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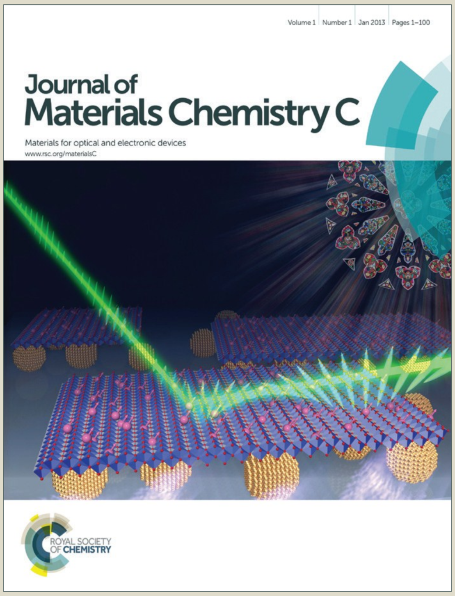

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ARTICLE

White light emitting soft materials from *off-the-shelf* ingredients

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Balanced white light emitting systems are important for applications in electronic devices. Of all types of white light emitting materials, gels have the special advantage of easy processability. Here we report two white light emitting gels, which are based on lanthanide cholate self assembly. The components are commercially available and the gels are prepared by simply sonicating their aqueous solutions (1-3 min), unlike any other known white light emitting systems. Their CIE co-ordinates, calculated from the luminescence data, fall in white light range with correlated color temperature of *ca.* 5600 K.

Introduction

Luminescent materials have attracted much attention for their various applications as light sources and color displays, such as in cell phones, computer and television display screens, fluorescent lamps etc.[1a] They are also widely used for sensing and bio-imaging.[1a-b] In particular, white light emitting luminescent materials have received considerable interest because of their wider application potentials.[1-3] A variety of white light emitting systems have been reported in the literature,[1-4] prepared by trichromatic (combination of three primary colors red, green and blue - RGB) or by dichromatic processes (by mixing two complementary colors, *e.g.*, yellow and turquoise). Many hybrid materials,[2] organic materials,[3] nanomaterials[1,4a,4b,2e] and inorganic salts[4c-e] have been reported to produce white light. Among these systems, supramolecular gels offer special advantages as they are viscoelastic soft solids with flexibility and easy processability, creating a wider scope for applications.[2d,3b,5f]

While a variety of chromophores and luminophores have been used to prepare white light emitting materials, lanthanide based systems are among the most frequently used ones. Lanthanides are known for their characteristic photoluminescence with sharp emission peaks. A wide range of colors can be generated by choosing different metals complexed with suitable ligands, *e.g.,* red (Eu^{3+}, Pr^{3+}, Sm^{3+}), green (Tb^{3+}, Er^{3+}) and blue (Tm^{3+}, Ce^{3+}, Dy^{3+} ions).[3b] They also have long lifetimes thereby allowing elimination of the short-lived background emission such as the autofluorescence from biological samples. Lanthanides are therefore becoming one of the most widely used materials in sensing, lighting and display,[2-5] especially in phosphor-based lighting systems. But due to their low molar extinction coefficients (of the forbidden f–f transitions), a sensitizer is required for an observable luminescence.[5a-b] With a suitable sensitizer (organic or inorganic), the luminescence of lanthanides can be greatly enhanced. Many studies on the sensitization of lanthanides and its applications have been conducted.[5]

Considering the flexibility and easy processability of a soft gel, we reasoned that it would be of great advantage if we could incorporate the lanthanides in supramolecular gels to prepare a white light emitting system. Moreover, most of the other reported lanthanide based white light emitting systems require tedious synthesis or/and high temperature methods, but our system can be prepared rapidly at room temperature. This report highlights our preliminary work on two such systems, and a comparison with a few chosen published systems (Table 1).

Table 1 Comparison of Lanthanide (Ln) based white light emitting systems.

Ln based white light emitting materials	# Steps	T (˚C)	Time taken
Eu^{3+} and Tb^{3+} co-doped In_2O_3 nanocrystals[1a]	2	110-330	>5 h
Coumarin, Rhodamine 6G and Eu^{3+} system [2c]	5	rt-90	>45 h
Eu^{3+}-doped Tb^{3+} MOF[2d]	1	150	>3 d
LnMOF[2e]	1	180	>4 d
Ir^{3+} and Eu^{3+} Complexes[2a]	8	rt	>6 h
This work, WEG1 and WEG2	1	rt	1-3 min

Experimental

The starting materials employed were Sodium cholate (≥99%), $Tb(OAc)_3$ (99.9 %), $Eu(OAc)_3$ (99.9%), $Zn(OAc)_2$ (99.99%), 2,3-dihydroxynaphthalene (99%) and pyrene (98%). All the chemicals were obtained from Sigma-Aldrich and were used without further purification except for 2,3-dihydroxynaphthalene (DHN) and pyrene which were used after recrystallization. The emission and excitation spectra were obtained using a Horiba Flurolog-3 fluorescence spectrometer. The CIE diagram and quantum yield were measured

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† Electronic Supplementary Information (ESI) available: [Job plot and binding constant determination of metal-DHN complexes are included in the supporting information.] See DOI: 10.1039/x0xx00000x

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using Edinburgh Instruments FLS980 fluorescence spectrometer equipped with an integrating sphere. Dynamic rheology was performed using TA instruments AR1000. SEM and TEM imaging were done in FEI Sirion XL30 FEG SEM and FEI Tecnai T20 S-TWIN TEM respectively. All photographic images were taken using Sony DSC-H70.

The gels (880 µL) were prepared in 10 x 75 mm test tubes by mixing the aq. metal salt solutions and adding aq. NaCh solution (premixed with appropriate quantities of DHN or pyrene), and sonicating in a cleaning bath thoroughly (1-3 min). The gels can form at concentrations as low as 0.3 mM Lanthanides and 0.9 mM NaCh,[6] but in this report the lanthanide and NaCh concentrations were kept roughly at 5/15 mM producing a mechanically strong gel, which was transparent enough for optical measurements.

Results and discussion

Calcium cholate gel was first reported in 1913 by Schryver, who termed it as a “clot”.[7] We, and others have recently reported metallocholate gels with several other metal ions.[8] We first discovered lanthanide cholate based luminescent hydrogels. The sensitization of Tb^{3+} by 2,3-dihydroxynapthalene (DHN) and Eu^{3+} by pyrene in the respective cholate gels were reported from our group.[9] The DHN doped Tb^{3+} cholate gel showed green luminescence (Fig. 1a & 2a) while pyrene doped Eu^{3+} cholate gel showed a magenta color (mixture of blue from pyrene and red from Eu^{3+}, Fig. 1b).

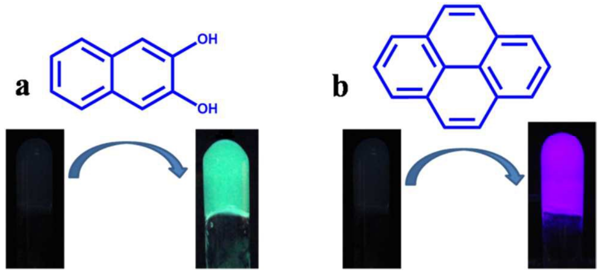

Fig. 1 (a) Sensitization of Tb^{3+} by DHN in $TbCh_3$ gel; (b) Sensitization of Eu^{3+} by pyrene in $EuCh_3$ gel.

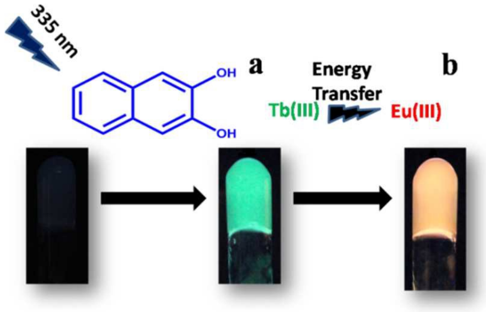

Fig. 2 (a) Sensitization of Tb^{3+} by DHN and (b) energy transfer to Eu^{3+} in cholate gel.

Furthermore, Tb^{3+} to Eu^{3+} energy transfer occurred when the Tb^{3+} cholate gel was doped with Eu^{3+}, enabling tuning of the gel luminescence from green to yellow to pink to red, depending on the Tb^{3+}/Eu^{3+} ratio.[10]

Thus our initial work resulted in two systems, each with two primary colors. Blue and red colors are present in system 1 (Fig 1b) while system 2 (Fig 2b) has green and red colors. It was therefore reasonable to think that the addition of an appropriate amount of green color to system 1, and blue to system 2 would lead to white light.

We hypothesized that the addition of Tb^{3+} (with its sensitizer DHN) to system 1 should in principle generate the three sets of primary colors, which in the correct proportion should lead to a white light emitting gel. We showed earlier that at 40:1 Tb^{3+}:Eu^{3+} ratio, emission from the gel was in the yellow region.[10] We optimized the final concentrations of the components by adjusting this ratio. The added pyrene increased red emission from Eu^{3+} and the gel looked reddish, so the Eu^{3+} concentration was lowered and to balance this with green emission from Tb^{3+}, DHN concentration was increased**.** The final optimized concentrations of the various components to obtain white light emitting gel WEG1 (Fig. 3) was: Tb^{3+} 4.55 mM, Eu^{3+} 28 µM, DHN 400 µM, pyrene 0.18 µM and NaCh 15.4 mM.

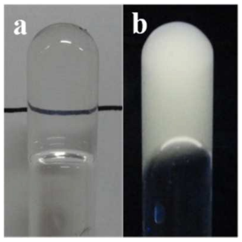

Fig. 3 White light emitting gel WEG1 (a) in ambient light and (b) under long wave UV lamp.

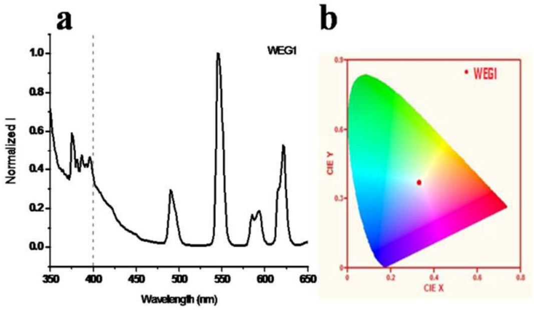

Fig. 4 (a) Normalized luminescence spectra (λ_{ex}=335 nm) (b) CIE (1931) co-ordinate diagram of WEG1.

The luminescence spectra of WEG1 (Fig 4a) showed characteristic peaks of pyrene (370-420 nm) which are responsible for the blue part of the spectra. Distinctive peaks of Tb^{3+} (498, 545, 584 and 621 nm) and Eu^{3+} (592 and 615 nm) furnished the green and red components, respectively. Combining these three primary colors, the resulting white light emitting system WEG1 had a CIE co-ordinate of 0.33, 0.37 (Fig. 4b), which falls in the white color range. The correlated color temperature (CCT) was calculated using McCamy’s formula[11] to be 5669K which falls in the daylight or electronic flashlight range, and can in principle be used for lighting applications.

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In system 2, the Tb^{3+}:Eu^{3+} ratio was kept at around 40:1, which led to yellow emission. Although DHN has an intrinsic blue emission, it was used in limited amounts and all of it got complexed to Tb^{3+} and Eu^{3+} thereby losing most of the blue fluorescence (due to its energy transfer to Tb^{3+}). We reasoned that the easiest way to add a blue component in this system would be to add a non-luminescent metal ion that complexes DHN, giving a blue component while retaining the sensitization of Tb^{3+}. Metal ions such as Cu^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+} and In^{3+} quenched Tb^{3+} and Eu^{3+} luminescence. However, we found that Zn^{2+} and Al^{3+} served the purpose quite well. Both complexed with DHN to give blue luminescence while retaining the sensitization of Tb^{3+} and its subsequent energy transfer to Eu^{3+}. In the presence of Al^{3+}, however, no gel was formed, and no further studies were done with it. Zn^{2+} itself formed a gel with NaCh (Fig. 5a), and in the presence of DHN it showed blue emission (Fig 5b). In the presence of Tb^{3+} and Eu^{3+}, the Zn-DHN complex retained the blue emission (Fig. 6). A detailed study of the binding of DHN to Tb^{3+}, Eu^{3+} and Zn^{2+} was carried out. Job's plot from the absorption data showed that all the metal ions formed 1:1 complex with DHN under these conditions (see SI). Binding constants (Table 2) determined from emission data[12] suggested that at comparable concentrations of the three metal ions, DHN will be distributed among the three.

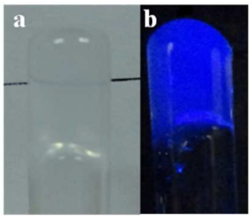

Fig. 5 $ZnCh_2$ gel (doped with DHN) (a) in ambient light (b) under long wave UV lamp.

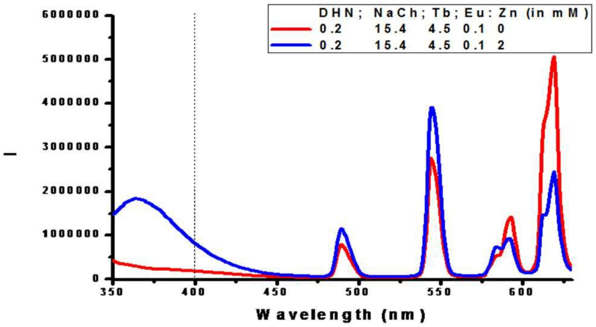

Fig. 6 Effect of Zn^{2+} on the spectra of Tb^{3+} and Eu^{3+} cholate gel (DHN- doped), (λ_{ex}=335 nm).

Table 2 logK values of metal DHN complexes at 25 °C

Complex	logK
Eu(III)DHN	6.8 (±0.2)
Tb(III)DHN	6.5 (±0.2)
Zn(II)DHN	7.1 (±0.2)

Therefore we presumed that a DHN-containing cholate gel with Zn^{2+}, Tb^{3+} and Eu^{3+} in appropriate quantities should produce white emission. Since the binding constant of Tb^{3+}/Eu^{3+}-DHN complex is comparable to the Zn-DHN complex, we needed comparable amounts of Zn^{2+} to shift the equilibrium appropriately to balance the overall emission. Thus the concentrations of the components were optimized to lead to a white light emitting gel, WEG2, as shown in Fig. 7, was with Tb^{3+} 4.55 mM, Eu^{3+} 110 µM, Zn^{2+} 2.84 mM, DHN-200 µM and NaCh 15.4 mM.

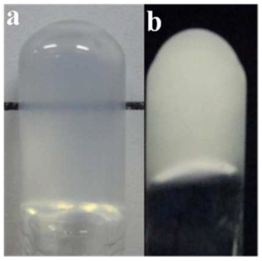

Fig. 7 White light emitting gel WEG2 (a) in ambient light and (b) under long wave UV lamp

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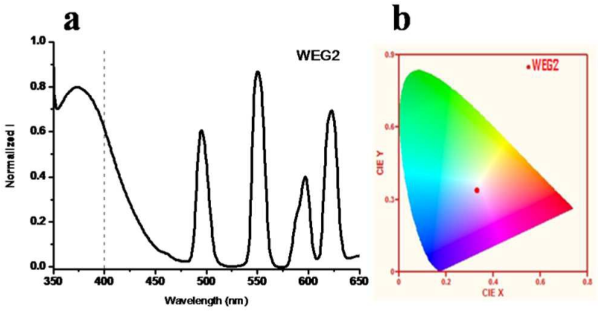
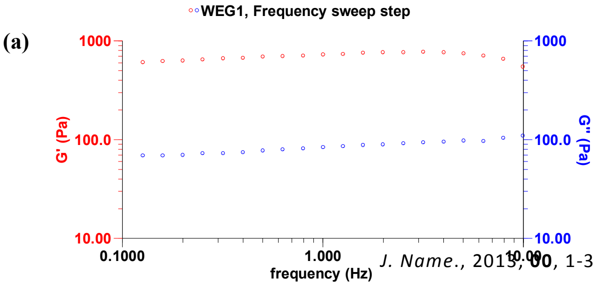


Fig. 8 (a) Normalized luminescence spectra (λ_{ex}=335 nm) (b) CIE (1931) co-ordinate diagram of WEG2.

The luminescence spectra of WEG2 (Fig. 8a) showed a broad peak from 360-450 nm that provided the blue component, coming from the Zn-DHN complex. Characteristic peaks of Tb^{3+} and Eu^{3+} that provide the green and red color were observed as in WEG1 and the CIE co-ordinates of (0.33, 0.34) were estimated (Fig. 8b). The CCT calculated as before was found to be 5609K which also falls in the daylight or electronic flashlight range (as in WEG1).

Quantum yields of the WEG1 and WEG2 gels were measured (using an integrating sphere in Edinburgh Instruments FLS980 system) to be 6% and 7%, respectively, which are better than the values reported for most lanthanide doped hybrid materials,[13] and trivalent lanthanide complexes in solution.[2c]

Mechanical strengths of WEG1 and WEG2 were investigated using dynamic rheology (Fig 9-10). Frequency sweep at constant stress of 1 Pa and stress sweep at frequency of 1 Hz were performed at 25°C (±0.1). The data are provided in Table 3.



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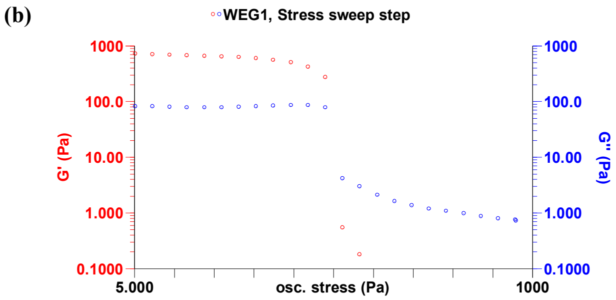

Fig. 9 (a) Frequency sweep and (b) stress sweep of WEG1

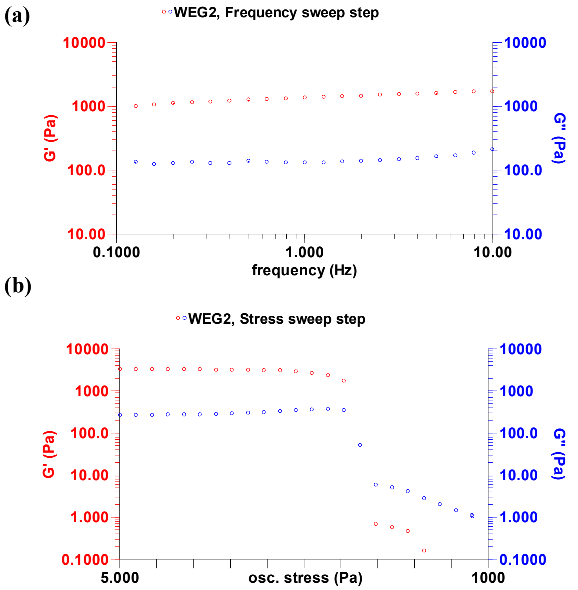

Fig. 10 (a) Frequency sweep and (b) stress sweep of WEG1

Table 3 Rheology data of WEG1 and WEG2

Gels	G'(Pa)	G"(Pa)	G'/G"	σ* (Pa)
WEG1	720	80	9	60
WEG2	1350	125	11	130

The higher storage modulus (G') and yield stress (σ*) values showed that WEG2 was mechanically stronger than WEG1. The stiffness value (G'/G") confirmed the viscoelstic nature of the material.

The morphology of the gels was probed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM (Fig. 11) and TEM (Fig. 12) images showed that both the gels have fine fibrous network of 20-35 nm diameter.

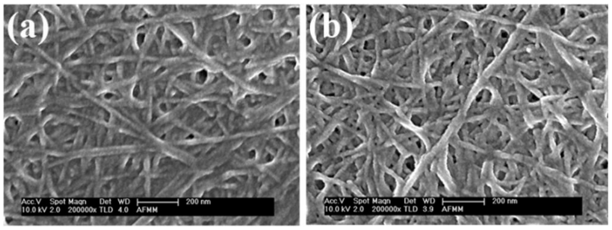

Fig. 11 SEM images (scale bar 200 nm) of (a) WEG1 (b) WEG2.

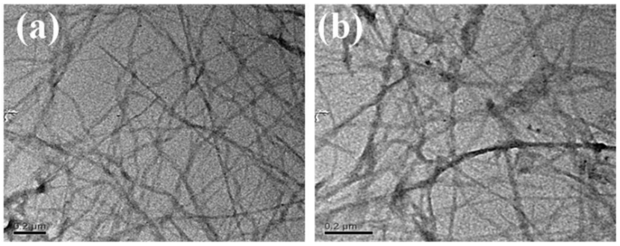

Fig. 12 TEM images (scale bar 200 nm) of (a) WEG1 (b) WEG2.

Conclusions

In conclusion, we believe this work demonstrates a remarkably simple approach for the development of two white light emitting gels by the combination of a number of commercially available materials. The quantum yields measured are higher than those measured for lanthanide derived white light emitting systems. We hope that further development along these lines will lead to systems with practical applications.

Acknowledgements

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Notes and references

1 (a) S. Ghosh, K. Das, G. Sinha, J. Lahtinen and S.K. De, *J. Mater. Chem. C*, 2013, **1**, 5557; (b) S. Mizukami, T. Yamamoto, A. Yoshimura, S. Watanabe and K. Kikuchi, *Angew. Chem. Int. Ed.*, 2011, **50**, 8750.

2 (a) P. Coppo, M. Duati, V.N. Kozhevnikov, J.W. Hofstraat and L.D. Cola, *Angew. Chem. Int. Ed.*, 2005, **44**, 1806; (b) D. Liu, Z. Zhang, H. Zhang and Y. Wang, *Chem. Commun.*, 2013, **49**, 10001; (c) G. He, D. Guo, C. He, X. Zhang, X. Zhao and C. Duan, *Angew. Chem. Int. Ed.*, 2009, **48**, 6132; (d) Z.F. Liu, M.F. Wu, S.H. Wang, F.K. Zheng, G.E. Wang, J. Chen, Y. Xiao, A.Q. Wu, G.C. Guo and J.S. Huang, *J. Mater. Chem. C*, 2013, **1**, 4634; (e) Y. Wei, Q. Li, R. Sa and K. Wu, *Chem. Commun.*, 2014,**50**, 1820; (f) D.K. Maiti and A. Banerjee, *Chem. Commun.*, 2013, **49**, 6909; (g)

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X. Cao, Y. Wu, K. Liu, X. Yu, B. Wu, H. Wu, Z. Gong and T. Yi, *J. Mater. Chem.*, 2012, **22**, 2650; (h) H. Zhang, X. Shan, L. Zhou, P. Lin, R. Li,E. Ma, X. Guoab and S. Du, *J. Mater. Chem. C*, 2013, **1**, 888; (i) D. Ma, X. Li and R. Huo, *J. Mater. Chem. C*, 2014, **2**, 9073.

3 (a) K.V. Rao, K.K.R. Datta, M. Eswaramoorthy and S.J. George, *Adv. Mater.*, 2013, **25**, 1713; (b) C. Vijayakumar, V.K. Praveen and A. Ajayaghosh, *Adv. Mater.*, 2009, **21,** 2059-2063; (c) Y. Zeng, Z. Li, Y. Liang, X. Gan and M. Zheng, *Inorg. Chem.*, 2013, **52**, 9590.

4 (a) Z. Xu, Q. Liao, X. Shi, H. Li, H. Zhang and H. Fu, *J. Mater. Chem. B*, 2013, **1**, 6035; (b) D. Wen and J. Shi, *Dalton Trans.*, 2013, **42**, 16621; (c) J. Brgoch, C.K.H. Borg, K.A. Denault, A. Mikhailovsky, S.P. DenBaars and R. Seshadri, *Inorg. Chem.*, 2013, **52,** 8010; (d) X. Zhang, Z. Zhao, X. Zhang, A. Marathe, D.B. Cordes, B. Weeksc and J. Chaudhuri, *J. Mater. Chem. C*, 2013, **1**, 7202; (e) D. Wen, J. Feng, J. Li, J. Shi, M. Wu and Q. Su, *J. Mater. Chem. C*, 2015, **3**, 2107.

5 (a) J.C.G. Bünzli and C. Piguet, *Chem. Soc. Rev.*, 2010, **39**, 189; (b) J.C.G. Bünzli, *Acc. Chem. Res.*, 2006, **39**, 53; (c) K. Hanaoka, K. Kikuchi, H. Kojima, Y. Urano and T. Nagano, *J. Am. Chem. Soc.*, 2004, **126**, 12470; (d) K. Hanaoka, K. Kikuchi, H. Kojima, Y. Urano and T. Nagano, *Angew. Chem., Int. Ed.*, 2003, **42**, 2996; (e) S. Mizukami, K. Tonai, M. Kaneko and K. Kikuchi, *J. Am. Chem. Soc.*, 2008, **130**, 14376; (f) V.K. Praveen, C. Ranjith and N. Armaroli, *Angew. Chem. Int. Ed.*, 2014, **53**, 365.

6 Y. Qiao, Y. Lin, S. Zhang, and J. Huang, *Chem. Eur. J.*, 2011, **17**, 5180.

7 S.B. Schryver, *Proc. R. Soc. Lond. B*,1913, **86**, 459.

8 (a) A. Chakrabarty, U. Maitra and A.D. Das, *J. Mater. Chem.*, 2012, **22**, 18268; (b) J.S. Shen, Y.L. Chen, J.L. Huang, J.D. Chen, C. Zhao, Y.Q. Zheng, T. Yu, Y. Yang and H.W. Zhang, *Soft Matter*, 2013, **9**, 2017; (c) Y. Qiao, Y. Lin, Y. Wang, Z. Yang, J. Liu, J. Zhou, Y. Yan and J. Huang, *Nano Lett.,* 2009, **9**, 4500.

9 (a) S. Bhowmik and U. Maitra, *Chem. Commun.*, 2012, **48**, 4624; (b) S. Bhowmik, S. Banerjee and U. Maitra, *Chem. Commun.*, 2010, **46**, 8642.

10 S. Banerjee, R. Kandanelli, S. Bhowmik and U. Maitra, *Soft Matter,* 2011, **7**, 8207.

11 C.S. McCamy*, Color Res. Appl.,* 1992*,* **17***,* 142.

12 C. Xu, C. Zhao, J. Ren and X. Qu, *Chem. Commun.*, 2011, **47**, 8043.

13 Y. Hasegawa, K. Sogabe, Y. Wada and S. Yanagida, *J. Lumin.*, 2003, **101**, 235

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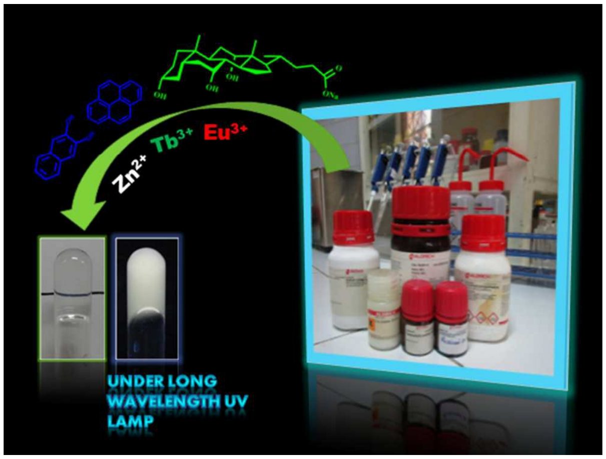

Text: Two white light emitting hydrogels were prepared by a careful combination of components which are all commercially available.

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