Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

The excited state dipole moments of betaine pyridinium investigated by an innovative solvatochromic analysis and TDDFT calculations.

Supporting Info

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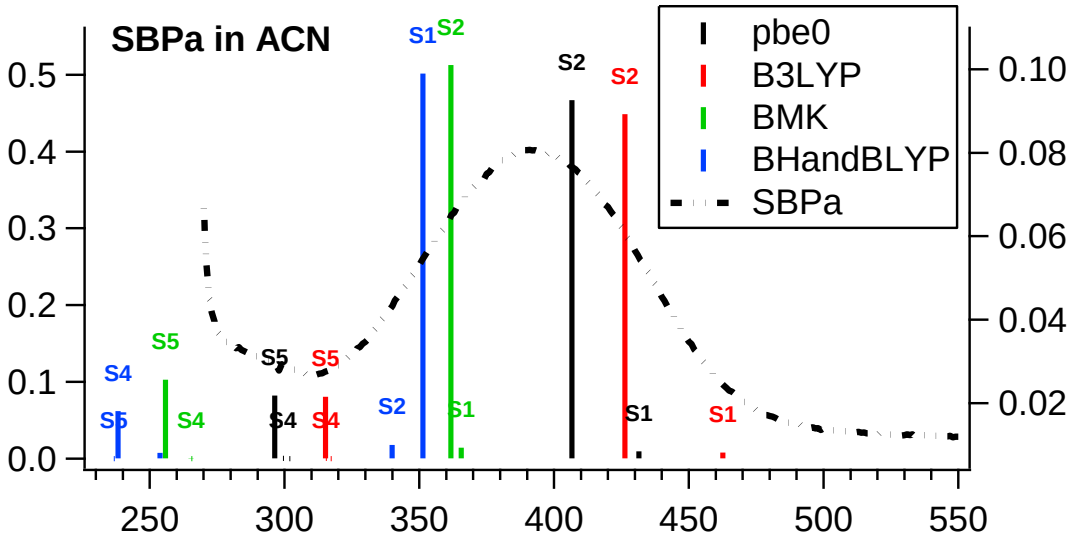


Figure SI1. Absorption spectrum of SBPa and PCM-TD-/6-311++G(2d,p)//PBE0/6-311G(d) oscillator strength for different functionals PBE0, B3LYP, BMK, BHandBLP in acetonitrile.

		ACN		THF		Toluene	
Exp		3.1872	$\Delta_{exp-theo}$	2.9590	$\Delta_{exp-theo}$	2.8307	$\Delta_{exp-theo}$
B3LYP	(20%)	2.9085 (S_2)	0.2787	2.8019 (S_2)	0.1571	2.5719 (S_2)	0.2588
PBE0	(25%)	3.0490 (S_2)	0.1382	2.9353 (S_2)	0.0237	2.6828 (S_2)	0.1479
BMK	(42%)	3.4279 (S_2)	-0.2407	3.3022 (S_2)	-0.3432	3.0032 (S_2)	-0.1725
BHandHLYP	(50%)	3.5291 (S_1)	-0.3419	3.3965 (S_1)	-0.4375	3.0672 (S_1)	-0.2365

Table SI1: Experimental and TDDFT theoritical CT band position in eV for different functionals. The main electronic state involved is indicated in parentheses.

	Basis	Vaccum	THF	ACN
PBE0	6-311++g(d,p)	4.92	4.52	4.74
	6-311g(d,p)	4.61	4.95	4.83
	6-31g	4.66	4.67	4.62

Table SI2: DFT/PCM Calculated Onsager radii (in Å) for SBPa in vacuum, in THF, and in acetonitrile using the PBE0 functional with different basis sets.

INNOVATIVE PHYSICAL SOLVATOCHROMIC DATA TREATMENT

The inputs of our algorithm are the experimental solvatochromic data $\{\nu_{Abs}^{sol}\}$ or $\{\nu_{Fluo}^{sol}\}$ and the solvent properties n and ε while the adjustable parameters are the molecular polarizability α and gas phase absorption/emission band maxima $\nu_{Abs}^{gaz}/\nu_{fluo}^{gaz}$. The main idea of this approach is based on the principle that the best set of $\nu_{Abs/Fluo}^{gaz}$ and α parameters should lead to the most accurate non-linear fit of the solvatochromic data according to eq 5 (main article). Thus, we have imagined to plot in a 2D map the variation of the mean square coefficient χ^2 characterizing this non linear fit as a function of both the $\nu_{Abs/Fluo}^{gaz}$ and α values. Analyzing this 2D map should allow to visualize directly the optimum values of $\nu_{Abs/Fluo}^{gaz}$ and α. The algorithm core (double implementation structure), illustrated in figure SI1, can be described as follows:

STEP 1: the experimental data $\{\nu_{Abs}^{sol}\}$ or $\{\nu_{Fluo}^{sol}\}$ measured for a given set of solvents $\{n, \varepsilon\}$ are selected. Appropriate intervals for the adjustable parameters $\nu_{Abs/Fluo}^{gaz}$ and α are chosen. The polarizability is scanned within the [0; 1.2] interval while ν_{Abs}^{gaz} and ν_{Fluo}^{gaz} are scanned within the [15000; 28000 cm^{-1}] and [10000; 17000 cm^{-1}] frequency intervals, respectively.

STEP 2:

a) a pair of $\nu_{Abs/Fluo}^{gaz}$ and α values is implemented in the loop. The 2 functions $g(n, \varepsilon, \alpha)$ and $h(n, \alpha)$ (eqs. 2 and 3) and $\Delta\nu_{Abs/Fluo} = \nu_{Abs/Fluo}^{sol} - \nu_{Abs/Fluo}^{gaz}$ (left side of eq. 4) are determined.

b) Then the $\Delta\nu_{Abs/Fluo}$ values are plotted for all solvents as a function of $g(n, \varepsilon, \alpha)$ and $h(n, \alpha)$ in a 3D graph $\Delta\nu_{Abs/Fluo}$ = f[$g(n, \varepsilon, \alpha)$, $h(n, \alpha)$].

c) Non-linear fits of $\Delta\nu_{Abs/Fluo}$ by the equation plane $K_1 g(n, \varepsilon, \alpha) - K_2 h(n, \alpha)$ (eq. 5) is performed and the fitted parameters K_1 and K_2 as well as χ^2 are stored.

Then the $\nu_{Abs/Fluo}^{gaz}$ and α values are incremented step by step within their respective intervals. For each set of values, the above operations a – c listed in step 2 are repeated until the overall chosen ranges are spanned by the procedure.

STEP 3: a 2D map of χ^2 as a function of the $\nu_{Abs/Fluo}^{gaz}$ and α values is built and its minimum value is detected. Alternatively, other interesting regions of the 2D map can be tested.

STEP 4: for the selected points chosen above, $\mu_g(S_0)$, $\mu_e(S_2)$ (abs) or $\mu_e(S_1)$ $\mu_g(S_0')$ (emiss) are computed from K_1 and K_2 according to eq.6-9 after implementing an Onsager radius of 4.75 Å (DFT calculations; see table SI2) and a phase value θ = 0 or π.

Solvatochromic Data Treatment Algorithm

GOAL= determinations of 2 dipole moments

3 inputs:
- Set of solvant values: $\{n, \varepsilon\}$
- Solvatochromic data: $\{\nu_{Abs}^{sol}\}$ or $\{\nu_{Fluo}^{sol}\}$

2 adjustable parameters:
- ν_{Abs}^{gaz} or ν_{Fluo}^{gaz} (gas phase!)
- and polarizability α.

2 outputs:

$\mu_g(S_0)$, $\mu_e(S_2)$ (absorption) or

$\mu_e(S_1)$, $\mu_g(S_0')$ (emission)

STEP 1

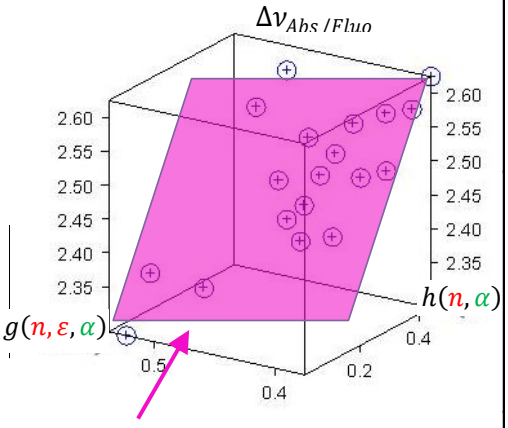
One chooses appropriate intervals for $[\nu_{Abs/fluo}^{gaz}]$ and $[\alpha]$.

STEP 2

a) For a pair of values $(\nu_{Abs/Fluo}^{gaz}; \alpha)$ one computes:
- $g(n, \varepsilon, \alpha)$
- $h(n, \alpha)$
- $\Delta\nu_{Abs/Fluo} = \nu_{Abs/Fluo}^{sol} - \nu_{Abs/Fluo}^{gaz}$

b) one plots 3D graph

$\Delta\nu_{Abs/Fluo} = f[g(n, \varepsilon, \alpha), h(n, \alpha)]$



c) Non-linear fit: $\Delta\nu_{abs/fluo} = K_1 g(n, \varepsilon, \alpha) - K_2 h(n, \alpha)$

⇒ **K_1, K_2 and χ^2 are stored**

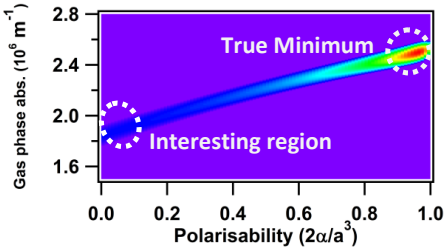
operation a)-c) repeated until both $[\nu_{Abs/fluo}^{gaz}]$ and $[\alpha]$ are spanned

STEP 3

2D Map are plotted

$\chi^2 = f(\nu_{Abs/Fluo}^{gaz}; \alpha)$

⇒ identification of true minimum or other relevant points



STEP 4

For the selected points :
- **K_1, K_2**
- **Onsager radius=4.75 Å**
- **Phase θ=0 or π**

absorption

$$\mu_g(S_0) = \frac{1}{\sqrt{4\pi\varepsilon_0 a^3}} \frac{K_1}{\sqrt{2(K_1 - K_2)}}$$

$$\mu_e(S_2) = \frac{(cos\theta)^{-1}}{\sqrt{4\pi\varepsilon_0 a^3}} \frac{K_2}{\sqrt{2(K_1 - K_2)}}$$

emission

$$\mu_g'(S_0') = \frac{1}{\sqrt{4\pi\varepsilon_0 a^3}} \frac{2K_2 - K_1}{\sqrt{2(K_1 - K_2)}}$$

$$\mu_e(S_1) = \frac{(cos\theta)^{-1}}{\sqrt{4\pi\varepsilon_0 a^3}} \frac{K_1}{\sqrt{2(K_1 - K_2)}}$$

figure SI2. Overall illustration of the 4 step algorithm related to the Innovative physical solvatochromic data treatment.

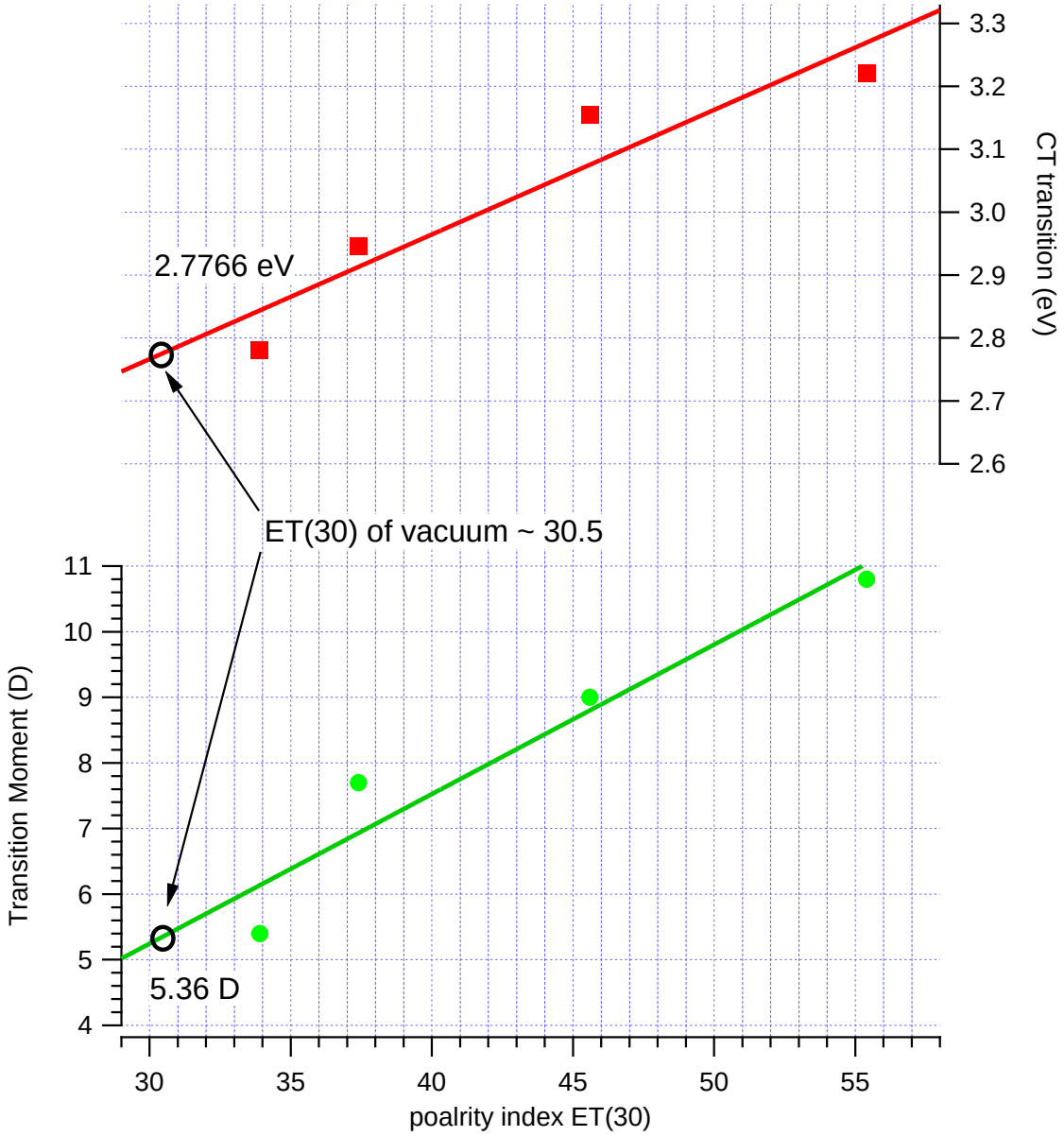


Figure SI3. Transition energy and transition moment of the solvatochromic CT band of SBPa (see fig 1 and Table 2) in Toluene, THF, ACN and MeOH. The extrapolated values for vacuum are indicated.