Tuning the fluorescence of 1-imino nitroxide pyrene with two chemical inputs: mimicking the performance of an "AND" gate

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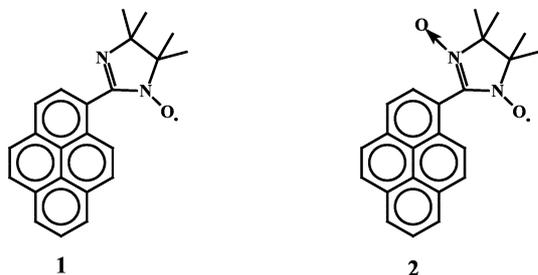[b] Graduate School, Chinese Academy of Sciences, Beijing 100080, China

The fluorescence of 1-imino nitroxide pyrene can be significantly enhanced only under the combined actions of Cys and CF₃COOH; such spectral change upon the actions of two chemical inputs mimics the performance of an "AND" gate.

Molecules with fluorescent cores and receptor units have been intensively investigated as luminescent PET (photoinduced electron transfer) signaling systems for over a decade.[1] These molecules show the potential to act as sensors of protons[2] and various metal ions.[3] More interestingly, the manner of fluorescence variation upon external stimulation (e.g. light irradiation and chemical inputs) observed for this type of molecule, in particular those with fluorescent cores flanked by two dissimilar receptor moieties, mimics the action of several logical operations (AND, NOT, OR, INHIBIT, XOR etc.),[4] exemplified by the original work of de Silva and coworkers.[5] It should be mentioned that spectral studies have been performed in solution in most cases, and thus such "logical operations" are limited to the solution phase.

Nitronyl nitroxides and imino nitroxides were initially discovered by Ullman in the 1970's and widely used as spin probes.[6] In 1991, the β-phase of p-nitrophenyl nitronyl nitroxide was found to be a bulk ferromagnet.[7] Since then, nitronyl nitroxide as well as the corresponding imino nitroxide has been intensively investigated for studies related to organic magnets. It was found that nitroxide was able to quench the excited states of fluorophores such as pyrene.[8] Besides, the imidazole unit of either nitronyl nitroxide or imino nitroxide can function as an electron donor. Accordingly, if imino nitroxide (or nitronyl nitroxide) is linked to a fluorescent core such as pyrene, two possible ways will be present to quench the fluorescence: one due to the presence of nitroxide, and the other one owing to the photoinduced electron transfer (PET) from the imidazole moiety to the fluorescent core (e.g. pyrene). These two quenching processes can be arrested by reactions with suitable chemical reagents (chemical inputs), and thus the fluorescence can be increased. Herein we present spectral studies of 1-imino nitroxide pyrene (1) under different conditions, and suggest the fluorescence change observed for the solution of 1 can be explained by an "AND" logic operation. These results demonstrate compound 1 may act as an "AND-type" chemical sensor. Consequently, imino nitroxide and nitronyl nitroxide are not only interesting as building blocks for organic magnets, but also appealing as chemical receptor units.
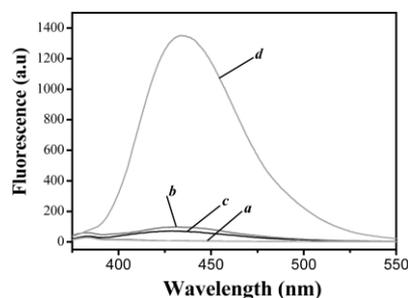
compounds that are scavengers of nitroxides, and as a result the fluorescence quenching due to the presence of the nitroxide moiety in 1 will be prohibited. For this purpose, cysteine (Cys, 1.5×10^{-4} M) was added to the solution of 1 (1.5×10^{-6} M). But, only slight fluorescence enhancement was observed (curve b in Fig. 1). Although the fluorescence intensity increased with the amounts of Cys added to the solution of 1, the fluorescence intensity at 434 nm increased only by about 5 times even when 100 equiv. of cysteine were used. Similar phenomena resulted if other thiol compounds instead of Cys were employed.

Protonation of the imidazole unit of 1 will reduce the electron donating ability, and hence the PET reaction from the imidazole unit to pyrene will be arrested. But, upon addition of CF₃COOH to the solution of 1 the fluorescence intensity was only slightly increased (curve c in Fig. 1). When 10 equiv. of CF₃COOH were added, the fluorescence intensity at 434 nm of the solution of 1 was enhanced by about 3 times compared with that of the pure solution of 1.[9]

However, the fluorescence intensity of the solution of 1 was significantly enhanced if the solution was sequentially reacted with Cys and CF₃COOH as demonstrated in Fig. 1 (curve d). Further experimental results showed that the reaction sequence of 1 with Cys and CF₃COOH had no effect on the fluorescence spectrum of the final solution. It should be noted that the fluorescence spectrum (λ_{max} = 434 nm) was red-shifted and became featureless as compared to that of pyrene. Quantitatively, the relative fluorescence quantum yields of 1 under different conditions were measured and they are listed in the table of Fig. 2. Obviously, the fluorescence of the solution of 1 was significantly increased only under the combined action of Cys and CF₃COOH. By using the principle of Boolean logic,[10] such fluorescence change in reponse to two chemical reagents can be interpreted by an "AND" operation with Cys (I1) and CF₃COOH (I2) as the chemical inputs and the fluorescence of 1 at 434 nm as the optical output (O1) as displayed in Fig. 2, in which the corresponding truth table is given. The fluorescence of the solution of 1 that had been treated with Cys and CF₃COOH was reduced to the original value by further addition of NaIO₄ and triethylamine, which can counteract the performance of Cys and CF₃COOH, respectively.

The fluorescence variation for the solution of 1 as discussed above can be explained as follows: separate reaction of 1 with Cys

Compound 1 was prepared by reduction of compound 2 with NaNO₂,† and compound 2 was synthesized according to the previous procedure.[6] As expected, the solution of compound 1 shows rather weak fluorescence. Imino nitroxide can be transformed to diamagnetic species after reaction with mercaptan

Fig. 1 Fluorescence spectra of 1 in THF with an excitation wavelength of 340 nm under different conditions: (a) pure solution of 1 (1.5×10^{-6} M); (b) after reaction with Cys (1.5×10^{-4} M); (c) after reaction with CF₃COOH (1.5×10^{-5} M); (d) after sequential reactions with Cys (1.5×10^{-4} M) and CF₃COOH (1.5×10^{-5} M).

Cys (*I1*) (concentration)	CF$_3$COOH (*I2*) (concentration)	Relative quantum yield[a]
0	0	0.0028
1.5×10^{-4} M	0	0.028
0	1.5×10^{-5} M	0.019
1.5×10^{-4} M	1.5×10^{-5} M	0.298

[a] Relative to 9,10-diphenylanthracene.

| *I1*	*I2*	*O1*[a]
0	0	0
1	0	0
0	1	0
1	1	1

[a] Fluorescence intensity of **1**

AND
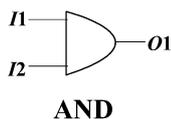
Fig. 2 The relative fluorescence quantum yields of **1** under different conditions (top); the corresponding truth table and the symbol of the "AND" logic gate (bottom).

and CF$_3$COOH (not in large excess) would lead to **3** and **4** respectively, and sequential reaction of **1** with both cysteine and CF$_3$COOH would lead to **5**. It is clear that the quenching process due to the PET reaction is still effective in **3**. Similarly, the quenching process due to the presence of nitroxide should also be effective in **4**. As a result the fluorescence of **1** after treatment with either Cys or CF$_3$COOH was weak. For **5**, however, both quenching processes are arrested, and hence the fluorescence of the solution can be significantly increased. Theoretical calculations were performed for **1**, **3**, **4** and **5**. The corresponding vertical transition energies and the oscillator strength on the basis of the optimized geometries were calculated,[11] and the results are in agreement with the experimental findings.

3   **4**   **5**
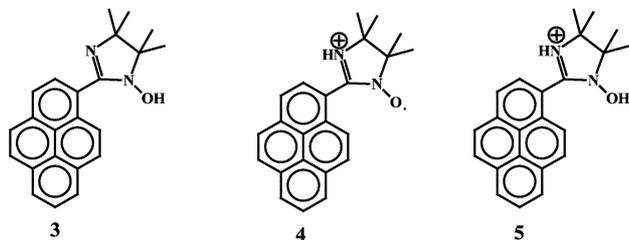
The same experiments were performed with 1-nitronyl nitroxide pyrene (**2**), and similar fluorescence spectral changes were observed. But, compared with compound **1** the fluorescence change with **2** was small after it was treated sequentially with Cys and CF$_3$COOH under the same conditions.

In summary, the fluorescence of 1-imino nitroxide pyrene (**1**) can be significantly increased only under the sequential reactions with Cys and CF$_3$COOH, and separate reaction with either Cys or CF$_3$COOH can not induce the fluorescence enhancement. Such fluorescence change upon two chemical inputs mimics the performance of an "AND" gate. Imino nitroxide is a paramagnetic species, and thus **1** and **4** are ESR active. Consequently, besides the fluorescence of the system, ESR signals can also be employed as the outputs. Hence, it is possible to mimic the function of new logic

circuits based on imino nitroxide derivatives. Further studies will include the synthesis of an analogue of **1** with long alkyl chains for the fabrication of LB films together with a suitable non-fluorescent amphiphilic compound, in order to conduct the corresponding spectral studies in the solid state and hence construct the solid-state "AND" logic gate.[12]

Notes and references

† Characterization data of compound **1**: mp 174–175 °C. FAB-MS: 342 (M + 1) (M), 343 (M + 2). IR (KBr, cm^{-1}): 1581.8, 1452.7, 1366.8, 1258, 1143, 852. ESR (methanol): 7 lines, $g = 2.00621$, $\alpha_N = 6.9$ mT. Anal. calcd. for C$_{23}$H$_{21}$N$_2$O: C 80.91; H 6.20; N 8.20%; found: C 80.70; H 6.19; N 8.16%.

1 See: A. P. de Silva, D. B. Fox, T. S. Moody and S. M. Weir, in *Optical Sensors and Switches*; Ed. V. Ramamurthy and K. S. Schanze, Marcel Dekker, Inc.: New York, Basel, 2001, Chapter 2, pp. 93–151.

2 See for example: (*a*) A. P. de Silva, H. Q. N. Gunaratne, J.-L. Habib-Jiwan, C. P. McCoy, T. E. Rice and J.-P. Soumillion, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1728; (*b*) A. P. de Silva, H. Q. N. Gunaratne, P. L. M. Lynch, A. J. Patty and G. L. Spence, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1611.

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8 See for example: (*a*) N. V. Blough and D. J. Simpson, *J. Am. Chem. Soc.*, 1988, **110**, 1915; (*b*) E. Szajdzinska-Pietek and M. Wolszczak, *Chem. Phys. Lett.*, 1997, **270**, 527.

9 If a large excess of CF$_3$COOH was used, the fluorescence intensity of the solution could be largely enhanced. This was in agreement with the fact that the ESR signal intensity of the solution was reduced under this condition as reported previously[6].

10 R. J. Mitchell, *Microprocessor Systems: An Introduction*; Macmillan: London, 1995.

11 The vertical transition energies and the oscillator strength were calculated on the basis of the optimized geometries (restricted-Hartree–Fock Austin Model 1 method for closed-shell compounds, and unrestricted-Hartree–Fock Austin Model 1 method for open-shell compounds), by means of Zerner's semiempirical intermediate neglect of differential overlap Hamiltonian (ZINDO) combined with a multi-reference double configuration interaction (MRD-CI) formalism.

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