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Synthesis, solvatochromism, and photophysical properties of the polymer-tetherable 3-[4-di(2-hydroxyethyl)amino]phenyl-l-(2-furyl)-2-propene-l-one

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Abstract

3-[4-Di(2-hydroxyethyl)amino]phenyl-l-(2-furyl)-2-propene-l-one DAFP has been synthesized as a model compound for the study of molecular interactions in the solid-state and liquid environments with different polarity. The UV/vis absorption spectra of this compound have been studied in 35 solvents of different polarity and hydrogen bonding ability. The solvent dependent UV/vis spectroscopic band shifts $\tilde{\nu}_{max}$ are analyzed using the empirical Kamlet–Taft solvent parameters π^* (dipolarity/polarizability), α (hydrogen bond donating capacity), and β (hydrogen bond accepting ability) in terms of the well-established linear solvation energy relationship (LSErs): $\tilde{\nu}_{max} = (\tilde{\nu}_{max})_0 + \mathbf{s}\pi^* + \mathbf{a}\alpha + \mathbf{b}\beta$. The solvent independent coefficients **s**, **a**, and **b** and $(\tilde{\nu}_{max})_0$ have been determined. To understand the environmental contribution to the fluorescence properties, the fluorescence spectra and fluorescence quantum yields of DAFP were investigated in 12 solvents at 293 K.

Keywords: LSE correlations; Long-wavelength UV/vis absorption band shift; Solvatochromism; α,β-Unsaturated ketones; Fluorescence; Time resolved spectroscopy

1. Introduction

Quantification of general properties of solvents, micelle environments and synthetic polymers has been studied by physical organic chemists for many years using suitable solvatochromic probes [1–15]. The responses of solvatochromic indicators on changing solvent environments have been used as the phenomenological basis for several empirical, "solvent polarity" scales [1a]. Among such quantitative scales, the Kamlet–Taft system [1,2] is the most inclusive with respect to all solvent types and it is well supported by theoretical reaction field models for the solvent influences upon the solvatochromic probes [2,3]. The general equation for the influence of solvent effects on a single solute is shown as Eq. (1) [1,2,4], where XYZ is the property to be correlated

$$\mathrm{XYZ} = (\mathrm{XYZ})_0 + \mathbf{h}\delta^2_{\mathrm{H}} + \mathbf{s}(\pi^* + \mathrm{d}\delta) + \mathbf{a}\alpha + \mathbf{b}\beta \qquad (1)$$

$(\mathrm{XYZ})_0$ is a property relating to a standard process, $\delta^2{}_{\mathrm{H}}$ is the solvent cohesive energy density (δ_{H} is the Hildebrand solubility parameter), π^* is the dipolarity/polarizability, δ represents a polarizability correction term, α is the hydrogen-bond donating (HBD) capacity, and β is the hydrogen-bond accepting (HBA) capacity [2]. This linear solvation energy (LSE) relationship is suitable for experimental proving of solvent effects, because it simply allows the separation of "dipolarity/polarizability" from other solvent–solute interactions such as hydrogen bonding by a multiple square correlation analysis. However, the parameters used in multi-parameter LSE relationships are seldom interrelated, featuring just different blends of fundamental intermolecular forces. This makes the interpretation of individual polarity parameters relating to non-specific or specific interaction mechanism in special cases ambiguous.

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Solvatochromic indicators have been also applied to observe the internally and externally polarity of surfaces of macromolecular and related materials [16–28]. The covalent incorporation of chromophores via functional group is an easy way to achieve information on local polarity of reactive polymer, i.e. polyurethanes or polyesters.

While solvatochromism can be often readily described by LSE relationships using the Kamlet–Taft solvent parameters, fluorescence properties such as quantum yield or Stokes shift also depend on the viscosity of the environment [29]. This is of importance since macromolecules of different flexibility are investigated using fluorochromic probes, because stiffness of the polymer chain significantly contributes to the viscosity.

Therefore, we intended to prepare 3-[4-di(2-hydroxyethyl)amino]phenyl-l-(2-furyl)-2-propene-1-one DAFP (Scheme 1). Compared with our previous work [15a], the difference between [4-di(2-hydroxyethyl)aminophenyl]-2-furylmethanone Fur(OH)$_2$ and DAFP is evidently, in the insertion of a single vinylene group between the carbonyl and the *N,N*-dihydroxyethylaminophenyl group to the backbone of Fur(OH)$_2$.

This novel fluorescent compound belongs to the α,β-unsaturated ketones of heterocyclic series. The presence of a single vinylene group between the dimethylaminophenyl and carbonyl group in this type of compounds is sufficient for the appearance of luminescence under ordinary conditions [30]. Therefore, exhibition room temperature emission for these compounds is of considerable interest. As previously reported, luminescence spectroscopy is widely applied to study the microstructure, electronic delocalization, exciton formation, redox processes, and solute–solvent interactions in various types of compounds [31–40]. The fluorescence quantum yield (Φ_f) values were found to be strongly influenced by different parameters, like environmental effects, viscosity, concentration of the dye solution and type of excitation source [38–40].

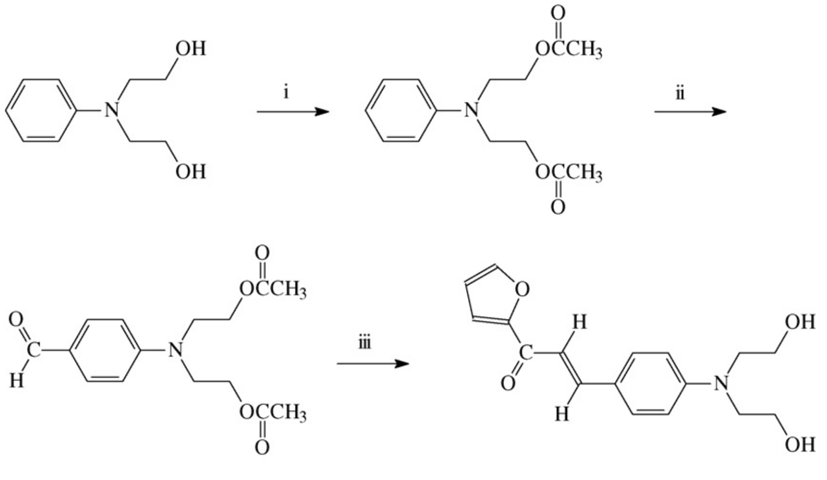
The goal of this paper is to report the synthesis and characterization of DAFP which can be incorporated to the polymeric backbone by reaction with reactive acid groups which enables the application of fluorescence techniques for the study of conformation, dynamics, and interactions of functional macromolecules.

2. Results and discussion

2.1. Solvent effects on the UV/vis absorption spectra and multiple LSE correlation analysis

The UV/vis absorption spectra of the solvatochromic UV/vis band (the longest wavelength band of the π–π* transition) of DAFP have been measured in 35 most common solvents at 293 K as shown in Table 1. Solvents are used with wide-ranging properties for which α, β, and π* are known [4]. With increasing the solvent polarity from cyclohexane (CH) to l,l,l,3,3,3-hexafluoro-2-propanol (HFP) (Table 1), the UV/vis absorption spectra of DAFP show a significant bathochromic shift of the long-wavelength UV/vis band. A representative series of UV/vis spectra is shown in Fig. 1 for DAFP.

The solvatochromic effect of DAFP (Table 1, Fig. 1) shows that the long-wavelength UV/vis absorption maximum ranges from $\lambda = 401$ nm in CH or tetrachloromethane (TCM) to $\lambda = 442$ nm in 1,2-ethane-1,2-diol or water, corresponding to $\Delta\lambda = 41$ nm ($\Delta\tilde{\nu} = 2320\,\text{cm}^{-1}$) stabilization energy between these solvents of extremely different polarity. This result indicates that compound DAFP is more polar in the excited singlet state than in the ground state. Going from non-polar solvent CH to polar solvent water, the extent of solvatochromic bathochromic shift for DAFP is similar to that of Fur(OH)$_2$ [15a]. However, the difference between the long-wavelength UV/vis absorption maximum of DAFP and Fur(OH)$_2$ in the same solvent is more significant ($\Delta\lambda = 54$ and 57 nm in case of CH and water, respectively). This result reflects the more extended conjugated system in the DAFP.



i: acetic anhydride; ii: dimethylformamide, phosphorus oxychloride.
iii: 2-acetyl furan, 20 % sodium hydroxide, methanol.

Scheme 1. Synthesis of 3-[4-di(2-hydroxyethyl)amino]phenyl-l-(2-furyl)-2-propene-l-one DAFP.

Table 1
UV/vis absorption maxima for DAFP in 35 solvents[a]

Solvent	$\tilde{\nu}_{max}$ DAFP (10^3 cm^{-1})	α	β	π^*
Cyclohexane	24.94	0.00	0.00	0.00
Tetrachloromethane	24.94	0.00	0.10	0.28
Diethylether	24.69	0.00	0.47	0.27
p-Xylene	24.51	0.00	0.12	0.43
Toluene	24.39	0.00	0.11	0.54
Benzene	24.33	0.00	0.10	0.59
Triethylamine	24.21	0.00	0.71	0.14
Ethyl acetate	24.15	0.00	0.45	0.55
1,4-Dioxane	24.10	0.00	0.37	0.55
Dichloromethane	24.07	0.13	0.10	0.82
Chloroform	24.04	0.20	0.10	0.58
1,2-Dimethoxy ethane	23.98	0.00	0.41	0.53
1,2-Dichloroethane	23.98	0.00	0.10	0.81
Tetrahydrofuran	23.92	0.00	0.55	0.58
Acetone	23.92	0.08	0.43	0.71
Acetonitrile	23.87	0.19	0.40	0.75
1,1,2,2-Tetrachloroethane	23.81	0.00	0.00	0.95
Benzonitrile	23.47	0.00	0.37	0.90
1-Octanol	23.36	0.77	0.81	0.40
1-Decanol	23.36	0.70	0.82	0.45
N,*N*-dimethylacetamide	23.31	0.00	0.76	0.88
N,*N*-dimethylformamide	23.31	0.00	0.69	0.88
1-Hexanol	23.31	0.80	0.84	0.40
Ethanol	23.26	0.86	0.75	0.54
Methanol	23.26	0.98	0.66	0.60
1-Propanol	23.20	0.84	0.90	0.52
Pyridine	23.15	0.00	0.64	0.87
Acetic acid	23.09	1.12	0.45	0.64
1-Butanol	23.04	0.84	0.84	0.47
2,2,2-Trifluoroethanol	23.04	1.51	0.00	0.73
Dimethylsulfoxide	22.99	0.00	0.76	1.00
1,1,1,3,3,3-Hexafluoro-2-propanol	22.78	1.96	0.00	0.65
Formamide	22.68	0.71	0.48	0.97
Ethane-1,2-diol	22.62	0.90	0.52	0.92
Water	22.62	1.17	0.47	1.09

[a] Solvatochromic parameters α, β, and π^* were taken from ref. [4].

The UV/vis absorption spectrum of the DAFP powder has been measured by means of diffuse reflectance spectroscopy (Fig. 1). The diffuse reflectance UV/vis spectrum shows three bands at λ_{max} 353, 436, and 486 nm. The bathochromic band systems shift of DAFP compared with that of Fur(OH)$_2$ as mentioned above is related to the more extent double bond conjugation in DAFP.

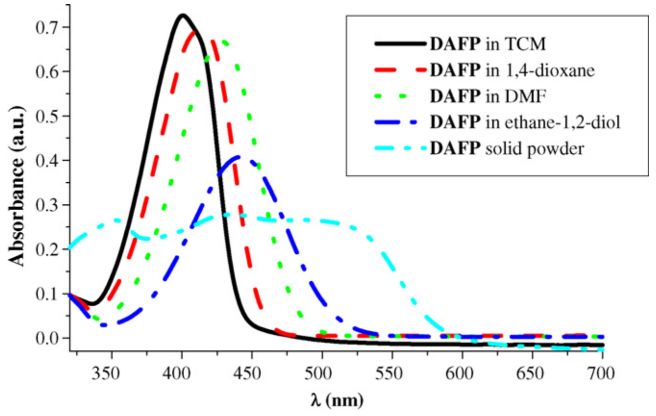


Fig. 1. UV/vis absorption spectra of DAFP in tetrachloromethane (TCM), *N*,*N*-dimethylformamide (DMF), ethane-1,2-diol, and in solid-state.

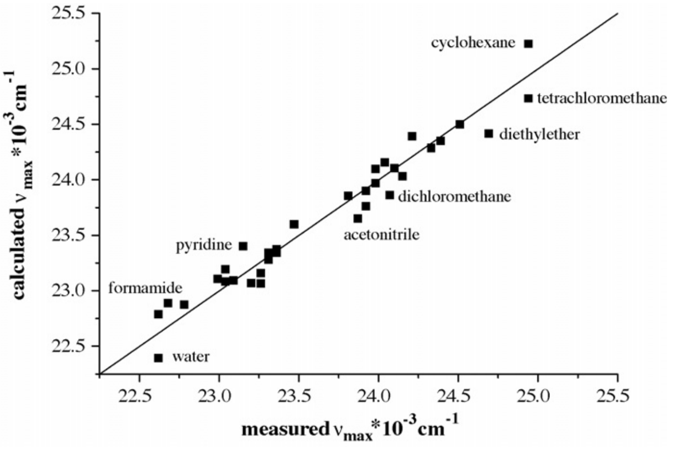


Fig. 2. Relationship between calculated and measured $\tilde{\nu}_{max}$ values for DAFP in 35 solvents of different polarity and hydrogen bond ability.

To evaluate the respective contributions of the dipolarity/polarizability of the solvent and its hydrogen-bonding ability in the ground and excited singlet state solute–solvent interactions of the aromatic amino ketones, the simplified form of the Kamlet–Taft LSE relationship XYZ = $\tilde{\nu}_{max}$ (probe) [1,2,4] was used (Eq. (2)).

$$\mathrm{XYZ} = (\mathrm{XYZ})_0 + \mathbf{s}(\pi^* + \mathrm{d}\delta) + \mathbf{a}\alpha + \mathbf{b}\beta \qquad (2)$$

The solvatochromic parameters α, β, and π^* for the square multiple correlation analysis were taken from ref. [4]. The wave numbers of the absorption maxima ($\tilde{\nu}_{max}$) as energy adequate measure have been used in the regression analysis.

The LSE relationships show a high quality in particular as indicated by correlation coefficients larger than 0.90 for special mathematical functions of $\tilde{\nu}_{max}$ with α, β, and π^*, respectively (Fig. 2).

The results of the multiple square correlation analysis are summarized in Table 2.

As shown from Table 2, the improvement of the correlation coefficient *r* seems to a remarkable change on going from a two-parameter equation to a three parameter equation.

The influence of the π^* on the bathochromic shift of $\tilde{\nu}_{max}$ DAFP is more pronounced than the α term (**s**/**a** ≈ 2, Table 2).

Table 2
Values of the solvent-independent correlation coefficients (α, β, and π^* of the Kamlet–Taft parameters α, β, and π^*), solute-property of a reference system (XYZ)$_0$, standard deviation (SD), significance (*F*) and number of solvents (*n*) for the solvatochromic probe DAFP

(XYZ)$_0$	**a**	**b**	**s**	*r*	SD	*n*	Probe > *F*
25.225	−0.721	−0.890	−1.441	0.975	0.152	35	< 0.0001
24.852	−0.779		−1.428	0.889	0.307	35	< 0.0001
24.656			−1.604	0.623	0.515	35	< 0.0001
25.247		−0.959	−1.472	0.970	0.151	18[a]	< 0.0001
25.049			−1.740	0.872	0.296	18[a]	< 0.0001

[a] Excluding solvents with $\alpha > 0$.

This demonstrates that the ability of the solvent to donate hydrogen bonds is weaker than do solute–solvent dipole–dipole interactions occurring preferably in the singlet excited-state of the DAFP. Thus, a satisfactory linear correlation with high significance is also observed between $\tilde{\nu}_{\max}$ DAFP and solely the Kamlet–Taft's solvation parameter π^* (Eq. (3)).

$$\tilde{\nu}_{\max} \times 10^{-3}\text{DAFP} = 24.656 - 1.604\pi^*,$$

$$n = 35 \quad r = 0.623 \quad \text{SD} = 0.515 \quad F < 0.0001 \qquad (3)$$

On going from a three-parameter equation with π^*, α, and β, to a two-parameter equation considering only π^* and α, a significant change in the correlation coefficient r for DAFP is produced (Eq. (4)).

$$\tilde{\nu}_{\max} \times 10^{-3}\text{DAFP} = 24.852 - 1.428\pi^* - 0.779\alpha,$$

$$n = 35 \quad r = 0.889 \quad \text{SD} = 0.31 \quad F < 0.0001 \qquad (4)$$

The negative sign of the **a** coefficient from the LSE relationships in Table 2 demonstrates that increasing solvent HBD ability also induces a red shift of $\tilde{\nu}_{\max}$. This indicates the formation of solute–solvent hydrogen bonds between the carbonyl oxygen and the HBD site of the solvent.

Also, it is worth noting that the **a** coefficient is significantly smaller than the **b** coefficient for the calculated LSE relationships. This demonstrates that the ability of the solvent to donate hydrogen bonds is weaker than its ability to accept hydrogen bonds of the –N(CH_2CH_2OH)$_2$-substituent.

2.2. *Solvent effects on fluorescence spectra*

Fluorescence spectra of DAFP are recorded in 12 solvents of diverse polarity and hydrogen bond ability (Table 3). Representative fluorescence spectra in four solutions (cyclohexane, acetone, ethanol, and water) are presented in Fig. 3. Quantum yields evaluated from the corrected emission spectra and fluorescence emission maxima are summarized in Table 3.

Table 3
Solvent-dependent fluorescence wave number ($\tilde{\nu}_f$), stokes shift ($\Delta\tilde{\nu}$) and fluorescence quantum yield (Φ_f) of DAFP

Solvent	$\tilde{\nu}_f$ (10^3 cm^{-1})	$\Delta\tilde{\nu}_s$ (10^3 cm^{-1})	$\Phi_f \times 10^{-3}$	η (mPa s)[a]
Cyclohexane	23.47	1.47	0.8	0.898
Toluene	21.51	2.88	18.6	0.553
Acetonitrile	21.51	2.36	181	0.341
Tetrahydrofuran	20.12	3.80	122	0.462
Chloroform	19.53	4.51	112	0.536
Acetone	18.52	5.40	200	0.303
Dimethylsulfoxide	18.26	4.74	355	1.991
Ethanol	17.70	5.56	23.7	1.083
Methanol	17.39	5.87	9.7	0.551
2,2,2-Trifluoroethanol	17.39	5.65	8.7	1.755
Ethane-1,2-diol[b]	17.04	5.58	33.4	13.76
Water	16.81	5.81	1.2	0.8903

[a] The dynamic viscosity, η, of solvents was taken from ref. [4b].
[b] The value of η for this solvent was taken from NCMS Solvents Data Base, http://solvdb.ncms.org/SOLV01.htm.

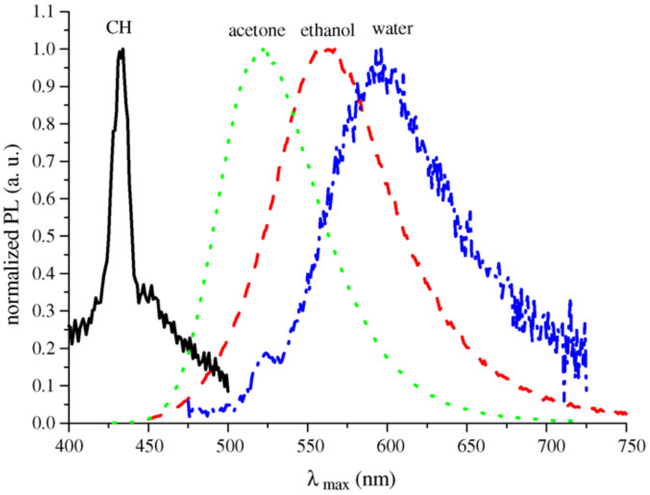


Fig. 3. Fluorescence spectra of DAFP in solvents with increasing polarity. From left to right: cyclohexane (CH), acetone, ethanol, water.

As can be seen in Fig. 3, the emission bands of DAFP in acetone, ethanol, and water are broader and less structured than that in cyclohexane. The emission spectra of DAFP show similar dependences on the solvent environment.

A more significant bathochromic shift of the emission maxima was observed with increasing solvent polarity (Fig. 3 and Table 3) in comparison with that shift of the absorption maxima (vide supra). The bathochromic shift from cyclohexane to water amounts to $\Delta\lambda = 169$ nm ($\Delta\tilde{\nu} = 6660$ cm^{-1}). This result confirms the existence of a significant positive solvatochromism. The pronounced Stokes shift values which rich to the maximum in polar HBD solvents indicating that the geometry of the ground and singlet excited-states could be rather different. The fluorescence quantum yields (Φ_f) varied strongly from 0.8×10^{-3} to 0.355, according to the nature of the solvent (Table 3). The highest value is recorded for strong polar dimethylsulfoxide whereas the smallest one is recorded for non-polar cyclohexane. This result indicates that solvent–solute interactions play a measurable role in modifying unimolecular decay constants for excited singlet electronic states. The aggregation of DAFP in non-polar cyclohexane enhances the non-radiative decay of the excited-state. Also, the interaction between the HBD solvents and the carbonyl group of DAFP decreases the value of the quantum yield whereas the interaction between the HBA solvents and the terminal hydroxyl groups of DAFP enhances the quantum yield.

Fig. 4 displays the plot of the calculated maxima of the fluorescence as a function of the corresponding experimental values for 12 solvents (Table 3).

The multiple square analyses of the wave number of the long-wavelength UV/vis absorption and emission bands of DAFP in the same 12 solvents are given by the Eqs. (5) and (6), respectively.

$$\tilde{\nu}_{\max} \times 10^{-3}\text{DAFP} = 25.071 - 1.315\pi^* - 0.679\alpha - 0.715\beta,$$

$$n = 12 \quad r = 0.979 \quad \text{SD} = 0.17 \quad F < 0.0001 \qquad (5)$$

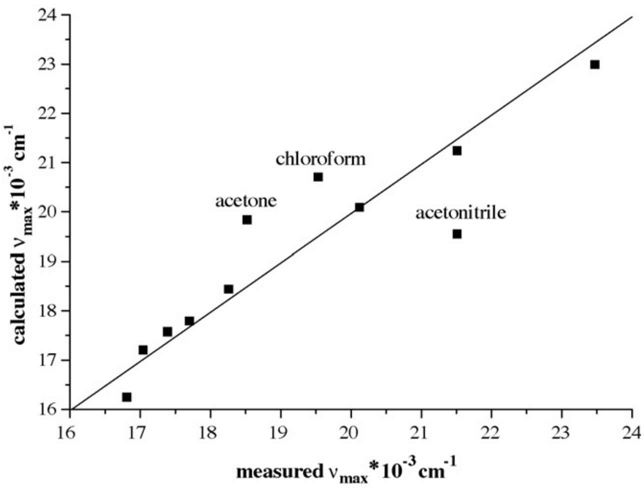


Fig. 4. Relationship between calculated and measured fluorescence $\tilde{\nu}_{max}$ values for DAFP in 12 solvents of different polarity and hydrogen bond ability.

$$\tilde{\nu}_{max} \times 10^{-3}\text{DAFP} = 22.988 - 2.750\pi^* - 2.251\alpha - 2.366\beta,$$

$$n = 12 \quad r = 0.920 \quad \text{SD} = 0.98 \quad F = 0.00128 \qquad (6)$$

It is clear from these equations that, in both of absorption and fluorescence, the polarity as well as the hydrogen bond donating or accepting ability of the solvent contribute to the stabilization of the excited-state. However, this effect is much more pronounced on the fluorescence side, as shown by the much higher **s**, **a**, and **b** coefficients of the solvatochromic parameters π^*, α, and β, respectively. The statistical contribution of π^* in Eq. (6) shows twice increase in comparison with that of Eq. (5). However, the values of coefficients **a** and **b** were increased approximately three-fold indicating that the influence of HBD and HBA solvent properties more pronounced in the charge transfer excited-state than that in the ground-state.

Results of quantum yield correlation analysis for 12 (protic and aprotic solvents) and 7 aprotic solvents (cyclohexane, toluene, chloroform, tetrahydrofuran, acetonitrile, acetone, and dimethylsulfoxide) using the multi-parameters α, β, π^*, and η are given by the Eqs. (7) and (8), respectively.

$$\Phi_f^* \times 10^{-3}\text{DAFP}$$
$$= -13.124 - 151.114\alpha + 63.948\beta + 236.253\pi^* - 3.874\eta,$$
$$r = 0.847 \quad n = 12 \quad \text{SD} = 73.405 \quad F = 0.04189 \qquad (7)$$

$$\Phi_f^* \times 10^{-3}\text{DAFP}$$
$$= -76.581 + 442.301\alpha + 280.003\beta + 66.713\pi^* + 75.148\eta,$$
$$r = 0.977 \quad n = 7 \quad \text{SD} = 44.284 \quad F = 0.08841 \qquad (8)$$

The influence of the α on the quantum yield of DAFP in both equations is more pronounced than the β term. Also, the influence of η in aprotic solvents is stronger than π^* (Eq. (8)).

Regarding the stability, the intensity of the emission maximum was found to decrease less than 2%. The measurement was carried out in acetone ($\lambda_{ex} = 417$ nm, $\lambda_{em} = 524$ nm) under constant illumination by the tungsten lamp of the spectrophotofluorometer. Prior to the measurements, the lamp was carefully heated for 3 h to reach working temperature. In case of acetone, time-resolved measurements showed a single-exponential fluorescence decay with a mean lifetime of $\tau = (1.909 \pm 0.008)$ ns and $\chi^2 = 0.99$ (Fig. 5). There is thus no evidence for conformational dynamics of the molecules affecting lifetime.

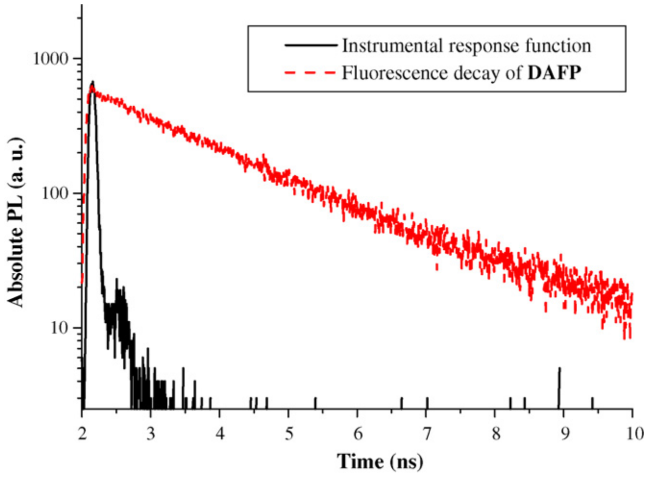


Fig. 5. Fluorescence decay of DAFP in acetone at excitation wavelength 400 nm.

3. Conclusion

A new fluorescent compound DAFP has been synthesized, and its spectroscopic properties studied. This compound reflects environment influences by manifold shifts of its absorption as well as emission band in the UV/vis absorption and emission spectra, respectively. The solvent influence on $\tilde{\nu}_{max}$ of DAFP, its solvatochromism, can be quantitatively expressed by means of a LSE relationship using the empirical Kamlet–Taft solvents parameter set. The LSE analyses show that dipolar interactions preferably contribute to the environmentally induced color changes. The intense orange color of the DAFP crystal is attributed to intermolecular interactions of the dipolar molecules in the solid-state.

The introduction of a vinyl functionality is expected to change solid-state structures in relation to UV/vis absorption properties, which makes this kind of compounds promising for investigating chromophores in terms of environmental effects relating to optical properties for application.

4. Experimental

4.1. Materials

Solvents from Merck, Fluka, Lancaster, and Aldrich were redistilled over appropriate drying agents prior to use [41,42]. Water was draught from a Millipore purification facility ($\rho > 20$ MΩ cm). The 2-acetyl furan from Merck, stated purity >99% was used as received.

4.2. Spectral measurement

The UV/vis absorption spectra were obtained by means of UV/vis spectrometer MCS 400 diode-array spectrometer from Carl Zeiss Jena, connected with an immersion cell (TSM 5) via glass-fiber optics. Fluorescence spectra were measured in solution (cell: Hellma QS) at 293 K by a Shimadzu RF-5001 PC spectrophotofluorometer in perpendicular geometry. The correction function for the emission spectra was obtained using a standard procedure described elsewhere [43]. The fluorescence quantum yields were determined relative to Coumarin 153 in ethanol [44]. Time-resolved measurements were carried out using the MCP-PMT 3908U (Hamamatsu) and the TCSPC (time-correlated single photon counting) module SPC-630 (Becker & Hickl). The sample was excited at the second harmonic (400 nm) of a Titan: Sapphire pulsed laser (80 MHz) in perpendicular geometry, with the light intensity not exceeding 3 μW, the accumulation time was 30 min. The instrumental response was taken with help of a scattering Al foil. Fluorescence decay curves were reconvoluted in a least-square fitting procedure [45].

NMR measurements were recorded at 20 °C on a VARIANT GEMINI 300 FT NMR spectrometer operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C. The signals of the solvent (CD_3OD) were used as internal standards. C, H, N quantitative analysis was performed with a Vario-EL from the company Elementaranalysen GmbH, Hanau.

4.3. Correlation analysis

Multiple regression analysis was performed with the Origin 5.0 statistic programs.

4.4. 3-[4-Di(2-hydroxyethyl)amino]phenyl-l-(2-furyl)-2-propene-l-one [DAFP]

The synthesis of 4-formyl-4′-[di(2-acetoxyethyl)amino]benzene was previously described [46].

A mixture of 2-acetylfuran (1.10 g, 10 mmol), 4-formyl-4′-[di(2-acetoxyethyl)amino]-benzene (2.93 g, 10 mmol) and 20% aqueous sodium hydroxide (5 mL) in methanol (20 mL) was stirred at room temperature for about 2 h. The resulting solid was washed with water (20 mL), dried and crystallized from ethanol affording the pure title compound DAFP; yield: 2.41 g (8 mmol, 80%) as orange crystals with m.p. 133–134 °C.

Found: C, 67.55; H, 6.29; N, 4.55; $C_{17}H_{19}NO_4$ [301.13], requires C, 67.76; H, 6.36; N, 4.65; ^{1}H NMR (CD_3OD): δ 7.83 (d, J = 8.85 Hz, 2H, ArH-2,6), 7.75 (dd, 1H, J = 1.74, 0.79 Hz FurH-5′), 7.48 (dd, J = 3.63, 0.79 Hz, 1H, FurH-3′), 7.40 (d, J = 15.40 Hz, 1H, COC*H*=CH), 6.80 (d, J = 8.85 Hz, 2H, ArH-3,5), 6.71 (dd, 3.63, 1.74 Hz, 1H, FurH-4′), 6.60 (d, J = 15.90 Hz, 1H, COCH=C*H*), 3.77 (t, J = 5.79 Hz, 4H, CH_2–O), 3.63 (t, J = 5.79 Hz, 4H, CH_2–N); ^{13}C NMR(CD_3OD): δ 180.5 (C=O), 155.6 (FurC-2′), 152.5 (ArC-4), 148.9 (CO*C*H=CH), 147.2 (FurC-5′), 132.5 (ArC-2,6), 124.0 (ArC-1), 119.2 (FurC-3′), 116.7 (COCH=*C*H), 114.1 (FurC-4′), 113.5 (ArC-3,5), 60.4 (CH_2–O), 55.2 (CH_2–N).

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