

SUPPORTING INFORMATION

Chiral Microneedles from an achiral Bis(BODIPY): Spontaneous Mirror Symmetry Breaking Leading to a Promising Photoluminescent Organic Material

Leire Gartzia-Rivero,[†] César Ray Leiva,[‡] Esther M. Sánchez-Carnerero,^{||} Jorge Bañuelos,^{*†} Florencio Moreno,[‡] Beatriz L. Maroto,[‡] Inmaculada García Moreno,[§] Lourdes Infantes,[¥] Bianchi Mendez,[⊥] Iñigo López Arbeloa,[†] and Santiago de la Moya^{*‡}

[†]Dpto. Química Física, Universidad del País Vasco (UPV/EHU), 644, 48080 Bilbao, Spain.

[‡]Dpto. Química Orgánica, Universidad Complutense de Madrid, Ciudad Universitaria s/n, 28040 Madrid, Spain.

^{||}Dpt. of Chemistry and RECETOX, Masaryk University, Kamenice 5, 62500 Brno, Czech Republic.

[§]Dpto. de Sistemas de Baja Dimensionalidad, Superficies y Materia Condensada, Instituto de Química Física Rocasolano, CSIC, Serrano 119, 28006 Madrid, Spain.

[¥]Dpto. de Cristalografía y Biología Estructural, Instituto de Química Física Rocasolano, CSIC, Serrano 119, 28006 Madrid, Spain

[⊥]Dpto. de Física de Materiales, Universidad Complutense de Madrid, Ciudad Universitaria s/n, 28040 Madrid, Spain.

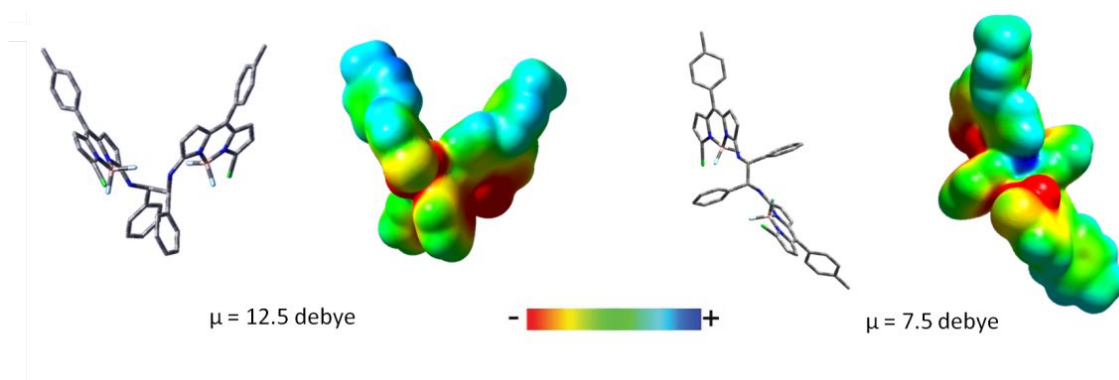


Figure S1. Computed preferred conformations and corresponding electron-density maps and permanent dipolar moments in CHCl_3 (B3LYP/6-31+G*) for *meso* **1** (left) and its chiral (*R,R*) stereoisomer (right). Note that achiral **1** adopts a pleated conformation, whereas its chiral diastereomer adopts an axially-chiral conformation with a preferred (*M*) helical configuration.

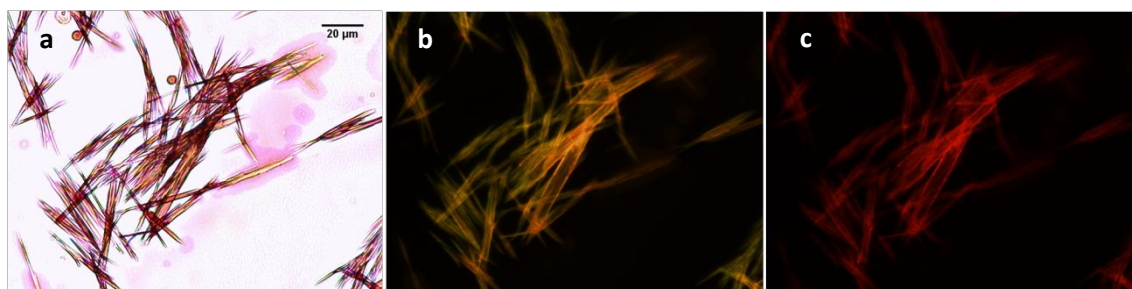


Figure S2. Transmission (a) and fluorescence images (b and c) of representative **1** needles under excitation with band-pass filter of 470/40 nm and monitoring the emission with a cut-off filter of 515 nm (b) and 580 nm (c).

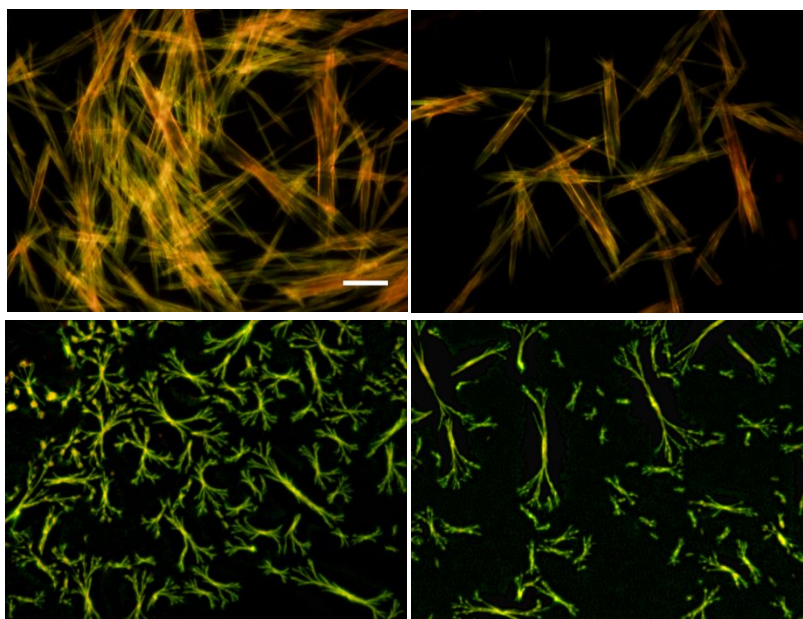


Figure S3. Fluorescence images of the two different morphologies detected for **1**: major totally-ripened crystalline needles obtained at higher dye concentrations (top); wires-enrolling fibers obtained at lower dye concentrations (bottom). Band-pass filter of 470/40 nm for the excitation; cut-off filter of 515 nm for recording the emission. 20- μ m Scale-bar.

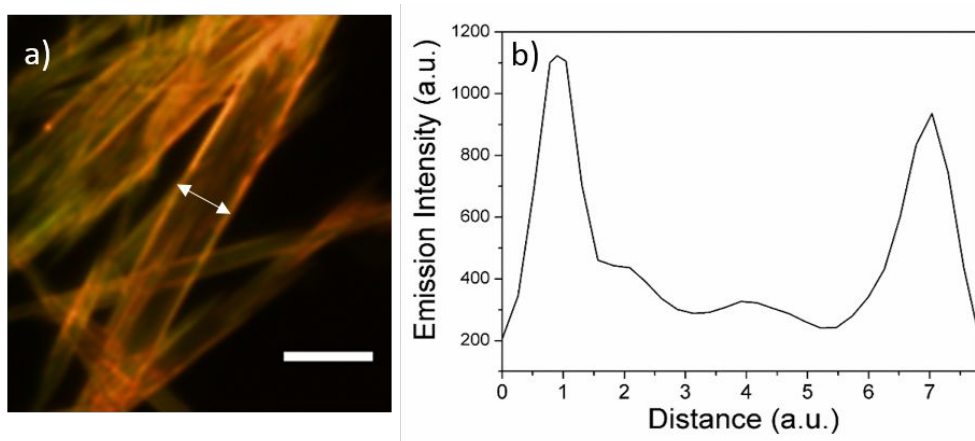


Figure S4. Fluorescence image of **1** needles showing energy migration towards the needle edges (a; 10- μ m scale-bar) and emission-intensity profile across the width of a single needle (b).

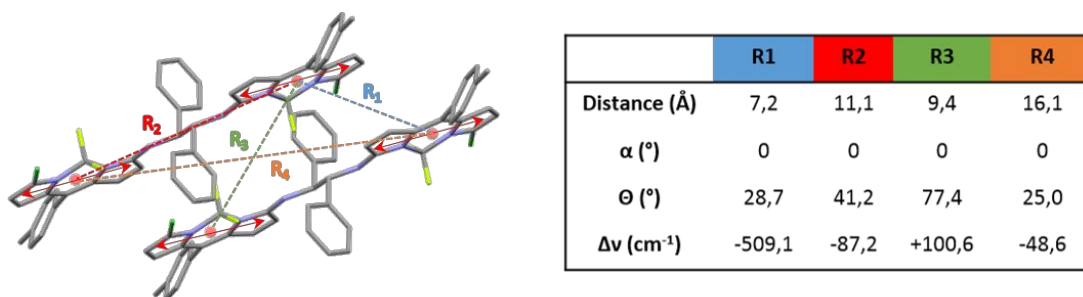


Figure S5. Calculated energy-splitting values ($\Delta\nu$; Davydov splitting) from possible dipole couplings (R1-R4) between nearest neighbor dipyrrens in the crystal structure obtained by X-Ray diffraction (key distances and angles are also given). Red double-head arrow show the transition dipole moment (along the longitudinal axis of the dipyrren).

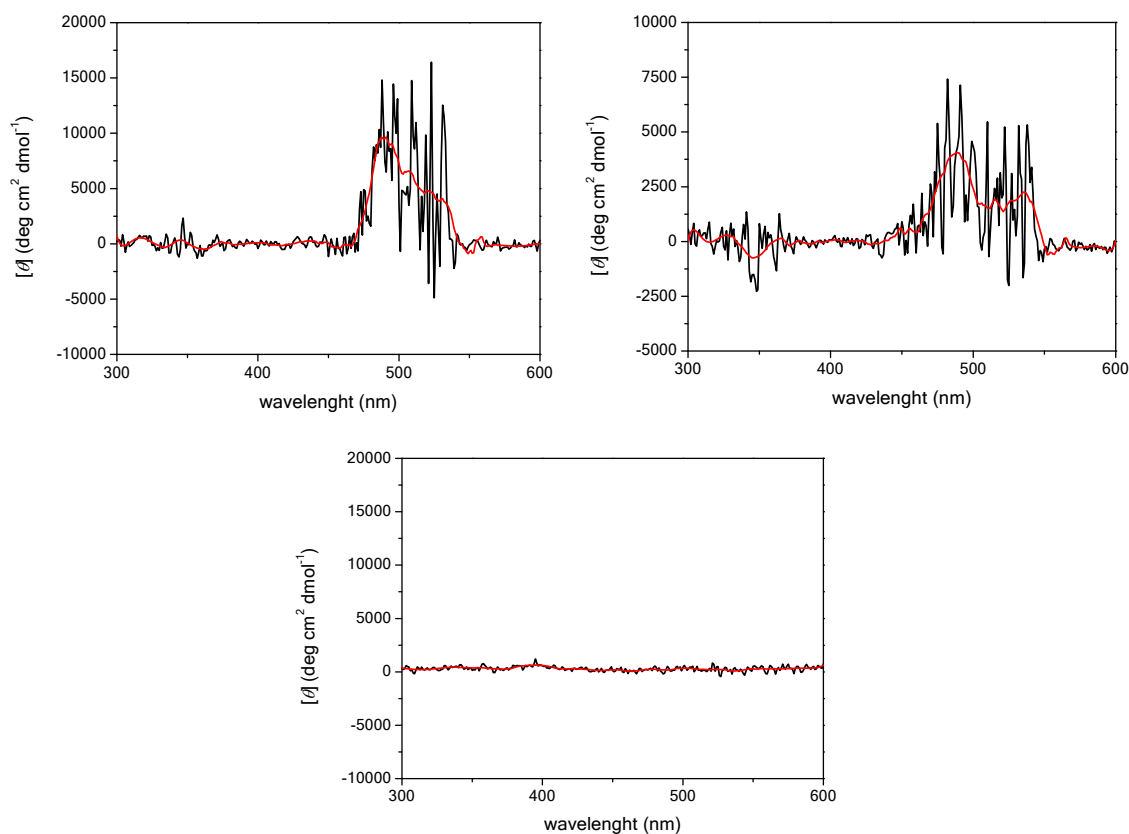


Figure S6. Examples of positive ECD spectra recorded from **1** needles dispersed in CHCl_3 at $1.4 \cdot 10^{-4}$ M (top, left) and $6.9 \cdot 10^{-5}$ M (top, right), and silent ECD spectra observed for individual **1** molecules at $6.9 \cdot 10^{-6}$ M (bottom). Formations of chiral nanostructured fibers is detected at high enough concentrations (top) by switching on the silent ECD (bottom) observed at a low enough concentration (disaggregated state). Red line indicates the estimated smoothed spectrum from the corresponding recorded (black line) spectrum.