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Sugar Building-Block as a Fine-Tunable Link for Electron-Donor - Electron-Acceptor Couples

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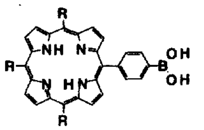
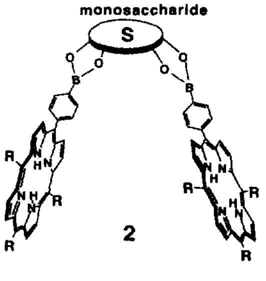
***Abstract*:** The structural factors of a saccharide link in an energy-transfer system using porphyrinatozinc-porphyrin couples and an electron-transfer system using porphyrinatozinc-anthraquinone couples have been estimated: it was found that the structual change in the saccharide scarcely affects the efficiency of the former system but does affect that of the latter system. © 1999 Elsevier Science Ltd. All rights reserved.

The distance and angle between two chromophoric groups or a donor-acceptor couple are the most important controlling factors governing the efficiency of energy and electron transfers. The typical example is seen in natural photosynthetic systems as a 'special pair'.[1] Thus, the reconstitution of the special pair in an artificial system is of current interest to many photochemists. Generally saying, however, the molecular design, actual synthesis and fine tuning of such porphyrin dimers with a specific distance and a specific 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 monosaccharide 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 previously synthesized compound **1**: we found that the 1:2 complexes **2** show the different spectroscopic properties, depending on the monosaccharide used as a link.[7]



1: R = 4-$C_6H_4OC_8H_{17}$



2

We here report the influence of the monosaccharide link on the energy-transfer efficiency between two porphyrin derivatives and the electron-transfer efficiency from a porphyrin group to a anthraquinone group. The syntheses of *o*-**3Zn** and *m*-**3Zn** were reported previously.[8,9] Compound *p*-**3** was synthesized according to the method used for the preparation of **1**[7] and metallated with Zn(OAc)$_2$ to yield *p*-**3Zn**. Saccharide-containing

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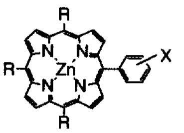
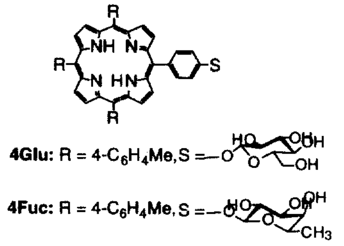
porphyrins **4Glu** and **4Fuc** and Saccharide-containing anthraquinones **5Glu** and **5Fuc** were synthesized in a manner similar to that reported by Oulmi *et al.*[10]

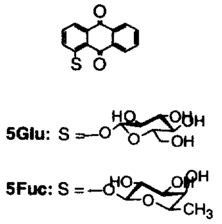


o-3Zn: R = C_6H_5, X = 2-$B(OH)_2$
m-3Zn: R = C_6H_5, X = 3-$B(OH)_2$
p-3Zn: R = 4-C_6H_4Me, X = 4-$B(OH)_2$



4Glu: R = 4-C_6H_4Me, S =

4Fuc: R = 4-C_6H_4Me, S =



5Glu: S =

5Fuc: S =

All compounds were identified by IR and ^1H NMR spectral evidence and elemental analyses. The complexation between the boronic acid group in the **3Zn** series compounds with the 4,6-diol group in **4Glu** and **5Glu** or the 3,4-diol group in **4Fuc** and **5Fuc** was attained by refluxing a CH_2Cl_2 solution of two reactants (1.0:1.0 molar ratio) for 2 h in a Soxhlet extractor depositing molecular sieve 3A in an upper cylindrical filter paper.

The energy-minimized structures of saccharide-linked complexes were estimated for the simplified phenyl skeletons (as shown in Fig. 1) using MM3.[11] Since the B atom adopts the sp^2-hybridization and strongly conjugates with the phenyl group, the $C_6H_5BO_2$ moiety lies in the same plane. This indicates that the sp^2-B is useful to restrict the conformational freedom. In D-glucose-linked complexes, the porphyrinatozinc position (a) or (b) scarcely affects the distance between the porphyrinatozinc and the acceptor. In L-fucose-linked complexes, in contrast, the distance is largely affected by the porphyrinatozinc position (a) or (b). One can thus regard that porphyrinatozinc occupies the position (a) in L-fucose-linked complexes if the energy- or electron-transfer occurs more efficiently in L-fucose-linked complexes than in D-glucose-linked complexes.

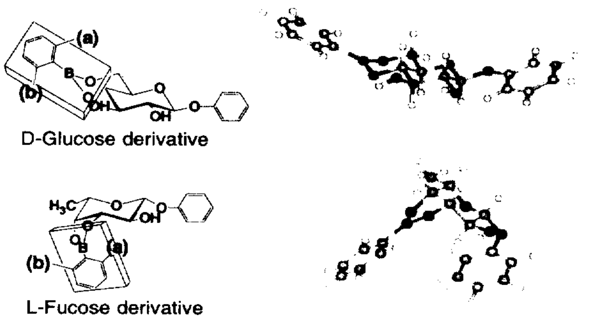


Fig. 1. Energy-minimized structures for the simplified diphenyl versions of D-glucose-linked and L-fucose-linked complexes.

The results of the energy-transfer in the porphyrinatozinc-porphyrin couples are shown in Fig. 2. The excitation wavelength is 546 nm where the absorbance ratio of porphyrinatozinc *versus* porphyrin becomes largest (2.0/1.0). The fluorescence spectrum for an equimolar mixture (1.00×10^{-6} mol dm^{-3} each) of *p*-**3Zn** and tri-*O*-acetylated **4Fuc** was basically equivalent to the sum of the two fluorescence spectra. This implies that the intermolecular energy-transfer is negligible at such a low concentration region. In contrast, the intramoleular energy-transfer did take place in the couples: emission of the porphyrinatozinc moiety (595 nm) decreased whereas that of the porphyrin moiety (650 nm) increased. It is seen from Fig. 2 that emission at 650 nm is due to both the *p*-**3Zn** moiety and the **4Fuc** moiety whereas emission at 595 nm mostly reflects that from the *p*-**3Zn**. Hence, we estimated the fluorescence intensity decrease at 595 nm for the quantitative comparison (Table 1). It is seen from Table 1 that the energy-transfer efficiencies are affected neither by the position of the boronic acid group nor by the structure of the saccharide link, the fluorescence intensities constantly decreasing by 60-

66 % relative to those of corresponding uncoupled **3Zn**. The fluorescence lifetimes monitored at 595 nm, however, indicate that the energy-transfer from **3Zn** occurs through two pathways based on the short-lived and the conventional long-lived species (Table 1). The energy-transfer process is influenced both by the position of the boronic acid group and by the structure of the saccharide link.

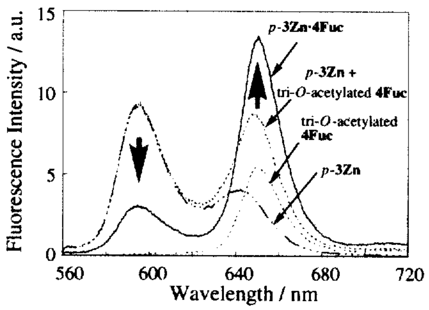


Fig. 2. Fluorescence spectra for *p*-**3Zn**, tri-*O*-acetylated **4Fuc**, a mixture of *p*-**3Zn** + tri-*O*-acetylated **4Fuc** and *p*-**3Zn·4Fuc** complexes: 25 °C, CH_2Cl_2, 1.00×10^{-6} mol dm^{-3} each, excitation 546 nm.

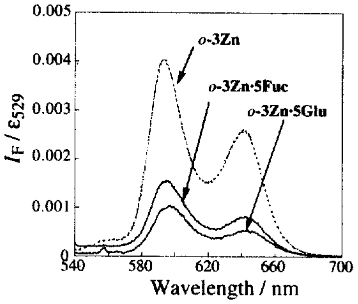


Fig. 3. Fluorescence spectra for *o*-**3Zn**, *o*-**3Zn·5Glu** and *o*-**3Zn·5Fuc** complexes: 25 °C, CH_2Cl_2, 1.00×10^{-5} mol dm^{-3}, excitation 529 nm. The ordinate is normalized by the absorption coefficient at 529 nm.

The electron-transfer efficiency for **3Zn·5Glu** and **3Zn·5Fuc** couples was estimated with 529 nm as an excitation wavelength. As summarized in Table 1, the fluorescence intensity at 595 nm was scarcely decreased in *m*- and *p*-isomers. In contrast, the fluorescence intensity largely decreased in *o*-isomers by 66 % (for *o*-**3Zn·5Fuc**)-84 % (for *o*-**3Zn·5Glu**) (Fig. 3). The results indicate that the electron-transfer efficiency is more sensitive to the distance factor.[12] As the electron-transfer occurs more efficiently in *o*-**3Zn·5Glu** than in *o*-**3Zn·5Fuc**, one can presume that the porphyrinatozinc moiety in *o*-**3Zn·5Fuc** mainly occupies the position (b) in Fig. 1.

The fluorescence lifetimes monitored at 595 nm were estimated to be 1.9 ns for uncoupled *o*-**3Zn**, 1.8 ns for uncoupled *m*- and *p*-**3Zn**. The time-

Table 1 Energy-transfer efficiencies in **3Zn·4Glu** and **3Zn·4Fuc** systems and electron-transfer efficiencies in **3Zn·5Glu** and **3Zn·5Fuc** systems [a]

Condensed couple	Decrease in the fluorescence intensity at 595 nm (%)	Fluorescence lifetime[d] (ns)	
o-**3Zn·4Glu**	65[b]	0.09 (79%)	1.8 (21%)
o-**3Zn·4Fuc**	66[b]	0.06 (75%)	1.8 (27%)
m-**3Zn·4Glu**	62[b]	0.31 (85%)	1.7 (15%)
m-**3Zn·4Fuc**	65[b]	0.18 (85%)	1.7 (15%)
p-**3Zn·4Glu**	60[b]	0.27 (92%)	1.6 (8%)
p-**3Zn·4Fuc**	62[b]	0.20 (90%)	1.6 (10%)
o-**3Zn·5Glu**	84[c]	0.10 (91%)	2.0 (9%)
o-**3Zn·5Fuc**	66[c]	0.08 (73%)	1.9 (27%)
m-**3Zn·5Glu**	0[c]	1.8 (100%)	
m-**3Zn·5Fuc**	0[c]	1.8 (100%)	
p-**3Zn·5Glu**	0[c]	1.8 (100%)	
p-**3Zn·5Fuc**	0[c]	1.8 (100%)	

[a] 25 °C, CH_2Cl_2, [couple] = 1.00×10^{-6} mol dm^{-3} for energy-transfer and 1.00×10^{-5} mol dm^{-3} for electron-transfer.

[b] Energy transfer efficiency expressed by the fluorescence intensity relative to that of corresponding uncoupled **3Zn** (*e.g.*, *o*-**3Zn·4Glu** relative to *o*-**3Zn**): excitation 546 nm.

[c] Electron-transfer efficiency expressed by the fluorescence intensity relative to that of corresponding uncoupled **3Zn**: excitation 529 nm.

[d] The percentage of the component for each emission species is shown in the parenthesis.

dependences for *m*- and *p*-isomers of **3Zn·5Glu** and **3Zn·5Fuc** obeyed the first-order kinetic equation and the lifetimes were all estimated to be 1.8 ns (Table 1). This again supports the view that the electron-transfer to the antharaquinone moiety can be virtually disregarded. For *o*-isomers, on the other hand, a new emission based on the short-lived species appeared as a major component in addition to the conventional long-lived species (Table 1). The lifetimes for the new species were shorter by *ca.* 21-fold. We consider that this species is related to the folded conformation in *o*-**3Zn·5Fuc** and *o*-**3Zn·5Glu**, featuring an intramolecular through-space electron-transfer.

In conclusion, the present study has demonstrated that the electron-transfer efficiency is sensitively affected by the structural factors in the saccharide link whereas the energy-transfer efficiency is not so mach. The results indicate that the electron-transfer efficiency is controllable by simply substituting the saccharide connecting the electron-donor and the electron-acceptor. Such a facile substitution of the link becomes possible for the first time by the utilization of the reversible boronic acid-saccharide interaction. We believe that judging from the variety of the saccharide structure, even the fine-tuning of the electron-transfer efficiency is possible in the electron-donor - saccharide - electron-acceptor ternary complexes.

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