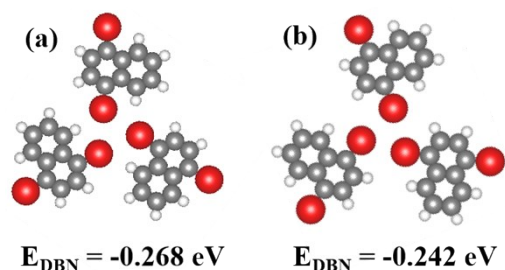


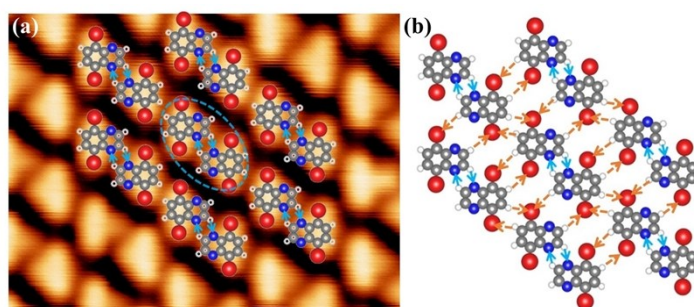
## Supplementary Information

### Surface self-assembly involving the interaction between S and N atoms

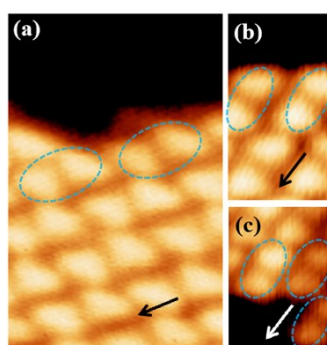
Tianhao Wu,<sup>‡a</sup> Na Xue,<sup>‡b</sup> Zhichao Wang,<sup>c</sup> Jie Li,<sup>d</sup> Yaru Li,<sup>d</sup> Wei Huang,<sup>ce</sup> Qian Shen,<sup>\*c</sup>  
Shimin Hou<sup>\*ad</sup> and Yongfeng Wang<sup>\*af</sup>



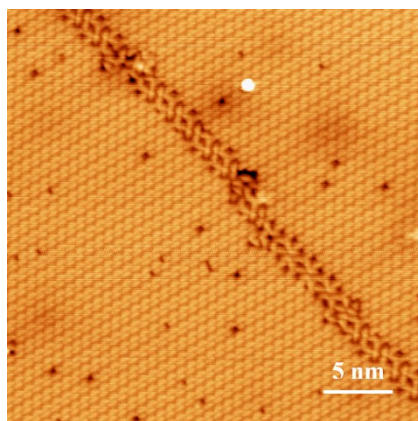
**Fig. S1** (a, b) DFT-optimized molecular models of the DBN trimers with opposite chirality, which appear alternately in the DBN molecular trimer array. The binding energies  $E_{\text{DBN}}$  of DBN trimers are determined to be  $-0.268 \text{ eV}$  and  $-0.242 \text{ eV}$  by substrate-free DFT calculations respectively.



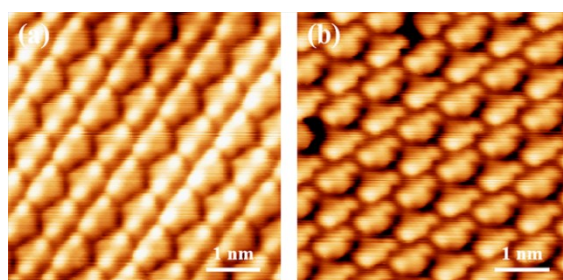
**Fig. S2.** (a) Seven optimized DBQX dimers are superimposed on the STM image. (b) The central dimer interacts with six others through Br-H...N hydrogen bonds.



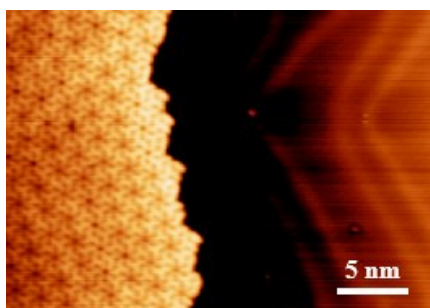
**Fig. S3** STM image of DBQX molecular island boundaries on Cu(111) ((a)  $V_S = 0.38 \text{ V}$ ,  $I_T = 60 \text{ pA}$ , (b)  $V_S = 0.52 \text{ V}$ ,  $I_T = 60 \text{ pA}$ , (c)  $V_S = 0.52 \text{ V}$ ,  $I_T = 60 \text{ pA}$ ). The structures circled by blue dotted lines indicate dimers connected N...H hydrogen bonds at the boundary. Arrows indicate the close-packed direction of the substrate.



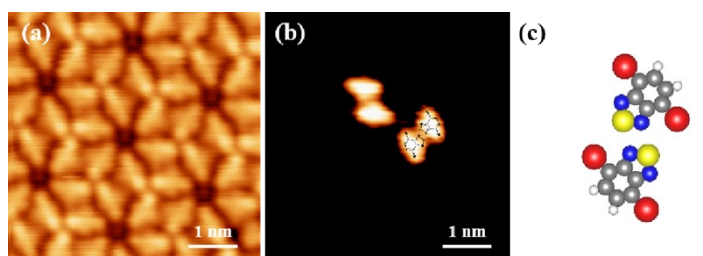
**Fig. S4** Large-scale STM image of DBQX molecules on Cu(111) ( $V_S = -1.10$  V,  $I_T = 60$  pA).



**Fig. S5** STM images of DBQX molecules on (a) Au(111) ( $V_S = -35$  mV,  $I_T = 100$  pA) and (b) Ag(111) ( $V_S = 0.27$  V,  $I_T = 60$  pA).



**Fig. S6** Large-scale STM image of DBBTA molecules on Au(111) ( $V_S = 0.23$  V,  $I_T = 60$  pA). Only one type of self-assembled pattern is observed and it does not change when varying molecular coverage.



**Fig. S7** (a, b) STM image of DBBTA molecules on Ag(111) ((a)  $V_S = -52$  mV,  $I_T = 100$  pA, (b)  $V_S = 50$  mV,  $I_T = 100$  pA). (c) DFT-optimized molecular model of the DBBTA dimer associating through S...N interactions.