

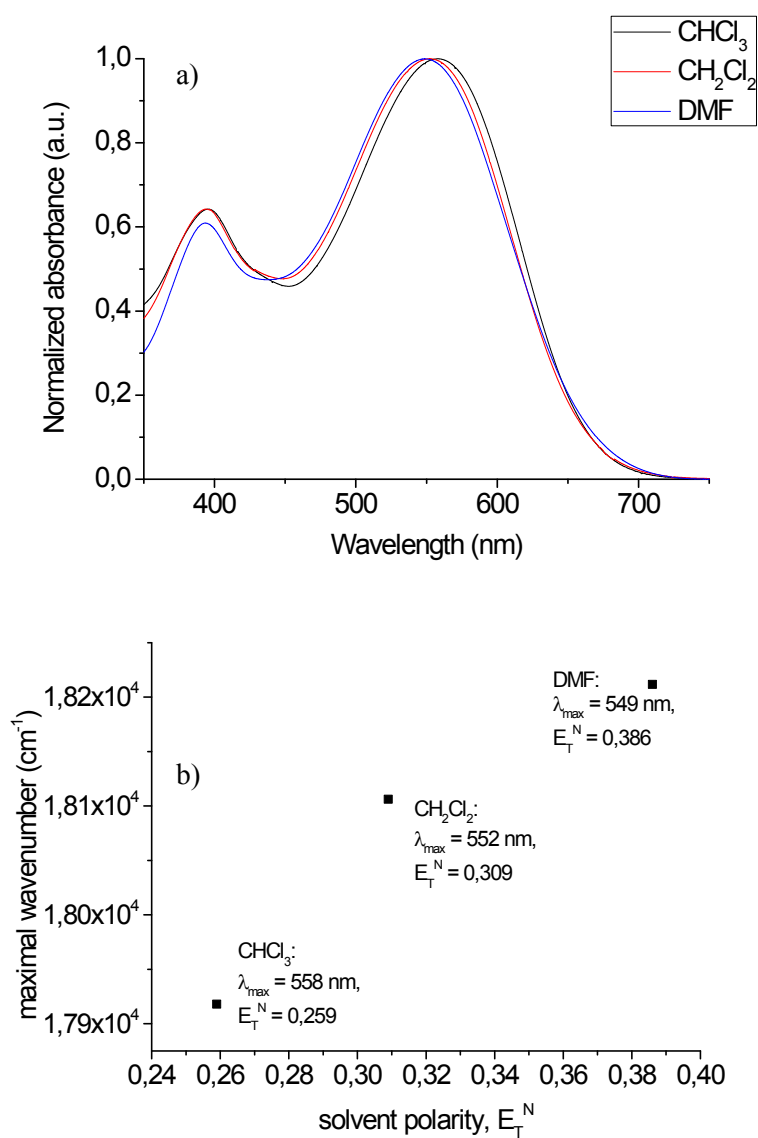
## SUPPORTING INFORMATION

### Synthesis, self-assembly and characterization of a novel push-pull thiophene-based chromophore on gold surface

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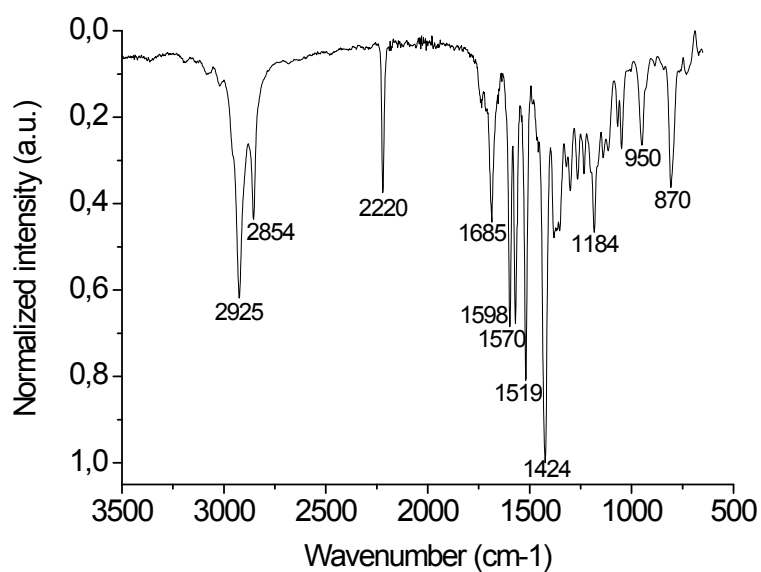
#### Contents

1. **Fig. 1** UV-Vis absorption spectra of molecule **10** in chloroform, dichloromethane, dimethylformamide and the maximal absorption wavenumber versus solvent polarity  $E_T^N$ . **S1**
2. **Fig. S2** Infrared spectrum of molecule **10**. **S2**
3. **Fig. S3** XPS spectra of SAM of **10** on Au (calibrated accordingly to C1s BE = 284.5 eV). **S3**
4. **Fig. S4** Typical Fowler-Nordheim plot from I(V) curve of SAM of **10** for the negative voltage part. The minimum (indicated by the arrow) corresponds to the transition voltage  $V_{T-}$  between direct ( $V < V_{T-}$ ) and Fowler-Nordheim ( $V > V_{T-}$ ) tunneling regimes, *i.e.*, to the alignment of the Fermi level with the molecular level the current flows through. Such analysis of I-V curves is known as Transition Voltage Spectroscopy (see Ref. 47 in the article). **S4**
5. **Fig. S5** Distribution of transition voltage values determined from different I-V curves. The Gaussian fit gives a maximum at  $\approx -0.55$  V. **S5**
6. Synthetic procedures for **8**, **9** and **10**. **S6-S7**



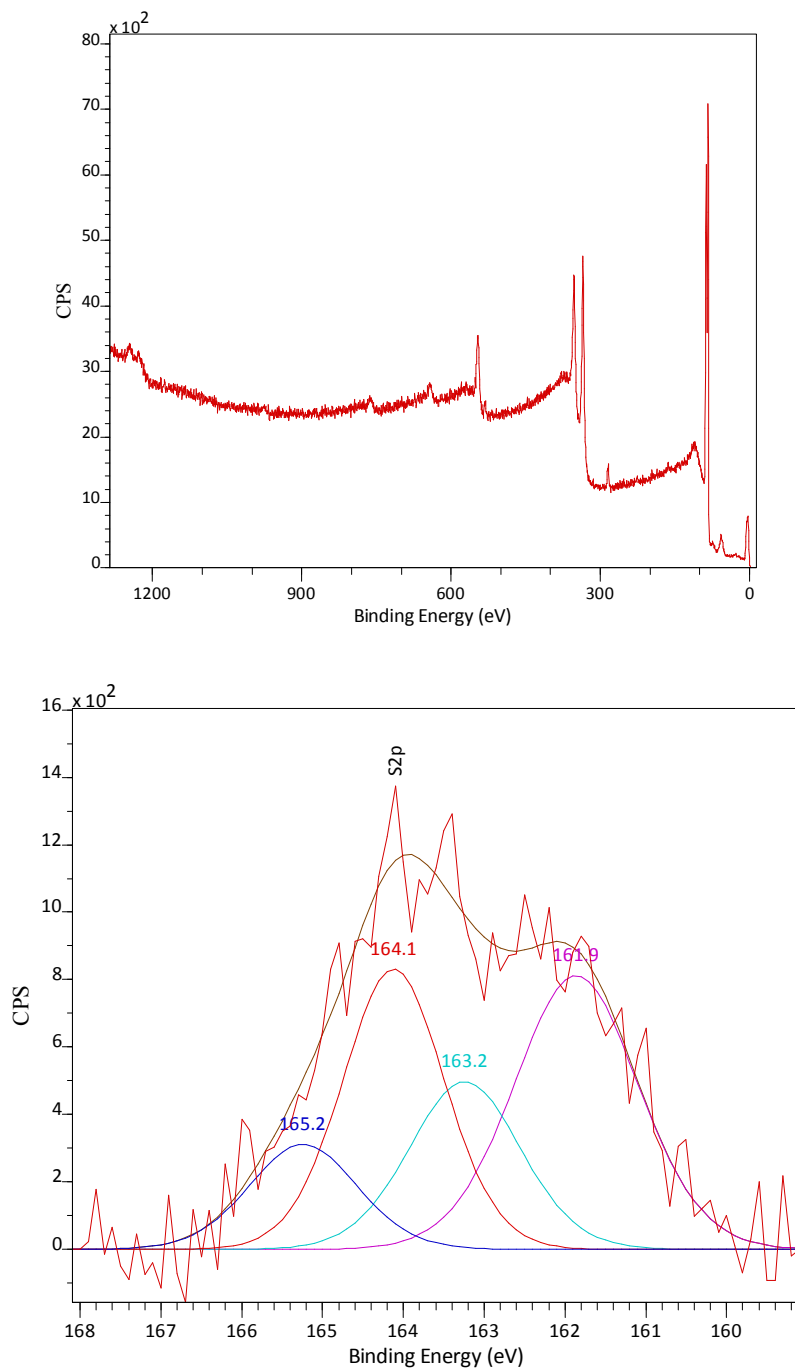
**Figure S1.** a) UV-Vis absorption spectra of molecule **10** in chloroform (black), dichloromethane (red), dimethylformamide (blue) and b) the maximal absorption wavenumber versus solvent polarity  $E_T^N$ <sup>1</sup>.

<sup>1</sup> C. Reichardt *Chemical Reviews*, **1994**, *94*, 2319–2358.



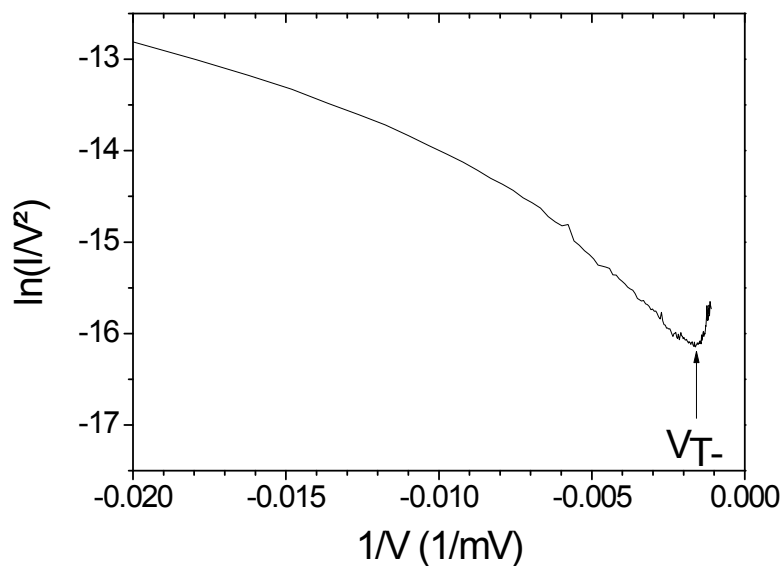
Wavenumber, cm <sup>-1</sup>	2925	2854	2220	1685	1598	1570
Attribution	$\nu(\text{C-H})$ aliphatic	$\nu(\text{C-H})$ aliphatic	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C=O})$ thioacetate	$\nu(\text{C=C})$ donor	$\nu(\text{C=C})$ acceptor
Wavenumber, cm <sup>-1</sup>	1519	1424	1184	950	870	
Attribution	$\nu_s(\text{C=C})$ bithiophene	$\nu(\text{C=C/C-C})$ conjugated	$\nu_s(\text{C-C})$	$\nu(\text{C-S})$ thiophene	$\nu(\text{C-S})$ thioacetate	

**Figure S2.** Infrared spectrum of molecule **10**.

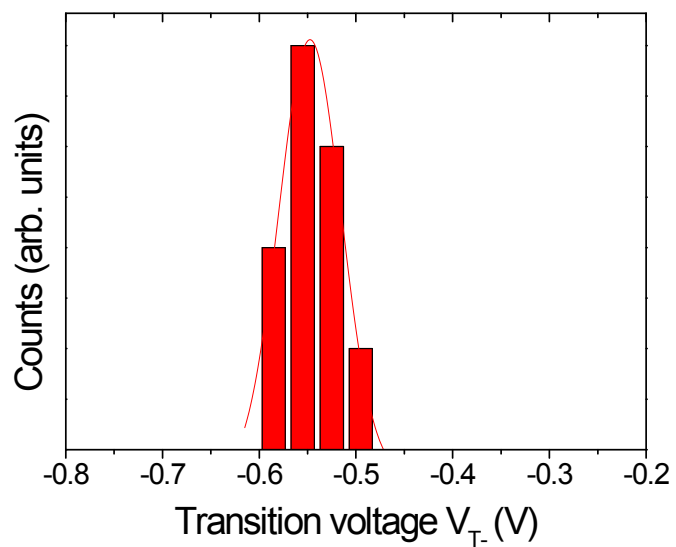


BE, eV	161.9	163.2	164.1	165.2
attribution	S <sub>2p<sub>3/2</sub></sub> S aromatic	S <sub>2p<sub>1/2</sub></sub> S aromatic	S <sub>2p<sub>3/2</sub></sub> S bind to Au	S <sub>2p<sub>1/2</sub></sub> S bind to Au

**Figure S3.** XPS spectra of SAM of **10** on Au (calibrated accordingly to C1s BE = 284.5 eV).



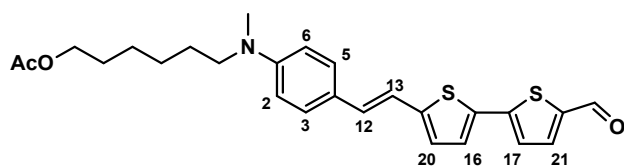
**Figure S4.** Typical Fowler-Nordheim plot from  $I(V)$  curve of SAM of **10** for the negative voltage part. The minimum (indicated by the arrow) corresponds to the transition voltage  $V_{T-}$  between direct ( $V < V_{T-}$ ) and Fowler-Nordheim ( $V > V_{T-}$ ) tunneling regimes, *i.e.*, to the alignment of the Fermi level with the molecular level the current flows through. Such analysis of  $I-V$  curves is known as Transition Voltage Spectroscopy (see Ref. 47 in the article).



**Fig. S5.** Distribution of transition voltage values determined from different I-V curves. The Gaussian fit gives a maximum at  $\approx -0.55$  V.

Synthetic procedures for **8**, **9** and **10**.

(*E*)-6-((4-(2-(5'-formyl-[2,2'-bithiophen]-5-yl)vinyl)phenyl)(methylamino)hexyl acetate (**8**)

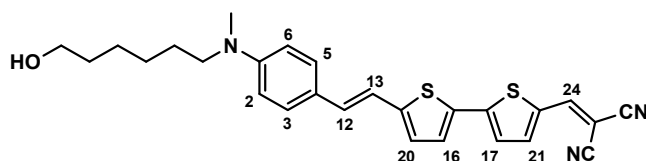


To a solution of [4-(*N*-methyl-*N*-6-acetoxyhexylamino)benzyl] triphenylphosphonium bromide **5** (1.00 g, 1.65 mmol) and 5'-[1,3]dioxolan-2-yl-[2,2'] bithienyl-5-carboxaldehyde **7** (0.40 g, 1.50 mmol) in 20 mL of a mixture (V:V) of anhydrous THF (10

mL) and CH<sub>3</sub>CN (10 mL) under Ar atmosphere at 0 °C was added portionwise sodium *tert*-butoxide (0.16 g, 1.65 mmol). The reaction was stirred at 0 °C and followed by <sup>1</sup>H NMR until the disappearance of the signal at 9 ppm corresponding to free aldehyde (about 2.5 hours). Hydrochloric acid (10 mL, 2M) was then added at 0 °C and the reaction mixture was further stirred 0.5 hours prior careful neutralization with an aqueous solution of sodium hydroxide (1M). Combined dichloromethane extracts were washed with water and dried over MgSO<sub>4</sub>. The organic phase was filtered and the solvent was removed under reduced pressure. The crude solid was passed through a pad of SiO<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub>) affording a crude mixture of the *cis/trans* isomers of **8** at ratio 3:7. The latter was dissolved into 50 mL of CHCl<sub>3</sub> and few crystals of iodine were added to the solution prior to reflux during 1 hour. The reaction mixture was cooled to room temperature, concentrated and purified by column chromatography over SiO<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub> then CH<sub>2</sub>Cl<sub>2</sub>: AcOEt (9:1), R<sub>f</sub> = 0.6) leading to 0.65 g of pure *trans*-**8** (93%) as a dark-red solid.

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ, ppm: 9.84(1 H, CHO, s), 7.65 (1 H, 21CH, d, J = 3.75 Hz), 7.36 (2 H, 3-CH & 5-CH, d, J = 8.75 Hz), 7.25 (1 H, 16CH, d, J = 3.75 Hz), 7.21 (1 H, 17CH, d, J = 3.75 Hz), 6.98 (1 H, 13CH, d, J = 15.75 Hz), 6.92 (1 H, 20CH, d, J = 3.75 Hz), 6.89 (1 H, 12CH, d, J = 15.75 Hz), 6.67 (2 H, 2-CH & 6-CH, d, J = 8.75 Hz), 4.06 (2 H, OCH<sub>2</sub>, t, J = 6.75 Hz), 3.35 (2 H, NCH<sub>2</sub>, t, J = 7.25 Hz), 2.98 (3 H, NCH<sub>3</sub>, s), 2.04 (3 H, CH<sub>3</sub>CO, s), 1.3 – 1.7 (8 H, aliphatic-CH<sub>2</sub>, 2 m). <sup>13</sup>C NMR (62.86 MHz, CDCl<sub>3</sub>) δ, ppm: 182.31, 171.16, 141.17, 137.41, 127.91, 126.85, 123.69, 123.64, 64.37, 58.47, 53.40, 28.57, 26.73, 25.82, 20.98, 18.44. ESI-MS: (Calcd) 468.1662; (Found) 468.1661 ([M+H]<sup>+</sup>).

(*E*)-2-((5'-(4-((6-hydroxyhexyl)(methylamino)styryl)-[2,2'-bithiophen]-5-yl)methylene)malonodinitrile (**9**)

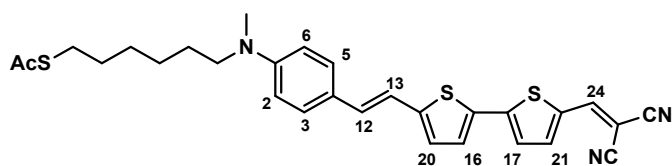


Compound **8** (0.65 g, 1.40 mmol) was dissolved in 20 mL of a mixture (V:V) of dichloromethane and methanol. To the solution was added 10 mL of a 10M aqueous solution of sodium hydroxide and stirred for 4 hours at room temperature. The reaction

mixture was then extracted twice with CH<sub>2</sub>Cl<sub>2</sub> and the organic phase was washed with water and dried over MgSO<sub>4</sub>. The organic phase was filtered and the solvent was removed under reduced pressure. The crude material was used without further purification in the next step. Thus the obtained intermediate (0.3 g) was dissolved in ethanol (100 mL) and malonodinitrile (0.14 g, 2.10 mmol) was added followed by 3 drops of Et<sub>3</sub>N and the reaction mixture was refluxed for 2 hours. Ethanol was removed under reduced pressure and the crude product was purified by column chromatography over SiO<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub>: AcOEt (95:5), R<sub>f</sub> = 0.3) affording **9** as a dark-violet solid in 95% yield for the 2 steps.

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ, ppm: 7.72 (1 H, 24CH, s), 7.62 (1 H, 21CH, d, J = 4 Hz), 7.39 (2 H, 3-CH & 5-CH, d, J = 8 Hz), 7.33 (1 H, 16CH, d, J = 4 Hz), 7.23 (1 H, 17CH, d, J = 4.25 Hz), 7.01 (1 H, 13CH, d, J = 15.75 Hz), 6.98 (1 H, 20CH, d, J = 4 Hz), 6.92 (1 H, 12CH, d, J = 15.75 Hz), 6.79 (2 H, 2-CH & 6-CH, br), 3.65 (2 H, OCH<sub>2</sub>, t, J = 6.5 Hz), 3.36 (2 H, NCH<sub>2</sub>, t, J = 7.5 Hz), 3.01 (3 H, NCH<sub>3</sub>, s), 1.3 – 1.7 (8 H, aliphatic-CH<sub>2</sub>, 2 m).

*(E)-S-(6-((4-(2-(5'-(2,2-dicyanovinyl)-[2,2'-bithiophen]-5-yl)vinyl)phenyl)(methyl)amino)hexyl)ethanethioate (10)*



Compound **9** (0.35 g, 0.74 mmol) was dissolved in 20 mL of anhydrous chloroform under Ar atmosphere. PBr<sub>3</sub> (0.3 g, 0.11 mL, 1.10 mmol) was added and the reaction mixture was stirred at room temperature during 48 h (during that time

the color changes from dark-violet to red). The reaction mixture was neutralized with a saturated aqueous solution of Na<sub>2</sub>CO<sub>3</sub>. Organic phase was separated, dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure affording a crude product that was used in the next step without further purification. The crude solid was dissolved in 20 mL of a mixture (1:3) EtOH/CH<sub>2</sub>Cl<sub>2</sub>) and potassium thioacetate (0.3 g, 2.60 mmol) was added. The reaction mixture was stirred overnight at room temperature. The titled product was purified by column chromatography over SiO<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub>, R<sub>f</sub> = 0.5) yielding 0.12 g (31 % yield) of **10** as a dark-violet solid.

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ, ppm: 7.66 (1 H, 24CH, s), 7.57 (1 H, 21CH, d, J = 4 Hz), 7.34 (2 H, 3-CH & 5-CH, d, J = 8.75 Hz), 7.29 (1 H, 17CH, d, J = 4 Hz), 7.18 (1 H, 16CH, d, J = 4 Hz), 6.95 (1 H, 13CH, d, J = 16 Hz), 6.92 (1 H, 20CH, d, J = 4 Hz), 6.87 (1 H, 12CH, d, J = 16 Hz), 6.67 (2 H, 2-CH & 6-CH, d, J = 8.75 Hz), 3.34 (2 H, NCH<sub>2</sub>, t, J = 7.25 Hz), 3.97 (3 H, NCH<sub>3</sub>, s), 2.86 (2 H, SCH<sub>2</sub>, t, J = 7.25 Hz), 2.32 (3 H, CH<sub>3</sub>COS, s), 1.2 – 1.7 (8 H, aliphatic-CH<sub>2</sub>, 2 m). <sup>13</sup>C NMR (62.86 MHz, CDCl<sub>3</sub>) δ, ppm: 195.85, 149.85, 149.70, 147.91, 140.22, 132.86, 131.94, 131.35, 128.12, 128.07, 127.88, 125.99, 123.85, 116.09, 114.48, 113.65, 112.08, 111.96, 74.90, 53.39, 38.39, 30.59, 29.44, 28.95, 28.57, 26.54. ESI-MS: (Calcd) 532.1546; (Found) 532.1542 ([M+H]<sup>+</sup>).