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Lanthanide luminescent logic gate mimics in soft matter: [H+] and [F-] dual-input device in a polymer gel with potential for selective component release

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The non-covalent incorporation of responsive luminescent lanthanide, Ln(III), complexes with orthogonal outputs from Eu(III) and Tb(III) in a gel matrix allows for *in situ* logic operation with colorimetric outputs. Herein, we report an exemplar system with two inputs ([H+] and [F-]) within a p(HEMA-*co*-MMA) polymer organogel acting as a dual-responsive device and identify future potential for such systems.

Molecular-based logic and computation has been developing since the first reports of the principles of storing logical states at the molecular level in 1988.[1] While representing a fundamentally young field of chemistry, a vast array of molecular systems have been reported to date either through single molecule[2] or supramolecular[3] paradigms. The parallel advances in receptor molecules for various ionic and molecular species, alongside probe species for chemical environment, have allowed for the construction of logic gates within solution- and solid-based chemical systems.[4] Logic systems of binary nature are most common, with "0" and "1" states only, while the calibrated properties of many chemical sensors have extended this to higher order, multi-level, logic.[5] Complexes, probes and sensors based on 4*f*-metal complexes have received much attention[6] and are appealing for their narrow-band emission spectra which are well resolved in spectroscopy and result in characteristic colours to the naked eye.[7] A range of luminescent and responsive lanthanide complexes have been developed to date by our group and by others exhibiting switching behaviour[7-8] with various solution analytes. Use of Ln(III) ions in logic functions has limited precedence in the literature from our research[9] and others[10] for a number of circuit types. The resistance of Ln(III)-centred emission to wavelength shifts with environmental change, such as the switching of states, is ideally suited to digitisation of intensity at well-defined wavelengths for outputs from a logic gate. The *in situ* applications of luminescent sensors have been demonstrated in

systems immobilised upon metal and mineral surfaces *via* various self-assembly techniques; inclusion within hybrid materials has been demonstrated effectively by Binnemans.[11] Polymeric and soft materials also have promise, with increasing versatility of sensitive ionogel materials.[12] We are interested in using polymer cross-linked hydrogel materials as intrinsic chemical devices.[13] Thus herein, we report the design and construction of a logic system with inputs of [H+] and [F-] through combination of two responsive emissive complexes of Eu(III) and Tb(III) with red and green emission, respectively.

Ligands that sensitise Eu(III) and Tb(III) emission were derived from scaffolds of dipicolinic acid (**dpa**), **1**, and **btp**[14], respectively. The self-assembly of mono-nuclear complexes of ligands of these types have been studied previously in our laboratory.[15] Both ligands, shown in Figure 1, were synthesised through optimised procedures in short, facile syntheses (Figure S1-4). Ligands **1** and **2** were then coordinated with Eu(OTf)$_3$ and Tb(OTf)$_3$, respectively, to produce complexes **Eu.1$_3$** and **Tb.2$_3$** that were emissive under excitation at λ_{ex} = 291 nm. These complexes were obtained by reaction of respective ligands and Ln(III) triflates in 3:1 ratio in CH$_3$OH under microwave-assisted heating. The resultant complexes were directly precipitated from diethyl ether and characterised as having 1:3 stoichiometry from emission lifetimes.[16]

The photophysical properties have been well characterised for **1**, **2** and their respective 1:3 complexes (Figure S5-7). The UV-Vis, fluorescence and time-gated emission properties the complexes, **Eu.1$_3$** and **Tb.2$_3$**, were responsive to simple analytes and distinguishable by their spectral features when

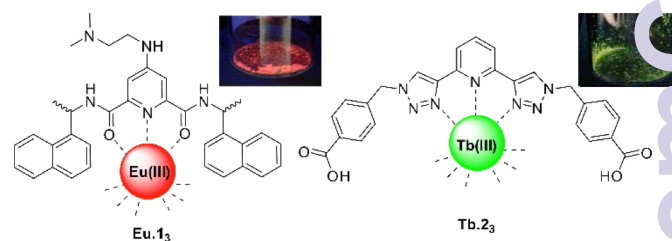Figure 1: Structures of ligand **1** and **2** and complexes with **Eu.1$_3$** and **Tb.2$_3$**. *Inset*: the emission arising from solid complexes irradiated under λ = 254 nm.

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analysed in parallel. These features showed responsive switching that, at mM detection limits, could be digitised to mimic the logic inputs "0" and "1" of Boolean logic and algebra. The visible nature of all these emissions allowed observation of "OFF" and "ON" to the naked-eye producing unique colours for all four output states of this two-input system. Complex **Eu.1$_3$**, showed fluorescence at 385 nm and characteristic Eu(III) phosphorescence that modulated with [H$^+$] giving significant enhancement of Eu(III)-centred emission upon protonation (*vide infra)*. This was due to reduction in photoinduced electron transfer (PET) quenching of the ligand excited states by the pendent amine, which is in competition with the energy transfer to Eu(III).

The **btp** motif has been previously explored in anion binding.[17] Our investigations of **Tb.2$_3$** with various anions showed unique emission and absorbance responses for interactions with F$^-$ compared to the other halides (Figure S8-16). The emission responses with F$^-$ were suitable to provide dual output channels. Here, the UV-Vis absorption of **Tb.2$_3$** was blue-shifted with concomitant enhancement in fluorescence emission upon addition of TBAF, resulting in complete 'switch-off' of Tb(III)-centred emission. This was assigned to F$^-$ induced dissociation of the 1:3 complexes producing uncoordinated ligand, **2**, which was no longer able to populate excited states of Tb(III) as was clearly visible from the changes in both the absorbance and emission spectra; no evidence for dissociation of **Eu.1$_3$** was observed (Figure S17).

These complexes were not mutually exclusive in their responses to [H$^+$] and [F$^-$] (Figure S9 and S18). However, the simultaneous monitoring of three output signals, at 490 nm and 615 nm from phosphorescence and at 338 nm from fluorescence, allowed for *four distinct states* to be identified.

Initially, solution studies of **Eu.1$_3$** and **Tb.2$_3$** were carried out in CH$_3$OH, where UV-Vis absorption, fluorescence and phosphorescence emission were recorded. The complexes showed substantially different quantum yield (Φ_{tot}) values, being 4% and 70% for **Eu.1$_3$** and **Tb.2$_3$**, respectively. Excitation of **Eu.1$_3$** and **Tb.2$_3$** at 291 nm gave a compromise between relative emission intensities where concentrations of [**Eu.1$_3$**] = 2.5 x 10^{-5} M and [**Tb.2$_3$**] = 5 x 10^{-6} M were used. The initial resting condition of the system, the (0,0) state, was characterised in solution to identify discrete signals from the two component complexes (Figure S19). Strong Tb(III) emission gave the solution a predominantly green colour; which varied upon input condition (*vide infra)*. The Ln(III)-centred emissions were monitored as time-gated luminescence given their ms lifetimes. Here the main Tb(III) transitions ($^5D_4\rightarrow{}^7F_J$) appeared at 490, 545, 585 and 621 nm; whereas the Eu(III) transitions of interest ($^5D_0\rightarrow{}^7F_J$) were observed at 595, 615 and 700 nm. While there was a substantial overlap of the 595 nm Eu(III) and 585 nm Tb(III) emissions, the remaining bands could be considered independent, and therefore appropriate for digitisation, Figure S19(a). The fluorescence spectra showed emission centred at 338, assigned to **Tb.2$_3$**, with a shoulder appearing at 385 nm which was assigned to **Eu.1$_3$**; allowing for the fluorescence to be addressed as an output channel.

The system was encapsulated into soft matter non-covalently, using a poly(HEMA-*co*-MMA) matrix that was prepared *via* a modified procedure based on our previously published methodology.[13a] HEMA, MMA and EGDMA were polymerised under free-radical polymerisation using AIBN, in the presence of complexes **Eu.1$_3$** and **Tb.2$_3$** (using CH$_3$CN as co-solvent) affording a hard brittle acrylic monolith. Emission enhancement was seen for both species upon encapsulation.
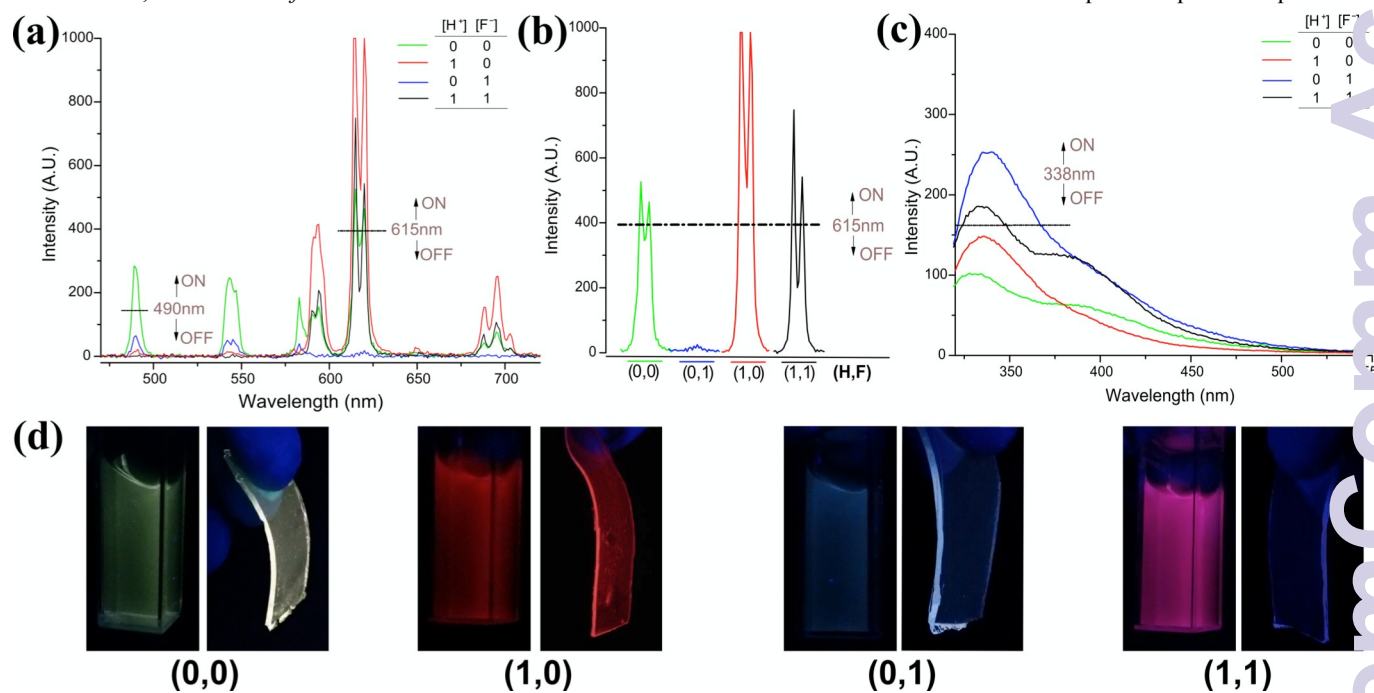
Figure 2: (a) Gel phosphorescence spectra of (0,0), (1,0), (0,1) and (1,1) input states with "ON"/"OFF" thresholds defined for λ = 490 and 615 nm. (b) Unstacked representation Δ*J* = 2 (615 nm) transition with "ON"/"OFF" threshold. (c) Gel fluorescence spectra of for (0,0), (1,0), (0,1) and (1,1) input states with "ON"/"OFF" threshold for λ = 338 nm. (d) Photographs of each input state as seen to the naked-eye in solution (left) and gel (right), when irradiated at λ$_{max}$ = 254 nm.

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therefore the ratio of **Eu.1₃** to **Tb.2₃** required to balance relative emission intensities was corrected to a 2:1 ratio. The hard materials were transparent and colourless under ambient light and yellow/green emissive under irradiation at 254 nm *c.f.* Figure 2c; indicating successful encapsulation of both complexes within the polymeric matrix. It was found that **Tb.2₃** readily dissociated within the polymer upon contact with excess water. Therefore the polymers were swelled in methanol to give soft organogel materials. Emission from both complexes was stable and no diffusion of the complexes from the material was observed during operation, indicating the internal porosity of the material was maintained within the organogels and, additionally, the swelled poly(HEMA-*co*-MMA) could be handled directly without structural damage. Irradiation of the swelled organogels gave rise to strong uniform emission (both fluorescence and Ln(III)-based), an indication of homogenous distribution of both compounds through the swelled matrix. Enhanced Eu(III)-emission intensity was consistent with reports of Φ_{tot} enhancement of other lanthanide complexes within dry poly(MMA) films.[18] Satisfyingly, this was also found to be the case for our swelled materials containing both **Eu.1₃** and **Tb.2₃**.

To construct the appropriate output truth-table, conditional changes were made to the (0,0) state and the response monitored. The two inputs of [H⁺] and [F⁻] were defined as: *(i)* 2 mM HCl and *(ii)* 1 mM TBAF, respectively, in CH₃OH. Swelled gels slides (30 mm × 10 mm × 1.2 mm) were suspended in a stirred CH₃OH solution and exposed to these inputs, Figure 3a. The phosphorescence, Figure 2a and b, and fluorescence emissions, Figure 2c, were subsequently probed under an operating temperature of 24 °C. In solution, the equilibrium that defines each state was reached rapidly and the emission changes occurred within minutes. However, the response times of the gels were found to be diffusion controlled, variable with gel thickness (diffusion length), and surface area (accessible pores). Hence, the gels were synthesised to a constant swell thickness; emission after 20 minutes was analysed. Changes were consistent with, but not identical to, solution studies of **Eu.1₃** and **Tb.2₃** and shows
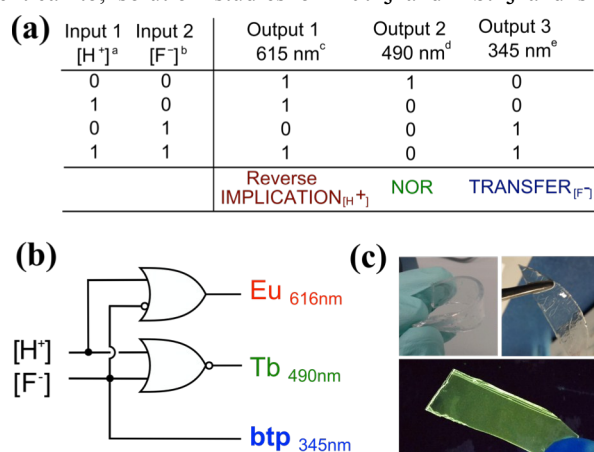

Figure 3 **(a)** Truth table of the logic functions. ᵃ [H⁺] = 2mM; ᵇ [F⁻] = 1 mM. **(b)** Circuit diagram representation of the logic gate functions. ᶜ Phosphorescence. ᵈ Fluorescence. **(c)** Photographs of **Eu.1₃** and **Tb.2₃** incorporated gels in swelled in H₂O (left) and CH₃OH (right) under ambient light; and after drying and irradiation at 254 nm demonstrating the (0,0) state.

analogous logic responses (Figure S19-20).

Upon acidification, yielding the (1,0) state, the intensity of the Eu(III) emission was enhanced, consistent with the PET mechanisms described above, while the Tb(III)-centred emission was concomitantly quenched, which is consistent with dissociation of **Tb.2₃**. A minor enhancement in the intensity of fluorescence associated with **2**, centred at 338 nm, was observed. Naked-eye observation of the sample showed that the initial (0,0) state was predominantly yellow/green in colour, Figure 2d. However, upon acidification, the sample became strongly red coloured, which was clearly visible to the naked-eye, being consistent with a dominant Eu(III)-centred emission within the gel. Fluoridation switched the (0,0) state to the (0,1) state. This caused a decrease in the Tb(III) emission to approximately the same extent as seen previously for the acidification, *ca.* 80%. This also resulted in the complete "switch-off" of the Eu(III)-centred emission. The changes in the Tb(III) emission were again assigned to dissociation of the **Tb.2₃** complex, being induced by F⁻, while the Eu(III) emission changes were due to deprotonation of the already protonated form of **Eu.1₃**,[19] which resulted in more efficient PET and reduced **1**→Eu(III) sensitisation. Concomitantly, the fluorescence emission spectra showed three-fold intensity enhancement in the 338 nm band of ligand **2**. This was reflected in the gel colour, which became light blue to the naked-eye.

The (1,1) input state was generated by: fluoridation followed by acidification; acid followed by fluoride; or the simultaneous addition. This resulted in substantial quenching of the Tb(III) emission 490 nm, with concomitant enhancement of the 615 nm Eu(III) emission, Figure 2a-c. Simultaneously, the fluorescence emission of **2** was enhanced compared to that seen in the (0,0) state. Here, the fluorescence emission (330-390 nm) was broad and dominant; the combined emission outputs gave purple emissive gels, as shown in Figure 2d.

To parameterise a logic circuit, that operated three different output logic functions, thresholds for "1" and "0" states were defined. Arbitrary threshold definition would allow the parameterisation of the system to different logic functions as a result of the continuous responses of **Eu.1₃** and **Tb.2₃** complexes. The chosen emission thresholds for the system, represented on the spectra in Figure 2a-c, were placed according to the criterion such that a consistent state should be derived within maximum error (≈ 5%) of the intensity value; maximising the information gained from and fidelity of the system. Each output was treated as a double-input-single-output device[5a] and the mimicked functions derived with these thresholds are summarised in the truth table, Figure 3a. In this system the Eu(III) luminescence corresponded to the **Reverse-IMPLICATION₍H⁺₎** logic operation, while the Tb(III) emission reported as a **NOR₍H⁺₎/₍F⁻₎** function. In turn, the fluorescence "OUTPUT 3", mimicked **TRANSFER₍F⁻₎** being "1" only when F⁻ is present, *i.e.* states (0,1) and (1,1). These three single-output logic 'gates' combined within the gel mimic a more complex double-input-three-output logic circuit, shown schematically in Figure 3b and animation provided as ESI.

Reverse switching of the polymer gel was not possible due to dissociation of **Tb.2₃**. Contrary to initial expectations from

hydrogel studies, the smaller 'free', or 'F⁻ bound', **btp** ligands, **2**, diffused from the interior. The leeching process was characterised in a preliminary fashion; spectra were recorded from washed gels and their respective supernatant solutions. Phosphorescence emission showed no leeching of either **Eu.1₃** or **Tb.2₃** from the cross-linked matrix (Figure S21). Fluorescence spectra showed a substantial increase in emission from **2** in the supernatant solution after exposure to the F⁻ stimulus for 60 minutes (Figure S22). UV-vis absorption spectra of the released material (Figure S23) showed features assignable to unbound ligand **2** demonstrating a selective component release. While a constraint, this can also be viewed as a demonstration of a stimulus-initiated ligand release; larger **Tb.2₃** complexes being retained within the gel matrix by steric encapsulation. Controlled release from polymer microgels is well explored,[20] and the design of functional complexes that undergo stimulated dissociation within such matrixes could allow application in selective ligand release with specific activity reporting through their emission properties. Further studies, however, are beyond the scope of the present work.

In conclusion, a molecular logic gate mimic consisting of outputs constructed from the use of Ln(III)- and ligand-centred emissions was developed. This system represents one of only a few examples to date of the use of 4*f* ions as outputs in molecular logic. The encapsulation of these within a polymer organogel gave luminescence changes within the microenvironment in response to the inputs [H⁺] and [F⁻], again being one of the first examples of such design. The responses of the materials to external stimuli were shown to mimic the **Reverse-IMPLICATION–TRANSFER–NOR** logic circuit, Figure 3b. The prospects of smarter responsive systems combining logic mimicry with easily processed materials are an exciting and promising approach to future applications. Our work in the development of second-generation materials, with improved control of release properties and aqueous application, are to be reported in the near future.

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