

*Supporting information materials for*

# Ordering of Molecules with $\pi$ -Conjugated Triangular Core by Switching Hydrogen Bonding and van der Waals Interactions

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## ***Synthesis of alkoxyated derivatives of DBA.***

**General.** We synthesized and purified the DBA derivative with methoxy groups (DBA-OC<sub>1</sub>) in accordance with a previous report<sup>S1</sup> and the DBA derivative with butoxy groups (DBA-OC<sub>4</sub>) as described here. All manipulations were performed in an inert gas (nitrogen or argon) atmosphere. All solvents were distilled or passed through activated alumina and copper catalyst in a Glass Contour solvent purification system before use. All commercially available reagents were used as received. Pd(PPh<sub>3</sub>)<sub>4</sub> was prepared following the literature.<sup>S2</sup> <sup>1</sup>H (400 MHz) and <sup>13</sup>C (100 MHz) NMR spectra were measured on a Bruker UltraShield Plus 400 spectrometer. The spectra measured in chloroform-*d* were referenced to residual solvent protons in the <sup>1</sup>H NMR spectra (7.26 ppm) and to solvent carbons in the <sup>13</sup>C NMR spectra (77.0 ppm). Other spectra were recorded using the following instruments: IR spectra, JASCO FT-IR-4200; Mass spectra, JEOL JMS-700 for EI ionization mode.

**Synthesis of 1,2-Dibutoxy-4-iodo-5-[(trimethylsilyl)ethynyl]benzene.** Under an argon atmosphere, 1,2-dibutoxy-4,5-diiodobenzene (3.39 g, 7.15 mmol),<sup>S3</sup> CuI (68 mg, 0.36 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (248 mg, 215 μmol) were placed in a three necked flask. Freshly distilled NEt<sub>3</sub> (30 mL) was added, then (trimethylsilyl)acetylene (1.0 mL, 3.5 mmol) was slowly added to the reaction mixture via a syringe. After stirring at room temperature for 1 h and at 50 °C for 2 h, the solvent was evaporated under vacuum. The products were purified with silica gel column (CH<sub>2</sub>Cl<sub>2</sub>/hexane = 1/4 and then 9/1) to give 1,2-dibutoxy-4-iodo-5-[(trimethylsilyl)ethynyl]benzene (1.18 g, 37%) as a pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.21 (s, 1H), 6.96 (s, 1H), 4.00–3.92 (m, 4H), 1.83–1.73 (m, 4H), 1.54–1.44 (m, 4H), 1.02–0.94 (m, 6H), 0.27 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 150.1, 148.9, 122.9, 121.7, 117.2, 107.0, 96.4, 90.6, 69.1, 69.0, 31.13, 31.09, 19.15, 19.14, 13.8, –0.09; IR (NaCl) 2958, 2872,

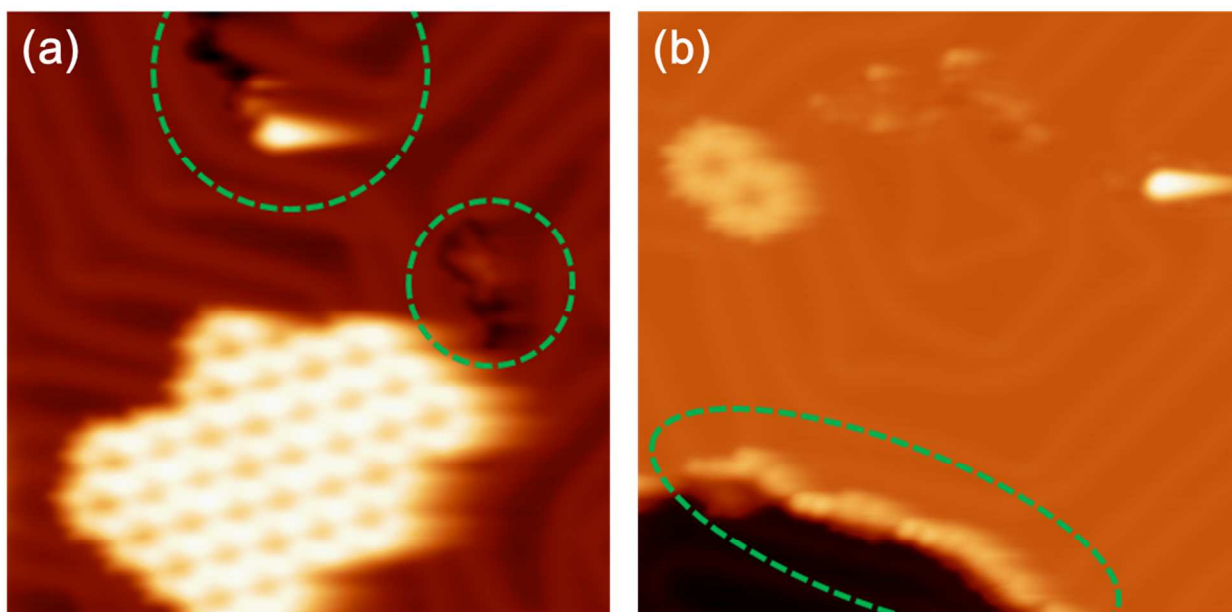
2153, 1586, 1502, 1467, 1376, 1251, 1213, 1182, 1025, 843, 759  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{19}\text{H}_{29}\text{O}_2\text{SiI}$ , 444.0982, found, 444.0961 ( $\text{M}^+$ ).

**Synthesis of 1,2-Dibutoxy-4-ethynyl-5-iodobenzene.** Deprotection of the trimethylsilyl group of 1,2-dibutoxy-4-iodo-5-[(trimethylsilyl)ethynyl]benzene (1.13 g, 2.54 mmol) was performed with  $\text{K}_2\text{CO}_3$  (1.05 g, 7.60 mmol) in MeOH (50 mL). After stirring at room temperature for 6 h, water and hexane were added, and the organic phase was washed with water and brine. The extract was dried over  $\text{MgSO}_4$ , and the solvents were evaporated to afford 1,2-dibutoxy-4-ethynyl-5-iodobenzene (830 mg, 88%) as white solids. This material was used in the next step without further purification. mp 80.5–82.0  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 (s, 1H), 6.99 (s, 1H), 4.04–3.90 (m, 4H), 3.28 (s, 1H), 1.86–1.72 (m, 4H), 1.58–1.40 (m, 4H), 1.04–0.92 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.5, 149.0, 123.0, 120.7, 117.9, 89.6, 85.5, 79.0, 69.11, 69.08, 31.10, 31.08, 19.20, 19.14, 13.8; IR (KBr) 3252, 2961, 2927, 2870, 1587, 1501, 1471, 1370, 1250, 1211, 1172, 1160, 1038, 823, 720  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{16}\text{H}_{21}\text{O}_2\text{I}$ , 372.0586, found, 372.0581 ( $\text{M}^+$ ).

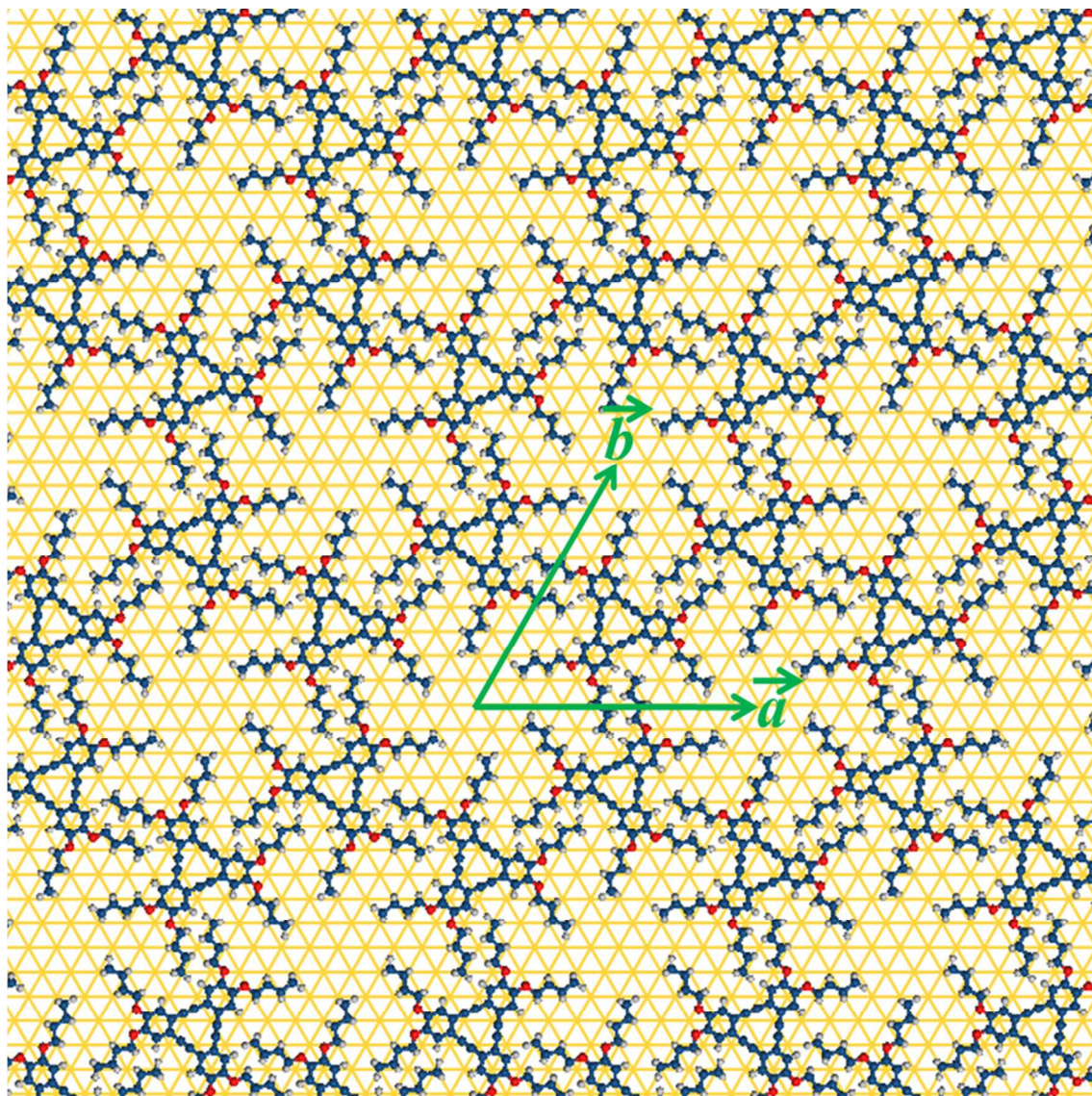
**Synthesis of Hexabutoxyhexadehydrotribenzo[12]annulene.** Under a nitrogen atmosphere, 1,2-dibutoxy-4-ethynyl-5-iodobenzene (800 mg, 2.15 mmol), CuI (123 mg, 646  $\mu\text{mol}$ ),  $\text{PPh}_3$  (169 mg, 644  $\mu\text{mol}$ ),  $\text{K}_2\text{CO}_3$  (890 mg, 6.44 mmol) and DMF (1.0 mL) were placed in a Schlenk tube. After stirring at 160  $^{\circ}\text{C}$  for 1 d, water was added. The products were extracted with  $\text{CHCl}_3$  (40 mL), the extract was washed with water and brine, and dried over  $\text{MgSO}_4$ . After evaporation of the solvents, the products were separated by the use of silica gel chromatography ( $\text{CH}_2\text{Cl}_2/\text{hexane} = 1/1$ ). Recrystallization from  $\text{CH}_2\text{Cl}_2/\text{hexane}$  (1/1) gave hexabutoxyhexadehydrotribenzo[12]annulene (175 mg, 33%) as yellow solids. mp 195.5–196.5  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.72 (s, 6H), 3.97 (t,  $J = 6.4$  Hz, 12H), 1.79 (tt,  $J = 6.8, 6.4$

Hz, 12H), 1.53–1.42 (m, 12H), 0.98 (t,  $J_{\text{H-H}} = 7.2$  Hz, 18H);  $^{13}\text{C}$  NMR (100 MHz) 149.2, 119.8, 115.9, 91.8, 68.8, 31.2, 19.2, 13.8; IR (KBr) 2956, 2871, 2210, 1592, 1510, 1474, 1348, 1222, 1070, 1037, 1009, 860, 748  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{48}\text{H}_{60}\text{O}_6$ , 732.4390, found, 732.4410 ( $\text{M}^+$ ).

**Figure S1.** STM images ( $40 \times 40 \text{ nm}^2$ ) showing that the herringbone reconstruction of the Au(111) surface is lifted by the DBA-OC<sub>4</sub> molecules. (a) STM image of DBA-OC<sub>4</sub>/Au(111) ( $V_s = 1.0 \text{ V}$ ,  $I_t = 0.1 \text{ nA}$ ). Green dashed circles indicate that the Au atoms ejected due to the strong surface-molecule contact are clustered as islands on terraces. (b) STM image of DBA-OC<sub>4</sub>/Au(111) ( $V_s = 2.0 \text{ V}$ ,  $I_t = 1.0 \text{ nA}$ ) representing that the Au atoms ejected due to the strong surface-molecule contact are grown out at edge of terrace (indicated by green dashed circle).

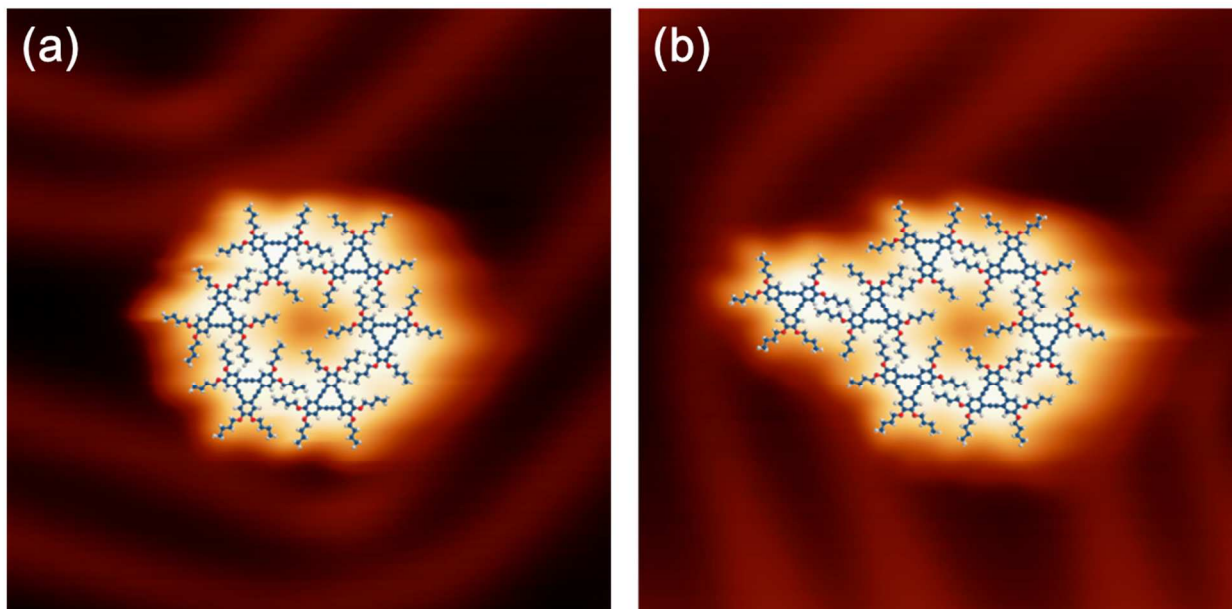


**Figure S2.** An extended honeycomb pattern of DBA-OC4 on the Au(111) surface. The lattice constants ( $a$  and  $b$ ) of the honeycomb network,  $28.8 \text{ \AA}$ , match the experimental values ( $29.2 \pm 1.0 \text{ \AA}$ ) very well.





**Figure S3.** STM images ( $13 \times 13 \text{ nm}^2$ ) obtained at the low-coverage region of DBA-OC<sub>4</sub>. (a) The smallest enclosed structure formed by DBA-OC<sub>4</sub> ( $V_s = 1.0 \text{ V}$ ,  $I_t = 0.2 \text{ nA}$ ). (b) The open structure formed by adding one DBA-OC<sub>4</sub> molecule to the smallest enclosed structure ( $V_s = 1.0 \text{ V}$ ,  $I_t = 0.5 \text{ nA}$ ). It indicates that the interdigitation pattern of DBA-OC<sub>4</sub> is stabilized via van der Waals (vdW) interactions regardless of coverage.



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