

Supporting Information

Water-soluble lanthanide coordination polymers particles with white-light emission and color tuning

Kaiqi Fan ^a, Xiaobo Wang ^b, Yongpeng Ma ^a, Yu Li ^a, Guanglu Han^{*a}, Zhigang Yin^{*a}, Jian Song^{*c}

Table of contents:

Experimental section	2
Figure S1	2
Figure S2	3
Figure S3	3
Figure S4	5
Figure S5	5
Figure S6	6
Figure S7	7
Figure S8	8
Table S1	8
Figure S9	8

Experimental section

1 Materials and reagents

Branched poly(ethylenimine) (PEI, Mw = 10000, 99%). Compound TPy was synthesized by the follow procedrues. All other reagents were of analytical reagent grade and used without further purification. Britton–Robinson (BR) buffer solutions was prepared by mixing 0.04 mol dm⁻³ of boric acid, phosphoric acid and acetic acid, and then adjusted to the required pH value with 0.2 mol dm⁻³ of NaOH solution. Ultrapure water with resistivity 18.2 MΩ·cm was used throughout the experiment.

1.1 Synthesis of TPy

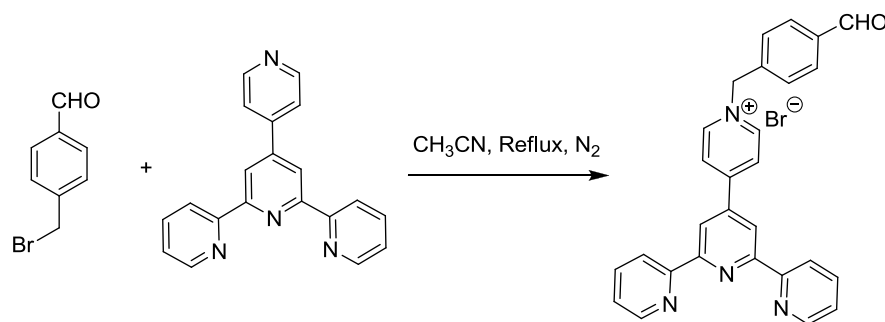


Fig. S1. Synthetic route to compound TPy.

A mixture of 4'-(4-Pyridyl)-2,2':6',2''-terpyridine (0.16 g, 0.52 mmol) and 4-(bromomethyl)benzaldehyde (0.308 g, 1.55 mmol) was added to acetonitrile (20 mL) under the protection of N₂ and the solution was stirred and refluxed for 24 h. After the mixture was cooled to room temperature, the resulting precipitate was filtered off, washed with acetonitrile, and recrystallized with CH₃OH/CHCl₃ (v/v=1/1) to obtain compound P with a yield of 78%. Mp: 210.1–211.2 °C. The ¹H and ¹³C NMR spectra of compound TPy are shown in Fig. S2-S3. ¹H NMR (400 MHz, DMSO-*d*₆, 298 K) δ (ppm): 10.06 (s, 1H), 9.42 (d, J = 6.6 Hz, 2H), 8.90 (s, 2H), 8.81 (dd, J = 18.3, 5.4 Hz, 4H), 8.70 (d, J = 7.9 Hz, 2H), 8.08 (td, J = 7.8, 1.4 Hz, 2H), 8.02 (d, J = 8.1 Hz, 2H), 7.79 (d, J = 8.1 Hz, 2H), 7.58 (dd, J = 7.0, 5.1 Hz, 2H), 6.11 (s, 2H). ¹³C NMR (400 MHz, DMSO-*d*₆, 298 K) δ (ppm): 193.29, 156.82, 154.65, 153.92, 149.91, 146.15, 144.37, 140.99, 138.24, 136.98, 130.64, 129.74, 127.04, 125.54, 121.70, 119.38, 62.80. HRESI-MS: *m/z* calcd for [M - Br]⁺ C₂₈H₂₁N₄O⁺, 429.1715; found 429.1719.

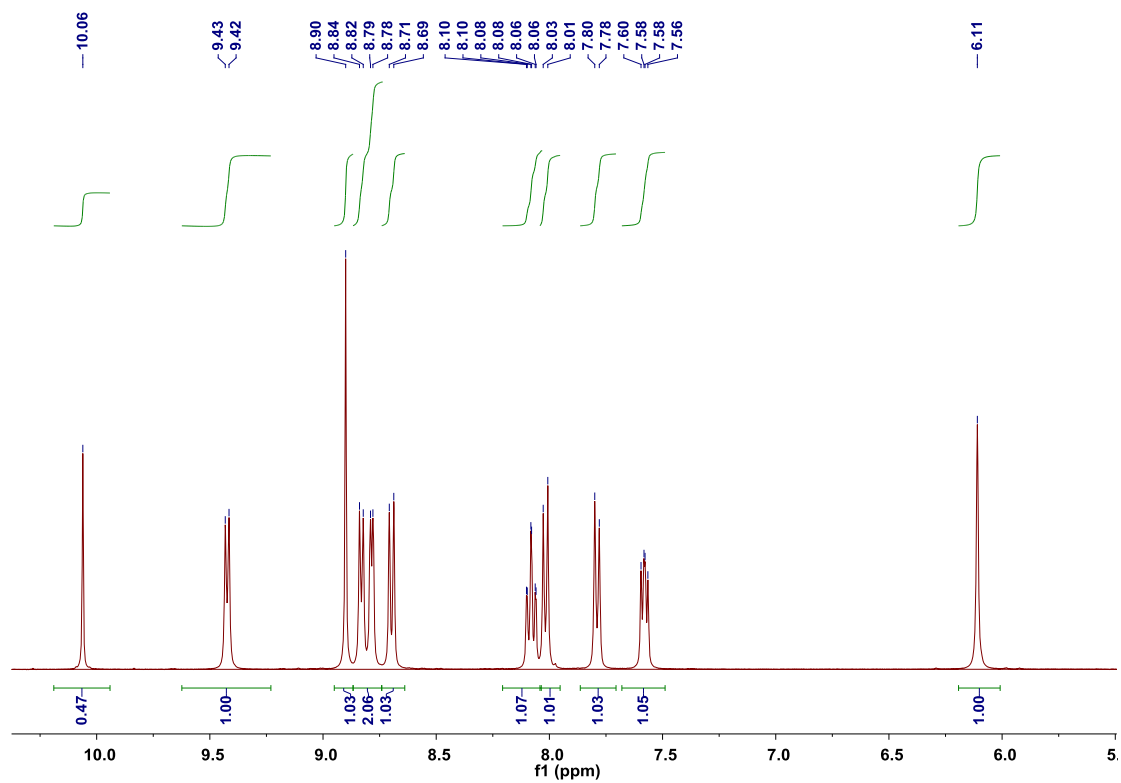


Fig. S2 ^1H NMR spectrum (400 MHz, DMSO- d_6 , 298 K) of compound TPy.

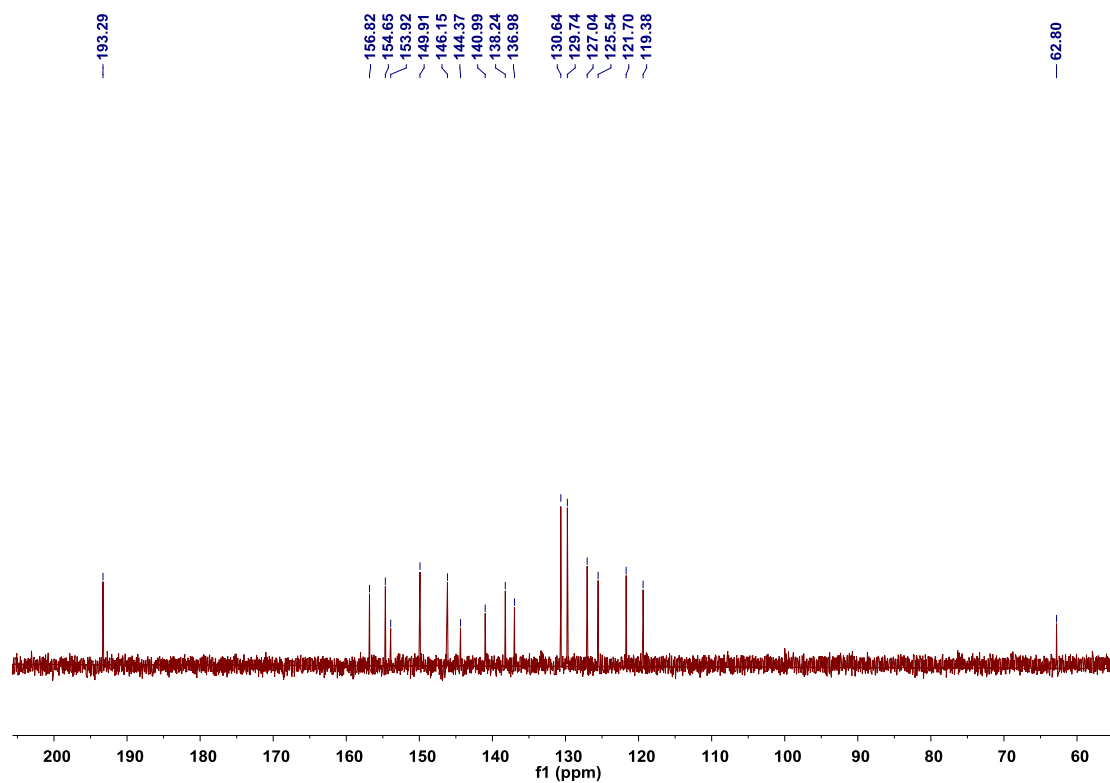


Fig. S3 ^{13}C NMR spectrum (400 MHz, DMSO- d_6 , 298 K) of compound TPy.

1.2 Synthesis of TPY/PEI polymer particles (TPY/PEI PPs)

The TPY/PEI PPs were prepared from PEI and compound TPY via Schiff base reaction. In brief, 100 μL of PEI (0.1 g/mL, 0.001 mmol) reacted with 800 μL of Britton–Robinson (BR) buffer (0.04 M, 0.032 mmol, pH 5) by stirring for about 10 min, and then TPY (0.02 g, 0.04 mmol) dissolved in 100 μL of DMSO was added. Subsequently, the mixture was stirred and heated at 80 $^{\circ}\text{C}$ for 4 h via hydrothermal treatment. The as-prepared TPY/PEI PPs solutions were purified with a dialysis membrane (molecular weight cutoff 3500 Da) for more than 24 h, and then the TPY/PEI polymer inside the dialysis bag were collected by lyophilization. Disperse it directly into a certain volume of water to obtain a certain concentration of TPY/PEI PPs solution.

1.3 Synthesis of Ln-CPPs

To the TPY/PEI PPs solution (0.02 g/mL, 600 μL), the aqueous solution of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}/\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.14 M, 50 μL) was added and the mixture was sonicated until a clear solution was attained. Next, the solutions were left undisturbed for 24 h at ambient temperature resulting in stable Ln-CPPs.

2 Instrumentation

NMR experiments: All 400 MHz NMR studies were carried out on a Bruker DPX 400 MHz spectrometer using cryo probe in D_2O and $\text{DMSO}-d_6$.

Mass spectrometry: Mass spectra were recorded on a TOF-QII high-resolution mass spectrometer.

Scanning Electron Microscope (TEM): The morphologies of the PPs were obtained by a Hitachi S-4800 SEM instrument operating at 3–5 kV. Samples were prepared by dropping the samples on the thin aluminum sheets. We then coated the samples with a thin layer of Au before the experiment.

FT-IR spectroscopy: IR spectra were collected by a FTS3000 spectrometer with KBr pellets. The samples were prepared by drying the PPs and Ln-CPPs on glass slides under vacuum for 24 h.

UV spectroscopy: UV spectroscopy was performed on a Jasco V-570 UV/vis/NIR spectrophotometer. The path length of the quartz cell was 1 mm.

Fluorescence emission spectroscopy: Steady state fluorescence and excitation spectra were acquired on either a Hitachi F-2500 fluorimeter or on an Edinburgh Instruments FLS980 phosphorimeter equipped with single monochromators. A photoluminescence decay curve was recorded at room temperature using the time-correlated single photon counting technique, with excitation at 330 nm. The quantum yield of Ln-CPPs was determined in an FLS980 fluorescence spectrophotometer (Edinburgh Instruments, Inc., Livingston, U.K.). The emission and excitation light was scattered and collected in an integrating sphere and detected with a photomultiplier with a detection range of 200–1010 nm. As for the Ln-CPPs that were dispersed in water, pure water was used as the reference. The quantum yield is calculated with the formula $\text{QY} = P_{\text{sample}} / (S_{\text{references}} - S_{\text{sample}})$ in which P_{sample} is the emission intensity and $S_{\text{references}}$ and S_{sample} represent the scattered light intensities of the reference and sample. The CIE color coordinates were calculated from the emission data using the color calculation software of FLS980 instrument.

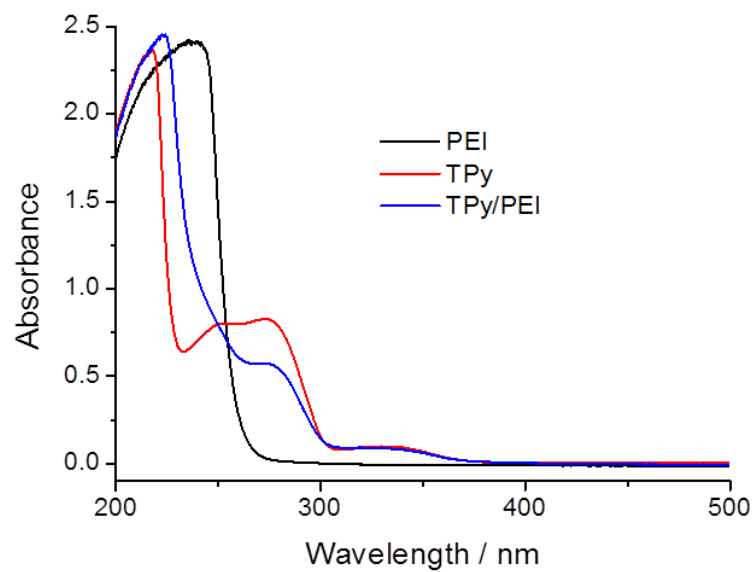


Fig. S4 UV-vis absorption spectra of PEI (0.5 mg/mL), TPy (1 mM in EtOH), and TPy/PEI PPs (0.5 mg/mL).

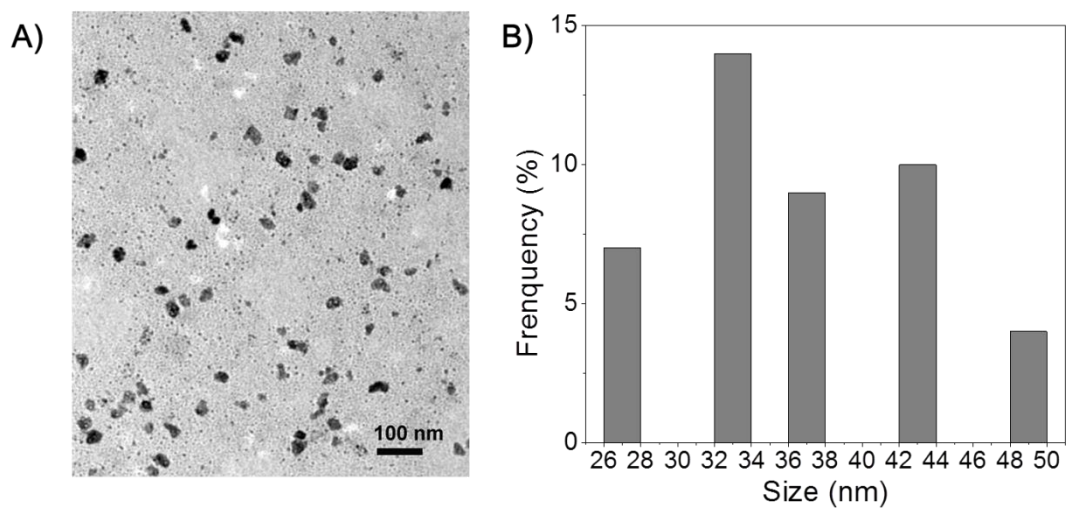


Fig. S5 (A) The TEM image of TPy/PEI PPs. (B) The particle size distribution histogram of TPy/PEI PPs.

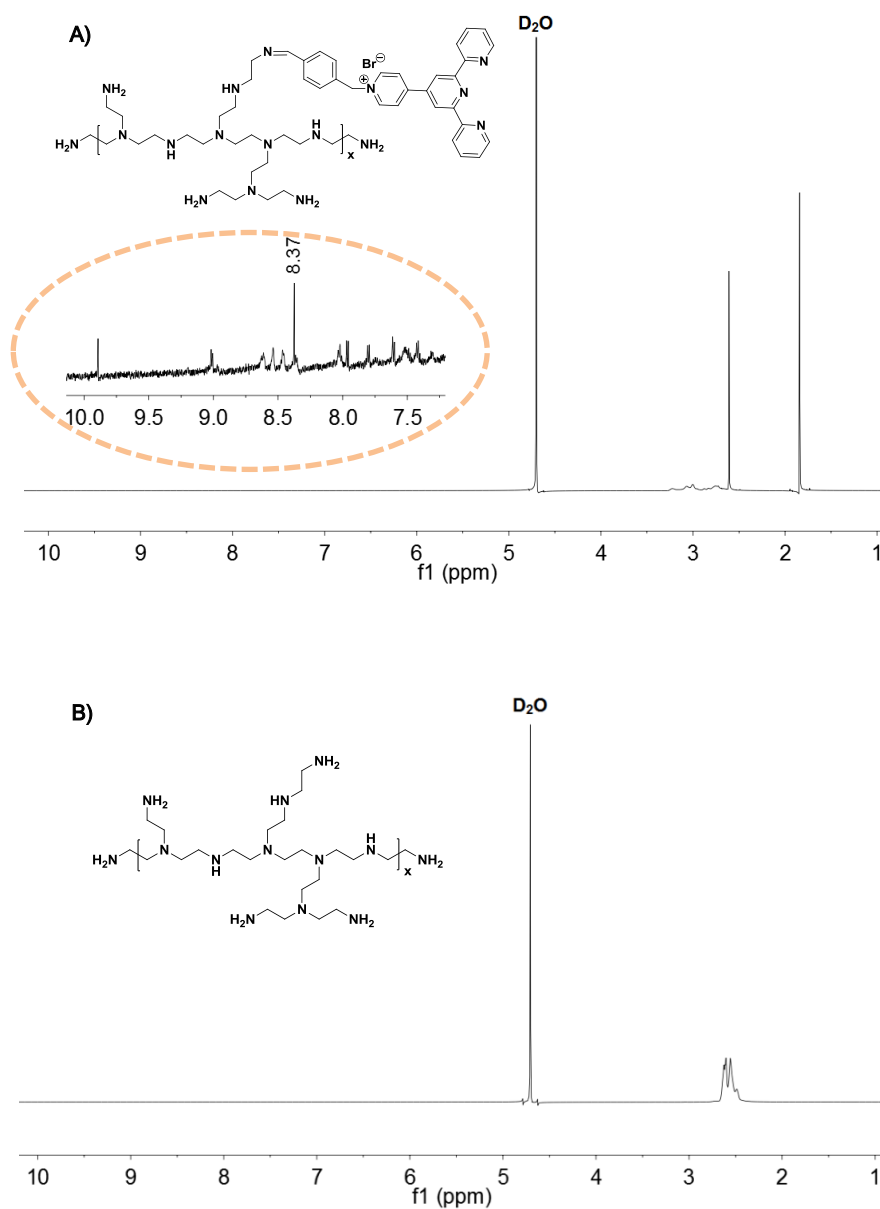


Fig. S6 ¹H NMR spectra of TPY/PEI PPs (A) and PEI (B) (D₂O, 400 MHz). Inset of A is a partial expansion of ¹H NMR spectrum of TPY/PEI PPs.

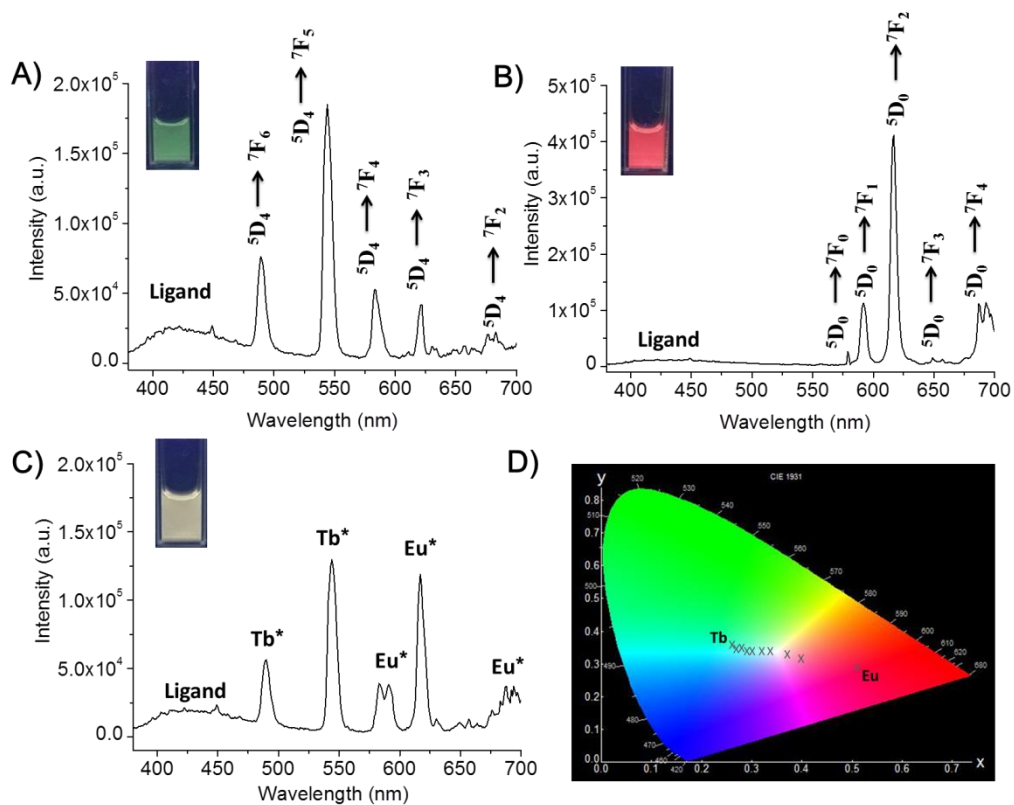


Fig. S7 Emission spectra of (A) Tb-CPPs, (B) Eu-CPPs, (C) Tb/Eu-CPPs and (D) the corresponding CIE 1931 chromaticity diagram ($\lambda_{ex} = 330$ nm), ($Tb^{3+}/Eu^{3+} = 1:0, 8:1, 7:1, 6:1, 5:1, 4:1, 3:1, 2:1, 1:1, 0:1$, respectively).

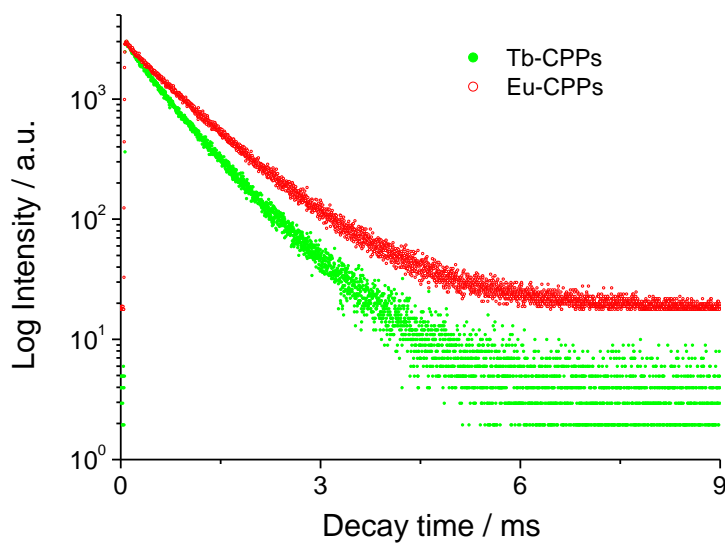


Fig. S8 Luminescence decay curves from $5D_0$ excited state of Eu(III) in Eu-CPPs 4 ($\lambda_{\text{ex}} = 330$ nm; $\lambda_{\text{em}} = 544$ nm) and from $5D_4$ excited state of Tb(III) in Tb-CPPs ($\lambda_{\text{ex}} = 330$ nm; $\lambda_{\text{em}} = 616$ nm) in H_2O .

Table S1. Luminescence Data (Lifetimes, τ , and Quantum Yields, Φ) for the Ln- CPPs in H_2O .

Complexes	Φ (%) ^a	τ (ms) ^b
Tb-CPPs	4.3	0.35
Eu-CPPs	11.3	0.81

^a Overall quantum yield in H_2O at a 330 nm excitation wavelength within an experimental uncertainty of $\pm 15\%$. ^b Luminescence decay lifetime measured for $5D_0$ (Eu^{III}) and $5D_4$ (Tb^{III}) excited states within an experimental uncertainty of $\pm 10\%$.

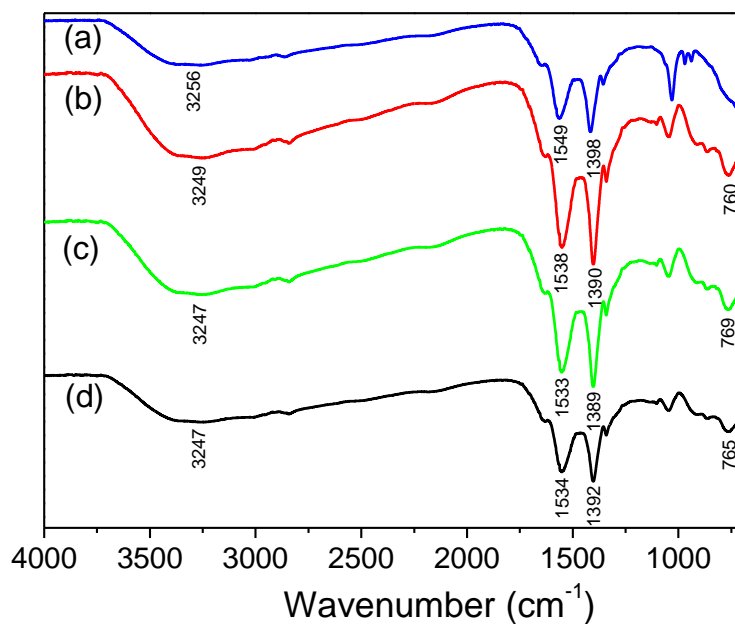


Fig. S9 FT-IR characterization of the TPY/PEI PPs (a), RL CPPs (b), GL CPPs (c) and WL CPPs (d).