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

Yong Yang,[a,b] Hai-Yu Hu[a,b] and Chuan-Feng Chen[a,*]

[a] *Beijing National Laboratory for Molecular Sciences, Center for Chemical Biology, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China*
[b] *Graduate School, Chinese Academy of Sciences, Beijing 100049, China*

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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.
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Host–guest chemistry and crystal engineering are two important fields of modern supramolecular chemistry.[1] In 1987, Allwood et al.[2] 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.[3] found that a BMP32C10 derivative **2** could form a folded, taco complex with paraquat, which has resulted in the construction of various supramolecular structures.[4,5]

Following our recent report that hydrazide structure motif exists as a dimer **3** in the solid state with high fidelity,[6] we designed a new supramolecular polymer strategy for the ordering arrangement of guest molecules using the hydrazide as a reliable supramolecular synthon.[7] 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[5,8] via quadruple N–H···O hydrogen bonds,[9] but a poly(taco structure)[10] 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_6^- counterion mediated supramolecular poly(taco complex) can also be found.

Synthesis of the host started with the reaction of 4-benzyloxy-2-hydroxybenzoic acid methyl ester **6**[11] and tetraethyleneglycol bis(*p*-toluenesulfonate) **7**[12] in acetone, using K_2CO_3 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_2CO_3 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**[13] 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

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

[*] Corresponding author. Tel.: +86 10 62588936; fax: +86 10 62554449; e-mail: cchen@iccas.ac.cn

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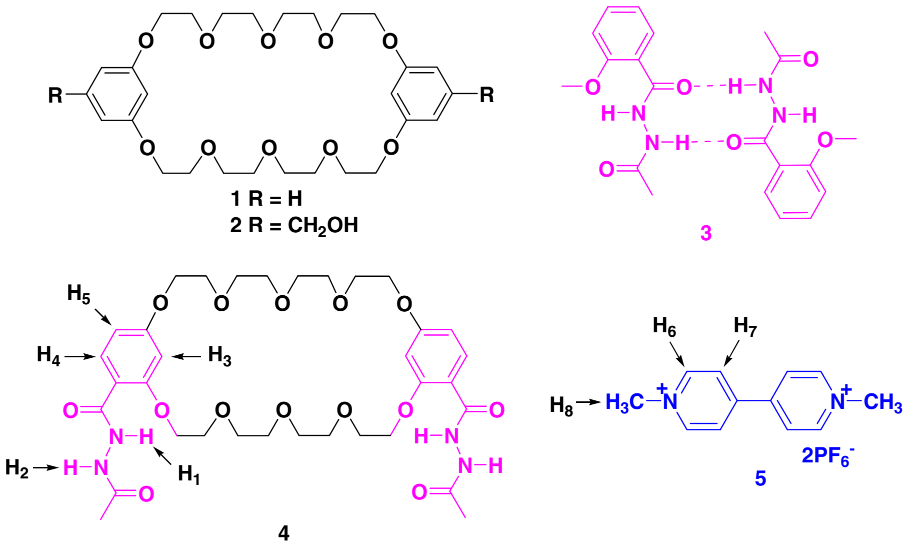
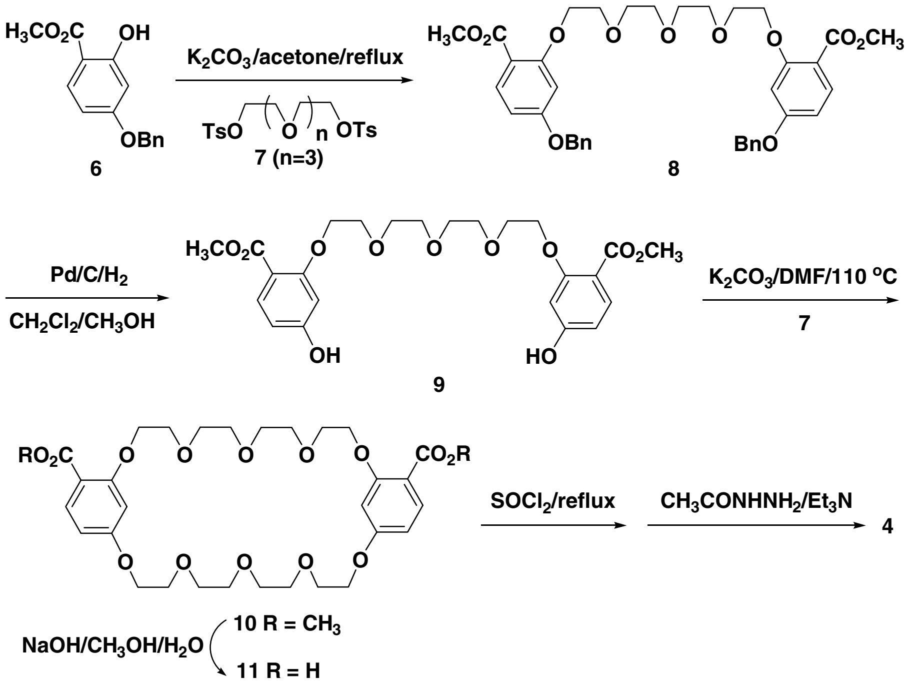


Figure 1. Chemical structures of **1** and **2**, a hydrazide-based supramolecular synthon **3**, and structure and proton designations of host **4** and guest **5** used in this study.



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

electron-poor pyridinium rings of **5**. As shown in Figure 2, the ^{1}H NMR spectrum of a solution of **4** and **5** in acetone-d_6 showed that the signals of aromatic protons, proton H_1 and some crown ether protons shifted upfield, while the signal of proton H_2 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.[14] From the Scatchard plot, the average apparent association constant for the complex was calculated to be $(2.8 \pm 0.7) \times 10^2\ \mathrm{M}^{-1}$.

ESI MS also confirmed the host–guest complexation. As a result, two relevant peaks at 1067.6 and 461.4 were found for $[\mathbf{4}\cdot\mathbf{5}-\mathrm{PF}_6^-]^+$ (8%) and $[\mathbf{4}\cdot\mathbf{5}-2\mathrm{PF}_6^-]^{2+}$ (100%), respectively. Moreover, a peak at 830.0 for $[\mathbf{4}_2\cdot\mathbf{5}-2\mathrm{PF}_6^-]^{2+}$ (68%) was also observed, which might be due to the formation of [3]complex $\mathbf{4}_2\cdot\mathbf{5}$.[15]

A single crystal of **4**,[16] 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 **4·5**[17] suitable for X-ray analysis, which is also block shaped but yellow due to change transfer between the electron-rich aromatic rings of host **4** and electron-poor pyridinium rings of guest **5**.