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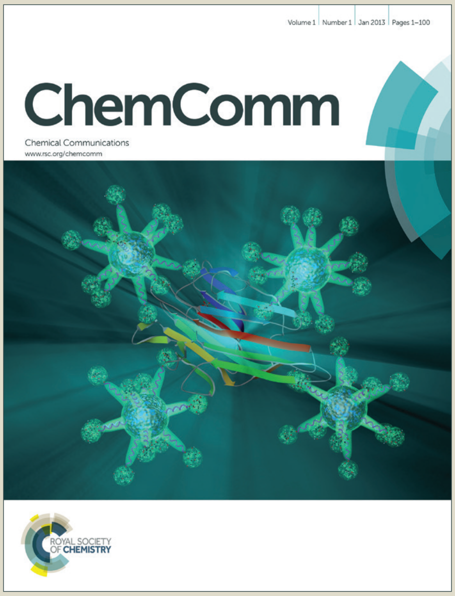

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# Self-assembly formation of a healable lanthanide luminescent supramolecular metallogel from 2,6-bis(1,2,3-triazol-4-yl)pyridine (btp) ligands

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Eoin P. McCarney,[a] Joseph P. Byrne,[a] Brendan Twamley,[a] Miguel Martínez-Calvo,[b] Gavin Ryan,[c] Matthias E. Möbius[c] and Thorfinnur Gunnlaugsson*[a]

**The synthesis of five new 2,6-bis(1,2,3-triazol-4-yl)pyridine (btp) ligands is described: the self-assembly behaviour of the tri-methyl ester, 1, with Eu(III) showed the formation of a luminescent 1:3 Eu:btp complex, $Eu1_3$, which was studied in solution and in the solid state; while the tri-carboxylic acid, 2, formed a hydrogel and its corresponding complex $Eu2_3$, gave rise to a strongly red luminescent healable metallogel.**

2,6-Bis(1,2,3-triazol-4-yl)pyridine (**btp**) based ligands are terdentate pyridine-centred heteroaromatic structures that have been shown to form stable coordination complexes with a variety of metal ions.[1-5] While the use of the **btp** binding motif has grown significantly in recent years,[3a] relatively few lanthanide (Ln(III)) complexes of **btp** have been studied,[1,2,3,5b] some of the first examples of which showed that **btp** can be used as a sensitising 'antenna' for ions such as Eu(III).[1a,5b] The **btp** structure provides a broad scope of functionalisation through the use of one pot 'click' chemistry.[3a,5] Recently, we developed the **btp** ligand **6**, Figure 1, and investigated its coordination, photophysical and electrochemical behaviour with various *d*-metal ions.[6] We showed that ester hydrolysis of **6**, followed by treatment with Ru(II) gave rise to the formation of a metallo-supramolecular gel. Building on this, we have developed Ln(III) bundles of **6** (and a range of its amino acid derivatives).[3c] The Ln(III) ions possess remarkable photophysical and magnetic properties[1,2,7] with applications in a diverse range of areas.[8-11] We, and others, have used them to template the formation of self-assembled supramolecular architectures from acyclic ligands.[12] They are ideal for template-directed generation of novel functional nanomaterials, such as gels,[13] work initiated by Rowan and co-workers.[14] Self-healing of supramolecular polymers is an increasingly topical area of research within supramolecular chemistry[13a,15] with host–guest chemistry playing a significant role.[16] Combining the 'guest' ability of Ln(III) ions with the versatile **btp** 'host' in the design of healable soft matter is our aim. With this in mind, we designed the **btp** ligands **1**-**5**, Figure 1, which possess carbonyl groups at both the 4-pyridyl position (**Y**) and the benzyl terminals (**Z**). This article will focus on **1** and **2**, featuring three methyl ester groups and three carboxylic acid groups, respectively. Ligands **3**-**5** are currently being investigated in our lab for future selective modification at **Y** and **Z** in an "orthogonal" manner. We show that structures **1** and **2** form Eu(III) complexes in 1:3 (**Eu:L**) stoichiometry, ligand **2** gives rise to a hydrogel while the Eu(III) complex of **2**, forms a metallogel in $CH_3OH$ solution endowed with the healable and luminescent properties of the Eu(III) ion.

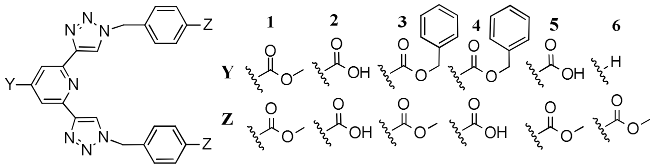

Fig. 1 **Btp l**igands fuctionalised at positions **Y** and **Z**.

The synthesis of **1** (Scheme S1, ESI) demonstrates the ease of formation and functionalisation of these **btp** ligands, **1**-**5** (all syntheses and full characterisations are described in detail in the ESI). Ligand **1** was formed in 85% yield, the key step being the CuAAC 'click' reaction between protected bis-alkyne **9** and azide **11**, which had been prepared *in situ* from commercially available methyl 4-(bromomethyl)benzoate, **10** (see ESI). Ester hydrolysis of **1** in aqueous NaOH gave **2** in high yield, 71%. The formation of $\mathbf{Eu1_3}$, and $\mathbf{Eu2_3}$ was achieved by reacting the appropriate ligand with $Eu(OTf)_3$ in $CH_3OH$ in 1:3 metal:ligand (M:L) stoichiometry under microwave irradiation at 80°C for 60 minutes followed by isolation using precipitation from diethyl ether. Complexes $\mathbf{Eu1_3}$, and $\mathbf{Eu2_3}$ were characterised using conventional methods (see ESI). The complexes of **3**-**5** will not be discussed in this communication.

Colourless, needle-like crystals of $\mathbf{Eu1_3}$ were successfully grown by diethyl ether diffusion into $CH_3CN$ from which the solid-state X-ray structure was determined at 150 K. The resulting structure, shown in Figure 2, crystallised in the triclinic space group $P\bar{1}$, demonstrating low symmetry in the Eu(III) complex. The structure showed each of the ligands coordinating the Eu(III) ion *via* the nitrogens of the pyridine and the two triazoles (through a *syn-syn* orientation)[1a,5b,17] giving an overall coordination environment of nine ($N_9$) for the Eu(III) ion. The crystal structure also showed that the methyl benzoate arms adopted *trans*-like conformation about the methylene linker with π-π interactions between the benzoate arms of neighbouring tris-complexes; each one of them facing 'outwards' from the Ln(III) centre, which could be further used as 'linking' points in the generation of novel material such as gels.[13a] The $^1H$

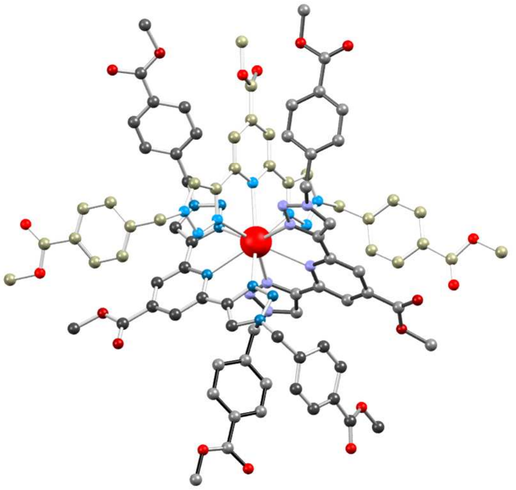

Fig. 2 Ball and stick model of the X-ray crystal structure of **Eu1$_3$**. Hydrogen atoms and counter-ions are omitted for clarity.

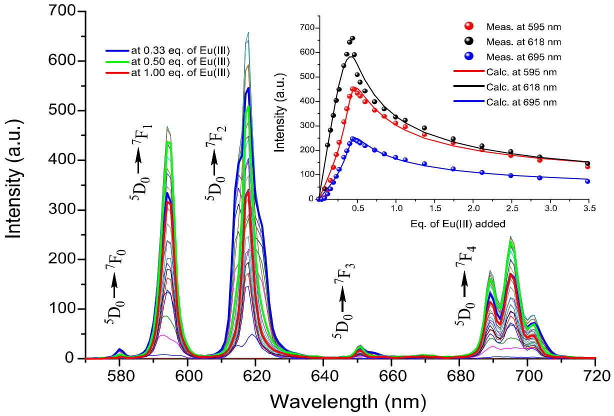

Fig. 3 Changes in Eu(III) centred luminescence spectra upon titration of **1** in $CH_3CN$ ($c$ = 1x10$^{-5}$M) against 0⟶3.5 eq. of $Eu(OTf)_3$ recorded at 25 $^o$C. (Inset) Experimental binding isotherms at band wavelengths. ($\lambda_{ex}$ = 325 nm).

NMR ($CD_3OD$, 400 MHz) analysis of **Eu1$_3$** also indicated that the same structure existed in solution (see ESI) as the geminal coupling between the methylene protons ($J$ = 14.6 Hz) was indicative of the loss of chemical equivalency with each proton losing free rotation about the methylene 'hinge'. Furthermore, the significant upfield shift of the pyridyl and triazolyl $^1$H and $^{13}$C resonances are indicative of the paramagnetic nature of the Eu(III) core.

Having analysed the photophysical properties of **Eu1$_3$** (see ESI) we next carried out titration studies to monitor the kinetic self-assembly behaviour of **1** with Eu(III) in $CH_3CN$ solution. Here, specific aliquots of a stock solution of $Eu(OTf)_3$ were added to a solution of **1** ($c$ = 1x10$^{-5}$ M) and the changes in the UV-Vis absorption and the emission spectra were monitored. Fluorescence quenching and population of the Eu(III) excited state caused by energy transfer from the **btp** antenna gave rise to metal centred emission at 580, 595, 617, 650, and 695 nm assigned to the $^5D_0 \rightarrow {}^7F_J$: $J$ = 0-4 transitions (Figure 3). Analysis of these changes at band wavelengths (inset) demonstrated that the emission enhanced sharply with increasing equivalents (eq.) of Eu(III) ion added. Thorough analysis of the Eu(III) spectral changes allowed for the stoichiometry in solution to be probed as the $\Delta J = 0$ band at 580 nm corresponded strongly to the formation of the 1:3 species (Figure S14, ESI). This, and the splitting pattern of the $\Delta J = 2$ band, are indicative of a single chemical species with $C_3$ symmetry in solution.[18] Moreover, it is worth pointing out that the X-ray crystal structure of **Eu1$_3$** showed that the $N_9$ coordination sphere formed a distorted triaugmented trigonal prism (Figure S27, ESI), a polyhedron normally associated with $D_{3h}$ site symmetry. Such variations between the solid and the solution state structures, having previously been observed in our group,[12a,12d,13a] allow for the symmetry adjustment ($C_3$ is a subgroup of $D_{3h}$) though, as expected, the luminescence spectra of **1** at 0.33 eq. of Eu(III) and that of **Eu1$_3$** in solution coincided closely (Figure S18, ESI).

Nonlinear regression analysis software (ReactLab Equilibria)[19] was used to determine both the speciation distribution and the stability constants for the formation of the **Eu(III):1$_n$** (n=1-3) self-assemblies in solution at 25 $^o$C. The binding isotherms were best fitted to 1:3, 1:2 and 1:1 M:L equilibria. The stability constants (expressed as $log\ \beta_{M:L}$) were determined as $log\ \beta_{1:3} = 22.3 \pm 0.2$; $log\ \beta_{1:2} = 16.2 \pm 0.2$ and $log\ \beta_{1:1} = 8.4 \pm 0.1$ for these stoichiometries, respectively. These compare well with those observed for related systems[3a,12a-d,k] and are reasonably high. The calculated speciation distribution diagrams from fitting the changes in the UV-Vis (Figure S15) showed that at 0.33 eq. of Eu(III) the 1:3 M:L species was present in 92.5% yield, with the ligand **1** becoming fully bound at slightly higher eq. of Eu(III). The formation of the 1:1 and 1:2 M:L species was also seen upon increasing the concentrations of Eu(III) with concomitant decrease in the abundance of the 1:3 M:L species and decrease in overall luminescence.

At low concentration the complexation between **1** and Eu(III) results in the formation of discrete supermolecules in solution, however, we are more interested in this process at higher concentrations. Currently, there exists a great deal of interest in the development of new supramolecular materials with various functional properties that are different from their monomeric or discrete molecular components.[20,21] Having explored the various photophysical properties of **1** upon addition of Eu(III), we set out investigating the possibility of using the **btp** ligands developed herein for soft-material applications. For supramolecular gel formation to be successful, the use of weak intermolecular or metal coordination interactions is of critical importance,[3a,13a,22] hence, the methyl esters of **1** were hydrolysed to the tri-carboxylic derivative **2** as a potential candidate for a low molecular weight gelator.[23] We foresaw that the acid moieties would function as 'bridging points' through hydrogen bonding interactions (*e.g.* carboxylic dimerisation). Initially, the use of the ligand **2** alone in the formation of soft matter was explored. The deprotonation of **2** in aqueous NaOH solution (pH 8) fully solubilised ligand **2**. Addition of dilute HCl until pH 6 resulted in the formation of an off-white 'cotton' like material that upon standing settled as a soft hydrogel material. Alternatively, centrifugation of the above pH 6 solution allowed recovery of the same hydrogel; the morphology was examined using Scanning Electron Microscopy (SEM). The SEM imaging (Figure 4a) showed that the hydrogel displayed a fibrous network of intertwined 'spaghetti' like strands of *ca.* 20–50 nm in diameter arranged in a tightly packed formation. This material under UV lamp excitation gave rise to blue coloured ligand based emission (Figure 4b). Thermogravimetric Analysis (TGA) was carried out on the ligand hydrogel, showing a loss in mass of 98.07% due to water content, giving it a weight percentage (wt. %) of 1.93±0.04 (see ESI).

Having investigated the ability of ligand **2** to form hydrogels, we then investigated the gelation of **Eu2$_3$**. We foresaw that the acid moieties would assemble through the carboxylic dimerisation, mentioned previously, or through the use of 'bridging' metal ions, such as *f*-metal ions. This was done in a two step one-pot procedure (see ESI). We treated a $CH_3OH$ solution of the **Eu2$_3$** complex with $Eu(OAc)_3$. Upon solvation of the Eu(III) salt (3 eq.), a white fluffy precipitate was generated. This mixture was irradiated again in the

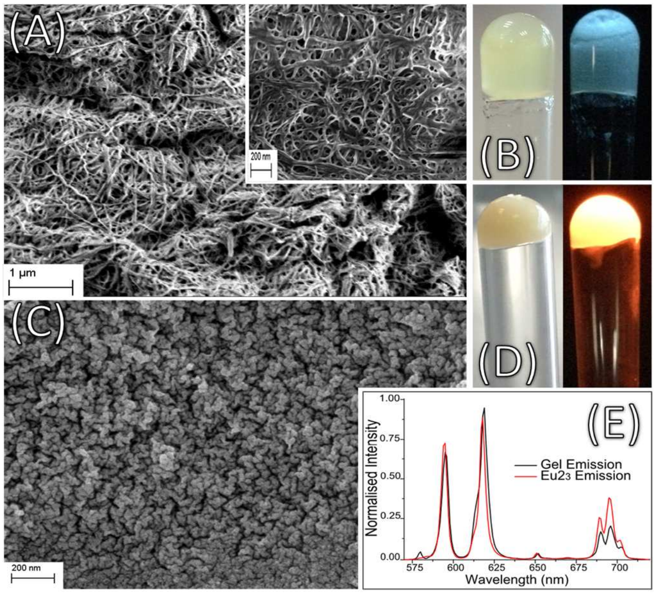

Fig. 4.(A) SEM images of hydrogel of **2** (scale bar 1 µm and inset at 200 nm). (B) Hydrogel of **2** (in daylight and under UV lamp at $\lambda_{ex}$ =365 nm). (C) SEM images of metallogel of **Eu2₃** (scale bar 200 nm). (D) Metallogel of **Eu2₃** (in daylight and under UV lamp at $\lambda_{ex}$ = 365 nm). (E) Eu(III) centred luminescence of **Eu2₃** complex in $CH_3OH$ (red) and of metallogel (black).

microwave for 30 minutes at 80 $^{o}$C giving rise to the formation of an off-white soft precipitate upon cooling. Upon centrifugation of this precipitate a gel was obtained. The same gel could be formed upon allowing the precipitate to settle over several hours. Furthermore, this gel was highly luminescent to the naked-eye (Figure 4d) with characteristic red Eu(III) emission. The gel was also shown to be highly robust and easily applicable to surfaces; it was applied on a quartz slide (Figure S20) which was then used for spectroscopic analysis. The emission spectra closely matched that observed for **Eu2₃** in solution for the $\Delta J$ = 1, 2 and 3, while the $\Delta J$ = 4 was structurally identical, but of lower intensity (Figure 4e). Moreover, unlike what was seen for **Eu2₃** in solution, the $\Delta J$ = 0 was observed in the gel-phase suggesting that a different Eu(III) coordination environment was being added to the system.[18] This was supported by comparing the gel's UV-Vis absorption spectrum to that of **Eu2₃** in solution (Figure S21). Band positions remained constant but a sharp hypochromic effect on $\pi \rightarrow \pi^*$ band indicated the Eu(III) interaction with the carboxylate arms of **Eu2₃** in the gel phase.

In order to characterise the newly formed Eu(III) environment observed in the metallogel, lifetime studies at different stages of the gelation process were conducted (see Table S3, ESI). Firstly, the radiative decay of the **Eu2₃** complex luminescence in $CH_3OH$ solution was found to be monoexponential with a lifetime ($\tau$) of 1.4 ± 0.1 ms. To this was added 2 eq. of $Eu(OAc)_3$, followed by microwave irradiation and collection of the metallogel. This was done in order to determine the lifetime of the still luminescent supernatant which was also shown to be monoexponential with $\tau$ = 1.4 ms, indicative of **Eu2₃**. Further addition of 1 eq. $Eu(OAc)_3$ was required to collect the maximum amount of metallogel removing any luminescent material from the supernatant. Lifetimes of the metallogel showed biexponential radiative decay indicative of the two Eu(III) environments. A long lived species ($\tau$ = 1.3 ± 0.1 ms) characteristic of the fully saturated **Eu2₃** and a shorter lived species ($\tau$ = 0.50 ± 0.05 ms) indicative of the 'bridging' Eu(III) centres.

SEM imaging of the **Eu2₃** metallogel demonstrated that incorporation of the Eu(III) ions formed a gel with different morphology to that of the hydrogel of **2**, Figure 4c; clearly showing the effect $Eu(OAc)_3$ had upon the nano-structure. Here, the SEM imaging showed a more condensed structure and lacked the enriched fibrous network seen in the gelation of **2**. TGA of the **Eu2₃** metallogel showed a loss in mass of 95.15% arising from the $CH_3OH$ content giving it a 4.85±0.08 wt. % (see ESI).

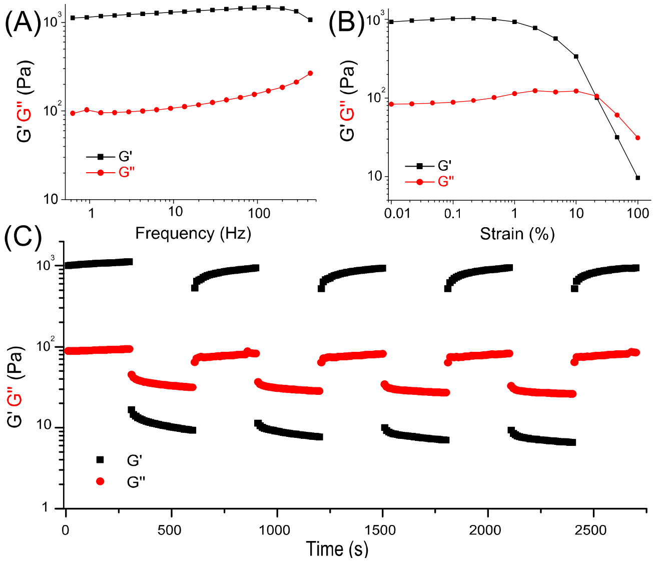

Fig. 5. Oscillatory rheology measurements of Eu(III) gel. (A) Frequency sweeps at 0.1% strain amplitude of the storage modulus G′(■) and loss modulus G″(●) are shown. (B) The corresponding strain dependence at a *f* = 1 Hz. (C) Recovery test for Eu(III) gel with alternating strain amplitudes of 20 % and 0.1 % at *f* = 1 Hz.

For better understanding of the mechanical properties of these novel hydrogel and metallogel materials, rheological studies (strain and frequency sweeps) were performed. The viscoelastic properties of the metallogel compared to those commonly seen for a cross-linked polymer system.[14,24] Little frequency dependence of the storage and loss moduli (G′ and G″ respectively) was observed in the linear viscoelastic region for both the ligand (see ESI) and Eu(III) gels (Figure 5a) and their response was solid-like (G′ > G″). However, for the ligand gel G″ approached G′ at high frequencies indicating a crossover to a liquid-like regime. The corresponding strain sweeps for the gels were also carried out (Figure 5b). At low strain amplitudes, the response was solid-like; the storage modulus remained constant until the yield strain was reached at which point the gel started to flow and G′ decreased. The Eu(III) gel had a storage modulus of about 1.0 kPa in the linear regime while G′ for the hydrogel was 0.8 kPa. The recovery properties of the gels were tested by imposing alternating strain amplitudes of 20% and 0.1% at a constant 1 Hz oscillation frequency. As shown (Figure 5c), the Eu(III) gel went from liquid-like (G″ > G′) to solid-like (G′ > G″) behaviour almost instantly with a quick recovery of within 50 seconds of the original values of the moduli in these two regimes, consistently over consecutive runs. This demonstrated that the Eu(III) gel is self-healing. The same behaviour was not observed for the ligand gel (Figure S26); the moduli values were not being recovered in the same smooth manner as for the Eu(III) gel. The difference in the rheology behaviour is due to the effect of the Eu(III) ion itself, acting as a cross-linker in the formation of the extended 3D network. Incorporation of the Eu(III) ion results in the formation of stronger materials, less subject to aging and more healable. It can be concluded that the $Eu(OAc)_{3,}$ is responsible for the 'bridging' of neighbouring tris-complexes through the carboxylate 'arms' of **Eu2₃**. The nature of the unsaturated Eu(III) 'bridges' possessing vacant coordination sites meant that bond breaking was occurring on the same timescale as bond formation as evident from the frequency sweeps.

In summary, a library of functionally modified **btp** ligands was developed using the successfully placed 4-pyridyl carbonyl group, the self-assembly behaviour of **1**, in particular, with Eu(III) was studied. The analogous compound, **2**, possessing three carboxylic acid groups functioned as a low molecular weight gelator giving rise to the formation of a hydrogel consisting of a fibrous network in aqueous solution. The corresponding luminescent metallogel of $\mathbf{Eu2_3}$ was formed and characterised spectroscopically. The gelation mechanism was investigated through radiative lifetime studies clearly showing two distinct Eu(III) environments present. Rheological studies demonstrated the important role the Eu(III) ion plays in the formation of the metallogel, both from the point of directing the initial self-assembly formation (*i.e.* 1:3 stoichiometry), as well as in 'bridging' between complexes *via* the carboxylate terminals which had a major effect on the morphology of the resulting healable gel material in contrast to that of the ligand hydrogel. This rheological comparison between ligand hydrogel and metallogel effectively demonstrates the value Ln(III) ions can contribute to these soft matter systems.

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## Notes and references

[a] School of Chemistry and Trinity Biomedical Science Institute, University of Dublin, Trinity College Dublin, Dublin 2 (Ireland).
[b] CIQUS, Universidade de Santiago, 15782, Santiago de Compostela (Spain).
[c] Sami Nasr Institute of Advanced Materials (SNIAM), School of Physics, Trinity College Dublin, University of Dublin, Dublin 2, Ireland.

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# Self-assembly formation of a healable lanthanide luminescent supramolecular metallogel from 2,6-bis(1,2,3-triazol-4-yl)pyridine (btp) ligands

Eoin P. McCarney, Joseph P. Byrne, Brendan Twamley, Miguel Martínez-Calvo, Gavin Ryan, Matthias E. Möbius and Thorfinnur Gunnlaugsson

The self-assembly and rheological studies of self-healing Eu(III) luminescent metallogels from a **btp** (2,6-bis(1,2,3-triazol-4-yl)pyridine) ligand is described.