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Ultrafast Photodissociation Dynamics of a Hexaarylbiimidazole Derivative with Pyrenyl Groups: Dispersive Reaction from Femtosecond to 10 ns Time Regions

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Abstract: The photodissociation dynamics of a hexaarylbiimidazole (HABI) derivative with two pyrenyl groups was investigated by time-resolved transient absorption spectroscopy and fluorescence measurements. Transient absorption spectroscopy revealed that photodissociation took place in the wide time region of <100 fs to 10 ns. On the other hand, fluorescence time profiles showed the dynamic red shift in the time region <100 ps. The apparent dispersive photodissociation process was attributed to the increase in the interaction between the pyrenyl moiety in the excited state and the other moiety in the ground state, resulting in the gradual increase of the activation energy for the crossing between the attractive potential surface of an excited pyrenyl unit and the repulsive potential surface.

1. Introduction

Photodissociation of a molecule into a radical species is one of the most important primary processes of photochemistry. Since the photodissociation has a time origin of the photoexcitation, direct detection of reaction profiles with high temporal resolution could provide precise information of the dynamics and mechanisms of the reaction, of which results may contribute to the comprehensive elucidation of general dissociation reactions in the thermal processes. Compared to the knowledge on the photodissociation of diatomic molecules and their recombination processes, much less is known on larger organic molecules dissociating into the radical pair in spite of their great importance. Direct observation of the formation and the recombination of the radical pair using transient absorption measurement techniques has been restricted to only a few aromatic molecules, such as tetraphenylhydrazine[1−6] and diphenyl disulfide derivatives.[6−12]

We recently reported the bond-cleavage dynamics of the photoreaction process of 2,2′-di(*ortho*-chlorophenyl)-4,4′,5,5′-tetraphenylbiimidazole (*o*-Cl-HABI) in benzene solution by means of femtosecond−nanosecond laser spectroscopy.[13] Hexaarylbiimidazoles (HABIs) are known to yield radicals upon UV light irradiation in both solid and solution. Various stimuli, such as heat, light, and pressure, readily cleave HABI into a pair of 2,4,5-triphenylimidazolyl radicals (TPIRs, lophyl radicals), which thermally recombine to reproduce their original imidazole dimer in inert environments without other reactions.[14−16] The photochromic behavior of HABIs can be attributed to the photoinduced homolytic reversible cleavage of the C−N bond between the imidazole rings. In organic solvents, the thermal transformation of TPIR to HABI requires several minutes to hours at room temperature. No emission signal from the excited

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state of *o*-Cl-HABI was detected by the steady-state fluorometer or femtosecond up-conversion measurement. The dissociation of *o*-Cl-HABI into the geminate radical pair occurs via the singlet excited state with a time constant of 80 fs. This time constant of the dissociation is comparable to those for diphenyl disulfide derivatives and tetraphenylhydrazine and strongly suggested that the repulsive nature of the potential energy surface along the C−N bond elongation axis takes an important role in the photodissociation and the nonadiabatic couplings between nearly degenerate electronic surfaces did not seriously affect the photodissociation of *o*-Cl-HABI.

On the other hand, the introduction of larger aromatic groups, instead of phenyl rings, is an efficient method to improve the photochromic properties of HABI derivatives which have higher sensitivity and an absorption band in the longer wavelength region. Because the photodissociation yield of HABI derivatrives is usually high (close to the unity), the larger absorption coefficient in the long wavelength region is an important factor to increase the total sensitivity of the molecule. However, the local attractive potential surface with lower energy area may affect the crossing of the surface to the repulsive one, leading to the decrease of the reaction yield. Because the time scale of the photodissociation is usually in the range of tens to hundreds of femtoseconds, the crossing between the attractive potential surface and the repulsive potential one could lead to an energy barrier to dissociation and molecules take more time before dissociation.[17] Hence, the detailed information on the dissociation involving surface hopping between the two intersecting diabatic potential energy surfaces is indispensable for the rational design of the improved derivatives. Along this line, we have directed our focus toward controlling the dynamics of the photodissociation process of HABI. While the overall process for larger organic molecules is complicated by the high dimensionality of the potential energy surfaces for the participating electronic states, we contemplated the possibility that the attractive potential surface along with the repulsive potential surface would be built up by the formation of the excimer state for an HABI derivative with pyrenyl units. In the present paper, we have investigated the excited-state dynamics of a newly designed HABI derivative with pyrenyl units by means of femtosecond−nanosecond laser spectroscopy. This new photochromic HABI shows weak fluorescence with a relatively large Stokes shift (2500−3500 cm^{-1}), indicating the large conformational changes in the first excited state. On the basis of the dynamic behaviors monitored by the fluorescence and the transient absorption, this broad emission was attributed to the excimer state of the pyrenyl units formed via the dynamic relaxation process in the attractive potential surface. In addition, this dynamic process led to "dispersive kinetics" for the production of the radicals giving rise to a time-dependent rate constant for the photodissociation. Though dispersive kinetics due to structural heterogeneity has been studied extensively,[18] this is the first observation for dispersive kinetics responsible for the structural relaxation of the excited state affecting the competitive bond-cleavage reaction path, to our knowledge. In the following, we will discuss the formation process of the radicals by comparing the rise of the radicals monitored by the transient absorption with the decay of the precursor state obtained by time-resolved fluorescence detection.

2. Experimental Section

2.1. Synthesis. 2.1.1. Materials. All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254). All reagents were purchased from TCI and Wako Co. Ltd. and were used without further purification. Benzil was recrystallized from ethanol. All reaction solvents were distilled on the appropriate drying reagents prior to use.

2.1.2. 4,5-Diphenyl-2-pyren-1-yl-1*H*-imidazole (1). 1-Pyrenecarbaldehyde (1.21 g, 5.26 mmol), benzil (1.45 g, 6.90 mmol), and ammonium acetate (14.0 g, 181 mmol) were stirred at 80 °C in acetic acid (140 mL) for 12 h. A yellow precipitate immediately formed and was collected by filtration and washed with water and then ethanol. The residue was dried in vacuo to give a yellow powder, 1.20 g (54%). ^{1}H NMR (DMSO, 500 MHz): δ 12.9 (s, 1H), 9.55 (d, $J = 9.2$ Hz, 1H), 8.52 (d, $J = 7.9$ Hz, 1H), 8.40 (d, $J = 7.9$ Hz, 1H), 8.35−8.29 (m, 3H), 8.24 (dd, $J = 10.4$ and 9.2 Hz, 2H), 8.11 (t, $J = 7.6$ Hz, 1H), 7.67 (d, $J = 7.3$ Hz, 2H), 7.61 (d, $J = 7.3$ Hz, 2H), 7.47 (t, $J = 7.6$ Hz, 2H), 7.41−7.36 (m, 3H), 7.27 (t, $J = 7.3$ Hz, 1H). FAB-MS: *m/z* 421 [M + H]$^+$.

2.1.3. 4,4′,5,5′-Tetraphenyl-2,2′-dipyren-1-yl-2′*H*-1,2′-biimidazole (Py-HABI). All manipulations were carried out with the exclusion of light. Under nitrogen, to a solution of **1** (830 mg, 0.984 mmol) in benzene (400 mL) was added the solution of potassium ferricyanide (14.0 g, 42.5 mmol) and KOH (7.00 g, 125 mmol) in water (100 mL), and the reaction mixture was vigorously stirred for 12 h. The organic layer was separated, exhaustively washed with water, and concentrated in vacuo. The residue was recrystallized from benzene/acetonitrile to give yellow crystals, 664 mg (80%). FAB-MS: *m/z* 839 [M + H]$^+$. NMR and mass spectra were shown in the Supporting Information.

2.2. Apparatus. Steady-state absorption and fluorescence spectra were measured with a Hitachi 3500 spectrometer and a Hitachi 850 fluorometer, respectively. The bandwidth in these spectral measurements was ca. 1 nm.

A picosecond laser photolysis system with a repetitive mode-locked Nd^{3+}:YAG laser was used for transient absorption spectral measurements in the ps−several ns time region.[19] The third harmonic (355 nm) with 15 ps fwhm and *ca.* 0.5 mJ energy and a white continuum generated by focusing a fundamental pulse into a 10 cm quartz cell containing D_2O and H_2O mixture (3:1) were, respectively, used as an excitation pulse and a monitoring light.

For the detection of dynamic behaviors in the shorter time region, a dual OPA laser system for transient absorption measurements was used.[20] The output of a femtosecond Ti:Sapphire laser

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(Tsunami, Spectra-Physics) pumped by the SHG of a cw Nd^{3+}:YVO_4 laser (Millennia V, Spectra-Physics) was regeneratively amplified with a 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%) and guided into each OPA. These two pulses were used for the kinetic measurements. For the spectral measurements, one of the pulses was guided to OPA and the other was employed for white light continuum generation. For the excitation at 400 nm, the SHG of the fundamental 800 nm laser pulse was used. Two sets of multichannel diode array (Hamamatsu, PMA-10) systems were used for transient absorption measurement. The pulse duration was estimated to be 200 fs from the cross correlation trace at the sample position.

A laser photolysis system combined with a Q-switched Nd^{3+}:YAG laser (DCR, 355 nm, output energy ca.1 mJ, fwhm 6 ns), a pulsed Xe lamp, and a gated multichannel photodiode array (Hamamatsu, PMA-50 system) with a polychromator (Acton, M4197) was used for the measurement of nanosecond−millisecond transient absorption spectra.[21] The wavelength resolution of the transient absorption spectroscopy in these three methods was ca. 5 nm.

Time profiles of the fluorescence in the subps−100 ps time region were measured by using a homemade fluorescence up-conversion apparatus.[22] A Ti:Sapphire laser system (Verdi-V8 pumped Mira 900, Coherent, Inc.) was used as a light source (120 fs, 76 MHz, 800 mW at 820 nm). The pulses were further compressed up to ~70 fs fwhm using a prism pair compressor. The second harmonic (ca. 20 mW) was generated in a 0.1 mm thin BBO crystal and focused onto the sample circulating in a flow cell (50 mL/min) with a 1 mm light path length, to generate the fluorescence. It was collected with a pair of parabolic mirrors and focused, together with the residual fundamental laser pulse, on a 0.4 mm BBO type I crystal to generate the up-converted signal at the sum frequency. After passing through a grating monochromator, it was detected by a photomultiplier (R1527P) coupled with a photon counter (C5410) system (both from Hamamatsu Photonics). As an instrumental response function, the cross-correlation signal between fundamental and its second harmonic pulses was used (fwhm ~130 fs).

Picosecond time-resolved fluorescence was measured with the second harmonic (400 nm) of Ti:sapphire laser (Spectra Physics, Tsunami) generated in a type I BBO crystal, and the repetition rate was reduced to 2 MHz by an EO modulator. The emission was detected at a magic angle configuration utilizing a polarizer and a half-wave plate. A photomultiplier tube (Hamamatsu Photonics, R3809U-50) with an amplifier (Hamamatsu Photonics C5594) and a counting board (PicoQuanta, PicoHarp 300) was used for signal detection. A monochromator was placed in front of the photomultiplier tube. The system response time was determined to be 25 ps fwhm from scattered light from a colloidal solution.

For the time-resolved measurement, benzene (Wako, Infinity Pure grade) was used as received. A cuvette with a 1 mm optical length was used for measurements in femtosecond−several tens of picosecond time regions, while a cuvette with a 2 mm or 1 cm optical length was employed for measurements in a longer time region. The sample solution was circulated during measurements. All the measurements were performed under O_2-free conditions at 22 ± 2 °C.

Results and Discussion

Figure 1 shows absorption spectra of Py-HABI in benzene solution before and after irradiation with UV light around 330 nm. Before UV irradiation, the main absorption at 340 nm was observed in addition to a weak band in the wavelength region >375 nm. Py-HABI has two kinds of imidazolyl rings, Im1 and Im2. Im1 is a resonant planar structure having the characteristic bond distances for a 6π electron system with electron-donating character. Im2 has two localized C═N double bonds and one sp^3 carbon connecting Im1 to be consistent with a 4π-electron system with electron-withdrawing character. An absorption band around 400 nm in Py-HABI could be tentatively assigned to the intramolecular charge-transfer (CT) like transition from the frontier molecular orbitals (MOs) delocalized over the pyrenyl moieties and Im1 to the LUMO localized mainly in Im2 on the basis of TD-DFT calculations (Figure S6 in the Supporting Information). On the other hand, new absorption bands at 510, 550, 820, and 935 nm appear after UV light irradiation. These new bands can be ascribed to the radical of Py-HABI, the lophyl radical Py-L, produced by photoinduced homolytic dissociation. The strong absorption band around 500−550 nm can be assigned to the transition mainly localized in the pyrenyl group in Py-L also on the basis of the TD-DFT calculation (Figures S7 and S8 in the Supporting Information). On the other hand, the broad absorption band ranging from 800 to 1000 nm can be ascribed to the CT band from the pyrenyl moiety to the imidazole ring. In the time region of several tens of minutes, these absorption bands disappear by radical recombination to result in the recovery of the parent Py-HABI, as shown in Scheme 1. The photodissociation yield of Py-HABI into Py-L was estimated to be almost unity (Supporting Information).

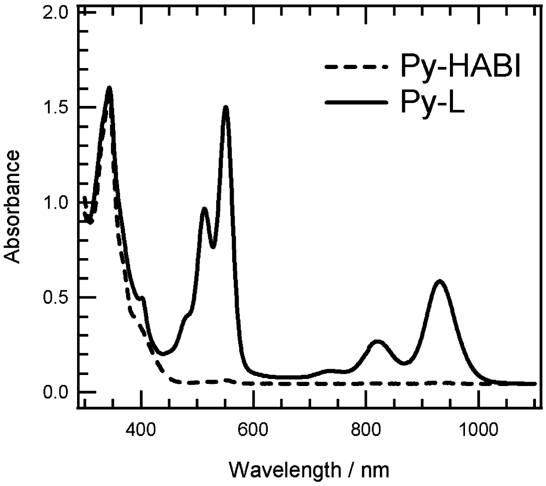

Figure 1. Absorption spectrum of Py-HABI in benzene solution (3.7 × 10^{-5} M) before (broken line) and after (solid line) UV irradiation.

Scheme 1

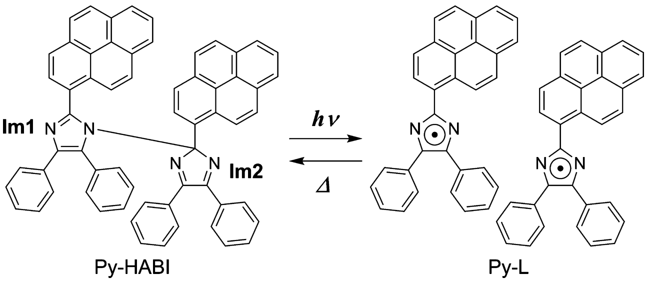

Figure 2 shows the fluorescence spectrum of Py-HABI in benzene solution, excited at 350 nm. A very broad emission with a maximum around 465 nm was observed. A Stokes shift of the fluorescence from the absorption in the steady-state

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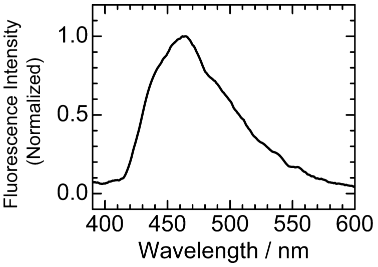

Figure 2. Fluorescence spectrum of Py-HABI in benzene solution (2.0 × 10^{-8} M), excited at 350 nm.

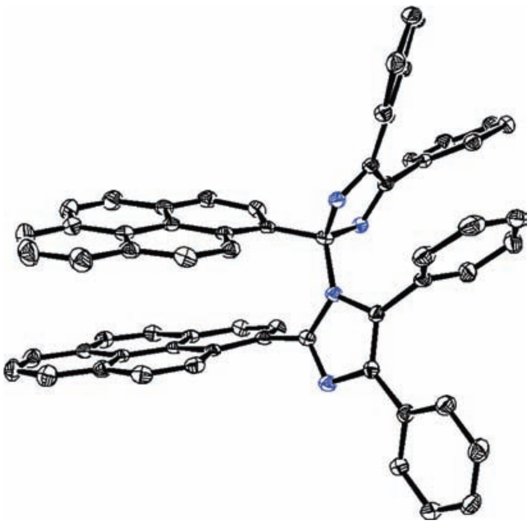

Figure 3. Crystal structure of Py-HABI with thermal ellipsoids (50% probability). The hydrogen atoms are omitted.

spectrum was estimated to be 3500 cm^{-1} on the assumption that the absorption maximum in the weak absorption band is located around 400 nm. Py-HABI in the crystalline phase was proven to have a molecular geometry with a face-to-face orientation of two pyrenyl groups by means of X-ray diffraction as shown in Figure 3 (see details of the experimental procedure in the Supporting Information), and the fluorescence in the crystalline phase was almost the same with the present one in benzene solution. In addition, the fluorescence band shape and its maximum are close to those of the excimer of pyrene[23] and no emission was observed for an HABI derivative where two pyrenyl groups were replaced with phenyl groups.[13] From the above results, the fluorescence of Py-HABI could be attributed to the pyrenyl moieties with mutual interaction.

Figure 4 shows time-resolved transient absorption spectra of Py-HABI in benzene solution, excited with a fs laser pulse at 400 nm. Absorption spectrum with maxima at 510 and 550 nm appears in the subps time region. This absorption spectrum can be safely assigned to Py-L, on the basis of the spectral band shape and its absorption maxima shown in Figure 1. With an increase in the delay time after the excitation, the absorption intensity gradually increases. The time profile of the transient absorbance at 550 nm in the early stage after the excitation is shown in Figure 5. To improve the time resolution, the output of OPA at 550 nm was employed as a monitoring light pulse in the measurement of the time profiles. As clearly shown in Figure 5a, the transient absorbance ascribable to Py-L appears in the subps time region and increases in a few ps time region.

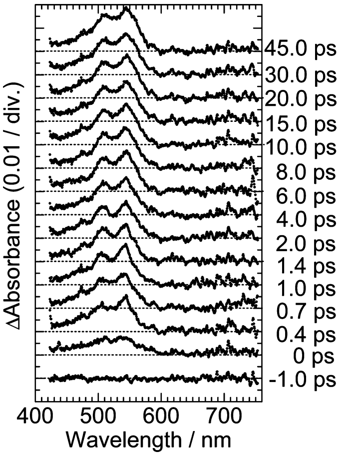

Figure 4. Transient absorption spectra of Py-HABI in benzene solution (1.5 × 10^{-2} M), excited with a fs laser pulse at 400 nm.

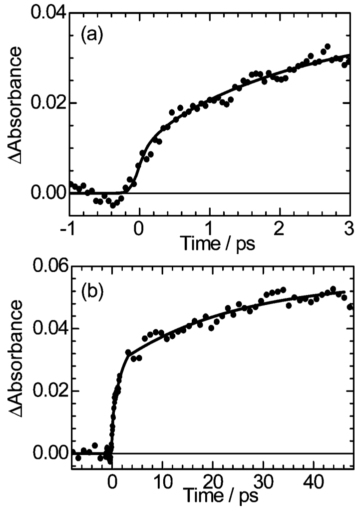

Figure 5. Time profile of transient absorbance of Py-HABI in benzene solution (1.5 × 10^{-2} M), excited with a fs laser pulse at 400 nm and monitored at 550 nm, (a) within the initial 3 ps after the excitation, and (b) within 50 ps time range after the excitation.

Figure 5b shows the time profile in the initial 50 ps following the excitation, indicating that the transient absorbance gradually increases also in the several tens of ps time region. By *tentatively* assuming the triple-exponential process, we analyzed the rise behaviors of the transient absorbance at 550 nm. The time constants obtained were, respectively, obtained 0.24, 2.6, and 25 ps. Details of the complex behaviors will be discussed in later sections.

Figure 6a shows the transient absorption spectra of Py-HABI in benzene solution, excited with a ps laser pulse at 355 nm. The absorption spectrum with maxima at 510 and 550 nm, which can be assigned to Py-L, appears within the response function of the apparatus of the picosecond laser pulse, and the absorption intensity gradually increases in the subns to several ns time region, together with a slight sharpening of the spectral band shape. The gradual sharpening of the spectral band shape might be related to the dissociation of the radical pair.[6b] Not only the spectral sharpening but also the increase in the intensity of the absorption band which was integrated in the 430−630-nm region was confirmed, indicating that the increase in the population of Py-L continues in a few ns time region.

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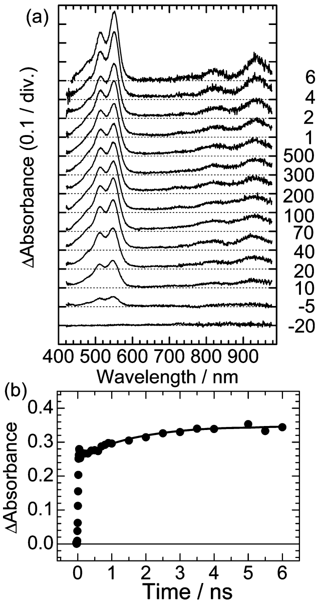


Figure 6. (a) Transient absorption spectra of Py-HABI in benzene solution (8.0×10^{-5} M), excited with a ps laser pulse at 355 nm. (b) Time profile of transient absorbance at 550 nm.

From the time profile of the transient absorbance at 550 nm in Figure 6b, the time constant of the rise in the several ns time region was estimated to be ca. 1.7 ns on the assumption that the rise kinetics was monophasic. We also applied ns laser photolysis measurement to the detection of the dynamic behaviors in the time region of several ns to ms (data are not shown). The rise of the transient absorbance was not observed in time regions > 10 ns. By summarizing the above results, it could be concluded that the formation of Py-L continues in a wide time region of <100 fs to ca. 10 ns.

To explore this complex behavior, we also applied the time-resolved detection of the fluorescence. Figure 7a shows time profiles of the fluorescence at 480 nm, obtained by the up-conversion method with a fs 400 nm laser pulse as an excitation source. In the initial 10 ps following the excitation, the rapid appearance of the fluorescence was followed by rapid decay in the several ps time region. For analysis of the time profile, we tentatively assumed the triple-exponential decay in the time window of the first 100 ps following the excitation. Time constants for these three time constants were, respectively, 0.26, 3.3, and 25 ps. These time constants were similar to those obtained for the rise of Py-L in the short time region as was shown in Figure 5, indicating that the fluorescence is due to the precursor species of Py-L. In addition, the pre-exponential factors of decay compounds were wavelength dependent although the time constants were almost independent of the monitoring wavelength (Figure 7b). The contribution of the shorter time constant is smaller in the time profile at 500 nm, while the pre-exponential factor of the shorter time constant is relatively large in the profile at 450 nm. In addition to the rapid decay within 10 ps following the excitation, one can find a long tail in the fluorescence decay. The decay of the fluorescence after several tens of ps following the excitation was also measured by means of single photon counting with an excitation pulse at 400 nm, and it was found that the decay in the several tens of ps to several tens of ns time region was monophasic with a decay time constant of 1.63 ns and independent of the monitoring wavelength (Figure S5 in the Supporting Information).

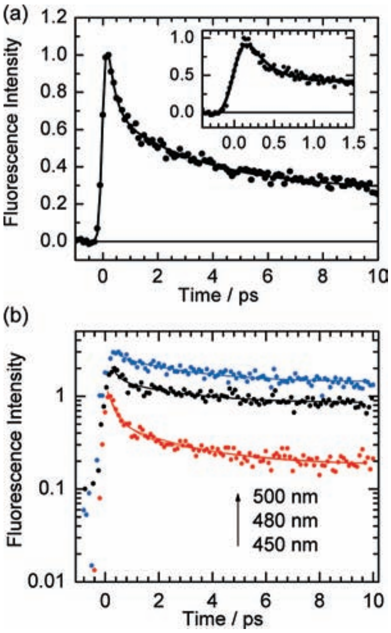


Figure 7. (a) Fluorescence time profiles of Py-HABI obtained by up-conversion measurements with a fs 400 nm laser as an excitation light monitored at 480 nm, and (b) wavelength dependence of the decay profiles.

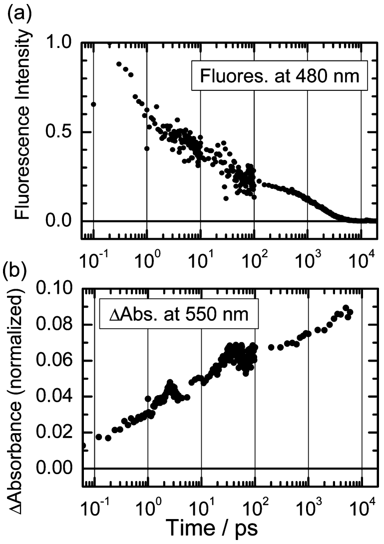


Figure 8. Time profiles of Py-HABI in benzene solution in wide time region of 0.1 ps−10 ns. (a) Fluorescence decay curve at 480 nm. (b) Time profile of transient absorbance at 550 nm.

Figure 8 shows time profiles of the transient absorbance at 550 nm and the fluorescence at 480 nm in the time region from ca. 100 fs to 10 ns. These time profiles were plotted by using Figures 4−7 and normalized on the basis of the overlapping time region of each profile. For the time profile of the fluorescence in the picoseconds to several tens of ns time region obtained by single photon counting is also listed. These figures clearly show that the decay of the fluorescence and the formation of Py-L occur with complex kinetics in a wide time region.

To elucidate these behaviors, we have analyzed time profiles in the following manner. The fluorescent intensity $I_F(t)$ at a delay time, t, is in general proportional to the radiative rate constant, k_F, as represented by eq 1.

$$I_F(t) = k_F[R(t)] \tag{1}$$

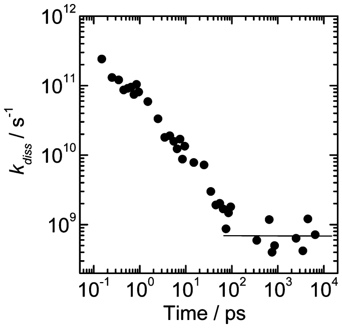


Figure 9. Time dependence of the photodissociation rate constant of Py-HABI in benzene solution. (See text) Solid line indicates the rate constant of 6.1×10^8 s^{-1}.

Here, $[R(t)]$ is the concentration of the fluorescent state. On the other hand, the formation of Py-L is written as

$$\frac{\mathrm{d}[P(t)]}{\mathrm{d}t} = 2k_{diss}[R(t)] \tag{2}$$

where $[P(t)]$ and k_{diss} are, respectively, the concentration of Py-L and the rate constant of photodissociation. Because the quantum yield of the photodissociation of Py-HABI resulting in the formation of Py-L is almost unity, k_{diss} could be much larger than k_F. On the basis of the above equations and the experimental results, we could estimate the rate constant of photodissociation, k_{diss}, by eq 3.

$$k_{diss}(t) \propto \frac{\Delta A_{550}(t + \Delta t) - \Delta A_{550}(t)}{2{\cdot}\Delta t{\cdot}I_F(t)} \tag{3}$$

Here, $\Delta A_{550}(t)$ is the transient absorbance at 550 nm at time t. In the actual calculation, the averaged value, $(I_F(t)+ I_F(t + \Delta t))/2$, was used and the time interval Δt was respectively set to be 0.1 ps for 0.1−1 ps, 1 ps for 1 −10 ps, 10 ps for 10−100 ps, 100 ps for 100 ps−1 ns, and 1 ns for 1−6 ns. The time dependence of the dissociation rate constant thus obtained is shown in Figure 9. In this figure, the rate constant in the ns region was set to be 6.1×10^8 s^{-1}, because the quantum yield of photodissociation was almost unity (see the Supporting Information) and the averaged rate constant of the rise of Py-L was ca. 1.7 ns (6.1×10^8 s^{-1}) as was shown in Figure 5. In addition, this time constant is in agreement with the fluorescent lifetime in the ns time region. Although the data are somewhat scattered, Figure 9 clearly shows that the reaction rate constant of photodissociation is strongly dependent on the delay time after the excitation. In the time region 0.1−100 ps after the excitation, it drastically decreases with an increase in the delay time.

The above result of the time dependence of the rate constant implies following two possible mechanisms of the photodissociation. The first mechanism is based on the coexistence of multistates where the conformation of Py-HABI just after the excitation has a wide distribution and the reaction rate constant is dependent on the conformation. That is, the molecule with the conformation favorable for the reaction undergoes rapid photodissociation, while that with unfavorable geometry may have a small reaction rate constant. In other words, the inhomogeneity of the conformation leads to the dispersive kinetics. In this case, the dynamic behaviors can be regarded as the integration of molecules with different rate constants.

The second mechanism is based on the dynamic relaxation model, where some relaxation process of the excited Py-HABI competes with the photodissociation reaction and the rate constant decreases with an increase in the time following the excitation. That is, the apparent activation energy of the photodissociation increases during this relaxation and the rate constant of the photodissociation is intrinsically time-dependent.

In beginning the discussion on the two mechanisms, it is worth mentioning that the photodissociation rate constant in the early stage after the excitation, which was estimated in Figure 9, is rather small (less than 5×10^{11} s^{-1}) compared to the fluorescence decay in the early stage after the excitation. The rate constant of the fluorescence decay at 480 nm immediately after the excitation was ca. 4.5×10^{12} s^{-1} (220 fs), as was shown in Figure 7a, and this value is almost 10 times larger than the rate constant of the photodissociation in the early stage after the excitation as estimated in Figure 9. This large difference indicates that the main process of the fluorescence decay in the early stage after the excitation is not the photodissociation. In addition, the internal conversion to the ground state is not the main deactivation of the fluorescence decay because the photodissociation yield was almost unity by steady state irradiation. These results indicate that the fluorescence decay involves some relaxation in the excited state. As was shown in Figure 7b, the pre-exponential factor of the short lifetime component was larger in the fluorescence decay at shorter wavelengths, implying that the fluorescence maximum of the excited state shifts toward the red wavelength region in the early stage after the excitation. The Stokes shift of the absorption and the fluorescence in the steady-state spectra was estimated to be 3500 cm^{-1} on the basis of the absorption maximum in the weak absorption band located around 400 nm as shown in Figure 2. Even if the absorption edge around 415 nm is used for estimation, the Stokes shift could be 2600 cm^{-1}. This large Stokes shift also supports the idea that some relaxation process takes place in the excited state. Although the contribution from the first mechanism of the coexistence of various conformations cannot be excluded entirely, these results strongly suggest that the dynamic relaxation process takes an essential role in the complex dynamic behaviors in the fluorescence decay and the formation of Py-L.

In addition to these two processes, the contribution from the excited state of the radical may take a role in these complex behaviors. Because Py-HABI in benzene solution could slightly undergo thermal dissociation in temperatures higher than 60−70 °C, the dissociation energy might be rather small. Hence, it seems necessary to discriminate the role of the electronically excited state of Py-L immediately after the production in the complex dynamics. To experimentally obtain the information on the excited state of Py-L, we measured the transient absorption spectra of Py-L in benzene solution. In this measurement, we irradiated UV light to the specimen in the reservoir tank to create the photostationary state of Py-L and circulated the solution. As we have already mentioned, the recombination of Py-L radicals takes place in a few tens of minutes time region. Hence, this procedure ensured the stable measurement of the transient absorption spectrum of Py-L in benzene solution, as shown in Figure 10a. The transient absorption spectrum immediately after the excitation shows a negative absorption band around 550 nm, which can be safely ascribed to the bleaching of Py-L. In addition, a broad positive absorption appears in the wavelength region >580 nm. With an increase in the delay time after the excitation, the positive absorption decreases and the negative signal recovers. Figure 10b shows the time profile of the transient absorbance monitored at 650 nm. In this measurement, we employed the output of OPA as a probe light for the improvement of the temporal resolution. The solid line in this

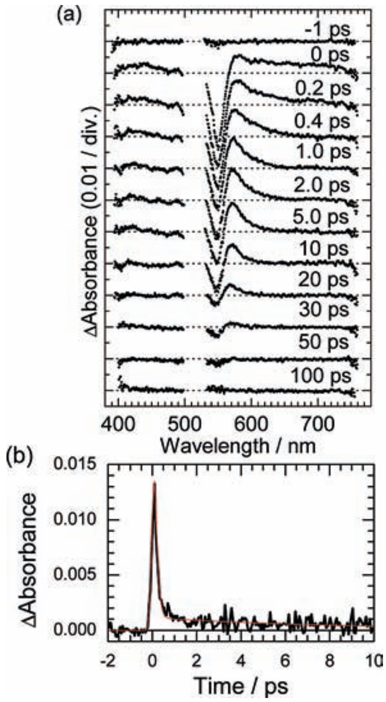
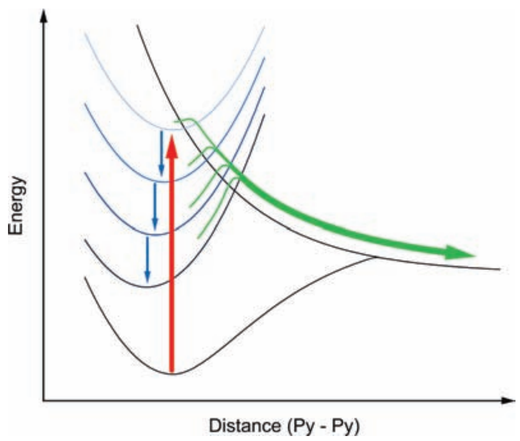


Figure 10. (a) Transient absorption spectra at Py-L in benzene solution, excited with a fs laser pulse at 510 nm. (b) Time profile of transient absorbance at 650 nm. The solid line in (b) is the result calculated with the biphasic decay with the faster and the slower time constants of 110 fs and 8.8 ps, respectively.

figure is the result analyzed with a biphasic decay function with time constants of 110 fs and 8.8 ps. The pre-exponential factor of the shorter time constant was 0.97 at this wavelength. Similar time constants were obtained for other monitoring wavelengths, but the pre-exponential factors were dependent on the monitoring wavelength. That is, the contributions of the longer time constants were pronounced in the wavelength region around 550−600 nm, while the pre-exponential factor of the shorter time constant was dominant in the regions around 450 nm and >640 nm. The transient absorption spectra at and after ca. 1 ps after the excitation show the positive band only in the wavelength region >580 nm in addition to the negative band around 550 nm, and these two bands decrease with a time constant of 8.8 ps. The temporal evolution of the spectra is characteristic of the cooling process where a vibratinally hot molecule with an absorption band in the longer wavelength region decreases together with the recovery of the molecule in thermal equilibrium with the environment. In addition, the time constant 8.8 ps is a typical value of the vibrational cooling. On the basis of the above results, we conclude that the longer time constant 8.8 ps is due to the vibrational cooling and the shorter time expresses the lifetime of Py-L in the excited state. The above results indicate that the contribution of the excited state of Py-L in the complex dynamics behaviors of the Py-L production is negligible.

The above results and discussion may lead to the following remarks on the mechanism of the complex kinetic behaviors of the photodissociation: (1) some relaxation processes of Py-HABI take place in the early stage after the excitation, and (2) the excited state of the nascent radical of Py-L does not contribute to the dispersive kinetics of the photodissociation in a wide time region even if the photodissociation of Py-HABI might lead to the production of the electronically excited state of Py-L. As we have already discussed in the previous sections, the relaxation processes in the excited state of Py-HABI may be attributed to the increase in the mutual interaction of pyrenyl moieties in the excited state. The previous result of the photodissociation on an HABI derivative which has phenyl groups instead of pyrenyl groups did not show any fluorescence and underwent radical formation with a time constant of 80 fs. This result also supports the above conclusion on the dispersive dynamics of Py-HABI. By summarizing the above results and discussion, the schematic potential energy curves could be represented as shown in Scheme 2 where the abscissa is given as the distance between two pyrenyl moieties. After the photoexcitation, the energy minimum of the locally excited state of pyrenyl moiety gradually lowers its energy with increasing time after the excitation. During this relaxation process, the minimum position of the locally excited state may shift toward the left (decrease in the distance between pyrenyl moieties) because of the increase in the interaction of two pyrenyl moieties. The lowering of the energy of the locally excited state as well as the slight shift of the potential curve toward the left-hand side in the abscissa may increase the apparent activation energy of the photodissociation to result in the decrease in the rate constant with an increase in the delay time. For *o*-Cl-HABI with phenyl groups, the energy level of the locally excited state is higher than the potential curve of the dissociation. In addition, the interaction between phenyl groups is rather small, as the equilibrium constant of intermolecular benzene excimer is less than unity.[24] Owing to these two effects, the photodissociation of *o*-Cl-HABI is rather simple, while that of Py-HABI shows the complex behaviors.

Scheme 2



Lastly, it is worth mentioning that the time dependence of the rate constant in Figure 9 seems to obey the power law of the time in the time region <100 ps. Although it is difficult to quantitatively elucidate the mechanism of the time evolution of $k_{diss}(t)$ at the present stage of the investigation, the gradual increase in the apparent activation energy of the dissociation takes an important role with an increase in the delay time after the excitation, as discussed in previous sections. The stabilization energy of the excimer is dependent on the mutual orientation and the distance between two aromatic groups.[24] The geometrical relaxation in the excited state of Py-HABI may cause the time-dependent activation energy to compete with the dissociation in the early stage after the excitation, leading to the complex temporal evolution of the time profile of $k_{diss}(t)$.

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(24) Vala, M. T.; Hiller, I. H.; Rice, S. A.; Jortner, J. *J. Chem. Phys.* **1967**, *44*, 23.

Compared to the photodissociation rate constant of *o*-Cl-HABI,[13] 1.25×10^{13} s^{-1}, the rate constant in the present Py-HABI at and after 100 ps following the excitation, 6.1×10^{8} s^{-1}, was more than 4 orders smaller. Provided that the frequency factor of the rate constant of the photodissociation is almost the same between these two systems, the apparent activation energy of Py-HABI is ca. 2000 cm^{-1} larger than that of the *o*-Cl-HABI system. Although the estimation based on the Arrhenius-type description of the rate constant is a rough approximation, the apparent activation energy for Py-HABI is similar to the value of the Stokes shift between the absorption and the fluorescence in the Py-HABI system.[25] This result also supports our conclusion that the stabilization of the excited state localized in the pyrenyl moiety is responsible for the complex dissociation dynamics.

Summary

We have studied the photodissociation dynamics of a hexaarylbiimidazole (HABI) derivative with two pyrenyl groups using transient absorption and fluorescence spectroscopic techniques. It was shown that radicals (Py-L) were formed within a broad time interval from sub-100 fs up to ca. 10 ns after exposure of light, exhibiting a complex dynamics behavior. The photodissociation reaction rate was strongly dependent on the delay time after the excitation, decreasing the rate with increasing delay time. It was concluded that a dynamic relaxation process involving stabilization of the excited state, localized in the pyrenyl moiety, is primarily responsible for the complex dissociation behavior, while the contribution of the Py-L excited state to the complex dynamics behavior of Py-L formation was negligible. Generally, it is an important to control the rate and the reaction quantum yield of the photochromic molecules to realize the desired photochromic properties. Although we have already developed fast photochromic HABI derivatives showing intense coloration with UV light irradiation and successive fast thermal bleaching within tens of milliseconds at room temperature,[16a] the detailed knowledge for controlling the reaction quantum yield would lead to the development of a highly sophisticated photochromic HABI system. These fast photochromic materials could be promising materials for certain applications, such as optical data processing and light modulators.

The introduction of the large aromatic group into the HABI is an effective method to control the dissociation reaction rate by modifying the surface crossing between the attractive potential surface and the repulsive one. The fluorescent lifetime of pyrene in solution[26] is ca. 400 ns in the monomer S_1 state and ca. 100 ns even in the excimer state. Hence, the reaction yield of the photodissociation is still almost unity, although the reaction rate constant decreased drastically by the excimer formation. The introduction of the aromatic group with a shorter lifetime as comparable with the reduced dissociation reaction rate constant, however, could lead to control of the dissociation rate and yield.

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(25) The stabilization energy in the excited state and destabilization energy in the ground state are generally responsible for the Stokes shift due to the excimer formation. Provided that both energies are the same, the stabilization energy is half of the Stokes shift. Strictly speaking, the actual activation energy is dependent on the potential energy surfaces. In the case that the crossing point between the surface of the locally excited state of pyrenyl moiety and the repulsive surface is not so strongly dependent on the stabilization process, the apparent activation energy after the relaxation is half of the Stokes shift value.

(26) Birks, J. B.; Lumb, M. D.; Munro, I. H. *Proc. R. Soc. London, Ser. A* **1963**, *275*, 575.