The optical signature of 2,6-bis((E)-2-(benzoxazol-2-yl)vinyl)naphthalene (BBVN) laser dye: A TDDFT Study

Essam Hammam, a Iqbal Ismail, b Jalal Basahi, b Talal Almeelbi b and Ibrahim Hassan b

a Department of Chemistry and Biochemistry, University of North Carolina Wilmington, 601 S. College Road, Wilmington, NC 28403, USA, Email: elbehadie@uncw.edu
b Center of Excellence in Environmental Studies, King Abdulaziz University, P.O. Box 80216, Jeddah 21589, Saudi Arabia

Table S1 Some selected structural parameters for the BBVN laser dye in both ground (GS) and first excited (ES) singlet states with the corresponding Mulliken atomic charges computed at the BMK/cc-pvdz level of theory in gas phase.

<table>
<thead>
<tr>
<th>Bond length (Å)</th>
<th>GS (S0)</th>
<th>ES (S1)</th>
<th>C</th>
<th>Atomic charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4-C5</td>
<td>1.4079</td>
<td>1.4167</td>
<td>C1</td>
<td>-0.016</td>
</tr>
<tr>
<td>C4-N7</td>
<td>1.3906</td>
<td>1.3756</td>
<td>C2</td>
<td>-0.015</td>
</tr>
<tr>
<td>C5-O9</td>
<td>1.3570</td>
<td>1.3524</td>
<td>C3</td>
<td>-0.037</td>
</tr>
<tr>
<td>N7-C8</td>
<td>1.3023</td>
<td>1.3188</td>
<td>C4</td>
<td>0.025</td>
</tr>
<tr>
<td>C8-C10</td>
<td>1.4536</td>
<td>1.4278</td>
<td>C5</td>
<td>0.150</td>
</tr>
<tr>
<td>C10-C11</td>
<td>1.3525</td>
<td>1.3827</td>
<td>C6</td>
<td>-0.056</td>
</tr>
<tr>
<td>C11-C12</td>
<td>1.4721</td>
<td>1.4331</td>
<td>N7</td>
<td>-0.246</td>
</tr>
<tr>
<td>C12-C13</td>
<td>1.3924</td>
<td>1.4305</td>
<td>C8</td>
<td>0.244</td>
</tr>
<tr>
<td>C13-C14</td>
<td>1.4208</td>
<td>1.3950</td>
<td>C9</td>
<td>-0.228</td>
</tr>
<tr>
<td>C14-C15</td>
<td>1.4362</td>
<td>1.4519</td>
<td>C10</td>
<td>-0.069</td>
</tr>
<tr>
<td>C15-C21</td>
<td>1.4208</td>
<td>1.3951</td>
<td>C11</td>
<td>0.033</td>
</tr>
<tr>
<td>C21-C20</td>
<td>1.3926</td>
<td>1.4323</td>
<td>C12</td>
<td>0.054</td>
</tr>
<tr>
<td>C20-C22</td>
<td>1.4710</td>
<td>1.4285</td>
<td>C13</td>
<td>-0.057</td>
</tr>
<tr>
<td>C22-C23</td>
<td>1.3521</td>
<td>1.3870</td>
<td>C14</td>
<td>0.054</td>
</tr>
<tr>
<td>C23-C24</td>
<td>1.4570</td>
<td>1.4261</td>
<td>C15</td>
<td>0.056</td>
</tr>
<tr>
<td>C24-N28</td>
<td>1.3018</td>
<td>1.3219</td>
<td>C16</td>
<td>-0.023</td>
</tr>
<tr>
<td>N28-C27</td>
<td>1.3888</td>
<td>1.3716</td>
<td>C17</td>
<td>-0.027</td>
</tr>
<tr>
<td>C27-C26</td>
<td>1.4085</td>
<td>1.4186</td>
<td>C18</td>
<td>-0.023</td>
</tr>
</tbody>
</table>

| Bond angles (°) | | | | |
|-----------------| | | | |
| C4-N7-C8        | 104.07 | 104.36 | C20| 0.055          |
| C5-O9-C8        | 104.68 | 104.80 | C21| -0.059         |
| C8-C10-C11      | 123.31 | 123.49 | C22| 0.047          |
| C10-C11-C12     | 126.71 | 125.90 | O23| -0.085         |
| Torsional angles (°) | | | | |
| O9-C8-C10-C11   | 0.0 | 0.0 | O25| -0.226         |
| C8-C10-C11-C12  | -180.0 | -180.0 | C26| 0.143          |
| C10-C11-C12-C13 | 0.0 | 0.0 | C27| 0.038          |
| N28-C27         | -0.251 | -0.254 | C29| -0.055         |

| Dipole Moment (D) | | | | |
|-------------------| | | | |
| 2.21              | 2.20 | C29| -0.055         |
|                   |     | C30| -0.017         |
|                   |     | C31| -0.015         |
|                   |     | C32| -0.041         |
Fig. S1 Molecular structures of EE-, EZ-, and ZZ-BBVN isomers.

Table S2 Dipole moments and dipole moment shifts ($\Delta D$, in Debye) upon photon absorption (abs) and emission (fl) obtained for BBVN at the BMK/cc-pvdz level at the optimal geometry of the ground state (GS) and excited state (ES) in the corresponding solvent.

<table>
<thead>
<tr>
<th>Dipole Moment</th>
<th>Gas phase</th>
<th>Dioxane ($\varepsilon=2.2099$)</th>
<th>Acetone</th>
<th>MeOH</th>
<th>CH$_3$CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0$(GS)</td>
<td>2.21</td>
<td>2.64</td>
<td>3.41</td>
<td>3.43</td>
<td>3.48</td>
</tr>
<tr>
<td>$S'$(GS)</td>
<td>2.38</td>
<td>2.86</td>
<td>3.51</td>
<td>3.53</td>
<td>3.58</td>
</tr>
<tr>
<td>$S_1$(ES)</td>
<td>2.20</td>
<td>2.92</td>
<td>3.87</td>
<td>3.89</td>
<td>3.96</td>
</tr>
<tr>
<td>$S'$(ES)</td>
<td>2.20</td>
<td>2.64</td>
<td>3.44</td>
<td>3.45</td>
<td>3.51</td>
</tr>
<tr>
<td>$\Delta D$(GS)$_{\text{abs}}$</td>
<td>0.17</td>
<td>0.22</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>$\Delta D$(ES)$_{\text{fl}}$</td>
<td>0.0</td>
<td>0.28</td>
<td>0.43</td>
<td>0.44</td>
<td>0.45</td>
</tr>
<tr>
<td>$\Delta \Delta D_{\text{fl-abs}}$</td>
<td>0.06</td>
<td>0.33</td>
<td>0.34</td>
<td>0.34</td>
<td>0.35</td>
</tr>
</tbody>
</table>

$\Delta D$(GS)$_{\text{abs}} = S_1'(GS) - S_0(GS)$, $\Delta D$(ES)$_{\text{fl}} = S_1(ES) - S_0'(ES)$, $\Delta \Delta D_{\text{fl-abs}} = \Delta D$(ES)$_{\text{fl}} - \Delta D$(GS)$_{\text{abs}}$