

Near-infrared (NIR) luminescent PMMA-based hybrid materials doped with Ln- β -diketonate (Ln = Nd or Yb) complexes



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ABSTRACT

Based on $[\text{Ln}(\text{L})_3(\text{H}_2\text{O})_2]$ (Ln = Nd, Yb or Er) complexes self-assembled from a trifluorinated acylpyrazole-type β -diketonate ligand **HL** ((Z)-3-methyl-1-phenyl-4-(2,2,2-trifluoro-1-hydroxyethylidene)-1H-pyrazol-5(4H)-one) and $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$, a series of NIR luminescent PMMA-supported hybrid materials $\text{PMMA}@\text{[Ln(L)}_3(\text{H}_2\text{O})_2]$ are obtained from physical doping. The immobilization of the luminescent species *via* physical and chemical interactions within the polymeric PMMA matrix also acting as co-sensitizer, endows the enhanced NIR luminescent properties ($\Phi_{em} = 0.85\text{--}0.97\%$) in comparison to the individual Ln^{3+} - β -diketonate complex ($\Phi_{em} = 0.53\text{--}0.79\%$) besides the improved thermal-stability properties.

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The characteristic photo-excited near-infrared (NIR) luminescent properties of Ln^{3+} (Ln = Nd, Yb or Er) ions are currently of special interest because of their potential applications in organic light-emitting diodes [1], tele-communication [2] and bio-analysis [3]. However, due to forbidden parity from the f–f transitions, introduction of suitable chromophores is necessary to obtain various Ln^{3+} complexes, where the organic chromophores are used as the sensitizers for the NIR luminescence of these Ln^{3+} ions (“antenna effect”) [4], indirectly. On the other hand, from the viewpoint of practical use, the NIR luminescent Ln^{3+} complexes are limited to a large extent by poor thermal stability and low mechanical strength. One of the simple but effective solutions [5] is through physical doping into a host polymer matrix such as poly(methyl methacrylate) (PMMA) to form a complex-containing hybrid material, from which, the distinctively improved thermal stability and mechanical properties could be expected [6]. Moreover, the possible recombination of charge carriers from PMMA matrix at the Ln^{3+} -centered trap site, endows the enhanced NIR luminescent performance due to the strengthened recombination energy transfer [7].

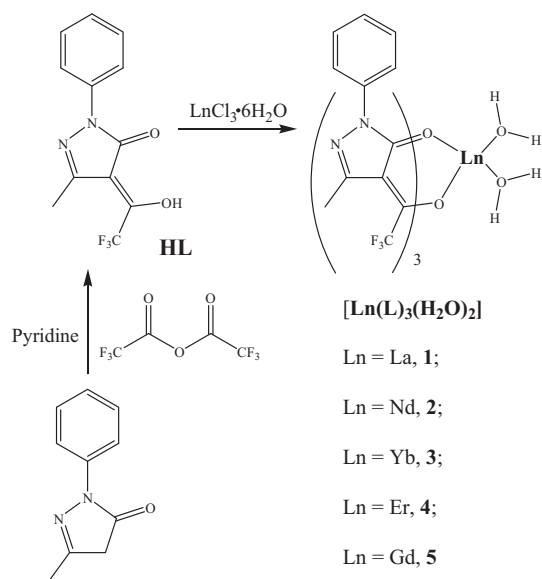
As a matter of fact, due to strong absorption within a large wavelength range, β -diketonate ligands and their derivatives are one among the most studied antenna molecules for sensitizing the characteristic luminescence of the Ln^{3+} ions in the obtained neutral trakis-(β -diketonate) [8–10] or anionic tetrakis-(β -diketonate) Ln^{3+} -complexes [11]. Especially the fluorinated [12] or aryl-modified β -diketonate ligands [13] with the

facilitated intersystem crossing appear to be suitable candidates on the sensitization of NIR emissions of some Ln^{3+} (Ln = Nd, Yb or Er) ions. Moreover, in contrast to the recent progress concerning PMMA doped with visible luminescent β -diketonate Ln^{3+} complexes [14], few examples of NIR luminescent PMMA-supported hybrid materials are reported [15]. Herein, a trifluorinated acylpyrazole-type β -diketonate ligand **HL** (**HL** = (Z)-3-methyl-1-phenyl-4-(2,2,2-trifluoro-1-hydroxyethylidene)-1H-pyrazol-5(4H)-one) with the promoted spin-orbit coupling is selected, and its NIR luminescent $[\text{Ln}(\text{L})_3(\text{H}_2\text{O})_2]$ (Ln = Nd, Yb or Er) complexes are doped into PMMA matrices, respectively. Furthermore, the improvement of the NIR luminescent and other physical properties of the hybrid materials is anticipated.

As shown in Scheme 1, the β -diketonate ligand **HL** was obtained in 93% yield from the trifluorinated acylation reaction with trifluoroacetic anhydride for 1-methyl-3-phenyl-1H-pyrazol-4(5H)-one in the presence of excess pyridine, and its dihydrate complexes $[\text{Ln}(\text{L})_3(\text{H}_2\text{O})_2]$ (Ln = La, **1**; Ln = Nd, **2**; Ln = Yb, **3**; Ln = Er, **4** or Ln = Gd, **5**) were easily assembled from further reaction with $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ and NaOH in EtOH– H_2O mixture, respectively. The ligand **HL** and complexes **1–5** were well characterized by EA, FT-IR and ^1H NMR, and X-ray quality crystals were obtained for **3**·EtOH as the representative of **1–5** with the crystallographic data in Tables 1–2s. **3**·EtOH crystallizes in the monoclinic system with the space group of $P2(1)/c$, where the asymmetric unit is composed of one neutral mononuclear $[\text{Yb}(\text{L})_3(\text{H}_2\text{O})_2]$ molecule and one solvate EtOH. As shown in Fig. 1, six O atoms (O1–O6) from three deprotonated L^- ligands chelate to the central Yb^{3+} ion (Yb1), and two O atoms (O7 and O8) from two coordinated H_2O saturate its eight-coordinate environment in a square *anti*-prismatic pattern,

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Scheme 1. Synthesis of the β -diketonate ligand **HL** and its Ln^{3+} complexes **1–5**.

exhibiting the typical neutral trakis-(β -diketonate) Ln^{3+} -complex framework [8]. It is worth noting that the two coordinated H_2O molecules occupy in the *trans*-position but not *cis*-position within the square plane, which should be due to the bulkiness effect of the CF_3 -substituent in the β -diketonate ligand.

The photophysical properties of **HL** and **2–5** have been examined in dilute MeCN solution at room temperature or 77 K, and summarized in Table 3s and Figs. 2 and 1–2s. As shown in Fig. 1s, the similar ligand-centered solution absorption spectra of 248–249 and 288–290 nm for **2–5** in the UV–visible region are observed, distinctively red-shifted by 19–20 and 8–10 nm in relative to that (229 and 280 nm) of the free β -diketonate ligand **HL** up coordination of Ln^{3+} ions. For **2–4**, in addition to the similar residual visible emissions ($\lambda_{em} = 470$ nm, $\tau < 1$ ns and $\Phi_{em} < 10^{-5}$), photo-excitation of the antennae at the range of 250–450 nm gives rise to the strong characteristic emissions of the Nd^{3+} ion (900, 1063 and 1335 nm; $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{j/2}$, $J = 9, 11, 13$) and the Yb^{3+} ion (979 nm; $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$) in the NIR region, respectively, while the characteristic NIR emission of the Er^{3+} ion for **4** is too weak to be observed, as shown in Fig. 2. The free β -diketonate ligand **HL** or **5** does not exhibit the NIR emission under the same condition, and just displays the strong ligand-based visible luminescence ($\lambda_{em} = 433$ nm, $\tau = 28.2$ ns and $\Phi_{em} = 3.4\%$ for the ligand; $\lambda_{em} = 470$ nm, $\tau = 36.7$ ns and $\Phi_{em} = 7.6\%$ for complex **5**) shown in Fig. 2s. At 77 K, **5** exhibits the typical phosphorescence ($\lambda_{em} = 519$ nm, $\tau = 0.21$ ms), from which the

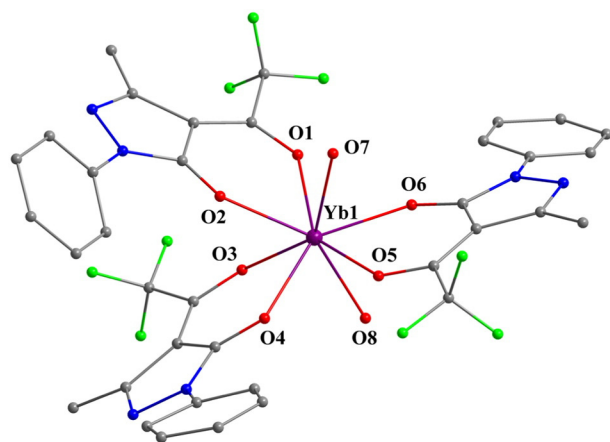


Fig. 1. Perspective drawing of **3·EtOH**, H atoms and solvate are omitted for clarity.

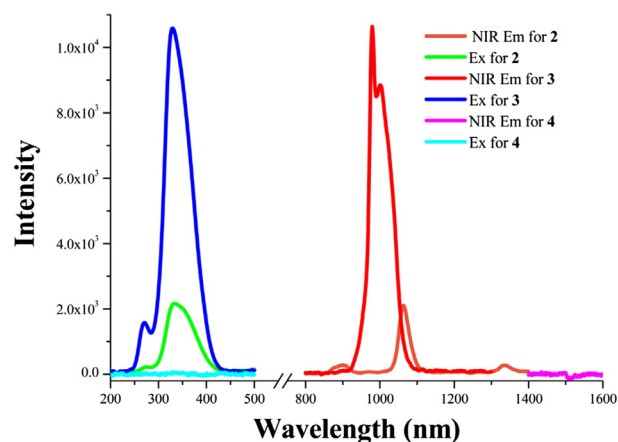


Fig. 2. NIR emission and excitation spectra of **2–4** in MeCN solution at 2×10^{-5} M at room temperature.

triplet ($^3\pi\pi^*$) energy level (19268 cm^{-1}) of the β -diketonate ligand **HL** is obtained. With regard to the singlet ($^1\pi\pi^*$) energy level (26667 cm^{-1}) of β -diketonate ligand **HL** estimated by referring to the wavelength of its UV–visible absorbance edge, the greater ΔE (7399 cm^{-1} , $^1\pi\pi^* - ^3\pi\pi^*$) than 5000 cm^{-1} endows the effective intersystem crossing process according to the Reinholdt's empirical rule [16]. Moreover, from the viewpoint of energy-level match, although the effective energy transfer in **4** is similar to those in **2** and **3** due to the triplet ($^3\pi\pi^*$) energy level (19268 cm^{-1}) of the β -diketonate ligand **HL** higher than each of the first excited state energy of Ln^{3+} ions (11257 cm^{-1} for $^4\text{F}_{3/2}$ of Nd^{3+} ion; 10400 cm^{-1} for $^2\text{F}_{5/2}$ of Yb^{3+} ion and 6610 cm^{-1} for $^4\text{I}_{13/2}$ of Er^{3+} ion), the large energy gap ($\Delta E = 12658 \text{ cm}^{-1}$) in **4** results in greater nonradiative energy loss during the energy transfer [17], which should be the reason to weak NIR luminescence for **4**. Furthermore, through time-resolved luminescence experiments for **2–3**, their respective luminescence decay curve can be fitted mono-exponentially with lifetimes in the microsecond range ($1.33 \mu\text{s}$ for **2** and $15.8 \mu\text{s}$ for **3**), and the intrinsic quantum yield (0.53% for **2** or 0.79% for **3**) of Ln^{3+} emission may be estimated by $\Phi_{Ln} = \tau_{obs}/\tau_0$ [18], where τ_{obs} is the observed emission lifetime and τ_0 is the “neutral lifetime”, *viz.* 0.25 or 2.0 ms for the Nd^{3+} or Yb^{3+} ion, respectively. As to the relatively higher intrinsic quantum yield of **3** (0.79%) than that of **2** (0.53%), it should be due to the quantity ($^4\text{I}_{j/2}$, $J = 9, 11, 13$) of accepting energy levels of the Nd^{3+} ion while only one ($^2\text{F}_{7/2}$) for the Yb^{3+} ion [19]. It is worth noting that both **2** and **3** exhibit the relatively shorter luminescent lifetimes than those of the reported trakis-(β -diketonate) Ln^{3+} -complexes with the N,N'- [20] or O, O'-chelated ancillary ligand [21], which should be ascribed to the –OH vibrational quenching [22] from the two coordinated H_2O molecules in the inner sphere of Ln^{3+} ions.

In consideration of the excellent performance of PMMA as one of the popular polymeric matrices with low cost, low optical absorbance and good mechanical property [23], PMMA-supported hybrid materials **PMMA@[Ln(L)₃(H₂O)₂]** ($\text{Ln} = \text{La}$, **1**; Nd , **2**; Yb , **3**; Er , **4** or Gd , **5**) with the molar ratio (100:1) of MMA to one of **1–5** are obtained from physical doping, respectively. The doped hybrid materials **PMMA@[Ln(L)₃(H₂O)₂]** based on **1–5** are well verified by FT-IR spectra, where the band absorptions in the range of $3293\text{--}3296 \text{ cm}^{-1}$ attributed to the coordinated H_2O in **1–5** almost disappeared, and the intense absorptions at $1738\text{--}1742 \text{ cm}^{-1}$ assigned to the $\nu(\text{C}=\text{O})$ vibration of **PMMA@[Ln(L)₃(H₂O)₂]** are slightly blue-shifted by $6\text{--}10 \text{ cm}^{-1}$ than that (1732 cm^{-1}) of pure PMMA. Both indicate that the two coordinated H_2O could be partially replaced by carbonyl groups from PMMA, and the coordination bonds between the $\text{C}=\text{O}$ groups of PMMA and Ln^{3+} ions are formed by doping [24] besides the van der Waals contacts and electrostatic forces. Further through the room temperature ^1H

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