## Supporting Information

# Spontaneous and Scanning-Assisted Desorption-Adsorption Dynamics in Porous Supramolecular Networks at the Solution-Solid Interface

Yuan Fang, <sup>\*a,d,e</sup> Oleksandr Ivasenko,<sup>a,d,f</sup> Ana Sanz-Matias,<sup>a,h</sup> Kunal S. Mali,<sup>a</sup> Kazukuni Tahara,<sup>g</sup> Yoshito Tobe, <sup>\*b,c</sup> Steven De Feyter<sup>\*a</sup>

- a. Division of Molecular Imaging and Photonics, Department of Chemistry, KU Leuven, Celestijnenlaan 200 F, 3001 Leuven, Belgium. E-mail: steven.defeyter@kuleuven.be.
- b. Department of Applied Chemistry, National Yang Ming Chiao Tung University, 1001 Ta Hsueh Road, Hsinchu 30030, Taiwan
- c. The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan. Email: tobe@chem.es.osaka-u.ac.jp
- d. Institute of Functional Nano & Soft Materials (FUNSOM), Joint International Research Laboratory of Carbon-Based Functional Materials and Devices, Soochow University, Suzhou, 215123, Jiangsu, PR China. E-mail: yfang2000@suda.edu.cn
- e. Jiangsu Key Laboratory of Advanced Negative Carbon Technologies, Soochow University, Suzhou, 215123, Jiangsu, PR China.
- f. Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou, 215123, Jiangsu, PR China.
- g. Department of Applied Chemistry, School of Science and Technology, Meiji University, 1-1-1 Higashimita, Tama-ku, Kawasaki, Kanagawa, 214-8571, Japan.
- h. The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

### AUTHOR INFORMATION

#### **Corresponding Author**

\*(Y.T.) E-mail: tobe@chem.es.osaka-u.ac.jp. Telephone: +81 66850 6225.

- \*(S.D.F.) E-mail: steven.DeFeyter@chem.kuleuven.be. Telephone: + 32 1632 7921.
- \*(Y.F.) E-mail: yfang2000@suda.edu.cn. Telephone: +86 18217381272

## **Methods:**

#### **STM experiments**

All STM images were acquired using an Agilent PicoLE system operating in constant-current mode with the tip immersed in the supernatant liquid. STM tips were prepared by mechanical cutting of Pt/Ir wire (80/20, diameter 0.25 mm). Several samples were investigated, and for each sample, multipul locations were probed. The imaging parameters  $I_{set}$  (tunnelling current) and  $V_{bias}$ (substrate bias) are described in the figure captions. Voltage pulsing of around 3V was repetitively applied until high-resolution images where black contours are visible. The substrate bias was always kept negative, indicating a tunnelling current from the substrate to the STM tip. All DBA derivatives used were synthesized using previously published synthesis protocols.<sup>1,2,3</sup> The solvent, 1-phenyloctane (Sigma, 98%) was used without further purification. Concentrated  $(1 \times 10^{-3} \text{ M})$ stock solutions of the achiral and chiral DBA derivatives were prepared by weighing the appropriate amount of solid powders. The solutions for dynamics experiments were prepared by mixing the stock solutions at a certain molar ratio and these were further diluted. Immediately before use, the HOPG substrate (grade ZYB, Advanced Ceramics) was freshly cleaved using adhesive tape. An open liquid cell (inner diameter = 3.1 mm) constructed of polytetrafluoroethylene (PTFE) was used to hold ~40 µl of the desired solution on the HOPG substrate (Supplementary Fig. 1).



**Figure S1.** The experimental setup for all samples. (a) Liquid cell (b) Schematic showing an open liquid cell arrangement for experiments at the solution-solid interface. (c) Picture of the liquid cell setup.

#### **Molecular Dynamics**

Molecular Dynamics simulations were performed in order to investigate the effect of a nearby tiplike object on the self-assembled cDBA structure.

First, initial structures were generated using 8 cDBA-OC12(R)-OC13(S) molecules interdigitated into a honeycomb structure. The method of the supramolecules<sup>4</sup> was used to obtain equilibrium lattice parameters of the cDBA (a = 4.72 nm, gamma = 60). Then, a quasi-commensurate bilayer graphene was added as well as a tip, placed 20 A away from the graphene surface, and 1065 molecules of phenyloctane (density = 0.84 g/ml) using packmol<sup>5</sup> forming a box of 9.37 × 8.36 × 6.20 nm<sup>3</sup>.

Initial structures with the tip at different heights (in 0.1 A intervals) were generated by tip displacement and optimization followed by NVT equilibration (300 ps, 298 K), considered as stabilization of the RMSD. These, as well as the production trajectories, were carried out using the OPLS-AA<sup>6, 7</sup> force field and the GROMACS<sup>8</sup> software package. The atomic positions of the tip and the graphene were restrained in place by a harmonic potential.

From every tip-height starting point, production trajectories were obtained at 298 K temperature, using the velocity-rescaling method.<sup>9</sup> A 2 ps timestep was used, facilitated by restraining the carbon-hydrogen bonds with the Lincs algorithm.<sup>10</sup> The particle-mesh Ewald method was used to include long-range electrostatic interactions.<sup>11</sup> Trajectory analysis was carried out with GromacsWrapper.<sup>12</sup> Upon request, GROMACS topology files are available.

#### **Probability estimation**

In the experimental observation (Fig 2b,c) of spontaneous desorption/adsorption 7 cDBA molecules either 1) did not desorb, or 2) after desorption have re-adsorbed in the same locations. The proposed calculation is a rough estimation of the likelihood of "2)", i.e. the probability to observe 7 out of 39 cDBA molecules re-adsorbed in the same location.  $C_n^m = C(n,m) = n!/m!(n-m)!$  is the number of possible m-combinations out of total n objects. Specifically:  $C_{39}^7$  is the number of possible combinations of choosing 7 out of 39 chiral molecules.  $C_{1101}^{39}$  is the number of possible combinations of total n objects. Specifically:  $C_{39}^7$  is the number of possible combinations of 20 chiral molecules re-adsorbing in different 1101 positions that were previously occupied by achiral DBAs.  $C_{1140}^{39}$  is the total number of possible combinations of 39 chiral molecules distributed within all 1140 adsorption cites after re-adsorption.

$$P(BC \text{ to } BC) = \frac{C_{\# \text{ of } BC}^{\# \text{ of } BC \text{ appear at the same location}} \cdot C_{\# \text{ of } BC \text{ appear at different location}}^{\# \text{ of } BC}}{C_{\# \text{ of } \text{ total adsorption sites}}^{\# \text{ of } BC}}$$

$$P(7) = \frac{C_{39}^7 \cdot C_{1101}^{32}}{C_{1140}^{39}} = 1.9 \times 10^{-4}$$







**Figure S2.** Scanning induced desorption dynamics of cDBA-OC12(*S*). (a-q) Selected STM images from a sequence obtained on the same area, recorded every 2 minutes, for 40 minutes with continued scanning, taken at 26 °C. The monolayer was formed from a 1-phenyloctane solution of DBA-OC12 containing 30 mol% cDBA-OC12-(*S*). a) is an original STM image without filtering. The wavy background surface was purposely chosen as a guide to help minimize thermal draft during scanning. For better visualization of the 'black contour' molecules, the background was filtered out using the FFT filtering in WSxM. Image a2 is the FFT filtered image of image a1. *I*<sub>set</sub>=0.2 nA, *V*<sub>bias</sub>=-0.2 V.



**Figure S3.** Scanning induced desorption dynamics of cDBA-OC12(*S*) at higher current set point (0.5 nA). (a-i) Full sequence of STM images obtained on the same area, recorded every 2 minutes, for 16 minutes with continued scanning, taken at 26 °C. The monolayer was formed from a 1-phenyloctane solution of DBA-OC12 containing 30 mol% cDBA-OC12(*S*). Black contour molecular are highlighted by coloured circles. The blue coloured circles in (a) correspond to the cDBA-OC12(*S*) that were observed in the first frame. A new color are applied to represent new cDBA-OC12(*S*) that have replaced DBA-OC12. It can be seen that in 4 mins all the original presented cDBA are all replaced by DBA-OC12. *I*<sub>set</sub>=0.5 nA,  $V_{\text{bias}}$ =-0.2 V.



**Figure S4.** Scanning induced desorption dynamics of cDBA-OC12(*S*)-OC13(*R*) at the 1-phenyloctane/HOPG interface taken at 26 °C ( $C = 2.5 \times 10^{-6}$  M containing 6 mol% cDBA-OC12(*S*) -OC13(*R*) and 94 mol% DBA-OC12. Selected STM images from a sequence obtained in

approximately the same area by 50 minutes of continuous STM scanning. Each image was obtained in about 2 minutes. Imaging conditions:  $I_{set} = 0.2$  nA,  $V_{bias} = -0.2$  V.



**Figure S5.** Molecular dynamics simulation of the early stages of tip-induced cDBAOC12(*S*) desorption. Snapshots demonstrate how tip, approached within the distances required to maintain the set-point current, deforms alkyl chain interdigitation and weakens cDBA adsorption. The tip is colored according to its distance from the surface: from blue (10 Å) to red (5 Å).





**Figure S6.** A demonstration of the local nature of cDBA removal at the 1-phenyloctane/HOPG interface taken at 21 °C (C =  $8 \times 10^{-6}$  M containing 70 mol% cDBA-OC12(*S*) and 30 mol% DBA-OC12). a) A 200 × 200 nm<sup>2</sup> scan. b-e) Zoomed-in images at the area outlined by the square in a). Selected STM images from a sequence obtained in approximately the same area by 26 minutes of continuous STM scanning. Each image was obtained in about 2 minutes. An estimated rate constant of the tip-induced desorption at 21 °C is ~0.116 s<sup>-1</sup>. f) By continuous scanning at the same 100 × 100 nm<sup>2</sup> area until most of the cDBA molecules are removed, followed by zooming out to obtain an image at 200 × 200 nm<sup>2</sup>. Figure 3e and Figure S5f are identical, but were used for different proposes. g) Without scanning in between, another 200 × 200 nm<sup>2</sup> image was taken at the

same location. (a'-g') Original images without processing. (a-g) Imaging conditions:  $I_{set} = 0.2$  nA and  $V_{bias} = -0.2$  V.

## **References:**

- 1. K. Tahara, H. Yamaga, E. Ghijsens, K. Inukai, J. Adisoejoso, M. O. Blunt, S. De Feyter and Y. Tobe, Nat. Chem., 2011, 3, 714-719.
- 2. E. Ghijsens, H. Cao, A. Noguchi, O. Ivasenko, Y. Fang, K. Tahara, Y. Tobe and S. De Feyter, Chem. Commun., 2015, 51, 4766-4769.
- 3. K. Tahara, S. Furukawa, H. Uji-i, T. Uchino, T. Ichikawa, J. Zhang, W. Mamdouh, M. Sonoda, F. C. De Schryver, S. De Feyter and Y. Tobe, J. Am. Chem. Soc. , 2006, 128, 16613-16625.
- 4. S. Conti and M. Cecchini, Phys. Chem. Chem. Phys., 2016, 18, 31480-31493.
- 5. L. Martínez, R. Andrade, E. G. Birgin and J. M. Martínez, J. Comput. Chem., 2009, 30, 2157-2164.
- 6. W. L. Jorgensen, D. S. Maxwell and J. Tirado-Rives, J. Am. Chem. Soc., 1996, 118, 11225-11236.
- 7. H. Heinz, R. A. Vaia, B. L. Farmer and R. R. Naik, J. Phys. Chem. C, 2008, 112, 17281-17290.
- 8. H. J. C. Berendsen, D. van der Spoel and R. van Drunen, Comput. Phys. Commun., 1995, 91, 43-56.
- 9. G. Bussi, D. Donadio and M. Parrinello, J. Chem. Phys., 2007, 126, 014101.
- 10. B. Hess, H. Bekker, H. J. C. Berendsen and J. G. E. M. Fraaije, J. Comput. Chem., 1997, 18, 1463-1472.
- 11. U. Essmann, L. Perera, M. L. Berkowitz, T. Darden, H. Lee and L. G. Pedersen, The Journal of Chemical Physics, 1995, 103, 8577-8593.
- 12. Oliver Beckstein, Pedro Lacerda, Jan Domański, David Dotson, Andrew White Max Linke, Ian Kenney and Cody, Andy Somogyi, Richard Gowers, Philip Loche and Mohamad Mohebifar. GromacsWrapper, https://github.com/Becksteinlab/GromacsWrapper