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Picosecond Dynamics of Excited 9,9′-Bianthryl Adsorbed on Porous Glass: Role of Symmetry Breaking in the Ground State[†]

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Excited-state dynamics of 9,9′-biantryl (BA) adsorbed on the porous glass, where the large motion of the surrounding medium or intramolecular motion of BA was not plausible, and temperature effects on it were investigated by means of steady-state fluorometry, absorption measurement, picosecond transient absorption spectroscopy, and time-resolved fluorescence measurement. Steady-state fluorescence and transient absorption spectroscopy revealed that the electronic structure of excited BA had strong charge transfer (CT) character as comparable as in the polar solutions both at room temperature and at 77 K, although the dielectric environments estimated by other inter- and intramolecular CT systems were in nonpolar or very weakly polar environments. The time constant of CT was determined to be 5−10 ps at 294 K. The CT time constant was slightly slower (ca. 20 ps) at 77 K but was much faster than that of BA in alcoholic solutions at room temperature. By integrating these results with those in solutions, the rapid CT state formation and the stabilization of the CT state were discussed from the viewpoint of the symmetry breaking in the ground state because of the heterogeneous adsorption of BA onto the glass surface.

Introduction

Photoinduced electron transfer (ET) and its related phenomena play fundamental and important roles in a number of photochemical reactions in the condensed phase and have been investigated from various viewpoints.[1−6] Among these investigations, much effort has been focused onto the elucidation of ET processes in solutions, and the relation between the solvation process and the rate of the ET reaction has been under vivid discussions.[4−6] In these studies, the photoinduced charge separation process of 9,9′-bianthryl (BA) and its analogues has been attracting much attention as typical models where the dynamic solvent motion takes an important role for the charge transfer.[4,6−23]

BA comprised of two identical anthryl moieties has no dipole moment in the ground state or in the excited state in nonpolar solutions. On the other hand, intramolecular charge transfer (CT) fluorescence appears in polar solutions, indicating that the charge separation takes place between these two identical groups. For the direct detection of the charge separation processes in polar solution, a number of investigations have been performed by means of ultrafast laser spectroscopy. For the excited-state dynamic behaviors in alcohol solutions, it was reported that the CT time constants were in agreement with the longitudinal dielectric relaxation time of the solvent.[12,13,18] On the other hand, the CT time in nonviscous aprotic solutions was slower than the solvent longitudinal relaxation time, but it was very close to the microscopic solvation time.[14−17] Although the dynamic behaviors of BA in nonviscous solutions are slightly different from those in alcohols, these results in polar solutions indicate that the solvation dynamics regulate the charge separation process. In addition, these results imply that the solvent dipole fluctuations around BA take a crucial role for the appearance of the unequal environments between two anthryl moieties, which triggers the charge separation accompanied by the symmetry breaking.

Although the fluctuation of the surrounding medium is strongly related to the electron transfer in solutions and in some cases the solvation process may regulate the rapid ET in solution as for BA, fast electron-transfer processes comparable to those in solutions are ubiquitous in various phases such as solids and heterogeneous systems where the large motion of the surrounding medium is not plausible.[24−28] Namely, the heterogeneous systems can provide various reaction environments different from solutions, and the design of such environments may supply potential tools for the control of electron transfer processes. For example, we have recently reported that the charge-separated state living more than 8 h at room temperature can be attained in the adsorbed system which enables the effective charge shift reaction and the trapping process of the ions to fix the long interionic distance.[25] In this respect, it is necessary to elucidate the underlying mechanism for the electron-transfer process in

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such heterogeneous systems[24−28] in comparison with those in solutions where the large fluctuation of the medium is very important. Moreover, information on the electron-transfer dynamics in these heterogeneous systems also provides in-depth insight into the dynamic behaviors in the homogeneous solution phase.

From such a viewpoint, we have investigated here the CT dynamics of BA adsorbed on porous glass. In the present adsorbed system, the large motion of the surrounding medium does not seem plausible. In addition, the dielectric constant experienced by the ion pair between tetracyanobenzene and anthracene[26,27] and by the intramolecular CT state in the porphyrin linked with anthryl groups[28] adsorbed on the porous glass were estimated to be ca. 4−5, indicating that the molecule adsorbed on the porous glass seems to be in nonpolar or very weakly polar environments. Because BA has molecular structure where two anthryl moieties have torsional angle of ca. 90° in the ground state,[20−22] it is rather difficult to be adsorbed on the surface in such a manner that both of moieties are equivalent. In addition, the surface is not flat in the molecular level. Hence, it is expected for BA to locate in the environment where two anthryl groups are unequal in the ground state although it is difficult to know how the BA molecule is adsorbed on the porous glass. Hence, the information on the dynamic behaviors in the adsorbed BA under an unsymmetrical environment can directly provide the detailed information on the role of the symmetry breaking in the CT process in the excited state.

Not only the characteristic behaviors of the environments but also the torsional motion of BA itself seem to be restricted in the adsorbed system. The angle between two anthracene planes at the minimum of the torsional angle was reported to be ca. 60° (120°) in nonpolar solutions,[20−22] whereas it was 90° in the ground state. The relaxation of the torsional angle in the initial stage after the excitation is reported to be also an important coordinate[12,13,17,18,20−22] in the dynamic behaviors in the excited state as well as the solvation coordinate. As will be shown later, the adsorption of BA on the porous glass induces the rapid CT reaction following the excitation. This rapid CT process and its temperature effect will be discussed by comparing the present results with those in solution phase.

Experimental Section

A porous glass plate (Corning, Vycor No.7930; mean pore radius = 4 nm, thickness =1 mm) was washed with nitric acid at 100 °C and repeatedly with distilled water, followed by heating at 400 °C for 48 h. BA (Molecular Probes Inc.) was used as received because the absorption and fluorescence spectra in various solvents were identical with the reference data. Adsorption was carried out in the following manner. The purified porous glass plate (ca. 1 cm × 1 cm) was put into a methylene chloride solution of BA (4.1×10^{-3} M) and stored at 30 °C for more than 24 h. The porous glass adsorbing BA was dried in a vacuum for more than 4 h and then stored in a quartz cuvette containing dried N_2 gas. The change of concentration of BA in the mother liquors from 10^{-4} to 10^{-2} M did not affect the dynamic behaviors, the steady-state fluorescence, or the ground-state absorption within the experimental error. However, the steady-state fluorescence maximum was dependent on the time after the sample preparation. This aging caused the fluorescence maximum shift within 10 nm. However, the aging effect was suppressed in the case where the specimen was stored at low temperature. *n*-hexane (Wako, Chromatograph Grade), ethytl acetate (Wako, Spectral Grade), and acetonitrile (Nakarai, Spectrosol) were used without further purification.

Steady-state fluorescence and absorption spectra were respectively recorded by a Hitachi F-4500 fluorometer and Hitachi 200-20 spectrophotometer. A microcomputer-controlled picosecond laser photolysis system with a handmade repetitive mode-locked Nd^{3+}:YAG laser was used for measurements.[29] A third harmonic pulse (355 nm) with 15 ps fwhm and ca. 0.5 mJ output power was used for the excitation. Monitoring white light was generated by focusing the fundamental light into a 10 cm D_2O-H_2O (3:1) cell. Two sets of the multichannel diode array (MCPD, Hamamatsu S3904-1024Q) combined with a polychromator were used for the detection of the monitoring light. The repetition rate of the excitation light was kept low (<0.3 Hz). For the adsorbed system, the sample positions were replaced after one or two exposures to avoid the degradation of the sample. A sample cell with 1 cm optical path length was used for the measurements of solution samples under picosecond laser excitation. Chirping of the monitoring light was corrected for the transient absorption spectra immediately after the excitation. Most of the data were accumulated over two measurements for the adsorbed system and four times for the solution samples.

To investigate the system with a very short lifetime, a double OPA femtosecond laser system for kinetic transient absorption measurements was used. The details of the system are described elsewhere.[30] Briefly, the output of a femtosecond Ti:sapphire laser (Tsunami, Spectra-Physics) pumped by SHG of a cw Nd^{3+}:YVO_4 laser (Millennia V, Spectra-Physics) was regeneratively amplified with 1 kHz repetition rate (Spitfire, Spectra-Physics). The amplified pulse (1 mJ/pulse energy and 85 fs fwhm) was divided into two pulses with the same energy (50%). These pulses are guided to two OPA systems (OPA-800, Spectra-Physics), respectively. OPA output pulses are converted to the SHG, THG, or FHG, each of which covers the wavelength region between 300 and 1200 nm with 1−10 mW output energy and 120 fs fwhm. One of these two pulses was used as a pump light, and the other one which is reduced to $<1/5000$ output power was utilized as a monitoring light. In the present measurement, SHG of the fundamental 800 nm light was used for the excitation. The pulse duration for the present wavelength pair (400 nm and 680 nm) at the sample position was estimated 130 fs from the cross correlation trace at the same position. The intensity of the light monitoring the sample excited with a pump pulse was detected by a photodiode and sent to the microcomputer for further analysis. For solution samples, the sample cell with 2 mm optical length was used.

Fluorescence decay curves were measured with a ps 2-Dimension streak camera (C4334, Hamamatsu).[31] A femtosecond pulse train (76 MHz, 1 W, 150 fs fwhm) from a cw self-mode-locked Ti:sapphire laser (Mira 900, Coherent) pumped with an Ar^+ laser (Innova 310, Coherent) was dumped to a 4 MHz train by a pulse picker (model 9200, Coherent). The obtained laser pulse was frequency doubled and used as an excitation light source. The excitation wavelength was about 390 nm, and its intensity was less than 1 nJ/pulse. For the measurements at 77 K, the sample cell was put in the quartz Dewar with flat windows. All measurements were performed under O_2 free condition.

Results and Discussion

Steady-State Absorption and Fluorescence Spectra. Figure 1 shows steady-state absorption spectrum of BA adsorbed on porous glass. As references, also exhibited are the spectra of BA in various solutions, which were in agreement with those reported previously.[7,8] Compared to the spectra in solution phase,

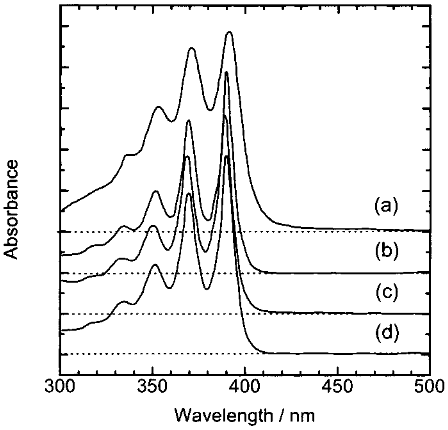

Figure 1. Steady-state absorption spectra of bianthryl at 293 K. (a) Adsorbed on the porous glass, (b) in *n*-hexane, (c) in ethyl acetate, and (d) in acetonitrile.

the band shape of the adsorbed system is rather broad. As will be shown later, the steady-state spectrum of the adsorbed system does not show apparent line-narrowing even at 77 K. Hence, the spectral broadening in the adsorbed system is mainly attributed to the heterogeneity of the adsorbed states.

In the adsorbed system, the absorption tail in the region of >400 nm is remarkable in its spectrum. Although it is difficult to derive a clear conclusion at the present stage of the investigation, some different transition such as CT absorption may be involved in the absorption spectrum in the condition where both of the anthryl moieties are unequal in the ground state. Actually, the solvent-dependent absorption tail was reported for the steady-state absorption of 10-cyanobinathryl[11,13] and 10-chlorobianthryl[12] in which the symmetry is broken by the introduction of the electron-accepting groups in one of the anthryl moieties. Another possibility for the spectral tail is an effect of distortion on the energetic potential surface of the electronically excited state of BA as well as that of the ground state. The inhomogeneous adsorption on the porous environment restricts the small motion of BA. Hence, the potential surfaces of BA in excited as well as ground states might differ from those in the solution phase, as will be discussed later. Presumably, both the CT character in the electronic structures and the shapes of the potential surfaces in the adsorbed environment contribute to the spectral tail. Although the spectral band shape is slightly different from those in the solution phase, it is worth noting that the absorption maxima on the adsorbed system are almost similar to those in the solution phase, suggesting that the ground-state molecular structure in the adsorbed state is similar to that in the solution phase.

Steady-state fluorescence spectra of BA adsorbed on the porous glass and those in several solvents are shown in Figure 2. The fluorescence spectra in the solution phase were in agreement with those reported previously.[7,8] In *n*-hexane, the fluorescence spectrum was attributed to the non-CT state. The increase in the solvent polarity opens the charge separation pathway, and the CT state accompanied with symmetry breaking is stabilized with further increase in the solvent polarity. The fluorescence band shape of the adsorbed system is very close to that in acetonitrile, indicating that the charge separation takes place in the adsorbed system. The absence of the non-CT emission (as observed in *n*-hexane) points out the very rapid CT process taking place even in the adsorbed system. In addition, the fluorescence maximum suggests that the local environment of the adsorbed BA is of high polarity as comparable as in acetonitrile. The fluorescence maximum and spectral band shape were almost identical with those for BA adsorbed on the porous glass reported by Nakashima and Phillips,[19] although their fluorescence spectrum involved the LE emission. This difference might be due to the treatment of the porous glass and/or a small amount of anthracene monomer that was mixed in their specimen.

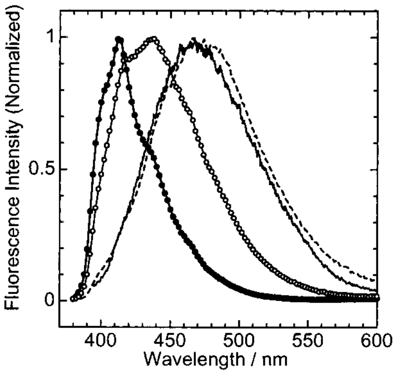

Figure 2. Steady-state fluorescence spectra of bianthryl at 293 K. Excitation wavelength was 355 nm. Solid line with no symbol, adsorbed on the porous glass; broken line with no symbol, in acetonitrile; closed circle, in *n*-hexane; and open circle, in ethyl acetate.

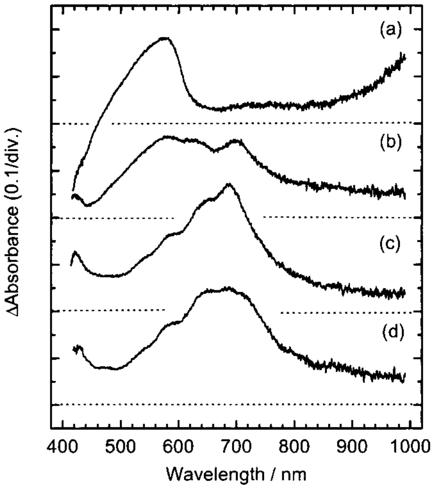

Figure 3. Transient absorption spectra of bianthryl observed at 100 ps following the excitation with a 355 nm laser pulse with 15 ps pulse width. (a) In *n*-hexane, (b) in ethyl acetate, (c) in acetonitrile, and (d) adsorbed on the porous glass.

As mentioned in the introductory section, the dielectric constant experienced by the adsorbed molecular systems was estimated to be ca. 4−5 by the fluorescence of the intermolecular CT complex such as the anthracene−tetracyanobenzene system[26,27] and the intramolecular CT system such as porphyrin linked with anthracene moieties.[28] The polarity experienced by the above anthracene systems indicated that the molecule adsorbed on the porous glass was in nonpolar or very weakly polar environments. In addition, the dielectric constant of 3.1 was reported by the dielectric measurement by applying 100 Hz AC,[32] which was very close to the above value obtained by the "molecular probes". The specific behaviors of the BA fluorescence maximum will be discussed in later part.

Transient Absorption Spectra in Equilibrium Excited States. Figure 3 shows the transient absorption spectra of BA in several solvents and in the adsorbed system, excited with a 15 ps 355 nm laser pulse and monitored at 100 ps. Because the initial relaxation in the early stage after the excitation was completed at 100 ps, these spectra can be regarded as being due to the equilibrium excited state in each of the environments.

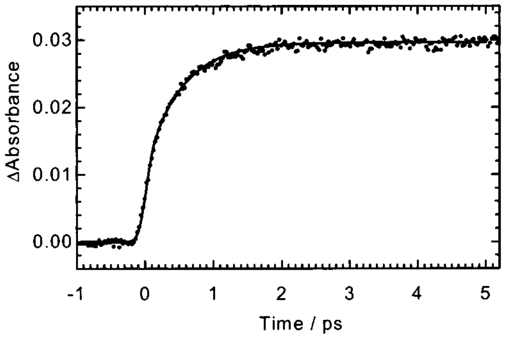

Figure 4. Time profile of the transient absorbance of bianthryl in acetonitrile, monitored at 680 nm following the excitation with a femtosecond 400 nm laser pulse with 85 fs fwhm. The solid line is the curve calculated on the basis of pulse duration of pump and probe pulses and the time constant of 0.55 ps.

The transient absorption spectra in the solution phase were in agreement with those reported previously.[12,13] The spectrum in *n*-hexane solution shows an absorption maximum at 585 nm, which was ascribed to the delocalized excited state over two anthryl moieties with non-CT character.[12] On the other hand, the absorption spectrum in acetonitrile was attributed to the charge-separated and symmetry-broken state.[12] In solvents of intermediate polarity, the transient absorption of BA was reported[12] to be approximately reproduced by the linear combination of the spectra in *n*-hexane and acetonitrile as the spectrum in ethyl acetate in Figure 3. Compared to the spectra in solution phase, the band shape of the transient spectrum of the adsorbed system was very close to that in acetonitrile in which the contribution of the CT state was dominant. The transient absorption spectroscopy also indicated that the charge separation actually takes place in the adsorbed condition and the CT state had a large contribution as suggested in the fluorescence spectrum in Figure 2.

Time Evolution of Transient Absorption. To elucidate the time constant of the formation of the CT state in the adsorbed BA system, we applied the femtosecond laser system. However, the high repetition rate of the laser pulse (1 kHz or 100 Hz) induced the degradation of the sample within a few seconds under the femtosecond laser exposure. Hence, we have compared to the formation time constant of CT state in acetonitrile as reference.

Figure 4 shows the time profile of the transient absorbance of BA in acetonitrile, monitored at 680 nm following the excitation with a femtosecond 400 nm laser pulse with 85 fs fwhm. The monitoring wavelength corresponds to the absorption band of the CT state. The solid line in Figure 4 is the result calculated on the basis of the pulse duration at the sample position and the time constant of the absorption growth of 0.55 ps. For the analysis of the time profile, the first-order rise of the absorption growth was assumed. The charge separation time constant was reported to be 0.7 ps by means of the fluorescence up-conversion technique monitoring the decay of the precursor non-CT emission.[14−16] The present time constant is slightly shorter than the previous value. This may be due to the difference of the detection techniques and the excitation wavelength, the observation of the transient absorption of the CT state following the 400 nm excitation, or the monitoring of the decay of the non-CT emission after the excitation at 362.5 nm. Anyhow, the subpicosecond charge separation was confirmed also from the rise of the transient absorption of the CT state in acetonitrile.

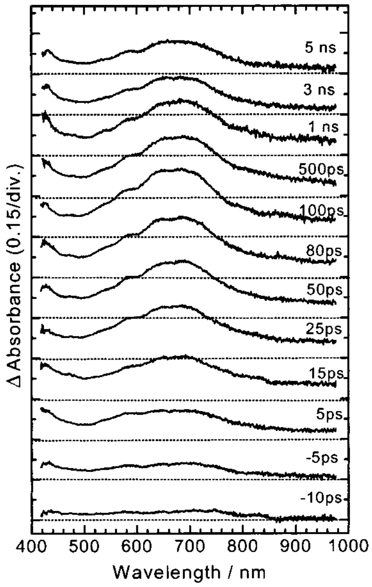

Figure 5. Time-resolved transient absorption spectra of bianthryl adsorbed on the porous glass, excited with a 355 nm laser pulse with 15 ps fwhm.

Figure 5 shows the time evolution of the transient absorption spectra of BA adsorbed on the porous glass, excited with a 15 ps laser pulse at 355 nm. The transient absorption spectrum with its maximum around 690 nm, which is ascribable to the intramolecular CT state, increase in the several tens of picoseconds following the excitation and gradually decreases in a several nanosecond time region. The time profile of the transient absorbance at 690 nm in the early stage after the excitation is exhibited in Figure 6a. The solid lines in this figure are the calculated curves on the basis of the pulse duration and the time constant of the charge separation. The time profile of the transient absorbance at 690 nm of BA in acetonitrile solution, of which charge separation time constant was 0.55 ps as shown in Figure 4, was confirmed to be identical with the response function of the apparatus within the experimental error under the 15 ps laser pulse excitation.

In the leading part of the absorption growth in Figure 6a, the transient absorbance increases almost identically with the response function of the apparatus. This quick rise of the transient absorbance may be partly due to the tail of the absorption because of the non-CT state. Actually, the relative absorption intensity around 590 nm, where the non-CT state had an absorption maximum as shown in Figure 3, was rather strong as observed in the transient absorption spectra in the early stage after the excitation in Figure 5 (e.g. at 5 ps). In the trailing part of the absorption rise in Figure 6a, the deviation from the response function was observed. The time constant of the rise was estimated to be ca. 5−10 ps. It should be remarked that the present adsorbed system is in heterogeneous condition. Hence, the present time constant should be regarded as the averaged or longest time constant of the charge-separation in the present heterogeneous condition. Namely, the charge separation might take place in some specific site with a much shorter time constant. Anyhow, it can be concluded that the very rapid charge separation took place even in the adsorbed system with a time constant <5−10ps.

Figure 6b shows the time profile at 690 nm in a wider time window, indicating that the CT state gradually decreases in several nanosecond time region. On the basis of the assumption that the decay profile in the present time window is biphasic, the time constants and amplitude factors were respectively obtained to be 0.55 (16%) and 11.7 ns (84%). The fluorescence decay profile monitored at 480 nm following the excitation at

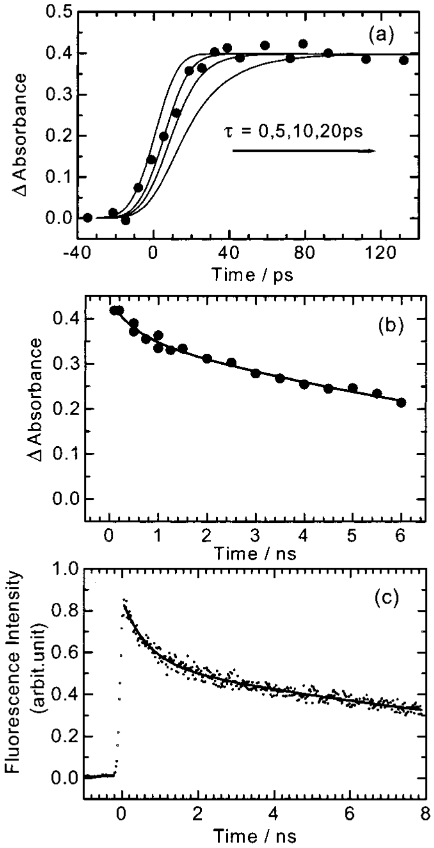

Figure 6. Time profile of transient absorbance of bianthryl adsorbed on the porous glass, monitored at 690 nm following the excitation with a 355 nm laser pulse with 15 ps fwhm. (a) Dynamic behaviors in the early stage after the excitation. Solid lines are the curves calculated on the basis of pulse duration of pump and probe pulses and the time constants. (b) Time profile in the several nanosecond time region. The solid line is the calculated curve on the basis of double-exponential decay function with time constants of 0.55 and 11.7 ns. The amplitude factors for the faster and the slower time constants were respectively 0.16 and 0.84 (see text). (c) Time profile of the fluorescence of BA adsorbed on the porous glass at 480 nm following the excitation at 390 nm. The solid line is the calculated curve on the basis of double-exponential decay function with time constants of 0.66 and 14.7 ns. The amplitude factors for the faster and the slower time constants were respectively 0.35 and 0.65 (see text).

390 nm is exhibited in Figure 6c. For the analysis of the time profile in the present window, the biphasic decay function was assumed as for the transient absorption in Figure 6b. The time constants and amplitude factors were respectively obtained to be 0.66 (35%) and 14.7 ns (65%). Although the amplitude factors of the fluorescence decay were different from those of transient absorption decay, similar time constants were obtained. The difference in the amplitude factors between the fluorescence decay and the time function of the transient absorbance indicates that the radiative rate constants of BA adsorbed on the porous glass have a difference which may be dependent on the adsorbed site.

On the fluorescence decay, it was also observed that the amplitude factors were dependent on the monitoring wavelength of the fluorescence. From our preliminary measurement, the temporal evolution of the fluorescence spectra was observed for BA adsorbed on porous glass. Although the fluorescence maximum evolved from ca. 440 to 475 nm in a subnanosecond to several nanosecond time region, the transient absorption spectra did not show the appreciable temporal evolution. This result was quite different from those observed in the results in

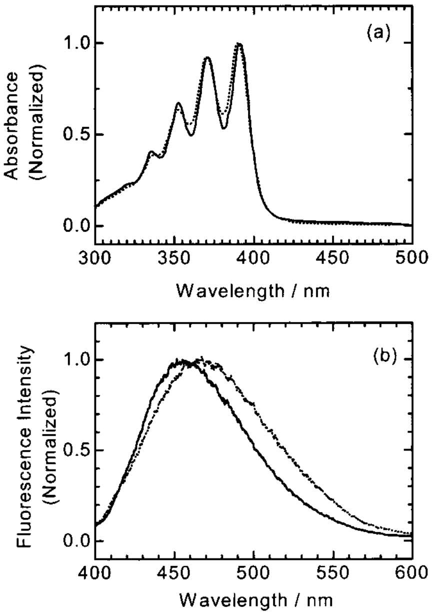

Figure 7. Temperature effect on steady-state spectra of bianthryl adsorbed on the porous glass. (a) Steady-state absorption spectra; solid line at 77 K and dotted line at 294 K. (b) Fluorescence spectra excited at 350 nm; solid line at 77 K and dotted line at 294 K.

solution phase, where the fluorescence maxima and the spectral shape of the transient absorption have a strong correlation.[12]

Excited-State Dynamics at 77 K. The CT state formation in the excited state was investigated also at 77 K. Figure 7a shows the steady-state absorption spectrum of BA adsorbed on the porous glass at 77 K. Although the band shape at 77 K is slightly sharper than the spectrum at room temperature (dotted line in Figure 7), the degree of the line-narrowing at 77 K is rather small in the comparison with the temperature effect of the spectrum in solution phase. As mentioned in the explanation in Figure 1, the small temperature effect of the absorption spectral band shape is mainly attributable to the inhomogeneous broadening. The spectral shape of the fluorescence at 77 K indicates that the CT process actually takes place even at low temperatures. However, the fluorescence maximum at 77 K was blue-shifted by *ca.* 10 nm from that at 294 K, suggesting that some molecular motion with activation process was responsible for the CT fluorescence.

Time-resolved transient absorption spectra of BA adsorbed on the porous glass at 77 K are exhibited in Figure 8. Although the spectral band shape at 77 K is slightly sharp compared to that at 294 K in Figure 5, it is still very close to the spectrum in acetonitrile at 294 K (Figure 3). The time profile of the transient absorbance at 690 nm in the early stage after the excitation is shown in Figure 9, indicating that the rise of the CT state at 77 K is estimated to be ca. 20 ps. Although the time constant at 77 K was slightly slower than that at 294 K, the charge separation took place within a few tens of picosecond. Summarizing the above results, it is concluded that BA adsorbed on the porous glass undergoes very rapid CT state formation even at 77 K.

Role of Symmetry Breaking in the CT State Production. As was shown above, the CT state was observed for BA adsorbed on the porous glass in the early stage following the picosecond laser excitation. The time constant of the charge separation was less than 5−10 ps at 294 K and less than a few tens of picoseconds even at 77 K. These time constants were much shorter than those in alcohol solutions at room temperature.[12,13] In addition, the CT emission maximum at room

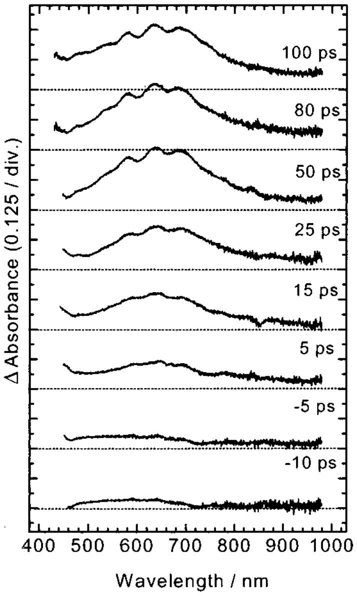

Figure 8. Time-resolved transient absorption spectra of bianthryl adsorbed on the porous glass at 77 K, excited with a 355 nm laser pulse with 15 ps fwhm.

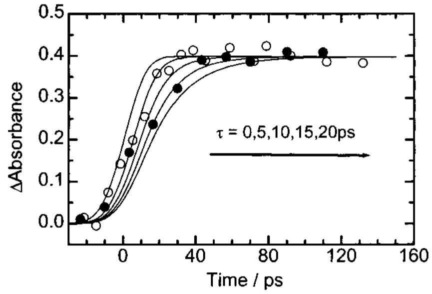

Figure 9. Time profile of transient absorbance of bianthryl adsorbed on porous glass at 77 K (closed circles), monitored at 690 nm following the excitation with a 355 nm laser pulse with 15 ps fwhm. Solid lines are the curves calculated on the basis of pulse duration of pump and probe pulses and the time constants. The results at 294 K (open circles) are also exhibited for the comparison.

temperature is located at a longer wavelength as comparable to that in acetonitrile although the polarity on the porous glass is not so polar. We will discuss these two problems in the following.

As mentioned in the introductory section, a lot of investigations have been performed for the charge separation processes of BA and its related analogues. From these investigations, it has been revealed that the charge separation process in polar solution phase is mainly controlled by the solvation dynamics.[12−18] On this problem, Martin et al. recently pointed out that the charge separation process in unsubstituted BA in polar solution was different from those of BA analogues in which two nonequivalent moieties were connected such as 10-cyanobianthryl.[18] That is, the very rapid inertial conformational relaxation in the non-CT excited state of BA was followed by the charge separation reaction involving both an intramolecular torsion coordinate and a solvation component. On the other hand, the BA analogues with unequal moieties underwent the CT reaction within 500 fs and were followed by the diffusive solvation process. The enhancement of the charge separation rate was also reported for chloro-BA,[12] although the substitution of a chlorine atom does not drastically affect the electronic structure of BA.

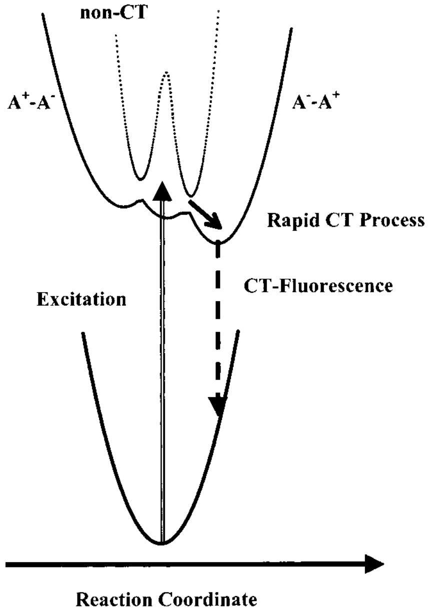

Figure 10. Schematic potential curves of biantheryl adsorbed on porous glass.

These results mean that the introduction of a substituent into an anthryl moiety causing the broken symmetry accelerates the CT reaction. The effect of substitution on the rate of CT is attributable to a couple of factors. One is the modification of the electronic structure increasing CT interactions in the ground and excited states. Indeed, the absorption spectrum of cyano-BA in its ground state exhibited tail-like absorption in the longer wavelength region, which may be ascribed to the CT absorption.[13] The rate of CT in cyano-BA is much faster than the average solvation times in alcoholic solvents as stated above. The other factor is the symmetry breaking in the arrangement of solvent molecules. The nonzero dipole moment in the ground state prepares a solvent polarization immediately after the excitation. This symmetry breaking in its initial excited state is favorable for the CT, whose direction is regulated by the initial solvation arrangement.

The present rapid CT process may be interpreted within this picture. As previously described, the absorption spectrum of BA adsorbed on the porous glass strongly suggests the CT interaction between the two anthryl moieties. Furthermore, intramolecular symmetry in terms of two anthryl moieties is broken because of the adsorption in the ground state. This CT interaction and symmetry breaking are considered to be quite effective for the rapid CT process. Adiabatic potential curves of free energy for the present adsorption system are schematically illustrated in Figure 10 on the basis of above discussion. The reaction coordinate is associated with vibrational coordinates of BA, the adsorbent, and BA−adsorbent interactions, and the reaction coordinate involves the direction of CT. The rapid CT takes place from the initial state (non-CT state) to the CT state (denoted as $A^-{-}A^+$ in the figure), which should be stabilized because of the BA−adsorbent specific interaction because the CT fluorescence is so red-shifted as in acetonitrile. Indeed, Honma et al. found CT fluorescence even from the BA−acetone complex in a supersonic jet and pointed out the importance of an antisymmetric arrangement of a few (> 1) acetone molecules in the complex for the CT state formation.[23] Hence, it seems valid that the CT state of BA is stabilized because of the adsorption by which the mutual relation of the two anthryl rings is asymmetric. Thus, the energy level of the CT state becomes lower than that of the non-CT state as well as the other CT state (denoted as A^+-A^- in the figure), and the CT reaction proceeds rapidly along the reaction coordinate.

Finally, we consider the "fluctuation" responsible for the motion on the reaction coordinate. In such a solid system, candidates of the effective mode of fluctuation for the CT are limited. The first one is the intramolecular torsional motion, which has been regarded as the key factor regulating the CT of BA and related TICT systems. Also in the present system, we consider that this low-frequency mode takes an important role because the overlap of the molecular orbital between both the anthryl rings is necessary to the formation of a CT state. In addition, the molecular vibration of BA could cause the fluctuation of the electric field experienced by the BA itself, as we suggested for a relevant adsorption system.[28] The lattice vibration of the adsorbent might also stimulate the above processes. The temperature effect on the CT observed slightly reflects that these low-frequency fluctuations are coupled with the rapid CT. Another factor accelerating the CT is the fluctuation of silanol groups (Si−OH) on the porous glass and water molecules captured at this site because of hydrogen bonding. However, the density of the silanol groups on the surface of the adsorbent is low (2−5 groups per 100 Å^2),[33] and the hydrophobic treatment of the adsorbent scarcely affects the CT dynamics.[26,27] Hence, these possibilities do not seriously affect the CT dynamics.

Concluding Remarks

For BA and related so-called TICT molecules, it has long been believed that the presence of a solvent is indispensable to induce CT. In the present study, we have shown that the efficient CT can be brought about in a heterogeneous solid system in which BA is adsorbed on porous glass. The electronic structure of excited BA has strong CT character as comparable in the polar solvent, which was confirmed by fluorescence and transient absorption spectroscopy. The time constant of CT was determined to be 5−10 ps at 294 K, which is slightly sensitive to temperature. The present CT process is much faster than that of BA in alcoholic solutions, although large fluctuation of the surrounding medium is absent. The rapid CT is attributed to the symmetry breaking in the ground state because of the adsorption. The present results on the adsorbed system support the idea that the solvent dipole fluctuations around BA in solutions take a crucial role for the appearance of the unequal environments between two anthryl moieties, which triggers the charge separation accompanying with the symmetry breaking.

For the adsorbed system, small fluctuations such as intramolecular torsional motion and/or other vibrations were suggested to promote the rapid CT, and the CT state generated is stabilized because of the antisymmetric environment. The relaxation of the CT sate is somewhat complicated and might be understood in terms of inhomogeneity of adsorption environment. To elucidate detailed mechanism underlying the generation and relaxation processes of the CT state in the present system, further spectroscopic studies with varying ambient temperature are underway.

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