

Estimation of Ground and Excited State Dipole Moments of Coumarin Derivatives by Solvatochromic Method

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Abstract- The ground state (μ_g) and excited state (μ_e) dipole moments of two coumarin derivatives namely diethyl 2-acetamido-2-((3-oxo-3H-benzo[f]chromen-1-yl)methyl)malonate (2DAM) and ethyl 2-((7-methyl-2-oxo-2H-chromen-4-yl)methyl)-3-oxobutanoate (2EMCO) were estimated in various solvents. The dipole moments were estimated from Lippert, Bakshiev and Kawaski-Chamma-Viallet equations by using the variation of Stokes shift with the solvent dielectric constant and refractive index. Ground state dipole moments were also calculated theoretically by DFT studies using Gaussian 03 software. It was observed that the excited state dipole moments calculated by solvatochromic shift method were greater than the ground state dipole moments indicating a substantial redistribution of the π -electron densities in a more polar excited state for both the coumarin derivatives.

Index Terms- Coumarin derivatives, Solvatochromic shift method, Ground state and excited state dipole moments and DFT studies.

I. INTRODUCTION

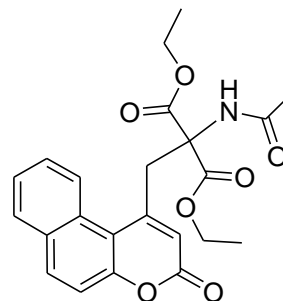
Photophysics of fluorescent organic compounds gives a better knowledge of excited state properties which in turn will help in the designing of newer molecules and understanding their performance in specific applications. Determination of ground state and excited state dipole moments of dye molecules is important because the values of dipole moments provide information about the change in electronic distribution after excitation, charge distribution in the molecule and to judge the site of attack by nucleophilic and electrophilic reagents in some photochemical reactions. The excited state dipole moments of some fluorescent molecules such as studied here also determine the tunability range of the emission energy as a function of the polarity of the medium. Coumarins are well known laser dyes for the blue – green spectral region. Coumarins and their derivatives are finding lot of applications in different fields of Science and technology [1-2]. They exhibit a strong fluorescence in UV and VISIBLE region. Hence they are more suitable for the use as colorants, dye laser media and also as NLO chromospheres. In medicine, coumarins are used as fluorescent probes to determine the rigidity and fluidity of living cells and its surrounding medium. They also possess distinct biological activity and have been described as potential agents for anticancer. Several

workers have made both experimental and theoretical studies on ground state and excited state dipole moments by using solvatochromic shift method and other methods on fluorescent organic molecules like coumarins, thiophene, imidazoles, indoles, purins etc.[3-21].

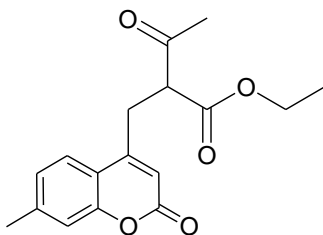
In our present work we report the effect of both polar and non-polar solvents on the absorption spectra and emission spectra of both the coumarins molecules. We have estimated the ground state and excited state dipole moments using solvatochromic shift method. Theoretical calculations were carried out by using Gaussian 03 program [22, 23] to supplement the experimental results. As per as these molecules are concerned, there are no reports on the calculation of dipole moments both in the ground state and in the excited state.

II. MATERIALS AND METHODS

The fluorescent coumarin molecules namely 2DAM and 2EMCO were synthesized in our laboratory using standard methods [24]. The molecular structure of these molecules are given in Fig.1. The solvents used in the present study namely toluene (TL) and 1,4-dioxane (DX) trichloroethane (TCE), tetrahydrofuran (THF), dichloromethane (DCM), dichloroethane (DCE), dimethylsulphoxide (DMSO) n-hexane (n-HX), n-heptane (n-HPT) and acetonitrile (AN) were obtained from S-D Fine Chemicals Ltd., India and they were of spectroscopic grade. The required solutions were prepared at fixed concentration of solutes 1×10^{-4} M in each solvent. The absorption and emission spectra were recorded using Perkin Elmer UV-Vis spectrophotometer and Perkin Elmer fluorescence spectrophotometer. All these measurements were carried out at room temperature.



Diethyl 2-acetamido-2-((3-oxo-3H-benzo[f]chromen-1-yl)methyl)malonate(2DAM)



ethyl 2-((7-methyl-2-oxo-2H-chromen-4-yl)methyl)-3-oxobutanoate(2EMCO)

Fig. 1: The molecular structure of 2DAM and 2EMCO

III. THEORY

3.1 Computational calculations.

The ground state dipole moments of these two molecules were calculated by quantum chemical calculations. All the computations were carried out using Gaussian 03 program on a Pentium- 4 PC and the basis set level used is B3LYP/6-31 g*. Corresponding optimized molecular geometries of 2DAM and 2EMCO are as shown in Fig.2 and Fig.3. The arrow mark indicates the direction of the dipole moment.

3.2 Experimental calculation of excited state dipole moments.

The three independent equations for the calculation of the excited state dipole moments of the solute molecules are as follows.

Lippert equation [27]

$$\overline{\vartheta}_a - \overline{\vartheta}_f = m_1 F_1(D, n) + const \quad (1)$$

Bakshiev equation[28]

$$\overline{\vartheta}_a - \overline{\vartheta}_f = m_2 F_2(D, n) + const \quad (2)$$

Kawaski-Chamma-Viallet equation[29]

$$\frac{\overline{\vartheta}_a + \overline{\vartheta}_f}{2} = m_3 F_3(D, n) + const \quad (3)$$

Here $F_1(D, n)$, $F_2(D, n)$ and $F_3(D, n)$, are Lippert polarity function, Bakshiev polarity function and Kawaski-Chamma-Viallet polarity function respectively. They are given in terms of dielectric constant (D) and refractive index (n) of the solvents as follows.

$$F_1(D, n) = \left[\frac{D-1}{2D+1} - \frac{n^2-1}{2n^2+1} \right] \quad (4)$$

$$F_2(D, n) = \left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2} \right] \left(\frac{2n^2+1}{n^2+2} \right) \quad (5)$$

$$F_3(D, n) = \left(\frac{2n^2+1}{2(n^2+2)} \right) \left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2} \right] + \frac{3(n^4-1)}{2(n^2+2)^2} \quad (6)$$

A plot of $\frac{\overline{\vartheta}_a - \overline{\vartheta}_f}{\overline{\vartheta}_a + \overline{\vartheta}_f}$ v/s $F_1(D, n)$, $\frac{\overline{\vartheta}_a - \overline{\vartheta}_f}{\overline{\vartheta}_a + \overline{\vartheta}_f}$ v/s

$F_2(D, n)$ and $\frac{\overline{\vartheta}_a - \overline{\vartheta}_f}{2}$ v/s $F_3(D, n)$ gives a linear plot with respective slopes m_1 , m_2 and m_3 . These slopes are given by

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad (7)$$

$$m_2 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad (8)$$

$$m_3 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \quad (9)$$

Where μ_g and μ_e are ground state and excited state dipole moments, h is the Planck constant, c is the speed of light and 'a' is Onsager's cavity radius[30]. By assuming ground state and excited state dipole moments are parallel following equations are obtained from equation (8) and (9).

$$\mu_g = \frac{(m_3 - m_2) [hca^3]^{1/2}}{2} \quad (10)$$

$$\mu_e = \frac{(m_3 + m_2) [hca^3]^{1/2}}{2} \quad (11)$$

$$\mu_e = \frac{(m_3 + m_2)}{(m_3 - m_2)} \times \mu_g \quad \text{For } m_3 \text{ greater than } m_2 \quad (12)$$

IV. RESULTS AND DISCUSSIONS

Stokes shifts were calculated from $\lambda_{f \text{ max}}$ rather than 0 - 0 emission transition and are presented in Table.1 and Table.2 along with the solvent polarity functions of solvents used in our present work. The possible resonance structures for the solute molecules are given in Fig.4 (a) & (b) and typical absorption and emission spectra of both the molecules are given in Fig.5. and Fig.6. We have used ten solvents whose dielectric constants vary from 2.4 to 48. Lippert plot, Bakshiev plot and Kawaski-

Chamma-Viallet plots are constructed for normal fluorescence spectrum of 2DAM and 2EMCO. These plots are linear with an excellent correlation coefficient and represented in Fig.7 to Fig.9. The small deviation from the linearity may be attributed to specific solute solvent interactions. With the increase in solvent polarity the emission peak shifts towards red by nearly 10nm in case of 2DAM and 30 nm in case of 2EMCO. This red shift also indicates strong host guest interactions. The slopes and corresponding correlation coefficients are presented in Table.3.

Ground state dipole moments were calculated using equation (10). Excited state dipole moments were calculated using Lippert equation, Bakshiev equation and Kawaski-Chamma-Viallet equations. Ground state dipole moments were also calculated theoretically using Gaussian 03 program and the basis set level used is B3LYP/6-31 g*. All these values are given in Table.4. It may be noted that the excited state dipole moments calculated from Lippert equation, Bakshiev equation and Kawaski-Chamma-Viallet equations were greater than the ground state dipole moments. The small discrepancies in the values of excited state dipole moments may be in part, due to the various assumptions and simplifications made in the use of above mentioned equations.

V. CONCLUSIONS

We have studied the photo physical properties of two coumarin derivatives namely 2DAM and 2EMCO using solvatochromic shift method. Both polar and non-polar solvents were employed in our study. With the increase in the solvent polarity we have noticed a red shift of 10nm in case of 2DAM and 30 nm in case of 2EMCO. This indicates a strong interaction between solvent and solute molecules and $\pi \rightarrow \pi^*$ transition. The excited state dipole moment ranges from 2.6435D to 3.4725D for 2DAM and 3.8636D to 6.3904D in case of 2EMCO. There is a considerable increase in the excited state dipole moments compare to ground state dipole moments indicating a substantial redistribution of π - electron densities in a more polar excited state for two Coumarins. To the best of our knowledge this is the first report on the dipole moments of these two coumarin derivatives and this should be of great practical importance in many fields as mentioned in the introduction.

FIGURES GRAPHS AND TABLES:

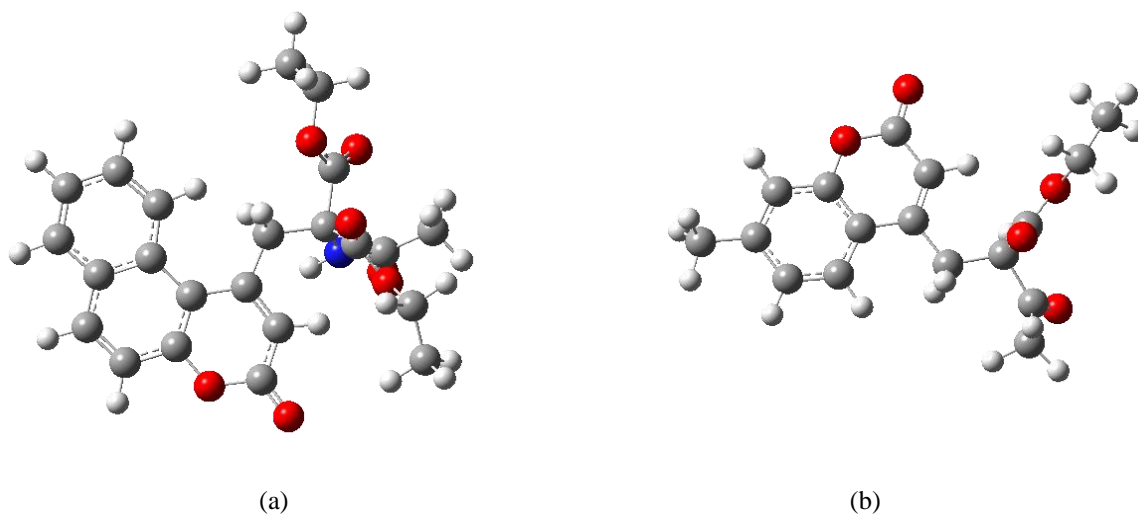


Fig.2: Optimized molecular geometry of 2DAM (a) and 2EMCO (b)

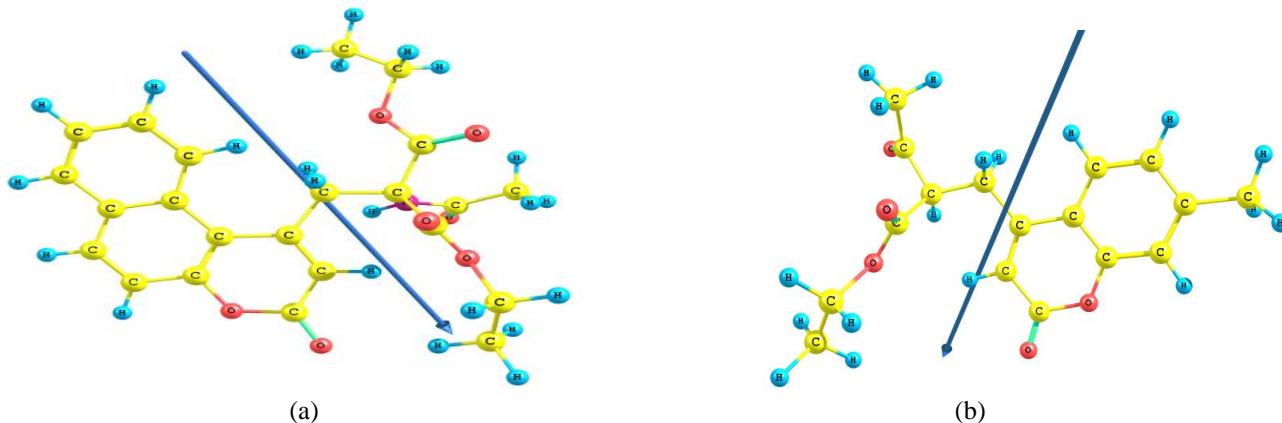


Fig.3: The ground state optimized molecular geometries of MDTC 2DAM (a) and 2EMCO (b)

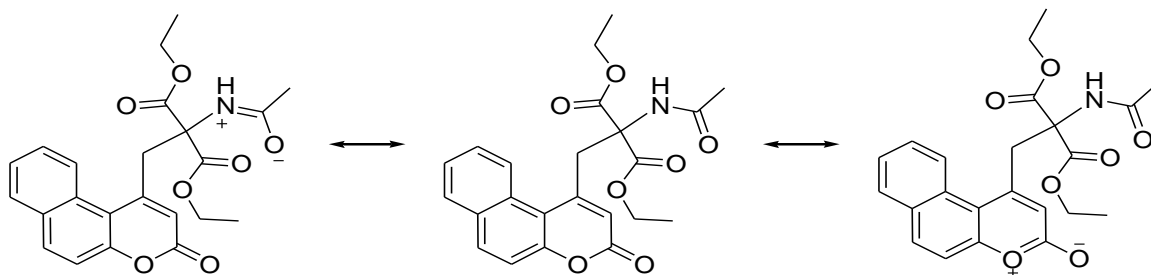


Fig. 4 (a): Resonance structure of 2DAM

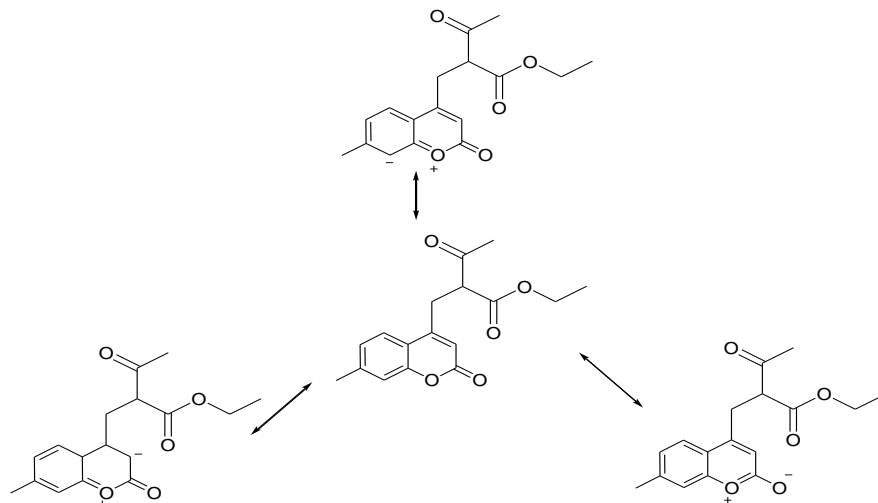


Fig. 4 (b): Resonance structure of 2 EMCO

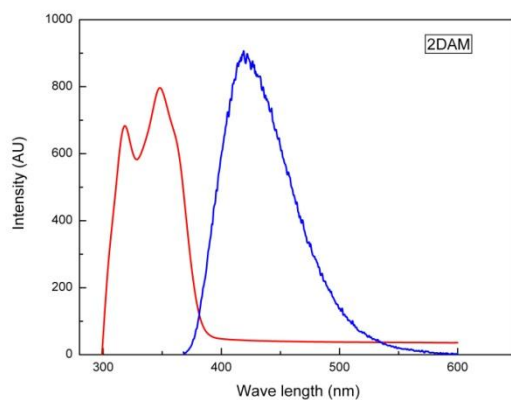


Fig. 5: Absorption emission spectra of 2DAM in acetonitrile.

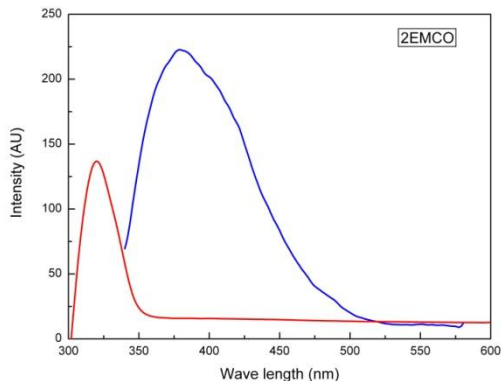


Fig. 6: Absorption emission spectra of 2 EMCO in acetonitrile

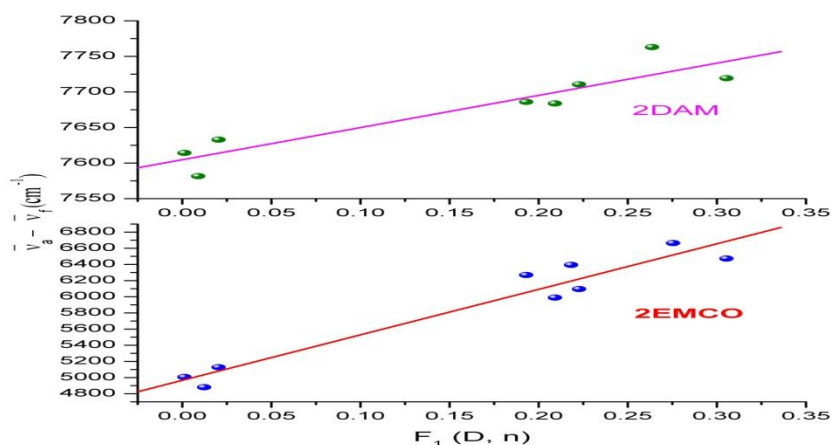


Fig. 7: The variation of stoke shift with $F_1(D,n)$ using Lippert equation for 2DAM and 2EMCO

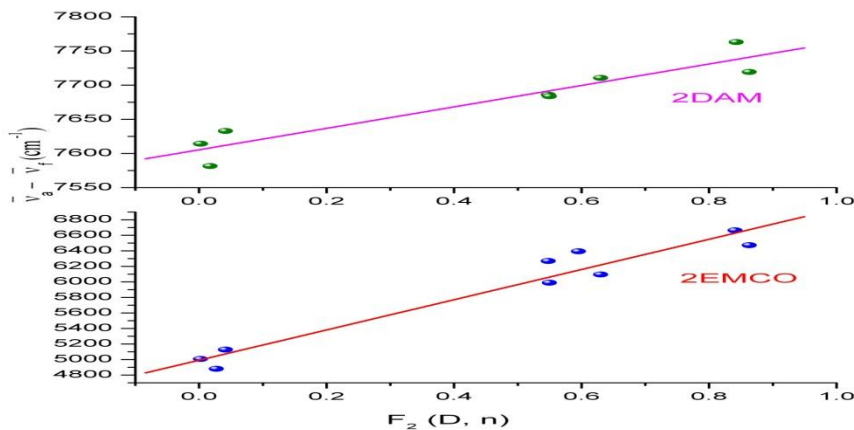


Fig. 8: The variation of stoke shift with $F_2(D,n)$ using Baksheiv equation for 2DAM and 2EMCO

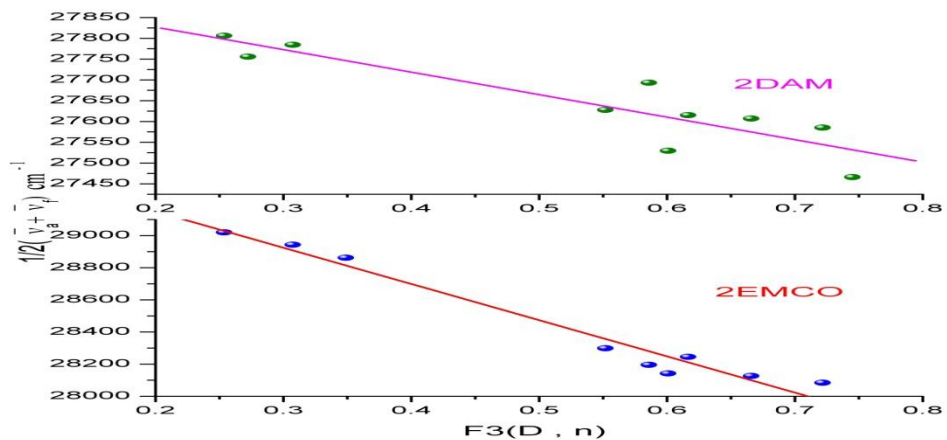


Fig. 8: The variation of stoke shift with $F_3(D, n)$ using Kawaski-Chamma-Viallet equation for 2DAM and 2EMCO

Table.1: Solvatochromic data of 2DAM in different solvents and solvent polarity functions.

Solvent	F ₁ (D,n)	F ₂ (D,n)	F ₃ (D,n)	λ _a (nm)	λ _f (nm)	$\Delta\bar{\nu} = \bar{\nu}_a - \bar{\nu}_f$	$\frac{\bar{\nu}_a + \bar{\nu}_f}{2}$
n-HX	0.0013	0.0025	0.2537	316	416	7607.10	27842.01
n-HPT	0.009	0.01734	0.2724	317	417	7564.92	27763.27
TOL	0.0123	0.02700	0.3488	320	417	7269.18	27615.40
1,4DX	0.0204	0.04140	0.3074	316	418	7722.12	27784.50
TCE	0.193	0.54780	0.6009	319	422	7651.27	27522.32
THF	0.2092	0.54950	0.5519	318	420	7637.01	27628.03
DCM	0.2182	0.59520	0.5859	319	424	7763.05	27466.43
DCE	0.2227	0.63000	0.6165	318	421	7693.57	27599.75
DMSO	0.2636	0.8425	0.745	319	424	7763.05	27466.43
AN	0.3054	0.863	0.6658	318	421	7693.57	27599.75

F₁(D,n): Lippert polarity function, F₂(D,n): Bakshiev polarity function, F₃(D,n): Kawaski-Chamma-viallet polarity function.

Table.2: Solvatochromic data of 2EMCO in different solvents and solvent polarity functions.

Solvent	F ₁ (D,n)	F ₂ (D,n)	F ₃ (D,n)	λ _a (nm)	λ _f (nm)	$\Delta\bar{\nu} = \bar{\nu}_a - \bar{\nu}_f$	$\frac{\bar{\nu}_a + \bar{\nu}_f}{2}$
n-HX	0.0013	0.0025	0.2537	317	375	4879.07	29106.20
n-HPT	0.009	0.01734	0.2724	317	400	6545.74	28272.87
TOL	0.0123	0.027	0.3488	319	378	4892.93	28901.49
1,4DX	0.0204	0.0414	0.3074	317	380	5229.95	28930.39
TCE	0.193	0.5478	0.6009	320	400	6250.00	28125.00
THF	0.2092	0.5495	0.5519	320	395	5933.54	28283.22
DCE	0.2227	0.63	0.6165	319	397	6159.04	28268.43
AN	0.3054	0.863	0.6658	319	401	6410.30	28142.80

F₁(D,n): Lippert polarity function, F₂(D,n): Bakshiev polarity function, F₃(D,n): Kawaski-Chamma-viallet polarity function.

Table.3: Slopes, Correlation coefficients and Number of data for 2DAM and 2EMCO.

Correlations	Compound	Slope	Correlation coefficient	No of data
Lippert Correlation	2DAM	452.61	0.9270	8
	2EMCO	5663.05	0.9702	9
Bakshiev Correlation	2DAM	156.98	0.9503	7
	2EMCO	1946.78	0.9737	9
Kawaski-Chamma-Viallet Correlation	2DAM	-541.19	-0.9025	10
	2EMCO	-2253.54	-0.9836	9

Table.4: Ground and excited state dipole moments of 2DAM and 2EMCO

Compound	Radius (a) (Å ⁰)	μ _g ^a (D)	μ _g ^b (D)	μ _e ^c (D)	μ _e ^d (D)	μ _e ^e (D)	μ _e ^f (D)
2DAM	4.4912	5.7633	1.4547	2.6435	3.4725	2.6430	2.6428
2EMCO	4.0484	4.3149	0.2821	3.8636	6.3904	3.8635	3.8636

$$\text{Debye(D)} = 3.33564 \times 10^{-30} \text{Cm} = 10^{-18} \text{esu cm.}$$

^a Calculated by Gaussian Software.

^b The ground states dipole moments calculated using Eq. 10.

^c The excited states dipole moments calculated using Eq. 11.

^d The experimental excited state dipole moments calculated from Lippert's equation.

^e The experimental excited state dipole moments calculated from Bakshiev equation.

^f The experimental excited state dipole moments calculated from Kawaski-Chamma-viallet equation.

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