

Supplement Information

Lanthanide metal-organic frameworks with nitrogen functional sites for highly selective and sensitive detection of NADPH

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Compared with organic ligands, the vibrational absorption peak of carbonyl group in Ln-MOFs becomes weaker and shifts from 1682 cm^{-1} , 1682 cm^{-1} , 1684 cm^{-1} to 1647 cm^{-1} , 1654 cm^{-1} , 1659 cm^{-1} , respectively. Which indicates the carboxyl group coordinated with lanthanide ions.

Figure S7. Fluorescence responses of Eu(BPDC- x N) ($x = 0, 1, 2$) toward NADH.

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1. Experimental procedures

1.1 Sample preparation

Organic ligand 4,4'-biphenyldicarboxylic acid (H₂BPDC-0N), 6-(4-carboxyphenyl)nicotinic acid (H₂BPDC-1N), [2,2'-bipyridine]-5,5'-dicarboxylic acid (H₂BPDC-2N) were purchased from Ji'nan Henghua Co. Ltd. the sensing targets NADPH and NADH were obtained from Shanghai Sahn Technology Co. Ltd. All other reagents and solvents were commercially available and used without further purification.

Synthesis of Eu(BPDC-0N): A mixture of Eu(NO₃)₃·6H₂O (6.47 mg), ligand H₂BDPC-0N (3.51 mg) and modulator 2-FBA (24.38 mg) was dissolved in DMF/H₂O (730 μL/20 μL), then added 20 μL nitric acid (3.5 mol·L⁻¹ in DMF), the reactants were dissolved evenly by ultrasound for 15 min, the solution was sealed in 5 ml bottle and transferred to 110 °C oven for 2 days. After cooling down to room temperature. Colorless crystals were obtained in a yield of 33% based on ligand, washed by DMF and EtOH three times, respectively, and dried at 80 °C overnight.

Synthesis of Eu(BPDC-1N): A mixture of Eu(NO₃)₃·6H₂O (6.47 mg), ligand H₂BDPC-1N (3.52 mg) and modulator 2-FBA (16.23 mg) was dissolved in DMF/H₂O (730 μL/20 μL), then added 40 μL nitric acid (3.5 mol·L⁻¹ in DMF), the reactants were dissolved evenly by ultrasound for 15 min, the solution was sealed in 5 ml bottle and transferred to 110 °C oven for 2 days. After cooling down to room temperature. light purple crystals were obtained in a yield of 47% based on ligand. washed by DMF and EtOH three times, respectively, and dried at 80 °C overnight.

Synthesis of Eu(BPDC-2N): A mixture of Eu(NO₃)₃·6H₂O (6.47 mg), ligand H₂BDPC-2N (3.52 mg) and modulator 2-FBA (24.38 mg) was dissolved in DMF/H₂O (2.92 mL/40 μL), then added 60 μL nitric acid (3.5 mol·L⁻¹ in DMF), the reactants were dissolved evenly by ultrasound for 15 min, the solution was sealed in 5 ml bottle and transferred to 110 °C oven for 3 days. After cooling down to room temperature. Purple red crystals were obtained in a yield of 17% based on ligand. washed by DMF and EtOH three times, respectively, and dried at 80 °C overnight.

1.2 NADPH/NADH detection

The 1 mL sample suspension (0.5 mg·mL⁻¹) prepared by dispersing Ln-MOFs in water was added to a cuvette that is cleared on all sides. At the same time, different concentrations of NADPH or NAD aqueous solution were prepared and *in situ* added it to the above cuvette, and test its luminous performance. During the experiment, the solution was stirred at a constant rate to maintain the homogeneity of the solution.

2. Measurement and analysis

2.1 PXRD

Powder X-ray diffraction (PXRD) patterns ranging from 3° to 50° were collected on a PANalytical X'Pert Pro X-ray diffractometer using a Cu-Kα (λ=1.542 Å) beam with the recording rate of 5°/min at room temperature. Bruker SMART APEX- II single crystal diffractometer with a CCD detector was employed to implement the crystallographic measurements for Eu(BPDC-xN)(x=0,1,2), using graphite-monochromatic Mo Kα radiation (λ=0.71073 Å) at 296 K. CrysAlisPro was used to conduct the determination of the unit cell and data collection. The data reduction was carried out with Bruker SAINT. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. The cell parameters determination and data collection was performed directly by

CrysAlisPro program. The crystal structure was determined by direct methods and refined by the full-matrix least-squares method with SHELX-2014 program package. All non-hydrogen atoms were located successfully from Fourier maps and were refined anisotropically. The H atoms on the ligands were placed in idealized positions and refined using a riding model. The disordered lattice solvent molecules and ions could not be located successfully from Fourier maps in the refinement cycles. The scattering from the highly-disordered lattice guest molecules were removed using SQUEEZE procedure implemented in the PLATON package.

2.2 TGA

Thermogravimetric analyses (TGA) was obtained on a Netzsch TG209F3 under N₂ atmosphere with a heating rate of 10 K/min. the testing temperature was set from 40 °C to 800 °C.

2.3 PL

Fluorescence signals of probes were recorded on a Hitachi F4600 fluorescence spectrometer. Xenon lamp serves as an excitation light source. In real experiment, scanning speed was set at 240 nm·min⁻¹, excitation and emission slits width and detector voltage were adjusted to get a proper fluorescence intensity, the test condition remained constant in the whole experiment.

2.4 FTIR

Fourier transform infrared (FTIR) spectra were recorded within 4000-400cm⁻¹ range on Thermo Fisher Nicolet iS10 spectrometer using KBr pellets. The pellets were prepared by mixing the sample with KBr (v:v =1:20). The mixture was then carefully grinded and compressed under the pressure of 20KPa to form a transparent pellet.

2.5 UV

UV-Vis adsorption spectra of NADPH and NADH were performed on UV-2600 spectrometer (Shimadzu Corp, Japan), the testing range was set from 200 to 700 nm.

2.6 DECAY

Fluorescence lifetime of MOFs were studied by using Edinburgh FLS920, μ F900 was used as light source when measuring fluorescence lifetime of lanthanide ions, laser was used for ligand's fluorescence lifetime analysis. The detector was Red PMT.

2.7 ICP

inductively coupled plasma massspectrometry was performed on Thermo IRIS Intrepid II XSP

2.8 MTT experiment

The biotoxicity of Eu(BPDC-2N) was assessed by MTT colorimetric assay. PC12 cells were cultured in culture medium containing Eu(BPDC-2N) of 5, 20, 50, 80, 100 μ g·mL⁻¹ initial concentration for 24 h, respectively.

3. Tables and Figures

Table s1. Crystallographic Data Collection of Eu(BPDC-1N) and Eu(BPDC-2N).

Sample	Eu(BPDC-1N)	Eu(BPDC-2N)
Chemical formula	C ₃₀ H ₁₂ Eu ₃ N ₁₂ O ₁₉	C ₁₄₄ H ₇₂ Eu ₁₂ N ₂₄ O ₆₇
Formula weight	1300.40	5033.77
Temperature (K)	293(2)	173
Wavelength (Å)	0.71073	0.71073
Crystal system	Cubic	Cubic
Space group	<i>Fm</i> $\bar{3}$ <i>m</i>	<i>Fm</i> $\bar{3}$ <i>m</i>
<i>a</i> (Å)	27.6237(8)	27.498(6)
<i>b</i> (Å)	27.6237(8)	27.498(6)
<i>c</i> (Å)	27.6237(8)	27.498(6)
<i>V</i> (Å ³)	21078.8(18)	20792(15)
<i>Z</i>	8	2
Density (calculated g·cm ⁻³)	0.820	0.804
Absorbance coefficient (mm ⁻¹)	1.799	1.819
<i>F</i> (000)	4936	4792
Crystal size (mm ³)	0.2 × 0.2 × 0.2	0.2 × 0.2 × 0.2
<i>R</i> (int)	0.1374	0.0464
Goodness of fit on <i>F</i> ₂	1.257	1.125
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0751, 0.2001	0.0222, 0.0589
<i>R</i> ₁ , <i>wR</i> ₂ (all data) ^a	0.1184, 0.2591	0.0252, 0.0604
Largest difference peak and hole (e Å ⁻³)	3.278, -1.705	1.017, -0.386

$$R_1 = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|}; wR_2 = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum wF_o^2} \right]^{1/2}$$

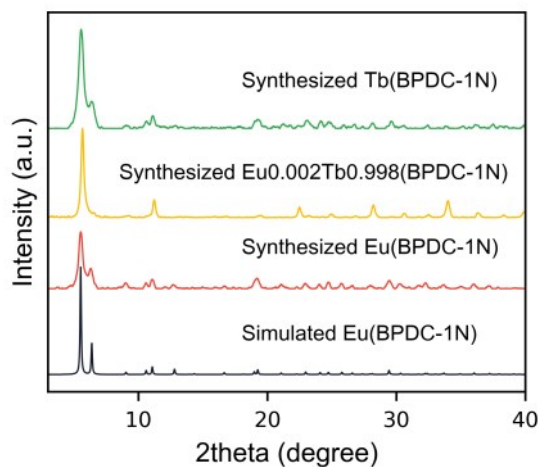


Figure S1. PXRD patterns of simulated and synthesized Ln-MOFs.

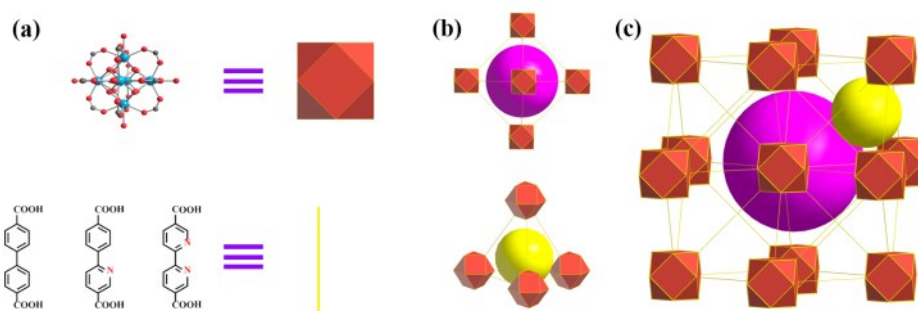


Figure S2. a) Hexanuclear cluster based on Eu^{3+} ions and organic ligands. b) Octahedral cage and tetrahedral cage. c) Crystal structure of $\text{Eu}(\text{BPDC-}x\text{N})$ ($x=0,1,2$). Eu, sky-blue; C, gray; O, red; H atoms and free solvent molecules are omitted for clarity.

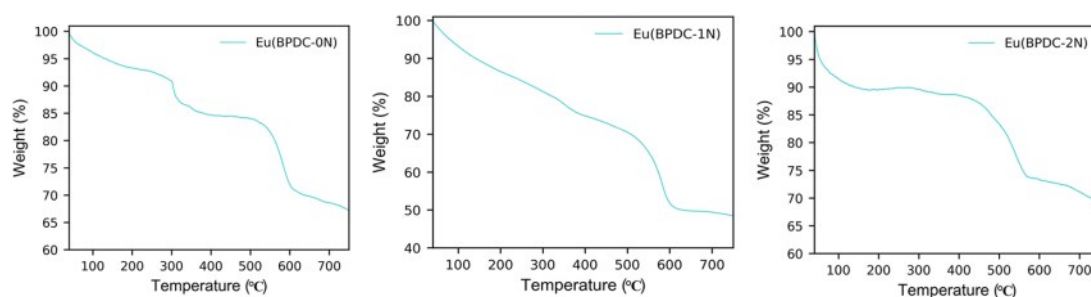


Figure S3. TGA curves of $\text{Eu}(\text{BPDC-}x\text{N})$ ($x=0,1,2$).

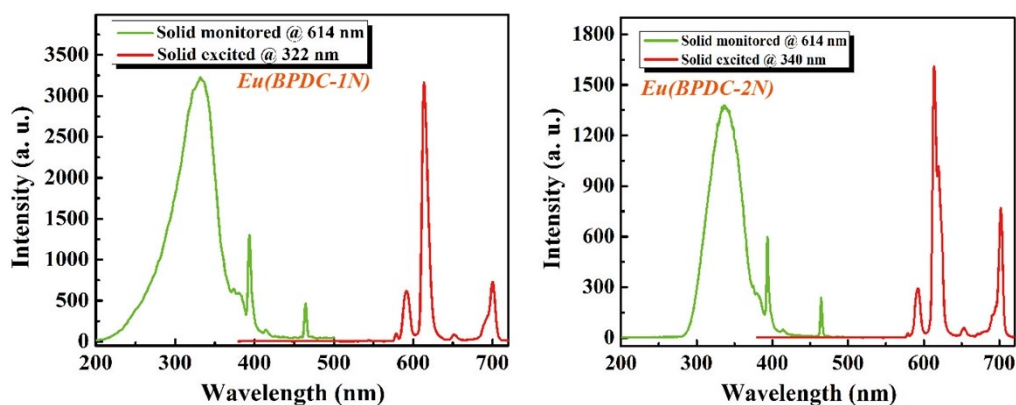


Figure S4. Excitation and emission spectra of Eu (BPDC-1N) and Eu (BPDC-2N)

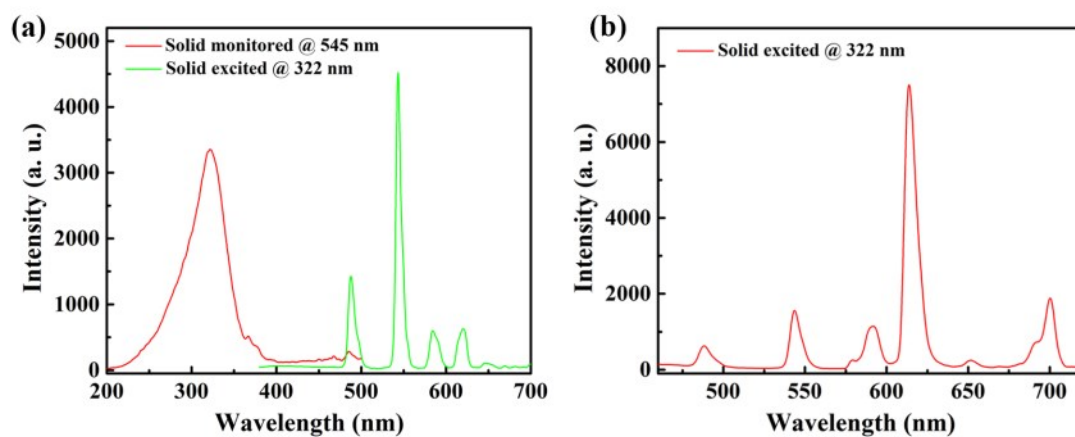


Figure S5. Excitation and emission spectra of Tb(BPDC-1N) (a) and $\text{Eu}_{0.002}\text{Tb}_{0.998}$ (BPDC-1N) (b) at solid state.

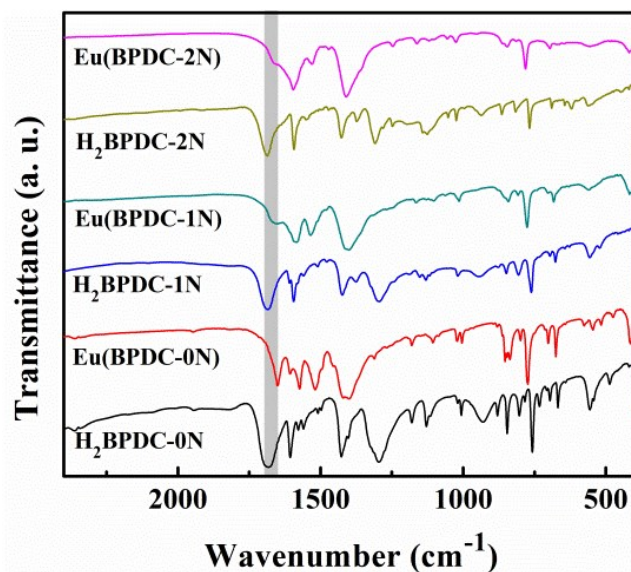


Figure S6 FT-IR spectra of organic ligands H₂BPDC-*x*N (*x*=0,1,2) and Eu(BPDC-*x*N) (*x*=0,1,2). Compared with organic ligands, the vibrational absorption peak of carbonyl group in Ln-MOFs becomes weaker and shifts from 1682 cm⁻¹, 1682 cm⁻¹, 1684 cm⁻¹ to 1647 cm⁻¹, 1654 cm⁻¹, 1659 cm⁻¹, respectively. Which indicates the carboxyl group coordinated with lanthanide ions.

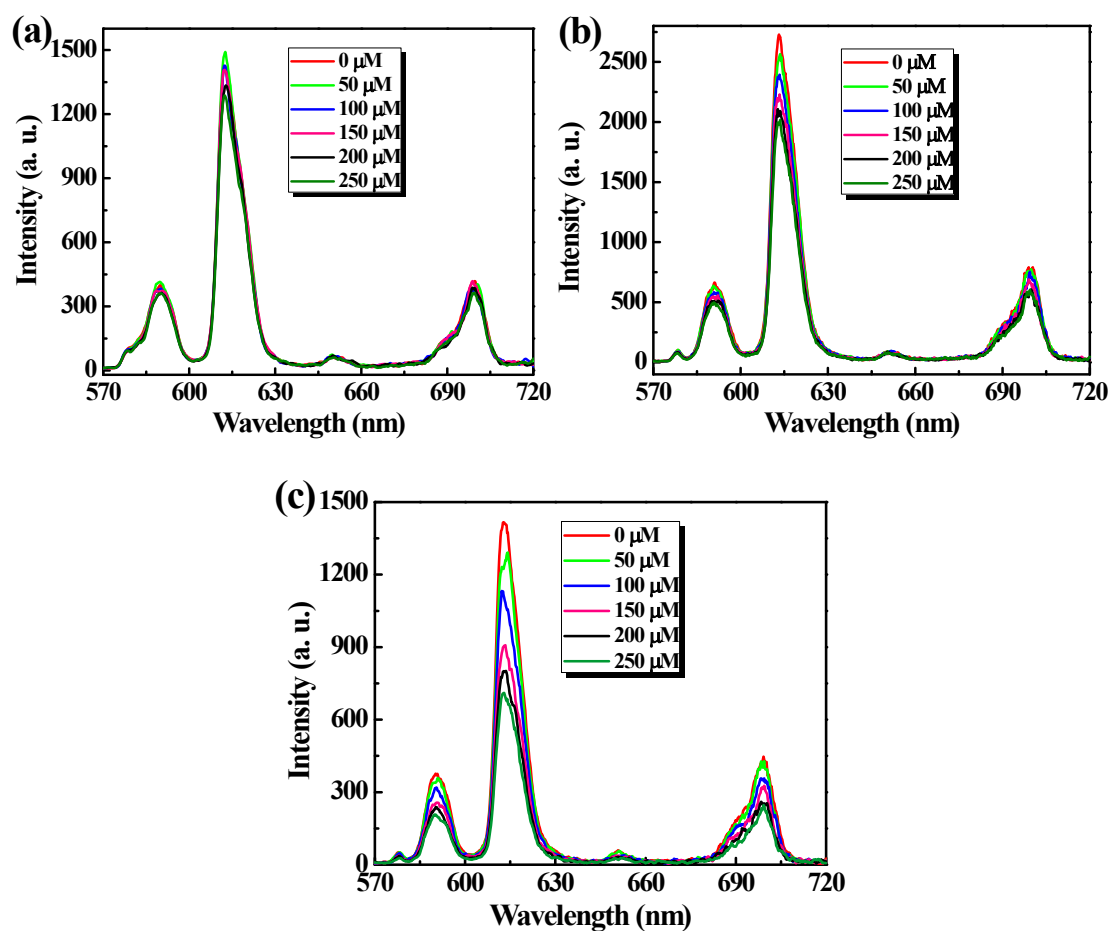


Figure S7. Fluorescence responses of Eu(BPDC-*x*N) (*x* = 0, 1, 2) toward NAD.

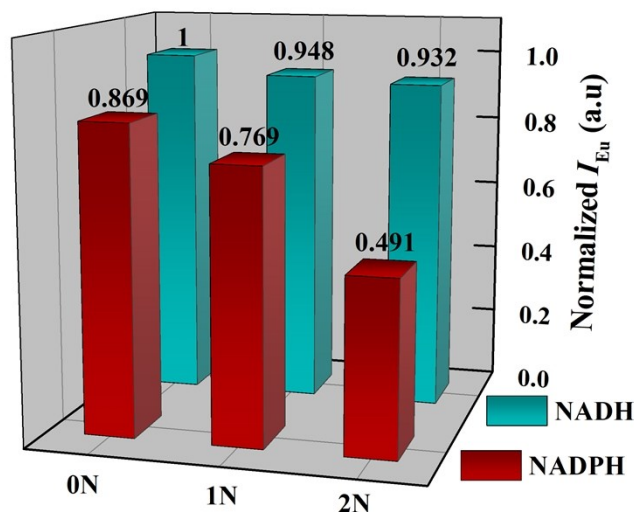


Figure S8. Fluorescence quenching of **Eu(BPDC- x N)** ($x = 0, 1, 2$) toward NADH and NADPH.

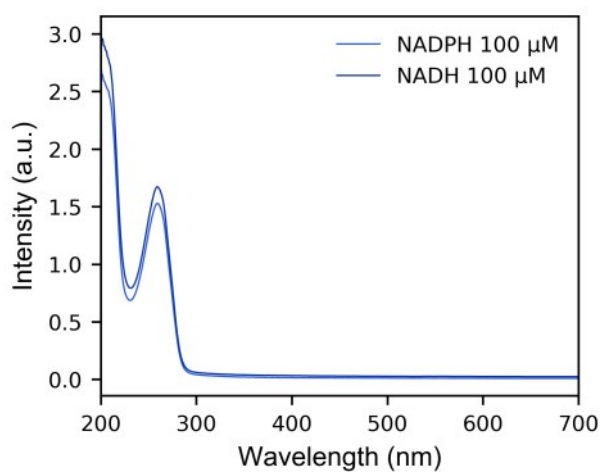


Figure S9. Absorption spectra of NADPH and NADH in water.

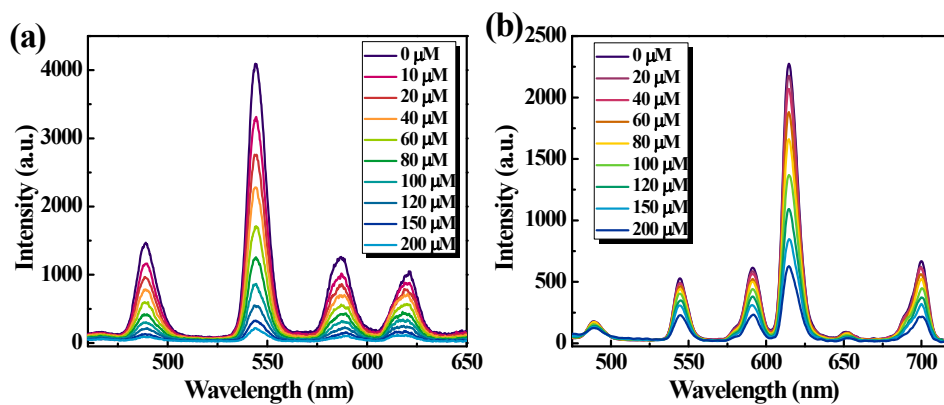


Figure S10 Fluorescence responses of (a) **Tb(BPDC-1N)** and (b) **Eu_{0.002}Tb_{0.998}(BPDC-1N)** toward NADPH.

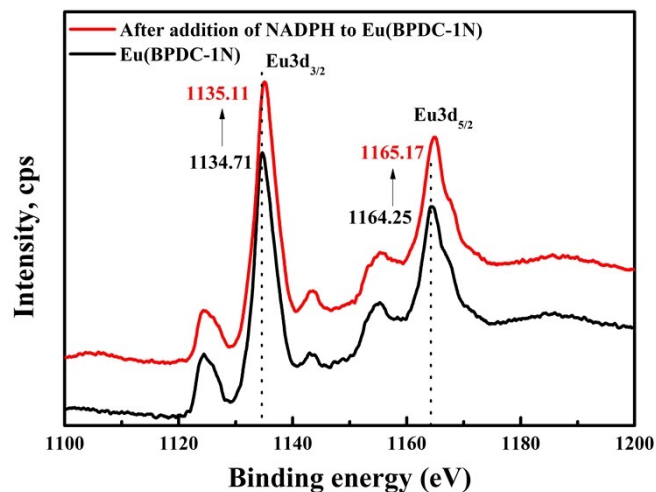


Figure 11. The XPS spectra of 3d electrons of Eu

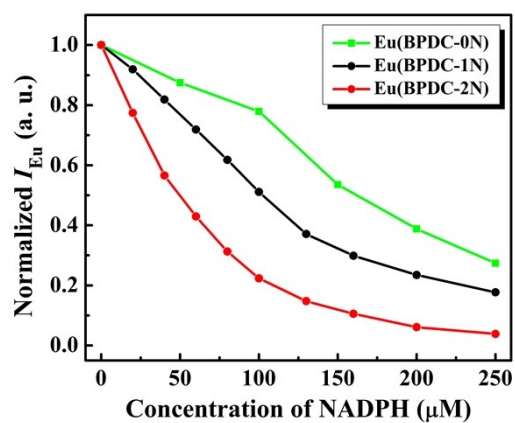


Figure S12. Normalized intensity of Eu(BPDC-xN) ($x = 0, 1, 2$)