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Electronic Supplementary Information

Fluorescent Pillarene Coordination Polymer

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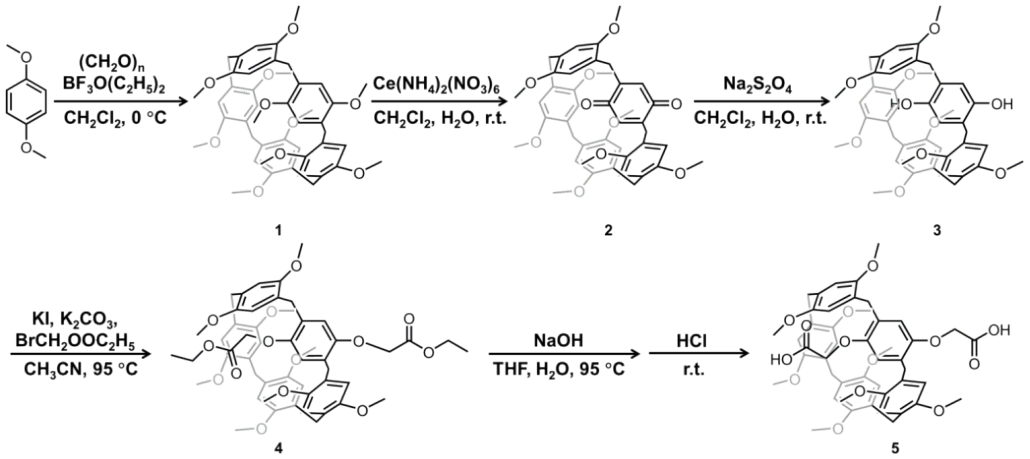
Materials and Characterization

All solvents and chemicals were purchased from commercial sources and used as received. CP5 and its noncyclic monomer were synthesized according to a modified procedure (see the Supporting Information). ^{1}H NMR spectra and solid-state cross-polarization magic angle spinning (CP/MAS) ^{13}C NMR spectra were recorded on a Bruker AVANCE III 300 MHz NMR spectrometer and Bruker Digital Avance III HD 400 WB (400 MHz) NMR spectrometer, respectively. Powder X-ray diffraction (PXRD) analyses were carried out on a PANalytical B.V. Empyrean powder diffractometer. Scanning electron microscopy (SEM) images were obtained on Hitachi SU8082 instrument. Dynamic light scattering (DLS) results were obtained on a Zetasizer Nano ZS instrument. Transmission electron microscopy (TEM) images and elemental mapping were recorded on a JEM 2100F instrument with energy dispersive spectroscopy (EDS). Thermogravimetric analysis (TGA) was carried out on a TGA/Q500 instrument. The surface area and pore size distribution analysis of samples were performed with a Micrometrics 3Flex Surface Characterization Analyzer. The surface compositions of samples were obtained by X-ray photoelectron spectroscopy (XPS) measured on a PREVAC XPS/UPS System and the binding energies were calibrated with respect to the signal to the C 1s peak. Ultraviolet-visible (UV-vis) measurements and fluorescence spectra were recorded on Shimadzu UV-2550 instrument and Shimadzu RF-5301PC spectrofluorometer, respectively. The time-resolved fluorescence decay curves were measured on a FLS920 instrument.

Experimental Procedures



Scheme S1. Synthetic routes to CP5 linker.

Synthesis of compound 1[S1]:

Paraformaldehyde (0.450 g, 15 mmol) was added into a solution of 1,4-dimethoxybenzene (7 g, 50 mmol) in dichloromethane (60 ml) under the protection of nitrogen. Then, boron trifluoride diethyl etherate ($BF_3O(C_2H_5)_2$, 0.75 mL, 6 mmol) was added into the above solution and kept stirring at 0 °C for 130 min. After that, $NaHCO_3$ aqueous solution was added to quench the reaction followed by extracting with dichloromethane. The obtained organic layer was dried with $MgSO_4$ and then concentrated *via* rotary evaporation to obtain the crude product. Subsequently, purified compound 1 was obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) (yield, 46 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 6.80 (s, 10H), 3.78 (s, 10H), 3.67 (s, 30H).

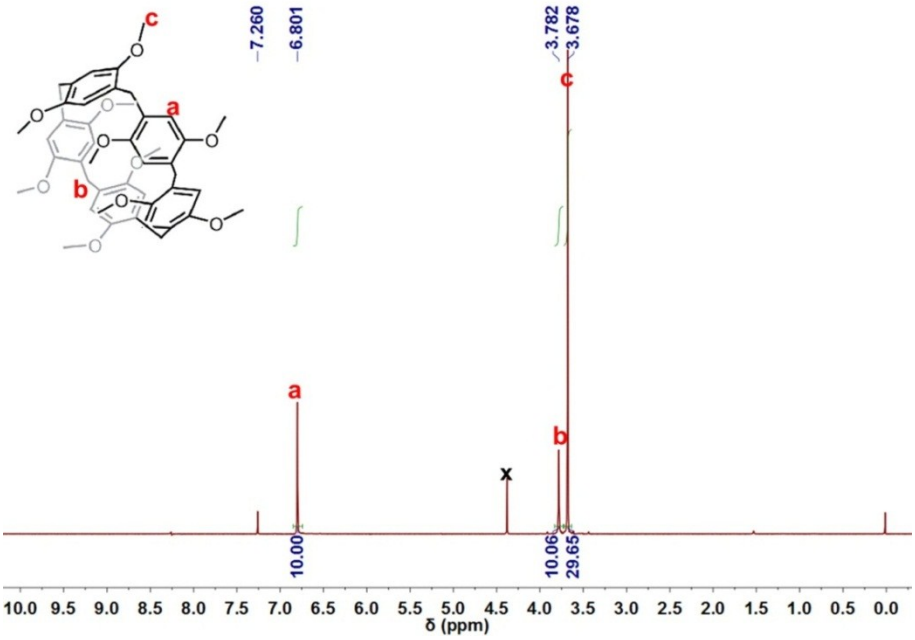


Figure S1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of compound 1.

Synthesis of compound 2[S2]:

To a solution of compound 1 (2 g, 2.67 mmol) in dichloromethane (200 mL), aqueous solution of ammonium ceric nitrate (2.92 g, 5.33 mmol) was added dropwise. After stirring at room temperature for 1 h, the crude product was extracted with dichloromethane and then concentrated by rotary evaporation. A red powder of compound 2 was further obtained by silica gel column chromatography (petroleum ether/dichloromethane = 1: 1) (yield, 77 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 6.85 (s,

2H), 6.81 (s, 2H), 6.80 (s, 2H), 6.67 (s, 4H), 3.79 (s, 6H), 3.75 (s, 6H), 3.72 (s, 6H), 3.71 (s, 6H), 3.63 (s, 6H), 3.59 (s, 4H).

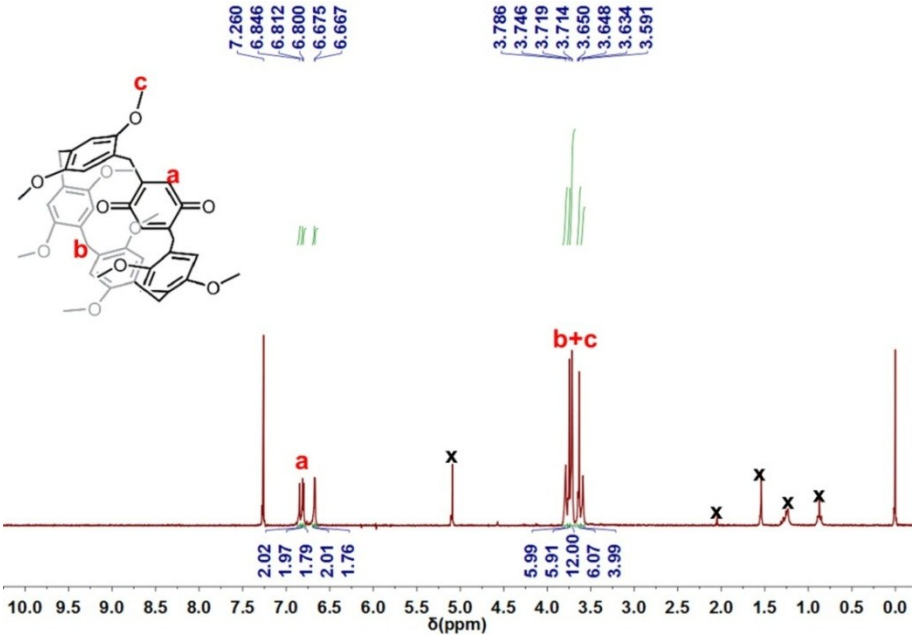


Figure S2. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of compound 2.

Synthesis of compound 3[S2]:

Compound 2 (1 g, 1.38 mmol) was dissolved in dichloromethane (20 mL) to obtain a red solution. Then, aqueous solution of $Na_2S_2O_4$ (2.4 g, 13.8 mmol) was added into the above solution and kept vigorous stirring until the reaction solution became white. A white compound 3 was obtained after extraction with dichloromethane and dried under vacuum. (yield, 90 %). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.18 (s, 2H), 6.92 (s, 2H), 6.87 (s, 2H), 6.84 (s, 2H), 6.62 (s, 2H), 6.60 (s, 2H), 3.84 (s, 6H), 3.78 (s, 12H), 3.75 (s, 6H), 3.70 (s, 6H), 3.68 (s, 4H).

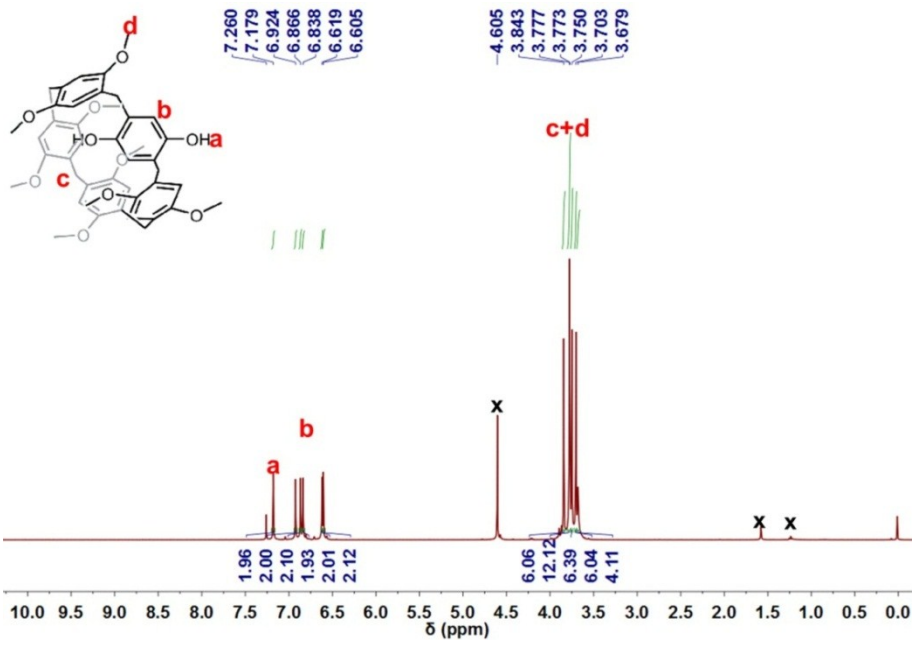


Figure S3. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of compound 3.

Synthesis of compound 4[S3]:

Compound 3 (0.5 g, 0.69 mmol) was dissolved in CH_3CN (50 mL) followed by the addition of K_2CO_3 (0.39 g, 2.8 mmol) and KI (46 mg, 0.28 mmol). After stirring at room temperature for 30 min, ethyl bromacetate (0.23 mL, 2.1 mmol) was added into the above mixture and refluxed at 95 °C for 24 h. Next, the obtained mixture was filtered and washed with dichloromethane, the residue was concentrated by evaporating under vacuum and crystallizing in a mixture of petroleum ether and dichloromethane. A purified compound 4 was finally obtained by filtration and dried under vacuum. (yield, 33 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 6.86 (s, 2H), 6.85 (s, 2H), 6.84 (s, 2H), 6.79 (s, 2H), 6.71 (s, 2H), 4.56 (s, 4H), 3.75 (m, 10H), 3.75 (s, 6H), 3.73 (s, 6H), 3.70 (s, 6H), 3.68 (s, 6H), 3.17 (q, J = 7.1, 6.7 Hz, 4H), -0.20 (t, J = 7.1 Hz, 6H).

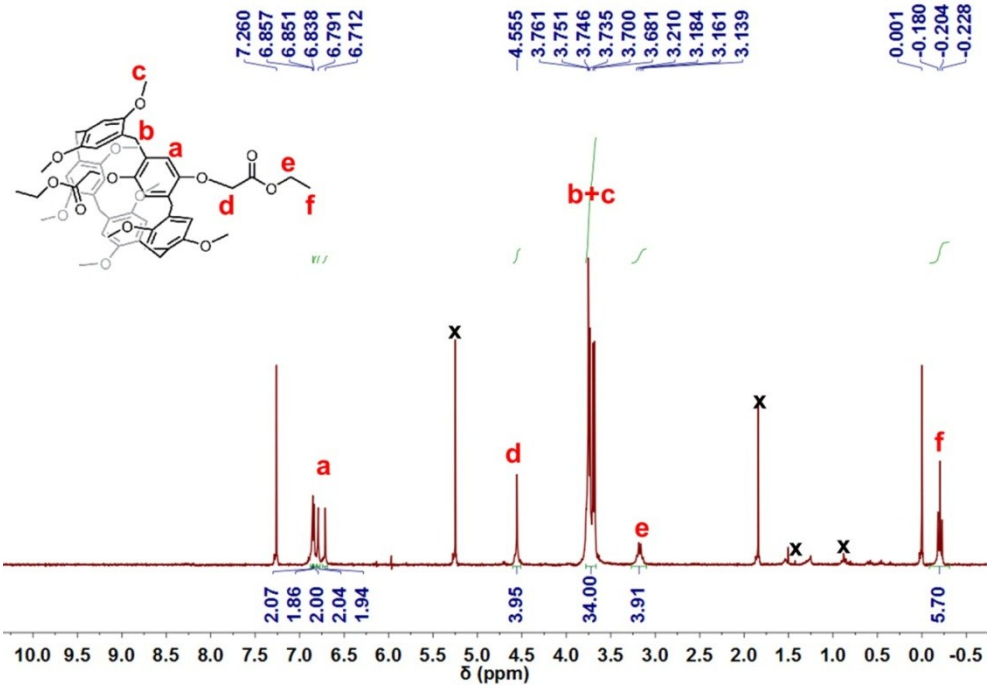


Figure S4. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of compound 4.

Synthesis of compound 5[S3]:

Compound 4 (0.2 g, 0.22 mmol) was dissolved in tetrahydrofuran (25 mL) and reacted with aqueous sodium hydroxide (89 mM, 15 mL) at 95 °C for 24 h. After cooling to room temperature, the mixture was concentrated by rotary evaporation and acidified with HCl. Then, the precipitated compound 5 was collected by filtration and dried under vacuum. (yield, 55 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 6.80 (s, 2H), 6.79 (s, 2H), 6.76 (s, 2H), 6.65 (s, 2H), 6.57 (s, 2H), 4.52 (s, 4H), 3.82 (s, 4H), 3.77 (s, 6H), 3.70 (s, 6H), 3.69 (s, 6H), 3.65 (s, 6H), 3.64 (s, 6H).

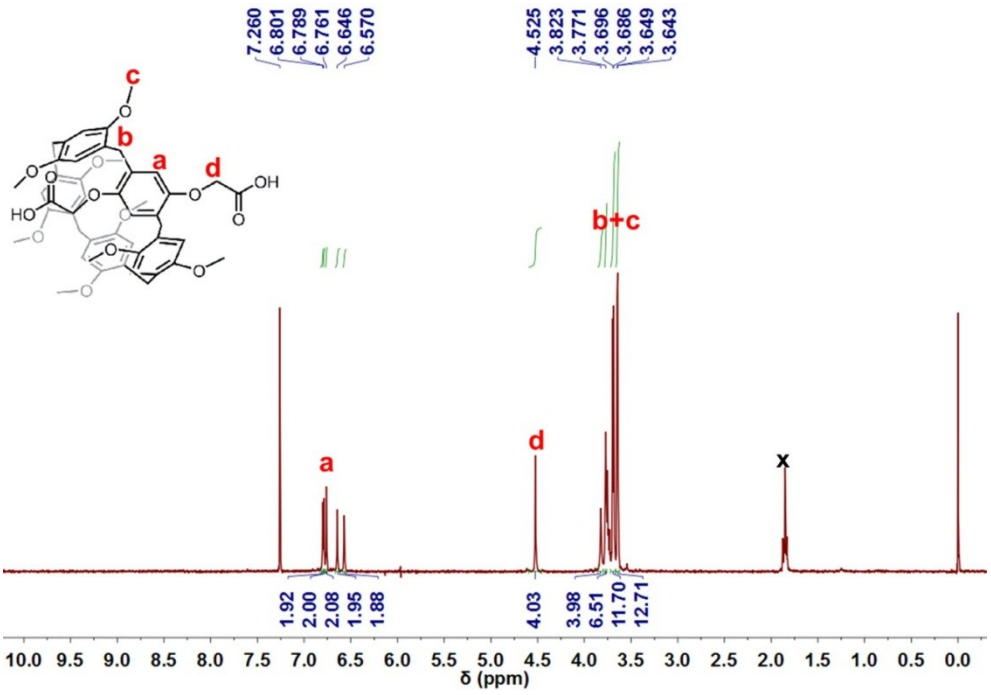
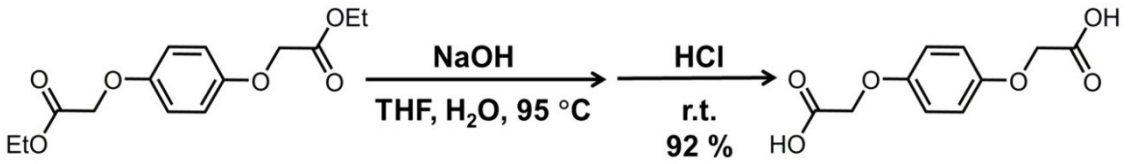


Figure S5. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of compound 5.

Synthesis of noncyclic monomer of CP5:



Scheme S2. Synthetic route to 1,4- phenylenebis(oxy)diacetic acid.

1,4-phenylenebis(oxy)ethyl diacetate (0.2 g, 0.71 mmol) was dissolved in tetrahydrofuran (10 mL) and reacted with aqueous sodium hydroxide (200 mM, 10 mL) at 95 °C for 24 h. After cooling to room temperature, the mixture was concentrated by rotary evaporation and acidified with HCl. Then, the precipitated product was collected by filtration and dried under vacuum. (yield, 92 %). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 12.92 (s, 2H), 6.83 (d, J = 2.2 Hz, 4H), 4.59 (d, J = 2.2 Hz, 4H).

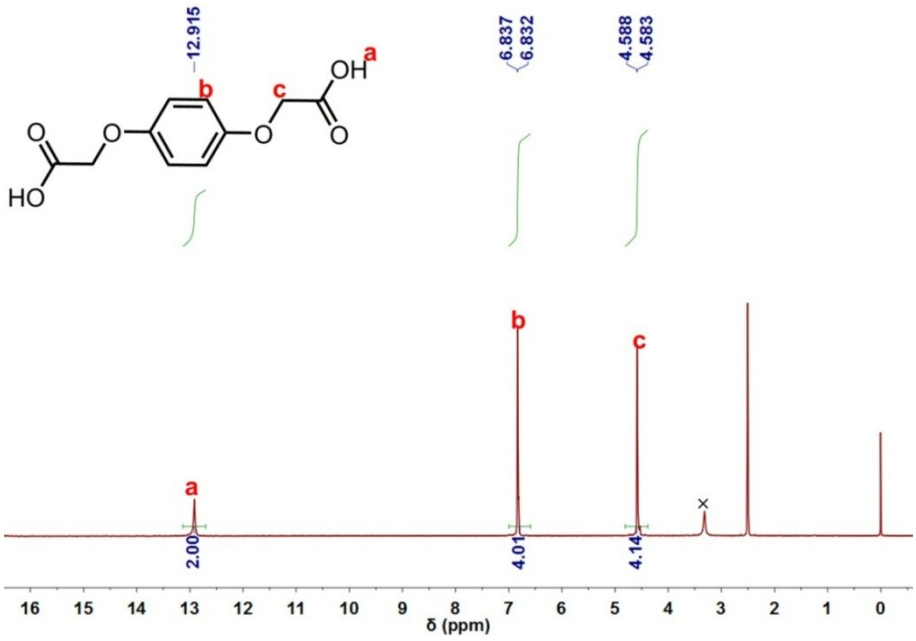


Figure S6. ^{1}H NMR spectrum (500 MHz, DMSO-*d6*, 298 K) of monomer compound.

Synthesis of CP5-PCP:

CP5-PCP was obtained hydrothermally by mixing $Cr(NO_3)_3$•$9H_2O$ (48.02 mg, 0.12 mmol), CP5 (100.56 mg, 0.12 mmol) and sodium acetate (6 mg, 0.04 mmol) aqueous solution (25 mL). The reaction was carried out under stirring at a constant speed of 500 rpm at 100 °C in a pressure tube for 2 days. Finally, the creamy product was separated by centrifugation and washed with N,N-dimethylformamide, ethanol, and water, respectively, for several times.

Synthesis of noncyclic monomer-based coordination polymer (M-CP):

M-CP was prepared as a counterpart in a similar way, briefly, $Cr(NO_3)_3$•$9H_2O$ (48.02 mg, 0.12 mmol) and noncyclic monomer, 1,4-phenylenebis(oxy)diacetic acid (27.14 mg, 0.12 mmol), were added into 25 mL of aqueous solution containing sodium acetate (6 mg, 0.04 mmol). The mixture was reacted in a pressure tube for 2 days at 100 °C under 500 rpm stirring, followed by centrifuging and washing with N,N-dimethylformamide, ethanol, and water, respectively, for several times to obtain M-CP.

Sensing of Fe^{3+}

Experiments were conducted to examine the potential for detecting metal ions. Firstly, a suspension solution (100 μg mL^{-1}) was prepared by dispersing powder samples of CP5-PCP in distilled water, and 200 μL M(Cl)x (Mn^{+} = Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Fe^{3+}, Al^{3+},

Eu^{3+}, and Er^{3+}) solution was added into the 2 mL above suspension solution to form a suspension containing metal ions with a final concentration of 500 μM, respectively. Then, the fluorescence of each suspension was recorded immediately. Similarly, interference metal ion with final concentration of 500 μM was added into the suspension solution containing Fe^{3+} with a final concentration of 500 μM to further investigate the fluorescence recognition of Fe^{3+} ions. During the whole experiments, the total volume of suspension was 2200 μL. Subsequently, the fluorescence quenching induced by Fe^{3+} was investigated to confirm whether the developed CP5-PCP could be used to quantitative detection of Fe^{3+}. Thus, 200 μL Fe^{3+} solutions with different concentrations (final concentrations were 0～500 μM) were added into 2 mL CP5-PCP suspension solution (100 μg mL^{-1}) and the fluorescence intensities were recorded, respectively.

Sensing of acetone

To further study the effect of common organic solvents on the CP5-PCP fluorescence. CP5-PCP powder was dispersed in 2 mL dichloromethane (DCM), ethanol (EtOH), acetonitrile (ACN), *N,N*-dimethylformamide (DMF), ethyl acetate (EA), dimethyl sulfoxide (DMSO), acetone, and water to prepare a suspension of 50 μg/mL, respectively. Taking CP5-PCP suspension in water as a reference, it is obvious that only acetone caused significant fluorescence quenching. Therefore, the fluorescence suppression caused by acetone was further studied to evaluate whether the developed CP5-PCP could be used to quantitative detection of acetone. Concretely, different amounts of acetone (acetone/water, v/v, 0 % – 2%) were added into 2 mL CP5-PCP suspension in water (50 μg/mL) and the fluorescence changes of CP5-PCP were recorded, respectively.

Sensing of nitrophenols

Inspired by the above experimental results, phenolic compounds were also investigated to evaluate whether they could induce the fluorescence changes of CP5-PCP. Accordingly, 200 μL of phenolic compounds (e.g., phenol, phloroglucinol, 2,4,6-tribromophenol, o-nitrophenol (o-NP), m-nitrophenol (m-NP), p-nitrophenol (p-NP), 2,4,6-trinitrophenol (TNP)) with final concentration of 455 μM were added into 2 mL ethanol suspensions of CP5-PCP (100 μg mL^{-1}) and their fluorescence intensities were recorded, respectively. It could be observed that electron-deficient nitrophenols analytes, *o*-NP, *m*-NP, *p*-NP, and TNP demonstrated significant fluorescence quenching performance, thus, the fluorescence quenching caused by different concentrations of *o*-NP (0～909 μM), *m*-NP(0～909 μM), *p*-NP(0～455 μM), and TNP(0～455 μM) were further studied to evaluate whether the fluorescent

CP5-PCP could be applied to quantitative detection of the above nitrophenols analytes. Specific experimental processes were to add 200 μL different concentrations of the above analytes into 2 mL ethanol suspensions of CP5-PCP (100 μg mL^{-1}), then, the relationships between analytes concentrations and fluorescence intensities were recorded and analyzed, respectively.

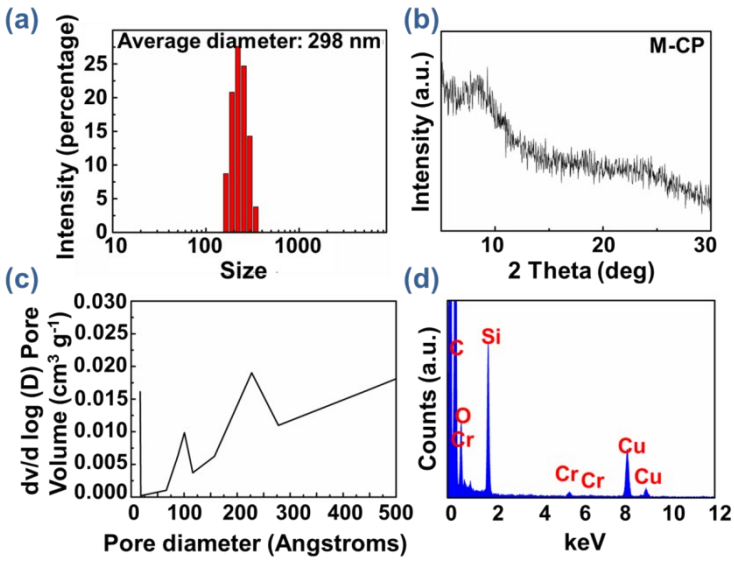


Figure S7. a) DLS results of CP5-PCP. b) PXRD measurements of counterpart M-CP. c) The pore size distribution analysis of CP5-PCP. d) EDS spectrum of CP5-PCP.

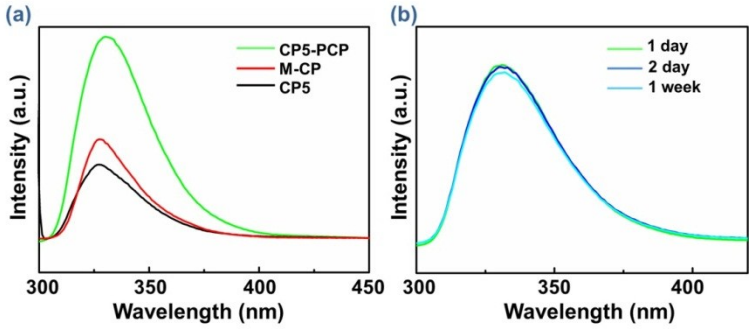


Figure S8. a) Emission spectra of CP5-PCP under the excitation at 285 nm (green), M-CP under the excitation at 285 nm (red), and CP5 ligand linker (black) under the excitation at 294 nm. b) Day-to-day fluorescence stability of CP5-PCP. Experimental conditions: slit widths: Ex. 5 nm, Em. 3 nm; [materials] = 100 μg mL-1 in water.

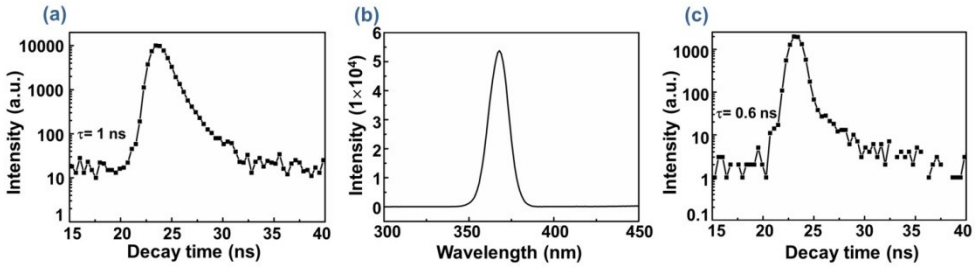


Figure S9. a) Fluorescence decay profile of CP5-PCP. Experimental conditions: λex = 285 nm; λem = 330 nm; [CP5-PCP]: 100 μg mL^{-1} in water. b) Fluorescence intensity of the CP5-PCP powder. c) Fluorescence decay profile of the CP5-PCP powder.

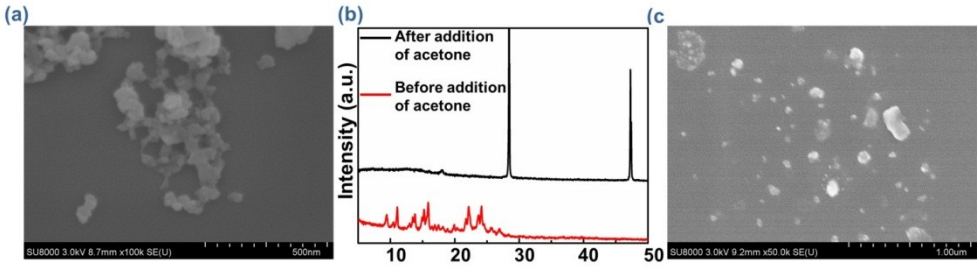


Figure S10. a) SEM image of coordination polymer constructed from Fe^{3+} and CP5. b) PXRD patterns of CP5-PCP before and after the detection of acetone. c) SEM image of CP5-PCP after the detection of acetone.

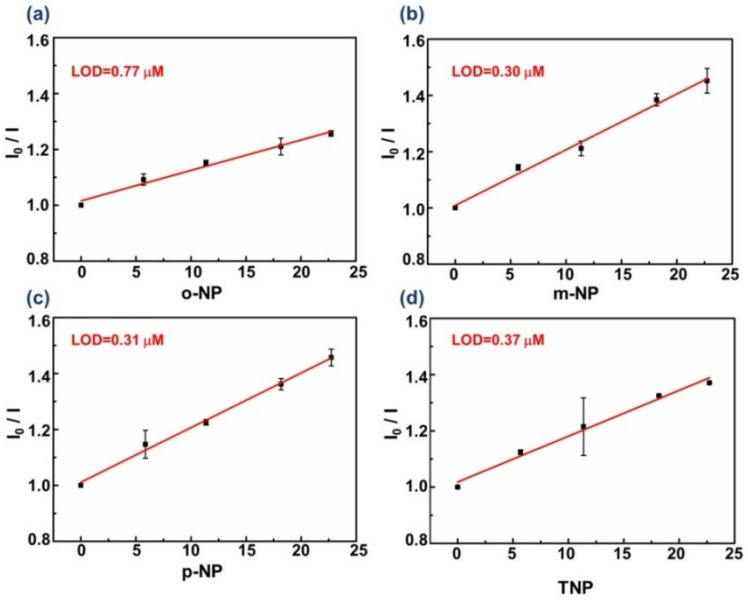


Figure S11. Relationships between the degree of fluorescence quenching of CP5-PCP and the concentration of analytes.

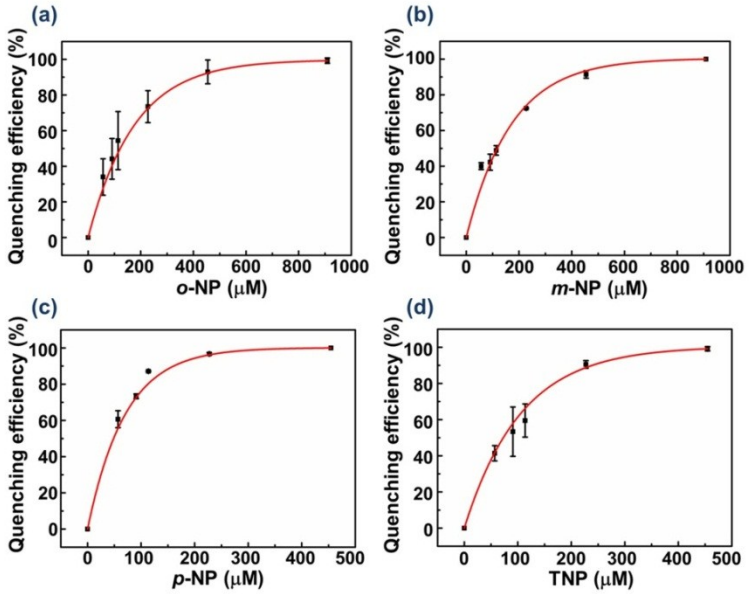


Figure S12. Relationships between I_0/I and concentrations of o-NP (a); m-NP (b); p-NP (c); TNP (d). And their detection limits (LODs) calculated based on the 3σ.

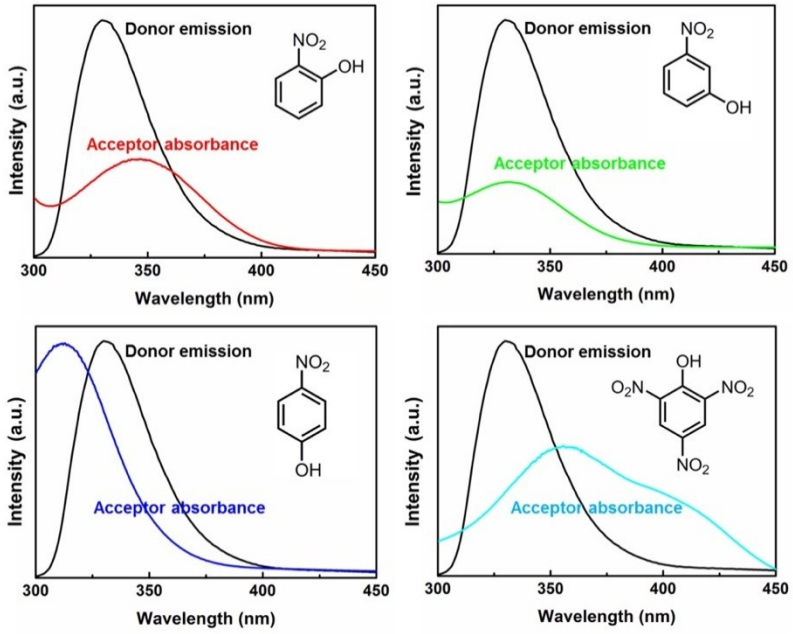


Figure S13. Overlaps of emission spectra of CP5-PCP and absorbance spectra of free nitroaromatic explosives o-NP at 500 μM (red), m-NP at 500 μM (green), p-NP (blue) at 125 μM, TNP (bright-blue) at 125 μM after normalization.

References

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