Journal of Photochemistry and Photobiology A: Chemistry 220 (2011) 54–63

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Synthesis and photophysical properties of 2,6-dicyano-*p*-phenylenediamine

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ARTICLE INFO

Article history:
Received 17 November 2010
Received in revised form 12 March 2011
Accepted 20 March 2011
Available online 27 March 2011

Keywords:
Solvatochromism
2,6-Dicyano-p-phenylenediamine
Photophysical properties
pK_a
pK_a*

ABSTRACT

The photophysical and electrochemical properties of *p*-phenylenediamine (PPD) are strongly affected by the addition of cyano groups to the aromatic ring. In 2,3,5,6-tetracyano-*p*-phenylenediamine (TCPPD) the photophysics is governed mostly by the solvent basicity (β) whereas in 2,6-dicyano-N,N,N′,N′-tetramethyl-*p*-phenylenediamine (DCTMPPD) by the solvent polarity/polarizability (π*). In order to study the interactions of cyano-substituted PPDs with the solvent molecules in more detail as well as to clarify the role and origin of hydrogen bonding differences for TCPPD and DCTMPPD, another cyano substituted PPD, 2,6-dicyano-*p*-phenylenediamine (DCPPD) has been synthesized. The photophysical properties have been measured in a wide range of solvents. The fluorescence lifetimes (from 14 ns to 20 ns) and quantum yields (from 0.7 to 0.85) are not very sensitive to the environment. The solvatochromism is analyzed by a linear solvation energy relationship (LSER) using parameters developed by Kamlet, Taft and co-workers. It has been found that both absorption and emission of DCPPD depend on specific as well as non-specific interactions of the solute with the solvent molecules. The ground and excited state pK_a values for DCPPD have also been determined.

1. Introduction

p-Phenylenediamines (PPDs) constitute an interesting family of molecules because of their useful electrochemical and spectrochemical properties which are governed by the substitution on the aromatic ring as well as on the nitrogen of the $-NH_2$ groups [1–5]. Thanks to their low oxidation potential and formation of stable semiquinone radical cations [6], PPDs are used in electrochromism, hair coloration and in color films and paper as color developer [7]. Their properties depend on both the position and nature of the substituents and the medium [8–10].

Until recently PPDs were not renowned for being highly fluorescent molecules. This has been drastically changed by the inclusion of electron withdrawing groups (–CN) on the aromatic ring [11,12]. 2,6-dicyano-N,N,N′,N′-tetramethyl-*p*-phenylenediamine (DCTMPPD) and 2,3,5,6,-tetracyano-*p*-phenylenediamine (TCPPD) were found to have fluorescence quantum yields and lifetimes much larger than any formerly known PPDs [13–15]. In the case of DCTMPPD the fluorescence quantum yield in different solvent ranges from 0.37 to 0.58 with relatively large fluorescence lifetime from 12 ns to 23 ns and very low triplet production yield [11]. The significant increase in both fluorescence quantum yield and lifetime is larger in TCPPD. In TCPPD the quantum yield is above 0.7 in most of the solvents and its lifetime is around 20 ns (even up to 0.89 in ethyl ether with fluorescence lifetime of 23.1 ns).

Another interesting feature is the electrochemical behavior of TCPPD. It is the first PPD derivative which undergoes reversible reduction (−0.72 V vs SCE) while not showing reversible oxidation [12]. This is because of the removal of electron density from the $-NH_2$ group by the introduction of four electron withdrawing –CN groups at the aromatic ring.

The solvatochromic studies for the above two cyano substituted PPDs have shown that DCTMPPD interacts with solvent molecules mainly through non-specific interactions while in TCPPD the solvent basicity is responsible for solvatochromic shifts.

Studying solvent solute interactions, which include non-specific (electrostatic) and specific interactions (hydrogen bonding) depends on many different parameters. Therefore, generally no single parameter or macroscopic property can be used to characterize the solvent effects on the solute properties. The solvent–solute interactions can be analyzed using the combination of solvent properties in the manner of linear solvation energy relationships that

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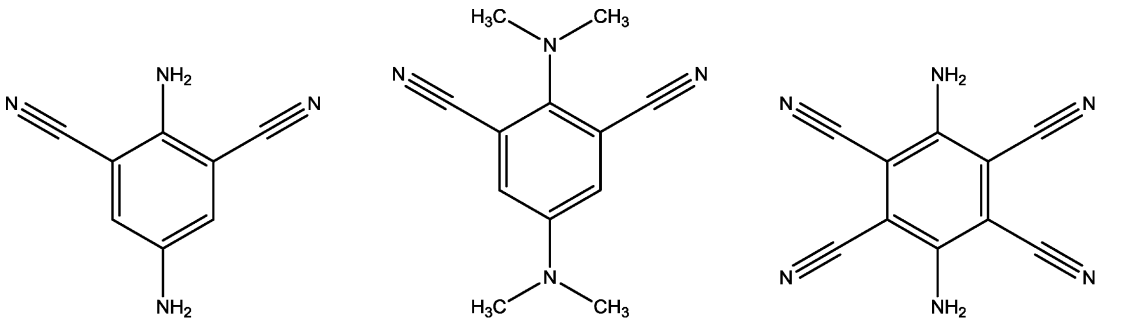
doi:10.1016/j.jphotochem.2011.03.018



Scheme 1.

take a general mathematical form as expressed in Eq. (1),

$$ABC = ABC_o + \sum_i x_i X_i \quad (1)$$

where *ABC* is the solvent dependent property of interest and ABC_o is its value in the gas phase. X_i are the parameters of the solvent, like solvent acidity, basicity, polarizability, di-polarity etc., and x_i stands for the solute sensitivity to the corresponding solvent property. Therefore, in order to disentangle the influence of so many solvent properties in the photophysics of aromatic molecules, a large number of solvents must be studied. Additionally, most solvents show a combined effect and no homogeneous series for each of the parameters in question does really exist. The information thus obtained can be in principle used to predict the behavior of the excited state in a number of environments and it is the starting point for further photophysical characterization works.

Despite the former, the precise role of the nitrile and amino groups in the former two molecules is not yet absolutely clear. Thence, a new cyano substituted derivative of PPD, 2,6-dicyano-*p*-phenylenediamine (DCPPD) has been synthesized in order to study the dramatic change in the photophysical properties of TCPPD and DCTMPPD (see structures in Scheme 1) as compared to each other and to PPD [14,15]. Using a non-methylated compound with only two nitrile groups, the role of hydrogen bonding in the solvatochromism of these cyano PPDs with respect to the nitrile substitution is expected to be addressed.

DCPPD has been structurally characterized using spectroscopic techniques such as IR, NMR (^{1}H and ^{13}C) and mass spectrometry. The photophysical properties (absorption and fluorescence maxima, Stokes shift, 0–0 transition energy, fluorescence quantum yield and lifetime) of DCPPD have been obtained in different solvents. The solvents used in this study encompass polar protic (alcohols and H_2O) highly polar aprotic (DMSO, DMF, HMPA etc.) and apolar to slightly polar aprotic ones (alkanes, aromatics, ethers and esters). The ground and excited state proton transfer equilibria (pK_a and pK_a^*) have also been studied. The solute–solvent interactions have been analyzed by applying multi-parameter linear regression analysis using Kamlet–Taft parameters (π^*, α and β) [16–19]. The structures of DCTMPPD, DCPPD and TCPPD are shown in Scheme 1.

2. Material and methods/experimental

2.1. Reagents

The starting material 5-nitroisophthalic acid (98%, Alfa Aesar), P_2O_5 (Fluka), diethylene glycol (99%, ROTH), hydroxylammonium-chloride (98%, Merck), $NaHCO_3$ (99.7%, Riedel-de Haën), $MgSO_4$ (99%, Aldrich) and NH_3 soln. (33%, ROTH), citric acid (99.5%, Roth) and Na_2HPO_4 (puris p.a., Fluka) were used as received. $SOCl_2$ (99%, Fluka) was distilled just before use. Solvents used were of spectroscopic grade (where necessary dried and distilled before using).

2.2. Synthesis

2,6-Dicyano-*p*-phenylenediamine (DCPPD) was synthesized using 5-nitroisophthalic acid as starting material. The carboxylic (–COOH) groups in nitroisophthalic acid were first converted into acid chloride (–COCl), then acid amide ($-CONH_2$), which upon dehydration gave dicyano-nitrobenzene. The amination followed by reduction of dicyano-nitrobenzene gives the desired DCPPD (6). The systematic layout for the synthesis of DCPPD is shown in Scheme 2.

2.2.1. Synthesis of 5-nitroisophthaloyl chloride (1)

5-Nitroisophthaloyl chloride was synthesized using 5-nitroisophthalic acid as starting material. 10 g of 5-nitroisophthalic acid (47.4 mmol) were refluxed with 30 mL of freshly distilled thionyl chloride, $SOCl_2$, until a clear solution was obtained (20 h). The solution was filtered to remove undissolved residues. Unreacted $SOCl_2$ was removed by the rotavapor, yielding 10.46 g (42.4 mmol; 89%) of 5-nitroisophthaloyl chloride (m.p. 68 °C; lit. [20] 66–68 °C).

2.2.2. Synthesis of 5-nitroisophthalamide (2)

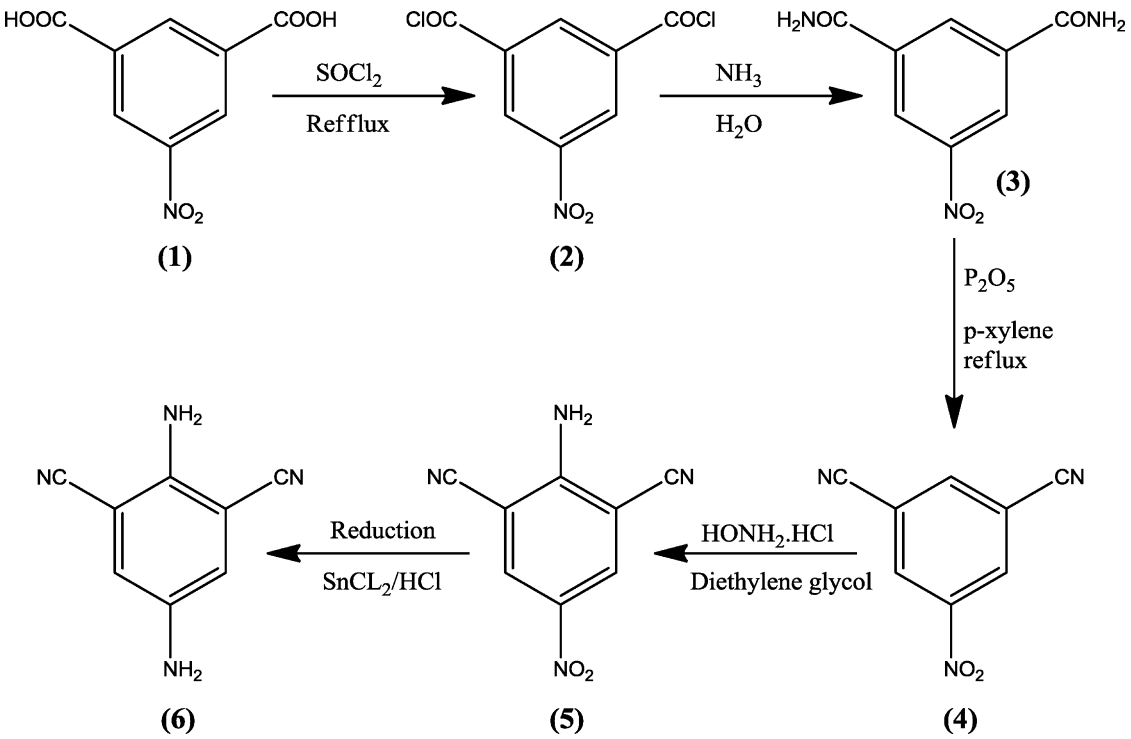
8.5 g of 5-Nitroisophthaloyl chloride (34.4 mmol) were added portion-wise under continuous stirring in 50 mL cold solution of (1:1) H_2O and 33% NH_3 aq. soln. This reaction mixture was stirred for 2 h. The reaction was exothermic and white precipitates were formed immediately after the addition of NH_3 soln. This turbid mixture was stirred for half an hour to ensure the completion of the reaction. The mixture was then filtered, washed with excess of water and dried at 110 °C yielding 7.1 g (33.6 mmol; 98%) of 5-nitroisophthalamide (2) (m.p. 314–315 °C; lit. [20] above 300 °C).

2.2.3. Synthesis of 1,3-dicyano-5-nitrobenzene (3)

4 g of Diamide (2), was converted into 2.43 g of 1,3-dicyano-5-nitrobenzene (3) with 73% reaction yield by refluxing the mixture of 5-nitroisophthalamide and P_2O_5 in p-xylene for 9 h. The p-xylene solution was filtered hot and filtrate was concentrated to obtain white crystal of (3). (m.p. 205 °C; lit. [21] 203.5–205.5 °C). IR (KBr disk) ν/cm^{-1}; 2243 (CN), 1544(NO_2), 1356 (NO_2). ^{13}C NMR (DMSO-d_6) δ/ppm; 114.3 (C_1, C_3), 115.9 (2CN), 132.0 (C_4, C_6), 142.2 (C_2), 148.3 (C_5).

2.2.4. Synthesis of 2,6-dicyano-4-nitroaniline (4)

1,3-Dicyano-5-nitrobenzene (3) was converted into 1,3-dicyano-5-nitrobenzene (4) by the method described in Ref. [22]. 75% of crude product (4) was obtained and recrystallized from



Scheme 2.

pyridine. (m.p. 310 °C; lit. [22] 310–311 °C). IR (KBr disk) ν/cm^{-1}; 3385 (NH_2), 3227 (NH_2), 2239 (CN), 1662 (C=C), 1591(Ar–NH_2), 1507 (NO_2), 1491 (C=C), 1334 (NO_2), 1320 (Ar–NH_2). ^{13}C NMR (DMSO-d_6) δ/ppm; 96.3 (C_2, C_6), 114.9 (2CN), 135.0 (C_3, C_5), 135.8 (C_4), 155.5 (C_1).

2.2.5. Synthesis of 2,6-dicyano-p-phenylenediamine (5)

Reduction was carried out using a slurry of 2,6-dicyano-4-nitroaniline (4) in 95% ethanol and $SnCl_2.2H_2O$ in conc. HCl following the procedure given by Doornbos et al. [23]. 67% of the crude 2,6-dicyano-*p*-phenylenedimine (5) was obtained and recrystallized from methanol. m.p. 178 °C. IR (KBr disk) ν/cm^{-1}; 3389 (NH_2), 3352 (NH_2), 3195 (mixed NH_2), 2213 (CN), 1665 (C$^-$C), 1575 (Ar–NH_2), 1490 (C$^-$C), 1312 (Ar–NH_2). ^{1}H NMR (200 MH_z, CD_3CN) δ/ppm; 7.02 (2H, arom. CH), 4.12 (2H, broad, NH_2), 4.93 (2H, broad, NH_2). ^{13}C NMR (DMSO-d_6) δ/ppm; 99.4 (C_2, C_6), 116.4 (2CN), 123.9 (C_3, C_5), 142.1 (C_4), 144.7 (C_1). Mass (*m*/*z*); 158 (M^+, 100%), 131 ([M-HCN]$^+$, 19%), 104 (M-2HCN]$^+$, 24%).

2.3. Photophysical study

The absorption and fluorescence spectra have been recorded using 10 mm quartz cuvettes sealed with septum caps. Each sample is purged with argon for about 15 min before each measurement. The absorption spectra have been recorded by means of a Shimadzu UV-3101PC UV-VIS-NIR spectrophotometer with a band pass of 1 nm. Steady state fluorescence measurements (corrected emission and excitation spectra) were recorded using a Jobin–Yvon Spex FluoroMax-2 spectrofluorimeter (scan range 250–900 nm, band pass 2 nm). To avoid inner filter and re-absorption effects [24] in the fluorescence measurements, the concentration of DCPPD was chosen such that the absorbance did not exceed 0.1 at and beyond the excitation wavelength. All spectra have been represented in the transition dipole moment representation (TDM) [25].

Fluorescence quantum yields have been measured using a quinine bisulfate (QB) solution in 0.05 M H_2SO_4 (Φ = 0.53 [26]) as reference. The quantum yield is determined using Eq. (2) [27].

$$\Phi_{\text{samp}} = \frac{I_{\text{samp}}(1-10^{-\text{OD}_{\text{ref}}})}{I_{\text{ref}}(1-10^{-\text{OD}_{\text{samp}}})}\left(\frac{xcorr_{\text{samp}}}{xcorr_{\text{ref}}}\right)\left(\frac{n_{\text{samp}}}{n_{\text{ref}}}\right)^2\Phi_{\text{ref}} \quad (2)$$

where Φ_x represents fluorescence quantum yield, OD_x represents the optical density at the excitation wavelength, I_x is the spectrum corrected for variation in lamp intensity ($I = S/R$ where S is the raw signal from the emission detector and R is the photodiode reading of the lamp output at the excitation wavelength), n_x is refractive index of the corresponding solvent at 25 °C, $xcorr_x$ is the correction for the sensitivity of the photodiode, the subscripts '*samp*' and '*ref*' refer to the sample and quantum reference, respectively. Both, the sample and the reference were excited at their respective absorption maxima. This approach was preferred in order to avoid exciting in a region of common absorbance but of large derivatives in the absorption spectra, what would have introduced a large error in the measurements, and in order to use QB, a well established fluorescence standard insensitive to the oxygen content of the solution. The absorbance of both, the sample and the reference are less than 0.1 at the excitation wavelength. Time resolved fluorescence measurements have been performed on a home built single photon counting apparatus described elsewhere [28] exciting with a light emitting diode (LED 370 nm). All fluorescence measurements (steady state and time resolved) have been performed at 25 °C using an external temperature control unit.

Ground and excited state protonation equilibrium constants have been determined from absorption and emission of DCPPD at different pH/H_0. Citric acid and Na_2HPO_4 have been used in buffer solutions of different pH, ranging from pH 2 to 8 [29]. Dilute aqueous solutions of $HClO_4$ have been used in order to perform measurements below pH 2 [30]. Spectrophotometric methods have been used to investigate the ground and excited state acid base equilibria [31–33].

Various multiparametric approaches have been reviewed in the past [34–36]. One of the most generally applicable and most precisely elaborated approaches was developed by Kamlet, Abboud and Taft (KAT) [16–19]. The specific (hydrogen bond donating or

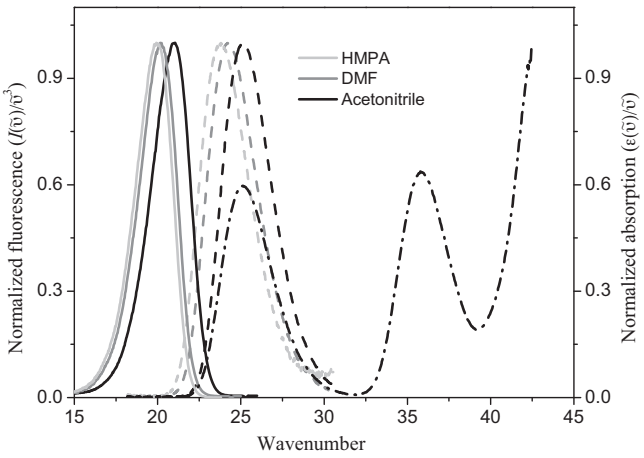


Fig. 1. Normalized fluorescence (solid line) and absorption (dashed line) spectrum of DCPPD in HMPA, DMF and acetonitrile. Dash-dot line is the complete normalized absorption spectrum of DCPPD in acetonitrile.

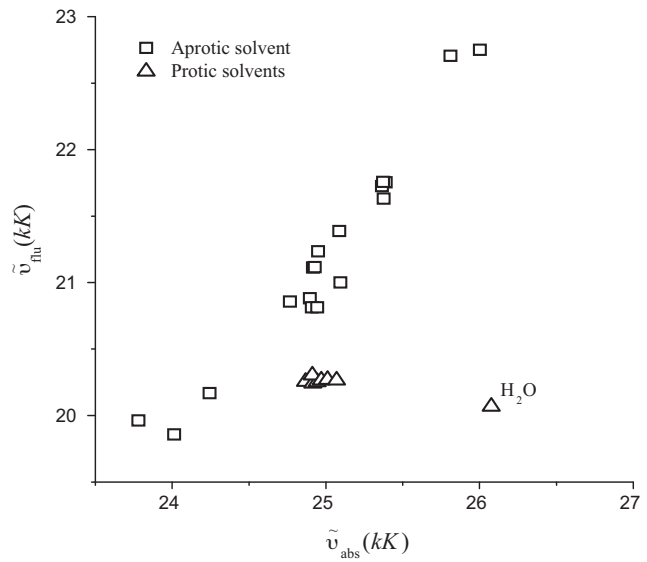


Fig. 2. Absorption maxima vs fluorescence maxima in different solvents.

accepting ability) and non-specific interactions are separately considered. The commonly used Kamlet–Taft equation is shown in Eq. (3)

$$\tilde{\upsilon} = \tilde{\upsilon}_o + s\pi^* + a\alpha + b\beta \quad (3)$$

where $\tilde{\upsilon}$ is the measured property (energy of the absorption or fluorescence maxima in our case) of the solute in a given solvent, $\tilde{\upsilon}_o$ is the calculated value for the gas phase, π^* is the solvent polarity/polarizability [17], α is the solvent hydrogen bond donating ability [18], β is solvent hydrogen bond accepting ability [19].

3. Results and discussion

3.1. Photophysical properties

The photophysical properties for 2,6-dicyano-*p*-phenylenediamine have been determined in 26 different solvents. These solvents were selected in order to cover an ample range of the Kamlet–Taft parameters (π^*, α and β) [16–19]. The solvents used to study the photophysical properties of DCPPD along with the corresponding parameters values are shown in Table 1.

The properties studied for DCPPD include the energy of absorption and fluorescence maxima, Stokes shift, E_{00}, fluorescence quantum yields and fluorescence lifetimes. The molar extinction coefficient, ε, of DCPPD is determined by using Lambert–Beer's law in DMSO ($4500 \pm 200\,M^{-1}\,cm^{-1}$ at 400 nm) and acetonitrile ($4800 \pm 100\,M^{-1}\,cm^{-1}$ at 397 nm). There are two well separated transitions observed for the absorption in different solvents (the absorption spectrum for acetonitrile is shown in Fig. 1). The LSER analysis is performed for the S_0 to S_1 transition which lies at lower energy (longer wavelength). Both, the absorption and fluorescence spectra are sensitive to the medium and shift upon changing the solvent. The shift in absorption and fluorescence spectra, measured in different solvents (acetonitrile, DMSO, HMPA), can be seen in Fig. 1. The photophysical properties of DCPPD are compiled in Table 1.

Generally if there are no specific solvent–solute interactions, the plot of the absorption maxima ($\tilde{\upsilon}_{abs}$) versus the fluorescence maxima ($\tilde{\upsilon}_{flu}$) is expected to be a straight line [37]. A clear deviation for the protic solvents (H_2O and alcohols) can be appreciated in Fig. 2. All the protic solvents fall below the expected trend line. This is an indication that specific solvent–solute interactions are present. Another interesting observation is that among the protic solvents there is a notable shift in the absorption maxima with almost no change in their fluorescence maxima. The $\tilde{\upsilon}_{abs}$ shifts from ~24,900 cm^{-1} (in 1-pentanol) to ~26,100 cm^{-1} (in H_2O), i.e., 1200 cm^{-1} whereas $\tilde{\upsilon}_{flu}$ changes only by about 200 cm^{-1} from 1-pentanol to H_2O. Also in Fig. 2, the relative position of absorption and fluorescence maxima in n-hexane and H_2O is interesting. There is almost no change in the absorption maxima but the fluorescence maxima in these solvents are at the two extremes. Contrary to the layman's opinion of "polarity" being the determining parameter in solvatochromism, this is an instructive example of the specific interactions totally compensating (or at least distorting) the effects of the former.

The fluorescence quantum yield, Φ, of DCPPD is high in almost all solvents (protic and aprotic). For most of the solvents it has a value in the range of 0.7–0.85 and the fluorescence lifetime, τ, is in the range of 14 ns to 20 ns. This observation indicates that the absorption and fluorescence transitions of DCPPD are very sensitive to the environment (depend on specific and/or non-specific interactions) while the fluorescence quantum yield and lifetime are not very sensitive to the nature of the surrounding medium.

3.2. Acid–base equilibria/pK_a and pK_a^*

The absorption and fluorescence spectra have been recorded at different pH (from 1 to 8) and H_0 scale (up to −5). A plot of absorption spectra at different pH is shown in Fig. 3. Going from pH 1 to H_0 −4.7, there is no further change in the absorption spectra of DCPPD. The formal concentration of DCPPD is strictly the same in solutions at different pH. Three isosbestic points (at 265 nm, 303 nm and 370 nm) are clearly observed. There are two species in the pH range from 6 to H_0 −4.69 in the ground state.

The ground state pK_a value is calculated using different methods, (a) from the relative intensity of the absorption of the protonated and unprotonated form, (b) using the Henderson–Hasselbalch method.

There is a decrease in the intensity of the unprotonated form (λ_{max} = 382 nm) with a corresponding increase in the intensity of the protonated form (λ_{max} = 356 nm) as the pH goes from 8 to 1. Fig. 4 shows the titration curves with the relative absorbance intensities of the two species, protonated (I'/I'_o) and unprotonated (I/I_o) involved in the acid–base equilibrium upon changing the pH of the solution. This figure has been constructed as follows: given the two spectra of the two pure species (from the extreme values of the pH scale) at every pH value the following over-determined linear

Table 1
Photophysical properties of DCPPD in different solvents, $\tilde{\upsilon}_{abs}$ absorption maxima, $\tilde{\upsilon}_{flu}$ emission maxima, $\Delta\tilde{\upsilon}$ Stokes shift, E_{00} 0–0 transition energy, Φ fluorescence quantum yield and τ fluorescence lifetime; kK = kilo-Kayser = 1000 cm^{-1}; THF tetrahydrofuran; HMPA hexamethylphosphoramide; DMF, N,N-dimethylformamide; DMSO, dimethyl sulfoxide; PC, propylene carbonate.

Sr. no.	Solvents	π^*	α	β	$\tilde{\upsilon}_{abs}$ (kK) ±0.06	$\tilde{\upsilon}_{flu}$ (kK) ±0.05	$\Delta\tilde{\upsilon}$ (kK) ±0.08	E_{00} (kJ/mol) ±0.5	Φ[a]	τ (ns) ±0.2
1	n-Hexane	−0.11	0	0	26.00	22.75	3.25	291.7	0.58	14.0
2	Cyclohexane	0	0	0	25.81	22.71	3.10	290.2	0.60	13.5
3	p-Xylene	0.45	0	0.12	25.39	21.75	3.64	282.0	0.69	16.0
4	Benzene	0.55	0	0.1	25.37	21.73	3.64	281.7	0.78	15.1
5	Toluene	0.49	0	0.11	25.37	21.76	3.61	281.9	0.74	15.5
6	Ethylbenzene	0.53	0	0.12	25.38	21.63	3.75	281.2	0.58	11.5
7	Butylether	0.18	0	0.46	25.09	21.39	3.70	278.0	0.81	17.5
8	Diethyl ether	0.24	0	0.47	24.95	21.24	3.71	276.3	0.77	19.3
9	Propylacetate	0.53	0	0.4	24.92	21.11	3.81	275.4	0.81	18.1
10	Ethylacetate	0.45	0	0.45	24.93	21.12	3.81	275.5	0.85	18.6
11	THF	0.55	0	0.55	24.77	20.86	3.91	272.9	0.61	18.5
12	Acetone	0.62	0.08	0.48	24.90	20.88	4.02	273.9	0.82	19.4
13	Benzonitrile	0.88	0	0.37	24.91	20.81	4.10	273.5	0.76	15.9
14	HMPA	0.87	0	1	23.78	19.96	3.82	261.7	0.71	19.7
15	Acetonitrile	0.66	0.19	0.4	25.09	21.00	4.09	275.8	0.82	19.5
16	DMF	0.88	0	0.69	24.24	20.17	4.07	265.7	0.77	18.9
17	DMSO	1	0	0.76	24.01	19.86	4.15	262.5	0.72	18.3
18	PC	0.83	0	0.4	24.94	20.81	4.13	273.7	0.86	17.6
19	1-Pentanol	0.4	0.84	0.86	24.87	20.26	4.61	269.9	0.83	18.6
20	2-Butanol	0.4	0.69	0.8	24.92	20.24	4.68	270.2	0.82	19.1
21	1-Butanol	0.47	0.84	0.84	24.94	20.25	4.69	270.4	0.77	19.0
22	2-Propanol	0.48	0.76	0.84	24.91	20.30	4.61	270.5	0.72	19.7
23	1-Propanol	0.52	0.84	0.9	24.97	20.27	4.70	270.6	0.80	19.3
24	Ethanol	0.54	0.86	0.75	25.01	20.27	4.74	270.9	0.73	19.9
25	Methanol	0.6	0.98	0.66	25.07	20.27	4.80	271.2	0.81	20.5
26	Water	1.09	1.17	0.47	26.08	20.07	6.01	276.0	0.65	15.1
27	Water									
(H_o = −3.98)	–	–	–	28.09	25.12	2.97	318.4	–	–	

[a] Fluorescence quantum yields were usually reported with 10% error [55].

system of equations was solved:

$$S(\mathrm{pH}) = aA + bB$$

where A and B are the two pure spectra and S(pH) is the spectrum at any given pH, a and b are the coefficients, i.e., the relative intensities. Both sigmoidal curves intersect at a pH of 3.5 which is the pK_a value for DCPPD.

Additionally, the Henderson–Hasselbalch method (Eq. (5), shown in Fig. 5) has been applied for the determination of the pK_a value for the above acid–base equilibrium.

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{A - A_{\mathrm{DCPPDH}^+}}{A_{\mathrm{DCPPD}} - A}\right) \quad (5)$$

where A_{DCPPD} and $A_{DCPPDH+}$ are the absorbance of the pure neutral DCPPD and its pure protonated form at a determined wavelength, while A denotes the absorbance at this wavelength at any given pH.

Steady state fluorescence titration and Förster cycle [38–41] have been used for the estimation of the excited state pK_a* value. Steady state fluorescence spectra have been obtained by excitation at the isosbestic point lying at the longest wavelength, namely at 370 nm. Fluorescence spectra of DCPPD at different pH are shown in Fig. 6. The titration curves of fluorescence for the relative intensities of both protonated (I'/I') and unprotonated (I/I_o) forms against different pH and H_0 values are shown in Fig. 7. The two curves obtained are not at all symmetrical with respect to each other. The emission intensity of the unprotonated form decreases but no corresponding increase in the emission intensity of the protonated form is

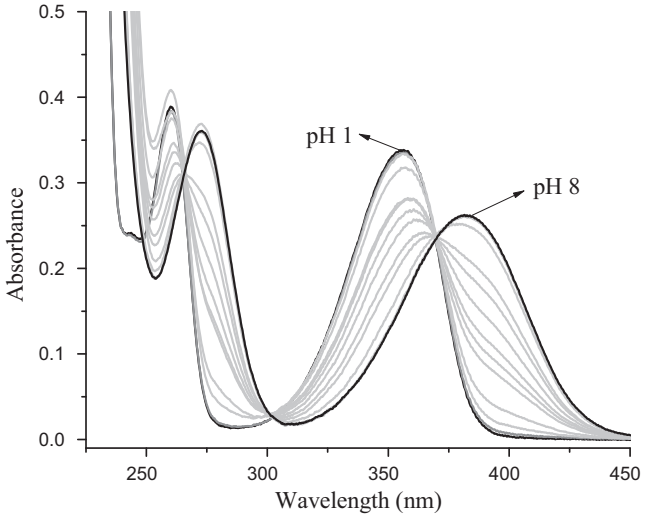


Fig. 3. Absorption spectra of DCPPD at different pH (1–8) showing three isosbestic points (265 nm, 303 nm and 370 nm).

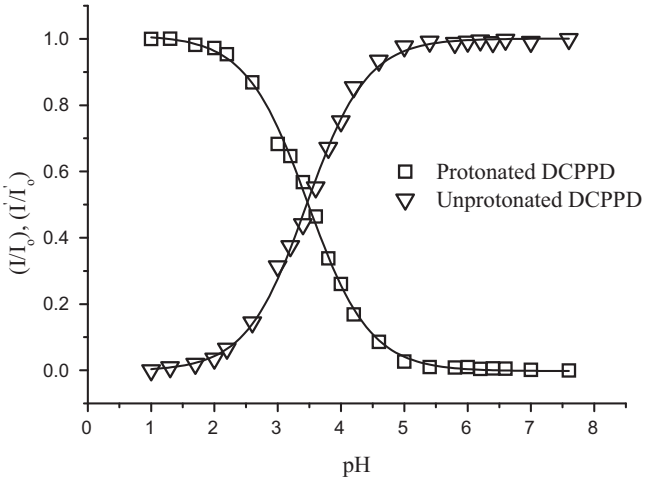


Fig. 4. Relative absorption intensities of the protonated and unprotonated DCPPD vs solution pH.

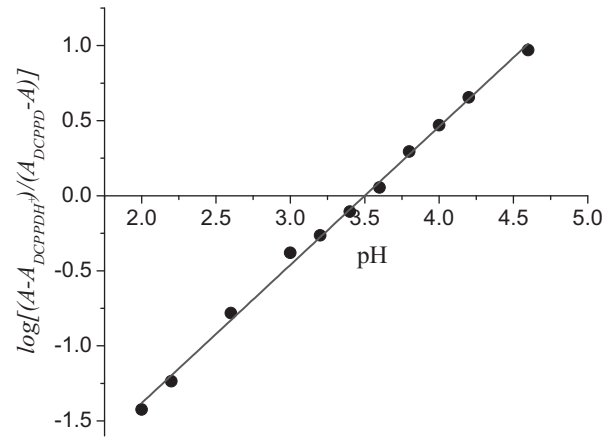


Fig. 5. Evaluation of the pH dependence of the absorption spectrum using the Henderson–Hasselbach equation.

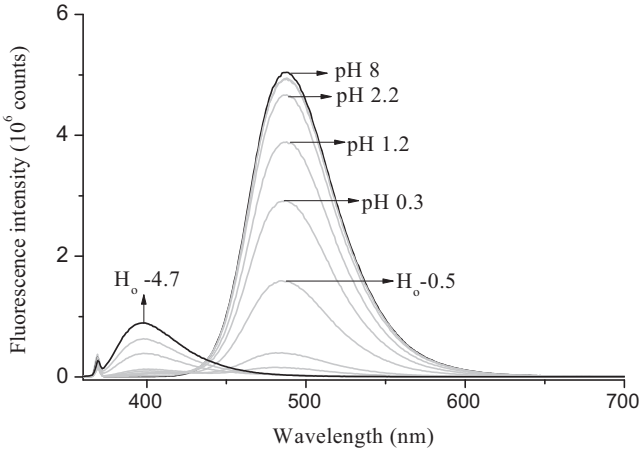


Fig. 6. Fluorescence spectra of DCPPD at different pH and H_0 values (*pH* 8 to H_0 -4.7) excited at 370 nm.

observed in the same range of pH/H_0. This may indicate the quenching of the excited state at higher proton concentrations. Such a quenching behavior has been observed for other amino substituted aromatic compounds [42–47] and also for phenylenediamines [48]. We have tried to simulate these curves with a single set of kinetic equations taking into account the quenching processes but did not succeed to reproduce the experimental observations. Additional experiments are being prepared to clarify this quite unusual situation. A third non-emissive excited state species cannot be excluded as there is no clear isostilbic point (*cf.* Fig. 6).

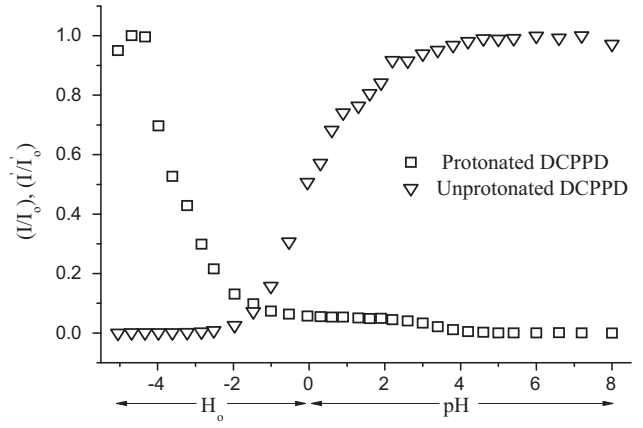


Fig. 7. Relative emission intensities of protonated and unprotonated DCPPD at different pH and H_0 values.

Anyhow, the estimation of the excited state equilibrium constant, pK_a^*, can be obtained by using the Förster cycle method [39]. It is based on ground state thermodynamics and electronic transition energies. Eq. (6) has been used to calculate the pK_a^*.

$$\Delta pK = pK_a - pK_a^* = \frac{E_{AH} - E_{A^-}}{2.303RT} \quad (6)$$

E_{AH} and E_{A-} are the 0–0 transition energies of protonated and unprotonated forms. Using Eq. (6) the calculated pK_a^* value is −3.9 which does not coincide at all with the inflection point of the *AH* form titration curve, which is placed around pH = 0.

Both methods (fluorescence titration and Förster cycle) for the estimation of the pK_a^* value are based on the assumption that the excited state proton transfer is very fast and that the acid–base equilibrium is established during the lifetime of the excited state, and that there are no deformations of the excited state forms – no large entropic differences between the ground and excited state processes [40,49]. However, we want to insist that in the present case proton induced fluorescence quenching can compete with the proton transfer reaction in the excited state and other excited state species cannot be ruled out. Under such conditions, the most reliable value for the pK_a^* can only be obtained by a dynamic analysis [50–52]. The time resolved study of the quenching mechanism will be discussed in detail in a future work and is beyond the scope of the present study.

3.3. Solvatochromism/linear solvation energy relationship (LSER)

A linear solvation energy relationship (LSER) has been applied to analyze the relative contributions of the different solvent properties to the solvent–solute interactions. The solvent induced shifts in the absorption and fluorescence spectra are analyzed by means of a semi-empirical solvent parameter scale developed by Kamlet and Taft (π^*, α and β). Two linear relationships (Eqs. (7a) and (7b)) have been obtained by plotting the experimental versus the corresponding theoretical values of the absorption, $\tilde{\upsilon}_{abs}$, and fluorescence maxima, $\tilde{\upsilon}_{flu}$, using all Kamlet–Taft parameters.

$$\tilde{\upsilon}_{abs} = 25.84(\pm0.06) - 0.30(\pm0.10)\pi^* + 0.97(\pm0.08)\alpha - 1.83(\pm0.11)\beta \quad (7a)$$

$R = 0.972$ and $n = 26$

$$\tilde{\upsilon}_{flu} = 22.53(\pm0.05) - 1.22(\pm0.09)\pi^* - 0.27(\pm0.06)\alpha - 1.79(\pm0.10)\beta \quad (7b)$$

$R = 0.992$ and $n = 26$

The coefficient of π^*, *s*, is the least important in absorption as can be seen (in Eq. (7a)) by its low value, is higher standard deviation and the relatively lower *t*-Student's value. However the absolute value of '*s*' is substantially increased for the fluorescence transition. DCPPD has some polar character in the ground state because of the presence of the two strong electron withdrawing cyano groups at the 2 and 6 positions. The polarity of DCPPD is remarkably increased after the electronic excitation possibly because of some internal charge redistribution concentrating negative charge on the CN groups. This enhanced polarity in the excited state manifests itself in a larger response of the DCPPD fluorescence towards solvent polarity. This means that DCPPD is more polar in the excited state than in the ground state ($\mu_e > \mu_g$) as is usually the case for molecules containing donor and acceptor groups [53,54].

The hydrogen bond donating ability α of the solvent is also relevant in the spectral shift of the absorption. The positive sign of α (in Eq. (7a)) indicates that the relaxed ground state of DCPPD is relatively more stabilized by the solvent hydrogen bond donating

ability than the FC excited state, or the latter more destabilized than the former. Supporting the first explanatory option one could argue that such an effect of solvent acidity could be due to the larger "availability" of the lone pair electrons residing on the nitrogen atom of the amino groups in the relaxed ground state, while in the excited state the CN groups tend to draw more charge than in the ground state. These electrons would be thus available to the surrounding solvent molecules for hydrogen bonding. As a consequence a hypsochromic shift in the absorption spectra in protic solvents, especially in the case of water, is observed. After the absorption electronic transition these electrons would be no longer readily available. Thence, the effect of the solvent acidity term would be much more reduced in the fluorescence as can be indeed inferred from its smaller coefficient in Eq. (7b).

Eqs. (7a) and (7b) show that the solvent hydrogen bond accepting ability, β, holds the major contribution to the solvatochromism in both absorption and fluorescence. The negative sign of b shows that both absorption and emission spectra of DCPPD are red shifted as a result of the solvent hydrogen bond accepting ability. The hydrogen atoms of the amino groups of DCPPD are available to interact with the H-bond accepting solvents both in the ground and excited states. However, in the excited states (Franck Condon and relaxed) the amino group is more acidic (*vide infra* Section 3.2). Therefore, its ability to donate protons to the solvent is largely increased in the excited states (FC and relaxed) as compared to the corresponding ground states (relaxed and FC). Analogically, as a result of H-bonding to the solvent, the excited states (FC and relaxed) of DCPPD may be much more stabilized as compared to the ground states (hence producing the observed red shift in $\tilde{\upsilon}_{abs}$ and $\tilde{\upsilon}_{flu}$ with the increase of β). Obviously, the alternative explanation, though not mutually exclusive with the former, would be a destabilization of ground states with respect to the excited ones as the relative acidity of ground and excited amino groups in water is not simply directly correlated to its H-bonding ability in organic solvents.

The linear correlation between the experimental transition maxima (absorption or fluorescence) with the corresponding calculated values using all the parameters of Kamlet and Taft has been plotted in Fig. 8(a) and (b). The results of the LSER analysis using the Kamlet–Taft parameters are summarized in Table 2.

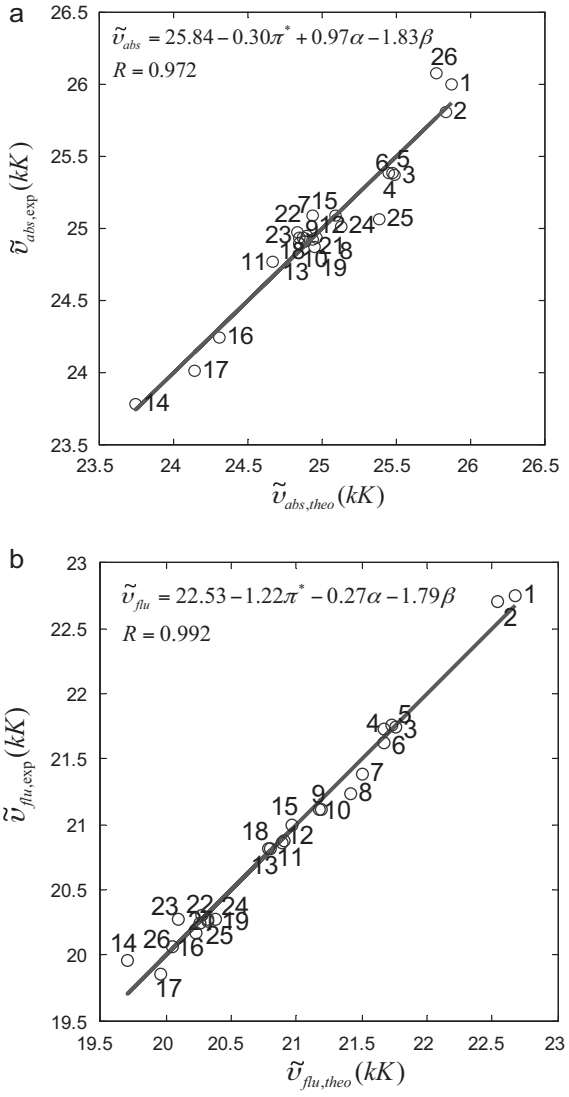


Fig. 8. (a) Plot of the experimental absorption maxima vs corresponding theoretically calculated values using all Kamlet–Taft parameters (α, β and π^*). The numbers correspond to the solvent shown in Table 1. (b) Plot of the experimental fluorescence maxima vs the corresponding theoretically calculated values using all Kamlet–Taft parameters (α, β and π^*). The numbers correspond to the solvent shown in Table 1.

3.4. Solvatochromic comparison with DCTMPPD and TCPPD

The values of '*s*' for both DCPPD and DCTMPPD for the emission transition are comparable. These high values indicate the increased polarity in the excited state for both, DCPPD and DCTMPPD. The smaller value of '*a*' for the absorption in DCTMMPD compared to that of DCPPD may be the result of steric hindrance for the approaching solvent hydrogen. The small values of '*a*' in the emission analysis can be attributed to the low response of both solutes (DCPPD and DCTMPPD) towards the solvent hydrogen bond donating ability.

The hydrogen atoms of the amino groups of DCPPD are substituted with methyl groups to give DCTMPPD. Therefore only C–H hydrogen atoms of the aromatic ring in DCTMPPD are available for solvent molecules to interact through their hydrogen bond accepting ability (β). The aromatic hydrogen atoms, however, are not prone to take part in hydrogen bonding. The LSER analysis for the absorption ($\tilde{\upsilon}_a^{cg}$) and emission centers of gravity ($\tilde{\upsilon}_f^{cg}$) using all Kamlet–Taft parameters are shown in the last column of Table 2 (data taken from Ref. [11]). It can clearly be seen that the value of '*b*' becomes very small in both absorption and emission when compared to that of DCPPD, moreover comparable in magnitude to its standard deviation. This evidences that both, the absorption and the emission spectra of DCTMPPD are not at all influenced by the solvent basicity. For DCPPD, the solute molecule photophysical properties are mostly affected by the H-bonding with the solvent as shown by the previous LSER analysis (*cf.* Eqs. (7a) and 7b)).

Thus DCPPD more or less behaves like DCTMPPD but with an additional sensitivity for the solvent hydrogen bond accepting ability β.

TCPPD is obtained by the inclusion of two more cyano groups into the aromatic ring of DCPPD, at positions 3 and 5. The solvatochromism for the electronic absorption transition is mainly governed by the solvent basicity parameter, β, in both DCPPD and TCPPD. This is because of the presence of the protons at the amino groups in these molecules. However, in the case of DCPPD the solvent acidity parameter, α, also has a considerable influence on the displacement of the absorption band. The introduction of two more cyano groups (at positions 3 and 5) into the aromatic

Table 2
Parameters from LSER analysis using all Kamlet–Taft parameters (α, β and π^*) for all three cyano substituted PPDs. *R* is the regression coefficient and the values in parenthesis are the corresponding Student's *t*-values.

LSER parameters for Absorption maxima			
Parameters	Solute molecules		
	DCPPD	TCPPD[a]	DCTMPPD[b]
$\tilde{\upsilon}_o$ (kK)	25.84 ± 0.06 (415.2)	20.66 ± 0.07 (265.9)	25.75 ± 0.09 (282.2)[c]
s (kK)	−0.30 ± 0.10 (−3.0)[d]	−0.31 ± 0.11 (−2.8)[d]	−0.53 ± 0.13 (−4.0)
a (kK)	0.97 ± 0.08 (12.7)	0.45 ± 0.08 (5.6)	0.17 ± 0.12 (1.4)[d]
b (kK)	−1.83 ± 0.11 (−16.3)	−1.87 ± 0.09 (−19.2)	0.08 ± 0.18 (0.42)[d]
R	0.972	0.973	0.674
LSER parameters for emission maxima			
$\tilde{\upsilon}_o$ (kK)	22.53 ± 0.05 (424.1)	18.6 ± 0.15 (119.0)	20.13 ± 0.05 (378.0)[c]
s (kK)	−1.22 ± 0.09 (−14.2)	−0.5 ± 0.22 (−2.5)[d]	−1.45 ± 0.08 (−19.1)
a (kK)	−0.27 ± 0.06 (−4.15)	−0.1 ± 0.16 (−1.1)[d]	−0.34 ± 0.07 (−5.04)
b (kK)	−1.79 ± 0.10 (−18.6)	−2.3 ± 0.19 (−11.9)	−0.19 ± 0.11 (−1.8)[d]
R	0.992	0.946	0.981

[a] Data taken from Ref. [12].
[b] Data taken from Ref. [11].
[c] $\tilde{\upsilon}_o$ for DCTMPPD are not the absorption or emission maxima but the corresponding values for center of gravity.
[d] Meaningless due to low Student's *t*-value.

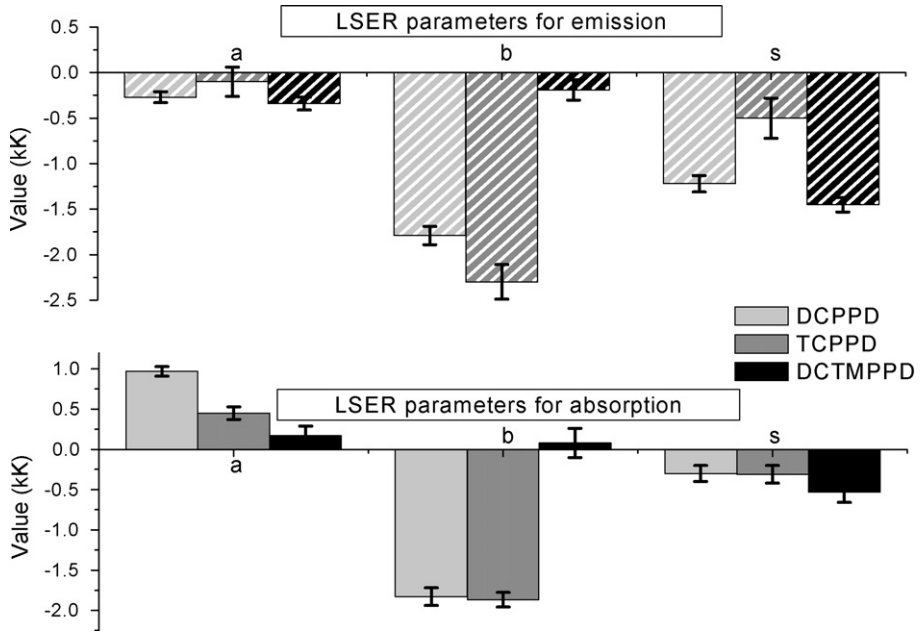


Fig. 9. LSER parameters for absorption and fluorescence transitions using all parameters of Kamlet–Taft (α, β and π^*).

ring of DCPPD transfers the electron density of the amino groups towards the cyano groups through the aromatic ring. This results in the decrease of the interaction of the solute with the solvent hydrogen bond donating ability, α, and lowers the value of '*a*' for TCPPD. TCPPD has no large permanent dipole moment due to its centro-symmetrical structure. Therefore contributions from the solvent dipolarity/polarizability term can be neglected for TCPPD (as attributed by the low Student's *t*-value for *s*). LSER results for the solvatochromism of all three PPDs are summarized in Table 2 and their comparison is shown in Fig. 9. It should be noted that there are some parameters in Table 2 which have low Student's *t*-value, thus showing their statistical insignificance. The fluorescence quantum yield of DCPPD (above 0.7 in most of the solvents) is comparable to that of TCPPD but somehow a little higher than that of DCTMPPD (up to 0.58). The lifetimes of all three PPD derivatives are comparable (mostly in the range from 16 ns to 22 ns). Both $\tilde{\upsilon}_{abs}$ and $\tilde{\upsilon}_{flu}$ are sensitive to the environment but there is no dramatic change in the fluorescence quantum yield and lifetime upon changing the solvents.

4. Conclusion

We have synthesized DCPPD, another highly fluorescent derivative of the cyano substituted PPD series (after DCTMPPD and TCPPD). The response of DCPPD towards the solvent acidity (α) as well as the solvent basicity (β) is higher compared to the solvent dipolarity/polarizability (π^*) for the absorption transition energy ($\tilde{\upsilon}_{abs}$). However, the effects of the solvent acidity and basicity are opposite to each other, Eq. (7a).

Using the Kamlet–Taft parameters, the response of DCPPD towards the solvent basicity (β) is similar (in magnitude and sign) for both absorption and fluorescence, namely a red shift in both $\tilde{\upsilon}_{abs}$ and $\tilde{\upsilon}_{flu}$. Also DCPPD is more polar in the excited state indicated by the large coefficient of the dipolarity/polarizability term in Eq. (7b).

The ground state pK_a for DCPPD is calculated to be 3.5 (±0.1). The excited stated proton transfer equilibrium constant (pK_a*) has been estimated using the Förster cycle and a steady state fluorescence titration. However, in present case, the exact value of the pK_a* can only be evaluated by a dynamic analysis for the excited state proton transfer.

By comparing DCPPD with the already studied cyano substituted derivatives PPD, DCTMPPD [11] and TCPPD [12] the solvatochromic studies have shown that the number of cyano groups is a major factor for the sensibility of the solvatochromism towards β. Thus, it is not only having easily accessible hydrogen atoms but also the number of cyano groups in the ring influences the response of β.

Acknowledgements

We would like to thank to Prof. Karl Gatterer, PTC/TU Graz, for IR spectra and Prof. Robert Saf, ICTM/TU Graz, for mass spectrometry. Thanks are due to Mr. Sarfraz Ahmad, Dept. of Pharmaceutical Chemistry, Uni-Graz, for the NMR spectra. M.Z. highly acknowledges financial support from the Higher Education Commission Pakistan.

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