Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron Letters 45 (2004) 8403–8407
Tetrahedron Letters

Towards the development of Eu(III) luminescent switching/sensing in water-permeable hydrogels

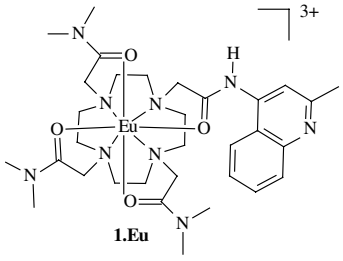
Thorfinnur Gunnlaugsson,[a,*] Colin P. McCoy[b,*] and Floriana Stomeo[a]

[a]*Department of Chemistry, Centre for Synthesis and Chemical Biology, Trinity College Dublin, Dublin 2, Ireland*
[b]*School of Pharmacy, The Queen's University of Belfast, 97 Lisburn Road, Belfast BT9 7BL, UK*

Received 1 July 2004; revised 26 August 2004; accepted 3 September 2004
Available online 25 September 2004

Abstract—The synthesis of the Eu(III) complex **1.Eu** and photophysical studies of this complex in solution are described. In water, the Eu(III) luminescence was 'switched on' in the presence of H^+, with large enhancements in the Eu(III) luminescence. The complex was then incorporated into poly[methylmethacrylate-*co*-2-(hydroxyethylmethacrylate)]-based hydrogels and the luminescent properties of the resulting polymeric films were investigated using confocal laser-scanning microscopy as well as using steady-state luminescence. The luminescence was shown to be 'switched on' in the soft material after adjusting the pH of the solution in which the **1.Eu**-incorporated film was immersed from alkaline to acid.

The development of luminescent devices is an active area of research. A large number of examples of luminescent switches, sensors and logic gates have been reported over the last few years.[1,2] These examples are usually studied in solution where the change in the luminescent properties of the device is caused by the use of external 'inputs' such as ions or molecules,[3] though several excellent examples exist of 'fully' optically-based devices, where both the 'input' and the 'output' are optical.[4] Examples of the former include chemosensors, where the recognition or sensing of a particular analyte causes the modulation of one or more of the physical properties of the sensors.[5] For practical purposes the incorporation of such a chemosensor into materials is highly desirable, giving it a platform for continuous flow analysis, as well as of on-line monitoring of essential electrolytes in critical care analysis.[6] We are interested in the development of such chemosensors for ions and molecules,[7,8] and recently we have incorporated several fluorescent 1,8-naphthalimide derivatives into poly[methylmethacrylate-*co*-2-(hydroxyethylmethacrylate)]-based hydrogels with the aim of developing novel luminescent devices.[9] Even though this approach was successful, the drawback to the use of such fluorescent materials is the short excited state lifetimes that can easily coincide with that of any biological background emission, that is autofluorescence. One way to overcome this is by employing long-lived and long wavelength emitting probes. For such purposes the use of lanthanide luminescence[10,11] is particularly attractive as the ions emit at long wavelengths and have relatively long-lived excited states (in the μs–ms time frame). However, the main drawback in the use of these emitting moieties is the difficulty of producing their excited state by direct excitation. This can be overcome by population of their excited state via sensitization from an appropriately energy-matched antenna.[10–12] This opens up the avenue of developing combined antenna–receptor moieties where the sensitization process can be modulated by a recognition event at the receptor part.[10,11] We, and others, have demonstrated such delayed luminescent switching and sensing in aqueous solutions, using synthetic lanthanide-based conjugates and self-assembly processes.[10–12] However, to the best of our knowledge, the incorporation of such 'switchable' lanthanide luminescent devices into



1.Eu

* Corresponding authors. Tel.: +353 1 608 2345; fax: +353 1 671 2826; e-mail: gunnlaut@tcd.ie

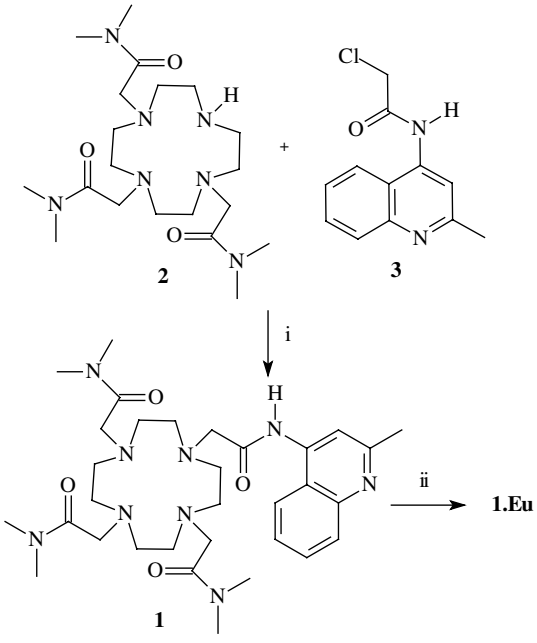
0040-4039/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2004.09.042

water-permeable hydrogels has not been achieved.[13] Here we describe the development of a lanthanide luminescent pH sensor **1.Eu** which shows reversible luminescence 'off–on' switching as a function of pH and the preliminary results of the noncovalent incorporation of this sensor into water-permeable hydrogels,[14] and the luminescent properties within the gel.

The design of **1.Eu** is based on the use of the tetraaza macrocycle cyclen (1,4,7,10-tetraazacyclododecane), which upon incorporation of four pendant arms such as carboxylates or carboxylic amides can form kinetically and thermodynamically stable complexes with lanthanide ions. It is also possible to functionalize selectively one (or more) of these pendant arms to allow for the incorporation of antenna moieties. We have used this metal coordination core for the incorporation of various antennae using combined antenna–receptor moieties. To demonstrate the feasibility of the incorporation of such a luminescent lanthanide complex into the hydrogels, we chose to use quinaldine chromophores, where the nitrogen moiety acts as a proton acceptor.[15] However, this is the first time that such a combined antenna–receptor is incorporated into a monofunctionalized cationic tetraamide Eu(III) complex, that is, only one antenna is incorporated.

The synthesis of **1.Eu** is shown in Scheme 1, and involves the reaction of the 2-(4,10-bis-dimethyl-carbamoylmethyl-1,4,7,10-tetraaza-cyclododec-1-yl)-*N*,*N*-dimethylacetamide **2**[16] with chloro-*N*-(2-methyl-4-quinolyl)ethanamide (**3**)[15] in DMF at 85 °C in the presence of Cs_2CO_3 and KI for 3 days. The ligand **1** was purified by precipitation from dry diethyl ether, giving **1** in 53% yield.[17] The two starting materials **2** and **3** have recently been reported by us.[15,16] The former was made in a single step by reacting the α-chloroamide of *N*,*N*-dimethyl-acetamide with cyclen in dry CH_3CN (in a 3:1 molar ratio of acetamide–cyclen) at 65 °C for 72 h in the presence of $NaHCO_3$. The product was then purified by column chromatography on alumina (gradient elution from CH_2Cl_2 to 60% NH_3 saturated MeOH/CH_2Cl_2 solution). The Eu(III) complex of **1** was made by refluxing together equivalent amounts of **1** and $Eu(CF_3SO_3)_3$ in dry CH_3CN under an inert atmosphere for 24 h. Upon cooling to room temperature the solution was poured into a stirring solution of dry diethyl ether, which resulted in a pale green solid in 84% yield.[18] The ^1H NMR of **1.Eu** in acetone-d_6 showed the characteristic europium shifted axial and equatorial cyclen protons, showing that the complex had been formed, and had adopted a square prismatic geometry in solution.[10] The ESMS of **1.Eu** also showed that complexation had occurred as a Eu(III) isotope pattern was observed for the complex as demonstrated for $(M + [triflate]/2)^+$ in Figure 1. By evaluating the lifetime of the Eu(III) excited state in both D_2O and H_2O, the complex was found to have one metal-bound water molecule.[10]

The **1.Eu** complex was finally incorporated into hydrogel matrices comprised of poly[methylmethacrylate-*co*-2-(hydroxyethylmethacrylate)] in a noncovalent manner,[9] using methylmethacrylate (MMA) and 2-(hydroxyethylmethacrylate) (HEMA) in three different ratios: 1:1 (MMA–HEMA, w/w), 1:3 (MMA–HEMA, w/w) and 100% HEMA. In all cases, ethylene glycol dimethacrylate was used as crosslinker and benzoyl peroxide as a radical initiator (both as 1% w/w of the total polymer). As **1.Eu** is cationic and hydrophilic, we chose to use a more water-permeable hydrogel matrix, by using higher percentages of HEMA, in comparison to our naphthalimide work.[9] The increased permeability to water was expected to decrease the time required for equilibration in response to pH changes. In order to achieve a homogeneous dispersion of **1.Eu** in the hydrogel, the complex (0.05% w/w) was dissolved in the appropriate monomer mixture prior to polymerization. After formation of the polymeric films, these were stored in neutral aqueous



Scheme 1. Synthesis of **1** and the Eu(III) complex **1.Eu**. Reagents and conditions: (i) DMF, 85 °C, Cs_2CO_3, KI, 3 days; (ii) $Eu(CF_3SO_3)_3$, dry CH_3CN, reflux.

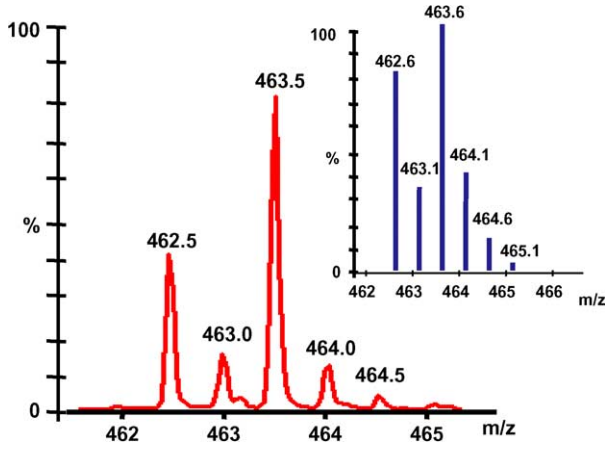


Figure 1. The electrospray mass spectrum of **1.Eu**, showing the isotopic distribution for $m/z = (M + [triflate]/2)^+$. Insert is the calculated isotopic distribution pattern for the same.

solution. Due to the different permeability grades of the films, a certain amount of **1.Eu** was found in the water where the hydrogel films were soaked over long-time storage (a period of days). Further investigations are required to determine the exact amount of the **1.Eu** released into solution as well as the kinetics of this process as a function of the hydrogel composition, but we do not believe that this is a major effect in the current study.

The photophysical properties of **1.Eu** were investigated both in water solution and in the above hydrogels. The changes in the absorption spectrum of the complex in water and in the presence of tetramethylammonium chloride (0.1 M, to maintain a constant ionic strength), as a function of pH are shown in Figure 2. In alkaline solution the complex has a broad absorption band due to the $\pi \rightarrow \pi^*$ transition which occurred at 300 nm. Upon acidification there was a significant shift to 319 nm, with a new band appearing at 261 nm, and with isosbestic points at 295 and 270 nm, respectively. In contrast to these results, the fluorescence emission spectra of **1.Eu** when excited at 330 nm gave rise to spectral changes that mirror those seen in the absorption spectrum, hence upon acidification (from alkaline solution) there was a distinctive shift in the emission spectra from 375 to 357 nm, and a subsequent enhancement of the emission intensity (from 350 to 700 a.u.). As stated above the efficiency of the population of the Eu(III) excited state is dependent on the ability of the antenna to sensitize the $^5D_0$ excited state. This will subsequently be seen in the intensity of the lanthanide luminescence that is due to the deactivation of the excited state to ^7F_J ($J = 1$, 2, 3 and 4) ground states. Hence, we chose 330 nm, where the difference between the absorption in alkaline versus acid solution is the greatest (cf. Fig. 2). Hence at this wavelength the efficiency of the sensitization of the $^5D_0$ excited state would be significantly pH dependent. The changes in the Eu(III) emission in solution as a function of pH are shown in Figure 3. Here the Eu(III) emission is clearly 'switched on' with large enhancements in the 580, 593, 615, 624, 654, 683 and 701 nm bands, respectively, representing the deactivation of the $^5D_0 \rightarrow {}^7F_J$ ($J = 0$, 1, 2, 3 and 4). Moreover, the luminescence switching was fully reversible, since addition of strong base (pH $\sim$ 10) quenched the emission, which could be subsequently 'switched on' again

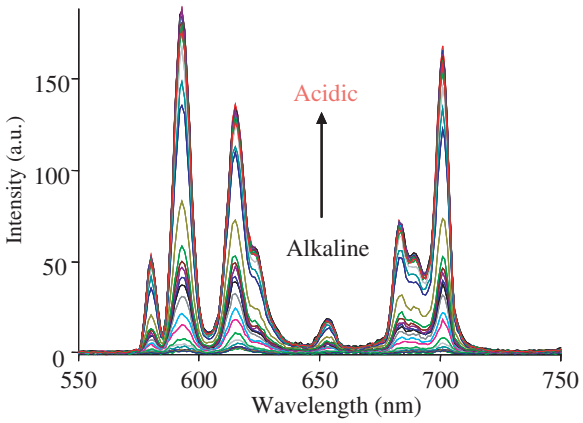


Figure 3. The changes in the Eu(III) emission of **1.Eu** in water as a function of pH.

by the addition of acid (pH = 1.6). By plotting the changes of any of these wavelengths as a function of pH (Fig. 4) it is clear that the emission changes almost linearly from ca. pH 3 to 8. These changes are mostly due to the protonation of the quinoline nitrogen moiety (between ca. 2.5 and 5) whereas the changes between ca. 6 and 8 are due to deprotonation of the quinoline carboxylic amide moiety, and mirror those seen in the fluorescence emission titration.[15a]

Having established the solution behaviour of **1.Eu** we analyzed the luminescent properties of the three lanthanide complex-incorporated hydrogel films. These were tested, in order of increasing hydrophilicity: 1:1 MMA/HEMA, 1:3 MMA/HEMA and 100% HEMA. For all films the Eu(III) emission was affected by going from alkaline to acidic media. This was achieved by soaking strips of the films in acidic or basic solutions for 1 h. The most hydrophilic (100% HEMA) and the most hydrophobic (1:1 MMA/HEMA) films showed an appreciable difference in the Eu(III) emission intensity, mirroring the behaviour in aqueous solution, where the emission was 'switched on' in acid (Fig. 5). It is worth remarking that the spectral fine structure obtained in solution is not so apparent in spectra recorded from films. We also recorded the changes in the Eu(III) emission after 24 h. The results for the 1:3,

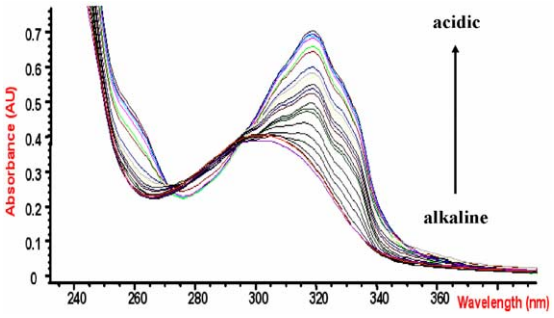


Figure 2. The changes in the absorption spectrum of **1.Eu** as a function of pH in water.

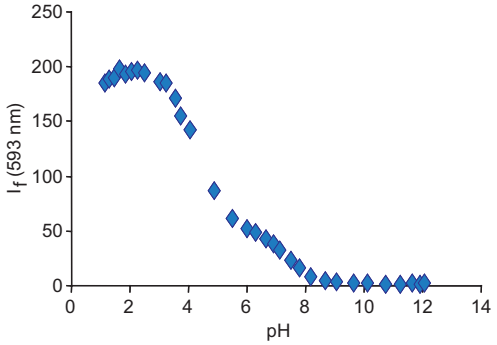


Figure 4. Changes in the Eu(III) emission at 593 nm as a function of pH.

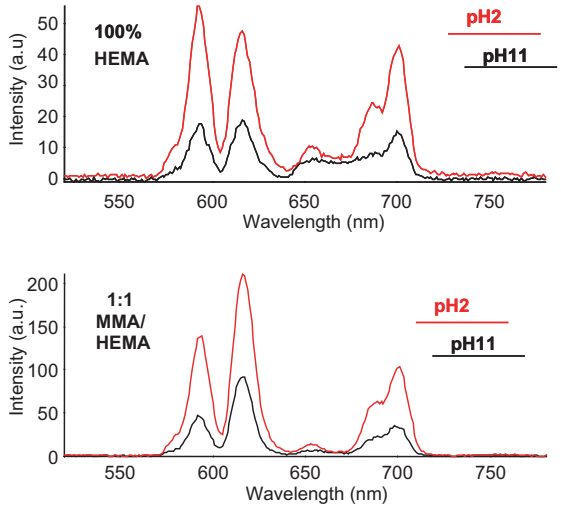


Figure 5. The change in the Eu(III) emission of the (top) 100% HEMA and 1:1 MMA/HEMA gels after 1 h soaking in either pH 2 or 11 solutions.

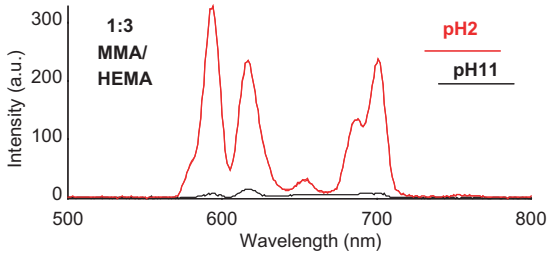


Figure 6. Luminescence emission spectra of **1.Eu** incorporated into MMA/HEMA (1:3) after soaking for 24 h.

MMA/HEMA hydrogel are shown in Figure 6. Here the Eu(III) emission has been fully 'switched off'. These results demonstrate that such 'off–on' pH dependent switching is possible both in solution and in the hydrogels. However, after such prolonged soaking some leaching had occurred as the solution gave rise to Eu(III) emission, indicating that the complex had diffused from the film. However, we did not quantify the degree of this leaching and it was not observed for the other films.

Luminescent measurements were also performed using confocal laser-scanning microscopy (CLSM) on **1.Eu** incorporated into the MMA/HEMA (1:3) hydrogel. Reflectance images showed that the complex was not homogeneously spread throughout the hydrogel. However, it was possible to observe the difference in emission between the films after soaking in acidic and basic solution for 24 h. As can be seen from the two images in Figure 7, the hydrogel incorporating 0.05% w/w of **1.Eu** at pH 2 shows the typical red emission of Eu(III), whereas at pH 11 the red emission is almost entirely quenched.

In conclusion, we have demonstrated that a cationic Eu(III)-based pH sensor can be incorporated into a soft material such as hydrogels. To the best of our knowledge this is the first time that such lanthanide based sensors have been incorporated into these types of

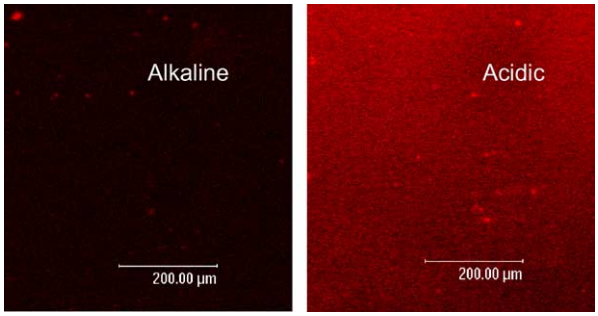


Figure 7. CLSM image of a section of hydrogel (MMA/HEMA, 1:3) incorporating 0.05% w/w **1.Eu** in acidic and basic media.

hydrogels. As **1.Eu** was not covalently bonded to any of the monomers used, there is a significant danger of leaching, where the water-soluble complex can diffuse from the gel into the environment, particularly upon prolonged storage. We are currently working towards overcoming this problem as well as working towards improving the 'switching' time between the 'off' and the 'on' stages, which are dependent on the diffusion rate of the analytes within the gel.

Acknowledgements

We thank Trinity College Dublin and the Queen's University Belfast, Center for Synthesis and Chemical Biology, Kinerton Ltd and The Royal Society (for a University Research Fellowship to McCoy) for financial support and Dr. John E. O'Brien for assisting with NMR and Dr. Ryan J. Morrow with the formation of hydrogels. We particularly thank Dr. Joseph P. Leonard for his continuous help.

References and notes

1. Rurack, K.; Resch-Genger, U. *Chem. Soc. Rev.* **2002**, *31*, 116; Rurack, K. *Spectrochem. Acta A* **2001**, *57*, 2161; Lavigne, J. J.; Anslyn, E. V. *Angew. Chem., Int. Ed.* **2001**, *40*, 3119; Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486; Fabbrizzi, L.; Licchelli, M.; Rabaioli, G.; Taglietti, A. F. *Coord. Chem. Rev.* **2000**, *205*, 85; Czarnik, A. W. *Acc. Chem. Res.* **1994**, *27*, 302.
2. Balzani, V. *Photochem. Photobiol. Sci.* **2003**, *2*, 459; Balzani, V.; Credi, A.; Venturi, M. *Pure Appl. Chem.* **2003**, *75*, 541; Brown, G. J.; de Silva, A. P.; Pagliari, S. *Chem. Commun.* **2002**, 2461; Ballardini, R.; Balzani, V.; Credi, A.; Gandolf, M. T.; Venturi, M. *Acc. Chem. Res.* **2001**, *36*, 445.
3. de Silva, A. P.; McCaughan, B.; McKinney, B. O. F.; Querol, M. *Dalton Trans.* **2003**, 1902; Raymo, F. M.; Giordani, S. *J. Am. Chem. Soc.* **2002**, *124*, 2004; Gunnlaugsson, T.; MacDónaill, D. A.; Parker, D. *Chem. Commun.* **2000**, 93.
4. Raymo, F. M. *Adv. Mater.* **2002**, *14*, 401.
5. Martínez-Máñez, R.; Sancenón, F. *Chem. Rev.* **2003**, *103*, 4419; Gale, P. A. *Coord. Chem. Rev.* **2000**, *199*, 181–233; Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486; Beer, P. D. *Chem. Commun.* **1996**, 689; de Silva, A. P.; Fox, D. B.; Huxley, A. J.; Moody, T. S. *Coord. Chem.*

Rev. **2000**, *205*, 41; de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515.
6. He, H.; Mortellaro, M. A.; Leiner, M. J. P.; Young, S. T.; Fraatz, R. J.; Tusa, J. K. *Anal. Chem.* **2003**, *75*, 549.
7. Gunnlaugsson, T.; Lee, T. C.; Parkesh, R. *Org. Biomol. Chem.* **2003**, *1*, 3265; Gunnlaugsson, T.; Kruger, P. E.; Lee, T. C.; Parkesh, R.; Pfeffer, F. M.; Hussey, M. G. *Tetrahedron Lett.* **2003**, *44*, 6575; Gunnlaugsson, T.; Nieuwenhuyzen, M.; Richard, L.; Thoss, V. *J. Chem. Soc., Perkin Trans. 2* **2002**, 141; Gunnlaugsson, T.; Davis, A. P.; Glynn, M. *Org. Lett.* **2002**, *4*, 2449; Gunnlaugsson, T.; Bichell, B.; Nolan, C. *Tetrahedron Lett.* **2002**, *43*, 4989; Gunnlaugsson, T.; Davis, A. P.; Glynn, M. *Chem. Commun.* **2001**, 2556.
8. Gunnlaugsson, T.; Kruger, P. E.; Jensen, P.; Pfeffer, F. M.; Hussey, M. G. *Tetrahedron Lett.* **2003**, *44*, 8909; Gunnlaugsson, T.; Kelly, J. M.; Nieuwenhuyzen, M.; O'Brien, A. M. K. *Tetrahedron Lett.* **2003**, *44*, 8571; Gunnlaugsson, T.; Leonard, J. P. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1980; Gunnlaugsson, T.; Nieuwenhuyzen, M.; Richard, L.; Thoss, V. *Tetrahedron Lett.* **2001**, *42*, 4725.
9. Gunnlaugsson, T.; McCoy, C. P.; Morrow, R. J.; Phelan, C.; Stomeo, F. *Arkivoc* **2003**, *8*, 216 http://www.arkat-usa.org/ark/journal/2003/McKervey/McKervey_index.htm.
10. Pope, S. J. A.; Faulkner, S. *J. Am. Chem. Soc.* **2003**, *125*, 10526; Shavaleev, N. M.; Moorcraft, L. P.; Pope, S. J. A.; Bell, Z. R.; Faulkner, S.; Ward, M. D. *Chem. Commun.* **2003**, 1134; Parker, D.; Dickins, R. S.; Puschmann, H.; Cossland, C.; Howard, J. A. K. *Chem. Rev.* **2002**, *102*, 1977; Parker, D. *Coord. Chem. Rev.* **2000**, *205*, 109; Parker, D.; Williams, J. A. G. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1305.
11. Gunnlaugsson, T.; Leonard, J. P. *Chem. Commun.* **2003**, 2424; Gunnlaugsson, T.; Harte, A. J.; Leonard, J. P.; Nieuwenhuyzen, M. *Supramol. Chem.* **2003**, *15*, 505; Gunnlaugsson, T.; Harte, A. J.; Leonard, J. P.; Nieuwenhuyzen, M. *Chem. Commun.* **2002**, 2134.
12. Gunnlaugsson, T.; Harte, A. J.; Leonard, J. P.; Senechal, K. *Chem. Commun.* **2004**, 782; Gunnlaugsson, T.; Harte, A. J.; Leonard, J. P.; Senechal, K. *J. Am. Chem. Soc.* **2003**, *125*, 12062; Faulkner, S.; Burton-Pye, B. P.; Kahn, T.; Martin, L. R.; Wray, S. D.; Skabara, P. J. *Chem. Commun.* **2002**, 1668.
13. Parker and co-workers have recently incorporated luminescent sensors into sol gels: Blair, S.; Kataky, R.; Parker, D. *New J. Chem.* **2002**, *26*, 530; Blair, S.; Lowe, M. P.; Mathieu, C. E.; Parker, D.; Senanayake, P. K.; Kataky, R. *Inorg. Chem.* **2001**, *40*, 5860.
14. (a) There are a few reports on the use of lanthanide ions in polyelectrolyte hydrogels and in polymer gels: Smirnov, V. A.; Sudhadolski, G. A.; Philippova, O. E.; Khokhlov, A. R. *J. Phys. Chem. B.* **1999**, *103*, 7621; Smirnov, V. A.; Philippova, O. E.; Sudhadolski, G. A.; Khokhlov, A. R. *Macromolecules* **1998**, *31*, 1162; (b) Other reports on the use of lanthanide ions in polymeric systems include: Liu, H. G.; Lee, Y. I.; Qin, W. P.; Jang, K. W.; Kim, S. S.; Feng, X. S. *J. Appl. Polym. Sci.* **2004**, *92*, 3524; Itaya, T.; Honda, T.; Kusumoto, N.; Matsumoto, A.; Inoue, K. *Polymer* **2003**, *44*, 2927; Beltran, J. B.; Cordoncillo, E.; Escribano, P.; Viana, B.; Sanchez, C. *J. Sol–Gel Sci. Technol.* **2003**, *26*, 977; Nishide, H.; Cho, M. D.; Kaku, T.; Okamoto, Y. *Macromolecules* **1993**, *26*, 2377; Yoshino, N.; Paoletti, S.; Kido, J.; Okamoto, Y. *Macromolecules* **1985**, *18*, 1513.
15. (a) Gunnlaugsson, T.; MacDónaill, D. A.; Parker, D. *J. Am. Chem. Soc.* **2001**, *123*, 12866; (b) Gunnlaugsson, T. *Tetrahedron Lett.* **2001**, *42*, 8901.
16. Gunnlaugsson, T.; Leonard, J. P.; Mulready, S.; Nieuwenhuyzen, M. *Tetrahedron* **2004**, *60*, 105.
17. *Synthesis of 2-{4,7-bis-dimethylcarbamoylmethyl-10-[(2-methyl-quinolin-4-ylcarbamoyl)-methyl]-1,4,7,10-tetraaza-cyclododeca-yl}-N,N-dimethyl-acetamide* (**1**). Compound **1** (0.272 g, 0.636 mmol), Cs_2CO_3 (0.228 g, 0.7 mmol), KI (0.116 g, 0.7 mmol) and **3** (0.164 g, 0.7 mmol) were added to DMF (35 mL). The mixture was heated at 80 °C under an inert atmosphere for 72 h. The solution was filtered and the solvent removed under reduced pressure. A dark orange viscous residue was obtained (0.359 g, 0.57 mmol) which was purified by precipitation from diethyl ether to give a brown solid in 53% yield. Calculated for $C_{32}H_{51}N_9O_4$: $(M + H)^+$ *m/z*: 626.4142. Found: 626.4163; δ_H (400 MHz, ($CDCl_3$) 10.5 (1H, s, N*H*), 8.75 (1H, d, *J* = 8.5, Ar-*H*), 7.93 (1H, s, Ar-*H*), 7.89 (1H, d, *J* = 8.5 Hz, Ar-*H*), 7.57 (1H, t, *J* = 6.0 Hz, Ar-*H*), 7.43 (1H, t, *J* = 6.0 Hz, Ar-*H*), 3.86 (2H, s, HNCOCH_2), 2.70 (43H, m, N–CH_3, CH_2CON(CH_3)$_2$, cyclen CH_2); δ_C (100 MHz, ($CDCl_3$)) 172.1, 170.4, 170.3, 158.3, 148.0, 141.8, 128.7, 127.7, 124.6, 123.4, 119.7, 112.6, 57.6, 54.5, 54.4, 35.7, 35.6, 35.0, 28.8, 26.5, 25.2; *m/z*: 626.33 $(M + H)^+$, 313.67 $(M + 2H/2)^+$.
18. *Synthesis of 2-{4,7-bis-dimethylcarbamoylmethyl-10-[(2-methyl-quinolin-4-ylcarbamoyl)-methyl]-1,4,7,10-tetraaza-cyclododeca-yl}-N,N-dimethyl-acetamide Eu(III)* (**1.Eu**). Compound **1** (0.095 g, 0.15 mmol) and Eu(III) trifluoromethane sulfonate (0.1 g, 0.16 mmol) were added to a 25 mL single neck round bottom flask that contained freshly dried MeCN (10 mL). After three freeze–pump–thaw cycles, the solution was placed under an argon atmosphere and left stirring at reflux for 24 h. The resulting solution was cooled to room temperature and then added dropwise to dry diethyl ether (100 mL) with stirring. The resulting precipitate was isolated to give **1.Eu** as a pale green solid in 84% yield. δ_H (400 MHz, CD_3OCD_3) 12.7, 10.4, 8.0, 6.9, 3.1, 2.2, 1.6, −5.5, −6.2, −7.0, −8.5; *m/z*: 463.5 $(M + [triflate]/2)^+$, 259.4 $(M/3)^+$, 388.6 $(M/2)^+$.