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# A polyaromatic dumbbell-based micelle capable of binding large dyes under organic solvent-rich conditions

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Micelles are typical molecular assemblies formed in water. To develop new micelles usable even under organic solvent-rich conditions, we designed and synthesized a dumbbell-shaped polyaromatic amphiphile composed of two bent bisanthracene dimers linked by a long dicationic spacer. The dissolved dumbbells quantitatively assemble into a spherical polyaromatic micelle with a core diameter of  $\sim 2$  nm in water, exhibiting extremely high stability against dilution (up to  $1.2 \mu\text{M}$ ). Through a simple grinding–sonication protocol, organic and metal–organic dyes are efficiently encapsulated by the micelle in water. Strikingly, the resulting host–guest composites retain excellent stability even after addition of a large amount of organic solvent (e.g., 75% v/v methanol), owing to multiple chelate-type  $\pi$ – $\pi$  and CH– $\pi$  interactions. The importance of both the long spacer and the dumbbell design is demonstrated by control experiments using an analogous dumbbell possessing a shorter spacer and an amphiphilic semi-dumbbell.

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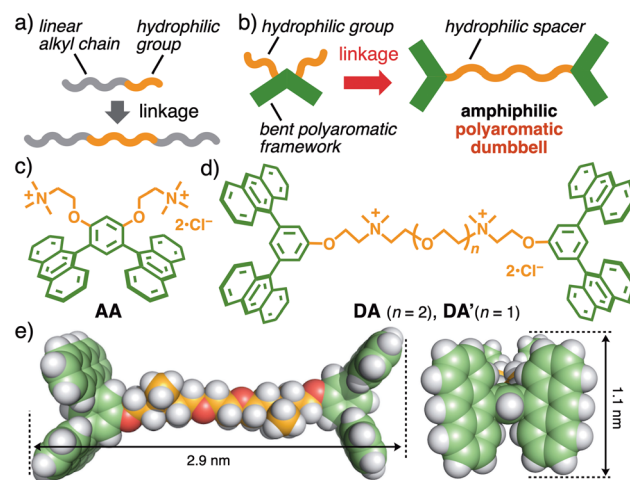
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## Introduction

Micelles, typical molecular assemblies in water, provide both advantages and disadvantages in terms of host functions.<sup>1</sup> One of the advantages is that the size and shape of the host frameworks are widely adaptable to the bound guest molecules, unlike molecular cages and capsules formed from covalent, hydrogen, and/or coordination bonds.<sup>2–4</sup> As a disadvantage, the resultant host–guest composites are unstable in both organic solvents and aqueous organic solvents, owing to facile host dissociation and weak host–guest interactions. There have been many reports on micelles with improved assembly stability in water through covalent linkage of linear alkyl amphiphiles (Fig. 1a).<sup>5,6</sup> However, high stability of micellar host–guest composites against the addition of organic solvent has hardly been realized even using such linked amphiphiles. Our group has developed polyaromatic amphiphile AA (Fig. 1b, left and 1c), featuring a bent anthracene dimer with two ionic hydrophilic groups,<sup>7</sup> which generates polyaromatic micelle (AA)<sub>n</sub>, with relatively strong host abilities, in water.<sup>8</sup> To accomplish high organic solvent compatibility, which can further enhance the practical utility of micelles (e.g., as cleaning and synthetic tools), we designed an amphiphilic polyaromatic dumbbell (Fig. 1b, right), composed of two bent anthracene dimers linked by a single hydrophilic spacer.

Here we report (i) the synthesis of DA ( $n = 2$ , Fig. 1d) and its grinding–sonication-assisted assembly into a new polyaromatic micelle in water and (ii) its high assembly stability against dilution compared to related derivatives, and (iii) the strong binding of various dyes (e.g., fullerene, organic, metal–



**Fig. 1** Linkage of (a) linear alkyl amphiphiles (previous work) and (b) bent polyaromatic amphiphiles (this work), to realize the stabilization of host–guest composites against aqueous organic solvents. (c) Bent polyaromatic amphiphile AA reported previously<sup>7</sup> and (d) amphiphilic polyaromatic dumbbells DA and DA'. (e) Optimized structure (DFT, B3LYP/6-31G(d,p) level) of DA: side and bottom views.

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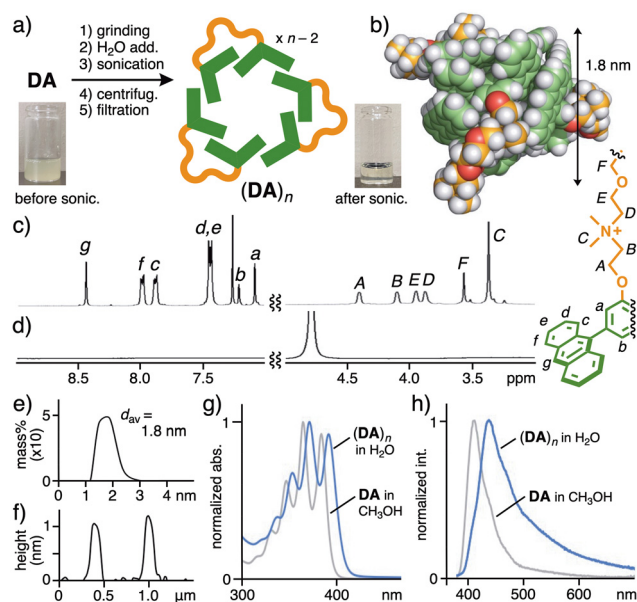
organic, and polymer dyes) even in organic solvent-rich (up to 75% v/v) aqueous solution.

Polyaromatic micelle ( $\text{AA}_n$ ) possesses wide-ranging encapsulation abilities toward aromatic compounds in water, based on the hydrophobic effect, and efficient  $\pi$ - $\pi$  and CH- $\pi$  interactions.<sup>7,8</sup> For the design of a micelle with strong host-guest interactions in aqueous organic media, we incorporated its bent polyaromatic part as the guest binding site into the structure of **DA** (Fig. 1d and e). Two of the bent frameworks were connected on the convex site with a flexible penta(ethylene oxide) spacer embedding two ammonium groups (1.8 nm in length) to enable chelate-type guest binding and reduce repulsive cation-cation interactions within the host.<sup>9</sup> Relocation of the hydrophilic spacer furthermore increased the partial aromatic stackings within **DA** as well as between **DA**s, resulting in improved assembly stability, relative to that of previous micelles formed from amphiphilic polyaromatic oligomers.<sup>10</sup> Analogous dumbbell **DA'** (Fig. 1d), possessing a shorter dicationic spacer ( $n = 1$ ), and an amphiphilic semi-dumbbell (**VA**) were prepared to study the effect of spacer length and the necessity of the linkage, respectively.

## Results and discussion

### Formation of the polyaromatic dumbbell-based micelle

Polyaromatic dumbbell-based micelle ( $\text{DA}_n$ ) was quantitatively obtained from amphiphile **DA** dissolved in water *via* grinding-sonication-assisted self-assembly. **DA** was synthesized in five steps starting from 1,3-dibromo-5-methoxybenzene in 26% overall yield (Fig. S1–19).<sup>11</sup> The construction of the bent anthracene dimer by Suzuki–Miyaura coupling and its dimerization through amine quaternization are the key steps. While **DA** (1.2 mg, 1.0  $\mu\text{mol}$ ) was virtually insoluble in water (1.0 mL) by simple stirring at room temperature, a clear aqueous solution of micelle ( $\text{DA}_n$ ) (0.4 mM based on **DA**) was obtained through sequential manual grinding (1 min), water addition, sonication (40 kHz, 150 W, 10 min), centrifugation (14 800 rpm, 10 min), and membrane filtration (200 nm pore size; Fig. 2a). Compared to the  $^1\text{H}$  NMR spectrum of **DA** in  $\text{CDCl}_3$  (Fig. 2c), that of ( $\text{DA}_n$ ) in  $\text{D}_2\text{O}$  (0.4 mM based on **DA**) showed completely broadened signals ( $H_{\text{a-g}}$  and  $H_{\text{A-F}}$ ), indicating the tight assembly of  $n$ -**DA** through the hydrophobic effect and chelate-type, multiple  $\pi$ -stacking interactions (Fig. 2d).<sup>12</sup> The formation of a well-defined assembly with an average core diameter of 1.8 nm in water was indicated by DLS analysis (Fig. 2e). The dry-state AFM analysis also supported the formation of small particles ( $d = \sim 1$  nm; Fig. 2f and S37).<sup>13</sup> The combination of experimental and molecular modeling studies suggested that the product is on average composed of ( $\text{DA}_3$ ), where the partial inter- and intramolecular stacking of **DA**s generates a spherical polyaromatic core ( $d = 1.8$  nm), surrounded by curved hydrophilic spacers (Fig. 2b). The assembled structure was also supported by UV-visible and fluorescence analyses. The anthracene-based absorption bands of ( $\text{DA}_n$ ) in  $\text{H}_2\text{O}$  were red-shifted ( $\Delta\lambda_{\text{max}} = +7$  nm), relative to



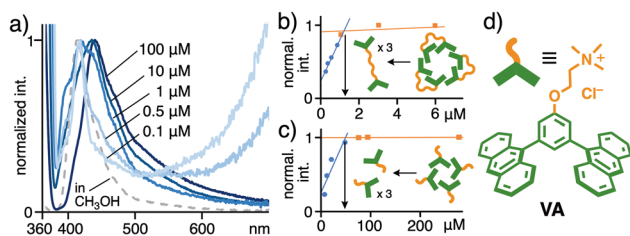
**Fig. 2** (a) Selective formation of polyaromatic micelle ( $\text{DA}_n$ ) in water *via* a grinding–sonication protocol. (b) Optimized structure (MM) of ( $\text{DA}_3$ ).  $^1\text{H}$  NMR spectra (400 MHz, r.t., 0.4 mM based on **DA**) of (c) **DA** in  $\text{CDCl}_3$  and (d) ( $\text{DA}_n$ ) in  $\text{D}_2\text{O}$ . (e) DLS chart ( $\text{H}_2\text{O}$ , r.t.) of ( $\text{DA}_n$ ) (0.1 mM based on **DA**) and (f) the AFM-based height profile (dry, r.t., mica) of ( $\text{DA}_n$ ). (g) UV-visible spectra (r.t., 0.4 mM based on **DA**) of ( $\text{DA}_n$ ) in  $\text{H}_2\text{O}$  and **DA** in  $\text{CH}_3\text{OH}$  and (h) their fluorescence spectra ( $\lambda_{\text{ex}} = 370$  nm).

those of monomer **DA** in  $\text{CH}_3\text{OH}$  ( $\lambda_{\text{max}} = 365$  nm, Fig. 2g). The emission band of ( $\text{DA}_n$ ) in  $\text{H}_2\text{O}$  upon excitation at 370 nm was likewise red-shifted ( $\Delta\lambda_{\text{max}} = +29$  nm) and broadened, as compared with that of **DA** in  $\text{CH}_3\text{OH}$  ( $\lambda_{\text{max}} = 414$  nm) at the same concentration (Fig. 2h), further suggesting strong  $\pi$ -stacking interactions.

### Stability against dilution and the importance of the dumbbell design

The dumbbell-shaped structure of the polyaromatic amphiphile increased the stability of the obtained micelle against water dilution, as evidenced by concentration-dependent fluorescence and NMR analyses. Stepwise dilution of micelle ( $\text{DA}_n$ ) in  $\text{H}_2\text{O}$  (100 to 0.1  $\mu\text{M}$  based on **DA**) resulted in a gradual blue-shift of the emission maximum and decrease in emission intensity at 450 nm (Fig. 3a), owing to gradual disassembly. The corresponding concentration–intensity plot indicated the critical micelle concentration (CMC) of **DA** being 1.2  $\mu\text{M}$  (Fig. 3b).<sup>14</sup> In a similar way, the amphiphilic semi-dumbbell **VA** (Fig. 3d) featuring a single ammonium side-chain assembled into micelle ( $\text{VA}_n$ ) in  $\text{H}_2\text{O}$ , as suggested by NMR, UV-visible, fluorescence, DLS, and molecular modeling analyses (Fig. S20–26 and S39–43). The CMC was estimated to be 50  $\mu\text{M}$  (Fig. 3c and S41),<sup>11</sup> which revealed more than a 40-fold increase in stability upon dimerization. Relative to ( $\text{AA}_n$ ) (CMC = 1 mM),<sup>7</sup> the dilution stability of ( $\text{DA}_n$ ) was thus improved by a factor of  $\sim 830$ , through a combination of facilitated intra/

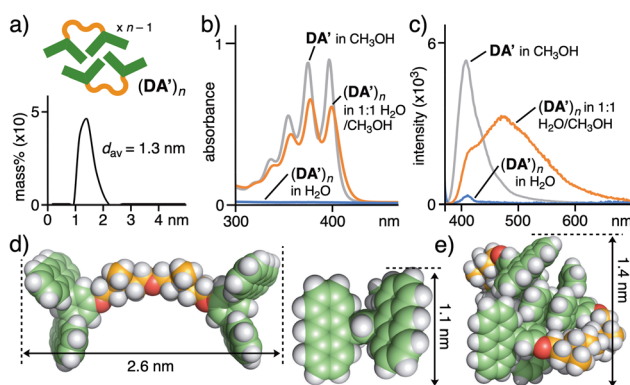




**Fig. 3** (a) Concentration-dependent fluorescence spectra ( $\text{H}_2\text{O}$ , r.t.,  $\lambda_{\text{ex}} = 370$  nm) of micelle  $(\text{DA})_n$  and (b) their concentration versus emission intensity plots ( $\lambda_{\text{det}} = 450$  nm). (c) Concentration versus emission intensity plots ( $\text{H}_2\text{O}$ , r.t.,  $\lambda_{\text{ex}} = 370$  nm,  $\lambda_{\text{det}} = 480$  nm) of  $(\text{VA})_n$ . (d) Amphiphilic semi-dumbbell VA.

intermolecular  $\pi$ - $\pi$  interactions, reduced electrostatic repulsion, and chelate-type assembly.

The importance of spacer length was verified using the dumbbell derivative  $\text{DA}'$ , which possesses a contracted ethylene oxide spacer ( $n = 1$ ; Fig. 1d and S27–32). While  $\text{DA}'$  exhibited essentially no solubility in water using the grinding-sonication protocol described above (Fig. S44 and S45), the dissolution and formation of small micelle  $(\text{DA}')_n$  (1.0 mM based on  $\text{DA}'$ ), with an average core diameter of 1.3 nm, was observed in a 1:1  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  mixture, as indicated by UV-visible and DLS analyses (Fig. 4a). The UV-visible spectrum suggested the assembly, due to a red-shift of the anthracene-based absorption band of  $\text{DA}'$  ( $\Delta\lambda_{\text{max}} = +4$  nm), as compared to that in  $\text{CH}_3\text{OH}$  (Fig. 4b). The emission band of  $(\text{DA}')_n$  at  $\lambda_{\text{max}} = 478$  nm upon irradiation at 370 nm was also red-shifted by +60 nm relative to that of monomer  $\text{DA}'$  in  $\text{CH}_3\text{OH}$  (Fig. 4c). On the basis of these findings, molecular modeling studies suggested the assembly of  $\text{DA}'$  into dimer  $(\text{DA}')_2$  in a  $\pi$ -stacked, face-to-face fashion, even in the presence of 50% v/v  $\text{CH}_3\text{OH}$  (Fig. 4d, e and S47).<sup>15</sup>

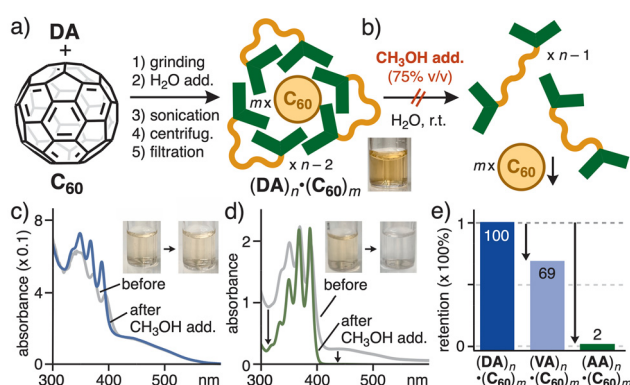


**Fig. 4** (a) DLS chart (1:1  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ , r.t., 0.1 mM based on  $\text{DA}'$ ) of micelle  $(\text{DA}')_n$ . (b) UV-visible spectra (r.t., 0.4 mM based on  $\text{DA}'$ ) of  $(\text{DA}')_n$  in  $\text{H}_2\text{O}$  and 1:1  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ , and  $\text{DA}'$  in  $\text{CH}_3\text{OH}$  and (c) their fluorescence spectra ( $\lambda_{\text{ex}} = 370$  nm). Optimized structures of (d)  $\text{DA}'$  (front and bottom views) and (e)  $(\text{DA}')_2$  (DFT, B3LYP/6-31G(d,p) level and MM, respectively).

### Dye binding under organic solvent-rich conditions

Besides the high stability of micelle  $(\text{DA})_n$  against water dilution, the efficient formation of its host-guest composites and their high stability against the addition of organic solvent were revealed in the following studies. Fullerene  $\text{C}_{60}$  ( $\text{C}_{60}$ ) was used as a typical hydrophobic dye and a mixture of  $\text{DA}$  (0.9 mg, 0.8  $\mu\text{mol}$ ) and  $\text{C}_{60}$  (0.1 mg, 0.2  $\mu\text{mol}$ ) was ground for 1 min using an agate mortar and pestle (Fig. 5a). After the addition of  $\text{H}_2\text{O}$  (2.5 mL), the suspension was sonicated with a probe sonicator (40 kHz, 150 W, 10 min, 0  $^\circ\text{C}$ ), centrifuged, and filtered to give a clear brown solution containing host-guest composite  $(\text{DA})_n(\text{C}_{60})_m$ . The product size and composition were revealed by a combination of DLS (*i.e.*, 2.3 nm in diameter; Fig. S49a), UV-visible, and molecular modeling analyses (*i.e.*,  $n : m = 3 : 1$ ; Fig. S49b).<sup>11</sup> The efficient encapsulation of  $\text{C}_{60}$  was confirmed by the UV-visible analysis. On the basis of the intensity of new absorption bands ( $\lambda = 440$  nm) derived from encapsulated  $(\text{C}_{60})_m$ , the uptake ability of  $(\text{DA})_n$  was slightly lower than that of  $(\text{AA})_n$  under the same conditions (0.8-fold; Fig. 5c, d, and S48). Next, methanol (1.5 mL) was added to  $(\text{DA})_n(\text{C}_{60})_m$  in  $\text{H}_2\text{O}$  (0.5 mL, 0.3 mM based on  $\text{DA}$ ) at room temperature (Fig. 5b) and the resultant pale brown solution (75% v/v methanol, 75  $\mu\text{M}$  based on  $\text{DA}$ ) was again analyzed by UV-visible spectroscopy after centrifugation and filtration.<sup>16</sup> The spectrum was nearly identical to that of  $(\text{DA})_n(\text{C}_{60})_m$  in  $\text{H}_2\text{O}$  (75  $\mu\text{M}$  based on  $\text{DA}$ ; Fig. 5c). The relative retention efficiency of the host-guest composite was estimated to be  $\sim 100\%$  (Fig. 5e), from the intensity change in the guest band at 440 nm. The band intensity of the diluted solution was nearly unchanged (82% retention) at room temperature even after 1 month (Fig. S51c), revealing excellent stability against methanol dilution.

In sharp contrast, the  $\text{C}_{60}$ -based absorption bands of  $(\text{AA})_n(\text{C}_{60})_m$  and  $(\text{VA})_n(\text{C}_{60})_m$  in water (150  $\mu\text{M}$  based on  $\text{AA}$  and  $\text{VA}$ ) decreased upon addition of methanol (Fig. 5d and S50a),



**Fig. 5** (a) Encapsulation of  $\text{C}_{60}$  by micelle  $(\text{DA})_n$  in water and (b) stability of host-guest composite  $(\text{DA})_n(\text{C}_{60})_m$  against  $\text{CH}_3\text{OH}$  dilution. UV-visible spectra (r.t., 75/150  $\mu\text{M}$  based on  $\text{DA}/\text{AA}$ , 1 cm path-length quartz cell) of (c)  $(\text{DA})_n(\text{C}_{60})_m$  and (d)  $(\text{AA})_n(\text{C}_{60})_m$  and  $(\text{VA})_n(\text{C}_{60})_m$  before and 1 h after the addition of  $\text{CH}_3\text{OH}$  (75% v/v). (e) Relative stabilities of  $(\text{DA})_n$  or  $(\text{AA})_n(\text{C}_{60})_m$  in water after  $\text{CH}_3\text{OH}$  addition.

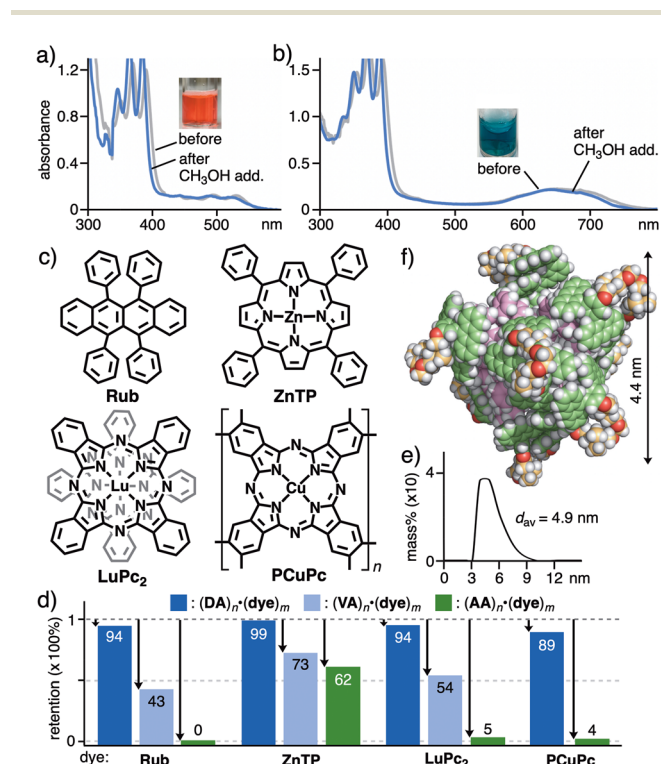


owing to the release of bound *m*-C<sub>60</sub>, under the same conditions. Their retention efficiencies were estimated to be 2% and 69% after 1 h, respectively (Fig. 5e). Typical alkyl amphiphiles (*i.e.*, sodium dodecyl sulfate (SDS)) showed poor uptake abilities toward C<sub>60</sub> and no retention abilities toward the bound C<sub>60</sub> under the same conditions (Fig. S52).<sup>11</sup> Host-guest composite (DA)<sub>n</sub>·(C<sub>60</sub>)<sub>m</sub> also showed high stability against the addition of DMSO, acetone, and acetonitrile (75% v/v each), with the retention efficiencies being ~100%, 97%, and 99%, respectively (Fig. S50b). Similar encapsulation and retention (~100%) were also observed for higher fullerene C<sub>70</sub> by using (DA)<sub>n</sub> under the same conditions (Fig. S53). These results indicated that both the bent polyaromatic frameworks and the connected hydrophilic chain of DA are of importance for tight host-guest interactions under organic solvent-rich aqueous conditions.

High stability against methanol-rich conditions was also demonstrated for host-guest composites containing organic and metal-organic dyes as well as polymer dyes. Subjecting DA (0.9 mg, 0.8 μmol) and rubrene (Rub; 0.1 mg, 0.2 μmol) to the established grinding-sonication protocol yielded a clear red solution containing (DA)<sub>n</sub>·(Rub)<sub>m</sub> (Fig. 6a and c). The obtained UV-visible spectrum of the aqueous solution exhibited new dye-derived absorption bands at 400–560 nm, which remained

largely unchanged (94% retention) upon the 75% v/v addition of methanol (Fig. 6d). On the other hand, 43% and no retention of Rub were observed in the case of (VA)<sub>n</sub> and (AA)<sub>n</sub> under similar conditions, respectively. To elucidate the structural origin of the high stability of (DA)<sub>n</sub>·(Rub)<sub>m</sub>, the DA:Rub ratio was determined to be 4:5 by the <sup>1</sup>H NMR integral analysis of the isolated host-guest composite in CDCl<sub>3</sub>, facilitated by sufficient solubility of both DA and Rub in this solvent (Fig. S55). In combination with the DLS-derived particle diameter of 4.9 nm on average (Fig. 6e), molecular modeling analyses indicated the formation of (DA)<sub>8</sub>·(Rub)<sub>10</sub> as the main species in solution (Fig. 6f). In the structure, roughly spherical aggregate (Rub)<sub>10</sub> is fully enclosed by the sixteen polyaromatic panels of eight DAs, stabilized through multiple π-π and CH-π interactions.

Metal-organic dyes such as Zn(II)-tetraphenylporphyrin (ZnTP) and Lu(III)-bisphthalocyaninato (LuPc<sub>2</sub>; Fig. 6c) were encapsulated by (DA)<sub>n</sub> (Fig. S57 and S58). The retention efficiencies upon 75% v/v methanol addition were estimated to be 99% and 94% for DA, 73% and 54% for VA, and 62% and 5% for AA, respectively (Fig. 6d). Notably, metal-organic polymer dyes, *i.e.*, poly-Cu(II)-phthalocyanines (PCuPc; Fig. 6c) were also effectively encapsulated and retained (89%) upon methanol addition, as judged by the broad dye-derived absorption band at 550–750 nm in the UV-visible spectra (Fig. 6b and d). In contrast, PCuPc was hardly encapsulated by (VA)<sub>n</sub> in water and nearly all of PCuPc was released from (AA)<sub>n</sub>·(PCuPc)<sub>m</sub> upon methanol addition (Fig. 6d and S60). Host-guest composites derived from (DA)<sub>n</sub> and polythiophenes (PT) as organic polymer dyes likewise exhibited high stability under methanol-rich conditions (Fig. S61). The above results highlight the host function of (DA)<sub>n</sub> toward various dyes as well as the high dye retention abilities in methanol-rich solution.



**Fig. 6** UV-visible spectra (r.t., 75 μM based on DA, 1 cm path-length quartz cell) of (a) (DA)<sub>n</sub>·(Rub)<sub>m</sub> and (b) (DA)<sub>n</sub>·(PCuPc)<sub>m</sub> before and after the addition of CH<sub>3</sub>OH (75% v/v). (c) Organic and metal-complex dyes Rub, ZnTP, LuPc<sub>2</sub>, and PCuPc. (d) Relative stabilities of (DA or VA or AA)<sub>n</sub>·(dye)<sub>m</sub> in water after CH<sub>3</sub>OH addition. (e) DLS chart (H<sub>2</sub>O, r.t., 0.1 mM based on DA) of (DA)<sub>n</sub>·(Rub)<sub>m</sub>. (f) Optimized structure (MM) of (DA)<sub>8</sub>·(Rub)<sub>10</sub>.

## Conclusions

We have designed and prepared a new micelle with high stability and high dye-binding ability under organic solvent-rich conditions. Amphiphilic polyaromatic dumbbells, featuring two bent anthracene dimers linked by a long flexible spacer, quantitatively assembled in water into a spherical polyaromatic micelle composed of three dumbbells on average. The micelle exhibited extremely high stability against dilution (up to 1.2 μM), around 830-fold higher compared to a non-dumbbell-based polyaromatic micelle. Various organic and metal-organic dyes were efficiently encapsulated by the micelle in water. Importantly, the corresponding host-guest composites showed unusually high stability against the addition of a large amount of organic solvent (75% v/v; *e.g.*, methanol, DMSO, and acetone), with the aid of the hydrophobic effect and multiple chelate-type π-π and CH-π interactions. We anticipate that the present “organostable” micelle will enable new host functions not only in water but also in aqueous organic



solvent media, e.g., for applications in painting materials, extraction/separation tools, and catalysis.

## Author contributions

L. C., A. S., K. T., and M. Y. designed the work, carried out research, analyzed data, and wrote the paper. All authors discussed the results and commented on the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. Experimental procedures, and NMR, MS, UV-visible, emission, AFM, DLS, and theoretical data. See DOI: <https://doi.org/10.1039/d6qo00227g>.

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- 11 See the SI. Chloride counter anions were used for the amphiphiles due to the insolubility of the corresponding iodide salts in water.
- 12 The saturated concentration of (**DA**)<sub>n</sub> in water was estimated to be 0.4 mM based on **DA** through the UV-visible study.
- 13 The observed smaller dimensions most probably arise from the strong interactions between the less protected, polyaromatic framework of (**DA**)<sub>n</sub> and the mica surface.
- 14 The concentration-dependent <sup>1</sup>H NMR analysis also indicated the CMC being less than 50 μM in water, owing to the highly broadened signals (Fig. S33c).<sup>11</sup>
- 15 Aromatic micelle (**DA'**)<sub>n</sub> encapsulated fullerene C<sub>60</sub> in a 1 : 1 mixture of H<sub>2</sub>O/CH<sub>3</sub>OH, albeit with a lower efficiency than **DA** and **VA**.
- 16 The assembled structure of (**DA**)<sub>n</sub> remained mostly intact in 25 : 75 D<sub>2</sub>O/CD<sub>3</sub>OD (0.1 mM based on **DA**) at room temperature as estimated by <sup>1</sup>H NMR analysis (Fig. S33d).

