

Use of the SPP Scale for the Analysis of Molecular Systems with Dual Emissions Resulting from the Solvent Polarity

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The solvent polarity/polarizability (SPP) scale is shown to be highly useful for analyzing the solvatochromic behavior of molecular systems emitting dual fluorescence by virtue of the solvent polarity. Stokes' shift data are presented on a test set of seven solutes in 58 solvents correlating with the SPP (single parameter polarity/polarizability index). SPP values for seven further solvents are given, extending the previously available list.

KEY WORDS: Dual emission; charge transfer; solvatochromism; twisted intramolecular charge transfer.

INTRODUCTION

Aromatic bicromophores exhibiting dual fluorescence are of great interest⁽¹⁻⁴⁾ on account of the fact that the extra fluorescence emitted is frequently related to the formation of a highly polar excited structure. Such polar forms usually result from a charge transfer—an electric charge transfer is believed to be involved in such significant naturally occurring processes as vision and photosynthesis. These processes are also of interest with a view to producing laser light, storing solar power, and possible future developments including organic conductors and superconductors.

More than 30 years ago, Lippert *et al.*⁽⁵⁾ showed *p*-*N,N*-dimethylaminobenzonitrile to emit the “normal” fluorescence for closely related benzene derivatives and extra, “anomalous” fluorescence at a lower energy. They ascribed their findings to a solvent-induced reversal of excited states. Since then, the phenomenon has been found to occur in a variety of molecular structures⁽¹⁻⁴⁾ and associated with the solvent involvement in

charge separation processes. In fact, the solvent polarity is believed to facilitate the formation of the more polar form by favoring a twisted intramolecular charge transfer (TICT) mechanism.

The solvatochromism of this type of system was first addressed in the pioneering work of Schneider and Lippert⁽⁶⁾ on 9,9'-bianthryl. Because the two excited forms of these systems must have rather a different dipole moment, their solvatochromism will exhibit a bilinear dependence on the solvent polarity. Schneider and Lippert⁽⁷⁾ showed 9,9'-bianthryl to conform to such hypothesized dependence, even though the segment encompassing the less polar solvents was of zero slope. This is in contradiction with the information subsequently obtained for this system in the gas phase.

Our group⁽⁸⁾ recently developed a single-parameter solvent polarity/polarizability (SPP) scale based on the solvatochromism of 2-(*N,N*-dimethylamino)-7-nitrofluorene and 2-fluoro-7-nitrofluorene that was subsequently extended to 136 solvents and the gas phase.^(8,9) This SPP scale encompasses values between 1 for DMSO and 0 for the gas phase (*i.e.*, the absence of solvent).

In this paper we revisit the solvatochromism of aromatic systems exhibiting dual fluorescence in the light of the new SPP scale. Also, the SPP values for seven new solvents are reported.

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Table I. Wavenumber of the Maximum of the First Absorption Band of the Probe ($\tilde{\nu}_{\text{DMANF}}$) and the Homomorph ($\tilde{\nu}_{\text{FNF}}$): Difference Between $\tilde{\nu}_{\text{DMANF}}$ and $\tilde{\nu}_{\text{FNF}}$ ($\Delta\tilde{\nu}$; cm^{-1}) and Their SPP Values (at 25°C)

Solvent	$\tilde{\nu}_{\text{DMANF}}$	$\tilde{\nu}_{\text{FNF}}$	$\Delta\tilde{\nu}$	SPP
Decalin	24,678	30,586	5,908	0.574
Dibutylamine	24,507	30,535	6,028	0.630
Dimethylcarbonate	24,179	30,377	6,198	0.711
Dibutyl oxalate	23,708	30,169	6,461	0.835
Dibutyl adipate	23,561	30,085	6,524	0.864
4-Methyl-2-pentanone	23,602	30,173	6,571	0.887
Butyronitrile	23,452	30,084	6,632	0.915

This paper demonstrates the usefulness of the SPP scale for analysing solvatochromism, with special emphasis on the ability to include spectroscopic evidence for the gas phase (*i.e.*, the absence of solvent) in the analysis.

EXPERIMENTAL

Absorption spectra were recorded on a Shimadzu 2100 UV-vis spectrophotometer. The monochromator was calibrated with respect to wavelength using the 486.0- and 656.1-nm lines from a deuterium lamp. The Shimadzu spectrophotometer was replaced with a Cary 5 model whenever a cell of 0.005-cm pathlength was required. Both instruments were routinely checked for wavelength accuracy using holmium oxide and didymium filters. All spectral measurements were made at 25°C using a matched pair of quartz cells of 1 cm pathlength. The cell of 0.005-cm pathlength was used for 4-methylpentanone, for which solvent cutoff posed some problems otherwise. The maximum wavelength was below the arithmetic mean of at least eight spectra whose maxima were shifted by less than 0.2 nm. All tabulated wavenumbers given in this work are direct conversions of experimental values.

2-Fluoro-7-nitrofluorene (FNF) was purchased from Aldrich and used as supplied (99% purity). 2-*N,N*-Dimethylamino-7-nitrofluorene (DMANF) was synthesized as described elsewhere.⁽⁸⁾ All the solvents studied (butyronitrile, dimethyl adipate, dibutyl oxalate, dimethyl carbonate, dibutylamine, 4-methylpentanone, and decalin) were obtained from Aldrich at the highest available purity and used as supplied.

RESULTS AND DISCUSSION

The solvatochromism of chromophores is usually assessed via the Stokes shift, *i.e.*, the frequency differ-

ence between the absorption ($\tilde{\nu}_a$) and emission maximum ($\tilde{\nu}_e$) of the chromophore in a given solvent, which can be determined using the expressions derived by Lippert^(5,10) or Mataga *et al.*⁽¹¹⁻¹³⁾ from the theory put forward by Ooshika,⁽¹⁴⁾

$$\tilde{\nu}_a - \tilde{\nu}_f = \frac{2}{hca^3} \left(\frac{\epsilon - 1}{2\epsilon + 2} - \frac{n^2 - 1}{2n^2 + 1} \right) (\mu^* - \mu)^2 + \text{cons}$$

or the more universal relationship derived by Bakhshiev⁽¹⁵⁾ on the basis of the Onsager model:⁽¹⁴⁾

$$\tilde{\nu}_a - \tilde{\nu}_f = \frac{2}{hca^3} \left[\left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) \frac{2n^2 + 1}{n^2 + 2} \right] \left(\mu^2 - \mu^{*2} - 2\mu\mu^* \cos\alpha \right) + \text{cons}$$

In the above equations, h is the Planck constant, c the speed of light, a the Onsager cavity radius, n_D the solvent refractive index, μ the dipole moment of the chromophore in the ground state, and μ^* that in the excited state involved in the transition concerned.

Each chromophore possesses a given μ and μ^* value; hence, its Stokes shift in a series of solvents will fit a polarity-polarizability relation of the type

$$\tilde{\nu}_a - \tilde{\nu}_f = m \times f(\text{polarity/polarizability}) + \text{cons}$$

Therefore, if a different excited state of a higher dipole moment occurs above a given solvent polarity, the solvatochromic behavior of the chromophore will result in a slope change and hence in a bilinear graph.

Let us now revisit the solvatochromic behavior of some particularly significant chromophores (*viz.*, unsubstituted and substituted biaryls) by replacing the $f(\epsilon, n)$ term in the above solvatochromic equation with the corresponding SPP values of the solvents, which were either reported elsewhere^(8,9) or determined in this work (see Table 1).

Table I lists the $\tilde{\nu}_{\text{DMANF}}$ and $\tilde{\nu}_{\text{FNF}}$ values, the difference between both ($\Delta\tilde{\nu}$), and the corresponding SPP value for each solvent tested, calculated from the equation reported in Ref. 8:

$$\text{SPP}_{\text{solv}} = \frac{\Delta\tilde{\nu} - 4692}{2119}$$

Table II lists the experimental data of the chromophores analyzed in this work; the corresponding SPP values, for each of the solvent used, are included.

9,9'-Bianthryl

9,9'-Bianthryl(BA) is no doubt the most thoroughly studied biaryl compound. The dual fluorescence of this

Table II. Experimental Data of the Different Chromophores, Stoke's Shift (cm^{-1}), and Wavenumber of the Fluorescence Maximum (cm^{-1}), Analyzed in the Present Work: The SPP (at 25°C) of the Solvent Employed Are Included

Solvent	SPP ^a	BA ^b	BACOH ^c	C153 ^d	DMAC ^e	C337 ^f	BBPY ^g	TBBP ^h
<i>n</i> -Hexane	0.519	1,540	2,400 (1532)	3,440	7,784	22,222	22,900	19,830
<i>n</i> -Heptane	0.526		2,389 (1584)			21,978		
2,2,4-Trimethylpentane	0.533	1,580	2,456 (1650)					
Cyclohexane	0.557	1,510	2,322 (1517)	3,370	7,569	22,222		
Methylcyclohexane	0.563		2,267 (1571)					
Decalin	0.574	1,540						
<i>n</i> -Hexadecane	0.578		2,322 (1694)					
<i>m</i> -Xylene	0.616		2,397					
<i>p</i> -Xylene	0.617		2,343					
Triethylamine	0.617			3,910				
Dibutyl amine	0.630		2,143					
Carbon tetrachloride	0.632	1,440	2,651 (1752)		8,330			
<i>o</i> -Xylene	0.641		2,451					
Dibutyl ether	0.652	1,670	2,210 (1811)				22,500	19,550
Toluene	0.655		2,451		8,730	21,598		
Benzene	0.667	1,870	2,451		9,046	21,505		
Methyl <i>t</i> -butyl ether	0.687		2,651					
Ethyl ether	0.694	1,780	2,718	4,130			21,900	
1,4-Dioxane	0.701	1,990	2,851		9,992	21,505		
Dimethyl carbonate	0.711		3,180					
Butyl acetate	0.784		2,919	4,640				
Isoamyl acetate	0.752	2,040						
<i>n</i> -Octanol	0.785		2,866					
Methyl acetate	0.785	2,540						
Chloroform	0.786	2,540	2,980		9,525	21,053		
Ethyl acetate	0.795	2,320	3,180			21,053		
<i>n</i> -Pentanol	0.817		3,076					
Chlorobenzene	0.824		2,914					
Bromobenzene	0.824	2,100				21,097		
Isobutanol	0.832	2,550				20,618		
Dibutyl oxalate	0.835		3,734					
<i>n</i> -Chlorobutane	0.837		2,866				21,500	19,400
<i>n</i> -Butanol	0.837		3,076	5,290	9,881			19,300
Tetrahydrofurane	0.838		3,112	4,730	9,920		21,200	19,300
Cyclohexanol	0.847	2,250	3,112					
<i>n</i> -Propanol	0.847		3,024	5,390				19,150
2-Propanol	0.848	2,520	3,283	5,230	9,979			
Ethanol	0.853	3,340	3,536	5,470	9,921	20,408		18,700
Methanol	0.857	3,590	3,881	5,660	10,419	20,325		18,440
Dimethyl adipate	0.864		3,266					
Dichloromethane	0.876	3,020	3,534		9,705	20,920	20,700	
2-Butanone	0.881		3,685					
Acetone	0.881	3,380	3,832	5,130	10,447	20,618		
1,2-Dichloroethane	0.890		3,534					
4-Methyl-2-pentanone	0.997		3,435					
Acetonitrile	0.895	4,040	4,355	5,230	6,216	20,618	19,350	17,900
2,2,2-Trifluoroethanol	0.908			4,930				
1,2-Dichlorobenzene	0.911	2,520						
<i>n</i> -Butyronitrile	0.915						20,300	18,300
Ethylene glycol	0.932	4,080	4,248					
Acetic anhydride	0.920	3,510						

Table II. Continued

Solvent	SPP ^a	BA ^b	BACOH ^c	C153 ^d	DMAC ^e	C337 ^f	BBPY ^g	TBBP ^h
Pyridine	0.922	3,500						
Propylene carbonate	0.930		4,380	5,190				
Glycerol	0.954	4,250						
<i>N,N</i> -Dimethylformamide	0.954		4,015	5,180		20,408		
Water	0.960					20,000		
<i>N,N</i> -Dimethylacetamide	0.970		3,873					
Dimethyl sulfoxide	1.000		4,319	5,230		20,202		

^a SPP values correspond to Refs. 8 and 9, or they have been evaluated in this work.

^b Stoke's shifts of BA are taken from Ref. 6.

^c Stoke's shifts of BACOH are taken from Ref. 22.

^d Stoke's shifts of C153 are taken from Ref. 28.

^e Stoke's shifts of DMAC are taken from Ref. 29.

^f Wavenumbers of the fluorescence maximum of C337 are taken from Ref. 31.

^g Wavenumbers of the fluorescence maximum of BBPY are taken from Ref. 32.

^h Wavenumbers of the fluorescence maximum of TBBP are taken from Ref. 33.

ⁱ The Stoke's shifts in parentheses are evaluated using the first maximum of the fluorescence of BACOH; see Table 1 of Ref. 22.

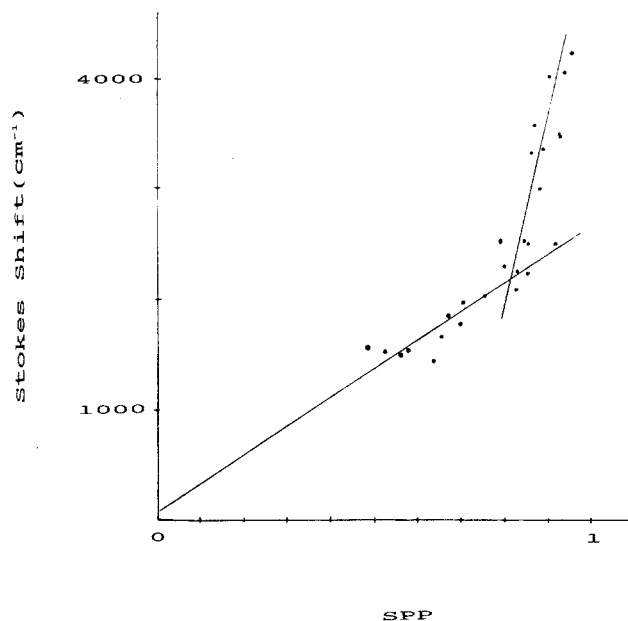


Fig. 1. Graphical plot of Stoke's shift versus SPP values (at 25°C) for 9,9'-bianthracene (BA) dissolved in 28 solvents listed in Table II.

compound was discovered by Schneider and Lippert⁽⁶⁾ in 1968. These authors⁽⁷⁾ demonstrated that the solvatochromism of this compound exhibits a bilinear variation with the solvent polarity and ascribed the fact that the segment corresponding to the less polar solvents had a zero slope to a orthogonal molecular arrangement of the aryl nuclei, both in the ground and in the excited electronic state; for obvious symmetry reasons, the dipole moments for both states must thus be zero.

Figure 1 shows a plot of the measured Stokes shift for the 28 solvents studied in Ref. 7 against their SPP values. As can be seen, the graph is bilinear; however, the segment encompassing the less polar solvents has a nonzero slope, contrary to the prediction of Schneider and Lippert.⁽⁷⁾ Extrapolation of the graph to SPP = 0 (*i.e.*, the gas phase) reveals that the Stokes shift in the gas phase must be close to zero, which also contradicts the results of Schneider and Lippert⁽⁷⁾ (*viz.*, *ca.* 1500 cm⁻¹).

Based on the recently reported laser-induced fluorescence spectra for BA obtained under supersonic jet conditions (*i.e.*, in the gas phase at an absolute temperature of a few degrees Kelvin),⁽¹⁷⁻²¹⁾ the equilibrium geometry in the excited state is not orthogonal but, rather, exhibits a torsional angle of *ca.* 70°, in contrast to the ground state. Also, the Stokes shift for the gas phase can be determined from the information on BA recently obtained by supersonic jet spectroscopy,^(17,19,21) according to which such a shift is zero—this fully confirms our previous hypothesis based on the analysis of Fig. 1.

9,9'-Bianthracene-10-carboxaldehyde

Recently, Acree *et al.*⁽²²⁾ obtained the absorption and fluorescence spectra for 9,9'-bianthracene-10-carboxaldehyde(BACOH) in 45 solvents and plotted the Stokes shift for the 42 solvents whose dielectric constants and refractive indices were known against Lippert's Δf function and the Bilot-Kawski $f(\epsilon, n)$ function,⁽²³⁾ with very small correlation coefficients (0.88 and 0.89, respectively). The plots, shown in Figs. 1 and

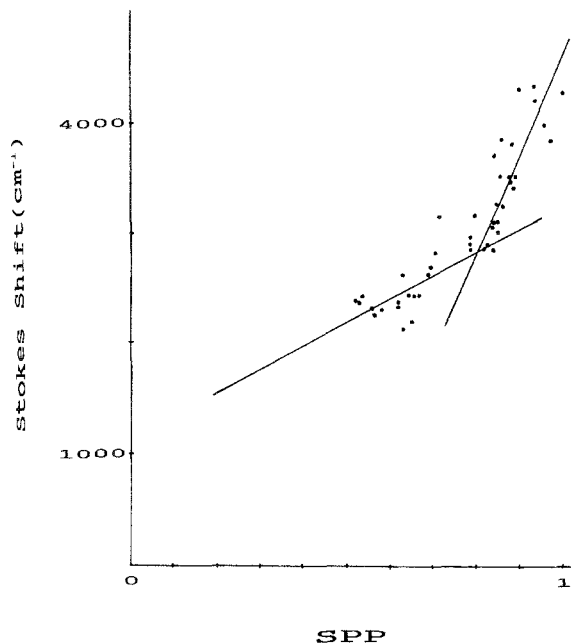


Fig. 2. Graphical plot of Stoke's shift versus SPP values (at 25°C) for 9,9'-bianthracene-10-carboxaldehyde (BACOH) dissolved in 45 solvents listed in Table II.

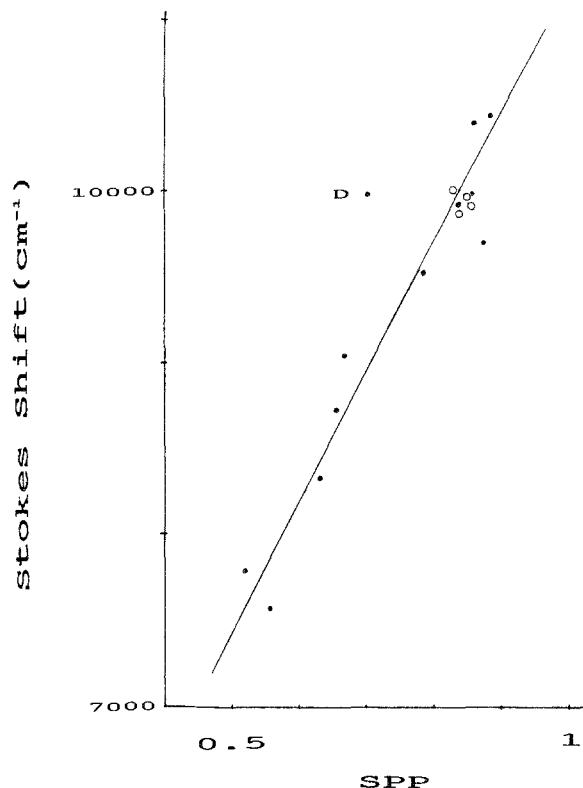


Fig. 4. Graphical plot of Stoke's shift versus SPP values (at 25°C) for 3-*N,N*-(dimethylamino)-2*H*-1-benzopyran-2-one (DMAC) dissolved in 16 solvents listed in Table II. (O) Protic solvents. D, 1,4-dioxane.

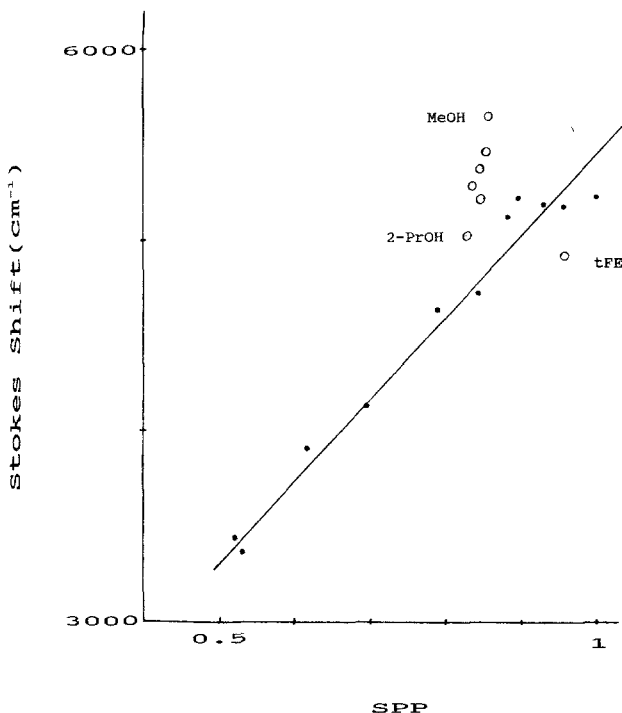


Fig. 3. Graphical plot of Stoke's shift versus SPP values (at 25°C) for coumarin 153 (C153) dissolved in 18 solvents listed in Table II. (O) Protic solvents.

2 of the above reference, are also hardly bilinear, contrary to what one would expect from the behaviour of the parent compound (BA). It is rather surprising that replacing the proton at C₁₀ in BA for an aldehyde group may result in such a disparate behaviour.

Figure 2 shows a plot of the Stokes shifts for the 45 solvents as a function of their SPP values. As expected, the plot is clearly bilinear; the increased scatter may be the result of specific interactions involving the aldehyde group. Surprisingly, extrapolation of the lower polarity segment leads to a gas-phase Stokes shift of *ca.* 1000 cm⁻¹, which is in contradiction with the shift for BA. Because the Stokes shifts for all the solvents were calculated from the emission data given in column 7 in Table I and the less polar solvents exhibit a peak in the blue region of the emission spectra, the calculated shifts may be diminished in *ca.* 1000 cm⁻¹ a similar amount, so the Stokes shift for the gas phase would be negligible.

Coumarin 153

Coumarin 153 is a solvatochromic probe that exhibits a single, low-lying excited state and a straightfor-

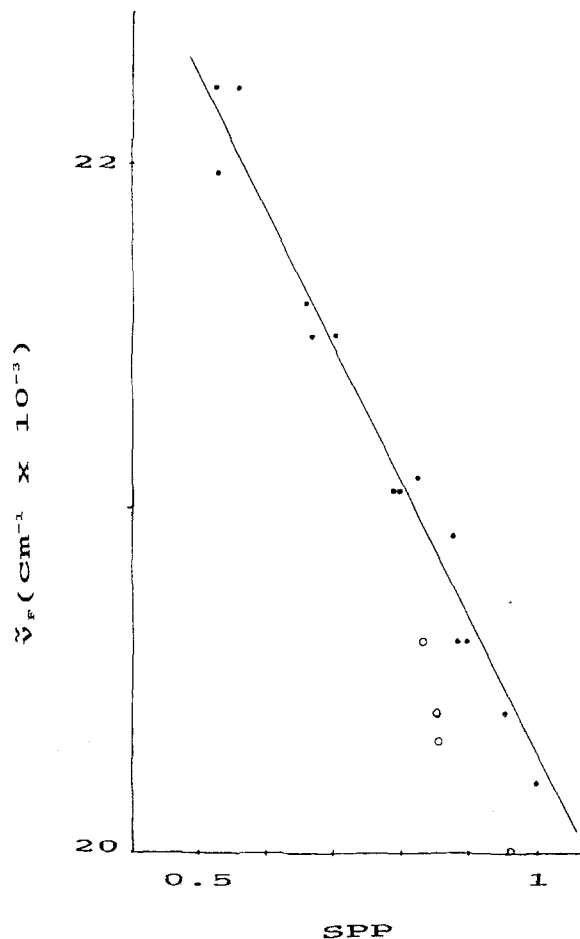


Fig. 5. Graphical plot of wavenumber of the fluorescence maximum versus SPP values (at 25°C) for coumarin 337 (C337) dissolved in 18 solvents listed in Table II. (O) Protic solvents.

ward solvatochromic behavior.⁽²⁴⁻²⁸⁾ Because of its rigid structure, it can take part in no TICT process. Figure 3 shows a plot of the Stokes shifts for this probe, as measured by Maroncelli and Fleming⁽²⁸⁾ in 18 solvents, against their SPP values—that for *N*-methylpropionamide could not be determined owing to its very high cost. As can be seen, the plot is monolinear for the nonprotic solvents; also, the values for the alcoholic solvents are clearly shifted to an extent proportional to their hydrogen bonding acidity. The anomalous behavior of 2,2,2-trifluoroethanol in this respect may be the result of the probe being protonated in such a strongly acidic solvent.

3-(*N,N*-dimethylamino)-2*H*-1-benzopyran-2-one (DMAC)

Gaplovsky *et al.*,⁽²⁹⁾ who analyzed the solvatochromic behavior of this coumarin derivative, found it

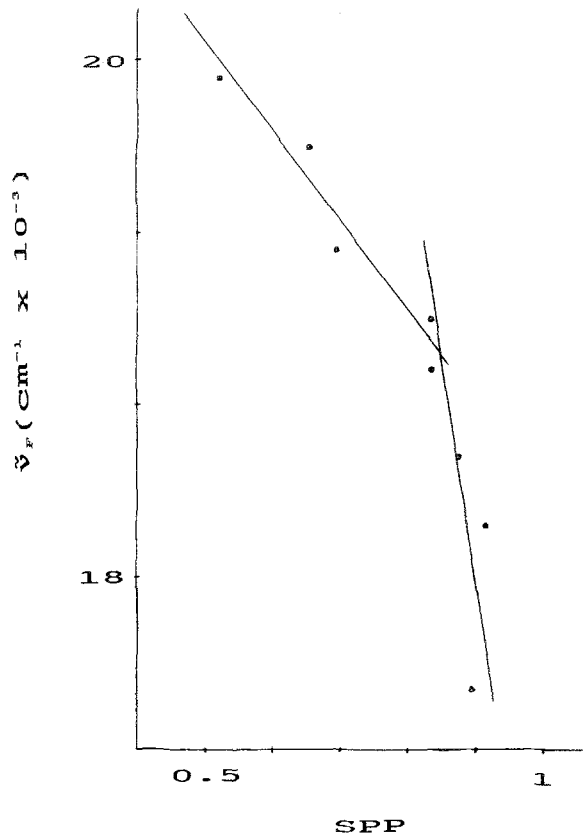


Fig. 6. Graphical plot of wavenumber of the fluorescence maximum versus SPP values (at 25°C) for 5,5'-bibenz-(a)-pyrenyl (BBPY) dissolved in eight solvents listed in Table II.

to exhibit a clearly bilinear behavior toward Et30;⁽³⁰⁾ however, a plot of its Stokes shift relative to Et30 exhibited an anomalously greater slope in the segment corresponding to the less polar solvents. As can be seen from Fig. 4, the variation of the solvatochromism of this probe with the SPP of the solvents studied is clearly monolinear for both protic and nonprotic solvents.

Coumarin 337

Because dual fluorescence originates in the excited electronic state, the above-described bilinear trend is merely a reflection of the solvatochromic behavior of the system emission. Therefore, one need only analyze the emission solvatochromism to determine whether a single or several excited electronic states are involved and whether they differ in terms of polarity in the latter case.

Coumarin 337 possesses a rigid structure, so it can take part in no TICT process—it will therefore exhibit a monolinear trend. Figure 5 shows plot of the fluorescence emission data for this probe in the 18 solvents

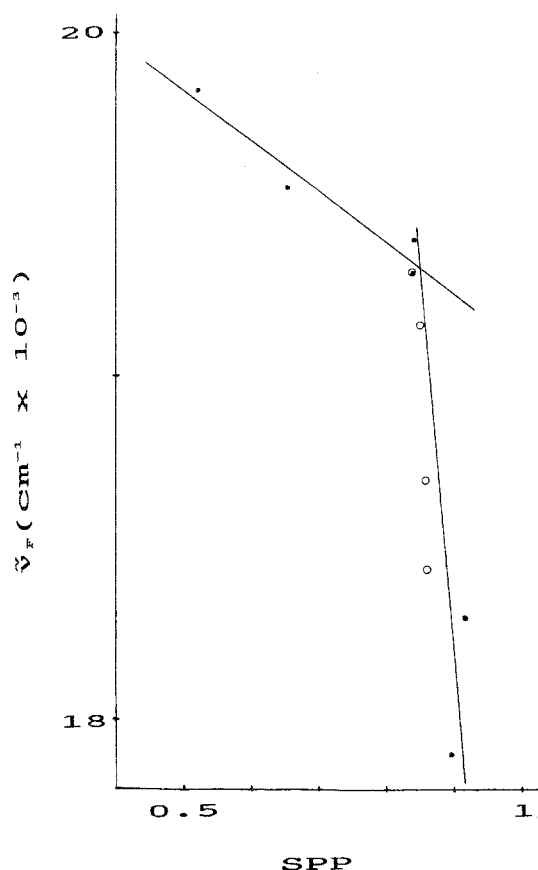


Fig. 7. Graphical plot of wavenumber of the fluorescence maximum versus SPP values (at 25°C) for 3,3'-(8,8',11,11'-tetra-*t*-butyl)biperylenyl (TBBP) dissolved in 10 solvents listed in Table II. (○) Protic solvents.

studied by Abdel-Mottaleb *et al.*⁽³¹⁾ against the SPP value for each solvent. As can be seen, there is very good correlation except for alcoholic solvents, which interact specifically via hydrogen bonding with the coumarin probe.

5,5'-Bibenz-(*a*)-pyrenyl(BBPY)

Zander and Rettig⁽³²⁾ studied charge separation in this biaryl system and, based on the results of an analysis of the temperature-dependence of the fluorescence, they determined the TICT emission values for the system in various solvents including *n*-hexane. Figure 6 shows a plot of the data reported by these authors for eight solvents against their SPP values. The bilinear trend observed clearly shows that the maxima belong to two different electronic states dependent on the solvent polarity, of which that lying in the segment corresponding to the more polar solvents is also the more polar.

3,3'-(8,8',11,11'-Tetra-*t*-butyl)biperylenyl (TBBP)

Recently, Dobkowsky *et al.*⁽³³⁾ studied the behavior of this probe in 10 solvents. As can be seen from a plot of their reported values against the SPP values, the bilinear trend observed is the result of the polarity of the excited electronic state increasing with increase in the solvent polarity.

CONCLUSIONS

As shown above, the SPP scale is a highly useful tool for determining whether the solvent polarity can modify the emitting electronic state of a chromophore in such a way as to alter its dipole moment. The results obtained in this work support the assumption that SPP values are more accurately descriptive of solvent polarity than are the dielectric constant and refractive index functions usually employed for this purpose.

As confirmed by our results, the Stokes shift for bianthryl (BA) in the gas phase is very small. Also, contrary to the expectations, the emission maxima for the ITC band of 5,5'-bibenz-(*a*)-pyrenyl obtained by Zander and Rettig using a spectral deconvolution method exhibit a bilinear trend.

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