Supporting Information

Macrocyclization-Induced Phosphorescent Enhancement of Pyridinium-based Macrocycles

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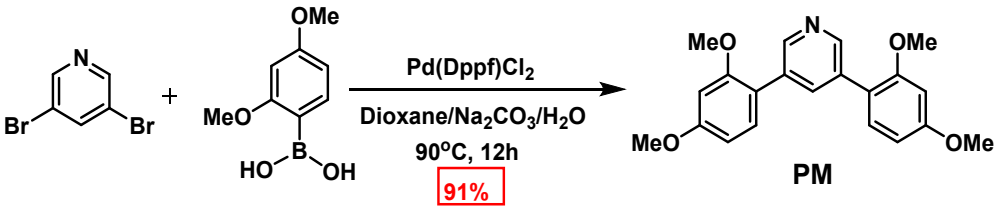
Table of Contents

Section I. Materials/Methods/Instrumentation

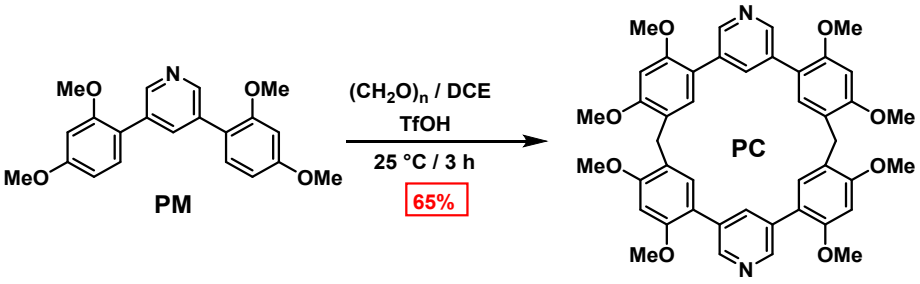
All reagents and solvents were commercially available and used without further purification, unless otherwise noted. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker Avance 500 MHz spectrometer. High-resolution mass spectra (HRMS) was determined on a SCIEX, X-500R QTOF instrument. Photoluminescence spectra and lifetime were obtained on FLS900 and FLS1000. Fluorescence and phosphorescence quantum efficiencies were measured on HAMAMATSU C9920-02. Melting points were obtained on an X-4 digital melting point apparatus. Single crystal X-ray diffraction data were collected on Bruker smart Apex 2, Bruker D8 Venture. The electrostatic potential maps of PC and PC•2Cl were performed by using Gaussian 09 program with B3LYP-D3(BJ)/6-31G + (d, p) and B3LYP-D3(BJ)/6-31G ++ (d, p) level, respectively.

Section II. Synthetic Protocols



Scheme S1. Synthesis of monomer PM.

Under the protection of N_2 atmosphere, 3,5-dibromopyridine (2.4 g, 10 mmol), 2,4-dimethoxybenzeneboronic acid (5.5 g, 30 mmol), and [1,1'-Bis(diphenylphosphino) ferrocene] dichloropalladium (II) ($Pd(Dppf)Cl_2$, 0.73 g, 1.0 mmol) were dissolved in dioxane (150 mL). The sodium carbonate (3.2 g, 30 mmol) in water (15 mL) was added into the solution and stirred for 12 h at 90 °C. Upon cooling to room temperature, water (150 mL), dichloromethane (150 mL) was added and stirred. After filtration of the solution, the solution was partitioned between dichloromethane and water. The product was extracted from the organic layer and evaporated under reduced pressure. The product was purified by column chromatography on silica gel (eluent: dichloromethane), resulted in the white product **PM** (3.2 g, 91%). M. p. 157-158 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 8.65 (s , 2H), 7.94 (s , 1H), 7.29 (d, J = 10.0 Hz, 2H), 6.61-6.58 (m, 4H), 3.86 (s, 6H), 3.82 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 160.99, 157.78, 148.10, 137.39, 133.30, 131.35, 120.20, 104.92, 99.10, 55.64, 55.56. HRMS (ESI) m/z: $[M+H]^+$ calculated for $[C_{21}H_{22}NO_4]^+$, 352.1543; found, 352.1563.



Scheme S2. Synthesis of macrocycle **PC**.

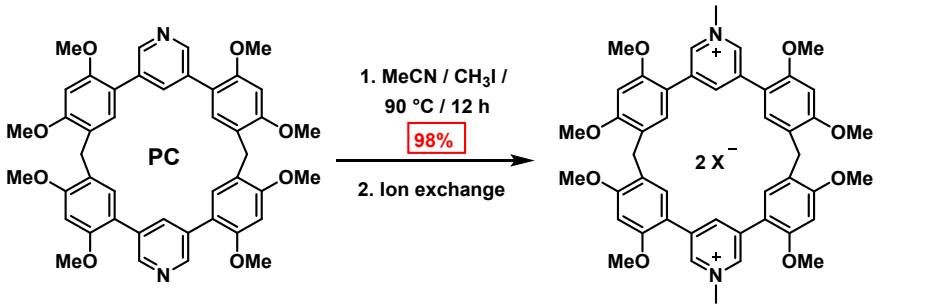
To the solution of **PM** (3.5 g, 10 mmol) in 1, 2-dichloroethane (200 mL) was added paraformaldehyde (0.90 g, 30 mmol). Trifluoromethanesulfonic acid (0.45 ml, 5.0

mmol) was then added to the reaction mixture. The mixture was stirred at 25 °C for 3 hours. Then the reaction was quenched by addition of 200 mL saturated aqueous $NaHCO_3$. The solution was partitioned between dichloromethane and saturated aqueous $NaHCO_3$. The product was extracted from the organic layer. The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The product was purified by column chromatography on silica gel (eluent: 3/1, v/v, dichloromethane: ethyl acetate), resulted in the white product **PC** (0.69 mg, 19%). M. p. >320 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 8.76 (s, 4H), 7.33 (s, 2H), 6.80 (s, 4H), 6.57 (s, 4H), 3.86 (s, 12H), 3.86 (s, 12H), 3.85 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 158.44, 155.68, 148.55, 136.35, 134.22, 131.67, 121.16, 118.85, 95.35, 55.80, 55.70, 28.17. HRMS (ESI) m/z: $[M+H]^+$ calculated for $[C_{44}H_{43}N_2O_8]^+$, 727.3014; found, 727.3011.

Table S1. Screening of reaction conditions for **PC**

Entry	Solvents	Catalysts	Concentrations [mM]	Reaction time	Yields (%)[a]
1	DCM	$BF_3.Et_2O$	5	1.5 h	15
2	$CHCl_3$	$BF_3.Et_2O$	5	2.0 h	37
3	DCE	$BF_3.Et_2O$	5	1.8 h	35
4	CH_3CN	$BF_3.Et_2O$	5	2.4 h	18
5	DCM	TfOH	5	3.0 h	39
6	$CHCl_3$	TfOH	5	4.0 h	42
7	DCE	TfOH	5	3.0 h	65
8	CH_3CN	TfOH	5	3.5 h	21
9	DCE	$FeCl_3$	5	2.3 h	11
10	DCE	$AlCl_3$	5	2.4 h	12

[a] Yields of isolated product; DCM: dichloromethane; DCE: 1,2-dichloroethane.



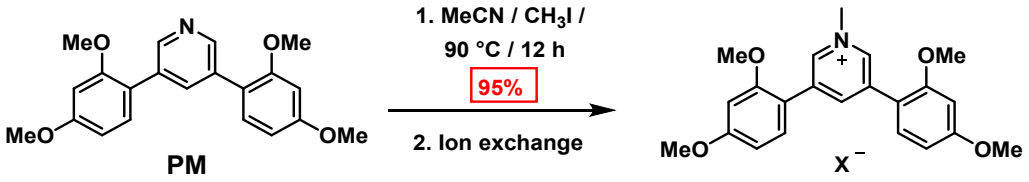
X= I, **PC•2I**; X=Cl, **PC•2Cl**; X= Br, **PC•2Br**

Scheme S3. Synthesis of macrocycles PC•2X.

*Synthesis of **PC•2I** and **PC•2Cl**. **PC*** (3.6 g, 5.0 mmol) and methyl iodide (1.2 mL, 20 mmol) were dissolved in 25 mL anhydrous acetonitrile and then refluxed for 12 h. Upon cooling to room temperature, the reaction mixture was concentrated and the resulting yellow precipitate was washed with ethyl ether. A yellow solid (**PC•2I**) was obtained in a 98% yield (4.9 g). After dispersing the yellow solid in 100 mL deionized water, saturated NH_4PF_6 aqueous solution were added and stirred for 24 h at 65 °C. After standing for a while, the precipitate was filtered and then dried under vacuum to obtain 4.8 g yellow solid in 94% yield. Subsequently, to the solution of the macrocycle with counterion of PF_6^- (0.42 g, 0.4 mmol) in CH_3CN (10 mL) was added tetrabutylammonium chloride and stirred until no solid appear any more. After standing for a while, the precipitate was filtered and washed with CH_3CN (10 mL × 3). A pale yellow solid (**PC•2Cl**) was obtained in a 43% yield (0.14 g). M. p. >320 °C; ^{1}H NMR (500 MHz, D_2O, 298 K) δ 8.83 (s , 4H), 7.74 (s , 2H), 6.69 (s, 4H), 6.56 (s, 4H), 4.42 (s, 6H), 3.85 (s, 12H), 3.66 (s, 12H), 3.66 (s, 4H). ^{13}C NMR (125 MHz, D_2O, 298 K) δ 159.79, 156.09, 141.97, 141.93, 141.49, 137.63, 120.61, 113.25, 96.12, 55.89, 55.69, 48.57, 28.39. HRMS (ESI) m/z: $[1/2M+H]^+$ calculated for $[C_{23}H_{25}NO_4]^+$, 379.1773; found, 379.1771.

*Synthesis of **PC•2Br**.* To the solution of the macrocycle with counterion of $PF6^-$ (0.42 g, 0.4 mmol) in CH_3CN (10ml) was added tetrabutylammonium bromide and stirred at room temperature until no solid appear any more. After standing for a while, the precipitate was filtered and washed with acetone (5 mL × 3). A pale yellow solid (**PC•2Br**) was obtained in a 62% yield (0.27 g). M. p. >320 °C; ^{1}H NMR (500 MHz,

DMSO-d_6, 298 K) δ 9.00 (s , 4H), 8.71 (s , 2H), 7.01 (s, 4H), 6.82 (s, 4H), 4.40 (s, 6H), 3.89 (s, 12H), 3.87 (s, 12H), 3.80 (s, 4H). ^{13}C NMR (125 MHz, DMSO-d_6, 298 K) δ 159.56, 155.68, 142.46, 142.23, 137.89, 132.12, 120.52, 113.33, 95.95, 56.23, 56.02, 48.32, 27.69. HRMS (ESI) m/z: $[1/2M+H]^+$ calculated for $[C_{23}H_{25}NO_4]^+$, 379.1773; found, 379.1769.



X= I, **PM•I**; X=Cl, **PM•Cl**; X= Br, **PM•Br**

Scheme S4. Synthesis of monomers **PM•X**.

PM•Cl was prepared in 38% yield as a pale yellow powder according to a procedure similar to that described for **PM•2Cl**. M. p. 138-139 °C; ^{1}H NMR (500 MHz, D_2O, 298 K) δ 8.47 (s , 2H), 7.86 (s , 1H), 7.03 (d, J = 10.0 Hz, 2H), 6.58-6.56 (m, 2H), 6.48 (d, J = 5.00 Hz, 2H), 4.16 (s, 3H), 3.83 (s, 6H), 3.74 (s, 6H). ^{13}C NMR (125 MHz, D_2O, 298 K) δ 162.09, 157.11, 142.67, 140.63, 137.14, 130.84, 113.92, 106.43, 98.61, 55.58, 55.52, 48.02. HRMS (ESI) m/z: $[M+H]^+$ calculated for $[C_{22}H_{25}NO_4]^+$, 367.1773; found, 367.1773.

PM•Br was synthesized in 65% yield as a pale yellow powder according to a procedure similar to that described for **PM•2Br**. M. p. 127-128 °C. ^{1}H NMR (500 MHz, DMSO-d_6, 298 K) δ 9.02 (s , 2H), 8.69 (s , 1H), 7.55 (d, J = 10.0 Hz, 2H), 6.80-6.75 (m, 4H), 4.42 (s, 3H), 3.87 (s, 6H), 3.86 (s, 6H). ^{13}C NMR (125 MHz, DMSO-d_6, 298 K) δ 162.32, 157.57, 143.74, 142.17, 136.60, 131.65, 114.95, 106.35, 99.16, 56.09, 55.69, 48.12. HRMS (ESI) m/z: $[M+H]^+$ calculated for $[C_{22}H_{25}NO_4]^+$, 367.1773; found, 367.1732.

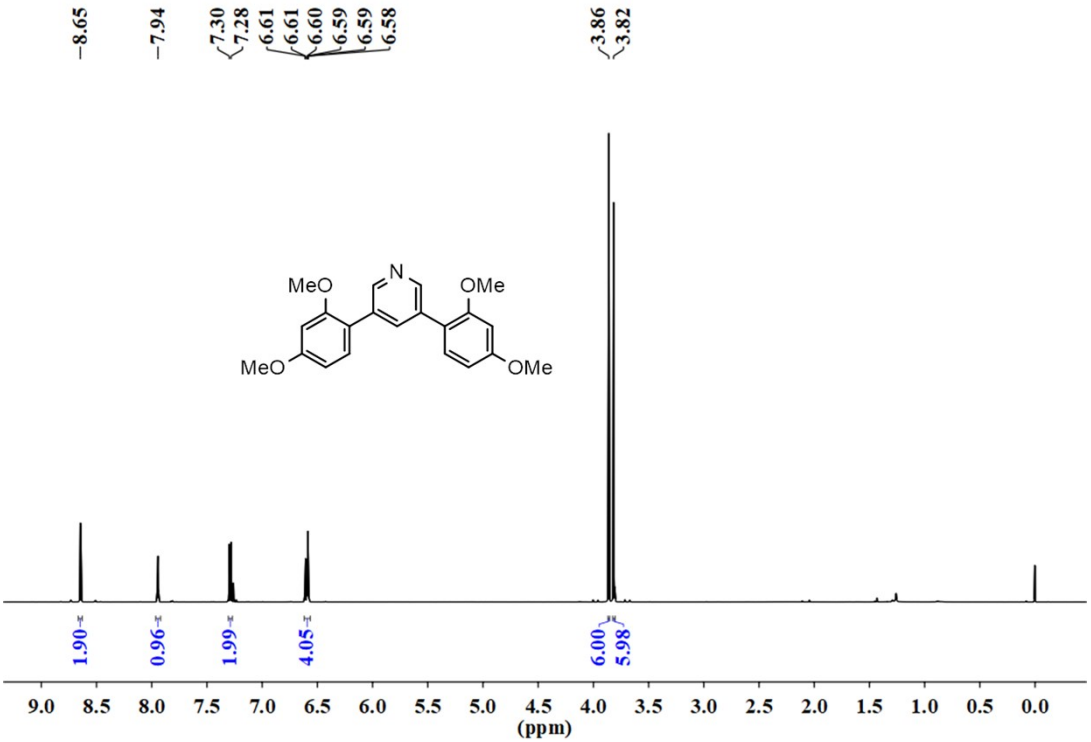


Figure S1 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **PM**.

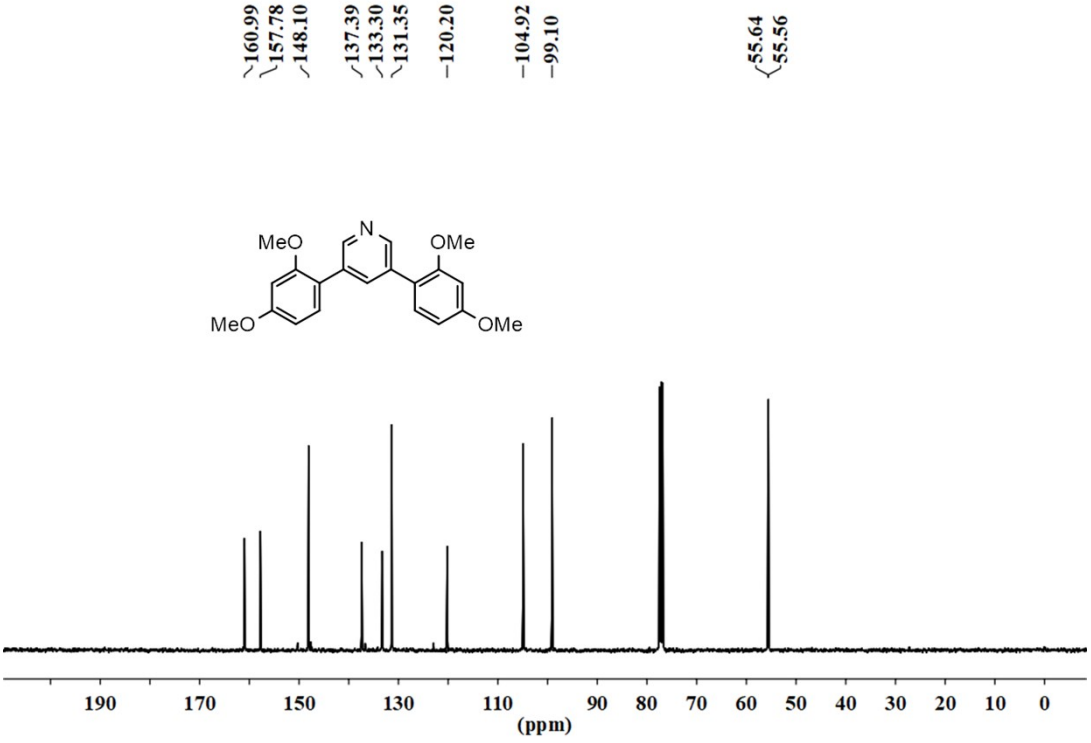


Figure S2 ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **PM**.

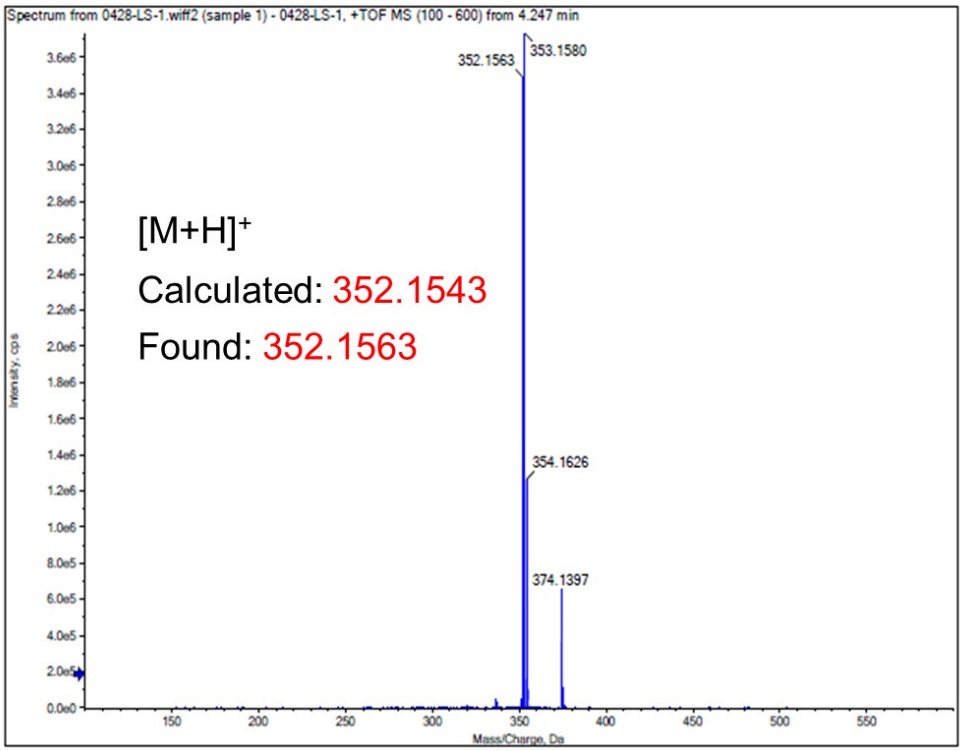


Figure S3 HMRS spectrum of **PM**.

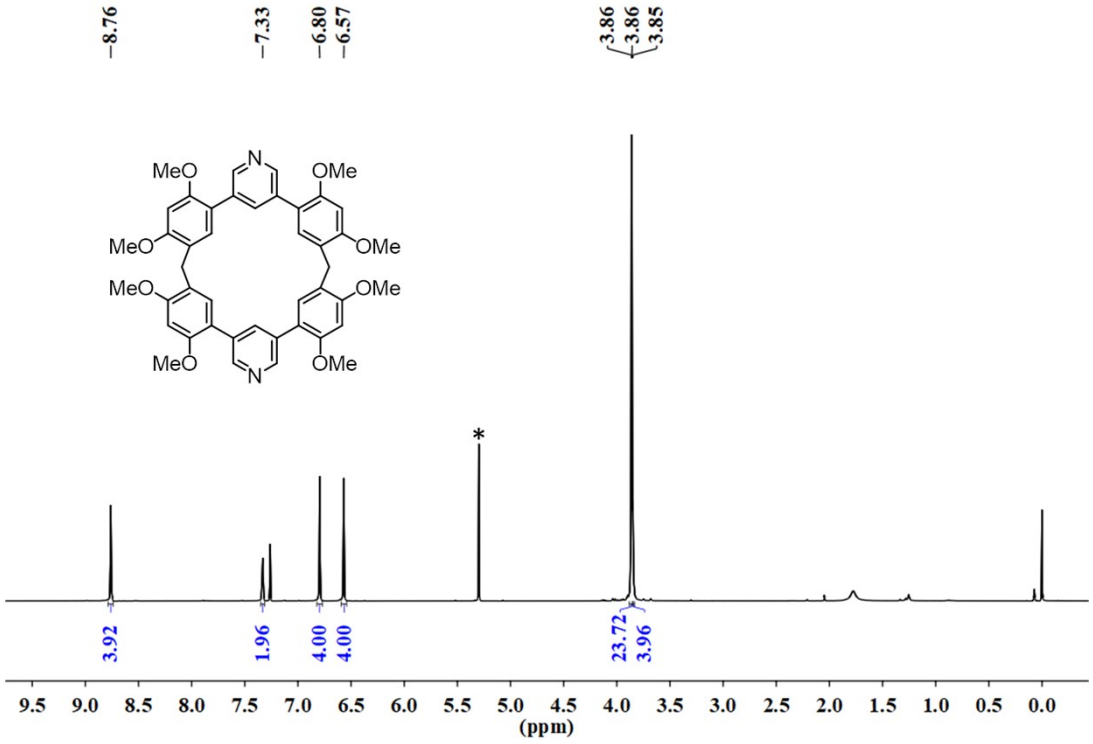


Figure S4 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **PC**. (* = dichloromethane peak signals).

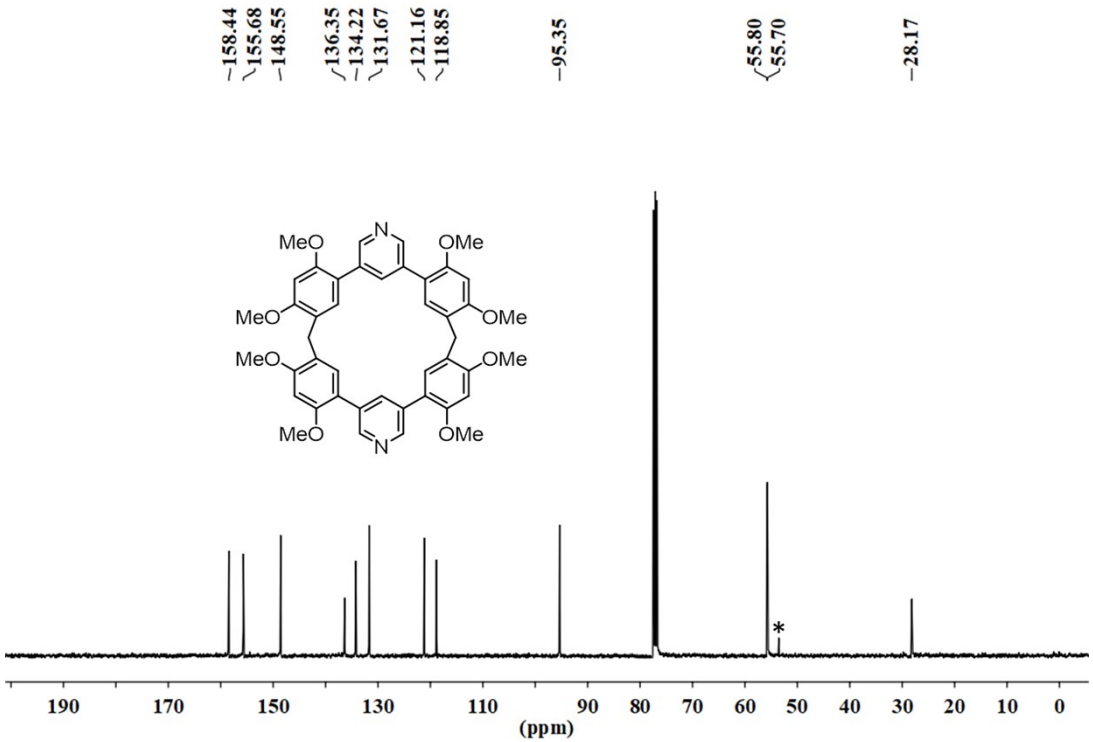


Figure S5 ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **PC**. (* = dichloromethane peak signals).

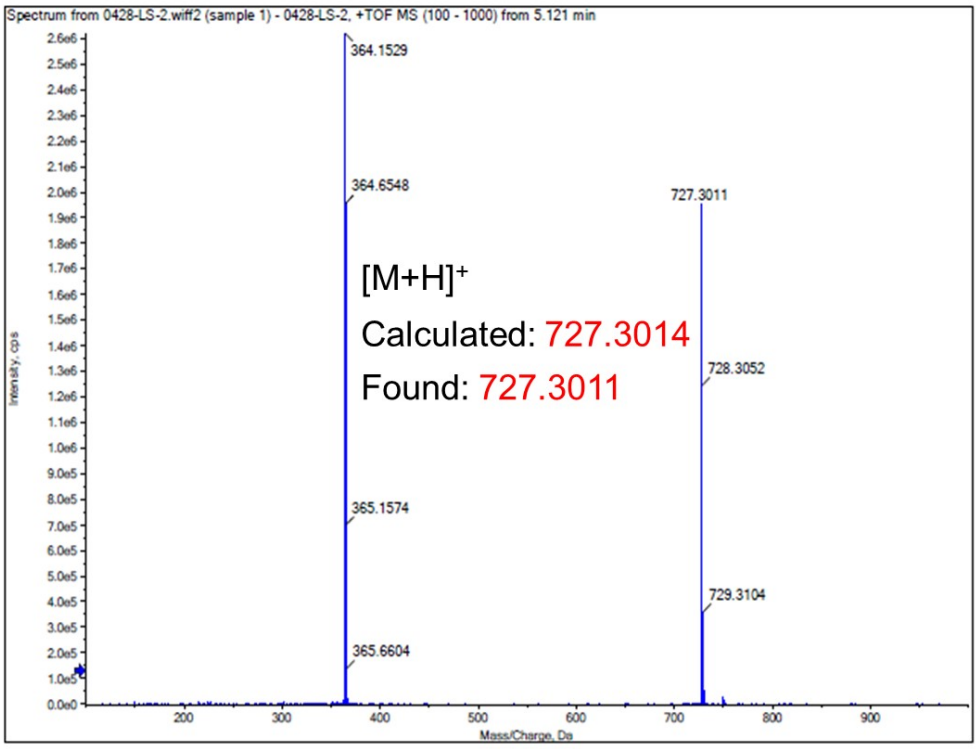


Figure S6 HMRS spectrum of **PC**.

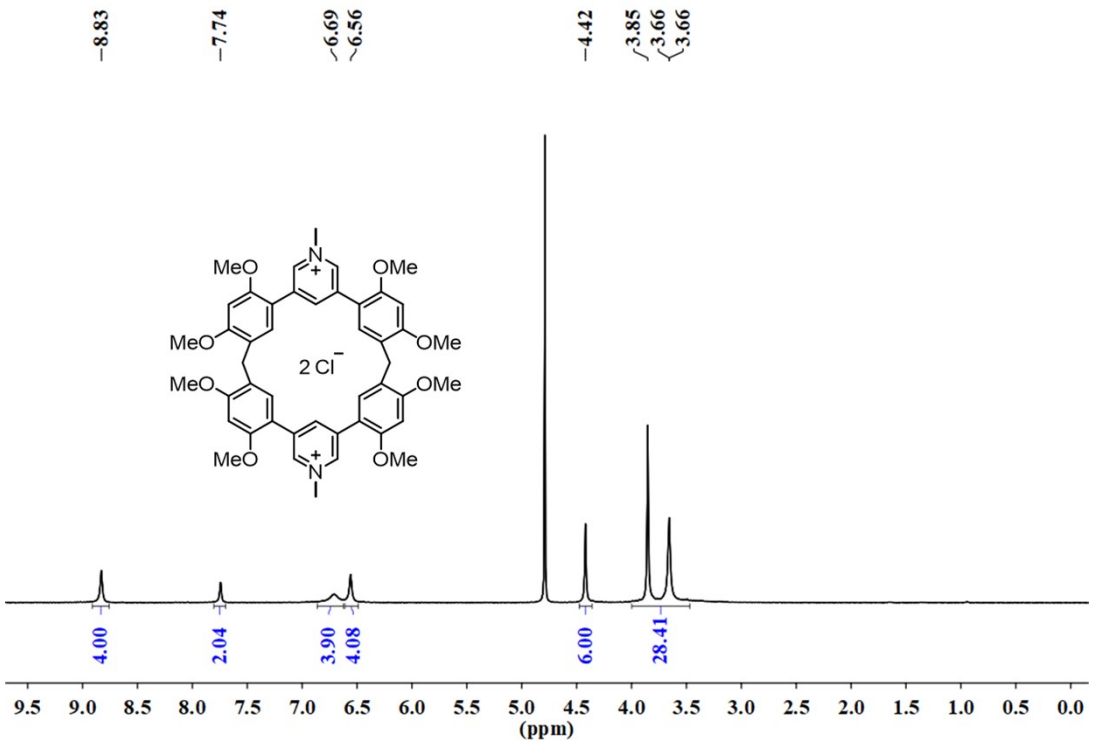


Figure S7 ^{1}H NMR spectrum (500 MHz, D_2O, 298 K) of **PC•2Cl**.

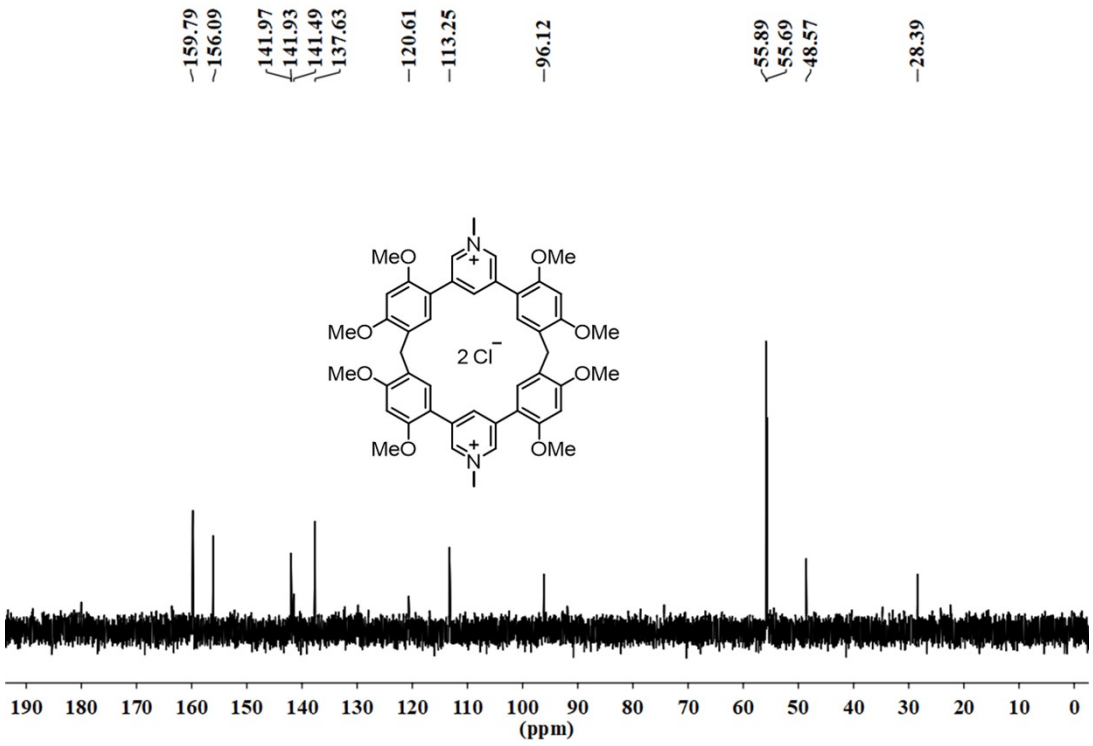


Figure S8 ^{1}C NMR spectrum (125 MHz, D_2O, 298 K) of **PC•2Cl**.

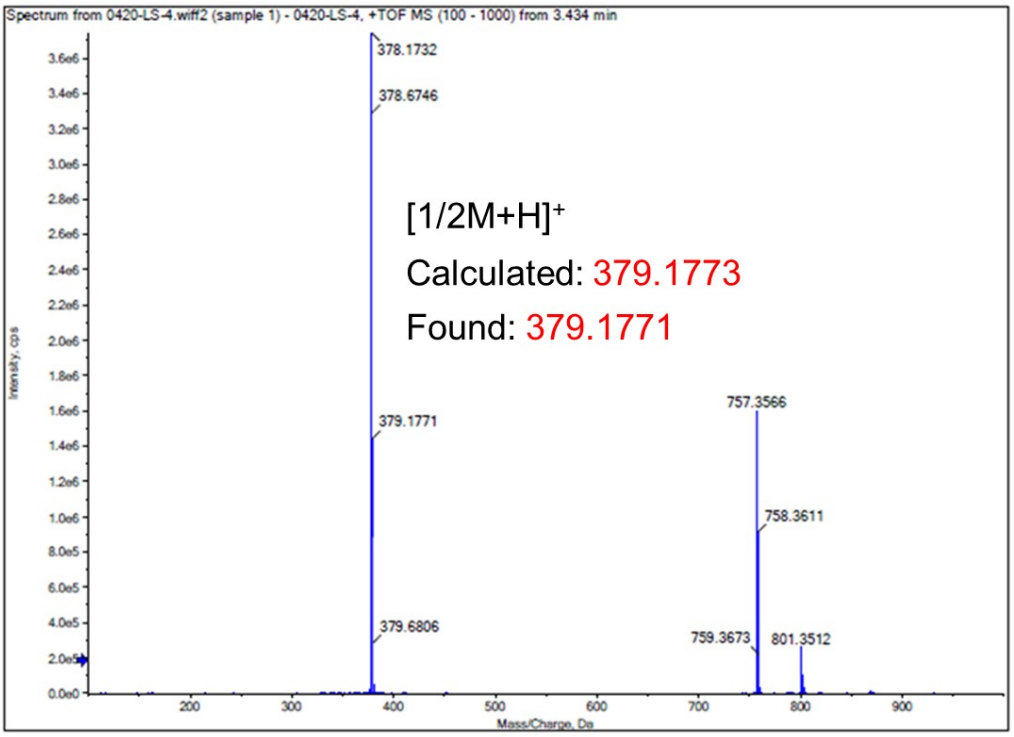


Figure S9 HMRS spectrum of **PC•2Cl**.

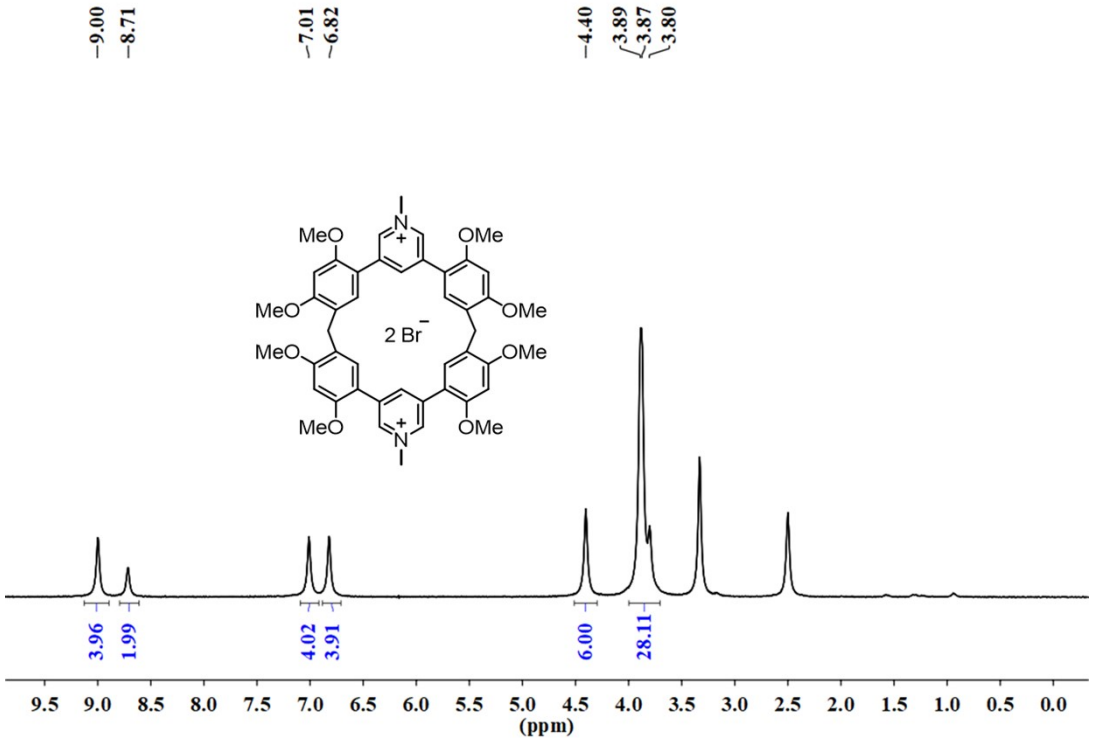


Figure S10 ^{1}H NMR spectrum (500 MHz, DMSO-d_6, 298 K) of **PC•2Br**.

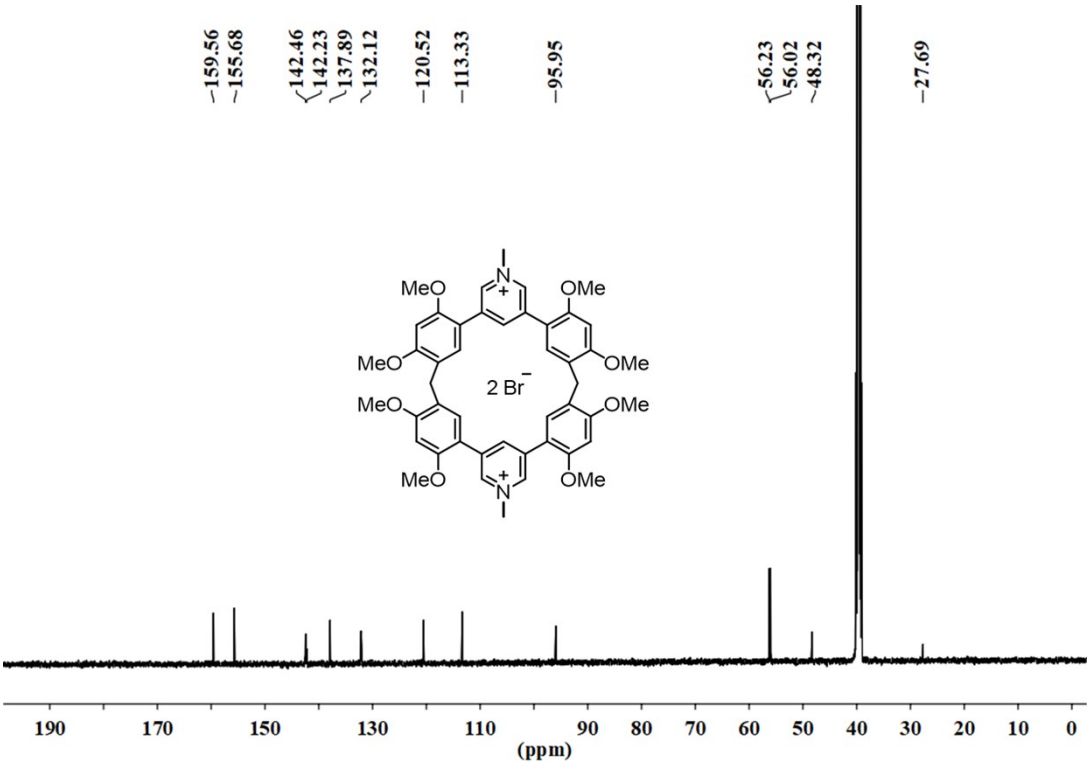


Figure S11 ^{1}C NMR spectrum (125 MHz, DMSO-d_6, 298 K) of **PC•2Br**.

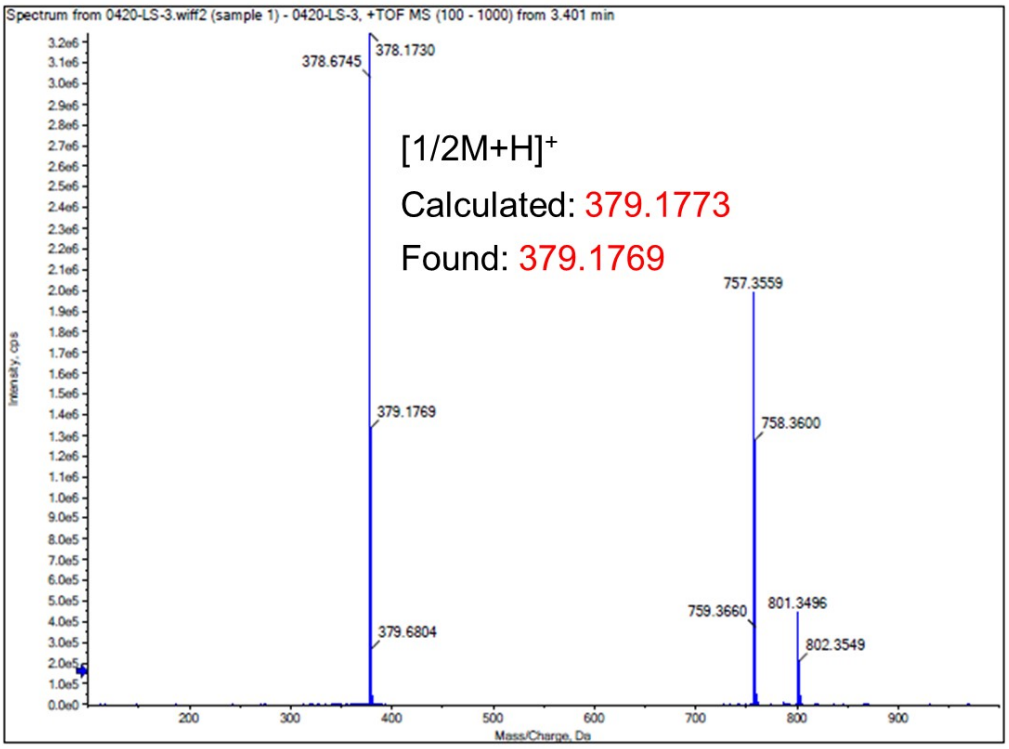


Figure S12 HMRS spectrum of **PC•2Br**.

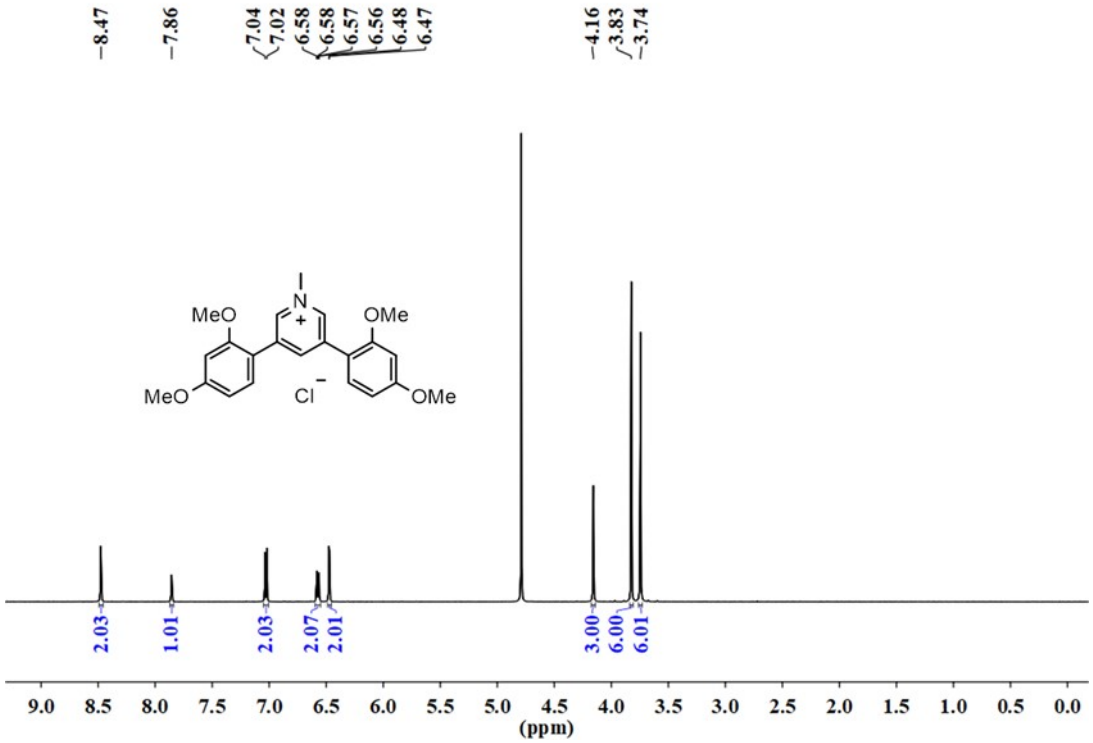


Figure S13 ^{1}H NMR spectrum (500 MHz, D_2O, 298 K) of **PM•Cl**.

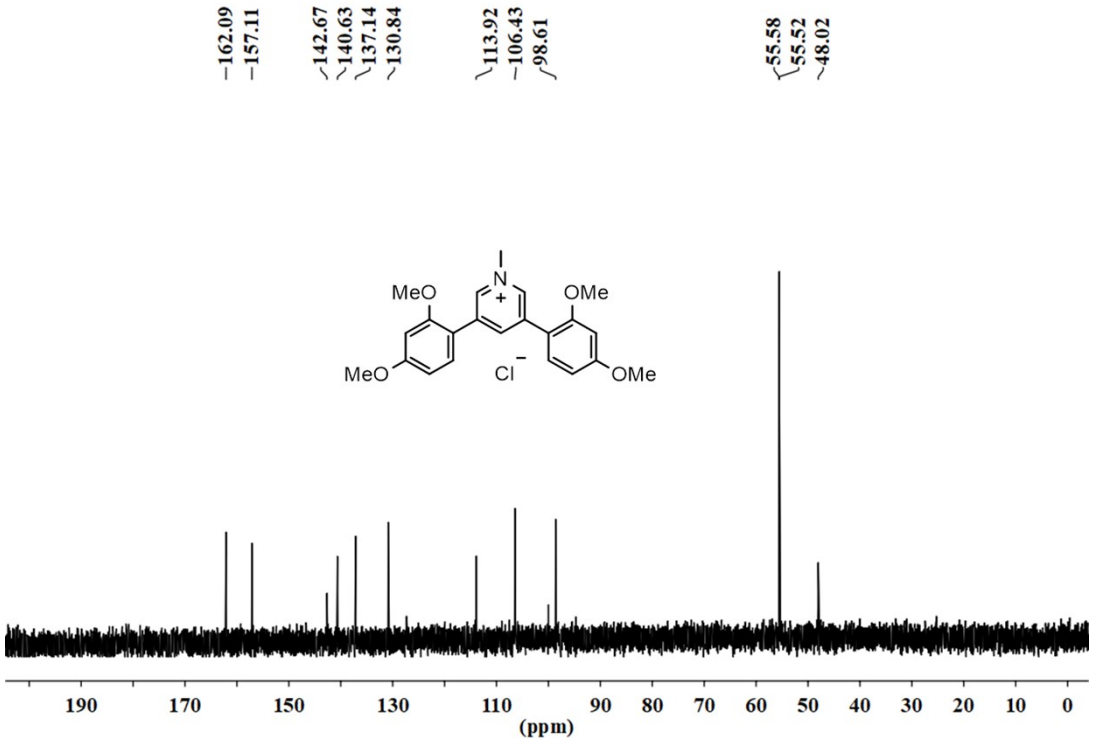


Figure S14 ^{1}C NMR spectrum (125 MHz, D_2O, 298 K) of **PM•Cl**.

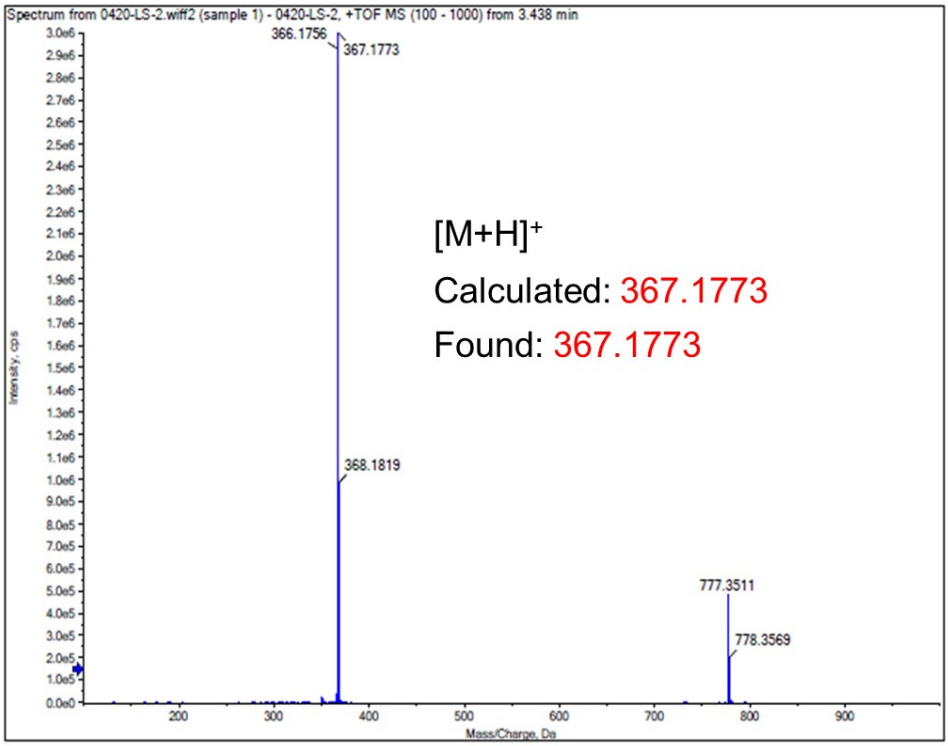


Figure S15 HMRS spectrum of **PM•Cl**.

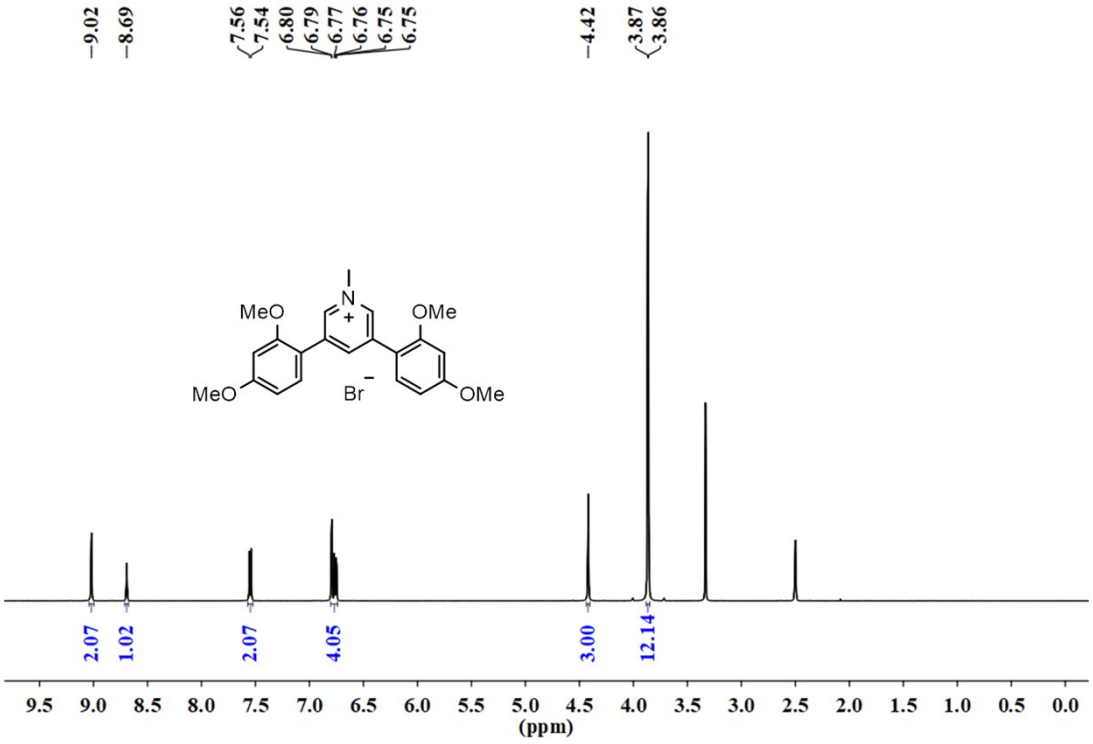


Figure S16 ^{1}H NMR spectrum (500 MHz, DMSO-d_6, 298 K) of **PM•Br**.

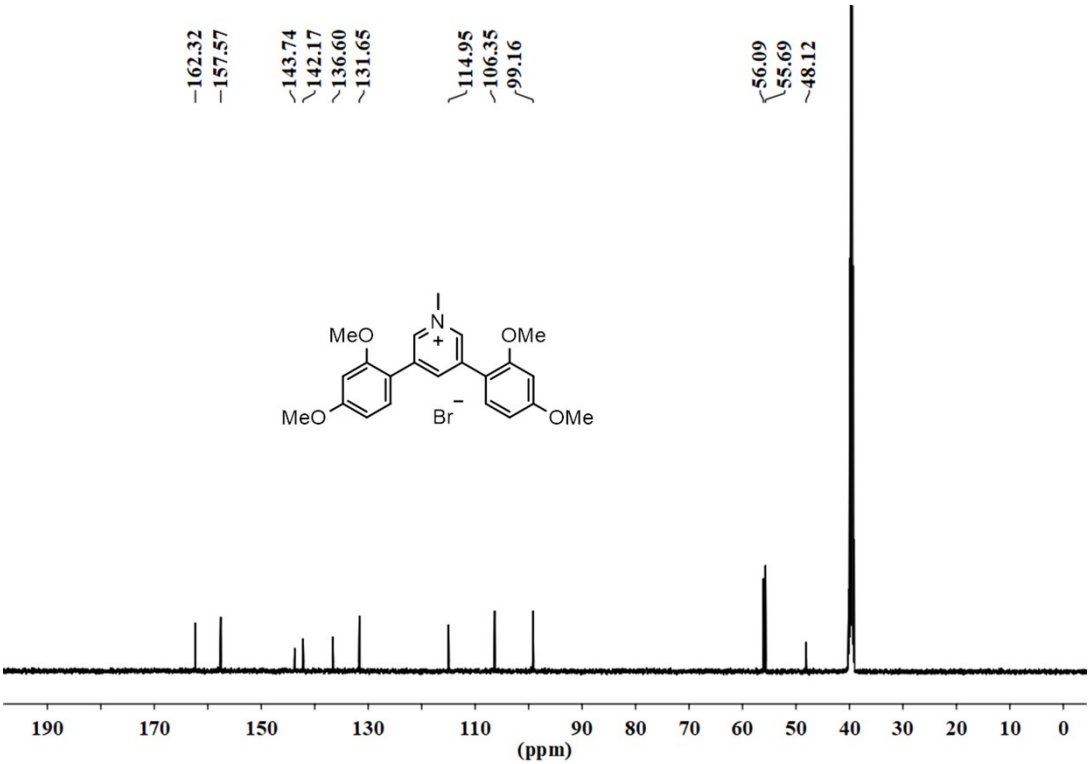


Figure S17 ^{1}C NMR spectrum (125 MHz, DMSO-d_6, 298 K) of **PM•Br**.

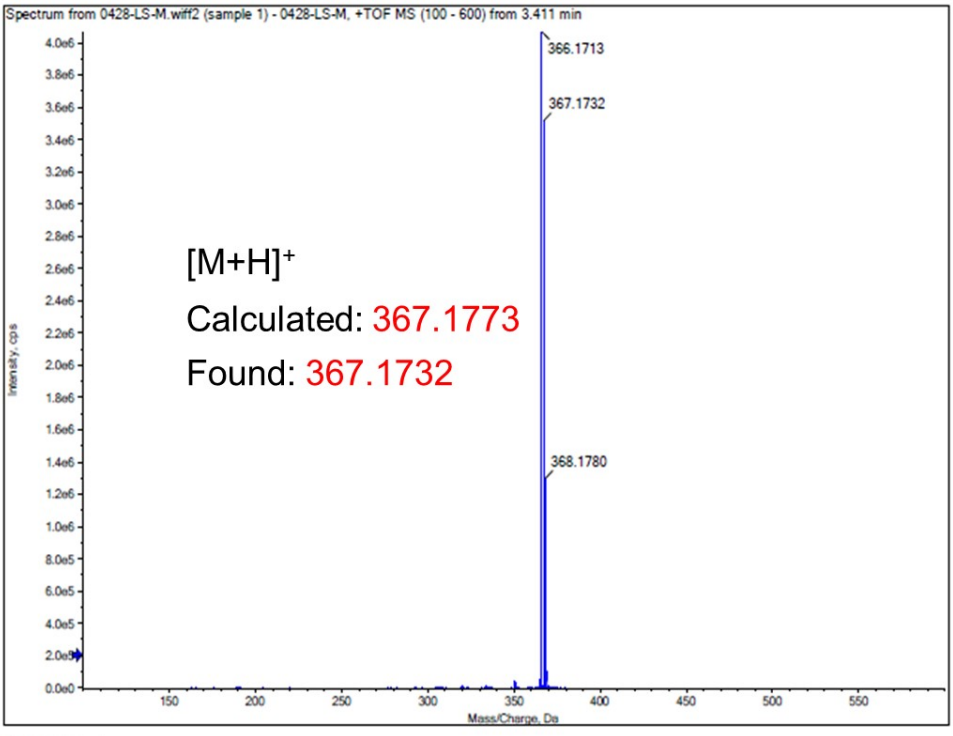


Figure S18 HMRS spectrum of **PM•Br**.

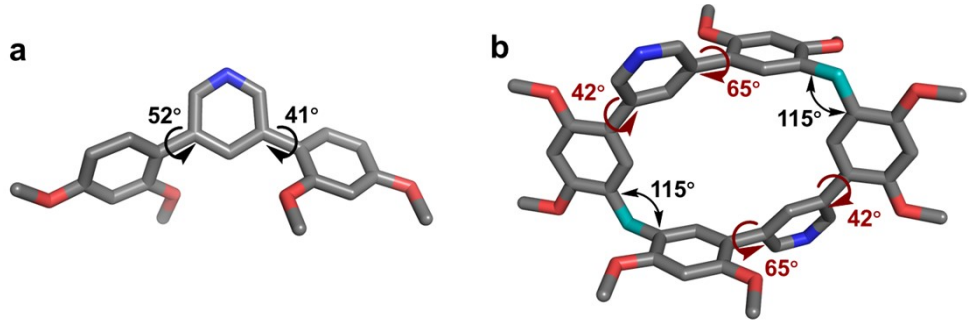


Figure S19. The single crystal structures of (a) monomer **PM** and (b) macrocycle **PC**. All hydrogen atoms were omitted for clarity and methylene were colored as deep cyan.

Section III. Photophysical properties

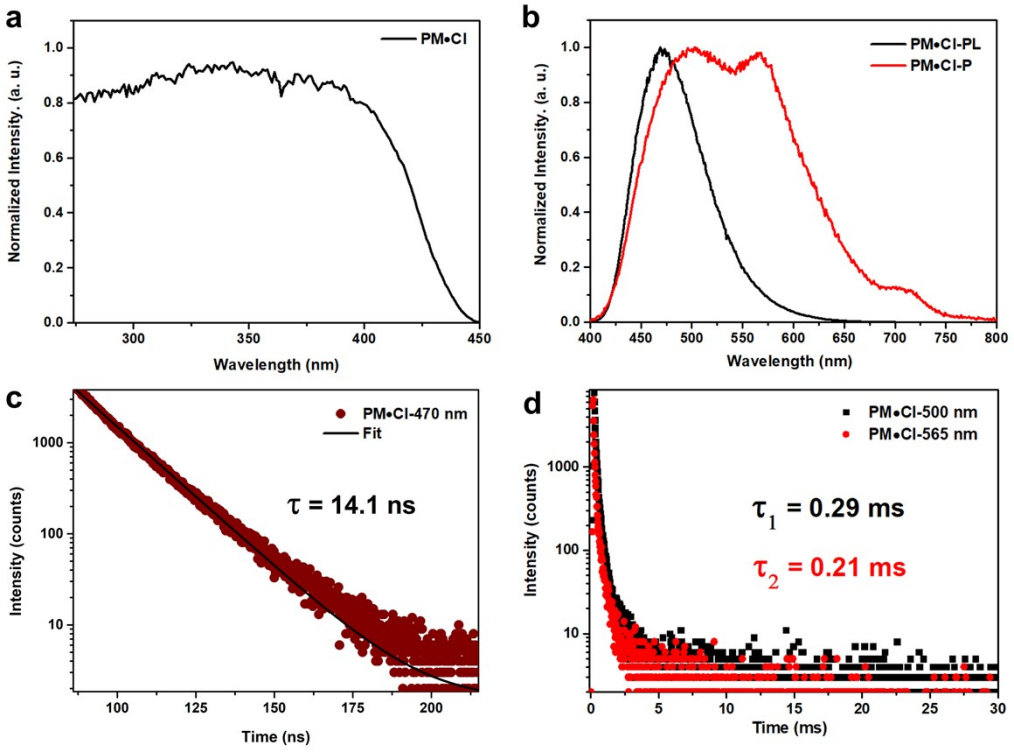


Figure S20. (a) Excitation spectra of **PM•Cl** at 470 nm; (b) Photoluminescence (black) and phosphorescence spectra (red) of **PM•Cl** under 350 nm excitation; (c) Time resolved PL decay of **PM•Cl** @470 nm in solid at room temperature; (d) Time resolved PL decay of **PM•Cl** @500 nm and 565 nm in solid state at room temperature.

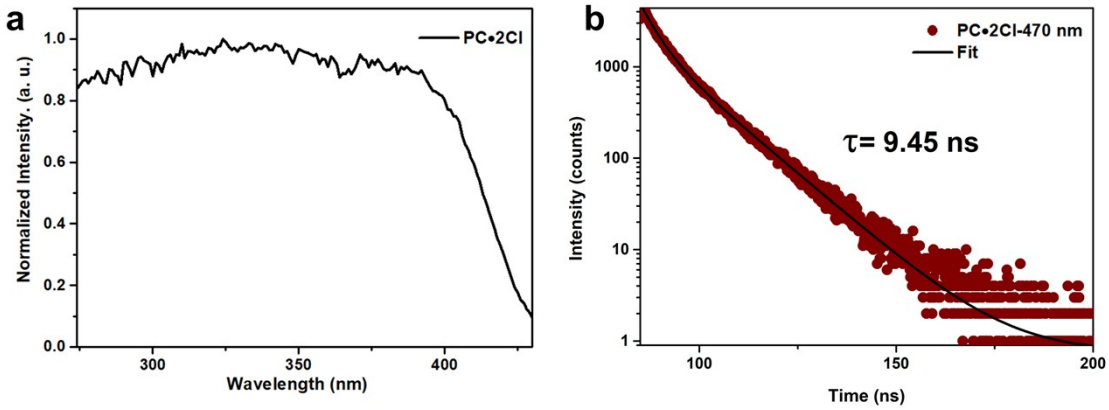


Figure S21. (a) Excitation spectra of **PC•2Cl** at 470 nm; (b) Time resolved PL decay of **PC•2Cl** @470 nm in solid state at room temperature.

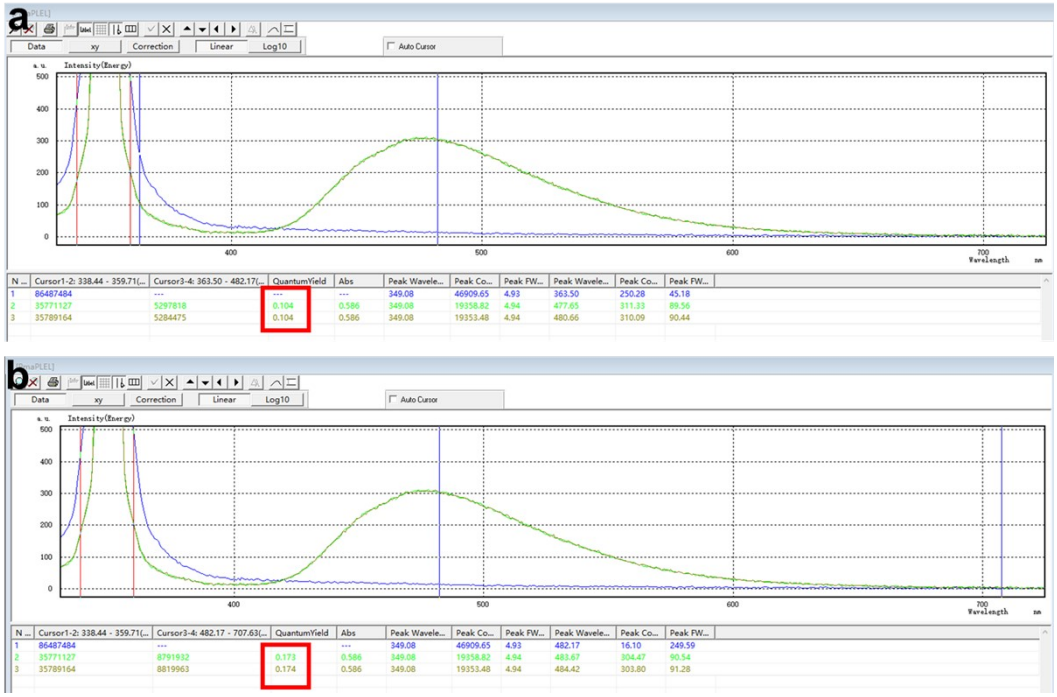


Figure S22. (a) Fluorescence and (b) phosphorescence quantum efficiency of **PM•Cl**.

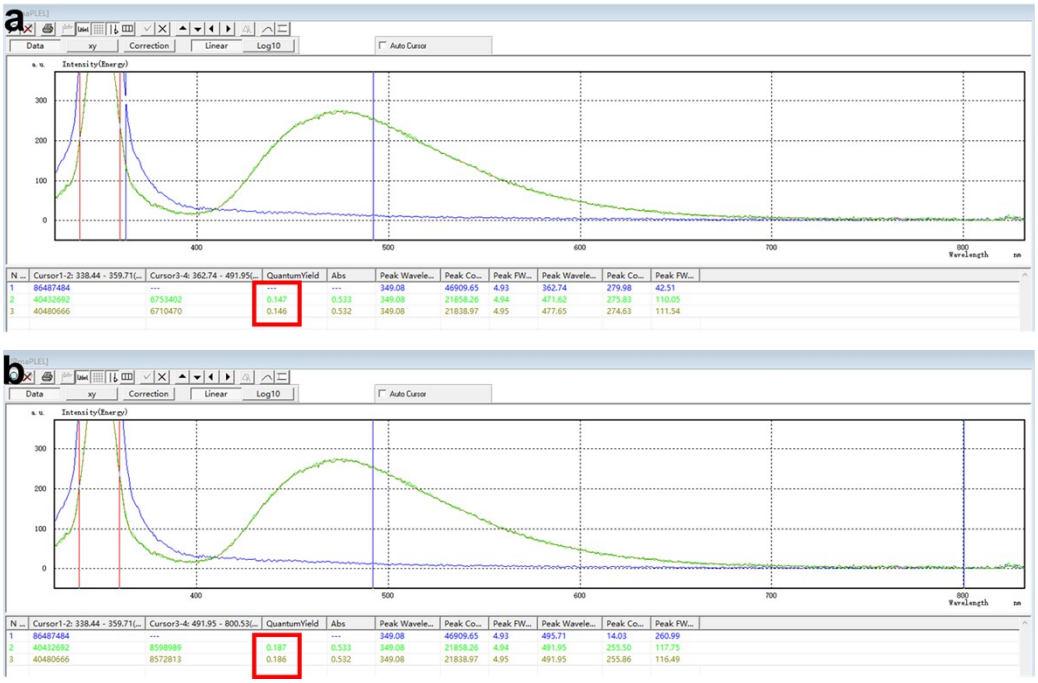


Figure S23. (a) Fluorescence and (b) phosphorescence quantum efficiency of **PC•2Cl**.

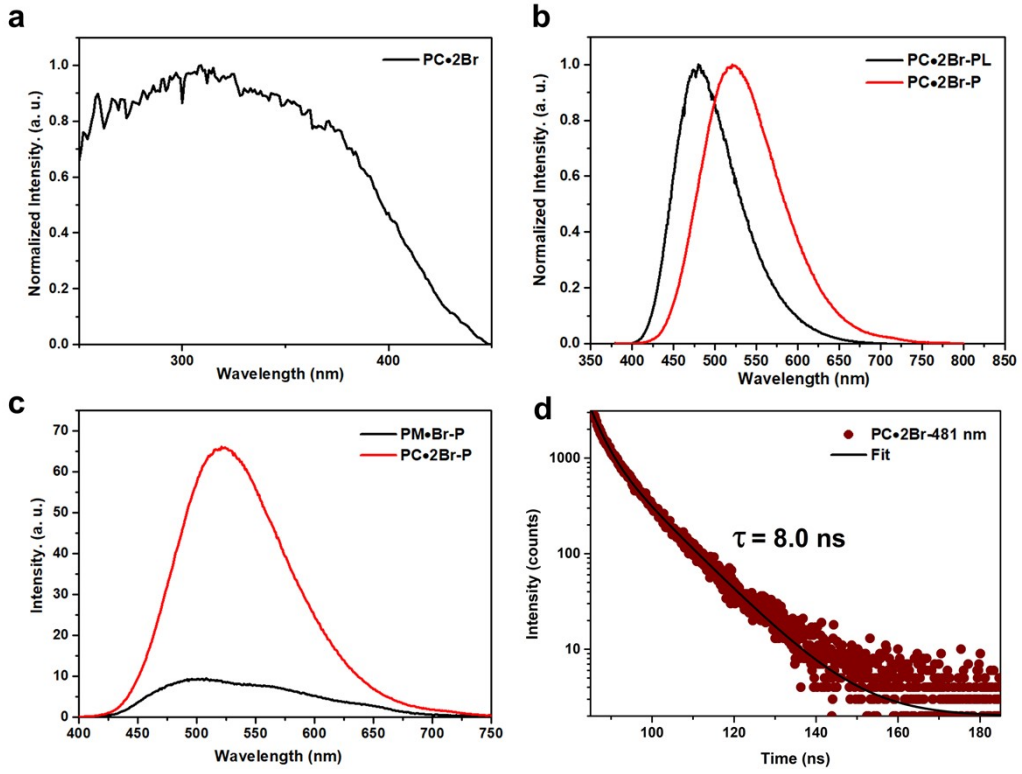


Figure S24. (a) Excitation spectra of **PC•2Br** at 481 nm; (b) Photoluminescence (black) and phosphorescence spectra (red) of **PC•2Br** under 340 nm excitation; (c) Phosphorescence spectra of **PM•Br** (black) and **PC•2Br** (red) after 340 nm excitation; (d) Time resolved PL decay of **PC•2Br** @481 nm in solid at room temperature.

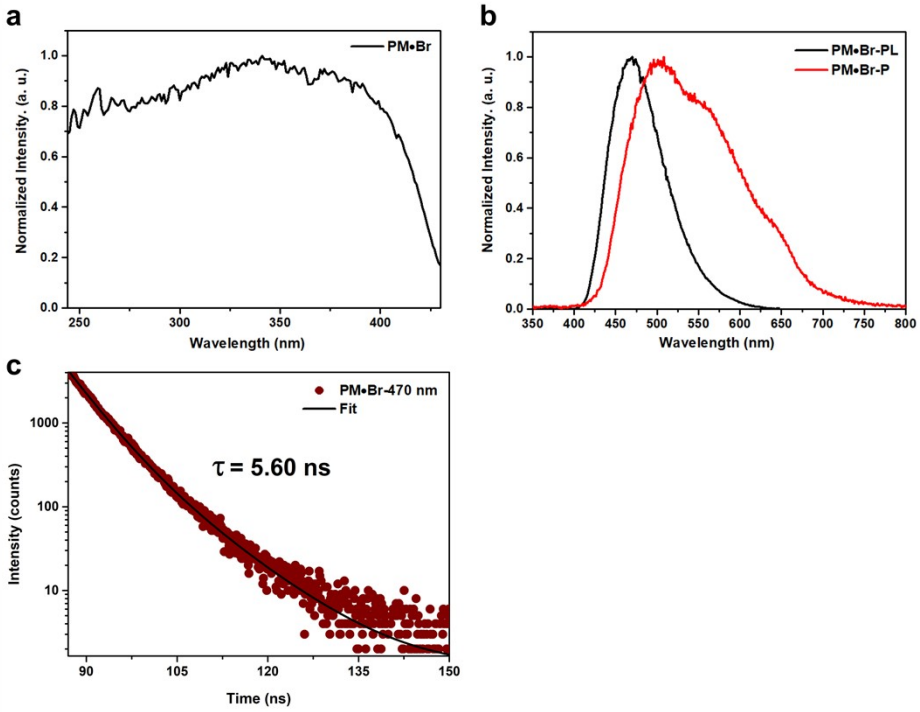


Figure S25. (a) Excitation spectra of **PM•Br** at 470 nm; (b) Photoluminescence (black) and phosphorescence spectra (red) of **PM•Br** under 340 nm excitation; (c) Time resolved PL decay of **PM•Br** @470 nm in solid at room temperature.

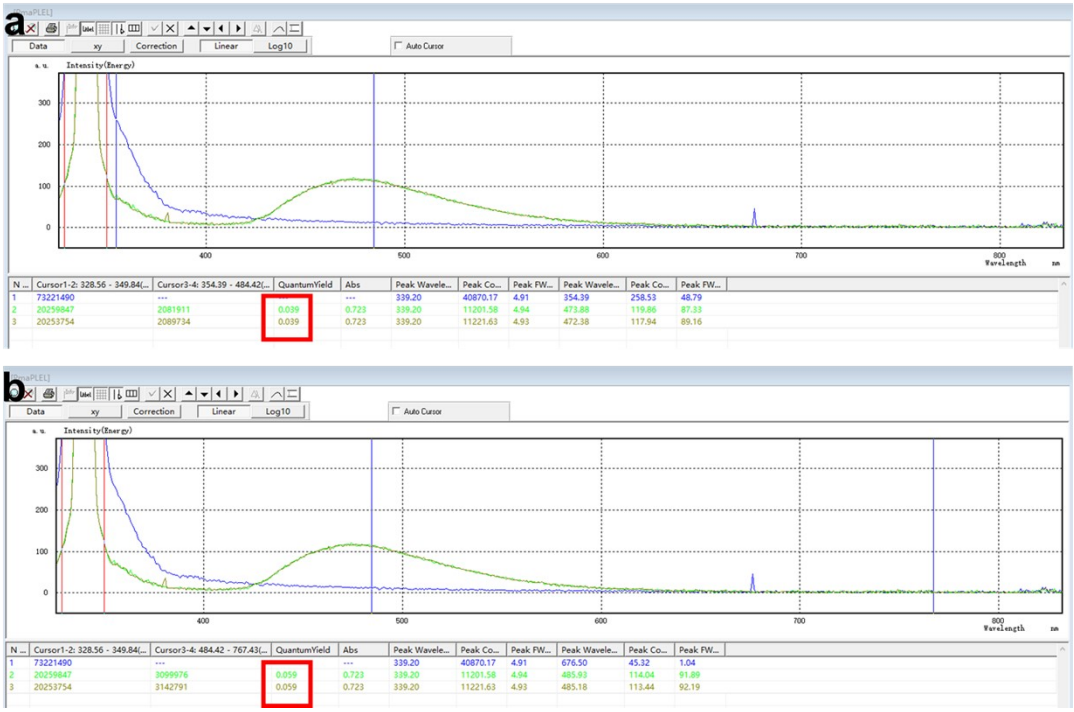


Figure S26. (a) Fluorescence and (b) phosphorescence quantum efficiency of **PM•Br**.

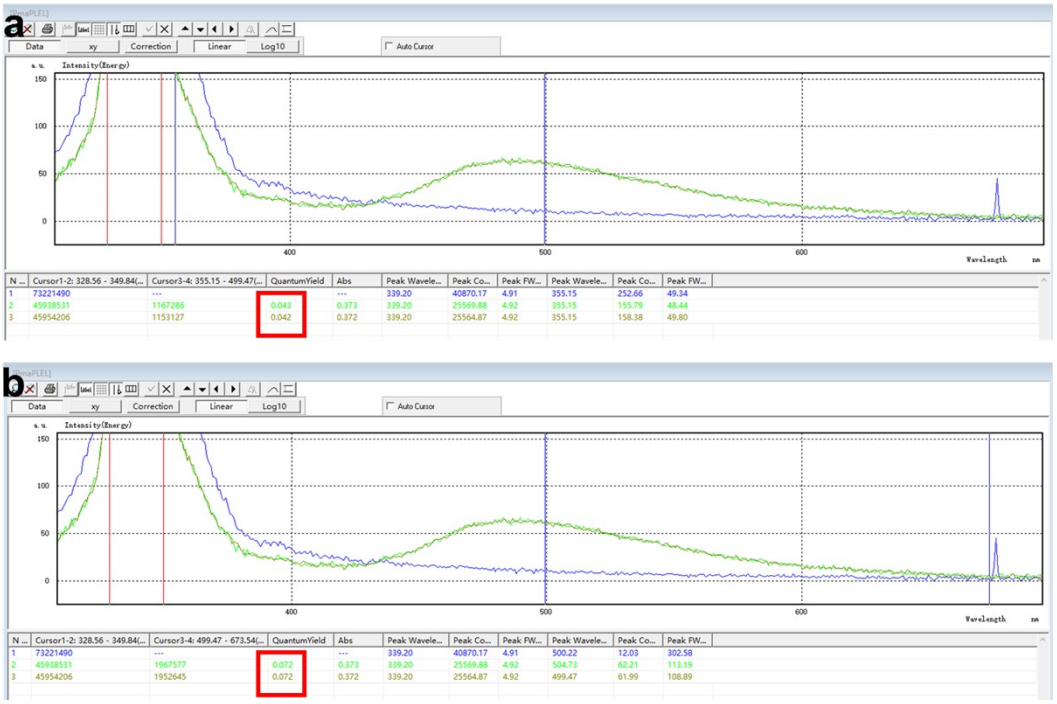


Figure S27. (a) Fluorescence and (b) phosphorescence quantum efficiency of **PC•2Br**.

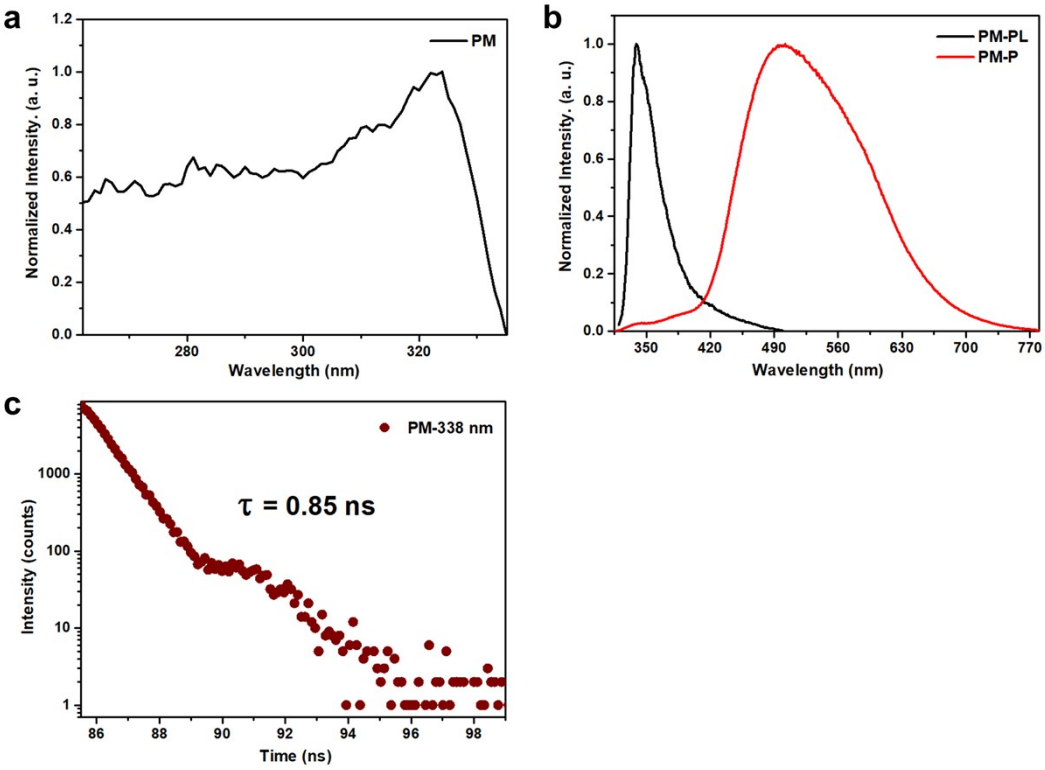


Figure S28. (a) Excitation spectra of **PM** at 310 nm; (b) Photoluminescence (black) and phosphorescence spectra (red) of **PM** under 310 nm excitation; (c) Time resolved PL decay of **PM** @338 nm in solid state at room temperature.

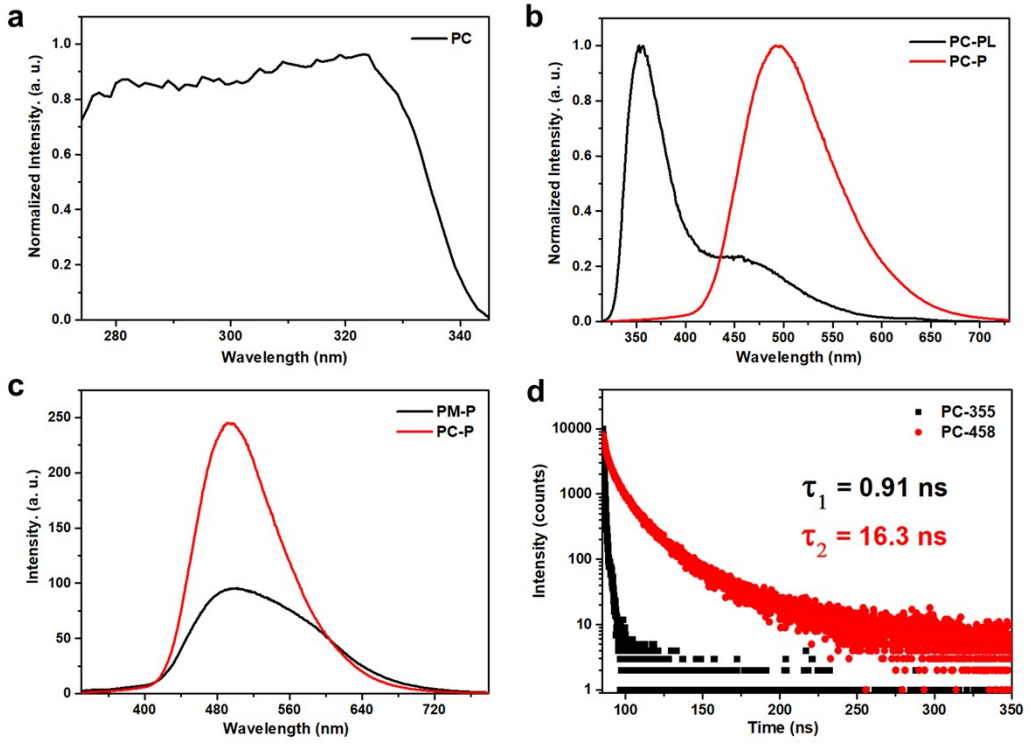


Figure S29. (a) Excitation spectra of **PC** at 355 nm; (b) Photoluminescence (black) and phosphorescence spectra (red) of **PC** under 310 nm excitation; (c) Phosphorescence spectra of **PM** (black) and **PC** (red) after 310 nm excitation; (d) Time resolved PL decay of **PC** @355 nm and 458 nm in solid state at room temperature.

Figure S30. (a) Fluorescence and (b) phosphorescence quantum efficiency of **PC**.

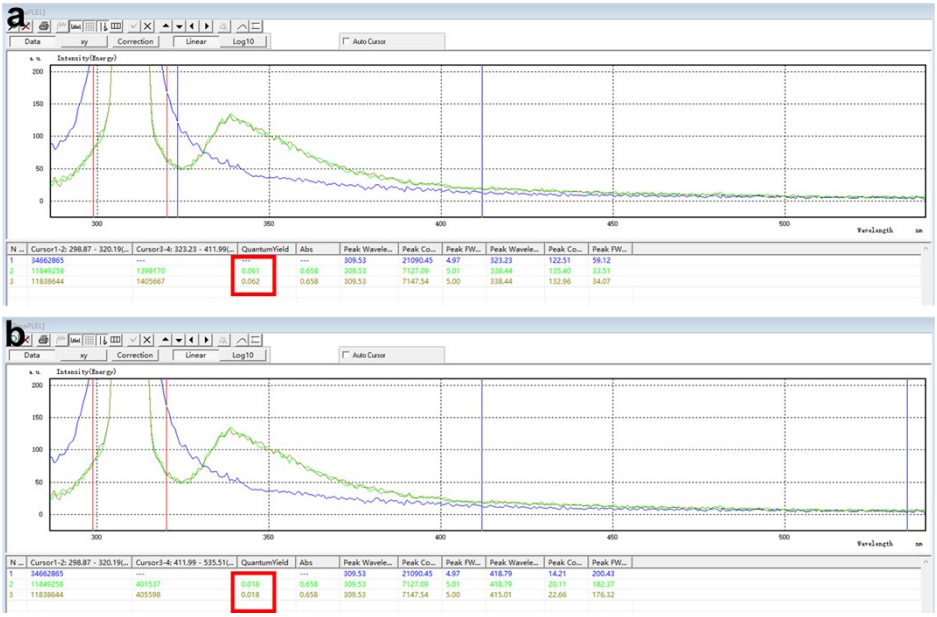


Figure S31. (a) Fluorescence and (b) phosphorescence quantum efficiency of **PM**.

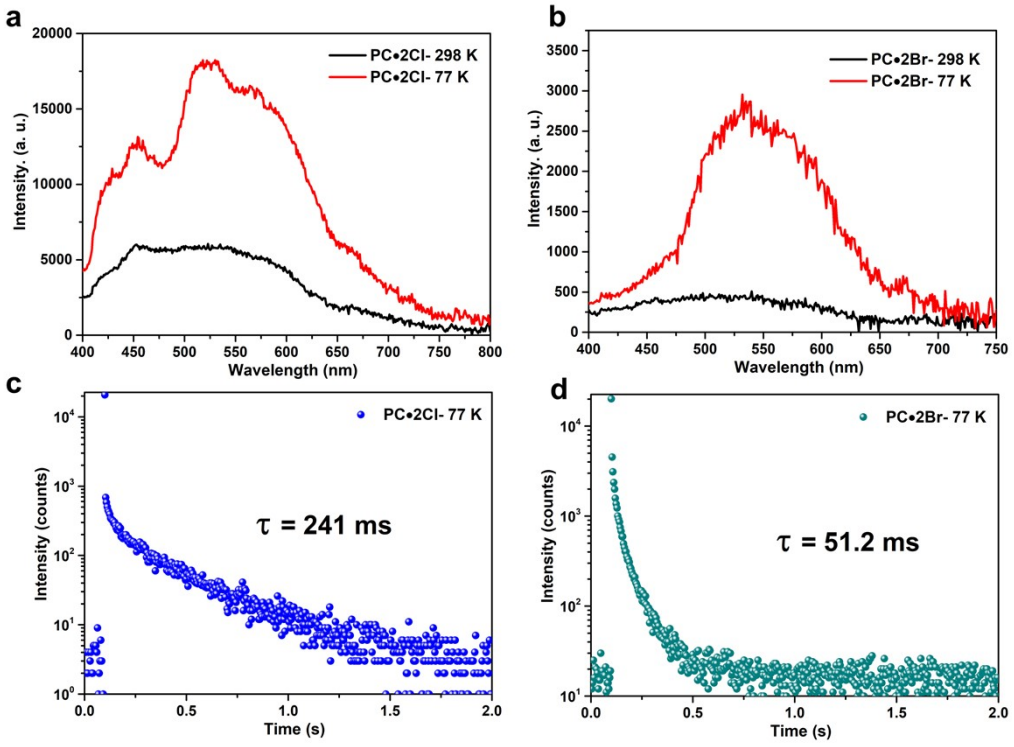


Figure S32. (a, b) Phosphorescent spectra of **PC•2Cl** and **PC•2Br** in solid state at 298 K and 77 K. (c, d) Time resolved PL decay of **PC•2Cl** and **PC•2Br** in solid state at 77 K.

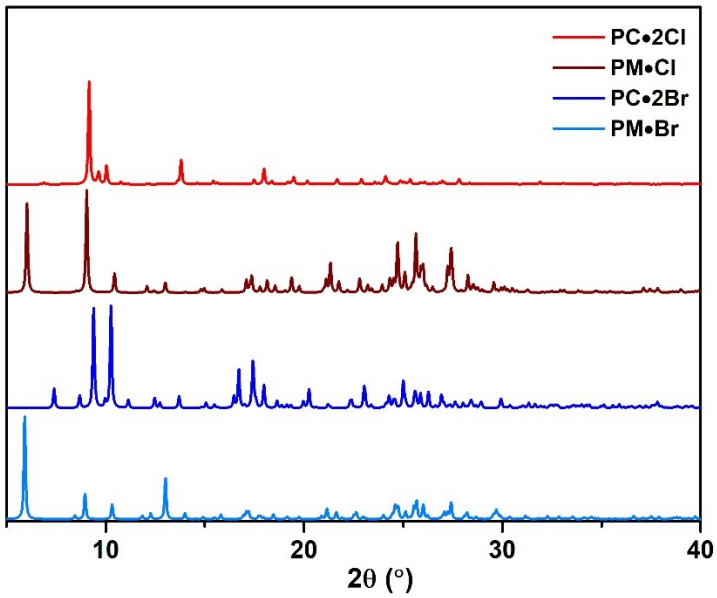


Figure S33. Simulated XRD of macrocycles **PC•2Br** and **PC•2Cl** and monomers **PM•Cl** and **PM•Br** based on single crystals.

The simulated PXRD of macrocycles PC•2Br and PC•2Cl and monomers PM•Cl and PM•Br were compared. Macrocycles possessed totally different XRD pattern with their monomers, indicating the difference of their superstructures.

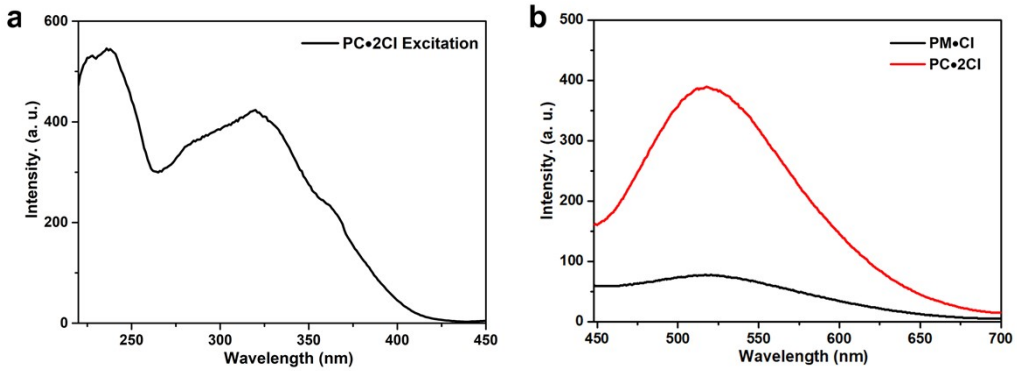


Figure S34. (a) Excitation spectra of **PC•2Cl**. (b) Photoluminescence spectra of **PM•Cl** (black) and **PC•2Cl** (red) in aqueous solution under 320 nm excitation. ([**PM•Cl**] = 2×10^{-6} mol/L; [**PC•2Cl**] = 1×10^{-6} mol/L)

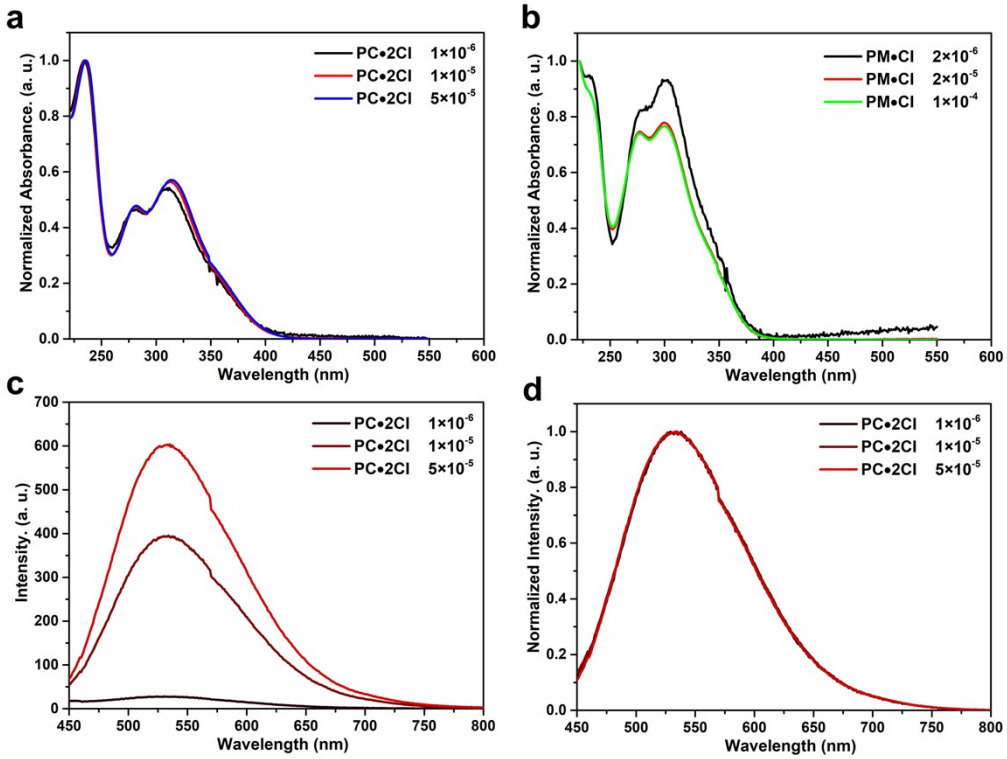


Figure S35. (a, b) The concentration-dependent UV-Vis absorption spectra of **PC•2Cl** and **PM•Cl** in aqueous solution. (c, d) The concentration-dependent photoluminescence spectra and normalized photoluminescence spectra of **PC•2Cl** in aqueous solution. (1×10^{-6}, 1×10^{-5}, and 5×10^{-5} mol/L for **PC•2Cl**; 2×10^{-6}, 2×10^{-5}, and 1×10^{-4} mol/L for **PM•Cl**). As one **PC•2Cl** possess two **PM•Cl** unites, the concentration of **PM•Cl** is twice of **PC•2Cl** to keep the same concentration of chromophores.

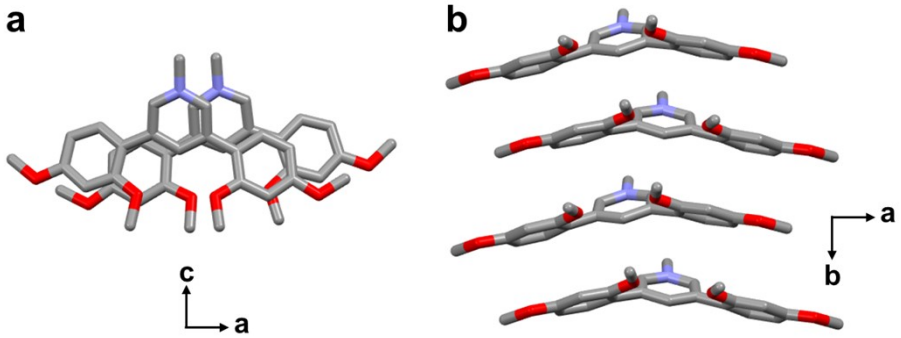


Figure S36. Single crystal structures of **PM•Cl** in b axis (a) and c axis (b). Color assign: C, gray; O, red; N, blue.

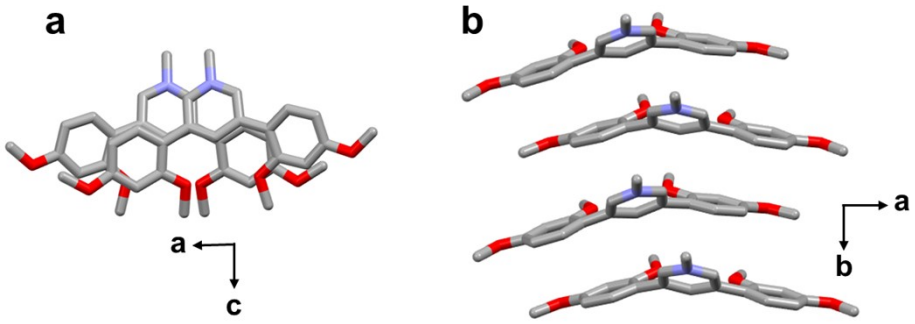


Figure S37. Single crystal structures of **PM•Br** in b axis (a) and c axis (b). Color assign: C, gray; O, red; N, blue.

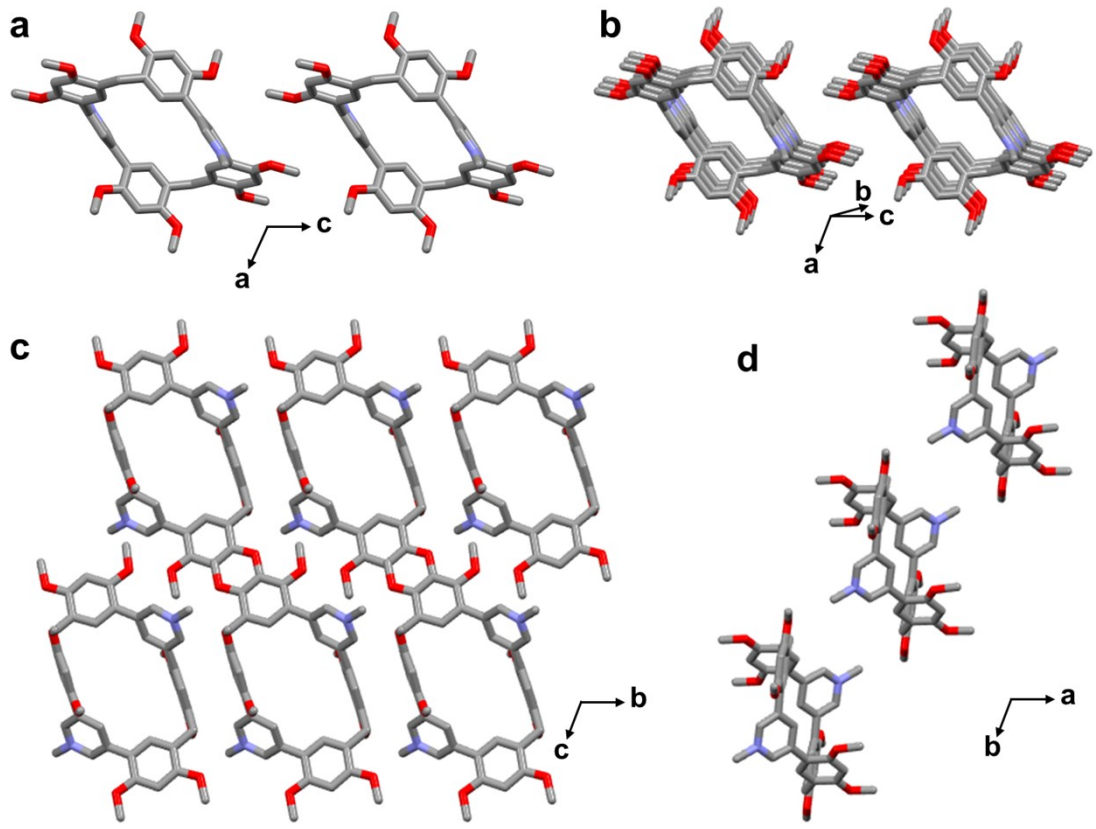


Figure S38. Single crystal structures of **PC•2Cl**. (a) packing mode in b axis; (b) packing mode in sliding b axis; (c) packing mode in a axis; (d) packing mode in c axis. Color assign: C, gray; O, red; N, blue.

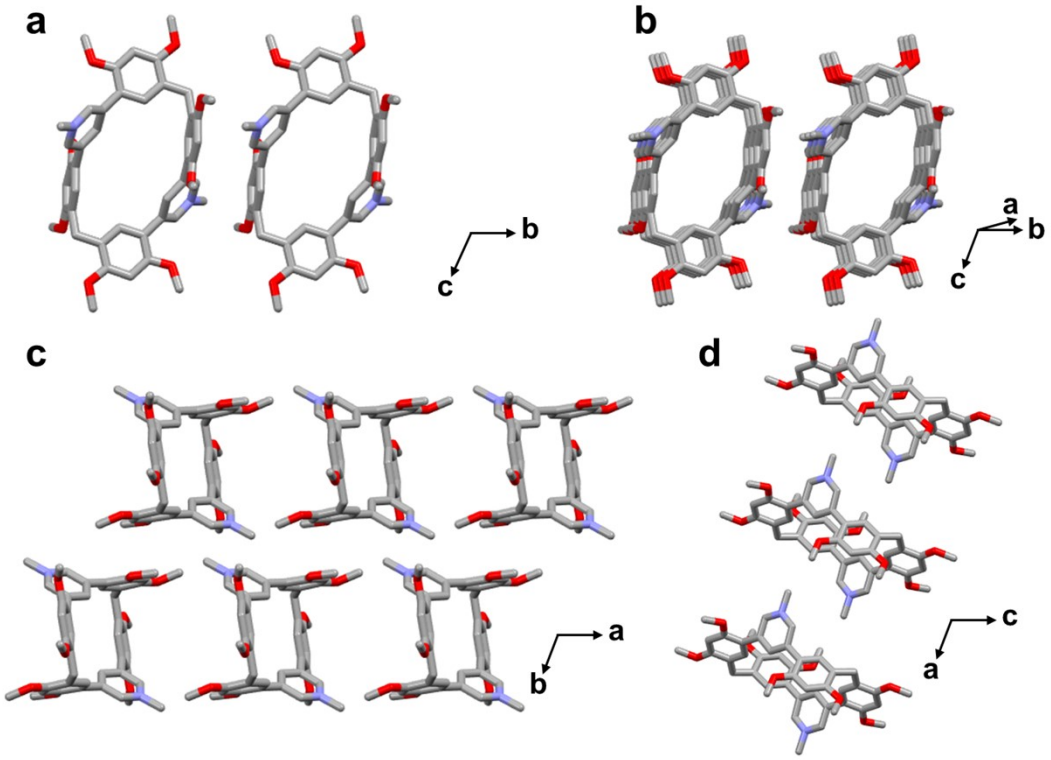


Figure S39. Single crystal structures of **PC•2Br**. (a) packing mode in a axis; (b) packing mode in sliding a axis; (c) packing mode in c axis; (d) packing mode in b axis. Color assign: C, gray; O, red; N, blue.

Section IV. Single-Crystal Structures of macrocycles and monomers

Crystal structure of PC (CCDC: 2169351)

Method: Single crystals, suitable for X-ray crystallography, were obtained as colorless block by slow vapor diffusion of isopropyl ether (1.5 mL) into a chloroform (3 mL) solution of **PC** (5 mg) at room temperature for 7 days. Crystal data of **PC** was collected on Bruker smart Apex 2.

Table S2. Crystal data and structure refinement for **PC.**

CCDC	2169351	
Empirical formula	$C_{46}H_{44}Cl_6N_2O_8$	
Formula weight	965.53	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.4158(9) Å	α=65.199(2)°.
	b = 11.2534(9) Å	β=66.882(2)°.
	c = 12.4707(9) Å	γ=65.616(2)°.
Volume	1165.21(16) $Å^3$	
Z	1	
Density (calculated)	1.376 Mg/m^3	
Absorption coefficient	0.423 mm^{-1}	
F(000)	500	
Crystal size	0.150 x 0.120 x 0.100 mm^3	
Theta range for data collection	2.332 to 24.999°.	
Index ranges	-12<=h<=12, -13<=k<=13, -14<=l<=14	
Reflections collected	18685	
Independent reflections	4088 [R(int) = 0.0884]	
Completeness to theta = 25.242°	97.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6648	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4088 / 33 / 326	
Goodness-of-fit on F^2	1.015	
Final R indices [I>2sigma(I)]	R_1 = 0.0749, wR2 = 0.1683	
R indices (all data)	R_1 = 0.1403, wR2 = 0.2143	

Crystal structure of PC•2Cl (CCDC: 2169350)

Method: Single crystals, suitable for X-ray crystallography, were obtained as pale yellow block by slow vapor diffusion of isopropyl ether (2 mL) into an ethanol (3 mL) solution of **PC•2Cl** (8 mg) at room temperature for 5 days. Crystal data of **PC•2Cl** was collected on Bruker smart Apex 2.

Table S3. Crystal data and structure refinement for **PC•2Cl.**

CCDC	2169350	
Empirical formula	$C_{46}H_{48}Cl_2N_2O_8$	
Formula weight	827.76	
Temperature	296.15 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 11.2342(16) Å	α= 94.218(5)°.
	b = 11.3547(19) Å	β= 105.649(5)°.
	c = 13.700(2) Å	γ = 118.707(4)°.
Volume	1432.6(4) $Å^3$	
Z	1	
Density (calculated)	0.959 g/cm^3	
Absorption coefficient	0.155 mm^{-1}	
F(000)	436.0	
Crystal size	0.12 × 0.1 × 0.1 mm^3	
Radiation	MoKα (λ = 0.71073)	
Theta range for data collection	4.41 to 55.002°	
Index ranges	$-14 \leq h \leq 13$, $-14 \leq k \leq 14$, $0 \leq l \leq 17$	
Reflections collected	13450	
Independent reflections	6451 [Rint = 0.0562, Rsigma = 0.0817]	
Data / restraints / parameters	6451/51/559	
Goodness-of-fit on F^2	1.159	
Final R indices [I>2sigma(I)]	R_1 = 0.0984, wR_2 = 0.2549	
R indices (all data)	R_1 = 0.1153, wR_2 = 0.2901	
Largest diff. peak and hole	0.93 and -0.52 e.$Å^{-3}$	

Crystal structure of PM•Cl (CCDC: 2169353)

Method: Single crystals, suitable for X-ray crystallography, were obtained as pale yellow block by slow vapor diffusion of isopropyl ether (2 mL) into an ethanol (2 mL) solution of **PM•Cl** (6 mg) at room temperature for 4 days. Crystal data of **PM•Cl** was collected on Bruker smart Apex 2.

Table S4. Crystal data and structure refinement for **PM•Cl.**

CCDC	2169353
Empirical formula	$C_{24}H_{30}ClNO_5$
Formula weight	447.94
Temperature	190.0 K
Crystal system	Orthorhombic
Space group	Pbcn
Unit cell dimensions	a = 29.2816(17) Å α= 90°. b = 7.4273(4) Å β= 90°. c = 20.7305(12) Å γ= 90°.
Volume	4508.5(4) $Å^3$
Z	8
Density (calculated)	1.320 g/cm^3
Absorption coefficient	1.166 mm^{-1}
F(000)	1904.0
Crystal size	0.12 × 0.1 × 0.1 mm^3
Radiation	GaKα (λ = 1.34139)
Theta range for data collection	7.42 to 106°
Index ranges	$-34 \leq h \leq 31$, $-8 \leq k \leq 8$, $-24 \leq l \leq 24$
Reflections collected	33827
Independent reflections	3977 [Rint = 0.1014, Rsigma = 0.0610]
Data / restraints / parameters	3977/0/287
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R_1 = 0.0513, wR_2 = 0.1278
R indices (all data)	R_1 = 0.0734, wR_2 = 0.1438
Largest diff. peak and hole	0.43 and - 0.42 e.$Å^{-3}$

Crystal structure of PM•Br (CCDC: 2169352)

Method: Single crystals, suitable for X-ray crystallography, were obtained as pale yellow block by slow vapor diffusion of isopropyl ether (1 mL) into an ethanol (3 mL) solution of **PM•Br** (10 mg) at room temperature for 4 days. Crystal data of **PM•Br** was collected on Bruker smart Apex 2.

Table S5. Crystal data and structure refinement for **PM•Br.**

CCDC	2169352	
Empirical formula	$C_{22}H_{24}BrNO_4$	
Formula weight	446.33	
Temperature	296.15 K	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 29.843(6) Å	α= 90°.
	b = 7.4061(17) Å	β= 90°.
	c = 20.906(4) Å	γ= 90°.
Volume	4620.6(17) $Å^3$	
Z	8	
Density (calculated)	1.283 g/cm^3	
Absorption coefficient	1.804 mm^{-1}	
F(000)	1840.0	
Crystal size	0.12 × 0.1 × 0.1 mm^3	
Radiation	MoKα (λ = 0.71073)	
Theta range for data collection	3.896 to 55.012°	
Index ranges	$-38 \leq h \leq 37$, $-8 \leq k \leq 9$, $-27 \leq l \leq 26$	
Reflections collected	37756	
Independent reflections	5308 [Rint = 0.1225, Rsigma = 0.0938]	
Data / restraints / parameters	5308/0/258	
Goodness-of-fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R_1 = 0.0517, wR_2 = 0.1353	
R indices (all data)	R_1 = 0.0723, wR_2 = 0.1498	
Largest diff. peak and hole	0.64 and - 0.60 $e.Å^{-3}$	

Crystal structure of PC•2Br (CCDC:2065557)

Method: Single crystals, suitable for X-ray crystallography, were obtained as pale yellow block by slow vapor diffusion of diethyl ether (2 mL) into a DMF (3 mL) solution of **PC•2Br** (5 mg) at room temperature for 10 days. Crystal data of **PC•2Br** was collected on Bruker smart Apex 2.

Table S6. Crystal data and structure refinement for **PC•2Br.**

CCDC	2065557	
Empirical formula	$C_{46}H_{48}Br_2N_2O_8$	
Formula weight	916.68	
Temperature	150.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.9754(6) Å	α= 93.242(2)°.
	b = 11.4978(6) Å	β= 105.007(2)°.
	c = 12.5999(6) Å	γ =115.658(2)°.
Volume	1358.12(12) $Å^3$	
Z	1	
Density (calculated)	1.121 g/cm^3	
Absorption coefficient	1.536 mm^{-1}	
F(000)	472.0	
Crystal size	0.17 × 0.16 × 0.15 mm^3	
Radiation	MoKα (λ = 0.71073)	
Theta range for data collection	4.006 to 55.024°	
Index ranges	$-14 \le h \le 14$, $-14 \le k \le 14$, $-16 \le l \le 16$	
Reflections collected	62345	
Independent reflections	6205 [Rint = 0.0490, Rsigma = 0.0346]	
Data / restraints / parameters	6205/0/267	
Goodness-of-fit on F^2	1.147	
Final R indices [I>2sigma(I)]	R_1 = 0.0539, wR_2 = 0.1439	
R indices (all data)	R_1 = 0.0552, wR_2 = 0.1446	
Largest diff. peak and hole	0.55 and -0.45 e.$Å^{-3}$	

Crystal structure of PM (CCDC: 2169354)

Method: Single crystals, suitable for X-ray crystallography, were obtained as colorless block by slow vapor diffusion of hexane (1 mL) into a dichloromethane (2 mL) solution of **PM** (8 mg) at room temperature for 3 days. Crystal data of **PM** was collected on Bruker smart Apex 2.

Table S7. Crystal data and structure refinement for **PM.**

CCDC	2169354	
Empirical formula	$C_{21}H_{21}NO_4$	
Formula weight	351.39	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 7.434(2) Å	α= 90°.
	b = 8.594(3) Å	β= 92.767(5)°.
	c = 27.816(8) Å	γ= 90°.
Volume	1775.1(9) $Å^3$	
Z	4	
Density (calculated)	1.315 Mg/m^3	
Absorption coefficient	0.091 mm^{-1}	
F(000)	744	
Crystal size	0.190 x 0.170 x 0.110 mm^3	
Theta range for data collection	2.481 to 25.009°	
Index ranges	-8<=h<=8, -10<=k<=9, -32<=l<=33	
Reflections collected	12875	
Independent reflections	3124 [R(int) = 0.0510]	
Completeness to theta = 25.009°	99.6 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3124 / 0 / 239	
Goodness-of-fit on F^2	1.060	
Final R indices [I>2sigma(I)]	R_1 = 0.0449, wR_2 = 0.1204	
R indices (all data)	R_1 = 0.0547, wR_2 = 0.1291	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.251 and -0.293 $e.Å^{-3}$	