SUPPLEMENTARY INFORMATION

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

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Experiment details

Chemicals. Chemicals were purchased from commercial sources. All solvents were analytical grade and without further purification. $Eu(NO_3)_3{\cdot}xH_2O$ were prepared by dissolving oxides (Eu_2O_3) in concentrated nitric acid (HNO_3). MOF-253 (Al(OH)(bpydc)) is synthesized according to the references. [S1]

Synthesis of MOF-253. MOF-253 was prepared from hydrothermal reaction of $AlCl_3{\cdot}6H_2O$ (151 mg, 0.625 mmol), 2,2'-bipyridine-5,5'-dicarboxylic acid (153 mg, 0.625 mmol) and 10 mL N,N'-dimethylformamide (DMF) at 120 °C for 24 hrs. The resulting white microcrystalline powder was then collected with by centrifugation and washed with DMF. The solid products were washed with methanol viasoxhlet extraction for 24 hrs, and then was collected by filtration and finally dried at 200 °C under vacuum for 12 hrs to give [Al (bpydc)(OH)], MOF-253 (165 mg, 90 %). Anal. Calcd for $C_{12}H_7AlN_2O_5$: C, 50.34; H, 2.45; N, 9.79. Found: C, 50.25; H, 2.52; N, 9.64.

Synthesis of MOF-253-EuX (X = 1 and 8). The preparation of MOF-253-Eu1 was carried out as follows: The compound Al(OH)(bpydc) (52 mg, 0.18 mmol), solution of $Eu(NO_3)_3{\cdot}xH_2O$ in the acetonitrile (1 mL, 1.8 mmol/L) and acetonitrile (15 mL) were added to a Tefloncapped 20 mL scintillation vial and heated on a hotplate at 65 °C for 24 hrs. The resulting white solid product was collected by centrifugation and washes with acetonitrile by ultrasonic three times. The resulting product was collected by filtration and heated at 60 °C for 12 hrs under vacuum to give $[Al(bpydc)(OH)(Eu(NO_3)_3)_{0.01}]$, MOF-253-Eu1 (45 mg, 86 %). ICP analysis showed that the molar ration of Al^{3+}/Eu^{3+} was 1: 0.0098. Anal. Calcd for $C_{12}H_7AlEu_{0.01}N_{2.03}O_{5.09}$: C, 49.78; H, 2.43; N, 9.82. Found: C, 49.98; H, 2.37; N, 9.72. MOF-253-Eu8 was prepared in a similar manner.

Synthesis of MOF-253-Eu1-TTA. The preparation of MOF-253-Eu1-TTA was carried out as follows: The MOF-253-Eu1 (44 mg, 0.15 mmol), solution of TTA in the acetonitrile (0.45 mL, 50 mmol/L), thriethylamine in the acetonitrile (0.45 mL, 50 mmol/L) and acetonitrile (15 mL) were added to a Tefloncapped 20 mL scintillation vial and heated on a hotplate at 65 °C for 24 hrs. The resulting white solid product was collected by centrifugation and washes with acetonitrile by ultrasonic three times and dried at 60 °C under vacuum for 12 hrs to give $[Al(bpydc)(OH)(Eu(NO_3)_3)_{0.01}(TTA)_{0.03}]$, MOF-253-Eu1-TTA (42 mg, 80 %). Anal. Calcd for $C_{12.24}H_{7.09}AlEu_{0.01}N_2O_{5.06}S_{0.03}F_{0.09}$: C, 49.95; H, 2.42; N, 9.52. Found: C, 49.77; H, 2.25; N, 9.29.

Synthesis of $Eu(TTA)_3$(bipyridyl) The $Eu(NO_3)_3{\cdot}6H_2O$ (446 mg, 1 mmol), 2-thenoyltrifluoroacetone (TTA) (666 mg, 3 mmol) and triethylamine (303 mg, 3 mmol) was dissolved in 15 mL ethanol. The solution was yellow and clear. The bipyridyl (156 mg, 1 mmol) was added and deposit appears immediately. The deposite was collected by filtration and cleaning with ethanol. After drying under vacuum, the product was white powder (802 mg). Yield is 87 %. Anal. Calcd for $C_{34}H_{23}EuF_9N_2O_6S_3$: C, 41.90; H, 2.38; N, 2.87. Found: C, 41.94; H, 2.36; N, 2.78.

Preparation of MOF-PEMA thin film. MOF-PEMA is dissolved in THF. The solution of MOF-PEMA in THF is doped on the glass. MOF-PEMA thin film could be achieved after removing THF by volatilizing.

Preparation of MOF-PEMA-X(X=3.5 and 10). 1 mL of liquid monomer EMA was added to a glass model containing 3.5 wt% of nano sized MOF-253-Eu1-TTA. The mixture was sonicated at room temperture for 2 h. Then, 4 mg of initiator (AIBN) was added, and the mixture has been refluxed for 6 hours in THF. And then, the solution has removed by vacuum. The polymer material has been done. MOF-PEMA-10 was prepared in a similar manner.

Assembling LEDs based on MOF-PEMA. Firstly, we try to realize the LED based on MOF-PEMA by simple dip coating produce to LED lamp. But the result is not satisfactory. The electroluminescent spectra of LED realized by simple dip coating produce exhibit a strong board band on the blue area. The blue light severely impacted the color of light from LED. In the LED lamp, the chip is packed by epoxy resin. Pure Epoxy resin has not obvious photoluminescence property. However, the commercial epoxy resin is added antioxidant. The antioxidant could emit strong blue light. This is why bright blue light could be observed while the UV LED lamp is working (Actually, the UV light can not be observed by naked eye).[S2] Hence, we packed the GaN chip by silica gel firstly, and then the MOF-PEMA is coating on the silica gel. The coating method is the same to preparation of MOF-PEMA thin film.

Absolute quantum yield (QY). Absolute quantum yield (QY) of hybrid materials based on MOF-253 measurements is made by exciting the powder samples with diffuse light within an integrating sphere under the excitation at 395 nm.

Comparison experiment of Eu^{3+} ion characteristic emission intensity. MOF-253-Eu1-TTA (29.4 mg) is dispersed to 50 mL alcohol to achieve a solution of MOF-253-Eu1-TTA (2 mmol/L) in alcohol. $Eu(TTA)_3$(bipyridyl) is dissolved in alcohol to achieve a solution of $Eu(TTA)_3$(bipyridyl) (0.02 mmol/L) in alcohol. In the two kind of alcohol solution, the concentration of Eu^{3+} ion is the same. The emission spectra of the two kind of liquid samples are obtained by excitation at 375 nm.

Physical characterization. The elemental analyses of nitrogen and carbon element the hybrids are measured with a Vario ELIII elemental analyzer. X-ray diffraction patterns (SAXRD) are recorded on a Rigaku D/ max-Rb diffractometer equipped with a Cu anode in a 2θ range from 5 to 45 °. Scanning electronic microscope (SEM) was measured on Hitachi S-4800. Transmission electron microscope (TEM) experiments were conducted on a JEOL2011 microscope operated at 200 kV or on a JEM-4000EX microscope operated at 400 kV. Nitrogen adsorption/desorption isotherms are measured by using a Nova 1000 analyzer under the liquid nitrogen temperature. Luminescence excitation and emission spectra of the solid samples are obtained on Edinburgh FLS920 spectrophotometer. Luminescence lifetime measurements are carried out on an Edinburgh FLS920 phosphorimeter using a microsecond pulse lamp as excitation source. Temperature dependence of the luminescence spectra are carried out on Oxford optista DN2. The measurement of metal ion was performed on Agilent 7700X inductively coupled plasma-mass spectrometer (ICPMS).

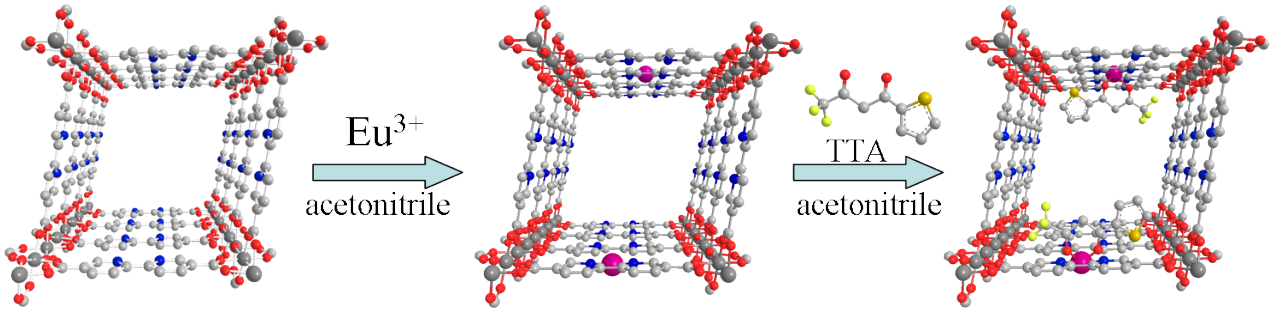

Figure S1 Synthesis and representative structure of MOF-253 with subsequent insertion of Eu^{3+} into open bipyridine ligand sites and modified by TTA. Dark-gray spheres represent Al atoms, while red, blue, and gray spheres represent O, N, and C atoms, respectively; H atoms are omitted for clarity. The figure was drawn by using structural data taken from the literature.[S1]

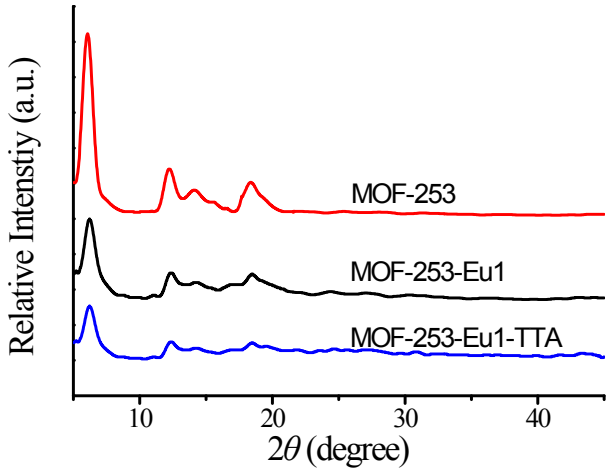

Figure S2 Powder x-ray diffraction patterns (PXRD) for MOF-253, MOF-253-Eu1 and MOF-253-Eu1-TTA, the PXRD of MOF-253 is consistent with reported literature.[S1]

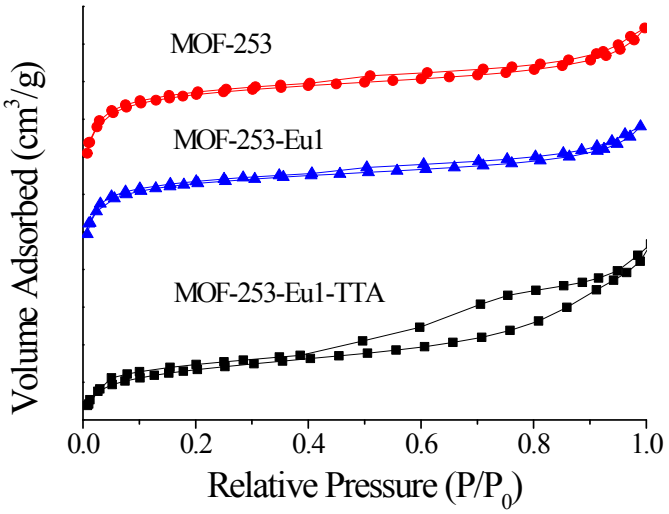

Figure S3 N_2 adsorption-desorption isotherms of MOF-253, MOF-253-Eu1 and MOF-253-Eu1-TTA, the Langmuir surface areas of MOF-253, MOF-253-Eu1 and MOF-253-Eu1-TTA were calculated to be 1183, 923 and 386 m^2/g, the Langmuir surface area of as-synthesized MOF-253 was considerably lower than Yaghi's work, but is consistent with other work about MOF-253. [S3]

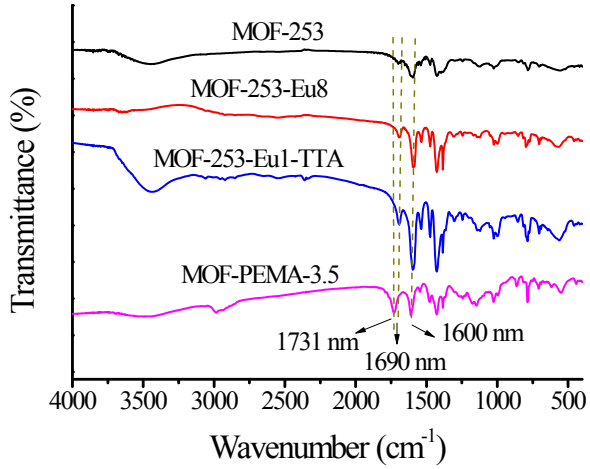

Figure S4 FT-IR spectra of MOF-253, MOF-253-Eu8, MOF-253-Eu1-TTA and MOF-PEMA-3.5.

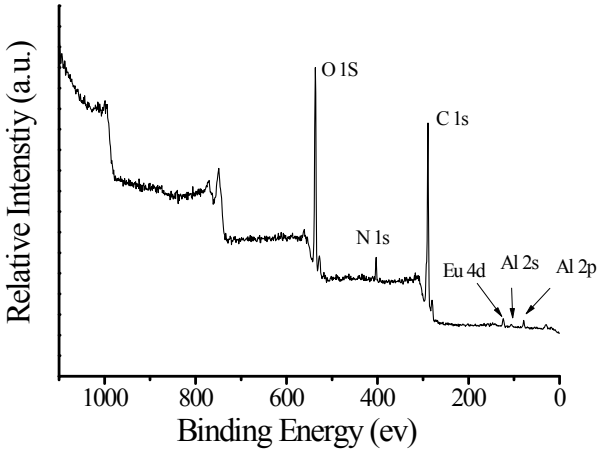

Figure S5 XPS spectra for MOF-253-Eu8

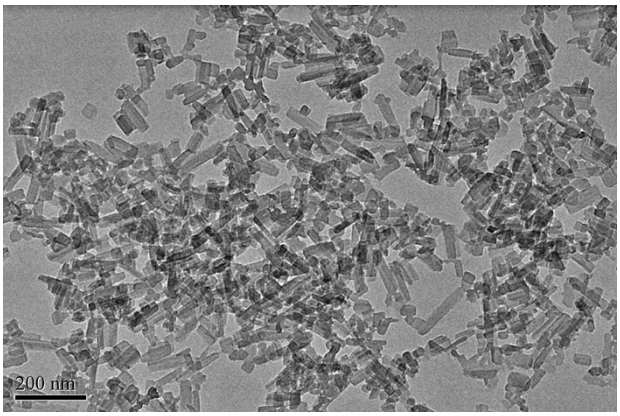

Figure S6 TEM image of MOF-253

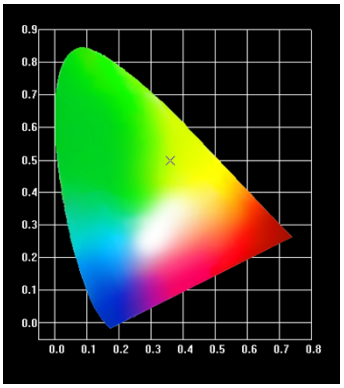

Figure S7 The CIE plot of MOF-253

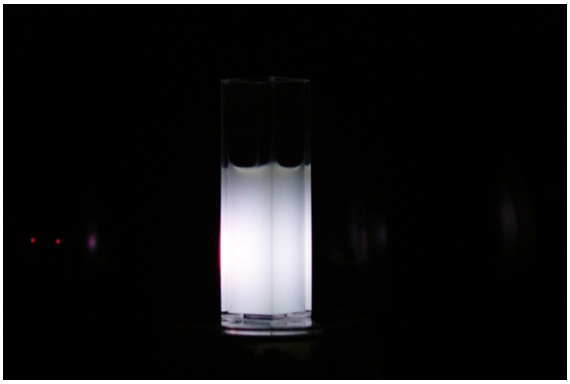

Figure S8 The photograph of MOF-253 suspension exciting white light under 395 nm, 10 mg MOF-253 powder disperse in ethanol, this photograph is shot on the Edinburgh FLS920 spectrophotometer.

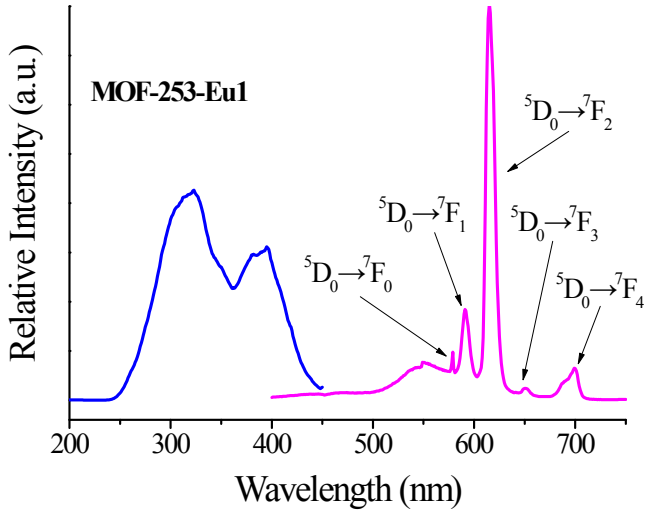

Figure S9 The excitation and emission spectra of MOF-253-Eu1, λ_{em} = 614 nm and λ_{ex} = 330 nm

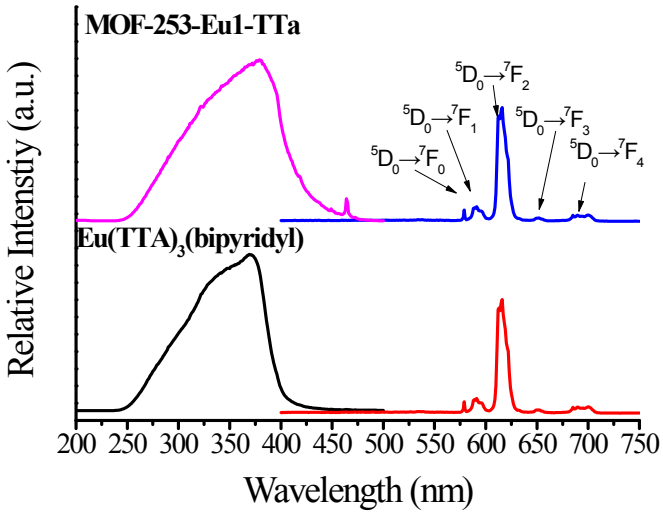

Figure S10 The excitation and emission spectra of MOF-253-Eu1 (λ_{em} = 614 nm and λ_{ex} = 375 nm) and $Eu(TTA)_3$(bipyridyl) (λ_{em} = 614 nm and λ_{ex} = 375 nm)

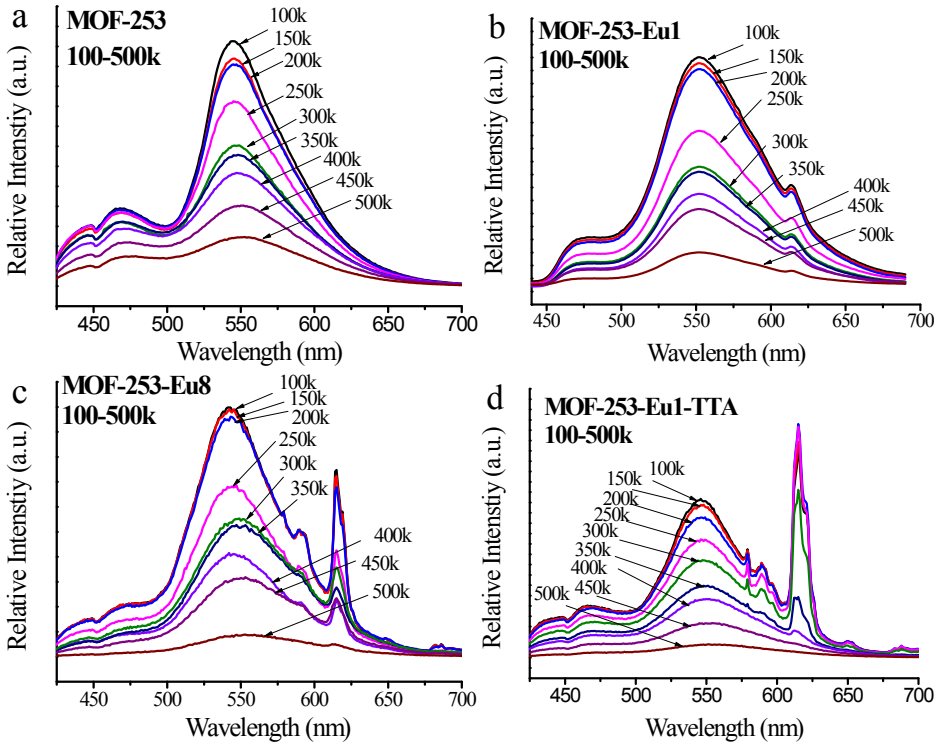

Figure S11 The emission spectra (λ_{ex}=395 nm) of the MOF-253-based hybrid materials at different temperature: a for MOF-253 (100-500 K), b for MOF-253-Eu1 (100-500 K), c for MOF-253-Eu8 (100-500 K), d for MOF-253-Eu1-TTA (100-500 K)

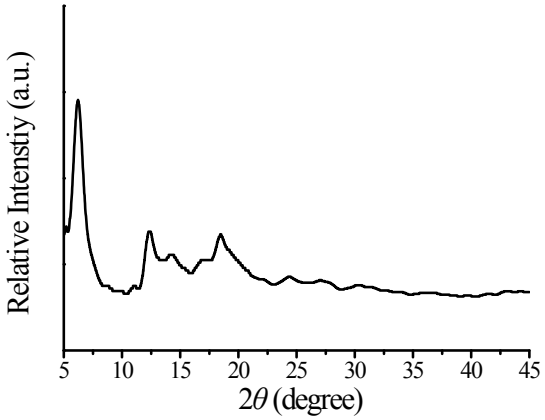

Figure S12 The PXRD of MOF-253-Eu1-TTA after temperature experiment.

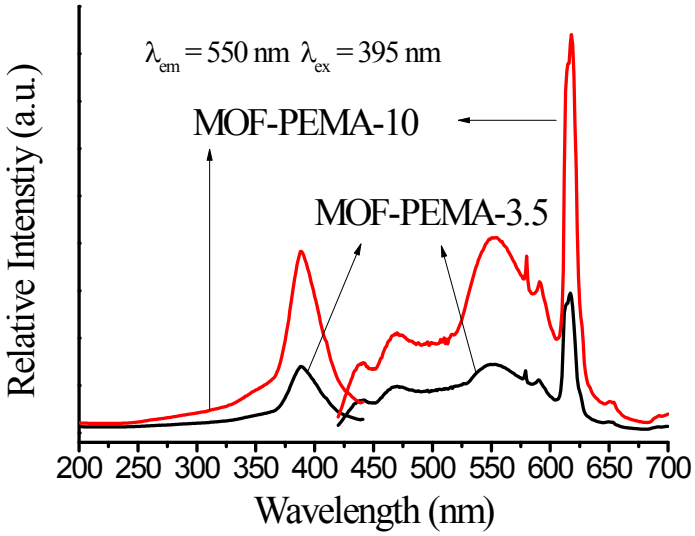

Figure S13 The excitation and emission spectra of MOF-PEMA-3.5 (black) (2mmol/L in THF) and MOF-PEMA-10 (red) (2mmol/L in THF), λ_{ex} = 395 nm and λ_{em} = 550 nm.

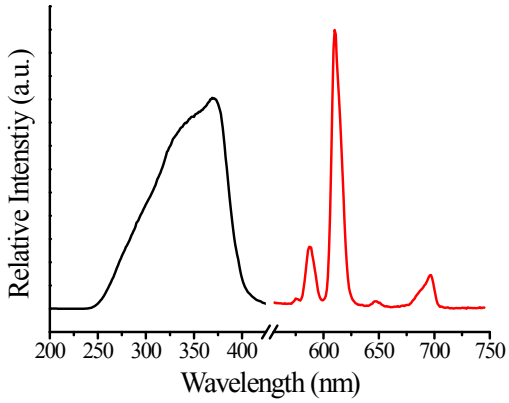

Figure S14 The excitation and emission spectra of MOF-PEMA-3.5, λ_{ex} = 375 nm and λ_{em} = 614 nm

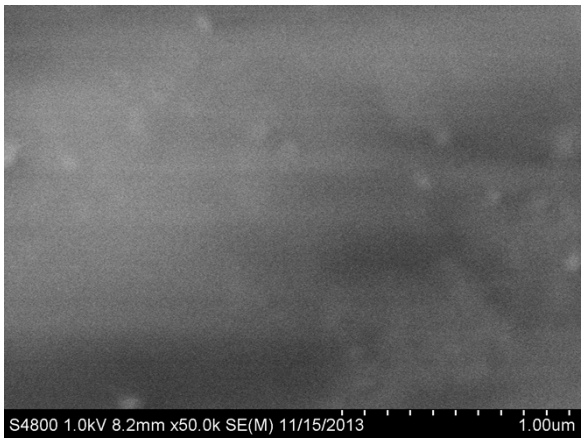

Figure S15 SEM images of MOF-PEMA-3.5 thin film viewed from surface

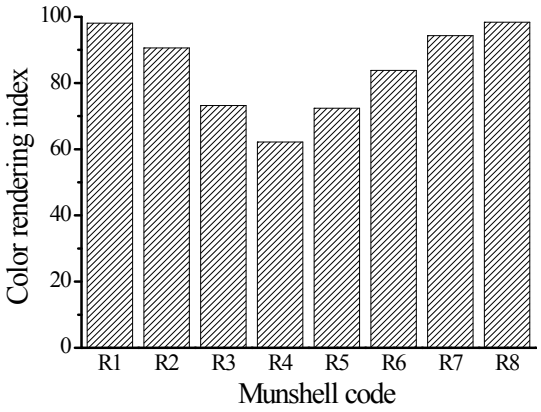

Figure S16 Color rendering indexes of MOF-PEMA-10 LED

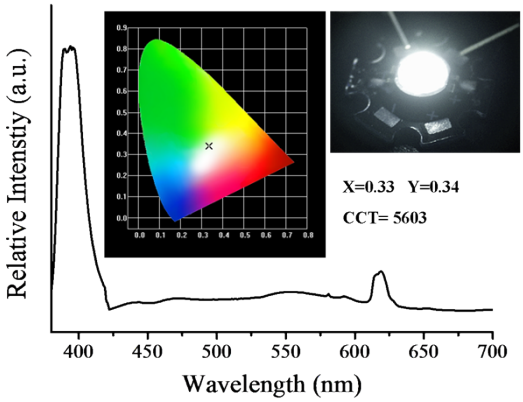

Figure S17 Electroluminescent spectrum of MOF-PEMA-3.5 LED, the inset is CIE plot, X=0.33 Y=0.34, the photograph is the natural white light from MOF-PEMA-3.5 LED under 350 mA

Table S1 The luminescent intensity of MOF-253, MOF-253-Eu8 and MOF-253-Eu1-TTA at 550 nm and 614 nm from 100-250 K

Temperature (K)	MOF-253 (a.u)	MOF-253-Eu1 (a.u.)		MOF-253-Eu8 (a.u.)		MOF-253-Eu1-TTA (a.u.)	
	550 nm	550 nm	614 nm	550 nm	614 nm	550 nm	614 nm
100	74898	74690	25931	71694	56056	75404	100033
150	69757	73397	25034	70675	54241	72569	104374
200	68594	72849	23480	70288	50875	66606	113008

REFERENCES

S1. E. D. Bloch, D. Britt, C. Lee, C. J. Doonan, F. J. Uribe-Romo, H. Furukawa, J. R. Long, O. M. Yaghi, *J. Am. Chem. Soc.* **2010**, *132*, 14382-14384.

S2. J. He, M. Zeller, A. D. Hunter and Z. T. Xu, *J. Am. Chem. Soc.*, 2012, **134**, 1553.

S3. F. Carson, S. Agrawal, M. Gustafsson, A. Bartoszewicz, F. Moraga, X. D. Zou, B. Martin-Matute, *Chem-Eur. J.* **2012**, *18*, 15337-15344.