

Supplementary information for

Chiral functionalization of solid surfaces with amino acid derivatives: diazonium grafting regulated by enantioselective processes

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1 Experimental details

1.1 Materials

All the chemicals and solvents, including Boc-4-Amino-L-phenylalanine(L-PheN, 98%, Aladdin), Boc-4-Amino-D-phenylalanine(D-PheN, 98%, Aladdin), isamyl nitrite (98%, J&K Chemicals), anhydrous ethanol (99.5%, Aladdin), (R)-2-butanol (98%, Bide), (S)-2-butanol (98%, Bide), hydrochloric acid (36%-38%,Yonghua) and H_3PO_2 (Macklin, 50wt.%), were used as received from commercial suppliers. Ultrapure water with a resistivity of 18.2 M Ω .cm @ 25 °C was used in all the experiments. A freshly cleaved surface of HOPG (grade ZYB, Bruker, USA) or a flame-annealed Au(111) film on mica (Georg Albert PVD Company, Germany) were used as substrate for functionalization.

1.2 Procedures for sample preparation

1.2.1 Functionalization of Au(111) :

First, a piece of flamed-annealed Au(111) on mica was covered with the aqueous solution of ascorbic acid (0.1 mL, 20 mM) or hypophosphorous acid (0.1 mL, 20 mM). Then a 0.98 mL aqueous solution of phenylalanine derivative (L-PheN or D-PheN,20 mM) was mixed with 0.02 mL aqueous solution sodium nitrite (0.1 M) and placed at 0 °C. To induce the formation of diazonium salts at 0 °C, 1 mL hydrochloric acid (0.1 M) was added to the above prepared solution and being shook for 10 s. After that, 0.1 mL solution of fresh prepared diazonium salt was immediately dropcasted on the surface that has already been covered by the solution of reducing agent. 10 minutes later, the surface was rinsed with ethanol and water for more than 3 times, and dried in nitrogen gas flow for STM measurements.

1.2.2 Functionalization of HOPG :

Graphite surface modified by L-PheN or D-PheN : First, a piece of fresh-cleaved graphite was covered with the methanol solution of ascorbic acid (0.05 mL, 20 mM). This time the diazonium salt solution was prepared by dissolving L-PheN or D-PheN in 6 M hydrochloric acid with a concentration of 20 mM. Then 0.98 mL L-PheN (or D-PheN) solution was mixed with 10 μL isoamyl nitrite and 10 μL anhydrous ethanol at low temperature to produce the diazonium salt. 10 minutes after depositing the solution of diazonium salt on the graphite surface that has already been covered with methanol solution of the AA, the surface was washed with ethanol and water for more than 3 times and dried in nitrogen gas flow. To increase the degree of surface functionalization, the same process was repeated

for several times.

Graphite surface modified by L-PheN and D-PheN : First, a piece of fresh-cleaved graphite was covered with the methanol solution of ascorbic acid (0.05 mL, 20 mM). Also the diazonium salt solution was prepared by dissolving L-PheN or D-PheN in 6 M hydrochloric acid with a concentration of 20 mM. Then 0.98 mL L-PheN (or D-PheN) solution was mixed with 10 μ L isoamyl nitrite and 10 μ L anhydrous ethanol at low temperature to produce the diazonium salt (the whole procedure was done in 5 minutes). 10 minutes after depositing the solution of diazonium salt on the graphite surface that has already been covered with methanol solution of the AA, the surface was washed with ethanol and water for more than 3 times and dried in nitrogen gas flow. The same process was repeated for 5 times to get a chirally modified surface of L-PheN or D-PheN. After that, D-PheN was used to functionalize the surface that has been modified by L-PheN for additional 5 times, while L-PheN was used to functionalize the surface that has been modified by D-PheN for additional 5 times.

Graphite surface modified by L-PheN in the presence of chiral solvents : First, a piece of fresh-cleaved graphite was covered with the (R)-2-butanol (or (S)-2-butanol) solution of ascorbic acid (0.05 mL, 20 mM). Also the diazonium salt solution was prepared by dissolving L-PheN in 6 M hydrochloric acid with a concentration of 20 mM. Then 0.98 mL L-PheN solution was mixed with 10 μ L isoamyl nitrite and 10 μ L anhydrous ethanol at low temperature to produce the diazonium salt. 10 minutes after depositing the solution of diazonium salt on the graphite surface that has already been covered with butanol solution of the AA, the surface was washed with ethanol and water for more than 3 times and dried in nitrogen gas flow. The same process was repeated for 10 times to get a chirally modified surface of L-PheN in the presence of chiral solvents.

Note: We were aware of the fact the t-butyloxy carbonyl (Boc) protecting group is sensitive to acid, but the Boc protecting group is ideal to avoid multilayer grown in surface grafting. We have tested the stability of Boc group in 6M hydrochloric acid with TLC analysis (Fig. S7). We found that the protecting groups (at least the majority of the protecting groups) are able to withstand the treatment of acid for a much longer time than we took to prepare samples.

1.3 Characterization

1.3.1 STM measurements. All STM experiments were performed at room temperature (24-30 $^{\circ}$ C)

using a Bruker MS-10 machine operating in constant-current mode. STM tips were prepared by mechanical cutting from Pt/Ir wire (80%/20%, diameter 0.25 mm, Goodfellow, UK). Imaging parameters (Iset: the setpoint tunneling current; Vbias: the bias voltage applied between sample and tip) are indicated in the figure captions. Vbias is referenced to the sample. STM imaging is performed in the quasi-constant-current mode (height mode). It normally takes more than a day to obtain enough images, and both large scale images and close-up images were obtained at different sites, by moving the sample plate (after every six images) by a few millimeters. Surface coverage of grafted moieties was done in two steps. At the first step, images taken at different locations were grouped into different sessions (4-7 images). In each image the number of surface species was counted and, in each session, the average value was calculated. After that, the surface coverage of a sample, and corresponding weighted standard deviation σ were determined.

1.3.2 AFM measurements. AFM measurements were performed at room temperature using a Bruker (Dimension Icon) and a Park XE-100 machine operating at room temperature with a tapping mode. The functionalized graphite and gold substrates were washed with water and ethanol and then dried in nitrogen flow for AFM measurements.

1.3.3 Raman Measurements. Raman spectroscopic measurements were performed on a France HORIBA JobinYvon, LabRAM HR-800 Raman spectroscopy with wavelength of 514 nm and a laser spot of 800 μ m. Power of the laser was set to 5 mW. The accumulation time for all spectra was 10 s.

2. Supplementary figures

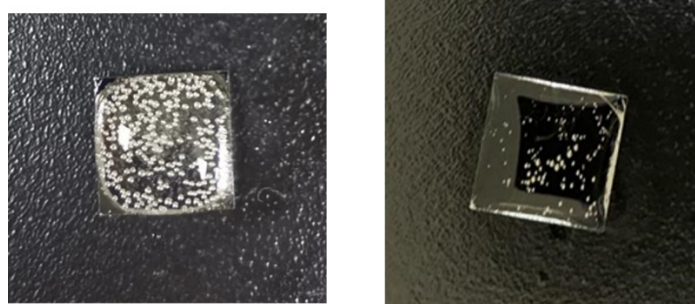


Fig. S1 Photographs of the graphite surfaces upon the mixing of diazonium salts of L-PheN (left) and D-PheN (right) with ascorbic acid.

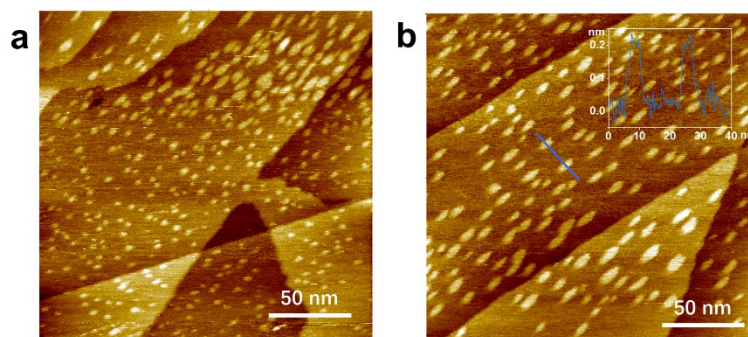


Fig. S2 Representative STM images of the Au(111) surfaces upon the reduction of diazonium salts of L-PheN (left) and D-PheN (right) with H_3PO_2 .

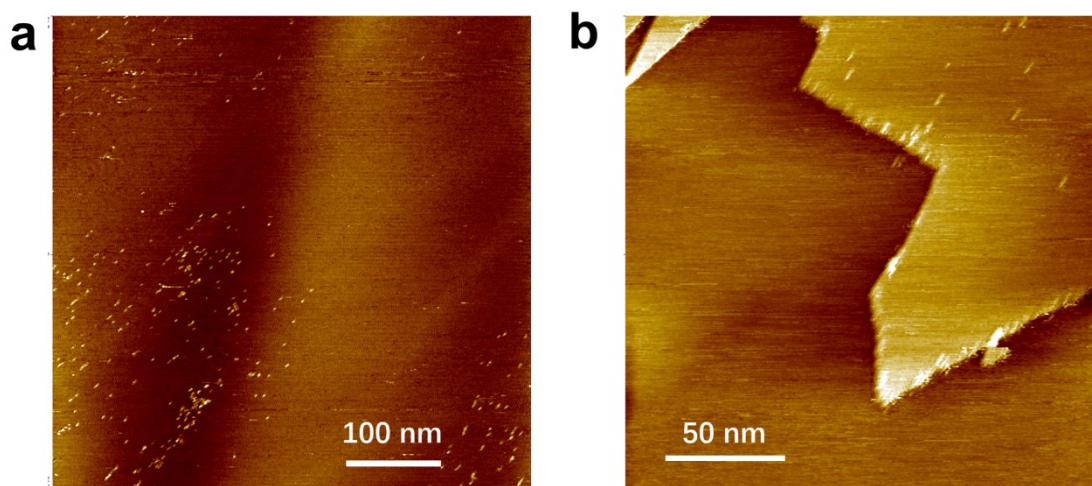


Fig. S3 Representative STM images of the HOPG surfaces upon the reduction of diazonium salts of L-PheN (left) and D-PheN (right) with ascorbic acid in a single round of surface functionalization.

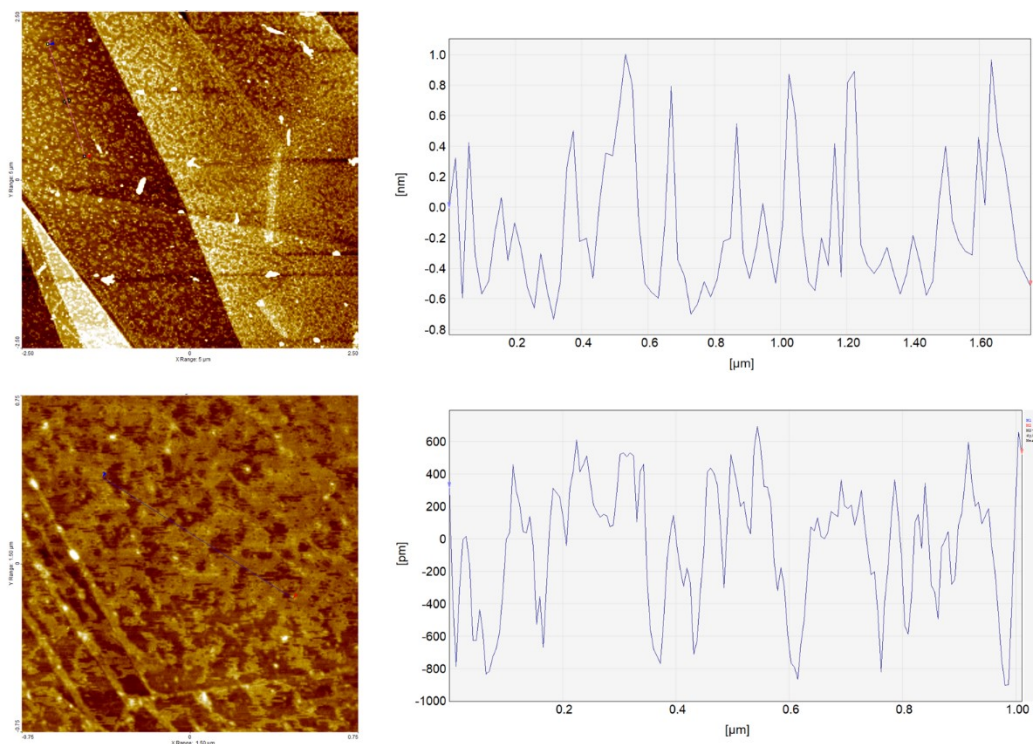


Fig. S4 Additional AFM images of the HOPG surfaces upon the reduction of diazonium salts of L-PheN with ascorbic acid for 10 rounds of surface functionalization.

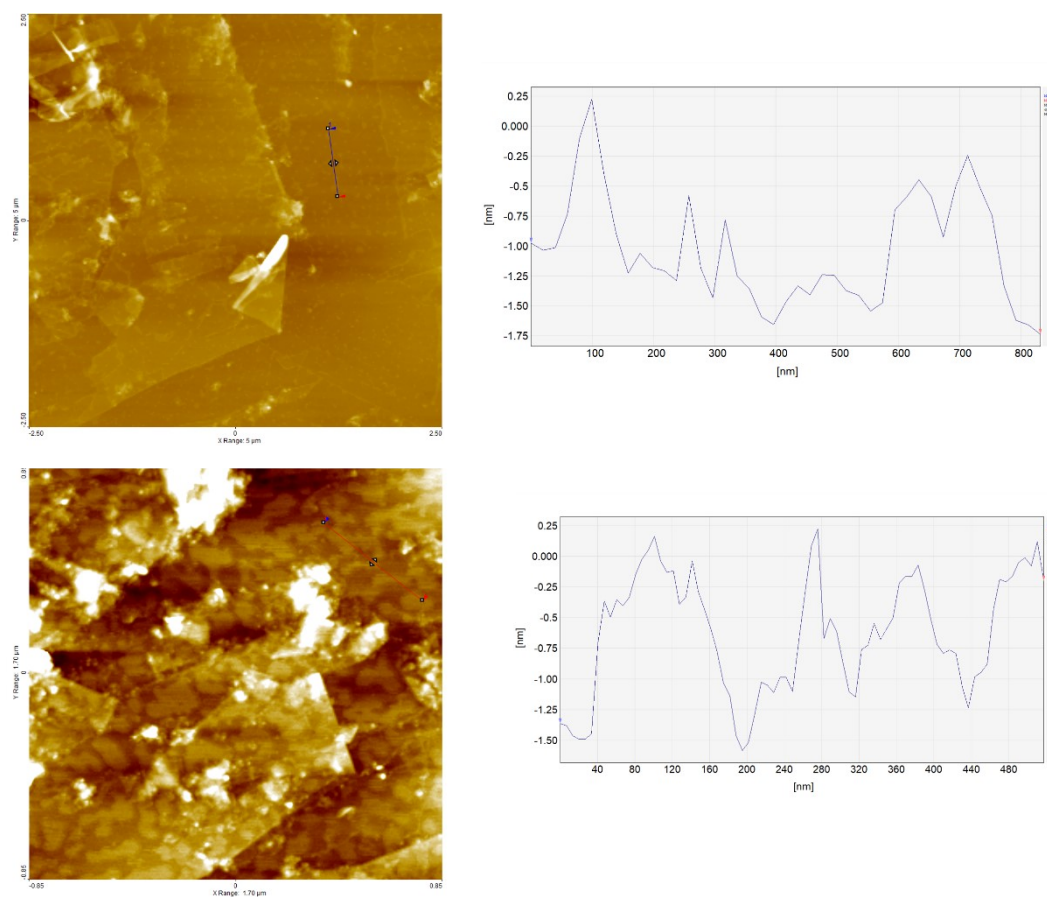


Fig. S5 Additional AFM images of the HOPG surfaces upon the reduction of diazonium salts of D-Phen with ascorbic acid for 10 rounds of surface functionalization.

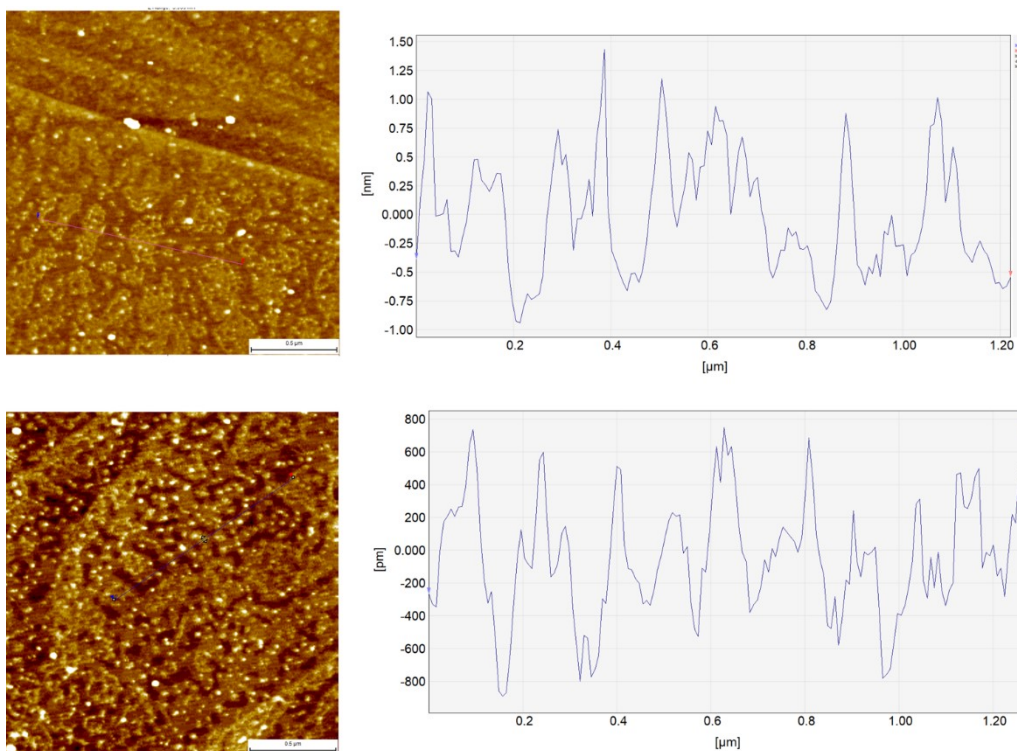


Fig. S6 AFM images of the HOPG surfaces after top) 5 rounds of surface functionalization with D-PheN and 5 rounds with L-PheN, and bottom) 5 times of surface functionalization with L-PheN and 5 times with D-PheN.

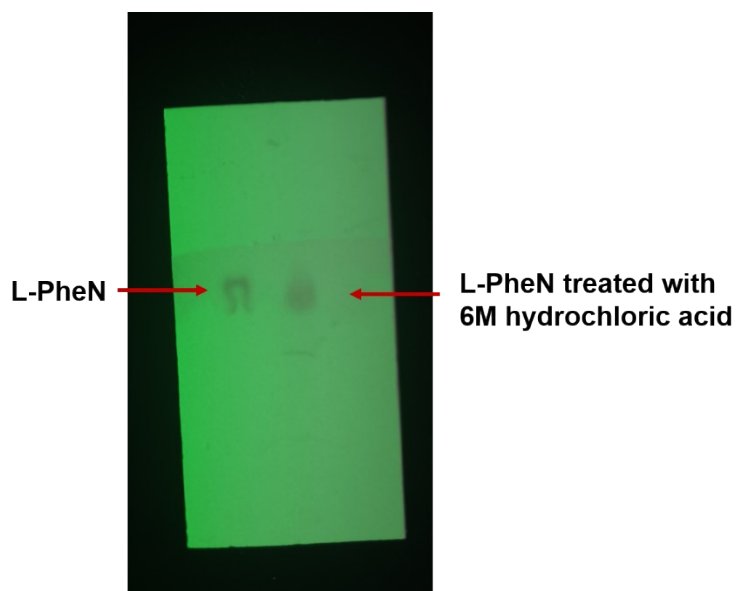


Fig. S7 TLC picture of the L-PheN and L-PheN treated with 6M HCl for more than 30 minutes, showing that majority of the protecting group of L-PheN remain intact. The eluent is methanol. The hydrochloric acid was neutralized by triethylamine before TLC analysis.