

## REVIEW

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 Cite this: *Mater. Chem. Front.*,  
 2020, 4, 46

## Assembling features of calixarene-based amphiphiles and supra-amphiphiles

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Macrocyclic amphiphiles as an emerging family of artificial amphiphiles have gained considerable attention in recent years on account of their fascinating recognition and assembly properties. Benefiting from a preorganized framework, facile modification and host–guest recognition ability, calixarenes have been widely used to fabricate self-assemblies of both amphiphiles and supra-amphiphiles. In this review, we organized hundreds of reported amphiphilic calixarenes based on their structures and systematically summarized assembling features of calixarene-based amphiphiles and supra-amphiphiles. For amphiphilic calixarenes, the size and conformation of skeletons significantly affect their assembly behaviors, such as lower critical aggregation concentration (CAC) and more diverse morphology than conventional amphiphiles. Besides, we also focus on emerging topics like uniformity, compactness, and kinetic properties of calixarene aggregation. For supra-amphiphiles, the binding affinities of calixarenes endow them with the ability to induce guest assembly. In addition, complexation of guests also improves amphiphilic calixarene aggregation. The obtained assemblies not only possess the advantages of low CAC and compact packing, but also respond to various stimuli. Finally, we pointed out several research topics of calixarene-based amphiphiles and supra-amphiphiles to be further developed in the future, such as the relationship between molecular structures and assembly properties, crosslinking, co-assembly, and utilization of cavities. We hope this review could be a guidance for studying amphiphilic assemblies based on calixarenes and other macrocyclic compounds.

 Received 29th July 2019,  
 Accepted 27th September 2019

DOI: 10.1039/c9qm00489k

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### 1. Introduction

Amphiphiles are molecules that contain both a hydrophobic component and a hydrophilic component connected by covalent bonds.<sup>1</sup> Inspired by nature, synthetic amphiphilic molecules

enrich the concept of amphiphiles. Based on the number and properties of polar head(s)/hydrophobic tail(s) as well as their manner of connection, amphiphiles are classified as conventional amphiphiles (single head/single tail), bolaamphiphiles, gemini amphiphiles, double and triple chain amphiphiles, catanionic amphiphiles, amphiphilic polymers, *etc.*<sup>2</sup> Owing to their unique structures, amphiphiles can assemble into aggregates such as micelles, vesicles, lyotropic liquid crystals, 2D monolayers and 3D multilayers,<sup>1</sup> resulting in important

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biological functions and various applications in our daily life and industry.<sup>3</sup>

As an emerging family of artificial amphiphiles, macrocyclic amphiphiles have gained considerable attention in recent years on account of their fascinating recognition and assembly properties.<sup>3,4</sup> Just as their name implies, macrocyclic amphiphiles are obtained by introducing hydrophilic groups and lipophilic groups to the preorganized scaffold. They incorporate both bola-type and gemini-type amphiphiles into a single molecule from the viewpoint of structural characteristics. Besides, the unique advantage of macrocyclic amphiphiles is the host-guest recognition. Macrocyclic amphiphiles are deemed as “surfactants with host-guest recognition sites”,<sup>5</sup> whose macrocyclic binding sites are distributed on the surface of the amphiphilic assembly. Up to now, cyclodextrin,<sup>6</sup> calixarene<sup>7</sup> and pillararene<sup>8,9</sup> have been the commonly used compounds to construct macrocyclic amphiphiles.

On the other hand, by combining supramolecular chemistry and amphiphiles, supra-amphiphiles have attracted widespread attention of scientists.<sup>10</sup> In contrast to amphiphiles based on covalent bonds, supra-amphiphiles refer to amphiphiles constructed on the basis of noncovalent interactions or dynamic covalent bonds, which are very useful in the fabrication of nanomaterials with a high degree of structural complexity. Functional groups can be attached to supra-amphiphiles by employing various noncovalent interactions, greatly avoiding tedious covalent syntheses. Moreover, the dynamic and reversible nature of noncovalent interactions endows the resultant supramolecular architectures with excellent stimuli-responsive features. Due to their unique advantages, supra-amphiphiles are being widely and actively investigated in materials and biomedical sciences nowadays.<sup>11,12</sup>

Calixarenes are the third generation of macrocyclic compounds composed of phenolic units linked by methylene groups at the *o*-positions of phenolic hydroxyl groups. Their history dates back to the late nineteenth century, but they did not receive wide attention for a long time until Gutsche and coworkers studied calixarenes as mimic enzymes.<sup>13</sup> Calixarenes have several sites for derivation and their sizes can be adjusted.

Moreover, chemical modification, especially with water soluble groups, could significantly enhance their binding affinity. Benefiting from these properties, calixarenes have been described as macrocycles which have “(almost) unlimited possibilities”<sup>14</sup> and have been widely used to fabricate amphiphiles and supra-amphiphiles. There have been a couple of reviews about calixarene-based amphiphiles and supra-amphiphiles. In 2010, Helttunen and Shahgaldian summarized self-assembly of amphiphilic calixarenes and resorcinarenes in water, and classified aggregates by their morphology.<sup>15</sup> Later, Garcia-Rio and coworkers published a review which focuses on a promising series of calixarene, *p*-sulfonatocalixarene,<sup>16</sup> while Klymchenko and coworkers focused on amphiphilic calixarenes as gene delivery vehicles.<sup>17</sup> Recently, Guo and coworkers discussed assembly behaviors of calixarene-based amphiphiles and supra-amphiphiles, and focused on their applications in drug delivery and protein recognition.<sup>18</sup> Up to now, calixarene-based amphiphiles and supra-amphiphiles have been widely used in many fields such as sensing,<sup>19</sup> adsorption and extraction,<sup>20,21</sup> catalysis,<sup>22</sup> inorganic-organic hybrid materials,<sup>23</sup> preparation of chiral materials<sup>24</sup> and photoluminescent materials,<sup>25</sup> and biomedical applications.<sup>18,26-35</sup>

In this review, we will summarize calixarene-based amphiphiles and supra-amphiphiles reported up to now and focus our special attention on their assembling features in aqueous solution. The structure of this review will be such that we first summarize and comprehensively list chemical structures of amphiphilic calixarenes, including upper-rim hydrophilic amphiphiles, lower-rim hydrophilic amphiphiles and bola-type amphiphiles, followed by their assembling features. Next we summarize the self-assemblies of calixarene-based supra-amphiphiles and their assembling features, focusing on complexation-induced aggregation (guest-induced aggregation of host, host-induced aggregation of guest, and mutual inducement).

## 2. Calixarene-based amphiphiles

### 2.1 Fabricating amphiphilic calixarenes by covalent modification

Calixarenes possess several sites which are easily modified, such as an upper rim, lower rim, and methylene bridge. As a result, more than four hundred amphiphilic calixarenes were obtained by simply modifying hydrophilic or hydrophobic groups on scaffolds. Most works focused on amphiphilic calixarenes in the cone conformation,<sup>36</sup> in which hydrophilic and hydrophobic groups are decorated on opposite rims, resulting in upper-rim hydrophilic amphiphiles and lower-rim hydrophilic amphiphiles (Scheme 1). Moreover, the adjustable conformation of calixarenes makes it easy to modify them on the basis of an alternate conformation, or stabilize the alternate conformation after modification. The obtained compounds are bola-type amphiphiles. We comprehensively list these three classes of amphiphilic calixarenes reported up to now in Schemes 2–4 and Tables 1–3 in order to facilitate readers for following this field and further studies.



**Dong-Sheng Guo**

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**Scheme 1** Schematic illustration of various types of calixarene-based amphiphiles.

As we can see from the schemes, most amphiphilic calixarenes are based on calix[4]arene. Calix[5]arene, calix[6]arene, calix[8]arene, calix[9]arene, and thiacalix[4]arene are also involved. For upper-rim hydrophilic amphiphiles, almost all the common substitutions which are possible for phenols have been carried out at the upper rim. For example, a sulfonate group is widely introduced because of its excellent water-solubility and convenient one-step reaction. A nitro group and a halogen (or benzyl halide) group were also attached to the upper-rim by a one-step reaction. Further derivatization from them results in numerous functional groups such as the phosphate group, guanidinium group, carboxylic group, amino group, azide group and so on. It is noteworthy that carboxylic group and amino group could involve in amide condensation, and the azide group could react with an alkynyl compound. These well-established reactions provide the possibility of decorating calixarene with almost everything, such as cyclodextrin, PEG, saccharide, and cholesterol. On the other hand, the hydrophobic moieties of most upper-rim hydrophilic amphiphiles were introduced by alkyl halides reacting with phenolic hydroxyl at the lower rim. Meanwhile, similar nucleophilic substitution has been applied for PEG chains, resulting in lower-rim hydrophilic amphiphiles. The upper-rim attached hydrophobic chain of most lower-rim hydrophilic amphiphiles were introduced at the cyclic formation step, *i.e.*, using *p*-alkylphenol as a reactant. Among them, the most popular *p*-alkylphenol is *p*-*tert*-butylphenol. In addition, the alkyl chain can be connected to the methylene, being introduced at the cyclic formation step as well. For bola-type amphiphiles, their conformations were usually controlled by template metal ions, for example, calix[4]arene tends to form alternative conformers in the presence of cesium carbonate. Since all these factors (skeleton, hydrophobic chain length, hydrophilic group, and conformation) affect the hydrophilic–hydrophobic balance,

amphiphilic calixarenes with various assembly properties have been obtained by taking advantage of convenient synthesis.

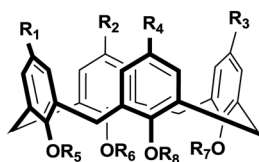
## 2.2 Assembling features of amphiphilic calixarenes

### 2.2.1 Low critical aggregation concentration (CAC).

When we study the assembly behavior of a specific amphiphile, CAC is a widely used parameter indicating self-assembling ability of amphiphiles. CAC is the concentration at which an amphiphile starts aggregating. Electrical conductivity, surface tension, light scattering and fluorescence intensity are the most commonly used parameters to determine the CAC value. Plots which show the dependence of measured physical properties on concentration of amphiphiles usually show a change of slope around CAC. CAC also relates to temperature and solvent. Under the same conditions, it is generally acknowledged that lower CAC represents stronger assembling ability, because lower CAC means lower monomer concentration in equilibrium between the monomer and assembly.<sup>3</sup>

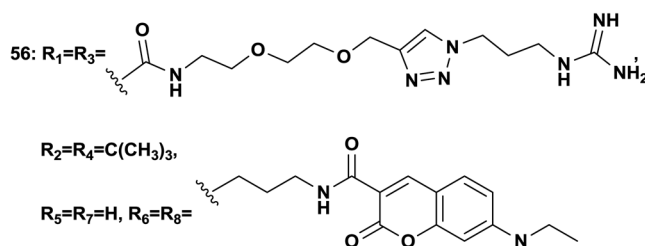
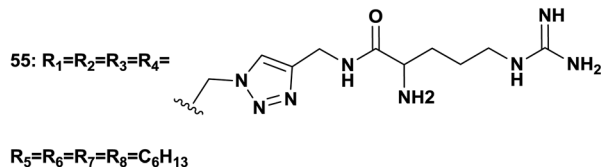
Reported CAC values of amphiphilic calixarenes are summarized in Table 4. It is easy to notice that a large proportion of amphiphilic calixarenes have quite low CACs (<1 mM) compared with common surfactants. For example, the CACs of sodium butyl benzene sulfonate, sodium hexyl benzene sulfonate, sodium octyl benzene sulfonate, and sodium dodecyl benzene sulfonate (SDBS) are 100 mM, 30 mM, 14 mM, and 1.5 mM, respectively. The CACs of the corresponding amphiphilic calix[4]arenes **3**, **6**, **8**, and **9** are 3.2 mM, 0.488 mM, 0.085 mM, and 0.02 mM, respectively. As a reference compound, the CAC of the gemini-type SDBS derivate is 0.9 mM. If we consider generalized monomer concentration, the CAC of the gemini-type SDBS derivate is 1.8 mM monomer, which is similar to SDBS, while the CAC of calix[4]arene **9** is 0.08 mM monomer, which is 19 times lower than that of SDBS. The lower CAC of calixarene undoubtedly originates from the cyclic oligomeric structure. From the viewpoint of entropy, amphiphiles in the assemblies have a lower degree of freedom than that in bulky water, so the entropy of amphiphiles (not including water molecules) decreases during the assembly process. The oligomer structure of calixarene leads to much lower entropy loss than the corresponding monomer, resulting in lower CAC as well as a more sensitive response to the structural difference.<sup>279</sup>

For example, CACs decrease more rapidly with longer alkyl chains of amphiphilic sulfonatocalix[*n*]arenes (SC*n*As) than that of sodium benzene sulfonate surfactants, as Basilio and co-workers proposed. They systematically investigated the relationship between CACs and the hydrophobic chain length of amphiphilic SC*n*As **3**, **6**, and **8** from the viewpoint of thermodynamics by ITC in detail, and obtained their free energy of micellization ( $\Delta G_M^\circ$ ).<sup>53,54</sup> They proposed that the  $\Delta G_M^\circ$  is the sum of contributions of each part of the molecule to the total free energy, such as ionic groups and counterions, aromatic rings, oxygen atoms that connect the aromatic rings to the alkyl chains, methylene group of the bridges, methylene groups of the alkyl chains, and terminal methyl groups of the chains. Among these, the free energy of transferring a methyl group from water to the micellar interior ( $\Delta G_M^\circ(\text{CH}_3)$ ) is equal to that

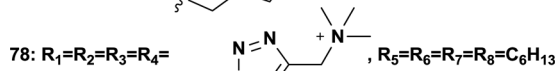
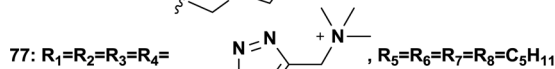
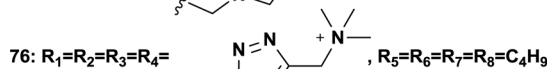
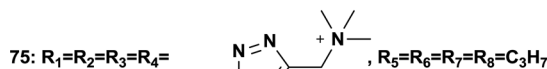
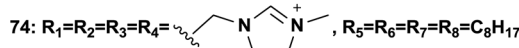
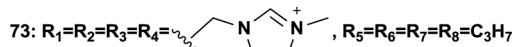


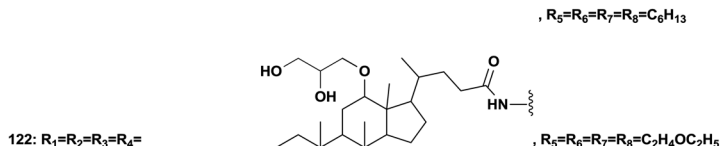
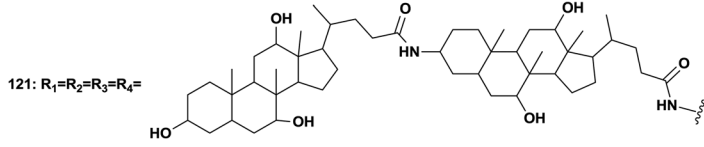
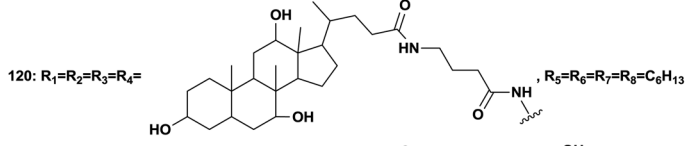
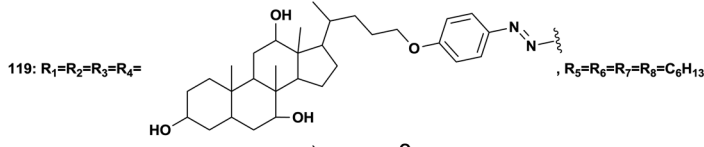
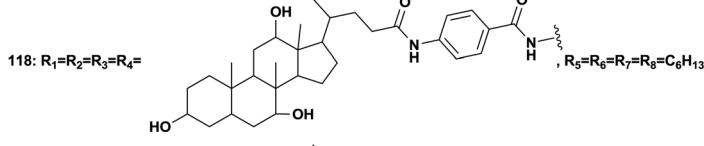
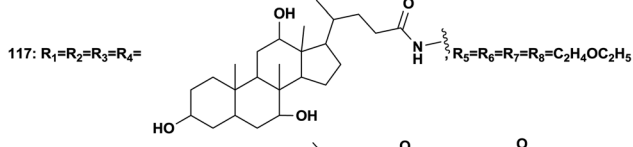
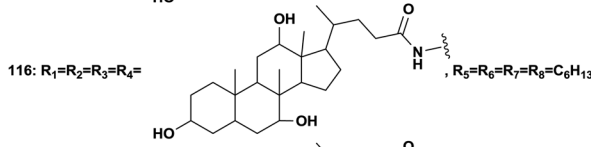
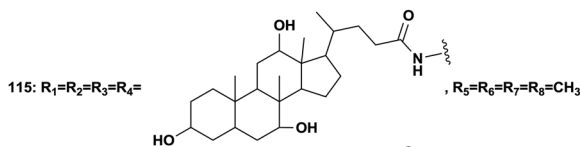
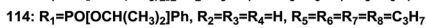
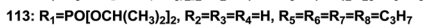
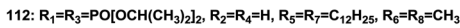
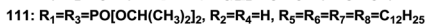
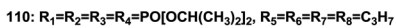
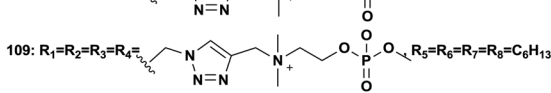
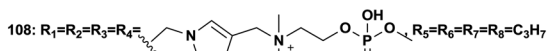
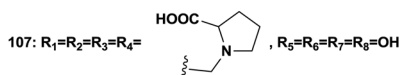
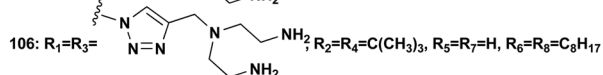
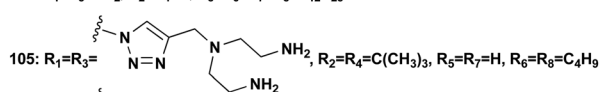
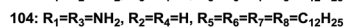
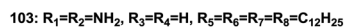
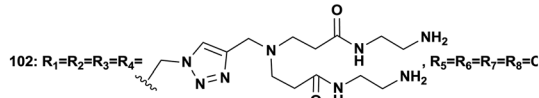
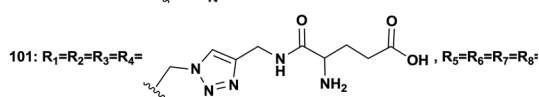
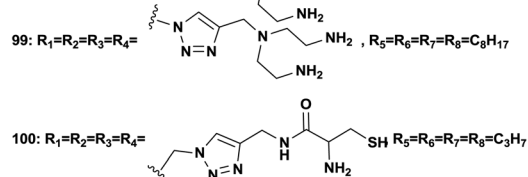
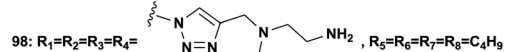
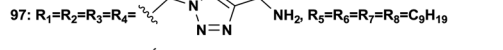
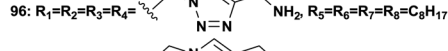
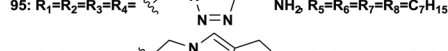
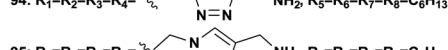
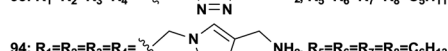
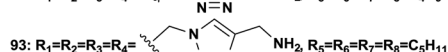
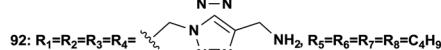
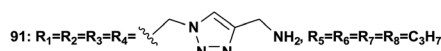
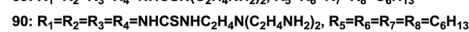
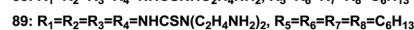
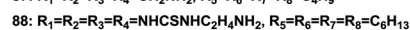
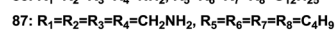
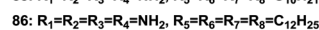
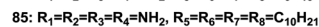
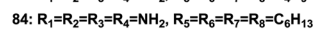
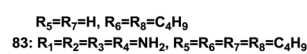
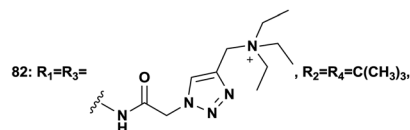
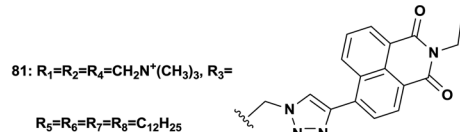
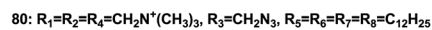
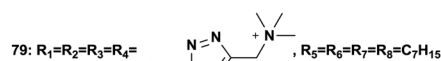
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 2:  $R_1=R_2=R_3=R_4=SO_3^-$ ,  $R_5=R_6=R_7=R_8=-CH_2-CH=CH_2$   
 3:  $R_1=R_2=R_3=R_4=SO_3^-$ ,  $R_5=R_6=R_7=R_8=C_4H_9$   
 4:  $R_1=R_2=R_3=R_4=SO_3^-$ ,  $R_5=R_6=R_7=R_8=C_5H_{11}$   
 5:  $R_1=R_2=R_3=R_4=SO_3^-$ ,  $R_5=R_6=R_7=R_8=CH_2CH(CH_3)C_2H_5$   
 6:  $R_1=R_2=R_3=R_4=SO_3^-$ ,  $R_5=R_6=R_7=R_8=C_6H_{13}$   
 7:  $R_1=R_2=R_3=R_4=SO_3^-$ ,  $R_5=R_6=R_7=R_8=C_7H_{15}$   
 8:  $R_1=R_2=R_3=R_4=SO_3^-$ ,  $R_5=R_6=R_7=R_8=C_8H_{17}$   
 9:  $R_1=R_2=R_3=R_4=SO_3^-$ ,  $R_5=R_6=R_7=R_8=C_{12}H_{25}$   
 10:  $R_1=R_2=R_3=R_4=PO_3H_2$ ,  $R_5=R_6=R_7=R_8=C_6H_{13}$   
 11:  $R_1=R_2=R_3=R_4=PO_3H_2$ ,  $R_5=R_6=R_7=R_8=C_8H_{17}$   
 12:  $R_1=R_2=R_3=R_4=PO_3H_2$ ,  $R_5=R_6=R_7=R_8=C_{10}H_{21}$   
 13:  $R_1=R_2=R_3=R_4=PO_3H_2$ ,  $R_5=R_6=R_7=R_8=C_{12}H_{25}$   
 14:  $R_1=R_2=R_3=R_4=PO_3H_2$ ,  $R_5=R_6=R_7=R_8=C_{14}H_{29}$   
 15:  $R_1=R_2=R_3=R_4=PO_3H_2$ ,  $R_5=R_6=R_7=R_8=C_{18}H_{37}$   
 16:  $R_1=R_2=R_3=R_4=CH_2PO_3H_2$ ,  $R_5=R_6=R_7=R_8=C_6H_{13}$   
 17:  $R_1=R_2=R_3=R_4=CH_2PO_3H_2$ ,  $R_5=R_6=R_7=R_8=C_8H_{17}$   
 18:  $R_1=R_2=R_3=R_4=CH_2PO_3H_2$ ,  $R_5=R_6=R_7=R_8=C_{12}H_{25}$   
 19:  $R_1=R_2=R_3=R_4=PO(OH)(OC_2H_5)$ ,  $R_5=R_6=R_7=R_8=C_4H_9$   
 20:  $R_1=R_2=R_3=CH_2PO_3H_2$ ,  $R_4=CH_2-N=N=N$ ,  $R_5=R_6=R_7=R_8=C_6H_{13}$   
 21:  $R_1=R_2=R_3=R_4=COOH$ ,  $R_5=R_6=R_7=R_8=C_3H_7$   
 22:  $R_1=R_2=R_3=R_4=COOH$ ,  $R_5=R_6=R_7=R_8=C_6H_{13}$   
 23:  $R_1=R_2=R_3=R_4=COOH$ ,  $R_5=R_6=R_7=R_8=C_8H_{17}$   
 24:  $R_1=R_2=R_3=R_4=COOH$ ,  $R_5=R_6=R_7=R_8=C_{12}H_{25}$   
 25:  $R_1=R_2=R_3=R_4=CH_2NHCH(CH_3)COOH$ ,  $R_5=R_6=R_7=R_8=C_{10}H_{21}$   
 26:  $R_1=R_2=R_3=R_4=NHCOC_2H_4COOH$ ,  $R_5=R_6=R_7=R_8=C_3H_7$   
 27:  $R_1=R_2=R_3=R_4=NHCOC_2H_4COOH$ ,  $R_5=R_6=R_7=R_8=C_4H_9$   
 28:  $R_1=R_2=R_3=R_4=NHCOC_2H_4COOH$ ,  $R_5=R_6=R_7=R_8=C_5H_{11}$   
 29:  $R_1=R_2=R_3=R_4=NHCOC_2H_4COOH$ ,  $R_5=R_6=R_7=R_8=C_{12}H_{25}$   
 30:  $R_1=R_2=R_3=R_4=NHCOC_3H_6COOH$ ,  $R_5=R_6=R_7=R_8=C_3H_7$   
 31:  $R_1=R_2=R_3=R_4=COOH$ ,  $R_5=R_7=C_3H_7Ph$ ,  $R_6=R_8=C_3H_7$   
 32:  $R_1=R_2=R_3=COOH$ ,  $R_4=R_5=R_7=H$ ,  $R_6=R_8=CH(CH_3)_2$   
 33:  $R_1=R_2=R_3=COOH$ ,  $R_4=R_5=R_7=H$ ,  $R_6=R_8=C_3H_7$   
 34:  $R_1=R_2=R_3=CH_2COOH$ ,  $R_4=R_5=R_6=R_7=H$ ,  $R_8=CH_3$   
 35:  $R_1=R_2=R_3=CH_2COOH$ ,  $R_4=R_5=R_6=R_7=H$ ,  $R_8=C_2H_5$   
 36:  $R_1=R_2=R_3=CH_2COOH$ ,  $R_4=R_5=R_6=R_7=H$ ,  $R_8=C_3H_7$   
 37:  $R_1=R_2=R_3=CH_2COOH$ ,  $R_4=R_5=R_6=R_7=H$ ,  $R_8=C_4H_9$   
 38:  $R_1=R_2=R_3=CH_2COOH$ ,  $R_4=R_5=R_6=R_7=H$ ,  $R_8=C_5H_{11}$   
 39:  $R_1=R_2=R_3=CH_2COOH$ ,  $R_4=R_5=R_6=R_7=H$ ,  $R_8=C_6H_{13}$   
 40:  $R_1=R_2=R_3=CH_2COOH$ ,  $R_4=R_5=R_6=R_7=H$ ,  $R_8=C_7H_{15}$   
 41:  $R_1=R_2=R_3=CH_2COOH$ ,  $R_4=R_5=R_6=R_7=H$ ,  $R_8=C_8H_{17}$   
 42:  $R_1=R_2=R_3=CH_2COOH$ ,  $R_4=R_5=R_6=R_7=H$ ,  $R_8=C_9H_{19}$   
 43:  $R_1=R_2=R_3=CH_2COOH$ ,  $R_4=R_5=R_6=R_7=H$ ,  $R_8=C_{10}H_{21}$   
 44:  $R_1=R_2=R_3=CH_2COOH$ ,  $R_4=R_5=R_6=R_7=H$ ,  $R_8=C_{12}H_{25}$   
 45:  $R_1=R_2=R_3=CH_2COOH$ ,  $R_4=R_5=R_6=R_7=H$ ,  $R_8=C_{10}H_{21}$   
 46:  $R_1=R_2=R_3=R_4=NHCOPhCONHC(C_2H_4COOH)_3$ ,  
 $R_5=R_6=R_7=R_8=C_{12}H_{25}$   
 47:  $R_1=R_3=NHCOCH_2CONHC(C_2H_4COOH)_3$ ,  
 $R_2=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=C_{12}H_{25}$

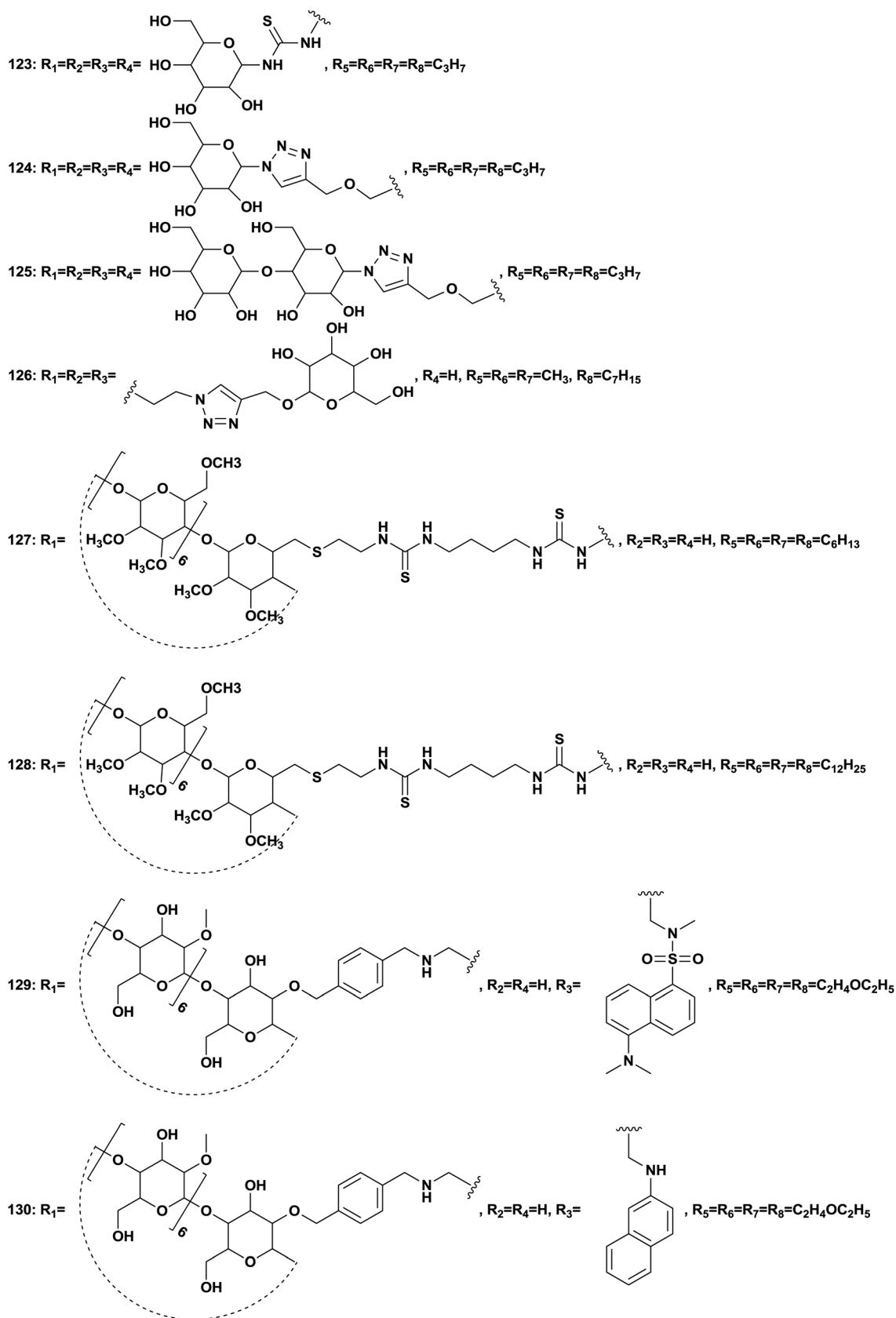
- 48:  $R_1=R_2=R_3=R_4=NHC(NH_2)_2^+$ ,  $R_5=R_6=R_7=R_8=C_4H_7$   
 49:  $R_1=R_2=R_3=R_4=NHC(NH_2)_2^+$ ,  $R_5=R_6=R_7=R_8=C_6H_{13}$   
 50:  $R_1=R_2=R_3=R_4=NHC(NH_2)_2^+$ ,  $R_5=R_6=R_7=R_8=C_8H_{17}$   
 51:  $R_1=R_2=R_3=R_4=NHC(NH_2)_2^+$ ,  $R_5=R_6=R_7=R_8=C_{12}H_{25}$   
 52:  $R_1=R_2=R_3=R_4=CH_2NHC(NH_2)_2^+$ ,  $R_5=R_6=R_7=R_8=C_6H_{13}$   
 53:  $R_1=R_2=R_3=R_4=NHC(NH_2)_2^+$ ,  $R_5=R_6=R_7=R_8=C_2H_4OC_2H_5$   
 54:  $R_1=R_2=R_3=R_4=NHCOCH(NH_2)C_3H_6NHC(NH_2)_2^+$ ,  $R_5=R_6=R_7=R_8=C_6H_{13}$

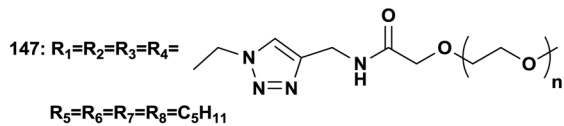
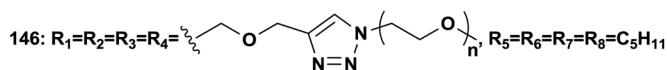
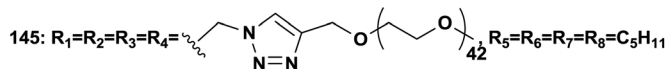
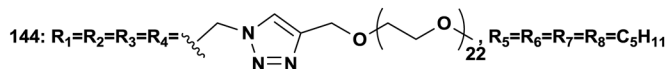
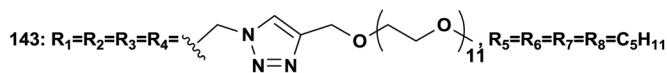
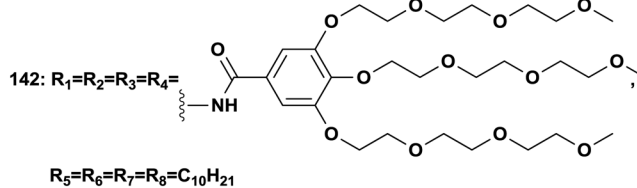
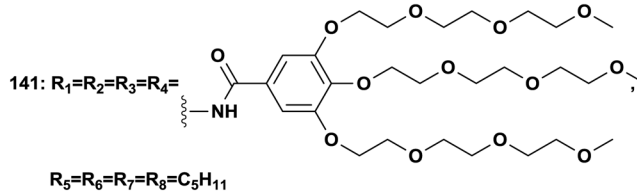
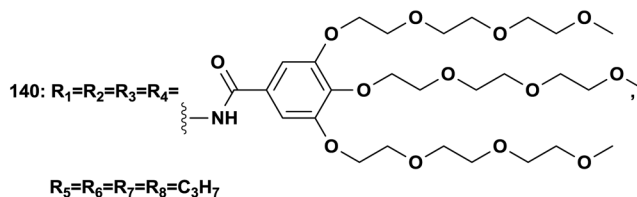
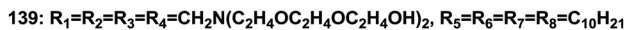
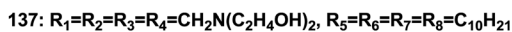
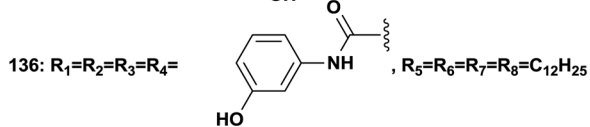
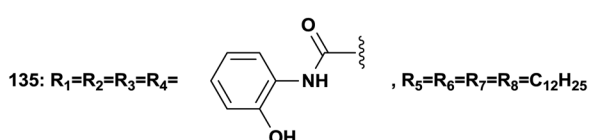
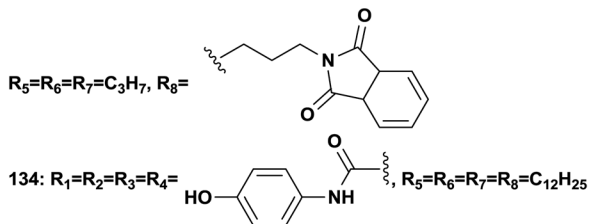
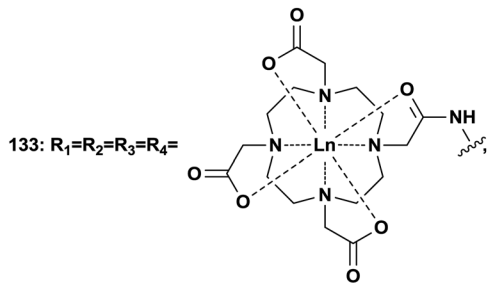
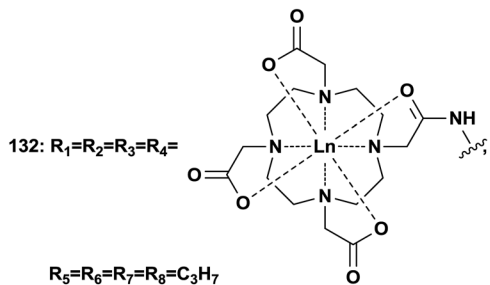
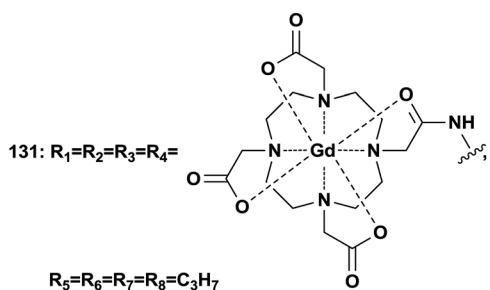


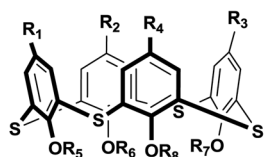
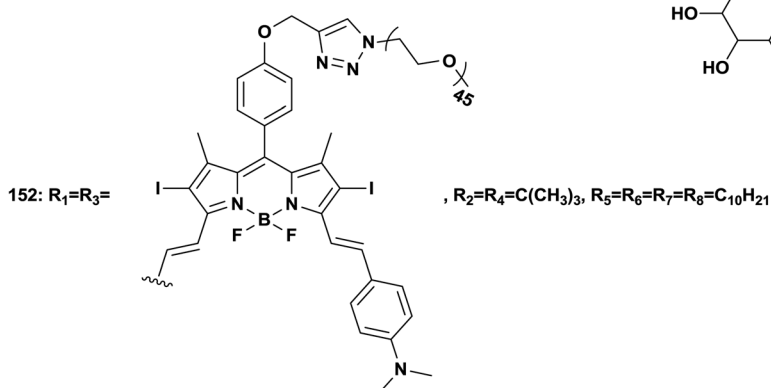
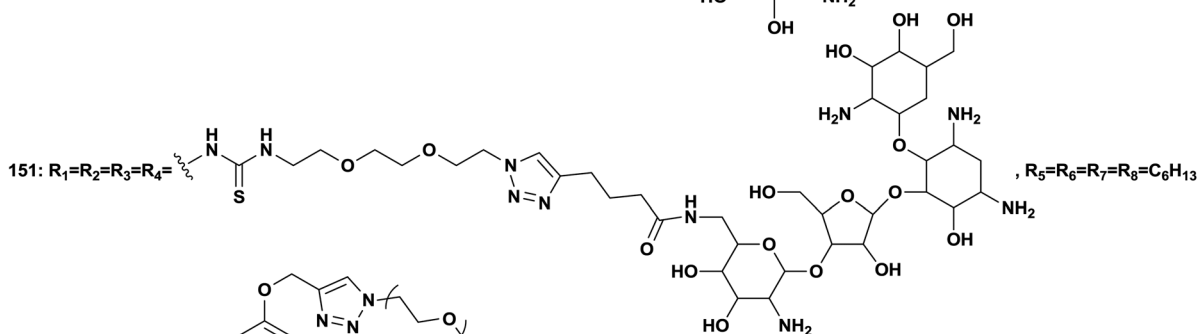
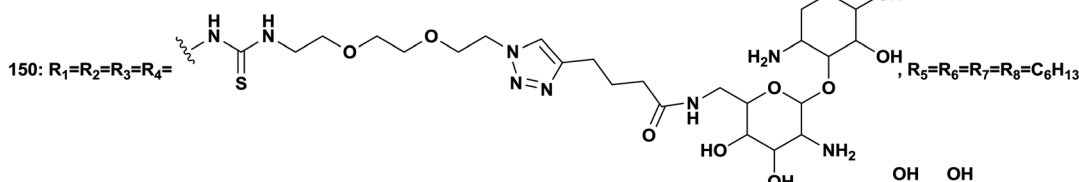
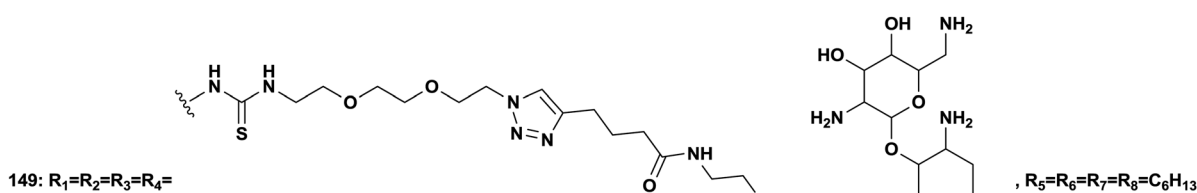
- 57:  $R_1=R_2=R_3=R_4=N^+(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=C_3H_7$   
 58:  $R_1=R_2=R_3=R_4=CH_2N^+(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=C_3H_7$   
 59:  $R_1=R_2=R_3=R_4=CH_2N^+(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=C_6H_{13}$   
 60:  $R_1=R_2=R_3=R_4=CH_2N^+(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=C_8H_{17}$   
 61:  $R_1=R_2=R_3=R_4=CH_2N^+(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=C_{12}H_{25}$   
 62:  $R_1=R_2=R_3=R_4=COOC_2H_4N^+(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=C_{12}H_{25}$   
 63:  $R_1=R_2=R_3=R_4=CH_2N^+(CH_3)_2CH_2C\equiv CH$ ,  $R_5=R_6=R_7=R_8=C_8H_{17}$   
 64:  $R_1=R_2=R_3=R_4=CH_2N^+(CH_3)_2C_2H_4OH$ ,  $R_5=R_6=R_7=R_8=C_3H_7$   
 65:  $R_1=R_2=R_3=R_4=CH_2N^+(CH_3)_2C_2H_4OH$ ,  $R_5=R_6=R_7=R_8=C_6H_{13}$   
 66:  $R_1=R_2=R_3=R_4=CH_2N^+(CH_3)_2C_2H_4OH$ ,  $R_5=R_6=R_7=R_8=C_8H_{17}$   
 67:  $R_1=R_2=R_3=R_4=CH_2N^+(CH_3)_2C_2H_4OH$ ,  $R_5=R_6=R_7=R_8=C_{12}H_{25}$   
 68:  $R_1=R_2=R_3=R_4=CH_2N^+(CH_3)_2C_2H_4OH$ ,  $R_5=R_6=R_7=R_8=C_{16}H_{33}$   
 69:  $R_1=R_2=R_3=R_4=CH_2N^+(CH_3)_2C_2H_4OH$ ,  $R_5=R_7=C_3H_7$ ,  $R_6=R_8=C_{16}H_{33}$   
 70:  $R_1=R_2=R_3=R_4=CH_2N^+(CH_3)(C_2H_4OH)_2$ ,  $R_5=R_6=R_7=R_8=C_3H_7$   
 71:  $R_1=R_2=R_3=R_4=CH_2N^+(CH_3)_2C_2H_4NH_2$ ,  $R_5=R_6=R_7=R_8=C_3H_7$   
 72:  $R_1=R_2=R_3=R_4=CH_2N^+(CH_3)_2C_2H_4NH_2$ ,  $R_5=R_6=R_7=R_8=C_8H_{17}$



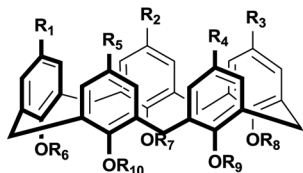








153:  $R_1=R_2=R_3=PO(OC_2H_5)_2$ ,  $R_4=R_5=R_6=R_7=H$ ,  $R_8=C_{10}H_{21}$



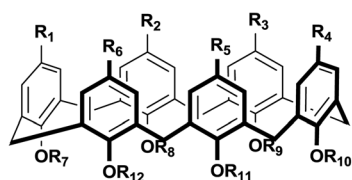
154:  $R_1=R_2=R_3=R_4=R_5=COOH$ ,  $R_6=R_7=R_8=R_9=R_{10}=C_{12}H_{25}$

155:  $R_1=R_2=R_3=R_4=R_5=NHC(NH_2)_2^+$ ,  $R_6=R_7=R_8=R_9=R_{10}=C_3H_6CH(CH_3)_2$

156:  $R_1=R_2=R_3=R_4=R_5=NHC(NH_2)_2^+$ ,  $R_6=R_7=R_8=R_9=R_{10}=C_{12}H_{25}$

157:  $R_1=R_2=R_3=R_4=R_5=N^+(CH_3)_3$ ,  $R_6=R_7=R_8=R_9=R_{10}=C_3H_6CH(CH_3)_2$

158:  $R_1=R_2=R_3=R_4=R_5=COOC_2H_4N^+(CH_3)_3$ ,  $R_6=R_7=R_8=R_9=R_{10}=C_{12}H_{25}$



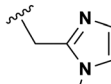
159:  $R_1=R_2=R_3=R_4=R_5=R_6=SO_3^-$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=C_3H_7$

160:  $R_1=R_2=R_3=R_4=R_5=R_6=SO_3^-$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=C_4H_9$

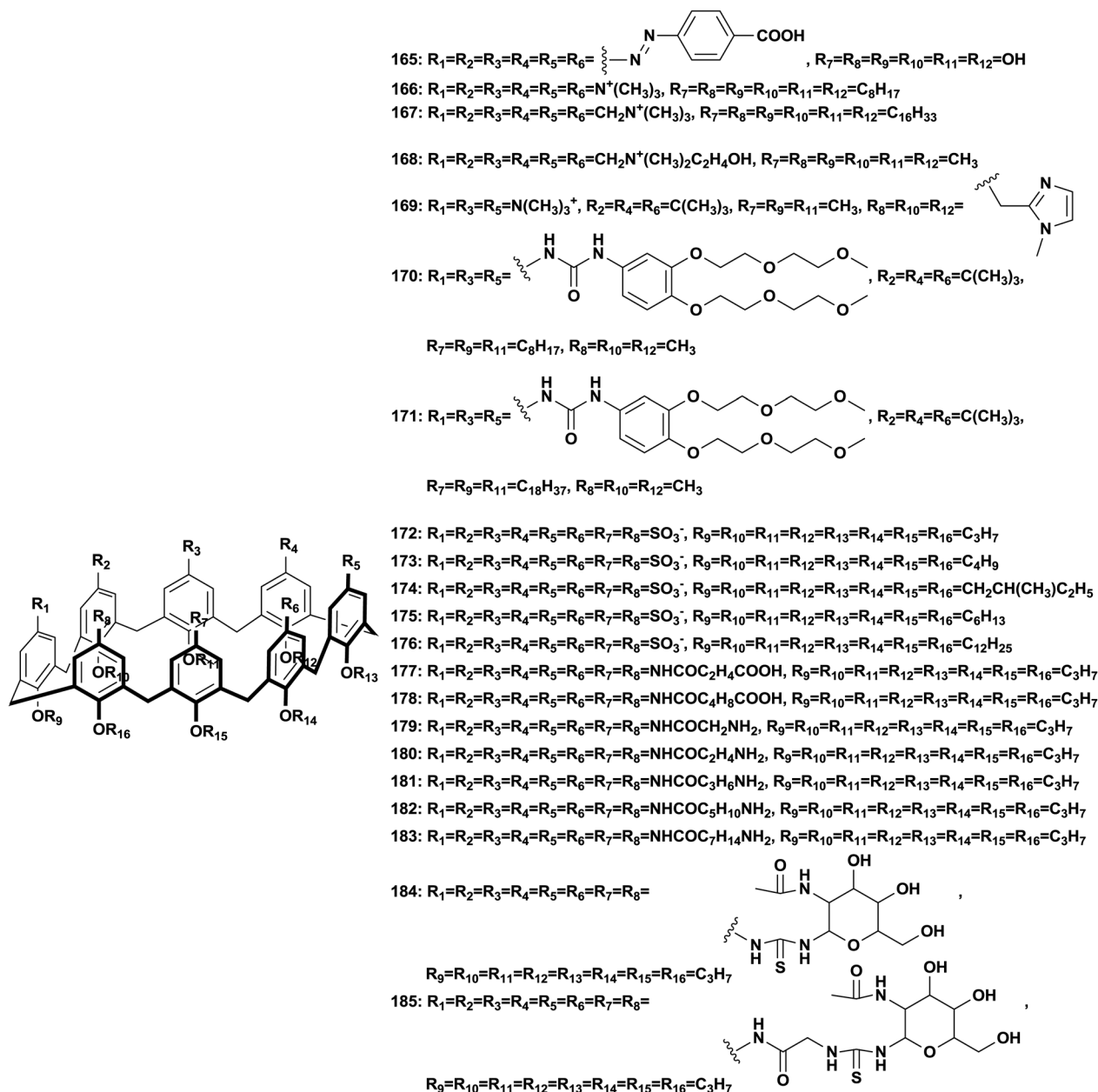
161:  $R_1=R_2=R_3=R_4=R_5=R_6=SO_3^-$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=CH_2CH(CH_3)C_2H_5$

162:  $R_1=R_2=R_3=R_4=R_5=R_6=SO_3^-$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=C_6H_{13}$

163:  $R_1=R_2=R_3=R_4=R_5=R_6=SO_3^-$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=C_{12}H_{25}$

164:  $R_1=R_3=R_5=SO_3^-$ ,  $R_2=R_4=R_6=C(CH_3)_3$ ,  $R_7=R_9=R_{11}=CH_3$ ,  $R_8=R_{10}=R_{12}=$  





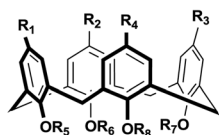
Scheme 2 Structures of upper-rim hydrophilic amphiphilic calixarenes.

of methylene groups ( $\Delta G_M^\circ(\text{CH}_2)$ ) add a constant (which can be represented by  $\Delta G_M^\circ(\text{CH}_3) = \Delta G_M^\circ(\text{CH}_2) + k$ , in which  $k$  is a constant). Therefore, the overall contribution of alkyl chains equals the free energy change for transferring one  $\text{CH}_2$  unit from the aqueous medium to the micellar interior ( $\Delta G_M^\circ(\text{CH}_2)$ ) multiplied by the carbon number of the alkyl chain, while other parts remain constant despite the change in carbon number. So the slope of  $\Delta G_M^\circ$  against carbon number is ( $\Delta G_M^\circ(\text{CH}_2)$ ).<sup>53,54</sup>

Since  $\Delta G_M^\circ$  is proportional to  $\log \text{CAC}$ , we plotted  $\log 4\text{CAC}$  of four amphiphilic SC4As with 4, 6, 8, 12 carbons and  $\log \text{CAC}$  of the corresponding monomer, *versus* the number of carbon atoms in the hydrophobic chain (Fig. 1), and the slope of linear

fitting is proportional to ( $\Delta G_M^\circ(\text{CH}_2)$ ). Results show a negative slope which reflects that the hydrophobic interaction contributes more favourably to the micellization process in the presence of longer alkyl chains. More importantly, the slope of calixarenes ( $-0.27$ ) is lower than the value generally observed for single-chain surfactants ( $-0.22$ ), which means  $\Delta G_M^\circ$  decreases more rapidly with longer alkyl chains of amphiphilic SCnAs than that of sodium sulfonate surfactants. This may be due to the existence of intramolecular interactions between the alkyl chains of the free monomers.<sup>53</sup>

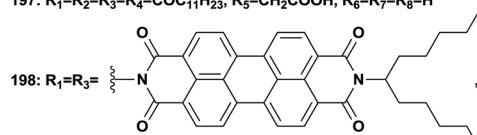
Similar to the difference between monomers and oligomers, in general, larger size of the skeleton results in a lower degree of entropic cost,<sup>279</sup> thus should lead to lower CAC, which is



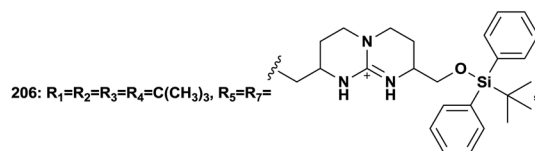
186:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=C_3H_6SO_3^-$   
 187:  $R_1=R_2=R_3=R_4=H$ ,  $R_5=R_6=R_7=R_8=C_3H_6SO_3^-$

188:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=C_2H_4PO_4H_2$   
 189:  $R_1=R_2=R_3=R_4=COC_9H_{11}$ ,  $R_5=R_6=R_7=R_8=H$   
 190:  $R_1=R_2=R_3=R_4=COC_7H_{15}$ ,  $R_5=R_6=R_7=R_8=H$   
 191:  $R_1=R_2=R_3=R_4=COC_9H_{19}$ ,  $R_5=R_6=R_7=R_8=H$   
 192:  $R_1=R_2=R_3=R_4=COC_{11}H_{23}$ ,  $R_5=R_6=R_7=R_8=H$   
 193:  $R_1=R_2=R_3=R_4=C_3H_6C_8F_{17}$ ,  $R_5=R_6=R_7=R_8=CH_2CONH(C_2H_4O)_3C_2H_4PO_4H_2$

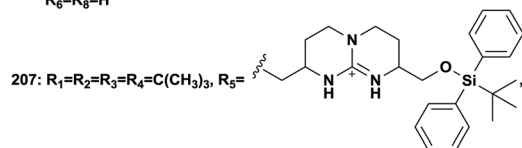
194:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=CH_2COOH$   
 195:  $R_1=R_2=R_3=R_4=C(CH_3)_2CH_2C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=CH_2COOH$   
 196:  $R_1=R_2=R_3=R_4=C_3H_6C_8F_{17}$ ,  
 $R_5=R_6=R_7=R_8=CH_2CONH(C_2H_4O)_3C_2H_4N(CH_2COOH)_2$   
 197:  $R_1=R_2=R_3=R_4=COC_{11}H_{23}$ ,  $R_5=R_6=R_7=R_8=CH_2COOH$ ,  $R_9=R_{10}=R_{11}=H$



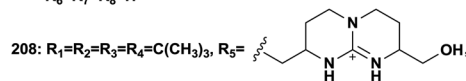
$R_2=R_4=R_5=R_7=H$ ,  $R_6=R_8=C_3H_6CONHC(C_2H_4COOH)_3$   
 199:  $R_1=R_2=R_3=R_4=H$ ,  $R_5=R_6=R_7=R_8=C_3H_6NHC(NH_2)_2^+$   
 200:  $R_1=R_2=R_3=R_4=H$ ,  $R_5=R_6=R_7=R_8=C_6H_{12}NHC(NH_2)_2^+$   
 201:  $R_1=R_2=R_3=R_4=C_3H_7$ ,  $R_5=R_6=R_7=R_8=C_3H_6NHC(NH_2)_2^+$   
 202:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=C_3H_6NHC(NH_2)_2^+$   
 203:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=C_4H_8NHC(NH_2)_2^+$   
 204:  $R_1=R_2=R_3=R_4=C_6H_{13}$ ,  $R_5=R_6=R_7=R_8=C_3H_6NHC(NH_2)_2^+$   
 205:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=C_2H_4NHC(NH_2)_2^+$ ,  $R_9=R_{10}=H$



$R_6=R_8=H$



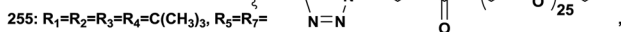
$R_6=R_7=R_8=H$



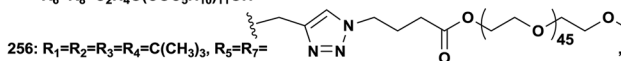
$R_6=R_7=R_8=H$

209:  $R_1=R_2=R_3=R_4=H$ ,  $R_5=R_6=R_7=R_8=C_3H_6N^+(CH_3)_3$   
 210:  $R_1=R_2=R_3=R_4=H$ ,  $R_5=R_6=R_7=R_8=C_6H_{12}N^+(CH_3)_2C_2H_4OH$   
 211:  $R_1=R_2=R_3=R_4=H$ ,  $R_5=R_6=R_7=R_8=C_3H_6NH_2$   
 212:  $R_1=R_2=R_3=R_4=C_3H_6C_8F_{17}$ ,  
 $R_5=R_6=R_7=R_8=CH_2CONH(C_2H_4O)_3C_2H_4NH_2$   
 213:  $R_1=R_2=R_3=R_4=C_2H_5$ ,  $R_5=R_6=R_7=R_8=H$   
 214:  $R_1=R_2=R_3=R_4=C_4H_9$ ,  $R_5=R_6=R_7=R_8=H$   
 215:  $R_1=R_2=R_3=R_4=C_6H_{13}$ ,  $R_5=R_6=R_7=R_8=H$

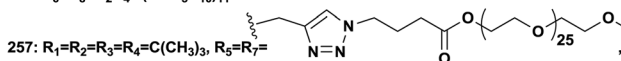
216:  $R_1=R_2=R_3=R_4=COC_9H_{11}$ ,  $R_5=R_6=R_7=R_8=H$   
 217:  $R_1=R_2=R_3=R_4=COC_7H_{15}$ ,  $R_5=R_6=R_7=R_8=H$   
 218:  $R_1=R_2=R_3=R_4=COC_9H_{19}$ ,  $R_5=R_6=R_7=R_8=H$   
 219:  $R_1=R_2=R_3=R_4=COC_{11}H_{23}$ ,  $R_5=R_6=R_7=R_8=H$   
 220:  $R_1=R_2=R_3=R_4=COC_{13}H_{27}$ ,  $R_5=R_6=R_7=R_8=H$   
 221:  $R_1=R_2=R_3=R_4=COC_{15}H_{31}$ ,  $R_5=R_6=R_7=R_8=H$   
 222:  $R_1=R_2=R_3=R_4=N_2PhCH_3$ ,  $R_5=R_6=R_7=R_8=H$   
 223:  $R_1=R_2=R_3=R_4=C_3H_6C_8F_{17}$ ,  $R_5=R_6=R_7=R_8=H$   
 224:  $R_1=R_2=R_3=R_4=N_2PhCl$ ,  $R_5=R_6=R_7=R_8=H$   
 225:  $R_1=R_3=COC_{17}H_{35}$ ,  $R_2=R_4=H$ ,  $R_5=R_6=R_7=R_8=H$   
 226:  $R_1=R_2=R_3=R_4=COC_{11}H_{23}$ ,  $R_5=R_6=PO(OC_2H_5)_2$ ,  $R_7=R_8=H$   
 227:  $R_1=R_2=R_3=R_4=COC_{11}H_{23}$ ,  $R_5=CH_2COOC_2H_5$ ,  $R_6=R_7=R_8=H$   
 228:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=CH_2COOC_2H_5$   
 229:  $R_1=R_2=R_3=R_4=C(CH_3)_2CH_2C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=C_2H_4OH$   
 230:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_6H$   
 231:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_{10}H$   
 232:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_{16}H$   
 233:  $R_1=R_2=R_3=R_4=C_4H_9$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_{16}H$   
 234:  $R_1=R_2=R_3=R_4=C_9H_{19}$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_8H$   
 235:  $R_1=R_2=R_3=R_4=C_9H_{19}$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_{12}H$   
 236:  $R_1=R_2=R_3=R_4=C_9H_{19}$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_{16}H$   
 237:  $R_1=R_2=R_3=R_4=C_6H_{12}CH(CH_3)_2$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_4H$   
 238:  $R_1=R_2=R_3=R_4=C_6H_{12}CH(CH_3)_2$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_8H$   
 239:  $R_1=R_2=R_3=R_4=C_6H_{12}CH(CH_3)_2$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_9H$   
 240:  $R_1=R_2=R_3=R_4=C_6H_{12}CH(CH_3)_2$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_{12}H$   
 241:  $R_1=R_2=R_3=R_4=C_6H_{12}CH(CH_3)_2$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_{16}H$   
 242:  $R_1=R_2=R_3=R_4=C_6H_{12}CH(CH_3)_2$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_{20}H$   
 243:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_{14}H$   
 244:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_{18}H$   
 245:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_{34}H$   
 246:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_{45}H$   
 247:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_{56}H$   
 248:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_{67}H$   
 249:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_{110}H$   
 250:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_{150}H$   
 251:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_{200}H$   
 252:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=(C_2H_4O)_{250}H$   
 253:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=CH_2COO(C_2H_4O)_{20}C_{16}H_{33}$   
 254:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=C_2H_4(OC_2H_4)_{12}OCH_3$ ,  $R_7=R_8=H$



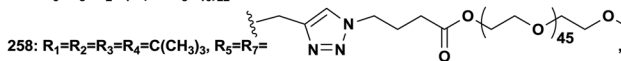
$R_6=R_8=C_2H_4O(COC_5H_{10})_{11}OH$



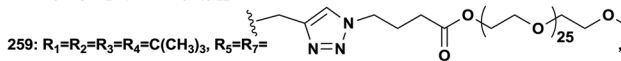
$R_6=R_8=C_2H_4O(COC_5H_{10})_{11}OH$



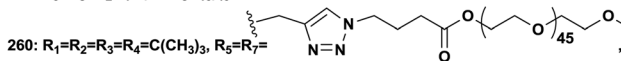
$R_6=R_8=C_2H_4O(COC_5H_{10})_{22}OH$



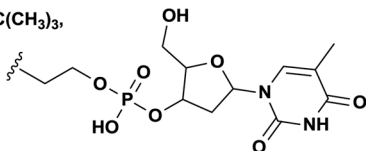
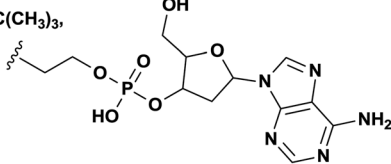
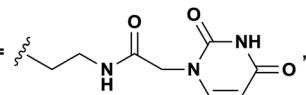
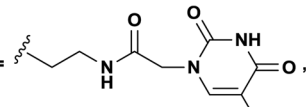
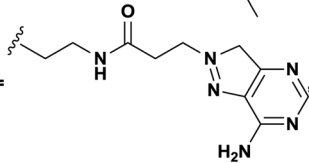
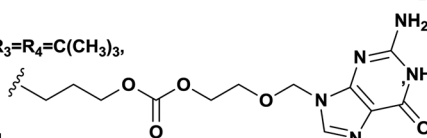
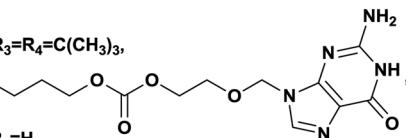
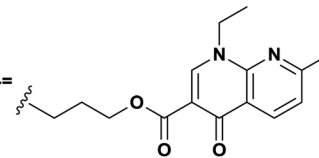
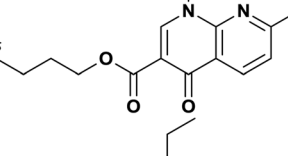
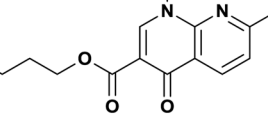
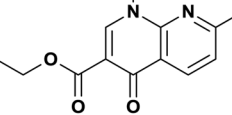
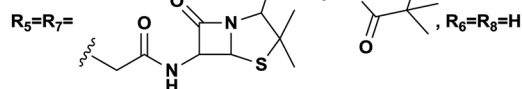
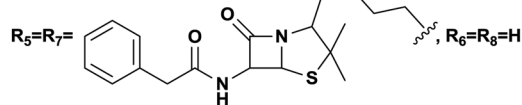
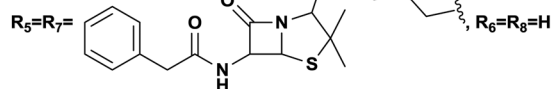
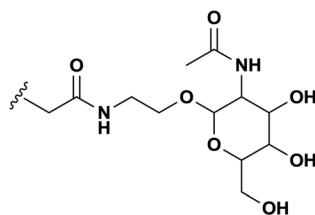
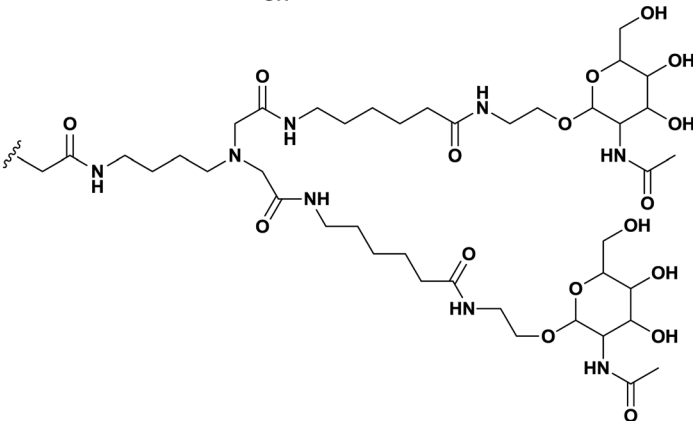
$R_6=R_8=C_2H_4O(COC_5H_{10})_{22}OH$

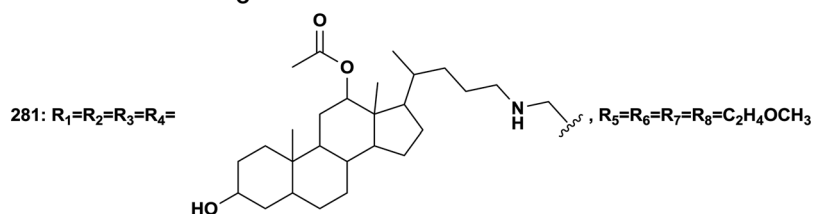
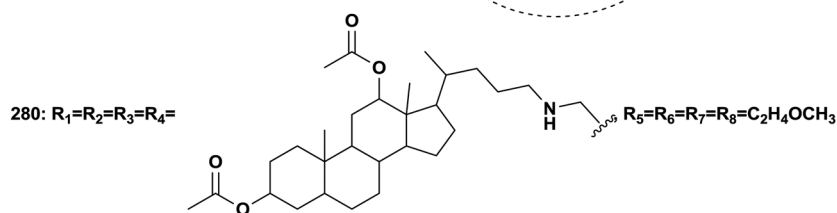
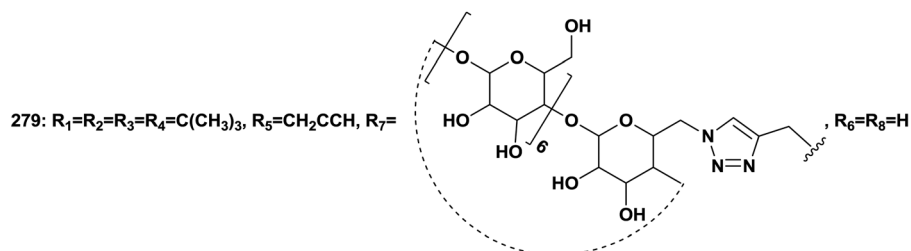
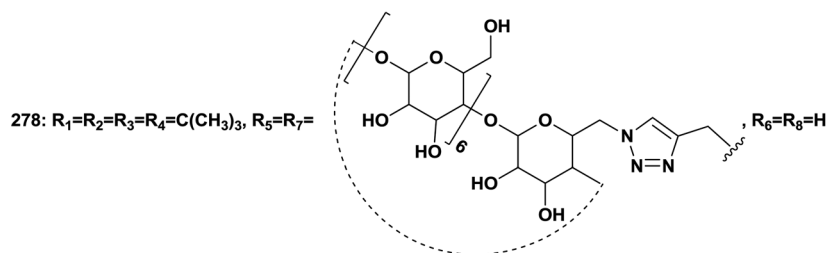
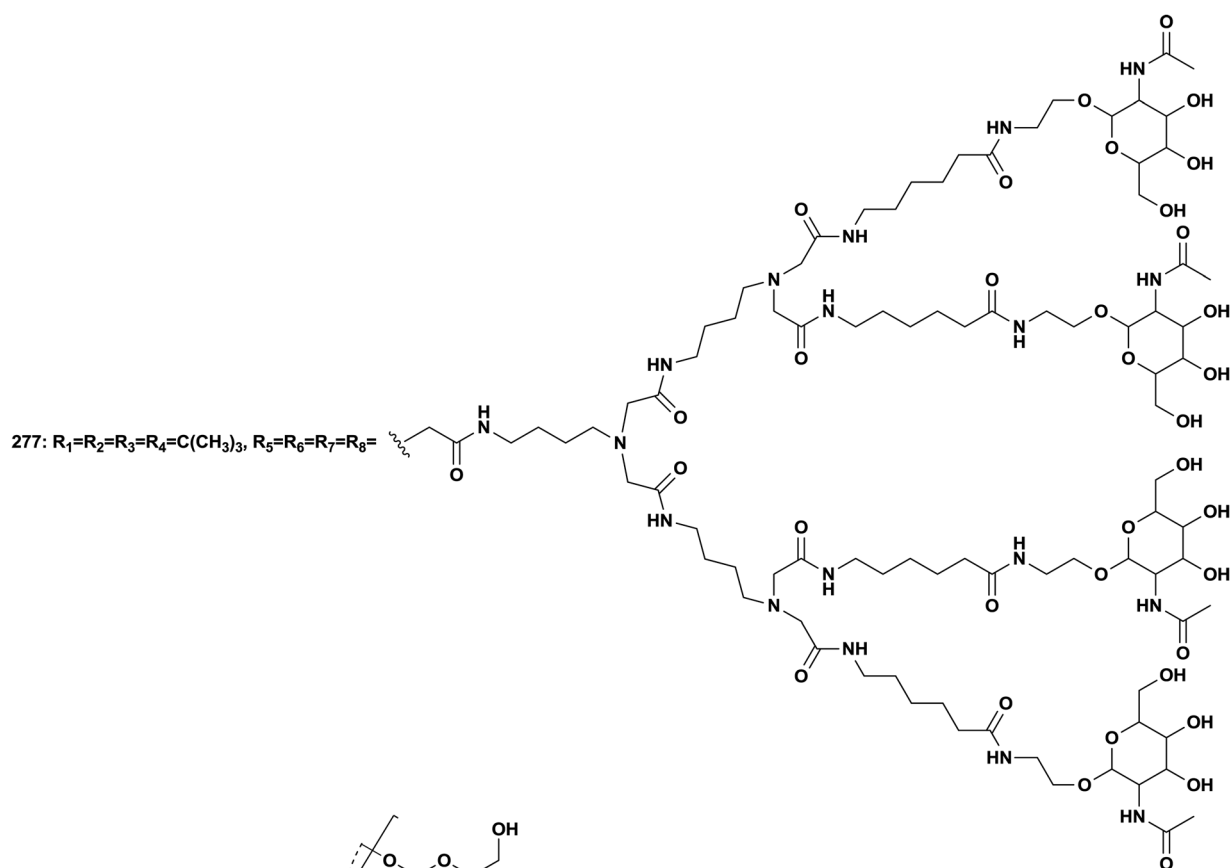


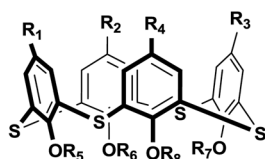
$R_6=R_8=C_2H_4O(COC_5H_{10})_{40}OH$



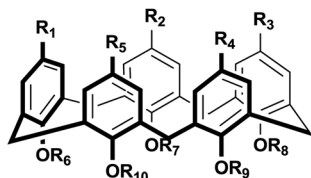
$R_6=R_8=C_2H_4O(COC_5H_{10})_{40}OH$

261:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ , $R_5=R_6=R_7=R_8=$ 262:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ , $R_5=R_6=R_7=R_8=$ 263:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_7=$  $R_6=R_8=H$ 264:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_7=$  $R_6=R_8=H$ 265:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_7=$  $R_6=R_8=H$ 266:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ , $R_5=R_7=$  $R_6=R_8=H$ 267:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ , $R_5=$  $R_6=R_7=R_8=H$ 268:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_7=$  $R_6=R_8=H$ 269:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=$  $R_6=R_7=R_8=H$ 270:  $R_1=R_2=R_3=R_4=H$ ,  $R_5=R_7=$  $R_6=R_8=H$ 271:  $R_1=R_2=R_3=R_4=H$ ,  $R_5=$  $R_6=R_7=R_8=H$ 272:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ , $R_5=R_7=$ 273:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ , $R_5=R_7=$ 274:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ , $R_5=R_7=$ 275:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=$ 276:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=$ 

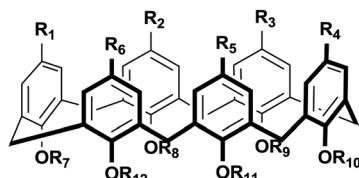




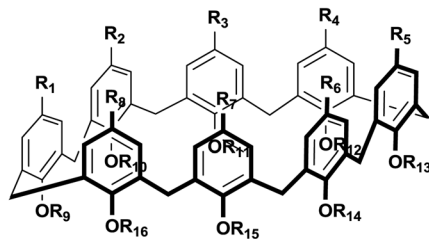
- 282:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=C_3H_6SO_3^-$   
 283:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=CH_2CONHC_3H_6N^+(CH_3)_3$   
 284:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=CH_2CONHC_3H_6N^+(CH_3)_2CH_2Ph$   
 285:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=CH_2CONHC_3H_6N^+(CH_3)_2C_2H_5$   
 286:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=CH_2CONHC_3H_6N^+(CH_3)_2C_3H_6Ph$   
 287:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=CH_2CONHC_3H_6N^+(CH_3)_2CH_2COOC_2H_5$   
 288:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=CH_2CONHC_3H_6N^+(C_2H_5)_2CH_3$   
 289:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=CH_2CONHC_2H_4N^+(C_2H_5)_2CH_2CONHCH_2COOC_2H_5$   
 290:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=CH_2CONHC_3H_6N^+(CH_3)_2CH_2CONHCH_2COOC_2H_5$   
 291:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=(C_2H_4O)_{14}CH_3$ ,  $R_6=R_7=R_8=H$   
 292:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=CH_2CONHC_3H_6N^+(CH_3)_2C_3H_6SO_3^-$   
 293:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=CH_2CONHC_3H_6N^+(CH_3)_2C_4H_8SO_3^-$



- 294:  $R_1=R_2=R_3=R_4=R_5=C(CH_3)_3$ ,  $R_6=R_7=R_8=R_9=R_{10}=C_4H_8SO_3^-$   
 295:  $R_1=R_2=R_3=R_4=R_5=C(CH_3)_3$ ,  $R_6=R_7=R_8=R_9=R_{10}=(C_2H_4O)_{12}CH_3$   
 296:  $R_1=R_2=R_3=R_4=R_5=CH_3$ ,  $R_6=R_7=R_8=R_9=R_{10}=(C_2H_4O)_{12}CH_3$

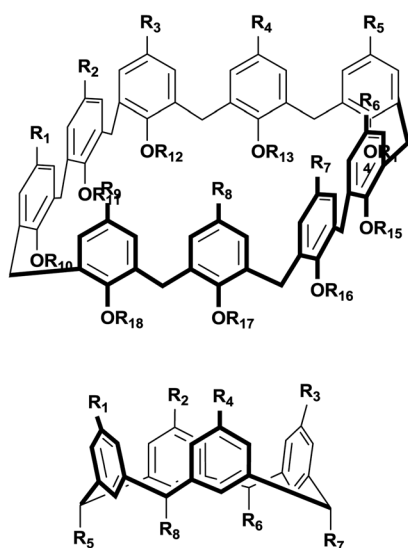


- 297:  $R_1=R_2=R_3=R_4=R_5=R_6=H$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=C_3H_6SO_3^-$   
 298:  $R_1=R_2=R_3=R_4=R_5=R_6=C_4H_9$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=C_3H_6SO_3^-$   
 299:  $R_1=R_2=R_3=R_4=R_5=R_6=C(CH_3)_3$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=C_3H_6SO_3^-$   
 300:  $R_1=R_2=R_3=R_4=R_5=R_6=C_6H_{13}$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=C_3H_6SO_3^-$   
 301:  $R_1=R_2=R_3=R_4=R_5=R_6=C_{12}H_{25}$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=C_3H_6SO_3^-$   
 302:  $R_1=R_2=R_3=R_4=R_5=R_6=COC_3H_7$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=C_4H_8SO_3^-$   
 303:  $R_1=R_2=R_3=R_4=R_5=R_6=COC_5H_{11}$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=C_4H_8SO_3^-$   
 304:  $R_1=R_2=R_3=R_4=R_5=R_6=COC_7H_{15}$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=C_4H_8SO_3^-$   
 305:  $R_1=R_2=R_3=R_4=R_5=R_6=H$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=CH_2COOH$   
 306:  $R_1=R_2=R_3=R_4=R_5=R_6=COC_3H_7$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=CH_2COOH$   
 307:  $R_1=R_2=R_3=R_4=R_5=R_6=COC_5H_{11}$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=CH_2COOH$   
 308:  $R_1=R_2=R_3=R_4=R_5=R_6=COC_7H_{15}$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=CH_2COOH$   
 309:  $R_1=R_2=R_3=R_4=R_5=R_6=C(CH_3)_3$ ,  $R_7=C_3H_6COOH$ ,  $R_8=R_9=R_{10}=R_{11}=R_{12}=H$   
 310:  $R_1=R_2=R_3=R_4=R_5=R_6=C(CH_3)_3$ ,  $R_7=R_9=R_{11}=C_2H_4NH_2$ ,  $R_8=R_{10}=R_{12}=CH_3$   
 311:  $R_1=R_2=R_3=R_4=R_5=R_6=C(CH_3)_3$ ,  $R_7=R_{10}=CH_2CONHC_3H_6NH_2$ ,  $R_8=R_9=R_{11}=R_{12}=H$   
 312:  $R_1=R_2=R_3=R_4=R_5=R_6=COC_3H_7$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=CH_2COOC_2H_5$   
 313:  $R_1=R_2=R_3=R_4=R_5=R_6=COC_5H_{11}$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=CH_2COOC_2H_5$   
 314:  $R_1=R_2=R_3=R_4=R_5=R_6=COC_7H_{15}$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=CH_2COOC_2H_5$   
 315:  $R_1=R_2=R_3=R_4=R_5=R_6=COC_3H_7$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=(C_2H_4O)_2CH_3$   
 316:  $R_1=R_2=R_3=R_4=R_5=R_6=COC_5H_{11}$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=(C_2H_4O)_2CH_3$   
 317:  $R_1=R_2=R_3=R_4=R_5=R_6=COC_7H_{15}$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=(C_2H_4O)_2CH_3$   
 318:  $R_1=R_2=R_3=R_4=R_5=R_6=C(CH_3)_3$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=COCH_3$   
 319:  $R_1=R_2=R_3=R_4=R_5=R_6=C(CH_3)_3$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=[CH_2CH(CH_3)O]_xH$   
 320:  $R_1=R_2=R_3=R_4=R_5=R_6=C(CH_3)_3$ ,  $R_7=R_8=R_9=R_{10}=R_{11}=R_{12}=[CH_2CH(CH_3)O]_x[COOCH_2C(CH_3)_2CH_2O]_yH$   
 321:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=H$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=C_3H_6SO_3^-$   
 322:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_3$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=C_3H_6SO_3^-$   
 323:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=COC_7H_{15}$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=C_4H_8SO_3^-$   
 324:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=COC_{15}H_{31}$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=C_4H_8SO_3^-$   
 325:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=H$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=CH_2COOH$   
 326:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_3$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=C_3H_6COOH$   
 327:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=COC_7H_{15}$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=CH_2COOH$   
 328:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=COC_{15}H_{31}$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=CH_2COOH$   
 329:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=COC_7H_{15}$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=C_3H_6COOH$   
 330:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=COC_{15}H_{31}$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=C_3H_6COOH$   
 331:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_2CH_2C(CH_3)_3$ ,  
 $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=CH_2COOH$



- 332:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=H$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=C_3H_6NHC(NH_2)_2^+$   
 333:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=COC_7H_{15}$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=H$   
 334:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=COC_9H_{19}$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=H$   
 335:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=COC_{11}H_{23}$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=H$   
 336:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=COC_{13}H_{27}$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=H$   
 337:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=COC_{15}H_{31}$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=H$   
 338:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=COC_7H_{15}$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=C_3H_6CN$   
 339:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=COC_{15}H_{31}$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=C_3H_6CN$   
 340:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_2CH_2C(CH_3)_3$ ,  
 $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=CH_2COOC_2H_5$   
 341:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=COC_7H_{15}$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=CH_2COOC_2H_5$   
 342:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=COC_{15}H_{31}$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=CH_2COOC_2H_5$   
 343:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=COC_7H_{15}$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=C_3H_6COOC_2H_5$   
 344:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=COC_{15}H_{31}$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=C_3H_6COOC_2H_5$   
 345:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=H$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_3H$   
 346:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_3$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_3H$   
 347:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_2CH_2C(CH_3)_3$ ,  
 $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_3H$   
 348:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=OCH_2Ph$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_3H$   
 349:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=H$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_6H$   
 350:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_3$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_6H$   
 351:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_2CH_2C(CH_3)_3$ ,  
 $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_6H$   
 352:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=OCH_2Ph$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_6H$   
 353:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=H$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_9H$   
 354:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=OH$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_9H$   
 355:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_3$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_9H$   
 356:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_2CH_2C(CH_3)_3$ ,  
 $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_9H$   
 357:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=OCH_2Ph$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_9H$   
 358:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_3$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_{12}H$   
 359:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=OCH_2Ph$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_{12}H$   
 360:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=OCH_2Ph$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_{18}H$   
 361:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=COC_7H_{15}$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=C_2H_4OCH_3$   
 362:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=COC_{15}H_{31}$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=C_2H_4OCH_3$   
 363:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=COC_7H_{15}$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_2CH_3$   
 364:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=COC_{15}H_{31}$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_2CH_3$   
 365:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=H$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_3CH_3$   
 366:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_3$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_3CH_3$   
 367:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_2CH_2C(CH_3)_3$ ,  
 $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_3CH_3$   
 368:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=OCH_2Ph$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_3CH_3$   
 369:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_3$ ,  
 $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=CH_2COO(C_2H_4O)_{20}C_{16}H_{33}$   
 370:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_3$ ,  
 $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=CH_2COO(C_2H_4O)_{22}C_{16}H_{33}$   
 371:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_3$ ,  
 $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=C_{10}H_{21}COO(OC_2H_4)_2OCH_3$

- 372:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=H$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_3THP$   
 373:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_3$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_3THP$   
 374:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_2CH_2C(CH_3)_3$ ,  
 $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_3THP$   
 375:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=OCH_2Ph$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_3THP$   
 376:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=H$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_6THP$   
 377:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_3$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_6THP$   
 378:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_2CH_2C(CH_3)_3$ ,  
 $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_6THP$   
 379:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=OCH_2Ph$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_6THP$   
 380:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=OCH_2Ph$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_6PMB$   
 381:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=H$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_9PMB$   
 382:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_3$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_9PMB$   
 383:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_2CH_2C(CH_3)_3$ ,  
 $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_9PMB$   
 384:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=OCH_2Ph$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_9PMB$   
 385:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_3$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_{12}PMB$   
 386:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=OCH_2Ph$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_{12}PMB$   
 387:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=OCH_2Ph$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_{18}PMB$   
 388:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=OCH_2Ph$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_6CH_2Ph$   
 389:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=OCH_2Ph$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_9CH_2Ph$   
 390:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=H$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_{12}CH_2Ph$   
 391:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_3$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_{12}CH_2Ph$   
 392:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_2CH_2C(CH_3)_3$ ,  
 $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_{12}CH_2Ph$   
 393:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=OCH_2Ph$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_{12}CH_2Ph$   
 394:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=H$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_{18}CH_2Ph$   
 395:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_3$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_{18}CH_2Ph$   
 396:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_2CH_2C(CH_3)_3$ ,  
 $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_{18}CH_2Ph$   
 397:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=OCH_2Ph$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_{18}CH_2Ph$   
 398:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=H$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_{24}CH_2Ph$   
 399:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_3$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_{24}CH_2Ph$   
 400:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=C(CH_3)_2CH_2C(CH_3)_3$ ,  
 $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_{24}CH_2Ph$   
 401:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=OCH_2Ph$ ,  $R_9=R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=(C_2H_4O)_{24}CH_2Ph$   
 402:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=R_9=COC_5H_{11}$ ,  $R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=R_{17}=R_{18}=H$   
 403:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=R_9=COC_7H_{15}$ ,  $R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=R_{17}=R_{18}=H$   
 404:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=R_9=COC_9H_{19}$ ,  $R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=R_{17}=R_{18}=H$   
 405:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=R_9=COC_{11}H_{23}$ ,  $R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=R_{17}=R_{18}=H$   
 406:  $R_1=R_2=R_3=R_4=R_5=R_6=R_7=R_8=R_9=COC_{13}H_{27}$ ,  $R_{10}=R_{11}=R_{12}=R_{13}=R_{14}=R_{15}=R_{16}=R_{17}=R_{18}=H$

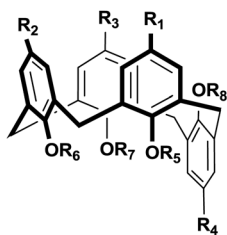


- 407:  $R_1=R_2=R_3=R_4=C_6H_{12}CH(CH_3)_2$ ,  $R_5=R_6=R_7=R_8=O(C_2H_4O)_{16}H$

Scheme 3 Structures of lower-rim hydrophilic amphiphilic calixarenes.

indeed supported by some reported values. For example, Shinkai and co-workers reported that in amphiphilic SCnAs **3**, **160**, **173**, which have 4, 6, and 8 repeat units respectively, the

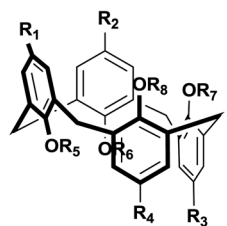
CAC values decrease from 2.5 mM to 1.0 mM and then to 0.7 mM with increasing ring size.<sup>49</sup> Zhao and co-workers synthesized amphiphilic calix[6]arene **305** and calix[8]arene **325** by



408:  $R_1=R_3=R_6=R_8=H$ ,  $R_2=R_4=COOH$ ,  $R_5=R_7=COPh$

409:  $R_1=R_3=R_6=R_7=H$ ,  $R_2=R_4=COOH$ ,  $R_5=R_8=COPh$

410:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=C_3H_6NHC(NH_2)_2^+$



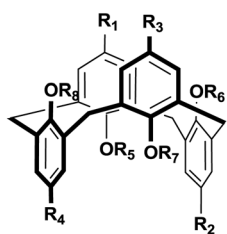
411:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=C_3H_6NHC(NH_2)_2^+$

412:  $R_1=R_2=R_3=R_4=COOH$ ,  $R_5=R_6=R_7=R_8=C_3H_7$

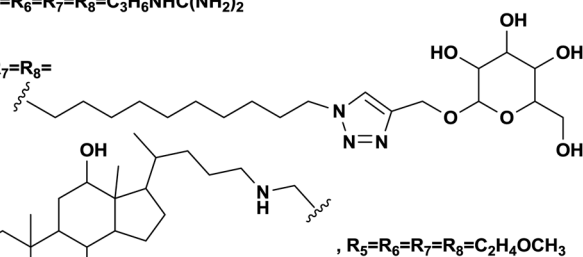
413:  $R_1=R_2=R_3=R_4=COOH$ ,  $R_5=R_6=R_7=R_8=CH(CH_3)_2$

414:  $R_1=R_2=R_3=COOH$ ,  $R_4=H$ ,  $R_5=R_6=R_7=R_8=CH(CH_3)_2$

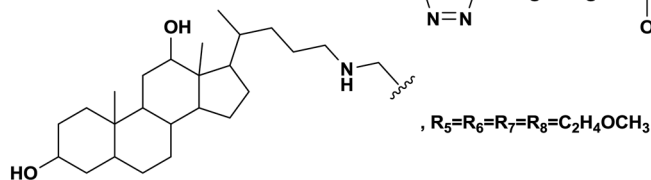
415:  $R_1=R_2=R_3=R_4=C(CH_3)_3$ ,  $R_5=R_6=R_7=R_8=C_3H_6NHC(NH_2)_2^+$



416:  $R_1=R_2=R_3=R_4=H$ ,  $R_5=R_6=R_7=R_8=$

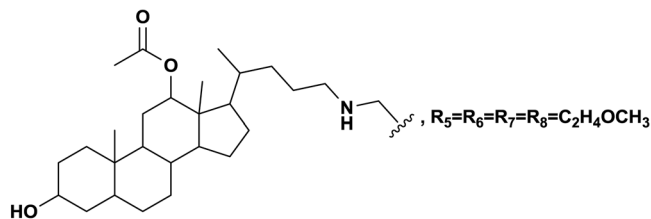


417:  $R_1=R_2=R_3=R_4=$



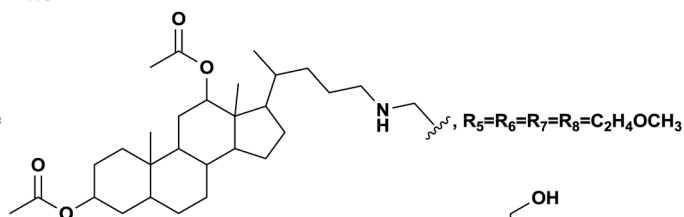
,  $R_5=R_6=R_7=R_8=C_2H_4OCH_3$

418:  $R_1=R_2=R_3=R_4=$



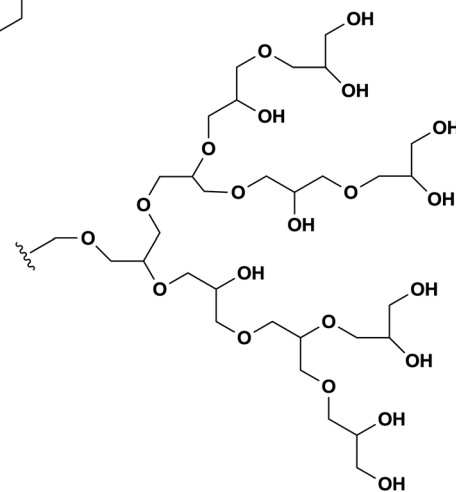
,  $R_5=R_6=R_7=R_8=C_2H_4OCH_3$

419:  $R_1=R_2=R_3=R_4=$

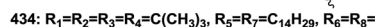
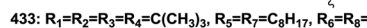
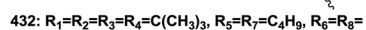
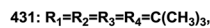
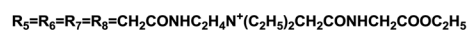
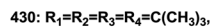
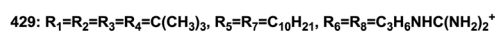
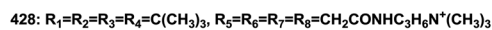
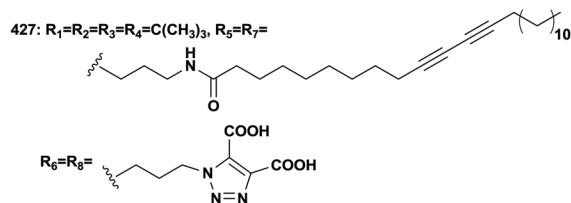
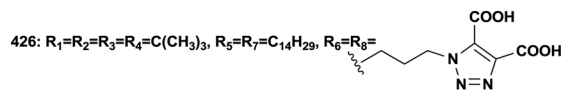
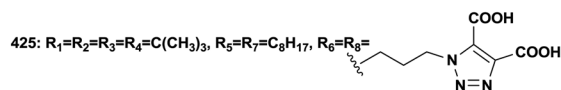
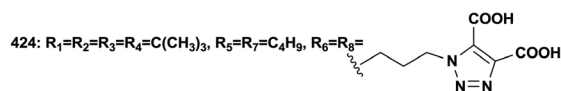
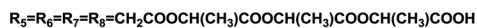
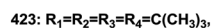
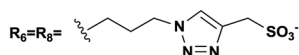
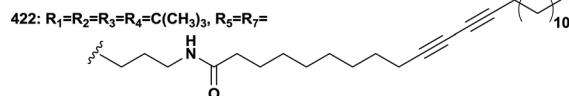
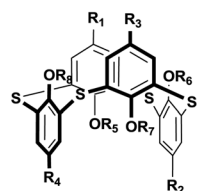
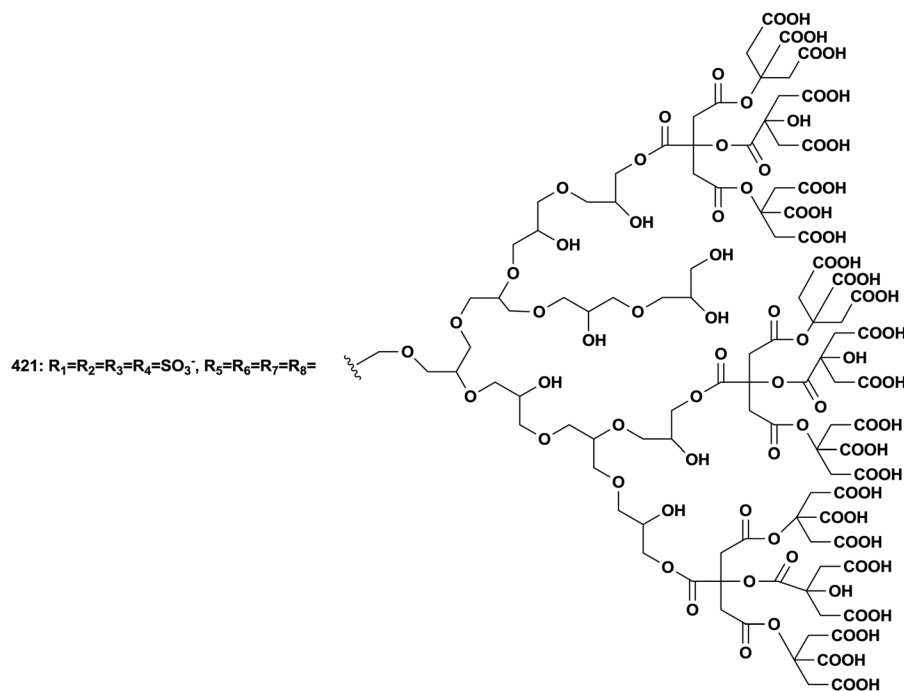


,  $R_5=R_6=R_7=R_8=C_2H_4OCH_3$

420:  $R_1=R_2=R_3=R_4=SO_3^-$ ,  $R_5=R_6=R_7=R_8=$









Scheme 4 Structures of bola-type amphiphilic calixarenes.

introducing acetoxy groups into the hydroxyls of calixarenes.<sup>259</sup> They interpreted the decrease in CAC (5.79–3.05  $\mu\text{M}$ ) with increasing phenyl groups (6–8) as strengthening of the hydrophobic interactions. However, other examples didn't show any significant trend. For instance, Xu and coworkers found the CAC of choline-modified calix[5]arene **158** (5.5  $\mu\text{M}$ ) is slightly higher than that of the corresponding calix[4]arene, **62** (5.2  $\mu\text{M}$ ).<sup>46</sup> Shinkai and coworkers reported that the CACs of lower-rim sulfonic group modified **186**, **299** and **322** are 0.55 mM, 0.58 mM and 0.40 mM by conductivity at 30  $^{\circ}\text{C}$ , respectively.<sup>49</sup> These unexpected phenomena may be explained by the shape of the skeleton and the conformation in bulk solution. As an example of conformation influencing CAC, Basilio and co-workers studied amphiphilic SCnAs **6**, **162** and **175**. The CAC values increase

(from 0.488 to 0.750 mM) with increasing number of monomeric units (from 4 to 8).<sup>54</sup> The calix[4]arene derivative, which is preorganized into the cone conformation, is favourable for the formation of globular aggregates. The calix[6]arene and calix[8]arene derivatives do not adopt cone conformations in bulk solution. Further thermodynamic studies show that changing these conformations to the more favourable cone conformer in the aggregates implied an energetic cost that contributed to making the micellization Gibbs free energy ( $\Delta G_M^{\circ}$ ) less efficient. The other example related to conformations was reported by Arimori and coworkers.<sup>132</sup> CAC of amphiphilic calix[4]arene **412** in a cone conformation is 10  $\mu\text{M}$  whereas in a 1,3-alternate conformation, **412** could not aggregate at a concentration of even up to 10 mM. This difference implies that the conformation of calixarene is a critical factor of CAC.

Table 1 References of upper-rim hydrophilic amphiphilic calixarenes in Scheme 2

| Compound | Ref.                        | Compound | Ref.                     | Compound | Ref.            | Compound | Ref.                               |
|----------|-----------------------------|----------|--------------------------|----------|-----------------|----------|------------------------------------|
| 1        | 37                          | 48       | 107                      | 94       | 122 and 124     | 140      | 142 and 143                        |
| 2        | 44                          | 49       | 45, 112 and 113          | 95       | 124             | 141      | 142 and 143                        |
| 3        | 49–59                       | 50       | 45, 112 and 113          | 96       | 124             | 142      | 142, 143 and 146                   |
| 4        | 62–66                       | 51       | 117–121                  | 97       | 122             | 143      | 63 and 150                         |
| 5        | 79                          | 52       | 45                       | 98       | 136             | 144      | 63 and 150                         |
| 6        | 52–54, 58, 64 and 82–89     | 53       | 108                      | 99       | 136             | 145      | 150                                |
| 7        | 64 and 95                   | 54       | 108 and 128              | 100      | 139             | 146      | 63                                 |
| 8        | 53, 54, 64 and 106          | 55       | 108                      | 101      | 63 and 140      | 147      | 63                                 |
| 9        | 56, 62, 82, 86, 109 and 110 | 56       | 131                      | 102      | 63              | 148      | 168                                |
| 10       | 114                         | 57       | 127 and 132              | 103      | 94              | 149      | 170                                |
| 11       | 114 and 116                 | 58       | 74, 75, 127, 134 and 135 | 104      | 94              | 150      | 170                                |
| 12       | 114 and 126                 | 59       | 138                      | 105      | 136             | 151      | 170                                |
| 13       | 114 and 126                 | 60       | 42 and 116               | 106      | 136             | 152      | 176                                |
| 14       | 114                         | 61       | 42 and 43                | 107      | 161 and 162     | 153      | 177                                |
| 15       | 129                         | 62       | 46 and 47                | 108      | 167             | 154      | 25 and 179                         |
| 16       | 130                         | 63       | 60                       | 109      | 167             | 155      | 180 and 181                        |
| 17       | 116                         | 64       | 71–77                    | 110      | 172             | 156      | 180                                |
| 18       | 43                          | 65       | 77                       | 111      | 174             | 157      | 107                                |
| 19       | 61, 104, 105 and 137        | 66       | 72 and 74–77             | 112      | 174             | 158      | 46                                 |
| 20       | 130                         | 67       | 77 and 100–103           | 113      | 172             | 159      | 37                                 |
| 21       | 38–40                       | 68       | 77                       | 114      | 172             | 160      | 49, 59, 82, 106, 148 and 186       |
| 22       | 45                          | 69       | 77                       | 115      | 141             | 161      | 79                                 |
| 23       | 45                          | 70       | 115                      | 116      | 141 and 182–184 | 162      | 5, 49, 53, 54, 82, 86, 147 and 148 |
| 24       | 42, 45, 67–70               | 71       | 76                       | 117      | 145 and 182     | 163      | 5, 37, 86, 106, 147 and 151–154    |
| 25       | 23                          | 72       | 76 and 77                | 118      | 141             | 164      | 155                                |
| 26       | 90                          | 73       | 76 and 127               | 119      | 183             | 165      | 158                                |
| 27       | 90                          | 74       | 72 and 76                | 120      | 141             | 166      | 49 and 160                         |
| 28       | 90                          | 75       | 63                       | 121      | 141             | 167      | 165 and 166                        |
| 29       | 111                         | 76       | 63                       | 122      | 145             | 168      | 73                                 |
| 30       | 90                          | 77       | 133                      | 123      | 149             | 169      | 171                                |
| 31       | 38                          | 78       | 63                       | 124      | 123             | 170      | 173                                |
| 32       | 40                          | 79       | 66 and 95                | 125      | 157             | 171      | 173                                |
| 33       | 40                          | 80       | 43                       | 126      | 159             | 172      | 37                                 |
| 34       | 41                          | 81       | 43                       | 127      | 163 and 164     | 173      | 49                                 |
| 35       | 41                          | 82       | 48                       | 128      | 163 and 164     | 174      | 79                                 |
| 36       | 41                          | 83       | 61                       | 129      | 169             | 175      | 53 and 54                          |
| 37       | 41                          | 84       | 78                       | 130      | 169             | 176      | 37 and 153                         |
| 38       | 41                          | 85       | 81                       | 131      | 127             | 177      | 144                                |
| 39       | 41                          | 86       | 93 and 94                | 132      | 175             | 178      | 144                                |
| 40       | 41                          | 87       | 61, 104 and 105          | 133      | 175             | 179      | 144                                |
| 41       | 41                          | 88       | 108                      | 134      | 178             | 180      | 144                                |
| 42       | 41                          | 89       | 108                      | 135      | 178             | 181      | 144                                |
| 43       | 41                          | 90       | 108                      | 136      | 178             | 182      | 144                                |
| 44       | 41                          | 91       | 122–125                  | 137      | 185             | 183      | 144                                |
| 45       | 80                          | 92       | 124                      | 138      | 185             | 184      | 156                                |
| 46       | 91 and 92                   | 93       | 124                      | 139      | 185             | 185      | 156                                |
| 47       | 92 and 96–99                |          |                          |          |                 |          |                                    |

On the other hand, similar to conventional surfactants, CACs of amphiphilic calixarenes are directly related to their hydrophobic/hydrophilic groups and affected by environments (temperature, pH, ionic strength and solvent).

For example, Rodik and co-workers synthesized a series of choline modified amphiphilic calixarenes **64–66** and **69** bearing various lengths of alkyl chains at the lower rim.<sup>77</sup> They found that CACs decreased (390–0.75  $\mu\text{M}$ ) with the increase in the chain length (3–16  $\text{CH}_2$  units). And we have already discussed before that CACs decrease more rapidly with longer alkyl chains.

Introducing extra interactions such as hydrogen bonds is an efficient way to enhance assembly, decreasing the CAC. Consoli and co-workers synthesized two amphiphilic calix[4]arenes **261** and **262** decorated with nucleotides at the lower rim.<sup>229</sup>

The CAC of **262** bearing adenine nucleotides (0.22 mM) is lower than that of **261** bearing thymine nucleotides (0.51 mM), which is consistent with the capacity of adenine to establish stronger stacking interactions with respect to thymine nucleobase.

High salt concentration could reduce electrostatic repulsion of like charges at the hydrophilic head group, resulting in a lower CAC value. Rodik and co-workers synthesized amphiphilic calix[4]arenes **64** and **66** bearing cationic choline groups at the upper rim and alkyl chains at the lower rim.<sup>72</sup> Their CACs were found to be decreased from pure water (0.37 mM for **64** and 0.048 mM for **66**) to 20 mM Tris buffer (0.067 mM for **64** and 0.0062 mM for **66**). Mchedlov-Petrosyan and co-workers found that the CAC of **64** decreased (4–0.12 mM) with increasing concentration of NaCl as well.<sup>73</sup>

Table 2 References of lower-rim hydrophilic amphiphilic calixarenes in Scheme 3

| Compound | Ref.                                      | Compound | Ref.             | Compound | Ref.        | Compound | Ref.        | Compound | Ref. |
|----------|---|----------|------------------|----------|-------------|----------|-------------|----------|------|
| 186      | 49, 187 and 188                           | 236      | 208              | 286      | 235 and 236 | 336      | 243         | 386      | 245  |
| 187      | 37 and 49                                 | 237      | 200              | 287      | 235 and 236 | 337      | 243 and 244 | 387      | 245  |
| 188      | 194                                       | 238      | 200, 204 and 223 | 288      | 237         | 338      | 244         | 388      | 245  |
| 189      | 197                                       | 239      | 204 and 227      | 289      | 247         | 339      | 244         | 389      | 245  |
| 190      | 197                                       | 240      | 200              | 290      | 247         | 340      | 248         | 390      | 245  |
| 191      | 197                                       | 241      | 200 and 223      | 291      | 249         | 341      | 244         | 391      | 245  |
| 192      | 190, 197 and 201                          | 242      | 200              | 292      | 232 and 250 | 342      | 244         | 392      | 245  |
| 193      | 203                                       | 243      | 191              | 293      | 250         | 343      | 244         | 393      | 245  |
| 194      | 210                                       | 244      | 191              | 294      | 251–254     | 344      | 244         | 394      | 245  |
| 195      | 199 and 212                               | 245      | 191              | 295      | 257         | 345      | 245         | 395      | 245  |
| 196      | 203                                       | 246      | 191              | 296      | 257         | 346      | 245         | 396      | 245  |
| 197      | 193                                       | 247      | 191              | 297      | 49          | 347      | 245         | 397      | 245  |
| 198      | 92  | 248      | 191              | 298      | 49          | 348      | 245         | 398      | 245  |
| 199      | 113 and 198                               | 249      | 191              | 299      | 49          | 349      | 245         | 399      | 245  |
| 200      | 198                                       | 250      | 191              | 300      | 49          | 350      | 245         | 400      | 245  |
| 201      | 113                                       | 251      | 191              | 301      | 49          | 351      | 245         | 401      | 245  |
| 202      | 45, 198 and 230                           | 252      | 191              | 302      | 246         | 352      | 245         | 402      | 262  |
| 203      | 45  | 253      | 209              | 303      | 246         | 353      | 245         | 403      | 262  |
| 204      | 113 and 198                               | 254      | 211              | 304      | 246         | 354      | 245         | 404      | 262  |
| 205      | 238                                       | 255      | 213              | 305      | 259         | 355      | 245         | 405      | 262  |
| 206      | 189                                       | 256      | 213              | 306      | 246         | 356      | 245         | 406      | 262  |
| 207      | 189                                       | 257      | 213              | 307      | 246         | 357      | 245         | 407      | 22   |
| 208      | 189                                       | 258      | 213              | 308      | 246         | 358      | 245         |          |      |
| 209      | 198                                       | 259      | 213              | 309      | 263         | 359      | 245         |          |      |
| 210      | 102                                       | 260      | 213              | 310      | 264         | 360      | 245         |          |      |
| 211      | 198                                       | 261      | 194 and 229      | 311      | 242         | 361      | 244         |          |      |
| 212      | 202 and 203                               | 262      | 194 and 229      | 312      | 246         | 362      | 244         |          |      |
| 213      | 207                                       | 263      | 234              | 313      | 246         | 363      | 244         |          |      |
| 214      | 207                                       | 264      | 234              | 314      | 246         | 364      | 244         |          |      |
| 215      | 207                                       | 265      | 234 and 241      | 315      | 246         | 365      | 245         |          |      |
| 216      | 190, 207 and 215–220                      | 266      | 192              | 316      | 246         | 366      | 245         |          |      |
| 217      | 190, 207, 215, 216, 219, 221 and 222      | 267      | 192              | 317      | 246         | 367      | 245         |          |      |
| 218      | 190, 207 and 215–219                      | 268      | 196              | 318      | 195         | 368      | 245         |          |      |
| 219      | 190, 193, 201, 207, 215, 216, 225 and 226 | 269      | 196              | 319      | 255         | 369      | 256         |          |      |
| 220      | 207 and 216                               | 270      | 196              | 320      | 255         | 370      | 258         |          |      |
| 221      | 207 and 216                               | 271      | 196              | 321      | 49          | 371      | 258         |          |      |
| 222      | 231                                       | 272      | 206              | 322      | 49          | 372      | 245         |          |      |
| 223      | 233                                       | 273      | 206              | 323      | 244         | 373      | 245         |          |      |
| 224      | 231                                       | 274      | 206              | 324      | 244         | 374      | 245         |          |      |
| 225      | 239 and 240                               | 275      | 214              | 325      | 259         | 375      | 245         |          |      |
| 226      | 190                                       | 276      | 214              | 326      | 260 and 261 | 376      | 245         |          |      |
| 227      | 193                                       | 277      | 214              | 327      | 244         | 377      | 245         |          |      |
| 228      | 195                                       | 278      | 224              | 328      | 244         | 378      | 245         |          |      |
| 229      | 199                                       | 279      | 224              | 329      | 244         | 379      | 245         |          |      |
| 230      | 200                                       | 280      | 228              | 330      | 244         | 380      | 245         |          |      |
| 231      | 200                                       | 281      | 228              | 331      | 248         | 381      | 245         |          |      |
| 232      | 200, 204 and 205                          | 282      | 188 and 232      | 332      | 198         | 382      | 245         |          |      |
| 233      | 208                                       | 283      | 235–237          | 333      | 243 and 244 | 383      | 245         |          |      |
| 234      | 208                                       | 284      | 235–237          | 334      | 243         | 384      | 245         |          |      |
| 235      | 208                                       | 285      | 235 and 236      | 335      | 243         | 385      | 245         |          |      |

Similarly, the pH value could change the protonation states of hydrophilic heads, influencing charge interactions, resulting in a CAC change. Fujii and co-workers synthesized a new amphiphilic calix[4]arene **91** with hydrophilic amino end groups.<sup>122</sup> With pH increasing from 3 (below the  $pK_a$  of amino group) to 8 (above the  $pK_a$  of amino group), the CAC decreased (from 0.11 to 0.042 mM). Further, they prepared a new calix[4]arene-based lipid **101** containing glutamic acid as the hydrophilic group.<sup>63,140</sup> The  $\alpha$ -amine and the  $\gamma$ -carboxylic acid groups of the glutamic acid moiety allowed a continuous change in the state of the head group from cationic to zwitterionic and then to anionic with increasing pH. The CAC at pH 7.5 (1.0  $\mu$ M) was

lower than that obtained under other pH conditions (4.4  $\mu$ M at pH 3.2 and 1.8  $\mu$ M at pH 10) because the intermolecular electrostatic repulsions are cancelled by the zwitterionic nature.

**2.2.2 Diverse morphology.** Besides CAC, morphology is another important property of amphiphilic assembly. It is not only an interesting topic in fundamental research, but also related to potential applications. NMR, DOSY, small-angle X-ray scattering (SAXS), and photo correlation spectroscopy (PCS) are methods that could be used to measure the size and shape of aggregates, while transmission electron microscopy (TEM), scanning electron microscopy (SEM), and AFM could provide us with more intuitional pictures. We summarize self-assembling

Table 3 References of bola-type amphiphilic calixarenes in Scheme 4

| Compound | Ref. | Compound | Ref. | Compound | Ref. | Compound | Ref. |
|----------|------|----------|------|----------|------|----------|------|
| 408      | 40   | 420      | 265  | 432      | 266  | 444      | 267  |
| 409      | 40   | 421      | 265  | 433      | 266  | 445      | 267  |
| 410      | 230  | 422      | 268  | 434      | 266  | 446      | 269  |
| 411      | 230  | 423      | 270  | 435      | 271  | 447      | 269  |
| 412      | 40   | 424      | 272  | 436      | 271  | 448      | 273  |
| 413      | 40   | 425      | 272  | 437      | 271  | 449      | 273  |
| 414      | 40   | 426      | 269  | 438      | 271  | 450      | 273  |
|          |      |          | and  |          |      |          |      |
|          |      |          | 272  |          |      |          |      |
| 415      | 230  | 427      | 268  | 439      | 271  | 451      | 273  |
| 416      | 274  | 428      | 232  | 440      | 271  | 452      | 242  |
|          |      |          |      |          |      |          | and  |
|          |      |          |      |          |      |          | 275– |
|          |      |          |      |          |      |          | 277  |
| 417      | 228  | 429      | 120  | 441      | 271  | 453      | 273  |
| 418      | 228  | 430      | 247  | 442      | 271  | —        | —    |
| 419      | 228  | 431      | 247  | 443      | 267  | —        | —    |

morphologies of all reported amphiphilic calixarenes in aqueous solution in Table 5, which does not include Langmuir–Blodgett films formed at the air–water interface.

Compared with corresponding conventional surfactants, self-assemblies of amphiphilic calixarenes show diverse morphologies. For example, sodium dodecyl sulphate (SDS) forms spherical micelles with an average radius of 2.09 nm.<sup>280</sup> Its corresponding calixarene, amphiphilic sulfonatocalix[4]arene **9**, forms micelles with an average radius of 6.9 nm<sup>109</sup> and the hexameric derivative **163** forms aggregates with various sizes (radii from about 70 nm to 195 nm) depending on the concentration.<sup>154</sup> For positively charged surfactants, dodecylguanidine hydrochloride forms micelles as well,<sup>281</sup> while the amphiphilic guanidinium-modified calix[4]arene **51** is able to form SLN with an average radius of 73 nm.<sup>117</sup> Such great differences mainly come from their unique skeletons. It is well known that the critical packing parameter (CPP) proposed by Israelachvili and coworkers is a parameter to estimate the morphology of an amphiphilic assembly.<sup>282</sup> Definition of the CPP value is  $P = V_H/(a_0l_c)$ , where  $V_H$  is the volume occupied by hydrophobic groups in the assembly core,  $a_0$  is cross-sectional area occupied by the hydrophilic group at the assembly–solution interface, and  $l_c$  is the chain length of the hydrophobic group in the assembly core. However, the CPP is hard to precisely apply in the case of macrocyclic amphiphiles. Various sizes and conformations of skeletons result in complicated, unpredictable, and diverse morphologies.

For example, Zhao and coworkers reported fully carboxylic acid modified amphiphilic calix[6]arene **305** and calix[8]arene **325**.<sup>259</sup> The mean radius of aggregates of **305** ( $111.2 \pm 17.4$  nm) is larger than that of **325** ( $89.8 \pm 14.8$  nm). Similarly, Xu and coworkers investigated choline modified amphiphilic calix[4]arene **62** and calix[5]arene **158**.<sup>46</sup> Despite their similar CAC values, the average radius of vesicles of **62** (75 nm) is almost two fold that of **158** (40 nm) (Fig. 2). The explanation of decreasing diameter with a larger skeleton is controversial; it may be related to an enhanced hydrophobic effect, different symmetry, or lower entropy loss. Exceptionally, Basilio and coworkers reported that an ellipsoidal micelle of amphiphilic sulfonatocalix[8]arene **175**

has a longer main semiaxis (7.3 nm) than that of calix[6]arene **162** (6.6 nm), which is the result of a more flexible conformation of calix[8]arene.<sup>54</sup>

Conformation is also an important factor. Stoikov's group reported a series of quaternary ammonium-modified amphiphilic calix[4]arenes which have the same decoration and different conformations (**283**, **289** and **290** in cone conformation and **428**, **430** and **431** in 1,3-alternate conformation).<sup>232,247</sup> At a concentration of 0.3 mM, the radius of assembly of **283** (227 nm) is larger than that of **428** (71 nm). At a concentration of 1 mM, the radius of assembly of **289** (70.8 nm) is larger than that of **430** (49.9 nm) while the radius of assembly of **290** (37.7 nm) is smaller than that of **431** (46.4 nm). We assume that conformations of skeletons in assemblies affect the curvature and sizes of assemblies due to different aggregation modes.

Certainly, the length of hydrophobic chains and the structure of hydrophilic head groups could affect the morphologies of aggregates. For instance, increasing the hydrophobic chain from 6 carbons to 9 carbons causes different morphologies of amphiphilic aminocalix[4]arenes **94** and **97** assemblies, which are micelle and cylinder respectively (Fig. 2).<sup>122</sup> For a series of amphiphilic calixarenes that show similar aggregation morphologies, some of them present a trend in size. Jebors and coworkers reported several SLNs assembled by acylcalix[9]arenes with different lengths of the carbon chain (**402–406**). The sizes of their aggregates decrease with increasing carbon atoms (radii decrease from 108 nm to 41 nm).<sup>262</sup> Similarly, Burirov and coworkers studied two kinds of amine modified amphiphilic calixarenes with 4 carbons (**98** and **105**) and 8 carbons (**99** and **106**) as the hydrophobic chain, respectively.<sup>136</sup> **98** and **99** are completely modified whereas **105** and **106** are partially modified. Aggregates of **98** and **105** show larger radii (88 nm and 97 nm, respectively) than those of **99** and **106** (70 nm and 77 nm, respectively), respectively. In principle, more and longer hydrophobic chains lead to a stronger hydrophobic effect, resulting in more compact packing, which leads to smaller aggregates. However, there are contrary examples such as a series of cyclodextrin modified amphiphilic calixarenes **127** and **128**, whose aggregate size increases with increasing carbon chain (radii increase from 65 nm to 95 nm).<sup>163,164</sup> This phenomenon may be related to the large volume of cyclodextrin. Besides, the aggregates of bola-type amphiphilic calixarenes **432–434** are of the same size, although they bear 4-carbon chains, 8-carbon chains, and 14-carbon chains, respectively.<sup>266</sup> In brief, we just find limited examples of hydrophobic chains affecting the morphology with a certain trend, while in many cases, morphologies vary irregularly with chain length.

Hydrophilic head affecting the aggregation morphology is an even more complicated topic. Factors such as volume, hydration energy, and interactions between hydrophilic head groups may give us a clue, but it is still difficult to predict aggregate morphologies from their structure. Here we just name several examples that may provide some ideas. Stoikov and coworkers<sup>235–237,247</sup> synthesized several amphiphilic butylthiacalix[4]arenes with quaternary ammonium, as well as amide (**289**, **290**), ester (**287**), benzene (**284**), or phthalimide

Table 4 CACs of amphiphilic calixarenes

| Compound              | CAC (mM)                         | Condition <sup>a</sup>                        | Method <sup>b</sup>                 | Ref. |
|-----------------------|----------------------------------|---|-------------------------------------|------|
| 3                     | 2.5                              | 30 °C   | Conductivity                        | 49   |
| 3                     | 3.05                             | 15 °C   | ITC                                 | 53   |
| 3                     | 3.20                             |   | ITC                                 | 53   |
| 3                     | 3.40                             | 35 °C   | ITC                                 | 53   |
| 3                     | 3.73                             | 45 °C   | ITC                                 | 53   |
| 3                     | 4.16                             | 55 °C   | ITC                                 | 53   |
| 3                     | 3.18                             |   | Conductivity                        | 54   |
| 4                     | $(8.98 \pm 2.69) \times 10^{-2}$ | 10 mM NaCl                                    | Fluorescence                        | 65   |
| 4                     | $(5.84 \pm 4.49) \times 10^{-2}$ | 15 mM NaCl                                    | Fluorescence                        | 65   |
| 4                     | 0.566                            | 50 mM NaCl                                    | Fluorescence                        | 66   |
| 6                     | 0.54                             |   | Fluorescence                        | 84   |
| 6                     | 0.32                             | D <sub>2</sub> O                              | DOSY                                | 84   |
| 6                     | 0.450                            | 15 °C   | ITC                                 | 53   |
| 6                     | 0.488                            |   | ITC                                 | 53   |
| 6                     | 0.520                            | 35 °C   | ITC                                 | 53   |
| 6                     | 0.600                            | 45 °C   | ITC                                 | 53   |
| 6                     | 0.689                            | 55 °C   | ITC                                 | 53   |
| 6                     | 0.491                            |   | Conductivity                        | 54   |
| 6                     | 0.040                            | 10 mM NaCl                                    | Fluorescence                        | 64   |
| 7                     | 0.020                            | 10 mM NaCl                                    | Fluorescence                        | 64   |
| 8                     | 0.0700                           | 15 °C   | ITC                                 | 53   |
| 8                     | 0.0850                           |   | ITC                                 | 53   |
| 8                     | 0.0940                           | 35 °C   | ITC                                 | 53   |
| 8                     | 0.112                            | 45 °C   | ITC                                 | 53   |
| 8                     | 0.150                            | 55 °C   | ITC                                 | 53   |
| 8                     | 0.0911                           |   | Conductivity                        | 54   |
| 9                     | 0.02                             |   | Fluorescence                        | 109  |
| 15                    | 0.0285                           |   | AFM                                 | 129  |
| 21                    | 0.65                             | pH 10 NaHCO <sub>3</sub> , <i>I</i> = 0.123 M | UV-vis                              | 38   |
| 31                    | 0.045                            | pH 10 NaHCO <sub>3</sub> , <i>I</i> = 0.123 M | UV-vis                              | 38   |
| 31                    | 0.035                            | pH 10 NaHCO <sub>3</sub> , <i>I</i> = 0.123 M | UV-vis                              | 38   |
| 34                    | 1                                | pH 6, 20 °C                                   | Surface tension                     | 41   |
| 34                    | 1.3                              | pH 8, 20 °C                                   | Surface tension                     | 41   |
| 35                    | 1.6                              | pH 6, 20 °C                                   | Surface tension                     | 41   |
| 35                    | 1.3                              | pH 8, 20 °C                                   | Surface tension                     | 41   |
| 36                    | 1.3                              | pH 6, 20 °C                                   | Surface tension                     | 41   |
| 36                    | 1                                | pH 8, 20 °C                                   | Surface tension                     | 41   |
| 37                    | 1.2                              | pH 6, 20 °C                                   | Surface tension                     | 41   |
| 37                    | 1.1                              | pH 8, 20 °C                                   | Surface tension                     | 41   |
| 38                    | 1.3                              | pH 6, 20 °C                                   | Surface tension                     | 41   |
| 38                    | 1.2                              | pH 8, 20 °C                                   | Surface tension                     | 41   |
| 39                    | 1.2                              | pH 6, 20 °C                                   | Surface tension                     | 41   |
| 39                    | 1                                | pH 8, 20 °C                                   | Surface tension                     | 41   |
| 40                    | 1.2                              | pH 6, 20 °C                                   | Surface tension                     | 41   |
| 40                    | 1.1                              | pH 8, 20 °C                                   | Surface tension                     | 41   |
| 41                    | 1.2                              | pH 6, 20 °C                                   | Surface tension                     | 41   |
| 41                    | 0.2                              | pH 8, 20 °C                                   | Surface tension                     | 41   |
| 42                    | 0.1                              | pH 6, 20 °C                                   | Surface tension                     | 41   |
| 42                    | 0.4                              | pH 8, 20 °C                                   | Surface tension                     | 41   |
| 43                    | 0.5                              | pH 6, 20 °C                                   | Surface tension                     | 41   |
| 43                    | 0.1                              | pH 8, 20 °C                                   | Surface tension                     | 41   |
| 44                    | 0.1                              | pH 6, 20 °C                                   | Surface tension                     | 41   |
| 44                    | 0.1                              | pH 8, 20 °C                                   | Surface tension                     | 41   |
| 46                    | 0.023                            |   | Conductivity                        | 91   |
| 46                    | 0.056                            | pH 7 Na <sup>+</sup> /K <sup>+</sup> PB       | Fluorescence                        | 91   |
| 46                    | 0.037                            | pH 9 Na <sup>+</sup> borate                   | Fluorescence                        | 91   |
| 46                    | 0.041                            | pH 7 Na <sup>+</sup> /K <sup>+</sup> PB       | Fluorescence                        | 91   |
| 46                    | 0.0021                           | pH 9 Na <sup>+</sup> borate                   | Fluorescence                        | 91   |
| 46                    | 0.073                            | pH 7 Na <sup>+</sup> /K <sup>+</sup> PB       | Fluorescence                        | 91   |
| 46                    | 0.052                            | pH 9 Na <sup>+</sup> borate                   | Fluorescence                        | 91   |
| 46                    | 0.04                             | pH 7 Na <sup>+</sup> /K <sup>+</sup> PB       | Fluorescence                        | 91   |
| 46                    | 0.043                            | pH 9 Na <sup>+</sup> borate,                  | Fluorescence                        | 91   |
| 47                    | ≤0.04                            | <i>I</i> = 0.07 M                             | Fluorescence                        | 98   |
| 49                    | 0.2                              | D <sub>2</sub> O                              | <sup>1</sup> H NMR                  | 112  |
| 57                    | 0.01                             | 17 °C   | Surface tension                     | 132  |
| 57                    | 0.01                             | 30 °C   | Fluorescence                        | 132  |
| 57                    | 3.8                              |   | <sup>1</sup> H NMR                  | 127  |
| 58 (I <sup>-</sup> )  | 8.7                              |   | <sup>1</sup> H NMR                  | 127  |
| 58 (Cl <sup>-</sup> ) | 0.00879                          | 22–23 °C                                      | Surface tension                     | 75   |
| 58 (Cl <sup>-</sup> ) | 9.8                              | 22–23 °C; 30 °C                               | UV-vis, osmolality, surface tension | 134  |

Table 4 (continued)

| Compound | CAC (mM)                       | Condition <sup>a</sup>          | Method <sup>b</sup>           | Ref. |
|----------|--------------------------------|---------------------------------|-------------------------------|------|
| 62       | 0.0052                         |                                 | Fluorescence                  | 46   |
| 64       | 0.37                           |                                 | Fluorescence                  | 72   |
| 64       | 0.067                          | 20 mM Tris, pH 7.4              | Fluorescence                  | 72   |
| 64       | 0.081                          | 20 mM Tris, pH 7.4, 150 mM NaCl | Fluorescence                  | 72   |
| 64       | 4                              |                                 | UV-vis                        | 73   |
| 64       | 0.12                           | 0.05 mM NaCl                    | UV-vis                        | 73   |
| 64       | 0.367                          | 22–23 °C                        | Surface tension               | 75   |
| 64       | 0.39                           |                                 | Fluorescence                  | 77   |
| 64       | 0.068                          | 20 mM PB, pH 7.4                | Fluorescence                  | 77   |
| 64       | 0.064                          | 20 mM PB, pH 7.4, 150 mM NaCl   | Fluorescence                  | 77   |
| 65       | 0.026                          |                                 | Fluorescence                  | 77   |
| 65       | 0.0098                         | 20 mM PB, pH 7.4                | Fluorescence                  | 77   |
| 65       | 0.0044                         | 20 mM PB, pH 7.4, 150 mM NaCl   | Fluorescence                  | 77   |
| 66       | 0.048                          |                                 | Fluorescence                  | 72   |
| 66       | 0.0062                         | 20 mM Tris, pH 7.4              | Fluorescence                  | 72   |
| 66       | 0.003                          | 20 mM Tris, pH 7.4, 150 mM NaCl | Fluorescence                  | 72   |
| 66       | 0.019                          |                                 | Fluorescence                  | 77   |
| 66       | 0.0044                         | 20 mM PB, pH 7.4                | Fluorescence                  | 77   |
| 66       | 0.0027                         | 20 mM PB, pH 7.4, 150 mM NaCl   | Fluorescence                  | 77   |
| 66       | 0.0478                         | 22–23 °C                        | Surface tension               | 75   |
| 67       | 0.008                          |                                 | Fluorescence                  | 101  |
| 69       | 0.00075                        |                                 | Fluorescence                  | 77   |
| 69       | 0.001                          | 20 mM PB, pH 7.4                | Fluorescence                  | 77   |
| 72       | 0.017                          |                                 | Fluorescence                  | 77   |
| 72       | 0.0036                         | 20 mM PB, pH 7.4                | Fluorescence                  | 77   |
| 72       | 0.0030                         | 20 mM PB, pH 7.4, 150 mM NaCl   | Fluorescence                  | 77   |
| 72       | 0.014                          | 20 mM acetate, pH 5             | Fluorescence                  | 77   |
| 73       | 1.4                            |                                 | <sup>1</sup> H NMR            | 127  |
| 74       | 0.01                           |                                 | Fluorescence                  | 72   |
| 74       | 0.0029                         | 20 mM Tris, pH 7.4              | Fluorescence                  | 72   |
| 74       | 0.0018                         | 20 mM Tris, pH 7.4, 150 mM NaCl | Fluorescence                  | 72   |
| 82       | 0.33                           |                                 | Fluorescence                  | 48   |
| 91       | 0.11                           | 50 mM NaCl, pH 3.0              | Fluorescence                  | 122  |
| 91       | 0.042                          | 50 mM NaCl, pH 8.0              | Fluorescence                  | 122  |
| 91       | 0.11                           | pH 8.0 Tris-HCl, 50 mM NaCl     | Fluorescence                  | 123  |
| 91       | 0.11                           | pH 3.0, 50 mM NaCl              | UV-vis                        | 124  |
| 94       | 0.0040                         | 50 mM NaCl, pH 3.0              | Fluorescence                  | 122  |
| 97       | 0.0029                         | 50 mM NaCl, pH 3.0              | Fluorescence                  | 122  |
| 98       | 0.0045                         | MES pH 6.5                      | Fluorescence                  | 136  |
| 98       | 0.0050                         | MES pH 6.5                      | Fluorescence                  | 136  |
| 99       | 0.0028                         | MES pH 6.5                      | Fluorescence                  | 136  |
| 99       | 0.0050                         | MES pH 6.5                      | Fluorescence                  | 136  |
| 101      | $(4.4 \pm 0.2) \times 10^{-3}$ | 50 mM NaCl, pH 3.0              | Fluorescence                  | 140  |
| 101      | $(1.0 \pm 0.1) \times 10^{-3}$ | 50 mM NaCl, pH 8.3              | Fluorescence                  | 140  |
| 101      | $(1.8 \pm 0.2) \times 10^{-3}$ | pH 10, 50 mM NaCl               | Fluorescence                  | 140  |
| 101      | 0.0044                         | pH 3.2                          | —                             | 63   |
| 101      | 0.0010                         | pH 7.5                          | —                             | 63   |
| 101      | 0.0018                         | pH 10                           | —                             | 63   |
| 105      | 0.0064                         | MES pH 6.5                      | Fluorescence                  | 136  |
| 105      | 0.79                           | MES pH 6.5                      | Fluorescence                  | 136  |
| 106      | 0.0048                         | MES pH 6.5                      | Fluorescence                  | 136  |
| 106      | 0.16                           | MES pH 6.5                      | Fluorescence                  | 136  |
| 108      | $(1.8 \pm 0.2) \times 10^{-3}$ | 150 mM NaCl                     | Fluorescence                  | 167  |
| 109      | $(5.0 \pm 1.0) \times 10^{-4}$ | 150 mM NaCl                     | Fluorescence                  | 167  |
| 124 (D)  | 0.13                           | pH 8.0 Tris-HCl, 50 mM NaCl     | Fluorescence                  | 123  |
| 124 (L)  | 0.10                           | pH 8.0 Tris-HCl, 50 mM NaCl     | Fluorescence                  | 123  |
| 125      | 0.00154                        | 50 mM NaCl                      | Fluorescence                  | 157  |
| 126      | 0.025                          |                                 | Fluorescence, surface tension | 159  |
| 131      | 0.21                           | 37 °C                           | Relaxivity                    | 278  |
| 132      | 2.3                            |                                 | Relaxivity                    | 175  |
| 133      | 0.12                           |                                 | Relaxivity                    | 175  |
| 140      | 0.019                          |                                 | Fluorescence                  | 142  |
| 141      | 0.015                          |                                 | Fluorescence                  | 142  |
| 142      | 0.013                          |                                 | Fluorescence                  | 146  |
| 142      | 0.013                          |                                 | Fluorescence                  | 142  |
| 143      | 0.00014                        | 50 mM NaCl                      | Fluorescence                  | 150  |
| 144      | 0.00027                        | 50 mM NaCl                      | Fluorescence                  | 150  |
| 145      | 0.0045                         | 50 mM NaCl                      | Fluorescence                  | 150  |
| 158      | 0.0055                         |                                 | Fluorescence                  | 46   |
| 160      | 1                              | 30 °C                           | Conductivity                  | 49   |

Table 4 (continued)

| Compound            | CAC (mM)  | Condition <sup>a</sup> | Method <sup>b</sup> | Ref. |
|---------------------|---|------------------------|---------------------|------|
| 162                 | 0.5   | 30 °C                  | Surface tension     | 5    |
| 162                 | 0.67  | 30 °C                  | Conductivity        | 5    |
| 162                 | 0.5   | 30 °C                  | Fluorescence        | 5    |
| 162                 | 0.636   | 15 °C                  | ITC                 | 53   |
| 162                 | 0.751   |                        | ITC                 | 53   |
| 162                 | 0.850   | 35 °C                  | ITC                 | 53   |
| 162                 | 0.904   | 45 °C                  | ITC                 | 53   |
| 162                 | 0.957   | 55 °C                  | ITC                 | 53   |
| 162                 | 0.734   |                        | Conductivity        | 54   |
| 163 (micelle)       | 0.6   |                        | DLS                 | 154  |
| 163 (domain)        | $1 \times 10^{-4}$  |                        | DLS                 | 154  |
| 163 (nanoassociate) | $1 \times 10^{-6}$  |                        | DLS                 | 154  |
| 164                 | 0.1   |                        | UV-vis              | 155  |
| 166                 | 0.1   | 30 °C                  | Surface tension     | 49   |
| 166                 | 0.16  | 30 °C                  | Conductivity        | 49   |
| 170                 | $(7.9 \pm 0.5) \times 10^{-3}$  |                        | Fluorescence        | 173  |
| 171                 | $(8.0 \pm 0.2) \times 10^{-3}$  |                        | Fluorescence        | 173  |
| 173                 | 0.5   | 30 °C                  | Surface tension     | 49   |
| 173                 | 0.7   | 30 °C                  | Conductivity        | 49   |
| 175                 | 0.700   | 15 °C                  | ITC                 | 53   |
| 175                 | 0.750   |                        | ITC                 | 53   |
| 175                 | 0.810   | 35 °C                  | ITC                 | 53   |
| 175                 | 0.894   | 45 °C                  | ITC                 | 53   |
| 175                 | 0.994   | 55 °C                  | ITC                 | 53   |
| 175                 | 0.729   |                        | Conductivity        | 54   |
| 186                 | 0.56  | 30 °C                  | Surface tension     | 49   |
| 186                 | 0.55  | 30 °C                  | Conductivity        | 49   |
| 223                 | 0.0005  |                        | UV-vis              | 257  |
| 230                 | 0.4   | 10% DMF aqueous        | Surface tension     | 200  |
| 231                 | CAC <sub>1</sub> : 0.95; CAC <sub>2</sub> : 5.0 <sup>c</sup>                        | 10% DMF aqueous        | Surface tension     | 200  |
| 232                 | CAC <sub>2</sub> : 2.2; CAC <sub>3</sub> : 80 <sup>c</sup>                          |                        | Surface tension     | 200  |
| 232                 | 2   |                        |                     | 205  |
| 233                 | 2.2   |                        |                     | 208  |
| 234                 | 2.1   |                        |                     | 208  |
| 236                 | 2.1   |                        |                     | 208  |
| 237                 | 0.1   | 10% DMF aqueous        | Surface tension     | 200  |
| 238                 | CAC <sub>1</sub> : 0.6; CAC <sub>2</sub> : 3.8; CAC <sub>3</sub> : 75 <sup>c</sup>  |                        | Surface tension     | 200  |
| 238                 | 6.5   |                        | Viscosity           | 200  |
| 238                 | CAC <sub>1</sub> : 0.95; CAC <sub>2</sub> : 6.0; CAC <sub>3</sub> : 60 <sup>c</sup> | 10% DMF aqueous        | Surface tension     | 200  |
| 238                 | 27  | 10% DMF aqueous        | Viscosity           | 200  |
| 239                 | 2.1   |                        |                     | 204  |
| 239                 | 2.7   |                        |                     | 227  |
| 240                 | CAC <sub>1</sub> : 0.2; CAC <sub>2</sub> : 2.0; CAC <sub>3</sub> : 16 <sup>c</sup>  |                        | Surface tension     | 200  |
| 240                 | 78  |                        | Viscosity           | 200  |
| 240                 | CAC <sub>1</sub> : 0.95; CAC <sub>2</sub> : 7.6; CAC <sub>3</sub> : 60 <sup>c</sup> | 10% DMF aqueous        | Surface tension     | 200  |
| 240                 | CAC <sub>2</sub> : 36; CAC <sub>3</sub> : 65 <sup>c</sup>                           | 10% DMF aqueous        | Viscosity           | 200  |
| 241                 | CAC <sub>1</sub> : 0.18; CAC <sub>2</sub> : 4.5 <sup>c</sup>                        |                        | Surface tension     | 200  |
| 241                 | 5.5   |                        | Viscosity           | 200  |
| 242                 | CAC <sub>1</sub> : 0.13; CAC <sub>2</sub> : 0.9 <sup>c</sup>                        |                        | Surface tension     | 200  |
| 242                 | 2.5   |                        | Viscosity           | 200  |
| 261                 | 0.51  |                        | Fluorescence        | 229  |
| 262                 | 0.22  |                        | Fluorescence        | 229  |
| 294                 | 0.64  | D <sub>2</sub> O       | DOSY                | 252  |
| 294                 | 1.15  | D <sub>2</sub> O       | DOSY                | 254  |
| 296                 | 0.0045  |                        | UV-vis              | 257  |
| 298                 | 0.43  | 30 °C                  | Conductivity        | 49   |
| 299                 | 0.61  | 30 °C                  | Surface tension     | 49   |
| 299                 | 0.58  | 30 °C                  | Conductivity        | 49   |
| 300                 | 0.21  | 30 °C                  | Surface tension     | 49   |
| 300                 | 0.25  | 30 °C                  | Conductivity        | 49   |
| 305                 | 0.00579   |                        | Fluorescence        | 259  |
| 322                 | 0.15  | 30 °C                  | Surface tension     | 49   |
| 322                 | 0.40  | 30 °C                  | Conductivity        | 49   |
| 325                 | 0.00305   |                        | Fluorescence        | 259  |
| 407                 | CAC <sub>1</sub> : 0.19; CAC <sub>2</sub> : 6.9 <sup>c</sup>                        |                        | Surface tension     | 22   |
| 416                 | 0.016   |                        | Fluorescence        | 274  |
| 432                 | $(91 \pm 5) \times 10^{-3}$   | pH 7.4 Tris, pyrene    | Fluorescence        | 266  |
| 432                 | $(2.0 \pm 0.1) \times 10^{-3}$  | pH 7.4 Tris, EY        | Fluorescence        | 266  |
| 433                 | $(59 \pm 3) \times 10^{-3}$   | pH 7.4 Tris, pyrene    | Fluorescence        | 266  |



Table 4 (continued)

| Compound | CAC (mM)                       | Condition <sup>a</sup> | Method <sup>b</sup> | Ref. |
|----------|--------------------------------|------------------------|---------------------|------|
| 433      | $(2.6 \pm 0.2) \times 10^{-3}$ | pH 7.4 Tris, EY        | Fluorescence        | 266  |
| 434      | $(33 \pm 2) \times 10^{-3}$    | pH 7.4 Tris, pyrene    | Fluorescence        | 266  |
| 434      | $(2.0 \pm 0.1) \times 10^{-3}$ | pH 7.4 Tris, EY        | Fluorescence        | 266  |
| 443      | 0.024                          |                        | Fluorescence        | 267  |
| 444      | 0.025                          |                        | Fluorescence        | 267  |
| 445      | 0.009                          |                        | Fluorescence        | 267  |

<sup>a</sup> The condition is 25 °C in pure water if no label. *I* is the ionic strength. EY is Eosin Y. <sup>b</sup> ITC: isothermal titration microcalorimetry, DOSY: diffusion-ordered spectroscopy, AFM: atomic force microscopy, NMR: nuclear magnetic resonance. <sup>c</sup> The nomenclature and values of CAC<sub>1</sub>, CAC<sub>2</sub>, and CAC<sub>3</sub> were taken from the original literature without any change.

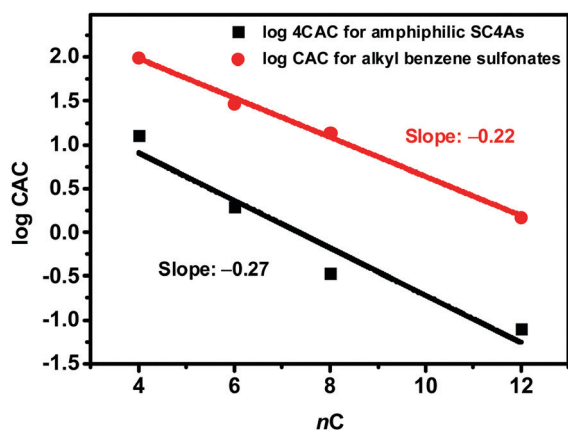


Fig. 1 Variation of the CAC with the number of carbons (*nC*) per alkyl chain for amphiphilic SC4As and alkyl benzene sulfonates.

(286) as hydrophilic groups. The 287 assembly has a significantly smaller radius (1.9 nm) than those of 284 (30.7 nm), 286 (7.3 nm), 289 (> 70.8 nm, Tris buffer) and 290 (> 37.7 nm, Tris buffer), owing to the small size of the ester. Similar results were reported by Shahgaldian and coworkers on diethylphosphate and phosphate modified calixarene, 192 (130 nm) and 226 (163 nm), respectively.<sup>190</sup> On the other hand, Li and coworkers reported cyclodextrin modified calixarene 279 and 278, which possess one and two  $\beta$ -cyclodextrins respectively.<sup>224</sup> In pure water, 279 forms small linear or dot like assemblies, whereas 278 shows large sheet like aggregations (Fig. 2). This phenomenon could be explained by hydrogen bonds between cyclodextrins. Besides, Klymchenko's group synthesized amphiphilic calixarenes modified by choline (66) and a *N*-(2-aminoethyl)-*N,N*-dimethylammonium group (72).<sup>76,77</sup> DLS results showed the micelles of 72 (3.04 nm) are little larger than those of 66 (2.82 nm), probably due to the larger hydration shell of amino groups as compared to hydroxyls. However, there are some examples showing that the morphology is not significantly influenced by different hydrophilic head groups. For example, Burilov and coworkers compared assembly behavior of amphiphilic thiocalix[4]arenes bearing carboxyl (427) and sulfonic (422) groups, respectively; these two compounds show similar shape and size.<sup>268</sup> Compounds 212, 196, and 193, reported by Martin and coworkers, which possess amine, aminodiacetate, and phosphate groups, respectively, present similar results.<sup>202,203</sup>

The morphologies of assemblies are largely related to experimental conditions<sup>283</sup> such as concentration. For example, Padnya and coworkers reported a series of quaternary ammonium based thiocalix[4]arenes 289 and 290, whose aggregate sizes increase with decreasing concentration (radii increase from 70.8 nm to 244.4 nm and from 37.7 nm to 226.9 nm, respectively, with concentration decrease from 1 mM to 1  $\mu$ M).<sup>247</sup> The authors assume that this phenomenon can be explained by the existence of two kinds of aggregates, spherical aggregates and elongated self-associates.

On the other hand, properties of solvents may modulate the morphology of amphiphilic calixarene assemblies, mainly by influencing the interactions of hydrophilic head groups. For instance, the polarity of solvent affects hydrogen bonds, resulting in a change in the packing mode of some amphiphiles. Liang and coworkers synthesized amphiphilic calix[6]biscrowns 450 and 451 possessing amide groups, interacting with each other *via* hydrogen bonds, at the hydrophilic part.<sup>273</sup> Their morphologies underwent a clear transition from spherical to tubular aggregates when the solvent polarity, *i.e.* content of water in water/ethanol solution, is increased (Fig. 2), whereas analogues 448 and 449, without any amide linkage, only showed a size decrease upon the same change in solvent polarity. Similarly, two cyclodextrin modified amphiphilic calix[4]arenes 278 and 279,<sup>224</sup> which we have already mentioned before, also present different assembly patterns in different solvents. With decreasing polarity, the morphology of 279 transferred from dots to linear aggregates and then to vesicles; meanwhile, 278 changed from sheet-like to bundle-like aggregations. All these examples show that lower solvent polarity enhances hydrogen bonds between head groups, resulting in larger aggregates.

pH of the solution is a common factor to modulate assembly morphology, by influencing electrostatic interactions and hydrophobicity. For groups whose  $pK_a$  values are in a regular range, such as amine, carboxyl acid, and pyridine, adjusting the pH could change the number of charges they possess. More like charges at the hydrophilic head cause stronger repulsion, resulting in a larger curvature. For example, Martin and coworkers reported a phosphate modified amphiphilic calix[4]arene 196, whose major assembly morphology is bilayer at pH 4.1 while small micelles at pH 12.<sup>203</sup> On the other hand, Houmadi and coworkers reported a sulfonatocalix[6]arene 164 with imidazolyl groups at the upper rim.<sup>155</sup> At pH 6.5, the average radius of its assembly is 25 nm, which is much smaller than those at pH 7.8 (25–125 nm) and

Table 5 Morphologies of amphiphilic calixarenes

| Compound | Morphology <sup>a</sup> | Radius <sup>b</sup> (nm)                        | Condition <sup>c</sup>   | Method <sup>d</sup> | Ref. |
|----------|-------------------------|---|--------------------------|---------------------|------|
| 3        | Ellipsoidal micelle     | Minor: 1.15, major: 6.6 (prolate); 3.5 (oblate) | D <sub>2</sub> O         | DOSY                | 54   |
| 4        | Spherical micelle       | $R_s$ : 2.13; $R_g$ : 1.64 ± 0.02               | 10 mM NaCl               | SAXS                | 65   |
| 4        | Spherical micelle       | $R_s$ : 2.19; $R_g$ : 1.73 ± 0.03               | 15 mM NaCl               | SAXS                | 65   |
| 6        | Ellipsoidal micelle     | Major: 4.6                                      | D <sub>2</sub> O         | DOSY                | 84   |
| 6        | Ellipsoidal micelle     | Minor: 1.40, major: 8.9 (prolate); 4.6 (oblate) | D <sub>2</sub> O         | DOSY                | 54   |
| 6        | Spherical micelle       | $R_s$ : 2.40; $R_g$ : 1.97                      | 10 mM NaCl               | SAXS                | 64   |
| 7        | Spherical micelle       | $R_s$ : 2.65; $R_g$ : 2.15                      | 10 mM NaCl               | SAXS                | 64   |
| 8        | Ellipsoidal micelle     | Minor: 1.65, major: 7.8 (prolate); 4.3 (oblate) | D <sub>2</sub> O         | DOSY                | 54   |
| 8        | Spherical micelle       | $R_s$ : 2.10                                    | 10 mM NaCl               | SAXS                | 64   |
| 9        | Micelle                 | 6.9   |                          | DLS, AFM            | 109  |
| 11       | Micelle                 | 2.1–2.8   | Various pH               | DLS                 | 114  |
| 12       | SLN                     | 85  |                          | DLS, AFM            | 126  |
| 12       | SLN                     | 78 ± 1  | 0.1 mM NaCl              | DLS, AFM            | 126  |
| 12       | SLN                     | 81 ± 2  | 1 mM NaCl                | DLS, AFM            | 126  |
| 12       | SLN                     | 81 ± 1  | 15 mM NaCl               | DLS, AFM            | 126  |
| 12       | SLN                     | 80 ± 1  | 145 mM NaCl              | DLS, AFM            | 126  |
| 12       | SLN                     | 66 ± 1  | 0.1 mM KCl               | DLS, AFM            | 126  |
| 12       | SLN                     | 76 ± 3  | 1 mM KCl                 | DLS, AFM            | 126  |
| 12       | SLN                     | 86 ± 1  | 5 mM KCl                 | DLS, AFM            | 126  |
| 12       | SLN                     | 83 ± 2  | 140 mM KCl               | DLS, AFM            | 126  |
| 12       | SLN                     | 85 ± 1  | 145 mM KCl               | DLS, AFM            | 126  |
| 12       | SLN                     | 64 ± 1  | 0.1 mM CaCl <sub>2</sub> | DLS, AFM            | 126  |
| 12       | SLN                     | 60 ± 1  | 0.5 mM CaCl <sub>2</sub> | DLS, AFM            | 126  |
| 12       | SLN                     | 59 ± 1  | 1 mM CaCl <sub>2</sub>   | DLS, AFM            | 126  |
| 12       | SLN                     | 105 ± 1   | 2 mM CaCl <sub>2</sub>   | DLS, AFM            | 126  |
| 12       | SLN                     | 371 ± 13  | 2.5 mM CaCl <sub>2</sub> | DLS, AFM            | 126  |
| 12       | SLN                     | 1206 ± 1179                                     | 3 mM CaCl <sub>2</sub>   | DLS, AFM            | 126  |
| 12       | SLN                     | 1429 ± 433                                      | 4 mM CaCl <sub>2</sub>   | DLS, AFM            | 126  |
| 12       | SLN                     | 1560 ± 485                                      | 5 mM CaCl <sub>2</sub>   | DLS, AFM            | 126  |
| 12       | SLN                     | 815 ± 1393                                      | 145 mM CaCl <sub>2</sub> | DLS, AFM            | 126  |
| 12       | SLN                     | 74 ± 2  | 0.1 mM MgCl <sub>2</sub> | DLS, AFM            | 126  |
| 12       | SLN                     | 64 ± 1  | 0.5 mM MgCl <sub>2</sub> | DLS, AFM            | 126  |
| 12       | SLN                     | 62 ± 1  | 1 mM MgCl <sub>2</sub>   | DLS, AFM            | 126  |
| 12       | SLN                     | 104 ± 1   | 2 mM MgCl <sub>2</sub>   | DLS, AFM            | 126  |
| 12       | SLN                     | 141 ± 6   | 2.5 mM MgCl <sub>2</sub> | DLS, AFM            | 126  |
| 12       | SLN                     | 507 ± 25  | 3 mM MgCl <sub>2</sub>   | DLS, AFM            | 126  |
| 12       | SLN                     | 1048 ± 497                                      | 5 mM MgCl <sub>2</sub>   | DLS, AFM            | 126  |
| 12       | SLN                     | 1247 ± 435                                      | 10 mM MgCl <sub>2</sub>  | DLS, AFM            | 126  |
| 12       | SLN                     | 1141 ± 647                                      | 20 mM MgCl <sub>2</sub>  | DLS, AFM            | 126  |
| 12       | SLN                     | 962 ± 1314                                      | 30 mM MgCl <sub>2</sub>  | DLS, AFM            | 126  |
| 12       | SLN                     | 757 ± 493                                       | 145 mM MgCl <sub>2</sub> | DLS, AFM            | 126  |
| 13       | SLN                     | 69  |                          | DLS, AFM            | 126  |
| 13       | SLN                     | 69 ± 1  | 0.1 mM NaCl              | DLS, AFM            | 126  |
| 13       | SLN                     | 69 ± 1  | 1 mM NaCl                | DLS, AFM            | 126  |
| 13       | SLN                     | 68 ± 2  | 15 mM NaCl               | DLS, AFM            | 126  |
| 13       | SLN                     | 66 ± 2  | 145 mM NaCl              | DLS, AFM            | 126  |
| 13       | SLN                     | 70 ± 1  | 0.1 mM KCl               | DLS, AFM            | 126  |
| 13       | SLN                     | 68 ± 1  | 1 mM KCl                 | DLS, AFM            | 126  |
| 13       | SLN                     | 65 ± 1  | 5 mM KCl                 | DLS, AFM            | 126  |
| 13       | SLN                     | 66 ± 1  | 140 mM KCl               | DLS, AFM            | 126  |
| 13       | SLN                     | 66 ± 2  | 145 mM KCl               | DLS, AFM            | 126  |
| 13       | SLN                     | 69 ± 3  | 0.1 mM CaCl <sub>2</sub> | DLS, AFM            | 126  |
| 13       | SLN                     | 58 ± 2  | 0.5 mM CaCl <sub>2</sub> | DLS, AFM            | 126  |
| 13       | SLN                     | 52 ± 1  | 1 mM CaCl <sub>2</sub>   | DLS, AFM            | 126  |
| 13       | SLN                     | 191 ± 6   | 2 mM CaCl <sub>2</sub>   | DLS, AFM            | 126  |
| 13       | SLN                     | 525 ± 22  | 2.5 mM CaCl <sub>2</sub> | DLS, AFM            | 126  |
| 13       | SLN                     | 1117 ± 467                                      | 3 mM CaCl <sub>2</sub>   | DLS, AFM            | 126  |
| 13       | SLN                     | 1345 ± 860                                      | 4 mM CaCl <sub>2</sub>   | DLS, AFM            | 126  |
| 13       | SLN                     | 1239 ± 1172                                     | CaCl <sub>2</sub> 5 mM   | DLS, AFM            | 126  |
| 13       | SLN                     | 1567 ± 3019                                     | 145 mM CaCl <sub>2</sub> | DLS, AFM            | 126  |
| 13       | SLN                     | 95 ± 65   | 0.1 mM MgCl <sub>2</sub> | DLS, AFM            | 126  |
| 13       | SLN                     | 64 ± 1  | 0.5 mM MgCl <sub>2</sub> | DLS, AFM            | 126  |
| 13       | SLN                     | 60 ± 2  | 1 mM MgCl <sub>2</sub>   | DLS, AFM            | 126  |
| 13       | SLN                     | 136 ± 2   | 2 mM MgCl <sub>2</sub>   | DLS, AFM            | 126  |
| 13       | SLN                     | 229 ± 20  | 2.5 mM MgCl <sub>2</sub> | DLS, AFM            | 126  |
| 13       | SLN                     | 837 ± 30  | 3 mM MgCl <sub>2</sub>   | DLS, AFM            | 126  |
| 13       | SLN                     | 1365 ± 399                                      | 5 mM MgCl <sub>2</sub>   | DLS, AFM            | 126  |

Table 5 (continued)

| Compound | Morphology <sup>a</sup>  | Radius <sup>b</sup> (nm)                 | Condition <sup>c</sup>                            | Method <sup>d</sup> | Ref. |
|----------|--|--|---|---------------------|------|
| 13       | SLN  | 650 ± 650                                | 10 mM MgCl <sub>2</sub>                           | DLS, AFM            | 126  |
| 13       | SLN  | 1425 ± 256                               | 20 mM MgCl <sub>2</sub>                           | DLS, AFM            | 126  |
| 13       | SLN  | 848 ± 1237                               | 30 mM MgCl <sub>2</sub>                           | DLS, AFM            | 126  |
| 13       | SLN  | 1242 ± 625                               | 145 mM MgCl <sub>2</sub>                          | DLS, AFM            | 126  |
| 18       | Vesicle  | 54 ± 3                                   | 10 mM PB 7.2, 154 mM NaCl                         | DLS                 | 43   |
| 24       | Mixture of large or small vesicles, distorted vesicles and rod-like micelles | R <sub>h</sub> : 43; R <sub>g</sub> : 58 | 0.1 M NH <sub>3</sub> aqueous                     | SLS, DLS, cryo-TEM  | 42   |
| 24       | Liquid crystal   | —  | 5 N NH <sub>3</sub> aqueous                       | OPM                 | 42   |
| 24       | Mixture of SLNs and lipid layers   | 100 (SLN)                                | —   | PCS, AFM            | 67   |
| 25       | Spherical aggregate  | 100–125                                  | pH 3  | FE-SEM, EF-TEM      | 23   |
| 25       | Necklace-like aggregate  | 250                                      | pH 7  | FE-SEM, EF-TEM      | 23   |
| 26       | Nanofiber  | 750                                      | H <sub>2</sub> O–EtOH 9 : 1                       | DLS, FE-SEM, TEM    | 90   |
| 29       | Multilamellar vesicle  | 84 ± 24                                  | —   | DLS, FE-SEM, TEM    | 111  |
| 34       | Micelle  | —  | pH 6  | —                   | 41   |
| 34       | Micelle  | —  | pH 8  | —                   | 41   |
| 35       | Micelle  | —  | pH 6  | —                   | 41   |
| 35       | Micelle  | —  | pH 8  | —                   | 41   |
| 36       | Micelle  | —  | pH 6  | —                   | 41   |
| 36       | Micelle  | —  | pH 8  | —                   | 41   |
| 37       | Micelle  | —  | pH 6  | —                   | 41   |
| 37       | Micelle  | —  | pH 8  | —                   | 41   |
| 38       | Micelle  | —  | pH 6  | —                   | 41   |
| 38       | Micelle  | —  | pH 8  | —                   | 41   |
| 39       | Micelle  | —  | pH 6  | —                   | 41   |
| 39       | Micelle  | —  | pH 8  | —                   | 41   |
| 40       | Micelle  | —  | pH 6  | —                   | 41   |
| 40       | Micelle  | —  | pH 8  | —                   | 41   |
| 41       | Micelle  | —  | pH 6  | —                   | 41   |
| 41       | Micelle  | —  | pH 8  | —                   | 41   |
| 42       | Micelle  | —  | pH 6  | —                   | 41   |
| 42       | Micelle  | —  | pH 8  | —                   | 41   |
| 43       | Micelle  | —  | pH 6  | —                   | 41   |
| 43       | Micelle  | —  | pH 8  | —                   | 41   |
| 44       | Micelle  | —  | pH 6  | —                   | 41   |
| 44       | Micelle  | —  | pH 8  | —                   | 41   |
| 46       | Mixture of rod-like and spherical micelles                                   | 3.6 (rod-like); 4.2 (spherical)          | Na <sup>+</sup> and K <sup>+</sup> PB, pH 7       | Cryo-TEM            | 91   |
| 46       | Spherical micelle  | 3.2                                      | Na <sup>+</sup> borate, pH 9                      | Cryo-TEM            | 91   |
| 46       | Membrane with a uniform pattern of pores                                     | —  | pH 4  | Cryo-TEM            | 91   |
| 47       | —  | 3  | pH 7.2  | PGSE NMR            | 97   |
| 47       | Hollow spherical cage  | 3.8                                      | 27 mM Na <sup>+</sup> and K <sup>+</sup>          | Cryo-TEM            | 97   |
| 47       | Micelle  | 4.0–4.5                                  | 27 mM K <sup>+</sup> , pH 7.0                     | Cryo-TEM            | 99   |
| 47       | Micelle  | 3.2–3.7                                  | 27 mM Na <sup>+</sup> and K <sup>+</sup> , pH 7.0 | Cryo-TEM            | 99   |
| 49       | —  | 3.27                                     | D <sub>2</sub> O                                  | DOSY                | 112  |
| 51       | SLN  | 73 ± 3                                   | —   | DLS                 | 117  |
| 57       | Micellar aggregate   | 1–2                                      | 30 °C   | DLS                 | 132  |
| 58       | Vesicle  | 40–650                                   | —   | DLS, TEM            | 134  |
| 60       | Liquid crystal   | —  | —   | OPM                 | 42   |
| 61       | Micelle  | 2.7 ± 0.3                                | 10 mM PB, pH 7.2, 154 mM NaCl                     | DLS                 | 43   |
| 62       | Vesicle  | 75                                       | —   | DLS                 | 46   |
| 63       | Micelle  | 2.5                                      | 75 mM Na <sub>2</sub> SO <sub>4</sub>             | DLS                 | 60   |
| 64       | Micelle  | ~2                                       | —   | DLS                 | 71   |
| 64       | —  | ~2                                       | —   | DLS, TEM            | 73   |
| 64       | Micelle  | 1.47                                     | 20 mM Tris, pH 7.4                                | DLS                 | 77   |
| 65       | Micelle  | 2.74                                     | 20 mM Tris, pH 7.4                                | DLS                 | 77   |
| 66       | Micelle  | 3.2                                      | —   | DLS                 | 72   |
| 66       | Micelle  | 2.82                                     | 20 mM Tris, pH 7.4                                | DLS                 | 77   |
| 67       | Micelle  | 20                                       | —   | DLS                 | 101  |
| 67       | Micelle  | 3.69                                     | 20 mM Tris, pH 7.4                                | DLS                 | 77   |
| 68       | —  | 150–200                                  | 20 mM Tris, pH 7.4                                | DLS                 | 77   |
| 69       | Micelle  | 4.14                                     | 20 mM Tris, pH 7.4                                | DLS                 | 77   |
| 72       | Micelle  | 3.04                                     | 20 mM Tris, pH 7.4                                | DLS                 | 77   |
| 72       | Micelle  | 3.28                                     | 20 mM acetate, pH 5.0                             | DLS                 | 77   |
| 74       | Micelle  | 3.2                                      | —   | DLS                 | 72   |
| 75       | Spherical micelle  | —  | 50 mM NaCl  | SAXS                | 63   |
| 76       | Spherical micelle  | —  | 50 mM NaCl  | SAXS                | 63   |

Table 5 (continued)

| Compound | Morphology <sup>a</sup>                    | Radius <sup>b</sup> (nm)              | Condition <sup>c</sup>      | Method <sup>d</sup> | Ref. |
|----------|--|---------------------------------------|-----------------------------|---------------------|------|
| 77       | Spherical micelle                          | —                                     | 50 mM NaCl                  | SAXS                | 63   |
| 77       | Spherical micelle                          | —                                     | 100 mM NaCl                 | SAXS                | 63   |
| 77       | Spherical micelle                          | —                                     | 200–300 mM NaCl             | SAXS                | 63   |
| 77       | Mixture of various micellar shapes         | —                                     | >400 mM NaCl                | SAXS                | 63   |
| 78       | Spherical micelle                          | —                                     | 50 mM NaCl                  | SAXS                | 63   |
| 79       | Spherical micelle                          | —                                     | 50 mM NaCl                  | SAXS                | 63   |
| 82       | Micelle                                    | 14                                    | 0.33 mM                     | DLS                 | 48   |
| 82       | Vesicle or aggregate of micelles           | 70                                    | 1 mM                        | DLS                 | 48   |
| 86       | SLN  | 95                                    |                             | PCS                 | 93   |
| 91       | Spherical micelle                          | —                                     | pH < 6, 50 mM NaCl          | AFM                 | 122  |
| 91       | Mixture of rod-like and spherical micelles | —                                     | 3 < pH < 8, 50 mM NaCl      | AFM                 | 122  |
| 91       | Connected network                          | —                                     | pH = 10, 50 mM NaCl         | AFM                 | 122  |
| 91       | Cylindrical micelle                        | —                                     | pH 8.0, 50 mM NaCl          | AFM                 | 122  |
| 91       | Spherical micelle                          | 2.05                                  | pH 4.2, 50 mM NaCl          | SAXS                | 122  |
| 91       | Cylindrical micelle                        | 1.68                                  | pH 7.5, 50 mM NaCl          | SAXS                | 122  |
| 91       | Micelle                                    | $R_g: 1.67$                           | —                           | SAXS                | 125  |
| 91       | Spherical micelle                          | $R_h: 2.05; R_g: 1.47 \pm 0.11$       | 50 mM NaCl, pH 3.0          | SAXS                | 124  |
| 92       | Spherical micelle                          | $R_h: 2.10; R_g: 1.58 \pm 0.15$       | 50 mM NaCl, pH 3.0          | SAXS                | 124  |
| 93       | Spherical micelle                          | $R_h: 2.25; R_g: 1.94 \pm 0.17$       | 50 mM NaCl, pH 3.0          | SAXS                | 124  |
| 94       | Spherical micelle                          | —                                     | pH < 6, 50 mM NaCl          | AFM                 | 122  |
| 94       | Vesicular micelle                          | —                                     | pH = 8, 50 mM NaCl          | AFM                 | 122  |
| 94       | Mixture of rod-like and spherical micelles | —                                     | pH = 6, 50 mM NaCl          | AFM                 | 122  |
| 94       | Cylindrical micelle                        | —                                     | pH 6.3, 50 mM NaCl          | AFM                 | 122  |
| 94       | Spherical micelle                          | 2.75                                  | pH 4.3, 50 mM NaCl          | SAXS                | 122  |
| 94       | Cylindrical micelle                        | 2.0                                   | pH 6.3, 50 mM NaCl          | SAXS                | 122  |
| 94       | Plate micelle                              | 1.91                                  | pH 7.8, 50 mM NaCl          | SAXS                | 122  |
| 94       | Spherical micelle                          | $R_h: 2.75; R_g: 2.52 \pm 0.19$       | 50 mM NaCl, pH 3.0          | SAXS                | 124  |
| 95       | Cylindrical micelle                        | $R_h: 2.20; R_g: 1.70 \pm 0.10$       | 50 mM NaCl, pH 3.0          | SAXS                | 124  |
| 96       | Cylindrical micelle                        | $R_h: 2.35; R_g: 1.87 \pm 0.13$       | 50 mM NaCl, pH 3.0          | SAXS                | 124  |
| 97       | Rod-like micelle                           | —                                     | pH < 6, 50 mM NaCl          | AFM                 | 122  |
| 97       | Cylindrical micelle                        | 2.40                                  | pH 4.7, 50 mM NaCl          | SAXS                | 122  |
| 98       | —  | $88 \pm 6$                            | 50 mM MES, pH 6.5           | DLS, SLS            | 136  |
| 99       | —  | $70 \pm 27$                           | 50 mM MES, pH 6.5           | DLS, SLS            | 136  |
| 100      | Dot-like micelle                           | 2.25                                  | 50 mM NaCl, pH 3.0          | SAXS, AFM           | 139  |
| 101      | Spherical micelle                          | 2.15                                  | 50 mM NaCl, pH 3.0          | SAXS                | 140  |
| 101      | Spherical micelle                          | 2.35                                  | 50 mM NaCl, pH 5.4          | SAXS                | 140  |
| 101      | Finite cylindrical micelle                 | 1.90                                  | 50 mM NaCl, pH 6.2          | SAXS                | 140  |
| 101      | Infinite cylindrical micelle               | 1.80                                  | 50 mM NaCl, pH 7.4          | SAXS                | 140  |
| 101      | Infinite cylindrical micelle               | 1.80                                  | 50 mM NaCl, pH 8.3          | SAXS                | 140  |
| 101      | Finite cylindrical micelle                 | 1.98                                  | 50 mM NaCl, pH 9.2          | SAXS                | 140  |
| 101      | Spherical micelle                          | 2.38                                  | 50 mM NaCl, pH 10           | SAXS                | 140  |
| 102      | Spherical micelle                          | —                                     | 50 mM NaCl                  | SAXS                | 63   |
| 105      | —  | $97 \pm 2$                            | 50 mM MES, pH 6.5           | DLS, SLS            | 136  |
| 106      | —  | $77 \pm 9$                            | 50 mM MES, pH 6.5           | DLS, SLS            | 136  |
| 108      | Micelle                                    | $R_g: 1.76$                           | 150 mM NaCl                 | DLS, SAXS, AFM      | 167  |
| 109      | Micelle                                    | $R_g: 2.46$                           | 150 mM NaCl                 | DSL, SAXS, AFM      | 167  |
| 123      | —  | $10.1 \pm 0.8$                        | PBS                         | DLS                 | 149  |
| 124      | Vesicle                                    | 10–30                                 | 50 mM NaCl/Tris-HCl, pH 7–8 | DLS, TEM            | 123  |
| 125      | Cylindrical micelle                        | $R_h: 2.50$                           | 50 mM NaCl, pH 7.0, 25 °C   | SAXS                | 157  |
| 125      | Spherical micelle                          | $R_h: 2.85; R_g: 2.81$                | 50 mM NaCl, pH 7.0, 40 °C   | SAXS                | 157  |
| 125      | Spherical micelle                          | $R_h: 2.72; R_g: 2.73$                | 50 mM NaCl, pH 12, 25 °C    | SAXS                | 157  |
| 125      | Spherical micelle                          | $R_h: 2.58; R_g: 1.80$                | 50 mM NaCl, pH 12, 40 °C    | SAXS                | 157  |
| 126      | Globular micelle                           | $R_h: 3; R_g: 2.43$                   |                             | DLS, SAXS           | 159  |
| 127      | SLN  | 65                                    |                             | DLS, AFM            | 163  |
| 127      | Nanosphere                                 | $65 \pm 1$                            |                             | DLS, cryo-TEM       | 164  |
| 127      | Nanocapsule                                | $60 \pm 1$                            |                             | DLS, cryo-TEM       | 164  |
| 128      | SLN  | 95                                    |                             | DLS, AFM            | 163  |
| 128      | Nanosphere                                 | $95 \pm 1$                            |                             | DLS, cryo-TEM       | 164  |
| 128      | Nanocapsule                                | $76 \pm 1$                            |                             | DLS, cryo-TEM       | 164  |
| 129      | Vesicle                                    | 25–50                                 |                             | DLS, TEM            | 169  |
| 130      | Fiber                                      | 25 (radius), several micrometers long |                             | DLS, TEM            | 169  |
| 131      | Micelle                                    | 2.2                                   |                             | DLS                 | 278  |
| 137      | Vesicle                                    | 100                                   |                             | DLS, TEM, FE-SEM    | 185  |
| 138      | Vesicle                                    | 18                                    |                             | DLS, TEM, FE-SEM    | 185  |
| 138      | Micelle                                    | 3                                     | pH 5                        | DLS, TEM            | 185  |

Table 5 (continued)

| Compound | Morphology <sup>a</sup>  | Radius <sup>b</sup> (nm)                        | Condition <sup>c</sup>                     | Method <sup>d</sup>   | Ref. |
|----------|--|---|--|-----------------------|------|
| 139      | Micelle  | 3   |  | DLS, TEM              | 185  |
| 140      | Micelle  | 2.9   |  | DLS                   | 142  |
| 140      | Micelle  | 2.8   |  | TEM                   | 142  |
| 140      | Irregular NP   | 7–16  |  | TEM                   | 142  |
| 141      | Micelle  | 3.5   |  | DLS                   | 142  |
| 141      | Micelle  | 3.6   |  | TEM                   | 142  |
| 141      | Sole like NP   | 13–43   |  | TEM                   | 142  |
| 141      | Solid micelle  | 3.6   |  | TEM                   | 143  |
| 142      | Irregular NP   | 8–50  |  | TEM                   | 146  |
| 142      | Mixture of micelles and NPs                                      | 3 (micelle); 40 (NP)                            |  | HR TEM                | 146  |
| 142      | Mixture of micelles and NPs                                      | 3 (micelle); 25 (NP)                            |  | Cryo-TEM              | 146  |
| 142      | Micelle  | 1.8   |  | DLS                   | 146  |
| 142      | Micelle  | 1.8   |  | DLS                   | 142  |
| 142      | Micelle  | 2.5   |  | TEM, HR TEM, cryo-TEM | 142  |
| 142      | Irregular NP   | 8–50  |  | TEM, HR TEM, cryo-TEM | 142  |
| 142      | Solid micelle  | 2.5   |  | TEM                   | 143  |
| 143      | Micelle  | $R_h$ : 2.90; $R_g$ : $2.26 \pm 0.14$           | 50 mM NaCl                                 | SAXS                  | 150  |
| 144      | Micelle  | $R_h$ : 3.60; $R_g$ : $2.63 \pm 0.12$           | 50 mM NaCl                                 | SAXS                  | 150  |
| 145      | Micelle  | $R_h$ : 4.10; $R_g$ : $3.75 \pm 0.34$           | 50 mM NaCl                                 | SAXS                  | 150  |
| 147      | Spherical micelle  | —   | 50 mM NaCl                                 | SAXS                  | 63   |
| 148      | —  | 118   |  | PCS                   | 168  |
| 154      | —  | 88  | 10 mM HEPES, pH 8.0                        | DLS                   | 179  |
| 158      | Vesicle  | 40  |  | DLS                   | 46   |
| 162      | Ellipsoidal micelle  | Minor: 2.10, major: 3.45                        |  | SAXS                  | 147  |
| 162      | Ellipsoidal micelle  | Minor: 1.40, major: 6.6 (prolate); 3.7 (oblate) | D <sub>2</sub> O                           | DOSY                  | 54   |
| 163      | Micelle  | Minor: 3.25, major: 10.675                      |  | SAXS                  | 147  |
| 163      | Micelle (>0.6 mM)  | ~123–190  |  | DLS, NTA              | 154  |
| 163      | Domain (100–0.1 μM)  | ~70–190   |  | DLS, NTA              | 154  |
| 163      | Nanoassociate (10–1 nM)  | ~160–195  |  | DLS, NTA              | 154  |
| 164      | Vesicle  | 25–125  | pH 7.8                                     | TEM, AFM, DLS         | 155  |
| 164      | Vesicle  | ≤50   | pH 7.8, sonicate 1 h                       | AFM                   | 155  |
| 164      | Vesicle  | 25  | pH 6.5                                     | TEM                   | 155  |
| 164      | Vesicle  | 225   | pH 8.5                                     | TEM, DLS              | 155  |
| 164      | Micelle  | 1.3   | 1 mM AgClO <sub>4</sub>                    | TEM                   | 155  |
| 168      | —  | 30–100  | 0.1 mM                                     | DLS, TEM              | 73   |
| 168      | —  | 33–250  | 0.2 mM                                     | DLS, TEM              | 73   |
| 168      | —  | 40–150; 250–350                                 | 0.6 mM                                     | DLS, TEM              | 73   |
| 168      | —  | 50–350  | 0.8 mM                                     | DLS, TEM              | 73   |
| 168      | —  | 55–400  | 1.0 mM                                     | DLS, TEM              | 73   |
| 168      | —  | 35–55; 80–200                                   | 4.0 mM                                     | DLS, TEM              | 73   |
| 168      | —  | 65–350  | 6.0 mM                                     | DLS, TEM              | 73   |
| 168      | —  | 75–400  | 8.0 mM                                     | DLS, TEM              | 73   |
| 168      | —  | 35–60; 150–250                                  | 10.0 mM                                    | DLS, TEM              | 73   |
| 170      | Vesicle  | 60 ± 15   | 8 μM                                       | Cryo-TEM, DLS         | 173  |
| 170      | Vesicle  | 50, 230   | 20 μM                                      | Cryo-TEM, DLS         | 173  |
| 171      | Flattened bilayer  | 108   | 7.4 μM                                     | Cryo-TEM, DLS         | 173  |
| 171      | Flattened bilayer  | 150   | 15 μM                                      | Cryo-TEM, DLS         | 173  |
| 175      | Ellipsoidal micelle  | Minor: 1.40, major: 7.3 (prolate); 4.0 (oblate) | D <sub>2</sub> O                           | DOSY                  | 54   |
| 184      | Vesicle  | 150 ± 50  | pH 4.5–12                                  | SLS, DLS              | 156  |
| 184      | Micelle  | 5   | pH 3                                       | SLS, DLS              | 156  |
| 185      | Vesicle  | 150 ± 50  | pH 4.5–12                                  | SLS, DLS              | 156  |
| 185      | Micelle  | 5   | pH 3                                       | SLS, DLS              | 156  |
| 192      | SLN  | 130   | PBS  | PCS                   | 190  |
| 193      | Mixture of micelles and large aggregates                         | 12; 49; 133                                     | Acetate pH 4.1                             | DLS, TEM              | 203  |
| 193      | Mixture of micelles and large aggregates                         | 8–10  | Borate pH 8.6                              | DLS, TEM              | 203  |
| 196      | Mixture of spherical micelles and large aggregates               | 9–10  | HCl pH 1.2; phthalate pH 3; acetate pH 4.1 | DLS, TEM              | 203  |
| 196      | Mixture of spherical micelles and large aggregates               | 20–30   | Borate pH 8.6                              | DLS, TEM              | 203  |
| 196      | Mixture of spherical micelles, bilayers and cylindrical micelles | —   | PB pH 12                                   | DLS, TEM              | 203  |

Table 5 (continued)

| Compound | Morphology <sup>a</sup>                       | Radius <sup>b</sup> (nm)                       | Condition <sup>c</sup>                   | Method <sup>d</sup> | Ref.        |
|----------|---|--|--|---------------------|-------------|
| 197      | SLN   | 97   |  | PCS                 | 193         |
| 198      | Mixture of tubular and ribbon-like aggregates | 4–10 (radius), 8–100 (length)                  | 1 mM                                     | Cryo-TEM            | 92          |
| 198      | Fiber   | Liquid crystalline lamellar phase              | 30% THF aqueous                          | Cryo-TEM            | 92          |
| 199      | —   | —  |  | AFM                 | 198         |
| 200      | —   | —  |  | AFM                 | 198         |
| 205      | Vesicle                                       | 100–250  | EtOH                                     | TEM, AFM            | 238         |
| 212      | Vesicle                                       | 34, 125  |  | DLS, TEM            | 202         |
| 212      | Fiber   | 109  | MeOH                                     | DLS, TEM            | 202         |
| 216      | SLN   | 170  | PBS                                      | PCS                 | 190         |
| 217      | SLN   | 177  | PBS                                      | PCS                 | 190         |
| 218      | SLN   | 175  | PBS                                      | PCS                 | 190         |
| 219      | SLN   | 74   | Produced using THF                       | PCS, AFM            | 225 and 226 |
| 219      | SLN   | 74   | Produced using EtOH                      | PCS                 | 226         |
| 219      | SLN   | 98   | Produced using acetone                   | PCS                 | 226         |
| 219      | SLN   | 107  | Produced using MeOH                      | PCS                 | 226         |
| 219      | SLN   | 114  | 0.2 g L <sup>-1</sup>                    | PCS                 | 226         |
| 219      | SLN   | 132  | 0.3 g L <sup>-1</sup>                    | PCS                 | 226         |
| 219      | SLN   | 136  | 0.4 g L <sup>-1</sup>                    | PCS                 | 226         |
| 219      | SLN   | 130  | 0.5 g L <sup>-1</sup>                    | PCS                 | 226         |
| 219      | SLN   | 81   | 3% THF in production                     | PCS                 | 226         |
| 219      | SLN   | 86   | 4% THF in production                     | PCS                 | 226         |
| 219      | SLN   | 108  | 5% THF in production                     | PCS                 | 226         |
| 219      | SLN   | 103  | 6% THF in production                     | PCS                 | 226         |
| 219      | SLN   | 103  | 8% THF in production                     | PCS                 | 226         |
| 219      | SLN   | 110  | 10% THF in production                    | PCS                 | 226         |
| 219      | SLN   | 75   | 0.1 M NaCl                               | PCS                 | 226         |
| 219      | SLN   | 80   | 0.1 M NaI                                | PCS                 | 226         |
| 219      | SLN   | 83   | 0.1 M CH <sub>3</sub> CO <sub>2</sub> Na | PCS                 | 226         |
| 219      | SLN   | 75   | 0.1 M NaHCO <sub>3</sub>                 | PCS                 | 226         |
| 219      | SLN   | 73   | 0.1 M KNO <sub>3</sub>                   | PCS                 | 226         |
| 219      | SLN   | 93   | 0.1 M KH <sub>2</sub> PO <sub>4</sub>    | PCS                 | 226         |
| 219      | SLN   | 65   |  | PCS                 | 215         |
| 219      | SLN   | 175  | PBS                                      | PCS                 | 190         |
| 219      | SLN   | 75   |  | PCS, AFM            | 193         |
| 219      | SLN   | 69   |  | PCS                 | 225         |
| 219      | SLN   | 70   | Carbopol 980 aqueous                     | PCS                 | 225         |
| 219      | SLN   | 73   | Carbopol 2020 aqueous                    | PCS                 | 225         |
| 219      | SLN   | 83   | Hyaluronic acid aqueous                  | PCS                 | 225         |
| 219      | SLN   | 76   | Xanthane aqueous                         | PCS                 | 225         |
| 223      | Vesicle                                       | 25–35, 100                                     |  | TEM                 | 233         |
| 223      | Lamellar-like vesicle                         | 25–500   | MeOH                                     | TEM                 | 233         |
| 223      | Fiber   | —  | CHCl <sub>3</sub>                        | TEM                 | 233         |
| 223      | Inverted micelle                              | 13   | Perfluorohexane                          | TEM                 | 233         |
| 223      | Circular assembly                             | 50 (radius), 25–30 (height)                    |  | AFM                 | 257         |
| 224      | SLN   | 74   | 0.1 M NaH <sub>2</sub> PO <sub>4</sub>   | PCS                 | 226         |
| 224      | SLN   | 73   | 0.1 M KCl                                | PCS                 | 226         |
| 226      | SLN   | 163  | PBS                                      | PCS                 | 190         |
| 227      | SLN   | 92   |  | PCS                 | 193         |
| 231      | —   | 140–200  | 0.8–7 mM, 10% DMF aqueous                | DLS                 | 200         |
| 232      | Micelle                                       | R <sub>g</sub> : 25.6                          | 0.1 mM                                   | SAXS                | 205         |
| 232      | Micelle                                       | R <sub>g</sub> : 30.5                          | 0.5 mM                                   | SAXS                | 205         |
| 232      | Micelle                                       | R <sub>g</sub> : 35.2                          | 1.0 mM                                   | SAXS                | 205         |
| 232      | Micelle                                       | 8–6  | 0.1–10 mM                                | DLS                 | 205         |
| 237      | —   | 62–130   | 0.09–3 mM, 10% DMF aqueous               | DLS                 | 200         |
| 238      | —   | 14–8   | 0.25–16 mM                               | DLS                 | 200         |
| 239      | Mixture of micelle-like aggregates and layers | 4  |  | DLS                 | 227         |
| 240      | —   | 8–4  | 0.15–16 mM                               | DLS                 | 200         |
| 241      | —   | 9–5  | 0.15–16 mM                               | DLS                 | 200         |
| 242      | —   | 15–5   | 0.25–20 mM                               | DLS                 | 200         |
| 247      | Spherical particle                            | R <sub>h</sub> : 107.1; R <sub>g</sub> : 120.4 |  | DLS, SLS, AFM       | 191         |
| 248      | Spherical particle                            | R <sub>h</sub> : 108.0; R <sub>g</sub> : 120.3 |  | DLS, SLS, AFM       | 191         |
| 249      | Spherical particle                            | R <sub>h</sub> : 98.6; R <sub>g</sub> : 122.0  |  | DLS, SLS, AFM       | 191         |
| 250      | Spherical particle                            | R <sub>h</sub> : 121.7; R <sub>g</sub> : 135.0 |  | DLS, SLS, AFM       | 191         |
| 251      | Spherical particle                            | R <sub>h</sub> : 106.8; R <sub>g</sub> : 131.0 |  | DLS, SLS, AFM       | 191         |
| 252      | Spherical particle                            | R <sub>h</sub> : 77.7; R <sub>g</sub> : 91.0   |  | DLS, SLS, AFM       | 191         |
| 255      | —   | 14.3   |  | DLS, TEM            | 213         |
| 256      | —   | 5.5  |  | DLS, TEM            | 213         |

Table 5 (continued)

| Compound                            | Morphology <sup>a</sup>                                     | Radius <sup>b</sup> (nm)             | Condition <sup>c</sup>              | Method <sup>d</sup> | Ref. |
|-------------------------------------|---|--------------------------------------|-------------------------------------|---------------------|------|
| 257                                 | —   | 79.5                                 |                                     | DLS, TEM            | 213  |
| 258                                 | —   | 10.3                                 |                                     | DLS, TEM            | 213  |
| 259                                 | —   | 34.7                                 |                                     | DLS, TEM            | 213  |
| 260                                 | —   | 17.7                                 |                                     | DLS, TEM            | 213  |
| 261                                 | Mixture of grape-like superstructures and non-linear chains | 60–85, 600–900 (length)              |                                     | SEM, TEM            | 229  |
| 262                                 | Mixture of micelles and large spherical aggregates          | 100–130; 350                         |                                     | DLS, SEM, TEM       | 229  |
| 278                                 | Sheet-like monolayer  | 1.3                                  |                                     | AFM, TEM            | 224  |
| 278                                 | Bundles of sticks   | 1.4–16.6 (radius), 500–3500 (length) | DMSO–H <sub>2</sub> O 1 : 9         | AFM, TEM            | 224  |
| 278                                 | Vesicle   | 25                                   | Acetone–H <sub>2</sub> O 1 : 9      | AFM, TEM            | 224  |
| 279                                 | Linear or dot-like aggregate                                | —                                    |                                     | AFM, TEM            | 224  |
| 279                                 | Vesicle   | 25                                   | DMSO–H <sub>2</sub> O 1 : 9         | AFM, TEM            | 224  |
| 282                                 | —   | 241 ± 30                             | 3 mM                                | DLS                 | 232  |
| 282                                 | —   | 240 ± 37                             | 0.3 mM                              | DLS                 | 232  |
| 282                                 | —   | 84 ± 4                               | 30 μM                               | DLS                 | 232  |
| 282                                 | —   | 131 ± 13                             | 3 μM                                | DLS                 | 232  |
| 283                                 | —   | 87 ± 11                              | 3 mM                                | DLS                 | 232  |
| 283                                 | —   | 227 ± 47                             | 0.3 mM                              | DLS                 | 232  |
| 283                                 | —   | 203 ± 15                             | 30 μM                               | DLS                 | 232  |
| 283                                 | —   | 415 ± 33                             | 3 μM                                | DLS                 | 232  |
| 284 (Br <sup>−</sup> )              | Particle  | 90.5 ± 11.5                          |                                     | DLS                 | 237  |
| 284 (NO <sub>3</sub> <sup>−</sup> ) | Particle  | 30.7 ± 8.4                           |                                     | DLS                 | 235  |
| 284 (NO <sub>3</sub> <sup>−</sup> ) | Particle  | 24 ± 3                               |                                     | DLS                 | 236  |
| 286                                 | Particle  | 7.3 ± 1.3                            |                                     | DLS                 | 235  |
| 286                                 | Particle  | 8 ± 1                                |                                     | DLS                 | 236  |
| 287                                 | Particle  | 1.9 ± 0.4                            |                                     | DLS                 | 235  |
| 289                                 | Spherical particle  | 70.8                                 | 5 mM Tris–HCl, pH 7.5, 1 mM (CA)    | DLS                 | 247  |
| 289                                 | Spherical particle  | 80.8                                 | 5 mM Tris–HCl, pH 7.5, 0.8 mM (CA)  | DLS                 | 247  |
| 289                                 | Spherical particle  | 104.5                                | 5 mM Tris–HCl, pH 7.5, 0.1 mM (CA)  | DLS                 | 247  |
| 289                                 | Spherical particle  | 194.8                                | 5 mM Tris–HCl, pH 7.5, 10 μM (CA)   | DLS                 | 247  |
| 289                                 | Spherical particle  | 244.4                                | 5 mM Tris–HCl, pH 7.5, 1 μM (CA)    | DLS                 | 247  |
| 290                                 | Spherical particle  | 37.7                                 | 5 mM Tris–HCl, pH 7.5, 1 mM (CA)    | DLS                 | 247  |
| 290                                 | Spherical particle  | 72.8                                 | 5 mM Tris–HCl, pH 7.5, 0.8 mM (CA)  | DLS                 | 247  |
| 290                                 | Spherical particle  | 100.6                                | 5 mM Tris–HCl, pH 7.5, 0.1 mM (CA)  | DLS                 | 247  |
| 290                                 | Spherical particle  | 122.4                                | 5 mM Tris–HCl, pH 7.5, 10 μM (CA)   | DLS, TEM            | 247  |
| 290                                 | Spherical particle  | 226.9                                | 5 mM Tris–HCl, pH 7.5, 1 μM (CA)    | DLS                 | 247  |
| 292                                 | —   | 211 ± 37                             | 0.3 mM                              | DLS                 | 250  |
| 292                                 | —   | 168 ± 24                             | 30 μM                               | DLS                 | 250  |
| 292                                 | —   | 159 ± 102                            | 3 μM                                | DLS                 | 250  |
| 292                                 | —   | 99 ± 3                               | 0.3 mM (CA), 0.3 mM Ag <sup>+</sup> | DLS                 | 250  |
| 292                                 | —   | 174 ± 61                             | 30 μM (CA), 30 μM Ag <sup>+</sup>   | DLS                 | 250  |
| 292                                 | —   | 218 ± 77                             | 3 μM (CA), 3 μM Ag <sup>+</sup>     | DLS                 | 250  |
| 292                                 | —   | 166 ± 12                             | 0.3 mM (CA), 0.3 mM Ag <sup>+</sup> | DLS                 | 250  |
| 292                                 | —   | 265 ± 135                            | 3 mM                                | DLS                 | 232  |
| 292                                 | —   | 211 ± 37                             | 0.3 mM                              | DLS                 | 232  |
| 292                                 | —   | 168 ± 24                             | 30 μM                               | DLS                 | 232  |
| 292                                 | —   | 159 ± 102                            | 3 μM                                | DLS                 | 232  |
| 293                                 | —   | 378 ± 47                             | 0.3 mM                              | DLS                 | 250  |
| 293                                 | —   | 265 ± 135                            | 30 μM                               | DLS                 | 250  |
| 293                                 | —   | 118 ± 103                            | 3 μM                                | DLS                 | 250  |
| 293                                 | —   | 195 ± 42                             | 30 μM (CA), 30 μM Ag <sup>+</sup>   | DLS                 | 250  |
| 293                                 | —   | 189 ± 31                             | 3 μM (CA), 3 μM Ag <sup>+</sup>     | DLS                 | 250  |
| 294                                 | Micelle   | (17.0 ± 1.3)–(24.4 ± 1.4)            | 2–10 mM, D <sub>2</sub> O           | DOSY, AFM           | 252  |
| 294                                 | Mixture of premicelles and large aggregates                 | 100; 300                             | 0.5 mM                              | DOSY, DLS           | 254  |
| 294                                 | Mixture of aggregate  | 50–100; 25                           |                                     | AFM                 | 254  |
| 296                                 | Homogeneous assembly  | 30–40 (radius), 3–5 (height)         |                                     | AFM                 | 257  |
| 305                                 | Spherical particle  | 111.2 ± 17.4.                        | PBS pH 7.4                          | DLS, TEM            | 259  |
| 311                                 | Vesicle   | —                                    | H <sub>2</sub> O–EtOH 1 : 3         | TEM                 | 242  |

Table 5 (continued)

| Compound | Morphology <sup>a</sup> | Radius <sup>b</sup> (nm)                               | Condition <sup>c</sup>                        | Method <sup>d</sup> | Ref. |
|----------|-------------------------|--|---|---------------------|------|
| 325      | Spherical particle      | 89.8 ± 14.8  | PBS pH 7.4                                    | DLS, TEM            | 259  |
| 370      | —                       | 100–110  | 0.33–10 g L <sup>-1</sup>                     | DLS                 | 258  |
| 371      | —                       | R <sub>h</sub> : 100–300; R <sub>g</sub> : 70–140      | 0.8 mg L <sup>-1</sup> –1.2 g L <sup>-1</sup> | DLS                 | 258  |
| 402      | SLN                     | 108  |   | DLS                 | 262  |
| 402      | SLN                     | 74   | Produced using acetone                        | DLS                 | 262  |
| 402      | SLN                     | 215  | Produced using EtOH                           | DLS                 | 262  |
| 402      | SLN                     | 106  | 0.2 g L <sup>-1</sup>                         | DLS                 | 262  |
| 402      | SLN                     | 125  | 0.3 g L <sup>-1</sup>                         | DLS                 | 262  |
| 402      | SLN                     | 123  | 0.4 g L <sup>-1</sup>                         | DLS                 | 262  |
| 402      | SLN                     | 139  | 0.5 g L <sup>-1</sup>                         | DLS                 | 262  |
| 402      | SLN                     | 117  | 5% glycerol                                   | DLS                 | 262  |
| 402      | SLN                     | 99   | 10% glycerol                                  | DLS                 | 262  |
| 402      | SLN                     | 114  | 15% glycerol                                  | DLS                 | 262  |
| 402      | SLN                     | 102  | 20% glycerol                                  | DLS                 | 262  |
| 402      | SLN                     | 104  | 25% glycerol                                  | DLS                 | 262  |
| 403      | SLN                     | 72   |   | DLS                 | 262  |
| 404      | SLN                     | 70   |   | DLS                 | 262  |
| 405      | SLN                     | 50   |   | DLS                 | 262  |
| 406      | SLN                     | 41   |   | DLS                 | 262  |
| 407      | —                       | R <sub>h</sub> : 4.242; R <sub>g</sub> : 3.288 ± 0.044 | 0.5 mM  | DLS, SAXS           | 22   |
| 407      | —                       | R <sub>h</sub> : 3.296; R <sub>g</sub> : 2.555 ± 0.128 | 1 mM  | DLS, SAXS           | 22   |
| 407      | —                       | R <sub>h</sub> : 34.06; R <sub>g</sub> : 2.640 ± 0.014 | 5 mM  | DLS, SAXS           | 22   |
| 407      | —                       | R <sub>h</sub> : 4.074; R <sub>g</sub> : 3.158 ± 0.002 | 10 mM   | DLS, SAXS           | 22   |
| 407      | —                       | 5; 100   |   | DLS                 | 22   |
| 415      | Particle                | 3 ± 0.2; 10 ± 1  |   | DLS                 | 236  |
| 420      | Tube                    | 15 (radius), 70–300 (length)                           |   | SEM                 | 265  |
| 421      | Tube                    | 10 <sup>6</sup> (radius), 10 <sup>8</sup> (length)     |   | SEM, AFM            | 265  |
| 422      | Vesicle                 | 370 ± 28   | 10 mM Tris, pH 7.4                            | DLS                 | 268  |
| 422      | Vesicle                 | 158 ± 3  | 10 mM Tris, pH 7.4, 65 °C                     | DLS                 | 268  |
| 422      | Vesicle                 | 268 ± 13   | 10 mM Tris, pH 7.4, irradiated                | DLS                 | 268  |
| 422      | Vesicle                 | 133 ± 5  | 10 mM Tris, pH 7.4, 65 °C, irradiated         | DLS                 | 268  |
| 427      | Vesicle                 | 440 ± 40   | 10 mM Tris, pH 7.4                            | DLS                 | 268  |
| 427      | Vesicle                 | 130 ± 10   | 10 mM Tris, pH 7.4, 65 °C                     | DLS                 | 268  |
| 427      | Vesicle                 | 245 ± 40   | 10 mM Tris, pH 7.4, irradiated                | DLS                 | 268  |
| 427      | Vesicle                 | 120 ± 1  | 10 mM Tris, pH 7.4, 65 °C, irradiated         | DLS                 | 268  |
| 428      | —                       | 150 ± 13   | 3 mM  | DLS                 | 232  |
| 428      | —                       | 71 ± 16  | 0.3 mM  | DLS                 | 232  |
| 428      | —                       | 136 ± 38   | 30 μM   | DLS                 | 232  |
| 428      | —                       | 100 ± 19   | 3 μM  | DLS                 | 232  |
| 429      | SLN                     | 66   |   | DLS, SEM            | 120  |
| 430      | Spherical particle      | 49.9   | 5 mM Tris–HCl, pH 7.5, 1 mM (CA)              | DLS                 | 247  |
| 430      | Spherical particle      | 52.2   | 5 mM Tris–HCl, pH 7.5, 0.8 mM (CA)            | DLS                 | 247  |
| 430      | Spherical particle      | 103.7  | 5 mM Tris–HCl, pH 7.5, 0.1 mM (CA)            | DLS                 | 247  |
| 430      | Spherical particle      | 119.8  | 5 mM Tris–HCl, pH 7.5, 10 μM (CA)             | DLS                 | 247  |
| 430      | Spherical particle      | 448.0  | 5 mM Tris–HCl, pH 7.5, 1 μM (CA)              | DLS                 | 247  |
| 431      | Spherical particle      | 46.4   | 5 mM Tris–HCl, pH 7.5, 1 mM (CA)              | DLS                 | 247  |
| 431      | Spherical particle      | 69.9   | 5 mM Tris–HCl, pH 7.5, 0.8 mM (CA)            | DLS                 | 247  |
| 431      | Spherical particle      | 212.9  | 5 mM Tris–HCl, pH 7.5, 0.1 mM (CA)            | DLS                 | 247  |
| 431      | Spherical particle      | 412.3  | 5 mM Tris–HCl, pH 7.5, 10 μM (CA)             | DLS                 | 247  |
| 431      | Spherical particle      | 502.0  | 5 mM Tris–HCl, pH 7.5, 1 μM (CA)              | DLS                 | 247  |
| 432      | —                       | 62 ± 9   | 50 mM Tris, pH 7.4                            | DLS                 | 266  |
| 433      | —                       | 66 ± 2   | 50 mM Tris, pH 7.4                            | DLS                 | 266  |
| 434      | —                       | 62 ± 1   | 50 mM Tris, pH 7.4                            | DLS                 | 266  |
| 443      | Vesicle                 | 42 ± 2   | 0.025 mM                                      | DLS                 | 267  |
| 443      | Vesicle                 | 47 ± 1   | 0.05 mM                                       | DLS                 | 267  |
| 443      | Vesicle                 | 53 ± 1   | 0.1 mM  | DLS                 | 267  |
| 443      | Vesicle                 | 50 ± 2   | 0.25 mM                                       | DLS                 | 267  |
| 443      | Vesicle                 | 42 ± 1   | 0.5 mM  | DLS                 | 267  |
| 443      | Vesicle                 | 64 ± 2   | 0.75 mM                                       | DLS                 | 267  |
| 443      | Vesicle                 | 62 ± 2   | 1.0 mM  | DLS                 | 267  |



Table 5 (continued)

| Compound | Morphology <sup>a</sup>        | Radius <sup>b</sup> (nm)                  | Condition <sup>c</sup>   | Method <sup>d</sup> | Ref. |
|----------|--------------------------------|---|--|---------------------|------|
| 444      | Vesicle                        | 31 ± 1                                    | 0.01 mM  | DLS                 | 267  |
| 444      | Vesicle                        | 24 ± 1                                    | 0.025 mM   | DLS                 | 267  |
| 444      | Vesicle                        | 26 ± 1                                    | 0.05 mM  | DLS                 | 267  |
| 444      | Vesicle                        | 25 ± 1                                    | 0.1 mM   | DLS                 | 267  |
| 444      | Vesicle                        | 24 ± 1                                    | 0.25 mM  | DLS                 | 267  |
| 444      | Vesicle                        | 25 ± 1                                    | 0.5 mM   | DLS                 | 267  |
| 444      | Vesicle                        | 31 ± 1                                    | 0.75 mM  | DLS                 | 267  |
| 444      | Vesicle                        | 31 ± 1                                    | 1.0 mM   | DLS                 | 267  |
| 448      | Vesicle                        | 40  | H <sub>2</sub> O–EtOH 1 : 2  | TEM, SEM, AFM, DLS  | 273  |
| 449      | Vesicle                        | 70  | H <sub>2</sub> O–EtOH 1 : 1  | TEM, SEM, AFM, DLS  | 273  |
| 449      | Vesicle                        | 46  | H <sub>2</sub> O–EtOH 3 : 1  | TEM, SEM, AFM, DLS  | 273  |
| 450      | Spherical aggregate            | 60–90                                     | H <sub>2</sub> O–EtOH 1 : 1  | TEM, SEM, AFM, DLS  | 273  |
| 450      | Tubular aggregate              | 28 (radius)                               | H <sub>2</sub> O–EtOH 3 : 1  | TEM, SEM, AFM, DLS  | 273  |
| 451      | Spherical aggregate            | 60–90                                     | H <sub>2</sub> O–EtOH 1 : 1  | TEM, SEM, AFM, DLS  | 273  |
| 451      | Tubular aggregate              | 28 (radius)                               | H <sub>2</sub> O–EtOH 3 : 1  | TEM, SEM, AFM, DLS  | 273  |
| 452      | Vesicle                        | 145                                       | H <sub>2</sub> O–EtOH 1 : 3  | TEM, AFM, DLS       | 242  |
| 452      | Mixture of vesicles and fibers | —   | H <sub>2</sub> O–EtOH 2 : 3  | SEM, TEM            | 242  |
| 452      | Fiber                          | 50–100 (radius), 10 <sup>4</sup> (length) | H <sub>2</sub> O–EtOH 1 : 1  | TEM, SEM, AFM       | 242  |
| 452      | Nanotube                       | 30–40                                     | 0.5 g L <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub> , H <sub>2</sub> O–EtOH 2 : 1 | TEM                 | 275  |
| 452      | Nanotube                       | —   | 0.5 g L <sup>-1</sup> AgNO <sub>3</sub> , H <sub>2</sub> O–EtOH 2 : 1              | TEM                 | 275  |
| 453      | Tubular aggregate              | —   | H <sub>2</sub> O–EtOH 3 : 1  | TEM, SEM, AFM, DLS  | 273  |

<sup>a</sup> NP: nanoparticle, SLN: solid lipid nanoparticle. <sup>b</sup> Radii are obtained from papers directly or calculated from diameters. Part of data which is not shown in papers clearly is read from figures which contain these data.  $R_s$  is the radius of the shell.  $R_g$  is the gyration radius.  $R_h$  is the hydrodynamic radius. <sup>c</sup> The condition is 25 °C in pure water if no label. CA is the corresponding amphiphilic calixarene. <sup>d</sup> SLS: static light scattering, cryo-TEM: cryogenic transmission electron microscopy, HR TEM: high resolution transmission electron microscopy, NTA: nanoparticle tracking analysis method, PGSE: pulse gradient spin echo, FE-SEM: field-emission scanning electron microscopy, EF-TEM: energy-filtered transmission electron microscopy, OPM: optical polarization microscopy, FFF-MALS: field flow fractionation combined with multi-angle light scattering.

pH 8.5 (225 nm). This phenomenon could be explained by protonation of imidazolyl group affecting the hydrophilic and hydrophobic balance.

Salt concentration influencing assembly is another interesting topic, and it is also related to further application in biological systems. Houel and coworkers did a systematic study on salt concentration affecting assembly using phosphonate-modified calix[4]arenes **12** and **13**.<sup>126</sup> In the presence of monovalent cations (Na<sup>+</sup>, K<sup>+</sup>), no apparent change in size was observed over a concentration range from 0.1 mM to 145 mM. In contrast, divalent cations could cause a significant size increase as the concentration is increased from 2 mM. The authors assumed that divalent cations have the ability to crosslink the assemblies.

**2.2.3 Uniform assembly.** Constructing precisely defined aggregates not only represents an enormous interest and challenge for fundamental research, but also has been widely used in fields such as pharmaceuticals, catalysts, sensors, film precursors, and information storage. As reported by Cui and coworkers, monodisperse nanoparticles with a size variation of less than 5% show unique properties and higher performances as compared with the corresponding polydisperse nanoparticles.<sup>284</sup> The major advantage of monodisperse particles may be attributed to the uniform properties of individual particles, which makes the property of whole particles strictly controllable.<sup>285</sup> However, most of the common surfactants self-assemble into polydisperse assemblies. Thus, lots of effort has been dedicated to developing reliable preparation methods such as freeze–thaw and extrusion; however, a tedious operating procedure is needed. An alternative is appropriate design of amphiphilic building blocks,

since the information determining their specific supramolecular assembly architecture must be encoded in their molecular structure. Fortunately, amphiphilic calixarenes are promising candidates due to their unique assembly properties. Many aggregations based on calixarenes presented fantastic monodisperse<sup>92,93,111,142,191,202,226,252,259,262,277</sup> and unique aggregation numbers ( $N_{agg}$ s). The reported  $N_{agg}$ s are listed in Table 6.

In 2004, Kellermann and coworkers reported the first completely uniform and structurally precise micelle, whose structure was determined by cryo-TEM and 3D reconstruction techniques.<sup>97</sup> The micelle is formed spontaneously by exactly seven **47** molecules (Fig. 3), which is a T-shaped compound and with third generation dendritic heads. Later, they reported another uniform micelle formed by twelve **46** molecules, which is with second generation dendritic heads.<sup>91</sup> Compared with molecule **47**, the smaller space required by **46** allows denser packing, resulting in a larger  $N_{agg}$  value.

The Sakurai group systematically studied assembly behavior of a series of calixarene micelles, whose head groups, including sulfonate group,<sup>64,65</sup> primary amine group,<sup>63,122,124</sup> quaternary amine group,<sup>63</sup> cysteine,<sup>139</sup> glutamic acid,<sup>140</sup> polyamidoamine,<sup>63</sup> mono/disaccharides,<sup>63,157</sup> PEG,<sup>63,150</sup> and so on, were conjugated with calixarene at the upper rim by a click reaction. Using methods including SAXS, AUC, AF4-MALS and LS, the morphologies and  $N_{agg}$  values of these micelles were determined. They found that these  $N_{agg}$  values coincide with the vertex numbers of regular polyhedral structures when  $N_{agg}$  are less than 30, so they named these small micelles as platonic micelles since the regular polyhedral structures are called platonic solids. They proposed

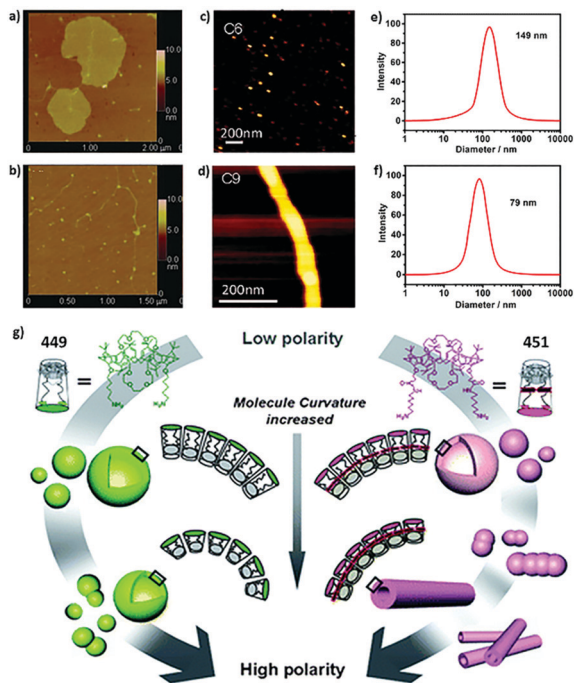


Fig. 2 AFM images of (a) **278** and (b) **279** in pure water. Reprinted with permission from ref. 224. Copyright 2012 from Science China Press and Springer-Verlag Berlin Heidelberg. AFM images of (c) **94** and (d) **97** in 50 mM NaCl, pH 3. Reprinted with permission from ref. 122. Copyright 2012 from American Chemical Society. DLS data of (e) **62** and (f) **158** in water. Reprinted with permission from ref. 46. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (g) Schematic representation for morphology transitions in self-assembly of **449** and **451** with changes in medium polarity. Reprinted with permission from ref. 273. Copyright 2011 from Royal Society of Chemistry.

that the formation of platonic micelles is a result of the maximal coverage ratio, which means the ratio of the total area of the caps to the surface area of the sphere (Fig. 4).

It is clear that the equilibrium interfacial area between the hydrophilic and hydrophobic domains ( $a_0$ ) has a significant effect on the  $N_{\text{agg}}$ , which was proved by studying a series of amphiphilic calixarenes bearing PEGs with different molecular weights as hydrophilic head groups.<sup>150</sup> Experiment results showed that amphiphile containing PEG of  $550 \text{ g mol}^{-1}$  forms a dodecamer while that of  $1000 \text{ g mol}^{-1}$  forms an octamer, since the former one has smaller  $a_0$ . Both of the micelles are monodispersed; meanwhile, high molecular weight PEG ( $2000 \text{ g mol}^{-1}$ ) leads to polydisperse micelles, because PEG 2000 exhibits a greater affinity for water and higher mobility than PEG 550 and 1000, resulting in a too large  $a_0$  to form stable monodisperse micelles.

The  $a_0$  value could be easily influenced by the solvent environment. As an example, high salt concentration decreases repulsion among head groups, resulting in smaller  $a_0$ , thus leading to larger  $N_{\text{agg}}$ .<sup>63,65</sup> Also, for head groups containing an amine or carboxyl group, pH variation may protonate or deprotonate them, resulting in a change in repulsion interaction among these head groups. Consequently, the  $a_0$  value increases with larger repulsion and *vice versa*, leading to different  $N_{\text{agg}}$ , or even a transition of morphology. For instance, amino-modified

compounds **87** and **88** form spheres at pH 3.0 while form cylinders at higher pH.<sup>122</sup>

A more complicated example is the glutamic acid containing **100**,<sup>140</sup> since it allows a continuous change in the state of its head groups from cationic to zwitterionic and then to anionic with increasing pH, resulting in a morphological transformation from spherical to cylindrical and again to spherical. Their  $N_{\text{agg}}$  at pH 3.0 and 10 were determined as 6 and 12 respectively. The molecular modeling results showed that the glutamic acid moieties exhibited folded-back structures with deprotonated carboxylic acid, resulting in a smaller hydrophilic volume than that with the protonated amino groups, causing increased  $N_{\text{agg}}$  from pH 3.0 to pH 10. It is also noteworthy that its  $l_c$  could also change during pH variation, because anions at pH 10 are more far away from the center of the molecule than cations at pH 3.0.

The ionized state change induced by pH change could also influence the hydrogen bond formation. Disaccharides containing **120** provides an interesting example.<sup>157</sup> The micellar morphologies are cylindrical at pH 7.0 and micelles with  $N_{\text{agg}}$  of 20 at pH 12 (25 °C), due to the cleavage of the hydrogen bonds by deprotonation of the hydroxyl groups in the sugar molecules. Similarly, temperature also affects hydrogen bonds. As a result, compound **120** forms micelles with  $N_{\text{agg}}$  of 24 at 40 °C (pH 7), and forms micelles with  $N_{\text{agg}}$  of 12 at 40 °C (pH 12).

As we mentioned before,  $l_c$  is also important to the  $N_{\text{agg}}$  of aggregates. According to packing parameter theory,  $N_{\text{agg}}$  is proportional to  $l_c^2$ , whose trend is consistent with experimental results of a series of quaternary amine group bearing calixarenes.<sup>63</sup> As the number of carbons in the alkyl chain increases from 3 to 7,  $N_{\text{agg}}$  increases discretely from 8 to 12, and then to 20. However, a series of amine group bearing calixarenes show a different behavior.<sup>124</sup> Their platonic micelles bearing butyl, heptyl, and hexyl chains remain at 12-mer. This phenomenon and discrete  $N_{\text{agg}}$  may indicate that the coverage ratio defined by the Tammes problem is more suitable than packing parameter theory in the case of investigating small micelles.

To test the universality of the platonic micelles, Sakurai's group also studied assembly behavior of a series of amphiphilic SC4As **4**, **6–8**.<sup>64,65</sup>  $N_{\text{agg}}$ s of these micelles increase from 4 to 17 to 24 and then to cylindrical structures with increasing alkyl chain length from pentyl to hexyl to heptyl and then to octyl, respectively. Although the values of 17 and 24 do not agree with the vertex numbers of regular polyhedra, but they match the local maxima in the Thomson problem considering the Coulomb potential for the calculation of the best packing on a sphere with multiple identical spherical caps.

**2.2.4 Compact packing.** Compactness of assemblies is another crucial factor for the performances of various applications, for example, construction of a reliable drug delivery system<sup>180</sup> or an efficient light harvesting material.<sup>46</sup> However, compared with CAC and morphology, such a significant assembly property did not attract much attention, and there is no unified definition of compactness up to now. In general, the microviscosity of assemblies presents their compactness, which could be measured by fluorescence polarization ( $P$ ). The shape of the IR or NMR peak reflects the environment surrounding a bond or nucleus, and is also used as a measure of compactness.

Table 6  $N_{agg}$ s of amphiphilic calixarene assemblies

| Compound | $N_{agg}$ | Condition <sup>a</sup>                   | Method <sup>b</sup> | Ref.        |
|----------|-----------|--|---------------------|-------------|
| 4        | 4         | 10 mM NaCl                               | SAXS, AF4-MALS, AUC | 64 and 65   |
| 4        | 6         | 15 mM NaCl                               | SAXS, AF4-MALS, AUC | 65          |
| 6        | 17        | 10 mM NaCl                               | SAXS, AF4-MALS, AUC | 64          |
| 7        | 24        | 10 mM NaCl                               | SAXS, AF4-MALS, AUC | 64          |
| 46       | 12        | pH 7                                     | Cryo-TEM            | 91          |
| 47       | 7         | 27 mM Na <sup>+</sup> and K <sup>+</sup> | Cryo-TEM            | 97          |
| 75       | 8         | 50 mM NaCl                               | SAXS, AF4-MALS, AUC | 63          |
| 76       | 8         | 50 mM NaCl                               | SAXS, AF4-MALS, AUC | 63          |
| 77       | 12        | 50 mM NaCl                               | SAXS, AF4-MALS, AUC | 63          |
| 77       | 12        | 100 mM NaCl                              | SAXS                | 63          |
| 77       | 20        | 200–300 mM NaCl                          | SAXS                | 63          |
| 78       | 12        | 50 mM NaCl                               | SAXS, AF4-MALS, AUC | 63          |
| 79       | 20        | 50 mM NaCl                               | SAXS, AF4-MALS, AUC | 63          |
| 91       | 6         | 50 mM NaCl, pH 3.0                       | SAXS, AF4-MALS, AUC | 122 and 124 |
| 92       | 12        | 50 mM NaCl, pH 3.0                       | SAXS, AF4-MALS, AUC | 124         |
| 93       | 12        | 50 mM NaCl, pH 3.0                       | SAXS, AF4-MALS, AUC | 124         |
| 94       | 12        | 50 mM NaCl, pH 3.0                       | SAXS, AF4-MALS, AUC | 122 and 124 |
| 100      | 12        | 50 mM NaCl, pH 3.0                       | SAXS, AF4-MALS, AUC | 122 and 124 |
| 101      | 6         | pH 3.2                                   | SAXS, AF4-MALS      | 139         |
| 101      | 12        | pH 10                                    | SAXS, AF4-MALS      | 63          |
| 101      | 6         | 50 mM NaCl, pH 3.0                       | SAXS, FFF-MALS      | 140         |
| 101      | 12        | 50 mM NaCl, pH 10                        | SAXS, FFF-MALS      | 140         |
| 102      | 8         | 50 mM NaCl                               | SAXS, AF4-MALS      | 63          |
| 125      | 24        | 50 mM NaCl, pH 7.0, 40 °C                | SAXS, AF4-MALS, AUC | 157         |
| 125      | 20        | 50 mM NaCl, pH 12                        | SAXS, AF4-MALS, AUC | 157         |
| 125      | 21        | 50 mM NaCl, pH 12, 40 °C                 | SAXS, AF4-MALS, AUC | 157         |
| 143      | 20        | 50 mM NaCl                               | SAXS, AF4-MALS      | 63          |
| 143      | 12        | 50 mM NaCl                               | SAXS, FFF-MALS      | 150         |
| 144      | 8         | 50 mM NaCl                               | SAXS, FFF-MALS      | 150         |
| 145      | 3–4       | 50 mM NaCl                               | SAXS, FFF-MALS      | 150         |
| 146      | 12        | 50 mM NaCl                               | SAXS, AF4-MALS      | 63          |
| 147      | 3.6       | 50 mM NaCl                               | AF4-MALS            | 63          |

<sup>a</sup> The condition is 25 °C in pure water if no label. <sup>b</sup> AUC: analytical ultracentrifugation. AF4-MALS: multiangle light scattering coupled with asymmetric field flow fractionation.

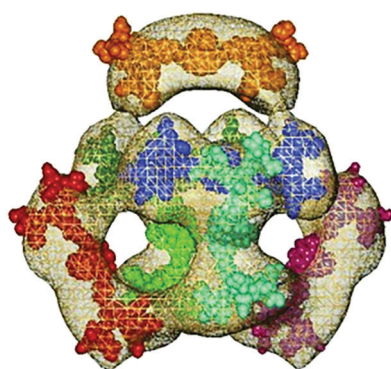


Fig. 3 A structurally precise micelle formed by exactly seven **47** molecules is determined by 3D reconstruction techniques. Reprinted with permission from ref. 97. Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Due to their preorganized structures, amphiphilic calixarene assemblies show different compactness from that of the corresponding monomers. Shinkai and co-workers investigated the microviscosity of a series of amphiphilic calixarenes above their CACs by measuring  $P$ .<sup>49</sup>  $P$  values of a series of sulfonic group modified amphiphilic calixarenes **162**, **299**, **300**, and **322** (0.033–0.106) are higher than those of SDS (0.020) and hexadecyltrimethylammonium chloride (0.016), which means

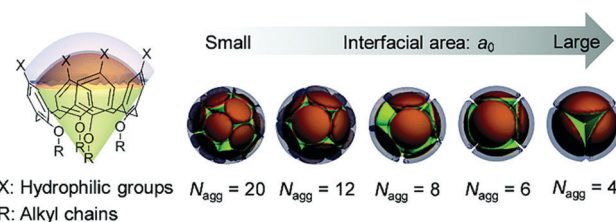


Fig. 4 Chemical structure of a calix[4]arene-based amphiphile and the schematic illustration of the effect of the size of interfacial area on the  $N_{agg}$  of the micelles composed of the amphiphiles. Reprinted with permission from ref. 65. Copyright 2018 from Royal Society of Chemistry.

more compact packing of calixarene micelles than conventional surfactant micelles.

Cho and co-workers reported that alanine-modified calix[4]arene **25** self-assembles into a hollow necklace-like structure at neutral pH.<sup>23</sup> IR spectra showed strong hydrogen bonding between the carbonyl groups and the highly organized, closely packed hydrocarbon chains exhibiting sharp IR bands.

As an assembly property, compactness is also influenced by pH and salt concentration, which modulate head group interactions. For example, Becherer and co-workers reported that carboxylic group modified calix[4]arene **46** micelles are clearly smaller at pH 9 than those at neutral pH, which can be concluded that denser packing of the micelles occurs under

basic conditions in comparison with the aggregates obtained at neutral pH.<sup>91</sup> The required smaller space of head groups allows denser packing.

Xu and co-workers demonstrated choline-modified calixarene (62 and 158) based molecular light-harvesting platforms, whose spectrum tunability is affected by assembly compactness.<sup>46</sup> When they increased the ionic strength of solvent, the ionic heads packed closer resulted in more compact aggregation, which led to higher energy-transfer efficiency and acceptor emission.

Although there have been only limited examples related to the compactness until now, we believe more and more systematic investigations will come up soon, since it is necessary for developing materials with better performance and reliability.

**2.2.5 Slow kinetics.** All four properties we mentioned above are related to thermodynamics, while kinetics, which is an interesting fundamental research topic as well as important basis of material preparation, is also essential. Due to the development of instruments and characterization methods, such as 2D exchange spectroscopy (2D EXSY), stop-flow, and time-resolved spectroscopy, kinetics of amphiphilic aggregation was investigated in detail. Originating from their multivalent feature, some amphiphilic calixarenes meet the higher energy barrier of assembly–bulky water exchange compared to conventional amphiphiles, resulting in slower kinetics.

As Basilio and co-workers reported, in contrast to conventional surfactants, the exchange rate of amphiphilic SC4A 6 between solution and micelle is slow on the NMR time scale.<sup>84</sup> The rate constants were determined by 2D EXSY experiments and these constants were found to be several orders of magnitude lower than those of conventional surfactants and comparable to those of other amphiphilic calixarenes and gemini surfactants. The explanation for this result presumably lies in the fact that the sole barrier felt by the amphiphile entering the micelle arises from long-range electrostatic repulsions due to the micellar charge. As 6 is a preorganized surfactant with four negative charges at the upper rim, this could increase the activation barrier and consequently slow down the rate constant for the association.

Takahashi and co-workers observed that quaternary ammonium modified 77 micelles transit from a dodecamer to an icosamer induced by a rapid increase in the NaCl concentration ( $c_{\text{NaCl}}$ ), using a stopped-flow device and time-resolved SAXS.<sup>133</sup> The  $N_{\text{agg}}$  remained at 12 during the first 60 s after the increase in  $c_{\text{NaCl}}$ , and then abruptly increased to 20 (Fig. 5). They speculated that the following kinetic process might take place: (1) the micelles with  $N_{\text{agg}} = 12$  become metastable after the  $c_{\text{NaCl}}$  increases to 290 mM. (2) Within the micelles, fluctuation of 77 takes place, providing sufficient space for the insertion of other 77 molecules in a process that might be very slow. (3) Once one 77 has been inserted into the metastable micelle,  $N_{\text{agg}}$  rapidly increases to 20.

Similar examples of amphiphilic calixarenes forming metastable “kinetic trap” states were reported, with more diverse morphologies.<sup>286</sup> For example, Strobel and co-workers reported that carboxylatocalix[4]arene 24 self-assembles into vesicles and long thin features that could possibly be rod-like micelles in dilute solution according to light scattering and cryo-TEM

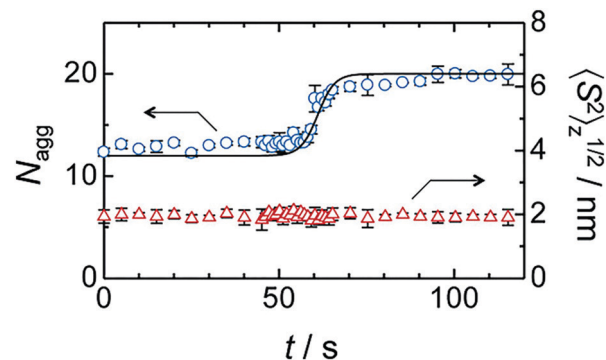


Fig. 5 Time evolution of  $N_{\text{agg}}$  (blue circles) and the radius of gyration  $\langle S^2 \rangle_z^{1/2}$  (red triangles). The solid curve for  $N_{\text{agg}}$  represents the fitted model curve. Reprinted with permission from ref. 133. Copyright 2017 from Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

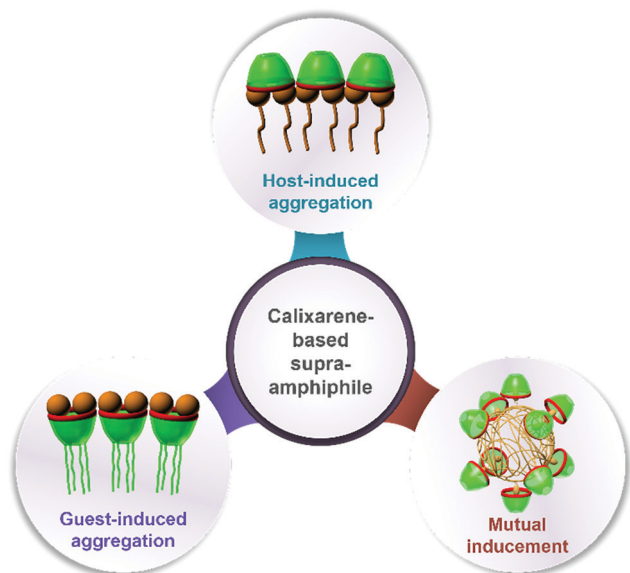
experiments.<sup>42</sup> Houmadi and co-workers reported that 164 self-assembles into vesicles in freshly prepared solution.<sup>155</sup> Vesicles of similar size and shape but with larger membrane shells were observed by TEM in 1 day old solutions, whereas giant vesicles appear after 1 week.

Despite scant examples, we have enough reason to predict a prosperous development of amphiphilic calixarene assembly kinetics. In general, highly kinetic systems at or close to equilibrium show uniform aggregate shapes and sizes, whereas systems with slow kinetics exhibit rather broad shape and size distributions.<sup>42</sup> Consequently, kinetics is critical for preparation procedures of amphiphilic calixarene assemblies. The tailored preparation process is needed for fabricating well-designed assemblies according to their kinetics features. Moreover, the slow assembling kinetics of amphiphilic calixarenes can be applied in extensive fields, such as controlled release in drug delivery systems and dissipative self-assembly systems.

### 3. Calixarene-based supra-amphiphiles

Amphiphilic macrocycles possess cavities, which endow them with binding affinity to various guests. Taking this advantage, guests could modulate the aggregation behavior of amphiphilic macrocycles. By host–guest interactions as well, non-amphiphilic macrocycles own the ability to influence the aggregate properties of some surfactants. The concept of “supra-amphiphiles” proposed by Zhang and co-workers covers those behaviors, describing amphiphiles constructed on the basis of non-covalent interactions or dynamic covalent bonds.<sup>10,287–292</sup>

Specific to water soluble calixarenes, they interact with guests including dyes, drugs, and biomacromolecules by hydrophobic interactions,  $\pi$ – $\pi$  interactions, electrostatic interactions and so on. Furthermore, their unique skeletons provide multivalent interaction sites. As a result, these guests efficiently affect the aggregation of amphiphilic calixarenes, and the aggregation behavior of these guests could be modulated by calixarenes conveniently. Based on the amphiphilicity of the host and guest



Scheme 5 Schematic illustration of various types of calixarene-based supra-amphiphiles.

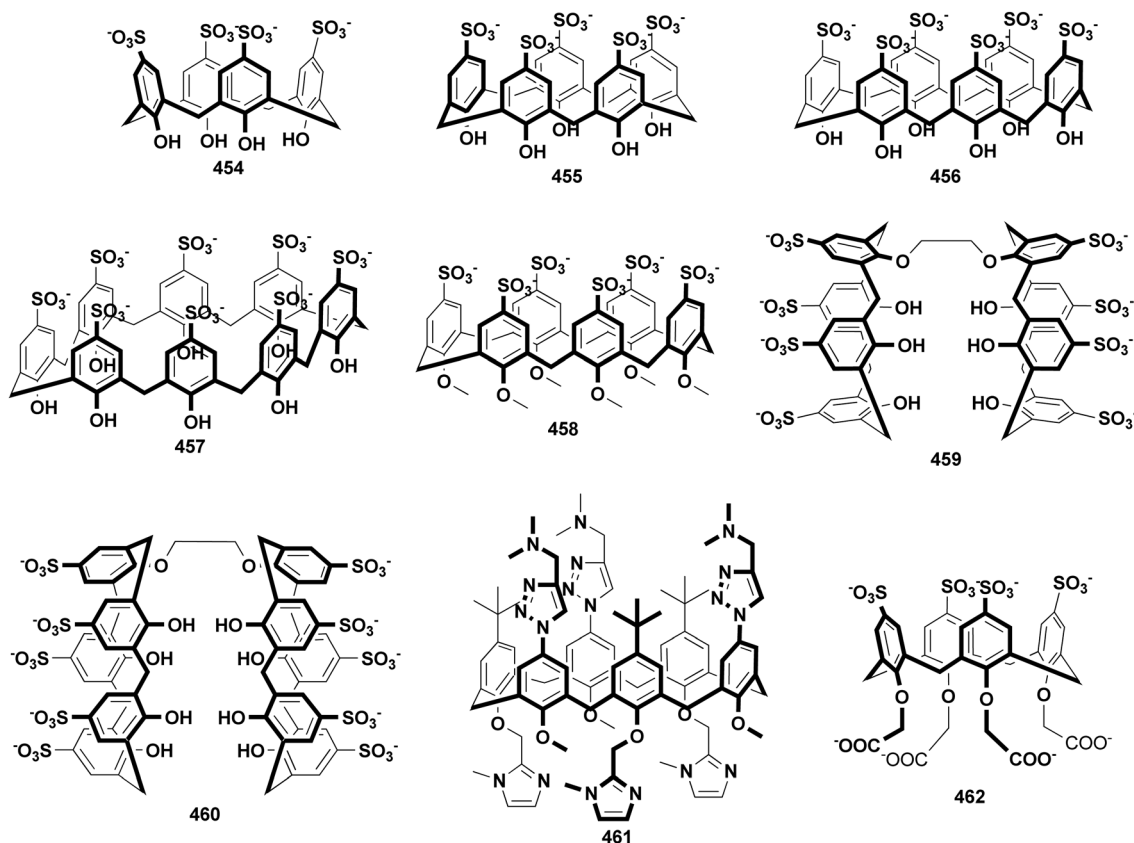
molecules, the assembling features of calixarene-based supra-amphiphiles can be divided into guest-induced aggregation of host, host-induced aggregation of guest and mutual induction (Scheme 5).

Chemical structures of host and guest molecules which have been used to construct supra-amphiphiles are summarized in Schemes 6, 7 and Tables 7, 8.

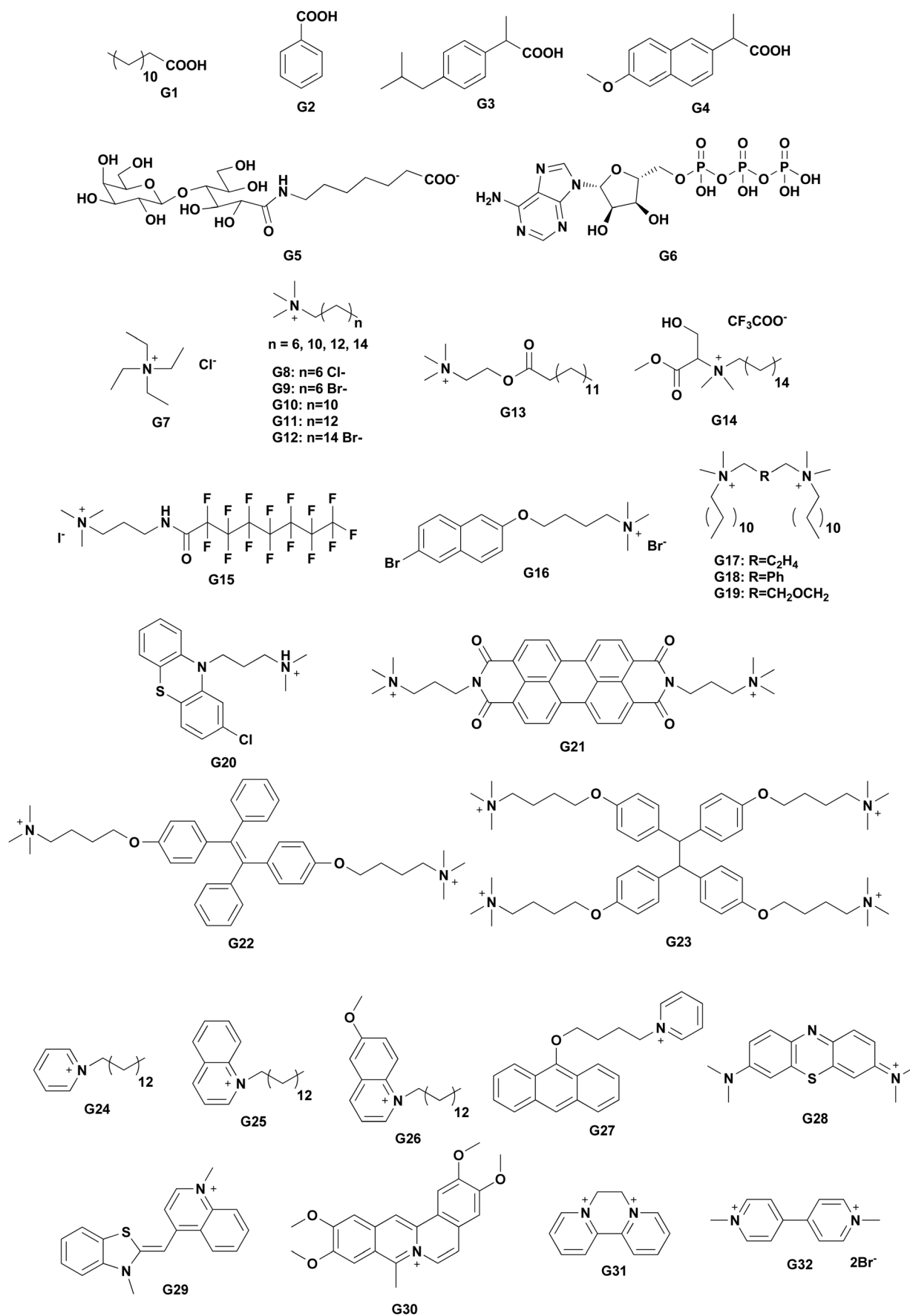
### 3.1 Guest-induced aggregation of host

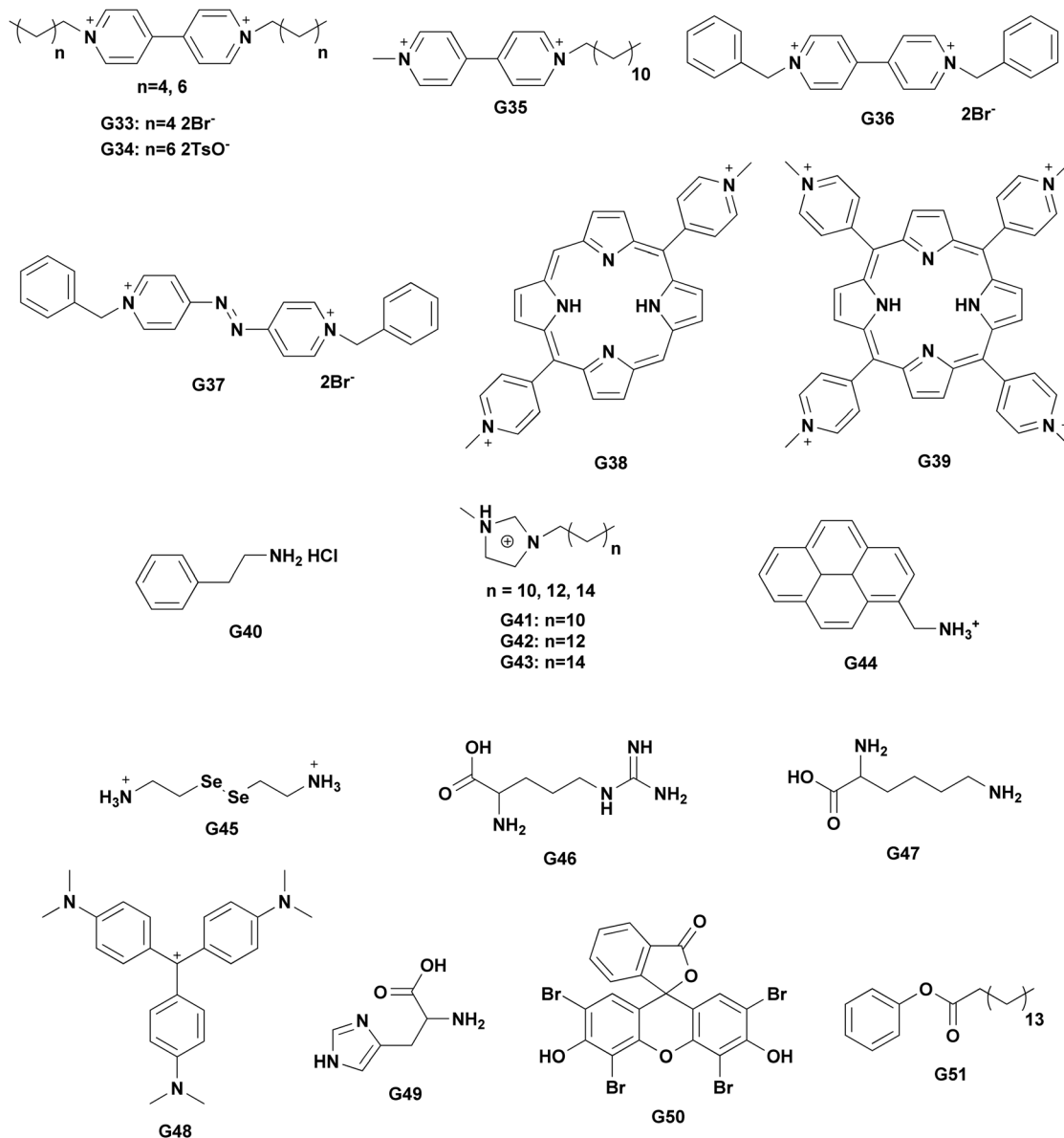
**3.1.1 Guest-decreased CAC.** A series of typical host molecules whose aggregation could be induced by guests is amphiphilic SC $n$ As owing to their good water solubility and binding affinity (Table 9). The interaction with cationic guests reduces electrostatic repulsion between their sulfonic groups, resulting in a smaller CAC. For instance, Hu and coworkers reported the aggregation of amphiphilic calix[4]arene **3** induced by diquat (**G31**).<sup>55</sup> In the absence of **G31**, the CAC value of **3** is 3.18 mM, while it decreases about 12 times (0.25 mM) in the presence of **G31**. Later, Fernandez-Abad and coworkers reported that DSMI (**G7**) could also decrease the CAC of **3** to 1.4 mM.<sup>57</sup> Moreover, it is also reported that the CAC of analogue **6** decreases in the presence of **G45**.<sup>88</sup>

Aggregation of calixarenes bearing sulfonic groups at the lower rim could also be induced by cationic guests. Gattuso and coworkers synthesized an amphiphilic calix[5]arene **294**, and DOSY results showed that its CAC was 0.64 mM.<sup>252</sup> In the presence of **G40**, its CAC decreases to 0.35 mM.<sup>251,252</sup> The inclusion of guests into the cavity of **294** is clearly proved by DOSY results, while some guests involved in the assembly are located outside the cavity. It is noteworthy that the CAC values of guests also decrease upon addition of **294**.



Scheme 6 Structures of hydrophilic host molecules which have been used to construct supra-amphiphiles.





Scheme 7 Structures of guest molecules which have been used to construct supra-amphiphiles.

Table 7 References of host molecules which have been used to construct supra-amphiphiles in Scheme 6

| Compound | Ref.                 | Compound | Ref.             | Compound | Ref. |
|----------|----------------------|----------|------------------|----------|------|
| 454      | 293–308              | 457      | 293, 296 and 307 | 460      | 309  |
| 455      | 298, 309 and 310     | 458      | 311–315          | 461      | 316  |
| 456      | 293, 296 and 317–319 | 459      | 303 and 320      | 462      | 321  |

Following the same principle, anionic guest induced cationic calixarene aggregation was also reported by Wang and coworkers.<sup>138</sup> The CAC value of a quaternary ammonium-modified calix[4]arene **59** decreases by 45 times in the presence of ATP (**G6**). Similarly, Burilov and coworkers synthesized several ammonium modified amphiphilic thiocalix[4]arenes (**432–434**) and studied their

aggregation behavior in the absence and presence of Eosin Y (**G50**).<sup>266</sup> CAC values of all these thiocalix[4]arenes, no matter the length of the hydrophobic chain, showed a significant decrease (at least 15 folds) with addition of **G50**.

**3.1.2 Guest-regulated morphology.** Besides decreasing CAC, guest promoted amphiphilic calixarene assembly also presents a transfer of morphology. Since the electrostatic repulsion is reduced by guests, the amphiphilic calixarenes tend to form larger aggregates.

For example, **6** forms small micelles in the absence of a guest, while forms aggregates with 81 nm average radius in the presence of **G45**, which was proved by DLS, TEM, and significant Tyndall effect.<sup>88</sup> Similar results were reported in the study of **59** in the presence of **G6** (Fig. 6).<sup>138</sup>

Moreover, guest induced larger aggregates could further form hydrogels. Liu's group reported several hydrogels constructed by

**Table 8** References of guest molecules which have been used to construct supra-amphiphiles in Scheme 7

| Compound | Ref.        | Compound | Ref. | Compound | Ref. | Compound | Ref.            |
|----------|-------------|----------|------|----------|------|----------|-----------------|
| G1       | 322         | G14      | 305  | G27      | 306  | G40      | 252             |
| G2       | 322         | G15      | 302  | G28      | 293  | G41      | 317             |
| G3       | 322         | G16      | 320  | G29      | 295  | G42      | 307 and 317–319 |
| G4       | 322         | G17      | 300  | G30      | 296  | G43      | 317             |
| G5       | 316         | G18      | 300  | G31      | 55   | G44      | 310             |
| G6       | 138         | G19      | 300  | G32      | 162  | G45      | 88              |
| G7       | 57          | G20      | 304  | G33      | 162  | G46      | 161             |
| G8       | 311         | G21      | 298  | G34      | 173  | G47      | 161             |
| G9       | 312         | G22      | 303  | G35      | 297  | G48      | 301             |
| G10      | 311–315     | G23      | 308  | G36      | 162  | G49      | 161             |
| G11      | 294 and 319 | G24      | 319  | G37      | 162  | G50      | 266             |
| G12      | 311         | G25      | 319  | G38      | 309  | G51      | 211             |
| G13      | 299         | G26      | 319  | G39      | 309  | —        | —               |

proline modified calix[4]arene **107**, in the presence of different guests.<sup>161,162</sup> **107** itself forms spherical aggregates with a wide size dispersion. However, upon mixing with **G32**, **G33**, **G36**, **G37**, **G46**, **G47**, and **G49**, the morphology of **107** changed to fibers, resulting in a binary hydrogel. AFM, SEM, and TEM results showed that the fiber shapes differed with guests. For example, the fibers of the **107**–**G46** are composed of long and branched fibers, while **107**–**G49** are shorter and twisted. And a denser network with stacks of rod-like nanofibers was observed in **107**–**G47** (Fig. 6).

### 3.2 Host-induced aggregation of guests

As we mentioned before, when a cationic surfactant **G45** is used to promote aggregation of an anionic amphiphilic calixarene **6**, the CAC value of **G45** decreases as well. This mutually inducing phenomenon further provides us the idea that hydrophilic calixarenes should also have the ability to enhance aggregation of amphiphiles. In fact, calixarene-induced aggregation (CIA) was first reported in 2001,<sup>321</sup> and has become more popular since 2009. The most typical hosts are SCnAs, which are capable of binding hundreds of guests with impressive affinity and promoting self-assembly of about 30 molecules in aqueous media. The concept of CIA was proposed in 2012, which means an appropriate concentration of SCnAs could lower some amphiphilic molecules' CAC, enhance aggregate stability and compactness, and regulate the degree of order in the aggregates. This strategy could be applied to aromatic fluorescent dyes, surfactants, drugs, and biomacromolecules. Some of them have been summarized in previous reviews by García-Río<sup>16</sup> and our group.<sup>3,323</sup> Herein, instead of listing all the results in this field, we focus on the properties of CIA assembly with assistance of some typical works.

From the viewpoint of intermolecular interactions, the hydrophobic interaction is the main driving force of conventional surfactant micelle formation, while electrostatic repulsion of its head group is unfavorable for assembly. SCnAs possessing multivalent negative charges could lower the potential energy

of electrostatic repulsion efficiently. As a result, in the presence of SCnAs, surfactants tend to show lower CAC, more regular arrangement, and more compact packing (Table 10).

**3.2.1 Host-decreased CAC.** A representative example of CIA is SC4A (**454**) inducing myristoylcholine (**G13**) aggregation. In this work, the CAC value of **G13** decreased significantly by a factor of *ca.* 100 with addition of an appropriate amount of **454**. Similar results were reported on various guests such as gemini surfactants **G17**–**G19**,<sup>300</sup> 1-pyrenemethylammonium (**G44**),<sup>310</sup> 1-methyl-3-tetradecylimidazolium (**G41**),<sup>317</sup> cationic serine-based surfactant **G14**<sup>305</sup> and so on. In general, the CAC value depends on the ratio of guest and SCnA, and the appropriate ratio was often determined by transmittance measurements. If the SCnA concentration is much less than that of the surfactant, there is no enough opposite charges to reduce electrostatic repulsion efficiently. On the other hand, too much SCnA concentration provides excess cavities to include surfactants, resulting in disassembling. However, García-Río and coworkers reported that sulfonatocalix[6]arene hexamethyl ether (**458**) concentration hardly effected the CAC value of the mixed system, while micelle concentration was highly dependent on **458** concentration. This phenomenon may be explained as the weak binding affinity of **458**, which has a flexible conformation without hydrogen bonds at the lower rim since methylation of lower-rim hydroxyls results in loss of hydrogen bonds, leading to a flexible conformation of **458**.

**3.2.2 Host-regulated morphology.** Following the same principle as guest induced amphiphilic calixarene aggregation, SCnAs reduced electrostatic repulsion of surfactants also leads to a larger size aggregation with a smaller curvature. Many examples of arrangement transfer from small micelles to vesicles were reported, with a significant Tyndall effect. For instance, the aggregation of **454** and an asymmetric viologen **G35** was studied by DLS, TEM, and SEM.<sup>297</sup> The DLS result showed that the average diameter of the aggregates was 362 nm, with a narrow size distribution. TEM and SEM images showed the hollow spherical morphology, indicating convincingly the vesicular structure. Moreover, the thickness of the bilayer membrane obtained was about 7 nm, which was almost equal to the total height of lengths of two **G35** and two **454**.

Harangozo and coworkers reported a nanoparticle consisting of **G42** and SC6A (**456**).<sup>307</sup> Small angle neutron scattering (SANS) and cryo-TEM results indicated that the diameter of the multilayered nanoparticles was around 160 nm. Interestingly, they found that the nanoparticles have a tendency to transform into supramolecular micelles (around 6 nm diameter) in the presence of NaCl (Fig. 7c), which may be due to additional ions interfering the hydrate structure around the hydrophobic chains and the cross-sectional area of this supra-amphiphile.

Besides the size of assemblies, SCnA could also modulate their shape. Guo and coworkers studied the morphology of the SC5A **455** and **G21** aggregates.<sup>298</sup> The TEM image of free **G21** showed some irregular arrangement without a specific topological structure, while nano-rod structures with an average length of 220 nm appeared in the presence of **455**. These rods are considered to be composed of bundles of fibers, resulting from the hierarchical assembly of calixarenes (Fig. 7).



Table 9 Morphologies of guest-induced host assemblies and CACs of corresponding hosts

| Host | Guest | Morphology  | Radius (nm)                                       | CAC          | Quantity (host : guest) | Condition <sup>a</sup> | Method                           | Ref. |
|------|-------|---|---|--------------|-------------------------|------------------------|----------------------------------|------|
| 3    | —     | —   | —   | 3.18 mM      | —                       | —                      | —                                | 55   |
| 3    | G31   | —   | —   | 0.25 mM      | 1 : 1                   | —                      | Fluorescence                     | 55   |
| 3    | G7    | —   | —   | 1.4 mM       | 3 mM (guest)            | —                      | Conductivity                     | 57   |
| 6    | —     | Micelle   | —   | 330 μM       | —                       | —                      | Fluorescence                     | 88   |
| 6    | G45   | Multi-lamellar sphere                                   | 81  | 35 μM        | 50 μM (guest)           | —                      | DLS, TEM                         | 88   |
| 62   | —     | Micelle   | 2.7   | 0.9 mM       | —                       | —                      | ITC, DLS                         | 138  |
| 62   | G6    | Vesicle   | 247   | 0.02 mM      | 1 : 1                   | —                      | UV-vis, DLS, SEM, TEM, AFM       | 138  |
| 111  | —     | Micelle   | 20–100  | 1.2 mM       | —                       | pH 3.0                 | CD, DLS, AFM, TEM, SEM           | 161  |
| 111  | G46   | Branched fiber  | 10 <sup>3</sup> –10 <sup>4</sup> (length)         | —            | 1 : 4                   | pH 3.0                 | AFM, TEM, SEM                    | 161  |
| 111  | G49   | Twisted fiber   | 10 <sup>3</sup> –3 × 10 <sup>3</sup> (length)     | —            | 1 : 4                   | pH 3.0                 | AFM, TEM, SEM                    | 161  |
| 111  | G47   | Network   | —   | —            | 1 : 4                   | pH 3.0                 | AFM, TEM, SEM                    | 161  |
| 111  | G32   | Rod-like fiber  | —   | —            | 1 : 1                   | pH 3.0                 | AFM, SEM                         | 162  |
| 111  | G33   | Rod-like fiber  | —   | —            | 1 : 1                   | pH 3.0                 | AFM, SEM                         | 162  |
| 111  | G36   | Network   | 2 × 10 <sup>3</sup> –5 × 10 <sup>3</sup> (length) | —            | 1 : 1                   | pH 3.0                 | AFM, SEM                         | 162  |
| 111  | G37   | Network   | —   | —            | 1 : 1                   | pH 3.0                 | AFM, SEM                         | 162  |
| 142  | —     | Mixture of micelles and NPs                             | 2.5; 40   | 13 μM        | —                       | —                      | DLS, HR TEM                      | 322  |
| 142  | G4    | Mixture of hollow micelles and hollow rod-like micelles | 6   | —            | 1 : 1                   | —                      | DLS, HR TEM, cryo-TEM            | 322  |
| 142  | G3    | Mixture of micelles and NPs                             | 5   | —            | 1 : 1                   | —                      | DLS, HR TEM, cryo-TEM            | 322  |
| 143  | G1    | Hollow micelle  | 5–10  | —            | 1 : 1                   | —                      | DLS, HR TEM, cryo-TEM            | 322  |
| 143  | G2    | Linear micelle  | 3.8 (radius), 50–400 (length)                     | —            | 1 : 1                   | —                      | DLS, HR TEM, cryo-TEM            | 322  |
| 170  | —     | Vesicle   | 60 ± 15   | 7.9 ± 0.5 μM | —                       | —                      | Fluorescence, DLS                | 173  |
| 170  | G34   | Mixture of micelles, vesicles and super-aggregates      | <10; >25; 50–100                                  | 7.2 ± 0.3 μM | 1 : 1                   | —                      | Fluorescence, DLS, cryo-TEM, TEM | 173  |
| 254  | G51   | Vesicle   | 40–155  | —            | 10 : 1                  | Dioxane : water 5 : 1  | TEM, DLS                         | 211  |
| 254  | G51   | Vesicle   | 85  | —            | 5 : 1                   | Dioxane : water 5 : 1  | TEM, DLS                         | 211  |
| 254  | G51   | Spherical micelle                                       | 65  | —            | 1 : 1                   | Dioxane : water 5 : 1  | TEM, DLS                         | 211  |
| 254  | G51   | Micelle   | ~150  | —            | 1 : 5                   | Dioxane : water 5 : 1  | TEM, DLS                         | 211  |
| 254  | G51   | Mixture of network aggregates and spherical micelles    | ~200  | —            | 1 : 10                  | Dioxane : water 5 : 1  | TEM, DLS                         | 211  |
| 432  | —     | —   | 62 ± 9  | 91 ± 5 μM    | —                       | 50 mM Tris pH 7.4      | Fluorescence                     | 266  |
| 432  | G50   | —   | 45 ± 3  | 2.0 ± 0.1 μM | 10 : 1                  | 50 mM Tris pH 7.4      | Fluorescence, DLS                | 266  |
| 433  | —     | —   | 66 ± 2  | 59 ± 3 μM    | —                       | 50 mM Tris pH 7.4      | Fluorescence                     | 266  |
| 433  | G50   | —   | 53 ± 2  | 2.6 ± 0.2 μM | 10 : 1                  | 50 mM Tris pH 7.4      | Fluorescence, DLS                | 266  |
| 434  | G50   | —   | 58 ± 4  | 2.0 ± 0.1 μM | 10 : 1                  | 50 mM Tris pH 7.4      | Fluorescence, DLS                | 266  |
| 434  | —     | —   | 62 ± 1  | 33 ± 2 μM    | —                       | 50 mM Tris pH 7.4      | Fluorescence                     | 266  |
| 294  | —     | Micelle   | 2.44  | 0.64 mM      | —                       | D <sub>2</sub> O       | DOSY, AFM                        | 252  |
| 294  | G40   | Micelle   | —   | 0.35 mM      | 1 : 1                   | D <sub>2</sub> O       | DOSY                             | 252  |

<sup>a</sup> The condition is 25 °C in pure water if no label.

**3.2.3 Host-enhanced packing compactness.** Direct evidence of enhancing the packing compactness is the XRD results of **G21**. As reported by Guo and coworkers, free **G21** shows a  $\pi$ - $\pi$  stacking distance of 3.54 Å, while the results are 3.42 and 3.39 Å in the presence of **454** and **455**, respectively (Fig. 7a).<sup>298</sup>

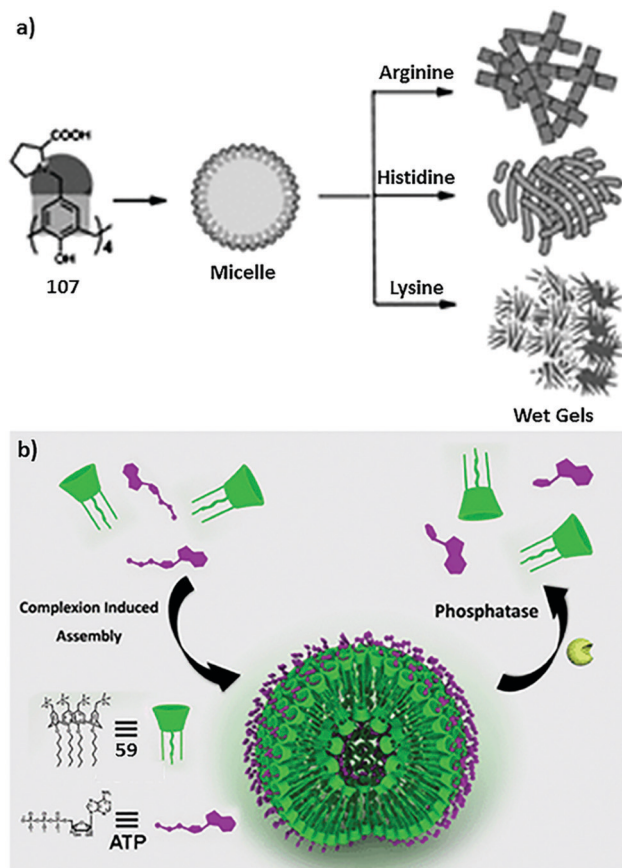
However, measuring XRD is not suitable for every assembly. So the García-Río group and the Biczok group took hydrophobicity of assembly as a parameter for compactness comparison. They assumed that a more hydrophobic assembly means more compactness.

Basilio and coworkers measured the hydrophobicity of dodecyltrimethylammonium bromide (**G10**) assembly by measuring the hydrolysis rate of two kinetic probes.<sup>314</sup> Hydrolysis rates at different surfactant concentrations were plotted and fitted, from which the binding constant of the kinetic probe between the micelles and the bulk water ( $K_m^S$ ) was obtained. The  $K_m^S$  value of **G10** in the absence of **458** is smaller than that in the presence of **458**, which means the addition of **458** leads to stronger hydrophobicity of aggregates.

Biczok and coworkers investigated the polarity of interfacial layers by using a fluorescent probe, from whose maximum fluorescence emission wavelength, the local polarity around the probe can be determined.<sup>307</sup> The polarity results were in the order **456**–**G42** supramolecular micelle < **457**–**G42** supramolecular micelle < **G42** micelle, which indicated more compact stacking of micelles.

### 3.3 Mutual inducement

In addition to the aforementioned two complexation-induced aggregation strategies, mutual inducement involves a larger range of host and guest molecules to fabricate supra-amphiphiles. For example, amphiphilic hosts and amphiphilic guests generate new supra-amphiphiles with different CACs and morphologies.<sup>251,304,324</sup> Hydrophilic hosts and hydrophobic drugs form supra-amphiphiles which can be applied in medical diagnosis and treatment.<sup>325,326</sup> Hydrophilic hosts and polymers, especially biomacromolecules like protein, DNA, and chitosan, are able to mutually induce aggregation.<sup>77,205,227,304,327–330</sup> Supra-amphiphiles consisting of



**Fig. 6** (a) Schematic illustration of gel generation from gelator **107** induced by basic amino acids. Reprinted with permission from ref. 161. Copyright 2011 from Royal Society of Chemistry. (b) Schematic illustration of the self-assembly of **59** with ATP (**G6**) and its phosphatase-response. Reprinted with permission from ref. 138. Copyright 2013 from Royal Society of Chemistry.

various kinds of host and guest molecules not only enrich the supra-amphiphile concept but also promise potential applications such as drug delivery and gene transfection.

## 4. Conclusion and outlook

In this review, we systematically summarized the assembling features of calixarene-based amphiphiles and supra-amphiphiles. Hundreds of amphiphilic calixarenes were fabricated by facile covalent modification, including upper-rim hydrophilic amphiphiles, lower-rim hydrophilic amphiphiles and bola-type amphiphiles. Compared with conventional amphiphiles, amphiphilic calixarenes usually show lower CACs and more diverse morphologies. Moreover, amphiphilic calixarenes are able to form uniform assemblies with precise  $N_{agg}$ s. The assemblies of amphiphilic calixarenes pack more compactly than those of common surfactants and their assembling kinetics is much slower. The preorganized framework of calixarenes is the most important factor to influence these unique assembly properties. In general, a larger number of repeat units lead to higher assembling tendency when the conformation is fixed, and the cone conformation is more beneficial to aggregation than the alternative conformation.

On the other hand, benefiting from their cavities, aggregation of amphiphilic calixarenes could be induced by various guests. Similarly, hydrophilic calixarenes possess the ability to enhance the assembly of amphiphilic guests. These induced aggregation phenomena are due to additional attractive interactions decreasing the repulsion of head groups of amphiphiles. Construction of such supra-amphiphiles avoids tedious synthesis, and the obtained assemblies also bear the properties of low CAC, regular morphology, and compact packing.

With prosperous development, there are still some promising objectives and challenges for the development of this area. First, the fundamental studies of assembly behaviors, such as the relationship between molecular structures and assembly properties, compactness and kinetics, need to be systematical investigated urgently. Up to now, hundreds of amphiphilic calixarenes as well as their CACs and morphologies have been reported, but there is no appropriate rule to describe how these properties depend on structures, which is extremely important to rational design of amphiphilic calixarenes with superior performance. On the other hand, compactness and kinetics behavior are featured properties of amphiphilic calixarenes, but only demonstrated in limited works. More attention is needed in the future because they are not only the important fundamental topics, but also related to further applications. For example, compact vesicles provide reliable platforms for capsuling cargo and constructing fluorescence materials with high efficiency,<sup>46,180</sup> while the kinetics feature is critical for preparation procedures of these materials.

Second, crosslinking represents a convenient avenue to obtain assemblies with better stability. For instance, Shulov and coworkers proposed a new platform for bioimaging by cyanine 3 and cyanine 5 corona crosslinked calixarene micelles.<sup>60</sup> The obtained protein-sized nanoparticles present excellent stability in various environments, showing a high fluorescence signal to noise ratio without dye leakage. Crosslinking can also be employed on the basis of supra-amphiphiles. Peng and coworkers constructed a novel supramolecular crosslinked vesicle by post-modification of a dynamic SC4A-(dodecyloxybenzyl)tripropargylammonium vesicle with the “click” reaction.<sup>331</sup> The obtained vesicle is stable enough in diverse and complex surroundings and can be disrupted with specific chemical stimuli to realize controlled release. These pioneering works demonstrate the advantages of the crosslinking strategy, which may inspire more fascinating applications in the future.

Third, by combining amphiphilic calixarenes with various kinds of other amphiphiles, such as conventional surfactants, phospholipids or macrocyclic amphiphiles, the obtained co-assemblies exhibit different assembly behaviors. Co-assembled amphiphiles may introduce attractive interactions between hydrophilic head groups of amphiphilic calixarenes, leading to lower CACs and various morphologies.<sup>66</sup> Moreover, calixarene conformations may be regulated by co-assembling, resulting in better binding affinity.<sup>86</sup> Besides, co-assembly of different amphiphilic macrocycles enables heteromultivalent recognition.<sup>179</sup>

Last but not least, although the cavities of calixarenes are well utilized in supra-amphiphiles, they have not attracted much attention in calixarene amphiphilic assemblies up to now.

Table 10 Morphologies of host-induced guest assemblies and CACs of corresponding guests

| Host | Guest | Morphology                                    | Radius (nm)                            | CAC                         | Quantity (host:guest)    | Condition <sup>a</sup>            | Method   | Ref. |
|------|-------|---|--|-----------------------------|--------------------------|-----------------------------------|--|------|
| 461  | G5    | Vesicle                                       | 150–300                                | 74 $\mu\text{M}$            | 1:3                      | pH 6.8                            | Surface tension, DLS, TEM                        | 316  |
| 461  | G5    | Vesicle                                       | 220–310                                | —                           | 1:3                      | pH 4–11                           | DLS  | 316  |
| —    | G8    | Micelle                                       | —                                      | 340 $\mu\text{M}$           | —                        | —                                 | Surface tension                                  | 311  |
| 458  | G8    | Micelle                                       | —                                      | 23 $\mu\text{M}$            | 1 mM (host)              | —                                 | Surface tension                                  | 311  |
| —    | G9    | Micelle                                       | —                                      | 310 mM                      | —                        | —                                 | Surface tension                                  | 311  |
| 458  | G9    | Micelle                                       | —                                      | 25 mM                       | 1 mM (host)              | —                                 | Surface tension                                  | 311  |
| —    | G10   | Micelle                                       | 0.9                                    | 14 mM                       | —                        | —                                 | Surface tension, fluorescence, DLS               | 311  |
| 458  | G10   | Micelle                                       | 3.0                                    | 0.20 mM                     | 5:1                      | —                                 | Surface tension, fluorescence, DLS               | 311  |
| 458  | G10   | Micelle                                       | 3.3                                    | 0.20 mM                     | 5:2                      | —                                 | Surface tension, fluorescence, DLS               | 311  |
| 458  | G10   | Micelle                                       | 3.5                                    | 0.20 mM                     | 1:1                      | —                                 | Surface tension, fluorescence, DLS               | 311  |
| 458  | G10   | Micelle                                       | 6.1                                    | 0.20 mM                     | 1:10                     | —                                 | Surface tension, fluorescence, DLS               | 311  |
| 458  | G10   | Micelle                                       | 3.0                                    | 0.20 mM                     | 1:20                     | —                                 | Surface tension, fluorescence, DLS               | 311  |
| 458  | G10   | Micelle                                       | 1.6                                    | 0.20 mM                     | 1:40                     | —                                 | Surface tension, fluorescence, DLS               | 311  |
| 458  | G10   | Micelle                                       | 1.1                                    | 0.20 mM                     | 1:80                     | —                                 | Surface tension, fluorescence, DLS               | 311  |
| 454  | G11   | Vesicle, small NP                             | 250–2500                               | —                           | 50 mM, 1:2.5             | —                                 | Nomarski light microscopy                        | 294  |
| 454  | G11   | Vesicle                                       | 57.2 $\pm$ 0.4                         | —                           | 2 mM, 1:2.5              | —                                 | DLS, TEM   | 294  |
| 456  | G11   | Spherical and ellipsoid NP                    | 46                                     | —                           | 1:6–7                    | —                                 | DLS  | 319  |
| 456  | G11   | Supramolecular micelle                        | 3.4 $\pm$ 0.3                          | —                           | 1:4                      | 15 mM NaCl, 10 $^{\circ}\text{C}$ | DLS  | 319  |
| 456  | G11   | Supramolecular micelle                        | —                                      | 20 $\mu\text{M}$            | 1:2, 3                   | 50 mM NaCl                        | DLS  | 319  |
| —    | G12   | —   | —                                      | 14 mM                       | —                        | —                                 | Fluorescence                                     | 319  |
| 458  | G12   | Micelle                                       | —                                      | 0.16 mM                     | 0.1 mM (host)            | —                                 | Surface tension, conductivity                    | 313  |
| 458  | G12   | Micelle                                       | —                                      | 0.16 mM                     | 0.5 mM (host)            | —                                 | Surface tension, conductivity                    | 313  |
| 458  | G12   | —   | —                                      | 0.3 mM                      | 0.5 $\mu\text{M}$ (host) | —                                 | Surface tension, conductivity                    | 313  |
| 458  | G12   | —   | —                                      | 0.4 mM                      | 1 $\mu\text{M}$ (host)   | —                                 | Surface tension                                  | 315  |
| 458  | G12   | —   | —                                      | 20 mM                       | 0.2 $\mu\text{M}$ (host) | —                                 | Surface tension                                  | 315  |
| 458  | G12   | —   | —                                      | 0.3 mM                      | 2 $\mu\text{M}$ (host)   | —                                 | Fluorescence                                     | 315  |
| 458  | G12   | —   | —                                      | 0.2 mM                      | 0.5 mM (host)            | —                                 | Fluorescence                                     | 315  |
| —    | G13   | Micelle                                       | —                                      | 2.5 mM                      | —                        | —                                 | —  | 299  |
| 454  | G13   | —   | —                                      | 16 $\mu\text{M}$            | 0.02 mM (host)           | —                                 | UV-vis   | 299  |
| 454  | G13   | —   | —                                      | 31 $\mu\text{M}$            | 0.05 mM (host)           | —                                 | UV-vis   | 299  |
| 454  | G13   | —   | —                                      | 31 $\mu\text{M}$            | 0.08 mM (host)           | —                                 | UV-vis   | 299  |
| 454  | G13   | Vesicle                                       | 97                                     | —                           | 1:10                     | —                                 | UV-vis, DLS, TEM, SEM, cryo-TEM, HR TEM          | 299  |
| —    | G14   | Micelle                                       | 4.3 $\pm$ 0.7                          | (162 $\pm$ 8) $\mu\text{M}$ | —                        | 35 $^{\circ}\text{C}$             | Surface tension, NMR, light microscopy, cryo-TEM | 305  |
| 454  | G14   | Micelle                                       | 30 $\pm$ 2                             | (93 $\pm$ 2) mM             | 1:250                    | 35 $^{\circ}\text{C}$             | Surface tension, NMR, light microscopy, cryo-TEM | 305  |
| 454  | G14   | Micelle                                       | —                                      | (13 $\pm$ 1) mM             | 1:100                    | 35 $^{\circ}\text{C}$             | Surface tension, NMR, light microscopy, cryo-TEM | 305  |
| 454  | G14   | Micelle                                       | 29 $\pm$ 3                             | (6.5 $\pm$ 0.8) mM          | 1:70                     | 35 $^{\circ}\text{C}$             | Surface tension, NMR, light microscopy, cryo-TEM | 305  |
| 454  | G14   | Mixture of bilayer-based tubules and vesicles | 12 $\pm$ 1                             | —                           | 1:25                     | 35 $^{\circ}\text{C}$             | Surface tension, NMR, light microscopy, cryo-TEM | 305  |
| 454  | G14   | Mixture of bilayer-based tubules and vesicles | 6.0 $\pm$ 0.2                          | —                           | 1:15                     | 35 $^{\circ}\text{C}$             | Surface tension, NMR, light microscopy, cryo-TEM | 305  |
| —    | G15   | —   | —                                      | 6.0 mM                      | —                        | —                                 | Fluorescence, surface tension                    | 302  |
| 454  | G15   | —   | —                                      | 70 $\mu\text{M}$            | 20 $\mu\text{M}$ (host)  | —                                 | Fluorescence, surface tension                    | 302  |
| 454  | G15   | —   | —                                      | 80 $\mu\text{M}$            | 50 $\mu\text{M}$ (host)  | —                                 | Fluorescence, surface tension                    | 302  |
| 454  | G15   | —   | —                                      | 100 $\mu\text{M}$           | 80 $\mu\text{M}$ (host)  | —                                 | Fluorescence, surface tension                    | 302  |
| 454  | G15   | Spherical aggregate                           | 196                                    | —                           | 4:15                     | —                                 | DLS, TEM, SEM                                    | 302  |
| 459  | G16   | Platelet-like micelle                         | 300 (length); 100 (width); 20 (height) | —                           | 1.2:2                    | 25 $^{\circ}\text{C}$             | TEM, AFM   | 320  |

Table 10 (continued)

| Host | Guest | Morphology                              | Radius (nm)              | CAC      | Quantity (host:guest) | Condition <sup>a</sup> | Method                         | Ref. |
|------|-------|---|--------------------------|----------|-----------------------|------------------------|--------------------------------|------|
| 459  | G16   | Cross-linked NP                         | —                        | —        | 1.2:2                 | 37 °C                  | DLS, TEM                       | 320  |
| —    | G17   | —                                       | —                        | 1 mM     | —                     | —                      | —                              | 300  |
| 454  | G17   | —                                       | —                        | 2.5 μM   | 0.02 mM (host)        | —                      | UV-vis                         | 300  |
| 454  | G17   | —                                       | —                        | 5.3 μM   | 0.04 mM (host)        | —                      | UV-vis                         | 300  |
| 454  | G17   | —                                       | —                        | 7.3 μM   | 0.06 mM (host)        | —                      | UV-vis                         | 300  |
| 454  | G17   | Vesicle                                 | 66.2                     | —        | 2:5                   | —                      | DLS, TEM, SEM, AFM             | 300  |
| —    | G18   | —                                       | —                        | 1 mM     | —                     | —                      | —                              | 300  |
| 454  | G18   | —                                       | —                        | 3.1 μM   | 0.02 mM (host)        | —                      | UV-vis                         | 300  |
| 454  | G18   | —                                       | —                        | 3.2 μM   | 0.04 mM (host)        | —                      | UV-vis                         | 300  |
| 454  | G18   | —                                       | —                        | 3.7 μM   | 0.06 mM (host)        | —                      | UV-vis                         | 300  |
| 454  | G18   | Vesicle                                 | 62.3                     | —        | 2:5                   | —                      | DLS, TEM, SEM, AFM             | 300  |
| —    | G19   | —                                       | —                        | 1 mM     | —                     | —                      | —                              | 300  |
| 454  | G19   | —                                       | —                        | 3.7 μM   | 0.02 mM (host)        | —                      | UV-vis                         | 300  |
| 454  | G19   | —                                       | —                        | 5.0 μM   | 0.04 mM (host)        | —                      | UV-vis                         | 300  |
| 454  | G19   | —                                       | —                        | 6.6 μM   | 0.06 mM (host)        | —                      | UV-vis                         | 300  |
| 454  | G19   | Vesicle                                 | 49.0                     | —        | 2:5                   | —                      | DLS, TEM, SEM, AFM             | 300  |
| —    | G20   | —                                       | —                        | 0.14 mM  | —                     | —                      | Conductivity                   | 304  |
| 454  | G20   | —                                       | —                        | 0.125 mM | 50 μM (host)          | —                      | UV-vis                         | 304  |
| 454  | G20   | Multilamellar sphere                    | $R_h$ : 141, $R_g$ : 108 | —        | 1:4                   | —                      | DLS, SLS, TEM                  | 304  |
| 454  | G21   | Mixtures of fibers and something larger | 96                       | —        | —                     | —                      | DLS                            | 298  |
| 454  | G21   | Mixture of fibers and columnar stacks   | 100                      | —        | —                     | —                      | DLS, TEM, SEM, AFM             | 298  |
| —    | G22   | Spherical aggregate                     | 55                       | —        | —                     | —                      | Surface tension, DLS, TEM, AFM | 303  |
| 454  | G22   | —                                       | —                        | 0.14 mM  | 1:2                   | —                      | Surface tension                | 303  |
| 454  | G22   | Multilamellar spherical aggregate       | 30                       | —        | 1:2                   | —                      | DLS, TEM, AFM                  | 303  |
| 459  | G22   | Spherical and linear aggregate          | 60                       | —        | 1:4                   | —                      | DLS, TEM, AFM                  | 303  |
| —    | G23   | —                                       | 240                      | 90 μM    | —                     | —                      | DLS                            | 308  |
| 454  | G23   | —                                       | 72                       | 0.8 μM   | 1:1                   | —                      | DLS                            | 308  |
| 456  | G24   | Spherical and oblate lamellar NP        | 15–48                    | —        | 1:2–7                 | —                      | DLS                            | 319  |
| 456  | G24   | Supramolecular micelle                  | $2.4 \pm 0.2$            | —        | 1:3                   | 50 mM NaCl, 15 °C      | DLS                            | 319  |
| 456  | G24   | Supramolecular micelle                  | —                        | —        | 1:2                   | 50 mM NaCl             | DLS                            | 319  |
| 456  | G25   | Spherical lamellar NP                   | 20–39                    | 16 μM    | 1:2                   | —                      | Fluorescence                   | 319  |
| 456  | G26   | Spherical NP                            | 25–41                    | —        | 1:2–6                 | —                      | DLS                            | 319  |
| 454  | G27   | —                                       | —                        | 0.078 mM | 1:2–6                 | —                      | DLS                            | 319  |
| 454  | G27   | —                                       | —                        | 0.062 mM | 0.05 mM               | —                      | UV-vis                         | 306  |
| 454  | G27   | —                                       | —                        | 0.103 mM | 0.02 mM               | —                      | UV-vis                         | 306  |
| 454  | G27   | Spherical NP                            | 133.36                   | —        | 0.08 mM               | —                      | UV-vis                         | 306  |
| —    | G35   | —                                       | —                        | 20 mM    | 2:5                   | —                      | DLS, TEM                       | 306  |
| 454  | G35   | —                                       | —                        | 0.02 mM  | —                     | —                      | —                              | 297  |
| 454  | G35   | —                                       | —                        | 0.04 mM  | 0.02 mM (host)        | —                      | UV-vis                         | 297  |
| 454  | G35   | —                                       | —                        | 0.07 mM  | 0.05 mM (host)        | —                      | UV-vis                         | 297  |
| 454  | G35   | Vesicle                                 | 181                      | —        | 0.08 mM (host)        | —                      | UV-vis                         | 297  |
| 460  | G38   | Fiber-like                              | $10^4$ (length)          | —        | 1:2                   | —                      | DLS, TEM, SEM                  | 297  |
| 460  | G39   | Flake-like                              | $1.5-1.7$ (height)       | —        | 1:5                   | 0.1 M PB, pH 7.2       | AFM, SEM                       | 309  |
| 455  | G39   | NP                                      | $0.8-0.9$                | —        | 1:2                   | 0.1 M PB, pH 7.2       | AFM, SEM                       | 309  |
| 456  | G41   | NP                                      | $65 \pm 10$              | —        | 1:1                   | 0.1 M PB, pH 7.2       | AFM                            | 309  |
| 456  | G41   | NP                                      | $88 \pm 28$              | —        | 1:2                   | —                      | DLS                            | 317  |
| 456  | G41   | NP                                      | 80–190                   | —        | 1:5                   | —                      | DLS                            | 317  |
| 456  | G42   | NP                                      | $80 \pm 30$              | —        | 1:3–120               | —                      | DLS                            | 317  |
| 456  | G42   | NP                                      | 75–150                   | —        | 1:1                   | —                      | DLS                            | 317  |
| 456  | G42   | Lamellar spherical aggregate            | 65–100                   | —        | 1:1–200               | —                      | DLS                            | 317  |
| 456  | G42   | Multilayered spherical aggregate        | 35–75                    | —        | 1:2                   | —                      | DLS, cryo-TEM, SANS            | 317  |
| —    | G42   | —                                       | —                        | —        | 1:20                  | —                      | DLS, cryo-TEM, SANS            | 317  |

Table 10 (continued)

| Host | Guest | Morphology                  | Radius (nm) | CAC     | Quantity (host : guest) | Condition <sup>a</sup> | Method        | Ref. |
|------|-------|-----------------------------|-------------|---------|-------------------------|------------------------|---------------|------|
| —    | G42   | Micelle                     | 2.3 ± 0.2   | —       | —                       | 20 mM NaCl             | DLS           | 318  |
| 456  | G42   | NP                          | 33–100      | —       | 1:6                     | 0–110 mM NaCl          | DLS           | 318  |
| 456  | G42   | NP                          | 33–119      | —       | 1:5                     | 0–110 mM NaCl          | DLS           | 318  |
| 456  | G42   | NP                          | 25–87       | —       | 1:4                     | 0–40 mM NaCl           | DLS           | 318  |
| 456  | G42   | Supramolecular micelle      | 3.0 ± 0.2   | —       | 1:4                     | 40–53 mM NaCl          | DLS           | 318  |
| 456  | G42   | NP                          | 28–69       | —       | 1:3                     | 0–25 mM NaCl           | DLS           | 318  |
| 456  | G42   | Supramolecular micelle      | 3.0 ± 0.2   | —       | 1:3                     | 25–33 mM NaCl          | DLS           | 318  |
| 456  | G42   | NP                          | 33–94       | —       | 1:2                     | 0–15 mM NaCl           | DLS           | 318  |
| 456  | G42   | Supramolecular micelle      | 3.0 ± 0.2   | —       | 1:2                     | 15–17 mM NaCl          | DLS           | 318  |
| 456  | G42   | Supramolecular micelle – NP | 3–250       | —       | 1:2                     | 15 mM NaCl, 27–33 °C   | DLS           | 318  |
| 456  | G42   | Supramolecular micelle – NP | 3–250       | —       | 1:2                     | 50 mM NaCl, 33–38 °C   | DLS           | 318  |
| 456  | G42   | NP                          | 80          | —       | 1:3                     | 15 mM NaCl, 20 °C      | DLS           | 318  |
| 456  | G42   | Supramolecular micelle      | 3           | —       | 1:3                     | 15 mM NaCl, 25 °C      | DLS           | 318  |
| 456  | G42   | NP                          | 185         | —       | 1:3                     | 15 mM NaCl, 30 °C      | DLS           | 318  |
| 456  | G42   | NP                          | 36 ± 10     | —       | 1:4                     | —                      | Cryo-TEM      | 318  |
| 456  | G42   | Supramolecular micelle      | <8          | —       | 1:4                     | 53 mM NaCl             | Cryo-TEM      | 318  |
| 456  | G42   | Micelle                     | —           | 720 μM  | —                       | 50 mM NaCl             | Fluorescence  | 318  |
| 456  | G42   | —                           | —           | 15 μM   | 1:2                     | 50 mM NaCl             | Fluorescence  | 318  |
| 456  | G42   | —                           | —           | 15 μM   | 1:1                     | 50 mM NaCl             | Fluorescence  | 318  |
| 456  | G42   | —                           | —           | 15 μM   | 1:3                     | 50 mM NaCl             | Fluorescence  | 318  |
| 456  | G42   | —                           | —           | 15 μM   | 1:3.6                   | 50 mM NaCl             | Fluorescence  | 318  |
| 454  | G42   | NP                          | 100         | —       | 1:2                     | 0–0.08 mM NaCl         | DLS, cryo-TEM | 307  |
| 454  | G42   | NP                          | 100         | —       | 1:4                     | 0–0.07 mM NaCl         | DLS, cryo-TEM | 307  |
| 457  | G42   | NP                          | 23–45       | —       | 1:2–9                   | —                      | DLS           | 307  |
| 457  | G42   | NP                          | 45          | —       | 1:6.8–8.8               | 0–50 mM NaCl           | DLS           | 307  |
| 457  | G42   | Supramolecular micelle – NP | 2.5–350     | —       | 1:4.9                   | 30 mM NaCl, 45–55 °C   | DLS           | 307  |
| 457  | G42   | Supramolecular micelle – NP | 2.5–320     | —       | 1:4.9                   | 50 mM NaCl, 50–55 °C   | DLS           | 307  |
| 457  | G42   | NP – supramolecular micelle | 45–2.5      | —       | 1:5.8                   | 0–50 mM NaCl           | DLS           | 307  |
| 457  | G42   | NP – supramolecular micelle | 38–2.5      | —       | 1:3.9                   | 0–50 mM NaCl           | DLS           | 307  |
| 457  | G42   | —                           | —           | 15 μM   | 1:2.0                   | 50 mM NaCl             | Fluorescence  | 307  |
| 457  | G42   | —                           | —           | 12 μM   | 1:5.9                   | 50 mM NaCl             | Fluorescence  | 307  |
| 456  | G43   | NP                          | 55 ± 13     | —       | 1:1                     | —                      | DLS           | 317  |
| 456  | G43   | NP                          | 60–90       | —       | 1:1–200                 | —                      | DLS           | 317  |
| —    | G44   | —                           | —           | 0.27 mM | —                       | —                      | Fluorescence  | 310  |
| 455  | G44   | —                           | —           | 0.07 mM | 0.02 mM (host)          | —                      | Fluorescence  | 310  |
| 455  | G44   | —                           | —           | 0.09 mM | 0.05 mM (host)          | —                      | Fluorescence  | 310  |
| 455  | G44   | —                           | —           | 0.08 mM | 0.08 mM (host)          | —                      | Fluorescence  | 310  |
| 455  | G44   | Vesicle                     | 49.4        | —       | 1:4                     | —                      | DLS, TEM, SEM | 310  |

<sup>a</sup> The condition is 25 °C in pure water if no label.

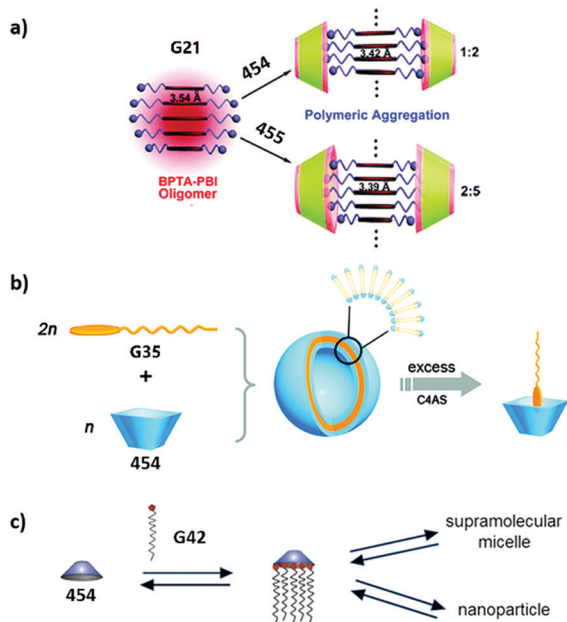


Fig. 7 (a) Schematic illustration of the complex-induced aggregation of BPTA-PBI (**G21**) by **454** and **455**. Reprinted with permission from ref. 298. Copyright 2012 from Royal Society of Chemistry. (b) Schematic representation of the construction of a supramolecular binary vesicle based on the host-guest complexation of **454** with **G35**. Reprinted with permission from ref. 297. Copyright 2011 from American Chemical Society. (c) Illustration of **454** induced **G42** formation of nanoparticles and supramolecular micelles. Reprinted with permission from ref. 307. Copyright 2016 from American Chemical Society.

Actually, binding and assembling abilities complement each other and influence each other. As we mentioned above, aggregation enhances the binding ability by regulating the calixarene conformation.<sup>86</sup> Furthermore, by utilizing the host-guest recognition cavity of calixarenes on the assembly surface, the morphology of the assembly can be controlled by guests, non-covalent modification of specific functional groups can be performed, and multidimensional and hierarchical self-assemblies can be achieved.

In summary, aiming on these objectives and challenges will lead to a deep understanding of the assembling features of amphiphiles and supra-amphiphiles based on calixarenes, and also enrich their construction motifs and strategies, which are essential to develop functional materials based on calixarenes. Moreover, although this review focused on calixarenes, the conclusions are also transferable to other macrocyclic amphiphiles and supra-amphiphiles.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was supported by the NSFC (51873090 and 21672112), the Fundamental Research Funds for the Central Universities

and the Innovation Project of Hebei Province (19241303D), which are gratefully acknowledged.

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