Rational design of a new class of diffusion-inhibited HABI with fast back-reaction

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ABSTRACT: The fast reversible photochromic molecule was synthesized with the aid of triphenylimidazolyl radicals (TPI·) and naphthalene linker. The crystal structure, photochemical properties, and kinetics of the target compound (1,8-TPID-naphthalene) were investigated. 1,8-TPID-naphthalene photochemically cleaved into 1,8-bisTPI·-naphthalene and the color of the solution changed from colorless to green. ESR spectroscopy detected the light-induced triplet radical pair in frozen matrix. After the UV irradiation is ceased, the back-reaction of 1,8-bisTPI·-naphthalene occurred by thermal conversion in the dark. The kinetic study on the back-reaction revealed that the reaction obeys the first-order kinetics with 2.04 s of half-life time at 295 K. The activation energy and frequency factor of the back-reaction were determined as 42.0 kJ/mol and $9.25 \times 10^6 \, s^{-1}$, respectively. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: photochromism; Hexaarylbiimidazole (HABI); radical cleavage; first-order kinetics; fast back-reaction; diffusion-inhibited; photoresponsive material; triplet radical pair

INTRODUCTION

The development of a fast reversible photochromic material is a major challenge for the photochemistry and material science because of their potential applications including smart windows, solar protection lenses and decorative objects. The photochromism of hexaarylbii-midazoles (HABIs) was discovered by Hayashi and Maeda in 1960s.[1] HABI derivatives can be prepared by oxidation of the corresponding triphenylimidazole (lophine) derivatives. HABIs readily cleave into a pair of triphenylimidazolyl radicals (TPI·) both thermally and photochemically, and TPI· will thermally recombine to reproduce the dimer of TPI·s, which is abbreviated as TPID in this manuscript. With respect to the molecular structure, TPID is identical with HABI. There are a number of spectroscopic studies on the photochemical reaction of HABI and its derivatives.[2] The typical mechanism for the photochromism of HABIs consists of two reactions as shown in Chart 1, namely light-induced radical cleavage and thermal back-reactions. At the earlier stage of the chemistry of HABIs, several kinetic studies on the thermal back-reactions of TPI·s have been reported. Although Willis and

co-workers postulated a complex kinetic behavior involving ionic and radical intermediates,[3] Hayashi and Maeda[1h] demonstrated that the kinetics of TPI· clearly obeys the second-order rate law. Recently, we have reported the acceleration of the back-reaction of bistpy-HABI (bis(terpyridyl)hexaarylbiimidazole).[4] The formation of iron(II) complex of bistpy-HABI resulted in the acceleration of the back-reaction even though the detailed mechanism is still obscure. This back-reaction also obeyed the second-order kinetics, and the recombination rate constant drastically increased from 48.4 L mol^{-1} s^{-1} to 504.6 L mol^{-1} s^{-1} (at 302 K) on the coordination of iron(II). In this case, the lowering of the activation energy barrier from 48.6 kJ/mol (free bistpy-HABI) to 24.3 kJ/mol (metal-coordinated bistpy-HABI) predominantly achieved the acceleration of the recombination rate.

In our previous reports, thermal behavior of the TPI· derivative, tF-BDPI-2Y (1,4-bis-(4,5-diphenylimidazol-2-ylidene)-2,3,5,6-tetrafluorocyclohexa-2,5-diene) have been discussed (Chart 2).[5] The dimerization reaction of tF-BDPI-2Y was found in solution at 293 K, while tF-BDPI-2Y was crystallized at 200 K because of the existence of the activation energy barrier toward the recombination reaction. On irradiation with UV light to the colorless benzene solution of tF-BDPI-2YD at room temperature, the dimer immediately cleaved into tF-BDPI-2Y and the solution intensively colored. Here, an instantly reversible

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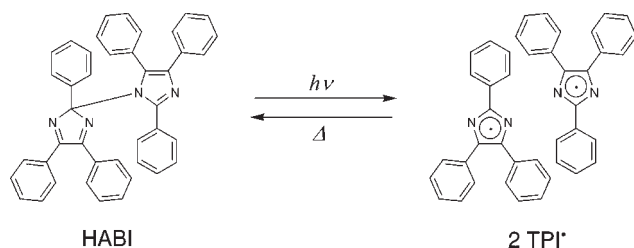E-mail: jiro_abe@chem.aoyama.ac.jp

Chart 1. Photochromism of conventional HABI

photochromic molecule can be designed if one imagines the one-photon reaction of tF-BDPI-2YD. The strategy for the molecular design begins with the virtual one-photon reaction depicted in Chart 2. The light-induced fluorinated TPI· pair will immediately recombine because the radical pair is restricted in their diffusion and the reaction centers are held in close proximity even in solution. Hence, this class of structure is assumed to be optimum for the achievement of very fast back-reaction of HABIs. In the restricted field such as a crystalline phase, it is known that the back-reaction of TPI· pair instantly undergoes. For example, the recombination reaction of chlorine-substituted TPI· pair completes within several milliseconds in the crystal at room temperature. We have directed toward, with the assistance of naphthalene linker as a diffusion inhibition unit, to fabricate a fast reversible photochromic molecule with HABI (Scheme 1). In this paper, we would like to

introduce the strategy with the aim of accelerating the back-reaction rate of HABIs based on the rational molecular designing. The synthesis, crystal structure, and photochemical properties will be described.

EXPERIMENTS

Synthesis

1,8-TPID-naphthalene was synthesized as shown in Scheme 1. All reagents except benzyl (recrystallized from ethanol) were used as commercially supplied. Although it is commercially available, p-formylphenylboronic acid can be synthesized from p-bromobenzaldehyde. Benzene, acetic acid, and toluene were distilled prior to use.

4,5-diphenyl-2-(4′-phenylboronicacid)imidazole (1)

p-formylphenylboronic acid (1.00 g, 6.67 mmol), benzyl (1.47 g, 6.99 mmol), and ammonium acetate (25.7 g, 0.333 mol) were gently refluxed in acetic acid (150 ml) for 20 h then allowed to cool to room temperature. The white slurry that precipitated by the neutralization by aqueous NH_3 was filtered off. The crude slurry was
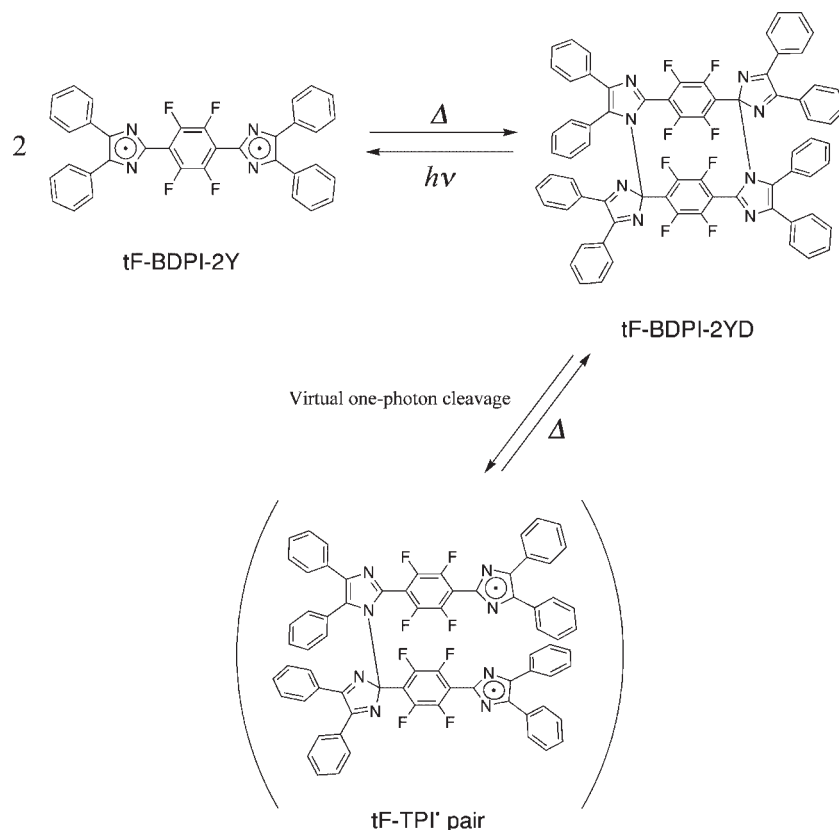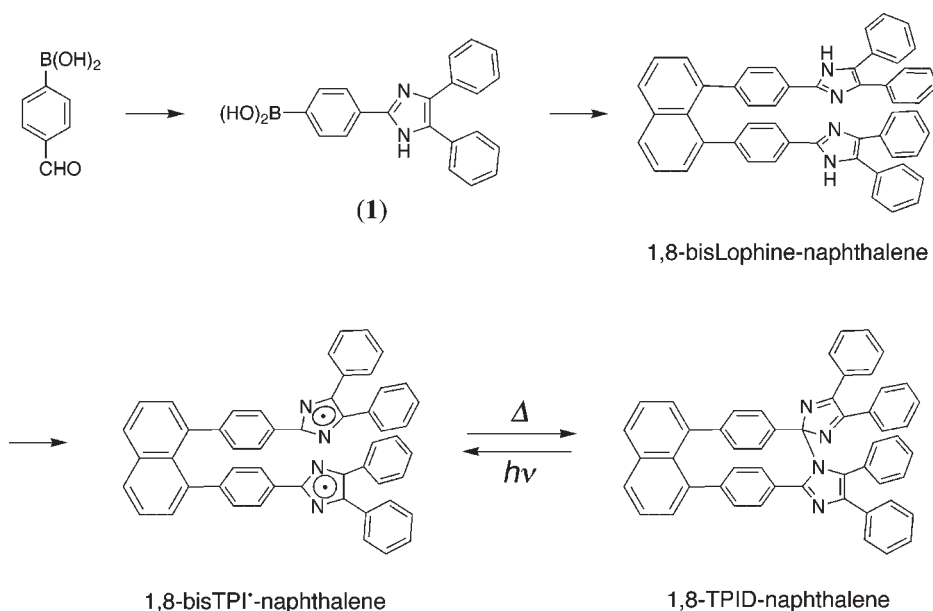

Chart 2. Photochromism and virtual one-photon reaction of tF-BDPI-2Y

Scheme 1. Synthesis of 1,8-TPID-naphthalene

dissolved in ethyl acetate and the solution was frequently washed with brine then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was treated by silica-gel column chromatography ($CHCl_3$: MeOH = 5:1). 4,5-diphenyl-2-(4′-phenylboronic acid)imidazole was obtained as white powder (1.10 g; yield 48.7%). ^{1}H NMR (500 MHz, DMSO-d^6): δ (ppm) 7.17 ∼ 8.12 (m, 16 H), 12.63 (s, 1 H). Anal. Calcd for $C_{21}H_{17}BN_2O_2 \cdot 2.5H_2O \cdot 0.25AcOEt$: C, 64.88; H, 5.94; N, 6.88. Found: C, 64.50; H, 5.09; N 7.07.

1,8-bisLophine-naphthalene

To a solution of 1,8-diiodonaphthalene (260 mg, 0.684 mmol)[6] in benzene (27 ml) and ethanol (27 ml), 680 mg (2.00 mmol) of **1** and $Pd(PPh_3)_4$ (111 mg, 96.1 μmol) was added. Sodium carbonate (438 mg, 4.13 mmol) in water (18 ml) was added, and the reaction mixture was refluxed overnight with exclusion of the light. After cooling to room temperature, the mixture was poured into $CHCl_3$ (150 ml) and brine (150 ml). The organic layer was separated and the aqueous layer was extracted three times with $CHCl_3$. Combined organic layer was washed with brine (×1) and water (×1) then dried over Na_2SO_4. The solvent was removed *in vacuo* and the residue was treated by silica-gel column chromatography ($CHCl_3$:AcOEt = 5:1). 1,8-bisLophine-naphthalene was obtained as pale yellow powder (420 mg; yield 85.7%). Recrystallization from hot AcOEt gave colorless, block crystal of 1,8-bisLophine-naphthalene · 2AcOEt. ^{1}H NMR (500 MHz, DMSO-d^6): δ (ppm) 6.60 ∼ 7.65 (m, 34 H), 11.85 (s, 2 H). Anal. Calcd

for $C_{52}H_{36}N_4 \cdot 2(C_4H_8O_2)$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.10; H, 6.01; N 6.32.

1,8-TPID-naphthalene

All manipulations include recrystallization were carried out with exclusion of the UV light. To the benzene (9 ml) solution of 1,8-bisLophine-naphthalene · 3AcOEt (188 mg, 0.192 mmol), the solution of potassium ferricyanide (1.9 g, 5.8 mmol) and KOH (1.3 g, 23 mmol) in H_2O (9 ml) was added. The mixture was vigorously stirred for 1.5 h, then the organic layer was separated and exhaustively washed with deionized water. Though the oxidation of 1,8-bisLophine-naphthalene gave the corresponding 1,8-bisTPI·-naphthalene, the intramolecular dimerization reaction of the TPI· moieties lead quickly to the formation of 1,8-TPID-naphthalene. The solvent was removed under reduced pressure to give a crude product of 1,8-TPID-naphthalene. The purification was carried out by silica-gel column chromatography ($CHCl_3$:AcOEt = 20:1). The solvent was removed and the residue was washed with acetonitrile. 1,8-TPID-naphthalene was isolated as slightly green-colored powder (83.3 mg; yield 60.9%). ^{1}H NMR (500 MHz, DMSO-d^6): δ (ppm) 6.69 ∼ 8.14 (m). Anal. Calcd for $C_{52}H_{34}N_4 \cdot 0.4MeCN \cdot 0.4H_2O$: C, 85.87; H, 4.91; N, 8.35. Found: C, 85.89; H, 5.09; N 8.12. The slow evaporation of dilute CH_3CN solution of 1,8-TPID-naphthalene under nitrogen stream gave transparent, thin-plate single-crystal suitable for the X-ray crystallographic analysis (crystal A in Table 1). The recrystallization from hot CH_3CN/benzene (8:1) mixture is also

Table 1. Crystallographic parameters of 1,8-TPID-naphthalenes

	Crystal A	Crystal B
Crystal preparation	Slow evap of CH_3CN	$CH_3CN:C_6H_6 = 8:1$
Formula	$C_{52}H_{34}N_4$	$(C_{52}H_{34}N_4)_2 \cdot 2C_6H_6 \cdot CH_3CN$
Formula weight	714.83	1626.93
Temperature/K	90	90
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Crystal dimension/mm^3	$0.15 \times 0.03 \times 0.01$	$0.35 \times 0.20 \times 0.10$
a/Å	9.902 (9)	9.7666 (5)
b/Å	14.179 (5)	21.1009 (10)
c/Å	15.231 (5)	22.2607 (11)
α/deg	117.357 (4)	106.569 (3)
β/deg	103.858 (6)	99.922 (3)
γ/deg	92.981 (6)	94.037 (3)
V/Å^3	1811.12 (18)	4296.4 (4)
Z	2	2
$R_1(wR)$ for $I > 2\sigma(I)$	0.0571 (0.0751)	0.0626 (0.1419)
$R(wR)$ for all data	0.1658 (0.0938)	0.1501 (0.1894)
G.O.F.	1.001	1.002

acceptable. This method afforded solvated compound, crystal B as listed in Table 1.

X-ray crystallographic analysis

The diffraction data of the single crystal of 1,8-TPID-naphthalene was collected on the Bruler APEX II CCD area detector (MoK_α, $\lambda = 0.71073$ nm). During the data collection, the lead grass doors of the diffractometer were covered to exclude the room light. The data refinement was carried out by the Bruker APEXII software package with SHELXT program.[7] All non-hydrogen atoms were anisotropically refined. The crystallographic parameters are listed in Table 1.

Photochemical studies

The ESR signal of the light-induced radical pair of 1,8-bisTPI·-naphthalene in frozen toluene matrix was recorded on a JEOL JES-TE200 spectrometer operating at the X-band equipped with a digital temperature controller model 9650 (Scientific Instruments, Inc.). The sample solution in a quartz tube (ϕ 3.2 mm) was degassed by the freeze-pump-thaw method.

The time-resolved visible-NIR absorption spectra were measured on a S-2600 multi-channel spectrometer (Soma optics Ltd.). The time-course spectra at 620 nm were recorded on an UV-3100 spectrophotometer equipped with a TCC-260 temperature controller (Shimadzu corporation).

Light from a xenon lamp passed thorough a band-pass filter (360 nm, *ca.* 0.2 mW/cm^{-1}; LAX 100, Asahi bunko Ltd.) was used for the ESR and time-resolved absorption spectra measurements. The light irradiation for the time-course study was performed by Keyence UV-400

series UV-LED lamp (UV-50H type) equipped with a UV-L6 lens unit (365 nm, *ca.* 800 mW/cm^2).

RESULTS AND DISCUSSION

The molecular structure of 1,8-TPID-naphthalene was unambiguously determined by X-ray crystallography as the ORTEP drawing shown in Fig. 1.[8] Two TPI· moieties afforded a photochromic 1,2′-biimidazole dimer by intramolecular radical recombination. The bond length between C1 and N1 (1.494 Å) was almost identical with that found in tF-BDPI-2Y dimer (1.499 Å). The other bond lengths are reasonable as compared with conventional HABIs. The bridging benzene rings are held in close proximity to each other and their mean planes were positioned at a slight tilt angle of 3.2 degree. The contact distances between the bridging benzenes are also shown in Figure 1. The torsion angle between the mean planes of naphthalene and benzene rings are 54.2 and 52.0 degree, respectively.

The light-induced radical pair of 1,8-bisTPI·-naphthalene was investigated by ESR spectroscopy. The frozen toluene solution of 1,8-TPID-naphthalene (1.61×10^{-3} M) was irradiated with 360 nm of UV light for 5 min at 84 K. As it is always observed for the HABI family, the formation of triplet TPI· pair was confirmed by a characteristic fine structure as shown in Fig. 2. The zero-field splitting parameter was obtained as 11.8 mT ($|2D/hc| = 0.0110$ cm^{-1}). An estimation by means of point-dipole approximation revealed that the distance between spin-density centers is 6.18 Å. This distance is comparable with those found in other light-induced TPI· pairs in frozen matrices or crystal.[9] The time-dependent signal decay arose from the back-reaction or disproportionation was not observed at 84 K, but the ESR signal disappeared due to the recombination of TPI· pairs as the
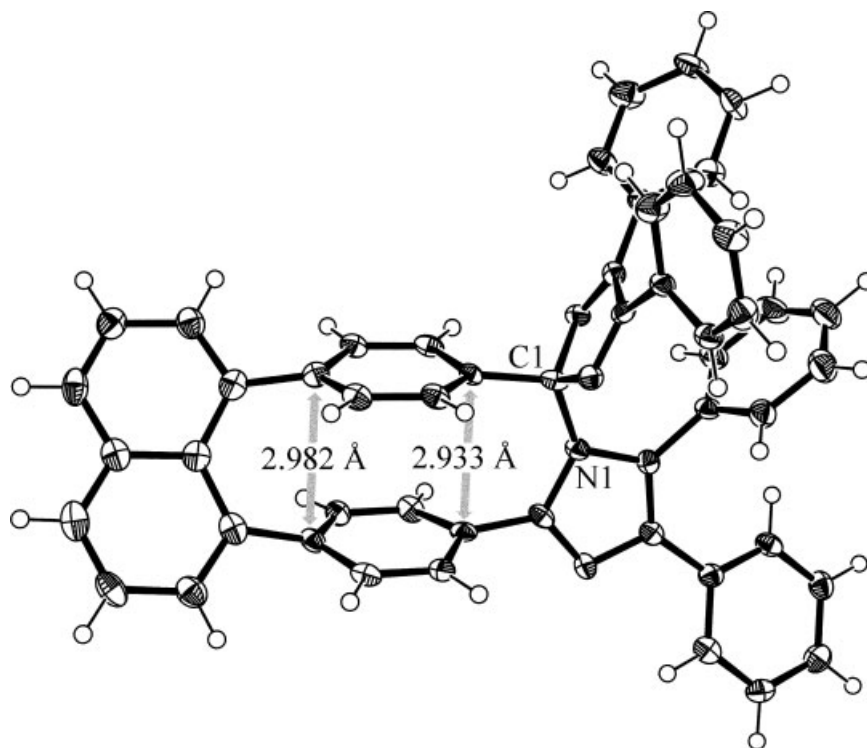
Figure 1. ORTEP drawing for 1,8-TPID-naphthalene with 50 % probability thermal ellipsoid

temperature increased to room temperature region. At a temperature above the melting point of toluene, light-induced ESR signal showed time decay with exclusion of the light.

The kinetics of the back-reaction was investigated by means of vis-NR absorption spectra. The photoreaction of 1,8-TPID-naphthalene in degassed toluene (3.53×10^{-4} M) was performed by irradiation with 365 nm of UV light in a well-stirred quartz cell (light-path length = 10 mm) equipped with a thermostat. Upon irradiation, an intense absorption band with $\lambda_{max} =$ 585 nm that attributable to the absorption of 1,8-

bisTPI·-naphthalene appeared and the color of the solution changed from colorless to green. Absorption spectral change of the light-induced 1,8-bisTPI·-naphthalene measured at 295 K is shown in Fig. 3. The absorption band immediately began to decrease as the light irradiation was turned off. A thing worthy to note is the existence of the shoulder band whose absorption maximum at approximately 620 nm and broad absorption band at longer wavelength (>750 nm). Interestingly,
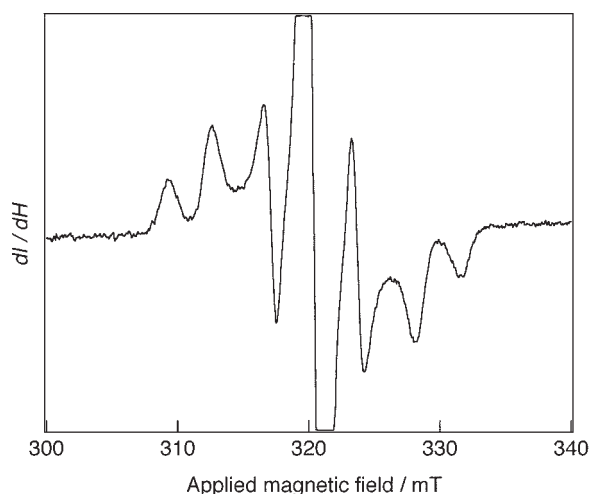

Figure 2. ESR signal of the light-induced triplet radical pair of 1,8-bisTPI·-naphthalene in frozen toluene
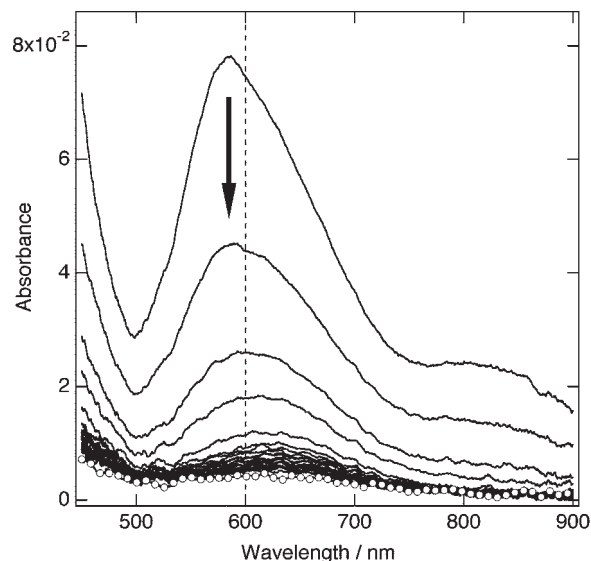

Figure 3. Absorption spectral change of 1,8-bisTPI·-naphthalene in degassed toluene at 295 K with the time interval of 1.5 s. The broken line at 600 nm is eye-guide. The line with circles shows the initial spectrum

these two absorption bands were affected by a bubbling of oxygen gas to the optical cell. As shown in Fig. 4, the absorption decay at 580 nm accelerated and longer wavelength absorption disappeared in the presence of oxygen. The initial spectral behavior recovered on the removal of oxygen by continuous bubbling of argon gas. These phenomena strongly support the existence of the contribution from the triplet state to the absorption spectra. The absorption band at 620 nm may be presumably assignable to that of singlet TPI· pair that led to the radical recombination. To our knowledge, the spectral observation of the triplet state of TPI· pair in solution has not been reported previously. The detailed mechanism of the recombination process is currently under investigation.

Taking into account above insight, the time course spectra for the radical recombination reactions of 1,8-bisTPI·-naphthalene were probed at 620 nm of wavelength after 10 s of light irradiation followed by a few seconds of delay-time after the irradiation was ceased. The first-order kinetic plot is depicted in Fig. 5. The rate constant was obtained as $8.46 \times 10^{-2}\,s^{-1}$ at 273 K and was found to increase with temperature. The temperature dependence of the kinetic constant of the recombination reaction followed an Arrhenius kinetics (Fig. 6). The activation energy barrier and the frequency factor determined from the plot are 42.0 kJ/mol and $9.25 \times 10^{6}\,s^{-1}$, respectively. The activation energy is comparable to those of conventional HABI family that obey the second-order kinetics. On the basis of the kinetic parameters, the rate constant and half-life time at 295 K ($\ln2/k_{295K}$) was estimated by the extrapolation to be $0.339\,s^{-1}$ and 2.04 s. It is noteworthy that this recombination reaction is extremely fast, and the kinetics clearly obeys the first-order as shown in Fig. 5, whereas several kinetic studies of HABIs based on the second-order have
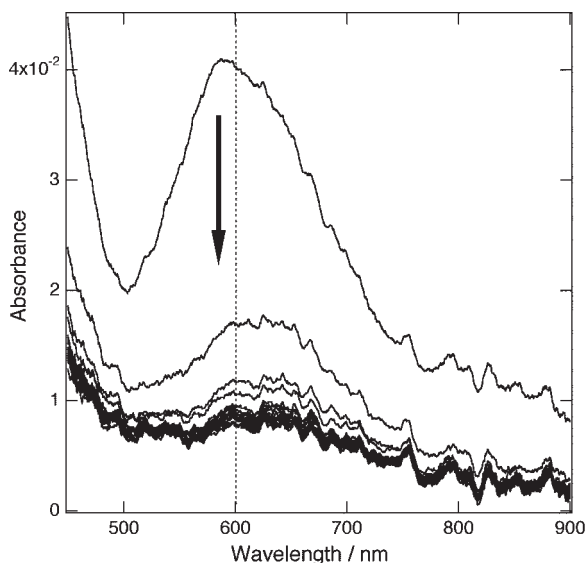
Figure 5. The first-order kinetic plot for 1,8-bisTPI·-naphthalene in toluene. For the graphical clarity, results at four temperatures are represented

been reported. The intramolecular recombination of diffusion-inhibited two radical centers of 1,8-bisTPI·-naphthalene allowed the kinetics to be the first-order. It is known that HABIs occur the solid state photoreaction as well as in the solution, but the back-reaction in the solid state does not obey the second-order law.[1(e)] The detailed investigation for the mechanism and kinetics of the back-reaction in the solid state have not been explored.

In conclusion, the fast reversible HABI derivative, 1,8-TPID-naphthalene, was designed with the aid of naphthalene linker, and a significant acceleration of the recombination reaction of light-induced radical pairs was achieved. The kinetic study of 1,8-bisTPI·-naphthalene revealed an unequivocal first-order behavior whose

Figure 4. Absorption spectral change of 1,8-bisTPI·-naphthalene in toluene with existence of oxygen with the time interval of 1.5 s. The broken line at 600 nm is eye-guide
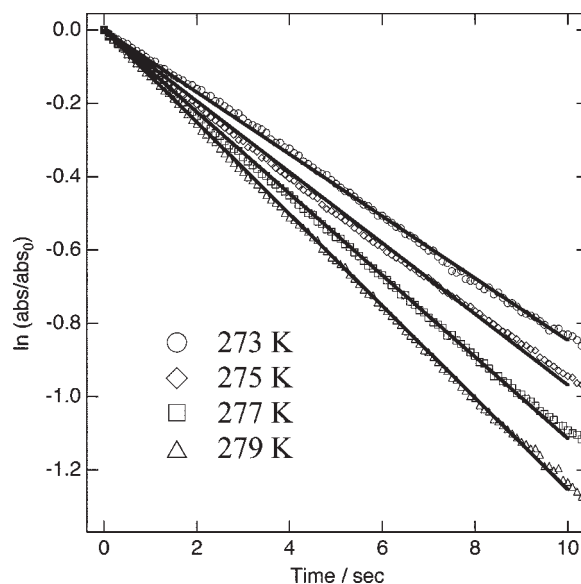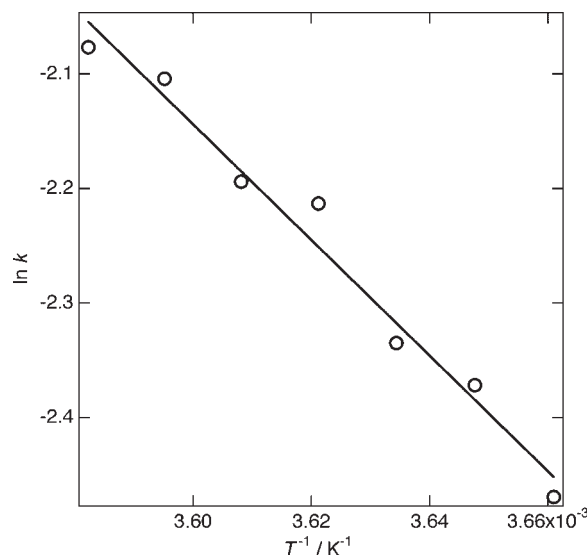
Figure 6. Arrhenius plots for the first-order kinetics of 1,8-bisTPI·-naphthalene

half-life time is 2 s at room temperature. These results established a new paradigm of the molecular designing for the photochemistry and functional material science.

Acknowledgements

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