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Supporting Information

Color tunable covalent organic polymer luminescent probes for selective sensing of metal ions and nitroaromatic explosives

Lin Guo, Dapeng Cao*

State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, P. R. China

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S1. Experimental Section

All reagents, unless otherwise stated, were obtained from commercial sources (Alfa Aesar, Sigma Aldrich) and were used without further purification.

S1.1 Synthesis of COPs

The synthesis of COPs was carried out by Yamamoto reaction, using the two monomers of TBB and TBP. The specific synthesis methods are as follows.

1,5-Cyclooctadiene (cod, 0.50 mL, 3.96 mmol, dried with CaH_2) was added to a solution of bis(1,5-cyclooctadiene)nickel(0)([Ni(cod)2], 1.125 g, 4.09 mmol), and 2,2’ -bipyridyl(0.640g, 4.09mmol) in dry dimethylformamide (DMF) (65mL). The mixture was stirred until completely dissolved. 1,3,6,8-Tetrabromopyrene (TBP) and 1,3,5-tris(4-bromophenyl)benzene (TBB) were subsequently added to the resulting purple solution in different ratio, as shown in table 1. The reaction vessel was heated at 80° C overnight under a nitrogen atmosphere. The above reaction is carried out in a glove box. After cooling to room temperature, concentrated HCl was added to the deep purple suspension, which would be changed into aqua transparent solution. After filtration, the residue was washed by $CHCl_3$(5×15mL), tetrahydrofuran (THF) (5×15 mL) and H_2O (5×15 mL), respectively, and dried in a vacuum oven. The dried sample (named as COP-61, COP-62, COP-63, COP-64, COP-65) was placed in containers and stored in a desiccator. Elemental analysis calcd (%) for $C_{102}H_{77}$: C94.08, H 5.92; found (%): C 86.84, H 3.833.

The synthetic steps and reaction conditions of the other four COPs (COP-62, COP-63, COP-64, COP-65) are same as COP-61. The amounts of the two monomers

(TBP and TBB) are listed in Table S1, and the elemental analysis results are shown in Table S2.

Table S1 The amount of TBP and TBB of the five COPs.

Materials	ratio of TBP:TBB	TBP/mmol	TBB/mmol
COP-61	2:3	0.3140	0.4710
COP-62	1:1	0.3925	0.3925
COP-63	3:2	0.4710	0.3140
COP-64	4:1	0.6280	0.1570
COP-65	9:1	0.7065	0.0785

Table S2 Summary of Elemental analysis results of the five COPs

materials	Elemental analysis Calculated/%		Elemental analysis found/%	
	C	H	C	H
COP-61	94.08	5.92	86.84	3.833
COP-62	95.81	4.19	82.88	3.873
COP-63	96.00	4.00	85.96	3.56
COP-64	96.44	3.56	81.03	3.91
COP-65	96.69	3.31	85.83	3.645

S1.2 Characterization of Materials

Thermo gravimetric analysis (TGA) data was obtained on a STA449C (NETZSCH) instrument, with a heating rate of 10°C min^{-1} under flowing N_2. FTIR spectroscopy was performed on an AC-80MHZ (Bruker) instrument with the wave range of 4000 - 400 cm^{-1}. Scanning electron microscope (SEM) images were obtained on a Hitachi S-4700 SEM instrument. Elemental analysis (C, N and H) was performed on a Thermo Fisher scientific Elemental Analyzer (Ea1112, Beijing Research Institute of Chemical Industry, SINOPEC). UV-vis absorption were recorded using TU-1901

spectrophotometers. Fluorescence lifetime and fluorescence quantum yield were measured by LifeSpec-ps spectrometer, and the lifetimes and quantum yields were fitteded by the FLS980 Edinburgh Instruments software. The fluorescent spectra of solid state powder monomers and the COP materials were measured by Hitachi F-7000 Fluorescence Spectrophotometer, and the widths of the excitation slit are 5 nm and emission slit is 10 nm for the COPs, test voltage is 420v.

S.2 Luminescent measurements

The fluorescent spectra of solid state powder monomers and the five COPs were measured by a fluorescence spectrometer (Hitachi F7000). The photoluminescence (PL) properties of the five samples in various solvent emulsions were investigated at room temperature.

To examine the potential of the COPs for sensing metal ions, the synthesized COPs (1 mg) was immersed in 10 mL DMF solutions containing $M(NO_3)_x$ (M= Pb^{2+}, Cu^{2+}, Cr^{3+}, Co^{2+}, Fe^{3+}, Cd^{3+}, Ni^{2+}, Mg^{2+}, and Zn^{2+}) to form the metal ion incorporated COP suspension for luminescence studies. For practical application, we studied the luminescent property of the COPs immersed in 10% (wt) ethanol aqueous solution for sensing metal ions. The widths of the excitation slit are 5 nm and emission slit is 10 nm for the COPs.

To explore the sensing properties of the COPs for nitroaromatic explosives, the fluorescence spectra of methanol solutions of the COPs (1mg/10mL) were recorded by successive addition of aliquots of PA, 2,4-dinitrotoluene (DNT), m-dinitrobenzen (mDNB), and m-dinitrobenzen (pDNB). The widths of the excitation slit are 5 nm and

emission slit is 10 nm for the COPs.

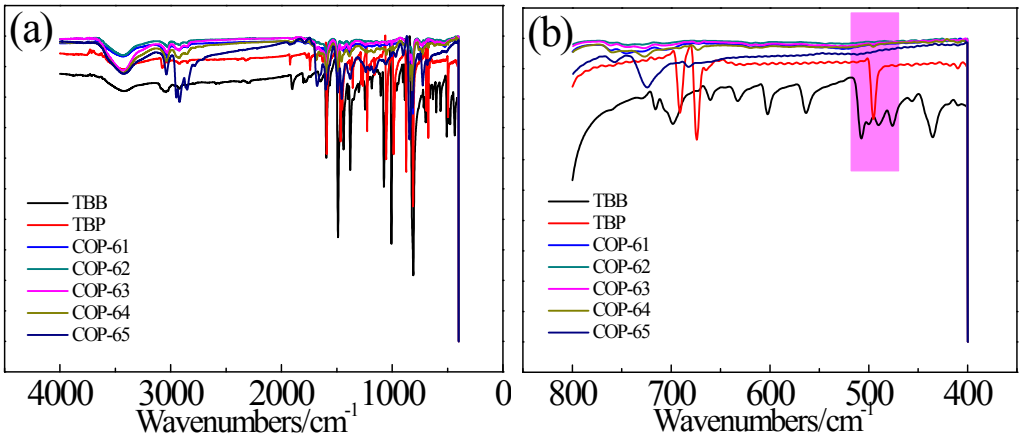


Figure S1. FTIR spectra of the TBB (black), TBP (red) and the five COPs (blue: COP-61; green: COP-62; pink: COP-63; gray green: COP-64; navy blue: COP-65) from 400-4000 cm^{-1} (a) and 400-800 cm^{-1} (b). The characteristic absorption bands for Carbon-Bromine are highlighted via pink region (see the bottom panel), clearly showing the lack of bromine in the COPs and indicating the formation of the polymeric COPs structure.

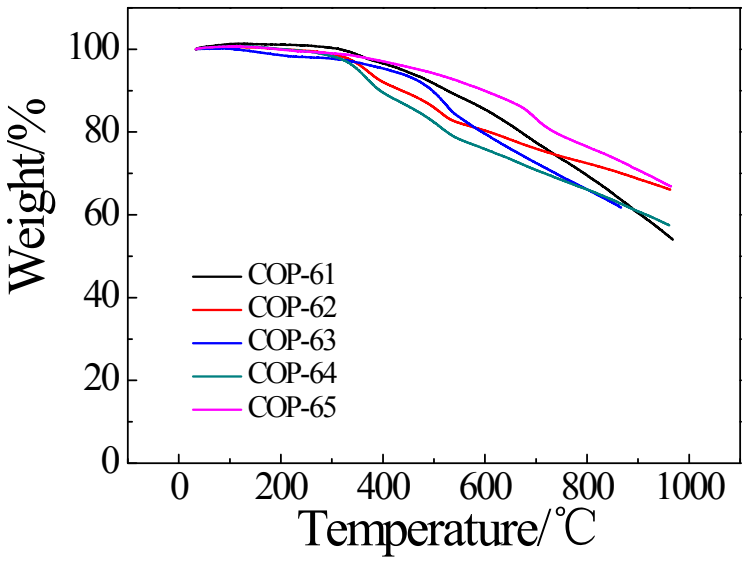


Figure S2. TGA trace of COP-61, COP-62, COP-63, COP-64, COP-65.

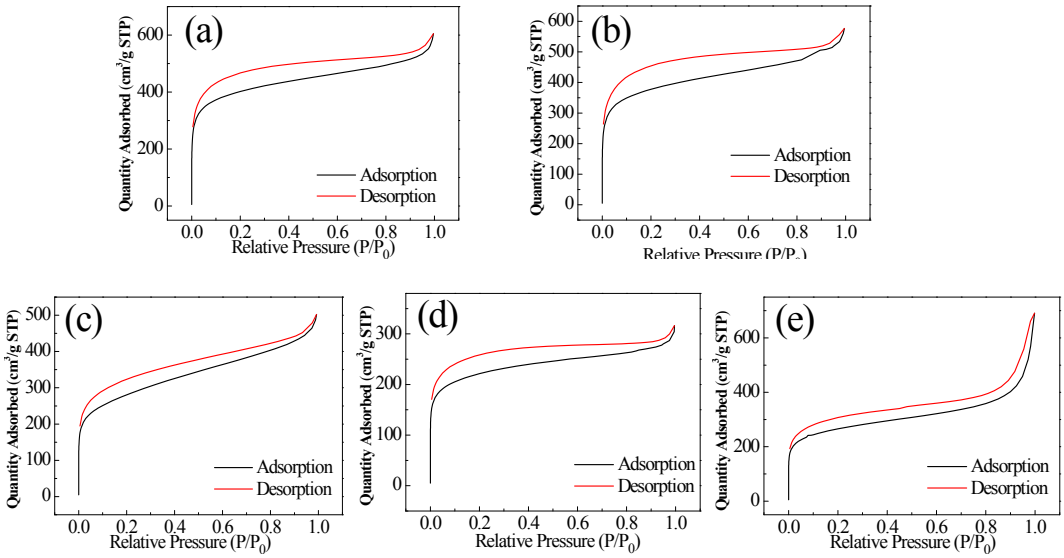


Figure S3. N_2 adsorption isotherms at T =77K. Black and red line represent adsorption and desorption, respectively. (a) COP-61, (b) COP-62, (c) COP-63, (d) COP-64, (e) COP-65.

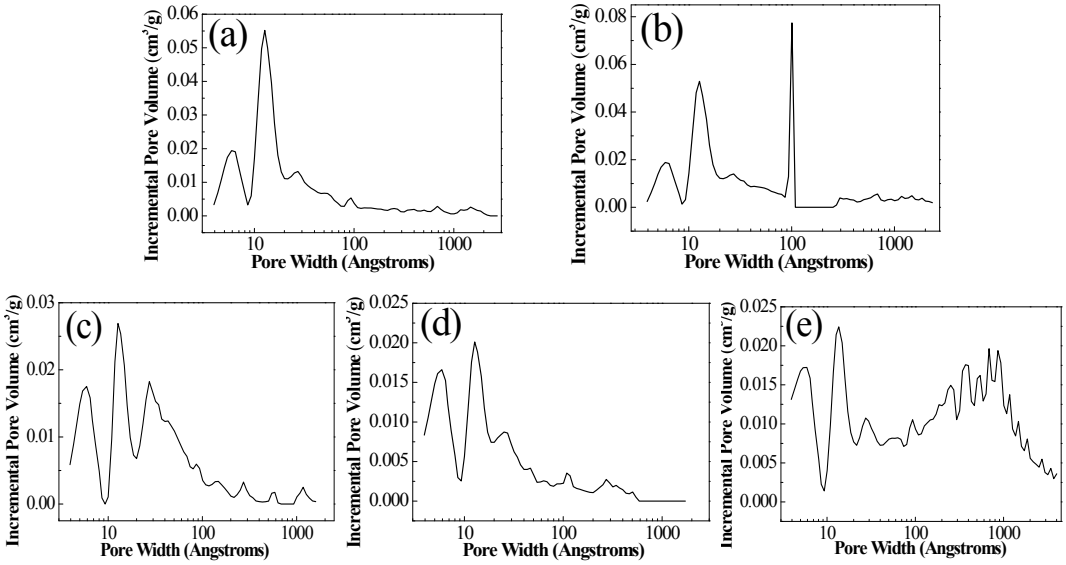


Figure S4. Nonlocal density functional theory (NLDFT) pore size distributions of products by incremental pore volume. (a) COP-61, (b) COP-62, (c) COP-63, (d) COP-64, (e) COP-65.

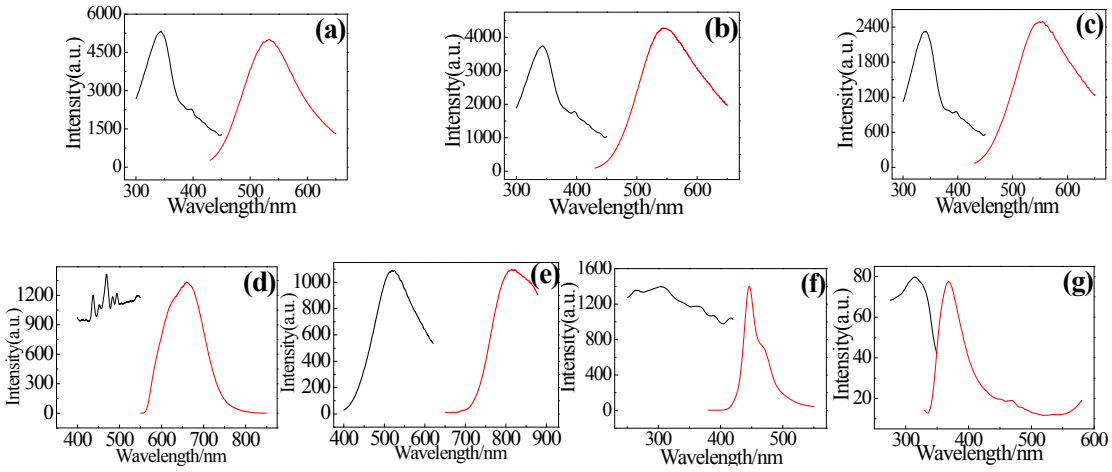


Figure S5. The excitation (dotted black line) and PL spectra (solid red line) of the solid COPs.

(a) COP-61, (b) COP-62, (c) COP-63, (d) COP-64, (e) COP-65, (f) TBP, (g) TBB

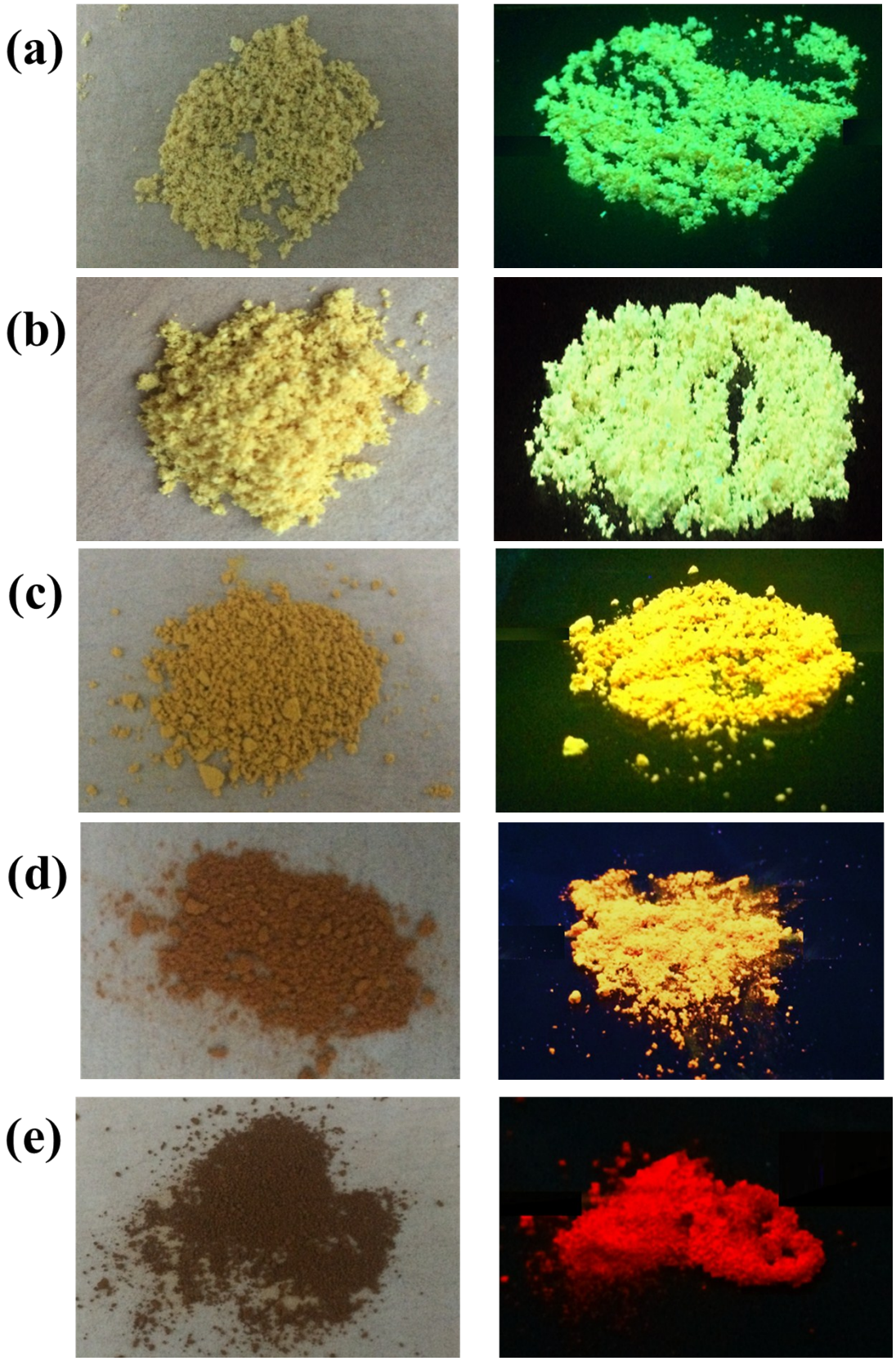


Figure S6. Photographs of the COPs under ambient conditions (left), and under irradiation with UV light (right) (excite=365 nm using a portable UV lamp). (a) COP-61; (b) COP-62; (c) COP-63; (d) COP-64; (e) COP-65.

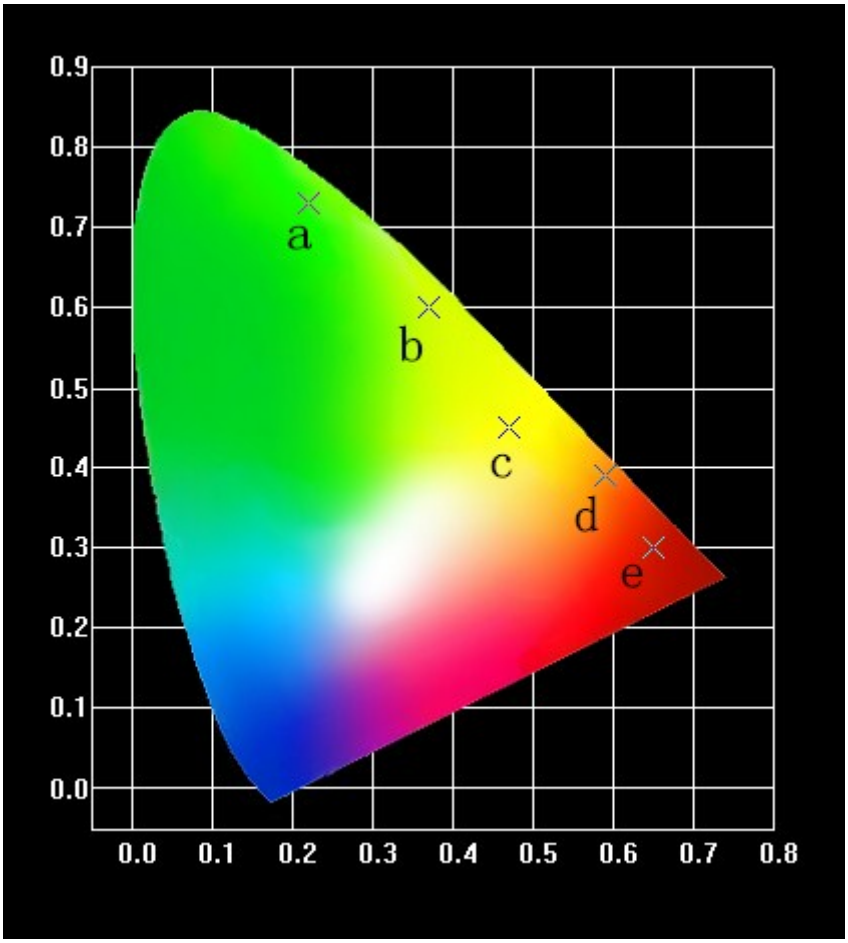
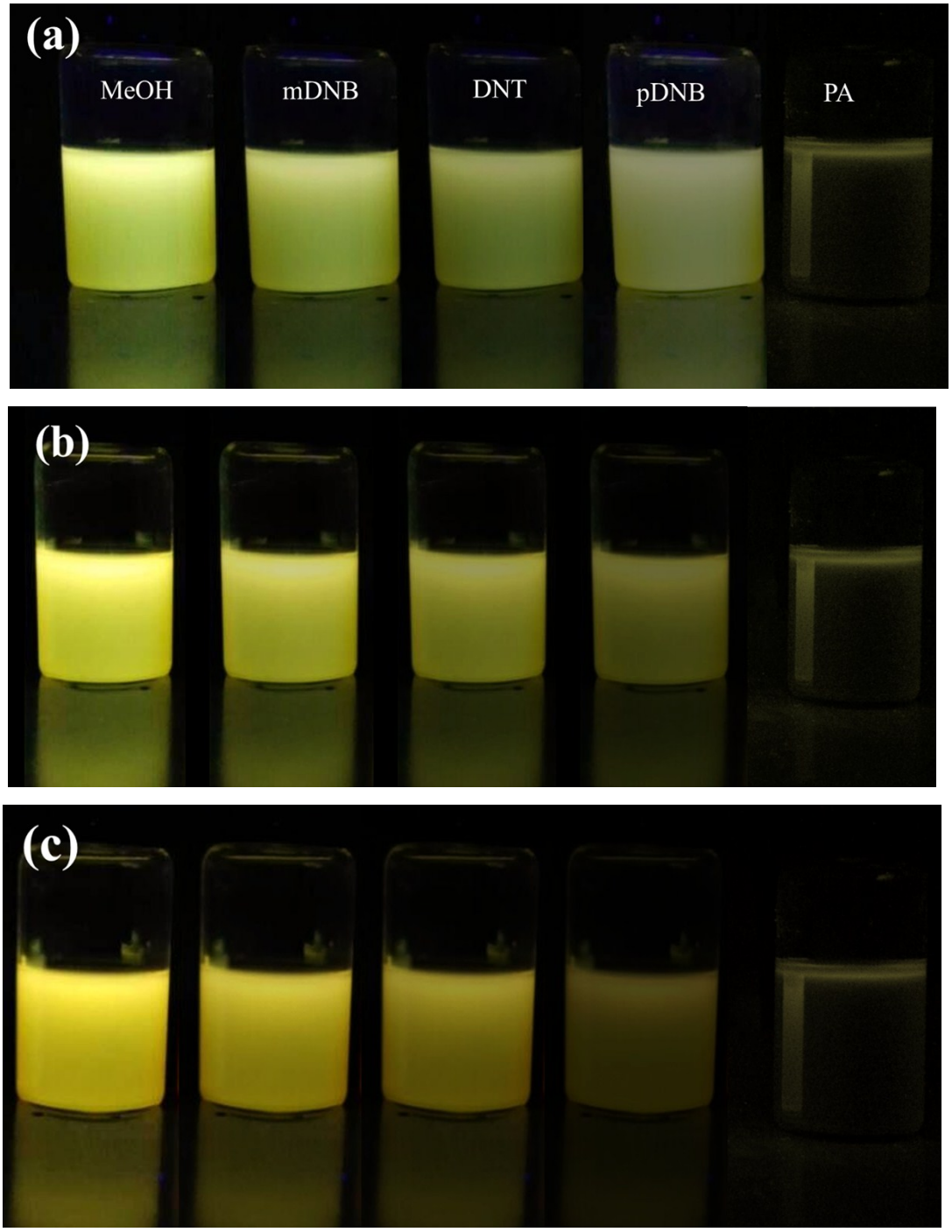


Figure S7. CIE chromaticity diagram of the COPs under ambient conditions, and the excited emission is 365 nm. (a) COP-61; (b) COP-62; (c) COP-63; (d) COP-64; (e) COP-65.


(a)
MeOH
mDNB
DNT
pDNB
PA
(b)
(c)

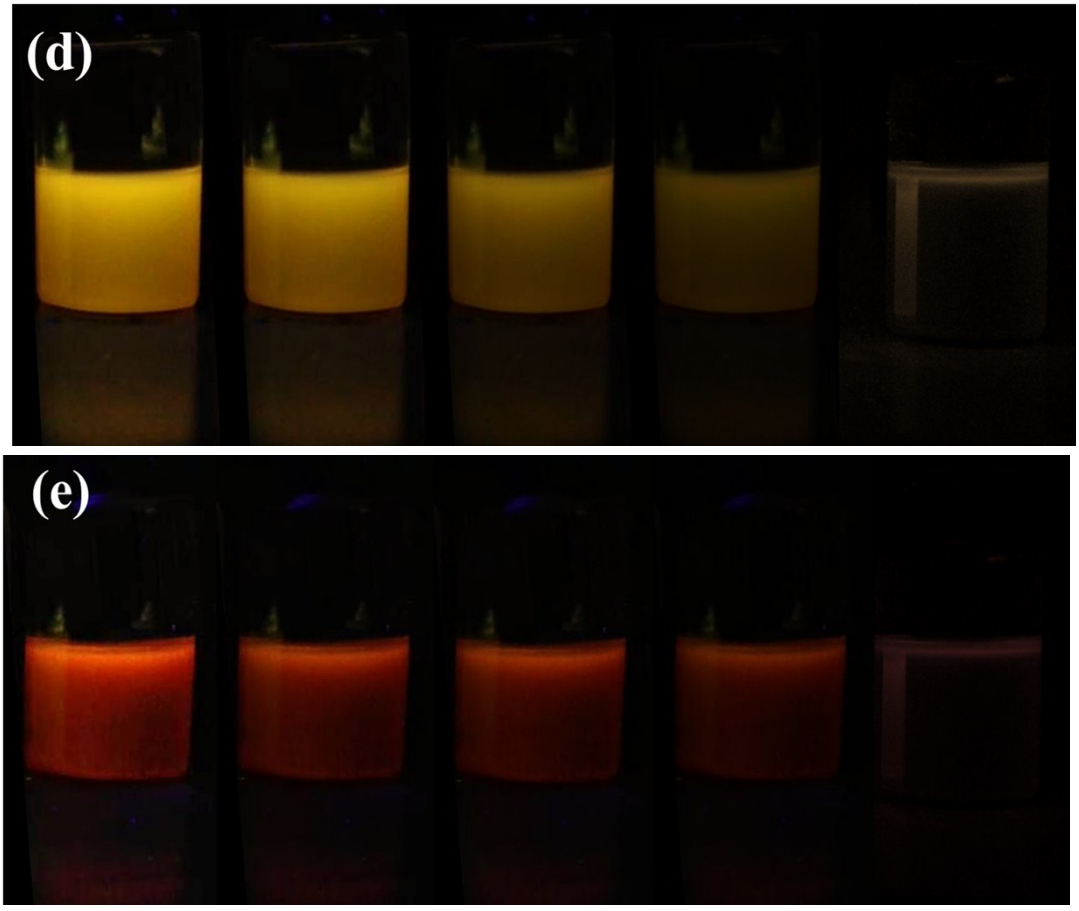


Figure S8. The luminescent photographs of suspensions of the five COPs and COP + mDNB, DNT, pDNB, PA (from left to right) in methanol solutions excited under λexcite=365nm using a portable UV lamp. (a) COP-61; (b) COP-62; (c) COP-63; (d) COP-64; (e) COP-65.

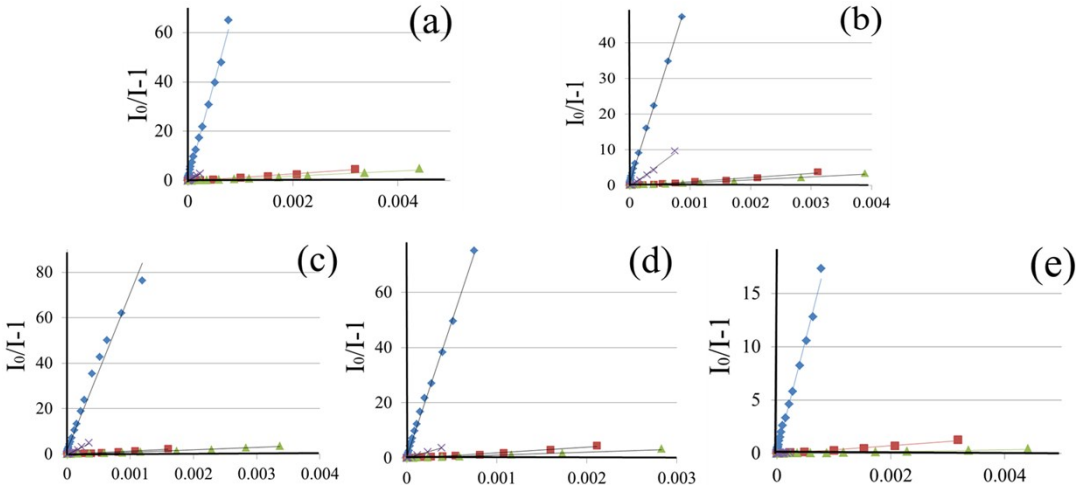


Figure S9. The Stern-Volmer constants with PA, pDNB, DNT, mDNB analytes for the COPs. (a) COP-61; (b) COP-62; (c) COP-63; (d) COP-64; (e) COP-65. ◆(PA); ■(pDNB); ▲(DNT); ✖ (mDNB).

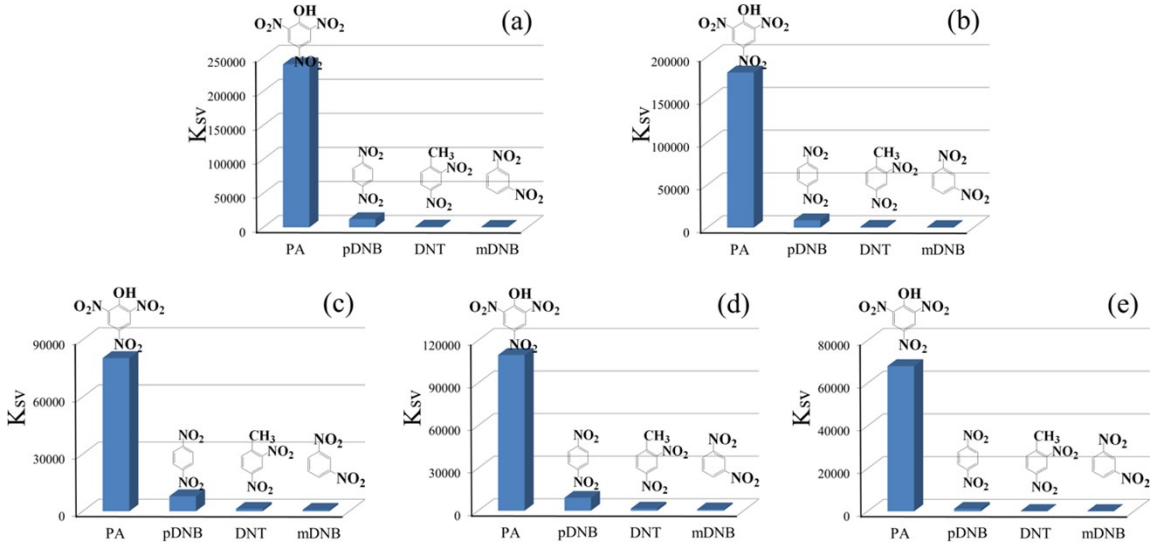


Figure S10. the Stern-Volmer constants with PA, pDNB, DNT, mDNB analytes for the COPs. (a) COP-61; (b) COP-62; (c) COP-63; (d) COP-64; (e) COP-65.

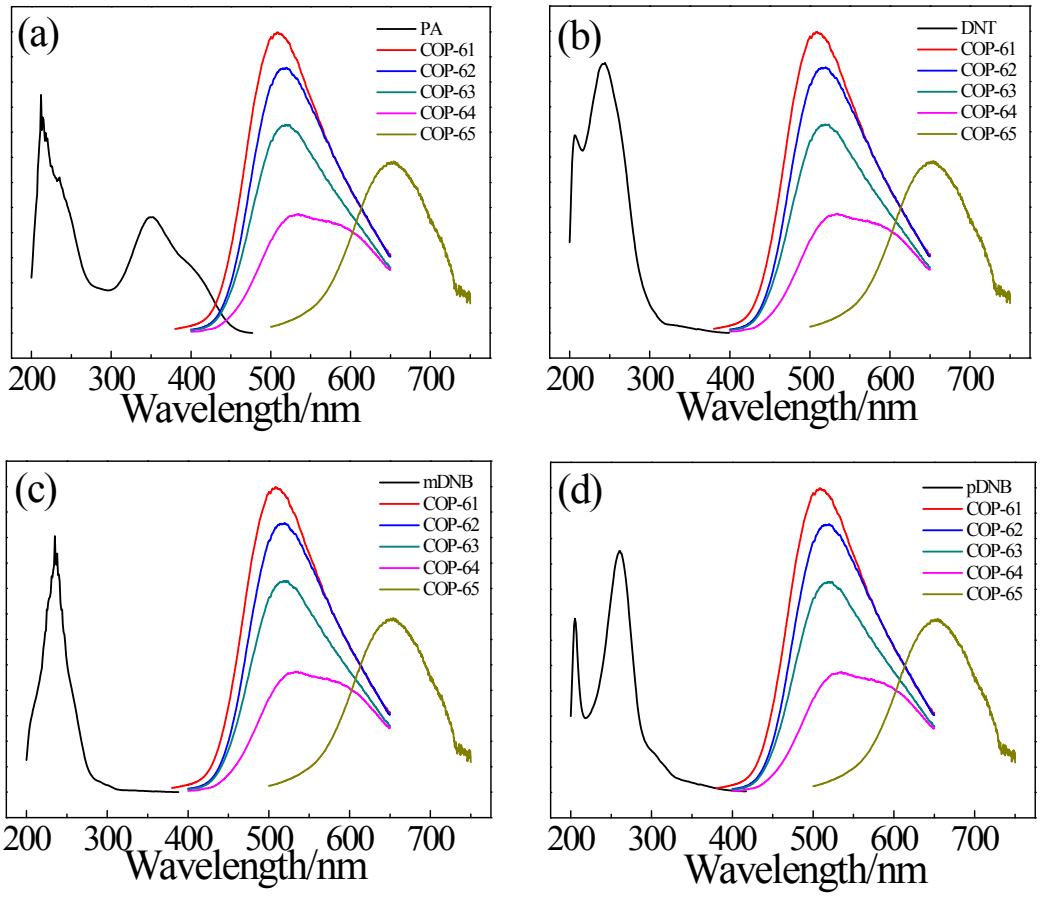
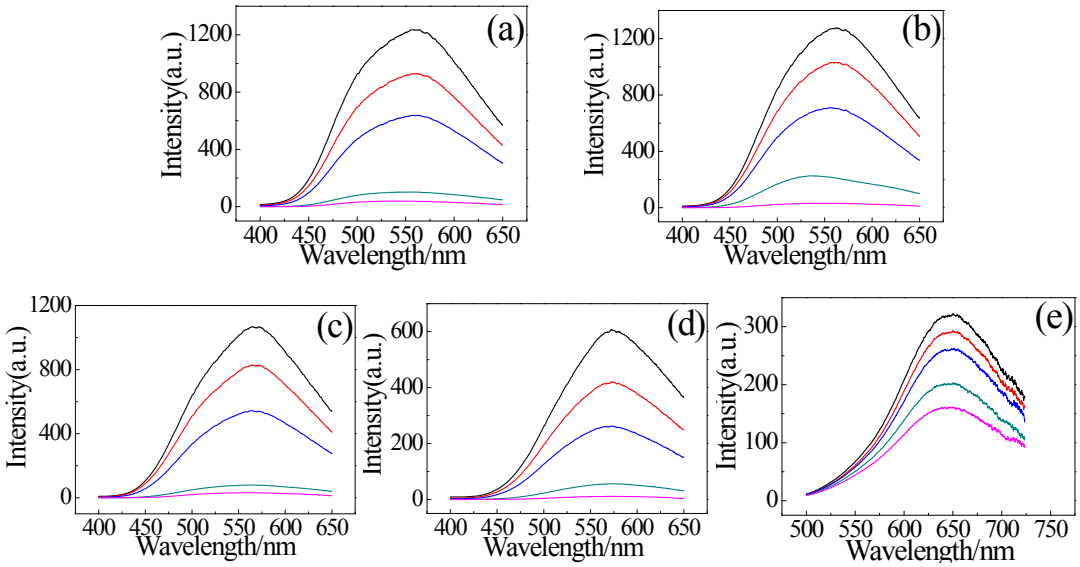


Figure S11. The absorption spectrum of nitroaromatic explosives and the emission spectrum of the five COPs.



Fifure S12. PL spectra of COPs in DMF solutions containing $Fe(NO_3)_3$ of different concentrations. From top to bottom, the Fe^{3+} concentrations in DMF are 0, 1×10^{-5}, 1×10^{-4}, 3×10^{-4} and 1×10^{-3} mol L^{-1}, respectively. (a) COP-61; (b) COP-62; (c) COP-63; (d) COP-64; (e) COP-65.

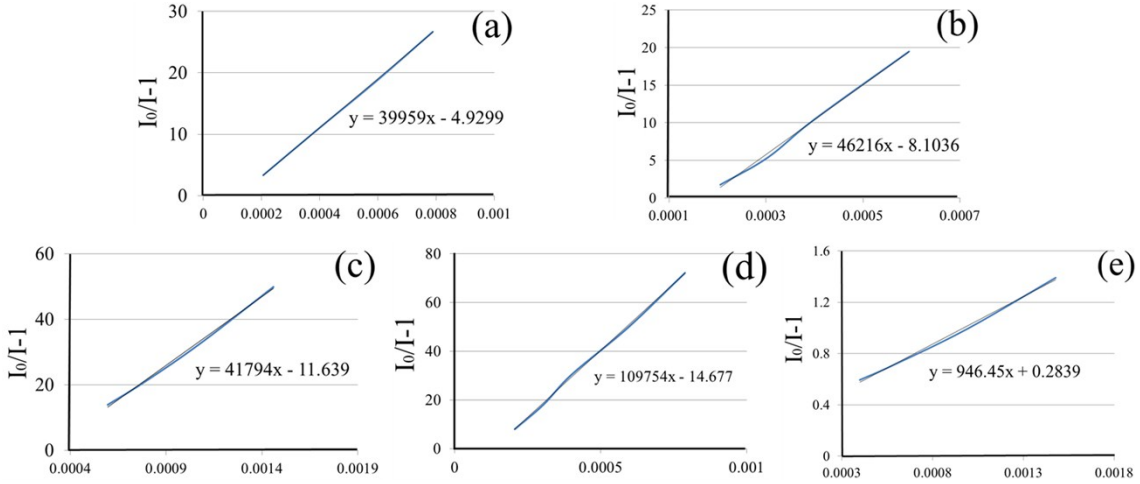


Figure S13. Stern–Volmer plots of the COPs for sensing Fe^{3+}. (a) COP-61; (b) COP-62; (c) COP-63; (d) COP-64; (e) COP-65.

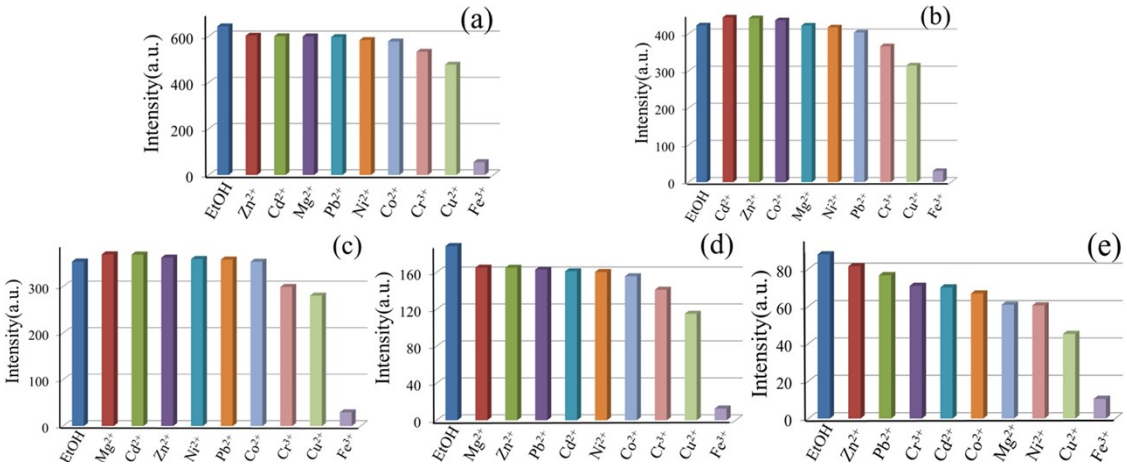


Figure S14. The luminescence intensity of the five COPs interacting with different metal ions in 1×10^{-3} mol·L^{-1} 10% (wt) ethanol aqueous solution of $M(NO_3)_x$. (a) COP-61; (b) COP-62; (c) COP-63; (d) COP-64; (e) COP-65.

Table S3. The porosity properties of the COPs.

Materials	BET SSAs [m^2/g]	Langmuir SSAs [m^2/g]	Pore volume [cm^3/g]	Pore size [Å]
COP-61	1302.95	1911.08	0.9354	6.5, 15
COP-62	1208.72	1812.28	0.8918	6, 13, 100
COP-63	931.636	1424.11	0.7769	7, 13, 120
COP-64	716.811	1050.44	0.4894	7.5, 15, 100
COP-65	869.978	1280.31	1.0684	10~2000

Table S4. The Stern-Volmer constants with PA, pDNB, DNT, mDNB analytes for the COPs.

materials	Ksv(M^{-1}) PA	Ksv(M^{-1}) pDNB	Ksv(M^{-1}) DNT	Ksv(M^{-1}) mDNB
COP-61	239719	12100	1220	750
COP-62	181538	8617	973	645
COP-63	80425	7890	1250	770
COP-64	97869	9308	2000	1101
COP-65	67990	1165	149	117

Table S5. The lifetime of the COPs dispersed in MeOH after add PA.

	Lifetime/ns			
	concentration of PA in the dispersed COP solutions/mmol·L^{-1}			
materials	0	0.001	0.01	0.1
COP-61	1.55	1.54	1.57	1.51
COP-62	1.47	1.48	1.42	1.43
COP-63	1.36	1.34	1.37	1.32
COP-64	1.21	1.23	1.19	1.22
COP-65	1.05	1.03	1.06	1.08