

Magnetic Field Effect on the Fluorescence of *m*-Phenylenebis-(phenylmethylene) in a Rigid Glass at 77 K

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The magnetic field effect (≤ 0.59 T) on the quintet–quintet fluorescence of *m*-phenylenebis(phenylmethylene) (MPBP) was studied in a rigid glass, decaline–cyclohexane (3:1) mixture, at 77 K. The fluorescence decay rate of MPBP increases in a magnetic field. The effect on the MPBP fluorescence is explained in terms of the Zeeman mixing of excited quintet sublevels of MPBP.

The magnetic field effects (MFEs) on fluorescence of triplet carbenes have been studied in detail by Migirdicyan and her collaborators.¹ The lifetime of triplet–triplet fluorescence of diphenylmethylene (DPM) in a hexane rigid matrix at 4.2–30 K decreases by application of a magnetic field (< 0.1 T). The effects are interpreted in terms of the Zeeman mixing of “excited triplet” sublevels. Therefore, it is interesting to know how a magnetic field affects the fluorescence decay of a reactive intermediate with higher spin multiplicity.

In this paper, the MFE on the fluorescence of *m*-phenylenebis(phenylmethylene) (MPBP) was examined in a rigid glass at 77 K by laser-induced fluorescence. Magnetic field dependence (MFD) of the fluorescence decay in MPBP is very similar to that in DPM. The results are interpreted in terms of the Zeeman mixing of the excited quintet sublevels in MPBP.

Experimental

Materials: 1,3-Bis(α -diazobenzyl)benzene (BDB) and diphenyldiazomethane (DDM) were synthesized in the manners similar to those described elsewhere.^{2,3} The purest grades of decaline and cyclohexane (Nacalai Tesque, Inc.) were used as supplied and were mixed in the volume ratio of 3:1 to prepare a decaline–cyclohexane mixed solvent (DCH). All sample solutions (10^{-4} – 10^{-5} mol dm⁻³) were deaerated by several freeze–pump–thaw cycles. Spectroscopic measurements were carried out at 77 K by immersing sample cells in liquid nitrogen.

The laser-induced fluorescence was measured using an XeCl

excimer laser (Lumonics, EX-500, 308 nm) as an exciting light source and a polychromator (Hamamatsu, C5094)–streak camera system (Hamamatsu, C4334) as a detection system.⁴ A xenon arc lamp with a bandpass filter (300–400 nm) or the 308-nm light from the laser was used for photolysis light. Magnetic fields were applied by an electromagnet (TOKIN, SEE-9), whose residual field was canceled to < 0.3 mT by applying a dc current.

Results and Discussion

Photoirradiation of BDB in a DCH rigid glass at 77 K leads to a reaction intermediate whose absorption band appears at 300–320 nm. Figure 1a shows time-resolved fluorescence spectra of BDB in the glass after photoirradiation of a 308-nm light. The spectra are composed of a short-lived band at 400–450 nm and a relatively long-lived band at 450–600 nm. The lifetime of the former is about 9 ns, whereas the decay curves of the latter band are nonexponential, as will be described later. The steady-state fluorescence spectrum obtained by integration of the time-resolved spectra is also shown in the inset of Fig. 1a. A shoulder band at 470 nm observed in the time-resolved spectrum at a 9 ns delay is not apparent in the steady-state spectrum because of its short lifetime.

Optical absorption and luminescence spectra of quintet MPBP generated from BDB have been studied in detail in a DCH rigid glass at 77 K.^{5,6} Two diazo groups in BDB are cleaved by one photon, yielding MPBP as a major reaction intermediate. MPBP has an intense absorption band at ca. 316 nm. By correlating EPR and steady-state fluorescence intensities, the fluorescence band peaking at ca. 485 nm with a life-

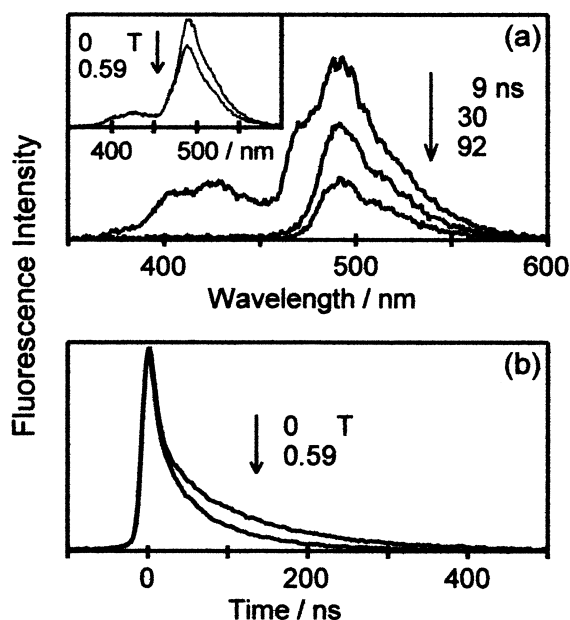


Fig. 1. (a) Time-resolved fluorescence spectra of BDB in an MCH rigid glass at 77 K after photoirradiation of a 308 nm light. Inset: Steady-state fluorescence spectra obtained by integration of the time-resolved spectra in the absence and presence of a magnetic field of 0.59 T. (b) Magnetic field effect on the fluorescence decay curve observed at 480–540 nm in the absence and presence of a magnetic field of 0.59 T.

time of ca. 150 ns is assigned to the excited quintet state of MPBP. By comparison with these reported optical data of MPBP, the fluorescence spectrum peaking at ca. 490 nm in Fig. 1a is assigned to the quintet-quintet fluorescence of MPBP. The short-lived fluorescence appearing around 470 nm in the time-resolved spectra cannot be assigned, since the transient spectra with higher time-resolution are not obtained due to the pulse width of the laser (ca. 10–15 ns). On the other hand, the fluorescence band at 400–450 nm would be ascribed to a stable photoproduct.

The MFE on the steady-state fluorescence spectrum of MPBP is shown in the inset of Fig. 1a. The intensity in the 450–600 nm region decreases by about 30% by application of a magnetic field of 0.59 T, whereas the intensity of the 400–450 nm band is magnetic-field insensitive. Figure 1b shows the MFE on the fluorescence decay of MPBP at 77 K. Here, the fluorescence intensities in the 480–550 nm region are analyzed in order to minimize contamination of the unknown fluorescence around 470 nm. The decay rate increases in a magnetic field of 0.59 T. Decay curves are nonexponential regardless of magnetic field and are analyzed tentatively by assuming a double exponential decay.

$$I(t) = I_f \exp(-t/\tau_f) + I_s \exp(-t/\tau_s) \quad (1)$$

where τ_f and τ_s are the lifetimes of the fast and slow decay components, respectively, I_f and I_s being the respective pre-exponential factors. Errors involved in the present analysis are about $\pm 10\%$. The lifetime τ_s of the slow decay component is 122 ns at zero field and is dependent on the magnetic field. The values of τ_f , I_f and I_s are 14 ns, 0.6, and 0.4, respectively, at zero field and are almost magnetic-field independent. Figure 2 shows the MFD of τ_s . The lifetime τ_s decreases with increasing magnetic field and is 82 ns at 0.59 T.

The MFD of the fluorescence decay of MPBP in a rigid glass of diethyl ether–ethyl alcohol–pentane (5:5:1) mixture (EPA) at 77 K is very similar to that in a DCH rigid glass at 77 K shown in Fig. 1b. At zero field, τ_s is 139 ns and this decreases down to 86 ns with increasing magnetic field from zero to

0.59 T, whereas the values of τ_f , I_f and I_s are about 17 ns, 0.4, and 0.6, respectively, and are almost magnetic-field independent.

For the purpose of comparison, the MFE on the fluorescence decay of DPM generated from DDM is also examined in a DCH rigid glass at 77 K. The steady-state fluorescence spectrum of triplet DPM peaking at ca. 485 nm is similar to that of quintet MPBP depicted in the inset of Fig. 1a. Furthermore, its fluorescence decay curves are also nonexponential and magnetic-field dependent. The curves are analyzed using Eq. 1, by analogy with the analysis of the MPBP fluorescence. The values of τ_f , I_f and I_s are about 25 ns, 0.4, and 0.6, respectively, at zero field and are almost magnetic-field independent. Figure 2 shows the MFD of the lifetime τ_s of DPM. It decreases from 115 ns to 79 ns with increasing the magnetic field from zero to 0.59 T.

The fluorescence of MPBP corresponds to the spin-allowed transition between excited and ground quintet states. Since the radiative transition is independent of spin sublevels, the radiative decay rate constants from the five spin sublevels are equal. On the other hand, each sublevel may have a different nonradiative decay rate constant. This is because it may have different symmetry and it may be coupled by spin-orbit coupling to different triplet and/or singlet states. In a low-temperature rigid glass, the rates of spin lattice relaxation among quintet sublevels are not fast compared to the decay rate of each quintet sublevel. Each sublevel decays with each own decay rate constant at zero field. By application of a magnetic field, all five quintet sublevels are mixed by the Zeeman interaction and, therefore, the decay rates change by application of a magnetic field, as discussed in the case of excited triplet DPM.¹

The lifetime and MFD of excited quintet MPBP are similar to those of excited triplet DPM. This fact may be understandable if the excitation is concerned dominantly with the molecular orbitals localized to the one divalent carbon.

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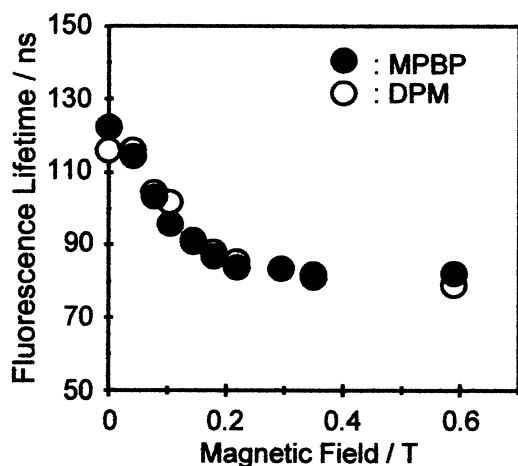


Fig. 2. Magnetic field dependence of the fluorescence lifetime of MPBP (●) and DPM (○).