Supporting Information

Polyaromatic Molecular Tubes with a Subnanometer Pore and the Guest-Induced Emission Enhancement Behavior

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Materials and methods

Solvents and reagents: TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., KANTO CHEMICAL CO., INC., Sigma-Aldrich Co., and Cambridge Isotope Laboratories, Inc. 2,3,6,7-Tetramethoxy-9,10-anthraquinone\(^{(1)}\) was synthesized according to previously published procedures.

References:

Synthesis of 2a

1,3-Dibromo-5-(methoxymethoxy)benzene (0.943 g, 3.04 mmol) and dry THF (50 mL) were added to a 2-necked 200 mL glass flask filled with N₂. A hexane solution (2.65 M) of n-butyllithium (1.0 mL, 2.7 mmol) was added dropwise to the flask at –80 ºC under N₂. After the mixture was stirred at –80 ºC for 1 h, a dry THF solution (25 mL) of 9,10-anthraquinone (0.211 g, 1.01 mmol) was added to the solution. The resultant mixture was further stirred at –80 ºC for 1 h and then warmed to r.t. for 12 h. After the obtained solution was concentrated under reduced pressure, acetic acid (20 mL), NaH₂PO₄•H₂O (0.322 g, 3.04 mmol), and NaI (0.456 g, 3.04 mmol) were added to the solids. The mixture was stirred at 70 ºC for 12 h. The resultant solution was poured into water and then the products were extracted with CH₂Cl₂. The crude product was purified by silica-gel column chromatography (hexane:ethyl acetate = 10:1) to give 2a as a white solid (0.601 g, 9.44 mmol, 93% yield).

¹H NMR (500 MHz, CDCl₃, r.t.): δ 7.68 (dd, J = 3.5 Hz, 4H), 7.37 (dd, J = 3.3 Hz, 4H), 7.30 (t, J = 2 Hz, 2H), 7.22 (t, J = 1.5 Hz, 2H), 6.99-6.99 (m, 2H), 4.17 (t, J = 4.5 Hz, 4H), 3.77 (t, J = 4.5 Hz, 4H), 3.46 (s, 6H). ¹³C NMR (125 MHz, CDCl₃, r.t.): δ 159.6 (C₉), 141.9 (C₉), 135.8 (C₉), 129.6 (C₉), 126.9 (CH), 126.8 (CH), 123.0 (C₉), 117.4 (CH), 116.6 (CH), 71.0 (CH₂), 67.9 (CH₃), 59.5 (CH₂). FT-IR (KBr, cm⁻¹): 3064, 2981, 2927, 2876, 2815, 2360, 2343, 1590, 1571, 1424, 1381, 1365, 1259, 1236, 1180, 1126, 1060, 1032, 934, 855, 777, 689, 669. MALDI-TOF MS (dithranol): m/z Calcd. for C₃₂H₂₈Br₂O₄ 636.38, Found 636.13 [M⁺]. HR MS (ESI): m/z Calcd. for C₃₂H₂₈O₄Br₂ [M + Na]⁺ 659.0229, Found 659.0230.
Figure S1. $^1$H NMR spectrum (500 MHz, CDCl$_3$, r.t.) of 2a.

Figure S2. $^{13}$C NMR spectrum (125 MHz, CDCl$_3$, r.t.) of 2a.
Figure S3. HSQC spectrum (400 MHz, CDCl₃, r.t.) of 2a.

Figure S4. MALDI-TOF MS spectrum (dithranol) of 2a.
Compound **2a** (0.448 g, 0.703 mmol), Ni(cod)$_2$ (0.287 g, 1.04 mmol), 2,2’-bipyridyl (0.179 g, 1.14 mmol), and dry DMF (300 mL) were added to a 2-necked 500 mL glass flask filled with N$_2$ and then the mixture was stirred at 90 ºC for 24 h. After the reaction was quenched with H$_2$O, the mixture was concentrated under reduced pressure. The obtained residue was extracted with CH$_2$Cl$_2$. The crude product was purified by silica-gel column chromatography (CHCl$_3$:acetone = 10:1) and GPC to give **1a** as a yellow solid (0.050 g, 0.035 mmol, 15% yield).

$^1$H NMR (500 MHz, CDCl$_3$, r.t.): δ 7.64 (dd, $J = 3.3$ Hz, 4H), 7.61 (s, 2H), 7.21 (dd, $J = 3.3$ Hz, 4H), 7.17 (s, 2H), 7.05 (s, 2H), 4.28 (t, $J = 4.5$ Hz, 4H), 3.85 (t, $J = 4.5$ Hz, 4H), 3.52 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$, r.t.): δ 159.4 (C$q$), 140.9 (C$q$), 140.6 (C$q$), 136.5 (C$q$), 129.5 (C$q$), 126.9(CH), 125.1 (CH), 122.5 (CH), 116.5 (CH), 112.0 (CH), 71.3 (CH$_2$), 67.7 (CH$_2$), 59.5 (CH$_3$). FT-IR (KBr, cm$^{-1}$): 3061, 2923, 2874, 2359, 2341, 1585, 1390, 1365, 1327, 1236, 1126, 1067, 1032, 1029, 845, 768. MALDI-TOF MS (dithranol): $m/z$ Calcd. for C$_{96}$H$_{84}$O$_{12}$ 1428.60, Found 1429.25 [M$^+$]. HR MS (ESI): $m/z$ Calcd. for C$_{96}$H$_{84}$O$_{12}$ [M + Na]$^+$ 1452.5889, Found 1452.5890.
Figure S5. $^1$H NMR spectrum (500 MHz, CDCl$_3$, r.t.) of 1a.

Figure S6. $^{13}$C NMR spectrum (125 MHz, CDCl$_3$, r.t.) of 1a.
Figure S7a. NOESY spectrum (400 MHz, CDCl$_3$, r.t.) of 1a (aliphatic region).

Figure S7b. NOESY spectrum (400 MHz, CDCl$_3$, r.t.) of 1a.
Figure S7c. NOESY spectrum (400 MHz, CDCl₃, r.t.) of 1a (aromatic region).

Figure S8. HSQC spectrum (400 MHz, CDCl₃, r.t.) of 1a.
Synthesis of 2,3,6,7-tetramethoxy-9,10-anthraquinone  

A CH₃CN solution (2.1 mL) of 1,2-dimethoxybenzene (4.244 g, 30.71 mmol) and acetaldehyde (1.708 g, 38.78 mmol) was added dropwise to a 2-necked 200 mL glass flask containing concentrated sulfuric acid (15 mL) at 0 ºC. After the mixture was stirred at 0 ºC for 1 h, water was added to the solution. After the neutralization by a NaOH aqueous solution, the resultant mixture was filtered and washed with water, CH₃OH, and hexane to afford 2,3,6,7-tetramethoxy-9,10-dimethylanthracene as a white solid (2.620 g, 8.027 mmol). The white solid, Na₂Cr₂O₇•2H₂O (6.028 g, 33.56 mmol), and AcOH (40 mL) were added to a 2-necked 200 mL glass flask filled with N₂. After the mixture stirred at 70 ºC for 1 h, water was added to the flask at r.t. The crude product was filtered and washed with water, CH₃OH, and hexane to afford 2,3,6,7-tetramethoxy-9,10-anthraquinone as a yellow solid (1.569 g, 4.778 mmol, 31% yield).
\[ ^1H \text{NMR (500 MHz, CDCl}_3, \text{r.t.): } \delta \ 7.68 \text{ (s, 4H), } 4.07 \text{ (s, 12H). MALDI-TOF MS (dithranol): } m/z \ \text{Calcd. for } C_{18}H_{16}O_6 328.09, \text{ Found } 328.07 [M]^+ \].

**Figure S10.** \(^1H\) NMR spectrum (500 MHz, CDCl\(_3\), r.t.) of 2,3,6,7-tetramethoxy-9,10-anthraquinone.

**Synthesis of 2b**

KH-388, (362, 369, 379, 383)

1,3-Dibromo-5-(methoxymethoxy)benzene (4.097 g, 13.84 mmol) and dry THF (70 mL) were added to a 2-necked 200 mL glass flask filled with N\(_2\). A hexane solution (2.69 M) of \(n\)-butyllithium (5.0 mL, 13 mmol) was then added dropwise to the flask at –80 °C under N\(_2\). After the mixture was stirred at –80 °C for 1 h, a dry THF solution (100 mL) of 2,3,6,7-tetramethoxy-9,10-anthraquinone (2.048 g, 6.237 mmol) was added to the solution. The resultant mixture was further stirred at –80 °C for 1 h and then warmed to r.t. for 12 h. After the obtained solution was concentrated under reduced pressure,
acetic acid (50 mL), NaH2PO2•H2O (0.743 g, 7.01 mmol), and NaI (0.995 g, 6.86 mmol) were added to the solids. The mixture was stirred at 70 °C for 12 h. The resultant solution was poured into water and then the products were extracted with CH2Cl2. The crude product was purified by silica-gel column chromatography (hexane:ethyl acetate = 10:1) to give 2b as a white solid (1.559 g, 2.140 mmol, 34% yield).

1H NMR (500 MHz, CDCl3, r.t.): δ 7.39 (dd, J = 2.0 Hz, 2H), 7.31-7.29 (m, 2H), 7.13-7.11 (m, 2H), 6.83 (s, 14H), 5.23-5.23 (m, 4H), 3.80 (s, 12H), 3.51-3.50 (m, 6H).

13C NMR (125 MHz, CDCl3, r.t.): δ 158.3 (Cq), 149.3 (Cq), 142.7 (Cq), 131.6 (Cq), 127.8 (CH), 125.6 (Cq), 123.1 (Cq), 119.1 (CH), 118.1 (CH), 103.7 (CH), 94.7 (CH3), 56.4 (CH3), 55.8 (CH3). FT-IR (KBr, cm−1): 3441, 3067, 2998, 2953, 2826, 1596, 1563, 1530, 1493, 1464, 1429, 1245, 1206, 1150, 1121, 1080, 1030, 999, 849, 753. MALDI-TOF MS (dithranol): m/z Calcd. for C34H32Br2O8 728.04, Found 727.99 [M]+. E.A.: Calcd. for C34H32O8Br2•(C6H14)0.14: C, 56.51; H, 4.62; Br, 21.58. Found: C, 56.28; H, 4.33; Br, 21.32.

**Figure S11.** 1H NMR spectrum (500 MHz, CDCl3, r.t.) of 2b.
Figure S12. $^{13}$C NMR spectrum (125 MHz, CDCl$_3$, r.t.) of 2b.

Figure S13. HSQC spectrum (400 MHz, CDCl$_3$, r.t.) of 2b.
Synthesis of molecular tube 1b’  

**KH-390, (363, 375, 377, 386, 392)**

Compound **2b** (0.630 g, 0.865 mmol), Ni(cod)$_2$ (0.493 g, 1.79 mmol), 2,2’-bipyridyl (0.064 g, 0.41 mmol), and dry DMF (450 mL) were added to a 2-necked 500 mL glass flask filled with N$_2$ and then the mixture was stirred at 90 ºC for 24 h. After the reaction was quenched with water, the mixture was concentrated under reduced pressure and the residue was extracted with CH$_2$Cl$_2$. The crude product was purified by silica-gel column chromatography (CHCl$_3$:acetone = 10:1) and GPC to give **1b’** as a yellow solid (0.047 g, 0.028 mmol, 10% yield).
$^1$H NMR (500 MHz, CDCl$_3$, r.t.): $\delta$ 7.64 (s, 6H), 7.37 (s, 6H), 7.24 (s, 6H), 6.90 (s, 12H), 5.34 (m, 12H), 3.62 (s, 36H), 3.57 (s, 18H). $^{13}$C NMR (125 MHz, CDCl$_3$, r.t.): $\delta$ 158.2 (C$_q$), 148.9 (C$_q$), 141.6 (C$_q$), 141.4 (C$_q$), 132.5 (C$_q$), 125.6 (C$_q$), 124.1 (CH), 118.2 (CH), 113.9 (CH), 103.9 (CH), 94.8 (CH$_2$), 56.3 (CH$_3$), 55.4 (CH$_3$). FT-IR (KBr, cm$^{-1}$): 3469, 2949, 2828, 1583, 1493, 1433, 1373, 1241, 1204, 1151, 1126, 1083, 1032, 851, 755. MALDI-TOF MS (dithranol): $m/z$ Calcd. for C$_{102}$H$_{96}$O$_{24}$ 1705.63, Found 1705.35 [M]$^+$. E.A.: Calcd. for C$_{102}$H$_{96}$O$_{24}$•(C$_6$H$_{14}$)$_{0.3}$: C, 70.55; H, 5.56. Found: C, 70.22; H, 5.59.

Figure S15. $^1$H NMR spectrum (500 MHz, CDCl$_3$, r.t.) of 1b'.
Figure S16. $^{13}$C NMR spectrum (125 MHz, CDCl$_3$, r.t.) of 1b'.

Figure S17a. NOESY spectrum (400 MHz, CDCl$_3$, r.t.) of 1b'.
Figure S17b. NOESY spectrum (400 MHz, CDCl₃, r.t.) of 1b' (aromatic region).

Figure S18. HSQC spectrum (400 MHz, CDCl₃, r.t.) of 1b'.
Figure S19. MALDI-TOF MS spectrum (dithranol) of 1b'.

Synthesis of molecular tube 1b

KH-385, (378, 380, 395)

Tube 1b' (33.2 mg, 0.0195 mmol), concentrated HCl (3 mL), THF (5 mL), and water (2 mL) were added to a 100 mL glass flask and the mixture was stirred at r.t. for 4 h. After the resultant mixture was concentrated under reduced pressure, the crude product was washed with water and CHCl₃, and then purified by silica-gel column chromatography (hexane:acetone = 1:1) to give deprotected tube 1b" as a white solid (¹H NMR (500 MHz, d₆-acetone, r.t.): δ 8.85 (s, 6H), 7.49 (dd, J = 2.0, 2.0 Hz, 6H), 7.25 (s, 6H), 7.02 (dd, J = 2.5, 1.5 Hz, 6H), 3.53 (s, 36H)). NaH (60% in oil; 24.0 mg,
0.600 mmol) was washed with hexane in a 100 mL glass flask under N₂. The obtained tube 1b’” and dry THF (10 mL) were added to the flask and then the mixture was stirred at r.t. for 1 h. 1,3-Propanesultone (0.055 g, 4.5 mmol) was added dropwise to the flask and the resultant mixture was stirred overnight at r.t. The mixture was concentrated under reduced pressure and the crude product was washed with hexane, acetone, and 1-propanol to afford 1b as a yellow solid (29.6 mg, 0.0128 mmol, 66% yield).

¹H NMR (500 MHz, CD₃OD, r.t.): δ 7.63 (s, 6H), 7.23 (s, 6H), 7.08 (s, 6H), 6.87 (s, 12H), 4.35 (t, J = 6.3 Hz, 12H), 3.56 (s, 32H), 3.09 (t, J = 7.5 Hz, 12H), 2.37 (q, J = 6.9 Hz, 12H). ¹³C NMR (125 MHz, CD₃OD, r.t.): δ 161.2 (Cₖ), 150.2 (Cₜ), 142.9 (Cₜ), 142.9 (Cₜ), 134.0 (Cₜ), 126.8 (Cₜ), 123.6 (CH), 117.5 (CH), 112.9 (CH), 104.9 (CH), 68.1 (CH₂), 55.8 (CH₃), 49.5-48.5 (overlapped with MeOH), 26.5 (CH₂). FT-IR (KBr, cm⁻¹): 3459, 2941, 1637, 1585, 1530, 1493, 1433, 1376, 1239, 1125, 1043, 851, 755, 528. ESI-TOF MS (CH₃OH): m/z 361.2 [1b – 6Na⁺]⁻, 438.0 [1b – 5Na⁺]⁻, 553.3 [1b – 4Na⁺]⁻, 745.4 [1b – 3Na⁺]⁻.

![Figure S20](image.png)

Figure S20. ¹H NMR spectrum (500 MHz, d₆-acetone, r.t.) of 1b’”.
Figure S21. $^1$H NMR spectrum (500 MHz, CD$_3$OD, r.t.) of 1b.

Figure S22. $^{13}$C NMR spectrum (125 MHz, CD$_3$OD, r.t.) of 1b.
Figure S23a. NOESY spectrum (400 MHz, CD$_3$OD, r.t.) of 1b.

Figure S23b. NOESY spectrum (400 MHz, CD$_3$OD, r.t.) of 1b (aliphatic region).
**Figure S23c.** NOESY spectrum (400 MHz, CD$_3$OD, r.t.) of 1b (aromatic region).

**Figure S24.** HSQC spectrum (400 MHz, CD$_3$OD, r.t.) of 1b.
Figure S25. ESI-TOF MS spectrum (CH$_3$OH) of 1b.

Figure S26. $^1$H NMR spectra (500 MHz, 0.4 mM) of tube 1b in (a) CD$_3$OD at r.t. and in D$_2$O at (b) r.t. and (c) 70 °C.
Figure S27. (a) Particle size distribution (H2O, 0.4 mM, r.t.) of 1b by DLS analysis and (b) the optimized structure of 1b.

Figure S28. (a) UV-vis (0.2 mM, r.t.) and (b) fluorescence spectra (λex = 375 nm, 0.2 mM, r.t.) of 1b’ in CH2Cl2 and 1b in H2O and CH3OH.

Synthesis and properties of 1b ⊃ 3a-d and 1b ⊃ 4a-c

KH-425 (421)

n-Decane (3a; 0.12 mg, 0.84 μmol) was added to an aqueous solution (0.4 mL) of tube 1b (1.00 mg, 0.43 μmol) in a glass test tube. The solution was stirred at r.t. for 1 h.
After filtration, the formation of 1:1 host-guest complex 1b⊃3a was confirmed by 1H NMR, UV-vis, fluorescence, and ESI-TOF MS analyses. 1:1 Host-guest complexes 1b⊃3b-d and 1b⊃4a-c were also obtained by the same procedure.

1b⊃3a: 1H NMR (500 MHz, D2O, 70 ºC): δ 7.84 (s, 6H), 7.32-7.31 (m, 12H), 6.95 (s, 12H), 4.45 (br, 12H, overlapped by H2O), 3.68 (br, 36H), 3.25 (br, 12H), 2.42 (br, 12H), 0.04 (br, 4H), −0.02 (br, 6H), −0.28 (br, 4H), −0.54 (br, 4H), −0.73 (br, 4H). ESI-TOF MS (H2O): m/z 384.9 [1b⊃3a−6Na+]6−, 466.5 [1b⊃3a−5Na+]5−, 589.1 [1b⊃3a−4Na+]4−.

1b⊃3b (2,2,4,4,6,8,8-heptamethylnonane): 1H NMR (500 MHz, D2O, 70 ºC): δ 7.77 (s, 6H), 7.30 (s, 6H), 7.20 (s, 6H), 6.83 (br, 12H), 4.45 (br, 12H, overlapped by H2O), 3.61 (s, 36H), 3.16 (s, 12H), 2.32 (s, 12H), −0.11 (s, 9H), −0.24 (br, 2H), −0.42 (br, 2H), −0.62 (br, 2H), −0.72 (br, 6H), −1.00 (br, 3H), −1.02–1.15 (m, 5H). ESI-TOF MS (H2O): m/z 396.9 [1b⊃3b−6Na+]6−, 480.9 [1b⊃3b−5Na+]5−, 606.8 [1b⊃3b−4Na+]4−.

1b⊃3c (bicyclohexyl): 1H NMR (500 MHz, D2O, 70 ºC): δ 7.86 (s, 6H), 7.35 (s, 6H), 7.30 (s, 6H), 6.93 (br, 12H), 4.45 (br, 12H, overlapped by H2O), 3.69 (s, 36H), 3.25 (s, 12H), 2.41 (s, 12H), 0.73 (br, 2H), 0.13 (br, 4H), −0.11 (br, 2H), −0.29 (br, 4H), −0.59 (br, 4H), −1.00–1.01 (m, 6H). ESI-TOF MS (H2O): m/z 388.9 [1b⊃3c−6Na+]6−, 471.3 [1b⊃3c−5Na+]5−, 595.1 [1b⊃3c−4Na+]4−.

1b⊃3d (trans-decalin): 1H NMR (500 MHz, D2O, 70 ºC): δ 7.71 (s, 6H), 7.23 (s, 6H), 7.21 (s, 6H), 6.84 (br, 12H), 4.45 (br, 12H, overlapped by H2O), 3.56 (s, 36H), 3.14 (s, 12H), 2.31 (s, 12H), 0.21 (br, 4H), −0.34–0.39 (m, 8H), −1.06 (br, 4H), −1.18 (br, 2H). ESI-TOF MS (H2O): m/z 384.2 [1b⊃3d−6Na+]6−, 465.6 [1b⊃3d−5Na+]5−, 587.8 [1b⊃3d−4Na+]4−.

1b⊃4a (biphenyl): 1H NMR (500 MHz, D2O, 70 ºC): δ 7.76 (s, 6H), 7.31 (s, 6H), 6.93-6.92 (m, 18H), 6.57 (s, 2H), 6.00 (s, 4H), 5.58 (s, 4H), 4.45 (br, 12H, overlapped by H2O), 3.61 (s, 36H), 3.24 (s, 12H), 2.41 (br, 4H). ESI-TOF MS (H2O): m/z 383.0 [1b⊃4a−6Na+]6−, 466.1 [1b⊃4a−5Na+]5−, 585.8 [1b⊃4a−4Na+]4−.

1b⊃4b (naphthalene): 1H NMR (500 MHz, D2O, 70 ºC): δ 7.69 (s, 6H), 7.21 (s, 6H), 7.04 (s, 6H), 6.81 (s, 12H), 6.36 (br, 4H), 6.21 (br, 4H), 4.40 (br, 12H), 3.50 (s, 36H), 3.16 (br, 12H), 2.32 (br, 4H). ESI-TOF MS (H2O): m/z 382.6 [1b⊃4b−6Na+]6−, 463.8 [1b⊃4b−5Na+]5−, 585.3 [1b⊃4b−4Na+]4−.

1b⊃4c (1,4-naphthoquinone): 1H NMR (500 MHz, D2O, 70 ºC): δ 7.69 (s, 6H), 7.37 (br, 4H), 7.20 (s, 6H), 7.13 (s, 6H), 7.08 (br, 4H), 6.83 (s, 12H), 6.59 (br, 4H), 4.45 (br, 12H, overlapped by H2O), 3.48 (s, 24H), 3.14 (s, 12H), 2.35 (s, 12H).
Figure S29. $^1$H NMR spectra (500 MHz, 1.1 mM, D$_2$O, 70 ºC) of (a) 1b॥3d, (b) 1b॥4b, (c) 1b॥4c, and (d) 1b.

Figure 30. (a) UV-vis (0.1 mM, H$_2$O, r.t.) and (b) fluorescence spectra ($\lambda_{ex} = 375$ nm, 0.1 mM, H$_2$O, r.t.) of 1b॥3d, 1b॥4b, 1b॥4c, and 1b.
Competitive binding experiments of 3a-d and 4a-c by 1b

n-Decane (3a; 0.05 mg, 0.4 µmol) and 2,2,4,4,6,8,8-heptamethylnonane (3b; 0.08 mg, 0.4 µmol) were added to a D₂O solution (0.5 mL) of tube 1b (0.50 mg, 0.22 µmol) in a glass test tube. The solution was stirred at r.t. for 1 h. After filtration, the formation and ratio of host-guest complexes were confirmed by ¹H NMR. Competitive binding experiments of 3a and 3c, 3b and 3c, 3b and 3d, 4a and 4c, and 3c and 4a by tube 1b were examined under the similar conditions. Naphthalene (4b) shows slight water solubility so that we excluded the competitive binding experiments.

(a)  
(b)  
(c)  
(d)  
(e)  
(f)  

3b 88%  
3a 12%  
3c 100%  
3a 0%  
3c 69%  
3b 21%  
3d 0%  
4c 100%  
4a 0%  
3c 10%
Figure S31. $^1$H NMR spectra (500 or 400 MHz, 0.5 mM, D$_2$O, 70 ºC) after the competitive binding experiments of (a) 3a and 3b, (b) 3a and 3c, (c) 3b and 3c, (d) 3b and 3d, (e) 4a and 4c, and (f) 3c and 4a by tube 1b. The binding rates were determined by the signal integration.

Guest exchange experiment of 1b$\uparrow$3a by 4a

Biphenyl (4a; 0.06 mg, 0.4 µmol) was added to a D$_2$O solution of 1b$\uparrow$3a (0.53 mg, 0.22 µmol) in a glass test tube and the solution was stirred at r.t. for 1h. The guest exchange was confirmed by $^1$H NMR analysis.

Figure S32. $^1$H NMR spectra (400 MHz, 0.5 mM, D$_2$O, 70 ºC) (a) before and (b) after addition of 4a to 1b$\uparrow$3a.

Table S1. Volume and length of guests 3a-d and 4a-c by DFT calculation (B3LYP/6-31G*).

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KH-417-2