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A stable Alq3@MOF composite for white-light emission

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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 promising white phosphor in the WLEDs.

White-light-emitting diodes (WLEDs) have evoked particular interest in the next-generation solid state lighting stem from their broad applications in illumination, indicators, backlights and displays.¹⁻² Existing problems are in urgent to solve in traditional lighting, such as high energy consumption, environment 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 longer 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 the WLEDs.

Metal-organic frameworks (MOFs) have emerged as very promising luminescent materials due to their adjustable fluorescent characteristic by decorating organic ligands and changing metal centres (building blocks).^{4,5} Furthermore, the luminescent properties can be improved thanks to the 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 Li group made a large outstanding works in yellow phosphors. They designed and synthesized a new type

of highly efficient yellow-emitting phosphors by combining aggregation-induced emission (AIE) ligands with d¹⁰ metals in 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,6c}. Guo and Li realized direct white-light emission by taking advantages of trinuclear d¹⁰ M^I clusters (M=Cu, Ag, Au) and delicate organic ligands that facilitate the 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 Although 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 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 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, for 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-emitting by encapsulating Alq3 (yellow-green emission) into blue emission MOF (Scheme 1). Further, the obtained MOF composite will be constructed to WLEDs, so excellent air stability is crucial for porous MOFs. The exceptionally high stability is a prerequisite to guarantee the framework intactness, especially with inclusion of guest molecules working as phosphors. However, most porous MOFs have poor stability, thus it remains a great challenge to obtain

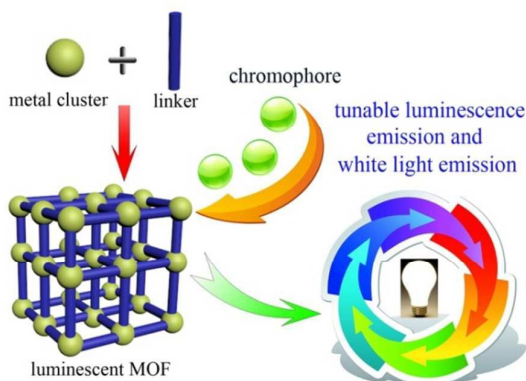
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luminescent MOFs with permanent porosity and high stability simultaneously.



Scheme 1 Schematic illustration of the encapsulation of a chromophore into a luminescent MOF for tunable luminescence emission and white-light emission.

In this work, we chose 4,4',4''-nitrotribenzoic 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) based on the following considerations: (i) To build non-interpenetrating MOFs, one available method is to use mixed ligands and cage-like polyhedral cages. H_3TPA linker possesses certain length for building MOF with suitable pore diameters, which will ensure the entrapment of guest Alq3 into 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 porosity and stability of **NENU-521** to achieve efficient white-light emission by encapsulating Alq3 into the cavity of MOF. The assembled WLED using the **Alq3@NENU-521** as 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 continuous turned on for one month. To our knowledge, this is the first reported that white-light MOF material 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). The asymmetric unit contains 5/3 $Zn_4(\mu_4-O)$ clusters 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). There are two kinds of $Zn_4(\mu_4-O)$ clusters in **NENU-521**. One $Zn_4(\mu_4-O)$ cluster (I) is encapsulated by six carboxylate groups from four TPA^{3-} and two TDA^{2-} ligands. Another $Zn_4(\mu_4-O)$ cluster (II) is connected to six carboxylate groups from six TPA^{3-} ligands (Fig. S3). H_3TPA , H_2TDA ligands and $Zn_4(\mu_4-O)$ clusters form four kinds of cages (including two mesopores and two micropores) with different sizes (Fig. 1). A-cage (22 Å in diameter, measured between the closest opposite atoms, excluding van der Waals radii) is formed by

twelve $Zn_4(\mu_4-O)$ SBUs (6 I and 6 II), and eight TPA^{3-} linkers (Fig. 1a), B-cage (20.6 Å) from by twelve $Zn_4(\mu_4-O)$ SBUs (6 I and 6 II), six TPA^{3-} and six TDA^{2-} linkers (Fig. 1b), C-cage (10.6 Å) through four SBUs (1 I and 3 II), two TPA^{3-} and three TDA^{2-} linkers (Fig. 1c), and 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 pillared-layer structure. Two-dimensional layers are formed by $Zn_4(\mu_4-O)$ clusters (I), TPA^{3-} , and TDA^{2-} ligands. The adjacent layers are further connected by $Zn_4(\mu_4-O)$ clusters (II) and TPA^{3-} linkers to give rise to an overall 3D pillared-layer structure (Fig. S4). 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), which is previously unreported. The effective free volume of **NENU-521** calculated by PLATON¹³ is 76.4 % of the crystal volume 70,679 Å³ of 92,471 Å³ 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/cm³.

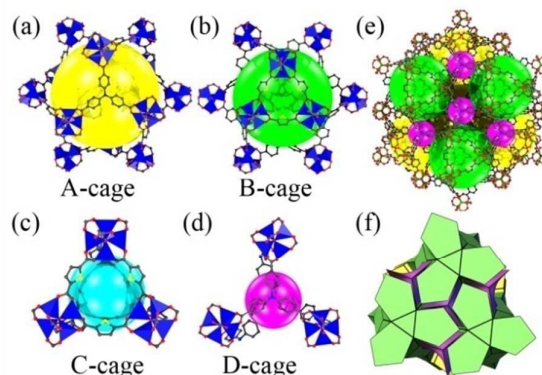


Fig. 1 (a) A-cage, (b) B-cage, (c) C-cage, (d) D-cage in **NENU-521**, (e) Ball and stick representations of the 3D structure of **NENU-521**, and (f) The (3, 6)-connected augmented net as a natural tiling.

The synthesized **NENU-521** was fully activated by the procedure described in the supporting information and the integrity of the framework was confirmed by the PXRD and the IR (Fig. S6 and S7). The N_2 sorption isotherm of the activated **NENU-521** at 77K shows a characteristic type IV (containing hysteresis) behaviour for mesopores and micropores concurrent materials. The pore size distribution indicates peaks in 5 ~ 10 Å and 20 ~ 25 Å, which is accordance with the results from the single crystal structure analyses (Fig. S8). Calculated from the nitrogen adsorption data, the BET surface area, Langmuir surface area and pore volume are approximately 2765 m² g⁻¹, 3191 m² g⁻¹ and 1.45 cm³ g⁻¹ respectively.

Alq3 complex was selected as encapsulant for its relatively small size (~ 1 nm) which allows access to the MOF. In an initial attempt, **NENU-521** (40 mg) was immersed into 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).

The ICP experiment showed that ~ 5.32 wt% Alq3 was embedded into the framework with respect to Zn (Table S2). We speculated that Alq3 molecules with sizes of ~ 1 nm would enter into the mesopores of the frameworks. With the increase of Alq3 molecules into 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 in $20 \sim 25$ Å disappeared further verified our speculation that Alq3 has interred into the mesopores of NENU-521 (Fig. S8). The IR and PXRD patterns proved that the framework of NENU-521 did not degrade when the Alq3 were introduced (Fig. S6 and S7).

The luminescent properties of NENU-521 and H₃TPA ligand in the solid state were investigated. Compared with the H₃TPA ligand, NENU-521 exhibited obvious enhanced blue emission with peak at 435 nm may be attributed to the deprotonation of H₃TPA and the coordination of the ligand to Zn (Fig. S10 and S12).¹⁴ The Commission International de l'Eclairage (CIE) coordinate for NENU-521 was (0.179, 0.144). The value is close to that of (0.14, 0.08) of 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 broad and strong peak at 521 nm (Fig. S11 and S12). Alq3 in powder yielded CIE and quantum yield of (0.293, 0.510) and 60.5 % (Table S2).

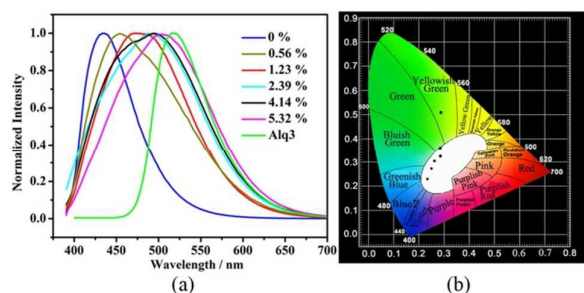


Fig. 2 (a) Room temperature solid emission spectra and (b) the CIE coordinates of NENU-521 and Alq3@NENU-521 with different concentrations of Alq3. All measurements were performed at an excitation wavelength of 370 nm.

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, significant bathochromic shift (435 to 502 nm) with concomitant broaden emission was observed for the fixed MOF amount. Tunable fluorescence emission from blue to green-yellow was realized by encapsulating different concentrations of Alq3 complex (Scheme S1). At the optimal concentration of 4.14 wt%, the spectrum exhibited a clear broaden emission, with 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-emitting (Alq3) and blue-light-emitting (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). The value of CCT calculated was 7796 K, thus the white light material can be used as 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). 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), and the emission spectra of the Alq3@NENU-521 exhibited distinct bathochromic shift with broaden emission (Fig. 2a).

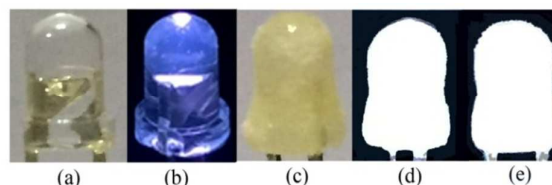


Fig. 3 Photographs of the LEDs. (a) A 3 mm ultraviolet LED (not turned on). (b) The same LED had a blue tinge (turned on). (c) The LED coated with 4.14 wt% Alq3@NENU-521 phosphors (not turned on). (d) The obtained WLED was turned on and generated bright white light. (e) The same WLED placed in the air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

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 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 with continuous turned on for one month (Fig. 3e). To sum up, the stable and cheap Alq3@NENU-521 phosphor has potential applications in WLED as a result of their good quality.

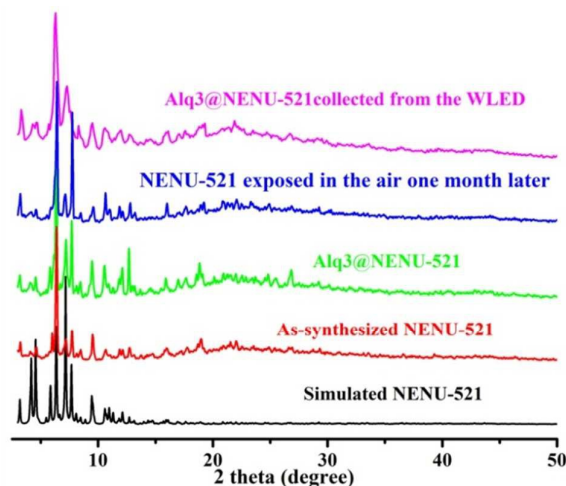


Fig. 4 X-Ray powder diffraction patterns of simulated NENU-521 (black), as-synthesized NENU-521 (red), 5.32 wt% contained Alq3@NENU-521 (green), NENU-521 exposed in the air for one month (blue) and Alq3@NENU-521 collected from the WLED with continuous turned on for one month (purple) respectively.

Good agreement between the simulated and experimental PXRD patterns verified the purity of the as-synthesized **NENU-521** (Fig. 4). **NENU-521** can maintain their pristine shape despite a few cracks appearing after exposed in the air for one month (Fig. S1). **NENU-521** and **Alq3@NENU-521** were confirmed stable after exposure in the air more than one month (Fig. 4 and S6). The **Alq3@NENU-521** was collected from the prepared WLED with continuous turned on for one month. The collected **Alq3@NENU-521** sample was washed with dichloromethane to remove glue and confirmed stable by 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 ($\lambda_{\text{ex}} = 370 \text{ nm}$), which keeps almost the same as before. The reason that **Alq3@NENU-521** can keep 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 are strong in contrast with 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 coordinate (0.291, 0.327) and the quantum yield up to 11.4 %. The assembled WLED using **Alq3@NENU-521** as phosphor exhibited bright cold white-light. It is worth noting that the obtained WLED can still maintain bright white light with continuous turned on for one month. This is the first reported that white-light-emitting MOF can be used in the 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 MOF 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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