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Unprecedented Cucurbituril-Based Ternary Host-Guest Supramolecular Polymers Mediated through Included Alkyl Chains

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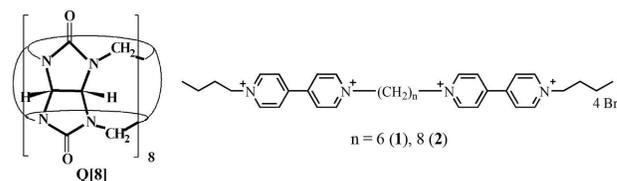**Novel supramolecular polymers constructed from Q[8] and 1',1''-(alkylene-1,4-diyl)bis(1-butyl)-4,4'-bipyridine-1,1'-diium)bromide (alkylene = hexylene, octylene) (1, 2) have been fabricated and characterized on the basis of a series of**
10 **NMR, SEM, and DLS techniques. In particular, single crystal X-ray diffraction analysis clearly reveals their ternary host-guest construction nature by mediating the Q[8] host molecule through two terminal butyl chains (that are simultaneously included inside the host cavity) of two guest**
15 **molecules depending on multiple hydrogen bonding interactions between the host and guest molecules as well as between the host and host molecules with the total energy amounting to as high as 161.2 kJ/mol. This represents the first example of ternary host-guest supramolecular polymers**
20 **that are mediated through alkyl chains instead of aromatic moieties included.**

Supramolecular polymers have attracted increasing research interests in the past decade due to their important roles in life[1] and potential applications in photovoltaic devices,[2] drug
25 delivery,[3] porous membranes,[4] and catalysts[5] associated with their useful features including responsiveness to stimuli,[6] self-healing,[7] and degradability.[8] In line with the construction of the most important naturally occurring supramolecular polymer, DNAs, many artificial supramolecular polymers including the
30 binary host-guest species have been prepared depending on hydrogen bonding interaction with relatively strong intensity and direction between the monomeric molecules.[9,10] This however is not true for the ternary host-guest supramolecular polymers, which are constructed usually depending on either host-enhanced
35 π-π interaction or host-stabilized charge transfer interaction between the functional groups (that are simultaneously included inside the host molecule) of two guest molecules.[11,12] As a consequence, ternary host-guest supramolecular polymers were usually constructed by mediating corresponding macrocyclic host
40 molecule with two guest molecules bringing either π-π interaction formation aromatic moiety like anthracene and naphthalene[13] or charge transfer interaction formation electron-donating/electron-accepting pair like the methyl viologen and naphthol moieties.[14] To the best of our knowledge, there still
45 exists no report on the ternary host-guest supramolecular polymer system that is mediated through two alkyl groups instead of two aromatic moieties (of two guest molecules) that are

simultaneously included inside the host molecule.

On the other hand, as one of the important functional
50 macrocyclic compounds, cucurbit[n]urils (Q[n]) with tunable cavity have been disclosed to exhibit good host-guest supramolecular polymer formation property because of their high binding constants with the guest molecules.[15] In particular, the Q[8] species has been among the most widely employed
55 cucurbit[n]uril members in constructing stable ternary host-guest supramolecular polymers due to its relatively large cavity, which enables the simultaneously inclusion of both aromatic functional groups of two guest molecules.[13,14,16] In the present work, this macrocyclic compound was employed again as the host
60 compound to construct novel host-guest supramolecular polymers Q[8]@n (n = 1, 2) with the guest compounds 1',1''-(alkylene-1,4-diyl)bis(1-butyl)-4,4'-bipyridine-1,1'-diium)bromide (alkylene = hexylene, octylene) (1, 2), Scheme 1. Surprisingly, single crystal X-ray diffraction analysis clearly reveals their construction nature
65 by mediating the Q[8] host molecule through two terminal butyl chains (that are simultaneously included inside the host cavity) instead of two aromatic pyridine moieties of two guest molecules in the solid state depending on multiple hydrogen bonding interactions with different modes between the host and guest
70 molecules as well as between the host and host molecules. This seems also true for Q[8]@n (n = 1, 2) formed in solution on the basis of spectroscopic in particular the NMR investigation results. The present result represents the first example of ternary host-guest supramolecular polymers that are mediated through alkyl
75 chains instead of aromatic moieties that are included in the host molecule.

Scheme 1. Schematic molecular structures of Q[8] and 1',1''-(alkylene-1,4-diyl)bis(1-butyl)-4,4'-bipyridine-1,1'-
80 diium)bromide (alkylene = hexylene, octylene) (1, 2).

Host Q[8] was prepared according to a published procedure.[17] Two 1-butyl-4,4'-bipyridinium units were linked together with a linear alkyl chain as the potential guest molecules to construct the ternary host-guest supramolecular polymer with Q[8]. Reaction
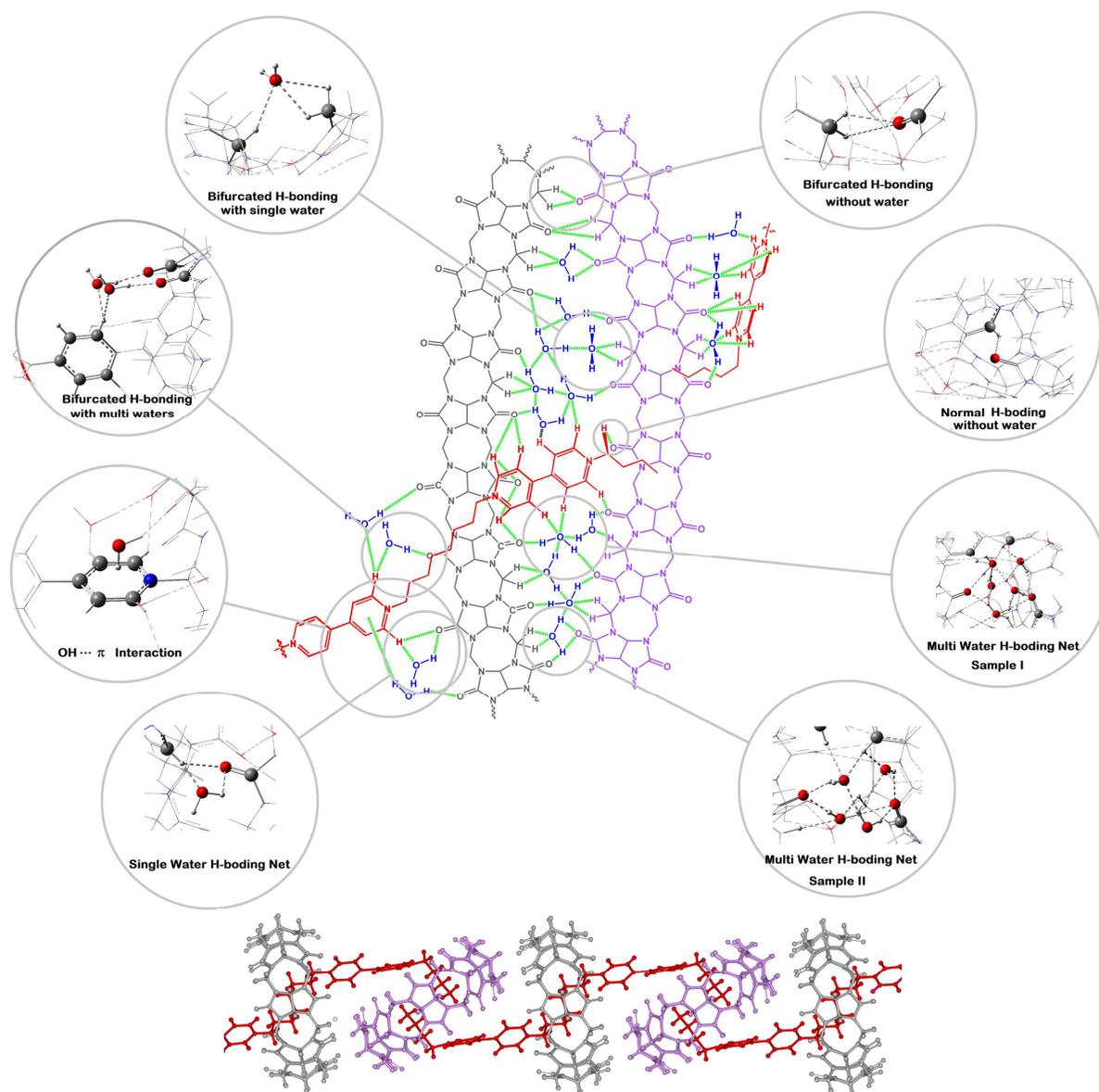
Fig. 1 Crystal structure and various hydrogen bonds existing between the host and guest as well as between the host and host molecules in Q[8]**@2**.

between 1-butyl-4,4'-bipyridinium and 1,n-dibromoalkane in refluxing DMF afforded the guest compounds 1',1"-(alkylene-1,4-diyl)bis(1-butyl)-4,4'-bipyridine-1,1'-diium)bromide (alkylene = hexylene, octylene) (**1**, **2**) in good yield (73.8−79.2%). It is worth mentioning that the two viologen dication moieties incorporated in these two guest compounds lend these two compounds good water-solublity, rendering the reaction being able to occur with water soluble Q[8] in aqueous solution. Indeed, the corresponding ternary host-guest supramolecular polymers Q[8]@ **n** (**n** = 1, **2**) were provided *via* aqueous solution reaction of Q[8] with **1** and **2** on the basis of single crystal X-ray diffraction analysis and a range of spectroscopic techniques as detailed below.

Single crystals of the supramolecular polymers Q[8]@**n** (**n** = 1,

2) were obtained by slow evaporation of the solvent from the aqueous reaction mixture of corresponding guest and cucurbit[8]uril in air. Q[8]@**1** and Q[8]@**2** crystallize in the triclinic system with a *P-1* space group and monoclinic system with a *P2/n* space group, respectively. As can be seen in Fig. 1, for the ternary supramolecular polymer Q[8]@**2**, the outer butyl groups of two independent guest molecules are located inside the cavity of one Q[8] host in a head-to-tail orientation with the viologen moieties sitting just outside the portal of Q[8], while the octylene chain that connects the two viologen moieties in the guest molecule is completely encapsulated by another Q[8] molecule, resulting in the formation of one dimensional superamolecular chain depending on multiple hydrogen bonding

interactions with various kinds of different bonding modes between the host and guest molecules as well as between the host and host molecules. For the readers' convenience, all the hydrogen bonding interactions involved in the present supramolecular polymeric system Q[8]@**2** have been clarified on the basis of the framework revealed by single crystal X-ray diffraction analysis with the help of theoretical analysis using the density functional theory of PBE-D(Grimme)/DND(3.5).[18] As shown in Fig. 1, the host and guest hydrogen bonds include two C-H⋯O=C hydrogen bonds between the pyridine moiety and carbonyl oxygen atom of Q[8], one C-H⋯O=C hydrogen bond between butyl chain and carbonyl oxygen atom of Q[8], two bifurcated $(C-H)_2 \cdots O=C$ hydrogen bonds between the pyridine moiety and carbonyl oxygen atom of Q[8], two C-$H_2 \cdots O(H_2) \cdots (H-C)_2$ hydrogen bonds between the -CH_2- group of Q[8] and two -CH groups in the pyridine moiety with the help of one water molecule, one C-H⋯(OH-H⋯O=C)₂ hydrogen bond between one –CH group of pyridine moiety and two carbonyl oxygen atoms of Q[8] with the help of two water molecules, one $Py(\pi) \cdots$H-O-H⋯O=C hydrogen bond between one pyridine moiety and one carbonyl oxygen atom of Q[8] with the help of one water molecule. While the host and host hydrogen bonds include two bifurcated C-$H_2 \cdots O=C$ hydrogen bonds between the two Q[8] molecules as well as two C-$H_2 \cdots O$-$H_2 \cdots O=C$ hydrogen bonds between the -CH_2 group of one Q[8] and the carbonyl oxygen atom of another Q[8] with the help of one water molecule. In addition, as also clearly shown in Fig. 1, two very much complicated hydrogen bonding networks involving both the –CH_2 groups and carbonyl oxygen atoms of two Q[8] molecules and the –CH groups of pyridine moieties with the help of multiple water molecules (actually four and six, respectively) also play a very important role in leading to the formation of the one-dimensional supramolecular chain from host and guest molecules. Nevertheless, calculation over the basic building block unit for the supramolecular polymer of Q[8]@**2** composed of two host and one guest molecules reveals that the total energy of all the hydrogen bonds amounts to as high as 161.2 kJ/mol, which easily accounts for the formation of stable supramolecular polymer Q[8]@**2** in either solid state or solution state even at room temperature as detailed below.

Fig. S3 (ESI†) displays the two dimensional crystal structure of Q[8]@**2**. As can be seen, the 1D superamolecular chain as building block further packs into a two dimensional supramolecular network also *via* the O-H⋯O hydrogen bonding interaction between the water molecules and the portal carbonyl groups of Q[8] as well as the O-H⋯Cl hydrogen bonding interaction between the water molecules and the tetrachloro zincate anions filled between the neighboring supramolecular chains.[19] This is also true for Q[8]@**1**, Fig. S4 and S5 (ESI†).

In addition, both the two species of Q[8] host molecules intrinsically with D_{8h} symmetrical conformation in Q[8]@**n** (**n** = **1**, **2**) undergo ellipsoidal deformation due to the inclusion of alkyl chains in their cavity, which is clearly revealed by the different O⋯O distances between the two terminal carbonyl portals of each Q[8] molecule ranging from 9.150 to 10.802 Å for Q[8]@**1** and from 9.680 to 10.301 Å for Q[8]@**2**. At the end of this section, it is worth noting that when forming ternary host-guest supramolecular polymers with the guest molecule containing

aromatic moieties, the Q[8] compound usually chooses to host the aromatic moieties instead of the alkyl groups (of the guest molecules) inside its cavity due to the relatively stronger interaction of Q[8] with the aromatic moiety than with alkyl chain.[20] This actually is also true for other macrocyclic compounds as host with the so-called "pseudo-aromatic" molecular structure.[13b-d,21]
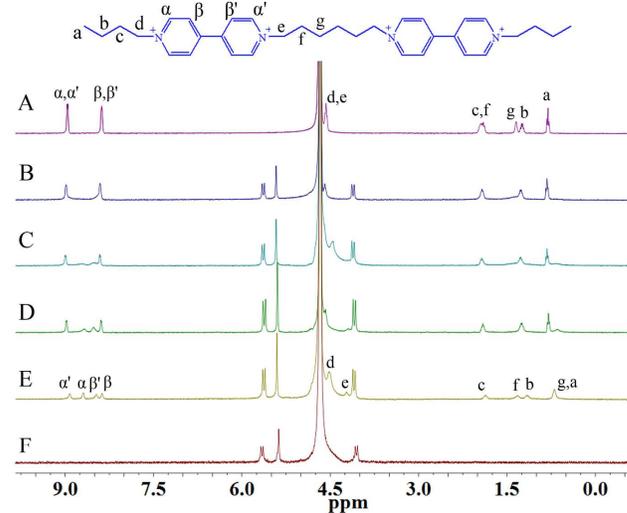

Fig. 2 ¹H NMR spectra of **1** (A), **1** and Q[8] in the ratio of 0.6 (B), 1.1 (C), 1.5 (D), 2.0 (E), and Q[8] (F) in D_2O.

In order to investigate the complexation of Q[8] with **1** and **2** in solution, ¹H NMR titration experiments were performed by adding increasing amount of Q[8] into the solution of **1** and **2** in D_2O. As clearly shown in Fig. 2 and Table S1 (ESI†), only one set of two signals were observed at δ 8.96 and 8.38 ppm, respectively, for the two sets of aromatic protons (H_α, H_β and $H_{\alpha'}$, $H_{\beta'}$) of the viologen dication moieties in the ¹H NMR spectrum of the free guest compound **1** due to their almost same (at least very much similar) chemical environments between H_α and $H_{\alpha'}$ as well as between H_β and $H_{\beta'}$ protons. However, the ¹H NMR spectrum of the mixture of **1** and Q[8] in D_2O is not a simple superimposition of the spectrum of pure **1** and that of pure Q[8] in the same deuterated solvent, Fig. 2. In line with the result reported previously,[22] addition of the host compound Q[8] into the D_2O solution of guest **1** does not induce any noticeable change in the signals attributed to the Q[8] aliphatic protons. This, however, is definitely not true for the signals due to the protons in particular the aromatic protons of the guest compound **1**. As can be seen in Fig. 2, when more than 1.0 (until 2.0) equiv. of Q[8] was added into the solution of **1** in D_2O, the set of signal at δ 8.96 ppm attributed to the H_α and $H_{\alpha'}$ protons of free guest **1** started to split. In particular, when 2.0 equiv. of Q[8] was added, this set of signal clearly splits into two sets of signals at δ 8.69 and 8.93 ppm, respectively. This is also true for set of signal due to the H_β and $H_{\beta'}$ protons of free guest **1** at δ 8.38 ppm into the two sets of signals at δ 8.38 and 8.48 ppm for the mixture of Q[8] and **1** in the ratio of 2:1 in D_2O, Fig. 2, indicating the complexation between the host Q[8] and guest **1** in the ratio of 2:1. Taking the single crystal X-ray diffraction analysis result for supramolecular polymer Q[8]@**1** into account, the supramolecular structure formed between Q[8] and **1** in the ratio of 2:1 in solution could

then be visualized as the one similar to that in solid state with two species of Q[8] host molecules: One Q[8] molecule includes two terminal butyl groups of two independent guest molecules while the other one encapsulates the central hexylene chain that connects the two viologen dication moieties in the guest molecule of **1**, resulting in the differentiation of the pyridinium moiety connecting the butyl group from the one connecting the hexylene chain in the viologen dication moieties of **1** in terms of NMR spectroscopy. As a natural result, NMR differentiation also occurs on the protons between the butyl group and hexylene chain in **1**, Fig. 2 and Table S1 (ESI†), the closer the protons to the aromatic pyridinium moiety, the more obvious the NMR differentiating effect. This is actually also true for the case of Q[8] with **2** in D$_2$O, Fig. S7 and Table S1 (ESI†).
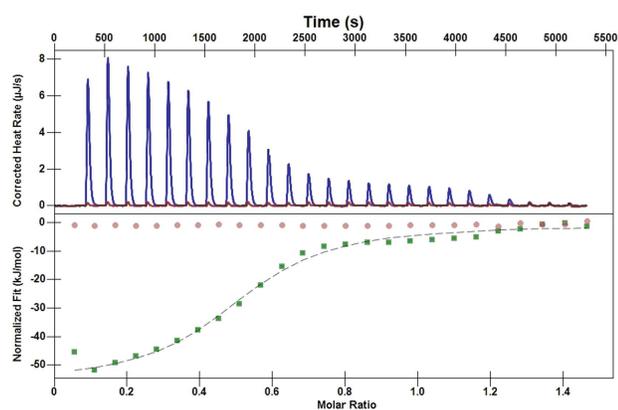

Fig. 3 ITC data for the binding of Q[8] with **1** in aqueous solution at 25°C.

Isothermal titration calorimetry (ITC) measurements have been revealed to be able to provide the quantitative information for the host-guest complexation including both the binding affinity and thermodynamic origin. As a consequence, a solution of **1** or **2** (1.2 mM) was consecutively injected into the solution of Q[8] (0.10 mM) at 25°C to record the exothermic binding isotherm, Fig. 3, resulting in the resolution of the binding molar ratio value of N = 0.509 and 0.491, respectively. This result is very much close to the expected one of 0.5, suggesting the binding stoichiometry of either **1** or **2** to Q[8] is 1:2. In addition, the association constant of K_a = (4.87 ± 0.23) × 10^5 and (8.49 ± 0.17) × 10^5 M^{-1} for Q[8] with **1** and **2**, respectively, was also afforded on the basis of corresponding experimental result. Such a high binding constant suggests the relatively strong host-guest interaction between Q[8] and **1** or **2**, indicating the construction of stable supramolecular polymers of Q[8]@**n** (**n** = **1**, **2**) in water. Meanwhile, the relatively large negative enthalpy value of Q[8]@**n** (**n** = **1**, **2**) deduced reveals that the assembly process of supramolecular polymers of Q[8] with either **1** or **2** is typically driven by a favorable enthalpy change, Table S2 (ESI†).

Electronic absorption spectroscopy was usually utilized to afford information about the binding mode(s) among the host and/or guest molecules in particular for the systems involving π-π interaction between aromatic functional moieties. However, in the present case, as shown in Fig. S10 (ESI†), addition of 2.0 equiv. of Q[8] into the solution of **1** or **2** in water induces almost

no change in the electronic absorption spectrum: except the very much slight change in the intensity, the absorption band around 263 nm keeps almost unshifted. The result clearly reveals the lack of π-π interaction between the guest molecules in solution, suggesting the similar binding modes among the building blocks of host and/or guest molecules to those in solid state supramolecular polymers.

Diffusion-ordered NMR spectroscopy (DOSY) was usually employed to confirm the formation of supramolecular polymers in solution since the results could directly correlate the ^{1}H NMR signals between the host and guest molecules with corresponding diffusion coefficient[23]. In the present case, the DOSY spectra of a series of samples with different ratio between **n** (**n** = **1**, **2**) and Q[8] in D$_2$O were recorded. As exhibited in Fig. 4 , the average diffusion coefficient obtained for the host compound Q[8] is revealed to be 2.90 × 10^{-10} m^2 s^{-1}, which amounts to 3.09 × 10^{-10} and 3.05 × 10^{-10} m^2 s^{-1}, respectively, for the guest compound **1** and **2**. Mixing the host and guest compounds together by adding Q[8] in D$_2$O into the D$_2$O solution of the guest compound leads to a decrease in the average diffusion coefficient. Nevertheless, along with the increase in the ratio of Q[8] to guest, the average diffusion coefficient of the complex gets further decreased with the lowest average diffusion coefficient value of 1.21× 10^{-10} for Q[8]@**1** and 1.07× 10^{-10} m^2 s^{-1} for Q[8]@**2** being reached at the molar ratio of 2.0 between Q[8] and guest. Such a dramatic decrease in the diffusion coefficient suggests that the host and guest building blocks diffuse as one entity, indicating the formation of a large polymeric species between Q[8] and guest. In addition, the SEM image from aqueous solution (c = 0.50 mM) of Q[8] and **2** provides direct visual information for the formation of linear polymeric structure with diameter of ca. 510 nm, Fig. S13 (ESI†).
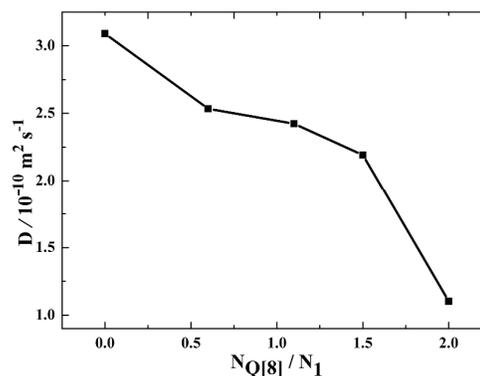

Fig. 4 Average diffusion coefficient of **1** with different ratios of Q[8].

Dynamic light scattering (DLS) performed in dilute solution was quite often employed to monitor the formation of linear supramolecular polymer. Fig. 5 shows the DLS data of polymer Q[8]@**1**. As can be found, mixing Q[8] and **1** at the molar ratio of 1:1 leads to the observation of one hydrodynamic diameter distribution centered at 98 nm due to the formation of polymer chains with a low degree of polymerization. When the molar ratio between Q[8] and **1** was changed to 2:1, a new hydrodynamic diameter distribution centered at 265 nm instead of the old one was observed, indicating the formation of much larger

supramolecular entities due to the further assembly of host molecules with polymer chains formed at the molar ratio of 1:1. As shown in Fig. S14 (ESI†), mixing Q[8] and **2** at the molar ratio of 1:1 induces the appearance of two hydrodynamic diameter distributions. The one centered at 6 nm could be ascribed to the pseudorotaxane structure (instead of the linear supramolecular polymer) between Q[8] and **2**, while the other one centered at 105 nm was contributed by polymer chains of Q[8]@**2**. When the Q[8] and **2** molar ratio was changed to 2:1, two relatively wide peaks were observed from 80 to 250 nm. The one centered at 122 nm is ascribed to the existence of polymer chains with a relatively low degree of polymerization and the other centered at 220 nm indicates the formation of large supramolecular assemblies with high molecular weight.
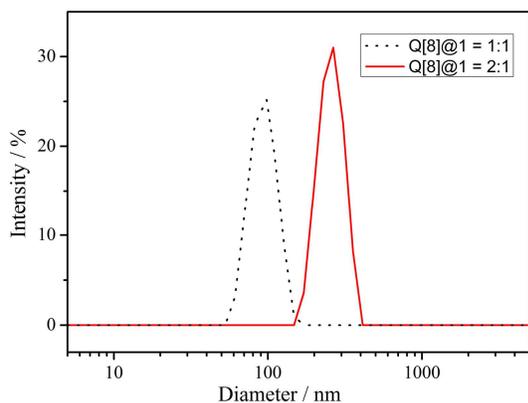

Fig. 5 DLS data of Q[8]@**1**.

Briefly summarizing above, two novel ternary host-guest supramolecular polymers have been successfully constructed from cucurbit[8]uril and 1',1''-(alkylene-1,4-diyl)bis(1-butyl)-4,4'-bipyridine-1,1'-diium)bromide, depending on multiple hydrogen bonding interactions with different modes between the host and guest molecules as well as between the host and host molecules, and structurally characterized on the basis of single crystal X-ray diffraction analysis. This appears also true in solution according to NMR, SEM, and DLS investigation results. In particular, theoretical analysis in combination with the single crystal X-ray diffraction analysis result renders it possible to clarify all the hydrogen bonds involved in the supramolecular polymeric systems with the total energy amounting to as high as 161.2 kJ/mol. Taking into account the important role of the natural supramolecular polymers formed depending mainly on multiple water-aided hydrogen bonding instead of π-π interactions, new host-guest supramolecular polymers that are mediated through alkyl chains instead of aromatic moieties included are expected to induce increasing research interests due to their potential life science-related significance.

Acknowledgements

Notes and references

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† Electronic Supplementary Information (ESI) available: [Synthesis and characterization, method for the determination of association constants, ^{1}H NMR, ITC, TEM images, DLS profile, Electronic absorption spectra and crystallographic data]. See DOI: 10.1039/b000000x/

1 (a) N. Joh, A. Min, S. Faham, J. P. Whitelegge, D. Yang, V. L. Woods and J. U. Bowie, *Nature*, 2008, **453**, 1266; (b) A. Luzar and D. Chandler, *Nature*, 1996, **379**, 55; (c) H. Luecke and F. A. Quiocho, *Nature*, 1990, **347**, 402; (d) X. Yan, S. Li, J. B. Pollock, T. R. Cook, J. Chen, Y. Zhang, X. Ji, Y. Yu, F. Huang and P. J. Stang, *Proc. Natl. Acad. Sci. U.S.A.*, 2013, **110**, 15585; (e) S. Dong, B. Zheng, F. Wang, and F. Huang, *Acc. Chem. Res.*, 2014, DOI: 10.1021/ar5000456.

2 J.-M. Lehn, *Prog. Polym. Sci.*, 2005, **30**, 814.

3 F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer and A. P. H. J. Schenning, *Chem. Rev.*, 2005, **105**, 1491.

4 E. Krieg, H. Weissman, E. Shirman, E. Shimoni and B. Rybtchinski, *Nat. Nanotechnol.*, 2011, **6**, 141.

5 (a) L. Yu, Z. Wang, J. Wu, S. Tu and K. Ding, *Angew. Chem. Int. Ed.*, 2010, **49**, 3627; (b) P. A. Korevaar, S. J. George, A. J. Markvoort, M. M. J. Smulders, P. A. J. Hilbers, A. Schenning, T. F. A. De Greef and E. W. Meijer, *Nature*, 2012, **481**, 492; (c) M. Hatano and K. Ishihara, *Chem.Commun.*, 2012, **36**, 4273.

6 (a) S. Yagai, T. Nakajima, K. Kishikawa, S. Kohmoto, T. Karatsu and A. Kitamura, *J. Am. Chem. Soc.*, 2005, **127**, 11134; (b) S. Yagai, T. Iwashima, K. Kishikawa, S. Nakahara, T. Karatsu and A. Kitamura, *Chem. Eur. J.*, 2006, **12**, 3984; (c) M. Burnworth, L. M. Tang, J. R. Kumpfer, A. J. Duncan, F. L. Beyer, G. L. Fiore, S. J. Rowan and C. Weder, *Nature*, 2011, **472**, 334; (d) F. Wang, B. Zheng, K. Zhu, Q. Zhou, C. Zhai, S. Li, N. Li and F. Huang, *Chem. Commun.*, 2009, 4375; (e) S. Dong, Y. Luo, X. Yan, B. Zheng, X. Ding, Y. Yu, Z. Ma, Q. Zhao and F. Huang, *Angew. Chem. Int. Ed.*, 2011, **50**, 1905; (f) S. Dong, B. Zheng, D. Xu, X. Yan, M. Zhang and F. Huang, *Adv. Mater.*, 2012, **24**, 3191; (g) X. Yan, D. Xu, X. Chi, J. Chen, S. Dong, X. Ding, Y. Yu and F. Huang, *Adv. Mater.*, 2012, **24**, 362; (h) M. Zhang, D. Xu, X. Yan, J. Chen, S. Dong, Bo Zheng and F. Huang, *Angew. Chem. Int. Ed.*, 2012, **51**, 7011; (i) X. Yan, T. R. Cook, J. B. Pollock, P. Wei, Y. Zhang, Y. Yu, F. Huang and P. J. Stang, *J. Am. Chem. Soc.*, 2014, **136**, 4460; (j) F. Wang, C. Han, C. He, Q. Zhou, J. Zhang, C. Wang, N. Li, F. Huang, *J. Am. Chem. Soc.*, 2008, **130**, 11254; (k) F. Wang, J. Zhang, X. Ding, S. Dong, M. Liu, B. Zheng, S. Li, L. Wu, Y. Yu, H. W. Gibson and F. Huang, *Angew. Chem. Int. Ed.*, 2010, **49**, 1090.

7 (a) X. Yan, F. Wang, B. Zheng and F. Huang, *Chem. Soc. Rev.*, 2012, **41**, 6042; (b) P. Cordier, F. Tournilhac, C. Soulie-Ziakovic and L. Leibler, *Nature*, 2008, **451**, 977; (c) X. Yan, D. Xu, J. Chen, M. Zhang, B. Hu, Y. Yu and F. Huang, *Polym. Chem.*, 2013, **4**, 3312.

8 (a) S. G. Zhang, *Nat. Biotechnol.*, 2003, **21**, 1171; (b) J. Gao, Y. N. He, H. P. Xu, B. Song, X. Zhang, Z. Q. Wang and X. G. Wang, *Chem. Mater.*, 2007, **19**, 14.

9 (a) X. Yang, F. Hua, K. Yamato, E. Ruckenstein, B. Gong, W. Kim and C. Y. Ryu, *Angew. Chem. Int. Ed.*, 2004, **43**, 6471; (b) B. Zheng, F. Wang, S. Dong and F. Huang, *Chem. Soc. Rev.*, 2012, **41**, 1621; (c) F. Huang and H. W. Gibson, *Prog. Polym. Sci.*, 2005, **30**, 982; (d) F. Wang, C. Han, C. He, Q. Zhou, J. Zhang, C. Wang, N. Li and F. Huang, *J. Am. Chem. Soc.*, 2008, **130**, 11254; (e) F. Wang, J. Zhang, X. Ding, S. Dong, M. Liu, B. Zheng, S. Li, L. Wu, Y. Yu, H. W. Gibson and F. Huang, *Angew. Chem. Int. Ed.*, 2010, **49**, 1090.

10 (a) C. Nuckolls and T. J. Katz, *J. Am. Chem. Soc.*, 1998, **120**, 9541; (b) P. J. Prest, R. B. Prince and J. S. Moore, *J. Am. Chem. Soc.*, 1999, **121**, 5933; (c) C. C. Lee, C. Grenier, E. W. Meijer and A. P. H. J. Schenning, *Chem. Soc. Rev.*, 2009, **38**, 671; (d) X. Yan, B. Jiang, T. R. Cook, Y. Zhang, J. Li, Y. Yu, F. Huang, H. Yang and P. J. Stang, *J. Am. Chem. Soc.*, 2013, **135**, 16813.

11 (a) X. Ma, Q. Wang, D. Qu, Y. Xu, F. Ji and H. Tian, *Adv. Funct. Mater.*, 2007, **17**, 829；(b) K. M. Park, J.-A. Yang, H. Jung, J. Yeom, J. S. Park, K.-H. Park, A. S. Hoffman, S. K. Hahn and K. Kim, *ACS Nano*, 2012, **6**, 2960; (c) Z. Zhang, Y. Luo, J. Chen, S. Dong, Y. Yu, Z. Ma and F. Huang, *Angew. Chem. Int. Ed.*, 2011, **50**, 1397; (d) X. Ji, Y. Yao, J. Li, X. Yan and F. Huang, *J. Am. Chem. Soc.*, 2012, **135**, 74; (e) B. Xia, B. Zheng, C. Han, S. Dong, M. Zhang, B. Hu, Y. Yu and F. Huang, *Polym. Chem.*, 2013, **4**, 2019.

12 (a) D. González-Rodrígue and A. P. H. J. Schenning, *Chem. Mater.*, 2011, **23**, 310；(b) H. J. Kim, J. Heo, W. S. Jeon, E. Lee, J. Kim, S. Sakamoto, K. Yamaguchi and K. Kim, *Angew. Chem. Int. Ed.,* 2001, **40**, 1526; (c) U. Rauwald and O. A. Scherman, *Angew. Chem., Int. Ed.*, 2008, **47**, 3950; (d) F. Biedermann, U. Rauwald, J. M. Zayed and O. A. Scherman, *Chem. Sci.*, 2011, **2**, 279.

13 (a) Y. L. Liu, R. C. Fang, X. X. Tan, Z. Q. Wang and X. Zhang, *Chem. Eur. J.*, 2012, **18**, 15650; (b) Y. L. Liu, K. Liu, Z. Q. Wang and X. Zhang, *Chem. Eur. J.*, 2011, **17**, 9930; (c) Y. Liu, Z. Huang, X. Tan, Z. Wang and X. Zhang, *Chem. Commun.,* 2013, **49**, 5766; (d) R. C. Fang, Y. L. Liu, Z. Q. Wang and X. Zhang, *Polym. Chem.*, 2013, **4**, 900.

14 (a) Y. H. Ko, K. Kim, J. K. Kang, H. Chun, J. W. Lee, S. Sakamoto, K. Yamaguchi, J. C. Fettinger and K. Kim, *J. Am. Chem. Soc.*, 2004, **126**, 1932; (b) K. Kim, D. Kim, J. W. Lee, Y. H. Ko and K. Kim, *Chem. Commun.*, 2004, 848; (c) Y. Liu, Y. Yu, J. Gao, Z. Wang and X. Zhang, *Angew. Chem. Int. Ed.*, 2010, **49**, 6576.

15 (a) Z. J. Zhang, Y. M. Zhang and Y. Liu, *J. Org. Chem.*, 2011, **76**, 4682; (b) X. Xiao, Q.-H. Hu, Zhu Tao, Y.-Q. Zhang, S.-F. Xue, Q.-J. Zhu and G. Wei, *Chem. Phys. Lett.,* 2011, **514**, 317; (c) L. Isaacs, *Chem. Commun.*, 2009, **6**, 619; (d) K. Kim, *Chem. Soc. Rev.*, 2002, **31**, 96; (e) X.-J. Cheng, L.-L. Liang, K. Chen, N.-N. Ji, X. Xiao, J.-X. Zhang, Q.-J. Zhu S.-F. Xue, X.-L. Ni and Z. Tao, *Angew. Chem. Int. Ed.*, 2013, **52**, 7252; (f) X. Xiao, Q. Wang, Y. -H. Yu, Z.-Y. Xiao, Z. Tao, S.-F. Xue, Q.-J., J.-X. Liu and X.-H. Liu, *Eur. J. Org. Chem.,* 2011, **12**, 2366; (g) X. Xiao, L. He, Z. Tao, S.-F. Xue, Q.-J. Zhu and A. Day, *Supramol. Chem.*, 2010, **22**, 194; (h) X. Xiao, Y.-Q. Zhang, Q.-J. Zhu S.-F. Xue and Z. Tao, *Sci China Ser B: Chem.*, 2009, **52**, 475; (i) X. Xiao, J. X. Liu, Z. F. Fan, K. Chen, Q. J. Zhu, S. F. Xue and Z. Tao, *Chem. Commun.*, 2010, **46**, 3741.

16 (a) D. A. Uhlenheuer, J. F. Young, H. D. Nguyen, M. Scheepstra and L. Brunsveld, *Chem. Commun.*, 2011, **47**, 6798; (b) D. T. Dang, H. D. Nguyen, M. Merkx and L. Brunsveld, *Angew. Chem. Int. Ed.*, 2013, **52**, 2915; (c) H. D. Nguyen, D. T. Dang, J. L. J. van Dongen and L. Brunsveld, *Angew. Chem. Int. Ed.*, 2010, **49**, 895.

17 J. Kim, I. S. Jung, S. Y. Kim, E. Lee, J. K. Kang, S. Sakamoto, K. Yamaguchi and K. Kim, *J. Am. Chem. Soc*., 2000, **122**, 540.

18 (a) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865; (b) S. *J.* Grimme, *Comput. Chem.*, 2006, **27**, 1787; (c) B. *J.* Delley, *Chem. Phys.,* 1990, **92**, 508.

19 X.-L. Ni, X. Xiao, H. Cong, Q.-J. Zhu, S.-F. Xue and Z. Tao, *Acc. Chem. Res.*, 2014, **47**, 1386.

20 P. Hobza and K. Müller-Dethlefs, *Non-covalent Interactions: Theory and Experiment*. RSC Publishing, Thomas Graham House, Science Park, Milton Road, Cambridge, 2010; (b) I. G. Kaplan, *Intermolecular Interactions-Physical Picture, Computational Methods and Model Potentials*. John Wiley and Sons Ltd, Atrium, Southern Gate, Chichester, West Sussex, 2006.

21 (a) L. Yang, H. Yang, F. Li and X. Zhang, *Langmuir*, 2013, **29**, 12375; (b) K. Liu, Y. Kang, Z. Wang and X. Zhang, *Adv. Mater.*, 2013, **25**, 5530.

22 K.-D. Zhang, J. Tian, D. Hanifi, Y. Zhang, C.-H. Andrew, T.-Y. Zhou, L. Zhang, X. Zhao, Y. Liu and Z.-T. Li, *J. Am. Chem. Soc.*, 2013, **135**, 17913.

23 (a) S.-L. Li, T.-X. Xiao, B.-J. Hu, Y.-J. Zhang, F. Zhao, Y. Ji, Y.-H. Yu, C.-Lin and L.-Y. Wang, *Chem. Commun.*, 2011, **47**, 10755; (b)

B. J. B. Folmer, R. P. Sijbesma and E. W. Meijer, *J. Am. Chem. Soc.*, 2001, **123**, 2093; (c) T. Haino, A. Watanabe, T. Hirao and T. Ikeda, *Angew. Chem. Int. Ed.*, 2012, **51**, 1473; (d) X. Yan, M. Zhou, J. Chen, X. Chi, S. Dong, M. Zhang, X. Ding, Y. Yu, S. Shao and F. Huang, *Chem. Commun.*, 2011, **47**, 7086.

Unprecedented Cucurbituril-Based Ternary Host-Guest Supramolecular Polymers Mediated through Included Alkyl Chains

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Novel ternary host-guest supramolecular polymers constructed from Q[8] and 1',1"-(alkylene-1,4-diyl)bis(1-butyl)-4,4'-bipyridine-1,1'-diium)bromide with included alkyl chains as the mediating functional groups have been fabricated and structurally characterized for the first time.