Luminescent molecular logic gates: the two-input inhibit (INH) function

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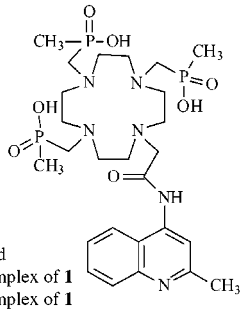
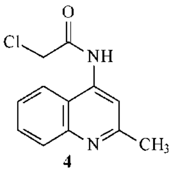
The Tb(III) complex 3, is the first example of a molecular logic gate corresponding to a two-input INHIBIT function, $A \wedge B'$ where the 'output', a sharp, line-like, terbium emission, is only observed with two chemical inputs (i) the presence of protons and (ii) the absence of molecular oxygen.

Developments in supramolecular chemistry and nanotechnology have stimulated interest in the construction of simple electronic or photonic driven systems and networks that function as molecular-level devices.[1] Examples include simple host–guest complexes as well as more advanced switches,[2] wires,[3] grids,[4] shuttles[5] and molecular machines.[6] Mimicking the functions of semiconductor logic gates used in modern computing is of particular interest,[7] where the relationship between input and the output may be described by truth tables, where 1 represents an active input/output and 0 an inactive one.[8] For a two input system there are 16 different logic gate functions.[8b]† Some of these functions have recently been demonstrated where ions and molecules are used as inputs,[7] including the ID (or YES), AND, OR and NOT logic functions designed by de Silva *et. al.*[9] and the XOR function designed by Balzani *et al.*[10] Among the remaining logic gates is the inhibit (INH) function which can be interpreted as a particular integration of an AND and a NOT logic functions, where the output signal is inhibited by one of the active inputs.‡ Recently the more complex three-input integrated INH logic gate was demonstrated.[11] However, the fundamental two-input INH gate has not been reported.



1 Free ligand
2 Eu(III) complex of **1**
3 Tb(III) complex of **1**



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Here, we demonstrate that in water the Tb(III) based quinolyl derived macrocyclic 1,4,7,10-tetraazacyclododecane (cyclen) conjugate, **3**, yields such an INH logic gate. The two inputs are H^+ (the nitrogen moiety of the quinoline acting as a proton acceptor) and O_2 (or rather the absence of O_2, since this input is not asserted when O_2 is present). The output signal is a delayed line like Tb luminescence (owing to the deactivation of the Tb $^5D_4$ excited state to the ^7F_J, $J = 6, 5, 4$ and 3), occurring at long wavelengths. These are important features since sharp, long wavelength emissions give minimal signal interference, critical for high performance signalling systems. Tb was chosen because, unlike Eu(III), pyridine based Tb and related complexes are known to be spectroscopically sensitive to O_2,[12] opening the possibility of a gate with O_2 as a second input. Moreover, lanthanide based cyclen derivatives have been shown to be kinetically stable in water.[13]

The syntheses of the α-chloroamide **4**, the free ligand in **1** and the Eu complex **2**, have previously been described; **2** was designed as a delayed Eu luminescence pH sensor.[14] **3**, the Tb complex of **1**, was synthesised in a similar manner to **2**, and obtained in 55% yield after treating **1** with $Tb(CF_3SO_3)_3$ in refluxing acetonitrile, followed by a purification on alumina. Complexation was established by electrospray (ES^+) mass spectrometry and ^{31}P NMR.§

The absorption spectrum of **3** showed a similar pH dependence to **2** and **4**, with λ_{max} at 314 nm ($\log \varepsilon = 4.18$) and a band at 261 nm under acid conditions with λ_{max} shifting to 295 nm ($\log \varepsilon = 4.0$) in the presence of base (isosbestic points at 299 and 271 nm). The Eu luminescence (occurring from $^5D_0$, $E = 17200\ cm^{-1}$)[15] of **2** (1×10^{-5} mol dm^{-3}) in H_2O under ambient conditions ([O_2] *ca.* 0.23 mmol dm^{-3}) was highly pH dependent when excited at 330 nm, with a 250 fold luminescence enhancement (LE) observed upon addition of acid ([CF_3CO_2H] = 3 mmol dm^{-3}/pH = 2.5). This pH dependence signals the protonation of the remote quinoline nitrogen moiety ($pK_a = 5.8$) and the 'tuning' of the so-called antenna effect, the energy transfer mechanism from the singlet excited state (S_1) of the chromophore (*via* the triplet, T_1) to the lanthanide excited state.[12,13]¶

The Tb luminescence of **3** (appearing at 491.5, 547.5, 588.0 and 623.0 nm, $J = 6, 5, 4$ and 3 respectively) was somewhat different. The excited state emission from $^5D_4$ ($E = 20500\ cm^{-1}$) was only weakly observed in alkaline solution under ambient conditions, with only a 1.7 fold enhancement upon acidification as seen in Fig. 1(a) ([CF_3CO_2H] = 1.26 mmol dm^{-3}/pH = 2.9) when excited at 330 nm. The corresponding fluorescence changes were more apparent; both a hypsochromic shift from 373 to 357 nm (isoemissive point at 387 nm) and intensity changes were observed upon acidification (two shoulders at 371 and 345 nm).

The measurements were repeated in degassed solution ('freeze–pump–thaw', [O_2] < 10^{-6} mol dm^{-3}). In alkaline solution the Tb emission spectrum and lifetime ($\tau_{Tb} = 0.39$ ms) were unaffected (owing to the inefficient population of the lanthanide excited state¶). However, in acid solution degassing yielded a *ca.*50 fold increase in the Tb luminescence intensity at 547.5 nm [Fig. 1(b)], and an almost threefold increase in the lifetime ($\tau_{Tb} = 0.98$ ms); these conditions 'switch on' the Tb emission [note the different scales in Fig. 1(a) and 1(b)]. The fluorescence spectra were however only marginally affected by the removal of O_2.

The small Tb emission in aerated acidic solution arises from the fact that the T_1 state of the quinoline (T_1 $E = 21978\ cm^{-1}$, as measured for the protonated form of **4**) is partly quenched by an ambient level of O_2. The Tb $^5D_4$ state can also participate in a back-energy transfer mechanism to the T_1 state (the energy difference being 1478 cm^{-1}); these combined processes lead to efficient quenching of the $^5D_4$ state (*i.e.* the Tb emission is switched off). Upon removal of O_2 this quenching process is largely suppressed leading to more efficient population of the Tb $^5D_4$ state (the antenna effect is more efficient) and switching on of the Tb emission.[12]

From the perspective of logic functions, the Eu emission (**2**) is determined only by the presence of single ionic input (H^+), back energy transfer from $^5D_0$ is inefficient and the complex is

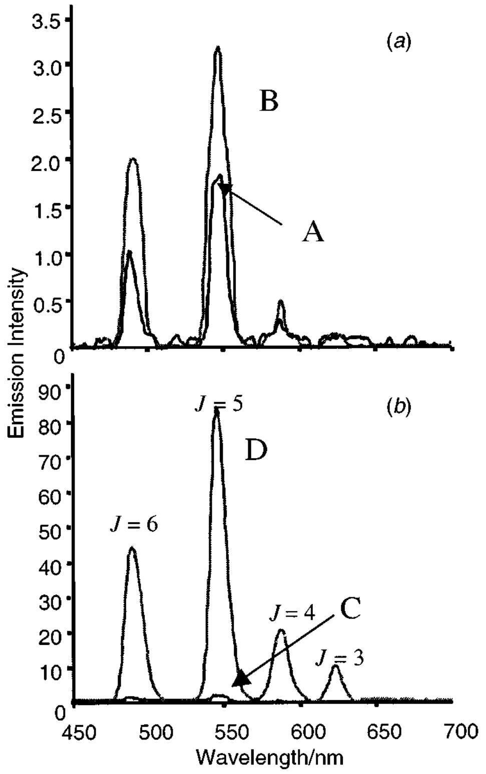

Fig. 1 Tb(III) emission of **3** (1×10^{-5} mol dm^{-3}) in water at 293 K, 10.0 mmol dm^{-3} NMe_4ClO_4 (to maintain constant ionic strength): (a) in *aerated* solution at: (A) pH = 11, (B) pH = 2.9; (*b*) in *degassed* solution at: (C) pH = 11, (D) pH = 2.9. Note the difference in the intensity scales.

thus insensitive to O_2,[7] and can as such be regarded as a pass logic function (YES[9] or ID[8b] logic gate). The emission of the Tb complex (**3**) is more interesting and is switched on *only* in the presence of H^+ and absence of O_2. Under other circumstances, the absence of H^+, the presence of O_2, or both, no significant Tb emission is observed (based on discrimination in LE factors; *ca.* 50 when O_2 *absent cf.* 1.7 with O_2 *present*, at 547.5 nm, Fig. 1). This behaviour may be conveniently described using logic notation,[7,9] written $A \wedge B'$, where A and B represent the H^+ and O_2 inputs respectively. The corresponding truth table is shown in Fig. 2(a), where an active output (X = 1, corresponding to emission) is obtained only when A = 1 and B = 0.[8] This logic gate is the inhibit (INH) function, Fig. 2(b).

(a)

A	B	X
0	0	0
0	1	0
1	0	1
1	1	0

(b)

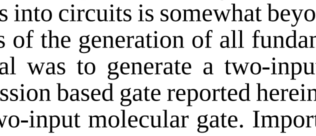

Fig. 2 (a) A truth table for the INH logic gate; inputs A and B correspond to the H^+ and O_2 respectively; X [Tb(III) emission], is the output signal. (b) The INH gate represented using a conventional gate notation; an active output signal (Tb emission) is obtained when A = 1 and B = 0.

Even though more advanced practical integration of such molecular level logic gates into circuits is somewhat beyond the horizon, progress depends of the generation of all fundamental logic operations. Our goal was to generate a two-input INH logic gate, and the Tb emission based gate reported herein is the first example of such a two-input molecular gate. Importantly, unlike many previous molecular logic gates where the output is a broad emission,[7,9,11] the output signal for **3**, is a set of line-like Tb emission bands occurring at long wavelengths (Stokes shifts of 160–300 nm for J = 6–3, respectively) with narrow bandwidth (*ca.* 10 nm) giving rise to a high signal quality. Complex **3**, is thus an important contribution to the development of molecular logic devices, not least since the current silicon based computer chips are expected to reach their physical limits in the near future.[16]

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Notes and references

† The ONE and ZERO functions are trivial, the output being a 1 or 0 respectively, regardless of the input. Four functions depend on a single input, namely both ID and both INV (or NOT) functions. The remaining ten are functions of two inputs, and of these AND, OR, XOR, NAND, NOR and EQU (or XNOR) satisfy commutation. The last four functions corresponding to INH and IMP gates do not satisfy commutation.

‡ The INH function, $A \wedge B'$, should not be confused with the NAND function, $(A \wedge B)'$.

§ ES$^+$: m/z 802.94 (15, $M^+ + 1$), 826.30 (13, $M + Na^+$). ^{31}P NMR (101 MHz, CH_3CN): δ 441.71 (br s) and 427.76 (br s) *cf.* δ 42.95 and 33.54 for **1**.

¶ Population of the quinoline S_1 (λ_{ex} = 330 nm) and subsequent population of the lanthanide excited state (the antenna effect) is inefficient in alkaline solution since the chromophore is only weakly absorbing at this wavelength. On acidification the S_1 population is greatly enhanced since absorption is shifted to longer wavelengths.

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