Sugar-controlled Association and Photoinduced Electron Transfer in Boronic-acid-appended Porphyrins

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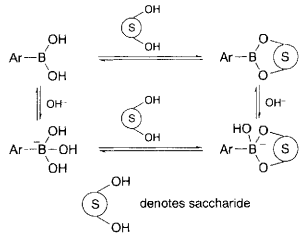
Complexation–decomplexation equilibria between boronic-acid-appended porphyrins and naphthalenedisulfonates or anthraquinonedisulfonates can be efficiently controlled by the addition of saccharides: this finding is readily applied to the saccharide-control of photoinduced electron-transfer processes.

Boronic acids can form covalently bonded complexes with diols (including saccharides) rapidly and reversibly in aqueous solution and therefore are useful as a functional group to design artificial receptors for saccharides.[1,2] It is known that the complexation induces three different changes in the boronic acid function: (i) it becomes more hydrophilic, (ii) the anionic charge (*i.e.* sp^3-hybridized B^-) is developed because of the apparent drop of the pK_a value [1,3–5] and (iii) it becomes chiral. Meanwhile, it is known that charged porphyrins bind oppositely charged molecules with the aid of electrostatic interactions.[6,7] It thus occurred to us that complexation–decomplexation equilibria in boronic-acid-appended porphyrins would be controlled by creation of anionic charges by the binding of saccharides to the boronic acid moieties. With these systems in mind we synthesized boronic-acid-appended porphyrins **1a** and **1b**. At a pH where two of four boronic acids are dissociated, they are dicationic overall and should favourably bind dianionic guest molecules. However, the saccharide addition facilitates the dissociation of the two undissociated boronic acids and **1** should become neutral over all. Then, we expected that the porphyrin–guest complex should be decomplexed (Scheme 1).

Compounds **1a** and **1b** were synthesized by the reaction of 5,10,15,20-tetrapyridylporphyrin‡ with 2-bromomethylphenylboronic acid and 4-chloromethylphenylboronic acid, respectively. The bromide salt of **1a** was ion-exchanged to give the chloride salt.† The products were identified by IR and ^1H NMR spectroscopy and elemental analyses.

First, we carried out potentiometric titration of **1a** and **1b** with aqueous NaOH solution (25 °C, 2.5 vol% methanol, [**1**] = 1.00×10^{-3} mol dm^{-3}): the pK_a values were estimated to be 6.94, 7.73, 8.86 and 10.30 for **1a** and 6.91, 7.92, 8.98 and 10.85 for **1b**. To create dicationic species (*i.e.* to dissociate two boronic acids) we set the solution pH to 8.2 for **1a** and 8.4 for **1b**.

The Soret band of **1b** decreases with increasing naphthalene-1,5-disulfonate (1,5-NDS) concentration. The similar spectral change was observed for the addition of other dianionic guest molecules listed in Table 1. The maximum value in the continuous variation plots and the linearity in the Benesi–Hildebrand plots support the view that they form a 1:1 complex. The association constants (K) determined from the Benesi–Hildebrand plots are summarized in Table 1. Examination with their CPK molecular models suggests that the distance between two sulfonate groups in anthraquinone-2,6-disulfonate (2,6-ADS) is comparable with that between two distal pyridinium cations in **1** when the anthraquinone moiety is π-complexed with the porphyrin plane. Hence, the complex can be stabilized by both the electrostatic interaction and the π–π interaction. In contrast, the distance between two sulfonate groups in other four compounds is comparable with that between two adjacent pyridinium cations. It seems difficult, therefore, for the complexes to adopt the structure in which both the electrostatic interaction and the π–π interaction act cooperatively. The difference in complementarity between **1** and guest molecules should be reflected by the difference in the K values. As seen from Table 1, the K values for 2,6-ADS are considerably larger than those for 1,5-, 2,6-, 2,7-NDS and 1,5-ADS.



Scheme 1

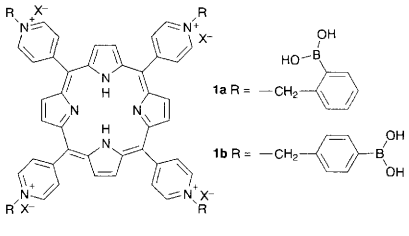


Table 1 Association constants (K) for dicationic **1a** (at pH 8.2) and **1b** (at pH 8.4)[a]

Dianionic guest	K/dm^3 mol^{-1} with **1a**	with **1b**
1,5-NDS	6.84×10^3	1.20×10^3
2,6-NDS	9.56×10^3	2.92×10^3
2,7-NDS	6.75×10^3	2.53×10^3
1,5-ADS	1.56×10^4	3.70×10^3
2,6-ADS	3.66×10^5	4.97×10^5

[a] 25 °C, water (0.10 mol dm^{-3} phosphate buffer): methanol 300:1 *v/v*, pH 8.2 for **1a** and 8.4 for **1b**, [**1**] = 1.00×10^{-5} mol dm^{-3}.

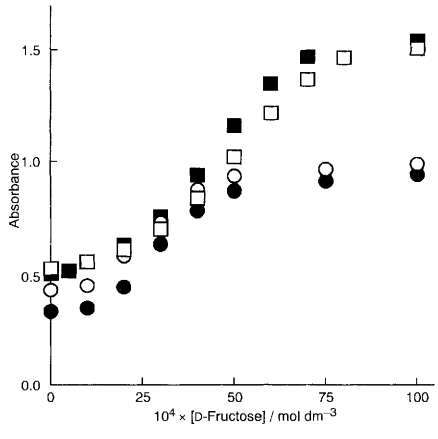
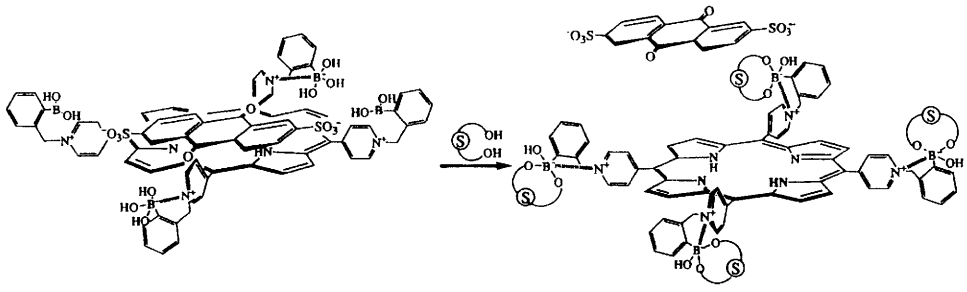


Fig. 1 Absorbance change induced by the ADS addition and the subsequent D-fructose addition; [**1a**] = [**1b**] = 1.00×10^{-5} mol dm^{-3}, pH 8.2 for **1a** and 8.4 for **1b**, 25 °C, MeOH–H_2O 1:300 *v/v*, 0.10 mol dm^{-3} phosphate buffer. The D-fructose concentration was varied while the ADS concentration was maintained constant (1.00×10^{-3} mol dm^{-3} for 1,5-ADS and 2.00×10^{-5} mol dm^{-3} for 2,6-ADS); □ **1a** plus 1,5-ADS, ■ **1a** plus 2,6-ADS, ○ **1b** plus 1,5-ADS, ● **1b** plus 2,6-ADS.



Static Quenching Dynamic Quenching

Scheme 2 Complexation–decomplexation of **1a** and 2,6-ADS

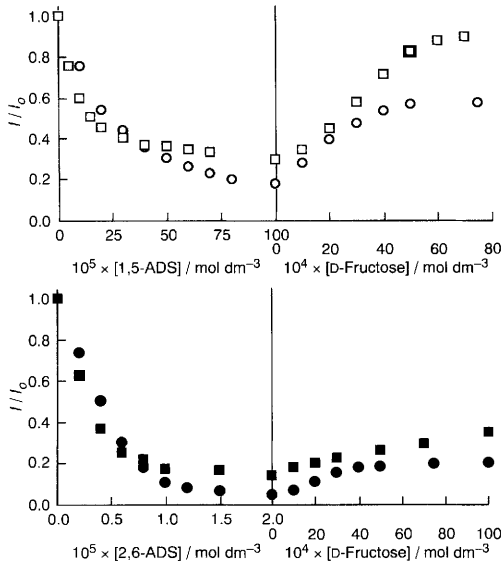


Fig. 2 Fluorescence intensity change (at 663 nm) induced by the ADS addition and the subsequent D-fructose additions; excitation wavelength 450 nm (isosbestic point in the absorption spectra). Other measurement conditions are recorded in caption for Fig. 1: □ **1a** plus 1,5-ADS, ■ **1a** plus 2,6-ADS, ○ **1b** plus 1,5-ADS and ● **1b** plus 2,6-ADS.

Here, we tested whether decomplexation of the **1**–ADS complexes can be controlled by added saccharides. For this purpose D-fructose was chosen because it always shows the highest affinity with monoboronic acids.[1,3–5] When D-fructose was added to the aqueous solution containing **1a** plus 1,5-ADS or **1a** plus 2,6-ADS, the absorbance of the Soret band (424.5 nm) gradually increased and the initial absorbance in the absence of ADS was regenerated (Fig. 1). The results indicate that 1,5-ADS and 2,6-ADS are entirely dissociated from the complexes because of the anionic charges developed on the boron atoms by the D-fructose binding. On the other hand, the initial absorbance of **1b** was only partially regenerated even by the addition of a great excess amount of D-fructose (67% for **1b** plus 1,5-ADS and 62% for **1b** plus 2,6-ADS). The difference between **1a** and **1b** is attributed to the stability of the complexes: that is, in **1a** the stable intramolecular zwitterion pairs can be formed between N^+ and saccharide-generated B^-, which facilitate the dissociation of ADS whereas in **1b** such intramolecular $N^+ \cdots B^-$ zwitterion pairs cannot be formed, so that the ADS dissociation is not so efficient as in **1a**.

Lastly, we tested whether photoinduced electron transfer from **1** to ADS can be controlled by the D-fructose addition. As shown in Fig. 2, the I/I_0 decreased with increasing ADS concentration and at the constant ADS concentration it increased with increasing D-fructose concentration. As expected from the result that the D-fructose-induced dissociation of the **1b** complexes is not so efficient, the I/I_0 increase on the addition of D-fructose occurs only partly (60% for **1b** plus 1,5-ADS and 21% for **1b** plus 2,6-ADS). In the **1a** complexes which are entirely dissociated by the D-fructose addition, the I/I_0 for the **1a**–1,5-ADS complex increases efficiently up to 91% of the initial I/I_0 in the absence of 1,5-ADS but that for the **1a**–2,6-ADS complex increases only up to 11%. Since the Stern–Volmer plots for these systems ([**1a**] = 1.00×10^{-5}, [D-fructose] = 7.00×10^{-3}, [1,5-ADS] = 0–7.50×10^{-4}, [2,6-ADS] = 0–4.00×10^{-5} mol dm^{-3}) are linear with K_{sv} = 0.01 for 1,5-ADS and 2.13 dm^3 mol^{-1} for 2,6-ADS, the decrease in I/I_0 for **1a** in Fig. 2 is attributed to dynamic quenching.

In conclusion, the complexation–decomplexation processess in boronic-acid-appended porphyrins can be illustrated as in Scheme 2. Photoinduced electron transfer from dicationic **1** to dianionic ADS occurs efficiently in a pseudo-intracomplex manner. Addition of D-fructose dissociates the complexes and the electron transfer mechanism changes from static quenching to dynamic quenching. This is a novel and convenient method to control the efficiency of photoinduced electron transfer that imitates the incipient stage of photosynthesis.

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Footnotes

† The $ClCH_2$ group in **1b** can be derived by a conventional reaction route, $CHO \rightarrow CH_2OH \rightarrow CH_2Cl$. In the synthesis of **1a**, however, the 2-CH_2OH group intramolecularly reacts with the boronic acid group. Hence, **1a** was synthesized by direct bromination of 2-methylphenylboronic acid with NBS followed by the ion-exchange with Cl^-. The ion-exchange treatment is indispensable for fluorescence measurements.

‡ 5,10,15,20-Tetrapyridylporphyrin was purchased from Aldrich.

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