Exploitation of a novel 'on–off' photoinduced electron-transfer (PET) sensor against conventional 'off–on' PET sensors†

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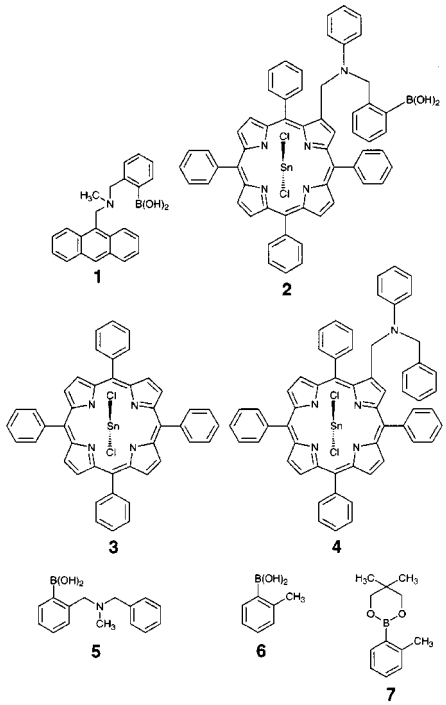
A novel PET sensor for sugar sensing which changes its fluorescence intensity in an 'on–off' manner was designed from (tetraphenylporphyrinato)tin(IV)

The concept of photoinduced electron-transfer (PET) sensors has been exploited by de Silva, Czarnik and others for spectroscopic sensing of metal ions and ionic, organic compounds.[1,2] It was later shown that this concept can be successfully applied to spectroscopic sensing of neutral molecules: for example, in a 2-aminomethylphenylboronic acid skeleton the Lewis acidity of the boronic acid group is markedly intensified upon complexation with saccharides, which eventually suppresses the fluorescence quenching efficiency of the amino group.[3–5] A typical example is compound **1** in which the



relative fluorescence intensity increases upon complexation with saccharides.[3] This is a typical '*off–on–type*' PET sensor. It occurred to us that judging from the various requirements for the quantitative analyses of saccharides, a reversed '*on–off–type*' PET sensor would be also useful for spectroscopic sensing. With these objectives in mind we synthesized compound **2** bearing a (tetraphenylporphyrinato)tin(IV) moiety as a fluorescent site[6] and a 2-aminomethylphenylboronic acid group as a saccharide-binding site. Computer simulations[7] suggested that, upon binding to the boronic acid moiety, the ligands are

† Electronic supplementary information (ESI) available: colour version of Fig. 1. See http://www.rsc.org/suppdata/cc/1999/2011/

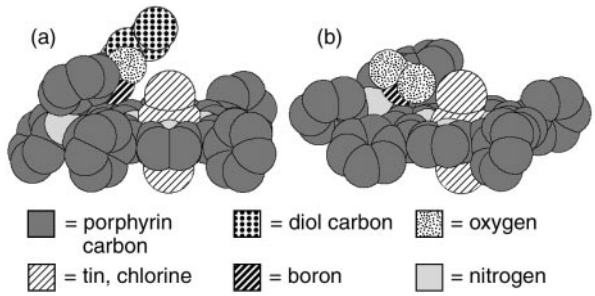


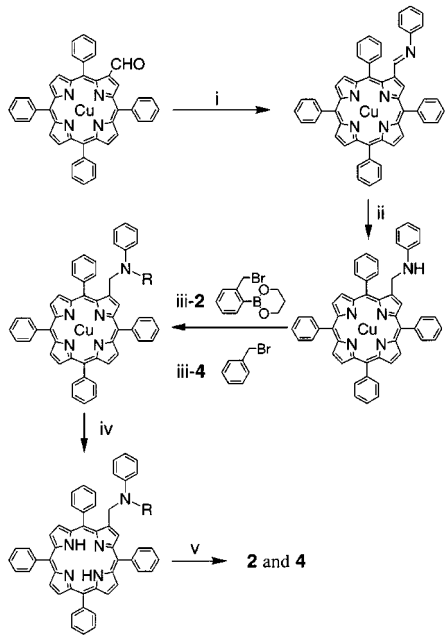
Fig. 1 Minimum energy structures for (a) butane-1,2-diol complexed **2** (b) free **2**: butane-1,2-diol; hydrogens have been omitted for clarity. The B–N distance in (a) is 4.6 Å and in (b) is 3.06 Å. This distance in the free porphyrin can be reduced to allow B–N interaction by thermal motions but steric buffeting between the ligand and the porphyrin prevents this from occurring upon complexation of the diol. Colour version available at http://www.rsc.org/suppdata/cc/1999/2011/

suspended over the plane of the porphyrin where the boron and nitrogen atoms are too far apart to interact (Fig. 1). In the case of the free receptor, however, the boron and tertiary nitrogen can come close enough to interact, including an '*exo*' interaction within the cleft of the adjacent *meso* phenyl rings. Hence, if diol complexation reduces the B–N interaction, **2** should act as a novel 'on–off–type' PET sensor. Compounds **3** and **4**[5] were used as reference compounds related to **2**.

Compounds **2** and **4** were synthesized according to Scheme 1 and identified by ^{1}H NMR and mass (SIMS) spectral evidence and elemental analyses. Initially, we carried out spectroscopic measurements in an aqueous system (25 °C, water : MeOH, 1 : 1 v/v). As expected the fluorescence intensity (I) decreased with increasing saccharide concentrations (pH 10.0 [**2**] = 2.0×10^{-7} mol dm^{-3}, λ_{ex} 417 nm, λ_{em} 605 nm; *e.g.*, I/I_0 = 0.92 and 0.78 at [D-fructose] = 1.0×10^{-3} and 1.0×10^{-2} mol dm^{-3}). We noticed, however, that the fluorescence is sensitive to slight changes in pH and buffer concentration because of axial ligand (Cl^-) substitution.‡ To avoid the complexity arising from axial ligand substitution, the fluorescence measurements were carried out in dichloromethane (but not in aqueous solution) to clarify the mechanism for the fluorescence decrease.

Fig. 2(a) shows the fluorescence spectra of **2**, **3** and **4** in the absence of saccharides: the excitation wavelength is 431 nm near the Soret band. Since the absorbance of these three compounds is similar to each other at this wavelength, one can directly compare their fluorescence intensities. It can be seen from Fig. 2(a) that the fluorescence intensity of **4** (at 605 nm) is only 10.8% of that of **3**, indicating that the intramolecular amino group in **4** efficiently quenches the fluorescence of the (tetraphenylporphinato)tin(IV) moiety. In **2**, on the other hand, the fluorescence intensity was reduced to 31.6% of that of **3**. This implies that the partial B–N interaction does exist but the amino group still retains the fluorescence quenching ability.

Fig. 2(b) shows the fluorescence spectra of **2** in the presence of an excess of a variety of diols; as expected from the original



Scheme 1 *Reagents and conditions* [yields]: i, aniline, benzene, reflux [89%]; ii, $NaBH_3CN$, THF, r.t. [58%]; iii, K_2CO_3, THF, reflux [iii **2**; 29%, iii **4**; 50%]; iv, HCl(g), $CHCl_3$, r.t. [iv **2**; 69%, iv **4**; 80%]; v, $SnCl_2$, DMF, 120 °C [**2**; 68%, **4**; 70%].

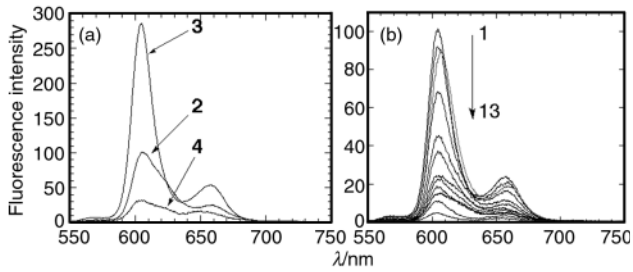


Fig. 2 (a) Fluorescence spectra of **2**, **3** and **4** (2.00×10^{-7} mol dm^{-3}) at 25 °C in CH_2Cl_2: excitation at 431 nm. (b) Fluorescence spectra of **2** (2.00×10^{-7} mol dm^{-3}) in the presence of various diols and saccharides (3.00×10^{-3} mol dm^{-3}) at 25 °C in dichloromethane: excitation 424 nm: 1, none; 2, pinacol; 3, dimethyl L-tartarate; 4, pentane-2,4-diol; 5, *cis*-cyclohexane-1,2-diol; 6, 1,2-diphenylethane-1,2-diol; 7, 2,2-dimethylpropane-1,3-diol; 8, (2*R*,3*R*)-butane-2,3-diol; 9, catechol; 10, butane-1,2-diol; 11, butane-1,3-diol; 12, 1,2,5,6-*O*-bis(isopropylidene)-D-mannitol; 13, (*R*)-1-phenylethane-1,2-diol.

molecular design, complexation with diols decreased the fluorescence intensity of **2**. As a general trend, sterically bulky diols such as (*R*)-1-phenylethane-1,2-diol and 1,2,5,6-*O*-bis(isopropylidene)-D-mannitol and diols with a high affinity for the boronic acid group such as butane-1,2-diol and butane-1,3-diol (frequently used as a protecting group for the boronic acid group) reduced the fluorescent intensity to a large extent. The fluorescence spectra of **3** and **4** were scarcely changed by the addition of these diols, indicating that the spectral change is due to the boronic acid–diol interaction. From plots of the fluorescence intensity *vs.* [diol] for selected diols, the association constants (K_{ass}) were estimated: $K_{ass} = 1.9 \times 10^4$ dm^3 mol^{-1} for 2,2-dimethylpropane-1,3-diol (DMPD), 2.6×10^2 dm^3 mol^{-1} for cyclohexane-1,2-diol, 5.0×10^3 dm^3 mol^{-1} for pentane-2,4-diol and 1.0×10^5 dm^3 mol^{-1} for catechol.

To obtain further insights into the fluorescence decrease induced by the addition of diols we measured ^1H and ^{11}B NMR spectra. In ^1H NMR spectroscopy (600 MHz, $CDCl_3$, 25 °C) DMPD gave a singlet peak at δ 2.16 for the OH protons. When an equimolar amount of **2** (5.0×10^{-3} mol dm^{-3}) was added, this peak nearly disappeared. This change indicates that DMPD forms a six-membered cyclic boronate ester with **2**. It is known that complexation of **5** in aqueous solutions causes an upfield shift of the boron signal of *ca.* 12.0 ppm.[8] In ^{11}B NMR spectroscopy [192 MHz, $CDCl_3$, 25 °C, external standard $B(OMe)_3$] we confirmed that the boron peak for **7** appears at a chemical shift higher by 2.4 ppm than that for **6**. These results indicate that the up-field shift is induced by both the B–N interaction and diol complexation. Compound **2** gave a singlet peak at δ 13.0 but upon addition of an equimolar amount of DMPD (2.5×10^{-2} mol dm^{-2}) a new strong peak appeared at δ 9.0. The shift width is only 4.0 ppm which is sufficiently rationalized by simple complexation with DMPD. We believe, therefore, that even though DMPD is bound to the boronic acid moiety in **2**, the B–N interaction is not specifically intensified as in the case of the previous 'off–on–type' PET sensors. To the best of our knowledge, this is the first example of an 'on–off–type' PET sensor for sugar sensing.[9]

The present study has demonstrated that a novel 'on–off–type' PET sensor can be designed by skilful utilization of steric crowding. Hence, it is now possible to choose either 'on–off–type' or 'off–on–type' PET sensors according to the experimental requirements. This indicates the high potential and versatility of combining the B–N interaction with the PET systems.

Notes and references

‡ Supporting information is available on request.

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5 More recently, Cooper and James reported a PET chemosensor with an anthracene fluorophore appending an *o*-aminomethylphenyl boronic acid group and a crown ether group which selectively binds glucosamine: C. R. Cooper and T. D. James, *Chem. Commun.*, 1997, 1419.

6 It is known that the amino group is capable of quenching the fluorescence of the (tetraphenylporphinato)tin(IV) moiety: R. Grigg and W. D. J. A. Norkert, *J. Chem. Soc., Chem. Commun.*, 1992, 1298.

7 Computer simulations were performed using CDiscover as implemented by Insight II ver. 98.0 on a Silicon Graphics Octane workstation. Conformations were explored with molecular dynamics simulations using the ESFF forcefield at 500 K for 40 ps with subsequent minimisation of low energy conformations.

8 C. R. Cooper, N. Spencer and T. D. James, *Chem. Commun.*, 1998, 1365.

9 An alternative mechanism was briefly considered after mass spectrometry consistently demonstrated the loss of one chloride ligand during measurements. Although this phenomenon could result simply from losing chloride to achieve a positive charge, we also considered the possibility of displacement of chloride by a boron-attached oxygen to yield a B–O–Sn self-complexed macrocycle. IR and NMR experiments produced no evidence for this interaction, however, and it was therefore discarded.

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