

Multifunctional porous organic polymers as an ideal platform for gas uptake, metal ion sensing, and cell

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Characterization

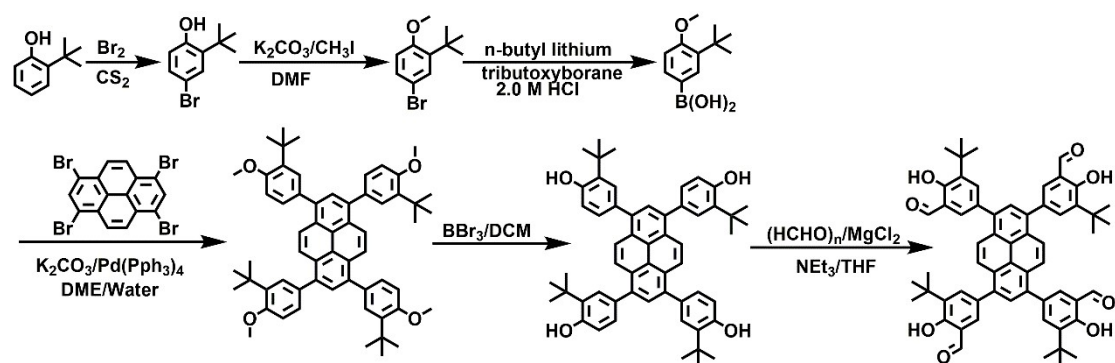
The infrared spectra were recorded from 500 to 3500 cm^{-1} on an Avatar FT-IR 360 spectrometer by using KBr pellets. Elemental analyses were measured by an Elementar model vario EL cube analyzer. Field emission scanning electron microscopy was recorded on a SU8020 model HITACHI microscope. Powder X-ray diffraction data were performed on a PANalytical BV Empyrean diffractometer by depositing powder on glass substrate, from $2\theta = 4.0^\circ$ to 35° with 0.02° . Thermogravimetric analysis (TGA) was performed on a TA Q500 thermogravimeter with the heating at a rate of $10^\circ\text{C min}^{-1}$ from 35°C to 800°C under nitrogen. Nitrogen sorption isotherms were measured at 77 K with a JW-BK 132F analyzer. The absolute fluorescence quantum yields were measured on Edinburgh FLS920 by using an integrating sphere. Photoluminescence spectra were recorded on a Cary Eclipse Fluorescence Spectrophotometer. SI-CMP was dispersed in THF to yield a nearly transparent dispersion which was immediately subjected to fluorescence spectroscopy. After the addition ions, time-dependent fluorescence spectra were recorded.

Experimental section

Materials

Anhydrous tetrahydrofuran (THF, stabilized with BHT), acetone, carbon disulfide, chloroform, dioxane, mesitylene, acetic acid, 2-tert-butylphenol, hydrazone monohydrate, methyl iodide, and other chemicals were obtained from TCI, Wako, J&K Scientific, and Sigma-Aldrich.

Synthesis process for monomer



Scheme 1. Synthetic route of monomer

4-bromo-2-(tert-butyl) phenol : To a stirred solution of 2-tert-butylphenol (10.0 g, 66.5 mmol) in carbon disulfide (15 mL) was added a solution of bromine (10.7 g, 66.5 mmol) in carbon disulfide (5 mL) through dropping at 0 °C. The solution was stirred overnight at room temperature. Solvent was removed with a rotary evaporator to give a residue, and then the crude product was distilled under vacuum to give colorless oil (12.9 g, 85%). ¹H NMR (400 MHz, CDCl₃): 7.34 (d, Ar–H, 1H), 7.14-7.18 (dd, Ar–H, 1H), 6.54 (d, Ar–H, 1H), 4.87 (s, OH, 3H), 1.44 (s, C(CH₃), 9H) ppm.

4-bromo-2-(tert-butyl)-1-methoxybenzene: Substituted 4-bromo-2-(tert-butyl) phenol (5.0 g, 66 mmol), methyl iodide (9.4 g, 66 mmol), and anhydrous potassium carbonate (6.97 g, 66 mmol) were added in DMF (30 mL) at room temperature. The system was stirred at 15 h. The reaction was quenched by adding distilled water and extracted with ethyl acetate, and dried over anhydrous sodium sulfate. The solvent was evaporated and the residue was purified by column chromatograph. The product was isolated as a colorless powder (5.2 g, 98%). ¹H NMR (400 MHz, CDCl₃): 10.27 (s, Ar–H, 1H), 7.80 (d, Ar–H, 1H), 7.64 (d, Ar–H, 1H), 3.94 (s, OCH₃, 3H), 1.44 (s, C(CH₃), 9H) ppm.

3-(tert-butyl)-4-methoxyphenyl boronic acid: Under nitrogen, 4-bromo-2-(tert-butyl)-1-methoxybenzene (3.0 g, 12 mmol) in THF (50 mL) was added 1.6 M n-butyl lithium/hexane solution (9.3 mL, 14.8 mmol) at -78 °C, and the resulting mixture was stirred for 2 h. The tributoxyborane (3.7 g, 16 mol) was added to the solution and the mixture was gradually warmed up to room temperature. After the mixture was stirred further at room temperature for 12 h and the organic layer was washed with 2.0 M HCl (30 mL). The solution extracted with dichloromethane and dried over anhydrous sodium sulfate. The solvent was evaporated and the residue was purified by column chromatography on silica gel. The product was isolated as a colorless powder (1.95 g, 76%). ¹H NMR (400 MHz, DMSO): 7.76 (s, B(OH)₂, 2H), 7.68 (s, Ar–H, 1H), 7.64 (d, Ar–H, 1H), 6.91 (s, Ar–H, 1H), 3.81 (s, OCH₃, 3H), 1.33 (s, C(CH₃), 9H) ppm.

1,3,6,8-tetrakis(3-(tert-butyl)-4-methoxyphenyl) pyrene

(3-(tert-butyl)-4-methoxyphenyl) boronic acid (0.96 g, 4.0 mmol), potassium carbonate (0.612 g, 5.8 mmol), tetrakis(triphenylphosphine) Pd(0) (0.11 mg, 0.09 mmol), and 1,3,6,8-tetrabromopyrene (300 mg, 0.58 mmol) were added

in round bottom schlenk flask and kept under vacuum for 5 minutes. Under nitrogen flow, methoxymethane DME (10 mL) and water (10 mL) was added dropwise to the above reaction mixture. The solution was degassed through three freeze–pump–thaw cycles and then the system was heated at 100 °C for 48 h at nitrogen protection. The mixture was gradually warmed up to room temperature. The precipitate has been removed by filtration, washed several times with water and DME, and ether to give the greenish product (0.33 g, 67%). ¹H NMR (400 MHz, CDCl₃): 8.18 (s, Ar-H, 4H), 7.60 (s, Ar-H, 2H), 7.50 (s, Ar-H, 4H), 7.49 (s, Ar-H, 4H), 7.05 (d, Ar-H, 4H), 3.95 (d, OCH₃, 12H), 1.44 (s, C(CH₃), 36H) ppm.

4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl) tetrakis-(2-(tert-butyl)phenol)

Under nitrogen, 1,3,6,8-tetrakis(3-(tert-butyl)-4-methoxyphenyl) pyrene (0.11 g, 0.13 mmol) and BBr₃ (0.26 g, 1.03 mmol) in dry CH₂Cl₂ 30 mL were stirred for 48 h at 50 °C. The mixture was gradually warmed up to room temperature. The resulting mixture was slowly poured into cold water (50 mL), extracted with dichloromethane and dried over anhydrous sodium sulfate. The solvent was evaporated and the residue was purified by silica gel column chromatography using methylene chloride/ethyl acetate (20:1, v/v) as an eluent to give a green powder in 89% yield (91 mg). ¹H NMR (400 MHz, CDCl₃): 8.16 (s, Ar-H, 4H), 7.96 (s, Ar-H, 2H), 7.56 (d, Ar-H, 4H), 7.35-7.38 (dd, Ar-H, 4H), 6.84 (d, Ar-H, 4H), 4.90 (d, OCH₃, 12H), 1.48 (s, C(CH₃), 36H) ppm.

5,5',5'',5'''-(pyrene-1,3,6,8-tetrayl) tetrakis(3-(tert-butyl)-2-hydroxybenzaldehyde)

Under nitrogen protection, anhydrous magnesium dichloride (191 mg, 2.0 mmol) and paraformaldehyde (90 mg, 3.0 mmol), and anhydrous THF (20 mL) were added and stirred for 5 min. Triethylamine (0.30 mL, 2.12 mmol) was added dropwise by syringe and the mixture was stirred for 10 min. 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrakis(2-(tert-butyl)phenol) (0.20 g, 0.21 mmol) is also added dropwise. And then, this mixture is immersed in an oil bath at about 80 °C for 24 h. After cooling to room temperature, the organic layer was washed with 2.0 M HCl (30 mL). The solution was extracted with ethyl acetate and dried over anhydrous sodium sulfate. The solvent was evaporated and the residue was purified by silica gel column chromatography to give a pale-yellow powder in 87% yield (0.19 g). ¹H NMR (400 MHz, CDCl₃): δ = 11.93 (s, OH, 4H), 9.99 (s, CHO, 4H), 8.15 (s, Ar-H, 4H), 7.99 (s, Ar-H, 2H), 7.84 (d, Ar-H, 4H), 7.71 (d, Ar-H, 4H), 1.54 (d, C(CH₃), 36H) ppm.

Synthesis process for M-MOP-1

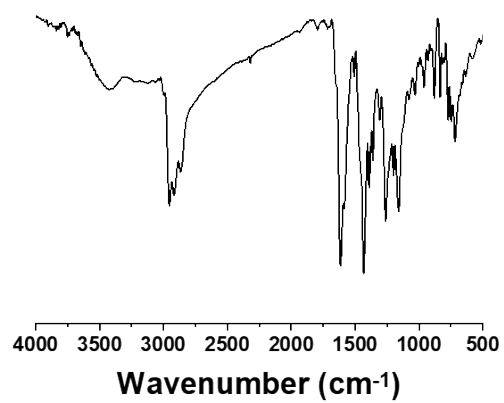
M-MOP-1: A 10 mL pyrex tube was charged with 5,5',5'',5'''-(pyrene-1,3,6,8-tetrayl) tetrakis (3-(tert-butyl)-2-hydroxybenzaldehyde (30 mg, 0.066 mmol), hydrazone hydrate (4 μL, 0.132 mmol), dioxane (1 mL), and AcOH (0.1 mL, 3 M). The mixture was sonicated for 2 minutes, degassed through three freeze–pump–thaw cycles, and sealed under vacuum. The reaction was heated at 120 °C yielding a yellow solid at the bottom of the tube which was isolated by centrifugation and washed with anhydrous tetrahydrofuran and dried under vacuum at 100 °C for 10 h to afford pale yellow powder in 87% isolated yield.

Synthesis process for M-MOP-2

M-MOP-2: A 10 mL pyrex tube was charged with 5,5',5'',5'''-(pyrene-1,3,6,8-tetrayl) tetrakis (3-(tert-butyl)-2-

hydroxybenzaldehyde (30 mg, 0.066 mmol), 1,4-phenylenediamine (14.3, 0.132 mmol), dioxane (1 mL), and AcOH (0.1 mL, 3 M). The mixture was sonicated for 2 minutes, degassed through three freeze-pump-thaw cycles, and sealed under vacuum. The reaction was heated at 120 °C yielding a yellow solid at the bottom of the tube which was isolated by centrifugation and washed with anhydrous tetrahydrofuran and dried under vacuum at 100 °C for 10 h to afford pale yellow powder in 90% isolated yield.

(a)



(b)

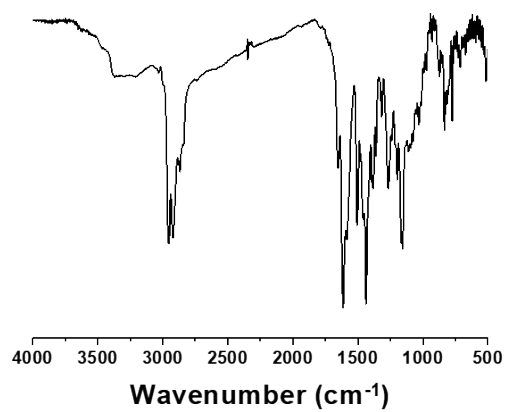


Fig. S1. FT IR spectra of (a) M-POP-1 and (b) M-POP-2.

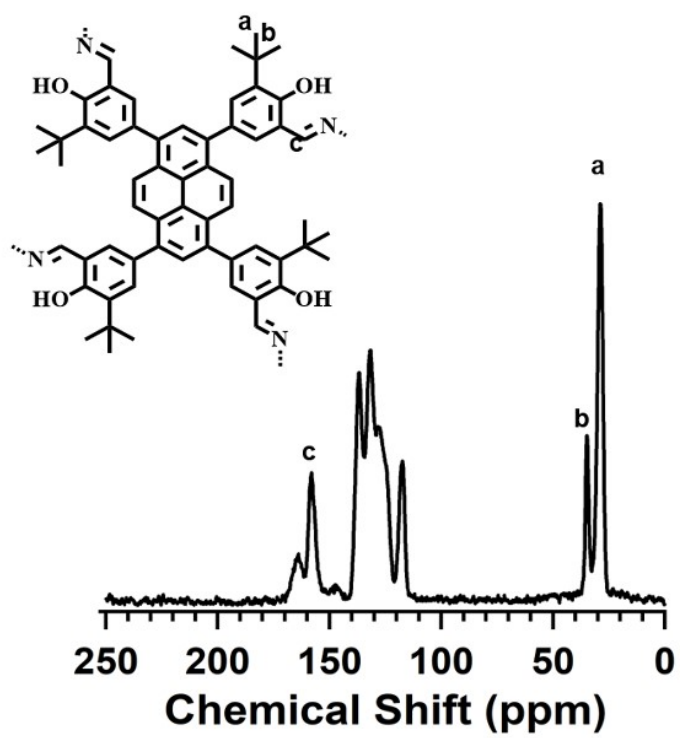


Fig. S2. ¹³C NMR spectrum of M-POP-1.

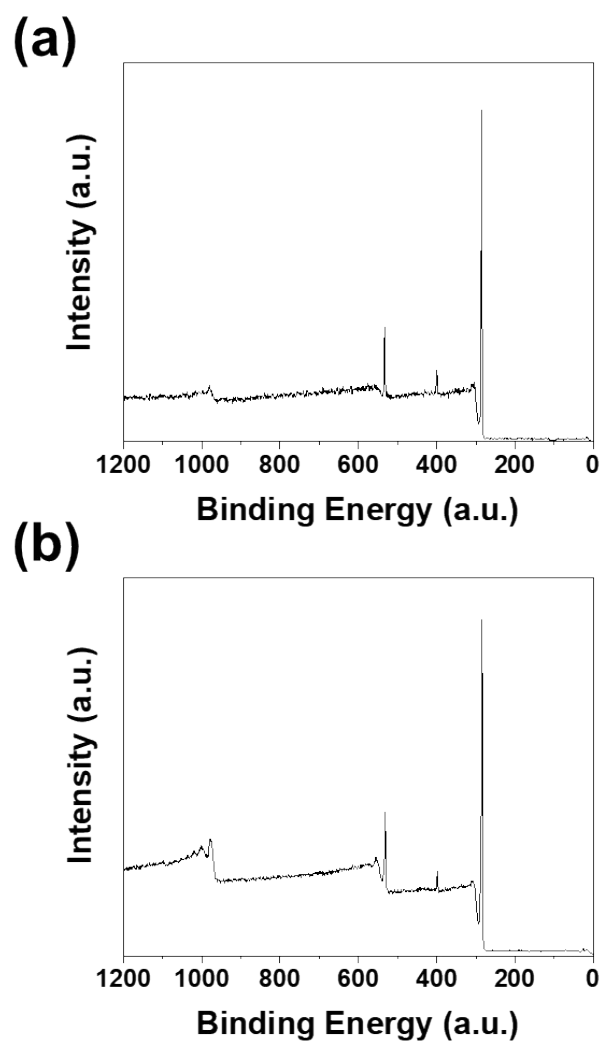


Fig. S3. XPS spectra of (a) M-POP-1 and (b) M-POP-2.

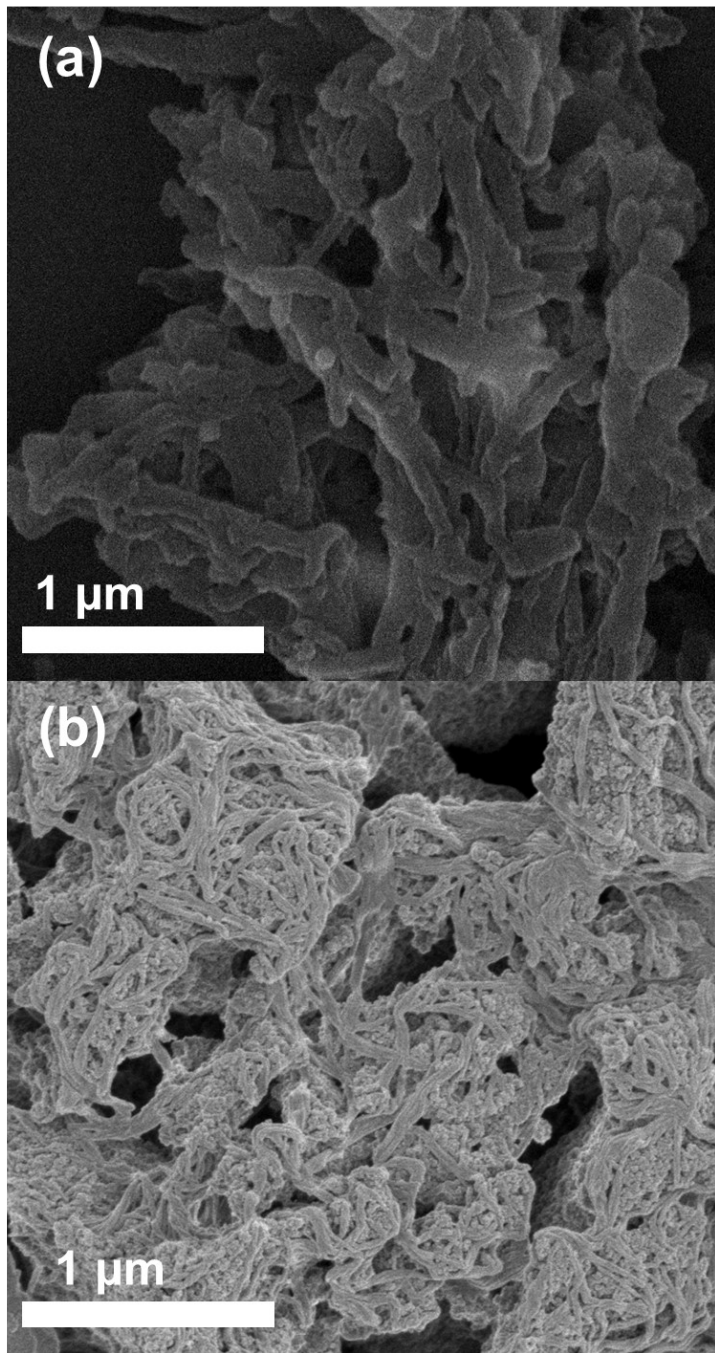
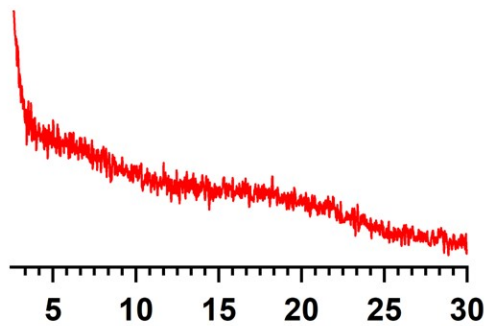


Fig. S4. SEM images of (a) M-POP-1 and (b) M-POP-2.

(a)



(b)

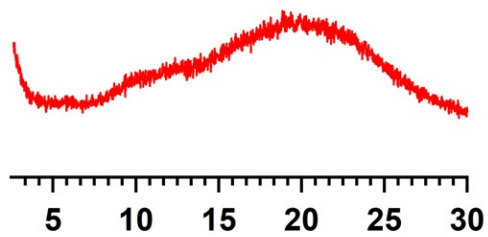


Fig. S5. PXR D patterns of (a) M-POP-1 and (b) M-POP-2.

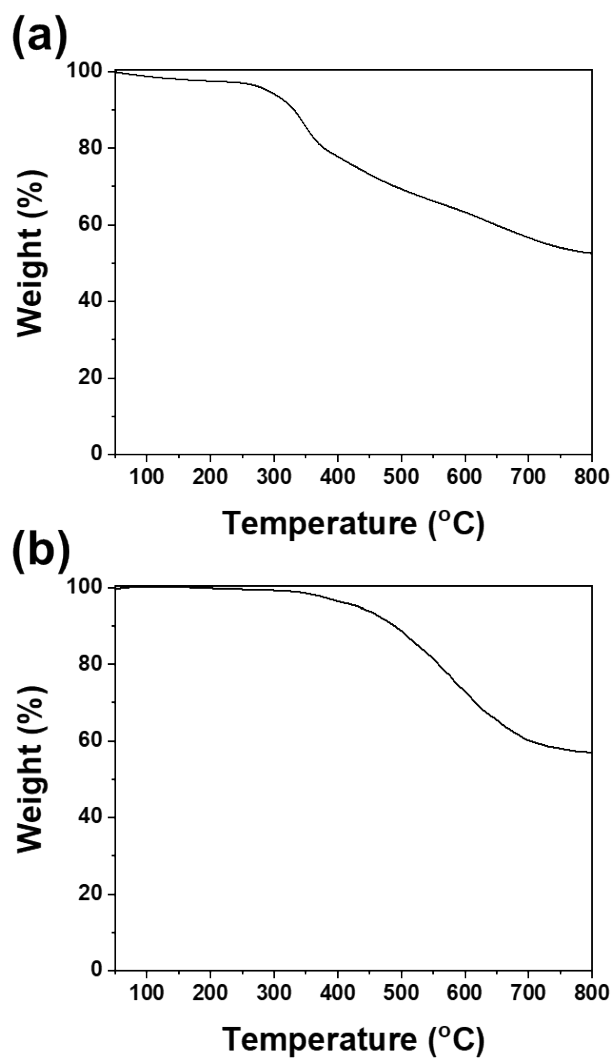


Fig. S6. TGA curves of (a) M-POP-1 and (b) M-POP-2 under nitrogen atmosphere.

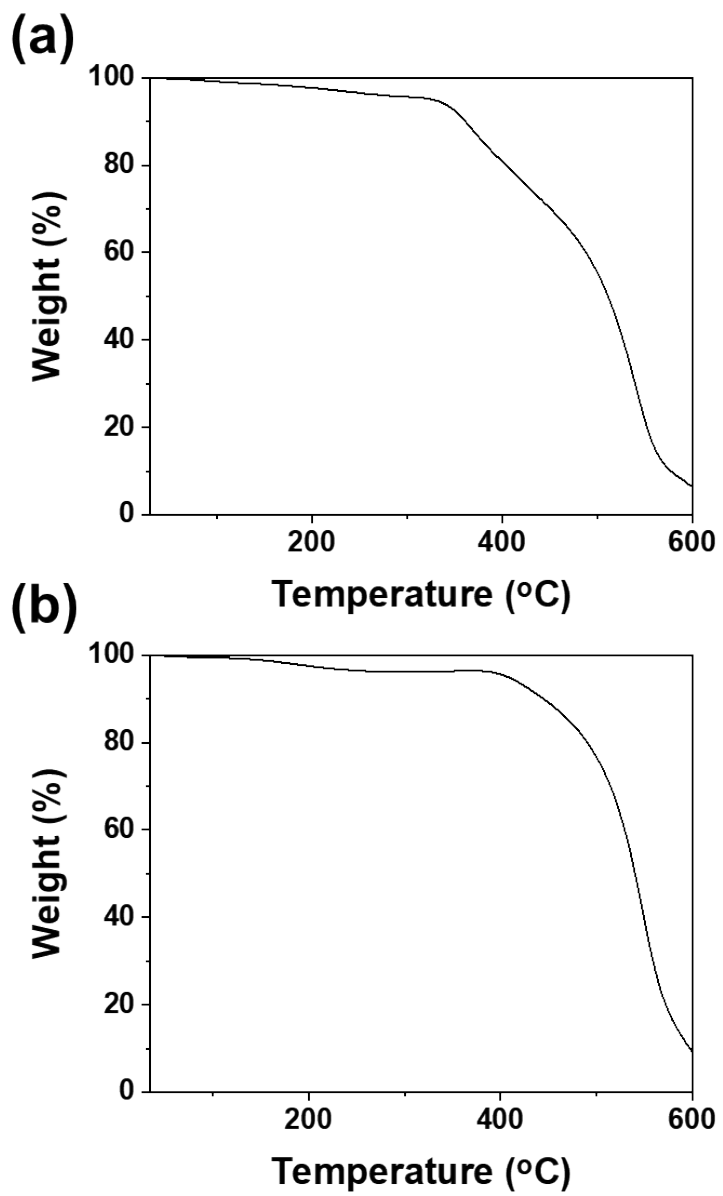


Fig. S7. TGA curves of (a) M-POP-1 and (b) M-POP-2 under air conditions.

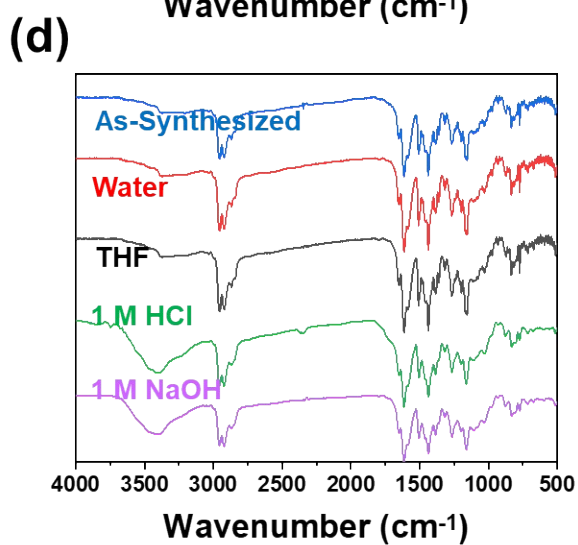
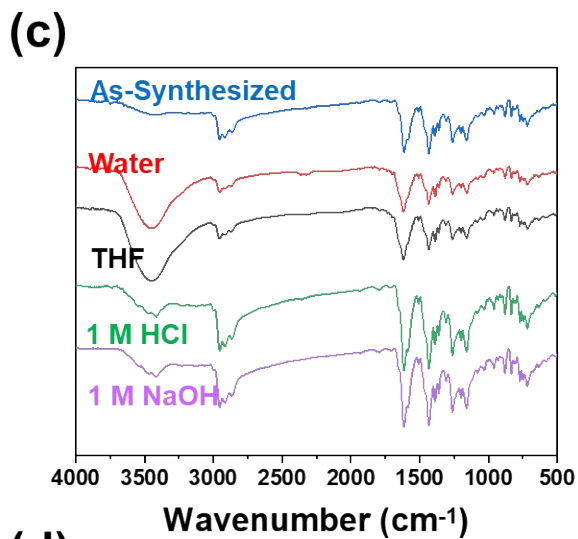


Fig. S8. FT IR spectra of (a) M-POP-1 and (b) M-POP-2 under different conditions.

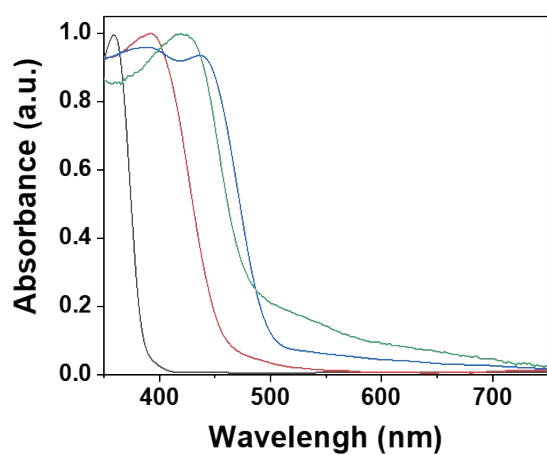


Fig. S9. Absorption spectra of 5,5',5'',5'''-(pyrene-1,3,6,8-tetrayl) tetrakis (3-(tert-butyl)-2-hydroxybenzaldehyde (red), 1,4-phenylenediamine (black), M-POP-1 (green), and M-POP-2 (blue).

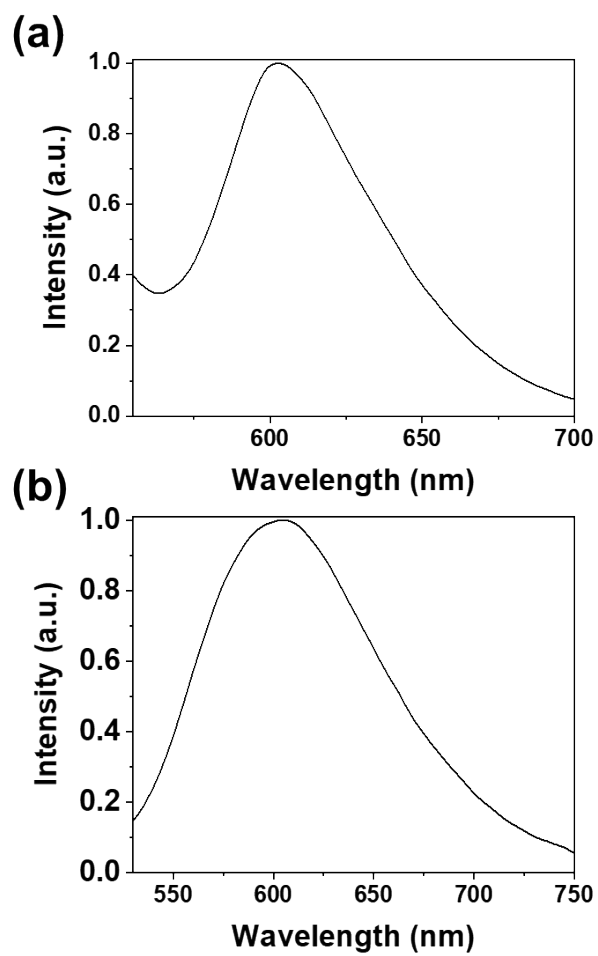


Fig. S10. Fluorescence spectra of (a) M-POP-1 and (b) M-POP-2 powder.

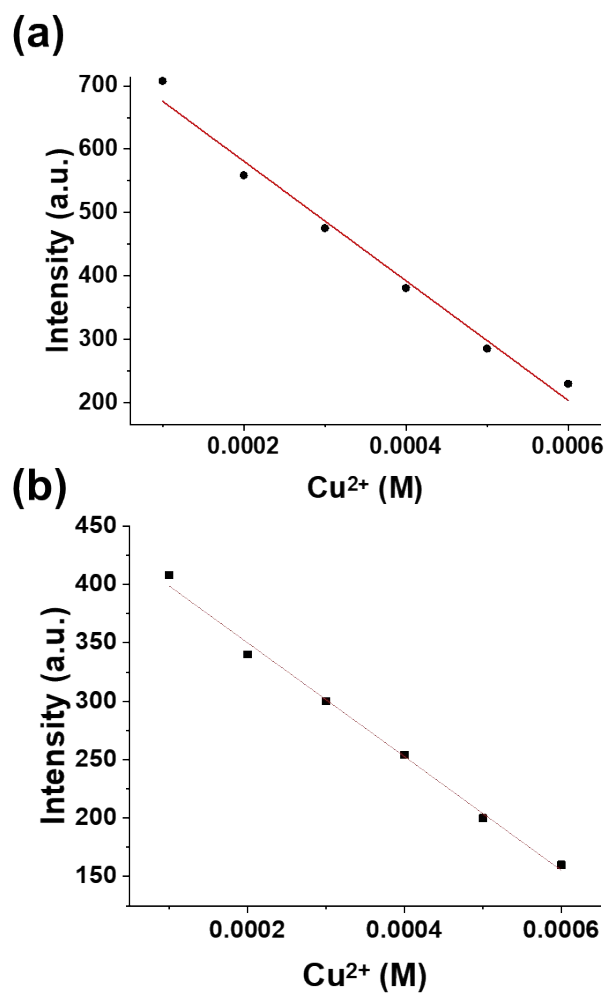


Fig. S11. PL intensity of (a) M-POP-1 and (b) M-POP-2 as a function of Cu^{2+} concentration.

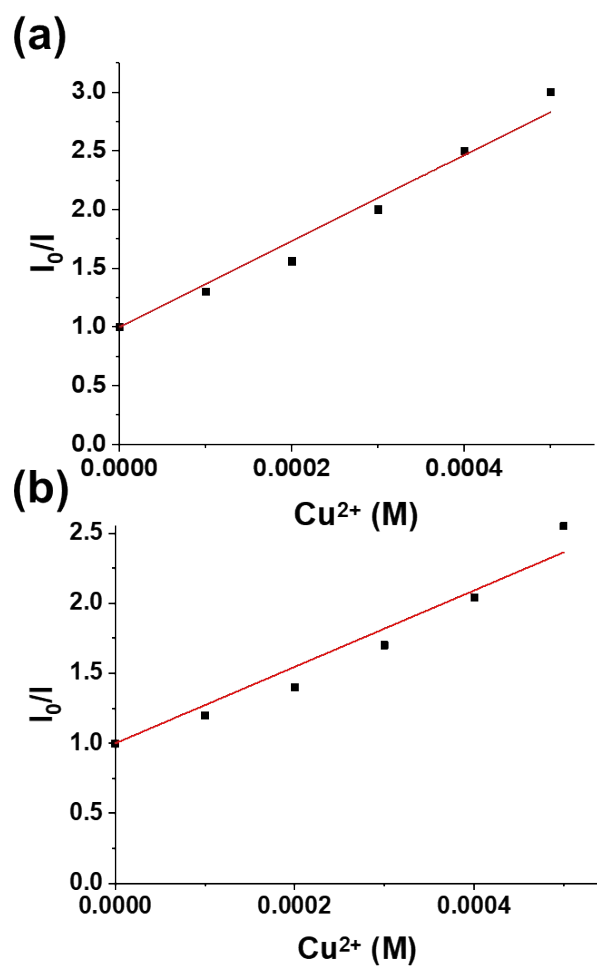


Fig. S12. PL intensity of (a) M-POP-1 and (b) M-POP-2 as a function of Cu^{2+} concentration.

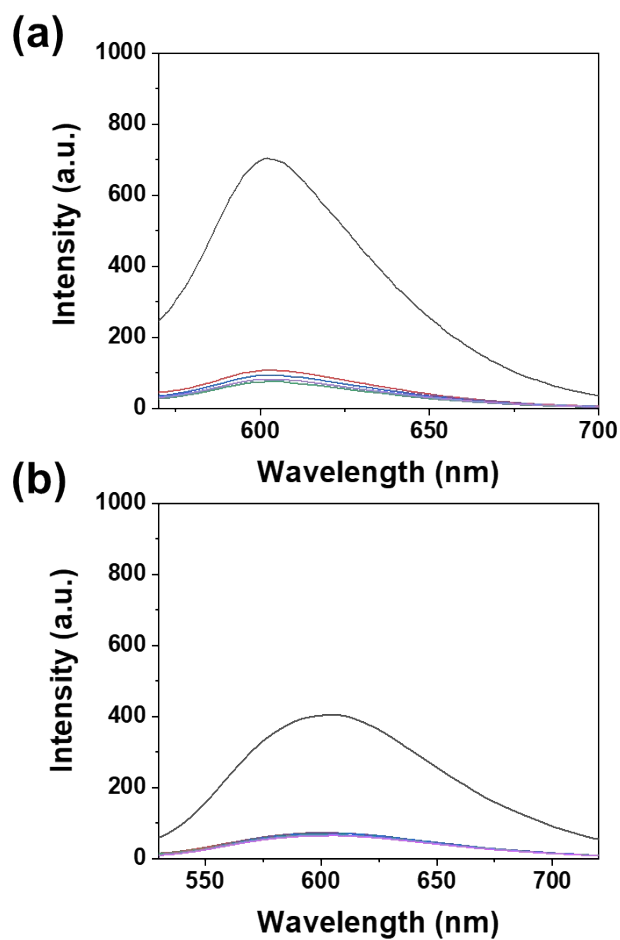


Fig. S13. PL spectra of (a) M-POP-1 and (b) M-POP-2 with Cu^{2+} and different anions (Cl^- , OAc^- , SO_4^{2-} , and NO_3^-).

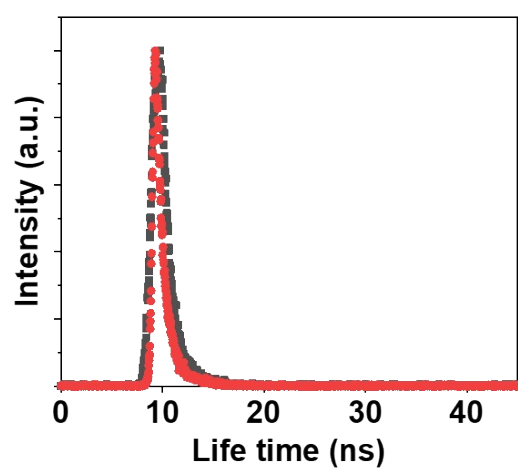
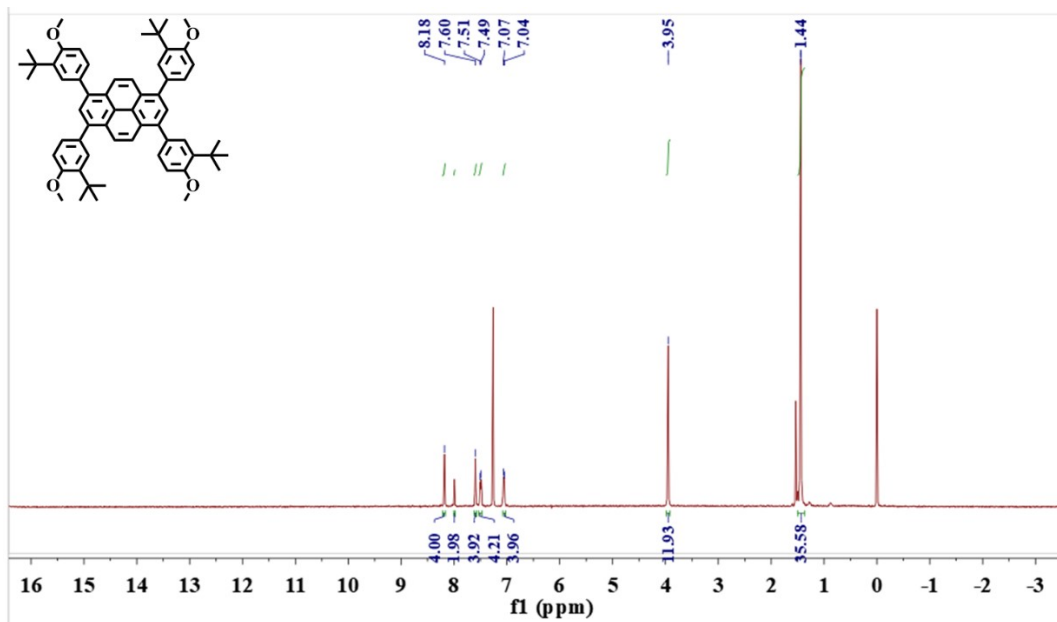
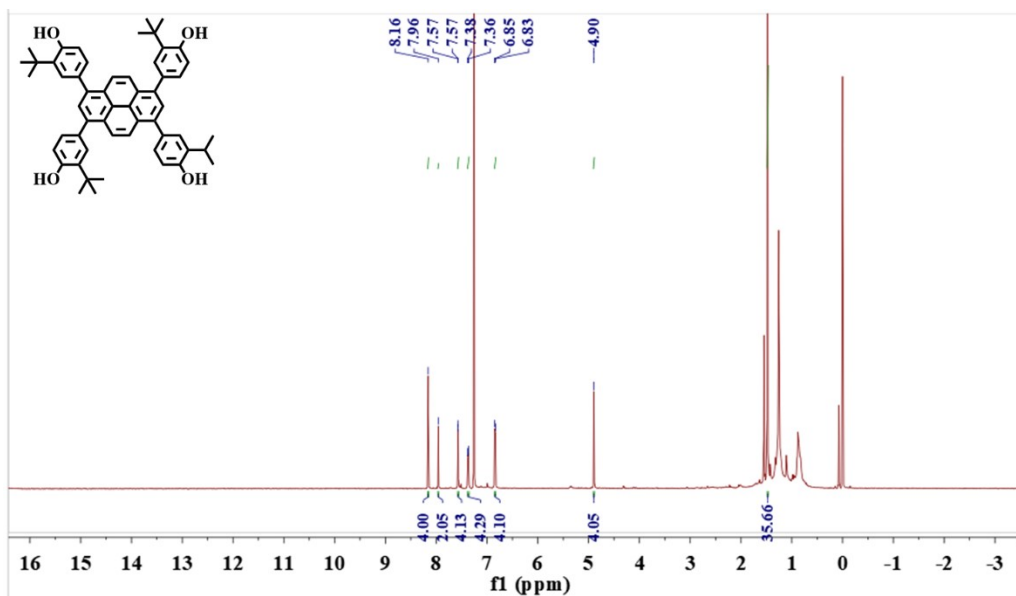


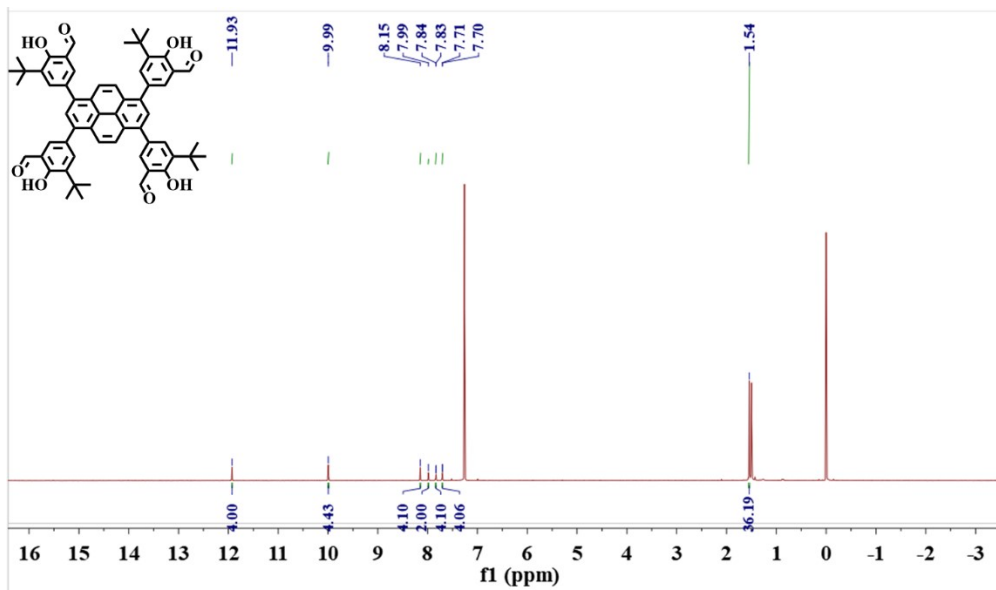
Fig. S14. Life time data of M-POP-1 (black) and M-POP-1@ Cu^{2+} (red).



1,3,6,8-tetrakis(3-(tert-butyl)-4-methoxyphenyl) pyrene



4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl) tetrakis(2-(tert-butyl)phenol)



5,5',5'',5'''-(pyrene-1,3,6,8-tetrayl) tetrakis(3-(tert-butyl)-2-hydroxybenzaldehyde)