

# From PASS 1 to YES to AND logic: building parallel processing into molecular logic gates by sequential addition of receptors

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The synthesis and photophysical characterization of a novel molecular logic gate **4**, operating in water, is demonstrated based on the competition between fluorescence and photoinduced electron transfer (PET). It is constructed according to a 'fluorophore-spacer-receptor<sub>1</sub>-spacer-receptor<sub>2</sub>' format where anthracene is the fluorophore, receptor<sub>1</sub> is a tertiary amine and receptor<sub>2</sub> is a phenyliminodiacetate ligand. Using only protons and zinc cations as the chemical inputs and fluorescence as the output, **4** is demonstrated to be both a two-input AND and INH logic gate. When **4** is examined in context to the YES logic gates **1** and **2**, and the two-input AND logic gate **3** and three-input AND logic gate **5**, each with one or more of the following receptors including a tertiary amine, phenyliminodiacetate or benzo-15-crown-5 ether, logic gate **4** is the missing link in the homologous series. Collectively, the molecular logic gates **1–5** corroborate the PET 'fluorophore-spacer-receptor' model using chemical inputs and a light-signal output and provide insight into controlling the fluorescence quantum yield of future PET-based molecular logic gates.

## Introduction

A significant goal in the fields of materials science, nanotechnology and supramolecular chemistry is the design of multi-functional molecular devices with built-in orthogonality with respect to the function of individual components, yet cooperativity as a whole.<sup>1</sup> Hence, the development of molecular systems capable of performing digital information processing by Boolean logic operations continues to grow.<sup>2</sup> Molecules capable of carrying out a variety of sensing functions simultaneously, and that compute a composite result autonomously, have great potential for real-life applications.<sup>3,4</sup> In the area of luminescence sensing and molecular logic gates, the 'fluorophore-spacer-receptor' modular configuration, based on the competition between intramolecular photoinduced electron transfer (PET) and fluorescence, continues to be a popular design principle.<sup>5</sup> Its general applicability comes from a rational model that allows for various components, in particular the receptor sites, to operate in parallel in terms of substrate binding, yet collectively in terms of quenching the fluorophore emission.<sup>6</sup> Furthermore, with a well-established theory for PET, the designer has considerable forecasting power with respect to the feasibility of the electron transfer reaction, which can be predicted from simple thermodynamic calculations.<sup>7</sup>

The development of luminescent molecular logic gates starts from a selective choice of a fluorophore, preferably one with a reasonable quantum yield of fluorescence.<sup>8</sup> Any fluorescent or

luminescent polyaromatic hydrocarbon dye generally satisfies the elementary PASS 1 logic gate. Independent of the absence or presence of an input, the dye continues to emit a light signal. A natural progression was towards switches<sup>9</sup> or sensors<sup>10</sup> with two states by selection of the appropriate receptor for a specific analyte at a defined concentration.

Single-input 'off-on' PET systems that serve as sensors, or in digital terms as YES logic gates, have found application in biomedical diagnostics<sup>11</sup> and cell imaging.<sup>12</sup> Since PET-based luminescent systems are necessarily modular, we can develop sets of molecular logic gates with more than one receptor. The next advancement from YES logic is the cumulative addition of two YES gates in parallel with respect to the fluorophore, which are attached strategically, most often, with a methylene spacer. The first example incorporated switching functions dependent on exceeding the binding thresholds of receptors for protons and sodium ions.<sup>13</sup> A system with this arrangement is more commonly referred to as an AND logic gate.<sup>14,15</sup> The significance of incorporating three YES gates operating in parallel with three PET processes (or more in polymer films)<sup>16</sup> has demonstrated that redundancy does not impend device performance<sup>17</sup> and has opened the potential for new applications such as the development of 'off-on-off'<sup>18</sup> molecular systems and a 'lab-on-a-molecule' prototype.<sup>4</sup>

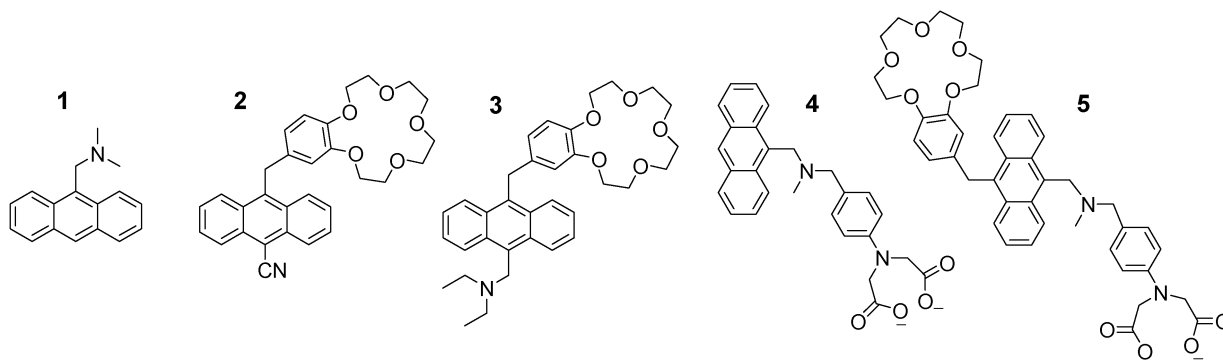
In this paper, we first describe the synthesis, photophysical characterization and operation of a novel two-input logic gate **4**, which on binding Zn<sup>2+</sup> and H<sup>+</sup> is shown to behave according to two-input AND and INH Boolean operations. Then, we compare the photophysical properties of a series of previously reported molecular logic gates<sup>4,15,19,20</sup> with an anthracene fluorophore based on the 'fluorophore-spacer-receptor' motif. Our starting point is the anthracene molecule, the reference PASS 1 logic gate.<sup>21</sup> We continue with one-input YES logic gates **1** and **2** for H<sup>+</sup><sup>19</sup> and Na<sup>+</sup>,<sup>20</sup> respectively, building up to two-input AND logic gates<sup>15</sup> **3** with a

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**Scheme 1** The structures of the logic gates 1–5.

‘fluorophore–spacer–receptor<sub>1</sub>–spacer–receptor<sub>2</sub>’ format for  $\text{Na}^+$  and  $\text{H}^+$ , and the new logic gate **4** for  $\text{Zn}^{2+}$  and  $\text{H}^+$ , and finally examining three-input logic gate **5** for all three analytes<sup>4</sup> as illustrated in Scheme 1. Logic gate **4** fills in the gap within a homologous series of fluorescence molecular logic gates, and provides perspective and insight into the rational design of ever more complex molecular logic gates with parallel processing capability.

## Results and discussion

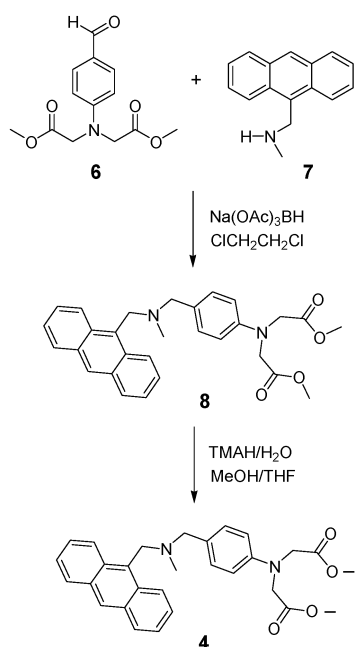
The synthesis of the target anthracene sensor **4** was prepared by a two step synthesis as shown in Scheme 2. The intermediate diester precursor **8** was obtained by reacting 4-*N,N*-bis-(methoxycarbonyl-methyl)amino-benzaldehyde **6** with aminomethylantracene **7** by reduction amination using sodium triacetoxyborohydride.<sup>22</sup> In the second step, the desired product was obtained by hydrolysis with excess tetramethylammonium hydroxide in a solution of methanol and tetrahydrofuran.

A dilute aqueous solution of  $10^{-5}$  M **4** exhibits an absorption spectrum with maximum wavelengths at 349, 367 and

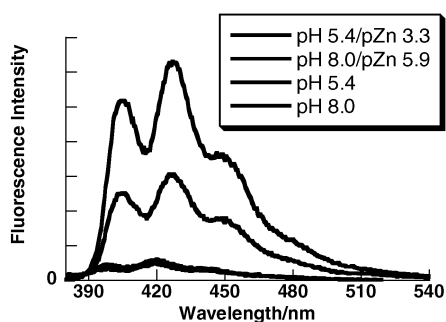
387 nm with molar extinction coefficients of 7600, 8000 and  $5500 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ . On titration with methanesulfonic acid or/and zinc sulfate the ground state UV-visible spectrum showed no significant change in the absorbance, and no new bands were observed. These observations are expected when the fluorophore and receptor modules are adequately isolated by methylene spacers.

The AND logic function of **4** was tested in water by observing the emission spectrum under four different experimental conditions with  $\text{H}^+$  and  $\text{Zn}^{2+}$  inputs (see Fig. 1 and Table 1). Excitation at 366 nm in the absence of either chemical inputs results in essentially no fluorescence with a quantum yield of only 0.02. This is in agreement with two thermodynamically favourable PET processes in the normal region of the Marcus parabola, though we have no further evidence regarding this assertion.<sup>7</sup> Addition of only methanesulfonic acid does not yield a substantial fluorescence signal either. In principle, the fluorescence signal should also be minimal with excess zinc sulfate at high pH. However, the chemical nature of  $\text{Zn}^{2+}$  restricts the lowest possible  $[\text{H}^+]$  that can be easily measured to about pH 8.0. The fluorescence signal decreases at pH values greater than 8, but the solution becomes turbid due to the precipitation of  $\text{Zn}(\text{OH})_2$ . However, when both chemical inputs are in excess of their binding thresholds, the fluorescence quantum yield is 0.19. Observance of AND logic behaviour was obtained in an IDA buffer solution at a pH of 5.4 with the  $[\text{Zn}^{2+}]$  equal to  $4.6 \times 10^{-4}$  M. Low input levels correspond to either zero in the case  $\text{Zn}^{2+}$ , or in the case of  $\text{H}^+$ , at a level that leaves the tertiary amine unprotonated about the physiological region of pH 8.

The logic characteristics of **4** can also be viewed as a two-input INHIBIT gate.<sup>23</sup> This is a case of logic reconfiguring arranged by alteration of input levels.<sup>24</sup> A higher concentration of  $\text{H}^+$  (low pH value) acts to veto the output result so that an output of 1 only results when  $\text{Zn}^{2+}$  is high and  $\text{H}^+$  is low. The low and high input levels of  $\text{H}^+$  correspond to  $10^{-5.4}$  M and  $10^{-2.0}$  M, respectively. At a pH of 2.0, the fluorescence from **4** is completely quenched resulting in the ‘off’ mode. The switching factor between the two digital states is *ca.* 10-fold. The dramatic switching factor may result as follows. At low pH the carboxylate units are protonated, which results in essentially no binding between the carboxylic acid units with the  $\text{Zn}^{2+}$ . Intramolecular hydrogen bonding of the phenyliminodiacetic acid moiety with the  $\pi$  orbitals of the



**Scheme 2** The synthesis of the logic gate **4**.



**Fig. 1** AND logic output fluorescence spectra of  $10^{-5}$  M **4** in water excited at 366 nm as a function of proton and zinc cation concentration.

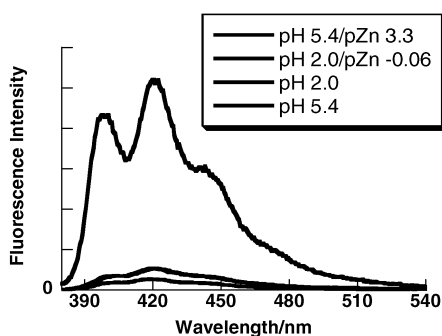
**Table 1** Truth table for the AND function for logic gate **4**<sup>a</sup>

Input <sub>1</sub> ( $H^+$ ) <sup>b</sup>	Input <sub>2</sub> ( $Zn^{2+}$ ) <sup>c</sup>	Output emission ( $\phi_F$ ) <sup>d</sup>
0 (low)	0 (low)	0 (low, 0.02)
0 (low)	1 (high)	0 (low, 0.08)
1 (high)	0 (low)	0 (low, 0.02)
1 (high)	1 (high)	1 (high, 0.19)

<sup>a</sup>  $10^{-5}$  M **4** excited at the isosbestic point of 366 nm in deionized water. <sup>b</sup> High and low input levels of  $H^+$  correspond to  $10^{-5.4}$  M and  $10^{-8.0}$  M adjusted with methanesulfonic acid and tetramethylammonium hydroxide (TMAH). <sup>c</sup> The high input levels of  $Zn^{2+}$  maintained with a  $Zn^{2+}$ -IDA buffer at pH values of 5.4 and 8.0 correspond to pZn values of 3.3 and 5.9, respectively. Calculations are based on  $\log \beta_{Zn^{2+}-IDA} = 7.3$  and  $\log \beta_{H^+-IDA} = 9.4$ . The low input level of  $Zn^{2+}$  corresponds to no added  $Zn^{2+}$ . <sup>d</sup> Output is considered high when  $\phi_F > 0.10$ .  $\phi_F$  obtained by comparison with 9,10-bis[(hydroxyethyl)aminoethyl]anthracene ( $\phi_F = 0.66$ )<sup>15</sup> in 1 : 4 MeOH : H<sub>2</sub>O (v/v) at pH = 3.5.  $\phi_F$  uncertainty is  $\pm 10\%$ .

excited anthracene system aids in quenching the fluorescence as the three-atom chain between aromatic units allows for conformational mobility.<sup>25</sup> Fig. 2 and Table 2 summarize the INHIBIT logic characteristics of **4**. It is also worthy to note that when the whole pH range from 2 to 10 is examined, **4** is also a  $Zn^{2+}$ -enabled,  $H^+$ -driven 'off-on-off' system.<sup>18</sup>  $H^+$ -driven 'off-on-off' cases fit ternary logic.<sup>26</sup>

The threshold ion binding constants for **4**, and the other logic gates, were determined by fluorescence titration experiments with the zinc metal cations or protons (or sodium cations) in methanol, 1 : 1 methanol-water or water. The



**Fig. 2** INHIBIT logic output fluorescence spectra of  $10^{-5}$  M **4** in water excited at 366 nm as a function of proton and zinc cation concentration.

**Table 2** Truth table for the INHIBIT function for logic gate **4**<sup>a</sup>

Input <sub>1</sub> ( $H^+$ ) <sup>b</sup>	Input <sub>2</sub> ( $Zn^{2+}$ ) <sup>c</sup>	Output emission ( $\phi_F$ ) <sup>d</sup>
0 (low)	0 (low)	0 (low, 0.01)
0 (low)	1 (high)	1 (high, 0.19)
1 (high)	0 (low)	0 (low, 0.02)
1 (high)	1 (high)	0 (low, 0.02)

<sup>a</sup>  $10^{-5}$  M **4** excited at the isosbestic point of 366 nm in deionized water. <sup>b</sup> Low and high input levels of  $H^+$  correspond to  $10^{-5.4}$  M and  $10^{-2.0}$  M adjusted with methanesulfonic acid and tetramethylammonium hydroxide (TMAH). <sup>c</sup> The high input levels of  $Zn^{2+}$  maintained with a  $Zn^{2+}$ -IDA buffer at pH values of 5.4 and 2.0 corresponding to pZn values of 3.3 and -0.06, respectively. Calculations are based on  $\log \beta_{Zn^{2+}-IDA} = 7.3$  and  $\log \beta_{H^+-IDA} = 9.4$ . The low input level of  $Zn^{2+}$  corresponds to no added  $Zn^{2+}$ . <sup>d</sup> Output is considered high when  $\phi_F > 0.10$ .  $\phi_F$  obtained by comparison with 9,10-bis[(hydroxyethyl)aminoethyl]anthracene ( $\phi_F = 0.66$ )<sup>15</sup> in 1 : 4 MeOH : H<sub>2</sub>O (v/v) at pH = 3.5.  $\phi_F$  uncertainty is  $\pm 10\%$ .

incorporation of the phenyliminodiacetate ligand, which introduces two negative charges, readily allowed for the study of **4** and **5** in aqueous solution. In cases where there is more than one receptor, the concentration of the other analytes was held in excess. The intensity  $I_F$  - pM profiles (note pM =  $-\log [M^+]$ ) from the titration experiments resulted in a sigmoidal curve typically over two logarithm units and were fitted according to eqn (1).<sup>27</sup>

$$\log[(I_{F_{\max}} - I_F)/(I_F - I_{F_{\min}})] = -\log [M^+] - \log \beta_M \quad (1)$$

Specifically, for the various logic gates we examined the concentration dependence of the fluorescence in the presence of  $H^+$ ,  $Zn^{2+}$  and  $Na^+$  where  $-\log [H^+] = \text{pH}$ ,  $-\log [Zn^{2+}] = \text{pZn}$ , and  $-\log [Na^+] = \text{pNa}$ . From the  $I_F$  - pM titrations, the binding constant  $\beta_M$ , which is the concentration when 50% of a receptor population is occupied by a specific analyte, is obtained.

Table 3 shows the fluorescence quantum yields and binding constants for the logic gates **1-5** shown in Scheme 1. The data for **1** are taken from literature values measured in water whereas the data for **2** and **3** were measured in methanol.<sup>15,20</sup> The parameters for **4** and **5** were obtained in aerated alcoholic or aqueous solutions. The objective of amassing this collection of data is to rationalize trends and distinguish irregularities, for instance, why **1** has an efficient fluorescence quantum yield of 0.71, in comparison to **5**, which has an inefficient fluorescence quantum yield of only 0.02. Our reference point is the anthracene fluorophore, although we would also be justified in using 9-methylanthracene, as each logic gate molecule has at least one methylene spacer. The literature fluorescence quantum yields for these two polyaromatic compounds in deaerated ethanol solution are 0.27 and 0.33, respectively.<sup>21</sup> Aerated ethanol solution quantum yields are about 20% lower. One would think that a reasonable assumption is that the maximum quantum yield for any sensor or logic gate with an anthracene fluorophore would be limited to these numbers. However, at first glimpse at Table 3, the reader is likely struck by the substantial emission quantum yield of 0.71 for the protonated 9-[(dimethylamino)methyl]anthracene.<sup>19</sup> This increase is due to electronic effects from protonation of the amino group. The  $\text{CH}_2\text{NMe}_2$  skeleton has a Hammett  $\sigma_p = 0.01$  whereas on protonation the  $\text{CH}_2\text{N}^+\text{HMe}_2$  group

**Table 3** Comparison of the quantum yield of fluorescence and binding constants for the logic gates **1–5**

Parameters	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>5</b>
Solvent	H <sub>2</sub> O	MeOH	MeOH	H <sub>2</sub> O	MeOH–H <sub>2</sub> O	H <sub>2</sub> O
$\phi_F^a$	0.71	0.22	0.22	0.19	0.07	0.02
$-\log \beta_{Na^+}$	—	3.0	2.7	—	0.9	–0.3
$-\log \beta_{H^+} = pK_a^b$	8.6	—	8.9	7.7	7.8	7.8
$-\log \beta_{Zn^{2+}}$	—	—	—	3.3	3.1	3.1

<sup>a</sup> All quantum yields  $\phi_F$  correspond to maximum values in the presence of excess protons and/or sodium cations and/or zinc cations.

<sup>b</sup> The aniline nitrogen centre has a  $pK_a = 4.2$  for **4**.

has a Hammett  $\sigma_p = 0.43$ . This parallels in comparison to 9-cyanoanthracene with a quantum yield of 0.93 and a  $\sigma_p = 0.66$ .<sup>28</sup> The dimethylamino and methylene groups adhere to their intended roles of ‘receptor’ and ‘spacer’ when the nitrogen atom is unprotonated. However, when the nitrogen atom is protonated the ‘spacer–receptor’ relationship loses its ideality because electric fields are transmitted across the short distance.<sup>29</sup> Not only is the PET pathway prevented as the nitrogen electron lone pair is bound to a proton, the (dimethylamino)methyl plays a rather under-rated role of contributing a fluorescence enhancement factor. Hence, the remarkable fluorescence quantum yield of 0.71 for **1** results from the cooperative contribution of no PET quenching and enhanced inductive/field effects.

A Na<sup>+</sup>-driven YES gate **2** results on replacing the CH<sub>2</sub>NMe<sub>2</sub> group in **1** with a benzo-15-crown-5-ether and outfitting the anthracene unit with a CN group.<sup>20</sup> The mere substitution of the CH<sub>2</sub>NMe<sub>2</sub> group with a benzo-15-crown-5-ether constitutes a Na<sup>+</sup>-independent PASS 1 gate with a quantum yield of 0.22.<sup>20</sup> The CN moiety is required to lower the anthracene LUMO for PET to be feasible. Replacement of the CN group with CH<sub>2</sub>NH<sup>+</sup>Me<sub>2</sub> maintained at a constant H<sup>+</sup> concentration is also a Na<sup>+</sup>-driven YES gate **3** in addition to a two-input AND logic gate.<sup>15</sup> Hence, compounds **2** and **3** both containing a benzo-15-crown-5-ether and an electron-withdrawing group have identical quantum yields of fluorescence in methanol.<sup>19,20</sup>

In the case of both **2** and **3**, the maximum fluorescence output is similar to what would be expected relative to anthracene taking into account the experimental values in Table 3 are in aerated solution. An identical emission quantum yield was observed when an AND logic gate with two benzo-15-crown-5-ethers, a tertiary amine and two anthracene fluorophores was demonstrated.<sup>17</sup> The decrease in quantum yield efficiency of **3** compared to **1** is due to a residual PET from the benzo-15-crown-5 ether to the excited anthracene, even when the (dimethylamino)methyl group is protonated. This type of behaviour results from the inability of a sodium ion to inadequately lower the HOMO energy of the benzo-15-crown-5 ether receptor, so a residual PET still competes with fluorescence as confirmed by a picosecond flash photolysis study.<sup>30</sup> Hence, the example suggests the energetics for PET, when favourable, will tend to dominate any electronic enhancement when the receptor binding is weak.

The success of **4** depends on the phenyliminodiacetate receptor for Zn<sup>2+</sup> which was pioneered by the Gunnlaugsson group.<sup>31</sup> A  $\log \beta_{Zn^{2+}}$  of 3.8 was determined in water, which is

similar to that for **4**. As for the fluorescence quantum yield of the corresponding anthracene-based system, no direct comparison can be made as it was not reported.<sup>31</sup> Other useful sensors for Zn<sup>2+</sup> and H<sup>+</sup> have been reported recently.<sup>24,32</sup>

An interesting observation for **4** worthy of a comment is the resulting quantum yield of 0.19 in the ‘on’ state (Table 3, entry 4). This result is similar to the maximum observed fluorescence quantum yields for **2** and **3** in methanol of 0.22, which both have a benzo-15-crown-5-ether. Thus, the binding of a proton at the tertiary amine and zinc cation at the phenyliminodiacetate by **4** results in an almost maximal fluorescence switching ‘on’. The benzo-15-crown-5 moiety in **5** has minimal, if any, influence on the proton and zinc binding constants as they are identical to those for **4**. Thus, the 10% decrease in fluorescence emission of **4** versus **2** and **3** is likely due to the difference in protic solution (*i.e.* water versus methanol). However, the fluorescence quantum yield for **5**, with all three receptors occupied by their respective analytes, is an order of magnitude lower in comparison to the quantum yield of **4**. This decrease in efficiency can be attributed to the residual PET from the benzo-15-crown-5 ether to the excited anthracene.<sup>28</sup> In retrospect, this is not surprising considering the  $-\log \beta_{Na^+}$  for sodium by benzo-15-crown-5 ether is –0.3 in water, which is three orders of magnitude lower than the binding constant for **2** in methanol. In 1 : 1 methanol–water, the  $-\log \beta_{Na^+}$  is definitely greater at 0.9 than in aqueous solution alone. Besides altering the solvent composite, a remedy for overcoming this shortcoming would be to replace the benzo-15-crown-5 ether in **5** with a stronger receptor for sodium in water such as *N*-(2'-methoxyphenyl)aza-15-crown-5 ether.<sup>11</sup>

## Conclusions

Compound **4**, which can be configured as an AND or an INH logic gate, senses for protons and zinc cations by communicating a fluorescence signal. The proton and zinc binding constants in water for **5** are identical to those for **4**. Thus, the order of magnitude lower fluorescence output observed for **5** relative to **4** is attributed to the weak binding of sodium ions to the benzo-15-crown-5-ether in aqueous solution, which does not effectively deactivate the photoinduced electron transfer pathway. This knowledge is useful for the rational design of functional molecules, such as complex molecular logic gates, with host–guest recognition properties. Whereas the driving force for electron transfer can be accurately predicted from electron transfer theories, predicting the quantum yield is still, at times, more an art than a science. However, by building on the past knowledge of simple models and Hammett parameters, we have some predictive power as to variations in fluorescence quantum yields. Taken as a whole, the series of related molecules provides insight into the rational design of ever more complex molecular logic gates with built-in orthogonality and cooperativity.<sup>1</sup>

## Experimental

### Instrumentation

Melting points were recorded on an Electrothermal 9100 capillary melting point apparatus and are not corrected. UV-visible spectra were recorded on a Perkin-Elmer Lambda 9



UV/vis/NIR spectrophotometer. Fluorescence experiments were performed on a Perkin-Elmer LS 55 luminescence spectrometer. pH measurements were performed with a Cranwell CR99 pH meter standardized with buffers at pH 4 and 7. Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer on NaCl plates as a thin film from CH<sub>2</sub>Cl<sub>2</sub>. Nuclear magnetic resonance spectra were recorded on a Bruker DPX spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> at 300.1 and 125.8 MHz. Chemical shifts are reported in ppm *versus* tetramethylsilane ( $\delta$  = 0.00) for <sup>1</sup>H NMR and CDCl<sub>3</sub> ( $\delta$  = 77.00) for <sup>13</sup>C NMR. LSIMS mass spectrometry was performed at 70 eV on a VG MS902 high-resolution mass spectrometer.

## Synthesis

Chemicals were readily available from Aldrich and used as received. 225 mg (0.85 mmol) of 4-*N,N*-bis(methoxycarbonylmethyl)amino-benzaldehyde **6** were reacted with 182 mg (0.82 mmol) of aminomethylanthracene **7** by reduction amination in 10 mL of 1,2-dichloroethane dried over molecular sieves. The compounds **6** and **7** were reacted with 290 mg (1.4 mmol) of sodium triacetoxyborohydride in the presence of a few drops of acetic acid.<sup>22</sup> The solution was stirred at room temperature for 48 h. Afterwards, the solution was diluted with 20 mL of dichloromethane, washed 3 times with saturated sodium bicarbonate, dried over sodium sulfate, filtered and evaporated to yield an orange gum. The crude ester **8** was purified by flash chromatography on silica gel using a hexanes–ethyl acetate eluant (*R*<sub>f</sub> = 0.45). A yellow crystalline solid was recovered in 31% yield.

Compound **8** (ester): mp 85–87 °C;  $\nu_{\text{max}}$ (NaCl)/cm<sup>−1</sup>: 3051, 2952, 2842, 2782, 1749, 1616, 1522, 1435, 1385, 1340, 1263, 1194, 1174, 1007, 885, 787;  $\delta_{\text{H}}$ (300 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>): 2.18 (s, 3H, −NCH<sub>3</sub>), 3.61 (s, 2H, CH<sub>2</sub> spacer<sub>1</sub>), 3.74 (s, 6H, OCH<sub>3</sub>), 4.14 (s, 4H, −NCH<sub>2</sub>CO−), 4.44 (s, 2H, CH<sub>2</sub> spacer<sub>2</sub>), 6.57 (d, 2H), 7.20 (d, 2H), 7.41–7.54 (m, 4H, anthracene), 7.96–8.02 (m, 2H, anthracene), 8.38–8.47 (m, 3H, anthracene);  $\delta_{\text{C}}$ (126 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>): 41.97, 52.06, 53.33, 53.42, 61.88, 112.13, 124.73, 125.13, 125.46, 127.28, 128.89, 129.15, 130.25, 130.63, 131.29, 131.41, 146.82, 171.39; *m/z*(EI): 471(M + H, 9), 470(M<sup>•+</sup>, 25), 411(9), 292(10), 291(16), 280(5), 279(19), 251(20), 250(100), 221(12), 220(7), 219(12), 192(33), 191(77), 178(14), 165(9), 147(12), 118(37), 97(12), 86(39), 84(63); LSIMS *m/z*: calcd for C<sub>29</sub>H<sub>30</sub>N<sub>2</sub>O<sub>4</sub> (M<sup>•+</sup>) 470.2206, found 470.2206.

The logic gate **4** was obtained by dissolving 60 mg (0.13 mmol) of **8** in a mixture of 5 mL of tetrahydrofuran (THF) and 3 mL of methanol (MeOH) in the presence of excess (~0.4 mL) tetramethylammonium hydroxide (TMAH) and refluxed for 6 h. The solvent was evaporated, and the resulting orange gum was dissolved in 7 mL of water and filtered. A yellow solid **4** was precipitated by acidification with 2 drops of concentrated HCl. Collection by vacuum filtration resulted in a 26% yield.

## Acknowledgements

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