Supramolecular Chemistry

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Europium-Directed Self-Assembly of a Luminescent Supramolecular Gel from a Tripodal Terpyridine-Based Ligand**

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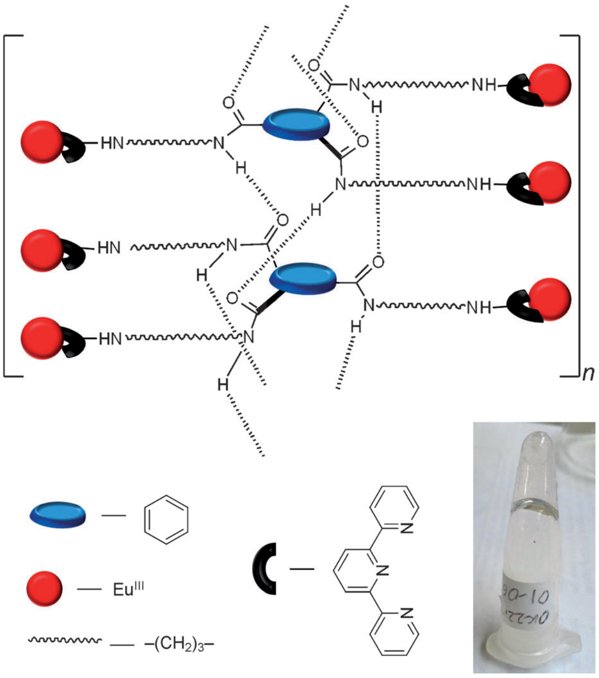
Dedicated to Professor John M. Kelly

The formation of complex and functional molecular structures triggered by the use of small templates and self-assembly processes is central to polymer and supramolecular chemistry, nanotechnology, and in the generation of novel materials.[1] The use of metal-directed synthesis is recognized as being a key approach in the formation of such self-assemblies.[2] Concomitantly, the formation of molecular gels by the controlled assembly into fibrous architectures has also gained significant interest, but such soft materials have found and have enormous application potentials across different subjects and disciplines.[3,4] Consequently, a wide range of gelators based on organic molecules for the generation of organo and hydrogels have been developed to date.[3] These systems are known to self-assemble unidirectionally, mainly through weak interactions, such as dispersion forces, hydrogen bonding, π–π, and electrostatic interactions. In contrast, the use of metal-directed gelation in developing such supramolecular structures has only recently been explored.[4] These approaches, usually in synergy with the aforementioned forces, enable the formation of more ordered structures, in multiple directions (i.e. 2D and 3D) with added complexity and function.[4] The lanthanides (Ln^{III}) are of specific interest for such applications, owing to their unique magnetic and photophysical properties,[5] which can be modulated through ligand design by simply taking advantage of their high coordination requirement/numbers (ca. 8–12).[6] Consequently the lanthanides have found their applications in sensing, medical diagnostics, and telecommunications.[7] To date, most Ln^{III}-containing hydrogels[8] and organogels have been obtained by noncovalently incorporating such complexes in the gelator matrix, that is, as "standalone" coordination complexes.[8a] The Ln^{III} ions can also be introduced into self-assembled structures of organic molecules where they act as bridging units that enable the formation of branched 2D and 3D coordination polymers and networks.[4,9] In a similar manner they direct the formation of supramolecular structures[10] and materials as we recently demonstrated with the generation of optically active amphiphilic Eu^{III}-based self-assembly complexes that give rise to the formation of luminescent lanthanide Langmuir–Blodgett monolayers exhibiting circularly polarized luminescence.[11] Building on these encouraging results, we report herein the formation and



Scheme 1. A schematic representation of the possible formation of threefold hydrogen bonding in helices of the terpyridine-based tripodal ligand (**L**) showing the europium binding sites on the outside of the helix. The inset shows formation of a transparent $EuCl_3$-**L** gel in a H_2O/CH_3OH solvent mixture.

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physical analysis of novel luminescent Eu^{III}-based hydrogels formed by self-assembly of the tripodal ligand **L**, which is shown in Scheme 1. The ligand structure is based on the C_3-symmetrical benzene-1,3,5-tricarboxamide (BTA) central core, which facilitates the initial self-assembly of ligand **L** into helices stabilized through threefold hydrogen bonding.[12] This core is connected to three 2,2′:6′,2″-terpyridyl (tpy) moieties through covalent carboxamide spacers; the tpy moiety enables the coordination of Ln^{III} ions and the concomitant formation of higher-order self-assembly gels. The second role of the tpy moiety is to function as a sensitizing antenna for the population of the $^5D_0$ excited state of Eu^{III}.[13]

The synthesis of ligand **L** was achieved in two steps (Scheme S1 in the Supporting Information) by first obtaining the amine derivative of tpy (Figure S1 in the Supporting Information) and subsequently reacting with BTA by using a standard peptide coupling reaction to deliver the target ligand in approximately 90% yield as a white powder. The ^{1}H NMR spectrum (600 MHz, CD_3OD; Figure S2A in the Supporting Information) of ligand **L** shows the presence of the BTA protons as a sharp singlet at $\delta = 8.68$ ppm, which is indicative of the C_3 symmetry of **L**. The presence of the amide bonds was confirmed by a broad resonance occurring at $\delta = 9.07$ ppm (400 MHz, $(CD_3)_2SO$, Figure S2B in the Supporting Information), as well as by the N–H vibrations in the IR spectra at approximately 3200 cm^{-1}. The formation of ligand **L** was also confirmed by HR-MALDI MS with m/z 1073.49, which matches the calculated isotopic distribution pattern of $[\mathbf{L}+\mathrm{H}]^+$. The phase transition of ligand **L** was determined for the powder sample by using differential scanning calorimetry (DSC), giving a glass transition temperature (T_g) of 173.7 °C.

The absorption spectrum of ligand **L** (1×10^{-5} M) in methanol solution showed a band centered at approximately 280 nm ($\log\varepsilon = 4.85$), assigned to the tpy $\pi\rightarrow\pi^*$ transition. Excitation at this wavelength gives rise to a fluorescence emission with λ_{max} at 410 nm (Figure S3 in the Supporting Information). The interaction of ligand **L** with Eu^{III} ions was studied in methanol solution, using $EuCl_3$. The changes in the absorption, fluorescence, and in the delayed Eu^{III}-centered emission spectra were all monitored, and these are shown in Figure 1 A–C, respectively. From Figure 1 A it is clear that upon binding to Eu^{III} ions, the absorption spectrum of ligand **L** was bathochromically shifted, with the appearance of a shoulder at approximately 320 nm, thereby indicating the formation of a (Eu/**L**) complex with a 1:1 stoichiometry (Figure 1 A, Figure S4A in the Supporting Information). Similar complex formation has been seen by Piguet and co-workers[10d] between a "strain-free" flexible covalent tripod ligand, called L8, and Ln^{III} ions. The concomitant changes in fluorescence emission spectra of ligand **L** upon excitation at 280 nm are shown in Figure 1 B. The broad emission band centered at approximately 410 nm, assigned to tpy, was significantly affected upon binding to Eu^{III} ions: the band was quenched by approximately 70% and slightly blue-shifted (Figure 1 B, Figure S4B in the Supporting Information). This quenching is a direct consequence of a complex formation between Eu^{III} ions and tpy moieties; this complex formation resulted in an energy transfer from ligand **L** to the $^5D_0$ excited state of Eu^{III}, which concomitantly deactivates to the ^7F_J ($J = 0$–4) ground states, thereby giving rise to the characteristic line-like emission at 580, 595, 616, 650, and 696 nm, respectively (Figure 1 C). The above titrations were also carried out using $Eu(CF_3SO_3)_3$ and $Eu(NO_3)_3$ to investigate the effect of the counter ion[14] upon binding of Eu^{III} ions to ligand **L** (Figures S5–S8 in the Supporting Information). The results of the titrations suggested the formation of a 1:1 Eu/**L** complex (Figure S9 in the Supporting Information). This observation was further confirmed by the presence of m/z signals corresponding to $[\mathrm{Eu}\mathbf{L}(CF_3SO_3)_2]^+$, $[\mathrm{Eu}\mathbf{L}(CF_3SO_3)_3+\mathrm{H}^+]^+$, and $[\mathrm{Eu}\mathbf{L}(CF_3SO_3)_4+2\mathrm{H}^+]^+$ in HR-MALDI MS of the same solutions (Figure S10 in the Supporting Information) and by following the transformations in the ^{1}H NMR spectrum (600 MHz, CD_3OD) of ligand **L** (1.31×10^{-3} M) upon addition of Eu^{III} (Figure S11 in the Supporting Information).

The changes in the UV/Vis, fluorescence, and the Eu^{III}-centered emission in Figure 1 were all analyzed by fitting the overall changes using the nonlinear regression analysis program SPECFIT.[15] The evolving factor analysis in all cases reveals the presence of three absorbing or fluorescent species and two for the Eu^{III}-centered emission (Table S1 in the Supporting Information). Of these changes, the changes in the absorption spectra gave excellent fits and the binding constants for the 1:1 as well as for the 3:2 species are shown in

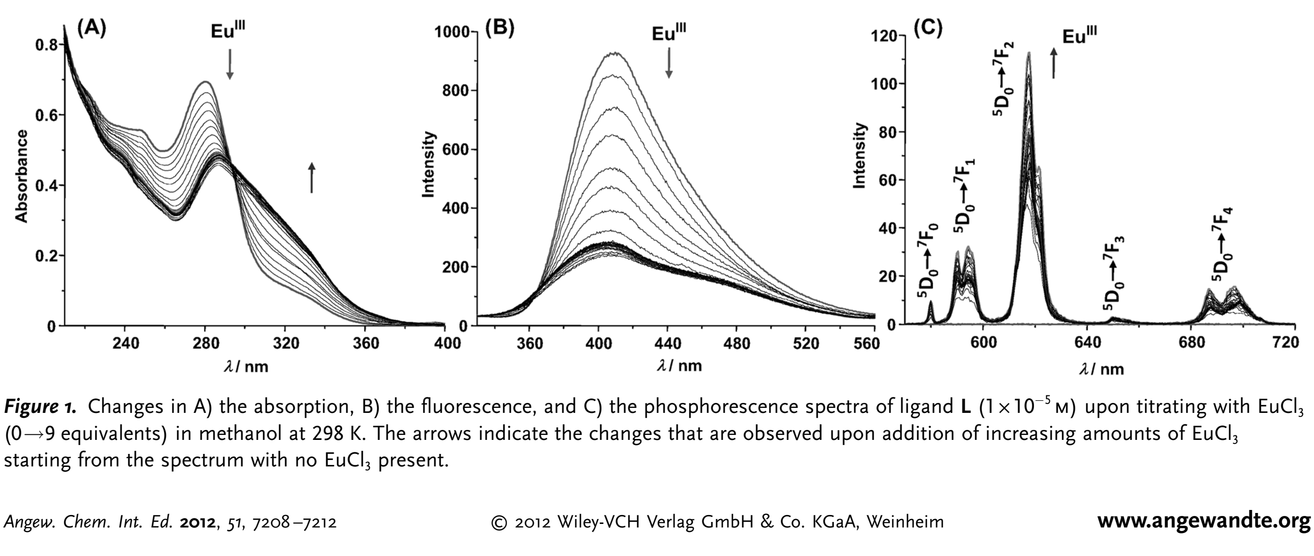

Figure 1. Changes in A) the absorption, B) the fluorescence, and C) the phosphorescence spectra of ligand **L** (1×10^{-5} M) upon titrating with $EuCl_3$ (0→9 equivalents) in methanol at 298 K. The arrows indicate the changes that are observed upon addition of increasing amounts of $EuCl_3$ starting from the spectrum with no $EuCl_3$ present.

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Table 1; this observation is contrary to the formation of solely 1:1 complex observed by Piguet and co-workers[10d] for the self-assembly of their ligand L8 and Eu^{III} ions studied in acetonitrile solution. The different behavior between our system and that of Piguet and co-workers can possibly be attributed to the nature of the BTA anchor, which makes ligand **L** more rigid compared to the "strain-free" ligand L8 (as depicted in Scheme S2 in the Supporting Information). The formation of 3:2 complexes have been reported by Bretonnière et al.[16] for a tpy-based tripodal ligand in the presence of various Ln^{III} ions. The speciation-distribution diagram resulting from the fits to the changes in Figure 1 A (Figure S12 in the Supporting Information) showed that within the addition of one equivalent of Eu^{III} the most predominant species in solution was the 1:1 Eu/**L** stoichiometry, being formed in 80 % yield. However, the 3:2 species also began to form after the addition of 0.5 equivalents of Eu^{III} and was formed in approximately 80 % yield after the addition of nine equivalents of $EuCl_3$ (see Figures S13 and S14 in the Supporting Information for $Eu(NO_3)_3$ and $Eu(CF_3SO_3)_3$). These results clearly demonstrate that the equilibrium process $Eu + \mathbf{L} \rightleftarrows Eu_1/\mathbf{L}_1$ can be shifted to higher stoichiometry, $Eu_n/\mathbf{L}_m$, which would facilitate the formation of higher-order self-assemblies in a manner described above, where the lanthanide ion would function as a "supramolecular glue" between such complexes (Figures S4B, C–S8B, C, S15 in the Supporting Information). The binding constants obtained from the fluorescence and Eu^{III}-centered emission titrations are shown in Table S2 in the Supporting Information.

Table 1: Binding constants obtained by fitting the changes in absorption spectra.

EuX_3[a]	Species	$\log\beta_{M/L}$
$Eu(CF_3SO_3)_3$	$\log\beta_{1:1}$	7.2 ± 0.3
	$\log\beta_{3:2}$	23.3 ± 0.4
$EuCl_3$	$\log\beta_{1:1}$	7.3 ± 0.2
	$\log\beta_{3:2}$	24.9 ± 0.5
$Eu(NO_3)_3$	$\log\beta_{1:1}$	6.6 ± 0.2
	$\log\beta_{3:2}$	23.8 ± 0.4

[a] In all cases the salts were used in the hexahydrate form $EuX_3{\cdot}6\,H_2O$.

After the photophysical properties of ligand **L** in the presence of Eu^{III} ions had been explored, the formation of self-assembled gels was undertaken next by using ligand **L** and Eu^{III} ions (with Cl^-, $CF_3SO_3^-$, and NO_3^- as counter ions). The formation of supramolecular polymers based on organic molecules that contain the central BTA unit has been carried out in aqueous solution by Meijer and co-workers.[12b] Such supramolecular polymerization has been described as being mainly driven by hydrogen-bonding interactions.[3e] In principle, our solvent system was chosen to mimic this formation; but it was found to be necessary to use methanol as a co-solvent to ensure full solubility of ligand **L**. Consequently, a variety of H_2O/CH_3OH ratios were employed. Of these, the use of a 5:95 H_2O/CH_3OH solvent mixture gave rise to the formation of a supramolecular ($EuCl_3$-**L**) (metallo-) gel, which was found to be both stable and highly transparent as demonstrated in an inset in Scheme 1. Concomitantly, the gelation of ligand **L** (0.25–0.3 wt %) alone was undertaken. Here again, a transparent gel was formed from **L** in a 70:30 H_2O/CH_3OH mixture upon slow evaporation of solvents after standing for several weeks at room temperature.

Initially ligand **L** was mixed with $EuCl_3{\cdot}6\,H_2O$ in 1:1, 2:1, and 3:1 (Eu/**L**) molar ratios in the aforementioned H_2O/CH_3OH mixture, which yielded on all occasions transparent gels upon standing under ambient conditions. Of these, the 1:1 and 2:1 stoichiometries yielded gels that were more liquid in nature and less easy to analyze in comparison to that formed using the 3:1 molar ratio; this behavior would suggest that all the tpy ligands were possibly engaged in the coordination to Eu^{III} ions.

The weight percentages of solvent (H_2O and CH_3OH) within the Eu^{III} gels formed above, compared to the corresponding solid components of **L** and $EuCl_3$-**L** gels, were determined by using thermogravimetric analysis (TGA) in an air atmosphere (Figures S16, S17 in the Supporting Information). These measurements showed that once the concentration of **L** became approximately 0.3 wt % (with CH_3OH ca. 28 wt % and H_2O ca. 71.7 wt %) gelation occurred. In contrast, $EuCl_3$-**L** gelation occurred at approximately 9 wt % (with CH_3OH ca. 82 wt % and H_2O ca. 9 wt %). Based on these results, and literature data,[12] we suggest that the formation of $EuCl_3$-**L** gels occurs by means of strong, threefold intermolecular hydrogen bonding with possibly additional π–π stacking between the tpy moieties (as depicted in Scheme 1). This initial supramolecular polymerization was further confirmed by monitoring the ^1H NMR (600 MHz, CD_3OD) spectra of ligand **L** at 1.31×10^{-3} M (c_1), 1.31×10^{-4} M (c_2), and 1.31×10^{-5} M (c_3) concentrations, where c_3 is comparable to the concentration at which the spectroscopic titrations were performed above (Figure S18 in the Supporting Information). As expected, the ^1H NMR spectra of ligand **L** revealed signal broadening for the BTA protons at high concentration of **L** (c_1) and that upon dilution, significant sharpening of the signals for these same protons occurred, which is indicative of reduced intermolecular interactions between **L**–**L** molecules. HR-MALDI analysis of a concentrated sample of ligand **L** showed *m/z* peaks assigned to species such as $\mathbf{L}_2$, $\mathbf{L}_3$ and $\mathbf{L}_4$ and thereby further confirmed such intermolecular interactions between **L** molecules (Figure S19 in the Supporting Information).

All the Eu^{III} gels formed above were found to be luminescent, where the Eu^{III}-centered emission was the most prominent and informative. The coordination of tpy to Eu^{III} ions was confirmed for the $EuCl_3$-**L** gels upon excitation of the tpy ligand at 280 nm (Figure S20 in the Supporting Information), which gave rise to characteristic metal-centered Eu^{III} emission at 595, 616, 650, and 696 nm. This emission of the $EuCl_3$-**L** gel was structurally similar to that seen in solution: the ratio between $\Delta J = 1$ and 2 was the same as in solution, and some degree of fine splitting was observed for the gel sample for the $\Delta J = 2$ transition. Moreover, the excitation spectra matched that seen in the absorption spectra with $\lambda_{em} = 616$ nm, thereby demonstrating the successful sensitization by the tpy antennae.

To investigate the morphology and possibly reveal the orientation of the supramolecular polymers within these gels,

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dried samples of both **L** and $EuCl_3$-**L** gels were analyzed by scanning electron and transmission electron microscopy (SEM and TEM) as well as by energy-dispersive X-ray spectroscopy (EDX; Figure S21 in the Supporting Information). The results from the SEM and TEM analyses showed drastic differences between these gels as is evident from Figure 2 A, B for **L** and $EuCl_3$-**L**, respectively. For these analyses, ultra-thin gel layer samples were made by suspending these gels on copper/lacey carbon TEM grids. The fibrous nature of the **L** gel consisting of long intertwining bundles of strings is evidenced from the SEM analysis shown in Figure 2 A, and these are similar to those seen by others using organic structures based on the BTA unit. In contrast, $EuCl_3$-**L** gave rise to the formation of more ordered gels (Figure 2 B), where the strands appear to be locally aligned within a domain or a larger "rope-type" self-assembly of strands, with a random arrangement of each domain (see the Supporting Information for additional images, Figure S22). More detailed structural features of these strands were obtained by scanning transmission microscopy using high-angle annular dark-field imaging (HAADF STEM), which showed the fiber width to be approximately 20 nm for **L** (Figure 2 C), and to be in the area of 20–25 nm for the fibers of the $EuCl_3$-**L** gel (Figure 2 D). It is important to point out that both microscopy imaging and diffraction information obtained for **L** (as shown in Figure 2 C) were limited by the rapid degradation under the electron beam, while this was not found for the $EuCl_3$-**L** samples to the same extent. This higher stability further highlights the importance of Eu^{III} within these structures and its ability to act as a "supramolecular glue" in an intermolecular manner, thereby resulting in the formation of higher-order self-assemblies. Hence, this reinforces the structure in comparison to that seen for **L**, thus indicating stronger intrastrand coordination-bond interactions, as depicted in Scheme 1. Several attempts were made to obtain electron diffraction patterns during the TEM analysis for both the **L** and $EuCl_3$-**L** gels. However, we were only able to get reliable data from the latter; this observation is yet again addition but indirect confirmation of the importance of the Eu^{III} in the formation of a stable $EuCl_3$-**L** gel morphology. A higher-magnification TEM image of the $EuCl_3$-**L** strands is shown in Figure 3 A, with the associated electron diffraction pattern shown in Figure 3 B. The diffraction pattern reveals the presence of two separate repeat distances within the structure. The intensity of the outer ring is textured and indicates a structure consisting of distances on the scale of 0.36 nm. Maximum intensity here is parallel to the direction of the strands, thus indicating that this structural feature is preferably noticed along the strand direction. We tentatively assign this feature to the distance between the BTA moieties (depicted as a blue arrow in Figure 3 C); this distance results in the formation of a supramolecular helical polymer stabilized by hydrogen bonding. X-ray diffraction data obtained by using single crystals of various BTA-containing organic derivatives have indeed shown that these distances are normally found to be between 0.36 to 0.47 nm for such systems.[12,17] The inner ring shown in Figure 3 B, represents a distance of 0.98 nm, which is perpendicular to the direction of the strands. We believe that this distance corresponds to a repetitive unit that includes ligand **L** and Eu^{III} ions (depicted as a red arrow in Figure 3 C). The results obtained from the diffraction pattern clearly indicate the structural order parallel and perpendicular to the direction of the strands in the manner depicted above; this order gives higher stability and a more ordered gel.

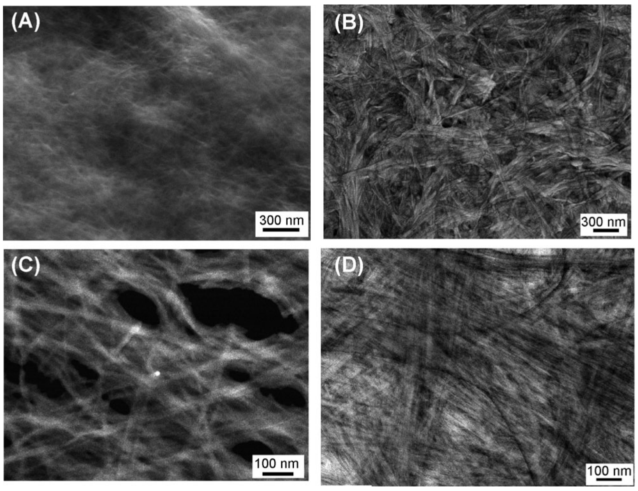

Figure 2. SEM images of: A) ligand **L** and B) $EuCl_3$-**L** supramolecular gels on silicon surfaces. HAADF STEM images of: C) ligand **L** and D) $EuCl_3$-**L** gels on lacey carbon TEM grids ((B) sample has been coated in a thin layer of palladium to improve imaging).

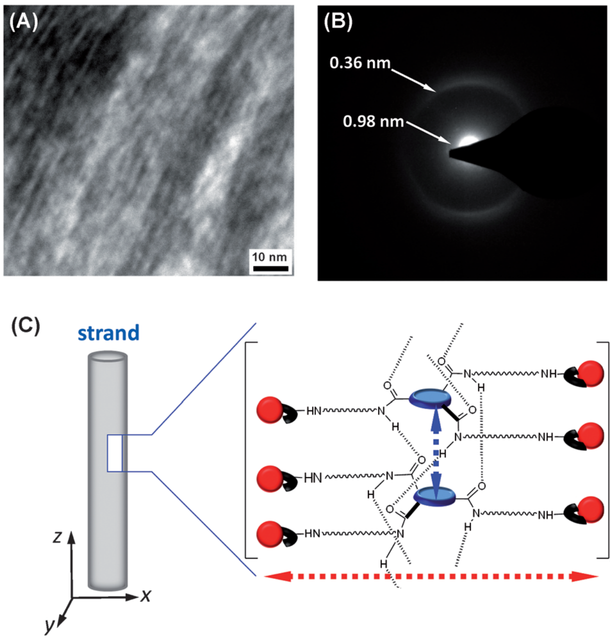

Figure 3. A) TEM image of $EuCl_3$-**L** supramolecular gel. B) Electron diffraction pattern. C) Schematic representation of the self-assembly of **L** molecules and Eu^{III} ions within $EuCl_3$-**L** gels. The blue and red arrows correspond to the distances 0.36 and 0.98 nm (shown in (B)), respectively.

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In conclusion, we have developed luminescent Eu^{III}-directed self-assembly gels from the tripodal tpy-based ligand **L**. These gels were studied using a variety of techniques, which revealed, particularly for EuCl_3-**L**, the important role that Eu^{III} plays in macroscopic organization of such systems. The TEM results along with diffraction patterns obtained for the EuCl_3-**L** gel suggest that initial supramolecular polymerization of ligand **L** takes place, and that this allows for preorganization of **L** in a manner that enables Eu^{III} ions to function as a "glue" by intermolecularly connecting such supramolecular polymers through coordination of Eu^{III} ions to more than one tpy unit in adjacent strands. This intermolecular connection results in the formation of a luminescent metallogel with improved order and physical properties.

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