

## Supporting Information

### Nanoscale Chemical Patterning of Graphite at Different Length Scales

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*STM characterization of chemically patterned surfaces.*

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Comparison of pattern transfer fidelity of C<sub>50</sub>H<sub>102</sub> and DMTC SAMNs (**Figure S2**).

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Additional STM data: CA grafted surfaces at different potentials and durations (**Figure S6-S8**).

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STM images: Comparison between topography and current images (**Figure S12**).

STM images: The influence of solvent rinsing on the stability of grafted units (**Figure S13**).

#### 3. NMR data

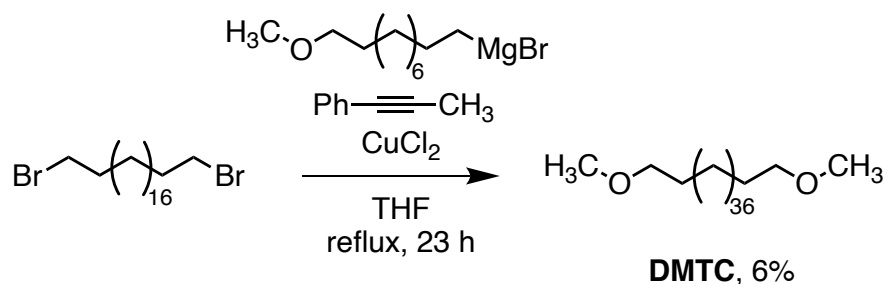
<sup>1</sup>H (500 MHz) and <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz) NMR spectra of DMTC in CDCl<sub>3</sub> (**Figure S14**).

## 1. Materials and methods

3,5-ditertbutylaniline (98%, Aldrich), tetradecane (99%, TCI), and pentacontane (97%, Aldrich) were used as received. 1,40-dimethoxytetracontane was synthesized as follows:

### a) Synthesis of DMTC:

**Scheme 1.** Synthesis of DMTC.



**General.** THF was passed through activated alumina and copper catalysts in a Glass Contour solvent purification system before use. All commercially available reagents were used as received.

$^1\text{H}$  (500 MHz) and  $^{13}\text{C}$  (100 MHz) NMR spectra were measured on a JEOL ECA-500 or ECA-400 spectrometer. For NMR measurements, chloroform-*d* was used as the solvent, and the spectra were referenced to a tetramethylsilane signal in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (0.00 ppm). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **DMTC** are shown in Figure S13. Recycling HPLC separation was undertaken with a JAI LC-5060 recycling chromatograph using 600 mm  $\times$  20 mm JAIGEL-1H and 2H GPC columns with  $\text{CHCl}_3$  as the eluent. Other spectra were recorded using the following instruments: IR spectra, JACSCO FT/IR-410; mass spectra, JMS-T100GCV (TOF); melting point (mp), Stuart Scientific SMP3. Oil baths were used as the heat sources for the following reactions.

**Synthesis of 1,40-Dimethoxytetracontane (DMTC).** Under Ar atmosphere, Mg (530 mg, 21.8 mmol) and THF (5 mL) were added to a Schlenk tube. 1-Bromo-10-methoxydecane<sup>1</sup> (2.65 mL, 11.2 mmol) was slowly added, and the resulting Grignard reagent was diluted with THF (4 mL). The Grignard reagent was added via a syringe to a mixture of  $\text{CuCl}_2$  (34.2 mg, 254  $\mu\text{mol}$ ), 1,20-dibromoicosane (1.11 g, 2.52 mmol), THF (2 mL), and 1-phenyl-1-propyne (0.15 mL, 1.2 mmol) in a two-necked flask. The Schlenk tube was washed with THF (1 mL) and the solution was also added to the two-necked flask. After stirring at 70  $^\circ\text{C}$  for 23 h, the reaction was quenched by the addition of sat.  $\text{NH}_4\text{Cl}$  aq. (25 mL). The products were extracted with hot  $\text{CHCl}_3$ . The organic phase was washed with water and brine, and dried over  $\text{MgSO}_4$ . After the removal of the solvents, the residue was subjected to column chromatography on silica gel (hexane/ $\text{CH}_2\text{Cl}_2$ , from 1/1 to 0/1)

and a recycling HPLC to afford **DMTC** (93.9 mg, 6%) as white solid. mp 86.1–87.0 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 19.9 °C)  $\delta$  3.36 (t,  $J$  = 7.0 Hz, 4H), 3.33 (s, 6H), 1.60–1.50 (m, 4H), 1.39–1.21 (m, 72H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25.0 °C)  $\delta$  73.0, 58.5, 29.7, 29.6, 29.5, 26.2; IR (KBr) 2916, 2849, 1472, 1463, 1393, 1214, 1200, 1188, 944, 730, 719  $\text{cm}^{-1}$ ; MS (FD)  $m/z$  calc. For  $\text{C}_{42}\text{H}_{86}\text{O}_2$  ( $\text{M}^+$ ): 622.6628, found 622.6625.

### **b) Preparation of templating SAMNs**

The physisorbed SAMN which served as a template for patterned electrochemical grafting was prepared by adding a small volume (20  $\mu\text{L}$ ) of a 10 mM solution of templating molecules (**DMTC** or  $\text{C}_{50}\text{H}_{102}$ ) dissolved in tetradecane onto the working electrode. The system was then allowed to equilibrate under ambient conditions for 10 minutes and then subjected to electrochemical grafting as follows.

### **c) Electrochemical grafting**

All electrochemical experiments were performed using a home-built electrochemical cell and a Autolab PGSTAT101 potentiostat (Metrohm Autolab BV, The Netherlands). Freshly cleaved highly oriented pyrolytic graphite (HOPG) carrying the physisorbed monolayer of the template molecules was used as the working electrode while a Pt wire served as a counter electrode. Ag/AgCl electrode was used as a reference electrode. The electrolyte was prepared by adding 0.1 mL of  $\text{NaNO}_2$  to 4.9 mL of a 1 mM solution of 3,5-bis(*tert*-butyl) aniline in 50 mM HCl. The freshly prepared electrolyte was then carefully added into the electrochemical cell without disturbing the organic interface over the working electrode. The HOPG substrate was dismantled after the electrochemical grafting process and cleaned by rinsing with ultrapure water (18.2 M $\Omega$ ) and acetonitrile and then dried under nitrogen flow.

### **d) Raman spectroscopy**

The Raman spectroscopy measurements were carried out using a confocal Raman microscope (Monovista CRS+, S & I GmbH) using a 532 nm He–Ne laser directed on the surface through an objective (OLYMPUS, BX43 100x, N.A. 0.7). After grafting, the rinsed and dried sample was analyzed under ambient conditions. The Raman scattering was collected using the same objective and guided to a Raman spectrograph (S&I GmbH) equipped with a cooled-charge coupled device (CCD) camera operated at -100 °C (Andor Technology, DU920P-BX2DD). The Raman spectra were plotted and analyzed using Igor and Origin 2020 software. The  $I_D/I_G$  is calculated by taking the ratio of intensities at 1350  $\text{cm}^{-1}$  (D-band) and 1600  $\text{cm}^{-1}$  (G-band) after subtracting the background.

### e) Scanning probe microscopy (STM and AFM)

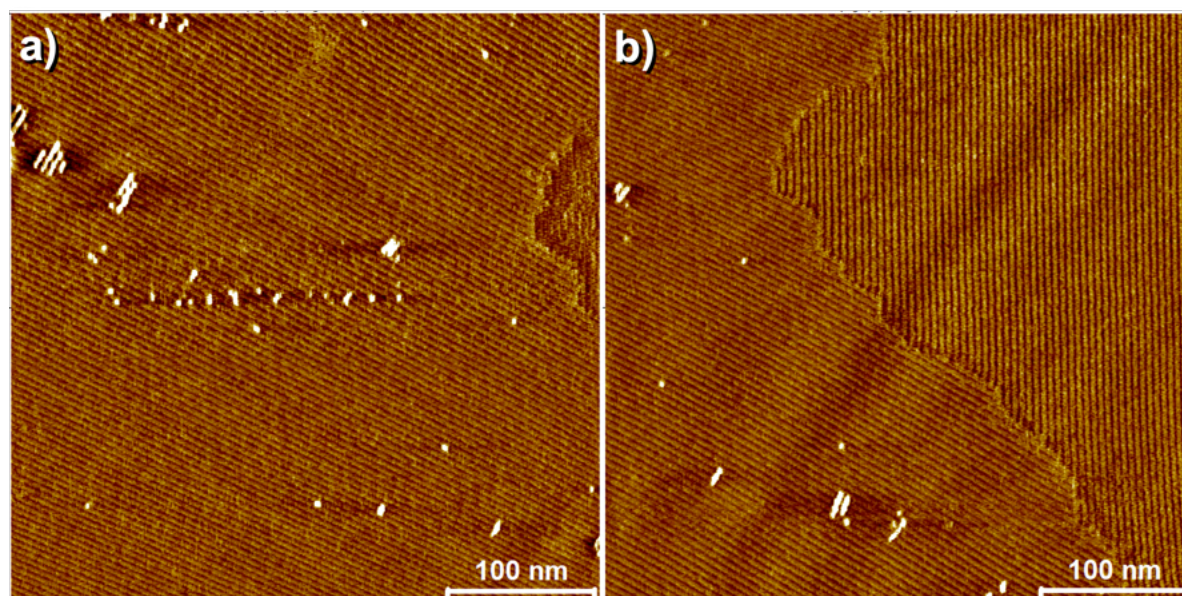
All STM experiments were performed at room temperature at the tetradecane/graphite interface using a PicoLE (Keysight Technologies) machine operating in constant-current mode. STM tips were prepared by mechanical cutting of Pt/Ir wire (80%/20%, diameter 0.25 mm).

Characterization of **DMTC**: Prior to STM imaging, a drop of **DMTC** solution was placed onto a freshly cleaved surface of highly oriented pyrolytic graphite (grade ZYB, Advanced Ceramics Inc., Cleveland, OH, USA). The experiments were repeated in two or three sessions using different tips to check for reproducibility and to avoid experimental artifacts, if any. For image calibration, recording of the **DMTC** monolayer image was followed by imaging the graphite substrate underneath it under the same experimental conditions, except for increasing the current and lowering the bias. Raw STM images of the **DMTC** monolayers were calibrated by using the STM images of the HOPG lattice obtained immediately after recording the monolayer image as a reference. Scanning probe image processor software (SPIP, version 6.5.1, Image Metrology ApS) was used for image calibration. The images are Gaussian filtered. The imaging parameters are indicated in the figure caption: tunnelling current ( $I_{set}$ ) and sample bias ( $V_{bias}$ ).

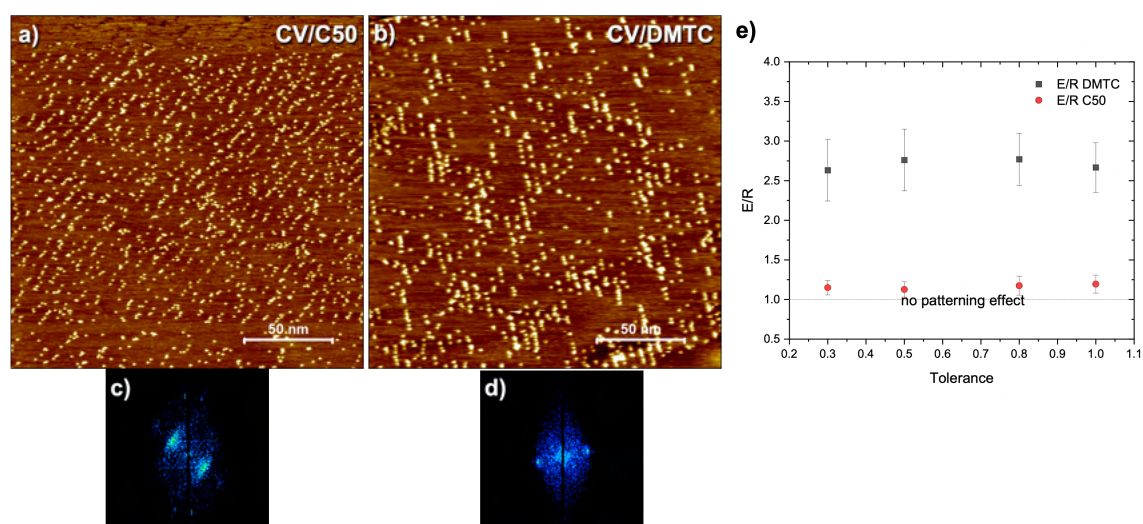
Characterization of chemically patterned surfaces: The STM characterization of the chemically patterned surfaces was carried out after addition of tetradecane to the surface. Throughout the main text, we have presented the current images since they present better STM contrast compared to the topography images. Some representative topography images are presented below in Figure S5-S8, S11.

AFM characterization of chemically patterned surfaces: The rinsed and dried substrates were characterized using AFM. AFM imaging was performed with Multimode 8 (Bruker) microscope equipped with a Nanoscope V controller operating in tapping mode. OMCL-AC240TS-R3 probes with spring constant  $\sim 2$  N/m and resonance frequency around 70 kHz were used for AFM imaging.

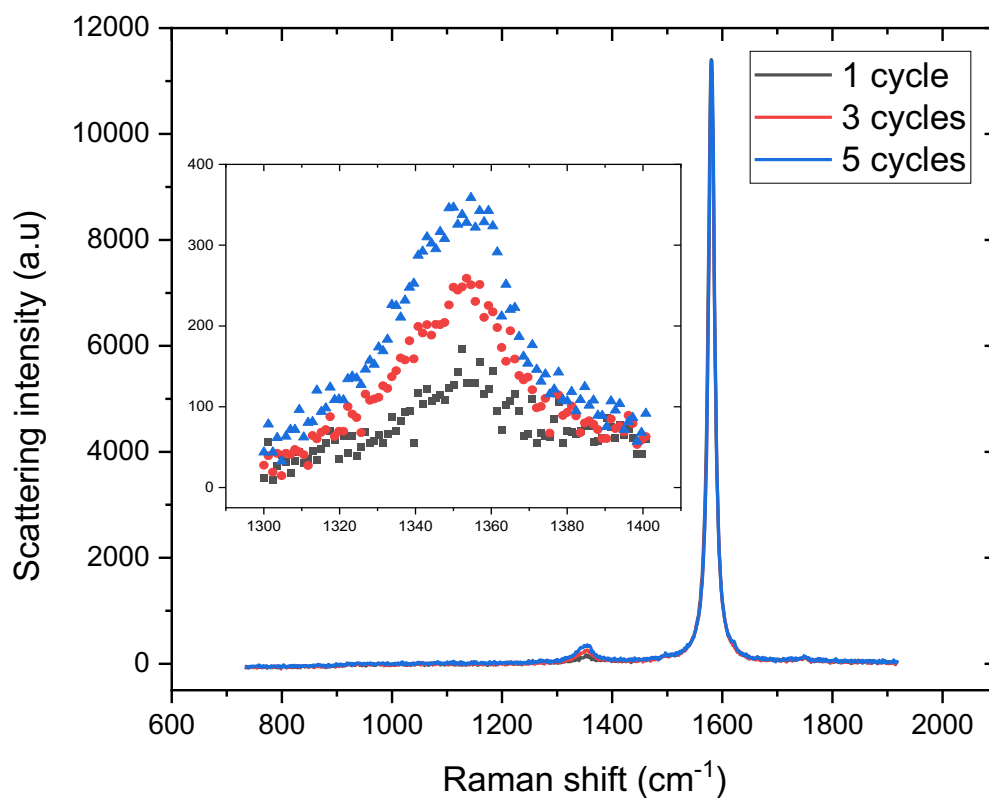
## 2. Additional/Supporting Data (Raman, STM and AFM)



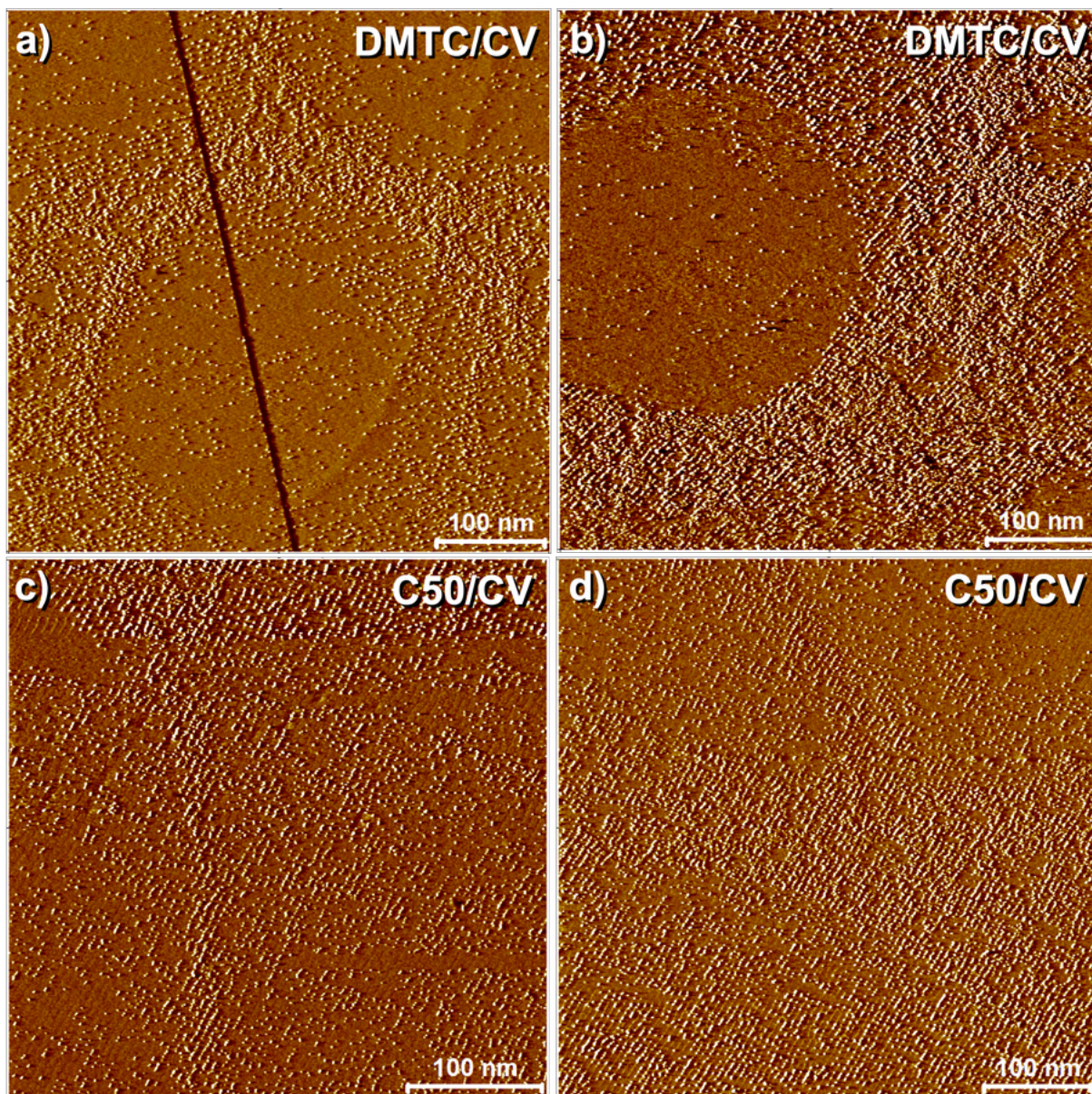
**Figure S1.** Large scale STM images of **DMTC** SAMN formed at the tetradecane/HOPG interface.  $[\text{DMTC}] = 1.0 \times 10^{-4} \text{ M}$ . Domains spreading over areas as large as  $500 \text{ nm} \times 500 \text{ nm}$  were observed. Imaging parameters (a, b):  $V_{\text{bias}} = -0.7 \text{ V}$ ,  $I_{\text{set}} = 0.08 \text{ nA}$ .



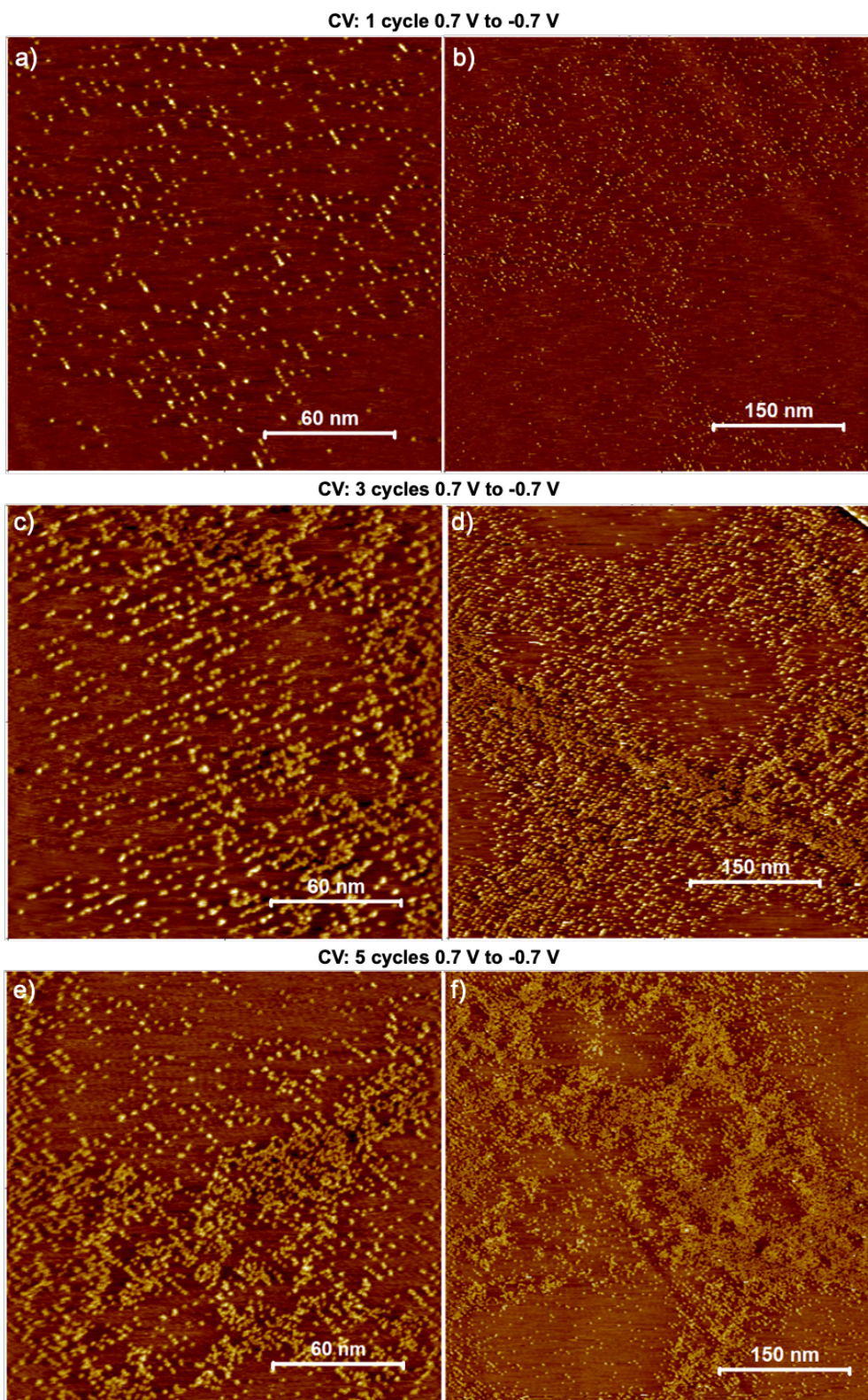
**Figure S2.** Comparison of pattern transfer fidelity of  $\text{C}_{50}\text{H}_{102}$  and **DMTC** SAMNs. (a, b) Representative STM images of the chemically patterned substrates obtained using  $\text{C}_{50}\text{H}_{102}$  (a) and **DMTC** (b) as template. (c, d) Corresponding 2D-FFT of the STM images. Note that the frequency peaks are much sharper in case of **DMTC** (d) than those for  $\text{C}_{50}\text{H}_{102}$  (c) template. The covalent grafting was carried out using CV. Analysis was based on 13 STM images of **DMTC** and 7 ( $200 \text{ nm} \times 200 \text{ nm}$ ) STM images in case of  $\text{C}_{50}\text{H}_{102}$ . CV parameters: (+ 0.7 to -0.7 V (scan rate = 0.1 V/s) versus Ag/AgCl).



**Figure S3.** Raman spectra showing the gradual increase in the D-band with increasing CV cycles for DMTC templated covalent grafting. The inset shows magnified region around the D-band. Corresponding  $I_D/I_G$  ratios are 0.012, 0.023, 0.030 for 1, 3 and 5 CV cycles respectively. CV parameters: + 0.7 to -0.7 V (0.1 V/s) versus Ag/AgCl.

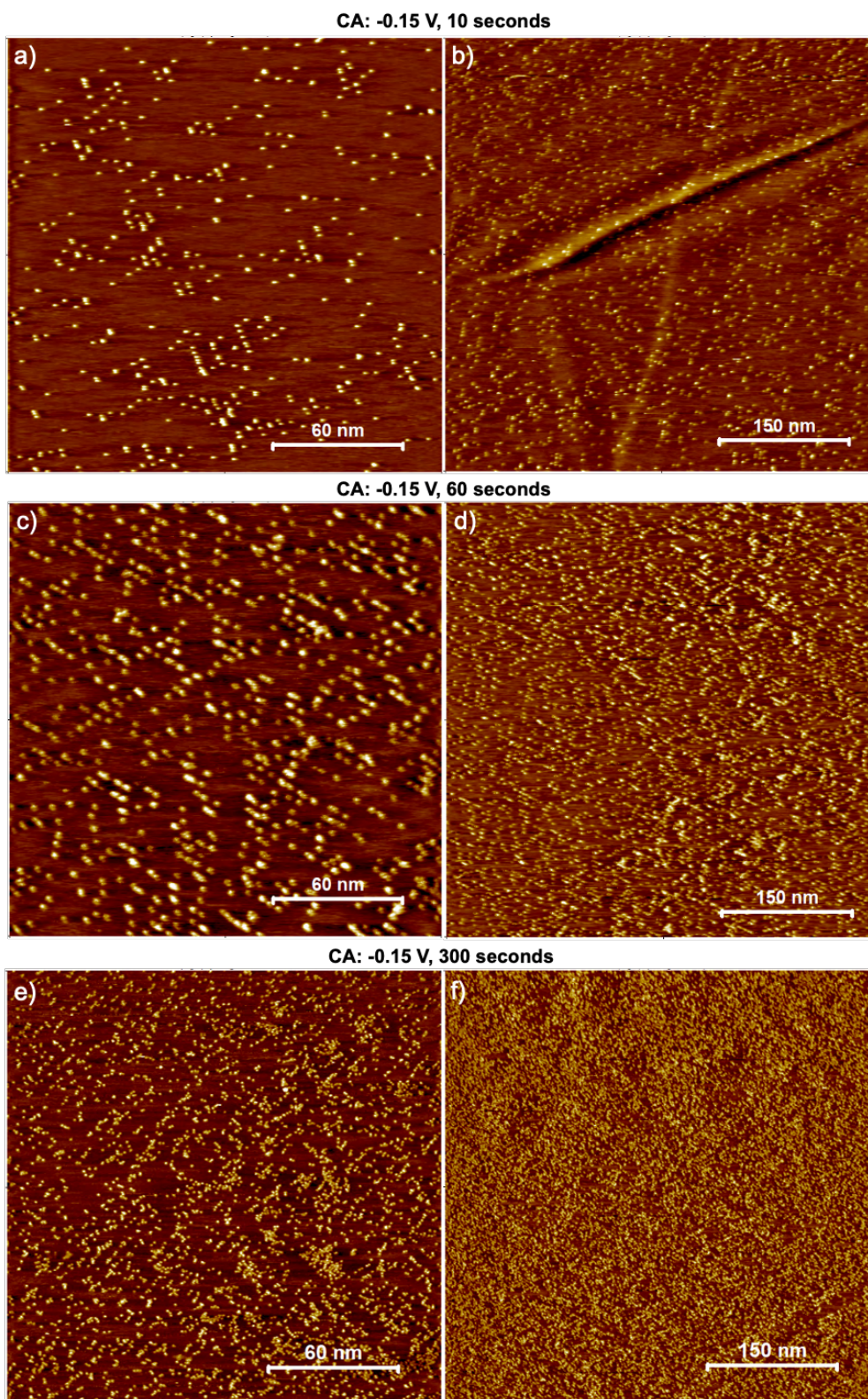


**Figure S4.** Representative STM images showing slightly higher propensity for intra-row grafting when **DMTC** (a, b) is used as the template for chemical patterning using CV compared to that when  $C_{50}H_{102}$  (c, d) is used, especially when higher number of potential sweeps are used. CV parameters: + 0.7 to -0.7 V (0.1 V/s) versus Ag/AgCl (three CV cycles).

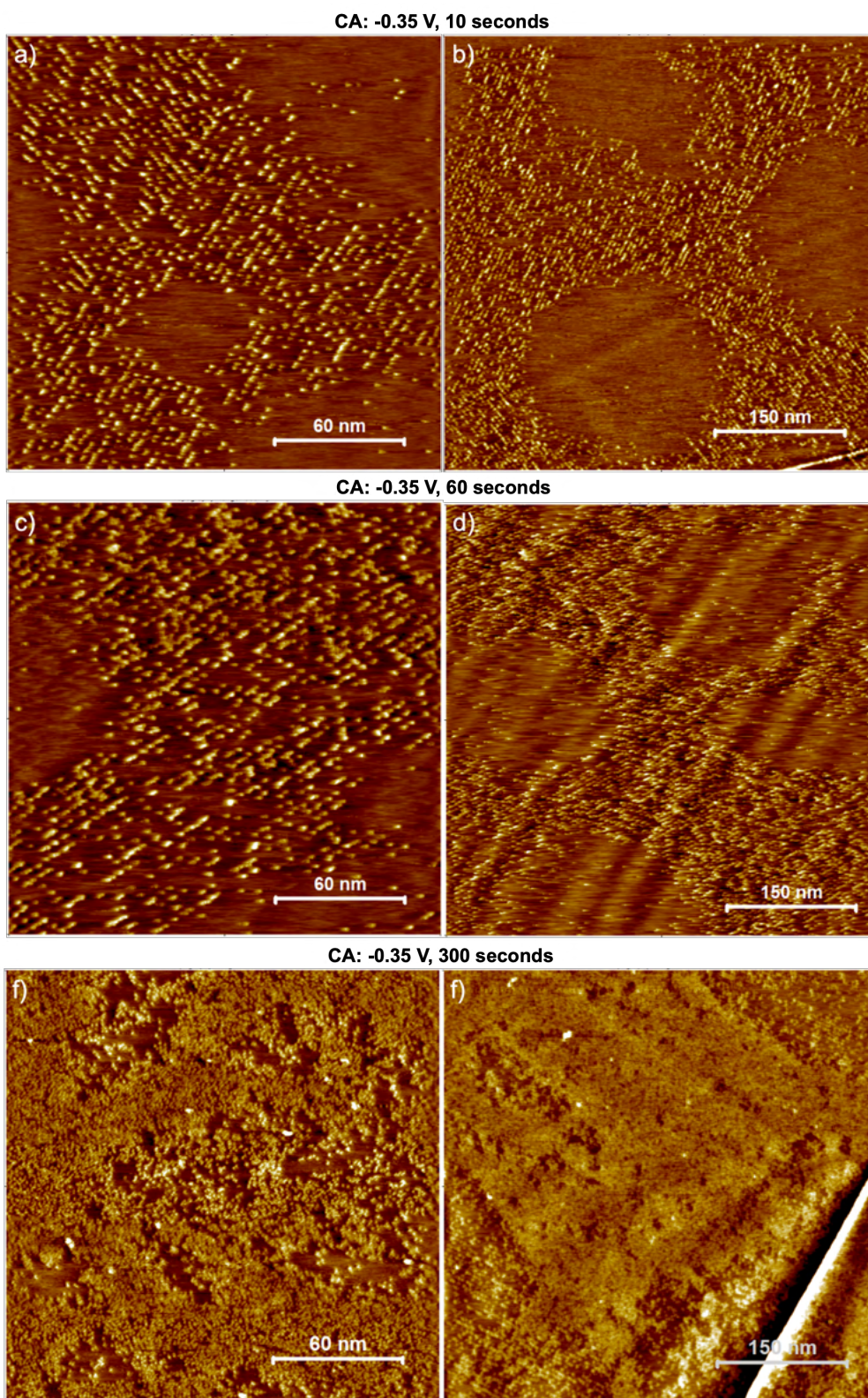


**Figure S5.** STM topography images showing the patterned graphite surface obtained using **DMTC** as the template and using CV as the grafting method with increasing number of potential sweeps. Scan rate = 0.1 V/s. Imaging parameters: (a: -1.1 V, 0.04 nA), (b: -1.1 V, 0.04 nA), (c: -1.0 V, 0.05 nA), (d: -1.1 V, 0.04 nA), (e: -0.95 V, 0.05 nA), (f: -0.95 V, 0.05 nA)

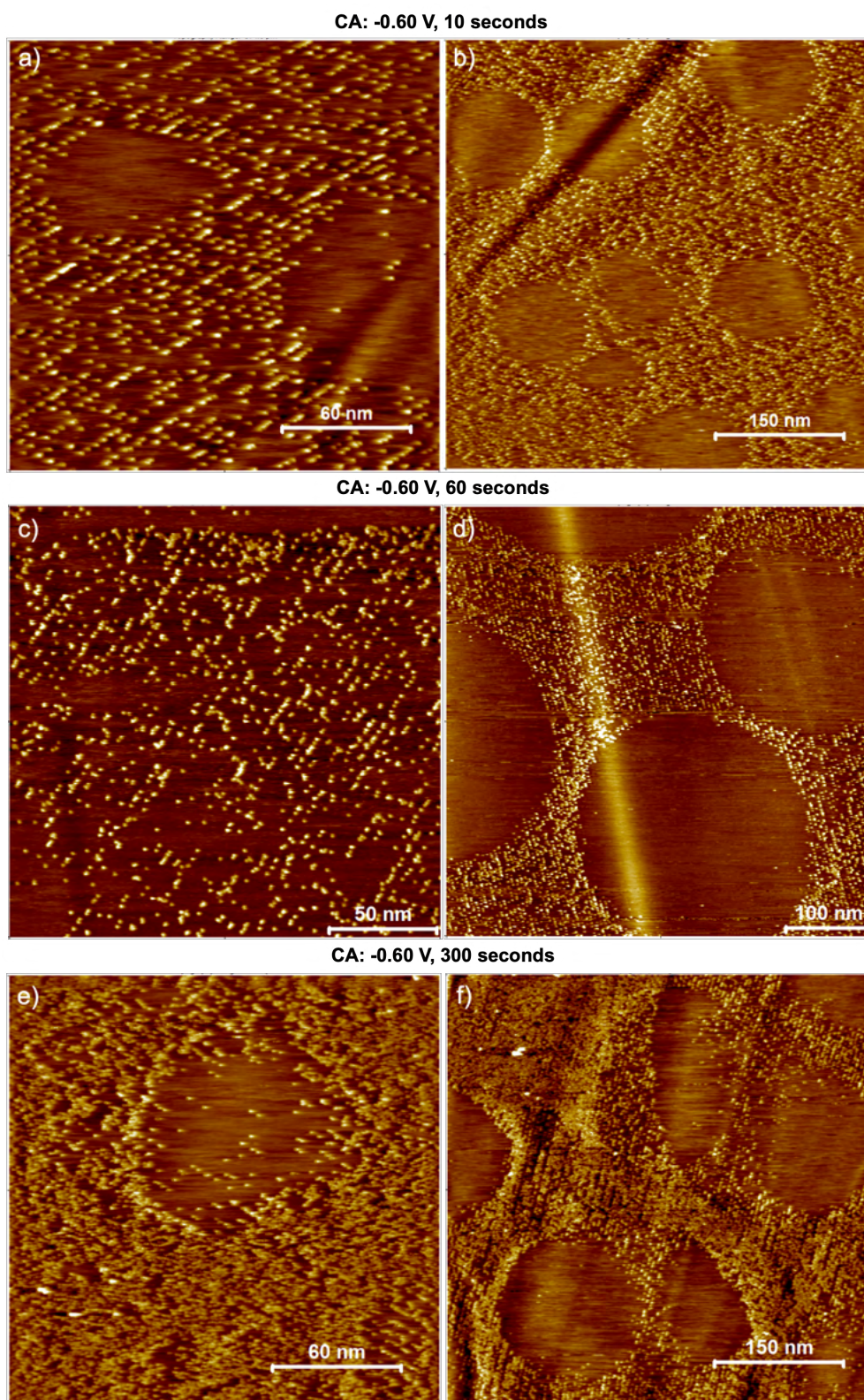




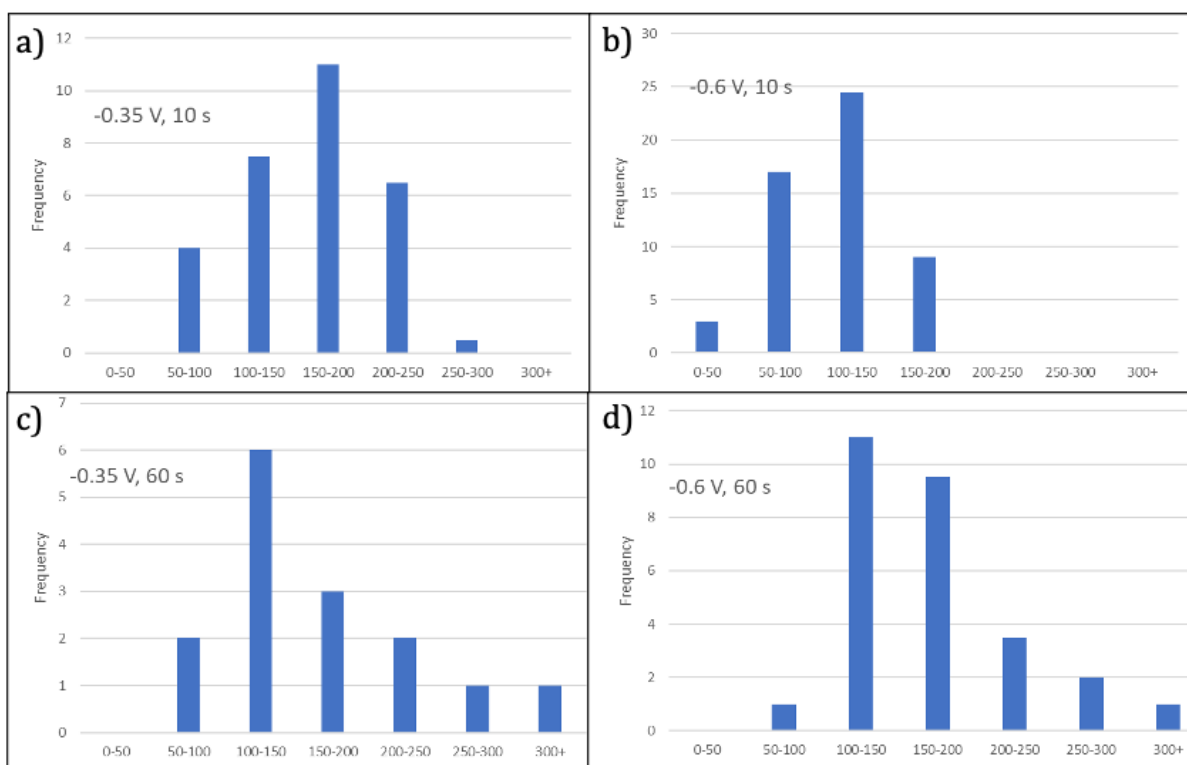
**Figure S6.** STM topography images showing the patterned graphite surface obtained using **DMTC** as the template and using CA as the grafting method at a constant potential (-0.15 V) with increasing duration. Imaging parameters: (a: -1.0 V, 0.04 nA), (b: -1.2 V, 0.05 nA), (c: -1.0 V, 0.05 nA), (d: -1.0 V, 0.05 nA), (e: -1.1 V, 0.04 nA), (f: -1.1 V, 0.04 nA).



**Figure S7.** STM topography images showing the patterned graphite surface obtained using **DMTC** as the template and using CA as the grafting method at a constant potential (-0.35 V) with increasing duration. Imaging parameters: (a: -1.0 V, 0.04 nA), (b: -1.0 V, 0.04 nA), (c: -1.0 V, 0.04 nA), (d: -1.0 V, 0.04 nA), (e: -1.0 V, 0.04 nA), (f: -1.0 V, 0.04 nA).

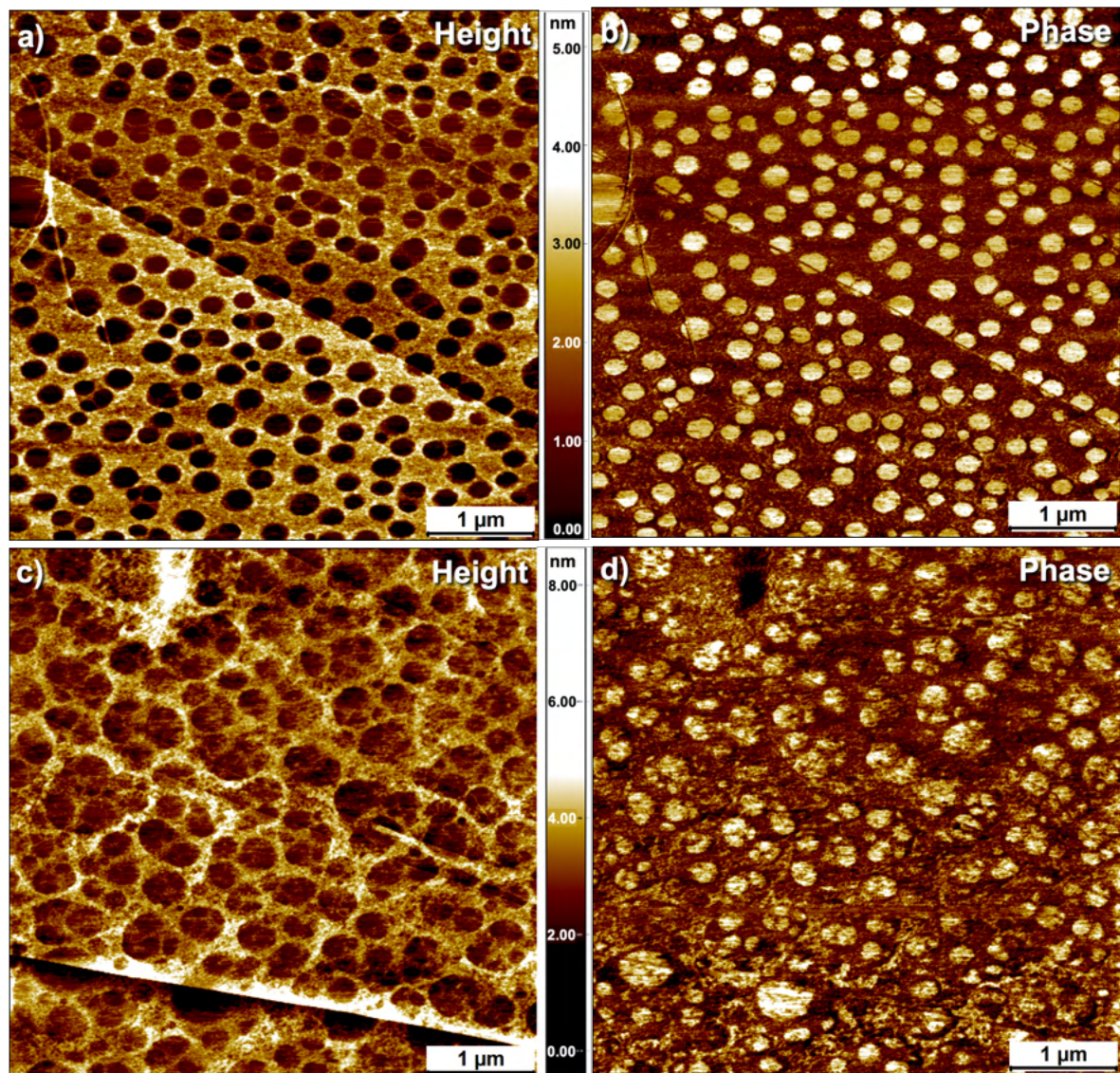


**Figure S8.** STM topography images showing the patterned graphite surface obtained using **DMTC** as the template and using CA as the grafting method at a constant potential (-0.35 V) with increasing duration. Imaging parameters: (a: -1.0 V, 0.04 nA), (b: -1.0 V, 0.04 nA), (c: -0.9 V, 0.06 nA), (d: -0.9 V, 0.06 nA), (e: -1.2 V, 0.04 nA), (f: -1.0 V, 0.05 nA).

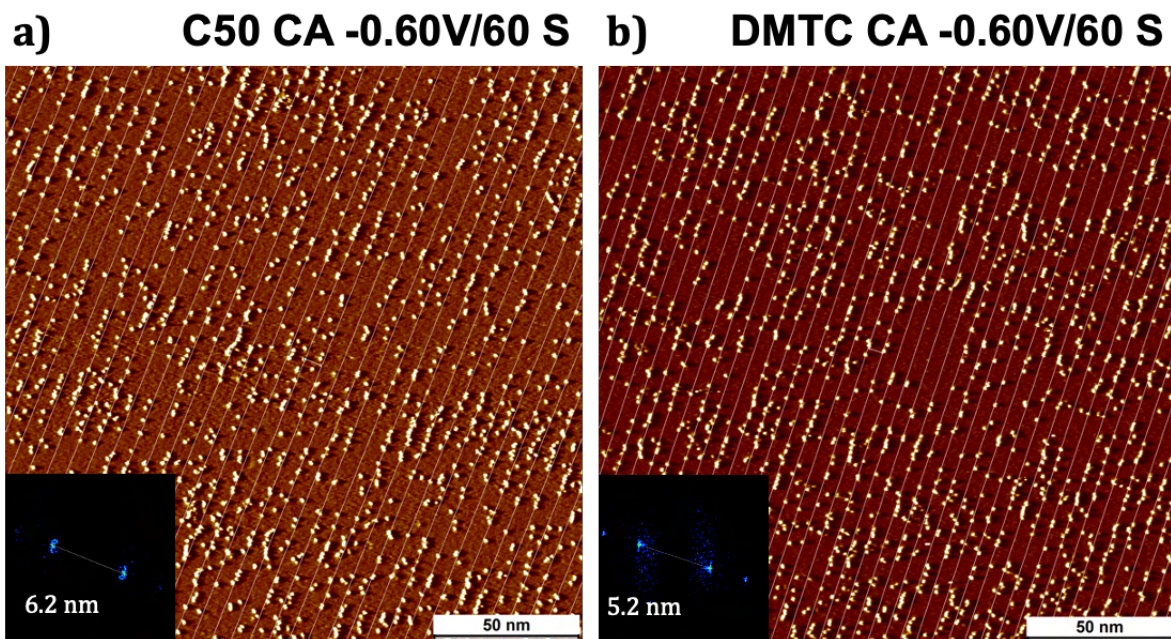


**Figure S9.** Size distribution of nanocorrals as a function of the magnitude of the applied potential and the duration of CA obtained from large scale STM images where the surface was patterned using DMTC.

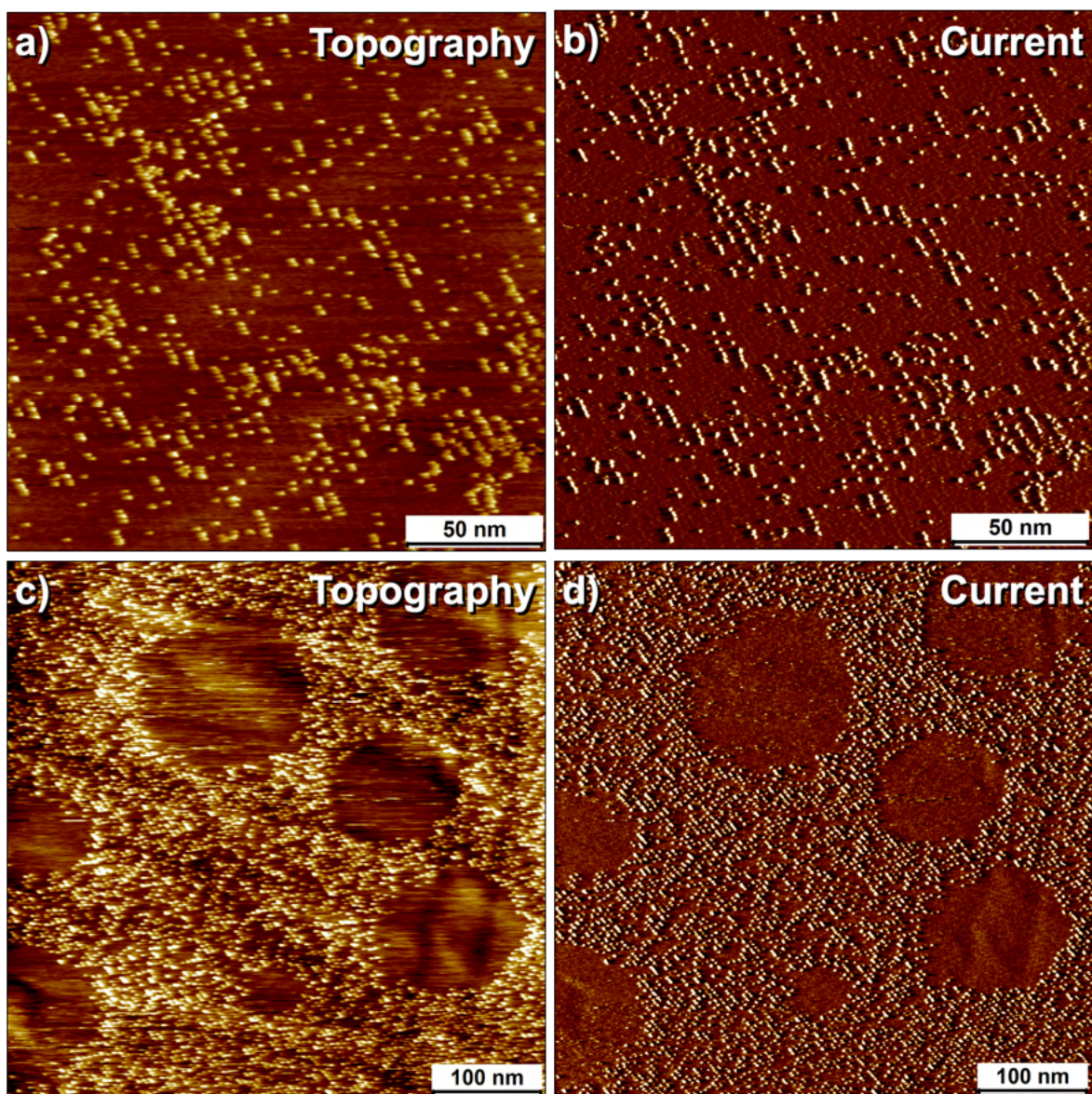
Additional AFM data showing height and phase images:



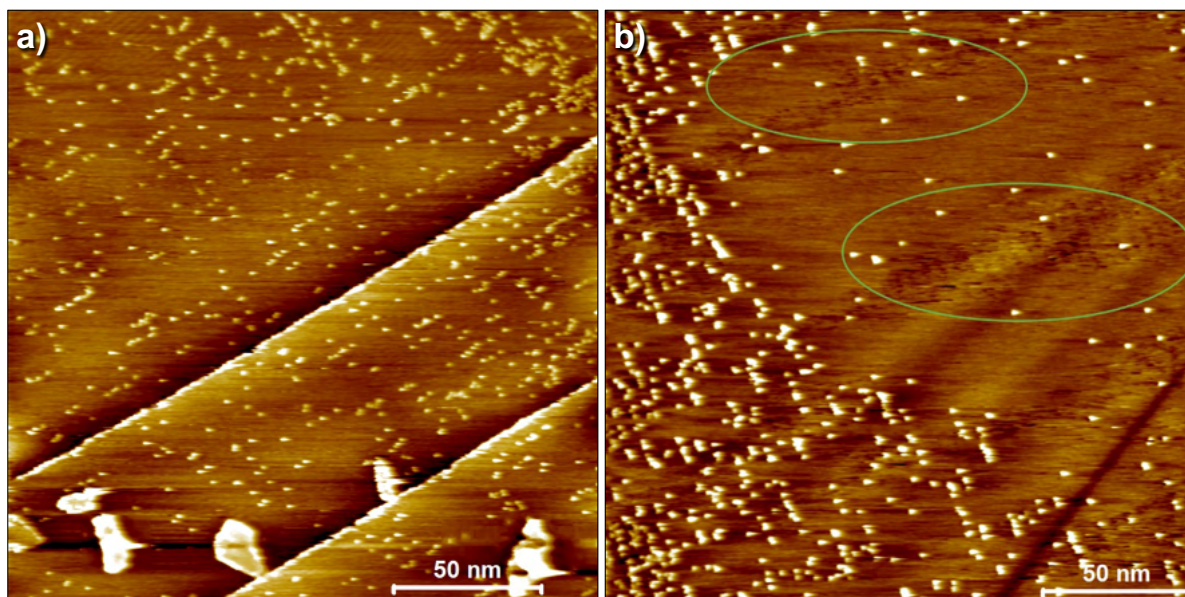
**Figure S10.** AFM height and phase images showing distinct phase contrast within the corrals. Panel (a) and (c) are the same height images presented in Figure 4c and 4b, respectively. (b) and (d) show the corresponding phase images.



**Figure S11.** The same STM images as those provided in Figure 6a, b in the main text but with lines that provide a guide to the eye. The quantitative pattern transfer fidelity analysis provided in Figure 6e in the main text further confirms that the pattern transfer is better in the case of DMTC compared to that in the case of  $C_{50}H_{102}$ .



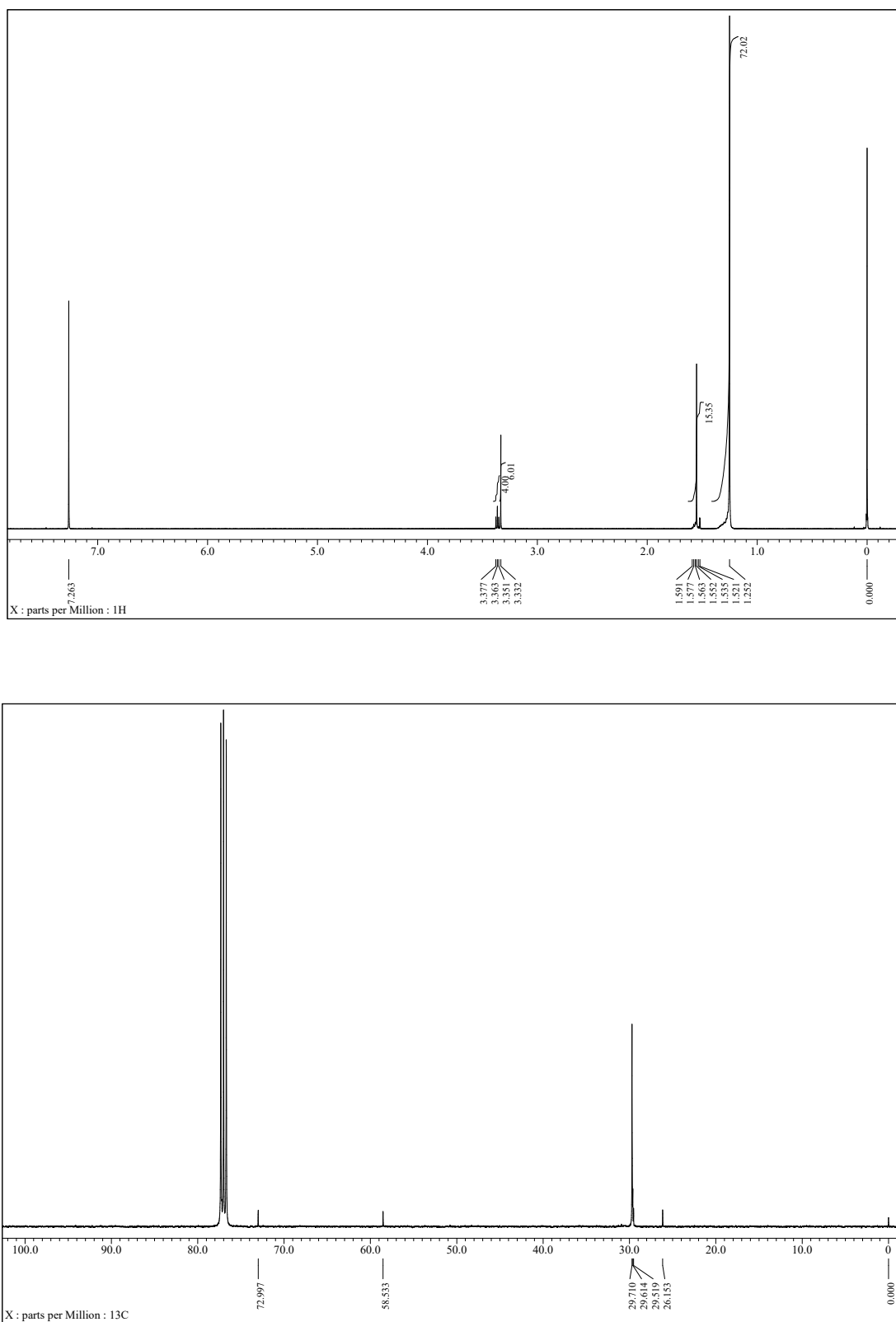
**Figure S12:** STM data showing the topography and current images. As stated in the experimental section, we chose to use current images in view of better contrast. (a, b) Topography and current images of the chemically patterned surface obtained using **DMTC** as template and using CV as the method of grafting. Panel (b) presents the same image as in Figure 1(e) in the main text. (c, d) Topography and current images of the chemically patterned surface obtained using **DMTC** as template and using CA as the method of grafting. Panel (b) presents the same image as in Figure 3(d) in the main text. (a, b) Imaging parameters:  $V_{bias} = -0.9$  V,  $I_{set} = 0.04$  nA. (c, d) Imaging parameters:  $V_{bias} = -0.9$  V,  $I_{set} = 0.05$  nA.



**Figure S13.** (a, b) STM topography images showing the surface morphology of the DMTC monolayer templated grafted surface after rinsing with hot (80 C) tetradecane. Majority of the grafted unit stay bonded to the surface after the rinsing procedure which removes most of the template monolayer. In some areas, the DMTC monolayer stays even after the rinsing step (green ovals in panel b). Imaging parameters:  $V_{bias}=-0.9$  V,  $I_{set}=0.04$  nA.



### 3. NMR data



**Figure S14.** <sup>1</sup>H (top, 500 MHz) and <sup>13</sup>C{<sup>1</sup>H} NMR (bottom, 100 MHz) NMR spectra of DMTC in CDCl<sub>3</sub>.

## References:

- (1) Wenzl, I.; Yam, C. M.; Barriet, D.; Lee, T. R. Structure and Wettability of Methoxy-Terminated Self-Assembled Monolayers on Gold. *Langmuir* **2003**, *19*, 10217-10224.