Synthesis and Photophysical Properties of Porphyrin-Tetracyanoanthraquinodimethane-Porphyrin Triad: Photon-Dependent Molecular Switching

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One-photon excitation of one of the two porphyrins within porphyrin-tetracyanoanthraquinodimethane-porphyrin triad with picosecond laser pulse leads to single reduction of the acceptor by intramolecular electron transfer, while an additional delayed excitation of the non-excited porphyrin results in double reduction of the acceptor.

Molecule-based electronic switches, wires, and microsensors have been investigated vigorously in recent years.[1] Since photoinduced energy and electron transfer (ET) processes within a molecule can occur in ultrafast time scale such as femto- and picosecond regions, it is possible to develop efficient optoelectronic devices which respond rapidly and reversibly.[2,3]

We have designed electron donor-acceptor-donor (D-A-D) molecule **1** consisting of two zincporphyrins tethered to a tetracyanoanthraquinodimethane (TCAQ) unit (Figure 1). TCAQ exhibits two-electron, single-wave reduction electrochemically, and the resulting dianion radical TCAQ^{2-} has different shape and intensity in the absorption of the UV-visible and near-infrared spectra compared with those of monoanion radical TCAQ^{-}.[4] Therefore, depending on the input excitation mode, one and two photons excitation of the porphyrins in **1**, the TCAQ moiety could be reduced to TCAQ^{-} and TCAQ^{2-}, respectively, via intramolecular charge separation (CS) from the excited singlet states of the porphyrins to TCAQ. It is known that the central ring in TCAQ is bent into a boat form and the two fused benzene rings are not in coplanarity because of the steric repulsion between the cyano substituents and the perihydrogen atoms of the central anthracene skeleton. On the other hand, the structure of dianion species TCAQ^{2-} is assumed to be quite different from the neutral one. Thus, the two $[C(CN)_2]^-$ groups rotate around the single bond connecting $C(CN)_2$ and anthracene groups. The dianion structure is probably stabilized compared with those in the monoanion where the steric interactions are not fully relieved. Therefore, it is expected that two-photon excitation in **1** leads to the formation of long-lived charge-separated state as output, while one-photon excitation results in the formation of the short-lived charge-separated state if the rotational rate of $C(CN)_2$ is faster than that for the charge recombination (CR). However, these possibilities have not been addressed so far.[5]

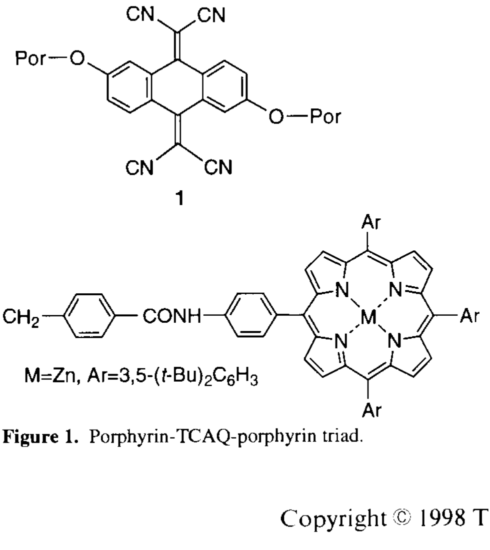
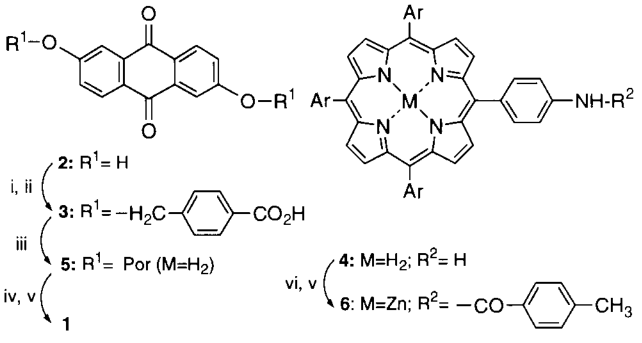


Figure 1. Porphyrin-TCAQ-porphyrin triad.



Scheme 1. Conditions: i, methyl 4-bromomethylbenzoate, K_2CO_3, DMF; ii, KOH, EtOH; iii, **4**, $SOCl_2$, benzene; iv, $CH_2(CN)_2$, $TiCl_4$, pyridine, CH_2Cl_2; v, $Zn(OAc)_2$, $CHCl_3$; vi, 4-methylbenzoic acid, $SOCl_2$, benzene.

Coupling reaction of **2** and methyl 4-bromomethylbenzoate in the presence of K_2CO_3 in DMF followed by the basic hydrolysis afforded **3** in 85% yield (Scheme 1). Porphyrin-anthraquinone-porphyrin triad **5** was prepared by the coupling reaction of aminoporphyrin **4** and acid chloride of **3** in 75% yield. $TiCl_4$-catalyzed reaction[6] of **5** with malononitrile in CH_2Cl_2 and subsequent metallation with $Zn(OAc)_2$ gave **1** in 31% yield.[7] Reference **6** was synthesized by the coupling reaction of **4** and 4-methylbenzoylchloride and the similar metallation.

The absorption spectrum of **1** in dioxane is almost the same as that of **6**, indicating that there is no strong interaction among the three chromophores. Differential pulse voltammetry of **1** in CH_2Cl_2 using 0.1 M Bu_4NClO_4 showed two-electron, single oxidation peak for the porphyrins at 0.87 V and two-electron, single reduction for the TCAQ at - 0.30 V vs Ag/AgCl.

The fluorescence lifetime of **1** in dioxane was measured by single-photon counting technique exciting at 400 nm where the porphyrins absorb mainly, and monitoring at 660 nm where the fluorescence is due to only the porphyrin. The decay curve was fitted by dual exponential decays with time constants of 180 ps ($=\tau_{S1}$; $A_1=0.27$) and 620 ps ($=\tau_{S2}$; $A_2=0.57$). Judging from the fact that the lifetime of **6** is 1800 ps ($=\tau_0$), the excited singlet state of the porphyrin is quenched by the TCAQ moiety via intramolecular ET.[5] The fast and slow CS components may be ascribed to the different conformations within **1** because of the flexible oxymethylene spacer between the donor and acceptor.

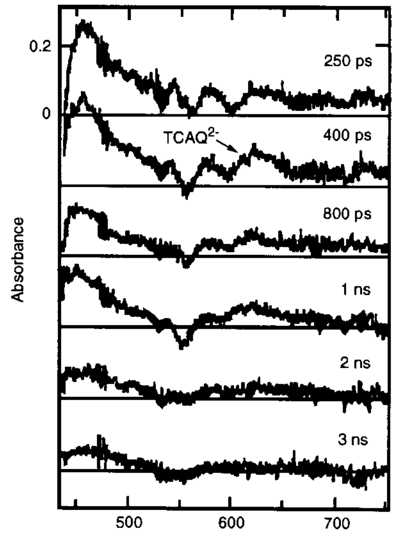


Figure 2. Differential time-resolved transient absorption spectra of **1** in dioxane via two-photon excitation. The delay times between the first excitation and measurement are indicated on the right.

The transient spectra of **1** in dioxane at the delay time of subnanosecond region after the excitation with 532 nm pulse showed 620-nm band, which can be assigned to $TCAQ^-$.[4] Time profile of the absorbance at 620 nm was analyzed by two rise components with time constants of 180 ps and 600 ps and a single decay component with time constant of 1500 ps ($=\tau_{ion}$). The time constants of dual rise components in the transient spectra are in good agreement with those in the fluorescence lifetime measurement, supporting the formation of two different conformations in **1**. Based on the lifetimes, the rate constants of CS ($k_{CS}=1/\tau_S-1/\tau_0$) and CR ($k_{CR}=1/\tau_{ion}$) in **1** are found to be 5.0×10^9 s^{-1} and 1.1×10^9 s^{-1} for CS and 6.7×10^8 s^{-1} for CR.

In the two-pump pulse experiment, a single 532-nm pulse again produced $D^+\text{-}A^-\text{-}D$. A second 555-nm pulse, where the absorbance due to the non-excited porphyrin is much higher compared with those due to the other transient species, was employed to produce $D^+\text{-}A^{2-}\text{-}D^+$.[8] In order to excite the $D^+\text{-}A^-\text{-}D$ selectively the delay time (233 ps) for the second pulse was used. The transient differential spectra of **1** in dioxane are shown in Figure 2.[9] The spectra correspond to the process where the first pulse produces the faster CS state followed by the second excitation of the non-excited porphyrin to generate the second CS. There is no substantial change of the absorption around 400-800 nm for $TCAQ^-$ and $TCAQ^{2-}$ because of no large difference in peak positions between them.[10] Time profile of the absorbance at 456 nm, which corresponds to the $S_n \leftarrow S_1$ absorption of the porphyrin ($^1ZnP^*$) and the absorption of the zincporphyrin cation radical (ZnP^+), was analyzed by two exponential decays with time constants of 400 ps ($=\tau_S'$) and 1200 ps ($=\tau_{ion}'$). These two values are not consistent with those in ET processes via one-photon excitation. On the other hands, the transient absorbance at 620 nm corresponding to $TCAQ^-$ and $TCAQ^{2-}$ arises with 400 ps and decays with 1200 ps. Considering the rise of the anion band at 620 nm and the good agreement of the time constants at 456 and 620 nm, 620-nm band can be assigned to be $TCAQ^{2-}$. Thus, successive two-photon excitation with different wavelengths produces $TCAQ^{2-}$ as output, whereas one-photon excitation generates $TCAQ^-$ as shown in Figure 3.[11] Based on the time constants, the rate constants were calculated to be 1.3×10^9 s^{-1} ($=k_{CS}'=(1/\tau_S')-(1/\tau_{ion})-(1/\tau_0)$) for the generation of $TCAQ^{2-}$ and 8.3×10^8 s^{-1} ($=k_{CR}'=1/\tau_{ion}'$) for the decay of $TCAQ^{2-}$. However, there is no evidence for longer lifetime in $TCAQ^{2-}$.

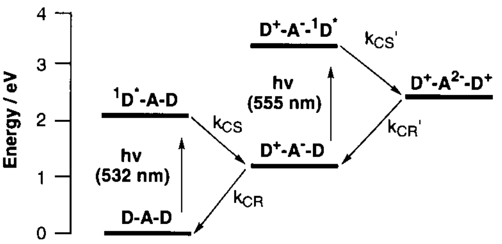


Figure 3. Energy level diagram of **1** in dioxane.

In conclusion, photon-dependent molecular switching using two different excitation wavelengths has been realized in porphyrin-TCAQ-porphyrin triad. The system may be applicable to polymers and films where output signals could be detected by monitoring light. In contrast, we could not observe the dianion state with longer lifetime compared with the monoanion state, indicating that lifetime is not enough to rotate the dicyanomethylene bond. Molecular design to prolong lifetime in the dianion state compared with the present system will make it possible to develop molecular switch based on the difference of the lifetime in the CS state. We are working on this line.

References and Notes

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7 Spectral data for **1**: ^1H NMR (270MHz, $CDCl_3$) δ 1.52 (s, 108H), 5.36 (s, 4H), 7.31 (dd, J=8, 2 Hz, 2H), 7.65 (d, J=8 Hz, 4H), 7.78 (t, J=2 Hz, 2H), 7.79 (t, J=2 Hz, 4H), 7.83 (d, J=2Hz, 2H), 8.02 (d, J=8 Hz, 4H), 8.06 (d, J=8 Hz, 4H), 8.08 (d, J=2Hz, 4H), 8.10 (d, J=2 Hz, 8H), 8.15 (s, 2H), 8.23 (d, J=8 Hz, 2H), 8.26(d, J=8 Hz, 4H), 8.98 (d, J=4 Hz, 4H), 9.01 (s, 8H), 9.02 (d, J=4 Hz, 4H). TOF-MS 2625 ($M+H^+$).

8 Attempt using light intensity-dependent excitation was unsuccessful because of photoionization of the porphyrins due to multi-photon absorption.

9 (The transient differential absorption spectra) = (total transient spectra) - ($D^+\text{-}A^-\text{-}D$) - ($_{620}D^*\text{-}A\text{-}D^*$) - ($_{620}D^*\text{-}A\text{-}D$) - ($D\text{-}A\text{-}_{180}D^*$) - ($D\text{-}A\text{-}_{620}D^*$) - (D-A-D); The abbreviation of 180 and 620 corresponds to the fast and slow CS components. The bracket represents photodynamic processes.

10 Absorptions of $TCAQ^-$ and $TCAQ^{2-}$ produced by photoinduced ET may be different from those produced electrochemically.[4] We could not observe the characteristic band of $TCAQ^-$ at 900-1200 nm, because of the limit of detector.

11 The energies of the charge-separated states are estimated from differential pulse voltammetric measurements of **1** in CH_2Cl_2. No corrections have been made for any Coulombic effects because it is difficult to assess the effect due to the low polarity of dioxane.