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Blue-Light Excitable, Quantum Yield Enhanced Yellow-Emitting Zirconium-Based MOF Phosphors formed by Immobilizing Organic Chromophores

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ABSTRACT □ We demonstrate that two new zirconium based metal-organic frameworks can be constructed from organic chromophore ligands. Both compounds show intense yellow emission when excited by blue light, with notable fluorescence red shift and quantum yield enhancement compared to the organic chromophore.

Light-emitting-diode (LED) bulbs are regarded as the future lighting devices to fully replace traditional incandescent and fluorescent lighting systems because of their low power consumption, high efficiency and long lifetime. It has been estimated that nearly 90% of general lighting devices will be LED-based by 2030 in United States, which would result in about 300 TWh of annual energy saving.¹ The simplest white LED (WLED) can be assembled by coating a yellow phosphor onto a blue LED chip which generates white light as a result of mixing blue and yellow emission from the blue LED chip and the yellow phosphor, respectively.² The currently widely used yellow phosphors have a large dependence on rare-earth elements (REEs), such as the cerium (III)-doped yttrium-aluminum garnet (YAG:Ce). However, the global supply of REEs (e.g. yttrium and cerium in YAG:Ce) has been and will remain at a deficit relative to demand. In light of their supply, cost, and negative impact on the environment, it is of global importance to develop REE-free alternative phosphors for the implementation of WLED devices.

Organic chromophores are promising alternative lighting phosphors, and incorporating them into metal-organic frameworks (MOFs) can further boost their performance as it will lead to tunable optical properties, enhanced emission and improved thermal stability. It has been shown that luminescent MOFs (LMOFs) built on organic chromophore-based ligands often exhibit higher quantum yields (QYs) than the chromophoric ligands themselves because immobilization of these chromophores onto the MOF structures limit

the molecular vibrations, torsions, and rotations which may result in nonradiative excitation decay in the molecular chromophore.³⁻⁶ LMOF materials have found great potential as lighting phosphors as well as chemical sensors.⁷⁻⁸ In this work, we demonstrate the construction of two new zirconium based LMOFs built on a pre-designed organic chromophore H₄tcnpe, 1,1,2,2-tetrakis(4-(6-carboxy-naphthalen-2-yl)phenyl)ethylene. The resulting Zr-MOF shows high thermal stability, dramatically enhanced quantum yield, and fluorescence red shift compared to the organic linker.

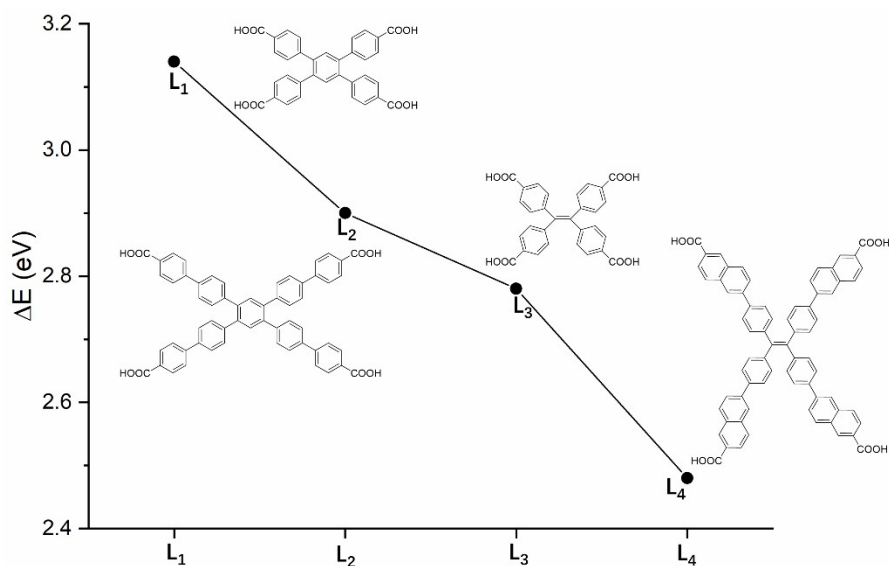


Figure 1. Estimated HOMO-LUMO energy gaps of ligands by DFT calculations.

Tetraphenylethylene (tpe) is a typical aggregation-induced emission (AIE) moiety, and its carboxylate form, tetrakis(4-carboxyphenyl)ethylene (H₄tcpe) has been extensively used for the construction of LMOFs.^{4, 9-11} H₄tcpe has a decent internal quantum yield (IQY) of 47% (Excited at 455 nm). However, its

emission energy is too high as a yellow phosphor ($\lambda_{em} = 480$ nm). In order to lower the emission energy of this ligand, we attempted to extend the arm from the tpe core. Thus we designed and synthesized the organic chromophore H₄tcnpe. The estimated HOMO-LUMO energy gap (ΔE) for H₄tcnpe is 2.48 eV based on the DFT calculations, notably lower than that of H₄tcpe (2.78 eV).⁶ Experimental UV-Vis spectrum shows H₄tcnpe has an energy gap of 2.55 eV, and photoluminescence spectrum indicates it emits at 524 nm, but with a fairly low IQY (17.7%) under blue light excitation ($\lambda_{ex} = 455$ nm). This is consistent with its excitation spectrum which suggests it is barely blue excitable (Figure. 3a).

The incorporation of H₄tcnpe into MOFs has been realized by solvothermal reactions. Heating a mixture of ZrOCl₂•8H₂O, H₄tcnpe, and an acid modulator in DMF gives rise to yellowish block-shaped crystals (See Supplementary Information for synthesis details). Single-crystal X-ray diffraction analysis reveals that the use of formic acid/acidic acid and benzoic acid leads to two new MOFs with similar structure but different terminal ligands. With formic acid/acidic acid, a compound with formula of Zr₆(μ_3 -O)₄(μ_3 -OH)₄(tcnpe)₂(H₂O)₄(OH)₄ (denoted as **1** and **LMOF-602**) is obtained and with benzoic acid the formula would be Zr₆(μ_3 -O)₄(μ_3 -OH)₄(tcnpe)₂(BA)₄(OH)₄ (denoted as **2** and **LMOF-603**, BA= benzoic anhydride). **1** and **2** crystallize in the space group of *Cmcm* and *Pbcn*, respectively, but with the same SBU and connectivity. The structures are built on 8-connected Zr₆O₄(OH)₄(COO)₈ SBUs propagated through tcnpe⁴⁻ linkers to form a 3D net. Two identical nets

interpenetrate forming the final framework featuring **scu** topology.¹² It is worth noting that these structures are different from PCN-94 (Zr-tcbpe, H₄tcbpe = 1,1,2,2-tetrakis(4-(4-carboxy-phenyl)phenyl)ethane) which is built on 12-connected Zr₆O₄(OH)₄(COO)₁₂ SBUs and features a **ftw** type structure.¹³ This is reasonable as H₄tcbpe has an aspect ratio that is close to 1 while the value for H₄tcnpe is as high as 1.63, making it unfavourable for the formation of 12-connected SBUs. In our previous report we have suggested that the connectivity of Zr₆ SBUs in Zr-MOFs built on planar, tetratopic carboxylate linkers as well as their topology largely depend on the aspect ratio of the organic ligand.¹⁴⁻¹⁶ When the geometry of the organic ligand is close to a square, it favours a **ftw** type structure with 12-connected SBUs. In contrast, if the ligand is rectangle-shaped with an aspect ratio that is notably larger than 1, it will most likely lead to the formation of a ftw-derivative topology (i.e. **scu**, **she**, **sql**) with 8-, 6-, or even 4-connected Zr₆ SBUs.

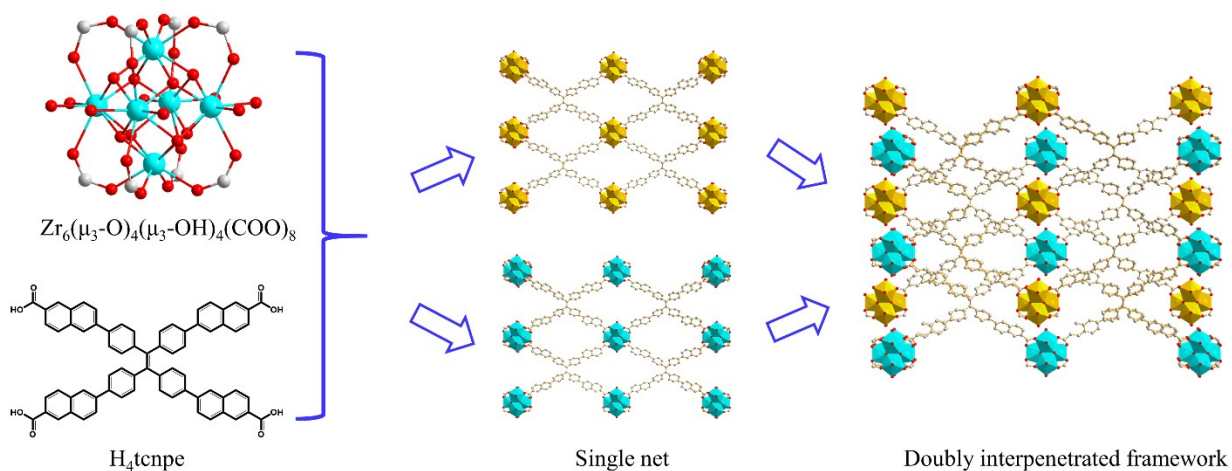


Figure 2. Structure illustration of **1** and **2** (terminal coordinated ligands are omitted for clarity).

Phase purity of the as-synthesized materials was confirmed by powder X-ray diffraction (PXRD) analysis where the experimental patterns agree well with the simulated ones derived from their crystal structures (Figures S6-S7). Thermogravimetric analysis (TGA) suggests that **1** features a plateau up to 500 °C following an initial weight loss before 300 °C (Figure S8). In contrast, the TGA curve of **2** indicates a continuous weight loss which should be attributed to the existence of the coordinated benzoic anhydride molecules (Figure S9).

The optical absorption spectra of the two compounds were collected at room temperature and shown in Figure S11. Estimated band gaps are 2.25-2.3 eV for both compounds. The photoluminescence spectra of the two MOFs were obtained at room temperature and compared with that of the organic ligand, as shown in Figure. 3. The excitation spectrum of H₄tcnpe indicates it is barely excitable by blue light, with emission intensity that is less than 50% of that excited by UV light. The excitation spectra of **1** and **2**, in sharp contrast to that of the organic linker, suggest that they are evidently blue excitable, and with a peak wavelength of 450-455 nm, right at the blue region. The emission spectrum shows H₄tcnpe emits at the blue-green with a maximum peak wavelength of 521 nm. Interestingly, when the organic molecule is incorporated into MOFs, both **1** and **2** emit at 570 nm, with a ~50

nm red shift from the emission wavelength of H₄tcnpe. This is very different from the case of PCN-94 where the Zr-based MOF (emits at 470 nm) show a blue shift compared to the organic linker (emits at 545 nm). As previously reported based on theoretical calculation results, the large red or blue shift of emission upon incorporation of a ligand into MOF structure can be mainly attributed to the breakdown or reformation of the delocalized conjugation system.¹³

The Commission International de l'Eclairage (CIE) coordinates of **1** and **2** are (0.47, 0.51) and (0.45, 0.53) under 455 excitation, respectively. Compared to the CIE of YAG:Ce³⁺ (0.41, 0.55), the emission of **1** and **2** are closer to red, indicating they can be promising yellow phosphors for a warmer white light which is highly desirable. **1** and **2** show very similar optical properties, indicating the terminal ligands have little influence on the photoluminescence of these MOFs.

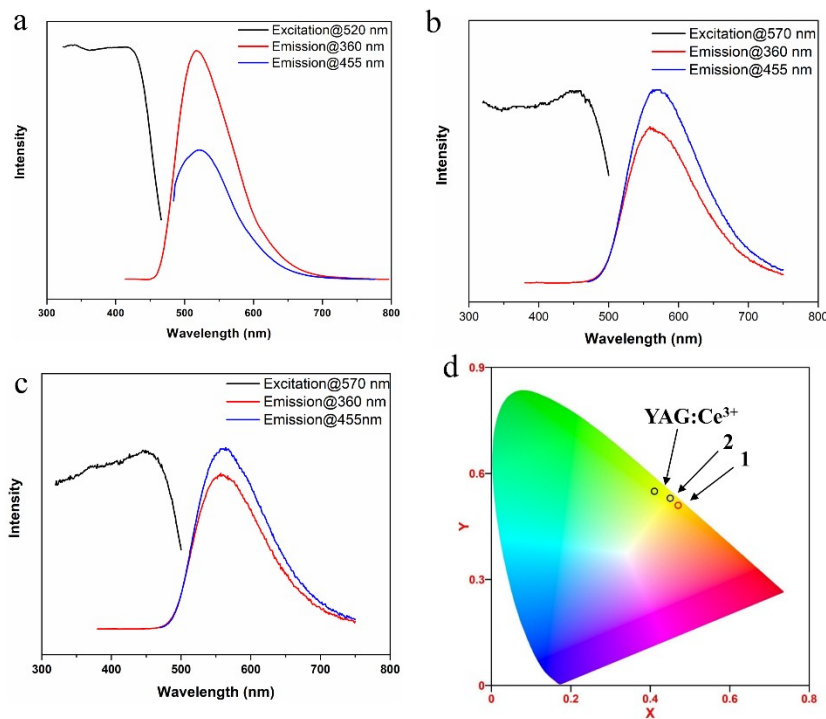


Figure 3. Optical properties of H₄tcnpe, **1**, and **2**. Excitation and emission spectra of H₄tcnpe (a), **1** (b), **2** (c), and CIE coordinates of **1** and **2**, compared to YAG:Ce³⁺ (d).

Photoluminescence efficiencies of the two MOFs were evaluated by internal quantum yield (IQY) measurements and compared with that of the organic linker. The IQY measurements were performed under excitation wavelengths of 360 and 455 nm. Consistent with their photoluminescence excitation spectra, both materials are highly excitable by blue light. The IQYs for **1** are 38.7% and 45.5% at 360 and 450 nm, respectively, and the values for **2** are 36.2% and 42.2%, respectively, at the same wavelengths. Compared to the IQY of the organic chromophore H₄tcnpe (17.7% at 450 nm), the increase of 157% and 138% (at 455 nm excitation) for **1** and **2** represents a substantial

improvement over the organic ligand. This can be attributed to the reduction of nonradiative excitation decay of the organic chromophore when rigidified in the MOF framework which limits the molecular vibrations, torsions, and rotations, as having been confirmed in the previous studies. The thermal stability of the two Zr-MOFs was also evaluated. After being heated at 150 °C for 24 hours, **1** showed essentially no loss in IQY, with a value of 44.5%, indicating its good thermal stability.

In summary, we have demonstrated in this work the successful incorporation of an organic chromophore into metal-organic framework materials. The organic chromophore is pre-screened for suitable HOMO-LUMO energy gap and its immobilization into MOFs leads to substantial enhancement in the quantum yield and a red shift in emission wavelength. The Zr-MOFs emit a warmer yellow light at 570 nm and have an increase of 157% and 138% in the quantum yield (at 455 nm excitation) compared with the ligand. Our strategy indicates LMOFs with enhanced and ideal emission energy may be achieved by incorporation of well-designed AIE-type molecular chromophores.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Chemicals and methods, synthetic details of the organic ligand and MOFs, materials characterization data (TGA, PXRD, Absorption spectra etc.)

Accession Codes

CCDC 1955130, 1955131 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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