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Fluorescent nanoscale zinc(II)-carboxylate coordination polymers for explosive sensing†

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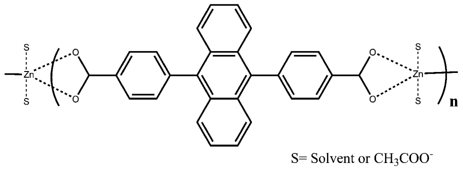
Fluorescent nanoscale coordination polymers with cubic morphology and long range ordered structure were fabricated and exhibited efficient sensing for both nitroaromatic explosive and nitromethane due to large surface area to volume ratio and strong binding affinity to explosive molecules.

Chemical sensors for rapid detection of explosives are important for the versatile applications in security screening, industrial process control, and environment monitoring.[1,2] Many explosive compounds possess electron withdrawing nitroaromatic groups, and often act as good electron acceptors. Electron donor conjugated polymers have been seen as one of the most promising candidates for detection of nitroaromatic explosives, mainly because the efficient exciton migration intrinsic to the long-range conjugation results in high sensitivity for fluorescence quenching by electron acceptors.[3,4] However, previous investigations were mainly focused on detection of nitroaromatic explosives.[5–7] Detection of nitroaliphatic explosives (*e.g.*, nitromethane) is limited by their high volatility and weak binding to conjugated polymers and other small conjugated molecules employed as sensory materials.[8]

Coordination polymers, constructed from metal ion connectors and polydentate bridging ligands, have drawn growing interest in chemistry and materials science due to their unique and highly tailorable properties and potential applications in heterogeneous catalysis, drug delivery, imaging, and sensing.[9,10] Scaling down these materials has recently led to development of an exciting new class of highly tailorable nanomaterials known as nanoscale coordination polymers (NCPs) or infinite coordination polymer particles.[11] Compared with purely inorganic or organic nanomaterials, new properties or enhanced performance can arise from NCPs by careful selection of the organic building blocks and metal species.[12–14] Here we report on a π-conjugated ligand, 9,10-bis(*p*-carboxyphenyl) anthracene (BCPA), which can be coordinated with zinc(II) ions, and self-assembled into cubic NCP particles with strong fluorescence (Scheme 1). Moreover, they demonstrate fast, highly efficient fluorescence quenching upon interaction with nitroaromatic explosives (*e.g.*, DNT, TNT), as well as nitroaliphatic explosives (*e.g.*, nitromethane).



Scheme 1 Molecular structure of the BCPA ligand and its coordination with zinc ions to form a coordination polymer (Zn–BCPA).

9,10-Diphenylanthracene (DPA) is an important functional molecule with high fluorescence. Its dicarboxylate derivative, BCPA, was synthesized following the previously reported method.[15] The π-conjugated system of BCPA acts as both the source of fluorescence emission and the chemical recognition element (binding site). Zinc ions were used as the metal connectors because of their high complexation affinity to carboxylate and nondetrimental nature to fluorescence.

In a typical synthesis, BCPA (4 mg) was dissolved into THF solvent (5 mL), into which a solution of THF (5 mL) containing two equivalents of $Zn(OAc)_2$ was added dropwise. Upon addition of $Zn(OAc)_2$, the clear solution of BCPA gradually turned turbid, indicating the formation of NCPs. The solution was kept under gentle stirring at room temperature for 6 hours. The NCP particles thus formed exhibited bright blue fluorescence emission upon UV excitation as depicted in the inset of Fig. 1, where also shown are the emission and excitation spectra of the Zn–BCPA NCPs in comparison to that measured on the BCPA ligand. Although the emission of BCPA is red shifted to some extent upon complexed with zinc ions, there seems no evidence that the emission spectrum is composed of overlapped monomer and excimer peaks since the shape of the spectrum of BCPA and Zn–BCPA remains the same. This phenomenon is similar to what was previously observed for the polymers containing anthracene or 9,10-diphenylanthracene as the pendant groups.[16,17] The red shift observed is likely owing to the strong electronic coupling between the neighboring anthryl groups. This electronic coupling is equivalent to the weekly bound excimer state, and efficient energy migration may occur between the anthracene groups.

To characterize the morphology of the NCPs particles, precipitate was collected by centrifugation and washed several

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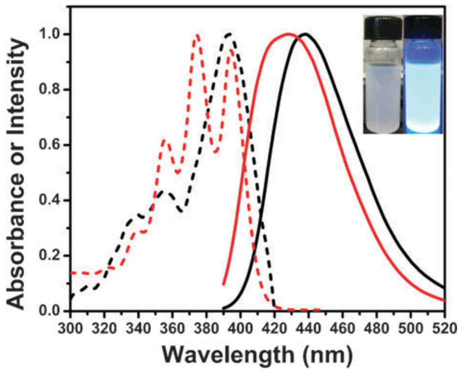

Fig. 1 The red lines are normalized UV-Vis absorption (dashed) and emission (solid, excitation at 370 nm) spectra of BCPA and the black lines are emission (solid, excitation at 370 nm) and excitation (dashed, emission at 438 nm) spectra of Zn–BCPA NCPs, for which the absorption can hardly be measured due to the light scattering. Insets are the photoimages of Zn–BCPA NCPs under daylight and UV illumination at 354 nm, respectively.

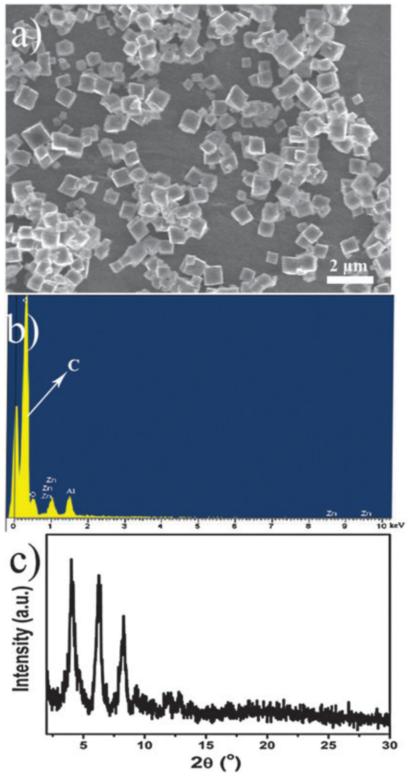

Fig. 2 (a) SEM image, (b) EDX data and (c) PXRD spectra of the Zn–BCPA NCPs.

times with THF. As imaged by a field-emission scanning electron microscope (Fig. 2a), the particles are in cubic shape with dimensional size ranging between 500 nm and 1 µm. The chemical composition of the NCP particles was characterized with energy-dispersive X-ray (EDX) spectroscopy, which showed that the particles were consisted of zinc, carbon and oxygen (Fig. 2b). The trace amount of aluminium as demonstrated in the spectrum was from the sample substrate. Following this chemical composition measurement, powder X-ray diffraction (PXRD) was performed to study the bulk crystalline structure within the cubic particles. The sharp diffraction peaks in the 2θ range from 2° to 10° as shown in Fig. 2c indicated that the NCP particles thus fabricated indeed possess long-range intermolecular order, as previously observed for other NCPs.[14] The well-defined cubic-like morphology of the particles was likely resulted from the thermodynamically preferred intermolecular arrangement as typically evidenced in molecular self-assemblies.

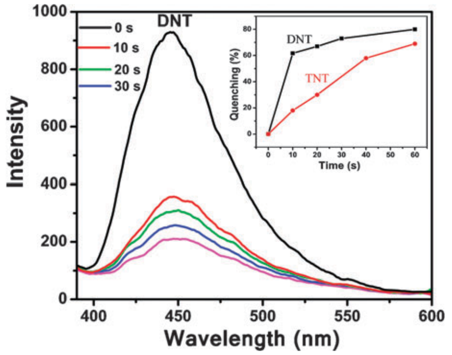

Fig. 3 Emission spectra of Zn–BCPA NCPs upon exposure to the saturated vapor of DNT (*ca.* 100 ppb) at various time intervals. The inset shows the time-course of emission quenching by saturated vapor of DNT and TNT (*ca.* 5 ppb). Experiments were performed following the same setup as described in ref. 6.

The Zn–BCPA NCPs with strong emission in solid state make them ideal to be employed as fluorescence sensor materials for vapor detection of chemical reagents. To explore the sensing capability for oxidative explosives, the emission spectra of a drop-cast thin film of the NCPs (*ca.* 1 µm of thickness) were recorded upon exposure to the saturated vapor of DNT or TNT at various time intervals. As shown in Fig. 3, the film demonstrated fast and efficient fluorescence quenching to both DNT and TNT. Within only 10 seconds of exposure to DNT, the emission was quenched by about 62%. Upon continuous exposure for longer time, the quenching reached its equilibrium plateau, at *ca.* 80%. The emission quenching response to TNT was slower than that to DNT (inset of Fig. 3), mainly due to the 20 times higher vapor pressure of the latter. Nonetheless, this level of sensitivity to TNT is comparable to that as obtained for the best performing conjugated polymer thin films.[3]

Encouraged by the initial success in vapor sensing of the nitroaromatic explosives, we attempted to extend the sensing capability of Zn–BCPA NCPs to the nitroaliphatic explosives, specifically, nitromethane, which represents one of the highly volatile explosives, with vapor pressure of 36 000 ppm at room temperature. The high volatility, in conjunction with the weak oxidizing power (*i.e.*, low electron affinity), makes nitromethane still a challenge for detection by current sensing techniques. Up to date, only few reports can be found on the fluorescence-quenching based vapor detection of nitromethane under ambient conditions.[8]

To perform the sensing of nitromethane, Zn–BCPA NCPs or BCPA were drop-cast onto one of the inner walls of a sealed quartz cuvette. Appropriate volume of saturated nitromethane vapor was injected (through a syringe) into the cuvette so that the vapor pressure of nitromethane was able to be diluted

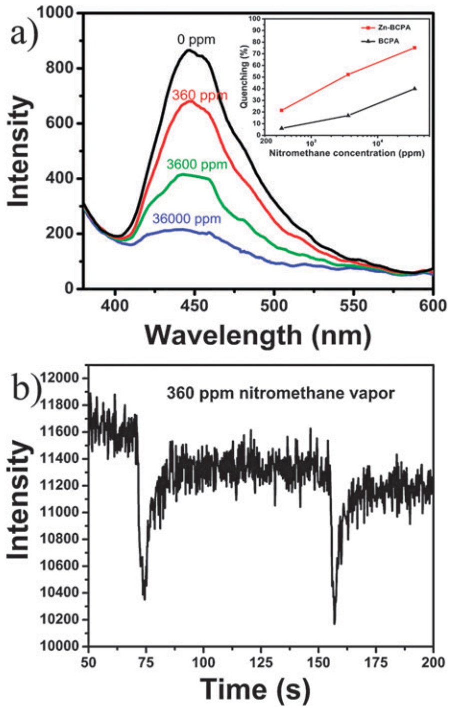

Fig. 4 (a) Emission spectra of Zn–BCPA NCPs upon exposure to various concentrations of nitromethane vapor. The inset shows the emission quenching of Zn–BCPA and the BCPA film as a function of vapor concentration of nitromethane. (b) Emission intensity as monitored at 450 nm for a film of Zn–BCPA NCPs upon blowing over with 360 ppm nitromethane vapor.

down to varying levels as shown in Fig. 4. As shown in Fig. 4a, the emission intensity of Zn–BCPA NCPs was dramatically decreased in the presence of nitromethane. Even when the vapor pressure of nitromethane was diluted down to 360 ppm (*i.e.*, 1% dilution of the saturated vapor), the emission of Zn–BCPA NCPs could still be quenched as significant as 21%. Upon increasing the vapor pressure up to 36 000 ppm, the emission quenching reached almost 100%. Considering the fact that a regular photomultiplier tube (PMT) can detect photon intensity change down to 1% or below, the detection limit of nitromethane as presented in Fig. 4a has already reached the range of a few ppm. For comparison, the same emission quenching measurements were also performed on the film of BCPA (inset of Fig. 4a). Apparently, the quenching efficiency of BCPA is much lower than that as observed for the Zn–BCPA NCPs. Under the vapor pressures of 360 and 36 000 ppm, the emission of BCPA was quenched by only 6% and 40%, respectively. The increased sensing efficiency obtained for the Zn–BCPA NCPs is largely due to the large surface area to volume ratio of the particles and their strong binding affinity to the analyte molecules (for which the presence of zinc ions is believed to enhance the interaction with nitro-compound).[18]

To further explore the potential for infield detection of explosives, we monitored the change of emission intensity of Zn–BCPA NCPs at 448 nm when 360 ppm of nitromethane vapor was introduced by blowing over the thin film. The measurement was carried out with an Ocean Optics USB 2000 spectrometer, in conjunction with an open sample holder.[8] As presented in Fig. 4b, instant emission quenching (*ca.* 10%) was observed when the vapor of nitromethane was blown in at a flow rate of 2–5 mL s^{-1}, and the quenching response was found also highly reversible. A combination of the instant response and low detection limit earns a strong potential for the Zn–BCPA NCPs for being employed in the detection of nitromethane upon optimization with the real device systems.

The mechanism of the fluorescence quenching observed above can be attributed to the photoinduced electron transfer from the excited NCPs (as electron donor) to the surface adsorbed electron acceptor (*e.g.*, DNT, TNT and nitromethane). The enhanced excited state (exciton) migration caused by the strong resonance coupling between the neighboring anthryl groups was believed to facilitate the interfacial charge transfer, resulting in amplified emission quenching. Such quenching amplification, in combination with the large surface area of NCP particles, enables efficient vapor detection of volatile reagents, especially nitromethane.

In conclusion, we have demonstrated the coordination-directed self-assembly of π-conjugated molecules into cubic meso-particles with long-range ordered structures. The NCPs thus synthesized exhibit strong fluorescence emission, and efficient emission quenching upon interaction with the nitro-based explosives including DNT, TNT and high volatile nitromethane, making them promising sensory materials for infield explosives monitoring.

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