

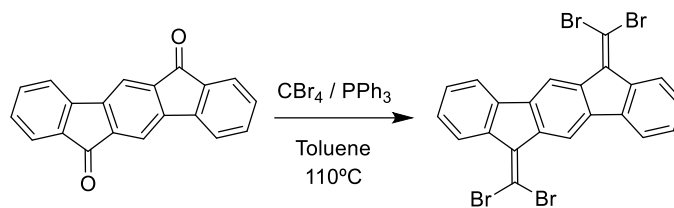
Supporting Information

Cumulene-like bridged indeno[1,2-b]fluorene π -conjugated polymers synthesized on metal surfaces

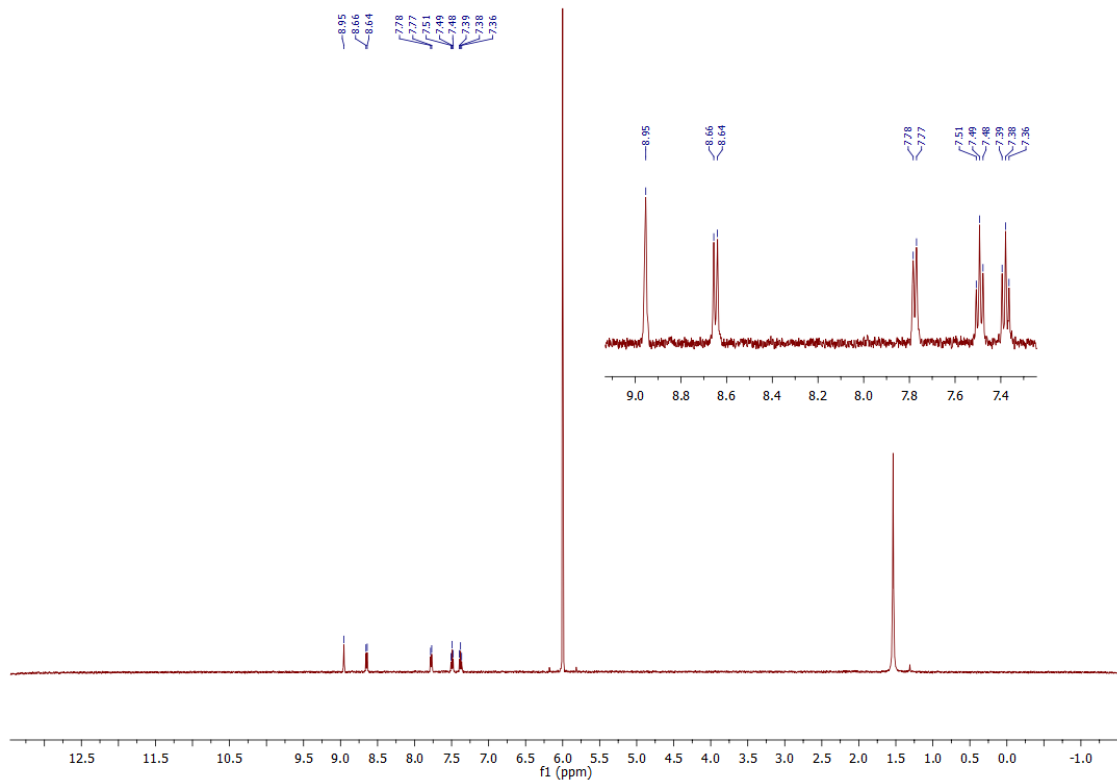
Cristina Martín-Fuentes^a José I. Urgel,^{a,*} Shayan Edalatmanesh,^b Eider Rodríguez-Sánchez,^a José Santos,^{a,d} Pingo Mutombo,^{b,c} Kalyan Biswas,^a Koen Lauwaet,^a Rodolfo Miranda,^{a,e} Pavel Jelínek,^{b,c,*} Nazario Martín,^{a,d,*} and David Écija^{a,*}

- 1. Precursor synthesis and characterizations**
- 2. Experimental methods**
- 3. Additional experimental and computational results**
- 4. Computational details**
- 5. References**

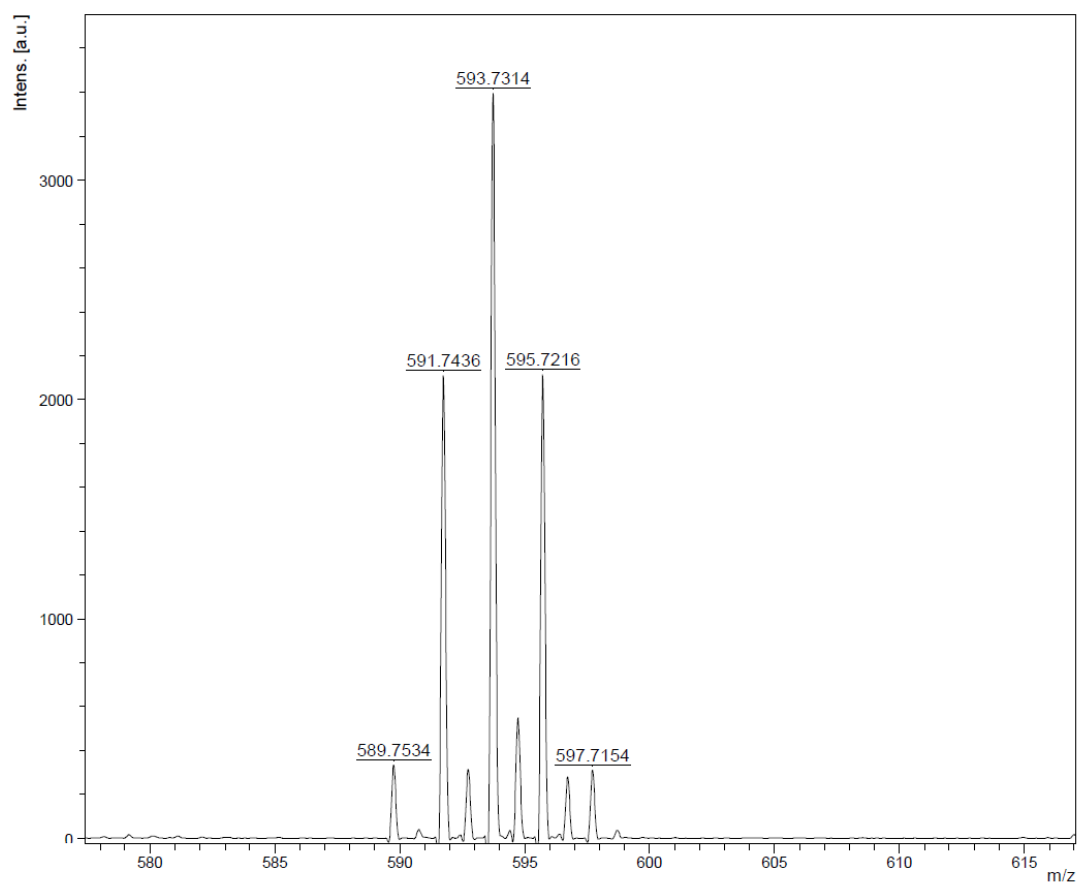
1. Precursor synthesis and characterizations



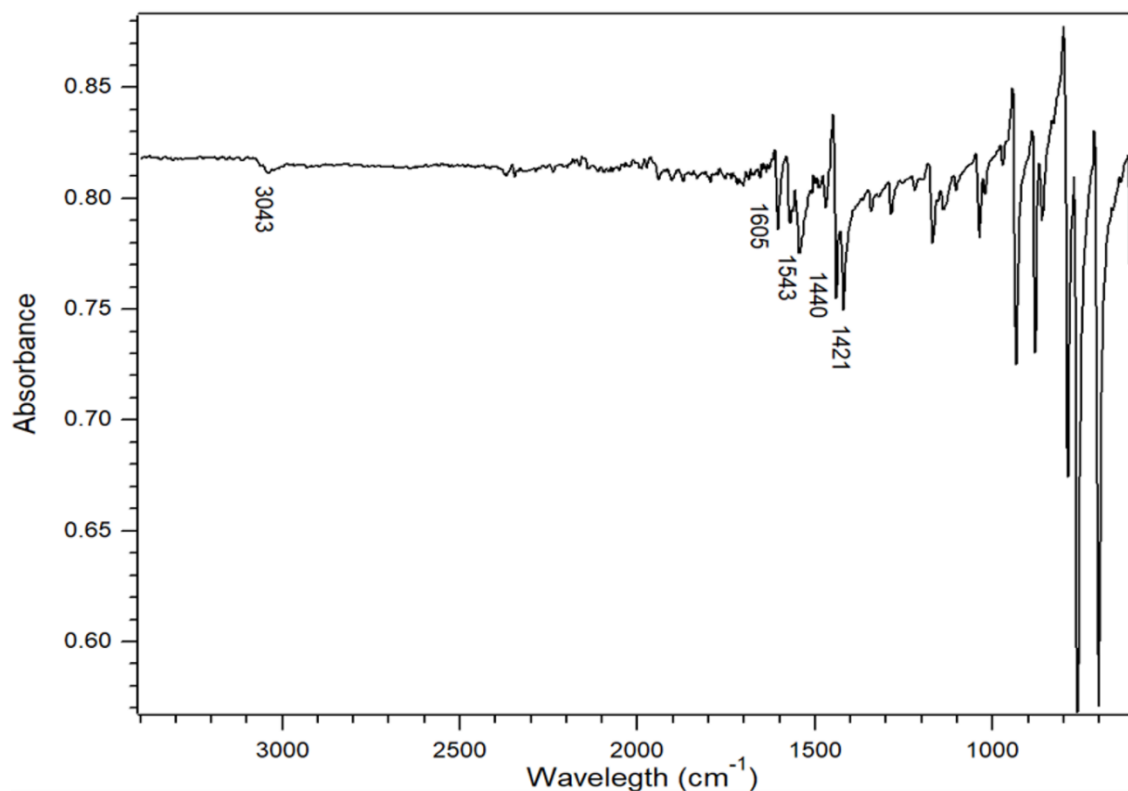
6,12-bis(dibromomethylene)-6,12-dihydroindeno[1,2-b]fluorene (1): A mixture of CBr₄ (2.43 g, 7.08 mmol) and PPh₃ (3.74 g, 14.17 mmol) in anhydrous toluene (100 mL) is stirred at room temperature for 20 min. Then indeno[1,2-b]fluorene-6,12-dione (500 mg, 1.77 mmol) is added and the resulting mixture is refluxed for 12 h. Upon cooling down to room temperature, methanol (200 mL) is added and the resulting precipitate is collected by filtration and thoroughly washed with methanol. The obtained solid is isolated as a yellow powder (753 mg, 1.27 mmol, 72%) with limited solubility in most common organic solvents, the lack of solubility prevented from recording the ¹³C NMR spectrum. ¹H NMR (Cl₂CDCDCl₂, 500 MHz): δ/ppm 8.95 (s, 2H), 8.65 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 7.3 Hz, 2H), 7.51-7.48 (m, 2H), 7.39-7.36 (m, 2H); FTIR (neat): 3043, 1605, 1543, 1440, 1421 cm⁻¹; HRMS calcd. for C₂₂H₁₀Br₄[M⁺], 593.9380; found 593.7314 *m/z*.



¹H NMR (500 MHz, Cl₂CDCl₂, 298 K) of compound 1.



HRMS (MALDI-TOF) of compound **1**.



FT- IR ATR spectrum of compound **1**.

2. Experimental methods

Experiments were performed in a custom-designed ultra-high vacuum system (base pressure below 4×10^{-10} mbar) hosting a commercial low-temperature microscope with STM/AFM capabilities from Scienta Omicron and located at IMDEA Nanoscience.

The substrates (Au(111), Ag(111) and Ag(100), MaTeck GmbH) were prepared by repeated cycles of Ar⁺ sputtering ($E = 1$ keV, SPECS IQE 11/35) and subsequent annealing to 740 K for 10 minutes. All STM images shown were taken in constant current mode, unless otherwise noted, with electrochemically etched tungsten tips, at a sample temperature of 4.3 K (LakeShore). Scanning parameters are specified in each figure caption. Molecular precursor **6,12-bis(dibromomethylene)-6,12-dihydroindeno[1,2-b]fluorene** was thermally deposited (Kentax TCE-BSC) onto three different clean surfaces (Au(111), Ag(111) and Ag(100)) held at room temperature with a typical deposition rate of 0.4 Å/min (sublimation temperature of 190°C), controlled by a quartz micro balance (LewVac). After deposition of 6,12-bis(dibromomethylene)-6,12-dihydroindeno[1,2-b]fluorene, on Au(111) the sample was post-annealed to 200 °C for 20 min to induce the debromination.

Non-contact AFM measurements were performed with a tungsten tip attached to a Qplus tuning fork sensor (Omicron).¹ The tip was a posteriori functionalized by a controlled adsorption of a single CO molecule at the tip apex from a previously CO-dosed surface.² The functionalized tip enables the imaging of the intramolecular structure of organic molecules.³ The sensor was driven at its resonance frequency (26 kHz for Qplus) with a constant amplitude of ~60 pm. The shift in the resonance frequency of the sensor (with the attached CO-functionalized tip) was recorded

in a constant-height mode (Omicron Matrix electronics and MFLI PLL by Zurich Instruments for Omicron). The STM and nc-AFM images were analyzed using WSxM.⁴

3. Additional experimental and computational results

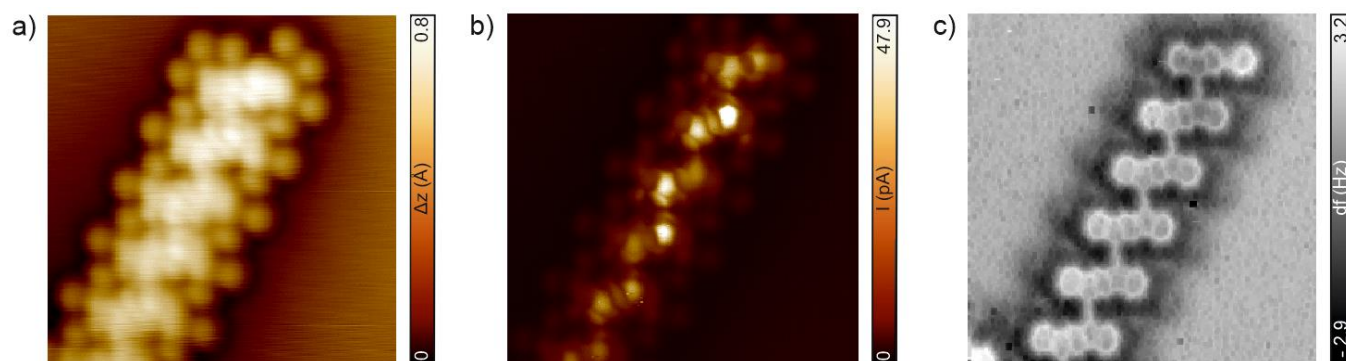


Figure S1. Cumulene-linked indeno[1,2-b]fluorene polymeric chain on Ag(111). a) Zoom-in STM image of the polymer chain comprising five indeno[1,2-b]fluorene units on Ag(111) after deposition at RT. Scanning parameters: $V_b = 50\text{mV}$, $I_t = 30\text{pA}$; Image size: 4 nm x 4 nm. b) High-resolution constant-height STM image of (a). Scanning parameters: $V_b = 5\text{ mV}$. c) Constant-height frequency-shift nc-AFM image of (a) acquired with a CO-functionalized tip. Open feedback parameters: $V_b = 5\text{ mV}$.

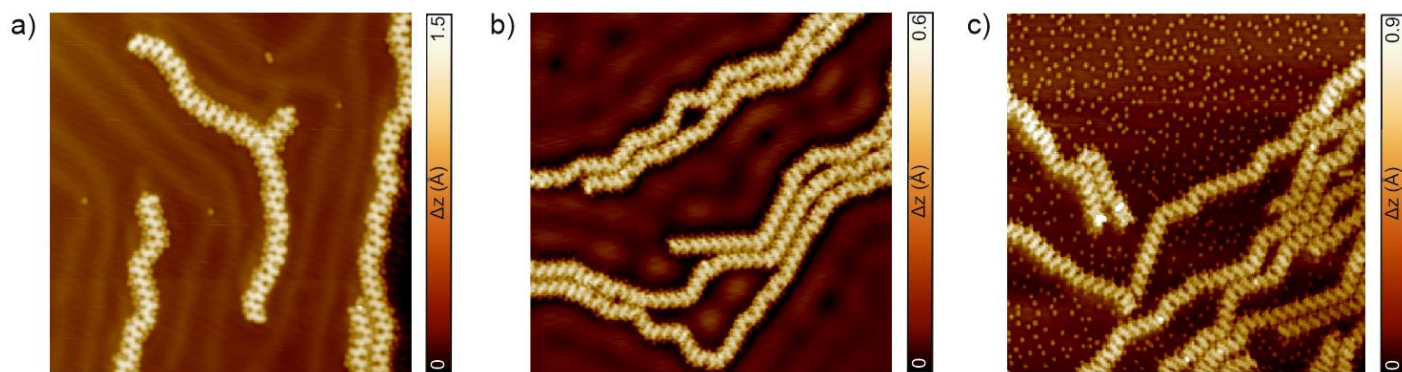


Figure S2. Synthesis of indeno[1,2-b]fluorene polymers on Au(111), Ag(111) and Ag(100). Large-scale STM images of cumulene-like bridged indeno[1,2-b]fluorene polymers formed on three different metal surfaces: Au(111) (a), Ag(111) (b) and Ag(100) (c). Scanning parameters: a) Au(111), $V_b = 200\text{mV}$, $I_t = 80\text{pA}$; b) Ag(111), $V_b = 50\text{mV}$, $I_t = 10\text{pA}$; c) Ag(100), $V_b = 50\text{mV}$, $I_t = 10\text{pA}$. All images size: 25 nm x 25 nm.

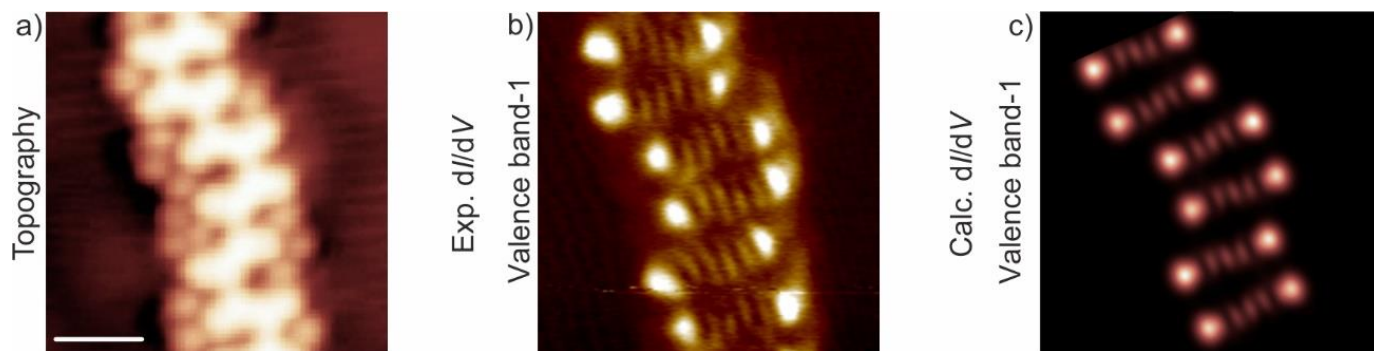


Figure S3. Constant-current dI/dV maps of indeno[1,2-b]fluorene π -conjugated polymers on Au(111) showing the VB-1. a) High-resolution STM image of the polymer chain comprising six indeno[1,2-b]fluorene units. Scanning parameters: $V_b = 50$ mV, $I_t = 100$ pA. Image size: 4 nm x 4 nm. b,c) Constant-current differential conductance (dI/dV) map and corresponding DFT calculated dI/dV map at the energetic position corresponding to the VB-1. Tunneling parameters for the dI/dV maps: $V_b = -1.5$ V, $I_t = 600$ pA.

4. Computational details

Total energy DFT and SPM calculations

Density functional theory (DFT) calculations were performed using the FHI-AIMS code⁵ using B3LYP exchange-correlation functional⁶ to describe the electronic properties of the freestanding polymer. In all the calculations, we employed the light settings for the atomic basis sets. The atomic structures were thoroughly relaxed until the Hellman-Feynman forces were smaller than 10^{-2} eVÅ⁻¹. The infinite chain has been calculated using periodic boundary conditions and the atomic structure and the unit cell were optimized using 18 k-points. The band structure shown on Figure 2c was calculated using 50 k-points. We employed PP-STM code^{7,8} to simulate constant-height dI/dV maps which were shown on Fig. 3f,g. CO-tip was represented by a linear combination of s-like (14%) and p_x, p_y -like (86%) orbitals without tip relaxation at tip-sample distance 5.5 Å.

5. References

- 1 *Appl. Phys. Lett.*, 2000, **76**, 1470–1472.
- 2 L. Bartels, G. Meyer, K.-H. Rieder, D. Velic, E. Knoesel, A. Hotzel, M. Wolf and G. Ertl, *Phys. Rev. Lett.*, 1998, **80**, 2004–2007.
- 3 L. Gross, F. Mohn, N. Moll, P. Liljeroth and G. Meyer, *Science*, 2009, **325**, 1110–1114.
- 4 *Rev. Sci. Instrum.*, 2007, **78**, 013705.
- 5 V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler, *Comput. Phys. Commun.*, 2009, **180**, 2175–2196.
- 6 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372–1377.
- 7 S. Hoshino, *Phys. Rev. B*, 2014, **90**, 115154.
- 8 O. Krejčí, P. Hapala, M. Ondráček and P. Jelínek, *Phys. Rev. B*, 2017, **95**, 045407.