Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information (ESI)

Impact of chirality on the aggregation modes of L-phenylalanine- and D-glucose-decorated phenylene-thiophene oligomers

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Experimental details

General

Chiral phenylene-thiophene oligomers **1–3** were synthesized according to our previous work.[1] Commercial grade solvents were purchased from Sigma-Aldrich, purified by employing conventional procedures[2-3] and stored over activated molecular sieves under nitrogen atmosphere.

Spectroscopy characterization in solution

UV-Vis absorption (Abs) spectra in solution were recorded at room temperature using a Jasco V-650 spectrophotometer.

Electronic circular dichroism (ECD) in solution were recorded at room temperature using a Jasco J-710 spectropolarimeter.

Thin films preparation

Thin film samples of each chiral oligomer were prepared by drop casting technique: ~ 100 µL of a chloroform solution of each compound (concentration: 1.0×10^{-3} M) were deposited dropwise on a quartz plate, followed by slow evaporation in an atmosphere saturated with chloroform vapors. The concentration of the starting solution was optimized in order to obtain thin films with an optical density (OD) ranging between 0.4 and 0.6 at the maximum absorbance wavelength.

Spectroscopy characterization in thin films

UV-Vis absorption (Abs) spectra of thin films were recorded at room temperature using a Jasco V-650 spectrophotometer.

Electronic circular dichroism (ECD) spectra of thin films were recorded at room temperature using a Jasco J-710 spectropolarimeter. In all cases, at least 5 independent thin film samples were prepared and subjected to full Abs and ECD analysis. Invariance of the ECD amplitudes upon sample rotation (*i.e.*, by rotating sample through successive 45° increments around the optical axis) and flipping (*i.e.*, by recording two ECD spectra: one with the organic film facing the light source, *front*, and one with the organic film facing the detector, *back*) was also testified: in no cases we could observed significant variations. Each ECD spectrum was normalized to maximum absorbance in order to avoid any mistake possibly associated to sample inhomogeneity.

IR spectra of thin films were recorded with a Perkin Elmer Spectrum Two Spectrophotometer equipped with a 2×2 mm Diamond crystal. The spectra were recorded in the range 4000-400 cm^{-1} with a 2 cm^{-1} resolution, using a 0.25 cm^{-1} acquisition interval and acquiring 16 scans for each sample.

Computational details

The computational model of chiral oligomer **1** was obtained by means of the following procedure, using Spartan'10 (Wavefunction, Inc., Irvine CA, 2010), with standard parameters and convergence criteria. A molecule of **1** was built and optimized with MMFF (Merck Molecular Force Field) after addition of a minimum set of restraints to keep the π-conjugated moiety planar. During this operation, the linear alkyl chain remained in a zigzag conformation. Six distinct units of the optimized oligomer **1** were then placed on top of each other. From this starting architecture, various structures were generated by modifying a few quantities including the twist between the π-conjugated chains and the conformation around α-amino acid units. Such structures were then allowed to relax by means of MMFF geometry optimizations. The computational model in **Figure 3** represents to the most stable (MMFF energy) result obtained, showing a network of hydrogen bonds.

Supplementary Figures

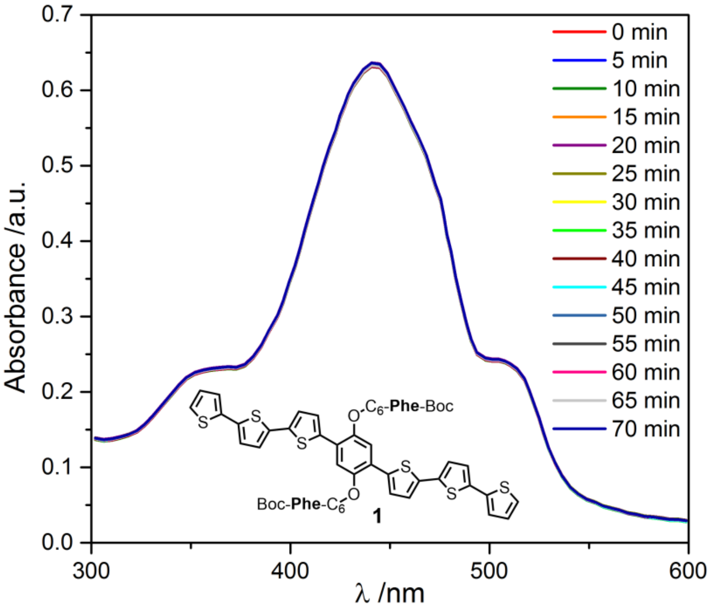

Figure S1. Evolution of the UV-Vis absorption spectrum of L-phenylalanine-functionalized phenylene-thiophene oligomer **1** in 99% MeOH as a function of time. Sample concentration: $6 \cdot 10^{-5}$ M; cell length: 0.2 cm.

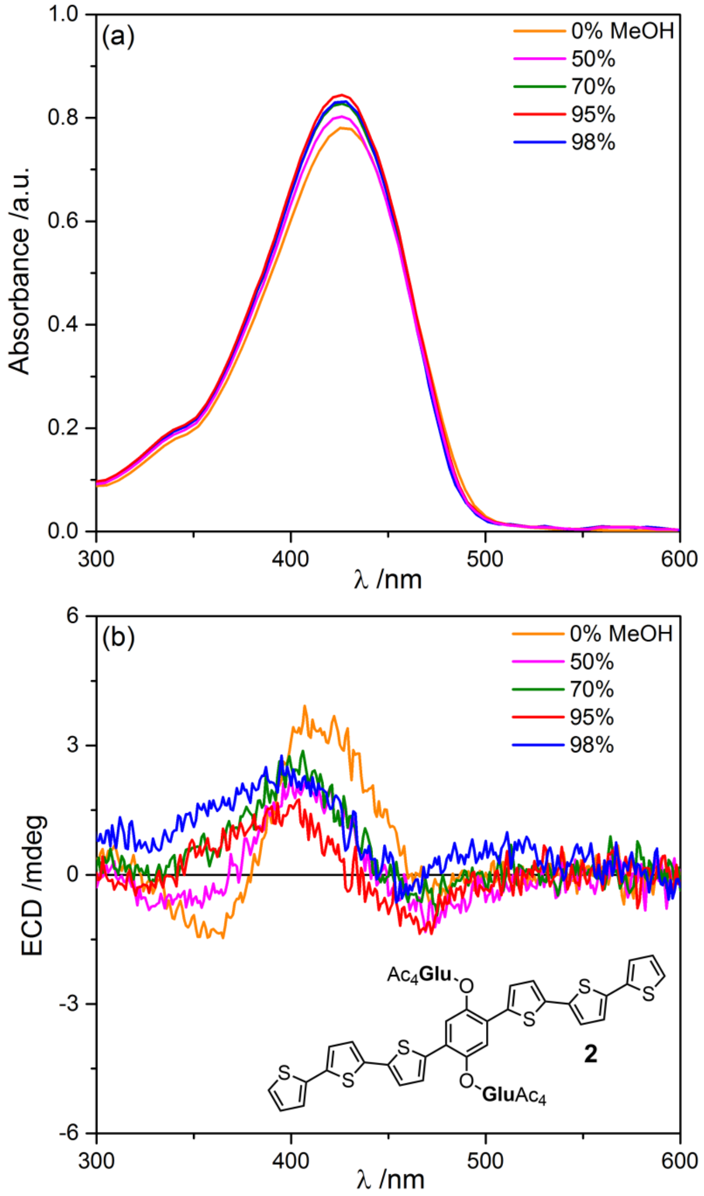

Figure S2. (Chiro)optical characterization of D-glucose-functionalized phenylene-thiophene oligomer **2** in solution: (a) UV-Vis absorption and (b) ECD spectra in $CHCl_3$/MeOH mixtures with increasing amounts of MeOH. Sample concentration: $6 \cdot 10^{-5}$ M; cell length: 0.2 cm.

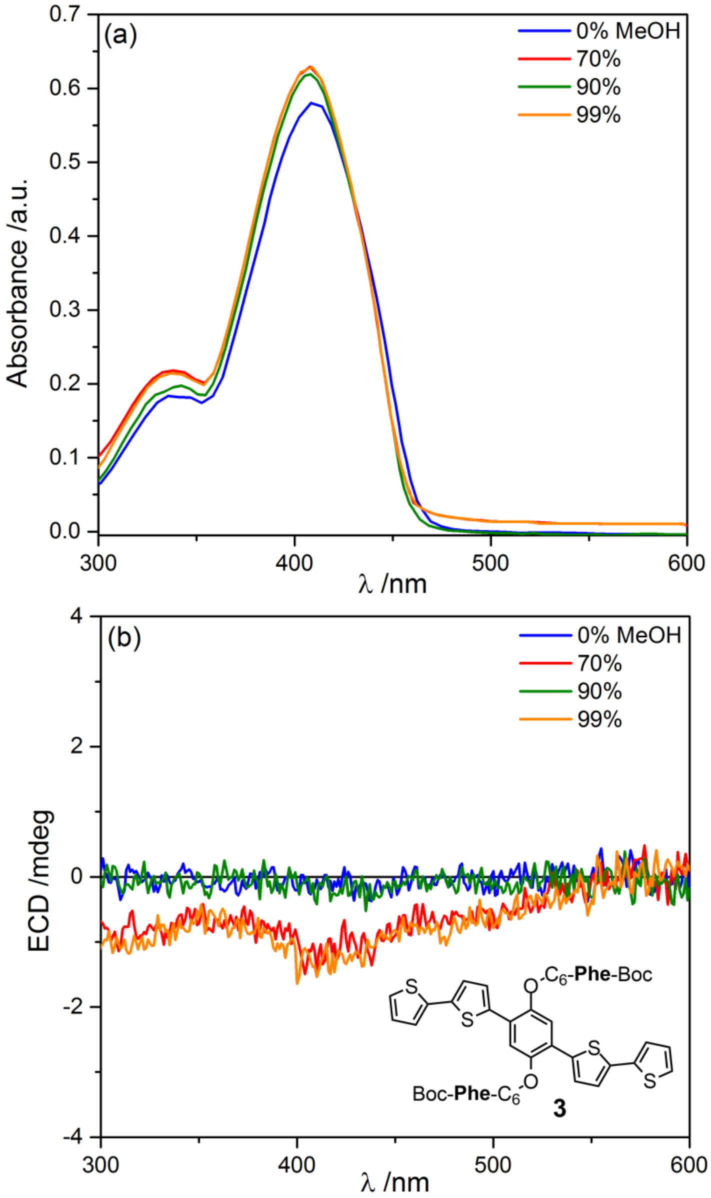

Figure S3. (Chiro)optical characterization of L-phenylalanine-functionalized phenylene-thiophene oligomer **3**: (a) UV-Vis absorption and (b) ECD spectra in $CHCl_3$/MeOH mixtures with increasing amounts of MeOH. Sample concentration: $6 \cdot 10^{-5}$ M; cell length: 0.2 cm.

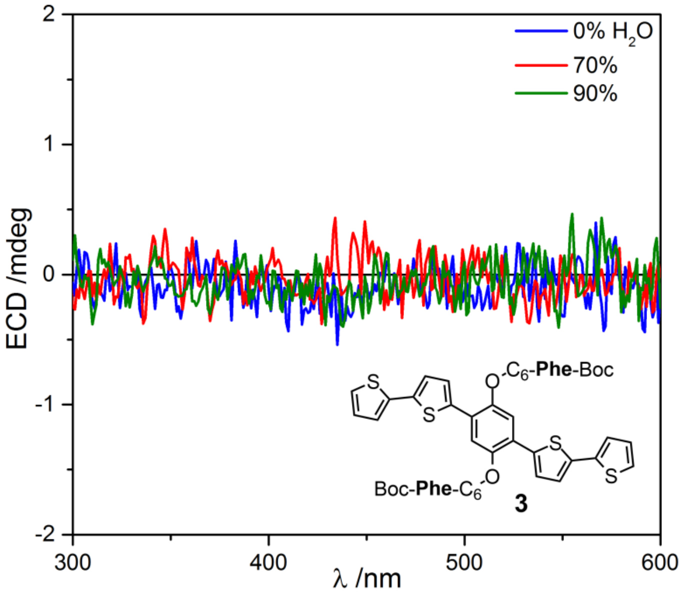

Figure S4. Chiroptical characterization of L-phenylalanine-functionalized phenylene-thiophene oligomer **3**: ECD spectra in THF/H_2O mixtures with increasing amounts of H_2O. Sample concentration: $6 \cdot 10^{-5}$ M; cell length: 0.2 cm.

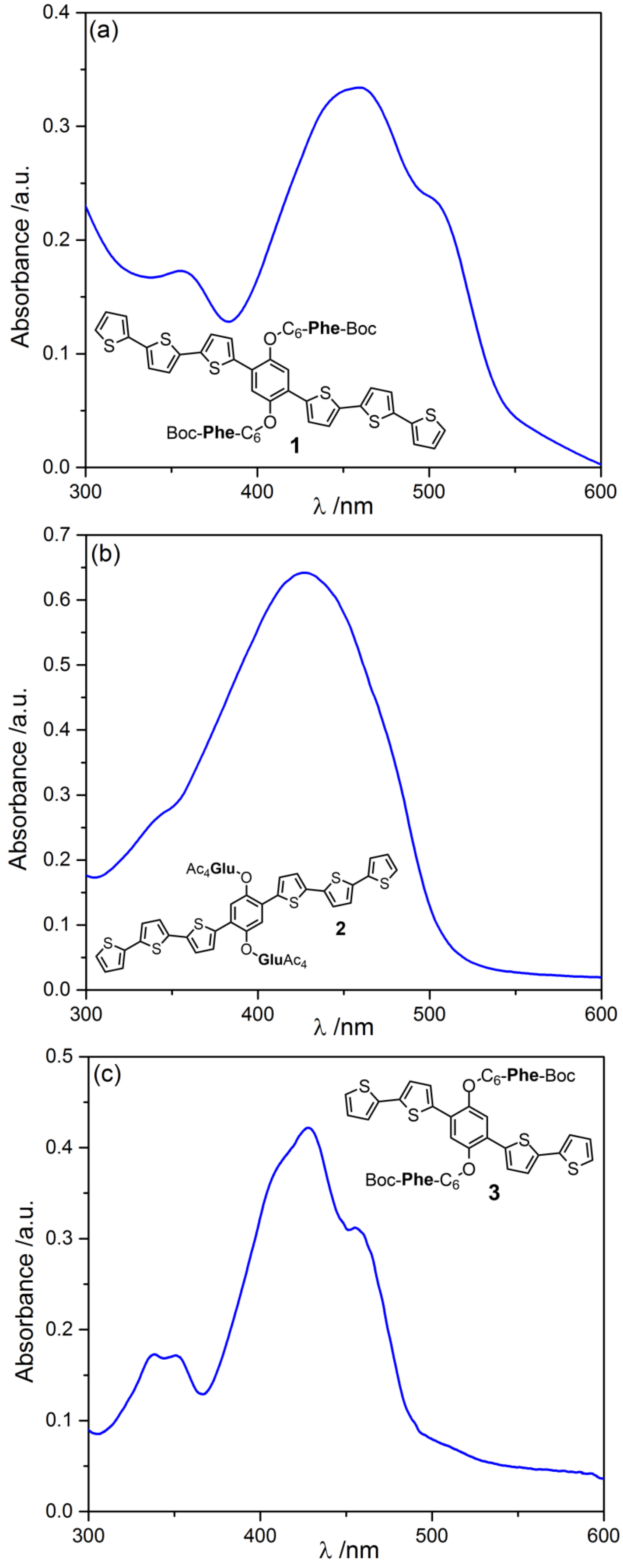

Figure S5. UV-Vis absorption spectra recorded for chiral phenylene-thiophene oligomer **1–3** as thin films prepared by drop casting from a $CHCl_3$ solution: (a) L-phenylalanine-functionalized oligomer **1** (**DC-1**) as freshly prepared sample; (b) peracetylated D-glucose-functionalized oligomer **2** (**DC-2**); (c) L-phenylalanine-functionalized oligomer **3** (**DC-3**).

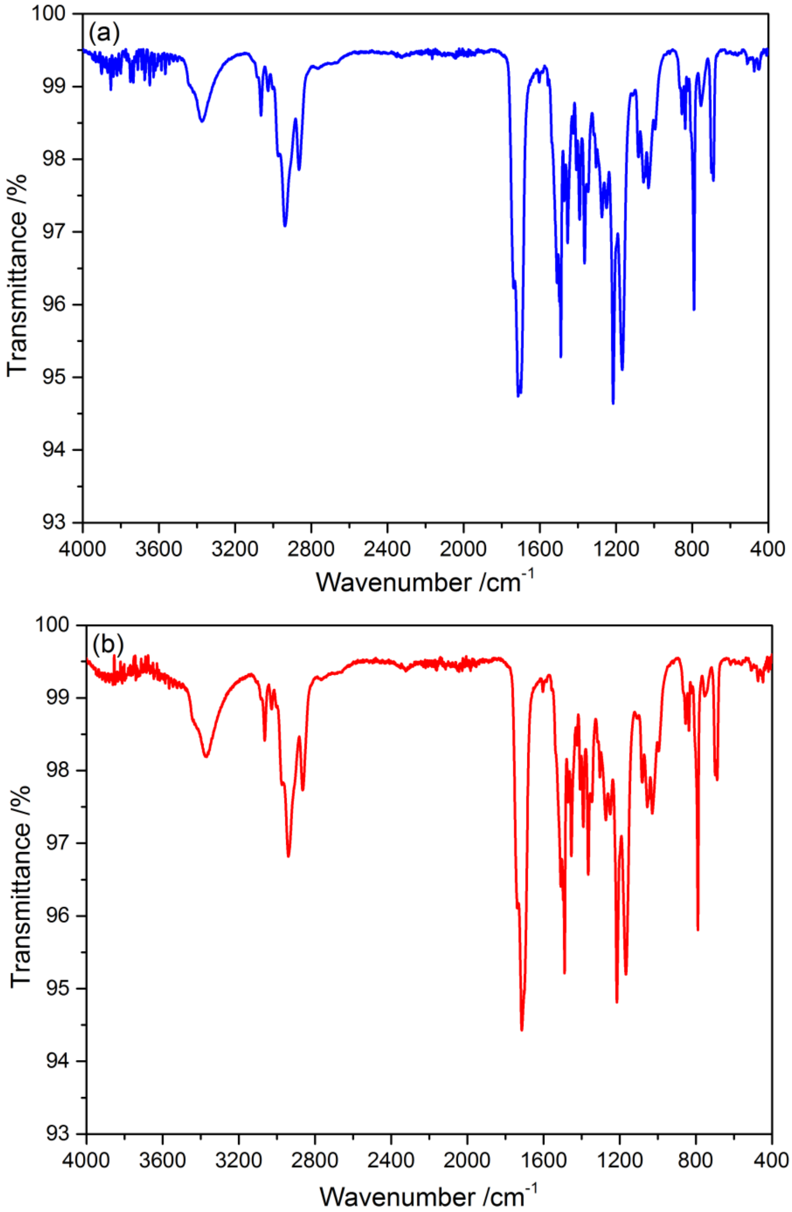

Figure S6. IR spectra recorded for L-phenylalanine-functionalized oligomer **1** as thin films prepared by drop casting from a $CHCl_3$ solution (**DC-1**): (a) as freshly prepared sample (blue line); (b) after 24 h of solvent annealing (red line).

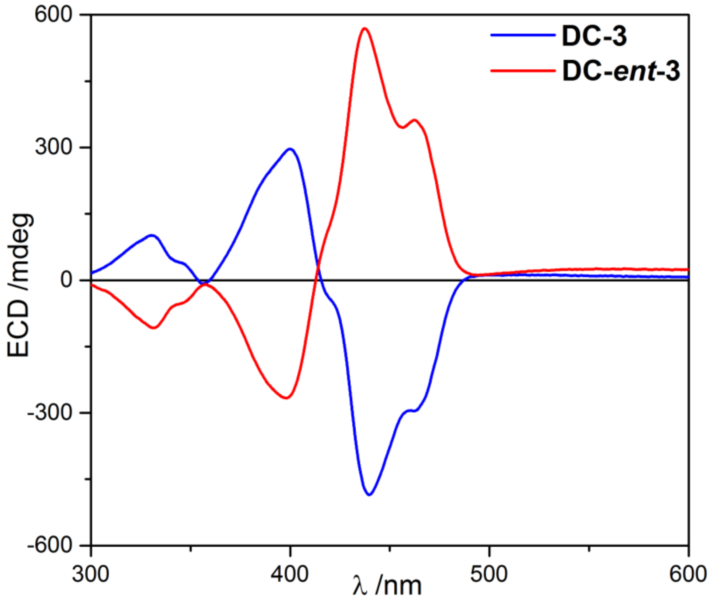

Figure S7. ECD spectra (normalized with respect to maximum absorbance) recorded for L-phenylalanine-functionalized phenylene-thiophene oligomer **3** (**DC-3**, blue line) and D-phenylalanine-functionalized phenylene-thiophene oligomer ***ent*-3** (**DC-*ent*-3**, red line) as thin films prepared by drop casting from a $CHCl_3$ solution.

References

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[2] W. L. F. Armarego, C. L. Lin Chai, *Purification of Laboratory Chemicals*, 5th ed., Butterworth-Heinemann: Sydney, **2003**.

[3] A. I. Vogel, *Textbook of Practical Organic Chemistry*, 5th ed., Longman Scientific and Technical: Harlow, UK, **1989**.