

An Intensely Luminescent Metal–Organic Framework Based on a Highly Light-Harvesting Dicyclo-Metalated Iridium(III) Unit Showing Effective Detection of Explosives

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Supporting Information

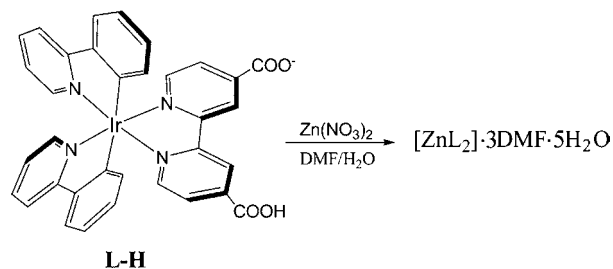
ABSTRACT: An intense visible yellow-orange emission with long lifetime and enhanced quantum yield has been achieved for a metal–organic framework based on a highly light-harvesting dicyclo-metalated iridium(III) unit, which shows effective detection of nitroaromatic explosives on the ppm scale.

The metal–organic frameworks (MOFs) designed with active functional units have attracted considerable attention over the past decades because the functional units that are incorporated into MOFs can create materials with potential applications in catalysis,¹ gas storage,² chemical sensing,³ and biomedical imaging.⁴ Recently, MOFs integrating different molecular components have been reported to be able to achieve light harvesting and further applied in luminescent sensing and photocatalysis.⁵ For example, Lin and co-workers have reported ruthenium(II) MOFs with strong visible-light absorption and long-distance energy migration via triplet charge-transfer excited states, and the MOFs show efficient fluorescence quenching in the presence of quencher.⁶ Uvdal et al. presented that excitation of a UV chromophore constituting the struts of nanoscale MOFs could increase light absorption.⁷ The achievements mentioned above afford us a powerful tool to design and construct intense luminescent MOFs with strong light-harvesting units. Iridium(III)-based complexes have received some attention as antennae by Huang et al.⁸ and other groups⁹ because of their ability to achieve sensitization in the visible spectrum and relatively long luminescent lifetimes. Thus, iridium(III)-derivated MOFs appear to have promising properties as luminescent materials for the abilities of iridium(III) units to absorb light in the visible via metal-to-ligand charge-transfer (MLCT) excitation. In this Communication, we report a highly luminescent heteronuclear MOF $[\text{Zn}(\text{L})_2] \cdot 3\text{DMF} \cdot 5\text{H}_2\text{O}$ (**1**; $\text{L} = [\text{Ir}(\text{ppy})_2(\text{dcbpy})]$, $\text{ppy} = 2\text{-phenylpyridine}$, $\text{dcbpy} = 2,2'\text{-bipyridine-4,4'-dicarboxylate}$, and $\text{DMF} = N,N\text{-dimethylformamide}$) based on iridium(III) units. **1** exhibits efficient visible-light harvesting and strong visible yellow-orange emission with long lifetimes and high quantum yields and displays detection of nitroaromatic explosives on the ppm scale. As far as we know, iridium(III)-based luminescent MOFs showing detection of explosives are rare. Further, the

intense emission of yellow-orange light in **1** provides us a visible change in the detection of trace amounts of analytes. The properties of **1** make it more convenient and sensitive for potential application.

L-H ligand was prepared according to a literature method¹⁰ and reacted with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in $\text{DMF}/\text{H}_2\text{O}$ at 90°C for 24 h to obtain orange thin-plate crystals of **1** (Scheme 1).¹¹ The

Scheme 1. Synthesis of Luminescent Heteronuclear MOF **1**



phase purity of **1** was confirmed by comparing the powder X-ray diffraction (PXRD) patterns of the sample with the simulated ones based on the single-crystal structure (Figure S1 in the Supporting Information, SI). **1** crystallizes in the noncentrosymmetric space group $Pna2_1$, as revealed by the single-crystal X-ray diffraction study. The asymmetric unit of **1** contains two **L** ligands and one Zn center. The Zn center adopts a tetrahedral geometry by coordinating with four carboxylate O atoms from four **L** ligands, and each **L** ligand connects two Zn centers to form a torsional double-stranded chain structure with a torsion angle of 108.3° between the adjacent cycles (Figure 1a). The distance between the adjacent Zn centers in the chain is 8.60 Å. The chains pack with each other via supermolecular interactions to give rise to a 3D stacking framework with two types of channels, as shown in Figure 1b. The large open channels in **1** are occupied by solvents, and the combination of single-crystal X-ray diffraction, thermogravimetric analysis (TGA)–quadrupole mass spectrometry (Figure S2 in the SI), and elements analysis afforded the final formula of $[\text{Zn}(\text{L})_2] \cdot 3\text{DMF} \cdot 5\text{H}_2\text{O}$ for **1**.

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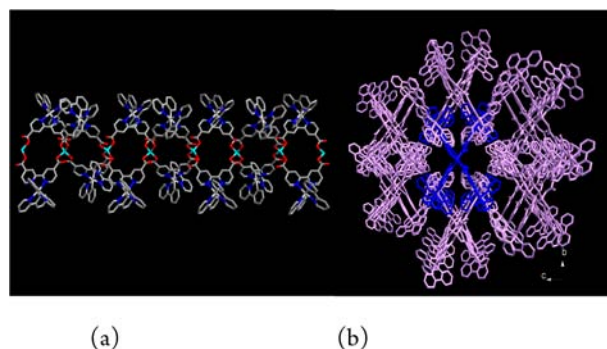


Figure 1. (a) Torsional double-stranded chain structure. (b) View of the 3D stacking framework via the *a* axis.

Diffuse-reflectance UV–vis measurements show that L-H exhibits strong absorption bands from 200 to 600 nm, arising from the $\pi-\pi^*$ transition of the aromatic rings and MLCT transition, which display almost no shift in **1** (Figure S3 in the SI). The fluorescence of the free L-H ligand displays a strong emission band at 575 nm in the solid state, and the as-made **1** fluoresces with an emission maximum at 602 nm (Figure S4 in the SI), indicating that the fluorescence of **1** is generated by the L-H ligand. The tiny red shift may be attributed to coordination of the L-H ligands with Zn centers and the stability of the coordination framework. More interesting, the fluorescence lifetime of L-H was determined to be 7.81 μs (Figure S5 in the SI), while it is almost doubled to 14.53 μs in **1**. Such a long-lifetime photoluminescent MOF is rare in the reported fluorescent MOFs.¹² Furthermore, the quantum yield (a measure of the emission efficiency of a fluorochrome and defined as the number of photons emitted divided by the number of photons absorbed) increases largely from 6.8% to 23.6%, while L-H is coordinated to form a Ir/Zn–organic framework of **1**. Such a large increase of the quantum yield in **1** is probably due to the fact that the coordination function reduces the odds of vibration-coupled internal conversion of the excitation state and the rigidity of the coordination framework reduces the odds of nonradiative transitions.¹³ In a word, the relatively long lifetime and high quantum yield of **1** speak volumes for its good performance on light-harvesting and luminescent sensing.

In view of the above-mentioned superior photoluminescent properties of **1**, the detection of explosives was studied further. For the sensing experiments, microscale crystals of **1** were prepared by modified procedures (see the SI). Scanning electron microscopy (SEM) images showed that stick-shaped particles of **1** were on the micrometer scale (Figure 2a,b). The microcrystals of **1** were dispersed in methanol without changing its original

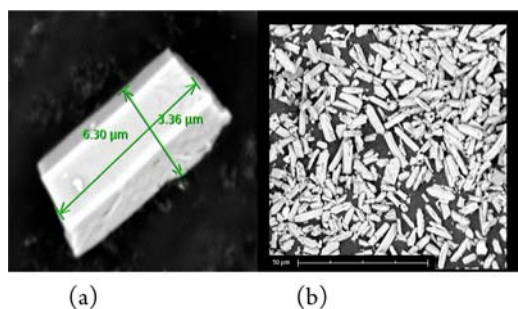


Figure 2. (a) SEM image of a single crystal of **1** with a measured value. (b) SEM image of plenty of microscale **1**.

framework, as confirmed by the PXRD patterns, and without photoluminescent changes. We found that the addition of small amounts of all of the selected nitroaromatics had a distinct quenching effect on the luminescence intensity of the dispersed microscale **1** in methanol. The quenching efficiency (%) was estimated using the formula $(I_0 - I)/I_0 \times 100\%$, where I_0 is the maximum fluorescence intensity of **1** before addition of the analytes. As shown in Figure 3a, detectable luminescence

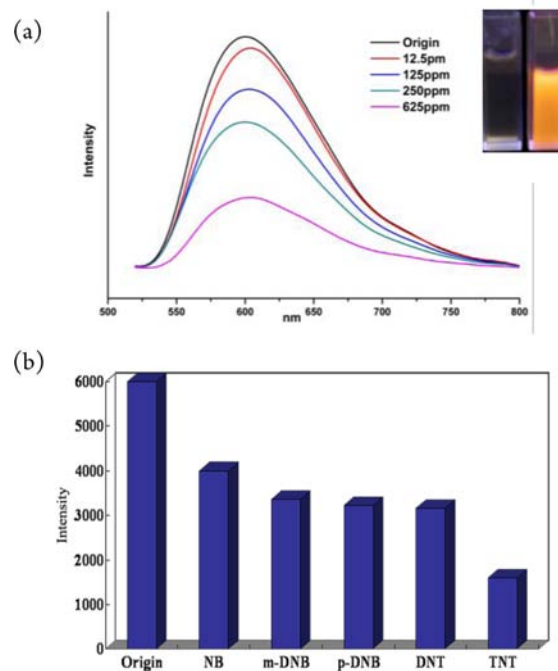


Figure 3. (a) Fluorescence intensity of **1** with TNT at different concentrations. Inset: photograph showing the change of the original fluorescence of **1** (right) and the decreased fluorescence upon the addition of TNT in **1** (left). (b) Fluorescence intensity of **1** with different analytes at room temperature.

responses of trinitrotoluene (TNT) were observed at the ppm scale, the quenching efficiency reached 70% at a concentration of 625 ppm, and the order of quenching efficiencies for the selected nitroaromatics at the same concentration was TNT > DNT \approx *p*-DNB \approx *m*-DNB > NB (Figure 3b; DNT = dinitrotoluene; DNB = dinitrobenzene; NB = nitrobenzene). Meanwhile, the microcrystals increased the sensitivity to a large extent, and the sensing could be instantly observed in a few seconds (Figure S6 in the SI). The mechanism might be electron transfer from the electron-donating framework of **1** to high electron-withdrawing $-\text{NO}_2$ groups of nitroaromatics, resulting in a detectable luminescence quenching, which is similar to those in the other reported MOFs.¹⁴ The well dispersion of the microcrystals of **1** in methanol enabled the nitroaromatic molecules to be effectively contacted with the microparticles of **1** and might facilitate the host–guest interaction between **1** and the analytes. Moreover, the large optical band gap (ca. 2.02 eV; Figure S7 in the SI) indicates that **1** in the excited state is highly reductive, providing the driving force for electron transfer to the nitroaromatics.¹⁵ So, the above-observed luminescence quenching behaviors were attributed to the electron-deficient nature of the nitroaromatics and the high-electron-rich framework structure of **1**. Such significant quenching effects of **1** by

nitroaromatic molecules indicated the potential application of **1** for detection of a small amount of nitroaromatic explosives.

In conclusion, a rare intensely luminescent MOF **1** based on a strong light-harvesting dyclo-metallated iridium(III) unit has been successfully constructed. **1** has high absorption in the visible spectrum and displays a strong visible yellow-orange emission, which can effectively detect nitroaromatic explosives on the ppm scale. Furthermore, the quenching can be ocularly observed. The convenience and sensitivity of detection make **1** a promising material to trace the nitroaromatic explosives. Our group will proceed to study the assembly and properties of MOFs with highly light-harvesting units.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental details, X-ray crystallographic data in CIF format, TGA, PXRD, optical absorption and diffuse-reflectance spectra, photoluminescence, and luminescent decay lifetimes of **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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(11) Crystal details for complex **1**: $C_{77}H_{75}ZnIr_2N_{11}O_{16}$, $M = 1860.33$, orthorhombic, $Pna2_1$, $a = 17.196(3)$ Å, $b = 12.963(2)$ Å, $c = 32.342(6)$ Å, $V = 7210(2)$ Å³, $Z = 4$, $D_c = 1.714$ g·cm⁻³, $F_{000} = 3704$, $\mu = 4.09$ mm⁻¹, $T = 173(2)$ K, $R1 = 0.0364$, and $wR2 = 0.002$ for 15840 reflections with $I > 2\sigma(I)$.

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