Electronic Supplementary Information

Construction of 2D nanoporous network by coupling on-surface dynamic imine chemistry and dipole-stabilized self-assembly

Jie-Yu Yue,[a,b] Marios Markoulides,[c] Andrew C. Regan,[d] Shu-Ying Li,[a,b] Nikos Chronakis,[e] André Gourdon,[c] Ting Chen,[a] Hui-Juan Yan,[a] and Dong Wang*[a,b]

[a] *Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, P. R. China.*

E-mail: wangd@iccas.ac.cn; Fax: +86 (0) 10 82616935

[b] *University of CAS, Beijing 100049 (P. R. China).*

[c] *CEMES-CNRS, UP8011, BP 94347, Nanosciences Group, 29 rue Jeanne Marvig, 31055, Toulouse, France.*

[d] *School of Chemistry, The University of Manchester, Manchester, M13 9PL, UK.*

[e] *Department of Chemistry, University of Cyprus, 2109, Aglantzia, Nicosia, Cyprus.*

Materials and methods

A Nanoscope IIIa SPM (Digital Instruments, Santa Barbara, CA) was employed for STM experiments. STM tips were made by mechanically cutting a Pt/Ir wire (90:10). All the STM images were collected in constant-current mode at ambient conditions at room temperature and were displayed without further processing.

Molecule A and [1", 1': 4', 1":4", 1"] triphenyl-4, 4"'-dicarbaldehyde (molecule B), were synthesized by the reported literature.[1, 2] The ^{1}H NMR and ^{13}C NMR spectra were in accordance with the reported literature. [1, 1'-biphenyl]-4, 4'-dicarboxaldehyde (molecule C), 4'-formyl-biphenyl-4-carboxylic acid ethyl ester (molecule E) and 4-biphenylcarboxaldehyde (molecule F) were purchased from J&K. [1, 1'-biphenyl]-4-carbaldehyd (molecule D) was purchased from TCI. THF was served as the solvent and was purchased from TCI. All the chemicals used in this study, unless otherwise specified, were utilized without further purification.

The typical synthesis procedure

4 μL THF solution containing molecule A with the concentration about 10^{-5} mol/L and molecule B/C with concentration about 10^{-5} mol/L were deposited on freshly cleaved HOPG surface, respectively. Then the treated HOPG was shifted to an autoclave with several $CuSO_4 \cdot 5H_2O$ powder (about 1 g) at the bottom. The autoclave was then sealed and placed into a heating oven at 150/120 °C for 3h. After cooling down, the

HOPG was taken out for STM characterization.

The control experiments

Molecule A and molecule D/E/F were served as precursors. 4 μL THF solution containing molecule A with concentration about 10^{-5} mol/L and molecule D/E/F with concentration about 10^{-5} mol/L were deposited on freshly cleaved HOPG surface, respectively. Then the treated HOPG and several $CuSO_4 \cdot 5H_2O$ powder were shifted to an autoclave. The autoclave was closed and heated at 120 °C for 3h. After the reaction, the HOPG was cooled down to room temperature and taken out for STM characterization.

Supplementary figures

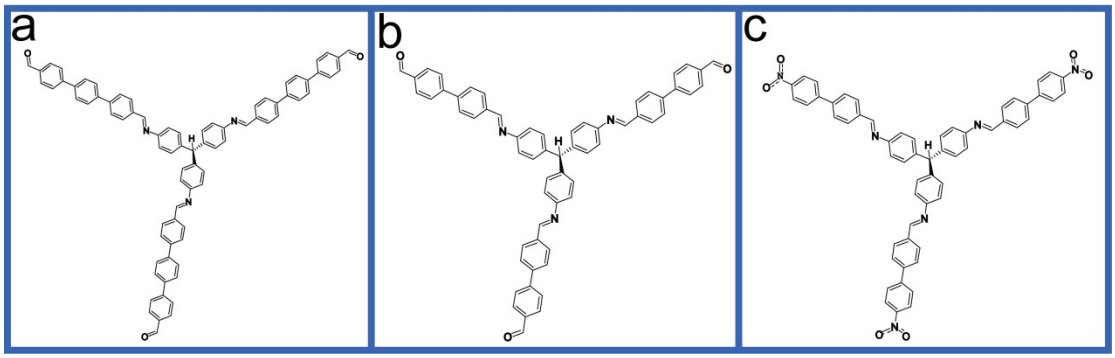

Fig. S1 (a) Chemical structure of imine oligomer AB_3. (b) Chemical structure of imine oligomer AC_3. (c) Chemical structure of imine oligomer AD_3.

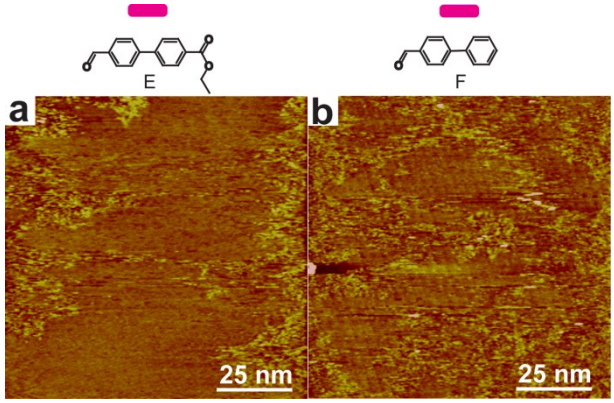

Fig. S2. Chemical structure of molecule E and F and STM image of the reaction results. (a) The reaction between molecule A and E. (b) The reaction between molecule A and F. Imaging conditions: (a) V_{bias} = 700 mV, I_t = 500 pA; (b) V_{bias} = 700 mV, I_t = 550 pA.

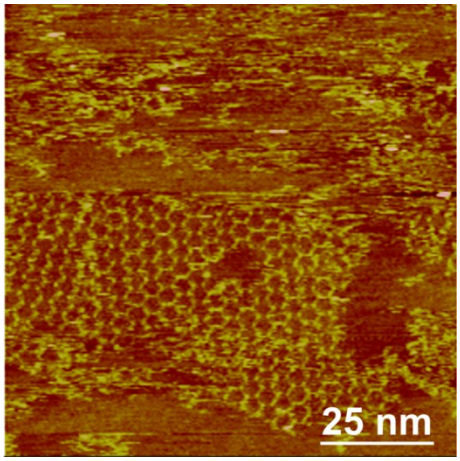

Fig. S3 STM image of the reaction between molecule A and B at 200 °C. Imaging conditions: V_{bias} = 700 mV, I_t = 500 pA.

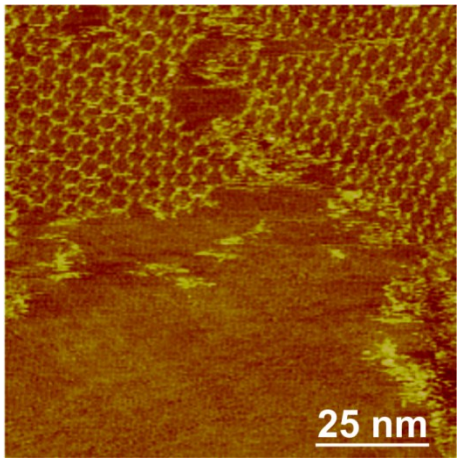

Fig. S4 STM image of the reaction between molecule A and B at 150 °C with the concentration of molecule A at 5×10^{-6} M and the concentration of molecule B at 10^{-6} M. Imaging conditions: $V_{bias} = 700$ mV, $I_t = 500$ pA.

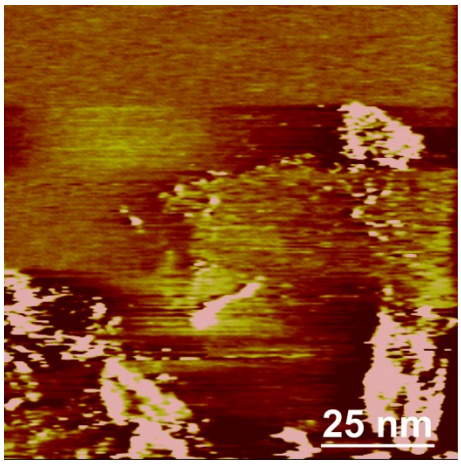

Fig. S5 STM image of the reaction between molecule A and B at 150 °C with the concentration of molecule A and B at 10^{-3} M. Imaging conditions: $V_{bias} = 700$ mV, $I_t = 500$ pA.

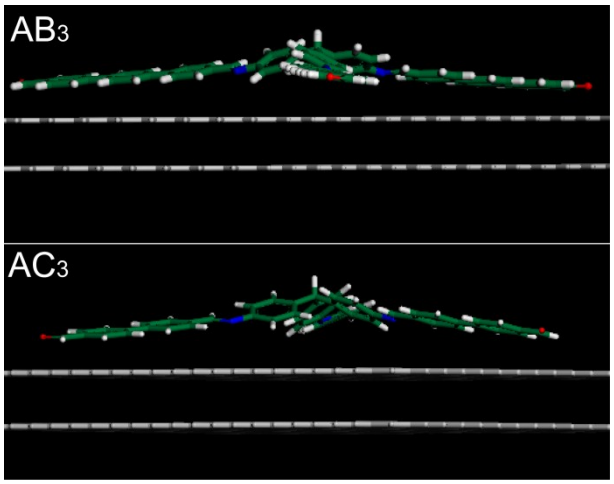

Fig. S6 The side view of imine oligomers AB_3 and AC_3 on the HOPG.

References

1 N. Chronakis, M. Markoulides, C. Efthymiou and A. Tasiopoulos, *Synlett*, 2015, **26**, 2659-2662.

2 M. Kozáková, M. Buděšínský and J. Hodačová, *Synth. Commun.*, 2005, **35**, 161-167.

3 L. Ascherl, T. Sick, J. T. Margraf, S. H. Lapidus, M. Calik, C. Hettstedt, K. Karaghiosoff, M. Döblinger, T. Clark, K. W. Chapman, F. Auras and T. Bein, *Nat. Chem.*, 2016, **8**, 310-316.