Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information for

Bidirectional light-induced conductance switching in molecular wires containing dimethyldihydropyrene unit

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1. Methods and experimental procedure

Absorption spectra were recorded using either a Varian Cary 50 Scan or a Varian Cary 300 UV-visible spectrophotometer equipped with a temperature controller unit. *^{1}H NMR spectra* were recorded on a Bruker Avance-400 MHz spectrometer in CD_3CN. Chemical shifts (ppm) are referenced to residual solvent peaks.

Atomic force Microscopy: the surface topography was determined by atomic force microscopy (AFM) under ambient air. The topographical features of the sample surfaces were scanned using an AFM soft tapping with Picoplus mode (Molecular Imaging Scientec, les Ulis, France). The tapping mode was performed using a sharp silicon cantilever [Tap150Al-G by Budget Sensor (Sofia, Bulgaria) with Aluminium Reflex Coating]. The cantilever was recorded with a resonance frequency of 150 kHz and a stiffness constant of 5 Nm-1. The RMS roughness values of the scans were calculated using the Gwyddion 2.19 program covered by GNU General Public License.

X-ray photoelectron spectroscopy measurements were performed using a Thermo VG Scientific ESCALAB 250 system fitted with a micro-focused, monochromatic Al Kα (hν = 1486.6 eV) 200 W X-ray source. The X-ray spot size was 500 μm. The samples were stuck on sample holders using conductive double-sided adhesive tape and pumped overnight in the fast entry lock at $\sim 5\times10^{-8}$ mbar prior to transfer to the analysis chamber. The pass energy was set at 100 and 40 eV for the survey and the narrow scans, respectively. Data acquisition and processing were achieved with the Avantage software, version 4.67. Spectral calibration was determined by setting the main C(1s) component at 285 eV. Atomic percentages have been determined using this software and taking into account photoemission cross sections, analyzer transmission, and variation of electron mean free paths with kinetic energy.

Conductivity measurements: the ITO/(Zn-tpy-DHP-tpy)n /Ti junctions were assembled by deposition of a titanium film onto the functionalized ITO surface using electron beam physical vapour deposition. I-V curves were measured by a Keithley 4200-SCS programmable electrometer. The voltage ramp was applied as a staircase function with steps of 50 mV and with an interval of at least 5 s between steps. These parameters were chosen based on the estimated resistive-capacitive (RC) time constants of the junctions (Cjunction ~ 10^{-10} F). For the same thin film, several measurements were made by varying the distance between the titanium patterns. The current values obtained for the same film are fairly close and therefore reproducible.

$Zn(BF_4)_2 \cdot xH_2O$ was purchased from Aldrich. (2,2':6',2''-terpyridine-4-yl)benzenephosphonic acid was prepared according to previously described procedure.[1] Indium tin oxide (ITO) coated glass slides with 30 Ω/sq surface resistivity and a thickness of 6000 Å were purchased from Solems (France).

Synthesis of tpy-DHP-tpy: 2,7-di-tert-butyl-4,9-di-(N-(4'-(4-methylphenyl)-2,2':6',2''-terpyridin-yl)pyridin-4-yl)-trans-10b,10c-dimethyl-10b,10c-dihydropyrene hexafluorophosphate. A degassed solution of 4'-(4-(Bromomethyl)phenyl)-2,2':6',2''-terpyridine (161.4 mg, 0.40 mmol) dissolved in 4 mL of CH_2Cl_2 was added to a stirred solution of 2,7-di-*tert*-butyl-4,9-di-(4-pyridyl)-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (100 mg, 0.20 mmol) in 100 mL of degassed acetonitrile. The reddish mixture was then refluxed for 15 hours under argon atmosphere. After cooling the mixture to room temperature, the solvent was concentrated under reduced pressure and the residue was then precipitated with diethylether. The product was then dissolved in methanol and reprecipitated in an aqueous solution of KPF_6 to afford the ion exchange. The red powder is then filtered, washed with water and dried. (52%).

^1H NMR (500 MHz, 298 K, CD_3CN): δ (ppm) 8.96 (4H, d, J = 6.4 Hz); 8.90 (2H, s); 8.86 – 8.77 (6H, m); 8.77 – 8.69 (10H, m); 8.51(4H, d, J = 4.5 Hz); 8.09 (4H, d, J = 6.2

Hz); 7.99 (4H, td, J = 7.7, 1.8 Hz); 7.82 (4H, d, J = 6.8 Hz); 7.47 (4H, dd, J = 6.2 Hz); 5.95 (4H, s, H); 1.63 (18H, s); -3.62 (6H, s) Exact mass (m/z): calcd: 571.2856, $[M-2PF_6]^{2+}$, found: 571.2851.

^1H NMR [CPD form] (500 MHz, 298 K, CD_3CN): δ (ppm) 8.77 (4H, s); 8.75 – 8.69 (8H, m); 8.66 (4H, d, J = 6.6 Hz); 8.11 (4H, d, J = 6.8 Hz); 8.04 (4H, d, J = 8.1 Hz); 7.98 (4H, td, ^1J = 7.7 ^2J = 1.8 Hz); 7.69 (4H, d, J = 8.1 Hz); 7.47 (4H, dd, ^1J = 7.7 ^2J = 1.8 Hz); 7.41 (2H, s); 7.12 (2H, s); 6.75 (2H, s); 5.77 (4H, s); 1.48 (6H, s); 1.20 (18H, s).

^{13}C [DHP form] NMR (75 MHz, CD_3CN) δ/ppm: 159.92, 157.28, 156.54, 151.07, 150.36, 150.05, 144.94, 140.87, 138.91, 135.08, 134.73, 131.33, 130.75, 130.12, 129.22, 125.28, 123.39, 122.10, 121.44, 119.45, 64.35, 49.91, 37.20, 31.68, 31.39, 15.39.

2. Layer by layer deposition

ITO coated surfaces were used as substrates. They were cleaned by rinsing them with large amounts of ethanol and dried under an air stream then treated using ultraviolet-ozone for 15 min. The first anchoring layer was spontaneously formed by dipping the ITO surfaces overnight and at room temperature into a 1 mM chloroform solution of (4-([2,2':6',2"-terpyridine]-4'-yl)benzyl)phosphonic acid. The substrates were then washed with large amounts of ethanol and dried under an air stream. Using the Layer-by-Layer method, the subsequent self-assembled layers onto the previously pre-functionalized ITO surfaces were formed by alternative dipping the pre-functionalized ITO surfaces into ethanol solutions, 0.1 M, of the $Zn(BF_4)_2 \cdot xH_2O$ salt and into diluted 1:1 (vol:vol) chloroform:ethanol solutions of terpyridine derivatives (1 mM) in ambient air. The dipping time was 2 min in each solution (unless stated otherwise). Between each dipping step, the functionalized surface was carefully rinsed and sonicated with ethanol. The dipping and rinsing steps were performed at room temperature.

3. Contact angles measurements

Contact angles (CA) of water droplets on modified ITO surfaces were recorded under ambient conditions using a video tensiometer system to prove the change in hydrophobicity/hydrophilicity induced after surface modifications by coordination reactions (figure 1). The interfacial contact angle of the water droplet was found to be 70 ± 1° on a freshly cleaned ITO surface and thus considerably larger than 49 ± 1° found for the functionalized ITO/tpy surface. This increase of wettability was due to the nitrogen atoms of terpyridine facing the water droplet. The complexation with zinc cation leads to an ITO/tpy-Zn substrate with a water contact angle of 33 ± 1°, suggesting a more hydrophilic surface since solvent molecules are coordinated to the Zn2+ unit. Coordination of tpy-DHP-tpy increased the contact angle to 44 ± 1° due to exposure of the uncoordinated nitrogen atom of tpy to water.

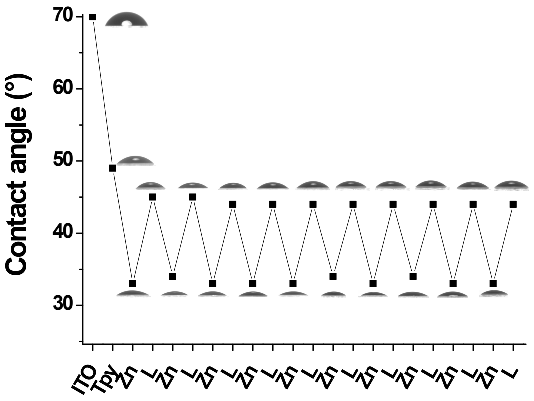

Figure 1: Contact angle during the Layer-by-Layer synthesis of ITO/(Zn-tpy-DHP-tpy)n metallopolymer (Zn: $Zn(BF_4)_2 \cdot 6H_2O$ L: tpy-DHP-tpy)

4. Optical images in the macroscopic scale of the thin film Zn-tpyDHP-tpy)$_{16}$

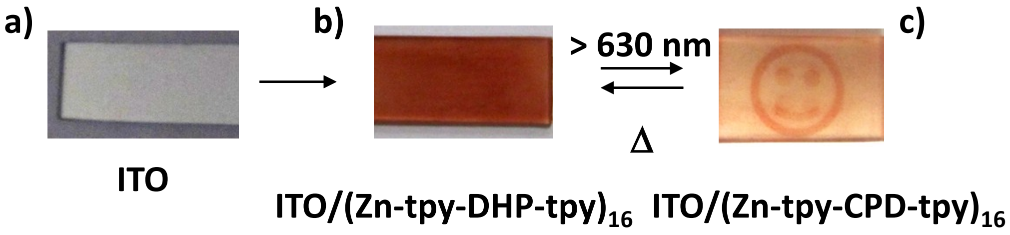

Figure 2. a) ITO substrate, b) after (Zn-tpyDHP-tpy)$_{16}$ deposition, c) after red light irradiation with a smile-mask

5. XPS data

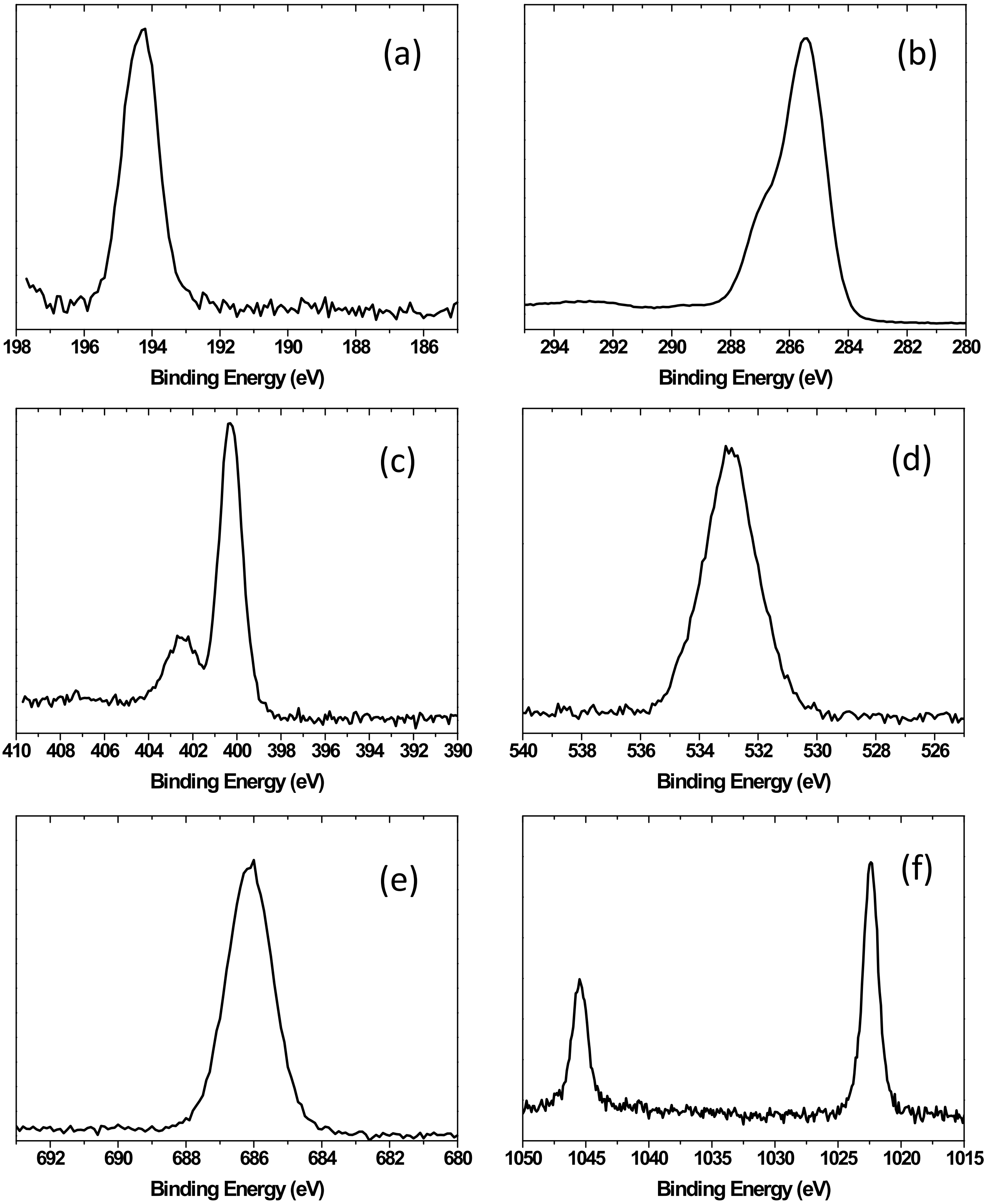

Figure 3. High resolution XPS spectra of the ITO/**(Zn-tpy-DHP-tpy)$_{16}$** substrates, at the (a) B (1s), (b) C (1s), (c) N (1s), (d) O (1s), (e) F (1s), (f) Zn (2p3) core levels.

6. AFM Images and thickness measurements

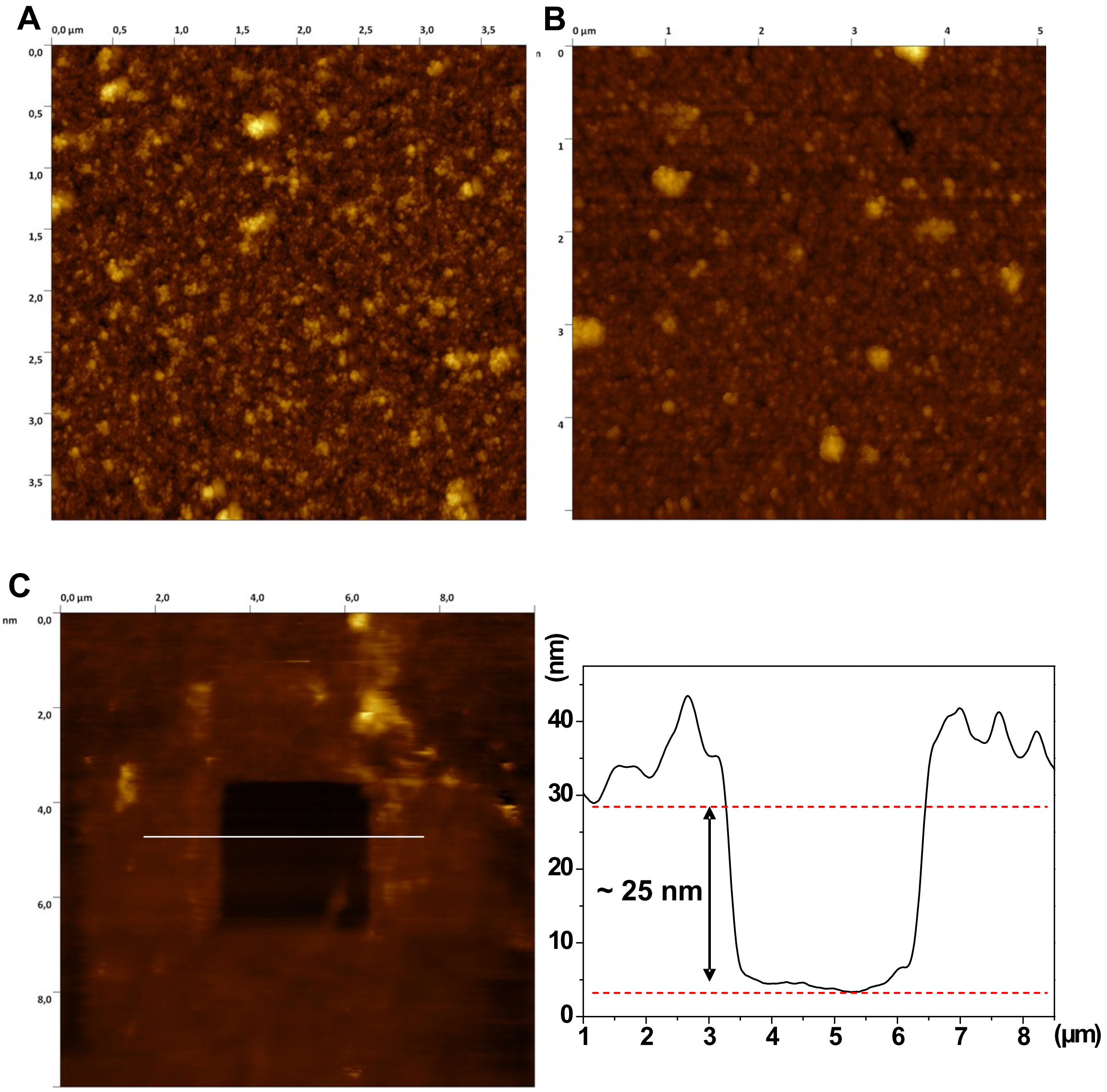

Figure 4. AFM Images of (A) ITO/***(Zn-tpy-DHP-tpy)***$_{16}$, (B) ITO/***(Zn-tpy-DHP-tpy)***$_{5}$ and (C) AFM scratch images and thickness measurement of ITO/***(Zn-tpy-DHP-tpy)***$_{10}$

7. Additional electrical measurements

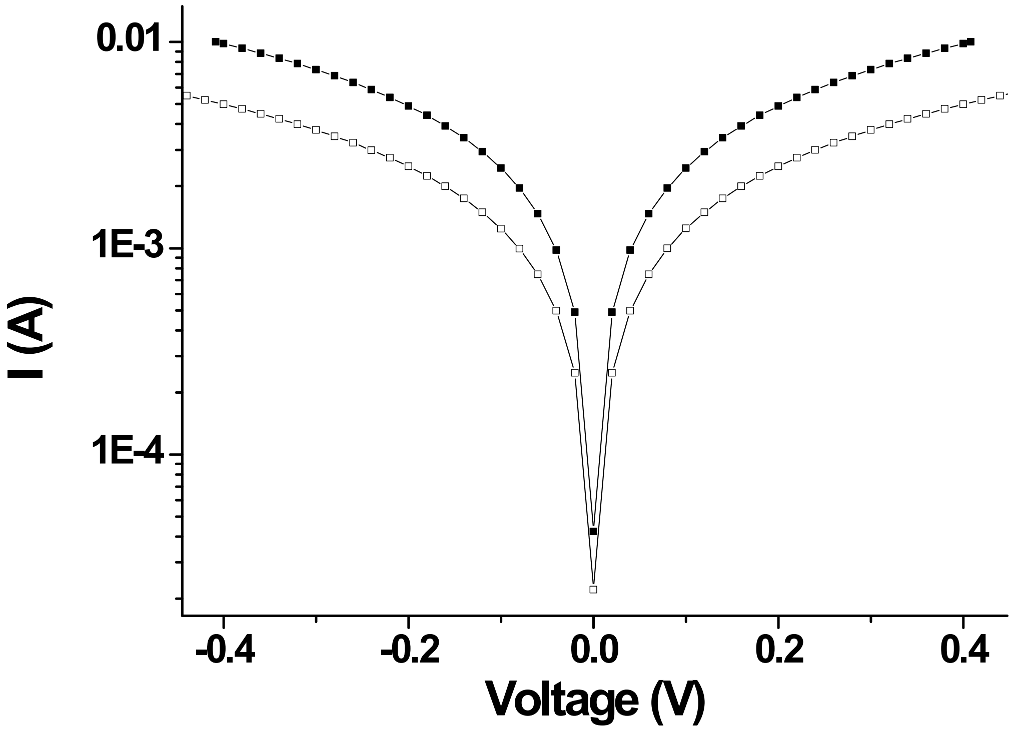

Figure 5.) *I*−V curves of the ITO/***(Zn-tpy-DHP-tpy)$_2$*** /Ti multilayer before (full square) and after (empty square) red irradiation.

8. References

(1) Spampinato, V.; Tuccitto, N.; Quici, S.; Calabrese, V.; Marletta, G.; Torrisi, A.; Licciardello, A. *Langmuir* **2010**, *26* (11), 8400–8406.