# Supporting information

# Superstructure manipulation and electronic measurement of monolayers constituted by a discotic liquid crystalline with intrinsic dipole moment using STM/STS

Kum-Yi Cheng,<sup>b</sup> Chih-Hsun Lin,<sup>b</sup> Mei-Chun Tzeng,<sup>c</sup> Ayyaz Mahmood,<sup>a</sup> Muhammad Saeed,<sup>a</sup>

Chun-hsien Chen,\*b Chi Wi Ong,\*c Shern-Long Lee\*a

- a. Institute for Advanced Study, Shenzhen University, Shenzhen, Guangdong, China 518060.
- b. Department of Chemistry and Center for Emerging Material and Advanced Devices, National Taiwan University, Taipei, Taiwan, 10617.
- c. Department of Chemistry, National Sun Yat-sen University, Kaohsiung, Taiwan, 80424.

\*E-mail: sllee@szu.edu.cn, chhchen@ntu.edu.tw, cong@mail.nsysu.edu.tw

## **Content of Supporting Information**

## S1.1 Experimental section: STM and STS

## **S1.2 Simulations**

- **Fig. S1.** The molecular potential energy maps and dipole moments vectors of **1** simulated by DFT calculations
- **Fig. S2.** Representative models for the two polymorphs of **1**.
- Fig. S3. STM results for the examination of solvent effect of the present study.
- **Fig. S4.** The section-profile analyses revealing the difference in the apparent height for the two polymorphs of **1**.
- Fig. S5. The STS measurements of the two polymorphs of 1.

#### S1.1 Experimental section: STM and STS

The synthesis of **1** was described in our previous report. <sup>(S1)</sup> All experiments were performed at room temperature (e.g., 24 °C). Solutions of **1** were prepared in 1-phenyloctance, octanoic acid or n-tetradecane (analytical-level solvent) for STM measurement (sample biased). The STM images were acquired at the liquid-solid interface by a MultiMode NanoScopeIIIa (Bruker) with typical imaging parameters of  $E_{\text{bias}}$  and  $i_{\text{tunnelling}}$  being  $-0.9\sim0.9$  V and ranging from 10 to 300 pA, respectively. Pt/Ir tips (80%/20%, diameter 0.25 mm) were mechanically cut. The images were repeated in several sessions and calibrated by an SPIP software (scanning probe image processor, Image Metrology ApS) *via* imaging the graphite substrate underneath.

Tunnelling spectra were obtained at the liquid-solid interface with the feedback-loop closed, thus determining the tip-sample distance. Due to noise, 10 % of the STS curves were discarded. To reduce thermal drift, prior to recording the I-V curves, we first scanned a large-area surface and then zoomed-in on a small area including the selected points for STS measurements. <sup>(S2)</sup> This practice ensures that we can reliably record STS curves at specific locations. The dI/dV traces were acquired through a lock-in amplifier.

#### **S1.2 Simulations**

Ground state geometry optimizations of **1** with different functional groups were performed with DFT/B3LYP method and 6-311g(d,p) basis set in gas-phase using Gaussian09 package.<sup>(S3)</sup> The molecular potential energy map and dipole moment of the molecule were simulated at DFT/B3LYP/6-311g(d,p). An isovalue of 0.02 was used for drawing the surface.



**Fig. S1.** The molecular potential energy maps and dipole moments vectors of **1** with functional groups OH (left), OCH<sub>3</sub> (middle), and OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (right). The figures on the left and right are same, just with different color codes. The surfaces are drawn with an iso-value of 0.02. The atoms in the Figures on the right are colored according to their calculated charges. Calculations performed at B3LYP/6-311g(d,p) using force keyword to compute the dipole moment as a proper analytic derivative of the energy.

The electronegative oxygen and nitrogen atoms cause the molecule to be polar and thus increasing the magnitude of intrinsic dipole moment, which results in the larger polarity of the molecule and a lower band gap. The lower band gaps indicate larger intramolecular charge transfer (ICT) for **1** with larger alkyl chains. The large intrinsic dipole moment is proposed to be responsible for the phase transitions of the polymorphs of the targeted molecule under the tuning of the electrical polarity of substrate.



**Fig. S2.** Representative models for the two polymorphs of **1**. The floating alkoxylated chains are showed in the models. (a,b) top view and (c,d) side-view models.



Fig. S3. STM results for the examination of solvent effect of the present study. Solvent: (a) octanoic acid, (b) n-tetradecane. The use of solvents such as octanoic acid or n-tetradecane did not lead to any significant effect. Imaging conditions:  $E_{\text{bias}}$ , -900 mV;  $i_{\text{tunnelling}}$ , 150 pA.



**Fig. S4.** The section-profile analyses revealing the difference in the apparent height for the two polymorphs of **1**. (a) Red and blue lines in the STM image indicate the height measurements for **packing i** (the red arrow) and **packing ii** (the blue arrow). (b,c) The section profiles of **packing i** and **packing i-ii**. The difference in height for **packing i** and **packing ii** is *ca*. 0.15 nm, indicating that the **packing i** has a higher conductance, which may result from a lying-down orientation.



**Fig. S5.** The STS measurements of the two polymorphs of **1**. Star marks in panel a and b display the locations in STM images for STS recording. Lower panels show the IV and dI/dV curves with standard deviations. The red and black data are the STS of **packing i** (panel a) and **packing ii** (panel b), respectively. The results show that the band gap of **packing i** is smaller than that of **packing ii**.

#### **References:**

- (S1) M. C. Yeh, Y. L. Su, M. C. Tzeng, C. W. Ong, T. Kajitani, H. Enozawa, M. Takata, Y. Koizumi, A. Saeki, S. Seki and T. Fukushima, *Angew. Chem. Int. Ed.*, 2013, **52**, 1031.
- (S2) S. L. Lee, Z. Yuan, L. Chen, K. S. Mali, K. Mullen and S. De Feyter, *J. Am. Chem. Soc.*, 2014, 136, 4117.
- (S3) M. J. G Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb *et al.* Gaussian 09, Revision D.01 2009.