Electronic Supplementary Information (ESI)

Excited-State Properties of Fluorenones: Influence of Substituents, Solvent and Macrocyclic Encapsulation

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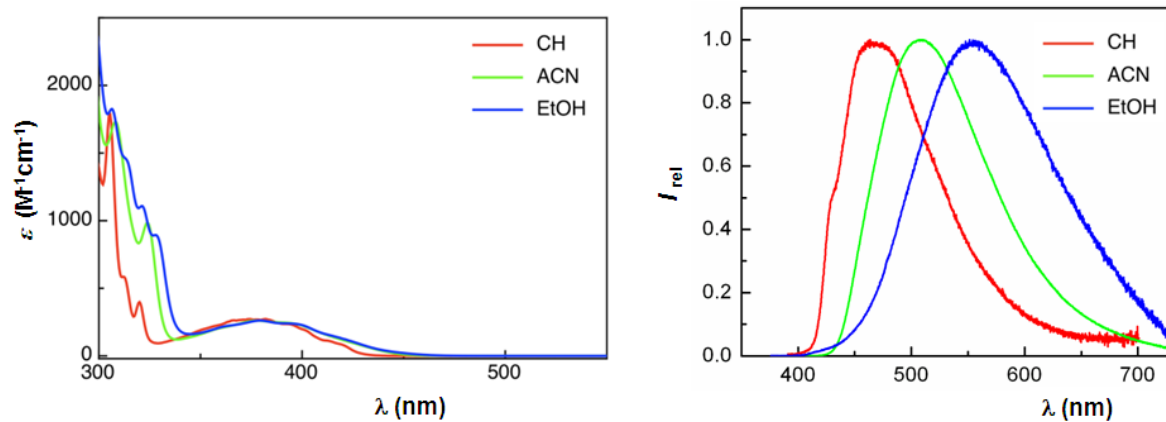

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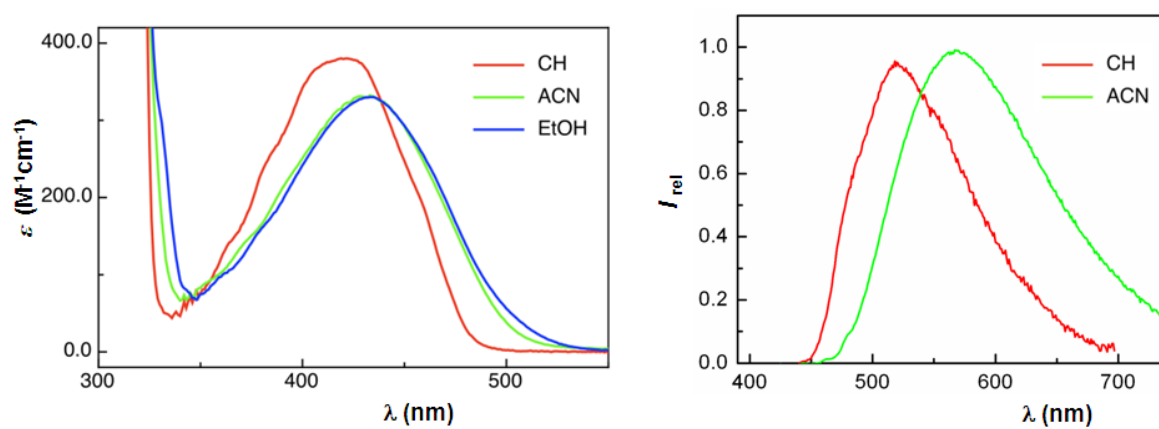

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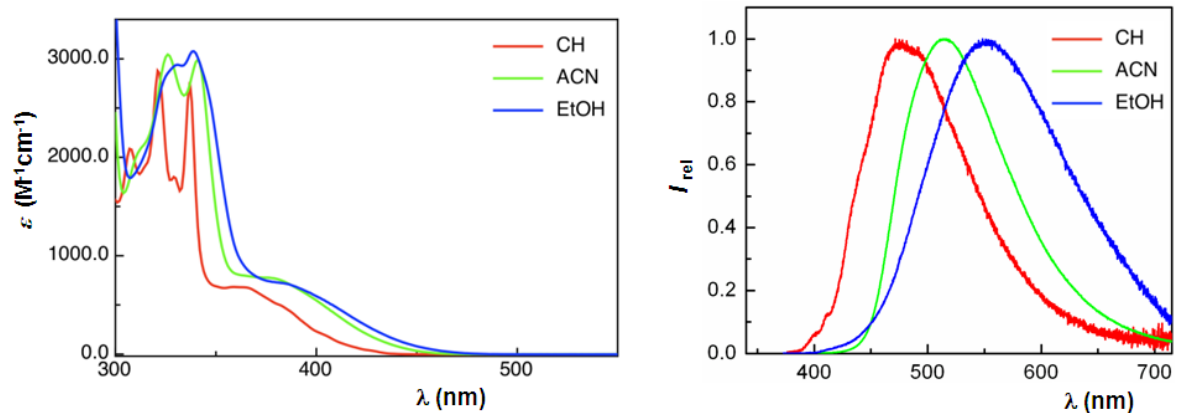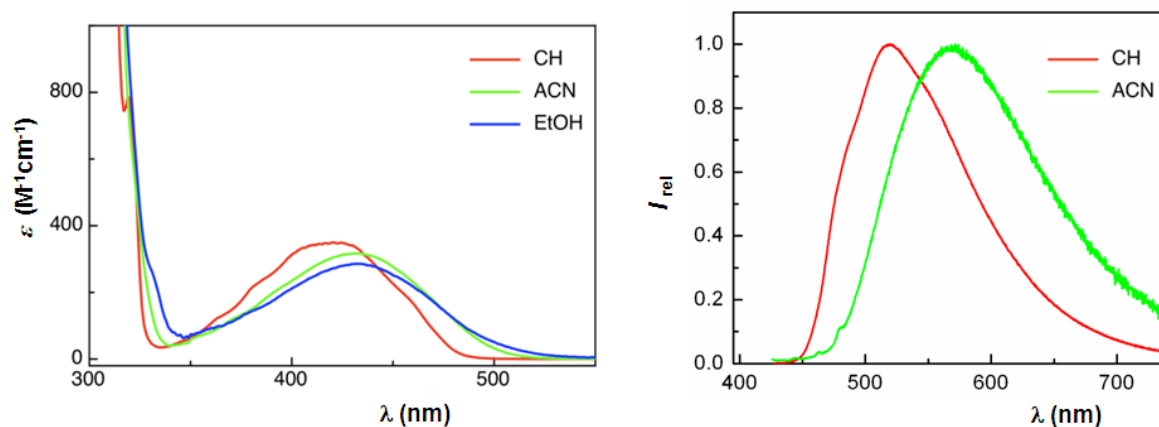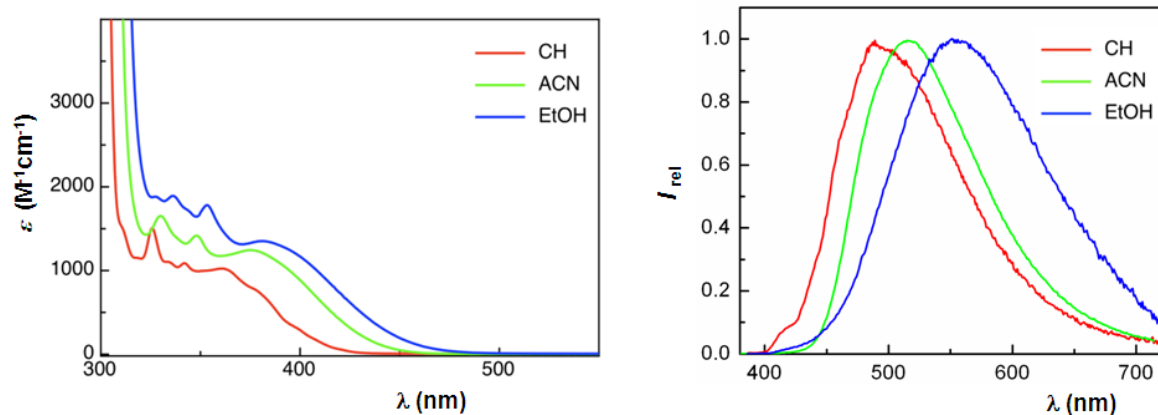
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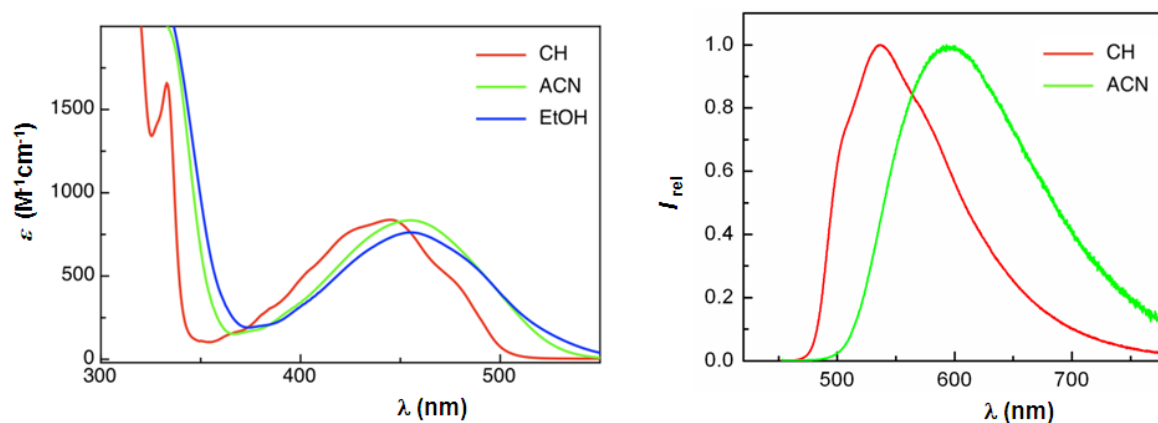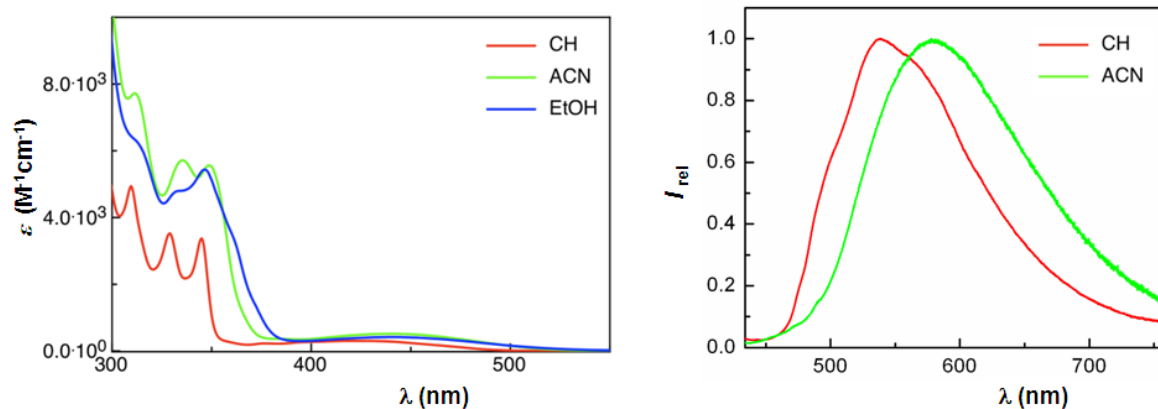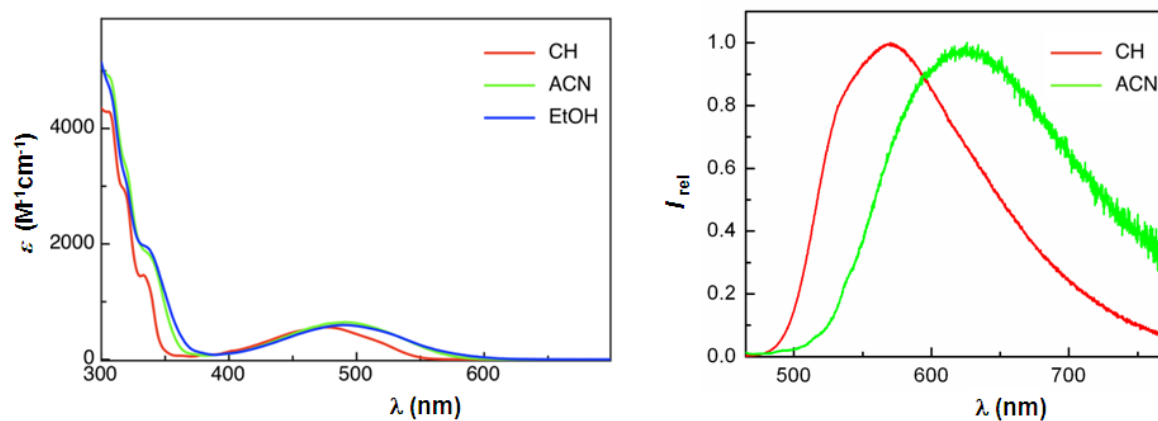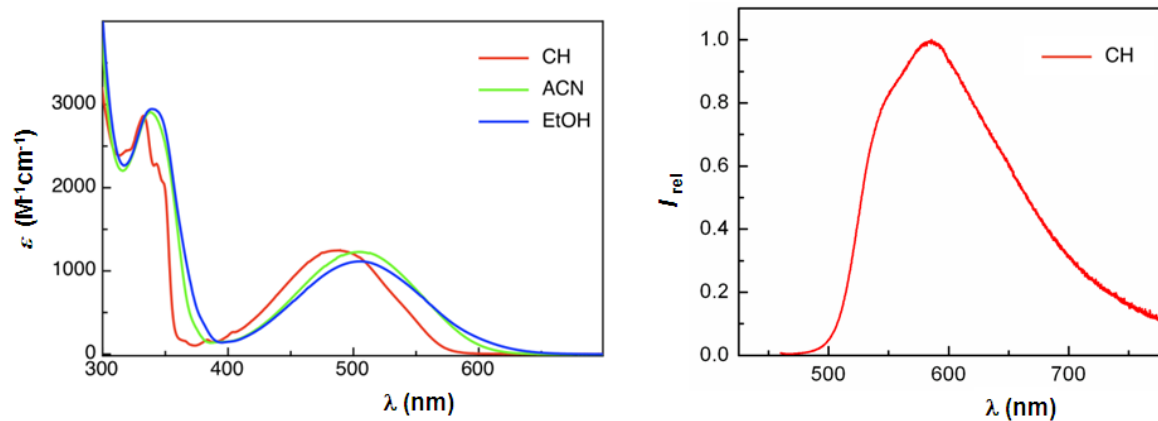
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2 Determination of Ground and Excited State Dipole Moments of Methoxy-Substituted Regioisomeric Fluorenones 2 and 3: A Comparative Study

In general, the theory of solvent effects on the emission properties of fluorophores is based on the fact that the fluorophore molecule is considered as a dipole in a continuous medium of uniform dielectric constant and that this model necessarily does not contain any chemical interactions. However, the interactions between the solvent and fluorophore dipoles affect the energy difference between the ground and excited states, which in turn is responsible for spectral shifts. In this regard, the solvatochromic shifts in different solvents allow the estimation of ground (μ_g) and excited state (μ_e) dipole moments. The ratio of μ_e and μ_g can be determined by applying the Bakshiev formulation[1] (Eq. 1) and Chamma and Viallet equations[2] (Eq. 2).

The formulation of Bakshiev and Chamma and Viallet equations are based on simplified assumptions, e.g., μ_e and μ_g, are almost collinear, the solute molecule is modelled as a spherical cavity with a rigid dipole at the centre and the cavity radius remains same both in the ground and excited states. These formulations ignore the molecular aspects of solvation.[3]

In accordance with the Bakshiev formulation,

$$\bar{v}_a - \bar{v}_f \ = \ \frac{2(\mu_e - \mu_g)^2}{a^3 hc} f_1(D,n) \ + \ constant$$

$$= \ S_1 f_1(D,n) \ + \ constant \qquad \ldots \ldots \text{Eq. 1}$$

Where, the slope of the linear fit of $(\bar{v}_a - \bar{v}_f)$ versus $f_1(D,n)$ can be expressed by:

$$S_1 = \frac{2(\mu_e - \mu_g)^2}{a^3 hc}$$

Again, in accordance with the Chamma and Viallet equations, we have:

$$\frac{(\bar{v}_a + \bar{v}_f)}{2} = -\frac{2(\mu_e^2 - \mu_g^2)}{a^3 hc} f_2(D,n) + constant$$

$$= S_2 f_2(D,n) + constant \quad \ldots .. \, \text{Eq. 2}$$

Where, the slope of the linear fit of $\frac{(\bar{v}_a + \bar{v}_f)}{2}$ versus $f_2(D,n)$ can be expressed by:

$$S_2 = -\frac{2(\mu_e^2 - \mu_g^2)}{a^3 hc}$$

Here, $\bar{v}_a$ and $\bar{v}_f$ are respectively the absorption and fluorescence maxima, n and D are the refractive indices and the dielectric constants of the solvents, respectively, 'a' is the Onsager cavity radius (in Å) and 'c' and 'h' are the velocity of light and Planck's constant respectively. The polarity functions f_1 and f_2 can be expressed as:

$$f_1(D,n) = \left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right]\left(\frac{2n^2+1}{n^2+2}\right) \ldots \ldots .. \, \text{Eq. 3}$$

$$f_2(D,n) = \frac{1}{2}f_1(D,n) + \frac{3}{2}\frac{(n^4-1)}{(n^2+2)^2} \ldots \ldots .. \, \text{Eq. 4}$$

The numerical values of the functions f_1 and f_2 for different solvents have been shown in Table 1. From Eq. 3 and Eq.4, we get the ratio of the dipole moment in the excited and ground states.

$$\boxed{\frac{\mu_e}{\mu_g} = \frac{|S_1 - S_2|}{|S_1 + S_2|}} \ldots \ldots .. \, \text{Eq. 5}$$

As can be seen from Eq. 5, the relation is independent of 'a', and this in fact points out that the ratio of μ_e and μ_g can be determined precisely without any knowledge of the Onsager cavity radius.[3]

In order to get a feel of polarization dependence of spectral profiles, however, the $E_T(30)$ function, i.e. molar transition energy, which is an empirical measure of solvent polarity and is based on solvatochromic behaviour of a betaine dye as a probe solute, is of particular interest. However, to avoid certain dimensionality problems, the normalized $E_T(30)$ function, viz., E_T^N is often employed.[3] An empirical correlation of spectral shift with E_T^N has been developed by Ravi and co-workers,[4] according to which,

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

Where $\Delta\mu_B$ and a_B designate dipole moment change on excitation and Onsager radius, respectively, for betaine dye. Similarly, the terms $\Delta\mu$ and a are the corresponding values for the unknown molecule under study. The values of solute radii were in turn estimated by calculating the Van der Waals volumes ($V_{VdW} = \frac{4}{3}\pi a^3$) using the technique developed by Michael H. Abraham and co-workers.[5] The values of E_T^N in different solvents are shown in Table 1.

A linear plot of the Stokes shift versus E_T^N results in the slope 'm' which can be expressed as:

$$m = 11307.6 \left[\left(\frac{\Delta\mu}{\Delta\mu_B}\right)^2 \left(\frac{a_B}{a}\right)^3\right]$$

For the probe molecule, betaine dye,[6] $\Delta\mu_B = 9\,D$ and $a_B = 6.2$ Å. With these values in hand, it turns out that

$$\Delta\mu = \left(\mu_e - \mu_g\right) = \sqrt{\frac{m \times 81}{11307.6 \left(\frac{6.2}{a}\right)^3}}$$

Thus, by knowing the ratio $\frac{\mu_e}{\mu_g}$ and the difference $\left(\mu_e - \mu_g\right)$, the experimental values of ground and excited state dipole moments can be easily determined.[3]

We have employed the above protocol to determine the ground and excited state dipole moments for 2- and 3-methoxy fluorenones **2** and **3**. The detailed calculations are given in the following.

2.1 Determination of Onsager Cavity Radius for Regioisomeric Fluorenones 2 and 3

The estimation of van der Waals volume (V_{vdW}) for the helicenes was done theoretically using the atomic and bond contributions of van der Waals volume (VABC). According to Abraham and co-workers,[5] the van der Waals volume (Å^3/molecule) can be calculated from the following formula:

$$V_{vdw} = \sum (\text{all atom contributions}) - 5.92N_{\text{B}} - 14.7\,R_{\text{A}} - 3.8\,R_{\text{NA}}$$

where, N_{B} is the number of bonds, R_{A} is the number of aromatic rings, and R_{NA} is the number of non-romantic rings.

If the total number of atoms in the molecule is N, then the number of bonds present (N_{B}) can be calculated using the relation:

$$N_{\text{B}} = N - 1 + R_{\text{A}} + R_{\text{NA}}$$

The van der Waals volumes[5] (V_{vdW}) for carbon, hydrogen and oxygen are considered to be as 20.58, 7.24 and 14.71 Å^3 respectively. For both the fluorenones **2** and **3** the molecular formula is: $C_{14}H_{10}O_2$. Thus, the sum of all atom contribution for each of these molecules turns out to be:

$$\sum(\text{all atom contributions}) = (14 \times 20.58) + (10 \times 7.24) + (2 \times 14.71)$$

$$= 288.12 + 72.4 + 29.42$$

$$= 389.94$$

The number of bonds present in **2** or **3** can be calculated as:

$$N_B = N - 1 + R_A + R_{NA}$$

$$= (14 + 10 + 2) - 1 + 3$$

$$= 28$$

Thus, the calculated van der Waals volumes (V_{vdW} in Å^3) for **2** and **3** should be given by:

$$V_{vdw} = \sum(\text{all atom contributions}) - 5.92N_B - 14.7\,R_A - 3.8\,R_{NA}$$

$$= 389.94 - (5.92 \times 28) - (14.7 \times 3) - (3.8 \times 0)$$

$$= 389.94 - 165.76 - 44.1$$

$$= 180.08$$

Now, if we consider the Onsager radius to be 'a' (in Å) for a spherical molecule, then the van der Waals volume (V_{vdW} in Å^3) can be regarded as,

$$V_{vdW} = \frac{4}{3}\pi\,a^3$$

Thus, for a molecule such as **2** or **3**, the relation turns out to be,

$$\frac{4}{3}\pi\, a^3 = 180.08$$

$$\text{i.\,e.,} \quad a^3 = 180.08 \times \frac{3}{4\pi} = 42.99$$

$$\text{Thus,} \quad a = 3.50 \text{ Å}$$

2.2 Comparative Data for the Regioisomeric Fluorenones 2 and 3 as Polarity Probes

Fluorenone Probe	**2**	**3**
Molecular Formula	$C_{14}H_{10}O_2$	$C_{14}H_{10}O_2$
$\sum$ (all atom contributions)	389.94	389.94
N_B	28	28
Van der Waals volume: V_{vdW} (Å^3)	180.08	180.08
Onsager cavity radius: a (Å)	3.50	3.50

2.3 Estimation of Solvent Shift Data for Regioisomeric Fluorenones 2 and 3

Table S1 Solvent Properties and Polarity Functions.

Solvent	Dielectric Constant (D) at 25 °C	Refractive Index (n) at 25 °C	Polarity Function f_1 (D, n)	Polarity Function f_2 (D, n)	E_T^N (*)
Cyclohexane	1.88	1.426	0.036	0.290	0.150
Benzene	2.28	1.501	0.005	0.340	0.117
1,4-Dioxane	2.25	1.422	0.05	0.311	0.164
Ethylacetate	6.02	1.372	0.489	0.498	0.228
Acetonitrile	37.5	1.344	0.865	0.666	0.472
Ethanol	24.6	1.361	0.813	0.652	0.654

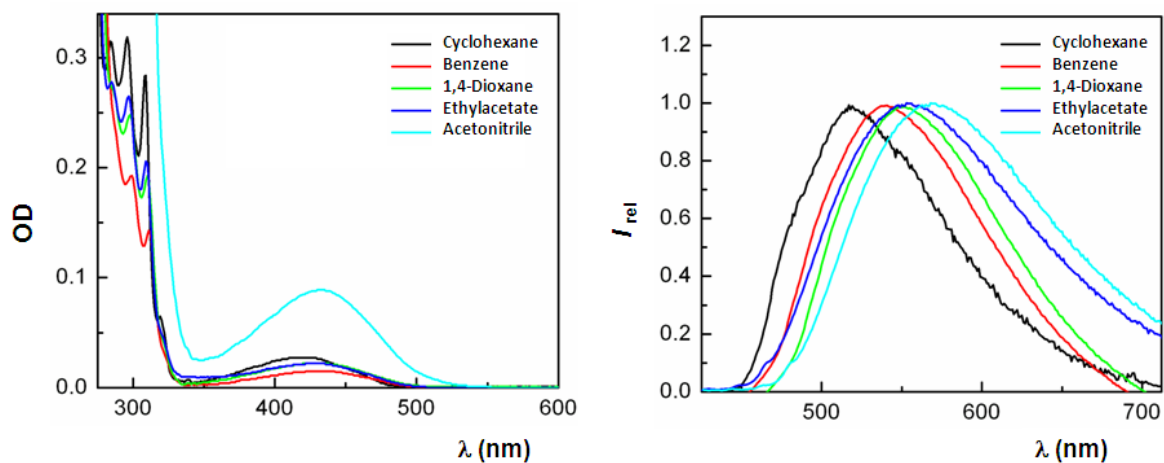(*) for standard values of E_T^N see ref. 7.

Fig. S10 UV-vis absorption (left) and fluorescence (right) spectral profiles of fluorenone **2** in different solvents.

Table S2 Solvent Shift Data for Fluorenone **2**.

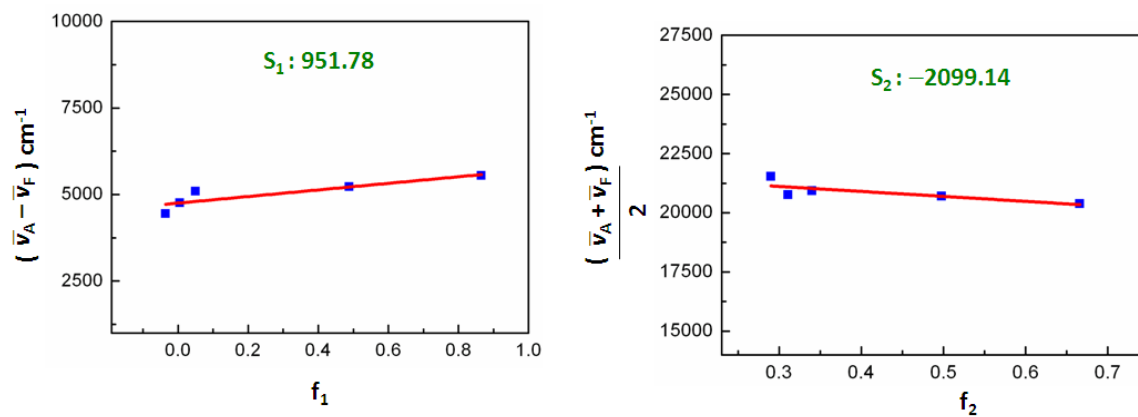| Solvent	λ_a (nm)	$\bar{v}_a$ (cm^{-1})	λ_f (nm)	$\bar{v}_f$ (cm^{-1})	$(\bar{v}_a - \bar{v}_f)$ (cm^{-1})	$(\bar{v}_a + \bar{v}_f)/2$ (cm^{-1})
Cyclohexane	421.0	23752.97	518.0	19305.02	4447.95	21528.99
Benzene	429.0	23310.02	539.0	18552.88	4757.13	20931.45
1,4-Dioxane	429.0	23310.02	549.0	18214.94	5095.08	20762.48
Ethylacetate	429.0	23310.02	553.0	18083.18	5226.84	20696.60
Acetonitrile	432.0	23148.15	568.0	17605.63	5542.52	20376.89

Fig. S11 Plot of solvent shift data versus polarity functions f_1 and f_2 for different solvents using fluorenone **2** as the probe.
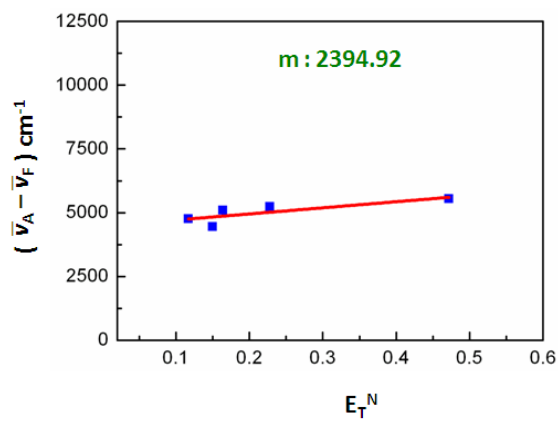

Fig. S12 Plot of Stokes shift versus E_T^N for different solvents using fluorenone **2** as the polarity probe.

Table S3 Experimentally Determined Dipole Moment Values of Fluorenone **2**.

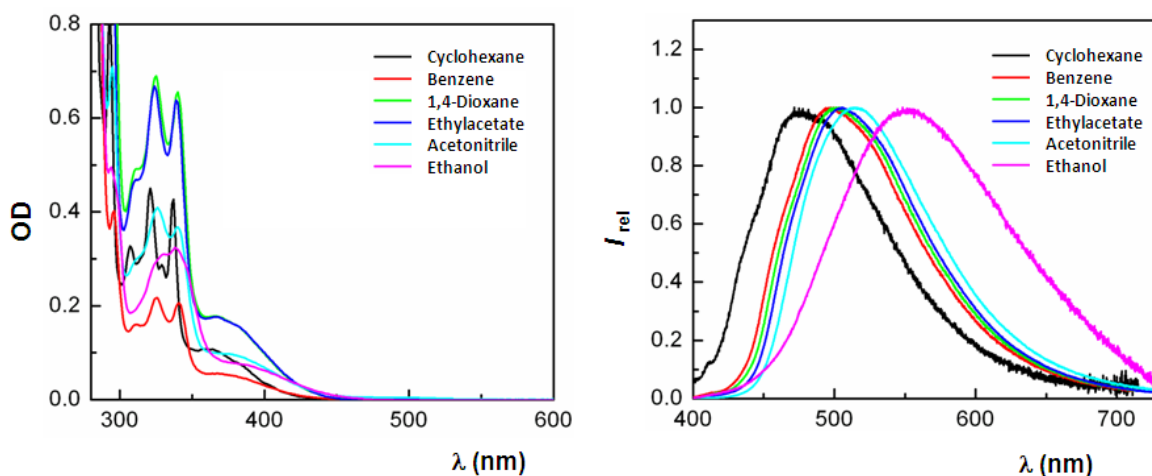| Property	Estimated Value
S_1	951.78
S_2	-2099.14
$\dfrac{\mu_e}{\mu_g} = \dfrac{\lvert S_1 - S_2 \rvert}{\lvert S_1 + S_2 \rvert}$	2.66
m	2394.92
a (Å)	3.5
$\Delta\mu = (\mu_e - \mu_g)$(D)	1.76
μ_e (D)	2.82
μ_g(D)	1.06

Fig. S13 UV-vis absorption (left) and fluorescence (right) spectral profiles of fluorenone **3** in different solvents.

Table S4 Solvent Shift Data for Fluorenone **3**.

| Solvent	λ_a (nm)	$\bar{v}_a$ (cm^{-1})	λ_f (nm)	$\bar{v}_f$ (cm^{-1})	$(\bar{v}_a - \bar{v}_f)$ (cm^{-1})	$(\bar{v}_a + \bar{v}_f)/2$ (cm^{-1})
Cyclohexane	365.0	27397.26	472.0	21186.44	6210.82	24291.85
Benzene	364.0	27472.52	495.0	20202.02	7270.5	23837.27
1,4-Dioxane	367.0	27247.96	499.0	20040.01	7207.95	23643.99
Ethylacetate	368.0	27173.91	505.0	19801.98	7371.93	23487.95
Acetonitrile	379.0	26385.22	510.0	19607.80	6777.42	22996.51
Ethanol	387.0	25839.79	549.0	18214.94	7624.85	22027.37
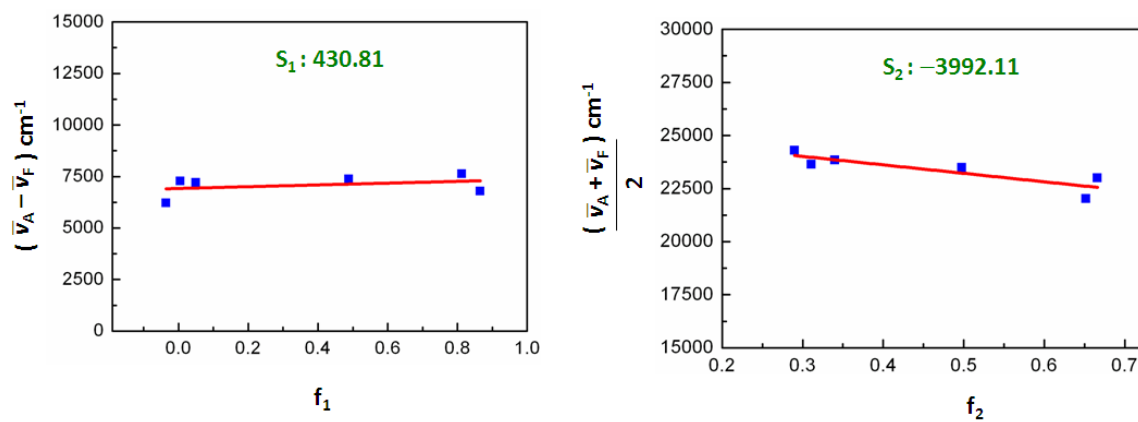
Fig. S14 Plot of solvent shift data versus polarity functions f_1 and f_2 for different solvents using fluorenone **3** as the probe.
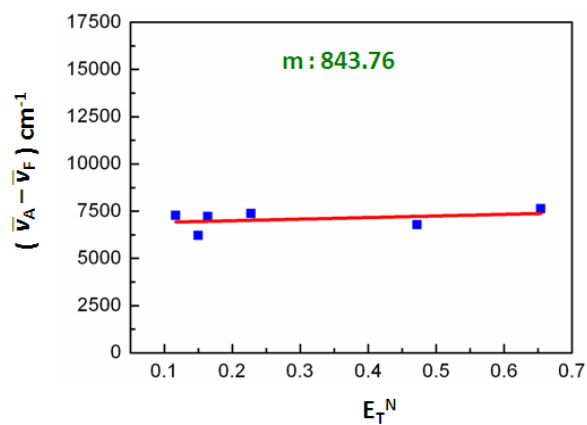

Fig. S15 Plot of Stokes shift versus E_T^N for different solvents using fluorenone **3** as the polarity probe.

Table S5 Experimentally Determined Dipole Moment Values of Fluorenone **3**.

Property	Estimated Value
S_1	430.81
S_2	-3992.11
$\dfrac{\mu_e}{\mu_g} = \dfrac{|S_1 - S_2|}{|S_1 + S_2|}$	1.24
m	843.76
a (Å)	3.5
$\Delta\mu = (\mu_e - \mu_g)$(D)	1.04
μ_e (D)	5.37
μ_g(D)	4.33

Table S6 Comparative Experimental Data of the Dipole Moments of Fluorenones **2** and **3**.

Property	Estimated Values	
	Fluorenone **2**	Fluorenone **3**
μ_g(D)	1.06	4.33
μ_e (D)	2.82	5.37
$\dfrac{\mu_e}{\mu_g}$	2.66	1.24
$\Delta\mu = (\mu_e - \mu_g)$(D)	1.76	1.04

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