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

Supporting Info

Zuzanna Pawlowska, Aude Lietard, Stéphane Aloïse*, Michel Sliwa, Abdenacer Idrissi, Olivier Poizat and Guy Buntinx.

Laboratoire de Spectrochimie Infrarouge et Raman (UMR 8516 du CNRS), Université des Sciences et Technologies de Lille, Bat C5, 59655 Villeneuve d’Ascq Cedex, France.

Stéphanie Delbaere

Université Lille Nord de France, UDSL, Laboratoire de Spectrochimie Infrarouge et Raman (UMR 8516 du CNRS), 3 rue du Professeur Laguesse BP83, F-59006 Lille, France.

Aurélie Perrier, François Maurel

Laboratoire Interfaces, Traitements, Organisation et Dynamique des Systèmes, CNRS UMR 7086, Université Paris Diderot, Bât. Lavoisier, 15 rue Jean Antoine de Baif, 75205 Paris Cedex 13, France.

Patrice Jacques

Ecole Nationale Supérieure de Chimie de Mulhouse, Université de Haute-Alsace, 3 rue Alfred Werner, 68093 Mulhouse, France

Jiro Abe,

Department of Chemistry, School of Science and Engineering, Aoyama Gakuin University 5-10-1 Fuchinobe, Sagamihara, Kanagawa 229-8558, Japan.

*stephane.aloise@univ-lille1.fr
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, BHandBLYP in acetonitrile.

<table>
<thead>
<tr>
<th>Run</th>
<th></th>
<th>ACN</th>
<th>THF</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp</td>
<td></td>
<td>3.1872</td>
<td>2.9590</td>
<td>2.8307</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.9085 (S₂)</td>
<td>2.8019 (S₂)</td>
<td>2.5719 (S₂)</td>
</tr>
<tr>
<td>B3LYP</td>
<td>(20%)</td>
<td>0.2787</td>
<td>0.1571</td>
<td>0.2588</td>
</tr>
<tr>
<td>PBE0</td>
<td>(25%)</td>
<td>3.0490 (S₂)</td>
<td>2.9353 (S₂)</td>
<td>2.6828 (S₂)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1382</td>
<td>0.0237</td>
<td>0.1479</td>
</tr>
<tr>
<td>BMK</td>
<td>(42%)</td>
<td>3.4279 (S₂)</td>
<td>3.3022 (S₂)</td>
<td>3.0032 (S₂)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-0.2407</td>
<td>-0.3432</td>
<td>-0.1725</td>
</tr>
<tr>
<td>BHandHLYP</td>
<td>(50%)</td>
<td>3.5291 (S₁)</td>
<td>3.3965 (S₁)</td>
<td>3.0672 (S₁)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-0.3419</td>
<td>-0.4375</td>
<td>-0.2365</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Run</th>
<th>Basis</th>
<th>Vacuum</th>
<th>THF</th>
<th>ACN</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE0</td>
<td>6-311++g(d,p)</td>
<td>4.92</td>
<td>4.52</td>
<td>4.74</td>
</tr>
<tr>
<td></td>
<td>6-311g(d,p)</td>
<td>4.61</td>
<td>4.95</td>
<td>4.83</td>
</tr>
<tr>
<td></td>
<td>6-31g</td>
<td>4.66</td>
<td>4.67</td>
<td>4.62</td>
</tr>
</tbody>
</table>

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 \( \{v_{\text{Abs}}^{\text{sol}}\} \) or \( \{v_{\text{Fluo}}^{\text{sol}}\} \) and the solvent properties \( n \) and \( \varepsilon \) while the adjustable parameters are the molecular polarizability \( \alpha \) and gas phase absorption/emission band maxima \( v_{\text{Abs}}^{\text{gaz}} \) or \( v_{\text{Fluo}}^{\text{gaz}} \). The main idea of this approach is based on the principle that the best set of \( v_{\text{Abs/Fluo}}^{\text{gaz}} \) and \( \alpha \) 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 \( \chi^2 \) characterizing this non-linear fit as a function of both the \( v_{\text{Abs/Fluo}}^{\text{gaz}} \) and \( \alpha \) values. Analyzing this 2D map should allow to visualize directly the optimum values of \( v_{\text{Abs/Fluo}}^{\text{gaz}} \) and \( \alpha \). The algorithm core (double implementation structure), illustrated in figure SI1, can be described as follows:

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

**STEP 2:**

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

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

c) Non-linear fits of \( \Delta v_{\text{Abs/Fluo}} \) by the equation plane \( K_1g(n, \varepsilon, \alpha) - K_2h(n, \alpha) \) (eq. 5) is performed and the fitted parameters \( K_1 \) and \( K_2 \) as well as \( \chi^2 \) are stored.

Then the \( v_{\text{Abs/Fluo}}^{\text{gaz}} \) and \( \alpha \) 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 \( \chi^2 \) as a function of the \( v_{\text{Abs/Fluo}}^{\text{gaz}} \) and \( \alpha \) 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 \( \theta = 0 \) or \( \pi \).
Solvatochromic Data Treatment Algorithm

**GOAL:** determinations of 2 dipole moments

**3 inputs:**

- Set of solvant values: \([n, \varepsilon]\)
- Solvatochromic data: \([\nu^\text{sol}_{\text{Abs}}] \text{ or } [\nu^\text{sol}_{\text{Fluo}}]\)

**2 adjustable parameters:**

\(\nu^{\text{gaz}}_{\text{Abs}} \text{ or } \nu^{\text{gaz}}_{\text{Fluo}}\) (gas phase) and polarizability \(\alpha\).

**2 outputs:**

\(\mu(S_0), \mu(S_2)\) (absorption) or \(\mu(S_1), \mu(S'_0)\) (emission)

**STEP 1**

One chooses appropriate intervals for \([\nu^{\text{gaz}}_{\text{Abs/Fluo}}]\) and \([\alpha]\).

**STEP 2**

a) For a pair of values \((\nu^{\text{gaz}}_{\text{Abs/Fluo}}, \alpha)\)

one computes:

- \(g(n, \varepsilon, \alpha)\)
- \(h(n, \alpha)\)
- \(\Delta \nu^{\text{Abs/Fluo}} = \nu^{\text{gaz}}_{\text{Abs/Fluo}} - \nu^{\text{gaz}}_{\text{Abs/Fluo}}\)

b) one plots 3D graph

\(\Delta \nu^{\text{Abs/Fluo}} = [g(n, \varepsilon, \alpha), h(n, \alpha)]\)

c) Non-linear fit: \(\Delta \nu^{\text{Abs/Fluo}} = K_1 g(n, \varepsilon, \alpha) - K_2 h(n, \alpha)\)

\(\Rightarrow K_1, K_2 \text{ and } \chi^2 \text{ are stored}\)

**operation a)-c) repeated until both } [\nu^{\text{gaz}}_{\text{Abs/Fluo}}] \text{ and } [\alpha] \text{ are spanned}\)

**STEP 3**

2D Map are plotted

\(\chi^2 = f(\nu^{\text{gaz}}_{\text{Abs/Fluo}}, \alpha)\)

\(\Rightarrow\) identification of true minimum or other relevant points

**STEP 4**

For the selected points:

- \(K_1, K_2\)
- Onsager radius=4.75 Å
- Phase \(\theta=0 \text{ or } \pi\)

\(\mu_g(S_0) = \frac{1}{\sqrt{4\pi\varepsilon_0a^2}} K_1\)

\(\mu_g(S_2) = \frac{1}{\sqrt{4\pi\varepsilon_0a^2}} \frac{2(K_1 - K_2)}{K_2 - K_1}\)

\(\mu_g(S'_0) = \frac{1}{\sqrt{4\pi\varepsilon_0a^2}} \frac{2(K_1 - K_2)}{2K_2 - K_1}\)

\(\mu_g(S_1) = \frac{1}{\sqrt{4\pi\varepsilon_0a^2}} K_1\)

\(\mu_g(S'_1) = \frac{1}{\sqrt{4\pi\varepsilon_0a^2}} \frac{2(K_1 - K_2)}{2K_2 - K_1}\)

Figure S12. 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.