

Photoinduced Charge-Transfer Association of Tetracyanoquinodimethane with Aminobiphenyls

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The molecular association of acceptors with electron donors is studied in the highly-polar solvent CH_3CN . Tetracyanoquinodimethane (TCNQ) forms a stable charge-transfer complex with donor molecules such as 4-aminobiphenyl (4-AB), benzidine (BD) and 2-aminobiphenyl (2-AB) with high association constants. The complexes of TCNQ with 4-AB or BD show new absorption bands at around 800 and 500 nm, which can be identified as reduced $\text{TCNQ}^{\cdot-}$ and TCNQ^{2-} species, respectively. These bands grow quickly upon photo-irradiation, implying that the charge-transfer complexes are easily formed in an excited state. Conversely, a small spectral manifestation of the charge transfer was observed in the case of 2-AB complex. It is demonstrated that the structural orientation between the geminate ion pairs could play an important role in building a stable complex.

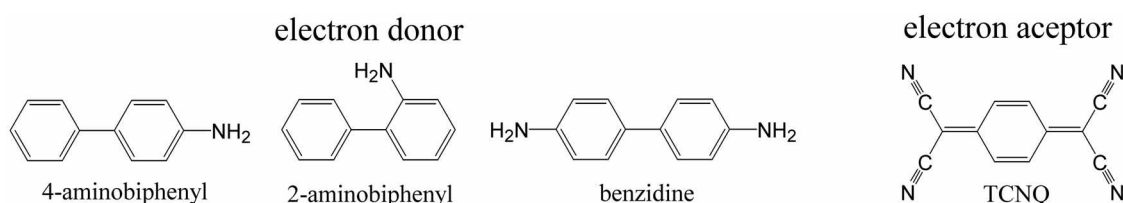
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Introduction

The charge-transfer complexes originating from the interaction between an electron donor and acceptor molecules in bimolecular equilibria have been an important research topic in physical chemistry and biochemistry over the past decades.¹⁻⁴ The charge-transfer systems in molecular optoelectronic devices such as molecular-based transistors, wires, and rectifiers, or in the doping of organic semiconducting polymers, are currently important issues in materials science.⁵⁻⁸ For instance, 7,7',8,8'-tetracyanoquinodimethane (TCNQ) has been widely used as a strong electron acceptor to form highly conducting charge-transfer complexes.⁹⁻¹² Since the first report of the tetrathiafulvalene/TCNQ complex as an "organic metal" in 1973, a number of subsequent studies related to charge-transfer complexes have been reported.¹³ Especially, the partial para-magnetism and electrical conductivity of TCNQ has received a significant amount of attention.¹⁴ To this end, one of the more prevalent strategies for the preparation of electro-magnetically novel materials is the reaction of electron donors (including amine compounds) with electron acceptors (such as TCNQ) to generate semi-conducting or superconducting complexes. Another technique is the enhancement of conductivity due to the doping of ionic species or mineral acids.¹⁵

Aromatic amines such as 4-aminobiphenyl (4-AB), 2-aminobiphenyl (2-AB), and benzidine (BD) are well-known chemical carcinogens.^{16,17} It has been suggested that these aromatic amines are likely to be more mutagenic, due to their relative ease of oxidation, as oxidation has been considered a primary step of the mutagenic process.^{18,19} However, it has also been reported that the mutagenicity of aromatic amines does not entirely correlate with their oxidation potentials,²⁰ implying that the mutagenic process through charge transfers can be affected by factors other than the oxidation potential.

To demonstrate how oxidative aminobiphenyl derivatives play a critical role in the mutagenic process through electron transfers, this study focuses on the redox behavior of the TCNQ acceptor for the following reasons: TCNQ is a planar π -acceptor with reversible redox potentials in a reasonable reduction potential ($E_{\text{red}}^{\text{V}}$) range, and the reduced TCNQ is stable in solution and can be rigorously characterized *via* isolation as a pure crystalline. It should be noted that the driving-force contribution ($\Delta G_{\text{ET}}^{\circ}$) is the primary factor for interpreting the formation of a charge-transfer complex. The charge-transfer complex formation is ascribed to interaction of the electron-poor π -orbital system of the acceptor with the electron-rich π -orbitals of the donor. Thus, charge-transfer complex formation can be affected by the orientation of



Scheme 1

the π -orbital interaction between the donor and acceptor molecules. This paper presents in detail the charge-transfer complexes of TCNQ with three aminobiphenyl derivatives having different π -conjugations, as shown in Scheme 1. Subsequent electronic absorption measurement of the systems is used to investigate the molecular association in terms of charge-transfer interaction.

Experimental Section

TCNQ, 4-AB and 2-AB were purchased from Aldrich Co. and BD purchased from Fluka Co. All aminobiphenyl derivatives were purified using recrystallization in ethanol. In the case of TCNQ, the chemical was further purified by a sublimation technique at 210 °C. CH₃CN (Merck, HPLC degree) was then used to prepare the solutions. The concentration of the electron acceptor TCNQ was fixed, and the concentration of the donor molecules was controlled through the addition of a stock solution. In brief, the same volume of TCNQ stock solution was added to a different volume of donor stock solution, thereby keeping the total volume constant so that the concentration of TCNQ would remain constant (2×10^{-5} M) through variation in the donor concentration.

The absorption spectra were recorded with a Shimadzu UV-3101PC spectrophotometer. Because the formation of charge-transfer complexes occurs slowly in a ground state, the spectra of each solution were measured after storage for 6 days in the dark, intercepting the light. In this case, the absorption spectra on TCNQ/donors complexes did not change anymore. These solutions show the stability for months under the room temperature and room-light condition. The absorption measurement for kinetics of photoinduced charge transfer complexes was performed using on a spectrophotometer (Myungjin Crystec Co. MPDS-1024) with a 1024-channel photodiode array detector, making it possible to obtain on-line spectra during photoirradiation (light source: 70 W tungsten-halogen lamp).

Results and Discussion

Charge-transfer complex between TCNQ and 4-amino-biphenyl. Figure 1 shows the absorption spectra of the TCNQ/4-AB complex in CH₃CN. The development of a broad band at around 500 nm was concomitant with a decrease of the neutral TCNQ band at 400 nm and an anion radical of TCNQ (TCNQ $^{\cdot-}$) band at around 840 nm;^{21,22} the absorption band at 500 nm was attributed to dianion TCNQ (TCNQ $^{2-}$).^{21,22} Two structural bands for TCNQ $^{\cdot-}$ at 740 and 840 nm grew gradually according to an increase of the 4-AB concentration (Figure 1, inset), but the absorption intensity reduced again in a high concentration of 4-AB of over 4×10^{-5} M (Figure 2). The isosbestic point was observed at around 420 nm, indicating an equilibrium between the TCNQ, TCNQ $^{\cdot-}$, and TCNQ $^{2-}$ species. It seems that the formation of the 1:1 and 2:1 inclusion complexes between the TCNQ and 4-AB processes were stepwise *via* the

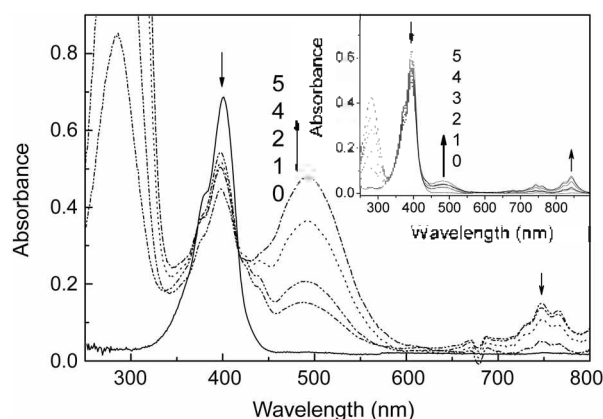


Figure 1. Absorption spectra of the mixtures of TCNQ (2×10^{-5} M) and 4-AB in CH₃CN. Concentration of donor molecule in (0) 0; (1) 4×10^{-5} ; (2) 8×10^{-5} ; (4) 1.6×10^{-4} ; and (5) 2.0×10^{-4} M, respectively. Inset figure, absorption spectra are measured at a low concentration of 4-AB in (0) 0; (1) 4×10^{-6} ; (2) 8×10^{-6} ; (3) 1.2×10^{-5} ; (4) 1.6×10^{-5} ; and (5) 2.0×10^{-5} M, respectively.

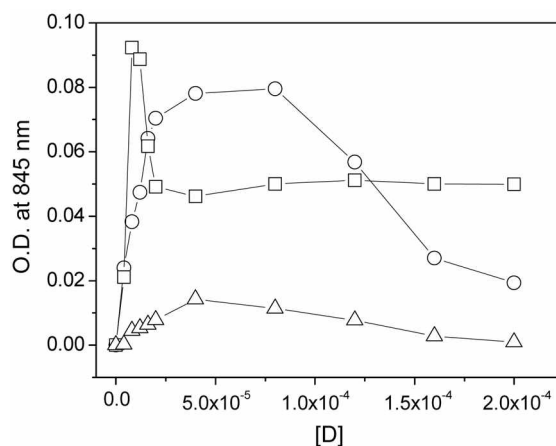
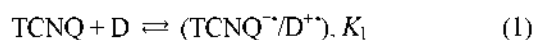


Figure 2. (A) Absorbance change of TCNQ $^{\cdot-}$ monitored at 845 nm in presence of donor molecules (0 – 2.0×10^{-4} M) in CH₃CN: (○) 4-AB, (△) Bz, and (□) 2-AB.

following two equilibriums:



where the 1:1 TCNQ $^{\cdot-}$ /4-AB $^{\cdot+}$ complex is formed with TCNQ at a low concentration of 4-AB of below 4×10^{-5} M. Then, the 1:1 TCNQ $^{\cdot-}$ /4-AB $^{\cdot+}$ complex is consecutively converted to TCNQ $^{2-}$ /2D $^{\cdot+}$ in the high concentration range of 4-AB.

Figure 3 shows the plot of absorbance (Abs.) as a function of donor (D, 4-AB) concentration according to the classical Benesi-Hildebrand equation²³ for the $\text{D} + \text{A} \rightleftharpoons \text{DA}$ equilibrium.

$$\frac{[A]}{\text{Abs}} = \frac{1}{\epsilon} + \frac{1}{\epsilon K[D]} \quad (3)$$

Eq. (1) allows for an estimation of the complex formation constant K and the apparent extinction coefficient ϵ at a given absorption wavelength of the donor-acceptor (DA) complex. In Eq. (3), the complex DA only absorbs at

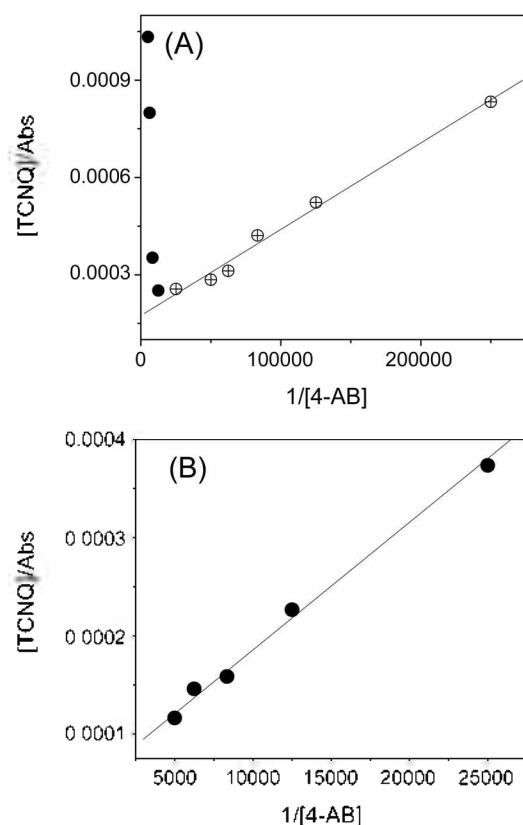


Figure 3. Benesi-Hilderbrand plot of TCNQ/4-AB in CH_3CN ; the absorbance changes are monitored at 845 nm (A) and 500 nm (B). In order to calculate the formation constant, K_2 , the initial concentration of $[\text{TCNQ}^-]$ is assumed to be identical to $[\text{TCNQ}]$ at over 4×10^{-5} M of 4-AB.

monitoring wavelengths such as 500 or 840 nm; thus, ϵ is identical to ϵ_{DA} . In a low concentration of 4-AB, the plots of the inverse of the optical density in the region of the absorption of TCNQ^- as a function of $1/[\text{4-AB}]$ are linear, thereby allowing the calculation of the complex formation constants. This result implies that the stoichiometry of the association is 1:1 in a low concentration of 4-AB. The K_1 values for the TCNQ complexes are listed in Table 1.

From the slope and its intercept of the first linear curve monitored at 845 nm, as shown in Figure 3, the formation constant of the 1:1 $\text{TCNQ}^-/\text{4-AB}^-$ complex K_1 was determined to be $65,100 \pm 5,200 \text{ M}^{-1}$, which is large enough for a strong interaction of TCNQ with 4-AB. In addition, from the linear curve monitored at 500 nm the formation constant of the 1:2 $\text{TCNQ}^{2-}/(\text{4-AB}^-)_2$ complex K_2 was determined to be $\text{ca. } 4,300 \pm 300 \text{ M}^{-1}$, which is much smaller than for K_1 .

Table 1. Complex formation constants and extinction coefficients for the electron donor (4-AB, 2-AB or BD) and acceptor (TCNQ) complexes in CH_3CN

	TCNQ/4-AB	TCNQ/BD	TCNQ/2-AB
$K_1 (\text{M}^{-1})$	$65,100 \pm 3,200$	$\sim 258,000$	nd
$K_2 (\text{M}^{-1})$	$4,300 \pm 300$	$6,200 \pm 100$	$1,900 \pm 40$
$\log \epsilon_1 (\text{M}^{-1}\text{cm}^{-1})$	3.76 ± 0.04	—	—
$\log \epsilon_2 (\text{M}^{-1}\text{cm}^{-1})$	4.25 ± 0.05	4.36 ± 0.04	4.12 ± 0.09

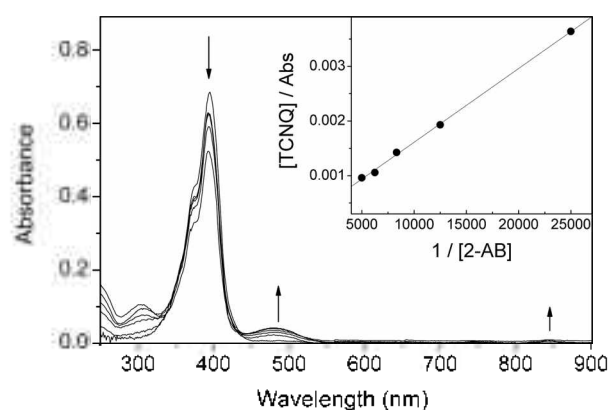


Figure 4. Electronic absorption spectra of the mixtures of TCNQ (2×10^{-5} M) and 2-AB in CH_3CN ; concentration of donor molecule in (0) 0; (1) 4×10^{-5} ; (2) 8×10^{-5} ; (3) 1.2×10^{-4} ; (4) 1.6×10^{-4} ; and (5) 2.4×10^{-4} M, respectively. Inset: Benesi-Hilderbrand plot of TCNQ/2-AB in CH_3CN , the absorbance changes are monitored at 500 nm.

This is in good accordance with our suggestion for consecutive equilibrium reactions.

Charge-transfer complex between TCNQ and 2-amino-biphenyl. A small absorption change in the TCNQ/2-AB complex was observed, as shown in Figure 4. The complex formation constant for $\text{TCNQ}^-/\text{2-AB}^+$ was hard to determine, because of very low absorbance at 845 nm; however, the plot obtained at 500 nm according to Eq. (3) is linear (Figure 4, inset). The complex formation constant of 1:2 $\text{TCNQ}^{2-}/(\text{2-AB}^+)_2$ is smaller than for other complexes, indicating that the association of the TCNQ/2-AB complex is weak compared to other systems.

In addition, spectral change in the TCNQ/2-AB system was comparatively small. The fact that the oxidation potential (Tables 2 and 3) of 2-AB is comparable with other donors was initially surprising, though subsequent consideration of the orientation between the donor and acceptor molecules described below verified that this result was hardly anomalous. The dihedral angle between two phenyl moieties of 2-AB is 85 degrees, as calculated using a semi-empirical calculation (PM3 method), due to the steric hindrance of the amino group. The dihedral angles of 4-AB and BD were each calculated to be about 47 degrees, with corresponding absorption bands observed around 281 and 287 nm, respectively, indicating that the π -conjugations

Table 2. Half-wave redox potential and Gibbs free energies (ΔG) for photoinduced electron-transfer processes in electron donor (4-AB, 2-AB or BD) and acceptor (TCNQ) systems in CH_3CN

	$E_{\text{ox}} (\text{V})^a$ vs. SCE	$E_{\text{red}} (\text{V})^b$ vs. SCE	E_{00} (eV) ^c	ΔG_{et} (eV)
TCNQ	—	0.17	3.10	—
4-AB	0.69	—	—	-2.58
2-AB	0.79	—	—	-2.48
BD	0.36, 0.63	—	—	-2.91 ^d , -2.64 ^d

^avalues were from ref. 20. ^bvalues were from ref. 26 and 27. ^cvalues were from ref. 21. ^dThe values of BD denote the first and second oxidation potentials.

Table 3. Half-wave redox potential and Gibbs free energies (ΔG) for photoinduced electron-transfer processes in electron donor (4-AB, 2-AB or BD) and acceptor (TCNQ^{•-}) systems in CH₃CN

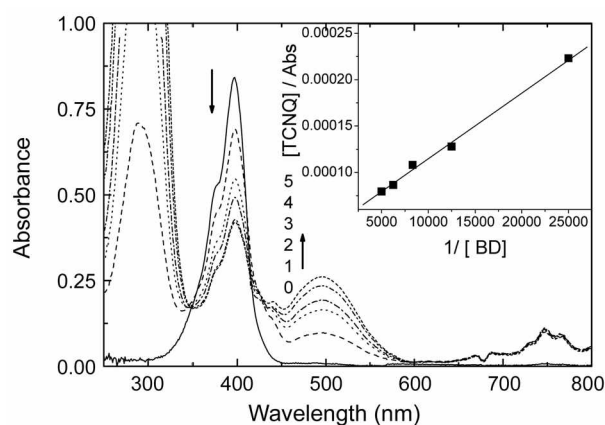
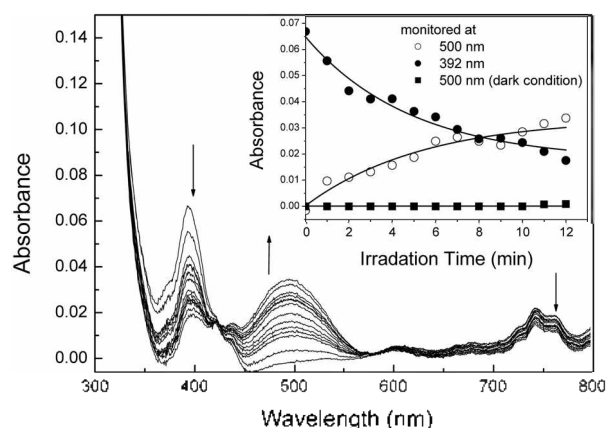
	E_{ox}^0 (V) ^a vs. SCE	E_{red}^0 (V) ^b vs. SCE	E_{00} (eV) ^c	ΔG_{et} (eV)
TCNQ ^{•-}	—	-0.37	1.46	—
4-AB	0.69	—	—	-0.40
2-AB	0.79	—	—	-0.30
BD	0.36, 0.63	—	—	-0.73 ^d , -0.46 ^d

^avalues were from ref. 20, ^bvalues were from ref. 26 and 27. ^cvalues were from ref. 21. ^dThe values of BD denote the first and second oxidation potentials.

were extended. However, the absorption maximum of 2-AB appeared at 225 nm with a shoulder around 250 nm, likely due to the interruption of electronic communication between the two phenyl moieties. Although 2-AB has a comparable oxidation potential as either 4-AB or BD, the interaction of TCNQ with 2-AB is weak, showing only a small change of absorption at 845 or 500 nm. This result implies that ion pairing between TCNQ and 2-AB is not favorable because of the structural inhibition of the π - π interaction. Based on these findings, it can be further inferred that the π - π interaction plays an important role in the formation of charge-transfer complexes using planar organic donors and acceptor molecules.

Charge-transfer complex between TCNQ and benzdine. Figure 5 shows absorption spectra of TCNQ/BD complex in CH₃CN. TCNQ^{•-} is generated in applying very low concentration of BD as shown in Figure 2. The absorption intensity for the TCNQ^{•-} complex at 845 nm grows quickly even in a concentration of 2×10^{-5} M (Figure 2). This means that the association between TCNQ and BD is very strong. Actually, the K_1 for TCNQ^{•-}/BD^{•+} obtained at 845 nm is quite large, $\sim 258,000$ M⁻¹, compared to the other complexes.

Photoinduced charge-transfer complex formation. Photoinduced charge-transfer complex formation was investi-

**Figure 5.** Electronic absorption spectra of the mixtures of TCNQ (2×10^{-5} M) and BD in CH₃CN; concentration of donor molecule in (0) 0; (1) 4×10^{-5} ; (2) 8×10^{-5} ; (3) 1.2×10^{-4} ; (4) 1.6×10^{-4} ; and (5) 2.0×10^{-4} M, respectively. Inset: Benesi-Hildebrand plot of TCNQ/BD in CH₃CN, the absorbance changes are monitored at 500 nm.**Figure 6.** Absorption spectra for the mixture of TCNQ (2×10^{-5} M) and BD (2×10^{-4} M) system in CH₃CN upon photoirradiation. Irradiation interval is 5 min and the light source is a 70 W tungsten-halogen lamp with a 350 nm cut-off filter. The measuring time is set at 1 ms to reduce any photoreaction. Inset: kinetic profile monitored at 392 nm (filled circle) and 500 nm (open circle), respectively; the bottom line (filled square) denotes a reference measured in a dark condition without irradiation.

gated based on kinetic measurements obtained using absorption spectroscopy. The sample solution was irradiated immediately after mixing of TCNQ (2×10^{-5} M) and BD (2×10^{-4} M). Upon photoirradiation, a broad band at around 500 nm developed and was accompanied with a decrease of the TCNQ neutral band at 400 nm, as shown in Figure 6. In the inset of Figure 6, the absorbance of TCNQ^{•-} monitored at 500 nm grows quickly compared with that stored in a dark room to shield the light. This indicates that charge-transfer complexes easily form *via* the photoinduced electron-transfer (PET) process in an excited state. Note that though we prepared the TCNQ/BD solution with extreme care, the trace absorption band for anion radical of TCNQ (TCNQ^{•-}) at above 700 nm could not be completely eliminated. This means that the reduction process of TCNQ occurs easily under weak light.

The likelihood of PET process occurring could be inferred based on the free-energy change ΔG . The ΔG associated with electron-transfer for the excited singlet state (S_1) of TCNQ was evaluated using the Rehm-Weller equation (5)^{24,25}

$$\Delta G_{et} = F(E_{ox}^0 - E_{red}^0) - E_{00} - \frac{e^2}{\epsilon r} \quad (5)$$

where E_{ox}^0 and E_{red}^0 are the oxidation and reduction potentials for the donor and acceptor, respectively. These two parameters were obtained earlier using electrochemical measurements, the values of which are in Table 1. Here, E_{00} denotes the lowest excited electronic state where the PET reaction occurs. The final term is the coulombic stabilization term, when the solvent has a large dielectric constant value, e.g. CH₃CN ($\epsilon \sim 35.84$), the Coulomb energy term might be neglected. In our systems, a contribution from the coulombic term was assigned for CH₃CN ($e^2/\epsilon r < 0.1$ eV) and the free energy calculation was employed. The ΔG values for PET between TCNQ and the aminobiphenyls are presented in

Table I. The negative values of ΔG ($\Delta G < 0$) clearly imply that PET from the donors to TCNQ is exothermic and energetically probable in an excited state.

Conclusion

The acceptor TCNQ reacts with each of the donors 4-AB, 2-AB and BD in CH_3CN at room temperature to form stable charge-transfer complexes, formulated as 1:1 ($\text{TCNQ}^{\cdot-}/\text{D}^{\cdot+}$) in low donor concentrations. In high donor concentrations, TCNQ formed new colored complexes such as 2:1 ($\text{TCNQ}^{2-}/2\text{D}^{\cdot+}$), which have an absorption band at around 500 nm. These charge-transfer complexes clearly show absorption bands related to their ionic species. These results confirm that the CT process essentially involves the complete electron transfer from the donor to the acceptor. Upon irradiation, the formation of complexes progresses quickly, and no complexes reversibly fade. In this way, stable photoproducts could be efficiently formed through the photoinduced charge-transfer processes. We are extending our time-resolved spectroscopic studies to include systems which realize stable photoproducts.

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