Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Acid-base-controlled and dibenzylammonium-assisted aggregation induced emission enhancement of poly(tetraphenylethene) with an impressive blue shift

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Additional data

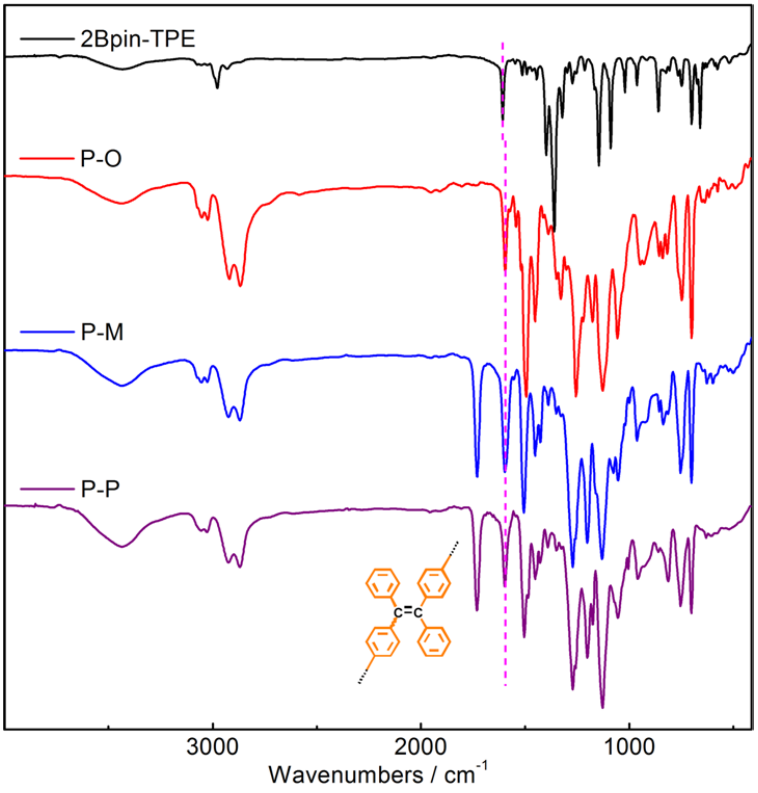


Fig. S1 Infrared spectra of 2Bpin-TPE, **P-O**, **P-M** and **P-P**.

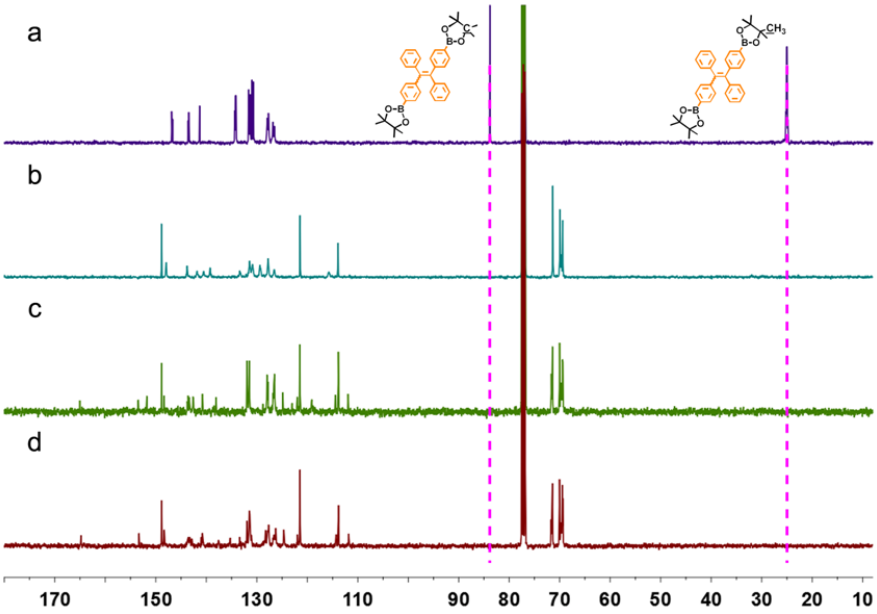


Fig. S2 ^{13}C NMR spectra of 2Bpin-TPE, **P-O**, **P-M** and **P-P**.

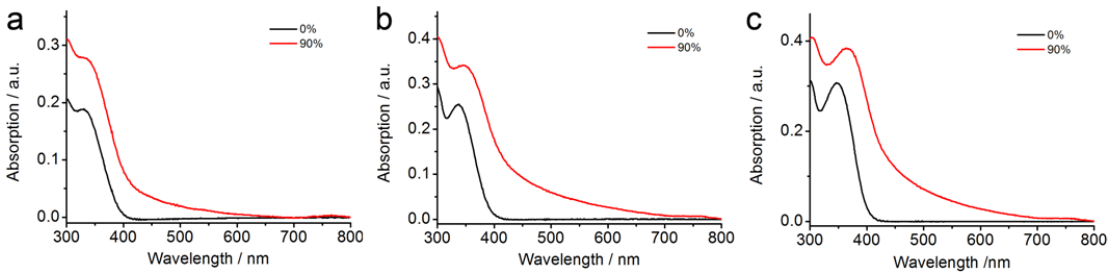


Fig. S3 Absorption spectra of **P-O** (a), **P-M** (b) and **P-P** (c) in the THF/water mixture solvents with 0% and 90% water content.

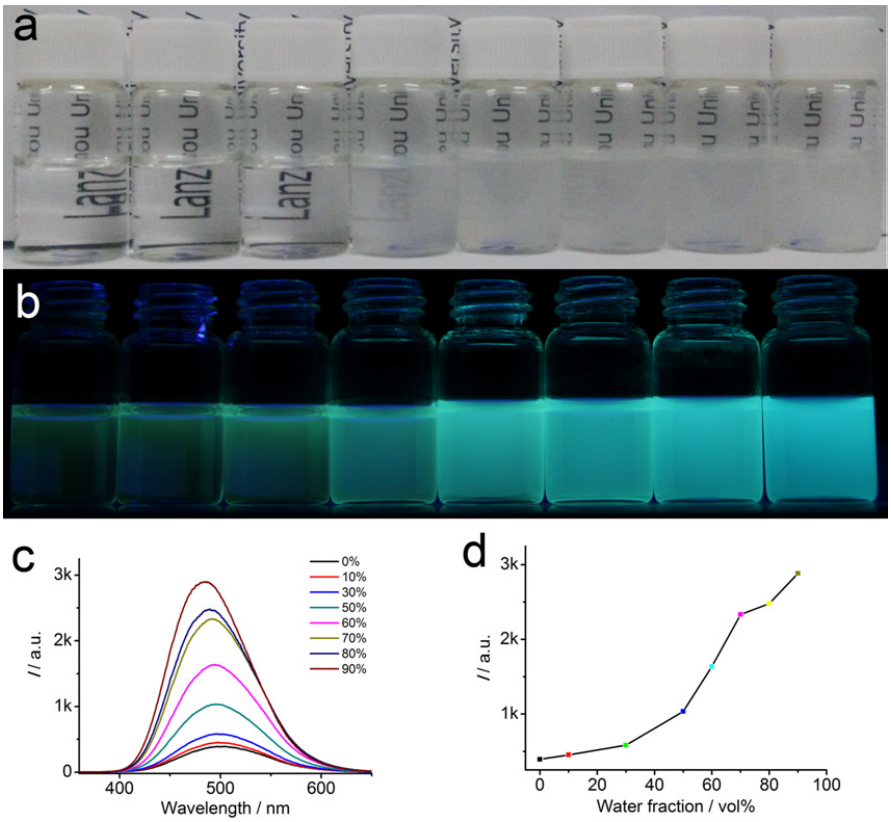


Fig. S4 Photographs of **P-O** in THF-Water mixture solvents with different fractions of water under ambient light (a) and UV irradiation (b). Photoluminescence spectra (c) and the plot of emission intensity (d) of **P-O** in THF-Water mixture solvents. The concentration was 100 μM.

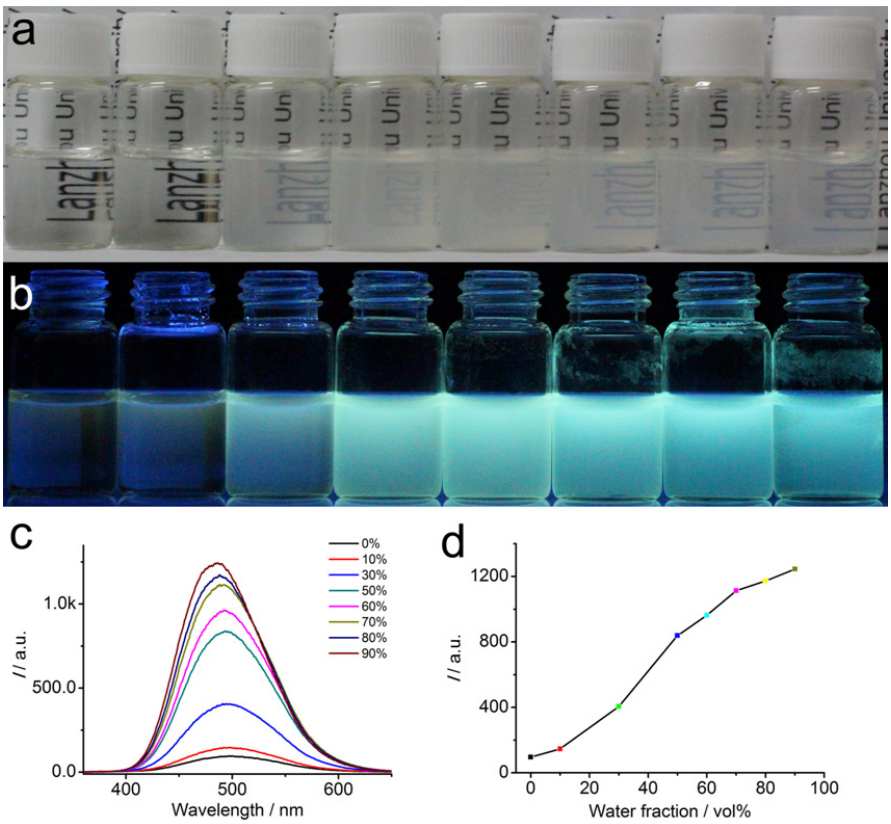


Fig. S5 Photographs of **P-M** in THF-Water mixture solvents with different fractions of water under ambient light (a) and UV irradiation (b). Photoluminescence spectra (c) and the plot of emission intensity (d) of **P-M** in THF-Water mixture solvents. The concentration was 100 μM.

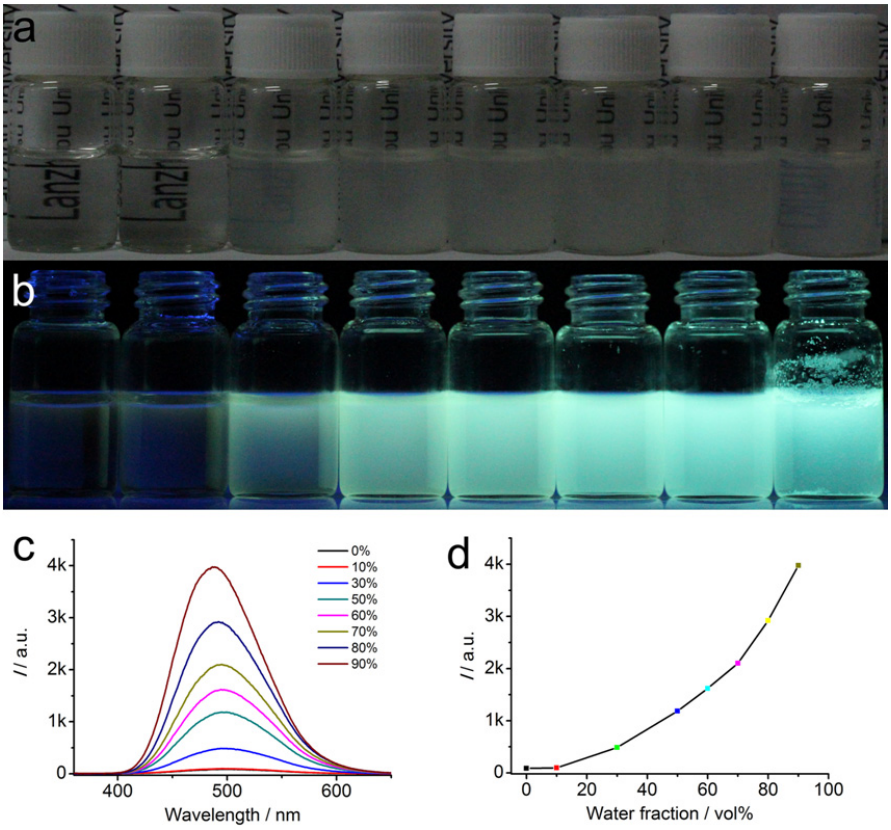


Fig. S6 Photographs of **P-P** in THF-Water mixture solvents with different fractions of water under ambient light (a) and UV irradiation (b). Photoluminescence spectra (c) and the plot of emission intensity (d) of **P-P** in THF-Water mixture solvents. The concentration was 100 μM.

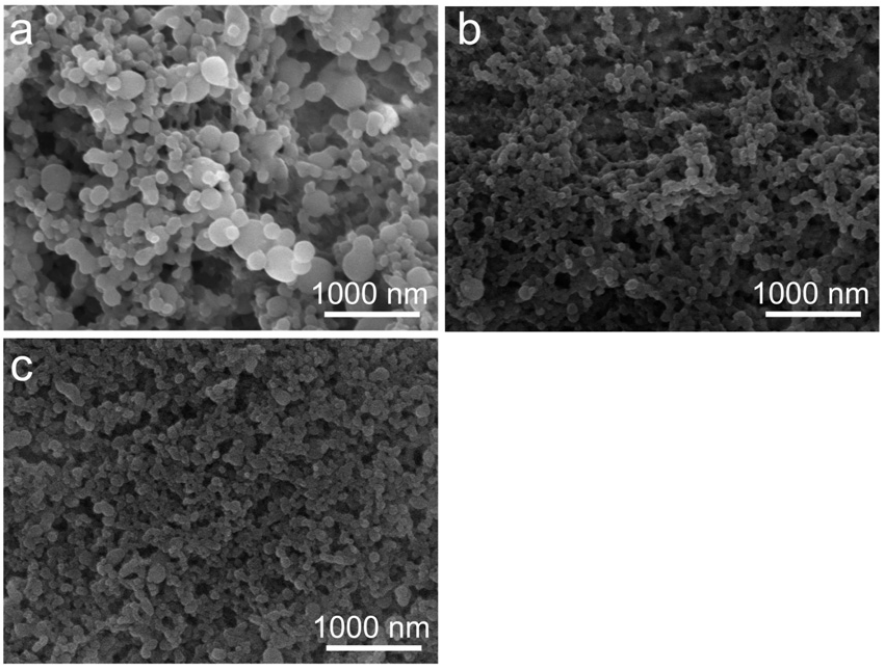


Fig. S7 SEM images of **P-O** (b), **P-M** (c) and **P-P** (d) in the THF-Water mixture solvent with 90% water content. The concentration was 100 μM

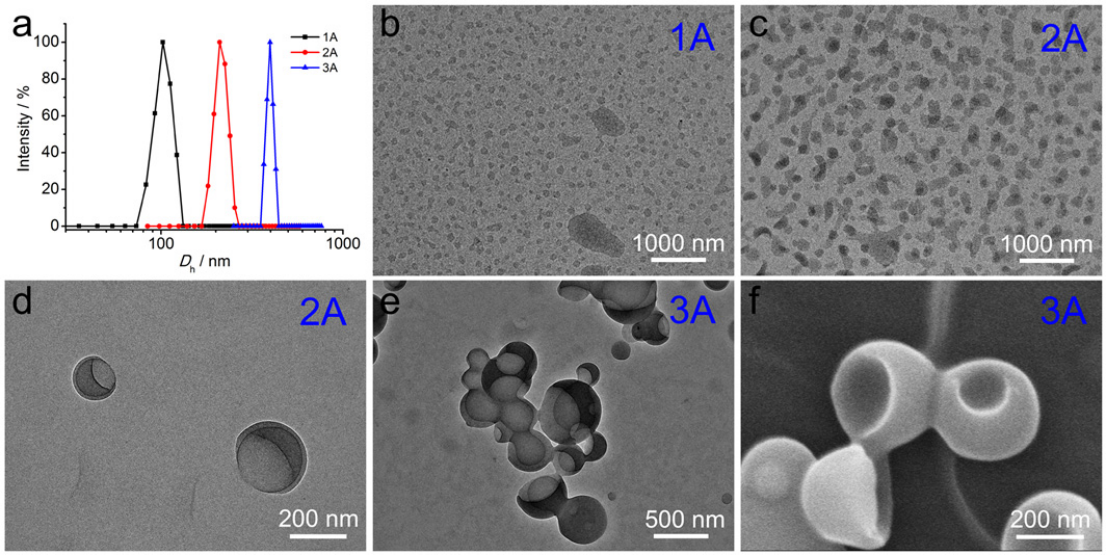
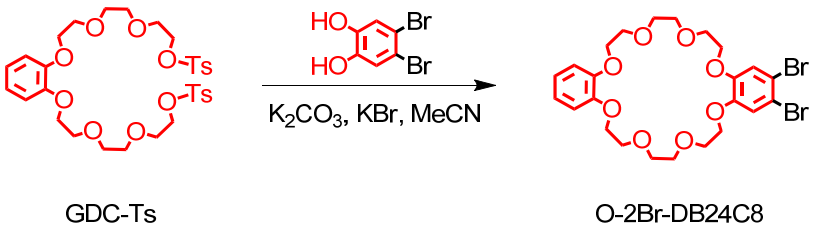


Fig. S8 DLS plot (a), TEM and SEM images (b-i) of **P-O**/**C12-2** in THF solution after the first, second and third acidification.

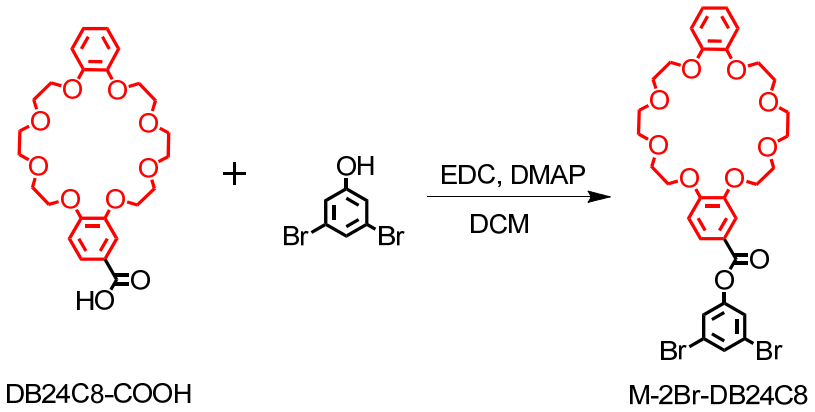
Synthesis



Scheme S1 Synthesis of **O**-2Br-DB24C8.

O-2Br-DB24C8**:**

Into a 500 mL Schlenk tube were added 4,5-dibromobenzene-1,2-diol (535.8 mg, 2 mmol), K_2CO_3 (1.1 g, 8 mmol) and catalytic amount of KBr. The tube was degassed with Ar and 250 mL MeCN was added. The mixture was stirred at reflux for 30 min. After the temperature was cooled to room temperature, GDC-Ts (1.366 g, 2 mmol) dissolved in 50 mL MeCN was injected into the tube. The mixture was stirred at reflux for two days. The formed solid was removed by filtration and washed with ethyl acetate. The crude product was purified by column chromatography (silica gel) using ethyl acetate as eluent to give a white solid in 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ), 7.06 (s, 2H), 6.88 (m, 4H), 4.10 (m, 8H), 3.90 (m, 8H), 3.81 [m, 8H]. ^{13}C NMR (100 MHz, $CDCl_3$, δ), 148.91, 148.81, 121.50, 118.17, 115.23, 113.95, 77.48, 77.16, 76.84, 71.52, 71.40, 70.04, 69.88, 69.70, 69.43. HR-ESI-MS (m/z), $[M+Na]^+$ calculated: 629.0179, found: 629.0173, Error = 1.0 ppm.

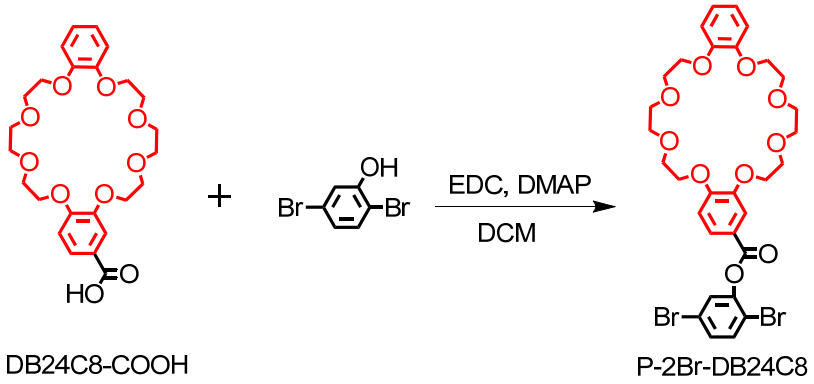


Scheme S2 Synthesis of **M**-2Br-DB24C8.

M-2Br-DB24C8:

Into a 100 mL a round-bottomed flask were added DB24C8-COOH (1 mmol), EDC (2 mmol), DMAP (1 mmol) and DCM (30 mL). The mixture was stirred in an ice-bath for 15 min, then 3,5-dibromophenol (1 mmol) was slowly added. The reaction mixture was warmed to room temperature

after 30 min. The reaction was monitored by TLC and stopped until the reactants disappeared completely. The crude product was extracted by DCM and washed with saturated brine, HCl (5%) and water. Further purification was achieved by flash column chromatography (silica gel) using ethyl acetate as eluent to give a white solid in 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ), 7.78 (d, 1H), 7.57 (m, 2H), 7.35 (m, 1H), 6.88 (m, 5H), 4.22 (m, 4H), 4.15 (m, 4H), 3.95 (m, 8H), 3.84 [m, 8H]. ^{13}C NMR (100 MHz, $CDCl_3$, δ), 164.13, 153.85, 151.82, 148.79, 148.42, 131.62, 124.98, 124.43, 122.81, 121.42, 120.87, 114.41, 113.77, 111.87, 77.48, 77.16, 76.84, 71.60, 71.37, 69.97, 69.76, 69.58, 69.38. HR-MS (m/z), $[M+Na]^+$ calculated: 749.0390, found: 749.0396, Error = 0.8 ppm.



DB24C8-COOH P-2Br-DB24C8

Scheme S3 Synthesis of **P**-2Br-DB24C8.

P-2Br-DB24C8:

Into a 100 mL a round-bottomed flask were added DB24C8-COOH (1 mmol), EDC (2 mmol), DMAP (1 mmol) and DCM (30 mL). The mixture was stirred in an ice-bath for 15 min and then 2,5-dibromophenol (1 mmol) was slowly added. The reaction mixture was warmed to room temperature after 30 min. The reaction was monitored by TLC and stopped until the reactants disappeared completely. The crude product was extracted by DCM and washed with saturated brine, HCl (5%) and water. Further purification was achieved by flash column chromatography (silica gel) using ethyl acetate as eluent to give a white solid in 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$, *δ*), 7.86 (d, 1H), 7.65 (s, 1H), 7.51 (d, 1H), 7.45 (s, 1H), 7.26 (d, 1H), 6.88 (m, 5H), 4.22 (m, 4H), 4.15 (m, 4H), 3.95 (m, 8H), 3.85 [m, 8H]. ^{13}C NMR (100 MHz, $CDCl_3$, δ), 163.67, 153.93, 149.19, 148.87, 148.50, 134.27, 130.47, 127.43, 125.23, 121.46, 121.29, 120.89, 115.51, 114.61, 113.83, 111.99, 77.48, 77.16, 76.84, 71.69, 71.57, 69.82, 69.66, 69.48, 69.40. HR-MS (m/z), $[M+Na]^+$ calculated: 749.0390, found: 749.0394, Error = 0.5 ppm.

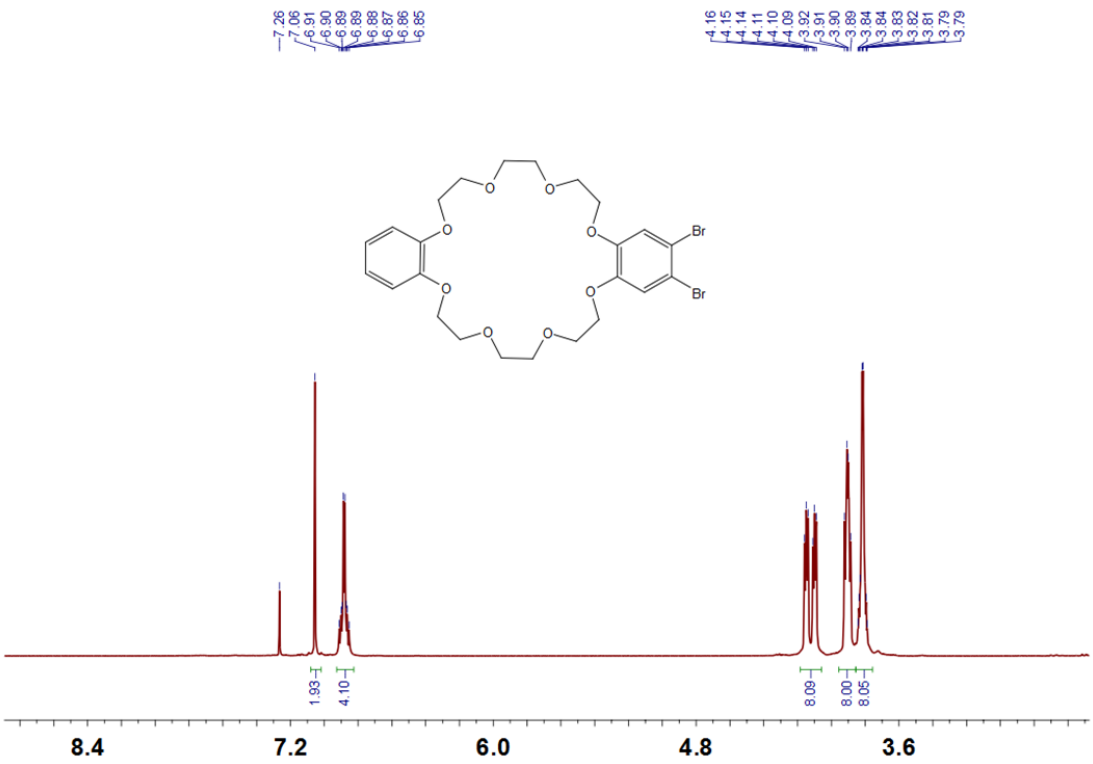


Fig. S9 ^{1}H NMR spectrum of **O**-2Br-DB24C8.

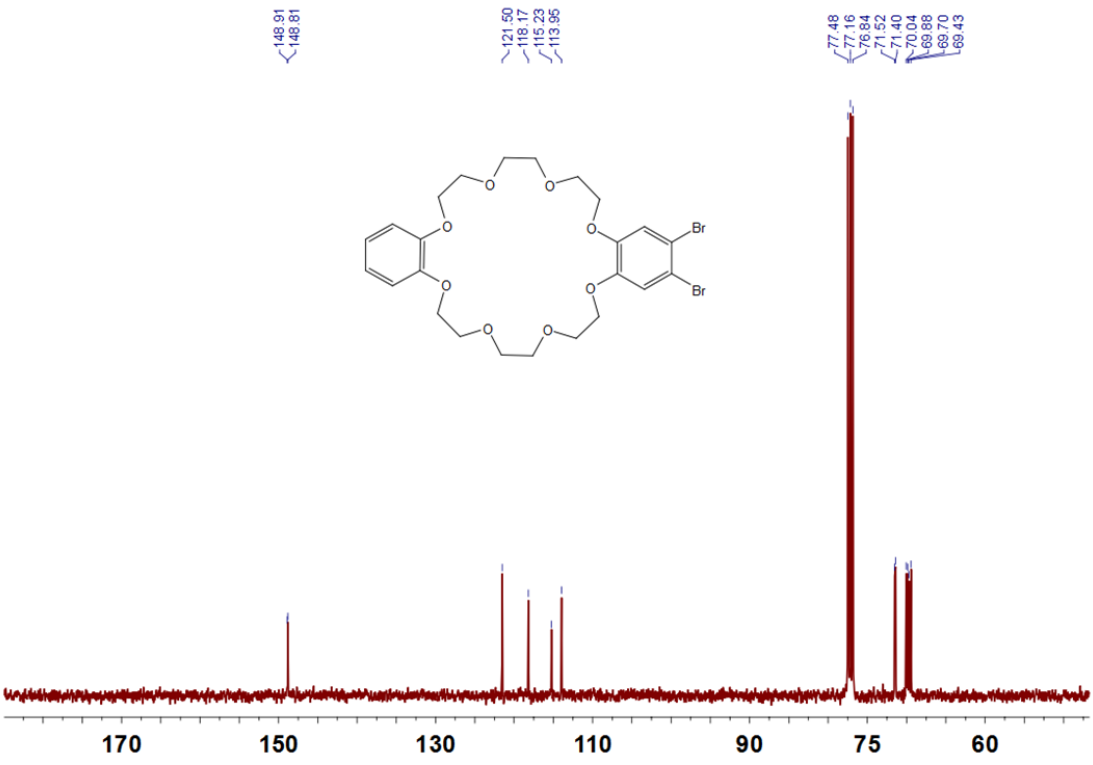


Fig. S10 ^{13}C NMR spectrum of **O**-2Br-DB24C8.

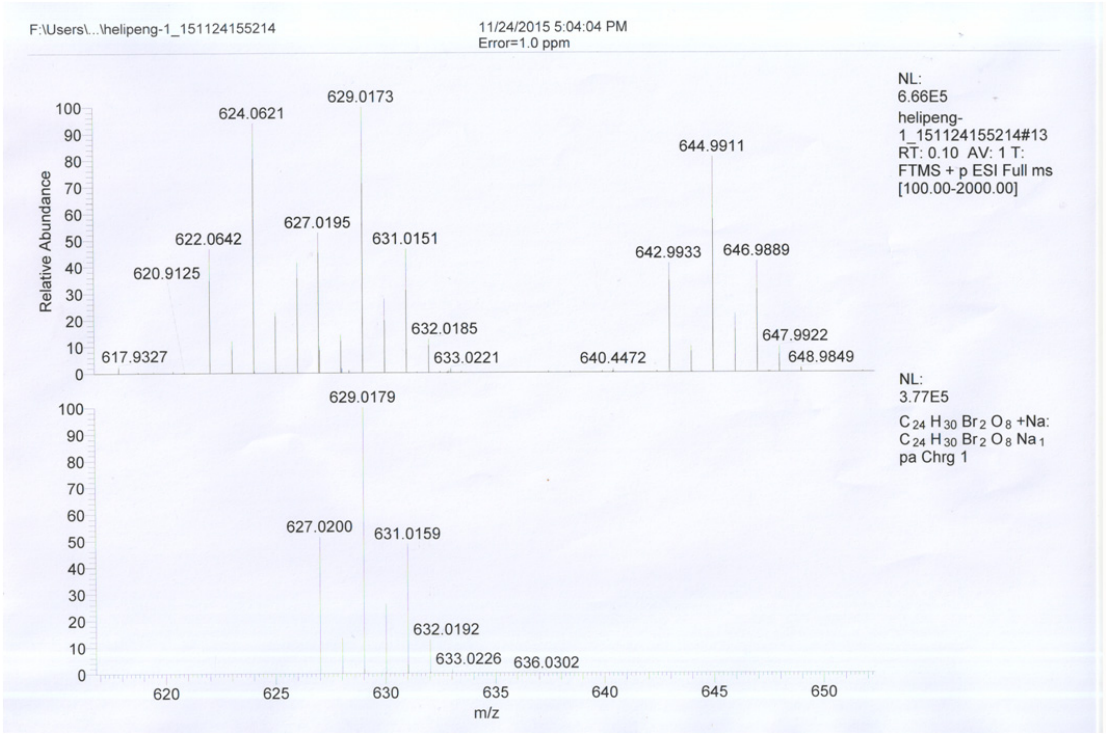


Fig. S11 HR-ESI-MS of **O**-2Br-DB24C8.

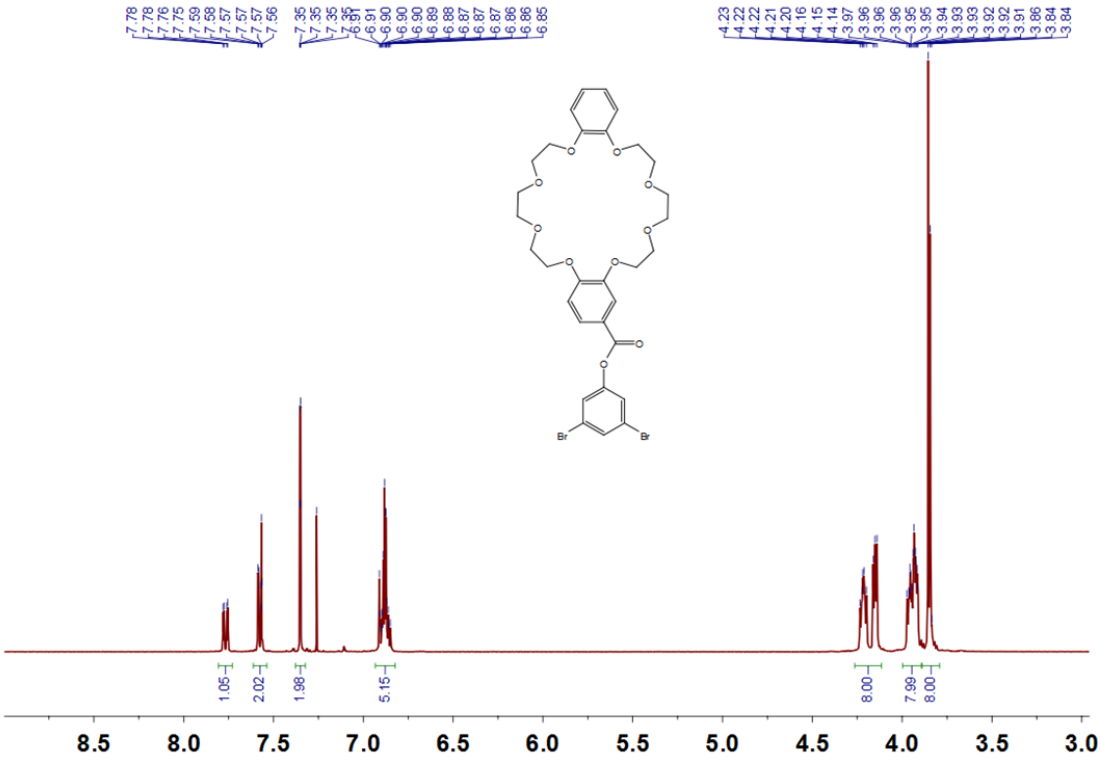


Fig. S12 ^{1}H NMR spectrum of **M**-2Br-DB24C8.

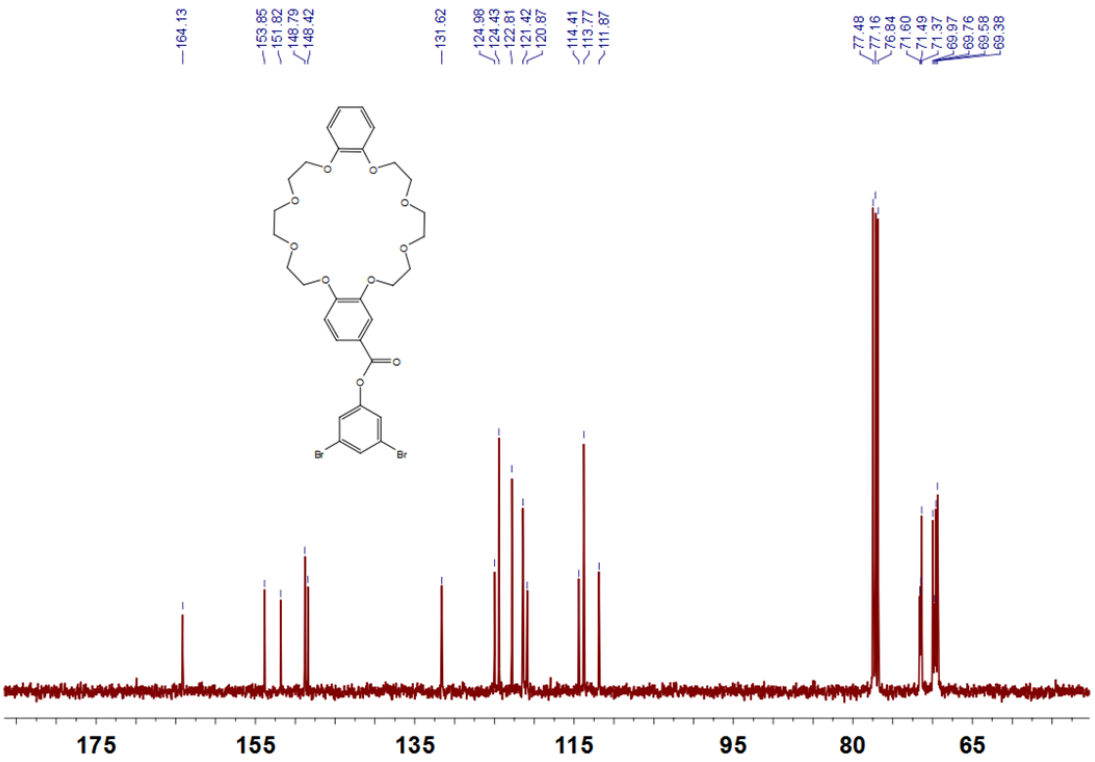


Fig. S13 ^{13}C NMR spectrum of **M**-2Br-DB24C8.

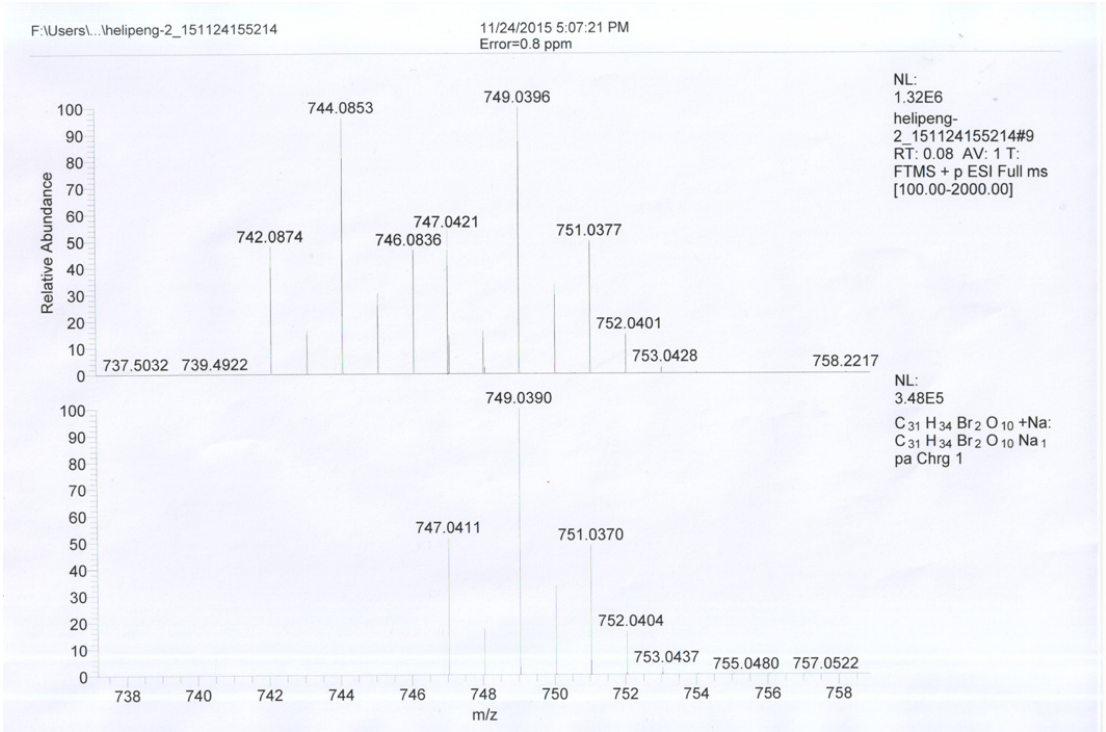


Fig. S14 HR-ESI-MS spectrum of **M**-2Br-DB24C8.

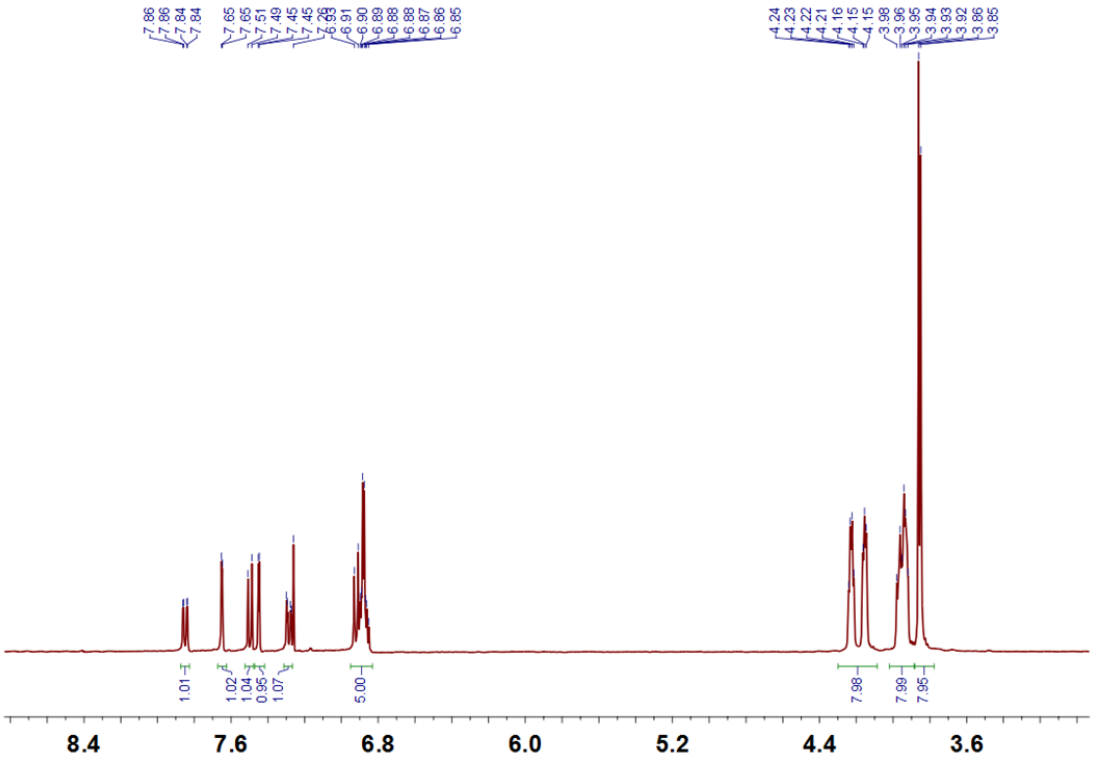


Fig. S15 ^{1}H NMR spectrum of **P**-2Br-DB24C8.

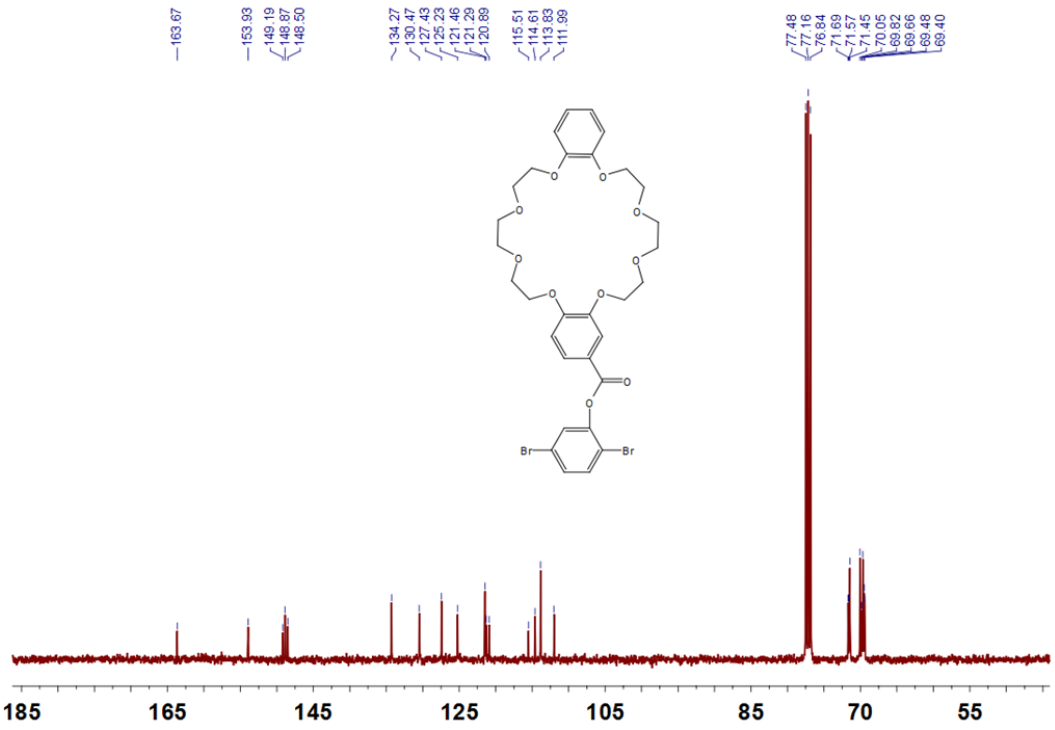


Fig. S16 ^{13}C NMR spectrum of **P**-2Br-DB24C8.

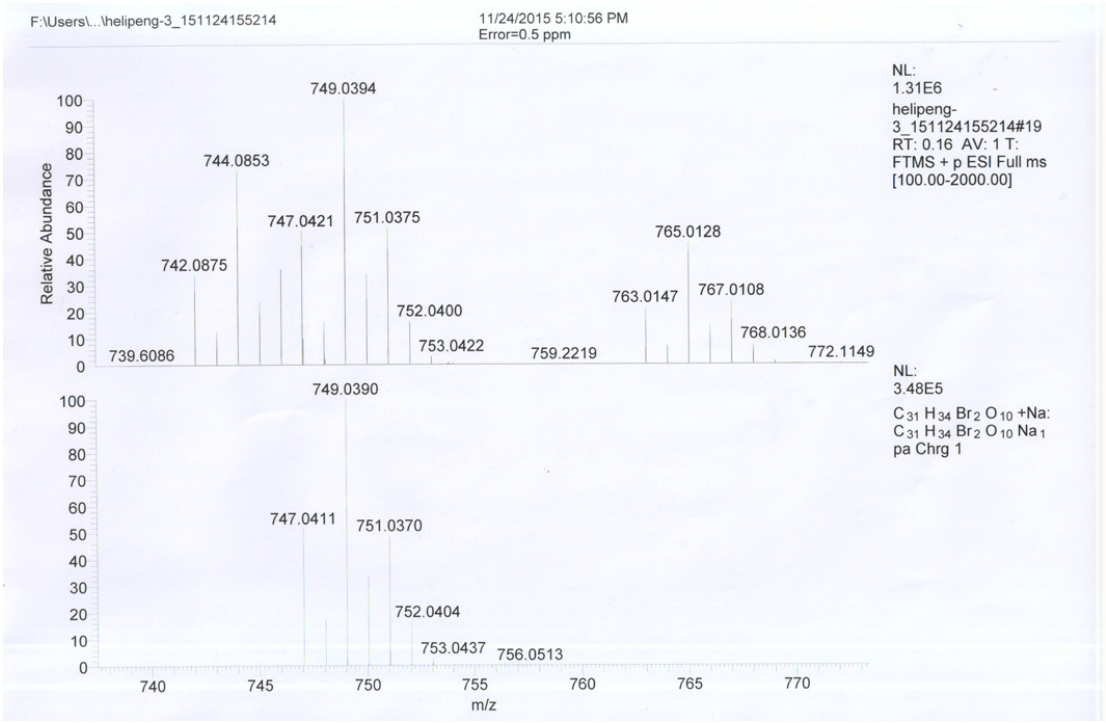


Fig. S17 HR-ESI-MS spectrum of **P**-2Br-DB24C8.