

Supporting information for

Poly(MMA-co-FMA) as a Platform for Tuning Emission by Clicking with Luminescent Lanthanide Complexes

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Experimental section

Azobis(isobutyronitrile) (AIBN) was purified by recrystallization twice from absolute ethanol prior to use. Furfuryl methacrylate (FMA) and methyl methacrylate (MMA) were passed through basic alumina columns to remove inhibitor, respectively. All other chemicals were commercial products of reagent grade and were used without further purification.

The amounts of C, N and H of the complexes were measured using an Elementar Vario Micro Cube Elemental analyses (EA). Infrared spectra (IR) were recorded on a Nicolet Nexus-6700 spectrophotometer (ThermoFisher) in the region 4000-400 cm^{-1} using KBr pellets. ^1H NMR spectra of the samples were recorded on a Bruker plus 400 spectrometer with SiMe_4 as the internal standard in CDCl_3 and/or DMSO-d_6 at room temperature. The molecular weight was measured using a 1260 Infinity (Agilent) gel permeation chromatography (GPC) instrument with a refractive index detector. Calibration curves were determined using monodisperse poly(methyl methacrylate) with *N,N*-dimethylformamide as the mobile phase. The thermal gravimetric analysis (TGA) was conducted on a TGA-1 thermo gravimetric analyzer (Mettler Toledo, Switzerland) at a heating rate of 20 $^\circ\text{C}\cdot\text{min}^{-1}$ under air atmosphere from 50 to 800 $^\circ\text{C}$. Steady-state photoluminescence (PL) emission and excitation spectra were collected at room temperature in DMSO solution using steady-state spectrometer (FLS-920, Edinburgh) with a 450 W Xe lamp as the steady-state excitation source. A microsecond flash Xe lamp was used as the excitation source for the excited-state decay lifetimes

measurements (QM 40, Photo Technology International). Decay curves were fitted according to the double exponential function ($I = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$). The luminescence absolute overall quantum yield (Φ) for a sample in solution at room temperature was based on the absolute method using a 450 W Xe lamp and a calibrated integrating sphere (150 nm, BaSO₄ coating) in the QM 40 Fluorescence Spectrometers, and calculated by the following equation:

$$\Phi = [E_{in}(\lambda) - (1-\alpha)E_{out}(\lambda)]/[X_{empty}(\lambda)\alpha]$$

$$\alpha = [X_{out}(\lambda) - X_{in}(\lambda)]/X_{out}(\lambda)$$

In these equations, $E_{in}(\lambda)$ and $E_{out}(\lambda)$ are the integrated luminescence as a result of direct excitation of the sample and secondary excitation, respectively. The latter emission is due to reflected excitation light from the sphere walls hitting the sample. $X_{empty}(\lambda)$ is the integrated excitation profile with the empty sphere. α is the BaSO₄ film absorptance. $X_{in}(\lambda)$ is the integrated excitation when the sample lies directly in the excitation path and $X_{out}(\lambda)$ is the integrated excitation when the excitation light first hits the sphere wall. All of the spectra were recorded with the same excitation and emission monochromator slits.

The Commission Internationale de l'Eclairage (CIE) coordinate of each sample were calculated based on the international CIE standards.

Synthesis of the ligand 5-Maleimido-1,10-phenanthroline (MP).

MP was prepared according to a modified literature procedure.¹ A suspension of 1,10-phenanthroline-5-amine (800 mg, 4.1 mmol) and maleic anhydride (2.00 g, 20.4 mmol) in CH₂Cl₂ (40 mL) was heated to reflux for 4 h. After cooling to room temperature, the solid was filtered and washed with CH₂Cl₂. Then the dried solid (760 mg, 2.6 mmol) was added to a suspension of NaOAc (4.0 g) in Ac₂O (40 mL) and heated for 1 h at 100 °C. After cooling to room temperature, the mixture was poured into ice-water (200 mL) and stirred until the Ac₂O was decomposed completely. After extraction with CH₂Cl₂ (3×150 mL), the organic phase was washed with H₂O (3×150 mL), dried over MgSO₄, and concentrated to 20 mL. The addition of hexane (100 mL)

provoked precipitation of the product, which was isolated as a light yellow solid; yield: 398 mg (0.7 mmol, 49.2%). ^1H NMR (400 MHz, CDCl_3 , δ): 9.3-9.4 (m, 2H, Ar-H), 8.37-8.39 (m, 1H, Ar-H), 8.04-8.06 (m, 1H, Ar-H), 7.83 (s, 1H, Ar-H), 7.71-7.81 (m, 2H, Ar-H), 7.08 (s, 2H, -COCHCHCO-).

Synthesis of complexes Eu(DBM)₃MP, Tb(p-BBA)₃MP, La(BTZ)₃MP.

Eu(DBM)₃MP. A solution of dibenzoylmethane (0.673 g, 3 mmol), 5-maleimido-1,10-phenanthroline (0.275 g, 1 mmol), and sodium hydroxide (0.12 g, 3 mmol) in 8 mL mixed solvent (ethanol: dichloromethane = 5:3) was heated at 50 °C for 30 min with stirring. Europium chloride hexahydrate (0.367 g, 1 mmol) was dissolved in 4 mL of ethanol and added dropwise to the stirred ligand solution, inducing precipitation of a light yellow solid. The reaction was kept at 50 °C for another 2 h and then cooled to room temperature. The product was filtered and washed with warm ethanol, and dried for 24 h in a vacuum oven at 60 °C. Yield: 1.02 g (90.9%). Calc. for $\text{C}_{61}\text{H}_{45}\text{O}_8\text{N}_3\text{Eu}$: C, 66.55; H, 4.09; N, 3.82%. Found: C, 65.28; H, 3.98; N, 3.65%.

Tb(p-BBA)₃MP. A solution of p-BBA (0.679 g, 3 mmol), 5-maleimido-1,10-phenanthroline (0.275 g, 1 mmol), and sodium hydroxide (0.12 g, 3 mmol) in 8 mL mixed solvent (ethanol: dichloromethane = 5:3) was heated at 50 °C for 30 min with stirring. Terbium chloride hexahydrate (0.37 g, 1 mmol) was dissolved in 4 mL of ethanol and added dropwise into the stirred ligand mixed solution, inducing precipitation of a light yellow solid. The reaction was kept at 50 °C for another 2 h. Finally, the precipitate was obtained by filtration, washing with hot anhydrous ethanol and drying in a vacuum at 60 °C for 24 h. Yield: 0.87 g (78.2%). Calc. for $\text{C}_{58}\text{H}_{36}\text{O}_{11}\text{N}_3\text{Tb}$: C, 66.55; H, 4.09; N, 3.82%. Found: C, 62.90; H, 4.05; N, 3.27%.

La(BTZ)₃MP. A solution of BTZ (0.682 g, 3 mmol), 5-maleimido-1,10-phenanthroline (0.275 g, 1 mmol) in 8 mL mixed solvent (ethanol: dichloromethane = 5:3 v:v) was heated at 50 °C for 30 min with stirring. Lanthanum chloride heptahydrate (0.37 g, 1 mmol) was dissolved in 4 mL of ethanol and added dropwise into the stirred ligand mixed solution. The pH of the mixed solution was then

neutralized to 7–8 with a $1.0 \text{ mol}\cdot\text{L}^{-1}$ sodium hydroxide ethanol solution and the light yellow precipitate appeared. The reaction was kept at $50 \text{ }^\circ\text{C}$ for another 4 h. Finally, the precipitate was obtained by filtration, washing with hot ethanol and drying in a vacuum at $60 \text{ }^\circ\text{C}$ for 24 h. Yield: 0.67 g (61.3%). Calc. for $\text{C}_{55}\text{H}_{33}\text{O}_5\text{N}_6\text{S}_3\text{La}$: C, 60.44; H, 3.02; N, 7.89%. Found: C, 60.09; H, 3.13; N, 7.76%.

Synthesis of Poly(MMA-co-FMA).

Synthesis of copolymers were carried out in a feed ratio of 5:1 and 20:1 of MMA and FMA, respectively. We denote as **P5** and **P20**, respectively. In a typical experiment, MMA (1.50 g, 15 mmol), FMA (0.50 g, 3 mmol), AIBN (29.6 mg, 0.18 mmol) were dissolved in 5 mL dried 1,4-dioxane. The solution was degassed by three freeze–evacuate–thaw cycles before immersion into a preheated oil bath. Then keep stirring at $70 \text{ }^\circ\text{C}$ for 18 h. After cooling to room temperature, the obtained viscous mixture was diluted with 1, 4-dioxane (10 mL). The product was isolated by precipitation in ice-cold methanol twice and dried for 24 h in a vacuum oven at $60 \text{ }^\circ\text{C}$.

For poly(MMA-co-FMA) (**P5**): yield: 94.0%. ^1H NMR (400MHz, CDCl_3): δ 0.9-1.9 (- CH_3 and $>\text{CH}_2$ protons of the main-chain backbone), 3.5 (s, 3H, $-\text{OCH}_3$ of PMMA), 4.9 (s, 2H, $-\text{OCH}_2-$ of PFMA), 6.4 (m, 2H, $=\text{CH}-\text{CH}=\text{}$ of the furan ring), 7.4 (s, 1H, $=\text{CH}-\text{O}-$ of the furan ring). The copolymer has 84% MMA and 16% FMA, as determined by ^1H NMR. M_n (GPC) and M_w/M_n of the polymer were 30700 g mol^{-1} and 2.0, respectively.

For poly(MMA-co-FMA) (**P20**): yield: 88%. ^1H NMR (400MHz, CDCl_3): δ 0.9-1.9 (- CH_3 and $>\text{CH}_2$ protons of the main-chain backbone), 3.5 (s, 3H, $-\text{OCH}_3$ of PMMA), 4.9 (s, 2H, $-\text{OCH}_2-$ of PFMA), 6.3 (m, 2H, d, $\text{CH}-\text{CH}$ of the furan ring), 7.4 (s, 1H, $=\text{CHO}-$ of the furan ring). The copolymer has 94% MMA and 6% FMA, as determined by ^1H NMR. M_n (GPC) and M_w/M_n of the polymer were 23600 g mol^{-1} and 1.5, respectively.

Preparation of the Ln³⁺-containing metallopolymers by Diels-Alder cycloaddition reaction (D-A reaction)

P20 and Eu(DBM)₃MP in an equal molar ratio (refer to the reactive groups of furanyl to maleimide) were dissolved in 10 mL DMF. The mixture solution was degassed for 25 min and subsequently stirred at 100 °C for 48 h. The product was isolated by precipitation in 500 mL of ice-cold diethyl ether, washed with diethyl ether and warm ethanol for several times and then dried for 24 h in a vacuum oven at 60 °C to give a sample named **P20-Eu**.

P20-Tb(p-BBA)₃MP (P20-Tb) and **P20-La(BTZ)₃MP (P20-La)** were prepared in the same way as **P20-Eu**.

Synthesis of Eu³⁺-Tb³⁺-La³⁺-grafted metallopolymers by successive D-A reactions.

P5-Tb(p-BBA)₃MP (P5-Tb) was synthesized in the same way of the preparation of **P20-Eu** except that the feed molar ratio of **P5** and Tb(p-BBA)₃MP with the reactive groups of furan and maleimide was 2:1.

P5-Tb(p-BBA)₃MP-Eu(DBM)₃MP (P5-Tb₅₀Eu₁) was prepared by the D-A reaction between **P5-Tb** and Eu(DBM)₃MP with a Tb/Eu feed molar ratio of 50:1.

P5-Tb(p-BBA)₃MP-Eu(DBM)₃MP (P5-Tb₅₀Eu_{1.7}) was prepared by the D-A reaction between **P5-Tb** and Eu(DBM)₃MP with a Tb/Eu feed molar ratio of 50:1.7.

P5-Tb₅₀Eu₁La₃ was prepared using **P5-Tb₅₀Eu₁** to click with La(BTZ)₃MP by a feed molar ratio of 50:1:3 (Tb/Eu/La).

P5-Tb₅₀Eu₁La₁ was prepared using **P5-Tb₅₀Eu₁** to click with La(BTZ)₃MP by a feed molar ratio of 50:1:1 (Tb/Eu/La).

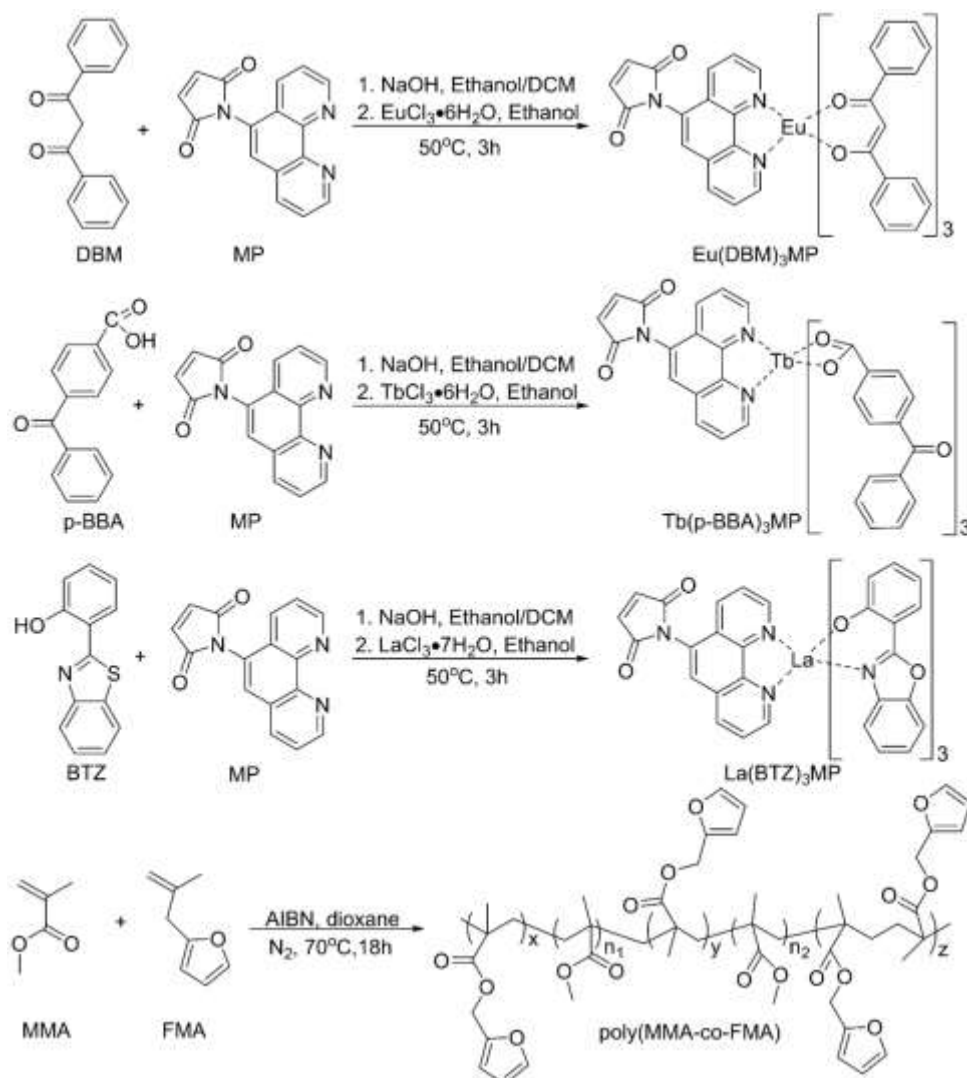
Synthesis of Eu³⁺-Tb³⁺-La³⁺-grafted metallopolymers P5-TbEuLa by one-step D-A reaction

P5-Tb₅₀Eu₁La_{0.95} with a stipulated feed reactive groups molar ratio of **P5/Tb/Eu/La** = 100:50:1:0.95 prepared in the same way as shown for **P5-Tb** except that lanthanide

complexes of Tb(p-BBA)₃MP, Eu(DBM)₃MP and La(BTZ)₃MP with mixed molar ratio (Tb/Eu/La = 50:1:0.95) were used instead of Tb(p-BBA)₃MP.

References

- (1). M. T. Reetz, M. Rentsch, A. Pletsch, A. Taglieber, F. Hollmann, R. J. Mondière, N. Dickmann, B. Höcker, S. Cerrone and M. C. Haeger, *ChemBioChem*, 2008, **9**, 552-564.



Scheme S1. Synthesis of Eu(DBM)₃MP, Tb(p-BBA)₃MP, La(BTZ)₃MP and poly(MMA-co-FMA).

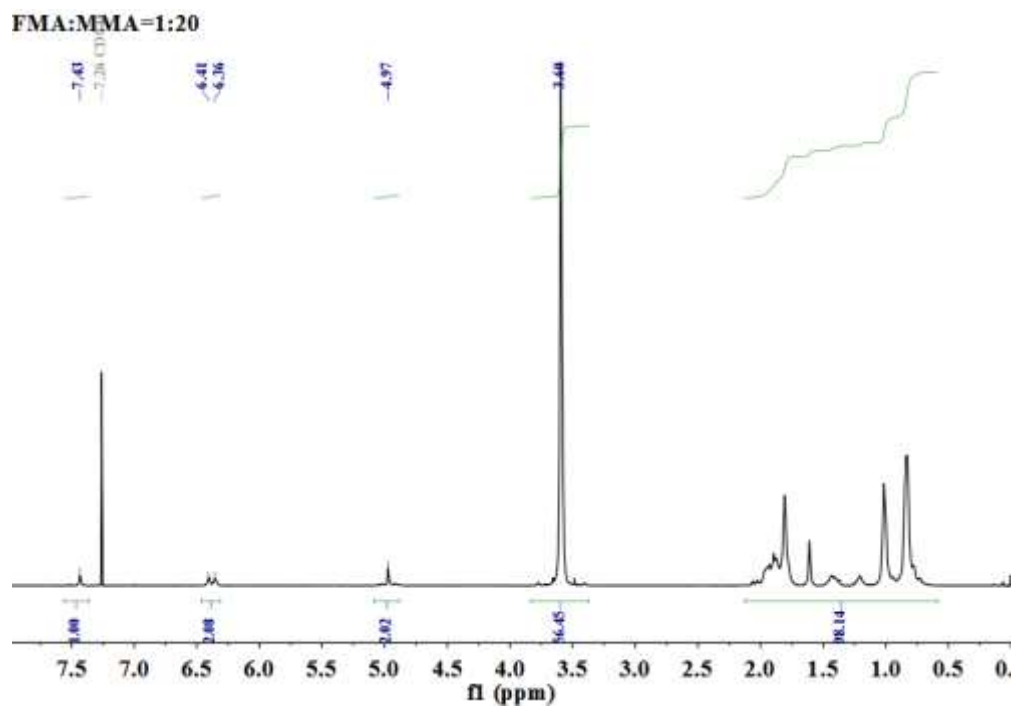


Figure S1. ¹H NMR spectrum of P20.

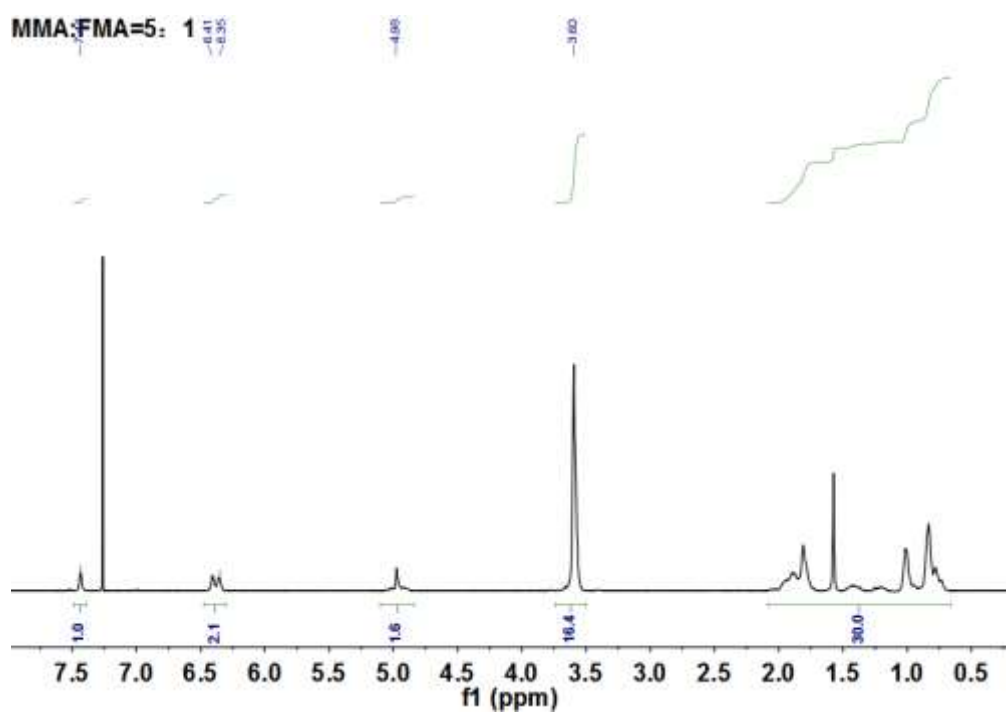


Figure S2. ¹H NMR spectrum of P5.

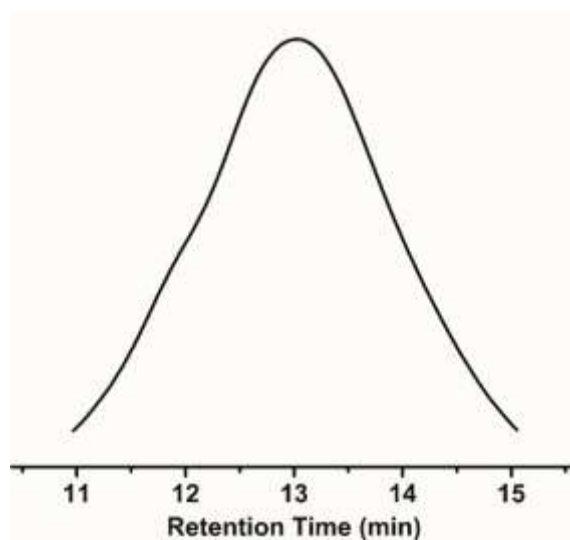


Figure S3. GPC Curve of **P5**.

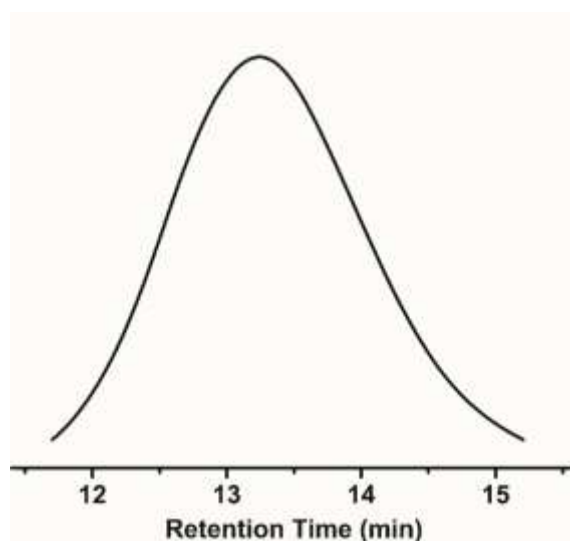


Figure S4. GPC Curve of **P20**.

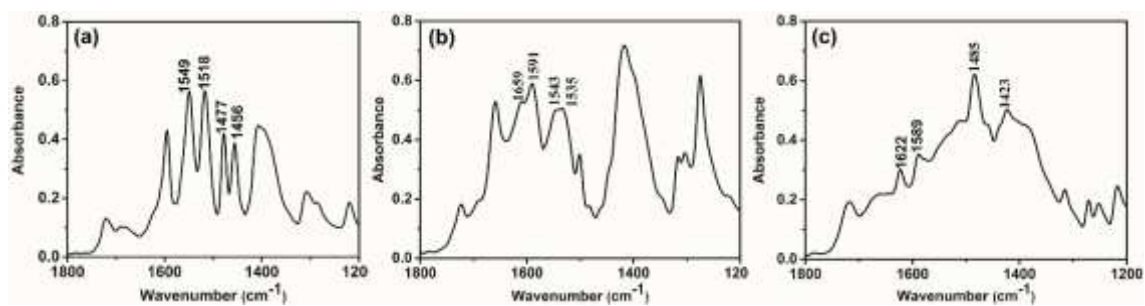


Figure S5. FT-IR spectra of (a) Eu(DBM)₃MP, (b) Tb(p-BBA)₃MP and (c) La(BTZ)₃MP.

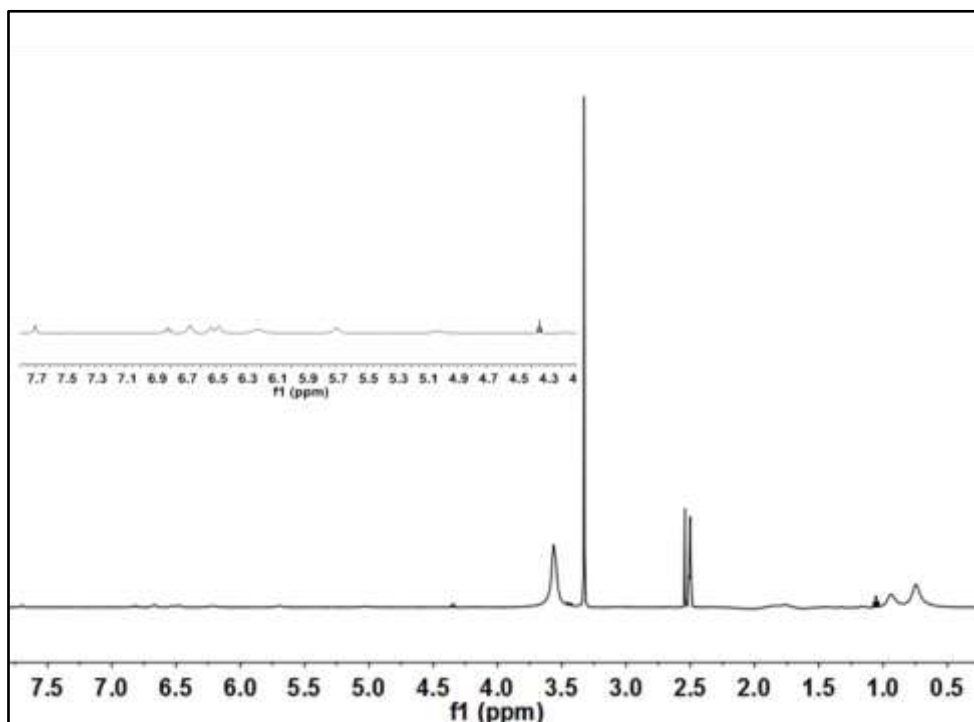


Figure S6. ¹H NMR spectra of **P20-Eu** in DMSO-d₆. The insert is local magnification of the spectrum of **P20-Eu**.

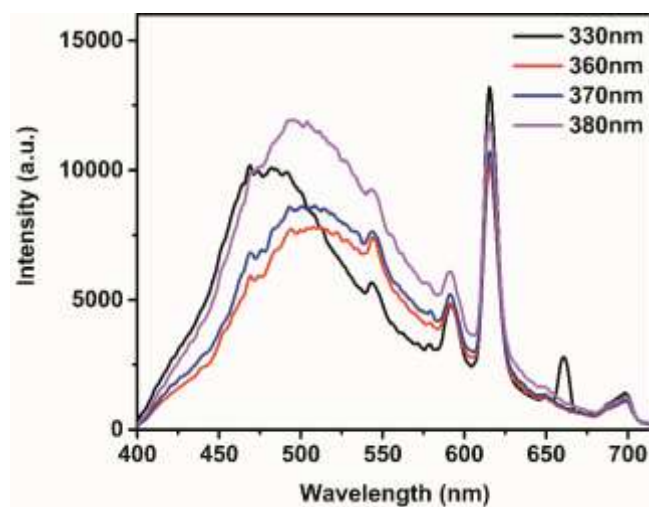


Figure S7. Emission spectra of the **P5-Tb₅₀Eu₁La_{0.95}** metallopolymer excited at different wavelengths at room temperature.

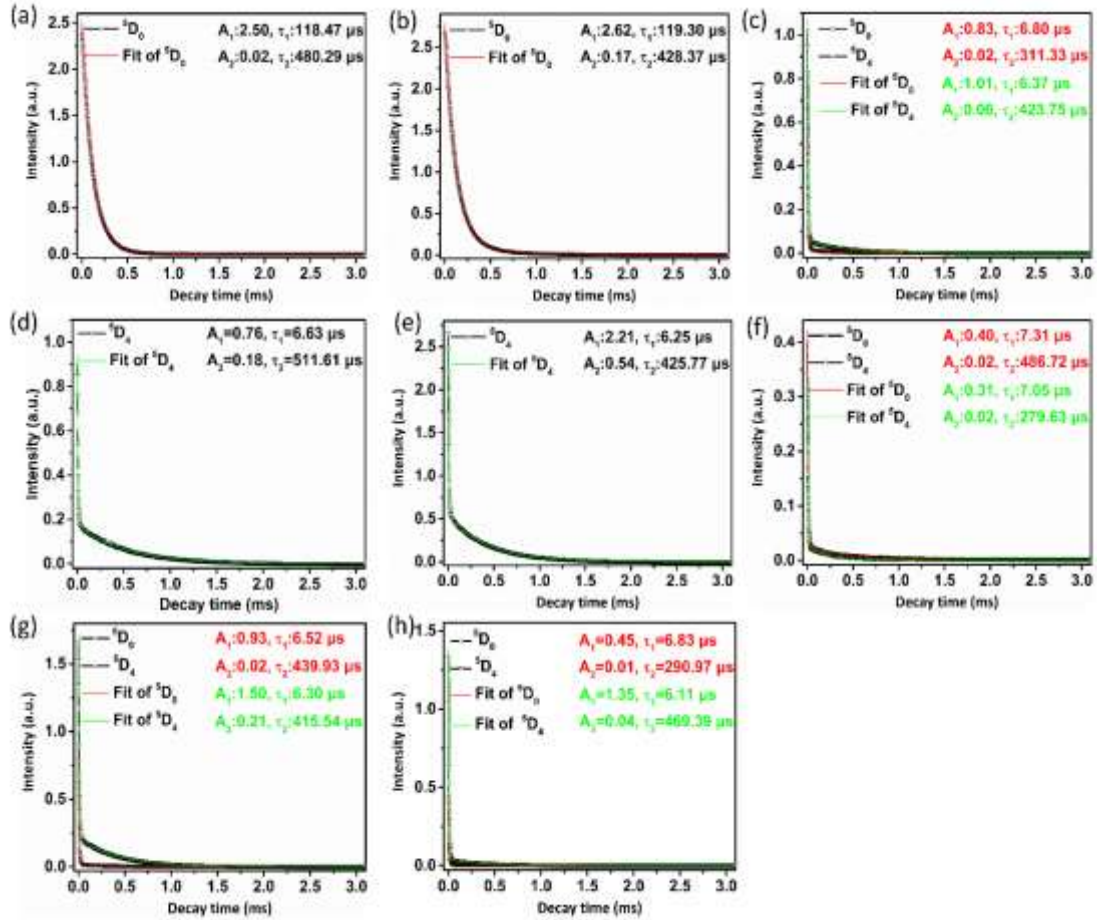


Figure S8. Decay curves of 5D_0 state (for Eu^{3+} , $\lambda_{\text{ex}} = 365 \text{ nm}$, $\lambda_{\text{monitored}} = 613 \text{ nm}$) and 5D_4 state (for Tb^{3+} , $\lambda_{\text{ex}} = 365 \text{ nm}$, $\lambda_{\text{monitored}} = 543 \text{ nm}$) of (a) $\text{Eu}(\text{DBM})_3\text{MP}$, (b) P20-Eu , (c) $\text{P5-Tb}_{50}\text{Eu}_1\text{La}_1$, (d) $\text{Tb}(\text{p-BBA})_3\text{MP}$, (e) P5-Tb , (f) $\text{P5-Tb}_{50}\text{Eu}_1\text{La}_3$ (g) $\text{P5-Tb}_{50}\text{Eu}_1$, (h) $\text{P5-Tb}_{50}\text{Eu}_{1.7}$.

The lifetime values of the excited state 5D_4 (Tb^{3+}) and 5D_0 (Eu^{3+}) in metallopolymer can be determined by the luminescent decay curves (Fig. S8). All decay curves could be well fit by a double-exponential function described as $I = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$, where τ_1 and τ_2 stand for the rapid and slow terms of the luminescent lifetime respectively, and A_1 and A_2 are the corresponding pre-exponential factors. These results imply the presence of different luminescent units in these hybrid materials.

The average decay time can be calculated by the formula of $\tau_{\text{av}} = (A_1 \cdot \tau_1^2 + A_2 \cdot \tau_2^2) / (A_1 \cdot \tau_1 + A_2 \cdot \tau_2)$, where τ_1 and τ_2 are the rapid and slow lifetimes, A_1 and A_2 are constants. The calculated average lifetimes of samples are listed as shown in the Table S1 below.

Table S1. The calculated average lifetime τ_{av} (μs) of samples.

lifetime	Eu(DBM) ₃ MP	P20-Eu	Tb(p-BBA) ₃ MP	P5-Tb	P5-Tb ₅₀ Eu ₁	P5-Tb ₅₀ Eu _{1.7}	P5-Tb ₅₀ Eu ₁ La ₁	P5-Tb ₅₀ Eu ₁ La ₃
Eu ³⁺	128.52	178.63	-	-	152.59	391.66	235.22	106.80
Tb ³⁺	-	-	485.00	401.97	334.00	211.54	376.06	319.25

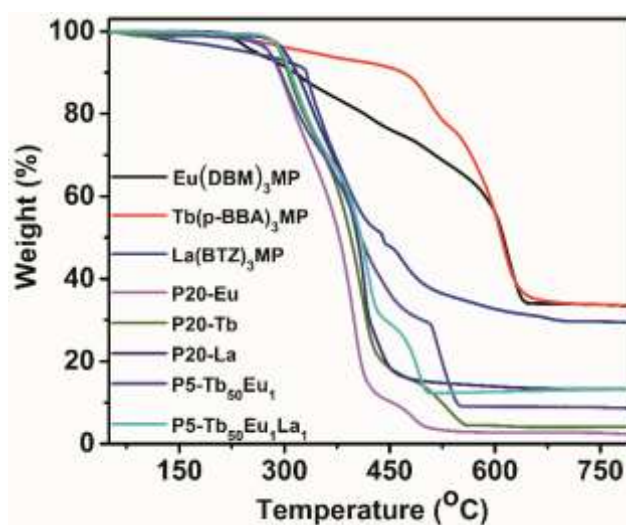


Figure S9. TGA curves of lanthanide complexes and lanthanide-containing polymers in air atmosphere with a heating rate of $20\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.