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Lanthanide Luminescence to Mimic Molecular Logic and Computing through Physical Inputs

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Abstract

The remarkable advances in molecular logic reported in the last decade demonstrated the potential of luminescent molecules for logical operations, a paradigm-changing concerning silicon-based electronics. Trivalent lanthanide (Ln^{3+}) ions, with their characteristic narrow line emissions, long-lived excited states, and photostability under illumination, may improve the state-of-the-art of molecular logical devices. Here is reported the use of monolithic silicon-based structures incorporating Ln^{3+} complexes for performing logical functions. Elementary logic gates (AND, INH and DEMUX), sequential logic (KEYPAD LOCK), and arithmetic operations (HALF ADDER and HALF SUBTRACTOR) exhibiting a switching ratio >60 % are demonstrated for the first time using non-wet conditions. Additionally, this is the first report showing sequential logic and arithmetic operations combining molecular Ln^{3+} complexes and physical inputs. Contrary to chemical inputs, physical inputs may enable the future concatenation of distinct logical functions and reuse of the logical devices, a clear step-forward towards input-output homogeneity that is precluding the integration of nowadays molecular logic devices.

1. Introduction

In a period of a few decades, the computers and related systems become smaller and smaller due to the substantial scaling shrinkage of silicon-based technology components.^[1-5] Whereas the first field-effect transistor has the dimensions of a palm of a hand, nowadays over 100 million equivalent components per mm² are packaged in a chip using state-of-the-art 10 nm lithography.^[6] Nevertheless, the increasing demand for further computing power and downscaling are not compatible with the inherent scale limitation of lithographic methods,^[7, 8] precluding much further miniaturization using the top-down approach followed so far. A disruptive step-forward towards bottom-up processing^[9, 10] will be perhaps the only possibility to expand the current computing power overcoming the inherent limitations of nowadays electronic devices.

In the early 90's, Prasanna de Silva *et al.*^[1] described the first general and practical approach to information processing and computing based on molecules able to perform logical operations. The first AND molecular logic gate was based on organic molecules, applying cations as the logical inputs and a change in the emission intensity of the organic molecules as the logical output.^[1] Basic logical gates were the first generation of logic devices in the 2000s.^[2, 3, 7, 11-17] Interrogating the molecules with ionic species, their optical properties were changed,^[17-19] giving a TRUE or FALSE logical output (logical outputs 1 and 0), and thus elementary Boolean functions were performed. Later on, it was recognized that the molecules can additionally perform logical operations of higher complexity, such as molecular multiplexers and demultiplexers or molecular binary adders and subtractors^[18, 20-25] All the above-mentioned molecular devices operate in wet conditions, so its immediate use was in biomedicine. Molecular and biomolecular computing/logic systems^[26-28], including supramolecules,^[16] proteins,^[14] DNA,^[29] DNA/conjugated polymer systems,^[17, 21] and enzyme based-systems^[30], were used to process chemical input signals mimicking most of the logical operations of semiconductor-based electronic devices.

As the signal processing is performed by molecules, parallel computing can be implemented, allowing an exponential gain on computing power in comparison with nowadays electronic devices.^[31] However, the characteristic broadband emission and fast decay times of organic compounds, conjugated to the well-known photobleaching, precludes multiplexing **using light as a logical input or output**, making difficult its implementation in applications other than proof of concept molecular logic devices.

The use of trivalent lanthanide ions (Ln^{3+}) as luminescent optical active centers in molecular logic is particularly attractive as these ions typically emit in a wide wavelength range covering the UV-VIS-NIR spectral regions, with characteristic line-like emission bands (<10 nm) and long-lived excited state lifetimes (>1 μs). Despite it is nowadays recognized that Ln^{3+} ions can improve the state-of-the-art of molecular logical devices, only a handful of papers have been published so far.^[11, 32-36] Up to now, all the logical gates based on Ln^{3+} ions respond to chemical inputs and thus operate exclusively in wet conditions, except the $\text{Eu}^{3+}/\text{Tb}^{3+}$ based self-assembled polymer monolayer functionalized Si surface proposed by some of us in 2016.^[36]

It is recognized in the literature that if physical inputs (*viz.* light, pressure, temperature) are used as inputs and outputs of a molecular logical device it will render advantages in the input-output homogeneity when the integration of distinct logical functions, no-contamination, and reuse of the device are demanded.^[37] It also permits higher integration of distinct logical functions because it does not require physical access, and monolithic structures may contain thousands of individual logic elements. For example, the optical inputs signals can be remotely delivered and read from the molecular devices as time-gated pulses (covering time ranges until the picosecond,^[37] faster cycling even in comparison to the electronic counterparts). All these potential benefits motivate the transfer of molecular logic devices from wet (chemical or physical inputs and physical outputs) to dry (exclusively physical inputs and outputs) operation conditions. Up to now all the works performing molecular logic and computing using

exclusively physical inputs (involving reversible photo transformations of photochromic molecules)^[37-41] operate, however, in wet conditions.

Here, we report a noteworthy step forward relative to the state-of-the-art examples presenting high-sophistication-level logical operations based exclusively on physical inputs and outputs and operating in non-wet conditions. By exploiting a $\text{Eu}^{3+}/\text{Tb}^{3+}$ -functionalized Si platform, that produces narrow and stable emission lines and that is fully compatible with existent Si-based electronic devices, we fabricate molecular logical arrays performing basic (AND, INH, DEMUX), sequential (KEYPAD LOCK), and arithmetic (HALF ADDER and HALF SUBTRACTOR) logic operations.

2. Results and Discussion

2.1. Fabrication and Structural Characterization of the Logical Arrays

The formation and the structure of the $\text{Eu}^{3+}/\text{Tb}^{3+}$ based self-assembled polymer monolayer functionalized Si surface are depicted in **Figure 1a**, and **Figure 1b** respectively. Original monocrystalline Si wafers were covered with a 1 μm thick layer of SiO_2 and the surface was activated by amination with 3-aminopropyl triethoxysilane (APTES). The functionalization with the Eu^{3+} and Tb^{3+} complexes was realized by Michael's addition to the surface amine groups of an acrylate poly(ethylene glycol) (PEG) polymer spacer terminated in a β -ketoester ligand (**Figure S1** and **Table S1** in Supporting Information). This group fixes the Eu^{3+} and Tb^{3+} ions to the surface allowing further complexation of these ions with light-harvesting DPA (2,6-pyridinedicarboxylic acid) ligands. Different types of coatings were prepared that differ in the length of the PEG polymer spacer (**Figure 1c**, **Table 1**). Samples with and without the addition of the Ln^{3+} ($\text{Ln}=\text{Eu}, \text{Tb}$) ions and DPA ligands and using two different reaction times for Michael addition of acrylate to surface amines were prepared (**Figures S2-S4** and **Tables S2-S4** in Supporting Information).

The extension of the reaction time from 24 h (samples **S1B-S6B**) to 48 h (samples **S1D-S6D**) did not result in a significant change in the composition and structure of the samples, and therefore samples of the series B and D are equivalent from the luminescence and structural point-of-view. The same applies to the samples without Eu^{3+} and Tb^{3+} ions prepared with a reaction time of 24 h (samples **S1A-S6A**) and 48 h (samples **S1C-S6C**).

The samples were analyzed by X-ray photoelectron spectroscopy (XPS) before and after the formation of the Eu^{3+} and Tb^{3+} complexes, confirming the functionalization of the Si surface and the incorporation of the Ln^{3+} ions (**Figure 2**)

Field emission scanning electron microscopy analysis of the samples show a very smooth surface and a uniform chemical composition for the samples with medium and small polymer chain lengths, whereas some degree of granulation and chemical heterogeneity is discerned for the sample with the longest polymer length. Atomic force microscopy analysis (Figures S5-S8 in Supporting Information) shows a clear increase of the surface roughness on the Ln^{3+} functionalized samples concerning amine-modified samples. This loss of functionalization effectiveness in long polymeric chain lengths is also observed in the Ln^{3+} -doped samples (**S1B** to **S6B**), and it is reflected in a lower concentration of Eu^{3+} and Tb^{3+} on the surface (Tables S2 and S3 in Supporting Information).

2.2. Photoluminescence

The photoluminescence of the samples prepared with distinct acacPEGA chain lengths or with different functionalization routes do not show notable differences (Figures S10-S17 in Supporting Information) and, thus, we selected for further investigation three representative samples treated at 48 h with the longest (**S1D**), middle (**S3D**) and shortest (**S6D**) polymer chain length.

The room temperature excitation spectra of the three samples, monitoring the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ (Tb^{3+}) and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (Eu^{3+}) transitions, are similar and dominated by broadband in the 250–290

nm range associated to the DPA ligand excited states (Figure S10 in Supporting Information).^[42] Increasing the temperature, the integrated areas of the $^5D_4 \rightarrow ^7F_5$ (Tb^{3+} , I_1) and $^5D_0 \rightarrow ^7F_2$ (Eu^{3+} , I_2) transitions decrease, by 70 and 30% respectively (**Figure 3** and Figure S12 in Supporting Information), meaning that the I_1/I_2 ratio is temperature-sensitive, as reported for other Eu^{3+}/Tb^{3+} -bearing materials.^[43-47] Figure S18 in Supporting Information presents the temperature evolution of the I_1/I_2 ratio in a single heating-cooling cycle for **S1D**, **S3D**, and **S6D**. During the heating from 295 to 369 K, the intensity ratio decreases linearly, probably due to the activation of nonradiative decay pathways involving the polymeric chains that depopulate the 5D_4 and 5D_0 emitting levels. The high energy of the DPA ligand triplet state, $\sim 27050\text{ cm}^{-1}$,^[46, 48] prevents the 5D_4 -to-ligand and 5D_0 -to-ligand energy back-transfer, discarding, then, any role of the ion-to-ligand back transfer in the decrease of the I_1/I_2 ratio as temperature increases. Furthermore, thermally activated Tb^{3+} -to- Eu^{3+} energy transfer is also settled out as no evidence of that transfer is found in the excitation spectra and lifetime measurements (in accord with the relatively low amount of the two ions, making the energy transfer extremely improbable). Moreover, the I_1/I_2 ratio shows a hysteretic behavior in a heating/cooling cycle (Figures S18 in Supporting Information). This is not related to the optical bistability of Ln^{3+} -bearing crystals excited with high power densities,^[49] but to changes in the conformation of the acacPEGA polymer chains, as reported previously by some of us in an analogous polymer.^[36, 50] On cooling, two linear regimes are distinctly discerned, whose intersection occurs at the same temperature for all the samples, ($T_c = 313 \pm 1\text{ K}$) (Figure S18 in Supporting Information). This indicates that the two regimes are independent of the polymeric chain length and different functionalization routes used (Figures S13-S14 in Supporting Information), reaffirming the crucial role of the temperature dependence of the polymer conformation on the temperature dependence of the I_1/I_2 ratio. The hysteretic response of the samples will be used in 2.3.2 to demonstrate sequential logical operations.

The thermometric response of these systems was accessed and summarized in Table S6 and Figures S18-S20 in Supporting Information. The maximum relative thermal sensitivities are 2.84, 2.23 and 2.27% K^{-1} for **S1D**, **S3D** and **S6D** respectively. These values are high enough to consider the application of these samples as luminescent molecular temperature probes (**Table 2**), particularly in the physiological range of temperatures interesting for biological applications. However, the focus of this manuscript is to use Ln^{3+} luminescence, including its temperature dependence, to mimic molecular logic and computing through physical inputs.

2.3. Molecular Logic Gates

2.3.1. Combinational Logic Functions

The Si arrays functionalized with Eu^{3+} and Tb^{3+} ions emitting centers can be employed for the construction of optically active molecular logic gates, using exclusively physical inputs and outputs. For the following discussion, we use **S1D** as an illustrative example. We tackle the design of molecular logics exploiting the heat and the excitation wavelength as logical inputs and several emission intensity ratios as the logical outputs (Figure 3d,e). The excitation light is always assumed as an input in the reports on all-optical or all-photonic logic gates,^[37, 51-54] however it is the first time that temperature increase (or heat) is being used as an input for molecular logical gates. Using simply the dependence of the emission spectra upon 271 nm excitation as the temperature is being raised (**Figure 4a**) we clearly observe changes in the emission profile that can be quantified using three ratiometric outputs: (i) I_1/I_2 , defined above, (ii) I_{2A}/I_{2B} , involving the intensity peak ratio of two Stark components of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition, Figure 4b, and (iii) I_{3A}/I_{3B} , an intensity peak ratio of two Stark components of the $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transition Figure 4c. The temperature evolution of these intensity ratios is plotted in Figure 4d,e. Whereas I_1/I_2 and I_{2A}/I_{2B} decrease 66 and 50%, respectively, as temperature increases 70 degrees, for I_{3A}/I_{3B} this same increment results in a 55% enhancement, relatively to the value at

300 K. These dissimilar evolutions upon heating induced the development of one inhibit (INH) and one AND logical gates.

Using the I_1/I_2 ratio (or I_{2A}/I_{2B}) as logical output we set a threshold value of 0.06 to define the logical output TRUE (1, when $I_1/I_2 > 0.06$) or FALSE (0, the opposite case). The logical inputs are the excitation at 271 nm (denoted by UV) and a temperature increase of 70 degrees (denoted by ΔT). This logical gate does not produce any output without UV and thus the logical output is 0. Only in the presence of excitation at 271 nm and in the absence of ΔT the logical output is 1 and, thus, this is the transfer function characterizing the INH logic gate (Figure 4a,c,e). We notice the high obtained switching ratio (66% of the initial value); defined as the relative change of the output signal when the logical output signals change from “1” and “0”.

The I_{3A}/I_{3B} ratio is used as logical output setting a threshold value of 0.8 to define the logical output TRUE (1, when $I_{3A}/I_{3B} > 0.8$) or FALSE (0, the opposite case). The logical inputs are the same defined for the INH logic gate. Again, this logical gate does not produce any output without 271 nm excitation and thus the logical output is 0. Only when the system is excited at 271 nm and heated by ΔT the logical output is 1 and, thus, this is the transfer function characterizing the AND logic gate (Figure 4b,d,f). This gate operates based on the distinct thermal population ratio of two 7F_4 Stark components. We observe that on one hand, the integrated intensity of the high-energy 7F_4 Stark component is almost temperature independent whereas that of the remaining ones displays a strong temperature dependence (Figure S17 in Supporting Information) evidencing the hypersensitive nature of the $^5D_0 \rightarrow ^7F_4$ Eu^{3+} transition.^[55] The switching ratio of this gate is about 60%, a similar value to that calculated from the data in reference ^[56] (67%).

Observing the inputs homogeneity on the two logical gates described above we design a port constituted by the integration of the AND and the INH logic gates. The resulting logical gate, presented in Figure 4g,h, is a 1:2 demultiplexer (DEMUX). This is a clear step forward relative

to our previous work^[36] (the first example using Eu^{3+} and Tb^{3+} emissions and temperature for logic applications), that reported the same DEMUX using a much complicated and time-consuming strategy.

2.3.2. Sequential Logical Functions

Contrarily to the combinational logic functions described in the previous section, in the sequential logic functions the output signal switches ON when a specific inputs order is set,^[57-59] implying a memory function of the device. The KEYPAD LOCK function has been reported previously employing both chemical^[58, 60-62] and physical^[37, 61, 63-68] inputs. Here, a KEYPAD LOCK was implemented using the temperature increment ΔT and the characteristic temperature T_c as physical inputs (**Figure 5a**). We set the logical value 0 for the ΔT input representing the switching off of the temperature controller and the T_c input in the $T < T_c$ range. The logical value 1 is set for the switching on of the temperature controller and $T = T_c$, respectively. Each input might be 0 or 1, leading to eight possible two-digit order combinations. From this state, when both physical inputs present the logical value 0, the output is strictly $(I_1/I_2)_0$. Regardless of the order in which the temperature controller is switched on ($\Delta T > 0$) while the second input is $T < T_c$, the output will be $(I_1/I_2)_c < (I_1/I_2) < (I_1/I_2)_0$. On the other hand, when the temperature is fixed to T_c and no heating source is acting (and *vice-versa*), the output will be $(I_1/I_2)_c$. When the heating is on, and then $T = T_c$, the output yields $(I_1/I_2)_c \leq I_1/I_2 < (I_1/I_2)_0$.

As the initial state, we consider the sample a room temperature (denoted by $(I_1/I_2)_0$, Figure 5a,c). The only possibility to open the KEYPAD LOCK is to have first the system at $T = T_c$ and then impose a ΔT such that $I_1/I_2 < (I_1/I_2)_c$.

2.3.3. Arithmetic Operations

A key requirement of digital computers is the ability to use logical functions to perform arithmetic operations. Traditionally the operation is implemented using an exclusively or (XOR for the sum digit) and an AND logical gate (for the carry digit). We notice that using the *UV*

and ΔT inputs it is not possible to recover the XOR transfer function, so we implement the HALF-ADDER operation using the temperature increase $\Delta T = T_H - T_C$ (Figure 5a,b, logical value 1 means heating and 0 means no temperature increase) and the characteristic temperature value $T = T_c$ as inputs, and combining the I_1/I_2 output and the relative thermal sensitivity, defined by Equation (1).

Defining the logical value “1” for I_1/I_2 ratio lower than the threshold value $(I_1/I_2)_H$ we recall the AND logic gate (for **S1D** $(I_1/I_2)_H = 0.025$). The $(I_1/I_2)_H$ is defined as the ratio of integrated intensities on cooling corresponding to the temperature T_C . The temperature T_H is defined as the temperature value for the heating regime for which the $(I_1/I_2)_H$ is obtained, Figure 5a. For the XOR logic gate we use the S_r output defining the logical value “1” when S_r is in the range $S_C < S_r < S_H$ corresponding to the S_r values at room temperature and at T_H . The resulting HALF-ADDER logical gates arrangement is presented in Figure 5e and the corresponding truth table in Figure 5f.

Other operations can be implemented by simply playing with the logic gates arrangement. Replacing the AND gate by an INH gate a HALF-SUBTRACTOR is implemented (see Figure 5g,h). In this case, the arithmetic difference between two binary numbers is given by the difference digit that corresponds to the XOR logic gate and the borrow that is given by an INH gate. To generate the INH gate we simply take the first logical output as the $I_1/I_2 = (I_1/I_2)_c$ (Figure S21 in Supporting Information).

3. Conclusions

In summary, monolithic structures consisting of Si surfaces functionalized with acacPEGA polymeric chains of controllable length and functionalized with Eu^{3+} and Tb^{3+} ions are reported for applications in molecular logic and computing using exclusively physical inputs. Basic (AND, INH and DEMUX), sequential (KEYPAD LOCK) and arithmetic (HALF ADDER and HALF SUBTRACTOR) logic operations are demonstrated using the excitation light and the

temperature as inputs and ratios of emission intensities and the relative thermal sensitivity as outputs. The system is fully reversible containing $\sim 10^6$ emitting centers per μm^2 . Comparing the integration density of the $\text{Eu}^{3+}/\text{Tb}^{3+}$ based self-assembled polymer monolayer functionalized Si surface with that of the modern Si-based chips ($\sim 10^2$)^[6], we realize that the former presents 10^4 times higher value. Concerning the molecular logical devices reported so far, this work demonstrates clear advantages on the integration of distinct logical functions and reuse of the device for several cycles. In this work, there is no physical contact of the inputs with samples (like in those operating in wet conditions) that result eventually in the device contamination. The implementation of the reported logical functions on a functionalized Si-chip also permits better integration with current electronic devices and the use of Ln^{3+} -based emitting centers is quite suitable for emission and excitation by commercial detectors and LED sources. Although a molecular computer able of substituting current conventional computers is still just an ambitious future vision,^[24] judiciously designing molecular systems that perform logic functions is paving the way for developing useful molecular logic applications. Most of the drawbacks of the devices reported so far can be mitigated if solid samples interrogated by physical inputs are used, preferentially giving narrow emitting lines. In this context, Ln^{3+} -based emitting centers will certainly play a central role, since the same ions are widely spread in optoelectronic devices, smoothing the interface between novel molecular and conventional electronic devices.

Experimental Section

Materials: Europium(III) chloride hexahydrate ($\text{EuCl}_3 \cdot (\text{H}_2\text{O})_6$, 99.9%), Terbium(III) chloride hexahydrate ($\text{TbCl}_3 \cdot (\text{H}_2\text{O})_6$, 99.9%), 2,6-Pyridinedicarboxylic acid (DPA, 99%), *tert*-butyl acetoacetate, APTES, Diethyleneglycol (DEG), PEGX (where X=200, 300, 400, 600, 1000 and 3000 Da is the Mw molecular weight), N,N-dimethylaniline (DMA), and acryloyl chloride (97%) were purchased from Aldrich and used as received.

Synthesis of the PEG polymer chains: The PEG chains were prepared as described in Supporting Information.

Preparation of SiO₂ coated wafers: p-type monocrystalline Si wafers (Okmetic) were coated with a SiO₂ layer of 1083.0±11.3 nm thickness by Plasma-Enhanced Chemical Vapor Deposition of TEOS (tetraethylorthosilicate) at 380°C, and a pressure of 1 atm.

Surface activation: The silicon wafers were cut in 1 ×1 cm² dices, washed with ethanol and acetone and dried under nitrogen. Surface hydroxylation was performed by O₃ treatment for 10 minutes using a UVO-cleaner Model 342 (Jelight Company Inc., USA).

Amine surface functionalization: Functionalization with amine groups was achieved by sol-gel reaction with APTES. The APTES coating was carried out by vapor deposition, as described in our previous publication.^[36] Briefly, the surfaces together with a vial containing 1 mL of APTES were placed inside a desiccator previously thermostated at 80°C and connected to a vacuum. The desiccator was pumped down and sealed off. The samples were left in contact with the APTES vapor for 3 hours. Afterward, the samples were washed with acetone, dried under nitrogen, and cured in an oven at 50–60°C for 20 minutes.

Grafting PEG polymer chains to the silicon substrates: The PEG polymer chains grafting were achieved by Michael's reaction of acrylate acacPEGA terminal groups with surface amine groups. After coating with APTES, the silicon surfaces were immersed in acacPEGA solution (samples **1b-6b**, 8 mM, Supporting Information) in the water at pH=8.5 and allowed to react at 60°C, washed with distilled water and dried under nitrogen flux. The reaction was carried out individually for each wafer in an Eppendorf containing 2 mL of an 8.9 mM aqueous solution of the polymer. Two series of silicon substrates with grafted polymer chains were prepared, labeled as **S1A-S6A** for a Michael reaction time of 24h and as **S1C-S6C**, for a Michael reaction time of 48h (Table 1).

Anchoring of lanthanide coordination compounds: Europium and terbium ions in a 1:3 molar ratio were attached to the polymer self-assembled monolayer by coordination to the β-ketoester polymer terminal groups in a 1:1 polymer/Ln³⁺ ratio. The polymer-coated wafers were placed in a vial with 2 mL of water, to which it was added 15.8 μL of NaOH 1M, 100 μL of a solution of EuCl₃(H₂O)₆ (1.44% w.) and 100 μL of a solution of TbCl₃(H₂O)₆ (4.42% w.), and the pH was adjusted to 6.7. After 3 hours, 340 μL of a solution of DPA (15.75 mg/mL, pH 6.76) was added. The complex was formed overnight. The surfaces were then thoroughly washed with distilled water and dried under nitrogen. Two series of samples were obtained, samples **S1B-S6B** (deriving from samples **S1A-S6A**), and samples **S1D-S6D** (deriving from samples **S1C-S6C**) (Table 1).

Surface characterization by XPS: The X-ray photoelectron spectroscopy (XPS) analysis was carried out using a Kratos Axis Ultra spectrometer employing a monochromatic Al K_α (1486,6 eV)10 mA, 15 kV) X-ray source and a power of 150 W. All samples were introduced in the analysis chamber simultaneously and were analyzed in the same experimental conditions. To avoid any induced effect in the chemistry of the samples, they were analyzed as received without any previous etching. Differential surface charging was minimized using a charge neutralizer system (flood gun). Survey spectra were recorded using an analyzer pass energy of 160 eV and 1.0 eV energy step. High-resolution spectra of C 1s, O 1s, N 1s, Si 2p, Eu 3d, and Tb 3d regions were collected using pass energy of 20 eV 0.1 eV energy step. The spectra were analyzed using CasaXPS® software. The background for all spectra was subtracted using a Shirley baseline. Due to the use of charge neutralizer, spectra need to be calibrated. Binding Energies (B.E.) were referenced to the C 1s (C-C) peak at 285.0 eV.

Photoluminescence characterization: The emission spectra were recorded with a modular double grating excitation spectrofluorimeter with a TRIAX 320 emission monochromator (Fluorolog-3, Horiba Scientific) coupled to an R928 Hamamatsu photomultiplier, using a front face configuration. A 450 W Xe arc lamp was used as the excitation source. Both recorded emission and excitation spectra were corrected with the spectrofluorimeter optical spectral response and the spectral distribution of the lamp intensity using a photodiode reference detector respectively. On the other hand, the temperature was controlled using an IES-RD31 controller and a Kapton thermofoil heater from Minco mounted on a copper holder and monitored using a thermocouple thermometer Barnant 100 (model 600-2820) with an accuracy of 0.1 K, accordingly to the manufacturer. The temperature ramp in the heating-cooling cycles is about 0.25 K min⁻¹.

Thermometric performance: The relative thermal sensitivity (S_r) was calculated using:

$$S_r = \frac{1}{\Delta} \left| \frac{\partial \Delta}{\partial T} \right| \quad (1)$$

and the temperature uncertainty using:

$$\delta T = \frac{1}{S_r} \frac{\delta \Delta}{\Delta} \quad (2)$$

being $\delta \Delta / \Delta$ the relative uncertainty in Δ calculated using:

$$\delta \Delta = \sqrt{\left(\frac{\delta I_1}{I_1} \right)^2 + \left(\frac{\delta I_2}{I_2} \right)^2} \quad (3)$$

where $\delta I_i / I_i$ ($i=1,2$) is calculated dividing the readout fluctuations of the baseline by the maximum value of each intensity, i.e. I_1 and I_2 . As the integrated areas are calculated from the same emission spectra $\delta I_1 = \delta I_2 = \delta I$. The experimental $\Delta = I_{Tb} / I_{Eu}$ values were fitted to straight lines (Table S6 in Supporting Information) and the resulting parameters were used to calculate S_r and δT .

Supporting Information

Supporting Information is available from the Wiley Online Library or from the authors.

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Figures

Figure 1. (a) Schematic diagram of Si surface functionalization with the self-assembled monolayers incorporating the Ln³⁺ ions showing the activation and functionalization steps. (b) The structural formula of monolayers functionalized with the Ln³⁺ ions. (c) Schematic representation of the **S1D**, **S3D**, and **S6D** samples. The details of the logic arrays structure and fabrication are summarized in Table 1.

Figure 2. XPS spectra of the C 1s region for short (samples **S6A**, **S6B**) medium (**S3A**, **S3B**) and long (**S1A**, **S1B**) acacPEGA chains in samples (a) A series (b) B series (Table 1 of the main text). The carbon oxidation states in acacPEGA are C-C (C_{1s}1 and C_{1s}2), C-O (C_{1s}3), O-C-O/C=O (C_{1s}4) and O-C=O (C_{1s}5). Remarkable differences are found in the C-O signal depending on the length of the acacPEGA chain. Series B and D, containing Eu³⁺ and Tb³⁺ ions, show the same behavior. (c) XPS spectra of **S3A** (before anchoring the complexes) and **S3B** (after anchoring the complexes). The Tb 3d and Eu 3d regions are highlighted to showing the differences resulting from the anchoring of the Ln³⁺ complexes. (d) Evolution of Eu 3d core level with the length of the acacPEGA organic chain, for short (**S6B**), medium (**S3B**) and large (**S1B**) chains.

Figure 3. (a) Emission spectra of **S6D** in the 295–369 K range under 271 nm excitation. The Tb^{3+} and Eu^{3+} transitions are signed in green and red respectively. The asterisk marks the spectral region of overlap between the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (Eu^{3+}) and the $^5\text{D}_4 \rightarrow ^7\text{F}_4$ (Tb^{3+}) transitions. The peak intensities I_1 , I_2 and I_3 are also identified. Magnification of (b) $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (displaying the I_{2A} and I_{2B} components) and (c) $^5\text{D}_0 \rightarrow ^7\text{F}_4$ (displaying the I_{3A} and I_{3B} components) transitions. The blue and red spectra correspond to the spectra measured at the lowest (295 K) and the highest (369 K) temperatures. Temperature dependence of the (d) I_1/I_2 intensity ratio and (e) I_{2A}/I_{2B} and I_{3A}/I_{3B} intensity ratios. The threshold values (above which the logical value of the ratio is “1” and below is “0”) are identified by the horizontal lines.

Figure 4. Bar plot of the **(a)** I_1/I_2 and **(b)** I_{3A}/I_{3B} intensity ratios of **S1D** displaying a transfer function of inhibit 1 (INH1) and AND logical gates, respectively. The inputs used are the temperature increase (or heating, ΔT) and the 271 nm excitation (UV). The corresponding truth tables are presented in **(c)** and **(d)** and the schematic of the logical gates in **(e)** and **(f)**. Combining the INH1 and AND logical gates the demultiplexer gate (DEMUX), in **(g)**, is obtained. **(h)** The truth table for the DEMUX gate.

Figure 5. An illustrative plot of the (a) I_1/I_2 intensity ratio and (b) S_r of **S1D**. The vertical pointy lines mark the characteristic temperatures T_c and T_H , whereas the horizontal ones indicate the corresponding values of I_1/I_2 (a) and S_r (b). The other lines in a) are the best fit to experimental data. In a and b, the shadowed regions mark the ranges in which the logical output is set as the logical value “1”. (c) Bar plot of KEYPAD LOCK using the heating (ΔT) and T_c as inputs. The ON state below the threshold (interrupted line) is only accessible when the inputs are applied in the correct sequence (first T_c and then ΔT) leading to the lock opening, as shown in (d). Logic gates of arithmetic operations for (e) sum or (g) subtract two binary numbers. The corresponding truth tables are presented in (f) and (h).

Tables

Table 1. The Si- functionalized surfaces are labeled accordingly to the molecular weight (M_w , Da) of the PEG chains and the Michael addition reaction times ($t=24$ hours or $t=48$ hours) employed in the thermal treatment of the Ln^{3+} doped and undoped samples. Details of the sample's synthesis are given in Supporting Information.

PEG M_w	without Ln^{3+} ions		with Ln^{3+} ions	
	24 h	48 h	24 h	48 h
3000	<i>S1A</i>	<i>S1C</i>	<i>S1B</i>	<i>S1D</i>
1000	<i>S2A</i>	<i>S2C</i>	<i>S2B</i>	<i>S2D</i>
600	<i>S3A</i>	<i>S3C</i>	<i>S3B</i>	<i>S3D</i>
400	<i>S4A</i>	<i>S4C</i>	<i>S4B</i>	<i>S4D</i>
200	<i>S5A</i>	<i>S5C</i>	<i>S5B</i>	<i>S5D</i>
100	<i>S6A</i>	<i>S6C</i>	<i>S6B</i>	<i>S6D</i>

Table 2. Excitation wavelength (λ , nm), temperature range (ΔT , K), maximum relative sensitivity (S_m , % K^{-1}), and corresponding temperature (T_m , K) of illustrative Ln^{3+} -based thermometers involving the intensity ratio of the $^5D_4 \rightarrow ^7F_5$ and $^5D_0 \rightarrow ^7F_2$ transitions.

Material	λ	ΔT	S_m	T_m	ref.
Tb ³⁺ /Eu ³⁺ co-doped organic-inorganic di-ureasil hybrid	325	298-333	7.1	298	[47]
Eu _{0.25} Tb _{0.75} (tfac) ₃ ·H ₂ O	330	280-317	5.14	295	[69]
Tb ³⁺ /Eu ³⁺ co-doped organic-inorganic di-ureasil hybrid incorporating γ -F ₂ O ₃ nanoparticles	358	12-303	3.0	125	[70]
S1D	271	295-369	2.84	369	This work
S3D	271	295-369	2.23	369	
S6D	271	295-369	2.27	369	
Na[(Gd _{0.8} Eu _{0.1} Tb _{0.1})SiO ₄]	483.5	12-450	2.0	20	[71]
Zn ₄ O(bdc) ₃ : Eu ³⁺ /Tb ³⁺	325	303-473	1.8	473	[72]
Tb _{0.957} Eu _{0.043} cpda	335	40-300	1.77	250	[73]
Eu ³⁺ /Tb ³⁺ dpa complexes in acacPEGA	280	296-338	1.43	323	[36]
Eu ³⁺ /Tb ³⁺ co-doped mesoporous silica decorated with dppz ligands	295	10-360	1.32	260	[74]
Eu _{0.37} Tb _{0.63} -btc metal organic framework	296	313-473	0.68	313	[75]
NaGdF ₄ :Yb ³⁺ /Tm ³⁺ @Tb ³⁺ /Eu ³⁺ nanoparticles	980	125-300	0.49	300	[76]
Na[(Gd _{0.8} Eu _{0.1} Tb _{0.1})SiO ₄]	483.5	10-425	0.3	300	[71]
Tb _{0.8} Eu _{0.2} L	322	40-300	0.15	300	[77]
[Tb _{0.3} Eu _{0.7} (D-cam)(Himdc) ₂ ·(H ₂ O) ₂] ₃	277	100-450	0.11	450	[78]

Htfac=1,1,1-trifluoro-2,4-pentanedione; H₂bdc=1,4-benzenedicarboxylic acid; H₂dpa=2,6-pyridinedicarboxylic acid; H₃cpda=5-(4-carboxyphenyl)-2,6-pyridinedicarboxylic acid; dppz=dipyridyl-pyridazine; H₃btc=1,3,5-benzenetricarboxylic acid; H₂L=1,3-bis(4-carboxyphenyl)imidazolium; D-H₂cam=D-camphoric acid; H₃imdc=4,5-imidazole dicarboxylic acid.

Monolithic silicon-based structures incorporating Ln^{3+} complexes in self-assembled polymeric layers are developed for mimicking molecular logic and computing. Elementary logic gates (AND, INH and DEMUX), sequential logic (KEYPAD LOCK), and arithmetic operations (HALF ADDER and HALF SUBTRACTOR) are demonstrated here for the first time in non-wet conditions.

Keywords lanthanide, luminescence, molecular logic, computing, physical input

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Lanthanide Luminescence to Mimic Molecular Logic and Computing through Physical Inputs