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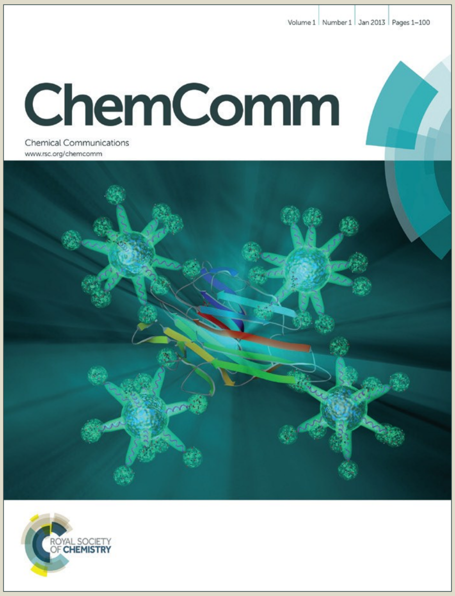

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Pure white-light and colour-tuning of Eu^{3+}-Gd^{3+}-containing metallopolymer

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Direct white-light (CIE coordinate of *x* = 0.333, *y* = 0.335, CCT of 5455 K and CRI of 82) with a high luminous efficiency (18.4%) was achieved in the first example of Eu^{3+}-Gd^{3+}-containing metallopolymer Poly(2-*co*-NVK-*co*-4), which also showed tuneable purplish-blue to white to yellow-green photoluminescence.

Ln^{3+}-containing metallopolymers,[1] distinctively different from Ln^{3+}-based supramolecular polymers,[2] arouse a special interest owing to the advantage of beneficial properties of both inorganic Ln^{3+} ion and organic macromolecule. Especially photophysical uniqueness of Ln^{3+} ion within makes its systems ideal for the development of luminescent metallopolymers with potential applications[3] for monochromatic polymer light-emitting diodes (PLEDs), sensors and memory devices. Nevertheless, if extended to white-light-emitting materials, and compared with great efforts to nanocrystals,[4] quantum dots,[5] small organic molecules,[6] polymers,[7] transition-metal-containing metallopolymers[8] and metal-organic frameworks (MOFs),[9] systems relied on hetero-Ln^{3+}-containing metallopolymers are still quite rare,[10] despite their prominent superiorities of both Ln^{3+}-endowed high colour purity and high luminous efficiency, and polymer-assisted exceptional stability and good film-forming properties. In this context, the common approach is through post-coordination from the firstly-prepared coordination-site-retained polymer skeletons with Eu^{3+} and Tb^{3+} complex units. In view of their white-light emissions, typical trichromatic (RGB) strategy[11] is based on a combination of red from Eu^{3+}, green from Tb^{3+} and compensatory blue from polymer. However, the balance of different colour contributions for ideal white-light-emitting remains a real challenge[10a] because of unmanageable Tb^{3+} to Eu^{3+} energy transfer. More importantly, the difficulty to a precise control of Eu^{3+} and Tb^{3+} concentrations is actually faced[10] due to usual wrapping of coordination sites by polymeric chains. As a matter of fact, theoretically, terpolymerization of polymerizable Eu^{3+} and Tb^{3+} complex monomers with the other functional organic monomer could easily give rise to another approach to formation of hetero-Ln^{3+}-containing metallopolymers, where white-light emission can also be generated from the trichromatic strategy above.[11] In comparison, the alternative approach endows a distinctive advantage of the much localized circumstance for each Ln^{3+} (Eu^{3+} or Tb^{3+}) ion. Even so, the method still suffers from the similar complicated Tb^{3+} to Eu^{3+} energy-transfer process.[10] For the further solution, a conceptual strategy to combination of Eu^{3+}-red or Tb^{3+}-green and Gd^{3+}-incorporated compensatory polymer emission is relatively suitable for an initiative exploration of white-light-emitting hetero-Ln^{3+}-containing metallopolymers, because the patent absence of Eu^{3+} or Tb^{3+} to Gd^{3+} energy transfer is unambiguous due to the extremely higher energy level of Gd^{3+} ion.[12] Interestingly enough, with judicious adjustments of both Ln^{3+} concentration and excitation wavelength, direct white-light emission could also be expected for the obtained Eu^{3+}(Tb^{3+})-Gd^{3+}-containing metallopolymer.

Herein, we report a novel type of PVK-supported Eu^{3+}-Gd^{3+}-containing metallopolymers **Poly(2-*co*-NVK-*co*-4)** terpolymerized from vinyl-functionalized tri-β-diketonate Ln^{3+}-complex monomers [Ln(DBM)$_3$(4-vp-2,2'-bpy)] (Ln = Eu, **2** or Ln = Gd, **4**) with NVK. Their emission trajectories can be modulated to definitely envision a pure white-light colour (*x* = 0.333 and *y* = 0.335) through the integration of red from Eu^{3+} and cyan from Gd^{3+}-incorporated polymer. This dichromatic strategy could open up a new while effective way to white-light-emitting Ln^{3+}-containing metallopolymer-type materials.

As shown in Scheme 1, the ancillary ligand 4-vp-2,2'-bpy was synthesized by the Stille coupling reaction and the subsequent Suzuki coupling reaction in a combined yield of 58%. Further through the reaction of equimolar amount of each of dihydrate complex precursors [Ln(DBM)$_3$(H$_2$O)$_2$] (Ln = La, Eu, Tb or Gd) and 4-vp-2,2'-bpy, the series of vinyl-containing Ln^{3+}-complexes [Ln(DBM)$_3$(4-vp-2,2'-bpy)] (Ln = La, **1**; Eu, **2**; Tb, **3** or Gd, **4**) were obtained, respectively. The ancillary ligand 4-vp-2,2'-bpy and its four complex monomers **1**-**4** were well-characterized by EA, FT-IR,

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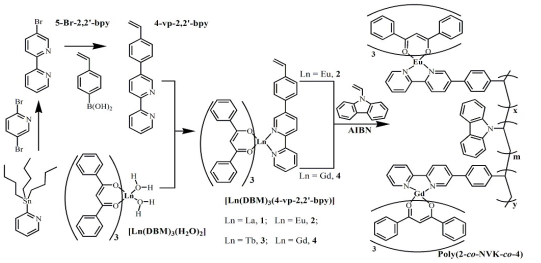

Scheme 1 Reaction scheme for the syntheses of 4-vp-2,2'-bpy, complex monomers **1**-**4** and metallopolymers **Poly(2-*co*-NVK-*co*-4)** (200:1; [**2**/**4** = 1:5 or 1:7]) terpolymerized from complex monomers **2**, **4** with NVK.

^{1}H NMR and ESI-MS. In the RT ^{1}H NMR spectrum (Figure S1) of La^{3+}-based complex **1**, besides a stipulated proton molar ratio (3:1) of DBM to 4-vp-2,2'-bpy, the proton resonances (δ = 6.84, 5.96 and 5.35 ppm) of the terminal functional vinyl group remain the same as those (δ = 6.82, 5.95 and 5.34 ppm) of 4-vp-2,2'-bpy despite the coordination of La^{3+} ion. Molecular structure of **3**·1.75H$_2$O·MeCN as the representative of complexes **1**-**4** was obtained by single-crystal X-ray diffraction analysis with crystallographic data in Tables S1-2. **3**·1.75H$_2$O·MeCN crystallizes with two independent mononuclear molecules and solvates H$_2$O and MeCN in the asymmetrical unit. As shown in Figure 1, within each mononuclear unit, three deprotonated DBM ligands with the similar O,O'-chelated mode and one 4-vp-2,2'-bpy ancillary ligand with the N^N-chelated mode coordinate to one Tb^{3+} ion in a square *anti*-prismatic pattern, resulting in the formation of a typical tris-β-diketonate Ln^{3+}-complex host structure.[13] The solvates are not bound to the framework, and they exhibit no observed interactions with the host structure. It is worth noting that the retained vinyl functional group with a typical C=C bond length of 1.301(16) or 1.318(17) Å from the 4-vp-2,2'-bpy in **3**·1.75H$_2$O·MeCN should be active in the following polymerization.

The photophysical properties of complex monomers **2**-**4** have been examined in dilute MeCN solution at RT or 77 K, and summarized in Figures 2 and S2. As shown in Figure S2, the similar ligands-centered solution absorption spectra of 247-248 and 344-348 nm for **2**-**4** in the UV-visible region are observed, where the lowest energy absorptions should be assigned to the π-π^* transition of DBM. For **2**, the photo-luminescence (Figure 2) just exhibits the Eu^{3+}-centered characteristic emissions ($^5D_0 \rightarrow {}^7F_J$, J = 0-4), giving the bright colour-purity red-light with a CIE (Commission International De L'Eclairage) chromatic coordinate of *x* = 0.664 and *y* = 0.332. As to **3**, photo-excitation (λ_{ex} = 410 nm) of the chromophores in the range of 275-440 nm just gives rise to weak residual visible emission (λ_{em} = 448 nm) assigned to the intra-ligand π-π^* transition, and no Tb^{3+}-centered characteristic emissions are observed. In contrast, different from the typical fluorescence (λ_{em} = 448 nm and τ = 2.1 ns) at RT, **4** displays the 0-0 transition phosphorescence (λ_{em} = 495 nm and τ = 11.2 μs) at 77 K, from which the triplet ($^3\pi$–π*) energy level at 20202 cm^{-1} is obtained. With regard to the singlet ($^1\pi$–π^*) energy level (25316 cm^{-1}) estimated by the lower wavelength of its UV-visible absorbance edge, the slightly larger energy gap ΔE^1 ($^1\pi$-π^* - $^3\pi$–π^*, 5114 cm^{-1}) than 5000 cm^{-1}, as shown in Figure S3, endows an effective intersystem crossing process according to Reinhouldt's empirical rule.[14] Nevertheless, further through the check of energy level match between the ligands-based $^3\pi$–π^* energy level and the first excited state level of $^5D_0$ (17286 cm^{-1}) for Eu^{3+} ion or $^5D_4$ (20545 cm^{-1}) for Tb^{3+} ion, the suitable energy gap ΔE^2 of 2916 cm^{-1} within the ideal 2500-4500 cm^{-1} range from Latva's empirical rule[15] confirms the effective sensitization of Eu^{3+} ion in **2**. While for **3**, the $^3\pi$–π^* energy level is even lower than $^5D_4$ (20545 cm^{-1}) of Tb^{3+} ion, and then the possible heavy non-radiative deactivation should result in the complete quenching of its Tb^{3+}-centered emissions. The Eu^{3+}-based ($^7F_2$, λ_{em} = 613 nm) lifetime of **2** has been measured to be τ_{obs} = 213 μs, and a high overall quantum yield ($\Phi_{\text{Eu}}^{\text{L}}$ = 39.6%) is obtained, attributing to relatively suitable energy level match besides the avoidance of vibrational quenching[16] in the inner coordination sphere of Eu^{3+} ion. Noticeably, the large optical absorbance of both DBM and 4-vp-2,2'-bpy involved renders their Gd-based complex **4** an attractive overall quantum yield (Φ_{em} = 10.2%) of cyan-light (*x* = 0.214 and *y* = 0.223).

Based on the relatively higher quantum yields for red-light of **2** and the cyan-emitting **4** and consideration of the excellent performance[17] of blue-emitting PVK as one of popular polymeric matrices with high mechanical intensity and good hole-transporting property, complex monomers **2** and **4** with active terminal vinyl group were terpolymerized with NVK in the presence of AIBN, as also shown in Scheme 1, resulting in the formation of PVK-supported Eu^{2+}-Gd^{3+}-containing metallopolmyers **Poly(2-*co*-NVK-*co*-4)** with a stipulated feed molar ratio of 200:1 ([**2**/**4** = 1:5 or 1:7]). To elucidate their AIBN-assisted free-radical polymerization,[18] the copolymer-type metallopolymer **Poly(NVK-*co*-1)** from the *iso*-structural while *anti*-ferromagnetic La^{3+}-based **1** and NVK with the

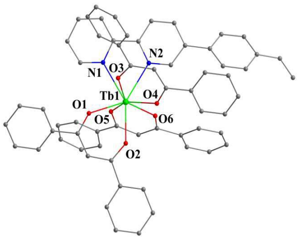

Figure 1 Perspective drawing of one independent mononuclear molecule of the asymmetrical unit in **3**·1.75H$_2$O·MeCN; H atoms, solvates H$_2$O and MeCN are omitted for clarity.

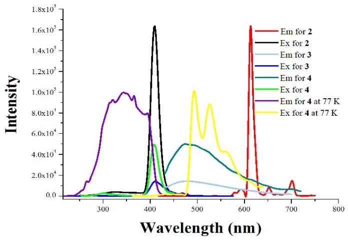

Figure 2 Visible emission and excitation spectra of complex monomers **2**-**4** in MeCN solution at 1 × 10^{-5} M at RT or 77 K.

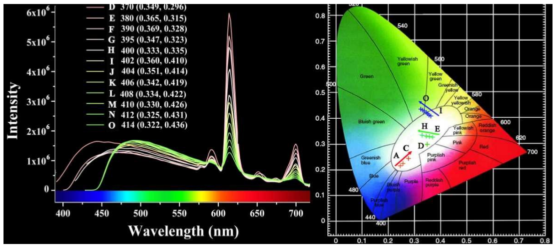

Figure 3 Emission spectra (Left) and corresponding CIE coordinates (Right) of **Poly(2-*co*-NVK-*co*-4)** (200:1; [**2**/**4** = 1:5]) in solid film upon excitations of λ_{ex} = 370-414 nm.

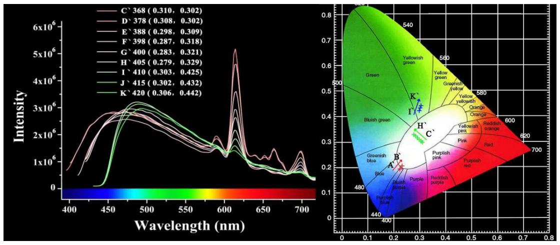

Figure 4 Emission spectra (Left) and corresponding CIE coordinates (Right) of **Poly(2-*co*-NVK-*co*-4)** (200:1; [**2**/**4** = 1:7]) in solid film upon excitations of λ_{x} = 368-420 nm.

same feed molar ratio of 200:1 was obtained for comparison. On the one hand, in the ^{1}H NMR spectrum (also shown in Figure S1) of La^{3+}-based **Poly(NVK-*co*-1)**, besides the combined and broadened proton resonances (δ = 9.08-0.50 ppm) of the polymerized **1** and NVK, the original proton resonances of the characteristic vinyl groups of both **1** and NVK disappear, indicating that the complex monomer is actually covalently-bonded into the PVK backbone. On the other hand, GPC results show that all the polydispersity indexes (PDI = M_w/M_n) of these metallopolymers are in the relatively narrow range of 1.12-1.21 due to the AIBN-initiated typical radical polymerization, in addition to similar M_n sizes (30898-31476 g/mol) from the same feed molar ratio of 200:1. PXRD patterns (Figure S4) of **Poly(2-*co*-NVK-*co*-4)** ([**2**/**4** = 1:5 or 1:7]) show only PVK-based amorphous peaks, also suggesting the low-concentration homogeneous distribution[19] of **2** and **4**. XPS quantitative analysis also verifies the stoichiometric atomic ratios (1:5.03 and 1:6.85) of Eu^{3+} to Gd^{3+} ion as desired feedings ([**2**/**4** = 1:5 and 1:7]), respectively. Moreover, their TG analysis shows a slight increase of 27 °C for the T_{onset} in comparison with pure PVK (Figure S5), and the decomposition with maxima around the higher temperature interval (450-462 °C) than that (285-306 °C) of **2** or **4**, which indicates that thermal stability of **Poly(2-*co*-NVK-*co*-4)** is significantly improved by polymerization. Furthermore, DR spectra (Figure S6) of **Poly(2-*co*-NVK-*co*-4)** exhibit relatively broader absorption bands than those of **2** and **4** in solution: where the absorptions at 259-261, 292-296 and 333-342 nm in the UV-visible region should be assigned to electronic transitions from organic moieties of PVK and the coordinated ligands. Due to the characteristic absorptions of Eu^{3+} or Gd^{3+} ion commonly appearing above 800 nm,[20] they are not detected in the corresponding samples.

The colour-tuning behaviours of **Poly(2-*co*-NVK-*co*-4)** ([**2**/**4** = 1:5 or 1:7]) were further investigated in the solid state at RT, and summarized in Figures 3-4 and S7-9. For **Poly(2-*co*-NVK-*co*-4)** ([**2**/**4** = 1:5]), photo-excitation (λ_{ex} = 350-414 nm) at a range of 340-460 nm (Figure S7) gives rise to a two-centered while broad-ranging emission of 400-750 nm assigned to the π–π^* transition of organic moieties and the $^5D_0 \rightarrow {}^7F_J$ transition of Eu^{3+} ion, respectively, and their relative intensity is strictly dependent on the excitation wavelength.[21] As shown in Figures S8 and 3, upon excitations at 350-360 nm, a blue-light emission centered at 430 nm attributing to the emission of PVK[17] dominates, and all the emitting colours (CIE coordinates 0.244-0.277, 0.216-0.0.240) are purplish-blue (Points A-C). When excited at 370-400 nm, the PVK-based emission significantly decreases, while its combination with the dominated red from Eu^{3+} ion and cyan from Gd^{3+}-incorporated polymer gives rise to the resultant colours (Points D-H) well falling within the white-light region. Especially, excitation of 400 nm is found to produce the high-quality white-light emission: the CIE coordinate (x = 0.333, y = 0.335) of this pure white-light emission (Point H) is very close to that (x = 0.333, y = 0.333) of ideal white-light, the colour rendering index (CRI) of 82 and the corrected colour temperature (CCT) of 5455 K are estimated, respectively. Moreover, the Eu^{3+}-centered (λ_{em} = 613 nm) lifetime of 860 μs and the lifetime of 53 ns from Gd^{3+}-incorporated PVK (λ_{em} = 480 nm) confirm that the pure white-light should unambiguously originate from both phosphorescence and fluorescence dichromatic-incorporation.[22] Noticeably, its quantum yield up to 18.4% is the highest among all reported white-light-emitting polymeric systems with Ln^{3+}-doping[23] or Ln^{3+}-grafting,[10, 24] as far as we know, and comparable to the best[25] (20.4%) of Ln^{3+}-MOFs reported to date. Moreover, due to the Eu^{3+}-centered red primary resource for **Poly(2-*co*-NVK-*co*-4)** ([**2**/**4**] = 1:5), the CIE coordinates of all the white-light emissions just drafting within a range of 0.02, the CCTs between 2500-6500 K and the CRIs above 80 endow its potential for WPLEDs with superior performance and practical lighting applications.[26] Further increasing the excitation wavelength (λ_{ex} = 402-414 nm), no band centered at 430 nm is observed, and the emission colours of **Poly(2-*co*-NVK-*co*-4)** ([**2**/**4**] = 1:5) locate at the yellow-green-light region (Points I-O; CIE (0.322-0.360, 0.410-0.436). By contrast, with an increase of relative Gd^{3+}-content in **Poly(2-*co*-NVK-*co*-4)** ([**2**/**4**] = 1:7), although the similar tuneable chromaticity of emission from purplish-blue (Points A'-B') to white (Points C'-H') to yellow-green (Points I'-K') is also realized by varying the excitation wavelength from 348-420 nm, as shown in Figures 4 and S9, the strengthened cyan-light from Gd^{3+}-incorporated polymer leads to distinctive shifts of the obtained white-light CIE coordinates (0.279-0.310, 0.302-0.329), despite the anticipated CRIs of 85-92. Worthy of noting, as to the promising white-light (Point C'), its lower quantum yield of 10.2% should be resulted from a new chromatic balance, even though two-centered species decay with a constant lifetime (857 μs) of Eu^{3+}-center while a slightly longer one (64 ns) from the higher Gd^{3+}-content, respectively, due to no aggregates formed upon low-concentration Ln^{3+}-grafting[27] in the host PVK matrix with a larger refractive index[17] besides the suppressed vibrational quench effect.[16]

In conclusion, through the terpolymerization of red-emitting [Eu(DBM)$_3$(4-vp-2,2'-bpy)] (**2**), cyan-light [Gd(DBM)$_3$(4-vp-2,2'-bpy)] (**4**) with NVK, we open up a new path to hetero-Ln^{3+}-containing metallopolymer with white-light and colour-tuneable properties. For the first example of Eu^{3+}-Gd^{3+}-containing metallopolymer **Poly(2-*co*-NVK-*co*-4)**, the intrinsic white-light emission can be easily optimized from a precise control of the Eu^{3+}-Gd^{3+} concentration and the excitation wavelength. Moreover, based on its higher luminous efficiency (18.4%) of pure white-light emission (CIE coordinate (0.333, 0.335); CCT between 2500-6500 K and CRI above 80), we anticipate that this study will raise the intriguing possibility to WPLEDs in future lighting application.

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