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A stable Alq3@MOF composite for white-light emission

A blue-emitting MOF was a host for encapsulating yellow-green-emitting Alq3 to obtain white-light and was used in WLEDs. It is the first report that a white-light-emitting MOF can be used for a long time with excellent stability.

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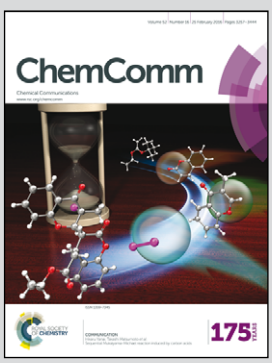

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A stable Alq3@MOF composite for white-light emission†

Wei Xie,[a] Wen-Wen He,[a] Dong-Ying Du,[a] Shun-Li Li,[b] Jun-Sheng Qin,[a] Zhong-Min Su,*[a] Chun-Yi Sun[a] and Ya-Qian Lan*[ab]

A stable mesoporous blue-emitting MOF NENU-521 was successfully constructed. NENU-521 can serve as a host for encapsulating Alq3 to obtain tunable and efficient white-light emission. The Alq3@NENU-521 composite possesses excellent stability and can be used as a promising white phosphor in WLEDs.

White-light-emitting diodes (WLEDs) have evoked particular interest in next-generation solid state lighting, which stems from their broad applications in illumination, indicators, backlights and displays.[1,2] The existing problems need to be urgently solved in traditional lighting, such as high energy consumption, environmental issues and health issues. White-light sources based on LEDs are gradually replacing incandescent bulbs and fluorescent lamps to provide a higher efficiency, lower energy consumption and long lasting option for solid state lighting. However there are some key factors to restrict the performance of WLEDs, including low luminous efficacy and poor quality of white-light using phosphors.[3] Therefore tremendous efforts have been dedicated to design and synthesize white phosphors with superior performance for use in WLEDs.

Metal–organic frameworks (MOFs) have emerged as very promising luminescent materials due to their adjustable fluorescence characteristics by decorating organic ligands and changing metal centres (building blocks).[4,5] Furthermore, the luminescence properties can be improved thanks to guest chromophores encapsulated into the cavities of MOFs.[6] Today, there are two common approaches to construct MOF-based WLEDs. One way is to combine a blue LED with yellow phosphors, and the Li group has done outstanding studies on yellow phosphors. They designed and synthesized a new type of highly efficient yellow-emitting phosphor by combining aggregation-induced emission (AIE) ligands with d^{10} metals in a MOF, and the obtained yellow phosphors can be effectively excited by blue LEDs to obtain highly efficient white light.[7] Another method is coating white phosphors on an ultraviolet LED.[6b,c] Guo and Li realized direct white-light emission by taking advantage of trinuclear d^{10} M^{I} clusters (M = Cu, Ag, Au) and delicate organic ligands that facilitate broad band emission in these systems.[8] Currently, the majority of MOF-based white-light materials rely heavily on the rare-earth elements (rare earths are bound to organic ligands as metal centers or doped into the pores of porous MOFs such as Eu, Tb and Dy).[9] White-light can be achieved by adjusting the proportion of different rare-earths, but at low quantum yield due to the low energy transfer between rare earths and organic ligands. Additionally, their high prices and supply risks have hindered the applications and developments of the rare-earth MOF materials. This requires that we design and synthesize efficient white-light-emitting MOF materials.

Previously our group realized white light by combining yellow emission from the encapsulated Ir complex with blue emission from the MOF.[6b] Compared to the Ir complex, Alq3 (tris(8-hydroxyquinoline)aluminium) is much cheaper. Strong emission in 520–530 nm and high decomposition temperature of Alq3 have evoked immense interest in organic light emitting diodes (OLEDs), photoluminescence, electroluminescence and field-emission fields.[10] The status of Alq3 has been unable to shake, because it almost meets all requirements of light-emitting materials. Our group first applied a nanotubular MOF as the host for encapsulating Alq3 to exhibit tunable luminescence emission.[11]

Here we introduce the strategy to achieve white-light-emission by encapsulating Alq3 (yellow-green emission) into the blue emission MOF (Scheme 1). Furthermore, the obtained MOF composite will be used to construct WLEDs, so excellent air stability is crucial for porous MOFs. The exceptionally high stability is a prerequisite to guarantee the framework intactness,

[a] *Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun 130024, Jilin, P. R. China. E-mail: zmsu@nenu.edu.cn, yqlan@njnu.edu.cn*

[b] *Jiangsu Key Laboratory of Biofunctional Materials, College of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210023, China*

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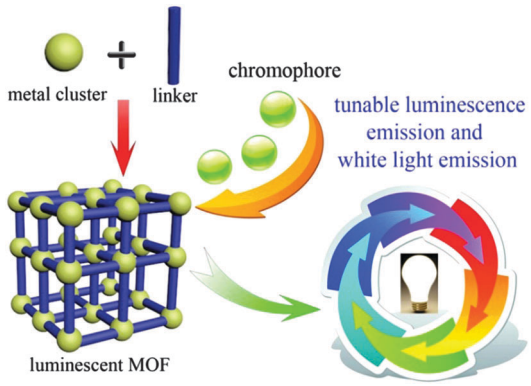

Scheme 1 Schematic illustration of the encapsulation of apposite chromophores into luminescent MOFs for tunable luminescence emission and white-light emission.

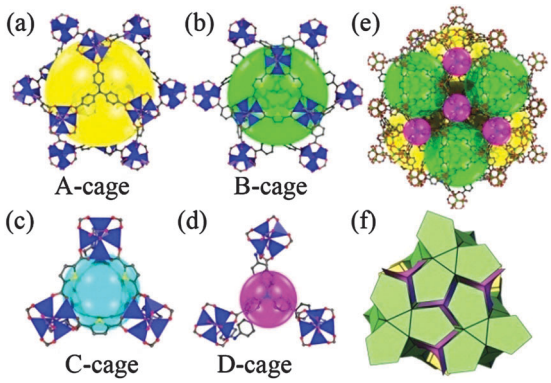

Fig. 1 (a) A-cage, (b) B-cage, (c) C-cage, (d) D-cage in **NENU-521**, (e) ball and stick representations of the 3D structure of **NENU-521**, and (f) the (3, 6)-connected augmented net as a natural tiling.

especially with the inclusion of guest molecules working as phosphors. However, most porous MOFs have poor stability, thus it remains a great challenge to obtain luminescent MOFs with permanent porosity and high stability simultaneously.

In this work, we chose 4,4′,4″-nitrilotribenzoic acid (H_3TPA), thiophene-2,5-dicarboxylic acid (H_2TDA) and $Zn(NO_3)_2{\cdot}6H_2O$ to synthesize a novel non-interpenetrating porous blue-emitting MOF $[(Zn_4O)_3(TPA)_4(TDA)_3(H_2O)_6][(Zn_4O)(TPA)_2]_2{\cdot}12DMF$ (**NENU-521**, NENU = Northeast Normal University) (Fig. S1, ESI†) based on the following considerations: (i) to build non-interpenetrating MOFs, one available method is to use mixed ligands and cage-like polyhedral cages. The H_3TPA linker possesses a certain length for building MOFs with suitable pore diameters, which will ensure the entrapment of guest Alq3 into the MOF. (ii) Triphenylamine and its derivatives emit strong emission at 450 nm,[12] which will result in a blue-emitting MOF. (iii) Zinc ions were selected as metal centres because they possess various coordination numbers and display photoactive properties when bound to organic ligands. Here we employ the porosity and stability of **NENU-521** to achieve efficient white-light emission by encapsulating Alq3 into the cavity of the MOF. The assembled WLED using **Alq3@NENU-521** as a phosphor exhibits bright white light. Furthermore, the **Alq3@NENU-521** sample collected from the WLED can still maintain the initial structure and constant quantum yield after the WLED is continuously turned on for one month. To our knowledge, this is the first report which states that white-light MOF materials can be used in WLEDs for a long time with excellent stability.

Single-crystal X-ray diffraction studies reveal that **NENU-521** crystallizes in the trigonal space group $R\bar{3}$ (Table S1, ESI†). The asymmetric unit contains 5/3 $Zn_4(\mu_4\text{-O})$ clusters as secondary building units (SBUs) consisting of four Zn cations and one μ_4-O atom, 8/3 deprotonated TPA^{3-} and one deprotonated TDA^{2-} ligands (Fig. S2, ESI†). There are two kinds of $Zn_4(\mu_4\text{-O})$ clusters in **NENU-521**. One $Zn_4(\mu_4\text{-O})$ cluster(I) is encapsulated by six carboxylate groups from four TPA^{3-} and two TDA^{2-} ligands. Another $Zn_4(\mu_4\text{-O})$ cluster(II) is connected to six carboxylate groups from six TPA^{3-} ligands (Fig. S3, ESI†). H_3TPA, H_2TDA ligands and $Zn_4(\mu_4\text{-O})$ clusters form four kinds of cages (including two mesopores and two micropores) with different sizes (Fig. 1). The A-cage (22 Å in diameter, measured between the closest opposite atoms, excluding van der Waals radii) is formed by twelve $Zn_4(\mu_4\text{-O})$ SBUs (6 I and 6 II) and eight TPA^{3-} linkers (Fig. 1a), the B-cage (20.6 Å) from by twelve $Zn_4(\mu_4\text{-O})$ SBUs (6 I and 6 II), six TPA^{3-} and six TDA^{2-} linkers (Fig. 1b), the C-cage (10.6 Å) through four SBUs (1 I and 3 II), two TPA^{3-} and three TDA^{2-} linkers (Fig. 1c), and the D-cage from four SBUs (1 I and 3 II) and three TPA^{3-} ligands (Fig. 1d). The structure was made up of these four kinds of cages packed in a 1 : 1 : 2 : 6 ratio (Fig. 1e). In some sense, the structure can also be seen as a pillared-layer structure. Two-dimensional layers are formed by $Zn_4(\mu_4\text{-O})$ clusters(I), TPA^{3-}, and TDA^{2-} ligands. The adjacent layers are further connected by $Zn_4(\mu_4\text{-O})$ clusters(II) and TPA^{3-} linkers to give rise to an overall 3D pillared-layer structure (Fig. S4, ESI†). From the viewpoints of topology, the SBUs serve as 6-connected nodes, whereas TPA^{3-} ligands as 3-connected nodes. As a result, **NENU-521** adopts a 3, 6-c nodal net (Fig. S5, ESI†), which is previously unreported. The effective free volume of **NENU-521** calculated by PLATON[13] is 76.4% of the crystal volume (70 679 $Å^3$ of 92 471 $Å^3$ unit cell volume), upon removal of the guest molecules. The calculated density of porous **NENU-521** after solvent removal is as low as 0.553 g cm^{-3}.

The synthesized **NENU-521** was fully activated by the procedure described in the ESI† and the integrity of the framework was confirmed by PXRD and IR (Fig. S6 and S7, ESI†). The N_2 sorption isotherm of the activated **NENU-521** at 77 K shows a characteristic type IV (containing hysteresis) behaviour for mesoporus and microporus concurrent materials. The pore size distribution indicates peaks at 5–10 Å and 20–25 Å, which is in accordance with the results from the single crystal structure analyses (Fig. S8, ESI†). Calculated from the nitrogen adsorption data, the BET surface area, Langmuir surface area and pore volume are approximately 2765 $m^2\ g^{-1}$, 3191 $m^2\ g^{-1}$ and 1.45 $cm^3\ g^{-1}$ respectively.

The Alq3 complex was selected as an encapsulant because of its relatively small size (~1 nm), which allows access to the MOF. In an initial attempt, **NENU-521** (40 mg) was immersed in DMF solutions of Alq3 (2×10^{-2} mol L^{-1}) for three days. An obvious colour change and the TGA curves indicate that Alq3

molecules were successfully encapsulated into **NENU-521** (Fig. S9 and S13, ESI†). The ICP experiment showed that ~5.32 wt% Alq3 was embedded into the framework with respect to Zn (Table S2, ESI†). We speculated that Alq3 molecules with sizes of ~1 nm would enter into the mesopores of the frameworks. With the increase of Alq3 molecules in the pores, the pores were occupied by guest Alq3 molecules and became small. The N_2 adsorption amount of **Alq3@NENU-521** decreased obviously and the peak at 20–25 Å disappeared, which further verified our speculation that Alq3 has interred into the mesopores of **NENU-521** (Fig. S8, ESI†). The IR and PXRD patterns proved that the framework of **NENU-521** did not degrade when Alq3 was introduced (Fig. S6 and S7, ESI†).

The luminescence properties of **NENU-521** and the H_3TPA ligand in the solid state were investigated. Compared with the H_3TPA ligand, **NENU-521** exhibited obvious enhanced blue emission with a peak at 435 nm, which may be attributed to the deprotonation of H_3TPA and the coordination of the ligand to Zn (Fig. S10 and S12, ESI†).[14] The Commission International de I'Eclairage (CIE) coordinate for **NENU-521** was (0.179, 0.144). The value is close to that of (0.14, 0.08) of a saturated blue emitter.[15] The quantum yield measured was 10.7%. These data showed that **NENU-521** can be used as an efficient blue-light-emitter. Alq3 emitted yellow-green emission with a broad and strong peak at 521 nm (Fig. S11 and S12, ESI†). Alq3 in powder yielded CIE and a quantum yield of (0.293, 0.510) and 60.5% (Table S2, ESI†).

Aiming at obtaining white-light emission, comparative emissions of the two components are needed. So the **Alq3@NENU-521** samples with different concentrations of Alq3 were prepared. The corresponding solid PL spectra were plotted in Fig. 2a. With the increase of Alq3 content, a significant bathochromic shift (435 to 502 nm) with concomitant broadened emission was observed for the fixed MOF amount. Tunable fluorescence emission from blue to green-yellow was realized by encapsulating different concentrations of the Alq3 complex (Scheme S1, ESI†). At an optimal concentration of 4.14 wt%, the spectrum exhibited a clear broadened emission, with a CIE coordinate of (0.291, 0.327), which is close to (0.33, 0.33) of the pure white light. This obtained white light consisted of yellow-green-emission (Alq3) and blue-light-emission (**NENU-521**) with suitable intensities. Other related color parameters such as the quantum yield and correlated color temperature (CCT) were also estimated. At this concentration, the value of the quantum yield obtained was 11.4%, which is higher among the reported white-light-emitting MOFs (Table S3, ESI†). The value of CCT calculated was 7796 K, thus the white light material can be used as a cold white-light source.

Clearly, the overlap in the absorption and emission spectra indicated that there was energy transfer between Alq3 and **NENU-521** (Fig. S14 and S15, ESI†). Such energy transfer behavior has been further confirmed by the lifetime measurements and the fluorescence emission spectra. The lifetimes of **Alq3@NENU-521** became longer with the increase of Alq3 content (Table S2, ESI†), and the emission spectra of **Alq3@NENU-521** exhibited a distinct bathochromic shift with broadened emission (Fig. 2a).

To facilitate our system for the white-light application, the WLED assemblies were fabricated using this material by the following method.[6b,16] The method employed **Alq3@NENU-521** (Alq3: 4.14 wt%) as a white phosphor and 3 mm commercially available ultraviolet LEDs. At 3.8 V voltage, the assembled WLED exhibits bright white light (Fig. 3). The obtained WLED can still maintain illuminating bright white light when continuously turned on for one month (Fig. 3e). To sum up, the stable and cheap **Alq3@NENU-521** phosphor has potential applications in WLEDs as a result of its good quality.

Good agreement between the simulated and experimental PXRD patterns verified the purity of the as-synthesized **NENU-521** (Fig. 4). **NENU-521** can maintain its pristine shape despite a few cracks appearing after being exposed in air for one month (Fig. S1, ESI†). **NENU-521** and **Alq3@NENU-521** were confirmed to be stable after exposure to air for more than one month (Fig. 4 and Fig. S6, ESI†). **Alq3@NENU-521** was collected from the prepared WLED with continuous turning on for one month. The collected **Alq3@NENU-521** sample was washed with dichloromethane to remove glue and it was confirmed to be stable by the PXRD pattern (Fig. 4). Furthermore, the quantum yield of the collected **Alq3@NENU-521** sample was also measured and a value of 11.2% was obtained (λ_{ex} = 370 nm), which is almost the same as before. The reason that **Alq3@NENU-521** can maintain high quantum yield could be explained by the following aspects. **NENU-521** itself can be used as an efficient blue-light-emitter with excellent stability. Alq3 molecules were located into the pores of the MOF, which partially reduced non-radiative decay by restricting molecular vibration, rotation and torsion. On the other hand, the interaction between Alq3 and the framework is

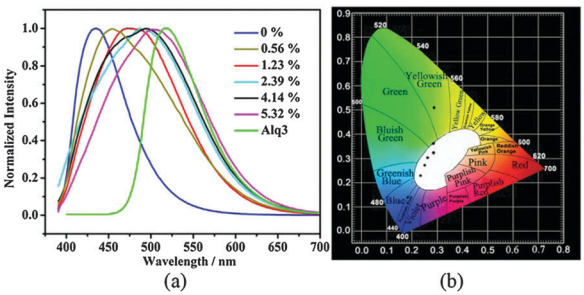

Fig. 2 (a) Room temperature solid emission spectra and (b) the CIE coordinates of **NENU-521** and **Alq3@NENU-521** with different concentrations of Alq3. All measurements were performed at an excitation wavelength of 370 nm.

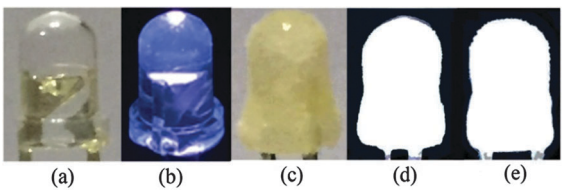

Fig. 3 Photographs of the LEDs. (a) A 3 mm ultraviolet LED (not turned on). (b) The same LED having a blue tinge (turned on). (c) The LED coated with 4.14 wt% **Alq3@NENU-521** phosphors (not turned on). (d) The obtained WLED turned on and generating bright white light. (e) The same WLED placed in air for one month (continuously turned on).

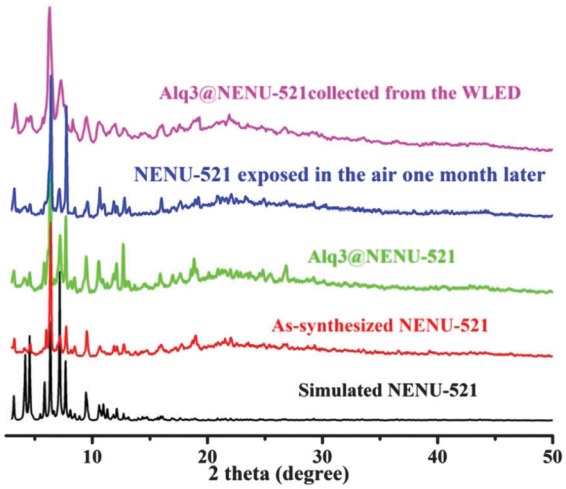

Fig. 4 X-Ray powder diffraction patterns of simulated **NENU-521** (black), as-synthesized **NENU-521** (red), 5.32 wt% **Alq3@NENU-521** (green), **NENU-521** exposed in air for one month (blue) and **Alq3@NENU-521** collected from the WLED when continuously turned on for one month (purple) respectively.

strong in contrast to rare-earths, for example π–π conjugation, which is also helpful for the light emission.[8,17]

In summary, we adopted mixed ligands to synthesize a porous and blue-emitting MOF **NENU-521** with superduper stability. Alq3 was selected as the encapsulant based on its complementary yellow-green emission and small size. The prepared **Alq3@NENU-521** (Alq3: 4.14 wt%) composite can generate bright white-light emission with CIE coordinates (0.291, 0.327) and the quantum yield up to 11.4%. The assembled WLED using **Alq3@NENU-521** as a phosphor exhibited bright cold white-light. It is worth noting that the obtained WLED can still maintain bright white light when continuously turned on for one month. This is the first report which states that a white-light-emitting MOF can be used in WLEDs for a long time with exceptionally high stability. This work provides a new approach to obtain white-light by encapsulating luminescence-active chromophores into luminescent MOFs and to fabricate WLEDs with superior performance. Further study will focus on more stable, efficient and energy-efficient white-light-emitting materials.

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