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Spontaneous Formation of Novel Luminescent Dinuclear Lanthanide Complexes That Emit in the Visible and Near-IR Regions

Claire Butler,[†] Sandrine Goetz,[†] Christopher M. Fitchett,[‡] Paul E. Kruger,[*,‡] and Thorfinnur Gunnlaugsson[*,†]

[†]School of Chemistry, Center for Synthesis and Chemical Biology, Trinity College Dublin, Dublin 2, Ireland

[‡]Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch 8041, New Zealand

S Supporting Information

ABSTRACT: The reaction of tetrasodium-4,4′,6,6′-tetracarboxy-2,2′-bipyridine (Na_4L) with various lanthanide ions yields a family of isostructural supramolecular $\{Na_2[Ln_2L_2]\}$ complexes (**1**−**4**), where Ln^{III} = Eu, Nd, Gd, and Tb. Strikingly, these complexes luminesce in buffered H_2O or D_2O solutions in either the visible or near-IR regions, despite their high hydration states.

There continues to be significant interest surrounding the synthesis and characterization of coordination polymers (CPs) because of their potential utility.[1] Porous CPs or metal−organic frameworks, in particular, attract much attention because the presence of void space within these materials may provide them with associated commercial applications in such areas as molecular separations, gas storage, and catalysis and as the active components in sensors.[2] Nevertheless, there still remains a need to develop novel CPs that possess unique function or added complexity.[3] The majority of CPs developed to date are based on the use of transition-metal ions. However, the use of lanthanide ions in the synthesis of CPs is also highly attractive because their high coordination requirements not only confer complex structural features to such assemblies but also provide unique magnetic, catalytic, and luminescent properties.[4] With this in mind, we set out to develop novel functional visible- and near-IR-emitting CPs formed by using f-directed synthesis. We have employed this approach successfully in the formation of luminescent lanthanide supramolecular systems[5] such as chiral molecular bundles and dinuclear triple helicates[6] and in the formation of functional Eu(III) luminescent gold nanoparticles.[7]

We recently reported the synthesis of the novel rigid tetradentate ligand 4,4′,6,6′-tetracarboxy-2,2′-bipyridine (H_4L) with the view of using it in the formation of lanthanide metal ion complexes and CPs.[8] This was, in part, inspired by the work of Bünzli, who employed the 6,6′-dicarboxy-2,2′-bipyridine analogue in the formation of highly luminescent lanthanide complexes,[9] but also with the knowledge that the oxophilic nature of the lanthanide ions renders H_4L ideal for coordination to them, and its rigid potentially chelating character lends some degree of predictability to the mode of coordination. We have shown that H_4L is capable of forming discrete eight-coordinate mononuclear complexes or CPs when coordinated to lanthanide ions with 2:1 or 1:1 ligand-to-metal stoichiometries, respectively.[8] However, the poor solubility of these species obviated any solution-based studies. We now extend our work here to include the self-assembly of aqueous *soluble* 2:2 Ln/L species and report the synthesis and structural and full photophysical characterization of $\{Na_2[Ln_2L_2]\}$ complexes [Ln = Eu (**1**), Nd (**2**), Gd (**3**), Tb (**4**)] by using Na_4L.

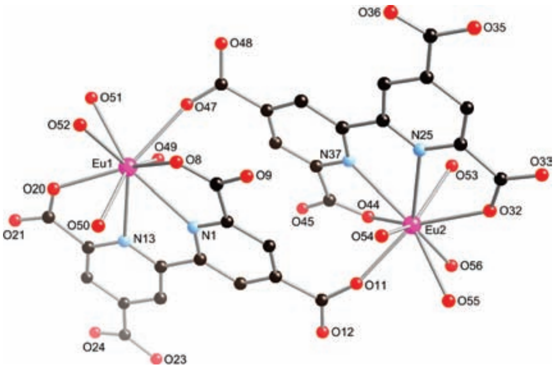

Figure 1. Molecular structure and atom numbering scheme for **1**. Bipyridyl and water molecule hydrogen atoms, lattice water molecules, and sodium counterions are omitted for clarity.

Compounds **1**−**4** were prepared by simply adding the appropriate lanthanide nitrate salt to Na_4L in water, followed by stirring at room temperature for 48 h, after which time they were allowed to slowly evaporate under ambient conditions to yield crystalline products that were isolated directly by filtration and obtained in 25−30% yield. Partial microanalytical data on **1**−**4** were consistent with 1:1 metal-to-ligand ratios, and their IR spectra are broadly similar, possibly attesting to a common structure and comparable coordination of the ligand about each metal center (see the Supporting Information). They showed the presence of carboxylate groups of L^{4-} with $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$ at ca. 1590 and 1360 cm^{-1}, respectively. Crystals of **1**−**3** were suitable for full single-crystal X-ray diffraction studies from which their structures were determined.[10] Because **1**−**3** were found to be isostructural, the structural discussion will be limited to **1** (see the Supporting Information).

The atom numbering scheme and atom connectivity for **1** are shown in Figure 1. The structure was refined in the triclinic $P\bar{1}$ space group, and all crystallographic data pertaining to **1**−**3** are brought together in Table S1 (Supporting Information). The structure of **1** consists of a dinuclear core with two unique Eu(III) metal centers, two L^{4-} ligands, and two sodium atoms that

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account for charge balance. Each Eu(III) metal center is nine-coordinate, and while being crystallographically unique, they have comparable coordination environments and so may be discussed together, with pertinent differences being highlighted. The coordination spheres about Eu1 and Eu2 are made from the L^{4-} ligand chelating in a tetradentate fashion via two bipyridyl nitrogen atoms and two 6,6′-carboxylate oxygen atoms. Four-coordinated water ligands and a 4-carboxylate oxygen atom from an adjacent L^{4-} ligand completes the Eu1 and Eu2 coordination spheres. The coordination of L^{4-} is such that it interacts with two Eu(III) metal centers, with the 4-carboxylate group linking between them. Eu1 and Eu2 are displaced from the tetradentate N_2O_2 binding plane of L^{4-} toward the linking 4-carboxylate oxygen atom (O47 and O11) of an adjacent L^{4-} ligand by ca. 0.65 and 0.72 Å, respectively. Hydrated Na^+ ions also coordinate to the dinuclear fragment by coordination to an oxygen atom from the coordinated carboxylate groups. Extensive hydrogen bonding between coordinated and lattice water molecules is evident within the structure. These interactions are augmented by offset face-to-face $\pi-\pi$ interactions between each dinuclear unit involving the L^{4-} ligands (3.62 Å separation at closest contact), which propagate down the crystallographic *a* axis to create a hydrogen-bonded CP.

Having established the solid-state structures of **1**−**4**,[10] we next evaluated their photophysical properties in water, with 0.1 M TEAP to maintain a constant ionic strength. The absorption spectra of **1**−**4** were broadly similar to that of Na_4L (λ_{max} = 305 nm; $\varepsilon = 1.06 \times 10^4\ M^{-1}\ cm^{-1}$), with the appearance of a broad absorption band with λ_{max} at ca. 327 nm, all being slightly red-shifted, and two additional bands/shoulders at 274 and 285 nm signifying coordination to the lanthanide(III) ions to L (see the Supporting Information). Excitation of λ_{max} gave rise to ligand-centered emission, for all of these complexes, which in the case of **3** ($\varepsilon = 2.2 \times 10^4\ M^{-1}\ cm^{-1}$) had λ_{max} at 345 nm, tailing into the 400 nm region (see the Supporting Information). The fluorescence emission for **3** was also significantly greater in intensity than those for **1**, **2**, and **4**, suggesting that the singlet excited state of these latter complexes was deactivated by competitive processes, such as energy transfer to their respective lanthanide(III) excited states, which in the case of Gd(III), is not achievable because of the unfavorably high energy of the $^6P_{7/2}$ excited state of Gd(III).[11] Indeed, when the delayed emission of the **1** and **4** complexes was recorded in a buffered solution (pH 7.5), the characteristic metal-centered Eu(III) and Tb(III) emissions were observed at long wavelengths, demonstrating deactivation of the $^5D_0$ and $^5D_4$ excited states of Eu(III) and Tb(III), respectively (see the Supporting Information). Furthermore, the emission arising from the $^5D_4$ excited state of Tb(III) was found to be independent of the presence of O_2. In a similar manner, the near-IR (NIR) Nd(III) emission from **2** was also observed but only in a pD 7.5 buffered D_2O solution, where deactivation of the $^4F_{3/2} \rightarrow {}^4I_J$ states ($J = {}^9/_2, {}^{11}/_2, {}^{13}/_2, {}^{15}/_2$) were clearly observed at 900, 1053, and 1323 nm, respectively (see the Supporting Information).[11] The sensitization process from the singlet excited state via T_1 to the $^4F_{3/2}$ excited state of Nd(III) was also verified by observing the NIR emission upon excitation at different wavelengths (Figure 2) using an excitation−emission profile in D_2O.

The crystal structures of the complexes revealed very high hydration states in the solid state with four bound water molecules per metal center (Figure 1). Similarly, in solution the hydration state (q) for both **1** and **4** was found to remain high.

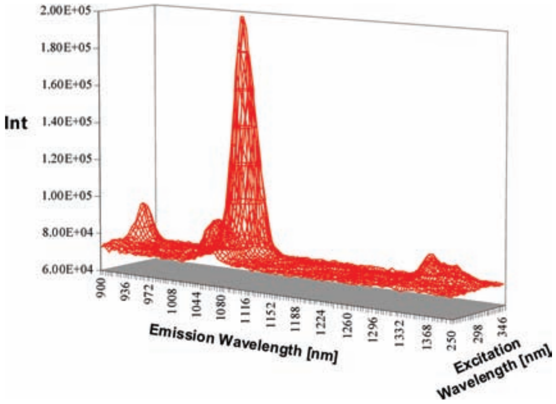

Figure 2. Excitation−emission profile of **2** when recorded in D_2O, at pD 7.5 using *N*-2-(hydroxyethyl)piperazine-*N*′-2-ethanesulfonic acid (HEPES) buffer; showing NIR emission occurring upon deactivation of the $^4F_{3/2}$ excited states to the ^4I_J ground states.

In the case of Eu(III), the excited-state decay was best fit to the monoexponential decay, giving lifetimes of 0.209 and 2.387 ms in H_2O and D_2O, respectively, from which q of 4.5 ± 0.5 was determined, whereas for Tb(III), the lifetimes in H_2O and D_2O were found to be 0.670 and 1.965 ms, respectively, giving q of 4.6 ± 0.5. The quantum yield for the Eu(III) emission of **1** was also determined and found to be 2 ± 0.02% (at pH 8.5), which is significantly smaller than that reported by Bünzli for the 6,6′-dicarboxy-2,2′-bipyridine analogue. However, this comparatively low quantum yield of **1** is not that surprising given the high number of metal-bound water molecules, which are effective Eu(III) excited-state quenchers.[12] These results confirm the structural integrity of the $Na_2Ln_2L_2$ stoichiometry in solution. This was also confirmed by carrying out titration studies of Na_4L against each lanthanide ion and observing the changes in the emission, fluorescence, and metal-centered emission in buffered pH 7.4 solutions.

The changes in the absorption spectra of Na_4L upon titration with Eu(III) are shown in Figure 3A, where λ_{max} at 307 nm ($\pi \rightarrow \pi^*$) was red-shifted by ca. 20 nm with the formation of an isosbestic point at 313 nm. Analysis of these changes showed that within 0−0.5 equiv of Eu(III) the absorption increased at long wavelength, before decreasing slightly between 0.5 and 1 equiv, leveling off after the addition of 1 equiv (see the Supporting Information). This is a clear indication of the initial formation of a 1:2 Eu^{III}/L complex prior to the formation of either the 1:1 or, more likely, the 2:2 structure. This phenomenon was also observed in the fluorescence emission spectra of Na_4L, where additionally Job's plot analysis also confirmed the formation of a product in a 1:1 stoichiometry (see the Supporting Information) and in the time-delayed Eu(III) emission, with the largest changes being observed for the hypersensitive $\Delta J = 2$ transition, which is electric-dipole-dependent; see Figure 3B. Again, here the Eu(III) emission was greatly enhanced up to the addition of 0.5 equiv, followed by quenching with subsequent additions (see Figure 3B, inset). This trend was also seen by carrying out Job's plot analysis (see the Supporting Information). We assign these changes to the formation of the 2:2 complex, which is highly hydrated, as demonstrated above, and these metal-bound water molecules would give rise to quenching in the Eu(III) emission. Consequently, the same titrations were carried out in a D_2O solution, the results of which are shown in Figure 3C. Analysis of

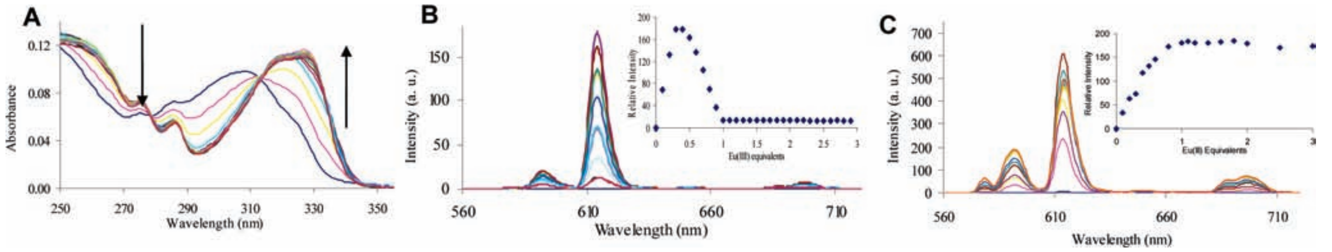

Figure 3. (A) Changes in the absorption spectrum of Na_4L upon titration with $Eu(ClO_4)_3$ in 0.04 M TEAP, at pH 7.5 (0.04 M HEPES). (B) Corresponding changes in the Eu(III) emission spectra in the $\Delta J = 2$ transition.

these changes (Figure 3C, inset, and those observed in Figure 3B) clearly demonstrated formation of the 1:1 or 2:2 complex, with the existence of the latter being confirmed by fitting of the changes in the Eu(III) emission spectra using nonlinear regression analysis (see the Supporting Information). Here, the changes were best fit to the formation of both Na_2EuL_2 and $Na_2Eu_2L_2$ (**1**) complex formation, with a log β = 13.23 and 19.38 (0.24) for these two complexes in buffered H_2O and log β = 11.76 and 18.28 (0.48) in D_2O solutions (see the Supporting Information) in the presence of 0.1 M TEAP and log β = 16.40 and 26.29 in the presence of 0.04 M TEAP. Speciation distribution diagrams also showed formation of the 2:2 complexes (see the Supporting Information), confirming a self-assembly formation in solution that leads to $Na_2Ln_2L_2$, as observed in the solid state. Analysis of the changes in Figure 3A also confirmed this self-assembly formation for Eu(III). The changes in the Tb(III) emission were also analyzed, and again formation of the 1:2 and 2:2 complexes was confirmed as a log β = 18.46 and 27.40 (0.24) 0.04 M TEAP.

The above results clearly demonstrate that Na_4L does not give rise to the formation of CPs upon reaction with various lanthanide ions but rather the spontaneous formation of 2:2 $Na_2Ln_2L_2$ complexes, which was monitored by observing the changes in the photophysical properties of these self-assemblies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray crystallographic data in CIF format and synthesis and characterization of L and $Na_2Ln_2L_2$ (Table S1 and Figures S1−S17). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: paul.kruger@canterbury.ac.nz (P.E.K.), gunnlaut@tcd.ie (T.G.).

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■ REFERENCES

(1) (a) Batten, S. R.; Neville, S. M.; Turner, D. R. *Coordination Polymers: Design, Analysis and Application*; Royal Society of Chemistry: Cambridge, U.K., 2009. (b) Janiak, C. *Dalton Trans.* **2003**, 2781. (c) Robson, R. *Dalton Trans.* **2008**, 5113. (d) Robin, A. Y.; Fromm, K. M. *Coord. Chem. Rev.* **2006**, *250*, 2127.

(2) (a) MacGillivray, L., Ed. *Metal−Organic Frameworks: Design and Application*; John Wiley & Sons: New York, 2010. (b) James, S. L. *Chem. Soc. Rev.* **2003**, *32*, 276.(c) Schroder, M., Ed. . *Topics in Current Chemistry*; Springer: Berlin, 2010; Vol. 293, pp 1−262.

(3) (a) Janiak, C.; Vieth, J. K. *New J. Chem.* **2010**, *34*, 2366. (b) Uemura, T.; Yanai, N.; Kitagawa, S. *Chem. Soc. Rev.* **2009**, *38*, 1228. (c) Eliseeva, S. V.; Bunzli, J. C. G. *Chem. Soc. Rev.* **2010**, *39*, 1. (d) Hill, R. J.; Long, D. L.; Champness, N. R.; Hubberstey, P.; Schroder, M. *Acc. Chem. Res.* **2005**, *38*, 335.

(4) (a) Huang, Y. G.; Jiang, F. L.; Hong, M. C. *Coord. Chem. Rev.* **2009**, *253*, 2814. (b) De Lill, D. T.; Cahill, C. L. *Prog. Inorg. Chem.* **2007**, *55*, 143. (c) de Bettencourt-Dias, A. *Dalton Trans.* **2007**, 2229. (d) Harbuzaru, B. V.; Corma, A.; Rey, F.; Jord, J. L.; Ananias, D.; Carlos, L. D.; Rocha, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 6476. (e) Xiao, Y.; Cui, Y.; Zheng, Q.; Xiang, S.; Qian, G.; Chen, B. *Chem. Commun.* **2010**, *46*, 5503. (f) Devic, T.; Serre, C.; Audebrand, N.; Marrot, J.; Férey, G. *J. Am. Chem. Soc.* **2005**, *127*, 12788. (g) Tanase, S.; Reedijk, J. *Coord. Chem. Rev.* **2006**, *250*, 2501.

(5) (a) dos Santos, C. M. G.; Harte, A. J.; Quinn, S. J.; Gunnlaugsson, T. *Coord. Chem. Rev.* **2008**, *252*, 2512. (b) Leonard, J. P.; Nolan, C. B.; Stomeo, F.; Gunnlaugsson, T. *Top. Curr. Chem.* **2007**, *281*, 1. (c) Plush, S. E.; Gunnlaugsson., T. *Org. Lett.* **2007**, *9*, 1919. (d) Leonard, J. P.; dos Santos, C. M. G.; Plush, S. E.; McCabe, T.; Gunnlaugsson, T. *Chem. Commun.* **2007**, 129. (e) Nonat, A. M.; Harte, A. J.; Sénéchal-David, K.; Leonard., J. P.; Gunnlaugsson, T. *Dalton Trans.* **2009**, 4703. (f) Cantuel, M.; Lincheneau, C.; Buffeteau, T.; Jonusauskaite, L.; Gunnlaugsson, T.; Jonusauskas, G.; McClenaghan, N. *Chem. Commun.* **2010**, *46*, 2486.

(6) (a) Lincheneau, C.; Peacock, R. D.; Gunnlaugsson, T. *Chem. Asian J.* **2010**, *5*, 500. (b) Stomeo, F.; Lincheneau, C.; Leonard, J. P.; Peacock, R. D.; McCoy, C. P.; Gunnlaugsson, T. *J. Am. Chem. Soc.* **2009**, *131*, 9636. (c) Comby, S.; Stomeo, S.; McCoy, C. P.; Gunnlaugsson, T. *Helv. Chem. Acta* **2009**, *92*, 2461. (d) Leonard, J. P.; Jensen, P.; McCabe, T.; O'Brien, J. E.; Peacock, R. D.; Kruger, P. E.; Gunnlaugsson, T. *J. Am. Chem. Soc.* **2007**, *129*, 10986.

(7) (a) Massue, J.; Quinn, S. J.; Gunnlaugsson, T. *J. Am. Chem. Soc.* **2008**, *130*, 6900. (b) Bonnet, C. S.; Massue, J.; Quinn, S. J.; Gunnlaugsson, T. *Org. Biomol. Chem.* **2009**, *7*, 3074. (c) Murray, N. S.; Jarvis, S. P.; Gunnlaugsson, T. *Chem. Commun.* **2009**, 4959.

(8) (a) Kelly, N. R.; Goetz, S.; Batten, S. R.; Kruger, P. E. *CrystEngComm* **2008**, *10*, 68. (b) Kelly, N. R.; Goetz, S.; Batten, S. R.; Kruger, P. E. *CrystEngComm* **2008**, *10*, 1018. (c) Kelly, N. R.; Goetz, S.; Hawes, C. S.; Kruger, P. E. *Tetrahedron Lett.* **2011**, *52*, 995.

(9) Bunzli, J. C. G.; Charbonniere, L. J.; Ziessel, R. F. *J. Chem. Soc., Dalton Trans.* **2000**, 1917.

(10) Crystals of **4** were not of sufficient quality to allow a full structural study, but the cell parameters were consistent with it being isostructural with **1**−**3**. CCDC: **1**, 810803; **2**, 810803; **3**, 810804. See the Supporting Information (Table S1).

(11) (a) Nonat, A. M.; Quinn, S. J.; Gunnlaugsson, T. *Inorg. Chem.* **2009**, *48*, 1646. (b) Sénéchal-David, K.; Pope, S. J. A.; Quinn, S. J.; Faulkner, S.; Gunnlaugsson, T. *Inorg. Chem.* **2006**, *45*, 10040.

(12) Beeby, A.; Clarkson, I. M.; Dickins, R. S.; Faulkner, S.; Parker, D.; Royle, L.; de Sousa, A. S.; Williams, G. J. A.; Woods, M. *J. Chem. Soc., Perkin Trans. 2* **1999**, 493.