Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Superbenzene-Bridged Bis(permethyl-β-cyclodextrin) as Convenient and Effective Probe for Trinitrophenol Exploder

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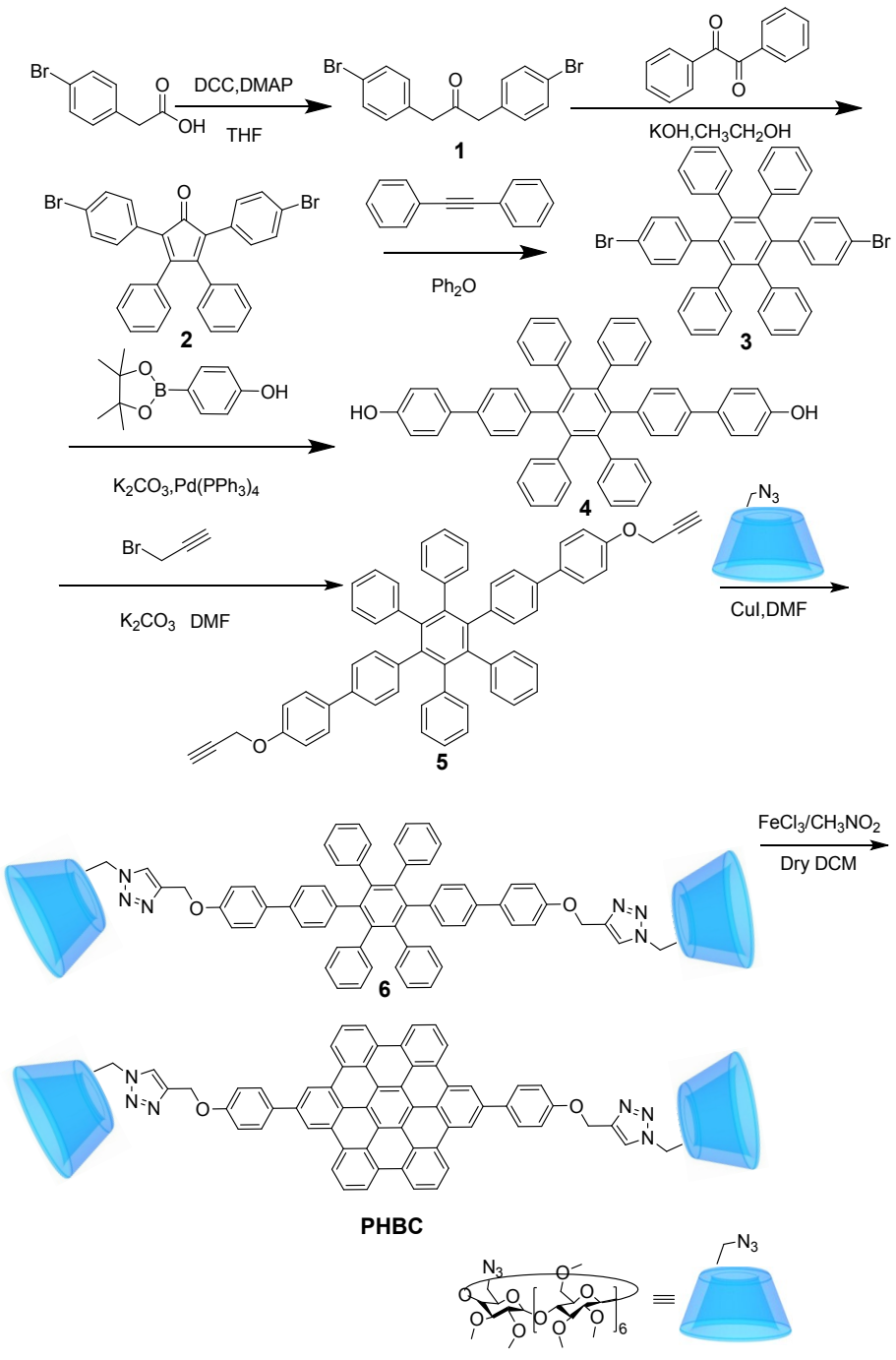
Experimental section

Materials. All chemicals were commercially available reagent grade unless noted. β-CD was recrystallized from water twice and dried in vacuo at 90°C for 24 h prior to use. Anhydrous CH_2Cl_2 and dry DMF were dried over CaH_2 for 24 h and then distilled prior to use. Column chromatography was performed on 200-300 mesh silica gel.

Instruments. NMR spectra were recorded on a Bruker AV400 instrument. UV/Vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer in a quartz cell (light path 10 mm) at 25°C. Steady-state fluorescence emission spectra were recorded in a conventional quartz cell (10 × 10 × 45 mm) at 25 °C on a Varian Cary Eclipse equipped with a Varin Cary single-cell peltier accessory to control temperature. TEM images were acquired by a high-resolution transmission electron microscope (Philips Tecnai G2 20 S-TWIN microscope) operating at an accelerating voltage of 200 keV. The samples were prepared by placing a drop of solution onto a carbon-coated copper grid and air-dried. The SEM images were recorded on a JEOL JSM-7500F scanning electronic microscope operating at an accelerating voltage of 30 keV. The fluorescence lifetimes were measured by time-correlated single photon counting on a FLS920 instrument (Edinburg Instruments Ltd., Livingstone, UK) with a H_2 pulse lamp.

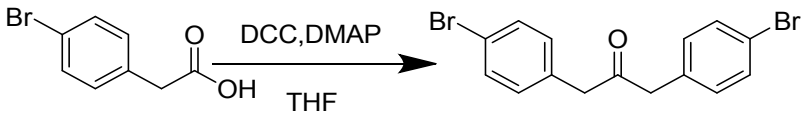
Synthesis and characterization.

Synthetic routes of PHBC:



Scheme 1. Synthetic routes of **PHBC**.

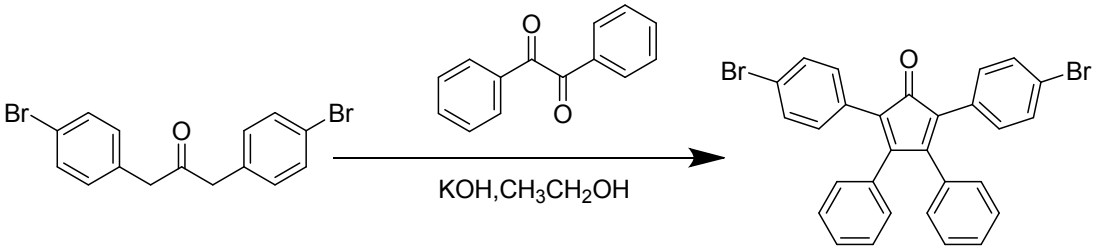
1.1 The synthesis of 1[1]



1

2-(4-Bromophenyl)acetic acid (8.00 g, 37.20 mmol) was added to a solution of **DCC** (8.06 g, 39.06 mmol) and **DMAP** (1.36 g, 11.16 mmol) in THF. The reaction mixture was stirred at room temperature for 3 h, then filtered and concentrated under vacuum. The residue was purified by chromatography to give **1** as a white solid (3.95 g, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.1 Hz, 4H), 7.01 (d, J = 8.1 Hz, 4H), 3.68 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.31, 132.64, 131.87, 131.23, 121.28, 48.48.

1.2 The synthesis of 2[2]

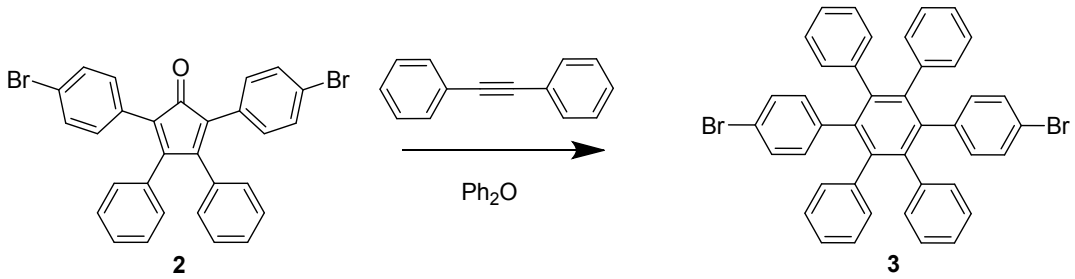


1 **2**

A solution of KOH (1.15 g, 20.55 mmol) in ethanol (50 mL) was added to a mixture of benzil (4.80 g, 22.83 mmol) and **1** (8.40 g, 22.83 mmol) in ethanol (100 mL). The reaction mixture was refluxed for 1 h and then cooled to 0 °C. The precipitate was collected by filtration to give **2** (10.20 g, 82%) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.5 Hz, 4H), 7.28 (d, J = 7.4 Hz, 2H), 7.19 (t, J = 7.5 Hz, 4H), 7.09 (d, J = 8.5 Hz, 4H),

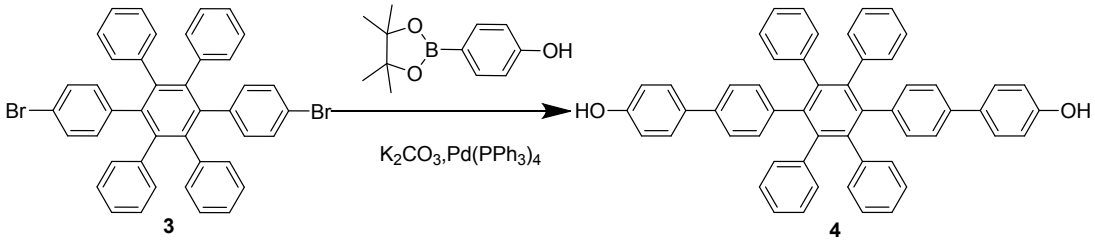
6.90 (d, J = 7.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.54, 155.00, 132.56, 131.64, 131.35, 129.49, 129.17, 128.90, 128.23, 124.37, 122.00.

1.3 The synthesis of 3[3]



1,2-Diphenylethyne (0.493 g, 2.77 mmol) and **2** (1.50 g, 2.77 mmol) was suspended in diphenylether. The reaction mixture was refluxed under N_2 for 24 h, then cooled to room temperature. The solvent was removed under vacuum, and the resulting residue was purified by chromatography to give compound **3** (1.68 g, 88%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, J = 8.4 Hz, 4H), 6.88 – 6.87 (m, 12H), 6.80 – 6.78 (m, 8H), 6.68 (d, J = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.54, 155.00, 132.56, 131.64, 131.35, 129.49, 129.17, 128.90, 128.23, 124.37, 122.00.

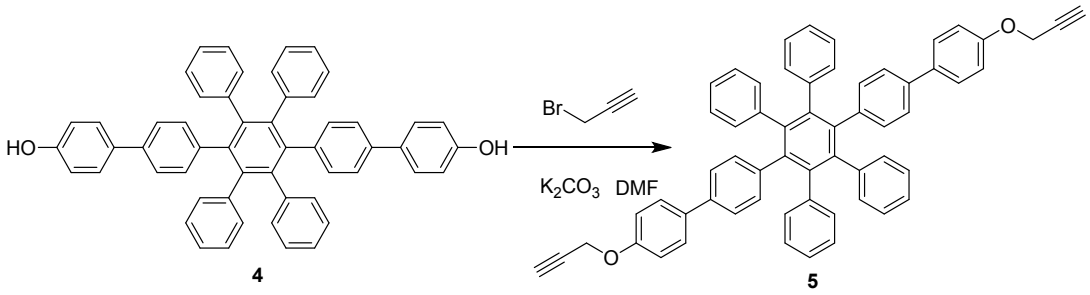
1.4 The synthesis of 4



$Pd(PPh_3)_4$ (0.83 g, 5% mol) and K_2CO_3 (2.00 g, 14.44 mmol) was added to a mixture of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (3.18 g, 14.44 mmol) and **3** (4.00 g,

5.78 mmol) in THF under N_2, and the reaction mixture was refluxed for 72 h. After the mixture was cooled to room temperature, acidified with diluted HCl, and then concentrated, the residue was washed with H_2O and dried under vacuum. The crude product **4** was used for next step directly without further purification.

1.5 The synthesis of 5



K_2CO_3 (0.31 g, 2.23mmol) was added to a solution of **4** (0.40 g, 0.56 mmol) in anhydrous DMF, which was stirred under N_2 for 30 min, and then propargyl bromide (0.33 g, 2.23mmol, 80 wt% solution in toluene) was added. The reaction mixture was heated at 50 ℃ for 48 h, cooled and poured into the ice water, then extracted with DCM. The organic layer was washed with H_2O, saturated NaCl solution, dried with anhydrous Na_2SO_4, filtrated and concentrated. The residue was purified by chromatography to give **5** (0.24 g, 54%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.8 Hz, 4H), 7.08 (d, J = 8.3 Hz, 4H), 6.95 (d, J = 8.8 Hz, 4H), 6.86 – 6.84 (m, 24H), 4.69 (d, J = 2.4 Hz, 4H), 2.50 (t, J = 2.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.75, 140.63, 140.46, 140.04, 139.31, 136.77, 134.29, 131.84, 131.47, 127.72, 126.68, 125.24, 124.72, 115.04, 78.55, 75.54, 55.86. MS (MALDI-TOF): m/z calcd for ($C_{60}H_{42}O_2$):794.32, found: 794.30.

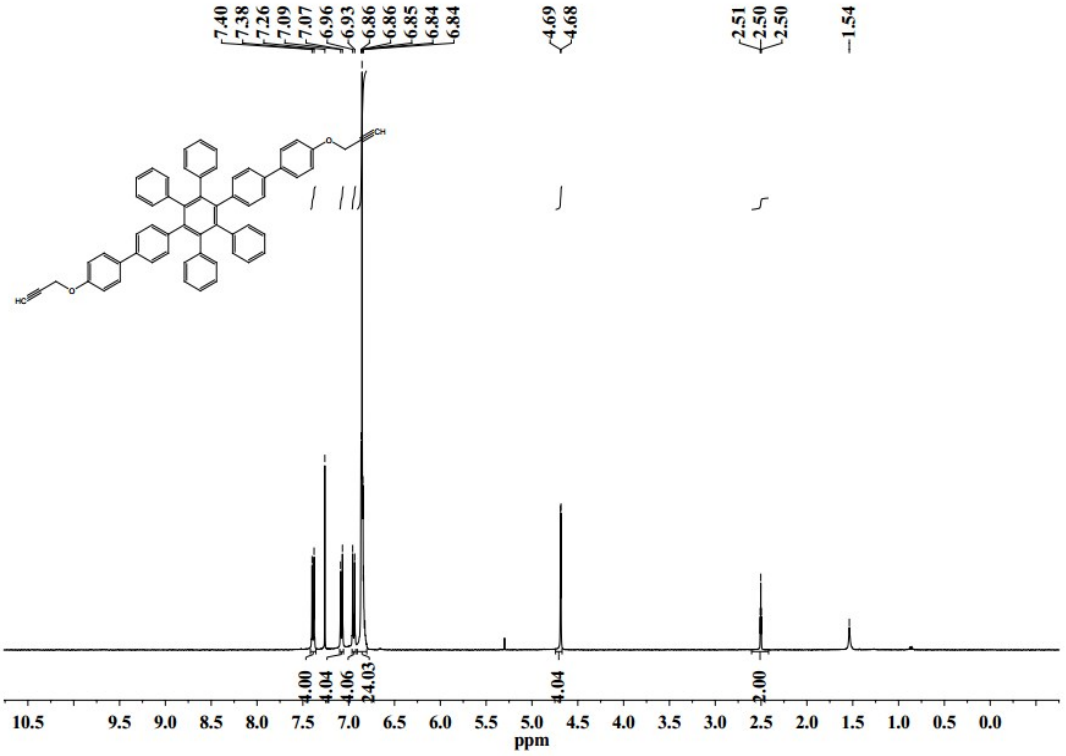


Figure S1. ^{1}H NMR (400 MHz) spectrum of **5** in $CDCl_3$ at 25 °C.

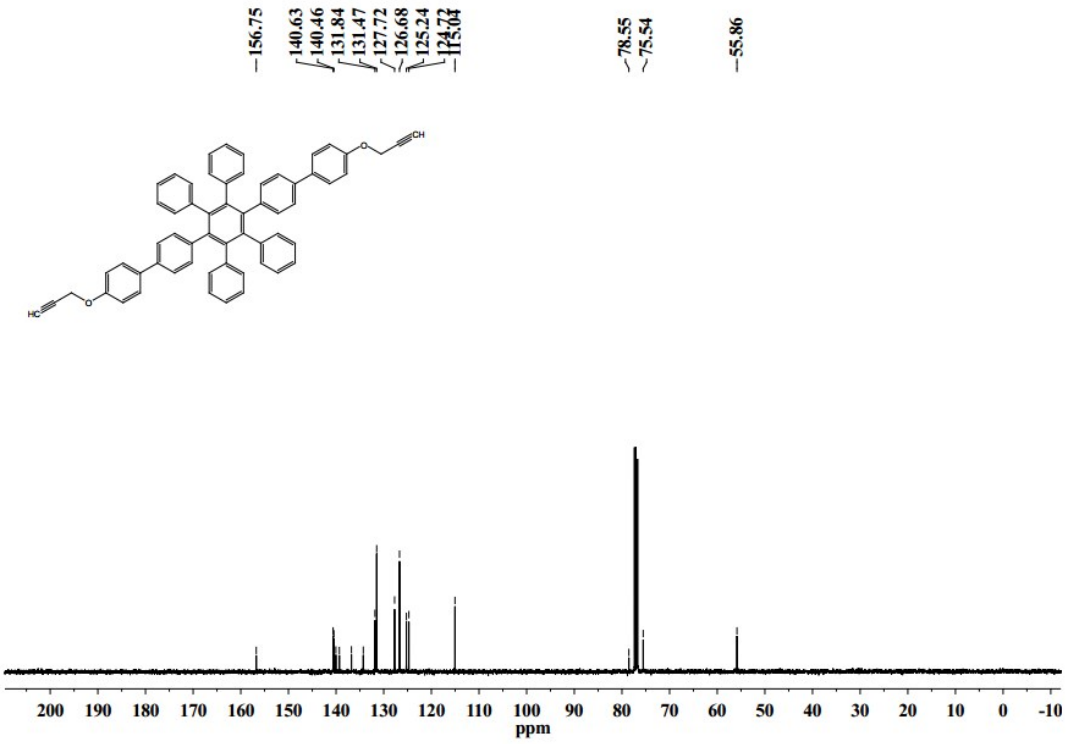
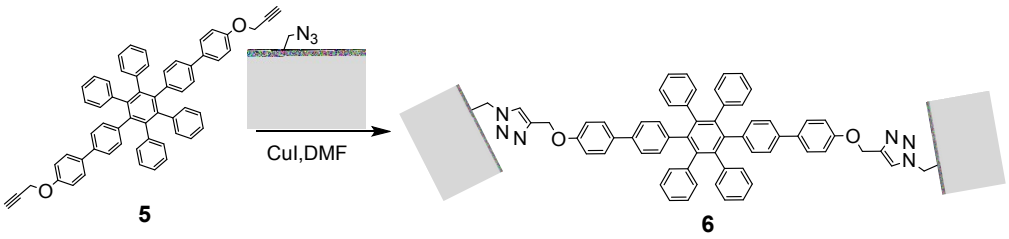


Figure S2. ^{13}C NMR (100 MHz) spectrum of **5** in $CDCl_3$ at 25 °C.

1.6 The synthesis of 6



CuI (47.6 mg, 0.25 mmol) was added to a solution of **5** (0.20 g, 0.25 mmol) and 6-deoxy-6-azido-permethyl-β-CD (0.91 g, 0.63 mmol) in dry DMF, and the reaction mixture was stirred at 60°C for 48 h. The solution was cooled to room temperature and filtrated. H_2O was added to the filtrate and then extracted with DCM. The organic layer was separated and then washed with H_2O, saturated NaCl solution, dried with anhydrous Na_2SO_4, filtrated and concentrated. The residue was purified by chromatography to give **6** (0.72 g, 78%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 2H), 7.36 (d, J = 8.6 Hz, 4H), 7.05 (d, J = 8.1 Hz, 4H), 6.96 – 6.78 (m, 28H), 5.25 (d, J = 3.5 Hz, 2H), 5.15 (m, 14H), 5.00 (d, J = 12.7 Hz, 2H), 4.71 – 4.65 (m, 2H), 4.18 – 2.86 (m, 202H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.48, 143.52, 140.60, 140.45, 139.97, 139.30, 136.72, 133.97, 131.84, 131.44, 127.76, 126.66, 125.22, 124.95, 124.63, 114.74, 99.26, 98.90, 98.80, 98.27, 83.00, 82.08, 81.96, 81.90, 81.78, 81.11, 80.25, 79.93, 79.35, 71.51, 71.26, 70.95, 70.75, 70.37, 62.06, 61.74, 61.48, 61.40, 61.32, 59.15, 59.11, 59.05, 59.01, 58.96, 58.84, 58.74, 58.68, 58.57, 58.42, 51.46; HR-MS (MALDI-TOF): *m/z* calcd for ($C_{184}H_{260}N_6O_{70}$+Na^+):3698.6933, found: 3698.6883.

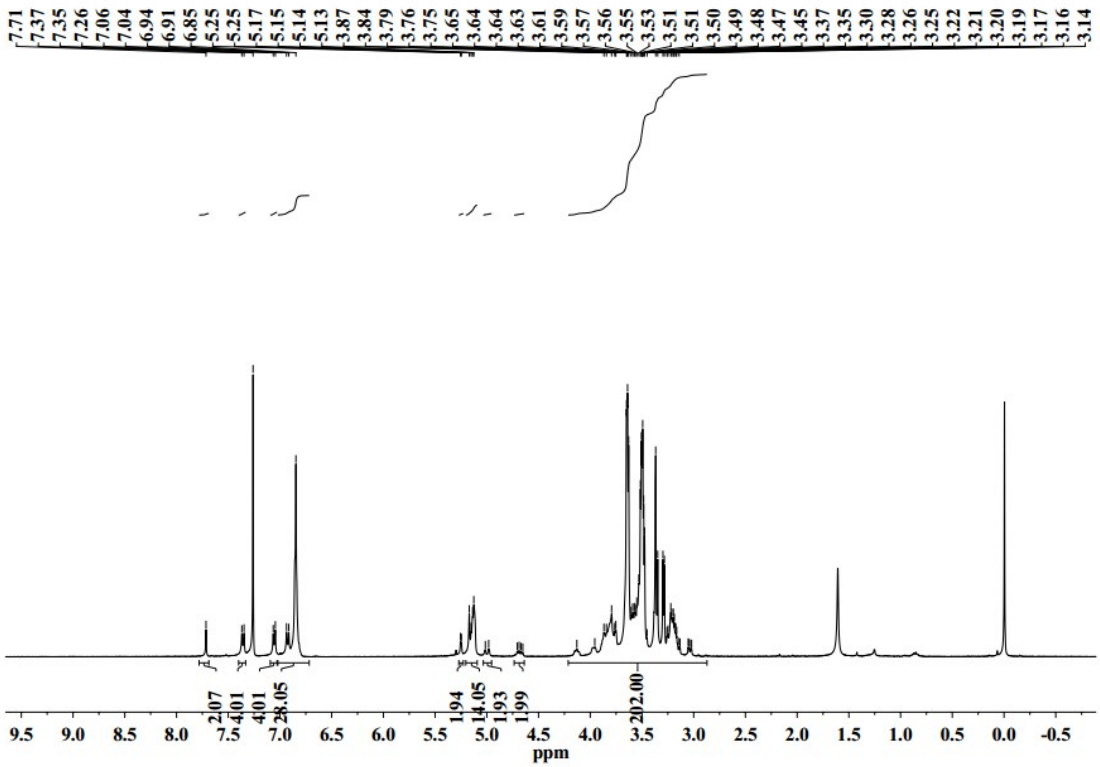


Figure S3. ^{1}H NMR (400 MHz) spectrum of **6** in $CDCl_3$ at 25 °C.

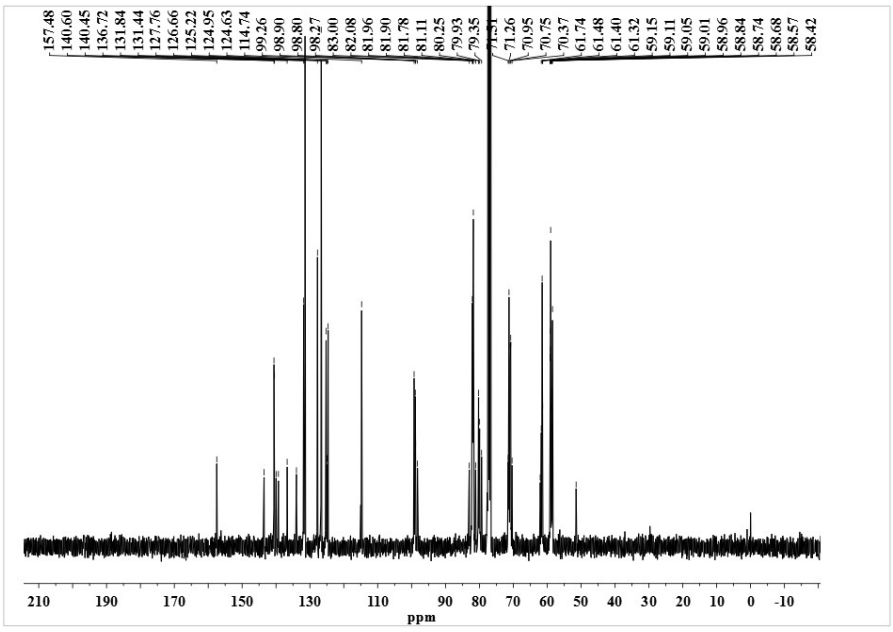


Figure S4. ^{13}C NMR (100 MHz) spectrum of **6** in $CDCl_3$ at 25 °C.

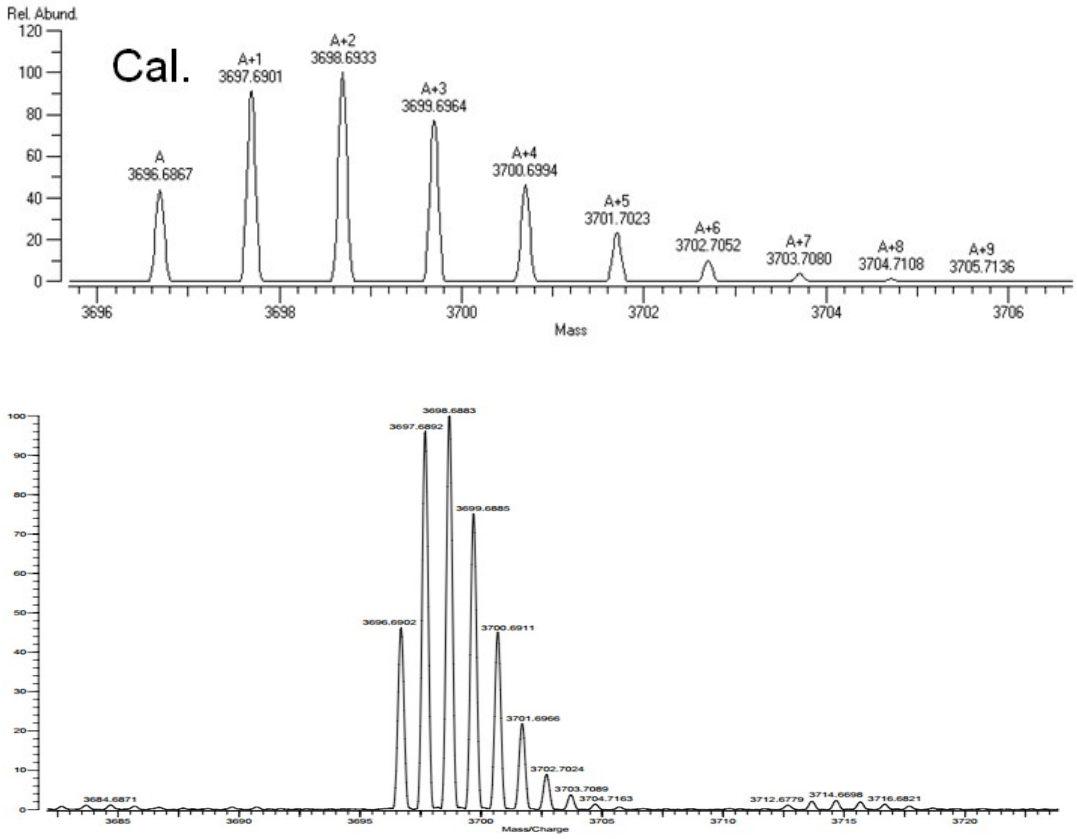
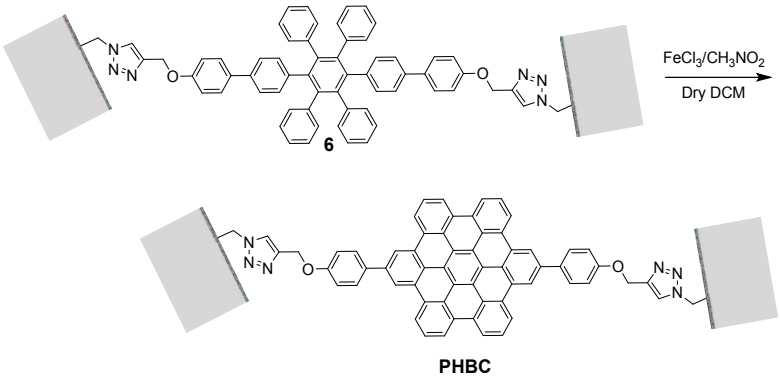


Figure S5. MALDI-MS spectrum of **6**.

1.7 The synthesis of PHBC[4]



Anhydrous $FeCl_3$ (0.64 g, 3.92mmol) in $MeNO_2$ (10 mL) was added to a solution of **6** (400

mg, 0.11 mmol) in dry DCM (200 mL) with argon bubbling through a glass tube. The reaction mixture was stirred for 3 h with continous argon bubbling, then the cooled MeOH (50 mL) was added to the reaction mixture to quench the reaction. The organic layer was washed with H_2O, saturated NaCl solution, dried with anhydrous Na_2SO_4, then filtrated and evaporated to dryness. The residue was purified by chromatography to give **PHBC** (0.25g, 63%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 – 8.25 (m, 12H), 7.94 – 7.89 (m, 6H), 7.52 (br, 4H), 7.36 (br, 4H), 5.47 – 5.41 (m, 4H), 5.26– 4.95 (m, 16H), 4.13 – 3.13 (m, 202H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.03, 143.59, 136.51, 134.83, 129.28, 128.77, 125.42, 123.59, 122.51, 120.60, 118.89, 115.22, 99.27, 98.89, 98.77, 98.38, 82.69, 82.21, 82.07, 82.02, 81.83, 81.61, 81.26, 80.36, 79.91, 79.80, 79.10, 71.61, 71.39, 70.98, 70.82, 70.75, 70.37, 62.27, 61.84, 61.48, 61.45, 61.39, 61.34, 59.35, 59.19, 59.04, 58.70, 58.65, 58.48, 58.43, 58.37, 51.38; HR-MS (MALDI-TOF): *m/z* calcd for ($C_{184}H_{248}N_6O_{70}$+ Na^+):3686.5994, found: 3686.5949.

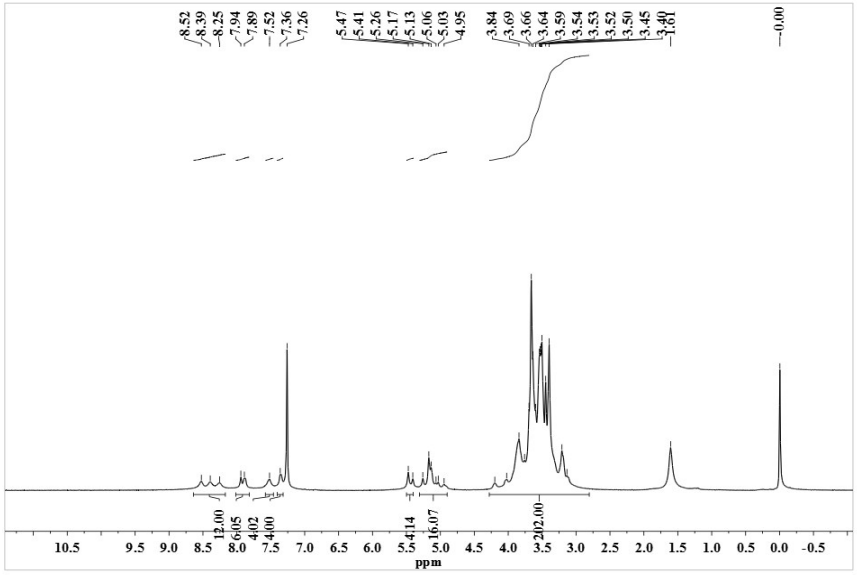


Figure S6. ^{1}H NMR (400 MHz) spectrum of **PHBC** in $CDCl_3$ at 25 °C.

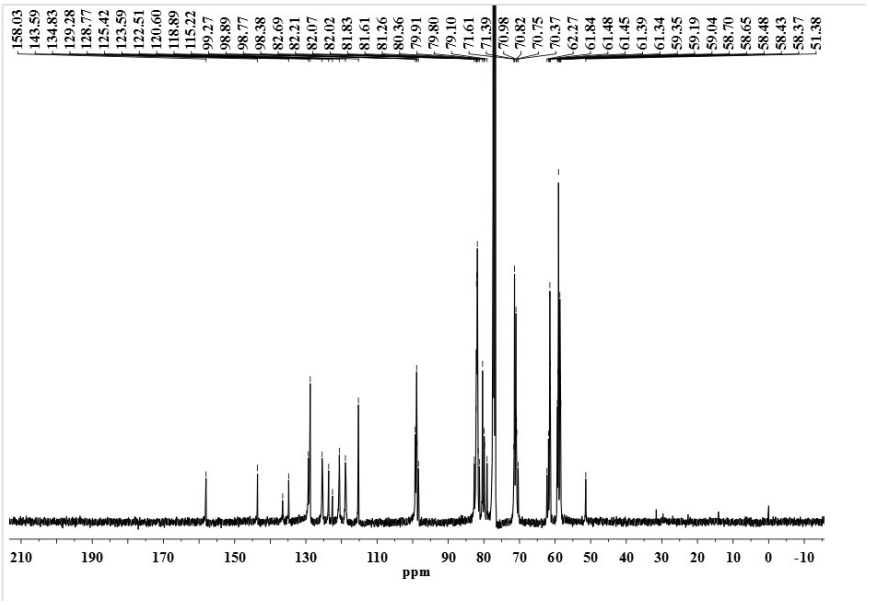


Figure S7. ^{13}C NMR (100 MHz) spectrum of **PHBC** in $CDCl_3$ at 25 °C.

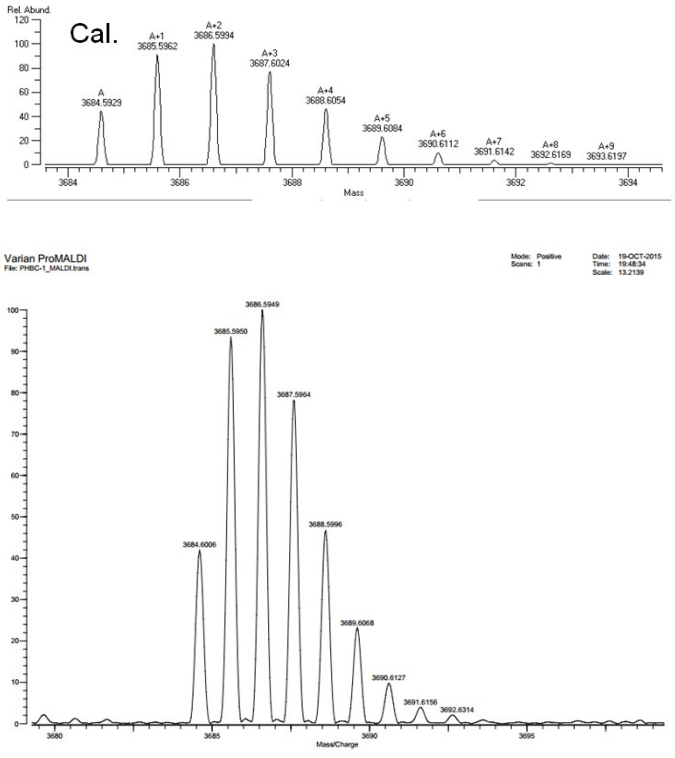


Figure S8. MALDI-MS spectrum of **PHBC**.

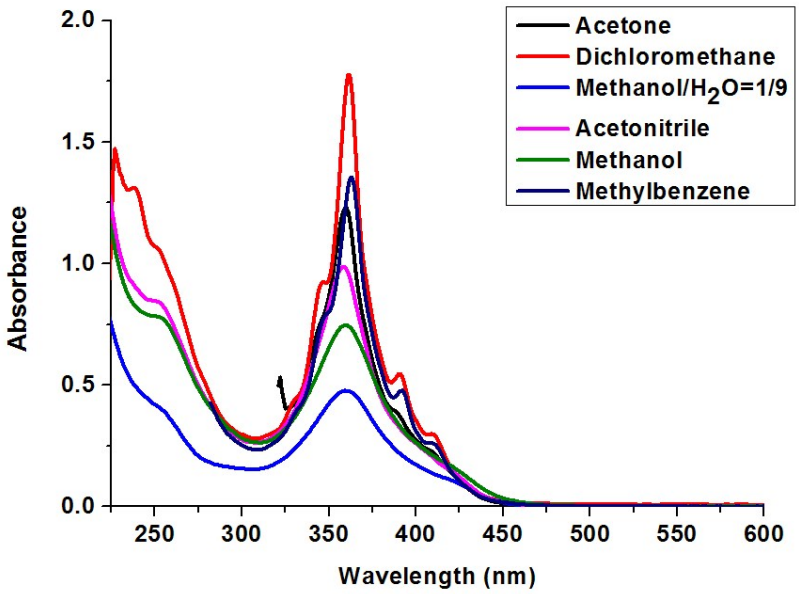


Figure S9. UV-vis spectra of **PHBC** (1.0×10^{-5} M) in different solvents at 25°C.

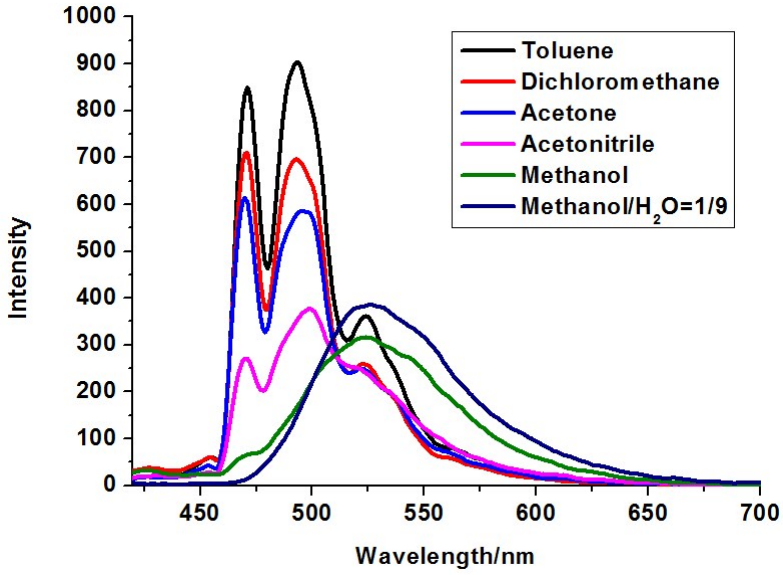


Figure S10. Emission spectra of **PHBC** (1.0×10^{-6} M , λ_{ex}=365 nm) in different solvents.

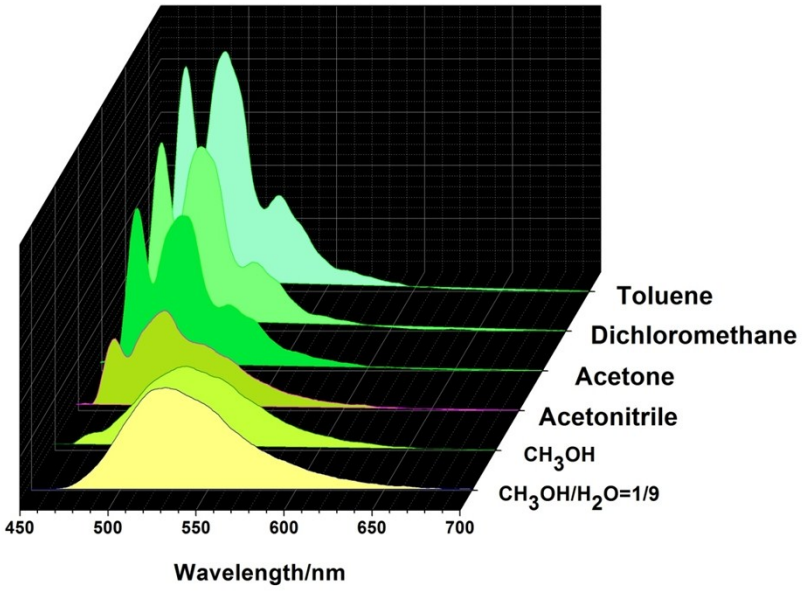


Figure S11. Emission spectra of **PHBC** (1.0×10^{-6} M, λ_{ex}=365 nm) in different solvents.

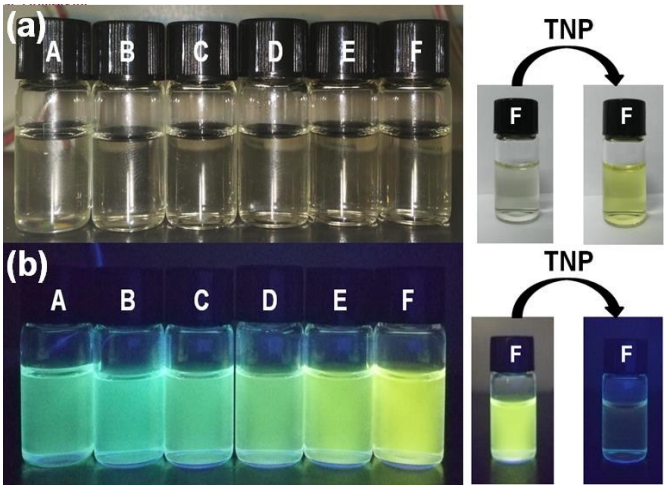


Figure S12. The color of **PHBC** in different solvents under (a)visible light and (b)UV light(365 nm): A) toluene, B) dichloromethane, C) acetone, D) acetonitrile, E) methanol, F) methanol/H_2O=1/9.

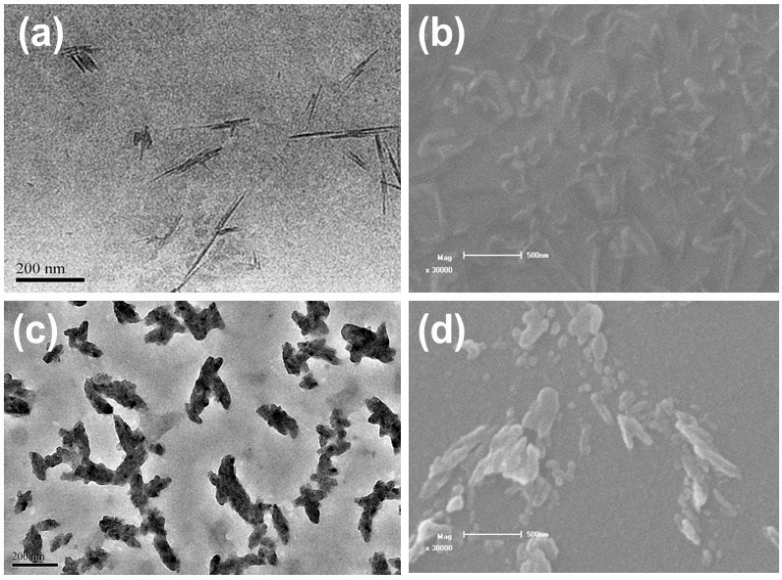


Figure S13.TEM (a,c) and SEM (b,d) images of **PHBC** in CH_3OH (a,b) and CH_3OH:H_2O =1:9 (c,d).

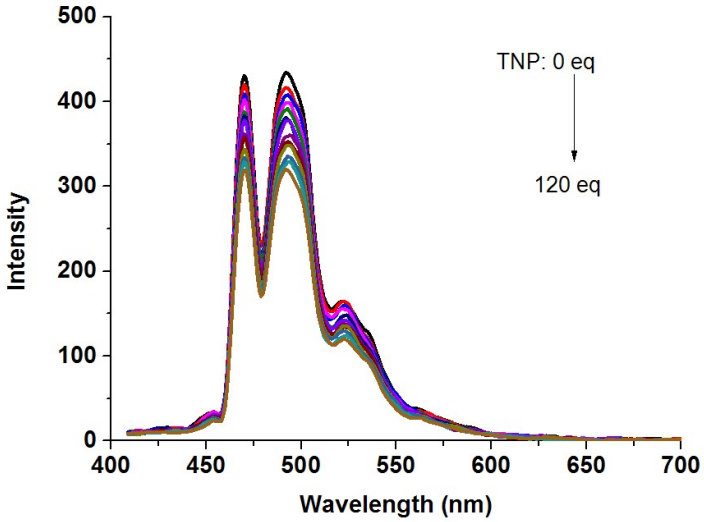


Figure S14. Emission spectra of **PHBC** (1.0×10^{-6} M in DCM, λ_{ex}=365 nm) in the presence of **TNP** (0-120 eq) at various concentrations.

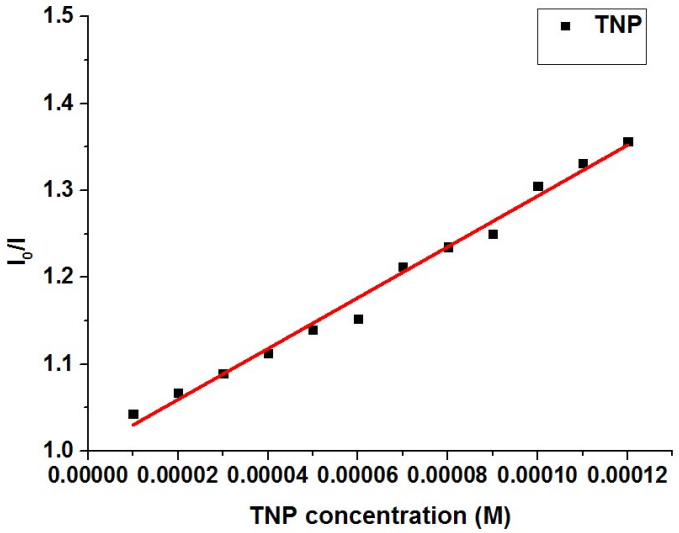


Figure S15. Stern−Volmer plot for quenching of **PHBC** with **TNP** in DCM.

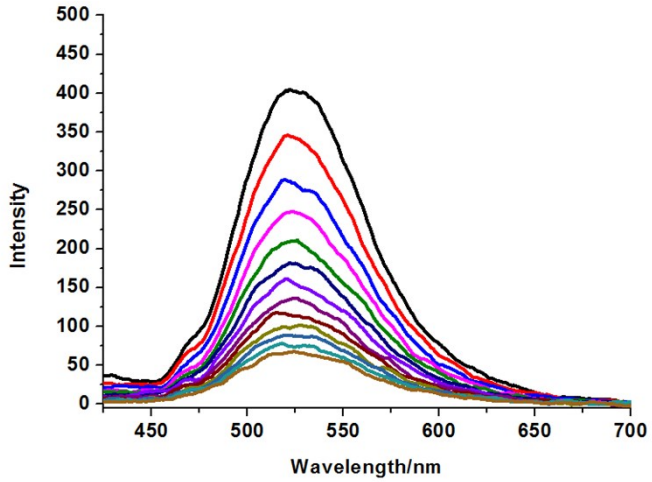


Figure S16. Emission spectra of **PHBC** (1.0×10^{-6} M in CH_3OH, λ_{ex}=365 nm) with **TNP** (0-120 eq) at various concentrations.

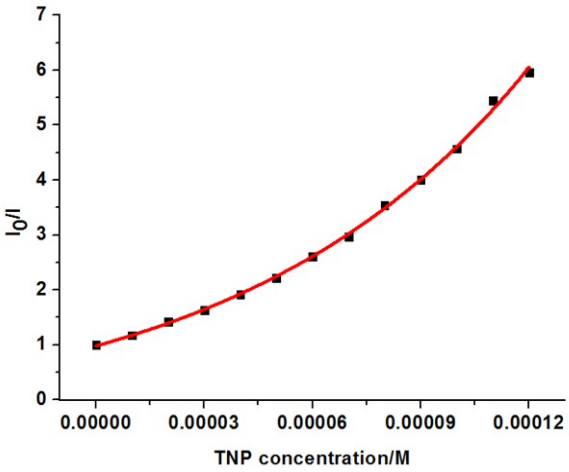


Figure S17. Stern−Volmer plot for quenching of **PHBC** with **TNP** in CH_3OH.

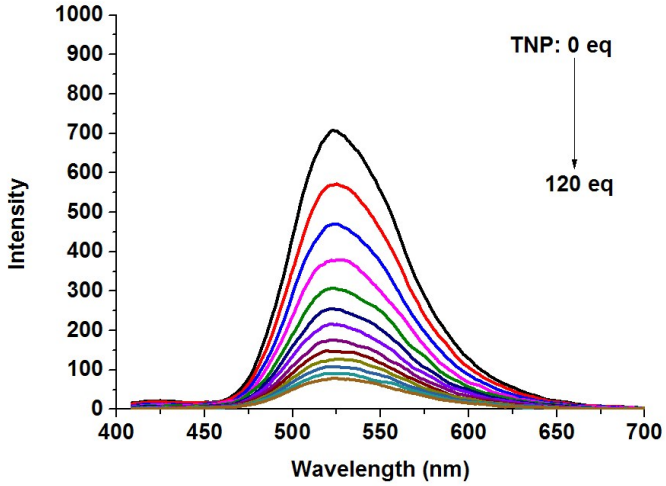


Figure S18. Emission spectra of **PHBC** (1.0×10^{-6} M in CH_3OH/H_2O=6/4, λ_{ex}=365 nm) with **TNP** (0-120 eq) at various concentrations.

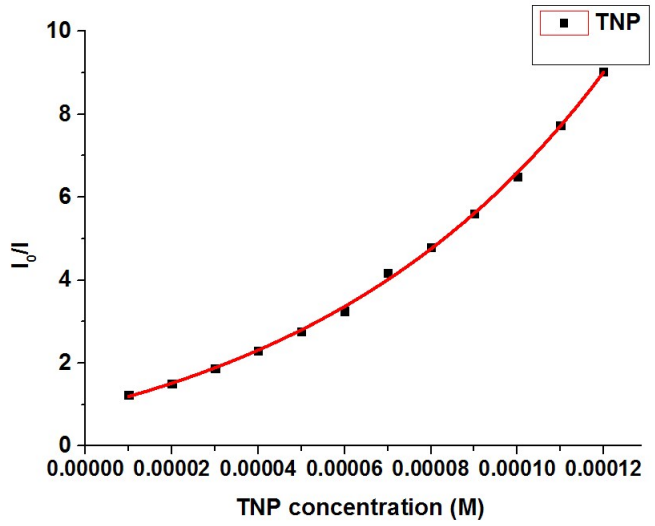


Figure S19. Stern−Volmer plot for quenching of **PHBC** with **TNP** in CH_3OH/H_2O =6/4.

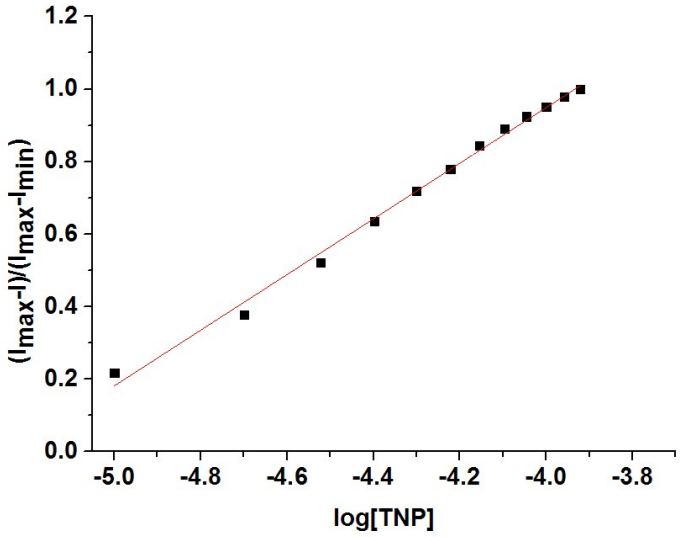


Figure S20. $(I_{max}-I)/(I_{max}-I_{min})$ vs log[**TNP**] plots for **PHBC** in CH_3OH/H_2O=6/4.

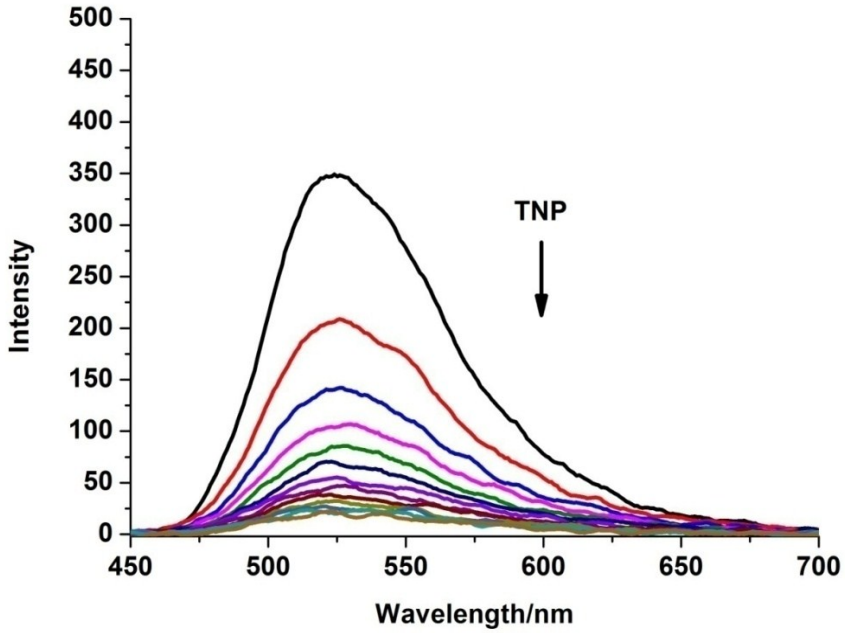


Figure S21. Emission spectra of **PHBC** (1.0×10^{-6} M in CH_3OH/H_2O=1/9, λ_{ex}=365 nm) with **TNP** (0-120 eq) at various concentrations.

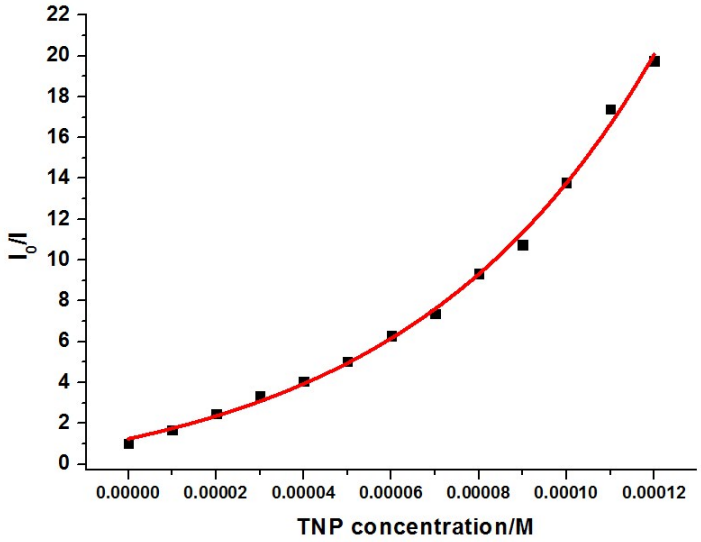


Figure S22. Stern−Volmer plot for quenching of **PHBC** with **TNP** in CH_3OH/H_2O =1/9.

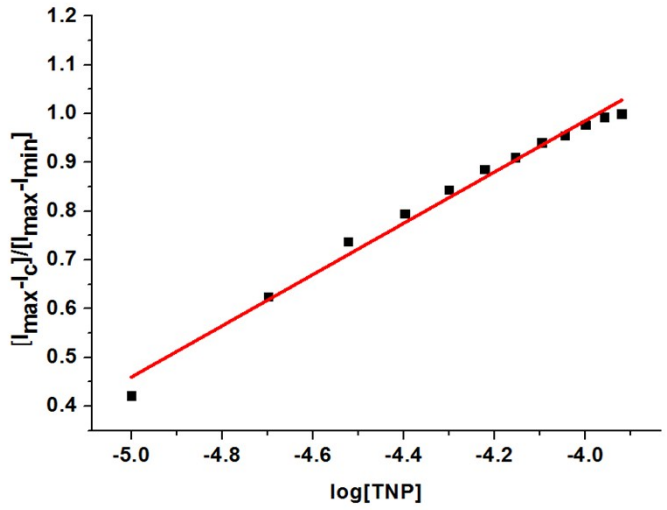


Figure S23. $(I_{max}-I)/(I_{max}-I_{min})$ vs log[**TNP**] plots for **PHBC** in CH_3OH/H_2O=1/9.

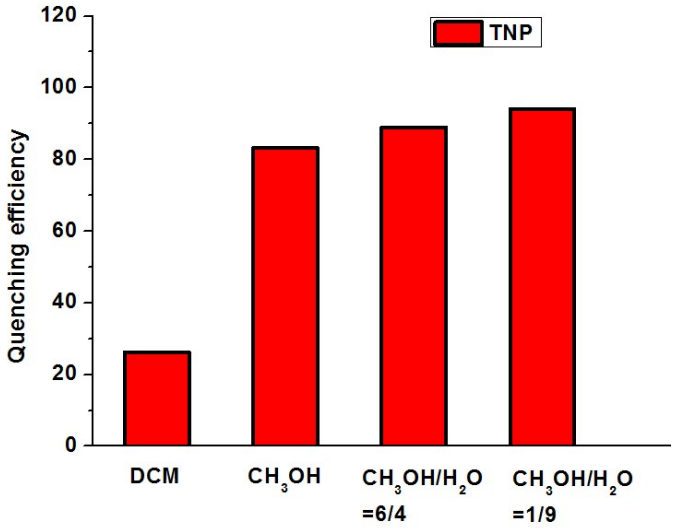


Figure S24. Quenching efficiency of **PHBC** (1.0×10^{-6} M, λ_{ex}=365 nm) with **TNP** (0-120 eq) at different solvents.

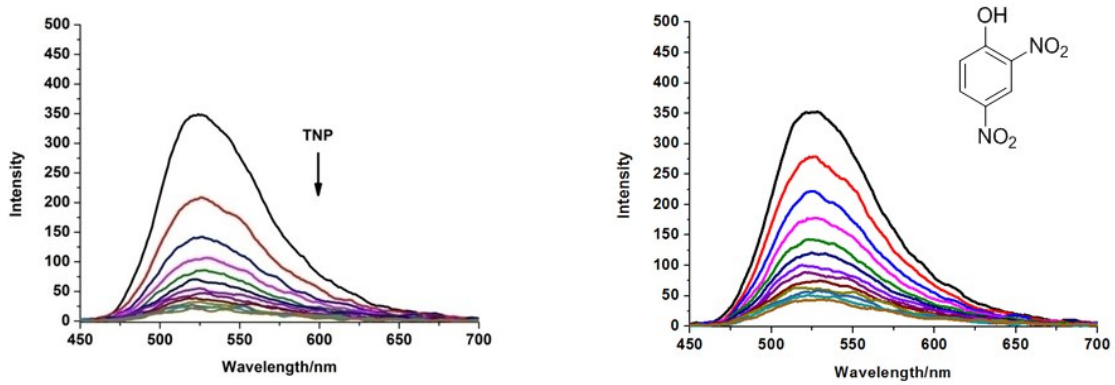


Figure S25. Emission spectra of **PHBC** (1.0×10^{-6} M in CH_3OH/H_2O=1/9, λ_{ex}=365 nm) toward different analytes (0-120 eq) at various concentrations.

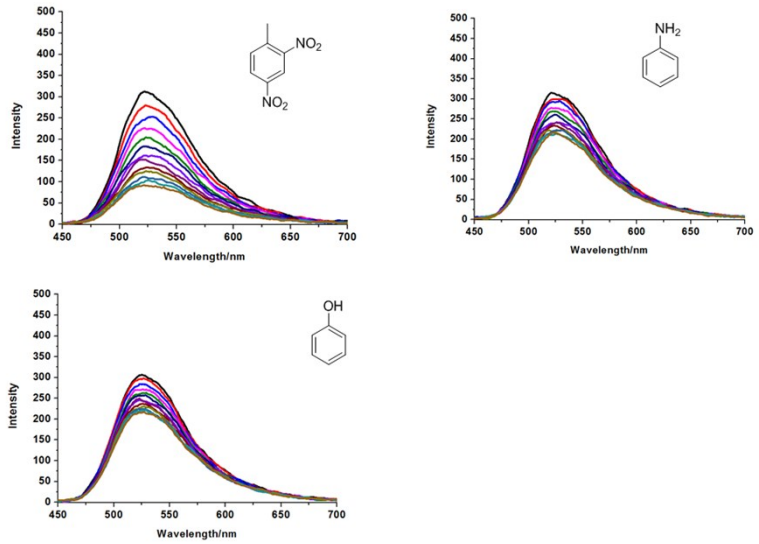


Figure S26. Emission spectra of **PHBC** (1.0×10^{-6} M in CH_3OH/H_2O=1/9, λ_{ex}=365 nm) toward different analytes (0-120 eq) at various concentrations.

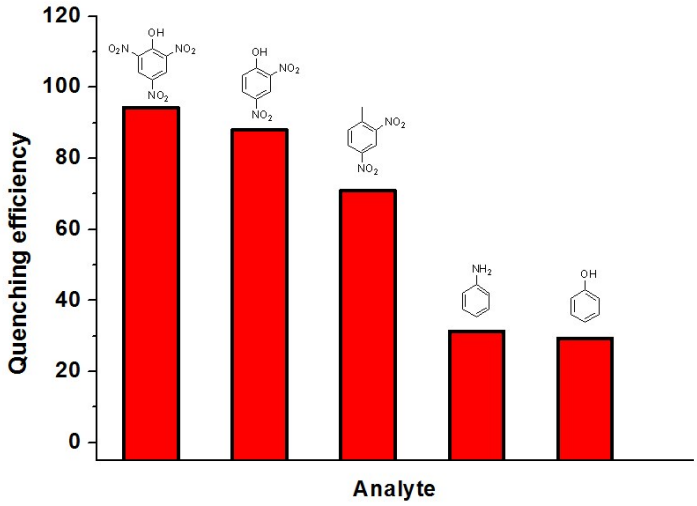


Figure S27. Quenching efficiency of **PHBC** (1.0×10^{-6} M, λ_{ex}=365 nm) toward different analytes (0-120 eq) in CH_3OH/H_2O=1/9.

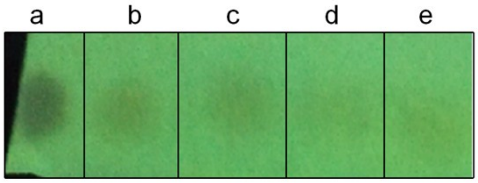
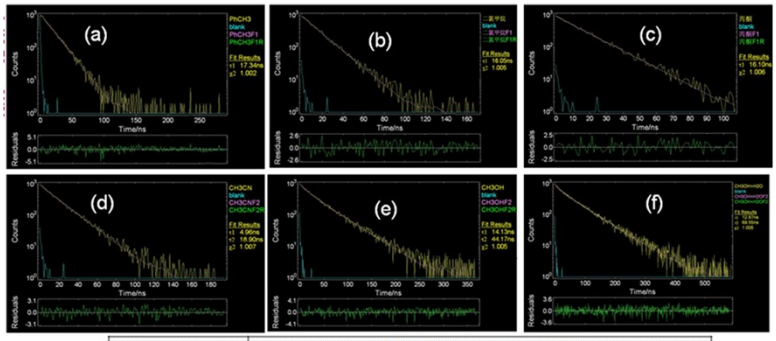


Figure S28. By applying a small spot of different concentrations of **TNP** ((a) 1×10^{-4} M, (b) 1×10^{-6} M, (c) 1×10^{-8} M, (d) 1×10^{-10} M, (e) 1×10^{-12} M on test strips made from aggregates of **PHBC.**



sample	Lifetime(ns)(%contribution)			
	τ_1	τ_2	τ	χ^2
PHBC in PhCH3	17.34		17.34	1.002
PHBC in DCM	16.05		16.05	1.005
PHBC in acetone	16.10		16.10	1.006
PHBC in CH_3CN	4.96(5.27%)	18.90(94.73%)	18.17	1.007
PHBC in CH_3OH	14.13(13.17%)	44.17(86.83%)	40.21	1.005
PHBC in CH_3OH/H_2O=1/9	12.87(6.43%)	69.55(93.57%)	65.91	1.005

Figure S29. The fluorescence lifetime of **PHBC (**1.0×10^{-5} M**)** in (a) $PhCH_3$, (b) DCM, (c) acetone, (d) CH_3CN, (e) CH_3OH and (f) CH_3OH/ H_2O=1/9 (λ_{ex}= 365 nm).

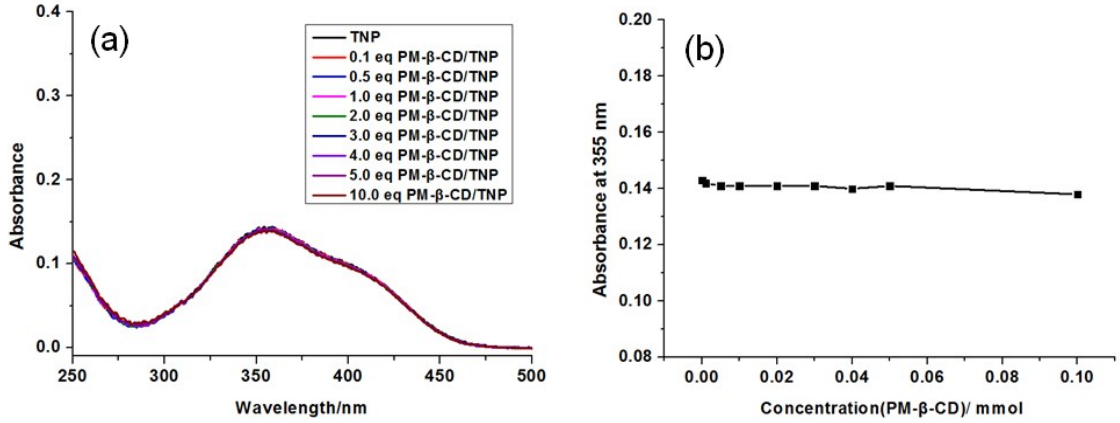


Figure S30. (a) UV-vis spectra of **TNP (**1.0×10^{-5} M**)** with the gradual addition of **PM-β-CD**. (b) Absorbance change of **TNP** with the gradual addition of **PM-β-CD** at 355 nm.

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