Influence of an electron-acceptor substituent type on the photophysical properties of unsymmetrically substituted diphenylacetylene

Małgorzata Szyszkowska, Irena Bylińska, Wiesław Wiczk*

Faculty of Chemistry, University of Gdańsk, Wita Stwosza 63, 80-308 Gdańsk, Poland

ABSTRACT

Unsymmetrically substituted diphenylacetylene derivatives containing a different type of an electron-acceptor substituent were synthetized and studied using spectroscopic methods in order to establish the influence of electron affinity of substituent on the photo physics of donor-acceptor pairs. Spectral and photophysical properties were studied in 14 solvents (non-polar, polar aprotic and protic). Influence of solvent properties on spectral and photophysical properties of studied compounds was analyzed using Catalan multi-parameter solvent scale. The change of the excited state dipole moment was estimated based on Bilot-Kawski theory.

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1. Introduction

Highly conjugated poly(*p*-phenylenethynylene)s are strongly fluorescing [1–11]. Likewise, asymmetric acetylene derivatives containing a polycyclic aromatic or hetero-aromatic hydrocarbon substituent on one side and phenyl or its derivative on the second side show intense fluorescence [12–20]. However, 1,2-diphenylacetylene (tolane, DPA) behave quite differently [21–28]. One of the most interesting photophysical properties of DPA is the loss of fluorescence that occurs following excitation of higher vibronic levels of the $^1B_{1u}$ state under the collision-free conditions of a supersonic free jet [21]. It also exhibits a strong temperature dependence of fluorescence quantum yield in solution [22,23]. The results of theoretical calculations made by Zgierski and Lim [24–26] indicate that while the lowest-energy excited singlet state is the B_{1u} ($\pi\pi^*$) state in the linear D_{2h} symmetry, the weakly fluorescent $\pi\sigma^*$ state of A_u symmetry is the lowest in energy in the bent C_{2h} symmetry. This leads to the crossing of the fluorescent $\pi\pi^*$ and weakly fluorescent $\pi\sigma^*$ state potential energy curves [27,28]. The transition from an initially excited $\pi\pi^*$ state to the $\pi\sigma^*$ 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

solution. The calculations made by Zgierski and Lim [24,25] also predicted that the attachment of an electron-withdrawing groups to DPA would increase the energy of the $\pi\sigma^*$ state and the $\pi\pi^*/\pi\sigma^*$ state switch would not be expected to occur. Moreover, the attachment of an electron-donating groups to DPA enhanced the state switch from the initially excited $\pi\pi^*$ to the $\pi\sigma^*$ state. These theoretically predictions have been confirmed experimentally [24,29,30]. Diphenylacetylene and its symmetrically substituted derivatives were mostly studied with an emphasis on theoretical calculations and picosecond absorption spectroscopy, while unsymmetrically substituted diphenylacetylene derivatives in phenyl rings were mostly studied by picosecond transient absorption spectroscopy [24,31–33]. Moreover, only for *p*-cyano-*p'*-methylthiodiphenylacetylene [34] and *p*-cyano-*p'*-N,N-dimethylaminodiphenylacetylene [35] the fluorescence in various solvents was reported.

1.1. Catalan solvent polarity scale

A general model which describes the properties of solvent and solvation does not exists. As a result, several empirical solvent polarity scales were proposed to characterize and rank empirically the polarity of the solvent. To study solute-solvent interactions multiparameter solvent polarity scales are widely used. The multiple linear regression approach based on a three-parameter scale of polarity of the solvent was introduced by Kamlet et al. [36].

Another, extended to a four-parameter, solvent polarity scale was introduced by Catalan [37] according to the equation:

$$y = y_0 + a_{SP}SP + b_{SdP}SdP + c_{SA}SA + d_{SB}SB \tag{1}$$

where y denotes a solvent-dependent physicochemical property in a given solvent and y_0 the statistical quantity corresponding to the value of property in the gas phase; SP, SdP, SA, and SB represent independent solvent parameters accounting for various types of solute-solvent interactions (SP denotes solvent polarizability, SdP—solvent dipolarity, SA—solvent's hydrogen bond donor strength and SB—hydrogen-bond acceptor strength); a_{SP}, b_{SdP}, c_{SA}, and d_{SB} are adjustable coefficients that reflect the sensitivity of the physical quantity y in a given solvent to the various solvent parameters.

1.2. Determination of excited state dipole moment of molecule by solvatochromic method

In the case of different electron densities in the electronic ground and excited state of a light-absorbing molecule, its dipole moment varies in these two states. Thus, a change of the solvent affects the ground and excited state differently. For non-polarizable solute, a linear dependence of absorption and emission frequency on the solvent polarity is predicted. Taking into consideration the linear and quadratic Stark's effect for spherical molecules with a radius a, and with approximation that the isotropic polarizability α of the solute of a molecule is $2\alpha/4\pi\varepsilon_0 a^3 = 1$, where a is Onsager's radius and ε_0 vacuum permittivity, following equations, obtained by Bilot–Kawski [38–40], allow to compute dipole moment in the excited state:

$$\tilde{v}_{abs} - \tilde{v}_{em} = m_1 f_{BK}(\varepsilon_r, n) + const \tag{2}$$

$$\tilde{v}_{abs} + \tilde{v}_{em} = -m_2[f_{BK}(\varepsilon_r, n) + 2g(n)] + const \tag{3}$$

the solvent polarizability functions $f_{BK}(\varepsilon_r, n)$ and $g(n)$ in Eqs. (2) and (3) are given by Eqs. (4) and (5):

$$f_{BK}(\varepsilon_r, n) = \frac{2n^2+1}{n^2+2}\left(\frac{\varepsilon_r-1}{\varepsilon_r+2} - \frac{n^2-1}{2n^2+1}\right) \tag{4}$$

$$g(n) = \frac{3(n^4-1)}{2(n^2+2)^2} \tag{5}$$

Using a slope obtained from Eqs. (2) and (3) and knowing the ground-state dipole moment μ_g, the excited-state dipole moment μ_e, can be calculated using the following equations:

$$m_1 = \frac{(\vec{\mu}_e - \vec{\mu}_g)^2}{2\pi\varepsilon_0 hca^3} = \frac{(\mu_e^2 + \mu_g^2 - 2\mu_e\mu_g\cos\Psi)}{2\pi\varepsilon_0 hca^3} \tag{6}$$

$$m_2 = \frac{(\mu_e^2 - \mu_g^2)}{2\pi\varepsilon_0 hca^3} \tag{7}$$

In these equations μ_e and μ_g are the dipole moments in the excited and ground state, respectively, a is Onsager's interaction radius of the solute, h is Planck's constant, c is the velocity of light in vacuum, n—refractive index, ε_r—relative dielectric constant and ε_0 is the permittivity of vacuum, thus $2\pi\varepsilon_0 hc = 1.105110440 \times 10^{-35}$ C^2. Generally, the dipole moments μ_e and μ_g are not parallel to each other but make an angle ψ. The use of Eqs. (6) and (7) leads to:

$$\mu_e = \sqrt{(\mu_g^2 + \frac{1}{2}m_2 hca^3)} \tag{8}$$

$$\cos\Psi = \frac{1}{2\mu_e\mu_g}\left[(\mu_g^2 + \mu_e^2) - \frac{m_1}{m_2}(\mu_g^2 - \mu_e^2)\right] \tag{9}$$

One of the most popular solvent polarity scale is the one parameter solvent polarity scale $E_T(30)$ or the normalized E_T^N parameter introduced by Reichardt et al. [41,42]. For non-hydrogen bond donor solvents, solvent polarity parameter $E_T(30)$ or E_T^N describes almost exclusively the electrostatic forces between solute and solvent [43]. Apart from the dependence of different spectral and photophysical properties, the correlation of the Stokes shift with this parameter can be applied to calculate the dipole moment change between the excited and ground state based on the equation proposed by Ravi et al. [44,45]:

$$\Delta v = \tilde{v}_{abs} - \tilde{v}_{em} = 11307.6\left[\left(\frac{\Delta\mu}{\Delta\mu_B}\right)^2\left(\frac{a_B}{a}\right)^3\right]E_T^N + const \tag{10}$$

where μ_B and a_B are the dipole moment change and Onsager's radius, respectively, for a pyridinium N-phenolatebetaine dye used to determine the E_T^N values ($\mu_B = 9$ D and $a_B = 6.2$ Å), whereas $\Delta\mu$ and a are the corresponding quantities for the molecule under study. The advantage of this equation is to minimize the problem associated with the Onsager's radius estimation since a ratio of two Onsager's radii is involved in the equation. Thus, based only on the Stokes' shift the change of the dipole moment in excited state can be calculated.

Because there is not much information about fluorescence spectroscopy of unsymmetrically substituted DPA derivatives, here we present results of the photophysical studies of substituted DPA derivatives containing an electron-accepting substituent (nitrile, ester or aldehyde group) or an electron-donor group (N,N-dimethyl amino) as well as an electron-donor acceptor pairs (D-π-A) in which as the electron-donor N,N-dimethyl amino group and the electron-acceptor nitrile or ester or aldehyde groups are present. The studies include measurements of the absorption and emission spectra as well as time-resolved fluorescence in different solvents to investigate the effects of type of substituent(s) on the photophysical properties of compound studied. Moreover, the influence of solvents properties on the photophysics on D-π-A compounds using the Catalan solvent polarity scale are analyzed. Based on the solvatochromic method the excited state dipole moment are calculated.

The structure, atom numbering and abbreviation of studied compounds are presented in Fig. 1.

2. Materials and methods

2.1. Synthesis

Studied compounds were synthetized according to Scheme 1. Iodobenzene, 4-iodobenzonitrile, methyl-4-iodobenzoate, phenylacetylene, 4-ethynyl-N,N-dimethylaniline and bis(triphenylphosphine)palladium(II) dichloride (Sigma–Aldrich) and 4-bromobenzaldehyde (Lancaster) were commercially available and used without further purification.

The progress of all reactions was monitored by TLC using Merck plates, Kieselgel 60 F$_{254}$. The products were isolated by means of column chromatography (Merck Kieselgel 60 (0.04–0.063 mm)) and/or semi-preparative RP-HPLC (Kromasil column, C-8, 5 μm, 250 mm long, i.d. 20 mm).

The identification of the product was based on: ^{1}H and ^{13}C NMR spectra (Bruker AVANCE III 500 MHz spectrometer) in CDCl$_3$, mass spectra (Bruker Daltonics HCTultra instrument) and Raman spectra (FRA-106 instrument).