Electronic Supplementary information for

“A family of solution-processable macrocyclic and open-chain oligothiophenes with atropoisomeric scaffolds: structural and electronic features for potential energy applications”

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Fig. S1. a): Superimposed $^1$H NMR spectra of $(R,R)$-2 and of $(R,R)$-2 + $(S,S)$-2 (d$_6$-DMSO, 40 °C); b): $^1$H NMR spectrum of (+) $(S,S,S)$-3 (d$_6$-DMSO, 40 °C); c): $^1$H NMR spectrum of the diastereomeric mixture of 3 (d$_6$-DMSO, 40 °C).

Fig. S2. HRLDI of the reaction mixture of the chemical oxidation of the diastereomeric mixture of 2a with FeCl$_3$. 
Fig. S3. HRLDI of compound 4 isolated after six selective precipitation cycles.

Fig. S4. $^1$H NMR spectra of the diastereomeric mixtures of compound 4 (top) and 2 (bottom). A significant shift of all peaks can be appreciated and, in particular, the signal around 6.8 ppm characteristic of compound 2 cannot be found in the spectrum of 4.
Fig. S5. Molecular structure of oligothiophene stereoisomers. Different views are presented for each oligomer.

Fig. S6. Molecular structure of oligothiophene:fullerene dyads. Different views are presented for each oligomer.
Fig S7. Optical micrographs of oligothiophene:fullerene blends. Materials ratios are the same used in devices. Marker length = 500 μm.
Fig. S8. Photovoltaic parameters of (a) P3HT and oligothiophene:PCBM solar cells, and (b) P3HT and oligothiophene:C₆₀ solar cells.
**Fig. S9.** UV-visible spectra of 1:1 oligothiophene:PCBM films.

**Fig. S10.** Synopsis of normalized CV patterns of open dimer 2a recorded as a function of the potential scan rate $v$ on GC electrode in CH$_2$Cl$_2$ + 0.1 M TBAPF$_6$. 
**Fig. S11.** Synopsis of normalized CV patterns of cyclic dimer 2 recorded as a function of the potential scan rate $v$ on GC electrode in CH$_2$Cl$_2$ + 0.1 M TBAPF$_6$.

**Fig. S12.** Synopsis of normalized CV patterns of cyclic trimer 3 recorded as a function of the potential scan rate $v$ on GC electrode in CH$_2$Cl$_2$ + 0.1 M TBAPF$_6$. 