

Supporting Information

1,2,3,4,5,6-hexakis(4-bromophenyl)benzene -based covalent organic polymers as specific luminescent probes for selectively sensing nitro-explosives

Xuezhen Song¹, Yixuan Mao², Shusheng Wang³, Jiayong Luo³, Shitao Wang^{*1}, Yun Qian^{*4},

Dapeng Cao^{*1}

1. State Key Lab of Organic-Inorganic Composites, Beijing University of Chemical Technology,
Beijing 100029, China
2. Beijing No. 80 High School, Beijing 100125, China
3. Jiangxi Guotai Longshi Technology Co. Ltd., Fengcheng, Jiangxi 331121, China
4. College of Electrical and Information Engineering, Beihua University, Jilin 132021, China

*Email: stwang@buct.edu.cn, qianyun_116@163.com or caodp@mail.buct.edu.cn

1. Experimental section

1.1 Synthesis of COPs

We used two groups of monomers, with TBP and DBP as a monomer while HBB and 6-HBB as another monomer to synthesize three COPs (COP-H1, COP-H2, and COP-H3) via a nickel-catalyzed Yamamoto-type cross-coupling reaction. The processes for the three COPs followed similar steps, only with difference in the monomers and their quantities. In particular, we presented the synthesis procedure of COP-H2 as a representative example. Firstly, 1,5-Cyclooctadiene (cod, 0.25 mL, 1.98 mmol, dried with CaH_2), 2,2'-bipyridyl (0.32 g, 2.05 mmol) and bis(1,5-cyclooctadiene)nickel(0) ($[\text{Ni}(\text{cod})_2]$, 0.56 g, 2.03 mmol) were added to the dry DMF in the pressure bottle, stirred at 40 °C for half an hour until completely dissolved. Then, TPB (0.1219 g, 0.235 mmol) and 6-HBB (0.1583 g, 0.157 mmol) were added to the resulting purple solution. The reaction vessel was heated at 90 °C overnight under argon atmosphere in glove box. After cooling to room temperature, the diluted HCl solution was added to the reaction vessel and continued stirring for 6h. The color of the solution changed markedly. The solution is stratified and the product is filtered. Then, after a series of filtration and washing by CHCl_3 (5×15 mL), THF (5×15 mL), MeOH (5×15 mL) and H_2O (5×15 mL), and the solid particles were dried in a vacuum oven of 120 °C for 24 h. The dried sample was placed in containers and stored in a desiccator.

1.2 Characterization of materials

Fourier Transform Infrared Spectrometer (FTIR) spectroscopy was performed on a VERTEX 70v instrument with the wave range of 4000–400 cm^{-1} . Thermo gravimetric analysis (TGA) data was obtained on a METTLER TGA/DSC3+ instrument. The temperature was from room temperature to 800 °C. Scanning electron microscope (SEM) images were obtained on a ZEISS Gemini SEM-300 instrument from Germany. UV – vis absorption spectra were measured with a TU1901 spectrophotometers.

1.3 Luminescent measurements

The fluorescence spectra of synthesized COP materials were measured by the Hitachi F7000 fluorescence spectrophotometer. The Nitro-explosives solution (1.0 mM) was prepared using DMF as the solvent. COP was dispersed in DMF to prepare a COP material solution (3 mg/20 mL). The photoluminescence (PL) performance of the synthesized COP materials in

DMF solution at room temperature were subsequently investigated.

1.4 Sensing characteristics of nitro-explosives

After 30 μL of different nitro-explosives (1mM) was added into COP (3mg/20mL) DMF solution, we promptly measured the fluorescence intensity after addition of nitro-explosives to evaluate the interaction between the COPs and the explosives. Ten kinds of nitro-explosives were tested in this paper, and they were o-nitrophenol (oNP), p-nitrophenol (pNP), m-nitrophenol (mNP), m-dinitrobenzene (mDNB), o-dinitrobenzene (oDNB), m-nitrotoluene (mNT), p-nitrotoluene (pNT), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrophenol (2,6-DNP), trinitrophenol (TNP).

1.5 Fluorescence titration experiments

For the titration process, nitro explosive solution (1 mM) was gradually added to the COP solution. After each addition, the solution was thoroughly mixed to ensure uniform distribution of the explosive. The fluorescence intensity was measured after each addition to monitor the change in the fluorescence response. The recorded data were fitted to the Stern-Volmer (ST) equation to calculate the Stern-Volmer constant (K_{sv}), which elucidates the quenching dynamics and the interactions between COP and the nitro-explosives.

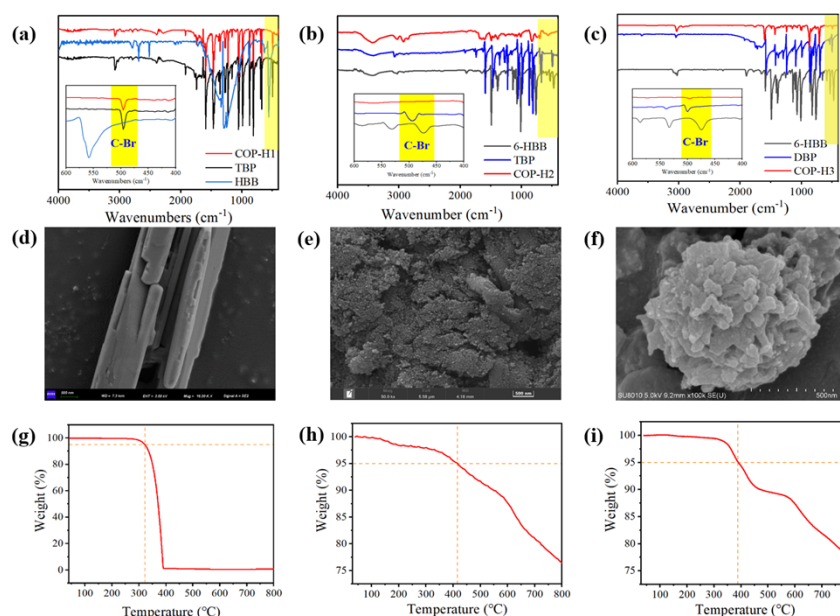


Figure S1. Characterization of materials (a~c): FTIR. (a)COP-H1 (b) COP-H2 (c) COP-H3. (d~f): SEM.(d) COP-H1, (e) COP-H2 (f) COP-H3. (g~i) TGA. (g) COP-H1,(h) COP-H2,(i) COP-H3.

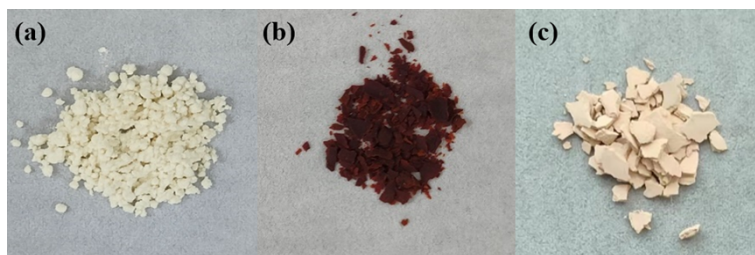


Figure S2. Photographs of the COPs at ambient conditions. (a)COP-H1; (b)COP-H2; (c)COP-H3.

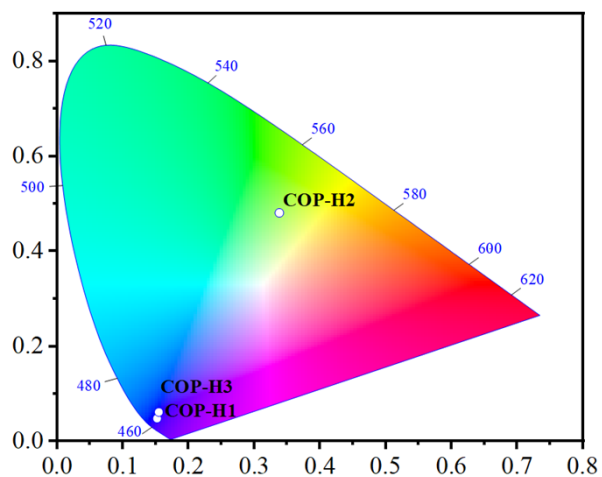


Figure S3. CIE chromaticity diagram of the COPs under ambient conditions, and the excited wavelength is the maximum excitation wavelength.

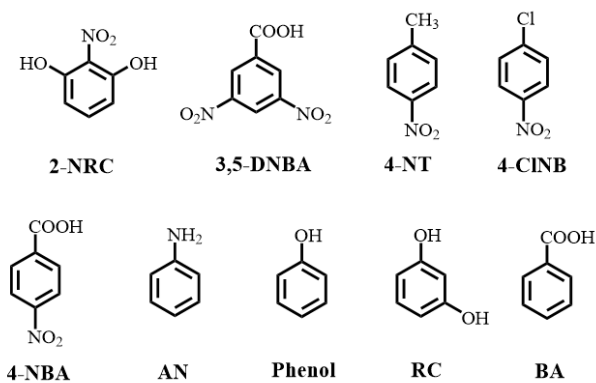


Figure S4. The chemical structures involved in the article.

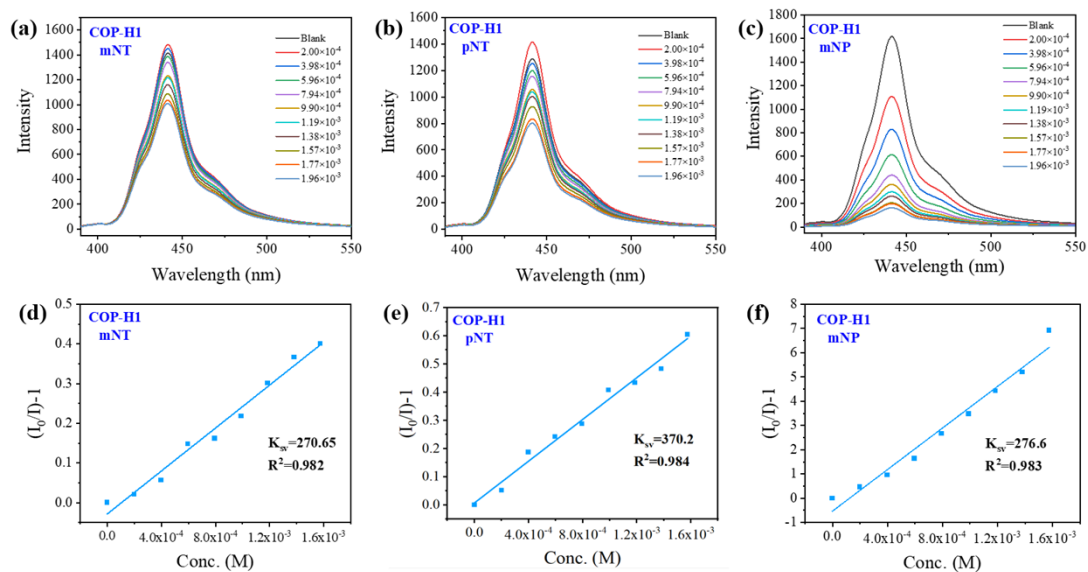


Figure S5. (a-c) PL spectra of COP-H1 in DMF solutions with different Nitro explosive concentrations. (a)mNT, (b)pNT, (c)mNP. (d-f) The corresponding Stern–Volmer plots of COP-H1. (d)mNT, (e)pNT, (f)mNP.

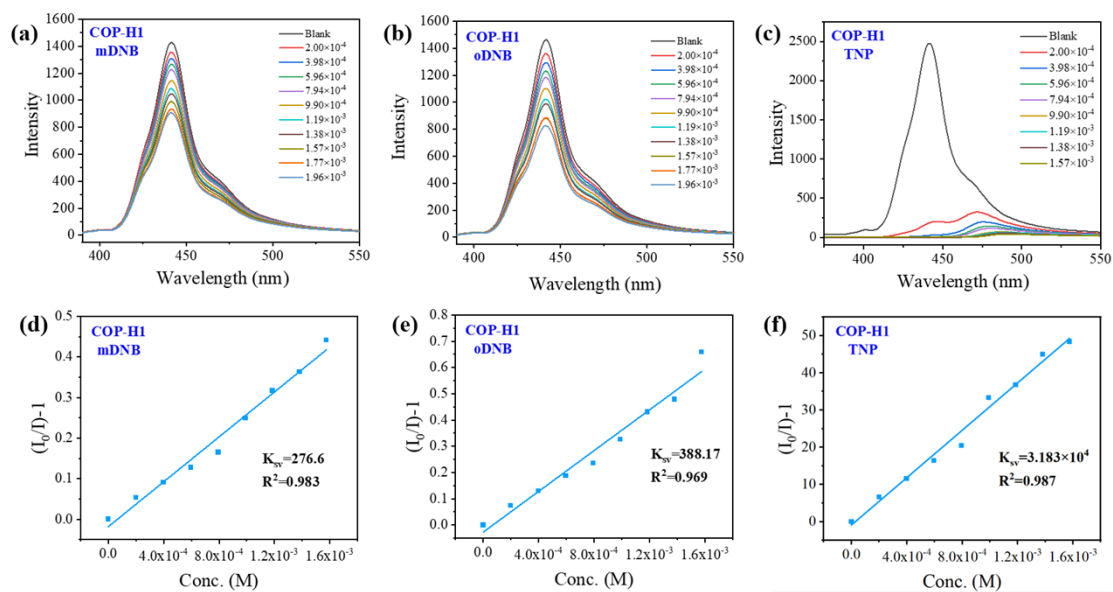


Figure S6. (a-c) PL spectra of COP-H1 in DMF solutions with different Nitro explosive concentrations. (a)mDNB, (b) oDNB, (c)TNP. (d-f) The corresponding Stern–Volmer plots of COP-H1. (d)mDNB, (e) oDNB, (f)TNP.

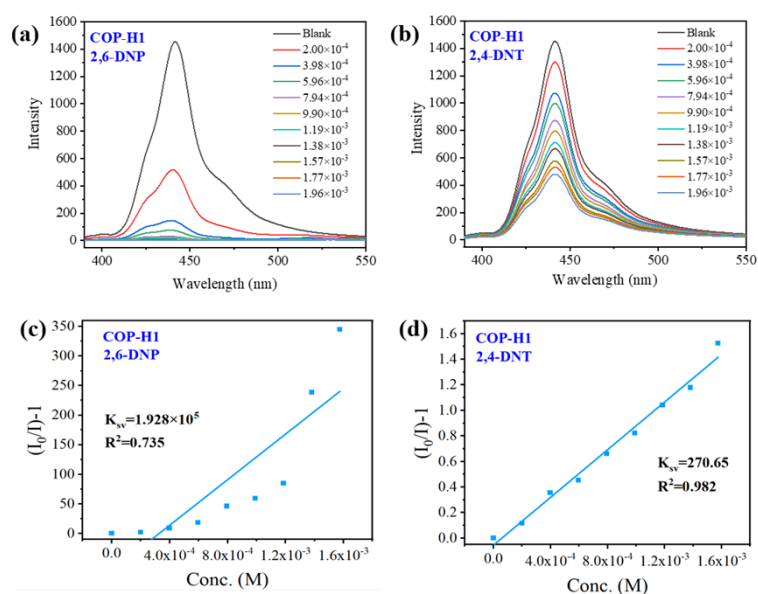


Figure S7. (a-b)PL spectra of COP-H1 in DMF solutions with different Nitro explosive concentrations.(a)2,6-DNP, (b) 2,4-DNT. (c-d) The corresponding Stern–Volmer plots of COP-H1. (c)2,6-DNP, (d) 2,4-DNT.

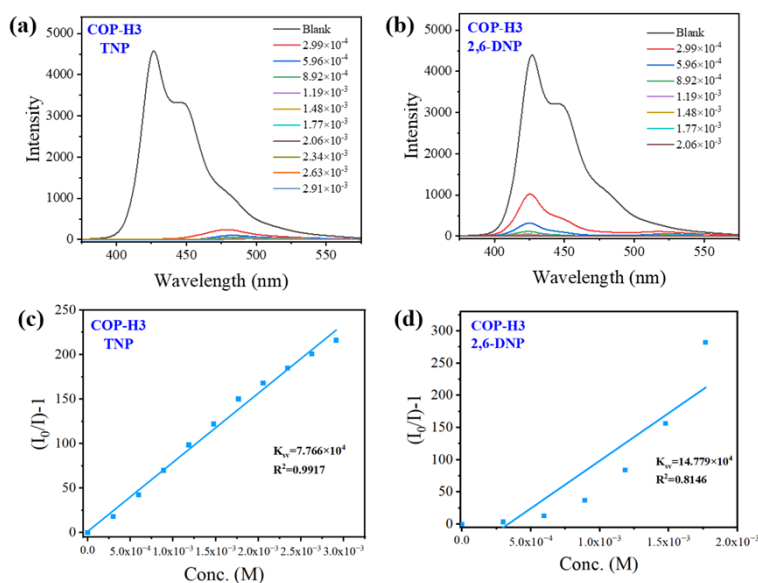


Figure S8. (a-b)PL spectra of COP-H3 in DMF solutions with different Nitro explosive concentrations.(a)TNP, (b) 2,6-DNP. (c-d) The corresponding Stern–Volmer plots of COP-H3. (c)TNP, (d) 2,6-DNP.

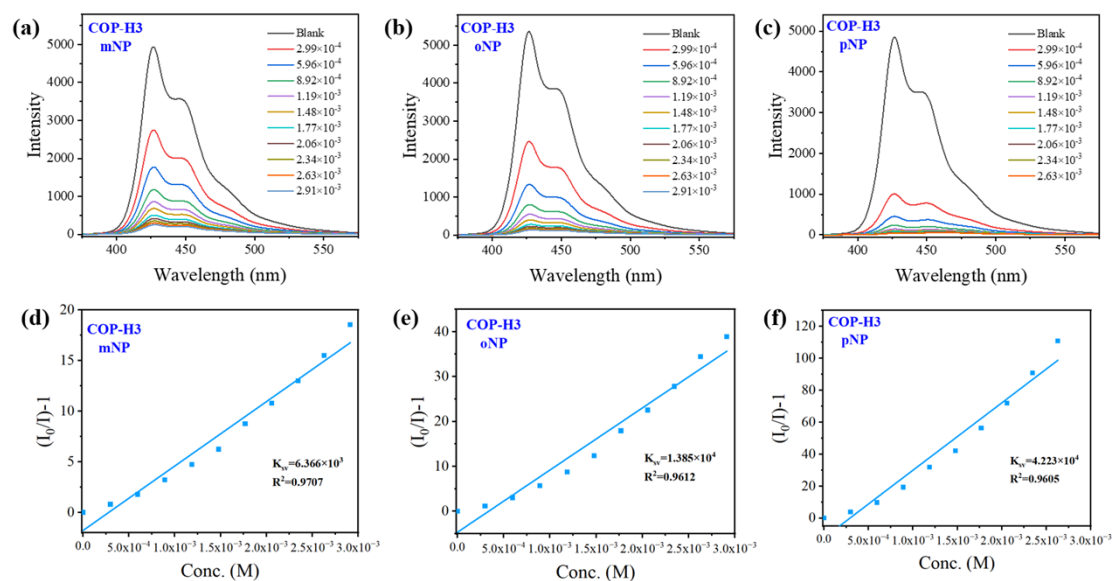


Figure S9. (a-c) PL spectra of COP-H3 in DMF solutions with different Nitro explosive concentrations. (a) mNP, (b) oNP, (c) pNP. (d-f) The corresponding Stern-Volmer plots of COP-H3. (d) mNP, (e) oNP, (f) pNP.

Table S1. The monomers of the COP materials, and the luminescent data of the solid COPs.

Material	Monomer 1	Monomer 2	$\lambda_{\text{ex}}(\text{nm})$	$\lambda_{\text{em}}(\text{nm})$	Intensity(a.u.)
COP-H1	TBP	HBB	277.2	441.2	1292
COP-H2	TBP	6-HBB	366.2	510.6	2631
COP-H3	DBP	6-HBB	345.2	426.8	4870

Table S2. K_{sv} of COP-H1 and COP-H3 for different nitro explosives

Nitro explosives	COP-H1	COP-H3
mNP	276.6	6.366×10^3
oNP	---	1.385×10^4
pNP	---	4.223×10^4
mNT	270.65	---
pNT	370.2	---
mDNB	276.6	---
oDNB	388.17	---
2,4-DNT	270.65	---
2,6-DNP	1.928×10^5	14.779×10^4
TNP	3.183×10^4	7.776×10^4