Dual Fluorescence of 1,2,4,5-Tetramethoxybenzene in 77 K Matrices Studied by Fluorescence Polarization

Nobuyuki Ichinose,* Kazutoyo Kishimoto, Jun-ichiro Kinugasa, Masahide Hagiri, and Toshihiro Nakayama*
Department of Chemistry and Materials Technology, Faculty of Engineering and Design, Kyoto Institute of Technology,
Matsugasaki Gosho-Kaidocho, Sakyo-ku, Kyoto 606-8585

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Anisotropy of the fluorescence spectrum of 1,2,4,5-tetrametoxybenzene (TEMB) in EPA matrix at 77 K showed a wavelength dependence indicating that the fluorescence was consisted of two components. This dual fluorescence can be explained by a modification of the $S_1(B_{2u}) \rightarrow S_0(A_g)$ transition moment of TEMB through the coupling with a synchronous in-plane or out-of-plane bending motion of the methoxyl groups.

Dual fluorescence has been a subject of photochemistry for these three to four decades. It is caused by several kinds of driving forces such as electron transfer, proton transfer, isomerization, and so on within the molecule in the lowest excited singlet state. We have studied the dual fluorescence phenomena caused by the large amplitude vibration such as the Jahn–Teller distortion,[1] proton transfer,[2] and other molecular deformation as a model of ultrafast chemical reactions. The dynamics of the molecular deformation proceeds in picosecond time region to give large spectral shift in the fluorescence spectra. However, some deformation only results in a slight spectral shift due to the small energy change. Conventional fluorescence spectroscopy could not distinguish such closely overlapped dual fluorescence. We now report a fluorescence polarization study on a dual fluorescence phenomenon of 1,2,4,5-tetramethoxybenzene[3] (TEMB) in 77 K matrices to distinguish the selection rules involved therein.

Absorption spectrum of TEMB in cyclohexane showed a peak corresponding to the $S_1 \leftarrow S_0$ transition at 292 nm with a molar extinction coefficient of 5300 $\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$. The width of the absorption spectrum was 3300 $\mathrm{cm^{-1}}$ (FWHM). Fluorescence spectrum of TEMB in cyclohexane showed a largely Stokes-shifted (6100 $\mathrm{cm^{-1}}$) peak at 360 nm and a spectral width of 4900 $\mathrm{cm^{-1}}$ (FWHM) (Figure 1). The fluorescence quantum yield was estimated to be 0.11 and the lifetime was estimated to be 1.5 ns from this value and the absorption data by the Strickler–Berg formalism.[4] The photophysical properties of TEMB indicates that the $S_1 \leftarrow S_0$ transition is allowed. Vibrational progression was not observed either in the absorption or in the fluorescence spectrum. The broadness of the fluorescence spectrum was not changed so much even in the 77 K low temperature matrices, while narrowing of the spectral width and weak vibrational structure was observed in the absorption spectrum. Although fluorescence spectrum of TEMB in 77 K EPA matrix was blue-shited by 1700 $\mathrm{cm^{-1}}$ (peaked at 336 nm), vibrational structure was not observed and the spectral width was narrowed by 600 $\mathrm{cm^{-1}}$ as compared to that in cyclohexane at room temperature (Figure 2).[5]

The width and Stokes-shift of the fluorescence spectrum of TEMB varied with viscosity of the media employed and also with polarity in part. This could be attributed to the presence of two fluorescence components, whose ratio in intensity is related to some molecular motion. Electronic transitions obeying different selection rules must have different polarization and will be distinguished by fluorescence polarization. Fluorescence anisotropy of TEMB measured in 77 K EPA matrix was not constant over the spectral range of 310–420 nm and decreased monotonously from 0.32 ± 0.04 to 0.10 ± 0.01 with the increase in the wavelength of the emission.[6] The fluorescence anisotropy ($r(\lambda)$) was analyzed as a function of wavelength (λ) assuming the overlapping of two fluorescence components ($I_1(\lambda)$ and $I_2(\lambda)$) with proper anisotropy values of $r_1 = 0.32$ and $r_2 = 0.10$ with fractions of $X_1(\lambda)$ and $X_2(\lambda)$ ($X_1(\lambda) + X_2(\lambda) = 1$), respectively. Total fluorescence spectrum ($I(\lambda)$) was decomposed into $I_1(\lambda)$ and $I_2(\lambda)$ solving the simultaneous equations concerning $I(\lambda)$ and $r(\lambda)$ (Eqs 1–4).

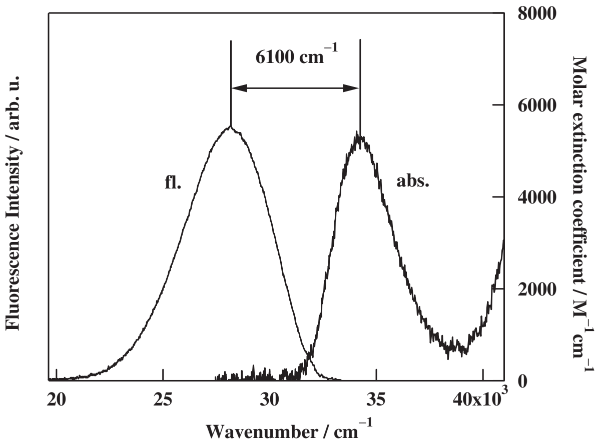

Figure 1. Stationary state absorption and fluorescence (excited at 290 nm) spectra of TEMB in cyclohexane at room temperature.

$$I(\lambda) = X_1(\lambda)I_1(\lambda) + X_2(\lambda)I_2(\lambda) \tag{1}$$

$$r(\lambda) = X_1(\lambda)r_1(\lambda) + X_2(\lambda)r_2(\lambda) \tag{2}$$

$$I_1(\lambda) = [(r(\lambda) - r_2)/(r_1 - r_2)]I(\lambda) \tag{3}$$

$$I_2(\lambda) = [(r_1 - r(\lambda))/(r_1 - r_2)]I(\lambda) \tag{4}$$

The results are shown in Figure 2. The obtained spectra showed peaks at 329 and 349 nm with widths of 3600 and 4300 $\mathrm{cm^{-1}}$. The relative integrated intensity was 1.6 (±0.1):1.0. The relative intensity of the second band increased to 1.0:2.7 (±0.3) in 77 K MCH/IP matrix which is softer than EPA.[7] The variation in the anisotropy was not due to the inhomogeneity of the matrix or the presence of rotational isomers. The excitation spectra monitored at 330 and 380 nm agreed completely.

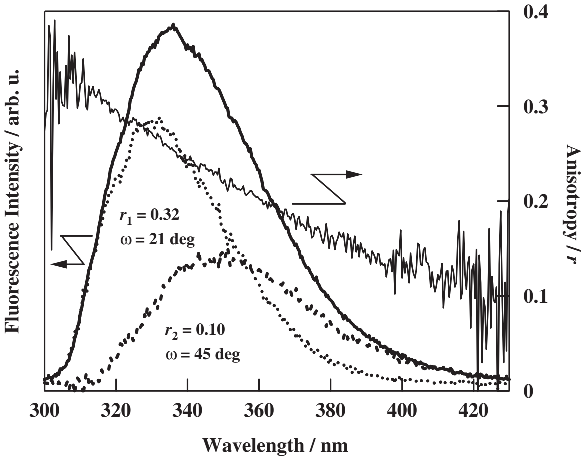

Figure 2. Fluorescence and fluorescence anisotropy spectra of TEMB in 77 K EPA matrix. Dotted and dashed spectra are decomposed spectra based on the fluorescence anisotropy values of 0.32 and 0.10, respectively (see text).

One can estimate the angle between the directions of transition moments for absorption and fluorescence (ω) from fluorescence anisotropy measured in isotropic rigid media from Eq 5.[8]

$$r = (3\cos^2\omega - 1)/5 \qquad (5)$$

We obtained a set of ω values, 21 and 45° for r_1 and r_2. This difference in the direction of the transition moments means that these emissions obey different selection rules. Group theoretical discussion, therefore, is required to explain the selection rule for the two transitions. Since the HOMO and LUMO of TEMB belong to the B_{1g} and B_{3u} representations of the D_{2h} point group,[9] respectively, if the methyl groups are ignored for the simplicity, the $S_1(B_{2u}) \leftarrow S_0(A_g)$ transition is a symmetrically allowed transition. Therefore, the fluorescence band with an anisotropy of 0.32 could be composed of progressions of transitions between totally symmetric vibrations ($a'_g \rightarrow a_g$) in the S_1 and S_0 states, respectively. On the other hand, another fluorescence band should be corresponding to the transition of $a_g \rightarrow b_{1g}$ or $a_g \rightarrow b_{3g}$ representations. Since the vibrations of b_{1g} and b_{3g} are in the same representations as rotations around the x- and z-axes, respectively, these vibrations would be synchronous in-plane and out-of-plane bending of oxygen atoms relative to the benzene ring, "twisting" and "waving" (Figure 3). Incorporation of the butterfly-like b_{3u} vibration in the $S_1 \rightarrow S_0$ transition, which has been reported for 1,2,4,5-tetrafluorobenzene (TEFB) to give molecular deformation in the S_1 state,[10] was ruled out as an origin of the rotation of the transition moment.[11] This could be due to the difference in the symmetry of the LUMO of TEFB (A_u)[9] and TEMB (B_{3u}) or due to the difference in the electronic properties of the substituents.

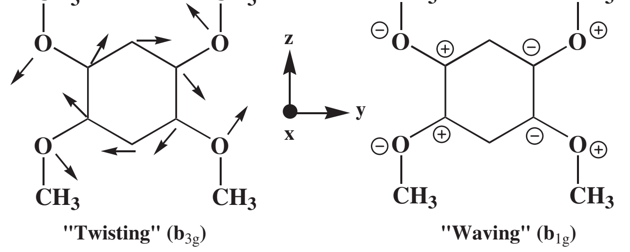

Figure 3. Possible vibrations which alter the direction of the transition moment of the $S_1(B_{3u}) \rightarrow S_0$ transition (see text).

The asymmetric relationship between the absorption and fluorescence spectra suggests the deformation of the potential surface of TEMB in the S_1 state. Although we could not observe any evidence for $a_g \rightarrow b'_{1g}$ or $a_g \rightarrow b'_{3g}$ transitions in the absorption spectrum,[12] it is clear that the TEMB fluorescence contains a component with a rotated polarization possibly due to the coupling with the b_{1g} or b_{3g} vibration. This dual fluorescence could explain the media-dependent Stokes-shift and the band width of TEMB fluorescence in room temperature solutions.

References and Notes

1 N. Ichinose, S. Iwasaki, M. Hagiri, J. Kinugasa, and T. Nakayama, in preparation.
2 M. Hagiri, N. Ichinose, J. Kinugasa, T. Iwasa, and T. Nakayama, *Chem. Lett.*, **33**, 326 (2004).
3 TEMB was synthesized from 2,5-dihydroxy-1,4-benzoquinone via 2,5-dimethoxy-1,4-benzoquinone according to the literature; H. Sato and F. P. Guengerich, *J. Am. Chem. Soc.*, **122**, 8099 (2000).
4 N. J. Turro, "Modern Molecular Photochemistry," Benjamin, Reading, MA (1978), Chap. 5, pp 88–90.
5 Glass forming solvents; EPA and MCH/IP are mixtures of diethyl ether:2-methylbutane:ethanol = 5:5:2 (v/v) and methylcyclohexane:2-methylbutane = 3:1 (v/v), respectively.
6 Vertically polarized fourth harmonic pulses (266 nm, 6 ns, 30 mJ pulse^{-1}) of a Nd:YAG laser (Continuum Surelite I-10) and a gated image-intensified multi-channel spectrometer (UNISOKU TSP-501) were used for the fluorescence and fluorescence anisotropy measurements. No fluorescence anisotropy was observed for TEMB in solution at room temperature indicating that any optical components did not produce erroneous polarization of the fluorescence. Since we did not observe any variation in the anisotropy for 1,4-dimethoxybenzene, artifactual anisotropy due to the experimental conditions was essentially negligible.
7 Fluorescence anisotropy in 77 K MCH/IP matrix was relatively low ($r_1 = 0.09 \pm 0.1$ and $r_2 = 0.06 \pm 0.1$) possibly owing to the rotational relaxation within the S_1 lifetime.
8 J. Michl and E. W. Thulsrup, "Spectroscopy with Polarized Light: Solute Alignment by Photoselection, in Liquid Crystals, Polymers, and Membranes," VCH, New York (1995), Chap. 7, pp 316–319.
9 Calculated by MOPAC2002, J. J. P. Stewart, *Int. J. Quantum. Chem.*, **58**, 133 (1996).
10 K. Okuyama, T. Kakinuma, M. Fujii, M. Mikami, and M. Ito, *J. Phys. Chem.*, **90**, 3948 (1986).
11 Although molecular deformation along the butterfly-like b_{3u} vibration modify the molecular symmetry of TEMB in the S_1 state into the C_{2v} point group, this will have no effect on the direction of the transition moment of TEMB fluorescence.
12 Polarized fluorescence excitation spectra corresponding to the $S_1 \leftarrow S_0$ transition (270–320 nm) showed a constant anisotropy at 370 nm ($r = 0.19$), indicating that fluorescent state of TEMB in 77 K EPA matrix were in equilibrium among the zero vibrational levels in the S_1 state.

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