In this work, we report a facile approach to prepare lanthanide metallopolymers with tunable photoluminescence by Diels–Alder reaction between poly(MMA-co-FMA) and lanthanide complexes. Emission colors including white light can be regulated by varying the feed ratios of the lanthanide complexes. This straightforward strategy gives us access to the construction of metallopolymers.

Nowadays, photoluminescent lanthanide (Ln$^{3+}$) complexes containing metallopolymers have merited intense attention in lighting sources, chemical sensors and optoelectronic devices, owing to the unique optical properties of lanthanide complexes, including sharp and intense luminescence, large Stokes shift, long excited-state lifetime, and excellent properties of the polymer matrix such as good transparency, superior mechanical strength, flexibility and ease of processing. Fine tuning of the emission color of luminescent materials, especially white-light emission, is of great significance for optical-device applications. For lanthanide (Ln$^{3+}$)-containing metallopolymers, tunable emission is generally generated by adjusting the ratios of emission intensities of lanthanide complexes, depending on the modulation of either chemical factors (Ln$^{3+}$ concentration and coordination environment) or physical parameters (excitation wavelength and temperature). With regard to non-stimuli-responsive fluorescent metallopolymers, tunable emissions are usually achieved by adjusting the relative amount of primary colors. The popular approach for this is to physically blend two or three lanthanide complexes with polymers. The major drawback, however, is the aggregation of the inserted lanthanide complexes which strongly affects the fluorescence intensity and stability. An alternative approach is to copolymerize fluorescent lanthanide complex monomers with monomers of host materials, which is able to avoid aggregation of the incorporated metal complexes while maintaining the photophysical properties. During the past few decades, there have been increasing investigations that focus on copolymerizing lanthanide complex monomers containing a reactive vinyl-containing ligand with another functional monomer to get metallopolymers. Unfortunately, the polymerizable complex monomers are hard to design and arduous to polymerize, which results in poor controllability of the amount of rare earth complexes in the polymers. Thus, facile methods for the fabrication of color tunable Ln$^{3+}$-complex grafted polymers are still lacking.

The Diels–Alder (D–A) click reaction, a highly selective 4 + 2 cycloaddition between electron-rich dienes and electron-poor dienophiles, has gained a great deal of attention due to its high specificity, nearly quantitative yield, and exceptional tolerance towards a wide range of functional groups and reaction conditions. This reaction has found specific applications in the attachment of drugs, ligands, and biomolecules to polymeric materials to obtain functional polymers. However, reported examples focusing on the preparation of Ln$^{3+}$ polymers using click reactions are very rare; in particular, the preparation of color-tunable emitting materials based on click reactions has not been reported in the open literature until now. Weng et al. attached a tris-(benzyltriazolylmethyl) amine ligand to a polystyrene with a high-temperature backbone resulting in a metallo-supramolecular polymer using the copper-catalyzed azide–alkyne cycloaddition reaction. In one of our previous works, we attempted to couple Eu(DBM)$_3$MP to copolymers of methyl methacrylate and anthracenylmethyl methacrylate using the D–A click reaction. Although the resultant product only emitted a single color of red light and the content of Eu(DBM)$_3$MP complexes in the polymer was low due to steric hindrance, our work proved that the click reaction was a powerful tool for the preparation of lanthanide complex-containing metallopolymers. Given that click reactions allow tailor-made functional precursors prior to performing a click reaction, if a “clickable” polymer and “clickable” lanthanide complexes emitting three primary colors can be designed and synthesized, it may be expected that tunable photoluminescence emission could be achieved by the D–A reaction.

In this work, we took advantage of the D–A click reaction for tunable emission via anchoring lanthanide complexes emitting...
different colors onto the polymer backbone. Our strategy for the fabrication of color-tunable fluorescence emitting metallopolymers involves the following three steps (Scheme 1). Firstly, a polymer backbone poly(MMA-co-FMA) having pendant furan groups as a click platform was synthesized. Secondly, three kinds of lanthanide complexes with MP as a “clickable” dienophile were synthesized emitting red, green and blue fluorescence, respectively. Thirdly, through D–A reaction between the MP ligands of the lanthanide complexes and the furan groups of poly(MMA-co-FMA), light emitting metallopolymers containing lanthanide complexes could be obtained. By changing the content of the three complexes introduced to the platform, light can be adjusted. Specifically, we can achieve this via D–A reaction by stepwise adding three kinds of complexes (Route 1) or directly adding different proportions of the complexes (Route 2) to platforms. In this article, we mainly utilized Route 1 to introduce our strategy.

As for a clickable platform, a tailor-made polymer matrix containing pendant furfuryl groups was prepared via free radical random copolymerization of furfuryl methacrylate (FMA) with methyl methacrylate (MMA). MMA-co-FMA is a high reactive diene that can react with the dienophile-containing lanthanide complexes. By adjusting the feed ratios of FMA and MMA, two kinds of polymers P5 and P20 were synthesized as platforms for D–A reaction, of which the feed ratios of MMA/FMA were 5/1 and 20/1, respectively. The compositions of the resultant poly(MMA-co-FMA)s were determined from their 1H NMR spectra (Fig. S1 and S2, ESI†), using the integration ratio of the peaks at 3.5 and 4.9 ppm arising from the CH3 protons belonging to the MMA units and CH2 protons belonging to the furan units, respectively. The ratios of FMA to MMA were 1/5 for P5 and 1/20 for P20, respectively, which were in agreement with their composition ratios directly calculated from their corresponding feed ratios, suggesting that the reactivity of both monomers is roughly the same. The molecular weight (Mn) and the polydispersity index (PDI) for each polymer were characterized by GPC (Fig. S3 and S4, ESI†).

The Mn values were 31 kg mol⁻¹ for P5 and 26 kg mol⁻¹ for P20, and the PDIs were 1.9 for P5 and 1.5 for P20. The PDIs of the copolymers are in a relatively broad range, which is due to chain transfer of FMA. 17

To introduce the “clickable” dienophile into lanthanide complexes to perform a D–A reaction with poly(MMA-co-FMA), we synthesized a MP ligand, a maleimide substituted derivative of 1,10-phenanthroline (see the ESI, † for details), used as a dienophile, and a second ligand as well to coordinate with different lanthanide metal ions. To realize tunable emission, Eu3⁺ primarily coordinated with dibenzoylmethane (DBM) was used for red color emission, and Tb3⁺ primarily coordinated with 4-benzoylbenzoic acid (p-BBA) was used for green color emission. As for blue emission, we skillfully used 2-(2-hydroxyphenyl)benzothiazole (BTZ), a blue emission source, to coordinate with La3⁺ to get a La(BTZ)3MP complex, since there is no suitable ligand for sensitization of blue-emitting lanthanide ions at room temperature under a 365 nm excitation wavelength. With MP as clickable groups, three MP-containing lanthanide complexes Eu(DBM)3MP, Tb(p-BBA)3MP and La(BTZ)3MP were synthesized, respectively (see the ESI, † for details). The successful synthesis of these complexes was confirmed by Elemental Analysis and FT-IR (Fig. S3, ESI†). The corresponding excitation and emission spectra of the three complexes in DMSO solution excited at 365 nm (room temperature) are displayed in Fig. 1. For Eu(DBM)3MP, the emission spectrum (Fig. 1a) exhibited five sharp emission bands at 578, 590, 613, 651 and 700 nm related to the 5D0 → 7Fj transitions of Eu3⁺, where J = 0–4, respectively. 20,21 It was dominated by the 5D0 → 7F2 band at 613 nm, which was responsible for the red emission color shown in the inset of Fig. 1a. For Tb(p-BBA)3MP, excitation at 365 nm resulted in line-shaped emission bands (Fig. 1b) at 488, 543, 584 and 619 nm, respectively, corresponding to the transitions of 5D4 → 7Fj (J = 6, 5, 4, and 3) of Tb3⁺. 22 The dominated 5D4 → 7F2 transition was responsible for the bright green emission color shown in the inset of Fig. 1b. Unlike the sharp emission lines from Eu3⁺ and Tb3⁺ complexes, La(BTZ)3MP had a broad emission band located in the blue region centered at 465 nm (Fig. 1c), which is ascribed to the π–π* transition of the BTZ ligand. 23–24 It’s worth noting that all three complexes can match a 365 nm UV chip well.

To demonstrate the effectiveness of the D–A reaction in the preparation of metallopolymers, we used P20 as a platform to click react with the three complexes to give monochromatic red, green and blue light, respectively. Eu(DBM)3MP, Tb(p-BBA)3MP and La(BTZ)3MP with P20 at equimolar ratios of reactive groups of MP to furan were efficiently coupled via D–A click reactions to give their corresponding complexes P20-Eu, P20-Tb and P20-La. The adduct of the complex and P20 was confirmed via 1H NMR (Fig. S6, ESI†), which shows that the peak of the proton of the furan ring at 7.4 ppm disappeared completely and a new triplet peak signal at 4.85 ppm emerged assigned to the bridgehead proton of the cycloadduct CH. As shown in Fig. 1a–c’, the emission colors of metallopolymers P20-Eu, P20-Tb and P20-La in DMSO solution excited at 365 nm were red, green and blue, respectively, quite similar to their corresponding complexes. As for the photoluminescence spectra, P20-Eu and P20-Tb exhibit similar

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Ln$^{3+}$-centered emission to that of their corresponding complexes. Compared with La(BTZ)$_3$MP, a slight blue shift to 448 nm in Ln$^{3+}$-centered emission to that of their corresponding complexes. The reason may be that the efficiency of the energy transfer. Thus, we investigated the photoluminescence (PL) quantum yield (QY), which is a principal characteristic of luminescent materials, can quantify the efficiency of the energy transfer. Therefore, we investigated the QYs of the as-prepared metallopolymers (10$^{-5}$ mol L$^{-1}$ in DMSO) upon excitation at 365 nm. The QYs were 5.40% for P5-Tb$_{50}$Eu$_{1.7}$-BBA, 14.57% for La(BTZ)$_3$MP, 589 nm and 615 nm (the red emission of Eu(DBM)$_3$MP), and 436 nm and 545 nm (the green emission of Tb(p-BBA)$_3$MP).

Fig. 1 Fluorescence excitation and emission spectra of complex Eu(DBM)$_3$MP (a), complex Tb(p-BBA)$_3$MP (b) and complex La(BTZ)$_3$MP (c), as well as P20-Eu (a'), P20-Tb (b') and P20-La (c') excited at 365 nm in DMSO. The insets show the photographs under the excitation of a 365 nm hand-held UV lamp.

The color tunability may be realized by adding different complexes to click with platforms stepwise, as shown in Route 1, Scheme 1. We here demonstrated P5 as a “clickable” platform to realize color-tunability. Heating the mixture of Tb(p-BBA)$_3$MP and P5 (a molar ratio of 1:2 relative to reactive groups) in DMSO, a metallopolymers, which we denoted as P5-Tb, emitting green light, was obtained, in which half of the furan groups were residual for further click reactions with lanthanide complexes. Upon addition of Eu(DBM)$_3$MP to P5-Tb with a Tb/Eu molar ratio of 50:1, the resulting adduct was a metallopolymers which we denoted as P5-Tb$_{50}$Eu$_1$. When excited at 365 nm, a yellow emission was observed. Corresponding fluorescence spectra show multiple peaks related to $^5D_0 \rightarrow ^7F_j$ transitions of the Eu$^{3+}$ ion and $^5D_1 \rightarrow ^7F_j$ transitions of the Tb$^{3+}$ ion (Fig. 2a). The CIE coordinate of P5-Tb$_{50}$Eu$_1$ was calculated to be (0.37, 0.33), located in the yellow region (point A in Fig. 2e), which shows the relative intensities of the red emission from Eu$^{3+}$ and the green emission from Tb$^{3+}$ are comparable. Further addition of Eu(DBM)$_3$MP to P5-Tb$_{50}$Eu$_1$, led to the generation of a metallopolymers which we denoted as P5-Tb$_{50}$Eu$_{1.7}$ (Tb: Eu in a 50:1.7 molar ratio) with CIE coordinate of (0.41, 0.38) and giving rise to orange color emission, as shown by point B in Fig. 2e. The intensity of emission from Eu$^{3+}$ was stronger than the intensity of emission from Tb$^{3+}$ (Fig. 2b). Finally, we used La(BTZ)$_3$MP emitting a blue color to click with its complementary yellow emission from P5-Tb$_{50}$Eu$_1$. After addition to P5-Tb$_{50}$Eu$_1$ with a molar ratio of Tb/Eu/La = 50:1:3, the color changed from yellow to greenish-yellow. The resulting adduct we named P5-Tb$_{50}$Eu$_1$La$_{1.7}$, emitted pure white light (Fig. S7, ESI†) with CIE coordinates of (0.31, 0.40) (point D in Fig. 2e). Fig. 2c displays the emission peaks of P5-Tb$_{50}$Eu$_1$La$_3$ at 460 nm (the blue emission of La(BTZ)$_3$MP), 488 nm and 545 nm (the green emission of Tb(p-BBA)$_3$MP), and 589 nm and 615 nm (the red emission of Eu(DBM)$_3$MP). The resulting adduct, which we named as P5-Tb$_{50}$Eu$_1$La$_1$, emitted white light with CIE coordinates of (0.33, 0.34) (point C in Fig. 2e) under 365 nm UV light (Fig. 2d). We summarized the luminescent colors of metallopolymers with different lanthanide complexes ratios in Table 1. It could be seen that, the method of utilizing D–A click chemistry between platforms and complexes to prepare tunable fluorescent materials is very effective.

As mentioned above, white light emission is usually highly required in many application fields. Based on the emission of the above complex P5-Tb$_{50}$Eu$_1$La$_3$, we decreased the amount of La(BTZ)$_3$MP to Tb/Eu/La = 50:1:1. It was found that the resulting adduct, which we named as P5-Tb$_{20}$Eu$_1$La$_1$, emitted white light with CIE coordinates of (0.33, 0.34) (point C in Fig. 2e) under 365 nm UV light (Fig. 2d). We summarized the luminescent colors of metallopolymers with different lanthanide complexes ratios in Table 1. It could be seen that, the method of utilizing D–A click chemistry between platforms and complexes to prepare tunable fluorescent materials is very effective.

Except for the above route (Route 1), metallopolymers with tunable emissions can also be prepared by adding different molar ratios of lanthanide complexes to click react with the platform in one-step (Route 2, Scheme 1). We herein prepared a metallopolymers which had a similar composition with white emission, P5-Tb$_{50}$Eu$_1$La$_1$, prepared by using a stepwise process. By mixing the three complexes at a molar ratio of Eu/Tb/La = 1:50:0.95 (our intended ratio is 1:50:1; however, the added La complex was slightly less than expected in practical operation) and subsequently heating with P5, we got a metallopolymers named P5-Tb$_{50}$Eu$_1$La$_{0.95}$. As expected, its emission was similar to that of P5-Tb$_{50}$Eu$_1$La$_1$, prepared using a stepwise-click process and it emitted pure white light (Fig. S7, ESI†).

The photoluminescence (PL) quantum yield (QY), which is a principal characteristic of luminescent materials, can quantify the efficiency of the energy transfer. Thus, we investigated the QYS of the as-prepared metallopolymers samples (10$^{-5}$ mol L$^{-1}$ in DMSO) under excitation at 365 nm. The QYS were 5.40% for Eu(DBM)$_3$MP, 4.99% for Tb(p-BBA)$_3$MP, 14.57% for La(BTZ)$_3$MP, 6.35% for P20-Eu, 4.08% for P20-Tb, 5.32% for P20-La, 5.24% for P5-Tb$_{50}$Eu$_1$, 4.33% for P5-Tb$_{50}$Eu$_{1.7}$, 5.90% for P5-Tb$_{50}$Eu$_1$La$_1$ and 5.89% for P5-Tb$_{50}$Eu$_1$La$_3$.
Furthermore, the luminescence decay curves of samples containing Eu³⁺ and/or Tb³⁺ were monitored at the characteristic emission of Eu³⁺ (5D0 → 7FJ) and Tb³⁺ (5D4 → 7FJ) (Fig. S8, ESI†). By fitting to a double exponential function, the average lifetimes $\tau_{av}$ were calculated (Table S1, ESI†). The fitting results suggested the presence of different coordination environments around the Eu³⁺ or Tb³⁺ ions in these complexes and metallopolymers. Compared to the mono-lanthanide metallopolymers, Eu³⁺ and Tb³⁺ containing hetero-lanthanide metallopolymers had a shorter $\tau_{av}$ of Tb³⁺ but a longer $\tau_{av}$ of Eu³⁺. In addition, by comparing the lifetimes of P5-Tb50Eu1 (τav = 152.59 μs for Eu³⁺, τav = 334 μs for Tb³⁺) and P5-Tb50Eu1.7 (τav = 391.66 μs for Eu³⁺, τav = 211.54 μs for Tb³⁺), we found that the lifetime of Eu³⁺ increased, while the lifetime of Tb³⁺ decreased with the increase of the Eu³⁺ content. This means that there may be an energy transfer between Eu³⁺ and Tb³⁺ ions. What needs to be pointed out is that the energy level of Tb³⁺ ($^5D_4 = 20500$ cm⁻¹) is higher than that of Eu³⁺ ($^5D_0 = 17500$ cm⁻¹). Based on the decay lifetimes and excited state energy levels of related ligands (DBM, MP and p-BBA) and lanthanide ions, we proposed a possible energy transfer process in the metallopolymers as shown in Scheme 2: (i) the organic ligand moieties DBM, MP and p-BBA absorb UV light and transit to the singlet excited state ($^1π-π^*$, S1) and then to the triplet state ($^3π-π^*$, T1) via intersystem crossing. (ii) A non-radiative energy transfer pathway from the T1 state of the ligand to the excited states of the Eu³⁺ and Tb³⁺ ion. (iii) In the Eu³⁺–Tb³⁺-containing metallopolymers, energy transfer occurs from the Tb³⁺ centers to Eu³⁺ centers.

The thermal properties of the Ln³⁺ metallopolymers were investigated by thermogravimetric analysis (TGA) measured under an air atmosphere at a heating rate of 20 °C min⁻¹. It was found that the metallopolymers showed a slight increase for the $T_{onset}$ in comparison with the lanthanide complexes, and decomposition with maxima located at a higher temperature interval than that of the complexes (Fig. S9, ESI†). P5-Tb50Eu1.7La0.95 remained stable up to 258 °C, indicating that the thermal stability of the metallopolymers is significantly improved. In view of the operation temperatures of LEDs below 150 °C, the prepared metallopolymers Poly(MMA-co-FMA)–Eu–Tb–La is thermally stable enough for the fabrication of LEDs.

## Conclusions

In summary, this study demonstrates that poly(MMA-co-FMA) obtained by the copolymerization of MMA and FMA can be used as a clickable platform for the synthesis of a series of photofluorescent homometallic and heterometallic lanthanide complexes containing poly(MMA-co-FMA)–Ln metallopolymers. In particular, direct white-light emission (CIE: $x = 0.33$, $y = 0.34$) with a quantum yield of 5.90% was achieved by P5-Tb50Eu1.7La0.95 upon excitation at 365 nm in DMSO. The strategy presented here is universal and gives straightforward access to the preparation of a variety of lanthanide metallopolymers, thereby opening new perspectives in the field of synthesis of fluorescent polymers where tunable fluorescence emissions are required.

## Conflicts of interest

There are no conflicts of interest to declare.

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Notes and references