



# A semi-empirical estimation of ground and excited state dipole moments of zinc phthalocyanine from solvatochromic shift data

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## Abstract

A semi-empirical determination of ground and excited state dipole moments of zinc phthalocyanine (ZnPc) from solvatochromic shifts is hereby presented. The ratio of the excited- and ground-state dipole moments of ZnPc ( $\frac{\mu_e}{\mu_g}$ ) was estimated by a combination of the Bakshiev and the Kawski-Chamma-Viallet's equations, while the difference in the excited- and ground-state dipole moments ( $\Delta\mu$ ) was estimated using the molecular-microscopic solvent polarity parameters ( $E_{\text{N}}^{\text{N}}$ ), alongside the Stokes' shifts ( $\Delta\nu$ ) in the various solvents. The dipole moment of ZnPc is significantly higher in the excited singlet state ( $\mu_e = 3.12$  D) than in the ground state ( $\mu_g = 1.50$  D). Obviously charge separation is greater in the excited state of ZnPc than in its ground state.

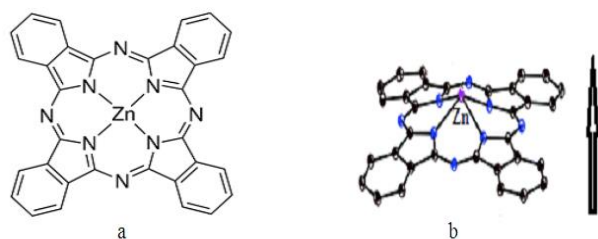
**Keywords:** Dipole Moment; Excited State; Ground State; Solvatochromism; Zinc Phthalocyanine.

## 1. Introduction

Phthalocyanine (Pc) is an organic macrocycle that is capable of forming stable complexes with several metals that have extensively found use as blue and green dyes and pigments. Pcs have been utilized in important functional materials in many fields. Apart from their traditional industrial applications, Pcs and their metalated derivatives (metallophthalocyanines, MPcs) have been utilized in many fields such as molecular electronics, optoelectronics, photonics, etc (Kadish et al. 2003, Sakamoto et al. 2004, de la Torre et al. 2004, Cid et al. 2007, Campidelli et al. 2008, Pinzon et al. 2008). The functions of MPcs are almost universally based on electron transfer reactions because of the 18 electron conjugated ring system found in their molecular structure.

MPcs present very interesting electronic properties, and are also very photoactive; this has necessitated investigations into their photophysical and photochemical properties (Ogunsipe et al. 2003, Ogunsipe and Nyokong 2005, Ogunsipe and Nyokong 2011). Most MPc molecules are non-polar because they belong to the  $D_{4h}$  point group; hence there are symmetry operations that take one end of the molecule into the other. Therefore, such molecules will have no dipole along or perpendicular to the symmetry axis. However, features like molecular distortion and ring substitution can induce polarity unto a hitherto non-polar MPc molecule (Kobayashi et al. 1971, Mack and Stillmann 1994). Knowledge of dipole moments is valuable in providing information about the change in the electronic charge distribution upon excitation, assessing parameters like polarizability in non-linear optical materials, understanding the nature of the emitting state, and also in the evaluation of the dielectric friction contribution to the rotational reorientation of polar solutes in solvents (Chandrasekhar et al. 2006).

Many procedures are available for the measurement of ground state dipole moment of a chemical system (Higasi 1953, Aaron et al. 1991); however, there is dearth of techniques for the estimation of the excited state dipole moment. The few available methods for accurate measurement of excited state dipole moment include electro-optical methods like electrochromism of absorption and fluorescent bands (Czekalla 1960), Stark splitting of rotational levels of the 0-0 vibrational bands and the effect of an external electric field on fluorescence anisotropy (Liptay 1974, Bawmann 1989). Nevertheless, these methods are not easily accessible because they involve the use of sophisticated equipment; and also because they might not be applicable to Pcs, MPcs and other large molecules. A convenient method for the estimation of ground and excited state dipole moments is based on the analysis of the solvatochromism of absorption and fluorescence data. This method is easily accessible as it involves only the measurement of absorption and fluorescence maxima, and has been used extensively (Nadaf et al. 2004, Husain et al. 2012). The solvatochromic method is based on a linear correlation between the wave numbers of the absorption and fluorescence maxima and a solvent polarity function which involves both dielectric constant ( $\epsilon$ ) and refractive index ( $n$ ) of the medium. The determination of ground and excited state dipole moments of fluorescent organic compounds is well documented (Nadaf et al. 2004, Kabatc et al. 2006, Husain et al. 2012), but there are no reports available in literature on the ground and excited state dipole moments of metallophthalocyanines. This work presents an estimation of the ground and excited state dipole moments of zinc phthalocyanine (ZnPc, Fig. 1) using the semi-empirical solvatochromic shift method.



**Fig. 1:** (A) Structure of ZnPc; (B) Structure Showing the Protrusion of Zn Out of the Plane of the Aromatic Ring.

## 2. Materials and methods

### 2.1. Materials

Zinc phthalocyanine (ZnPc) synthesized according to literature procedure (Tomoda et al. 1983). Solvents - trimethylamine, n-butylamine, tetrahydrofuran (THF), dichloromethane (DCM), N,N'-dimethylformamide (DMF), chloroform, dimethylsulphoxide (DMSO), toluene, and benzene were obtained from SAAR-CHEM; while pyridine, benzonitrile and 1-chlorophthalene were obtained from FLUKA.

### 2.2. Equipment

UV-visible spectra were recorded on a Shimadzu 2550 UV-Vis spectrophotometer. Fluorescence emission spectra were recorded on a Varian Eclipse spectrofluorometer.

### 2.3. Method

#### 2.3.1. Semi-empirical determination of dipole moment

Ground- and excited-state dipole moments of ZnPc are determined via a quantitative assessment of solute-solvent interactions (involving the use of solvent-induced spectral shifts, solvent polarity functions and the molecular-microscopic solvent polarity parameter).

The ratio of the excited- and ground-state dipole moments of ZnPc ( $\frac{\mu_e}{\mu_g}$ ) was determined by combining the Bakshiev (Bakshiev 1964) and the Kawski-Chamma-Viallet's (Kawski 1966, Chamma and Viallet 1970) equations. On the other hand, the use of the molecular-microscopic solvent polarity parameter yielded the term  $\mu_e - \mu_g$ . For polar fluorophores, charge separation is greater in the excited state; therefore,  $\mu_e$  is expected to be greater in magnitude than  $\mu_g$ .

#### 2.3.2. Bakshiev and kawski-chamma-viallet polarity functions

Bakshiev and Kawski-Chamma-Viallet equations were obtained from a simple quantum-mechanical second-order perturbation theory. Cognizance was also taken of the Onsager's model.

$$\bar{\nu}_a - \bar{\nu}_f = m_1 F_1(\epsilon, n) + k_1 \quad (\text{Bakshiev's equation}) \quad (1)$$

$$\frac{\bar{\nu}_a + \bar{\nu}_f}{2} = m_2 F_2(\epsilon, n) + k_2 \quad (\text{Kawski-Chamma-Viallet's equation}) \quad (2)$$

$\bar{\nu}_a$  and  $\bar{\nu}_f$  are absorption and fluorescence maximum wavenumbers ( $\text{cm}^{-1}$ ), respectively;  $\epsilon$  and  $n$  are the solvent's dielectric constant and refractive index, respectively;  $k_1$  and  $k_2$  are constants. The expressions  $F_1(\epsilon, n)$  and  $F_2(\epsilon, n)$  are defined as:

$$F_1(\epsilon, n) = \frac{\epsilon-1}{\epsilon+2} \frac{n^2-1}{n^2+2} \left[ \frac{2n^2+1}{n^2+2} \right] \quad (\text{Bakshiev's polarity function}) \quad (3)$$

$$F_2(\epsilon, n) = \frac{2n^2+1}{2(n^2+2)} \left[ \frac{\epsilon-1}{\epsilon+2} \frac{n^2-1}{n^2+2} \right] + \left[ \frac{3(n^4-1)}{2(n^2+2)^2} \right] \quad (\text{Kawski-Chamma-Viallet's polarity function}) \quad (4)$$

It follows that plots of  $\bar{\nu}_a - \bar{\nu}_f$  versus  $F_1(\epsilon, n)$ ; and  $\frac{\bar{\nu}_a + \bar{\nu}_f}{2}$  versus  $F_2(\epsilon, n)$  should give straight lines. The parameters  $m_1$  and  $m_2$  occurring in Eqs. 1 and 2 are linear functions of  $F_1$  and  $F_2$ , and can be determined from the slopes of the straight lines.  $m_1$  and  $m_2$  are also defined as follows:

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad (5)$$

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \quad (6)$$

$h$  being Planck's constant, and  $c$ , the velocity of light in vacuum. The Onsager's cavity radius ( $a$ ) of ZnPc is obtained from molecular volume, as given by Suppan's equation:

$$a = \sqrt[3]{\frac{3M}{4\pi\rho N}} \quad (7)$$

Where  $M$  is the ZnPc's molecular weight ( $577.91 \text{ g mol}^{-1}$ ),  $\rho$ , its density ( $1.50 \text{ g cm}^{-3}$  (Gao and Kahn 2002)); and  $N$ , the Avogadro's number. From Eq. 7,  $a_{\text{ZnPc}} = 5.35 \text{ \AA}$ .

Analysis of Eqs. 5 and 6 yielded the ratio  $\frac{\mu_e}{\mu_g}$ , given as:

$$\frac{\mu_e}{\mu_g} = \frac{m_1 + m_2}{m_2 - m_1} \quad (8)$$

#### 2.3.3. Molecular-microscopic solvent polarity parameter ( $E_T^N$ )

According to Reichardt (Reichardt and Harbusch-Gornert 1983, Reichardt 1994), the molecular-microscopic solvent polarity parameter ( $E_T^N$ ) has dimensionless values that are defined according to Eq. 9. Water and trimethylsilane are taken as extreme polar and non-polar reference solvents, with  $E_T^N$  equal to 1.0 and 0.0, respectively. All other solvents have values in-between these extreme values.

$$E_T^N = \frac{E_T(\text{Solvent}) - E_T(\text{TMS})}{E_T(\text{Water}) - E_T(\text{TMS})} = \frac{E_T(\text{Solvent}) - 30.7}{32.4} \quad (9)$$

The relationship among Stokes' shift ( $\bar{\nu}_a - \bar{\nu}_f$ ), the dipole moment difference term ( $\Delta\mu$ ) and  $E_T^N$  is given by Eq. 10 (Ravi et al. 1994):

$$\Delta\bar{\nu} = \bar{\nu}_a - \bar{\nu}_f = 11307.6 \left[ \left( \frac{\Delta\mu}{\Delta\mu_B} \right)^2 \left( \frac{a_B}{a} \right)^3 \right] E_T^N + \text{constant} \quad (10)$$

Where  $\Delta\mu$  and  $\Delta\mu_B$  ( $= 9 \text{ D}$ ) are the differences between the excited- and ground-state dipole moments of ZnPc and betaine, respectively;  $a$  and  $a_B$  are the Onsager cavity radii of ZnPc and betaine, respectively.

A plot of  $\Delta\bar{\nu}$  against  $E_T^N$  should give a straight light with slope  $m$  given as:

$$m = 139.6 \left( \frac{6.2}{a} \right)^3 \cdot (\Delta\mu)^2 \quad (11)$$

$\Delta\mu$  can then be calculated as:

$$\Delta\mu = \sqrt{\frac{m \cdot \left( \frac{6.2}{a} \right)^{-3}}{139.6}} \quad (12)$$

## 3. Results and discussion

### 3.1. UV-visible and fluorescence spectra

Fig. 2 shows the ground electronic absorption spectra of ZnPc in five solvents - DMSO, THF, pyridine, triethylamine and 1-chloronaphthalene. Solvent parameters - aromaticity, polarity, coordinating power and refractive index, which differ among various solvents are usually used in explaining the observed trend in the variation of Q-band position with solvent.

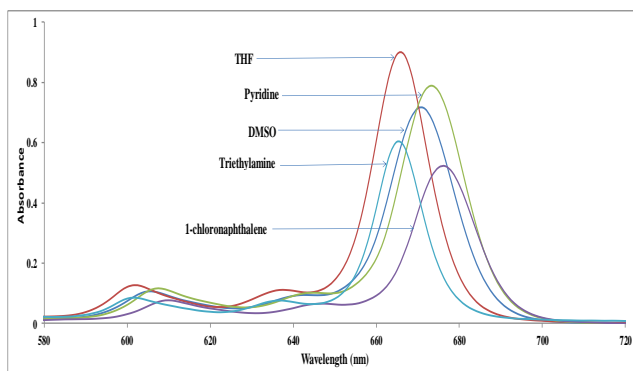


Fig. 2: Ground Electronic Absorption Spectra of ZnPC in Five Solvents.

It has been observed that aromatic solvents cause Q-band positions to occur at longer wavelengths (Ogunsipe et al. 2003); this is attributed to the interaction of the  $\pi$ -electron system of the aromatic solvent with the phthalocyanine ring, which facilitates  $\pi$ -back-donation, thus augmenting the ring's  $\pi$ -electron density and therefore destabilizing the highest occupied molecular orbital (HOMO). Consequently, ZnPc's Q-bands occur at longer wavelengths in the aromatic solvents – toluene, benzene, pyridine, benzonitrile and 1-chloronaphthalene (Table 1). In THF however the Q-band exists at 668 nm; the aromatic nature of the solvent is not enough to elicit any further bathochromic shift in Q-band position. This observation suggests that solvent's aromaticity is not sufficient to explain the changes in Q-band position with solvent. Fig. 3 depicts the variation of ZnPc's Q-band positions with the respective solvents' refractive indexes. The wavelength of maximum absorption increases with solvent's refractive index, which is due to the interaction between ZnPc's transition-dipole moment and solvent-polarization (Isago et al. 2004).

Table 1: Spectral Data for ZNPC in Various Solvents

	n	$\epsilon$	$\mu/D$	$\lambda_Q$ (Abs)/nm (Log $\epsilon$ )	$\lambda_Q$ (Ems) /nm	$\Delta\lambda_{\text{Stokes}}$ /nm
Triethylamine	1.401	2.45	0.72	666 (5.31)	671	5
n-butylamine	1.405	4.92	1.00	669 (5.46)	674	5
THF	1.406	7.47	1.69	668 (5.48)	672	4
*DCM	1.424	9.02	1.60	671 (5.27)	679	8
DMF	1.430	37.06	3.97	670 (5.37)	675	5
Chloroform	1.446	4.89	1.02	673 (5.29)	680	7
DMSO	1.479	46.71	3.96	672 (5.38)	679	7
*Toluene	1.497	2.43	0.38	672 (5.32)	676	4
*Benzene	1.501	2.274	0.00	672 (5.33)	676	4
Pyridine	1.509	13.22	2.21	674 (5.42)	681	7
Benzonitrile	1.528	25.20	4.28	674 (5.40)	681	7
1-CN	1.633	5.00	1.55	677 (5.24)	685	8

\*one drop of pyridine added to effect dissolution

The lack of linearity of Fig. 3 further demonstrates that a combination of solvent parameters is necessary to explicate solvatochromism in ZnPc and similar complexes.

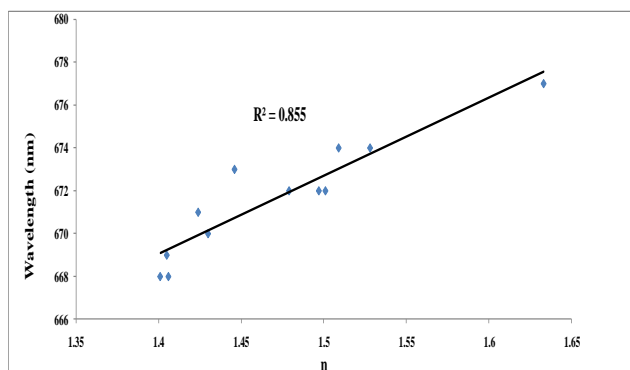


Fig. 3: Dependence of ZNPC'S Q-Band Absorption Position on Solvent's Refractive Index.

Fig. 4 shows the absorption and fluorescence emission spectra of ZnPc in THF. Stokes' shifts in the various solvents range between 4 and 8 nm. These small Stokes' shifts are due to the rigidity of the chromophore environment that excludes non-fluorescent relaxation to a ground state.

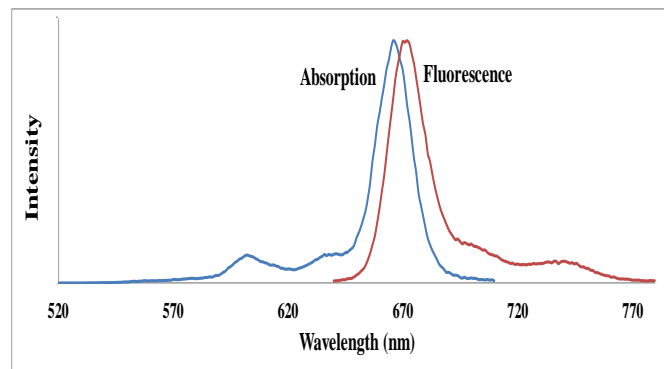


Fig. 4: Absorption and Fluorescence Spectra of ZnPc in THF.

Plots of polarity functions ( $F_1$  and  $E_T^N$ ) against Stokes' shift ( $\Delta\bar{\nu}$ ) (Figs. 5 and 7 respectively) and  $F_2$  against  $\frac{\bar{\nu}_A + \bar{\nu}_F}{2}$  (Fig. 6) show linear dependence of the polarity functions on the respective energy functions. However, it must be noted that the most polar solvents and the coordinating solvents in the range (DMF, DMSO, benzonitrile and pyridine, according to dipole moment,  $\mu$ , values; Table 2) were excluded from the plots; this was due to the failure to obtain linear fits when these solvents were included. It appears that the polarity functions  $F_1$ ,  $F_2$  and  $E_T^N$  do not adequately account for the high polarities of these solvents, as observed before (Ogunsipe 2018). Again, it appears that specific fluorophore-solvent interactions such as dipole-dipole interactions or electron-pair Donor/electron-pair acceptor interactions also contribute significantly to the overall solute-solvent interaction.

Table 2: Solvatochromic Data for the Determination of ZnPc's Ground State and Excited State Dipole Moments

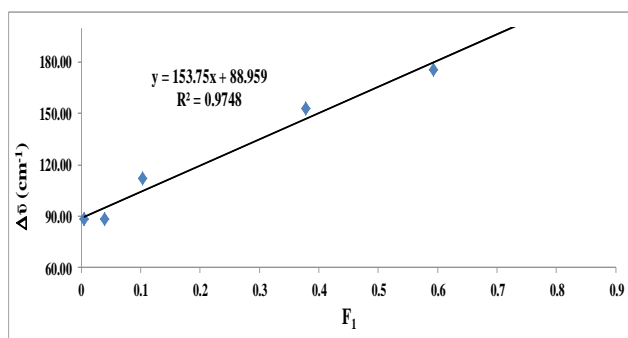
	$F_1$	$F_2$	$E_T^N$	$(\bar{\nu}_a - \bar{\nu}_f)$ /cm <sup>-1</sup>	$(\bar{\nu}_a + \bar{\nu}_f)$ /cm <sup>-1</sup>
Triethylamine	0.1030	0.3240	0.259	112	14959
n-Butylamine	0.4002	0.4752	0.762	111	14892
Dichloromethane	0.5932	0.5843	0.111	176	14815
Chloroform	0.3774	0.4909	0.386	153	14782
Toluene	0.0390	0.3549	1.00	88.1	14837
Benzene	0.0045	0.3403	0.654	88.1	14837

$$m_1 = 153.75; m_2 = 438.16; m = 386.66; \frac{\mu_e}{\mu_g} = 2.08; \Delta\mu = 1.62 \text{ D}; \mu_g = 1.50 \text{ D}; \mu_e = 3.12 \text{ D}$$

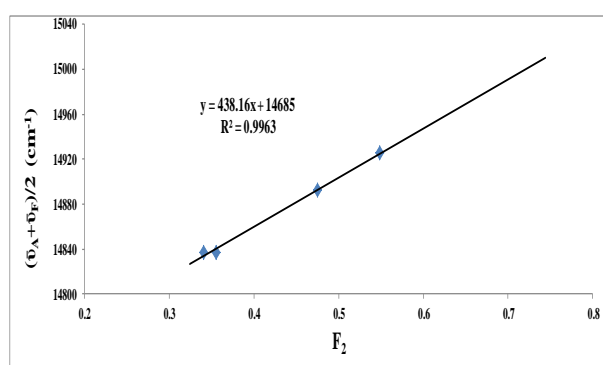
### 3.2. Zinc phthalocyanine structure and dipole moment

The geometry of the nuclear skeleton of a metallophthalocyanine is almost perfectly square planar with a  $\pi$ -electron system of  $D_{4h}$  symmetry comprising of a  $C_4$  principal axis of rotation, four perpendicular  $C_2$  axes and a horizontal mirror ( $\sigma_h$ ) plane (Fig. 1a); and this should confer an almost zero dipole moment on the molecule. However, some metals do not perfectly fit into the phthalocyanine (Pc) cavity, in which case the symmetry drops to  $C_{4v}$ . In ZnPc, there are four vertical mirror ( $\sigma_v$ ) planes in addition to the  $C_4$  axis. Zinc is displaced 45 pm from the plane of the aromatic ring, with Zn-N bond lengths of 206.1 pm, to form a domed shape (Kobayashi et al. 1971, Mack and Stillmann 1994) (Fig. 1b). The drop in symmetry from  $D_{4h}$  to  $C_{4v}$  in the ZnPc molecule should be responsible for its observed polarity. Even in the  $C_{4v}$  symmetry, the molecule cannot have a component of the dipole moment perpendicular to the symmetry axis ( $C_4$ ), because a dipole moment which exists in one direction perpendicular to the axis is cancelled by an opposing dipole. A dipole moment in these molecules can only be parallel to the molecular axis (Fig. 1b).

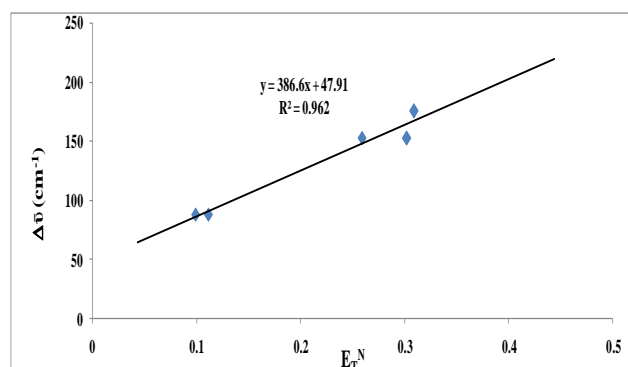
The treatment of solvatochromic data in this work, which is based on the plots involving the polarity functions ( $F_1$  vs  $\Delta\bar{\nu}$ ,  $F_2$  vs  $\frac{\bar{\nu}_A + \bar{\nu}_F}{2}$ , and  $E_T^N$  vs  $\Delta\bar{\nu}$ ), and their respective slopes ( $m_1$ ,  $m_2$  and  $m$ , Figs. 5, 6 and 7 respectively), culminated in the values of ground state and excited state dipole moments of ZnPc.



**Fig. 5:** Dependence of ZnPc's Stokes' Shift on the Bakshiev's Solvent Polarity Function ( $F_1$ , Eq. 3).



**Fig. 6:** Dependence of ZnPc's absorption/Fluorescence Wavenumber on the Kawski-Chamma-Viallet's Solvent Polarity Function ( $F_2$ , Eq. 4).



**Fig. 7:** Dependence of ZnPc's Stokes' shift on the molecular-microscopic solvent polarity parameter ( $E_T^N$ , Eq. 5).

The respective values of  $m_1$  and  $m_2$  and  $m$  were found to be 153.75, 438.16 and 386.66  $\text{cm}^{-1}$ , respectively; which resulted in the following values:  $\Delta\bar{\nu} = 1.62$  D and  $\frac{\mu_e}{\mu_g} = 2.09$  D. The values of ground state and excited state dipole moments were then calculated to be  $\mu_g = 1.50$  D, and  $\mu_e = 3.12$  D (Table 2). As expected, ZnPc is more polar in the excited state than in the ground state which, is attributed to a modification of electronic charge distribution in the excited singlet state relative to the ground state (altered charge separation upon excitation).

## 4. Conclusion

The dipole moment of ZnPc is significantly higher in the excited singlet state ( $\mu_e = 3.12$  D) than in the ground state ( $\mu_g = 1.50$  D), indicating a substantial redistribution of the  $\pi$ -electron densities in the more polar excited state. The most polar solvents and the co-

ordinating solvents were left out of the plot leading to the estimation of the dipole moments. It appears that specific fluorophore-solvent interactions such as dipole-dipole interactions or electron-pair

Donor/electron-pair acceptor interactions also contribute significantly to the overall solute-solvent interaction. It is worthwhile to stress that the solvatochromic shift method might not be as accurate as instrumental methods, due to approximations and oversimplifications made in the method. However, the method remains very convenient because it negates the use of expensive equipment and is easily accessible.

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