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Distinctive Solvent Effect on the Optical Spectra of Polar Molecules and its Relevance to Solvatochromic Scales

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Investigation of five chromophores bearing electron-donating groups in polar and nonpolar solvents revealed a substantial bathochromic shift in their optical spectra, observed already between the nonpolar, nonpolarizable solvent n-hexane and the nonpolar but polarizable solvent toluene. The magnitude of this shift is comparable to that observed between toluene and the highly polar solvent acetonitrile. Analysis based on various solvatochromic scales highlights the importance of both solvent and solute polarizability in the solvation process.

topics: solvatochromism, polar molecules, solvent polarizability

1. Introduction

Polarity and polarizability of the solvent influence the positions of the absorption and emission spectra of chromophores and are the origin of the Stokes shift [1]. Interactions between a solvent and a polar solute are governed primarily by electrostatic forces, including dipole–dipole, dipole–induced dipole, and induced dipole–induced dipole interactions. These solvent–solute electrostatic interactions alter the energies of the solute's electronic states and, consequently, affect the positions of its optical spectra. In the first theoretical model proposed by Ooshika [2] and later refined by Lippert [3], the solvent was treated as a dielectric continuum medium, while the chromophore was approximated as a point dipole. Within this framework, the energy of the solvent–solute interaction was related to the difference between the wavenumbers of the absorption and fluorescence spectra maxima, ϑ_{abs} and ϑ_{flu}, respectively, according to the following relation

$$\vartheta_{\mathrm{abs}}-\vartheta_{\mathrm{flu}}=\frac{2\Delta\mu^2}{hca^3}\left(\frac{\varepsilon-1}{2\varepsilon+1}+\frac{n^2-1}{2n^2+1}\right)+\text{const.} \tag{1}$$

where $\Delta\mu^2=(\mu_{\mathrm{e}}-\mu_{\mathrm{g}})^2$ denotes the difference between the dipole moments of the excited, μ_{e} and ground, μ_{g}, states; a is the cavity radius of the solute, ε and n are the dielectric constant and the refractive index of the solvent, respectively. Bakhishiev [4] developed a more complex solvatochromic scale, which accounts for not only the difference in the magnitude of the ground and excited state dipole moments, but also the change in direction. In such approach, the Stokes shift formula is expressed as follows

$$\vartheta_{\mathrm{abs}}-\vartheta_{\mathrm{flu}}=\frac{2\Delta\mu^2}{hca^3}\left(\frac{\varepsilon-1}{2\varepsilon+1}+\frac{n^2-1}{2n^2+1}\right)\frac{2n^2+1}{n^2+2}+\text{const.} \tag{2}$$

In both models, the solvent was considered polarizable, whereas the solute was not. Chamma and Viallet [5] extended the theory to include the case of a polar and polarizable solute, as well as a polarizable solvent, resulting in a more complex expression

$$\frac{\vartheta_{\mathrm{abs}}+\vartheta_{\mathrm{flu}}}{2}=\frac{(\mu_{\mathrm{e}}^2-\mu_{\mathrm{g}}^2)}{hca^3}\left[\left(\frac{\varepsilon-1}{2\varepsilon+1}+\frac{n^2-1}{2n^2+1}\right)\frac{2n^2+1}{n^2+2}+\frac{3(n^4-1)}{2(n^2+2)^2}\right]+\text{const.} \tag{3}$$

All of the above equations predict that for polar molecules with $\mu_{\mathrm{e}}>\mu_{\mathrm{g}}$, the solvatochromic shift increases in polar solvents. This phenomenon is well known, and both (1) and the Lippert–Mataga plot presenting the Stokes shift versus solvent polarity parameter f are commonly employed to estimate the change in the dipole moment of a chromophore upon electronic excitation [1, 3, 6–8]. It should be noted that other solvation mechanisms — such as hydrogen-bond formation between solute and solvent or dispersion [9] and other effects [10] — are referred to as specific solvent interactions and require the use of phenomenological scales, such as the single empirical parameter $E_{\mathrm{T}}(30)$ [11] or the multiparameter Kamlet–Taft correlation equation [12],

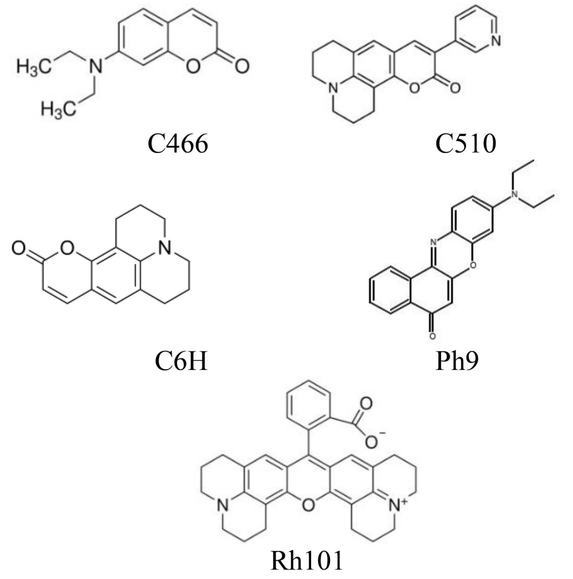

Fig. 1. Molecular structures of the compounds.

TABLE I

Parameters of the solvents used: dipole moment μ [Debyes], dielectric constant ε, refractive index n [15], and polarity parameter $f=\frac{\varepsilon-1}{2\varepsilon+1}-\frac{n^2-1}{2n^2+1}$.

Solvent	μ [Debyes]	ε	n	f
n-hexane	0	1.89	1.375	-8.2×10^{-5}
Toluene	0.36	2.379	1.497	0.013115
EtAc	1.88	6.02	1.372	0.19978
Acetone	2.85	20.7	1.3587	0.284307
ACN	3.45	37.5	1.344	0.306107

which are based on extensive measurements of the optical spectra of numerous molecules in a wide range of solvents [13].

In this work, we report an unexpected solvatochromic behavior observed for four polar dyes in five solvents, characterized by a substantial spectral shift occurring already between the nonpolar, nonpolarizable n-hexane and the nonpolar but polarizable toluene. The magnitude of this red shift is comparable to that observed between toluene and the highly polar acetonitrile. Our experimental study provides an explanation for this phenomenon and highlights the role of both solvent polarizability and the polarizability of the excited electronic state of the solute molecules.

2. Experimental methods

To restrict solvent–solute interactions solely to electrostatic forces and to exclude the solvent-specific effects such as hydrogen bonding or other factors like solvent viscosity, the selection of solvents in this study was limited to five: n-hexane, toluene, ethyl acetate (EtAc), acetone, and acetonitrile (ACN). All solvents were of spectroscopic grade. The properties of these solvents relevant to the present study are summarized in Table I (see also [15]). For the preliminary investigation, five commercially available dyes were selected: Coumarin 466 (C466), Coumarin 510 (C510), Coumarin 6H (C6H), Phenoxazone 9 (Ph9), and Rhodamine 101 (Rh101). The molecular structures of these compounds are shown in Fig. 1.

Absorption spectra were recorded using a Lambda 35 spectrophotometer (PerkinElmer). Fluorescence spectra were measured with an FLS1000 spectrofluorimeter (Edinburgh Instruments) and converted from wavelength to energy representation using the Jacobian transformation [14]. The Origin software package of OriginLab Corporation was employed for plotting and linear regression analysis of the solvatochromic shift data sets.

3. Results and discussion

All spectra are presented in Fig. 2, and the corresponding spectral parameters, i.e, the positions of the intensity maxima and Stokes shift values, are summarized in Table II, expressed in wavenumbers. A pronounced bathochromic shift is evident for emission spectra and, although to somewhat less extent, for absorption spectra of the polar compounds C466, C510, C6H, and Ph9, all of which contain electron-donating groups. However, a very little effect is observed for Rh101, in which two electron-donating groups are symmetrically substituted.

The Stokes shift, commonly regarded as a measure of solvatochromism, increases markedly from n-hexane to acetonitrile for the polar dyes. Interestingly, a substantial red shift is already observed between spectra recorded in the nonpolar, nonpolarizable n-hexane and the nonpolar but polarizable toluene. For instance, in the case of C466, the maximum of the fluorescence spectrum shifts by 1507 cm^{-1} between n-hexane and toluene, while the shift between toluene and acetonitrile amounts to 1438 cm^{-1} (Fig. 2, Table II). Likewise, the maximum of the 0–0 transition band exhibits a significant red shift of 1712 cm^{-1} between n-hexane and toluene, a value considerably larger than the shift observed between toluene and polar solvents. Similar behavior is found for the other polar chromophores investigated. A bathochromic shift, although smaller, is also observed in the absorption spectra, and a large change in spectral position between n-hexane and toluene is clearly visible (Fig. 2).

These observations are all the more remarkable because the solvatochromic models discussed above predict only minor spectral shifts in nonpolar solvents. Therefore, a more detailed investigation

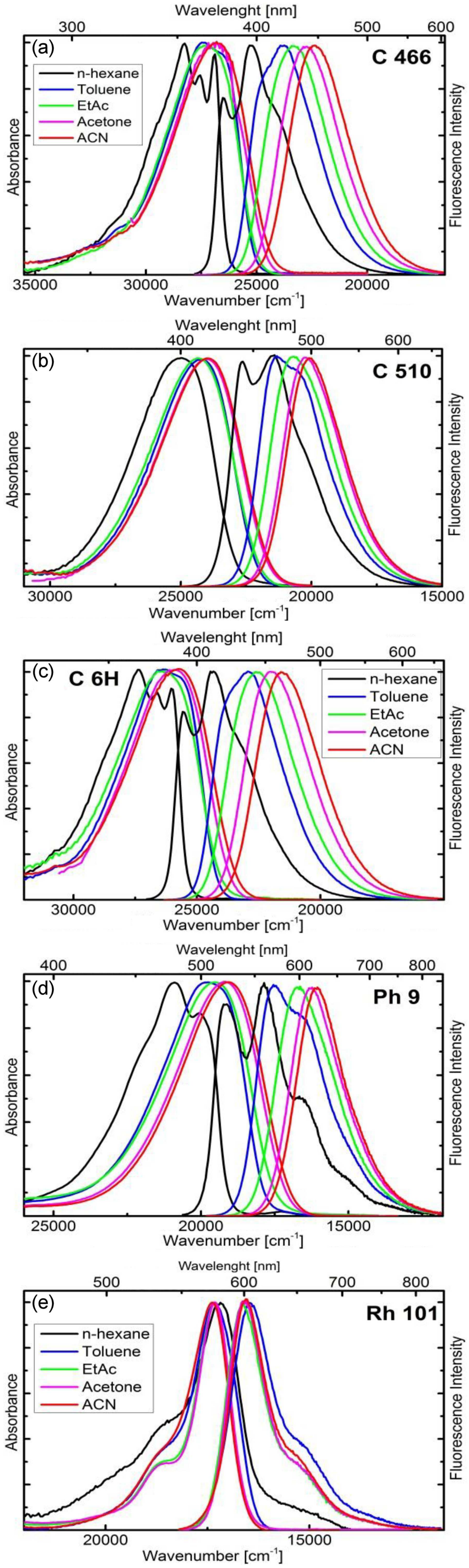

Fig. 2. Absorption and fluorescence spectra of (a–e) the compounds in solvents. Legend specifies solvents.

TABLE II

Wavenumbers of the absorption spectrum maximum ϑ_{abs}, fluorescence spectrum maximum ϑ_{flu}, and Stokes shift SS of polar molecules in solvents.

Molecule	Solvents	ϑ_{abs}	ϑ_{flu}	SS
C466	n-hexane	28248.6	25316.4	2932.2
C466	toluene	27472.5	23809.5	3663.0
C466	EtAc	27248.0	23419.2	3828.8
C466	acetone	26881.7	22779.0	4102.7
C466	ACN	26809.6	22371.4	4438.2
C510	n-hexane	25000.0	21413.3	3586.7
C510	toluene	24271.8	21322.0	2949.8
C510	EtAc	24330.9	20661.2	3669.7
C510	acetone	24038.5	20242.9	3795.6
C510	ACN	23980.0	20080.3	3899.7
C6H	n-hexane	27397.2	24390.2	3007.0
C6H	toluene	26385.2	22935.8	3449.4
C6H	EtAc	26315.8	22573.4	3742.4
C6H	acetone	25906.7	21978.0	3928.7
C6H	ACN	25773.2	21551.7	4221.5
Ph 9	n-hexane	20876.8	17857.1	3019.7
Ph 9	toluene	19762.8	17543.8	2219.0
Ph 9	EtAc	19493.2	16694.5	2798.7
Ph 9	acetone	19157.1	16286.6	2870.5
Ph 9	ACN	19047.6	16051.0	2996.6

was undertaken to evaluate the applicability of these theoretical models to the experimental results obtained for the studied chromophores.

The Lippert–Mataga plot of the Stokes shift, defined as the difference between the positions of the absorption and fluorescence intensity maxima, $\vartheta_{\mathrm{abs}} - \vartheta_{\mathrm{flu}}$, shown as a function of the solvent polarity parameter f (as defined in Table I and (1)), reveals considerable scatter in the experimental data (Fig. 3). According to the International Union of Pure and Applied Chemistry (IUPAC) definition, the Stokes shift is "the difference between the spectral positions of the band maxima (or the band origin) of the absorption and luminescence" [16].

For the four compounds studied, the difference between the wavenumber of the 0–0 transition, ϑ^{0-0}, and that of the intensity maximum, $\vartheta^{\max}$, is substantial; for example, in the case of C466 in n-hexane, these values differ by 1367 cm^{-1} for absorption and 1209 cm^{-1} for fluorescence. Both definitions of the Stokes shift are illustrated in Fig. 3, with the data sets corresponding to the band origin labeled with the '0–0' index in the legend. However, both data sets exhibit noticeable scatter.

To assess whether alternative solvatochromic scales provide a better correlation, the Stokes shift was also plotted as a function of Bakhshiev's solvent polarity function, $F_{\mathrm{B}} = f\,(2n^2{+}1)/(n^2{+}2)$,

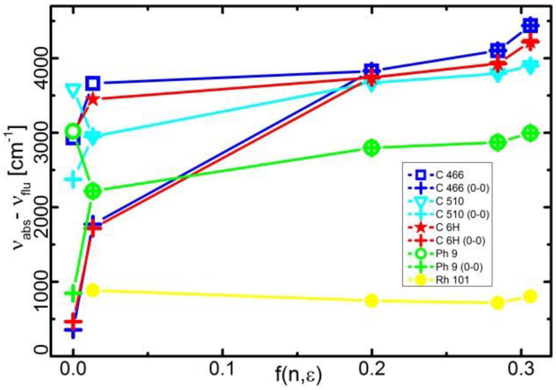

Fig. 3. Lippert–Mataga plot for compounds in solvents. Data points are connected with lines to make differences evident.

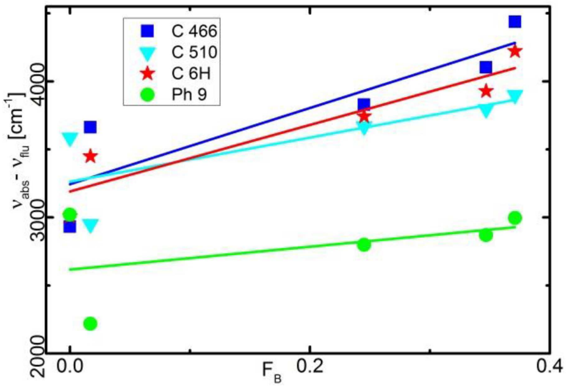

Fig. 4. Plot of Stokes shift versus Bakhishiev's solvent polarity function F_{B} for compounds in solvents (symbols) and straight lines are the best fit to data.

as defined in (2), and the mean wavenumber $(\vartheta_{abs}+\vartheta_{\mathrm{flu}})/2$ was plotted as a function of the Chamma–Viallet function, $F_{\mathrm{CV}} = F_{\mathrm{B}} + 3(n^4-1)/[2(n^2+2)^2]$, as defined in (3). These relationships are presented in Figs. 4 and 5, respectively.

Comparison of Figs. 3, 4, and 5 reveals that the scatter of data points is smallest in Fig. 5. This observation is supported by the results summarized in Table III, which lists the correlation coefficients (R values) representing the quality of the linear regression fits applied to the solvatochromic data sets. Clearly, the quality of the fit improves progressively from f to the F_{B} correlation and subsequently to the F_{CV} correlation, indicating that, in the description of solvation for polar chromophores, it is essential to account for the polarizability of the solute. Furthermore, the fits are noticeably better when the IUPAC definition of the Stokes shift is used (datasets labeled with the superscript 'b' for n-hexane and toluene) compared to the simpler definition based on the difference between the positions of the absorption and fluorescence maxima (datasets labeled with the superscript 'a').

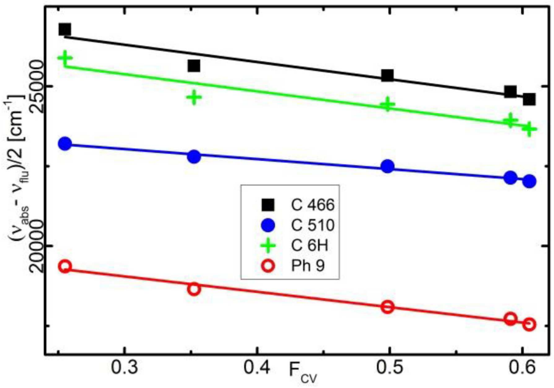

Fig. 5. Plot of mean of absorption and fluorescence wavenumbers versus Chamma–Viallet's solvent polarity function F_{CV} for compounds in solvents (symbols) including regression lines.

TABLE III

The R values obtained from linear regression of the Stokes shift scale or mean wavenumber to the Lippert f, Bakhishev F_{B}, and Chamma-Viallet F_{CV} function. The upper indexes 'a' and 'b' refer to data based on the difference between the maxima and the 0-0 transitions of the spectra, respectively.

Dye	f^a	f^b	$F_{\mathrm{B}}^{\mathrm{a}}$	$F_{\mathrm{B}}^{\mathrm{b}}$	$F_{\mathrm{CV}}^{\mathrm{a}}$	$F_{\mathrm{CV}}^{\mathrm{b}}$
C466	0.705	0.881	0.704	0.885	0.899	0.907
C510	0.465	0.867	0.463	0.871	0.977	0.977
C6H	0.83	0.882	0.829	0.885	0.864	0.918
Ph9	0.21	0.606	0.256	0.61	0.987	0.948

The effect of solvent polarity on the positions of absorption and fluorescence spectra was also considered by Kawski, who incorporated the mean isotropic polarizability, α, of the solute into his model [17–23]. Two equations were derived, one describing the Stokes shift and the other the average spectral position (absorption and emission maxima mean wavenumber) given respectively as

$$\vartheta_{\mathrm{abs}} - \vartheta_{\mathrm{flu}} = \frac{2\Delta\mu^2}{hca^3}\, f_{\mathrm{K}}(\varepsilon,n) + \mathrm{const.} \tag{4}$$

and

$$\frac{\vartheta_{\mathrm{abs}}+\vartheta_{\mathrm{flu}}}{2} = \frac{2(\mu_{\mathrm{e}}^2-\mu_{\mathrm{g}}^2)}{hca^3}\,[f_{\mathrm{K}}(\varepsilon,n)+g_{\mathrm{K}}(n)] + \mathrm{const.} \tag{5}$$

where Kawski's polarity parameters $f_{\mathrm{K}}(\varepsilon,n)$ and $g_{\mathrm{K}}(n)$ for spherical cavity with Onsager radius a are

$$f_{\mathrm{K}}(\varepsilon,n) = \frac{\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}}{\left(1 - \frac{2\alpha}{a^3}\frac{\varepsilon^2-1}{2\varepsilon^2+1}\right)\left(1 - \frac{2\alpha}{a^3}\frac{n^2-1}{2n^2+1}\right)^2} \tag{6}$$

and

$$g_{\mathrm{K}}(n) = \frac{\frac{n^2-1}{2n^2+1}\left[1 - \frac{\alpha}{a^3}\frac{n^2-1}{2n^2+1}\right]}{\left(1 - \frac{2\alpha}{a^3}\frac{n^2-1}{2n^2+1}\right)^2}. \tag{7}$$

For the isotropic polarizability of the solute, it is often assumed the condition $2\alpha/a^3 = 1$ [17]. However, in general, the polarizability α can be varied to construct a series of solute-specific polarity functions, allowing one to determine which value of α provides the best correlation with experimental data. In this work, the polarity functions $f_{\mathrm{K}}(\varepsilon, n)$ and $g_{\mathrm{K}}(n)$ were calculated for the five solvents used, considering several values of the $2\alpha/a^3$ parameter $(0, 0.5, 1.0, 1.5,$ and $2.0)$. These functions were then applied to the dye C466. Linear regression of the mean wavenumber of the 0–0 transition data set onto (5) yielded different adjusted values of R^2 corresponding to the parameters listed above: 0.906, 0.920, 0.891, 0.826, and 0.529, respectively. Although none of the regressions yielded fully satisfactory correlations, it is evident that values of $2\alpha/a^3 > 1$ are not statistically reasonable. Therefore, C466 does not appear to be highly polarizable, although the inclusion of the polarizability term may help to account for the pronounced spectral shift observed in toluene.

In this preliminary study, only five solvents were used, so the statistical significance of the conclusions remains limited. To improve the robustness of the analysis, a larger set of solvents should be investigated. Another constraint arises from the assumption of a spherical Onsager cavity and the treatment of the polar molecule as a point dipole. The cavity shape can be generalized to an ellipsoid, albeit at the cost of increased mathematical complexity and the need to determine the principal axes' lengths [24]. The additional assumption of alignment between the ground-state dipole moment and the transition moment is likely valid for C466, C510, C6H, and Ph9, as these dyes can be regarded as typical push–pull chromophores. Consequently, the selected compounds represent suitable candidates for further investigations on the role of molecular polarizability in solvatochromism and in solvent–solute electrostatic interactions.

4. Conclusions

The absorption and fluorescence spectra of four polar chromophores exhibit an unexpectable and pronounced spectral shift between the nonpolar, nonpolarizable n-hexane and the nonpolar but polarizable toluene. The shift is comparable in magnitude to the bathochromic shift observed between toluene and the highly polar acetonitrile, suggesting that highly dipolar dyes effectively polarize toluene and induce a reaction field that substantially lowers the energy of the first excited singlet state. This is a surprising effect, as models of solvatochromism predict a small shift for non-polar solvents.

Analysis of the spectral data using different models of the solvent polarity functions (see (1)–(5)) indicates that solute polarizability may also contribute to the unusually large solvatochromic shift observed in toluene, emphasizing the possible role of induced dipole–induced dipole interactions between solvent and solute molecules. However, a reliable quantitative evaluation of this phenomenon requires extending the study to a broader range of solvents to improve the statistical significance of the results. Then, the mechanism and specific factors responsible for this unexpected effect could be discussed in detail. This preliminary study is intended to announce and present the phenomenon of a large red shift in non-polar solvents.

References

[1] J.R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, New York (NY) 2006.

[2] Y. Ooshika, *J. Phys. Soc. Jpn.* **9**, 594 (1954).

[3] E. Lippert, *Z. Elektrochem.* **61**, 962 (1957).

[4] N.G. Bakshiev, *Opt. Spektosk. (USSR)* **16**, 821 (1964).

[5] A. Chamma, P.C.R. Viallet, *Acad. Sci. Paris C* **270**, 1901 (1970).

[6] N. Mataga, Y. Kaifu, M. Koizumi, *Bull. Chem. Soc. Jpn.* **29**, 465 (1956).

[7] G.V. Loukova, V.P. Vasiliev, A.A. Milov, V.A. Smirnov, V.I. Minkin, *J. Photochem. Photobiol. A* **327**, 6, (2016).

[8] C. Peebles, C.D. Wight, B.L. Iverson, *J. Mater. Chem. C* **3**, 12156 (2015).

[9] Š. Budzaák, A.D. Laurent, C. Laurence, M. Medved, D. Jacquemin, *J. Chem. Theory Comput.* **12**, 1919 (2016).

[10] S.-J. Kim, S. Lebègue, S. Ringe, H. Kim, *J. Phys. Chem. Lett.* **15**, 4575 (2024).

[11] C. Reichardt, *Angew. Chem. Int. Ed. Engl.* **18**, 98 (1979).

[12] M.J. Kamlet, R.W. Taft, *J. Am. Chem. Soc.* **98**, 377 (1976).

[13] J. Rouillon, C. Benitez-Martin, M. Grøtli, J. Andréasson, *Phys. Chem. Chem. Phys.* **27**, 4679 (2025).

[14] J. Mooney, P. Kambhampati, *J. Phys. Chem. Lett.* **4**, 3316 (2013).

[15] Dielectric Constant of Common Solvents, University of Washington Homepage, 2007.

[16] J.W. Verhoeven, *Pure Appl. Chem.* **68**, 2223 (1996).

[17] L. Bilot, A. Kawski, *Z. Naturforsch. A* **17**, 621 (1962).

[18] L. Bilot, A. Kawski, *Z. Naturforsch. A* **18**, 256 (1963).

[19] A. Kawski, *Acta Phys. Pol.* **29**, 507 (1966) (in German).

[20] A. Kawski, *Z. Naturforsch. A* **57**, 255 (2002).

[21] A. Kawski, *Progress in Photochemistry and Photophysics*, Vol. 5, Ed. J.F. Rabek, CRC Press, Boca Raton 1992.

[22] B. Shivaleela, G.G. Shivraj, S.M. Hanagodimath, *Results Chem.* **6**, 101046, (2023).

[23] N.E. Guesmi, *J. Fluorsc.* **33**, 2315 (2023).

[24] C.I.F. Böttcher, *Theory of Electric Polarization*, Elsevier, Amsterdam 1952.