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Metal–Organic Frameworks

A Fluorescent Sensor for Highly Selective Detection of Nitroaromatic Explosives Based on a 2D, Extremely Stable, Metal–Organic Framework

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Abstract: A 2D, extremely stable, metal–organic framework (MOF), **NENU-503**, was successfully constructed. It displays highly selective and recyclable properties in detection of nitroaromatic explosives as a fluorescent sensor. This is the first MOF that can distinguish between nitroaromatic molecules with different numbers of $-NO_2$ groups.

Chemical sensors for fast and highly selective detection of high explosives and explosivelike substances have attracted increasing attention concerning homeland security, environmental and humanitarian implications.[1] Although many explosive-detection technologies, such as typical canines or sophisticated instruments,[2] are widely utilized, these techniques are expensive and may not be easily accessible in most cases. Alternatively, fluorescence detection based on chemical sensing by using fluorescent materials has proven to be an excellent candidate for the rapid detection of explosives. Fluorescence-based detection has an advantage over traditional detection methods in virtue of the high sensibility, simplicity, short response time, and the ability to be applied in both solution and solid phase.[3] Nowadays, new molecular, oligomeric, polymeric, and nanoscale materials are usually used for fluorescence detection. These materials are capable of quick, efficient, and credible detection of various explosives.[4] However, there are still some hindrances, such as stability, toxicity, sensitivity, and biodegradability, thus it is a significant and challenging task to synthesize novel materials for fluorescence detection of explosives.

Metal–organic frameworks (MOFs) have been extensively investigated in chemistry and materials science owing to, not only the intriguing structural and chemical diversities, but also the functional properties and potential applications of these compounds.[5] Among these, multifunctional MOFs with functional sites, such as open metal sites, catalytically active metal sites, and photoactive metal sites,[6] have been of particular interests because of the promising application as chemical sensors.[7,8] Moreover, some ligands have also been designed, synthesized, and explored as fluorescent sensors.[9] In general, MOFs used to detect explosives are porous frameworks with 2D or 3D structures and nonporous frameworks with 2D sheets or nanoscale materials.[10] The sensitivity and recyclability of these MOFs, and especially the stability, need to be improved. Therefore, it is important to synthesize stable MOFs to be used for detection of explosives. In particular, the selection of the ligand plays a crucial role in the design and construction of the stable MOFs for fluorescence detection of explosives. We selected 4,4′,4′′-((2,2′,2′′-(nitrilotris(methylene))tris(1*H*-benzo[*d*]imidazole-2,1-diyl))tris(methylene))tribenzoic acid (H_3L, see the Supporting Information) and Cd^{II} to synthesize MOFs for detection of explosives based on the following reasons: 1) Numerous explosives are good electron acceptors with electron-deficient $-NO_2$ groups, including the hazardous explosives 2,4-dinitrotoluene (2,4-DNT), 2,4,6-trinitrotoluene (TNT), 2,4,6-trinitrophenol (TNP), and 1,3-dinitrobenzene (1,3-DNB), which are common chemical constituents of commercial explosives.[11] H_3L is a flexible tripodal ligand with aromatic π rings and nitrogen atoms with lone-pair electrons, which may help to adjust the position of ligands to provide intraligand interactions and promote luminescent character. 2) The coordination between organic ligands and metal ions, not only adds flexibility and diversity in the geometric structures of the MOFs, but also alters the electronic structures and surface functionalities of the MOFs; this can facilitate efficient exciton migration between MOFs and electron-deficient nitroaromatic analytes so as to achieve the means of detection.[12] 3) In addition, d^{10} metal ions, such as Zn^{II} and Cd^{II}, usually show high complexation affinity to carboxylate and do not interfer with fluorescence, because they can display varied coordination numbers and geometries, and exhibit outstanding luminescent properties.[13]

Herein, we report the synthesis of $[Cd_2Cl(H_2O)(L)]\cdot 4.5DMA$ (DMA = *N*,*N*-dimethylacetamide; **NENU-503**, NENU = Northeast Normal University) by the solvothermal reaction of $Cd(NO_3)_2\cdot 4H_2O$ and H_3L. **NENU-503** displays high stability in air for

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more than two weeks, and in both acidic and alkaline solutions. Meanwhile, **NENU-503** can detect nitroaromatic explosives fast and sensitively through fluorescence quenching. This is the first report on MOFs that can distinguish between nitroaromatic molecules with different numbers of $-NO_2$ groups. Although the toxicity of Cd^{II} cannot be ignored, especially when inhaled or exposed to skin, our results demonstrate a promising and proven approach for a highly selective detection of nitroaromatic explosives.

Single-crystal X-ray analysis reveals that **NENU-503** crystallizes in the monoclinic space group *C*2/*c* (see the Supporting Information, Table S1). The asymmetric unit of **NENU-503** includes two Cd^{2+} in different coordination environments, one L^{3-} ion, one Cl^- ion, and one coordinated H_2O molecule (Figure 1 a). The Cd1 atom is four-coordinate by three nitrogen atoms from one L^{3-} ion and a chlorine atom (Cd–N, 2.217–2.606 Å and Cd–Cl, 2.413 Å, see the Supporting Information, Table S2). The Cd2 atom is seven-coordinate by six carboxylate oxygen atoms from three L^{3-} ligands and one oxygen atom from a coordinated H_2O molecule (Figure 1 a). Three carboxylate groups from L^{3-} can coordinate three Cd2 atoms (see the Supporting Information, Figure S1a). Such connectivity modes give rise to a 2D sheetlike structure with (3,3) topology (Figure 1 b, c), which is packed along the *c* axis (see the Supporting Information, Figure S2). Furthermore, adjacent layers are connected through π–π stacking, yielding a 3D supramolecular motif (see the Supporting Information, Figure S3). **NENU-503** displays a microporous framework along the *c* axis (Figure 1 d). Moreover, under ambient conditions, that is, exposure to air for more than two weeks, no major changes to either the external appearance or to the PXRD patterns of **NENU-503** were detected; confirming extreme framework stability (see the Supporting Information, Figure S4). Surprisingly, **NENU-503** also exhibits outstanding chemical stability and unaltered PXRD results, suggesting that the crystallinity is retained, after exposure to aqueous solutions (HCl and NaOH) with pH values in the range of 2–12 (see the Supporting Information, Figure S5). Only a few MOFs that are stable in both acidic and basic solutions have been reported previously.[14] The thermal stability of **NENU-503** was studied by thermogravimetric analysis (TGA, see the Supporting Information, Figure S6).

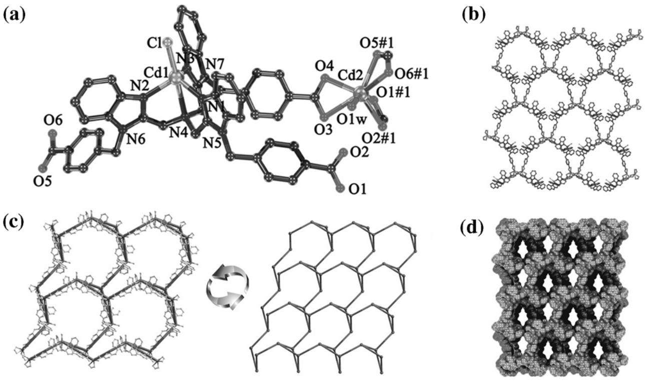

Figure 1. a) Coordination environments of Cd^{II} atoms in **NENU-503**. Symmetry code: #1 $-x+1, y, -z+3/2$. b) Ball-and-stick representation of the 2D sheetlike structure in **NENU-503**. c) 2D sheet with (3,3) topology of **NENU-503**. d) Space-filling representation of **NENU-503** viewed from the *c* axis. All the hydrogen atoms are omitted for clarity.

The photoluminescence (PL) spectra of **NENU-503** and H_3L in the solid state were recorded at room temperature. **NENU-503** exhibited an emission peak at 389 nm upon excitation at 331 nm (see the Supporting Information, Figure S7a). This emission band can be assigned to H_3L ligand-centered emission, because similar emission was observed at 424 nm ($\lambda_{ex}=345$ nm) for the free H_3L ligand (see the Supporting Information, Figure S7b). In addition, the fluorescence properties of **NENU-503** in different solvent emulsions were investigated (Figure 2 a). The predominant feature is that the PL intensities are largely dependent on the solvent molecules, particularly in the case of nitrobenzene (NB), which exhibits significant quenching behavior (see the Supporting Information, Figure S8a). The physical interaction of the solute and solvent plays a vital role in such fluorescence behavior. To examine sensing sensitivity towards NB in more detail, a batch of suspensions of **NENU-503** with gradually increasing NB con-

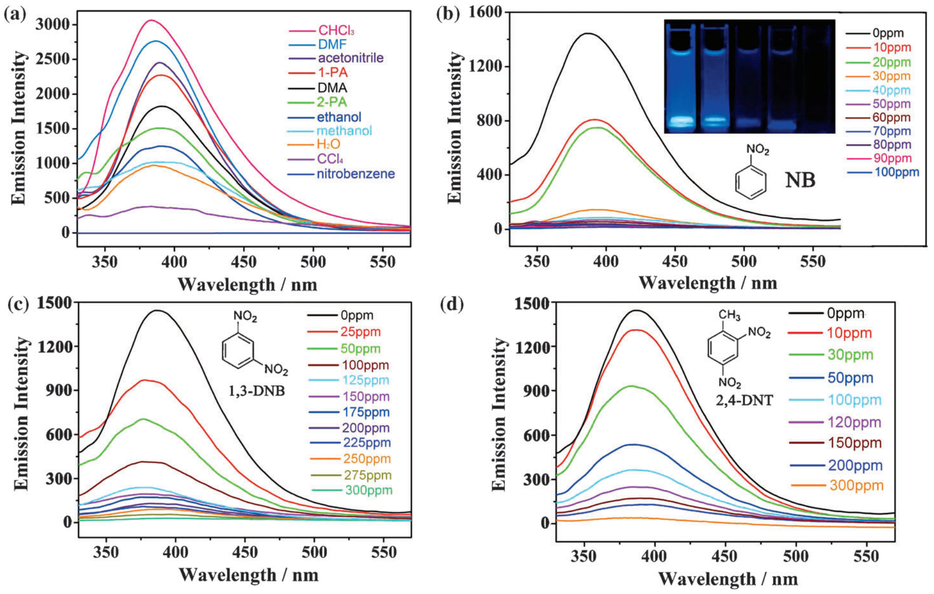

Figure 2. a) Emission spectra of **NENU-503** in different solvents (excited at 295 nm). b) Emission spectra of **NENU-503** in different concentrations of nitrobenzene in DMA (excited at 295 nm). Inset: a photograph taken under UV light (365 nm), showing the fluorescence quenching upon addition of nitrobenzene to **NENU-503**. c, d) Emission spectra of **NENU-503** in different concentrations of 1,3-DNB and 2,4-DNT in DMA (excited at 295 nm), respectively.

tents in *N*,*N*-dimethylacetamide (DMA) was prepared to monitor the emissive response (Figure 2b). The luminescence intensity decreased to 50% at 20 ppm, and complete quenching was received at 100 ppm (see the Supporting Information, Figure S8b). The finely ground powder of **NENU-503** is dispersed well in the solution. This enables NB to be closely adhered to the surface of the MOF particles and facilitates possible host–guest interactions. Therefore, electron transfer from the electron-donating framework to the highly electron-deficient NB molecule can take place upon excitation, resulting in fluorescence quenching.

Because the luminescence quenching is related to the electron-withdrawing $-NO_2$ group, we investigated the potential of **NENU-503** towards sensing a series of nitroaromatic explosives, such as 1,3-DNB, 2,4-DNT, TNT and TNP. High fluorescence quenching was monitored by PL spectroscopy ($\lambda_{ex}=$ 295 nm) when the analytes were added to DMA. The lowest concentration of complete quenching is 300 ppm for 1,3-DNB and 2,4-DNT (Figure 2c,d and Figure S9 in the Supporting Information), and 400 ppm for TNT and TNP (Figure S10 in the Supporting Information). The relationship between emission intensity and different concentrations of analytes (see the Supporting Information, Figure S11) and quenching efficiency at 50 ppm for analytes in DMA (see the Supporting Information, Figure S12) indicate that, among the different analytes tested, **NENU-503** displays the most effective detection for NB. Interestingly, the color of the solution turned orange upon incremental addition of TNT; this could be observed by the naked eye (Figure 3a). Therefore, we can detect TNT with high selectivity simply by registering the color change; this is extremely convenient and fast. The color changes observed in the presence of TNT may be ascribed to the formation of charge-transfer complexes between **NENU-503** (electron donor) and TNT (electron acceptor) through charge-transfer interactions upon excitation.[15] Upon closer examination of the PL spectra, we have found that the spectrum of 1,3-DNB is obviously blueshifted by 13 nm as compared with that of pure DMA (390 nm, Figure 2c), whereas it is apparently redshifted by 84 nm for TNP (Figure 3b) and only one emission band exists, namely, in the spectrum for TNP in DMA without **NENU-503** (see the Supporting Information, Figure S13). As mentioned above, the emission band of NB is at 390 nm. Therefore, **NENU-503** can be used to distinguish between nitroaromatic molecules with different numbers of $-NO_2$ groups, for example, NB, 1,3-DNB, and TNP, through the shift of the PL spectra (Figure 3c). Moreover, the PL spectra do not shift when performing the same

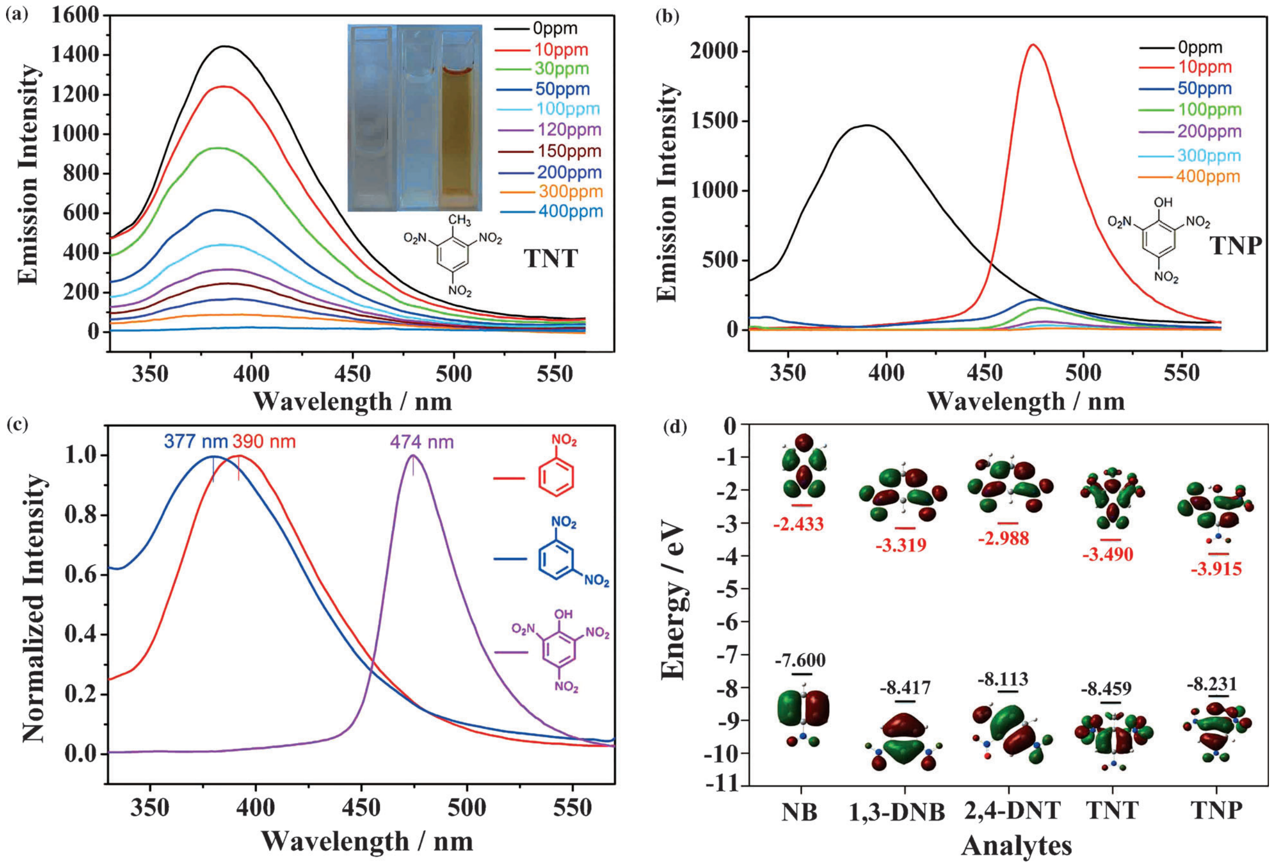

Figure 3. Emission spectra of **NENU-503** in different concentrations of a) TNT and b) TNP in DMA (excited at 295 nm). Inset in (a): color changes upon incremental addition of TNT solution (left: TNT; middle: **NENU-503** in DMA; right: **NENU-503** in DMA containing TNT). c) Emission spectra of **NENU-503** in NB, 1,3-DNB, and TNP (10 ppm in DMA). d) Shapes of HOMO and LUMO of the molecular orbitals considered and the relative energy level investigated by the B3LYP/6-31G** method.

experiment with only H_3L (see the Supporting Information, Figure S14). This indicates that this discrimination is due to **NENU-503**. Most previous reports of MOFs for detection of nitro-containing compounds investigate the effects of the concentration on fluorescence quenching, whereas the distinction between different nitro-containing compounds has rarely been reported.[16] This is the first time that a MOF can distinguish nitroaromatic compounds from each other through shifts of PL spectra. The shifts of the PL spectra may be due to the formation of exciplexes (excited complexes) by the interaction of analytes and MOFs in the excited states;[17] this phenomenon is less studied in MOFs. To further explore the reason for the shift of the PL spectra of TNP, we have monitored the PL spectra of phenol and *p*-nitrophenol in the presence of **NENU-503**. The emission band of phenol is at 390 nm, whereas the PL spectra are obviously redshifted by 10 nm for *p*-nitrophenol (400 nm) and 84 nm for TNP (474 nm, see the Supporting Information, Figure S15). Therefore, the redshift of the PL spectra for TNP results from $-OH$ and $-NO_2$ groups in combination with exciplexs. The framework is intact after detection of different analytes as confirmed by PXRD (see the Supporting Information, Figure S16).

The quenching efficiency can be quantitatively explained by the Stern–Volmer equation: $(I_0/I) = K_{sv}[A] + 1$, where I_0 and I are the fluorescence intensities before and after addition of the analyte, respectively, K_{sv} is the quenching constant (M^{-1}), $[A]$ is the molar concentration of the analyte. The Stern–Volmer plots for analytes are nearly linear at low concentrations. The plots subsequently deviate from linearity at higher concentrations (see the Supporting Information, Figure S17). The nonlinear nature of the plot of the analytes may be ascribed to self-absorption or an energy-transfer process.[3,18] This suggests that dynamic and static quenching coexist in the fluorescence quenching process. Fluorescence decays of **NENU-503** at different concentrations of analytes also verify this (see the Supporting Information, Figure S18).[18b] The fluorescence attenuation can be attributed to a photoinduced electron-transfer (PET) mechanism. MOFs constructed from d^{10} metal ions with highly localized electronic states are often characterized by narrow energy bands. Therefore, they can be regarded as giant "molecules" and the valence-band (VB) and conduction-band (CB) energy levels can be described in a fashion similar to that used for molecular orbitals (MOs).[10b] In general, the lowest unoccupied MOs (LUMOs) of analytes are low-lying π^*-type orbitals stabilized by the $-NO_2$ group through conjugation (Figure 3 d); the energy levels of these orbitals are lower than the CB energy levels of **NENU-503**. This can force electrons to transfer from the CB of **NENU-503** to the LUMO of the analyte, thus leading to fluorescence quenching upon excitation. Shapes and relative orbital energies of the highest occupied MO (HOMO) and LUMO of the molecular considered were calculated by density functional theory at the B3LYP/6-31G** level (see the Supporting Information, Table S3). Another possible reason for the quenching is resonance energy transfer. If the emission spectrum of the fluorophore (donor) has a certain degree of overlap with the absorption band of the analyte (acceptor), when the distance between them is appropriate, the resonance energy transfer can be observed from the donor to the acceptor. The efficiency and sensitivity of the fluorescence quenching can therefore be significantly improved.[3,19] The absorption bands of the analytes have a considerable degree of overlap with the PL spectrum of **NENU-503** in DMA (see the Supporting Information, Figure S19). As a result, the combination of photoinduced electron transfer and resonance energy transfer gives rise to the fluorescence quenching.

We also monitored the sensitivity of H_3L towards NB in DMA (see the Supporting Information, Figure S20). The quenching efficiency in the presence of **NENU-503** is 45, 93, and 100 % for 10, 50, and 100 ppm of NB, respectively, whereas for H_3L it is only 28, 56, and 78 %. This result indicates that the coordination between H_3L and Cd^{II} makes the electron transfer from **NENU-503** to analytes more effective. Furthermore, H_3L dissolves well in DMA, thus the stability of **NENU-503** is propitious to separate and recycle. In particular, **NENU-503** can be regenerated by centrifugation of the solution after use and washing several times with DMA.[20] The quenching efficiencies of cycles 1–6 are basically unchanged at about 90 %, displaying high recyclability and stability for detection applications (Figure 4). The PXRD pattern further confirms that the framework is retained after cycle 6 (see the Supporting Information, Figure S21).

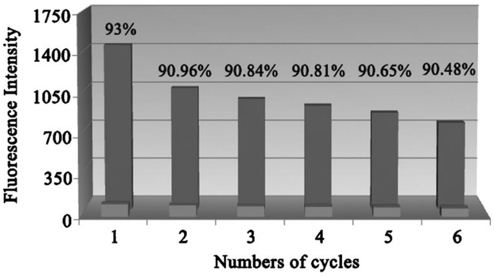

Figure 4. Reproducibility of the quenching ability of **NENU-503** dispersed in DMA and in the presence of 50 ppm NB. The dark-grey bars represent the initial fluorescence intensity and the light-grey bars represent the intensity upon addition a solution of 50 ppm NB in DMA. The percentages on the top represent quenching efficiency of every cycle.

In conclusion, we have successfully synthesized extremely stable **NENU-503** for quick and sensitive detection of nitroaromatic explosives through fluorescence quenching. Notably, we can easily detect TNT by the naked eye. This fluorescence quenching is ascribed to photoinduced electron transfer and resonance energy transfer. For the first time, a MOF can distinguish between NB, 1,3-DNB, and TNP with different numbers of $-NO_2$ groups by the shift of the PL spectra. High stability and recyclability of **NENU-503** make it an outstanding candidate in the field of detection of explosives. The present work opens a promising approach to design MOF-based sensors for explosives; this will probably be useful under more realistic conditions in the future.

Experimental Section

Synthesis of NENU-503

H_3L (0.03 g, 0.04 mmol), $Cd(NO_3)_2\cdot 4H_2O$ (0.16 g, 0.52 mmol), DMA (5 mL), H_2O (3 mL), and four drops of HCl (6 mol L^{-1}) were sealed in a Teflon-lined stainless steel container. The container was heated to 110 °C for four days, resulting in white crystals that were isolated by washing with DMA and dried at room temperature. Yield: 64% based on H_3L. IR (KBr): $\tilde{\nu}=3434$ (s), 2937 (m), 1625 (s), 1552 (s), 1401 (s), 1262 (m), 1187 (m), 1018 (s), 959 (w), 859 (w), 756 (m), 719 (w), 596 (m), 475 (w), 427 cm^{-1} (w); elemental analysis calcd (%) for $C_{66}H_{77.5}N_{11.5}O_{11.5}Cd_2$: C 53.69, H 5.30, N 10.91; found: C 53.62, H 5.38, N 11.01.

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Keywords: explosives · fluorescence · metal–organic frameworks · nitroaromatic molecules · sensors

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