Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Rational design of two-dimensional covalent tilings using a C_6-symmetrical building block via on-surface Schiff base reaction

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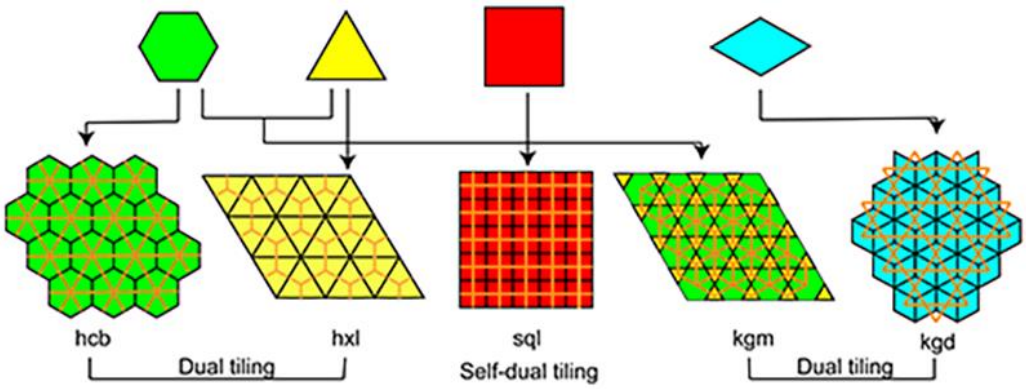
Contents

The five essential tiling and duality

Euclidean plane tilings by convex regular polygons have been widely used since antiquity. In geometry, regular hexagon, regular triangle, square and rhombus are the four elementary polygons, and tiling plane with simplex regular hexagon, regular triangle, square and rhombus can form the regular hcb tiling, regular hxl tiling, regular sql tiling and kgd tiling. In addition, combination regular hexagon with regular triangle can form the kgm tiling. Because of consisting of the above-mentioned simple polygons, the hcb, hxl, sql, kgm and kgd are the five essential tilings in Euclidean plane tilings.

The duality is intrinsic structure properties of tilings. Any polyhedron is associated with a second dual figure, where the vertices of one correspond to the faces of the other and the edges between pairs of vertices of one correspond to the edges between pairs of faces of the other. Hence, hcb and hxl are the dual tiling for each other, kgm and kgd are the dual tilings and sql belongs to self-dual tiling.



Scheme S1 The five essential tiling and duality relation

1. Synthetic procedures:

1.1 Materials & methods

Hexa(4-formylphenyl)benzene (HFPB) was synthesized according to the reported procedures[1]. 1H NMR and 13C NMR spectra agree well with the reported previously (Fig. S1). P-phenylenediamine (PPDA), 1,3,5-tris (4-aminophenyl) benzene (TAPB) and 4,4''-diamino-p-terphenyl (DATP) were purchased from J＆K and THF was purchased from TCI. The synthesis routes of 1,3-di(4-aminophenyl)benzene (DAPB) was described and the 1H NMR and 13C NMR spectra is shown in Fig. S2 and Fig. S3. PPDA and TAPB were used without further purification, HFPB and DFPB were purified after synthesis.

Scanning tunneling microscope (STM) experiments were carried out by using a Multimode STM (Bruker) at room temperature under ambient air condition. STM tips are mechanically cut Pt/Ir wires (90:10). All the STM images presented in the paper were recorded by using the constant current mode.

1.2 Synthesis

1.2.1 Synthesis of hexa(4-formylphenyl)benzene (HFPB)[1]:

Compound HFPB was synthesized according to the reported procedure. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 9.73 (s, 6H), 7.46-7.45 (m, 12H), 7.21–7.19 (m, 12H).

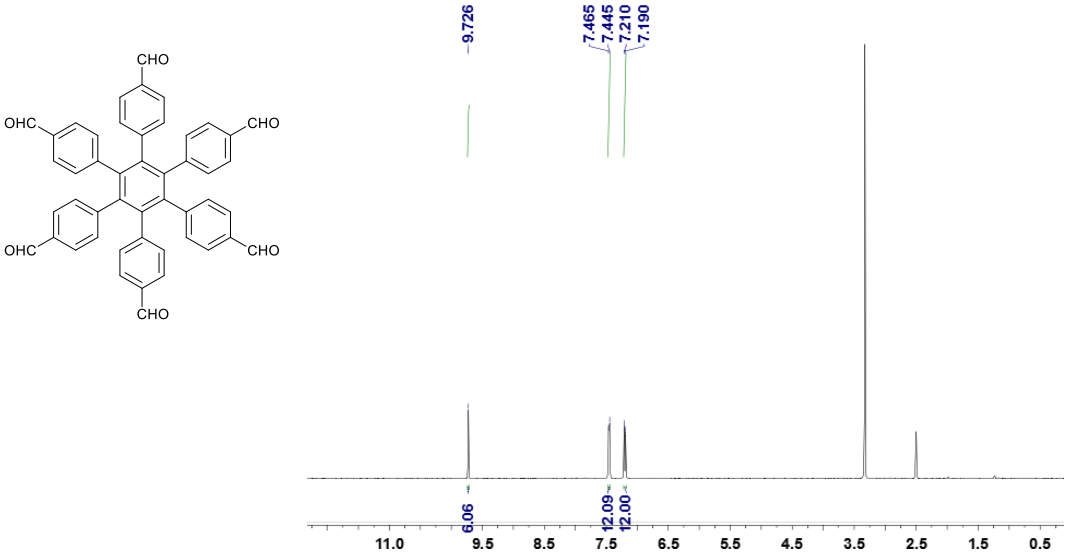


Fig. S1 ^{1}H NMR spectrum of hexa(4-formylphenyl)benzene (298K, 400 MHz, DMSO-d_6).

1.2.2 Synthesis of compound 1,3-di(4-aminophenyl)benzene (DAPB):

To a solution of 1,3-dibromobenzene (0.55 g, 2.34 mmol) and 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenylamine (1.29 g, 5.86 mmol) in dioxane were added K_2CO_3 (0.85 g, 9.36 mmol), distilled H_2O (8 mL), and $[PdCl_2(PPh_3)_2]$ (0.36 g, 0.51 mmol) under argon and the reaction mixture was refluxed overnight. The dioxane was then removed under vacuum and the residue obtained was treated with water, extracted with dichloromethane, and dried over anhydrous Na_2SO_4. The organic layer was evaporated, and the compound was purified by column chromatography using ethyl acetate as an eluent to give compound DAPB as white solid (0.3 g, 50%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.70 (s, 1H), 7.46-7.45 (m, 7H), 6.78–6.77 (m, 4H), 3.75 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 145.98, 141.68, 131.86, 129.10, 128.23, 124.80, 124.59, 115.50. MALDI-TOF, m/z: calcd for $C_{18}H_{16}N_2$ $[M]^+$ 260.1313; found, 260.231.

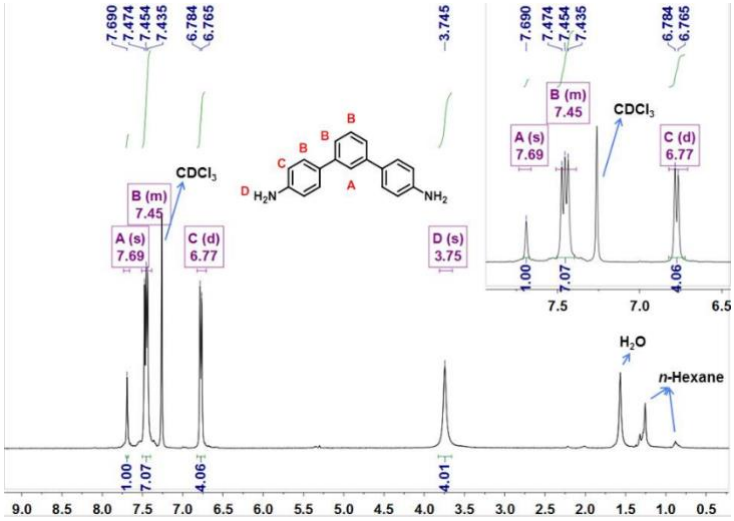


Fig. S2 ^1H NMR spectrum of 1,3-di(4-aminophenyl)benzene (298K, 400 MHz, $CDCl_3$).

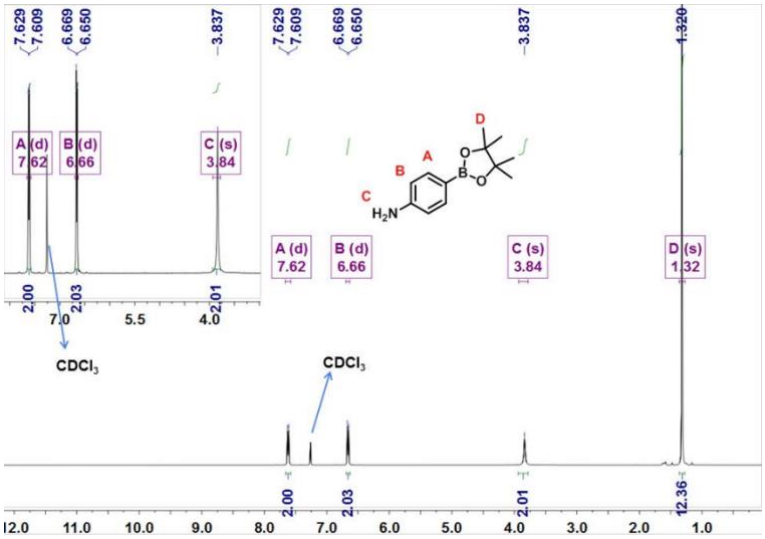


Fig. S3 ^1H NMR spectrum of 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenylamine (298K, 400 MHz, $CDCl_3$).

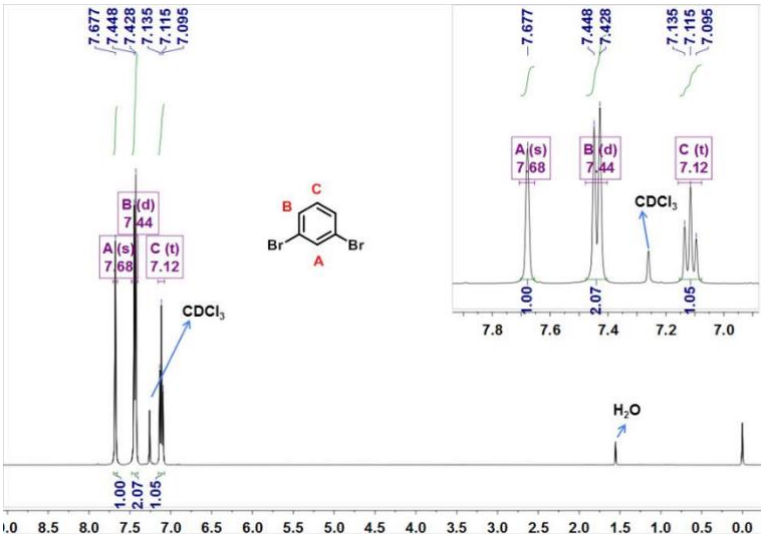


Fig. S4 ^{1}H NMR spectrum of 1,3-dibromobenzene(298K, 400 MHz, $CDCl_3$).

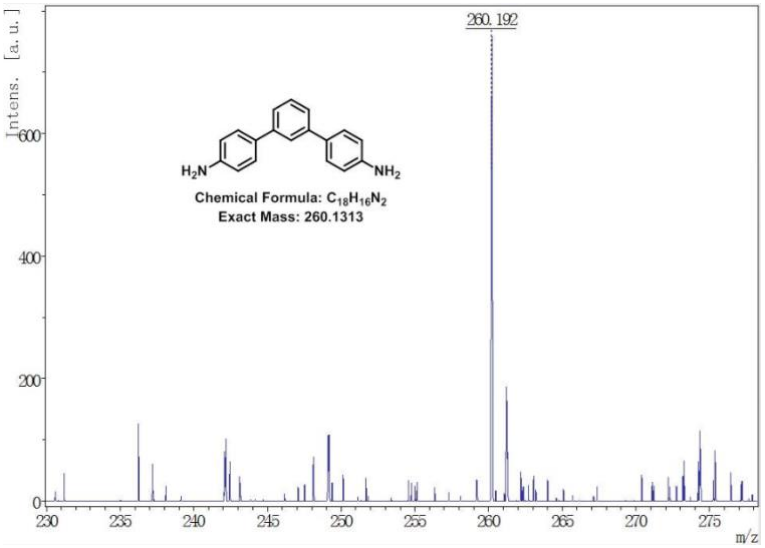


Fig. S5 MALDI-TOF-MS spectrum of 1,3-di(4-aminophenyl)benzene.

3. STM measurements

3.1 Experimental details:

3.1.1 Synthesis procedure of 2D covalent triangular tilings

In synthesis procedure for covalent triangular tilings, a droplet (~5 uL) tetrahydrofuran (THF) containing 1×10^{-5} M 3',4',5',6'-tetrakis(4-formylphenyl)-[1,1':2',1''-terphenyl]-4,4''-dicarbaldehyde (HFPB) was deposited on freshly cleaved highly oriented pyrolytic graphite (HOPG) surfaces and allowed to dry before located in a 100 mL Teflon-sealed autoclave. p-phenylenediamine (PPDA) powder (~0.2 mg) and $CuSO_4 \cdot 5H_2O$ power (~1.1 g) were added to the bottom of the 100 mL Teflon-sealed autoclave, but not in direct contact with the sample. After heating at 160°C for 3 h, the HOPG was cooled down to room temperature and taken out for STM characterization.

3.1.2 Synthesis procedure of 2D covalent rhombille tilings

For covalent rhombille tilings synthesis, 5 μL mixed THF solution containing molecule HFPB with concentration about 1×10^{-5} M and molecule TAPB with concentration about 2×10^{-5} M was deposited on freshly cleaved HOPG surface and allowed to dry. Then the HOPG loaded with precursors was put in a closed 100 mL Teflon-sealed autoclave with the presence of $CuSO_4 \cdot 5H_2O$ powder about 1.1 g. After heating at 160°C for 3 h, the HOPG was cooled down to room temperature and taken out for STM characterization.

3.1.3 Synthesis procedure of 2D covalent semi-regular tilings

For covalent semi-regular tilings synthesis, 5 μL mixed THF solution containing molecule HFPB with concentration about 5×10^{-6} M and molecule DAPB with concentration about 1.5×10^{-5} M was deposited on freshly cleaved HOPG surface and allowed to dry. Then the HOPG loaded with precursors was put in a closed 100 mL Teflon-sealed autoclave with the presence of $CuSO_4 \cdot 5H_2O$ powder about 1.1 g. After heating at 160°C for 3 h, the HOPG was cooled down to room temperature and taken out for STM characterization.

3.2 Additional STM data:

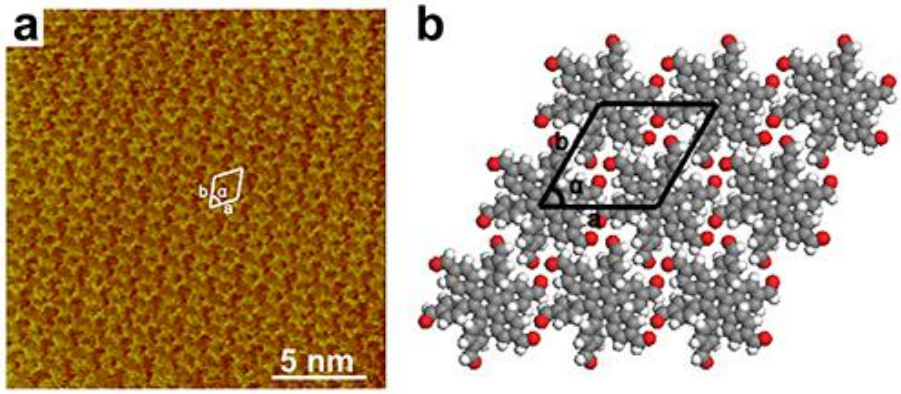


Fig. S6 (a) STM image of self-assembly of HFPB molecules on HOPG (c = 10^{-4} M). The measured lattice parameters are a = 1.6 nm ± 0.2 nm, b = 1.5 nm ± 0.2 nm, α = 57° ± 2°. (b) The structural model for HFPB assembly. Imaging conditions: V_{bias} = 700 mV, I_t = 510 pA

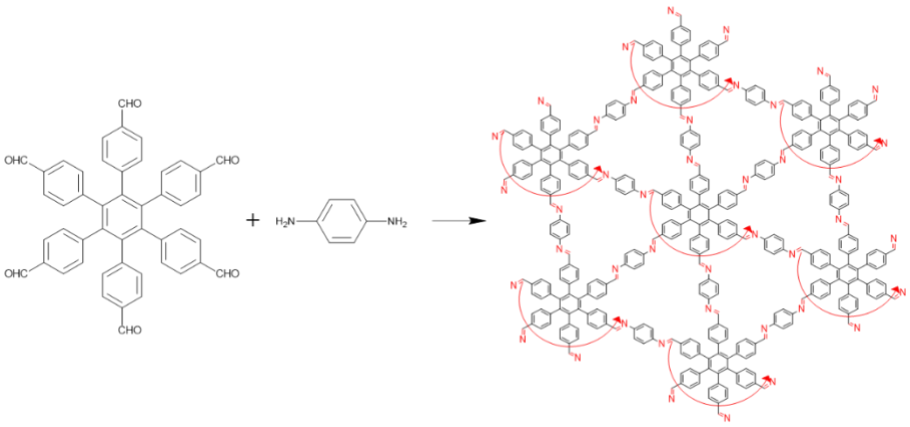


Fig. S7 Illustration for the construction of triangular (hxl) tiling from the combination of C6-symmetric and C2-symmetric monomers. The linkage C=N bond for imine based COFs results a kink configuration. The orientation of C=N can be heterodromous or homodroumous in construction COFs. For fabrication the triangular (hxl) tiling, the C=N bonds around a vertex adapt homodromous orientation to form the extended two-dimensional tiling. In contrast, a heterodromous orientation of imine bonds would result in incomplete bond formation. Similarly, the concerted arrangement of the C=N linkages should occur for the construction of other extended networks. However, the C=N orientation cannot be clearly resolved by the ambient STM because of the restriction of STM resolution.

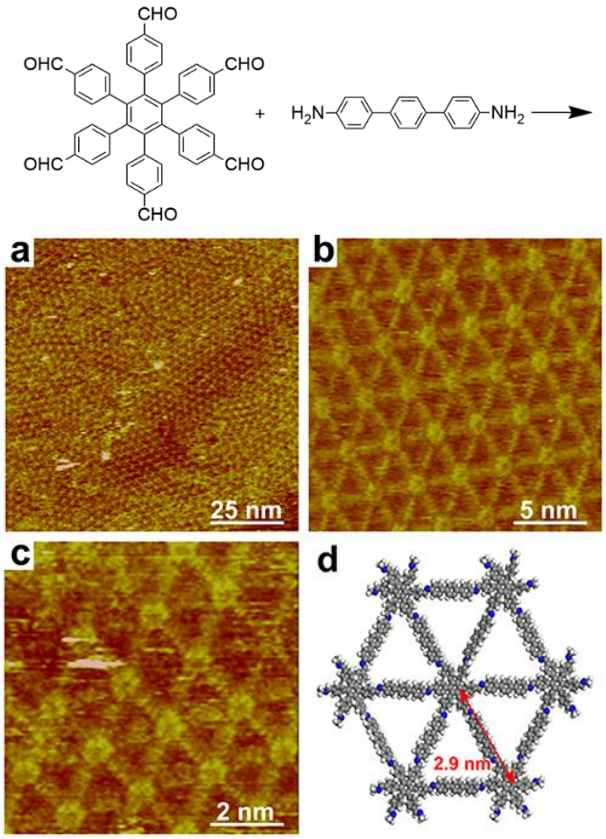


Fig. S8 (a) (b) Representative STM images of the sCOFs of triangular tiling obtained by condensation reaction of HFPB (1×10^{-5} M) with DATP (3×10^{-5} M) at 160°C. (c) High resolution STM image showing the structures of the triangular tiling. (d) Structure model. Imaging conditions: V_{bias} = 700 mV, I_t = 510 pA

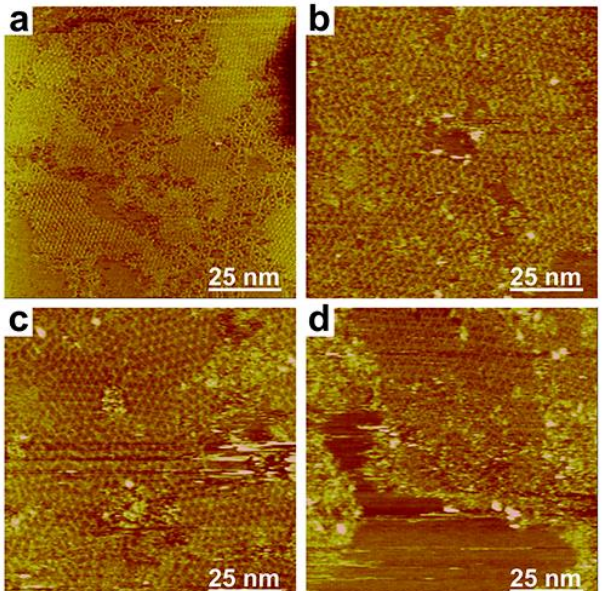


Fig. S9 STM images of the structures obtained from different molecular ratios of HFPB and DATP on HOPG. (a) STM image obtained for HFPB : DATP = 2:1. (b) STM image obtained for HFPB : DATP = 1:6. (c) STM image obtained for DFPB : DATP = 1:10. (d) STM image obtained for DFPB : DATP = 1:15. The concentration of HFPB is 1×10^{-5} M. Imaging conditions: (a) V_{bias} = 670 mV, I_t = 510 pA; (b) V_{bias} = 660 mV, I_t = 480 pA; (c) V_{bias} = 710 mV, I_t = 500 pA; (d) V_{bias} = 700 mV, I_t = 490 pA.

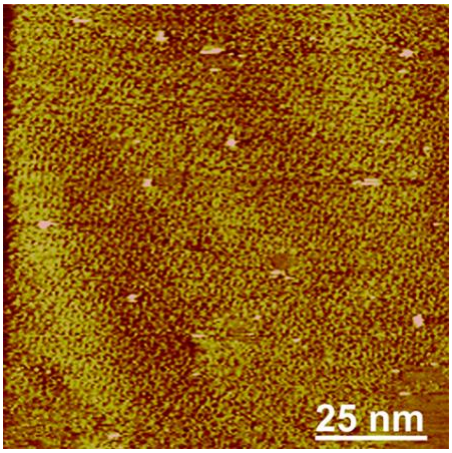


Fig. S10 The larger scale STM image of the rhombille (kgd) tiling fabricated via co-condensation reaction of HFPB (1×10^{-5} M) with TAPB (2×10^{-5} M) at 160°C. Imaging conditions: V_{bias} = 700 mV, I_t = 510 pA

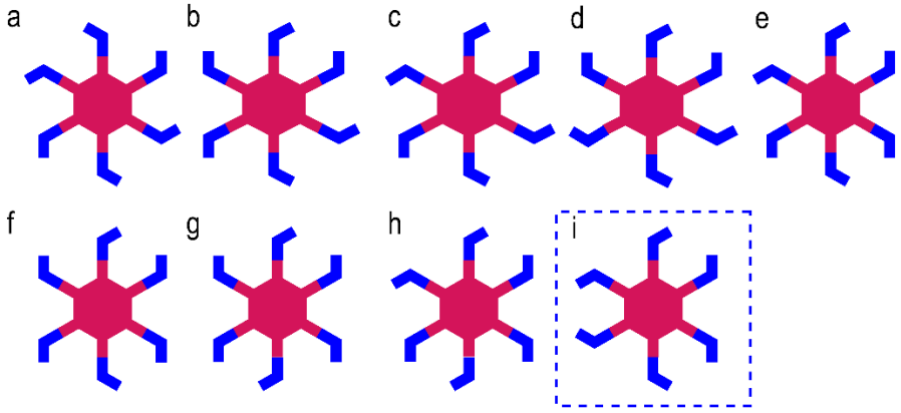


Fig. S11 Different architecture at vertex for reaction of C_6-symmetrical and C_{2v}-symmetrical building blocks. (a) (b) (c) (d) (e) (f) (g) (h) shown the eight disordered structures and (i) represents the connection mode of forming the highly ordered semi-regular tiling. (The related mirrored structures are not shown)

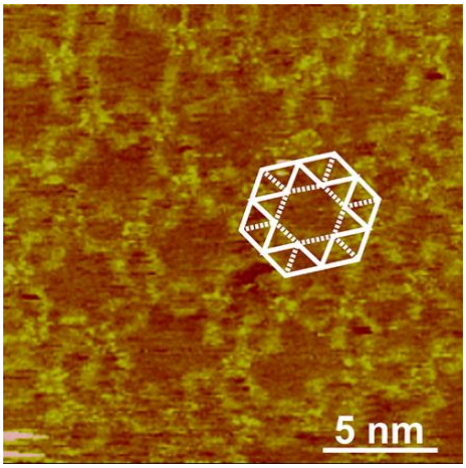


Fig. S12 The schematic diagram of dividing the semi-regular tiling into snub hexagonal tiling (five-vertex configurations: four triangles and one hexagon at each vertex). Every rhombus is divided into two triangles, and hexagram is divided into six triangles and hexagon. Imaging conditions: V_{bias} = 710 mV, I_t = 500 pA

3.3 Correction average STM images

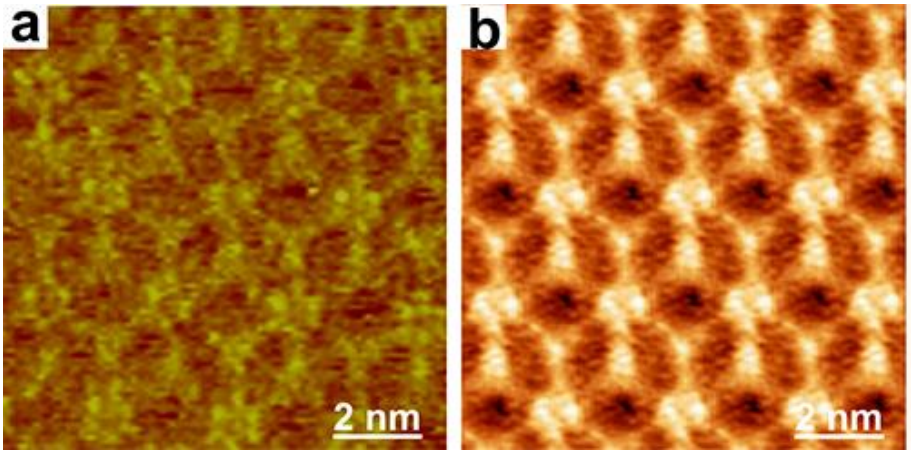


Fig. S13 (a)The high-resolution STM image and (b) the correlation average image of the rhombille (kgd) tiling fabricated via co-condensation reaction of HFPB (1×10^{-5} M) with TAPB (2×10^{-5} M) at 160°C. Imaging conditions: V_{bias} = 700 mV, I_t = 510 pA. (This process is carried out by using WSxM 5.0)[2]

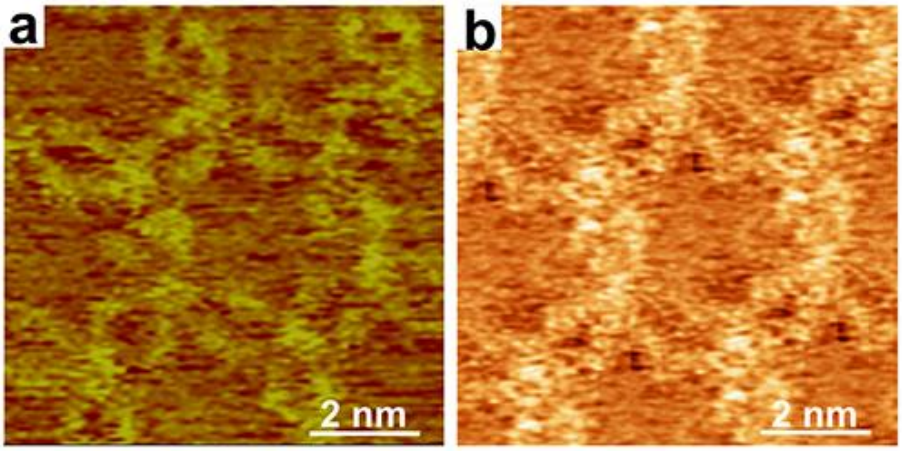


Fig. S14 (a)The high-resolution STM image and (b) the correlation average image of the semi-regular tiling fabricated via co-condensation reaction of HFPB (5×10^{-6} M) with DAPB (1.5×10^{-5} M) at 160°C. Imaging conditions: V_{bias} = 700 mV, I_t = 510 pA. (This process is carried out by using WSxM 5.0)[2]

4. ESI reference

1. B. Alahakoon, C. M. Thompson, A. X. Nguyen, G. Occhialini, G. T. McCandless and R. A. Smaldone., *Chem. Commun.*, 2016, **52**, 2843-2845.
2. I. Horcas, R. Fernandez, J.M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero and A. M. Baro. *Rev. Sci. Instrum.,* 2007, 78, 013705