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COMMUNICATION

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

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In this work, we reported 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 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, [1-6] owing to unique optical properties of lanthanide complexes, including sharp and intense luminescence, large Stokes shift, long excited-state lifetime, and excellent properties of polymer matrix such as good transparently, superior mechanical strength, flexibility and ease of processing.[7,8] 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, the tunable emission is generally generated by adjusting ratios of emission intensity 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.[9] The major drawback, whereas, is the aggregation of 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 material, which is able to avoid aggregation of incorporated metal complexes while maintaining the photophysical properties.[10] During the past decades, there has been increasing investigations that focus on copolymerizing lanthanide complex monomers containing a reactive vinyl-containing ligand with another functional monomer to get metallopolymers.[11-14] Unfortunately, the polymerizable complex monomers are hard to design and arduous to polymerize, which results in poor controllability of the amounts of rare earth complexes in polymers. Thus, facile methods for the fabrication of color tunable Ln^{3+}-complex grafted polymers are still lacking.

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 their high specificity, nearly quantitative yield, and exceptional tolerance towards a wide range of functional groups and reaction conditions. This reaction has been found specific applications for attachment of drugs, ligands, and biomolecules to polymeric materials to obtain functional polymers.[15-18] However, reported examples focused on the preparation of Ln^{3+} polymer by click reaction are very rare, especially the preparation of color-tunable emitting materials based on click reaction is not reported in open literatures till now. Weng *et al.* attached tris-(benzyltriazolylmethyl) amine ligand to the polyvinylbenzyl chloride backbone resulted in a metallo-supramolecular polymer via the copper-catalyzed azide–alkyne cycloaddition reaction.[19] In one of our previous work, we attempted to couple $Eu(DBM)_3MP$ to copolymer of methyl methacrylate and anthracenylmethyl methacrylate using D-A click reaction. Although the resultant product only emitted a single color of red light and the content of $Eu(DBM)_3MP$ complexes in the polymer was low due to steric hindrance, our work proved that click reaction was a powerful tool for preparation of lanthanide complex containing metallopolymer. Given that click reactions allow tailor-made functional precursors prior to perform a click reaction, if design and synthesize a “clickable” polymer and “clickable” lanthanide complexes emitting three primary colors, it may be expected that tunable photoluminescence emission could be achieved by D-A reaction.

In this work, we took advantage of D-A click reaction for tunable emission via anchoring lanthanide complexes emitting

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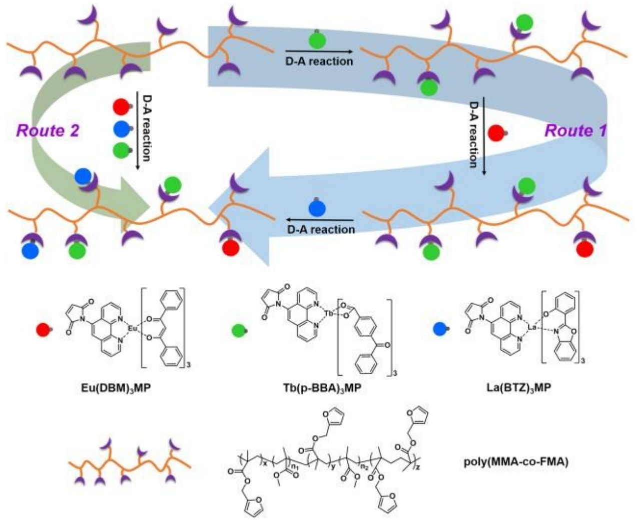

Scheme 1. Reaction scheme for the synthesis of Ln^{3+} complex grafted poly(MMA-co-FMA)-Ln (Ln = Eu, Tb and/or La) by D-A click reaction.

different colors onto the polymer backbone. Our strategy for fabrication of color-tunable fluorescence emitting metallopolymers involves three following steps (Scheme 1). Firstly, a polymer backbone poly(MMA-co-FMA) having pendent furan groups as a click platform was synthesized. Secondly, three kinds of lanthanide complexes with MP as "clickable" dienophile were synthesized emitting red, green and blue fluorescence, respectively. Thirdly, through D-A reaction between MP ligand of lanthanide complexes and 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 complexes (Route 2) to platforms. In this article, we mainly utilized Route 2 to introduce our strategy.

As for a clickable platform, the tailor-made polymer matrix containing pendant furfuryl groups was prepared via free radical random copolymerization of furfuryl methacrylate (FMA) with methyl methacrylate (MMA). 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 resultant poly(MMA-co-FMA)s were determined from their ^{1}H NMR spectra (Fig. S1 and Fig. S2), using the integration ratio of the peaks at 3.5 and 4.9 ppm arising from the CH_3 protons belonging to MMA units and CH_2 protons belonging to 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 polydispersity index (PDI) for each polymer were characterized by GPC (Fig. S3 and Fig. S4). The Mn values were 31 kg mol^{-1} for **P5** and 26 kg mol^{-1} for **P20**, PDI 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 "clickable" dienophile into lanthanide complexes to perform a D-A reaction with poly(MMA-co-FMA), we synthesized MP ligand, a maleimide substituted derivative of 1,10-phenanthroline (see ESI, for details), used as dienophile and the second ligand as well to coordinate with different lanthanide metal ions. To realize tunable emission, Eu^{3+} primarily coordinated with dibenzoylmethane (DBM) was used for red color emission, and Tb^{3+} primarily coordinated with 4-benzoylbenzoic acid (p-BBA) was used for green color emission, respectively. As for blue emission, we skillfully used 2-(2-hydroxyphenyl)benzothiazole (BTZ), a blue emission source, to coordinate with La^{3+} to get La(BTZ)$_3$MP complex, since there is no suitable ligand for sensitization of blue-emitting lanthanum ion at room temperature under 365 nm excitation wavelength. With MP as clickable groups, three MP-containing lanthanide complexes Eu(DBM)$_3$MP, Tb(p-BBA)$_3$MP and La(BTZ)$_3$MP were synthesized, respectively (see ESI, for details). The successful synthesis of these complexes was confirmed by Elemental Analysis and FT-IR (Fig. S5). The corresponding excitation and emission spectra of the three complexes in DMSO solution excited at 365 nm (room temperature) were displayed in Fig. 1. For Eu(DBM)$_3$MP, the emission spectrum (Fig. 1a) exhibited five shape bands at 578, 590, 613, 651 and 700 nm related to the $^5D_0$ - ^7F_J transitions of Eu^{3+}, where J = 0 – 4, respectively.[20,21] It was dominated by the $^5D_0 \rightarrow {}^7F_2$ band at 613 nm, which was responsible for the red emission color shown in the inset of Fig.1a. For Tb(p-BBA)$_3$MP, excited at 365 nm resulted in line-shaped emission bands (Fig. 1b) at 488, 543, 584 and 619 nm, respectively, corresponding to the transitions of $^5D_4$ - ^7F_J (J = 6, 5, 4, 3) of Tb^{3+}.[22] The dominated $^5D_4 \rightarrow {}^7F_5$ transition was responsible for the bright

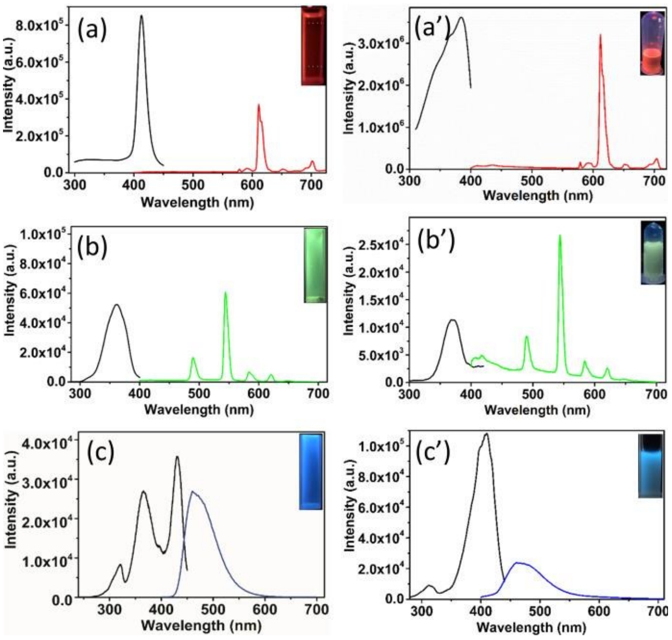

Fig.1 Fluorescence excitation and emission spectra of complex Eu(DBM)$_3$MP (a), complex Tb(p-BBA)$_3$MP (b) and complex La(BTZ)$_3$MP (c), as well as **P20-Eu** (a'), **P20-Tb** (b') and **P20-La** (c') excited at 365 nm in DMSO. The insets show the photographs under the excitation of a 365 nm hand-held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

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green emission color shown in the inset of Fig. 1b. Unlike the sharp emission lines from Eu^{3+} and Tb^{3+} complexes, $La(BTZ)_3MP$ had a broad emission band locating in the blue region centered at 465 nm (Fig. 1c), which is ascribed to the π-π* transition of 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 D-A reaction in preparation of metallopolymers, we used **P20** as a platform to click reacted with the three complexes to give monochromatic red, green and blue light, respectively. $Eu(DBM)_3MP$, $Tb(p\text{-}BBA)_3MP$ and $La(BTZ)_3MP$ with **P20** at equimolar ratio of reactive groups of MP to furan were efficiently coupled via D-A click reaction to give their corresponding **P20-Eu**, **P20-Tb** and **P20-La**. The adduct of complex and **P20** was confirmed by ^1H NMR (Fig. S6), which shows the peak disappeared completely of the proton of furan ring at 7.4 ppm and the emergence of new triplet peak signal at 4.85 ppm assigned to the bridgehead proton of the cycloadduct CH. As shown in Fig. 1a', 1b' and 1c', the emission colors of metallopolymers **P20-Eu**, **P20-Tb** and **P20-La** in DMF solution excited at 365 nm were red, green and blue, respectively, quite similar to their corresponding complexes. As to the photoluminescence spectra, **P20-Eu** and **P20-Tb** exhibit similar Ln^{3+}-centered emission to that of their corresponding complexes. Compared with $La(BTZ)_3MP$, a slight blue shift to 448 nm in metallopolymer **P20-La** was observed. The reason may be that the absorbed energy of the polymer chain is partially passed to the BTZ ligand, resulting in the decrease of energy loss of the nonradiative transition.[14,25]

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 $Tb(p\text{-}BBA)_3MP$ and **P5** (molar ratio of 1:2 relatives to reactive groups) in DMSO, a metallopolymer we denoted **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 $Eu(DBM)_3MP$ into **P5-Tb** by Tb/Eu molar ratio of 50:1, the resulting adduct was metallopolymer we denoted as **P5-Tb$_{50}$Eu$_1$**. When excited at 365 nm, a yellow emission was observed. Corresponding fluorescence spectrum shows multiple peaks related to $^5D_0 \rightarrow {}^7F_J$ transitions of the Eu^{3+} ion and $^5D_4 \rightarrow {}^7F_J$ transitions of the Tb^{3+} ion (Fig. 2a). The CIE coordinate of **P5-Tb$_{50}$Eu$_1$** is calculated to be (0.37, 0.33), located to the yellow region (point A in Fig. 2e), which shows that the relative intensities of the red emission from Eu^{3+} and green emission from Tb^{3+} are comparable. Further addition of $Eu(DBM)_3MP$ to **P5-Tb$_{50}$Eu$_1$**, leaded to the generation of metallopolymer we denoted **P5-Tb$_{50}$Eu$_{1.7}$** (Tb:Eu in 50:1.7 molar ratio) with CIE coordinates 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 $La(BTZ)_3MP$ emitting blue color to click with its complementary yellow emission from **P5-Tb$_{50}$Eu$_1$**. After adding to **P5-Tb$_{50}$Eu$_1$** by 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$_3$** with CIE coordinate of (0.31, 0.40) (point D in Fig. 2e). Fig. 2c displayed the emission peaks of **P5-Tb$_{50}$Eu$_1$La$_3$** at 460 nm (the blue emission of $La(BTZ)_3MP$), 488 nm, 545 nm (the green emission of $Tb(p\text{-}BBA)_3MP$) and 589 nm, 615 nm (the red emission of $Eu(DBM)_3MP$).

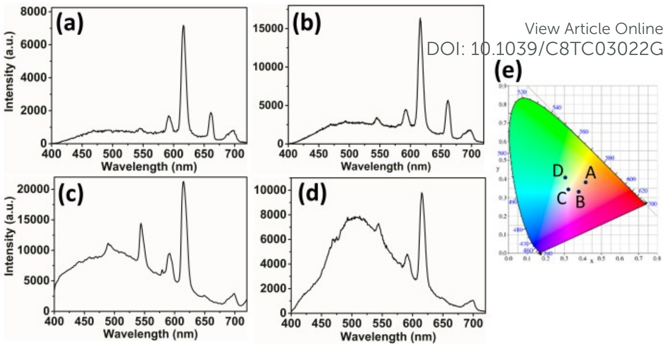

Fig. 2 The emission spectra of metallopolymers **P5-Tb$_{50}$Eu$_1$** (a), **P5-Tb$_{50}$Eu$_{1.7}$** (b), **P5-Tb$_{50}$Eu$_1$La$_3$** (c) and **P5-Tb$_{50}$Eu$_1$La$_1$** (d) excited at 365 nm. (e) CIE chromatography of **P5-Tb$_{50}$Eu$_1$** (point A), **P5-Tb$_{50}$Eu$_{1.7}$** (point B), **P5-Tb$_{50}$Eu$_1$La$_1$** (point C) and **P5-Tb$_{50}$Eu$_1$La$_3$** (point D) at 2.5×10^{-5} M in DMSO solution (R.T.).

As mentioned above, the white light emission is usually high required in many applicant fields. Based the emission of above **P5-Tb$_{50}$Eu$_1$La$_3$**, we decreased the amount of $La(BTZ)_3MP$ to Tb/Eu/La = 50:1:1. It was found that the resulting adduct we named as **P5-Tb$_{50}$Eu$_1$La$_1$** emitted white light with CIE coordinate 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 complex ratios in Table 1. It could be see 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), metallopolymer with tuning emission can also be prepared by adding different molar ratios of lanthanide complexes to click with the platform in one-step (Route 2, Scheme 1). We herein prepared a metallopolymer which had a similar composition with the white emission **P5-Tb$_{50}$Eu$_1$La$_1$** prepared by 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 expectant in practical operation) and subsequently heating with **P5** together, we got a metallopolymer 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 by stepwise-click process and emitted a pure white light (Fig. S7).

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 metallopolymer samples (10^{-5} mol L^{-1} in DMSO) under excited at 365 nm. The QYs were 5.40% for $Eu(DBM)_3MP$, 4.49% for $Tb(p\text{-}BBA)_3MP$, 14.57% for $La(BTZ)_3MP$, 6.35% for **P20-Eu**, 4.08% for **P20-Tb**, 5.52% for **P20-La**, 3.47% for **P5-Tb$_{50}$Eu$_1$**, 4.01% for **P5-Tb$_{50}$Eu$_{1.7}$**, 5.24% for **P5-Tb$_{50}$Eu$_1$La$_1$** and 5.89% for **P5-Tb$_{50}$Eu$_1$La$_3$**, respectively.

Furthermore, the luminescence decay curves of samples containing Eu^{3+} and/or Tb^{3+} were monitored at characteristic emission of Eu^{3+} ($^5D_0$) and Tb^{3+} ($^5D_4$) (Fig. S8). By fitting to a

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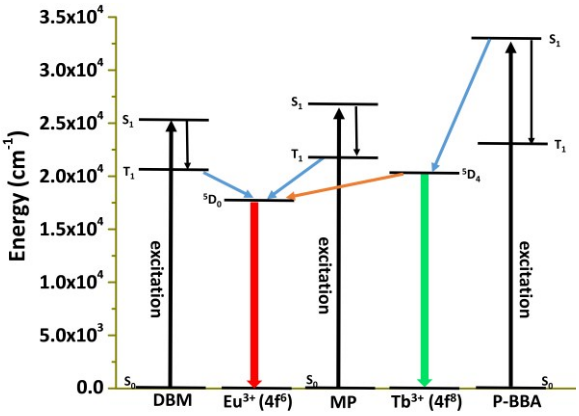
Table 1. The QYs of Eu, Tb and La complexes and various metallopolymers samples

Samples	Complexes			Approximate color regions	QY (%)
	Eu(DBM)$_3$MP	Tb(p-BBA)$_3$MP	La(BTZ)$_3$MP		
Eu(DBM)$_3$MP				red	5.40
Tb(p-BBA)$_3$MP				green	4.49
La(BTZ)$_3$MP				blue	14.57
P20-Eu	1	0	0	red	6.35
P20-Tb	0	1	0	green	4.08
P20-La	0	0	1	blue	5.52
P5-Tb	0	0.5	0	green	4.01
P5-Tb$_{50}$Eu$_{1.7}$	0.017	0.5	0	yellow	4.33
P5-Tb$_{50}$Eu$_1$	0.01	0.5	0	orange	5.24
P5-Tb$_{50}$Eu$_1$La$_1$	0.01	0.5	0.01	white	5.90
P5-Tb$_{50}$Eu$_1$La$_3$	0.01	0.5	0.03	greenish-yellow	5.89
P5-Tb$_{50}$Eu$_1$La$_{0.95}$	0.01	0.5	0.0095	white	5.77

double exponential function, the average lifetimes τ_{av} were calculated (Table SI, ESI). The fitting results suggested that the presence of different coordination environments around the Eu^{3+} or Tb^{3+} ions in these complexes and metallopolymers. Compared to the mono-lanthanide metallopolymer, Eu^{3+} and Tb^{3+} containing hetero-lanthanide metallopolymers had shorter τ_{av} of Tb^{3+} but a longer τ_{av} of the Eu^{3+}. In addition, by comparing the lifetimes of **P5-Tb$_{50}$Eu$_1$** (τ_{av} = 152.59 μs for Eu^{3+}, τ_{av} = 334 μs for Tb^{3+}) and **P5-Tb$_{50}$Eu$_{1.7}$** (τ_{av} = 391.66 μs for Eu^{3+}, τ_{av} = 211.54 μs for Tb^{3+}), we found that the lifetime of Eu^{3+} increased, while the lifetime of Tb^{3+} decreased with the increase of Eu^{3+} content. It means that there may be energy transfer between Eu^{3+} and Tb^{3+} ion.What needs to be pointed out is that the energy level of Tb^{3+} ($^5D_4$ = 20500 cm^{-1})[26] is higher than that of Eu^{3+} ($^5D_0$ = 17500 cm^{-1})[27]. Based on decay lifetimes and excited stated energy levels of related ligands (DBM, MP and p-BBA)[28] 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 transiting to the singlet excited state ($^1\pi$-π^*, S_1) and then to the triplet state ($^3\pi$-π^*, T_1) via intersystem crossing. (ii) non-radiative energy transfer pathway from the T_1 state of the ligand to excited states of the Eu^{3+} and Tb^{3+} ion. (iii) In the Eu^{3+}-Tb^{3+}-containing metallopolymers, energy transfer occurs from the Tb^{3+} centers to Eu^{3+} centers.

The thermal properties of the Ln^{3+} metallopolymers were investigated by thermogravimetric analysis (TGA) measured under air atmosphere at a heat rate of 20 °C min^{-1}. It was found that the metallopolymers showed slight increase for the T_{onset} in comparison with lanthanide complexes, and decomposition with maxima located at higher temperature interval than that of complexes (Fig. S9). **P5-Tb$_{50}$Eu$_1$La$_1$** remained stable up to 258 °C, indicating that thermal stability of metallopolymers are significantly improved. In view of the operation temperatures of LEDs below 150 °C,[29,30] the prepared metallopolymer Poly(MMA-co-FMA)–Eu–Tb–La is thermally stable enough for the fabrication of LEDs.



Scheme 2. Scheme of energy transfer in metallopolymers.

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 (5.90%) was achieved by **P5-Tb$_{50}$Eu$_1$La$_1$** upon excitation at 365 nm in DMSO. The strategy presented here is universal and give a straightforward access to the preparation of 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.

Acknowledgements

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Notes and references

1 L. D. Carlos, R. A. Ferreira, V. de Zea Bermudez, B. Julian-Lopez and P. Escribano, *Chem. Soc. Rev.*, 2011, **40**, 536-549.
2 P. Li, Y. Wang, H. Li and G. Calzaferri, *Angew. Chem., Int. Ed.*, 2014, **53**, 2904-2909.

View Article Online
DOI: 10.1039/C8TC03022G

3 S. Bhunia, N. Chatterjee, S. Das, K. Das Saha and A. Bhaumik, *ACS Appl. Mater. Interfaces*, 2014, **6**, 22569-22576.

4 X.-d. Wang, O. S. Wolfbeis and R. J. Meier, *Chem. Soc. Rev.*, 2013, **42**, 7834-7869.

5 C. Yang, J. Xu, Y. Zhang, Y. Li, J. Zheng, L. Liang and M. Lu, *J. Mater. Chem. C*, 2013, **1**, 4885-4901.

6 K. X. Song, L. He, L. Zhang and G. H. Tao, *Adv. Mater. Interfaces*, 2018, **5**, 1870002.

7 J. Feng and H. Zhang, *Chem. Soc. Rev.*, 2013, **42**, 387-410.

8 W. Kwon, S. Do, J. Lee, S. Hwang, J. K. Kim and S.-W. Rhee, *Chem. Mater.*, 2013, **25**, 1893-1899.

9 Y. Zhao, L. He, S. Qin and G.-H. Tao, *Polym. Chem.*, 2016, **7**, 7068-7077.

10 C. Peng, H. Zhang, J. Yu, Q. Meng, L. Fu, H. Li, L. Sun and X. Guo, *J. Phys. Chem. B*, 2005, **109**, 15278-15287.

11 W.-X. Feng, S.-Y. Yin, M. Pan, H.-P. Wang, Y.-N. Fan, X.-Q. Lü and C.-Y. Su, *J. Mater. Chem. C*, 2017, **5**, 1742-1750.

12 L. Liu, H. Li, P. Su, Z. Zhang, G. Fu, B. Li and X. Lü, *J. Mater. Chem. C*, 2017, **5**, 4780-4787.

13 Z. Zhang, Y.-N. He, L. Liu, X.-Q. Lü, X.-J. Zhu, W.-K. Wong, M. Pan and C.-Y. Su, *Chem. Commun.*, 2016, **52**, 3713-3716.

14 A. Zhang, N. Sun, L. Li, Y. Yang, X. Zhao, H. Jia, X. Liu and B. Xu, *J. Mater. Chem. C*, 2015, **3**, 9933-9941.

15 R. Pola, A. Braunová, R. Laga, M. Pechar and K. Ulbrich, *Polym. Chem.*, 2014, **5**, 1340-1350.

16 M. Shi, K. Ho, A. Keating and M. S. Shoichet, *Adv. Funct. Mater.*, 2009, **19**, 1689-1696.

17 B. Gacal, H. Durmaz, M. Tasdelen, G. Hizal, U. Tunca, Y. Yagci and A. Demirel, *Macromolecules*, 2006, **39**, 5330-5336.

18 O. I. Kalaoglu-Altan, R. Sanyal and A. Sanyal, *Biomacromolecules*, 2015, **16**, 1590-1597.

19 B. Yang, H. Zhang, H. Peng, Y. Xu, B. Wu, W. Weng and L. Li, *Polym. Chem.*, 2014, **5**, 1945-1953.

20 K. Binnemans, *Chem. Rev.*, 2009, **109**, 4283-4374.

21 V. Divya and M. Reddy, *J. Mater. Chem. C*, 2013, **1**, 160-170.

22 S. Sivakumar and M. Reddy, *J. Mater. Chem.*, 2012, **22**, 10852-10859.

23 Q.-D. Liu, R. Wang and S. Wang, *Dalton Trans.*, 2004, 2073-2079.

24 C. Seward, J. Pang and S. Wang, *Eur. J. Inorg. Chem.*, 2002, 1390-1399.

25 S. G. Roh, Y. H. Kim, K. D. Seo, D. H. Lee, H. K. Kim, Y. I. Park, J. W. Park and J. H. Lee, *Adv. Funct. Mater.*, 2009, **19**, 1663-1671.

26 W. Chen, R. Fan, H. Zhang, Y. Dong, P. Wang and Y. Yang, *Dalton Trans.*, 2017, **46**, 4265-4277.

27 H. F. Jiu, J. J. Ding, Y. Y. Sun, J. Bao, C. Gao and Q. J. Zhang, *J. Non-Cryst. Solids*, 2006, **352**, 197-202.

28 N. Sun, L. Li, Y. Yang, A. Zhang, H. Jia, X. Liu and B. Xu, *Opt. Mater.*, 2015, **49**, 39-45.

29 H. Wang, P. He, H. Yan and M. Gong, *Sens Actuators B Chem.*, 2011, **156**, 6-11.

30 A. Fischer, T. Koprucki, K. Gärtner, M. L. Tietze, J. Brückner, B. Lüssem, K. Leo, A. Glitzky and R. Scholz, *Adv. Funct. Mater.*, 2014, **24**, 3367-3374.

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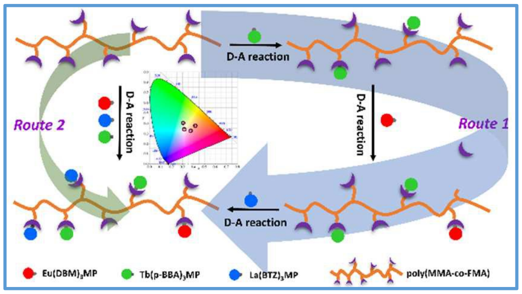
DOI: 10.1039/C8TC03022G



Lanthanide metallopolymers with tunable emission were prepared by skillfully designed Diels-Alder reaction.