Change of electron-transfer path-selectivity in a triad by F$^-$-coordination at a boronate-ester bridge

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In a triad comprising of a zinc porphyrin donor (ZP) appended to a naphthalene-1,8:4,5-tetracarboxylic diimide (NI) and a pyromellitic diimide (PI) through a boronate ester and an acetal bridge, respectively, F$^-$-coordination at the boronate bridge induced clear switching of the electron-transfer path from ^{1}ZP* → NI to ^{1}ZP* → PI.

Electron-transfer (ET) path-selectivity is one of the key issues in understanding the mechanism of primary charge separation in photosynthetic reaction centers (RCs).[1] In spite of the highly C_2 symmetric structure, only the L-branch is ET active in RC. This ET path-selectivity is strongly guided by the surrounding proteins in which electron carriers of the RC are embedded and it seems difficult to realize ET flow along the M-branch even in RCs of a variety of site-directed mutants.[2] Control of ET path-selectivity such that an unfavorable ET path can be made preferential over a favorable one without a drop in rate by external input will be quite useful not only for construction of artificial ET molecular devices but also in understanding the factors which govern biological ET reactions. In order to realize this control, the external input must trigger two effects, *i.e.* to *block* a *favorable* ET path and simultaneously to *accelerate* an *unfavorable* ET path. Here, we demonstrate that this ET path control is indeed possible in triad **1** comprising of a zinc porphyrin donor (ZP) appended to a naphthalene-1,8:4,5-tetracarboxylic diimide (NI) and a pyromellitic diimide (PI), through a boronate ester and an acetal bridge, respectively (Scheme 1). Important structural features are as follows; (1) the two bridges are similar in length,[3] (2) NI is a stronger electron acceptor than PI by 0.3 V,[4] and (3) intramolecular ET from ^{1}ZP* to NI across a boronate bridge can be suppressed upon F$^-$-coordination.[5]

In benzene, the fluorescence intensities of **1**, **2** and **3** relative to that of **4** were 0.45, 0.44 and 0.89, respectively. This fluorescence quenching suggests intramolecular charge separation (CS) between ^{1}ZP* and NI or PI which has been confirmed by picosecond-time resolved transient absorption spectra (Fig. 1).[6] Absorption peaks due to the radical anion were observed at 475, 610 and 790 nm (NI$^-$) for **2**, and at 721 nm (PI$^-$) for **3**, providing clear evidence for formation of NI$^-$–ZP$^+$ and ZP$^+$–PI$^-$,[4] respectively. The transient absorption studies revealed that excitation of ZP with 532 nm laser pulses in **2** and **3** yielded NI$^-$–ZP$^+$ with τ_{CSN} = 0.52 ns and ZP$^+$–PI$^-$ with τ_{CSP} = 1.1 ns, respectively.[7] Lifetimes of these ion pairs were both longer than 6 ns. Upon similar laser excitation of ZP in **1**, the absorbance due to ^{1}ZP* around 460 nm decayed with τ = 0.46 ns, and the transient absorption spectrum at 3 ns delay time is practically the same as that of **2** except for a small band at 721 nm due to PI$^-$, indicating that CS between ^{1}ZP* and NI is dominant in **1**. Comparison of decay time constants of ^{1}ZP* in **1**–**3** led to the conclusion that excitation of ZP in **1** leads to formation of NI$^-$–ZP$^+$ and ZP$^+$–PI$^-$ in a ratio of 11:1 (Scheme 2).

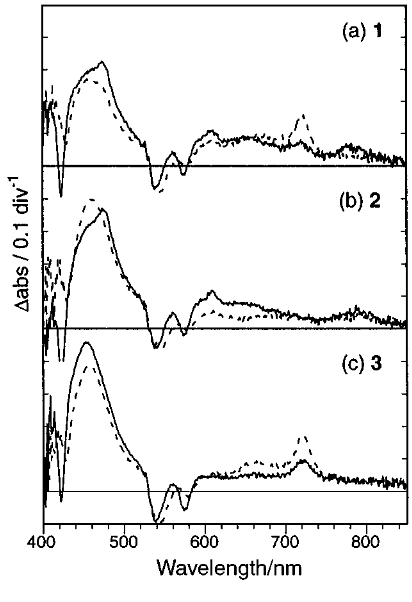
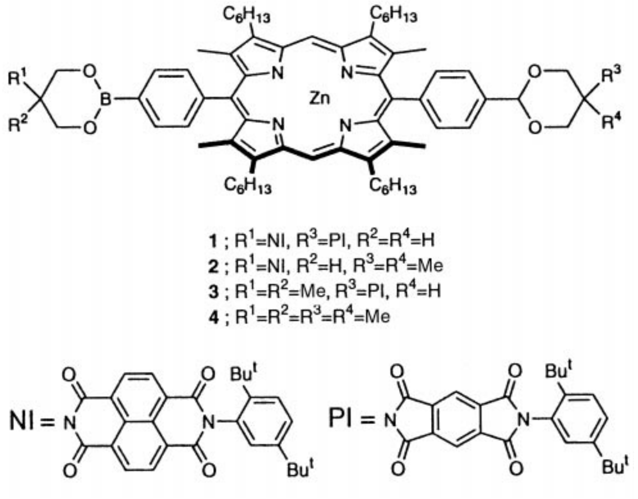
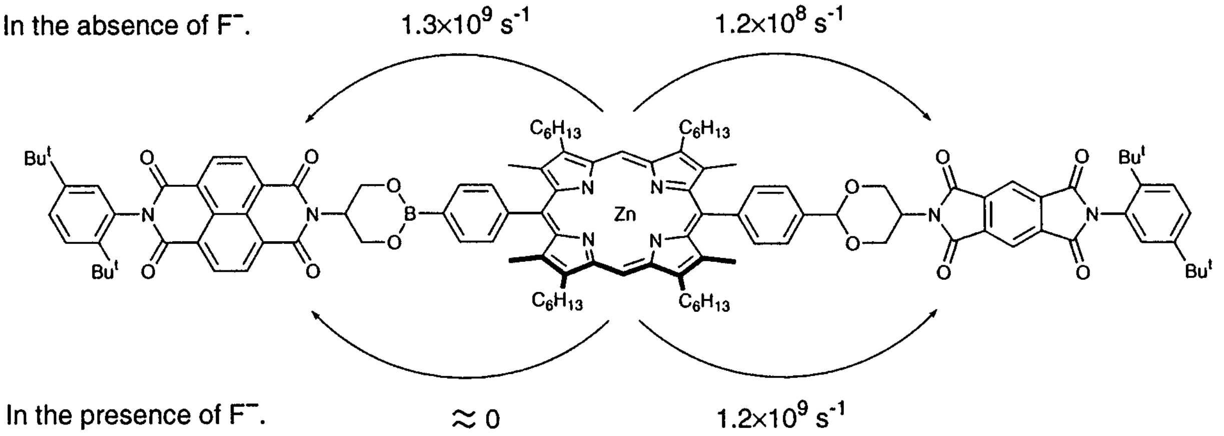


Fig. 1 Transient absorption spectra of (a) **1**, (b) **2** and (c) **3** in benzene at 3 ns; (——) no TBAF; (······) in the presence of 1.2 equiv. TBAF.

In the presence of 1.2 equiv. of tetra-*n*-butylammonium fluoride (TBAF), relative fluorescence intensities of **1**, **2** and **3** to **4** were 0.65, 0.98 and 0.72, respectively. The transient absorption spectra of **2** [Fig. 1(b), dotted line] are practically the same as those of **4** (not shown) from 20 ps to 6 ns delay times, featuring no CS but simple intersystem crossing of ^{1}ZP* → ^{3}ZP* with τ = 1.5 ns. Thus CS between ^{1}ZP* and NI in **2** is completely suppressed in a F$^-$-coordinated form as reported previously.[5] This CS suppression may be explained in terms of decreased electronic coupling between ^{1}ZP* and NI across a F$^-$-coordinated boronate bridge possibly due to the high energy LUMO of the bridge in comparison to that in a neutral bridge.[8] Considering the similar CS suppression in **1**, its fluorescence quenching should be ascribed to CS between ^{1}ZP* and PI. This



Scheme 1 Structures model **1** and reference molecules **2**–**4**.



Scheme 2 ET-path selectivity of **1** in the absence and presence of F^-.

has been confirmed by the transient absorption spectrum [Fig. 1(a), dotted line], which shows the appearance of a 721 nm absorption peak, thus indicating CS between $^1ZP^*$ and PI instead of NI. Here it is interesting to note that the F^--coordination not only blocks ET to NI but also accelerates ET to PI significantly. On the basis of the analysis of the time profile of the rise at 721 nm, the CS rate constant in F^--coordinated **1** has been determined to be $1.2 \times 10^9\ s^{-1}$, which is *ca.* 10 times larger compared to that occurring in neutral **1**. Similar acceleration of CS between $^1ZP^*$ and PI was also observed in F^--coordinated **3** ($k_{CS} = 6.5 \times 10^8\ s^{-1}$). The acceleration of CS between $^1ZP^*$ and PI upon F^--coordination on the boronate bridge can be explained on the basis of Coulomb interaction between the negative charge on the F^--coordinated boron atom and the ion-pair ZP^+–PI^-. In nonpolar solvents like benzene, the tetracoordinated boronate exists as a tight ion pair. However, it is reasonable to consider that electrostatic attraction between the negative charge at the tetracoordinated boronate and the positive charge at the ZP^+ must be most influential among other electrostatic interactions in the system and thus the F^--coordination eventually leads to a decrease in the energy level of ZP^+–PI^-, thereby enhancing CS reaction between $^1ZP^*$ and PI.

Switching of ET path-selectivity of **1** upon F^--coordination is summarized in Scheme 2, where the ET to NI is suppressed mainly by the electronic factor and the ET to PI is accelerated mainly by the nuclear factor. The boronate-bridged acceptor–donor–acceptor architectures will be useful, since they provide a convenient and efficient way to control the ET path selectivity in a predictable manner as such that ET over the boronate-bridge will be suppressed and ET in the opposite direction from the boronate bridge will be accelerated.

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