Acid/base controllable molecular switch based on a neutral phenanthroline guest penetrated pseudorotaxane†

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A ditopic macrocycle with a bisamide and a half dibenzo-crown ether component has been newly synthesized and its complexation behavior toward neutral phenanthroline derivatives is reported. The macrocycle can bind phenanthroline derivatives very strongly by hydrogen bonding and π-electron interaction, yielding pseudorotaxane structures. The inclusion complexes show a pH controllable reversible threading–dethreading molecular switching system.

Introduction

Various mechanically interlocked molecules such as rotaxanes and catenanes have been prepared towards future realization of molecular machines.[1] Moreover, intense recent research has been focused on technological applications of exploiting rotaxanes and catenanes as molecular sensors[2,3] and catalysts.[4] For example, Hiratani *et al.*[3] reported that three-dimensional cavities between axles and wheels in the rotaxanes are capable of binding particular alkali metal cations and one enantiomer of an aminoalcohol selectively.

Crown ethers and other macrocycles incorporating functional moieties with hydrogen bonding, ligation, and π–π stacking have been widely used in preparing rotaxanes as a ring component in order to accommodate secondary dialkylammonium salts,[5] paraquat derivatives,[6] amide esters,[7] and aromatic amine derivatives such as phenanthroline derivatives[8] and 2,2′-bipyridinium salts[9] as axle components. Nonetheless, investigation of new rotaxanes with respect to both components remains an important challenge. It is well-established that a strategy for the synthesis of rotaxanes is mainly interdigitation *via* π–π stacking,[6,9] hydrogen bonding[5,7,9] and ion-templated complexation.[8,10,11] However, it would seem to be restrictive that cationic hydrogen-bonded and ion-templated rotaxanes are applied for a molecular sensor,[9,12] presumably due to the complicated procedures on neutralizing the cationic species and removing the template ions.[13] On the other hand, there have also been extensive studies on rotaxane synthesis utilizing neutral axle components.[1,2,14] However, it should be desirable to study different types of threading of neutral axle components through macrocycles to synthesize interlocked molecules in order to apply for the molecular sensor and the catalyst.

Herein, we describe the formation of the inclusion complexes of heterocycles such as phenanthroline derivatives **2a** and **2b**, and a bipyridine **3**, with a ditopic macrocycle **1** bearing a bisamide and a half dibenzo-crown ether component. The formation of the complexes was characterized by ^{1}H NMR spectral changes and ^{1}H NMR spectroscopic titration experiments. The notable features of these assembled molecules include high stabilities and selectivities towards heterocycles, as well as pH controllable molecular switching abilities.

Results and discussion

Synthesis

Inspired by previously reported macrocycles,[10,11,15] the ditopic macrocycle **1** (Fig. 1) was designed to provide two amide hydrogen bond donating groups towards the aromatic amines as axle components. In addition, the π-electron-rich aromatic rings of the macrocycle **1** would also stabilize the π-electron-poor aromatic rings of neutral phenanthroline derivatives through the cooperative effects of π–π stacking. The macrocycle **1** was newly synthesized with the use of a simple three-step approach as shown in Scheme 1. The Williamson reaction between 4-cyanophenol and tri(ethylene glycol) ditosylate under basic conditions afforded the dinitrile **2** in 52% yield, followed by reduction to give the diamine **3** in 72% yield. Intermolecular [1+1] macrocyclization reaction between the diamine **3** and the isophthaloyl dichloride gave the

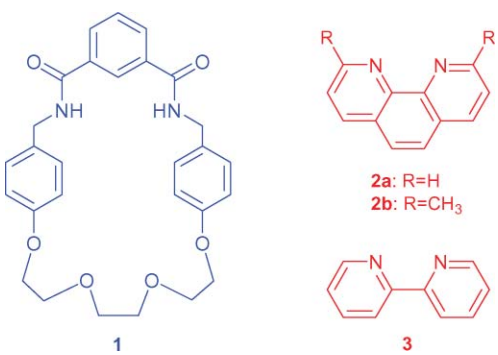

Fig. 1 Structure of the wheel and the axles for the [2]pseudorotaxanes.

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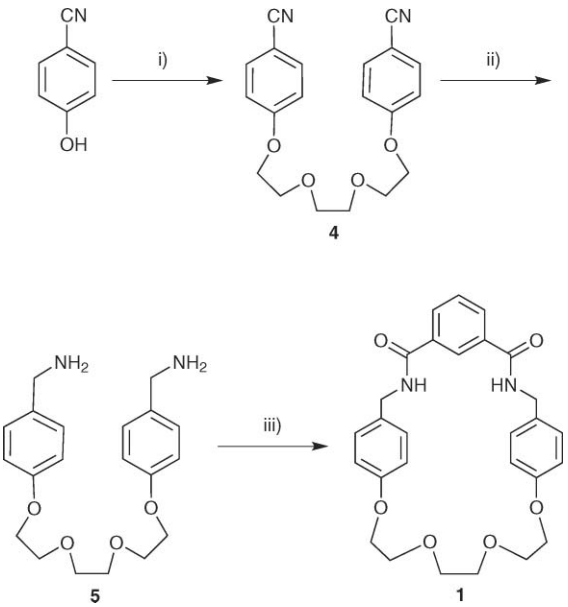
† Electronic supplementary information (ESI) available: Fig. S1: Partial ^{1}H NMR spectra of an equimolar mixture (19 mM) of **1** and **2b**; Fig. S2: Partial ^{1}H NMR spectra an equimolar mixture (19 mM) of **1** and **3**; Fig. S3–S7: ^{1}H NMR titration curves for **2a**, **2b** and **3** with **1**; Table S1: Association constants thermodynamic parameters for complexes of macrocycle **1** with **2a**, **2b** and **3**; Fig. S8: ^{1}H NMR spectra of an equimolar mixture (19 mM) of **1** and protonated phenanthroline (**2a**); Fig. S9: Variable temperature ^{1}H NMR spectral changes for **2a** with **1**. See DOI: 10.1039/b926010b



Scheme 1 Bisamide macrocycle synthesis. *Reagents and conditions*: (i) tri(ethylene glycol) ditosylate, K_2CO_3, CH_3CN, reflux, 44 h, 52%; (ii) $LiAlH_4$, THF, reflux, 4 h, 72%; (iii) isophthaloyl dichloride, Et_3N, THF, 14 h, 40%.

desired macrocycle **1** in 40% yield. The heterocycles **2a**, **2b**, and **3** as axle components are commercially available.

^{1}H NMR binding studies

The binding behavior of macrocycle **1** with phenanthroline derivatives was examined by the addition of 1 molar equivalent of amine to a solution of the macrocycle in *d*-chloroform. The ^{1}H NMR spectra of macrocycle **1**, phenanthroline (**2a**), and an equimolar mixture of **1** and **2a** (**1**⊃**2a**) in *d*-chloroform are shown in Fig. 2. Upon addition of phenanthroline (**2a**), significant downfield shifts in the macrocyclic amide (d) and the isophthalic aromatic protons (a, b, and c) were observed, indicating the formation of hydrogen bonding between the amide hydrogens of the macrocycle **1** and the nitrogen atoms of the phenanthroline (**2a**). In the spectrum of the complex **1**⊃**2a**, the upfield shifts in the signals of the benzylic phenyl protons (f and g) of the macrocyle **1** imply the existence of interactions between the electronically complementary aromatic rings of the macrocycle **1** and phenanthroline (**2a**). Therefore, the ^{1}H NMR spectrum of an equimolar mixture (19 mM) of the macrocycle **1** and phenanthroline (**2a**) in *d*-chloroform suggests the formation of the pseudorotaxane **1**⊃**2a** based on various supramolecular interactions. Other neutral heterocycles, 2,9-dimethylphenanthroline (**2b**) and 2,2′-bipyridine (**3**), also showed characteristic chemical shift changes similar to those of **2a** upon addition of an equimolar amount of the macrocycle **1** (see the ESI†). Thus, it is assumed that the macrocycle **1** binds to these heterocycles to form a [2]pseudorotaxane.

Job plots[16] (Fig. 3) based on ^{1}H NMR spectroscopic data measured in *d*-chloroform demonstrated that the complexes of **1**⊃**2a** and **1**⊃**2b** were of 1 : 1 stoichiometry in solution. The binding properties of the macrocycle **1** were estimated by quantitative ^{1}H NMR titration experiments of the macrocycle **1** with phenanthroline (**2a**), 2,9-dimethylphenanthroline (**2b**) and

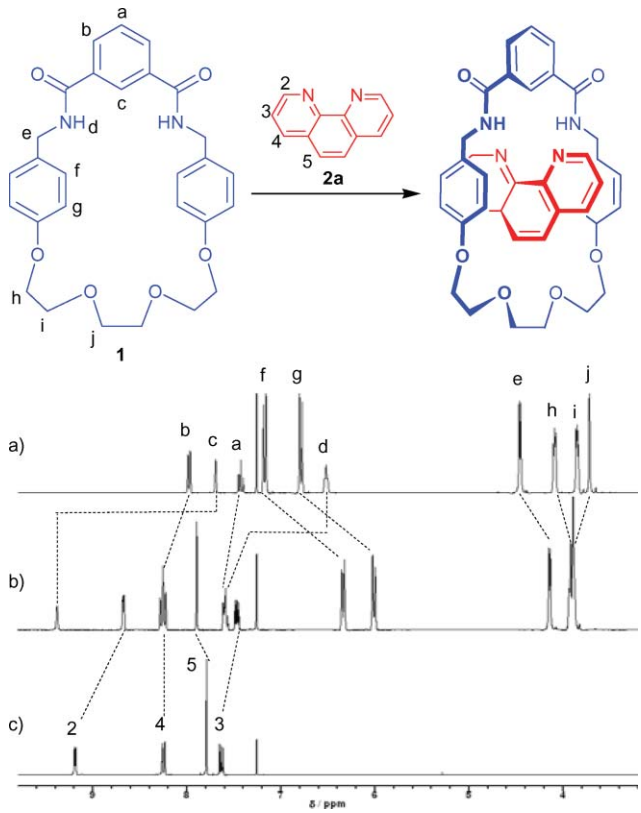


Fig. 2 Partial ^{1}H NMR spectra (300 MHz, $CDCl_3$, 293 K) of (a) **1**, (b) an equimolar mixture (19 mM) of **1** and **2a**, and (c) **2a**.

bipyridine (**3**) in *d*-chloroform and the ^{1}H NMR shift changes of the macrocyclic isophthalic aromatic proton (c), amide (d), and benzylic phenyl protons (f, g) were monitored (Fig. S3–S7, ESI†).[17] The association constants (K_a) for the complexation are shown in Table 1. Monitoring the downfield shift in protons (c and d) and the upfield shift in protons (f and g) upon amine addition allowed association constants to be determined. Due to very strong binding of 2,9-dimethylphenanthroline (**2b**) towards the macrocycle **1** in *d*-chloroform, 10% *d*-methanol in *d*-chloroform was used for comparison about the association constants (Fig. S7, ESI†). It is noteworthy that there is a marked, about 6-fold, increase in

Table 1 Association constants[a] for complexes of macrocycle **1** with phenanthroline derivatives **2a** and **2b**, and bipyridine (**3**) as determined by ^{1}H NMR titrations in *d*-chloroform at 293 K

	K_a/M^{-1}			
Guest	H_c[b]	H_d[b]	H_f[b]	H_g[b]
2a	470 ± 40	430 ± 40	470 ± 30	450 ± 45
2b	2580 ± 300	3130 ± 240	2480 ± 450	2420 ± 370
3	[c]	[c]	[c]	[c]

[a] Determined by four kinds of protons of macrocycle **1** based on the chemical shift change by the titration experiments followed by non-linear least square data treatment method reported by Hirose.[17] The starting concentration of the host [**1**] = 22 mM for **2a** and **3**, and [**1**] = 2.0 mM for **2b** were used for the titration. [b] H_c denotes proton (c), H_d denotes proton (d), H_f denotes proton (f), and H_g denotes proton (g), which were used for the calculations of K_a, respectively. [c] Shifts were too small to determine the binding constant; association constants are estimated at less than 20 M^{-1}.

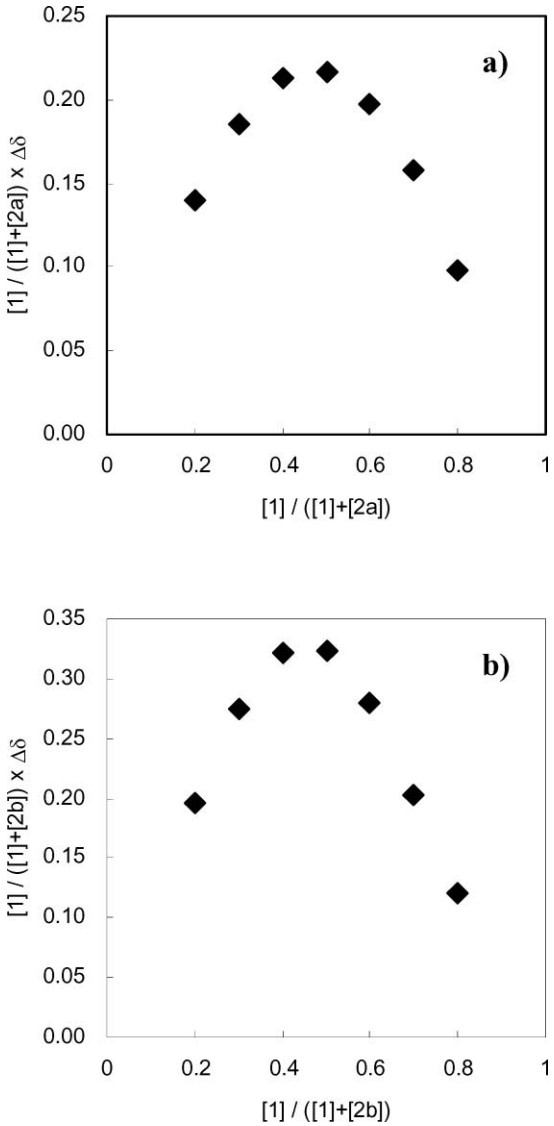


Fig. 3 Job plot showing the 1 : 1 stoichiometry of the complex between (a) **1** and **2a** in $CDCl_3$ and (b) **1** and **2b** in $CDCl_3$: [**1**] + [**2a**] = 4.0 mM; [**1**] + [**2b**] = 3.0 mM; $\Delta\delta$ = chemical shift change for proton (c) of **1**.

the macrocycle's binding affinity for 2,9-dimethylphenanthroline (**2b**) over unsubstituted phenanthroline (**2a**). Because the phenanthrolyl nitrogen atom of 2,9-dimethylphenanthroline (**2b**) is more basic than that of phenanthroline (**2a**) due to its high electron density resulting from the electron-donating methyl groups attached to the phenanthroline ring, it is likely that the binding affinity for 2,9-dimethylphenanthroline (**2b**) is higher than that for unsubstituted phenanthroline (**2a**). Interestingly, with the macrocycle **1**, bipyridine (**3**) is bound the most weakly of three aromatic amines. This highlights the cooperative recognition of phenanthroline derivatives by favorable hydrogen bond acceptor ability. In addition, the macrocycle **1** provides an optimal size and shape complementarity to these phenanthroline derivatives.

Acid–base controlled switching studies

The molecular switching properties of the pseudorotaxanes **1**⊃**2a** and **1**⊃**2b** by pH-controlled stimuli were investigated by adding acid and base to the pseudorotaxanes in *d*-chloroform. When 3 drops of trifluoroacetic acid as an acid stimulus were added into an equimolar mixture (19 mM) of the macrocycle **1** and phenanthroline (**2a**) in *d*-chloroform, the chemical shifts corresponding to benzylic phenyl protons (f and g) and to tri(ethylene glycol) ether protons (h, i, j) of the macrocycle **1** returned to almost their uncomplexed chemical shifts as shown in Fig. 4 (a) and (c), indicating that the protonated salt of **2a** was completely dethreaded from the macrocycle **1**.[18] These signal changes imply that the protonated salt of **2a** is located outside the macrocycle **1** and not associated with the ether oxygen atoms in the tri(ethylene glycol) moiety by hydrogen bonds.[9,19] After 4 drops of triethylamine as a base stimulus were added to this solution, neutral phenanthroline (**2a**) was bound back to the macrocycle **1**, since large upfield changes of the chemical shifts corresponding to benzylic phenyl protons (f and g) of the macrocycle **1** were observed again, as shown in Fig. 4 (b), (c) and (d) (see the ESI† about the same result for **1**⊃**2b**). Therefore, the threading–dethreading switching phenomena of the pseudorotaxanes between bisamide macrocycle **1** and neutral aromatic amines **2a** and **2b** can be controlled reversibly by changing the solution pH, due to the reversible protonation of the phenanthroline derivatives **2a** and **2b**.

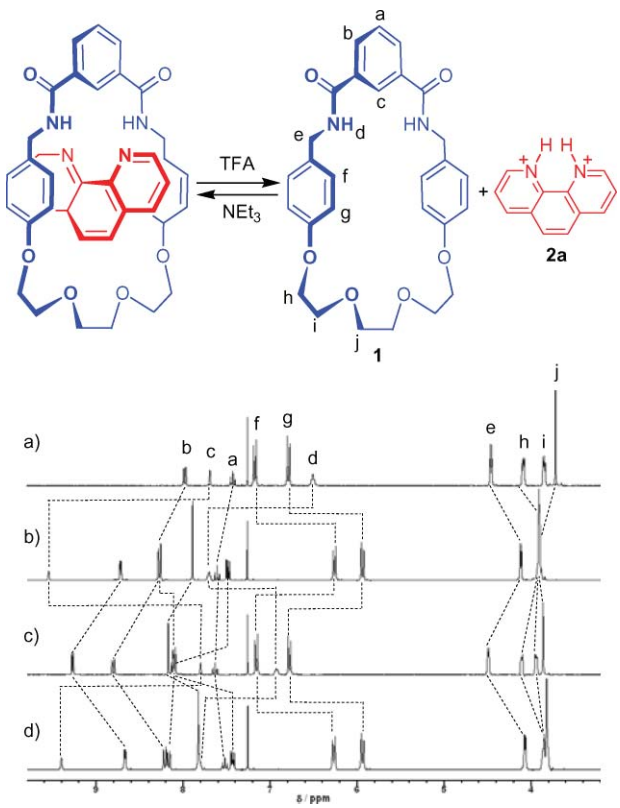


Fig. 4 Partial ^{1}H NMR spectra (300 MHz, $CDCl_3$, 293 K) of (a) **1**, (b) an equimolar mixture (19 mM) of **1** and **2a**, (c) the mixture obtained after adding trifluoroacetic acid (3 drops) to the solution in (b), and (d) the mixture obtained after adding triethylamine (4 drops) to the solution in (c).

NOE experiments are effective for useful information on further evidence of the threading–dethreading switching process. In the NOESY spectra of the pseudorotaxane **1**⊃**2a** in *d*-chloroform as shown in Fig. 5(a), clear correlations were observed between

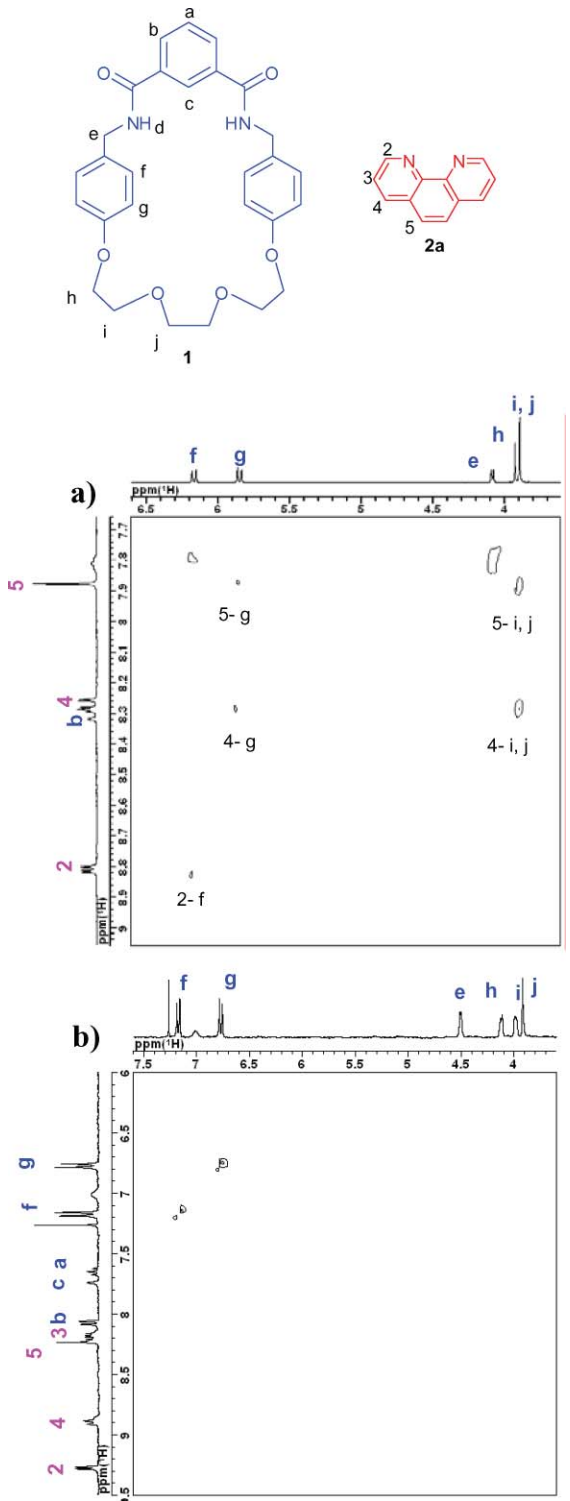


Fig. 5 Partial NOESY spectra (300 MHz, $CDCl_3$, 293 K) of an equimolar mixture (19 mM) of **1** and **2a** (a) before, and (b) after the addition of trifluoroacetic acid (3 drops).

the benzylic phenyl protons (f) of the macrocycle **1** and proton (2) of phenanthroline (**2a**), benzylic phenyl protons (g) of the macrocycle **1** and protons (4, 5) of phenanthroline (**2a**), benzylic phenyl protons (f) of the macrocycle **1** and protons (2) of phenanthroline (**2a**), and the oxyethylene protons (h, i, j) of the macrocycle **1** and protons (4, 5) of phenanthroline (**2a**), confirming that phenanthroline (**2a**) was incorporated within the macrocycle **1** in *d*-chloroform. When 3 drops of trifluoroacetic acid as an acid stimulus were added into the pseudorotaxane **1⊃2a** in *d*-chloroform, no distinct cross peaks were observed between the protons (f, g, h, i, j) of the macrocycle **1** and the protons (2, 4, 5) of phenanthroline (**2a**) in the NOESY spectra as shown in Fig. 5(b). These results clearly show the protonated phenanthroline is located outside the macrocycle **1**. In fact, when protonated phenanthroline (**2a**) was added into the macrocycle **1** in *d*-chloroform, ^{1}H NMR signals of oxyethylene protons (h, i, j) of the macrocycle **1** remained in the same positions as those of uncomplexed macrocycle **1** (Fig. S8, ESI†).

Conclusions

The design and synthesis of a ditopic macrocycle having a bisamide and a half dibenzo-crown ether component has been achieved. This ditopic macrocyclic structure has been shown to exhibit complexation behavior towards neutral aromatic amines by hydrogen bonding and π-electron interaction. As a result, we have developed a simple synthetic strategy for a pseudorotaxane by using phenanthroline derivatives without ion-templates and have proved the pseudorotaxane to be a pH-controllable reversible threading–dethreading molecular switch. We are currently continuing the construction of rotaxanes providing shuttling[1] and rotating[20] movements for molecular sensing applications utilizing the oxyethylene moieties as a binding site toward neutral or ionic sensing targets.

Experimental

All chemicals were of commercially-available reagent grade, and were used without further purification. THF was dried over sodium benzophenone ketyl and distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded with a Varian Mercury 300 spectrometer for solution in $CDCl_3$ and DMSO-d_6 with $SiMe_4$ as an internal standard. Mass spectra were measured on a JEOL JMS-DX-303 mass spectrometer. Elemental analyses were carried out with a Yanaco CHN-Corder MT-5 analyzer.

1,10-Bis(*p*-cyanophenyl)-1,4,7,10-tetraoxadecane (4)[21]

4-Cyanophenol (20.0 g, 0.168 mol), tri(ethylene glycol) ditosylate (30.8 g, 0.0672 mol) and potassium carbonate (69.7 g, 0.504 mol) were refluxed in acetonitrile (300 ml) for 44 h. After cooling to room temperature, the mixture was filtered and concentrated *in vacuo* to give a white solid, which was dissolved in CH_2Cl_2 (300 ml) and the solution was filtered three times with Celite. The organic layer was dried over anhydrous magnesium sulfate, filtered, and the solvent was evaporated to yield the crude product **4** as a white solid, which was subjected to column chromatography over silica gel (eluent: 50 : 50 hexane–ethyl acetate) to give the pure product **4** as a white solid (11.6 g, 52%). M.p. 107-108 °C (119 °C[19]); ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 3.75 (s, 4H), 3.88 (t, $J = 4.8$ Hz, 4H), 4.17 (t, $J = 4.8$ Hz, 4H), 6.96 (d, $J = 9.0$ Hz, 4H), 7.58 (d, $J = 9.0$ Hz, 4H); elemental analysis calcd (%) for $C_{20}H_{20}N_2O_4$: C 68.17, H 5.72; found: C 67.85, H 5.68.

1,10-Bis[*p*-(aminomethyl)phenyl]-1,4,7,10-tetraoxadecane (5)

To a suspension of $LiAlH_4$ (4.56 g, 0.120 mol) in THF (100 ml), a solution of **4** (5.48 g, 0.0156 mol) in THF (170 ml) was added dropwise over a period of 40 min at 0 °C. The resulting mixture was stirred for 30 min at room temperature and then refluxed for 4 h. After the mixture was cooled to room temperature, water (3 ml), 15% aqueous NaOH (3 ml) and water (8 ml) were added by turns. The mixture was stirred for 30 min and filtered. Water (250 ml) was added to the mixture and then it was extracted with CH_2Cl_2 (3 × 250 ml). The organic layer was dried over anhydrous magnesium sulfate, filtered, and the solvent was evaporated to yield the crude product **5** as a white solid (4.07 g, 72%). M.p. 131-135 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 3.76 (s, 4H), 3.79 (s, 4H), 3.86 (t, J = 4.9 Hz, 4H), 4.12 (t, J = 4.9 Hz, 4H) 6.88 (d, J = 8.7 Hz, 4H), 7.21 (d, J = 8.7 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 45.9, 67.5, 69.8, 70.8, 114.7, 128.2, 135.8, 157.7; elemental analysis calcd (%) for $C_{20}H_{28}N_2O_4$: C 66.64, H 7.83; found: C 66.62, H 7.80.

1,7-Diaza-13,16,19,22-tetraoxa-2,6-dioxo-3,5,9,12,23,26-tribenzocycloheptacosane (1)

5 (1.02 g, 2.83 × 10^{-3} mol) was dissolved in THF (140 ml). Separately, isophthaloyl dichloride (0.580 g, 2.86 × 10^{-3} mol) was dissolved in dry THF (40 ml). A three necked round-bottomed flask (500 ml) was charged with THF (150 ml) and NEt_3 (2 ml). *Via* two pressure-equalizing dropping funnels, both solutions were added simultaneously dropwise to the flask with stirring over a period of 2 h at room temperature. The reaction mixture was stirred under argon atmosphere overnight at room temperature. The solvent was evaporated under reduced pressure to leave a pale yellow solid. The residue was purified by silica gel chromatography (eluent: $CHCl_3$) to give the pure product **1** as a white solid (0.550 g, 40%). An analytical sample of **1** was obtained after recrystallization from dioxane–toluene. M.p.: 228-233 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 3.72 (s, 4H), 3.85 (t, J = 4.3 Hz, 4H), 4.10 (t, J = 4.3 Hz, 4H), 4.46 (d, J = 5.1 Hz, 4H) 6.51 (brs, 2H), 6.80 (d, J = 8.6 Hz, 4H), 7.18 (d, J = 8.6 Hz, 4H), 7.45 (t, J = 7.8 Hz, 1H), 7.69 (s, 1H), 7.99 (d, J = 7.8 Hz, 2H); ^{1}H-NMR (DMSO-d_6, 300 MHz): δ (ppm) 3.55 (s, 4H), 3.67-3.71 (m, 4H), 4.06-4.09 (m, 4H), 4.37 (d, J = 5.2 Hz, 4H), 6.88 (d, J = 8.4 Hz, 4H), 7.25 (d, J = 8.4 Hz, 4H), 7.56 (t, J = 7.8 Hz, 1H), 7.88 (d, J = 7.8 Hz, 2H), 8.01 (s, 1H), 8.61 (t, J = 5.2 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 42.7, 67.4, 68.9, 70.2, 114.6, 125.8, 128.9, 129.6, 130.2, 131.1, 135.2, 157.8, 166.4; HRMS(FAB): m/z: for $C_{28}H_{30}N_2O_6$: calcd: 490.2104; found: 490.2107; elemental analysis calcd (%) for $C_{28}H_{30}N_2O_6$: C 68.56, H 6.16; found: C 68.31, H 6.17.

Determination of the association constants (K_a)

All titration results were acquired by a Varian 300 MHz NMR spectrometer and performed with the starting concentration of host **1** at 22 mM for **2a** and **3**, and 2.0 mM for **2b**. Appropriate aliquots of guests **2a** and **3** at 890 mM, and **2b** at 20 mM solutions with a microsyringe. The protons (c, d, f, and g) for the host **1** were followed during the course of the titration. The complexation equilibrium was fast on the NMR time scale and gave signals at weight averaged chemical shifts of the free and complexed host. The association constants (K_a) for the complexation were obtained based on the chemical shift change by the titration experiment followed by non-linear least-square data treatment method with 95% confidence interval applied by Student's t-distribution reported by Hirose.[17] The volume change for the titrated solutions was properly accounted for in the Hirose's method. The limiting chemical shifts, Δ_0, which mean the difference in δ values for the protons of the host **1** in the uncomplexed and fully complexed species, and the standard deviations as the curve fitting errors for the association constants were determined by SOLVSTAT.[22]

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