

# Paraquat guest induced hydrogen-bonding modes of a hydrazide-derived bis(*meta*-phenylene)-32-crown-10 host in the solid state

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**Abstract**—A hydrazide-derived bis(*meta*-phenylene)-32-crown-10 host showed a dimeric structure via quadruple N–H···O hydrogen bonds, but a polymeric structure via two N–H···O hydrogen bonds and two C–H···O hydrogen bonds at each knot in the presence of paraquat in the solid state, which led to a novel poly(taco complex) and ordering arrangement of the guest molecules indirectly. © 2007 Published by Elsevier Ltd.

Host–guest chemistry and crystal engineering are two important fields of modern supramolecular chemistry.<sup>1</sup> In 1987, Allwood et al.<sup>2</sup> first reported the formation of 1:1 pseudorotaxane-type complex between bis(*meta*-phenylene)-32-crown-10 (BMP32C10) **1** and paraquat (*N,N'*-dimethyl-4,4'-bipyridinium salt). Recently, Gibson et al.<sup>3</sup> found that a BMP32C10 derivative **2** could form a folded, taco complex with paraquat, which has resulted in the construction of various supramolecular structures.<sup>4,5</sup>

Following our recent report that hydrazide structure motif exists as a dimer **3** in the solid state with high fidelity,<sup>6</sup> we designed a new supramolecular polymer strategy for the ordering arrangement of guest molecules using the hydrazide as a reliable supramolecular synthon.<sup>7</sup> With two hydrazide structure motifs attached to the periphery of a bis(*meta*-phenylene)-32-crown-10 host **4** (Fig. 1), the preorganization of the host via a hydrogen bonding mediated polymeric structure could be expected. Considering that the strong complexation between the host and paraquat guest existed, the ordering arrangement of the guest could thus be obtained indirectly. Here we report our findings that in the solid

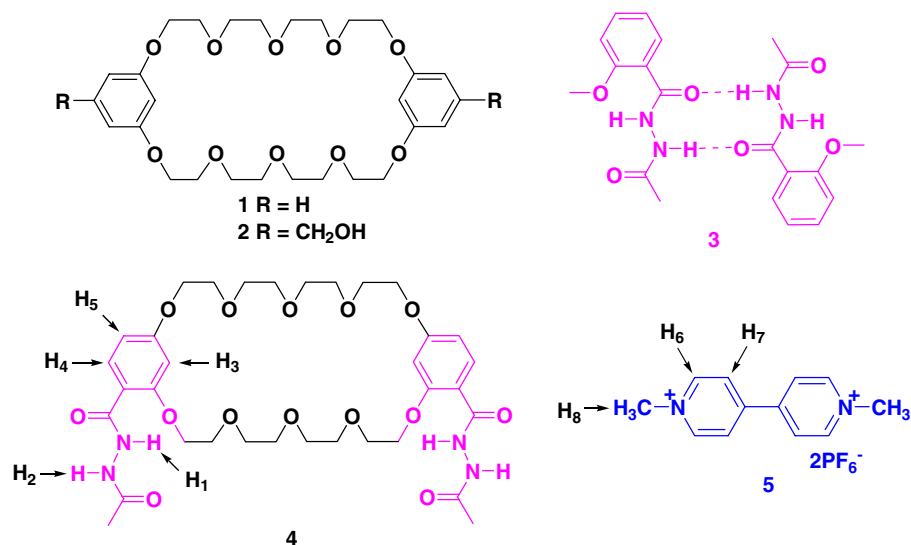
state host **4** shows a dimeric structure with a pseudo cylindrical macrotricyclic shape<sup>5,8</sup> via quadruple N–H···O hydrogen bonds,<sup>9</sup> but a poly(taco structure)<sup>10</sup> via two N–H···O hydrogen bonds and two C–H···O hydrogen bonds at each knot in the presence of paraquat. Moreover, a PF<sub>6</sub><sup>−</sup> counterion mediated supramolecular poly(taco complex) can also be found.

Synthesis of the host started with the reaction of 4-benzoyloxy-2-hydroxybenzoic acid methyl ester **6**<sup>11</sup> and tetraethyleneglycol bis(*p*-toluenesulfonate) **7**<sup>12</sup> in acetone, using K<sub>2</sub>CO<sub>3</sub> as base, to afford the mono polyether chain bridged product **8** in 81% yield. Deprotection of the benzyl groups under the catalytic hydrogenation conditions gave diol **9** in almost quantitative yield, which then reacted with bistosylate **7** under pseudo-high dilution condition using K<sub>2</sub>CO<sub>3</sub> as base in DMF to yield the ester-derived bis(*meta*-phenylene)-32-crown-10 **10** in 61% yield. Compound **10** was hydrolyzed to acid **11**, which was then converted to the acyl chloride and further coupled with acetohydrazide. Consequently, the target molecule bis(4-(*N'*-acetylhydrazinocarbonyl)-*meta*-phenylene)-32-crown-10 **4**<sup>13</sup> with two hydrazide motifs attached to its periphery was efficiently formed (Scheme 1).

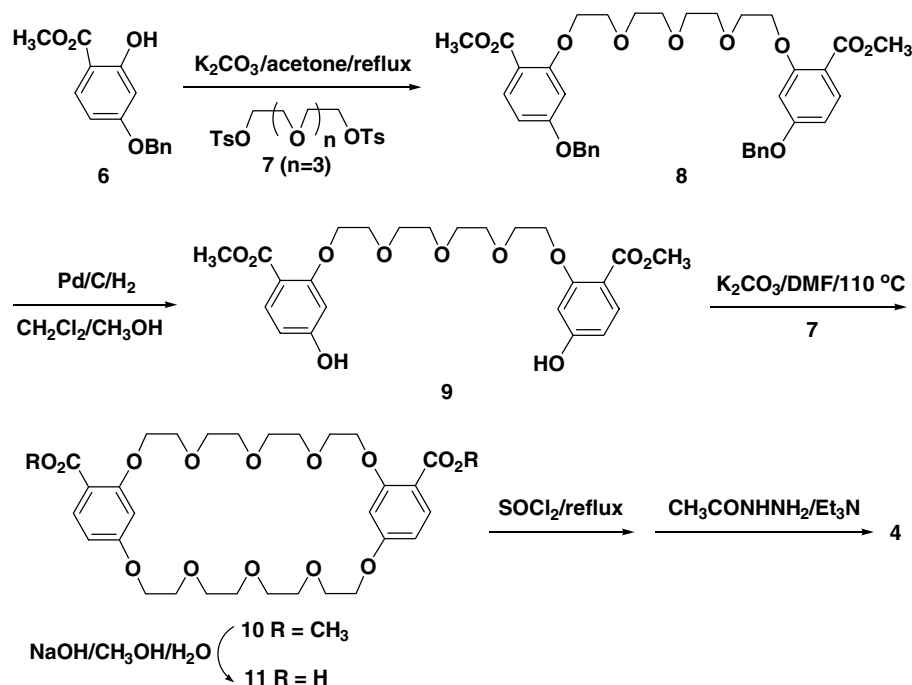
The host–guest complexation was first evidenced by a yellow solution when host **4** and guest **5** were equivalently mixed in acetone due to charge transfer interactions between the electron-rich aromatic rings of **4** and

**Keywords:** Paraquat; Hydrazide; Bis(*meta*-phenylene)-32-crown-10; Hydrogen bond; Self-assembly.

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**Figure 1.** Chemical structures of **1** and **2**, a hydrazide-based supramolecular synthon **3**, and structure and proton designations of host **4** and guest **5** used in this study.



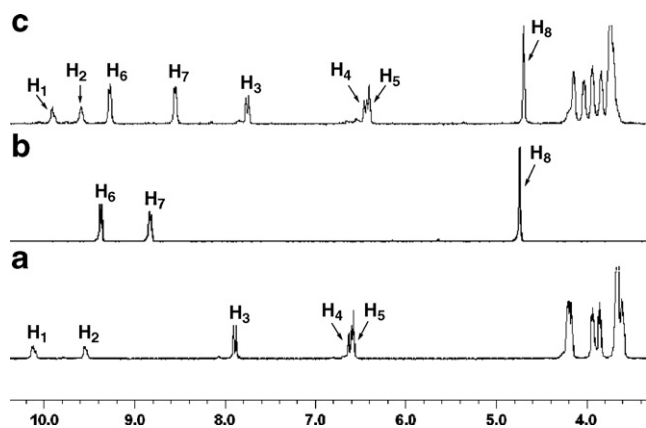
**Scheme 1.** Synthesis of host **4**.

electron-poor pyridinium rings of **5**. As shown in Figure 2, the <sup>1</sup>H NMR spectrum of a solution of **4** and **5** in acetone-*d*<sub>6</sub> showed that the signals of aromatic protons, proton H<sub>1</sub> and some crown ether protons shifted upfield, while the signal of proton H<sub>2</sub> shifted downfield. These are consistent with the formation of a new complex between **4** and **5**. The stoichiometry of the complex between **4** and **5** was further determined to be 1:1 by a mole ratio plot.<sup>14</sup> From the Scatchard plot, the average apparent association constant for the complex was calculated to be  $(2.8 \pm 0.7) \times 10^2 \text{ M}^{-1}$ .

ESI MS also confirmed the host–guest complexation. As a result, two relevant peaks at 1067.6 and 461.4 were

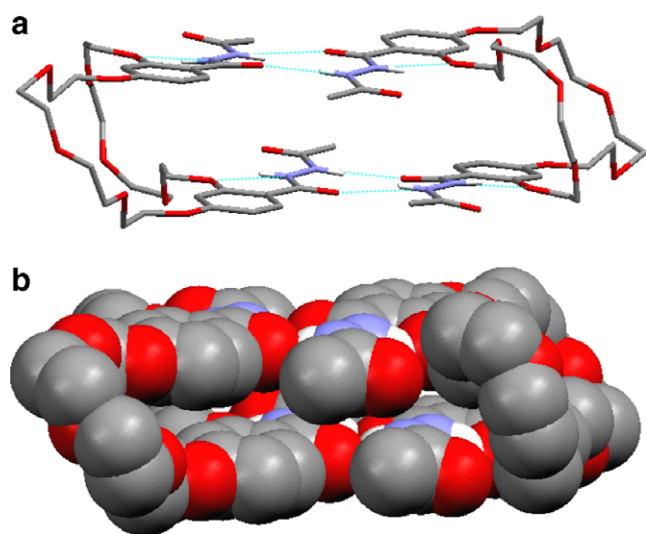
found for  $[\mathbf{4}\cdot\mathbf{5}-\text{PF}_6^-]^+$  (8%) and  $[\mathbf{4}\cdot\mathbf{5}-2\text{PF}_6^-]^{2+}$  (100%), respectively. Moreover, a peak at 830.0 for  $[\mathbf{4}_2\cdot\mathbf{5}-2\text{PF}_6^-]^{2+}$  (68%) was also observed, which might be due to the formation of [3]complex  $\mathbf{4}_2\cdot\mathbf{5}$ .<sup>15</sup>

A single crystal of **4**,<sup>16</sup> which is block shaped and colorless, suitable for X-ray analysis was obtained from slow cooling of its acetone solution. Accordingly, slow cooling of equimolar solution of **4** and **5** in acetone afforded a single crystal of complex  $\mathbf{4}\cdot\mathbf{5}$ <sup>17</sup> suitable for X-ray analysis, which is also block shaped but yellow due to charge transfer between the electron-rich aromatic rings of host **4** and electron-poor pyridinium rings of guest **5**.



**Figure 2.** Partial  $^1\text{H}$  NMR spectra (300 MHz, acetone- $d_6$ , 25  $^\circ\text{C}$ ) of (a) **4**, (b) **5**, and (c) **4** and 1 equiv **5**.  $[\mathbf{4}]_0 = 2.0$  mM.

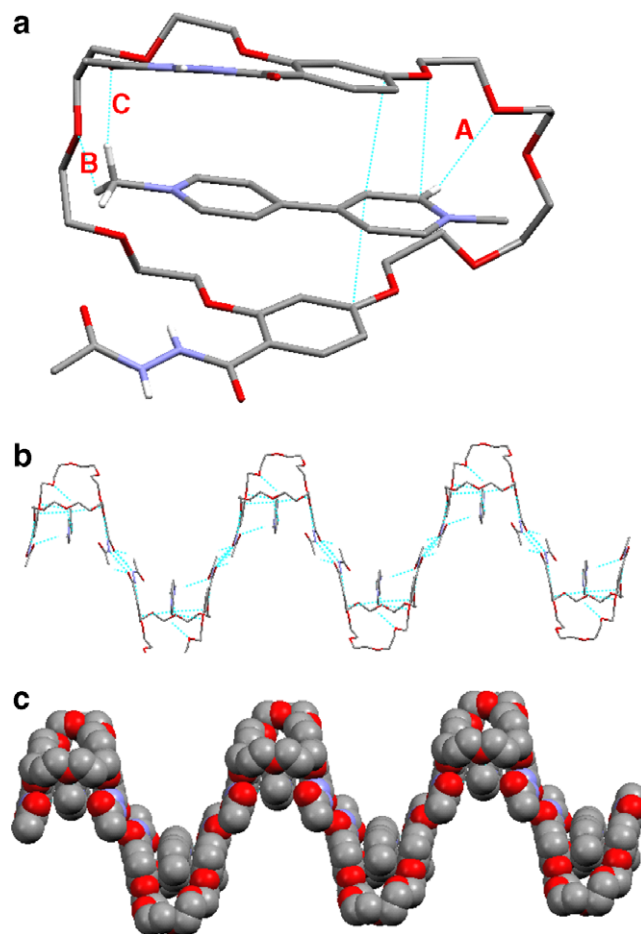
It was found that the hydrazide-derived BMP32C10 **4** showed a folded structure in the solid state (Fig. 3), which resulted in a dimer due to intermolecular hydrogen bonding between hydrazide groups. The dimer has a similar shape to the cylindrical bis(crown ether) host in which two BMP32C10 units are covalently linked.<sup>5</sup> As shown in Figure 3, in each monomer two highly favorable S(6) type<sup>18</sup> hydrogen bonds ( $d = 1.93$  Å,  $D = 2.61$  Å,  $\theta = 135.3^\circ$ , average) confine the hydrazide units to be coplanar with the two aromatic rings and expose four hydrogen bonding sites to interact intermolecularly. Bond length and angle parameters of intermolecular hydrogen bonds ( $d = 2.06$  Å,  $D = 2.90$  Å,  $\theta = 165.1^\circ$ , average) are similar to those of the supramolecular zipper system reported by us.<sup>6</sup> To our knowledge, this is the first example of cylindrical bis(crown ether) host constructed via quadruply hydrogen bonds.<sup>19</sup> The two aromatic rings are almost parallel, adopting an offset face-to-face  $\pi$ - $\pi$  stacking mode,



**Figure 3.** Two views of the X-ray structure of **4**. Solvent molecules and hydrogen atoms not involved in the hydrogen-bonding interactions are omitted for clarity. (a) Capped stick model of the dimeric structure, blue dotted lines indicate hydrogen bonds. (b) Space-filling model of the dimeric structure. Oxygen: red; carbon: grey; nitrogen: blue.

which might stabilize the hydrogen-bonded dimeric structure.<sup>20</sup> The dihedral angle and centroid-centroid distance between the two aromatic rings are  $4.35^\circ$  and  $4.86$  Å, respectively.

As shown in the X-ray structure (Fig. 4a), host **4** and paraquat **5** form a taco (or folded sandwich-type) complex **4·5**. In the complex, there existed multiple hydrogen bonds between one  $\alpha$ -pyridinium proton and two *N*-methyl protons in the guest and the ether oxygen atoms and one *N'*-acetylhydrazino oxygen atom in the host. Moreover, face-to-face  $\pi$ - $\pi$  stacking interactions between the two phenyl rings of the host and the pyridinium rings of the guest were also observed. These multiple noncovalent interactions resulted in the stable complex **4·5**. Compared with its uncomplexed conformation, the two aromatic rings of the host are just above each other, not adopting an off-set mode, with the dihedral angle and centroid-centroid distance of  $21.2^\circ$  and  $7.16$  Å. Moreover, the intramolecular hydrogen bonds ( $d = 2.04$  Å,  $D = 2.69$  Å,  $\theta = 131.8^\circ$ , average) did not



**Figure 4.** X-ray crystal structure of complex **4·5**. (a) Representation of host-guest interaction. Intermolecular hydrogen-bond distances in Å and C-H $\cdots$ O angles in deg.: A = 2.60, 136.7; B = 2.63, 129.9; C = 2.65, 151.0. (b) Capped stick model of the poly(taco complex). Blue dotted lines indicate hydrogen bonding and other short contacts. (c) Space-filling model of the poly(taco complex). Solvent molecules,  $\text{PF}_6^-$  counterions, and hydrogens not involved in the hydrogen bond interactions are omitted for clarity.

change much, but the intermolecular hydrogen bonding mode changed substantially. Perhaps the complexation with the guest made the aromatic rings of the host unparallel such that a dimeric structure for the host via quadruply N–H···O hydrogen bonds was no longer favored. Consequently, a polymeric structure with two N–H···O hydrogen bonds ( $d=2.20$  Å,  $D=2.99$  Å,  $\theta=152.0^\circ$ , average) and two C–H···O hydrogen bonds ( $d=2.67$  Å,  $D=3.47$  Å,  $\theta=140.2^\circ$ , average) at each knot was formed, which resulted in a novel poly(taco complex)<sup>21</sup> (Fig. 4b and c).

Furthermore, a PF<sub>6</sub><sup>−</sup> counterion mediated supramolecular poly(taco complex) was also found (Fig. 5a).<sup>22</sup> One PF<sub>6</sub><sup>−</sup> counterion located at the axis of the polymer structure acts as hydrogen bonding bridge to stabilize the noncovalent polymer by connecting one taco complex by one bifurcated hydrogen bond and one trifurcated hydrogen bond, and another one by two hydrogen bonds. Another PF<sub>6</sub><sup>−</sup> counterion located at the edge of the polymer structure also acts in concert with an acetone molecule to form a hydrogen bonding bridge to stabilize the supramolecular polymer structure. The supramolecular poly(taco complex) was also stabilized by hydrogen bonding between the two adjacent taco complexes. Thus, with the formation of two orthogonal supramolecular poly(taco complexes), a grid arrangement of guest molecules was obtained (Fig. 5b).

In summary, we have shown that the paraquat could substantially influence the modes of hydrogen bonding of the hydrazide-derived BMP32C10 host. Consequently, the host existed as a dimer via quadruple hydrogen bonds, but showed a polymeric structure via two N–H···O hydrogen bonds and two C–H···O hydrogen bonds at each knot in the presence of para-

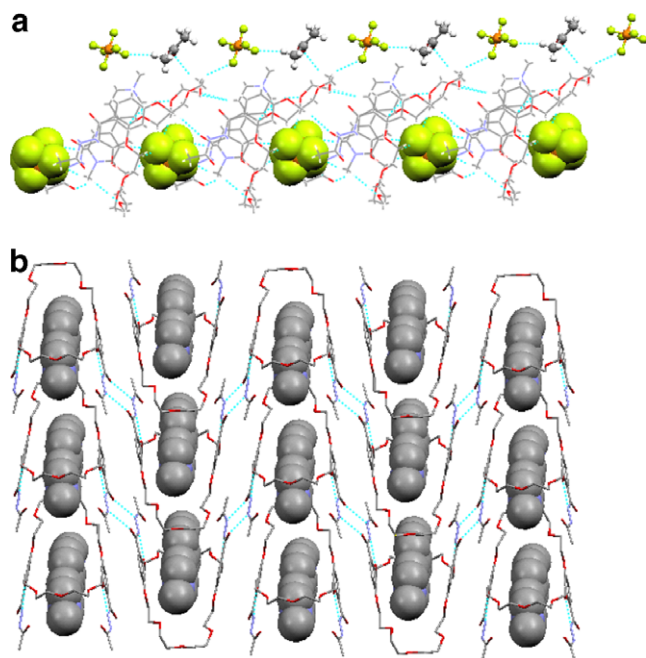
quat in the solid state, which led to a novel poly(taco complex). Moreover, a PF<sub>6</sub><sup>−</sup> counterion mediated orthogonal supramolecular poly(taco complex) was also found, which resulted in a grid arrangement of the guest molecules. The results presented here will be helpful for developing various new supramolecular systems with unique structures and properties, which are under way in our laboratory.

### Acknowledgements

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### References and notes

- Lehn, J.-M. *Supramolecular Chemistry*; VGH: New York, 1995.
- Allwood, B. L.; Shahriari-Zavareh, H.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1058–1061.
- Bryant, W. S.; Jones, J. W.; Mason, P. E.; Guzei, I.; Rheingold, A. L.; Fronczek, F. R.; Nagvekar, D. S.; Gibson, H. W. *Org. Lett.* **1999**, *1*, 1001–1004.
- (a) Huang, F.; Nagvekar, D. S.; Slebodnick, C.; Gibson, H. W. *J. Am. Chem. Soc.* **2005**, *127*, 484–485; (b) Huang, F.; Gibson, H. W. *J. Am. Chem. Soc.* **2004**, *126*, 14738–14739; (c) Huang, F.; Fronczek, F. R.; Gibson, H. W. *Chem. Commun.* **2003**, 1480–1481.
- (a) Huang, F.; Zakharov, L. N.; Rheingold, A. L.; Ashraf-Khorassani, M.; Gibson, H. W. *J. Org. Chem.* **2005**, *70*, 809–813; (b) Huang, F.; Gibson, H. W. *Chem. Commun.* **2005**, 1696–1698.
- Yang, Y.; Zhang, Y.; Tang, Y. L.; Chen, C. F. *New J. Chem.* **2006**, *30*, 140–142.
- Desiraju, G. R. *Chem. Commun.* **1997**, 1475–1482.
- (a) Zong, Q. S.; Chen, C. F. *Org. Lett.* **2006**, *8*, 211–214; (b) Zong, Q. S.; Zhang, C.; Chen, C. F. *Org. Lett.* **2006**, *8*, 1859–1862.
- For more multiple hydrogen-bonded systems, see: (a) Prins, L. J.; Reinhoudt, D. N.; Timmerman, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2382–2426; (b) Sijbesma, R. P.; Meijer, E. W. *Chem. Commun.* **2003**, 5–16.
- More examples of hydrogen-bonded polymeric structures, see: (a) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071–4097; (b) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, K. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601–1604; (c) Kim, S. J.; Jo, M.-G.; Lee, J. Y.; Kim, B. H. *Org. Lett.* **2004**, *6*, 1963–1966; (d) Du, Y.; Creighton, C. J.; Tounge, B. A.; Reitz, A. B. *Org. Lett.* **2004**, *6*, 309–312; (e) Pérez, C.; Rodríguez, M. L.; Foces-Foces, C.; Pérez-Hernández, N.; Pérez, R.; Martín, J. D. *Org. Lett.* **2003**, *5*, 641–644; (f) Ducharme, Y.; Wuest, J. D. *J. Org. Chem.* **1988**, *53*, 5787–5789.
- Robertson, D. W.; Beedle, E. E.; Krushinski, J. H.; Pollock, G. D.; Wilson, H.; Wyss, V. L.; Hayes, J. S. *J. Med. Chem.* **1985**, *28*, 717–727.
- Ouchi, M.; Inoue, Y.; Kanzaki, T.; Hakushi, T. *J. Org. Chem.* **1984**, *49*, 1408–1412.
- A solution of **11** (0.312 g, 0.5 mmol) in SOCl<sub>2</sub> (5 mL) was refluxed for 4 h and the excess SOCl<sub>2</sub> was then evaporated



**Figure 5.** Presentation of (a) PF<sub>6</sub><sup>−</sup> counterion mediated supramolecular poly(taco complex) and (b) grid arrangement of guest molecules.

- under reduced pressure. The residue was dissolved in dichloromethane (10 mL) and added dropwise into a solution of triethylamine (0.2 g, 2 mmol) and acetohydrazide (0.15 g, 2 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) over a period of 30 min with ice-water bath equipped. After complete addition, the ice-water bath was removed. The reaction mixture was stirred at room temperature for another 2 h, and more  $\text{CH}_2\text{Cl}_2$  (30 mL) added. The solution was washed with diluted 2 N HCl (20 mL), saturated  $\text{Na}_2\text{CO}_3$  aqueous solution (20 mL), and saturated brine (20 mL) successively. The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After the solvent was evaporated under reduced pressure, the crude product was recrystallized from methanol to give product **4** (0.367 g, 99.7% yield) as a white solid. Mp: 158–159 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  10.33 (d,  $J = 3.6$  Hz, 2H,  $H\text{-N}$ ), 9.86 (d,  $J = 3.6$  Hz, 2H,  $H\text{-N}$ ), 7.82 (d,  $J = 8.5$  Hz, 2H,  $H\text{-Ar}$ ), 6.68–6.65 (m, 4H,  $H\text{-Ar}$ ), 4.21–4.16 (m, 8H,  $\text{CH}_2$ ), 3.80–3.76 (m, 8H,  $\text{CH}_2$ ), 3.58–3.48 (m, 12H,  $\text{CH}_2$ ), 3.32–3.33 (m, 4H,  $\text{CH}_2$ ), 1.92 (s, 6H,  $\text{COCH}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  164.9, 160.6, 160.2, 156.0, 130.6, 111.0, 105.1, 98.3, 68.1, 68.0, 67.7, 66.9, 66.6, 66.5, 65.7, 18.4. IR (KBr,  $\text{cm}^{-1}$ ): 3211.9, 2937.1, 1655.6, 1605.5, 1261.2. MS (ESI):  $m/z$  737  $[\text{M}+\text{H}]^+$ , 759  $[\text{M}+\text{Na}]^+$ . Elemental Anal. Calcd for  $\text{C}_{34}\text{H}_{48}\text{N}_4\text{O}_{14}\cdot\text{H}_2\text{O}$ : C, 54.10; H, 6.68; N, 7.42. Found: C, 53.83; H, 6.55; N, 7.33.
14. Tsukube, H.; Furuta, H.; Odani, A.; Takeda, Y.; Kudo, Y.; Inoue, Y.; Liu, Y.; Sakamoto, H.; Kimura, K. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vogtle, F., Lehn, J.-M., Eds.; Elsevier: New York, 1996; Vol. 8, p 425.
  15. Similar [3]complexes reported by Huang et al. from BMP32C10 based cryptands and paraquat, see: (a) Huang, F.; Gibson, H. W.; Bryant, W. S.; Nagvekar, D. S.; Fronczek, F. R. *J. Am. Chem. Soc.* **2003**, *125*, 9367–9371; (b) Huang, F.; Lam, M.; Mahan, E. J.; Rheingold, A. L.; Gibson, H. W. *Chem. Commun.* **2005**, 3268–3270.
  16. *Crystal data for compound 4 (CCDC 608205)*:  $\text{C}_{37}\text{H}_{54}\text{N}_4\text{O}_{15}$ ,  $M_w = 794.84$ , crystal size:  $0.30 \times 0.30 \times 0.20$  mm<sup>3</sup>, crystal system: triclinic, space group:  $P(\bar{1})$ ,  $a = 9.758(2)$  Å,  $b = 13.528(3)$  Å,  $c = 17.004(4)$  Å,  $\alpha = 79.685(4)^\circ$ ,  $\beta = 76.503(4)^\circ$ ,  $\gamma = 71.592(4)^\circ$ ,  $U = 2057.5(8)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.283$  Mg/m<sup>3</sup>,  $T = 293(2)$  K,  $\mu = 0.100$  mm<sup>-1</sup>, 7205 reflections measured, 3206 unique ( $R_{\text{int}} = 0.0260$ ),  $R_1 = 0.0724$ ,  $wR_2 = 0.1942$ .
  17. *Crystal data for 45 (CCDC 608204)*:  $\text{C}_{49}\text{H}_{68}\text{F}_{12}\text{N}_6\text{O}_{15}\text{P}_2$ ,  $M_w = 1271.03$ , crystal size:  $0.22 \times 0.18 \times 0.16$  mm<sup>3</sup>, crystal system: triclinic, space group:  $P(\bar{1})$ ,  $a = 11.045(2)$  Å,  $b = 17.257(7)$  Å,  $c = 17.451(8)$  Å,  $\alpha = 75.946(16)^\circ$ ,  $\beta = 75.316(19)^\circ$ ,  $\gamma = 77.803(14)^\circ$ ,  $U = 3081.5(19)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.370$  Mg/m<sup>3</sup>,  $T = 294(2)$  K,  $\mu = 0.172$  mm<sup>-1</sup>, 10,174 reflections measured, 5102 unique ( $R_{\text{int}} = 0.0510$ ),  $R_1 = 0.1371$ ,  $wR_2 = 0.3729$ .
  18. For nomenclature, see: (a) Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120–126; (b) Etter, M. C.; Macdonald, J. C.; Bernstein, J. *Acta Crystallogr., Sect. B.* **1990**, *46*, 256–262; (c) Bernstein, J.; Davis, R. E.; Shimon, L.; Chang, N.-L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1555–1573.
  19. Gibson H.W. et al. recently reported water assisted formation of a dimeric structure and formation of a dimeric structure driven by dipole–dipole and face-to-face  $\pi$ -stacking interactions. (a) Huang, F.; Zakharov, L. N.; Rheingold, A. L.; Jones, J. W.; Gibson, H. W. *Chem. Commun.* **2003**, 2122–2123; (b) Huang, F.; Zhou, L.; Jones, J. W.; Gibson, H. W.; Ashraf-Khorassani, M. *Chem. Commun.* **2004**, 2670–2671.
  20. (a) Jurečka, P.; Hobza, P. *J. Am. Chem. Soc.* **2003**, *125*, 15608–15613; (b) Dąbkowska, I.; Gonzalez, H. V.; Jurečka, P.; Hobza, P. *J. Phys. Chem. A.* **2005**, *109*, 1131–1136; (c) Guo, D.; Sijbesma, R. P.; Zuilhof, H. *Org. Lett.* **2004**, *6*, 3667–3670.
  21. Huang et al. recently reported a supramolecular poly(taco complex), in which hydrogen bonding of the  $\text{PF}_6^-$  counterions with the urethane linkages of the guest played a key role. See Ref. 4c.
  22. Examples of  $\text{PF}_6^-$  anion assisted the assemblies in the solid state, see: (a) Ashton, P. R.; Cantrill, S. J.; Preece, J. A.; Stoddart, J. F.; Wang, Z.-H.; White, A. J. P.; Williams, D. J. *Org. Lett.* **1999**, *1*, 1917–1920; (b) Fyfe, M. C. T.; Glink, P. T.; Menzer, S.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **1997**, *36*, 2068–2070.