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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

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ABSTRACT

Unsymmetrically substituted diphenylacetylene derivatives containing a different type of an electronacceptor 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

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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-cyanop'-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].







^{*} Corresponding author. E-mail address: wieslaw.wiczk@ug.edu.pl (W. Wiczk).

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

$$y = y_0 + a_{SP}SP + b_{SdP}SdP + c_{SA}SA + d_{SB}SB$$
(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 $2\alpha/4\pi\epsilon_0 a^3 = 1$, 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:

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

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

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

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

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

$$m_1 = \frac{(\vec{\mu}_e - \vec{\mu}_g)^2}{2\pi\epsilon_0 hca^3} = \frac{(\mu_e^2 + \mu_g^2 - 2\mu_e\mu_g\cos\Psi)}{2\pi\epsilon_0 hca^3}$$
(6)

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

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 $2\pi\varepsilon_0hc = 1.105110440 \times 10^{-35}$ C². 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:

$$\mu_e = \sqrt{(\mu_g^2 + \frac{1}{2}m_2hca^3)} \tag{8}$$

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

$$\Delta \nu = \tilde{\nu}_{abs} - \tilde{\nu}_{em} = 11307.6 \left[\left(\frac{\Delta \mu}{\Delta \mu_B} \right)^2 \left(\frac{a_B}{a} \right)^3 \right] E_T^N + const$$
(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 μ m, 250 mm long, i.d. 20 mm).

The identification of the product was based on: ¹H and ¹³C NMR spectra (Bruker AVANCE III 500 MHz spectrometer) in CDCl₃, mass spectra (Bruker Daltonics HCTultra instrument) and Raman spectra (FRA-106 instrument).



4-(phenylethynyl)benzaldehyde PhacPhCHO



4-(phenylethynyl)benzonitrile PhacPhCN



methyl 4-(phenylethynyl)benzoate PhacPhCOOMe



4-((4-(dimethylamino)phenyl)ethynyl)benzaldehyde DMAPhacPhCHO



methyl 4-((4-(dimethylamino)phenyl)ethynyl)benzoate DMAPhacPhCOOMe



4-((4-(dimethylamino)phenyl)ethynyl)benzonitrile DMAPhacPhCN



N,*N*-dimethyl-4-(phenylethynyl)aniline DMAPhacPh

Fig. 1. Structure, atoms numbering and abbreviation of the studied compounds.



A: DMF, Cul, Pd(PPh₃)₄, TEA, T= 55°C, Ar (for PhacPhCHO and DMAacPhCHO) B: TEA, Cul, Pd[(Ph)₃P]₂Cl₂, T= 0°C (for PhacPhCN, PhacPhCOOMe, DMAPhacPh, DMAPhacPhCOOMe, DMAPhacPhCN)

R ₁	R ₂	-X	$R_1 R_2$
-H	-CHO	-Br	PhacPhCHO
	-CN	-1	PhacPhCN
	-COOCH ₃	-1	PhacPhCOOMe
-N(CH3) ₂	-H	-1	DMAPhacPh
	-CHO	-Br	DMAacPhCHO
	-COOCH ₃	-1	DMAacPhCOOMe
	-CN	-1	DMAacPhCN

Scheme 1. Synthesis of unsymmetrical diphenylacetylene derivatives.



Fig. 2. Normalized absorption spectra of PhacPhCOOMe in selected solvents.



Fig. 3. Normalized absorption spectra of DMAPhacPh in selected solvents.

Details of synthesis and identification of studied compounds are presented in ESI.

2.2. Spectroscopic measurements

The UV–vis absorption spectra of studied compounds in various solvents were measured using a PerkinElmer Lambda 40P spectrophotometer, whereas emission spectra were measured using a FluoroMax-4Horriba-Yobin spectrofluorimeter. Solvents of the highest available quality (spectroscopic or HPLC grade) were applied.

Fluorescence quantum yields were calculated using: 2-aminopiridine in 0.1 M H₂SO₄ (QY = 0.60) (for DMAPhacPh, PhacPhCHO and PhacPhCN, PhacPhCOOMe) and quinine sulphate in 0.5 M H₂SO₄ (QY = 0.546) (for DMAPhacPhCHO, DMAPhacPhCOOMe and DMAPhacPhCN) as reference and were corrected for different refractive indices of solvents. In all fluorimetric measurements, the optical density of the solution does not exceed 0.1. The fluorescence lifetimes were measured using a time-correlated single-photon counting apparatus (FT300 PicoQuant fluorescence lifetimes spectrometer) using subnanosecond pulsed diodes as the excitation source: PLS-290 (for PhacPhCHO, PhacPhCOOMe and PhacPhCN), PLS-320 for DMAPhacPh, PLS-340 (for DMAPhAcPh-COOMe) and LDH-375 (for DMAPhacPhCHO and DMAPhacPhCN). The half-width of the response function of the apparatus, measured using a Ludox solution as a scatter, was about 1.0 ns for pulse diode and about 150 ps for a diode laser. The emission wavelengths were isolated using a monochromator. Fluorescence decay data were fitted by the iterative convolution to the sum of exponents according to Eq. (11):

$$I(t) = \sum_{i} \alpha_{i} \exp(-t/\tau_{i})$$
(11)

where α_i is the pre-exponential factor obtained from the fluorescence intensity decay analysis and τ_i the decay time of the *i*-th component, using a software supported by the manufacturer. The adequacy of the exponential decay fitting was judged by visual inspection of the plots of weighted residuals as well as by the statistical parameter χ^2_R and shape of the autocorrelation function of the weighted residuals and serial variance ratio (SVR).

Linear and multi-parametric correlations were performed using Origin v. 9.0 software.

3. Results and discussion

3.1. Absorption spectroscopy

Absorption spectra of PhacPhCOOMe in selected solvents is presented in Fig. 2 while for PhacPhCN and PhacPhCHO in Figs. 1 and 2 ESI.

For diphenylacetylene derivatives containing an electronacceptor substituent the long-wave absorption band is shifted to the longer wavelength in comparison with parent molecule, while at shorter wavelengths than for symmetrically di-substituted DPA derivatives [29]. The polarity of solvent has a minor influence on the position of the absorption spectrum. For PhacPhCOOMe the maximum of absorption is located at 294 nm in polar acetonitrile, while at 297 nm for non-polar cyclohexane (Table 1). Changing a

Table 1

Spectral (ν_{abs} and ν_{fluo}) and photophysical parameters (fluorescence quantum yield (ϕ), fluorescence lifetime (τ), Stokes shift ($\Delta\nu$)), pre-exponential factor (α), quality of fit (χ^2_R) and radiative (k_r) and non-radiative (k_{nr}) rate constants of PhacPhCOOMe in different solvents.

solvent	v_{abs} (cm ⁻¹)	$v_{\rm fluo} ({\rm cm}^{-1})$	$\Delta \nu (\text{cm}^{-1})$	φ	τ (ns)	α	χ^2_{R}	$k_f \! \times 10^{-8} \; (s^{-1})$	$k_{nr} \times 10^{-8} \; (s^{-1})$
MeOH	32072	27503	4569	0.305	0.62	1.000	1.14	4.9	11.2
i-PrOH	31867	28316	3551	0.398	0.64	1.000	1.05	6.1	10.0
hexane	31766	31348	418	0.420	0.55	1.000	0.98	7.6	10.5
CH	31586	31133	453	0.421	0.59	1.000	1.19	7.1	9.8
hexadecane	31516	31027	489	0.429	0.55	1.000	1.03	7.6	10.4
1-Cl-hexadecane	31526	30581	945	0.441	0.59	1.000	1.10	7.5	9.5
MeCN	32092	28265	3827	0.277	0.52	1.000	1.19	5.3	14.9

Spectral (ν_{abs} and ν_{fluo}) and photophysical parameters (fluorescence quantum yield (ϕ) fluorescence lifetime (τ), Stokes shift ($\Delta \nu$)), pre-exponential factor (α), quality of fit (χ^2_R) and radiative (k_f) and non-radiative (k_{nr}) rate constants of DMAPhacPh in different solvents.

MeOH 30864 26882 3982 0.010 >0.15* 1.000 1.26 - - i-PrOH 31114 27397 3717 0.011 >0.17* 1.000 1.16 - - lso-octane 31746 29155 2592 0.280 0.35 1.000 0.93 8.7 1.46 hexadecane 31556 28820 2735 0.372 0.43 1.000 0.93 8.7 1.46 1-chlorohexadecane 30303 27740 2563 0.409 0.66 1.000 0.98 6.2 9.0 CH 31556 28986 2570 0.350 0.38 1.000 0.98 6.2 9.0 coluene 30647 27322 3324 0.390 0.58 1.000 0.94 6.7 24.1 acetone 30518 26846 3773 0.320 0.71 1.000 1.12 4.5 9.6 THF 30572 26490	solvent	v_{abs} (cm ⁻¹)	$v_{\rm fluo} ({\rm cm}^{-1})$	$\Delta \nu ({ m cm^{-1}})$	φ	τ (ns)	α	χ^2_R	$k_f \! \times 10^{-8} (s^{-1})$	$k_{nr} \! \times 10^{-8} \; (s^{-1})$
i-PrOH 31114 27397 3717 0.011 >0.17* 1.000 1.16 - - Iso-octane 31746 29155 2592 0.280 0.35 1.000 1.17 8.0 20.6 hexadecane 31556 28820 2735 0.372 0.43 1.000 0.93 8.7 14.6 1-chlorohexadecane 30303 27740 2563 0.409 0.66 1.000 0.98 6.2 9.0 CH 31556 28986 2570 0.350 0.38 1.000 0.99 9.2 17.1 toluene 30647 27322 3324 0.390 0.58 1.000 0.94 6.7 24.1 acetone 3058 24361 5998 0.103 1.83 1.000 1.13 0.6 4.9 1.4-dioxane 30618 26846 3773 0.320 0.71 1.000 1.12 4.5 9.6 THF 30414 25907 4508 0.244 0.34 0.789 1.28 - - -	MeOH	30864	26882	3982	0.010	>0.15*	1.000	1.26	-	-
Iso-octane 31746 29155 2592 0.280 0.35 1.000 1.17 8.0 20.6 hexadecane 31556 28820 2735 0.372 0.43 1.000 0.93 8.7 14.6 1-chlorohexadecane 30303 27740 2563 0.409 0.66 1.000 0.93 8.7 14.6 1-chlorohexadecane 30303 27740 2563 0.409 0.66 1.000 0.93 6.2 9.01 CH 3156 28986 2570 0.350 0.38 1.000 0.94 6.7 24.1 toluene 30647 27322 3324 0.390 0.58 1.000 0.94 6.7 24.1 acetone 30358 24361 5998 0.103 1.83 1.000 1.17 8.0 4.9 1.44 30618 26846 3773 0.220 0.71 1.000 1.12 4.5 9.6 THF 30572 26490 4082 0.314 0.37 0.951 1.16 - -	i-PrOH	31114	27397	3717	0.011	>0.17*	1.000	1.16	-	-
hexadecane 31556 28820 2735 0.372 0.43 1.000 0.93 8.7 14.6 1-chlorohexadecane 30303 27740 2563 0.409 0.66 1.000 0.98 6.2 9.0 CH 31556 28986 2570 0.350 0.38 1.000 0.99 9.2 17.1 toluene 30647 27322 3324 0.390 0.58 1.000 0.94 6.7 24.1 acetone 3058 24361 5998 0.103 1.83 1.000 1.13 0.6 4.9 1,4-dioxane 30618 26846 3773 0.320 0.71 1.000 1.12 4.5 9.6 THF 30414 25907 4508 0.244 0.34 0.789 1.28 - - MeTHF 30572 26490 A92 0.314 0.37 0.951 1.28 - - MeTHF 30534 26144 4391 0.250 1.16 1.000 0.95 - - DMFO<	Iso-octane	31746	29155	2592	0.280	0.35	1.000	1.17	8.0	20.6
1-chlorohexadecane 30303 27740 2563 0.409 0.66 1.000 0.98 6.2 9.0 CH 31556 28986 2570 0.350 0.38 1.000 0.99 9.2 17.1 toluene 30647 27322 3324 0.390 0.58 1.000 0.94 6.7 24.1 acetone 30358 24361 5998 0.103 1.83 1.000 1.13 0.6 4.9 1.4-dioxane 30618 26846 3773 0.320 0.71 1.000 1.12 4.5 9.6 THF 30414 25907 4508 0.244 0.34 0.789 1.28 - - MeTHF 30572 26490 4082 0.314 0.37 0.951 1.6 - - - L20 30845 27137 3708 0.110 0.35 0.929 0.97 - - DMF 30003 23613 6108 0.300 1.66 0.096 1.10 - - D	hexadecane	31556	28820	2735	0.372	0.43	1.000	0.93	8.7	14.6
CH 31556 28986 2570 0.350 0.38 1.000 0.99 9.2 17.1 toluene 30647 27322 3324 0.390 0.58 1.000 0.94 6.7 24.1 acetone 30358 24361 5998 0.103 1.83 1.000 1.13 0.6 4.9 1,4-dioxane 30618 26846 3773 0.320 0.71 1.000 1.12 4.5 9.6 THF 30414 25907 4508 0.244 0.34 0.789 1.28 - - MeTHF 30572 26490 4082 0.314 0.37 0.951 1.16 - - - Et20 30845 27137 3708 0.110 0.35 0.929 0.97 - - DMF 30534 26144 4391 0.250 1.16 1.000 0.95 - - DMF 3032 23613 6123 0.290 0.71 0.988 0.98 - - - DM	1-chlorohexadecane	30303	27740	2563	0.409	0.66	1.000	0.98	6.2	9.0
toluene306472732233240.3900.581.0000.946.724.1acetone303582436159980.1031.831.0001.130.64.91,4-dioxane306182684637730.3200.711.0001.124.59.6THF304142684637730.3200.711.0001.124.59.6THF305722649040820.3140.370.9511.16L20308452713737080.1100.350.9290.97L20305342614443910.2501.161.0000.95DMF30032389561080.3001.660.9061.10DMSO297352361361230.2900.710.9880.98MeCN303122406762450.1020.770.5251.10	СН	31556	28986	2570	0.350	0.38	1.000	0.99	9.2	17.1
acetone 30358 24361 5998 0.103 1.83 1.000 1.13 0.6 4.9 1,4-dioxane 30618 26846 3773 0.320 0.71 1.000 1.12 4.5 9.6 THF 30414 25907 4508 0.244 0.34 0.789 1.28 - - MeTHF 30572 26490 4082 0.314 0.37 0.951 1.16 - - Et20 30845 27137 3708 0.110 0.35 0.929 0.97 - - AcOEt 30534 26144 4391 0.250 1.16 1.000 0.95 - - DMF 3003 23895 610 0.300 1.06 0.906 1.10 - - DMSO 29735 23613 6123 0.290 0.71 0.988 0.98 - - MeCN 30312 24067 6245 0.102 <t< td=""><td>toluene</td><td>30647</td><td>27322</td><td>3324</td><td>0.390</td><td>0.58</td><td>1.000</td><td>0.94</td><td>6.7</td><td>24.1</td></t<>	toluene	30647	27322	3324	0.390	0.58	1.000	0.94	6.7	24.1
1,4-dioxane 30618 26846 3773 0.320 0.71 1.000 1.12 4.5 9.6 THF 30414 25907 4508 0.244 0.34 0.789 1.28 - - MeTHF 30572 26490 0.314 0.37 0.951 1.16 - - Et20 30845 27137 3708 0.110 0.35 0.929 0.97 - - - AcOEt 30534 26144 4391 0.250 1.16 1.000 0.95 - <td>acetone</td> <td>30358</td> <td>24361</td> <td>5998</td> <td>0.103</td> <td>1.83</td> <td>1.000</td> <td>1.13</td> <td>0.6</td> <td>4.9</td>	acetone	30358	24361	5998	0.103	1.83	1.000	1.13	0.6	4.9
THF 30414 25907 4508 0.244 0.34 0.789 1.28 - - MeTHF 30572 26490 4082 0.314 0.37 0.951 1.16 - - Et20 30845 27137 3708 0.110 0.35 0.929 0.97 - - AcOEt 30534 26144 4391 0.250 1.16 1.000 0.95 - - DMF 30003 23895 6108 0.300 1.06 0.906 1.10 - - DMSO 29735 23613 6123 0.290 0.71 0.988 0.98 - - MeCN 30312 24067 6245 0.102 0.77 0.525 1.10 - -	1,4-dioxane	30618	26846	3773	0.320	0.71	1.000	1.12	4.5	9.6
MeTHF 30572 26490 4082 0.314 0.37 0.951 1.16 - - Et20 30845 27137 3708 0.110 0.35 0.929 0.97 - - AcOEt 30534 26144 4391 0.250 1.16 1.000 0.95 - - DMF 30003 23895 6108 0.300 1.06 0.906 1.10 - - DMSO 29735 23613 6123 0.290 0.71 0.988 0.98 - - MeCN 30312 24067 6245 0.102 0.77 0.525 1.10 - -	THF	30414	25907	4508	0.244	0.34	0.789	1.28	-	-
MeTHF 30572 26490 4082 0.314 0.37 0.951 1.16 - - Et20 30845 27137 3708 0.110 0.35 0.929 0.97 - - AcOEt 30534 26144 4391 0.250 1.16 1.000 0.95 - - DMF 30003 23895 6108 0.300 1.06 0.906 1.10 - - DMSO 29735 23613 6123 0.290 0.71 0.988 0.98 - - MeCN 30312 24067 6245 0.102 0.77 0.525 1.10 - -						1.52	0.211			
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Et20 30845 27137 3708 0.110 0.35 0.929 0.97 - - AcOEt 30534 26144 4391 0.250 1.16 1.000 0.95 - - DMF 30003 23895 6108 0.300 1.06 0.906 1.10 - - DMSO 29735 23613 6123 0.290 0.71 0.988 0.98 - - MeCN 30312 24067 6245 0.102 0.77 0.525 1.10 - -						1.26	0.049			
AcOEt 30534 26144 4391 0.250 1.16 1.000 0.95 - - DMF 30003 23895 6108 0.300 1.06 0.906 1.10 - - DMSO 29735 23613 6123 0.290 0.71 0.988 0.98 - - MeCN 30312 24067 6245 0.102 0.77 0.525 1.10 - -	Et2O	30845	27137	3708	0.110	0.35	0.929	0.97	-	-
AcOEt 30534 26144 4391 0.250 1.16 1.000 0.95 - - DMF 30003 23895 6108 0.300 1.06 0.906 1.10 - - DMSO 29735 23613 6123 0.290 0.71 0.988 0.98 - - MeCN 30312 24067 6245 0.102 0.77 0.525 1.10 - -						1.21	0.071			
DMF 30003 23895 6108 0.300 1.06 0.906 1.10 - - - DMSO 29735 23613 6123 0.290 0.71 0.988 0.98 - - MeCN 30312 24067 6245 0.102 0.77 0.525 1.10 - -	AcOEt	30534	26144	4391	0.250	1.16	1.000	0.95	-	-
DMSO 29735 23613 6123 0.290 0.71 0.988 0.98 - - MeCN 30312 24067 6245 0.102 0.77 0.525 1.10 - -	DMF	30003	23895	6108	0.300	1.06	0.906	1.10	-	-
DMSO 29735 23613 6123 0.290 0.71 0.988 0.98 - - MeCN 30312 24067 6245 0.102 0.77 0.525 1.10 - -						3.02	0.094			
4.65 0.012 MeCN 30312 24067 6245 0.102 0.77 0.525 1.10 - -	DMSO	29735	23613	6123	0.290	0.71	0.988	0.98	-	-
MeCN 30312 24067 6245 0.102 0.77 0.525 1.10						4.65	0.012			
1 50 0 155	MeCN	30312	24067	6245	0.102	0.77	0.525	1.10	-	-
1.78 0.475						1.78	0.475			

solvent from non-polar CH to polar MeCN did not cause a significant changes in the shape of the long-wavelength absorption band however, in polar acetonitrile and protic solvents a small blue-shift and less distinct vibronic structure is observed. Similarly absorption spectra were recorded for nitrile and aldehyde derivatives with the difference that for aldehyde derivative the maximum of absorption is additionally red-shifted for about 10 nm compared to that of nitrile and ester (Tables 1 and 2 ESI). Moreover, absorption spectra of PhacPhCHO possess a long-wavelength tail (Fig. 2 ESI).

A greater impact on the position of the absorption band exerts an electron-donor substituent (Fig. 3).

The position of maximum of absorption is red-shifted compared to the derivatives containing an electron-acceptor substituent (Table 2). Moreover, in non-polar solvents absorption spectrum has a less clearly marked vibronic structure than for an electronacceptor containing derivatives, which disappears in more polar non-protic and protic solvents. Additionally, polar solvents shift the



A similar influence of solvents on position of absorption band was observed by Hirata et al. for aminophenyl(phenyl)acetylene [33].

Normalized absorption spectra of D- π -A pairs in selected solvents are presented in Figs. 4–6.

For compounds containing an electron-donor and an electronacceptor substituents (D- π -A) absorption spectra are red-shifted for about 40 nm (for DMAPhacPhCN and DMAPhacPhCOOMe) (Figs. 4 and 5), while for aldehyde derivative for about 60 nm (Fig. 6) compared to that of DMAPhacPh (Fig. 3). In non-polar solvents the vibronic structure is preserved although the shape of the spectrum is changed depending on the substituent. In the remaining solvents studied absorption bands are unstructured and red-shifted with increasing solvent polarity. The maxima of absorption spectra in all solvents studied are gathered in Tables 3–5 for DMAPhacPhCN, DMAPhacPhCOOMe and DMA-PhacPhCHO, respectively.



Fig. 4. Normalized absorption spectra of DMAPhacPhCN in selected solvents.



Fig. 5. Normalized absorption spectra of DMAPhacPhCOOMe in selected solvents.



Fig. 6. Normalized absorption spectra of DMAPhacPhCHO in selected solvents.

3.2. Fluorescence spectroscopy

Fluorescence spectra for PhacPhCOOMe are presented in Fig. 7, while for PhacPhCN in Fig. 3 ESI. Because of PhacPhCHO is very weakly fluorescent its spectra are not presented.

For diphenylacetylene derivatives containing an electronacceptor group their fluorescence spectra in the same solvent are similar to each other. In non-polar solvents emission spectra shown the same features as fluorescence spectra of symmetrically substituted diphenylacetylene [29] with well-formed vibronic structure. Moreover, in non-polar solvents substantial asymmetry between absorption and emission spectra is observed. Such phenomenon have been observed also for arylethynyl derivatives of *N*,*N*-dimethylaniline [19,20] as well as for phenylene ethynylene oligomers [29,46-49] and have been explained in terms of torsional disorder and guadratic coupling between the ground and the first excited state [50] or the exciton model developed by Liu et al. [51]. In polar protic and aprotic solvents the emission spectrum shift bathochromically and lose their vibration structure. There is a certain difference in the position of emission band in protic solvents for ester and nitrile derivatives. For PhacPhCN the position of maximum of fluorescence spectrum in acetonitrile coincidence with methanol, whereas for PhacPhCOOMe with that

Table 3

Spectral (ν_{abs} and ν_{fluo}) and photophysical parameters (fluorescence quantum yield φ) fluorescence lifetime (τ) Stokes shift ($\Delta \nu$)), pre-exponential factor (α), quality of fit (χ^2_R) and radiative (k_f) and non-radiative (k_{nr}) rate constants of DMAPhacPhCN in different solvents.

solvent	v_{abs} (cm ⁻¹)	$v_{\rm fluo} ({\rm cm}^{-1})$	Δu (cm ⁻¹)	φ	τ (ns)	α	χ^2_R	$k_f \! \times 10^{-8} (s^{-1})$	$k_{nr} {\times} 10^{-8} (s^{-1})$
MeOH	27330	18281	9049	0.006	_*	-	-	-	-
i-PrOH	27200	19608	7592	0.032	0.31	0.250	1.16	-	-
					0.53	0.750			
iso-octane	26900	26316	584	0.300	0.59	1.000	1.07	5.1	11.9
hexadecane	26596	25974	622	0.33	0.62	1.000	0.93	5.3	10.8
1-chlorohexadecane	26738	23607	3131	0.455	1.54	1.000	0.98	3.1	3.5
СН	26640	26110	530	0.380	0.67	1.000	1.11	5.7	9.3
toluene	26820	23419	3401	0.490	1.52	1.000	1.07	3.2	3.4
acetone	27200	18416	8804	0.066	1.26	1.000	1.10	0.5	7.4
1,4-dioxane	27320	22421	4809	0.400	2.27	1.000	1.17	1.8	2.6
THF	26960	19802	7158	0.099	1.26	1.000	1.12	0.8	7.2
MeTHF	27160	21367	5793	0.290	2.55	1.000	1.06	1.1	2.8
Et ₂ O	27420	22075	5345	0.330	2.05	1.000	1.17	1.6	3.3
AcOEt	27260	20747	6513	0.170	2.25	1.000	1.10	0.8	3.7
DMF	26820	17668	9152	0.029	0.77	1.000	1.00	0.4	12.6
DMSO	26550	17452	9098	0.024	0.60	1.000	1.12	0.4	16.3
MeCN	27310	17513	9797	0.024	0.64	1.000	1.07	0.4	15.3

Table 4

Spectral (ν_{abs} and ν_{fluo}) and photophysical parameters (fluorescence quantum yield (ϕ) fluorescence lifetime (τ), Stokes shift ($\Delta\nu$)), pre-exponential factor (α), quality of fit (χ^2_R) and radiative (k_f) and non-radiative (k_{nr}) rate constants of DMAPhacPhCOOMe in different solvents.

solvent	v_{abs} (cm ⁻¹)	$v_{\rm fluo} ({\rm cm}^{-1})$	$\Delta \nu (\text{cm}^{-1})$	φ	τ (ns)	α	χ^2_R	$k_f imes 10^{-8} (s^{-1})$	$k_{nr} \times 10^{-8} (s^{-1})$
MeOH	227855	21505	6350	0.001	_*	1.000	0.93	-	-
i-PrOH	27739	22650	5089	0.013	1.32	1.000	0.96	0.1	7.5
hexane	27435	26490	945	0.310	0.73	1.000	1.00	4.2	9.5
iso-octane	27360	27027	333	0.314	0.75	1.000	0.88	4.2	9.2
hexadecane	26991	26144	847	0.339	0.92	1.000	0.89	3.7	7.2
1-Cl-hexadecane	27816	23474	4342	0.351	1.35	1.000	1.09	2.6	4.8
CH	27064	26247	817	0.324	0.90	1.000	0.98	3.6	7.5
toluene	27624	23420	4204	0.428	1.51	1.000	1.09	2.8	3.8
1,4-dioxane	27739	22222	5517	0.303	2.38	1.000	1.01	1.3	2.9
THF	27633	20747	6886	0.150	2.43	1.000	1.03	0.6	3.5
MeTHF	28209	21528	6681	0.248	2.68	1.000	0.93	0.9	2.8
Et ₂ O	28209	21810	6399	0.216	0.40	0.669	0.87	-	-
					2.09	0.331			
AcOEt	28011	21254	6757	0.140	2.47	1.000	0.84	0.6	3.5
DMF	27211	19084	8127	0.065	1.70	1.000	0.99	0.4	5.5
DMSO	27027	18232	8795	0.053	1.92	1.000	1.03	0.3	4.9
MeCN	27739	18382	9357	0.134	1.48	1.000	1.00	0.9	5.8

Spectral (ν_{abs} and ν_{fluo}) and photophysical parameters (fluorescence quantum yield (ϕ) fluorescence lifetime (τ) Stokes shift ($\Delta\nu$)), pre-exponential factor (α), quality of fit (χ^2_R) and radiative (k_r) and non-radiative (k_{nr}) rate constants of DMAPhacPhCHO in different solvents.

solvent	v_{abs} (cm ⁻¹)	$v_{\rm fluo} ({\rm cm}^{-1})$	Δu (cm ⁻¹)	φ	τ (ns)	α	χ^2_R	$k_f \! \times 10^{-8} \; (s^{-1})$	$k_{nr} \times 10^{-8} \; (s^{-1})$
MeOH	26281	20277	6004	0.006	*	-	-	-	-
i-PrOH	26281	20243	6038	0.017	0.23	0.919	1.13	-	-
					1.39	0.081			
hexane	26076	25220	856	0.044	0.74	1.000	1.18	0.6	12.9
Iso-octane	26110	25126	984	0.056	0.71	1.000	1.00	0.8	13.3
hexadecane	25641	24845	796	0.093	0.92	1.000	1.09	1.0	9.8
1-Cl-hexadecane	26212	21622	4590	0.363	0.98	0.358	1.13	-	-
					2.15	0.642			
toluene	26212	21575	4637	0.337	0.95	0.355	0.92	-	-
					2.08	0.645			
СН	25773	24907	866	0.047	0.98	1.000	1.12	-	-
1,4-dioxane	26666	19881	6785	0.254	0.54	0.229	1.09	-	-
					1.83	0.771			
THF	26350	18726	7624	0.131	0.55	0.887	0.89	-	-
					2.09	0.113			
MeTHF	26178	19324	6854	0.223	1.02	0.596	1.11	-	-
					1.85	0.404			
Et ₂ O	26846	19880	6966	0.201	0.35	0.901	0.97	-	-
					1.47	0.099			
AcOEt	26666	19881	6785	0.174	0.96	0.704	0.94	-	-
					1.75	0.296			
DMF	26350	17513	8837	0.046	0.19	0.360	0.94	-	-
					1.26	0.520			
					2.81	0.120			
DMSO	25840	17286	8554	0.037	0.49	0.657	1.04	-	-
					2.62	0.343			
MeCN	26666	17360	9306	0.012	0.62	0.955	1.11	-	-
					3.90	0.045			

measured in 2-propanol, while in methanol emission spectrum of PhacPhCOOMe is most shifted to the red. This can be explained by the hydrogen bond network formation with protic solvent molecules. Both, the shape of emission band and the Stokes shift (Table 1 and Table 1 ESI) indicates that in non-polar solvents the emission of PhacPhCOOMe, PhacPhCN and DMAPhacPhCHO take place from local excited state, whereas in polar solvents from internal charge transfer state.

Fluorescence quantum yields of PhacPhCOOMe and PhacPhCN are quite large in the range of 0.3–0.5 (Table 1 and Table 1 ESI). Moreover, they are a little lower in polar and protic solvents compared to non-polar ones. However, for PhacPhCHO fluorescence quantum yields are very low, lower than 0.001 (Table 2 ESI)



Fig. 7. Normalized fluorescence spectra of PhacPhCOOMe in selected solvents, $\lambda_{exc}\!=\!295\,\text{nm}.$

indicating that the emission occurs from the $n\pi^*$ with state. This is confirmed by absorption spectra in which the $n\pi^*$ transition manifests itself as the long-wavelength tail as a result of the overlap of the intensive $\pi\pi^*$ with the $n\pi^*$ transition. Similarly to the fluorescence quantum yields also fluorescence lifetimes of PhacPhCOOMe and PhacPhCN are similar (Table 1 and Table 1 ESI), however for PhacPhCOOMe they are a little longer, especially in polar and protic solvents. Fluorescence intensity decays for both PhacPhCOOMe and PhacPhCN are mono-exponentials in all studied solvents. For ester derivative are in the range of 0.5 ns to 0.6 ns and are independent on solvent polarity, whereas for PhacPhCN are about 0.5 ns in non-polar solvent and shorter (0.3 ns) in polar and protic solvent.

Above presented results indicate that diphenylacetylene derivatives containing one an electron-acceptor group behave like symmetrically substituted derivatives in which the lowest excited state is the $\pi\pi^*$ of a linear structure which does not intersect with the $\sigma\pi^*$ for the bent structure [24–31]. It seems that the linear structure in the excited state is stabilized by the internal charge transfer from the phenyl group to the substituted phenyl group. However, a small solvatochromic effect indicated that excited state dipole moment is not much bigger than in the ground state.

Fluorescence spectra of diphenylacetylene derivative containing an electron-donor substituent (DMAPhacPh) in selected solvents are presented in Fig. 8

N,*N*-Dimethylamino as an electron-donor substituent influenced on the emission spectra of diphenylacetylene quite differently than an electron-acceptor substituent does. The emission spectra are much more bathochromically shifted and their shape is strongly modified by the solvent polarity. In the case of DMAPhacPh the maxima of emission bands are at 346 nm in CH, 360 nm in 1-Cl-hexadecane, 419 nm in MeCN, 427 nm in DMSO and 420 nm in MeOH (Fig. 8). A characteristic features include the dualband emission in polar solvents and long-wavelength tail in medium polarity solvents like: MeTHF, 1,4-dioxane or ethyl



Fig. 8. Normalized fluorescence spectra of DMAPhacPh in selected solvents, λ_{exc} = 320 nm.

acetate. Such a phenomenon was observed by Hirata et al. [33] for aminophenyl(phenyl)acetylene and interpreted as an emission from both the locally excited and charge-transfer state. It is worth noting that the phenomenon of dual emission does not occur for acetylene derivatives containing *N*,*N*-dimethylaminophenyl and polycyclic aromatic hydrocarbon as substituents [20]. Fluorescence quantum yields as well as fluorescence lifetime are diverse and depend on the type of solvent (Table 2). In protic solvents both fluorescence quantum yield and fluorescence lifetime are small compared to the other solvents studied probably due to the formation of hydrogen bond with solvent as in the case of derivatives containing polycyclic aromatic hydrocarbon as substituent [20].

For the donor model compound DMAPhacPh fluorescence lifetimes are more diversified and depend on the solvent (Table 2). In protic solvent they are too short to be measured using our equipment, and according to Hirata et al. [31,33] are shorter than 60 ps. For the saturated hydrocarbon solvents a single exponential fluorescence intensity decay is observed with the lifetime about 0.5 ns. In medium polar and polar solvent bi-exponential function is needed to correctly fitted to the fluorescence intensity decay (Table 2). However, is a certain inconsistency between our results



Fig. 10. Normalized fluorescence spectra of DMAPhacPhCOOMe in selected solvents, $\lambda_{exc}\text{=}350\,\text{nm}.$

and those published by Hirata et al. [31,33]. Contrary to us, Hirata et al. using a streak-camera technique found that in DMF, THF, diethyl ether DMAPhacPh has a single fluorescence lifetime.

Fluorescence spectra of D- π -A pairs are presented in Figs. 9–11.

In these cases emission spectra have the form of a single band. Fluorescence spectra in saturated hydrocarbons possesses vibronic structure, while a structureless broad fluorescence with a quite large solvatochromic shift in polar solvents is observed (Tables 3-5). For DMAPhacPhCN they are similar to previously published by Hirata [31] and the maxima of emission bands are at 383 nm in CH, 425 nm in 1-Cl-hexadecane, 474 nm in MeTHF, 548 nm in MeCN, 570 nm in DMSO and 545 nm in MeOH (Fig. 9 and Table 3). In the similar range are located the emission spectra of DMAPhacPhCOOMe, except that they are shifted slightly toward the short-wavelength (the maxima of emission bands are at 381 nm in CH, 427 nm in 1-Cl-hexadecane, 465 nm in MeTHF, 540 nm in MeCN, 547 nm in DMSO and 465 nm in MeOH) (Fig. 10 and Table 4). The most bathochromic shift of emission spectra are recorded for DMAPacPhCHO (at 401 nm in CH, 462 nm in 1-Clhexadecane, 517 nm in MeTHF, 576 nm in MeCN, 580 nm in DMSO and 477 nm in MeOH) (Fig. 11 and Table 5). The absorption



Fig. 9. Normalized fluorescence spectra of DMAPhacPhCN in selected solventsm, λ_{exc} = 355 nm.



Fig. 11. Normalized fluorescence spectra of DMAPhacPhCHO in selected solvents, λ_{exc} = 350 nm.

spectrum shows only a little red shift and a slight broadening with increasing solvent polarity, while the emission spectra show a large bathochromic shift. Also, Stokes shift which is large in polar solvent and small in non-polar ones. These results indicate that in non-polar solvents the emission take place from the local excited state whereas in polar solvent from the internal charge transfer state [31]. A trough-bond charge-transfer mechanism in the excited state for DMAPhacPhCN was also postulated by Ma et al. [52] based on the theoretical calculations.

As shown by Krystkowiak et al. [53] 1-chloro-n-alkanes are the best solvents that interact only non-specifically with many fluorescence probes [20,54–56] because they do not have π -electrons, do not form hydrogen bond and do not have charge-transfer character. However, comparing the emission spectra of DMAPhacPh and D- π -A pairs recorded in hexadecane and 1-chloro-hexadecane (Figs. 9-11) one can see a big difference in the shape and position of maximum of emission spectra in these two solvents. In hexadecane, like in other saturated hydrocarbon solvents, emission spectra possess a clear vibronic structure, while in 1-chloro-hexadecane are structureless, and substantial Stokes shift is recorded (Tables 3-5), similarly to the CT emission in polar solvents. However, a such differences are not seen in emission spectra of diphenylacetylene derivatives studied containing an electron-acceptor substituent (Fig. 7 and Figs. 3 and 4 ESI). This can be explained by interactions between the permanent solvent dipole and the permanent and induced dipoles of studied compounds [57], which results in emission from the chargetransfer. If a such weak interactions of bond dipole of solvent cause the states inversion this means that the difference of energy between these states is small.

Also noteworthy is a significant blue-shift of emission spectra in protic solvent observed for DMAPhacPhCOOMe and DMAPhacPh-CHO in comparison to that of DMAPhacPhCO. It seems that the hydrogen bonding in protic solvents may be responsible for this. As shown by Bylińska at al. [20] and Hirata et al. [35] molecules containing *N*,*N*-dimethylaniline and aromatic hydrocarbon linked by the acetylene unit form in excited state a hydrogen bond between amino group and protic solvent causing blue-shift and broadening of emission band. In the case of the studied compounds, lower electron affinity of ester and aldehyde group than that of nitrile increase the electron density on nitrogen atom of amino group increasing the strength of hydrogen bond and thereby reducing the charge separation. Additionally, there is the possibility of hydrogen bond formation by the ester or aldehyde group with protic solvent.

The fluorescence intensity decay of DMAPhacPhCN and DMAPhacPhCOOMe in all studied solvents (except in alcohols for DMAPhacPhCN and in ethyl ether for DMAPhacPhCOOMe) are described by a single-exponential function. In the case of DMAPhacPhCN (Table 3) the fluorescence lifetimes are about 0.6 ns in polar solvents and saturated hydrocarbons and in the range from 1.3 ns to 2.5 ns in the remaining studied solvents. In the case of DMAPhacPhCOOMe (Table 4) shorted the fluorescence lifetimes are in saturated hydrocarbons solvents (0.7-0.9 ns) and in polar solvents they are in the range from 1,3 to 1,5 ns. DMAPhacPhCHO is characterized by complex photophysics (Table 5). Only in saturated hydrocarbon solvents fluorescence intensity decay is mono-exponential (fluorescence lifetime are in the range of 0.7-1 ns) while for the remaining studied solvent twoor three exponentials function is needed to correctly describe the decay. This seems to be connected with the small difference of energy of close lying $n\pi^*$ and $\pi\pi^*$ states.

When fluorescence quantum yield is known single exponential fluorescence intensity decay allows to determine the radiative and non-radiative rate constants according to the equations; $k_r = \varphi/\tau$ and $k_{nr} = (1 - \varphi)/\tau$. Analyzing the data contained in Table 1 and

Table 1 ESI for PhacPhCOOMe and PhacPhCN, respectively, may be noted that the electron-affinity of electron-acceptor substituent modifies photophysical properties of compounds studied. Lower fluorescence quantum yield of PhacPhCN containing a stronger electro-acceptor substituent than that of PhacPhCOOMe are caused be higher values of non-radiative rate constant at comparable values of radiative rate constant. Due to the fact that for DMAPhacPh, containing electron-donor substituent, monoexponential decays of the fluorescence intensity was recorded in other solvents than for derivatives containing an electron-acceptor substituent the influence of type of the substituent on the photophysical properties cannot be evaluated. Based on Tables 3 and 4 is difficult to unambiguously evaluate the effect of electron affinity of the substituent on photophysical properties of D-A pairs. However, in polar solvents for both compounds the radiative rate constant is lower than in non-polar solvents while non-radiative rate constant is higher in nonpolar solvents with the exception for strongly polar DMF, DMSO and MeCN for DMA-PhacPhCN (Table 3).

3.3. Multiple-linear correlation

In order examine in more detail the solute-solvent interactions and know which solvent properties have the greatest impact on the spectral and photophysical parameters studied compounds multiple-linear correlation according to Catalan equation (Eq. (1)) for DMAPhacPh and D- π -A pairs was carried out and obtained results are gathered in Table 6.

For DMAPhacPh a good correlation of the absorption band maximum was obtained ($R^2_{adj} = 0.9341$) with the largest impact of solvent polarizability and dipolarity.

However, for D- π -A pairs the correlation is much worse ($R^2_{adj} = 0.5794$, $R^2_{adj} = 0.3232$, $R^2_{adj} = 0.5133$ for DMAPhacPhCN, DMAPhacCOOMe and DMAPhacCHO, respectively). The largest impact has the solvent polarizability, causing the bathochromic shift. Moreover, for DMAPhacPhCHO absorption some impact has also solvent dipolarity, whereas for DMAPhacPhCN and DMA-PhacPhCOOMe solvent basicity. Emission band maximum and Stokes shift correlate well with Catalan solvent polarity scale for all studied compounds. For DMAPhacPh and DMAPhacPhCN exclusively solvent dipolarity causes the bathochromic shift of fluorescence spectra and increase Stokes shift. For DMAPhacPhCHO beside solvent dipolarity also solvent basicity play substantial role, whereas for DMAPhacPhCOOMe solvent acidity with opposite effect to solvent dipolarity.

For two D-A pairs for which received a sufficient number of points correlations of radiative (k_r) and non-radiative rate (k_{nr}) constant with Catalan solvent polarity scale was carried out. The radiative rate constant in both cases correlates well $R^2_{adj} \ge 0.9$ and solvent dipolarity and solvent basicity play substantial role lowering its value. In contrast, non-radiative rate constant indicates a weak correlation $0.5 \le R^2_{adj} \ge 0.7$, and the value of this constant depends only on solvent acidity and basicity (with the opposite signs).

Due to various standard deviations of the measured values and the independent solvent parameters coefficients in Catalan equation, more quantitative measure of the impact of the individual properties of the solvent are standardized coefficients. These factors allow to determine the percentage share of the solvent polarity parameters on the measured solvent-dependent physicochemical property. The relevant data are presented in Table 7.

As shown in the above Table, the position of absorption band maximum for DMAPhacPh is determined in 55% by solvent dipolarity and in nearly equal amount by solvent polarizability and basicity, whereas for DMAPhacPhCN and DMAPhacPhCOOMe

Estimated from Eq. (1) adjusted coefficients (ν_x)_o, a_{SP}, b_{SdP}, c_{SB}, d_{SA} their standard error and adjustable correlation coefficient (r_{Adj}^2) of the multiple linear correlation analysis of absorption (ν_{abs}), fluorescence (ν_{fluo}) wavenumber, Stokes shift ($\Delta\nu_{SS}$ of studied compounds as a function of Catalan-four parameter solvent polarity scale. Additionally, the radiative rate constant (k_r) and non-radiative rate constant (k_{nr}) for DMAPhacPhCN and DMAPhacPhCOOMe are presented.

quantity	$(\nu_x)_0$	a _{SP}	b _{SdP}	C _{SB}	d _{SA}	R ² adj
DMAPhacPh						
v_{abs} (cm ⁻¹)	33519 ± 526	$-(3003\pm792)$	$-(1091 \pm 199)$	$-(472 \pm 322)$	1423 ± 1768	0.9341
	33371 ± 4834	$-(2739\pm706)$	$-(1036 \pm 179)$	$-(586 \pm 284)$	_	0.9366
$v_{\rm fluo} ({\rm cm}^{-1})$	30529 ± 1688	$-(2350 \pm 2450)$	$-(4882\pm 636)$	256 ± 1035	$-(2691\pm 5633)$	0.9347
	28940 ± 227	-	$-(4893 \pm 535)$	-	-	0.9409
$\Delta v_{\rm SS} ({\rm cm}^{-1})$	2990 ± 1350	$-(653 \pm 20231)$	3785 ± 508	$-(728\pm828)$	4159 ± 4528	0.9181
	2499 ± 190	-	3457 ± 295	-	-	0.9192
DMADL - DLCN						
DMAPHaCPHCN (cm^{-1})	20021 + 662	(2802 ± 006)	160 240	278 + 406	(2201 + 2224)	0 5200
V _{abs} (CIII)	20031 ± 002	$-(2092 \pm 990)$	160 ± 249	578 ± 400	$-(2301 \pm 2224)$ (1752 + 1084)	0.5598
	20040 ± 039 20052 + 590	$-(2952 \pm 901)$	_	564 ± 275	$-(1752 \pm 1984)$	0.5700
	29032 ± 389	$-(3200\pm 030)$	-	033±288	_	0.3794
$v_{\rm fun}$ (cm ⁻¹)	26270 ± 2761	-(378 + 4153)	$-(7705 \pm 1040)$	1940 + 947	$-(2872 \pm 9278)$	0 9383
	20210 2 2701	(0,0 ± 1100)	(1100 ± 1010)	10 10 ± 0 11	(2012 ± 0210)	0.0000
$\Delta v_{\rm ss} ({\rm cm}^{-1})$	225841 ± 3448	-	$-(8277\pm534)$	-	_	0.9524
33(1)/	2560 ± 3022	$-(2513 \pm 4545)$	7864 ± 1137	1458 ± 1852	507 ± 10154	0.9300
	1055 ± 388		8467 ± 601	_	_	0.9426
$k_{f} imes 10^{-8} (s^{-1})$	5.541 ± 3.310	0.937 ± 3.717	$-(3.7714 \pm 0.9900)$	$-(3.2898 \pm 1.3684)$	10.276 ± 12.884	0.8982
	5.196 ± 0.355	-	$-(3.1857\pm0.7174)$	$-(3.6649 \pm 1.2199)$	-	0.9057
$k_{nr} \times 10^{-8} (s^{-1})$	21.89 ± 11.170	$-(17.88 \pm 16.07)$	0.1235 ± 4.2859	$-(9.153\pm 5.936)$	212.72 ± 55.88	0.6692
	9.467 ± 1.945	-	-	$-(9.158\pm 3.370)$	189.98 ± 35.80	0.6914
DMAPhacPhCOOMe					(=== . ====)	
v_{abs} (cm ⁻¹)	29850 ± 1128	$-(3758 \pm 1659)$	141 ± 430	753 ± 596	$-(705\pm709)$	0.2600
	29324 ± 933	$-(2984 \pm 1350)$	-	733 ± 341	-	0.3222
··· (am -1)	20107 - 2244	(2220 ± 4770)	(7510 + 1007)	20 + 1714	4204 - 2027	0.0005
V _{fluo} (CIII)	28197 ± 3244	$-(3226 \pm 4770)$	$-(7518 \pm 1237)$	20 ± 1714	4304 ± 2037	0.8835
	20040 ± 403	-	$-(7738 \pm 700)$	-	4993 ± 1051	0.8984
Δv_{ee} (cm ⁻¹)	1652 ± 3770	-(527 + 5541)	7660 ± 1437	733 + 1991	$-(5009 \pm 2367)$	0.8566
1 <i>v</i> ₅₅ (em)	1399 ± 461	-(527 ± 5541)	8003 ± 801	-	$-(4853 \pm 1890)$	0.8787
	1999 ± 101		0003±001		(1055 ± 1050)	0.0707
$k_{\rm f} \times 10^{-8} (s^{-1})$	4.064 ± 1.527	-(0.050 + 2.291)	$-(1.8338 \pm 0.5635)$	$-(3.665 \pm 0.922)$	2.296 ± 2.178	0.9274
	4.031 ± 0.209	_	$-(1.8362 \pm 0.5207)$	$-(3.667 \pm 0.861)$	2.314 ± 1.890	0.9355
	3.962 ± 0.206	_	$-(1.9005 \pm 0.5305)$	$-(3.200 \pm 0.79)$	_	0.9322
			(
$k_{nr} \times 10^{-8} (s^{-1})$	13.746 ± 5.696	$-(8.630 \pm 8.435)$	$-(0.137 \pm 22.074)$	$-(6.857 \pm 3.392)$	19.450 ± 8.018	0.5222
	7.974 ± 0.780	_	_	$-(8.051 \pm 1.997)$	22.878 ± 7.006	0.5641
DMAPhacPhCHO						
v_{abs} (cm ⁻¹)	27800 ± 1161	$-(2703 \pm 1718)$	555 ± 583	467 ± 723	$-(6270\pm 6944)$	0.2866
	28804 ± 897	$-(4159 \pm 1341)$	680 ± 214	-	-	0.5133
. 1						
$v_{\rm fluo} (\rm cm^{-1})$	26655 ± 3532	$-(2794 \pm 5224)$	$-(6181 \pm 1774)$	$-(2976 \pm 2201)$	11096 ± 21117	0.9024
	24779 ± 452	-	$-(5715 \pm 1081)$	$-(3567 \pm 1748)$	-	0.9180
A	11.40 + 4500	01 + 6750	C027 + 2205	2444 - 2040	(117067 + 07017)	0.0574
$\Delta v_{\rm SS} ({\rm cm}^{-1})$	1140 ± 4509	$91 \pm 6/58$	6837 ± 2295	3444 ± 2848	$-(11/36/\pm 2/31/)$	0.8574
	1220±58/	-	טען ± 1401	4338 ± 2269	-	0.8/93

nearly in half by solvent polarizability and solvent basicity. Moreover, for DMAPhacPhCHO in equal amount by solvent polarizability and dipolarity. The position of the fluorescence band maximum and Stokes shift for DMAPhacPh and DMA-PhacPhCN in 100% depend on solvent dipolarity, while for DMAPhacPhCOOMe in 80% on solvent dipolarity and 20% solvent acidity, whereas for DMAPhacPhCHO in 70% on solvent dipolarity and 30% on solvent basicity. Thus, not only electron affinity of substituent but also the type of substituent expressed through the proton-acceptor properties has a significant impact on the solutesolvent interactions which modify their spectral and photophysical properties. However, multiple-linear correlation analysis shows that solvent polarizability has major influence on absorption solvatochromism, while position of the fluorescence band maximum as well as the Stokes shift mostly depend on solvent dipolarity, albeit solvent basicity and acidity have minor influence too. A similar solvent influence on the spectral and photophysical properties was observed for pull-push molecules containing *N*,*N*dimethylaniline and aromatic hydrocarbon linked by an acetylene unit [20]. The kind of electron-acceptor substituent only slightly modified the radiative rate constant. For DMAPhacPhCN the solvent dipolarity in 60% influence k_r while in 47%. for DMA-PhacPhCOOMe. A more pronounced of solvent properties is observed on the non-radiative rate constant. A solvent basicity has 32% and 55% impact on it for DMAPhacPhCN and DMAPhacPh-COOMe, respectively.

Estimated, based on data gathered in Table 6, standardized coefficients A_{SP} , B_{SdP} , C_{SB} , D_{SA} and their contribution (in%) to the dependence of absorption (ν_{abs}), fluorescence (ν_{fluo}) wavenumber and Stokes shift ($\Delta\nu_{SS}$) of studied compounds on the Catalan-four parameter solvent polarity scale. Additionally, coefficients A_{SP} , B_{SdP} , C_{SB} , D_{SA} and their contribution (in %) to the dependence of (k_r) and (k_{nr}) for two D-A pairs are also presented.

quantity	A _{SP}	B _{SdP}	C _{SB}	D _{SA}	%A _{SP}	%B _{SdP}	%C _{SB}	%D _{SA}
DMAPhacPh								
v_{abs} (cm ⁻¹)	-0.293	-0.671	-0.252	-	24.3	55	20.7	0
$v_{\rm fluo} ({\rm cm}^{-1})$	-	-0.983	-	-	0	100	0	0
$\Delta v_{\rm SS}~({ m cm}^{-1})$	-	0.973	-	-	0	100	0	0
DMAPhacPhCN								
v_{abs} (cm ⁻¹)	-0.796	-	-0.573	-	56.7	0	43.3	0
$v_{\rm fluo} ({\rm cm}^{-1})$	-	-0.989	-	-	0	100	0	0
$\Delta v_{ m SS}$ (cm ⁻¹)	-	0.984	-	-	0	100	0	0
$k_r (s^{-1})$	-	-0.535	-0.362	-	0	60.0	40.0	0
$k_{nr} (s^{-1})$	-	-	-0.426	0.899	0	0	32	68
DMAPhacPhCHO								
v_{abs} (cm ⁻¹)	-0.751	0.733	-	-	50.6	49.4	0	0
$v_{\rm fluo} (\rm cm^{-1})$	-	-0.075	-0.031	-	0	70.7	29.3	0
$\Delta u_{ m SS}~(m cm^{-1})$	-	0.805	0.352	-	0	69.6	30.4	0
DMAPhacPhCOOMe								
v_{abs} (cm ⁻¹)	-0.495	-	0.487	-	50.4	0	49.6	0
$v_{\rm fluo} (\rm cm^{-1})$	-	-1.075	-	0.294	0	78.5	0	21.5
$\Delta v_{\rm SS}$ (cm ⁻¹)	-	1.063	-	-0.267	0	79.9	0	20.1
$k_r (s^{-1})$	-	-0.477	-0.538	-	0	47.0	53.0	0
k_{nr} (s ⁻¹)	-	-	-0.945	0.765	0	0	55.0	45.0

3.4. Exited state dipole moment

The method depending on the internal electric field (solvatochromism) has been frequently used to determine the excited state dipole moment. Herein, solvent dependence of absorption and emission spectra is used to estimate the excited state dipole moment based on the Bilot-Kawski theory. Table 8 presents the values of slops (m_1 and m_2) obtained from a linear fit to Eq. (2) (Stoke's shift) and (3) (sum of position of absorption and emission maxima) and quality of linear fit (r^2). Moreover, dipole moment change in excited state ($\Delta \mu_{ex}$) calculated from Eq. (8) and angle between dipole moment in the ground and excited state calculated from Eq. (9) as well as the ground state dipole moment calculated using DFT method are also presented. Table 8 shows also the Onsager radius (a) value used in the calculation.

In the calculations of excited state dipole moment polar protic solvents were not included. Moreover, 1,4-dioxane was also excluded due to the fact that it behaves as a pseudo-polar solvent of variable polarizability function, which depends upon the solute's electric field, as result of conformation polarizability [58]. The quality of fit to Eqs. (2) and (3) are good. The excited state dipole moment changes show, that derivatives with the greater electron affinity substituent possess a greater excited state dipole moment. For DMAPhacPh dipole moment change is equal to $\Delta \mu_{ex}$ = 8.0 D and the angle between dipole moment in the ground and excited state is about 23°. For DMAPhacPhCN $\Delta \mu_{ex}$ = 15.4 D, while angle between dipole moment in the ground and excited

state increase to 63°. Taking into account the calculated ground state dipole moment (10 D) the excited state dipole moment is equal μ_{ex} = 25.4 D and is lower than that published by Hirata et al. (36 D) [33], which was obtained using Lippert-Mataga equation, however, greater than for *p*-cyano-*p*′methylthiodiphenylacetylene (19 D) [58]. For two remaining studied D- π -A pairs, DMAPhacPh-COOMe and DMAPhacPhCHO, dipole moment change in the excited state is equal $\Delta \mu_{ex}$ = 10.2 D and $\Delta \mu_{ex}$ = 7.8 D, respectively, with nearly the same angle between dipole moment in the ground and excited state (about 71°). Such large change of the dipole moment in the excited state indicate a substantial change in the charge distribution in the excited molecule.

Excited state dipole moment change can be also calculated using the relation between Stokes shift and E^T_N solvent polarity parameter according to Eq. (10). Thus, obtained values presented in Table 9 are comparable (about 2D larger for PhacPhCOOMe, PhacPhCHO and about 2D smaller for DMAPhacPhCN and DMAPhacPh) to those obtained from solvatochromic shift.

4. Conclusion

Diphenylacetylene and its symmetrically substituted derivatives containing an electron-donor groups are weakly fluorescing compounds contrary to the derivatives containing an electronacceptor groups which show a relatively high fluorescence

Table 8

Values of slops (m_1 and m_2), quality of fit (r^2), dipole moment change in the exited state ($\Delta \mu_{ex}$) and angle between dipole moments in the ground and excited state (φ) obtained from solvatochromic studies for DMAPhacPh, DMAPhacPhCN, DMAPhacPhCOOMe and DMAPhacPhCHO. The theoretically calculated dipole moment for ground state (μ_{gcal}) and Onsager radius value (a) are also presented.

compound	μ_{gcal} (D)	a (Å)	$m_1 ({\rm cm}^{-1})$	r ²	$m_2 ({\rm cm}^{-1})$	r ²	$\Delta \mu_{ ext{ex}}$ (D)	φ
DMAacPhe	3.4	5.6	3659 ± 285	0.9428	-6791 ± 695	0.8968	8.0	23°10′
DMAacPheCN	10.0	6.6	8199 ± 977	0.8761	-8403 ± 725	0.9312	15.4	63°12′
DMAacPheCOOCH ₃	5.9	6.6	8229 ± 1127	0.8001	-8003 ± 874	0.8643	10.2	70°59′
DMAacPheCHO	5.5	5.7	9001 ± 1024	0.8639	-8183 ± 690	0.9208	7.8	71°16′

Values of slops (*b*) obtained from a linear fits to Eq. (10), quality of fit (r^2), dipole moment change in the exited state ($\Delta \mu_{ex}$) obtained from the dependence of Stokes shift on E^T_N for DMAPhacPh, DMAPhacPhCO, DMAPhacPhCOOMe and DMAPhacPhCHO.

compound	$\mu_{gcal}(D)$	a (Å)	b	r^2	$\Delta\mu_{ex}$ (D)
DMAacPh	3.4	5.6	8582 ± 930	0.8938	6.7
DMAacPhCN	10.0	6.6	19714 ± 2656	0.8439	13.0
DMAacPhCOOCH ₃	5.9	6.6	18311 ± 2412	0.8252	12.6
DMAacPhCHO	5.5	5.7	18111 ± 2802	0.7875	10
betaine	9.0	6.2	-	-	

quantum yield. Introducing only one substituent to the diphenylacetylene skeleton changes its photophysical properties. Spectroscopic and photophysical studies of synthesized compounds show that unsymmetrically substituted diphenylacetylene derivatives are good fluorophores compounds. However, an electron-accepting substituent has much lower influence on photophysical properties of diphenylacetylene than an electron-donating one. While, PhacPhCOOMe and PhacPhCN show only weak solvatochromic effect, DMAPhacPh shows a significant solvatochromic effect caused by substantial charge redistribution in the excited state the effect of which is a large change of the excited state dipole moment. Moreover, dual emission band in moderate polar solvent revealed that locally excited and charge-transfer states have similar energy and simultaneous emissions from both states take place. Introducing to the DMAPhacPh skeleton an electronacceptor substituent substantially increase excited state dipole moment which value depends on the substituent electron affinity. Likewise to DMAPhacPh, for D- π -A pairs in non-polar solvent the charge-transfer state is situated slightly above locally excited state and a small electric field created by chlorine-carbon bond dipole in long saturated hydrocarbon solvent is sufficient to state inversion and emission from the charge-transfer state. Because of failure of time dependent density functional theory for long-range chargetransfer excited states [59–61], therefore we do not present the results of theoretical calculations of the excited states properties of compounds studied using DFT method. Based on the subpicosecond transient absorption spectroscopy and kinetics Fujiwara et al. [62] and Lee et al. [63] stated that the intramolecular charge transfer state proceeds by a two-step consecutive reaction in which highly polar $\pi\sigma^*$, formed from the initially excited $\pi\pi^*$ state by state switch, acts as a precursor of the internal charge transfer state. Moreover, the $\pi\pi^*\!\rightarrow\!\pi\sigma^*$ transition is strongly enhanced in polar solvents. It appears, although we have no experimental evidence for it in the form of transient absorption spectra, that the $\pi\sigma^*$ state plays a similar role in the studied compounds.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2016.03.023.

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