A solvatochromic dye for probing significantly the dipolarity/polarizability of HBD (hydrogen bond donating) environments

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The solvatochromism of the novel dye 4-*tert*-butyl-2-(dicyanomethylene)-5-[4-(diethylamino)benzylidene]-Δ^3-thiazoline (**1**) has been investigated in 26 solvents of different polarity. **1** exhibits a positive solvatochromism, its solvent-induced bathochromic UV/Vis absorption band shift ranges from n-hexane ($\lambda_{max} = 566$ nm) to dimethyl sulfoxide ($\lambda_{max} = 640$ nm). The molar absorption energy of the solvatochromic band shift of **1** can be well correlated with Kamlet–Taft's and Catalàn's solvent polarity scales. **1** is mainly sensitive to the solvent's dipolarity/polarizability (π^* of **SPP**^{N} term) rather than of its HBD (hydrogen-bond donating) or HBA (hydrogen-bond accepting) property. It is emphasized that the UV/Vis absorption band maximum of **1** in the strong HBD solvents acetic acid, 2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoropropan-2-ol fit well in the LSE (linear solvation energy) relationship with Kamlet and Taft's π^* and Catalàn's **SPP**^{N} scale, respectively, which makes this dye important as a dipolarity/polarizability indicator for various solid acids.

Introduction

Solvent polarity is among the most widely used concepts in chemistry.[1–8] Most solvent polarity scales are empirical and are based on kinetic, thermodynamic, or spectroscopic data relating to certain reference processes.[1,3,4] Significantly, different empirical solvent polarity scales have been shown to correlate well with each other, pointing to the existence of an underlying common feature.[1,3,7–10] Empirical solvent polarity scales based on spectroscopic measurements usually employ changes in the UV/Vis absorption maximum of an indicator in different solvents (solvatochromism).[1,6,9,10]

However, the interaction of a solvatochromic dye with a pure solvent or a solvent mixture is a composite of many effects.[1–4] Multiple intermolecular solute/solvent interactions can be described by the LSER (linear solvation energy relationship) of Kamlet and Taft [eqn. (1)].[11]

$$\mathrm{XYZ} = (\mathrm{XYZ})_o + m\delta_H{}^2 + a\alpha + b\beta + s(\pi^* + d\delta) \qquad (1)$$

$(\mathrm{XYZ})_o$ is the solute property of a reference system, *e.g.* a nonpolar medium, $\delta_H{}^2$ is a cavity term which relates to the Hildebrand solubility parameter, α describes the HBD (hydrogen-bond donating) acidity, β the HBA (hydrogen-bond accepting) ability, and π^* the dipolarity/polarizability of the solvents. δ is a polarizability correction term which is 1.0 for aromatic, 0.5 for polyhalogenated, and zero for aliphatic solvents; m, a, b, s, and d are solvent independent correlation coefficients.[1,11]

The original Kamlet–Taft solvent polarity parameters are averaged values derived from numerous solvent-dependent physicochemical processes.[11] However, their underlying interpretations are often based on intuition or preconceived opinion rather than on physically defined interaction mechanisms. As a matter of fact, the parameters used in multiparameter LSERs are often interrelated, featuring just different blends of fundamental intermolecular forces.[4,7,9,10] This makes the definition of individual polarity parameters relating to specific interaction mechanisms often questionable. Despite this critical argument, in the last two decades, the Kamlet–Taft parameters have been established for interpretation of a lot of physicochemical processes because of their usefulness in many applications.[12–17]

In the last six years, Catalàn's group established three related empirical solvent polarity scales: the **SPP**^{N} (dipolarity polarizability),[18a,b] the SB (solvent basicity),[18c] and the SA (solvent acidity) scale.[18d,e] Their advantage is that each scale is based with respect to well defined reference processes of two homomorph solvatochromic dyes.[18]

For instruction and motivation of this research, it is not scientifically sound that the dipolarity/polarizability (π^* term) of 2,2,2-trifluoroethanol (TFE) ($\pi^* = 0.73$) is larger than that of 1,1,1,3,3,3-hexafluoropropan-2-ol (HFI) ($\pi^* = 0.63$), because the dipole moment of HFI is greater than that of TFE.[11] In terms of the **SPP**^{N} scale, a reasonable order of dipolarity/polarizability seems available: the dipolarity of TFE (**SPP**^{N} = 0.960) is lower than that of HFI (**SPP**^{N} = 1.007).[18a,b] Perhaps, the large α value of HFI is a blend containing contributions from π^*. Related problems are sometimes reflected in several papers.[1,3,8–10]

There is a lack of solvatochromic dyes for which the UV/Vis absorption band shift references solely to one of the Kamlet–Taft α, β, and π^*, or Catalàn **SSP**^{N}, SB, and SA solvent parameters, respectively, when using a representative solvent set including nonpolar and strong HBD as well HBA solvents.[1b,9]

For determining α in protic environments, an excellent indicator is $\mathrm{Fe(phen)_2(CN)_2}$ [*cis*-dicyanobis(1,10-phenanthroline)-iron(II)][10b,19a,b] and related complexes of this type of compound.[19c] However, the UV/Vis shift of $\mathrm{Fe(phen)_2(CN)_2}$

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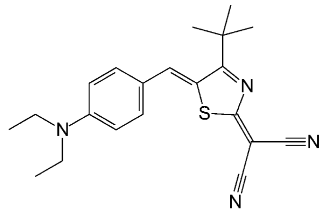

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Chart 1 Molecular structure of the novel solvatochromic dye **1**.

reflects contributions of π^* with 25%.[10b,19a] Despite this critical argument, we think this type of compound is the best for probing HBD environments.

For β, a suitable indicator is $\text{Cu(tmen)(acac)}^+\text{-B}(\text{C}_6\text{H}_5)_4^-$.[13d,14a,19a,b] However, it is only sparingly soluble in weak polar solvents and due to the low absorption coefficient [$\varepsilon = 250\ \text{l mol}^{-1}\text{cm}^{-1}$] rather large concentrations of this probe are required which restricts its application.

A UV/Vis indicator is required which is solely sensitive to the dipolarity/polarizability and not to the acidity and basicity including very strong HBD and HBA solvents such as TFE and HFI, or DMSO and triethylamine, respectively.[1,12,13] For instance, despite its excellent solvatochromic properties, the π^* sensitive solvatochromic dye 5-(*N*,*N*-dimethylamino)-5′-nitro-2,2′-bisthiophene[20] shows a nonlinear UV/Vis spectroscopic bathochromic shift on acidic surfaces like silica, similar to those in HFI or TFE.[13c]

In this paper we introduce a novel solvatochromic dye 4-*tert*-butyl-2-(dicyanomethylene)-5-[4-(diethylamino)benzylidene]-Δ^3-thiazoline (Chart 1)[21] which is mainly sensitive to the π^* and **SPP**$^\text{N}$ parameters, respectively, of solvent polarity including the strong HBD solvents TFE and HFI. Other dyes of similar structure show solvatochromic dependence on both π^* and α.[21–23]

Experimental

The complete synthesis of the dye and related compounds has been reported in ref. 21. In the final synthetic step, it was obtained by acetic anhydride catalyzed aldol condensation: 4.4 g of *N*,*N*-diethylaminobenzaldehyde and 5.1 g of the dicyanomethine thiazole derivate were refluxed in 20 ml of acetic anhydride for 5 min. Then the mixture was stirred overnight at room temperature and the dye precipitated. The crude crystals were washed with 100 ml of methanol and dried in vacuum at 60 °C. Yield: 90% (theor.), green needles, mp.: 241–243 °C (uncorrected).

The structure of the novel dye was confirmed by quantitative elemental analyses (molar mass:364.5 g mol^{-1}) $\text{C}_\text{found} = 69.2\%$ ($\text{C}_\text{theor} = 69.20\%$), $\text{N}_\text{found} = 6.8\%$ ($\text{N}_\text{theor.} = 6.64\%$), $\text{S}_\text{found} = 8.9$ ($\text{S}_\text{theor} = 8.8$), $\text{H}_\text{found} = 15.7\%$ ($\text{H}_\text{theor} = 15.37\%$) as well as ^{1}H and ^{13}C NMR spectroscopy. ^{1}H NMR: $\delta = 1.19$ ppm (t, CH_3–), $\delta = 1.48$ ppm (s, CH_3C–), $\delta = 3.43$ ppm (q, –CH_2–), $\delta = 6.7$ ppm and $\delta = 7.47$ ppm (d, CH aromatic H), and $\delta = 7.8$ ppm (s, –CH=). ^{13}C NMR: $\delta = 13.79$ ppm, $\delta = 32.51$ ppm, $\delta = 39.86$ ppm, $\delta = 46.25$ ppm, $\delta = 54.10$ ppm, $\delta = 113.47$ ppm, $\delta = 115.02$ ppm, $\delta = 117.02$ ppm, $\delta = 121.18$ ppm, $\delta = 129.67$ ppm, $\delta = 136.11$ ppm, $\delta = 140.65$ ppm, $\delta = 152.48$ ppm, $\delta = 183.11$ ppm, and $\delta = 191.19$ ppm.

Solvents were carefully dried and freshly distilled before use. Several solvents such as 1,1,1,3,3,3-hexafluoropropan-2-ol (HFI) and 2,2,2-trifluoroethanol (TFE) (Spectroscopic grade, ACROS) were used without any further purification.

For the UV/Vis measurements, a diode array spectrometer MCS 400 with fibre glass optics connected to a TSM 5 A immersion cuevette (by Carl Zeiss Jena GmbH) was used. The procedure for measuring the UV/Vis spectra of adsorbed dyes on solid acids in nontransparent slurries is reported in ref. 12*c*.

Results and discussion

The UV/Vis absorption maxima of dye **1** measured in 26 solvents and the corresponding empirical polarity parameters α, β, π^*, **SPP**$^\text{N}$, and the well established $E_\text{T}(30)$ are given in Table 1. Fig. 1 shows UV/Vis spectra of **1** measured in five solvents.

The UV/Vis band of the dye **1** shows a shoulder at lower wavelength ($\Delta\lambda = 50$ nm) which overlays with the main band.

The change of line-shape of the UV/Vis spectra with respect to the solvent is not strongly dependent on the solvent nature. Thus, the long wavelength UV/Vis absorption band can be clearly utilized for the solvatochromic property of the dye. Strong Brønsted acids like formic acid and aluminosilicate (see later) cause protonation and a retro-Knoevenagel reaction takes place induced by water traces. Then in the UV/Vis spectrum, a new UV/Vis absorption band at $\lambda_\text{max} = 430$ nm with a shoulder at $\lambda_\text{max} = 600$ nm is observed.

In increasing the solvent's dipolarity/polarizability, the maximum of the UV/Vis absorption band of **1** shifts to higher wavelength. It ranges between $\lambda_\text{max} = 566$ nm (in n-hexane) and $\lambda_\text{max} = 640$ (in dimethylsulfoxide) corresponding to $\Delta\lambda = 74$ nm ($\Delta\nu = 2040\ \text{cm}^{-1}$). Thus, the novel probe molecule can also be used for coloured liquids and materials, respectively, which cover the visible region up to $\lambda = 500$ nm. The specific advantage of the novel dye is that fairly strong HBD solvents TFE and HFI also fit well into the correlation of ν_max with the Kamlet–Taft π^* values [eqn. (2)], with n = number of solvents, sd = standard deviation,

Table 1 UV/Vis absorption maxima of dye **1**, measured in 27 various solvents at room temperature, and the empirical Kamlet–Taft solvent polarity parameters α, β, and π^*, Catalàn's **SPP**$^\text{N}$ (dipolarity/polarizability) as well as Reichardt's $E_\text{T}(30)$ values of these solvents

Solvent	α	β	π^*	**SPP**$^\text{N}$	$E_\text{T}(30)$/ kcal mol^{-1}	$\nu_\text{max} \times 10^{-3}$/ cm^{-1}	λ/nm
n-hexane	0.00	0.00	−0.04	0.519	31.0	17.67	566
cyclohexane	0.00	0.00	0.00	0.557	30.9	17.51	571
triethylamine	0.00	0.71	0.14	0.617	32.1	17.33	577
CCl_4	0.00	0.10	0.28	0.632	32.4	17.21	581
diethyl ether	0.00	0.47	0.27	0.694	34.5	17.12	584
p-xylene	0.00	0.12	0.43	0.617	33.1	17.01	588
toluene	0.00	0.11	0.54	0.655	33.9	16.95	590
benzene	0.00	0.10	0.59	0.667	34.3	16.92	591
THF	0.00	0.55	0.58	0.838	37.4	16.42	609
CH_3COOH	1.12	0.45	0.64	0.781	51.7	16.45	608
CHCl_3	0.20	0.10	0.58	0.786	39.1	16.39	610
anisole	0.00	0.32	0.73	0.823	37.1	16.31	613
CH_2Cl_2	0.00	0.10	0.82	0.876	40.7	16.29	614
acetone	0.08	0.43	0.71	0.881	42.2	16.21	617
DCE[a]	0.00	0.10	0.81	0.890	41.3	16.23	616
ethanol	0.86	0.75	0.54	0.853	51.9	16.18	618
methanol	0.98	0.66	0.6	0.857	55.4	16.15	619
butan-1-ol	0.84	0.84	0.47	0.837	49.7	16.16	619
TFE[b]	1.51	0.00	0.73	0.960	59.8	16.08	622
$\text{Cl}_2\text{CH–CHCl}_2$	0.00	0.00	0.95	0.887	39.4	16.08	622
nitromethane	0.22	0.06	0.85	0.907	46.3	16.05	623
HFI[c]	1.96	0.00	0.65	1.007	62.1	16.00	625
DMF	0.00	0.69	0.88	0.954	43.2	15.82	632
benzyl alcohol	0.60	0.52	0.98	0.886	50.4	15.75	635
ethane-1,2-diol	0.90	0.52	0.92	0.932	56.3	15.75	635
formamide	0.71	0.48	0.97	—	55.8	15.72	636
DMSO	0.00	0.76	1.00	1.000	45.1	15.65	639

[a] 1,2-Dichloroethane. [b] 2,2,2-Trifluoroethanol. [c] 1,1,1,3,3,3-Hexafluoropropan-2-ol.

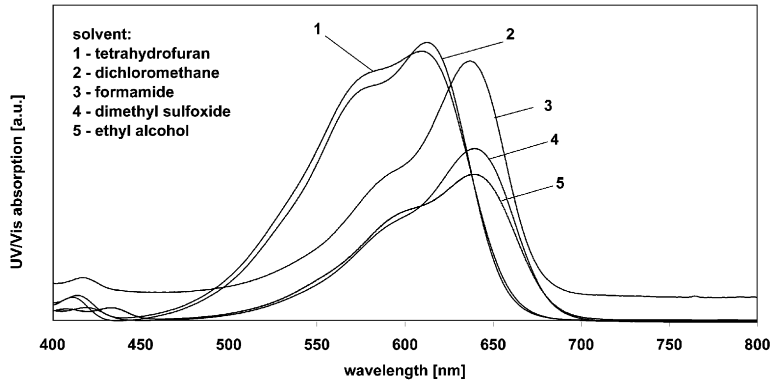

Fig. 1 UV/Vis transmission absorption spectra of **1** in THF, dichloromethane, formamide, ethanol, and DMSO.

F = significance.

$$\nu_{\max}(\mathbf{1})[\mathrm{cm}^{-1}] \times 10^{-2} = 17.5567(\pm 0.1032) - 1.422(\pm 0.1566)\,\pi^*$$
$$n = 27;\ r = 0.92;\ \mathrm{sd} = 0.232;\ F < 0.0001 \qquad (2)$$

Catalàn's **SPP**^{N} values can be directly determined with $\alpha_{\max}(1)$ [eqn. (3)].

$$\mathbf{SPP}^N = 4.6542(\pm 0.225) - 0.234(\pm 0.0137)\nu_{\max}(\mathbf{1})$$
$$n = 26;\ r = 0.961;\ \mathrm{sd} = 0.0393;\ F < 0.0001 \qquad (3)$$

Therefore, **1** is better suited as an indicator for solvent dipolarity/polarizability in strong HBD solvents than 5-(*N*,*N*-dimethylamino)-5′-nitro-2,2′-bisthiophene.[21]

Considering altogether the Kamlet–Taft solvent parameters α, β, and π^*, then an improved multiple correlation is obtained [eqn. (4)] (see Fig. 2):

$$\nu_{\max}(\mathbf{1})[\mathrm{cm}^{-1}] \times 10^{-3} = 17.6830 - 0.2597(\pm 0.0514)\alpha - 0.4063\ (\pm 0.0964)\,\beta - 1.6708(\pm 0.0978)\pi^*$$
$$(s/a = 5.49 \text{ and } s/b = 4.02)$$
$$n = 27;\ r = 0.97;\ \mathrm{sd} = 0.1398;\ F < 0.0001 \qquad (4)$$

The acidity term α plays no significant role upon the solvent induced bathochromic solvatochromic UV/Vis shift of **1**. It contributes only about 13% to the whole extent of the UV/Vis band shift of **1**. The basicity term contributes about 17%. However, we think the latter influence seems not of significant importance when **1** is used as a surface polarity indicator for solid acid catalysts, such as silica, alumina or aluminosilicate, because the value of the basicity term of solid acid catalysts appears to be rather low.

We think that Catalàn's **SPP**^{N} scale is better suited as a dipolarity/polarizability scale than the π^* scale for acidic solvents, because when using the SA values of TFE and HFI[18e] a worsening of the correlation [eqn. (3)] is found ($r = 0.4$).

The well established empirical $E_T(30)$ solvent polarity parameter can be also expressed by an LSE relationship using the Kamlet–Taft solvent parameters α and π^* [eqn. (5)].

$$E_T(30) = 31.2 + 15.2\alpha + 11.5\pi^*\ (a/s = 1.32)$$
$$n = 155;\ r = 0.98;\ \mathrm{sd} = 1.1 \qquad (5)$$

Eqn. (3) demonstrates that the $E_T(30)$ value for solvents contains contributions of the hydrogen bond donating capacity (60%) and dipolarity/polarizability (40%) of the solvents. The correlation of $\nu_{\max}(\mathbf{1})$ with $E_T(30)$ is shown in Fig. 3.

In the range of $30 < E_T(30) < 45$, a linear correlation with $\nu_{\max}(\mathbf{1})$ results [eqn. (6a)].

$$\nu_{\max}(\mathbf{1}) = 20.93091\ (\pm 0.38534) - 0.1151\ (\pm 0.01021)\ E_T(30)$$
$$r = 0.94;\ n = 18;\ \mathrm{sd} = 0.20752;\ F < 0.0001 \qquad (6a)$$

Since the HBD solvents are included, a poor correlation is obtained [eqn. (6b)].

$$\nu_{\max}(\mathbf{1}) = 18.45732\ (\pm 0.34213) - 0.04707\ (\pm 0.00774)\ E_T(30)$$
$$r = 0.77;\ n = 27;\ \mathrm{sd} = 0.376;\ F < 0.0001 \qquad (6b)$$

These results strongly support the suggestion that **1** preferentially responds to the dipolarity/polarizability of HBD

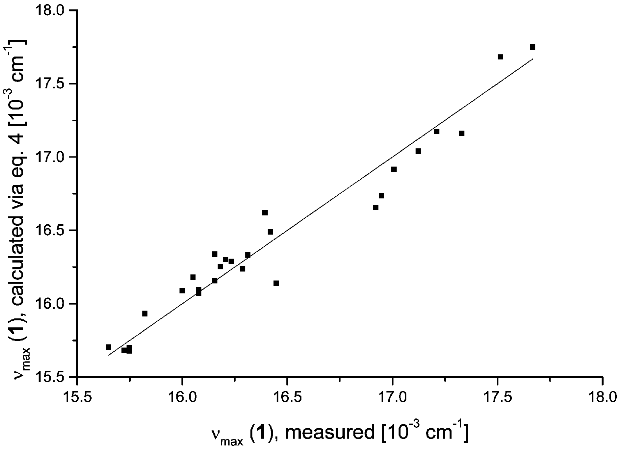

Fig. 2 Measured *versus* calculated $\nu_{\max}(\mathbf{1})$ values for 26 solvents [*via* eqn. (4)].

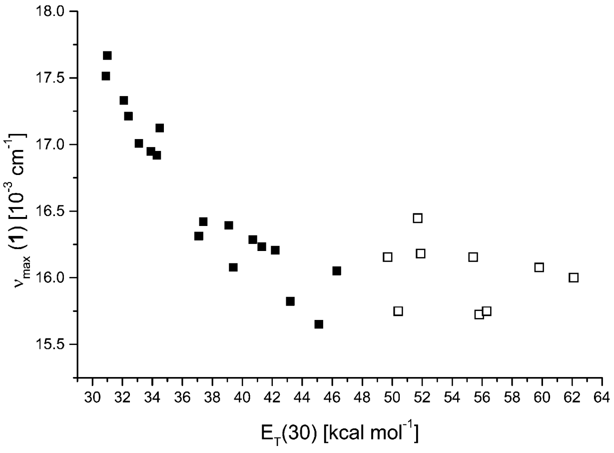

Fig. 3 $\nu_{\max}(\mathbf{1})$ as function of Reichardt's $E_T(30)$ value (■ aprotic solvents, □ protic solvents).

Table 2 UV/Vis absorption maxima of dye **1** when adsorbed on solid acids in dichloromethane. The α and π^* values of the solid acids were taken from refs. 12*d* and 13*g*

Solid/solvent	BET (surface area)/$m^2\ g^{-1}$	Pore diameter/nm	Producer	α	π^*	$\nu_{max} \times 10^{-3}/cm^{-1}$ (calculated)[a]	$\nu_{max} \times 10^{-3}/cm^{-1}$ (measured)	λ/nm
Al_2O_3	160	5.2	Condea	1.36	0.45	16.73/16.58	15.53	644
MCM-41	753	3.6	Mobil oil	0.9	1.10	15.53/15.61	15.70	637
KG 60	423	9.0	Merck	1.13	1.08	15.57/15.59	15.75	635
Siral 40	460	3.5	Condea	1.84	0.43	16.76/16.49	15.53	644

[a] Calculated by [eqn. (2)/eqn. (4)].

solvents and not to the HBD capacity, because it is insensitive in the range of $45 < E_T(30) < 65$ where the solvents vary in α but not in π^*.

The bathochromic UV/Vis band shift of **1** upon increasing the solvent dipolarity/polarizability is caused by the larger dipole moment of the excited state of the molecule. The *tert*-butyl group in the 4-position of the thiazole ring causes a strong twist between the aromatic and heterocyclic moieties which improves the intramolecular charge-transfer (CT) from the *para* 4-(*N*,*N*-dialkylamino) substituted aromatic ring as donor to the dicyanomethylene substituted thiazole ring as acceptor. The strong twisting of the molecule is responsible for the disturbance of charge compensation by directed conjugation. Therefore, the dye exhibits a sufficient solvatochromic UV/Vis band shift also in this section of the visible spectrum where conventional dyes usually show only a weak solvatochromic shift.[1]

When **1** is adsorbed on solid acid catalysts, it shows an unprecedented bathochromic shift, which is even larger when observed in strong dipolar solvents. The shape of the UV/Vis band of **1** adsorbed on silica or alumina is similar to those in dipolar solvents.However, the dipolarity/polarizability terms of silica, alumina, and aluminosilicates seem to be quite similar considering the UV/Vis band shift of **1**. Altogether, their dipolarities are close to the dipolarity of DMSO. When adsorbed on a highly acidic aluminosilicate batch with mobile Brønsted protons on the surface dye **1** becomes chemisorbed as indicated by new UV/Vis adsorption bands at $\lambda = 430$ nm and 460 nm. However, dye **1** is equally unstable to strong acidic and basic media when water traces are present on the surface. Then a reversible Knoevenagel reaction is possible which cannot be completely excluded on aluminosilicate where UV/Vis peaks of decomposition products are observed.[22] The results of sorptiochromism are given in Table 2.

Good agreement between predicted and measured ν_{max} values of **1** for weak solid acids (silicas) has been obtained using [eqns. (2) and (4)] and the α and π^* parameters of the solid acids, determined independently by means of $Fe(phen)_2(CN)_2$ and Michler's ketone as surface polarity indicators.[12c,13f,g] This result shows the reliability of the surface polarity parameters for silicas.[12e,13i] Probably, the order of magnitude of the π^* values, determined in our previous work,[12e] is too low for the strong solid acids alumina and aluminosilicate.

Conclusion

The results of this work have shown that **1** is a suitable solvatochromic probe for observing preferentially the dipolarity/polarizability of acidic environments. Therefore, this type of solvatochromic dye should be recommended as a novel polarity indicator for various environments including solvents as well as surfaces of solid materials.

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