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Generation of a triplet diradical from a donor–acceptor cross conjugate upon acid-induced electron transfer†

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Enhancement of the electron acceptor ability of a *para*-quinodiimine unit by double protonation leads to the proton-induced intramolecular electron transfer from the donor unit to the cross-conjugated acceptor, giving rise to ground state triplet diradical reversibly.

Cooperative transportation of a proton and an electron is often observed in biological systems, as observed in redox reactions carried out by flavoenzymes.[1] Such a phenomenon also plays a crucial role in the physical properties of molecular systems. Emeraldine, which consists of an equimolar mixture of poly-*p*-phenylenediamine and poly-*p*-quinodiimine, shows high electrical conductivity when it is protonated.[2] Di-protonation on the *p*-quinodiimine unit induces an electron transfer from the *p*-phenylenediamine unit, providing two equivalent cation-radicals of *p*-phenylenediamine as an electronic carrier along the polymer chain.

Such a protonation-induced electron transfer can be utilized for generating a high spin molecule. As an example of the protonation-induced spin manipulation, Ishiguro *et al.* demonstrated that the spin multiplicity of a cross-π-conjugate of a phenoxyl radical and a nitronyl nitroxide could be changed reversibly between the diradical and closed shell state when the pH of the solution was changed.[3] Morita *et al.* reported the similar phenomenon in a phenalenoxyl radical carrying a nitronyl nitroxide.[4] On the other hand, Wienk and Janssen observed the generation of ground state triplet dication-diradical species through an intermolecular electron transfer by adding acid to an equimolar mixture of fully reduced and fully oxidized forms of an oligoaniline in which two *para*-substituted rings are linked by a *m*-phenylene ring which act as a ferromagnetic coupler, although this is an intermolecular process.[5]

Here we designed a manipulating spin system in terms of protonation-induced electron transfer as an unimolar event, affording a ground state triplet species. As shown in Fig. 1, the role of donor or acceptor is specified to the appropriate molecular unit within a cross-π-conjugated molecular framework. Such conversion of spin states of the cross-π-conjugated molecule can be performed in a PVC film reversibly, accompanied by the color change. Accordingly, the current system can be utilized to develop a protonation-induced magnetic memory when the protonation-induced electron transfer occurs within one molecule.

A cyclic voltammogram of cross-π-conjugate **QA**[6] in an acetonitrile solution in the presence of tetra-*n*-butylammonium perchlorate as an electrolyte showed a redox wave at 0.95 V *vs.* Ag/AgCl. Since the oxidation potential is close to that of trianisylamine (TA) ($E_{1/2}$ = 0.84 V *vs.* Ag/AgCl), it is

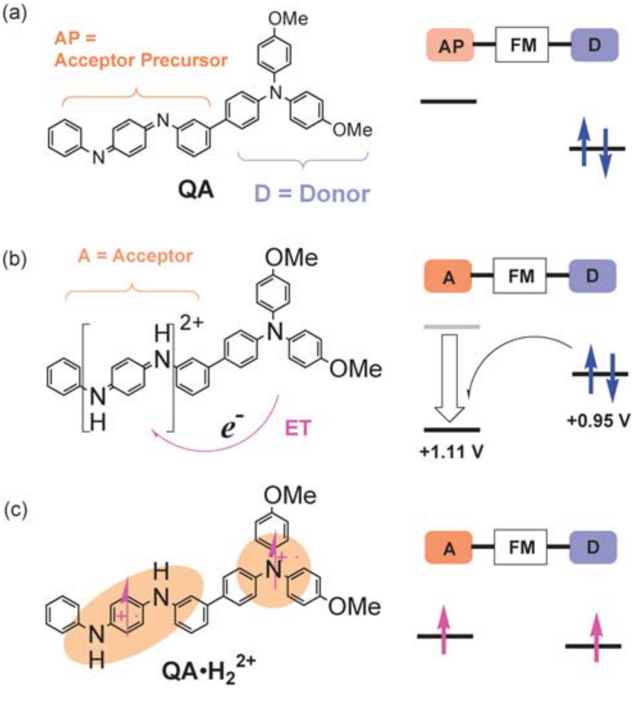

Fig. 1 Schematic drawing of a protonation-induced electron transfer and generation of high-spin species in **QA**. (a) The neutral dimer consists of a donor, an acceptor precursor (pro-acceptor) and a ferromagnetic coupler. (b) The *p*-quinodiimine moiety acquires the acceptor ability, after being doubly-protonated at the two nitrogen atoms, and the intramolecular electron transfer takes place from the dianisylphenylamine moiety. (c) A ground state triplet diradical is generated from the protonation-induced electron transfer and from the ferromagnetic interaction *via* the *m*-phenylene coupler between two unpaired electrons

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† Electronic supplementary information (ESI) available: Preparation methods for compounds **QA**, the details of the UV-vis spectral change upon titration of **QA** with TFA, ESR spectrum of $\mathbf{QA{\cdot}H_2^{2+}}$ in a PVC matrix, calculated spin distribution of $\mathbf{QA{\cdot}H_2^{2+}}$, IR spectrum of **QA** and $\mathbf{QA{\cdot}H_2{\cdot}(ClO_4)_2}$ with the theoretical simulations. See DOI: 10.1039/b804999h

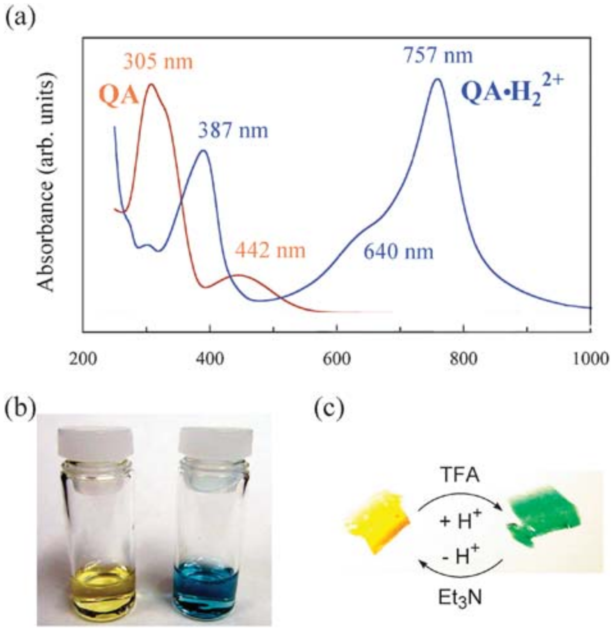

Fig. 2 UV-Vis spectral change of **QA** in dichloromethane solution titrated by trifluoroacetic acid (TFA). (a) UV-Vis spectra of **QA** and doubly protonated **QA** (**QA·H$_2$$^{2+}$**) in acetonitrile. (b) Acetonitrile solutions of **QA** (left: yellow colored solution) and **QA·H$_2$$^{2+}$** (right: deep blue). (c) Protonation induced electron transfer was also performed in a PVC film reversibly.

attributed to the oxidation process of the triarylamine unit of **QA**. On the other hand, the reduction wave could not be observed down to −1 V. In order to estimate the redox potential of the diprotonated form of the *p*-quinodiimine unit, the oxidation waves of *N*,*N′*-diphenyl-*p*-phenylenediamine (PA) were measured because it was a reference compound for the di-protonated and doubly reduced form of *p*-benzoquinodiimine (QI). The oxidation waves of PA were observed at +0.71 and +1.11 V in acetonitrile. The data clearly showed that the acceptor ability of the *p*-quinodiimine moiety was drastically increased by di-protonation referring to the second oxidation potential of PA (+1.11 V). Since this oxidation potential is higher than the oxidation potential (+0.84 V) of TA, the electron transfer from the triarylamine unit to the diprotonated quinodiimine unit of **QA·H$_2$$^{2+}$** must take place, affording the dication diradical species.[7]

The change in the electronic structure of **QA** upon titration with trifluoroacetic acid (TFA) to the dichloromethane solution of **QA** was monitored by UV-vis absorption spectroscopy as shown in Fig. 2. A yellow colored solution of cross-conjugate **QA** in dichloromethane shows two absorption peaks at 305 and 442 nm, the shorter peak being characteristic to the *p*-benzoquinodiimine unit. When the two equivalent TFA was added to the solution, the color of the solution turned to deep blue. Accompanied by the color change, a strong absorption band at 757 nm with a shoulder at 640 nm grew. Further addition of TFA did not cause any changes in the absorption spectrum. Since the band at 757 nm, which appears by the addition of TFA, is similar to the cation radical of trianisylamine,[8] it is certain that the single electron transfer occurs from triarylamine to the doubly protonated quinodiimine unit. The UV spectrum of the acidic solution was returned to the original one by the addition of the excess amount of triethylamine (TEA). This reversible color change was observed repeatedly.

Formation of the radical species upon protonation was observed by ESR measurement. An ESR spectrum of the frozen solution of diprotonated **QA** in dichloromethane containing TFA ([**QA**] : [TFA] = 1 : 5) showed a broad peak centered at g = 2.0036 flanked by two shoulders separated by 4.1 mT (Fig. 3). These fine structures can be assigned to a triplet diradical species with the zero field splitting parameters of D/hc = 0.0019 cm^{-1} E/hc = 0.0008 cm^{-1} on the basis of the second order perturbational simulation. Furthermore, the half-field resonance line due to the forbidden transition (ΔM_s = 2) was observed. These results are strong support for the generation of the triplet diradical species upon the di-protonation of **QA**.

Since the intensity of the triplet signal increased monotonously with decreasing temperature, the triplet is the ground state for the diradical. According to the MO calculation, coefficients of SOMOs distribute on the phenylenediamine or dianysilphenylamine moiety, respectively, and the distribution of both orbitals overlap on the *m*-phenylene ring. This electronic feature strongly suggests the presence of the ferromagnetic interaction between unpaired electrons.[9] The small D value of **QA·H$_2$$^{2+}$** was also reproduced on the basis of the spin distribution calculated by the above molecular orbital calculation.[10]

Formation of the diradical electronic structure of **QA·H$_2$$^{2+}$** was also supported by magnetic susceptibility data. Although the chloride salt of **QA·H$_2$$^{2+}$** was isolated as green precipitate by bubbling HCl gas into the trichloroethane solution of **QA**, the magnetic susceptibility of the salt was only 0.10 emu K mol^{-1} because of the charge transfer interaction between a highly electron deficient **QA·H$_2$$^{2+}$** moiety and a chloride anion with a relatively low redox potential. To avoid the charge donation from the counter anion, the perchlorate (ClO_4^-) salt of **QA·H$_2$$^{2+}$** (**QA·H$_2$·(ClO$_4$)$_2$**) was prepared as a deep blue powder by addition of an etheral solution saturated by perchloric acid. The chemical composition of the salt was confirmed by the elemental analysis. The **QA·H$_2$·(ClO$_4$)$_2$** salt showed paramagnetic property with the small

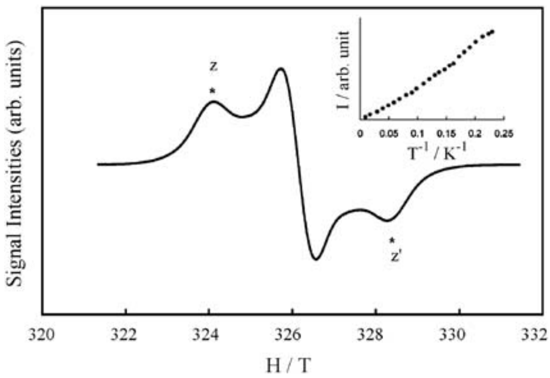

Fig. 3 (a) ESR spectrum of the doubly protonated **QA** (**QA·H$_2$$^{2+}$**) in a frozen solution of dichloromethane. Marked peaks are assigned as the z lines of the fine structure of the triplet state of the doubly protonated species. The inset shows the temperature dependence of the intensity of the triplet signal.

antiferromagnetic intermolecular interaction (θ = −7 K). Although the Curie constant of the salt (0.52 emu K mol^{-1}) was smaller than the predicted value for the **QA·H$_2$$^{2+}$** diradical (1.0 emu K mol^{-1}), the value is enough larger than that for the 1/2 spin complex (0.375 emu K mol^{-1}), suggesting that the diprotonated dication has the diradical electronic structure. The small Curie constant for the diradical structure might be due to the chemical bond formation between neighboring **QA·H$_2$$^{2+}$** molecules because the Curie constant of the salt approached to 0.375 emu K mol^{-1} after annealing at 400 K.

We also formed a polyvinylchloride film containing conjugate **QA** (1×10^{-4} mol g^{-1}). The reversible color change of the film upon addition of TFA and TEA was the same as that of the solution (Fig. 2c). The green colored film sample, made by treating with TFA, also exhibited the triplet ESR signal of the same D value with that in the frozen solution. These results suggest that the acid-induced electron transfer occurred as a unimolecular process, whereas Janssen's system requires the intermolecular collaboration.

In conclusion, cross-conjugate moleule **QA** turned out to produce a triplet dication diradical when strong acid was added. Such a type of acceptor, the acceptor ability of which is switchable by protonation, can be utilized widely to create manipulating functional molecular systems, provided that the cooperative proton–electron transfer takes place triggered by protonation.

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7 The difference between redox potentials of PA^{+}/PA^{2+} and TA/TA^{+} redox couples is 0.27 V. Judging from the difference of 0.27 eV in the redox potentials, the population of the PA^{+} + TA^{+} is 3.0×10^{5} times larger than that of PA^{2+} + TA at 300 K. Thus the electron transfer will take place almost completely when the PA^{2+} is generated by protonation of the QI in the presence of TA.

8 The cation radical of trianisylamine was generated in a fused cell for galvanometric and spectroscopic measurements. The absorption spectrum of the species generated in the cell at the oxidation potential of +0.84 V showed an absorption band at 700 nm, which was assigned to the cation radical of trianisylamine.

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