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Supporting Information

Aggregation-Induced Emission Based on Fluorinated Macrocycle: Visualizing the Spontaneous and Ultrafast Solid-State Molecular Motion at Room Temperature *via* F···F Interactions

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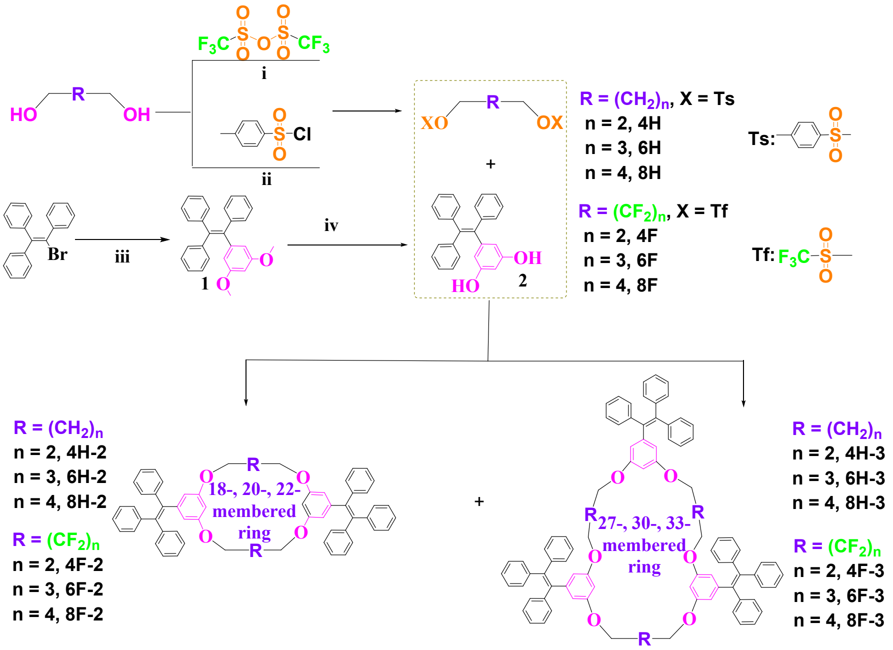
General experimental details and materials

Materials and Charaterization: All the reagents and solvents were commercially available and used as received. ^{1}H and ^{19}F were recorded on a 400 MHz/600MHz nuclear magnetic resonance spectrometer operating at 400 and 376 MHz respectively, Chemical shifts were reported relative to Me_4Si for ^{1}H and CCl_3F for ^{19}F. The solvent was either $CDCl_3$ unless otherwise specified. Thermogravimetric analysis (TGA) measurements worked at a heating rate of 10 ^oC min^{-1} with a Netzsch TG-209F3 (Germany) apparatus. Differential scaning calorimetry (DSC) was performed at a scan rate of 5 ºC min^{-1} on a Shimadzu TA-60WS (Japan) instrument. UV/Vis spectra were recorded with a Shimadzu UV-2700 (Japan) instrument. Fluorescence spectra were recorded with a Hitachi LTD spectrophotometer F-4600. Fluorescence lifetime measurements were executed using a Edinburgh FLS920 spectrofluorometer. X-ray diffraction (XRD) measurement was conducted on a Bruker D8 Advance X-ray diffractometer. The ground-state geometries were optimized by density functional theory (DFT) method with the B3LYP hybrid functional at the basis set level of 6-31G* in the gas state.

Synthesis and characterization

The polyfluoroalkyldiols, were reacted with trifluoromethanesulfonic anhydride to give trifluoromethanesulfonate esters[1], **4F**, **6F** and **8F**. Alkyl methyl *p*-toluenesulfonate, **4H**, **6H** and **8H**, were prepared by the reaction of corresponding alkyldiols with *p*-toluenesulfonyl chloride. As depicted in **Scheme 1**, (2-(3,5-dimethoxyphenyl)ethene-1,1,2-triyl)tribenzene, **1**, was obtained by Suzuki cross-coupling reaction[2] in 95% yield, whereafter, it was transformed into the corresponding phenol[3] **2** in 98% yield. Two kind of polyfluoroalkyl or alkyl linked macrocycles with two TPE cores (**4F-2**, **6F-2**, **8F-2**, **4H-2**, **6H-2, 8H-2)**, and three TPE cores (**4F-3**, **6F-3**, **8F-3**, **4H-3**, **6H-3, 8H-3**) were simultaneously obtained in 16%-64% yield *via* the reaction[4] of **2** with trifluoromethanesulfonate esters (**4F**, **6F** and **8F**) or alkyl methyl p-toluenesulfonate (**4H**, **6H** and **8H**) respectively.



i: pyridine, DCM, 0 ^{o}C~rt, 12 h; ii: triethylamine, DCM, 0 ^{o}C~rt, 12 h; iii: 0.01% mol Pd(PPh3)4, K2CO3, TBAB, toluene, 97 ^{o}C, 12 h; iv: BBr3, DCM, 0 ^{o}C, 8 h; v: K2CO3, CH3CN, 90 ^{o}C, 12 h.

Scheme 1. Synthesis of alkyl/polyfluoroalky functionalized TPE-based macrocycles.

Trifluoromethanesulfonic anhydride (12.5 mL, 74.04 mmol) was reacted respectively with 2,2,3,3-tetrafluoro-1,4-butanediol (4.0000 g, 24.68 mmol), 2,2,3,3,4,4-hexafluoro-1,5-pentanediol (5.2386 g, 24.68 mmol) and 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol (6.4667 g, 24.68 mmol) in dichloromethane (75 mL) and pyridine (5 mL) to get the corresponding compounds, 2,2,3,3-tetrafluorobutane-1,4-diyl bis(trifluoromethanesulfonate), **4F**, 2,2,3,3,4,4-hexafluoropentane-1,5-diyl bis(trifluoromethanesulfonate), **6F** and 2,2,3,3,4,4,5,5-octafluorohexane-1,6-diyl bis(trifluoromethanesulfonate), **8F**. Then the mixture was stirred at 0 ºC~rt for 12 h under nitrogen. The solution was added 50 mL dichloromethane and washed with water, brine and dried with anhydrous sodium sulfate. The solvent was removed under vacuum and the crude product was purified by column chromatography (petroleum/EtOAc=3/1) to give the target products.

P-toluenesulfonyl chloride (11.4390 g, 60 mmol) was reacted respectively with 1,4-butanediol (1.84 mL, 20 mmol), 1,5-pentanediol (2.08 mL, 20 mmol) and 1,6-hexanediol (2.3634g, 20 mmol) in dichloromethane (100 mL) and triethylamine (15 mL) to give butane-1,4-diyl bis(4-methylbenzenesulfonate), **4H**, pentane-1,5-diyl bis(4-methylbenzenesulfonate), **6H** and hexane-1,6-diyl bis(4-methylbenzenesulfonate), **8H**. Then the mixture was stirred at 0 ºC~rt for 12 h. The solution was added 25 mL dichloromethane and washed with water, brine and dried with anhydrous sodium sulfate. The solvent was removed under vacuum and the crude product was purified by column chromatography (petroleum/EtOAc=5/1) to give the target products.

2,2,3,3-tetrafluorobutane-1,4-diyl bis(trifluoromethanesulfonate) (**4F**): ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 5.06–4.60 (m, 4H). ^{19}F NMR (565 MHz, $CDCl_3$) δ (ppm): -73.96 (s, 4F), -120.37–120.47 (m, 4F).

2,2,3,3,4,4-hexafluoropentane-1,5-diyl bis(trifluoromethanesulfonate) (**6F**): ^{1}H NMR (600 MHz, DMSO-*d₆*) δ (ppm): 4.77 (t, *J* = 12.7 Hz, 4H). ^{19}F NMR (565 MHz, DMSO-d_6) δ (ppm): -74.67 (s, 6F), -120.29 (s, 4F), -124.99 (s, 2F).

2,2,3,3,4,4,5,5-octafluorohexane-1,6-diyl bis(trifluoromethanesulfonate) (**8F**): ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 4.83 (t, *J* = 12.1 Hz, 4H). ^{19}F NMR (565 MHz, $CDCl_3$) δ (ppm): -73.95 (s, 4F), -119.74 (s, 4F), -122.97 (s, 4F).

Butane-1,4-diyl bis(4-methylbenzenesulfonate) (**4H**): ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.78 (d, *J* = 8.2 Hz, 4H), 7.37 (d, *J* = 8.1 Hz, 4H), 4.01 (t, *J* = 5.3 Hz, 4H), 2.48 (s, 6H), 1.77–1.69 (m, 4H).

Pentane-1,5-diyl bis(4-methylbenzenesulfonate) (**6H**): ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.79 (d, *J* = 8.3 Hz, 4H), 7.37 (d, *J* = 8.0 Hz, 4H), 3.99 (t, *J* = 6.3 Hz, 4H), 2.48 (s, 6H), 1.65–1.60 (m, 4H), 1.40–1.36 (m, 2H).

Hexane-1,6-diyl bis(4-methylbenzenesulfonate) (**8H**): ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.76 (d, *J* = 8.2 Hz, 4H), 7.46 (d, *J* = 7.9 Hz, 4H), 3.94 (t, *J* = 6.2 Hz, 4H), 2.40 (s, 6H), 1.46 (s, 4H), 1.12 (d, *J* = 19.7 Hz, 4H).

Synthesis of **(2-(3, 5-dimethoxyphenyl) ethene-1, 1, 2-triyl)tribenzene (1)** : bromotriphenylethylene (3.3524 g, 10 mmol), 3, 5-dimethylphenylboronic acid (2.2297 g, 15 mmol), Tetrabutylammonium bromide (0.3224 g, 1 mmol) were dissolved in toluene (60 mL), adding K_2CO_3 (2.764 g, 20 mmol) dissolved in water (18 mL) and $Pd(PPh_3)_4$ (0.1155 g, 0.1 mmol) under nitrogen. The solution was stirred for 12 h at 97 ºC. After removing of the solvent under vacuum, the residue was diluted with CH_2Cl_2 (100 mL), washed with water and dried with anhydrous sodium sulfate. The crude product was purified by column chromatography (PE/EtOAc = 30/1) to obtain the product **1** (3.5297 g, 95%) , white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.20-7.00 (m, 15H), 6.25 (d, *J* = 1.8 Hz, 1H), 6.21 (d, *J* = 1.8 Hz, 2H), 3.56 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 159.95, 145.52, 143.91, 143.57, 143.24, 141.07, 140.90, 131.31, 131.25, 130.96, 127.76, 127.64, 126.50, 109.67, 99.24, 55.18. HRMS (EI$^+$) m/z: $C_{28}H_{24}O_2$ for $[M]^+$, calculated 392.1776, found 392.1773.

Synthesis of **5-(1,2,2-triphenylvinyl)benzene-1,3-diol (2)**: The compound **5** (10 mmol) was dissolved in 60 mL dichloromethane at 0 ºC and then BBr_3 (4.01 mL) was added dropwise without water. The solution was stirred for 8 h. Water was added dropwise to quench the reaction. Dilute the solution with dichloromethane, washed with water and dried with anhydrous sodium sulfate. The crude product was purified by column chromatography (PE/EtOAc = 5/1) to get the product **2** (3.5685g, 98%) , white solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 9.00 (s, 2H), 7.12-6.93 (m, 15H), 5.96 (s, 1H), 5.89 (d, J = 1.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 157.97, 148.13, 145.49, 145.41, 145.20, 143.16, 142.01, 133.26, 133.16, 133.02, 129.72, 129.66, 129.62, 128.67, 128.49, 113.14, 103.30. HRMS (EI$^+$) m/z: $C_{26}H_{20}O_2$ for [M]$^+$, calculated 364.1463, found 364.1464.

Synthesis of **4F-2, 4F-3, 6F-2, 6F-3, 8F-2, 8F-3, 4H-2, 4H-3, 6H-2, 6H-3, 8H-2** and **8H-3**: **5-(1,2,2-triphenylvinyl)benzene-1,3-diol (2)** (0.3641 g, 1 mmol) was reacted with the corresponding alkyl chain in dry acetonitrile (30 mL) and K_2CO_3(0.2764 g, 2 mmol) to obtain **4F-2, 4F-3, 6F-2, 6F-3, 8F-2, 8F-3, 4H-2, 4H-3, 6H-2, 6H-3, 8H-2** and **8H-3**. Then the mixture was stirred at 90 ºC for 12 h under nitrogen. The solution was added 50 mL dichloromethane and washed with water, brine and dried with anhydrous sodium sulfate. The solvent was removed under vacuum and the crude product was purified by column chromatography (petroleum/EtOAc=40/1) to give the target products.

4F-2: pure white solid, 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.13–6.99 (m, 30H), 6.31 (d, J = 1.7 Hz, 4H), 6.16 (s, 2H), 4.06 (s, 8H). ^{19}F NMR (565 MHz, $CDCl_3$) δ (ppm): -123.12 (s, 8F). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 157.76, 146.84, 143.46, 142.89, 142.44, 142.30, 139.71, 131.12, 127.89, 126.87, 114.75, 112.04, 100.12, 65.64. HRMS (ESI): $C_{60}H_{44}O_4F_8$ for [M]$^+$ calculated 980.30754, found 980.31064.

4F-3: pure white solid, yield, 35%. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.20–6.99 (m, 45H), 6.34 (d, J = 1.9 Hz, 6H), 6.19 (s,3H), 4.08 (d, J = 1.2 Hz, 12H). ^{19}F NMR (565 MHz, $CDCl_3$) δ (ppm): -121.35 (t, J = 13.0 Hz, 12F). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 158.12, 146.23, 143.62, 143.08, 142.58, 142.16, 139.86, 131.17, 127.85, 126.85, 115.15, 112.35, 102.25, 65.79. HRMS (ESI): $C_{90}H_{66}O_6F_{12}$ for [M]$^+$ calculated 1470.46267, found 1470.46623.

6F-2: pure white solid, yield, 61%. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm):

7.05–6.93 (m, 30H), 6.23 (d, *J* = 2.2 Hz, 4H), 6.16 (d, *J* = 2.0 Hz, 2H), 4.02 (t, *J* = 12.0 Hz, 8H). ^{19}F NMR (565 MHz, $CDCl_3$) δ (ppm): -119.30 (s, 8F), -126.71 (s, 4F). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 157.08, 145.39, 142.47, 141.94, 141.44, 141.19, 138.72, 130.14, 126.71, 125.85, 115.18, 113.47, 111.65, 101.81, 64.85. HRMS (ESI): $C_{62}H_{44}O_4F_{12}$ for $[M]^+$ calculated 1080.30891, found 1080.30425.

6F-3: pure white solid, yield, 30%. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.20–7.03 (m, 45H), 6.37–6.33 (m, 3H), 6.31 (d, *J* = 2.3 Hz, 4H), 4.12 (t, *J* = 12.4 Hz, 12H). ^{19}F NMR (565 MHz, $CDCl_3$) δ (ppm): -119.83 (s, 12F), -125.13 (s, 6F). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 157.94, 146.20, 143.64, 143.09, 142.59, 142.16, 139.90, 131.20, 127.88, 126.88, 116.50, 114.79, 111.83, 101.80, 65.33. HRMS (ESI): $C_{93}H_{66}O_6F_{18}$ for $[M]^+$ calculated 1620.46359, found 1620.45665.

8F-2: pure white solid, yield, 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): (ppm) 7.20–6.92 (m, 30H), 6.26 (d, *J* = 2.2 Hz, 4H), 6.22 (s, 2H), 4.07 (t, *J* = 11.9 Hz, 8H). ^{19}F NMR (565 MHz, $CDCl_3$) δ (ppm): -118.82 (s, 8F), -124.13 (s, 8F). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 158.30, 146.74, 144.07, 143.49, 142.97, 142.71, 140.26, 131.64, 128.21, 127.38, 112.74, 112.35, 111.59, 102.68, 66.24. HRMS (ESI): $C_{64}H_{44}O_4F_{16}$ for $[M]^+$ calculated 1180.29864, found 1180.29786.

8F-3: pure white solid, 31%. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.25–6.99 (m, 45H), 6.35 (t, J = 3.3 Hz, 9H), 4.14 (t, *J* = 12.4 Hz, 12H). ^{19}F NMR (565 MHz, $CDCl_3$) δ (ppm): -119.46 (s, 12F), -123.76 (s, 12F). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 158.00, 146.32, 143.62, 143.07, 142.56, 142.23, 139.84, 131.20, 127.90, 126.90, 114.64, 112.32, 110.95, 101.82, 65.60. HRMS (ESI): $C_{96}H_{66}O_6F_{24}$ for $[M]^+$ calculated 1770.44829, found 1770.44707.

4H-2: pure white solid, 51%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): (ppm) 7.14–6.94 (m, 30H), 6.18 (t, *J* = 14.0 Hz, 6H), 3.85–3.56 (m, 8H), 1.67 (s, 8H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 159.08, 145.58, 143.96, 143.60, 140.99 (d, *J* =4.5), 131.24, 127.64, 126.43, 110.80, 101.10, 68.00, 25.69. HRMS (ESI):

$C_{60}H_{52}O_4$ for [M + Na]$^+$ calculated 859.37365, found 859.37578.

4H-3: pure white solid, 44%.^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): (ppm) 7.16–6.97 (m, 45H), 6.26 (t, J = 2.1 Hz, 3H), 6.20 (d, *J* = 2.1 Hz, 6H), 3.73 (t, *J* = 5.8 Hz, 12H), 1.71 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 159.24, 145.46, 143.91, 143.62, 143.28, 140.98, 140.91, 131.26, 127.63, 126.46, 110.77, 100.67, 67.24, 25.37. HRMS (ESI): $C_{90}H_{78}O_6$ for [M + Na]$^+$ calculated 1277.57152, found 1277.56906.

6H-2: pure white solid, 40%. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): (ppm) 7.18–6.87 (m, 30H), 6.25–6.10 (m, 6H), 3.70 (t, *J* = 6.1 Hz, 8H), 1.60–1.54 (m, 8H), 1.52–1.45 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 159.64, 145.95, 144.37, 144.11, 143.74, 141.47, 141.36, 131.80, 128.07, 126.97, 111.07, 101.69, 67.83, 28.12, 22.15. HRMS (ESI): $C_{62}H_{56}O_4$ for [M + Na]$^+$ calculated 887.40979, found 887.40708.

6H-3: pure white solid, 45%. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.18–6.88 (m, 45H), 6.24 (s, 3H), 6.16 (d, *J* = 1.2 Hz, 6H), 3.67 (t, *J* = 6.0 Hz, 12H), 1.64–1.56 (m, 12H), 1.50–1.42 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 159.43, 145.41, 143.95, 143.67, 143.33, 141.04, 140.94, 131.28, 127.62, 126.40, 110.21, 100.68, 67.69, 28.71, 22.85. HRMS (ESI): $C_{93}H_{84}O_6$ for [M + Na]$^+$ calculated 1319.61846, found 1319.61601.

8H-2: pure white solid, 43%. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.13–6.97 (m, 30H), 6.22 (t, *J* = 2.2 Hz, 2H), 6.16 (d, *J* = 2.2 Hz, 4H), 3.68 (t, *J* = 6.2 Hz, 8H), 1.64–1.60 (m, 8H), 1.42 (s, 8H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 159.43, 145.41, 143.95, 143.69, 143.35, 141.07, 140.88, 131.29 (d, *J*=8.45), 127.62, 126.41, 110.24, 100.27, 67.34, 28.08, 25.06. HRMS (ESI): $C_{64}H_{60}O_4$ for [M + Na]$^+$ calculated 915.43900, found 915.43838.

8H-3: pure white solid, 21%. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.16–7.00 (m, 45H), 6.25 (t, *J* = 2.1 Hz, 3H), 6.20 (d, *J* = 2.1 Hz, 6H), 3.70 (t, *J* = 6.4 Hz, 12H), 1.63 (d, *J* = 5.9 Hz, 12H), 1.39 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 160.02, 146.06, 144.58, 144.33, 143.98, 141.66, 141.56, 131.94, 128.27, 127.08, 111.11, 101.04, 68.27, 29.55, 26.20. HRMS (ESI): $C_{96}H_{90}O_6$ for [M +

Na]$^+$ calculated 1361.66172, found 1361.66296.

Differential scanning calorimeter (DSC) and Thermogravimetric analysis (TGA) curves of macrocycles

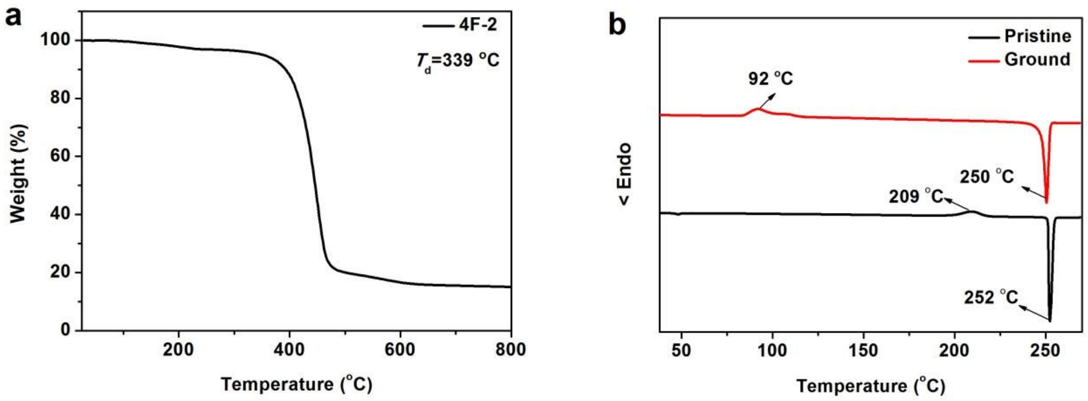


Fig. S1 TGA (a) and DSC (b) curves of **4F-2**

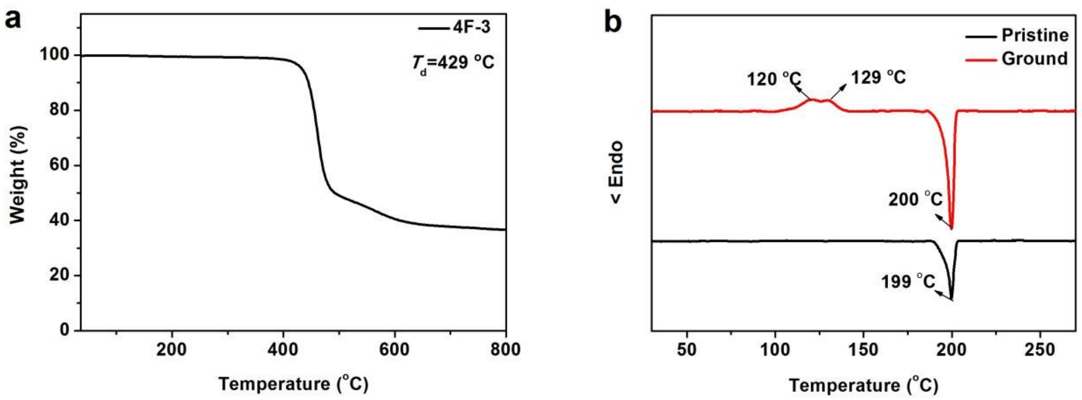


Fig. S2 TGA (a) and DSC (b) curves of **4F-3**

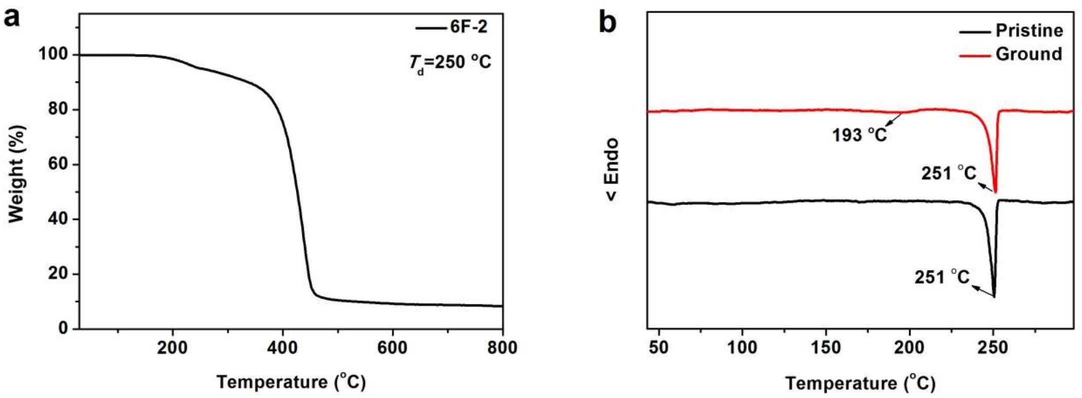


Fig. S3 TGA (a) and DSC (b) curves of **6F-2**

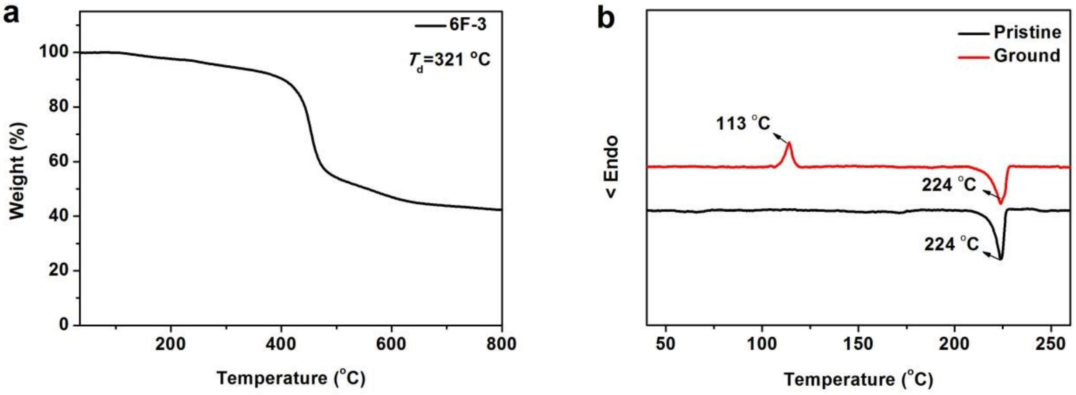


Fig. S4 TGA (a) and DSC (b) curves of **6F-3**

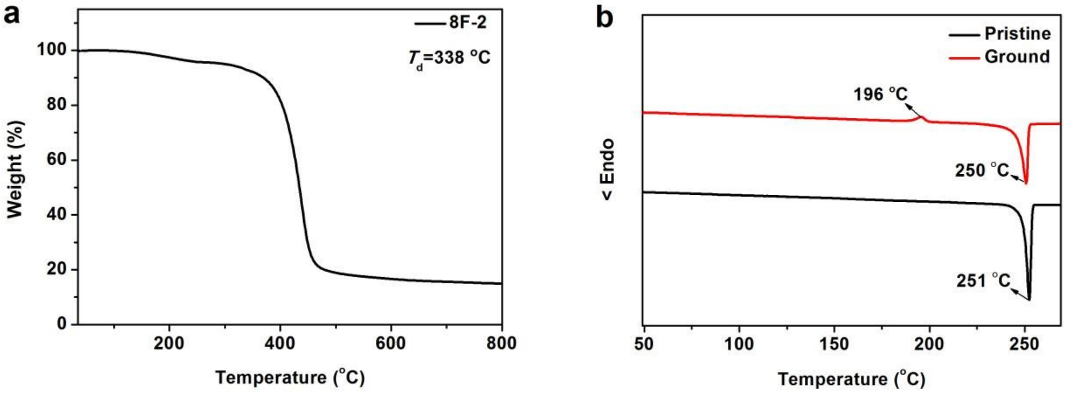


Fig. S5 TGA (a) and DSC (b) curves of **8F-2**

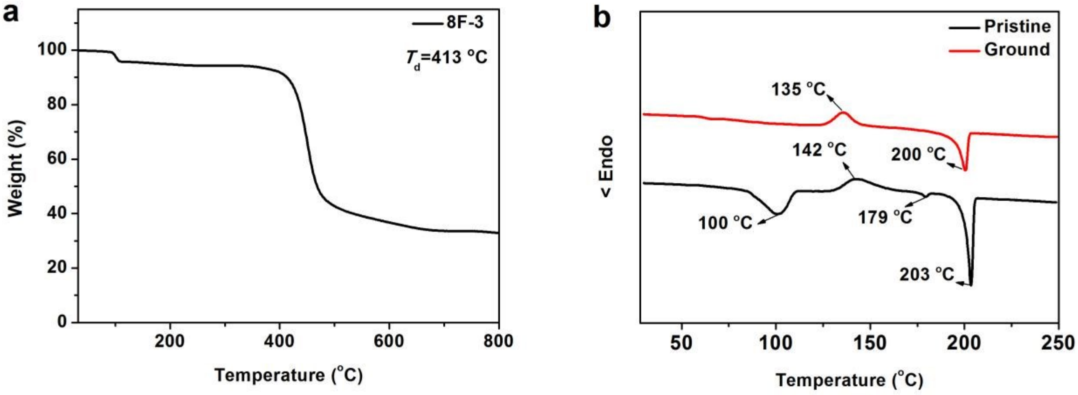


Fig. S6 TGA (a) andDSC (b) curves of **8F-3**

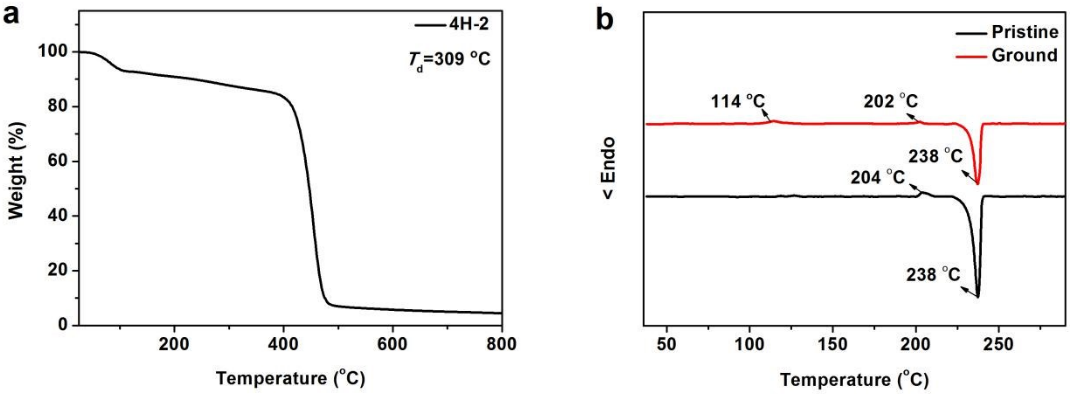


Fig. S7 TGA (a) and DSC (b) curves of **4H-2**

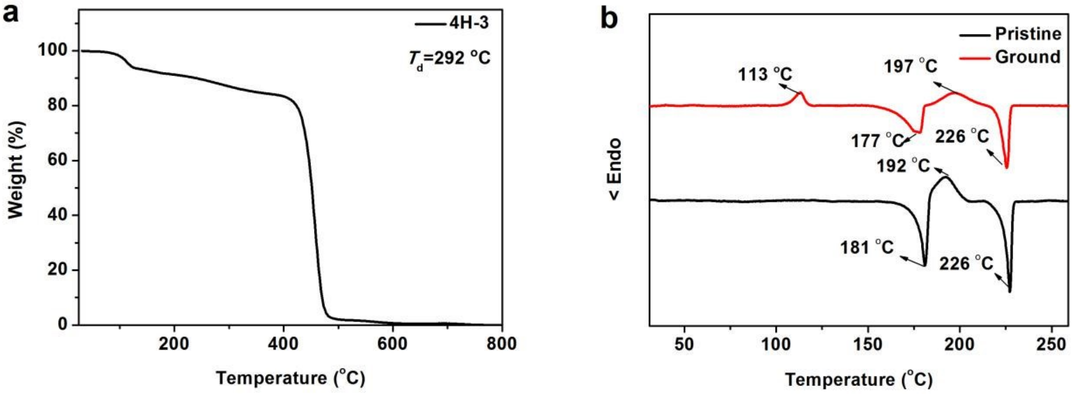


Fig. S8 TGA (a) and DSC (b) curves of **4H-3**

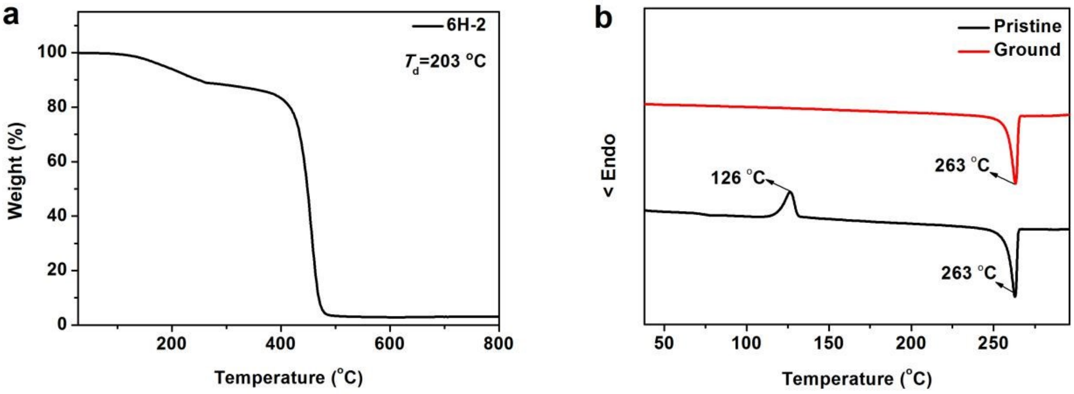


Fig. S9 TGA (a) and DSC (b) curves of **6H-2**

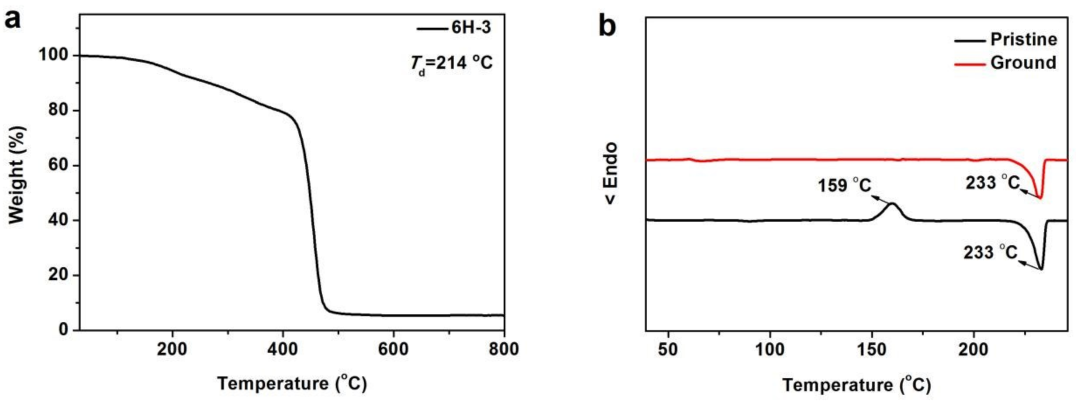


Fig. S10 TGA (a) and DSC (Right) curves of **6H-3**

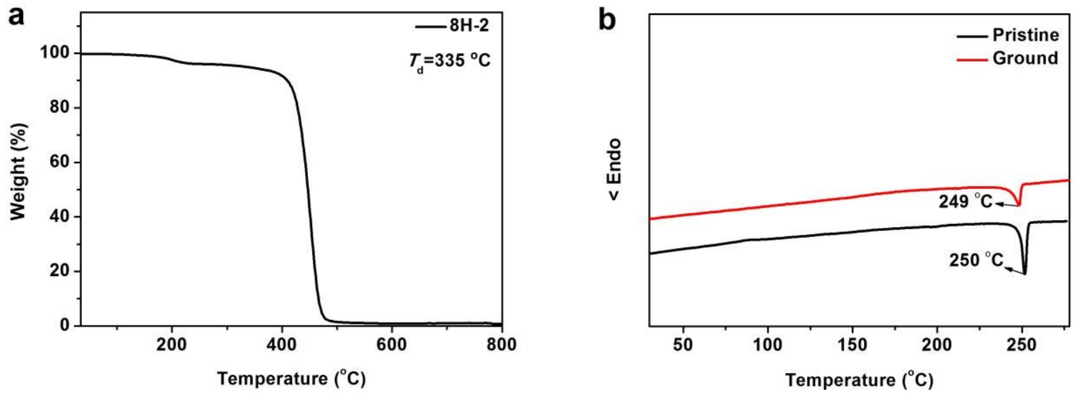


Fig. S11 TGA (a) and DSC (b) curves of **8H-2**

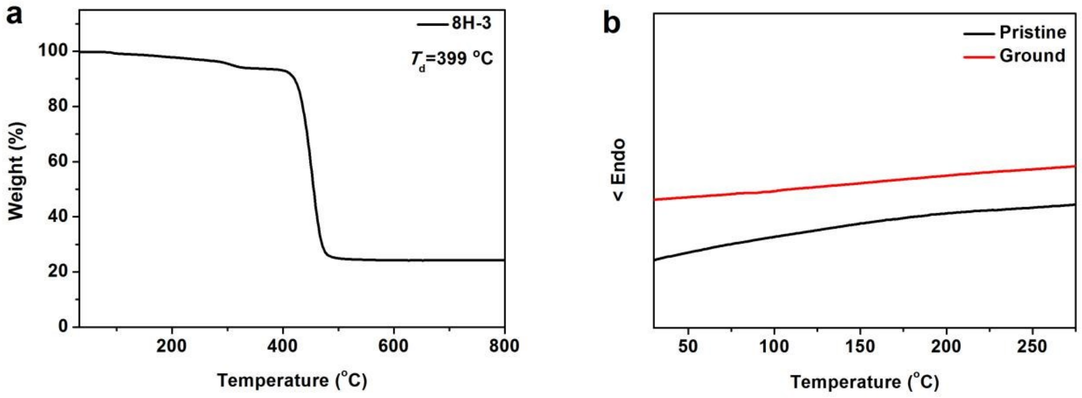


Fig. S12 TGA (a) and DSC (b) curves of **8H-3**

Table S1. Thermal behaviour of the macrocycles

compound	T_g/°C [a]	T_d/°C[b]
4F-2	P 209 G 92	339
4F-3	G 120, 129	429

4H-2	P 204 G 114, 202	309
4H-3	P181, 192 G 113, 177, 197	292
6F-2	G 193	250
6F-3	G 113	321
6H-2	P 126	203
6H-3	P 159	214
8F-2	G 196	338
8F-3	P 100, 142, 179 G 135	413
8H-2		335
8H-3		399

[a] T_g (glass transition temperature) were determined by DSC (peak temperature, first heating scan, 10°C min^{-1}) , P = pristine, G = ground, [b] Decomposition temperature.

Absoption and photoluminescence (PL) spectra of macrocycles in tetrahydrofuran /water mixtures with different water fractions

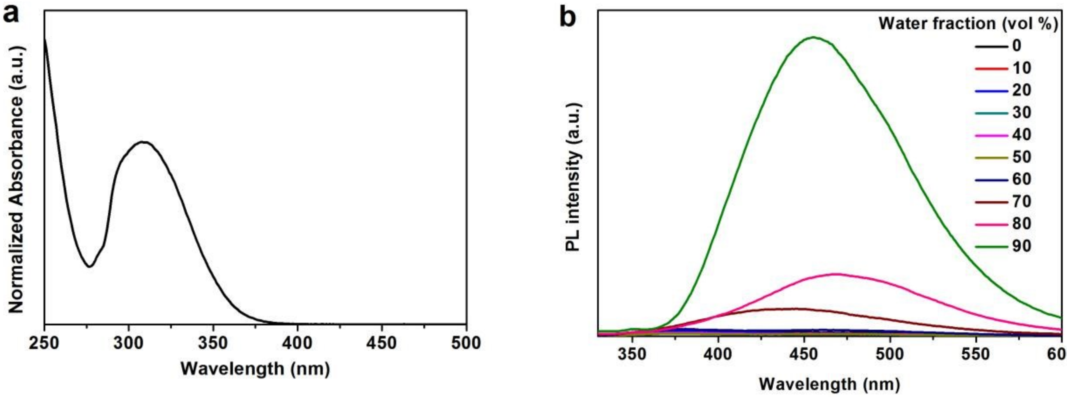


Fig. S13 (a) Absorption spectrum of **4F-2** in THF solution and (b) PL intensity spectra of **4F-2** in tetrahydrofuran/water mixtures with different water fractions

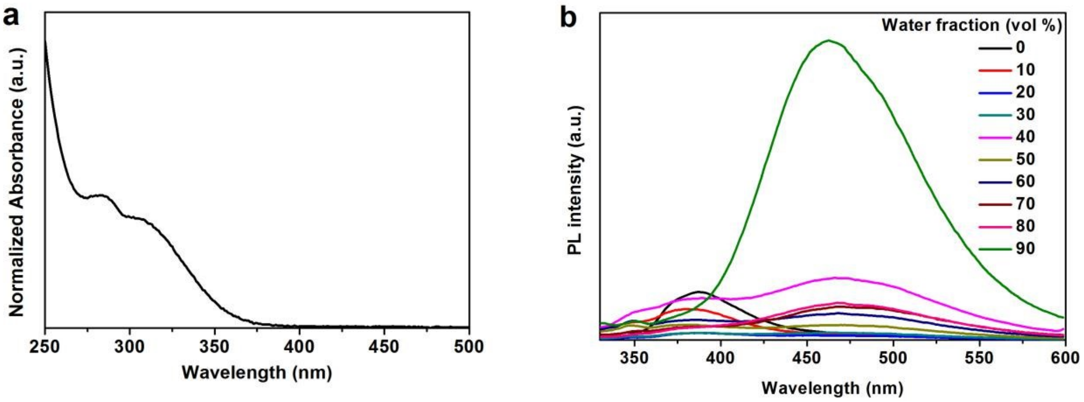


Fig. S14 (a) Absorption spectrum of **4F-3** in THF solution and (b) PL intensity spectra of **4F-3** in tetrahydrofuran/water mixtures with different water fractions

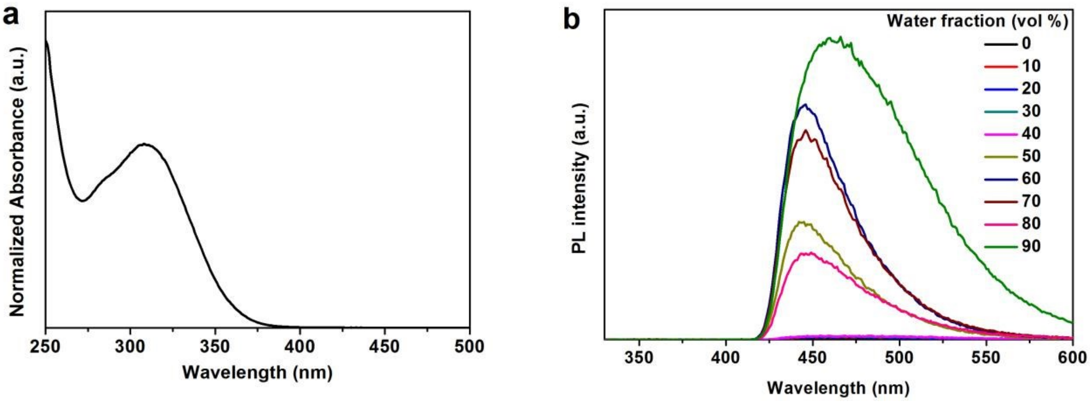


Fig. S15 (a) Absorption spectrum of **6F-2** in THF solution and (b) PL intensity spectra of **6F-2** in tetrahydrofuran/water mixtures with different water fractions

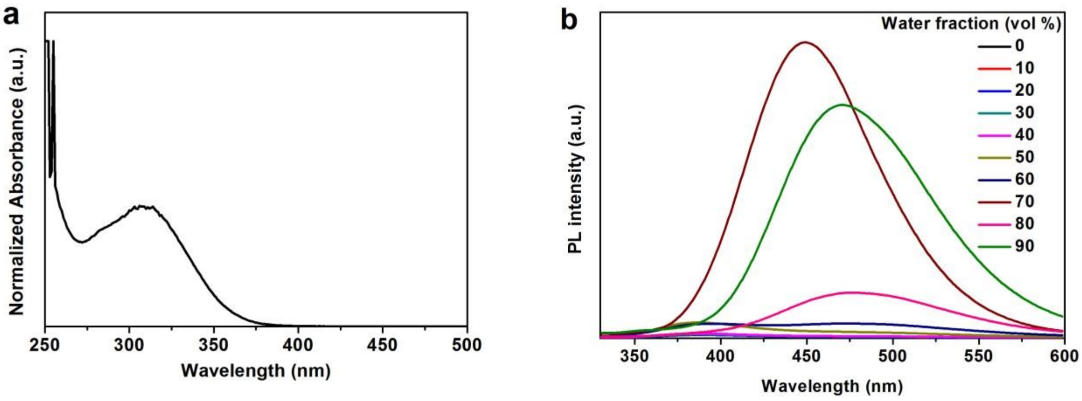


Fig. S16 (a) Absorption spectrum of **6F-3** in THF solution and (b) PL intensity spectra of **6F-3** in tetrahydrofuran/water mixtures with different water fractions

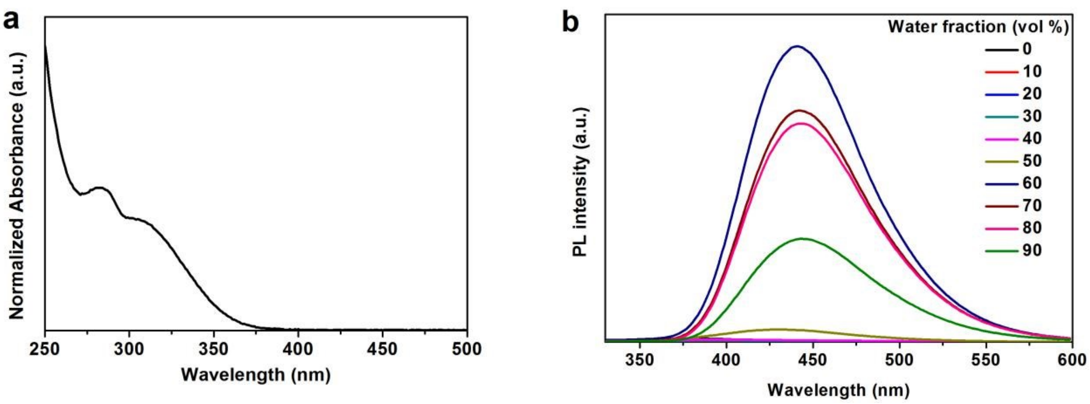


Fig. S17 (a) Absorption spectrum of **8F-2** in THF solution and (b) PL intensity spectra of **8F-2** in tetrahydrofuran/water mixtures with different water fractions

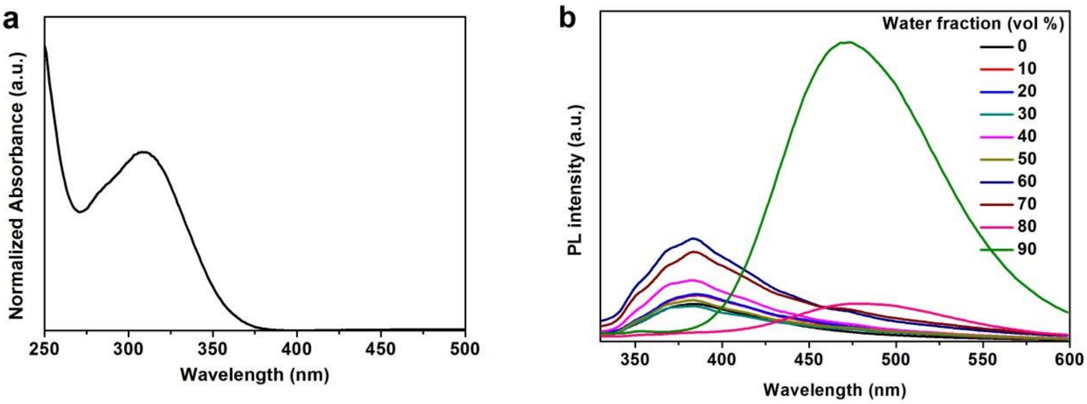


Fig. S18 (a) Absorption spectrum of **8F-3** in THF solution and (b) PL intensity spectra of **8F-3** in tetrahydrofuran/water mixtures with different water fractions

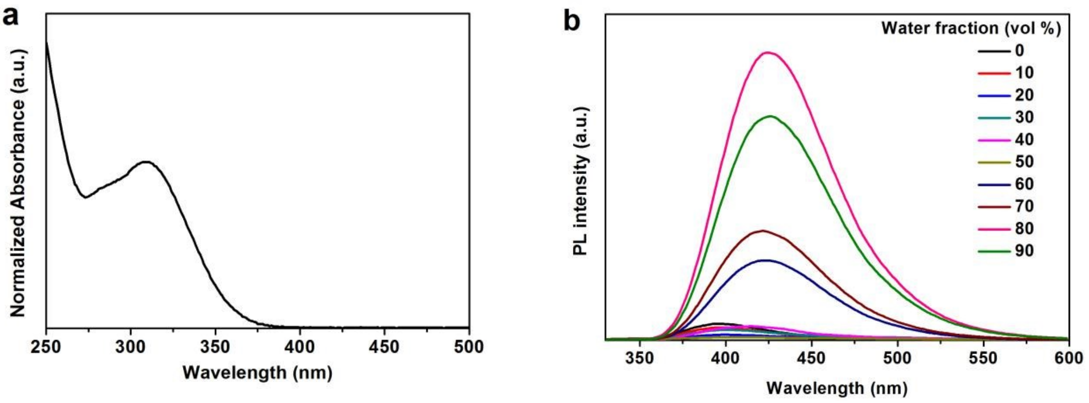


Fig. S19 (a) Absorption spectrum of **4H-2** in THF solution and (b) PL intensity spectra of **4H-2** in tetrahydrofuran/water mixtures with different water fractions

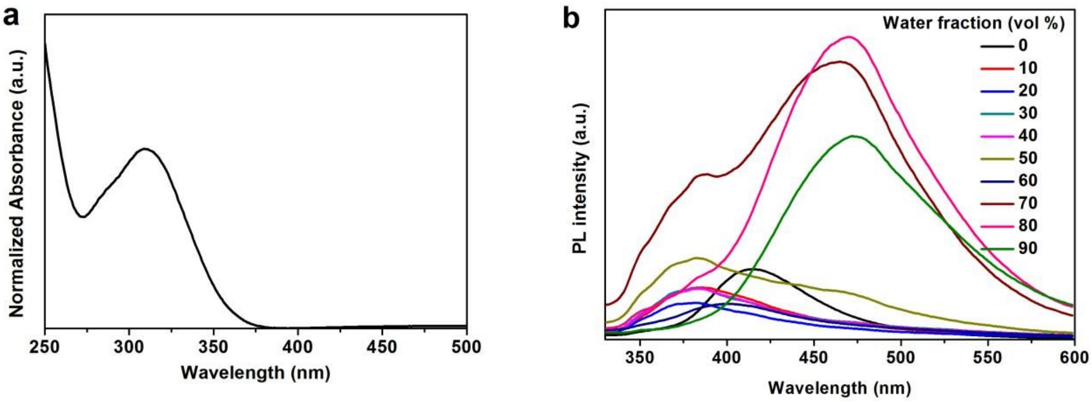


Fig. S20 (a) Absorption spectrum of **4H-3** in THF solution and (b) PL intensity spectra of **4H-3** in tetrahydrofuran/water mixtures with different water fractions

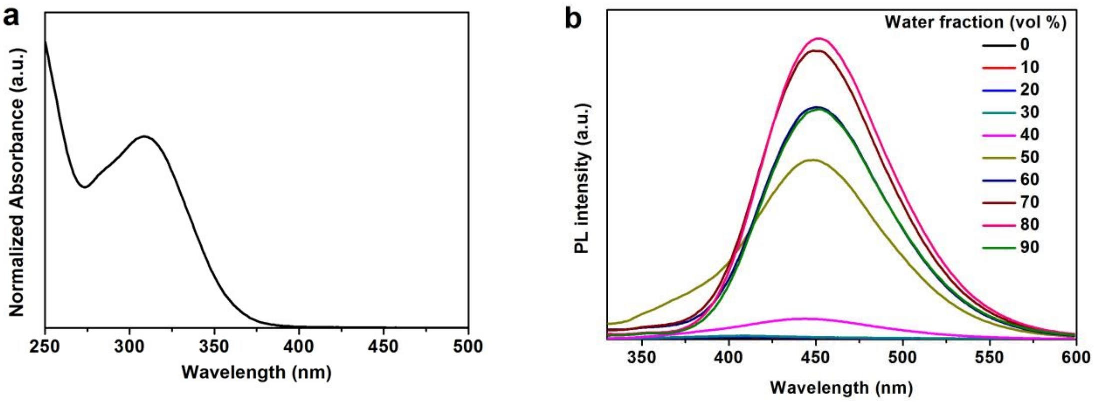


Fig. S21 (a) Absorption spectrum of **6H-2** in THF solution and (b) PL intensity spectra of **6H-2** in tetrahydrofuran/water mixtures with different water fractions

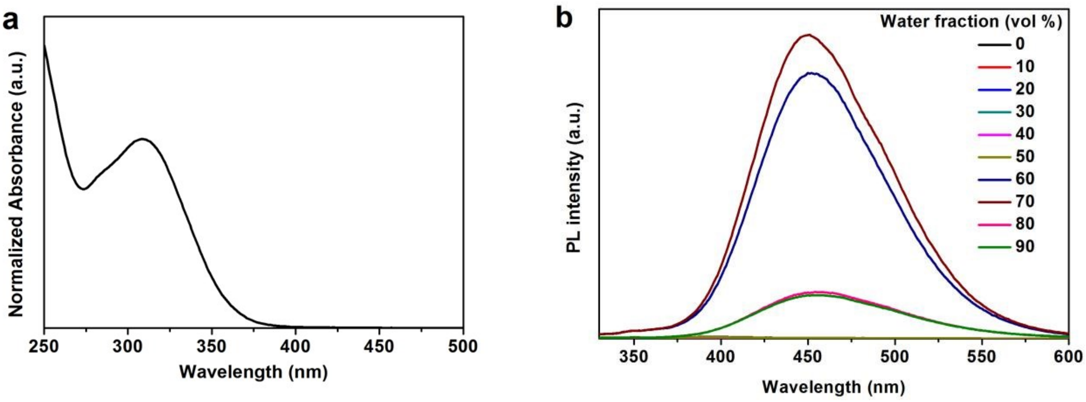


Fig. S22 (a) Absorption spectrum of **6H-3** in THF solution and (b) PL intensity spectra of **6H-3** in tetrahydrofuran/water mixtures with different water fractions

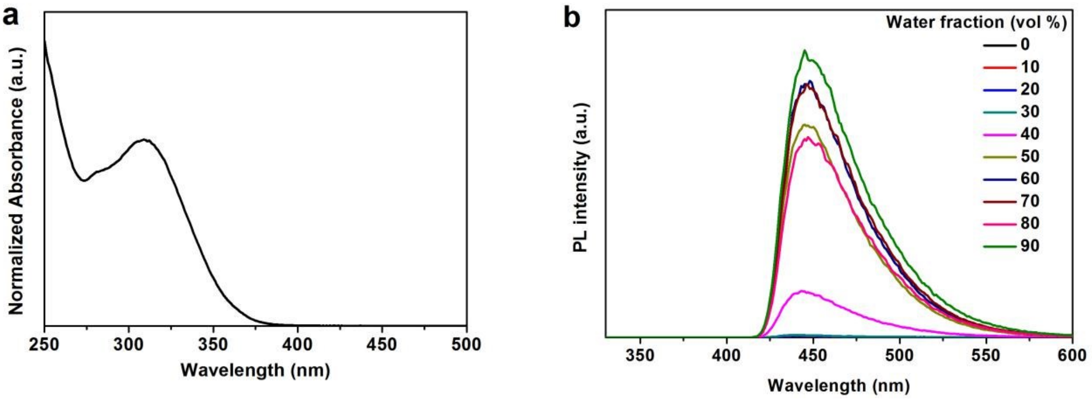


Fig. S23 (a) Absorption spectrum of **8H-2** in THF solution and (b) PL intensity spectra of **8H-2** in tetrahydrofuran/water mixtures with different water fractions

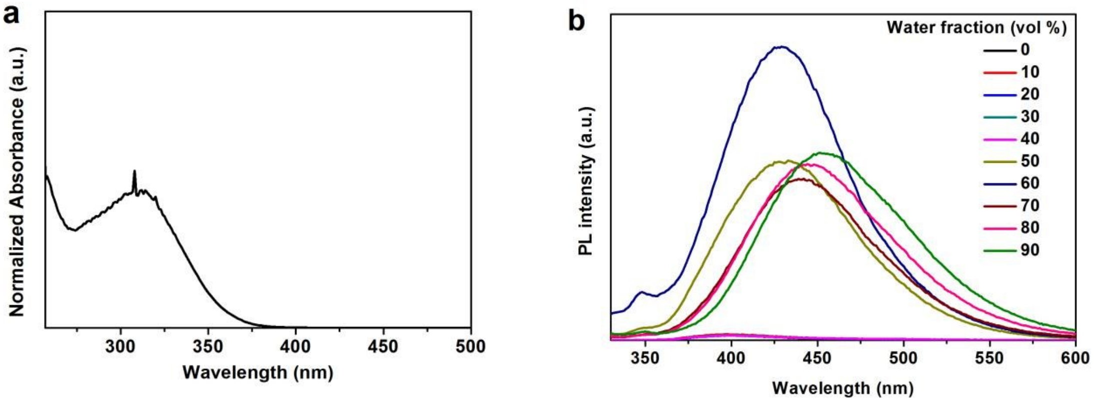


Fig. S24 (a) Absorption spectrum of **8H-3** in THF solution and (b) PL intensity spectra of **8H-3**in tetrahydrofuran/water mixtures with different water fractions

The normalized PL spectra of macrocycles in solid state

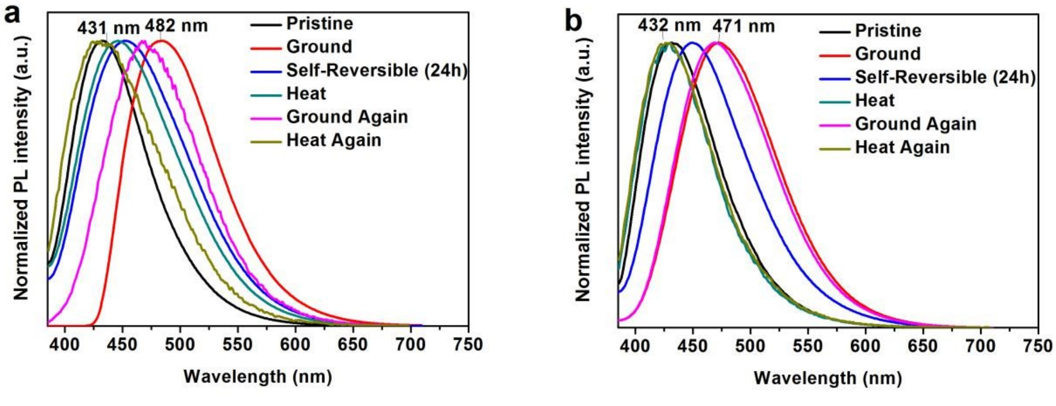


Fig. S25 Normalized PL spectra of **4F-2** (a) and **4H-2** (b) excited at 365 nm.

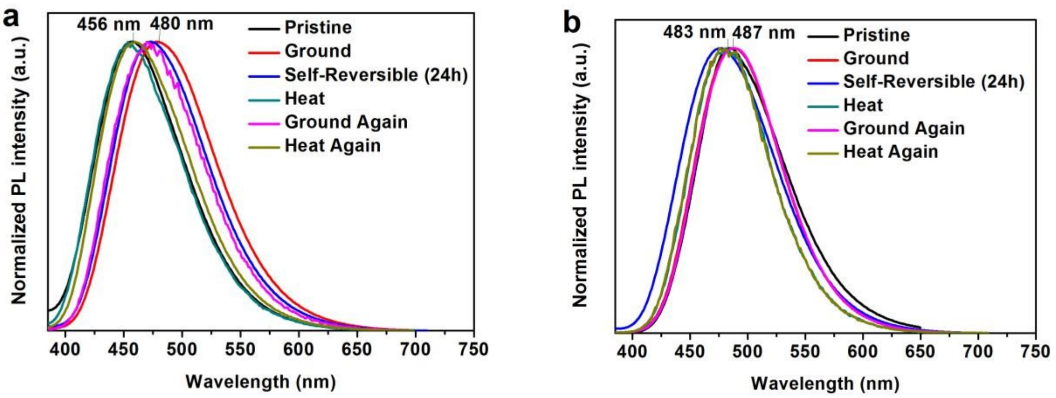


Fig. S26 Normalized PL spectra of **4F-3** (a) and **4H-3** (b) excited at 365 nm.

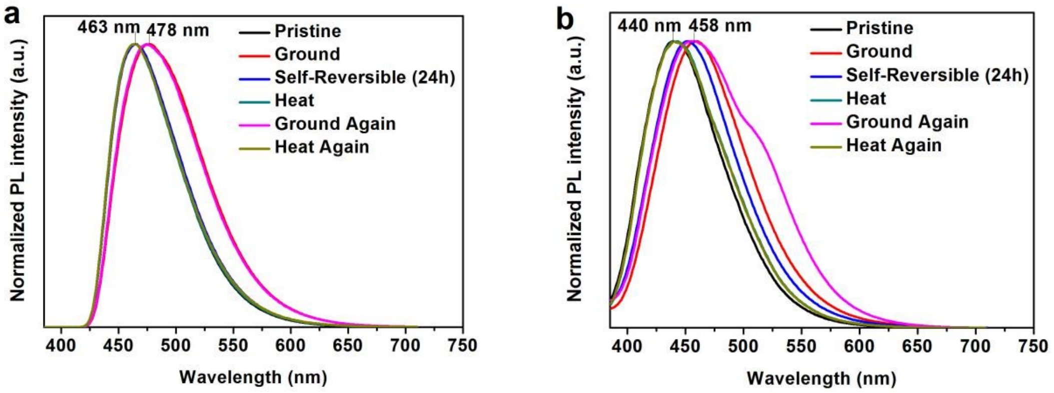


Fig. S27 Normalized PL spectra of **6F-2** (a) and **6H-2** (b) excited at 365 nm.

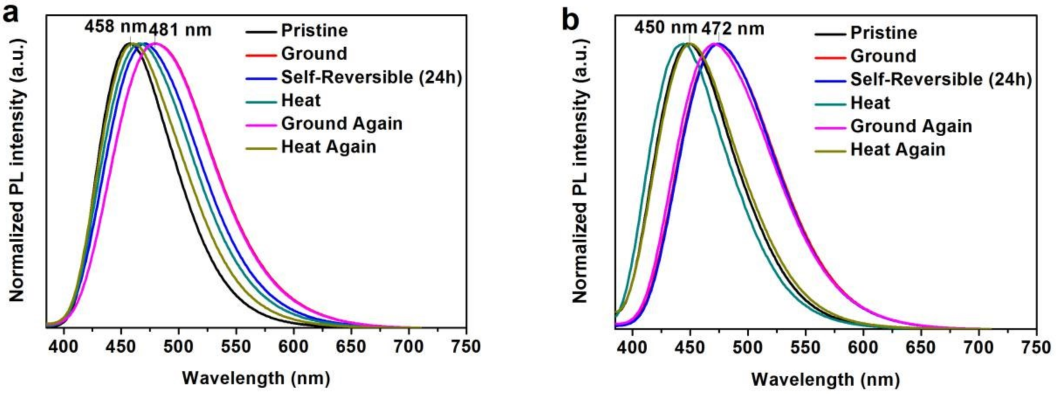


Fig. S28 Normalized PL spectra of **6F-3** (a) and **6H-3** (b) excited at 365 nm.

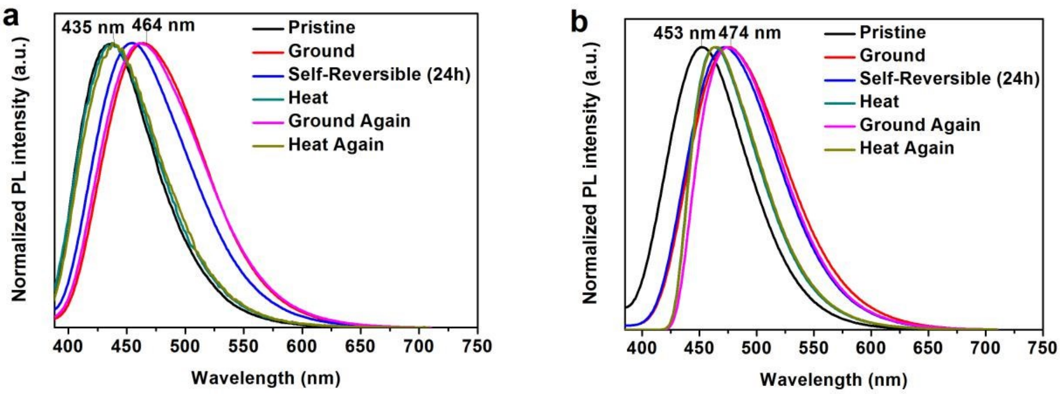


Fig. S29 Normalized PL spectra of **8F-2** (a) and **8H-2** (b) excited at 365 nm.

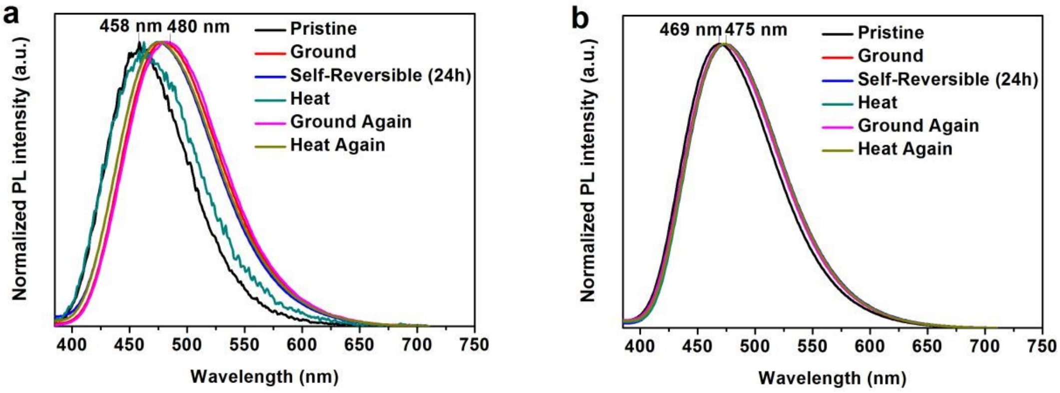


Fig. S30 Normalized PL spectra of **8F-3** (a) and **8H-3** (b) excited at 365 nm.

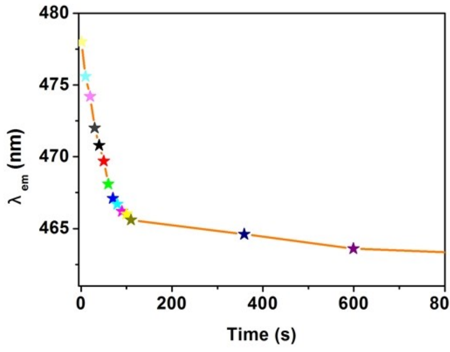


Fig. S31 The time dependent maximum emission wavelengths of the ground **6F-2** (in mortar).

Table S2. Photophysical data of the TPE-based macrocycles

Compound	λ_{em} [a] (nm)	λ_{em} [b] (nm)	$\Delta\lambda_{em}$ [c] (nm)	λ_{em} [d] (nm)	Φ_F [a](%)	Lifetime[a] (τ_F, ns)

4F-2	431	482	51	451	29.24	1.00
4H-2	432	471	39	449	47.64	3.96
6F-2	463	478	15	460 (463[e])	11.08	1.47
6H-2	440	458	18	452	9.10	0.82
8F-2	435	464	29	453	31.52	2.06
8H-2	453	474	21	472	11.45	3.13
4F-3	456	480	24	474	9.63	4.14
4H-3	483	487	4	478	46.66	5.22
6F-3	458	481	23	469	13.00	1.27
6H-3	450	472	22	471	19.30	2.72
8F-3	458	480	22	475	14.39	4.13
8H-3	469	475	6	473	9.40	3.90

[a] Pristine solid powders [b] Ground solid powders [c] Red shift of ground solid powders [d] Ground solid powders stand at room temperature for 24 h. [e] Ground solid powders stand at room temperature for 100 s.

The PL spectra of 4F-2 and 4H-3 in the presence of different monadic acids with different volumes

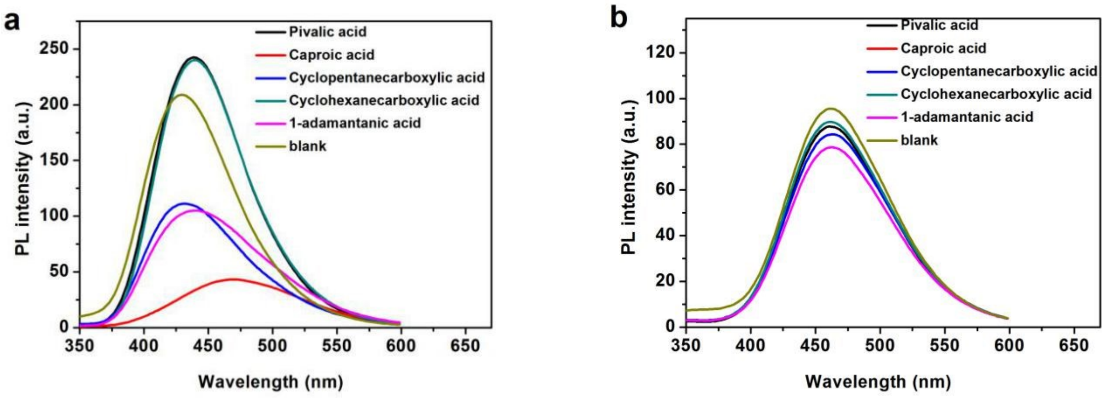


Fig. S32 The PL spectra of a) **4F-2** and b) **4H-3** in THF/water mixture (f_w = 90%) in the presence of 1.1 × 10^{-4} M of different monadic acidsof different volumes. [**4H-3**] = 1.0 ×

10^{-4} M.

The 1H NMR spectra of 4F-3, 1-adamantanic acid and mixture

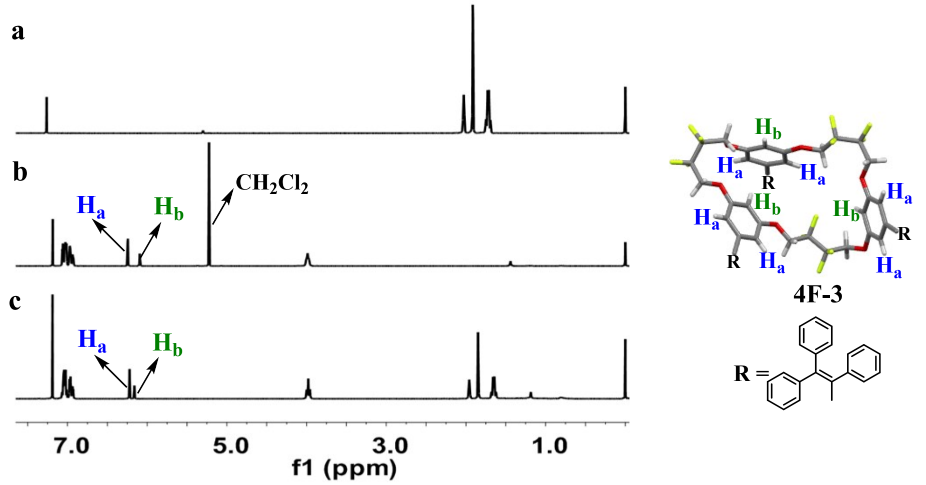


Fig. S33 ^{1}H NMR (600 MHz, $CDCl_3$) of (a) 1-adamantanic acid, (b) **4F-3** and (c) mixture of **4F-3** and 1-adamantanic acid (**4F-3**:1-adamantanic acid=1:1.1)

Theoretical calculations of macrocycles

To further understand the electronic structure of macrocycles, the geometry optimization was carried out by density functional theory (DFT) method at B3LYP/6-31G (d) leve^5 in the gas state. As described in Table 3, the ΔEHL (HOMO (The highest Occupied Molecular Orbital)-LUMO (The lowest Unoccupied Molecular Orbital) gap, $\Delta E_{HL} = E_{LUMO} - E_{HOMO}$) value of **6F-2** was larger than that of **6H-2**. interestingly, the HOMO of 6F-2 was distributed over the central double bond of two TPE cores, whereas the corresponding LUMO was mainly localized on the four phenyl groups of one TPE core and the central double bond of the other TPE core, which was different from its alkyl bridged analogue **6H-2**.

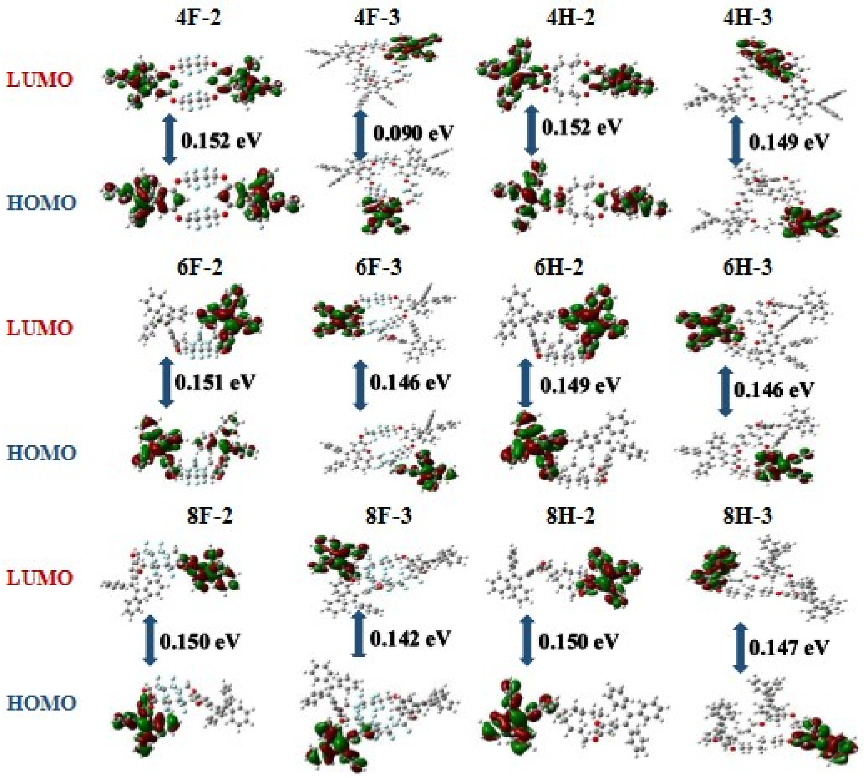


Fig. S34 Molecular orbital amplitude plots of HOMO and LUMO energy levels of macrocycles calculated at B3LYP/6-31+G(d) level based on the geometry optimization.

Table S3. Geometrical parameters of thel macrocycles calculated by Gaussian09

Compounds	Energy[a.u.]	E_{HOMO}[eV]	E_{LUMO}[eV]	ΔE_{HL}[eV]	$D^{[a, b]}$ [Å]
4F-2	-3412.442794	-0.199	-0.047	0.152	3.01-8.67^{a} 3.47-3.91^{b}
4H-2	-2618.554343	-0.195	-0.043	0.152	3.29-8.79^{b}
4F-3	-5118.764563	-0.169	-0.079	0.090	2.74-11.23^{a} 3.40-3.81^{b}
4H-3	-3928.663309	-0.204	-0.055	0.149	4.64-12.87^{b}
6F-2	-3887.986918	-0.202	-0.051	0.151	4.47-8.15^{a} 2.98-6.73^{b}
6H-2	-2697.175477	-0.199	-0.050	0.149	2.88-8.10^{a} 6.36-9.44^{b}
6F-3	-5832.000934	-0.196	-0.050	0.146	3.12-6.86^{b}
6H-3	-4046.629737	-0.201	-0.055	0.146	5.05-11.23^{b}
8F-2	-4363.556732	-0.197	-0.047	0.150	2.722-7.136^{b}
8H-2	-2775.803440	-0.194	-0.044	0.150	4.497-8.766^{b}
8F-3	-6546.957253	-0.204	-0.062	0.142	2.984-6.732^{b}

8H-3	-4164.586557	-0.203	-0.056	0.147	6.535-10.368[b]

D, the width of the cavity of compound [a] A single crystal [b] Macrocycle calculated at B3LYP/6-31G* level based on the geometry optimization.

Powder X-ray diffraction (PXRD) of 4F-2, 4H-2, 6F-3 and 6H-3

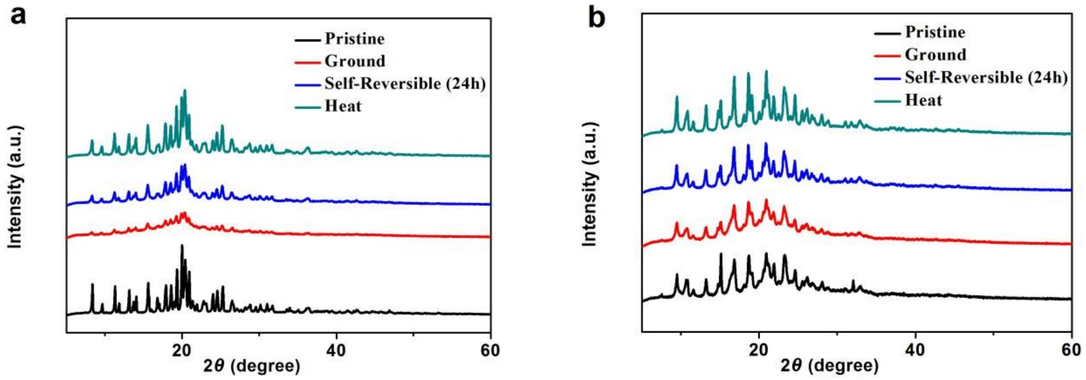


Fig. S35 PXRD patterns of a) **4F-2**, b) **4H-2**.

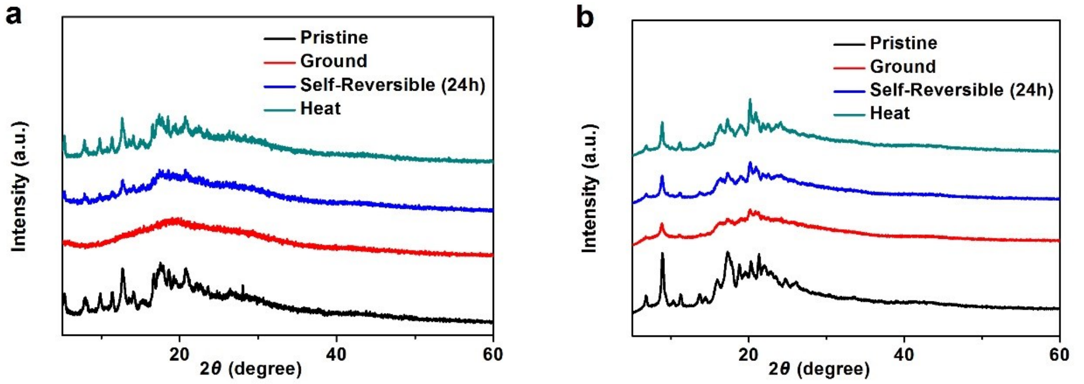


Fig. S36 PXRD patterns of a) **6F-3**, b) **6H-3**.

Single crystal structure of 4F-2 and 4F-3

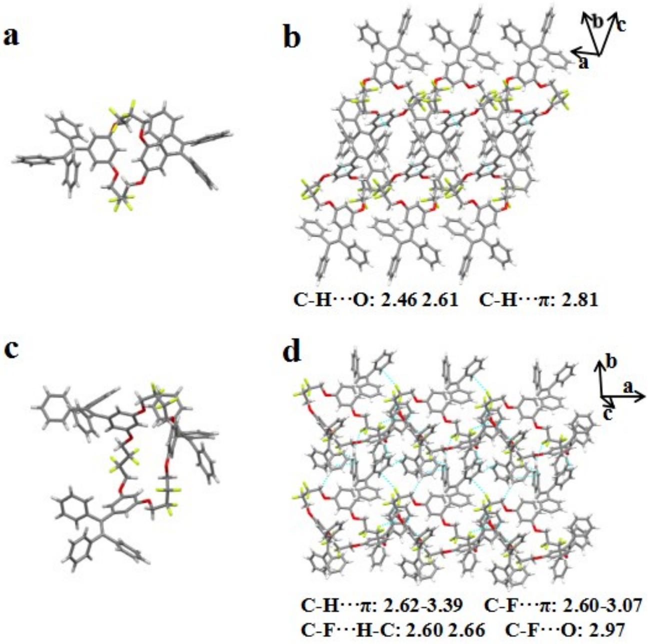


Fig. S37 Single crystal structures a) **4F-2** and c) **4F-3** and molecular packing of b) **4F-2** and d) **4F-3**.

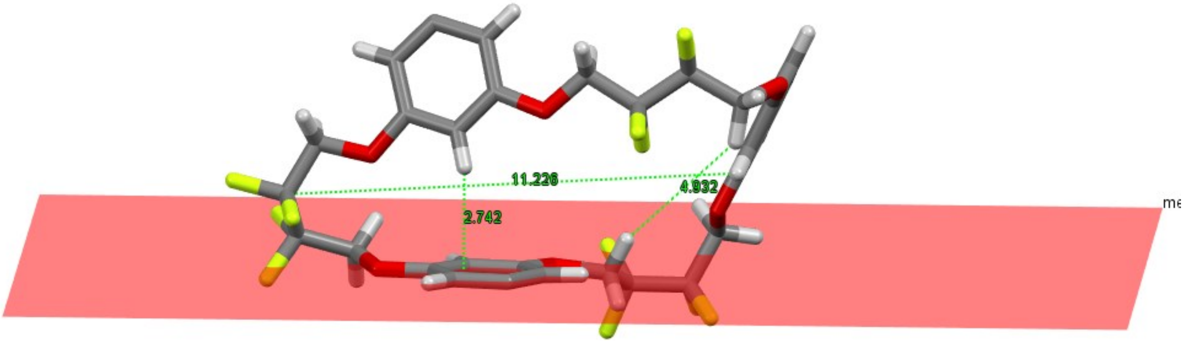


Fig. S38 cage width of single crystal **4F-3**

Crystal data and structure refinement of 4F-2, 4F-3, 6F-2 and 6H-2

Table S4. Crystal data and structure refinement for **4F-2** (CCDC 2017303)**.**

complex	**4F-2**
empirical formula	$C_{60}H_{44}F_8O_4$
formula weight	980.95
T (K)	296(2)
crystal system	Triclinic
space group	*P -1*
a (Å)	9.9525(2)
b (Å)	14.0868(3)
c (Å)	19.2659(4)

a (deg)	76.5590(10)
β(deg)	75.7270(10)
γ(deg)	80.8660(10)
V (Å^3)	2531.20(9)
Z	2
D calcd (Mg/m3)	1.287
μ/mm^{-1}	0.839
F (000)	1016
GOF	1.041
R1 [I > 2σ(I)] ^{a}	0.0869
ωR$_2$ (all data) ^{b}	0.2520
Data/restraints/parameters	8317 / 0 / 650
CCDC number	2017303

Table S5. Crystal data and structure refinement for **4F-3** (CCDC 2017304)**.**

complex	**4F-3**
empirical formula	C_{90} H_{66} F_{12} O6
formula weight	1471.42
T (K)	193(2)
crystal system	Triclinic
space group	*P -1*
a (Å)	12.0167(4)
b (Å)	13.5794(5)
c (Å)	22.8168(9)
a (deg)	93.7120(10)
β(deg)	95.6130(10)
γ(deg)	92.8560(10)
V (Å^3)	3691.7(2)
Z	2
D calcd (mg/m^3)	1.324
μ/mm^{-1}	0.102
F (000)	1524
GOF	1.044
R1 [I > 2σ(I)] ^{a}	0.0524
ωR$_2$ (all data) ^{b}	0.1344
Data/restraints/parameters	14467 / 1/ 974
CCDC number	2017304

Table S6. Crystal data and structure refinement for **6F-2** (CCDC 2017305)**.**

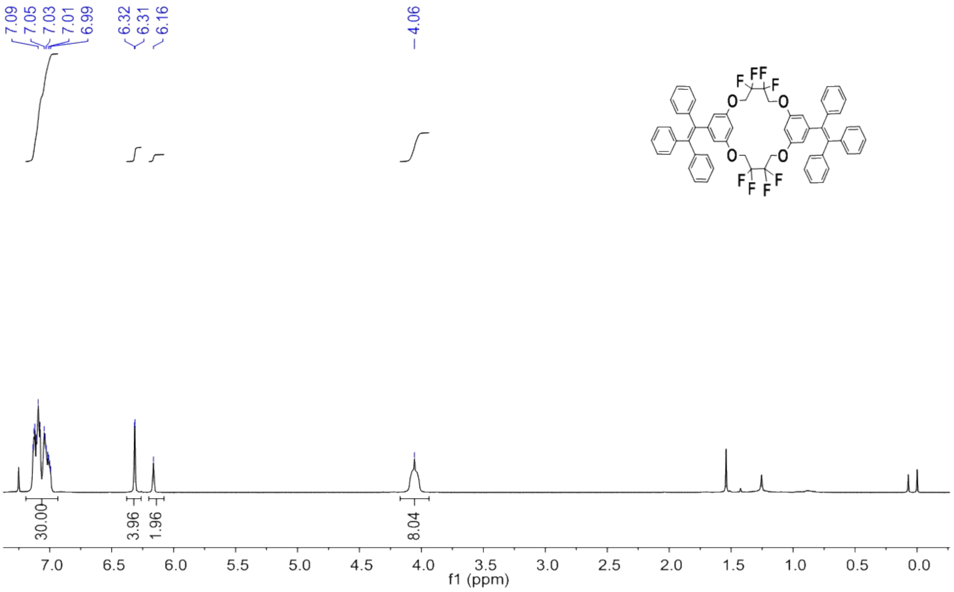
complex	**6F-2**
empirical formula	$C_{64}H_{46}Cl_6F_{12}O_4$
formula weight	1319.71
T (K)	293(2) K
crystal system	Triclinic
space group	*P -1*
a (Å)	9.0822(5)
b (Å)	12.8517(8)
c (Å)	13.3856(7)
a (deg)	100.129(2)
β(deg)	95.982(2)
γ(deg)	93.379(2)
V (Å^3)	1524.89(15)
Z	1
D calcd (mg/m^3)	1.437
μ/mm^{-1}	0.366
F (000)	672
GOF	1.041
R1 [I > 2σ(I)] [a]	0.0525
ωR$_2$ (all data) [b]	0.1554
Data/restraints/parameters	5635/ 48 / 433
CCDC number	2017305

Table S7. Crystal data and structure refinement for **6H-2** (CCDC 2017306)**.**

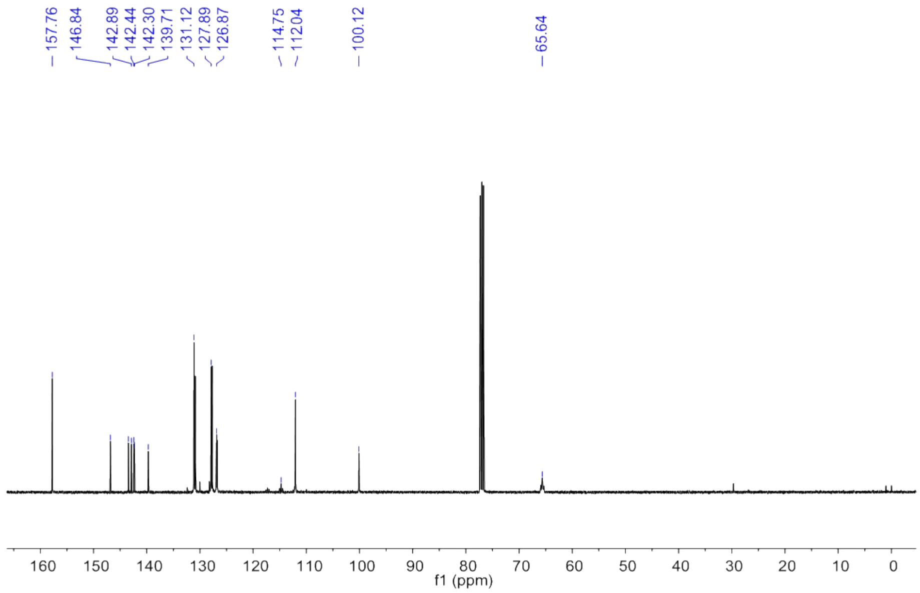
complex	**6H-2**
empirical formula	$C_{62}H_{56}O_4$
formula weight	865.06
T (K)	293(2) K
crystal system	Triclinic
space group	*P -1*
a (Å)	5.6038(2)
b (Å)	9.5867(4)
c (Å)	23.3111(9)
a (deg)	89.0650(10)
β(deg)	84.1400(10)
γ(deg)	74.9460(10)
V (Å^3)	1202.95(8)
Z	1
D calcd (mg/m^3)	1.194
μ/mm^{-1}	0.073
F (000)	460
GOF	1.030
R1 [I > 2σ(I)] [a]	0.0476

ωR$_2$ (all data) ^{b}	0.1138
Data/restraints/parameters	4677 / 72 / 334
CCDC number	2017306

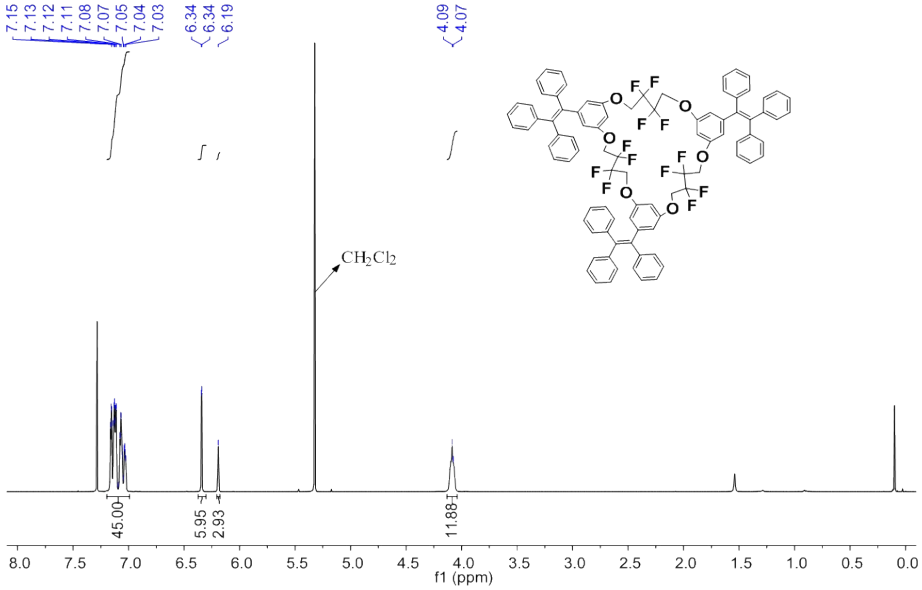
The NMR spectrum of macrocycles



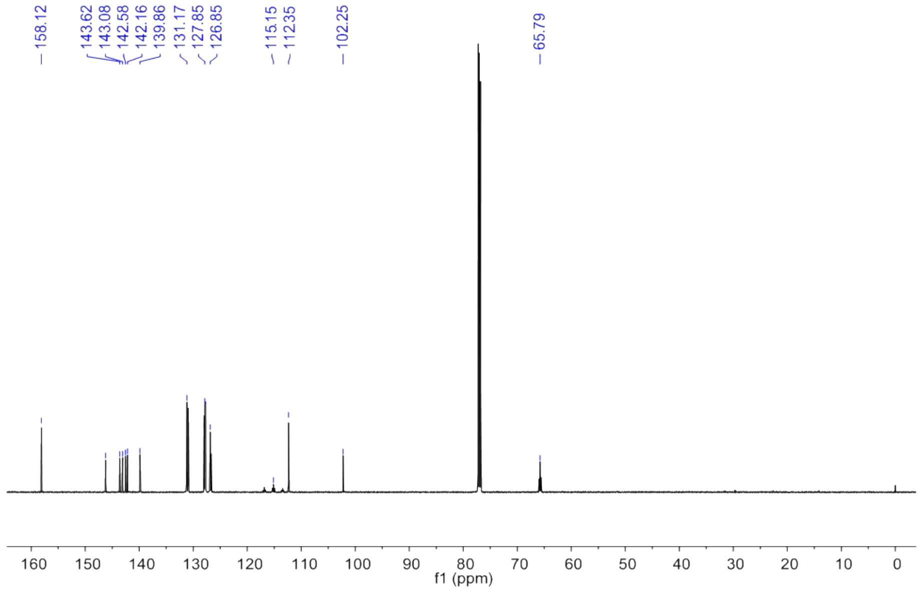
^{1}H-NMR spectrum of compound **4F-2** (CDCl$_3$, 400MHz)



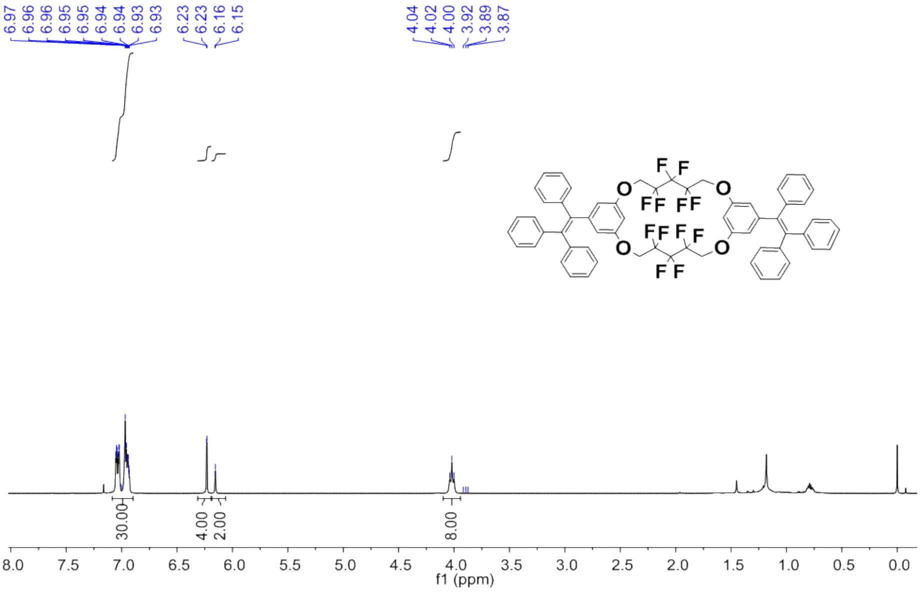
^{13}C-NMR spectrum of compound **4F-2** (CDCl$_3$, 400MHz)



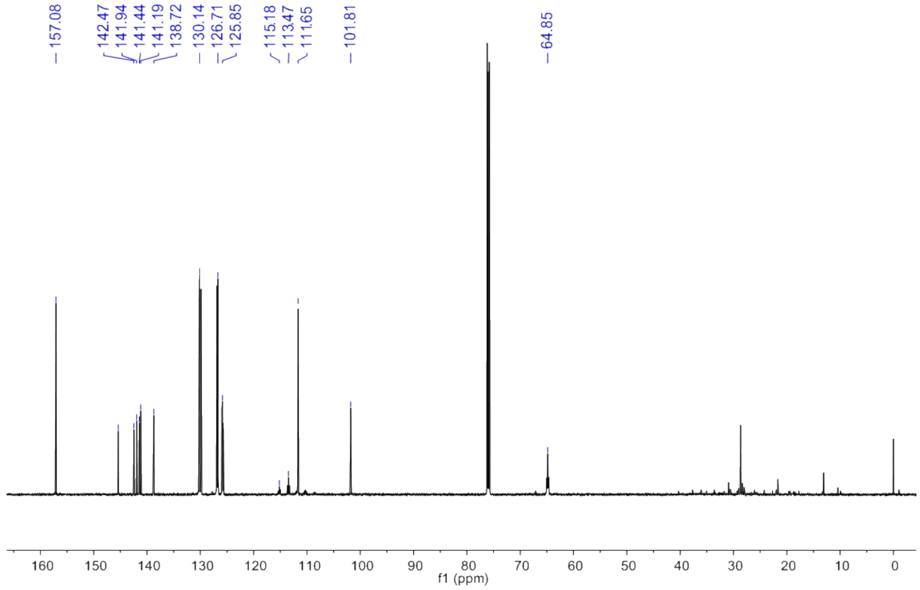
^{1}H-NMR spectrum of compound **4F-3** ($CDCl_3$, 600MHz)



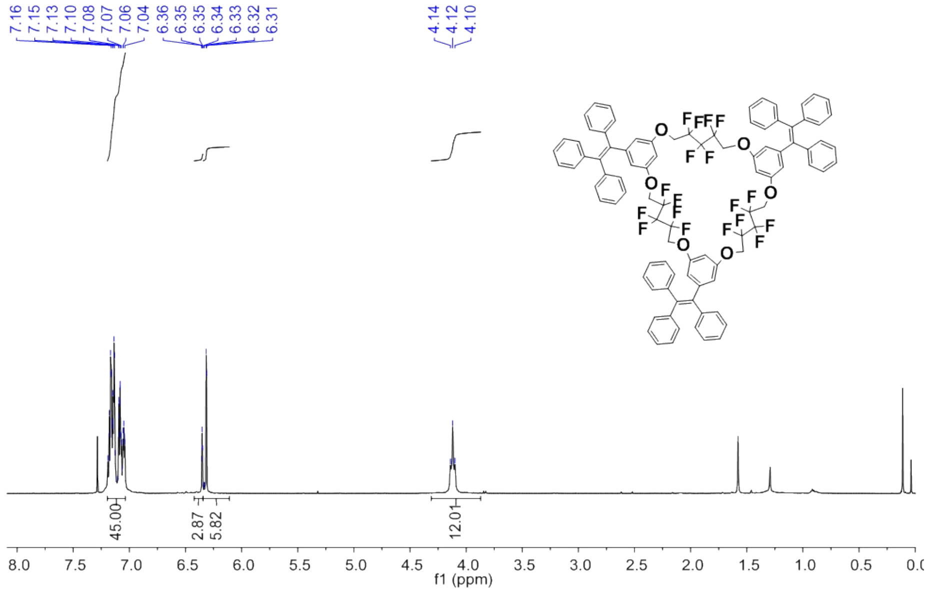
^{13}C-NMR spectrum of compound **4F-3** ($CDCl_3$, 600MHz)



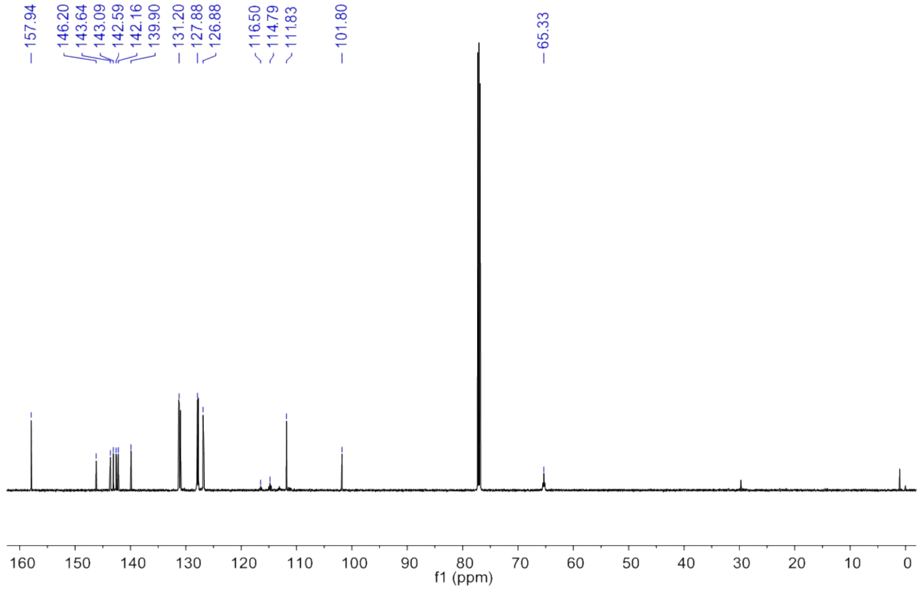
^{1}H-NMR spectrum of compound **6F-2** ($CDCl_3$, 600MHz)



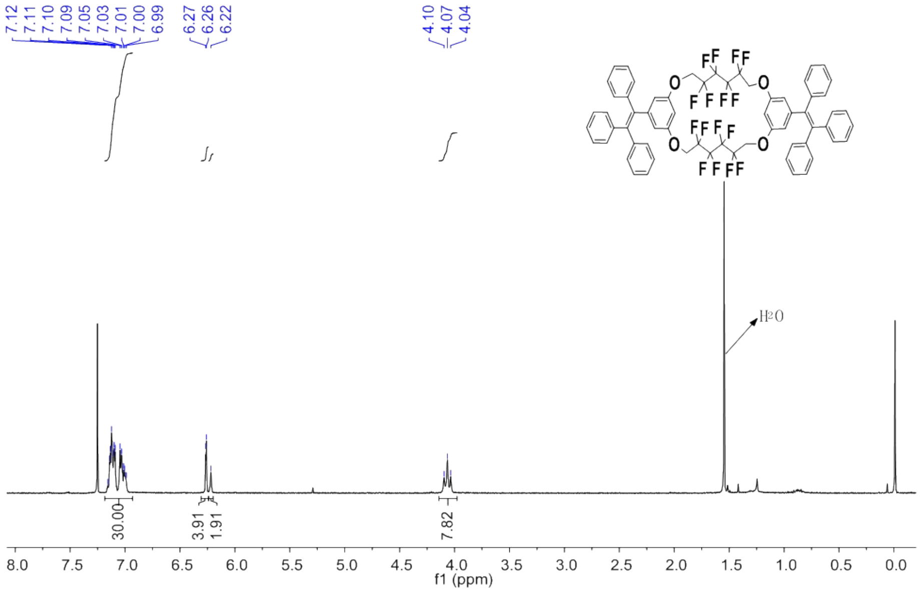
^{13}C-NMR spectrum of compound **6F-2** ($CDCl_3$, 600MHz)



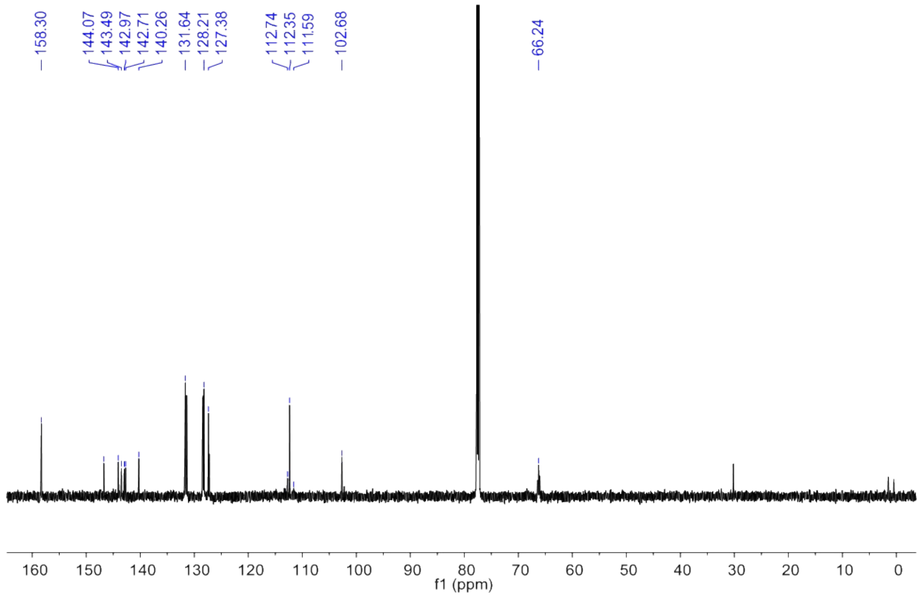
^{1}H-NMR spectrum of compound **6F-3** ($CDCl_3$, 600MHz)



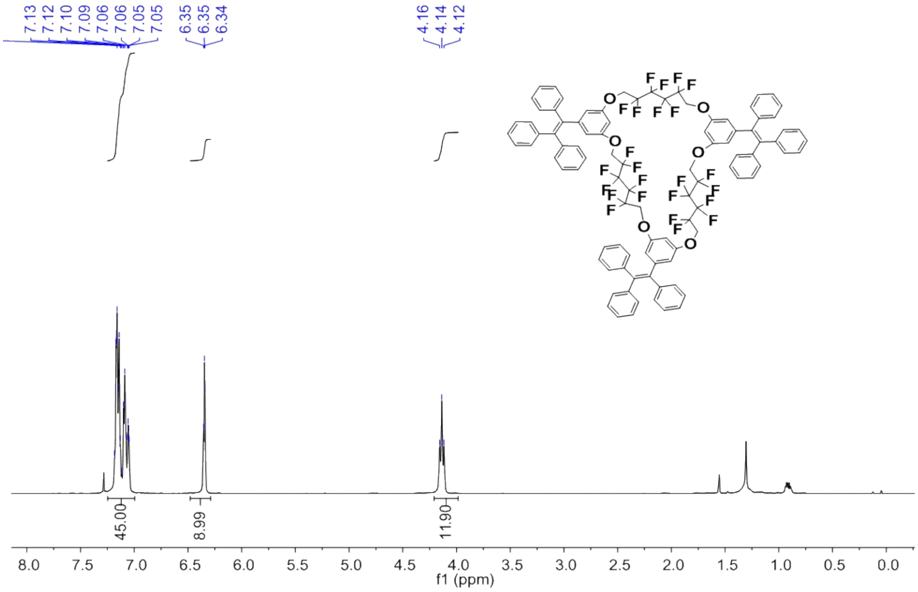
^{13}C-NMR spectrum of compound **6F-3** ($CDCl_3$, 600MHz)



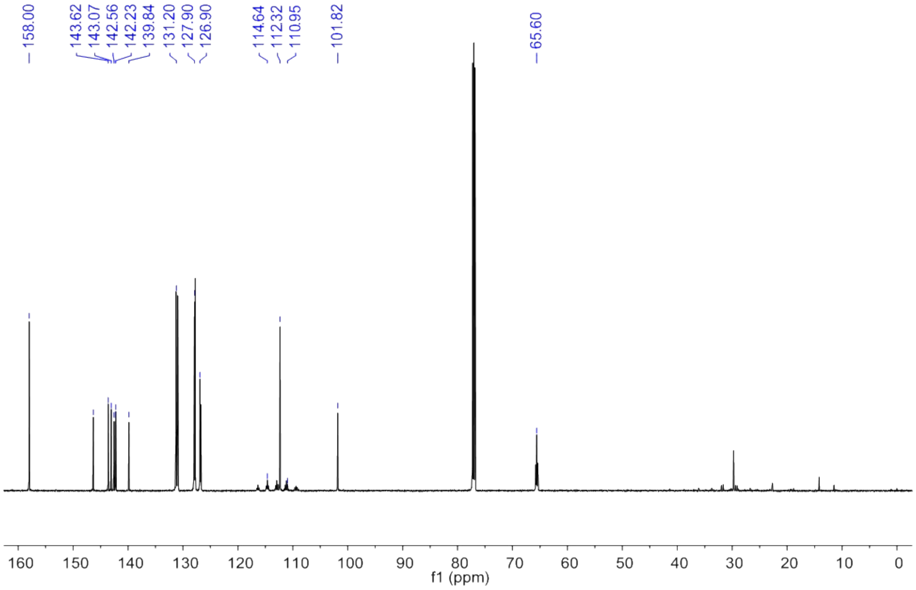
^{1}H-NMR spectrum of compound **8F-2** ($CDCl_3$, 400MHz)



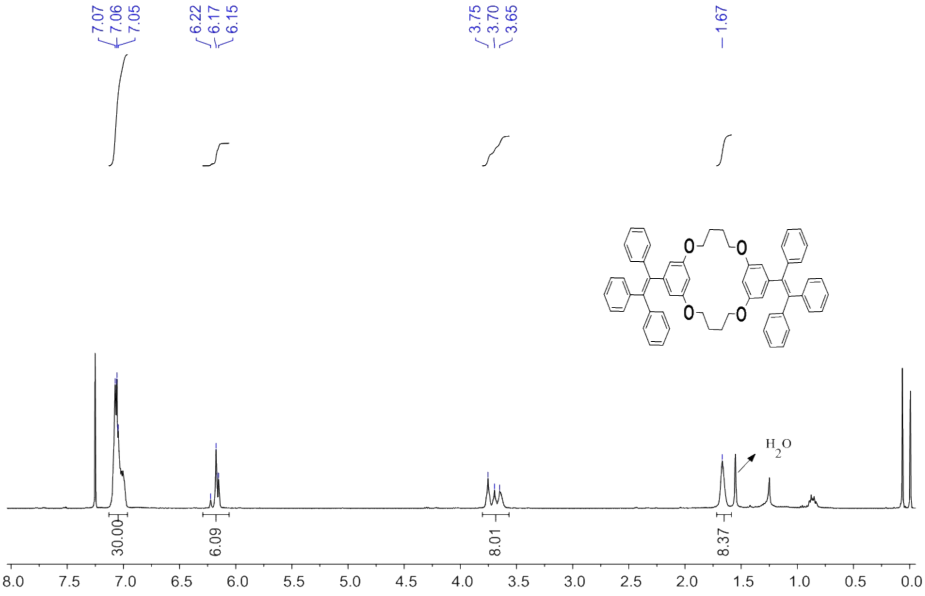
^{13}C-NMR spectrum of compound **8F-2** ($CDCl_3$, 600MHz)



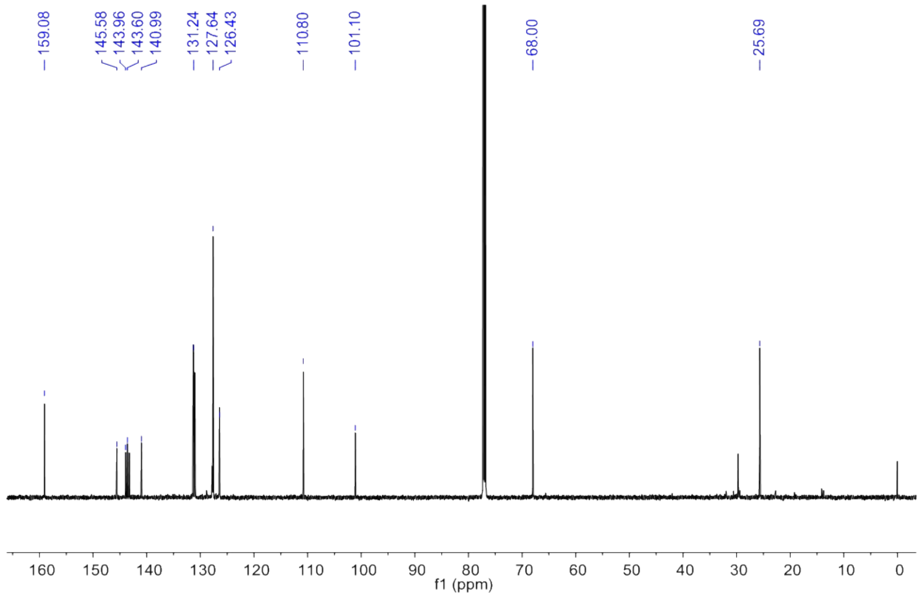
^{1}H-NMR spectrum of compound **8F-3** ($CDCl_3$, 600MHz)



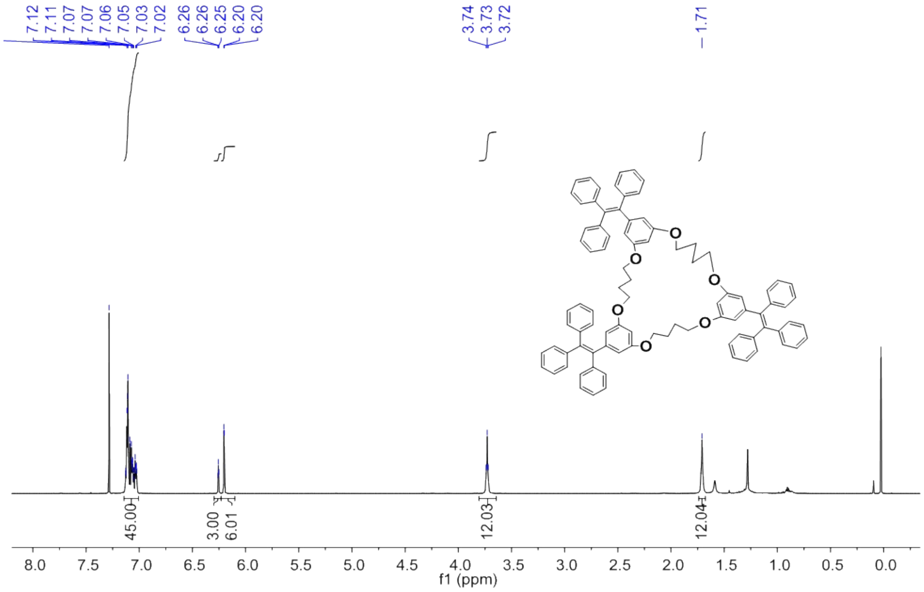
^{13}C-NMR spectrum of compound **8F-3** ($CDCl_3$, 600MHz)



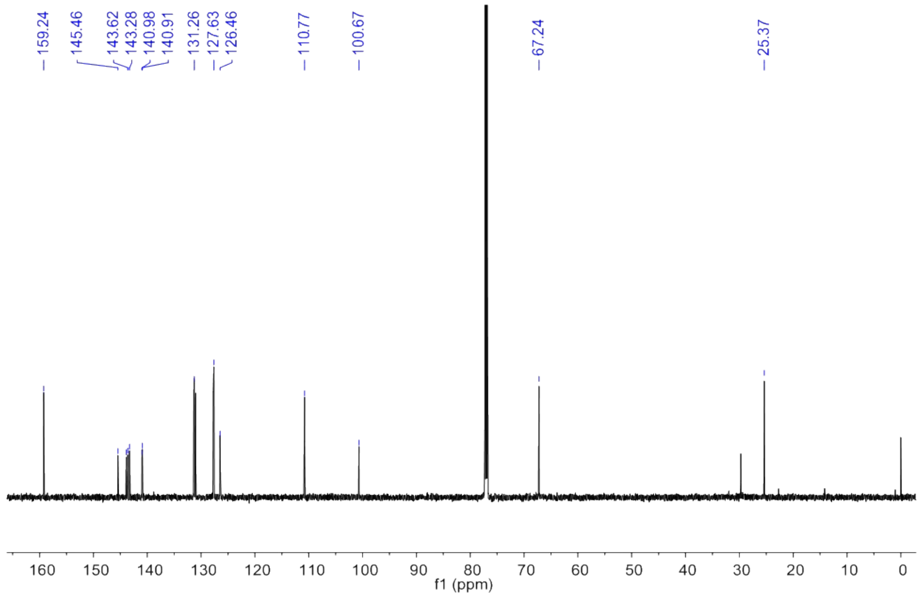
^{1}H-NMR spectrum of compound **4H-2** (CDCl$_3$, 400MHz)



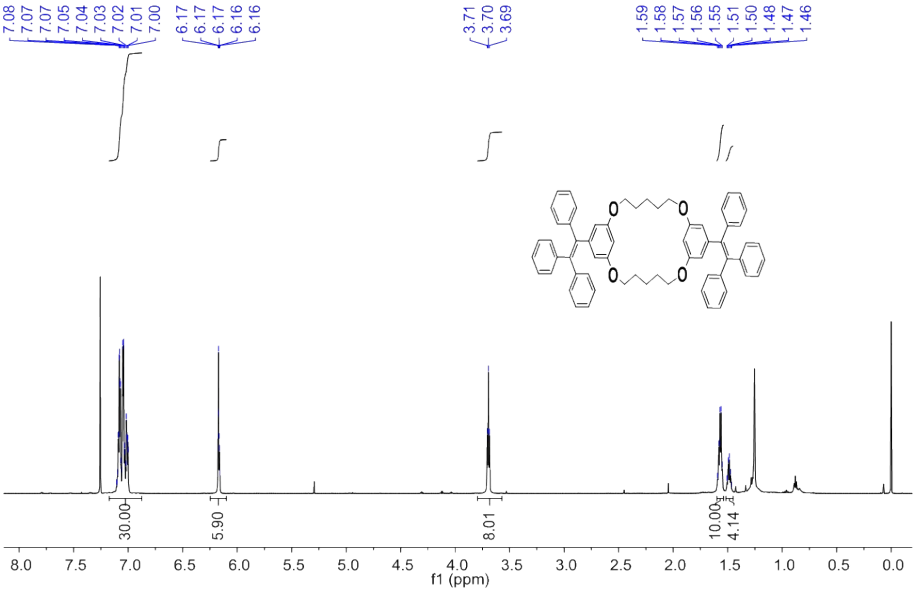
^{13}C-NMR spectrum of compound **4H-2** (CDCl$_3$, 600MHz)



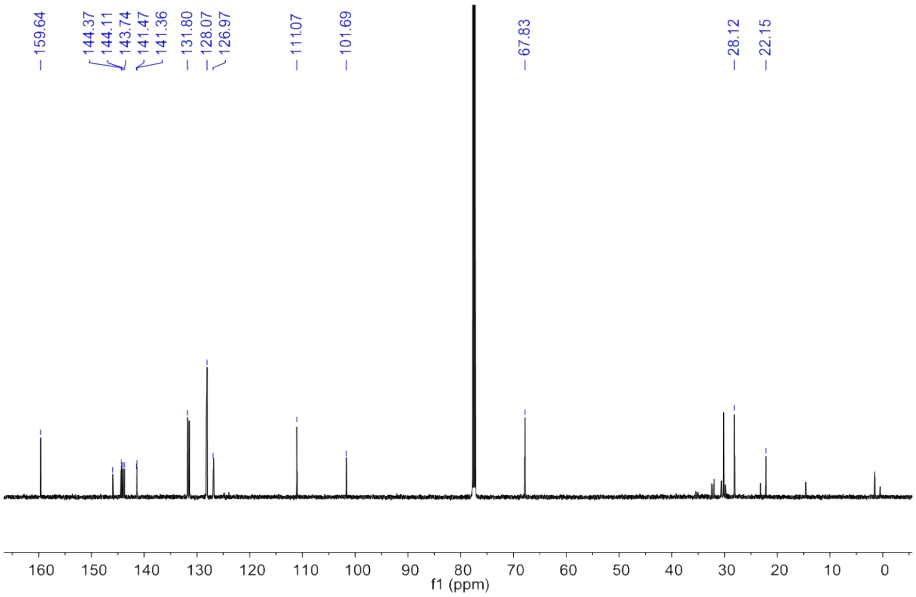
^{1}H-NMR spectrum of compound **4H-3** ($CDCl_3$, 600MHz)



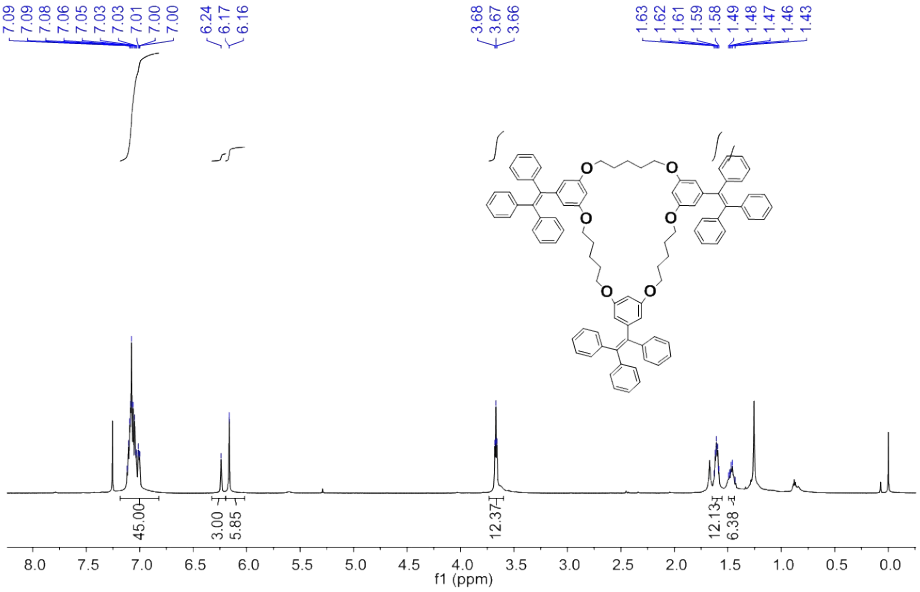
^{13}C-NMR spectrum of compound **4H-3** ($CDCl_3$, 600MHz)



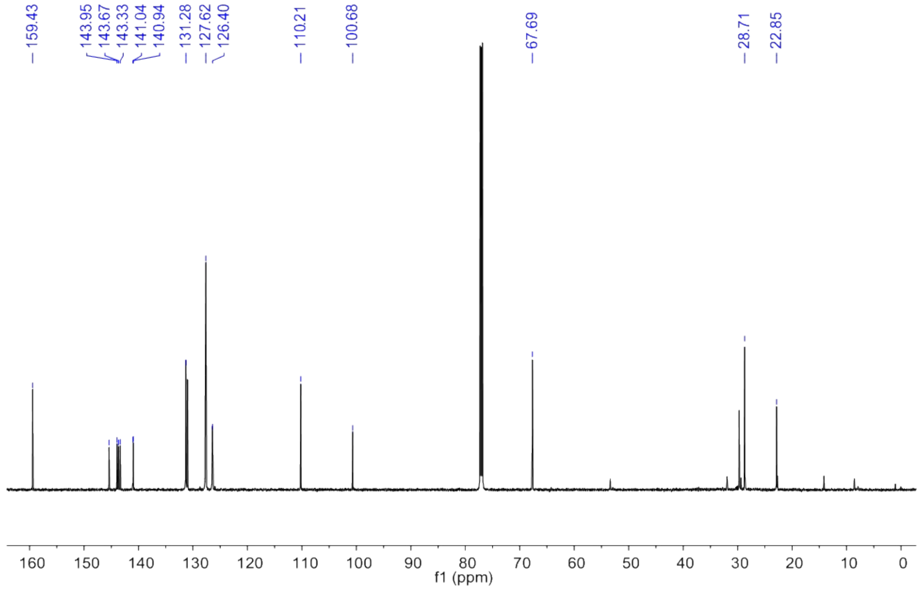
^{1}H-NMR spectrum of compound **6H-2** ($CDCl_3$, 600MHz)



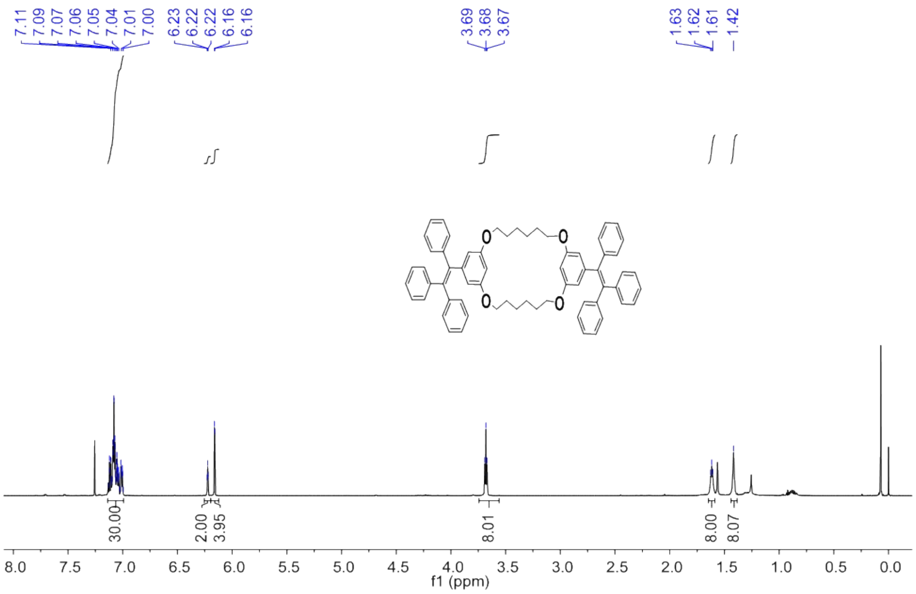
^{13}C-NMR spectrum of compound **6H-2** ($CDCl_3$, 600MHz)



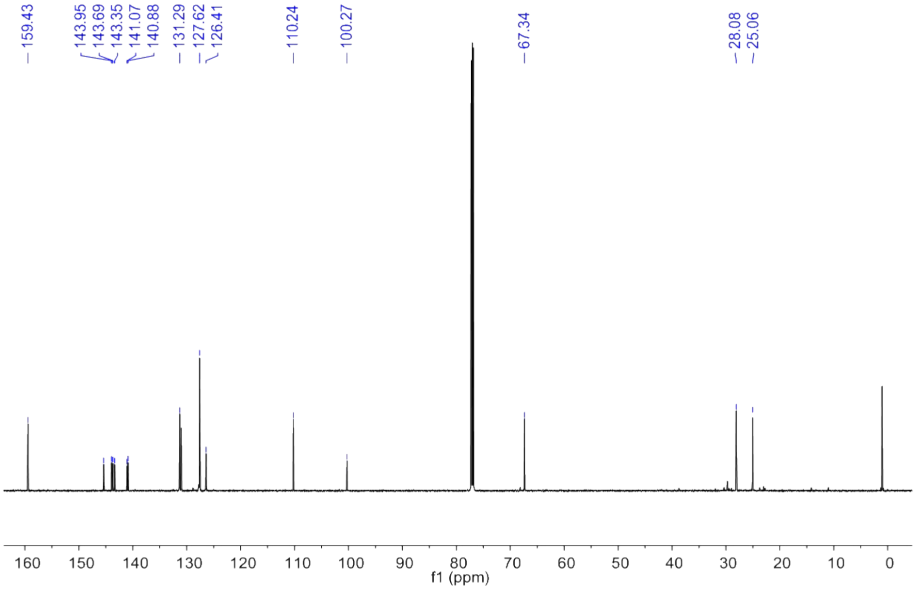
^{1}H-NMR spectrum of compound **6H-3** (CDCl$_3$, 600MHz)



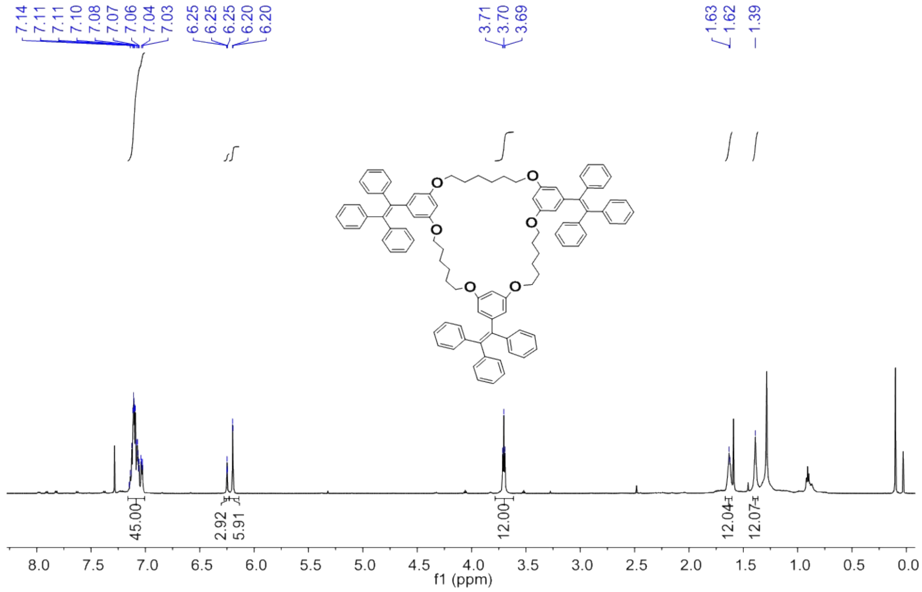
^{13}C-NMR spectrum of compound **6H-3** (CDCl$_3$, 600MHz)



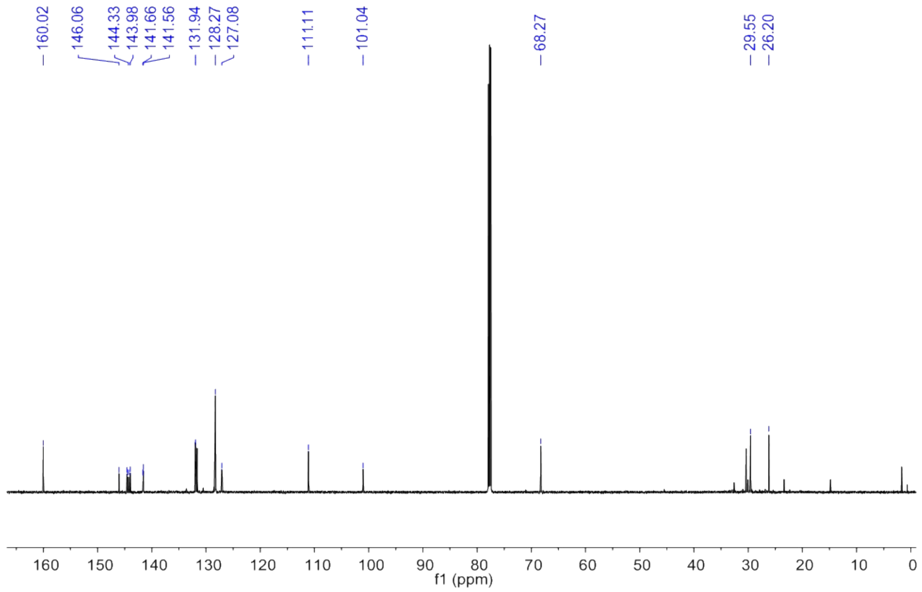
^{1}H-NMR spectrum of compound **8H-2** ($CDCl_3$, 600MHz)



^{13}C-NMR spectrum of compound **8H-2** ($CDCl_3$, 600MHz)



^{1}H-NMR spectrum of compound **8H-3** ($CDCl_3$, 600MHz)



^{13}C-NMR spectrum of compound **8H-3** ($CDCl_3$, 600MHz)

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