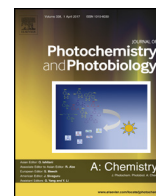




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Temperature-dependence of spectral and photophysical properties of polycyclic aromatic hydrocarbon derivatives of acetylene and buta-1,3-diyne

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ABSTRACT

Variable-temperature absorption and emission data over the range 80–300 K have been collected for acetylene and buta-1,3-diyne derivatives with polycyclic aromatic hydrocarbons as substituents, in 2-methyltetrahydrofuran (2-MeTHF). 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. Moreover, the dependency of fluorescence quantum yield on temperature indicates that the energy of activation of conformational changes for studied compounds is comparable or slightly larger than the activation energy of viscous flow of 2-MeTHF. Moreover, contrary to diphenyl derivatives of buta-1,3-diyne for which conformation changes are barrierless, polycyclic aromatic hydrocarbons derivatives are characterized by a relatively high activation energy.

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1. Introduction

Acetylene and buta-1,3-diyne derivatives containing a polycyclic aromatic hydrocarbon or heteroaromatic as a substituents have been applied to a variety of purposes. They can be used as polarity-sensitive probes [1–4], for labelling biological molecules and intracellular imaging [5,6], as oligonucleotide analogues [7], fluorescence switches [8–10], electrochemiluminescent materials [11–16] or to synthesize conjugated macromolecules [17–19]. Moreover, so-called pull–push chromophores containing electron donors and acceptors connected by a π -electron bridge (D– π –A) show a large nonlinear optical response (NLO) which allows to use them in second-order NLO applications [4,20–23]. Poly(arylene-ethylene)s find wide application in molecular engineering [24–26] and components of light-emitting diodes and solar cells [27,28]. Buta-1,3-diyne derivatives are less applicable than acetylene derivatives, however, substituted buta-1,3-diyne undergo 1,4-addition reactions in the solid state giving polydiacetylene [29] which can be used as a label-free fluorogenic chemosensor [18].

Photophysical properties of acetylene and buta-1,3-diyne derivatives containing a polycyclic aromatic hydrocarbon or

heteroaromatic substituents are completely different than 1,2-diphenylacetylene (DPA) and 1,4-diphenylbuta-1,3-diyne (DPB) derivatives. While DPA and DPB derivatives are weakly fluorescent at room temperature [30–38], derivatives containing polycyclic aromatic hydrocarbon or heteroaromatic substituents as well as highly conjugated poly(*p*-phenylenethynylene)s show intense fluorescence [4,39–46]. This difference in photophysical properties has been explained by Zgierski and Lim on the basis of theoretical calculations [35,36]. They indicate that the lowest-energy excited singlet state of DPA is the 1^1B_{1u} ($\pi\pi^*$) state in the linear D_{2h} symmetry, while $\pi\sigma^*$ state of 1^1A_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 $\pi\sigma^*$ state potential energy curves [33,37]. 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 dependence of fluorescence quantum yield on temperature has been shown that the bending motion involved in the $1^1B_{1u} \rightarrow 1^1A_u$ internal conversion of DPA requires overcoming a small intrinsic barrier (about 4 kJ/mol) and the fraction of the activation energy for the viscous flow, that is imposed on the relaxation of the excited state, is 0.98 [37,47]. A small intrinsic barrier is also characteristic for symmetrically substituted acetylene derivatives [48]. However, relaxation of the

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excited state of buta-1,3-diyne derivatives are barrierless [48]. High flexibility of DPB at ambient and even at cryogenic temperature was also postulated by Thulstrup et al. basing on the IR and UV linear dichroism study [49].

To explain in detail the differences in photophysical properties between diphenyl derivatives and polycyclic aromatic hydrocarbons derivatives of acetylene and buta-1,3-diyne spectral and photophysical studies in 2-methyltetrahydrofuran (2-MeTHF) in wide temperature range were performed and the differences and similarities between these two classes of compounds is discussed.

2. Materials and methods

Symmetrically substituted diarylacetylenes and diarylbuta-1,3-diyne: 1,2-di(naphtalen-1-yl)ethyne (1Nac), 1,2-di(naphtalen-2-yl)ethyne (2Nac), 1,4-di(naphtalen-1-yl)buta-1,3-diyne (1Nac2), and 1,4-di(naphtalen-2-yl)buta-1,3-diyne (2Nac2), 1,2-di(anthracen-9-yl)ethyne (Aac) and 1,4-di(anthracen-9-yl)buta-1,3-diyne (Aac2) presented in Fig. 1, were synthesized and isolated as described previously [46].

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 (HorribaYobin-Yvon) spectrofluorimeter. Low temperature absorption and luminescence spectra were obtained using an Optistat DN2 dewar and Mercury ITC controller from Oxford Instruments.

Fluorescence quantum yield at each temperature were calculated applying a reference method using published fluorescence quantum yield values for room temperature [1–3] as references. Quinine sulphate in 0.5 M H₂SO₄ ($\phi = 0.53$) was used for 1Nac, 2Nac, 1Nac2 and 2Nac2 and fluorescein in 0.1 M NaOH ($\phi = 0.87$) for Aac and Aac2. All values were corrected for the absorbance change with temperature at excitation wavelength, however were not corrected for the change of refractive index of 2-methyltetrahydrofurane (2-MeTHF) with temperature.

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

Variable-temperature measurements were made as follows: each sample optically thin (o.d. ~ 0.1) in a standard quartz fluorescence cuvette was placed in dewar and spectra or fluorescence intensity decay at room temperature were collected. The temperature of the sample was decreased. Increment was 5 K with the exception of high temperature region (close to the room temperature) for which $\Delta T = 10$ K. Before measurement the sample was stabilized at the new temperature to within ± 0.1 K. The measurements were carried out until the temperature reached 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

Figs. 2–4 show the absorption spectra of diarylacetylene (2Nac, 1Nac, Aac) measured at different temperatures, while Figs. 5–7

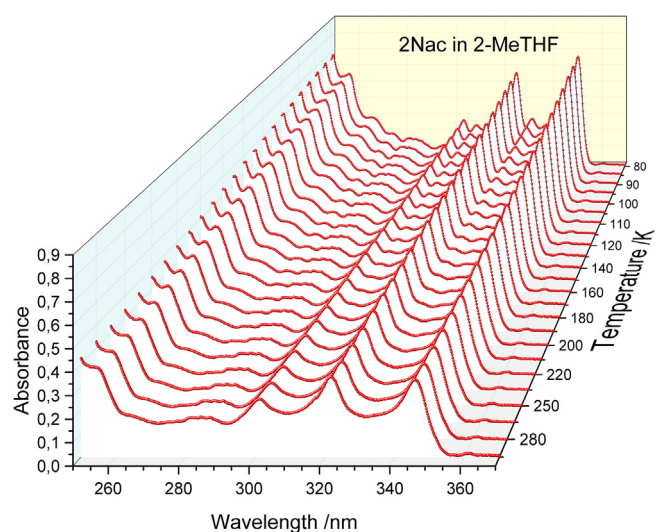


Fig. 2. Absorption spectra of 2Nac in 2-MeTHF at different temperatures.

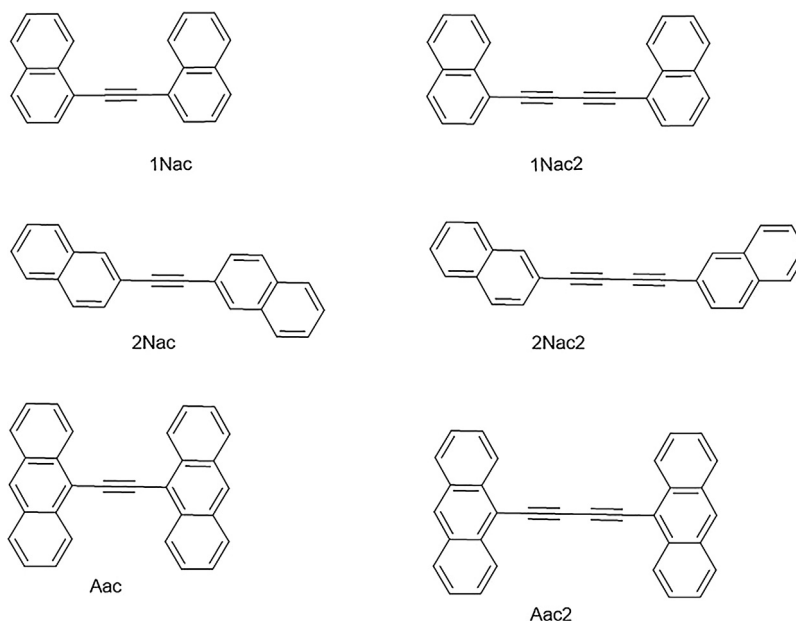


Fig. 1. Structure of studied compounds.

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