SUPPORTING INFORMATION FOR:

Oligothienoacenes versus oligothiophenes: Impact of ring fusion on the optical properties

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1 Molecular structure

![Molecular structure diagram]

Fig. S1 BLA values (Å) calculated for each thiophene ring of 7TA and 4T in the ground (S₀) and first excited (S₁) electronic states.

2 Optical properties

In order to rationalize the origin of the differences between the first transition energies in nTAs and nTs, several tests have been carried out to separate substitution, geometrical and electronic effects.

a) Substitution effect:
Geometry optimization at the BHLYP/6-31G** level has been performed on 2T-(SH)₂ (Fig. S2) and the vertical transition energy has been calculated on the optimized geometry. Our results indicate that substitution with sulphur atoms leads to a decrease of the optical bandgap with respect to 2T (4.25 eV vs. 4.39 eV), contrary to what is found for 3TA (4.66 eV). Thus, the differences between nTAs and nTs do not arise from a simple substituent effect.

b) Geometrical effect:
In order to evaluate the impact of the geometry on the S₀ → S₁ transition energy, TD-DFT calculations have been carried out on cis-2T, trans-2T, 2T-SH and 2T-(SH)₂, where the geometry of the backbone was kept frozen with bond lengths and angles from 3TA (see Fig. S2). In all cases, a decrease of the energy with respect to the value for the optimized 2T has been obtained, discarding the geometrical effect as the reason for the larger optical bandgap observed in 3TA.

c) Electronic effect:
The analysis of the energies of the HOMO and LUMO monoelectronic levels involved in the S₀ → S₁ transition of cis-2T, trans-2T, 2T-SH and 2T-(SH)₂ calculated at the
geometry of 3TA shows the same trends for the HOMO – LUMO gap that those found for the calculated vertical transition energies (see Fig. S2). A closer inspection of the frontier orbitals of 2T and 3TA shows a destabilization of the LUMO in 3TA due to an increase of the C-S antibonding interactions resulting from the participation of the sulphur atom of the bridge. The stabilization of the HOMO is ascribed to the additional electronic density introduced by the sulphur atoms in the bridge. In all, the HOMO – LUMO gap is increased resulting in a larger $S_0 – S_1$ transition energy compared to 2T.

In conclusion, the larger transition energies in nTAs in comparison to nTs arise from an electronic effect and are not related to a simple substituent or structural effect.

![Optimized bond lengths (Å) (only for 2T and 3TA), orbital and $S_0 \rightarrow S_1$ vertical excitation energies (eV) for 2T, 3TA, trans-2T, cis-2T, 2T-SH and 2T-(SH)$_2$. The geometries of trans-2T, cis-2T, 2T-SH and 2T-(SH)$_2$ were kept frozen with bond lengths and angles from 3TA.](image)

**Fig. S2** Optimized bond lengths (Å) (only for 2T and 3TA), orbital and $S_0 \rightarrow S_1$ vertical excitation energies (eV) for 2T, 3TA, trans-2T, cis-2T, 2T-SH and 2T-(SH)$_2$. The geometries of trans-2T, cis-2T, 2T-SH and 2T-(SH)$_2$ were kept frozen with bond lengths and angles from 3TA.
3 Vibronic coupling

![Simulated LT (solid line) and RT (dash line) spectra of absorption (right) and fluorescence (left) of 3TA, 5TA and 7TA (from bottom to top). Inserted Gaussian half-width $\gamma$ of 150 cm$^{-1}$ and 1250 cm$^{-1}$ at LT and RT for all compounds.](image_url)

**Fig. S3** Simulated LT (solid line) and RT (dash line) spectra of absorption (right) and fluorescence (left) of 3TA, 5TA and 7TA (from bottom to top). Inserted Gaussian half-width $\gamma$ of 150 cm$^{-1}$ and 1250 cm$^{-1}$ at LT and RT for all compounds.
Table S1. Frequencies (ν in cm\(^{-1}\)) and HR factors (S\(_k\)) of 2T and 3T for selected totally-symmetric normal modes (k) involved in the S\(_0\)↔S\(_1\) electronic transition in emission and excitation.

<table>
<thead>
<tr>
<th></th>
<th>2T</th>
<th>3T</th>
<th>4T</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Emission</td>
<td>Excitation</td>
<td>Emission</td>
</tr>
<tr>
<td>k</td>
<td>ν(_0^a)</td>
<td>S(_k)</td>
<td>ν(_1^a)</td>
</tr>
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</tbody>
</table>

\(^a\)ν\(_0\) and ν\(_1\) indicate the frequencies of the ground and first excited states, respectively.
Figure S4. Simulated stick spectra of absorption (solid line) and fluorescence (dotted line) of 2T, 3T and 4T (from bottom to top). Inserted Gaussian half-width $\gamma$ of 10 cm$^{-1}$ for all compounds.