

A “plug-and-play” approach to the preparation of transparent luminescent hybrid materials based on poly(methyl methacrylate), a calix[4]arene crosslinking agent and terbium ions.

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A novel methodology to prepare transparent luminescent hybrid materials is reported. Using a calixarene ionophore as a PMMA cross-linker avoids problems such as phase segregation, and produces a polymer monolith that can be loaded with the metal ion required for luminescence post-synthesis. This approach is versatile and will simplify the production of such materials.

Hybrid inorganic-organic materials offer the advantageous combination of the functional properties of the guest metal centres, such as luminescence and/or magnetism, with the thermal and mechanical properties of the host polymeric matrix.¹ Particular attention has been devoted in the last decade to the preparation of transparent polymeric materials exhibiting luminescent properties,² as these find applications in a variety of fields, *viz.* light emitting devices, optical displays, tuneable lasers, and sensors. Amongst the various classes of potential inorganic guests, luminescent lanthanoid compounds are particularly attractive due to their line-like quasi-monochromatic emissions in the visible or infrared spectra,^{3, 4} and potential application in non-linear optics,⁵ and as a result they have been used for the fabrication of such materials.^{6, 7} We have also recently shown that lanthanoid hydroxo clusters can be used for the fabrication of transparent reinforced emissive materials.⁸ The challenge in preparing these types of hybrid materials is the tendency towards phase segregation of the inorganic component from the organic polymer.⁹ This undesired phenomenon leads to a loss of homogeneity and transparency, significantly decreasing the quality of the final material. Various strategies have been proposed to overcome this,⁶ including: i) functionalisation of the lanthanoid complexes and nanoparticles with suitable solubilising groups; ii) direct attachment of these compounds, via covalent crosslinking, to the polymeric chains.

As part of our work focused on the preparation of transparent hybrid materials, we have turned our attention to the use of calix[4]arene sensitised lanthanoid complexes and their incorporation into polymeric matrices. Calixarene-containing polymers are not common, but have been accessed by functionalisation of a pre-formed polymeric material,¹⁰⁻¹³ and by reaction of a calixarene monomer.¹⁴⁻²³ The bulk of this work focuses on using well known behaviour of the calixarenes as receptors, for absorption of target species including cations,^{13, 17, 18} anions,¹¹ biological molecules,¹⁰ and neutral organic species^{14, 16}.

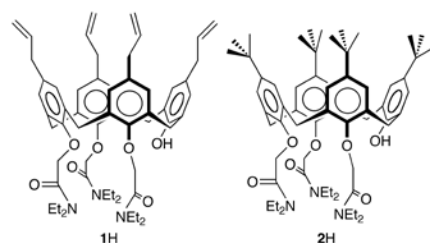
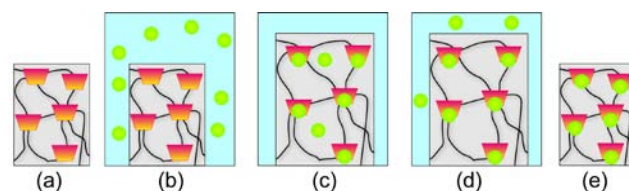


Fig. 1 Structures of the allyl functionalised (1H) and *p*-*tert*-butyl (2H) calix[4]arene trisamide ligands.



Scheme 1 Schematic representations of the preparation of luminescent materials by swelling: the calix[4]arene monolith (a) is immersed in a solution containing a Tb³⁺ salt (b); upon swelling the Tb³⁺ penetrates the material and occupies the coordination sites of the calix[4]arene (c); unbound Tb³⁺ is then removed by successive swelling in solvents (d) and eventually the material shrinks back to its original shape under reduced pressure (e).

We have exploited the allyl groups at the upper rim of the calix[4]arene **1H** (Fig. 1) to form poly(methyl methacrylate) (PMMA) crosslinked with luminescent lanthanoid complexes of **1**. The advantage of our procedure is that it does not require the pre-formation of the calix[4]arene metal complex, and instead introduces a novel two step procedure to obtain these hybrid materials. As depicted in Scheme 1, firstly, methyl methacrylate (MMA) is polymerised in the presence of **1H** to give a crosslinked polymer. Secondly, the crosslinked polymer is swollen with a solution containing a suitable lanthanoid salt, which can penetrate the PMMA material and coordinate to the calix[4]arene ligands within. Subsequent swelling (*i.e.* washing) steps and removal of the solvent yields the desired luminescent hybrid material. This methodology resolves issues related to the solubility of the inorganic precursor (or calix[4]arene metal complex) in the neat monomer or solvent system, as the organic soluble calix[4]arene is polymerised first, and then complexation can be performed using a second solvent system more suitable for the metal complexes. Moreover, the crosslinked nature of the matrix guarantees the original shape of the material is

preserved. To illustrate this novel procedure, we have prepared PMMA matrices crosslinked by Tb^{3+} complexes of **1**, and compared the emission profile of these materials with those of the analogous Tb^{3+} complex with calix[4]arene **2H**.

The *p-tert*-butylcalix[4]arene trisamide **2H** was prepared according to the literature,²⁴ while **1H** was prepared following the same alkylation procedure,[†] with the allyl functionalised calix[4]arene.²⁵ Crosslinked PMMA samples were obtained by bulk radical polymerisation of neat MMA with **1H** (0.2% mol. eq.), using azobisisobutyronitrile (0.13% mol. eq.) as the initiator, following the previously developed methodology.^{8, 26} Since **1H** is completely soluble in MMA, the amount of crosslinking agent in the reaction mixture can be easily varied without phase segregation occurring. At the end of the procedure, the polymerised material was removed from its glass container, giving transparent cylindrical monoliths with a 6 mm diameter. The PMMA monoliths were then swollen in a 1:1 ethanol/dichloromethane solution (4 mL) containing $\text{Tb}(\text{NO}_3)_3(\text{DMSO})_4$. The DMSO solvated Tb nitrate was chosen as an anhydrous metal source to minimise the potential for H_2O molecules to coordinate to the metal centres in the final product,²⁷ which can lead to vibrational quenching of the metal centred emission. A large excess of Tb relative to **1H** in the monolith was used to favour complexation of the available calix[4]arene sites within the material during the swelling stage.[‡] After the complexation step, the swollen monoliths were dried until the material returned to its original size. Subsequent swelling procedures were then performed twice with a 1:1 ethanol/dichloromethane mixture and then with ethanol to facilitate the removal of any unbound Tb salt. The fact that the hybrid material swelled in the presence of these solvents (volume increased by *ca.* 180%), rather than dissolved, confirms that **1H** has covalently crosslinked the PMMA chains.

In order to assess the photophysical properties of the final material, the monoliths were directly positioned on the cuvette holder of the fluorimeter. The materials were then excited at $\lambda_{\text{ex}}=320$ nm, exhibiting the typical green emission of trivalent Tb. To determine if the Tb cations had coordinated to the calix[4]arene sites within the material, the emission profile of the crosslinked PMMA hybrid was compared to the emission spectrum of a 1:1 ethanol/dichloromethane solution containing equimolar quantities of **2H** and $\text{Tb}(\text{NO}_3)_3(\text{DMSO})_4$. The spectra are shown in Fig. 2 and display the characteristic Tb^{3+} bands corresponding to the $^5\text{D}_4 \rightarrow ^7\text{F}_J$ transitions with $J=6-3$, characterised by a typically long emission lifetime ($\tau=0.774$ ms[†]).³ The most intense peak is the green-centred $^5\text{D}_4 \rightarrow ^7\text{F}_5$. Both the $^5\text{D}_4 \rightarrow ^7\text{F}_6$ and $^5\text{D}_4 \rightarrow ^7\text{F}_5$ bands exhibit multiple peaks originating from the $2J+1$ splitting of both the excited and ground states.²⁸ Notably, the emission profiles of the Tb-containing PMMA monoliths changed when comparing the spectra before and after the swelling stage to remove unbound Tb salts. While minor changes in the emission intensity may be due to different positioning of the monolith in the cuvette holder, it is possible that improvement of the photophysical properties is due to the removal of excess Tb which may have been causing concentration quenching.²⁹ The emission profile of the Tb containing crosslinked PMMA monoliths is

remarkably similar to the emission profile in solution, even to the extent of the fine structure exhibited by the two higher energy peaks ($^7\text{F}_J$, $J=6, 5$). This evidence strongly supports the conclusion that within the material, light emission of the Tb centres is originating by means of an antenna effect of the calix[4]arene, which efficiently transfers the energy of its triplet excited state to the $^5\text{D}_4$ state of the Tb^{3+} . This was confirmed by conducting a series of control experiments. No emission was detected by excitation at $\lambda_{\text{ex}}=320$ nm of an ethanolic solution of $\text{Tb}(\text{NO}_3)_3(\text{DMSO})_4$. No light emission was observed when a PMMA sample, crosslinked with ethylene glycol dimethacrylate, was swollen with a $\text{Tb}(\text{NO}_3)_3(\text{DMSO})_4$ solution (Fig. 3). Finally, the excitation spectrum of the polymer crosslinked by **1H** and containing Tb cations shows a maximum around 320 nm, with a peak shape similar to the absorption profile of **1H** (Fig. S8[†]).

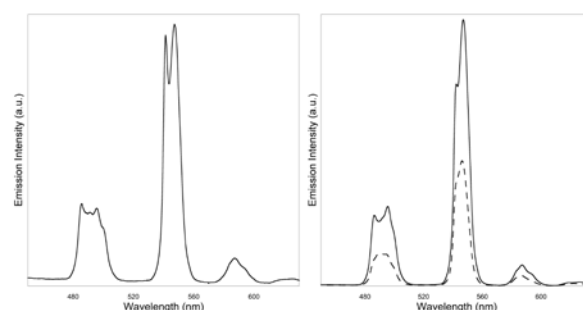


Fig. 2 Left: emission profile of $\text{Tb}(\mathbf{2})(\text{NO}_3)_2$ in a 1:1 ethanol/ CH_2Cl_2 solution. Right: solid state, room temperature emission profile of PMMA crosslinked with $\text{Tb}(\mathbf{1})(\text{NO}_3)_2$ before (dashed line) and after washing (solid line).

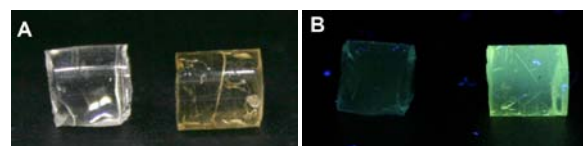


Fig. 3 Comparison of the hybrid materials crosslinked with either ethylene glycol dimethacrylate (left) or **1H** (right) and swollen in presence of $\text{Tb}(\text{NO}_3)_3(\text{DMSO})_4$. Picture A was taken under white light whereas B was taken under UV irradiation.

Having confirmed that the calix[4]arene chromophore is essential to observe the Tb-centred emission, we investigated the impact of small changes in the coordination environment of Tb cations bound to the calix[4]arene ligand on the fine structure of the emission spectra. In particular we have compared the emission originating from the complexation of $\text{Tb}(\text{NO}_3)_3(\text{DMSO})_4$ to **1H** with solutions containing equimolar quantities of: i) $\text{TbCl}_3(\text{H}_2\text{O})_6$ and **1H**; ii) $\text{Tb}(\text{NO}_3)_3(\text{DMSO})_4$ and **2H**; iii) $\text{TbCl}_3(\text{H}_2\text{O})_6$ and **2H**; iv) $\text{Tb}(\text{ClO}_4)_3(\text{DMSO})_4$ and **2H**. For the last complex, we were also able to isolate single crystals suitable for X-ray diffraction[†] (Fig. 4).

The structure, crystallised in the triclinic $P\bar{1}$ space group, shows an octacoordinated Tb centre bound to the phenolate O atom, the three ether and carbonyl O atoms of the amide arms, and lastly to a DMSO molecule. The structure is similar to the previously reported lanthanoid picrate complexes of this calix[4]arene, but here DMSO is bound to the metal centre rather than picrate.^{30, 31} By comparing all the emission spectra it is evident that differences in the chemical nature of the

upper rim do not affect the Tb-centred emission (see Figs. S4 and S6[†]). The profiles obtained from the Tb(NO₃)₃(DMSO)₄ solutions, when the ⁵D₄ excited state of Tb is populated either by energy transfer from **1**[†] or **2**[†], are virtually identical. In contrast, emission profiles with a different fine structure, especially related to the ⁵D₄→⁷F₆ and ⁵D₄→⁷F₅ bands, are obtained when Tb chloride or perchlorate salts are substituted for the Tb(NO₃)₃(DMSO)₄. These results indicate that the coordination spheres of the two emissive complexes in Fig. 2 are very similar, further confirming that the Tb ions are coordinated to the crosslinking calix[4]arenes during the swelling stage. These results also indicate that emission profiles of the trisamide calix[4]arene complexes may be fine-tuned by varying the co-ligand (DMSO in Fig. 4).

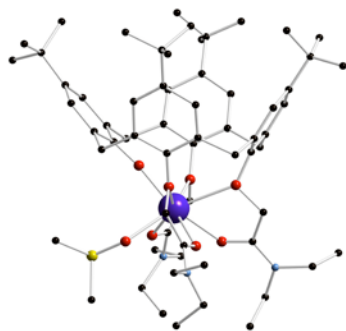


Fig. 4 X-ray crystal structure of [Tb(1)(DMSO)][ClO₄]₂ with ClO₄⁻ counteranions, hydrogens and lattice solvents omitted for clarity (colour scheme: C, black; O, red; N, blue; S, yellow; Tb, purple).

In conclusion, we have presented a novel methodology for the preparation of transparent and luminescent hybrid inorganic-organic materials. The two-step process involves firstly the crosslinking of the PMMA chains by copolymerisation of MMA in presence of the allyl-functionalised calix[4]arene. Secondly, the swelling step in the presence of Tb salts introduces the luminescent functionalities within the hybrid material. This methodology overcomes issues related to the solubility of the inorganic component in the polymerisation system, thus avoiding phase segregation and loss of transparency. Moreover, as the ligand itself is generally soluble in organic mixtures, this allows for fine-tuning of the photophysical and mechanical properties of the final material by variation of the concentration of the calix[4]arene in the reaction mixture. Current investigations are focused on the elaboration of this “plug-and-play” methodology to include metals with other properties (e.g. magnetism and other emission profiles) into the hybrid material and the use of different crosslinking ligands.

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Notes and references

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[†] Electronic Supplementary Information (ESI) available: synthetic details for **1H**; X-ray structural data of [Tb(1)(DMSO)][ClO₄]₂; emission and excitation spectra; excited state lifetime data. CCDC 801658 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. See DOI: 10.1039/b000000x/

[‡] A base is often added to enhance deprotonation of the phenol group in such complexation experiments,^{30,31} although complexation also occurs in the absence of base.²⁴ Here, base was not added to ensure hydroxides were not precipitated thus reducing transparency of the polymer monolith. Solution phase fluorescence measurements showed that complexation occurred in the presence and absence of added triethylamine, although complexation was enhanced with added base (Fig. S5).

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