SUPPORTING INFORMATION FOR:

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

Juan Aragó,[a] Pedro M. Viruela,[a] Johannes Gierschner,[a,b] Enrique Ortí[a] and Begoña Milián-Medina[a]*

[a] *Instituto de Ciencia Molecular, Universidad de Valencia, Valencia 46980 (Spain)*
[b] *Madrid Institute of Advanced Studies, IMDEA Nanoscience, Madrid (Spain)*
E-mail: b.milian.medina@uv.es

1 Molecular structure

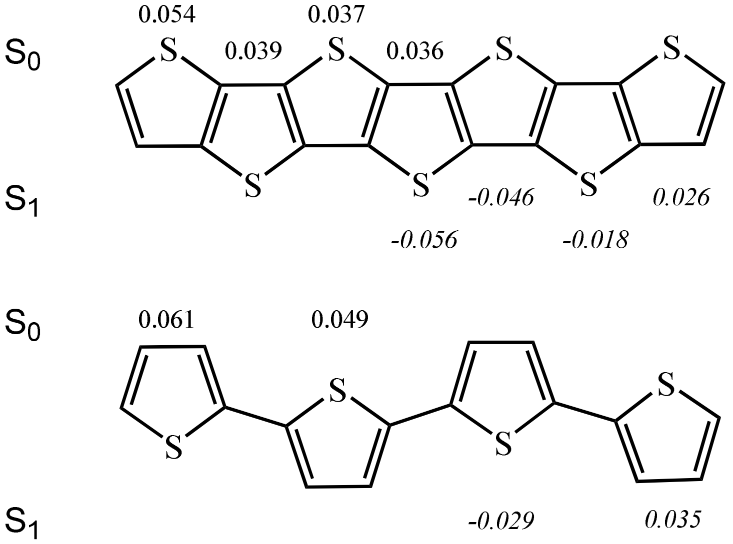

Fig. S1 BLA values (Å) calculated for each thiophene ring of **7TA** and **4T** in the ground (S_0) and first excited (S_1) electronic states.

2 Optical properties

In order to rationalize the origin of the differences between the first transition energies in ***n*TAs** and ***n*Ts**, 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 it is found for **3TA** (4.66 eV). Thus, the differences between ***n*TAs** and ***n*Ts** do not arise from a simple substituent effect.

b) Geometrical effect:
In order to evaluate the impact of the geometry on the $S_0 \rightarrow S_1$ 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 $S_0 \rightarrow S_1$ 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 ***n*TAs** in comparison to ***n*Ts** arise from an electronic effect and are not related to a simple substituent or structural effect.

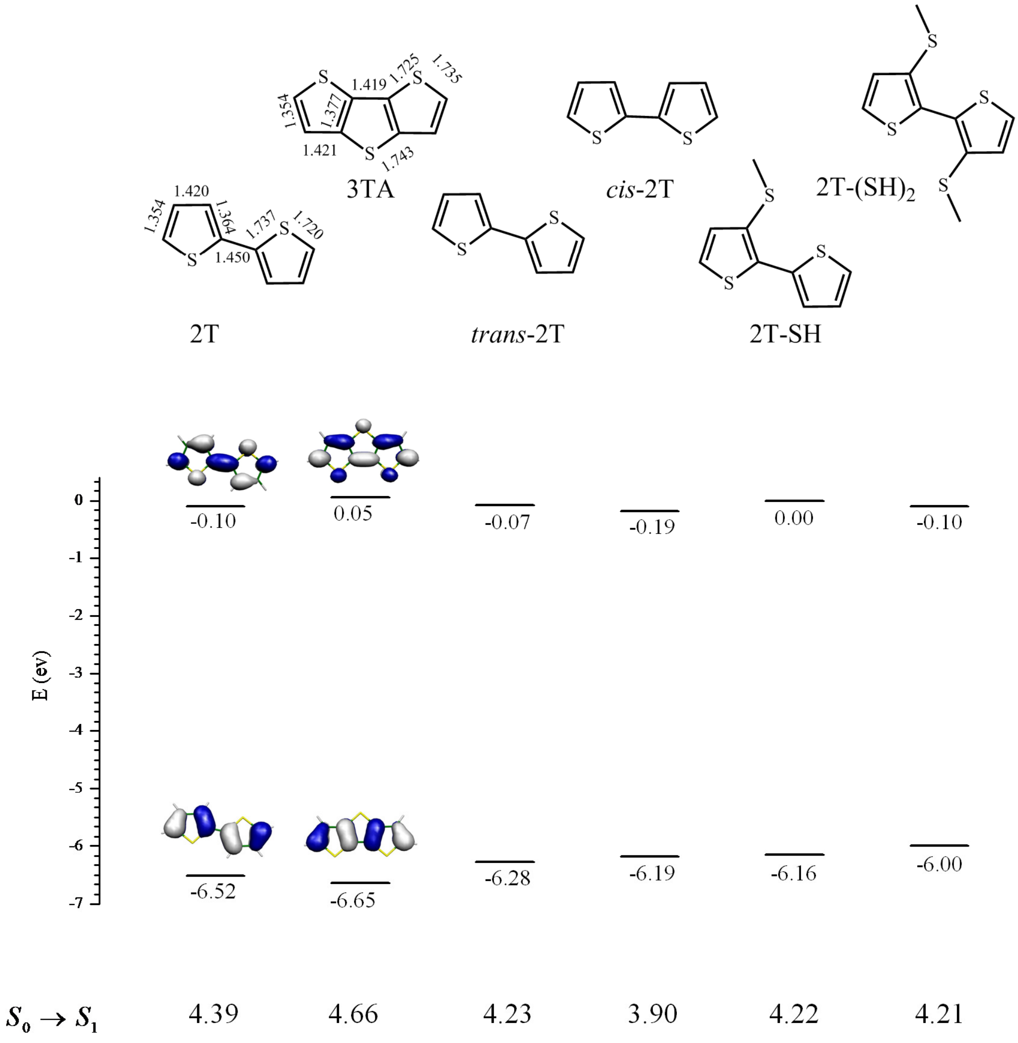

Fig. S2 Optimized bond lengths (Å) (only for **2T** and **3TA**), orbital and $S_0 \rightarrow S_1$ vertical excitation energies (eV) for **2T**, **3TA, trans-2T**, **cis-2T, 2T-SH** and **2T-(SH)₂**. The geometries of **trans-2T**, **cis-2T, 2T-SH** and **2T-(SH)₂** were kept frozen with bond lengths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

3 Vibronic coupling

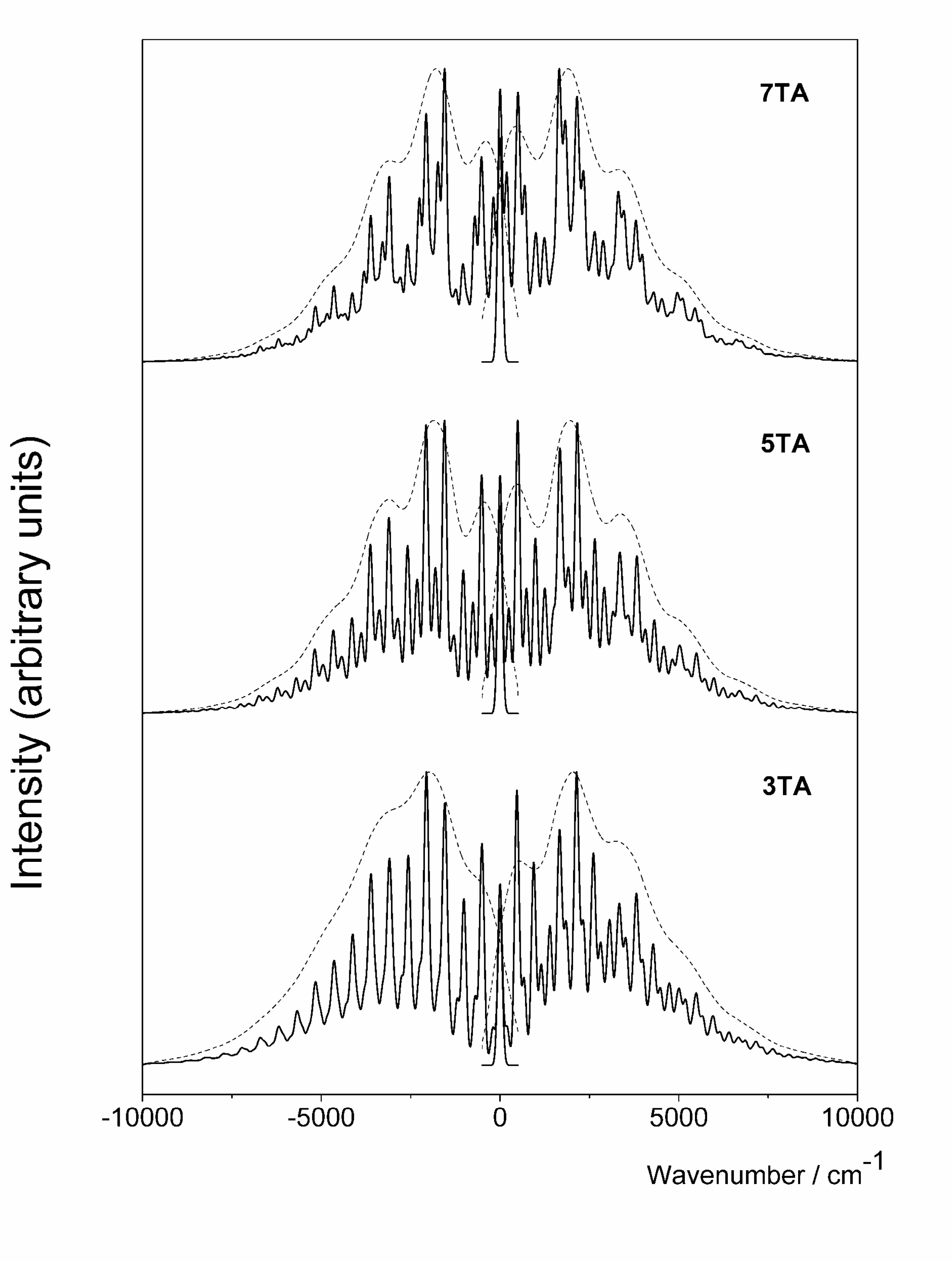

Fig. S3 Simulated LT (solid line) and RT (dash line) spectra of absorption (right) and fluorescence (left) of **3TA**, **5TA** and **7TA** (from bottom to top). Inserted Gaussian half-width γ of 150 cm^{-1} and 1250 cm^{-1} at LT and RT for all compounds.

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 $S_0 \leftrightarrow S_1$ electronic transition in emission and excitation.

	2T				**3T**				**4T**			
	Emission		Excitation		Emission		Excitation		Emission		Excitation	
k	ν_0[a]	S_k	ν_1[a]	S_k	ν_0[a]	S_k	ν_1[a]	S_k	ν_0[a]	S_k	ν_1[a]	S_k
I	304	0.15	296	0.14	216	0.45	215	0.42	166	0.60	167	0.64
II	395	0.36	395	0.37	352	0.29	358	0.31	334	0.28	344	0.25
III	712	0.83	688	0.64	729	0.45	711	0.42	735	0.30	721	0.33
IV	1575	1.19	1693	0.89	1587	1.08	1673	0.86	1585	0.92	1666	1.03
V	1690	0.08	1552	0.42	1670	0.05	1599	0.28	1660	0.18	1635	0.04

[a] ν_0 and ν_1 indicate the frequencies of the ground and first excited states, respectively

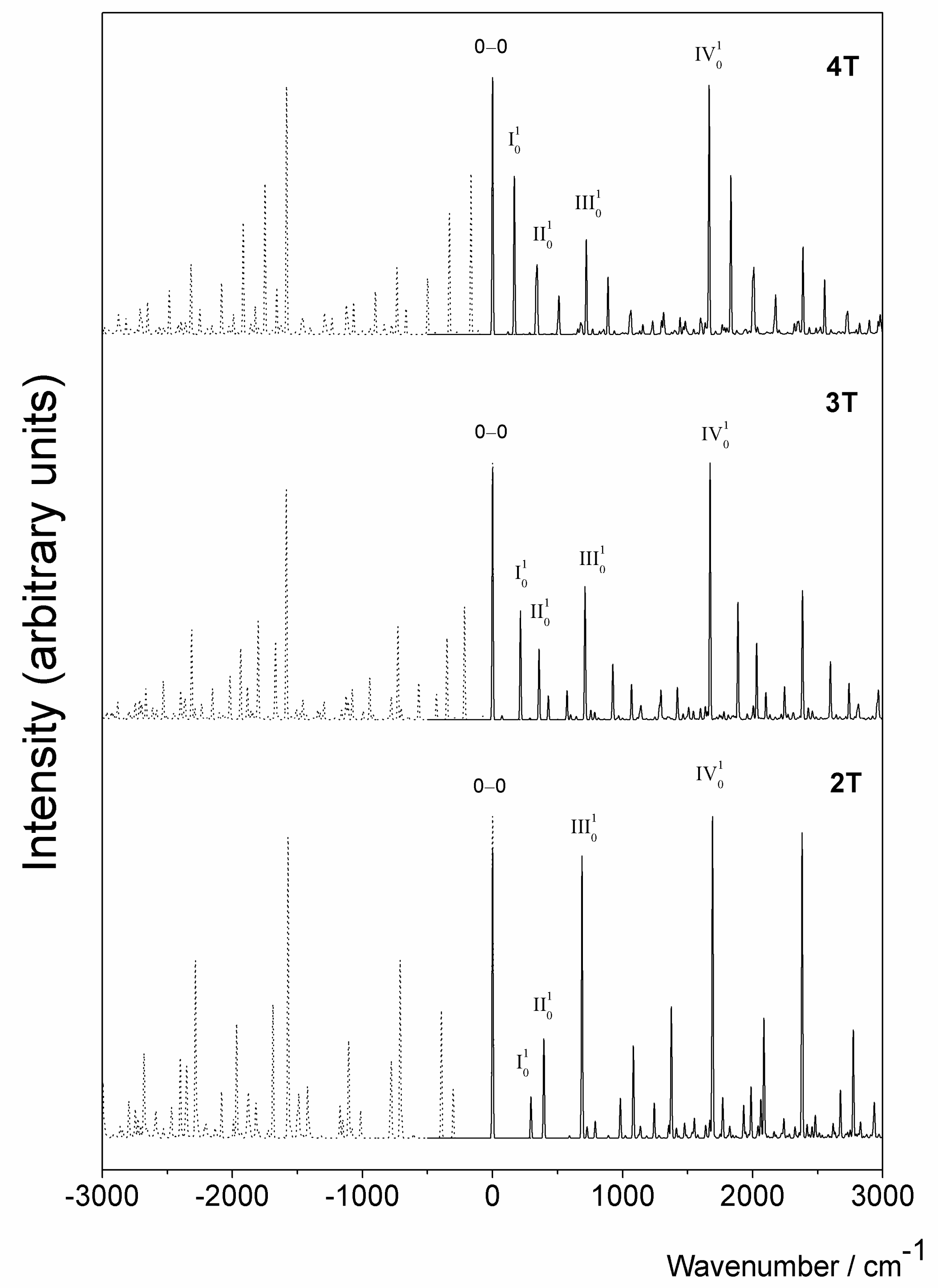

Figure S4. Simulated stick spectra of absorption (solid line) and fluorescence (dotted line) of **2T**, **3T** and **4T** (from bottom to top). Inserted Gaussian half-width γ of 10 cm^{-1} for all compounds.