

## A new type of [2] and [3]pseudorotaxane composed of $\beta$ -cyclodextrin and bisimidazolyl compounds

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**Abstract**—Employing bisimidazolyl compounds as guests, a new type of [2] and [3]pseudorotaxanes based on  $\beta$ -cyclodextrin were synthesized and characterized. From the crystallographic structural analysis and  $^1\text{H}$  NMR spectroscopy it has been found that the number of threaded cyclodextrin depends on the length of the guest molecule.

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In recent years, much attention has been paid to the pseudorotaxane and rotaxane supramolecules because of their interesting structures and properties, as well as potential applications for molecular devices.<sup>1</sup> Pseudorotaxane is a type of supramolecular assembly that consists of a cyclic molecule, acts as the wheel, that is host, and a threadlike molecule acts as the axle, that is guest. It is commonly used as precursor for the formation of permanently interlocked rotaxane by adding ‘stopper’ components, which are bulky enough to prevent unthreading.

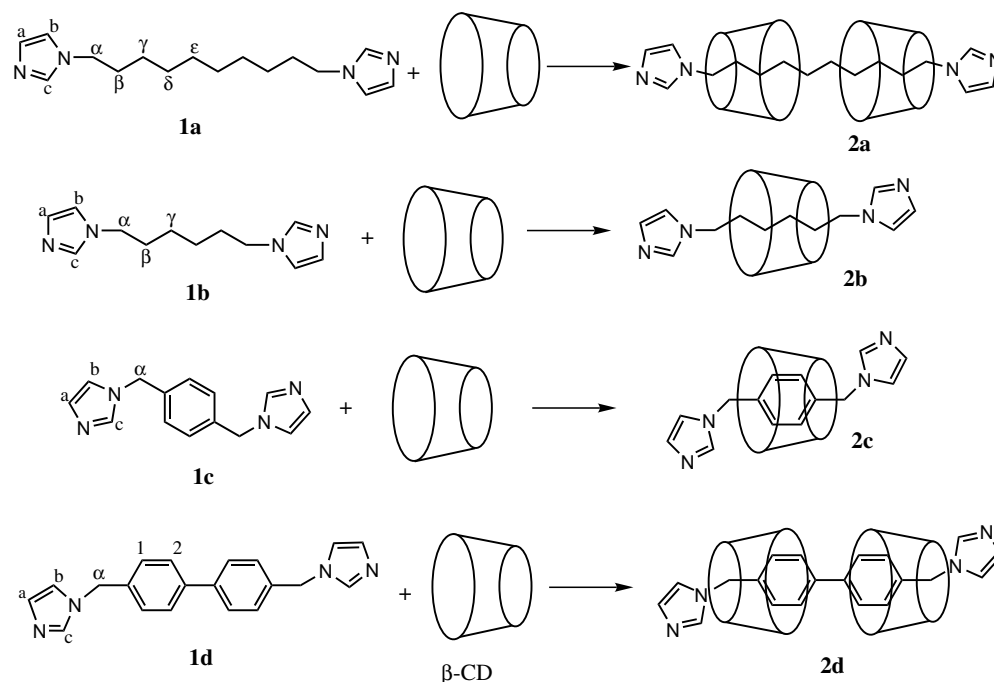
Although there are previous works about rotaxanes and pseudorotaxanes based on cyclodextrins,<sup>1a,f,2</sup> structural data of them are not plentiful. It is still a challenge to prepare new member of the rotaxanes with novel structures and special properties. The Mavridis’s group has determined the molecular structures of [3]pseudorotaxanes, in which a long aliphatic chain with carboxylic group or amino group thread through two molecules of  $\beta$ -CD.<sup>3</sup> Kamitori and co-workers reported the 2:1 complex of  $\alpha$ -CD/biphenyldicarboxylic.<sup>4</sup> Moreover, the single crystal X-ray diffraction analysis of a polymeric glycol-cyclodextrin polyrotaxane and two structures of pseudo-polyrotaxane composed of  $\beta$ -CD with poly(trimethylene oxide) and poly(propylene glycol) have been reported.<sup>5,6</sup> Recently, Anderson’s group determined the molecular structure of a stilbene cyclodextrin

[2]rotaxane.<sup>7</sup> However, to our knowledge, no [2] or [3]pseudorotaxane with the guest molecule involving imidazolyl group has been prepared. Here we describe the synthesis and characterization of a new type of  $\beta$ -CD pseudorotaxanes, in which bisimidazolyl compounds, that is **1a** (1,10-bis(imidazol-1-yl) decane), **1b** (1,6-bis(imidazol-1-yl)hexane), **1c** (1,4-bis(imidazol-1-ylmethyl)benzene) and **1d** (4,4’-(bis(imidazol-1-ylmethylene))biphenyl) are employed as guest to thread into  $\beta$ -CD (Scheme 1). Two structures of pseudorotaxanes, that is **2a** (**1a**/2 $\beta$ -CD) and **2c** (**1c**/ $\beta$ -CD) have been determined for the first time. Because of the N atom in terminal imidazole group of the guest molecule can coordinate with transition metal ion, these type of pseudorotaxanes may be converted to permanent metallo-rotaxanes, which would probably be furnished with specific photonic, electric or magnetic properties.

The four guest compounds **1a**, **1b**, **1c** and **1d** were prepared from relevant  $\alpha,\omega$ -dibromo-alkyl or -aromatic compounds with imidazole in a molar ratio of 1:2 in isopropyl alcohol under strong alkali (KOH) conditions by the method of Kikugawa.<sup>8</sup> All compounds gave satisfactory spectral and analytical results.<sup>9</sup> The pseudorotaxanes of **2a**, **2b**, **2c** and **2d** were synthesized by self-assembly of the guest compounds with  $\beta$ -CD in aqueous solution. The products were characterized by  $^1\text{H}$  NMR spectroscopy, elemental analysis and ESI-MS, respectively.<sup>10</sup> Single prismatic crystals were obtained by slow evaporation of the aqueous solution. The molecular structures were determined by a single crystal X-ray diffraction analysis.<sup>11</sup>

**Keywords:**  $\beta$ -Cyclodextrin; Pseudorotaxane; Bisimidazolyl compound; X-ray diffraction analysis;  $^1\text{H}$  NMR spectroscopy.

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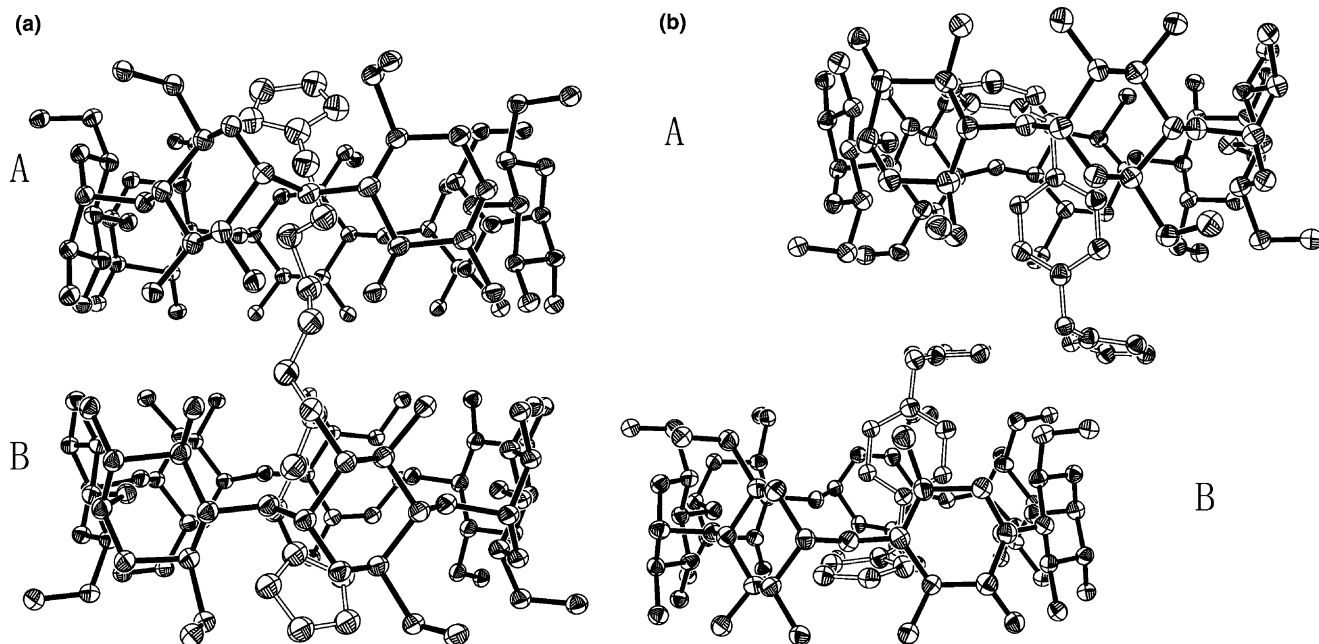


**Scheme 1.** Formation of the pseudorotaxanes.

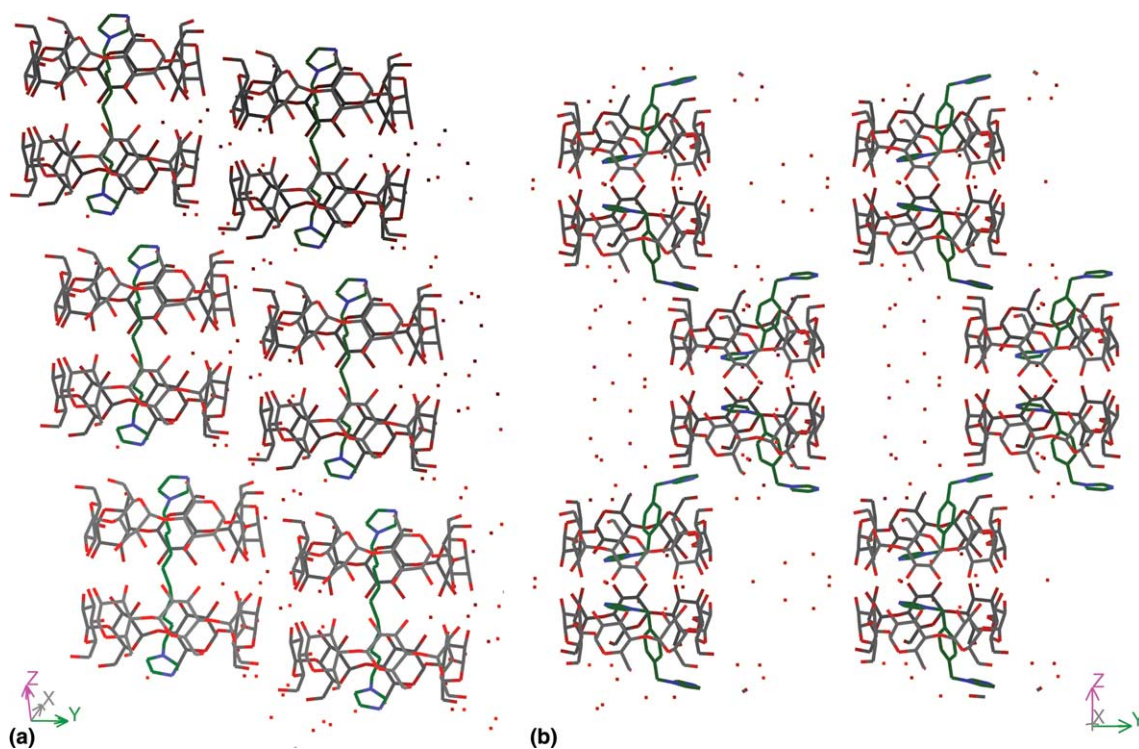
The molecular structure of **2a** (Fig. 1a) indicates that two  $\beta$ -CD rings are threaded on to **1a** molecule to form a [3]pseudorotaxane. The  $\beta$ -CD dimer is composed of the monomers A and B with the stacking of secondary to secondary faces. Each of the secondary hydroxyls of  $\beta$ -CD is H-bonded to those secondary hydroxyls both in the same and in the neighboring  $\beta$ -CD molecule of the dimer. The guest molecule spans the entire length of the  $\beta$ -CD dimer cavity with the imidazole groups slightly protruding from the primary faces of  $\beta$ -CDs. The mole-

cule packing of **2a** (Fig. 2a) shows that  $\beta$ -CDs constitute channels along  $c$  axis, which forms an angle of  $19.5^\circ$  with the axis of  $\beta$ -CD dimer. The space between the  $\beta$ -CDs is filled with water molecules, which is H-bonded to cyclodextrin hydroxyl and other water molecules.

While the structure of **2c** shows that each molecule of **1c** threads into the cavity of one  $\beta$ -CD to form a [2]pseudorotaxane (Fig. 1b). The benzene group of **1c** is included in the  $\beta$ -CD cavity, one imidazole group is located in the



**Figure 1.** Molecular structure of the [2] and [3]pseudorotaxanes (a) **2a**, (b) **2c** (50% probability ellipsoids; H atoms are omitted; the bonds of guest molecules are hollowed for clarity). In **2a**, the angles between the plane of the imidazole groups and the heptagons composed of seven O atoms of the  $\beta$ -CD are  $43.5^\circ$  and  $51.3^\circ$ , respectively. In **2c**, the corresponding angles are  $14.9^\circ$ ,  $12.1^\circ$  (of A unite) and  $2.9^\circ$ ,  $5.8^\circ$  (of B unite), respectively.



**Figure 2.** Packing style of pseudorotaxanes (a) **2a**, (b) **2c** (observed from *a* axis, the carbon atoms of guest molecules are green-colored for clarity).

secondary face of  $\beta$ -CD and the other slightly protrudes from the primary face. The crystallographic asymmetric unit contains two [2]pseudorotaxanes. From the molecule packing of **2c** (Fig. 2b), we can see that  $\beta$ -CD molecules also form face-to-face dimers, in which their secondary hydroxyl sides are linked by multiple hydrogen bonds. The two adjacent imidazole rings, which are located in the secondary faces of  $\beta$ -CD, exhibit a  $\pi$ - $\pi$  interaction with a centroid-centroid distance of 4.16 Å and an angle of 16.3°. In addition, the imidazole group in the primary face of  $\beta$ -CD assists in the formation of network via H-bond interaction with primary hydroxyl of the adjacent  $\beta$ -CD dimer. The  $\beta$ -CD dimers constitute brick-type molecular packing, which is different from the channel packing of **2a**. 'Cages' surrounded by dimers are filled with water molecules.

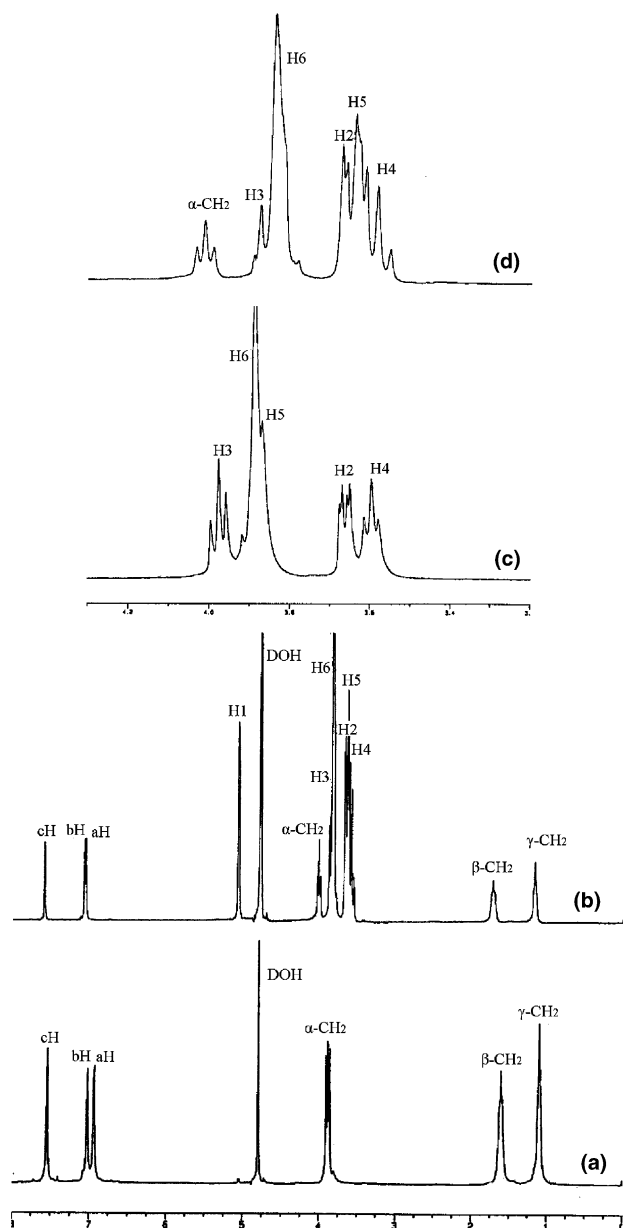
Apart from the single crystal X-ray diffraction analysis,  $^1\text{H}$  NMR spectroscopy is a powerful technique to investigate the formation of inclusion complex and the interaction between cyclodextrin and substrate.<sup>12,13</sup> Comparing to the  $^1\text{H}$  NMR spectroscopic data (Table 1) of free  $\beta$ -CD with that of **2b** (**2d**), 0.09 (0.14) and 0.22 (0.21) ppm upfield shifts were observed for H3 and H5 protons, which located in the cavity of  $\beta$ -CD, respectively. The chemical shifts of the resonance of H1, H2 and H4 protons on the outer surface were unaffected. Furthermore, the chemical shifts for H6 protons located in the narrower opening of  $\beta$ -CD, also moved to a higher field. For the guest molecule, the  $^1\text{H}$  NMR signals of alkylene of **1b** broadened and shifted upfield, while the signal of aH in imidazole group, which is close to the face of  $\beta$ -CD, moved downfield (about

**Table 1.** Chemical shifts of  $\beta$ -CD before and after formation of pseudorotaxane of **2a**, **2b**, **2c** and **2d** (ppm, in  $\text{D}_2\text{O}$ )

		H1	H2	H3	H4	H5	H6
Free		5.06	3.64	3.96	3.58	3.85	3.87
$\beta$ -CD							
<b>2a</b>	$\delta$	5.06	3.65	3.87	3.59	3.70	3.83
	$\Delta\delta$	0.00	+0.01	-0.09	+0.01	-0.15	-0.04
<b>2b</b>	$\delta$	5.06	3.65	3.87	3.58	3.63	3.84
	$\Delta\delta$	0.00	+0.01	-0.09	+0.00	-0.22	-0.03
<b>2c</b>	$\delta$	5.04	3.63	3.79	3.57	3.45	3.74
	$\Delta\delta$	-0.02	-0.01	-0.17	-0.01	-0.40	-0.13
<b>2d</b>	$\delta$	5.04	3.63	3.82	3.57	3.64	3.76
	$\Delta\delta$	-0.02	-0.01	-0.14	-0.01	-0.21	-0.11

0.11 ppm), compared with that of **2b** (Fig. 3). According to the integral area of the  $^1\text{H}$  NMR spectra, the molar ratio of  $\beta$ -CDs and guest molecules is 1:1 for **2b** and 2:1 for **2d**, respectively, which is consistent with element analysis and ESI-MS results. Furthermore, two-dimensional NOESY spectroscopy of **2b** (**2d**) revealed the correlation between alkylene protons of **1b** (phenyl protons of **1d**) and H3, H5 of  $\beta$ -CD. It indicates that the guest molecule had threaded through the cavities of one or two  $\beta$ -CDs to form the [2] or [3]pseudorotaxane, respectively.

In summary, bisimidazolyl compounds were used as guests for the first time to prepare a new kind of [2] or [3]pseudorotaxanes based on  $\beta$ -cyclodextrin. According to the crystal structural analysis and  $^1\text{H}$  NMR studies, we found that the guest molecules with longer alkylene chain or two benzene rings can thread two  $\beta$ -CDs to form the [3]pseudorotaxanes, while the guests with



**Figure 3.** The  $^1\text{H}$  NMR spectra (in  $\text{D}_2\text{O}$ ) of (a) **1b**, (b) **2b**, (c) partial spectra of  $\beta$ -CD (free) and (d) in **2b**.

shorter chain or one benzene thread only one  $\beta$ -CD ring to become the [2]pseudorotaxanes. It is worth noting that pseudorotaxanes show distinct molecular packing with the changing of guest molecules. Further investigation of metallo-rotaxane by adding complex 'stopper' to the ends of pseudorotaxane is in progress in our laboratory.

#### Acknowledgements

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- Selected data for the guest compounds: **1a**: yield 85%; elemental analysis calcd (%) for  $\text{C}_{16}\text{H}_{26}\text{N}_4$ : C, 70.03; H, 9.55; N, 20.42; found: C, 69.96; H, 9.66; N, 20.41;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.56 (2H, s,  $\text{cH}_{\text{im}}$ ), 7.14 (2H, s,  $\text{bH}_{\text{im}}$ ), 6.99 (2H, s,  $\text{aH}_{\text{im}}$ ), 4.01 (4H, t,  $J=6.9$  Hz,  $\alpha\text{-CH}_2$ ), 1.83–1.89 (4H, m,  $\beta\text{-CH}_2$ ), 1.27–1.44 (12H, m,  $\gamma\text{-}\epsilon\text{-(CH}_2)_3$ ); ESI-MS:  $m/z$  275 ( $[\text{M}+\text{H}]^+$ ).  
Compound **1b**: yield 50%;  $^1\text{H}$  NMR (500 MHz,  $\text{D}_2\text{O}$ ): 7.58 (2H, s,  $\text{cH}_{\text{im}}$ ), 7.06 (2H, s,  $\text{bH}_{\text{im}}$ ), 6.97 (2H, s,  $\text{aH}_{\text{im}}$ ), 3.92 (4H, t,  $J=6.3$  Hz,  $\alpha\text{-CH}_2$ ), 1.62–1.66 (4H, m,  $\beta\text{-CH}_2$ ), 1.12–1.16 (4H, m,  $\gamma\text{-CH}_2$ ); ESI-MS:  $m/z$  218 ( $[\text{M}+\text{H}]^+$ ).  
Compound **1c**: yield 80%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 7.66 (2H, s,  $\text{cH}_{\text{im}}$ ), 7.21 (4H, s,  $\text{H}_{\text{bz}}$ ), 7.18 (2H, s,  $\text{bH}_{\text{im}}$ ), 7.00 (2H, s,  $\text{aH}_{\text{im}}$ ), 5.23 (4H, s,  $\alpha\text{-CH}_2$ ); ESI-MS:  $m/z$  238 ( $[\text{M}+\text{H}]^+$ ).  
Compound **1d**: yield 71%; elemental analysis calcd (%) for  $\text{C}_{20}\text{H}_{18}\text{N}_4$ : C, 76.41; H, 5.77; N, 17.82; found: C, 76.36; H, 5.77; N, 17.82;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 7.58 (2H, s,  $\text{cH}_{\text{im}}$ ), 7.54 (4H, d,  $J=7.5$  Hz,  $2\text{H}_{\text{bz}}$ ), 7.23 (4H, d,  $J=7.5$  Hz,  $1\text{H}_{\text{bz}}$ ), 7.11 (2H, s,  $\text{bH}_{\text{im}}$ ), 6.93 (2H, s,  $\text{aH}_{\text{im}}$ ), 5.16 (4H, s,  $\alpha\text{-CH}_2$ ); ESI-MS:  $m/z$  315 ( $[\text{M}+\text{H}]^+$ ).  
 $\text{H}_{\text{im}}$  refers to imidazole protons and  $\text{H}_{\text{bz}}$  refers to benzene ring protons.
- General procedure for the preparation of pseudorotaxane **2a**, **2b**, **2c** and **2d**: a solution of **1a**, **1b**, **1c** and **1d**, respectively (1 mmol) in methanol (5 mL) was added to an aqueous solution (100 mL) of  $\beta$ -CD (1 mmol) at 40 °C water-bath. The mixture was filtered after stirring for 2 h at room temperature and the filtrate was allowed to stand at ambient temperature for several weeks. Colourless crystals were collected and were dried in vacuo at the presence of  $\text{P}_2\text{O}_5$  prior to the  $^1\text{H}$  NMR and element analysis. Yield 40%. Compound **2a**: elemental analysis

calcd (%) for  $C_{100}H_{166}N_4O_{70}$ : C, 47.21; H, 6.58; N, 2.20; found: C, 47.30; H, 6.64; N, 2.16;  $^1H$  NMR (500 MHz,  $D_2O$ , DSS): for  $\beta$ -CD,  $\delta$  5.06 (14H, d,  $J=3.3$  Hz, H1), 3.87 (14H, t,  $J=9.5$  Hz, H3), 3.83 (28H, s, H6), 3.70 (14H, d,  $J=9.5$  Hz, H5), 3.65 (14H, dd,  $J_{12}=3.3$  Hz,  $J_{23}=9.5$  Hz, H2), 3.59 (14H, t,  $J=9.5$  Hz, H4); for guest, 7.70 (2H, s,  $cH_{im}$ ), 7.15 (2H, s,  $bH_{im}$ ), 7.08 (2H, s,  $aH_{im}$ ), 4.06 (4H, t,  $J=6.9$  Hz,  $\alpha$ -CH<sub>2</sub>), 1.75 (4H, br,  $\beta$ -CH<sub>2</sub>), 1.15 (12H, br,  $\gamma$ - $\epsilon$ -(CH<sub>2</sub>)<sub>6</sub>); ESI-MS:  $m/z$  1227 ( $[M+2H]^{2+}/2$ ).

Compound **2b**: elemental analysis calcd (%) for  $C_{54}H_{88}N_4O_{35}$ : C, 47.93; H, 6.55; N, 4.14; found: C, 47.88; H, 6.56; N, 4.07;  $^1H$  NMR (500 MHz,  $D_2O$ , DSS): for  $\beta$ -CD,  $\delta$  5.06 (7H, d,  $J=3.3$  Hz, H1), 3.87 (7H, t,  $J=9.5$  Hz, H3), 3.84 (14H, s, H6), 3.65 (7H, dd,  $J_{12}=3.3$  Hz,  $J_{23}=9.5$  Hz, H2), 3.63 (7H, H5), 3.58 (7H, t,  $J=9.5$  Hz, H4); for guest, 7.59 (2H, s,  $cH_{im}$ ), 7.07 (2H, s,  $bH_{im}$ ), 7.05 (2H, s,  $aH_{im}$ ), 4.01 (4H, t,  $J=6.3$  Hz,  $\alpha$ -CH<sub>2</sub>), 1.72 (4H, br,  $\beta$ -CH<sub>2</sub>), 1.16 (4H, br,  $\gamma$ -CH<sub>2</sub>); ESI-MS:  $m/z$  677 ( $[M+2H]^{2+}/2$ ).

Compound **2c**: elemental analysis calcd (%) for  $C_{56}H_{84}N_4O_{35}$ : C, 48.98; H, 6.17; N, 4.08; found: C, 48.86; H, 6.36; N, 4.01;  $^1H$  NMR (500 MHz,  $D_2O$ , DSS): for  $\beta$ -CD,  $\delta$  5.04 (7H, d,  $J=3.3$  Hz, H1), 3.79 (7H, t,  $J=9.5$  Hz, H3), 3.74 (14H, s, H6), 3.63 (7H, dd,  $J_{12}=3.3$  Hz,  $J_{23}=9.5$  Hz, H2), 3.57 (7H, t,  $J=9.5$  Hz, H4), 3.45 (7H, d,  $J=9.5$  Hz, H5); for guest, 7.75 (2H, s,  $cH_{im}$ ), 7.16 (4H, s,  $H_{bz}$ ), 7.11 (2H, s,  $bH_{im}$ ), 7.06 (2H, s,  $aH_{im}$ ), 5.25 (4H, s,  $\alpha$ -CH<sub>2</sub>); ESI-MS:  $m/z$  687 ( $[M+2H]^{+}/2$ ).

Compound **2d**: elemental analysis calcd (%) for  $C_{104}H_{158}N_4O_{70}$ : C, 48.33; H, 6.16; N, 2.17; found: C, 48.27; H, 6.18; N, 2.27;  $^1H$  NMR (500 MHz,  $D_2O$ , DSS): for  $\beta$ -CD,  $\delta$  5.04 (14H, d,  $J=3.3$  Hz, H1), 3.82 (14H, t,  $J=9.5$  Hz, H3), 3.76 (28H, s, H6), 3.64 (14H, d,  $J=9.5$  Hz, H5), 3.63 (14H, dd,  $J_{12}=3.3$  Hz,  $J_{23}=9.5$  Hz, H2), 3.57 (14H, t,  $J=9.5$  Hz, H4); for guest, 7.87 (2H, s,  $cH_{im}$ ), 7.43 (4H, d,  $J=7.5$  Hz,  $2H_{bz}$ ), 7.35 (4H, d,  $J=7.5$  Hz,  $1H_{bz}$ ), 7.15 (2H, s,  $bH_{im}$ ), 7.08 (2H, s,  $aH_{im}$ ), 5.34 (4H, s,  $\alpha$ -CH<sub>2</sub>); ESI-MS:  $m/z$  1293 ( $[M+2H]^{+}/2$ ).

- Crystallographic data of **2a**·23H<sub>2</sub>O:  $C_{100}H_{212}N_4O_{93}$ , Mr=2958.71, triclinic, space group  $P1$ ,  $a=15.435(3)$ ,  $b=15.466(2)$ ,  $c=17.949(3)$  Å,  $\alpha=99.310(10)$ ,  $\beta=113.160(10)$ ,  $\gamma=103.110(10)^\circ$ ,  $V=3683.0(12)$  Å<sup>3</sup>,  $Z=1$ ,  $\rho_{calcd}=1.313$  g/cm<sup>-3</sup>,  $\mu(Mo_{K\alpha})=0.118$  mm<sup>-1</sup>,  $F(000)=1538$ . Intensities of 35665 reflections were measured with a Bruker Smart Apex CCD diffractometer at 293 K ( $\lambda(Mo_{K\alpha})=0.71073$  Å,  $2\theta < 56^\circ$ ), and 26,613 independent reflections ( $R_{int}=0.026$ ) were used in further refinement. The refinement converged to  $wR_2=0.1561$  and GOF=1.073 for all independent reflections ( $R_1=0.0547$  was calculated against  $F^2$  for 22,826 observed reflections with  $I > 2\sigma(I)$ ). CCDC 217565 contains the supplementary crystallographic data for this paper. This data can be obtained online free of charge (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336-033; or deposit@ccdc.cam.ac.uk). Crystallographic data of **2c**·8H<sub>2</sub>O:  $C_{56}H_{100}N_4O_{43}$ , Mr=1517.39, monoclinic, space group  $C2$ ,  $a=19.101(2)$ ,  $b=24.032(2)$ ,  $c=32.580(3)$  Å,  $\alpha=90$ ,  $\beta=93.763(12)$ ,  $\gamma=90^\circ$ ,  $V=14,923(2)$  Å<sup>3</sup>,  $Z=8$ ,  $\rho_{calcd}=1.329$  g/cm<sup>-3</sup>,  $\mu(Mo_{K\alpha})=0.116$  mm<sup>-1</sup>,  $F(000)=6464$ . Intensities of 40,378 reflections were measured with a Bruker Smart Apex CCD diffractometer at 293 K ( $\lambda(Mo_{K\alpha})=0.71073$  Å,  $2\theta < 56^\circ$ ), and 27,848 independent reflections ( $R_{int}=0.016$ ) were used in further refinement. The refinement converged to  $wR_2=0.1915$  and GOF=1.073 for all independent reflections ( $R_1=0.0605$  was calculated against  $F^2$  for 17,838 observed reflections with  $I > 2\sigma(I)$ ). CCDC 217566 contains the supplementary crystallographic data for this paper.
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