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# Two Different Charge Transfer States of Photoexcited 9,9′-Bianthryl in Polar and Nonpolar Solvents Characterized by Nanosecond Time-Resolved Near-IR Spectroscopy in the 4500−10 500 cm$^{-1}$ Region

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Transient absorption spectra of 9,9′-bianthryl (BA) in heptane, in acetonitrile, and in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (bmimTf$_2$N) are observed with a nanosecond time-resolved near-IR absorption spectrometer for the wavenumber range of 4500−10 500 cm$^{-1}$ (2200−950 nm). In nonpolar heptane solution, a broad absorption band is observed at 6700 cm$^{-1}$ (1500 nm), in addition to a strong absorption band of the locally excited (LE) state centered at 9800 cm$^{-1}$ (1020 nm). The broad band is assigned to a partial charge transfer (PCT) band. The decay time constants of the PCT band and the LE band are both (13 ± 1) ns. The agreement of the two decay constants strongly suggests that the PCT state is in equilibrium with the LE state in heptane. In acetonitrile, an absorption band of the charge transfer (CT) state is observed at 8000 cm$^{-1}$ (1250 nm). This band decays in (41 ± 2) ns. In bmimTf$_2$N, the CT band appears at 8500 cm$^{-1}$ (1180 nm) and decays in (34 ± 1) ns. The difference in peak position for the CT bands in acetonitrile and in bmimTf$_2$N, and the PCT bands in heptane, is explained well by the model based on the charge resonance between the two equivalent electronic structures of the CT state.

## 1. Introduction

Photoinduced charge transfer (CT) reaction is one of the most fundamental and important chemical reactions. The CT reaction in 9,9′-bianthryl (BA) has attracted much attention as a prototype of photoinduced intramolecular charge transfer reaction since the CT reaction was proposed by Schneider and Lippert.[1,2] A large number of ultrafast spectroscopic experiments on the CT reaction in BA have been performed in the UV/vis region in clusters,[3−11] in solutions,[12−29] or in ionic liquids.[30] When BA is irradiated by UV light, it is excited to the locally excited (LE) state in which one of the anthracene moieties is electronically excited. The CT reaction occurs between the two anthracene moieties after the UV irradiation in polar solvents, including ionic liquids, and it has been widely accepted that the CT reaction does not proceed in nonpolar solvents.

In order to examine the mechanism of the CT reaction in BA, we have performed femtosecond time-resolved near-IR absorption anisotropy spectroscopy as well as ordinary time-resolved near-IR absorption spectroscopy.[31−33] When BA is photoexcited in acetonitrile, there are two bands observed at 9800 cm$^{-1}$ (1020 nm) for the LE state and at 6450 and 7100 cm$^{-1}$ (1550−1400 nm) for the CT state at 0 ps. The 9800 cm$^{-1}$ band that decays in (0.37 ± 0.01) ps shows a transition moment perpendicular to the inter-ring C−C bond, whereas the broad band between 6450 and 7100 cm$^{-1}$ shows a transition moment parallel to the inter-ring C−C bond. When BA is photoexcited in heptane, two absorption bands are also observed at 0 ps. A CT band of BA is formed in heptane as well. We call this a partial CT (PCT) state,[33] because the band shape in heptane agrees with the shape observed at 0 ps in acetonitrile. In acetonitrile, however, the peak position of the PCT band gradually shifts to 8000 cm$^{-1}$ (1250 nm) to form a CT band within a few picoseconds from the excitation, which indicates that the PCT state is an intermediate in the CT reaction.

The presence of the PCT state is supported by the results of time-resolved UV/vis spectroscopy and time-resolved microwave conductivity measurements. From time-resolved UV/vis spectroscopy, it has been suggested that the CT reaction proceeds via an intermediate in polar solvents.[14,22−24] Time-resolved microwave conductivity measurements suggest that BA photoexcited in nonpolar solvents has a permanent dipole moment larger than zero. It has not been widely accepted, however, that the CT reaction proceeds in nonpolar solvents.[34]

These results suggest that the interaction between the PCT state and solvent molecules determines if the CT reaction proceeds or not. However, it has not yet been fully understood what roles the polar and nonpolar solvents play on the electronic structure of the LE, PCT, or CT states. If the PCT state has the lifetime identical with the LE state, then the equilibrium of these states is strongly supported. In this study, we measure nanosecond time-resolved spectra in the whole near-IR region of 4500−10 500 cm$^{-1}$ (2200−950 nm) in heptane, in acetonitrile,

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and in bmimTf$_2$N and show that the LE state is in equilibrium with the PCT state in heptane. We also discuss the difference in electronic structures of the PCT and CT states in these solvents.

## 2. Experimental Section

Transient absorption spectra were measured with a nanosecond time-resolved near-IR absorption spectrometer.[35,36] The spectrometer was developed based on a nanosecond time-resolved IR absorption spectrometer we constructed with a dispersive monochromator.[37,38] Briefly, sample solutions were photoexcited by the third harmonic of a pulsed Q-switched Nd:YAG laser (IB LASER DiNY pQ355, 355 nm, 250 Hz, 40 $\mu$J/pulse, 7 ns). Probe radiation in the near-IR region from a tungsten-halogen lamp (Hosobuchi Electric Lamp) was focused onto a sample point. Transmitted probe light was introduced into a dispersive monochromator (JASCO CT-50TFP) with a pair of off-axis ellipsoidal mirrors and was detected by a photovoltaic InSb detector with a preamplifier (Kolmar Technologies KISDP-1J1/DC). Electric signals from the detector were amplified with an AC-coupled main differential amplifier (NF Corporation 5305). The output of the main amplifier was monitored by a digital sampling oscilloscope (Tektronix DSA602). The overall time resolution of the spectrometer, determined by the bandwidth of the detector and the main amplifier, was estimated to be 40 ns. The spectral coverage was from 4500 cm$^{-1}$ (2200 nm) to 10 500 cm$^{-1}$ (950 nm). Sample solutions were stirred in a quartz cell with a 3 mm optical path.

We synthesized BA by reducing anthraquinone with zinc powder in acetic acid.[39] The product was first recrystallized from chlorobenzene and then from acetic acid. Steady-state UV/vis absorption spectra of purified BA in various solvents were identical with those in the literature.[1,2,7] Heptane (GC grade) was purchased from Nacalai Tesque, Inc. Acetonitrile (HPLC grade) was purchased from Kanto Chemical Co., Ltd. These solvents were used without further purification. 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (bmimTf$_2$N) was purchased from Kanto Chemical Co., Ltd. bmimTf$_2$N solution was kept under vacuum for longer than 2 h before the time-resolved measurements for removing water. The time profiles in heptane and in acetonitrile were measured under an Ar atmosphere.

## 3. Results and Discussion

**3.1. Heptane Solution.** Absorbance changes of BA induced by the photoexcitation at 355 nm in a solvent heptane were recorded by the time-resolved near-IR absorption spectrometer. The time-resolved spectra measured in heptane are shown in Figure 1. Two transient bands centered at 9800 cm$^{-1}$ (1020 nm) and 6700 cm$^{-1}$ (1500 nm) are clearly observed. They are assigned to the LE band and the PCT band, respectively, based on the observation in our previous femtosecond experiments.[31−33] The presence of the PCT state in heptane is consistent with the nonzero permanent dipole moment for the photoexcited BA in nonpolar solvents observed by the time-resolved microwave conductivity measurements.[34] With the use of a time-resolved near-IR spectrometer that covers a wide spectral range of 4500−10 500 cm$^{-1}$ (2200−950 nm), the peak position of the PCT band is distinctly determined to be 6700 cm$^{-1}$ (1500 nm). Note that the spectral coverage of our previous femtosecond time-resolved near-IR experiments[31−33] was limited to 6450−10 500 cm$^{-1}$ (1550−950 nm).

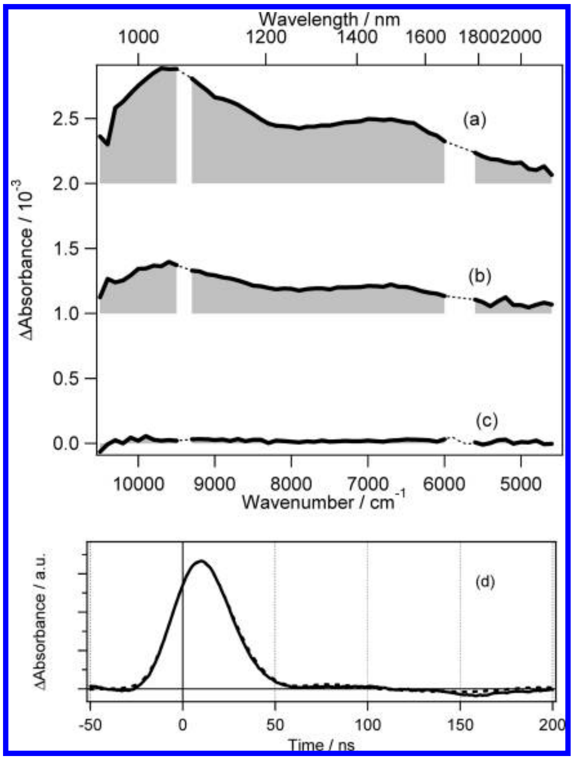

**Figure 1.** Time-resolved near-IR spectra of 9,9′-bianthryl photoexcited at 355 nm in heptane at 0 ns (a), 40 ns (b), and 80 ns (c). Spectral range where the measurement is strongly influenced by overtone near-IR absorption is represented by a dotted line. Time profiles of absorption intensity at 1020 nm (solid trace) and at 1250−1540 nm (dotted trace) of photoexcited 9,9′-bianthryl in heptane (d). Each time profile is normalized at the 0 ns.

Time profiles of the near-IR absorption at 9800 cm$^{-1}$ (1020 nm) and 6700 cm$^{-1}$ (1500 nm) represent the decay kinetics of the LE state and the PCT state. The observed time profiles are shown in Figure 1. The decay time constants were determined to be (13 ± 1) ns at 9800 cm$^{-1}$ (1020 nm), for the LE state, and (13 ± 1) ns at 6500−8000 cm$^{-1}$ (1540−1250 nm), for the PCT state, by the least-squares fitting analysis. The model function was convolution between a single exponential decay function and a Gaussian instrumental response function. The two time constants obtained above are identical with each other. The agreement of the time constants between the LE and the PCT states is consistent with a lack of changes in relative band intensities in a set of time-resolved spectra. The spectrum at 0 ns, which includes both the LE and PCT bands, is identical with those at 40 and 80 ns, when they are normalized at 9800 cm$^{-1}$ (1020 nm). The result strongly suggests that the PCT state in heptane is in equilibrium with the LE state. The LE and PCT states are equilibrated much faster than the instrument response time of 40 ns.

**3.2. Acetonitrile Solution.** In acetonitrile, obtained nanosecond time-resolved near-IR spectra are different from those in heptane. The obtained spectra are shown in Figure 2. Only one absorption band that has a peak at 8000 cm$^{-1}$ (1250 nm) and extends from 4500 to 10500 cm$^{-1}$ (2200−950 nm) appears within the instrumental response time.

The observed band is assigned to the CT state absorption, because the CT reaction completes in (0.37 ± 0.01) ps, much faster than the response time.[35] The assignment is consistent with the results from our femtosecond near-IR anisotropy measurement, in which a broad absorption band centered at 8000 cm$^{-1}$ (1250 nm) was assigned to the CT state absorption based on the direction of its transition absorption dipole moment along the inter-ring direction.[31−33]

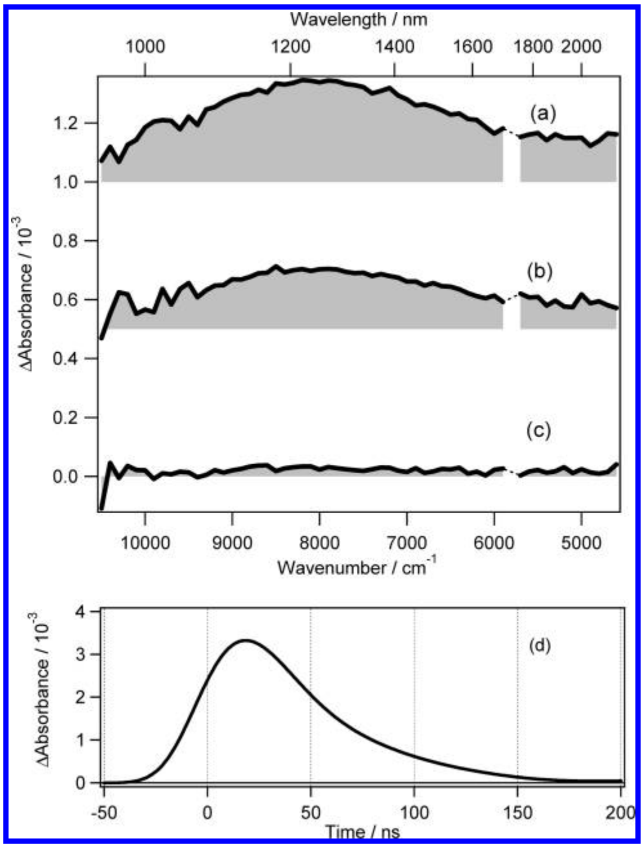

**Figure 2.** Time-resolved near-IR spectra of 9,9′-bianthryl photoexcited at 355 nm in acetonitrile at 0 ns (a), 40 ns (b), and 80 ns (c). Spectral range where the measurement is strongly influenced by overtone near-IR absorption is represented by dotted line. Time profile of absorption intensity at 1250−1540 nm of photoexcited 9,9′-bianthryl in acetonitrile (d).

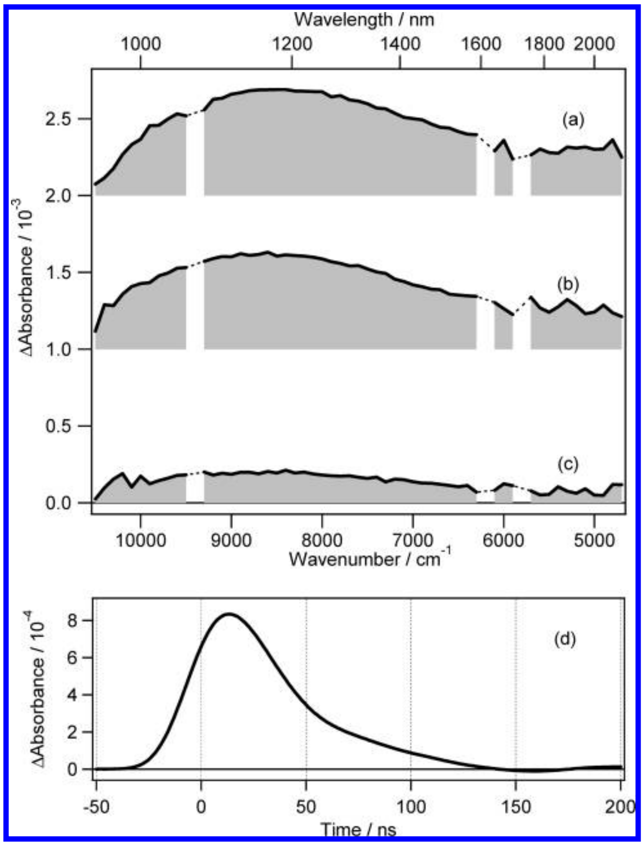

**Figure 3.** Time-resolved near-IR spectra of 9,9′-bianthryl photoexcited at 355 nm in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (bmimTf$_2$N) at 0 ns (a), 40 ns (b), and 80 ns (c). Spectral range where the measurement is strongly influenced by overtone near-IR absorption is represented by dotted line. Time profiles of absorption intensity at 1020 nm (solid trace) and at 1250−1540 nm (dotted trace) of photoexcited 9,9′-bianthryl in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (bmimTf$_2$N) (d).

Time dependence of the absorption intensity of the CT band is shown in Figure 2. The decay time constant of a single exponential function is determined to be (41 ± 2) ns by the least-squares fitting analysis. The obtained decay time constant of the CT band agrees with the decay time constants obtained by time-resolved fluorescence spectroscopy (35.26 ns) or time-resolved UV absorption spectroscopy (34.0 ns).[29]

**3.3. bmimTf$_2$N Solution.** Room temperature ionic liquids are composed of positive and negative ions. It is interesting to study their microscopic solvation environments as a reaction media. Time-resolved near-IR spectra were observed in an ionic liquid, bmimTf$_2$N. The result is shown in Figure 3. The spectra observed in bmimTf$_2$N are similar to those observed in acetonitrile. An absorption band that has a peak at 8500 cm$^{-1}$ (1180 nm) and extends from 4500 to 10500 cm$^{-1}$ (2200−950 nm) appears within the instrumental response time. The peak position is blue-shifted by 500 cm$^{-1}$ from the one in acetonitrile.

The observed band is assigned to the CT state absorption, because its band shape is similar to the CT band in acetonitrile. The LE band is not detected in bmimTf$_2$N as well as in acetonitrile. This assignment is consistent with the results of picosecond time-resolved visible absorption spectroscopy or picosecond time-resolved fluorescence spectroscopy reported by Nagasawa, Miyasaka and their collaborators.[30] The picosecond transient absorption spectra showed that the visible CT band rose within 1 ns. Picosecond fluorescence spectra showed dynamic Stokes shift completed by 10 ns in bmimTf$_2$N. The time dependence of the absorption intensity observed in bmimTf$_2$N is shown in Figure 3. The decay time constant of a single exponential function is determined to be (34 ± 1) ns by the least-squares fitting analysis. The obtained decay time constant of the CT band roughly agrees with the decay time constants obtained by time-resolved fluorescence spectroscopy (30.5 ns).[30]

**3.4. CT States in Polar and Nonpolar Solvents.** In the present experiment, the entire PCT band is clearly observed in heptane. Observation of the identical decay rate both for the PCT and LE states indicates that the two states are in equilibrium in heptane. The interaction with the surrounding solvent molecules should give nonequivalent environments for the two anthracene moieties, which might well result in the formation of the CT states. The induced dipole moment of the solvent is likely to play an essential role on the stabilization of the PCT state of BA in heptane (Figure 4). In polar solvents such as acetonitrile and bmimTf$_2$N, however, the PCT states are not in equilibrium with the LE state in the nanosecond time region. In these solvents, the PCT state is further stabilized to the fully charge transferred CT states by the strong interactions with the large permanent dipole moment of the solvent molecules or with the charge of the solvent ions.

Different natures of the CT states formed in the three solvents account for the difference in the observed time-resolved spectra. We compare the position, the bandwidth, and the decay time constant in the following. The position of the CT band in acetonitrile and in bmimTf$_2$N is 8000 cm$^{-1}$ (1250 nm) and 8500 cm$^{-1}$ (1180 nm), respectively, whereas it is 6700 cm$^{-1}$ (1500 nm) for the PCT band in heptane. The position of the CT band

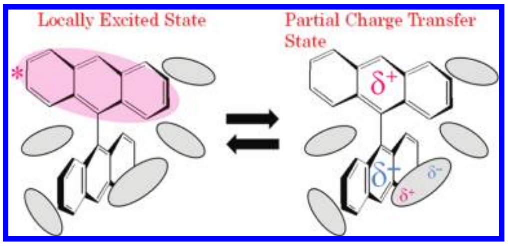

**Figure 4.** Electronic state dynamics of photoexcited 9,9′-bianthryl in nonpolar solvents observed in this study. In nonpolar solvents, the LE state of 9,9′-bianthryl is in equilibrium with the PCT state.

and the PCT band reflects the interaction between the two anthracene moieties. According to the model based on the charge resonance between $(\mathrm{ANT})^{\delta+} - (\mathrm{ANT})^{\delta-}$ and $(\mathrm{ANT})^{\delta-} - (\mathrm{ANT})^{\delta+}$, where ANT represents the anthryl group, the position of the CT (PCT) band represents the energy gap between the two charge resonance states.[33] The CT band in acetonitrile is blue-shifted by approximately 1300 $\mathrm{cm}^{-1}$ compared to the PCT band in heptane. The CT band in $\mathrm{bmimTf_2N}$ is further blue-shifted by approximately 500 $\mathrm{cm}^{-1}$. This result indicates that the energy splitting between the two states is large in the order of: in $\mathrm{bmimTf_2N}$ > in acetonitrile ≫ in heptane. This is consistent with our idea that the CT state in $\mathrm{bmimTf_2N}$ and in acetonitrile is significantly stabilized by the charge of the solvent ions or by the permanent dipole moment of the solvent molecules, whereas the PCT state in heptane is only weakly stabilized by the induced dipole moment of heptane.

The width of the near-IR absorption band is also different between the CT state in polar solvents and the PCT state in nonpolar solvents. The width of the CT band in $\mathrm{bmimTf_2N}$ and in acetonitrile is approximately 4000 $\mathrm{cm}^{-1}$ (fwhm), whereas it is approximately 2500 $\mathrm{cm}^{-1}$ (fwhm) for the PCT band in heptane. The width of the CT band is larger than the PCT band by 1500 $\mathrm{cm}^{-1}$. This result is indicative of larger fluctuation of the energy splitting between $(\mathrm{ANT})^{\delta+} - (\mathrm{ANT})^{\delta-}$ and $(\mathrm{ANT})^{\delta-} - (\mathrm{ANT})^{\delta+}$ in polar solvents than in nonpolar solvents.

The decay time constants are also different between the CT state in polar solvents and the PCT state in nonpolar solvents. The CT bands in acetonitrile and in $\mathrm{bmimTf_2N}$ decays in (41 ± 2) ns and (34 ± 1) ns, respectively, whereas the PCT band in heptane decays in (13 ± 1) ns. The difference in the decay time constant is well understood from the decay mechanism of the CT and PCT states. In polar solvents, the CT state decays directly to the ground state by the back CT reaction. Because the CT state is significantly stabilized by the solvent molecules, the activation energy of the back CT reaction is probably large. In nonpolar solvents, however, the PCT state is equilibrated with the LE state. Therefore, the LE state is the product of the back CT reaction of the PCT state. Because the LE and PCT states approach the equilibrium within the instrumental response time, the back CT reaction from the PCT to LE state is much faster than the decay of the CT state in polar solvents. Most probably, the activation energy of the back CT reaction for the PCT state in heptane is smaller than that of the CT state in acetonitrile and in $\mathrm{bmimTf_2N}$, because the PCT state in heptane is significantly less stabilized by the solvent than the CT state in acetonitrile and in $\mathrm{bmimTf_2N}$.

## 4. Conclusions

In the present study, the nanosecond time-resolved near-IR absorption spectra of 9,9′-bianthryl in heptane, in acetonitrile, and in $\mathrm{bmimTf_2N}$ have been observed. The LE state and the PCT state in heptane show absorption bands at 9800 and 6700 $\mathrm{cm}^{-1}$, and decay with the same time constant of (13 ± 1) ns, indicating that the LE state is in equilibrium with the PCT state in heptane. The CT state in acetonitrile shows a broad absorption band at 8000 $\mathrm{cm}^{-1}$ and decays in (41 ± 2) ns. The CT state in $\mathrm{bmimTf_2N}$ shows a blue shift by 500 $\mathrm{cm}^{-1}$ from the band in acetonitrile and decays in (34 ± 1) ns. The PCT state in heptane is only weakly stabilized by the induced dipole moment of the heptane molecules surrounding the excited 9,9′-bianthryl, whereas the CT state in acetonitrile and in $\mathrm{bmimTf_2N}$ is significantly more stabilized by the permanent dipole moment of the solvent molecules or the charge of the solvent ions.

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## References and Notes

(1) Schneider, F.; Lippert, E. *Ber. Bunsen-ges. Phys. Chem.* **1968**, *72*, 1155.
(2) Schneider, F.; Lippert, E. *Ber. Bunsen-ges. Phys. Chem.* **1970**, *74*, 624.
(3) Yamasaki, K.; Arita, K.; Kajimoto, O.; Hara, K. *Chem. Phys. Lett.* **1986**, *123*, 277.
(4) Kajimoto, O.; Yamasaki, K.; Arita, K.; Hara, K. *Chem. Phys. Lett.* **1986**, *125*, 184.
(5) Honma, K.; Arita, K.; Yamasaki, K.; Kajimoto, O. *J. Chem. Phys.* **1991**, *94*, 3496.
(6) Honma, K.; Kajimoto, O. *J. Chem. Phys.* **1994**, *101*, 1752.
(7) Fujiwara, T.; Fujimura, Y.; Kajimoto, O. *Chem. Phys. Lett.* **1996**, *261*, 201.
(8) Ishida, T.; Fujimura, Y.; Fujiwara, T.; Kajimoto, O. *Chem. Phys. Lett.* **1998**, *288*, 433.
(9) Fujiwara, T.; Egashira, K.; Ohshima, Y.; Kajimoto, O. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1365.
(10) Fujiwara, T.; Fujimura, Y.; Kajimoto, O. *J. Chem. Phys.* **2000**, *113*, 11109.
(11) Tanaka, K.; Honma, K. *J. Phys. Chem. A* **2002**, *106*, 1926.
(12) Nakashima, N.; Murakawa, M.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 854.
(13) Mataga, N.; Yao, H.; Okada, T.; Rettig, W. *J. Phys. Chem.* **1989**, *93*, 3383.
(14) Mataga, N.; Nishikawa, S.; Okada, T. *Chem. Phys. Lett.* **1996**, *257*, 327.
(15) Elich, K.; Kitazawa, M.; Okada, T.; Wortmann, R. *J. Phys. Chem. A* **1997**, *101*, 2010.
(16) Tsuboi, Y.; Kumagai, T.; Shimizu, M.; Itaya, A.; Schweitzer, G.; De Schryver, F. C.; Asahi, T.; Masuhara, H.; Miyasaka, H. *J. Phys. Chem. A* **2002**, *106*, 2067.
(17) Kahlow, M. A.; Kang, T. J.; Barbara, P. F. *J. Phys. Chem.* **1987**, *91*, 6452.
(18) Kang, T. J.; Kahlow, M. A.; Giser, D.; Swallen, S.; Nagarajan, V.; Jarzeba, W.; Barbara, P. F. *J. Phys. Chem.* **1988**, *92*, 6800.
(19) Barbara, P. F.; Jarzeba, W. *Acc. Chem. Res.* **1988**, *21*, 195.
(20) Kang, T. J.; Jarzeba, W.; Barbara, P. F.; Fonseca, T. *Chem. Phys.* **1990**, *81*, 149.
(21) Barbara, P. F.; Jarzeba, W. *Adv. Photochem.* **1990**, *15*, 1.
(22) Jurczok, M.; Plaza, P.; Martin, M. M.; Meyer, Y. H.; Rettig, W. *Chem. Phys.* **2000**, *253*, 339.
(23) Jurczok, M.; Plaza, P.; Rettig, W.; Martin, M. M. *Chem. Phys.* **2000**, *256*, 137.
(24) Jurczok, M.; Gustavsson, T.; Mialocq, J.-C.; Rettig, W. *Chem. Phys. Lett.* **2001**, *344*, 357.
(25) Kovalenko, S. A.; Lustres, J. L. P.; Ernsting, N. P.; Rettig, W. *J. Phys. Chem. A* **2003**, *107*, 10228.
(26) Anthon, D. W.; Clark, J. H. *J. Phys. Chem.* **1987**, *91*, 3530.
(27) Zachariasse, K. A.; Grobys, M.; von der Haar, Th.; Hebecker, A.; Il'ichev, Yu. V.; Jiang, Y. -B.; Morawski, O.; Kühnle, W. *J. Photochem. Photobiol. A* **1996**, *102*, 59.
(28) de Bekker, E. J. A.; Pugzlys, A.; Varma, C. A. G. O. *J. Phys. Chem. A* **2002**, *106*, 5974.

(29) Grabner, G.; Rechthaler, K.; Köhler, G. *J. Phys. Chem. A* **1998**, *102*, 689.

(30) Nagasawa, Y.; Itoh, T.; Yasuda, M.; Ishibashi, Y.; Ito, S.; Miyasaka, H. *J. Phys. Chem. B* **2008**, *112*, 15758.

(31) Takaya, T.; Hamaguchi, H.; Kuroda, H.; Iwata, K. *Chem. Phys. Lett.* **2004**, *399*, 210.

(32) Takaya, T.; Saha, S.; Hamaguchi, H.; Sarkar, M.; Samanta, A.; Iwata, K. *J. Phys. Chem. A* **2006**, *110*, 4291.

(33) Takaya, T.; Hamaguchi, H.; Iwata, K. *J. Chem. Phys.* **2009**, *130*, 014501.

(34) Piet, J. J.; Schuddeboom, W.; Wegewijs, B.; Grozema, F. C.; Warman, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 5337.

(35) Yabumoto, S.; Sato, S.; Hamaguchi, H. *Chem. Phys. Lett.* **2006**, *416*, 100.

(36) Yabumoto, S. Ph.D. Thesis, Development of Highly-sensitive and High-speed Nanosecond Time-resolved Mid-/Near-infrared Spectrometer and Its Application to Photochemistry of Aromatic Carbonyl Compounds; The University of Tokyo: 2008.

(37) Iwata, K.; Hamaguchi, H. *Appl. Spectrosc.* **1990**, *44*, 1431.

(38) Yuzawa, T.; Kato, C.; George, M. W.; Hamaguchi, H. *Appl. Spectrosc.* **1994**, *48*, 684.

(39) Magnus, A.; Hartmann, H.; Becker, F. *Z. Phys. Chem.* **1951**, *197*, 75.

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