

# Coordination control of intramolecular electron transfer in boronate ester-bridged donor–acceptor molecules

Hideo Shiratori,<sup>a</sup> Takeshi Ohno,<sup>b</sup> Koichi Nozaki,<sup>b</sup> Iwao Yamazaki,<sup>c</sup> Yoshinobu Nishimura<sup>c</sup> and Atsuhiko Osuka<sup>\*a†</sup>

<sup>a</sup> Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan

<sup>b</sup> Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, 560-8531, Japan

<sup>c</sup> Department of Chemical Process Engineering, Graduate School of Engineering, Hokkaido University, Sapporo, 060-8628, Japan

Acid–base reaction at the bridge in a donor–acceptor molecule can influence intramolecular electron-transfer reactions; this has been demonstrated in boronate ester bridged zinc porphyrin–diimide dyads in which intramolecular electron transfer reaction has been completely suppressed by coordination of F<sup>−</sup> on the bridge boron.

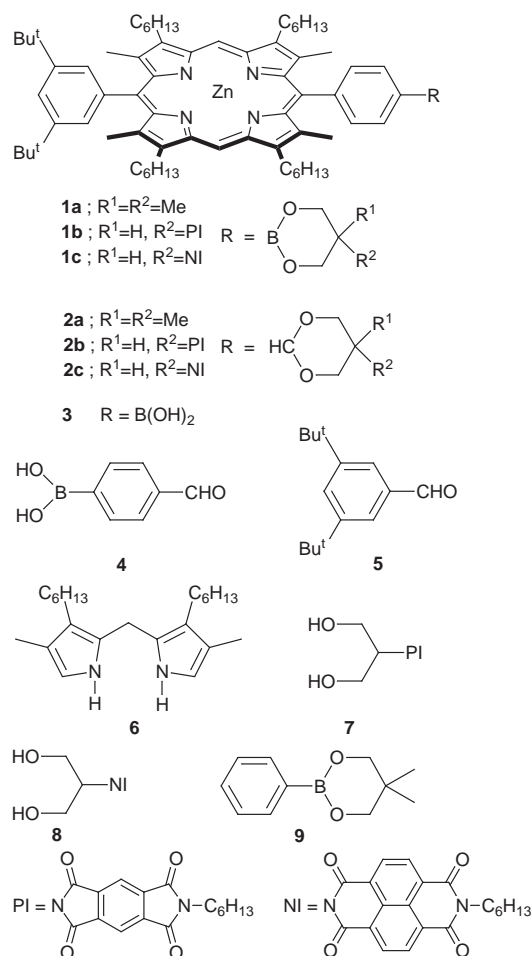
Intramolecular electron transfer (ET) is the subject of many studies that are aimed at elucidating the role of the various parameters which govern the ET rate.<sup>1</sup> Among these, the chemical identity and nature of the bridge that connects donor and acceptor are important, since ET reactions can be facilitated by appropriate molecular orbitals provided by the bridge.<sup>2</sup> When a donor–acceptor molecule undergoes ET with a rate tunable by external physical and/or chemical input, it may constitute a switching ET molecular system. We report here intramolecular photoinduced electron transfer in boronate ester bridged zinc porphyrin–pyromellitimide (ZP–PI, **1b**) and zinc porphyrin–1,8:4,5-naphthalenetetracarboxylic diimide (ZP–NI, **1c**) (Scheme 1) in which the Lewis acidic boronate ester may enable alteration of the ET rate upon base coordination. This has indeed been demonstrated by addition of fluoride anion (F<sup>−</sup>) which suppresses the ET.

Porphyrin **1a** was prepared according to the method reported by Toi *et al.*<sup>3</sup> Attempted hydrolysis of **1a** was unsuccessful in our hands under both basic<sup>3</sup> and acidic conditions.<sup>4</sup> Thus, boronic acid **3** was prepared by the cross-condensation of 4-formylphenylboronic acid **4** and 3,5-di-*tert*-butylbenzaldehyde **5** with dipyrromethane **6** followed by oxidation with *p*-chloranil under mild conditions (0 °C, 30 min) in 35% yield. Boron-bridged dyads **1b** and **1c** were prepared by refluxing a toluene solution of **3** in the presence of diol **7** or **8** with 84% and 90% isolated yields, respectively.

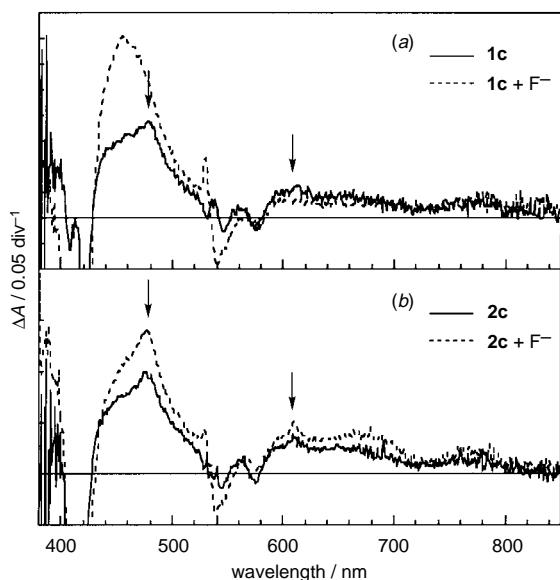
In benzene, the fluorescence of <sup>1</sup>ZP\* in **2b** and **2c** is quenched by the attached PI or NI; the relative fluorescence intensities of **2b** and **2c** to **2a** are 0.89 and 0.36, respectively, and the fluorescence decays of **2b** and **2c** measured by the time-correlated single photon counting technique have been found to obey a single exponential function with lifetimes of 1.21 ns and 0.49 ns, respectively, which are shorter than the lifetime (1.39 ns) of **2a**. The observed fluorescence quenching suggests charge separation (CS) between <sup>1</sup>ZP\* and PI or NI. The ET quenching has been confirmed by picosecond time resolved transient absorption spectroscopy. The transient absorption spectra taken for excitation with a 17 ps laser pulse at 532 nm revealed the appearance of a 715 nm absorption band due to PI<sup>−</sup> for **2b** (not shown) and of 480 nm and 610 nm bands due to NI<sup>−</sup> for **2c** [Fig. 1(b)],<sup>5</sup> respectively, clearly indicating ion-pair formation. Charge recombination kinetics of the ion pair to the ground state in **2b** measured by monitoring the 715 nm absorbance change follows a single exponential decay with  $\tau = 84 \pm 6$  ns, while the similar kinetic trace at 480 nm in **2c** follows a biphasic decay with  $\tau_1 = 77 \pm 16$  ns (66%) and  $\tau_2 = 380 \pm 100$  ns (34%).<sup>6</sup> The

boronate ester-bridged models, **1b** and **1c**, undergo essentially the same ET reactions as those of **2b** and **2c**; the relative fluorescence intensities of **1b** and **1c** to **1a** are 0.70 and 0.36, and the fluorescence lifetimes of **1b** and **1c** are 1.18 ns and 0.57 ns, respectively, which are both shorter than the lifetime (1.40 ns) of **1a**. Transient absorption spectroscopy also revealed the formation of the ion-pair state, and the lifetimes of the ion-pair state are  $40 \pm 5$  ns for **1b** (not shown) and  $13 \pm 1$  ns (60%) and  $290 \pm 10$  ns (40%) for **1c** [Fig. 1(a), solid line].

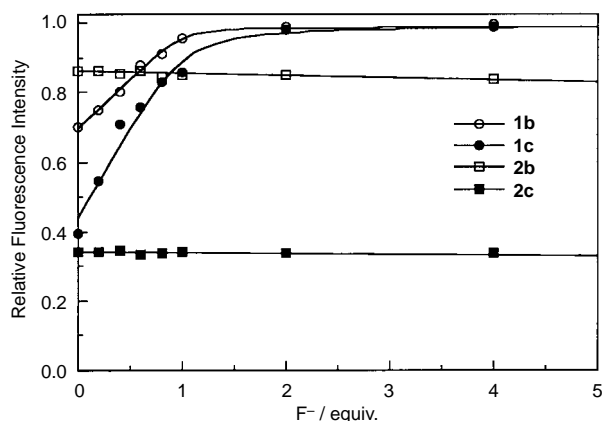
The ET dynamics were also examined in the presence of tetra-*n*-butylammonium fluoride (TBAF). In the <sup>11</sup>B NMR spectra taken in benzene, a broad boron signal of **1a** appearing at around 10 ppm with respect to a trimethylborate internal standard was shifted to −14 ppm upon an addition of 1 equiv. of TBAF, indicating the complete coordination of F<sup>−</sup> on the



Scheme 1 Structures of models studied



**Fig. 1** Transient absorption spectra of **1c** (a) and **2c** (b) in benzene, at a delay time of 6 ns. Solid lines: in the absence of  $F^-$ ; dotted lines: in the presence of 1.2 equiv.  $F^-$ .



**Fig. 2** Change of fluorescence intensities of diimide-linked models upon addition of  $F^-$ . Data for **1b,c** and **2b,c** were recorded relative to **1a** and **2a**, respectively. Concentrations of models were 1  $\mu$ M.

boron atom. Similar shifts were observed for **1b** and **1c**. Fig. 2 shows the effects of TBAF addition on the fluorescence intensities of **1b,c** and **2b,c**. It is evident that the fluorescence intensity of **1c** increased with increasing amount of TBAF and returned to the original unquenched level with ca. 1 equiv. of TBAF, while the fluorescence intensity of **2c** remained quenched to a constant level up to 5 equiv. of TBAF added. Essentially the same trend was observed for **1b** and **2b**. Upon addition of 5 equiv. TBAF, the short fluorescence lifetimes of free **1b** and **1c** were restored to the unquenched levels (1.56 and 1.57 ns, respectively), which are almost the same as that (1.58 ns) of the acceptor-free reference compound **1a** under the same conditions. In contrast to the ET reactions of **2b** and **2c**, which are rather independent of TBAF [Fig. 1(b)], the transient absorption spectra of **1b** and **1c** in the presence of 1.2 equiv. TBAF are practically the same as those of the acceptor-free **1c** with no indication of ion-pair formation [Fig. 1(a), dotted line].<sup>7</sup> Therefore it is concluded that the CS reactions in **1b** and **1c** are completely blocked by  $F^-$  coordination. Since restoring the initial ET activities of **1b** and **1c** after the addition of  $F^-$  is important for constructing a real ON/OFF system, the addition of a large amount of **9** to solutions of  $F^-$ -complexed **1b** and **1c** was examined but did not lead to the recovery of the ET activities. Finally, note that the CS reactions in **1b** and **1c** are also completely blocked in solvents with high donor numbers

such as DMF and triethylamine but such solvent effects are not observed for **2b** and **2c**.

At the present stage, it seems difficult to identify the main reason for this CS inhibition by  $F^-$  coordination. The energy levels of the ion-pair states, geometrical parameters, and electronic coupling should be changed upon  $F^-$  coordination. Since the addition of TBAF had almost no effect on the redox potentials of these models,<sup>8</sup> the energy levels of the ion-pair states do not change significantly, at least in polar DMF solution, but are more difficult to estimate in nonpolar benzene solution. Since the center-to-center distance between ZP and the boron is estimated to be longer than that between the boron and the diimide,<sup>9</sup> the negative charge at the boron may raise the energy level of the ion-pair state, thereby decreasing the  $k_{CS}$  value. A change from a neutral trigonal boron to a tetrahedral 'ate' anion induces a slight shortening of the donor-acceptor distance by 0.4 Å as well as changes in the molecular orbitals of the bridge that will alter the electronic coupling between ZP and the diimide acceptor, relevant for CS. The former structural change seems to be unimportant since comparable  $k_{CS}$  rates were observed for the structural analogues, **2b** and **2c**. The latter effect, which may be evaluated by considering the molecular orbitals of the phenylboronate **9**, causes a considerable increase in the LUMO energy of the bridge upon  $F^-$  coordination,<sup>10</sup> suggesting the decreased electronic coupling due to the high LUMO energy to be critical in the observed CS inhibition.

Coordination on a neutral bridging boron may provide a convenient method of controlling the intramolecular ET. The generality of this method will be tested in other ET systems and also in triplet-triplet energy transfer systems. Studies in this direction are ongoing and will be reported soon elsewhere.

This work was partly supported by a Grant-in-Aid for Scientific Research (No. 09440217) from the Ministry of Education, Science, Sports and Culture of Japan and by CREST (Core Research for Evolutional Science and Technology) of Japan Science and Technology Corporation (JST).

## Notes and References

† E-mail: osuka@kuchem.kyoto-u.ac.jp

- M. R. Wasielewski, *Chem. Rev.*, 1992, **92**, 435, and references therein.
- H. M. McConnell, *J. Chem. Phys.*, 1961, **35**, 508; S. Lason, *J. Am. Chem. Soc.*, 1981, **103**, 4034; M. N. Paddon-Row, *Acc. Chem. Res.*, 1994, **27**, 18, and references therein.
- H. Toi, Y. Nagai, Y. Aoyama, H. Kawabe, K. Aizawa and H. Ogoshi, *Chem. Lett.*, 1993, 1043.
- M. Takeuchi, Y. Chin, T. Imada and S. Shinkai, *Chem. Commun.*, 1996, 1867.
- A. Osuka, S. Nakajima, K. Maruyama, N. Mataga, T. Asahi, I. Yamazaki, Y. Nishimura, T. Ohno and K. Nozaki, *J. Am. Chem. Soc.*, 1993, **115**, 4577; A. Osuka, R.-P. Zhang, K. Maruyama, N. Mataga, Y. Tanaka and T. Okada, *Chem. Phys. Lett.*, 1993, **215**, 179.
- This biphasic decay behavior may be accounted for by considering the singlet-triplet intersystem crossing within the ion-pair since the rate of charge recombination is comparable to the rate of the singlet-triplet intersystem crossing of the ion-pair state. W. Udo, Y. Sakaguchi, H. Hayashi, G. Nohya, R. Yoneshima, S. Nakajima and A. Osuka, *J. Phys. Chem.*, 1995, **99**, 13930.
- The transient absorption spectra indicate that the  $S_1$  state of the ZP does not undergo any ET and is converted to the  $T_1$  state absorbing at 455 nm.
- The one-electron redox potentials of the donor and the acceptor moieties have been measured in DMF by cyclic voltammetry:  $E_{ox}(ZP) = 0.22$ ,  $E_{red}(PI) = -1.24$  and  $E_{ox}(NI) = -0.98$  V for **1a-c**, and  $E_{ox}(ZP) = 0.22$ ,  $E_{red}(PI) = -1.18$  and  $E_{red}(NI) = -0.94$  V for **2a-c** vs. ferrocene-ferrocenium ion.
- Estimated distance between the ZP and the boron is 9.4 Å and those between the boron and the diimide are 7.6 and 7.8 Å in **1b** and **1c**, respectively.
- MO calculations were performed using MacSpartan Plus (*ab initio*, 3-21G basis set). Calculated LUMO energies are 3.4, 8.2, and 4.1 eV for neutral **9**,  $F^-$ -coordinated **9**, and an acetal reference bridge, respectively.

Received in Cambridge, UK, 1st April 1998; 8/02473A