Pyrene-fused Bisphenazinothiadiazoles with Red to NIR Electroluminescence

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Supporting Information
<table>
<thead>
<tr>
<th>B3LYP 6-311+g(2d,p)</th>
<th>LUMO+2</th>
<th>LUMO+1</th>
<th>LUMO</th>
<th>HOMO</th>
<th>HOMO-1</th>
<th>HOMO-2</th>
<th>gap</th>
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<tbody>
<tr>
<td>1 (alternate)</td>
<td>-2.12</td>
<td>-3.47</td>
<td>-3.48</td>
<td>-5.72</td>
<td>-5.76</td>
<td>-6.27</td>
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<tr>
<td>1 (parallel)</td>
<td>-2.12</td>
<td>-3.47</td>
<td>-3.48</td>
<td>-5.77</td>
<td>-5.82</td>
<td>-6.29</td>
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<tr>
<td>2 (UD-DU-UD)</td>
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<td>-3.77</td>
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<td>-6.33</td>
<td>2.06</td>
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<tr>
<td>2 (DD-UU-DD)</td>
<td>-2.25</td>
<td>-3.76</td>
<td>-3.8</td>
<td>-5.86</td>
<td>-5.91</td>
<td>-6.33</td>
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<td>-4.07</td>
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<td>1.96</td>
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**Table S1.** Frontier orbitals computed with the B3LYP and BMK Hamiltonians with the 6-311+g(2d,p) basis set in dichloromethane on B3LYP-CH\textsubscript{2}Cl\textsubscript{2}-6-31g(d,p) geometries. All values in eV.
<table>
<thead>
<tr>
<th></th>
<th>LUMO(EA)</th>
<th>HOMO(IP)</th>
<th>GAP (EA+IP)</th>
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<tr>
<td>1 (alternate)</td>
<td>-3.52</td>
<td>5.66</td>
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<td>1 (parallel)</td>
<td>-3.53</td>
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<tr>
<td>2 (DD-UU-DD)</td>
<td>-3.82</td>
<td>5.79</td>
<td>1.97</td>
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<tr>
<td><strong>Experimental</strong></td>
<td><strong>LUMO</strong></td>
<td><strong>Opt. gap</strong></td>
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<td>-3.81</td>
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**Table S2.** Vertical ionization potentials (IP) and electron affinities (EA), gap (EA+IP) at the B3LYP level in CH₂Cl₂ from B3LYP-CH₂Cl₂-6-31g(d,p) geometries. All values in eV.
<table>
<thead>
<tr>
<th>B3LYP 6-311+g(2d,p)</th>
<th>eV</th>
<th>nm</th>
<th>Osc. Strength</th>
<th>Major contribs</th>
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</thead>
<tbody>
<tr>
<td>(alternate) 1</td>
<td>1.82</td>
<td>680</td>
<td>0.0811</td>
<td>H-1-&gt;LUMO (14%), HOMO-&gt;LUMO (15%), HOMO-&gt;L+1 (65%)</td>
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<tr>
<td>(alternate) 1</td>
<td>1.83</td>
<td>676</td>
<td>0.2306</td>
<td>H-1-&gt;LUMO (18%), H-1-&gt;L+1 (28%), HOMO-&gt;LUMO (46%)</td>
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<tr>
<td>(parallel) 1</td>
<td>1.87</td>
<td>664</td>
<td>0.0066</td>
<td>H-1-&gt;LUMO (23%), HOMO-&gt;L+1 (75%)</td>
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<tr>
<td>(parallel) 1</td>
<td>1.87</td>
<td>662</td>
<td>0.2873</td>
<td>H-1-&gt;L+1 (31%), HOMO-&gt;LUMO (67%)</td>
</tr>
<tr>
<td>(UD-DU-DD) 2</td>
<td>1.73</td>
<td>716</td>
<td>0.3575</td>
<td>HOMO-&gt;LUMO (90%)</td>
</tr>
<tr>
<td>(UD-DU-DD) 2</td>
<td>1.74</td>
<td>714</td>
<td>0.017</td>
<td>HOMO-&gt;L+1 (90%)</td>
</tr>
<tr>
<td>(UD-DU-DD) 2</td>
<td>1.80</td>
<td>688</td>
<td>0.0044</td>
<td>H-1-&gt;LUMO (90%)</td>
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<tr>
<td>(UD-DU-DD) 2</td>
<td>1.83</td>
<td>677</td>
<td>0.0657</td>
<td>H-1-&gt;L+1 (92%)</td>
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<td>(DD-UU-DD) 2</td>
<td>1.73</td>
<td>716</td>
<td>0.2036</td>
<td>HOMO-&gt;LUMO (68%), HOMO-&gt;L+1 (22%)</td>
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<td>(DD-UU-DD) 2</td>
<td>1.74</td>
<td>713</td>
<td>0.1598</td>
<td>HOMO-&gt;LUMO (24%), HOMO-&gt;L+1 (72%)</td>
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<td>1.81</td>
<td>685</td>
<td>0.0149</td>
<td>H-1-&gt;LUMO (91%)</td>
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<td>674</td>
<td>0.0632</td>
<td>H-1-&gt;L+1 (92%)</td>
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</table>

Table S3. TD-DFT transitions involving frontier orbitals at the B3LYP-CH$_2$Cl$_2$-6311+g(2d,p)/B3LYP-CH$_2$Cl$_2$-6-31(d,p) level (strongest transitions are in bold).
Figure S1. B3LYP-CH$_2$Cl$_2$-6311+g(2d,p)/B3LYP-CH$_2$Cl$_2$-6-31(d,p) level frontier orbitals from top to bottom: 1 alternate and parallel and 2 UD-DU-UD and DD-UU-DD.