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LETTERS

Laser-Induced Fluorescence of 1,3,5-Trimethoxybenzene Radical Cation in Solution at Room Temperature

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Laser excitation at 532 nm of 1,3,5-trimethoxybenzene radical cation ($\mathbf{1}^{\bullet+}$), which is generated by photoinduced electron transfer in aerated acetonitrile containing 1.4-dicyanonaphthalene and biphenyl (BP) as a sensitizer−cosensitizer system by the use of XeCl laser (308 nm), gave fluorescence around 620 nm. The assignment to that from the excited state of $\mathbf{1}^{\bullet+}$ ($\mathbf{1}^{\bullet+*}$) is based on the agreement of the rates for the formation of $\mathbf{1}^{\bullet+}$ obtained by laser-induced fluorescence and absorption spectroscopies. The fluorescence quantum yield for $\mathbf{1}^{\bullet+}$ is ca. 2×10^{-3}. There was no observable fluorescence from other di- and trimethoxybenzenes. It was revealed by molecular orbital and configuration interaction calculations that the fluorescence corresponds to the D_2−D_0 transition of $\mathbf{1}^{\bullet+}$. The high quantum yield of $\mathbf{1}^{\bullet+}$ would be attributable to the large energy separation between the emissive D_2 and a non-emissive D_3 states of $\mathbf{1}^{\bullet+}$ preventing their mixing which leads to the non-radiative decay.

The photochemistry of chemical intermediates such as excited radicals or higher excited states has attracted much interest from physical and synthetic points of view.[1] Radical ions have been of interest because their excitation affects their reactivity through the enhancement of redox properties or weakening of chemical bonding.[2−4] However, the physical properties of radical ions, such as fluorescence, have been investigated less because of the experimental requirement of a pair of pulsed lasers or a pulsed accelerator and a laser with a temporal control for the generation of radical ions and their excitation. Recent studies on excited radical ions in solution have revealed short lifetimes (<1 ns) and weak fluorescence possibly due to their low excitation energy which allows fast internal conversion.[5,6] To our knowledge, only a few radical ions have been reported to fluoresce in solution.[7,8] In addition, the assignment of fluorescence to excited radical ions is difficult due to the formation of fluorescent stable side products as has been pointed out by Fox.[7]

Observation of dynamics of fluorescent species is necessary for their assignment to excited radical ions.[8a] We have studied the laser-induced fluorescence (LIF) of radical cations of methoxybenzenes by excitation of their absorption bands in the visible region of 400−600 nm. The radical cations were generated within 1 μs after the first laser pulse via secondary electron transfer from the biphenyl radical cation ($BP^{\bullet+}$), which was also generated by photoinduced electron transfer to an

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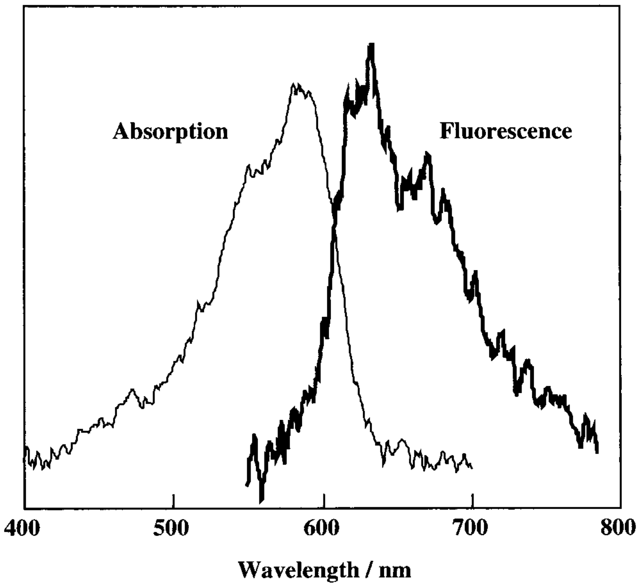


Figure 1. Absorption spectrum of $\mathbf{1}^{\bullet+}$ obtained by the laser flash photolysis of an aerated acetonitrile solution containing DCN (1×10^{-4} M), BP (0.02 M), and **1** (1.1×10^{-3} M) at 1 μs after the first 308-nm laser excitation and fluorescence spectrum obtained upon the 532-nm laser excitation at 1 μs after the first 308-nm laser excitation (see text).

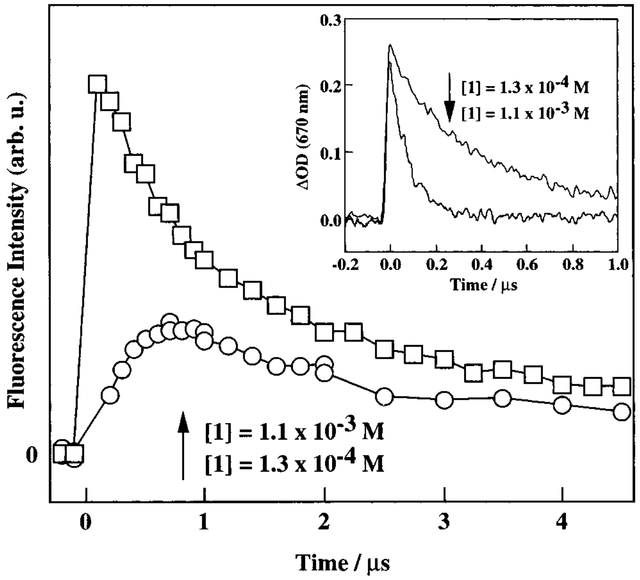


Figure 2. Plots of fluorescence intensity observed at 620 nm as a function of the delay time of the 532-nm laser pulse after the 308-nm laser excitation of aerated acetonitrile solutions containing DCN (1×10^{-4} M), BP (0.02 M), and **1** (1.3×10^{-4} and 1.1×10^{-3} M). Insert: decay curves of the transient absorption at 670 nm corresponding to those of $\mathrm{BP}^{\bullet+}$.

electron-accepting sensitizer, 1,4-dicyanonaphthalene (DCN). The LIF technique has a sufficient time resolution to distinguish the fluorescence of the radical ions kinetically from that of side products formed in the system as observed during the steady-state fluorescence spectroscopy of chemically or electrochemically generated radical ions. We now wish to report the fluorescence from the radical cation of 1,3,5-trimethoxybenzene (**1**) in solution observed by this technique.

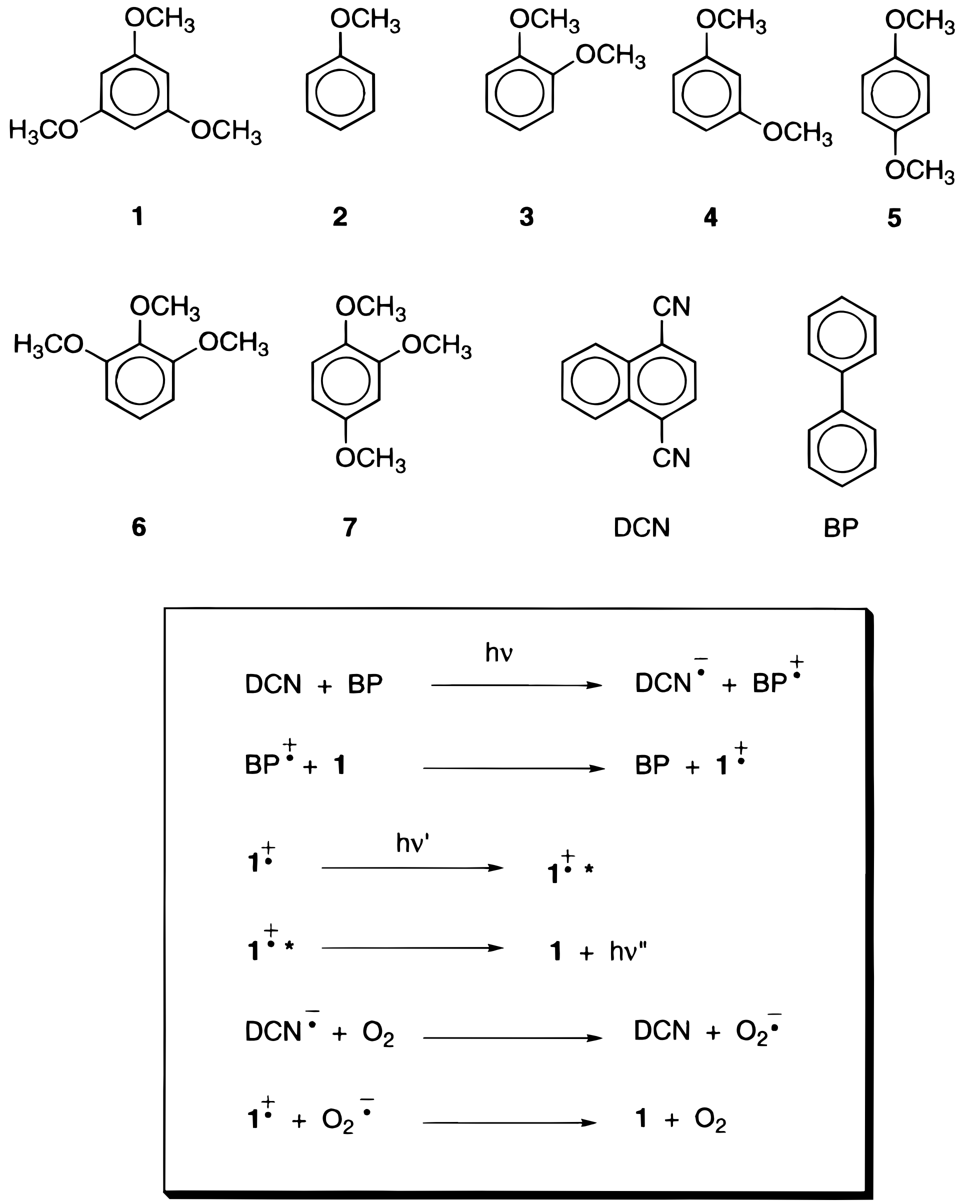
An aerated acetonitrile solution of **1** ($1-11 \times 10^{-4}$ M) containing DCN (1×10^{-4} M) as a sensitizer and BP (0.02 M) as a cosensitizer was excited with a XeCl laser (308 nm, 40–70 mJ pulse^{-1}). Transient absorption spectra immediately and at 1 μs after the laser pulse indicate nearly quantitative conversion of $\mathrm{BP}^{\bullet+}$ into $\mathbf{1}^{\bullet+}$. The radical cation of **1** shows an absorption around 500–600 nm with an extinction coefficient of 3800 M^{-1} cm^{-1} (590 nm). The transient absorption of the radical anion of DCN ($\mathrm{DCN}^{\bullet-}$) is readily quenched by oxygen giving transparent $\mathrm{O_2}^{\bullet-}$ within 500 ns (mostly within 100 ns). Excitation of this band at 532 nm with a second harmonic pulse of Nd/YAG laser (40 mJ pulse^{-1}) affords fluorescence around 620 nm (Figure 1). The fluorescence spectrum was measured with a gated multichannel spectrometer (Hamamatsu PMA-50, gate time 40 ns). The spectrum exhibits mirror image symmetry to the absorption spectrum strongly suggesting that the fluorescence is from excited $\mathbf{1}^{\bullet+}$ ($\mathbf{1}^{\bullet+*}$). The duration of the fluorescence obtained with a photomultiplier is almost the same as that of the laser excitation pulse, indicating a short fluorescence lifetime (τ) of <2 ns.

Plots of fluorescence intensity observed at 620 nm as a function of the delay time of the 532-nm pulse relative to the 308-nm pulse showed rise times dependent on the concentration of **1**, ≈700 ns at [**1**] = 1.3×10^{-4} M and <100 ns at [**1**] = 1.1×10^{-3} M (Figure 2). The plots reflect to the time profile of the concentration of ground state of $\mathbf{1}^{\bullet+}$ and not the decay of the excited state, $\mathbf{1}^{\bullet+*}$. The rise times obtained by LIF agreed with the decay time of $\mathrm{BP}^{\bullet+}$ transient absorption at 670 nm.[9] Both fluorescence and absorption obey second-order kinetics and the half-lives of the fluorescence intensity (1.5–2.0 and 4.0–4.5 μs) also agreed with those observed by the absorption of $\mathbf{1}^{\bullet+}$ at 580 nm though the rise was not observed by the absorption measurement due to its overlap with that of $\mathrm{BP}^{\bullet+}$ which has a large molar extinction coefficient at this wavelength (6000 M^{-1} cm^{-1}). The decay of $\mathbf{1}^{\bullet+}$ was attributed to charge recombination with $\mathrm{O_2}^{\bullet-}$. These results rule out the possibility of fluorescence from side products (Scheme 1).

The quantum yield (Φ_f) was determined to be $2(\pm 1) \times 10^{-3}$ from the integrated fluorescence intensity and the absorbance of $\mathbf{1}^{\bullet+}$ at 1 μs using the fluorescence of a cyclohexane solution of tetraphenyl zinc porphyrin (ZnTPP) obtained by excitation with the 532-nm pulse as a standard ($\Phi_\mathrm{f} = 0.03$).[10] The quantum yield is higher than those reported for triarylamine radical cations in solution ($\Phi_\mathrm{f} = 10^{-5}$).[7] From the observed extinction coefficient of $\mathbf{1}^{\bullet+}$ at 590 nm in acetonitrile, the oscillator strength (f) for the transition and the radiative rate constant (k_f) were calculated to be $f = 3.3 \times 10^{-2}$ and $k_\mathrm{f} = 9.5 \times 10^{6}$ s^{-1}. The reported radiative rate constants for the fluorescence from excited radical cations of fluorobenzenes in the gas phase agree with this value.[11] From the relationship of $\Phi_\mathrm{f} = k_\mathrm{f}\tau$, the fluorescence lifetime would be ca. 210 ps. This value is in fairly good agreement with reported lifetimes of excited radical cations in solution.[5b,6a]

As reported by Shida,[12] Steenken,[13] and Schnabel,[14] the radical cations of anisole (**2**), 1,2-, 1,3-, and 1,4-dimethoxybenzenes (**3**, **4**, and **5**), and 1,2,3- and 1,2,4- trimethoxybenzenes (**6** and **7**) show absorption maxima in the visible region (400–500 nm). We attempted similar measurements of LIF for these radical cations with the third harmonic pulses of a YAG laser for generation and dye laser pulses for excitation. Although no significant differences in chemical stability from that of $\mathbf{1}^{\bullet+}$ were observed, these radical cations gave no observable fluorescence ($\Phi_\mathrm{f} < 10^{-5}$). We have calculated radiative rate constants from the obtained oscillator strengths and the transition energies to be in the order of 10^{7} s^{-1} for the visible absorption. Therefore, nonradiative rate constants would be higher than 10^{12} s^{-1} and the lifetime of the excited state would be less than 1 ps. Such a fast nonradiative decay of the excited radical cation cannot be attributed to a chemical deactivation pathway such as a

SCHEME 1



nucleophilic attack and elimination of acetonitrile to the excited radical cation which does not give any product.

We have considered the electronic transitions of the radical cations by combination of a semiempirical MO calculation program and a configuration interaction (CI) calculation program.[15] The results are summarized in Table 1. The calculated oscillator strengths for D_2−D_0 transition of $\mathbf{1}^{\bullet+}$ − $\mathbf{7}^{\bullet+}$ are in good agreement with those obtained from the transient absorption spectra[13] and the energy separations among the D_0, D_1, D_2, and D_3 levels also agree fairly with those obtained from the reported photoelectron spectra of **2** and **5**.[17] The calculation revealed that the visible absorption spectra of the methoxybenzene radical cations are not due to transitions to the lowest excited state but to the second excited state. Therefore, the fluorescence observed here corresponds to the D_2−D_0 transition of $\mathbf{1}^{\bullet+}$. The energy separation between the D_1 and D_0 states for $\mathbf{1}^{\bullet+}$ (0.58 eV) is much smaller than the observed fluorescence wavelength (612 nm, 2.03 eV), also ruling out the possibility of D_1−D_0 fluorescence. The energy separations among the ground, first, second, and third excited states would be the most important factors controlling magnitude of the nonradiative rate constants competing with fluorescence. The D_2 state of $\mathbf{1}^{\bullet+}$ is separated well from the D_3 state (>1 eV) and also from the D_1 state. On the other hand, the D_2−D_3 energy separations are small for $\mathbf{2}^{\bullet+}$, $\mathbf{3}^{\bullet+}$, and $\mathbf{5}^{\bullet+}$−$\mathbf{7}^{\bullet+}$. Perhaps thermal activation of an emissive D_2 state to a non-emissive D_3 state operates as a

TABLE 1. Calculated Transition Energies (eV) and Corresponding Oscillator Strengths (*f*) for the Radical Cation of Methoxybenzenes Obtained by the ZINDO/S Method Based on the MO's Calculated by the AM1 Method

compd	D_0−D_1 (*f*)	D_0−D_2 (*f*) f_{exp}[a]	D_0−D_3 (*f*)
$\mathbf{1}^{\bullet+}$	0.58 (0.0003)	2.39 (0.0508) 0.032	3.54 (0.0513)
$\mathbf{2}^{\bullet+}$	0.94 (0.0001)	3.09 (0.1076) 0.056[b]	3.17 (0.0260)
$\mathbf{3}^{\bullet+}$	1.16 (0.0048)	3.03 (0.0732) 0.051[b]	3.17 (0.0252)
$\mathbf{4}^{\bullet+}$	1.06 (0.0045)	2.89 (0.0373) 0.047[b]	3.40 (0.0585)
$\mathbf{5}^{\bullet+}$	1.32 (0.0000)	2.81 (0.2035) 0.105[b]	2.95 (0.0079)
$\mathbf{6}^{\bullet+}$	0.67 (0.0033)	2.90 (0.0611) 0.056[b]	3.05 (0.0077)
$\mathbf{7}^{\bullet+}$	1.23 (0.0026)	2.77 (0.1012) 0.096[b]	2.98 (0.0357)

[a] Calculated from the width of the absorption band ($\Delta\nu_{1/2}$) and extinction coefficient (ϵ) obtained from transient absorption data, $f \approx \Delta\nu_{1/2}\epsilon/2.5 \times 10^8$. See, for example, Turro, N. *J. Modern Molecular Photochemistry*; Benjamin: Reading, MA, 1978; Chapter 5. [b] The value of ϵ in ref 13 was used.

nonradiative decay mechanism as discussed for the nonradiative decay of the excited state of the benzyl radical at room temperature.[18] Although the non-fluorescent nature of the D_2 state of $\mathbf{4}^{\bullet+}$ is not understood at present, the pseudo-D_{3h} symmetry of $\mathbf{1}^{\bullet+}$ as discussed for the gas-phase fluorescence of the 1,3,5-trifluorobenzene radical cation whose ground state is degenerate as a result of complete D_{3h} symmetry[11] also may contribute to the fluorescent nature of $\mathbf{1}^{\bullet+}$.

We have reported a relatively high fluorescence quantum efficiency in the visible region for $\mathbf{1}^{\bullet+*}$ which could provide a sensitive mechanistic probe for dynamics studies of radical ions in electron transfer phenomena by the combination with electron or energy transfer quenching of this species. Related work in progress will be reported elsewhere.[19]

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(9) The decay of $BP^{\bullet+}$ is faster than the rise of $\mathbf{1}^{\bullet+}$ because of charge recombination with $O_2^{\bullet-}$ in addition to the secondary electron transfer from **1** in particular at a low concentration of **1**. We have calculated the initial concentration of $BP^{\bullet+}$ to be $\approx 2.8 \times 10^{-5}$ M. The concentration of $O_2^{\bullet-}$ formed in the system would be the same. With the observed rate constant for the charge recombination of $BP^{\bullet+}$ of 1.2×10^{10} M^{-1} s^{-1} and that for the secondary electron transfer 2×10^{10} M^{-1} s^{-1}, the lifetime is calculated to be 463 and 77 ns at the concentrations of **1** of 1.3×10^{-4} and 1.1×10^{-3} M, respectively. The rise time of $\mathbf{1}^{\bullet+}$ was calculated to be 641 and 80 ns. These values are in good agreement with the observation through the fluorescence of $\mathbf{1}^{\bullet+}$, though the decay curves of the transient absorption at 590 nm were essentially the same as those observed at 670 nm because of the strong absorption of $BP^{\bullet+}$ overlapping with that of $\mathbf{1}^{\bullet+}$ and we could not obtain the rate constants from them.

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