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Transient Phenomena of Polyphenyls in the Higher Triplet Excited State

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Transient phenomena of polyphenyls (PP), such as biphenyl (BP), *p*-terphenyl (TP), and 1,3,5-triphenylbenzene (TPB) in the higher triplet excited states (T_n, $n \geq 2$), were investigated with the nanosecond−nanosecond (ns−ns) two-color two-laser excitation method. PP(T_n) was generated by the excitation of PP in the lowest triplet excited state (PP(T_1)) at the wavelength tuned to the absorption of PP(T_1). Bleaching of the transient absorption of BP(T_1) and TP(T_1) was observed during the second laser irradiation in the presence of chloroalkanes (RCl) such as carbon tetrachloride (CCl_4), dichloromethane (CH_2Cl_2), or 1,2-dichloroethane (DCE). In the case of TPB, clear bleaching of TPB(T_1) was observed in the presence of CCl_4, while no bleaching was observed in the presence of CH_2Cl_2 and DCE. No formation of $PP^{\bullet+}$ was detected during the quenching of PP(T_n) by RCl. Therefore, the bleaching of PP(T_1) is attributed to triplet energy transfer quenching of PP(T_n) by RCl followed by the C−Cl bond cleavage. The lifetimes (τ_{Tn}) of PP(T_n) were estimated from the dependence of the quenching efficiency on the RCl concentration. It was found that the τ_{Tn} value decreased with the increasing number of benzene rings, BP(T_n) (950 ps) > TP(T_n) (620 ps) > TPB(T_n) (360 ps). The quenching mechanism of PP(T_n) by RCl was discussed.

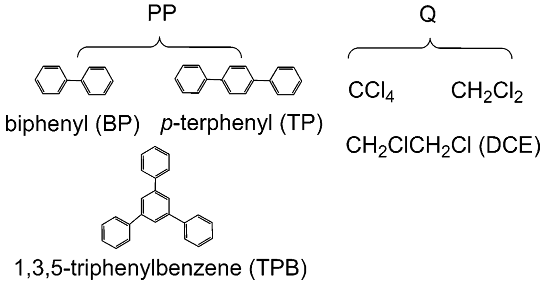
Introduction

Polyphenyls (PP), such as biphenyl (BP), *p*-terphenyl (TP), and 1,3,5-triphenylbenzene (TPB), are composed only of benzene rings without any other substituents. The electronic structure of PP can be interpreted in terms of the π conjugation in PP. Therefore, it is interesting to study the properties of PP from both theoretical and experimental points of view.[1,2] Among PP, BP is the smallest PP containing two nonfused benzene rings and has been extensively studied.[3−6] The structure of BP changes from nonplanar to near planar when BP is excited from the ground state to the excited states.[5,6] Similar structural change is expected for TP and TPB.[1,2] Selected data of PP, such as singlet excited state (S_1) energy ($E\mathrm{s}_1$), lifetime ($\tau\mathrm{s}_1$), lowest triplet excited state (T_1) energy (E_{T1}), lifetime (τ_{T1}), ionization potential (IP), redox potential ($E_{1/2}{}^{\mathrm{ox}}$ and $E_{1/2}{}^{\mathrm{red}}$), and absorption peaks of radical ions, are given in the Table 1.

The $E\mathrm{s}_1$ and E_{T1} values of BP are higher than those of TP and TPB. The ϕ_{T} of BP is much larger than that of TP. The IP, $E_{1/2}{}^{\mathrm{ox}}$, and $E_{1/2}{}^{\mathrm{red}}$ of BP are similar to those of TP. All radical ions of BP, TP, and TBP have clear absorption peaks in the shorter wavelength (340−600 nm) and longer wavelength (600−1200 nm) regions. Since the τ_{T1} of PP(T_1) is sufficiently long, PP(T_1) can be easily excited to give PP in the higher triplet excited states (T_n) before the deactivation of PP(T_1) to PP(S_0) through the intersystem crossing and/or T−T annihilation using the nanosecond−nanosecond (ns−ns) two-color two-laser excitation method. However, the properties of PP(T_n) have not been investigated, except for a report on BP(T_n).[8]

Recently, several fused aromatic hydrocarbons, such as naphthalene, dibenz[*a*,*h*]anthracene, and chrysene in the T_n states, have been investigated in our group.[9] We report here the transient phenomena of PP(T_n) with the ns−ns two-color two-laser photolysis method. The lifetimes of PP(T_n) (τ_{Tn}) are estimated from the efficiency dependence of the quenching of PP(T_n) by quencher (Q) on the Q concentration at room temperature. The quenching mechanism of PP(T_n) by Q is discussed. The structures of PP and Q used in this study are shown in Scheme 1.

SCHEME 1: Structures of Polyphenyls (PP) and Quenchers (Q) used in this Study



Experimental Section

Materials. Biphenyl (BP), *p*-terphenyl (TP), 1,3,5-triphenylbenzene (TPB), and benzophenone were purchased from Nacalai Tesque Inc. and recrystallized from ethanol before use. Carbon tetrachloride (CCl_4), dichloromethane (CH_2Cl_2), and 1,2-dichloroethane (DCE) were purchased from Wako Chem. Co. Hexane, cyclohexane, and methylcyclohexane were purchased from Nacalai Tesque Inc. All liquid compounds were spectral grade. Sample solutions were freshly prepared in a 1 cm × 1 cm × 4 cm rectangular Suprasil cell and deoxygenated by bubbling with argon (Ar) gas for 20 min before irradiation. All experiments were carried out at room temperature.

Nanosecond−Nanosecond Two-Color Two-Laser Flash Photolysis. The laser flashes at 266 and 355 nm were obtained

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TABLE 1: Properties of Polyphenyls[a]

PP	E_{S_1} (kJ/mol)	τ_{S_1} (ns)	ϕ_T	E_{T_1} (kJ/mol)	τ_{T_1} (μs)	IP (eV)	$E_{1/2}^{ox}$ (V)[b]	$E_{1/2}^{red}$ (V)	absorption peaks[c] radical cation (nm)	absorption peaks[c] radical anion (nm)
BP	418	16	0.84	274	130	7.95	+1.17	−2.55	365, 387, 703	380, 396, 408, 655
TP	385	0.95	0.11	244	450	7.78	+1.05	−2.57	426, 462, 965	445, 483, 906
TPB	375	42.6	−	269	−	−	−	−2.68	343, 394, 605, 1150	354, 410, 555, 1190

[a] PP, polyphenyls; BP, biphenyl; TP, *p*-terphenyl, TPB, 1,3,5-triphenylbenzene; E_{S_1}, S_1 state energy; τ_{S_1}, S_1 state lifetime; ϕ_T, intersystem crossing quantum yield from the S_1 state to the T_1 state; E_{T_1}, T_1 state energy; τ_{T_1}, T_1 state lifetime; IP, adiabatic ionization potential; $E_{1/2}^{ox}$, oxidation potential; $E_{1/2}^{red}$, reduction potential. All data are from Murov et al.[11] [b] $E_{1/2}^{ox} = 0.705 \times \text{IP} - 4.43$.[7] [c] Shida.[12]

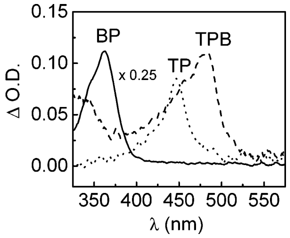


Figure 1. Transient absorption spectra obtained at 100 ns after a laser flash (3 mJ pulse^{-1}) during the 266 nm laser flash photolysis of BP (a) (solid line), TP (b) (dotted line), and TPB (c) (broken line) in Ar-saturated cyclohexane. The concentrations of BP, TP, and TPB were 1.5×10^{-4}, 4.2×10^{-5}, and 5.0×10^{-5} M, respectively.

from Nd:YAG lasers (Continuum, Surelite II-10 and Quantel, Brilliant). The diameter of the laser flash was 0.5 cm and the duration was 5 ns. The laser flashes at 450 (7 mJ pulse^{-1}) and 480 nm (9 mJ pulse^{-1}) were obtained from an OPO laser (Continuum, Surelite OPO) pumped by a Nd:YAG laser (355 nm, 150 mJ pulse^{-1}). The delay time of the second laser flash (355, 450, or 480 nm) after the first laser flash (266 or 355 nm) was set in the range of 10 ns to 10 μs by a four channel digital delay/pulse generator (Stanford Research Systems, Inc., Model DG 535). Two laser beams were overlapped through the sample. The probe light was obtained from a 450 W Xe lamp (Osram XBO-450) with a perpendicular intersection of the laser beams and then focused on a monochromator (Nikon G250). 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, 1 GHz). A Hamamatsu Photonics multichannel analyzer (C5967) system was used for measurement of the transient absorption spectra. The total system was controlled with a personal computer via a GP-IB interface. To avoid any damage to the sample solution by the probe light, a suitable cutoff filter was used in front of the sample.

Results and Discussion

Fast Internal Conversion of PP(T_n) to PP(T_1). The absorption spectra with peaks at 361, 445, and 480 nm were observed during the 266 nm laser (3 mJ pulse^{-1}) irradiation of BP, TP, and TPB, respectively, in Ar-saturated cyclohexane and are assigned to PP in the lowest triplet excited states (T_1) (Figure 1).[10,11] It is obvious that the absorption peak of the BP(T_1), TP(T_1), and TPB(T_1) is red shifted with the increase in the number of phenyl rings.

For generation of BP(T_n), BP(T_1) generated from the efficient intersystem crossing ($\phi_T = 0.84$) was excited by the second 355 nm YAG laser at 100 ns after the first 266 nm YAG laser flash. For generation of TP(T_n) and TPB(T_n), 450 and 480 nm OPO laser flashes were used as the second laser, respectively, to excite TP(T_1) and TPB(T_1) generated by the sensitization with benzophenone(T_1) during the 355 nm first YAG laser flash photolysis. The 266 nm excitation generates TP(S_1) and TPB(S_1), which are not desired to study the transient phenomena of TP(T_n) and TPB(T_n). The delay time for the second laser irradiation was 400 ns after the first laser in the case of TP and TPB. During the second laser irradiation of PP(T_1), no transient absorption change was observed (Figure 2b). Similar results were observed when cyclohexane was replaced by other nonpolar solvents, such as hexane and methylcyclohexane. This result indicates that no ionization from PP(T_n) occurred, but that fast internal conversion from PP(T_n) to PP(T_1) occurred in nonpolar solvents.

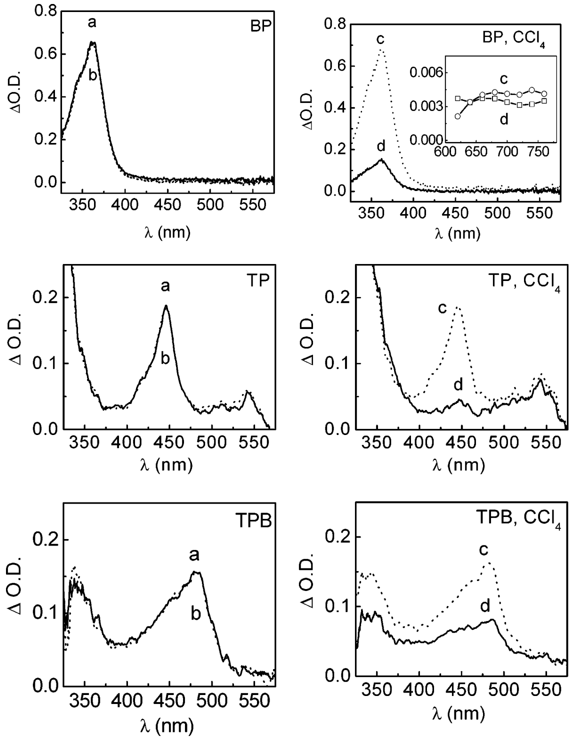


Figure 2. Transient absorption spectra of BP, TP, and TPB observed at 200, 500, and 500 ns, respectively, after the first laser irradiation (a) and at 100, 100, and 100 ns, respectively, after the second laser irradiation (b) during the ns−ns two-color two-laser flash photolysis of BP, TP, and TPB, respectively, in Ar-saturated cyclohexane at room temperature (left). In the absence of Q (c), and in the presence of 0.5 M CCl_4 (d), during the ns−ns two-color two-laser flash photolysis of PP. In the cases of TP and TPB, benzophenone was used as the triplet sensitizer (right).

Bimolecular Triplet Energy Transfer Quenching of PP(T_n) by RCl. In the presence of an electron acceptor such as CCl_4 in nonpolar solvents, the bleaching of the transient absorption of BP(T_1), TP(T_1), and TPB(T_1) ($\Delta\Delta$O.D.) was observed within the second laser flash (Figure 2d). The $\Delta\Delta$O.D. values increased with increasing CCl_4 concentration (Figure 3). No absorption peak assigned to $BP^{\bullet+}$, $TP^{\bullet+}$, and $TPB^{\bullet+}$ (Table 1) was observed.[12] On the other hand, when other chloroalkanes (RCl), such as CH_2Cl_2 and DCE, were used in place of CCl_4,

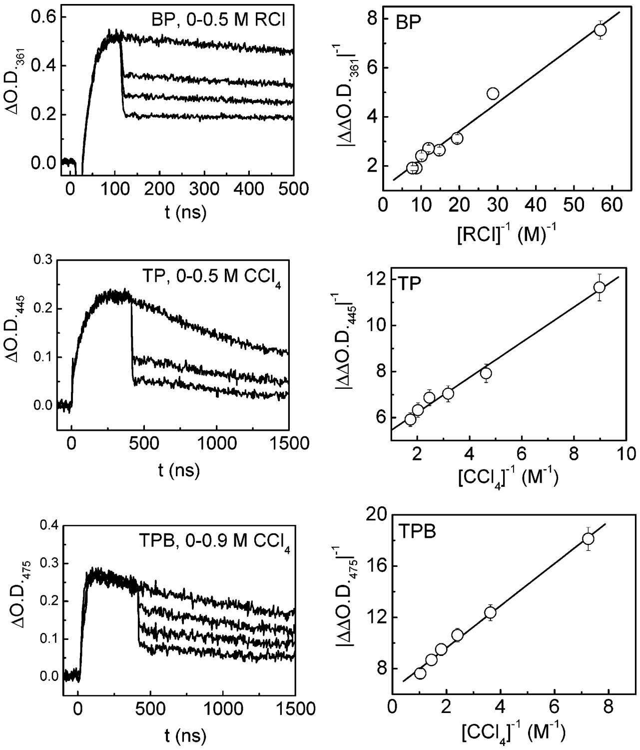


Figure 3. Kinetic traces of ΔO.D. of BP(T_1) at 361 nm, TP(T_1) at 445 nm, and TPB(T_1) at 475 nm in the absence and in the presence of various concentrations of RCl during the ns−ns two-color two-laser flash photolysis of PP in Ar-saturated cyclohexane (left), and the plots of $|\Delta\Delta\text{O.D.}|^{-1}$ vs $[\text{RCl}]^{-1}$ (right). The minus signal of the transient absorption of BP(T_1) observed immediately after the first laser flash is attributed to the fluorescence of BP(S_1). The growth of the transient absorption at 361 nm is attributed to the intersystem crossing from BP(S_1) to BP(T_1). The growth of the transient absorptions at 445 and 475 nm are attributed to the triplet−triplet energy transfer from benzophenone(T_1) to TP and TPB to give TP(T_1) and TPB(T_1).

similar bleaching was observed for the transient absorption of BP(T_1) and TP(T_1), but not for TPB(T_1). It is known that CCl_4, CH_2Cl_2, and DCE are all strong electron acceptors.[13,14] If a bimolecular electron transfer (ELT) reaction between PP(T_n) and RCl would occur, ΔΔO.D., together with the formation of the transient absorption of $PP^{\bullet+}$, could be observed in all the cases of the quenching of PP(T_n) by CCl_4, CH_2Cl_2, and DCE. Therefore, no ELT occurred, but triplet energy transfer (TENT) quenching of PP(T_n) by RCl did occur, followed by the PP(T_n)-sensitized C−Cl bond cleavage (as discussed in the following section).[9]

Lifetimes of PP(T_n). Based on the energy transfer from PP(T_n) to RCl, the lifetime of PP(T_n) (τ_{Tn}) can be calculated from the relationship between ΔΔO.D. and RCl concentration ([RCl]) using eqs 1−3,[14−17]

$$|\Delta\Delta\text{O.D.}|^{-1} = \beta + \beta(k_{\text{TENT}}\tau_{\text{Tn}}[\text{RCl}])^{-1} \tag{1}$$

$$k_{\text{TENT}} = k_{\text{diff}} + k_{\text{diff}}\,\sigma'/(\pi D\tau_{\text{Tn}})^{1/2} \tag{2}$$

$$k_{\text{diff}} = 4\pi N\sigma' D \tag{3}$$

where β is a constant depending on the experimental condition, τ_{Tn} is the lifetime of PP(T_n), k_{TENT} is the rate constant of TENT from PP(T_n) to RCl, N is Avogadro's number, σ' is the reaction distance, and D is the sum of the diffusion coefficients of PP(T_n) and the quencher molecule.[7] According to eq 1, the Stern−Volmer plots of $|\Delta\Delta\text{O.D.}|^{-1}$ vs $[\text{RCl}]^{-1}$ gave a linear line with an intercept of β and slope of $\beta(k_{\text{TENT}}\tau_{\text{Tn}})^{-1}$ (Figure 3). The τ_{Tn} values of BP(T_n), TP(T_n), and TPB(T_n) were calculated to be 950, 620, and 360 ps, respectively, with an assumption of $\sigma' = 0.6$ nm.[9,16,17] Because rapid internal conversion occurs completely from PP(T_n) to PP(T_1), τ_{Tn} depends on the energy gap between the T_1 and T_n states, $\tau_{Tn}^{-1} = k_{IC} \approx 10^{13} \exp(-\alpha\Delta E_{T_n-T_1})$, where α and k_{IC} are a constant and the rate constant of the internal conversion, respectively. Therefore, the τ_{Tn} and $\Delta E_{T_n-T_1}$ values decrease with increasing ring numbers, BP(T_n) > TP(T_n) > TPB(T_n).

Mechanism of Bimolecular Quenching of PP(T_n) by RCl. Based on the high bleaching ratio (70−90%) of the PP(T_1) absorption, the quenching of PP(T_n) by RCl efficiently occurred. Neither the PP radical cation ($PP^{\bullet+}$) nor the PP radical anion ($PP^{\bullet-}$) was observed, even when RCl was used as the solvent of the transient absorption measurements. Since the transient absorption spectra of $PP^{\bullet+}$ or $PP^{\bullet-}$ are entirely different from those of PP(T_1) and molar absorption coefficients (ϵ) of the absorption peaks of $PP^{\bullet+}$ or $PP^{\bullet-}$ are sufficiently high,[12] those radical ions can be easily detected. For example, the ϵ of $BP^{\bullet+}$ at 365, 387, and 703 nm are 9×10^3, 8×10^3, and 4.5×10^3 $M^{-1}cm^{-1}$, respectively.[8] Furthermore, TPB(T_n) was not quenched when CCl_4 was replaced by CH_2Cl_2 or DCE, despite the high electron acceptability.[14,15] Therefore, these results clearly indicate that an electron transfer (ELT) reaction from PP(T_n) to RCl does not occur. Similar experimental results to those of PP(T_n) have been reported in the cases of several fused aromatic hydrocarbons in the T_n state.[9]

The ELT from PP(T_n) to RCl would involve the dissociative ELT to cause the C−Cl bond cleavage of RCl, giving an R radical and a chloride ion. Recently, "sticky" dissociative ELT theory has been developed to describe such types of ELT.[18−20] For example, the electrochemical reductive cleavage of CCl_4 in *N*,*N*′-dimethylformamide (DMF) reveals that electron transfer and bond breaking are concerted.[18] According to the "sticky" dissociative ELT theory, the activation energy ($\Delta G^{\ddagger}$) of ELT is represented as eq 4

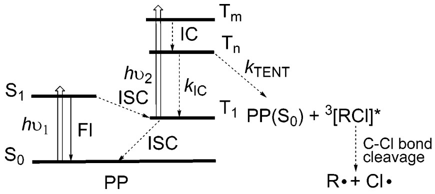
$$\Delta G^{\ddagger} = [((D_{\text{R}}^{1/2} - D_{\text{p}}^{1/2})^2 + \lambda)/4] \times [1 + (\Delta G - D_{\text{p}})/((D_{\text{R}}^{1/2} - D_{\text{p}}^{1/2})^2 + \lambda)]^2 \tag{4}$$

where D_R is the bond dissociation energies, D_p is the interaction energy of the radical−ion pair, λ is the total reorganization energy, and ΔG is the overall free energy changes. The ELT reaction rate constant (k_{ELT}) is expressed as eq 5

$$1/k_{\text{q}} = 1/k_{\text{diff}} + 1/k_{\text{ELT}} \tag{5}$$

where k_q is the experimental measured rate constant and k_{diff} is the diffusion-controlled rate constant. The D_R values of the C−Cl bond are 3.17 eV for CCl_4,[21] 3.25 eV for CH_2Cl_2,[22] and 3.52 eV for DCE.[23] Such large D_R values cause the substantial decrease in the ELT rate ($k_{ELT} < 10^8\ M^{-1}\ s^{-1}$).[9,24,25] The ELT from PP(T_n) to RCl may occur competitively with other rapid processes, such as internal conversion and TENT with the rate constant of $k_{TENT} = k_{diff}$, when the free energy change ($-\Delta G_{TENT}$) is larger than 13 kJ mol^{-1}.[26,27] From the E_{T1} values of PP(T_1) in Table 1 and the transient absorption edge of PP(T_1), the T_n state energies of PP(T_n) ($E_{PP(Tn)}$) were calculated to be 555, 483, and 486 kJ mol^{-1} for BP(T_n), TP(T_n), and TPB(T_n) (these calculated $E_{PP(Tn)}$ values correspond to PP(T_m) ($E_{PP(Tm)}$) in Scheme 2, see the below discussion), respectively, which are much larger than the D_R values of the C−Cl bond of RCl. Consequently, the occurrence of the TENT from PP(T_n) to RCl at k_{diff} is much faster than the ELT from PP(T_n) to RCl.[9]

SCHEME 2: Energy Level Diagram of PP and Transient Phenomena of PP(T_n) during the Two-Color Two-Laser Flash Photolysis[a]



[a] $h\nu_1$ and $h\nu_2$: the first and second laser excitation, Fl: fluorescence, IC: internal conversion, ISC: intersystem crossing, k_{IC} and k_{TENT}: the rate constants of IC and triplet energy transfer from PP(T_n) to RCl, respectively.

The TENT depends on the $E_{PP(Tn)}$ and D_R values. In the case of CCl_4, as Q for the TENT quenching of PP(T_n), $E_{PP(Tn)}$ is sufficiently high for the occurrence of the C−Cl bond cleavage. On the other hand, in the case of CH_2Cl_2 or DCE, as Q for TPB(T_n), no C−Cl bond cleavage occurred (no ΔΔO.D. of TPB(T_1) was observed), although the $E_{TPB(Tn)}$ values are higher than the D_R values of the C−Cl bond cleavage according to the above analysis. No occurrence of the C−Cl bond cleavage in the case of CH_2Cl_2 or DCE as Q for the TENT quenching of TPB(T_n) indicates that TPB(T_n, $2 \leq n < m$) with $\tau_{Tn} = 360$ ps is generated from fast internal conversion of the initially generated TPB(T_m) with very short lifetimes during the 480 nm laser irradiation. From the D_R values of CCl_4, CH_2Cl_2, and DCE, the $E_{TPB(Tn)}$ value of TPB(T_n) with $\tau_{Tn} = 360$ ps should be in the range of 306−314 kJ mol^{-1} (3.17−3.25 eV). Therefore, the energy gap between TPB(T_1) and TPB(T_n) is approximately 40 kJ mol^{-1}. It is obvious that the α value (<5 eV^{-1}), used for fused aromatic hydrocarbons(T_n) with $\tau^{-1} = k_{IC} \approx 10^{13} \exp(-\alpha\Delta E)$,[9,26] cannot be essentially used for PP(T_n) because of the large structural change between PP(S_0) and PP(T_n). The structure of PP(S_0) is nonplanar and twisted between benzene rings, while those of PP(T_1) are assumed to be planar.[1,2,5,6] Because of the short lifetimes of PP(T_n), the planar structures similar to those for PP(T_1) are reasonably assumed for PP(T_n).

Although $\sigma' = 0.6$ nm[9,16,17] was used to calculate the τ_{Tn} values of PP(T_n), the real σ' value may be much smaller than $\sigma' = 0.6$ nm in eqs 2 and 3 for PP(T_n). If so, the calculated τ_{Tn} values of PP(T_n) are longer than the real τ_{Tn} values.[28] Therefore, direct measurement of the τ_{Tn} value of PP(T_n) is desired to be carried out using the second picosecond laser, although such a laser is not available at present. Similar processes are expected in the cases of the TENT quenching of BP(T_n) and TP(T_n). The energy levels and quenching mechanism of PP(T_n) are shown in Scheme 2.

Before PP(T_1) decays into PP(S_0), PP(T_1) is excited with the second laser ($h\nu_2$) to generate PP(T_m), from which the fast internal conversion occurs to give PP(T_n) with the longest lifetime. Since the τ_{Tn} value of PP(T_n) is sufficiently long for bimolecular reactions to occur, bimolecular TENT from PP(T_n) to RCl and PP(T_n)-sensitized C−Cl bond cleavage occur in the presence of RCl with the dependence on the $E_{PP(Tn)}$ and D_R values.

Conclusions

Quenching of PP(T_n) such as BP(T_n), TP(T_n), and TPB(T_n) by RCl has been studied using the ns−ns two-color two-laser excitation method. In the presence of an electron acceptor such as CCl_4, efficient bleaching of the transient absorption of PP(T_1) was observed with no recovery of PP(T_1) during the second laser irradiation. The experimental results indicate the occurrence of the quenching of PP(T_n) without reproduction of PP(T_1). Neither a radical cation nor a radical anion of PP was observed, indicating that no ELT from PP(T_n) to RCl occurs. According to the dissociative ELT theory, the ELT rate from PP(T_n) to RCl could occur too slowly to be detected. The main quenching pathway of PP(T_n) by RCl is TENT. TENT from PP(T_n) to RCl and PP(T_n)-sensitized C−Cl bond cleavage of RCl occur with the dependence on the $E_{PP(Tn)}$ and D_R values. The τ_{Tn} values of BP(T_n), TP(T_n), and TPB(T_n) were estimated to be 950, 620, and 360 ps, respectively, from the RCl concentration dependence on the TENT quenching of PP(T_n) by RCl.

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