Supporting Information

A Red Luminescent Eu^{3+}Doped Conjugated Microporous Polymer for Highly Sensitive and Selective Detection of Aluminum Ions

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Contents

Section A. Materials and methods

1,3-Bis(4-bromophenyl)propane-1,3-dione and 1,4-diethynylbenzene were purchased from Aladdin. 1,3,5-Triethynylbenzene was purchased from TCI. Europium (III) acetate hydrate was purchased from Energy Chemical.

Recording Fourier Transform Infrared (FT-IR) Spectrum with FT-IR Frontier Infrared Spectrometer with Perkin-elmer Model. The solid UV-visible analyzer was used for shimadzu UV-3600. For the UV test, the blank sample test is first carried out with the solid barium sulfate powder as the background, and then the holder with solid samples of CMPs was mounted onto the window of the integration sphere. Solid-state ^{13}C CP/MAS NMR measurements was recorded using a Bruker AVANCE III 400 WB spectrometer at a MAS rate of 5 kHz and a CP contact time of 2 ms. Field-emission scanning electron microscopy (FE-SEM) images were performed on a JEOL model JSM-6700 operating at an accelerating voltage of 5.0 kV. The samples were prepared for SEM by drop-casting a tetrahydrofuran suspension onto mica substrate and then coated with gold. High-resolution transmission electron microscopy (HR-TEM) images were obtained on a JEOL model JEM-3200 microscopy. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB250Xi electron spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA). Metal content was analyzed by ICP-MS (NexION350X). Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from $2\theta = 1.5°$ up to 60° with 0.02° increment. TGA analysis was carried out using a Q5000IR analyser (TA Instruments) with an automated vertical overhead thermobalance. Before measurement, the samples were heated at a rate of 5 °C min^{-1} under a nitrogen atmosphere. Photoluminescence spectra were recorded on a JASCO model FP-8600 spectrofluorometer. The absolute quantum yield was determined by standard procedure with an integral sphere JASCO model ISF-834 mounted on the FP-8600 spectrofluorometer.

Nitrogen sorption isotherms were measured at 77 K with ASIQ (iQ-2) volumetric adsorption analyzer. Before measurement, the samples were degassed in vacuum at 150 °C for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume. The nonlocal density functional theory (NLDFT) method was applied for the estimation of pore size and pore size distribution.

Section B. Synthetic procedures

Synthesis of Phen-Eu@BPPD-LP

Firstly, 1.3.5-triethynylbenzene (0.031 g), 1,3-bis(4-bromophenyl)propane-1,3-dione(0.0765 g), $Pd_2(dba)_3$ (0.0183 g), PPh_3 (0.0053 g), CuI (0.0038 g), 1,10-o-phenanthroline (0.361 g), $Eu(OAc)_3 \cdot 6H_2O$ (0.87 g) were added to a 50 mL two-necked flask in turn. Next, the 8 mL of DMF and 2 mL of triethylamine were separately added into the flask, then the flask was exchanged 3 cycles under vacuum/N_2. After evacuating three times, it was filled with nitrogen gas, and then the reaction was heated to 120 °C for 48 h. After completion of the reaction, the obtained product was cooled to room temperature, and washed with ethanol and water. The collected products were then extracted by Soxhlet with water and ethanol for 12 h, respectively, and dried in a vacuum oven at 80 ℃ for 12 h, to give BPPD-CMP as light yellow powder (72% yield).

Synthesis of Phen-Eu@BPPD-LP

Firstly, 1,4-diethynylbenzene (0.038 g), 1,3-bis(4-bromophenyl)propane-1,3-dione (0.0765 g), $Pd_2(dba)_3$ (0.0183 g), PPh_3 (0.0053 g), CuI (0.0038 g), 1,10-o-phenanthroline (0.361 g), $Eu(OAc)_3 \cdot 6H_2O$ (0.87 g) were added to a 50 mL two-necked flask in turn. Next, the 8 mL of DMF and 2 mL of triethylamine were separately added into the flask, then the flask was exchanged 3 cycles under vacuum/N_2. After evacuating three times, it was filled with nitrogen gas, and then the reaction was heated to 120 °C for 48 h. After completion of the reaction, the obtained product was cooled to room temperature, and washed with ethanol and water. The collected products were then extracted by Soxhlet with water and ethanol for 12 h, respectively, and dried in a vacuum oven at 80 °C for 12 h, to give **Phen-Eu@BPPD-LP** as yellow powder (67% yield).

Synthesis of Eu@BPPD-CMP

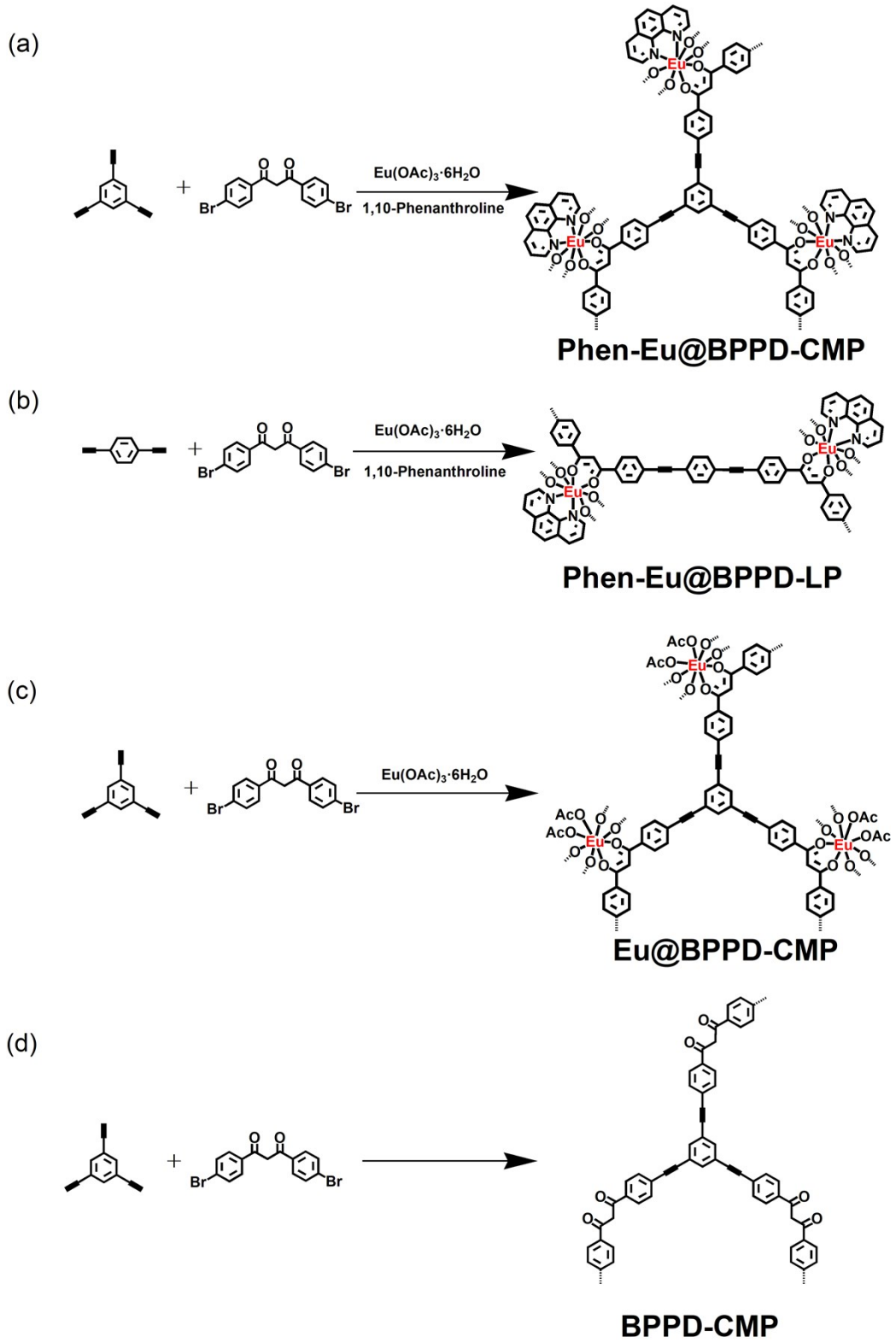
Firstly, 1,3,5-triethynylbenzene (0.031 g), 1,3-bis(4-bromophenyl)propane-1,3-dione (0.0765 g), $Pd_2(dba)_3$ (0.0183 g), PPh_3 (0.0053 g), CuI (0.0038 g), $Eu(OAc)_3 \cdot 6H_2O$ (0.87 g) were added to a 50 mL two-necked flask in turn. Next, the 8 mL of DMF and 2 mL of triethylamine were separately added into the flask, then the flask was exchanged 3 cycles under vacuum/N_2. After evacuating three times, it was filled with nitrogen gas, and then the reaction was heated to 120 °C

for 48 h. After completion of the reaction, the obtained product was cooled to room temperature, and washed with ethanol and water. The collected products were then extracted by Soxhlet with water and ethanol for 12 h, respectively, and dried in a vacuum oven at 80 °C for 12 h, to give **Eu@BPPD-CMP** as brown powder (70% yield).

Synthesis of BPPD-CMP

Firstly, 1,3,5-triethynylbenzene (0.031 g), 1,3-bis(4-bromophenyl)propane-1,3-dione (0.0765 g), $Pd_2(dba)_3$ (0.0183 g), PPh_3 (0.0053 g), CuI (0.0038 g) were added to the two-necked flask in turn. Next, the 8 mL of DMF and 2 mL of triethylamine were separately added into a 50 mL two-necked flask, then the flask was exchanged 3 cycles under vacuum/N_2. After evacuating three times, it was filled with nitrogen gas, and then the reaction was heated to 120 °C for 48 h. After completion of the reaction, the obtained product was cooled to room temperature, and washed with ethanol and water. The collected products were then were then extracted by Soxhlet with water and ethanol for 12 h, respectively, and dried in a vacuum oven at 80 °C for 12 h, to give **BPPD-CMP** as black powder (85% yield).

Scheme S1



Scheme S1 Schematic representations of (a) the Eu^{3+}-doped CMP Phen-Eu@BPPD-CMP composite, (b) the linear polymer analogue Phen-Eu@BPPD-LP, (c) Eu@BPPD-CMP without Phen units, and (d) BPPD-CMP, respectively.

Section C. ^{13}C NMR spectra

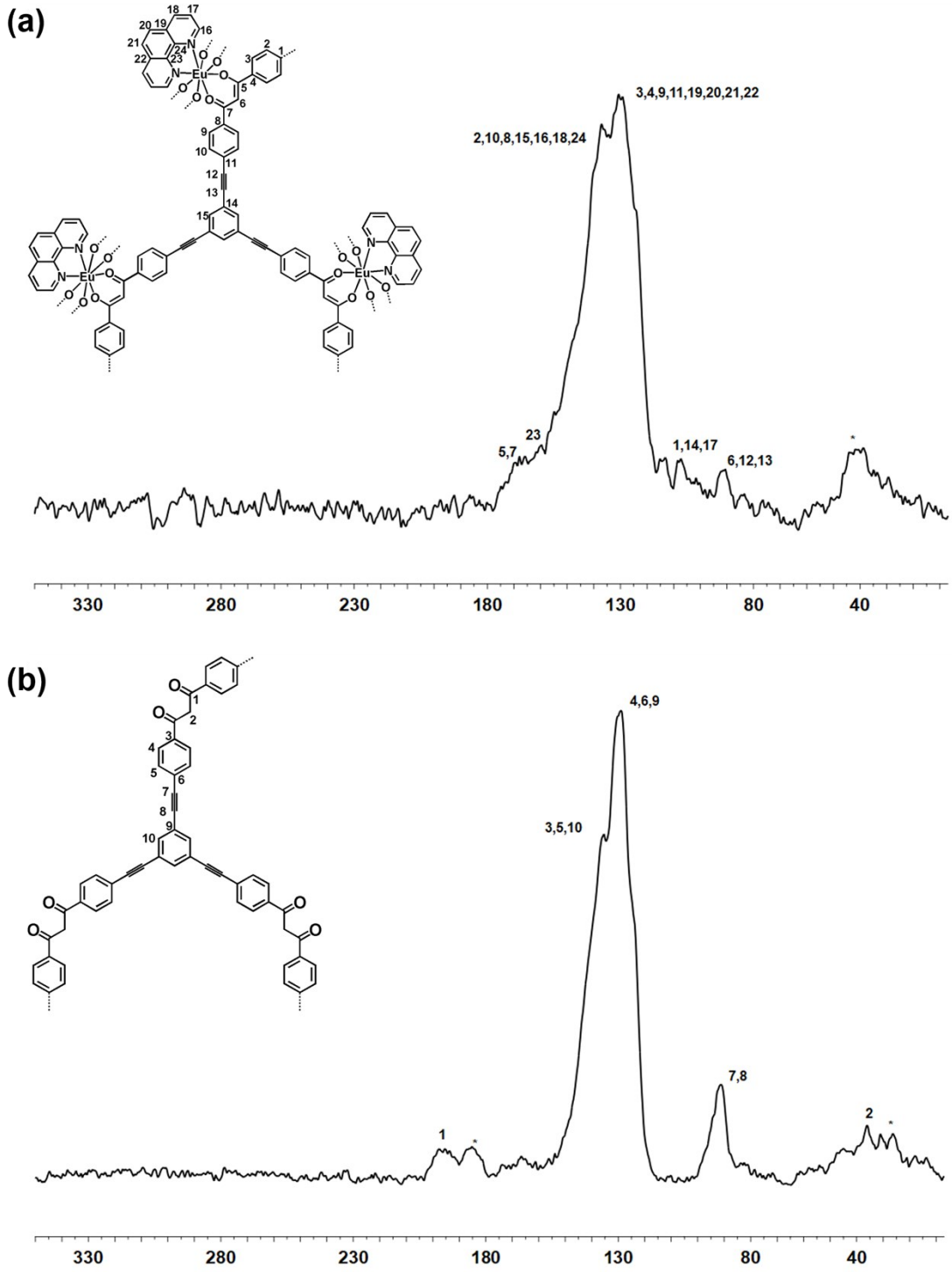


Fig. S1 The solid-state ^{13}C CP-MAS NMR of (a) Phen-Eu@BPPD-CMP and (b) BPPD-CMP.

Section D. XPS spectrum

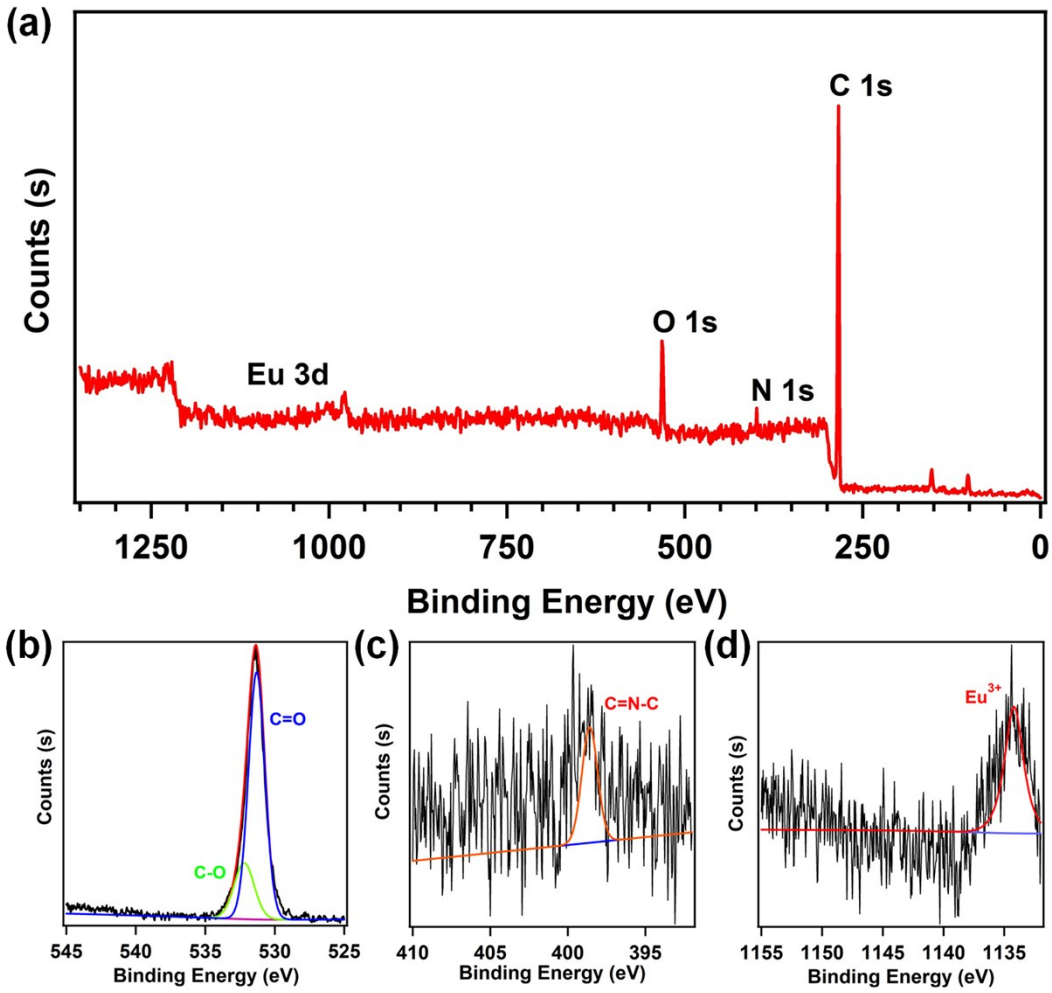


Fig. S2 (a) X-ray photoelectron spectroscopy of Phen-Eu@BPPD-CMP, (b) O 1s spectrum of Phen-Eu@BPPD-CMP, (c) N 1s spectrum of Phen-Eu@BPPD-CMP, (d) Eu 3d spectrum of Phen-Eu@BPPD-CMP.

Section E. FT-IR spectra

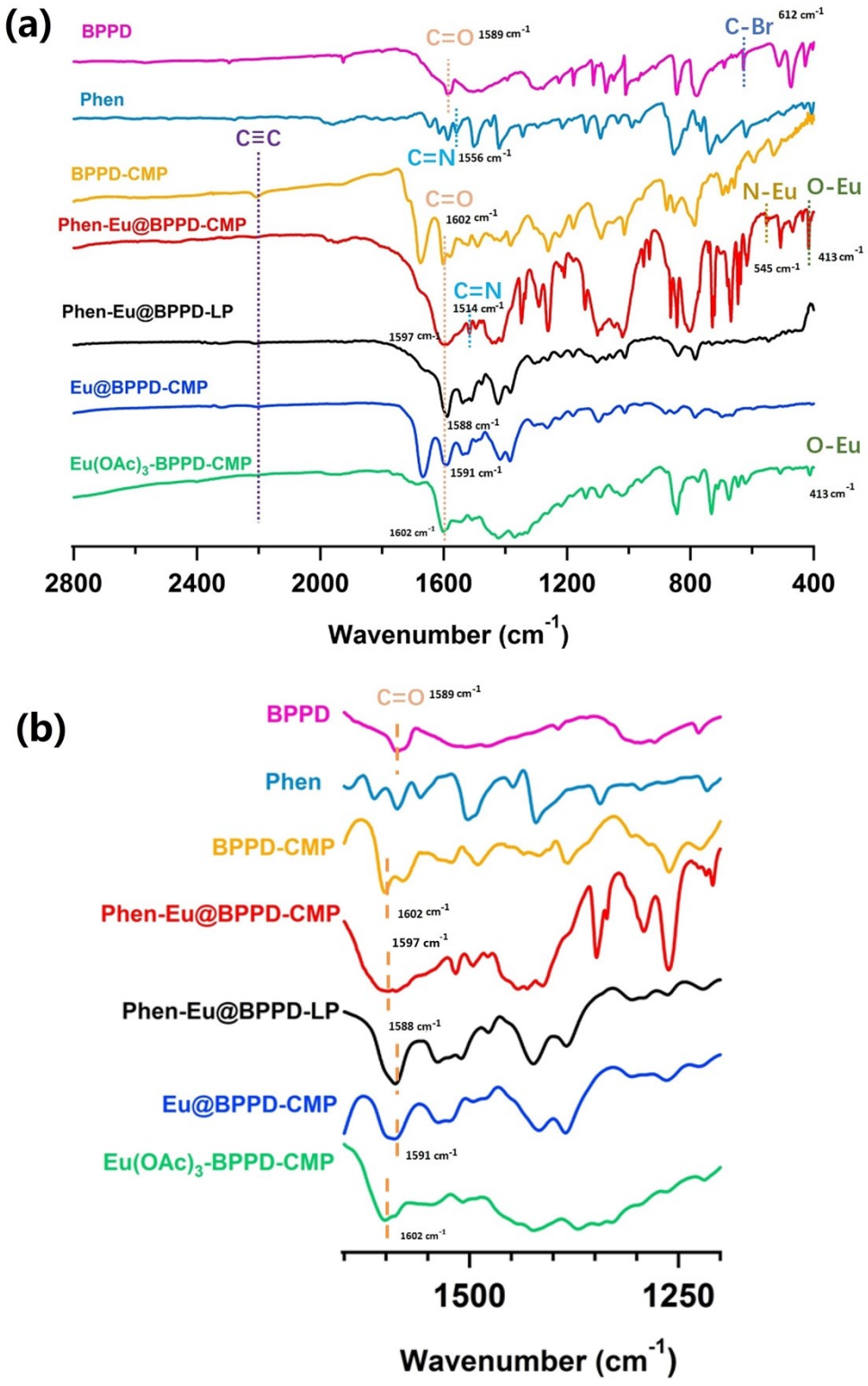


Fig. S3 (a) FT-IR spectra and (b) the amplified part in the FT-IR spectra of BPPD-CMP, Phen-Eu@BPPD-CMP, Phen-Eu@BPPD-LP, Eu@BPPD-CMP, and $Eu(OAc)_3$-BPPD-CMP, respectively.

Section F. Powder X-ray diffraction patterns

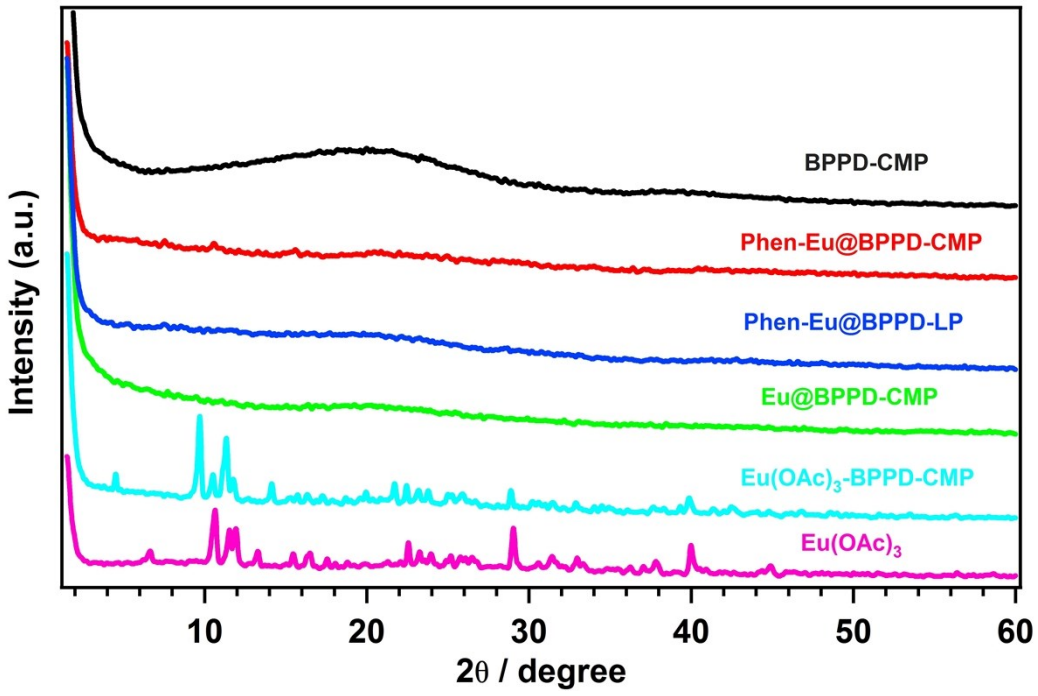


Fig. S4 Powder X-ray diffraction profiles of BPPD-CMP, Phen-Eu@BPPD-CMP, Phen-Eu@BPPD-LP, Eu@BPPD-CMP, $Eu(OAc)_3$-BPPD-CMP and $Eu(OAc)_3$, respectively.

Section G. FE-SEM images

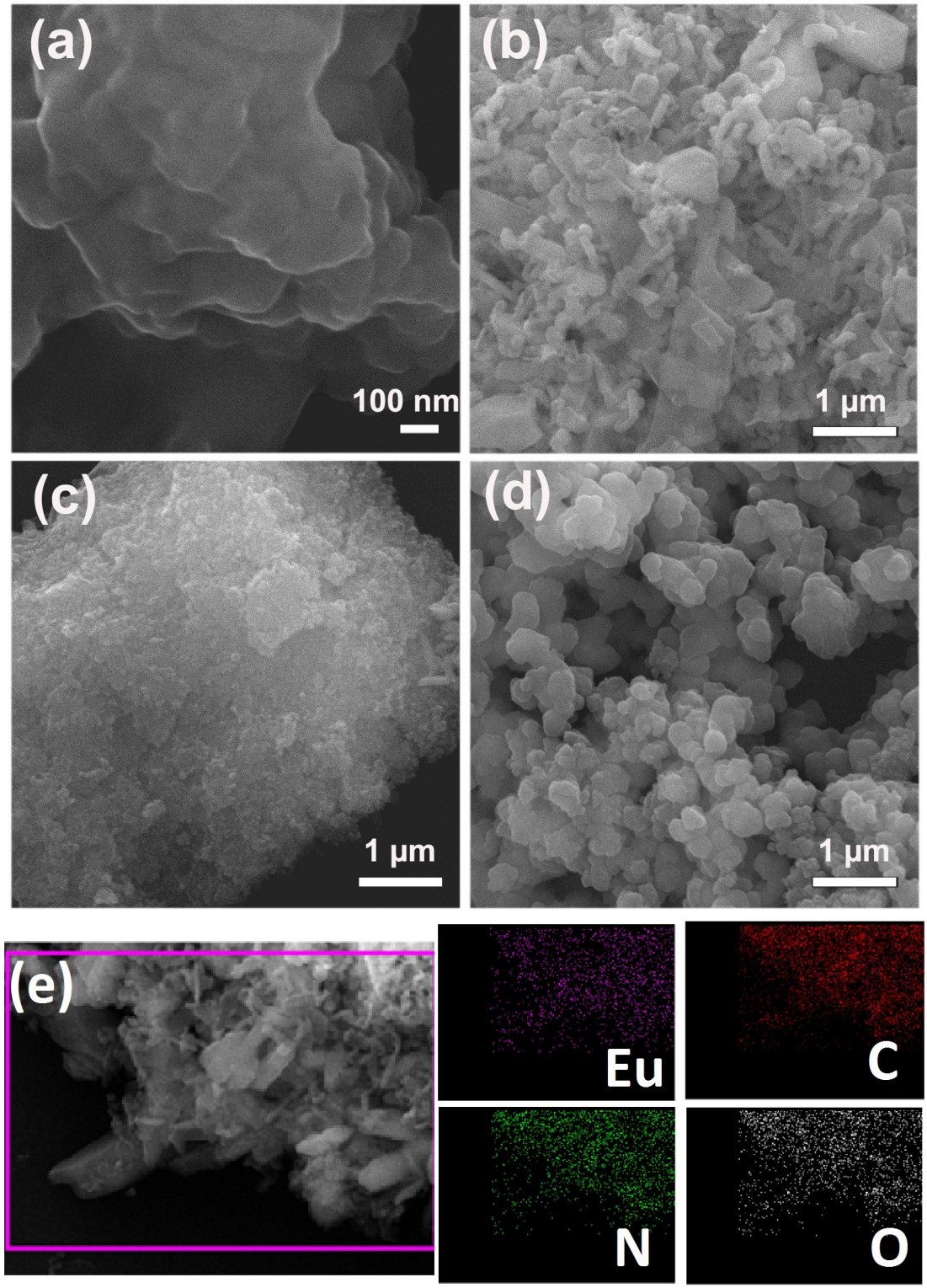


Fig. S5. FE-SEM images (a) BPPD-CMP, (b) Phen-Eu@BPPD-CMP, (c) $Eu(OAc)_3$-BPPD-CMP, and (d) Eu@BPPD-CMP, respectively. (e) EDS analysis of Eu (green), C (red), and N (violet) atoms in Phen-Eu@BPPD-CMP .

Section H. TEM images

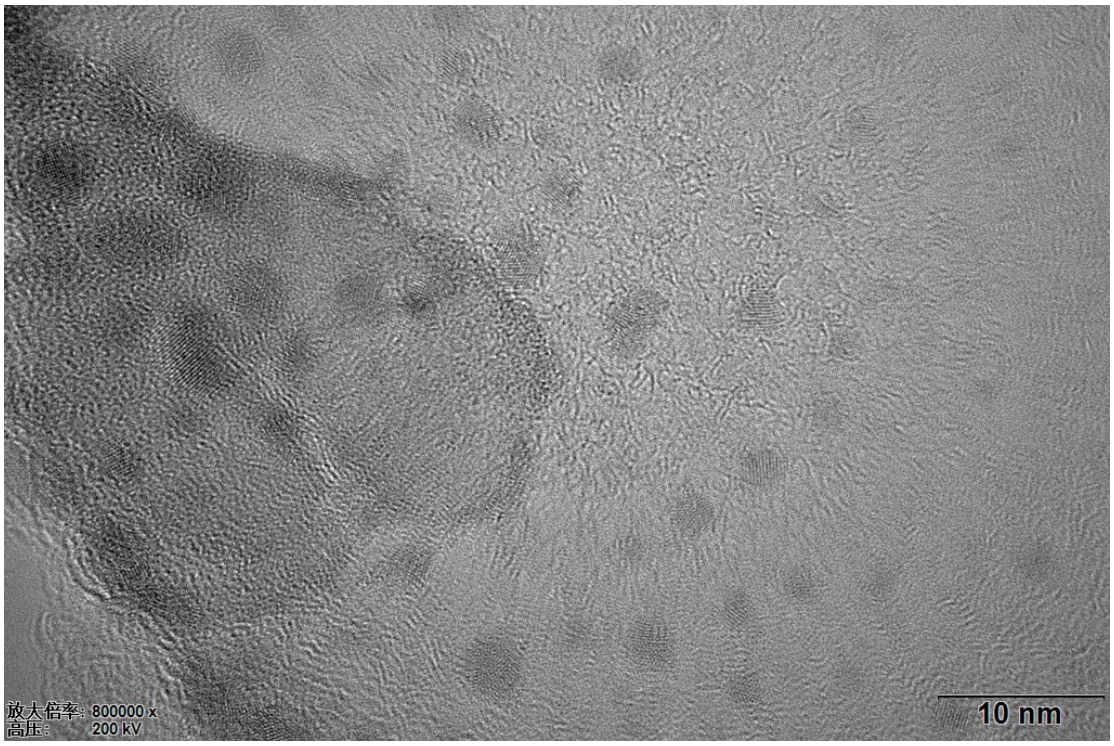


Fig. S6 TEM image of Phen-Eu@BPPD-CMP (the crystal dots in the image should be the distribution of the rare earth metal europium on the structure).

Section I. TGA curves

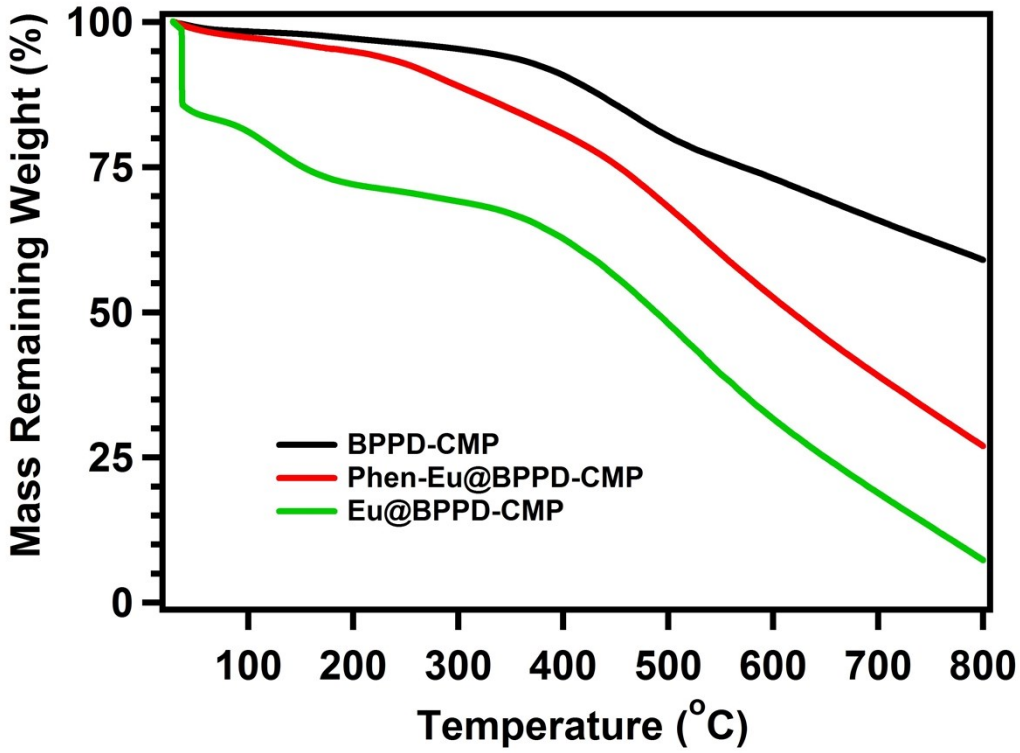


Fig. S7 TGA curves of BPPD-CMP, Phen-Eu@BPPD-CMP, and Eu@BPPD-CMP, respectively.

Section J. Pore property

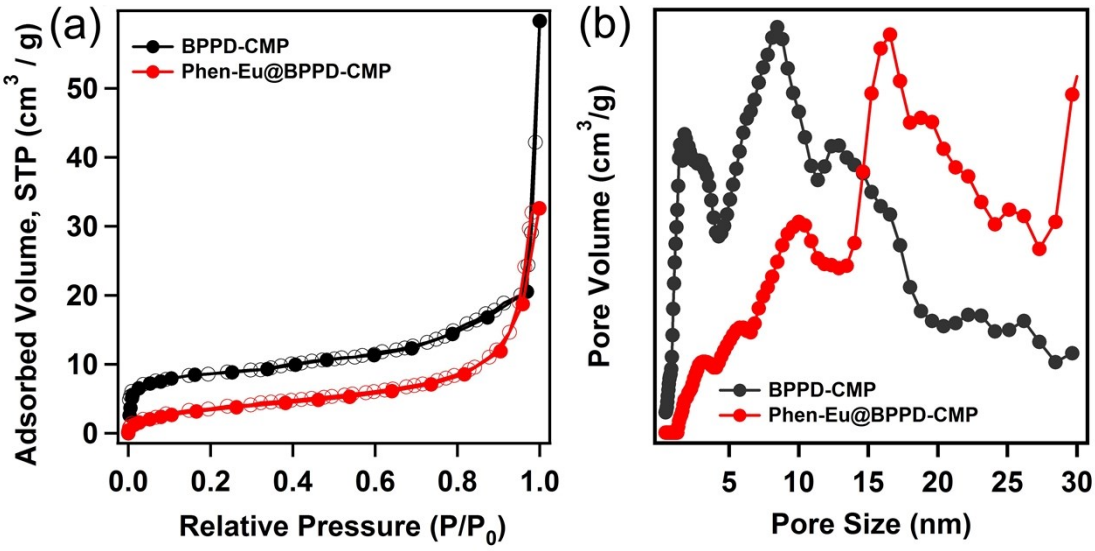


Fig. S8 (a) Nitrogen sorption curves and (b) pore size distribution curves of Phen-Eu@BPPD-CMP and BPPD-CMP.

Section K. Fluorescence Spectra

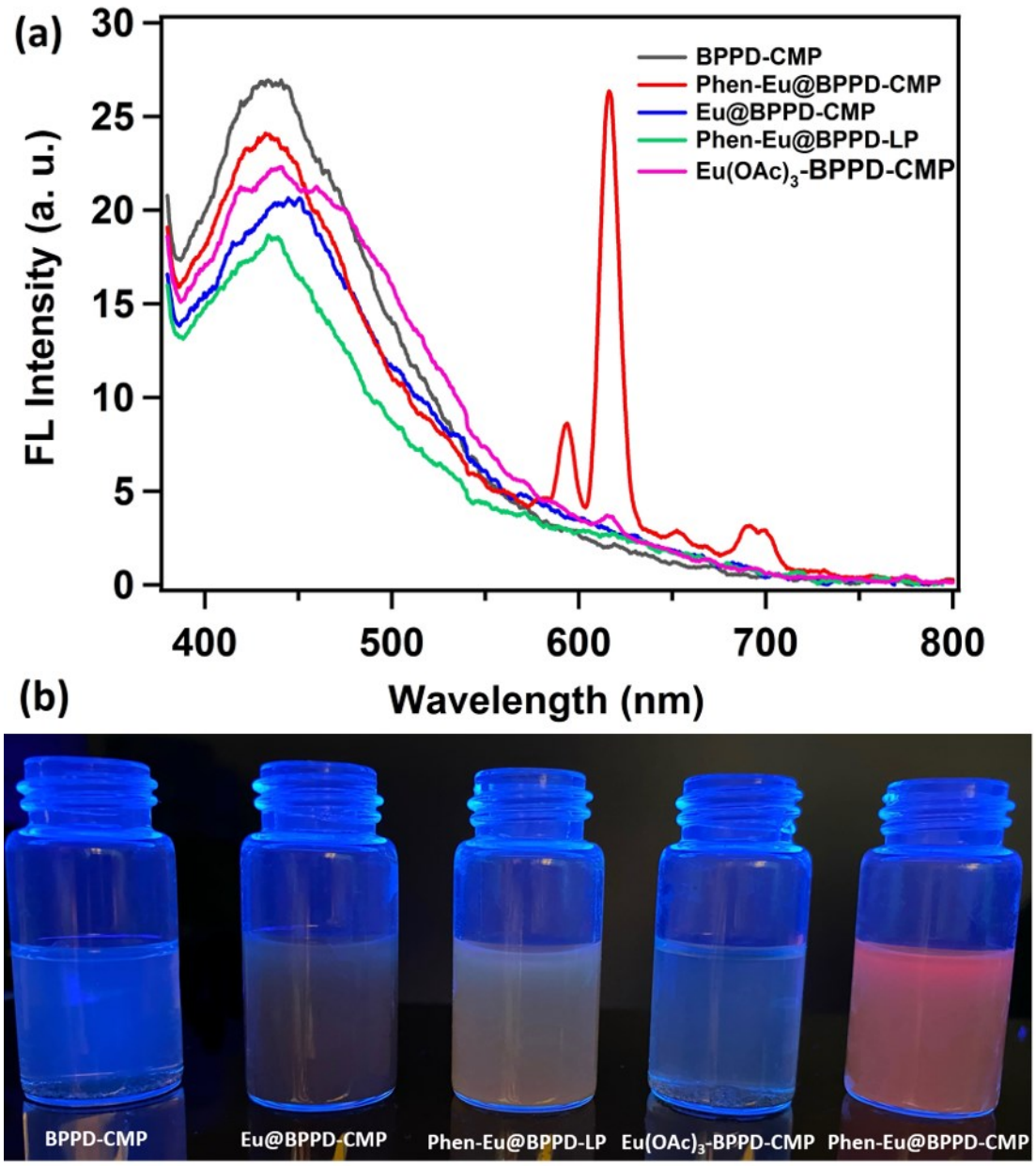


Fig. S9 (a) The solid-state fluorescence spectra of BPPD-CMP, $Eu(OAc)_3$-BPPD-CMP mixture, Phen-Eu@BPPD-LP, Eu@BPPD-CMP, and Phen-Eu@BPPD-CMP, respectively; (b) the fluorescence photographs of BPPD-CMP, Eu@BPPD-CMP, Phen-Eu@BPPD-LP, $Eu(OAc)_3$-BPPD-CMP mixture and Phen-Eu@BPPD-CMP in DMF under a 365 nm UV lamp, respectively.

Section L. The Solid-state Uv-Vis Spectra

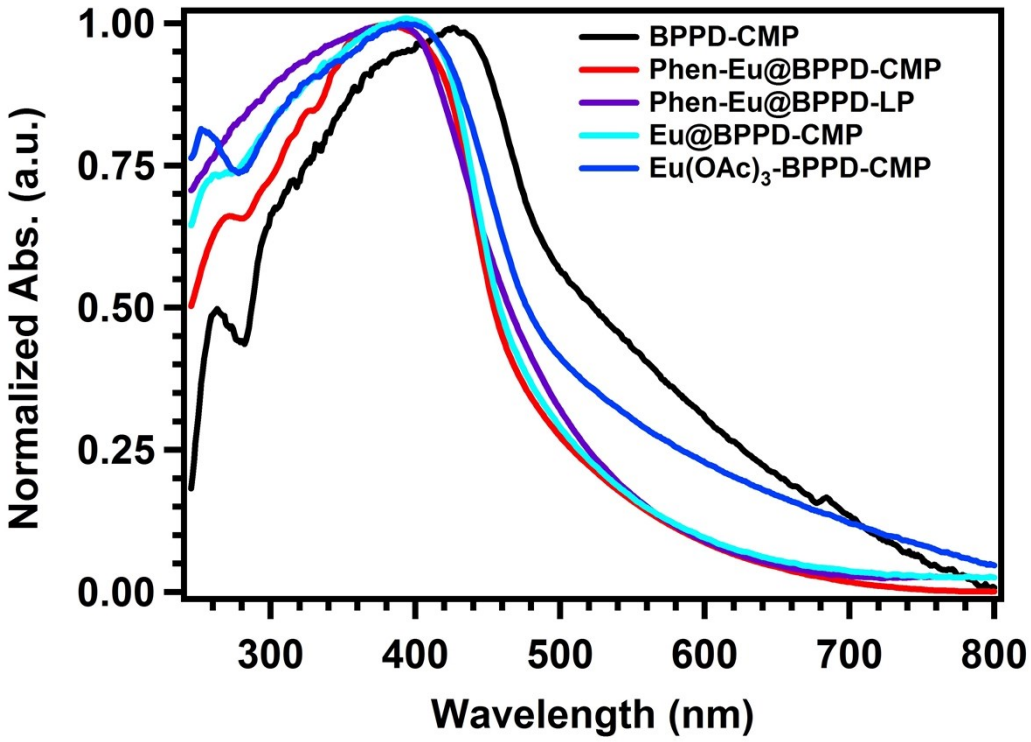


Fig. S10 The solid-state absorption spectra of BPPD-CMP, Phen-Eu@BPPD-CMP, Phen-Eu@BPPD-LP, Eu@BPPD-CMP, and $Eu(OAc)_3$-BPPD-CMP mixture, respectively.

Section M. The Stern-Völmer Curves

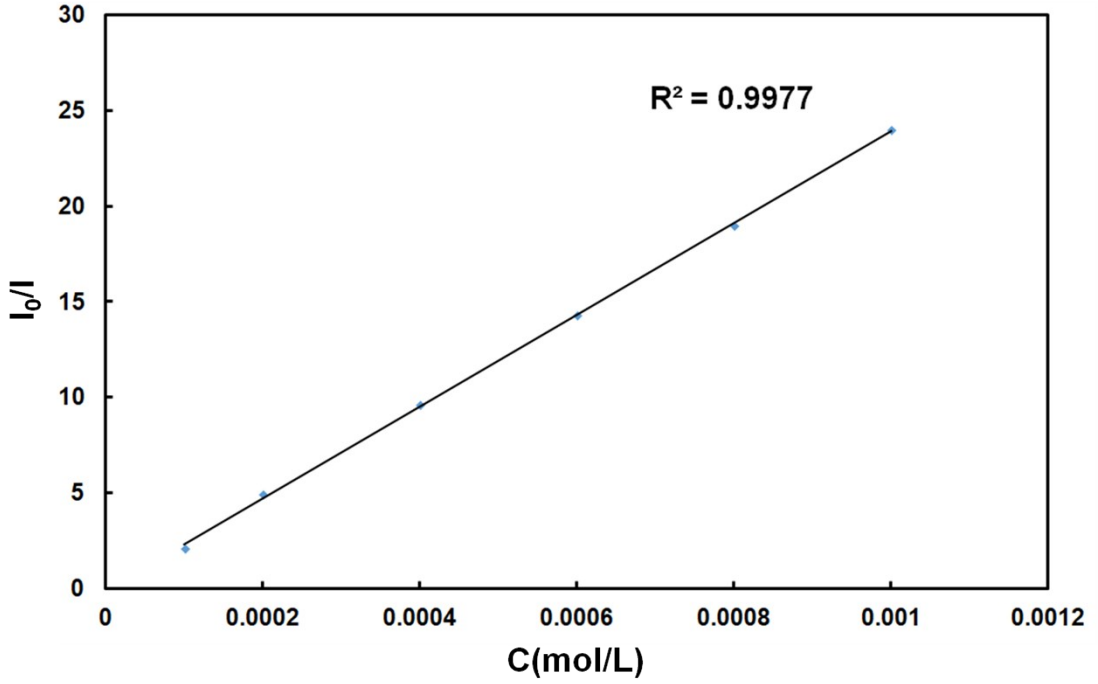


Fig. S11 The Stern-Völmer curve with doped Al^{3+} concentration in the range of 0.1-1 mM.

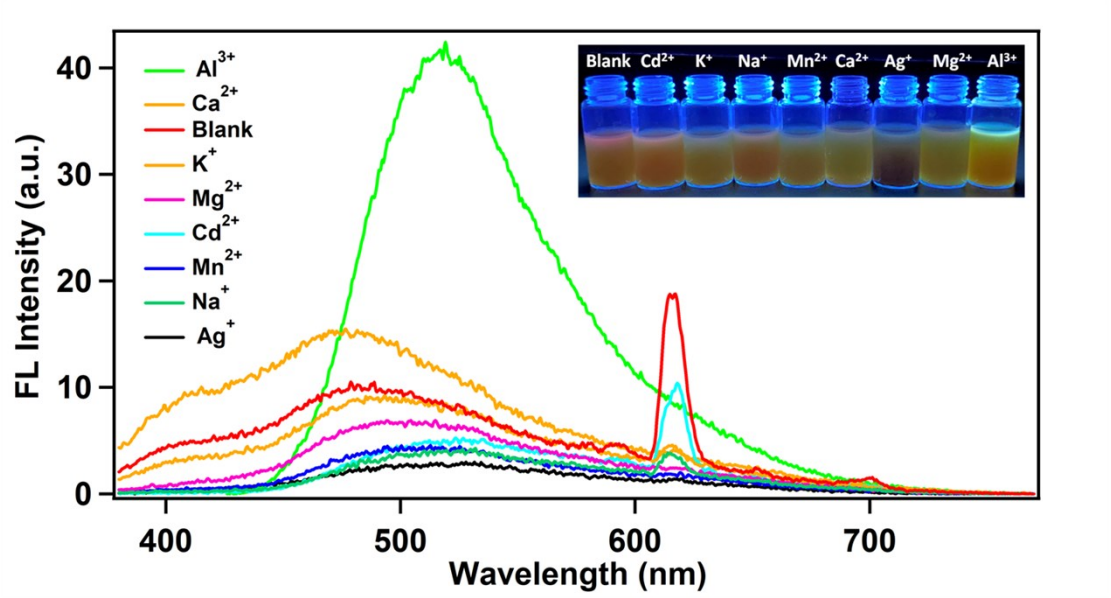


Fig. S12 Fluorescence emission spectra of Phen-Eu@BPPD-LP in the presence of different metal ions (the inset: the fluorescence photographs under a 365 nm UV lamp).

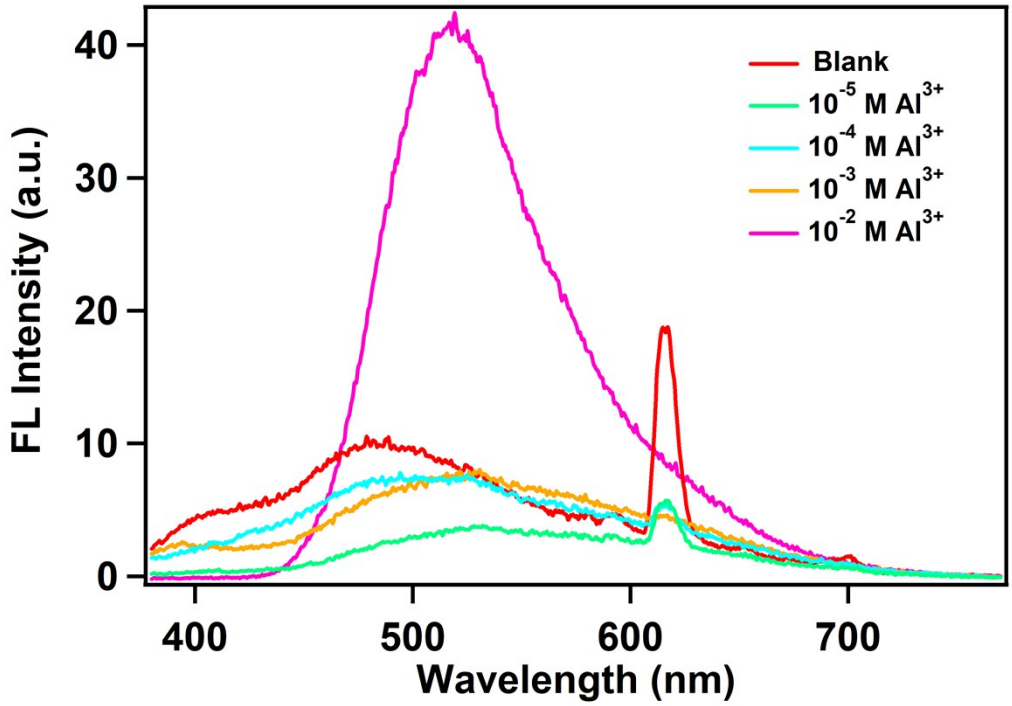


Fig. S13 Fluorescence emission spectra of Phen-Eu@BPPD-LP in the presence of Al^{3+} with the different concentrations in DMF.