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Invited feature article

Variable-temperature absorption and emission properties of 1,2-diphenylacetylene and 1,4-diphenylbuta-1,3-diyne derivatives

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ABSTRACT

Variable-temperature absorption and emission data over the range 80–300 K have been collected for 1,2-diphenylacetylene (DPA) and its derivatives, as well as 1,4-diphenylbuta-1,3-diyne (DPB) derivatives in 2-methyltetrahydrofuran (2-MeTHF). Moreover, the influence of temperature on fluorescence lifetime and quantum yield has also been investigated. A strong coupling between solvation dynamics and solute structure is observed in the low-temperature regime as well as at intermediate temperature where the structure of the compound is evolving in the course of excited-state relaxation. Moreover, the dependency of fluorescence quantum yield on temperature indicates that the energy of activation of radiationless transition for 1,2-diphenylacetylene and its derivatives is larger than the activation energy of viscous flow of 2-MeTHF, while for 1,4-diphenylbuta-1,3-diyne derivatives the opposite is observed. This finding implies that the conformational change of DPA and its derivatives in the excited state in 2-MeTHF shows an activation energy, contrary to DPB and its derivatives for which conformational changes are barrierless.

1. Introduction

Photophysical properties of 1,2-diphenylacetylene (DPA) and 1,4-diphenylbuta-1,3-diyne (DPB) are completely different than acetylene[1] or buta-1,3-diyne derivatives containing polycyclic aromatic hydrocarbons as substituent(s) [2–5]. While DPA [6,7] and DPB [7] are very weakly fluorescent at room temperature, derivatives containing polycyclic aromatic hydrocarbons or heteroaromatic substituent(s) [1–5,8–15] as well as highly conjugated poly(*p*-phenylenethynylene)s [16–19] show intense fluorescence.

One of the most interesting photophysical property of DPA is the loss of fluorescence that occurs following excitation of higher vibronic levels of the $^1B_{1u}$ state under collision-free conditions of a supersonic free jet [20]. It has been explained by Zgierski and Lim on the basis of theoretical calculations [21–23]. They indicate that the lowest-energy excited singlet state of DPA is the B_{1u} ($\pi\pi^*$) state in the linear D_{2h} symmetry, while $\pi\sigma^*$ state of A_u symmetry is the lowest in energy in the bent C_{2h} symmetry. This leads to the crossing of the fluorescent $\pi\pi^*$ state and weakly-fluorescent [24] $\pi\sigma^*$ state potential energy curves. The transition from initially excited $\pi\pi^*$ state to $\pi\sigma^*$ state requires crossing a small energy barrier, which explains the loss of fluorescence in the gas phase at higher excitation energies and the thermally activated quenching of fluorescence in the solution. The calculations made by Zgierski et al. [21,22] also predicted modification of the spectral and photophysical properties of DPA derivatives after attachment of an electron-withdrawing or an electron-donating group to DPA. For DPA with an electron-withdrawing group, the energy of $\pi\sigma^*$ increase and the $\pi\pi^* \rightarrow \pi\sigma^*$ state switch does not occur, while the attachment of an electron-donating group should enhance the state switch from an initially excited $\pi\pi^*$ to $\pi\sigma^*$ state. All these predictions have been experimentally confirmed [1,2,21–23,25–33]. The photophysical properties of DPA and its derivatives have been extensively studied in contrast to such properties of DPB and its derivatives which were studied to a much lesser extent [2,3,7,34,35]. For DPB the fluorescent state is assigned to 1^1B_{1u} and the presence of non-fluorescent relaxation pathway was also found in excess of about 2000 cm^{-1} above 1^1B_{1u} which was attributed to the closely lying 1^1A_u state, similarly to DPA [7]. Also, the influence of substituents in the phenyl ring of DPB causes similar effects as in the case of DPA [2]. DPB derivatives containing electron-accepting

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substituents have a greater fluorescence quantum yield and the absence of significant thermal quenching of emission, while these with electron-donating substituents show no measurable fluorescence at room temperature. Moreover, their fluorescence depends strongly on temperature. The fluorescence quantum yields of studied DPB derivatives are substantially lower than these of DPA derivatives as a result of greater conformational freedom of DPB and its derivatives. High flexibility of DPB at ambient and even at cryogenic temperature was also postulated by Thulstrup et al. [34] based on the IR and UV linear dichroism study.

Steady-state measurements of fluorescence quantum yield as a temperature function allowed to state that the fluorescent state of DPA is thermally deactivated with activation energy equal to 14 kJ/mol [6]. A big difference in fluorescence intensity at room and liquid nitrogen temperature was found for DPB and its derivatives, while there are no systematic studies on the effect of temperature on the photophysical properties of this class of compounds [2]. To further probe the non-radiative pathways that depopulate the singlet-excited state, the influence of temperature on the spectral and photophysical properties of DPA and DPB derivatives in 2-methyltetrahydrofuran (2-MeTHF) was investigated in order to know the differences and similarities between these two classes of compounds.

2. Materials and methods

Symmetrically substituted 1,2-diphenylacetylene and its derivatives: 1,2-bis(4-methoxyphenyl)ethyne (dOMeDPA), 1,2-bis(phenyl)ethyne (DPA), dimethyl 4,4’-(ethyne-1,2-diyl)dibenzoate (dCOOMeDPA), 4,4’-(ethyne-1,2-diyl)dibenzonitrile (dCNDPA), 4,4'-(ethyne-1,2-diyl)bis(*N*,*N*-dimethylaniline) (dDMADPA), 1,4-diphenylbuta-1,3-diyne derivatives: 1,4-bis(4-methoxyphenyl)-buta-1,3-diyne (dOMeDPB), dimethyl 4,4′-(buta-1,3-diyne-1,4-diyl)dibenzoate (dCOOMeDPB), 4,4′-(buta-1,3-diyne-1,4-diyl) dibenzonitrile (dCNDPB), 4,4′-(buta-1,3-diyne-1,4-diyl)-bis(*N*,*N*-dimethylaniline) (dDMADPB) were synthesized as described previously [1,2]. The structures of studied compounds are presented in Fig. 1 ESI.

2.1. Variable-temperature absorption and fluorescence measurements

Absorption spectra were measured using a Perkin-Elmer Lambda-40P spectrophotometer whereas fluorescence spectra were measured using a FluoroMax-4 (Horriba Yobin-Yvon) spectrofluorimeter. Low temperature absorption and luminescence spectra were obtained using an Optistat DN2 dewar and Mercury ITC controller from Oxford Instruments. In the absorption measurements, the sample concentration was about 10^{-5} M for DPA and its derivatives acetylene derivatives and $3 * 10^{-5}$ M for DPB derivatives, while in fluorimetric measurements the concentration of samples were the order of magnitude smaller ($1–3*10^{-6}$ M).

Fluorescence quantum yield at each temperature was calculated applying a reference method using published room temperature fluorescence quantum yield values [1,2] as references. For dOMeDPA, DPA and dCOOMeDPA, 2-aminopyridine in 0.1 M H_2SO_4 ($\varphi = 0.60$) was used, whereas for dDMADPA, dCNDPA, dCNDPB, dCOOMeDPB, dDMADPB and dOMeDPB – quinine sulphate in 0.5 M H_2SO_4 ($\varphi = 0.53$). All values were corrected for the absorbance change with temperature at excitation wavelength, however, they were not corrected for the change of the refractive index of 2-MeTHF with temperature because of lack of the appropriate data. The excitation wavelength (given in figure caption) coincided with the first vibronic band of the absorption spectrum to avoid thermal deactivation of excited state [1,2,6].

The fluorescence lifetimes were measured with a time-correlated single-photon counting CD-900 fluorescence lifetime spectrometer (Edinburgh Instruments) using an appropriate sub-nanosecond pulsed diode from Horriba as a light source

Variable-temperature measurements were performed as follows: each sample, optically thin (o.d.$\sim$0.1), in a standard quartz fluorescence cuvette was placed in dewar and spectra or fluorescence intensity decay was collected. Then the temperature of the sample was decreased, typically in a 5 K increment except for the high temperature region (close to the room temperature) for which $\Delta T = 10$ K. The sample was allowed to stabilize at the new temperature until the temperature does not change more than within ± 0.1 K. Afterwards a new proper measurement was made. This process was repeated until the lowest temperature had been taken (about 80 K). Care was taken to avoid moving the optical dewar within a full variable-temperature run.

3. Results and discussion

3.1. Absorption spectroscopy

3.1.1. DPA and its symmetrically substituted derivatives

The influence of temperature on photophysical properties of DPA will be discussed first, because it is a model compound for which partial data in 2-methyl-pentane (MP) and diethyl ether, pentane and alcohol, 5:5:3 solvent mixture (EPA) has been published by Ferrante at al. [6]. Absorption spectra of 1,2-diphenylacetylene in 2-MeTHF at different temperatures are presented in Fig. 1. They are similar to these already published [6].

It was found that lowering the temperature causes an increase of absorbance which is probably a result of the solvent contraction [36,37] rather than conformational changes of the studied compound (if so, probably in small extent). The vibronic structure of the spectrum becomes more pronounced at lower temperature resulting from the hindered rotation in the ground state caused by solvent viscosity increase [36,38–42]. The single progression of the most prominent vibronic structure at about 2000–2100 cm^{-1} is displayed from the origin that has been assigned to the C≡C stretching mode [1,7]. Moreover, other vibronic bands (about 1000 cm^{-1}), which may be attributed to the total symmetric vibrations of the phenyl ring, are visible in the absorption spectrum [1,7]. When the temperature decreases from the room temperature up to about 250 K, a small bathochromic shift of the position of the absorption band maximum is observed (about 4 nm, $\sim$450 cm^{-1}). In the temperature range from 250 K to 80 K, this shift is almost linear (Fig. 2 ESI).

For all studied derivatives of DPA a similar character of changes in the absorption spectrum can be observed – an increase in

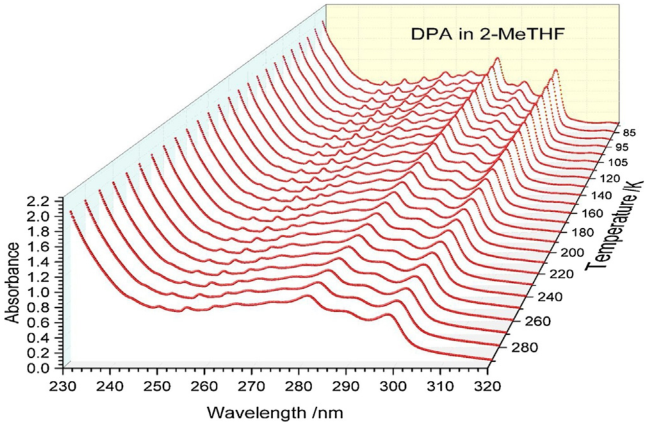

Fig. 1. Absorption spectra of DPA in 2-MeTHF at different temperatures.