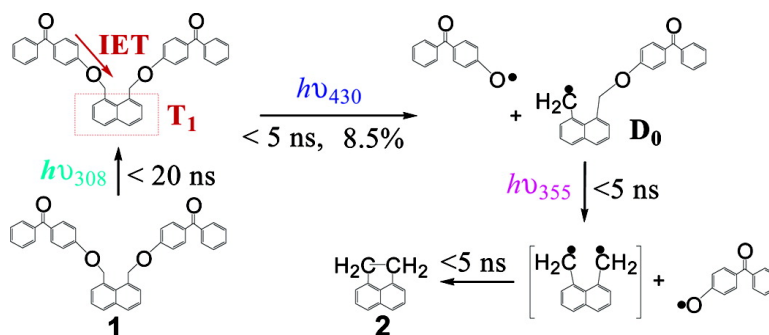


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Stepwise Photocleavage of Two C–O Bonds of 1,8-Bis[(4-benzoylphenoxy)-methyl]naphthalene with Three-Step Excitation Using Three-Color, Three-Laser Flash Photolysis

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Photoexcitation provides excitation energy for a molecule in which one bond can decompose depending on the characteristic of the excited state during a one-photon excitation process. On the other hand, two equivalent bonds in a molecule can be cleaved by two-photon processes through a concerted or stepwise mechanism. For example, a one carbon–chloride (C–Cl) bond cleavage occurred during low-intensity laser irradiation, while concerted two C–Cl bond cleavages occurred under high-intensity laser irradiation during the photolysis of 1,3-dichloro-1,3-diphenylpropane.¹ However, there are a few reports showing clear evidence of the stepwise cleavage of two equivalent bonds in a molecule. The two-color, two-laser or the three-color, three-laser flash photolysis technique is a powerful tool for studying the photochemistry of reactive intermediates such as radicals and radical ions generated from the preceding laser irradiation.^{1,2} This technique allows us to study stepwise cleavage of two equivalent bonds in a molecule. To provide clear evidence for the stepwise photocleavage of two equivalent bonds in a molecule, we report here two C–O bond cleavages of 1,8-bis[(4-benzoylphenoxy)methyl]naphthalene (1,8-(BPO–CH₂)₂Np, **1**) to give acenaphthene (**2**) with a three-step excitation using three-color, three-laser flash photolysis. Previously, it has been reported that **2** is efficiently produced by the laser irradiation of **1** or 1,8-bis(X–CH₂)₂naphthalene (X = Cl, Br, PhS, PhSe, and PhO) through two C–X bond cleavages,^{3,4} in which a two-photon process is assumed, but the reaction mechanism is still unclear.

A three-step, selective excitation was performed by the first (308 nm), second (430 nm), and third (355 nm) laser irradiations. The first selective excitation of the 4-benzoylphenyl group (BP) of **1** caused an intramolecular triplet energy transfer from BP(T₁) to the naphthyl group (Np) giving **1** in the lowest triplet state **1**(T₁). The second selective excitation of the Np(T₁) of **1**(T₁) caused formation of the naphthylmethyl radical (1-(BPO–CH₂)NpCH₂[•]) due to the first C–O bond cleavage. The third selective excitation of 1-(BPO–CH₂)NpCH₂[•] caused the formation of the biradical (1,8-([•]CH₂)₂-Np) due to the second C–O bond cleavage.

A transient absorption spectrum was observed during the 308 nm laser irradiation (5 mJ pulse⁻¹, 20 ns) of **1** (6.8 × 10⁻⁵ M) in Ar-saturated acetonitrile (ACN) at room temperature (Figure 1a). Absorption peaks at 400 and 425 nm were assigned to **1**(T₁), whose energy was localized at Np similar to the case of the previously reported monosubstituted 1-(BPO–CH₂)Np.^{5,6} The formation of **1**(T₁) was explained by the selective excitation of the BP of **1**(S₀) to S₁, which converted into T₁ in 100% yield,⁷ followed by an intramolecular triplet energy transfer from BP(T₁) to Np(S₀), producing Np(T₁) in 100% yield. No new peak was observed during

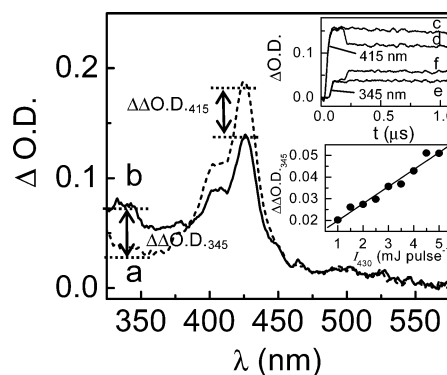


Figure 1. Transient absorption spectra obtained at 300 ns after the first (308 nm) laser (a, broken line) and at 100 ns after the second (430 nm) laser (b, solid line) during the laser flash photolysis of **1** in Ar-saturated ACN. The delay time of the two lasers was 200 ns. The inset (above) shows the time profiles of transient absorptions obtained at 415 and 345 nm during one-laser irradiation at 308 nm (c and e) and two-laser irradiation at 308 and 430 nm (d and f). The growth of the transient absorption in the time scale of a few tens ns was due to the formation of **1**(T₁) through intramolecular triplet energy transfer from BP(T₁) to Np. The inset (below) shows the plots of $\Delta\Delta\text{OD}_{345}$ of **1** vs 430 nm laser intensity (I_{430}).

the disappearance of **1**(T₁), suggesting that no reaction including the C–O bond cleavage occurred from **1**(T₁). The absence of the C–O bond cleavage can be rationalized by the large dissociation energy of the C–O bond (285 kJ mol⁻¹) compared with the triplet energy of **1**(T₁) (254 kJ mol⁻¹).^{5,7}

Immediately after the second (430 nm laser, 7 mJ pulse⁻¹) flash, the formation of a transient absorption band around 345 nm and bleaching of the peaks of **1**(T₁) at 400 and 425 nm were observed (Figure 1b). Because **1**(S₀) has no absorption at 430 nm, only **1**(T₁) was excited to give **1**(T_n) during the second (430 nm) laser irradiation. The bleaching of ΔOD_{415} ($\Delta\Delta\text{OD}_{415}$) during the second laser irradiation indicates the decrease in **1**(T₁) due to the occurrence of some reactions from **1**(T_n) without reproduction of **1**(T₁). From the comparison with the reported absorption spectrum of 1-NpCH₂[•], the absorption around 345 nm was assigned to 1-(BPO–CH₂)NpCH₂[•].^{5,6} These results reasonably show that the T_n state energy is higher than the C–O bond dissociation energy, and by analogy with our previous report,⁶ it delocalizes in the molecule including the C–O bonds. A linear line was obtained for the plots of $\Delta\Delta\text{OD}_{345}$ vs the 430 nm laser intensity (I_{430}) with a constant intensity of the first (308 nm laser, 5 mJ pulse⁻¹) (Figure 1, inset (below)). This result indicates that 1-(BPO–CH₂)NpCH₂[•] was produced by a one-photon process from **1**(T₁). The quantum yield (Φ) of the formation of 1-(BPO–CH₂)NpCH₂[•] from the photo-reaction of **1**(T₁) was calculated to be 0.085 ± 0.004 from the slope

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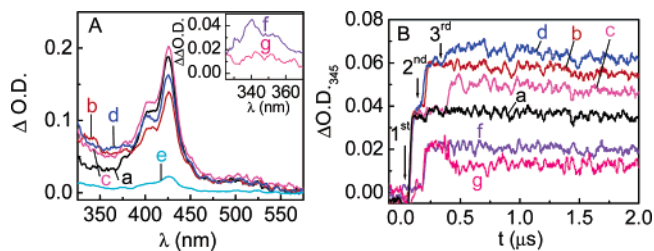


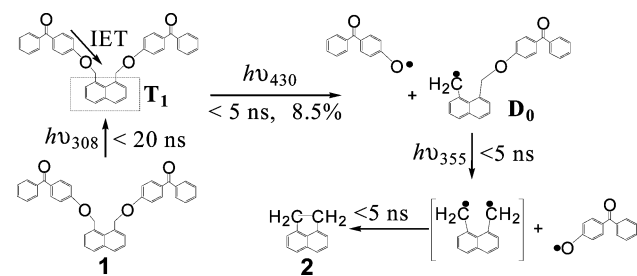
Figure 2. Three-color, three-laser photolysis of **1** (A, spectra; B, time profiles detected at 345 nm) in Ar-saturated ACN. The transient spectra observed during the irradiation of a 308 nm laser (at 500 ns after the laser pulse) (a), successive irradiation with 308 and 430 nm lasers (at 300 ns after the second laser pulse; delay time between the two lasers: 200 ns) (b), successive irradiation of 308 and 355 nm lasers (at 100 ns after the second laser pulse; delay time between the two lasers: 400 ns) (c), successive irradiation of 308, 430, and 355 nm lasers (at 100 ns after the third laser pulse; delay time between the lasers: 200 and 200 ns) (d), irradiation of a 355 nm laser (at 100 ns after the laser pulse) (e). The inset in A shows the spectra b – a (f) and d – c (g). In panel B, 1st, 2nd, and 3rd refer to the irradiation sequence order of 308, 430, and 355 nm lasers, respectively.

of the linear plots depicting the formation of ΔOD_{345} within a laser flash duration of 5 ns (ΔOD_{345}) vs I_{430} . It was found that the Φ value was 2-fold greater than that for the formation of 1-NpCH_2^* from $1\text{-}(\text{BPO}-\text{CH}_2)\text{Np}(\text{T}_n)$ (0.042 ± 0.004).⁶ According to our previous results on the lifetime (4.5 ps) of naphthalene(T_n),⁸ the T_n state energy of $\text{Np}(\text{T}_n)$ in **1**(T_n) was calculated to be 385 kJ mol^{-1} , which was higher than the C–O bond dissociation energy of 285 kJ mol^{-1} but not enough for the concerted cleavage of two C–O bonds. Therefore, it is suggested that only one C–O bond cleavage is possible from **1**(T_n), but with a 2-fold higher yield for the C–O bond cleavage compared with that of $1\text{-}(\text{BPO}-\text{CH}_2)\text{Np}(\text{T}_n)$. Consequently, one C–O bond cleavage with two-step, two-photon excitation is necessary for the formation of $1\text{-}(\text{BPO}-\text{CH}_2)\text{NpCH}_2^*$ from **1**(S_0).

Because $1\text{-}(\text{BPO}-\text{CH}_2)\text{NpCH}_2^*$ has an absorption at 355 nm, the third (355 nm, 10 mJ pulse^{-1}) laser irradiated $1\text{-}(\text{BPO}-\text{CH}_2)\text{NpCH}_2^*$ 200 ns after the second (430 nm) laser irradiation. The results of the three-color, three-laser photolysis of **1** are shown in Figures 2A and B.

The transient absorption spectrum of $1\text{-}(\text{BPO}-\text{CH}_2)\text{NpCH}_2^*$ was obtained by the subtraction of the spectrum observed after the first (308 nm) laser irradiation (a) from that after the first (308 nm) and the second (430 nm) laser irradiations (b), (b – a). The change in the transient absorption of $1\text{-}(\text{BPO}-\text{CH}_2)\text{NpCH}_2^*$ during the third (355 nm) laser irradiation was obtained after the subtraction of the spectrum obtained after the first (308 nm) and third (355 nm) laser irradiations (c) from that after the first (308 nm), second (430 nm), and third (355 nm) laser irradiations (d), (d – c). Bleaching of the transient absorption at 345 nm during the third (355 nm) laser irradiation was clearly observed. Results similar to those for **1** were observed for $1,4\text{-}(\text{BPO}-\text{CH}_2)_2\text{Np}$. However, bleaching of the transient absorption of 1-NpCH_2^* at 365 nm was not observed during the three-color, three-laser photolysis of $1\text{-}(\text{BPO}-\text{CH}_2)\text{Np}$ (Supporting Information). This result indicates that the third (355 nm) laser intensity (10 mJ pulse^{-1}) was not sufficiently high for the two-photon ionization of 1-NpCH_2^* to give 1-NpCH_2^{+} .⁹ It is clear that 1-NpCH_2^* in the excited state (D_n) decays to $1\text{-NpCH}_2^*(\text{D}_0)$ in 100% yield. These results indicate that $1\text{-}(\text{BPO}-\text{CH}_2)\text{NpCH}_2^*(\text{D}_0)$ was excited by the third (355 nm) laser flash to give $1\text{-}(\text{BPO}-\text{CH}_2)\text{NpCH}_2^*(\text{D}_n)$ from which no ionization occurred. Since **2** is produced as the final product in the photolysis of **1**, the bleaching of the transient absorption at 345 nm observed during the third (355 nm) laser irradiation is due to the C–O bond cleavage from

Scheme 1. Three-Color Three-Laser Flash Photolysis of **1** in Ar-Saturated ACN^a



^a Dotted squares show the excitation energy location. IET: intramolecular energy transfer.

$1\text{-}(\text{BPO}-\text{CH}_2)\text{NpCH}_2^*(\text{D}_n)$. It is suggested from a previous report⁶ that the molecular orbital of the D_n state is delocalized not only on the Np chromophore but also on the C–O σ orbital. Formation of **2** from $1\text{-}(\text{BPO}-\text{CH}_2)\text{NpCH}_2^*(\text{D}_n)$ may be explained by the radical backside attack mechanism or the second C–O bond cleavage to give the $1,8\text{-}(\text{CH}_2)_2\text{Np}$ biradical, which rapidly cyclizes to form **2**. However, since similar results were observed for $1,4\text{-}(\text{BPO}-\text{CH}_2)_2\text{Np}$, the formation of **2** is most likely explained by the $1,8\text{-}(\text{CH}_2)_2\text{Np}$ biradical mechanism. The absorption of $1,8\text{-}(\text{CH}_2)_2\text{Np}$, which was reported to appear at 500 nm,¹⁰ was not observed probably due to the small absorption coefficient, the formation of $1,8\text{-}(\text{CH}_2)_2\text{Np}$ at a low concentration, and fast cyclization of $1,8\text{-}(\text{CH}_2)_2\text{Np}$ that occurred within the laser duration (5 ns). The mechanism of the three-color, three-laser photochemistry of **1** to give **2** is shown in Scheme 1.

In summary, the stepwise cleavage of two C–O bonds in **1** occurred by the three-step excitation using the three-color, three-laser flash photolysis technique. The first C–O bond cleavage occurred under the first (308 nm) and second (430 nm) laser irradiations to give $1\text{-}(\text{BPO}-\text{CH}_2)\text{NpCH}_2^*(\text{D}_0)$ with a Φ value of 0.085 ± 0.004 . Subsequent cleavage of the second C–O bond occurred when $1\text{-}(\text{BPO}-\text{CH}_2)\text{NpCH}_2^*(\text{D}_0)$ was excited to $1\text{-}(\text{BPO}-\text{CH}_2)\text{NpCH}_2^*(\text{D}_n)$ under the third (355 nm) laser irradiation. This is the first report showing clear evidence of stepwise cleavage of two equivalent bonds in a molecule during the three-step, selective excitation.

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Supporting Information Available: Three-color, three-laser photolysis of $1\text{-}(\text{BPO}-\text{CH}_2)\text{Np}$ and $1,4\text{-}(\text{BPO}-\text{CH}_2)_2\text{Np}$ (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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