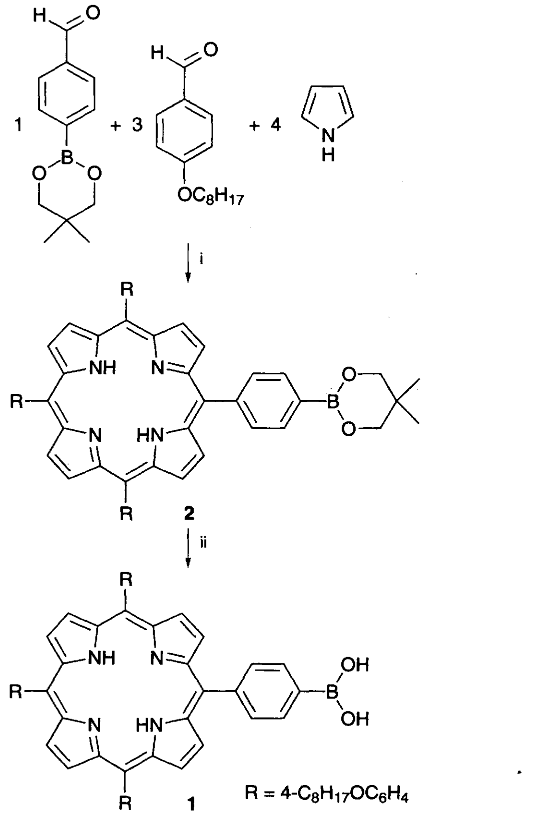
Sugar–boronic acid interactions in the formation of novel chiral porphyrin dimers with various porphyrin–porphyrin angles

Masayuki Takeuchi, Yakushu Chin, Tomoyuki Imada and Seiji Shinkai*

Department of Chemical Science & Technology, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan

Monoboronic acid-appended porphyrin 1 forms sugar–1 complexes (1:2) which have various porphyrin–porphyrin angles, depending on the sugar absolute configuration; the system is very useful in the study of the photochemical properties of dimeric porphyrins and the role of a so-called 'essential pair'.

The distance and angle of two porphyrin groups are the most important controlling factors governing the efficiency of electron transfers to and from porphyrins and are known to play a decisive role in photosynthetic systems as an 'essential pair'.[1] Thus, the reconstitution of the essential pair in an artificial system is of current interest to many photochemists. However, in most cases, the molecular design, actual synthesis and fine tuning of such porphyrin dimers with a specific distance and angle are very difficult.[2,3] Recently, we noticed that diol–boronic acid interactions are a very useful building-block to create oriented supramolecular assemblies.[4,5] In particular, it is known that monosaccharides can form saccharide–boronic acid complexes (1:2) and chirally arrange two pendent groups at a specific distance and angle, depending on the absolute configuration of the monosaccharides involved.[5,6] Judging from the variety and diversity of monosaccharides, one can expect that the fine-tuning of the distance and the angle of the porphyrin dimers may be achieved by simply mixing a boronic acid-appended porphyrin with monosaccharides. With these objects in mind we synthesized compound **1**. The three octyl groups in **1** were introduced to enhance the solubility in organic media.



Scheme 1 *Reagents and conditions*: i, Propionic acid reflux, 2 h; ii, TFA, 10% aq. H_2SO_4, stirred for 30 h, total yield 3.2%

Compound **1** (mp 211–214 °C) was synthesized according to Scheme 1 and identified by IR, ^{1}H NMR and mass spectral (FAB, *m/z* 1099 [M + glycerin + H − $2H_2O]^+$)† evidence and satisfactory elemental analysis.

The 1:2 complexes were prepared by refluxing a CH_2Cl_2 solution of saccharide and **1** (1.2:2.0 molar ratio) for 1.5 h in a Soxhlet extractor depositing molecular sieves (4 Å) in an upper cylindrical filter paper. D- and L-Fucose, D-arabinose, α-methyl-D-mannopyranoside and D- and L-threitol, which have only four OH groups and therefore react with two boronic acids, were used. The product structures with a 1:2 stoichiometry were confirmed by ^{1}H NMR spectral evidence[7] and elemental analysis. Theoretical calculations (MOPAC ver. 6)[6] indicated that fucose·$\mathbf{1}_2$, arabinose·$\mathbf{1}_2$, α-methyl-D-mannopyranoside·$\mathbf{1}_2$ and threitol·$\mathbf{1}_2$ have the porphyrin dihedral angles of 120, 53, 40 and 12°, respectively (Fig. 1).

The spectral parameters are summarized in Table 1. Examination of Table 1 reveals that the extinction coefficients per one porphyrin in saccharide·$\mathbf{1}_2$ are always smaller than that for **2** (used as a monomeric reference compound). Similarly, the relative fluorescence intensities (compared with I/ε_{430}) for saccharide·$\mathbf{1}_2$ are smaller (except D-fucose·$\mathbf{1}_2$) than that for **2**. The results indicate that two porphyrins in saccharide·$\mathbf{1}_2$ interact with each other in the ground state and/or in the excited state. Very interestingly, we discovered that both ε_{max} and I/ε_{430} are linearly correlated with the porphyrin dihedral angle (Fig. 2). The finding clearly establishes that the dihedral angle plays a decisive role in electronic properties of porphyrin dimers.

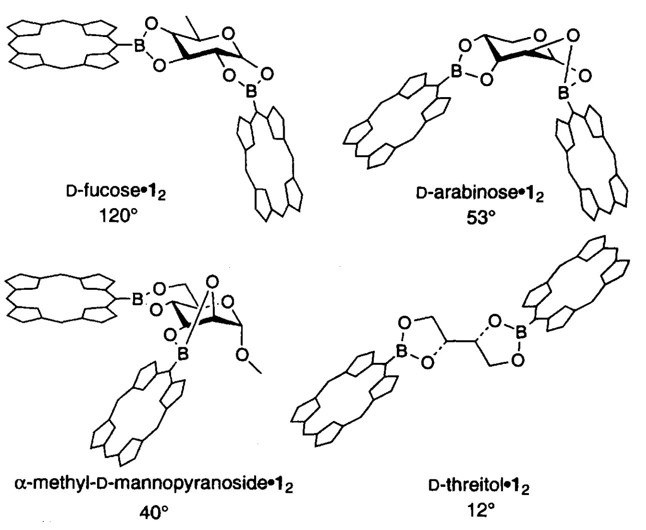


Fig. 1

Table 1 Spectral parameters[a]

	Absorption spectra		Fluorescence spectra	
Porphyrin	Soret band λ_{max}/nm	10^{-5} ε per porphyrin	λ_{EM}/nm[b]	I/ε_{430}
2 (monomer)	421	4.78	653	100
D-Fucose·$\mathbf{1}_2$	422	4.34	653	104.6
D-Arabinose·$\mathbf{1}_2$	422	3.66	653	97.0
α-Methyl-D-mannopyranoside·$\mathbf{1}_2$	422	3.77	653	95.3
D-Threitol·$\mathbf{1}_2$	422	3.47	653	93.1

[a] 25 °C, CH_2Cl_2, [**2**] = 2.00×10^{-6} mol dm^{-3}; [saccharide·$\mathbf{1}_2$] = 1.00×10^{-6} mol dm^{-3}. [b] Emission maximum wavelength. Excitation wavelength is 430 nm.

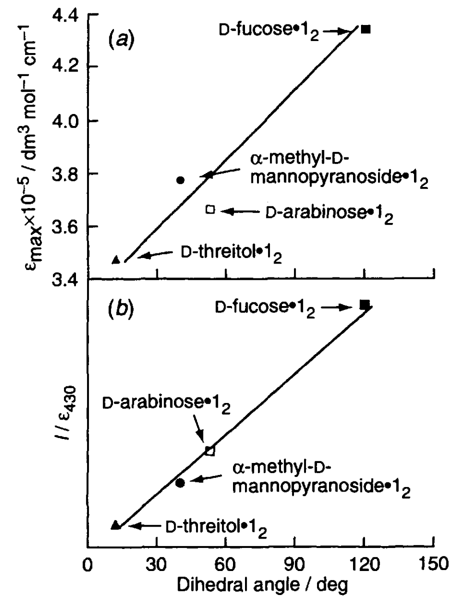


Fig. 2 Plots of (*a*) ε_{max} *vs.* dihedral angle and (*b*) I/ε_{430} *vs.* dihedral angle

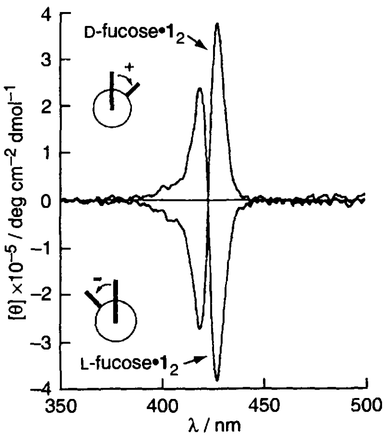
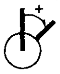
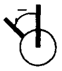
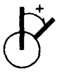


Fig. 3 Typical example of CD spectra; 25 °C, CH_2Cl_2, [fucose·$\mathbf{1}_2$] = 1.00×10^{-6} mol dm^{-3}

As expected, saccharide·$\mathbf{1}_2$, in which two porphyrins are forced to chirally orientate by a saccharide connector, gave a sharp exciton-coupling band: symmetrical spectra were always observed for D- and L-enantiomers (Fig. 3). The CD sign can be reasonably explained by the absolute configuration of used saccharides (Table 2). The results imply that this system is also useful for a convenient method of the saccharide structure determination by CD spectroscopy.

Table 2 CD parameters of saccharide·$\mathbf{1}_2$ complexes[a]

		λ_{max}, λ_{min} (θ)/nm (deg cm^{-2} dmol^{-1})	
Saccharide complex		First	Second
D-Fucose·$\mathbf{1}_2$		427.0 (3.8×10^5)	418.5 (-2.7×10^5)
L-Fucose·$\mathbf{1}_2$		427.0 (-3.8×10^5)	419.0 (2.4×10^5)
D-Arabinose·$\mathbf{1}_2$		427.0 (-3.4×10^5)	419.0 (2.8×10^5)
α-Methyl-D-mannopyranoside·$\mathbf{1}_2$		427.0 (-8.7×10^5)	419.0 (5.3×10^5)
D-Threitol·$\mathbf{1}_2$		427.5 (-4.0×10^5)	419.0 (1.8×10^5)
L-Threitol·$\mathbf{1}_2$		427.5 (3.9×10^5)	419.0 (-2.1×10^4)

[a] 25 °C, CH_2Cl_2, [saccharide·$\mathbf{1}_2$] = 1.00×10^{-6} mol dm^{-3}

Footnote

† This parent peak indicates that the boronic acid group reacts with glycerin, used as a matrix in the mass spectral measurement, to yield its boronate ester ($-2H_2O$).

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