

FORMATION OF A COMPLETE ELECTRON TRANSFER STATE OF 9,9'-BIANTHRYL IN A POLAR SOLVENT*

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It has been generally recognized that excited 9,9'-bianthryl in polar solvents achieves a partial charge-separation state, instead of a complete electron transfer state, even in high-polarity solvents like acetonitrile at room temperature. However, here we firstly found that 9,9'-bianthryl reaches the complete electron transfer state in a polar alkanenitrile solvent at lower temperature as elucidated by means of transient absorption and steady-state fluorescence spectroscopy. A stepwise increase in the fluorescence Stokes shift observed when temperature was reduced implies a formation of a state more polar than that dominated at the room temperature. At low temperature (165 K), the transient absorption spectra of 9,9'-bianthryl in butyronitrile gradually changed from the spectrum ascribed to the partial charge-separation state toward that of the complete electron transfer state. We suggest that at low temperature, due to the increase in the solvent polarity, the energetically stabilized electron transfer state should be predominant.

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1. Introduction

The photochemistry of 9,9'-bianthryl (BA) in the excited state in solution has been an object of extensive studies [1-8], regarded as a prototype of the twisted intramolecular charge-transfer (TICT) concept. In the ground state the two anthryl groups of BA are considered to be perpendicular to each other. The fluorescence and $S_n \leftarrow S_1$ absorption spectra of BA in nonpolar solvents are structured, but broader than those of anthracene, which have been attributed to the excitonic interaction between the anthryl chromophores with tilted conformation. In polar

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solvents at room temperature, the broadened and highly red-shifted fluorescence of BA implies the formation of the charge-separation (CS) state. It is recognized that in the excited state in polar solvents the energetically favorable CS state is achieved, whereas the excitonic state is predominant in nonpolar solvents. On the other hand, we reported that the transient absorption spectrum of BA in the equilibrated excited state even in acetonitrile (ACN), a commonly used high-polarity and nonviscous solvent, could not be reconstructed as a superposition of the cation and anion radical spectra of anthracene and/or 9-methylanthracene [5]. We thus ascribed the equilibrated excited state of BA in ACN to the partial CS state expressed by a notation of $A^{\delta+}-A^{\delta-}$, instead of a complete electron transfer (ET) state (A^+-A^-) where one electron is transferred from one anthryl half to another. It has been believed that for BA, due to the intramolecular torsional relaxation mode around the single bond connecting the anthryl halves, contribution from the excitonic interaction might slightly exist even in high-polarity solvents, which would bring about the partial CS state. It has been explained that owing to the energetical preference the partial CS state could be obtained even in high-polarity solvents instead of the complete ET state. The question can therefore be asked if the final electronic state would be characterized by the energetics among the corresponding electronic states, BA also might well achieve the complete ET in the excited states when a suitable circumstance could be arranged.

In this paper we report the results from the temperature dependence of the steady-state fluorescence and transient absorption spectra of BA. We found that in butyronitrile (BuCN) at low temperature (188–165 K) BA could form the complete ET at one or several hundreds of nanoseconds after the excitation.

2. Experimental section

Steady-state absorption spectra were observed by a Shimadzu UV-260 spectrometer. Corrected fluorescence spectra were recorded by a Hitachi 850E spectrophotometer. Transient absorption spectra earlier than 6 ns after the excitation were observed by using a second harmonics of an output of a dye laser (350 nm), under the time resolution of 10 ps [9]. For the detection of transient absorption spectra up to 800 ns at the wavelength region longer than 500 nm, a third harmonics of YAG laser (355 nm) was employed as an excitation source. A continuum emitted from a xenon lamp was used as a probe light. The spectra in the shorter wavelength region (> 330 nm) were observed by an intensified multichannel photodetector, using an excimer laser as an excitation source (351 nm).

Temperature regulation between 300–165 K for the steady-state fluorescence and transient absorption spectroscopy was achieved by changing the flow rate of a nitrogen gas stream evaporated from liquid nitrogen. When temperature was reduced close to the melting point of BuCN (161 K), special care was taken to keep the sample in the liquid phase. BA was the same sample as employed in our former investigation [5]. Spectrograde ACN and GR grade BuCN were used as solvents. BuCN was distilled after the dehydration by using calcium hydride and activated molecular sieves if necessary. The solutions were deoxygenated by flashing a nitrogen gas stream.

3. Results and discussion

3.1. Temperature dependence of the steady-state fluorescence spectra

Temperature dependence of the steady-state fluorescence spectra of BA in BuCN was recorded from 300 K to 165 K, and typical spectra are illustrated in Fig. 1. The observed spectrum around the room temperature (300 K) was broad-

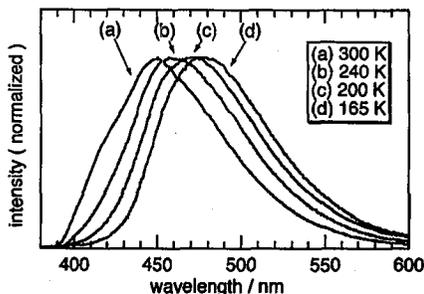


Fig. 1. Steady-state fluorescence spectra of BA in BuCN detected at 300 K (a), 240 K (b), 200 K (c), and 165 K (d).

ened and red-shifted as compared to the spectrum detected in nonpolar solvents, which would be attributed to the CS state to some extent. In the shorter wavelength region of the spectrum (415 nm), the spectral shoulder, even though it was a minor one, was observed which should be originated from the excitonic state. As the temperature is reduced, the spectra shift towards red chiefly reflecting the increase in the solvent polarity. The contribution from the excitonic state to the spectra decreases at lower temperature. We note here that at 300 K and 165 K the relative permittivity $\epsilon = 24$ and $\epsilon = 37$ for BuCN, respectively, whereas $\epsilon = 37$ for ACN at 300 K. The amount of the Stokes shift $\Delta\tilde{\nu}$ in BuCN at 300 K is obtained to be 3630 cm^{-1} , which is smaller than that observed in ACN (4520 cm^{-1}) at 297 K. Instead of the similar ϵ of BuCN at 165 K compared to that of ACN at room temperature, larger $\Delta\tilde{\nu}$ was observed in BuCN at 165 K (4750 cm^{-1}) than that detected in ACN at room temperature, which would suggest that a more polar state might be possible in BuCN at low temperature.

In general, the solvent-induced red-shift of fluorescence spectra can be plotted versus a solvent parameter as follows [10]:

$$hc\Delta\tilde{\nu} = \frac{2\mu^2}{a^3} \left[f(\epsilon) - \frac{1}{2}f(n) \right] \quad (1)$$

with

$$f(\epsilon) = \frac{\epsilon - 1}{2\epsilon + 1}, \quad f(n) = \frac{n^2 - 1}{2n^2 + 1},$$

where h and c are the Planck constant and the velocity of light, respectively. $\Delta\tilde{\nu}$ is the Stokes shift, μ denotes the excited state dipole moment of the solute molecule. a stands for the cavity radius of the solute molecule which is approximated to be spherical. n corresponds to the refractive index of the solvent. Equation 1 is a

reduced form of the Mataga-Lippert relation, where it is assumed that only the dipole moment in the equilibrated excited state has a substantial value. In order to apply Eq. (1) to our present experimental result on the fluorescence red-shift, the temperature dependence of ϵ can be known from the literature [11]. On the other hand, a reliable data-set of the temperature dependence of n could not be available. In Fig. 2 we thus plot $\Delta\tilde{\nu}$ versus $f(\epsilon) - (1/2)f(n)$ according to Eq. (1), where the value of n was fixed to that at the room temperature. As the temperature is reduced, a stepwise change of $\Delta\tilde{\nu}$ was observed around 230 K, which may imply

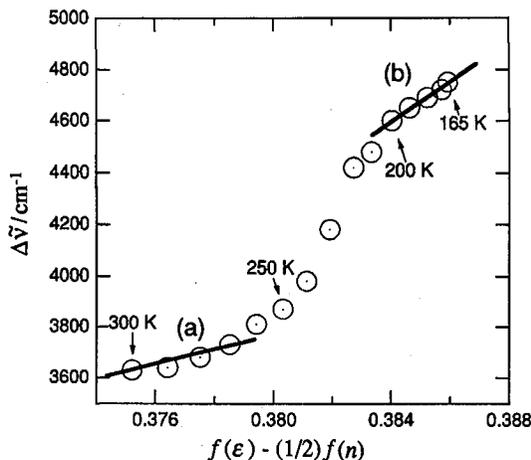


Fig. 2. Fluorescence Stokes shift $\Delta\tilde{\nu}$ of BA in BuCN plotted versus the parameter of solvent polarity observed by varying temperature. The range of temperature regulation was from 300 K to 170 K every 10 K, and 165 K. Typical values of temperature at which the measurement was performed are indicated in the figure as a guide.

TABLE

Estimated values of the excited state dipole moments μ of BA derived from the temperature-induced fluorescence red-shift.

Dipole moment	Temperature range [K]	μ [Debye]
μ_a^a	300–270	25
μ_b^b	200–165	41
μ_{RT}^c	293	20

^aEstimated from the slope (a) in Fig. 2.

^bEstimated from the slope (b) in Fig. 2.

^cEstimated from the solvatochromic fluorescence red-shift observed by changing solvents where the temperature was fixed at 293 K. Taken from our previous report [12].

a change of the electronic structure of the solute molecule. Alternately stated, a more polar state with a larger dipole moment might become predominant in the low temperature region. On the basis of Eq. (1), Table compares the estimated values of the excited state dipole moments μ_a and μ_b which are derived from the slopes a (the temperature range 300–270 K) and b (200–165 K), respectively, as indicated in Fig. 2. In order to calculate μ 's values on the basis of Eq. (1), $a = 6 \text{ \AA}$ was assumed for BA. Also given in Table is μ_{RT} obtained by varying solvents but the temperature was kept 293 K as reported elsewhere [12]. The estimated value of μ_b is much larger than μ_a or μ_{RT} , which implies that a more polar state would be substantial at lower temperature.

3.2. Transient absorption spectra at low temperature

In order to investigate the existence of the electronic structure change after the stepwise increase in $\Delta\tilde{\nu}$, transient absorption spectra of BA in BuCN at 165 K were thoroughly observed in the extended time scale. By means of the laser spectroscopy between 10 ps to 6 ns, the transient absorption spectrum gradually changed its shape from that assigned to the excitonic state to the partial CS state, where the rise time of the CS state absorption band τ_{CS} was estimated to be $\tau_{CS} = 50 \text{ ps}$. It should be stated here that in the time region earlier than 6 ns no further essential spectral changes were detected. We have thus performed transient absorption spectroscopy for later time domain.

Figure 3 illustrates the time dependence of the transient absorption spectra of BA in BuCN detected within the time domain of tens to hundreds of nanoseconds at 297 K (Figs. 3a, b) and 165 K (Figs. 3c, d). For the sake of comparison, Fig. 3b (d) is a normalized version of the spectra by the absorption peak intensity of Fig. 3a (c), respectively. At each temperature, 297 K and 165 K, the contribution from the longer wavelength region ($> 700 \text{ nm}$) increases with time. In particular, the relative increase in the absorption band in the wavelength region of $> 700 \text{ nm}$ was obviously detected at 165 K.

On the basis of the literature [13], typical absorption maxima of the cation radical of anthracene are located at 356 nm and 726 nm, whereas for the anion radical of anthracene a characteristic peak is at 367 nm and a broad absorption band is observed at 720–750 nm. Other maxima located around 400–500 nm, where the $T_n \leftarrow T_1$ absorption band of BA would be dominant, are not referred here. The absorption spectra of ion radicals of 9-methylanthracene (9MA) are available from our present work. In Fig. 4, we show the absorption spectra of the cation (Fig. 4a) and anion (Fig. 4b) radical bands of 9MA observed by adding 1,4-dicyanobenzene (DCNB) and *N,N*-diethylaniline (DEA), respectively. The spectra were detected in ACN solution at room temperature monitored with the time gate of 0–50 ns after the excitation. In Figs. 4a and b, the spectral maxima observed at 400 nm and 425 nm are attributed to the $T_n \leftarrow T_1$ absorption of 9MA. In Fig. 4a, the specific spectral maximum observed at 680 nm can be ascribed to the absorption of the cation radical of 9MA. The absorption of the anion radical of DCNB would contribute to the observed specific peak at 345 nm to some extent [14]. At the present point of time, the extinctions of the absorption spectra of the T_1 state of BA, the anion radical of DCNB, and the cation radical of 9MA

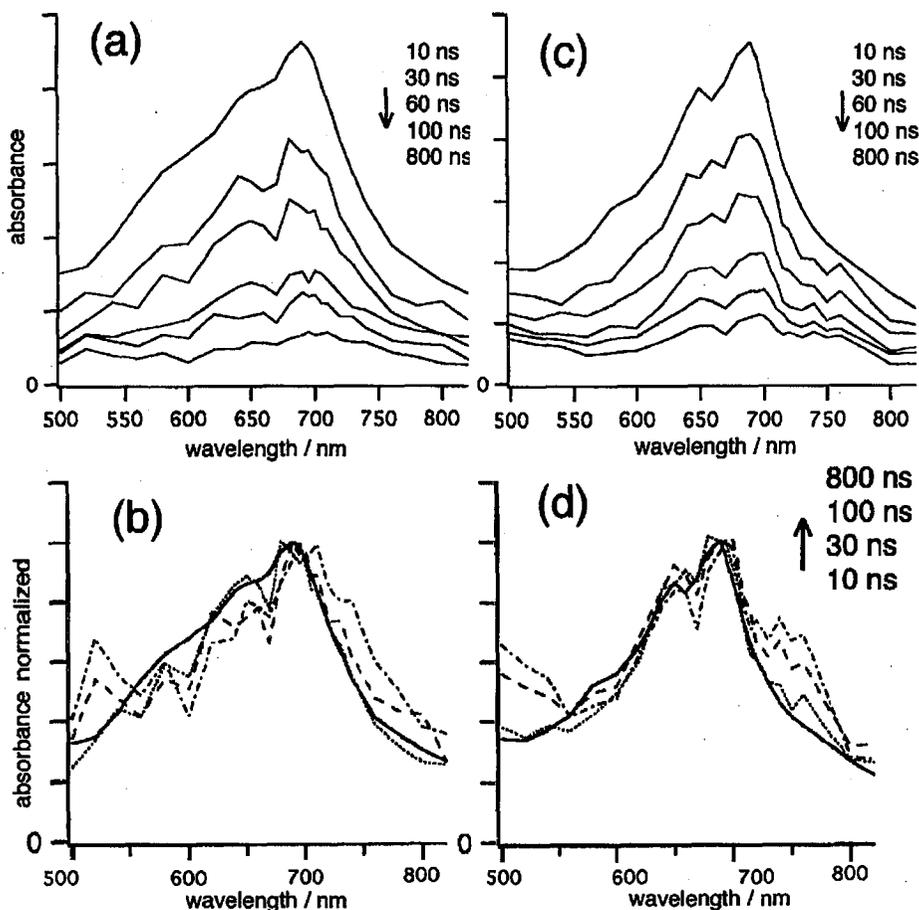


Fig. 3. Transient absorption spectra of BA in BuCN detected at 297 K (a, b) and 165 K (c, d). For the sake of comparison, the spectra shown in b (d) are normalized versions of a (c) by the spectral peak intensity, respectively. In Figs. 3b and d delay times after the excitation are: 10 ns (solid lines), 30 ns (dotted), 100 ns (dashed), and 800 ns (dot-and-dashed).

are not available. However, relying on the analogy with the case of anthracene, we would speculate that the absorption of the anion radical of 9MA might be located in the shorter wavelength region, say < 400 nm. In Fig. 4b, the specific peak at 370 nm and the broad absorption around 700 nm are assigned to the anion radical of 9MA, while the cation radical band of DEA appears at 465 nm.

We therefore conclude that the spectral shoulder with its maximum at 740 nm detected at hundreds of nanoseconds after the excitation especially at 165 K (Fig. 3d) can be just ascribed to the anion radical band of anthracene [13] or 9MA. We suggest that in the slower time region at low temperature, a more polar electronic state compared to the partial CS state, i.e. the complete ET could be sub-

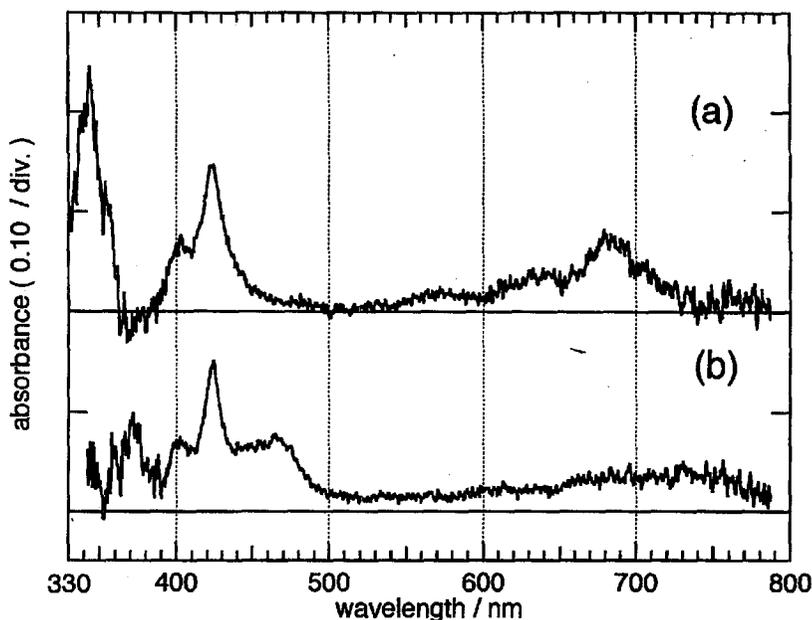


Fig. 4. Absorption spectra of cation (a) and anion (b) radicals of 9MA in ACN detected at room temperature, by adding 1,4-dicyanobenzene (a) and *N,N*-diethylaniline (b). See Sec. 3.2 for the assignment of the spectral bands observed here.

stantial. The observed time evolution of the spectra could then be attributed to the electronic structure change of BA from the partial CS to the complete ET states.

Owing to the characteristic absorption band of anthracene [13] or 9MA especially detected at the wavelength region shorter than 400 nm, transient absorption spectroscopy for that wavelength region is indeed desirable. Figures 5a and b depict the transient absorption spectra of BA in BuCN at 293 K (a) and 188 K (b), at 800 ns after the excitation. Also shown in Fig. 5c in the dashed line is the inverse of the steady-state absorption spectra of BA in BuCN at 293 K. For the transient spectra of BA in Figs. 5a and b, the strong absorption band with the maximum at 430 nm and with the shoulder at 410 nm is due to the $T_n \leftarrow T_1$ absorption of BA, at each temperature. It is described here that the contribution from the induced emission to the transient spectra in Figs. 5a and b, if exists, should be observed at longer than 400 nm as suggested by the steady-state fluorescence spectra (Fig. 1). We consequently assign that in the region shorter than 400 nm the spectra are the superposition of the absorption of the transient species and the breach due to the ground state absorption.

In Fig. 5a, the negative depressions at 370 nm and 390 nm just correspond to the maxima of the steady-state absorption spectra, respectively. In the region of shorter than 370 nm, a featureless positive band was observed. On the other hand, at 188 K (Fig. 5b) the spectral depressions were also detected at 370 nm

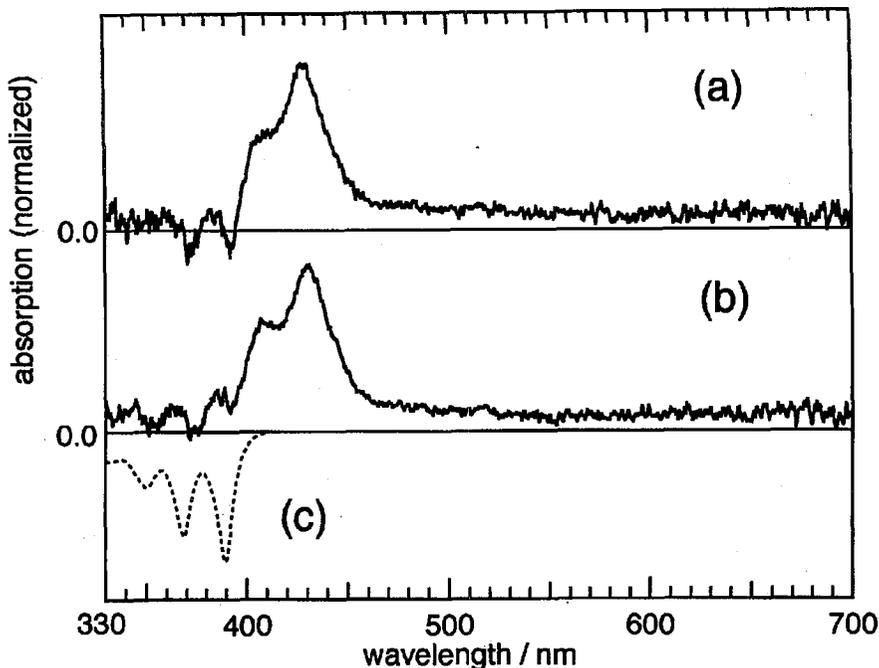


Fig. 5. Transient absorption spectra of BA in BuCN at 800 ns after the excitation detected at 293 K (a) and 188 K (b). Also shown in the dashed line (c) is the inverse of the steady-state absorption spectrum of BA in BuCN at 293 K.

and 390 nm owing to the ground state breaching. We should emphasize that at 188 K the depressions were no longer observed in the negative domain as was the case of 293 K, but were detected in the positive region in the spectrum, which would be indicative that some absorption band(s) could exist in this wavelength region. With a more closer look on Fig. 5b, the evident absorption band centered at 365 nm could be recognized, which was not detected at 293 K. We could assign this absorption band at 365 nm to the anion radical of 9MA and/or anthracene. We suppose that the apparent absorption maximum around 370 nm disappeared in the case of the spectrum of BA at 188 K because of the ground state breach. At 188 K we also observed the absorption maximum located at 345 nm, which is rather small but beyond the signal-to-noise ratio of the spectrum. We would speculate that the band might be originated from a cation radical of one of the anthryl chromophore of BA.

As a conclusion, together with the results from the transient absorption spectra discussed on the longer (> 700 nm) and shorter (< 400 nm) wavelength regions where characteristic absorption bands of ion radicals of anthracene or 9MA were observed, the complete ET between the anthryl chromophores of BA should be achieved in BuCN at low temperature. Furthermore, the stepwise increase in $\Delta\tilde{\nu}$ detected at low temperature as described in the former subsection would support the fact that a more polar state than the partial CS state would be dominant at low temperature. In accordance with the reduction of temperature, it is consid-

ered that the energetically preferable ET state became substantial because of the increase in polarity of the solvent. By means of the transient absorption measurements the complete ET state became predominant at one or several hundreds of nanoseconds after the excitation at low temperature. Before that time region, the partial CS state was detected. At the present stage of our investigation, the formation time of the complete ET state τ_{ET} cannot be exactly determined, although we have observed some snapshots of the transient absorption spectra at several delay times from which we obtained the evidence of the complete ET state. We would speculate at this point that τ_{ET} might be about some tens of nanoseconds to hundreds of nanoseconds, relying on the obvious absorption band already appeared at 100 ns after the excitation (Fig. 3d). On the other hand, as reported in our previous paper [8], the CS dynamics of BA would be coupled with the intramolecular torsional relaxation mode around the single bond connecting two anthryl moieties. We observed the torsional relaxation time τ_r of BA in methylcyclohexane at 160 K by detecting the time-resolved fluorescence spectra, the results of which will be published in our forthcoming paper. With the increase in time, the fluorescence spectra changed from that assigned to the perpendicular conformation to that ascribed to the tilted conformation, and τ_r was estimated to be 50 ps. Having in mind that viscosity η of methylcyclohexane at 160 K is estimated to be 22 cp while $\eta = 9$ cp for BuCN at 165 K relying on the literature [15], we speculate that τ_r in BuCN at 165 K would not so much deviate from that observed in methylcyclohexane, and it might be tens of picoseconds time region. As described at the beginning of this subsection we estimated that in BuCN at 165 K $\tau_{\text{CS}} = 50$ ps, which would be closely coupled with the intramolecular torsional relaxation process. After reaching the partial CS state another relaxation process to achieve the complete ET state could proceed, where τ_{ET} would be of tens to hundreds of nanoseconds because of the slower relaxation process of the solvent at low temperature. This is a plausible explanation for the entire picture of the complete ET state formation. Further discussions especially with respect to the dynamics part will be given in our forthcoming paper.

We have also made effort to measure the temperature dependence of the fluorescence lifetime τ_{fl} of BA in BuCN by means of a single-photon-counting method. At 297 K τ_{fl} was observed to be 37 ns where the fluorescence decayed as a single exponential curve, which is similar to τ_{fl} detected in ACN at room temperature (35 ns) [12]. As the temperature was reduced τ_{fl} became longer, for instance, at 240 K $\tau_{\text{fl}} = 46$ ns, where the stepwise increase in $\Delta\tilde{\nu}$ was still not observed (Fig. 2). At 200 K or lower, however, the time dependence of the fluorescence intensity could not be fitted as a single exponential decay. Moreover, the repetition rate of the excitation laser source of our present instrumental setup (4.1 MHz) was proven to be even too high for the determination of the longer fluorescent components such as hundreds of nanoseconds. At any rate, our preliminary result of the multi-exponential behavior of the fluorescence intensity at lower temperature would suggest the electronic structure change when temperature was reduced.

We should remark finally that at the present point of time we are unaware of any other report which experimentally shows the complete ET state of BA in polar solvents.

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