ARTICLE TYPE

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

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Rapid and sensitive detection of nitroaromatic explosives have attracted considerable attention due to their serious harm to our world. In this work, two porous luminescent covalent-organic polymers (COP-401 and COP-301) have been synthesized through copolymerization of double ligands. Results indicate that the two COPs with high thermal stability show significant luminescence quenching effects for nitroaromatic explosives. In particular, the two COPs 10 exhibit not only high sensitivity (about 1 ppm) for nitoraromatic explosives, but also extremely high selectivity for 2,4,6-Trinitrophenol (PA), which suggests that they are promising luminescent probe for highly sensitive and selective detection of nitroaromatic explosives, especially for PA.

15   Rapid and selective detection of nitroaromatic explosives has become one of the most pressing issues, because nitroaromatic explosives are serious pollution sources of water and important chemical species in mine fields, munitions remediation sites, military and security applications.[1-5] Currently, 20 nitroaromatic derivatives are being used world-wide to prepare different explosives. Among them, the detection of 2,4,6-Trinitrophenol (PA) has become very popular as it is widely used in dyes, fireworks, glass and leather industries. During commercial production and use, PA is released into the 25 environment, leading to the contamination of soil and aquatic biosystems.[6-10] Thus, it is an urgent need to develop an efficient and reliable sensor for detection of nitroaromatic explosives, especially for PA, owing to their serious pollution and potential threats for security.

30   Until now, a variety of methods of sensing nitroaromatic explosives have been reported.[11] Metal detectors, widely used as portable instrumentation for field explosive detection, cannot locate the plastic casing of modern land mines. Trained dogs are expensive and difficult to maintain, and are also easily fatigued.[12] 35 Physical detection methods for explosives include gas chromatography coupled with a mass spectrometer, surface-enhanced Raman spectroscopy, nuclear quadrupole resonance, energy-dispersive X-ray diffraction, neutron activation analysis, electron capture detection and cyclic voltammetry.[13-19] These 40 techniques are highly selective, but some are expensive and are not easily fielded in a small low-power package. Most detection methods for explosives are only applicable to vapor samples,[20-22] because of interference problems encountered in complex aqueous media.

45   As a complementary method, however, chemical sensors provide new means for the rapid detection of ultra-trace analytes from explosives, and can be easily incorporated into inexpensive and portable microelectronic devices.[23-30] Meanwhile, the fluorescence-based sensor schemes show very special promising. 50 Moreover, fluorescence method has individual advantage in many

circumstances. Therefore, the fluorescence-based detection is gaining increasing attention owing to its high sensitivity, simplicity, short response time and its ability to be employed both in solution and solid phase.[31-35] Numerous electron-rich 55 fluorescent conjugated polymers have been synthesized and used in the detection of trace amounts of nitroaromatic explosives.[36-38] Fluorescence-quenching-based chemical detection represents one of the most sensitive and convenient methods that have been widely employed in explosives identification.[39-43] By means of 60 the specific recognition of TNT antibodies, Goldman et al. fabricated some fluorescence immunoassays for TNT.[44] Li et al. synthesized two new luminescent metal–organic frameworks as probe materials to sense RDX.[45] Wang et al. reported a convenient and rapid paper sensor for PA-selective detection.[46] 65 Shyamal et al. reported a graphene-based composite, which could be potentially useful for selective detection of PA.[9] Although many chemical sensors with fluorescence toward nitroaromatic explosives have been proposed, developing quick and highly selective sensors for nitroaromatic explosives is still 70 an imperative issue.

    Covalent-organic polymers (COPs) are a new class of porous network materials, which are connected by stable covalent C-C bonds. Recent research indicates that COPs have shown great potential for a wide range of applications such as gas 75 storage and separation, luminescent sensing and template for new energy materials.[47-50] In particular, COPs are a kind of moisture-resistant porous materials, possessing high hydrothermal stability and large specific surface of 1000 ~ 3000 m^2g^{-1},[43] which may be promising reversible luminescent sensing materials. In this work, 80 we report two porous luminescent COP probes that are capable of fast and sensitive detection for nitroaromatic explosives.

    The synthesis route of the two COPs is depicted in Scheme 1. The porous COPs were successfully synthesized using 1,4-Dibromobenzene (DB) with 2,4,6-Tris-(4-bromo-phenyl)-[1,3,5] 85 -triazine (TBT) and 1,3,5-Tris(4-bromophenyl)benzene (TBB) respectively by copolymerization. The success of the phenyl–

phenyl coupling in the two porous COPs can be certified by the Fourier transform infrared (FTIR) measurement, as shown in Figure S1 and Figure S2 in Supporting Information, in which the absence of C-Br stretching peak around 500 cm^{-1} in the FTIR
5 spectra indicates that the Br functional groups in the reactant have been consumed completely by phenyl -phenyl coupling.
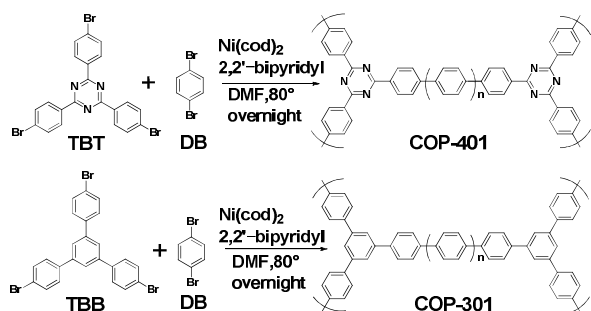
10 **Scheme1** Schematic representation of synthesis of COP-401 and COP-301 through 1,4-Dibromobenzene (DB) and 2,4,6-Tris-(4-bromo-phenyl)-[1,3,5]triazine TBT), 1,3,5-Tris(4-bromophenyl)benzene (TBB) respectively using nickel-catalyzed Yamamoto-type Ullmann cross-coupling reaction.
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The SEM image of COP-401 shows hollow pipe morphology (Figure 1 (a)), while the SEM image of COP-301 exhibits spherical shape (Figure 1 (b)). Figure 1(c) shows the TGA of two COPs under Ar atmosphere. There is nearly no
20 weight loss before 300°C for the two COPs, and less than 5% weight loss at T= 400°C. Beyond 550°C, COP-401 has a large weight loss, while COP-301 has a large weight loss after 650°C, i.e. the framework decomposition thresholds for COP-401 and COP-301 are about 550 and 650°C, respectively, which indicates
25 that both COPs are highly thermal stability.
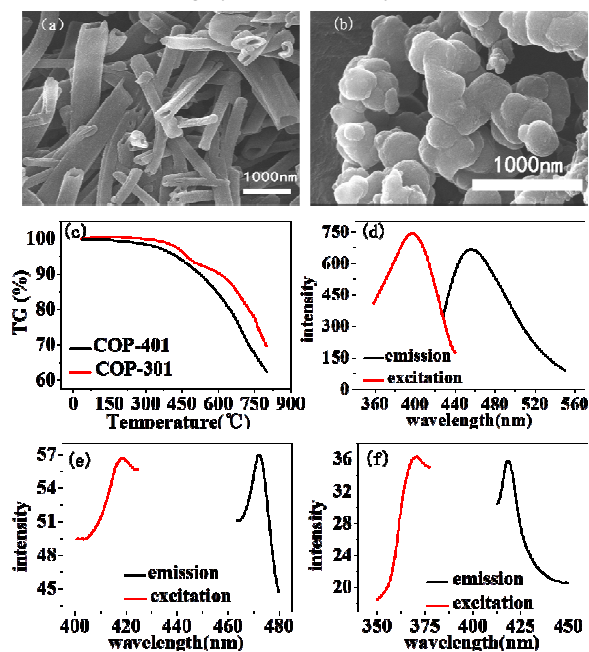
Figure 1 The characterizations of COP-401 and COP-301 **(a)** and **(b)** SEM images of COP-401and COP-301; **(c)** TGA trace of COP-401 (black) and COP-301 (red); **(d)** and **(e)** and **(f)** The excitation
30 (red) and photoluminescence spectra (black) of COP-401, TBT and DB

Figure 1 **(d-f)** show the solid-state photoluminescence (PL) spectra of the COP-401 and respective monomers (TBT and DB) at room temperature. Both organic linkers show the emission
35 peak upon excitation. Organic linker DB shows an emission at 418 nm upon excitation at 371 nm. TBT shows an emission at 472 nm upon excitation at 416 nm. The maximum emission peak of COP-401 is located at 456 nm upon excitation at 396 nm. Compared to TBT and DB, the luminescent behavior of the COP-
40 401 is probably caused by the ligand to ligand charge transfer, because the interactions between linkers can shorten the distance between the luminophores, enabling electron transfer between the luminophores.[38] Actually, the luminescent principles of COP-301 is similar to COP-401.The maximum emission peak of COP-301
45 is located at 432 nm, upon excitation at 372 nm (Figure S3a). The solid-state PL spectra of TBB monomer is shown in Figure S3b.

The ability of COPs to detect nitroaromatic explosives by luminescence quenching was investigated by adding successive aliquots of PA, TNT, DNT, mDNB, and NB into methanol
50 solutions of COP-401 and COP-301. The quenching behaviors of PL spectra of COP-401 and COP-301 upon addition of various concentrations of PA, TNT, DNT, mDNB, and NB are shown in Fig. 2a-2b and Figures S4-S5 in Supporting Information, respectively. All nitroaromatic explosives lead to the luminescent
55 quenching, compared to COP matrices. The luminescence intensity of nitroaromatic explosives-incorporated COPs is largely dependent on the concentration of the nitroaromatic explosives. With the increase of the nitroaromatic explosives concentration, the luminescence intensity decreases at different
60 levels. However, the quenching degree of the same COP for different nitroaromatic explosives is clearly different. Among the nitroaromatic explosives, the quenching effects of the two COPs for PA are very apparent, especially the sensing of COP-301 for PA.
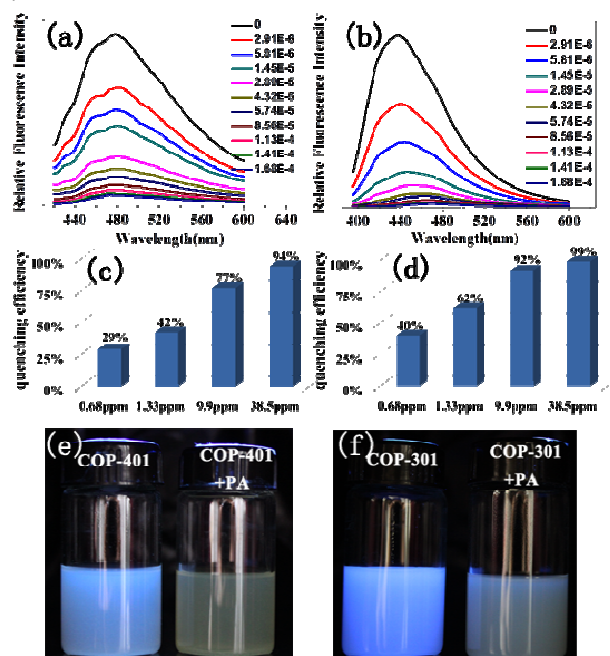
65 **Figure 2 (a)** and **(b)** Quenching of photoluminescence spectra of COP-401 and COP-301 with various concentrations of PA in methanol solutions. In each graph, the data for cutline refers to the concentrations of each analyte with M unit, and 0 refers to PL spectra without analyte; **(c)**
70 and **(d)** The quenching efficiency of COP-401 and COP-301 with various

concentrations of PA; **(e)** and **(f)** The luminescent photographs of suspensions of COP-401,COP-401+PA and COP-301, COP-301+PA in methanol solutions excited under λexcit = 365 nm using a portable UV lamp

5   In addition, both COP-401 and COP-301 can detect PA at very low concentration (＜ 1ppm), i.e. they show high sensitivity for PA. As shown in Figure 2c and 2d, when the concentration of PA is only 0.68 ppm, the quenching efficiency

10 of COP-401 is 29%, and the quenching efficiency of COP-301 is 40%. With the increase of the concentration of PA, the luminescent intensity decreases drastically. When the concentration of PA is 38.5 ppm, the quenching efficiency of COP-401 reaches 94%, while it is almost quenched completely

15 for COP-301. The visible bright blue emission of COP-401 and COP-301 in UV light vanishes upon the addition of the PA solution, which are quenched almost completely (Figure 2 (e) and (f)). Therefore, both COP-401 and COP-301 can be used to detect nitroaromatic explosives, especially for PA, with high sensitivity.

20 According to previous literature,[23] the quenching effect can be calculated quantitatively by the Stern-Volmer equation:

$$\frac{I_0}{I} = 1 + K_{SV}[M]$$

where I_0 is the initial fluorescence intensity without analyte, I is the fluorescence intensity after adding analyte of concentration

25 [M], and K_{SV} is the quenching coefficient. As shown in Figure 3 (a) and (b), a good linear Stern–Volmer relationship is observed in both COP-401 and COP-301 for each analyte, suggesting a dynamic quenching process.[51] The K_{SV} can be calculated by luminescent data. For nitroaromatic explosive-incorporated COP-

30 401, K_{SV}[PA], K_{SV}[TNT], K_{SV}[DNT], K_{SV}[mDNB] and K_{SV}[NB] are 8.3×10^4, 404, 319, 168 and 62, respectively. Similar behavior also appears in the case of COP-301, where K_{SV}[PA], K_{SV}[TNT], K_{SV}[DNT], K_{SV}[mDNB] and K_{SV}[NB] are 2.6×10^5, 2271, 997, 984 and 102, respectively. Interestingly, it is found

35 that the value of K_{SV}[PA] is higher than those of other fluorescent chemosensors for PA.[52-55] For example, the value of K_{SV}[PA] of a porous luminescent metal–organic framework for PA is 2.9×10^4 and K_{SV}[PA] of photoluminescent MoS$_2$ quantum dots (QDs) for PA is 4.3×10^4. In both cases of COP-401 and COP-301, the

40 quenching efficiencies are in the order of PA > TNT > DNT > mDNB > NB. Importantly, Figure 3 (c) and (d) show that both COP-401 and COP-301 exhibit extremely high selectivity for PA from nitroaromatic explosives. In particular, the quenching constant of COP-401 for PA is at least 201 times (K_{SV}[PA]:

45 K_{SV}[TNT]=201.1) greater than these for TNT and other nitroaromatic explosives, and the quenching constant of COP-301 for PA is at least is 116 times greater than these for other nitroaromatic explosives. The observation above indicates that the COP-401 and COP-301 might be a promising candidate to

50 selectively detect PA for security or environmental applications.

In both COP-401 and COP-301 cases, the quenching efficiencies are in the order of PA > TNT > DNT > mDNB > NB. To better understand this observation we measured absorption spectrum of PA and shown in Figure S6 in Supporting

55 Information. The absorption of PA and the emission of COPs have almost no spectral overlap, suggesting that it is not the energy transfer mechanism.[51, 56, 57] Therefore, we calculated the molecular orbits (MO) (Figure S7 in Supporting Information).

This quenching order can be explained by the donor–acceptor

60 electron transfer mechanism with COPs as the donor and PA as the acceptor. Upon excitation, the electrons in conduction band of COPs are transferred to the lowest unoccupied molecular orbital (LUMO) of the analytes, which results in quenching effect. With the increase of such electron withdrawing groups (-NO$_2$) in

65 analytes, the quenching efficiencies are therefore enhanced,[38] which can be explained by the order of LUMO levels of explosives, i.e. NB > mDNB > DNT > TNT > PA. As a result, the transferred electron efficiency follows the order of NB < mDNB < DNT < TNT < PA, therefore yielding the above

70 quenching order. In addition, the K_{SV}[PA] of COP-301 is three times higher than the K_{SV}[PA] of COP-401, mainly because the electronegativity of N is larger than C and the LUMO level of COP-301 is higher than that of COP-401 (see Figure S7). Accordingly, the electron transformation from conduction band

75 of COP-301 to LUMO of analyte becomes faster than that of COP-401 upon excitation, which results in higher quenching efficiencies of COP-301 for analyte, compared to COP-401.
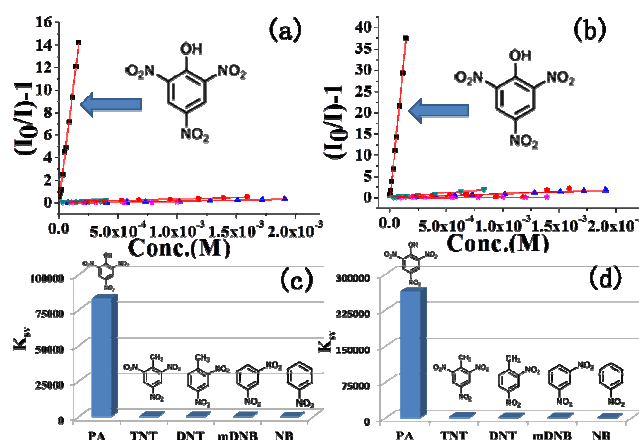
80 **Figure 3 (a)** and **(b)** Stern–Volmer plots of COP-401 and COP-301; ■ (PA), ● (DNT), ▲ (mDNB), ▼(TNT), ★ (NB); **(c)** and **(d)** The Stern–Volmer constants with PA, TNT, DNT, mDNB, NB analytes for COP-401 and COP-301.

85 In summary, we have synthesized two porous luminescent COPs by copolymerization. The two COPs possess high thermal stability and good luminescence intensities. Moreover, the two COPs show fast response and high sensitivity for detection of the nitroaromatic explosives, especially for PA. In particular,

90 K_{SV}[PA] of COP-301 and COP-401 for PA reaches 2.6×10^5 and 8.3×10^4, which is higher than other chemical sensors.[48-51] Furthermore, both COP-401 and COP-301 exhibit not only high sensitivity for PA at low concentration about 1 ppm, but also extremely high selectivity for PA, which suggests that the COPs

95 are promising luminescent probe for detection of nitroaromatic explosives, especially for PA.

Notes and References

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Table of content graphics

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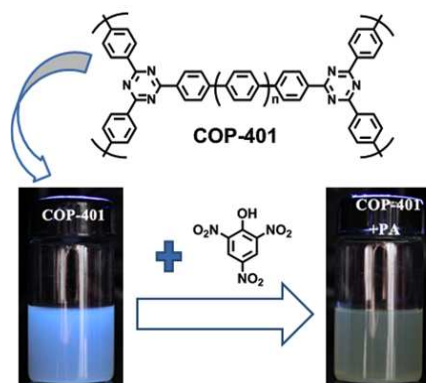
We have synthesized two luminescent covalent-organic polymers (COPs), which could be considered as promising luminescent probe for highly sensitive and selective detection of nitroaromatic explosives, especially for 2,4,6-trinitrophenol.