Electronic Supplementary Information

Tetraphenylethylene[3]arene: Synthesis, Structure, and Sensing of I^- ions

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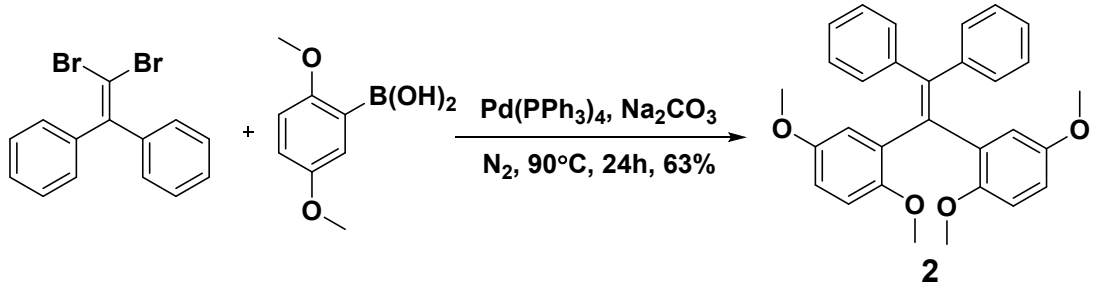
Contents

1. Materials and Methods.

All reactions were carried out with oven-dried glassware. Commercial reagents were used without further purification. Flash column chromatography was performed on 100-200 mesh silica gel. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker DMX 400 NMR spectrometer. Melting points were determined using WRR melting point apparatus and were uncorrected. High Resolution atmospheric-pressure chemical ionization mass spectra (APCI-MS) were determined by Bruker Daltonics. Inc, APEX II. FT-ICRMS. Electrospray ionization mass spectra (ESI-MS) were recorded on the Thermo Fisher® Exactive LC-MS spectrometer.

2. Synthesis of New Compounds.



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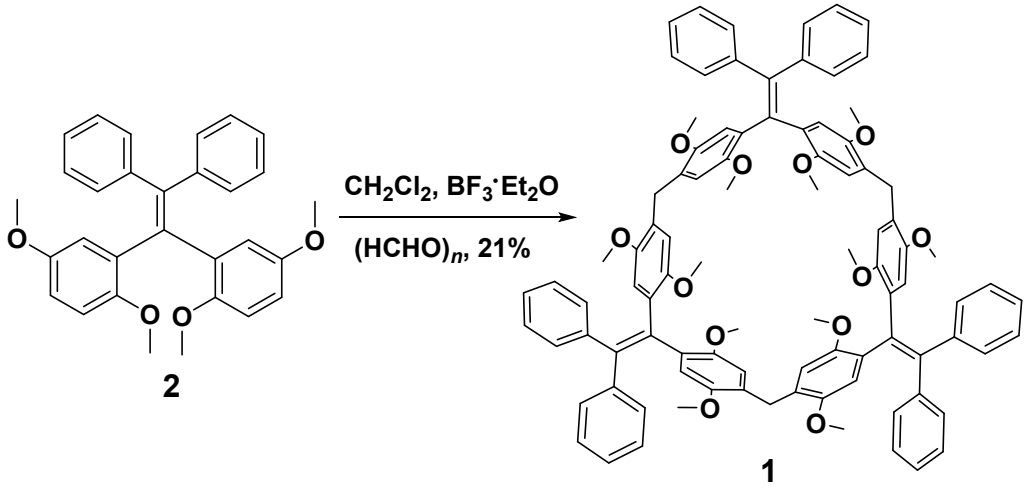
Compound 2: A mixture of (2,5-dimethoxyphenyl)boronic acid (910 mg, 5.0 mmol), Na_2CO_3 (690 mg, 5.0 mmol), (2,2-dibromoethene-1,1-diyl)dibenzene (336 mg, 1.0 mmol) and tetrakis(triphenylphosphine)palladium (139 mg, 0.12 mmol) in 50 mL 1,4-dioxane/water (v/v=4:1) in a flask was stirred at 90 °C for 24 h under N_2. After evaporating the solvents, resulting mixture was extracted with dichloromethane (3 × 50 mL) and then washed with water and brine successively. The organic layer was dried over anhydrous Na_2SO_4 and removed in vacuo and the residue was separated by column chromatography on silica gel (eluent: 1:2 DCM/Petroleum ether) to give compound **3** (285 mg, yield 63%) as yellow solid. M.p.: 171-172 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.06 (s, 4H), 6.94 – 6.82 (m, 6H), 6.61 (s, 2H), 3.78 (s, 6H), 3.73 (s, 6H), 3.58 (s, 2H), 3.35 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 153.1, 151.7, 151.3, 143.4, 133.6, 130.5, 128.7, 127.2, 126.3, 117.6, 117.2, 113.4, 113.0, 112.6,

112.5, 56.5, 56.1, 55.7, 55.7. HRMS (APCI) m/z: $[M+H]^+$ calcd for $C_{30}H_{29}O_4$, 453.2060; found, 453.2054.



Host 1: To a mixture of **2** (452 mg, 1.0 mmol) and paraformaldehyde (90 mg, 3.0 mmol) in dichloromethane (70 mL) was added boron trifluoride diethyl etherate (0.15 mL, 1.2 mmol). The mixture was stirred at room temperature for 2.5 h. Then the reaction was quenched by the addition of 50 mL water. The organic layer was separated and dried with anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was separated by column chromatography on silica gel (eluent: 1:100 ethyl acetate /DCM) to give **1** (146 mg, 21%) as yellow solids. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.07 (q, *J* = 7.7, 7.0 Hz, 30H), 6.49 (s, 6H), 6.36 (s, 6H), 3.73 (s, 6H), 3.41 (s, 18H), 3.07 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 151.2, 143.7, 142.3, 131.3, 130.7, 128.7, 127.3, 126.2, 115.6, 115.3, 56.3, 56.2, 29.6. M.p.: 274-276 °C. HRMS (APCI) m/z: $[M+Na]^+$ calcd for $C_{93}H_{84}O_{12}Na$, 1415.5855; found, 1415.5795.

3. ^{1}H NMR and ^{13}C NMR Spectral of New compounds.

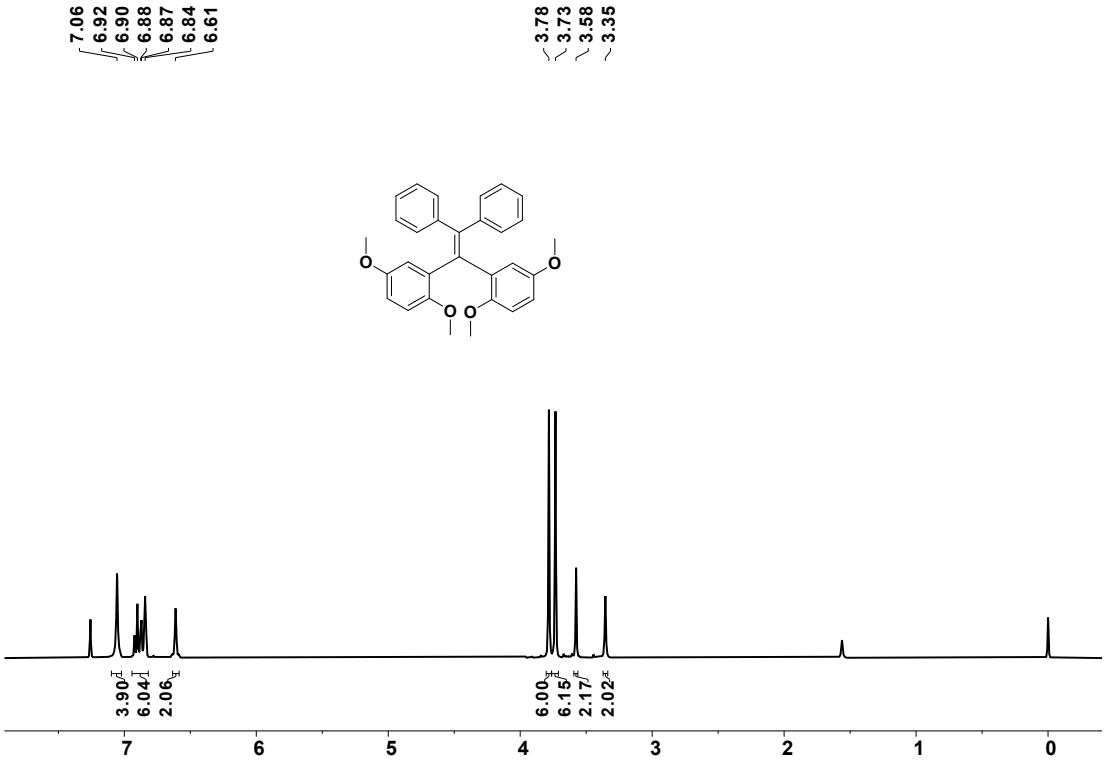


Figure S1.^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **2**

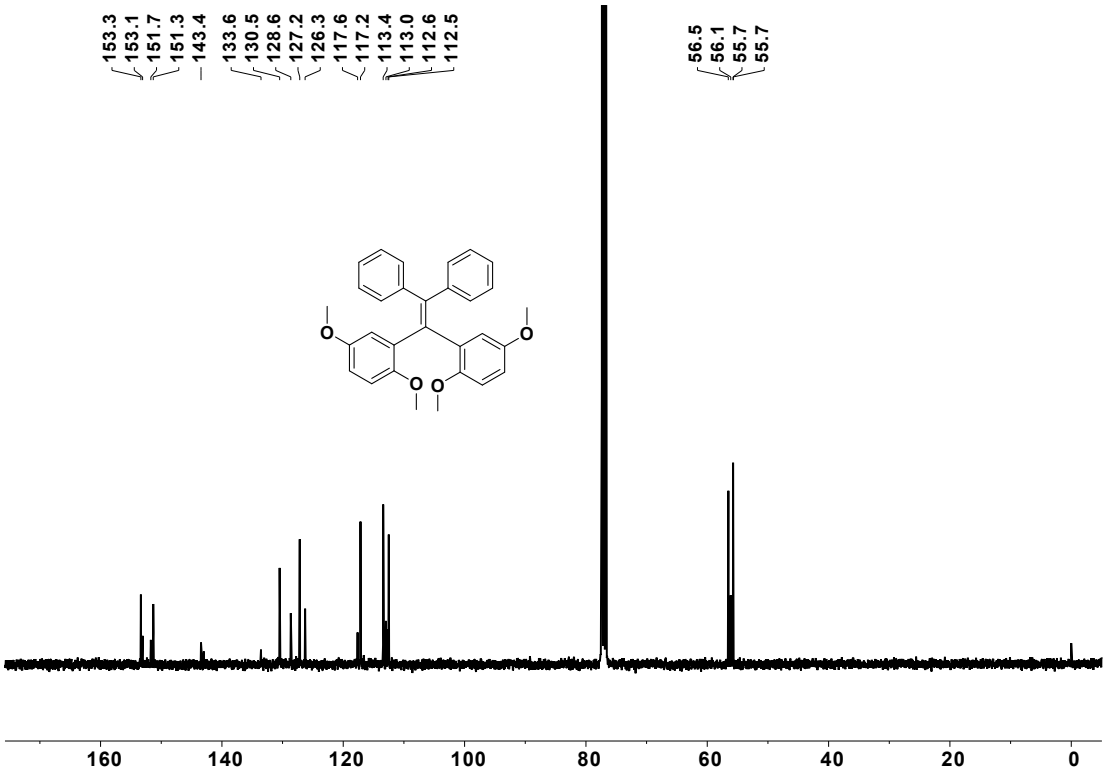


Figure S2.^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298K) of **2**

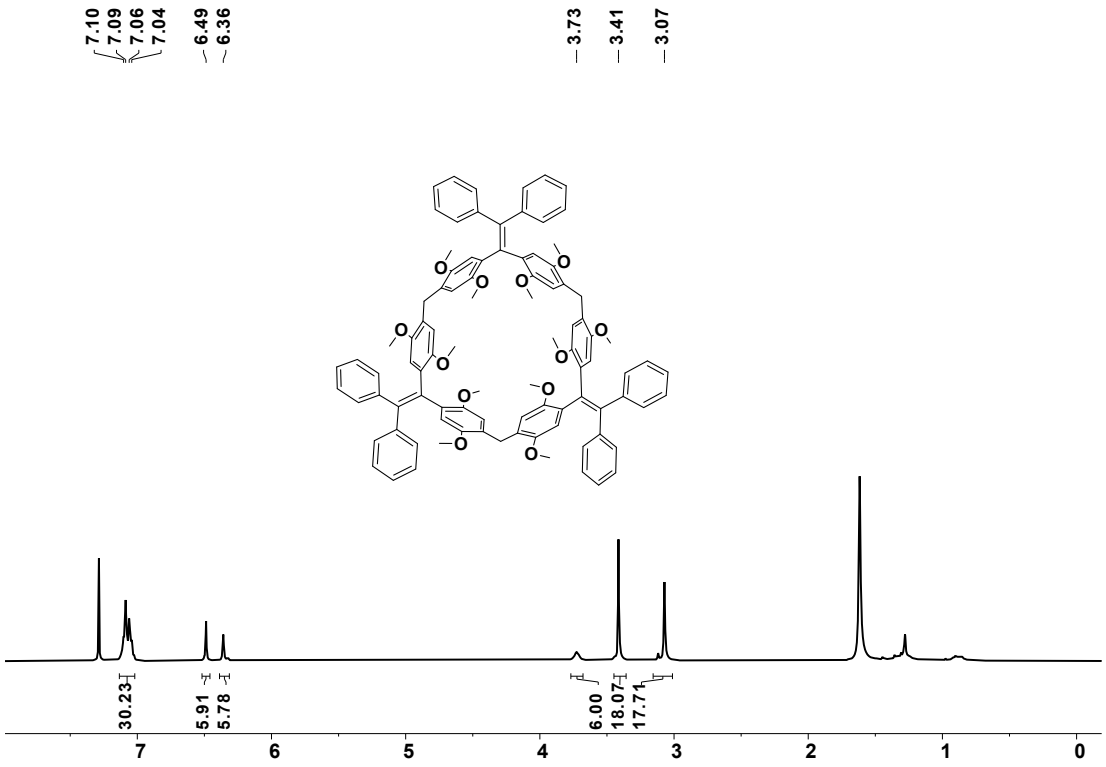


Figure S3.[1]H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **1**

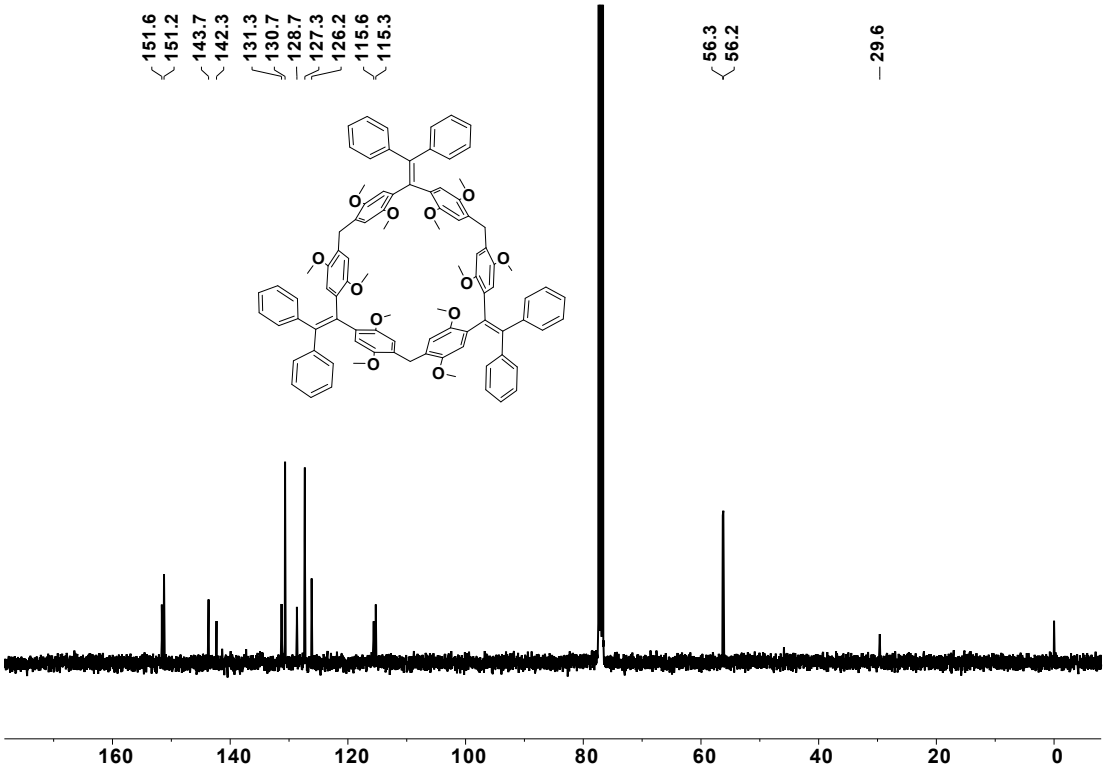


Figure S4.[13]C NMR spectrum (101 MHz, $CDCl_3$, 298K) of **1**

4. Quantum yield of host 1

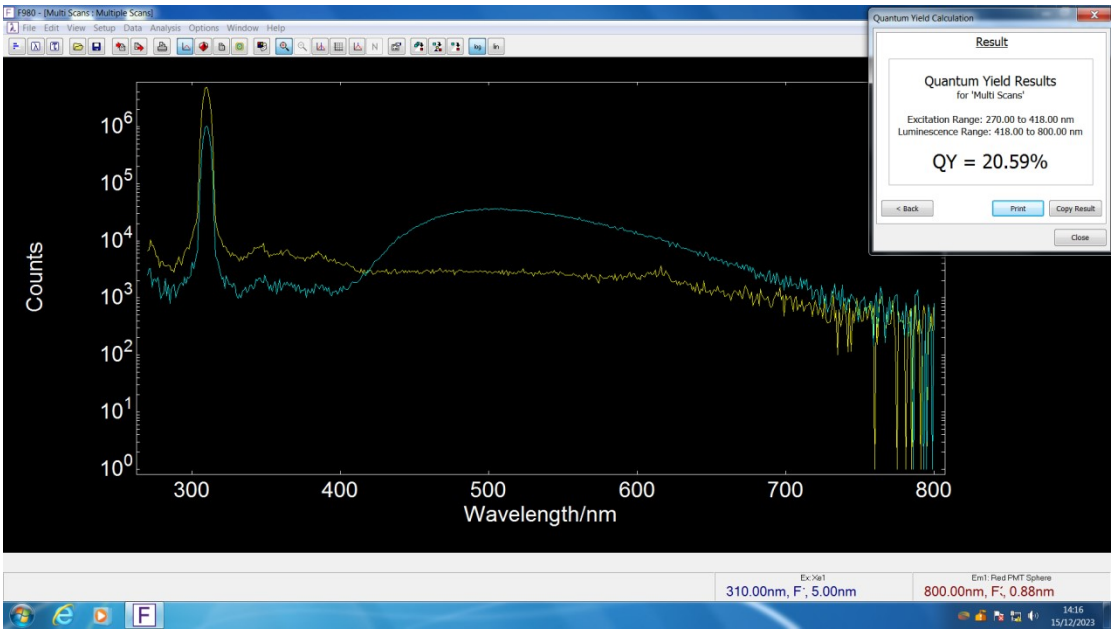


Figure S5. Quantum yield of **1** at solid state

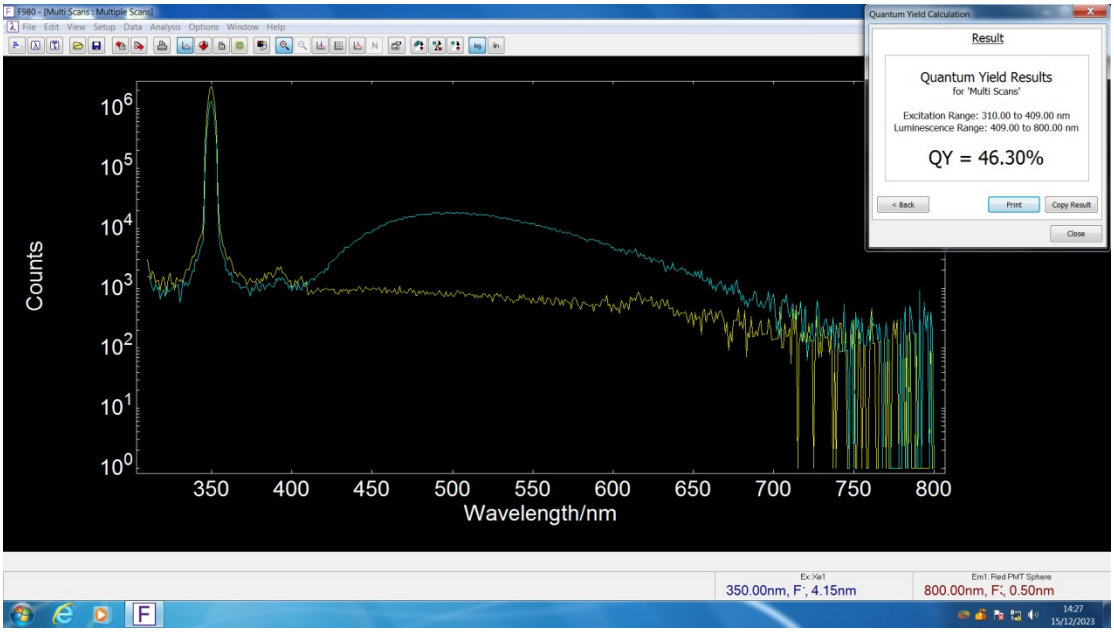


Figure S6. Quantum yield of **1** at solution of f_w =95%

5. ^{1}H NMR studies of Complexation of the Host and Guest

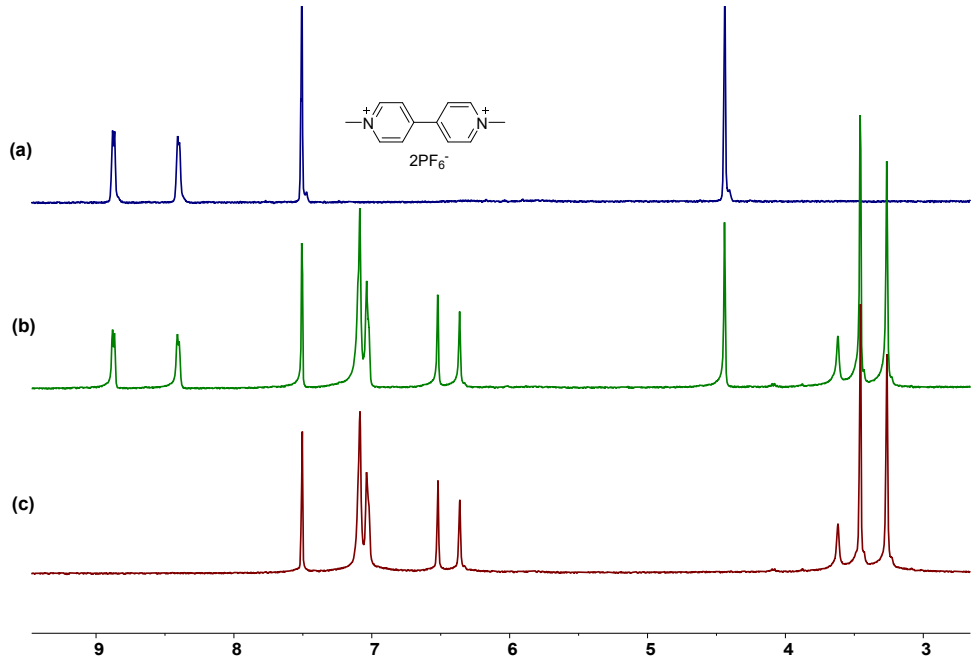


Figure S7. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$, V/V=1:1, 298 K) of (a) free paraquat, (b) **1** and 1.0 equiv. of paraquat, and (c) free **1**. $[\mathbf{1}]_0$ = 2.0 mM.

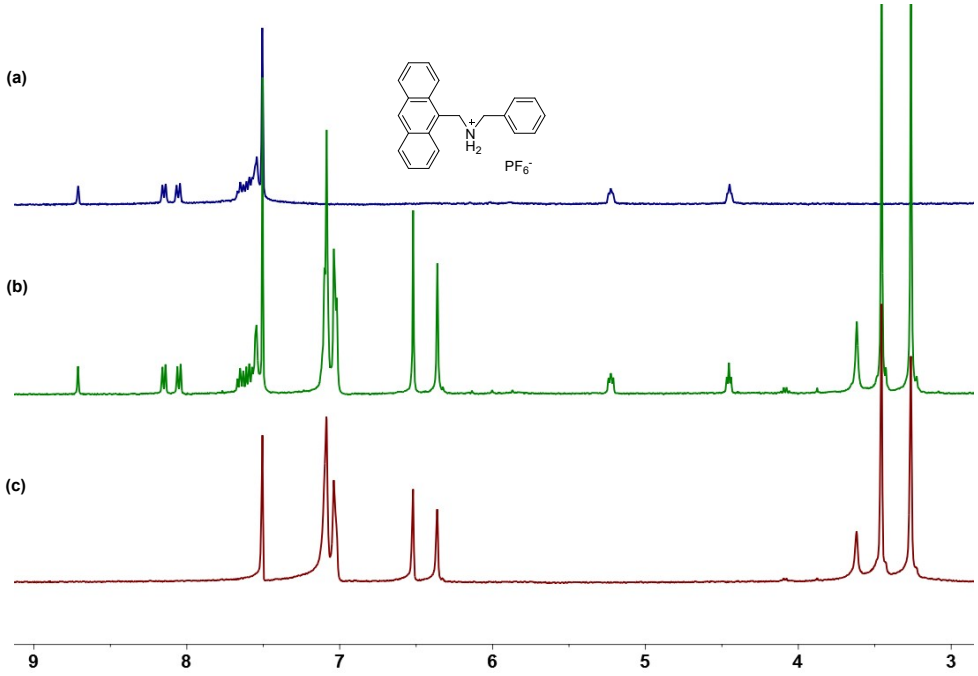


Figure S8. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$, V/V=1:1, 298 K) of (a) 1-(anthracen-9-yl)-N-benzylmethanaminium hexafluorophosphate, (b) **1** and 1.0 equiv. of 1-(anthracen-9-yl)-N-benzylmethanaminium hexafluorophosphate, and (c) free **1**. $[\mathbf{1}]_0$ = 2.0 mM.

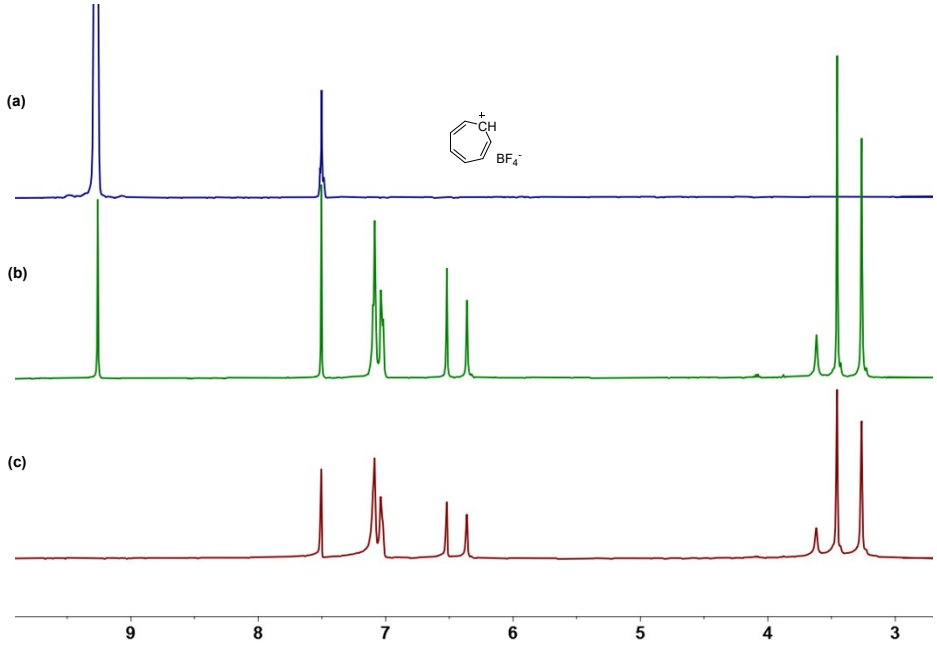


Figure S9. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$, V/V=1:1, 298 K) of (a) tropyliumtetrafluoroborate, (b) **1** and 1.0 equiv. of tropyliumtetrafluoroborate, and (c) free **1**. $[\mathbf{1}]_0$ = 2.0 mM.

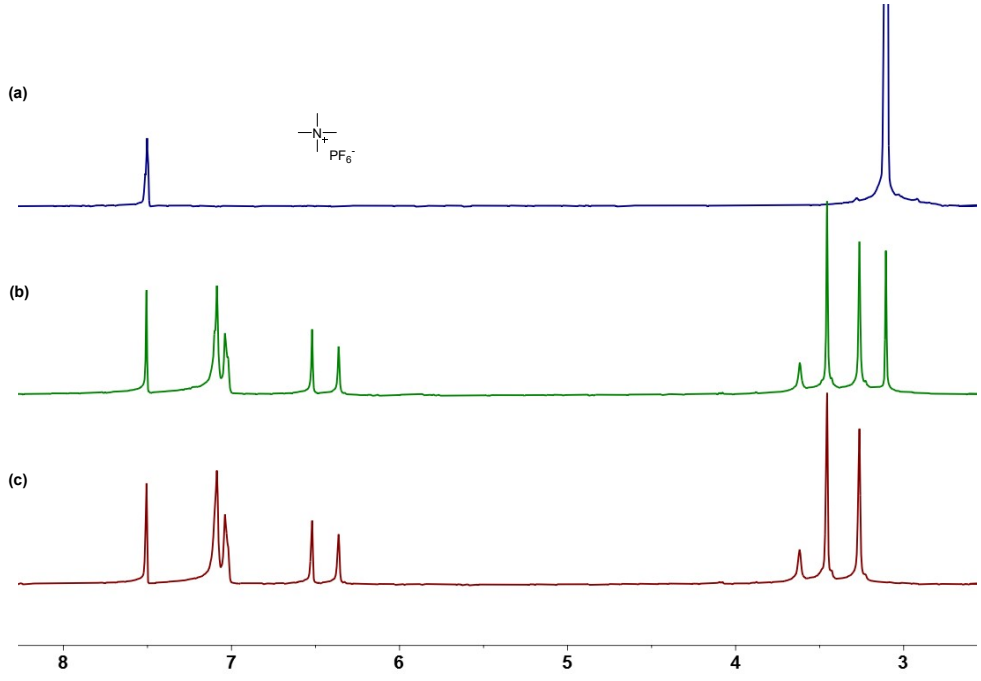


Figure S10. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$, V/V=1:1, 298 K) of (a) tetramethylammonium hexafluorophosphate, (b) **1** and 1.0 equiv. of tetramethylammonium hexafluorophosphate, and (c) free **1**. $[\mathbf{1}]_0$ = 2.0 mM.

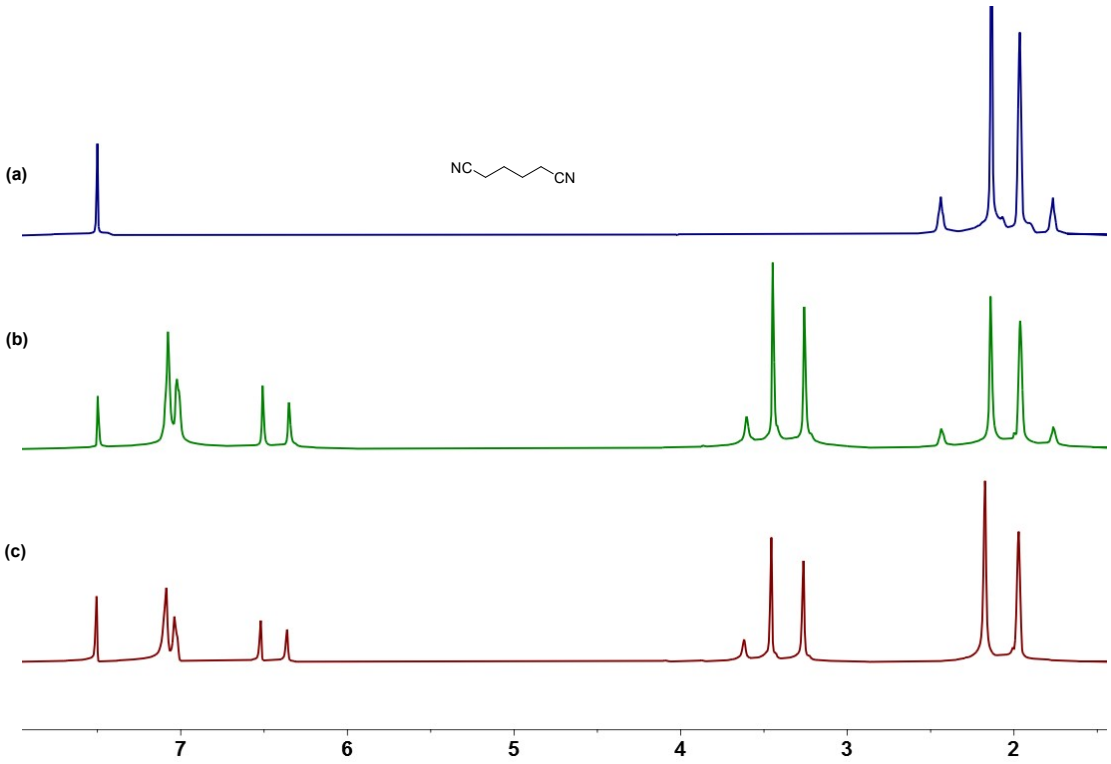


Figure S11. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$, V/V=1:1, 298 K) of (a) adiponitrile, (b) **1** and 1.0 equiv. of adiponitrile, and (c) free **1**. $[\mathbf{1}]_0$ = 2.0 mM.

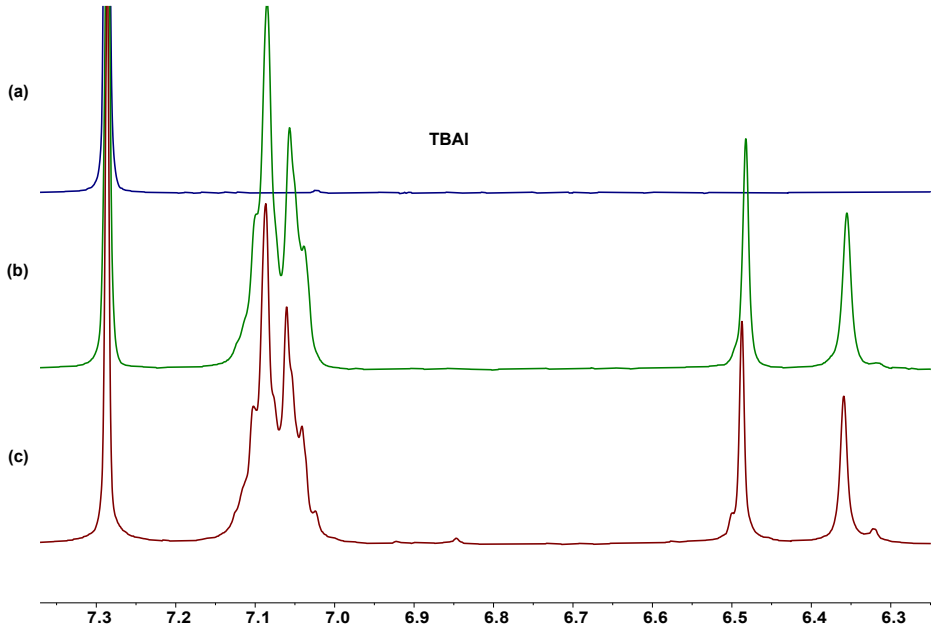


Figure S12. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of (a) free **TBAI**, (b) **1** and 1.0 equiv. of **TBAI**, and (c) free **1**. $[\mathbf{1}]_0$ = 2.0 mM.

6. Energy-minimized structure of 1@X^-

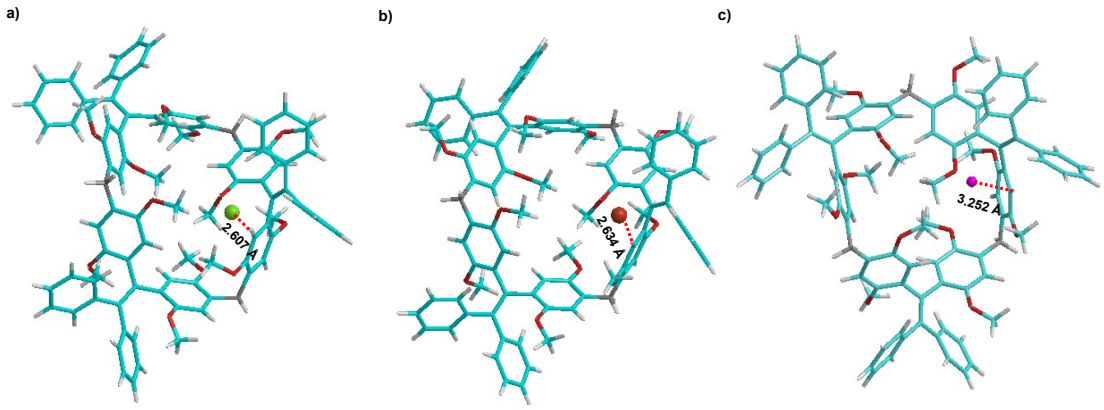


Figure S13. Energy-minimized structure of (a) **1**@$\mathbf{Cl^-}$; (b) **1**@$\mathbf{Br^-}$ and (c) **1**@ $\mathbf{I^-}$ at the level of B3LYP-D3/6-31G

7. Fluorescence spectra of 1 with TBACl and TBAF

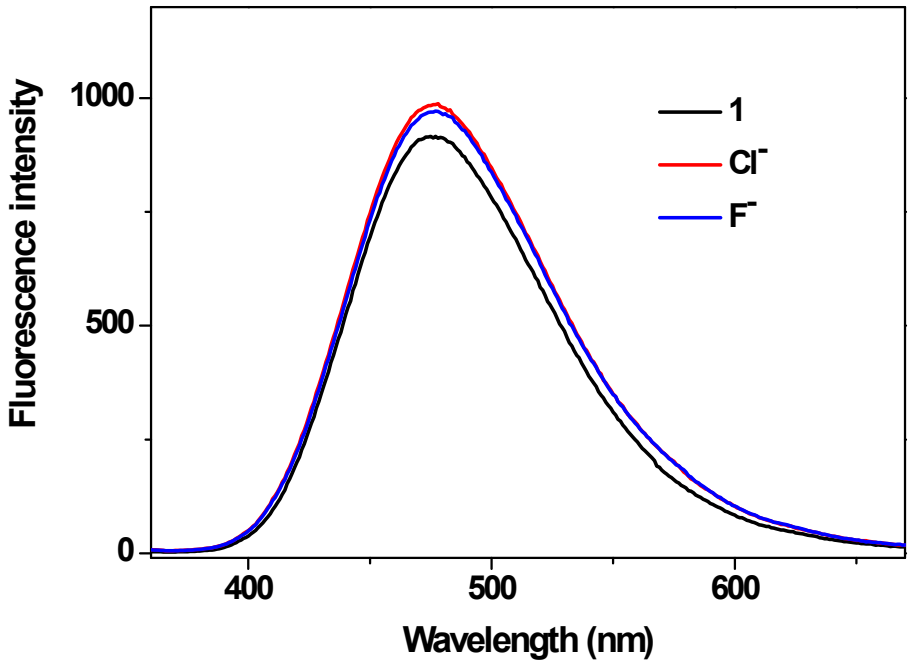


Figure S14. Fluorescence spectra of **1** in 95% H_2O THF/H_2O solution before and after the addition of 50.0. TBAX (X = F^-, Cl^-), $[\mathbf{1}]_0 = 1.0 \times 10^{-5}$ M.

8. ESI MS Studies of Host 1

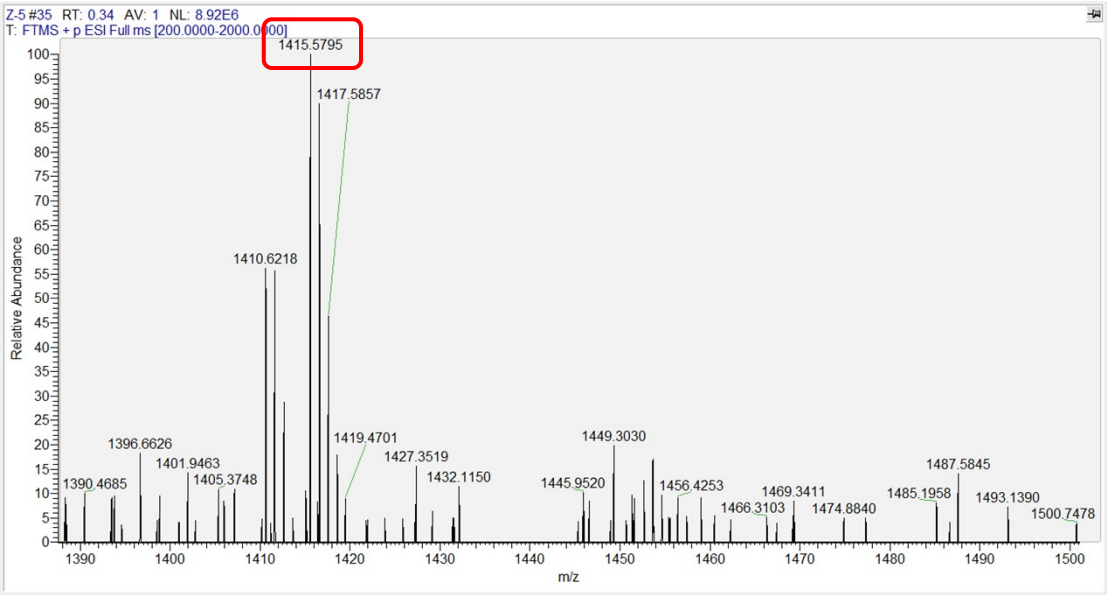


Figure S15. ESI Spectrum of **1**

9. Crystal data for host 1

Table 1 Crystal data and structure refinement for host 1.

Identification code	11_a
Empirical formula	$C_{93}H_{84}O_{12}$
Formula weight	1393.60
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	23.393(2)
b/Å	18.6985(19)
c/Å	19.754(2)
α/°	90
β/°	107.1040(10)
γ/°	90
Volume/Å^3	8258.3(15)
Z	4
ρ_{calc}g/cm^3	1.121
μ/mm^{-1}	0.073
F(000)	2952.0

Crystal size/mm^3	0.36 × 0.21 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.822 to 55.142
Index ranges	-29 ≤ h ≤ 30, -23 ≤ k ≤ 24, -25 ≤ l ≤ 25
Reflections collected	91466
Independent reflections	18781 [R_{int} = 0.0418, R_{sigma} = 0.0424]
Data/restraints/parameters	18781/2/958
Goodness-of-fit on F^2	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0732, wR_2 = 0.2217
Final R indexes [all data]	R_1 = 0.1250, wR_2 = 0.2624
Largest diff. peak/hole / e Å^{-3}	0.60/-0.50