Supporting Information for

Long Rylene Nanoribbons Express Polyacetylene-like Signatures on Their Edges

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Part 1. General information

Spectroscopic measurements. UV-Vis absorption spectra were obtained by using a Cary 5000 instrument equipped with a photomultiplier tube R928 and a Cooled PbD Photocell detection system or on a Jasco V-570. Emission spectra were recorded on a spectrofluorometer from Edinburgh Analytical (FLS920P) equipped with a Xenon lamp and on a Jasco FP-6600 spectrometer. All solvent used were of spectroscopic grade purchased from Aldrich. FT-Raman spectra were measured using the RAMII FT-Raman module of a VERTEX 70 FT-IR spectrometer. A continuous-wave Nd-YAG laser working at 1064 nm was employed for excitation, at a laser power in the sample not exceeding 30 mW. Raman scattering radiation was collected in a back-scattering configuration with a standard spectral resolution of 4 cm⁻¹. 2000 scans were averaged for each spectrum. The Raman spectra recorded using the 785 nm, 633nm and 532 nm excitations were collected by using the 1×1 camera of a Bruker Senterra Raman microscope by averaging spectra during 50 min with a resolution of 3–5 cm–1. A CCD camera operating at –50 °C was used. Variable temperature Raman measurements were performed in KBr pellets (to assure faster thermal equilibration) in the range between -180 °C and 150 °C, by using a Linkam FTIR600 stage cooled by liquid nitrogen and with a temperature stability of <0.1°C.

Spectroelectrochemical measurements. Spectroelectrochemical data were obtained by using an optically transparent thin-layer electrochemical (OTTLE) cell positioned either in the sample compartment of a Cary 5000 Spectrophotometer or of the Raman Senterra spectrometer. The working electrode (Pt minigrid, 32 wires per cm) potential was

controlled with an Electrochemical Analyzer BAS 100B and referenced to the Fc/Fc^+ couple. The supporting electrolyte was a 0.1 mol/L dichloromethane solution of tetrabutylammonium hexafluorophosphate (TBA-PF₆).

Part 2. Theoretical Calculations of CP-Per



Figure S1. Theoretical Raman spectrum of **CP- Per** calculated at the optimized CAM-B3LYP/6-31G* geometry.



coordinates corresponding to frequencies of 1391 cm⁻¹ (left) and 1592 cm⁻¹ (right) in the computed Raman spectrum of **CP- Per** (figure S1).





Figure S3. FT-Raman spectra of **CP-OR** in bulk. The inset corresponds to the benzenoid modes region.



Figure S4. FT-Raman spectra of **CP-OR** in bulk (bottom) and in different solvents (from top to bottom: o-dichlorobenzene, toluene and 2-methyltetrahydrofuran).



Figure S5. Vibrational normal coordinates corresponding to frequencies of 887, 1091, 1130, 1370 and 1514 cm⁻¹ (from top to bottom) in the computed Raman

spectrum of **CP- OR** at the displaced BS diradical structure (see the discussion in the text and Figures 3 and S6).



Figure

S6.

Comparison of the computed bond lengths for the optimized CS (red trace), optimized BS (green trace) and displaced BS (open shell geometry)diradical structure (see the discussion in the text) (dark-green trace) geometries of **CP-OR**. The insets show the bond numbering in the two peripheral polyacetylene-like CC chains.



Figure S7. Comparison of the computed bond length for the open shell singlet diradical (blue trace) and for the anion (pink trace) and cation (green trace) geometries of **CP-OR**. The insets show the bond numbering in the two peripheral polyacetylene-like CC chains.



Part 5. Spectroelectrochemical Study

Figure S8. UV-Vis-NIR absorption spectra of positive (top) and negatives (bottom) species of **CP-OR**, obtained electrochemically in a 0.1 M solution of $(Bu)_4NPF_6$ in CH_2CI_2 at room temperature.