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We describe the preparation and optical characterisation of a coronene tetracarboxylate salt (**CS**) in polyvinyl alcohol (PVA) thin films solution-processed from water, neat, and mixed with varying ratios of a europium trishexafluoroacetylacetoanto diaquo complex [Eu(hfac)$_3$(H$_2$O)$_2$]. Neat **CS**-PVA showed not only well-defined fluorescence peaks but also a long-lived phosphorescence emission, persisting for more than 1 second. Interaction between the **CS** and Eu(III) molecules, mediated *via* carboxylate coordination to the Eu(III), was attained by simple incorporation into the PVA polymer matrix and resulted in energy transfer from the coronone antenna to the europium centre. Under various blend ratios of **CS** and Eu(III) complex, total photoluminescence quantum yields of typically around 30% were achieved. The straightforward processing of this type of self-assembled chromophore-lanthanide system into a luminescent polymer film offers potential to be readily translated to other chromophores, lanthanides and polymers.

Introduction

There is widespread interest in luminescent lanthanide complexes for applications across topics including solar energy conversion,[1, 2] telecommunications,[3] display technologies,[4] biological sensing[4] and lasers.[5] Due to the low oscillator strength of f-f transitions, light harvesting by lanthanide complexes is generally achieved using a chromophoric ligand as antenna, such that excitation energy is transferred to the metal centre and subsequently emitted.[4-6] For many applications, the luminescent complex is embedded in a host material and a variety of these have been explored, including inorganic matrices and substrates,[7] liquid crystals,[8] dendrimers[9] and polymers.[10] Polymers, in particular, offer the opportunity to vary processing, materials and optical characteristics, and studies have investigated the use of polymethylmethacrylate,[2, 11-15] fluorinated polymer,[15] poly-*β*-hydroxybutyrate,[16] ethylvinylacetate[1] and ethylene glycol dimethacrylate as host matrices.[17] For example, we and others have explored the use of Eu-complex-doped polymer films as luminescent downshifting layers to enhance the efficiency of photovoltaic cells.[1, 2]

Studies of lanthanide complexes in polymer hosts, however, typically involve the immobilisation of pre-synthesised lanthanide complexes in the host material which limits the rate at which new materials can be prepared and assessed. For solution studies, it has been shown previously,[18, 19] that *in situ* interaction of a lanthanide centre with an organic chromophore featuring a carboxylate/phosphonate group capable of acting as a ligand, provides a rapid and effective means to explore good lanthanide-sensitiser combinations. To the best of our knowledge, this *in situ* self-assembly approach has not been applied previously to the preparation of emissive lanthanide-polymer films, despite the enormous scope for new materials discovery and the possibility for simplified materials synthesis, optimisation and processing that can be achieved.

Herein, we report the spectroscopic properties of coronene tetracarboxylate salt (**CS**), which shows long-lived phosphorescence, and its *in situ* blends with europium trishexafluoroacetylacetoanto diaquo complex [Eu(hfac)$_3$(H$_2$O)$_2$], in polyvinyl alcohol (PVA) films (Fig. 1). Absorption, steady-state and time-resolved emission, and photoluminescence quantum yield (PLQY) are reported, demonstrating broad UV light harvesting with energy transfer to Eu(III) and characteristic emission around 610 nm. This demonstrates the potential of this versatile general approach to luminescent polymer materials *via* self-assembly of the components during spin coating.

Coronene Salt (CS)   **(hfac)$_3$Eu^{III}(H$_2$O)$_2$**
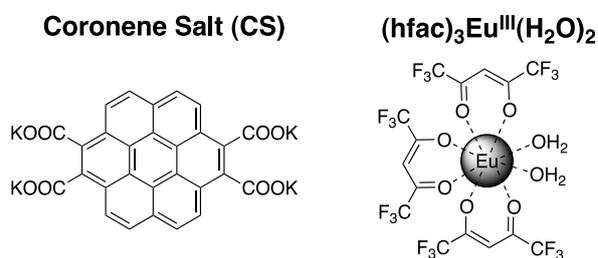
Figure 1. Molecular structures of the coronene salt (**CS**) and europium complex used in this study.

Results and Discussion

The presence of four carboxylate groups makes the **CS** molecule appropriate for study in aqueous solution, with limited solubility in common organic solvents. In aqueous solution, **CS** shows two

main absorption peaks centred at 311 and 348 nm (Fig. 2) with high molar absorption coefficients of 132 000 and 30 000 cm^{-1} M^{-1}, respectively. These are around half the values for the parent coronene, for which Patterson reported a value of 270 000 cm^{-1} M^{-1} at 305 nm,[25] suggesting that the carboxylate groups significantly modify the absorption properties.
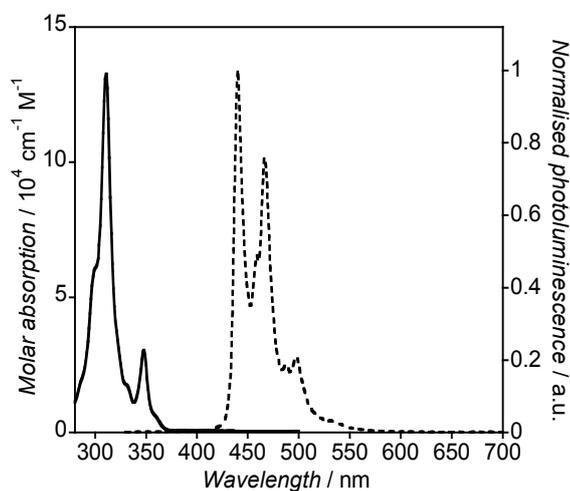
Figure 2. Absorption (*solid line*) and emission (*dashed line*) spectra of **CS** in deionised water recorded at 8.5 x 10^{-6} M and 1.4 x 10^{-7} M, respectively. Emission was excited at 311 nm.

The emission spectrum of **CS** in distilled water (Fig. 2) shows three main peaks, centred at 440, 465 and at 500 nm, independent of the excitation wavelength. The excitation spectrum matches the **CS** absorption confirming the origin of the emission (Fig. S1†). Emission from such polyaromatic salts has been a valuable tool to investigate aggregation kinetics and supramolecular assembly,[22] however, no aggregation was detected at the concentrations used in this study (Fig. S2†).
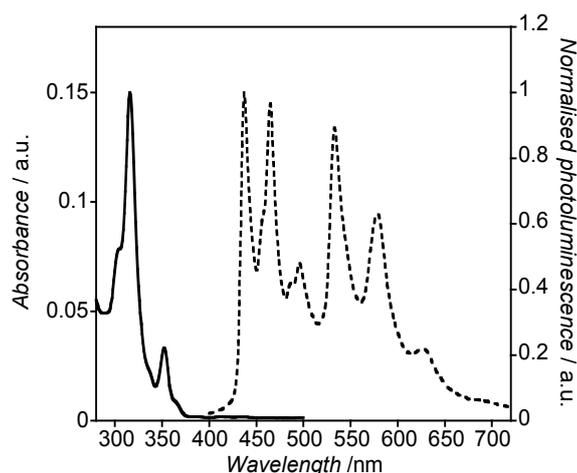
Figure 3. Absorption (*solid line*) and emission (*dashed line*) spectra of **CS** in PVA matrix. Emission was excited at 315 nm.

Further studies on the optical properties of **CS** were carried out after incorporation into a PVA matrix. Films were obtained by mixing **CS** in a concentrated PVA water solution, followed by spin coating. The optimal **CS** concentration for spectroscopic studies was found to be 1 mM, giving a maximum absorbance around 0.15. at the main **CS** absorption peak (315 nm). Solid-state pristine **CS**-PVA showed two main absorption bands, centered at 315 and 350 nm, slightly red-shifted compared with solution, perhaps due to some aggregation or simply to some inhomogeneity in the solid state (Fig. 3). On the other hand, the emissive properties of **CS**-PVA differ significantly from aqueous solution. As shown in Fig. 3, we observe broad emission, covering a range from 420 nm to 720 nm, with peaks at 438, 465, 534 and 578 nm. The emission can be assigned as fluorescence, from 420 nm to 520 nm, and phosphorescence, from 520 nm to 720 nm, based on the observed lifetimes (*vide infra*). The phosphorescence constitutes a significant proportion of the total emission inensity, with a long lifetime (greater than 1 s), as shown Fig. 4. The lowest excited singlet and triplet states of the parent coronene molecule are reported to be 2.88 eV and 2.41 eV respectively.[26] This combination of singlet and triplet emission in **CS**-PVA offers a spectral envelope similar to white light (Fig. S3†), which is normally derived from multiple independent emitters.

Fig. 4 shows the phosphorescence spectrum of **CS**-PVA at different time intervals after excitation. The spectrum has three peaks at 533, 580 and 628 nm and the emission shows a monoexponential decay with lifetime (τ) of 1.8 seconds. This value is in agreement with that reported for unsubstituted coronene dispersed in PMMA matrix where phosphorescence at room temperature has been observed,[27] accompanied by lifetime up to several seconds. The exceptionally long triplet lifetime is potentially beneficial for the sensitisation of Eu. The emissive state of Eu is around 17 300 cm^{-1} and the ligand triplet state is estimated from the phosphorescene spectrum at around 19 000 cm^{-1} which should be sufficient to allow efficient energy transfer from the chromophore to the Eu, aided by the long triplet lifetime.

A significant enhancement in the luminescence yield for **CS**-PVA composite, compared with **CS** in aqueous solution is observed (Table S1, S2†), and can be partly attributed to the oxygen-impervious property of PVA films minimising triplet quenching. The PLQY of **CS** in water solution at various concentrations was around 3%, despite thorough degassing to minimize oxygen quenching (Table S2†). The photoluminescence quantum yield for **CS**-PVA was measured in the concentration range 0.3 to 6 mM of **CS** in the precursor solution, rising to a maximum of 43% for the lowest concentration (Table S1†). Emission from concentrations below this was too weak for accurate measurement and the higher concentrations may be adversely affected by aggregation of **CS**,[28] which can lead to emission quenching.[29] Values around 65% for coronene films sublimed onto glass plates have been reported in the literature,[30] whereas spin-coated films in PMMA from highly-diluted solutions of coronene gave instead PLQY of about 20%,[31] which is in the range found here for PVA films, although significantly lower than our highest values. Persistent room temperature phosphorescence in amorphous organic materials at room temperature in air has been recognised as a rare and important phenomenon that has potential applications in a wide range of areas.[32]

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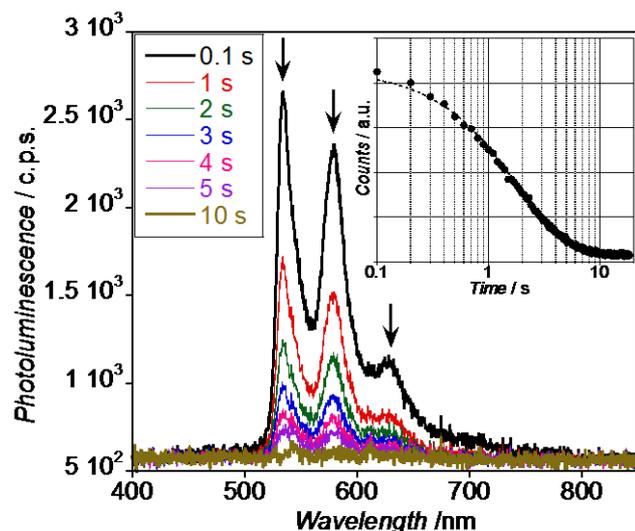
Figure 4. Transient phosphorescence spectra of pristine **CS** in PVA film at different time intervals after excitation and its time-resolved decay recorded at 533 nm (inset). Phosphorescence decay was fitted by a monoexponential function, giving a lifetime of 1.8 s.

Having studied the absorption and emissive properties of pristine **CS**, we proceeded to measure the photoluminescence of blends of **CS** with $[Eu(hfac)_3(H_2O)_2]$. Films were obtained by mixing different ratios of **CS** and Eu complex, as described in the experimental section. The Eu complex was selected to have two monodentate ligands, that could readily be replaced by carboxylates on the **CS,** and three hfac ligands to minimise C–H oscillators near the metal that might quench the luminescence. $[Eu(hfac)_3(H_2O)_2]$ itself has been shown previously to have a PLQY of 32% in DCM and 26% in PMMA.[11]
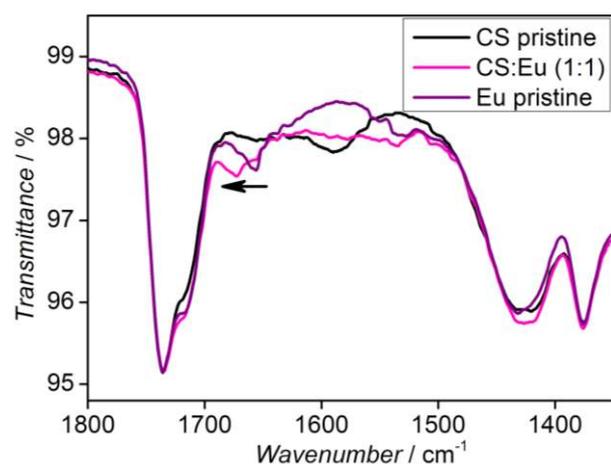
Figure 5. ATR-FTIR spectra of PVA films containing neat **CS** (black line), neat $Eu(hfac)_3(H_2O)_2$ (purple line) and a mixture of **CS**:Eu at a ratio of 1:1 (magenta line). Arrow indicates a shift of the carbonyl vibration peak of hfac on addition of **CS**. Eu and **CS** concentrations were kept at 1 mM in all films.

Prior to discussing the photoluminescence data, we first consider the ATR-FTIR spectra of PMMA films containing CS alone, Eu-

complex alone and a 1:1 ratio of these two (Fig. 5). We were unable to observe peaks from the **CS** carboxylates due to competing absorption in the PMMA, however in the **CS**:Eu mixture , we clearly observe a new peak around 1690 cm^{-1} that is present in neither of the other two films. This peak lies in the region associated with vibrations of the hfac ligand[33,34] and its modification in the presence of **CS** provides clear evidence of a spontaneous coordination interaction between the **CS** and Eu-complex when spin-coated together in PMMA.
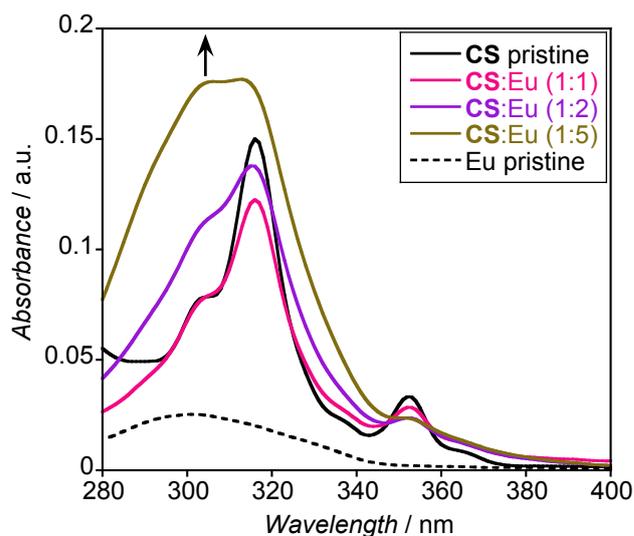
Figure 6. Absorption spectra of PVA films containing pristine **CS** (solid black line), **CS**:Eu mixtures at different ratios (solid coloured lines) and neat $[Eu(hfac)_3(H_2O)_2]$ (dashed black line). Arrow indicates the trend after incremental incorporation of the Eu complex. The ratio is shown in brackets as equivalents and [**CS**] was kept as 1 mM. Eu pristine concentration was 1 mM..

Upon addition of $[Eu(hfac)_3(H_2O)_2]$ to the spin-coating solution, the **CS** UV-absorption peaks remain essentially unaffected, although at higher concentrations, direct absorption by the Eu complex was also observed (Fig. 6).

Initially, photoluminesence properties of **CS**:Europium PVA blends were studied by exciting into the main absorption band at 315 nm. After incremental addition of the Eu complex, a clear trend was observed. As shown in Fig. S4, the intensity of emission from **CS** decreases as the concentration of the Eu complex in the film increases, becoming mostly quenched with higher Eu complex amounts (Fig. S4, inset). At the same time, the characteristic Eu emission bands appear and increase gradually. This could be an indication of energy transfer; however, this is not conclusive since the free complex can be excited directly at 315 nm, as shown by observation of signifcant emission from the pure Eu complex.

Excitation at 350 nm, where absorption by the Eu complex is negligible, permitted investigation of the photoluminescence response of the system to selective excitation (Fig. 7). The same trend is observed; a decrease of **CS** emission followed by an increment of Eu emission with increasing proportion of Eu, with very significant quenching of the **CS** emission at higher Eu concentrations (Fig. 7, inset). This unambiguously demonstrates that the **CS** is acting as an antenna for Eu excitation, which in turn strongly suggests complexation of the Eu centre *via* the **CS**

3

carboxylates, in keeping with the IR data (Fig. 5).

To further confirm energy transfer from **CS** to the Eu complex, excitation spectra were aquired by fixing the emission wavelength at 614 nm (the main Eu emission peak). As can be seen in Fig. 8, the excitation spectrum is clearly characteristic of **CS** for blends with a low Eu component (less than one equivalent), confirming its role as sensitiser. Direct europium-complex excitation can also be observed with a higher Eu component (Fig. 8 inset).

As the Eu concentration is increased up to one equivalent, the intensity of Eu emission, excited at 350 nm, increases steadily (Figure 7), consistent with the formation of increasing concentration of Eu-**CS** complex. Further increase of the Eu component, however, to **CS**:Eu = 1:2, gives no discernable increase in Eu emission intensity (Figure 7 inset). Further increase to a fivefold excess of Eu does result in an increase in Eu emission, however excitation via the long wavelength tail of the hfac absorption becomes significant at this high Eu concentration and the increased Eu emission can be attributed to direct excitation of Eu that is not complexed with **CS**. Furthermore, at Eu:CS ratios greater than 1:1, **CS** emission decreases considerably (Fig. S5†), although Eu intensity does not concomitantly increase. This implies that there is a quenching process in addition to energy transfer operative in the presence of excess Eu. Taken together, these observations suggest that the 1:1 ratio may provide an optimum stoichiometry for complexation and hence energy transfer between **CS** and Eu, with further addition of Eu leading only to quenching of **CS** rather than energy transfer.

Figure 8. Photoluminescence excitation spectra (at emission wavelength 614 nm) of PVA films containing neat **CS** (solid black line) or **CS**:Eu mixtures at high **CS**:Eu ratios (solid coloured lines). Inset shows excitation spectra for low **CS**:Eu ratios and for the Eu complex alone (solid dashed line). Arrows indicate the trend after incremental incorporation of [Eu(hfac)$_3$(H$_2$O)$_2$]. The ratio is shown in brackets as equivalents and [**CS**] was kept 1 mM. Eu pristine concentration was 1 mM.

Time-resolved photoluminescence studies were also performed exciting at both 315 nm and 350 nm and recording at the main Eu emission peak of 614 nm (Fig. S6, S7†). The decay data were fitted to a monoexponential function, giving lifetime values in the range 400 to 600 μs, with no clear trend among samples (Table S3†). The values are within the expected range for Eu complexes,[11] indicating that association with **CS** does not significantly affect the observed lifetime.

To determine the practical potential of the lanthanide-chromophore self-assembly process in polymer for applications such as luminescent downshifting, we determined the PLQY of the **CS**:Eu mixtures in PVA films excited at 350 nm, where **CS** is excited selectively without direct excitation of the (hfac)$_3$Eu moiety. As shown in Table 1, PLQY values were typically around 30%. The results showed variation over the approximate range 20 – 40% and the lack of a strong trend may be due to the heterogeneous nature of the solid-state samples exacerbated by subtle differences in the fabrication process and the need to use a higher (3 mM) conentration of **CS** for sufficient absorption at 350 nm. Taken alongside the clear evidence of energy transfer, however, the results signify moderate PLQY achieved for largely Eu-centred emission through *in situ* sensitisation by the coronene ligand.

Figure 7. Photoluminescence spectra, excited at 350 nm, of PVA films containing neat **CS** (solid black line) or **CS**:Eu mixtures with high **CS**:Eu ratios (solid coloured lines). The inset shows the Eu emission region for mixtures with low **CS**:Eu ratios, and for the Eu complex alone (dashed black line). Arrows indicate the trend after incremental incorporation of [Eu(hfac)$_3$(H$_2$O)$_2$]. The ratio is shown in brackets as equivalents and [**CS**] was kept 1 mM. Eu pristine concentration was 1 mM.

Table 1. Photoluminescence quantum yields of PVA films containing **CS**:Eu complex mixtures at different ratios. The ratio is shown in brackets as equivalents.

Sample	PLQY$_{350}$ / %[a]
CS pristine	20 ± 2
CS:Eu (1:0.1)	35 ± 4
CS:Eu (1:0.2)	42 ± 4
CS:Eu (1:0.5)	29 ± 3
CS:Eu (1:1)	21 ± 2
CS:Eu (1:2)	27 ± 3
CS:Eu (1:5)	n/a[b]

[a] Absorbance ~ 0.10 a.u. at λ_{ex} = 350 nm. [**CS**] = 3 mM. [b] Sample not prepared due to solubility limitation.

Conclusions

In summary, we report a straightforward spin-coating method in water to fabricate luminescent polymer films by achieving the *in situ* self-assembly of **CS** and a precursor Eu complex, evidenced by IR, and most likely through an Eu-carboxylate interaction. The films were studied by absorption, emission and excitation spectroscopies at a variety of concentration ratios, clearly demonstrating energy transfer from **CS** to the europium centre as well as reasonable PLQY. Effective energy transfer from **CS** to Eu can likely be attributed in part to the long phosphorescence lifetime demonstrated for the former which enables energy transfer with only a comparatively small driving force, hence light harvesting can be extended towards longer UV wavelengths. The *in situ* assembly approach promises easy variation of the lanthanide metal, the sensitising ligand and the host polymer, making this method suitable for application in light-harvesting or spectral conversion systems. The achievement of PLQYs typically around 30% with an initial trial system points towards higher values being possible with further optimisation of the components, the concentrations and the film processing.

Experimental Section

Materials. Coronene potassium tetracarboxylate salt (**CS**)[20-22] and tris(hexafluoroacetylacetoanto)europium(III) dihydrate (Eu(hfac)$_3$(H$_2$O)$_2$)[11] were synthetised according to literature procedures. The polymer matrix consisted of the water-soluble poly-vinylalcohol (PVA) Mowiol® 18-88 with a M$_W$ ~ 131 000.

Film preparation. The films were prepared on a 1 mm thick glass slide with an area of 1.5 x 2.5 cm. Glass slides were cleaned by sequential sonication in detergent "Decon 90", distilled water (x2) and iso-propanol (x2). The **CS** and Eu complex were mixed at different ratios, keeping [**CS**] = 1 mM to achieve convenient spectral intensities without saturation, with a previously prepared solution of 17 mg/mL PVA in distilled water. A few drops of methanol were added in order to improve the solubility of the Eu complex in water. Then, 100 µL of the PVA mixture was drop cast onto a glass slide and spin-coated for 60 seconds at 1000 r.p.m., followed by an additional 15 seconds at 4000 r.p.m. Thin films were stored in a desiccator over CaCl$_2$ for 72 hours in the dark before measurements.

FTIR-ATR mearuments. ATR-FTIR spectra were recorded using a Perkin Elmer Spectrum 65 spectrometer equipped with an OptKBr beamsplitter and a LiTa03 detector at a spectral resolution of 4 cm^{-1}. The thin films were mounted on a Miracle ATR attachement for analysis, using 8 scans for each measurement. Two different areas on each film were measured to ensure reproducibility.

Optical characterisation. Solution and solid-state UV-Visible absorption spectra were recorded using a Jasco V-670 UV/Vis/NIR spectrophotometer, controlled using the SpectraManager software. Solution samples were measured in a 1 cm cell at room temperature with distilled water as solvent. Steady-state and time-resolved photoluminescence (PL) were recorded with a Fluoromax-P luminescence spectrometer, controlled by the ISAMain software. For solid-state samples, front surface excitation was used and a 400 nm long pass filter was used to exclude scattered excitation light.

Photoluminescence quantum yield (PLQY). **CS**:Eu thin-film PLQY were determined via transmission and emission measurements in a spectrofluorimeter (Edinburgh Instruments FS920) using the integrating-sphere method described previously.[23, 24] In this case, [**CS**] was set as 3 mM, in order to obtain an absorbance close to 0.1 at 350 nm. Spectra were integrated over 400 – 730 nm. Note that (*i*) the samples containing the Eu complex alone did not exhibit sufficient absorption, thus the PLQY could not be determined and (*ii*) a homogeneous **CS**:Eu 1:5 thin-film was not achieved due to solubility limitations.

Supporting Information (see footnote on the first page of this article): † **CS** excitation spectrum in water, Beer-Lamber plot, chromaticity index diagram of **CS**-PVA, excitation spectra of **CS**:Europium blends in PVA, photoluminescence decays, PLQY values for pristine **CS** on PVA and water as well as **CS**:Eu PVA films lifetime values.

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