

A Direct White-Light-Emitting Metal–Organic Framework with Tunable Yellow-to-White Photoluminescence by Variation of Excitation Light

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White-light-emitting diodes (white LEDs) have broad applications in displays and lighting for the purpose of conserving energy and miniaturization of equipment.¹ They are generally produced through exciting multiphosphors by a UV LED, mixing a blue LED with a yellow phosphor, or blending multi-LEDs. One of the current academic interests is in the pursuing single white-light phosphors to avoid the intrinsic color balance, device complication, and high-cost problems when using multiphosphors or multi-LEDs. Examples are rare but still can be found in the research field of organic molecules or polymers,² metal-doped or hybrid inorganic materials,³ metal complexes,⁴ and nanomaterials.⁵

In the past two decades, metal–organic frameworks (MOFs) have received intense interest due to their potential applications in gas purification, gas separation, catalysis and sensors.⁶ Studies on the photoluminescence (PL) of MOFs are still in their infancy;⁷ however, novel PL phenomena have been discovered, such as tunable UV-to-visible emission by controlling guest molecules⁸ and ion sensing of PL.⁹ We here report a distinct direct white-light MOF, $[\text{AgL}]_n \cdot n\text{H}_2\text{O}$ (**1**, L = 4-cyanobenzoate), with tunable yellow-to-white PL by variation of excitation light.

Colorless crystalline complex **1** can be easily obtained by the stoichiometric reaction of deprotonated HL and AgNO_3 in water in the dark. Their phase purity was verified by elemental analysis, IR spectrum, thermogravimetric analysis (TGA), and powder X-ray diffraction (PXRD) determination (Figures S1–3, Supporting Information (SI)). The TGA result shows the complete loss of lattice water molecules at ~ 271 °C. Compound **1** presents a gentle absorption peak from ~ 460 nm to the near-IR region and a steep one with an absorption edge of 354 nm (Figure S4, SI).

Single-crystal X-ray diffraction analysis reveals that the crystal structure of **1** consists of wave-like 2-D MOFs and lattice water molecules. As shown in Figure 1a, the Ag atom is three-coordinated by two carboxylate O atoms and one cyano N atom, yielding a near T-shaped configuration. The Ag...Ag separation of 2.8303(4) Å in the centrosymmetric dimeric $[\text{Ag}_2(\text{O}_2\text{C})_2]$ cluster is close to that in metallic silver and hence indicative of a comparable metal...metal interaction. The Ag1–N11 bond distance of 2.436(2) Å is shorter than those found in Ag complexes of aromatic polynitrile ligands.¹⁰ The bond distances and bond angles of the L[−] ligand are in common values. The cocrordination of cyano N and carboxylate O atoms for the L[−] ligand is only found in two double salts reported by the Mak group.¹¹ The 2-D MOFs lying in the [0 1 0] and [2 0 −1] plane stack in parallel without interpenetration to generate the 3-D crystal structure of **1** with 10.832×6.650 Å² parallelogram-like channels approximately along the *a* direction (Figure S5, SI). As shown in Figure 1b, there are interlayer Ag...Ag interactions and π ... π stacking interactions among the layers. The ligand-unsupported interlayer Ag...Ag interactions of 3.3426(4) Å are weaker than the ligand-supported ones in the

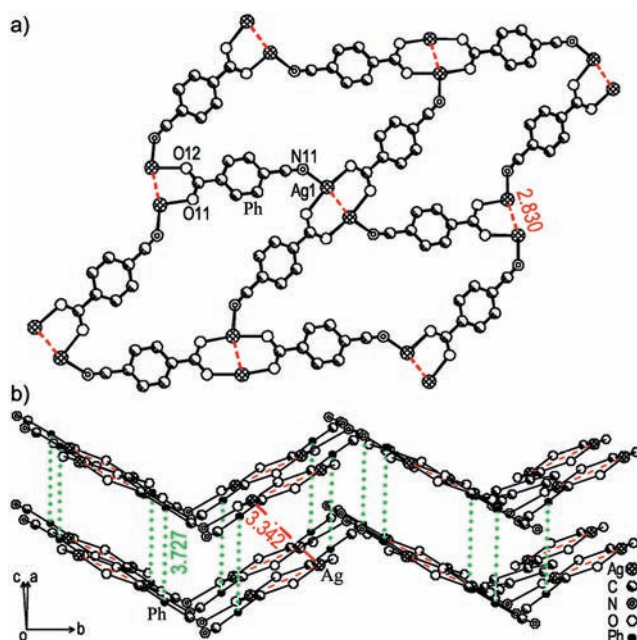


Figure 1. (a) 2-D layer and (b) their packing diagram. The phenyl (Ph) groups in (b) are denoted as solid black balls. H atoms and lattice water molecules are omitted for clarity.

$[\text{Ag}_2(\text{O}_2\text{C})_2]$ clusters mentioned above but stronger than that reported in the literature.¹² The interlayer π ... π stacking interactions are among the parallel phenyl groups of L[−] ligands with centroid-to-centroid distances of *ca.* 3.727 Å.

As shown in Figure 2, the solid-state sample of **1** displays a maximum emission at ~ 427 and ~ 566 nm when excited by 355- and 330-nm light, respectively. Also as shown in Figure 3, the decrease of the wavelength of excitation light lowers the intensity of the 427-nm peak but enhances that of a group of peaks at approximately 513, 566, and 617 nm and generates yellow PL finally. When adjusting the excitation light to the ~ 350 nm, the emission peaks at 427 and 566 nm are comparable in intensity, which results in direct white light to the naked eye (Figure 3, inset). The Commission Internationale de l'Éclairage (CIE) chromaticity coordinates of the white-light emissions excited by 350- and 349-nm light are approximately (0.31, 0.33) and (0.33, 0.34), respectively, close to that of pure white light (Figure S6, SI). Hence, the PL of **1** is tunable from yellow to white based on the variation of excitation light. This direct tunable PL is different from that of a reported porous zinc gallophosphate NTHU-4 by the Wang group that needs heat treatment and then guest exchange.^{3c} The external quantum yield of **1** is 10.86% when excited by 349-nm light.

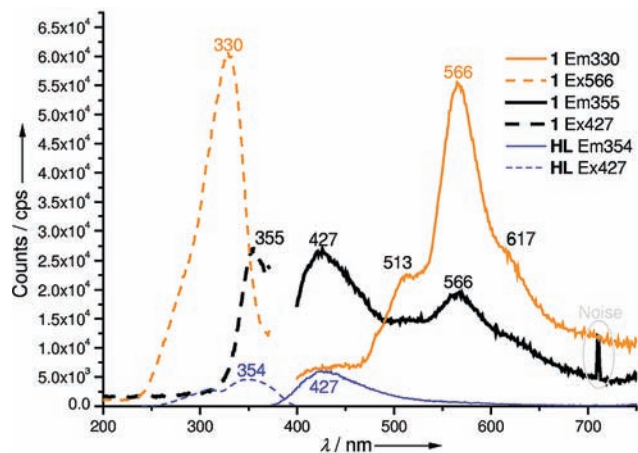


Figure 2. Solid-state PL spectra of **1** and HL at room temperature (Ex = excitation; Em = emission). The intensities between **1** and HL are not directly comparable, since their spectra were obtained using different slits.

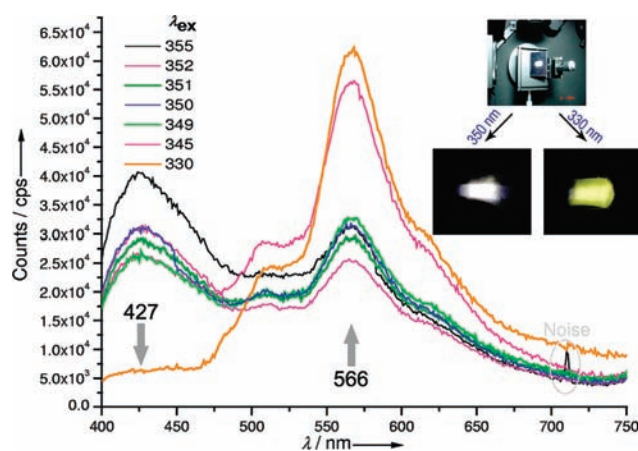


Figure 3. Solid-state PL spectra of **1** by variation of excitation light under the same metrical condition. Inset: PL images of a sample excited by 350- and 330-nm light, respectively.

The 427-nm peak and the group of peaks at 513, 566, and 617 nm have lifetimes of 0.87 ns and 2.60 ms, respectively, which indicates that they each have fluorescence and phosphorescence characteristics. The calculated density of states (DOS), performed with the CASTEP code based on the density functional theory using a plane-wave expansion of the wave functions, shows that the top of the valence band of **1** is dominated by the $p-\pi$ orbitals of L^- ligands mixed with partial Ag-4d states while the bottom of the conduction band is almost contributed by the $p-\pi^*$ antibonding orbitals of L^- ligands (Figure S7, SI). Theoretically speaking, ligand-centered and metal-to-ligand charge transfer (MLCT) coexist in the absorption transition of **1**. As depicted in Figure 2, the emission peak at 427 nm for **1** is similar to that of HL; hence it is reasonable to attribute this emission to the intraligand $\pi-\pi^*$ transition of L^- ligand. The group of low-energy emission peaks at 513, 566, and 617 nm can be mainly ascribed to the Ag-4d to $L^--\pi^*$ transition according to the theoretical calculation. There is precedence in the literature for low-energy MLCT emission in silver complexes.¹³ Compound **1** is sensitive to 300–370-nm UV light. Saturated illumination by the UV light almost halves the PL intensity of **1** (Figure S8; see details in SI).

In summary, we have synthesized a direct white-light MOF with tunable yellow-to-white PL by variation of excitation light. This material can be used as a single white phosphor for a white LED equipped with a recently reported deep UV GaN LED, which has light output at 325–350 nm. From the point of view of crystal engineering, we believe that introduction of pillar rigid building blocks would change the dimension of frameworks and further enhance their thermal stability. Replacement of Ag(I) by other soft Lewis acids, such as Pd(II) and Au(I), would be another promising route to obtain new direct white-light materials.

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Supporting Information Available: An X-ray crystallographic file in CIF format and a pdf file with experimental details and Figures S1–8. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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