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

Lin Guo[a] and Dapeng Cao*[a]

We adopt 1,3,6,8-Tetrabromopyrene (TBP) and 1,3,5-tris(4-bromophenyl)benzene (TBB) as double monomers to synthesize a series of porous covalent organic polymers (COPs) using Ni-catalyzed Yamamoto reaction. By manipulating the reactive ratios of two monomers, we successfully achieve the color tailoring of the resultant COP samples. Interestingly, the emission peaks of these porous COP samples cover a wide color range from 533 up to 815 nm, which is the first near-infrared luminescent porous organic material. Further study indicates that these porous COPs can be served as luminescent sensors for highly sensitive and selective sensing of nitroaromatic explosives and metal ions. These materials might also find more applications in photocatalysis, organic electronics and medical images.

Fast development of chemical industry and extensive applications of chemical products are leading to the contamination of soil and aquatic bio-systems and environmental deterioration.[1] Therefore, rapid sensing or detecting the metal ions and nitroaromatic explosives are attracting increasing attention since it is closely related to security, environmental and human being health implications.[2] Previous investigations indicate that the conjugated polymer-based fluorescence sensors can amplify the sensing sensitivity. A lot of metal–organic frameworks (MOFs)[3] and covalent–organic materials (COMs)[4] have been considered as promising reversible luminescent sensing materials, owing to their permanent porosity, conjugated groups and tunable framework structures. However, the low hydrothermal stability of some MOFs limits their industrial application.[4j] So, the COM materials become a better candidate as luminescent probe owing to its rich in extended π systems and high hydrothermal stability. A series of conjugated microporous polymer (CMP) materials have been synthesized and used as luminescent probes for detection of reactive gases NOx,[5] hazardous explosives,[6] oxidative ions and TNT[7].

Recently, light-emitting diodes (LEDs) are well known as the new generation lighting source.[8] Currently, most LEDs are based on group-III nitride crystals, and they often exhibit high efficiency in the blue wavelengths and decrease rapidly in red wavelengths.[9] Actually, it is still a great challenge to find novel materials covering all color contributions for generation of white emission. As an emerging technology, organic LEDs (OLEDs) with conjugated bond have exhibited great potentials owing to good processability, low operating voltages and facile color tunability.[10] As an efficient chromophore, pyrene may be a good monomer for synthesis of OLED materials. Jiang et al. used pyrenediboronic acid as the building unit to synthesize a photoconductive COF material for applications in optoelectronics.[11] Cooper et al. also adopted pyrene as monomer to prepare a series of CMP luminescent materials and

achieved the tailoring of emission peak up to L< 620 nm.[12] Allendorf et al. used the same ligands to synthesize two MOFs with different structures and found that the microstructure of MOF will affect the luminescent emission significantly,[13] which give us opportunity to tailor the luminescent emission of materials by manipulating the microstructures.

Here, by tuning the ratios of two monomers of 1,3,6,8-tetrabromopyrene (TBP) and 1,3,5-tris- (4-bromophenyl) benzene (TBB), we synthesize a series of porous covalent-organic polymers (COPs) by using Ni-catalyzed Yamamoto reaction. The resulting COP materials exhibit strong luminescence with wide emission peak ranges from 533 up to 815 nm, and color tailoring can be achieved. Moreover, these porous COPs also exhibit high sensitivity and selectivity for sensing of nitroaromatic explosives and metal ions.
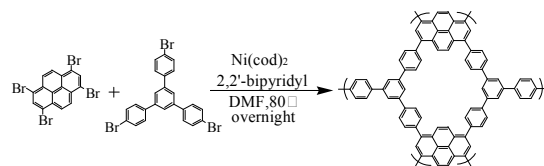
Scheme1 Synthetic route of the COPs by using 1,3,6,8-Tetrabromopyrene (TBP) and 1,3,5-tris(4-bromophenyl)benzene (TBB) as double monomers via the nickel-catalyzed Yamamoto-type Ull-mann cross-coupling reaction.

The synthetic scheme of the COPs is shown in Scheme 1. The five COP samples were synthesized in five different monomer ratios of 2:3, 1:1, 3:2, 4:1 and 9:1 by using Ni-catalyzed Yamamoto reaction. For convenience, the five COPs are marked as COP-61, COP-62, COP-63, COP-64 and COP-65, respectively. The detailed synthetic processes and the monomer ratios were presented in Section S1 and Table S1 and the elemental analysis data are listed in Table S2 in Supporting Information.

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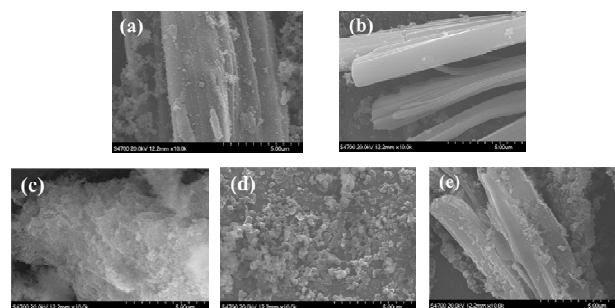
Figure 1. SEM images of the five COPs. (a) COP-61; (b) COP-62; (c) COP-63;(d) COP-64; (e) COP-65.

The success of the phenyl–phenyl coupling in the five porous COPs can be confirmed by the Fourier transform infrared (FTIR) (Figure S1). The absence of the C–Br stretching peak around 500 cm^{-1} in the FTIR spectra indicates that the Br functional groups in the reactant have been consumed completely by phenyl–phenyl coupling. Figure 1 shows the SEM images of the five COPs, where these COPs hold different morphologies. COP-61 shows hollow pipe morphology, and COP-62 and COP-65 exhibit the clear-cut layer texture, while COP-63 and COP-64 exhibit the spherical shape. Thermogravimetric analysis under N_2 (Figure S2) suggests that there is only 10% weight loss at about T=550, 450, 500, 400 and 600 °C for COP-61 ~ COP-65, which indicate that these COPs hold high thermal stability. The quantum yields of COP-61 ~ COP-65 are 2.52%, 2.33%, 2.08%, 1.85%, 1.57%, respectively. The porosity of these COPs is characterized by N_2 adsorption at T=77K (Figure S3 and S4). The BET specific surface areas of these porous COPs are 1302, 1208, 931, 716 and 869 m^2/g, respectively (Table S3)
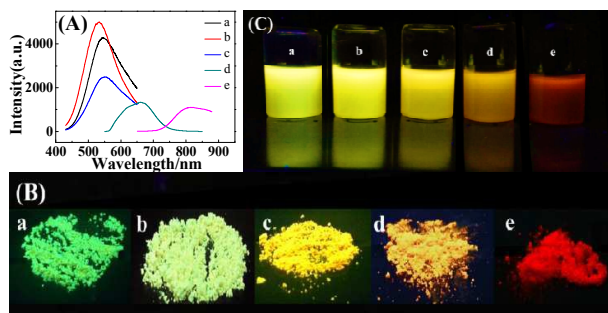
Figure 2. (A) PL spectra of the five solid COP materials. (B) The emitting colorful luminescence of five solid state COPs. (C) The emitting colorful luminescence of five COPs in DMF solution. (a) COP-61, (b) COP-62, (c) COP-63, (d) COP-64, (e) COP-65.

The solid-state photoluminescence (PL) spectra of the five COPs at room temperature are shown in Figure 2A, and the detailed excitation and emission PL spectra of five COPs and respective monomers are presented in Figure S5. The emission peaks of TBP and TBB are at 468 and 368nm respectively. Compared to TBB (the luminescence intensity of TBB is very weak and only 72), the luminescence intensity of the five COPs exhibits several orders of magnitude increase (in particular, COP-61 reaches 5500). Moreover, the emission peaks of the five COPs show significant red-shift. The observation above may attribute to the formation of extended π conjugation in the COPs. As shown in Figure 2A and Figure S5, COP-

61, COP-62 and COP-63 show single emission peak of 533, 543 and 555 nm when excited at 344 nm, whereas COP-64 presents a broad peak located at 655 nm upon the excitation at 469 nm. Interestingly, COP-65 shows a broad emission peak at 815 nm when excited at 532 nm, which is greatly longer than the emission peaks of all previously reported porous organic materials,[4c, 12, 14] and even be longer than some Ln-MOFs.[15] The significant redshift implies that the degree of polymerization in the synthesized COPs are very high.[12] The large emission may be also attributed to the hierarchically disordered channels, because COP-65 contains an extremely wide hierarchical channels from 1 to 200 nm (Figure S4e), and in the hierarchical pores, the optically isolated regions can be connected efficiently for charge transfer and therefore leads to the enhancement of π conjugation effects.[16] Interestingly, by manipulating the reaction ratio of monomer TBP and TBB, we successfully achieve the emission color tailoring of the resultant COP materials (see Figure 2A), because the different ratios of monomers would lead to different polymerization degrees and redshift of emission peaks.[17] Actually, the luminescence behavior of the five COPs is probably caused by the monomer to monomer charge transfer, because the interactions between linkers can shorten the distance between the luminophores, enabling electron transfer between the luminophores.[4e] Actually, COP-64 and COP-65 present a relatively broad emission peak, probably due to the presence of a distribution of chromophore in the COPs caused by the statistical distribution of monomer sequences (like TBP-TBP, TBP-TBB and TBB-TBB sequences).[12]

All the five COPs show strong solid state fluorescence with wide emitting colors ranging from yellow-green (COP-61), light yellow green (COP-62), yellow (COP-63), orange (COP-64) and red (COP-65) (see Figure 2B and Figure S6). The solid state properties of the COPs make them be potential candidates for applications in OLED. Compared to the luminescent emission peaks of the five solid COPs (as shown in Figure 2A), their emitting colors exhibit some differences (as shown in Figure 2B and Figure S6). This is because the luminescent photographs of the COPs are obtained under the UV lamp with the excited wavelength of 365 nm, which is not the maximum excitation wavelength. To explain the phenomena, we also used the CIE chromaticity diagram of the COPs under ambient conditions with the excited emission of 365 nm to determine their colors, and the CIE chromaticity diagram is shown in Figure S7. Definitely, the CIE chromaticity diagram is entirely same with the luminescent photographs of the COPs.

When the five COPs were dispersed in solvent DMF, they still exhibit similar color luminescence with the solid state samples, respectively (see Figure 2C), which allows us to use these color-tunable COPs as luminescent probe for sensing nitroaromatic explosives and metal ions in solutions.

The ability of COPs to detect nitroaromatic explosives by luminescence quenching has been investigated by adding successive aliquots of PA, DNT, mDNB, and pDNB into methanol solutions of the COPs. Compared to the COP matrices, all nitroaromatic explosives can lead to luminescence quenching (see Figure S8). The quenching degree of the same COP for different nitroaromatic explosives is clearly different, and the quenching effects of the five COPs for PA are more apparent, as shown in Figure 3, which means that these COPs exhibit high selectivity for

PA. In particular, the red luminescence of COP-65 is almost quenched entirely for PA (see Figure 3f). To better explore the quenching degree, we also calculated the quenching coefficient by the Stern-Volmer equation: $I_0/I=1+K_{sv}[M]$,[2b] where I_0 is the initial fluorescence intensity without the analyte, I is the fluorescence intensity after adding the analyte of concentration [M], and K_{sv} is the quenching coefficient. As shown in Figure S9, a good linear Stern–Volmer relationship is observed in all the COPs for each analyte.[4j, 18] In all the five COPs, the quenching efficiencies are in the order of PA > pDNB > DNT > mDNB. The K_{sv} of the five COPs (COP-61 ~ COP-65) for PA are 2.40×10^5, 1.82×10^5, 8.04×10^4, 9.79×10^4, 6.80×10^4, respectively (see Figure S10 and Table S4). In particular, the selectivities of COP-61 for PA against pDNB, DNT and mDNB reach 19.8, 196.5 and 319.6, respectively.
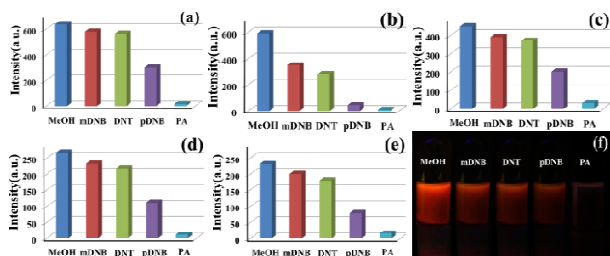
Figure 3. The PL quenching of five COPs for sensing nitroaromatic explosives in the same concentration of 1.0×10^{-5} mol·L^{-1} in methanol solutions. (a) COP-61; (b) COP-62; (c) COP-63; (d) COP-64; (e) COP-65; (f) The PL quenching photographs by adding different explosives into COP-65 suspension in methanol solutions, where PL is excited under λ_{ex}=365 nm using a portable UV lamp.
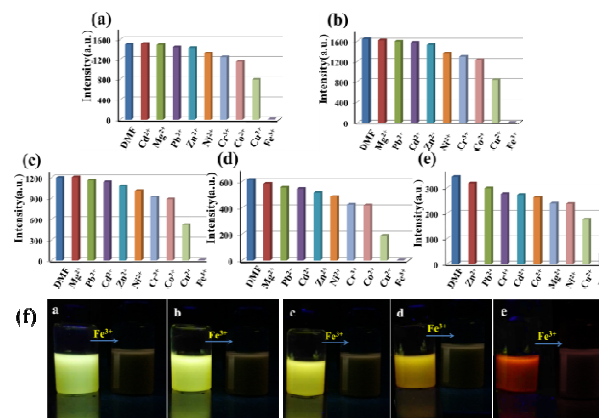
Actually, the luminescence intensity of nitroaromatic explosives-incorporated COPs largely depends on the concentration of the nitroaromatic explosives. With the increase of the nitroaromatic explosive concentration, the luminescence quenching effect becomes more apparent. Figure 4 shows the PL spectra of the COPs in methanol solutions containing PA of different concentrations. Results indicate that all the five COPs can detect PA at a very low concentration (< 1 ppm), and show extremely high sensitivity for PA.

To investigate the quenching mechanism, we measured the absorption spectrum of nitroaromatic explosives and the emission spectrum of the COP matrices, and shown in Figure S11. The absorption of PA and the emission of COPs have almost no spectral overlap, suggesting that it is not the energy transfer mechanism. Then, we measured the lifetime of the COPs dispersed in MeOH before and after adding PA of different concentrations, and listed in Table S5. Obviously, the mean lifetimes keep unchanged with the addition of PA, suggesting that it is a static quenching process of the five COPs.[2b] The quenching order can be explained by the donor-acceptor electron transfer mechanism with COPs as the donor and PA as the acceptor. With the increase of such electron withdrawing groups (for example, $-NO_2$) in analyte, the quenching efficiencies are therefore enhanced; and with the increase of such electron donating groups (for example, $-CH_3$) in analyte, the quenching efficiencies are weakened. Therefore, the quenching effects follow the order of transferred electron efficiency, mDNB < DNT < pDNB < PA.
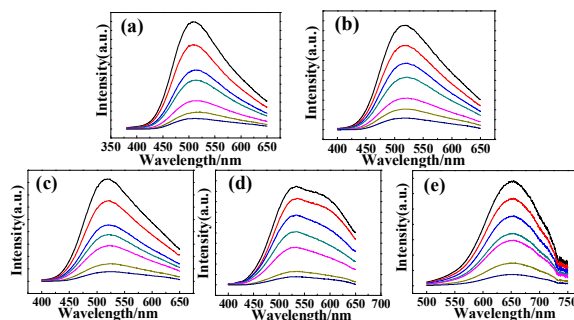
Figure 4. PL spectra of five COPs in methanol solutions with different PA concentrations. (a) COP-61; (b) COP-62; (c) COP-63; (d) COP-64; (e) COP-65. From top to bottom, the PA concentrations in methanol are 0, 1.02×10^{-7}, 5.13×10^{-7}, 1.02×10^{-6}, 5.13×10^{-6}, 1.02×10^{-5}, 5.13×10^{-5} mol·L^{-1}, respectively.

To explore the multifunctional applications of these COPs as luminescent probes, we further studied the ability of the COPs to detect metal ions by adding successive aliquots of $M(NO_3)_x$ (M= Pb^{2+}, Cu^{2+}, Cr^{3+}, Co^{2+}, Fe^{3+}, Cd^{3+}, Ni^{2+}, Mg^{2+}, and Zn^{2+}) into DMF solutions of the synthesized COPs. The luminescence quenching effects of the COPs upon addition of 1.0×10^{-3} mol·L^{-1} $M(NO_3)_x$ are shown in Figures 5. Interestingly, among the metal ions studied, the luminescence quenching of these COPs for Fe^{3+} is more pronounced, suggesting that the COPs exhibit high selectivity for Fe^{3+} sensing. After Fe^{3+} is added, the luminescence intensity of the five COP suspensions reduces to almost zero, suggesting that they are almost quenched completely. Figure 5f shows the pictures of almost completely quenching of luminescence after adding Fe^{3+}.

Figure 5. The luminescence intensity of the five COPs interacting with different metal ions in 1×10^{-3} mol·L^{-1} DMF solution of $M(NO_3)x$. (a) COP-61; (b) COP-62; (c) COP-63; (d) COP-64; (e) COP-65. (f) The PL quenching photographs by adding Fe^{3+} into five COP suspensions in DMF solutions, where PL is excited under λ_{ex}=365 nm using a portable UV lamp.

PL spectra of the COPs in DMF solutions containing $Fe(NO_3)_3$ of different concentrations are presented in Figure S12. By calculating the quenching coefficient using the Stern-Volmer equation, we obtained a good linear Stern-Volmer relationship for five Fe^{3+}/COP cases (Figure S13). Actually, the COPs for sensing Fe^{3+} have high quenching coefficient K_{sv}, which allows us to easily identify the

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existence of a small amount of Fe^{3+} ions. The possible mechanism of detecting metal ions is the donor–acceptor electron transfer mechanism, as reported elsewhere.[4l, 19] For practical application, we also studied the luminescent property of the COPs immersed in 10% (wt) ethanol aqueous solution for sensing metal ions, and found that these COPs shows similar luminescence quenching upon addition of $M(NO_3)x$ (M= Pb^{2+}, Cu^{2+}, Cr^{3+}, Co^{2+}, Fe^{3+}, Cd^{3+}, Ni^{2+}, Mg^{2+} and Zn^{2+}) (Figures S14). Even the COPs have much higher sensitivity for Fe^{3+} ions in 10% (wt) ethanol aqueous solution, suggesting that the COPs are a good candidate for practical application as sensors.

In summary, we have synthesized a series of porous COP luminescent probes through copolymerization of the monomers of TBP and TBB. By manipulating the ratios of TBP and TBB, we successfully achieve the luminescent color tailoring of these COPs. Interestingly, the luminescence of these COPs covers a wide wavelength range and the maximum emission peak of COP-65 reaches 815 nm, which is the first near infrared luminescent porous organic material. It may be attributed to the hierarchically disordered channels of COP-65 ranging from 1 to 200 nm, which is beneficial to efficiently connect the optically isolated regions for charge transfer and therefore leads to the enhancement of π conjugation effects. Further investigations indicate all the five COPs show very high selectivity and sensitivity for detection of PA (< 1 ppm) and Fe^{3+} (< 1 mM) at low concentrations, which suggest that the COPs are promising luminescent probes for detection of nitroaromatic explosives and metal ions, especially for PA and Fe^{3+}. These materials might also find more applications in photocatalysis, organic electronics and medical images.

Acknowledgements

Notes and references

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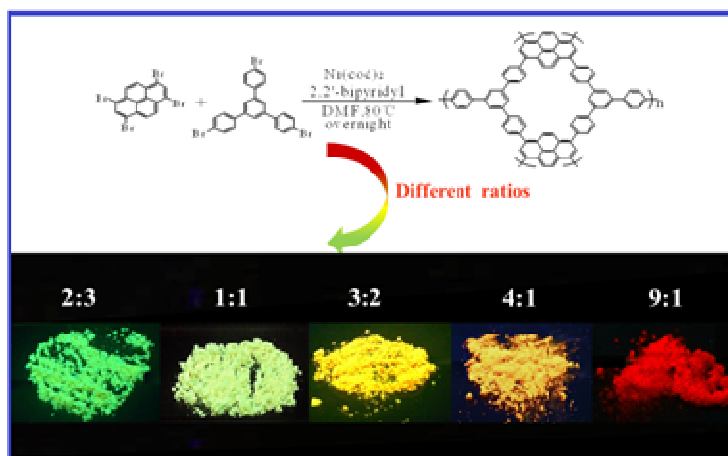
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Color tunable covalent organic polymer luminescent probes for selective sensing of metal ions and nitroaromatic explosives

Lin Guo and Dapeng Cao

The color tailoring of the porous covalent-organic polymers (COPs) are achieved successfully, and the first near-infrared luminescent COP with emission of 815 nm is obtained. These COPs can be served as luminescent sensors for highly sensitive and selective sensing of nitroaromatic explosives and metal ions.