

Laser-induced fluorescence and fluorescence lifetime of diphenylbenzobis(thiadiazole) in supersonic free jets

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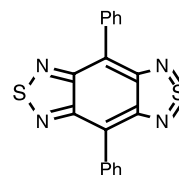
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Abstract

The technique of laser-induced fluorescence (LIF) spectroscopy in supersonic free jets was applied to diphenylbenzobis(thiadiazole) [Angew. Chem., Int. Ed. Engl. 33 (1994) 1977], in the excitation wavelength region of 500–595 nm. The position of the electronic origin was determined to be 589.81 ± 0.02 nm. The LIF excitation spectra indicate that the phenyl groups swing torsionally with large amplitude in the electronically excited state. The fluorescence lifetimes were measured at 11 major vibronic bands to vary between 42.0 and 43.4 ns, with no observable decrease for vibrational energies in the first excited singlet state up to 2605 cm^{-1} . The LIF spectrum and fluorescence lifetime of van der Waals complexes with xenon atoms were also measured. No heavy-atom effect on the fluorescence lifetimes was observed, and therefore the fluorescence quantum yields are expected to be unity even when the excited molecule had a high excess energy up to 2605 cm^{-1} . © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

λ^2, λ^4 -Benzobis(thiadiazole) (BBTD) derivatives have unique electronic structures consisting of heterocycles containing hypervalent sulfur atoms [1–5]. These heterocyclic molecules have high electron affinities and are expected to have unique photophysical properties [5]. No spectroscopic data are available in the gaseous phase of diphenylbenzobis(thiadiazole) (DPBBTD),



although the wavelengths of spectral maxima in the absorption and dispersed fluorescence spectra in methylene chloride were reported as 558 and 642 nm by Ono et al. [5].

Upon photo-excitation, the torsional motions of the phenyl groups in biphenyl [6–8], anthracene derivatives [9–12], and naphthalene/tetracene derivatives [13], often occur with large amplitude in the first excited singlet state (S_1). Although, the torsional potential energy surfaces are different in

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all these molecules and the present molecule DPBBTD, the phenyl groups in the excited DPBBTD molecule probably have torsional motions as well. From a molecular structural point of view, the torsional potential energy surfaces in the electronic ground (S_0) and S_1 states of DPBBTD are expected to be similar to those of biphenyl because the intramolecular interference between the H atom in the phenyl group and the N atom in the BBTD skeleton is rather insignificant.

In the present study, laser-induced fluorescence (LIF) spectra and fluorescence decay curves were observed for DPBBTD in supersonic free jets, and the electronic origin and fluorescence lifetimes were determined. The fluorescence lifetimes of van der Waals (vdW) complexes of DPBBTD with Xe atoms were also measured. From the spectral analysis, the torsional motions of the phenyl groups are discussed. The electronic relaxation processes of DPBBTD are also discussed by using the fluorescence lifetimes obtained in the present study.

2. Experimental

Bare DPBBTD and its vdW complexes with Xe atoms were prepared in supersonic free jets by the same method used for the generation of jet-cooled anthracene derivatives and their vdW complexes with rare-gas atoms (Ar, Kr, and Xe) [12,14–17]. In brief, gaseous DPBBTD was generated by heating the solid to ca. 423 K and the vapour was expanded into a vacuum chamber ($\sim 10^{-5}$ Torr) through a 150 μm cw-nozzle, with a Ne buffer gas of ca. 760 Torr. For the vdW complexes, the Ne gas was replaced with Xe gas. The laser beam, a dye laser pumped by a XeCl excimer laser (Lambda Physik LPX105 + FL3002), crossed the supersonic jet at 7 mm downstream of the nozzle. The fluorescence was detected through a band-pass filter (Toshiba R-60) in combination with a photomultiplier tube (Hamamatsu R331). In the measurement of excitation spectra, the intensity of the output signal, integrated with a boxcar averager (PAR Model 162), was recorded continuously as the laser wavelength was scanned. The laser wavelength was calibrated by the LIF measure-

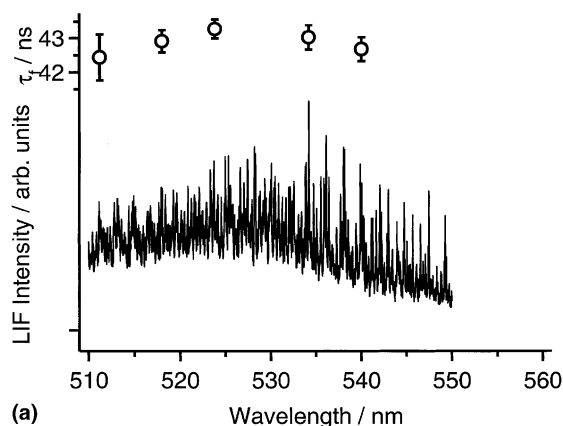
ment for jet-cooled 9-cyanoanthracene [14,15]. The laser line width was estimated to be less than 0.6 cm^{-1} by the spectral bandwidths observed in the present study. The temporal width of the laser pulse was ca. 10 ns. The fluorescence intensities were not corrected for the laser intensity. The fluorescence decay curves were recorded by a digital oscilloscope (LeCroy 7200). The fluorescence lifetimes were obtained by a conventional convolution method. The absorption spectrum of gaseous DPBBTD, generated by heating the solid to ca. 538 K in the sealed quartz cell, was observed by using a spectrometer (Shimadzu UV-210A).

3. Results and discussion

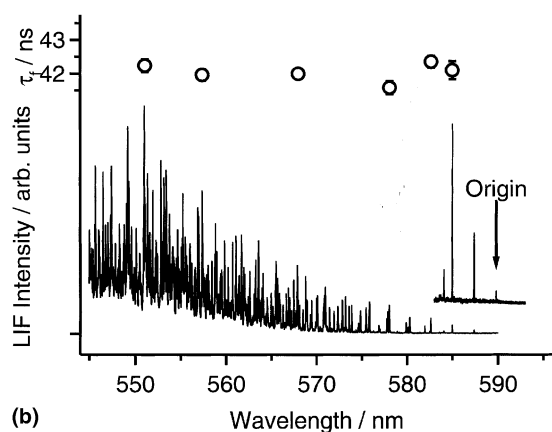
3.1. LIF excitation spectra

Fig. 1 shows the LIF excitation spectra in which a number of excitation bands of jet-cooled DPBBTD appear. As is expected from the absorption spectrum of DPBBTD measured in the gaseous phase at 538 K (Fig. 2) which is structureless and broad, the vibronic bands in the LIF spectra of the jet-cooled molecules are heavily congested and cover the whole wavelength region. The longest wavelength band is observed at $589.81 \pm 0.02\text{ nm}$ and is assigned to the electronic origin of the S_1 state. From the origin to the higher energy region, vibrational progressions with constant frequency intervals ($60\text{--}70\text{ cm}^{-1}$), which are due to torsional motions of the two phenyl groups, can be seen in the expanded spectrum (Fig. 3). The wave numbers for the observed bands are listed in Table 1. The intervals, i.e., vibrational frequencies, are slightly larger than those ($50\text{--}60\text{ cm}^{-1}$) observed in the LIF spectrum of 9,10-diphenylanthracene (DPA), [12] and comparable to the frequency of the torsional motion ($\sim 65\text{ cm}^{-1}$) for biphenyl in the S_1 state [6–8].

The progression covers a wide energy region, at least 500 cm^{-1} . In this Franck–Condon profile, the transition to the vibrational states with high quanta (~ 8) of torsion is a maximum, while the transition to the vibrational ground state is weak, i.e., the overlap between the zero-point vibrational wavefunctions in the S_0 and S_1 states is small. This



(a)



(b)

Fig. 1. LIF excitation spectra (solid lines) and fluorescence lifetimes τ_f (open circles) measured for DPBBTD in a supersonic free jet. The length of vertical bars represents a standard deviation on the lifetime analysis. Experimental reproducibility of the fluorescence lifetimes was less than ± 0.5 ns. Upper and lower spectra were measured in the regions of 510–550 nm and 545–595 nm using Coumarin-500 and Coumarin-540A, respectively, as laser dyes. The expanded spectrum in the region of 585–595 nm was measured in order to determine the position of the electronic origin.

indicates that the equilibrium conformation in the S_1 state is displaced from that in the S_0 state. Therefore, the amplitude of the torsional motions of phenyl groups in DPBBTD seems to be quite large. The large amplitude is probably a consequence of a limited intramolecular steric hindrance of the phenyl groups in DPBBTD. In the S_1 state, it is expected that the energy barrier due to the steric hindrance is no longer decisive and that a coplanar structure becomes the most stable [6–11].

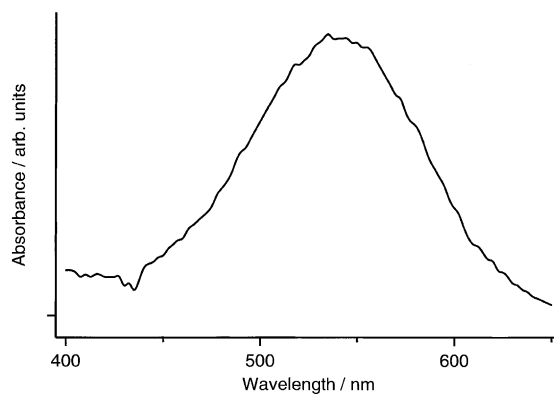


Fig. 2. Absorption spectrum of gaseous DPBBTD at 538 K. The band pass was 1 nm.

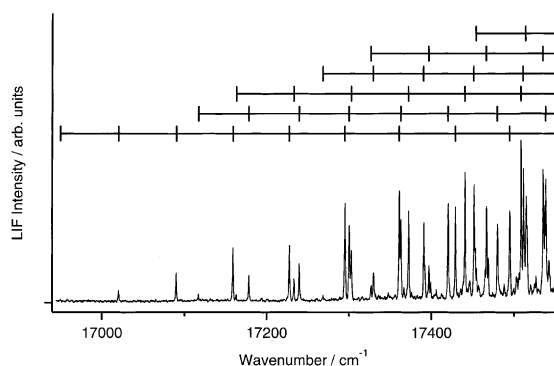


Fig. 3. LIF excitation spectrum of DPBBTD in a supersonic free jet shown using an expanded scale in the range 16945–17550 cm^{-1} . Band progressions associated with torsional vibrations of the phenyl groups and indicated. The progressions are labelled as numbers (1–6) for the present.

The band structure consists of a number of progressions. The constant intervals observed in the progressions indicate harmonic, torsional vibrations of the two phenyl groups. Therefore, the potential energy surface in the S_1 state is expected to have a single minimum where the two phenyl rings and the BBTD plane in DPBBTD are coplanar. The potential energy surface in the S_0 state should have an energy barrier at the coplanar conformation due to the intramolecular steric hindrance.

Since the harmonic, torsional vibrations (60–70 cm^{-1}) in the S_1 state are comparable to those (~ 65 cm^{-1}) for biphenyl [6–8], the torsional po-

Table 1
Energies of the observed bands ($\tilde{\nu}$) and their intervals for the vibrational progressions ($\Delta\tilde{\nu}$), in cm^{-1}

$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$
Progression 1		17360.8	60.4	17329.8	61.3
16949.9	–	17420.7	59.9	17391.0	61.2
17020.0	70.1	17480.4	59.7	17451.7	60.7
17089.9	69.9	17539.3	58.9	17512.0	60.3
17159.1	69.2	17598.0	58.7	17572.0	60.0
17227.4	68.3				
17295.3	67.9	Progression 3		Progression 5	
17362.9	67.6	17162.9	–	17326.8	–
17429.5	66.6	17233.0	70.1	17397.1	70.3
17495.4	65.9	17303.1	70.1	17467.0	69.9
17561.0	65.6	17372.3	69.2	17536.2	69.2
		17441.1	68.8	17606.0	69.8
Progression 2		17509.2	68.1		
17116.8	–	17576.0	66.8	Progression 6	
17178.3	61.5			17454.8	–
17239.6	61.3	Progression 4		17515.3	60.5
17300.4	60.8	17268.5	–	17576.0	60.7

The quoted $\tilde{\nu}$ values represent the peak position of the various bands. The uncertainties are $\pm 0.5 \text{ cm}^{-1}$.

tential energy surfaces of DPBBTD are expected to be similar to those of biphenyl. The biphenyl molecule has a twisted geometry in the S_0 state but it has a planar conformation in the S_1 state and its potential energy surface is almost harmonic along the torsional motion coordinate [6–8]. The interference between the two phenyl groups in biphenyl is too weak to form an effective energy barrier in the S_1 state. On the other hand, in the S_0 and S_1 states of 9-phenylanthracene, the anharmonic potential energy surfaces along the torsion angle between the phenyl and anthracene planes have an almost single and a double minimum, respectively, due to the strong steric hindrance [9–11]. In the case of DPBBTD, the phenyl groups and the BBTB skeleton probably have a torsion geometry in the S_0 state due to their intramolecular interference. In the S_1 state, however, the DPBBTD molecule is expected to have a planar conformation just as does the biphenyl molecule because the π -interaction is enhanced and the interference is probably ineffective.

3.2. Fluorescence lifetimes

The fluorescence lifetimes τ_f were obtained at specific strong excitation bands of jet-cooled DPBBTD, by least-squares fits of exponentials to

the fluorescence decay curves recorded. The τ_f values and their statistical errors obtained in the present study are plotted with the LIF spectra in Fig. 1 and the experimental reproducibility was less than 0.5 ns. The values of τ_f are seen to be quite large and almost constant (42.0–43.4 ns) over the vibrational progressions examined. These fluorescence lifetimes are significantly longer than the fluorescence lifetimes (15–35 ns) reported for the jet-cooled anthracene derivatives [18,19], which have a 14π -electron-system as DPBBTD does.

The electronic relaxation processes of DPBBTD can be discussed by analogy with the anthracene derivatives. Large values of τ_f (20 ~ 30 ns) have been observed for 9,10-dichloroanthracene (DCA) [16,20] and 9,10-dicyanoanthracene (DCNA) [17] at their electronic origins. These regarded as the natural radiative lifetimes, since, for these molecules the nonradiative transitions, i.e., intersystem crossing (ISC) from the S_1 to the T_2 electronic state, are not available [21,22]. The S_1 levels of these molecules are considered to be lower than the levels of T_2 state which has the most effective interaction with the S_1 state [16,17,20]. When the energy level of the vibrationally excited state in the S_1 state is higher than the T_2 level, even if the origin level is lower, the ISC is expected to be available. Actually, the ISC from the vibronic

levels with high excess energy has been observed for 9-cyanoanthracene [14,15,23], i.e., the τ_f values are shortened with an increase in the excess energy. Therefore, in the case of DCA and DCNA, the energy level of T_2 is much higher than the S_1 level. On the other hand, in the electronic relaxation processes of jet-cooled DPA, the ISC from any vibronic levels of the S_1 state to the T_2 state can occur due to the higher energy level of S_1 relative to T_2 [12], so that the τ_f values are significantly shorter (≤ 10.2 ns) than the radiative lifetime.

Based on arguments used for anthracene derivatives, the nonradiative relaxations from S_1 of DPBBTD are supposed to be unavailable as for DCA or DCNA. That is, the fluorescence quantum yield of jet-cooled DPBBTD is expected to be unity. This prediction can be verified by a check as to whether there is the heavy-atom effect [24–27] on the fluorescence lifetime, i.e., shortening in the fluorescence lifetime due to the acceleration of the ISC rate, for the DPBBTD-Xe vdW complexes.

3.3. vdW complexes with Xe atoms

LIF from the vdW complexes of DPBBTD with Xe atoms was also observed in the present study, as shown in Fig. 4. The LIF excitation yields a broad feature. This reflects the overlap of a number of vibronic bands arising from a distribution of various complexes different in the number and

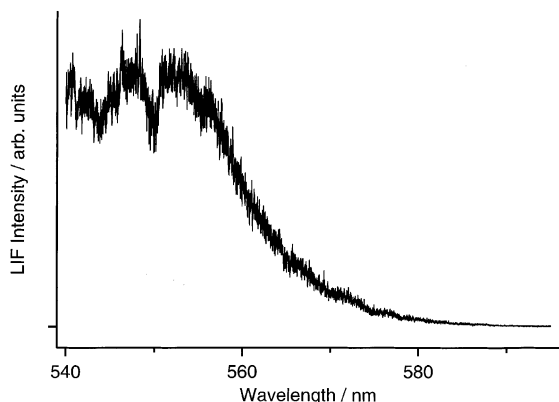


Fig. 4. LIF excitation spectrum of the vdW complexes of DPBBTD with Xe atoms. In the jet expansion, DPBBTD was seeded in ca. 760 Torr of Xe gas.

structure of coordinating Xe atoms [12,19]. The values of τ_f were obtained as 52.7 ± 0.3 and 49.5 ± 0.1 ns at the exciting wavelengths of 553 and 520 nm, respectively. The errors are only standard deviations on the lifetime analysis. As no short-period fluorescence lifetimes were observed, the heavy-atom effect on the fluorescence decay process of DPBBTD [23–26] is absent. It seems that ISC does not occur, even if the spin-orbit coupling is enhanced by the heavy-atom effect. Therefore the fluorescence quantum yields should be unity. Taking the argument of the fluorescence decay processes of the anthracene derivatives (see Section 3.2) into account, the energy level of the triplet state T_n , which interacts effectively with the S_1 state of DPBBTD, is located higher than the S_1 level, so that ISC from the S_1 to T_n is not allowed energetically. It also must be considered that the S_1 level relative to the T_n level is lowered by the coordination of Xe [12,27], but that is not important here because the constant τ_f values for bare DPBBTD obtained in the present study indicate that no vibronic levels above the T_n level were observed, i.e., the S_1 level is already much lower than T_n level. The energy gap between the S_1 and T_n levels is estimated to be larger than at least 2605 cm^{-1} , which is the highest excess energy for which the τ_f value was measured. The nonradiative process from S_1 to T_1 is ineffective as well, because, if not, this process should be enhanced by the heavy-atom effect leading to the shorter fluorescence lifetime for the Xe complexes at the electronic origin. The internal conversion process from S_1 to S_0 might have to be considered since the energy gap between S_1 and S_0 is significantly smaller than those for anthracene derivatives. However, such a process will not be effective for DPBBTD judging from the fact that the fluorescence lifetime remains practically constant with increasing excess energy.

The number of Xe atoms clustered on the DPBBTD molecule is unknown. Also, there is a possibility that the predissociation of one or more Xe atoms gives rise to form the bare DPBBTD molecule. However, the majority of fluorescence is not emitted from the bare molecule. Fluorescence from the DPBBTD-Xe $_n$ ($n \geq 1$) clusters should be observed. As shown in Fig. 5 the fluorescence decay curve measured for the vdW complexes is

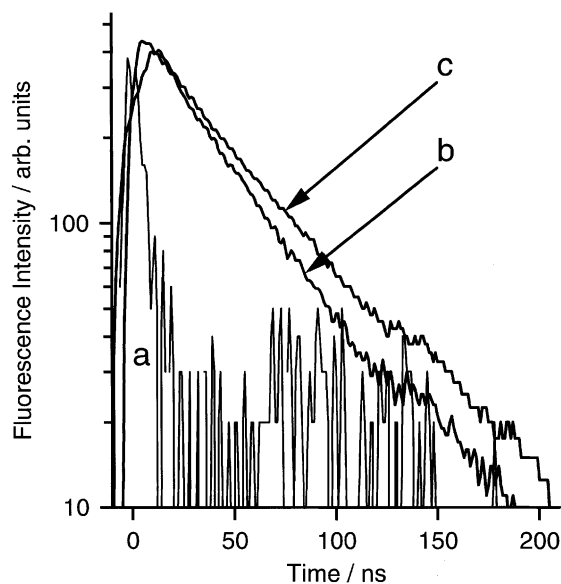


Fig. 5. Fluorescence decay curves of DPBBTD in a supersonic free jet and their vdW complexes. (a) Temporal profile of the laser pulse. The original data were multiplied by a factor of 10. (b) Fluorescence decay of bare DPBBTD observed in the 584.98 nm photoexcitation. (c) Fluorescence decay of the vdW complexes of DPBBTD with Xe observed in the 553 nm photoexcitation. The original data were multiplied by a factor of 2.5.

single-exponential and its decay rate is definitely slower than the fluorescence decay rate of the bare molecule. The decay curve for the vdW complexes does not have a significant component of the fluorescence decay indicating the lifetime of 42.0–43.4 ns. Moreover, there is no component of the decay curve indicating the heavy-atom effect at all. It is assumed that the clusters formed in the present experiment have several fXe atoms; the fluorescence from the DPBBTD-Xe_n ($n \geq 1$) clusters is observed even if the parent clusters are predissociated.

It should be noted that the values of τ_f measured for the vdW complexes were ca. 1.2 times longer than the values for the bare molecule. This is presumably because the magnitude of the oscillator strength is modified by the coordination of Xe [20,28,29]. Since this elongation of the τ_f value is more significant than that reported for anthracene derivatives [20,28,29], it is likely that the microscopic molecular environment surrounding DPBBTD has a strong influence on the electronic

transition. However, further investigations are required to know the true reasons why the τ_f value is increased by coordinating Xe atoms.

4. Conclusion

The characteristics of the LIF spectrum and the fluorescence lifetimes measured for the jet-cooled DPBBTD molecules are reported. The electronic origin of the S₁ state was observed at 589.81 ± 0.02 nm and numerous vibronic bands were observed in the LIF excitation spectra. Since the vibronic progressions indicate harmonic, torsional vibrations, the potential energy curves along the torsional coordinate of the phenyl groups in DPBBTD in the S₁ states are expected to have a single minimum at the coplanar conformation. No indication of nonradiative processes from the S₁ state was observed in the present study. The fluorescence quantum yields are therefore expected to be unity and also the energy level of the S₁ state should be lower than the level of the T_n state, which has the most effective interaction with the S₁ state.

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