Metal ion-modulated self-assembly of pseudo-suit[3]anes using crown ether-based terpyridine metalloprisms

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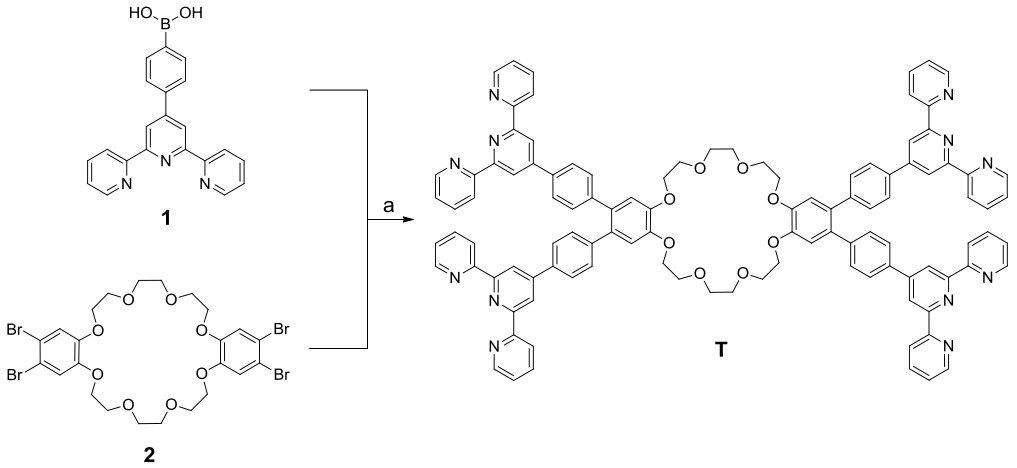
Materials and General Methods. Unless otherwise noted, reagents and solvents were received from Alfa Aesar, Sigma-Aldrich and used without further purification. Column chromatography was conducted using silica gel (75-200 μm) from Fuji Silysia GS series and basic Al_2O_3 (50-200 μm) from Acros. ^1H and ^{13}C NMR spectra were recorded at 25 °C on a Varian Mercury NMR 400 spectrometer, where chemical shifts (δ in ppm) were determined with respect to the nondeuterated solvents as a reference. The transmission electron microscope (TEM) images were recorded on a Hitachi Model H-7650 microscope operated at 120 kV or a JEOL EX-1200 microscope operated at 80 kV. TEM samples were prepared by drop-casting a sample solution (~10^{-8} M) onto a carbon-coated copper grid and dried *in vacuo* for 24 h.

Mass Spectrometry and Ion-Mobility Experiments. Mass spectrometry and traveling wave ion-mobility (TWIM) experiments were conducted on a Waters Synapt HDMS G2 with a LockSpray ESI source, using the same parameters in the literature.[1] Data were collected and analyzed by using MassLynx 4.1 and DriftScope 2.4 (Waters). The experimental collision cross-sections (CCSs) were obtained according to the literature procedure.[1] Matrix-assisted laser desorption/ionization coupled with time-of-flight detector (MALDI-TOF) mass spectrometry was conducted on a Bruker autoflex series spectrometer equipped with a nitrogen 337 nm laser. 1.0 μL of 2,5-dihydroxybenzoic acid (DHB) matrix solution (10 mg/mL in CH_3CN) was first deposited on a MALDI plate and air-dried. Aliquots of sample solution (1 mg/mL in $CHCl_3$) were then added onto the matrix spots for measurements.

Molecular Modeling. Energy-minimized structures were obtained following the same settings in the literature.[2] Calculations were proceeded with Anneal and Geometry Optimization functions in Forcite module of Materials Studio version 7.0 program (Accelrys Software, Inc.). For each structure, 200 conformations after annealing were generated and converted to collision cross-sections using projection approximation (PA) and trajectory method (TM) in MOBCAL.[3]

Synthesis of ligand **T**

4′-(4-Boronophenyl)-2,2′:6′,2″-terpyridine (**1**)[4] and 4,4′,5,5′-tetrabromodibenzo[24]crown-8 (**2**)[5] were synthesized according to the literature procedures.



Scheme S1. Synthesis of ligand **T**. *Reagents and conditions*: (a) $Pd(PPh_3)_4$, Na_2CO_3, toluene/H_2O/*t*-BuOH (3:3:1, v/v/v), reflux.

4,4′,5,5′-tetrakis[4-(4′-terpyridinyl)phenyl]dibenzo[24]crown-8 (T). To a degassed two-neck flask containing **2** (100.3 mg, 131.3 μmol), **1** (460.5 mg, 1.3 mmol), and Na_2CO_3 (138.0 mg, 1.3 mmol), a mixed solvent (70 mL) of toluene/H_2O/*t*-BuOH (3:3:1, v/v/v) was added. After being purged with N_2 for 30 min, $Pd(PPh_3)_4$ (58.3 mg, 50.5 μmol) was added into the mixture, which was then refluxed for 2 days under N_2. After cooling to room temperature, the aqueous layer was extracted with $CHCl_3$. The combined organic extract was dried over Na_2SO_4 and then evaporated to dryness under reduce pressure. The residue was purified by flash column chromatography (basic Al_2O_3, $CHCl_3$) and then recrystallized from MeOH to give **T** as a brown solid (180.2 mg, 0.11 mmol) in 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.71 (s, 8H), 8.69–8.64 (m, 8H), 8.62 (d, J = 7.9 Hz, 8H), 7.83 (td, J = 7.7 and 1.8 Hz, 8H), 7.80–7.75 (m, 8H), 7.32–7.26 (m, 16H), 7.03 (s, 4H), 4.29 (t, J = 4.2 Hz, 8H), 3.99 (t, J = 4.3 Hz, 8H), and 3.90 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.25, 155.80, 149.71, 149.04, 148.43, 142.05, 136.72, 136.30, 133.06, 130.43, 126.98, 123.65, 121.25, 118.73, 116.37, 71.37, 69.95, and 69.77. MALDI-TOF-MS: calcd. for $C_{108}H_{85}N_{12}O_8$ $[M+H]^+$: m/z = 1678.6647; found: 1678.6517 and calcd. for $C_{108}H_{84}N_{12}NaO_8$ $[M+Na]^+$: m/z = 1700.6466; found: 1700.6394.

^{1}H and ^{13}C NMR spectra of ligand **T**

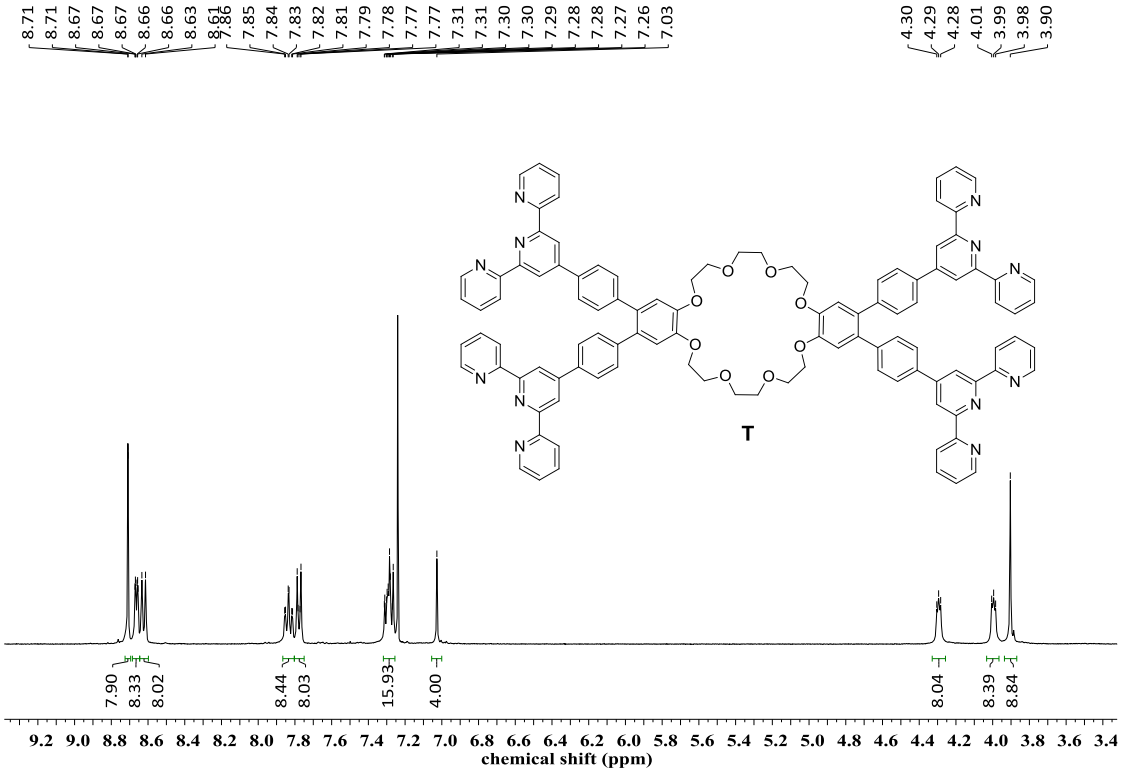


Fig. S1 ^{1}H NMR spectrum of **T** in $CDCl_3$.

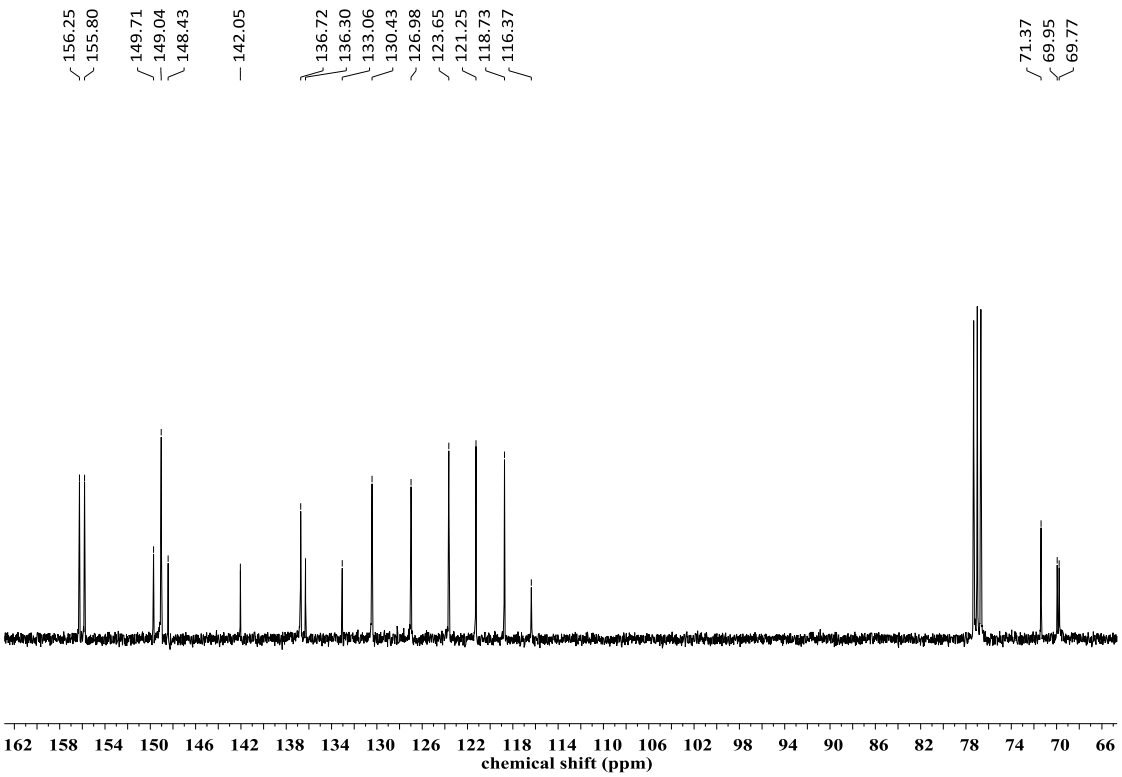


Fig. S2 ^{13}C NMR spectrum of **T** in $CDCl_3$.

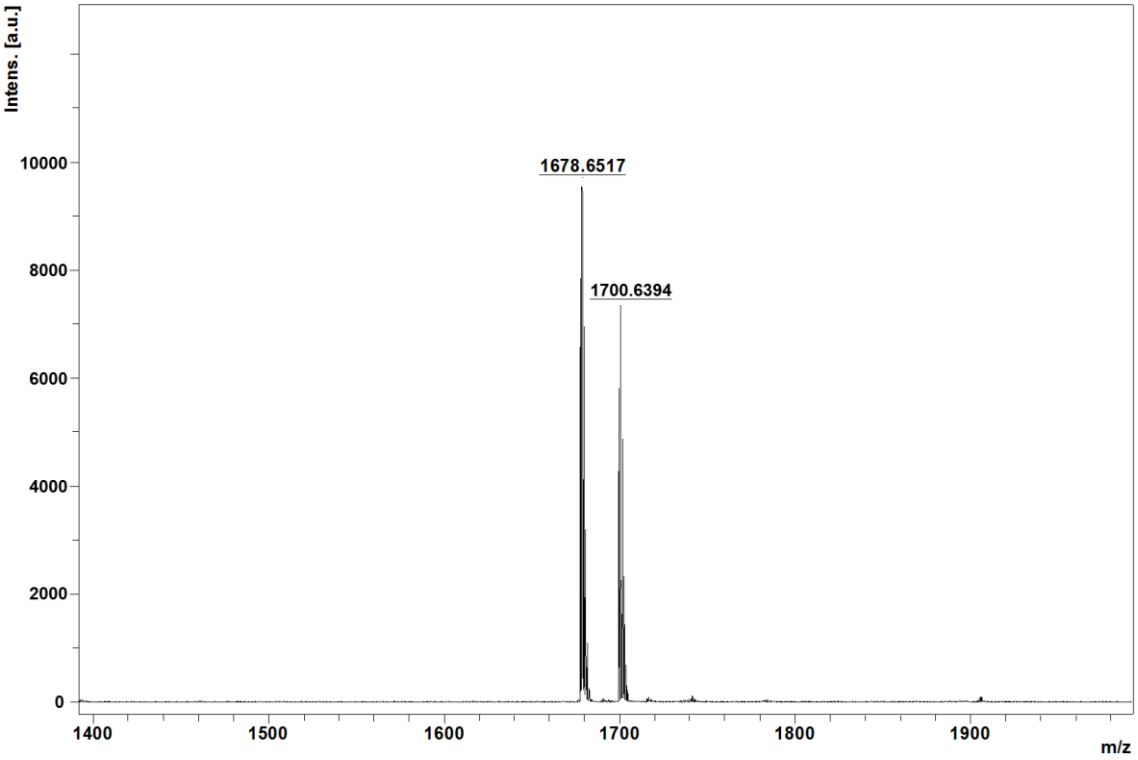


Fig. S3 MALDI-TOF-MS spectrum of **T**.

Complexation Reactions

[Cd$_6$T$_3$]. To a stirred $CHCl_3$ solution (5 mL) of **T** (20.5 mg, 12.2 μmol), a MeOH solution (5 mL) of $Cd(NO_3)_2{\cdot}4H_2O$ (7.7 mg, 24.9 μmol) was added. A small amount of $MeNO_2$ was added in order to improve the solubility. After the mixture was stirred for 30 min at 25 °C, an excess amount of NH_4PF_6 (82.0 mg, 0.5 mmol) was added to precipitate the counterion-exchanged complex (PF_6^-), and then the mixture was stirred for additional 30 min. The precipitate was filtered, washed with H_2O, and dried *in vacuo* to give [Cd$_6$**T**$_3$] (29.1 mg, 3.9 μmol) in 95% yield. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 8.88 (s, 24H), 8.62 (d, J = 8.2 Hz, 24H), 8.08 (d, J = 8.4 Hz, 24H), 7.95 (d, J = 4.2 Hz, 24H), 7.81 (dt, J = 7.8 and 1.6 Hz, 24H), 7.55 (d, J = 8.3 Hz, 24H), 7.18 (s, 12H), 7.02 (dd, J = 7.4 and 5.8 Hz, 24H), 4.43 (t, J = 10.1 Hz, 12H), 4.27 (d, J = 9.5 Hz, 12H), 4.00–3.87 (m, 36H), and 3.72–3.67 (m, 12H). ESI-MS (*m/z*): 1717.0066 $[M\text{-}4PF_6]^{4+}$ (calcd. *m/z* = 1717.0266), 1344.6158 $[M\text{-}5PF_6]^{5+}$ (calcd. *m/z* = 1344.6284), 1096.3457 $[M\text{-}6PF_6]^{6+}$ (calcd. *m/z* = 1096.3630), 919.0110 $[M\text{-}7PF_6]^{7+}$ (calcd. *m/z* = 919.0306), 786.1445 $[M\text{-}8PF_6]^{8+}$ (calcd. *m/z* = 786.0312), and 668.5806 $[M\text{-}PF_5\text{-}9PF_6]^{9+}$ (calcd. *m/z* = 668.5873).

[Zn$_6$T$_3$]. To a stirred $CHCl_3$ solution (10 mL) of **T** (41.0 mg, 24.5 μmol), a MeOH solution (10 mL) of $Zn(NO_3)_2{\cdot}6H_2O$ (15.1 mg, 49.9 μmol) was added. After the mixture was stirred for 30 min at 25 °C, an excess amount of NH_4PF_6 (159.4 mg, 1.0 mmol) was added to precipitate the counterion-exchanged complex (PF_6^-), which was filtered,

washed with H_2O, and redissolved in MeCN (210 mL). After the solution was stirred at 70 °C for 3 days, the mixture was poured into Et_2O to precipitate the complex, which was filtered, washed with H_2O, and dried *in vacuo* to give [Zn_6**T**$_3$] (58.0 mg, 8.1 μmol) in 99% yield. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 8.92 (s, 24H), 8.55 (d, J = 8.1 Hz, 24H), 8.12 (d, J = 8.3 Hz, 24H), 7.69 (d, J = 4.6 Hz, 24H), 7.65 (dt, J = 7.8 and 1.5 Hz, 24H), 7.57 (d, J = 8.2 Hz, 24H), 7.21 (s, 12H), 6.83 (dd, J = 7.0 and 5.4 Hz, 24H), 4.45 (t, J = 8.4 Hz, 12H), 4.29 (d, J = 9.0 Hz, 12H), 4.00–3.86 (m, 36H), and 3.72–3.68 (m, 12H). ESI-MS (*m/z*): 1646.2517 $[M\text{-}4PF_6]^{4+}$ (calcd. *m/z* = 1646.3130), 1288.0162 $[M\text{-}5PF_6]^{5+}$ (calcd. *m/z* = 1288.0592), 1049.1753 $[M\text{-}6PF_6]^{6+}$ (calcd. *m/z* = 1049.2206), 878.5874 $[M\text{-}7PF_6]^{7+}$ (calcd. *m/z* = 878.6216), 750.6469 $[M\text{-}8PF_6]^{8+}$ (calcd. *m/z* = 750.6744), and 637.1447 $[M\text{-}PF_5\text{-}9PF_6]^{9+}$ (calcd. *m/z* = 637.1625).

2D NMR spectra of [Cd_6**T**$_3$]

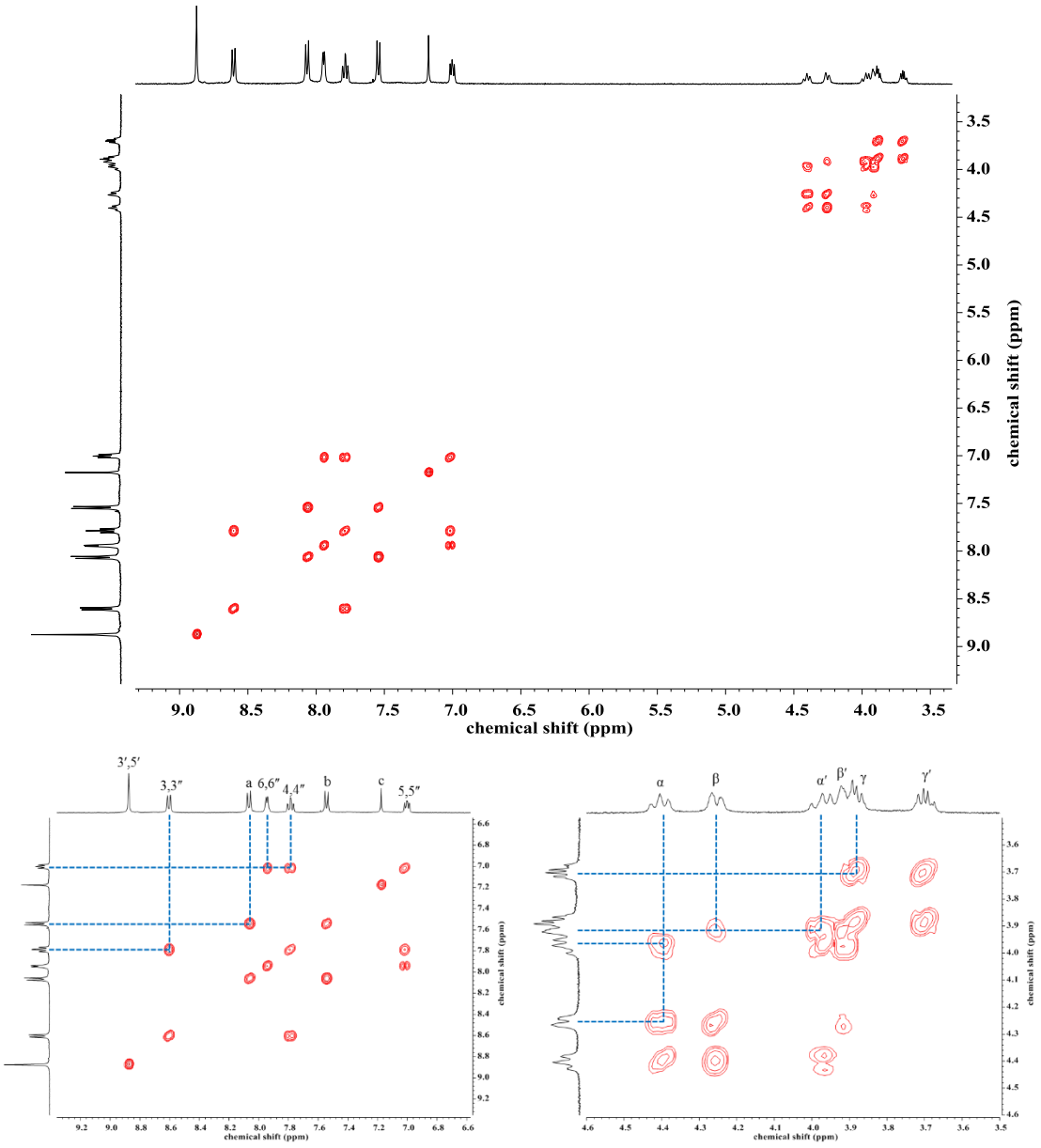


Fig. S4 COSY spectra of [Cd_6**T**$_3$] in CD_3CN.

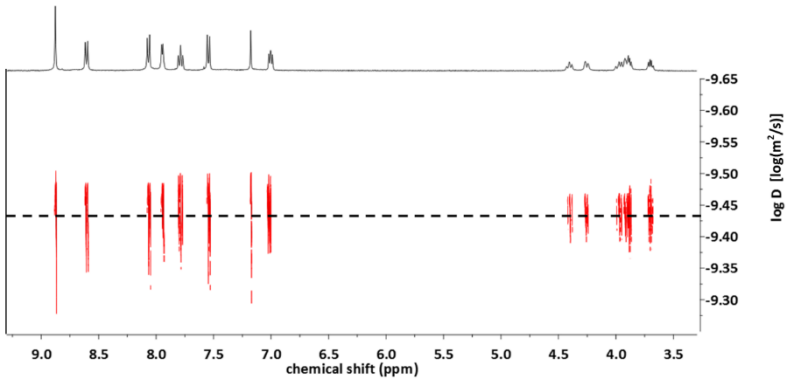


Fig. S5 DOSY spectrum of [Cd_6**T**$_3$] in CD_3CN.

2D NMR spectra of [Zn_6**T**$_3$]

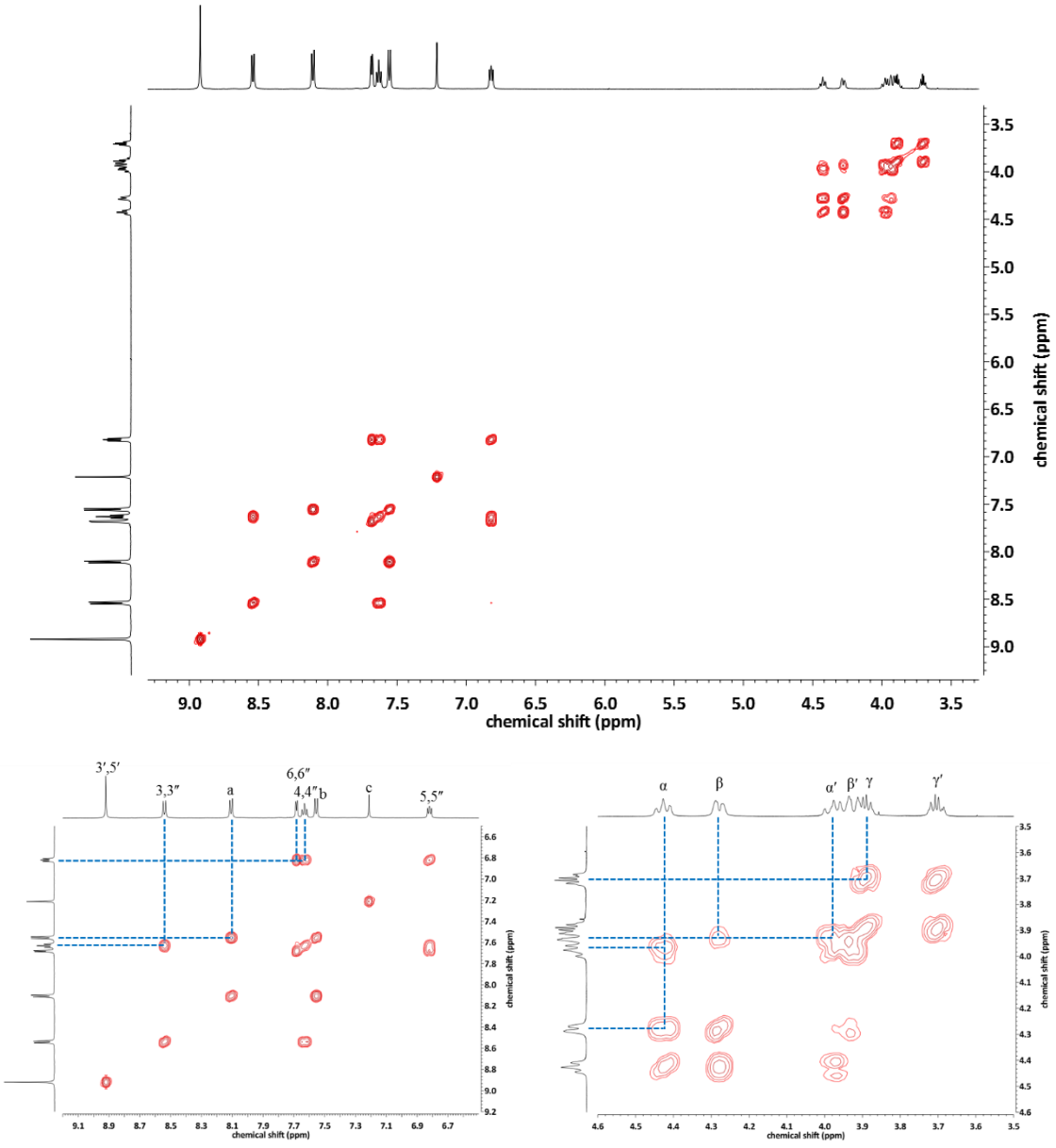


Fig. S6 COSY spectra of [Zn_6**T**$_3$] in CD_3CN.

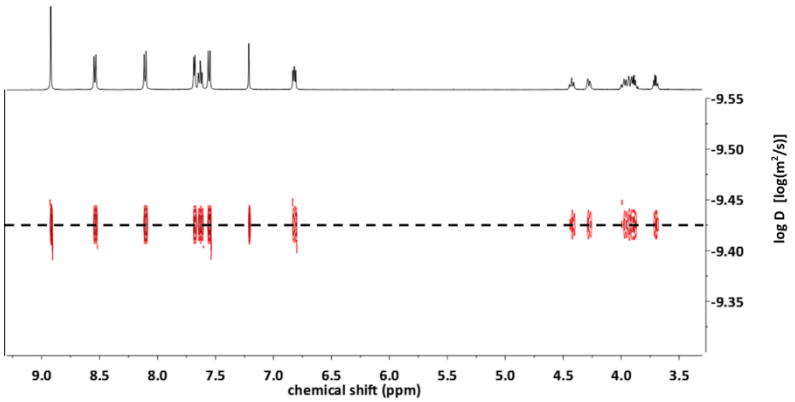


Fig. S7 DOSY spectrum of [Zn_6**T**$_3$] in CD_3CN.

ESI-MS spectra of $[Cd_6\mathbf{T}_3]$ and $[Zn_6\mathbf{T}_3]$

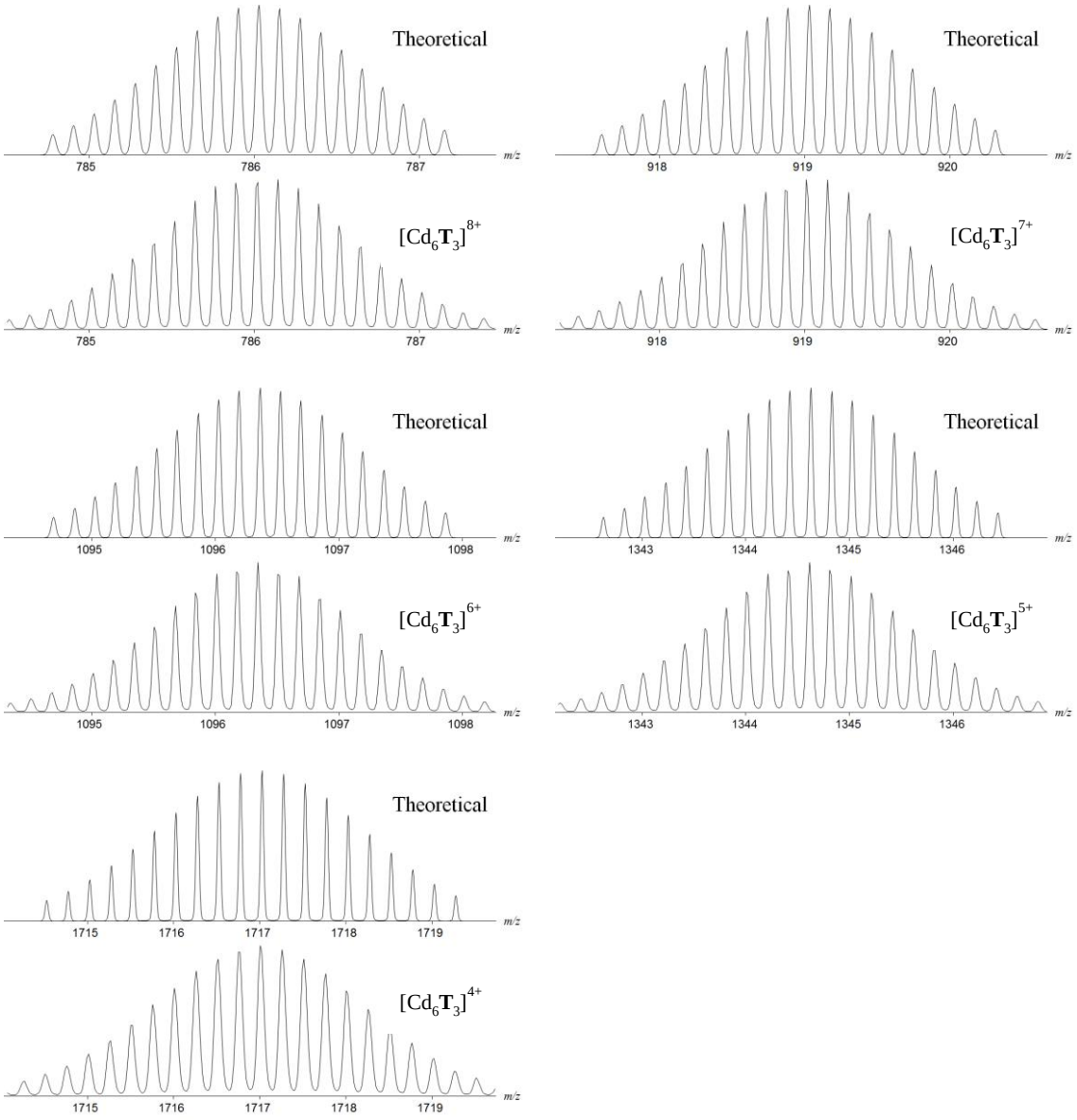


Fig. S8 Experimental and theoretical ESI-MS isotope patterns of $[Cd_6\mathbf{T}_3]$.

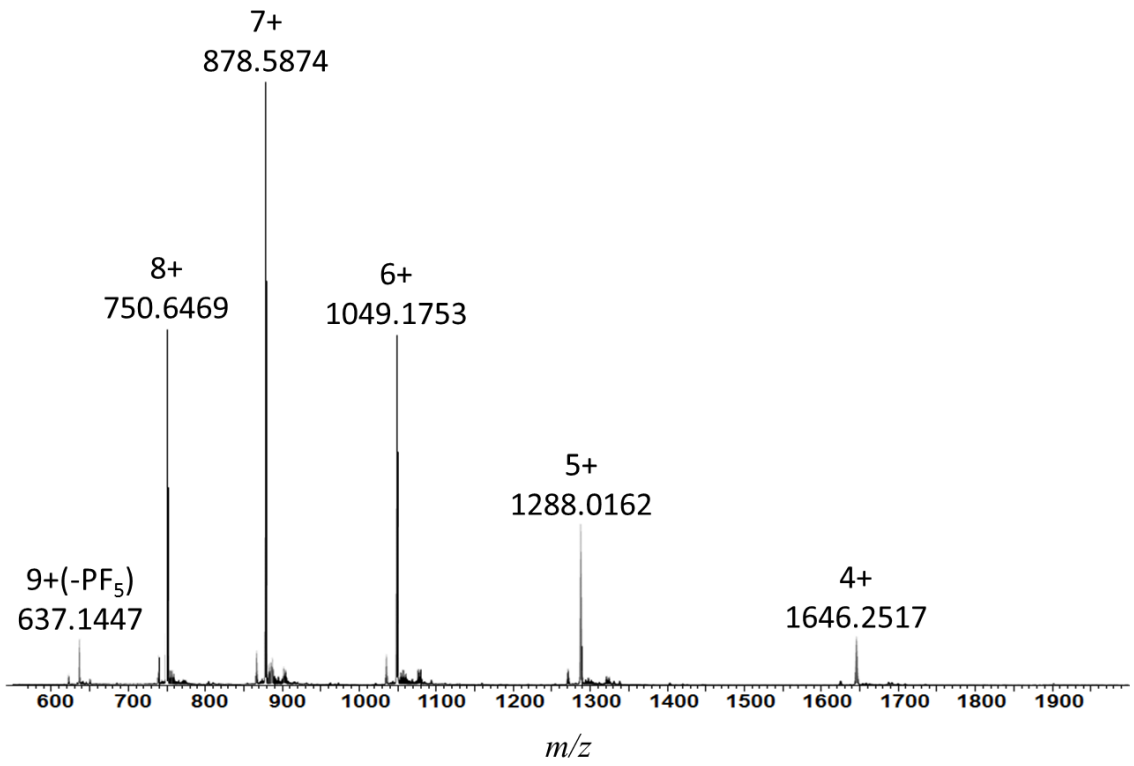


Fig. S9 ESI-MS spectrum of [Zn_6**T**$_3$].

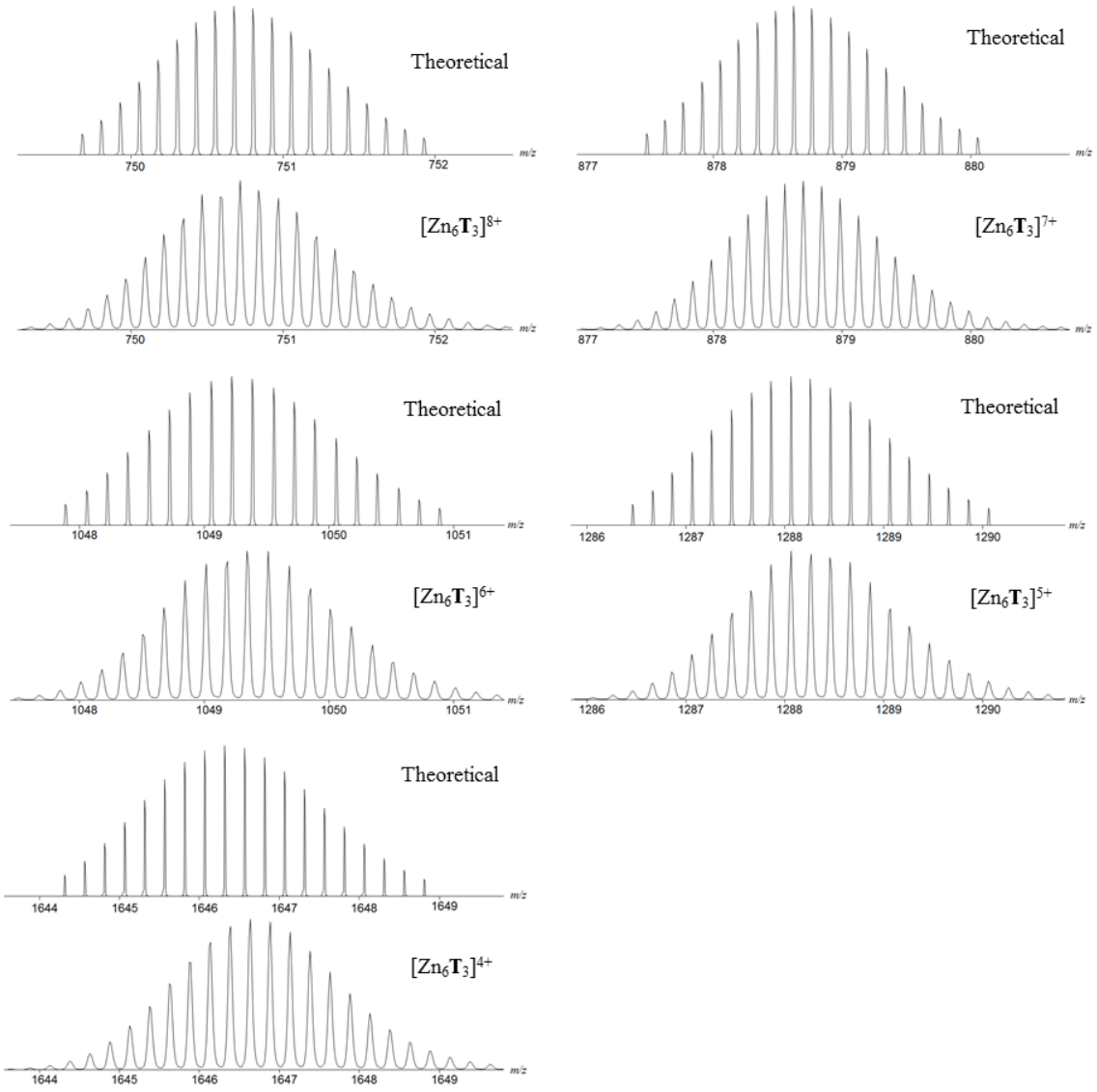


Fig. S10 Experimental and theoretical ESI-MS isotope patterns of $[Zn_6\mathbf{T}_3]$.

ESI-TWIM-MS plot of [Zn_6**T**$_3$]

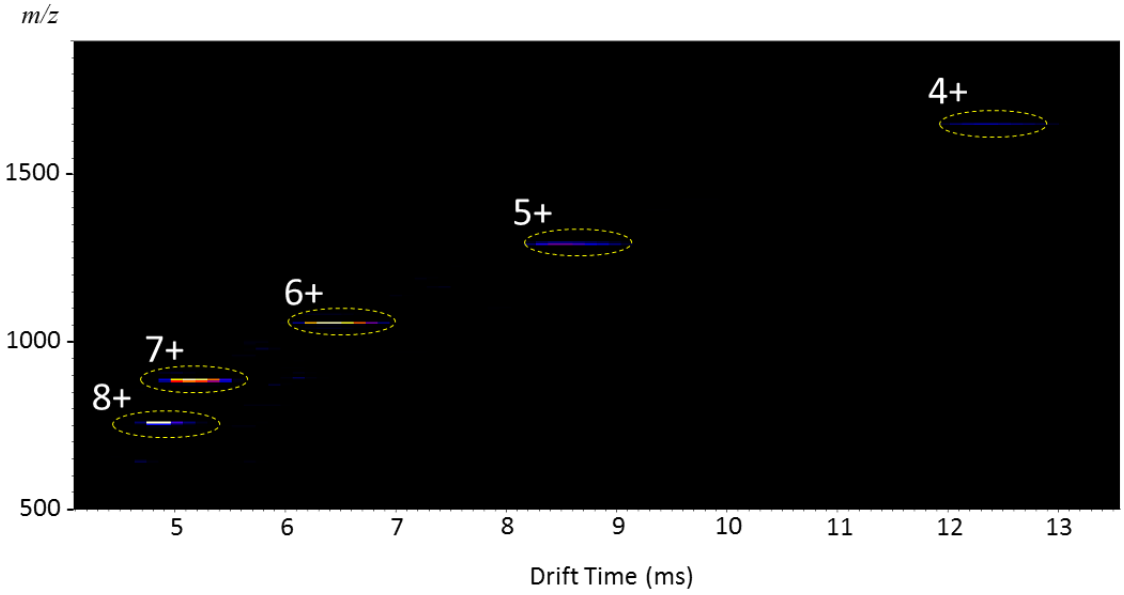


Fig. S11 ESI-TWIM-MS plot of [Zn_6**T**$_3$].

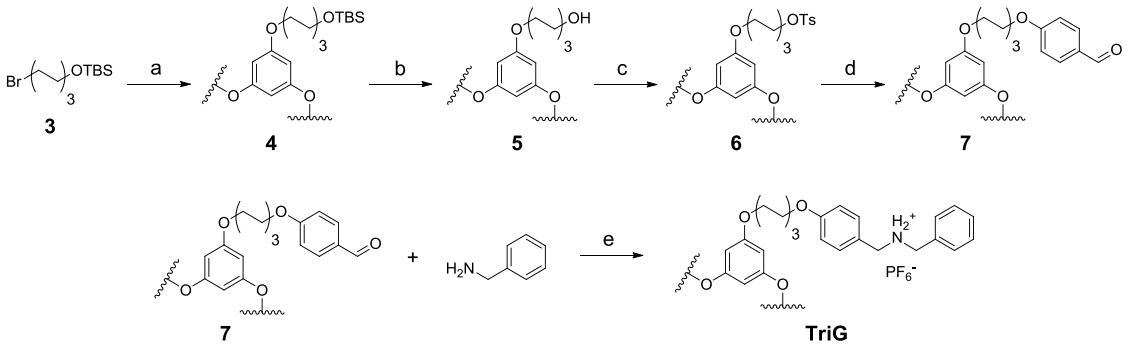
Table S1 Experimental and theoretical average collision cross-sections of [Cd_6**T**$_3$] and [Zn_6**T**$_3$].

Drift time (ms)	Exp. CCS (Å^2)	Exp. Avg. CCS (Å^2)	Calcd. Avg. CCS (Å^2)
	[Cd_6**T**$_3$]		
12.46 (4+)	829.8		
8.60 (5+)	796.0		699.1±4.2[a]
6.50 (6+)	774.7	803.8±34.9	829.0±15.1[b]
5.29 (7+)	768.8		
5.07 (8+)	849.4		
	[Zn_6**T**$_3$]		
12.13 (4+)	814.5		
8.38 (5+)	781.2		688.1±4.1[a]
6.28 (6+)	754.5	776.7±34.9	814.3±14.8[b]
4.96 (7+)	729.7		
4.74 (8+)	803.7		

[a] PA and [b] TM values obtained by using MOBCAL.

Synthesis of **TriG**

[(6-Bromohexyl)oxy](*tert*-butyl)dimethylsilane (**3**) were synthesized according to the literature procedure.[6]



Scheme S2 Synthesis of **TriG**. *Reagents and conditions*: (a) phloroglucinol, K_2CO_3, DMF, 90 °C; (b) TBAF, 0 °C; (c) TsCl, Et_3N, DCM, 0 °C; (d) 4-hydroxybenzaldehyde, K_2CO_3, MeCN, reflux; (e) 1) toluene, reflux, 2) $NaBH_4$, MeOH, 25 °C, 3) $HCl_{(aq)}$, 25 °C, 4) $NH_4PF_{6(aq)}$, MeCN, 25 °C.

Compound 4. To a stirred solution of **3** (6.7 g, 22.5 mmol), phloroglucinol (0.9 g, 6.8 mmol), and potassium carbonate (4.2 g, 30.7 mmol), anhydrous DMF (20 mL) was added. The mixture was stirred at 90 °C for 12 h, then poured into $NH_4Cl_{(aq)}$, and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane/EtOAc = 10:1, v/v) to afford **4** as a colorless oil (4.1 g, 5.4 mmol) in 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.03 (s, 3H), 3.88 (t, J = 6.5 Hz, 6H), 3.59 (t, J = 6.5 Hz, 6H), 1.74 (m, 6H), 1.60–1.29 (m, 18H), 0.87 (s, 27H), and 0.03 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.89, 93.72, 67.88, 63.14, 32.75, 29.25, 25.98, 25.87, 25.60, 18.36, -5.24, and -5.27. ESI-MS: calcd. for $C_{42}H_{85}O_6Si_3$ $[M+H]^+$: m/z = 769.5654; found: 769.5649.

Compound 5. To a THF solution (5 mL) of **4** (4.3 g, 5.6 mmol), a THF solution (1 M, 20 mL) of tetrabutylammonium fluoride was added at 0 °C. After the mixture was stirred at 25 °C for 12 h, the solvent was evaporated under reduced pressure and the residue was subjected to column chromatography (SiO_2, EtOAc) to give **5** as a colorless oil (2.4 g, 5.6 mmol) in 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.03 (s, 3H), 3.89 (t, J = 6.5 Hz, 6H), 3.64 (t, J = 6.6 Hz, 6H), 1.74 (m, 6H), and 1.65–1.33 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.82, 93.75, 67.79, 62.77, 32.60, 29.12, 25.82, and 25.45. ESI-MS: calcd. for $C_{24}H_{43}O_6$ $[M+H]^+$: m/z = 427.3060; found: 427.3026.

Compound 6. To an anhydrous DCM solution (10 mL) of **5** (2.4 g, 5.6 mmol) and *p*-toluenesulfonyl chloride (4.8 g, 25.2 mmol), triethylamine (4.8 mL, 33.6 mmol) was added at 0 °C. After the mixture was stirred at 25 °C for 12 h, the mixture was poured into H_2O and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane/EtOAc = 1:1, v/v) to give **6** as a yellow oil (2.2 g, 2.5 mmol) in 44% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.77 (d, J = 7.8 Hz, 6H), 7.32 (d, J = 7.9 Hz, 6H), 5.99 (s, 3H), 4.01 (t, J = 6.4 Hz, 6H), 3.84 (t, J = 6.4 Hz, 6H), 2.42 (s, 9H), 1.66 (m, 12H), and 1.37 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.77, 144.65, 133.06, 129.78, 127.80, 93.68, 70.45, 67.57, 28.93, 28.70, 25.42, 25.10, and 21.58. ESI-MS: calcd. for $C_{45}H_{60}O_{12}NaS_3$ $[M+Na]^+$: m/z = 911.3145; found: 911.3149.

Compound 7. To a flask containing **6** (1.4 g, 1.6 mmol), 4-hydroxybenzaldehyde (0.9 g, 7.1 mmol), and potassium carbonate (1.9 g, 14.1 mmol), anhydrous acetonitrile (20 mL) was added. The mixtures was refluxed for 36 h, then poured into $NH_4Cl_{(aq)}$, and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/EtOAc = 20:1, v/v) to afford **7** as a yellow oil (1.1 g, 1.5 mmol) in 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.86 (s, 3H), 7.80 (d, J = 8.3 Hz, 6H), 6.97 (d, J = 8.7 Hz, 6H), 6.04 (s, 3H), 4.03 (t, J = 6.4 Hz, 6H), 3.90 (t, J = 6.4 Hz, 6H), 1.80 (m, 12H), and 1.61–1.46 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 190.73, 164.10, 160.83, 131.92, 129.70, 114.67, 93.70, 68.16, 67.68, 29.08, 28.92, 25.78, and 25.70. ESI-MS: calcd. for $C_{45}H_{54}O_9Na$ $[M+Na]^+$: m/z = 761.3666; found: 761.3645.

Compound TriG. To a flask containing **7** (196.4 mg, 0.3 mmol) and benzylamine (85 mg, 0.8 mmol), anhydrous toluene (20 mL) was added. The mixture was refluxed for 12 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in a mixed solvent (20 mL) of CH_2Cl_2/MeOH (1:1, v/v). Subsequently, $NaBH_4$ (1.0 g, excess) was added into the mixture, which was stirred at 25 ^{o}C for 4 h. The reaction mixture was poured into H_2O and extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue suspended in hydrochloric acid (37%, excess) was stirred at room temperature for 0.5 h. The white precipitate was filtered and washed with CH_2Cl_2 to give the white solid, which was suspended in MeCN (5 mL). Saturated $NH_4PF_{6(aq)}$ was added into the suspension until the solid was totally dissolved. The solution was concentrated *in vacuo* and the precipitate was filtered and washed with H_2O to give **TriG** as a white solid (20.2 mg, 14.0 μmol) in 5% yield. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm)

7.45 (s, 15H), 7.37 (d, J = 8.7 Hz, 6H), 6.95 (d, J = 8.7 Hz, 6H), 6.04 (s, 3H), 4.18 (s, 6H), 4.14 (s, 6H), 4.00 (t, J = 6.5 Hz, 6H), 3.92 (t, J = 6.5 Hz, 6H), 1.76 (m, 12H), and 1.50 (m, 12H). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 161.94, 160.98, 132.66, 131.76, 130.95, 130.49, 129.93, 123.30, 115.66, 94.56, 68.79, 68.64, 52.08, 51.95, 29.78, 29.72, 26.40, and 26.35. ESI-MS (m/z): 1304.7002 $[M\text{-}PF_6]^+$ (calcd. m/z = 1304.5643), 1158.6903 $[M\text{-}H\text{-}2PF_6]^+$ (calcd. m/z = 1158.5924), and 1012.6776 $[M\text{-}2H\text{-}3PF_6]^+$ (calcd. m/z = 1012.6204).

^{1}H and ^{13}C NMR spectra of compounds **4**, **5**, **6**, **7**, and **TriG**

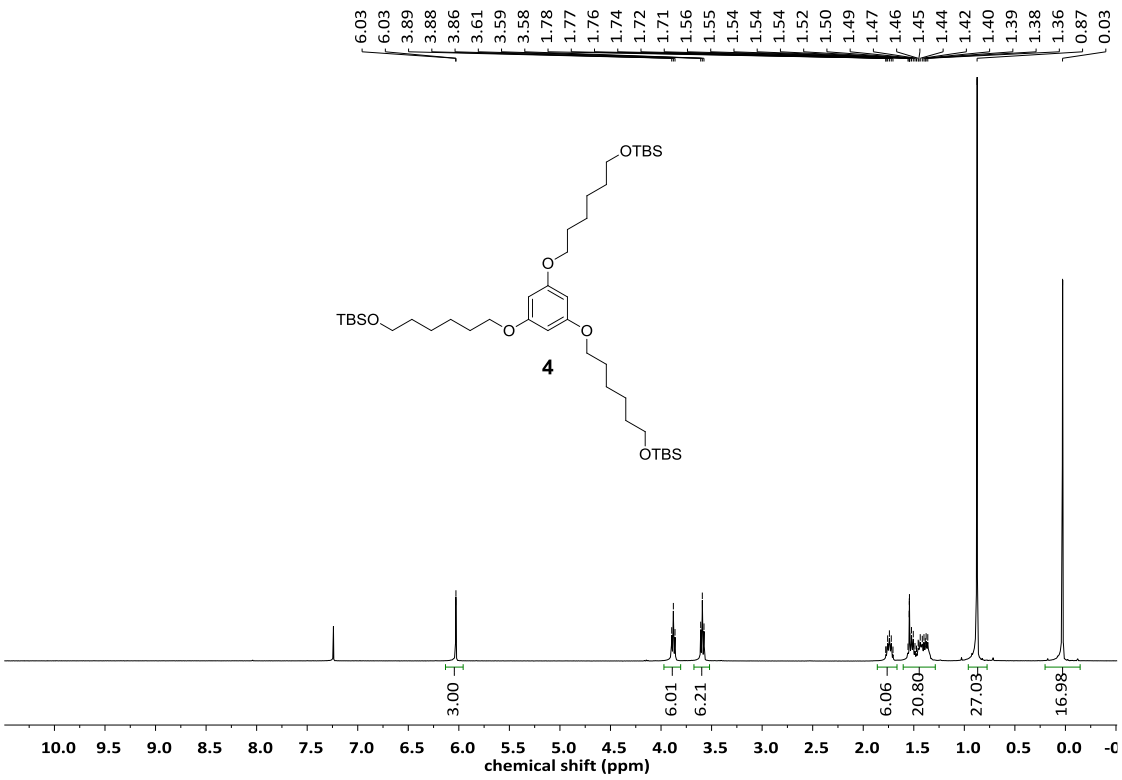


Fig. S12 ^{1}H NMR spectrum of **4**.

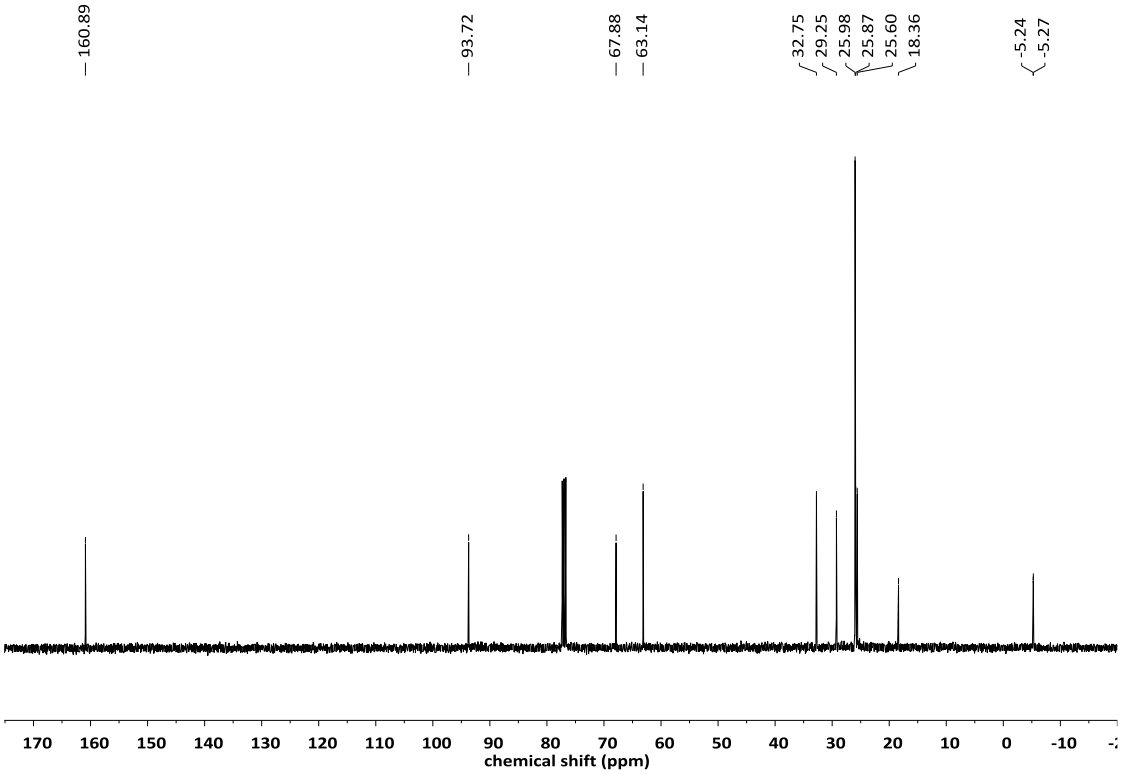


Fig. S13 ^{13}C NMR spectrum of **4**.

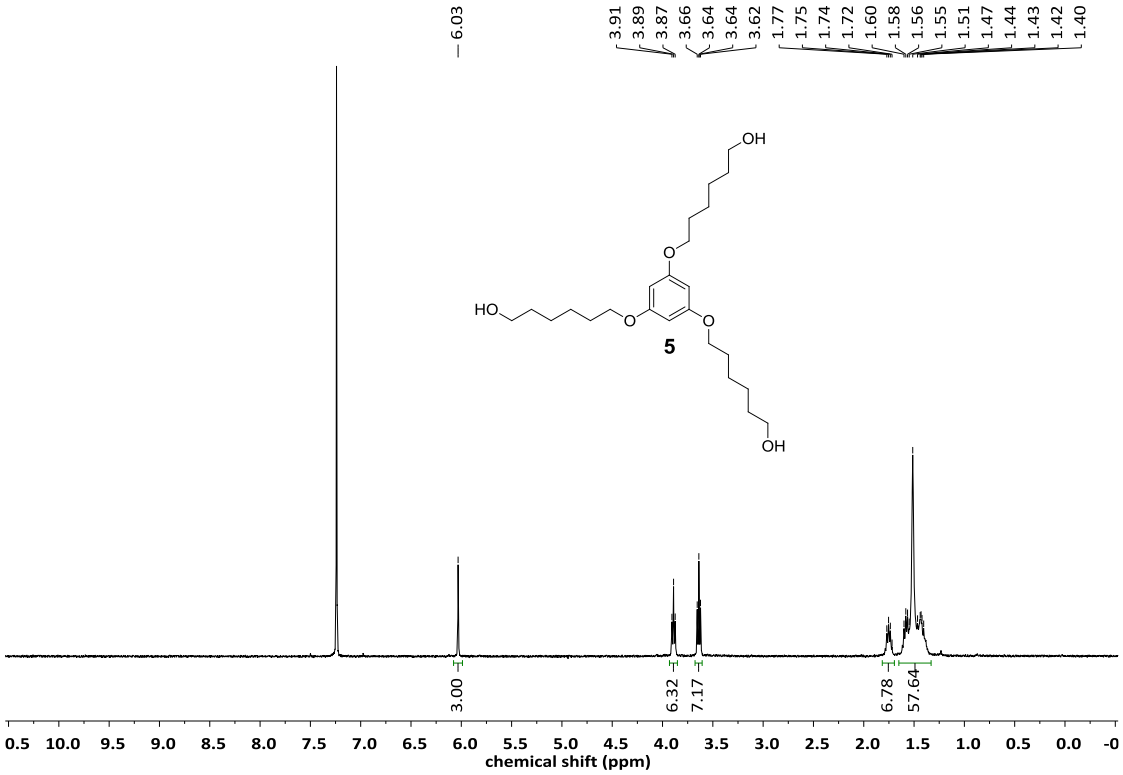


Fig. S14 ^{1}H NMR spectrum of **5**.

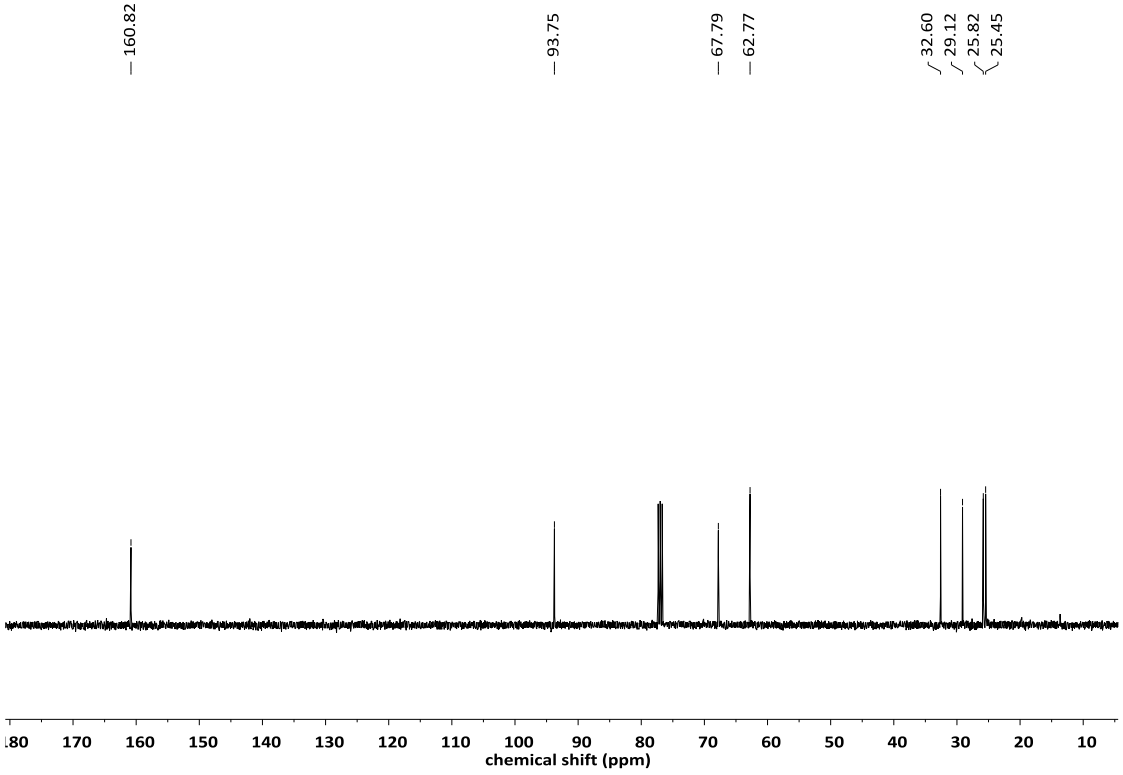


Fig. S15 ^{13}C NMR spectrum of **5**.

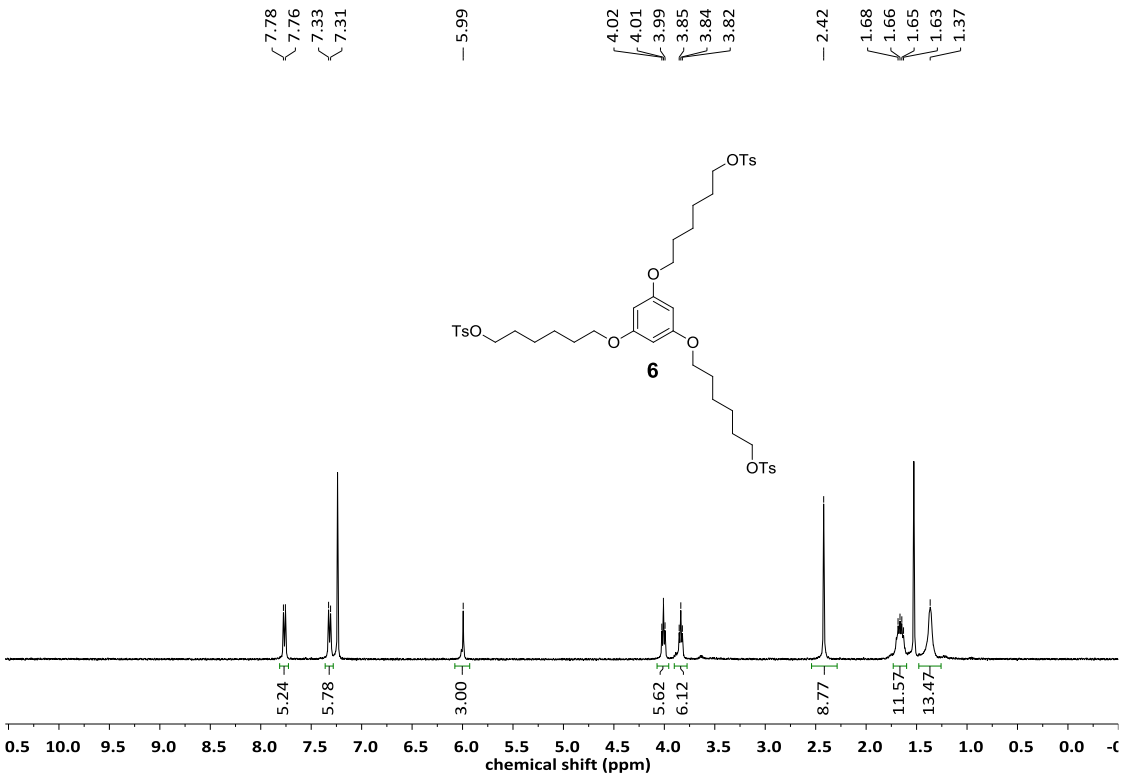


Fig. S16 ^{1}H NMR spectrum of **6**.

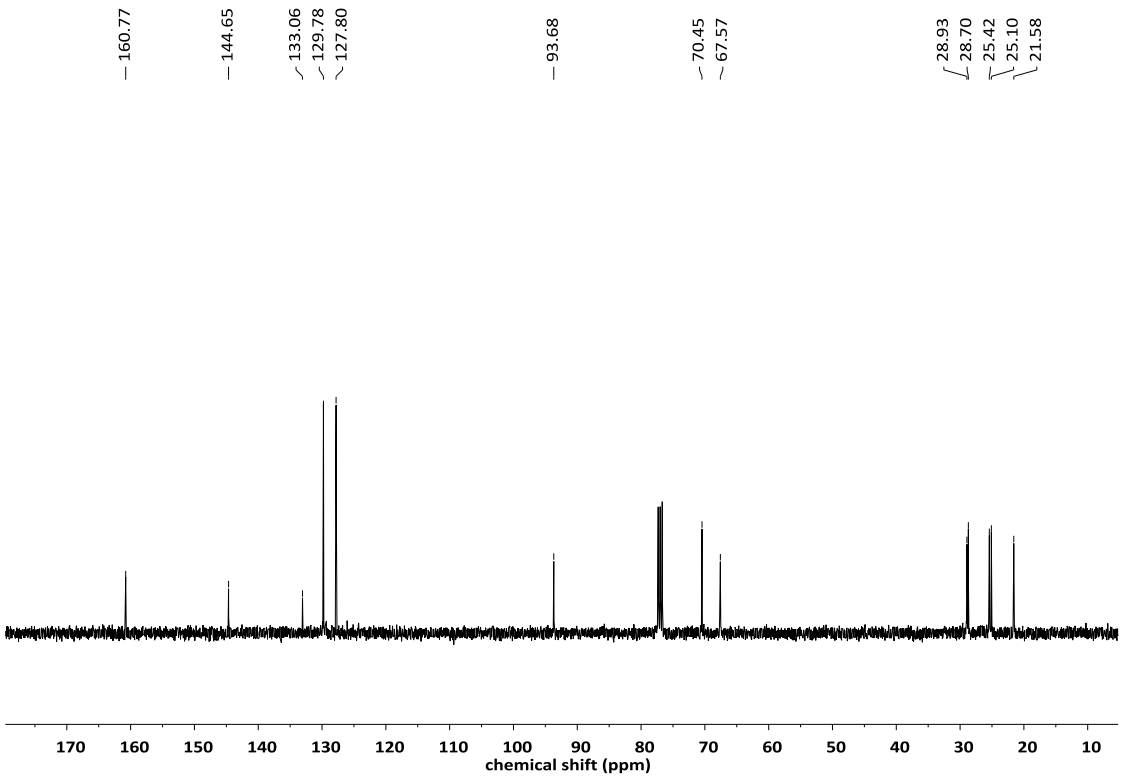


Fig. S17 ^{13}C NMR spectrum of **6**.

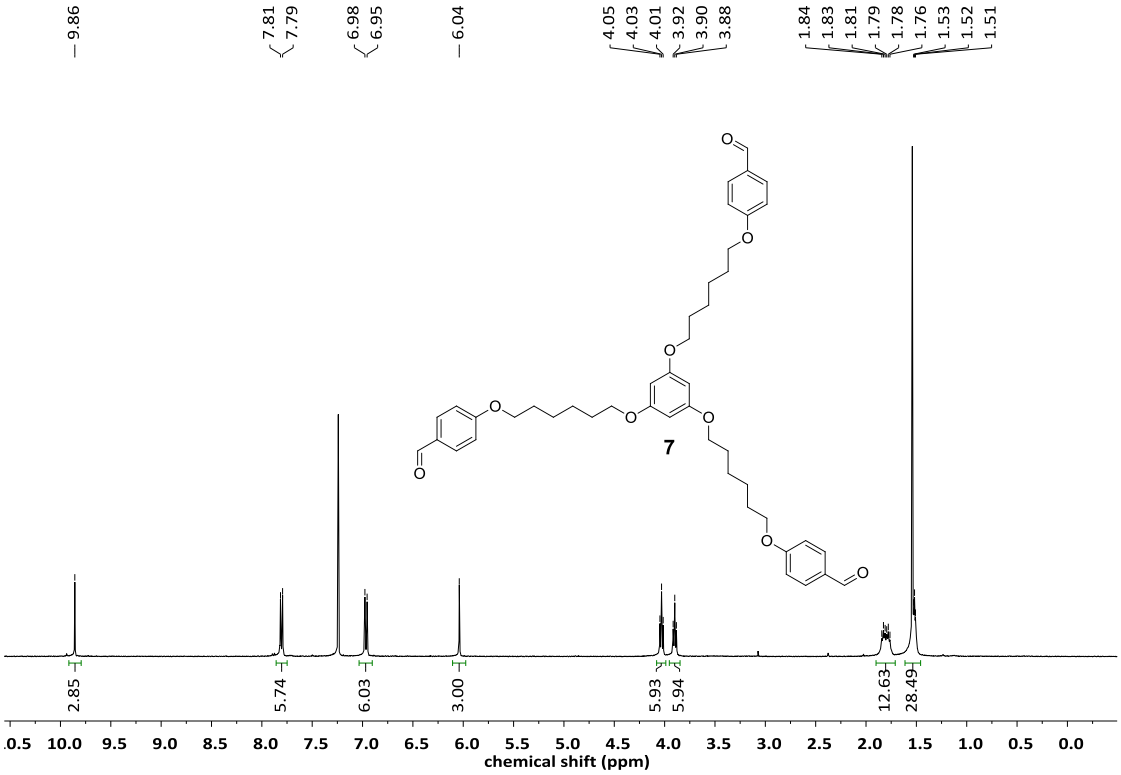


Fig. S18 ^{1}H NMR spectrum of **7**.

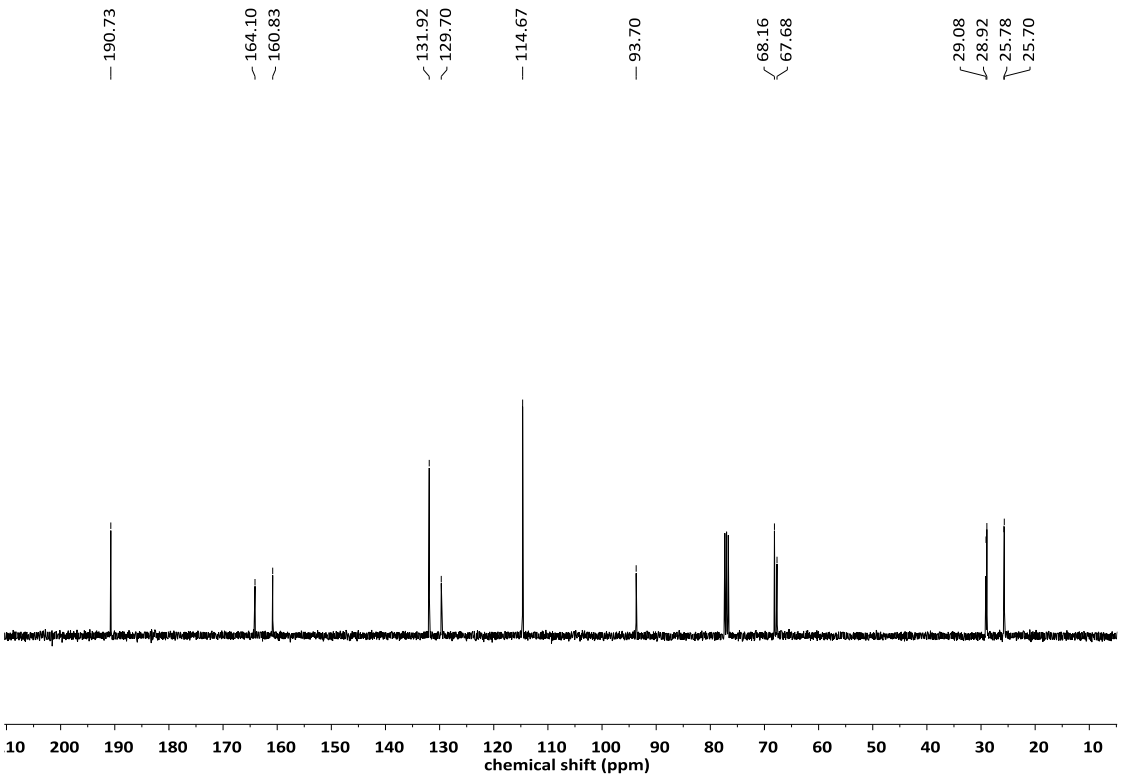


Fig. S19 ^{13}C NMR spectrum of **7**.

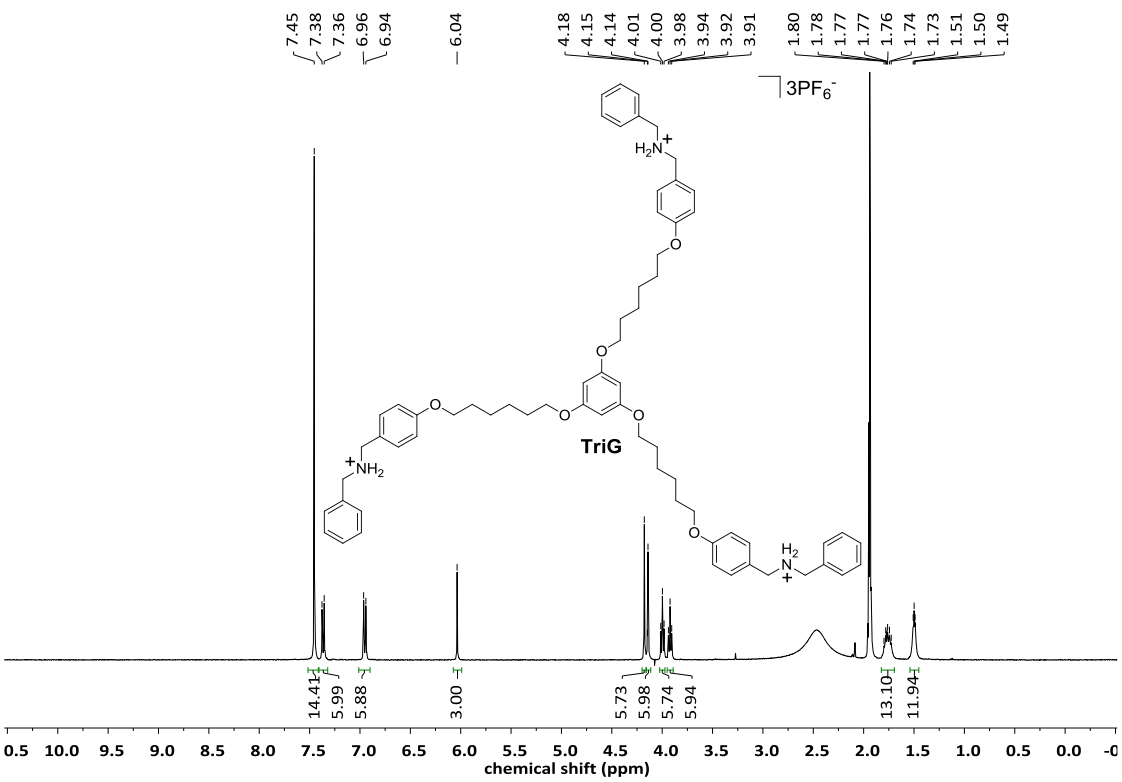


Fig. S20 ^{1}H NMR spectrum of **TriG**.

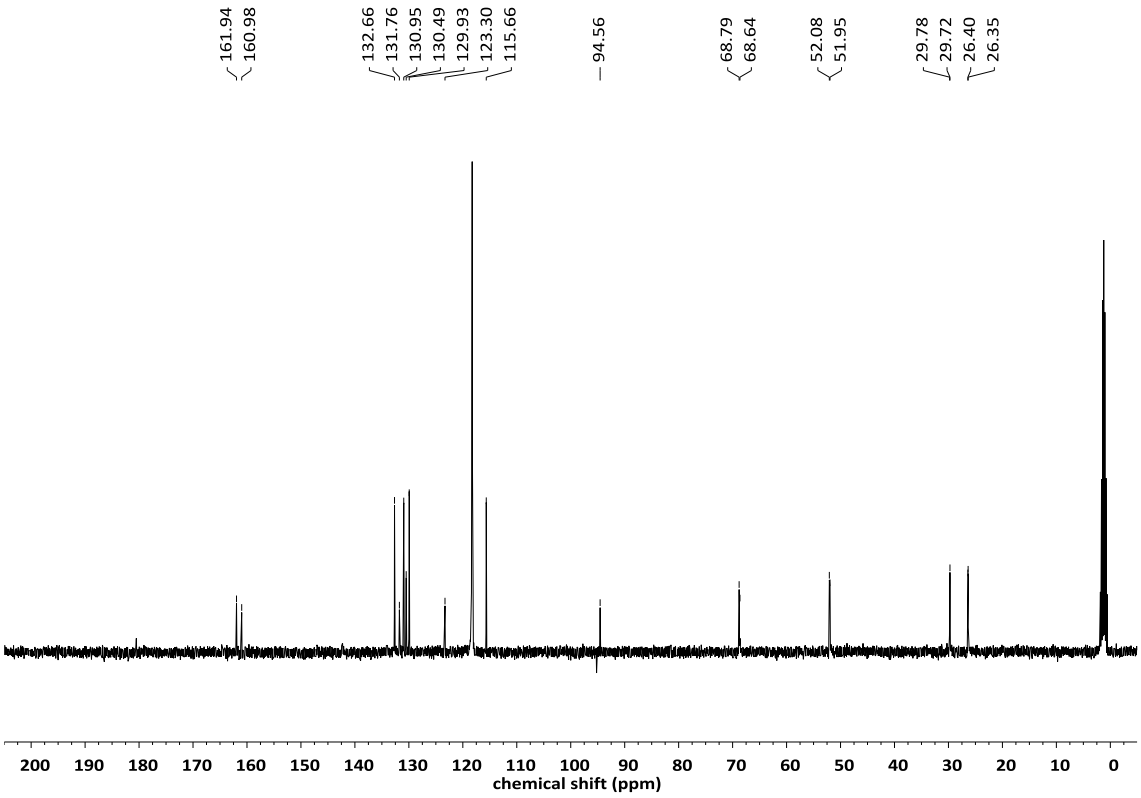


Fig. S21 ^{13}C NMR spectrum of **TriG**.

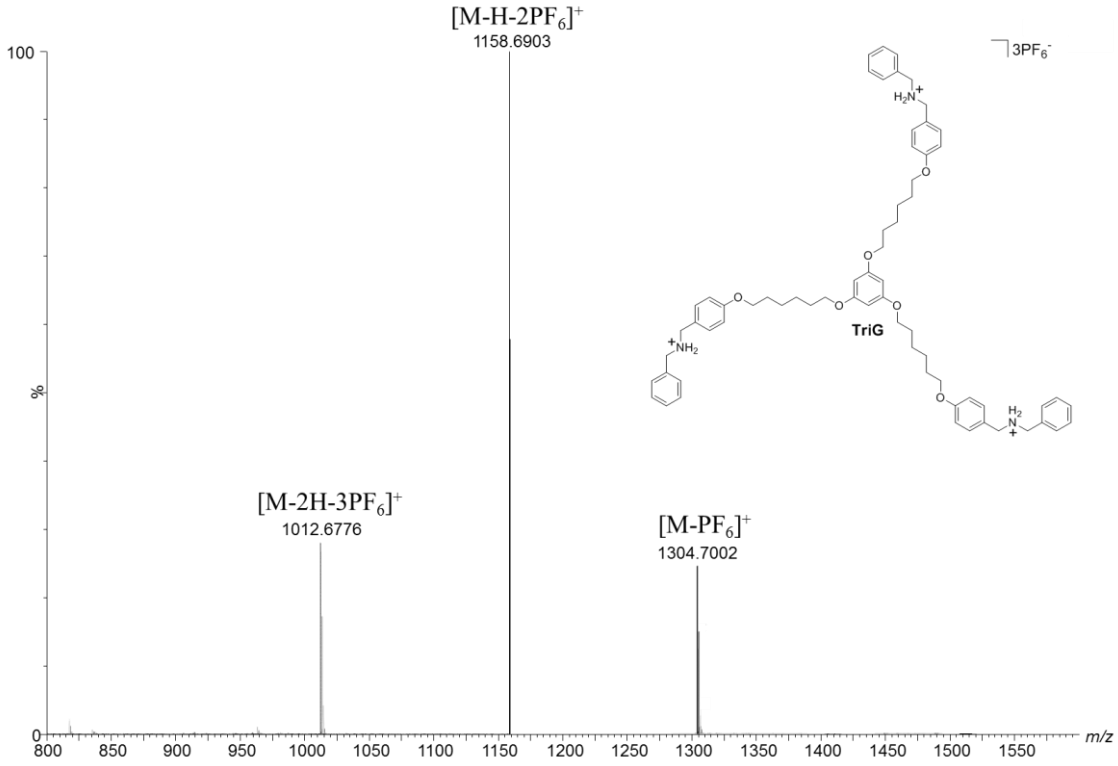


Fig. S22 ESI-MS spectrum of **TriG**.

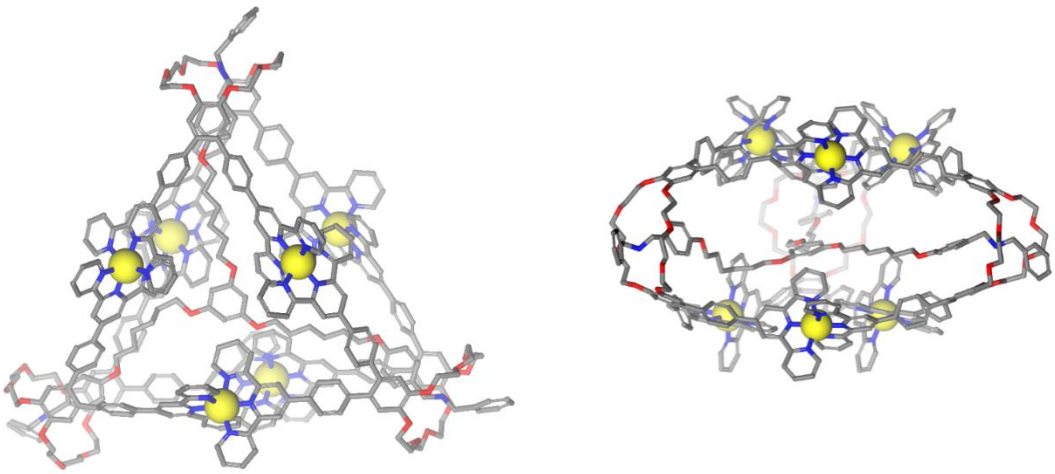


Fig. S23 Energy-minimized structures of $[Cd_6\mathbf{T}_3]\supset$**TriG**.

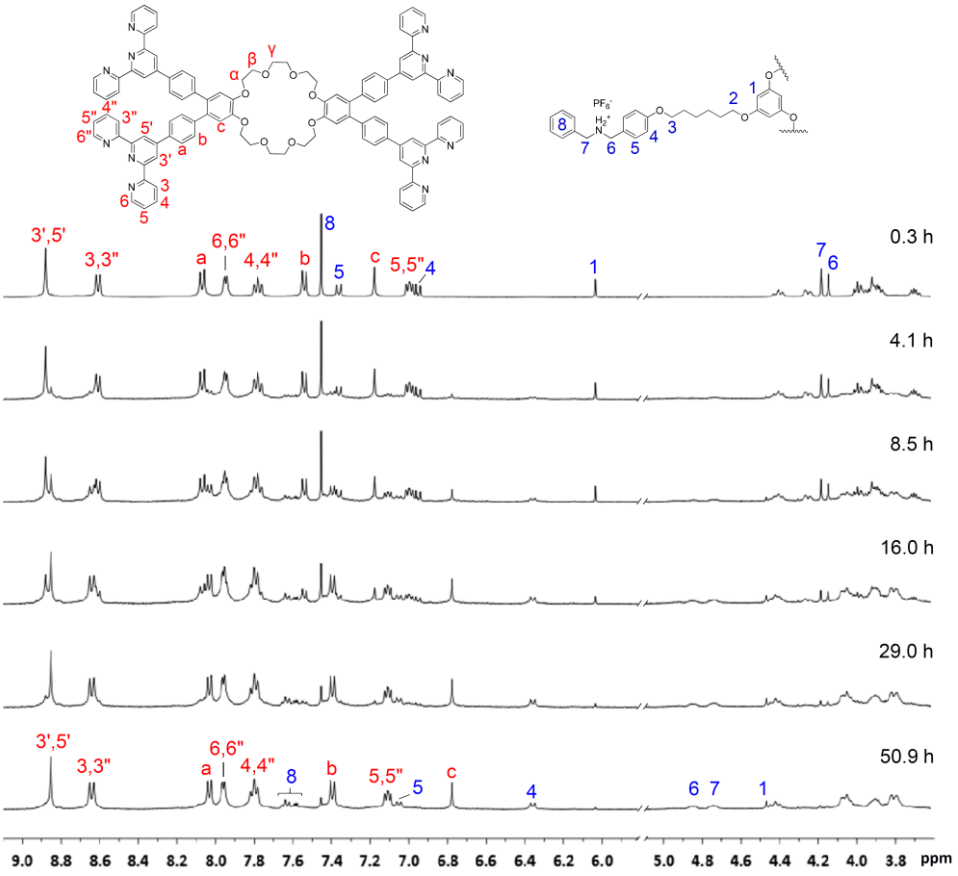


Fig. S24 Time-dependent ^{1}H NMR spectra of a mixture of [Cd_6**T**$_3$] (0.8 mM) and **TriG** in a molar ratio of 1:1 at 25 °C.

2D NMR spectra of [Cd_6**T**$_3$]⊃**TriG**

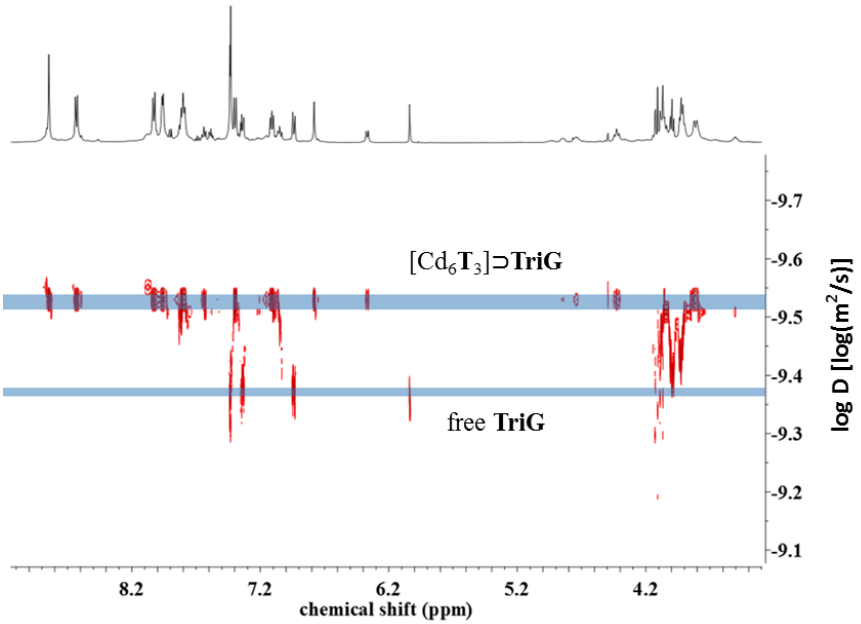


Fig. S25 DOSY spectrum of [Cd_6**T**$_3$]⊃**TriG** with excess **TriG** in CD_3CN.

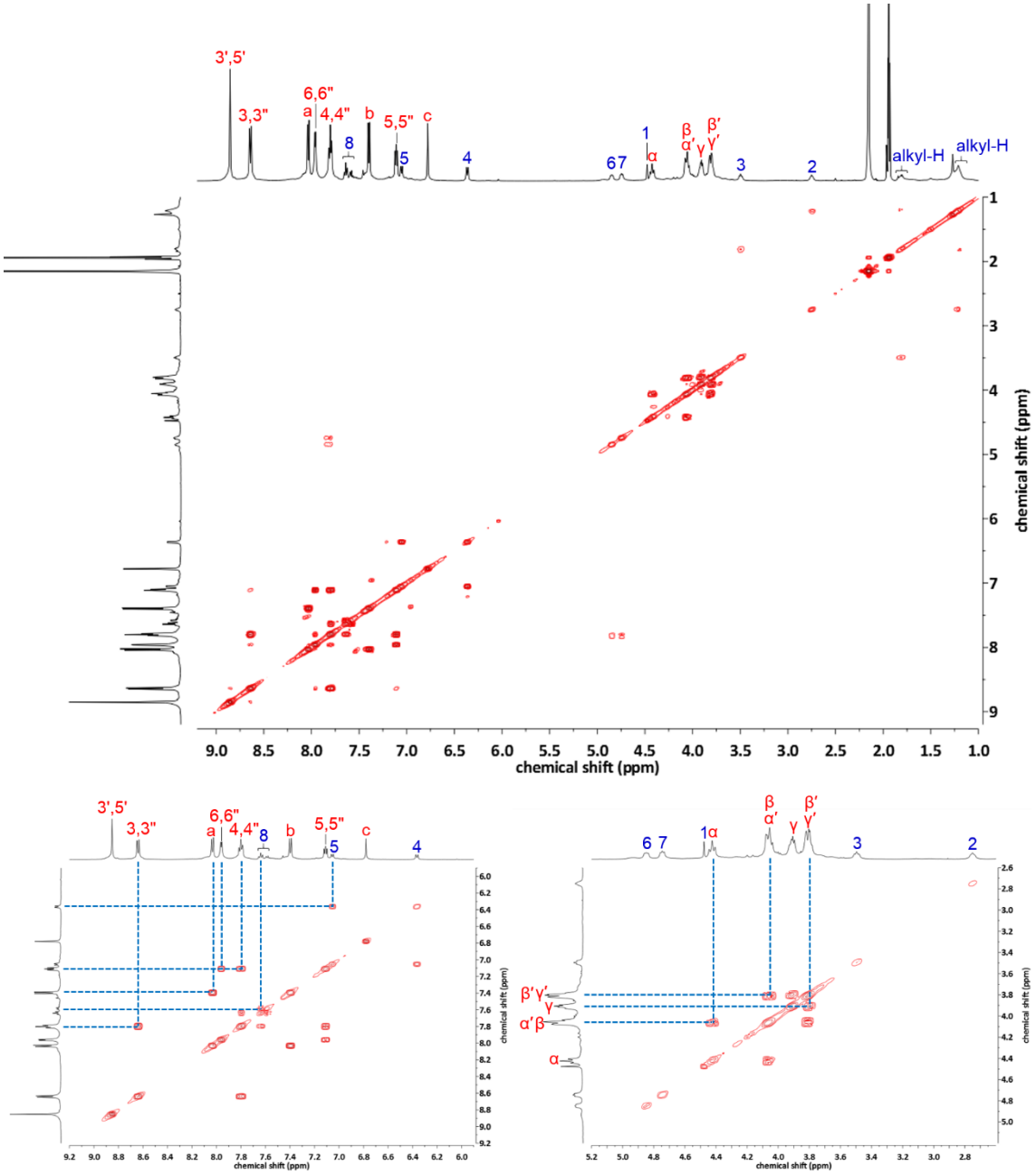


Fig. S26 COSY spectra of [Cd_6**T**$_3$]⊃**TriG**.

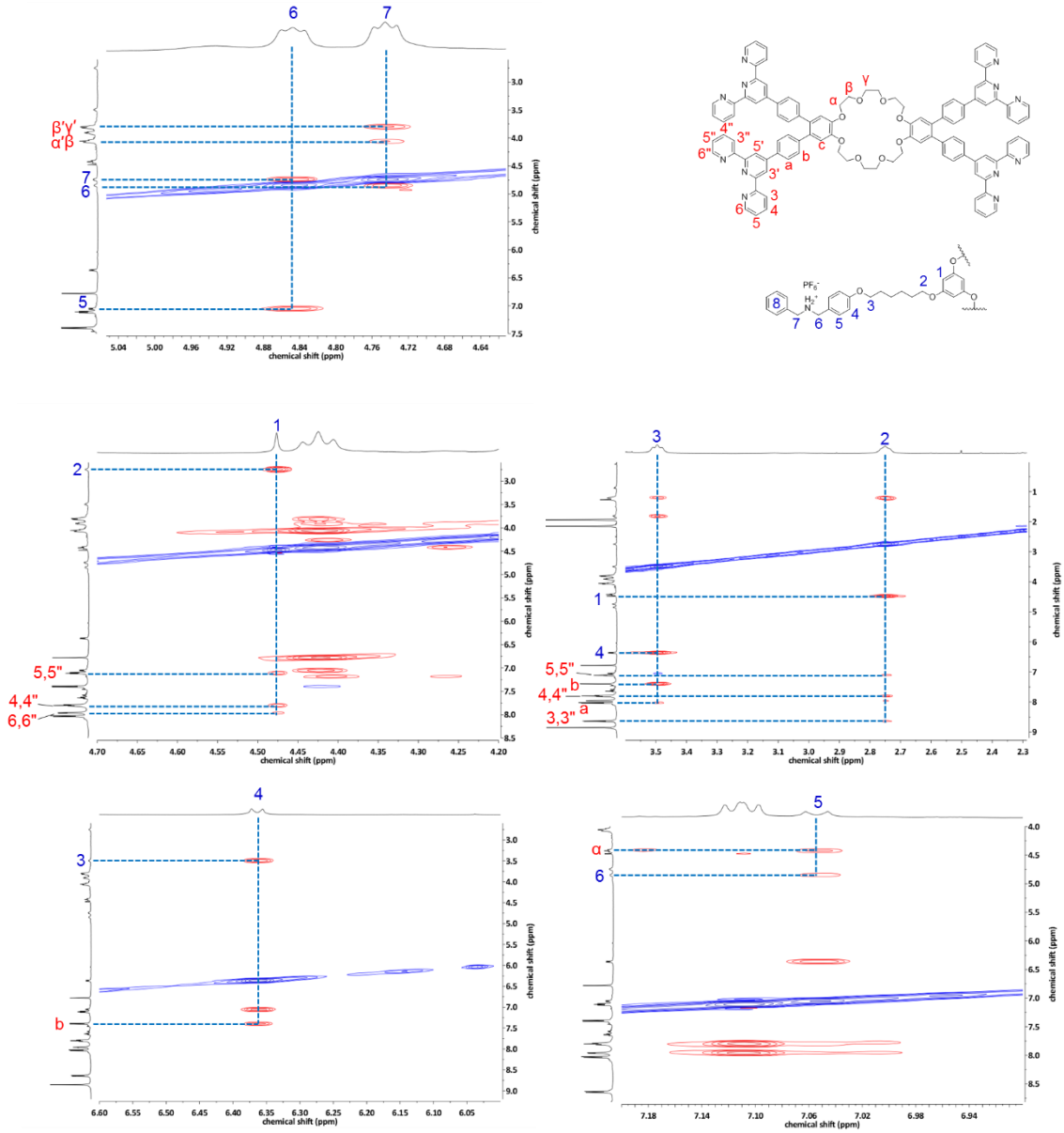


Fig. S27 ROESY spectra of $[Cd_6\mathbf{T}_3]\supset$**TriG** in CD_3CN.

ESI-MS spectra of $[Cd_6\mathbf{T}_3]\supset\mathbf{TriG}$

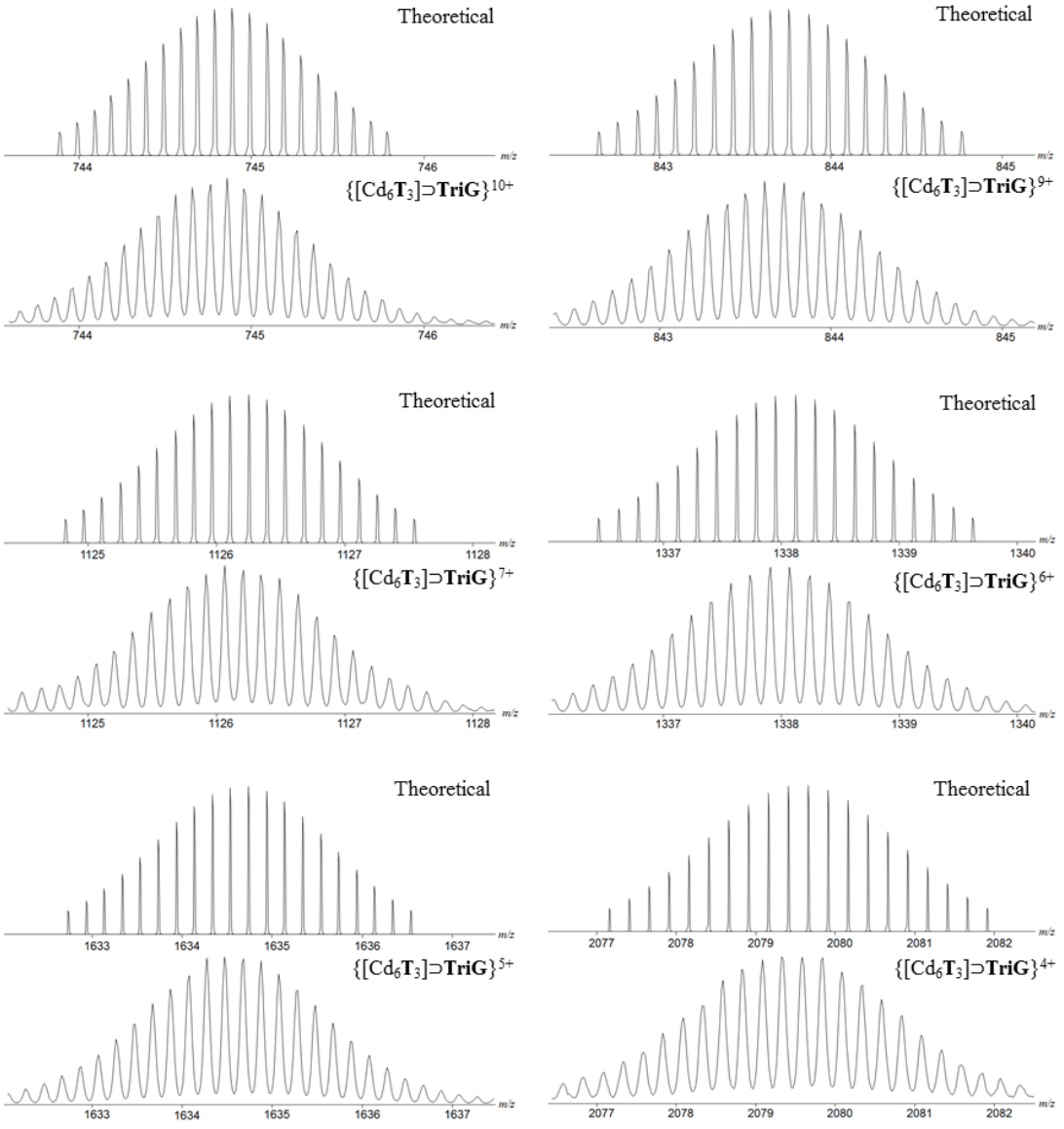


Fig. S28 Experimental and theoretical ESI-MS isotope patterns of $[Cd_6\mathbf{T}_3]\supset\mathbf{TriG}$.

Binding constant of $[Cd_6\mathbf{T}_3]\supset$**TriG**

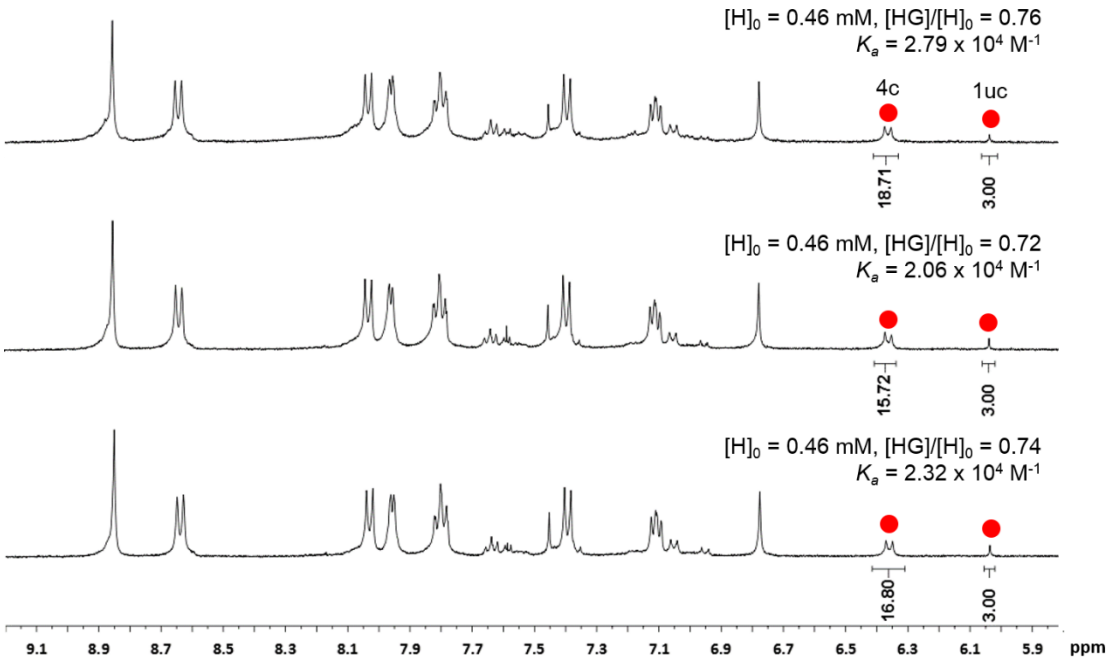


Fig. S29 ^{1}H NMR spectra of the mixture of $[Cd_6\mathbf{T}_3]$ (H) and **TriG** (G) at equilibrium in CD_3CN at 25 °C. The experiment was repeated three times, and "c" and "uc" denote the complexed and uncomplexed peaks of **TriG**, respectively.

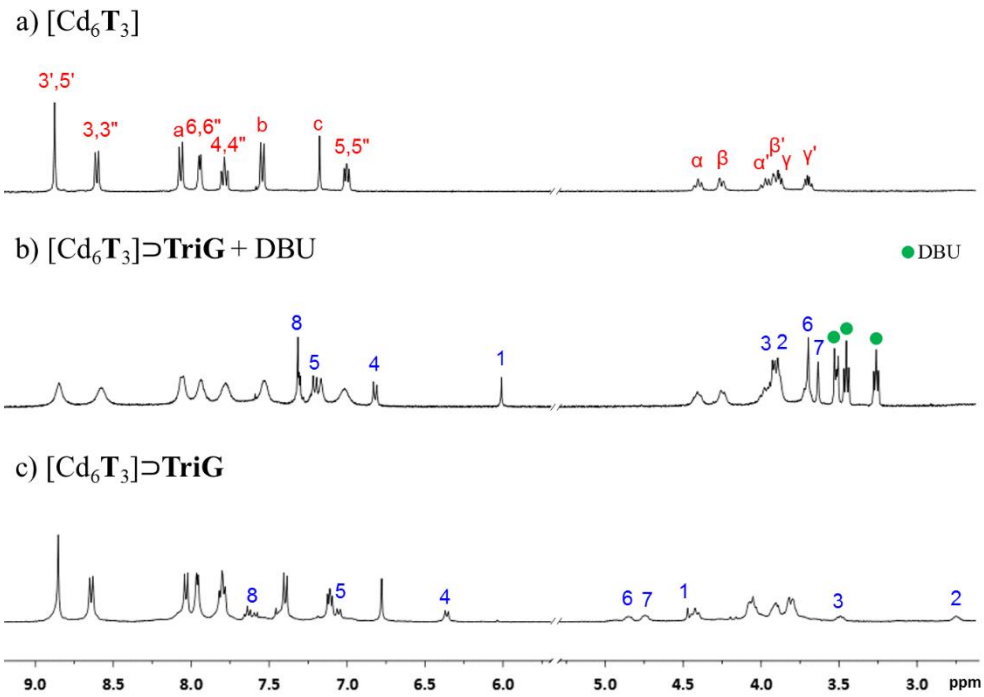


Fig. S30 ^{1}H NMR spectra of a) $[Cd_6\mathbf{T}_3]$, b) $[Cd_6\mathbf{T}_3]\supset$**TriG** + DBU, and c) $[Cd_6\mathbf{T}_3]\supset$**TriG**.

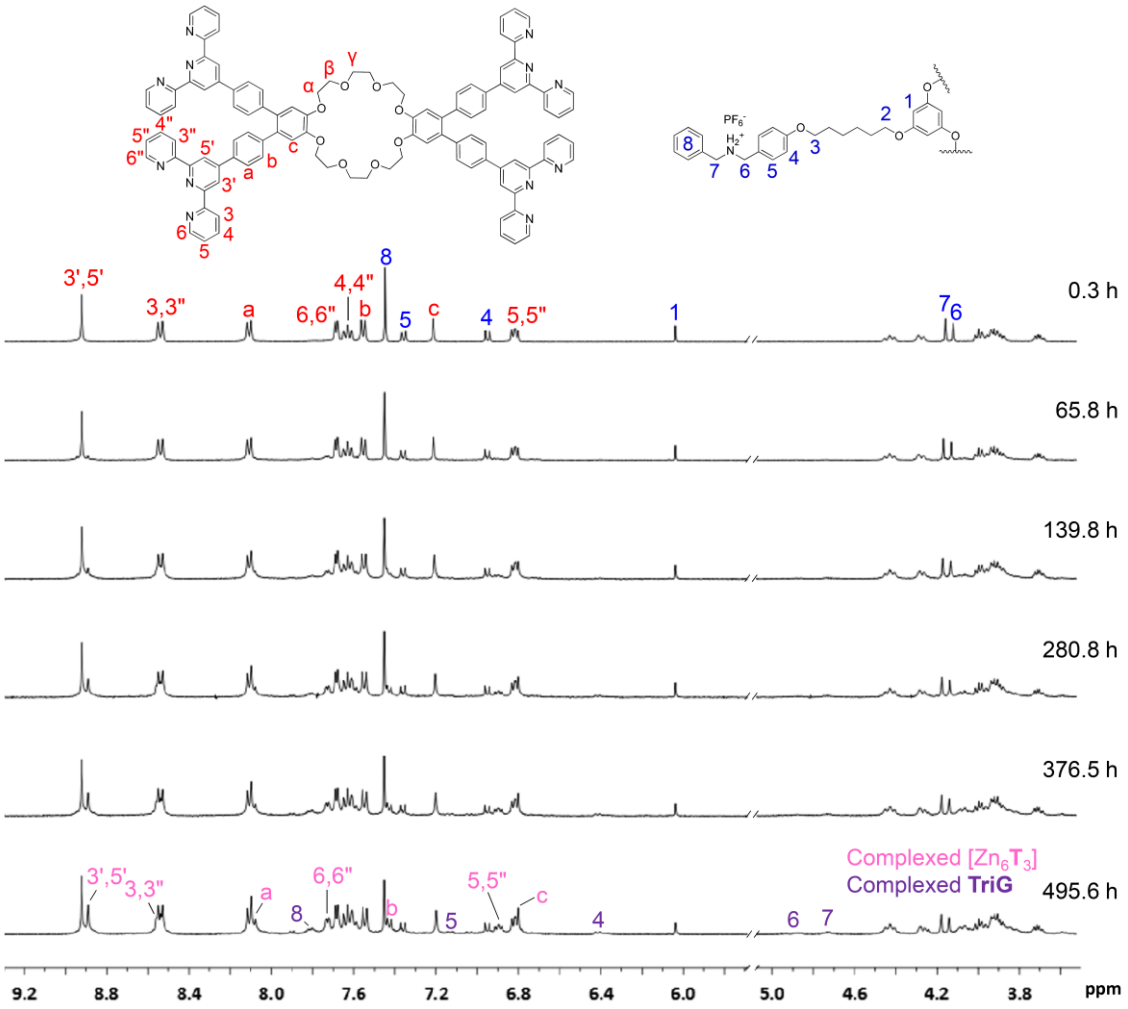


Fig. S31 Time-dependent ^{1}H NMR spectra of a mixture of [Zn_6**T**$_3$] (0.8 mM) and **TriG** in a molar ratio of 1:1 at 25 °C.

Synthesis and characterization of $[Zn_6\mathbf{T}_3]\supset$**TriG**

$[Zn_6\mathbf{T}_3]\supset$TriG. To a flask containing $[Zn_6\mathbf{T}_3]$ (4.0 mg, 0.6 μmol), an MeCN solution (0.7 mL) of **TriG** (2.5 mg, 1.7 μmol) was added. The mixture was refluxed for 48 h, cooled to room temperature, and dried *in vacuo*. The residue was washed with MeOH several times, and then dried *in vacuo* to give $[Zn_6\mathbf{T}_3]\supset$**TriG** (4.3 mg, 0.5 μmol) in 89% yield. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 8.89 (s, 24H), 8.56 (d, J = 8.2 Hz, 24H), 8.10 (d, J = 8.4 Hz, 24H), 7.82 (d, J = 6.7 Hz, 6H), 7.73 (d, J = 4.2 Hz, 24H), 7.68–7.65 (m, 9H), 7.63 (dt, J = 8.0 and 1.4 Hz, 24H), 7.44 (d, J = 8.2 Hz, 24H), 7.14 (d, J = 7.5 Hz, 6H), 6.92 (dd, J = 7.0 and 5.4 Hz, 24H), 6.80 (s, 12H), 6.42 (d, J = 8.0 Hz, 6H), 4.90–4.85 (m, 6H), 4.76–4.71 (m, 6H), 4.47 (t, J = 9.0 Hz, 12H), 4.24 (s, 3H), 4.09–4.04 (m, 24H), 3.97–3.81 (m, 36H), 3.62–3.54 (m, 6H), and 2.77–2.68 (m, 6H). ESI-MS (*m/z*): 2008.9843 $[M\text{-}4PF_6]^{4+}$ (calcd. *m/z* = 2008.9452), 1577.9901 $[M\text{-}5PF_6]^{5+}$ (calcd. *m/z* = 1578.1633), 1291.0007 $[M\text{-}6PF_6]^{6+}$ (calcd. *m/z* = 1290.9753), 1085.8601 $[M\text{-}7PF_6]^{7+}$ (calcd. *m/z* = 1085.8412), 931.8813 $[M\text{-}8PF_6]^{8+}$ (calcd. *m/z* = 931.9905), 812.3367 $[M\text{-}9PF_6]^{9+}$ (calcd. *m/z* = 812.3289), and 716.6113 $[M\text{-}10PF_6]^{10+}$ (calcd. *m/z* = 716.5995).

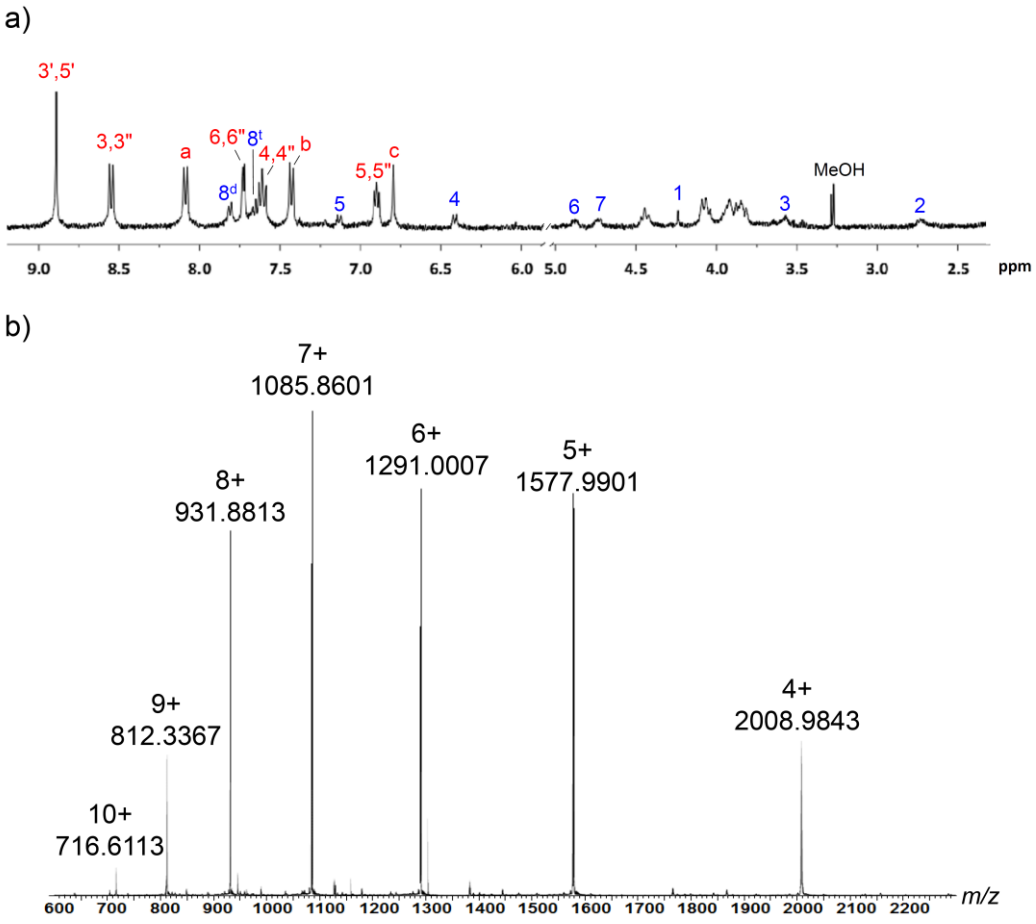


Fig. S32 a) ^{1}H NMR and b) ESI-MS spectra of $[Zn_6\mathbf{T}_3]\supset$**TriG**.

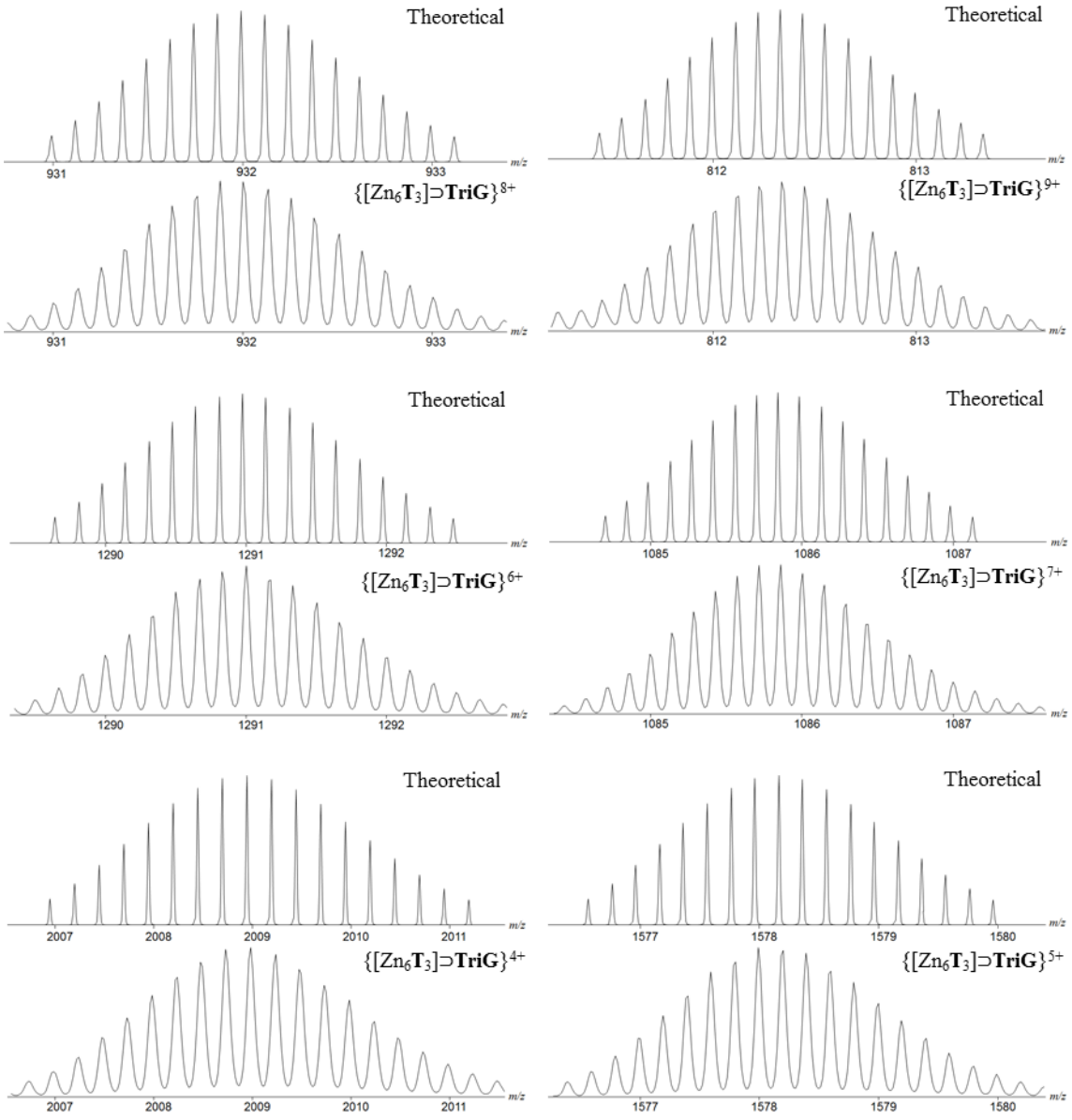


Fig. S33 Experimental and theoretical ESI-MS isotope patterns of $[Zn_6\mathbf{T}_3]\supset\mathbf{TriG}$.

Inclusion and transmetalation study

Sample preparation:

<u>^{1}H NMR</u>: To a sample vial containing [Zn_6**T**$_3$] (4.0 mg, 0.6 μmol) and [Cd_6**T**$_3$] (4.2 mg, 0.6 μmol), 0.7 mL CD_3CN was added. The solution was mixed thoroughly and settled at 25 °C for ^{1}H NMR measurement at different mixing timeframes. To study the effect of **TriG**, an CD_3CN solution (0.7 mL) of **TriG** (1.2 mg, 0.8 μmol) was added instead.

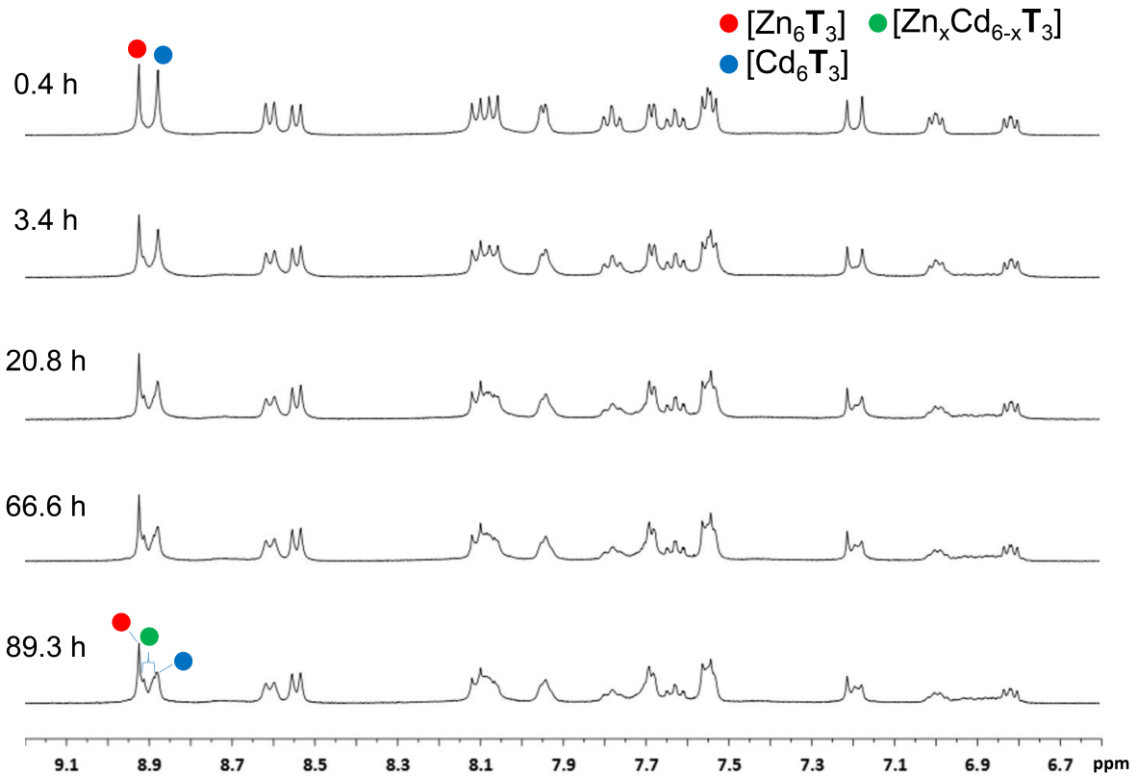


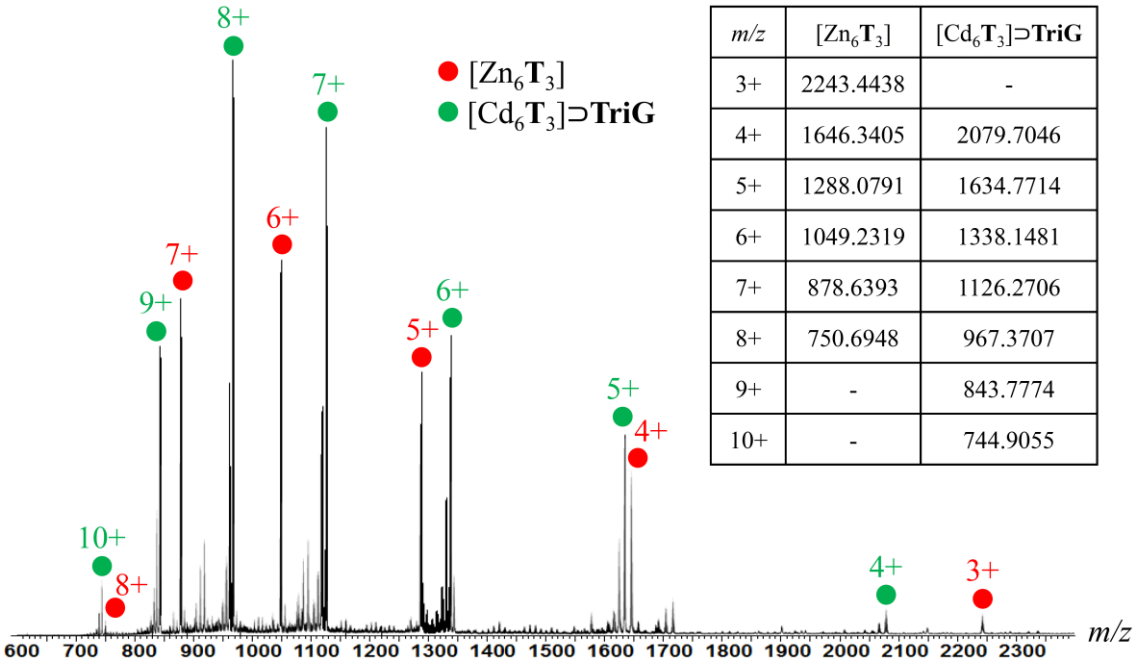
Fig. S34 Time-dependent ^{1}H NMR spectra of an equimolar mixture of [Zn_6**T**$_3$] and [Cd_6**T**$_3$].

<u>ESI-MS</u>: By using a similar procedure, two MeCN mixtures (with and without **TriG**) containing an equimolar amount of [Zn_6**T**$_3$] and [Cd_6**T**$_3$] were prepared. 50 μL of the mixture was taken and diluted 5 times with MeCN for ESI-MS measurement at different mixing timeframes.

Data analysis:

<u>ESI-MS</u>: The TOF intensities of all [M-6PF_6]$^{6+}$ ions, including [Cd_6**T**$_3$]$^{6+}$, [$ZnCd_5$**T**$_3$]$^{6+}$, [Zn_2Cd_4**T**$_3$]$^{6+}$, [Zn_3Cd_3**T**$_3$]$^{6+}$, [Zn_4Cd_2**T**$_3$]$^{6+}$, [Zn_5Cd**T**$_3$]$^{6+}$ and [Zn_6**T**$_3$]$^{6+}$, were measured for each sampling. It was found that [$ZnCd_5$**T**$_3$]$^{6+}$ and [Zn_2Cd_4**T**$_3$]$^{6+}$ were the two primary species in the absence of **TriG** after mixing for 40 h (Fig. S36a), so their relative intensities were normalized against all the 6+ ions. In the presence of **TriG**, the TOF

intensities of the inclusion complexes, including $[Cd_6\mathbf{T}_3]^{6+}\supset$**TriG**, $[ZnCd_5\mathbf{T}_3]^{6+}\supset$**TriG**, $[Zn_2Cd_4\mathbf{T}_3]^{6+}\supset$**TriG**, $[Zn_3Cd_3\mathbf{T}_3]^{6+}\supset$**TriG**, $[Zn_4Cd_2\mathbf{T}_3]^{6+}\supset$**TriG**, $[Zn_5Cd\mathbf{T}_3]^{6+}\supset$**TriG**, and $[Zn_6\mathbf{T}_3]^{6+}\supset$**TriG,** were measured and taken into account for normalization. Normalized intensities of the selected 6+ were then plotted against mixing time (Fig. S37).



m/z	$[Zn_6\mathbf{T}_3]$	$[Cd_6\mathbf{T}_3]\supset$**TriG**
3+	2243.4438	-
4+	1646.3405	2079.7046
5+	1288.0791	1634.7714
6+	1049.2319	1338.1481
7+	878.6393	1126.2706
8+	750.6948	967.3707
9+	-	843.7774
10+	-	744.9055

Fig. S35 ESI-MS spectrum of an equimolar mixture of $[Zn_6\mathbf{T}_3]$ and $[Cd_6\mathbf{T}_3]$ after mixed with **TriG** for 40 h. The major species are $[Zn_6\mathbf{T}_3]$ and $[Cd_6\mathbf{T}_3]\supset$**TriG**.

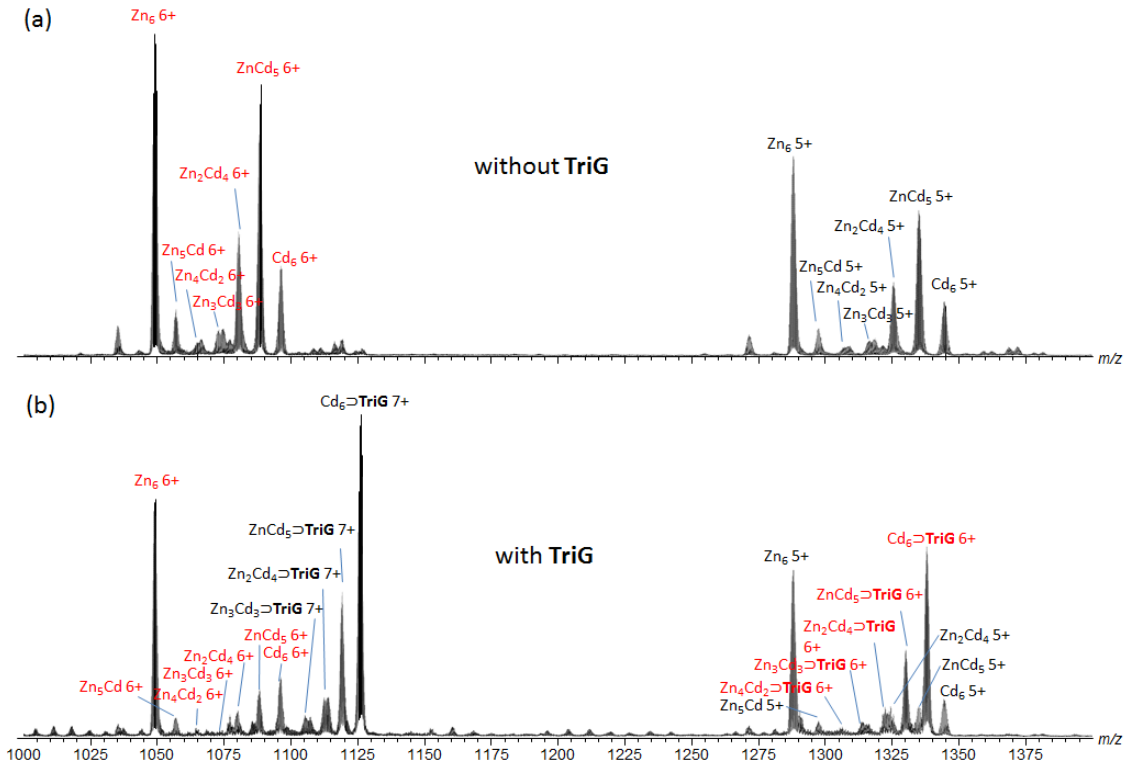
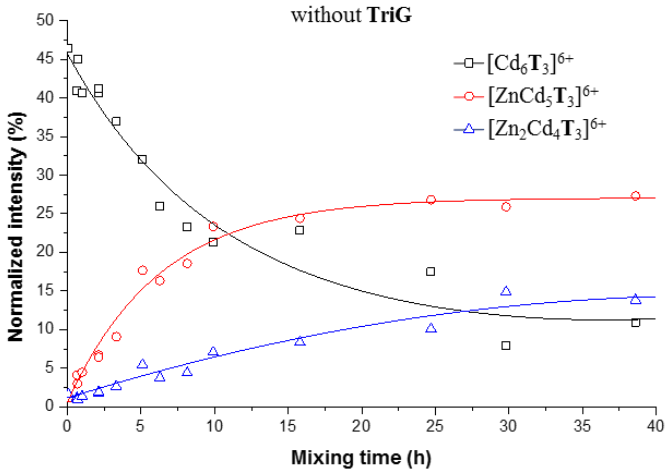
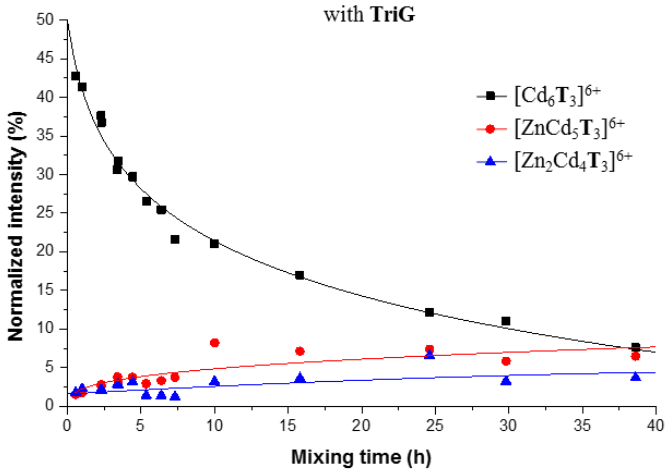


Fig. S36 Partial ESI-MS spectra of two MeCN mixtures (a) without and (b) with **TriG**, containing $[Zn_6\mathbf{T}_3]$ and $[Cd_6\mathbf{T}_3]$ (1:1) after mixing for 40 h.

(a)



(b)



(c)

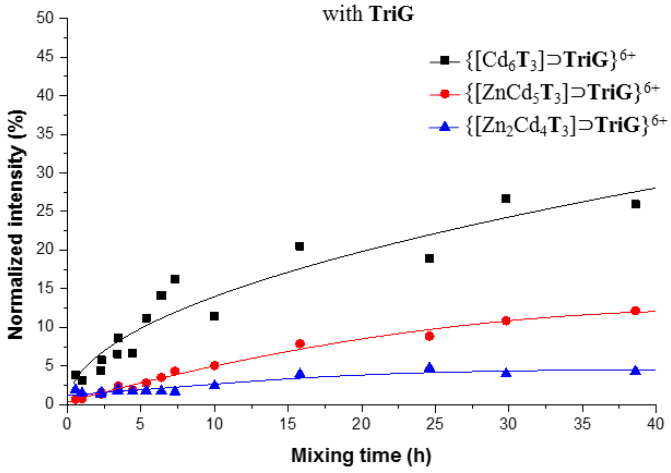


Fig. S37 ESI-MS trace plots of normalized intensities for the 6+ ions vs. mixing time (a) without and (b-c) with **TriG**.

Tandem mass spectrometry analysis

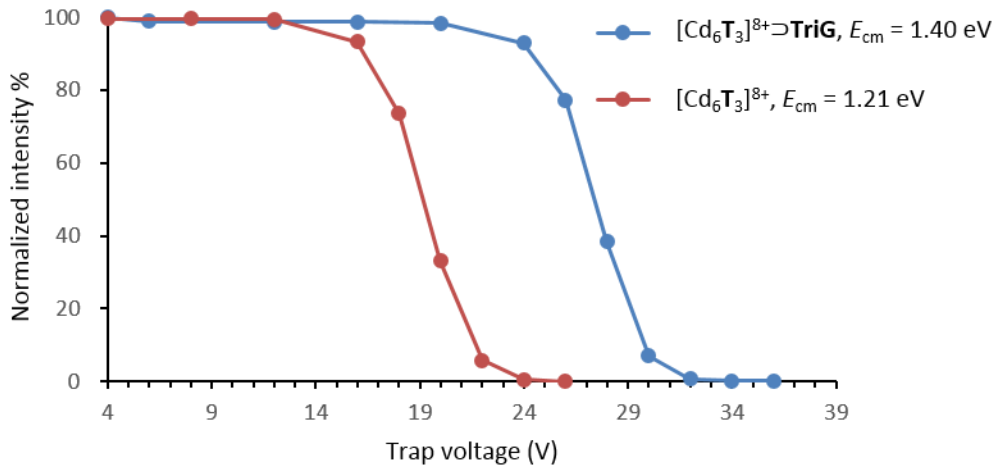


Fig. S38 Normalized intensities for $[Cd_6\mathbf{T}_3]^{8+}$ and $\{[Cd_6\mathbf{T}_3]\supset\mathbf{TriG}\}^{8+}$ as a function of trap voltage and their corresponding center-of-mass collision energies (E_{cm}).

References

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[2] Y.-T. Chan, X. Li, J. Yu, G. A. Carri, C. N. Moorefield, G. R. Newkome, C. Wesdemiotis, *J. Am. Chem. Soc.*, 2011, **133**, 11967.

[3] (a) A. A. Shvartsburg, M. F. Jarrold, *Chem. Phys. Lett.*, 1996, **261**, 86; (b) M. F. Mesleh, J. M. Hunter, A. A. Shvartsburg, G. C. Schatz, M. F. Jarrold, *J. Phys. Chem.*, 1996, **100**, 16082.

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