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Aggregation-Induced White Emission of Lanthanide Metallopolymer and Its Coating on Cellulose Nanopaper for White-Light Softening

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1.1. Materials and Methords

All chemicals were reagent grade and used without further purification. UV-vis spectra (200–800 nm) of the materials were recorded using a Cary 300 UV spectrophotometer. PL excitation spectra and steady-state visible fluorescence were measured with a PTI Alphascan spectrofluorometer (Photon Technology International) and visible decay spectra on a pico-N_2 laser system (PTI Time Master). The luminescent absolute overall quantum yield (Φ) of Poly-Eu-Tb-CNFs in solid state were determined by the steady-state spectrometer (FLS-980, Edinburgh) using a 450 W Xe lamp and an integrating sphere. Stress-strain curves of the nanopapers were obtained using a universal testing machine (CMT6503, Shenzhen, SANS Test Machine Co. Ltd.). The thickness of nanopaper was measured using a paper thickness meter (DC-HJY03, Sichuan, China, working precision is 0.001 mm). Surface morphology of the Poly-Eu-Tb was imaged based on scanning electron microscopy (SEM, JEOL, Japan). Poly-Eu-Tb aggregated particles were prepared using a simple precipitation method: 0.1 mg/mL DMF solution was quickly added into Diox and quick stir (v/v = 1/1). Further, the mixtures solution was lyophilized to yield the desired product. For comparison, non-aggregated particles were also prepared from pure DMF solution of Poly-Eu-Tb with the similar method. Leica TCS SP5 confocal

laser scanning microscopy (Leica microsystems CMS GmbH, Manheim, Germany) was applied to study the fluorescence of Poly-Eu nanopaper.

1.2. Synthesis of mono-lanthanide metallopolymer Poly-Tb, Poly-Eu and Poly-Gd

Tepyrine-based polymer (Poly) was prepared according to a published procedure.[1] Poly (100 mg) was dissolved in 10 mL of deionized water. Then, 3 mL DMF containing $TbCl_3 \cdot 6H_2O$ (0.018 mmol) was added to the solution, and the mixture was stirred for 6 h and then precipitated with diethyl ether. Subsequent filtration gave the product as a white solid which afforded Poly-Tb after drying in a ventilated for several days. Similarly, Poly-Eu and Poly-Gd were prepared.

1.3. Preparetion of cellulose nanofibrils (CNFs)

10 g of the pulverized poplar pulp board was taken and 60 mL of distilled water, 1 mL of glacial acetic acid, and 2 g of sodium chlorite were added, and the mixture was heated in a 75 °C constant temperature water bath. After 3 h, 0.5 mL of glacial acetic acid and 2 g of sodium chlorite were added, and the reaction was continued for 6 h until the product became white, and washed repeatedly with distilled water until the filtrate was not acidic, and dried in a vacuum oven at 50 °C to a constant weight. 5 g of the dried product was added to a mass fraction of 4% NaOH, and treated at 60℃ for 2 h, and then repeatedly washed with distilled water until the filtrate was not alkaline, and dried in a vacuum oven at 50℃ to a constant weight. Pure cellulose is obtained. After the pure cellulose was uniformly dispersed by an ultrasonic machine, the solution was treated at a rate of 3000 r/min for 20 min. The lower layer precipitate was collected and homogenized to prepare CNFs, which was extracted and filtered

and dried at room temperature to produce optical haze nanopaper.

1.4. Determination of lanthanide ions concentration

Lanthanide ions concentration was preliminary calculated using the formula [Ln] = [Eu] +[Tb] = $\frac{m}{[M_{unit} + M_{Ln}][V_{DMF} + V_{Doix}]}$, where m is the mass of Poly-Eu-Tb, M_{Ln} the molecular weight of Ln^{3+} ions, M_{unit} the molecular weight of each Tpy unit was connected to about 45 repeating HEAA units, and V the volume of DMF or Doix.

1.5 Synthesis of precursor polymer (Poly)

According to a published procedure,[1] Poly{(N-(2-hydroxyethyl)acrylamide)-*co*-(2-(4-(4-(4-vinylbenzyloxy)phenyl)-6-(pyridin-2-yl)pyridin-2-yl)pyridine)} (Poly) was prepared from N-(2-hydroxyethyl)acrylamide (1.0 mL, 7.8 mmol) and 2-(4-(4-(4-vinylbenzyloxy)phenyl)-6-(pyridin-2-yl)pyridin-2-yl)pyridine (62 mg, 0.14 mmol) in dimethylformamide (DMF) and initiator reazobisisobutyronitrile (10 mg, 0.06 mmol) at 70 °C for 48 h in a Fisher-Porter glass reactor. The sticky product was dissolved in deionized water (10 mL) and precipitated from acetone (50 mL). After filtration and drying at 45 °C under vacuum, Poly as white solid was collected. GPC: PDI = 1.29, M_n = 22,736 Da. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.36 (br, 6H, -Ar), 7.52 (br, 6H, -Ar), 7.10 (br, 6H, -Ar), 5.08 (s, 2H, -CH_2-), 4.69 (s, 90H, -OH and -NH), 3.49 (br, 90H, -CH_2-N), 3.14 (br, 90H, -CH_2-O), 2.04 (br, 45H, -CH-), 1.43 (br, 90H, -CH-). IR (KBr, cm^{-1}): 3416 (b), 3297 (b), 3102 (m), 2936 (m), 2881 (m), 1659 (vs), 1562 (s), 1442 (m), 1389 (m), 1358 (w), 1286 (m), 1253 (w), 1065 (s), 618 (m).

Table S1. Photophysical Properties of low concentrations Poly-Eu-Tb (0.1 mg/mL)

precipitated in Diox (V_{DMF}/V_{Diox} = 1:0, 1:1, 1:2, 1:3, 1:4 and 1:5).

Poly-Eu-Tb	Quantum yield	Lifetime (μs)	
(v/v)	(%)	λ_{em} = 618 nm	λ_{em} = 545 nm
1/0	0.6	1,246	532
1/1	1.5	1,295	559
1/2	2.7	1,255	537
1/3	4.6	1,267	534
1/3	6.8	1,277	538
1/4	8.7	1,293	542

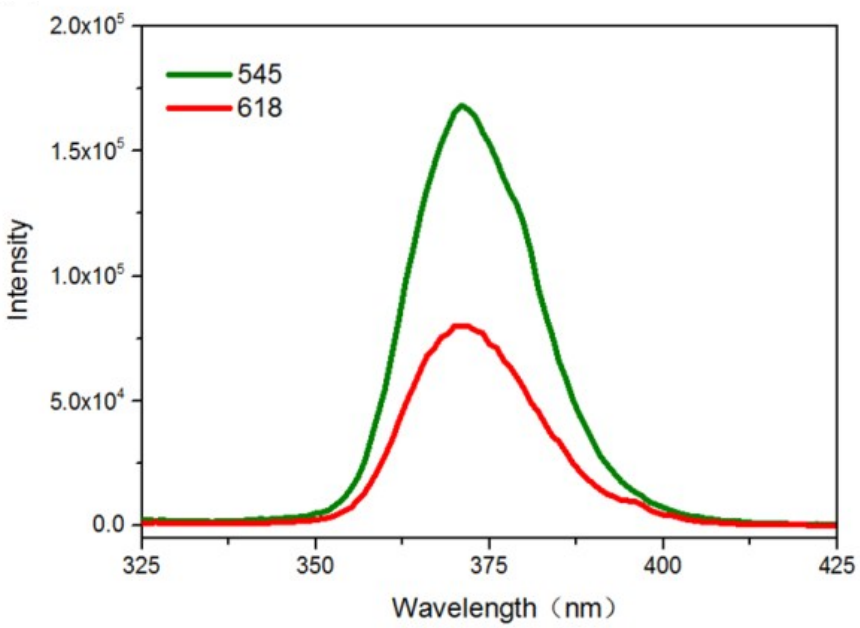

Fig. S1 Excitation spectra of Poly-Eu-Tb monitored at emission peaks of 545 and 618 nm, respectively.

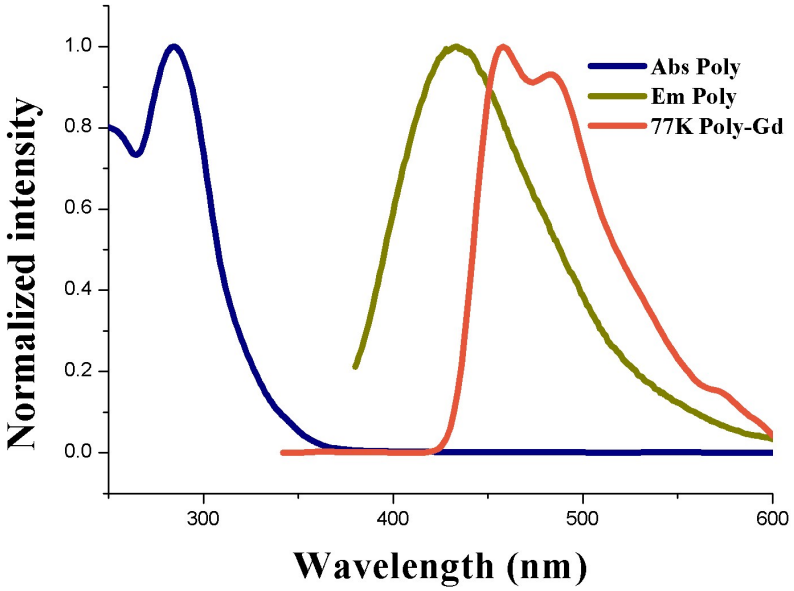

Fig. S2. UV-visible and emission spectra of Poly, and emission spectrum of Poly-Gd in DMF at 77K.

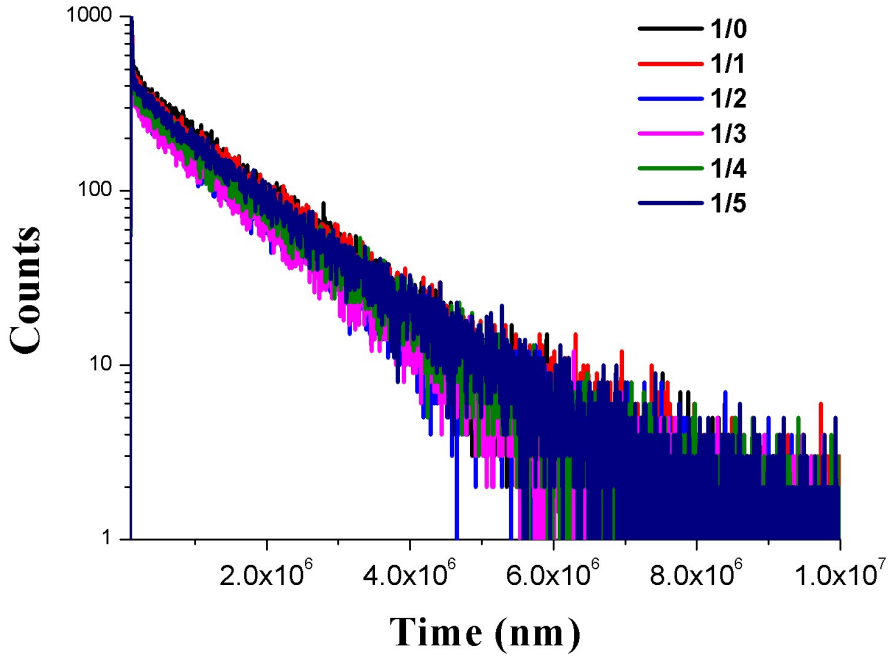

Fig. S3. Lifetime λ ($_{em}$ at 618 nm) of of low concentrations Poly-Eu-Tb (0.1 mg/mL) precipitated in Diox (V_{DMF}/V_{Diox} at 1:0, 1:1, 1:2, 1:3, 1:4, and 1:5).

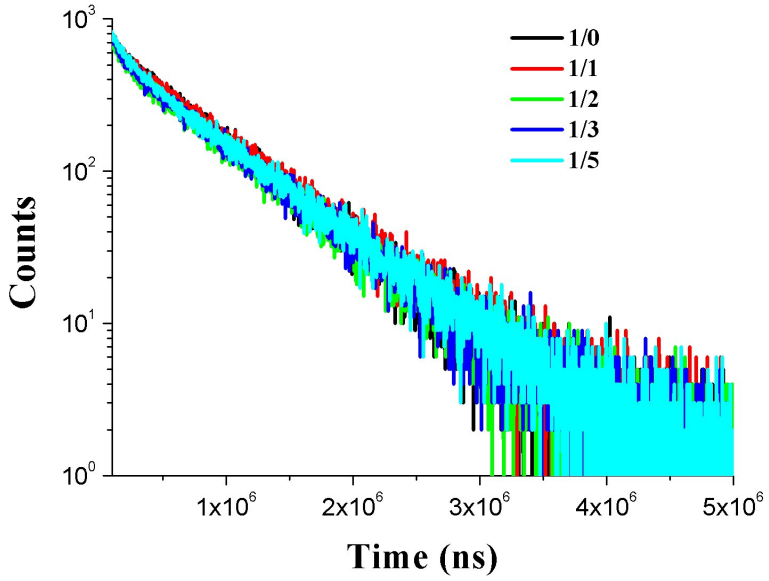

Fig. S4. Lifetime (λ_{em} at 545 nm) of of low concentrations Poly-Eu-Tb (0.1 mg/mL) precipitated in Diox (V_{DMF}/V_{Diox} at 1:0, 1:1, 1:2, 1:3, 1:4, and 1:5).

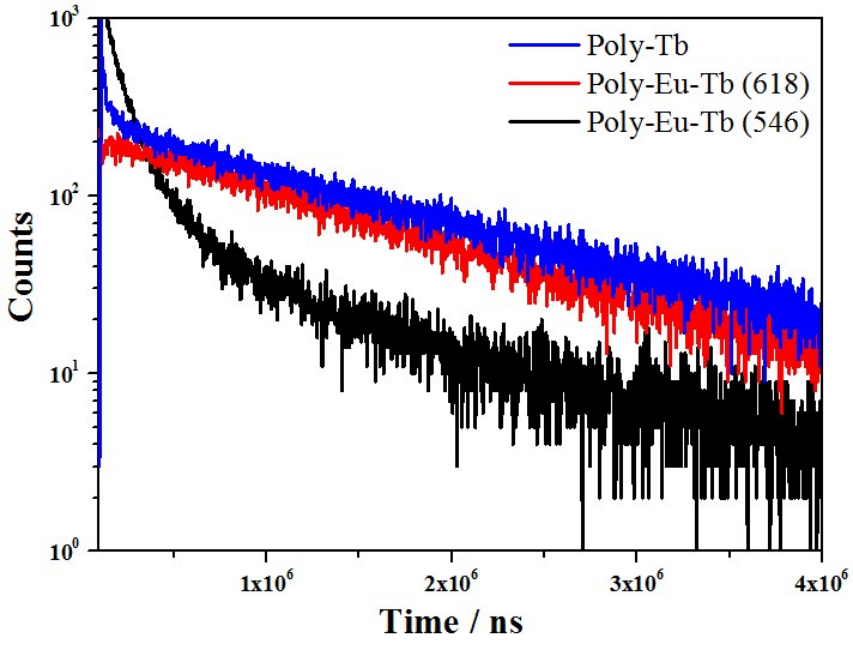

Fig. S5. The lifetime of Poly-Eu-Tb in pure DMF (λ_{em} = 546 nm and/or 618 nm).

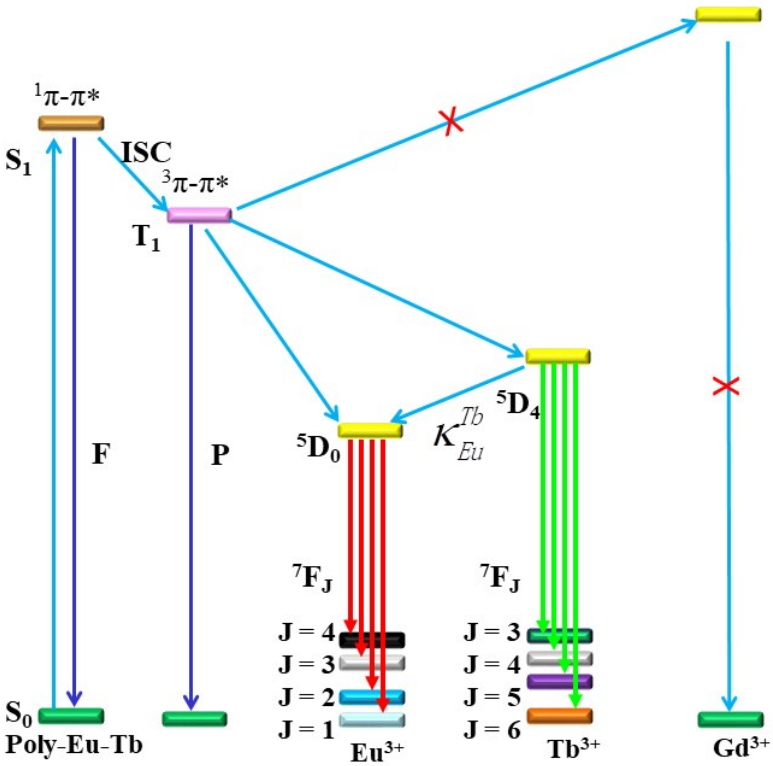

Fig. S6. The energy transfer process of Poly- Eu-Tb, Poly-Eu, Poly-Tb and Poly-Gd.

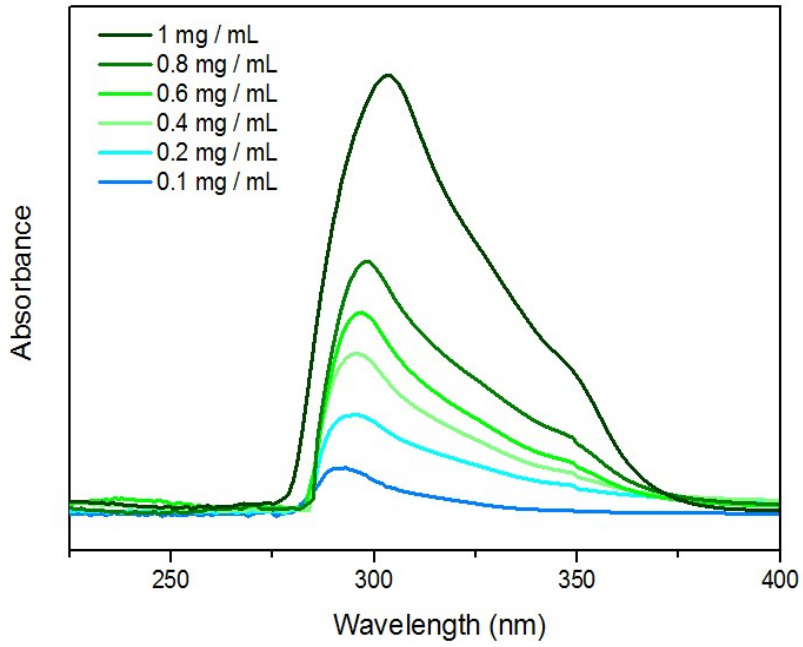

Figure S7. UV-visible spectra of Poly-Tb at different concentrations in DMF.

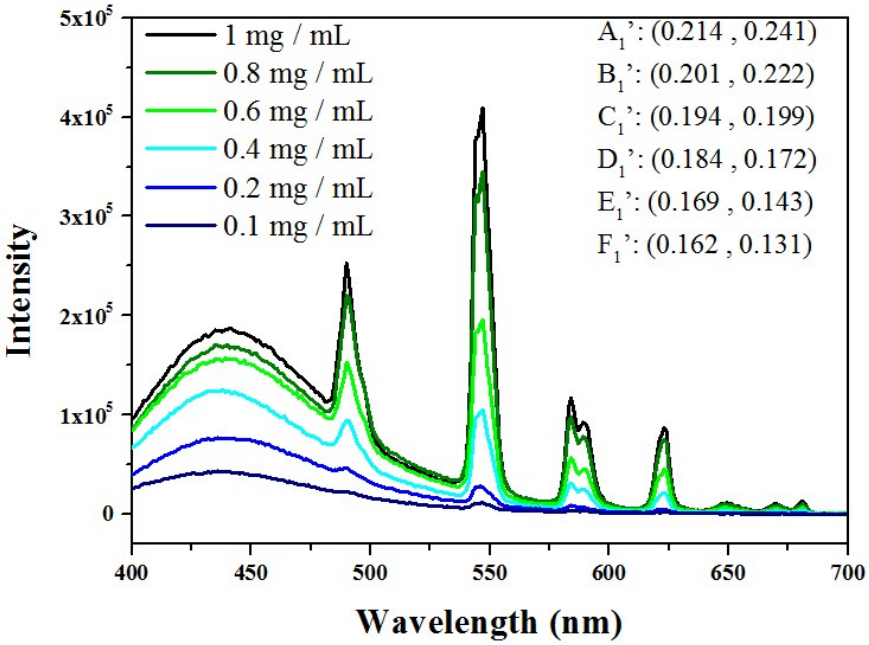

Figure S8. Emission spectra of Poly-Tb gradually reduced concentration from 1 to 0.1 mg/mL in pure DMF**.**

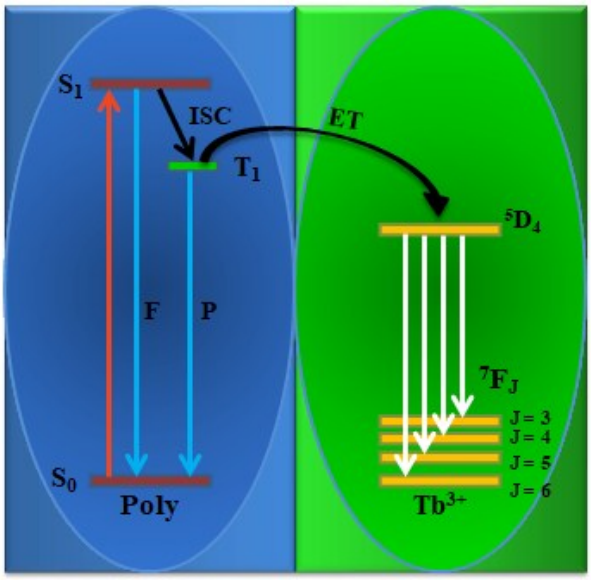

Figure S9. Schematic energy level diagram and energy transfer process of Tb^{3+} for Poly-Tb in the solid state.

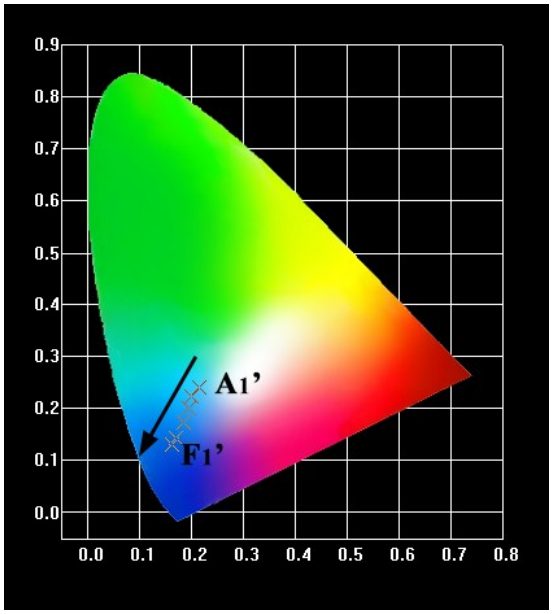

Figure S10. CIE chromaticity graphs of Poly-Tb gradually reduced concentration from 1 to 0.1 mg/mL in pure DMF**.**

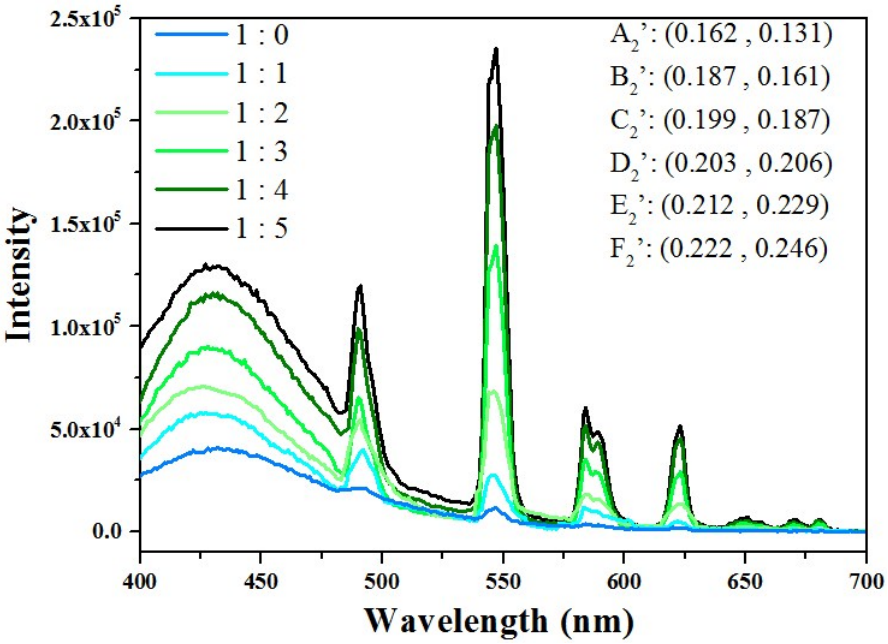

Figure S11. Emission spectra of Poly-Tb (0.1 mg/mL) after precipitated in Diox.

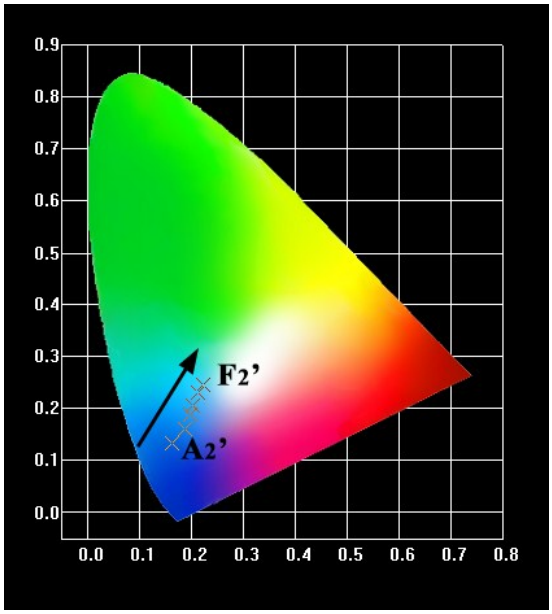

Figure S12. CIE chromaticity graphs of Poly-Tb (0.1 mg/mL) after reprecipitated in Diox.

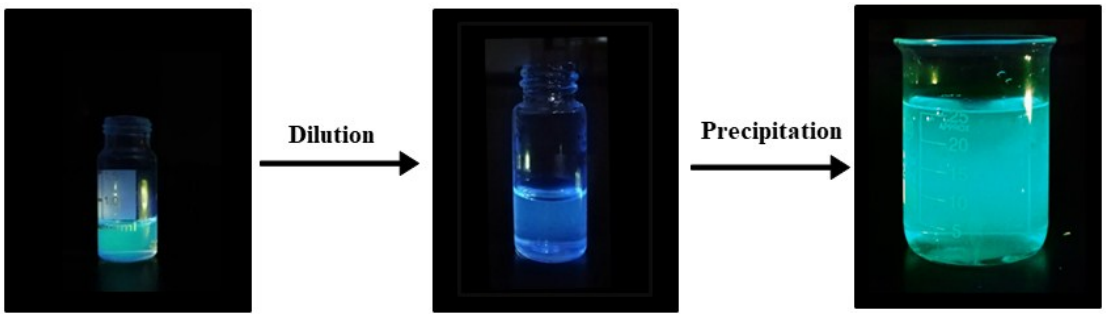

Figure S13. Luminescence behavior of Poly-Tb in pure DMF at 1mg/mL (left), pure DMF at 0.1mg/mL (middle); V_{DMF}/V_{Diox} = 1:5 (right).

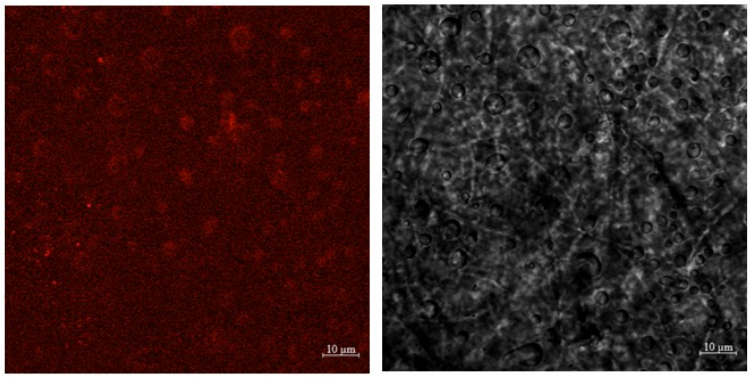

Figure S14. Fluorescence characterization of Poly-Eu nanopaper by confocal microscopy.

Reference

[1] Zhao Zhang, Hui Chang, Yifan Kang, Xinping Li, Huie Jiang, Bailiang Xue, Yaoyu Wang, Xingqiang Lü, Xunjin Zhu, Water soluble Ln(III)-based metallopolymer with AIE-active and ACQ-effect lanthanide behaviors for detection of nanomolar pyrophosphate, *Sensors and Actuators B: Chemical*, 282, 999-1007, **2019**.