

A molecular tool kit for the variable design of logic operations (*NOR*, *INH*, *EnNOR*)

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Supporting Information

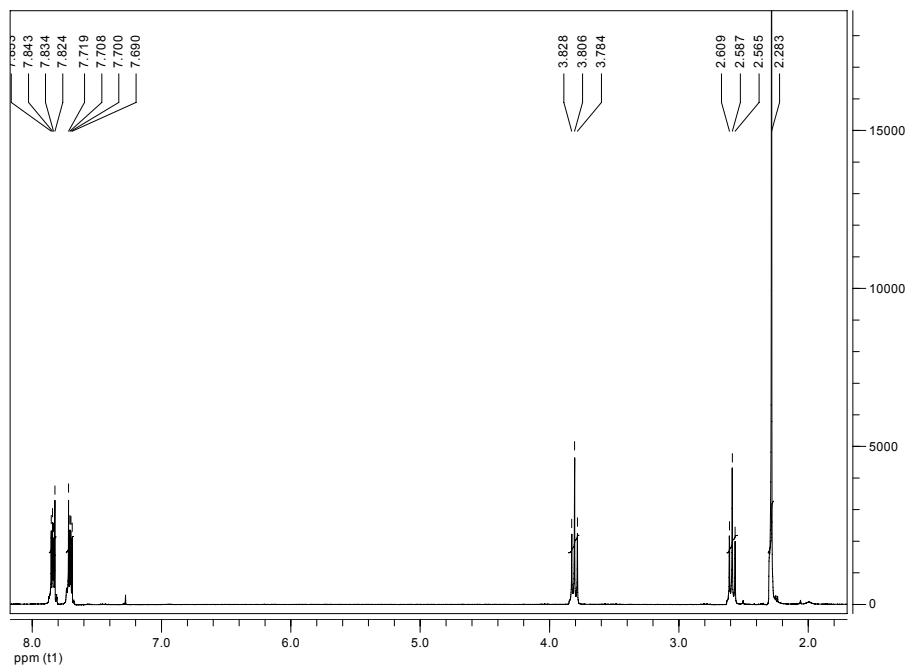
MATERIALS, METHODS, SYNTHESIS OF 1

Materials. Acetonitrile from ROMIL was of spectroscopic quality. The educts for the synthesis of **1** [phthalic anhydride (> 99 %, Aldrich), *N,N*-dimethylethylenediamine (> 98 %, Fluka)] were used as received. Terbium triflate (98%, anhydrous) and gadolinium triflate (98%, anhydrous) were from Aldrich. All tetra-*n*-butylammonium salts (chloride, iodide, bromide, nitrate, dihydrogenphosphate, perchlorate) were from Fluka (> 99 %). The removal of oxygen was accomplished by bubbling with argon. Titration data were fitted with the HYPERQUAD 2003 software.^{1,2} All measurements were done at room temperature (298 K), except indicated differently.

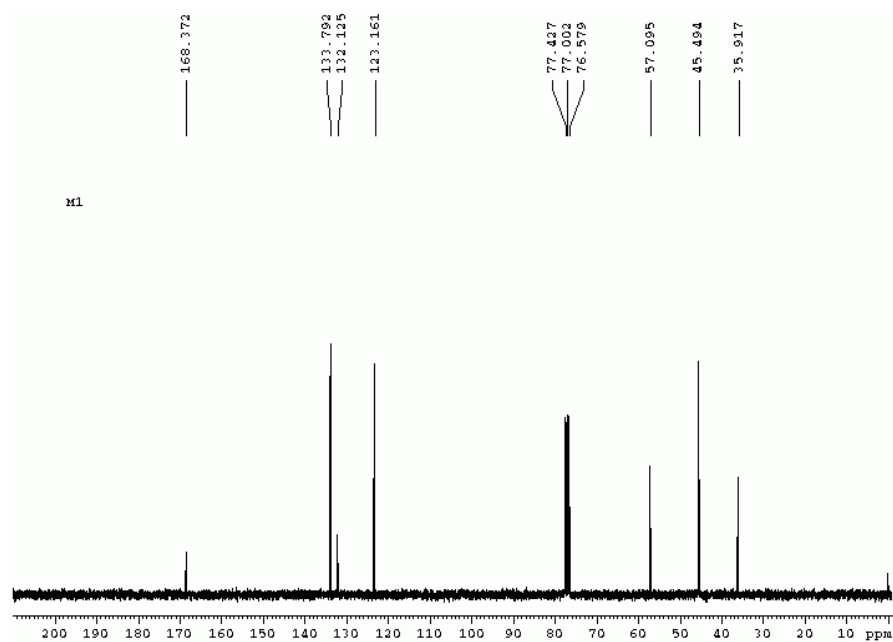
Synthesis of *N*-[(2-*N*',*N*'-dimethylamino)ethyl]phthalimide (1**).** Compound **1** has been reported before.³ We used a slightly modified procedure for its synthesis as described in the following. Phthalic anhydride (2.0 g, 13.5 mmol) was added under stirring and heating to an ethanolic solution (30 ml) of *N,N*-dimethylethylenediamine (1.5 g, 17 mmol). The resulting mixture was refluxed for 18 h. After cooling to room temperature a brownish precipitate formed which was filtered-off and re-crystallised from *n*-hexane. Compound **1** (0.9 g, 31 %) was obtained as a colourless solid (Found: C, 65.58; H, 6.48; N, 12.70. C₁₂H₁₄N₂O₂ requires C, 66.04; H, 6.47; N, 12.84 %); δ_{H} (300 MHz;

CDCl₃; Me₄Si) 2.28 (6H, s, Me₂N), 2.59 (2H, t, *J* 6.6, CH₂NMe₂), 3.81 (2H, t, *J* 6.6, CH₂N_{imide}), 7.69-7.72 (m, 2H, Ph), 7.82-7.85 (m, 2H, Ph); δ_C (75 MHz; CDCl₃; Me₄Si) 35.9, 45.5, 57.1, 123.2, 132.1, 133.8, 168.4.

¹H spectrum



¹³C spectrum



Absorption and Emission Spectroscopy. UV spectroscopic measurements were performed with a UV-8500 spectrometer from Techcomp Scientific Instrument. Tb(III) luminescence measurements were carried out with a Cary Eclipse spectrometer from Varian Instruments or a FL-3D spectrofluorimeter from Jobin-Yvon. Phosphorescence measurements were done with non-degassed samples on a Spex Fluorolog phosphorimeter at 77 K. Luminescence quantum yields were determined by using optically matched solutions of the Tb(III)-1 conjugate and quinine sulfate (Aldrich) in aerated 0.5 M sulfuric acid ($\Phi_f = 0.546$).⁴ Absorption and luminescence measurements (titration with Tb(III), quantum yields) were performed in presence of 0.05 M tetra-*n*-butylammonium perchlorate (TBAP). However, the effect of TBAP on Tb(III) luminescence lifetimes was found to be small: $\tau_{lum} = 1.1$ ms and 1.3 ms, with and without TBAP, respectively. On the other hand, in the case of anion additions the presence of TBAP gave rise to smaller enhancement factors than observed without TBAP. Therefore, the latter experiments were done without TBAP.

Laser-Flash Photolysis. Acetonitrile solutions (argon-outgassed for triplet state measurements; air-equilibrated or oxygen-saturated for triplet quenching by oxygen) were irradiated with a 308 nm laser pulse (GSI Lumonics Pulsemaster 846 excimer laser operating with a XeCl fill, fwhm *ca.* 10 ns, pulse energy 80 mJ). The decay kinetics (two averaged traces) of the phthalimide triplet state was followed at 340 nm, recorded with a transient digitiser, and analysed by means of nonlinear least-squares fitting. In the titration experiments with Tb(III) and trifluoroacetic acid the amplitude of the triplet-triplet absorption signal at 340 nm was determined from traces in a short time window (200 ns/div). Transient absorption spectra were recorded in the wavelength range of 300–600 nm.

ELECTRON TRANSFER THERMODYNAMICS, Tb(III) LIFETIMES VS. ANIONS

Calculation of Thermodynamics of Electron Transfer Quenching. The thermodynamics of intramolecular PET from the amine to the imide was calculated with the Rehm-Weller equation ($\Delta G_{\text{et}} = E_{\text{ox}} - E_{\text{red}} - E^* + C$). The following electrochemical potentials [*versus* SCE in polar solvent (MeCN, DMF)] and spectroscopic data were used: $E_{\text{ox}} = 0.96$ V for triethylamine as model,⁵ $E_{\text{red}} = -1.37$ V for *N*-methylphthalimide as model,⁶ $E^*(S_1) = 3.46$ eV and $E^*(T_1) = 3.03$ eV for *N*-(*N'*,*N'*-dimethylamino)methylphthalimide as model compound.⁷ The coulomb term C was taken as -0.06 eV.

Table S1. Tb(III) luminescence lifetime measurements in aerated MeCN solution ($[1] = 75 \mu\text{M}$, $[\text{Tb(III)}] = 75 \mu\text{M}$) in presence of different anions (without TBAP).

anion	number of equivalents	$\tau_{\text{lum}}/ \text{ms}$
CF_3SO_3^-	3 ^a	1.3
I^-	2	1.1
Br^-	2	1.3
Cl^-	2	1.6
NO_3^-	2	1.5
H_2PO_4^-	3	2.4

^a The triflate was added as Tb(III) salt, while in all other cases tetra-*n*-butylammonium salts were added to the triflate-containing solution.

ADDITIONAL FIGURES (SEE ALSO TEXT)

Fig. S1 Transient absorption (deaerated MeCN, $\lambda_{\text{exc}} = 308$ nm, 500 ns after laser flash) of **1** (150 μM) in presence of 1 eq. trifluoroacetic acid.

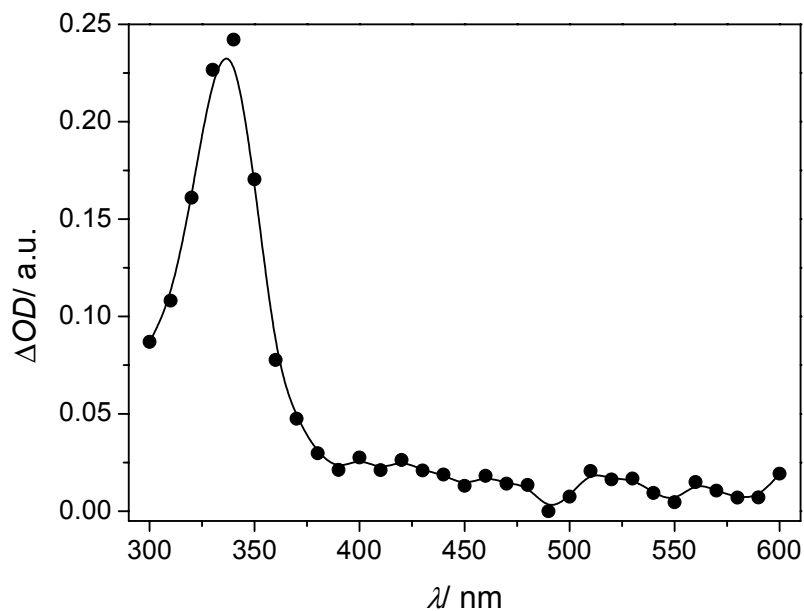
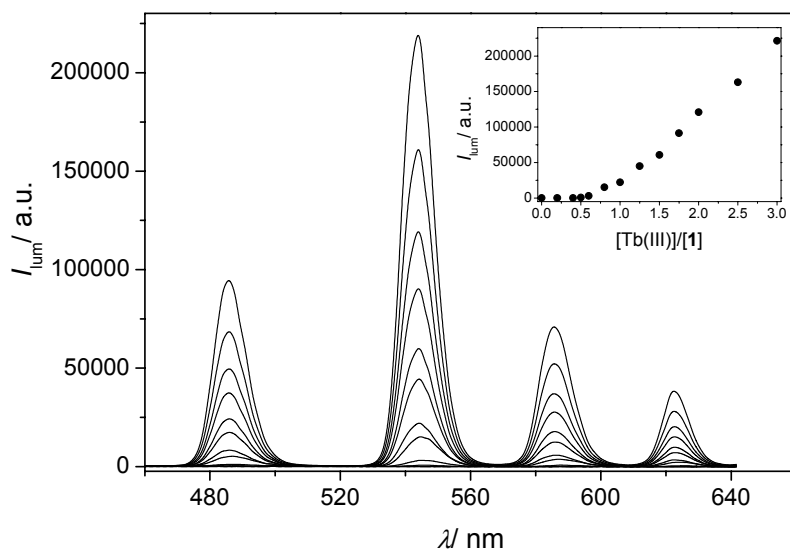


Fig. S2 Titration of **1** (75 μM) with Tb(III) in MeCN under argon. The inset shows the corresponding titration curve ($\lambda_{\text{exc}} = 285$ nm, $\lambda_{\text{obs}} = 544$ nm).



The observation of the Tb(III) luminescence in dependence on the lanthanide ion concentration yielded a different behaviour as compared to the titration observing the triplet-triplet absorption signal. Only at Tb(III) concentrations above 0.5 equivalents ($2[\text{Tb(III)}] > [1]$) the typical emission lines of the lanthanide were observed (inset Figure S1). The titration curve did not level-off until 3 equivalents of Tb(III). However, the triplet-triplet absorption titration showed clearly the formation of Tb1_3 and Tb1_2 , beside Tb1 . The absence of Tb(III) luminescence until 0.5 equivalents relates most likely to the fact that its observation might depend on the complex stoichiometry. Similar observations have been made for related naphthalimide-Eu(III) conjugates.⁸

Fig. S3 Normalised Tb(III) luminescence intensities of a 1:1 mixture with **1** (75 μM , MeCN) at $\lambda_{\text{obs}} = 544 \text{ nm}$ with different chemical inputs [TEA: 75 μM ; O_2 : 1.9 mM (air-equilibrated)]. The dashed line marks the threshold. The insets show the logic table and the respective logic representation of the *NOR* function.

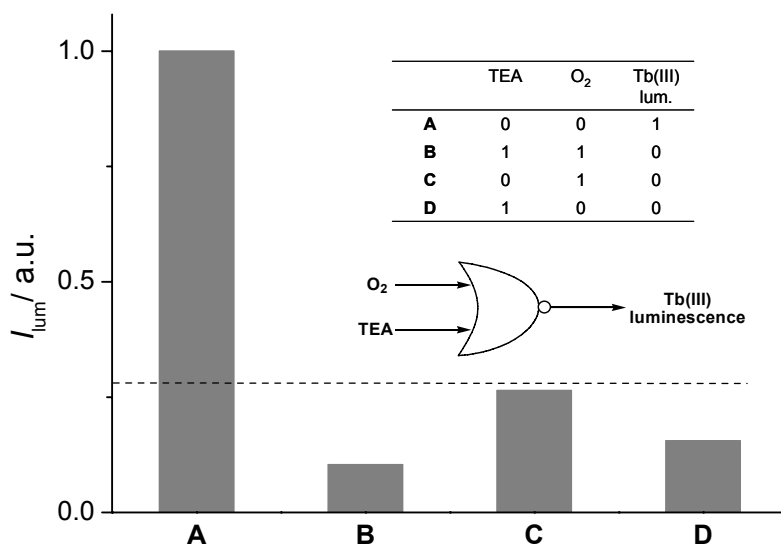


Fig. S4 Normalised Tb(III) luminescence intensities of a 1:1 mixture with **1** (75 μM , MeCN) at $\lambda_{\text{obs}} = 544 \text{ nm}$ with different chemical inputs [Cl^- : 150 μM ; O_2 : 1.9 mM (air-equilibrated)]. The dashed line marks the threshold. The insets show the logic table and the respective logic representation of the *INHIBIT* function.

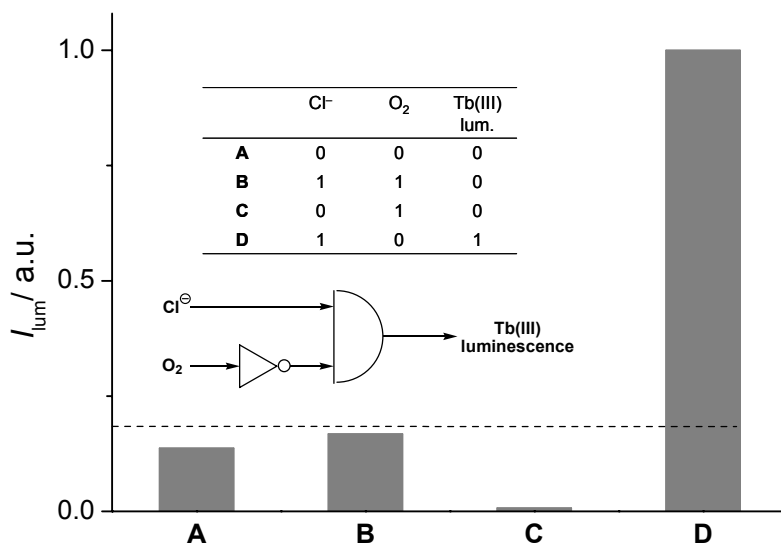


Fig. S5 Phosphorescence spectra ($\lambda_{\text{exc}} = 285 \text{ nm}$) of a 1:1 mixture of **1** (75 μM) and Gd(III) triflate in MeCN at 77 K.

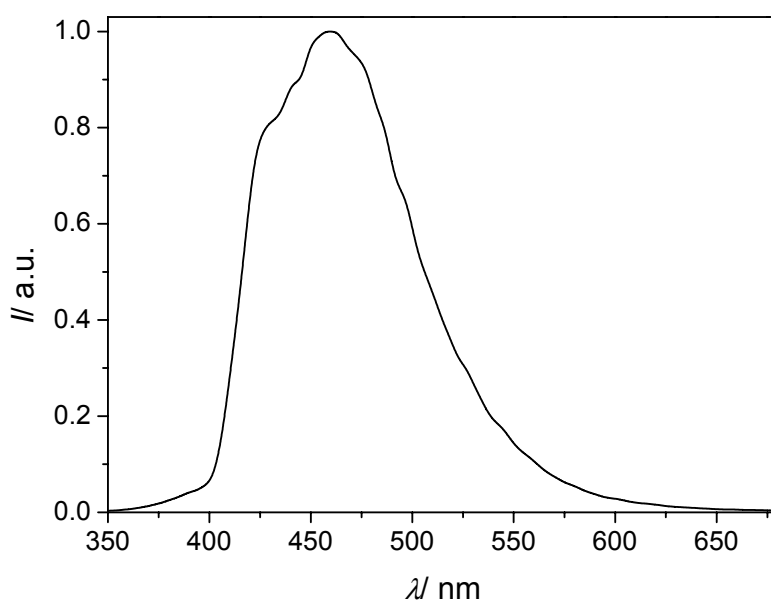
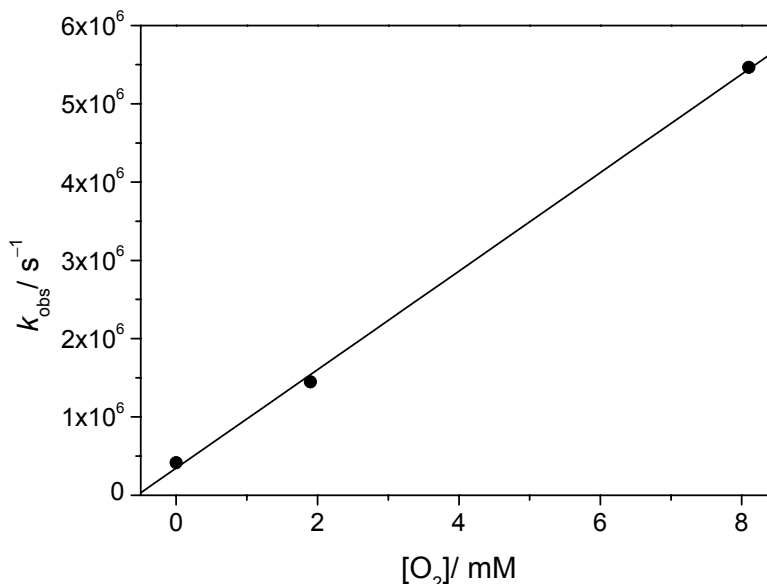


Fig. S6 Kinetic plot for the oxygen quenching of the excited triplet state of **1** (150 μM) in presence of 1 eq. Tb(III). Triplet decay rates were measured at $\lambda_{\text{obs}} = 340 \text{ nm}$ in absence of air ($[\text{O}_2] = 0 \text{ mM}$), air-equilibrated solution ($[\text{O}_2] = 1.9 \text{ mM}$) and oxygen-saturated solution ($[\text{O}_2] = 8.1 \text{ mM}$).



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