

## Supporting Information

### **Highly sensitive and selective detection of 2,4,6-trinitrophenol by covalent–organic polymer luminescent probes**

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## S1. Experimental Section

All reagents, unless otherwise stated, were commercially available and used without further purification.

### S1.1 Synthesis of COPs

1,5-Cyclooctadiene (cod, 0.50 mL, 3.96 mmol, dried with  $\text{CaH}_2$ ) was added to a solution of bis (1,5-cyclooctadiene)nickel(0)( $[\text{Ni}(\text{cod})_2]$ , 1.125 g, 4.09 mmol), and 2,2'-bipyridyl(0.640 g, 4.09 mmol) in dry dimethylformamide (DMF) (65mL). The mixture was stirred until completely dissolved. 2,4,6-Tris-(4-bromo-phenyl)-[1,3,5]-triazine (TBT) (0.1667 g, 0.314 mmol) and 1,4-Dibromobenzene (DB) (0.1111 g, 0.471 mmol) were subsequently added to the resulting purple solution. The reaction vessel was heated at 80° C overnight under a nitrogen atmosphere. 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  $\text{CHCl}_3$  ( $5 \times 15$  mL), tetrahydrofuran (THF) ( $5 \times 15$  mL) and  $\text{H}_2\text{O}$  ( $5 \times 15$  mL), respectively, and dried in vacuum to yield a cream powder (marked as COP-401). The dried sample was placed in containers and stored in a desiccator. Elemental analysis calcd (%) for  $\text{C}_{60}\text{N}_6\text{H}_{36}$ : C 85.71, H 4.29, N 10.00; found (%): C 78.64, H 4.696, N 9.668.

The synthetic steps and reaction conditions of COP-301 is the same as COP-401. However, the organic ligands for COP-301 are 1,3,5-Tris(4-bromophenyl)benzene (TBB) (0.1705 g, 0.314 mmol) and DB (0.1111 g, 0.471 mmol). Elemental analysis calcd (%) for  $\text{C}_{45}\text{H}_{28}$ : C 95.96, H 5.04; found (%): C 88.31,

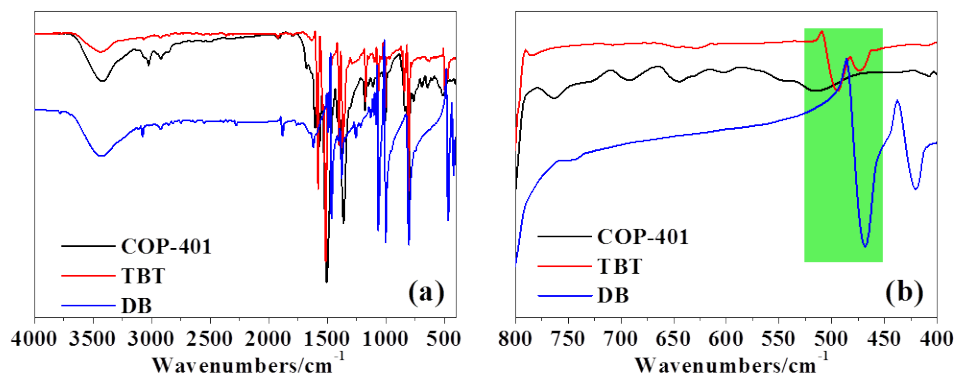
H 5.432.

## **S1.2 Characterization of Materials**

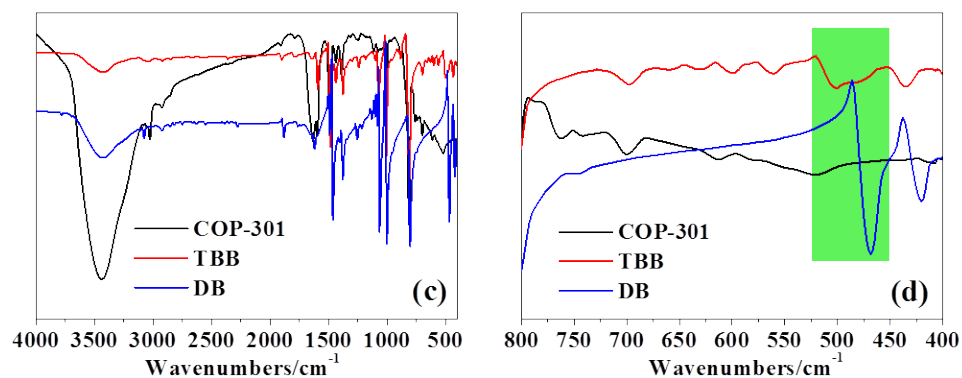
Thermogravimetric analysis (TGA) data was obtained on a STA449C (NETZSCH) instrument, with a heating rate of  $10^{\circ}\text{C min}^{-1}$  under flowing  $\text{N}_2$ . FTIR spectroscopy was performed on an AC-80MHZ (Bruker) instrument with the wave range of  $4000 - 400 \text{ cm}^{-1}$ . Scanning 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). The photoluminescence (PL) spectra were recorded by using Hitachi F-7000 Fluorescence Spectrophotometer.

## **S1.3 Luminescent measurements**

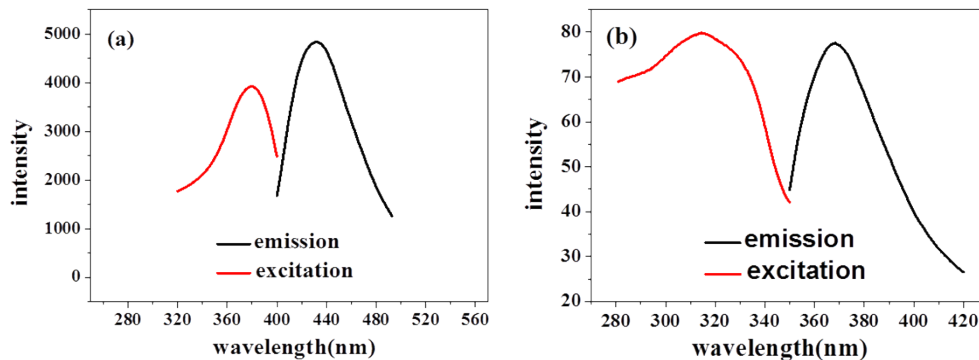
The fluorescent spectra of solid state powder monomers (TBT, TBB, DB) and the COP-401 and COP-301 were measured at room temperature. To explore the sensing properties of COPs for different nitroaromatic explosives, the two sample-solvent emulsions were prepared by introducing 2 mg of COP-401 and COP-301 powder into 10 mL of methanol, and the fluorescence spectra of methanol solutions of COP-401 and COP-301 were recorded by successive addition of aliquots of PA, 2,4,6-Trinitrotoluene (TNT) (standard solution from Aldrich), 2,4-dinitrotoluene (DNT), m-dinitrobenzen (mDNB), and nitrobenzene (NB). Prior to being added the nitroaromatic explosives, the COP methanol solutions should be stirred at least 24 hours to try best to disperse the COP powders in methanol solutions. Both excitation slit and emission slit are 5 nm for two COP samples.



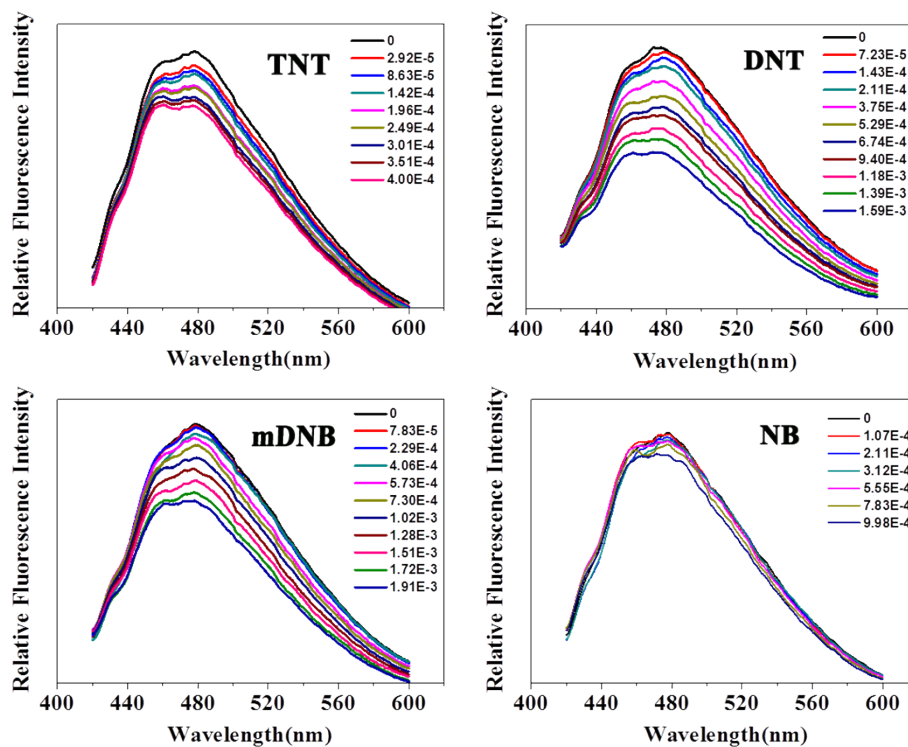
**Figure S1** FTIR spectra of the TBT (red), DB (blue) and the COP-401 (black) from 400-4000  $\text{cm}^{-1}$ (a) and 400-800  $\text{cm}^{-1}$ (b). The characteristic absorption bands for Carbon-Bromine are highlighted via green region (see the right panel), clearly showing the lack of bromine in the COP-401 and indicating the formation of the polymeric COP-401 structure.



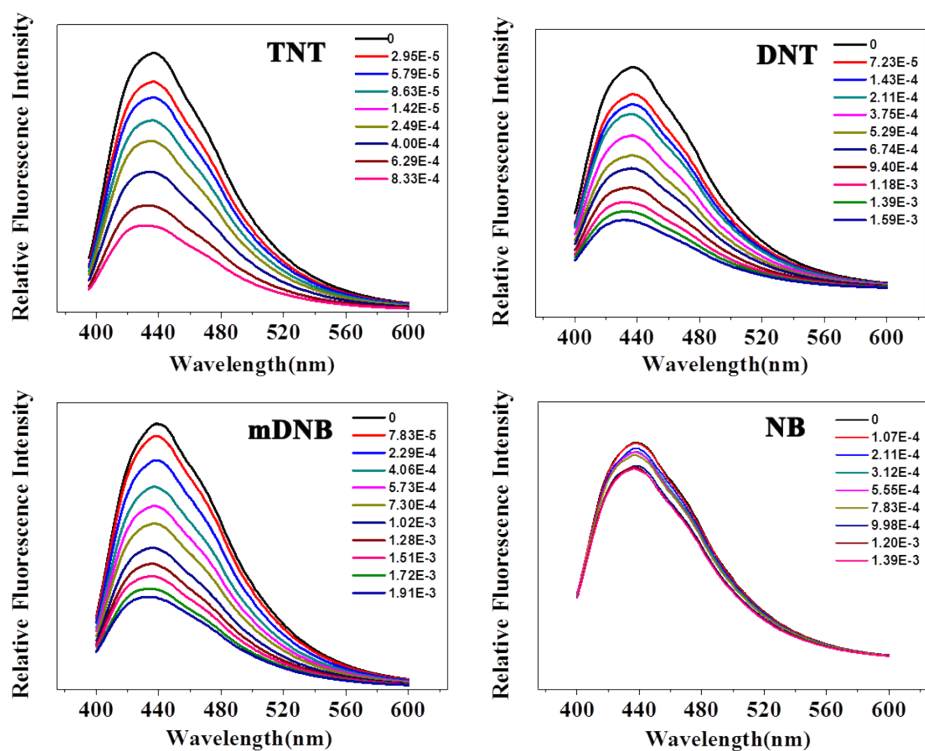
**Figure S2** FTIR spectra of the TBB (red), DB (blue) and the COP-301 (black) from 400-4000  $\text{cm}^{-1}$ (c) and 400-800  $\text{cm}^{-1}$ (d). The characteristic absorption bands for Carbon-Bromine are highlighted via green region (see the right panel), clearly showing the lack of bromine in the COP-301 and indicating the formation of the polymeric COP-301 structure.



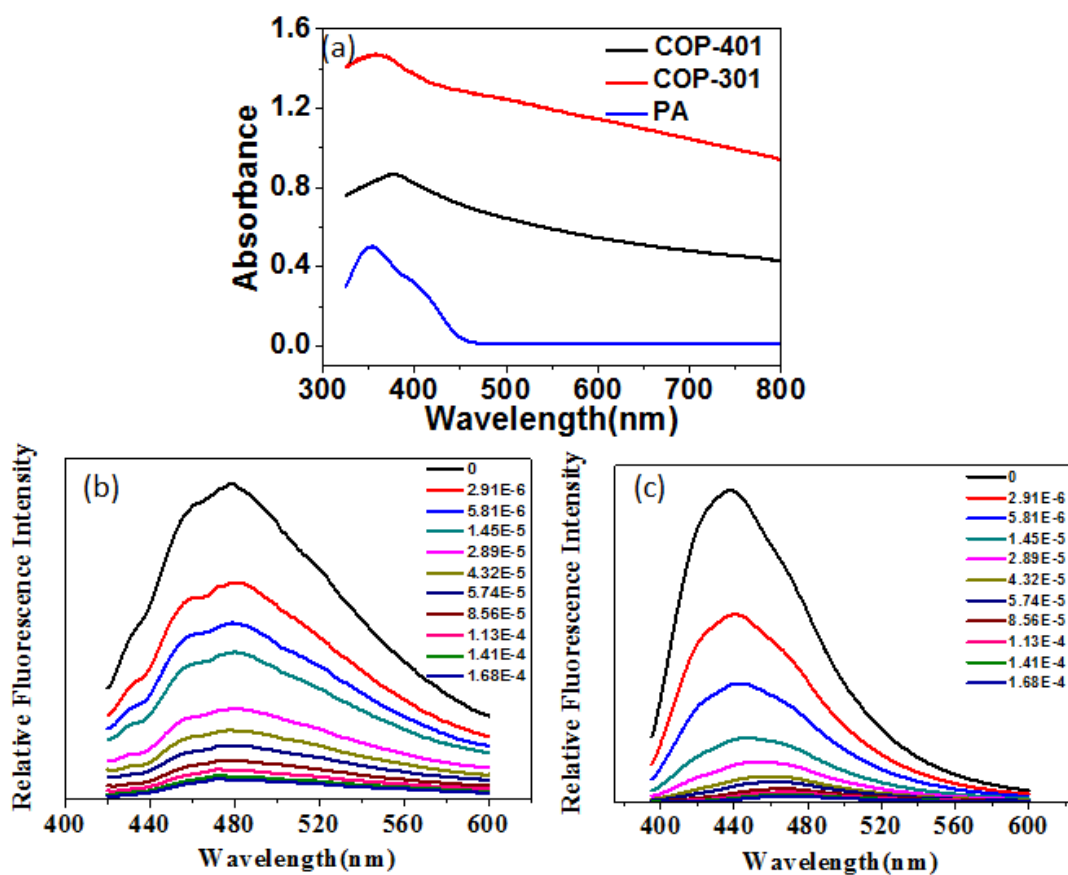
**Figure S3** The excitation (black) and PL spectra (red) of (a) COP-301; (b) TBB



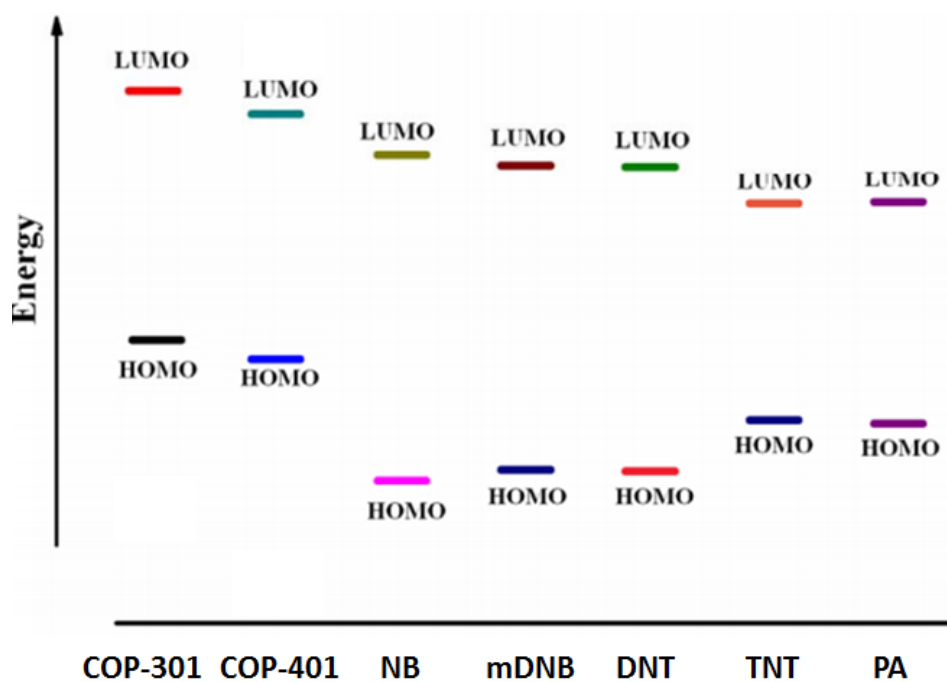
**Figure S4** Quenching of photoluminescence spectra of COP-401 with various concentrations of TNT, DNT, mDNB and NB in methanol solutions. In each graph, the data for cutline refers to the concentrations of each analyte with M unit, and 0 refers to PL spectra without analyte.



**Figure S5** Quenching of photoluminescence spectra of COP-301 with various concentrations of TNT, DNT, mDNB and NB in methanol solutions. In each graph, the data for cutline refers to the concentrations of each analyte with M unit, and 0 refers to PL spectra without analyte.



**Figure S6** (a) The absorption spectrum of COP-401, COP-301 and PA. (b) and (c) Quenching of photoluminescence spectra of COP-401 and COP-301 with various concentrations of PA in methanol solutions.



**Figure S7** HOMO and LUMO calculations for COP-301, -401 and the explosives. All the molecular orbital calculations were performed with the Gaussian 09 program at the B3LYP/6-31G\* level.