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 °C\( \cdot \)min\(^{-1}\) under air atmosphere from 50 to 800 °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 = A₁exp(−t/τ₁) + A₂exp(−t/τ₂)). 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:

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

\[
\alpha = \left[ X_{\text{out}}(\lambda) - X_{\text{in}}(\lambda) \right]/X_{\text{out}}(\lambda)
\]

In these equations, \( E_{\text{in}}(\lambda) \) and \( E_{\text{out}}(\lambda) \) 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. \( X_{\text{empty}}(\lambda) \) is the integrated excitation profile with the empty sphere. \( \alpha \) is the BaSO₄ film absorptance, \( X_{\text{in}}(\lambda) \) is the integrated excitation when the sample lies directly in the excitation path and \( X_{\text{out}}(\lambda) \) 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%). $^{1}$H 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)$_3$MP, Tb(p-BBA)$_3$MP, La(BTZ)$_3$MP.**

**Eu(DBM)$_3$MP.** 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 C$_{61}$H$_{45}$O$_8$N$_3$Eu: C, 66.55; H, 4.09; N, 3.82%. Found: C, 65.28; H, 3.98; N, 3.65%.

**Tb(p-BBA)$_3$MP.** 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 C$_{58}$H$_{36}$O$_{11}$N$_3$Tb: C, 66.55; H, 4.09; N, 3.82%. Found: C, 62.90; H, 4.05; N, 3.27%.

**La(BTZ)$_3$MP.** 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 mol•L⁻¹ sodium hydroxide ethanol solution and the light yellow precipitate appeared. The reaction was kept at 50 °C for another 4 h. Finally, the precipitate was obtained by filtration, washing with hot ethanol and drying in a vacuum at 60 °C for 24 h. Yield: 0.67 g (61.3%). Calc. for C₅₅H₃₃O₅N₆S₃La: 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 °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 °C.

For poly(MMA-co-FMA) (P5): yield: 94.0%. ¹H NMR (400MHz, CDCl₃): δ 0.9-1.9 (-CH₃ and >CH₂ protons of the main-chain backbone), 3.5 (s, 3H, -OCH₃ of PMMA), 4.9 (s, 2H, -OCH₂- of PFMA), 6.4 (m, 2H, =CH-CH= of the furan ring), 7.4 (s, 1H, =CH-O- of the furan ring). The copolymer has 84% MMA and 16% FMA, as determined by ¹H NMR. Mn (GPC) and Mw/Mn of the polymer were 30700 g mol⁻¹ and 2.0, respectively.

For poly(MMA-co-FMA) (P20): yield: 88%. ¹H NMR (400MHz, CDCl₃): δ 0.9-1.9 (-CH₃ and >CH₂ protons of the main-chain backbone), 3.5 (s, 3H, -OCH₃ of PMMA), 4.9 (s, 2H, -OCH₂- of PFMA), 6.3 (m, 2H, d, CH-CH of the furan ring), 7.4 (s, 1H, =CHO- of the furan ring). The copolymer has 94% MMA and 6% FMA, as determined by ¹H NMR. Mn (GPC) and Mw/Mn of the polymer were 23600 g mol⁻¹ and 1.5, respectively.
Preparation of the Ln$^{3+}$-containing metallopolymers by Diels-Alder cycloaddition reaction (D-A reaction)

P20 and Eu(DBM)$_3$MP 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)$_3$MP (P20-Tb) and P20-La(BTZ)$_3$MP (P20-La) were prepared in the same way as P20-Eu.

Synthesis of Eu$^{3+}$-Tb$^{3+}$-La$^{3+}$-grafted metallopolymers by successive D-A reactions.

P5-Tb(p-BBA)$_3$MP (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)$_3$MP with the reactive groups of furan and maleimide was 2:1.

P5-Tb(p-BBA)$_3$MP-Eu(DBM)$_3$MP (P5-Tb$_{50}$Eu$_1$) was prepared by the D-A reaction between P5-Tb and Eu(DBM)$_3$MP with a Tb/Eu feed molar ratio of 50:1.

P5-Tb(p-BBA)$_3$MP-Eu(DBM)$_3$MP (P5-Tb$_{50}$Eu$_{1.7}$) was prepared by the D-A reaction between P5-Tb and Eu(DBM)$_3$MP with a Tb/Eu feed molar ratio of 50:1.7.

P5-Tb$_{50}$Eu$_1$La$_3$ was prepared using P5-Tb$_{50}$Eu$_1$ to click with La(BTZ)$_3$MP by a feed molar ratio of 50:1:3 (Tb/Eu/La).

P5-Tb$_{50}$Eu$_1$La$_{1.1}$ was prepared using P5-Tb$_{50}$Eu$_1$ to click with La(BTZ)$_3$MP by a feed molar ratio of 50:1:1 (Tb/Eu/La).

Synthesis of Eu$^{3+}$-Tb$^{3+}$-La$^{3+}$-grafted metallopolymers P5-TbEuLa by one-step D-A reaction

P5-Tb$_{50}$Eu$_1$La$_{0.95}$ 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)$_3$MP, Eu(DBM)$_3$MP and La(BTZ)$_3$MP with mixed molar ratio (Tb/Eu/La = 50:1:0.95) were used instead of Tb(p-BBA)$_3$MP.

References


Scheme S1. Synthesis of Eu(DBM)$_3$MP, Tb(p-BBA)$_3$MP, La(BTZ)$_3$MP and poly(MMA-co-FMA).
Figure S1. $^1$H NMR spectrum of P20.

Figure S2. $^1$H 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. $^1$H NMR spectra of P20-Eu in DMSO-d$_6$. The insert is local magnification of the spectrum of P20-Eu.

Figure S7. Emission spectra of the P5-Tb$_{50}$Eu$_1$La$_{0.95}$ metallopolymer excited at different wavelengths at room temperature.
Figure S8. Decay curves of $^5D_0$ state (for Eu$^{3+}$, $\lambda_{\text{ex}} = 365$ nm, $\lambda_{\text{monitored}} = 613$ nm) and $^5D_4$ state (for Tb$^{3+}$, $\lambda_{\text{ex}} = 365$ nm, $\lambda_{\text{monitored}} = 543$ nm) of (a) Eu(DBM)$_3$MP, (b) P20-Eu, (c) P5-Tb$_{50}$Eu$_1$La$_1$, (d) Tb(p-BBA)$_3$MP, (e) P5-Tb, (f) P5-Tb$_{50}$Eu$_1$La$_3$ (g) P5-Tb$_{50}$Eu$_1$, (h) P5-Tb$_{50}$Eu$_{1.7}$.

The lifetime values of the excited state $^5D_4$ (Tb$^{3+}$) and $^5D_0$ (Eu$^{3+}$) in metallopolymers 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 $\tau_1$ and $\tau_2$ 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 $\tau_{av} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$, where $\tau_1$ and $\tau_2$ are the rapid and slow lifetimes, $A_1$ and $A_2$ are constants. The calculated average lifetimes of samples are list as shown in the Table S1 below.
Table S1. The calculated average lifetime $\tau_{av}$ (μs) of samples.

<table>
<thead>
<tr>
<th>lifetime</th>
<th>Eu(DBM)$_3$MP</th>
<th>P20-Eu</th>
<th>Tb(p-BBA)$_3$MP</th>
<th>P5-Tb</th>
<th>P5-Tb$<em>{50}$Eu$</em>{17}$</th>
<th>P5-Tb$_{50}$Eu$_1$La$_1$</th>
<th>P5-Tb$_{50}$Eu$_1$La$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu$^{3+}$</td>
<td>128.52</td>
<td>178.63</td>
<td>-</td>
<td>-</td>
<td>152.59</td>
<td>391.66</td>
<td>235.22</td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>_</td>
<td>_</td>
<td>485.00</td>
<td>401.97</td>
<td>334.00</td>
<td>211.54</td>
<td>376.06</td>
</tr>
</tbody>
</table>

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