

Phenol/phenolate-dependent on/off switching of the luminescence of 4,4-difluoro-4-bora-3a,4a-diaza-s-indacenes

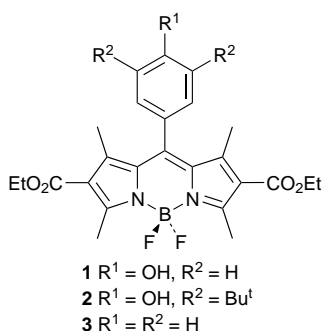
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Boradiazaindacenes **1 and **2** bearing phenolic subunits show deprotonation/protonation dependent fluorescence off/on-switching; the lack of emission of the phenolate forms is attributed to photoinduced electron transfer (PET) between the phenolate and indacene subunits.**

There is still considerable need for novel molecular probes for fluorescent analysis and materials science chemistry. Difluoroboryldipyromethene complexes are of high interest as fluorophores due to their favourable photophysical and optoelectronic properties.¹ Whilst the work on their syntheses,² photophysical properties³ and application as fluorophoric probes is well established, their potential for sensing by optoelectronic switching has been only partially explored. Previously, we have demonstrated that reversible redox activation of boradiazaindacenes gives rise to efficient electrochemically generated luminescence^{4,5a} (ECL). By using a non-fluorescent dimethylaminophenyl derivative, it could be shown that strong emission occurs on protonation.⁵ The present study is directed towards shifting the on/off switching of luminescence to higher pH. Therefore, the phenol/phenolate couples **1** and **2** have been investigated.



We synthesized the phenolic dyes **1** and **2**⁴ according to previously applied procedure.² Owing to the presence of methyl groups at positions C-1 and C-7, the phenyl and boraindacene systems are twisted and conjugatively uncoupled. This follows from an X-ray analysis^{5a} of a structurally similar compound and from the high-field NMR chemical shift of the methyl protons.⁴ Both **1** and **2** are therefore representatives of orthogonal fluorophor–receptor systems.⁶ A phenolate is formed by deprotonation, which may exhibit a PET-like quenching mechanism.⁷

The preliminary objective was to study the emissive properties of the phenol/phenolate equilibrium in organic solvents using an organic base for deprotonation. To avoid intermolecular charge transfer quenching, which is often observed in the presence of tertiary amines,⁸ we used pyridine as the proton acceptor.

Fig. 1 shows the fluorescence titrations of **1** dissolved in CHCl₃ by successive addition of pyridine. The fluorescence signals of **1** and **2** significantly decrease, whereas the wave-

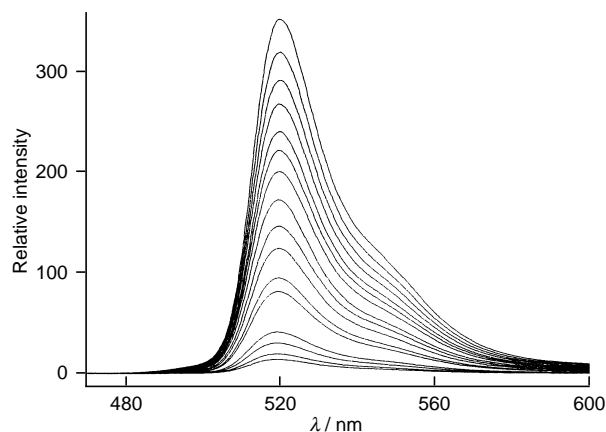


Fig. 1 Decrease of fluorescence intensity during titration of **1** on successive addition of pyridine (2.7 ml of dye; 2.1×10^{-5} mol l⁻¹ in CHCl₃, excitation at 500 nm, end concentration of pyridine: 3.2×10^{-1} mol l⁻¹)

length of emission remains unchanged. Reprotonation by addition of trifluoroacetic acid restores fluorescence. Switching between the fluorescent on/off states can be repeated without decomposition or formation of precipitates. To prove that the observed decrease in fluorescence intensity is due to the phenolic properties of **1** and **2**, the same titration experiments were performed with 8-phenylboradiazaindacene **3**.^{2c} No base-dependent response could be observed. By fluorescence titration experiments in a MeOH–H₂O mixture⁹ (1 : 1), the pK_a value of compound **1** was determined to be 10.4 ± 0.5 (see Fig. 2) which indicates the decoupling of the subunits.

The determination of pK_a values for **2** failed due to its poor solubility in the aqueous solvent mixture. Compounds **1** and **2** also have been embedded into a hydrogel matrix, according to a previously published procedure,⁹ with the aim of obtaining a material for use in sensors. Membranes were tested in a home-

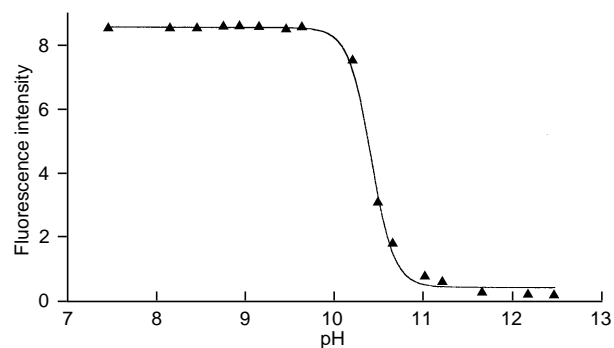


Fig. 2 Fluorescence intensity–pH profiles of **1** (pK_a 10.4) in a MeOH–H₂O (1 : 1): (▲) measured values, (—) sigmoidal fit; ionic strength of 150 mmol l⁻¹ (NaCl) (dye concentration: 2×10^{-6} mol l⁻¹; I_{NaCl} = 150 mmol l⁻¹; λ_{ex} = 490 nm; λ_{em} = 506 nm)

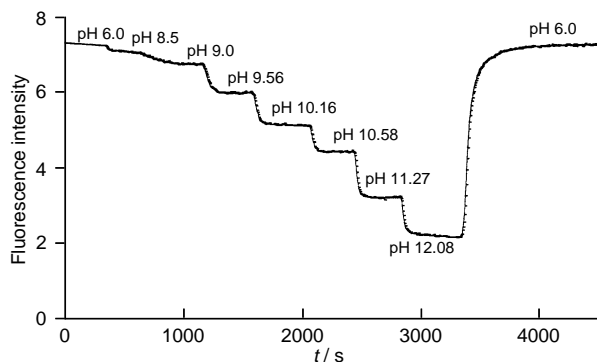


Fig. 3 Relative signal change, response time and reversibility of **1** incorporated in a hydrogel matrix on exposure to a flow of buffers. The pH values are inserted in the graph. Ionic strength is kept constant at 150 mmol l⁻¹ (NaCl); concentration: 39 mmol per kg of matrix.

made flow-through cell with respect to the response of various pH values. To minimize effects of ionic strength, sodium chloride (150 mmol l⁻¹) was added. Again, the base form is only weakly fluorescent due to electron transfer from the phenolate group (the receptor) to the indacene fluorophore. The excitation/emission maxima of the membrane for **1** and **2** are at 504/515 nm and 502/508 nm, respectively. However, excitation was performed at 500 nm in order to minimize straylight. Fig. 3 shows the response behaviour and reversibility characteristics of **1** embedded in the matrix. The response times were faster (2

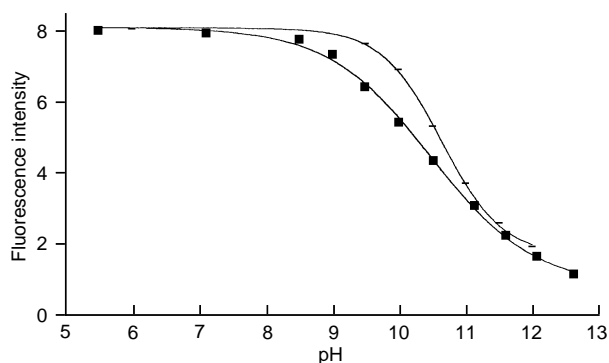


Fig. 4 pH titration plot of **1** and **2** incorporated in a hydrogel matrix: (■) **1** (pK_a 10.4) and (—) **2** (pK_a 10.8)

to 3 min) when going to lower pH than in the reverse direction (5 to 8 min).

The pH titration curves of sensors **1** and **2** exhibit the typical sigmoidal shape and are depicted in Fig. 4. The pK_a values of the two membranes are 10.4 and 10.8, respectively.

Footnotes and References

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- I. D. Johnson, H. C. Kang and R. P. Haughland, *Anal. Biochem.*, 1991, **198**, 228; J. Karolin, L. B.-A. Johansson, L. Strandberg and T. Ny, *J. Am. Chem. Soc.*, 1994, **116**, 7801; T. G. Pavlopoulos, M. Shah and J. H. Boyer, *Apl. Opt.*, 1988, **27**, 4998; O. Driessen and J. Lugtenburg, *J. High Resolut. Chromatogr. Commun.*, 1980, **3**, 405.
- (a) A. Treibs and F.-H. Kreuzer, *Liebigs Ann. Chem.*, 1968, **718**, 208; (b) E. Vos de Wael, J. A. Pardoen, J. A. van Koevinge and J. Lugtenburg, *Recl. Trav. Chim. Pays Bas*, 1977, **96**, 306; (c) H. Falk and G. Schoppel, *Monatsh. Chem.*, 1990, **121**, 67; (d) H. J. Wories, J. H. Koek, G. Lodder, J. Lugtenburg, R. Fokkens, O. Driessen and G. R. Mohn, *Recl. Trav. Chim. Pays Bas*, 1985, **104**, 288; (e) R. W. Wagner and J. S. Lindsey, *Pure Appl. Chem.*, 1996, **68**, 1373.
- H. Falk and A. Leodolter, *Monatsh. Chem.*, 1978, **109**, 883; J. Karolin, L. B.-A. Johansson, L. Strandberg and T. Ny, *J. Am. Chem. Soc.*, 1994, **116**, 7801.
- T. Gareis, Ph.D. Thesis, University of Regensburg, 1997; M. Kollmannsberger, Diploma Thesis, University of Regensburg, 1996.
- (a) M. Kollmannsberger, T. Gareis, S. Heintl, J. Breu and J. Daub, *Angew. Chem.*, 1997, **109**, 1391; *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1333; (b) T. Werner, C. Huber, S. Heintl, M. Kollmannsberger, J. Daub, O. S. Wolfbeis and Fresenius, *Z. Anal. Chem.*, in the press.
- R. A. Bissel, A. P. de Silva, H. Q. N. Gunaratne, P. L. M. Lynch, G. E. M. Maguire and K. R. A. Samankumara Sandanayake, *Chem. Soc. Rev.*, 1992, **21**, 187.
- For an introduction to photo induced electron transfer, see *Photoinduced Electron Transfer Part A-D*, ed. M. A. Fox and M. Chanon, Elsevier, Amsterdam, Oxford, 1988; A. P. de Silva and S. A. da Silva, *J. Chem. Soc., Chem. Commun.*, 1986, 1709; R. Grigg, J. M. Holmes, J. M. Jones and W. D. J. A. Norbert, *J. Chem. Soc., Chem. Commun.*, 1994, 185; J. P. Konopelski, F. Kotzyba-Hibert, J.-M. Lehn, J.-P. Desvergne, F. Fages, A. Castellan and H. Bouas-Laurent, *J. Chem. Soc., Chem. Commun.*, 1985, 433; M. E. Huston, K. W. Haider and A. W. Czarnik, *J. Am. Chem. Soc.*, 1988, **110**, 4460 and references cited therein.
- Y.-P. Sun, C. Bunker and B. Ma, *J. Am. Chem. Soc.*, 1994, **116**, 9692 and references cited therein.
- O. S. Wolfbeis, C. Huber and T. Werner, *Solid State Supramolecular Optical Sensors*, Proc. NATO Adv. Res. Workshop, *Chemosensors of Ion and Molecule Recognition*, ed. A. T. Czarnik and J. P. Desvergne, NATO Adv. Sci. Ser., part E, Kluwer, Dordrecht, Boston, London, 1997, in the press.

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