Supporting Information

Biphen[3]arene based on V-shaped units: Synthesis and Macrocyclization-enhanced Thermally Activated Delayed Fluorescence

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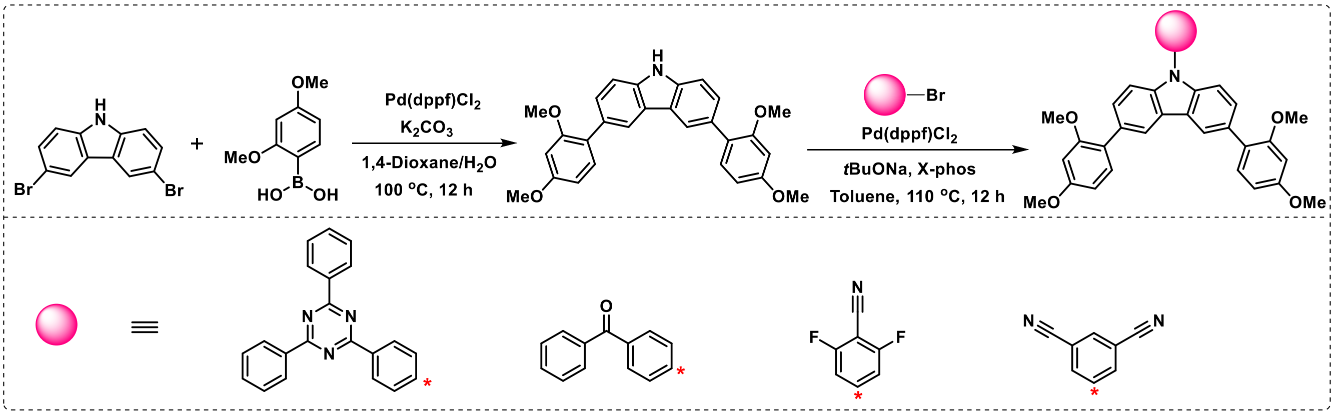
1. Materials and methods

All reagents were purchased commercially and used without further purification unless otherwise noted. [1]H NMR and [13]C NMR spectra were recorded using a Bruker Avance 400 MHz spectrometer. High-resolution mass spectra (HRMS) was determined on Shimadzu LCMS-IT-TOF and MALDI-TOF. Fluorescence spectroscopy was measured on Shimadzu RF-6000 and Edinburgh FLS980. Quantum efficiency and lifetime were measured on FLS980. Melting points were obtained on an X-4 digital melting point apparatus without correction. The electron distribution analysis was performed by Gaussian16 using density functional theory (DFT). B3LYP was chosen for the method, and the ground-state geometry was optimized with Gaussian16 software using the PBE0 hybrid functional and the 6-31G(d) basis set. The lowest singlet- and triplet-excited states were also calculated at their optimized ground-state geometries using the same functional and basis set. The methodology in recording the fluorescence and phosphorescence spectra: firstly, a low concentration toluene solution of monomers and macrocycles was prepared, and the temperature was lowered to 77K using liquid nitrogen. Then, low temperature fluorescence spectra directly collected and low temperature phosphorescence spectra is collected after turning off the excitation light for 8 ms (gate time) where prompt and delayed fluorescence have all disappeared.

2. Experimental details



Monomers. A 250 ml round bottom flask was charged with, 3,6-dibromocarbazole (3.25 g, 10.0 mmol), 2,4-diethoxybenzeneboronic acid (4.00 g, 22.0 mmol), [1,1'-Bis(diphenylphosphino)ferrocene] dichloropalladium (II) (Pd(Dppf)Cl_2, 0.73 g, 1.0 mmol), sodium carbonate (4.24 g, 40.0 mmol), a magnetic stir bar, 1,4-dioxane (100 mL) and water (15 mL). The reaction mixture was stirred for 12 h at 101 °C. After removal of solvent, the residue was purified by chromatography on silica gel to give products. Then, under the protection of N_2 atmosphere, the products (2.2 g, 5.0 mmol), brominated aromatic derivatives (5.5 mmol), Pd(Dppf)Cl_2 (0.37 g, 0.5 mmol), xantphos (0.578 g, 1.0 mmol) and *t*-

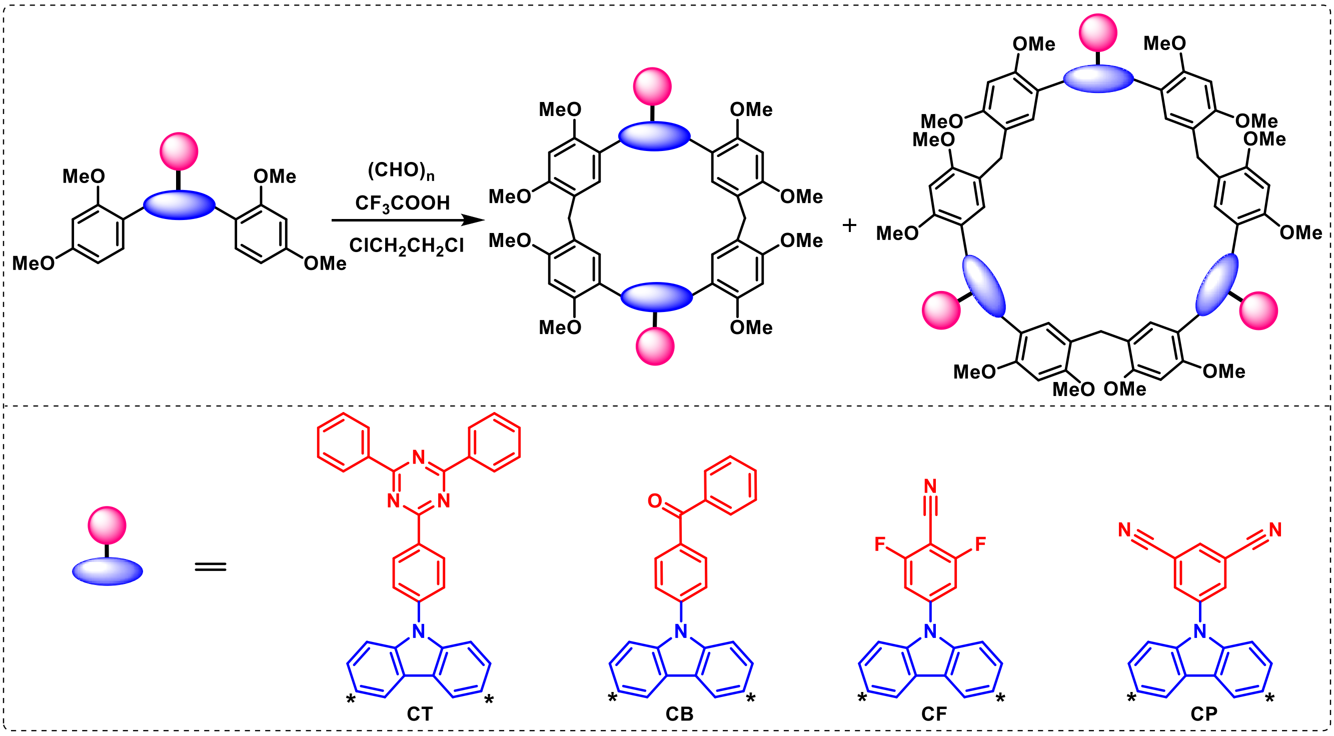
BuONa (1.44 g, 15.0 mmol) were added to a toluene (60 ml). The reaction mixture was stirred for 15 h at 110 °C. After removal of solvent, the residue was purified by chromatography on silica gel.

CT-1 ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ 9.014 (d, *J* = 8.4 Hz, 2H), 8.827 (dd, *J* = 8.0, 1.6 Hz, 4H), 8.264 (s, 2H), 7.851 (d, *J* = 8.4 Hz, 2H), 7.637-7.591 (m, 10H), 7.375 (d, *J* = 8.8 Hz, 2H), 6.629-6.601 (m, 4H), 3.871 (s, 6H), 3.831 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 298K) δ 171.8, 171.0, 160.0, 157.6, 139.6, 136.2, 132.7, 131.6, 130.8, 130.7, 129.1,128.7, 128.0, 126.5, 124.2, 121.3, 109.4, 104.6, 99.1,55.7, 55.5. m.p. 223-224 °C; HRMS (ESI) m/z: $[M+Na]^+$ calculated for $[C_{49}H_{38}N_4O_4Na]^+$, 769.2785; found, 769.2784.

CB-1 ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ 8.245 (s, 2H), 8.083 (d, *J* = 8.4 Hz, 2H), 7.912 (d, *J* = 6.8 Hz, 2H), 7.779 (d, *J* = 8.4 Hz, 2H), 7.644-7.533 (m, 7H), 7.366 (d, *J* = 8.8 Hz, 2H), 3.632-6.611 (m, 4H), 3.878 (s, 6H), 3.829 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 298K) δ 195.7, 160.1, 157.5, 139.4, 137.5, 132.6, 132.0, 131.6, 130.1, 128.5, 128.0, 126.1, 124.1, 121.3, 109.3, 104.6, 99.1, 55.7, 55.5. m.p. 103-104 °C; HRMS (ESI) m/z: $[M+Na]^+$ calculated for $[C_{41}H_{33}N_1O_5Na]^+$, 642.2251; found, 642.2253.

CF-1 ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ 8.222 (d, *J* = 1.2 Hz, 2H), 7.633-7.558 (m, 4H), 7.427 (d, *J* = 8.4 Hz, 2H), 7.345 (d, *J* = 8.8 Hz, 2H), 6.637-6.618 (m, 4H), 3.887 (s, 6H), 3.836 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 298K) δ 165.4, 162.9, 160.3, 157.5, 144.9, 138.2, 132.4, 131.5, 128.5, 124.8, 123.5, 121.6, 109.5, 109.2, 104.7, 99.1, 89.7, 55.7, 55.5. m.p. 278-279 °C; HRMS (ESI) m/z: $[M+H]^+$ calculated for $[C_{35}H_{26}N_2O_4F_2Na]^+$, 599.1753; found, 599.1755.

CP-1 ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ 8.230 (d, *J* = 1.2 Hz, 2H), 8.195 (d, *J* = 1.6 Hz, 2H), 7.963 (s, 1H), 7.625 (d, *J* = 2.0 Hz, 1H), 7.603 (d, *J* = 1.6 Hz, 1H), 7.427 (s, 1H), 7.406 (s, 1H), 7.348 (d, *J* = 8.8 Hz, 2H) 6.636-6.613 (m, 4H), 3.882 (s, 6H), 3.832 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 298K) δ 160.3, 157.5, 140.7, 138.6, 133.5, 132.7, 132.3, 131.5, 128.5, 124.5, 123.6, 121.7, 116.1, 115.9, 108.3, 104.7, 99.1, 55.7, 55.5. m.p. 135-136 °C; HRMS (ESI) m/z: $[M+H]^+$ calculated for $[C_{36}H_{27}N_3O_4Na]^+$, 588.1894; found, 588.1900.



Macrocycles. To the solution of monomer (1.00 mmol) in 1,2-dichloroethane (120 mL) was added paraformaldehyde (90.0 mg, 3.00 mmol). CF_3COOH (3.00 mL) was added to the reaction mixture in three times. Then, the mixture was stirred at room temperature for about 2 hours. Then the reaction was quenched by addition of 150 mL saturated aqueous $NaHCO_3$. The organic phase was separated and washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4 and evaporated. The products were purified by column chromatography on silica gel (eluent: dichloromethane: ethyl acetate gradually changing) to obtain target macrocycles. m.p. > 320 °C;

CT-2 ^{1}H NMR (400 MHz, $Cl_2DCCDCl_2$, 298K) δ 9.040 (d, *J* = 8.4 Hz, 4H), 8.823 (d, *J* = 7.2 Hz, 8H), 8.087 (s, 4H), 7.885 (d, *J* = 8.4 Hz, 4H), 7.677-7.551 (m, 20H), 6.974 (s, 4H), 6.572 (s, 4H), 3.954 (s, 4H), 3.853 (s, 12H), 3.793 (s, 12H). ^{13}C NMR (100 MHz, $Cl_2DCCDCl_2$, 298K) δ 171.6, 170.7, 157.3, 155.6, 141.7, 138.9, 135.9, 134.3, 132.7, 132.0, 131.5, 130.6, 128.9, 128.7, 126.2, 123.2, 123.1, 121.0, 120.6, 109.295.9, 56.0, 55.7, 29.4. m.p. > 320 °C; HRMS (MALDI-TOF) m/z: $[M]^+$ calculated for $[C_{100}H_{76}N_8O_8]^+$, 1517.5814; found, 1517.5791.

CT-3 ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ 8.962 (d, *J* = 8.0 Hz, 6H), 8.806 (d, *J* = 7.2 Hz, 12H), 8.215 (s, 6H), 7.761 (d, *J* = 8.4 Hz, 6H), 7.603-7.546 (m, 30H), 7.286 (s, 6H), 6.505 (s, 6H), 3.979 (s, 6H), 3.855 (s, 18H), 3.712 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, 298K) δ 171.8, 171.0, 157.5, 155.7, 141.9, 139.4, 136.2, 134.4, 132.6, 131.1, 130.6, 129.0, 128.7, 128.0, 126.3, 124.0, 123.0, 121.6, 121.3, 109.4, 559., 55.7, 28.5. m.p. > 320 °C; HRMS (MALDI-TOF) m/z: $[M]^+$ calculated for $[C_{150}H_{114}N_{12}O_{12}]^+$, 2275.8807; found, 2275.8670.

CB-2 ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ 8.115 (s, 4H), 8.064 (d, *J* = 8.4 Hz, 4H), 7.895 (d, *J* = 8.4 Hz, 4H), 7.769 (d, *J* = 8.4 Hz, 4H), 6.652-7.615 (m, 2H), 7.559-7.524 (m, 12H), 6.943 (s, 4H), 6.554 (s, 4H), 3.939 (s, 6H), 3.828 (s, 12H), 3.763 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 298K) δ 195.8, 157.6, 155.8, 139.2, 132.6, 132.0, 131.9, 131.6, 130.1, 128.5, 126.1, 124.0, 120.7, 109.0, 95.8, 56.0, 55.7, 29.8. m.p. 258-259 °C;HRMS (ESI) m/z: $[M+Na]^+$ calculated for $[C_{84}H_{66}N_2O_{10}Na]^+$, 1285.4610; found, 1285.4623.

CB-3 ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ 8.183 (s, 6H), 8.106 (d, *J* = 8.8 Hz, 6H), 7.880 (d, *J* = 4.4 Hz, 6H), 7.658 (d, *J* = 8.4 Hz, 6H), 7.614-7.578 (m, 8H), 7.541-7.504 (m, 12H), 7.255 (s, 6H), 6.483 (s, 6H), 3.947 (s, 6H), 3.838 (s, 18H), 3.700 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, 298K) δ 195.8, 157.6, 155.7, 139.2, 137.6, 132.6, 131.9, 131.3, 130.1, 128.5, 125.9, 124.0, 122.8, 121.6, 109.3, 95.8, 55.9, 55.7, 28.5. m.p. 272-273 °C; HRMS (ESI) m/z: $[M+Na]^+$ calculated for $[C1_{26}H_{99}N_3O_{15}Na]^+$, 1917.7002; found, 1917.7073.

CF-2 ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ 8.073 (s, 4H), 7.571-7.520 (m, 9H), 7.419 (d, *J* = 8.8 Hz, 5H), 6.894 (s, 4H), 6.552 (s, 4H), 3.909 (s, 4H), 3.837 (s, 12H), 3.771 (s, 12H). We failed to obtain ^{13}C NMR spectrum for CF-2 due to its poor solubility in organic solvents. m.p. > 320 °C; HRMS (ESI) m/z: $[M+Na]^+$ calculated for $[C_{72}H_{52}N_4F_4O_8Na]^+$, 1199.3613; found, 1199.3613.

CF-3 ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ 8.149 (s, 6H), 7.633 (d, *J* = 10.0 Hz, 6H), 7.497 (d, *J* = 8.8 Hz, 6H), 7.261 (d, *J* = 8.8 Hz, 6H), 7.177 (s, 6H), 6.449 (s, 6H), 3.864 (s, 6H), 3.830 (s, 18H), 3.705 (s, 18H). ^{13}C NMR (100 MHz, CD_2Cl_2, 298K) δ 165.4, 162.8, 157.7, 155.6, 144.7, 138.0, 132.7, 132.4, 128.6, 124.7, 122.1, 121.4, 121.3, 109.3, 109.2, 95.7, 89.5, 55.8,55.7, 28.0. m.p. > 320 °C; HRMS (ESI) m/z: $[M+Na]^+$ calculated for $[C_{108}H_{78}N_6F_6O_{12}Na]^+$, 1788.5508; found, 1788.5508.

CP-2 ^{1}H NMR (400 MHz, CD_2Cl_2, 298K) δ 8.189 (s, 4H), 8.096 (s, 6H), 7.955 (s, 2H), 7.557 (d, *J* = 9.6 Hz, 4H), 7.386 (d, *J* = 8.4 Hz, 4H), 6.905 (s, 4H), 6.558 (s, 4H), 3.931 (s, 4H), 3.839 (s, 12H), 3.775 (s, 12H). ^{13}C NMR (100 MHz, CD_2Cl_2, 298K) δ 157.8, 155.8, 140.7, 138.4, 133.5, 132.9, 132.5, 131.9, 129.1, 124.5, 122.8, 121.7, 120.7, 116.1, 115.9, 108.1, 95.7, 55.9, 55.7, 29.7. m.p. > 320 °C; HRMS (ESI) m/z: $[M+Na]^+$ calculated for $[C_{74}H_{54}N_6O_8Na]^+$, 1177.3895; found, 1177.3907.

CP-3 ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ 8.205 (s, 6H), 8.025 (s, 6H), 7.906 (s, 3H), 7.649 (d, *J* = 8.8 Hz, 6H), 7.331 (d, *J* = 8.8 Hz, 6H), 7.132 (s, 6H), 6.450 (s, 6H), 3.846 (s, 6H), 3.787 (s, 18H), 3.711 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, 298K) δ 157.6, 155.6, 140.3, 138.2, 133.2, 132.3, 128.6, 124.4, 122.0, 121.3, 116.2, 115.6, 108.4, 95.8, 55.8, 55.7, 27.6. m.p. > 320 °C; HRMS (ESI) m/z: $[M+Na]^+$ calculated for $[C_{111}H_{81}N_9O_{12}Na]^+$, 1755.5930; found, 1755.5907.

3. ^{1}H NMR, ^{13}C NMR, HMRS spectra

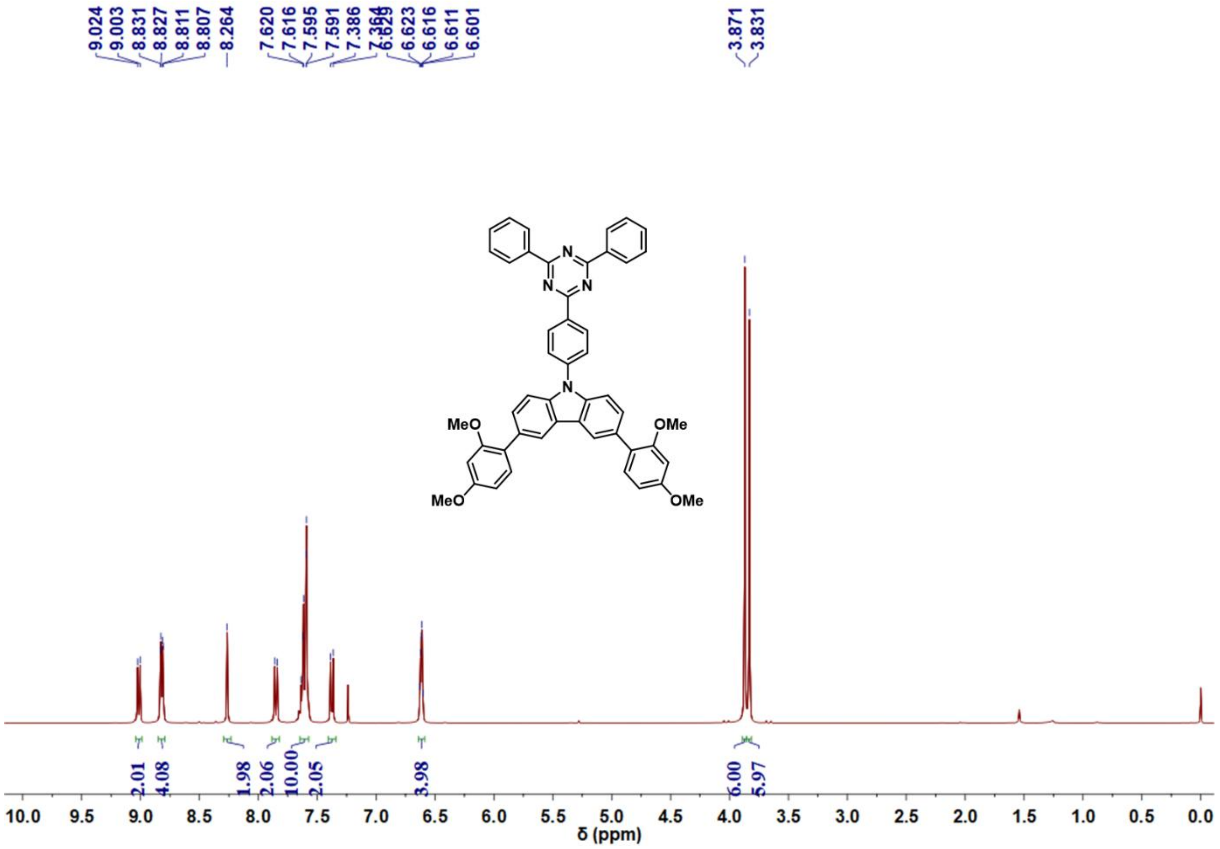


Fig. S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of monomer **CT-1**.

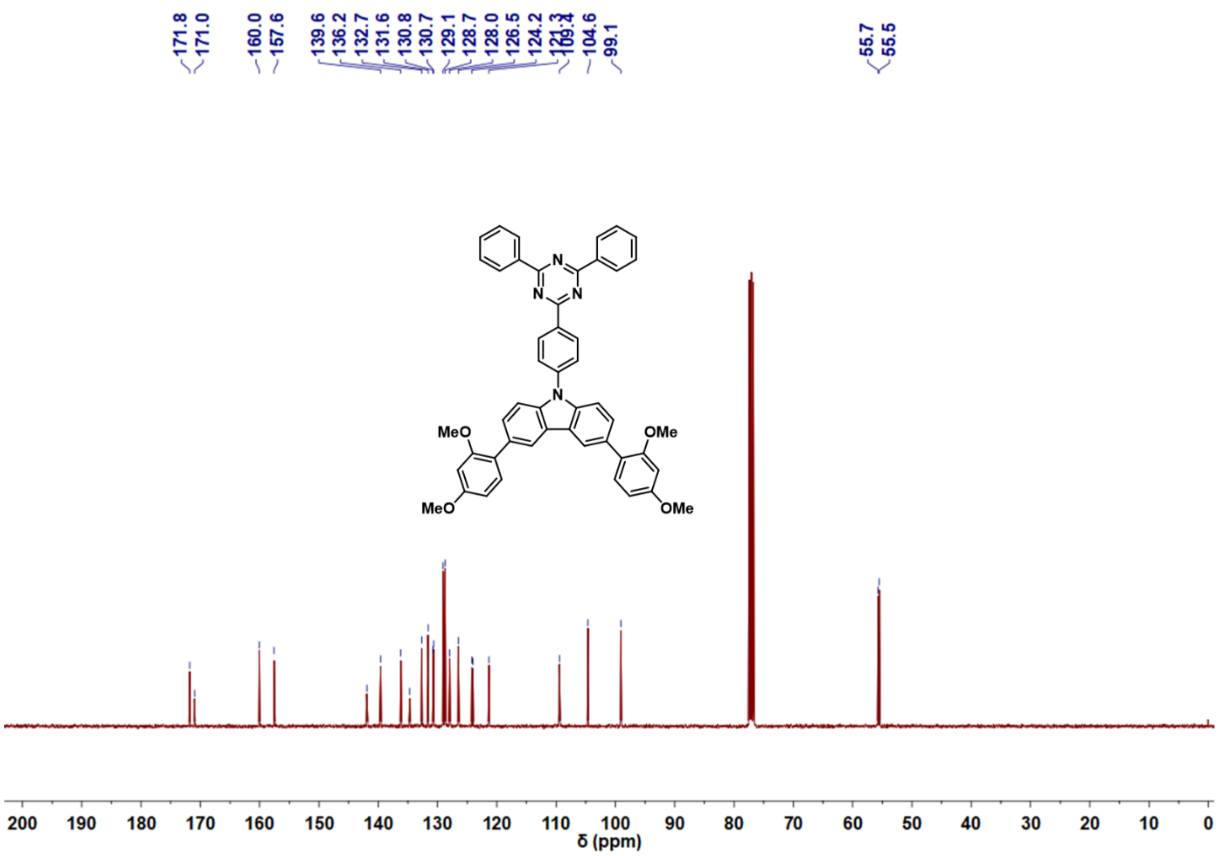


Fig. S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298K) of monomer **CT-1**.

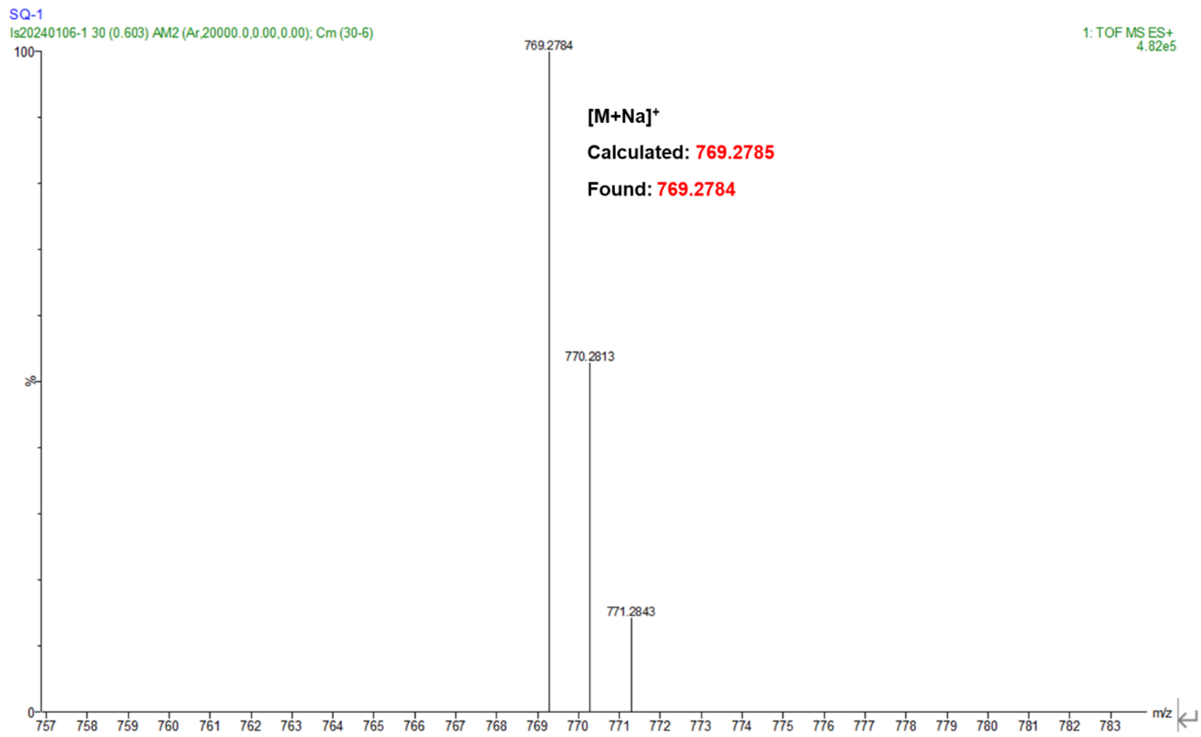


Fig. S3. HRMS spectrum of monomer **CT-1**.

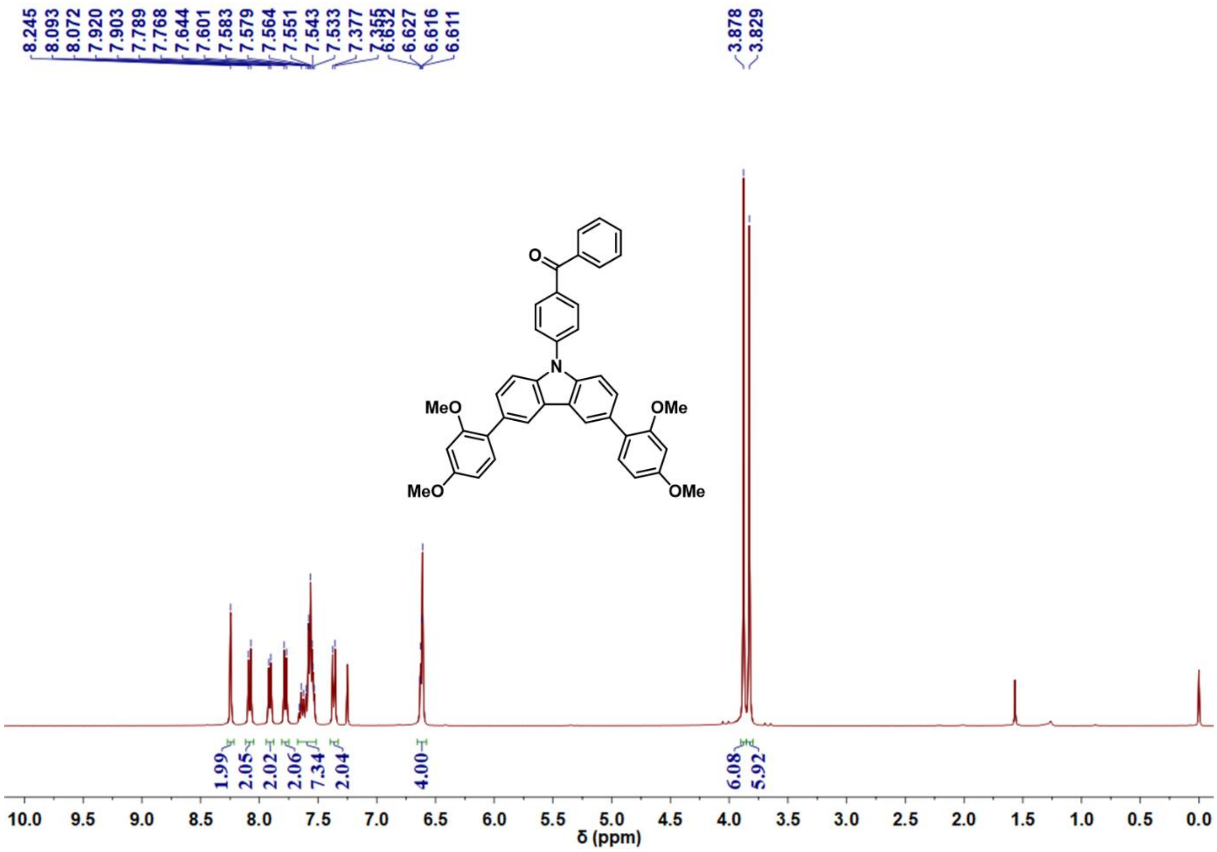


Fig. S4. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298K) of **CB-1**.

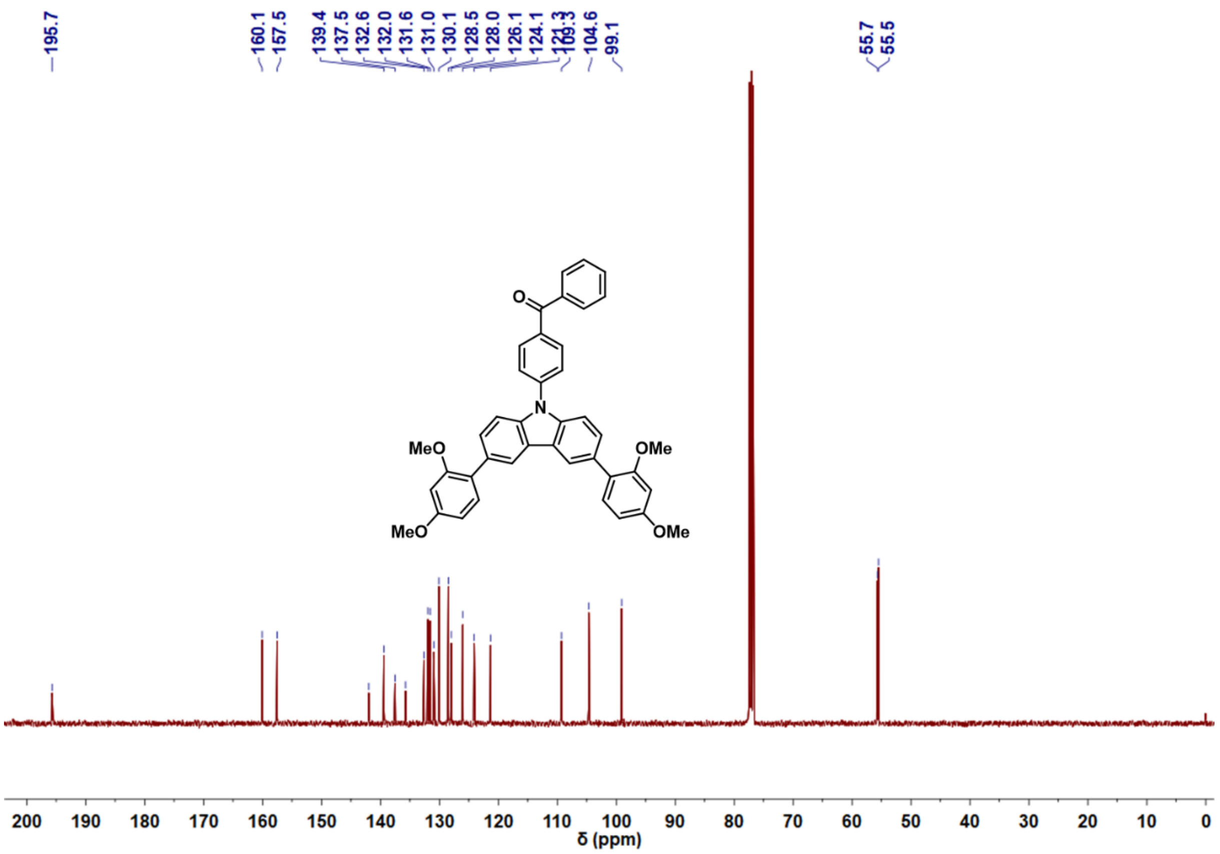


Fig. S5. ^{13}C NMR spectrum (100 MHz, CD_2Cl_2, 298K) of **CB-1**.

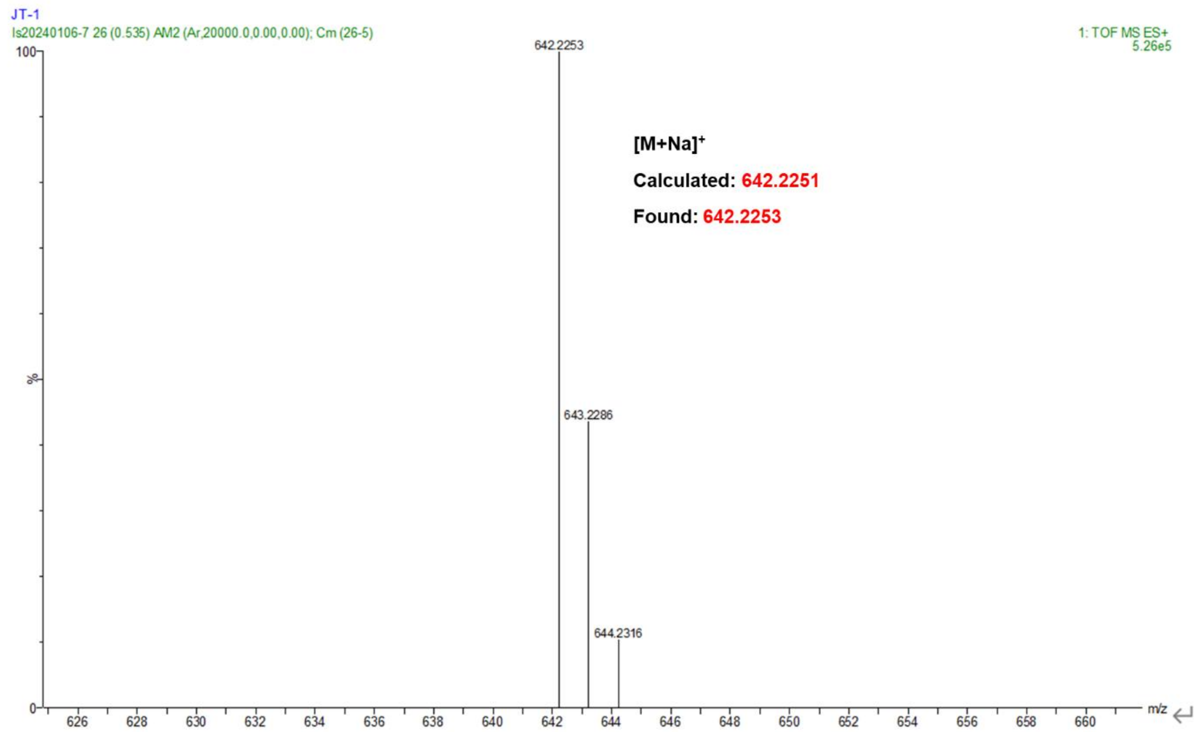


Fig. S6. HMRS spectrum of **CB-1**.

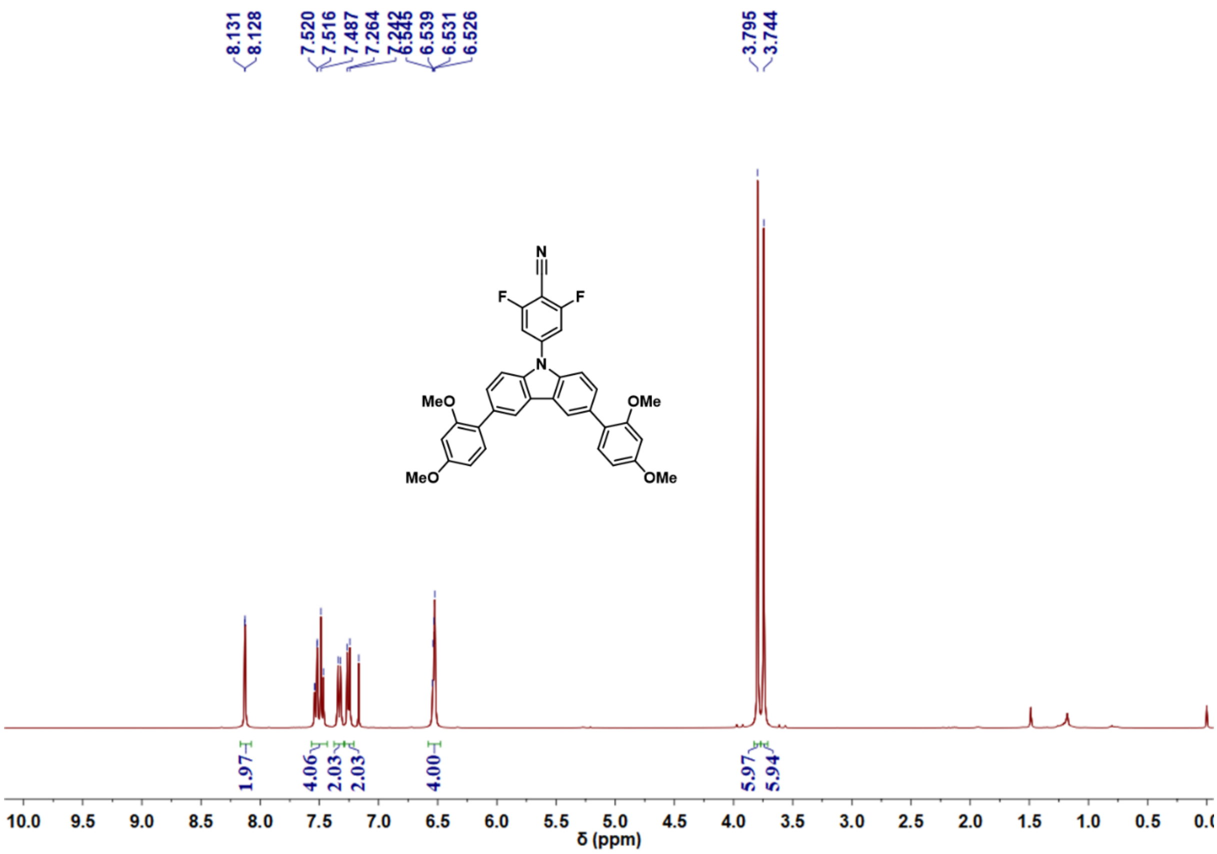


Fig. S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **CF-1**.

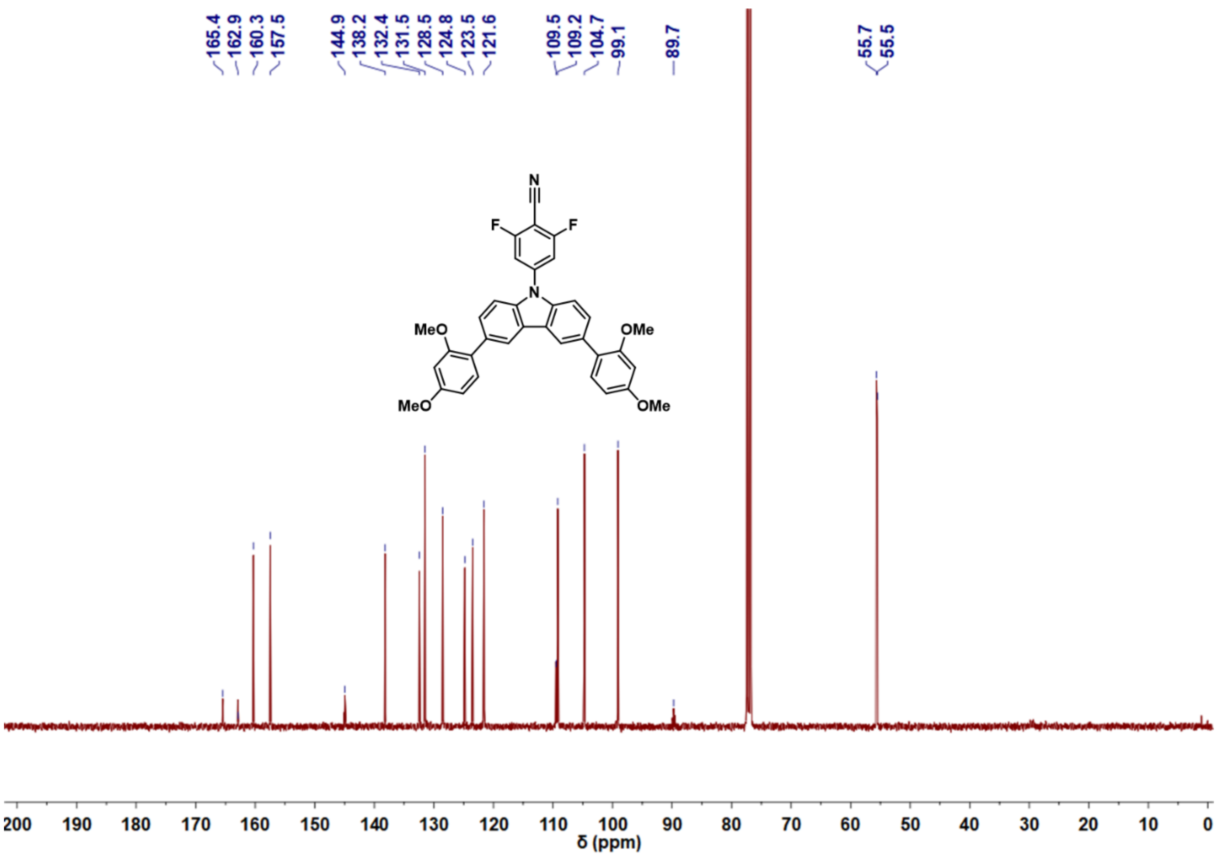


Fig. S8. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298K) of **CF-1**.

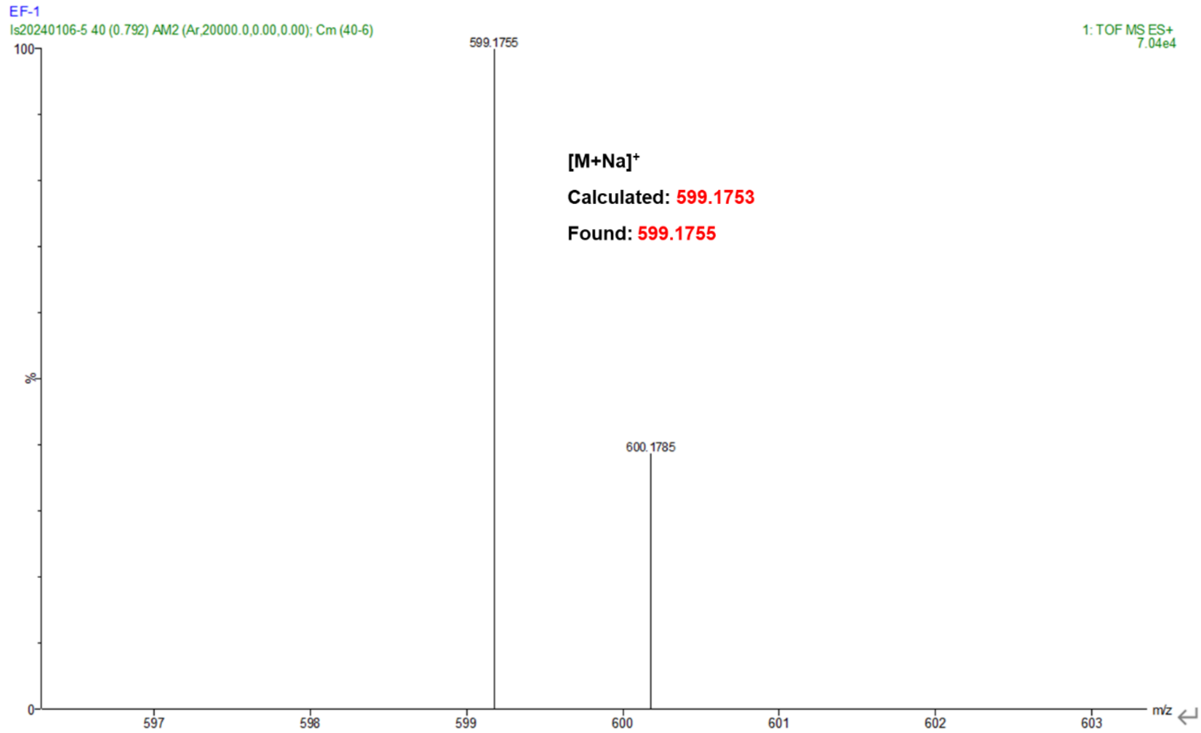


Fig. S9. HMRS spectrum of **CF-1**.

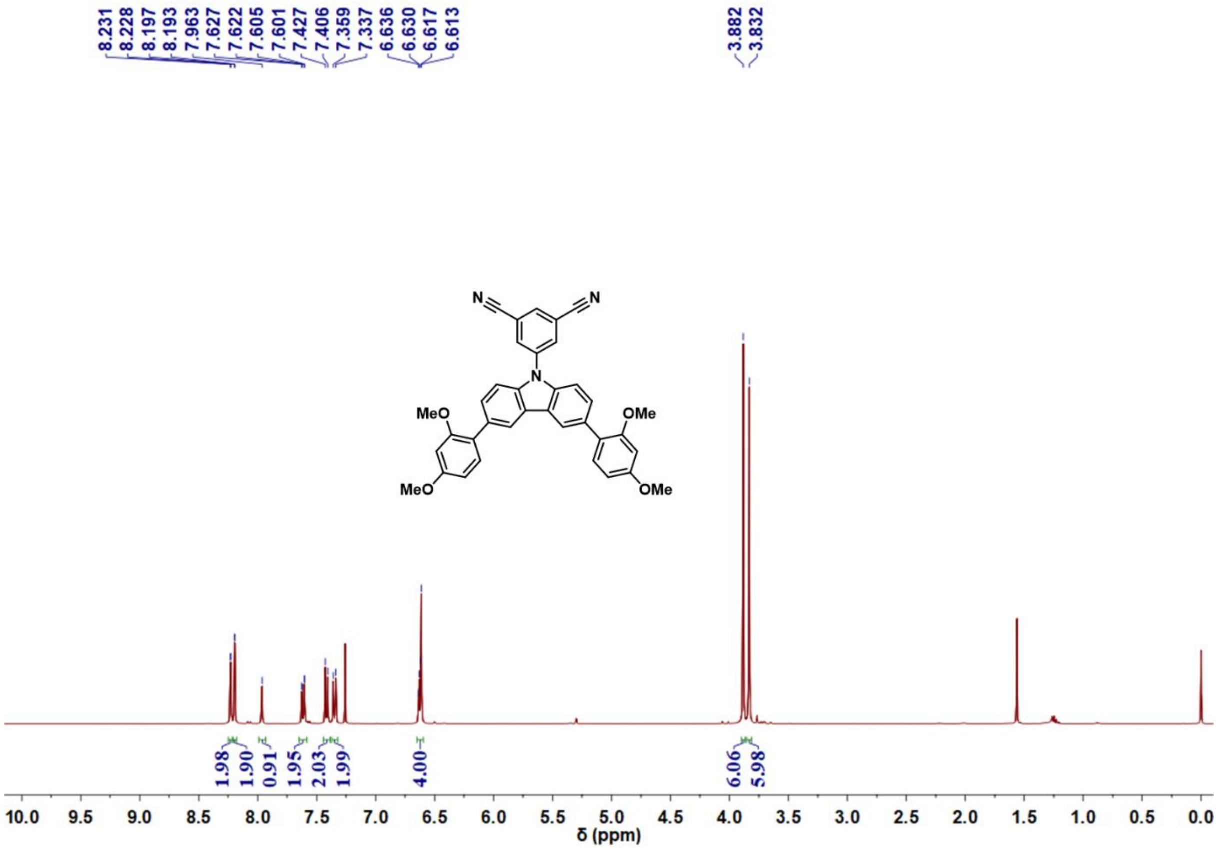


Fig. S10. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **CP-1**.

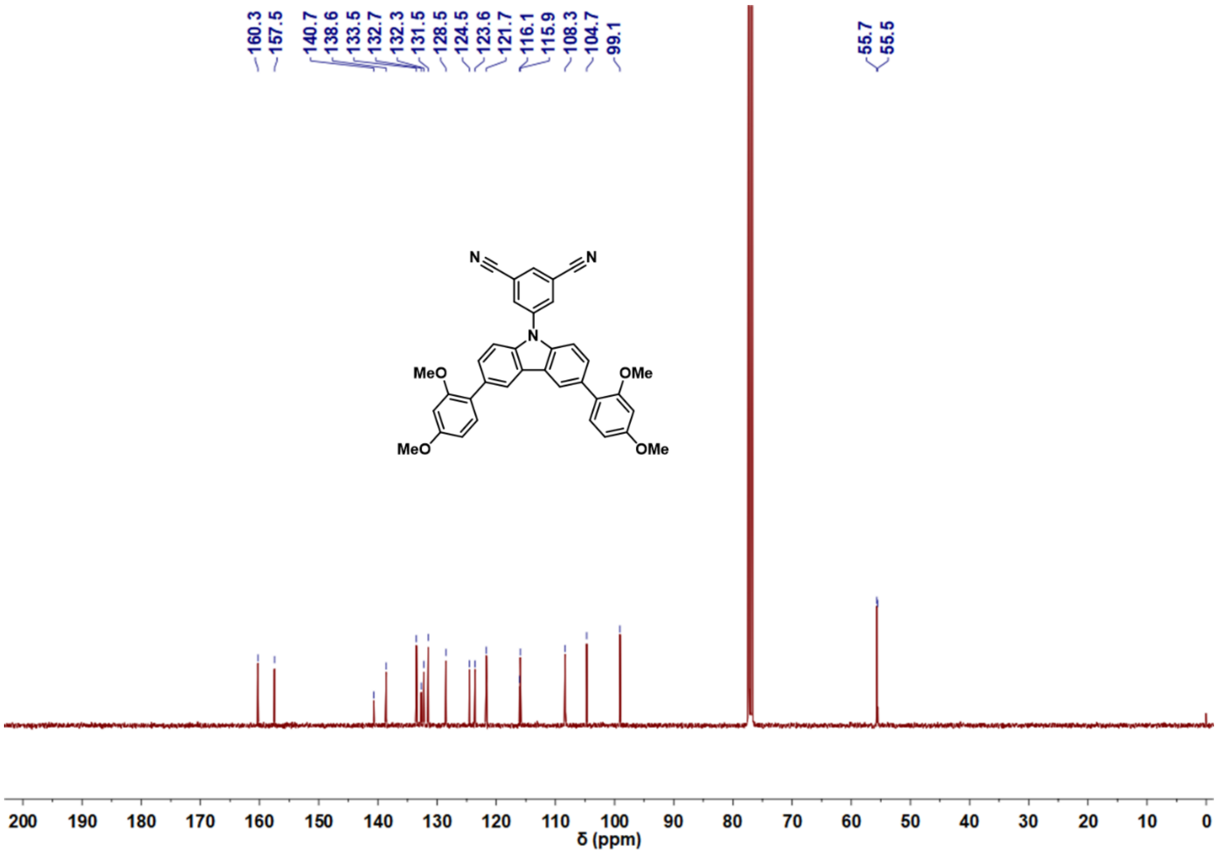


Fig. S11. ^{13}C NMR spectrum (400 MHz, $CDCl_3$, 298K) of **CP-1**.

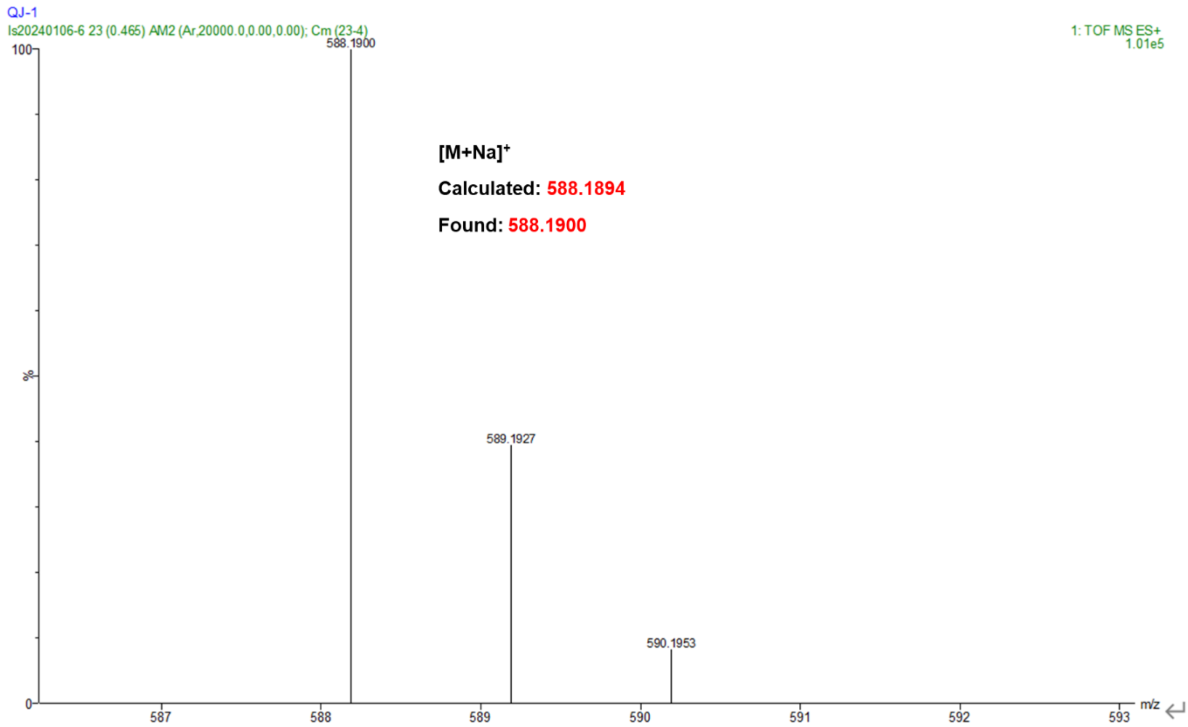


Fig. S12. HRMS spectrum of **CP-1**.

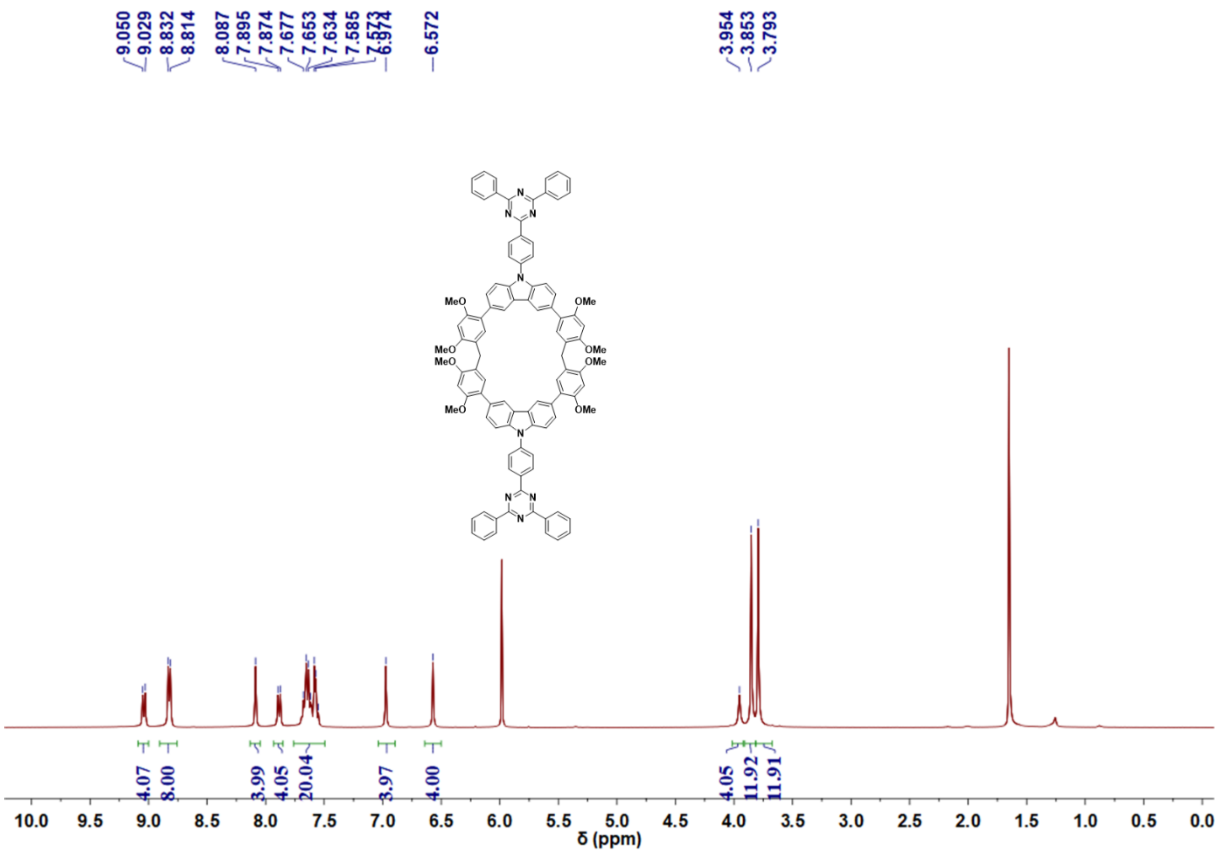


Fig. S13. [1]H NMR spectrum (400 MHz, $Cl_2DCCDCl_2$, 298K) of **CT-2**.

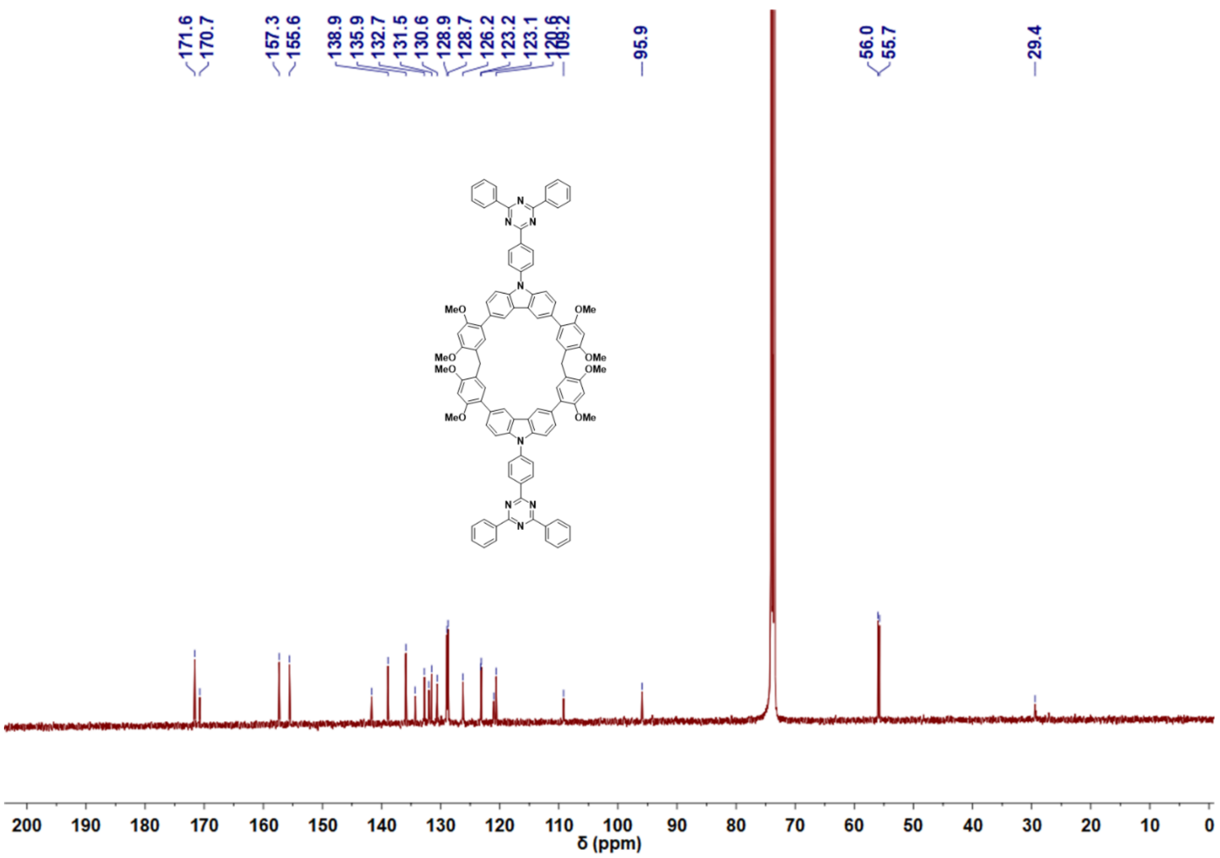


Fig. S14. [13]C NMR spectrum (400 MHz, $Cl_2DCCDCl_2$, 298K) of **CT-2**.

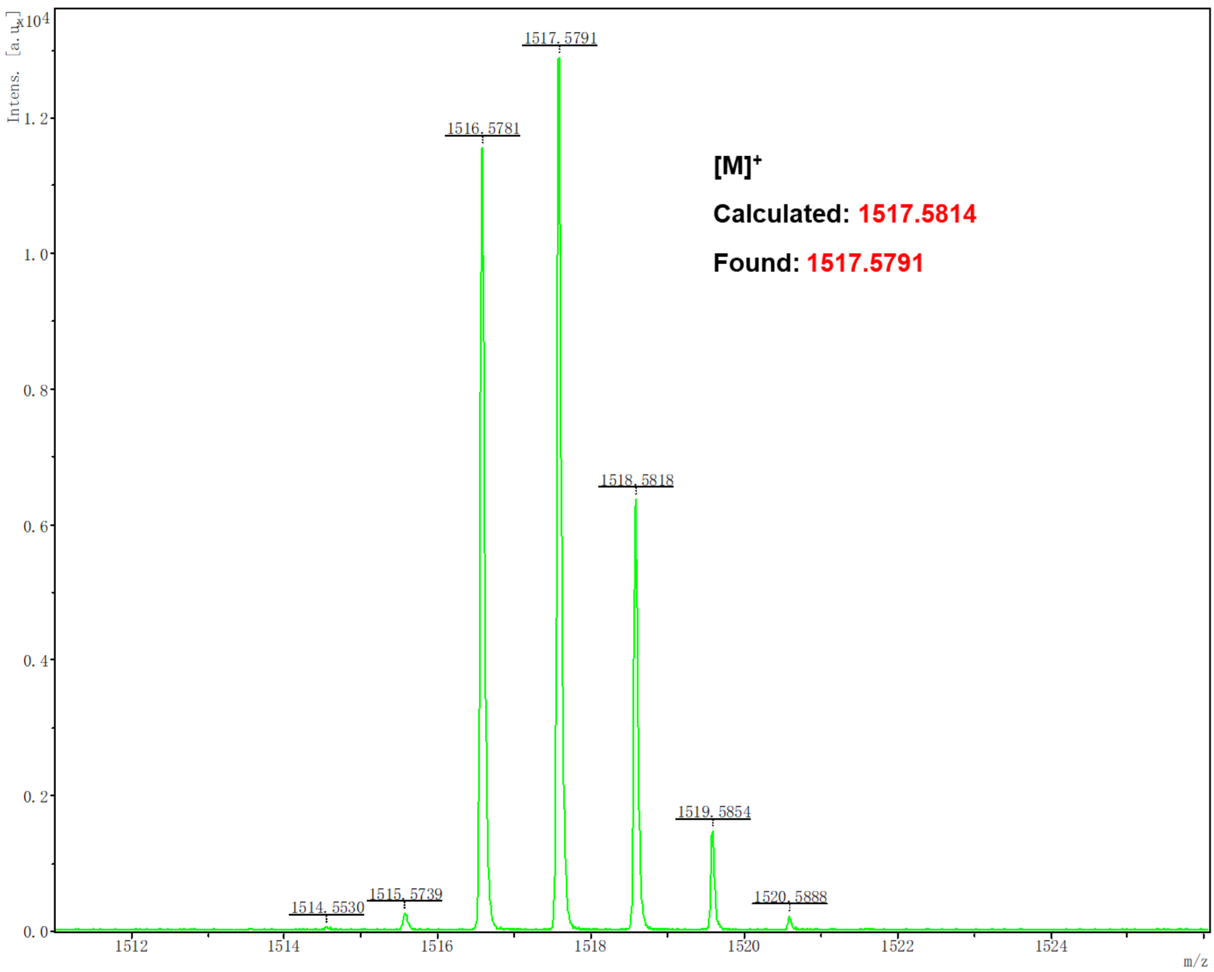


Fig. S15. HRMS spectrum of **CT-2**.

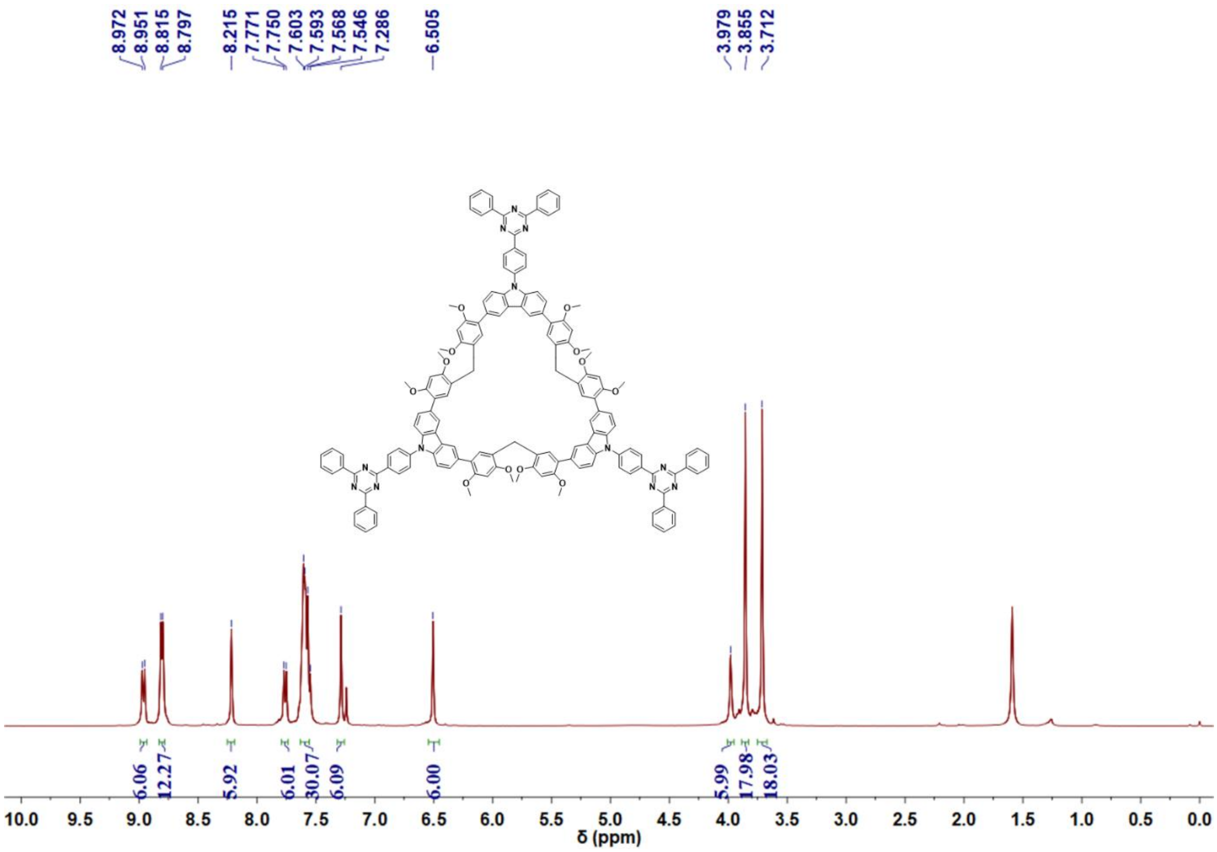


Fig. S16. [1]H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **CT-3**.

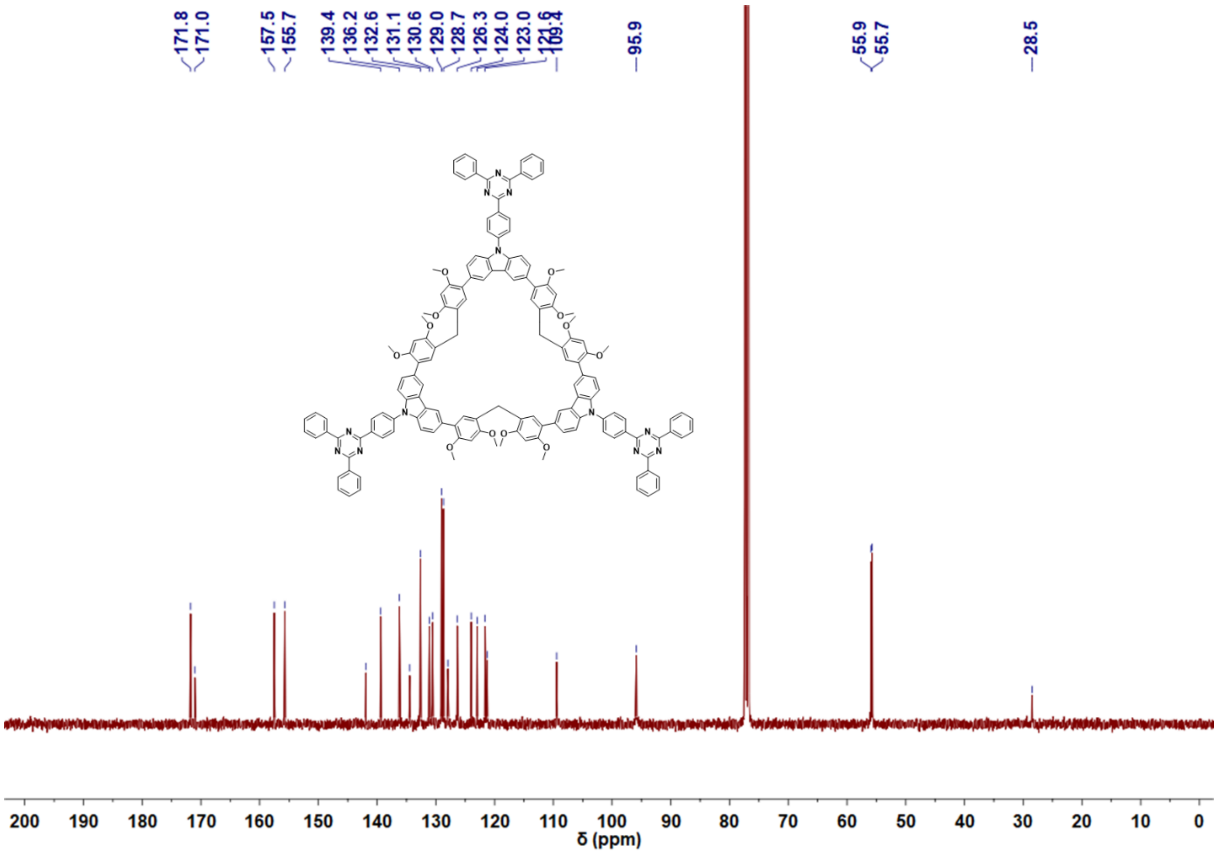


Fig. S17. ^{13}C NMR spectrum (400 MHz, $CDCl_3$, 298K) of **CT-3**.

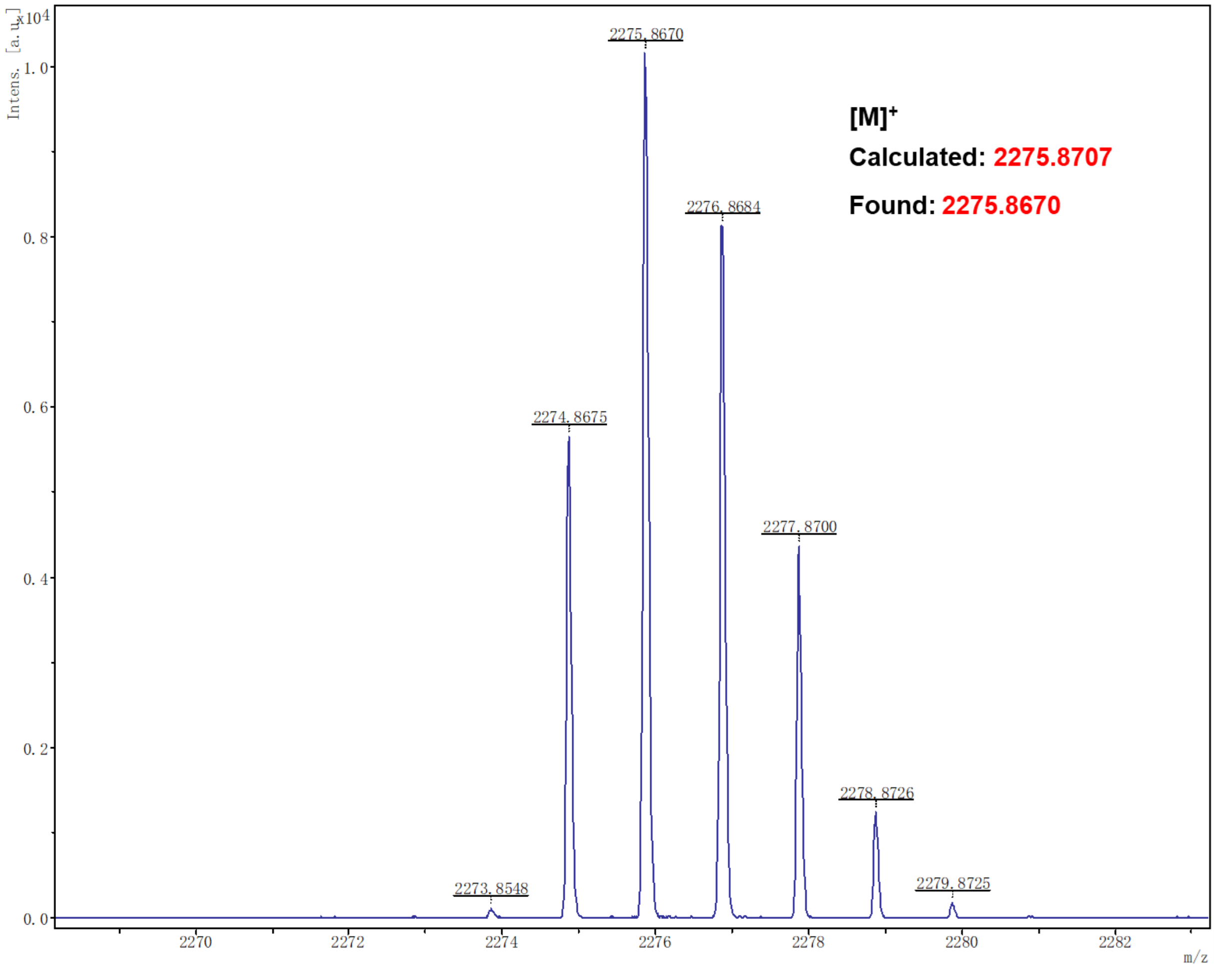


Fig. S18. HRMS spectrum of **CT-3**.

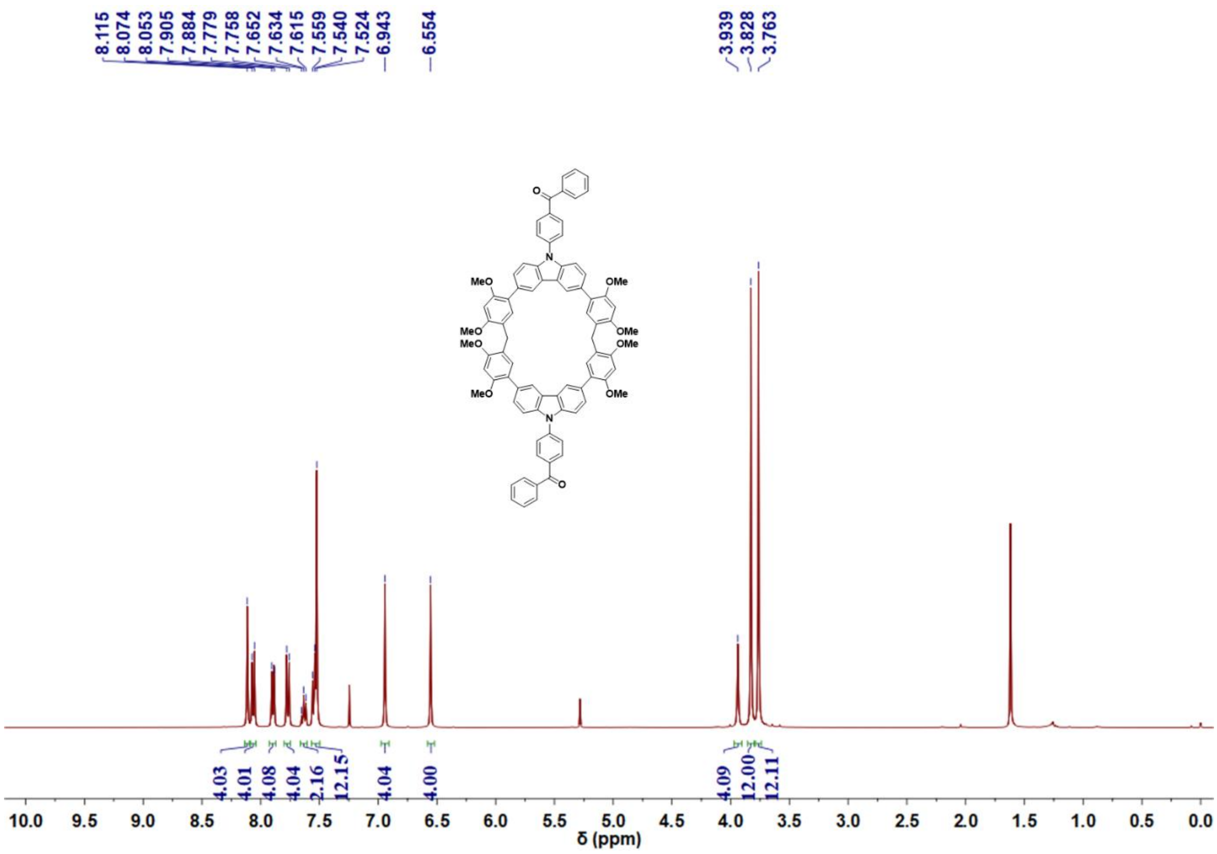


Fig. S19. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **CB-2**.

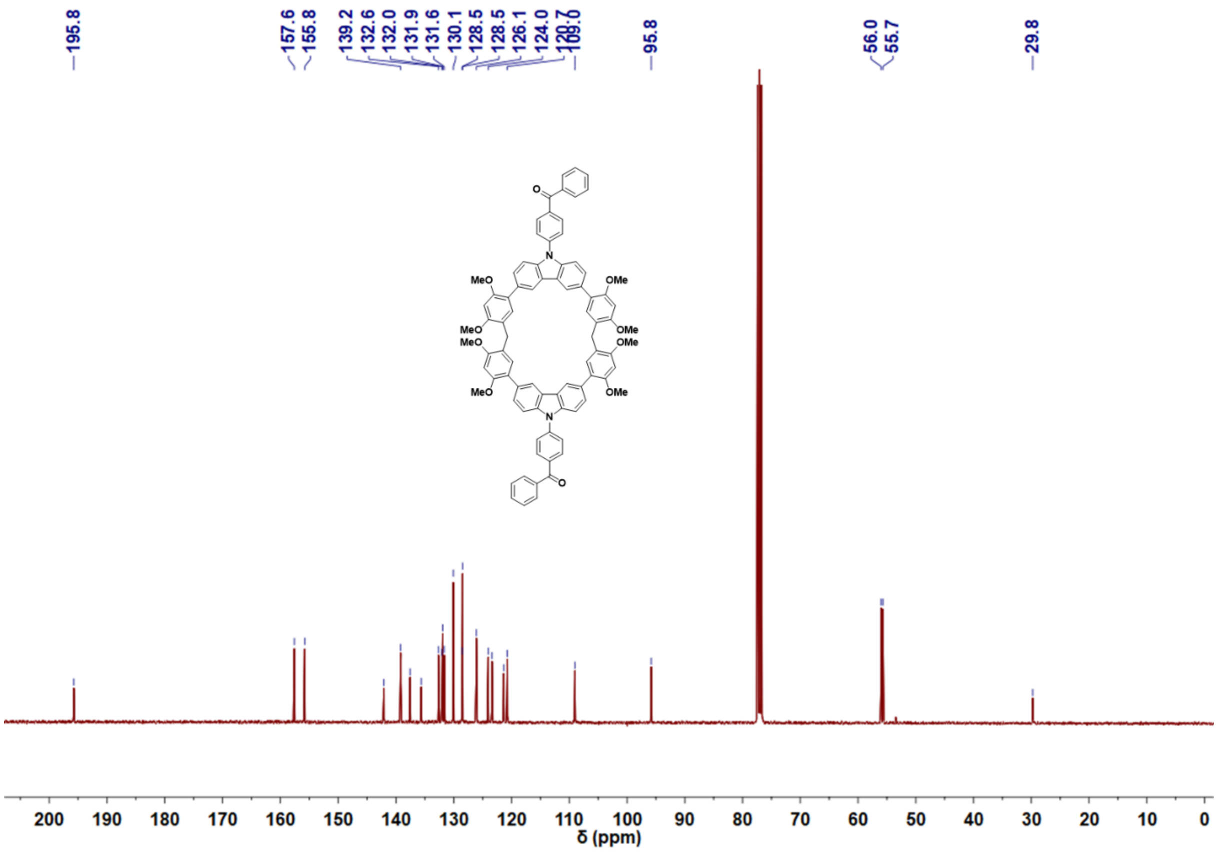


Fig. S20. ^{13}C NMR spectrum (400 MHz, $CDCl_3$, 298K) of **CB-2**.

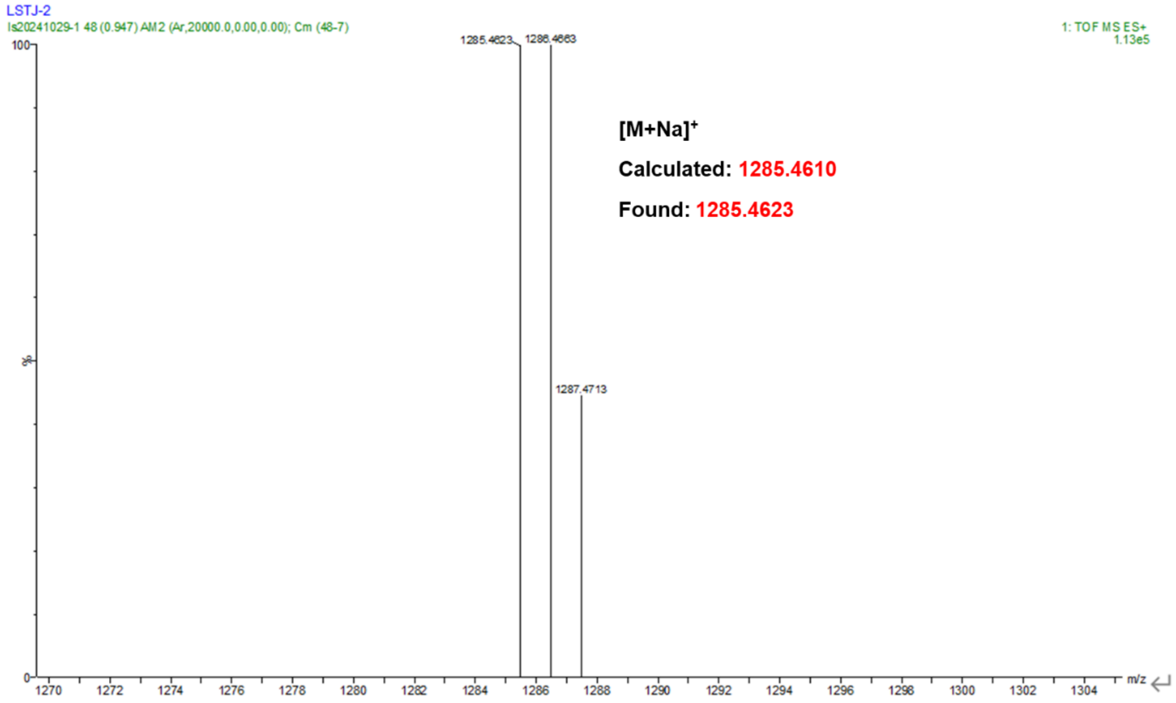


Fig. S21. HRMS spectrum of **CB-2**.

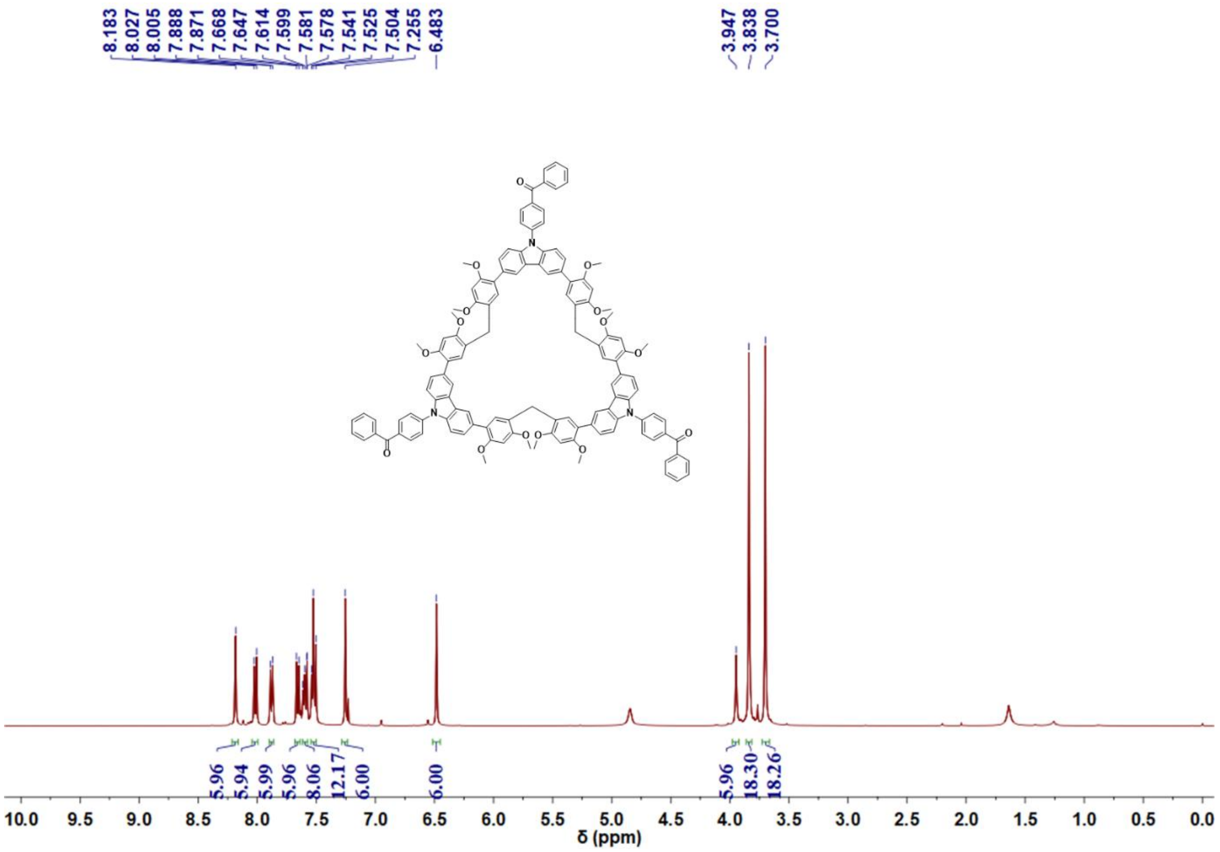


Fig. S22. [1]H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **CB-3**.

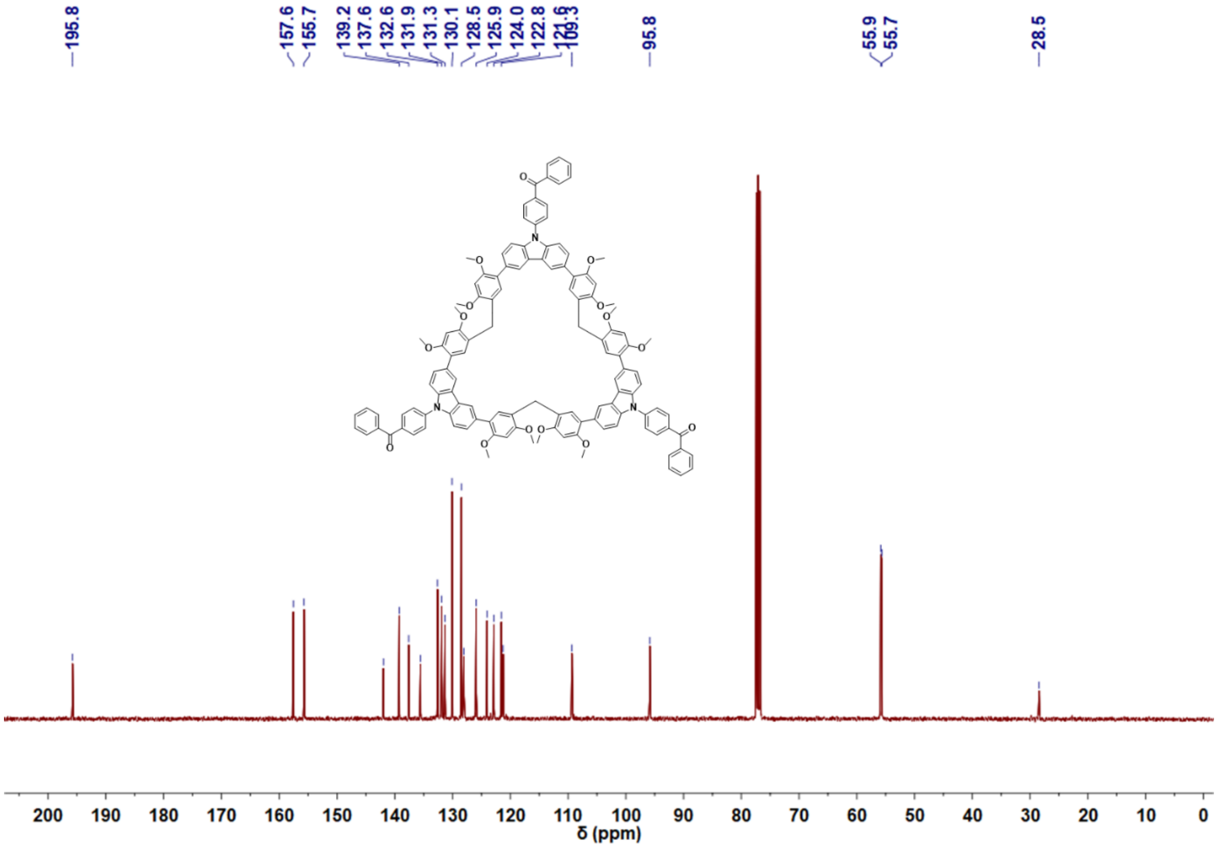


Fig. S23. ^{13}C NMR spectrum (400 MHz, $CDCl_3$, 298K) of **CB-3**.

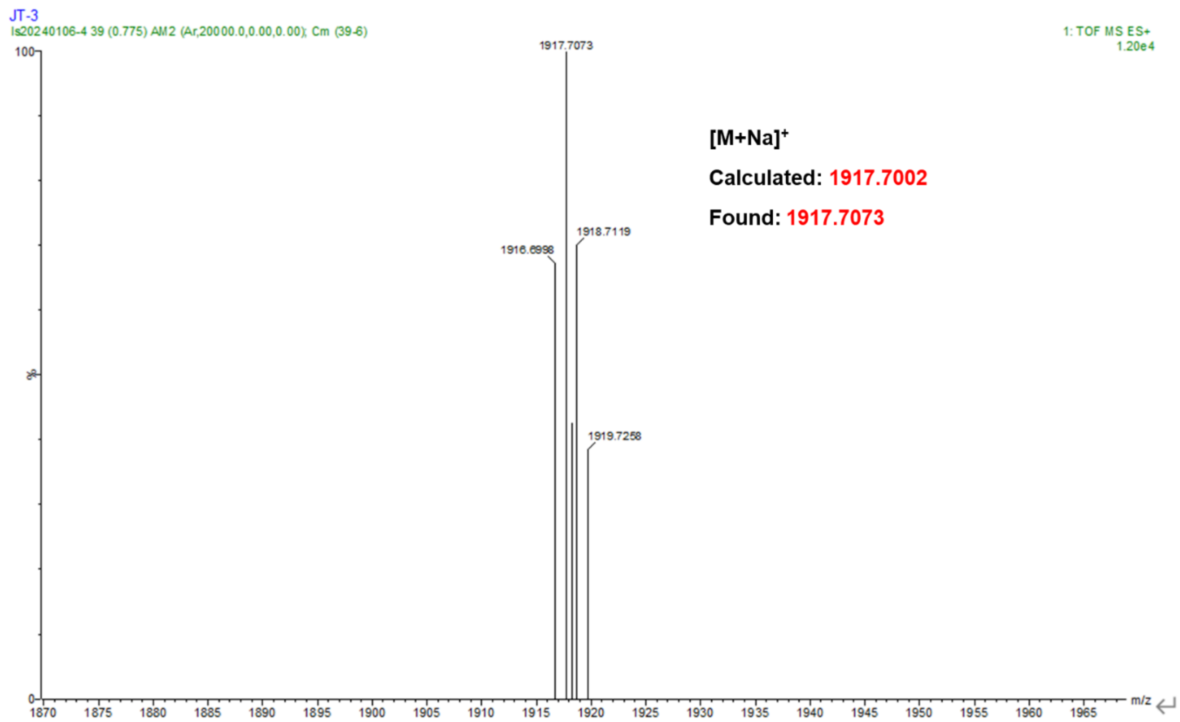


Fig. S24. HRMS spectrum of **CB-3**.

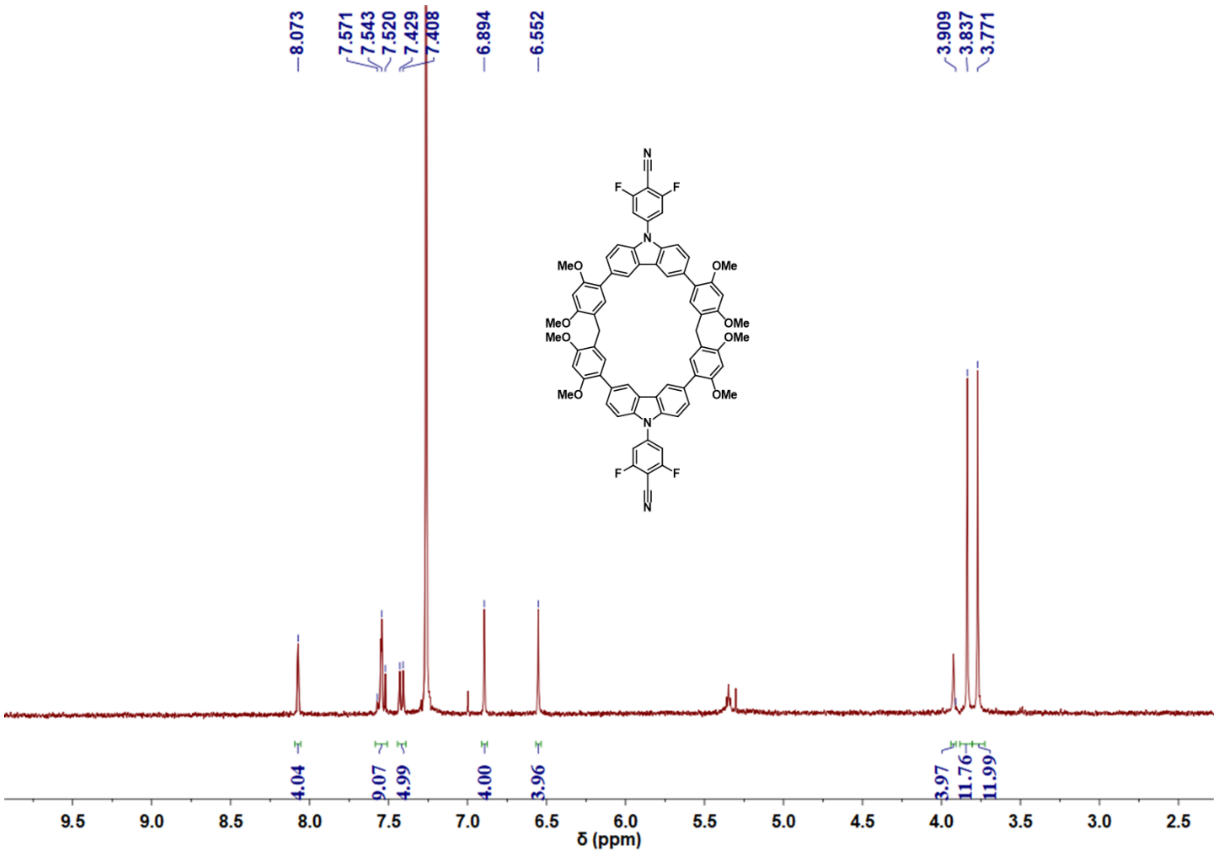


Fig. S25. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **CF-2**.

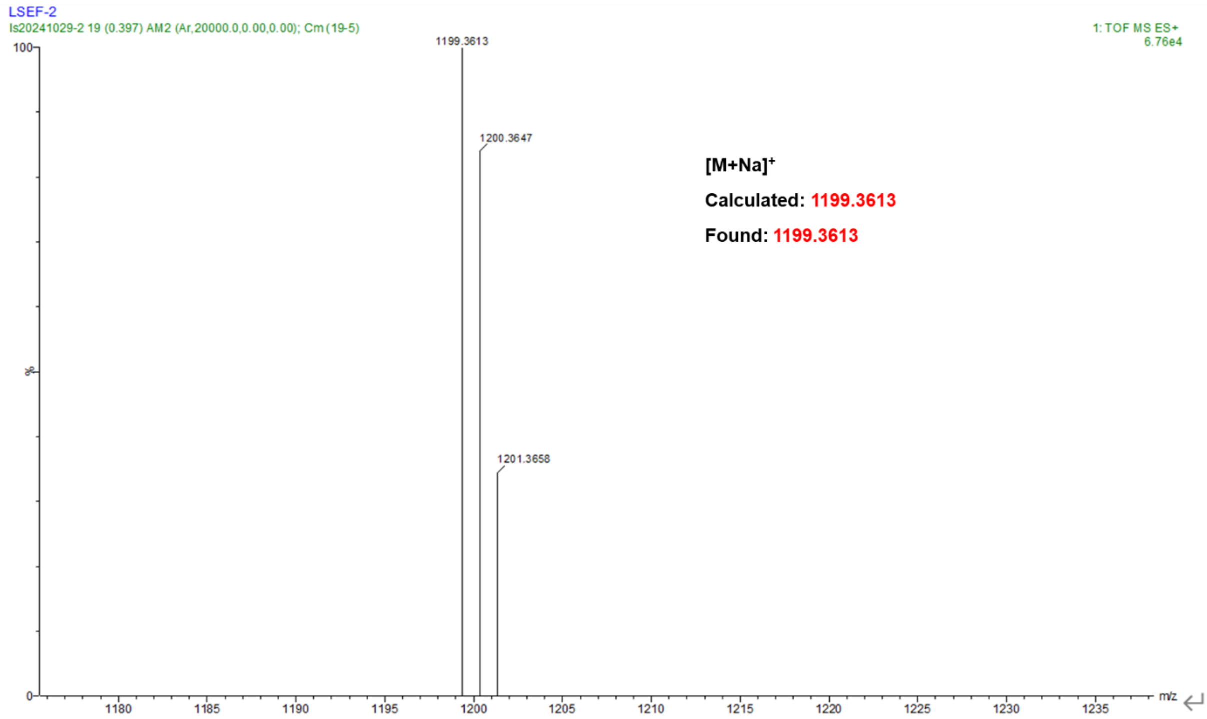


Fig. S26. HRMS spectrum of **CF-2**.

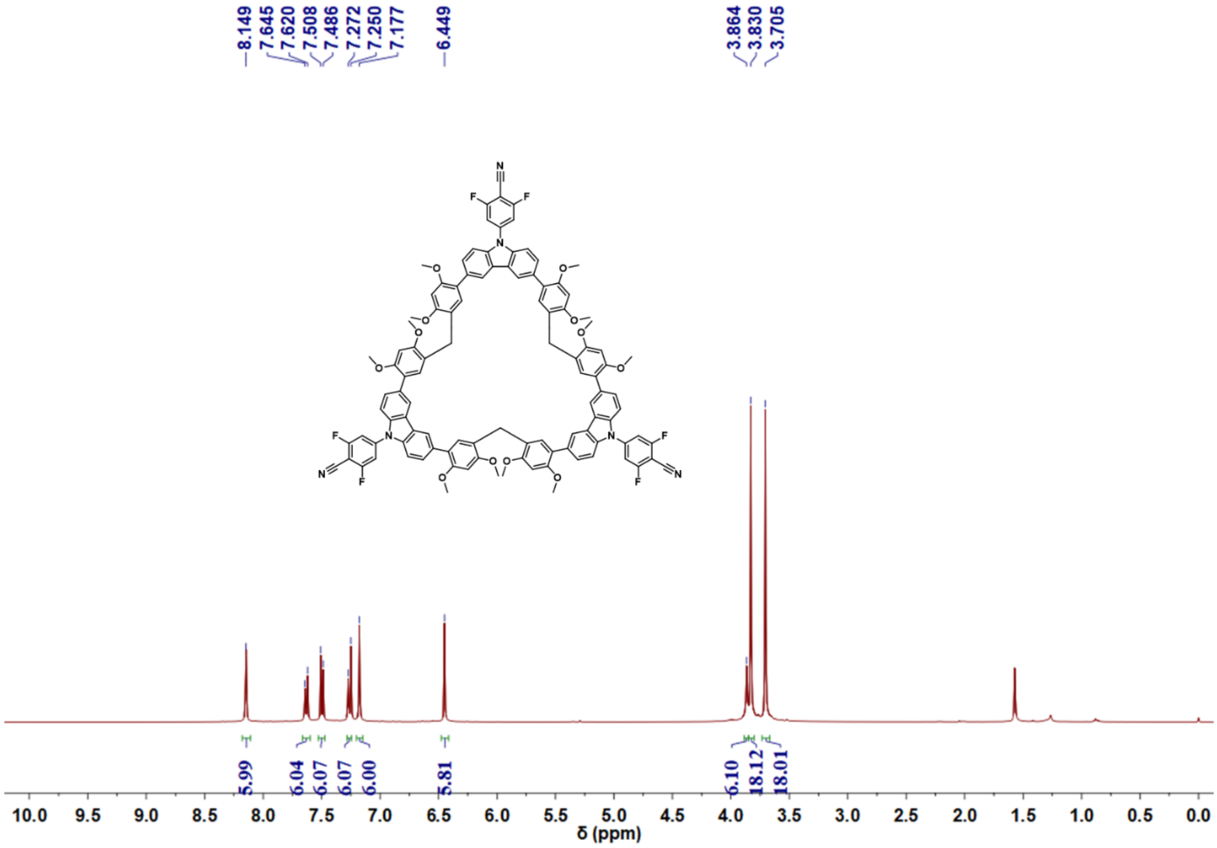


Fig. S27. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **CF-3**.

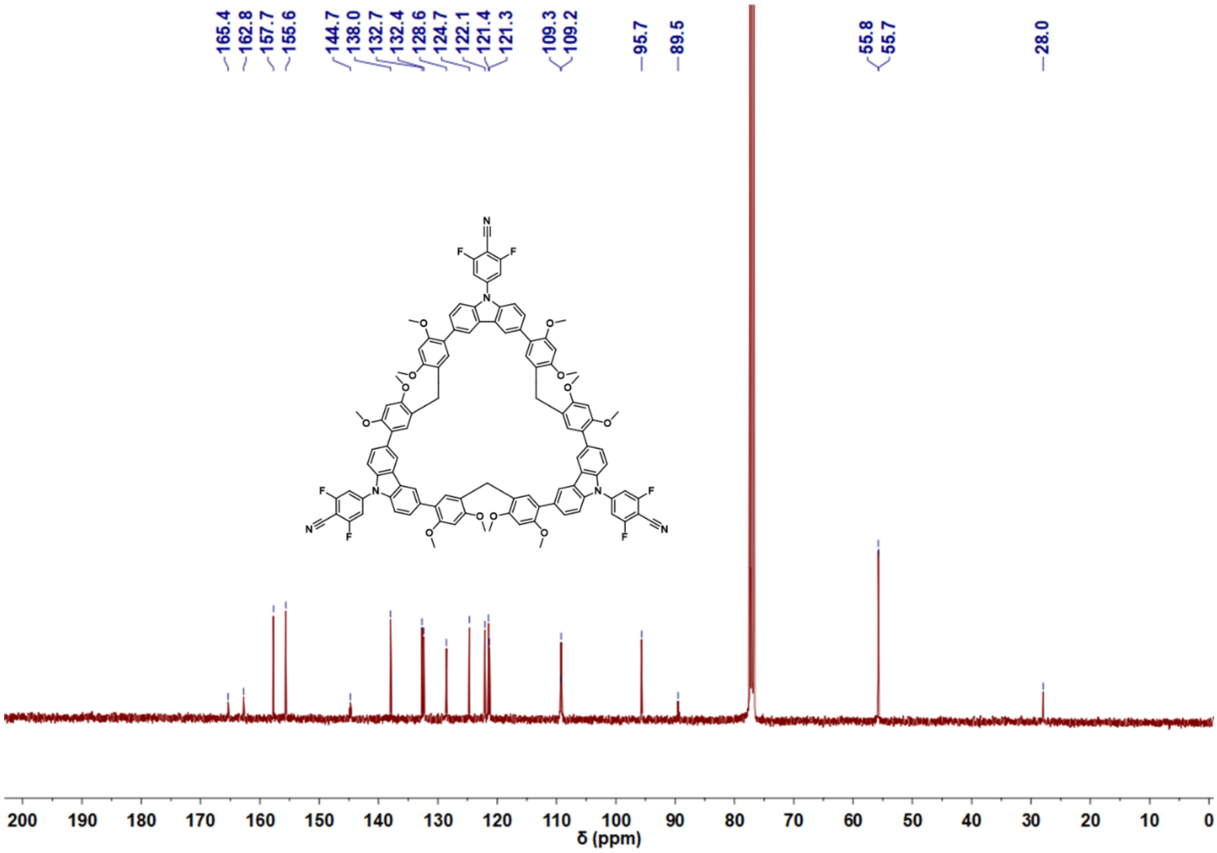


Fig. S28. ^{13}C NMR spectrum (400 MHz, $CDCl_3$, 298K) of **CF-3**.

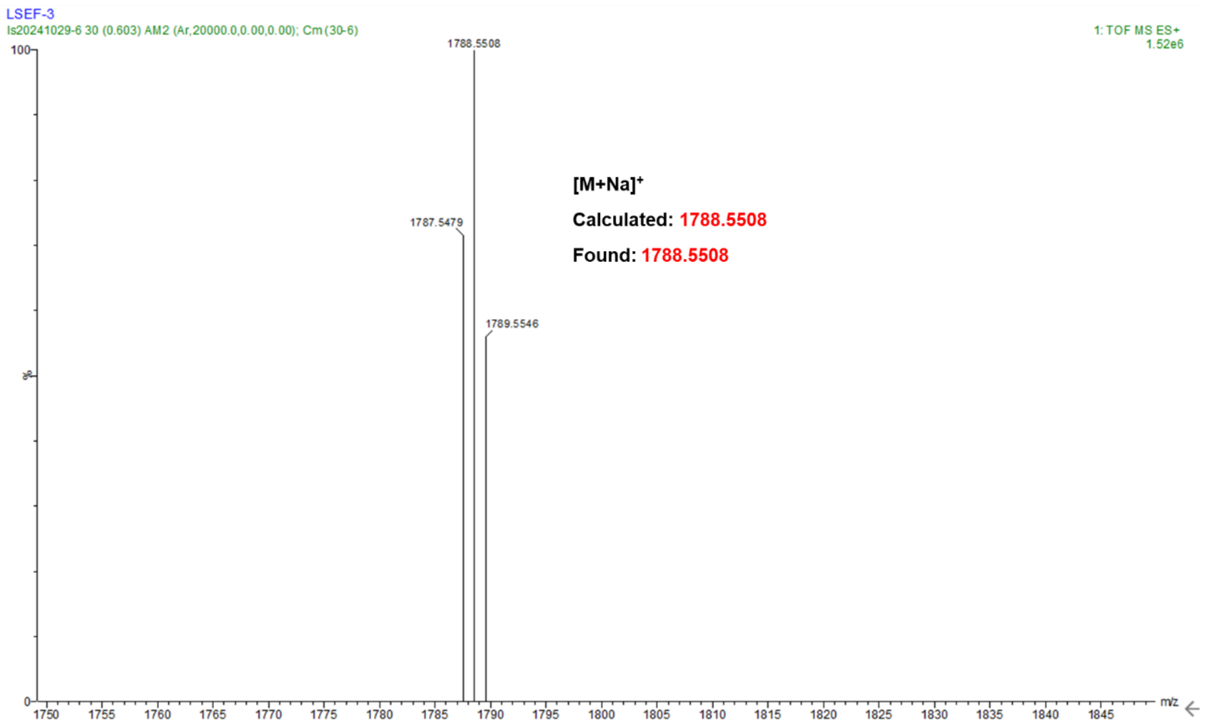


Fig. S29. HRMS spectrum of **CF-3**.

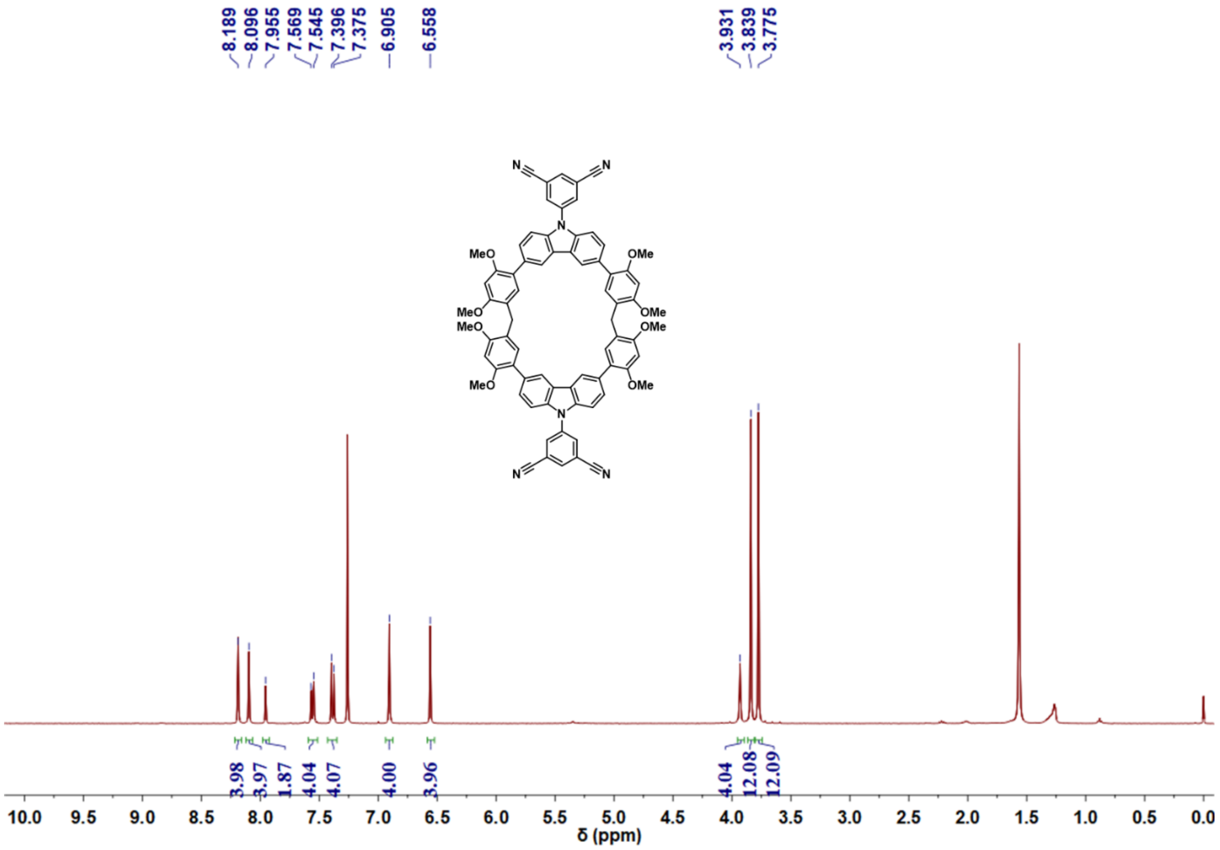


Fig. S30. ^{1}H NMR spectrum (400 MHz, $Cl_2DCCDCl_2$, 298K) of **CP-2**.

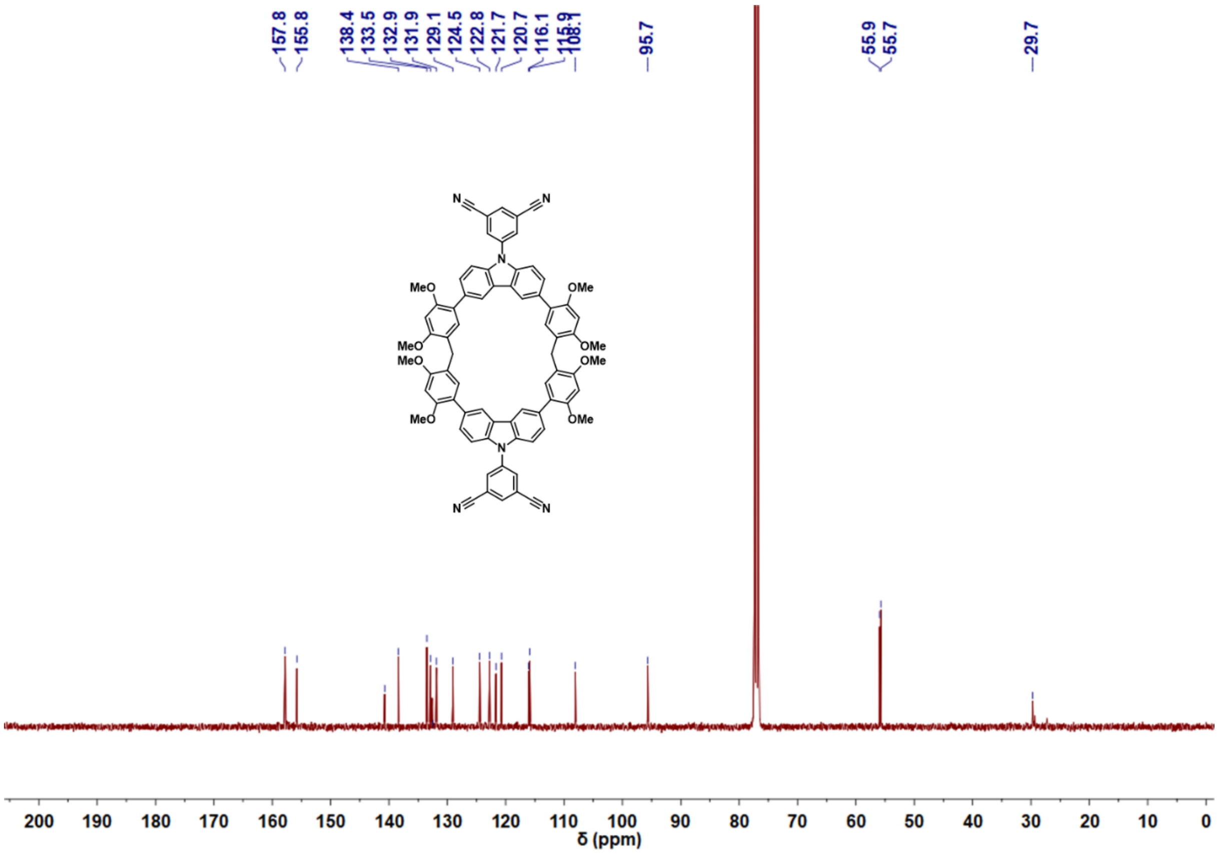


Fig. S31. ^{13}C NMR spectrum (400 MHz, $Cl_2DCCDCl_2$, 298K) of **CP-2**.

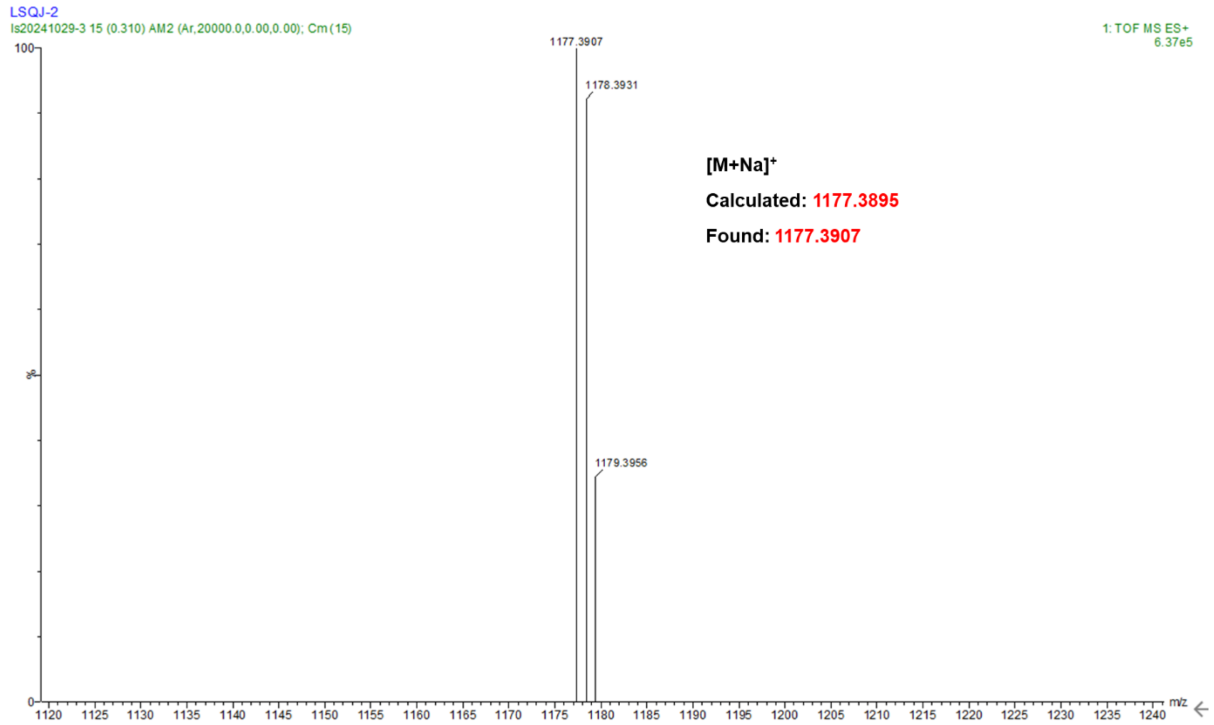


Fig. S32. HRMS spectrum of **CP-2**.

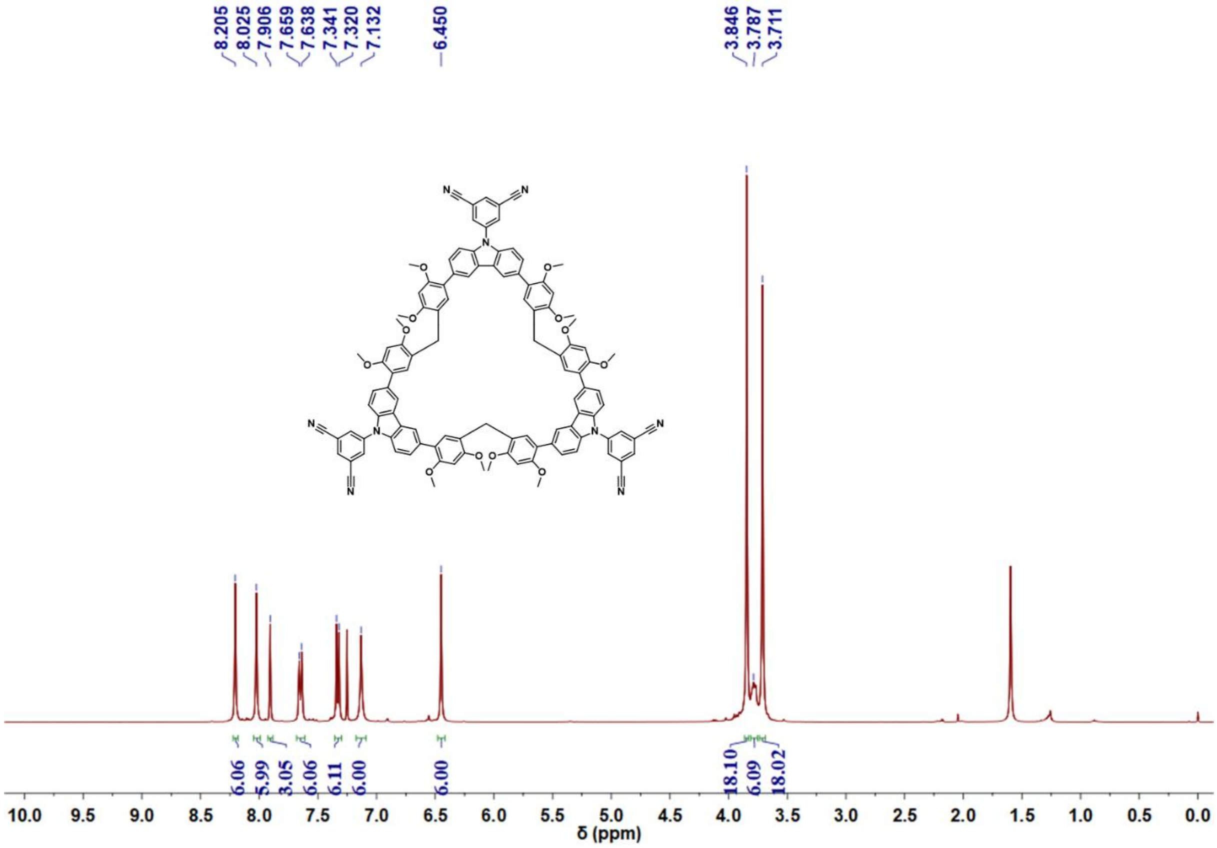


Fig. S33. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **CP-3**.

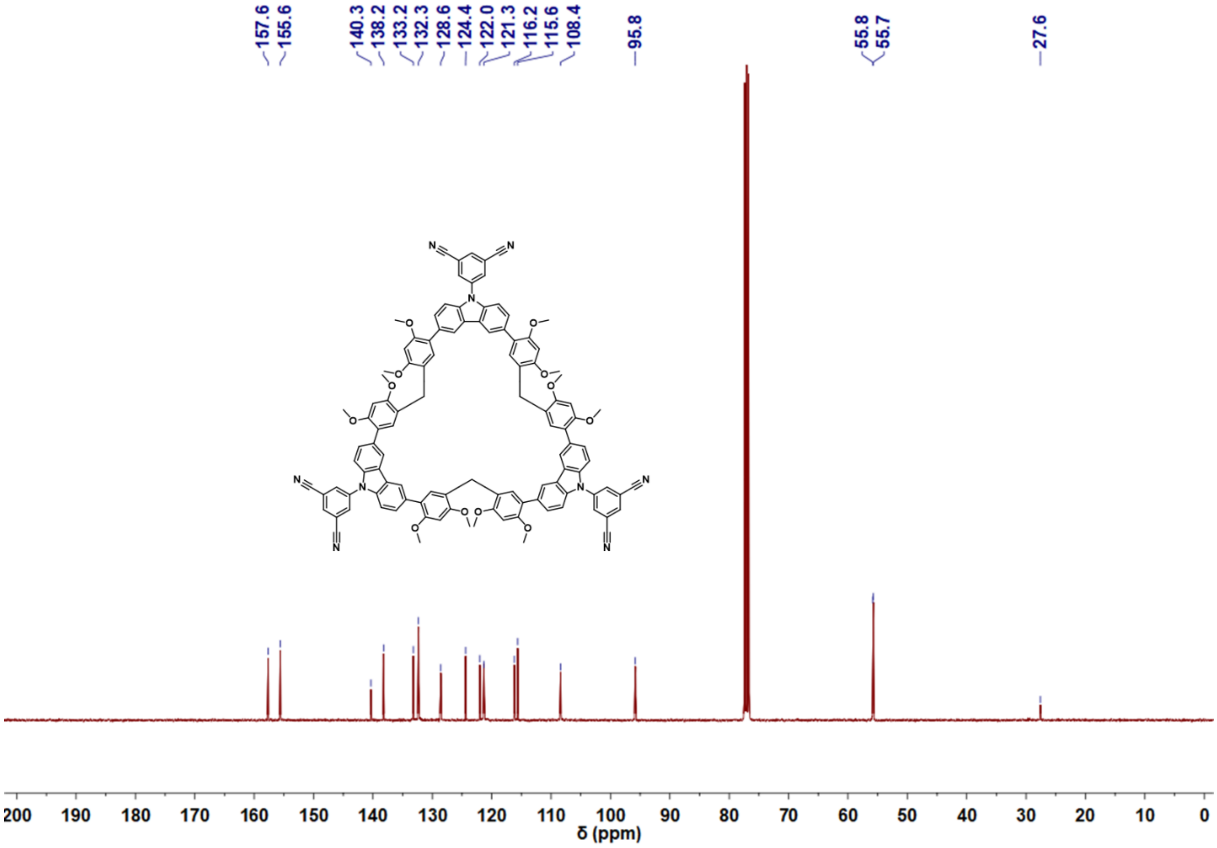


Fig. S34. ^{13}C NMR spectrum (400 MHz, $CDCl_3$, 298K) of **CP-3**.

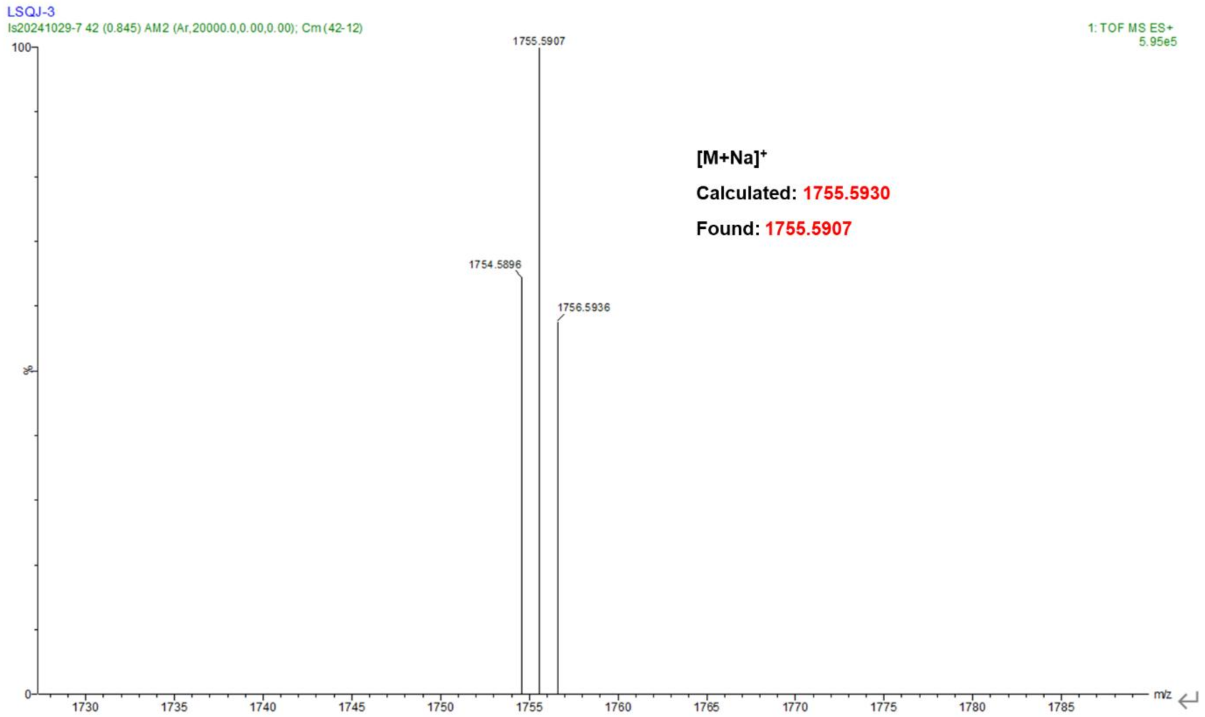


Fig. S35. HRMS spectrum of **CP-3**.

4. Photophysical properties

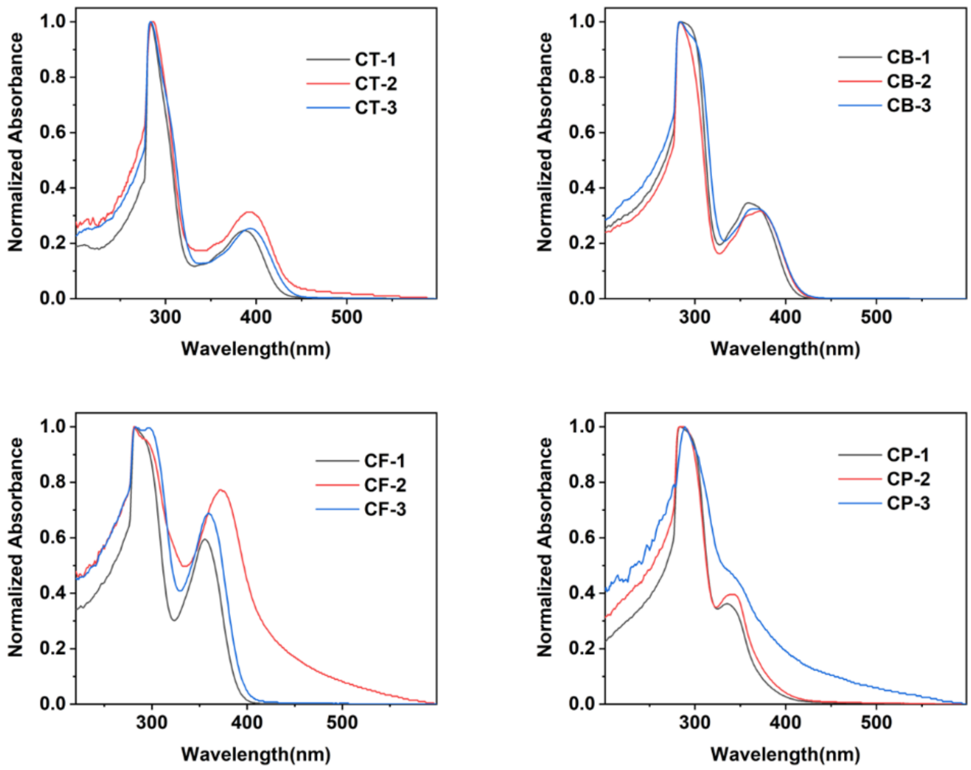


Fig.S36 Normalized UV-Vis absorption spectra of monomers and macrocycles in toluene solution.

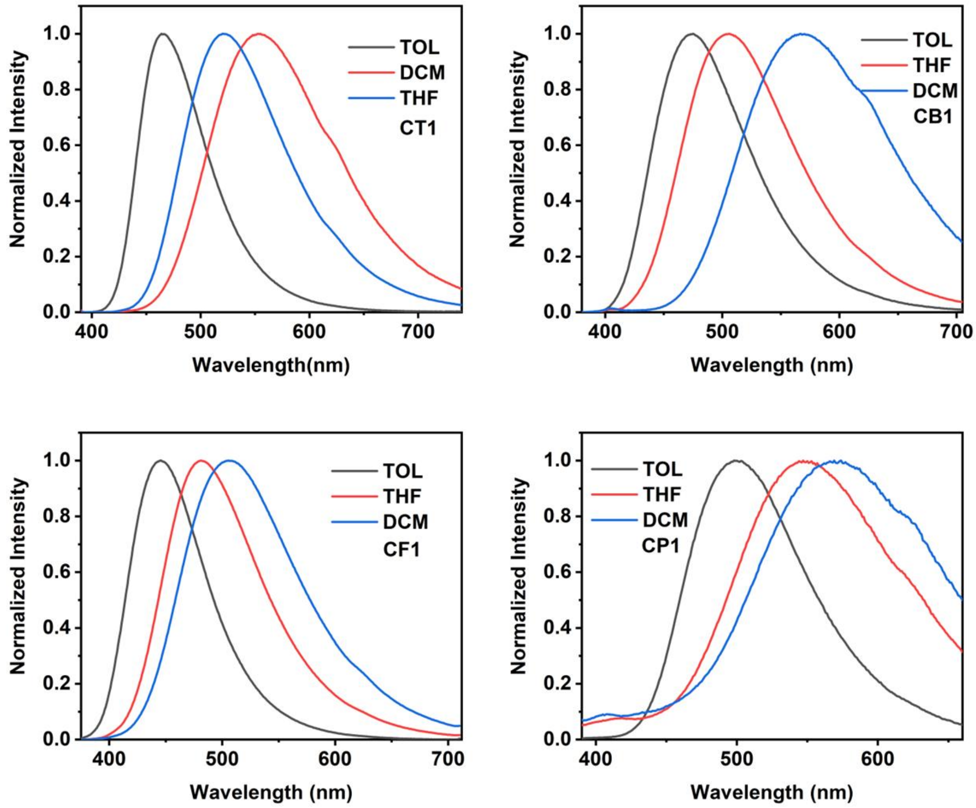


Fig. S37. Normalized fluorescence spectra of monomers in different solvents (1.0×10^{-5} M).

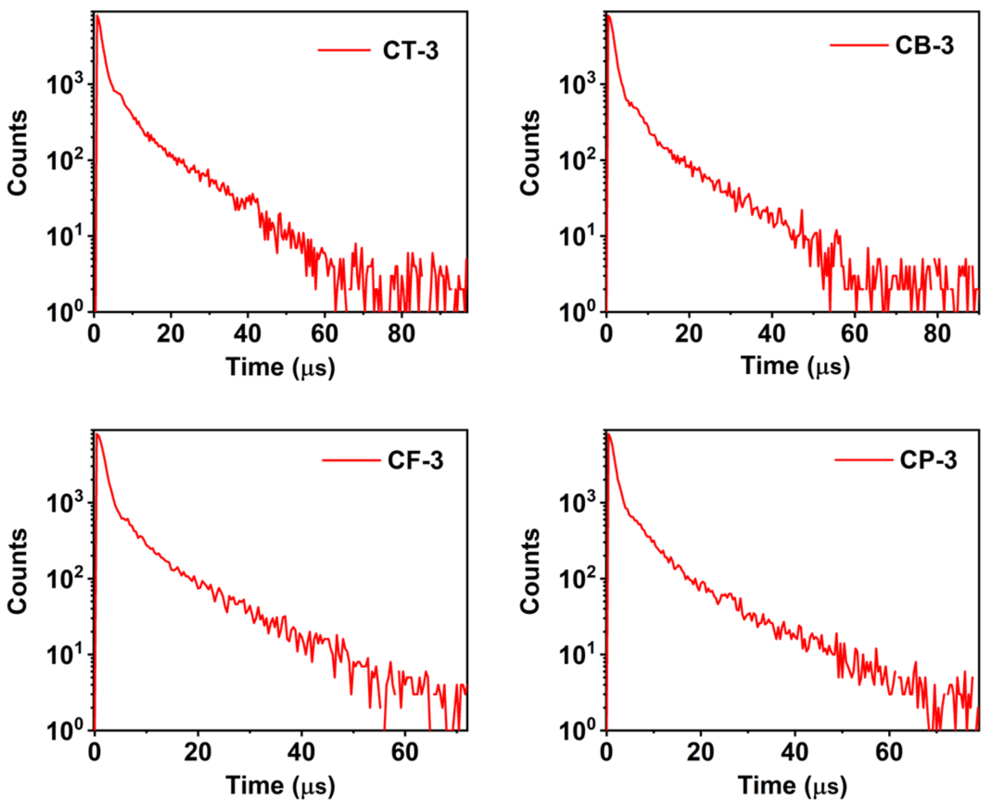


Fig. S38. Transient PL decay curve of trimeric macrocycles in toluene (1.0×10^{-5} mol/L) at room temperature.

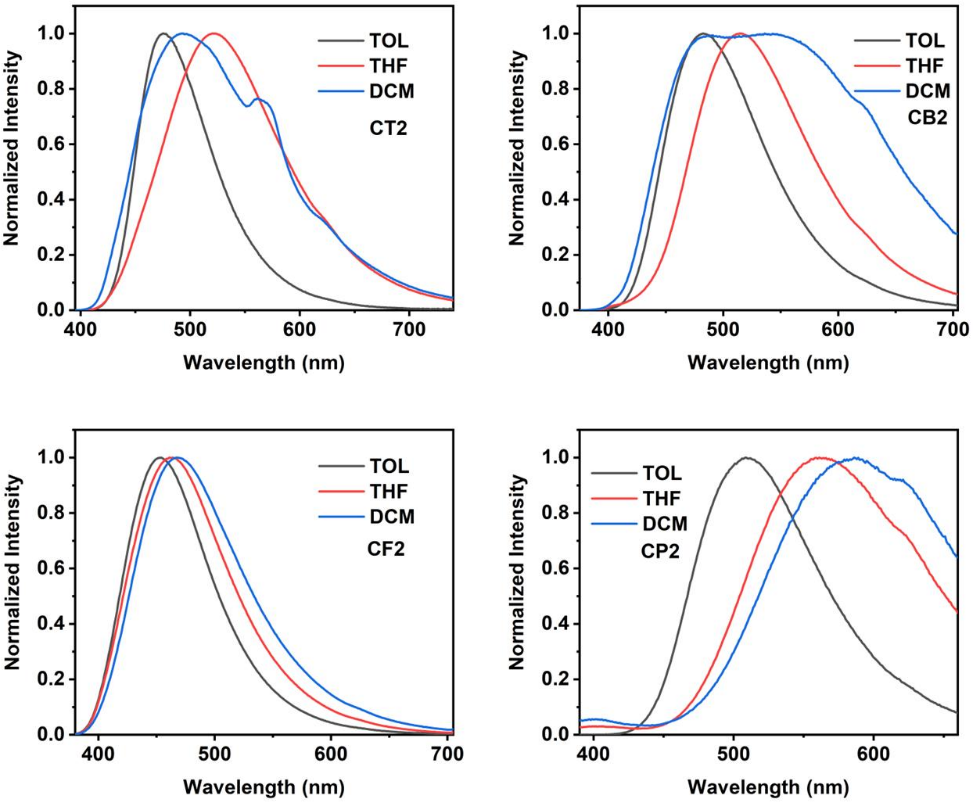


Fig. S39. Normalized fluorescence spectra of biphen[2]arene in different solvents (1.0×10^{-5} M).

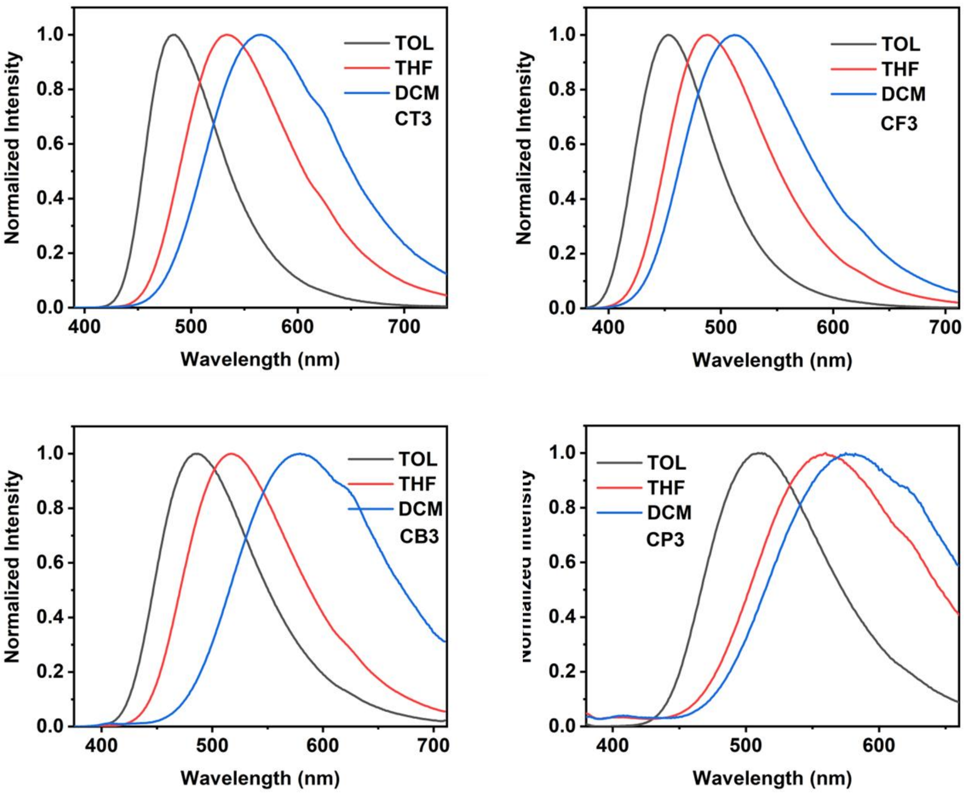


Fig. S40. Normalized fluorescence spectra of biphen[3]arene in different solvents (1.0×10^{-5} M).

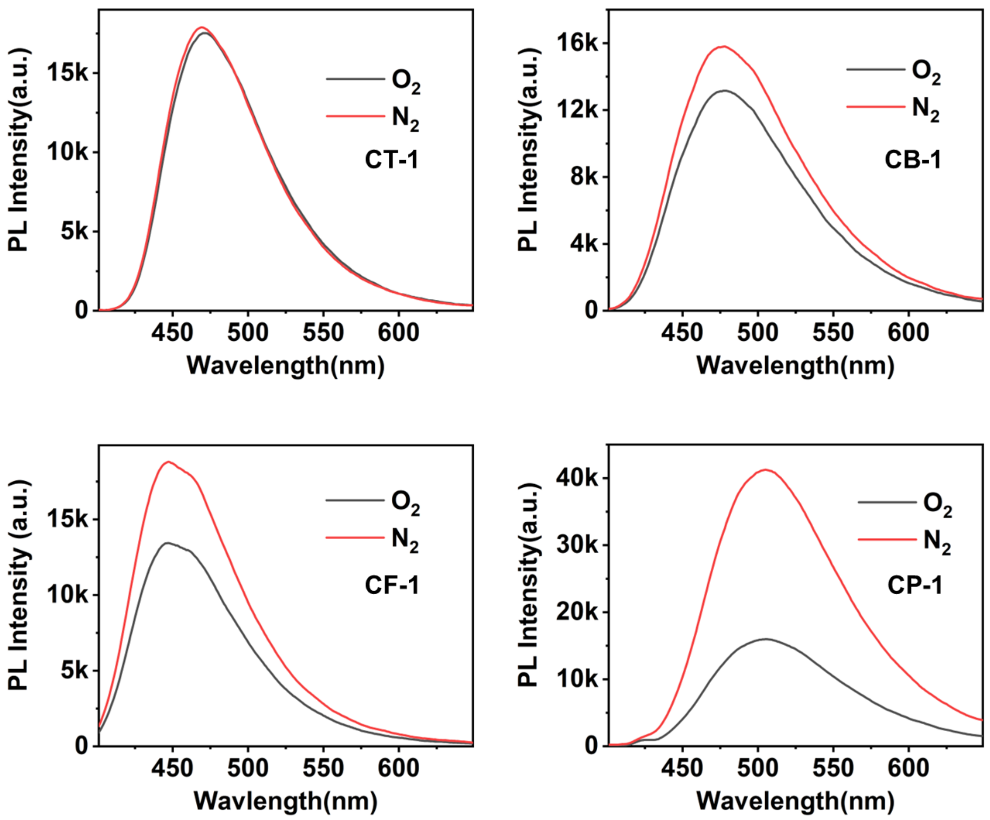


Fig. S41. PL spectra of monomers in toluene (1.0×10^{-5} mol/L) before and after nitrogen purging.

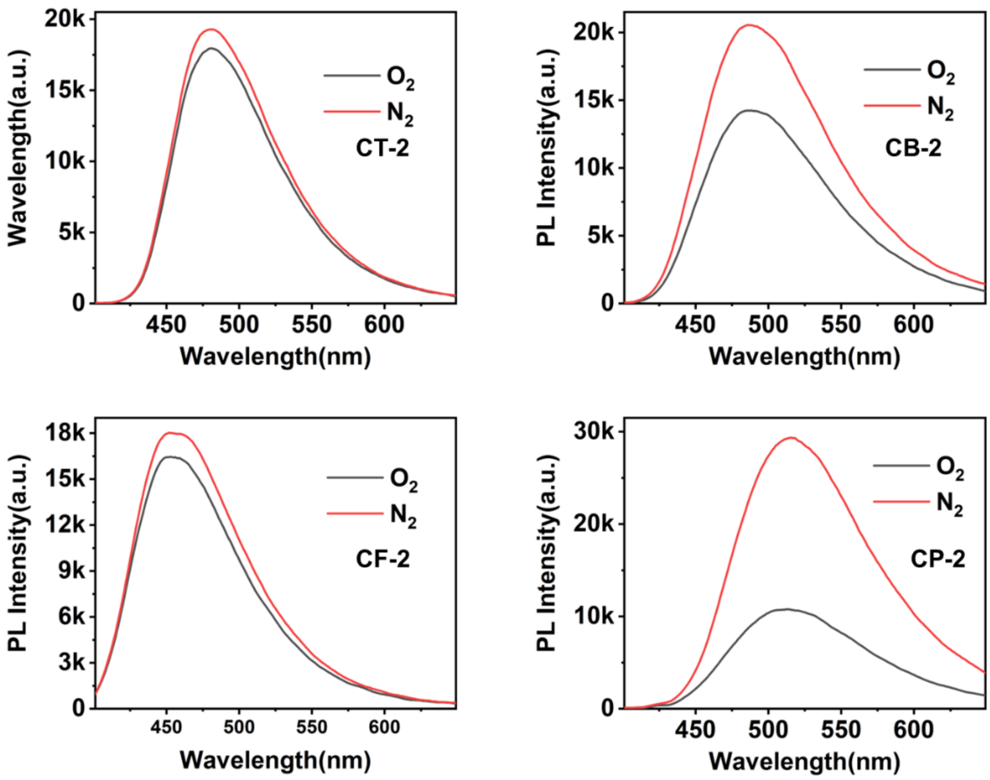


Fig. S42. PL spectra of biphen[2]arenes in toluene (1.0×10^{-5} mol/L) before and after nitrogen purging.

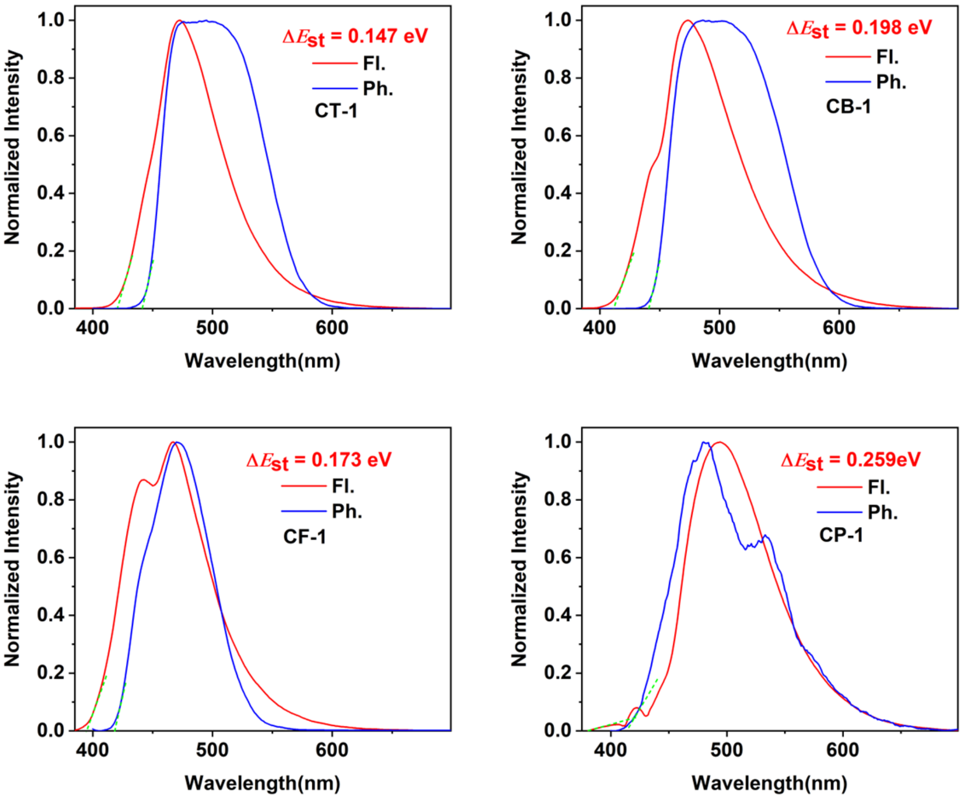


Fig. S43. Normalized fluorescence and phosphorescence spectra recorded at 77 K in toluene (1.0×10^{-5} mol/L) of monomers.

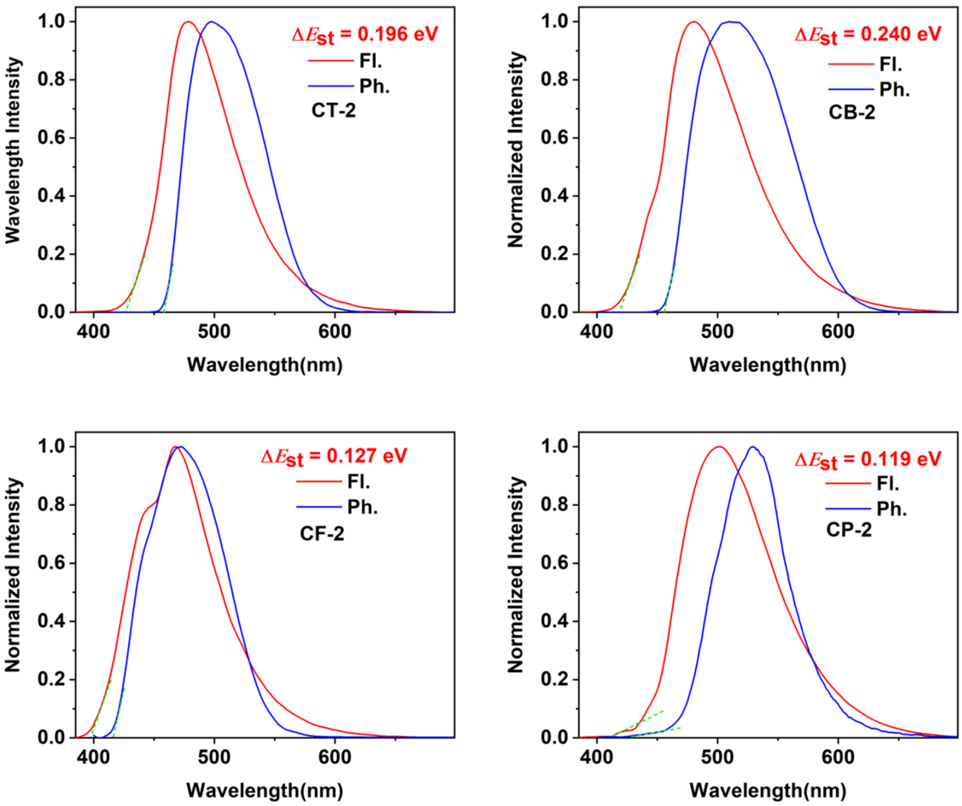


Fig. S44. Normalized fluorescence and phosphorescence spectra recorded at 77 K in toluene (1.0×10^{-5} mol/L) of biphen[2]arenes.

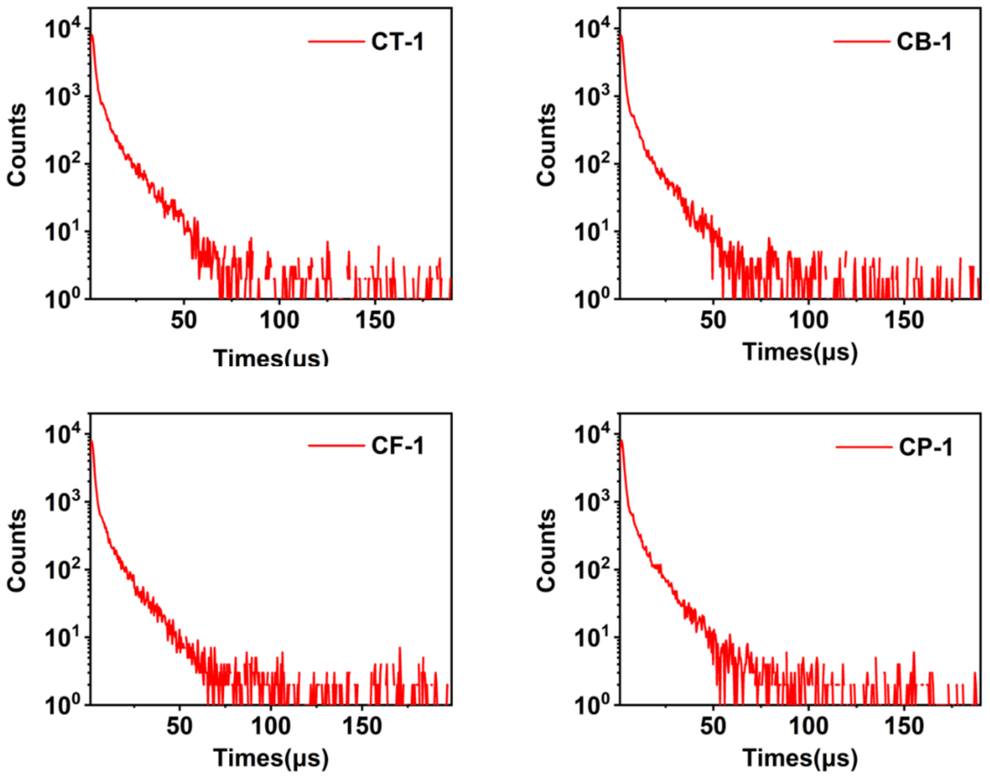


Fig. S45. Transient PL decay curve of monomers in toluene (1.0×10^{-5} mol/L) at room temperature.

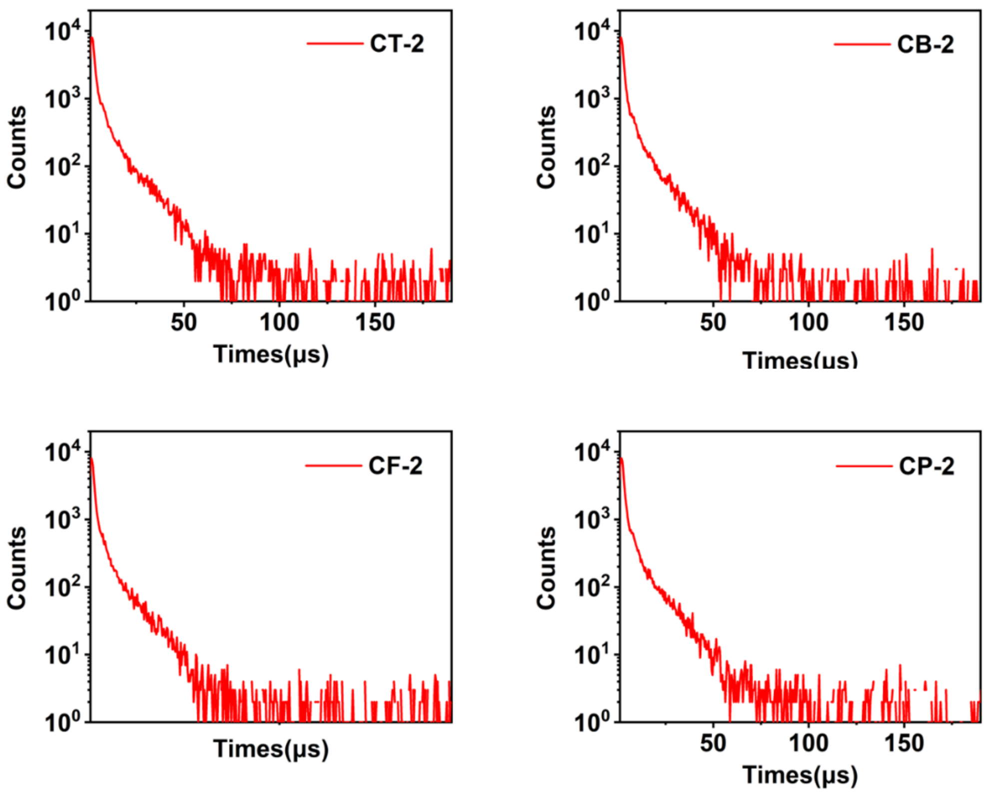


Fig. S46. Transient PL decay curve of biphen[2]arenes in toluene (1.0×10^{-5} mol/L) at room temperature.

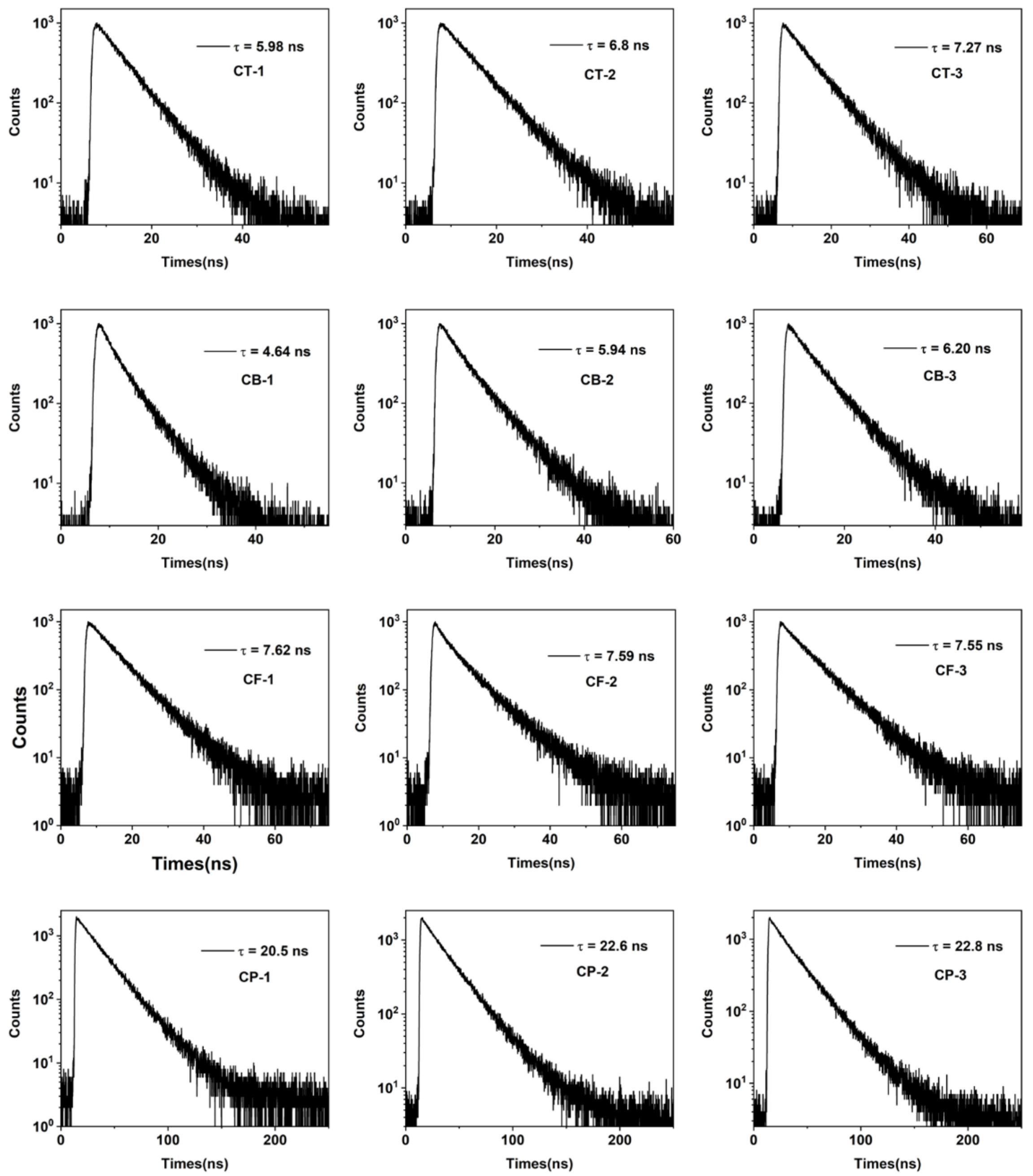


Fig. S47 Transient PL decay curves of monomers and macrocycles in toluene solution.

Table S1. Summary of photophysical data of monomers and macrocycles.

	τ_F[a] nS	τ_{TADF}[b] μS	Φ_{PL}[c] %	Φ_F[d] %	Φ_{TADF}[e] %	k_F[f] 10^7 s^{-1}	k_{TADF}[g] 10^5 s^{-1}	k_{ISC}[h] 10^7 s^{-1}	k_{RISC}[i] 10^5 s^{-1}	K_r[j] 10^7 s^{-1}	K_{nr}[k] 10^5 s^{-1}
CT-1	5.98	5.31	36.8	19.7	17.1	16.7	1.88	13.4	2.04	3.29	1.48
CT-2	6.8	4.85	34.3	20.7	13.6	14.7	2.06	11.7	1.70	3.05	1.71
CT-3	7.27	5.3	70.9	37.8	33.1	13.8	1.89	8.56	2.66	5.20	0.88
CB-1	4.64	4.08	14.7	9.4	5.3	21.6	2.45	19.5	1.51	2.03	2.31
CB-2	5.94	4.37	38.7	24.5	14.2	16.8	2.29	12.7	1.75	4.13	1.86
CB-3	6.20	4.29	36.4	23.3	13.1	16.1	2.33	12.4	1.70	3.76	1.93

CF-1	7.62	4.39	42.2	26.8	15.4	13.1	2.28	9.61	1.79	3.52	1.80
CF-2	7.59	4.32	73.4	47.4	26.0	13.2	2.31	6.93	2.41	6.25	1.17
CF-3	7.55	4.33	42.4	26.7	15.7	13.2	2.31	9.71	1.85	3.54	1.81
CP-1	20.5	4.65	10.8	6.3	4.5	4.88	2.15	4.57	1.65	0.306	2.05
CP-2	22.6	4.38	11.1	7.3	3.8	4.42	2.28	4.10	1.26	0.325	2.19
CP-3	22.8	4.50	16.1	9.4	6.7	4.39	2.22	3.97	1.74	0.414	2.06

[a]Prompt fluorescence lifetime obtained from transient PL experiments. [b]Delayed fluorescence lifetime obtained from transient PL experiments. [c]Total PLQY. [d]Fractional PLQY for prompt fluorescence calculated from transient PL experiments and total PLQY measurements. [e]Fractional PLQY for delayed fluorescence calculated from transient PL experiments and total PLQY measurements. [f]Rate constant of prompt fluorescence. [g]Rate constant of delayed fluorescence. [h]Rate constant of intersystem crossing. [i]Rate constant of reverse intersystem crossing. [j]Radiative decay rate constants. [k]Non-radiative decay rate constants

$k_p=1/\tau_F$

$k_{TADF}=1/\tau_{TADF}$

$k_{ISC}=k_F(1-\Phi_F)$

$k_{RISC}=k_F*k_{TADF}*\Phi T_{ADF} / k_{ISC}*\Phi_{TADF}$

$k_r=\Phi_F/\tau_F$

$k_{nr}=k_{TADF}-\Phi_F*k_{RISC}$

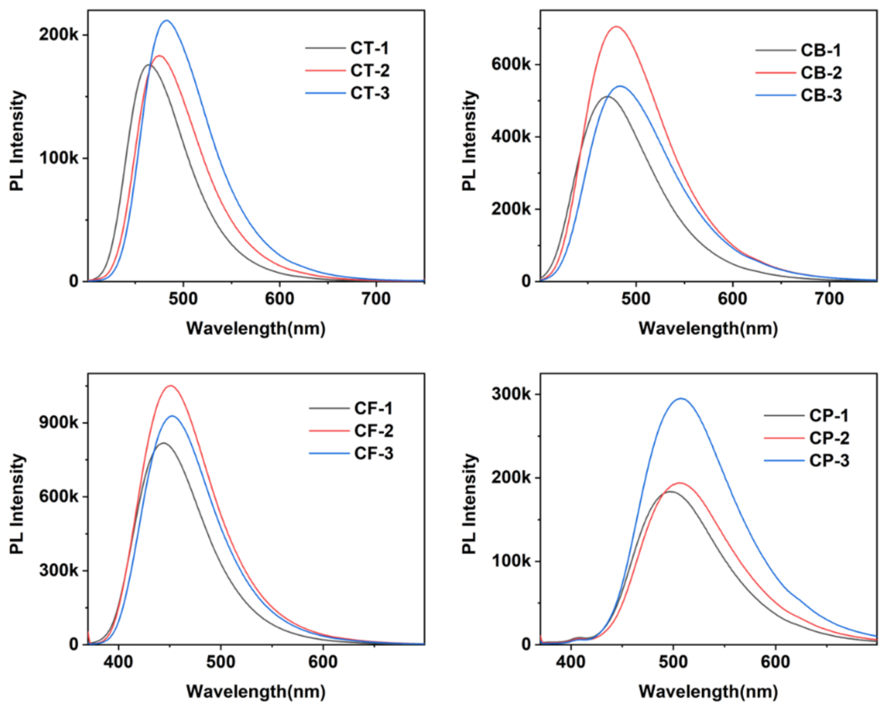


Fig.S48 PL spectra of monomers and macrocycles in toluene solution (monomer:3.0×10^{-5} mol/L; dimer macrocycle: 1.5×10^{-5} mol/L; trimer macrocycles: 1.0×10^{-5} mol/L).

Table S2. The photoluminescence quantum yield of monomers and macrocycles.

	CT-1	CT-2	CT-3	CB-1	CB-2	CB-3	CF-1	CF-2	CF-3	CP-1	CP-2	CP-3
Φ_{PL}(%)	68.7	72.2	70.9	34.9	35.6	36.4	36.9	65.71	42.4	9.53	12.0	16.1

5. Theoretical calculations

The quantum calculations were performed at the PBE0/6-31g level by using the time-dependent density functional theory (TD-DFT) method.

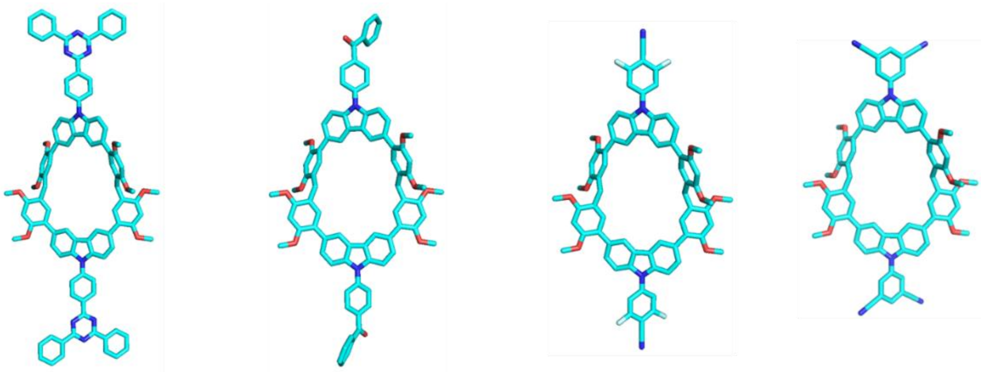


Fig. S49. The energy-minimized conformation of biphen[2]arenes.

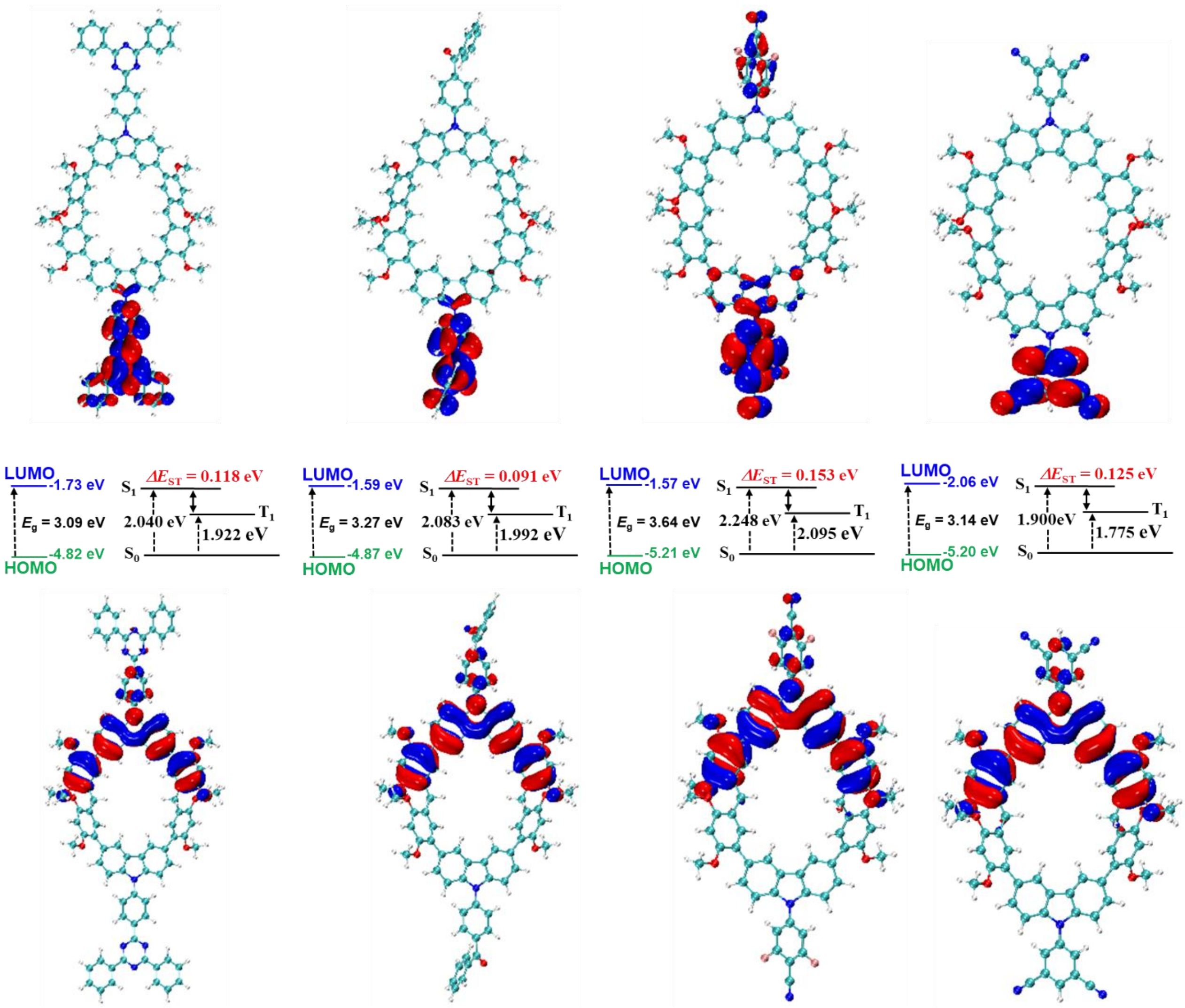


Fig. S50. The optimized ground state geometries, orbital distributions, and energy levels of the lowest-lying excited singlet and triplet states of biphen[2]arenes.