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Tunable emission in lanthanide coordination polymer gels based on a rationally designed blue emissive gelator

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Rational design and synthesis of a new low molecular weight gelator (LMWG) having 9,10-diphenylanthracene core and terminal terpyridine is reported. Tb^{III} and Eu^{III} ion coordination to LMWG results in green and pink emissive coordination polymer gels respectively with coiled nanofiber morphology. Further, control over stoichiometry of LMWG:Tb^{III}:Eu^{III} leads to yellow and white light emitting bimetallic gels.

Over past few decades, enormous research interest has been directed towards the development of new functional supramolecular gels from low molecular weight gelators (LMWGs).¹ Easy solution processability and dynamic nature of such soft materials hold great promise for applications in diverse fields, including biomedicine, nanoelectronics and catalysis.² Recently, the concept of coordination polymer gels (CPGs) has been emerged where coordination of metal ions to a suitably designed LMWG results in supramolecular selfassembled networks.³ Such soft organic-inorganic hybrids are highly promising since the incorporation of metal ions renders an opportunity to emulate its unique redox, optical, electronic and magnetic properties in supramolecular gels.^{3a, 4} Particularly, metallogel of lanthanide ions (Ln^{III}) are of specific interest as they show narrow band emissions (red: Eu^{III} , Pr^{III} , Sm^{III} ; green: Tb^{III} , Er^{III} ; blue: Tm^{III}, Ce^{III}) with high quantum yields when bind to suitable π -chromophoric linker.⁵ Such unique emission properties of Ln^{III} ions, stemming from sensitized f-f electronic transition has been investigated in bulk crystalline coordination polymers and exploited for solid state lighting and sensing applications.⁶ However, low solution processability greatly limits their application in device fabrication and biological sciences. In this regard, lanthanide coordination polymer gels (CGPs) are superior as reversible sol-gel behaviour enhances their processability and would facilitate easy fabrication of large-area and flexible displays, portable sensing kits.

Recently, white-light-emitting materials have merited immense research interest due to their potential application in solid state lighting.⁷ White-light-emitting materials can be trichromatic in which blue, green and red light emitting components are introduced to cover the entire visible spectral window. Such materials are superior compared to the monochromatic (that emits entire visible regions) and dichromatic (that emit in blue and yellow regions) due to the finer colour rendering properties and high quantum efficiencies.⁸ To date a handful of trichromatic white light emitting materials, suitable for solid state lighting applications have been reported. However, realization of white-light-emission based on CPG is yet to be accounted.

In this work, we report rational design of a new LMWG, 9,10-(4-carboxyphenyl)anthracenedi-{[3-([2,2';6',2'']terpyridin-4'ylami no)-propyl]-amide (**L**) having a blue emitting 9,10-diphenyl anthracene core and terminal terpyridine groups and its gelation properties. Coordination of **L** through terpyridine with Tb^{III} and Eu^{III} result in CPGs (**TbL** and **EuL**) which show green and pink emission respectively. Moreover, coordination of both Tb^{III} and Eu^{III} to **L** yields bimetallic CPGs (**TbEu1**, **TbEu2**) in which precise stoichiometric control over **L**:Eu^{III}:Tb^{III} ratio leads to tunable yellow and white emissions (Scheme 1).



Scheme1 Schematic showing the self-assembly of L though H-bonding and π - π stacking interactions and its coordination to Ln^{III} forming luminescent CPGs.

L is synthesized in one-step via amide coupling (see ESI for details) between 9, 10-(4-carboxyphenyl)anthracene and 2,2';6',2"

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terpyridin-4'-yl-propane-1,3-diamine and characterized using ¹H-NMR (Fig. S1, S2 and S3).⁹ Methanolic solution of L $(1 \times 10^{-4} \text{ M})$ shows a broad absorption in the range 280-310 nm which could be assigned to the π - π * transition of 9,10-diphenyl anthracene (ant) core and terminal terpyridine (tpy) groups (Fig. S4, S5). Excitation at 280 nm results in strong blue emission with maxima at 428 nm which can be considered as combined emission from ant and tpy (Fig. S6, S7). Interaction of \mathbf{L} with Tb^{III} ions is studied in methanol solution by gradually adding Tb^{III} (10⁻⁴ M) to solution of L (10⁻⁴ M) (Fig. 1a). With incremental addition of Tb^{III}, absorption spectrum shows a significant bathochromic shift at 280 nm with appearance of a broad shoulder at 327 nm, suggesting complexation of Tb^{III} to the **tpy** groups of \mathbf{L}^{10} . The corresponding emission spectra of the solution (λ_{ex} = 280 nm) shows a decrease in intensity at 428 nm with concomitant appearance of sharp peaks at 490 nm, 546 nm, 587 nm and 623 nm which can be attributed to ${}^{5}D_{4}$ - ${}^{7}F_{I}$ (J= 6-3) transitions of Tb^{III} (Fig. 1b). This sensitized emission further confirms the binding of Tb^{III} to the **tpy** of **L**.¹¹ Interestingly, emission of **L** at 428 nm is not supressed completely even after addition of 2 eq of Tb^{III} ions. This residual emission is attributed to the central ant core which probably does not involve in sensitization of Tb^{III} due to large spatial distance between ant and metal ion. Similar changes in absorption spectra are also observed in case of Eu^{III} ion (Fig. 1c). However, the emission spectra exhibits weak bands at 592 nm and 618 nm, assigned to the ${}^{5}D_{0}$ - ${}^{7}F_{1}$ and ${}^{5}D_{0}$ - ${}^{7}F_{2}$ transition of Eu^{III} and a feeble decrease in emission at 428 nm (Fig. 1d). This result indicates weak energy transfer from **tpy** to Eu^{III}.



Fig. 1 Spectral changes in (a), (c) absorption and (b), (d) emission of L on incremental addition of Tb^{III} and Eu^{III} in methanol respectively. Arrows indicate observed changes.

Heating solution of **L** (10^{-3} M) in CHCl₃/THF (2:1), followed by cooling at room temperature results in an opaque gel that remained stable upon inversion (Fig. 2a). Field emission scanning electron microscopy (FESEM)) images of xerogel reveal the fibrous morphology. Nanofibers are several micrometer long with approximate diameter of 40-50 nm (Fig. 2b, 2c and Fig. S8). Interestingly, presence of nanorings is also observed which are formed via coiling of nanofibers.¹² Transmission electron microscopy (TEM) images also support the existence of nanofibers and nano-rings. Formation of nanofibers can be explained based on the self-assembly of L as shown in the Scheme 1. In binary mixture of solvents like CHCl₃/THF, L assembles through the H-bonding between amide groups and π - π stacking between **ant** cores of

neighbouring L and forms fibrils. These fibrils on aggregation form fibers which further entangle to form typical fibrous gel architecture. The presence of H-bonding and π - π stacking in gel are supported by powder X-ray diffraction (PXRD) and Fourier transform infrared spectra (FTIR) analysis. PXRD of the xerogel shows broad peak at $2\theta = 21.8^{\circ}$, corresponding to the *d*-spacing value of 4.0 Å which supports the presence of π - π stacking in gel (Fig. S9). Moreover, FTIR of L xerogel on comparison with L exhibits decrease in -N-H and -C=O stretching frequency from 3436 cm⁻¹ to 3424 cm⁻¹ and from 1645 cm⁻¹ to 1638 cm⁻¹ respectively, indicating the presence of intermolecular H-bonding in this assembly (Fig. S10). The absorption spectrum of L xerogel shows maxima around 350 nm. Upon exciting at 350 nm it shows intense blue emission with maxima at 435 nm, originating from both ant core and tpy (Fig. S11). Emission spectra of gel film prepared on quartz substrate is also recorded and it shows similar emission behaviour with a maximum at 435 nm (Fig. S12).



Fig. 2 (a) Photographs of **L** gel under day and UV light, (b) FESEM image and (c) TEM image of **L** xeogel. (d) Photographs of **TbL** gel under day and UV light, (e) and (f) TEM images of **TbL** xerogel. (g) Comparison of PXRD of **L** (black), **TbL**(blue) and **EuL**(red) xerogel (low angle peak in **TbL** and **EuL** xerogel is highlighted in box). (h) Probable coordination environment around Tb^{III} in **TbL** which leads to the formation of coiled-nanofiber morphology.

Heating the mixture of **L** and $Tb(NO_3)_3.6H_2O$ (molar ratio=1:1) in the aforementioned CHCl₃/THF (1:1) solvent mixture followed by cooling results in a stable coordination polymer gel (CPG) (**TbL**) (Fig. 2d). Likewise, **EuL** is also prepared by using 1:1 molar ratio of **L** and Eu(NO₃)₃.6H₂O. The presence of coordinated Tb^{III} and Eu^{III} in respective **TbL** and **EuL** xerogels is confirmed by energy dispersive X-ray spectroscopy (EDXS) analysis (Fig. S13, S14). CHN analysis of **TbL** and **EuL** xerogels indicate the probable formula as [Tb(L)(NO₃)₃.2THF] and [Eu(L)(NO₃)₃.2THF] respectively. To get insight into the mode of packing in CPG, **TbL** xerogel is analysed by TEM and FESEM images. The **TbL** xerogel exhibits uniformly distributed coiled-nanofiber morphology with diameter of 80-150 nm (Fig. 2e, 2f, 2h and Fig. S15) which is higher than that of **L** nanofibers (40-50 nm). It is expected that the 1D self-assembled primary structure of LMWG with pendent **tpy** groups on

(a)

350 400

(c)

1000

800

tji 600

at 400

200

800

oug sity

uet 400

200

350 400

(e)

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400 1 (b)

300

200

100

1000 (d)

800

600

400

200

Intensity

(f)

400 450 500 550 600 650 700 750

Wavelength (nm)

350 400 450 500 550 600 650

Wavelength (nm)

700

ntensity

450 500 550 600 650 700

Eu

O TbL TbEul

650 700

Wavelength (nm)

450 500 550 600

Wavelength (nm)

 $\label{eq:rescaled_rescaled$

Emission spectrum of TbL xerogel displays characteristic peaks for Tb^{III} (λ_{ex} = 280 nm, Fig. S16) at 486 nm, 540 nm, 580 nm, 618 nm and L centred peak at 435 nm (Fig. 3a). Nevertheless, emission spectrum of EuL xerogel (λ_{ex} = 280 nm, Fig. S17) shows well preserved L centred peak at 435 nm along with sharp peaks for Eu^{III} at 590 nm, 615 nm (Fig. 3b). **TbL** and **EuL** gels show intense green and pink emissions respectively, under UV light (Fig. S18). Respective CIE (Commission International de L'Eclairage) coordinates of TbL and EuL emission are calculated to be (0.25, 0.43) and (0.26, 0.23) (Fig. 3e). The absolute quantum yield (QY) upon excitation at 340 nm is 4.2% for TbL and 12.4% for EuL and these values are comparable with other reported values of Tb^{III}/Eu^{III} based matallogel and coordination polymers.^{5c, 8b, 8c}As seen in Fig. 3a, emission spectrum of TbL extends from 400 nm to 600 nm in which blue (from L) and green (from Tb^{III}) parts are major components. Therefore, by further introducing a red component (from Eu^{III}) into TbL, the entire visible spectrum (400-800 nm) could be covered via RGB approach. To validate this hypothesis, bimetallic CPGs are prepared. Tb^{III} and Eu^{III} metal ions of different

ratios are simultaneously added into L solution during gelation. The bimetallic CPG TbEu1 with Tb^{III}:Eu^{III} = 1:1.2 is prepared which shows strong greenish yellow emission under UV light (Fig. S18). The corresponding emission spectrum displays bands characteristic of L, Tb^{III} and Eu^{III} in which emission from Tb^{III} at 545nm (green) predominant over Eu^{III} peaks at 590 nm and 615 nm (red) (Fig. 3c). The CIE coordinate of **TbEu1** is calculated to be (0.24, 0.38) (Fig. 3e). We envisioned that by further increasing $\mathrm{Eu}^{\mathrm{III}}$ concentration, the emission feature of bimetallic CPG could be further tuned towards white light. Finally, by changing the (Tb^{III}:Eu^{III}) ratio to 1:2, we are able to prepare CPG (TbEu2) which show near white light emission (Fig. 3d). The CIE coordinate of TbEu2 is calculated to be (0.28,0.34) (Fig. 3e).¹³ Upon excitation at 340 nm the absolute quantum yield (QY) of TbEu2 is found to be 5.0%. The presence of both Tb^{III} and Eu^{III} in **TbEu2** xerogel is confirmed by EDAX (Fig. S19). Excellent processability and colour tunability of these "soft hybrids" prompted us to exploit them for coating on various substrates. As seen in inset, Fig. 3a-d quartz substrates coated with corresponding gels show strong red, green, yellow and white light emission. The white light emitting gel has also been used to fabricate white-light-emitting-diode (WLED) by simply coating commercial blue LED with TbEu2. Upon turning on the LED, it displays bright white light (Fig. 3f).

In conclusion, the preceding results demonstrate a rational design of a LMWG having blue luminescent core ant and a metal chelator tpy which can also acts as a sensitizer for lanthanide ions. Coordination driven self-assembly of LMWG with Ln^{III} (Tb^{III}/Eu^{III}) resulted in bright green/pink luminescent coordination polymer gels. While, self-assembly of L with mixed metal ions with controlled stoichiometry of L:Tb^{III}:Eu^{III} yielded bimetallic coordination polymer gels with tunable emission including yellow and near white light. These soft coordination polymer nanostructures are easy processable and gentle heating of gels forms viscous liquids which can be easily transferred to solid substrate without any loss in emission intensity. Based on this approach a bright white light LED has been fabricated. We believe that our design strategy of trichromatic approach in coordination polymer gels would provide new perspective for developing robust and easy processable light emitting materials for potential applications in optoelectronics and sensing.

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Notes and references

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Journal Name

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A new blue emissive gelator has been synthesized and its self-assembly with ${\rm Tb}^{\rm III}$ and ${\rm Eu}^{\rm III}$ results in coordination polymer gels, which show tunable emission based on stoichiometric control over LMWG:Tb^{III}:Eu^{III}.