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Journal Name

COMMUNICATION

Lanthanide organic-inorganic hybrids based on functionalized metal-organic frameworks (MOFs) for near-UV white LED

Ye Lu and Bing Yan*
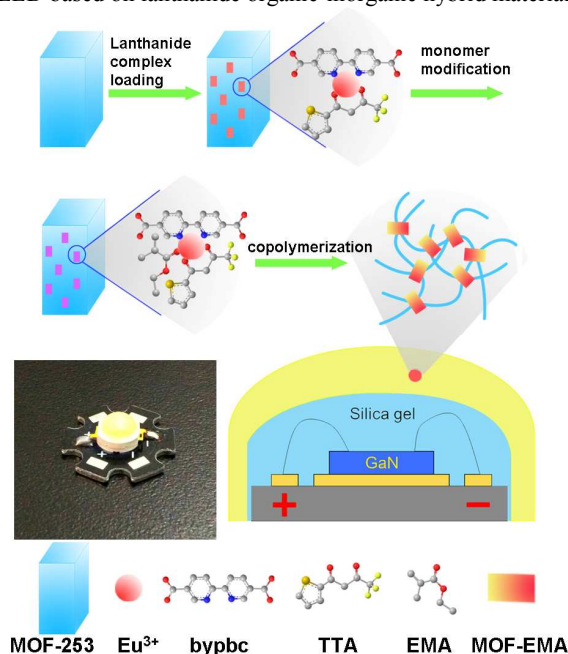
A novel near-UV white LED based on lanthanide organic-inorganic hybrid material is realized through postsynthetic modified MOFs and MOF-based polymer. The hybrids materials have high quantum yield and satisfactory luminescent stability; the assembled white LED has tuneable correlated color temperature and high color rendering index.

Current white LED for solid-state lighting is based on blue InGaN substrate that excites the yellow-emitting phosphor.[1] The combination of blue and yellow light produces a cold white light that can be made warm by combining with a red-emitting component, for example, Eu^{3+} ion.[2] In recent years, to further improve color rendering index (CRI) and reduce the influence of blue light (450 nm) from chip, another new approach have gained extensive attention, which use a near-UV LED chip (produce light 395 nm) and down-converts phosphor to realize white light.[3] But, the phosphor applied in near-UV white LED almost concentrates in traditional solid inorganic material.[4] Meanwhile, the exploration of using metal-organic framework (MOFs) as phosphor have became a attractive highlight, especially for white-light-emitting MOFs.[5] However, the reported white-light-emitting MOFs is not very suitable for common LED chip because the excitation wavelength of reported white-light-emitting MOFs is almost located in the ultraviolet area, while the wavelengths of common LED chip are 395 nm and 450 nm. Moreover, the UV LED chip is more expensive than near-UV LED chip, and the UV would accelerate plastic component aging.[5, 6]

Over the past few decades, lanthanide organic-inorganic hybrid materials have been achieved considerable attention, which is constructed by embedding molecular lanthanide complex to an inorganic host matrix, or alternatively, embedding an inorganic lanthanide compound to organic polymer matrix.[7] The early work of the this field focus on introducing lanthanide complexes to ordered porous silica material.[8] Recently, a particular interest is using MOFs as a host matrix to carry lanthanide complex because MOFs have richer luminescent property.[9] But much deeper problem, such as the interaction between different luminescent mechanism, the energy

transition from support to luminescent center and so on, has not been comprehensively and intensively discussed yet.[9d, 9e, 10] Lanthanide complex-based polymer is another important part of lanthanide organic-inorganic hybrid material.[11] Recently, a new progress of this field is to build lanthanide complex-based hybrid materials by polymerization of liquid monomer containing surface modified zeolite L (whose channels have incorporated lanthanide complexes).[12] This strategy successfully combines the superiority of porous materials and polymer materials. For MOFs, there is only few preliminary attempt of introducing MOFs to organic polymer, moreover, the synthesis methods almost belong to simple physically doping.[13] This intrigues our interest in combine this strategy and the inherent advantage of MOFs (rich luminescent property) to realize white LED based on lanthanide organic-inorganic hybrid material.

Figure 1. Procedure for obtaining MOF-PEMA LED, the inset is the LED based on MOF-PEMA.

Herein, we present a new method for near-UV white LED based on lanthanide organic-inorganic hybrid materials (Figure 1). Lanthanide complex are firstly encapsulated to MOFs (MOF-253) by postsynthetic method (PSM) (Figure S1), and then the modified MOF-253 is introduced into organic polymer by suitable monomer functionalization to achieve polymer hybrid materials based on MOFs. Finally, the MOF-based polymer is assembled on near-UV GaN chip to realize near-UV white LED. Moreover, an effective energy transfer from MOFs to the guest is discovered and proved.

MOF-253 with an uncoordinated bipyridyl group (2,2'- bipyridyl) is an ideal platform to carry lanthanide complex because bipyridyl could chelate and sensitize lanthanide ion simultaneously.[9a, 9b, 9c] Moreover, bipyridyl is an ubiquitous role in lanthanides coordination chemistry.[7] Meantime, the nanoscale of the size endows MOF-253 with inherent advantage in practical application. We have reported the application of nanosized MOF-253 in thin film assembling, pH sensing and intercellular sensing.[9a, 9b, 14]

Eu^{3+} ion is introduced to MOF-253 by PSM, the amount of Eu^{3+} ion is 1 and 8 % (molar ratio). The products are denoted as MOF-253-EuX (X = 1 and 8). MOF-253-Eu1 is further modified with TTA (TTA= 2-thenoyltrifluoroacetone) and denoted as MOF-253-Eu1-TTA. (The details see ESI) The modified MOF-253s are confirmed by PXRD (Figure S1), elemental analysis (see ESI), and nitrogen adsorption/desorption isotherms (Figure S2), respectively. After PSM, the framework is still integrated according to PXRD. The FT-IR spectroscopy also can improve this (Figure S3). Bands at 1600 and 1420 cm^{-1} are observed in the FT-IR spectra of MOF-253, MOF-253-Eu8 and MOF-253-Eu1-TTA, which can be ascribed to the absorption of carboxylic group and bipyridyl group, respectively. From X-ray photoelectron spectroscopy (XPS) of MOF-253-Eu8 (Figure S4), the binding energy of Eu 4d peak of MOF-253-Eu8 (124 eV) is shifted remarkably toward lower binding energy, compared with Eu 4d peak of Eu_2O_3 (128 eV). Such a big shift may be attributed to the strong coordination interaction between bipyridyl and Eu^{3+} ion. From the transmission electron microscopy (TEM) image of MOF-253 (Figure S5), MOF-253 is a rectangle, whose length and width is about 120 and 30 nm, respectively.

The excitation spectrum of MOF-253 is obtained by monitoring the emission at 550 nm, which is dominated by a broad band centered at about 380-400 nm (Figure 2); the emission spectra of MOF-253 present broad bands centered at about 550 nm under excitation at 395 nm. The point of emission spectra in CIE chromaticity diagram is in the yellow color area of (X = 0.33, Y = 0.47) (Figure S7), so white light can be observed under excitation by bluish violet light (λ_{ex} = 395 nm) because bluish violet light and yellow light could be integrated to realize white light (Figure S8). This method of obtaining white light is similar to commercial white LED based on yellow-emitting YAG: Ce^{3+} phosphor. The correlated color temperature (CCT) of MOF-253 is 5627, and the quantum yield (QY) is 33% (λ_{ex} = 395 nm), which is outstanding compared with reported white-light-emitting MOFs.[5a, 5c]
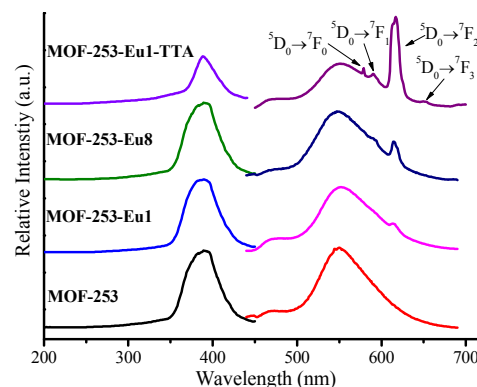
The luminescent spectra of MOF-253-Eu1, MOF-253-Eu8 and MOF-253-Eu1-TTA are shown in Figure 2 (λ_{ex}=395 nm, λ_{em}= 550 nm). The intensity of narrow-band at 614 nm is enhanced with the increase of Eu^{3+} ion or introduction TTA. The excitation band of MOF-253-Eu1-TTA is sharper than MOF-253-Eu1, which is due to the enhancement of Eu^{3+} characteristic luminescence. The CCT of

MOF-253-Eu1-TTA is 3189 (X = 0.43, Y = 0.42), and the QY of MOF-253-Eu1-TTA is 36% (λ_{ex} = 395 nm).

Eu^{3+} ion can also be used as luminescence center to be monitored. The emission spectra of MOF-253-Eu1 under excitation 330 nm (Figure S9) exhibit the Eu^{3+} characteristic transitions at 579, 591, 614, 650 and 692 nm, which are ascribed to the $^5D_0 \rightarrow {}^7F_J$ (J = 0-4) transitions, respectively; the excitation spectrum of MOF-253-Eu1 (λ_{em} = 614 nm) presents typical broad bands which is due to energy transfer from organic ligand, so called "antenna affect".[7a, 15] This can also prove the coordination interaction between bipyridyl and Eu^{3+} ion. The luminescent spectra of MOF-253-Eu1-TTA (λ_{em} = 614 nm, λ_{ex} = 375 nm) (Figure S10) also display the Eu^{3+} characteristic transitions at 579, 590, 614, 649 and 690 nm, which are ascribed to the $^5D_0 \rightarrow {}^7F_J$ (J = 0-4) transitions.

The emission spectra of MOF-253, MOF-253-Eu1, MOF-253-Eu8 and MOF-253-Eu1-TTA (λ_{ex} = 395 nm) in different temperature (100-500K) are shown in Figure S11. Generally, luminescence intensity would decrease with the increase of temperature because molecular thermal vibration is against luminescence. For MOF-253 (Figure S11a), the luminescent intensity in 450 K is about 75 % of that in 300 K. Though this is not excellent in comparison with traditional solid phosphor, it still fills within the promising range. For MOF-253-Eu1-TTA (Figure S11d), the luminescent spectrum is composed of a broad band from MOF-253 (550 nm) and a narrow-band from Eu^{3+} ion (614 nm). The luminescent intensity at 550 nm shows the similar changing rule with MOF-253, MOF-253-Eu1 and MOF-253-Eu8. But the luminescent intensity of narrow-band at 614 nm display opposite tendency in the low temperature. In the range of 100-200 K, the luminescent intensity of the narrow-band at 614 nm is increased with the raise of temperature (Figure 3a).

The abnormal luminescent phenomena may be related to the energy transfer from the framework to Eu^{3+} ion. The corresponding intensity at 550 nm and 614 nm in 100-200 k is listed in Table S1. Comparing the data of MOF-253-Eu1 and MOF-253-Eu1-TTA, it can be found that the relative intensity of MOF-253-Eu1-TTA at 550 nm decreases significantly faster than MOF-253-Eu1 from 100 to 200 K while the relative intensity of MOF-253-Eu1-TTA at 614 nm is rising in the same temperature range. This maybe ascribe to the energy loss of MOFs and the energy achievement of Eu^{3+} ion at the same time. For MOF-253-Eu1-TTA, Eu^{3+} ions have two kinds of ligand, TTA and bipyridine. The triplet energy level of TTA is among of Eu^{3+} ion and bipyridyl. So, the energy may be transfer from MOF to TTA and then to Eu^{3+} ion.[7a]

Figure 2. Luminescent spectra of MOF-253, MOF-253-Eu1, MOF-253-Eu8 and MOF-253-Eu1-TTA, λ_{ex} = 395 nm, λ_{em} = 550 nm.
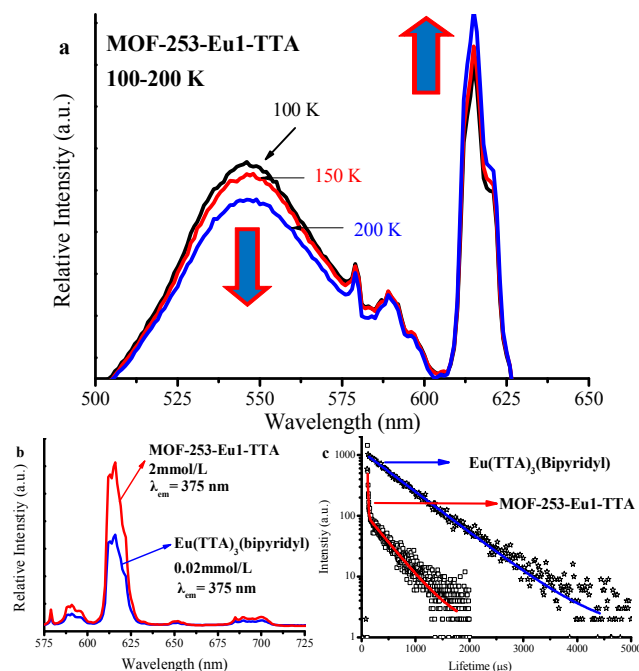
Figure 3. (a) Emission spectra (λ_{ex} = 395 nm) of the MOF-253-Eu1-TTA in different temperature (100-200K), (b) the emission spectra of the solution of MOF-253-Eu1-TTA (2 mmol/L) and Eu(TTA)$_3$(bipyridyl) (0.02 mmol/L) under excitation at 375 nm, (c) decay curve of MOF-253-Eu1-TTA (red) and Eu(TTA)$_3$(bipyridyl) (blue), λ_{ex} = 375 nm, λ_{em} = 614 nm.

To further prove this, Eu(TTA)$_3$(bipyridyl) is prepared and it is checked by elemental analysis and luminescent spectra (the details see ESI and Figure S10). The Eu^{3+} ion characteristic emission intensity of MOF-253-Eu1-TTA (2mmol/L in alcohol) is obviously stronger than that of Eu(TTA)$_3$(bipyridyl) (0.02mmol/L in alcohol) (Figure 3b), which the concentration of Eu^{3+} ion in the two kind of alcohol solution is the same (The details see ESI). Moreover, the $^5D_0$ lifetime of MOF-253-Eu1-TTA (395 μs) is shorter than Eu(TTA)$_3$(bipyridyl) (812 μs) in the ambient temperature (Figure 3c). In the two systems, Eu^{3+} ion all have four ligands, three TTA and one bipyridyl. All of the significant difference in lifetimes and Eu^{3+} ion characteristic emission intensity maybe attribute to the energy transfer from matrix to Eu^{3+} ion. And then, the energy transfer should be occurred not only in low temperature but also in ambient temperature. But the molecule vibration would deactivate the energy and decrease the luminescence of hybrids. Hence, only in low temperature, the deactivation effect from vibration of molecule is not strong enough so that the energy transfer process can be recorded at the luminescent spectra. The PXRD of MOF-253-Eu1-TTA after temperature experiment could prove the decrease of luminescent intensity is not from collapse of framework (Figure S12). Due to the energy transfer, MOF-253-Eu1-TTA could achieve satisfactory red luminescence under the low Eu^{3+} ion doping content (only 1 %, molar ratio). This also endows MOF-253-based hybrid material with inherent advantage in the application in near-UV white LED.[2]

The transparent MOF-253-based polymer hybrid materials are prepared according to the procedure outlined in Figure 1. Functionalization of MOF-253-Eu1-TTA with ethyl methacrylate (EMA) leads to MOF-253-Eu1-TTA-EMA (MOF-EMA). The transparent hybrid materials (MOF-PEMA) are finally prepared from the radical polymerization of the monomer EMA and MOF-EMA.

The method is similar to prepare the polymer materials based on zeolite L.[12] The amount of EMA is kept the same and additional MOF-EMA amounts equivalent to 3.5 and 10 % (weight ratio), denoted as MOF-PEMA-3.5 and MOF-PEMA-10. Comparison with the FT-IR spectroscopy of MOF-253-Eu1-TTA, the bands at 1420 cm^{-1} and 1600 cm^{-1} in the FT-IR spectra of MOF-PEMA-3.5 can prove the integrity of the framework (Figure S3). The absorption band of MOF-PEMA-3.5 at 1731 cm^{-1} is ascribe to the stretching vibration of C=O for polymerization.

The luminescent spectra of MOF-PEMA are shown in Figure S13. Under excitation at 395 nm, the emission spectra of MOF-PEMA-3.5 and MOF-PEMA-10 are similar to MOF-253-Eu1-TTA, which is constructed by a broad band from MOF-253 (550 nm) and a narrow-band from Eu^{3+} ion (614 nm). Moreover, the luminescent intensity of MOF-PEMA-10 is obviously stronger than MOF-PEMA-3.5 in THF solution with the same concentration. This could prove the integrity of framework during polymerization. Furthermore, this also indicates that the luminescence of PEMA is very weak so that the luminescence spectra and luminescent intensity of MOF-PEMA only depend on the added MOF-based hybrid materials and the added amount of MOF-based hybrid materials. Under excitation at 375 nm, Eu^{3+} ion characteristic emission can be achieved (Figure S14). After polymerization, the intensity ration of $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ alters from 7.9 (MOF-253-Eu1-TTA) to 3.7 (MOF-PEMA-3.5), which can be attributed to the coordination effect between carbonyl of EMA and Eu^{3+} ion. MOF-PEMA could be coated in glass to achieve the MOF-PEMA thin film (The details see ESI). From SEM images (Figure S15), the thin film surface is continuous and defect-free over a large area. MOF-PEMA-3.5 hybrid material has high transparency and could emit bright white light under excitation by 395 nm GaN chip (Figure 4).

MOF-PEMA could be further assembled on near-UV GaN chip to realize the near-UV white LED. (The details see ESI) The electroluminescent spectrum of MOF-PEMA-10 LED is shown in Figure5. The MOF-PEMA-10 white LED operated at 350 mA shows warm white light with CCT of 3742 K (X = 0.39, Y = 0.38) and a promising CRI (R_a) of 87.34 (Figure S16). The general CRI is designated by the symbol R_a, which is the average value of R_1 to R_8.[16] The numbers in parentheses indicate the Munsell color system.[17] MOF-PEMA-10 LED have higher R values than the commercial YAG: Ce^{3+} white LED (whose R_a is 78).[18] The white light from the MOF-PEMA LED could be adjusted by altering the content of MOF-EMA in the polymer. The LED assembled by MOF-PEMA-3.5 shows natural white light, the color coordinates is X = 0.33, Y = 0.34 and CCT is 5603 K. The electroluminescent spectrum of MOF-PEMA-3.5 LED is shown in Figure S17. Hence, the white light operated by MOF-PEMA LED could be changed from natural white to warm white.
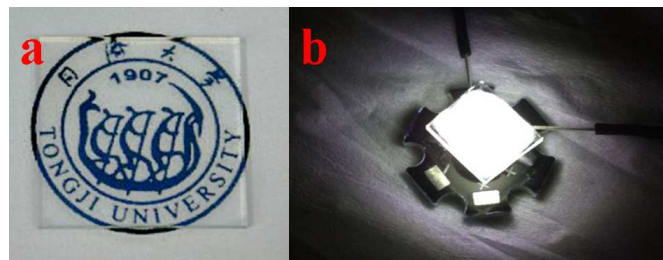
Figure 4. (a) The photograph of MOF-PEMA-3.5 hybrid materials and the bright white light from MOF-PEMA-3.5 hybrid materials under excitation by 395 nm GaN chip.
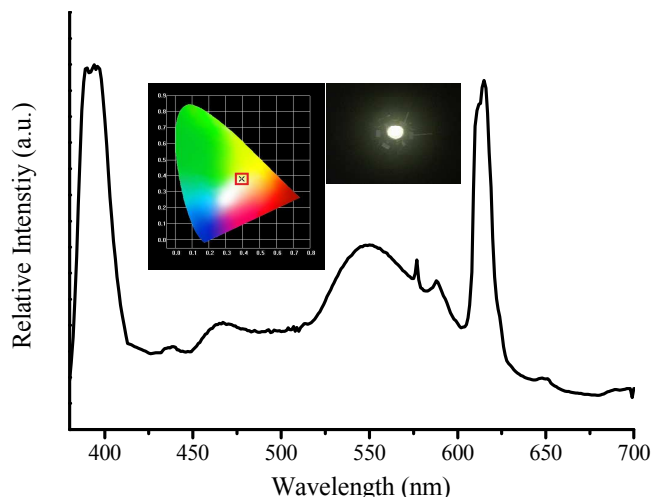
Figure 5. Electroluminescent spectrum of MOF-PEMA-10 LED, the inset is CIE plot, the photograph is the warm white light from MOF-PEMA-10 LED under 350 mA.

In summary, a new method for near-UV white LED based on lanthanide organic-inorganic hybrids materials is presented, which the modified MOF-253 by PSM is introduced to polymer by monomer functionalization to achieve the polymer hybrid materials based on MOFs. The highly transparent hybrid materials have high QY and satisfactory luminescent stability. And then, the MOF-based functionalization polymer is assembled on GaN chip to realize white LED with tunable CCT and high CRI. Moreover, the white light operated by MOF-PEMA LED could be adjusted from warm white to natural white. Furthermore, the effective energy transfer from matrix to Eu^{3+} ion is found and this kind of energy transfer could effectively heighten luminescence of fabricated lanthanide ion. Our investigation highlights the potential value of MOF as a novel platform for designing luminescent hybrid material with photoluminescence and electroluminescence.

Acknowledgements

Notes and references

Department of Chemistry, Tongji University, Shanghai 200092, P. R. China. Fax: (+86) 21-65982287; E-mail: byan@tongji.edu.cn

† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x/

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