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A highly luminescent entangled metal-organic framework based on pyridine-substituted tetraphenylethene for efficient pesticide detection

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A novel pillared-layered entangled luminescent metal-organic framework $[Zn_2(bpdc)_2(BPyTPE)]$ (1) (BPyTPE = (*E*)-1,2-diphenyl-1,2-bis(4-(pyridin-4-yl)phenyl)ethene) has been designed and constructed. The solvent-free 1 exhibits strong blue-green emission with an excellent fluorescence quantum yield of 99% and provides a facile and reversible method to sensitively and quantitatively detect trace pesticide of 2,6-dichloro-4-nitroaniline.

Molecules with aggregation-induced emission (AIE) can fluoresce strongly in the aggregated state and have exhibited great potentials in diverse research frontiers.[1] Tetraphenylethene (TPE) is emerging as a most popular AIE luminogen because of its simple molecular structure and splendid AIE nature, which has been widely used as an important building block for numerous luminescent materials.[2] Recently, considerable interests are focused on using TPE derivatives decorated with coordination groups, such as carboxylate or pyridine, to construct metal-organic frameworks (MOFs).[3] The incorporation of TPE units enables MOFs to emit strong fluorescence where the nonradiative decay by intramolecular motions of TPE units is restricted in rigid MOFs. The TPE-based luminescent MOFs (LMOFs) have shown great potential in an array of high-tech applications.[4] In particular, the LMOFs are promising fluorescence sensors to detect various substances, such as volatile organic compounds, mycotoxins and nitro explosives.[5,6] The essential sensing signals of changes in fluorescence intensity or wavelength are closely associated with the electron transfer from LMOFs to guests or vice versa.[7]

Pesticides are widely used in agriculture, but their residues can cause serious damages to ecological safety, and result in hazardous impacts on human health and life quality through the food chain. Hence, the rapid and selective detection of pesticides has become one of the most pressing issues concerning human health and environmental protection.[8] For example, 2,6-dichloro-4-nitroaniline (DCN) is a broad-spectrum pesticide belonging to toxicity class IV. It has been extensively employed for control of many diseases, such as wheat powdery mildew, cotton rotten bell, and fruit trees and vegetable rot. DCN degrades slowly and can persist for a long time in the environmental conditions. Currently, the common methods of DCN detection include ion mobility spectrometry, high performance liquid chromatographyor other assays requiring sophisticated instruments that are expensive and complicated.[9] To address this situation, in this contribution, we synthesize a TPE-based ligand exhibiting prominent AIE nature, and fabricate a novel pillared-layered LMOF using it as a pillar linker. The LMOF has a remarkably high fluorescence quantum yield (Φ_F) of 99%, and performs outstandingly in DCN detection with a low detection limit down to 0.13 ppm.

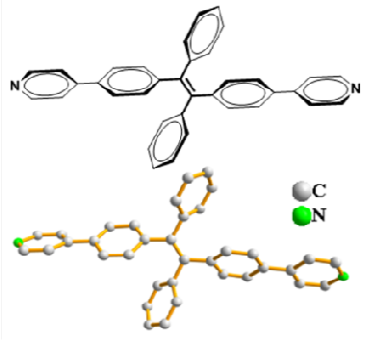

Fig. 1 Molecular and single-crystal structures of AIE-active BPyTPE.

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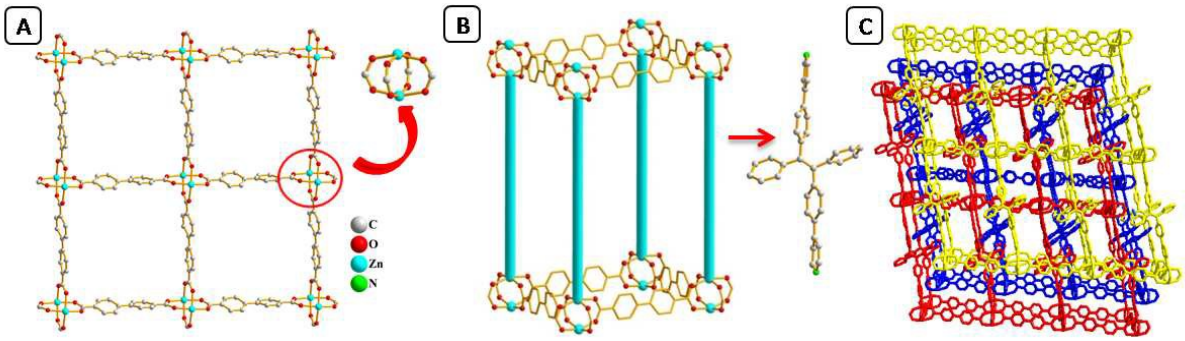

Fig. 2 (A) Topological representation of rhombic 4^4 two-dimensional paddle-wheel layer with an indicated structure of paddle-wheel SBU $[Zn_2(COO)_4]$. (B) Single net of complex **1** viewed along the a-axis, showing pores that are closed up the interpenetration. (C) Overall crystal structure of complex **1** demonstrating the three-fold interpenetration and 1D pore running along the b-axis. Hydrogen atoms are omitted, and solvent molecules are removed by using the SQUEEZE routine of PLATON for clarity.

The TPE-based ligand (*E*)-1,2-diphenyl-1,2-bis(4-(pyridin-4-yl)phenyl)ethene (BPyTPE) is synthesized according to the synthetic route outlined in Scheme S1. The crude product of BPyTPE is purified by column chromatography to afford pure target compound with a *trans*-conformation, which is confirmed by the single-crystal structure (Fig. 1). The treatment of BPyTPE with $Zn(NO_3)_2 \cdot 6H_2O$ and biphenyl-4,4′-dicarboxylic acid (H_2bpdc) in a mixed solvent of *N*,*N*-dimethylacetamide and *N*,*N*-dimethylformamide yields colorless cube-like crystals of complex **1**. The complex **1** belongs to triclinic crystal system, space group $P\bar{1}$ (Table S1). Each Zn^{2+} ion coordinates to four carboxylate oxygen atoms from different $bpdc^{2-}$ anions and one pyridine nitrogen atom of BPyTPE ligand, which can be seen as a tetragonal pyramid. The bond lengths of Zn-O/N are in the range of 2.000–2.038 Å, and the bond angles of O-Zn-O and O-Zn-N are approximately 86.380–89.714° and 95.406–105.058°, respectively. Two Zn^{2+} ions are bridged by four carboxylic groups to form a paddle-wheel secondary building unit (SBU) $[Zn_2(COO)_4]$.[5b] Each SBU is linked by coshared carboxylate groups of $bpdc^{2-}$ ligands, generating a rhombic 4^4 two-dimensional (2D) network with a cross section of 22.52×20.09 $Å^2$ (Fig. 2A). Two adjacent layers are connected by BPyTPE pillar linkers with an inter-layer distance of about 21.27 Å to furnish a stable three-dimensional (3D) framework (Fig. 2B). A three-fold interpenetration is observed for the overall structure of complex **1** (Fig. 2C), and the pore volume of complex **1** is calculated to be 1793.3 $Å^3$, corresponding to a void of around 33.2% per unit cell (5403.2 $Å^3$ total).[10] The geometrical conformation for BPyTPE in complex **1** is further investigated (Fig. S1, ESI†). It is found that BPyTPE in complex **1** adopts a more twisted conformation with larger dihedral angles between aromatic moieties than BPyTPE in single crystals (Table S2). There are only very weak π–π stacking interactions between the phenyl rings from $bpdc^{2-}$ ions and pyridine rings from BPyTPE ligands, with the distances of 3.540 and 3.707 Å (Fig. S2, ESI†), while no π–π stacking interactions are observed between TPE units that are mainly responsible for the light emission.

Complex **1** is stable in THF or water as indicated by powder X-ray diffraction patterns (PXRD) results (Fig. S3). It can undergo solvent exchanged with dichloromethane (DCM), followed by drying under vacuum at room temperature to furnish solvent-free **1** sample. The result of powder X-ray diffraction patterns confirms that solvent-free **1** retains the original framework without any collapsing (Fig. S3, ESI†). Thermogravimetric analysis of complex **1** reveals 22% initial weight loss by heating from room temperature to 145 °C in N_2 stream, which is attributed to the loss of solvent molecules. A plateau appears between 145 and 405°C, followed by a sharp weight loss (~53%) corresponding to the decomposition of the framework. However, there is no obvious weight change until 405°C of solvent-free **1**, indicating the solvent molecules in complex **1** have been removed completely (Fig. S4, ESI†).

BPyTPE shows an absorption maximum at 335 nm in THF solution (Fig. S5, ESI†), associated to the π–π* transition of the conjugated backbone. Like most TPE derivatives, BPyTPE is almost nonfluorescent in dilute THF solution because of the active intramolecular rotation. But as the aggregate formation by adding a large amount of water into the THF solution of BPyTPE, an emission peak at 502 nm enhances swiftly (Fig. 3A), which is ascribed to the restriction of intramolecular rotations and thus block of nonradiative decay of excited state. These emission behaviours demonstrate the AIE nature of BPyTPE. Solvent-free **1** exhibits strong blue-green emission at 490 nm (Fig. 3B), and complex **1** shows intense emission peaking at 498 nm, which is close to the emission of BPyTPE aggregate. The emission of solvent-free **1** is blue-shifted by 8 nm than that of complex **1**. This blue-shift phenomenon often

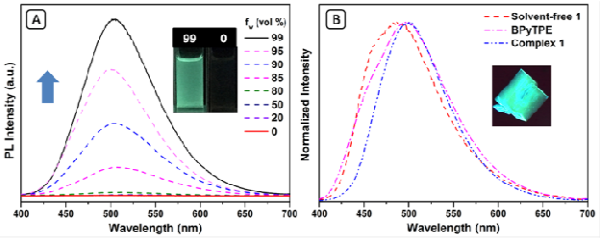

Fig. 3 (A) Photoluminescence (PL) spectra of BPyTPE in THF/water mixtures with various water fractions (f_w). Inset: photos of BPyTPE in THF/water mixtures (f_w = 99 and 0 vol%). (B) Solid-state PL spectra of complex **1**, solvent-free **1** and BPyTPE. Inset in B: the fluorescence photo of complex 1 (λ_{ex} = 365 nm).

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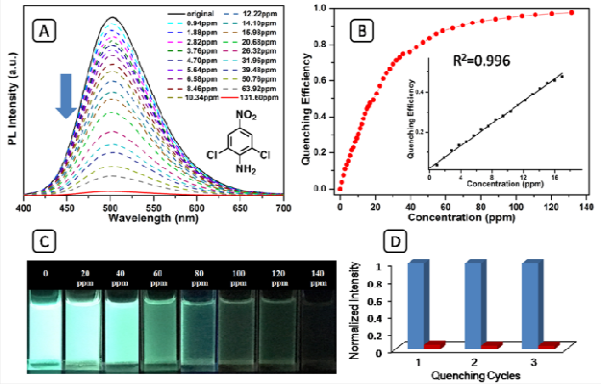

Fig. 4 (A) Fluorescence titration of solvent-free **1** in dichloromethane suspension of 2,6-dichloro-4-nitroaniline (DCN) with different concentrations (λ_{ex} = 365 nm). (B) Correlation between the quenching efficiency and concentration of DCN. (C) Fluorescence photos of solvent-free **1** in suspensions with gradually increased DCN. (D) The result of DCN for three continuous quenching cycles. The blue bars represent the initial fluorescence intensity and the red bars represent the intensity upon addition of DCN (96 ppm).

appears in reported LMOFs, which is probably due to the decreased inter ligand coupling. Both solvent-free **1** and complex **1** have excellent Φ_F values of 99% and 79%, respectively, determined by a calibrated integrating sphere, thanks to the AIE nature of BPyTPE ligand. Both values are much higher than that of BPyTPE solid (Φ_F = 43%), owing to the greatly reduced intramolecular motion of BPyTPE when coordinated within the rigid framework. Moreover, when the turbulence of highly disordered solvent molecules is removed, the excited state energy loss is depressed to minimal, rendering a remarkably high Φ_F approaching to unit of solvent-free **1**. BPyTPE solid, complex **1** and solvent-free **1** exhibit fluorescence lifetimes (τ) of 3.11, 2.85 and 2.39 ns, respectively. This tendency of shorter τ and higher Φ_F maybe result from the immediate release of excited energy via fluorescence, which is the same as the findings like other TPE-based MOF PCN-94.[3f,11]

The sensing application of solvent-free **1** in DCM suspension (0.15 mg mL^{-1}, Fig. S6 and Table S3, ESI†) is firstly evaluated by titration experiments with different electron rich aromatics, such as toluene, *m*-xylene, mesitylene and aniline (Fig. S7, ESI†). These tested samples can only slightly enhance the emission intensity. However, the emission of solvent-free **1** can be quenched by nitrobenzene, owing to the excited state electron transfer from donor (LMOFs) to acceptor (nitrobenzene guests). The quenching efficiency (QE) is estimated using the formula $(I_0–I)/I_0$, where I_0 and I are the emission intensities of solvent-free **1** before and after adding guest molecules. As shown in Fig. S8, the emission starts to decrease upon addition of 58 ppm nitrobenzene, and is quenched greatly at a concentration of 1800 ppm with a high quenching efficiency of 98%. It is found that the detection sensitivity of nitro aniline is much higher than those of nitrobenzene and 1,2,3,4,5-pentachloro-6-nitrobenzene at the same conditions (Fig. S9 and Fig. S14, ESI†). When 55 ppm *p*-nitroaniline is dispersed into the solvent-free **1** suspension, the emission is almost totally quenched (QE = 98%) (Fig. S10, ESI†). The detection limit is as low as ~4.9 × 10^{-2} ppm, calculated with 3σ/k (σ: standard deviation; k: slope).[4] The higher selectivity of solvent-free **1** towards nitro aniline (Fig. S11, ESI†) probably results from hydrogen bonding interactions (N-H···O) between amino of guests and oxygen of bpdc^{2-}.

The high sensitivities and low detection limits of solvent-free **1** towards nitro anilines inspire us to develop an assay for DCN, which has never been achieved by LMOFs previously. Fig. 4A and 4B show the spectra of decline in emission intensity and the linear quenching range of solvent-free **1** upon the addition of DCN (Fig. S12, ESI†). The strong emission of solvent-free **1** is quenched drastically, which can be observed by naked eye (Fig. 4C). A quantitative detection of DCN ranged from 0.94 to 16.92 ppm is established with a low detection limit of 0.13 ppm. To confirm the limit of detection, the fluorescence titration of DCN at low concentrations from 0.13 ppm to 0.80 ppm is further performed, and a linear proportion of I_0/I is obtained (Fig. S13, ESI†). Solvent-free **1** can be reused after centrifuging the suspension and washing with DCM by several times (Fig. 4D), without degradation in detection performance. According to China National food safety standard-Maximum residue limits for pesticides in food, the maximum residue limits for DCN is 7 ppm in fruits of nectarine and grapes, and 15 ppm in vegetables of carrots.[12] Obviously, solvent-free **1** can perform outstandingly in detection of the fruit fungicide of DCN and is competent to fulfill the requirements. To deepen insight into the mechanism for detecting DCN, the HOMO and LUMO energy levels of DCN and BPyTPE in complex **1** are calculated (Fig. S15, ESI†). The excited state electron transfer from the higher LUMO of BPyTPE (–1.77 eV) to that of DCN (–2.40 eV) may occur, resulting in severe fluorescence quenching. Therefore, the photoinduced electron-transfer (PET)[13] may be the sensing mechanism. Furthermore, hydrogen bonding interactions between complex **1** and DCN should also contribute to the good sensitivity of the detection.

In summary, we have synthesized a TPE-based ligand (BPyTPE) with a trans-conformation and prominent AIE property. Based on BPyTPE, we have developed a novel pillared-layered LMOF (complex **1**) with a three-fold interpenetration structure. Solvent-free **1** exhibits intense blue-green emission at 498 nm with a remarkably high Φ_F of 99%. The emission of solvent-free **1** can be quenched efficiently and selectively by nitro aniline. Based on solvent-free **1**, we establish a reversible method to sensitively and quantitatively detect trace pesticide DCN, with a linear range of 0.94–16.92 ppm and a low detection limit of 0.13ppm. To the best of our knowledge, using LMOF as a fluorescent sensor to efficiently detect DCN is very rare and the present assay method is a promising one capable of practical application. Further studies of detecting other pesticides as well as heavy metal pollutants with TPE-based LMOFs are in progress.

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