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A Kinetic Study on the Spin Polarization Switching of Benzil in the Presence of Triethylamine

Tetsuo Okutsu,* Masaki Ooyama, Katsuhiko Tani, and Hiroshi Hiratsuka
Department of Chemistry, Gunma University, Kiryu Gunma 376-85l5, Japan

Akio Kawai
Department of Chemistry, Tokyo Institute of Technology, 2-12-1 Ohokayama, Meguro-ku,
Tokyo 152-8551, Japan

Kinichi Obi
Department of Chemical and Biological Sciences, Japan Women's University, Mejirodai, Bunkyo-ku,
Tokyo, 112-8681, Japan

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Dual spin polarization of CIDEP signal of radicals produced in benzil/triethylamine in the benzene system was investigated by the time-resolved ESR and transient absorption technique. CIDEP signals showed absorption or emission depending on the concentration of triethylamine. Emissive CIDEP signal was observed below 10^{-3} M of triethylamine, whereas absorptive signal was observed above 10^{-1} M. The dual CIDEP signal was explained by the triplet mechanism (TM) and the radical−triplet pair mechanism (RTPM); the absorptive polarized TM signal was generated from the reaction of free triplet benzil with triethylamine, whereas the emissive polarized CIDEP signal was generated through the interaction between triplet benzil and benzil ketyl radical produced from the benzil−triethylamine complex.

Introduction

Benzil is a typical α-dicarbonyl molecule. Many studies on the photochemical reactions have been reported on benzil. The photochemical reactions of benzil have been studied by flash photolysis[1,2] and time-resolved ESR.[3−5] Benzil has attracted our attention because the CIDEP signals of produced radicals show dual spin polarization in the presence of various amines and phenols. For example, spin polarization of benzil ketyl and counter radicals produced in the benzil/aniline system is inverted twice depending on the concentration of quenchers, net emission at 1×10^{-3} M of aniline, net absorption at 1×10^{-1} M, and again inverted to emission at 10 M.[3]

It is well-known that benzil has two rotational isomers.[6−8] These isomers have been thought to be responsible for the dual spin polarization of CIDEP. Several studies have been made on the conformations of benzil. Benzil in the ground state has a nonplanar (skew) conformation in which the central carbonyl−carbonyl bond is twisted at an angle of 111°.[9] Therefore, the two benzoyl moieties are not in conjugation with each other. In the first excited singlet state, benzil has a trans-planar conformation. Morants and Wright reported that the skew benzil relaxed to the trans-planar conformation after the excitation.[10] Miyasaka and Mataga reported that conformational relaxation in the S_1 state was completed within a few picoseconds,[11] though the lifetime of the S_1 state was fairly long (ca. 2 ns). The conformation of the triplet state (T_1) was reported to be identical to that of the S_1 state; i.e., the conformations in the S_1 and T_1 states are thought to be unique.[12,13] Therefore, the dual CIDEP signal must have nothing to do with the existence of rotational isomers.

In our previous study,[3] the dual spin polarization of benzil in the presence of amines or phenols was interpreted to result from two different precursors. Absorptive polarized radicals were formed in the reaction of free triplet benzil whose $\Delta m_s = 2$ transition was known to be absorptive in the low-temperature experiment.[3] Emissive polarized radicals were produced through the photoreaction of benzil-quencher complex formed in the ground state. Assuming that the excited triplet complex gave an emissive CIDEP signal by the triplet mechanism (TM), it was successfully demonstrated that the polarization inversion occurred twice by changing the quencher concentration.

In a benzene solution of benzil in the presence of triethylamine (TEA), spin polarization inversion was also observed.[14] The inversion, however, could not be explained by the above mechanism. The inversion occurred only once; emission was observed at a very low concentration of TEA ($<10^{-3}$ M) and absorption at a high concentration ($>10^{-1}$ M). Mukai et al. also demonstrated dual spin polarization in benzil/TEA in 2-propanol solution.[15] They concluded that the different electronic states of benzil yielded different intermediate species with opposite spin polarization. They assigned that the absorptive polarized radical was the benzil anion radical produced through a one photon process, while the emissive polarized radical was the benzil ketyl radical formed from the higher triplet state T_n through a two photon process. The spin sublevel population of T_n produced from a higher singlet state through intersystem crossing (ISC) was assumed to be different from that of T_1 generated from S_1. This T_n state was thought to react with the solvent 2-propanol and produced the emissive polarized ketyl radical.

Recently, the quartet-precursor radical-triplet pair mechanism (RTPM) was revealed to play an important role in the spin

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* Corresponding author. E-mail: okutsu@chem.gunma-u.ac.jp.

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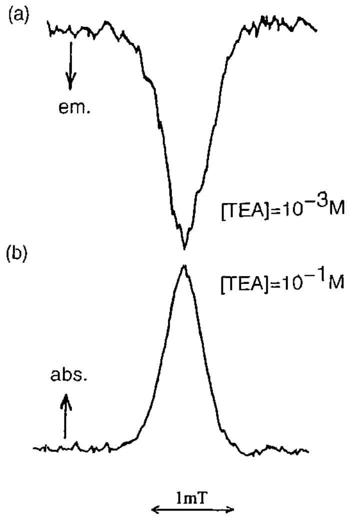

Figure 1. Concentration dependence of the CIDEP spectra on TEA obtained by laser photolysis in benzil (2 × 10^{-3} M)/TEA in benzene. Concentrations of TEA are (a) 1 × 10^{-3} M and (b) 10^{-1} M.

polarization.[16−18] Blättler and Paul reported that the benzil ketyl radical in 2-propanol solution was produced by a single-photon process from the lowest triplet and the two-photon process was via a higher triplet state. And they demonstrated that emissive polarization of benzil ketyl was due to RTPM.[19]

In this study, we have reinvestigated the switching mechanism of spin polarization in the photoreactions of benzil in the presence of TEA and revealed that, in addition to TM, RTPM also plays an important role in the spin polarization inversion; the net emissive CIDEP signal is due to RTPM, and the net absorptive signal is due to TM.

Experimental Section

Time-resolved ESR measurements were carried out using a Varian E-112 spectrometer at X-band without field modulation. Signals were accumulated in a boxcar integrator (Stanford SR-250). The gate of the boxcar was opened for 1.1−2.1μs after the laser pulse. An excimer laser (Lambda Physik LPX100) was used as an excitation light source. The details of the experimental apparatus for time-resolved ESR measurements were described previously.[20−22] For transient absorption measurements, a Nd^{3+}:YAG laser (Quanta-Ray GCR-130, 355 nm) was used as an excitation light source. The samples were flowed through a quartz cell with a flow rate of ca. 30 mL min^{-1}. A Unisoku TSP-601H laser system was used as signal detection.

GR grade benzil (Tokyo Kasei) was used in CIDEP and transient absorption experiments. GR grade triethylamine (Tokyo Kasei) was used without further purification. GR grade benzene (Kanto Kagaku) and GR grade 2-propanol (Kanto Kagaku) were used as solvents without further purification.

Results and Discussion

Figure 1 shows the CIDEP spectra obtained in laser photolysis of benzil in the presence of TEA. Benzene was used as a solvent. The spectrum in Figure la obtained at concentrations of 2.0 × 10^{-3} M benzil and l0^{-3} M TEA shows net emissive signals without hyperfine structure. This signal was assigned to the benzil ketyl radical. There is little difference in the *g*-values between the benzil ketyl radical and triethylamine radical, and thus, the net emissive CIDEP signal is produced by TM or RTPM. Figure lb shows a CIDEP spectrum obtained in the same system at a high concentration of TEA (0.1 M). The phase of CIDEP signal is inverted to absorption. According to TM, the polarization of produced radicals reflects that of the triplet precursor. Though the triplet state of benzil has absorptive character as known in the low-temperature experiments, the produced radicals in our system show both emissive and absorptive polarization depending on experimental conditions.

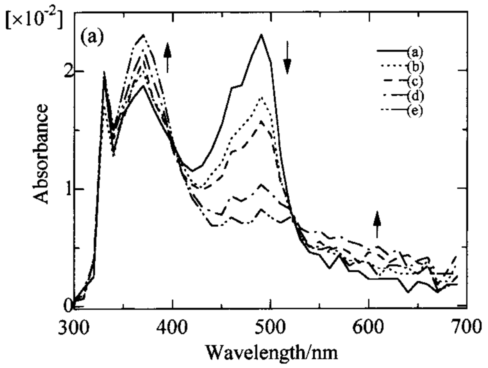

Figure 2. Transient absorption spectra obtained by laser photolysis in benzil (2 × 10^{-2} M)/TEA (5 × 10^{-4} M) in benzene at (a) 200, (b) 400, (c) 800, (d) 1600, and (e) 3200 ns after the laser pulse.

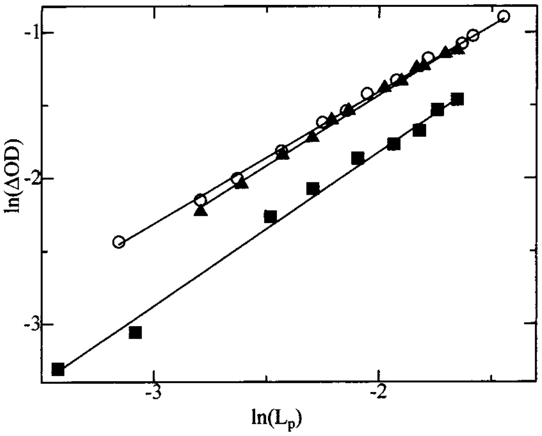

Figure 3. Laser power dependence of the production yield of benzil ketyl radical for (■) benzil anion radical, (○) benzil ketyl radical produced from the benzil/TEA system, and (▲) benzil ketyl radical produced from benzil in 2-propanol.

Transient absorption experiments were carried out to examine the generation mechanism of these radicals. Figure 2 shows the transient absorption spectra of the benzil in the presence of TEA in benzene. The spectrum obtained at 200 ns has peaks at 370 and 480 nm and a broad absorption around 600 nm. The peak at 480 nm is attributed to the T−T absorption of benzil, because the transient absorption spectrum of triplet benzil has a typical peak at 480 nm.[2] The peak at 370 nm is assigned to the benzil ketyl radical because the transient absorption spectrum of benzil ketyl radical shows a peak at 370 nm.[14] The longer wavelength transient absorption around 600 nm is ascribed to the benzil anion radical. We measured laser power dependence of the transient absorption signals of the ketyl and anion radicals in benzil/TEA in benzene and benzil in 2-propanol.

Figure 3 shows the logarithmic plots of the benzil ketyl and anion radicals vs laser power. Laser power dependencies gave slopes of 0.9 for the ketyl radical, 1.1 for the anion radical in the benzil/TEA system, and 1.1 for the ketyl radical in the benzil/2-propanol system. It is concluded that all radicals are produced through a one photon process with excitation at 355 nm. Since the laser power dependence on the CIDEP signal of the emissive polarized ketyl radical was 2, another photon should take part in the generation of the emissive spin polarization.

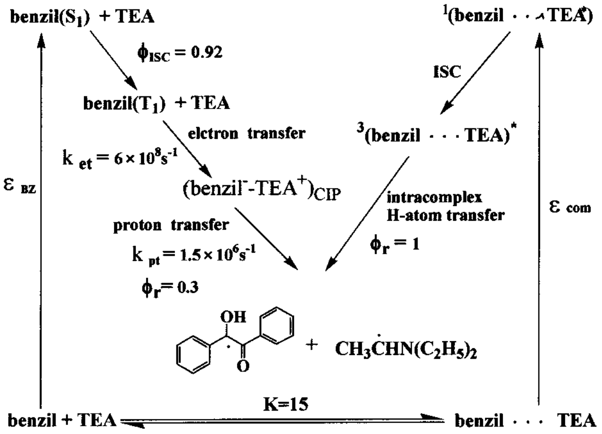

Figure 4. Reaction scheme to product benzil ketyl radical.

A detailed kinetic analysis was reported in the previous paper.[22] The whole reaction scheme and kinetic data in the benzil/TEA system are summarized in Figure 4. There is chemical equilibrium in the ground-state molecules,

$$\mathrm{B} + \mathrm{TEA} \overset{K}{\rightleftharpoons} \mathrm{B}\cdots\mathrm{TEA} \qquad (1)$$

where B is benzil and K is the equilibrium constant. Equilibrium constant K was obtained as ca. 15 M^{-1}.[22] Both chemical species, free benzil and its complex with TEA, are responsive to photoabsorption,

$$\mathrm{B} + h\nu \rightarrow {}^{1}\mathrm{B}^{*} \qquad (2)$$

$$(\mathrm{B}\cdots\mathrm{TEA}) + h\nu \rightarrow {}^{1}(\mathrm{B}\cdots\mathrm{TEA})^{*} \qquad (3)$$

and the singlet excited states of both species undergo intersystem crossing to the triplet states,

$${}^{1}\mathrm{B}^{*} \xrightarrow{\mathrm{ISC}} {}^{3}\mathrm{B}_{\mathrm{abs}}^{*} \qquad (4)$$

$${}^{1}(\mathrm{B}\cdots\mathrm{TEA})^{*} \xrightarrow{\mathrm{ISC}} {}^{3}(\mathrm{B}\cdots\mathrm{TEA})^{*} \qquad (5)$$

where the subscript "abs" represents absorption of spin polarization.

Free triplet benzil yields the contact ion pair (CIP) of benzil anion ($\mathrm{B}^{-}\cdots\mathrm{TEA}^{+}$), which decays with the rate constant of 1.5×10^{6} s^{-1} forming the ketyl radicals with absorptive polarization through TM.

$${}^{3}\mathrm{B}_{\mathrm{abs}}^{*} \xrightarrow{k_{\mathrm{sp}}} {}^{3}\mathrm{B}_{\mathrm{th}}^{*} \qquad (6)$$

$${}^{3}\mathrm{B}_{\mathrm{abs}}^{*} + \mathrm{TEA} \xrightarrow{k_{\mathrm{et}}} (\mathrm{B}^{-}\cdots\mathrm{TEA}^{+})_{\mathrm{abs}} \qquad (7)$$

$$(\mathrm{B}^{-}\cdots\mathrm{TEA}^{+})_{\mathrm{abs}} \xrightarrow{k_{\mathrm{pt}}} \mathrm{BH}_{\mathrm{abs}}^{\bullet} + \mathrm{TEA}^{\bullet} \qquad (8)$$

where ${}^{3}\mathrm{B}_{\mathrm{th}}^{*}$ is thermally distributed triplet benzil. k_{sp} is the spin relaxation rate of the triplet benzil which was measured as 1×10^{10} s^{-1} by optical induced magnetization.[23] k_{et} and k_{pt} are the CIP formation and proton-transfer rate constants, and their values are 6.0×10^{8} M^{-1} s^{-1} and 1.5×10^{6} s^{-1}, respectively. The decay of the triplet benzil is not needed to be included in the reaction scheme of the spin polarized ketyl formation due to the slow decay rate, 2.3×10^{4} s^{-1}, compared with spin relaxation rate. These kinetic parameters are listed in our previous study.[22] The rate equations for the above scheme are expressed as

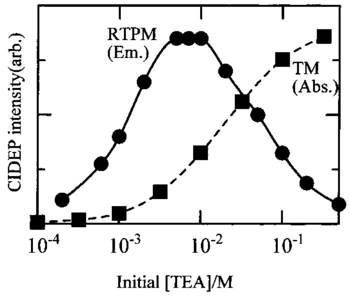

Figure 5. Kinetic simulation of the CIDEP intensities at $t = 1.5$ μs as a function of initial concentration of TEA. Emissive polarization due to RTPM is indicated by the solid line and absorptive polarization due to TM is indicated by the broken line.

$$\frac{\mathrm{d}[{}^{3}\mathrm{B}_{\mathrm{abs}}^{*}]}{\mathrm{d}t} = -(k_{\mathrm{sp}} + k_{\mathrm{et}}[\mathrm{TEA}])[{}^{3}\mathrm{B}_{\mathrm{abs}}^{*}] \qquad (9)$$

$$\frac{\mathrm{d}[(\mathrm{B}^{-}\cdots\mathrm{TEA}^{+})_{\mathrm{abs}}]}{\mathrm{d}t} = k_{\mathrm{et}}[{}^{3}\mathrm{B}_{\mathrm{abs}}^{*}][\mathrm{TEA}] \qquad (10)$$

$$\frac{\mathrm{d}[\mathrm{BH}_{\mathrm{abs}}^{\bullet}]}{\mathrm{d}t} = \alpha k_{\mathrm{pt}}\Phi_{\mathrm{r}}[(\mathrm{B}^{-}\cdots\mathrm{TEA}^{+})_{\mathrm{abs}}] \qquad (11)$$

where α is a factor for spin polarization generation. The value of α is not known and assumed as unity in the following calculation. $[{}^{3}\mathrm{B}_{\mathrm{abs}}^{*}]$ at $t = 0$ is considered to be equal to the initial concentration of triplet benzil, which was calculated from the molecular extinction coefficient of the ground state, the intersystem crossing quantum yield[24] ($\Phi_{\mathrm{isc}} = 0.92$), the equilibrium constant, and the excitation laser power. $[{}^{3}\mathrm{B}_{\mathrm{abs}}^{*}] = 1.5 \times 10^{-5}$ M at [benzil] $= 9 \times 10^{-3}$ M and 25 mJ pulse^{-1}. Φ_{r} is a quantum yield of the ketyl radical formation which is 0.31.[22] The concentration of $\mathrm{BH}_{\mathrm{abs}}^{\bullet}$ was obtained by solving the above rate equations numerically up to $t = 1.5$ μs. The results are plotted as a broken line in Figure 5 against initial concentration of TEA.

The CIDEP signals shown in Figure 1b was measured by opening the gate of the boxcar integrator from 1.1 to 2.1 μs. In this time range, only 13% of initially produced anion radicals survive in CIP as an average and 87% CIP dissociates to the ketyl radicals. The CIDEP spectrum in Figure 1b is, therefore, mainly due to the ketyl radical with some contribution of the anion radical and reflects the absorptive spin polarization of triplet benzil through TM.

Next, we will discuss the ketyl formation from the complex in the ground state.

$${}^{3}(\mathrm{B}\cdots\mathrm{TEA})^{*} \rightarrow \mathrm{BH}^{\bullet} + \mathrm{TEA}^{\bullet} \qquad (12)$$

The concentration of excited-state complex was calculated from the molecular extinction coefficient $\epsilon_{353}{}^{\mathrm{com}} = 490$ M^{-1} cm^{-1} of the complex[22] and excitation laser power by using the following equation:

$$[{}^{3}(\mathrm{B}\cdots\mathrm{TEA})^{*}] = \frac{I_{0}(1 - 10^{-\epsilon cl})}{N_{\mathrm{A}}V} \qquad (13)$$

Here I_0 is the excitation laser power and was estimated as 4.4×10^{16} photons when there is a 25 mJ pulse^{-1} at 355 nm, N_{A} is Avogadro number, and V is the volume of the cell used. The quantum yield of ketyl formation from the complex was confirmed to be unity.[22]

Now, we will focus our interest on the mechanism of spin polarization inversion. In our previous paper, we proposed that the spin polarization inversion is due to the complex formation: free benzil gives absorptive CIDEP through TM, whereas the complex of benzil with TEA yields the emissive one through TM, too, which is opposite to the spin polarization of the triplet state measured at 77 K. [3] We should, however, take back this idea because that spin polarization by TM from the photoexcitation of the complex cannot explain the second-order laser power dependence of the CIDEP signal intensity in this system.

Another mechanism to give emissive polarization is RTPM[16−18] which works between a spin relaxed triplet molecule and a free radical. According to RTPM, radicals always show emissive polarization regardless of the triplet spin polarization. The singlet excited state of the complex produced in reaction (3) yields the ketyl radical following ISC. These processes are thought to be too fast compared with Larmor precession rate to generate spin polarization and, hence, the produced radicals would not show CIDEP. The ketyl radicals produced in reaction (12) interact with spin relaxed triplet benzil formed in process (6), and emissive polarization is generated on the free radicals through RTPM.

$$^3\mathrm{B}^* + \mathrm{BH}^\bullet \xrightarrow{\mathrm{RTPM}} {}^1\mathrm{B} + \mathrm{BH_{em}}^\bullet \tag{14}$$

Intensity of the spin polarization due to RTPM is already calculated by Blättler and Paul, and we carried out the spin polarization estimation after their method.[19] These are expressed as

$$\frac{\mathrm{d}M_y}{\mathrm{d}t} = -T_2{}^{-1}M_y - \omega_1 M_z \tag{15}$$

$$\frac{\mathrm{d}M_z}{\mathrm{d}t} = \omega_1 M_y - T_1{}^{-1}(M_z - P_{\mathrm{eq}}[\mathrm{BH}^\bullet]) + Pk_{\mathrm{RTPM}}[^3\mathrm{B_{th}}^*][\mathrm{BH}^\bullet] \tag{16}$$

The triplet state of benzil decays,

$$^3\mathrm{B}^* \xrightarrow{k_0} {}^1\mathrm{B} \tag{17}$$

$$2\,^3\mathrm{B}^* \xrightarrow{k_{\mathrm{T-T}}} 2\,^1\mathrm{B} \tag{18}$$

$$^3\mathrm{B}^* + \mathrm{TEA} \xrightarrow{k_{\mathrm{et}}} \mathrm{B}^- + \mathrm{TEA}^+ \tag{19}$$

where k_0 is the single-exponential triplet decay rate $k_0 = 2 \times 10^4\ \mathrm{s}^{-1}$, $k_{\mathrm{T-T}}$ is the rate constant of the T−T annihilation $2k_{\mathrm{T-T}} = 1.3 \times 10^8\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, k_{RTPM} is the rate of the quenching of the triplet benzil by benzil ketyl radical $k_{\mathrm{RTPM}} = 10^{10}\ \mathrm{s}^{-1}$ which is the value of the diffusion-controlled rate, and k_{et} is the rate constant of electron transfer $k_{\mathrm{et}} = 6.0 \times 10^8\ \mathrm{s}^{-1}$.[22] Spin polarization intensity by RTPM is the simulated ESR time profile by numeric integration by solving the Bloch equations and kinetic treatments. The magnetization induced by RTPM in the *z*-component is coupled with microwave field amplitude ω and created the magnetization in the *y*-component. The parameters are unknown for T_1 and T_2 in our system. These values are quoted from the literature $T_1 = 6\ \mu\mathrm{s}$ and $T_2 = 0.25\ \mu\mathrm{s}^{-1}$,[19] which are the values in 2-propanol at −50 °C. These must be different from the value at our conditions in benzene solution at 25 °C; however, we can get some qualitative information of the CIDEP intensity which corresponds to the concentration of TEA. $\omega = 1.9 \times 10^5\ \mathrm{rad\ s}^{-1}$ was obtained in our system. $P/P_{\mathrm{eq}} = -60$ is used which is reported to be the adequate ratio of RTPM polarization. P_{eq} is the spin polarization of the Boltzmann distribution. Because of no two-photon process produces benzil ketyl in our system, $M_z(t = 0)/P_{\mathrm{eq}} = 0$ M was chosen as the initial condition.

The equations were solved numerically up to $t = 1.5\ \mu$s. [BH$^\bullet$] was calculated from eq 13. The results are shown in Figure 5 as a solid line against the initial concentration of TEA. Since the concentrations of the complex and hence produced ketyl are low at low concentration of TEA, RTPM does not work efficiently and emissive CIDEP signals are weak. The chemical equilibrium (1) moves to the right with the increase in TEA concentration, and the ketyl concentration becomes high enough to promote RTPM, where triplet benzil still survives. When TEA concentration is higher than 10^{-2} M, triplet benzil reacts with TEA to yield CIP and the efficiency of RTPM goes down. These are the reasons the emissive CIDEP intensity curve shows a peak around 10^{-2} M of TEA.

Absorptive polarized CIDEP is also plotted in the figure as a broken line in arbitrary unit. From the curves in Figure 5, it is easily understood that the polarization changes from emission to absorption with increase in TEA concentration.

These demonstrations reproduce the experimental results about the spin polarization inversion depending on the TEA concentrations.

Summary

Mechanism of spin polarization generation in photoreaction of the benzil/triethylamine system was investigated by using the time-resolved ESR and transient absorption techniques. The benzil ketyl radicals produced show spin polarization inversion depending on TEA concentration, emission at low and absorption at high concentrations. We have analyzed this double-faced polarization of CIDEP signal with kinetic data and revealed that photoexcitaion of the ground-state complex yields the ketyl radicals with emissive polarization through RTPM, and the triplet state of free benzil forms those with absorptive polarization through TM. This study demonstrates that RTPM readily occurs in an ordinary photochemical system under laser excitation condition.

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