Photonic logic gates based on metal ion and proton induced multiple outputs in 5-chloro-8-hydroxyquinoline based tetrapod

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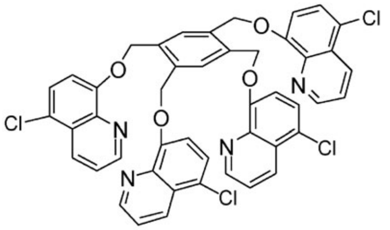
Tetrapod 1 shows opportunities for OR, NOR and INHIBIT logic gates based on fluorescence enhancement (FE) (Zn^{2+}, Cd^{2+}; 435–445 nm), fluorescence quenching (FQ) (Cu^{2+}, Ni^{2+}, Co^{2+}; 402 nm) and dual FQ (402 nm)—FE (510 nm) (H^+) outputs.

The current interest in molecular systems capable of performing logic operations is largely due to likely application of these systems as molecular devices in information processing and computation.[1] Molecular devices which function as wires,[2] switches,[3] diodes[4] and logic gates[5–10] have indeed been reported. Recently carrying the notions of solid state silicon based computing to the molecular world, molecular analogs of AND,[5] OR,[6] NOR,[7] XOR,[8] INHIBIT[9] and NAND[10] logic gates based on photoinduced electron transfer (PET) processes have also been described. Several logic functions integrated within a single molecule have been used, not only for recognizing the chemical inputs, but also for light signals.[11] On the basis of functional integration in a single molecule, a half adder[12] and half subtractor[13] have been constructed. It has been proposed that molecular logic gates could be powered by superior processing capabilities, which are based on a two input–multi output system. Each chemical input can be recognized within a single molecule, forming ideally distinct chemical states with corresponding characteristic signals. When the receptor is combined with the various analytes, the molecule can display "ON–OFF", "OFF–ON", ON–OFF–ON"[14] and "OFF–ON–OFF"[15] fluorescence emission phenomena which can be used for building logic gates.

8-Hydroxyquinoline based systems have attained prime significance due to their applications[16] in chromatography, detection of metal ions, organic light emitting diode devices and electrochemiluminescence *etc.*

As a part of our study on 8-hydroxyquinoline based ion sensing molecular devices[17] we now demonstrate that tetrapod **1** on addition of different metal ions provides varied outputs *viz.* fluorescence enhancement (FE), fluorescence quenching (FQ) and dual fluorescence quenching–fluorescence enhancement (FQ–FE) which have been used for developing truth tables for OR, NOR and INHIBIT logic gates.

The absorption band at λ_{max} 310 nm on excitation between 280–370 nm gives an emission at λ_{max} 402 nm in CH_3CN. All the emission studies have been performed by using excitation wavelength 360–365 nm. Tetrapod **1** (Scheme 1; 10 μM) on addition of $AgNO_3$ (1–30 μM) exhibited emission quenching and on further addition of $AgNO_3$ a new emission band at 432 nm appeared which achieved a plateau at >500 μM $AgNO_3$. On addition of Pb^{2+}, Hg^{2+}, Fe^{3+} or Cr^{3+}, the quenching (for <50 μM metal ion conc.) at 405 nm was followed by the appearance of a new emission band at 510 nm (>50–500 μM metal ion conc.). Therefore interaction of **1** with Ag^+, Pb^{2+}, Hg^{2+}, Fe^{3+} or Cr^{3+} offers a situation where three concentration dependent states: state 0 (high emission) = 0 μM metal ion; state 1 (low emission) = $<x$ μM and state 2 (high emission) = $>x$ μM metal ion are achieved. The addition of ~50 μM of Co^{2+}, Cu^{2+} or Ni^{2+} caused quenching (>90%) at 402 nm and addition of ~50 μM Zn^{2+} or Cd^{2+} led to >12 times enhancement along with a red shift of the



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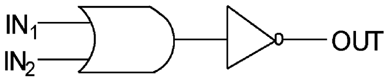
Scheme 1 Structure of tetrapod **1**.

A



B

IN_1 Cu^{2+}	IN_2 H^+	OUT 402 nm
0	0	1
1	0	0
0	1	0
1	1	0

Fig. 1 The logic table and symbolic representation of the NOR logic system under the action of two inputs (input I_1: state '0', Cu^{2+} = 0 μM; state '1', Cu^{2+} = 40 μM. Input I_2: state '0', H^+ = 0 μM; state '1', H^+ = 10 μM); output: state '0', Φ_F = 0.012; state '1', Φ_F = 0.17).

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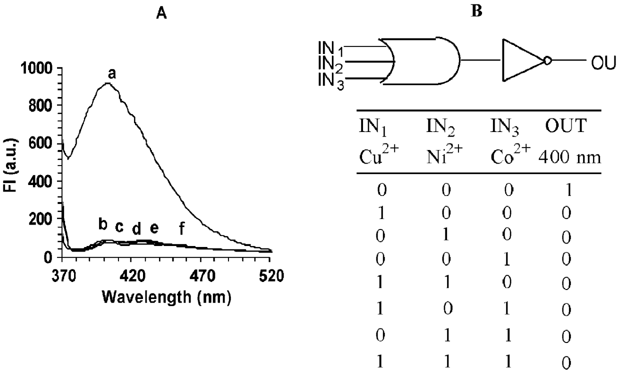
Table 1 Log β_{MXL} values for tetrapod **1** towards transition metal ions in pure CH_3CN

Entry	Metal ion	log β_{ML2}	log β_{ML}	log β_{M2L}	log β_{M4L}
1	Ag^+		5.77 ± 0.1	9.86 ± 0.12	17.1 ± 0.2
2	Hg^{2+}		5.59 ± 0.1	9.48 ± 0.08	17.8 ± 0.1
3	Pb^{2+}	15.9 ± 0.5	9.05 ± 0.4	12.7 ± 0.42	
4	Cr^{3+}		4.72 ± 0.1		16.3 ± 0.1
5	Cu^{2+}		5.60 ± 0.1		
6	Ni^{2+}	11.5 ± 0.1		9.19 ± 0.25	
7	Co^{2+}	11.9 ± 0.1		9.58 ± 0.22	
8	Zn^{2+}		6.51 ± 0.3	11.8 ± 0.30	
9	Cd^{2+}		6.49 ± 0.2	9.90 ± 0.32	
10	H^+	7.21 ± 0.2	11.9 ± 0.2		

emission band between 430–445 nm. The addition of $HClO_4$ (≤ 10 μM) caused quenching at 402 nm and subsequently on addition of $HClO_4$ > 10 μM led to a new emission band at 510 nm which reached a plateau ≤ 50 μM (5 equiv.). The spectral fitting of these data shows the formation of multiple stoichiometric complexes of **1** with metal ions (Table 1).

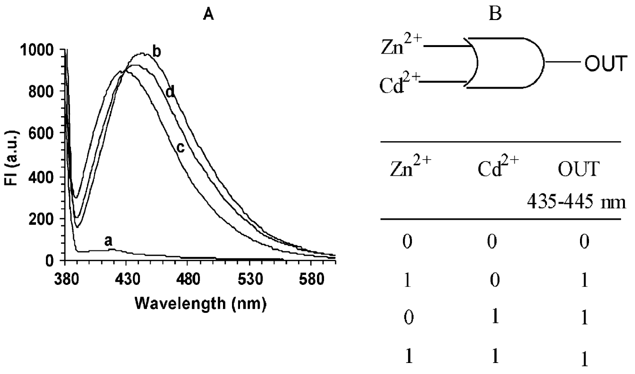
The absorption spectrum of **1** on addition of $HClO_4$ showed simultaneous decrease and increase in absorbance respectively, at 310 and 380 nm. Therefore, input of different metal ions and protons to tetrapod **1** gives multiple outputs *viz*. FE, FQ and dual FE–FQ phenomena. These phenomena permit the construction of truth tables for building OR, NOR and INHIBIT photonic logic gates. The addition of either Cu^{2+} (40 μM) or H^+ (10 μM) or both caused quenching of emission ($\sim$90%) of tetrapod **1** at 402 nm. The lowering in emission either by binding Cu^{2+} or H^+ or both resulted in a NOR logic gate with low output at 402 nm (Fig. 1).

Instead of using a combination of Cu^{2+} and H^+ as inputs, the combination of two or three metal ions (Co^{2+}, Ni^{2+} and Cu^{2+}) as inputs can be used to achieve a NOR gate. The pattern of fluorescence intensities as a function of cation input read as a NOR logic response as shown in the truth table[1a] given in Fig. 2. The spectra in Fig. 2 demonstrate the NOR logic response. NOR gates are of potential interest because they are considered as universal gates and when connected together enable the combinatorial creation of all other boolean operations.



IN$_1$ Cu^{2+}	IN$_2$ Ni^{2+}	IN$_3$ Co^{2+}	OUT 400 nm
0	0	0	1
1	0	0	0
0	1	0	0
0	0	1	0
1	1	0	0
1	0	1	0
0	1	1	0
1	1	1	0

Fig. 2 Molecular scale implementation of NOR logic gate. (A) Fluorescence emission spectra for **1** under different input conditions. a, blank (high, $\Phi_F = 0.11$); b, 1 + Cu^{2+} (40 μM, low, $\Phi_F = 0.012$); c, 1 + Ni^{2+} (60 μM, low, $\Phi_F = 0.012$); d, 1 + Co^{2+} (60 μM, low, Φ_F = 0.012); e, 1 + Cu^{2+} + Ni^{2+}; f , 1 + Cu^{2+} + Ni^{2+} + Co^{2+}. (B) Truth table for NOR logic gate.



Zn^{2+}	Cd^{2+}	OUT 435-445 nm
0	0	0
1	0	1
0	1	1
1	1	1

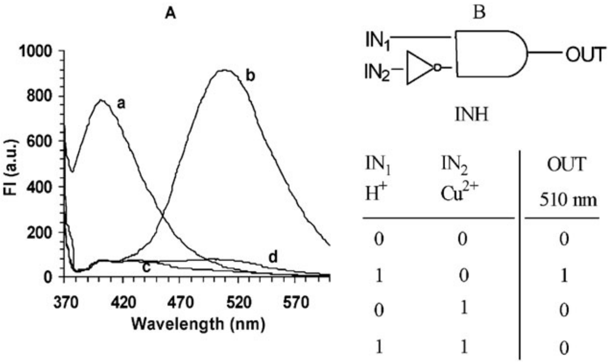
Fig. 3 Molecular scale implementation of OR logic gates. a, blank (low, $\Phi_F = 0.03$); b, 1 + Zn^{2+} (50 μM) (high, $\Phi_F = 0.41$); c, 1 + Cd^{2+} (50 μM) (high, $\Phi_F = 0.39$); d, 1 + Zn^{2+} + Cd^{2+} (high, $\Phi_F = 0.4$). (B) Logic symbol and truth table for OR gate.

The ability of tetrapod **1** to exhibit >12 times increase in fluorescence on addition of >50 μM Zn^{2+} or Cd^{2+} or both can be used for developing an OR logic gate. The truth table[1a] for the OR gate is shown in Fig. 3. The spectrum in Fig. 3 demonstrates the high emission state achieved by addition of Zn^{2+} or Cd^{2+} or both metal ions to **1**.

The ability of molecule **1** to exhibit a new emission band at 510 nm on addition of $HClO_4$ and its reversal on addition of Cu^{2+} has been used as an INHIBIT logic gate at 510 nm. An INHIBIT function is basically an AND operation where one input is reversed, *i.e.*, in our case, Cu^{2+} ion.

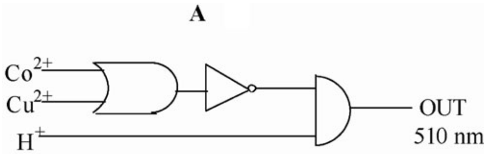
The addition of $HClO_4$ (40 μM) to tetrapod **1** quenches the fluorescence at 402 nm and gives a highly efficient new emission band at 510 nm (Fig. 4). The addition of Cu^{2+} (80 μM) as second input inhibits the formation of the emission band at 510 nm. The strongest luminescence ($\Phi_F = 0.17$) of **1** at 510 nm was observed in the absence of Cu^{2+} and the presence of perchloric acid, while all other combinations of these two inputs led to much weaker signals ($\Phi_F = 0.012$).

Therefore the emission of tetrapod **1** at 510 nm could be used to develop an INHIBIT logic gate whereas the emission at 402 nm achieved on addition of $HClO_4$ has been



IN$_1$ H^+	IN$_2$ Cu^{2+}	OUT 510 nm
0	0	0
1	0	1
0	1	0
1	1	0

Fig. 4 Molecular scale implementation of INHIBIT logic gates. a, blank; b, 1 + H^+ (40 μM); c, 1 + Cu^{2+} (80 μM); d, 1 + H^+ (40 μM) + Cu^{2+} (80 μM). (B) Logic symbol and truth tables for INH gate.



B

IN$_1$ H$^+$	IN$_2$ Co^{2+}	IN$_3$ Cu^{2+}	OUT 510 nm
1	0	0	1
0	1	0	0
1	1	0	0
0	0	0	0
1	0	1	0
0	1	1	0
1	1	1	0
0	0	1	0

Fig. 5 The logic table and the respective symbolic representation of the EnNOR function. λ_{em} = 510 nm with different chemical inputs [H$^+$: 40 μM, Cu^{2+}: 40 μM; Co^{2+}: 40 μM].

demonstrated in Fig. 1 to behave as a NOR logic gate. Finally, the three inputs discussed above, *i.e.*, Cu^{2+}, Co^{2+} and perchloric acid, were applied. The resulting logic scheme corresponds to a NOR function[18] (Cu^{2+} and Co^{2+}) which is only activated in the presence of the third input ($HClO_4$). The presence of perchloric acid has the function of control signal: whenever it is positive (*i.e.*, 1) the NOR gate is open (*i.e.*, 1), whenever it is negative (*i.e.*, 0) the NOR gate is closed (*i.e.*, 0). This behaviour is typical for an enabled NOR (EnNOR) gate (Fig. 5).[18]

Thus, the unique multiple emission properties of tetrapod **1** with proton and various metal ions provide opportunities for OR, NOR and INHIBIT gates.

Experimental

A solution of 5-chloro-8-hydroxyquinoline (895 mg, 5.0 mmol), NaH (pre-washed with hexane) (240 mg, 10.0 mmol) and tetrabutylammonium hydrogen sulfate (20 mg) (catalyst) in DMF (30 ml) was stirred at 0 °C. After 30 min, 1,2,4,5-tetrakis(bromomethyl)benzene (500 mg, 1.1 mmol) was added and stirring was continued at 0 °C. After completion of the reaction (TLC, 24 h), the solid residue was filtered off and washed with ethyl acetate. The combined filtrate was evaporated under vacuum and the solid residue was purified by column chromatography over silica-gel (60–120 mesh) using a mixture of CH_2Cl_2–ethyl acetate–MeOH (80 : 17 : 3, v/v) to obtain pure **1**, as a white solid (40%). Mp 300–302 °C ($CHCl_3$–CH_3OH), FAB Mass *m*/*z* 843, 845, 847, 849 (78 : 100 : 50 : 12) (M$^+$ + H); ^{1}H NMR ($CDCl_3$) (300 MHz): δ 5.60 (s, 4 × CH_2, 8H), 6.87 (d, J = 8.4 Hz, 4H, 4 × HQ-H7), 7.21 (d, J = 8.4 Hz, 4H, 4 × HQ-H6), 7.48 (dd, J_1 = 8.4 Hz, J_2 = 4.2 Hz, 4H, 4 × HQ-H3), 7.70 (s, 2H, ArH), 8.45 (dd, J_1 = 8.4 Hz, J_2 = 1.5 Hz, 4H, 4 × HQ-H4), 8.87 (dd, J_1 = 4.2 Hz, J_2 = 1.5 Hz, 4H, 4 × HQ-H2); ^{13}C NMR (CDCl3 + TFA): 69.1, 114.3, 123.4, 125.0, 128.2, 130.2, 131.1, 135.6, 143.8, 145.2, 147.1. Elemetal analysis: Found C, 65.59; H, 3.62; N, 6.45%. $C_{40}H_{36}Cl_4N_4O_4$ requires C 65.42; H, 3.58; N, 6.63; O, 7.58%.

UV-Vis and fluorescence experiments

UV-Vis spectroscopic analysis were carried out on a Shimadzu UV-1601 PC UV-Vis spectrophotometer by using slit widths of 1.0 nm and matched quartz cells. Fluorescence spectra were recorded on a Shimadzu RF1501 spectrofluorophotometer with a 1 cm quartz cell at 25 ± 0.1 °C. For performing the studies in acetonitrile, the solutions of **1** and metal nitrates/perchlorates were prepared in doubly distilled acetonitrile. The solution containing **1** (10 μM) was taken in a quartz cell and their absorption or fluorescence spectrum recorded. The addition of different concentrations of metal nitrates/perchlorates was carried out with a micropipette in aliquots of 1.5–3.0 μl (0.05–0.1 equiv.) in the same cell and each time the solution was allowed to stand for 3 min before recording the absorption or fluorescence spectrum.

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References

1 Recent reviews: (*a*) F. M. Raymo, *Adv. Mater.*, 2002, **14**, 401; (*b*) A. P. de Silva and N. D. McCleneghan, *Chem.–Eur. J.*, 2004, **10**, 574; (*c*) I. K. Cheah, S. J. Langford and M. Latter, *J. Supramol. Chem.*, 2005, **17**, 121; (*d*) J. M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995; (*e*) G. J. Ashwell, *Molecular Electronics*, Research Studies Press, Taunton, Somerset, 1992.

2 (*a*) W. B. Davis, W. A. Svec, M. A. Ratner and M. R. Wasielewski, *Nature*, 1998, **396**, 60; (*b*) B. Schlicke, P. Belser, L. De Cola, E. Sabbioni and V. Balzani, *J. Am. Chem. Soc.*, 1999, **121**, 4207; (*c*) V. Grosshenny, A. Harriman and R. Ziessel, *Angew. Chem., Int. Ed. Engl.*, 1996, **34**, 2705.

3 (*a*) R. W. Wagner, J. S. Lindsay, J. Seth, V. Palaniappan and D. F. Bocian, *J. Am. Chem. Soc.*, 1996, **118**, 3996; (*b*) N. Tamai, T. saika, T. Shimidzu and M. Irie, *J. Phys. Chem.*, 1996, **100**, 4689; (*c*) P. R. Ashton, V. Balzani, J. Becher, A. Credi, M. C. T. Fyfe, G. Mattersteig, S. Menzer, M. B. Nielsen, F. M. Raymo, J. F. Stoddart, M. Venturi and D. J. Williams, *J. Am. Chem. Soc.*, 1999, **121**, 3951; (*d*) P. L. Boulas, M. Gomez-Kaifer and L. Echegoyen, *Angew. Chem., Int. Ed.*, 1998, **37**, 216.

4 D. Gosztola, M. P. Niemczyk and M. R. Wasielewski, *J. Am. Chem. Soc.*, 1998, **120**, 5118.

5 (*a*) S. Iwata and K. Tanaka, *J. Chem. Soc., Chem. Commun.*, 1995, 1491; (*b*) A. P. de Silva, H. Q. N. Gunaratne and C. P. McCoy, *J. Am. Chem. Soc.*, 1997, **119**, 7891; (*c*) Y. Weizmann, R. Elanathan, O. Lioubashevski and I. Willner, *J. Am. Chem. Soc.*, 2005, **127**, 12666; (*d*) S. Muramatsu, K. Kinbara, H. Taguchi, N. Ishii and T. Aida, *J. Am. Chem. Soc.*, 2006, **128**, 3764; (*e*) M. N. Stojanovic, S. Semova, D. Kolpashchikov, J. MacDonald, C. Morgan and D. Stefanovic, *J. Am. Chem. Soc.*, 2005, **127**, 6914; (*f*) A. Okamoto, K. Tanaka and I. Saito, *J. Am. Chem. Soc.*, 2004, **126**, 9458; (*g*) S. Uchiyama, N. Kawai, A. P. de Silva and K. Iwai, *J. Am. Chem. Soc.*, 2004, **126**, 3032; (*h*) D. C. Magri, G. J. Brown, G. D. McClean and A. P. de Silva, *J. Am. Chem. Soc.*, 2006, **128**, 4950; (*i*) T. Gunnlaugsson, D. A. MacDonaill and D. Parker, *J. Am. Chem. Soc.*, 2001, **123**, 12866.

6 (*a*) A. P. de Silva, H. Q. N. Gunaratne and C. P. McCoy, *Nature*, 1993, **42**, 364; (*b*) A. P. de Silva, H. Q. N. Gunaratne and C. P. McCoy, *J. Chem. Soc., Chem. Commun.*, 1994, 1213; (*c*) P. Ghosh and P. K. Bharadwaj, *J. Am. Chem. Soc.*, 1996, **118**, 1553; (*d*) J. F. Callan, A. P. de Silva and N. D McClenaghan, *Chem. Commun.*, 2004, 2048.

7 (*a*) A. P. de Silva, I. M. Dixon, H. Q. N. Gunaratne, T. Gunnlaugsson, P. R. S. Maxwell and T. E. Rice, *J. Am. Chem. Soc.*, 1999, **121**, 1393; (*b*) Z. Wang, G. Zhang and P. Lu, *Org. Lett.*, 2005, **7**, 3669.

8 (*a*) A. Credi, V. Balzani, S. J. Langford and J. F. Stoddart, *J. Am. Chem. Soc.*, 1997, **119**, 2679; (*b*) M. N. Stojanovic, T. E. Mitchell and D. Stefanovic, *J. Am. Chem. Soc.*, 2002, **124**, 3555; (*c*) K. Szacilowski, W. Macyk and G. Stochel, *J. Am. Chem. Soc.*, 2006, **128**, 4550.

9 (*a*) J.-M. Montenegro, E. Parez-Inestrosa, D. Collado, Y. Vida and R. Suau, *Org. Lett.*, 2004, **6**, 2353; (*b*) A. Saghatelian, N. H. Volckar, K. M. Guckian, V. S.-Y. Lin and M. R. Ghadiri, *J. Am. Chem. Soc.*, 2003, **125**, 346; (*c*) S. D. Striaght, J. Andreasson, G. Kodis, S. Bandyopadhyay, R. H. Mitchell, T. A. Moore, A. L. Moore and D. Gust, *J. Am. Chem. Soc.*, 2005, **127**, 9403.

10 H. T. Baytekin and E. U. Akkaya, *Org. Lett.*, 2000, **2**, 1725.

11 (*a*) F. M. Raymo and S. Giordani, *J. Am. Chem. Soc.*, 2002, **124**, 2004; (*b*) F. M. Raymo and S. Giordani, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 4941.

12 (*a*) A. P. de Silva and N. D. McClenaghan, *J. Am. Chem. Soc.*, 2000, **122**, 3965; (*b*) M. N. Stojanovic and D. Stefanovic, *J. Am. Chem. Soc.*, 2003, **125**, 6673; (*c*) F. Remacle, S. Speiser and R. D. Levine, *J. Phys. Chem. B*, 2001, **105**, 5589.

13 (*a*) S. J. Langford and T. Yann, *J. Am. Chem. Soc.*, 2003, **125**, 11198; (*b*) A. Coskun, E. Deniz and E. U. Akkaya, *Org. Lett.*, 2005, **7**, 5187.

14 (*a*) A. P. de Silva, H. Q. N. Gunaratne and C. P. McCoy, *Chem. Commun.*, 1996, 2399; (*b*) H. Chao, B.-H. Ye, Q.-L. Zhang and L.-N. Ji, *Inorg. Chem. Commun.*, 1999, **2**, 338; (*c*) Y. Kubo, S. Obara and S. Tokita, *Chem. Commun.*, 1999, 2399.

15 (*a*) V. Amedola, L. Fabrizzi, C. Mangano, H. Miller, P. Pallavicini, A. Perrotti and A. Taglietti, *Angew. Chem., Int. Ed.*, 2002, **41**, 2533; (*b*) P. Pallavicini, V. Amedola, C. Massera, E. Munderm and A. Taglietti, *Chem. Commun.*, 2002, 2452.

16 (*a*) G. De Armas, M. Miro, A. Cladera, J. M. Estela and V. Cerda, *Anal. Chim. Acta*, 2002, **455**, 149; (*b*) R. T. Bronson, M. Montalti, L. Prodi, N. Zaccheroni, R. D. Lamb, N. K. Dalley, R. M. Izatt, J. S. Bradshaw and P. B. Savage, *Tetrahedron*, 2004, **60**, 11139; (*c*) J.-S. Youk, Y. H. Kim, E.-J. Kim, N. J. Youn and S.-K. Chang, *Bull. Korean Chem. Soc.*, 2004, **25**, 869; (*d*) L. Prodi, *New J. Chem.*, 2005, **29**, 20; (*e*) I. A. Bagatin and H. E. Toma, *New J. Chem.*, 2000, **24**, 841; (*f*) S. Wang, *Coord. Chem. Rev.*, 2001, **215**, 79; (*g*) B. D. Muegge, S. Brooks and M. M. Richter, *Anal. Chem.*, 2003, **75**, 1102.

17 (*a*) P. Singh and S. Kumar, *Tetrahedron Lett.*, 2006, **47**, 109; (*b*) P. Singh and S. Kumar, *Tetrahedron*, 2006, **62**, 6379.

18 M. de Sousa, B. de Castro, S. Abad, M. A. Miranda and U. Pischel, *Chem. Commun.*, 2006, 2051.