

Chiral sensing for induced circularly polarized luminescence using an Eu(III)-containing polymer and D- or L-proline†

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An Eu(III)-containing polymer can exhibit intense induced circularly polarized luminescence (CPL) in the presence of proline. In addition, the optical anisotropy factor (g_{lum}) of the polymer for $^5D_0 \rightarrow ^7F_1/7F_2$ transition was much higher than that of a single model molecule, which reveals the amplification effect of CPL arising from the conjugated polymer structure.

Enantioselective recognition of chiral molecules is one of the most important fundamental processes in nature and plays vital roles in asymmetric synthesis and biological systems.¹ More sophisticated chiroptical probes have recently brought fresh insights to the role of solvation and the local dielectric environment in the problem of light–matter interactions with chiral materials.² Circularly polarized luminescence (CPL) is now a ubiquitous tool for characterizing and quantifying natural and synthetic chiral systems.³ In the past several years, there has been growing interest in the CPL-active materials⁴ and chemical-stimuli-responsive CPL properties.⁵ Maeda and co-workers first observed anion-driven CPL enhancement response behaviour of chiral BINOL-based boron hybrid complexes.^{5a,b} Recently, Iwamura *et al.* have also found that the chiral sensing effect could be detected by using achiral europium(III) complexes in the presence of chiral 2-pyrrolidone-5-carboxylic acid.^{5c}

Although there have been some reports on CPL-induced chemical sensors, most of them are based on organic small molecules. So far there has been no report on polymer-based CPL sensors. Compared with organic small molecules, one of the most important questions is whether the achiral polymer sensor can offer a significantly higher luminescence dissymmetry factor g_{lum} by the induction of chiral molecules. Herein, $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R are the emission intensities of left and right circularly polarized luminescence, respectively.^{2a}

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Another question is whether the conjugated polymer can lead to the chiral sensing enhancement or the chiroptical signal amplification effect. These questions may be resolved by enhancing the purity of the chiroptical response from the intrinsic interaction between chiral molecules and the conjugated polymer structures, which can afford an opportunity to develop more sensitive CPL materials.

It is well known that chiral lanthanide(III) complexes are of great practical value because optical anisotropy factors (g_{lum} values) of f–f transitions are much higher than those of chiral organic molecules.^{5c,6} In our previous work, we reported the energy transfer from the conjugated polymer to the Eu(TTA)₃ moiety by choosing different excitation wavelengths for tunable chromaticity.⁷ In this work, we have further designed and synthesized an achiral Eu(III)-containing conjugated polymer **P3** in which the Eu(III) metal ion is tightly coordinated with the β-diketone unit in the polymer main chain. The higher optical anisotropy factor (g_{lum}) of the polymer for $^5D_0 \rightarrow ^7F_1/7F_2$ transition could be detected by induced CPL in the presence of D- or L-proline, which reveals the amplification effect of CPL arising from the conjugated polymer structure.

The neutral polymer **P1**, water-soluble polymer **P2**, Eu(III)-containing polymer **P3** and the corresponding model molecule are shown in Fig. 1. The neutral polymer **P1** could be obtained by the polymerization of 2,2'-((2,5-diiodo-1,4-phenylene)bis(oxy))bis(*N,N*-diethylethanamine) (**M1**) with 1,3-bis(4-ethynylphenyl)-3-hydroxyprop-2-en-1-one (**M2**) via a typical Pd-catalyzed Sonogashira cross-coupling reaction (Scheme S1, ESI†). Conversion of the neutral

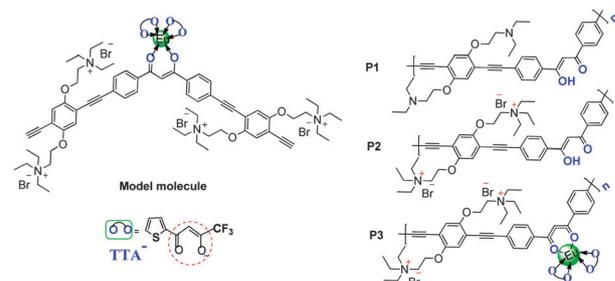


Fig. 1 Structures of the neutral polymer **P1**, water-soluble polymer **P2**, Eu(III)-containing polymer **P3** and the corresponding model molecule.

polymer **P1** to the cationic polymer **P2** was achieved by treating **P1** with bromoethane in THF–DMSO at 50 °C for 3 days. M_w , M_n and PDI of polymer **P1** were determined by gel permeation chromatography using polystyrene standards in THF and their values are 34 720, 32 800 and 1.05, respectively. The GPC result of polymer **P1** shows a high molecular weight. **P1** is soluble in THF and DMF solvent, but insoluble in methanol. **P2** exhibits good solubility in water and DMF. The water soluble polymer **P2** does not form the completely quaternized cationic polymer. By comparing the ^1H NMR spectra of the subunits M2, S2, and S4, the quaternization degree (QD) of **P2** could be determined using ^1H NMR spectroscopy as shown in Fig. S1 (ESI †). Based on the relative integrals of each pair of split peaks ($-\text{CH}_2\text{N}^-$, low field: the quaternized component, upfield: unquaternized component 8), the QD of **P2** is 42%. In addition, these spectral features support the view that a well-defined polymer **P2** structure was obtained as we expected. **P2** incorporating a β -diketone unit in the polymer backbone could directly coordinate with EuCl_3 and the TTA anion ligand (4,4,4-trifluoro-1-(thiophen-2-yl)butane-1,3-dione) to afford **P3** as a deep red solid in a solution of pH = 6.5. The β -diketone unit in the main chain backbone of **P2** does not completely coordinate with Eu ions according to their elemental analysis data. Furthermore, the molar ratio of sulfur and nitrogen could be obtained from elemental analysis results. The molar ratios of S and N obtained from elemental analysis is 0.51 [3.28/(32.0 \times 2):2.85/(14.01 \times 2)] indicating that the content of $\text{Eu}(\text{TTA})_2$ in **P3** is 51%. Herein, the content of Eu in **P3** is 7.74%, similar to the elemental analysis data obtained using ICP determination. 7

The fluorescence spectra of the model molecule, **P2** and **P3** were obtained in a mixed solution of DMSO and H_2O (v/v, 1.0%, 1×10^{-5} mol L^{-1} corresponding to the β -diketone unit). As evident from Fig. 2a, the water soluble polymer **P2** appears to exhibit a strong fluorescence emission centered at 410 nm upon excitation at 350 nm. The Eu(III)-containing polymer **P3** exhibits characteristic red fluorescence situated at 615 nm while excited at 350 nm, which can be assigned to the Eu(III) ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) transition. The weak emission peaks of Eu(III) at 577, 596 and 653 nm can be fingerprinted to Eu(III)'s $^5\text{D}_0 \rightarrow ^7\text{F}_0$, $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_3$ transitions, respectively. However, compared with **P2**, **P3** exhibits a weak fluorescence emission at 410 nm arising from the conjugated polymer backbone, demonstrating that the energy transfer process can partially take place from the polymer main chain conjugated backbone to the $\text{Eu}(\text{TTA})_2$ complex moiety. As evident from Fig. 2b, a perfect overlap between the excitation ($\lambda_{\text{moni}} = 615$ nm) and absorption spectra of **P3** can also support the hypothesis that the fluorescence emission of polymer **P3** at 410 nm shows obvious quenching due to efficient intramolecular energy transfer. 7,9 In addition, the fluorescence decay profiles of **P2** and **P3** were obtained with excitation at 345 nm and detection at 410 nm (Fig. 2c). The weighted average lifetimes ($\langle\tau^0\rangle$) 10 of **P2** and **P3** were 2.08 ns and 1.53 ns, respectively, which provides further evidence of efficient energy transfer. 11 And the mean square deviation χ^2 (CHISQ) values of **P2** and **P3** were 0.94866 and 0.85040 (Fig. S2, ESI †). Similar to **P3**, the model molecule also shows a sharp emission peak at 615 nm and a weak

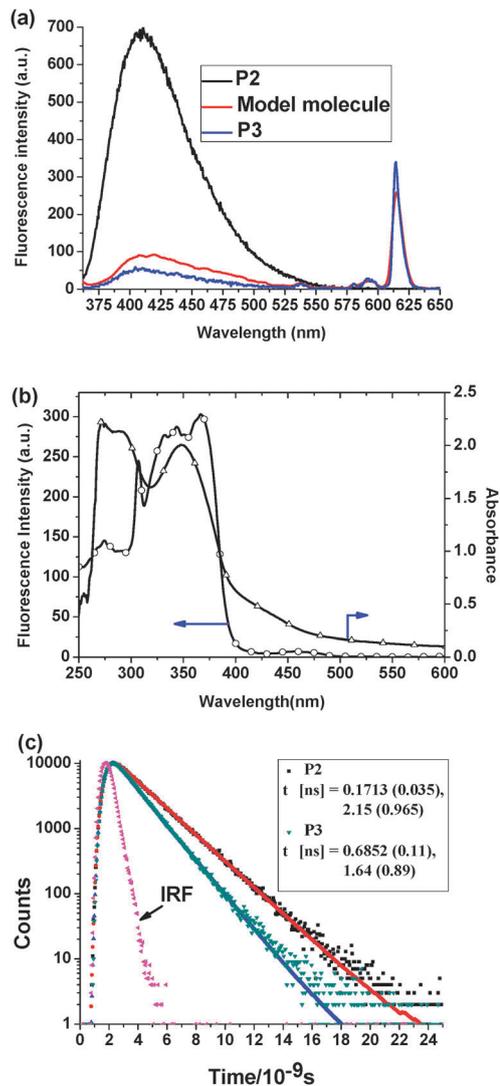


Fig. 2 (a) Fluorescence spectra of **P2**, **P3** and the model molecule in a mixed solution of DMSO and H_2O (v/v, 1.0%, 1×10^{-5} mol L^{-1} corresponding to β -diketone unit) $\lambda_{\text{ex}} = 350$ nm. (b) Fluorescence excitation (\circ) and absorption (Δ) spectra of **P3**: [**P3**] = 1×10^{-5} mol L^{-1} , $\lambda_{\text{moni}} = 615$ nm. (c) Time-resolved fluorescence decays (τ) of **P2** and **P3** in DMSO and H_2O (v/v, 1.0%, 1×10^{-5} mol L^{-1} corresponding to the β -diketone unit) obtained by excitation at 345 nm and detection at 410 nm.

emission peak at 410 nm with several weak emission peaks from 577 to 653 nm.

Fig. 3 shows the CPL and total luminescence spectra for an aqueous solution of **P3** and a model molecule in the presence and absence of proline (0.1 mol L^{-1} in DMSO and H_2O v/v, 1.0%). In the absence of proline, no CPL spectrum was observed. However, upon addition of D- or L-proline to the solution of **P3** and the model molecule, intense CPL signals situated at 596 nm of mirror image $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition could be clearly observed as shown in Fig. 3. More interestingly, we found that **P3** when used as a CPL-active sensor for enantioselective recognition of proline can exhibit better sensitivity and selectivity than the model molecule. With the model molecule, a g_{lum} value of +0.028 was observed for L-proline versus $g_{\text{lum}} = -0.036$ for D-proline (Fig. 3a). As for **P3**, the $^5\text{D}_0 \rightarrow ^7\text{F}_1$

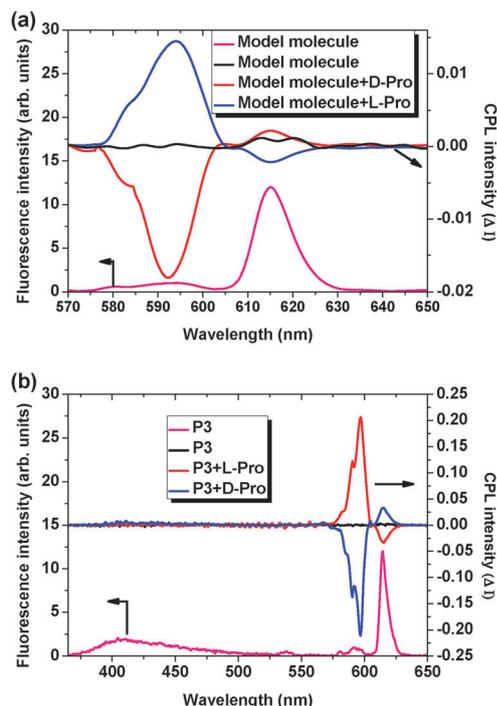


Fig. 3 Circular polarized luminescence (upper curves) and total luminescence (lower curves) spectra of model molecule (a) and **P3** (b) in DMSO and H₂O (v/v, 1.0%, 1×10^{-5} mol L⁻¹ corresponding to the β -diketone unit). (a) Spectra observed in the range of 570–650 nm in the presence and absence of L- and D-proline. The total luminescence spectrum was normalized to the peak of $^5D_0 \rightarrow ^7F_1$ transition. (b) Spectra observed in the wide range of 360–650 nm in the presence and absence of L- and D-proline. The total luminescence spectra were normalized to the peak of $^5D_0 \rightarrow ^7F_1$ transition ($\lambda_{\text{ex}} = 350$ nm).

magnetic-dipole transition at 596 nm gave a g_{lum} value of +0.41 for L-proline versus $g_{\text{lum}} = -0.42$ for D-proline (Fig. 3b). Thus **P3** can exhibit intense left circularly polarized luminescence (CPL) in the presence of L-proline in aqueous solution for $^5D_0 \rightarrow ^7F_1$ transition, while right-CPL was observed in the presence of D-proline for $^5D_0 \rightarrow ^7F_1$ transition. In addition, the CPL spectra of the $^5D_0 \rightarrow ^7F_2$ transition of **P3** also gave a low g_{lum} value of -0.0055 for L-proline versus $g_{\text{lum}} = +0.0056$ for D-proline. However, the g_{lum} value of the $^5D_0 \rightarrow ^7F_2$ transition for the model molecule was measured to be less than 0.001. We thought that a well-defined structure of the conjugated polymer main chain can lead to a specific guest-molecule orientation, which can be beneficial to obtain a higher luminescence dissymmetry factor.^{2a} Herein, this kind of specific guest-molecule orientation can be induced by the interaction between the Eu-containing polymer and L- or D-proline so that distinct contributions to the average g value can be observed. As for the single molecule, the lower g value can be attributed to cancellation effects in ensemble measurements of a randomly oriented bulk sample. Our research suggests that the amplification effect of chiral sensing for induced CPL could be realized by using an achiral Eu(III)-containing conjugated polymer and D- or L-proline.

An achiral Eu(III)-containing polymer can exhibit intense left circularly polarized luminescence (CPL) in the presence of L-proline in aqueous solution for $^5D_0 \rightarrow ^7F_1$ transition, while right-CPL was observed in the presence of D-proline for $^5D_0 \rightarrow ^7F_1$ transition.

More importantly, the optical anisotropy factor (g_{lum}) of the polymer for $^5D_0 \rightarrow ^7F_1/7F_2$ transition was much higher than that of the single model molecule demonstrating that the amplification effect of CPL could be produced by the conjugated polymer by the induction of chiral organic small molecules. This research work could provide a new strategy to obtain higher g_{lum} values for CPL-active polymer materials.

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