

Supporting Information

Structural Polymorphism in Self-Assembled Networks of a Triphenylene Based Macrocycle

Kunal S. Mali[†], Matthias Georg Schwab^{‡#}, Xinliang Feng[‡], Klaus Müllen^{‡} and Steven De Feyter^{†*}*

[†]Division of Molecular Imaging and Photonics, Department of Chemistry, KU Leuven-University of Leuven, Celestijnenlaan 200F, B 3001, Leuven, Belgium, [‡]Max-Planck Institute for Polymer Research, Ackermannweg 10, D-55128, Mainz, Germany

[#]Present address: BASF SE, Carl-Bosch-Straße 38, 67063 Ludwigshafen (Germany)

Address correspondence to: muellen@mpip-mainz.mpg.de; Steven.DeFeyter@chem.kuleuven.be

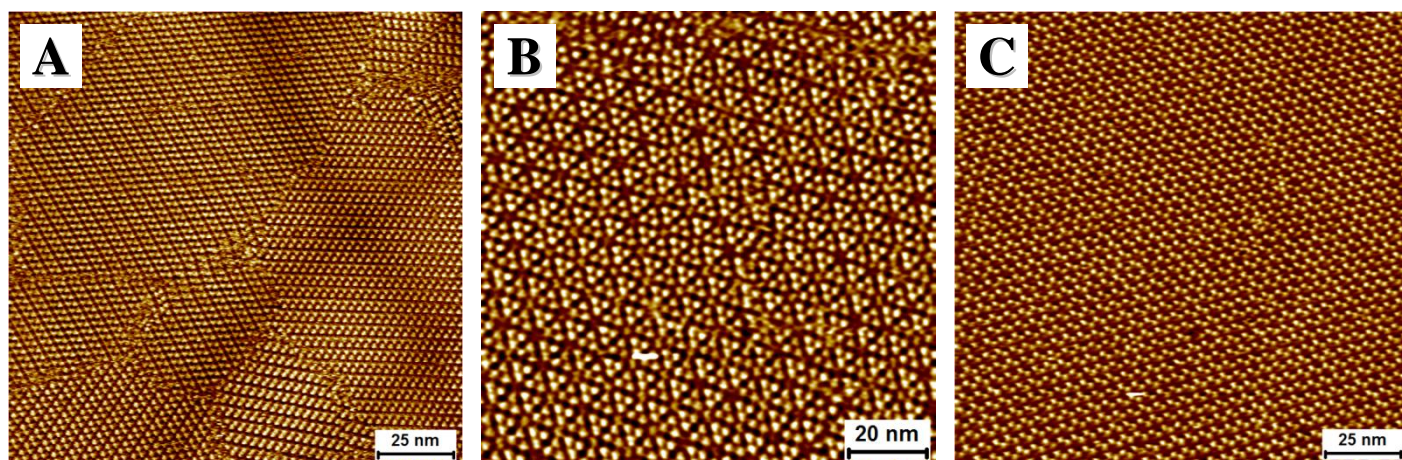


Figure S1: Large scale STM images of the (A) Linear and (B) trimeric hexagonal and (C) Honeycomb porous networks of **TTP** at the **TCB/HOPG** interface. Typical tunneling parameters range from $I_{set} = 100$ -200 pA and $V_{bias} = -750$ mV to -1.2 V.

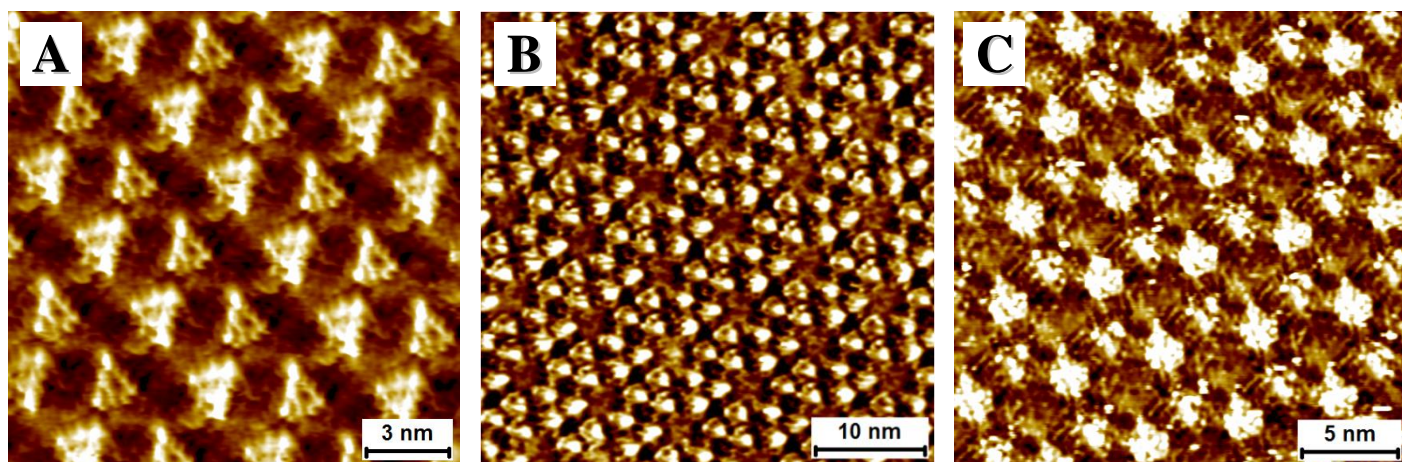
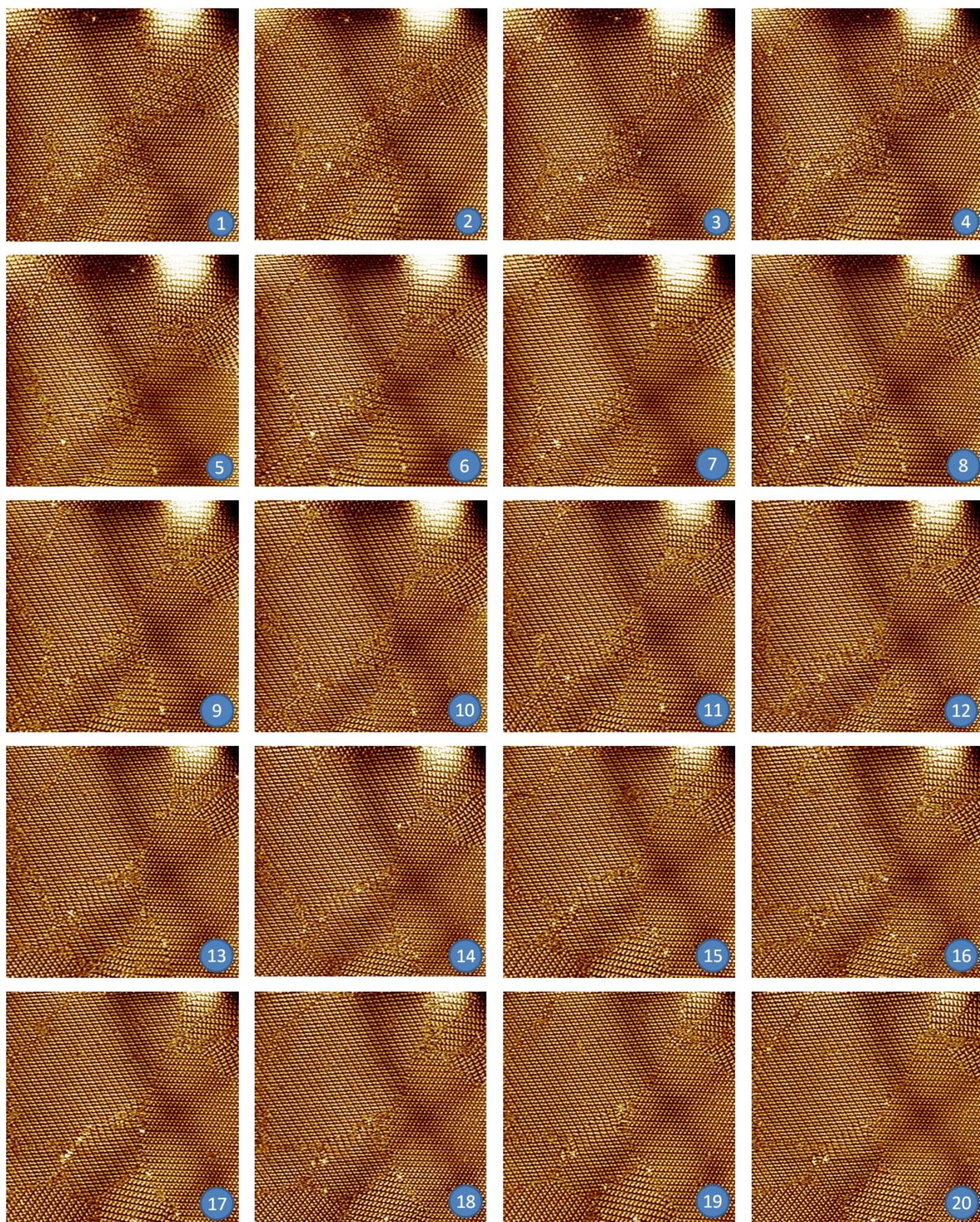


Figure S2: Additional HR-STM images of the (A) Linear and (B) trimeric hexagonal and (C) Honeycomb porous networks of **TTP** at the **TCB/HOPG** interface. Typical tunneling parameters range from $I_{set} = 100$ -200 pA and $V_{bias} = -750$ mV to -1.2 V.



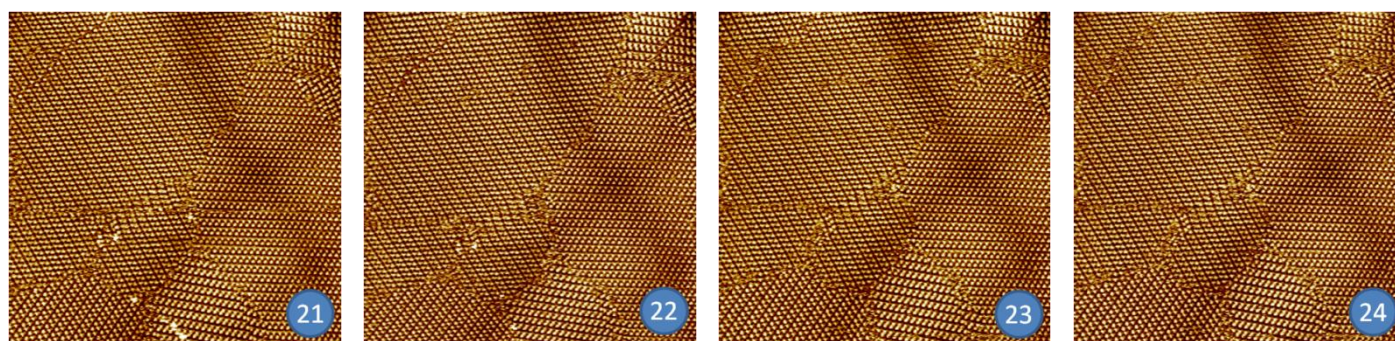


Figure S3: Time dependent STM images ($150 \times 150 \text{ nm}^2$, 84 seconds/frame) describing the ripening process of **TTP** linear phase which is coupled with the removal of the metastable trimeric hexagonal phase at the **TCB/HOPG** interface ($C_{\text{TTP}} = 6.2 \times 10^{-5} \text{ M}$). The hexagonal structures present at domain boundaries in (1) are also removed in time (24). The overall change in going from STM image (1) to (24) is shown in Figure 2 (G, H) of the main text: number of domains in (1) = 14 and in (24) = 10.

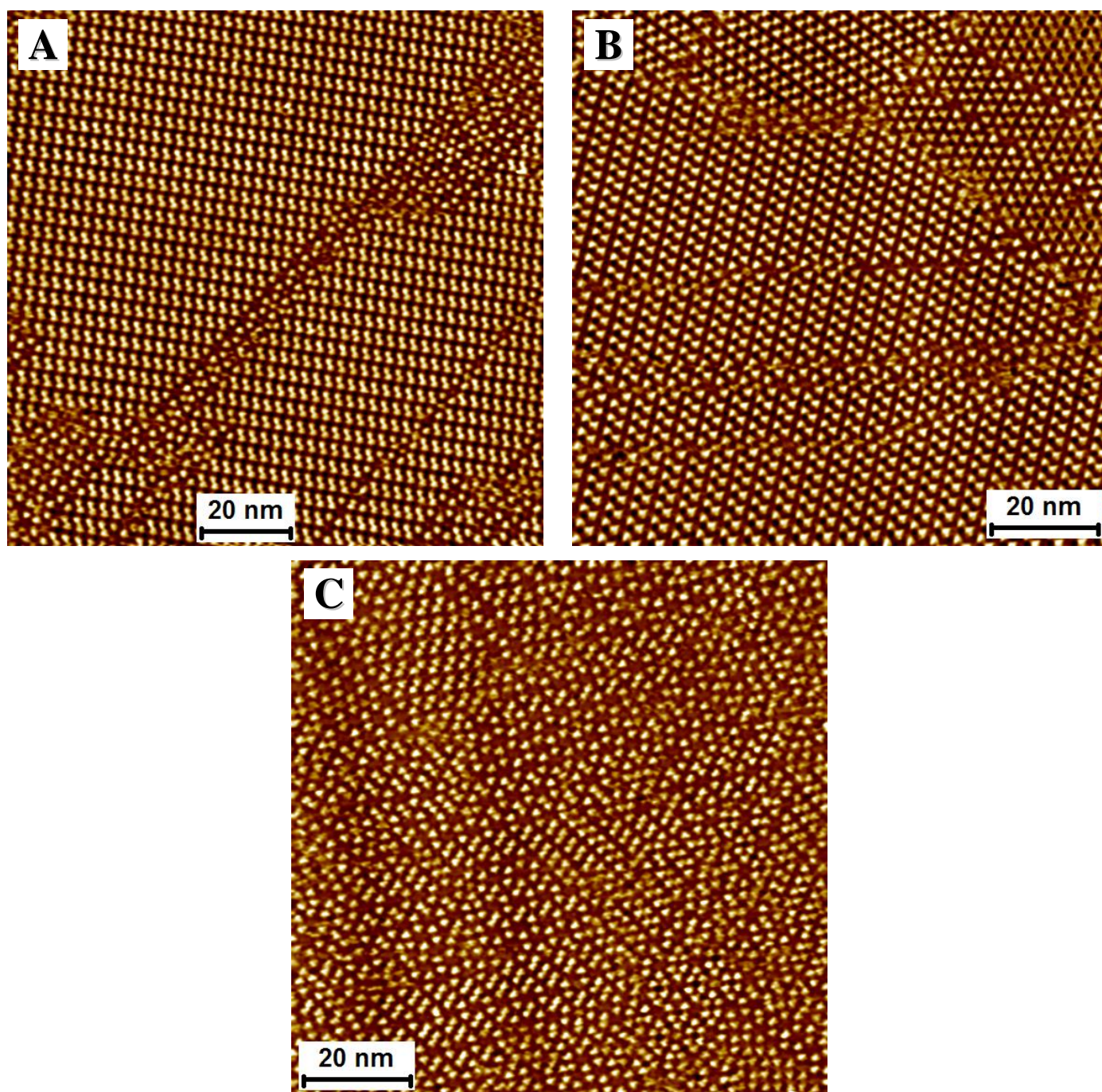


Figure S4: Large scale STM images showing coexistence of the hexagonal structures with large domains of linear polymorph at the TCB/HOPG interface. A smooth transition between the linear and hexagonal structures is clearly evident from the STM images given in (A) and (B). STM image in panel (C) shows intimately mixed domains of linear and honeycomb porous networks obtained after evaporation of TCB at 3.1×10^{-6} M after 30 minutes.

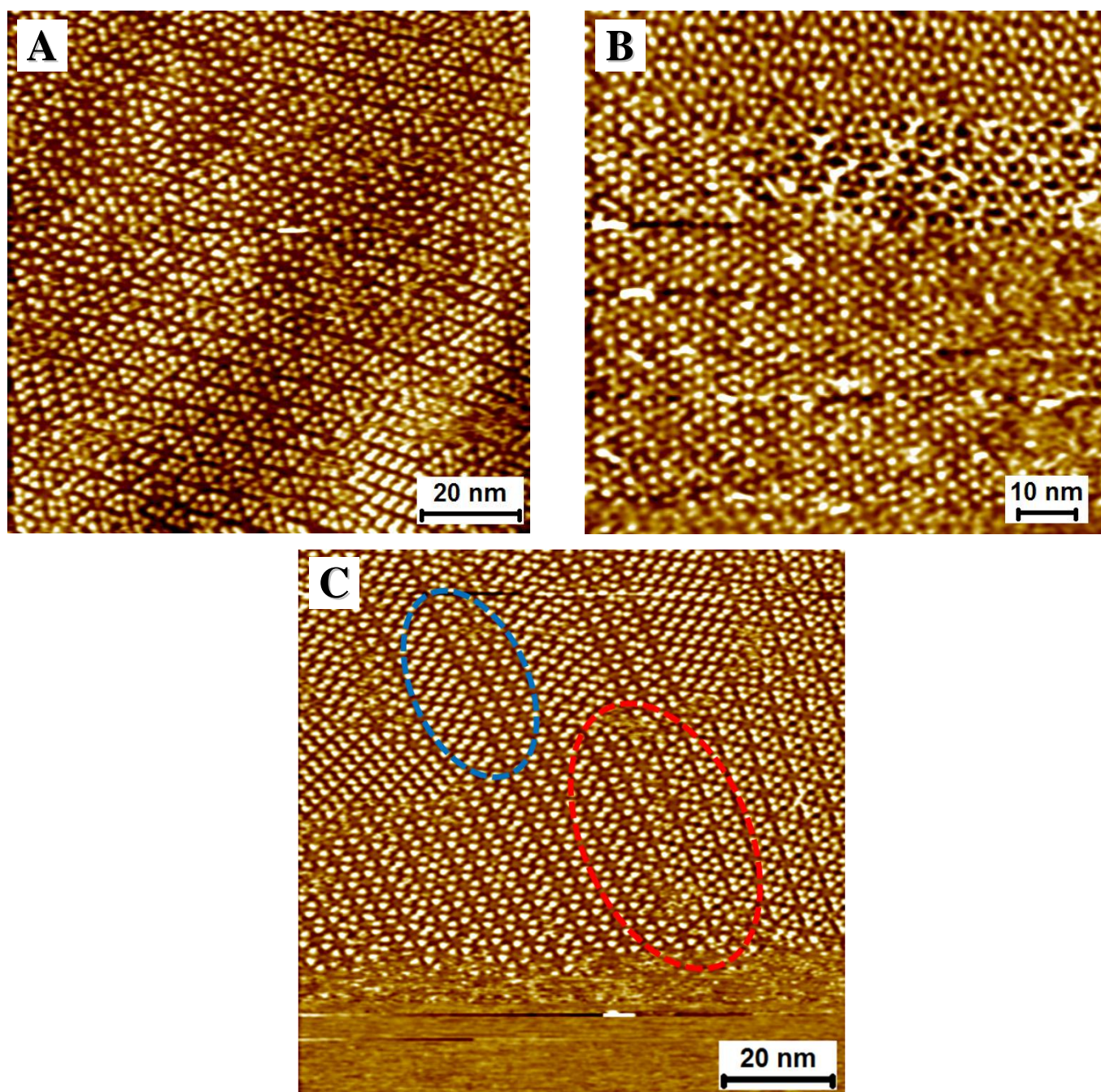


Figure S5: Large scale STM images showing coexistence of the trimeric hexagonal and honeycomb porous structures at the **TCB/HOPG** interface. A smooth transition between the trimeric hexagonal and honeycomb structures is clearly evident from the STM images given in (A) and (B). STM image in panel (C) shows all the three polymorphs. Blue oval shows the smooth transition between the linear and honeycomb polymorph whereas the red oval shows the smooth transition between the honeycomb porous and trimeric hexagonal structures.

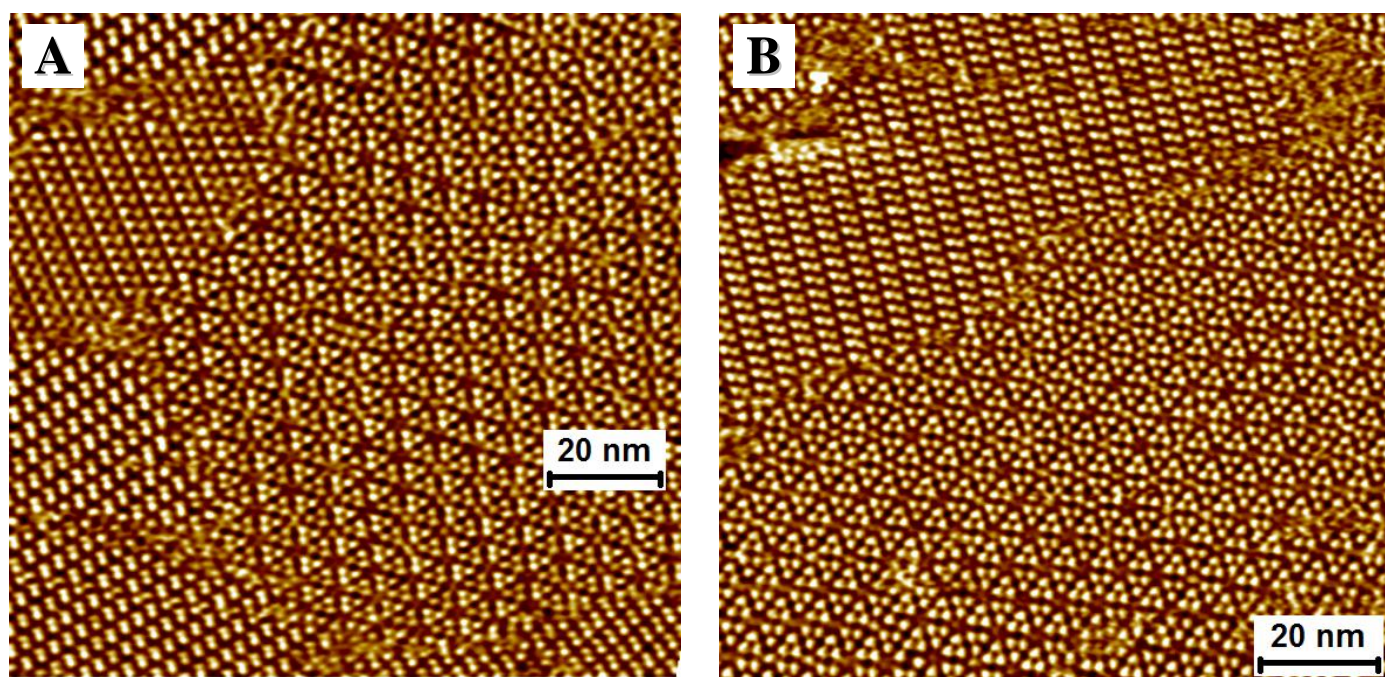


Figure S6: Large scale STM images showing coexistence of the domains of linear and trimeric hexagonal polymorph at the TCB/HOPG interface. The domain boundaries are always visualized as fuzzy and featureless.

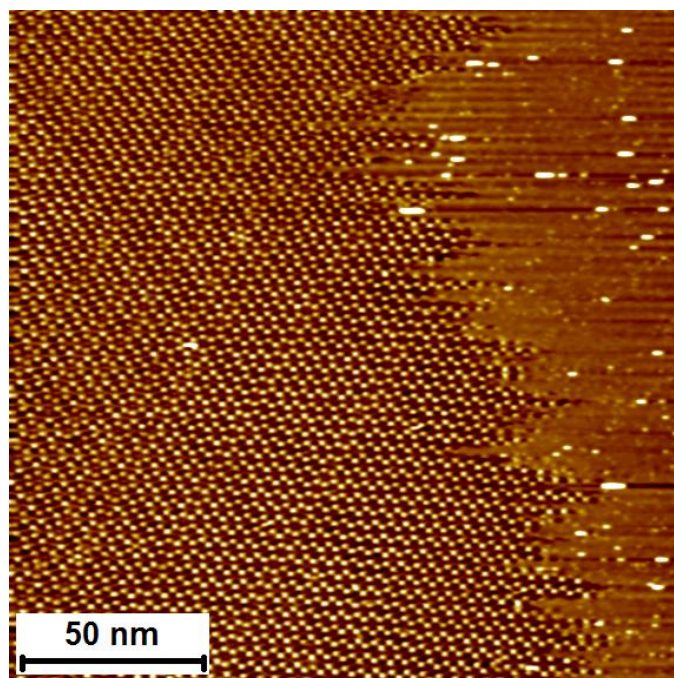


Figure S7: Large scale STM image showing submonolayer coverage of the honeycomb porous polymorph at the TCB/HOPG interface. $C_{\text{TTP}} = 1.5 \times 10^{-7}$ M.

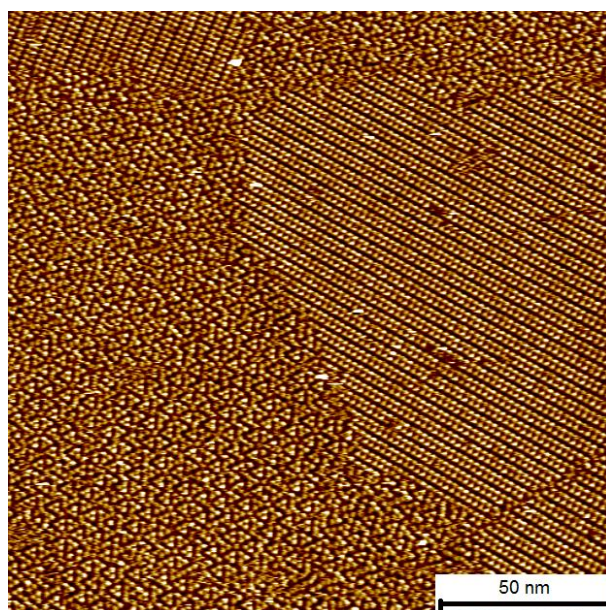


Figure S8: Large scale STM image showing coexistence of the trimeric and linear phase of **TTP** at the 1-phenyloctane/HOPG interface. $C_{\text{TTP}} = 3.0 \times 10^{-4}$ M. $I_{\text{set}} = 123$ pA, $V_{\text{bias}} = -1330$ mV

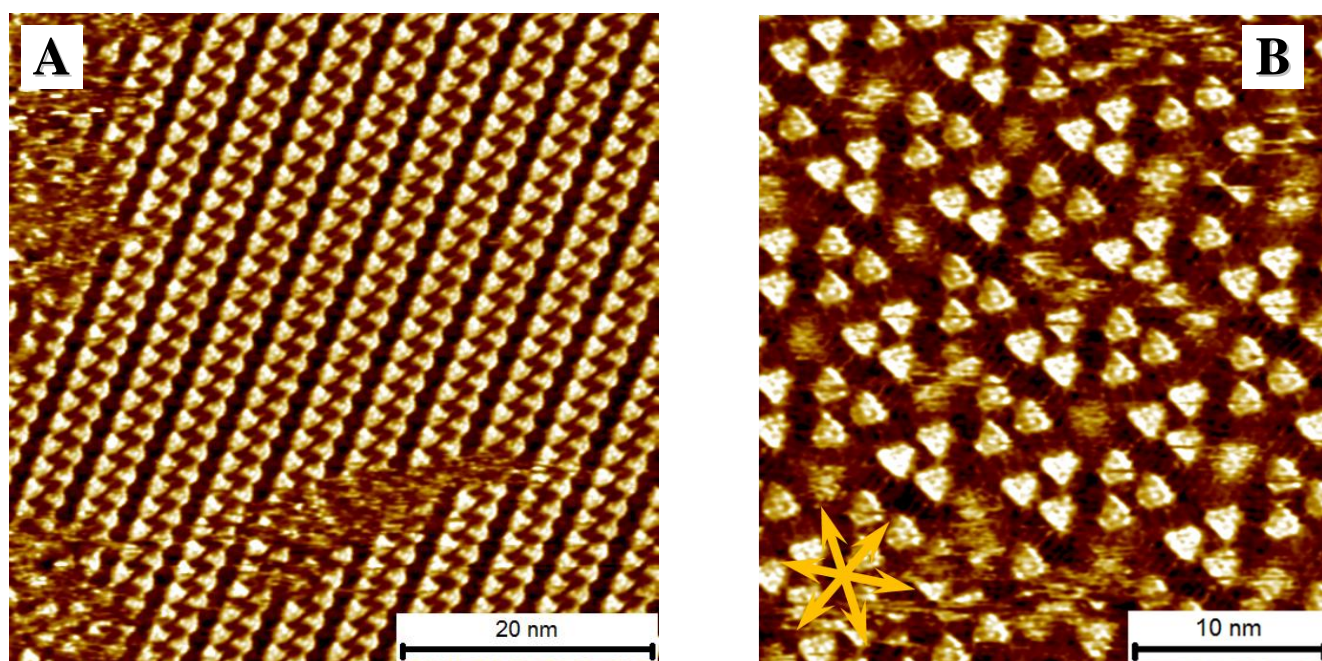


Figure S9: Additional small scale STM image showing linear (A) and trimeric (B) phase of **TTP** at the 1-phenyloctane/HOPG interface. $C_{\text{TTP}} = 3.0 \times 10^{-4}$ M. $I_{\text{set}} = 143$ pA, $V_{\text{bias}} = -1250$ mV