Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Efficient Screening of 2D Molecular Polymorphs at the Solution–Solid Interface

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Content:

Experimental Section:

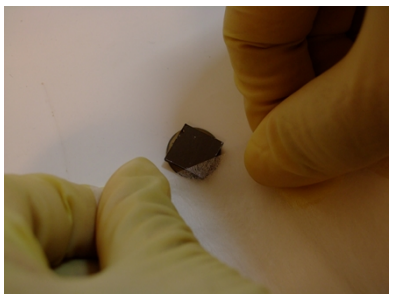
STM experiments

All experiments were performed at the solution-solid interface at room temperature (RT, 19－22°C) using a Nanoscope IIIa (Bruker) machine operating in constant-current mode. STM tips were prepared by mechanical cutting from Pt/Ir wire (80%/20%, diameter 0.25 mm). 1, 2, 4-trichlorobenzene (TCB, Sigma-Aldrich, ≥99%) and 1-octanoic acid (OA, Sigma-Aldrich, ≥99%) were used as the solvent without further purification. Prior to imaging, solid alkoxylated dehydrobenzo[12]annulene (**DBA-OC_{16}**), hexadecyl-substituted rhombic-shaped bis(dehydrobenzo[12]annulene (**bisDBA-C_{16}**), and 1,3,5-tris(4-carboxyphenyl)benzene (1,3,5-benzenetribenzoic acid (**BTB**), were dissolved in either TCB or OA in appropriate amount and a droplet of the sample solution was applied by a pipette onto a freshly cleaved surface of highly oriented pyrolytic graphite (HOPG, grade ZYB, Advanced Ceramics Inc., Cleveland, USA). The experiments were repeated in several sessions using different tips to check for reproducibility and to avoid experimental artifacts, if any. For analysis purposes, recording of a molecular image was followed by imaging the graphite lattice underneath it under the same experimental conditions, except for lowering the bias. The images were corrected for drift *via* Scanning Probe Image Processor (SPIP) software (Image Metrology ApS), using the recorded graphite images for calibration purposes, allowing a more accurate unit-cell determination. The unit-cell parameters were determined by examining at least 5 images and only the average values are reported. The imaging parameters are indicated in figure captions: sample bias (V_{bias}) and tunneling current (I_{set}).

The shear flow method

The flow process for molecular polymorph screening and separation consisted of the following protocol: Upon applying a 10-μL droplet of **DBA-OC_{16}**, **bisDBA-C_{16} or BTB** sample solution on HOPG, a piece of lens tissue or Kimwipe™ was employed to absorb the solvent. The linear flow rate was *ca.* 0.5－0.6 mm/s. This procedure produces a steady laminar flow. A photograph below illustrates the shear flow treatment with a piece of paper.[(1)]

The specific flow rate is essential for successfully uncovering and separating the polymorphs of a given compound. Since the flow rate and thus force triggered by the adsorption *via* tissues is determined by the volume of the solution droplet on HOPG, the simple flow method for uncovering and separation of polymorphs of a given compound will be successful only if a large enough volume is applied. For instance, a drop of 10-μL solvent leads to a linear flow rate of *ca.* 0.5—0.6 mm/s, which is effective for uncovering and separation of the molecular polymorphs in this study, whereas a solvent volume less than 3 μL is unable to create an effective flow for this purpose.



Histogram

Each histogram presented in the study showing the relative surface coverage of polymorphs of **DBA-OC_{16}**, **bisDBA-C_{16} and BTB** as a function of distance from the tissue contact line was acquired from at least 5 representative positions/distances, at least 4 100 × 100-nm^2 STM images and 3 experimental sessions.

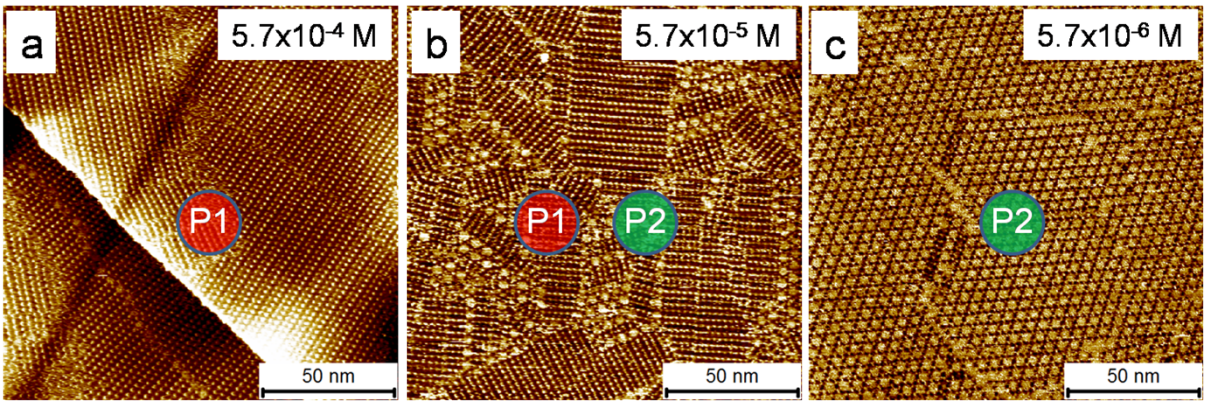


Figure S1. Concentration dependent polymorphism in **DBA-OC$_{16}$** monolayers Representative STM images of the 2D network of **DBA-OC$_{16}$** upon dropcasting at various concentrations. The concentrations of the 3 samples are noted in the Figures. Note that these images were taken at random positions on the as-prepared sample surfaces. Imaging conditions: V_{bias} = 500 mV, I_{set} = 100 pA.

Conc. (M)	Coverage (θ)			
	P1'	P2'	P3'	P4'
1.0×10^{-4}	8%	92%	0%	0%
1.0×10^{-5}	12%	87%	1%	0%
4.0×10^{-6}	3%	81%	15%	0%
3.0×10^{-6}	2%	69%	28%	0%
2.0×10^{-6}	3%	53%	43%	0%
1.5×10^{-6}	0%	0%	86%	14%
1.3×10^{-6}	0%	0%	81%	19%

Table S1. Relative surface coverage of the polymorphs of **bisDBA-C_{16}** on HOPG surface at various concentrations. This data is obtained from REF [(2)] P1'—P4' of **bisDBA-C_{16}** are defined in the Scheme 1 in the main text.

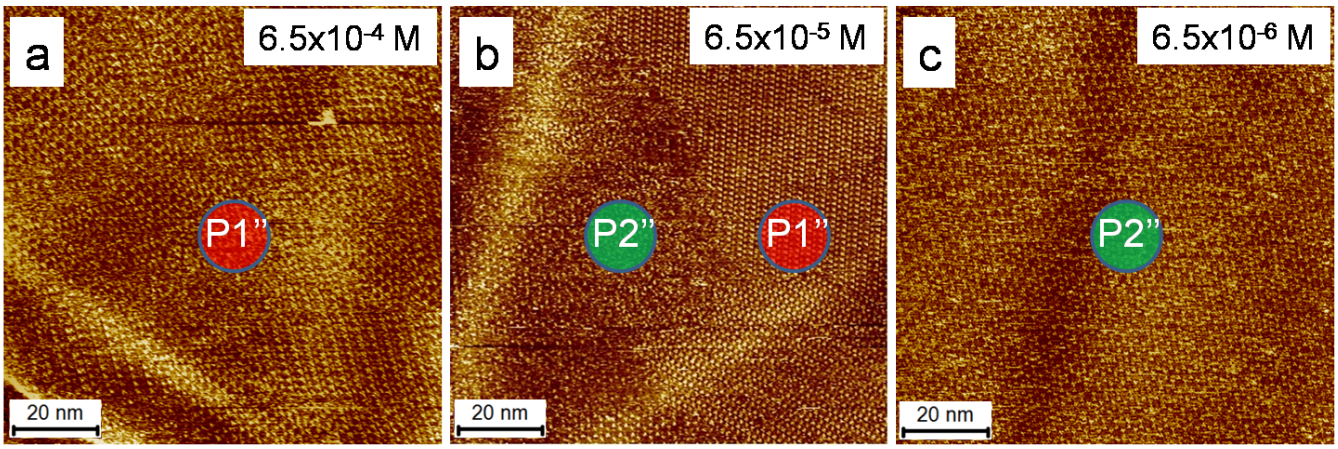


Figure S2. Concentration dependent polymorphism in BTB monolayers. Representative STM images of the 2D network of **BTB** acquired upon drop casting at different concentrations. The concentrations of the 3 samples are noted in the figures. Imaging conditions: V_{bias} = -600 mV, I_{set} = 100 pA.

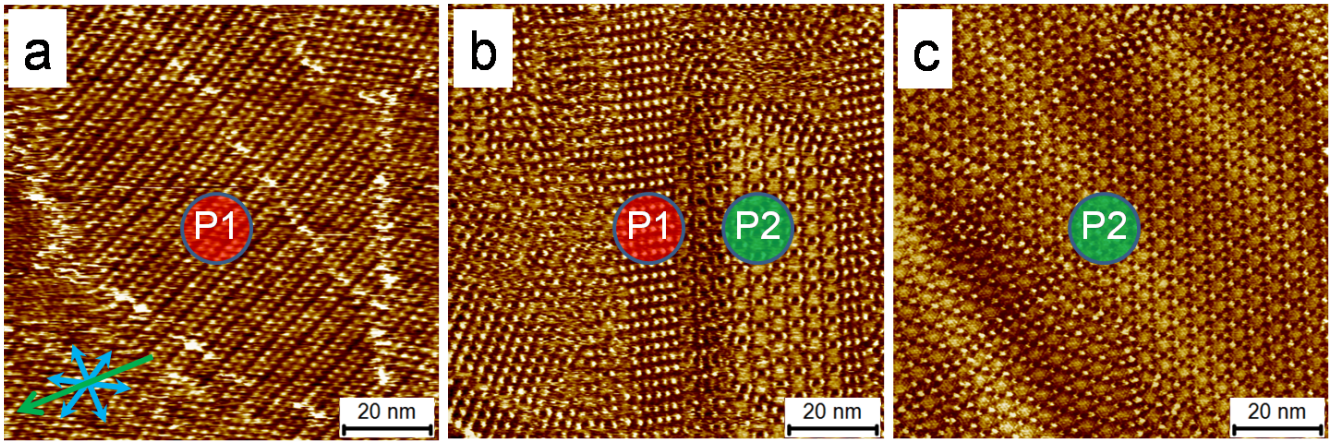


Figure S3. STM images of the 2D network of **DBA-OC$_{16}$** upon applying flow along the direction parallel to the normal to the main symmetry axes of HOPG lattice (**[DBA-OC$_{16}$]** = 5.5 x 10^{-6} M). Panels a—c were probed at a distance of *ca.* 0.5, 1.5 and 3 mm from the tissue paper contact line, respectively. P1 and P2 are the linear and porous type polymorphs of **DBA-OC$_{16}$**. This result is virtually identical to the one in Figure 1 in the main text except for the multiple small domains of the linear motifs of **DBA-OC$_{16}$**. Upon applying flow in a random direction, results are similar. These observations suggest that the flow method for polymorphs screening is independent of the flow direction applied. The green arrow in panel (a) indicates the direction along which the solution flow was applied during the sample preparation. The blue arrows on images indicate the 3-fold symmetry of the underlying HOPG. Imaging conditions: V_{bias} = 500 mV, I_{set} = 100 pA.

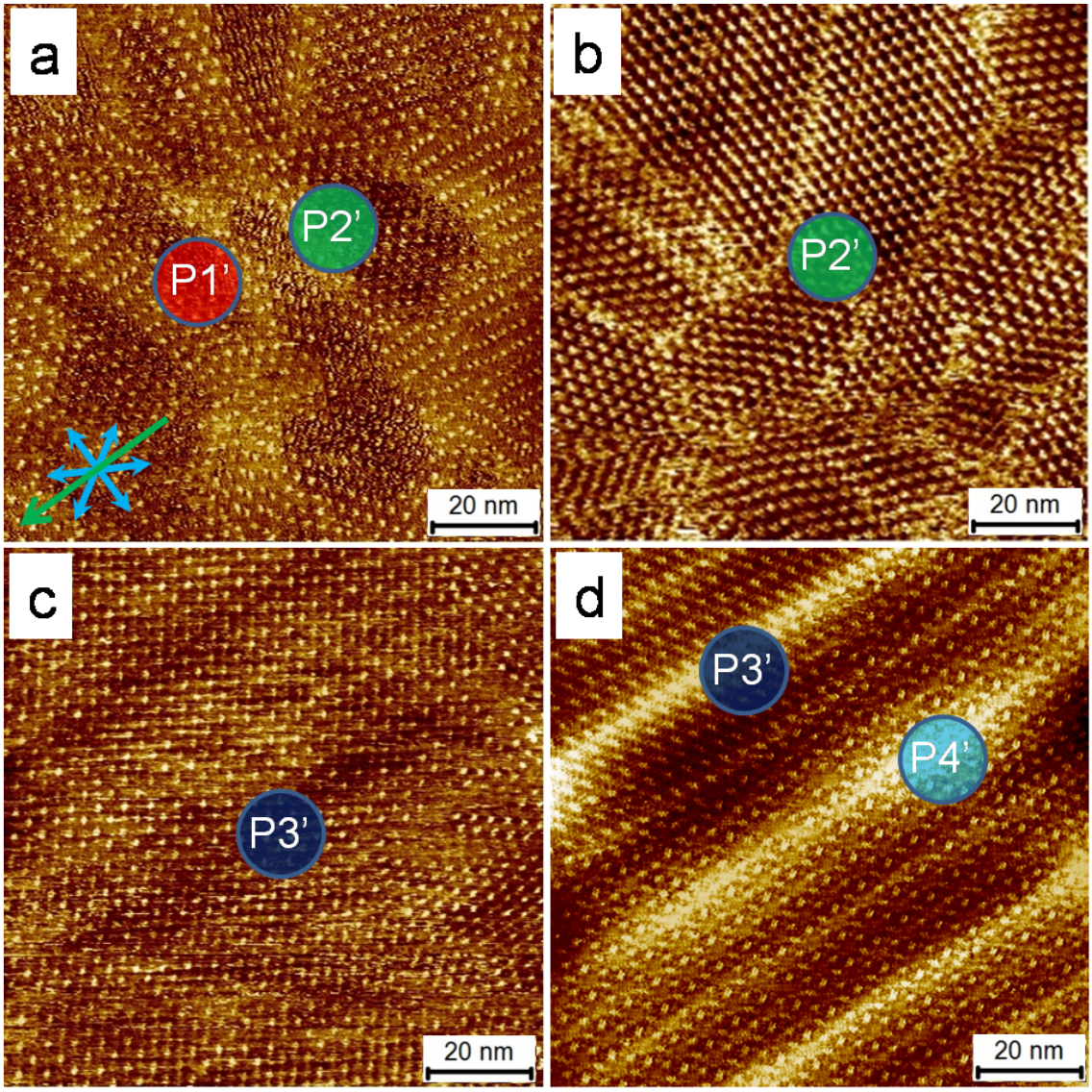


Figure S4. STM images of the 2D network of **bisDBA-C_{16}** after applying flow along the direction parallel to the normal to the main symmetry axes of HOPG lattice (**[bisDBA-C_{16}]** = 1.3 x 10^{-6} M). Panels a—d were probed at a distance of *ca.* 0.5, 1, 2 and 3 mm, from the tissue paper contact line, respectively. P1'—P4' of **bisDBA-C_{16}** are defined in the Scheme 1 in the main text. Upon applying flow along the main symmetry axes of HOPG, similar results are obtained. The blue arrows on images indicate the 3-fold symmetry of the underlying HOPG. Imaging conditions: V_{bias} = 600 mV, I_{set} = 100 pA.

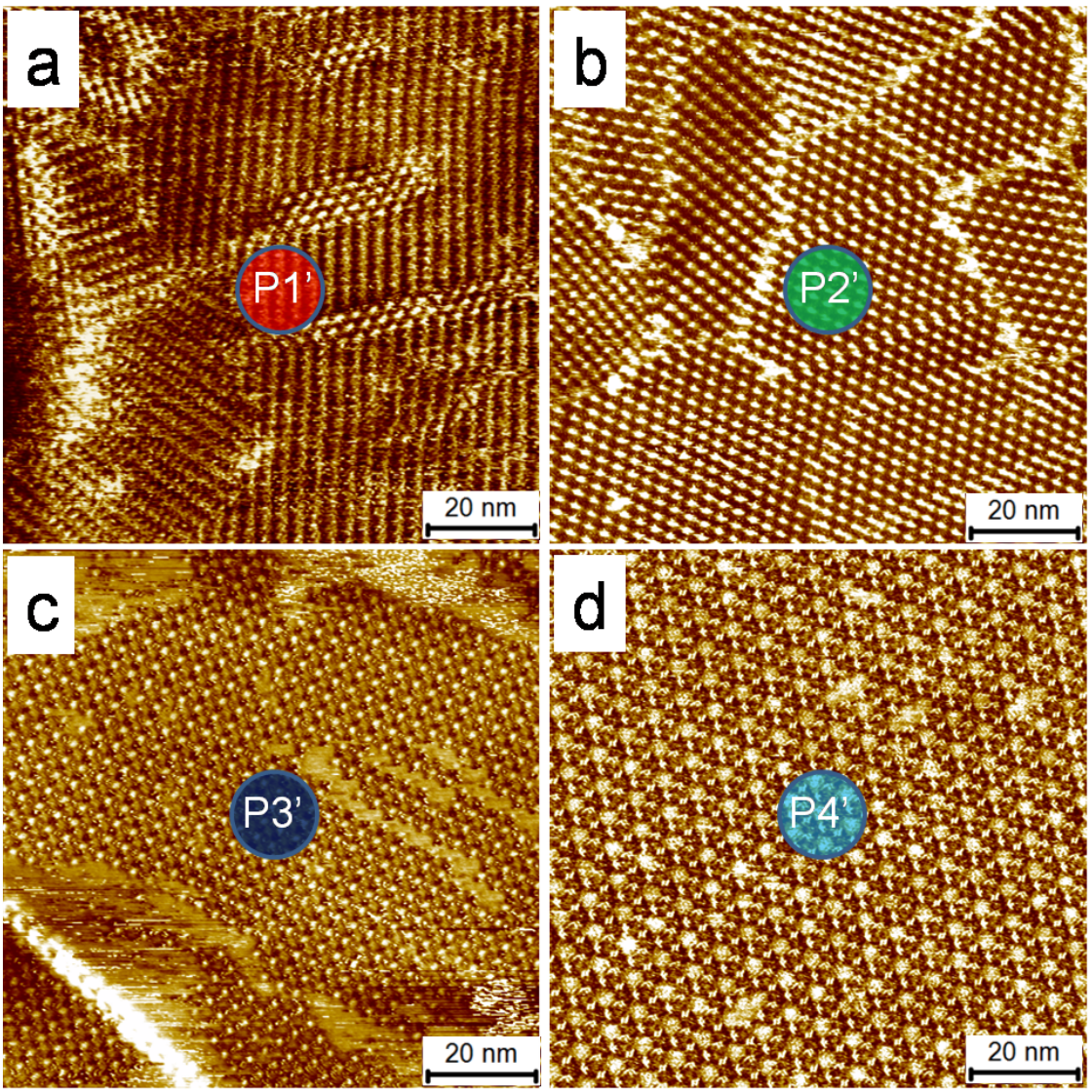


Figure S5. STM images showing that each of the polymorphs of **bisDBA-C_{16}** mainly appear in specific zones of the active area generated by flow. Panels a—d are networks P1'—P4' of **bisDBA-C_{16}** probed at a distance of *ca.* 0.5, 1, 2, and 3 mm from the tissue paper contact line, respectively. Imaging conditions: V_{bias} = 600 mV, I_{set} = 100 pA.

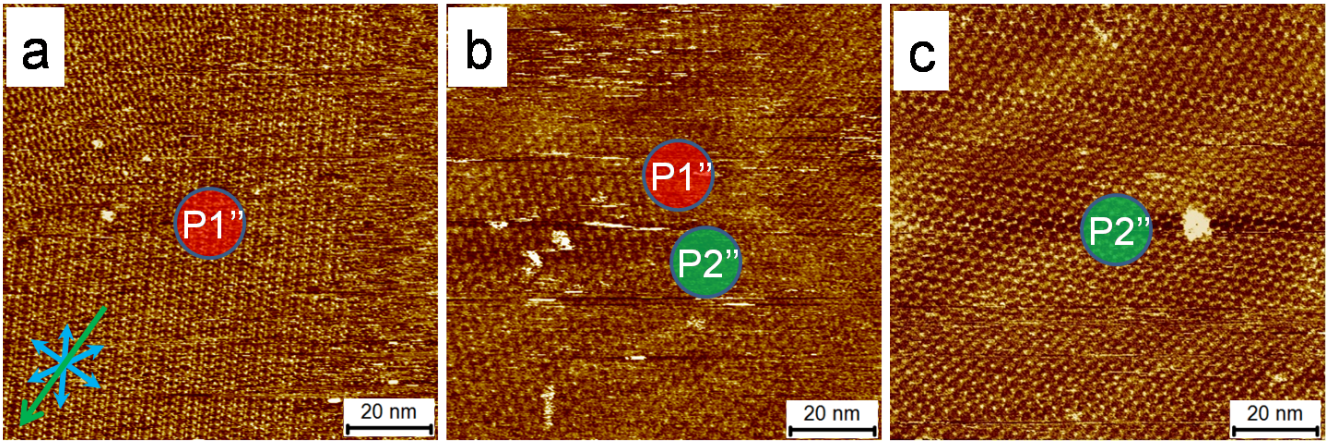


Figure S6. STM images of the 2D network of **BTB** after applying flow parallel to the normal to the main symmetry axes of HOPG lattice (**[BTB]** = 6.5 x 10^{-6} M). Panels a—c were probed at a distance of *ca.* 1, 2, and 3 mm from the tissue paper contact line, respectively. P1'' and P2'' are the densely packed and chicken-wire polymorphs of **BTB**. This result is virtually identical to the one in Figure 3 in the main text except for the multiple small domains of the densely packed polymorph of **BTB.** Applying a flow in a random direction produces similar results. The green arrow in panel a) indicates the flow direction applied during the process of the sample preparation. The blue arrows on images indicate the 3-fold symmetry of the underlying HOPG. Imaging conditions: V_{bias} = -600 mV, I_{set} = 100 pA.

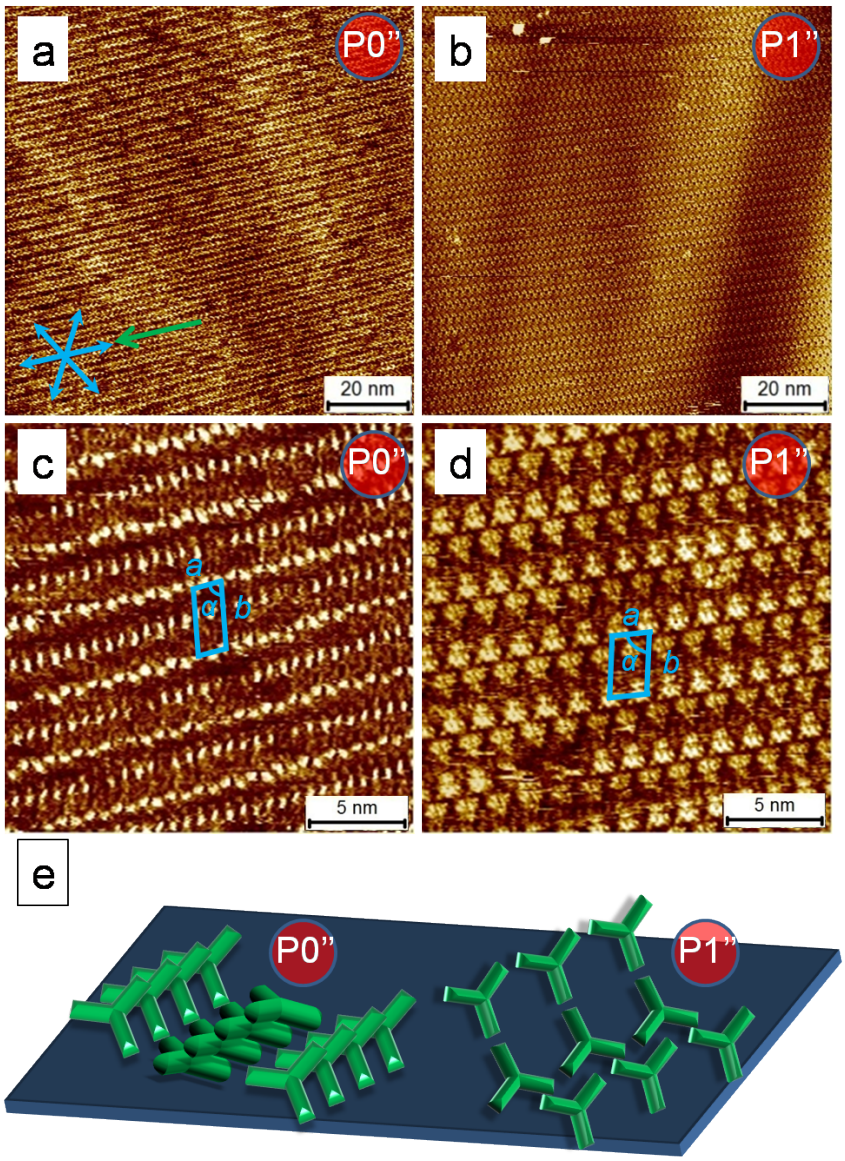


Figure S7. Impact of solute concentration on the flow method for screening of 2D molecular polymorphs: *The case of the high solute concentration* (**[BTB]** = 6.5 x 10^{-4} M). This relatively concentrated solution yielded a pair of polymorphs, one of which was previously in accessible at lower concentration (after flow). **BTB** forms a highly dense phase (defined P0'' here) upon using concentrated solutions together with previously observed P1''. Polymorph P0'' appears near the tissue paper contact line whereas *ca.* 1 mm away from the line, P1'' is observed. The P0'' structure has been previously reported by Lackinger et al. and they observed it upon drop casting a saturated solution of **BTB in OA**.[3] The green arrow in panel a) indicates the flow direction applied during the process of the sample preparation and the blue arrows indicate the 3-fold symmetry of the underlying HOPG. The unit-cell parameters of P0'' and P1'': a = 1.3 ± 0.2 nm, b = 3.3 ± 0.2 nm, α = 84.2 ± 2.8° and a = 1.8 ± 0.1 nm, b = 3.2 ± 0.2 nm, α = 74.4 ± 1.9°. Imaging conditions: V_{bias} = -600 mV, I_{set} = 100 pA.

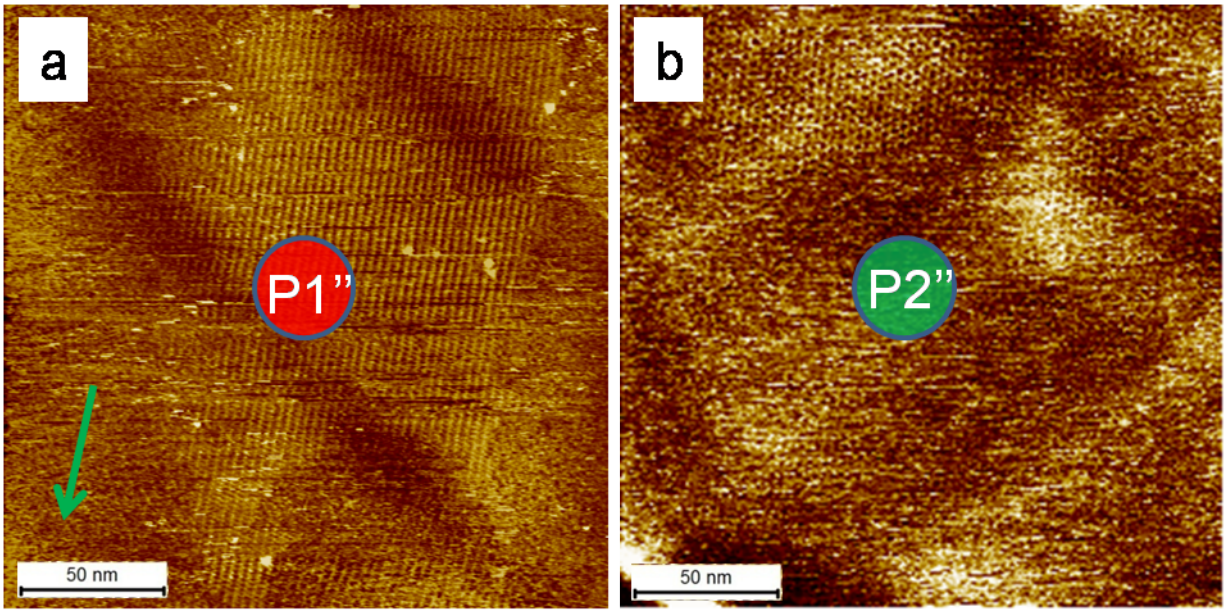


Figure S8. Impact of solute concentration on the flow method for screening of 2D molecular polymorphs: *The case of the sub-monolayer concentration*. To further check the impact of solute concentration, we took the **BTB** system as representative example in this study and ran an experiment in which the flow was applied on a sample with sub-monolayer concentration (**[BTB]** = 1.6 x 10^{-6} M). By using STM for mapping the as-prepared sample surface, we found that although appearing with low coverage, there is densely packed polymorph (P1'') of **BTB** near the tissue paper contact line (a). The areas far away from the contact line show sub-monolayer coverage of the low-density polymorph (P2'') (b). The green arrow in panel a) indicates the flow direction applied during the process of the sample preparation. Imaging conditions: V_{bias} = -600 mV, I_{set} = 100 pA.

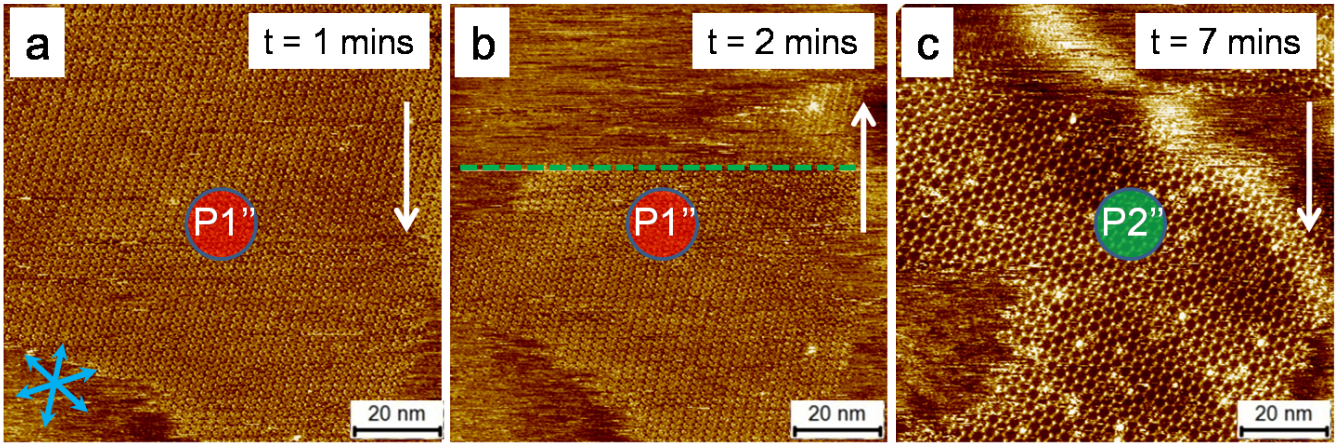


Figure S9. Regeneration of the low-density polymorph from flow generated densely packed polymorph using re-solvation in the case of **BTB**. Selected sequential STM scans (a-c) reveal that the transition of P1''into P2''occurs after adding a droplet of neat OA to the monolayer of P1'' obtained after flow treatment showed in Fig3 in the main text. Such phase transition could be ascribed to the *in situ* dilution effect where lowering the concentration of **BTB** favors the formation of low-density polymorph. Note that the transition of P2'' into P1'' could not be reversed upon evaporation of the solvent. The green dashed line in (b) approximately indicates the timing at which a neat solvent droplet was applied to the HOPG surface. The white and blue arrows on images indicate the STM scan directions and the 3-fold symmetry of the underlying HOPG, respectively. Imaging conditions: V_{bias} = -600 mV, I_{set} = 100 pA.

References

(1) S.-L. Lee, C.-Y. J. Chi, M.-J. Huang, C.-h. Chen, C.-W. Li, K. Pati, R.-S Liu. *J. Am. Chem. Soc.* 2008, **130**, 10454-10455.

(2) K. Tahara, S. Okuhata, J. Adisoejoso, S. Lei, T. Fujita, S. De Feyter, Y. Tobe. *J. Am. Chem. Soc.* 2009, **131**, 17583-17590.

(3) R. Gutzler, T. Sirtl, J. F. Dienstmaier, K. Mahata, W. M. Heckl,. M. Schmittel and M. Lackinger, *J. Am. Chem. Soc.* 2010, **132**, 5084-5090.