Supplementary information

Suppression of Charge Transfer States in Aryl Substituted 9,9’ – Bianthryl Derivatives


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Deconvolution of LE and CT emission spectra

The contribution of LE and CT state emission is evaluated by estimating contribution of LE emission spectra in polar environment, which is obtained in low polarity toluene environment. PLQY of each state can be obtained from overall population of LE and CT species or by comparing radiative decay rates.

DFT modeling of 9,9’ - bianthryl

Ground state

Fig. S1. Optimised geometry and HOMO and LUMO distribution of a refernece 9,9’ - bianthryl BA (a), BATph (b) and 9,9’ - bianthryl BA2ph (c) derivatives.
The geometry optimization of BA’s was carried out for both ground and excited states. Ground state geometry optimization was carried out as follows. First we start with PM6 model, then semi – empirical, Hartree – Fock and DFT. We use B3LYP functional with 6-31g (d,p) basis sets.

For excited state optimization we used TD-DFT methodology, also with B3LYP functional and 6-31g (d,p) basis sets. As a source, we use DFT - optimized geometry of the molecule from ground state. For CT state modeling we used a system of chromophore and solvent molecules in QM:QM point of view.

**HOMO – LUMO distribution: the electrochemical perspective**

To get deeper insight into the distribution of LE states, we compare properties of HOMO and LUMO energy levels in terms of oxidation and reduction reaction. The quality map of HOMO and LUMO energy levels for 9,9’ - bianthryl BA, BAtph and BA2ph is represented as differential pulse voltammetry (DPV) data in Fig. S2 and Table S2. For a reference 9,9’ - bianthryl BA (Fig. S2 a)) compound a sharp peak at 1.27 eV (- 5.63 eV compared to Fc/Fc+ couple) of DPV

### Table S1. Energy and oscillator strength of excited states of a reference 9,9’ - bianthryl BA, BAtph and BA2ph derivatives in optimized $S_0$ geometry.

<table>
<thead>
<tr>
<th></th>
<th>BA</th>
<th>BAtph</th>
<th>BA2ph</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nr.</td>
<td>Energy (eV)</td>
<td>Oscillator</td>
<td>Energy (eV)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>strength</td>
<td></td>
</tr>
<tr>
<td>LE₁</td>
<td>3.12</td>
<td>0.253</td>
<td>3.04</td>
</tr>
<tr>
<td>LE₂</td>
<td>3.24</td>
<td>0.000</td>
<td>3.18</td>
</tr>
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</table>
curve is observed which is a lowest electron energy level in a ground state of the molecule. This state is similar to HOMO energy level, as it represents electron extraction. At a higher energy levels (at around - 1.85 eV and - 2.51 eV compared to Fc/Fc\(^+\) couple) another sharp peak of DPV curve is observed. This represents the introduction of electron to the lowest possible excited state in the molecule and is equivalent to the LUMO energy level, while the second peak is for electron at even higher excited state. The obtained electrochemical band gap \(E_g\) is at around 3.12 eV, also similarly approximated by DFT at \(S_0\) geometry. For 10,10’ – aryl substituted BAph (Fig. S2 b) compound, similar HOMO and LUMO energy levels, followed by almost identical lineshape of DPV curves are observed.

Although 2,2’ – aryl substituted substituted 9,9’ - bianthryl BA2ph (Fig. S2 c) derivative demonstrated similar energy band gap \(E_g\) (2.99 eV), the HOMO and LUMO energy level map is drastically different. First of all, lowest electron energies in a ground and excited states are splitted, which also implies to disrupted resonance interaction between anthracene monomers. The electron energies in a HOMO is distributed evenly, as the intensities of DPV curve are similar. Meanwhile, the LUMO energy levels are dominated by one sharp peak, at 2.53 eV, followed by

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Fig. S2. Differential pulse voltammograms of 9,9’ - bianthyl derivatives BA (a), BA1ph (b) and BA2ph (c) in DMF solution (0.002 M). Measurements were carried out with glassy carbon working electrode and platinum/titanium auxiliary electrode and values calibrated against Fc/Fc\(^+\) couple. Scan rate 20 mV/s
two significantly smaller nearby excited states, also split at around 100 meV. These results confirm differences in DFT approximation, as well as redistribution of the absorption band compared to a reference 9,9’ - bianthryl BA and BAtph compounds.

Table S2. HOMO, LUMO and band gap energy levels of the 9,9’ - bianthryl derivatives. HOMO – LUMO energy levels were estimated by relationship: \( E_{\text{HOMO/LUMO}} = -(4.8 \text{ eV} + E_{\text{OX/RED}} - E_{\text{FC/FC}}) \)

<table>
<thead>
<tr>
<th>Comp.</th>
<th>( E_{\text{HOMO}} ) (eV) [a]</th>
<th>( E_{\text{LUMO}} ) (eV) [b]</th>
<th>( E_{g \text{ el.}} ) (eV) [c]</th>
<th>( E_{\text{HOMO}} ) (eV) [a]</th>
<th>( E_{\text{LUMO}} ) (eV) [b]</th>
<th>( E_{g \text{ el.}} ) (eV) [c]</th>
<th>( E_{g \text{ opt.}} ) (eV) [d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA</td>
<td>-5.64</td>
<td>-2.54</td>
<td>3.10</td>
<td>-5.63</td>
<td>-2.51</td>
<td>3.12</td>
<td>3.13</td>
</tr>
<tr>
<td>BAtph</td>
<td>-5.61</td>
<td>-2.62</td>
<td>2.99</td>
<td>-5.67</td>
<td>-2.61</td>
<td>3.06</td>
<td>2.99</td>
</tr>
<tr>
<td>BA2ph</td>
<td>-5.59</td>
<td>-2.53</td>
<td>3.05</td>
<td>-5.52</td>
<td>-2.53</td>
<td>2.99</td>
<td>2.95</td>
</tr>
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</table>

a) HOMO energy levels of the Biantracene BA and BA2ph derivatives  
b) LUMO energy levels of the Biantracene BA and BA2ph derivatives  
c) electrochemical band gaps of the Biantracene BA and BA2ph derivatives  
d) Optical band gap of the Biantracene BA and BA2ph derivatives.
**Fig. S3.** Transient absorption map (a), transient absorption spectra (b) and transient absorption decay (c) of 9,9’-bianthryl **BA** in polar, non-viscous acetonitrile environment. Pump pulse – at 385 nm (200 fs). SE – stimulated emission, LE – locally excited state, CT – charge transfer state.

**Fig. S4.** Transient absorption map (a), transient absorption spectra (b) and transient absorption decay (c) of 9,9’-bianthryl **BA tph** in polar, non-viscous acetonitrile environment. Pump pulse – at 385 nm (200 fs). SE – stimulated emission, LE – locally excited state, CT – charge transfer state.
Fig. S5. Transient absorption map (a), transient absorption spectra (b) and transient absorption decay (c) of 9,9′-bianthryl BA2ph in polar, non-viscous acetonitrile environment. Pump pulse – at 385 nm (200 fs). SE – stimulated emission, LE – locally excited state, CT – charge transfer state.
Fig. S6. Amplitudes of LE and CT states for 9,9’ – bianthryl BA a), BAtphe b) and BA2ph c). The decay of LE and the growth of CT states for 9,9’ – bianthryl BA d), BAtphe e) and BA2ph f) derivatives, approximated by global analysis in polar and non-viscous acetonitrile environment.
Fig. S7. Amplitudes of LE and CT states for 9,9’ – bianthryl BA a), BAtphe b) and BA2ph c). The decay of LE and the growth of CT states for 9,9’ – bianthryl BA d), BAtphe e) and BA2ph f) derivatives, approximated by global analysis in polar and viscous propylene carbonate environment.