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Reversible Intramolecular Triplet−Triplet Energy Transfer in Benzophenone-*N*-methylphthalimide Dyad

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In the present paper, we synthesized a series of benzophenone (BP)-*N*-methylphthalimide (MePI) dyads (**Cn**, **n** = 3, 6, and 9, where **n** denotes the number of methylene in the linker) and investigated the photochemical properties and intramolecular triplet−triplet energy transfer from BP(T_1) to MePI. Formation of two different intramolecular complexes was found, that is, a ground-state complex and a singlet exciplex. The formation of the triplet-equilibrium between MeBP and MePI was observed. The triplet-equilibrium constant (1.0 and 1.1 for **C6** and **C9**, respectively) and forward ((3.8 ± 1.3) × 10^7 and (3.9 ± 1.2) × 10^7 s^{-1} for **C6** and **C9**, respectively) and back ((3.8 ± 1.3) × 10^7 and (3.6 ± 1.2) × 10^7 s^{-1} for **C6** and **C9**, respectively) energy transfer rates were estimated from the result of transient absorption measurements. From the van't Hoff plots, enthalpy and entropy change for the equilibrium formation were estimated.

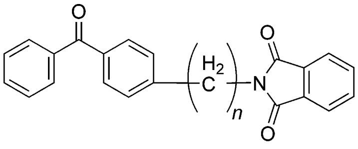
Introduction

Triplet−triplet energy transfer (TET) is an important and fundamental photochemical process and has been an intensively investigated subject.[1−3] When the energy levels of donor and acceptor are close to each other (within few kcal/mol), reversible TET becomes possible. The triplet-equilibrium formation is one of the important TET processes, and the equilibrium in complexes attracted much attention due to the application to temporal energy storage or elongation of excited-state lifetime.[4−7] Additionally, it is tempting to investigate the effect of the entropy change (ΔS) term on the TET process, since ΔS plays an important role in the triplet-equilibrium formation.[8−10]

Benzophenone (BP) has been widely applied to a variety of photoinduced reaction systems, such as photosensitizers,[11] light-harvesting antenna,[12] crosslinkers,[13] bioconjugates,[14] etc. The applicability of BP is owing to the quite high triplet quantum yields ($\Phi_T = 1$),[15] high triplet energy ($E_T = 68.6$ kcal mol^{-1}),[15] sufficiently long lifetime ($\tau_T = 50$ μs in polar solvent),[15] and reactivity of BP in the lowest triplet excited state (BP(T_1)). Gessner et al. reported the formation of triplet equilibrium in the BP−biphenyl and BP−tryphenylene systems.[8] Zhang et al. also investigated the triplet-equilibrium formation of BP. They compared the ΔS of triplet equilibrium in the nonrigid and rigid molecules and reported that ΔS depends on the relative change in conformational freedom between the ground and excited states.[9] However, those previous studies were carried out in an intermolecular system and there had been no study about the intramolecular triplet-equilibrium formation of BP.

In the present paper, we synthesized a series of BP-*N*-methylphthalimide (MePI) dyads (**Cn**, **n** = 3, 6, and 9, where **n** denotes the number of methylene in the linker, and the structures are shown in Chart 1) and investigated the photochemical properties and TET from BP(T_1) to MePI. Since the triplet energy levels of BP and MePI are close, it is expected that the triplet equilibrium is formed in the system. The study about the triplet-equilibrium of BP, which has been widely applied for photoinduced systems, is an important theme. Although the intermolecular TET from BP(T_1) to *N*-alkylated phthalimides was reported,[16] a detailed study on the intramolecular system had not been examined. Here, we investigated intramolecular triplet-equilibrium formation using the transient absorption measurement. Enthalpy change (ΔH) and ΔS for the equilibrium formation were estimated and contribution of ΔS was discussed. Complex formation of **Cn** was investigated using the emission and excitation spectra measurement and time-resolved emission measurement.

CHART 1: Structures of Cn



C3: *n* = 3
C6: *n* = 6
C9: *n* = 9

Experimental Section

Materials. A series of **Cn** dyads were synthesized as summarized in the Supporting Information. The structures of **Cn** are shown in Chart 1.

Nanosecond Laser Flash Photolysis. The nanosecond laser flash photolysis was carried out using the third harmonic oscillation (355 nm) of Nd^{3+}:YAG laser (Continuum, Surelite II-10; 30 mJ pulse^{-1}, 5 ns fwhm). The monitor light from a pulsed 450-W Xe arc lamp (Ushio, UXL-451-0) was collected by a focusing lens and directed to a grating monochromator (Nikon, G250). The monitor light was set perpendicular to the laser beam. The output of the monochromator was monitored using a photomultiplier tube (PMT) (Hamamatsu Photonics, R928). The signal from the PMT was recorded on a transient digitizer (Tektronix, TDS 580D four channel digital phosphor oscilloscope). A Hamamatsu Photonics multichannel analyzer

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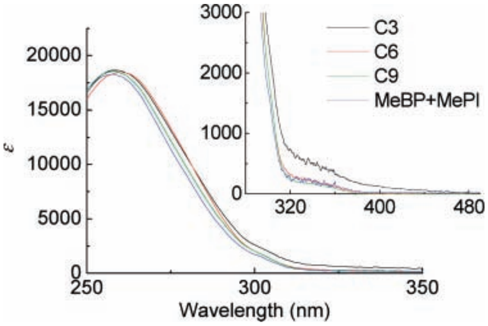


Figure 1. UV−vis absorption spectra of **Cn** and reference compound in acetonitrile. The inset is the enlarged graph.

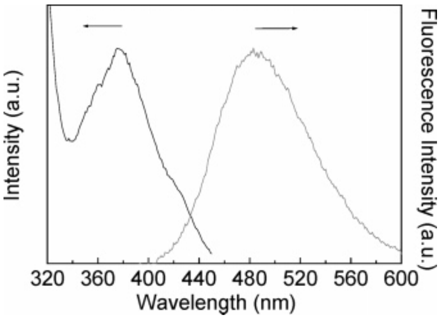


Figure 2. Normalized emission spectra (gray line) and excitation spectra (black line) of **C3** in acetonitrile.

(C5967) system was used for the measurement of the transient absorption spectra. The total system was controlled with a personal computer via a GP-IB interface. The time resolution of the whole system is less than 10 ns. To avoid stray light and pyrolysis of the sample by the probe light, a suitable sharp cut filter (Sigma Koki, SCF-50S-37L) was employed to measure kinetic traces.

Picosecond Laser Flash Photolysis. The picosecond laser flash photolysis was carried out using second harmonic oscillation (532 nm) of a Nd^{3+}:YAG laser (Continuum, RGA69-10; 3 mJ $pulse^{-1}$, 30-ps fwhm, 10 Hz). The fluorescence spectra were measured using a streak camera (Hamamatsu Photonics, C7700) equipped with a charge-coupled device camera (Hamamatsu Photonics, C4742-98). The time resolution of the whole systems is less than 100 ps.

UV−Vis Absorption and Fluorescence Spectral Measurements. The UV−vis absorption and fluorescence spectra were measured using a Shimazu UV-3100 and a Hitachi 850 spectrometer, respectively.

Results and Discussion

Absorption Spectra. The UV−vis absorption spectra of **Cn** are shown in Figure 1. The absorption of **C9** is slightly broadened compared with the superposition of the absorption of mixture of 4-methylbenzophenone (MeBP) and MePI. The absorption of **C6** is slightly red-shifted and broadened as **C9**. In the case of **C3**, the absorption is broadened and the weak shoulder from 300 to 400 nm was observed. The changes in the absorption spectra indicate the interaction between MeBP and MePI in the ground state.

Steady-State Emission and Excitation Spectra. **C3** showed an emission peak at around 480 nm by illumination of 355-nm light in acetonitrile at room temperature (Figure 2). **C6** and **C9** showed only weak emissions, so the detection was quite difficult.

The excitation spectrum of **C3** monitoring the emission intensity at 480 nm is shown in Figure 2. It seems that the excitation spectrum agreed with the shoulder from 300 to 400 nm observed in the UV−vis absorption spectrum. This fact indicates that the emission was derived from the ground-state complex in the excited state. It is suggested that the short center-to-center distance between MeBP and MePI (R_{DA}) of **C3** promotes the formation of complex.

TABLE 1: Triplet Quantum Yield (Φ_T), Fluorescence Maxima, and Lifetime of Emission (τ_{fl}) of Cn

compound	Φ_T	λ_{fmax}	τ_{f1} (ns)
C3	0.52	450, 490	0.89, 7.1
C6	0.66	440	6.8
C9	0.77	450	6.3

Time-Resolved Emission Spectra. The time-resolved emission spectra of **Cn** during the 355-nm picosecond laser flash photolysis are shown in Figure 3. Upon the 355-nm laser excitation, **C3** showed the two different emissions. One is the emission with a peak at 450 nm (the peak position was estimated by subtracting the overlap of emission observed at 10 ns), and another is the emission with a peak at 490 nm. The latter emission corresponds to the excited-state of complex (vide supra). The lifetime of emission peak at 450 nm (0.89 ns) is shorter than that peak at 490 nm (7.1 ns) (Table 1). In the cases of **C6** and **C9**, only one emission peak at around 440−450 nm was observed. The lifetime of emissions of **C6** and **C9** are similar to each other (6.8 and 6.3 ns, respectively) (Table 1). Since the lifetimes of the emissions peak at around 440−450 nm are shorter than that of MeBP(T_1) and MePI in the triplet excited state (MePI(T_1)) and the Φ_T of **Cn** significantly decreased compared with MeBP (vide infra), it is suggested that those emissions are attributed to singlet exciplex (Scheme 1).

Transient Absorption Measurement. Transient absorption spectra of **Cn** were measured using the nanosecond laser flash photolysis. Upon the 355-nm laser excitation of **Cn**, the transient absorption assigned to MeBP(T_1) was observed (Figure 4).[15] The Φ_T of **Cn** was obtained by using BP as a standard (Table 1). The Φ_T value of **Cn** decreased with decreasing R_{DA}, suggesting that the Φ_T values are decreased by the complex formation.

The kinetic traces of **Cn** at 530 nm are shown in Figure 5A. It should be noted that the kinetic traces of **C6** and **C9** showed fast and slow decay components. For **C3**, only slow decay component was observed. The lifetime of fast decay component of **C3** may be shorter than the instrument response function (<c.a. 10 ns). The kinetic trace of **C6** at 340 nm after the laser irradiation was expressed by the sum of fast decay and rise components (Figure 5B). Because MePI(T_1) shows an absorption peak at 340 nm, the fast rise corresponds to the TET from MeBP(T_1) to MePI.[16] The similar result was also obtained for **C9**. The lifetime of the slow component was measured in diluted solution to suppress the affection of triplet−triplet annihilation (data not shown). The lifetimes of the slow decay components of **C3**, **C6**, and **C9** are similar to each other (around 20 μs). Since their lifetimes are similar to that of MeBP(T_1), it is concluded that the slow components correspond to the deactivation via the intersystem crossing of **Cn** from the triplet excited state to the ground state.

It is suggested that the decay process of MeBP(T_1) for **C6** and **C9** is well explained when taking the triplet-equilibrium formation into account (Scheme 2).[4,8−10] Since the triplet energy levels of MeBP(T_1) and MePI(T_1) (ΔE_T) are significantly close (energy difference of $\Delta E_T = -1.4$ kcal mol^{-1}),[16] the triplet

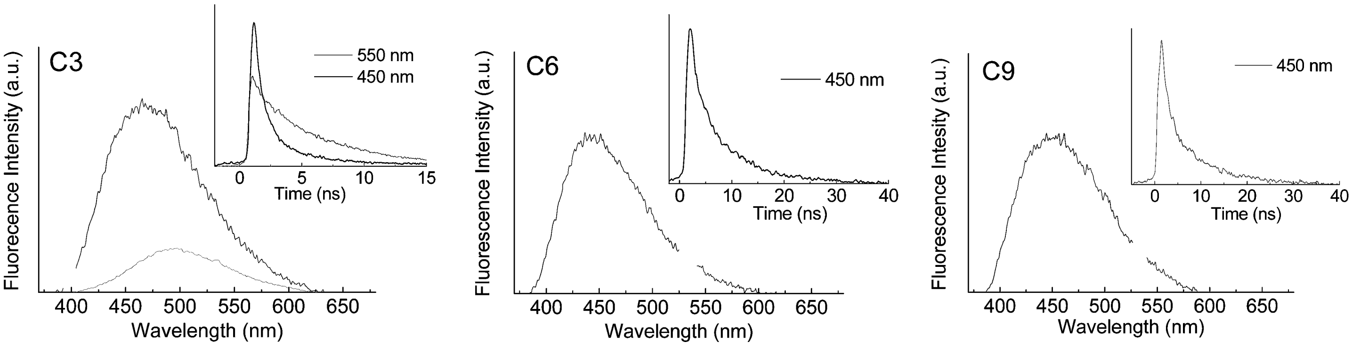


Figure 3. Time-resolved emission spectra of **Cn** in acetonitrile upon (black line) and 10 ns (gray line) after laser irradiation. Inset shows the kinetic traces of emission. The spike upon the laser irradiation is fluorescence of MeBP. The blank at around 532 nm was due to the residual SHG of Nd^{3+}:YAG laser.

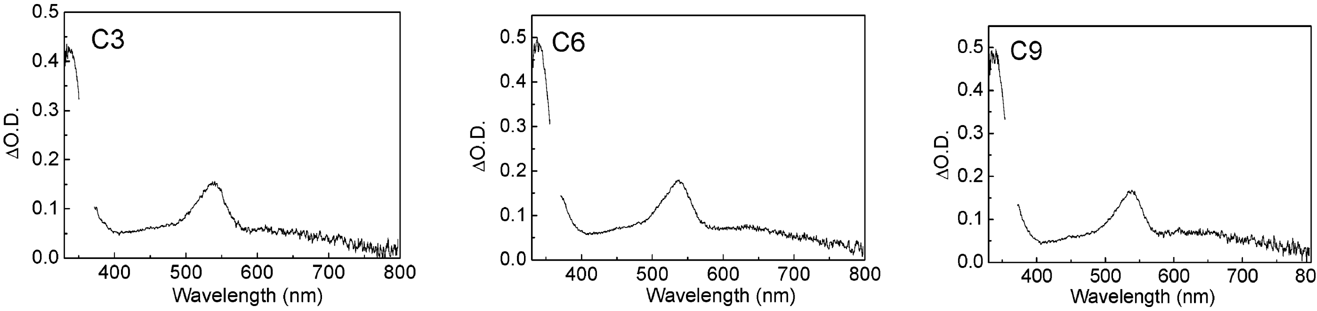
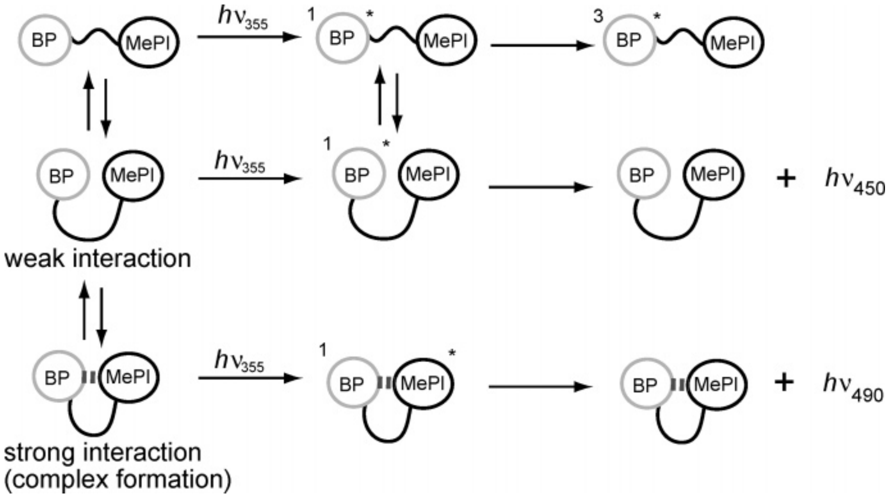


Figure 4. Transient absorption spectra of **Cn** at 10 ns after the 355-nm laser excitation in Ar-saturated acetonitrile.

SCHEME 1: Schematic Diagram Showing Processes of Cn after the Excitation[a]



[a] Upon the excitation of 355-nm laser, $BP(S_1)$ was generated at first. $BP(S_1)$ decays through two different processes: one is the intersystem crossing from $BP(S_1)$ to $BP(T_1)$; the other is the formation of singlet exciplex. When BP and MePI form a complex in the ground state, the excited state of the complex is formed by the excitation.

equilibrium would be established by the intramolecular triplet−triplet energy transfers between MeBP and MePI.

The triplet-equilibrium constant (K_{eq}) is defined by

$$K_{eq} = \frac{[MePI(T_1)]_{eq}[MeBP]}{[MeBP(T_1)]_{eq}[MePI]} \qquad (1)$$

where $[MePI(T_1)]_{eq}$ and $[BP(T_1)]_{eq}$ are concentrations of MePI(T_1) and MeBP(T_1) at equilibrium. In the present condition, [MeBP] is the same as [MePI]. Under the assumption that the fast decay corresponds to the TET from $BP(T_1)$ to MePI, the K_{eq} value can be estimated to be 1.0 and 1.1 for **C6** and **C9**, respectively, from the ratio of fast decay component of MeBP(T_1).

Since the decay rates of $MeBP(T_1)$ and $MePI(T_1)$ ($k_{ISC1} = 5.0 \times 10^4\ s^{-1}$ and $k_{ISC2} = 4.4 \times 10^4\ s^{-1}$, respectively) are considered to be much smaller than forward and back energy transfer rates (k_f and k_b, respectively), the intersystem crossing can be neglected during the triplet-equilibrium formation. Under the above condition, the decay of fast component is expressed by eq 2[17]

$$1 - \frac{[MePI(T_1)]}{[MePI(T_1)]_{eq}} = \exp\{-(k_f + k_b)t\} \qquad (2)$$

where $[MePI(T_1)]_{eq}$ can be expressed as $[MeBP(T_1)]_0 - [MeBP(T_1)]_{eq}$. From the fitting of kinetic traces, $k_f + k_b$ values for **C6** and **C9** were estimated to be both $(7.5 \pm 2.5) \times 10^7\ s^{-1}$. When

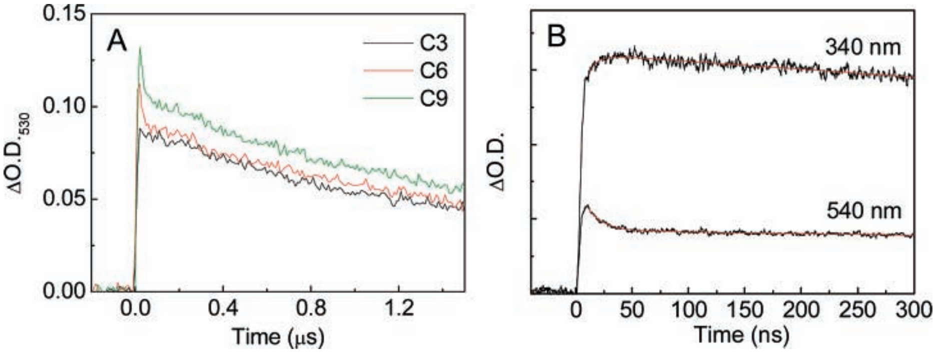


Figure 5. Kinetic traces of **Cn** at 530 nm in Ar-saturated acetonitrile during the 355-nm laser flash photolysis (A). Kinetic traces of **C6** at 530 and 340 nm in Ar-saturated acetonitrile during the 355-nm laser flash photolysis (B). The red lines are the best fit.

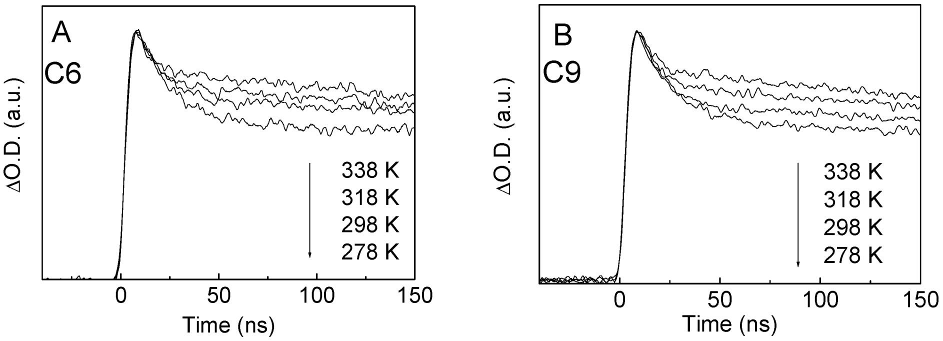
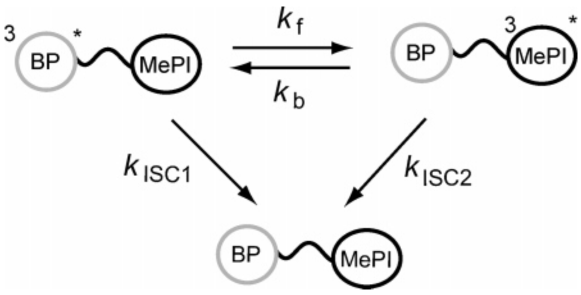


Figure 6. Normalized kinetic traces of **C6** and **C9** at several temperatures in Ar-saturated acetonitrile during the 355-nm laser flash photolysis ((A) and (B), respectively).

SCHEME 2: Schematic Diagram Showing Latter Processes of Cn after the Excitation[a]



[a] The decay process of **Cn**(T_1) was explained as follows: first, BP(T_1) forms the triplet equilibrium; second, BP(T_1) and MePI(T_1) decay via intersystem crossing.

the triplet equilibrium is formed, the relation expressed by the eq 3 should be established

$$k_f([\mathrm{MeBP}(T_1)]_0 - [\mathrm{MePI}(T_1)]_{eq}) = k_b[\mathrm{MePI}(T_1)]_{eq} \quad (3)$$

From eq 3, k_f values for **C6** and **C9** were estimated to be (3.8 ± 1.3) × 10^7 and (3.9 ± 1.2) × 10^7 s^{-1}, respectively, and k_b values for **C6** and **C9** were estimated to be (3.8 ± 1.3) × 10^7 and (3.6 ± 1.3) × 10^7 s^{-1}, respectively. The similarity of k_f and k_b values for **C6** and **C9** may reflect the similar geometry of **C6** and **C9** in the triplet excited state (vide infra). K_{eq} is also expressed by eq 4

$$K_{eq} = k_f/k_b \quad (4)$$

The K_{eq} values estimated by eq 4 (1.0 and 1.1 for **C6** and **C9**, respectively) agreed with the obtained K_{eq} values from eq 1. The agreement supports the correctness of estimated K_{eq} values.

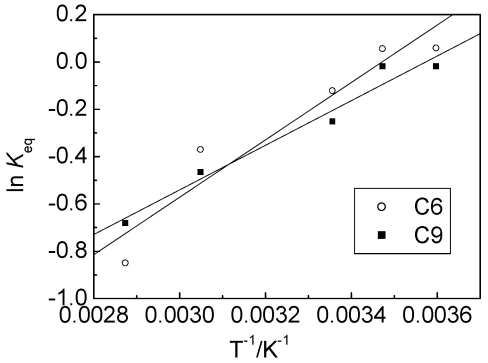


Figure 7. van't Hoff plots of K_{eq} for **C6** and **C9** in acetonitrile.

Temperature Effect for the TET. The temperature effect on the intramolecular TET was investigated for the further characterization of triplet equilibrium. The normalized kinetic traces of **C6** and **C9** at several temperatures are shown in Figure 6. The ratio of the fast decay component is decreased with increasing temperature. Following the increase of temperature from 278 to 348 K, K_{eq} values of **C6** and **C9** were changed from 1.0 to 0.5 and from 1.1 to 0.43, respectively. The fact indicates that the complex formation is exothermic process. The van't Hoff plots of K_{eq} for **C6** and **C9** are shown in Figure 7. The van't Hoff equation is given in terms of Δ*S* and Δ*H* for the equilibrium formation (eq 5)

$$\ln K_{eq} = \Delta S/R - (\Delta H/R)T^{-1} \quad (5)$$

From eq 5, Δ*H* for **C6** and **C9** were estimated to be −1.9 and −2.4 kcal mol^{-1}, respectively. Those values are similar to the ΔE_T (−1.4 kcal/mol). Δ*S* for **C6** and **C9** were estimated to be −6.6 and −8.3 cal mol^{-1} K^{-1}, respectively.

Δ*S* plays an important role in the triplet-equilibrium formation because both its sign and magnitude can significantly affect the equilibrium constant.[4,8−10] Zhang et al. reported that ΔS depends on the relative change in conformational freedom between the ground and excited states.[9] The obtained ΔS values were different from that of MeBP estimated in the previous paper.[9] Taking the rigidity of MePI into account, it is concluded that the methylene chain connecting BP and MePI significantly decreases the ΔS value.

The free energy change (ΔG) for the equilibrium formation is expressed as eq 6

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

At 298 K, the ΔG values of both **C6** and **C9** are calculated to be 0.1 kcal mol^{-1}, almost 0. It is suggested that the connection of BP and MePI by methylene chain decreases the ΔS value and negatively affect the formation of triplet equilibrium. The triplet-equilibrium formation is driven by the ΔH.

In the case of **C3**, the fast decay component of MeBP(T$_1$) was shorter than the instrument response function (<c.a. 10 ns). It is suggested that the short R_{DA} and strong interaction between BP and MePI affects the k_f and k_b. The ground-state complex formation also supports the strong interaction. The decay of **C6** and **C9** are similar to each other although the R_{DA} is significantly different. Additionally, the ΔH and ΔS values of the triplet-equilibrium formation for **C6** and **C9** are also not very different. It is suggested that the geometry of **C6** and **C9** in the triplet excited state may be similar due to the interaction between MeBP and MePI and flexibility of long methylene chain. The similar emissions of **C6** and **C9** suggest the similar molecular geometry of them (i.e., similar distance between MeBP and MePI).

Conclusions

In the present paper, we investigated the intramolecular triplet-equilibrium formation between MeBP and MePI. Two different intramolecular complexes were observed, that is, the ground-state complex and singlet exciplex. The ground-state complex formation was observed only in the case of **C3**, indicating that the ground-state complex formation significantly depends on the R_{DA}. The emission spectra of the singlet exciplex of **Cn** were similar, while the lifetimes were affected by the R_{DA}. The formation of the triplet equilibrium between MeBP(T$_1$) and MePI(T$_1$) was observed. From the van't Hoff plots in the range from 278 to 338 K, ΔH and ΔS for the equilibrium formation were estimated. It was revealed that the ΔS was significantly affected by the linkage of BP and MePI using methylene chain. Those results display new example of intermolecular triplet equilibrium and provide new findings to the photochemistry of BP. The distance effect on the triplet-equilibrium was not investigated well due to the formation of the complexes between MeBP and MePI; the investigation employing the system without complex formation is necessary for the further study.

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Supporting Information Available: Synthesis of **Cn** and estimation of decay rate constant of MePI(T$_1$). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The equation was obtained by solving the following equation, $d[\mathrm{MePI(T_1)}]/dt = k_f([\mathrm{MeBP(T_1)}]_0 - [\mathrm{MePI(T_1)}]) - k_b[\mathrm{MePI(T_1)}]$.