Coupling Covalent and Noncovalent Electron Transfer in a Catenane-type Donor-Sensitizer-Acceptor Triad

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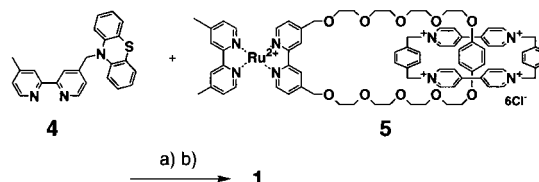[†]*Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 812-8581*
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A catenane-type triad consisting of a donor (phenothiazine), a sensitizer (Ru(2,2'-bipyridine)$_3$) and an acceptor (cyclobis(paraquat-p-phenylene)) was prepared by stepwise coordination. Multistep noncovalent and covalent electron transfer was successfully carried out in this triad.

One of the most fascinating developments in supramolecular chemistry during the past decade is the construction of artificial photosynthetic systems with elaborate structures.[1] A number of covalently linked donor-acceptor supramolecules have been prepared to understand the controlling factors of photosynthetic electron transfer (ET). Some of them such as triads, tetrads and pentads have displayed a long lifetime with a high quantum yield for the final charge-separated (CS) state, showing that photoinduced multistep ET is an effective strategy for photoconversion of energy.[2] In addition, noncovalently bonded supramolecular assemblies of sensitizer-acceptor complexes have also been extensively investigated so as to understand ET events through noncovalent interactions.[3] Systems involving both covalent and noncovalent ET processes, however, are very limited so far.[4] Here we report a novel donor-sensitizer-acceptor triad (**1**, PTZ-Ru^{2+}(bpy)$_3$-BXV^{4+}), in which the acceptor (cyclobis(paraquat-p-phenylene), BXV^{4+}) and the sensitizer (Ru(bpy)$_3$) are noncovalently linked in a catenane type, and the sensitizer is covalently linked with the donor (phenothiazine, PTZ) (Figure 1). Upon photoexcitation, covalent and noncovalent ET processes are successfully coupled in this supramolecule.
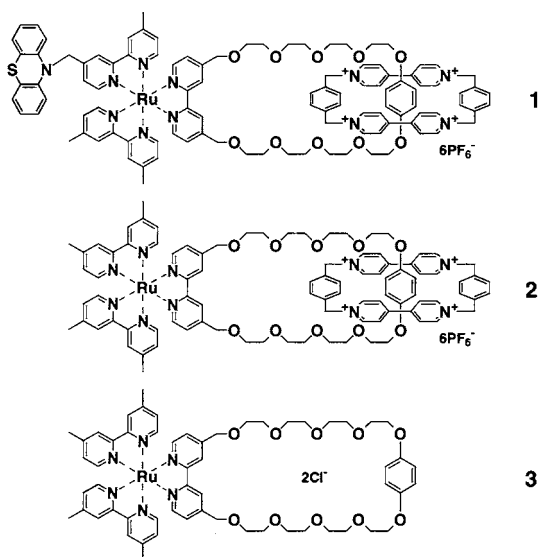

Figure 1. Structures of the triad and the reference compouds.

Scheme 1. Reagents and conditions: a) EtOH, reflux under N$_2$ in the dark, 24 hrs. b) NH$_4$PF$_6$, 57% yield.

Compound **1** was synthesized by refluxing the PTZ-bpy (**4**)[5] with the BXV^{4+}-catenated Ru(bpy)$_2$ complex (**5**)[4] in EtOH under N$_2$ for 24 h. After column chromatography on silica gel (eluents: MeOH / 2M NH$_4$Cl aq. / MeNO$_2$, 7:2:1 followed by MeOH / 2M NH$_4$Cl aq. / MeNO$_2$, 4:2:3) and anion exchange, **1(PF$_6$)$_6$** was obtained in 57% yield.[6] Although four stereoisomers in the Ru coordination sphere may exist in **1**, these isomers have not been separated in this study. The syntheses of compounds **2** and **3** have been reported previously.[7]

The absorption spectrum of **1** in CH$_3$CN is essentially a linear combination of the absorption spectra of PTZ and **2**, indicating no evidence for strong interaction among the chromophores in the ground state. Fluorescence spectra of **1** and **2** in CH$_3$CN are strongly quenched as compared with that of **3** when excited at the MLCT band (λ_{EX} = 460 nm, $A_{460 \text{ nm}}$ = 0.30) under the same conditions. The relative intensities for **1** and **2** to that of **3** are 0.0037 and 0.0057, respectively. These results confirm the fast noncovalent ET from the excited state of the Ru^{2+}(bpy)$_3$ component to the BXV^{4+} unit via oxidative quenching in both **1** and **2**. The rate constant (k_{ox}) for this noncovalent ET process was calculated to be 2.0×10^8 s^{-1} in CH$_3$CN using the emission intensities of **2** and **3** and the emission lifetime of **3** (847 ns).[7,8] Furthermore, the relative emission intensities of **1** and **2** show that presence of the donor (PTZ) in **1** results in further quenching of the emission as compared with that of **2**. This suggests that photoinduced ET from PTZ to the excited state of Ru^{2+}(bpy)$_3$, i.e. PTZ-*Ru^{2+}(bpy)$_3$-BXV^{4+} → PTZ$^{+•}$-Ru^{2+}(bpy)$_2$(bpy$^{-•}$)-BXV^{4+}, takes place in **1** via reductive quenching. Similar results have been reported for structure-related PTZ-Ru(bpy)$_3$ dyads by Meyer and coworkers.[9] The energies of PTZ-*Ru^{2+}(bpy)$_3$-BXV^{4+} and PTZ$^{+•}$-Ru^{2+}(bpy)$_2$(bpy$^{-•}$)-BXV^{4+} are estimated to be 2.16 eV and 2.08 eV, respectively, confirming that the reductive quenching is thermodynamically favorable. The emission quenching in **1** (k_q) should be the combination of both the oxidative and reductive quenching, i.e. $k_q = k_{ox} + k_{red}$. The k_q of **1** was calculated to be 3.1×10^8 s^{-1} using the emission intensities of **1** and **3** and the emission lifetime of **3**.[8] Thus, the rate constant for the reductive quenching (k_{red}) was estimated to be 1.1×10^8 s^{-1}, which is in agreement with the previous report.[9]
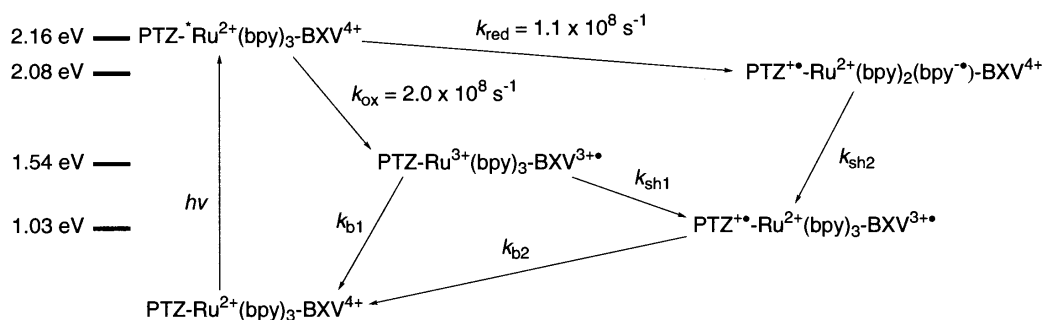
As shown in Figure 2, pulsed laser excitation of a CH$_3$CN

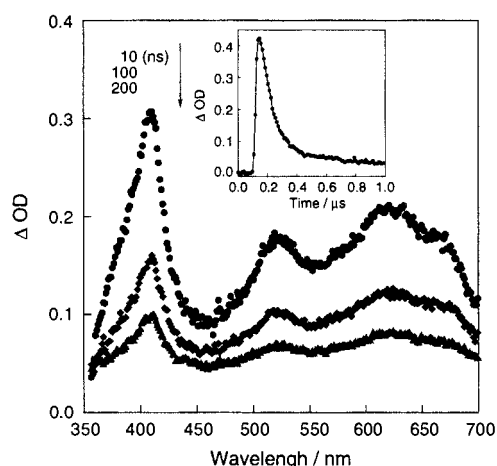**Figure 3.** Schematic energy diagram for the photoinduced reactions of **1**.

Figure 2. Transient absorption spectra of PTZ-Ru(bpy)$_3^{2+}$-BXV^{4+} triad (35 μM) in deaerated CH$_3$CN at 10 ns, 100 ns and 200 ns after 355 nm-laser photolysis (10 mJ/pulse). Inset: Time profile monitored at 620 nm.

solution of **1** (35 μM) at 460 nm leads to the prompt appearances of absorption bands at 400 nm, 520 nm and 620 nm. The bands at 400 nm and 620 nm are characteristic of the radical cation of bipyridinium salt (i.e. BXV$^{3+\bullet}$),[4,7] and the band at 520 nm is characteristic of PTZ$^{+\bullet}$.[9] The difference spectrum corresponds to a superposition of the spectra of PTZ$^{+\bullet}$ and BXV$^{3+\bullet}$, consistent with the formation of the charge separated state, PTZ$^{+\bullet}$-Ru^{2+}(bpy)$_3$-BXV$^{3+\bullet}$. Since the formation of the CS state is faster than our instrumental resolution, the formation mechanism remains unclear. Based on the emission study, we considered that the CS state might be generated *via* both the oxidative and reductive quenching, followed by rapid charge shifts, as shown in Figure 3. Since k_{ox} is faster than k_{red}, the oxidative quenching pathway should be dominant in the formation of the CS state. Laser excitation of **2** in CH$_3$CN (35 μM) also generates its CS state (Ru^{3+}(bpy)$_3$-BXV$^{3+\bullet}$) immediately, which displays transient absorption at 400 nm and 620 nm (BXV$^{3+\bullet}$) and bleaching of the MLCT band (data not shown).

The decay behavior of the CS state, PTZ$^{+\bullet}$-Ru^{2+}(bpy)$_3$-BXV$^{3+\bullet}$, is considerably complicated (inset of Figure 2). Analysis of the decay kinetics at 620 nm yielded two components. The shorter component dominates (85%) and decays with a lifetime of 90 ns, whereas the longer component decays with a lifetime of 1.66 μs (15%). Analysis of the decay kinetics of the CS state of **2** (data not shown) yielded two components with

the shorter component dominating (85%) and decaying with lifetime of 25 ns. Comparison of the lifetimes of PTZ$^{+\bullet}$-Ru^{2+}(bpy)$_3$-BXV$^{3+\bullet}$ and Ru^{3+}(bpy)$_3$-BXV$^{3+\bullet}$ confirms that coupling of the covalent ET process with the noncovalent ET process in **1** has profound effect on the CS state lifetime. In addition, the quantum yield of PTZ$^{+\bullet}$-Ru^{2+}(bpy)$_3$-BXV$^{3+\bullet}$ was determined to be 0.55, which is about 3.5 times as high as that of Ru^{3+}(bpy)$_3$-BXV$^{3+\bullet}$ (0.16).

In conclusion, covalent and noncovalent ET processes were successfully coupled in a catenated donor-sensitizer-acceptor triad. The CS state lifetime and quantum yield of this supramolecule (**1**) are significantly improved as compared with those of the reference dyad (**2**).

References and Notes

†††† A postdoctoral fellow of the Japan Society for the Promotion of Science (JSPS).

††††† A JSPS fellow for Japanese Junior Scientists.

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6   **1**(PF$_6$)$_6$: ESI-Tof MS for C$_{106}$H$_{109}$N$_{11}$O$_{10}$SRuP$_6$F$_{36}$ (cald. M = 2699.99): *m/z* = 1205.09 (M - 2PF$_6$)$^{2+}$, 755.03 (M - 3PF$_6$)$^{3+}$, 689.35 (M - 3PF$_6$ - PTZ)$^{3+}$, 530.52 (M - 4PF$_6$)$^{4+}$, 481.23 (M - 4PF$_6$ -PTZ)$^{4+}$, 395.21 (M - 5PF$_6$)$^{5+}$. Elemental Anal. calcd for C$_{106}$H$_{109}$N$_{11}$O$_{10}$SRuP$_6$F$_{36}$·CH$_3$OH: C, 47.04; H, 4.17; N, 5.63%. Found: C, 47.30; H, 4.47; N, 5.43%. UV-vis. spectrum in CH$_3$CN: 460 nm (MLCT band, ε = 14300 M^{-1}cm^{-1}).

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8   The rate constants of k_{ox} and k_q were calculated by the following equation: $k = (1/\tau_0)(I_0/I - 1)$, where τ_0 is the emission lifetime of **3**, and I_0 and I are the emission intensities of **3** and **2** (for k_{ox}) or **1** (for k_q), respectively.

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