Dynamic nature of excited states of donor-acceptor TADF materials for OLEDs: how theory can reveal structure-property relationships.

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Table S1: Relative energies between axial and equatorial (in kcal/mol) conformers for D-A and D-A-D compounds calculated at the PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene).

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<th>Compound</th>
<th>Conformer</th>
<th>$\Delta E$ (kcal/mol)</th>
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Table S2: Relative energies between axial and equatorial (in kcal/mol) conformers for D-A and D-A-D compounds calculated at the PBE0-D3(BJ)/def2TZVP level of theory with the PCM module for solvent (toluene).
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**Table S3:** Sₑ and T₁ excitations energies and their associated singlet-triplet energy gap (ΔEST) for the equatorial conformer as well as the attachment and detachment densities overlap and distance difference between attachment and detachment densities centroids of the different compounds calculated at the TDA-PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene). Oscillator strengths (O.S.) for S₁ electronic transitions as well as the symmetry point group of the ground state optimized geometries (in parenthesis next to the molecule names) are also reported.
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**Table S4:** S₁ and T₁ excitations and their associated singlet-triplet energy gap (ΔE<sub>ST</sub>) for the equatorial conformer of the different compounds calculated at the TDA-PBE0-D3(BJ)/def2TZVP level of theory with the PCM module for solvent (toluene). Oscillator strengths (O.S.) for S₁ electronic transitions as well as the symmetry point group of the ground state optimized geometries (in parenthesis next to the molecule names) are also reported.
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<th>Energy (eV)</th>
<th>O.S.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2PXZ-OXD (Cs)</td>
<td>2.799</td>
<td>-</td>
<td>2.543</td>
<td>-</td>
<td>3.158</td>
<td>-</td>
</tr>
<tr>
<td>2PXZ-TDZ (Cs)</td>
<td>3.470</td>
<td>1.730</td>
<td>3.211</td>
<td>1.807</td>
<td>3.750</td>
<td>1.439</td>
</tr>
<tr>
<td>2PXZ-TAZ (C1)</td>
<td>0.671</td>
<td>0.668</td>
<td>0.592</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Energy (eV)</th>
<th>O.S.</th>
<th>Energy (eV)</th>
<th>O.S.</th>
<th>Energy (eV)</th>
<th>O.S.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2PTZ-OXD (Cs)</td>
<td>2.811</td>
<td>-</td>
<td>2.529</td>
<td>-</td>
<td>3.142</td>
<td>-</td>
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<tr>
<td>2PTZ-TDZ (Cs)</td>
<td>3.505</td>
<td>1.691</td>
<td>3.207</td>
<td>1.410</td>
<td>3.716</td>
<td>1.947</td>
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<tr>
<td>2PTZ-TAZ (C1)</td>
<td>0.693</td>
<td>0.678</td>
<td>0.574</td>
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</table>

**Table S5**: S₁ and T₁ excitations and their associated singlet-triplet energy gap (ΔEₘ) for the axial conformer of the different compounds calculated at the TDA-PBE0-D3(BJ)/def2TZVP level of theory with the PCM module for solvent (toluene). Oscillator strengths (O.S.) for S₁ electronic transitions as well as the symmetry point group of the ground state optimized geometries (in parenthesis next to the molecule names) are also reported.
<table>
<thead>
<tr>
<th></th>
<th>PXZ-OXD (Cs)</th>
<th>PXZ-TDZ (Cs)</th>
<th>PXZ-TAZ (C1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S_0$</td>
<td>$S_1$</td>
<td>$T_1$</td>
</tr>
<tr>
<td>Angle (°)</td>
<td>83.08</td>
<td>90.31</td>
<td>89.69</td>
</tr>
<tr>
<td></td>
<td>PTZ-OXD (Cs)</td>
<td>PTZ-TDZ (Cs)</td>
<td>PTZ-TAZ (C1)</td>
</tr>
<tr>
<td></td>
<td>$S_0$</td>
<td>$S_1$</td>
<td>$T_1$</td>
</tr>
<tr>
<td>Angle (°)</td>
<td>79.33</td>
<td>89.82</td>
<td>90.16</td>
</tr>
<tr>
<td></td>
<td>2PXZ-OXD (C2V)</td>
<td>2PXZ-TDZ (C2V)</td>
<td>2PXZ-TAZ (C2)</td>
</tr>
<tr>
<td></td>
<td>$S_0$</td>
<td>$S_1$</td>
<td>$T_1$</td>
</tr>
<tr>
<td>Angle (°)</td>
<td>84.60</td>
<td>89.65</td>
<td>90.35</td>
</tr>
<tr>
<td></td>
<td>2PTZ-OXD (Cs)</td>
<td>2PTZ-TDZ (C2V)</td>
<td>2PTZ-TAZ (C2)</td>
</tr>
<tr>
<td></td>
<td>$S_0$</td>
<td>$S_1$</td>
<td>$T_1$</td>
</tr>
<tr>
<td>Angle (°)</td>
<td>81.18</td>
<td>88.38</td>
<td>89.54</td>
</tr>
</tbody>
</table>

**Table S6:** Equilibrium D-A torsion angles (in degrees) for ground state ($S_0$) and, singlet ($S_1$) and triplet ($T_1$) excited state (Tamm-Dancoff) optimization at PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene).
<table>
<thead>
<tr>
<th>State</th>
<th>PXZ-OXD</th>
<th>PXZ-TDZ</th>
<th>PXZ-TAZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>T₁</td>
<td>99.9</td>
<td>99.9</td>
<td>99.3</td>
</tr>
<tr>
<td>S₁</td>
<td>99.9</td>
<td>99.9</td>
<td>99.8</td>
</tr>
<tr>
<td>T₂</td>
<td>92.9</td>
<td>92.1</td>
<td>93.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>State</th>
<th>PTZ-OXD</th>
<th>PTZ-TDZ</th>
<th>PTZ-TAZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>T₁</td>
<td>99.6</td>
<td>99.8</td>
<td>93.0</td>
</tr>
<tr>
<td>S₁</td>
<td>99.9</td>
<td>99.9</td>
<td>99.8</td>
</tr>
<tr>
<td>T₂</td>
<td>88.4</td>
<td>92.0</td>
<td>96.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>State</th>
<th>2PXZ-OXD</th>
<th>2PXZ-TDZ</th>
<th>2PXZ-TAZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>T₁</td>
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<td>96.4</td>
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<tr>
<td>T₂</td>
<td>92.2</td>
<td>96.4</td>
<td>85.9</td>
</tr>
<tr>
<td>S₁</td>
<td>92.6</td>
<td>96.6</td>
<td>87.0</td>
</tr>
<tr>
<td>S₂</td>
<td>92.6</td>
<td>96.6</td>
<td>87.1</td>
</tr>
<tr>
<td>T₃</td>
<td>46.9</td>
<td>91.9</td>
<td>47.0</td>
</tr>
<tr>
<td>T₄</td>
<td>46.9</td>
<td>47.3</td>
<td>47.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>State</th>
<th>2PTZ-OXD</th>
<th>2PTZ-TDZ</th>
<th>2PTZ-TAZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>T₁</td>
<td>92.1</td>
<td>96.5</td>
<td>69.7</td>
</tr>
<tr>
<td>T₂</td>
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<td>96.5</td>
<td>69.6</td>
</tr>
<tr>
<td>S₁</td>
<td>93.2</td>
<td>96.9</td>
<td>87.4</td>
</tr>
<tr>
<td>S₂</td>
<td>93.2</td>
<td>96.9</td>
<td>87.3</td>
</tr>
<tr>
<td>T₃</td>
<td>88.1</td>
<td>91.9</td>
<td>61.6</td>
</tr>
<tr>
<td>T₄</td>
<td>45.5</td>
<td>45.5</td>
<td>61.7</td>
</tr>
</tbody>
</table>

**Table S7:** Composition of the excited states transitions in terms of the HONTO to LUNTO transitions.