

# Ordering the Self-Assembly Structures via Intermolecular Br $\cdots$ S interactions

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## 1. $^1\text{H}$ NMR data of two DTBDT derivatives

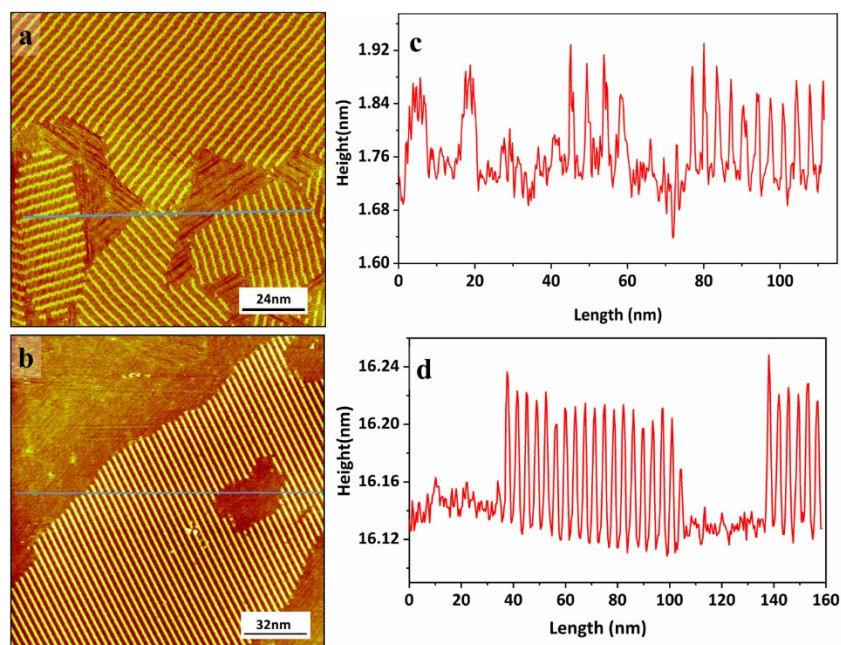
### H-DTBDT

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm) 7.64 (d,  $J = 7.15$  Hz, 2H), 7.44 (d,  $J = 7.15$  Hz, 2H), 7.29 (d,  $J = 4.35$  Hz, 2H), 6.90 (d,  $J = 4.35$  Hz, 2H), 2.91 (t,  $J = 9.57$  Hz, 4H), 1.77 (m, 4H), 1.43 (m, 4H), 1.25 (m, 60H), 0.87 (t,  $J = 8.52$  Hz, 6H).

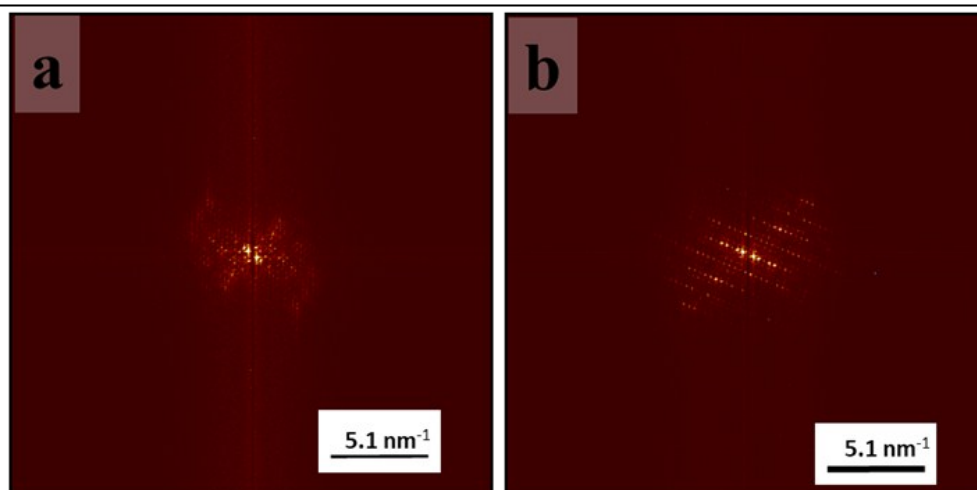
### Br-DTBDT

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm) 7.60 (d,  $J = 7.1$  Hz, 2H), 7.48 (d,  $J = 7.1$  Hz, 2H), 7.27 (s, 2H), 2.88 (t,  $J = 9.68$  Hz, 4H), 1.76 (m, 4H), 1.45 (m, 4H), 1.25 (m, 60H), 0.88 (t,  $J = 8.55$  Hz, 6H).

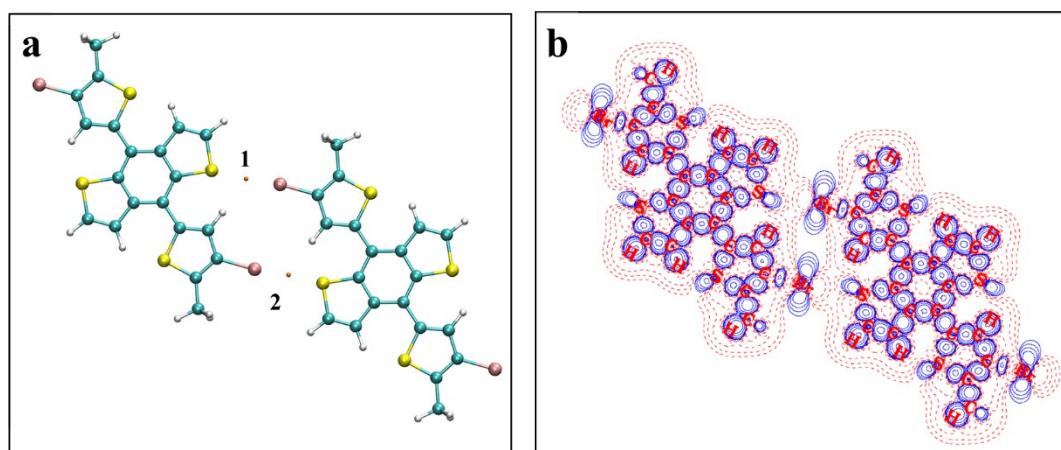
## 2. Images



**Fig. S1** (a) and (b) Large-scale STM images of the monolayer formed by H-DTBDT Br-DTBDT at the 1-phenyloctane/HOPG interface, respectively. ( $I_{\text{set}} = 520$  pA,  $V_{\text{bias}} = 600$  mV; scale bar: (a)  $120 \times 120$  nm $^2$ , (b)  $160 \times 160$  nm $^2$ ). (c) and (d) the height profile corresponding to the blue line in (a) and (b), respectively.



**Fig. S2** (a) and (b) Two-dimensional fast Fourier transform of the high-resolution images of H-DTBDT (Fig. 4b) and Br-DTBDT (Fig. 5b), respectively.



**Fig S3.** (a) Molecular graph showing intermolecular bond critical points (BCPs) for the dimer of Br-DTBDT molecules (small orange dots marked as 1 and 2). (b) Deformation charge density map in the plane for the dimer. Positive contours are shown with blue lines, and negative contours are shown with red lines.