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New fluorescent probes for monitoring polymerisation reactions
1. Synthesis, solvatochromism and emission properties

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Abstract

The synthesis of three new highly fluorescent compounds is reported and the basic spectroscopic properties of them described, discussed and compared with those of some structurally related fluorescent compounds usually used as fluorescent probes. The effect of the solvent on ambient temperature absorption and fluorescence spectra, and the solvatochromic properties observed for both ground and first excited states of all the probes were used to evaluate their first excited dipole moments using the solvatochromic shift method (Bakhshiev's correlation). © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Fluorescent probes; Solvatochromism; Dipolar moments; Polymerisation

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1. Introduction

In the last few years many physicochemical studies have been undertaken in order to understand physical and chemical processes that occur at the molecular level. Among the techniques encountered in the literature, fluorescence spectroscopy of probes sensitive to their microenvironment has been particularly used. Our objective was to find fluorescence probes sensitive to both viscosity and polarity changes. To satisfy these requirements, fluorescent molecular rotors were selected. These probes, upon electronic excitation, lead to the formation of an initial intramolecular charge transfer (ICT) state with partial electron transfer, generally followed by a twisting of the molecule to give a complete electron transfer in a twisted ICT (TICT) state, in which the donor orbital is perpendicular to the acceptor orbital. Depending on the molecule structure, both ICT and TICT states can be radiative, especially in fluid polar media, as for example 4-(*N*,*N*-dialkylamino)benzene derivatives.

These flexible fluorescent dye molecules have been proven to be sensitive to both the local viscosity (rigidity) [1,2] and local polarity [3,4] of the surroundings. Recently, polarity-sensitive absorbance or fluorescent probes have been tested to monitor water uptake in polymers [5–7].

Moreover, dicyano- and tricyanovinylderivatives have been also described as good chromophores for NLO applications [8].

In order to correlate the polarity influence of the solvent on the absorption maxima and fluorescence emission wavelengths, we used the polarity parameters which expressed the best local interactions between the solute and the solvent, i.e., the $E_T(30)$ (defined by Dimroth and Reichardt [9,10]) and π^* values (from Kamlet, Abboud and Taft [11,12]).

The π^* scale is based on solvent-induced shifts of the longest wavelength $\pi \to \pi^*$ absorption band of seven nitroaromatic indicators[1], in which this electronic transition is connected with an intramolecular charge transfer from the electron–donor part (–OMe, –NR_2, –alkyl). The values of their solvatochromic shifts are averaged to prevent the inclusion of specific probe/solvent interactions. It is accepted that π^* values measure dispersive, inductive, and electrostatic probe/solvent interactions and correspond to a blend of polarisability and dipolarity of the solvent. For non-aromatic and non-polyhalogenated aliphatic solvents π^* correlates approximately linearly with the permanent

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[1] 4-Ethylnitrobenzene, 4-methoxynitrobenzene, 4-(diethylamino)-nitrobenzene, 3-(diethylamino)-nitrobenzene, 2-(methylamino)-5-methylnitrobenzene, 4-methoxy-ß-nitrostyrene, and 4-(dimethylamino)benzophenone.

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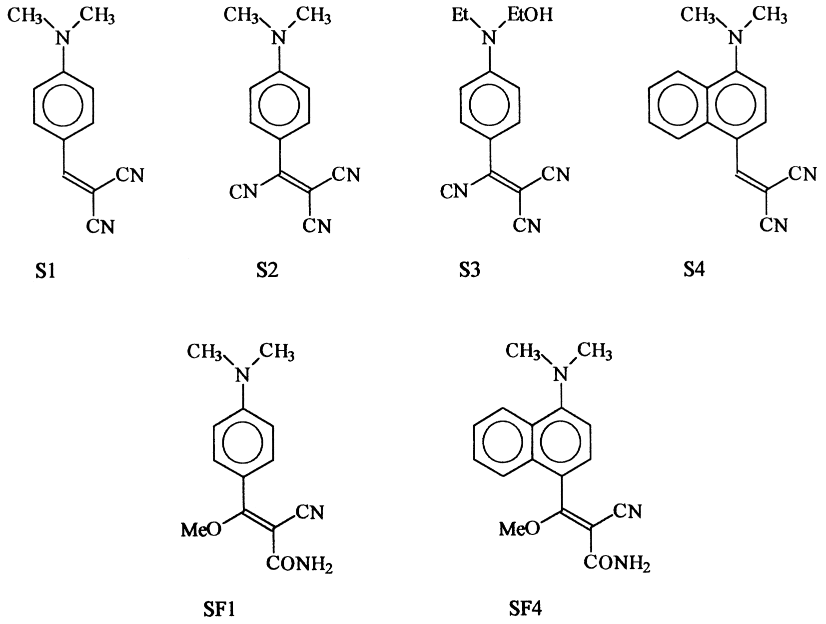


Scheme 1.

dipole moment of the solvent molecules. A new procedure for defining π^* values using only 4-methoxynitrobenzene and 4-(dimethylamino)nitrobenzene has been recently recommended [13]. In the present work, we have used the π^* values found in the literature [14] for the dye 4-(dimethylamino)nitrobenzene because it has the highest structural similarity with our chromophores.

The $E_T(30)$ scale is another commonly used indicator of solvent polarity, and their values are based on the negative solvatochromic pyridinium *N*-phenolate betaine dye as probe molecule.

In this work, we report the synthesis of three new solvatochromic fluorescent probes, as well as the influence of solvents of various polarity on the electronic absorption and fluorescence spectra, and the evaluation of their dipole moments in the excited singlet state using the Bakhshiev solvatochromic method. The structures studied in this work are shown in Scheme 1.

2. Experimental

2.1. Synthesis

4-Dicyanovinyl-*N*,*N*-dimethylaniline (S1), 4-dicyanovinyl-*N*,*N*-dimethylaminonaphthalene (S4), 4-tricyanovinyl-*N*,*N*-dimethylaniline (S2), and 4-tricyanovinyl-*N*-methyl-*N*-(2-hydroxyethyl)-aniline (S3) were synthesised according to procedures described in the literature [15,16]. *p*-*N*,*N*-dimethylaminophenyl-2-cyano-3-methoxy-2-propenamide (SF1) and *p*-*N*,*N*-dimethylaminonaphthyl-2-cyano-3-methoxy-2-propenamide (SF4) were synthesised by modification of the former procedure by adding to the corresponding dicyanovinyl derivative one equivalent of sodium methoxide, and hydrolising the intermediate with water at 70°C afterwards refluxing for 4 h in methanol. Purification of the probes was done by column chromatography (eluent: hexane–diethylether) and recrystallisation (in a mixture of ethanol–toluene) until their spectroscopical data and elemental mass analysis showed complete purity of the substances.

Yields: S1=48%; S2=57%; S3=59%; S4=69%; SF1=12%; SF4=10%.

The spectroscopical data for the compounds not described previously in the literature are given below.

2.1.1. ^{1}H-NMR

S4 (δ ppm, $CHCl_3$): 8.47 (s, 1H, $-C\underline{H}=C-$); 8.46 (d, 1H, C_2–Ar); 7.9 (d, 1H, C_8–Ar); 7.7–7.5 (m, 2H, $C_{6,7}$–Ar); 7.0 (d, 1H, C_3–Ar); 3.1 (s, 6H, $-N(C\underline{H}_3)_2$).

SF1 (δ ppm, $CHCl_3$): 7.5 (d, 2H, $C_{3,5}$–Ar); 6.75 (d, 2H, $C_{2,6}$–Ar); 5.56 (s, 2H, $CON\underline{H}_2$); 4.03 (s, 3H, $OC\underline{H}_3$); 3.04 (s, 6H, $-N(C\underline{H}_3)_2$).

SF4 (δ ppm, $CHCl_3$): 8.25 (d, 1H, C_3–Ar); 7.6–7.2 (m, 4H, $C_{5,6,7,8}$–Ar); 7.15 (d, 1H, C_2–Ar); 5.65 (s, 2H, $CON\underline{H}_2$); 4.1 (s, 3H, $OC\underline{H}_3$); 3.0 (s, 6H, $-N(C\underline{H}_3)_2$).

2.1.2. ^{13}C-NMR

S4 (δ ppm, $CHCl_3$): 157.7; 155.2; 133.5; 130.3; 128.4; 126.8; 126.2; 125.4; 122.4; 119.9; 115.3; 114.2; 112.0; 77.7; 44.4.

SF1 (δ ppm, DMSO):166.1; 161.4; 151.5; 129.8; 120.2; 116.2; 111.3; 82.5; 54.6; 39.7.

SF4 (δ ppm, $CHCl_3$): 165.59; 160.4; 152.08; 131.00; 127.57; 126.86; 126.80; 125.76; 125.46; 124.74; 124.54; 114.74; 112.93; 85.00; 54.62; 44.55.

2.2. Spectral measurements

Solvents were analytical grade (Merck, Aldrich) and were used without further purification. Absorption spectra were recorded with a Perkin–Elmer UV–VIS Lambda 16 spectrometer and fluorescence spectra were taken on a Perkin–Elmer LS 50B spectrophotometer using the absorption maximum wavelength as the excitation wavelength and varying the slits in order to achieve a better spectra for the different probes. Fluorescence quantum yields were determined by comparing with 9,10-diphenylanthracene fluorescence in cyclohexane which has been shown to have a quantum yield of 0.99. The optical densities of all the probes were in the range 0.3–1.0 at the absorption maximum.

2.3. Theoretical calculations

Semiempirical calculations were performed using the original parameters of the program AM1 [17] based on the restricted Hartree–Fock (RHF). This method is included in MOPAC version 6.0 [18], using as graphic interface and data analysis the Cerius2 program [19]. This semiempirical method is commonly accepted to allow a better description of the lone-pair/lone-pair repulsion in several compounds [20]. The MOPAC version 6.0 program ran on a Silicon Graphics Indigo R10000 workstation.

Geometries were optimised in internal coordinates. The optimisation was stopped when Herbert or Peter tests were satisfied in the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method [21]. The PRECISE option was applied for semiempirical calculations during the optimisation process with the gradient norm set to 0.01. The calculations were carried out with full geometry optimisation (bond length, bond angles and dihedral angles) without any assumption of symmetry.

Mulliken population analyses [22] charges used to discuss the electron distributions and dipolar moments are adequate for present purposes since they reflect the tend in populations and charges which seem to be important rather than their actual values, regarding differential reactivity.

2.4. Dipole moment determination

In order to determine the excited state singlet dipole moments by the solvatochromic method the Bakhshiev's formula [23] was used:

$$\nu_{\mathrm{A}} - \nu_{\mathrm{F}} = \frac{2(\mu_{\mathrm{e}} - \mu_{\mathrm{g}})^2}{hca_0^3} F_1 \qquad (1)$$

where ν_{A} and ν_{F} are the wavenumbers (cm^{-1}) of the absorption and emission maxima, respectively, μ_{g} and μ_{e} are the permanent dipole moments in the ground and first excited states, respectively, a_0 is the Onsager cavity radius and F_1 is defined as follows (solvent polarity function):

$$F_1 = \left[\frac{D-1}{D+2} - \frac{2n^2+1}{n^2+2}\right] \frac{2n^2+1}{n^2+2} \qquad (2)$$

where D is the solvent dielectric constant and n is the solvent refractive index.

3. Results and discussion

3.1. Synthesis

The fluorescent probes S1–S4 were prepared according to the procedures described by McKusick and Sulzberg.

Serendipitously, upon purification of S1 (Rf=0.38) we isolated SF1 (Rf=0.08; <1% yield) as a minor pure highly fluorescent component from the crude reaction mixture. Taking into account that methanol and water have to be present during the preparation of S1, the formation of SF1 was rationalised by the next sequence (Scheme 2): first, formation of cetinimide I by regioselective Michael addition of methanol to the cyanovinyl moiety of S1, and second, oxidation of I followed by hydroxyl addition to the cetinimide portion of II.

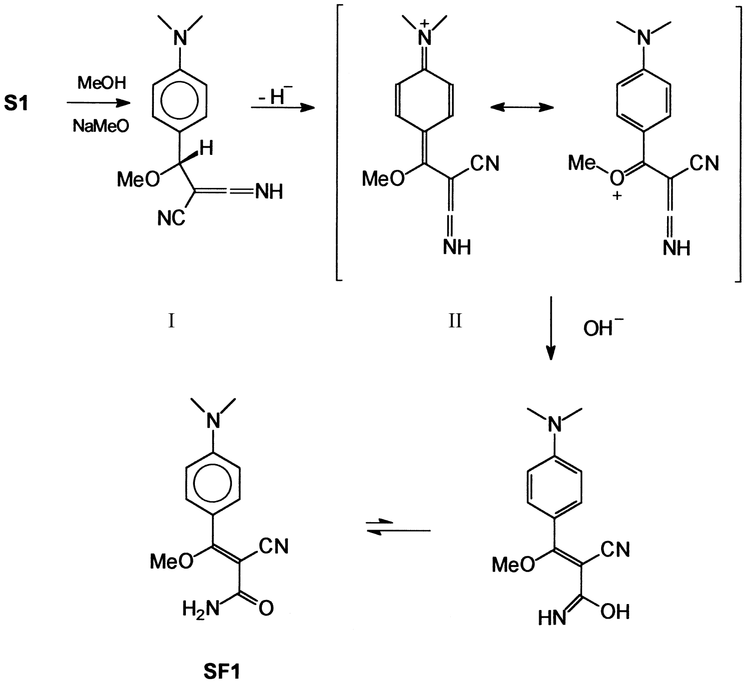
With the above mechanistic proposal in mind, SF1 and SF4 were prepared by adding to a methanolic solution of S1 or S4, respectively, one equivalent of sodium methoxide followed by refluxing for 4 h and then hydrolysis at 70°C.

3.2. Absorption and emission properties

A description of the absorption and emission properties of the dyes S1–SF4 are summarised in Table 1, and the quantum yields are shown in Table 2. Absorption molar coefficients for the new probes are compiled in Table 3.

All the electronic absorption spectra present two main bands, whose maxima are located in the 230–280 nm and λ>300 nm regions. The shortest wavelength bands are attributed to the $\pi \to \pi^*$ transitions whereas the long-wavelength bands, generally characterised by higher molar absorption coefficients, are attributed to CT transitions. On varying the solvent polarity, relatively long shifts in the absorption maxima are observed (20–35 nm). The fluorescence emission spectra of the probes show only one peak in polar solvents whereas double fluorescence emission can be only seen for S1 (λ=554 nm) and S4 (λ=511 nm, shoulder) in cyclohexane. The fluorescence maxima of the probes are significantly red shifted on increasing solvent polarity for the malononitriles ($\Delta\lambda$ up to 39 nm for S1), SF1 and SF4 compounds ($\Delta\lambda$ up to 79 nm), whereas tricyanovinyl derivatives S2 and S3 are less sensitive towards solvent polarity ($\Delta\lambda$=25 nm).

Quantum yields of probes S1–S4 are very low, and independent of the solvent polarity. This agrees with the data stated in literature for the particular case of S1 [24,25] and seems to be a general behaviour for the other cyanovinyl derivatives studied by us. Quantum yields for SF1 and SF4



Scheme 2.

are much higher, especially in polar non-hydrogen bonding solvents. It has been postulated before [26] that for sterically hindered derivatives of molecules which approaches in the ground state the perpendicular geometry of the highly emitting TICT state, the formation of it will be favoured after excitation. SF1 and SF4 are highly torsionated molecules (see below) and this could be the explanation for the significant increase in quantum yield values. Strong differences in ϕ_f values have also been reported for several stilbenes [27,28] depending on the possibility of rotation of the single bonds that connect the attractor and donor moieties.

The correlations of the absorption and emission maxima wavelengths with $E_T(30)$ and π^* values are shown in Figs. 1–4.

Table 2
Fluorescence quantum yields of the probes in different solvents

Solvent	S1	S2	S3	S4	SF1	SF4
Cyclohexane					0.33	0.03
Ether					0.78	0.05
Chloroform					0.89	0.3
THF			$<10^{-3}$		0.88	0.28
Ethyl acetate					0.82	0.19
Acetone					0.62	0.13
Methanol					0.023	0.0014

As can be seen, both the absorption and the emission maxima correlate well with solvent polarity parameters. Due to the structural similarities of the probes with the *p*-nitro-*N*,*N*-dimethylaminobenzene, they correlate better

Table 1
Absorption (λ_{abs}) and emission (λ_{em}) maxima wavelength of the probes

Solvent	S1		S2		S3		S4		SF1		SF4	
	λ_{abs}	λ_{em}	λ_{abs}	λ_{em}	λ_{abs}	λ_{em}	λ_{abs}	λ_{em}	λ_{abs}	λ_{em}	λ_{abs}	λ_{em}
Cyclohexane	413	444	482	–	488	–	428	490	–	390	–	427
Ether	415	458	497	552	503	560	434	502	331	419	322	452
Chloroform	433	467	516	575	516	567	462	521	330	428	319	469
THF	428	473	510	572	517	572	448	518	336	442	326	471
Ethyl acetate	423	475	505	568	515	572	443	520	333	444	323	475
Acetone	430	483	514	577	522	582	454	524	334	458	328	487
Methanol	429	482	514	570	517	584	450	525	332	466	324	506
Ethanol	430	480	513	–	520	–	454	525	333	463	325	490
i-Propanol	428	483	513	–	519	–	451	524	332	456	325	485
n-Butanol	428	480	513	–	520	–	452	524	332	455	325	486
Water	–	–	–	–	–	–	–	–	–	469	–	460

Table 3
Molar absorption coefficient of S4, SF1, SF4 in different solvents[a]

$\varepsilon\times10^{-2}$ (mol l^{-1} cm^{-1})											
Probe	Cyclohexane	Ethyl ether	Chloroform	THF	Ethyl acetate	Acetone	Methanol	Ethanol	*i*-Propanol	*n*-Butanol	Water
S4	246	275	306	297	238	323	242	242	234	254	–
SF1	–	165	154	192	218	169	±	±	±	±	–
SF4	–	131	134	218	222	–	±	±	±	±	–

[a] (–): Non soluble; (±): slightly soluble.

with π^* scale than with $E_T(30)$, as expected. Nevertheless, the correlation coefficients are good enough with both scales. The slopes of the lines are indicative of the sensitiveness of the different probes towards solvent polarity. As can be seen in Figs. 2 and 4, the emission maxima of S1 and S4 present the same sensitivity towards polarity, this is, the same slope in both plots. The same fact is found for SF1 and SF4. This means that in the case of these functionalities, the size of the probe does not affect very much the solute–solvent interactions when a benzene ring is substituted by a naphthalene ring.

It is important to note that the probes S1–S4 are sensitive to solvent polarity in both the ground and excited singlet states, being the new probes SF1 and SF4 sensitive to polarity only in their emission properties.

Parallel to the synthesis of these molecules, a theoretical study was carried out by semiempirical AM1 computational calculations, in order to reckon the dipolar moments and to get insight of their geometric differences. The main geometrical parameters in the ground state of the probes are shown in Table 4 and Scheme 3.

The existence of electronic conjugation between the pendant groups can be seen by the changes of the distances $d_{N_1–C_4}$ and $d_{C_7–C_8}$, whereas the distance $d_{C_8–C_9}$ is an in-

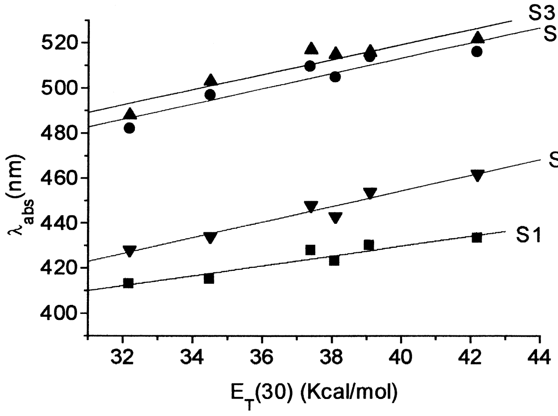


Fig. 1. Correlation of maxima absorption wavelength of the probes with $E_T(30)$ empirical polarity parameter.

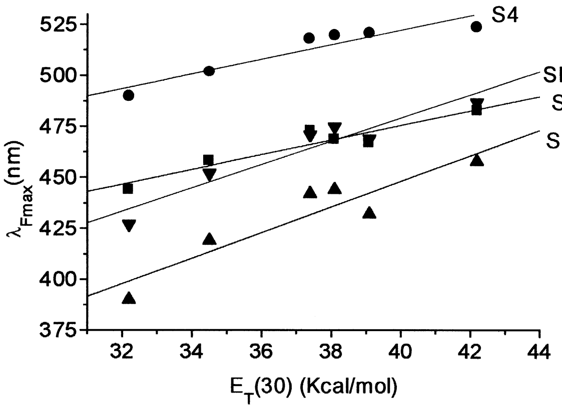


Fig. 2. Correlation of maxima emission wavelength of the probes with $E_T(30)$ empirical polarity parameter.

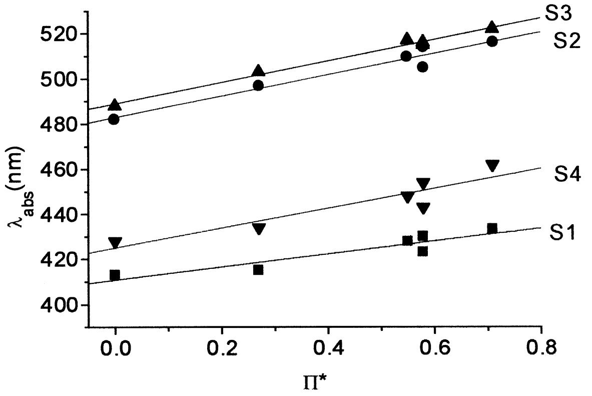


Fig. 3. Correlation of maxima absorption wavelength of the probes with π^* empirical polarity parameter.

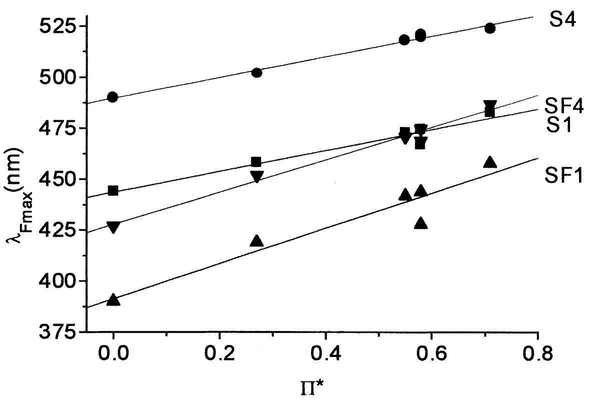


Fig. 4. Correlation of maxima emission wavelength of the probes with π^* empirical polarity parameter.

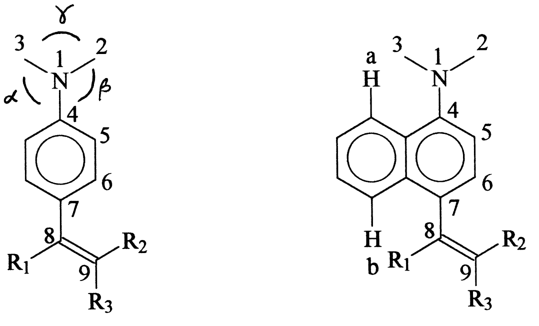
Table 4
Geometrical parameters (Scheme 3) for the molecules of this work

Compound	d(N–C_4)	d(C_7–C_8)	d(C_8–C_9)	$\alpha+\beta+\gamma$	DH1[a]	DH2[b]	DH3[c]	Volume (Å^3)	μ_g (D)
S1	1.396	1.444	1.355	354	−14.9	−15.2	31.9	197.7	6.65
S2	1.393	1.455	1.363	356	−12.7	14.1	40.3	215.4	6.83
S3	1.399	1.456	1.362	352	−20.1	−51.0	41.9	234.1	5.64
S4	1.421	1.450	1.354	345	−24.1	−71.3	42.7	243.5	8.59
SF1	1.396	1.461	1.361	355	−12.4	15.5	45.8	233.2	8.59
SF4	1.422	1.469	1.362	345	−24.7	−71.9	68.7	279.1	8.5

[a] DH1=α=dihedral angle C_3–N–C_4–C_{10}.
[b] DH2=β=dihedral angle C_2–N–C_4–C_5.
[c] DH3=γ=dihedral angle C_6–C_7–C_8–C_9.

dicator of the attached groups of the olefinic bond. As can be seen in Scheme 3, there is a steric interaction in the naphthalene moiety between the dialkylamino group and hydrogen ‘a’, and between the olefinic group and hydrogen ‘b’. This steric hindrance can be quantified by the dihedral angles $H_{C_2-N_1-C_4-C_5}$ and $H_{C_6-C_7-C_8-C_9}$, where a higher value means a higher interaction.

In the minimum energy configuration, the dimethylamino moiety is close to planar with the aromatic ring for the probes which have a benzene ring. Bond lengths are similar in these compounds and correspond to the expected values. For those probes which have a naphthalene ring, the steric hindrance between hydrogen ‘a’ and C_3 takes the dimethylamino group out of the plane of the aromatic ring. Then, an increase in N_1–C_4 bond length is observed. The difference in planarity of the attractor groups is notable for all probes (but again is higher for S4 and SF4) and bond lengths show only little conjugation with the aromatic rings, especially in those cases of a naphthalene ring. Although our findings of approximate planarity between dimethylamino and aromatic moieties are consistent with previous reports of TICT probes, the observation of long wavelength CT emission for the torsionated structures would appear to contrast with the general view of intramolecular charge transfer states in highly donor–aryl–acceptor systems. In our systems, the significant dihedral angle between the aromatic ring and the electron acceptor moiety does not affect, apparently, to an effective charge separation to effect low energy solvatochromic emission sensitivity. This effect has been also recently reported for the similar structure 1,1 -dicyano -2 -[6-dimethylamino)naphthalen-2-yl]propene [29], as well as for other more simple dicyanoderivatives [30,31].



Scheme 3.

3.3. Excited singlet state dipole moments

Dipolar moments in the excited state for the new fluorescent probes have been estimated using the Bakshiev’s solvatochromic method (Fig. 5 and Table 5), and using the

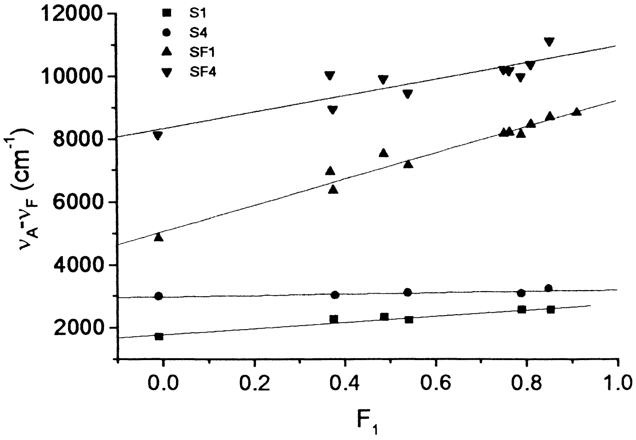


Fig. 5. Bakshiev’s correlation for S1, S4, SF1 and SF4.

Table 5
Slope of Bakshiev’s correlation and calculated excited state dipolar moments for the new probes

Probe	Slope[a] (cm^{-1})	μ_e (D)
S1	985	24.05
S4	216	14.68
SF1	4160	47.32
SF4	2613	42.08

[a] From Fig. 5.

calculated parameters for V and μ_g. The excited state dipolar moments for the probes calculated with Eq. (1) are shown in Table 5. Some assumptions have been taken. The Onsager cavity radius a_0 which appears in many solvatochromic shift equations, as in Eq. (1), approximates the dipole moment of a molecule by a point dipole in the centre of a spherical cavity with radius a. For non-spherical molecules such as those discussed here, a is very badly defined. A suggestion by Lippert [32] is to take a as 40% of the long axis of an ellipsoid enclosing the molecule, but this treatment is not appropriate for comparing molecules of very different sizes. In this work, we have calculated by semiempirical methods the Van der Waals volume and, following Suppan et al. [33], estimate the Onsager cavity radius by a cubic lattice model as $8a^3=V$.

As can be seen, the values of μ_e obtained for SF1 and SF4 are much higher than those of S1 and S4, and this explains the higher sensitivity towards polarity of these new compounds.

4. Conclusions

Three new fluorescent compounds have been synthesised, and their spectroscopic properties studied and compared with other well known fluorescent probes.

The new probes are highly fluorescent molecules, and their emission band strongly depend on the polarity of the solvent. For SF1 and SF4 there is a variation of maximum wavelength and fluorescence quantum yield, whether for S1–S4 only dependence in wavelength is found. Additionally, S4 presents sensitiveness towards polarity in its absorption band.

So, the new compounds are very promising as fluorescent probes for sensing polarity changes in their microenvironment.

Given the excellent properties of SF1 and SF4 as fluorescent sensors of polarity, different synthetic routes are currently being explored in order to increase the low yield obtained in their synthesis.

Acknowledgements

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