SUPPORTING INFORMATION

The Construction of Complex Multicomponent Supramolecular Systems *via* the Combination of Orthogonal Self-Assembly and Self-Sorting Approach

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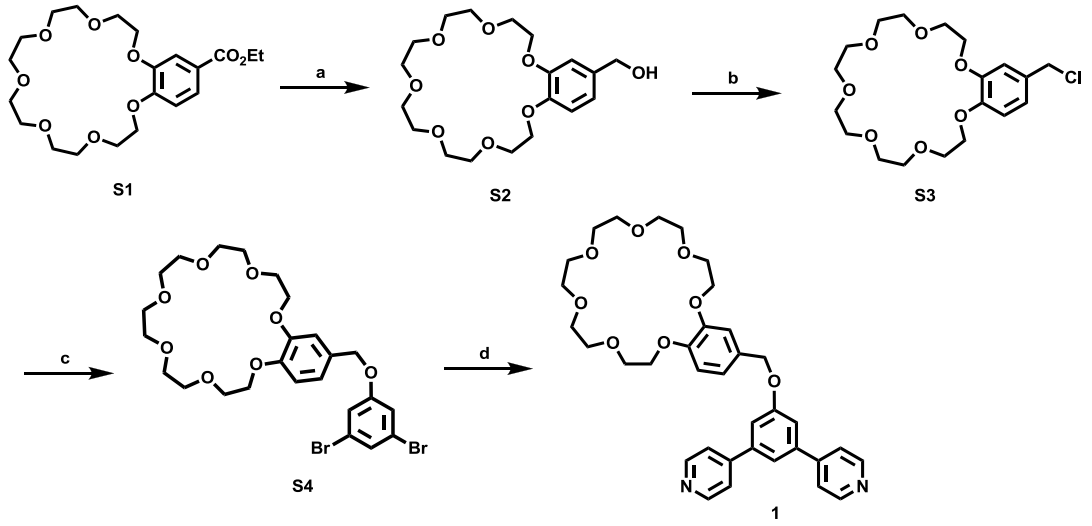
1. General Information.

All reagents were of analytical purity and used without further treatment. TLC analyses were performed on silica-gel plates, and flash chromatography was conducted using silica-gel column packages purchased from Qingdao Haiyang Chemical Co., Ltd. (China). The 120° DB24C8-containing donor building block **2**,[1] 120° di-Pt(II) acceptors **3**,[2] and compounds **S1**,[3] **S5**,[4] and **S6**[5] were prepared according to the established methods.

^{1}H NMR and ^{31}P NMR spectra were recorded on Bruker 400 MHz or 500 MHz Spectrometer (^{1}H: 400 MHz or 500 MHz; ^{31}P: 161.9 MHz) at 298 K. The ^{1}H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals, and ^{31}P NMR resonances are referenced to an internal standard sample of 85% H_3PO_4 (δ 0.0). Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet, br = broad. Mass spectra were recorded on a Waters LCT Premier XE spectrometer with acetonitrile or methanol as solvent.

2. The Synthesis of 21C7-Containing Building Block 1 and Guest Compounds 4 and 5.

Scheme S1. **Synthesis of 120° Angular B21C7 Containing Donor Subunit 1** [a]



[a]Key: (a) $LiAlH_4$, THF, reflux, overnight, 82% ; (b) $SOCl_2$, pyridine, CH_2Cl_2, room temperature, 3 h, 55%; (c) 3,5-dibromophenol, K_2CO_3, acetone, reflux, overnight, 63%; (d) pyridin-4-ylboronic acid, Na_2CO_3, $Pd(PPh_3)_4$, DME/EtOH/H_2O, 80 °C, 24 h, 64%.

Synthesis of S1:

3, 4-Dihydroxybenzaldehyde (1.28 g, 7.04 mmol), K_2CO_3 (2.91 g, 21.11 mmol), and KPF_6 (3.88 g, 21.11mmol) were dissolved in dry CH_3CN (150 mL). A solution of 3, 6, 9, 12, 15-pentaoxaheptadecane-1, 17-diyl bis(4-methylbenzenesulfonate) (4.16 g, 7.04 mmol) in CH_3CN (50 mL) was added and then stirred for 72 h under reflux. The cooled solution was evaporated to dryness and extracted with CH_2Cl_2. The extract was evaporated to yield a viscous oil, which was purified by flash column chromatography (ethyl acetate: methanol = 10:1 v/v) to yield the compound **S1** as a claybank solid (1.88 g, 63%). ^{1}H NMR ($CDCl_3$,400 MHz): δ 7.63–7.66 (m, 1H), 7.54 (m, 1H), 6.84 (m, 1H), 4.30–4.35 (q, J_1 = 6.8Hz, J_2 = 14 Hz,2H,), 4.20 (m, 4H), 3.94 (m, 4H), 3.79 (m, 4H), 3.72 (m, 4H), 3.65 (m, 8H), 1.36 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 166.5, 152.7, 148.2, 124.2, 123.7, 114.8, 70.7, 70.3, 69.7, 69.54, 69.0, 68.8, 61.1, 14.5. MS (EI): m/z, 428.20; HRMS (EI-TOF): Calcd. For $[C_{21}H_{32}O_9]^+$: 428.2046, Found: 428.2047.

Synthesis of S2:

To a suspension of $LiAlH_4$ (139 mg, 3.65 mmol) in 20mL THF at 0 °C, the compound **S1** (624 mg, 1.46 mmol) in 10 mL THF was slowly added dropwise. The resultant solution was allowed to warm to room temperature and then reflux overnight. The reaction mixture was quenched with water. Then the reaction mixture was filtered through celite and the clear filtrate was concentrated *in vacuo* to yield compound **S2** as a colorless oil (465 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$):δ 6.90 (s, 1H), 6.81–6.86 (m, 2H), 4.55 (s, 2H), 4.12–4.15 (m, 4H,), 3.86–3.88 (m, 4H), 3.72–3.75(m, 4H), 3.63–3.68 (m, 4H), 3.62 (m, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.1, 147.4, 135.0, 120.4, 113.6, 112.7, 72.7, 70.5, 70.3, 70.1, 70.0, 69.8, 69.5, 69.2, 68.0, 67.8, 64.8, 62.8, 61.5, 29.9, 29.8, 25.7. MS (EI): m/z, 386.19; HRMS (EI-TOF): Calcd. For $[C_{19}H_{30}O_8]^+$: 386.1941, Found:386.1939.

Synthesis of S3:

To a solution of pyridine (1.61 g, 20.40 mmol) and thionyl chloride (2.43 g, 20.40 mmol) in CH_2Cl_2 (10 mL) was added a solution of compound **S2** (1.58 g, 4.01mmol) in CH_2Cl_2 (5 mL). The solution was stirred at room temperature for 1 h. Chloroform (30 mL) was added and the reaction mixture was poured over cold water (100 mL). The aqueous layer was extracted with CH_2Cl_2 (2×50 mL) and the combined organic layers was washed with water (2×50 mL), 1 *M* $NaHCO_3$ (2 ×50 mL), and the saturated brine solution (50 mL), then dried ($MgSO_4$) and concentrated *in vacuo* to yield compound **S3** as a claybank oil (900 mg, 55%).^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90–6.93 (m, 2H), 6.70–6.87 (m, 1H), 4.54 (s, 2H), 4.14–4.18 (m, 4H), 3.90–3.93 (m, 4H), 3.77–3.79 (m, 4H), 3.72–3.73 (m, 4H), 3.62 (m, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz):δ 148.8, 148.7, 148.1, 147.8, 143.8, 134.8, 131.5, 130.5, 128.6, 121.7, 121.1, 119.9, 116.6, 115.1, 114.4, 113.9, 113.7, 113.0, 70.8, 70.7, 70.6, 70.2, 70.2, 69.5, 69.0, 68.9, 64.6, 46.4, 29.6. MS (EI): m/z, 404.16; HRMS (EI-TOF): Calcd. For $[C_{19}H_{29}ClO_7]^+$: 404.1602, Found: 404.1599.

Synthesis of S4:

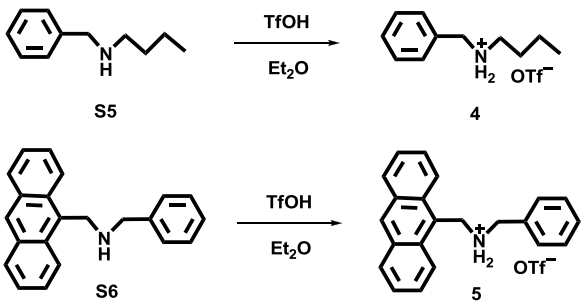
To a stirred mixture of 3, 5-dibromopheneol (185 mg, 0.45 mmol) and compound **S3** (105 mg, 0.41 mmol) in acetone (pre-dried by Na_2SO_4, 15 mL), K_2CO_3 (453 mg, 3.28 mmol) was added. The resultant suspension was refluxed for 12 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate was concentrated *in vacuo* to give a yellow oily residue, which was purified by flash column chromatography (ethyl acetate: CH_2Cl_2 = 5:1 v/v) to yield compound **S4** as a claybank oil (220 mg, 63%).^{1}H NMR (CD_3COCD_3,400 MHz): δ 7.32 (m, 1H), 7.21-7.31 (m, 2H), 7.13 (m, 1H), 7.04–6.98 (m, 2H), 5.10 (s, 2H), 4.16–4.19 (m, 4H), 3.71–3.87 (m, 4H), 3.70–3.71 (m, 4H), 3.63–3.69 (m, 4H), 3.59 (m, 8H). ^{13}C NMR (CD_3COCD_3, 100 MHz): δ 161.3, 149.9, 130.1, 126.9, 123.7, 122.0, 118.4, 115.0, 114.8, 71.4, 71.3, 71.3, 71.2, 71.1, 70.3,

69.7, 69.7. MS (EI): m/z, 618.05; HRMS (EI-TOF): Calcd. For $[C_{25}H_{32}Br_2O_8]^+$: 618.0464, Found: 618.0461.

Synthesis of 1:

A solution of **S4** (150 mg, 0.24 mmol) in dimethoxyethane (10 mL) was stirred for 5 min at room temperature under a nitrogen atmosphere. Then tetrakis(triphenylphosphine)palladium(0) (56 mg, 0.05 mmol) was added at room temperature and the resulting light-yellow solution was heated to 80 °C and stirred for 5 min. At this time, a solution of pyridine-4-boronic acid (180 mg, 1.46 mmol) in ethanol (10 mL) was added, followed by a solution of sodium carbonate (154 mg, 1.46 mmol) in water (1.0 mL). The resultant light-yellow suspension was stirred for 15 h at reflux temperature. Then the reaction mixture was cooled down to room temperature and diluted with water (10 mL) and ethyl acetate (25 mL). The two layers were separated, and the aqueous layer was extracted with ethyl acetate (25 mL). The combined organic extracts were washed with water (50 mL) and brine solution (50 mL), then dried over anhydrous magnesium sulfate. Filtration and concentration of the solvent gave the crude residue that was purified by column chromatography on silica gel (CH_2Cl_2/THF 1:2) to afford **1** (96 mg, 64%) as a white solid. Mp: 145°C. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 8.67 (d, J = 6.0 Hz, 4H), 7.56 (d, J= 6.0 Hz, 4H), 7.51 (t, 1H), 7.32 (d, J = 6.0 Hz, 2H), 7.03(br, 2H), 6.91(br, 2H), 5.12 (s, 2H), 4.15 (m, 4H), 3.86 (m, 4H), 3.71 (m, 4H), 3.65 (m, 4H), 3.60 (m, 8H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 160.4, 150.8, 149.6, 149.5, 148.0, 141.0, 130.0, 122.1, 121.3, 118.8, 114.6, 71.4, 71.3, 71.2, 71.0, 70.8, 70.1, 69.7, 69.6.; MS (ESI): 617.39 ($[M+H]^+$), Anal. Calcd. For $C_{35}H_{40}N_2O_8$: C, 68.17; H, 6.54; N, 4.54. Found: C, 68.02; H, 6.44; N, 4.48.

Scheme S2. Synthesis of Guest Compounds 4 and 5



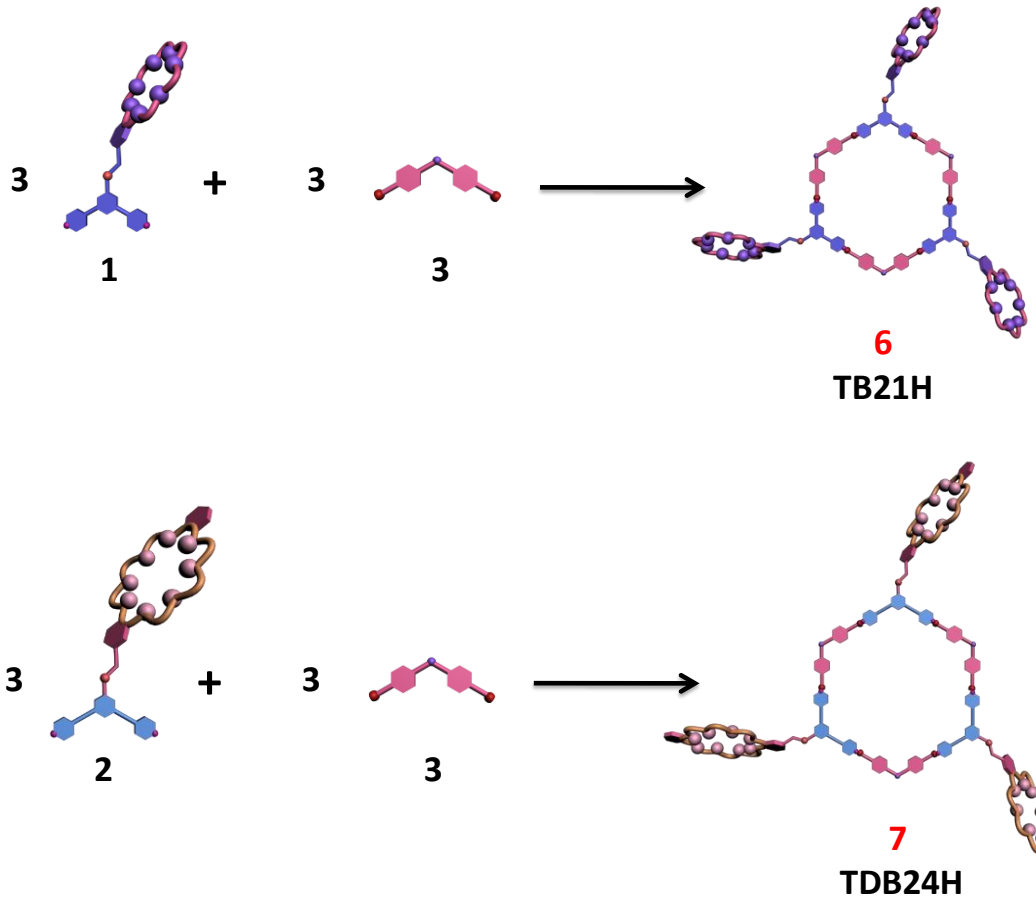
Trifluoromethanesulfonic acid (375 mg, 2.50 mmol) was added to diethyl ether (~10 mL) at room temperature. Amines (2.0 mmol, for **S5**, 326 mg; for **S6**, 542 mg) were added to the stirred acid solution. A white precipitate was immediately observed, collected via vacuum filtration, washed with diethyl ether, and dried (For **4**, 250 mg, 80%; for **5**, 380 mg, 85%).

4, M.p. 123 °C. ^{1}H NMR (CD_3CN, 400 MHz): δ 7.49 (m, 5H), 4.18 (s, 2H), 3.03–3.07 (m, 2 H), 1.63–1.71 (m, 2H), 1.35–1.44 (m, 2H), 0.93-0.97(m, 2H); ^{13}C NMR (CD_3CN, 100 MHz) δ 13.7, 20.3, 28.5, 48.7, 52.5, 130.1, 130.7, 131.1, 131.7.; MS (EI): 164 [*M*-OTf]$^{+}$; Anal. Calcd. For $C_{12}H_{18}F_3NO_3S$: C, 46.00; H, 5.79; N, 4.47; Found: C, 45.79; H, 5.66; N, 4.63.

5, M.p. 204 °C. ^{1}H NMR (CD_3CN, 400 MHz): δ 4.52 (s, 2H), 5.27 (s, 2H), 7.54–7.69 (m, 9H), 8.12 (d, J = 9.0 Hz, 2H), 8.17 (d, J = 9.0 Hz, 2H), 8.75 (s, 1H); ^{13}C NMR (CD_3CN, 100 MHz) δ 44.1, 53.0, 122.0, 124.1, 126.6, 128.6, 130.2, 130.5, 131.0, 131.3, 131.5, 131.9, 132.3; MS (EI): 297 [*M*-OTf]$^{+}$; Anal. Calcd. For $C_{23}H_{20}F_3NO_3S$: C, 61.74; H, 4.51; N, 3.13; Found: C, 61.79; H, 4.56; N, 3.26.

3. The Construction of the Individual Hexagonal Metallacycles and Tris[2]pseudorotaxanes

Scheme S3. The Construction of the Individual Hexagonal Metallacycles 6 and 7



Preparation of Tris-B21C7 Hexagon 6. To a mixture of 120° **B21C7** containing building blocks **1** (1.97 mg, 0.00312 mmol) and 120° di-Pt(II) acceptor **3** (4.28 mg, 0.00312 mmol) in a small vessel was added 0.5 mL dichloromethane-d_2 solution drop by drop with continuous stirring. The reaction mixture was stirred for another 2 h at room temperature and employed for the further characterizations directly.

Preparation of Tris-DB24C8 Hexagon 7. To a mixture of 120° **DB24C8** containing building blocks **2** (1.71 mg, 0.00226 mmol) and 120° di-Pt(II) acceptor **3** (2.96 mg, 0.00226 mmol) in a small vessel was added 0.5 mL dichloromethane-d_2 solution drop by drop with continuous stirring. The reaction mixture was stirred for another 2 h at room temperature and employed for the further characterizations directly.

Figure S1. **^{1}H NMR Spectrum of the Metallacycle 6 in CD_2Cl_2.**

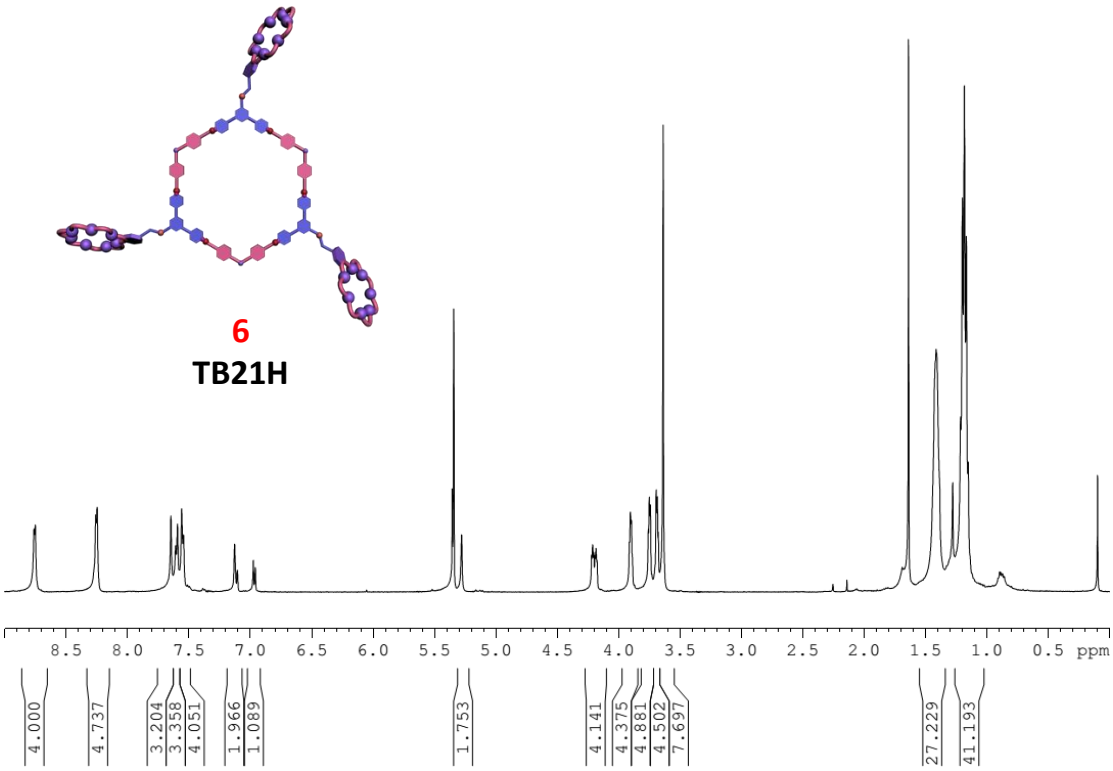


Figure S2. **^{1}H NMR Spectrum of the Metallacycle 7 in CD_2Cl_2.**

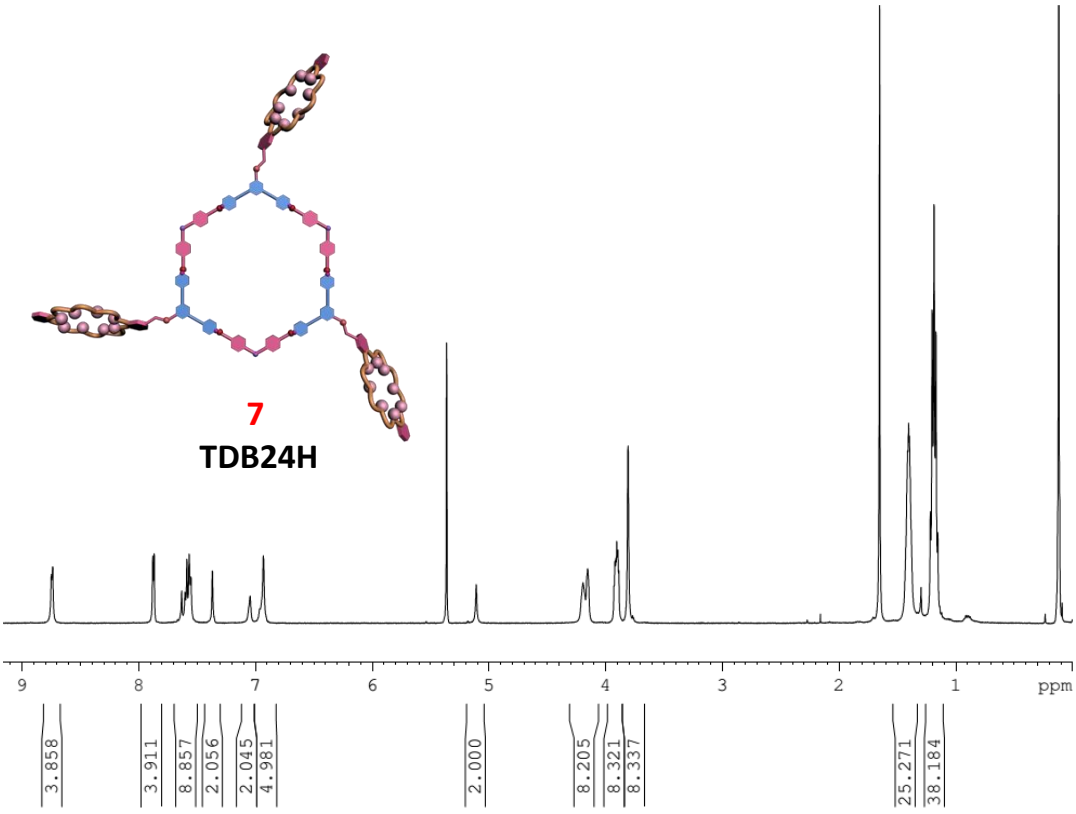


Figure S3. **NOESY Spectrum of the Metallacycle 6 in CD_2Cl_2.** (In this spectrum, the correlations between the protons of the pyridine moiety in donor building block **1** and the ethyl protons of the phosphine ligand in acceptor building block **3** could be clearly identified, thus indicating the formation of the target metallacycle **6**).

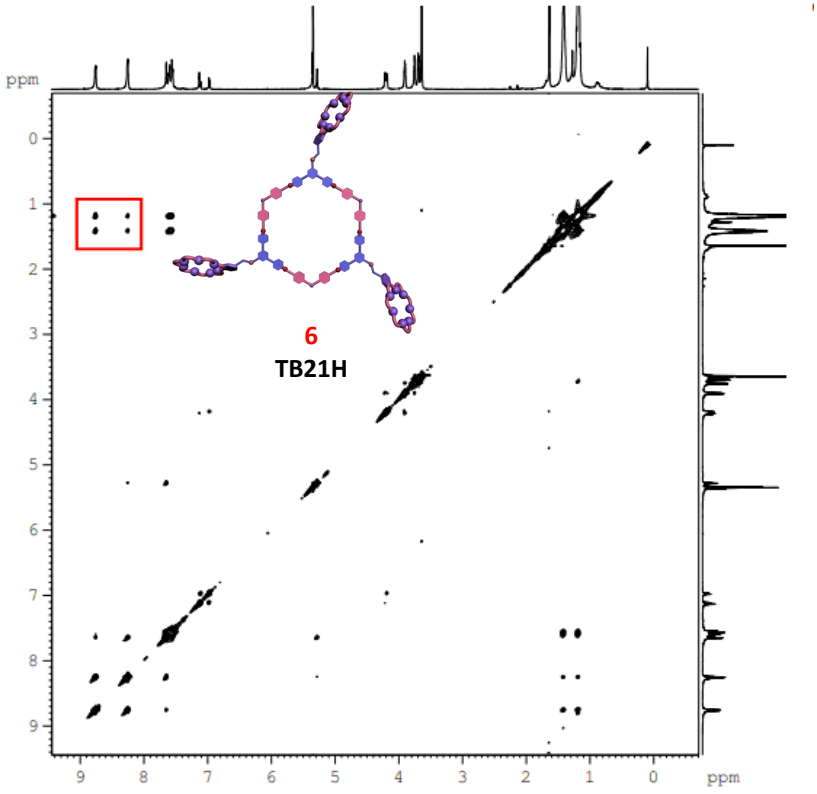


Figure S4. **DOSY Spectrum of the Metallacycle 6 in CD_2Cl_2.** (In this spectrum, all protons show the same diffusion coefficient, thus suppoting the metallacycle **6** as the only self-assembly product.)

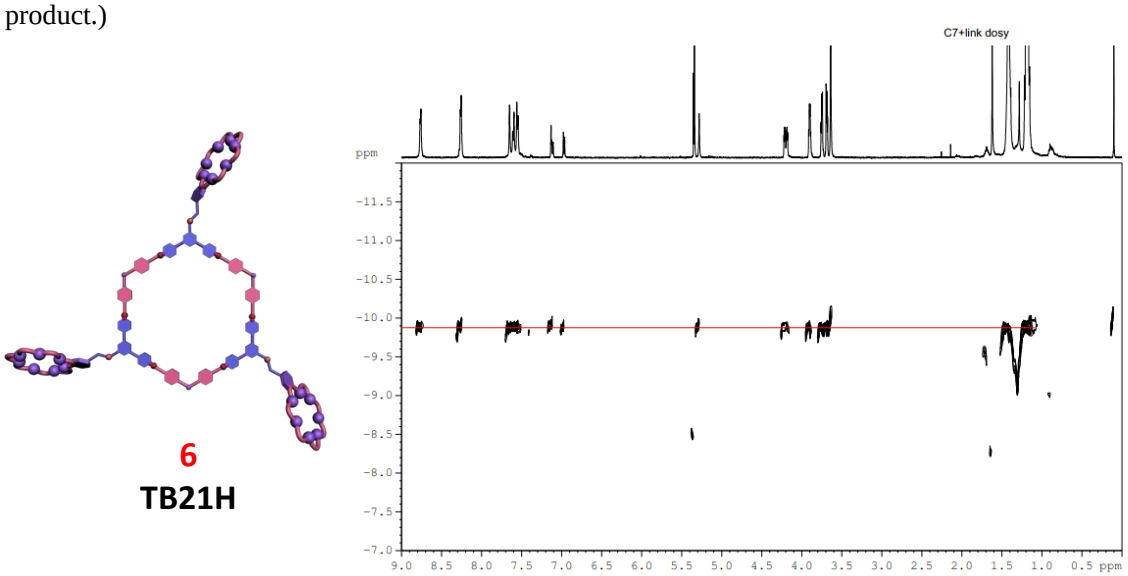


Figure S5. **NOESY Spectrum of the Metallacycle 7 in CD_2Cl_2.** (In this spectrum, the correlations between the protons of the pyridine moiety in donor building block **2** and the ethyl protons of the phosphine ligand in acceptor building block **3** could be clearly identified, thus indicating the formation of the target metallacycle **7**).

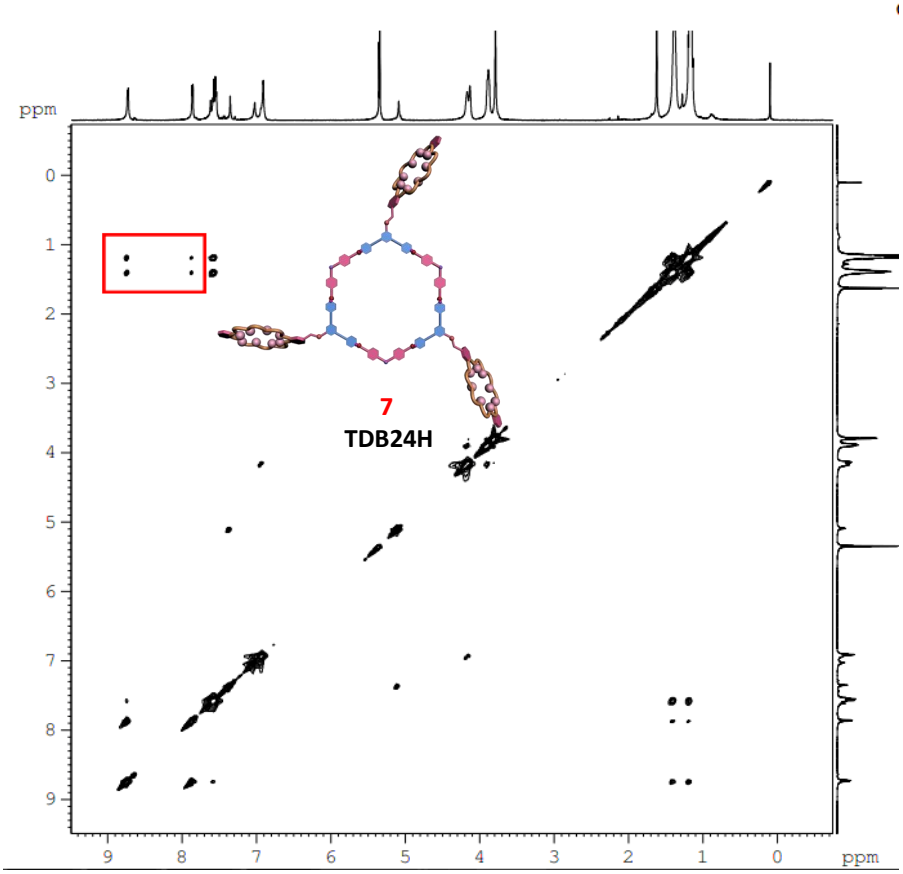
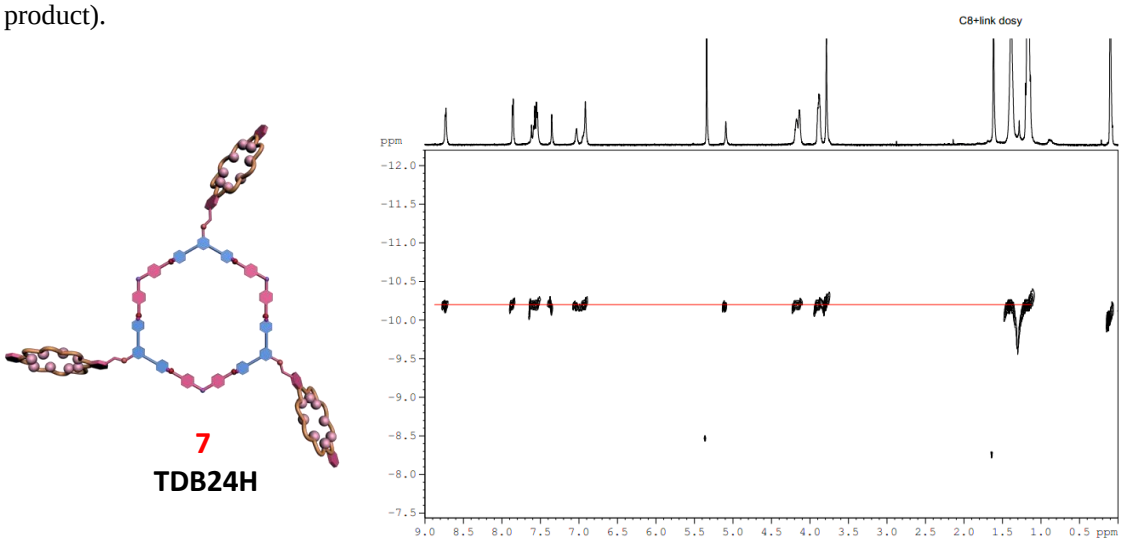
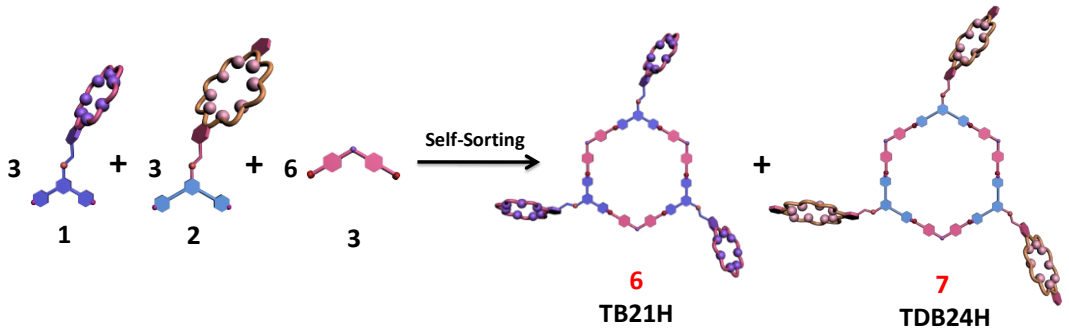


Figure S6. **DOSY Spectrum of the Metallacycle 7 in CD_2Cl_2.** (In this spectrum, all protons show the same diffusion coefficient, thus supporting the metallacycle **7** as the only self-assembly product).



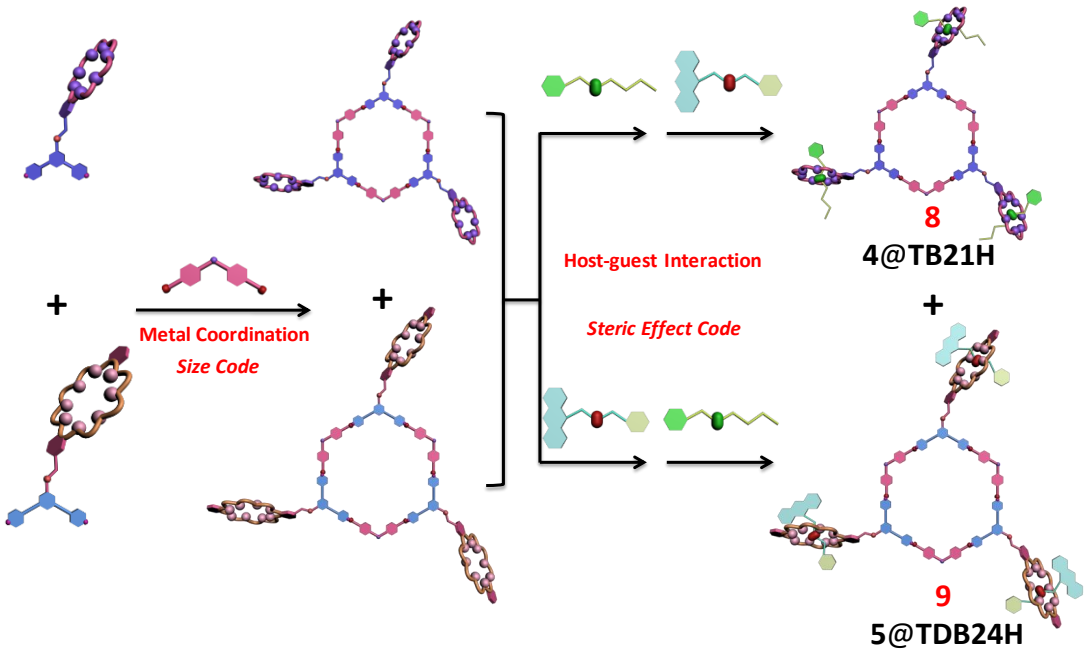
4. Experimental details of Size-Controlled Self-Sorting Process and the Construction of Multicomponent Supramolecular System

Size-Controlled Self-Sorting Process: To a mixture of 120° crown ether containing building blocks **1** (1.79 mg, 0.00290 mmol), **2** (2.20 mg, 0.00290 mmol), and 120° di-Pt(II) acceptor **3** (7.79 mg, 0.00580 mmol) in a small vessel was added 0.5 mL dichloromethane-d_2 solution drop by drop with continuous stirring. The reaction mixture was stirred for another 2 h at room temperature and employed for the further characterizations directly.

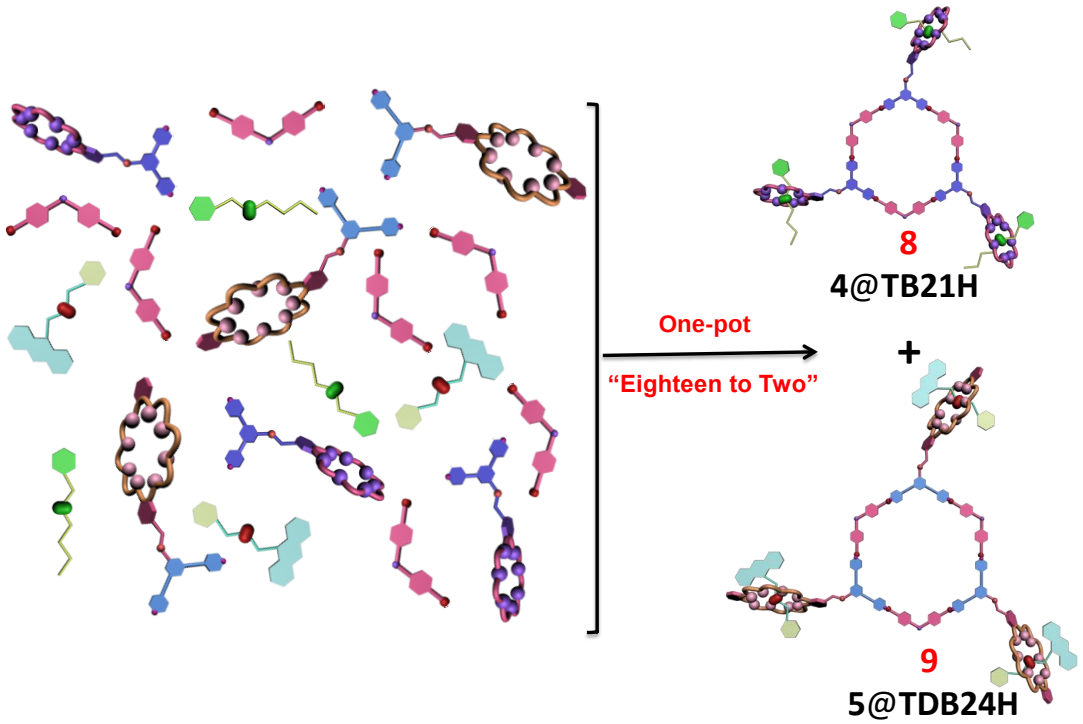


The Construction of Multicomponent Supramoleclar System: ***Method I (the stepwise fashion):*** The solution of the mixture of above-mentioned multiple crown ether containing metallacycles **6** and **7** (11.78 mg) was added to the guest **4** (0.91 mg, 0.00290 mmol) in a small vessel drop by drop with continuous stirring. The complexation mixture was stirred for another 1 h at room temperature. After the necessary characterizations, the resultant mixture solution was then added to the guest **5** (1.30 mg, 0.00290 mmol) in a small vessel. After 1 h stirring at room temperature, the resultant multicomponent supramolecular system was obtained, which was used for the further characterizations directly. Similar experimental operation was employed when the guests were added in a different sequence.

Method II (the one-pot fashion): To a mixture of 120° crown ether containing building blocks **1** (1.57 mg, 0.00255 mmol), **2** (1.93 mg, 0.00255 mmol), 120° di-Pt(II) acceptor **3** (6.83 mg, 0.00510 mmol), guest **4** (0.80 mg, 0.00255 mmol), and guest **5** (1.14 mg, 0.00255 mmol) in a small vessel was added 0.5 mL dichloromethane-d_2 solution drop by drop with continuous stirring. The reaction mixture was stirred for another 1 h at room temperature and employed for the further characterizations directly.



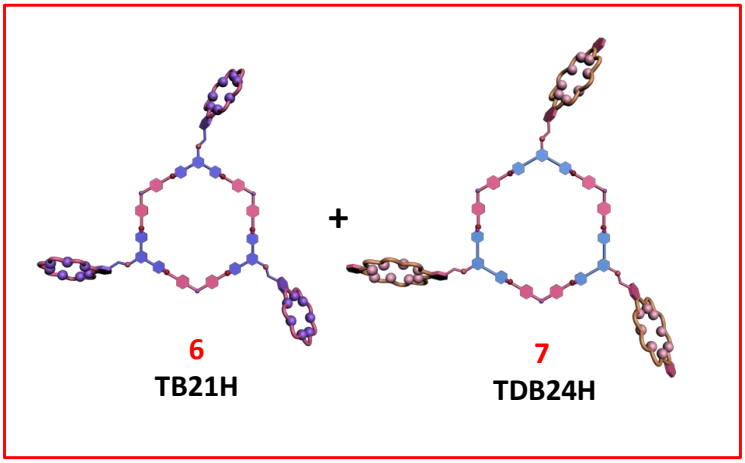
Method I (the stepwise fashion)



Method II (the one-pot fashion)

5. 2D NMR Spectra of the Size-Controlled Self-Sorting System

Figure S7. **NOSEY Spectrum of the Size-Controlled Self-Sorting System in CD_2Cl_2.** (In this spectrum, the correlations between the proton of the pyridine moieties in donor building block **1** and **2** and the ethyl protons of the phosphine ligand in acceptor building block **3** could be clearly identified, thus indicating the formation of the target metallacycles via size-controlled self-sorting).



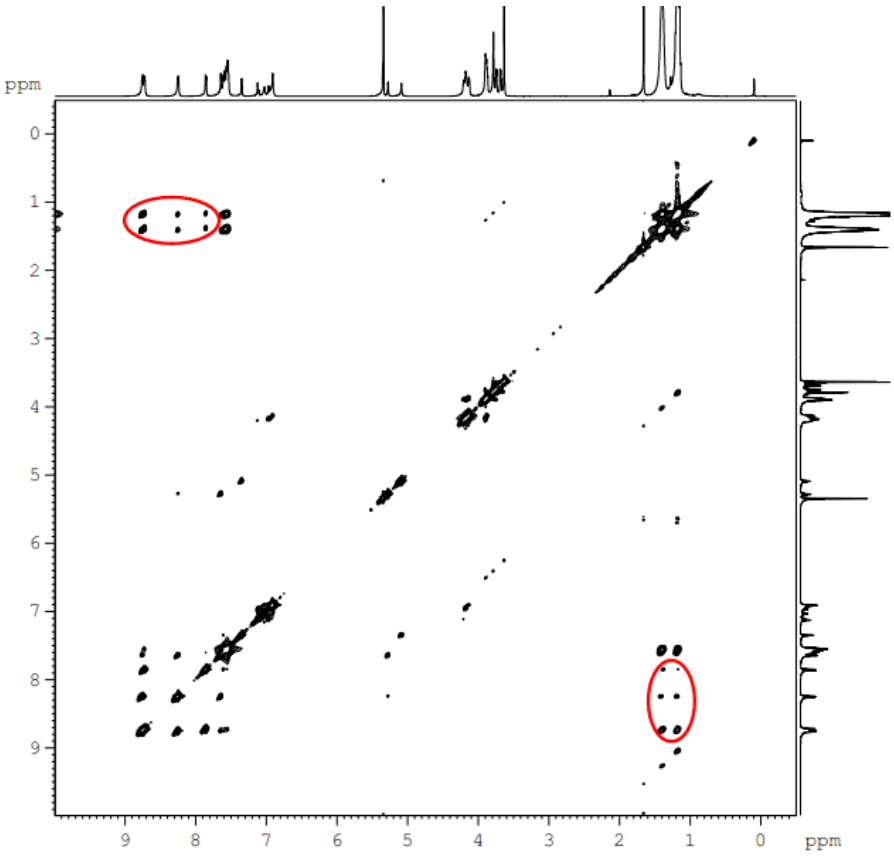
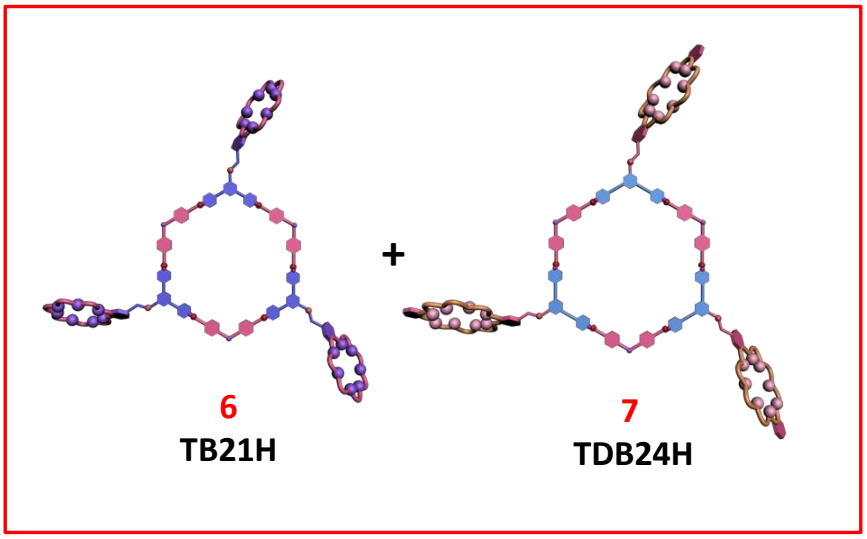
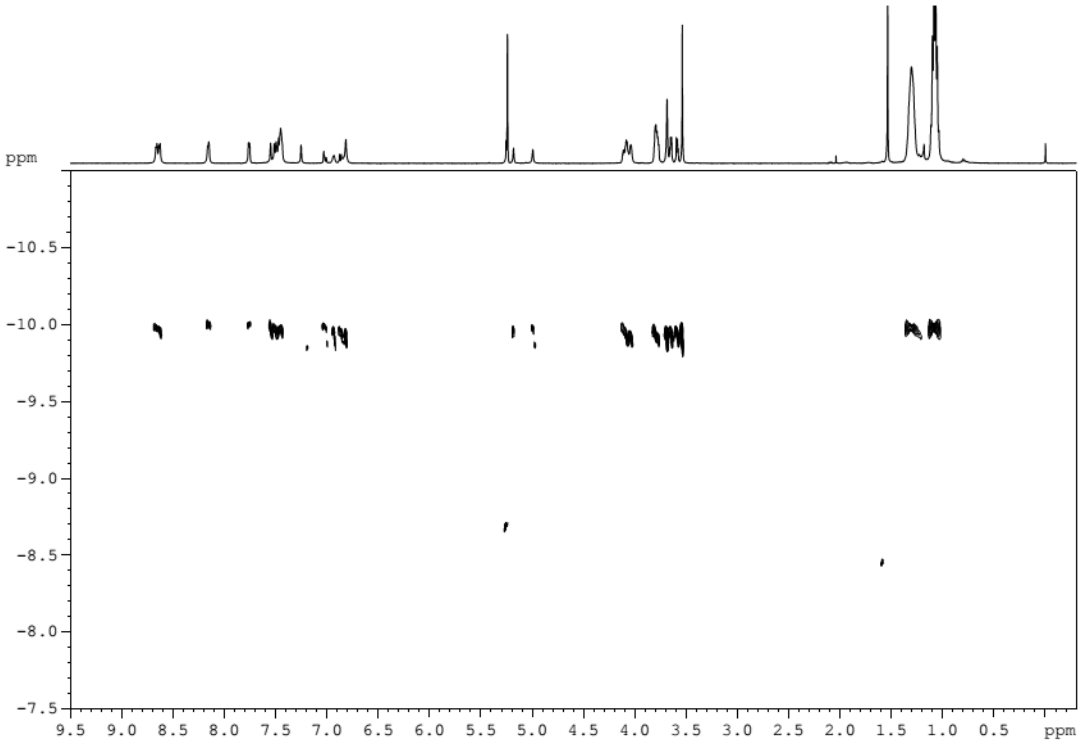


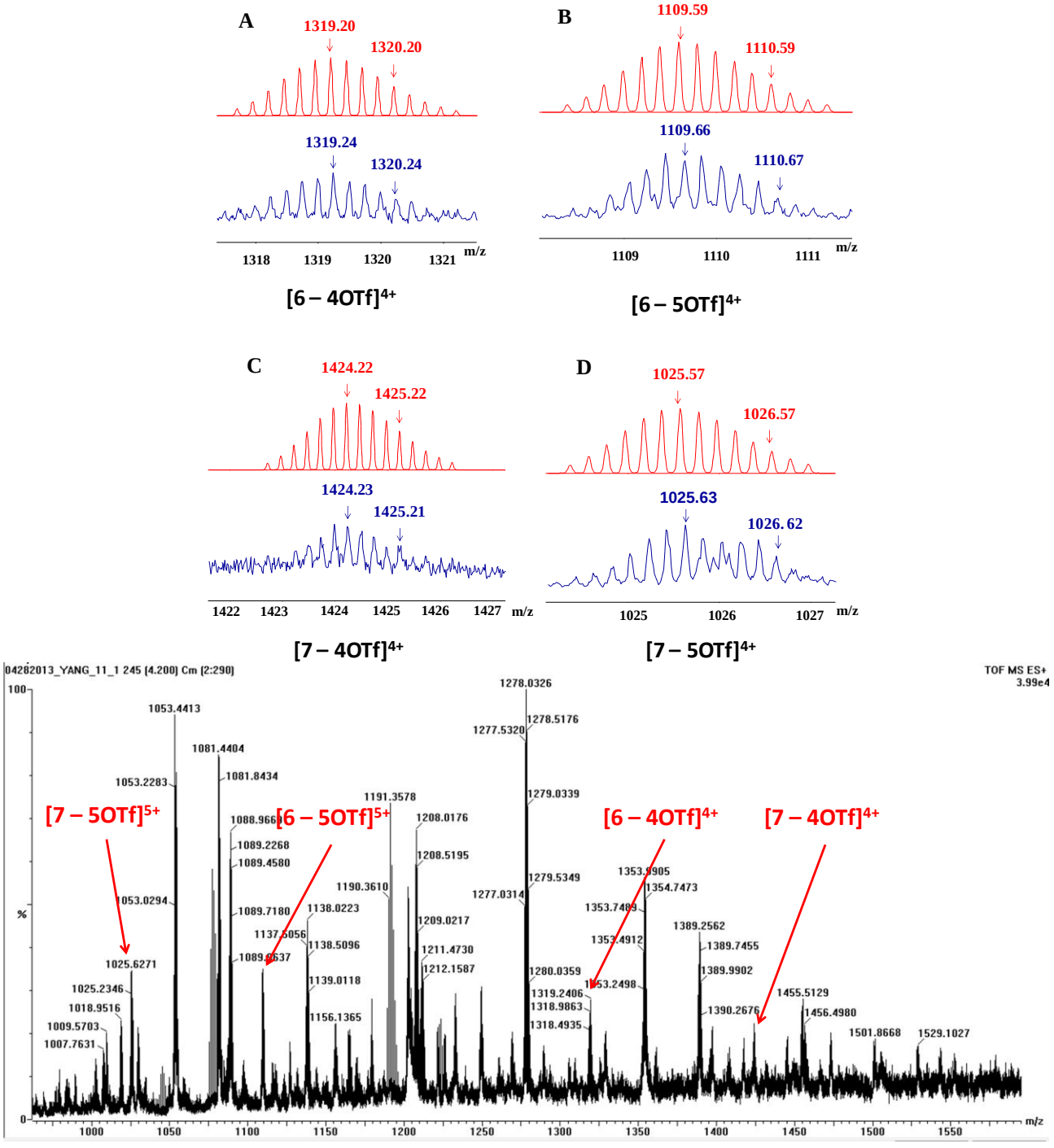
Figure S8. **DOSY Spectrum of the Size-Controlled Self-Sorting System in CD_2Cl_2.** (Unfortunately, the expected different diffusion coefficients of these two different metallacylces was not obtained, possibly due to the slight difference of the diffusion coefficients of **6** and **7**).





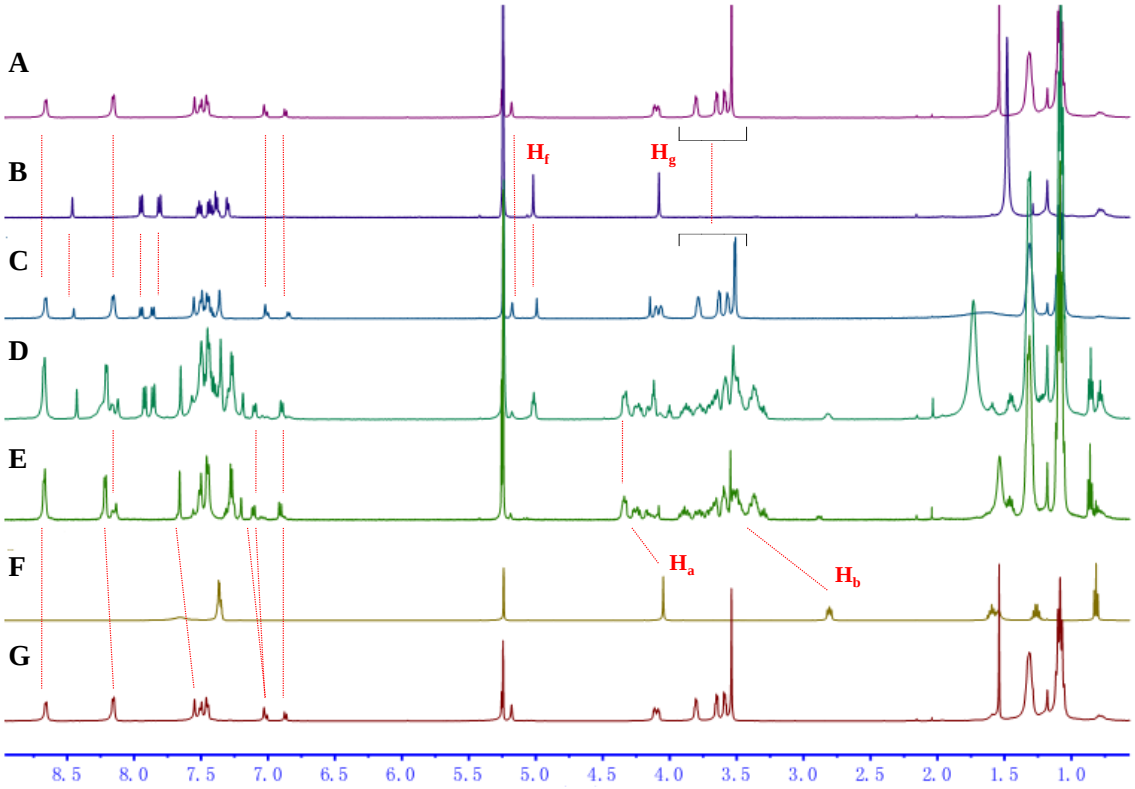
6. ESI-TOF Mass Spectra of the Size - Controlled Self-Sorting System

Figure S9. **Calculated (top) and Experimental (bottom) ESI-TOF-MS Spectrum of Multiple Crown Ether Containing Hexagonal Metallacycle 6 (A, B) and 7 (C, D) in the Size-Controlled Self-Sorting System.**



7. Individual Complexation Studies of Metallacycles 6, 7 and Guests 4, 5

Figure S10. **Partical ^{1}H NMR (500 MHz, CD_2Cl_2, 298K) of Free Metallacycle TB21H (A, G), 4 (F), 5 (B) and Complxation Systems TB21H and 4 (E), TB21H and 5 (C) and TB21H, 4 and 5 (D).(For all individual complexation systems, each component is mixed in equilmolar ration for the crown ether and guest moiety. For complexation system TB21H, 4 and 5 (D), the ration for TB21H, 4 and 5 is 1:3:3.)**



The ^{1}H NMR spectrum confirmed the existence of complexation in a slow exchange manner between **TB21H and 4**, in which two sets of peaks attributed to the complexed and uncomplexed signals of guest **4** were observed. The H_a and H_b protons on guest **4** experienced significant downfield shifts with respect to the free **4 (E)**. While no complexation was observed in the 1:3 mixture of **TB21H** and **5**, since no obvious shifts for both **TB21H** and **5** were observed **(C)**. When **TB21H**, **4**, and **5** were mixed in a 1:3:3 ration, only the complextion between **TB21H** and **4** was found as shown in Spectrum **(D)**.

Figure S11. **NOSEY Spectrum of the Complexation System of TB21H and Guest 4 in CD_2Cl_2.** (Because of the overlaps of the protons in the host **B21C7** moiety and guest **4** no obvious correlations of the tris[2]pseduorotaxane **8** were observed.)

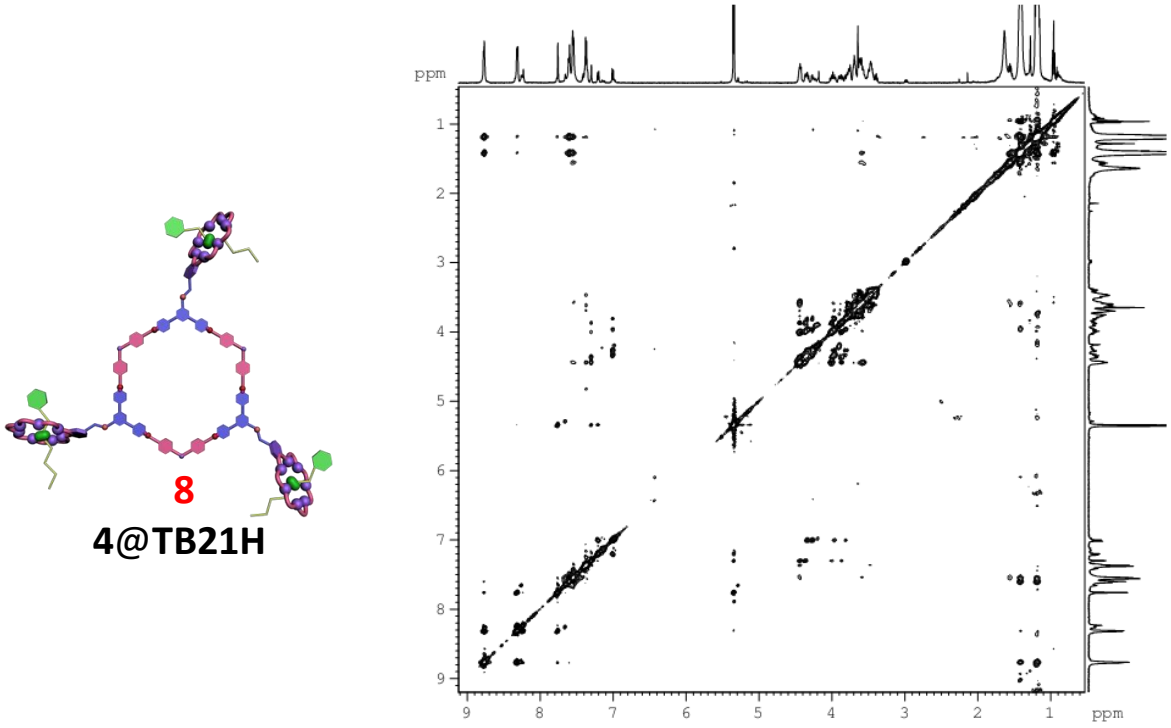


Figure S12. **DOSY Spectrum of the Complexation System of TB21H and Guest 4 in CD_2Cl_2.** (The formation of the resultant tris[2]pseduorotaxane **8** could be confirmed by the decrease of the diffusion coefficient of **8** compared with the free metallacycle **6**).

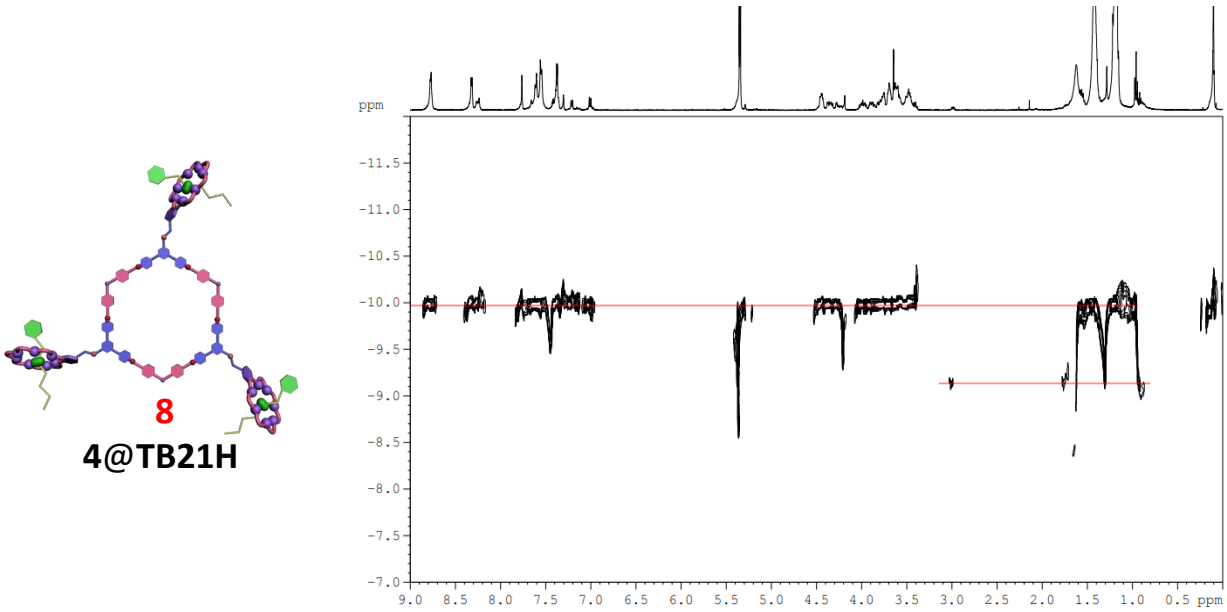
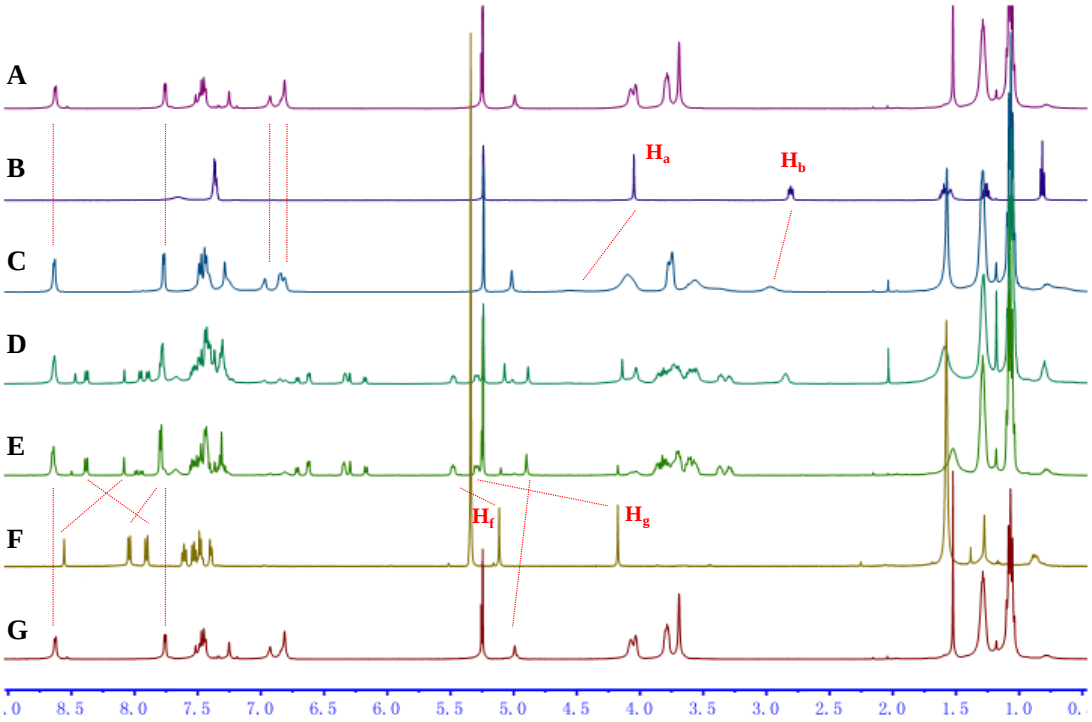


Figure S13. **Partical ^{1}H NMR (500 MHz, CD_2Cl_2, 298K) of Free Metallacycle TDB24H (A, G), 4 (B), 5 (F) and Complxation Systems TDB24H and 4 (C), TDB24H and 5 (E) and TDB24H, 4 and 5 (D). (For all individual complexation systems, each component is mixed in equilmolar ration for the crown ether and guest moiety. For complexation system TDB24H, 4 and 5 (D), the ration for TDB24H, 4 and 5 is 1:3:3.)**



The ^{1}H NMR spectrum confirmed the existence of complexation in a slow exchange manner between **TDB24H** and **5**, in which two sets of peaks attributed to the complexed and uncomplexed signals of guest **5** were observed. The H_f and H_g protons on guest **5** experienced significant downfield shifts with respect to the free **5 (E)**. While a fast exchange system was observed for **TDB24H** and **4**. The peaks attributed to guest **4** were disappeared and new broad peaks were observed **(C)**. When **TDB24H**, **4**, and **5** were mixed in a 1:3:3 ration, the complextion between **TDB24H** and both guests was found, as shown in Spectrum **(D)**.

Figure S14. **ROSEY Spectrum of the Complexation System of TDB24H and Guest 4 in CD_2Cl_2.** (Clear correlations between the guest **4** and the **DB24C8** moiety in TDB24H were observed, thus indicating the formation of tris[2]pseduorotaxane **8**).

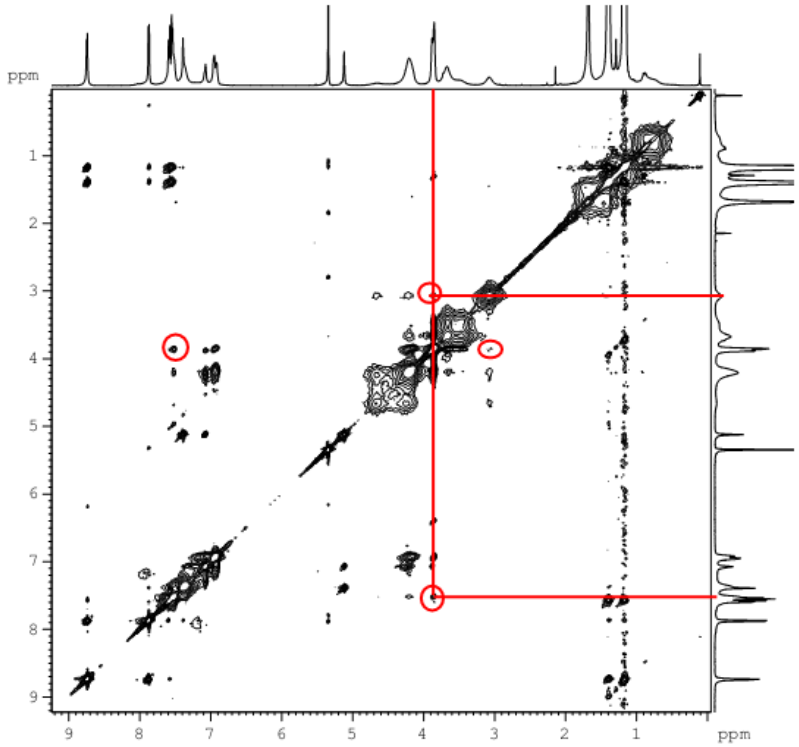


Figure S15. **DOSY Spectrum of the Complexation System of TDB24H and Guest 4 in CD_2Cl_2.** (The formation of the tris[2]pseduorotaxane of TDB24H and guest **4** could be further confirmed by the decrease of the diffusion coefficient compared with free metallacycle **7**).

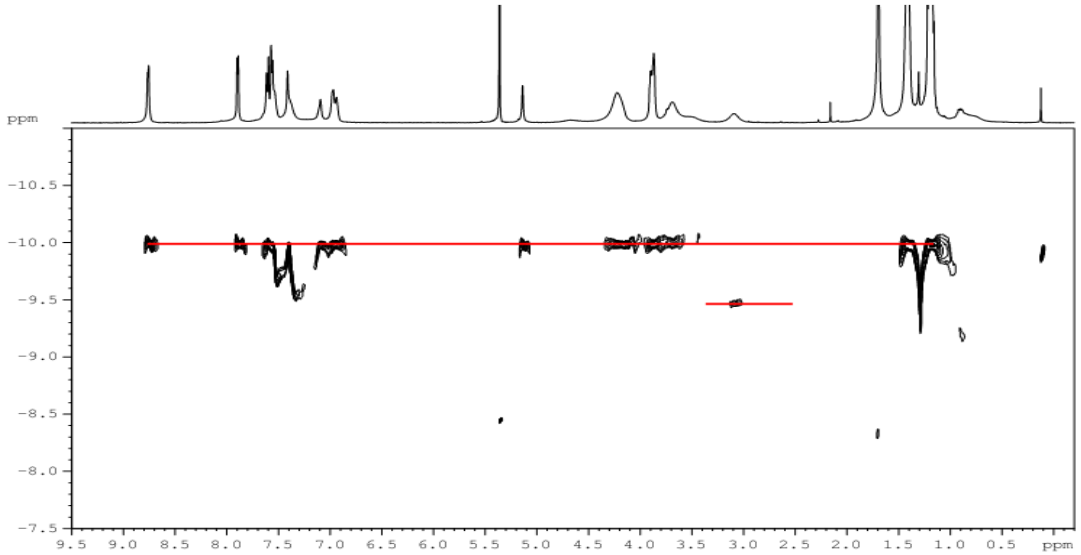


Figure S16. **NOSEY Spectrum of the Complexation System of TDB24H and Guest 5 in CD_2Cl_2.** (Clear correlations between the guest **5** and the **DB24C8** moiety in TDB24H were observed, thus indicating the formation of tris[2]pseduorotaxane **9**).

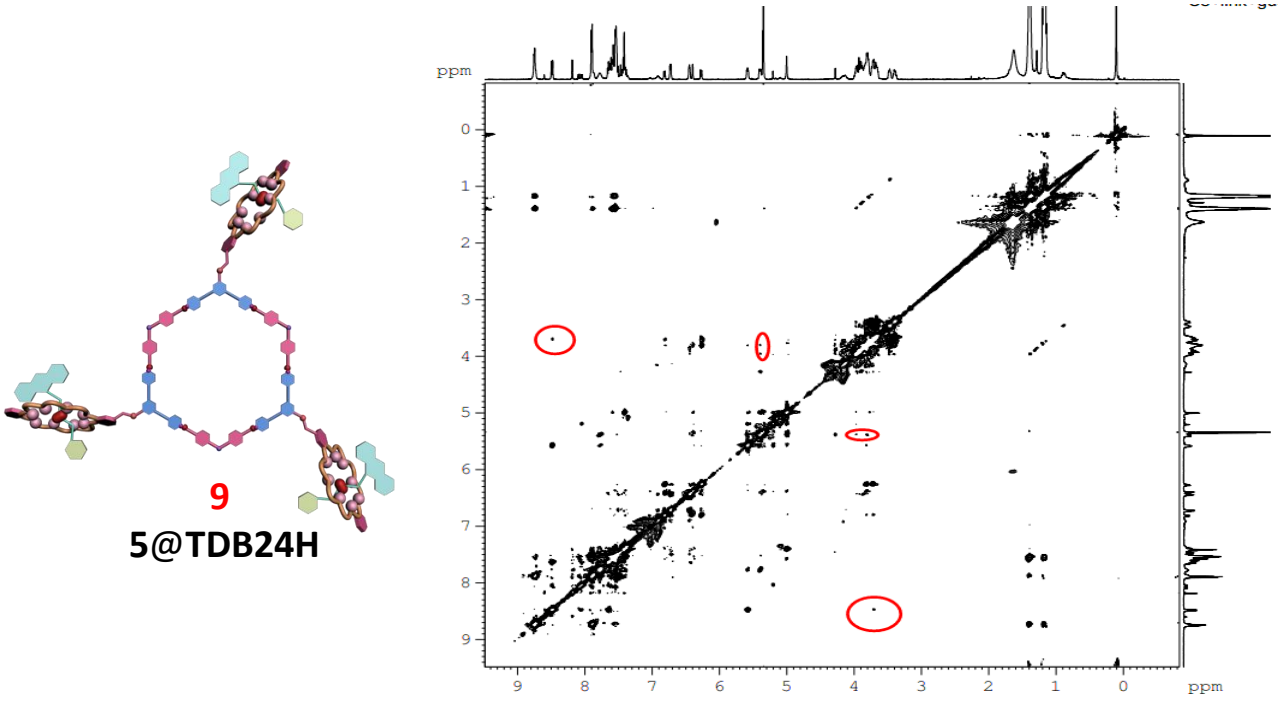
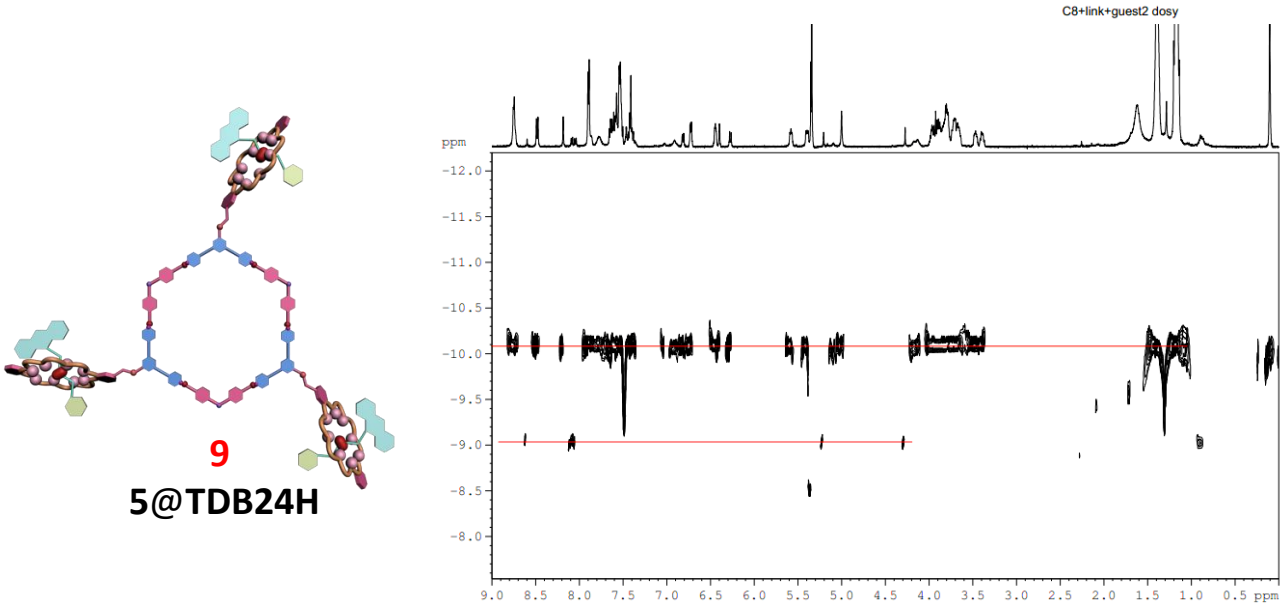
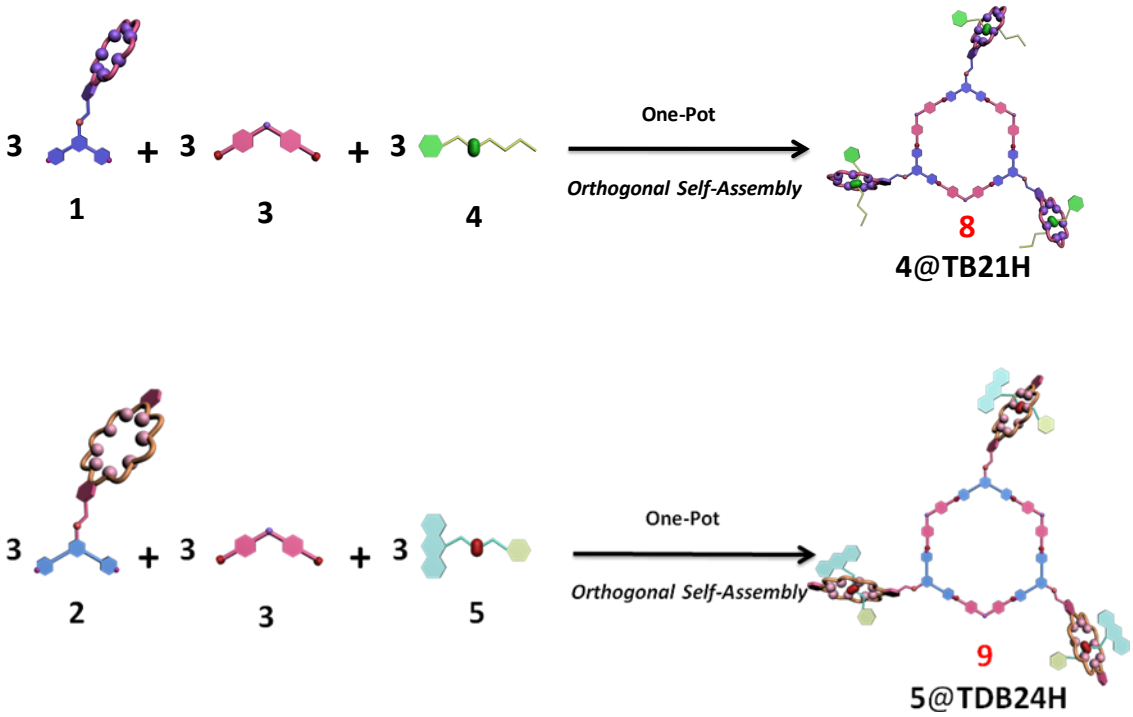


Figure S17. **DOSY Spectrum of the Complexation System of TDB24H and Guest 5 in CD_2Cl_2.** (The formation of the tris[2]pseduorotaxane **9** could be further confirmed by the decrease of the diffusion coefficient compared with free metallacycle **7**).



8. The Construction of the Individual Tris[2]pseudorotaxanes

Scheme S4. The Construction of the Individual Tris[2]pseudorotaxanes 8 and 9 via Orthogonal Self-Assembly Approach.



Preparation of Tris[2]pseudorotaxanes 4@TB21H: 8. To a mixture of 120° B21C7 containing building blocks **1** (1.38 mg, 0.00224 mmol), 120° di-Pt(II) acceptor **3** (2.93 mg, 0.00224 mmol), and guest **4** (0.70 mg, 0.00224 mmol) in a small vessel was added 0.5 mL dichloromethane-d_2 solution drop by drop with continuous stirring. The reaction mixture was stirred for another 1 h at room temperature and employed for the further characterizations directly.

Preparation of Tris[2]pseudorotaxanes 5@TDB24H: 9. To a mixture of 120° DB24C8 containing building blocks **2** (1.64 mg, 0.00217 mmol), 120° di-Pt(II) acceptor **3** (2.84 mg, 0.00217 mmol), and guest **5** (0.97 mg, 0.00217 mmol) in a small vessel was added 0.5 mL dichloromethane-d_2 solution drop by drop with continuous stirring. The reaction mixture was stirred for another 1 h at room temperature and employed for the further characterizations directly.

Figure S18. **^{1}H NMR Spectrum of the Tris[2]pseudorotaxanes 4@TB21H (8) in CD_2Cl_2.**

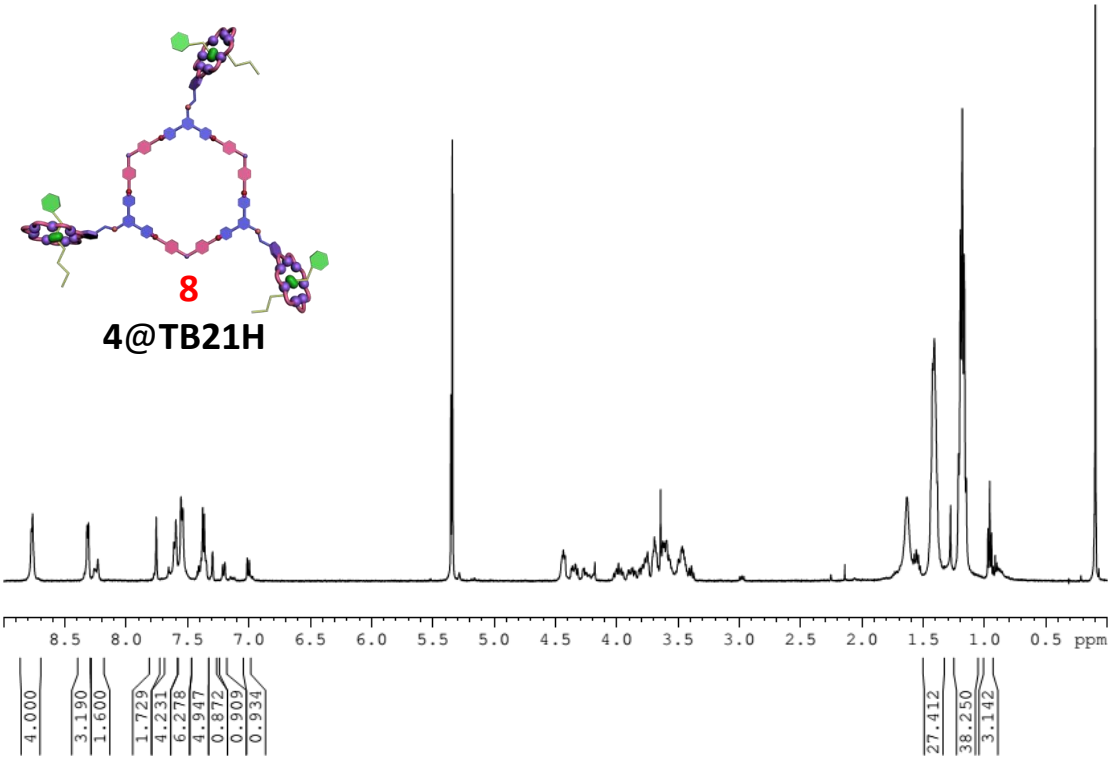
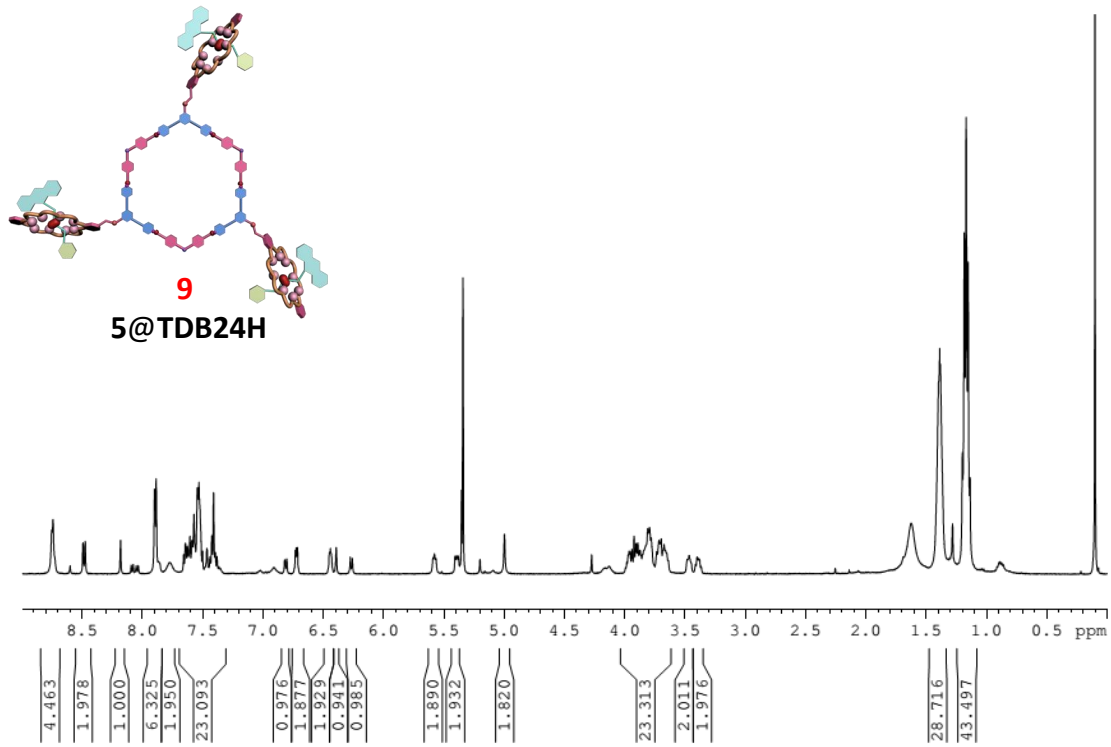


Figure S19. **^{1}H NMR Spectrum of the Tris[2]pseudorotaxanes 5@TDB24H (9) in CD_2Cl_2.**



9. NMR Spectrua of the Final Multicomponent Supramolecular System

Figure S20. **Partical ^{1}H NMR (500 MHz, CD_2Cl_2, 298K) of Metallacycle 6 and 7 (A, E); the Complexation System 6, 7 and 4 (1:1:3 ration) (*Method I - Step I*) (B); 6, 7 and 5 (1:1:3 ration) (*Method II - Step I*) (D); and the Final Multicomponent Supramolecular System (C), the detail statement of the stepwise approach was showed in the main text (*The stepwise approach for the construction of the MSS are shown at the top*).**

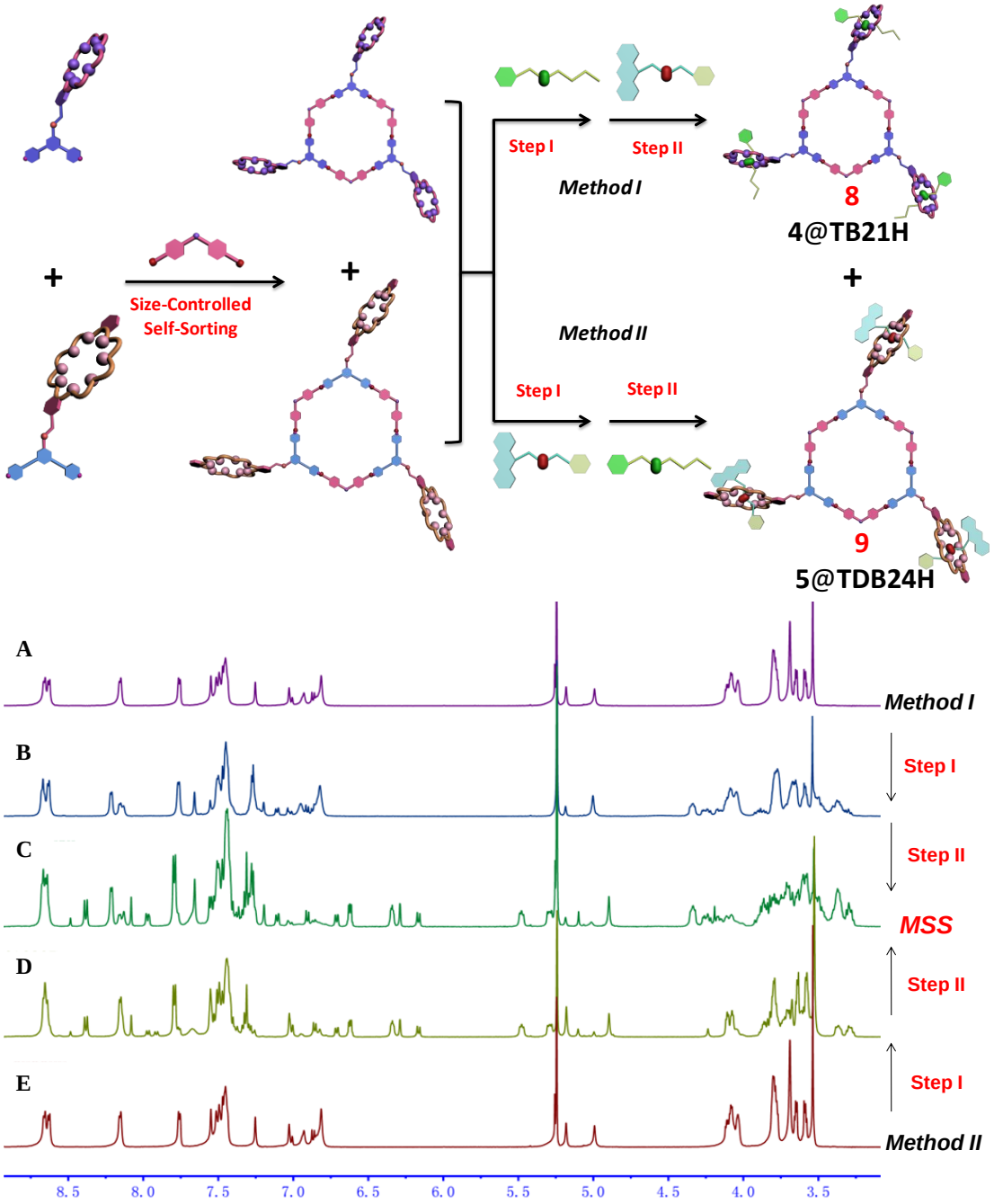


Figure S21. **ROESY Spectrum of the Complexation System of TB21H, TDB24H, and Guest 4 in CD_2Cl_2 (In a 1:1:3 ration) (*Method I - Step I*).**

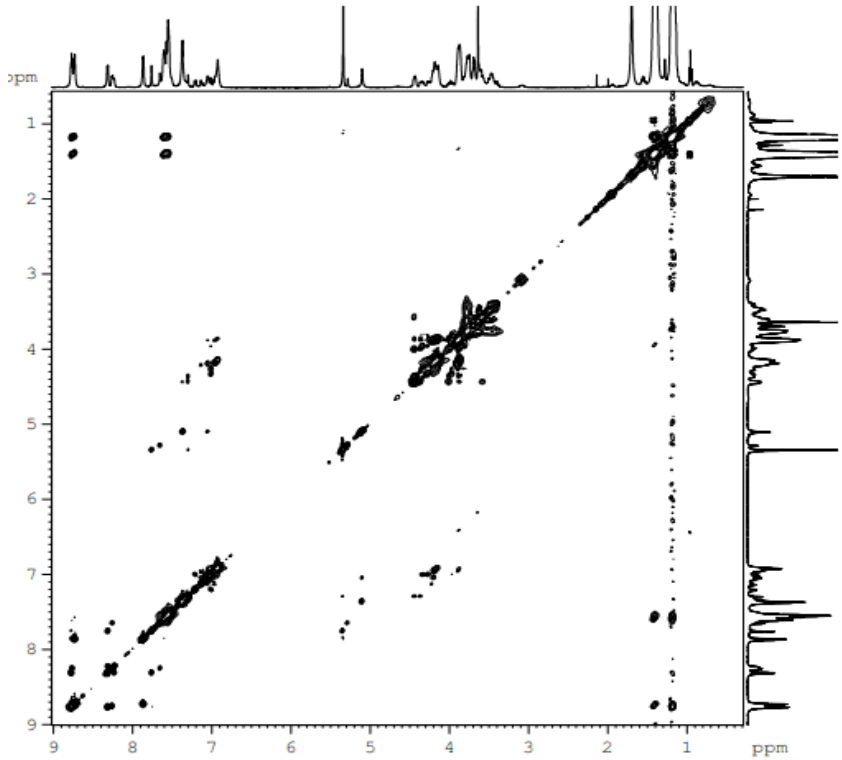


Figure S22. **DOSY Spectrum of the Complexation System of TB21H, TDB24H, and Guest 4 in CD_2Cl_2 (In a 1:1:3 ration) (*Method I - Step I*).**

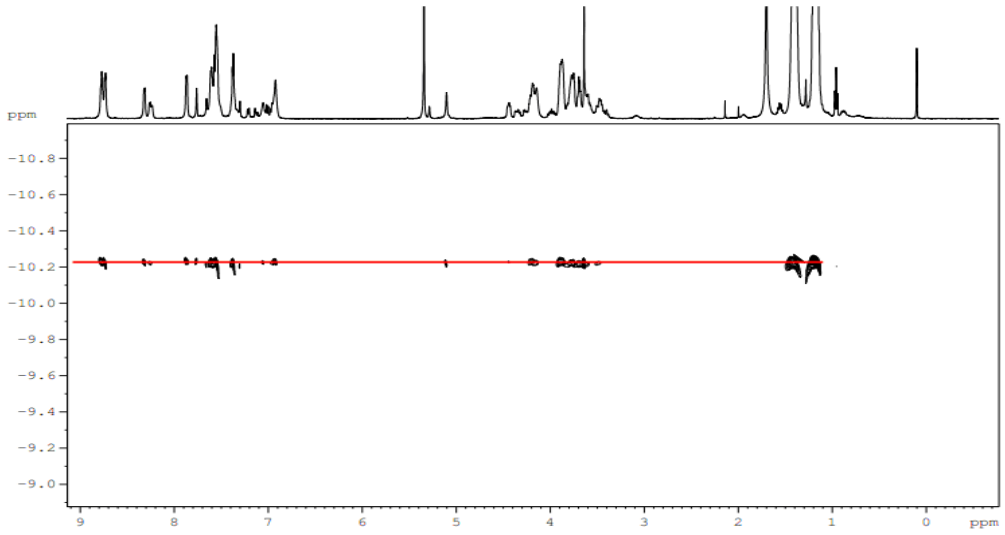


Figure S23. **NOESY Spectrum of the Complexation System of TB21H, TDB24H, and Guest 5 in CD_2Cl_2 (In a 1:1:3 ration) (*Method II - Step I*).**

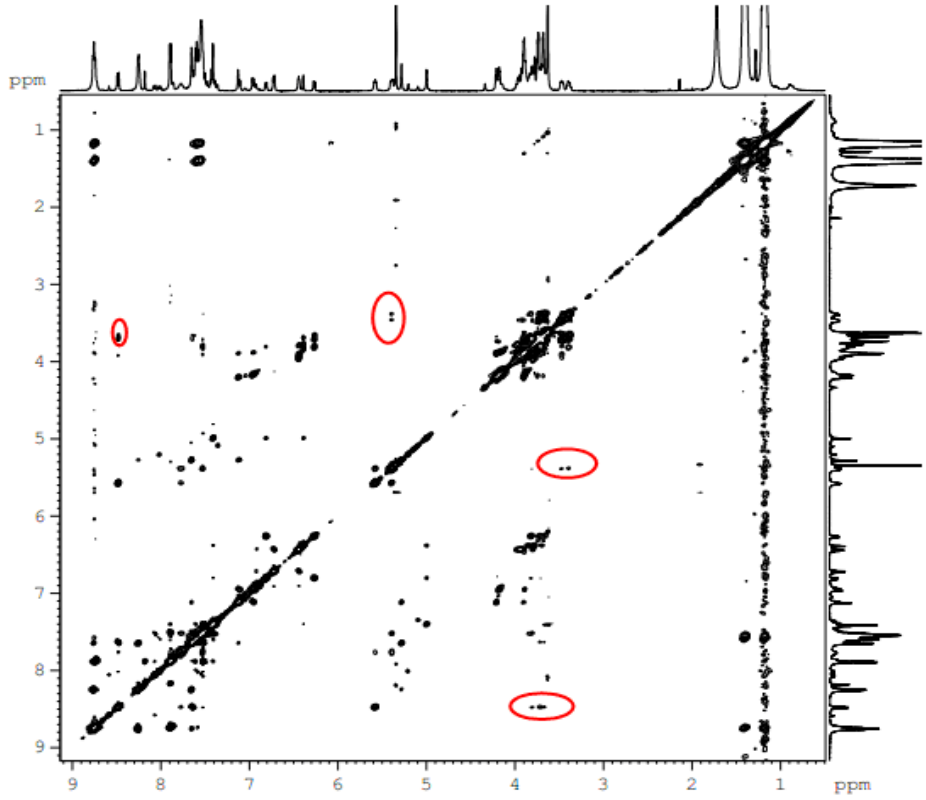


Figure S24. **DOSY Spectrum of the Complexation System of TB21H, TDB24H, and Guest 5 in CD_2Cl_2 (In a 1:1:3 ration) (*Method II - Step I*).**

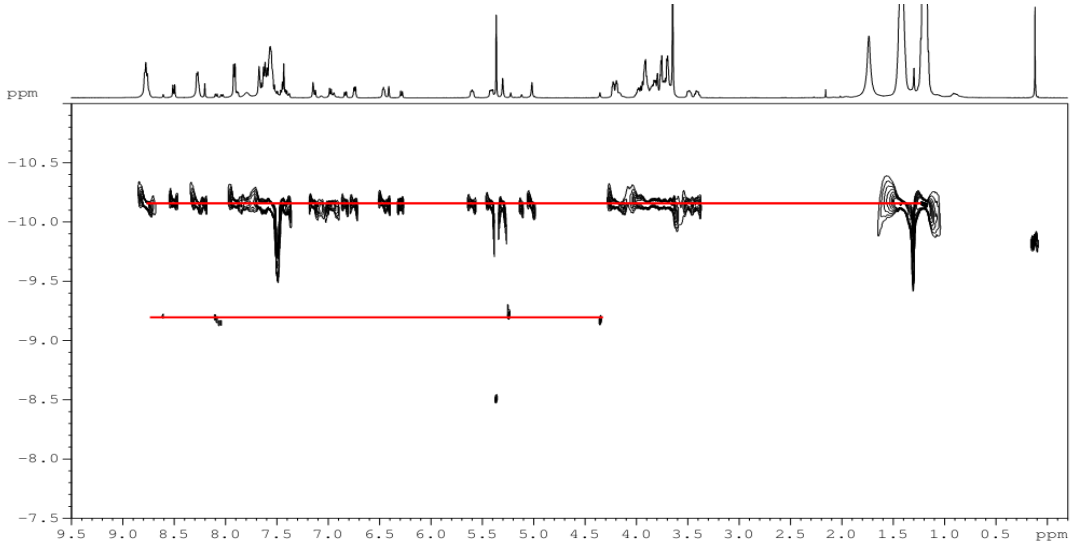
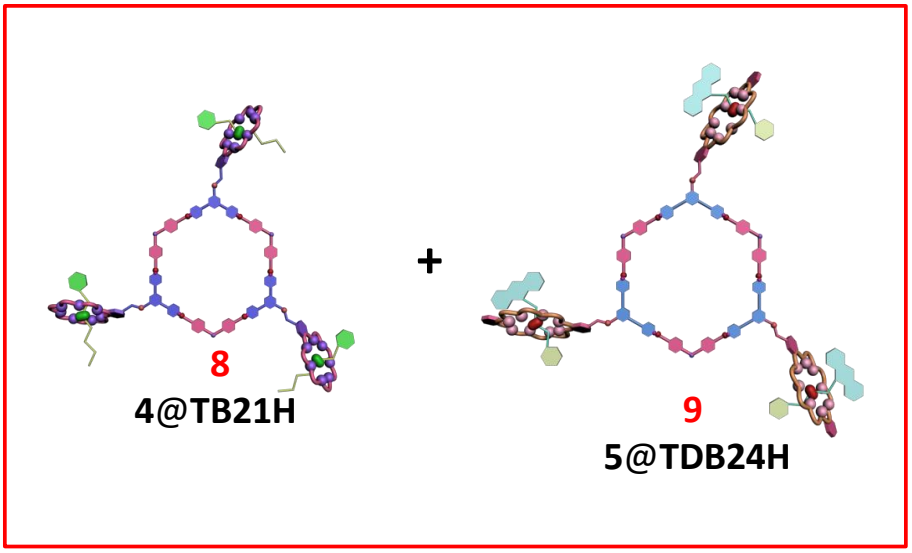


Figure S25. **NOESY Spectrum of the Final Multicomponent Supramolecular System in CD_2Cl_2.** (Clear correlations between the guest **5** and the **DB24C8** moiety in **TDB24H** were revealed, while the correlations between the guest **4** and the **B21C7** moiety in **TB21H** were not observed due to the overlaps among the related protons).



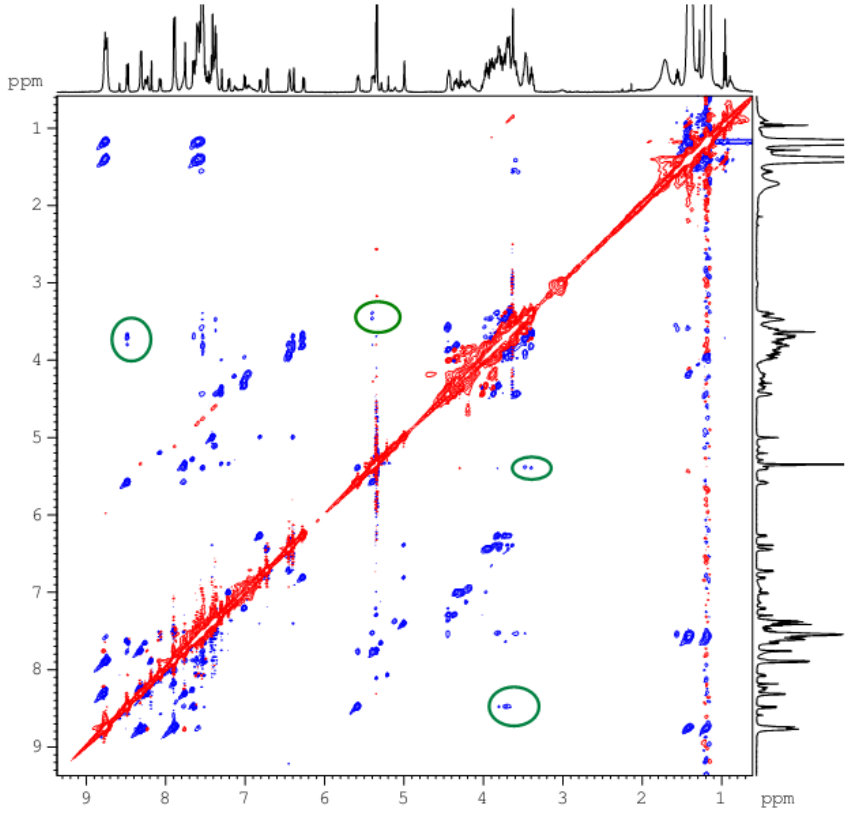
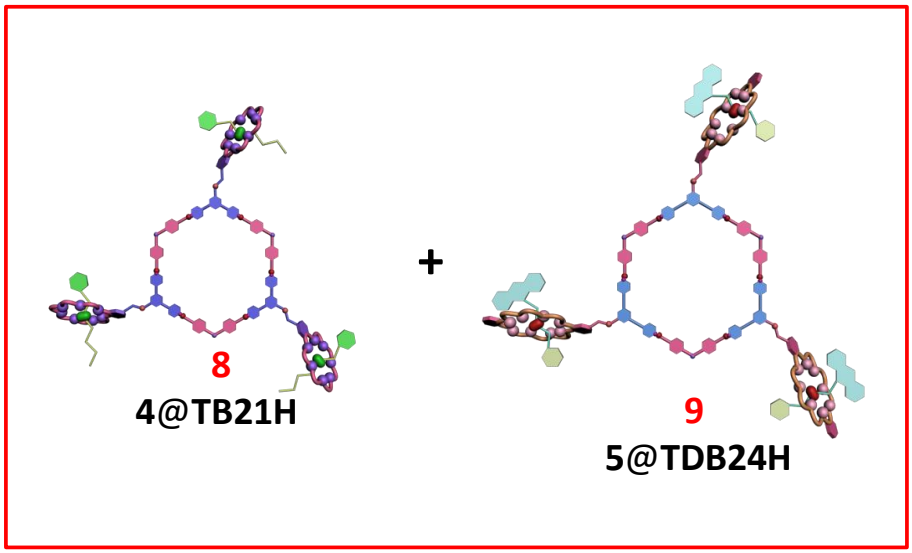
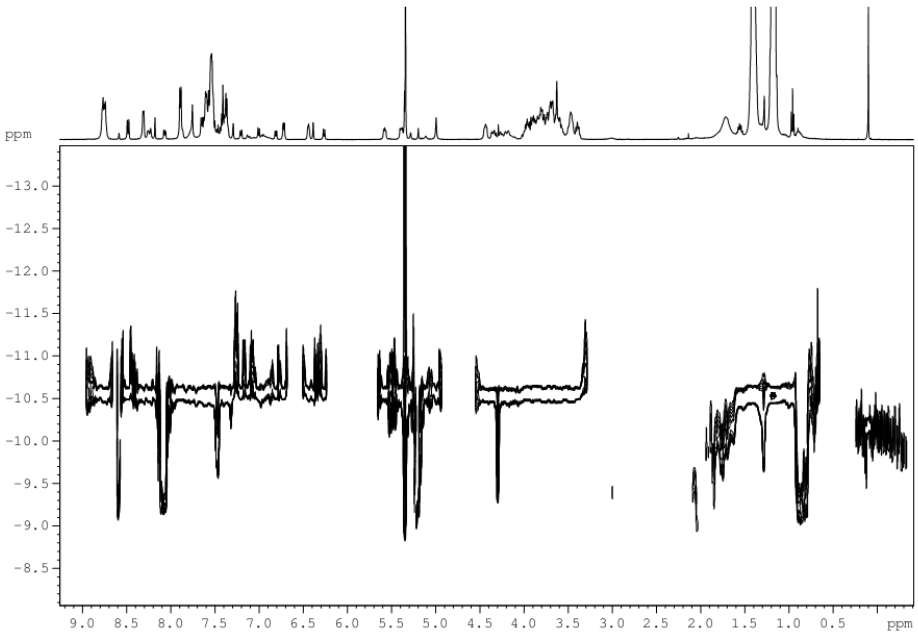


Figure S26. **DOSY Spectrum of the Final Multicomponent Supramolecular System in CD_2Cl_2.**





10. ESI-TOF Mass Spectra of the Final Multicomponent Supramolecular System

Figure S27. **Self-Sorted Complexation of the individual Building Blocks 1, 2 and Guests 4, 5.** As shown below, the self-sorted complexation system derived from these four components (B) revealed a superposition of the spectra of the two individual and separate complexation systems 4@1 (A) and 5@2 (C), thus clearly indicating the high-fidelity self-sorting complexation.

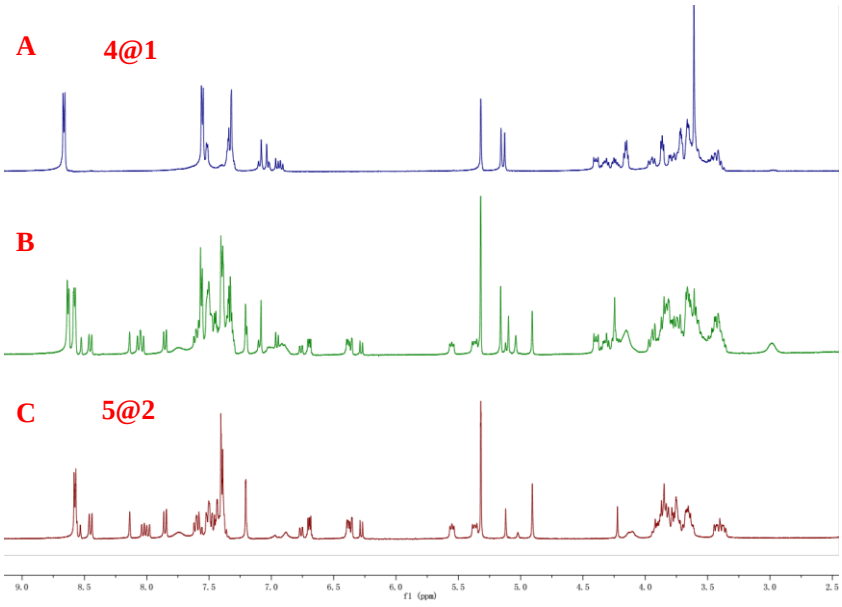


Figure S28. **ESI-TOF-MS Spectrum of the Self-Sorting System of the individual Building Blocks 1, 2 and Guests 4, 5.**

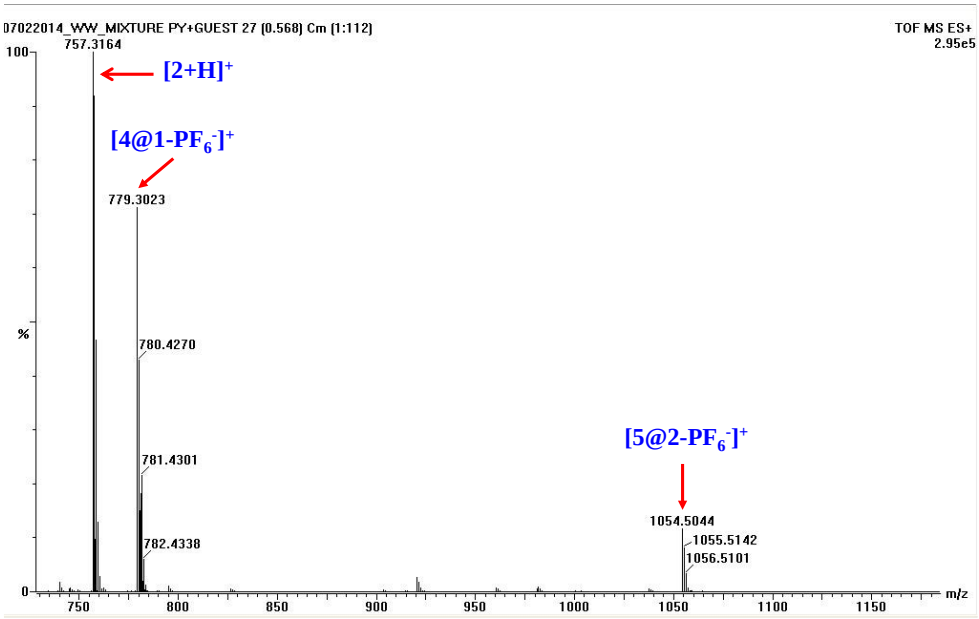
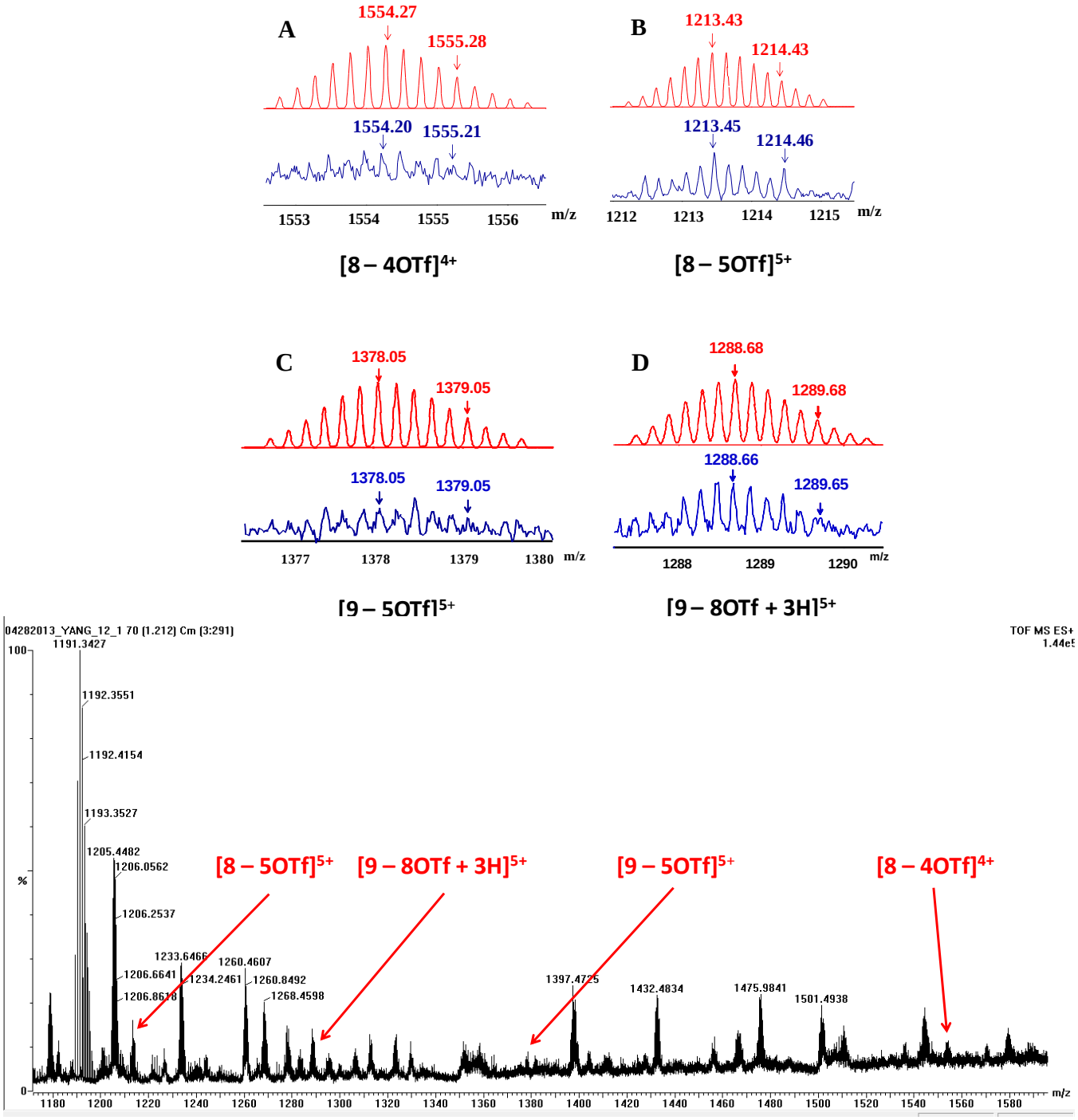


Figure S29. **Calculated (top) and Experimental (bottom) ESI-TOF-MS Spectrum of the Novel Metallacycle based Tris[2]pseudorotaxanes 8 (A, B) and 9 (C, D) in the Final Multicomponent Supramolecular System.**



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