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Displacement assay detection by a dimeric lanthanide luminescent ternary Tb(III)–cyclen complex: high selectivity for phosphate and nitrate anions†

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The luminescent dimeric ternary lanthanide–cyclen complexes (**2**-(Ln.**1**)₂; Ln = Tb/Eu) were designed and both their self-assembly formation and their ability to detect anions *via* displacement assays were investigated using spectrophotometric titrations in MeOH solution. The formation of **2**-(Tb.**1**)₂ and **2**-(Eu.**1**)₂ was investigated in solution, and determination of the binding constants and stoichiometry showed that the former was formed almost exclusively over the 1:1 complex **2**-(Tb.**1**) after the addition of two equivalents of **2**; while for **2**-(Eu.**1**)₂ a mixture of both stoichiometries existed even after the addition of four equivalents of **2**. Of these two systems, **2**-(Tb.**1**)₂ was studied in details as a probe for anions, where significant changes were observed in the photophysical properties of the complex; with the characteristic Tb(III)-centred emission being fully *switched off* upon the sensing of phosphates and nitrate, giving rise to the formation of a H₂PO₄[−]:Tb.**1** complex in a 1:2 stoichiometry upon sensing of H₂PO₄[−] by **2**-(Tb.**1**)₂, while NO₃[−] gave 1:1 complex formation and two equivalents of NO₃[−]:Tb.**1**.

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Introduction

Phosphates and nitrate are essential anions in biology and industry. Consequently, the design of luminescent and colorimetric sensors for the detection of such anions (*e.g.* phosphate, pyrophosphate, AMP, ADP and ATP) and polyanions (*e.g.* DNA, RNA, *etc.*) has become an increasingly topical area of research within supramolecular chemistry.^{1–3} The use of visible-emitting Ln(III)-based systems in the design of targeting luminescent sensors is particularly attractive, as we⁴ and others⁵ have demonstrated in the past. This stems from the distinct long wavelength emissions and long excited state lifetimes inherent to these metal ions, which allow for time-resolved detection in biological media, overcoming background scattering and auto-fluorescence.⁶ As part of this programme, we have developed several examples of Ln(III)–cyclen complexes for such sensing,^{4,7} as well as self-assembly lanthanide complexes based on dipicolinic acid (**dpa**) derivatives.⁸ Similarly, Parker *et al.*, Faulkner *et al.* and others have developed responsive systems for anions based on Ln(III)–cyclen complexes.^{9–11}

The use of luminescent ternary Ln(III)–cyclen complexes for application in luminescent displacement assays¹² for ion sensing is particularly attractive¹³ as these can be formed in solution through the use of Ln(III)-directed self-assembly synthesis.^{14,15} The target ion then displaces one, or more, labile ligands from the ternary lanthanide ion complex, giving rise to concomitant changes in the photophysical properties of the self-assembly. Herein, we describe an example of a displacement assay for anions based on a cyclen-**dpa** based ternary self-assembly structure. The sensor, **2**-(Ln.**1**)₂ is a bis-ternary Ln(III)–cyclen complex formed by reacting the **dpa** derivative **2** with two equivalents of Ln.**1** (Ln = Eu or Tb) *in situ*, Scheme 1.

We demonstrate that **2**-(Tb.**1**)₂, is a particularly effective displacement sensor, which is selective for phosphate and nitrate. To the best of our knowledge this is the first example of this kind of luminescent bis-ternary cyclen lanthanide complexes to be developed as displacement assays for anions. Moreover, this is also the first time that such cyclen based lanthanide displacement assays for the sensing of nitrate has been demonstrated, but this anion is a common environmental pollutant due to its use in fertilisers.

Results and discussion

The synthesis and characterisation of **1** and its Ln(III) complexes, Ln.**1** (where Ln = Eu or Tb), have been previously

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Scheme 1 Schematic illustration of $2-(\text{Tb.1})_2$ (emission switched on) and the displacement assay upon addition of anion (emission switched off).

reported by us.¹⁶ The synthesis of the ditopic ligand **2** was achieved in a few steps as shown in Scheme 2, starting from the commercially available chelidamic acid **6**. Esterification of **6** was achieved in refluxing ethanol with catalytic amount of sulphuric acid for 4 hours, giving **7** in 70% yield, as an oil that later solidified upon drying under vacuum. Compound **7** was then reacted with the linker **5** in anhydrous DMF in the presence of K_2CO_3 , under elevated temperature (see Experimental), followed by aqueous acidic workup, giving **8** as a white solid in 44% yield. The linker **5** (Scheme 2) was synthesised in two steps from **3** using the classical Finkelstein reaction (of the di-tosylated derivative **4**) in moderate yield. The conversion of **8** into **2** was simply achieved by treating **8** with neat ethylamine (40% w/v in toluene) at 60 °C for 72 hours. This was followed by precipitation upon the addition of the reaction mixture to ice, followed by filtration and

Fig. 1 The ^1H NMR (400 MHz) of compound **2**.

further purification of the desired product by flash silica column chromatography (gradient elution 100:0→95:5 CH_2Cl_2 -MeOH) yielding **2** as a white solid in 32% yield. The ^1H NMR of **2** is depicted in Fig. 1, clearly show the C_2 symmetry of the ligand, but using HSQC experiments (see ESI†) allowed for full assignment of the structure. Moreover, HRMS (ES^+) showed the appearance of m/z at 611.2805, attributed to the $[\text{2} + \text{Na}]^+$ species. Both the synthesis and characterisation of the cyclen ligand **1** and the corresponding $\text{Ln}(\text{III})$ complexes, **Ln.1**, (where $\text{Ln} = \text{Eu}$ or Tb) have been reported by us previously.^{15b,16}

The self-assembly formation of **2** [1×10^{-5} M] and **Ln.1** to give $2-(\text{Ln.1})_2$ was monitored in MeOH solution by a series of photophysical titrations at room temperature (see ESI Scheme S1†). Here, the changes in the UV-Vis absorption, fluorescence emission and the lanthanide-centred emission were all monitored to probe this self-assembly process upon titration with $\text{Eu}(\text{III})$ and $\text{Tb}(\text{III})$ complexes of **1**. For both systems, the changes in the lanthanide-centred emission were the most

Scheme 2 Synthesis of (i) the spacer **5** and (ii) the ligand **2**.

Fig. 2 Changes in the absorption spectra of **2** (1×10^{-5} M) upon titration of **Tb.1** (0 $\rightarrow$ 4 eq.) in MeOH ($\lambda_{\text{exc}} = 279$ nm). Inset: binding isotherms at 250 nm demonstrating the formation of the 1 : 2 complex.

notable. The changes in the UV-Vis absorption spectra of **2** upon binding to **Tb.1** is shown in Fig. 2, with the changes seen at 250 nm shown as inset. The 2 : 1 stoichiometry was clearly evident from the absorption titration. Identical changes were seen for **Eu.1** and **Tb.1** (see ESI†); with the absorption of **2** being blue shifted and slightly enhanced upon the addition of **Ln.1**. However, as discussed below the saturation point, and hence, the formation of the 2 : 1 complex was not as clear for **Eu(III)** (see ESI†) an indication of a lesser affinity of **Eu.1** for **2**. For both titrations, the changes in the fluorescence emission of **2** were quenched upon the addition of **Ln.1**.

Upon excitation of various wavelengths in the absorption spectra above for **2** (such as at 220 and 240 nm) and monitoring the Ln(III) centred emission, it was apparent that the ligand was able to successfully populate the excited states of both **Eu(III)** and **Tb(III)**. This was further confirmed by analysis of the excitation spectra, which was structurally similar to that seen in the absorption spectra (see ESI†). We choose to use an excitation of 279 nm, which is assigned to the $n \rightarrow \pi^*$ of the **dpa** antenna **2**, in our measurements, but this also provided successful sensitisation of the lanthanide excited states occurred as is evident from Fig. 2 for **Tb(III)**. Here, upon addition of **Ln.1** and excitation of **2** at 279 nm, both self-assembly systems gave rise to line-like emission spectra corresponding to the **Eu(III)** $^5D_0 \rightarrow ^7F_J$ ($J = 0-4$) and **Tb(III)** $^5D_4 \rightarrow ^7F_J$ ($J = 6-0$) transition, respectively, as seen in Fig. 3 for **Tb(III)**, thus demonstrating the successful sensitisation of the Ln(III) excited states of both complexes by **2**. In both instances, enhancements were seen in the lanthanide emission up to the addition of 2 equivalents of **Ln.1**, after which the emission became saturated (*c.f.* inset Fig. 3). This 2 : 1 stoichiometry signifies the formation of the desired **2-(Ln.1)₂**, ternary species in solution.

The self-assembly formation between **2** and **2-Ln.1** was further analysed by fitting the changes in the spectroscopic data using the non-linear regression analysis program SPECFIT®. In agreement with the evolving factor analysis, the fits generated for both cyclen complexes accounted for the

Fig. 3 Evolution of the **Tb(III)**-centred emission for the titration of **2** (1×10^{-5} M) with **Tb.1** (0 $\rightarrow$ 4 eq.) in MeOH ($\lambda_{\text{exc}} = 279$ nm), showing the switching on of emission. Inset: binding isotherms at 490 nm, 545 nm, and 583 nm.

stepwise formation of two luminescent ternary complex formations, namely **2-Ln.1** and **2-(Ln.1)₂**, in solution. The binding constants for these two processes were determined as $\log \beta_{1:1} = 5.2 \pm 0.2$, and $\log \beta_{2:1} = 11.0 \pm 0.1$ for **Tb.1** (see ESI† for fits), while for **Eu.1** $\log \beta_{1:1} = 4.9 \pm 0.2$, and $\log \beta_{2:1} = 11.9 \pm 0.1$ were determined for the 1 : 1 and the 2 : 1 (**Ln.1** : **2**) stoichiometries, respectively. From these titrations, the percentage formation of **2-(Tb.1)₂** was evaluated as being *ca.* 82% and 98% at 2 and 4 equivalents of **Tb.1**, respectively. Moreover, the large difference in the binding affinity of the 2 : 1 complex over that of the 1 : 1 system, is interesting, as it seems to indicate the possibility that its formation could be an example of positive cooperative binding whereby the binding of the first **Tb.1**, complex to **2**, to give **2-Tb.1**, promotes increased affinity for the second binding event and hence drives the formation of **2-(Ln.1)₂**. It is also worth highlighting that, in the case of **Tb.1**, the overall stability of **2-(Tb.1)₂** was somewhat larger than that observed in the titration of **2** with **Eu.1**, and that the percentage formation of **2-(Eu.1)₂** was significantly lower at 2 equivalents of **Eu.1**, being only 42%, *vs.* that seen for **Tb.1**. This we also saw by observing the changes in the absorption spectra above. We have seen in the past that such **Tb(III)**-cyclen complexes often have higher affinity for anions (such as salicylic acid) over that seen for structurally identical **Eu(III)** complexes¹⁷ and it is possible that such preference is also seen here in the ternary complex formation between **2** and **Tb.1** compared to that of **Eu.1**.

The formation of **2-(Ln.1)₂** was also evaluated by probing the hydration state (the *q*-value) of **2-(Ln.1)₂** *vs.* that of **Ln.1**; the latter we have previously shown to give $q = 2$ (*i.e.* two metal bound water molecules).¹⁷ The luminescent lifetime measurements for **Eu(III)**, showed that in the presence of ligand **2** (upon excitation at 279 nm) excited state lifetimes of $\tau = 0.48 \pm 0.01$ ms and $\tau = 0.56 \pm 0.03$ ms were measured in MeOH and MeOD, respectively. This gave $q \approx 0$ (*i.e.* no metal bound water molecules), further supporting the successful self-assembly formation of **2-(Ln.1)₂** in solution. Having successfully formed

Fig. 4 Changes in the phosphorescence spectra of 2-(Tb.1)₂ ([2] = 1×10^{-5} M) upon titrating with H₂PO₄⁻ (0 → 4 eq.) in MeOH (λ_{exc} = 279 nm). Inset: changes in emission intensity (black) and percentage quenching (red) at 545 nm.

2-(Ln.1)₂ we next evaluated the ability of these supramolecular ternary structures to detect anions through luminescent displacement assays. While these were formed for both systems, due to its higher stability constant the focus of this communication will be on the Tb(III) system. The ability of 2-(Tb.1)₂ to participate in anion displacement assays was investigated using tetrabutylammonium (TBA) salts of acetate, chloride, nitrate, phosphate and pyrophosphate.

The changes seen in the Tb(III)-centred emission of 2-(Tb.1)₂ upon titration with H₂PO₄⁻ led to quenching in the 2-(Tb.1)₂ emission due to the displacing of the two equivalents of Tb.1 from the 2-(Tb.1)₂ self-assembly, as shown graphically in Scheme 1. The overall changes observed in the Tb(III) emission are shown in Fig. 4 as a function of H₂PO₄⁻ equivalents, with the changes in the 545 nm transition being shown as an inset. Analysis of these changes showed that the emission was *ca.* 90% quenched upon the addition of 1 equivalent of H₂PO₄⁻; being fully quenched after the addition of a second equivalent. These changes were further analysed by using non-linear regression analysis, which gave excellent fits; showing two stepwise equilibrium processes for the displacement of Tb.1 by H₂PO₄⁻, with an initial binding constant of $\log \beta_{1:1} = 6.6 \pm 0.1$, followed by the second displacement process with a $\log \beta_{1:2}$ of 13.8 ± 0.1 . These results demonstrated that the displacement of the two equivalents of Tb.1 from 2-(Tb.1)₂ resulted in the formation of a new Tb(III) self-assembly in solution, consisting of the binding of two equivalents of Tb.1 to a single anion. This is evident from the speciation distribution diagram in Fig. 5. This was quite an unexpected result, as it was anticipated that the 1:1 complex formation would be more favourable. In fact, the 1:2 stoichiometric species was found to be favoured, reaching 80% formation after the addition of 1 equivalent of H₂PO₄⁻. Moreover, comparison of these displacement assay results with that of the formation of 2-(Tb.1)₂, indicated that the ternary complex formation between Tb.1 and H₂PO₄⁻ was significantly more favoured;

Fig. 5 Speciation-distribution diagram obtained from the fit of the phosphorescence titration of 2-(Tb.1)₂ ([2] = 1×10^{-5} M) with H₂PO₄⁻ (0 → 4 eq.) in MeOH (λ_{exc} = 279 nm).

being *ca.* 1.4 orders of magnitude greater than that seen for the association constant between 2 and Tb.1 (to yield 2-(Tb.1)₂). The changes in the UV-Vis absorption spectra were also monitored during these titrations, and were seen to be reversed compared to those seen above for the formation of 2-(Tb.1)₂, indicating the full dissociation of 2-(Ln.1)₂ to give 2, and H₂PO₄⁻·(Tb.1)₂, respectively.

Having shown that H₂PO₄⁻ could be recognised by the above displacement assay, we carried out similar titrations with other anions. Here, both CH₃CO₂⁻ and Cl⁻ only gave rise to minor quenching in the lanthanide-centred emission (*ca.* 8% and 4% at 4 eq. of anions, respectively; see ESI†). In contrast, pyrophosphate (H₂P₂O₇²⁻) gave rise to complete quenching in the Tb(III) luminescence (see ESI†). The changes observed as a function of equivalents of H₂P₂O₇²⁻ at 546 nm demonstrated that the Tb(III) emission was quenched by *ca.* 83% after the addition of 0.5 equivalents of H₂P₂O₇²⁻ and that the emission was fully quenched after only 0.8 equivalents of the anion (see ESI†). Unfortunately, fitting these changes using both linear and non-linear regression analysis gave unreliable binding constants due to a multiple binding equilibrium, but we have previously seen such complex binding for H₂P₂O₇²⁻ using cyclen urea based Tb(III) sensors.^{4a}

Nitrate is another important biological anion that is also commonly found in fertilisers. As such it is also a well-known environmental pollutant for which the detection on farmlands, in lakes and rivers is an essential requirement. Being intrigued by the formation of the 1:2 stoichiometry for the displacement of Tb.1 from 2-(Tb.1)₂ by H₂PO₄⁻, we wondered if nitrate could be detected in a similar manner; but here we expected that the 1:1 would be the only possible stoichiometry. Indeed, NO₃⁻ gave rise to quenching in the Tb(III) emission. However, unlike that seen for both H₂PO₄⁻ and H₂P₂O₇²⁻ this quenching was only 60% after the addition of three equivalents of the NO₃⁻, Fig. 4a, and even upon saturation in the emission changes at the addition of 25 equivalents, the Tb(III) emission was only 89% quenched. Nevertheless, these results

clearly demonstrate that 2-(Tb.1)_2 can be employed for the sensing of nitrated in competitive media. Treatment of the spectroscopic data gave a binding constant similar to that seen for H_2PO_4^- , but by treating the quenching data using Stern–Volmer fitting, Fig. 4b, dynamic quenching was demonstrated. This yielded a $\log \beta_{1:1}$ value of 4.70 ± 0.01 ; a slightly higher binding constant than that seen for the formation of 2-(Tb.1)_2 . To the best of our knowledge this is the first time that NO_3^- has been sensed by a cyclen based lanthanide complex by a displacement assay mechanism. These results demonstrate the flexibility of this ternary displacement assay for probing anions of both physiological and industrial relevance using systems based on 2-(Tb.1)_2 , where the selectivity can be summarised as $\text{H}_2\text{P}_2\text{O}_7^{2-} > \text{H}_2\text{PO}_4^- > \text{NO}_3^- \gg \text{Cl}^-$ and CH_3CO_2^- (Fig. 6).

Conclusions

In summary, we have shown that dimeric ternary Ln(III) –cyclen complexes can be formed in solution based on the general

self-assembly structure 2-(Ln.1)_2 , and that these self-assemblies can function as anion displacement probes, with 2-(Tb.1)_2 acting as a sensor or probe for the detection of $\text{H}_2\text{P}_2\text{O}_7^{2-}$, H_2PO_4^- and NO_3^- . In comparison the displacement of 2 from 2-(Eu.1)_2 upon the addition of these anions was only minor. We are currently exploring the use of lanthanide based displacement assays for sensing of ions and molecules in greater detail, and the application of structures such as 2 in the formation of higher order self assemblies by coordination to dimetallic lanthanide complexes.

Experimental

Materials and methods

All chemicals were purchased from Sigma-Aldrich Ireland Ltd, Acros Organics, and TCI Ltd, and were used without further purification, unless otherwise stated. Deuterated solvents for NMR analysis were all obtained from Apollo Scientific. Dry solvents were prepared in accordance with standard procedures described by Vogel, with distillation prior to each use.¹ Chromatographic columns were performed manually using either silica gel 60 (230–240 mesh ASTM) or aluminium oxide (activated, neutral, Brockman I STD grade, 150 mesh). Chromatographic columns were also run on a Teldyne Isco Combiflash Companion automatic machine using pre-packed silica or alumina columns. Thin-layer chromatography (TLC) was conducted using both Merck Kiesegel 60 F_{254} silica plates and Polygram Alox N/UV₂₅₄ aluminium oxide plates, and observed by UV light or developed in an iodine chamber. Melting Points were determined using an Electrothermal IA900 digital melting point apparatus. NMR spectra were recorded using either a Bruker Spectrospin DPX-400 instrument, operating at 400.13 MHz for ^1H NMR and 100.6 MHz for ^{13}C NMR, or a Bruker AV-600 instrument, operating at 600.1 MHz for ^1H NMR and 150.2 MHz for ^{13}C NMR. All NMR spectra were measured at 293 K. Chemical shifts are expressed in parts per million (ppm or δ) relative to the non-deuterated solvent peak and, for ^1H NMR spectra, are reported alongside the number of protons, splitting pattern, coupling constant where applicable, and proton assignment (in that order). Multiplicities are abbreviated as follows; singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). Electro mass spectra were recorded using a Mass Lynx NT V 3.4 on a Waters 600 controller connected to a 996 photodiode array detector, with HPLC grade carried solvents. Accurate molecular weights were determined by a peak-matching method, using leucine enkephaline ($\text{H-Tyr-Gly-Gly-Phe-Leu-OH}$) as the standard reference ($m/z = 556.2771$); all accurate mass were reported within ± 5 ppm of the expected mass. Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer fitted with a universal ATR sampling accessory.

4,4'-((Ethoxy-ethoxy)ethyl)-bis(diethylester-2,6-pyridine) (8). Compound 7 (0.85 g, 3.55 mmol, 2.20 eq.) and anhydrous K_2CO_3 (0.67 g, 4.85 mmol, 3.00 eq.) were stirred in anhydrous DMF (30 mL) at 25 °C for 30 min. Compound 4 (0.60 g,

Fig. 6 (a) Changes in the Tb(III) emission of 2-(Tb.1)_2 ($[2] = 1 \times 10^{-5}$ M) upon addition of NO_3^- (0 $\rightarrow$ 25 eq.) in MeOH. (b) The Stern–Volmer fitting of the Tb(III) emission data at 545 nm.

1.62 mmol, 1.00 eq.) was added and the solution was heated at 80 °C for 72 h. The solvent was then removed under reduced pressure and CH₂Cl₂ was added to the residue. The organic layer was washed twice with 1% aqueous acetic acid and H₂O before drying over MgSO₄. Solvent evaporation under reduced pressure afforded a crude yellow oil, which was subsequently recrystallised from EtOH to give **8** as a white solid (0.42 g, 0.71 mmol, 44% yield); m.p. 77–79 °C; HRMS (*m/z*) (ES⁺) Calculated for C₂₈H₃₆N₂O₁₂Na *m/z* = 615.2166 [M + Na]⁺. Found *m/z* = 615.2156; ¹H NMR (400 MHz, CDCl₃) δ_H: 7.80 (4H, s, py-H), 4.45 (8H, q, *J* = 7.2 Hz, CH₂CH₃), 4.30 (4H, t, *J* = 4.5 Hz, CH₂), 3.90 (4H, t, *J* = 4.5 Hz, CH₂), 3.74 (4H, s, CH₂), 1.43 (12H, t, *J* = 7.2 Hz, CH₂CH₃); ¹³C NMR (100 MHz, CDCl₃) δ_C: 166.77, 164.69, 150.17, 114.44, 71.00, 69.26, 68.26, 62.45, 14.20; IR ν_{max} (cm⁻¹): 3076, 2983, 2933, 2905, 1742, 1706, 1594, 1567, 1478, 1435, 1371, 1369, 1342, 1328, 1244, 1230, 1158, 1134, 1102, 1067, 1023, 994, 938, 887, 866, 817, 786, 732, 701.

4,4'-(Ethoxy)-ethoxyethyl)-bis(diethylamide-2,6-pyridine) (2). Compound **8** (0.15 g, 0.25 mmol, 1.00 eq.) and ethylamine (40 wt% in toluene) (50 mL) were heated together at 60 °C for 72 h. The reaction mixture was then poured onto ice, resulting in the precipitation of a brown solid. Upon melting of the ice, the solid was isolated by filtration and dissolved in CH₂Cl₂. The organic phase was washed twice with H₂O before drying over MgSO₄. The solvent was then removed under reduced pressure to give a crude brown solid. Purification by flash silica column chromatography (gradient elution 100:0 → 95:5; CH₂Cl₂–MeOH) yielded **2** as a white solid (0.05 g, 0.08 mmol, 32% yield). m.p. 222–224 °C; HRMS (*m/z*) (ES⁺) Calculated for C₂₈H₄₀N₆O₈Na *m/z* = 611.2805 [M + Na]⁺. Found *m/z* = 611.2808; ¹H NMR (600 MHz, CDCl₃) δ_H: 8.20 (4H, t, *J* = 5.9 Hz, NH), 7.82 (4H, s, py-H), 4.04 (4H, t, *J* = 4.5 Hz, CH₂), 3.77 (4H, t, *J* = 4.5 Hz, CH₂), 3.65 (4H, s, CH₂), 3.48 (8H, m, CH₂CH₃), 1.22 (12H, t, *J* = 7.3 Hz, CH₂CH₃); ¹³C NMR (150 MHz, CDCl₃) δ_C: 167.87, 163.64, 151.07, 111.46, 71.08, 69.31, 67.95, 34.63, 15.01; IR ν_{max} (cm⁻¹): 3310, 3080, 2972, 2934, 2876, 1737, 1647, 1601, 1523, 1445, 1366, 1281, 1241, 1144, 1129, 1056, 1044, 997, 885, 875, 817, 752, 695.

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Notes and references

- (a) A. E. Hargrove, S. Nieto, T. Zhang, J. L. Sessler and E. V. Anslyn, *Chem. Rev.*, 2011, **111**, 6603; (b) C. Caltagirone, P. A. Gale, J. R. Hiscock, S. J. Brooks, M. B. Hursthouse and M. E. Light, *Chem. Commun.*, 2008, 3007; (c) A. M. Mallet, Y. Liu and M. Bonizzoni, *Chem. Commun.*, 2014, **50**, 5003; (d) N. A. Esipenko, P. Koutnik, T. Minami, L. Mosca, V. M. Lynch, G. V. Zyryanov and P. Anzenbacher, *Chem. Sci.*, 2013, **4**, 3617; (e) Y. Zhou, Z. Xu and J. Yoon, *Chem. Soc. Rev.*, 2011, **40**, 2222; (f) X. Li, X. Gao, W. Shi and H. Ma, *Chem. Rev.*, 2014, **114**, 590; (g) J. A. Kitchen, E. M. Boyle and T. Gunnlaugsson, *Inorg. Chim. Acta*, 2012, **381**, 236; (h) C. M. G. dos Santos and T. Gunnlaugsson, *Supramol. Chem.*, 2009, **21**, 173.
- (a) P. A. Gale and T. Gunnlaugsson, *Chem. Soc. Rev.*, 2010, **39**, 3595–3596; (b) R. M. Duke, E. B. Veale, F. M. Pfeffer, P. E. Kruger and T. Gunnlaugsson, *Chem. Soc. Rev.*, 2010, **39**, 3936; (c) T. Gunnlaugsson, M. Glynn, G. M. Tocci (née Hussey), P. E. Kruger and F. M. Pfeffer, *Coord. Chem. Rev.*, 2006, **250**, 3094; (d) H. Akiba, J. Sumaoka and M. Komiyama, *ChemBioChem*, 2009, **10**, 1773.
- (a) E. B. Veale, G. M. Tocci, F. M. Pfeffer, P. E. Kruger and T. Gunnlaugsson, *Org. Biomol. Chem.*, 2009, **7**, 3447; (b) C. M. G. dos Santos, T. McCabe and T. Gunnlaugsson, *Tetrahedron Lett.*, 2007, **48**, 3135; (c) J. A. Kitchen, E. M. Boyle and T. Gunnlaugsson, *Inorg. Chim. Acta*, 2012, **381**, 236; (d) R. M. Duke and T. Gunnlaugsson, *Tetrahedron Lett.*, 2007, **48**, 8043; (e) R. M. Duke, J. E. O'Brien, T. McCabe and T. Gunnlaugsson, *Org. Biomol. Chem.*, 2008, **6**, 4089.
- (a) C. M. G. dos Santos and T. Gunnlaugsson, *Dalton Trans.*, 2009, 4712; (b) S. E. Plush and T. Gunnlaugsson, *Dalton Trans.*, 2008, 3801; (c) S. E. Plush and T. Gunnlaugsson, *Org. Lett.*, 2007, **9**, 1919; (d) J. P. Leonard, C. M. G. dos Santos, S. E. Plush, T. McCabe and T. Gunnlaugsson, *Chem. Commun.*, 2007, 129; (e) A. J. Harte, P. Jensen, S. E. Plush, P. E. Kruger and T. Gunnlaugsson, *Inorg. Chem.*, 2006, **45**, 9465.
- (a) M. L. Cable, J. P. Kirby, H. B. Gray and A. Ponce, *Acc. Chem. Res.*, 2013, **46**, 2576; (b) M. L. Cable, D. J. Levine, J. P. Kirby, H. B. Gray and A. Ponce, in *Advances in Inorganic Chemistry: Inorganic Photochemistry*, ed. R. Van Eldik, Elsevier, San Diego, vol. 63, 2011, p. 145; (c) M. L. Cable, J. P. Kirby, D. J. Levine, M. J. Manary, H. B. Gray and A. Ponce, *J. Am. Chem. Soc.*, 2009, **131**, 9562.
- (a) S. J. Bradberry, A. J. Savyasachi, M. Martinez-Calvo and T. Gunnlaugsson, *Coord. Chem. Rev.*, 2014, **273–274**, 226; (b) C. M. G. dos Santos, A. J. Harte, S. J. Quinn and T. Gunnlaugsson, *Coord. Chem. Rev.*, 2008, **252**, 2512.
- (a) S. Comby, E. M. Surender, O. Kotova, L. K. Truman, J. K. Molloy and T. Gunnlaugsson, *Inorg. Chem.*, 2014, **53**, 1867; (b) T. Gunnlaugsson and J. P. Leonard, *Chem. Commun.*, 2005, 3114.
- (a) C. Lincheneau, B. Jean-Denis and T. Gunnlaugsson, *Chem. Commun.*, 2014, **50**, 2857; (b) O. Kotova, J. A. Kitchen, C. Lincheneau, R. D. Peacock and T. Gunnlaugsson, *Chem. – Eur. J.*, 2013, **19**, 16181; (c) C. Lincheneau, R. M. Duke and T. Gunnlaugsson, *Org. Biomol. Chem.*, 2012, **10**, 6069.
- (a) S. J. Butler and D. Parker, *Chem. Soc. Rev.*, 2013, **42**, 1652; (b) D. G. Smith, R. Pal and D. Parker, *Chem. – Eur. J.*, 2007, **13**, 1111.

- 2012, **18**, 11604; (c) E. J. New, D. Parker, D. G. Smith and J. W. Walton, *Curr. Opin. Chem. Biol.*, 2010, **14**, 238; (d) S. Pandya, J. Yu and D. Parker, *Dalton Trans.*, 2006, 2757; (e) D. Parker and R. Pal, *Org. Biomol. Chem.*, 2008, **6**, 102; (f) D. Parker and R. Pal, *Chem. Commun.*, 2007, 474.
- 10 (a) T. J. Sorensen, L. R. Hill, J. A. Tilney, O. A. Blackburn, M. W. Jones, M. Tropiano and S. Faulkner, *Eur. J. Inorg. Chem.*, 2014, 2520; (b) L. R. Hill, O. A. Blackburn, M. W. Jones, M. Tropiano, T. J. Sorensen and S. Faulkner, *Dalton Trans.*, 2013, **42**, 16255; (c) T. J. Sorensen, M. Tropiano, O. A. Blackburn, J. A. Tilney, A. M. Kenwright and S. Faulkner, *Chem. Commun.*, 2013, **49**, 783; (d) S. J. A. Pope, B. P. Burton-Pye, R. Berridge, T. Khan, P. J. Skabara and S. Faulkner, *Dalton Trans.*, 2006, 2907.
- 11 (a) Ci. M. G. dos Santos and T. Gunnlaugsson, *Supramol. Chem.*, 2009, **21**, 173; (b) M. S. Tremblay, Q. Zhu, A. A. Martí, J. Dyer, M. Halim, S. Jockusch, N. J. Turro and D. Sames, *Org. Lett.*, 2006, **8**, 2723; (c) R. K. Mahajan, I. Kaur, R. Kaur, S. Uchida, A. Onimaru, S. Shinoda and H. Tsukube, *Chem. Commun.*, 2003, 2238.
- 12 (a) A. T. Wright and E. V. Anslyn, *Chem. Soc. Rev.*, 2006, **35**, 14; (b) S. L. Wiskur, H. Ait-Haddou, J. J. Lavigne and E. V. Anslyn, *Acc. Chem. Res.*, 2001, **34**, 963.
- 13 (a) J. Massue, S. J. Quinn and T. Gunnlaugsson, *J. Am. Chem. Soc.*, 2008, **130**, 6900; (b) N. S. Murray, S. P. Jarvis and T. Gunnlaugsson, *Chem. Commun.*, 2009, 4959; (c) J. P. Leonard, C. B. Nolan, F. Stomeo and T. Gunnlaugsson, *Top. Curr. Chem.*, 2007, **281**, 1.
- 14 O. Kotova, S. Comby and T. Gunnlaugsson, *Chem. Commun.*, 2011, **47**, 6810.
- 15 (a) M. Cantuel, C. Lincheneau, T. Buffeteau, L. Jonusauskaite, T. Gunnlaugsson, G. Jonusauskas and N. D. McClenaghan, *Chem. Commun.*, 2010, **46**, 2486; (b) C. M. G. dos Santos, P. B. Fernández, S. E. Plush, J. P. Leonard and T. Gunnlaugsson, *Chem. Commun.*, 2007, 3389.
- 16 (a) T. Gunnlaugsson, A. J. Harte, J. P. Leonard and M. Nieuwenhuyzen, *Chem. Commun.*, 2002, 2134; (b) T. Gunnlaugsson, A. Harte, J. P. Leonard and M. Nieuwenhuyzen, *Supramol. Chem.*, 2003, **15**, 505.
- 17 A. Beeby, I. M. Clarkson, R. S. Dickins, S. Faulkner, D. Parker, L. Royle, A. S. de Sousa, J. A. G. Williams and M. Woods, *J. Chem. Soc., Perkin Trans. 2*, 1999, 493.