

Short communication

First example of PMMA-supported and highly luminous color-purity red-light metallopolymer based on a tris- β -diketonate Zn^{2+} - Eu^{3+} -complex



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ABSTRACT

Through the copolymerization of a complex monomer $[\text{Zn}(\text{L})(4\text{-vinyl-Py})\text{Eu}(\text{TTA})_3]$ (**2**; $\text{H}_2\text{L} = N,N'$ -bis(salicylidene)cyclohexane-1,2-diamine; 4-vinyl-Py = 4-vinyl-pyridine and HTTA = 2-thenoyltrifluoroacetate) with MMA (methyl methacrylate), the first example of PMMA-supported and highly luminous ($\Phi_{\text{Eu}}^{\text{red}} = 63.1\%$) color-purity red-light metallopolymer poly(MMA-co-**2**) based on a tris- β -diketonate Zn^{2+} - Eu^{3+} -complex is obtained.

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Attributed to the long-lived (μs to ms) lifetime and the high color-purity in red-light emission of Eu^{3+} ion, there has been of special interest on the development of Eu^{3+} -based optical materials with potential applications in monochromatic red-light [1] or panchromatic white-light OLEDs (organic light-emitting diodes) [2], barcode materials [3] and fluoro-immunoassays [4]. Nevertheless, the inherent limit of low molar absorption coefficients ($\epsilon = 0.01\text{--}10 \text{ M}^{-1}$) due to the parity forbidden f-f transitions of Eu^{3+} ion, has led to a considerable introduction of suitable chromophores to act as sensitizers for the effective sensitization of characteristic narrow line-like emissions of Eu^{3+} ion (antenna effect) [5]. As a matter of fact, an ideal Eu^{3+} -based optical material, especially for optoelectronic applications, should require exceptionally high thermal stability and good mechanical property [6].

To date, HTTA is proved to be one of the most popular chromophores for Eu^{3+} -complexes because of its strong optical absorption and suitable $^1\pi\text{-}\pi^*$ ($25,000 \text{ cm}^{-1}$) and $^3\pi\text{-}\pi^*$ ($20,600 \text{ cm}^{-1}$) excited energy levels for the efficient intra-molecular energy transfer to Eu^{3+} ion [7]. In this context, most of Eu^{3+} -complexes adopt a binary tris- β -diketonate configuration, where the remaining coordination sites are saturated by one neutral organic ancillary ligand in N,N' -chelate [8], N,N',N'' -chelate [9], or $P = \text{O}$ -linked mode [10]. The involvement of these ancillary ligands is highlighted from avoidance of direct oscillator-induced quenching effect [11], while not impactful enough to further decrease the $^3\pi\text{-}\pi^*$ energy level. On the other hand, due to poor mechanical property and relatively low thermal stability for

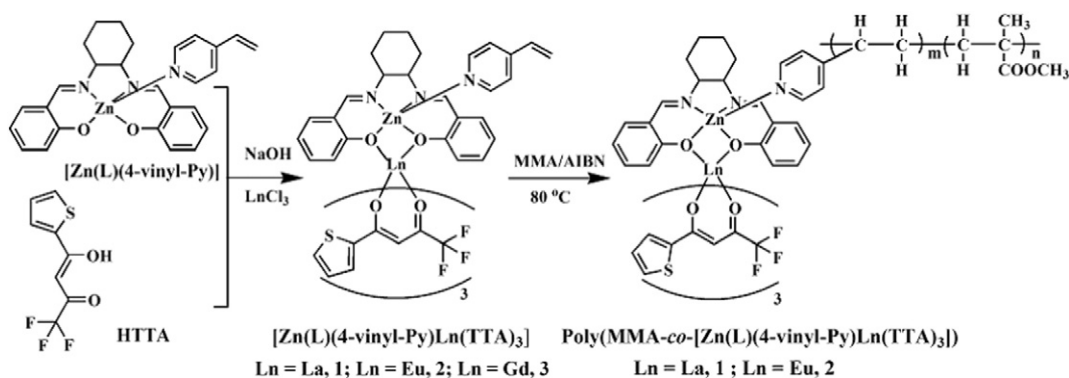
those tris- β -diketonate Eu^{3+} -complexes, they have no choice but to be applied as organic-inorganic hybrid materials through doping [12] or grafting [13] into one stable inorganic or organic host matrix.

Our recent report [14] of the series of Zn-Ln -complexes ($\text{Ln} = \text{Nd}$, Yb , Er or Gd) self-assembled from both one Zn-Salen complex and three same β -diketonate ligands showed that the Zn-Salen portion could be realized as the O,O' -chelate ancillary ligand to form typical binary tris- β -diketonate Ln^{3+} -complexes [10]. More importantly, the combination of Zn-Salen complex and β -diketonate ligand within actually enabled a further decrease of the $^3\pi\text{-}\pi^*$ energy level besides the availabilities to strengthening the optical absorption and enhancing the thermal stability. These stimulate us an exploration on the TTA-based tris- β -diketonate hetero-binuclear Zn^{2+} - Eu^{3+} -complex, and its highly luminous and color-purity red-light emission is expected. Additionally, by introducing an active vinyl group into the $(\text{TTA})_3\text{-Zn}^{2+}\text{-Eu}^{3+}$ -complex system, the first example of PMMA-supported and Zn^{2+} - Eu^{3+} -containing grafting-type metallopolymer is constructed, where the improved physical properties including significantly enhanced color-purity red-light emission of Eu^{3+} ion are also anticipated. Herein, through self-assembly from a precursor $[\text{Zn}(\text{L})(4\text{-vinyl-Py})]$ with HTTA and $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ ($\text{Ln} = \text{La}$, Eu or Gd), three new $(\text{TTA})_3\text{-Zn}^{2+}\text{-Eu}^{3+}$ -complexes ($[\text{Zn}(\text{L})(4\text{-vinyl-Py})\text{Ln}(\text{TTA})_3]$; $\text{Ln} = \text{La}$, **1**; $\text{Ln} = \text{Eu}$, **2** or $\text{Ln} = \text{Gd}$, **3**) are obtained, respectively. And based on copolymerizations of the efficient color-purity red-luminescence complex monomer **2** with MMA in different feed molar ratios, the series of metallopolymer poly(MMA-co-**2**) are formed, respectively.

As shown in Scheme 1, the precursor $[\text{Zn}(\text{L})(4\text{-vinyl})]$ was obtained in a good yield of 81% from the reaction of an equimolar amount of the

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Scheme 1. Reaction scheme for synthesis of three tris- β -diketonate Zn^{2+} - Ln^{3+} -complex monomers **1–3** and their PMMA-supported metallopolymers poly(MMA-*co*-**1**) and poly(MMA-*co*-**2**).

Salen-type Schiff-base ligand H_2L and $Zn(OAc)_2 \cdot 2H_2O$ in the presence of 4-vinyl-Py. Moreover, through the self-assembly of the deprotonated $(TTA)^-$ ligand, the precursor $[Zn(L)(4\text{-vinyl})]$ and $LnCl_3 \cdot 6H_2O$ ($Ln = La, Eu$ or Gd), three Zn^{2+} - Eu^{3+} -complexes ($[Zn(L)(4\text{-vinyl-Py})Ln(TTA)_3]$; $Ln = La, 1$; $Ln = Eu, 2$ or $Ln = Gd, 3$) were isolated as yellow microcrystalline solids, respectively. The precursor $[Zn(L)(4\text{-vinyl})]$ and its complexes **1–3** were well-characterized by EA, FT-IR (Fig. 1S) and ESI-MS (in Supporting information). It is worth noting that, despite a regret of no X-ray single-crystal diffraction data for each of three complexes as the analogue of the binary tris- β -diketonate Zn^{2+} - Yb^{3+} -complex [14], the similar combined proton resonances ($\delta = 8.53$ – 1.43 ppm) of both the deprotonated $(TTA)^-$ ligand and the precursor $[Zn(L)(4\text{-vinyl})]$ in a stipulated molar ratio of 3:1 for the anti-ferromagnetic complex **1** in the 1H NMR spectrum (shown in Fig. 2S) should well consolidate the binary tris- β -diketonate Zn^{2+} - La^{3+} configuration. Moreover, the new proton resonances ($\delta = 6.74, 6.11$ and 5.53 ppm) assigned to the terminal functional vinyl group ($-\text{CH}=\text{CH}_2$) of 4-vinyl-Py in **1** almost remain the same as those ($\delta = 6.75, 6.15$ and 5.54 ppm) of 4-vinyl-Py in the precursor of $[Zn(L)(4\text{-vinyl-Py})]$ despite the coordination of La^{3+} ion. Furthermore, ESI-MS spectra of complexes **1–3** in MeCN display the similar patterns and exhibit the strong mass peak at m/z 1294.35 (**1**), 1307.41 (**2**) or 1312.70 (**3**) attributed to the major species $[M-H]^+$ of complexes **1–3**, respectively, also further confirming that

the respective $(TTA)_3$ - Zn^{2+} - Eu^{3+} -binuclear molecule unit is stable in the respective dilute solution.

For the absorption spectra of complexes **2–3** in solution shown in Fig. 3S, the similar combined ligand-centered absorptions of 230–232, 264–265 and 338–340 nm while distinctively red-shifted relative to those (268 and 330 nm) of the free HTTA or those (218, 254 and 314 nm) of the free Salen-type Schiff-base ligand H_2L due to the coordination of metal ions in the UV-visible region are observed. However, in comparison with those (230, 262 and 350 nm) of the precursor $[Zn(L)(4\text{-vinyl-Py})]$, the lower energy absorptions are all slightly blue-shifted by 10–12 nm due to the further coordination of Ln^{3+} ion. For complex **2**, photo-luminescence (in Fig. 2) upon $\lambda_{ex} = 376$ nm just exhibits the Eu^{3+} -centered characteristic while ligand-field splitting emissions ($^5D_0 \rightarrow ^7F_J, J = 0-4$). Moreover, the evidence of a single peak at 579 nm assigned to the $^5D_0 \rightarrow ^7F_0$ transition, together with a large intensity ratio of about 29 between the “hyper-sensitive” $^5D_0 \rightarrow ^7F_2$ transition (613 nm) and the $^5D_0 \rightarrow ^7F_1$ transition (594 nm), also verifies that there has only one luminescent Eu^{3+} species with a low symmetrical coordination character for complex **2** in solution [15], giving rise to the bright color-purity red-light with a CIE (Commission International De L’Eclairage) chromatic coordinate (0.665, 0.334). As for complex **3**, upon photo-excitation ($\lambda_{ex} = 387$ nm) of the chromophores in the range of 310–440 nm at RT, a wide-ranging visible

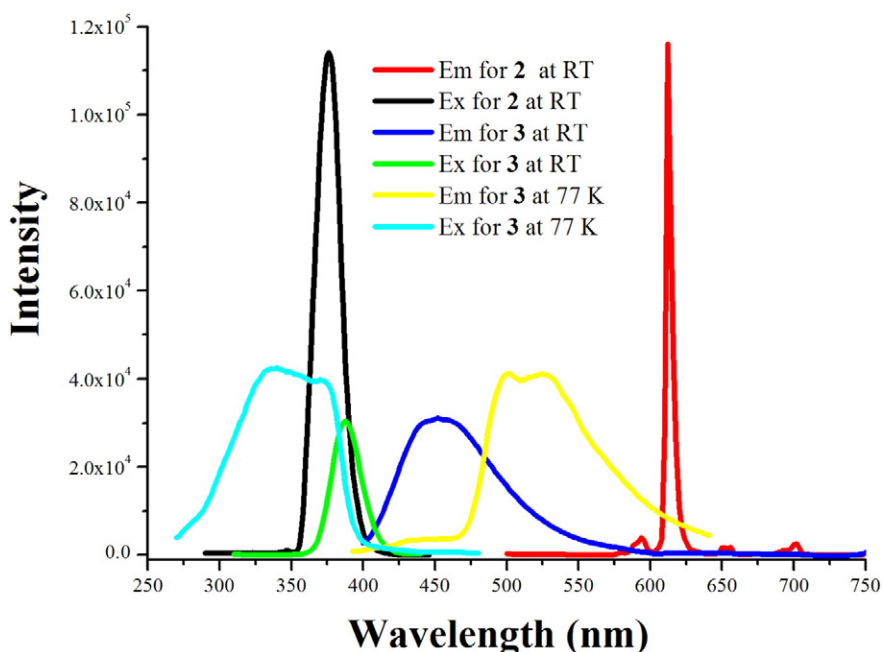


Fig. 1. Visible emission and excitation spectra of complexes **2–3** in absolute MeCN solution at 1×10^{-5} M at RT or 77 K.

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