

RESEARCH ARTICLE

View Article Online

View Journal | View Issue



Cite this: *Inorg. Chem. Front.*, 2017, 4, 547

Encapsulation of an iridium complex in a metal–organic framework to give a composite with efficient white light emission†

Wei Xie,^a Jun-Sheng Qin,^a Wen-Wen He,^a Kui-Zhan Shao,^a Zhong-Min Su,^{*a} Dong-Ying Du,^{*a} Shun-Li Li^b and Ya-Qian Lan^{*a,b}

We successfully synthesized a novel anionic luminescent metal–organic framework (MOF) (**NENU-524**) with a lonsdaleite topology. **NENU-524** contains a trigonal prismatic unit $\{Zn_8(btca)_6(2-NH_2-bdc)_3\}$ that can be regarded as a double secondary building unit with an unusual triply bound triangular frustum geometry. The prepared **NENU-524** had a permanent porosity and excellent stability in air. **NENU-524** was used as a platform to encapsulate yellow-emitting $[Ir(ppy)_2(bpy)]^+$ cations in the nanotube channels of the blue-emitting MOF via an ion-exchange process. The $[Ir(ppy)_2(bpy)]^+@NENU-524$ MOF ($[Ir(ppy)_2(bpy)]^+$ concentration 3.86 wt%) emitted a pure white light with CIE coordinates of (0.300, 0.336) and a high quantum yield of up to 15.2%. The white light-emitting diodes assembled using $[Ir(ppy)_2(bpy)]^+@NENU-524$ as a white phosphor emitted a bright white light, suggesting that the composite is a promising material for use in lighting. The assembled white light-emitting diodes continued to emit a bright white light for up to one month. This simple and feasible approach could be used to develop luminescent luminophor@MOFs composites for practical applications.

Received 28th November 2016,

Accepted 11th January 2017

DOI: 10.1039/c6qi00528d

rsc.li/frontiers-inorganic

Introduction

White light sources based on light-emitting diodes (LEDs) are increasingly used in solid-state lighting as a result of their high efficiency, low energy consumption, long lifetime and environmental friendliness.¹ Three methods are used to create white light: blending multi-LED chips; exciting yellow phosphors with a blue LED; or coating a UV LED with a white phosphor (or multiple phosphors).² Using white light phosphors has the advantages of low cost, simplified devices and a good intrinsic colour balance.³ It is therefore important to study white light phosphors that meet the criteria required for use in white light illumination.

Metal–organic frameworks (MOFs), a class of promising fluorescent materials, have received considerable attention because their luminescent performance can be adjusted by

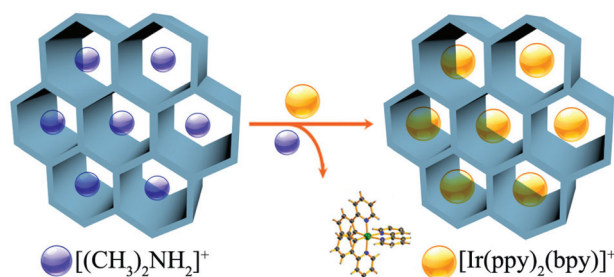
changing the organic ligands and metal nodes. In addition to their structural diversity, the guest luminophores accommodated in the cavities can improve and modulate the optical properties of MOFs.^{4–6} Many luminescent MOFs have been reported and show potential for use in fields such as luminescent sensors, photocatalysis, non-linear optics and biomedical imaging.^{7,8} However, MOFs that emit white light are less common and are heavily dependent on co-doping with lanthanide (Ln) ions.^{9,10} The transmission of energy from the organic ligands to Ln is low and Ln-based MOFs generally have low quantum yields.¹¹ In addition, Ln is both rare and very expensive. Thus it is worth exploring other MOFs that emit white light with high quantum yields.

If luminophores with high emission could be wrapped into the pores of MOFs to create luminophor@MOF composites, then the transmission ranges could be expanded to produce efficient white light emission by making full use of the emission from both the MOF and the luminophore guest. This has been achieved by novel strategies such as encapsulating cationic luminophores into luminescent anionic MOFs via ion-exchange processes to obtain luminophor@MOFs. For example, Qian and coworkers¹² prepared a MOF ⊃ dye composite through this strategy to realize white light emission. Our group also obtained efficient white light emission by combining the emission from a blue-emitting MOF and a yellow-emitting iridium complex.^{5c} However, unlike Ln-based

^aInstitute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun 130024, Jilin, P. R. China. E-mail: zmsu@nenu.edu.cn, yqian@nenu.edu.cn

^bJiangsu Key Laboratory of Biofunctional Materials, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210023, China

†Electronic supplementary information (ESI) available: Experimental details, crystal data, structural information, PXRD, FT-IR, TGA, fluorescence measurements, and additional figures. CCDC 1422972. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6qi00528d



Scheme 1 Schematic diagram of the encapsulation of cationic $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ into a luminescent anionic MOF via an ion-exchange process.

MOFs, which have been widely investigated, such lumino-phor@MOFs with white light emission have rarely been studied. Stability is a key factor in restricting the application and development of MOFs. Good stability guarantees the intactness of the framework and facilitates the enclosure of guest molecules. The design and preparation of MOF composites with high stability is still challenging.

We report here a novel anionic MOF $[(\text{CH}_3)_2\text{NH}_2]_2[\text{Zn}_8(\text{btca})_6(2\text{-NH}_2\text{-bdc})_3]\cdot 8\text{DMF}$ (**NENU-524**; NENU = Northeast Normal University) with a one-dimensional nanotube channel. This was successfully synthesized by heating benzotriazole-5-carboxylic acid (H_2btca), 2-amino-1,4-benzenedicarboxylic acid ($2\text{-NH}_2\text{-H}_2\text{bdc}$) and $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ under solvothermal conditions. The **NENU-524** sample had excellent stability in air. The anionic blue-emitting MOF was then used as a platform to incorporate yellow-emitting $[\text{Ir}(\text{ppy})_2(\text{bpy})][\text{PF}_6]$ (bpy = 2,2'-bipyridine, Hppy = 2-phenylpyridine) through an ion-exchange process to prepare the $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+@ \text{NENU-524}$ composite (Scheme 1). Iridium^{III} complexes are increasingly being used as fluorescent materials as a result of their diverse emission and high efficiency.¹³ The $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+@ \text{NENU-524}$ ($[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ 3.86 wt%) composite emitted a pure white light with Commission International de l'Eclairage (CIE) coordinates of (0.300, 0.336) and a quantum yield of up to 15.2%. We used the as-synthesized $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+@ \text{NENU-524}$ composite to create white light-emitting diodes (WLEDs) that emitted a bright white light in air for up to one month.

Results and discussion

The compound **NENU-524** crystallizes in the hexagonal $P6_3/m$ space group based on single-crystal X-ray diffraction (XRD) analysis. The asymmetrical unit of **NENU-524** includes two types of Zn ions: one deprotonated btca^{2-} linker and one $2\text{-NH}_2\text{-bdc}^{2-}$ ligand. Zn1 exhibits six coordination with three carboxylate O atoms from three $2\text{-NH}_2\text{-bdc}^{2-}$ ligands and three N atoms from three btca^{2-} linkers in an octahedral geometry. Zn2 shows a tetrahedrally coordinated geometry through two N atoms from two btca^{2-} ligands and two carboxylate O atoms from one btca^{2-} ligand and one $2\text{-NH}_2\text{-bdc}^{2-}$ ligand (Fig. S1, ESI†). All the bond lengths of the Zn–N and Zn–O bonds are in

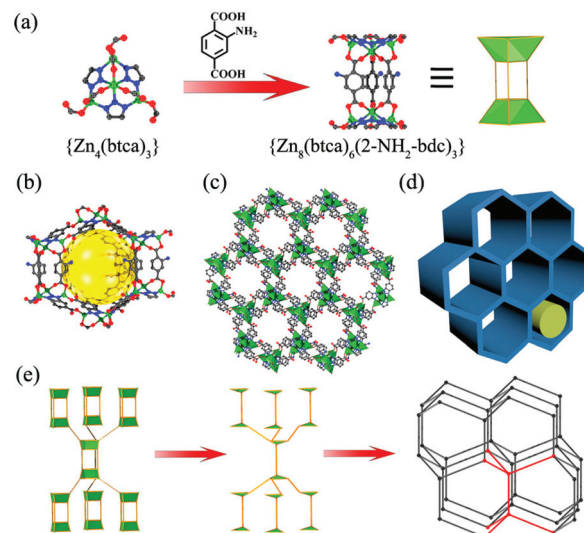


Fig. 1 Structure of **NENU-524**: (a) trigonal prismatic unit; (b) microporous cage; (c, d) 3D representation of the open framework viewed along the *c*-axis; and (e) the lon topology of **NENU-524**.

the normal range.¹⁴ One Zn1 and three Zn2 are connected through three btca^{2-} fragments to give one tetranuclear Zn cluster $\{\text{Zn}_4(\text{btca})_3\}$; three $2\text{-NH}_2\text{-bdc}^{2-}$ ligands bridge two $\{\text{Zn}_4(\text{btca})_3\}$ clusters to form a trigonal prismatic building unit $\{\text{Zn}_8(\text{btca})_6(2\text{-NH}_2\text{-bdc})_3\}$ ¹⁵ (Fig. 1a). The most interesting feature of the structure is the trigonal prismatic unit $\{\text{Zn}_8(\text{btca})_6(2\text{-NH}_2\text{-bdc})_3\}$, which can be regarded as a double secondary building unit (SBU) with an unusual triply bound triangular frustum geometry. **NENU-524** also has a microporous cage formed by two $\{\text{Zn}_4(\text{btca})_3\}$ clusters and three $\{\text{Zn}_8(\text{btca})_6(2\text{-NH}_2\text{-bdc})_3\}$ units (Fig. 1b). The $\{\text{Zn}_8(\text{btca})_6(2\text{-NH}_2\text{-bdc})_3\}$ double SBUs propagate through btca^{2-} fragments to make a 3D non-interpenetrated anionic framework (Fig. 1c, d and S2 ESI†). There are 1D open hexagonal channels of *ca.* $13.18 \times 13.18 \text{ \AA}^2$ parallel to the *c*-axis and *ca.* $12.27 \times 14.63 \text{ \AA}^2$ along the *b*-axis (Fig. S3 and S4†). The channels and cavities are occupied by the DMF solvent and $[(\text{CH}_3)_2\text{NH}_2]^+$ cations originated from the decarbonylation of DMF. Calculated results from PLATON software¹⁶ showed that the effective porosity of **NENU-524** was 74.6% (7893 \AA^3 of the total 10587 \AA^3) on removal of the guest molecules.

From the viewpoint of topology, if each tetranuclear $\{\text{Zn}_4(\text{btca})_3\}$ SBU serves as a four-connected node (Fig. 1e), then the **NENU-524** framework can be described as a 3D network with a rare lonsdaleite (**lon**) topology. However, each double SBU $\{\text{Zn}_8(\text{btca})_6(2\text{-NH}_2\text{-bdc})_3\}$, as a six-connected node, was further linked by btca^{2-} fragments to yield an **acs** net (Fig. S5†). To some extent, the connection of the $\{\text{Zn}_4(\text{btca})_3\}$ units and the H_2btca ligands resulted in a 2D layer and the adjacent layers were further jointed by the $2\text{-NH}_2\text{-bdc}^{2-}$ pillars to give a 3D open pillared layer network (Fig. S4†).

The purity of the fresh **NENU-524** phase was confirmed by matching the simulated powder XRD pattern with that of the as-synthesized **NENU-524** sample. The as-synthesized

NENU-524 sample was also exposed to air for one month or placed in water for 12 h; the **NENU-524** framework remained intact (Fig. S6†), showing the composite's superb stability in air. The calculated high porosity inspired us to carry out the N_2 sorption test. The as-synthesized **NENU-524** was activated according to the method reported in the ESI.† The N_2 sorption of the activated **NENU-524** at 77 K showed a typical type I behaviour (Fig. S13†). The N_2 adsorption test for the activated **NENU-524** gave BET and Langmuir surface areas of 1635.6 and 2476.3 $m^2 g^{-1}$, respectively. The pore volume of the sample was 0.984 $cm^3 g^{-1}$. The porosity distribution showed a main peak in the range *ca.* 10–15 Å, which agrees with the result of the crystal structure analyses (Fig. S13†).

Similar to anionic MOFs,^{17,18} the endogenous $[(CH_3)_2NH_2]^+$ cations easily underwent ion exchange with exogenous cations. We therefore used **NENU-524** in cation-exchange experiments with transition metals. Fresh **NENU-524** samples were immersed in solutions of cadmium nitrate, copper nitrate, cobalt nitrate and nickel nitrate in DMF. The colour of the samples changed from light yellow to teal (Cu^{2+}), red (Co^{2+}), and reseda green (Ni^{2+}) (Fig. S9, ESI†). No colour change was observed for Cd^{2+} . The retention of the structural integrity of **NENU-524** before and after the ion-exchange experiments was verified by the powder XRD and FTIR patterns (Fig. S10 and S11†). After the cation-exchange experiments, the samples were analysed by inductively coupled plasma atomic emission spectrometry (Table S2†). About 0.35 Cd^{II} , 0.59 Cu^{II} , 0.48 Co^{II} and 0.44 Ni^{II} were enclosed within the MOF cavities per formula unit.

We studied the luminescent properties of **NENU-524**. On excitation at 370 nm at room temperature, crystals of **NENU-524** in the solid state showed a blue emission maximum at 444 nm with the emission mainly based on the 2- NH_2 -H₂bdc ligand (Fig. S14 and S15†). The blue emission had CIE coordinates of (0.163, 0.052), close to the (0.14, 0.08) of the saturated blue emitter.¹⁹ The quantum yield of the as-synthesized **NENU-524** was 7.2% on excitation at 370 nm. These data suggest that **NENU-524** may have potential applications as an efficient emitter of blue light.

White light emission can be realized by combining blue emission with yellow emission. Therefore, in addition to the blue emission from **NENU-524**, a yellow-emitting component is also required. We chose the $[Ir(ppy)_2(bpy)]^+[PF_6]^-$ complex as an encapsulant as a result of its yellow emission and high quantum yield. $[Ir(ppy)_2(bpy)]^+$ has a relatively small size of *ca.* $10 \times 11 \text{ \AA}^2$, which is sufficient for entry into the pores of the MOF *via* ion exchange. A DMF solution of $10^{-4} \text{ mol L}^{-1}$ $[Ir(ppy)_2(bpy)][PF_6]$ showed a strong yellow emission about at 580 nm under excitation at 370 nm (Fig. S16†). We tried to obtain a white light emitter by adjusting the amount of $[Ir(ppy)_2(bpy)]^+$ encapsulated (Fig. 2).

In an initial attempt, **NENU-524** was soaked in a $10^{-4} \text{ mol L}^{-1}$ solution of $[Ir(ppy)_2(bpy)]^+$ in DMF for 10 days. The successful exchange of $[(CH_3)_2NH_2]^+$ by $[Ir(ppy)_2(bpy)]^+$ cations was accompanied by a clear change in colour (Fig. S18†). Inductively coupled plasma atomic emission spectrometry showed that

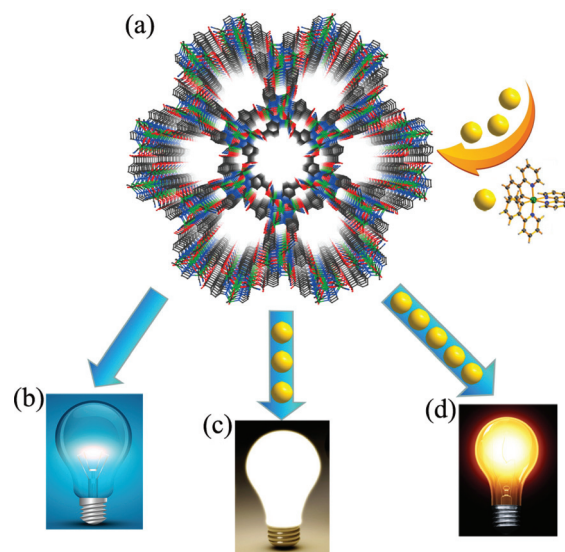


Fig. 2 Schematic illustration of the encapsulation of $[Ir(ppy)_2(bpy)]^+$ into **NENU-524**. (a) Ball and stick representation of the 3D network of **NENU-524**. (b) Emission of blue light by **NENU-524**. (c) $[Ir(ppy)_2(bpy)]^+@NENU-524$ ($[Ir(ppy)_2(bpy)]^+$ 3.86 wt%) emits a bright white light. (d) $[Ir(ppy)_2(bpy)]^+@NENU-524$ ($[Ir(ppy)_2(bpy)]^+$ 7.33 wt%) emits yellow light on excitation with a standard laboratory 365 nm UV lamp.

the mass fraction of the encapsulated $[Ir(ppy)_2(bpy)]^+$ was *ca.* 7.33 wt% with respect to Zn (Table S3†). The cavities became smaller when occupied by the $[Ir(ppy)_2(bpy)]^+$ cations as the ion-exchange process progressed. The amount of N_2 adsorbed by the activated $[Ir(ppy)_2(bpy)]^+@NENU-524$ sample clearly decreased compared with **NENU-524** and the pore width distribution disappeared, evidence that $[Ir(ppy)_2(bpy)]^+$ had been encapsulated in the cavities of **NENU-524** (Fig. S13†). The powder XRD pattern for $[Ir(ppy)_2(bpy)]^+@NENU-524$ was almost identical to the parent **NENU-524**, indicating that the crystal structure had not been destroyed during the ion-exchange process. The $[Ir(ppy)_2(bpy)]^+@NENU-524$ samples remained stable after exposure to air for one month (Fig. S12†). No obvious emission band was observed from the emission spectrum of the filtrate after the immersion of $[Ir(ppy)_2(bpy)]^+@NENU-524$ (10 mg) in 10 mL of DMF for one day (Fig. S16†). These results demonstrated that the strong electrostatic forces between cationic $[Ir(ppy)_2(bpy)]^+$ and the anionic framework could effectively limit the release of the $[Ir(ppy)_2(bpy)]^+$ cations from the cavities of the MOF.

As expected, $[Ir(ppy)_2(bpy)]^+@NENU-524$ simultaneously showed two emission peaks around 445 and 570 nm in the solid luminescent spectrum. The emission at 445 nm derived from **NENU-524**, whereas the band at 570 nm may be attributed to $[Ir(ppy)_2(bpy)]^+$ (Fig. 3a, pink curve). The emission spectrum also further indicated that the $[Ir(ppy)_2(bpy)]^+$ had been successfully encapsulated in the channels of **NENU-524**. The corresponding CIE coordinates were (0.336, 0.416) for the sample with a high quantum yield of 20.2% (Table S3†). Its yellow emission could be clearly seen (Fig. S18†) under a

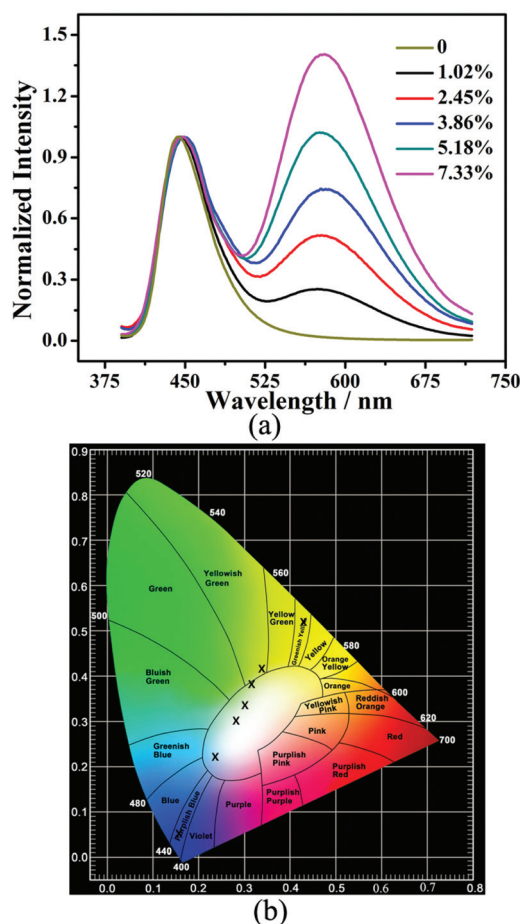


Fig. 3 (a) Solid emission spectra of **NENU-524** and $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+@ \text{NENU-524}$ with different concentrations of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ at room temperature. (b) CIE coordinates of the samples and $[\text{Ir}(\text{ppy})_2(\text{bpy})]\text{PF}_6$ complex in DMF solvent (10^{-4} mol L^{-1}). All measurements were conducted at $\lambda_{\text{ex}} = 370$ nm.

365 nm UV lamp. For comparison, we also studied the fluorescence properties of a thoroughly ground mixture of **NENU-524** and $[\text{Ir}(\text{ppy})_2(\text{bpy})]\text{PF}_6$ (7.33 wt%) under the same conditions. The finely ground mixture did not show an obvious emission band for $[\text{Ir}(\text{ppy})_2(\text{bpy})]\text{PF}_6$ (Fig. S17†). These results indicated that the $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ cations were enclosed in the channels of **NENU-524**, which effectively prevented their oscillation and aggregation and restrained non-radiative energy transfer.

To further research the white light emission, we needed to balance the intensities of the emission from $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ and **NENU-524**. White light could be obtained by controlling the amounts of encapsulated $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$. A series of samples with different amounts of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ was conveniently produced by varying the immersion time. We measured the solid emission spectra of the samples (Fig. 3a). The spectra show that the intensities of the 570 nm emission band increased with increasing amounts of encapsulated $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$, whereas the emission intensities of the 445 nm peak remained almost constant. The emission colours

of the series of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+@ \text{NENU-524}$ samples varied from blue to yellow as the amount of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ cation was varied. We obtained the optimum white light with CIE coordinates of (0.300, 0.336) (Fig. 3b) when the amount of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ cation was 3.86 wt%. These coordinate are close to the CIE (0.33, 0.33) of a perfect white illuminant. The quantum yield was 15.2%, which is fairly high compared with previously reported data for white light MOFs (Table S4†). White light emission under radiation by a 365 nm UV lamp is shown in Fig. S18.† $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+@ \text{NENU-524}$ had a high quantum yield because when the $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ cations were enclosed in the MOF, oscillation and aggregation were effectively prevented.^{5b,c}

The fluorescence emission spectra of the $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+@ \text{NENU-524}$ composites showed a simple dual emission from **NENU-524** and $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ and therefore we speculated that there was no energy transfer between $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ and **NENU-524**. The intensity of the second emission of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ at 570 nm increased monotonically as the amount of the ion increased and was independent of the first peak from **NENU-524** (Fig. 3a). The absorption spectra and the photoluminescent emission spectra of these two independent species were almost non-overlapping, further confirming that there was no energy transfer between **NENU-524** and the Ir complex (Fig. S19 and S20†). We also measured the lifetimes of **NENU-524** and $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+@ \text{NENU-524}$. The lifetime of the solid **NENU-524** sample was 1.02 ns and the lifetimes of 3.86 and 7.33 wt% of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ samples of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+@ \text{NENU-524}$ were 0.86 and 0.91 ns, respectively. The encapsulation of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ into **NENU-524** had almost no effect on the lifetime, verifying that there was hardly any energy transfer between **NENU-524** and $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$.

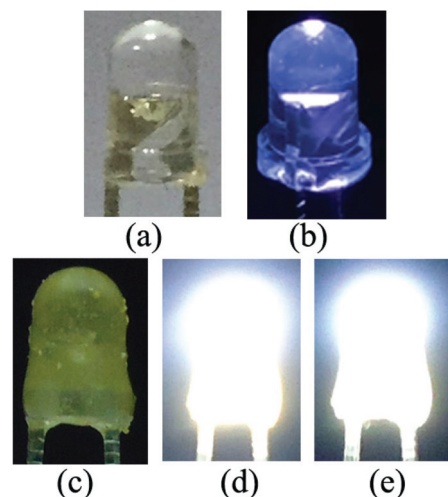


Fig. 4 (a) Photograph of a commercially available 3 mm UV LED. (b) Photograph of the same LED emitting a blue tinge when turned on. (c) The WLED assembled using 3.86 wt% $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+@ \text{NENU-524}$. (d) The coated WLED emitted a bright white light when turned on. (e) The assembled WLED emitted white light when turned on continuously for one month.

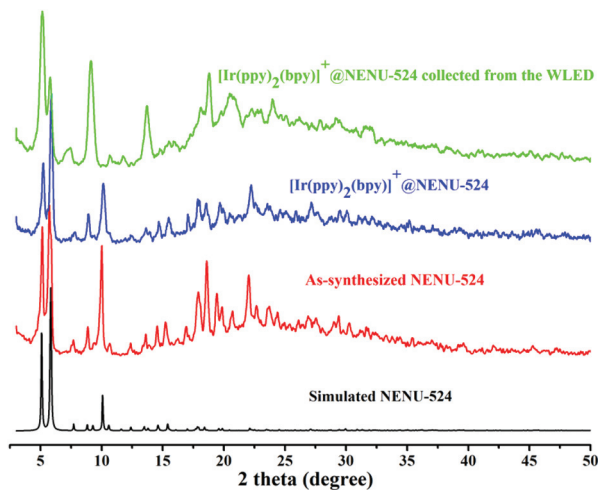


Fig. 5 Powder XRD pattern of NENU-524: black, simulated; red, as-synthesized; blue, 7.33 wt% $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+@ \text{NENU-524}$; and green, $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+@ \text{NENU-524}$ collected from the assembled WLED after one month of continuous use.

To further investigate the potential of this iridium complex incorporated into a MOF for lighting applications, a WLED device was fabricated by simply coating a thin layer of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+@ \text{NENU-524}$ onto the surface of a commercially available UV (365 nm) LED.^{5b,c,20} The fabricated WLED emitted a bright white flash at 3.8 V (Fig. 4d). The resultant WLED continued to emit a bright white light when continuously turned on for a month in air at room temperature (Fig. 4e). After one month of continuous use, we collected the $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+@ \text{NENU-524}$ sample from the assembled WLED and confirmed its stability by powder XRD (Fig. 5). The collected sample had a quantum yield of 14.9%, almost the same as that of the as-synthesized $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+@ \text{NENU-524}$ white light phosphor. On the basis of these results, the white phosphor $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+@ \text{NENU-524}$ has the potential to be used in practical lighting devices as a result of its good colour quality and high stability.

Conclusions

We successfully prepared a novel blue-emitting anionic MOF. NENU-524 has a **lon** net topology based on a novel double SBU trigonal prismatic unit. NENU-524 showed excellent stability in air. The encapsulation of yellow-emitting $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ into the anionic MOF through an ion-exchange process not only led to tunable emission, but, more importantly, generated a bright white light. The white phosphor emitted a pure white light with CIE coordinates of (0.300, 0.336) and a high quantum yield of up to 15.2%. The WLED assembled using the $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+@ \text{NENU-524}$ white phosphor emitted a bright white light and was stable for at least one month. This novel approach can be easily implemented with other fluorescent MOFs for white light emission and may promote the development of white light materials.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 21622104, 21371099, 21401021 and 21471080), the NSF of Jiangsu Province of China (No. BK20130043 and BK20141445), the Priority Academic Program Development of Jiangsu Higher Education Institutions and the Foundation of Jiangsu Collaborative Innovation Center of Biomedical Functional Materials.

Notes and references

- (a) L. D. Carlos, R. A. S. Ferreira, V. de Zea Bermudez, B. Julián-López and P. Escribano, *Chem. Soc. Rev.*, 2011, **40**, 536–549; (b) J. Kido, M. Kimura and K. Nagai, *Science*, 1995, **267**, 1332–1334; (c) J. He, M. Zeller, A. D. Hunter and Z. Xu, *J. Am. Chem. Soc.*, 2012, **134**, 1553–1559; (d) T. Fleetham, J. Ecton, Z. Wang, N. Bakken and J. Li, *Adv. Mater.*, 2013, **25**, 2573–2576; (e) E. R. Dohner, A. Jaffe, L. R. Bradshaw and H. I. Karunadasa, *J. Am. Chem. Soc.*, 2014, **136**, 13154–13157.
- (a) Z. Zhao, J. W. Y. Lam and B. Z. Tang, *Curr. Org. Chem.*, 2010, **14**, 2109; (b) Y. Ner, J. G. Grote, J. A. Stuart and G. A. Stozing, *Angew. Chem., Int. Ed.*, 2009, **48**, 5134–5138; (c) G. He, D. Guo, C. He, X. Zhang, X. Zhao and C. Duan, *Angew. Chem., Int. Ed.*, 2009, **48**, 6132–6135; (d) K. C. Tang, M. J. Chang, T. Y. Lin, H. A. Pan, T. C. Fang, K. Y. Chen, W. Y. Hung, Y. H. Hsu and P. T. Chou, *J. Am. Chem. Soc.*, 2011, **133**, 17738–17745.
- (a) M. C. Gather, A. Köhnen and K. Meerholz, *Adv. Mater.*, 2011, **23**, 233–248; (b) G. M. Farinola and R. Ragni, *Chem. Soc. Rev.*, 2011, **40**, 3467–3482.
- (a) S. Diring, K. Sumida and S. Kitagawa, *Chem. Soc. Rev.*, 2014, **43**, 5700–5734; (b) K. Kim, *Nat. Chem.*, 2009, **1**, 603–604; (c) X. T. Rao, T. Song, J. K. Gao, Y. J. Cui, Y. Yang, C. D. Wu, B. L. Chen and G. D. Qian, *J. Am. Chem. Soc.*, 2013, **135**, 15559–15564.
- (a) Z. Dou, J. Yu, Y. Cui, Y. Yang, Z. Wang, D. Yang and G. Qian, *J. Am. Chem. Soc.*, 2014, **136**, 5527–5530; (b) W. Xie, W. W. He, D. Y. Du, S. L. Li, J. S. Qin, Z. M. Su, C. Y. Sun and Y. Q. Lan, *Chem. Commun.*, 2016, **52**, 3288–3291; (c) C. Y. Sun, X. L. Wang, X. Zhang, C. Qin, P. Li, Z. M. Su and J. Li, *Nat. Commun.*, 2013, **4**, 2717–2724; (d) H. He, E. Ma, Y. Cui, J. Yu, Y. Yang, T. Song, C. Wu, X. Chen, B. Chen and G. Qian, *Nat. Commun.*, 2016, **7**, 11087–11094.
- (a) Y. J. Cui, W. F. Zou, R. J. Song, J. C. Yu, W. Q. Zhang, Y. Yang and G. D. Qian, *Chem. Commun.*, 2014, **50**, 719–721; (b) J. Yu, Y. Cui, C. D. Wu, Y. Yang, B. Chen and G. Qian, *J. Am. Chem. Soc.*, 2015, **137**, 4026–4029.
- (a) R. Chakrabarty, P. S. Mukherjee and P. J. Stang, *Chem. Rev.*, 2011, **111**, 6810–6918; (b) Y. J. Cui, Y. F. Yue, G. D. Qian and B. L. Chen, *Chem. Rev.*, 2012, **112**, 1126–1162; (c) Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815–5840.

- 8 (a) D. Zhao, Y. Cui, Y. Yang and G. Qian, *CrystEngComm*, 2016, **18**, 3746–3759; (b) H. Xu, C.-S. Cao, X.-M. Kang and B. Zhao, *Dalton Trans.*, 2016, **45**, 18003–18017; (c) D. E. Williams, E. A. Dolgoplova, P. J. Pellechia, A. Palukoshka, T. J. Wilson, R. Tan, J. M. Maier, A. B. Greytak, M. D. Smith, J. A. Krause and N. B. Shustova, *J. Am. Chem. Soc.*, 2015, **137**, 2223–2226; (d) M.-S. Wang and G.-C. Guo, *Chem. Commun.*, 2016, **52**, 13194–13204.
- 9 (a) Y. Cui, B. Chen and G. Qian, *Coord. Chem. Rev.*, 2014, **273**, 76–86; (b) M. Zhu, Z. M. Hao, X. Z. Song, X. Meng, S. N. Zhao, S. Y. Song and H. J. Zhang, *Chem. Commun.*, 2014, **50**, 1912–1914; (c) Y. Liu, M. Pan, Q. Y. Yang, L. Fu, K. Li, S. C. Wei and C. Y. Su, *Chem. Mater.*, 2012, **24**, 1954–1960; (d) Y. Lu and B. Yan, *Chem. Commun.*, 2014, **50**, 15443–15446.
- 10 (a) J. He, J. Huang, Y. He, P. Cao, M. Zeller, A. D. Hunter and Z. Xu, *Chem. – Eur. J.*, 2016, **22**, 1597–1601; (b) B.-B. Du, Y.-X. Zhu, M. Pan, M.-Q. Yue, Y.-J. Hou, K. Wu, L.-Y. Zhang, L. Chen, S.-Y. Yin, Y.-N. Fan and C.-Y. Su, *Chem. Commun.*, 2015, **51**, 12533–12536; (c) W. Xie, S. R. Zhang, D. Y. Du, J. S. Qin, S. J. Bao, J. Li, Z. M. Su, W. W. He, Q. Fu and Y. Q. Lan, *Inorg. Chem.*, 2015, **54**, 3290–3296; (d) Y. Wei, Q. Li, R. Sa and K. Wu, *Chem. Commun.*, 2014, **50**, 1820–1823.
- 11 (a) S. V. Eliseeva and J.-C. G. Bünzli, *Chem. Soc. Rev.*, 2010, **39**, 189–227; (b) J.-C. G. Bünzli, *Chem. Rev.*, 2010, **110**, 2729–2755; (c) D. F. Sava, L. E. Rohwer, M. A. Rodriguez and T. M. Nenoff, *J. Am. Chem. Soc.*, 2012, **134**, 3983–3986; (d) X. T. Rao, Q. Huang, X. L. Yang, Y. J. Cui, Y. Yang, G. D. Qian, B. L. Chen and G. D. Qian, *J. Mater. Chem.*, 2012, **22**, 3210–3214.
- 12 Y. J. Cui, T. Song, J. C. Yu, Y. Yang, Z. Y. Wang and G. D. Qian, *Adv. Funct. Mater.*, 2015, **25**, 4796–4802.
- 13 R. D. Costa, E. Ortí, H. J. Bolink, F. Monti, G. Accorsi and N. Armaroli, *Angew. Chem., Int. Ed.*, 2012, **51**, 8178–8211.
- 14 (a) Y. Q. Lan, H. L. Jiang, S. L. Li and Q. Xu, *Adv. Mater.*, 2011, **23**, 5015–5020; (b) J. S. Qin, D. Y. Du, W. L. Li, J. P. Zhang, S. L. Li, Z. M. Su, X. L. Wang, Q. Xu, K. Z. Shao and Y. Q. Lan, *Chem. Sci.*, 2012, **3**, 2114–2118.
- 15 (a) J. S. Qin, D. Y. Du, M. Li, X. Z. Lian, L. Z. Lian, L. Z. Dong, M. Bosch, Z. M. Su, Q. Zhang, S. L. Li, Y. Q. Lan, S. Yuan and H. C. Zhou, *J. Am. Chem. Soc.*, 2016, **138**, 5299–5307; (b) Y. W. Li, L. F. Wang, K. H. He, Q. Chen and X. H. Bu, *Dalton Trans.*, 2011, **40**, 10319–10321.
- 16 (a) P. van der Sluis and A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 194–201; (b) A. L. Spek, *PLATON, A multipurpose crystallographic tool*, Utrecht University, The Netherlands, 2001.
- 17 (a) J. Yu, Y. Cui, C. Wu, Y. Yang, Z. Wang, M. O'Keeffe, B. Chen and G. Qian, *Angew. Chem., Int. Ed.*, 2012, **51**, 10542–10545; (b) J. Yu, Y. Cui, H. Xu, Y. Yang, Z. Wang, B. Chen and G. Qian, *Nat. Commun.*, 2013, **4**, 2719–2725.
- 18 (a) J. An, S. J. Geib and N. L. Rosi, *J. Am. Chem. Soc.*, 2009, **131**, 8376–8377; (b) J. An, C. M. Shade, D. A. Chengelis-Czegán, S. Petoud and N. L. Rosi, *J. Am. Chem. Soc.*, 2011, **133**, 1220–1223; (c) D. T. Genna, A. G. Wong-Foy, A. J. Matzger and M. S. Sanford, *J. Am. Chem. Soc.*, 2013, **135**, 10586–10589.
- 19 L. Wang, Y. Jiang, J. Luo, Y. Zhou, J. Zhou, J. Wang, J. Pei and Y. Cao, *Adv. Mater.*, 2009, **21**, 4854–4858.
- 20 M. Roushan, X. Zhang and J. Li, *Angew. Chem., Int. Ed.*, 2012, **51**, 436–439.