Supporting Information *for*

Engineering Two-Dimensional Multilevel Supramolecular Assemblies from a Bifunctional Ligand on Au(111)

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1) Summary of complementary bonding motifs.

In Table S1, we have summarized the number of the complementary bonding motifs for DBA-I and the three alkali-coordination nanostructures (DBA·Na-II, DBA·Cs-I and -II), according to our analysis of the corresponding DFT optimized atomic structural models. The chemical interactions of Br···Br, Br···O, Br···H and O···H are determined according to previous literatures [21,44-46].

Table S1. Summary complementary bonding motifs.

Structure	DBA-I [a]		DBA·Na-II		DBA·Cs-I			DBA·Cs-II		
Level	2nd	3rd	1st	2nd	1st	2nd	3rd	1st	2nd	3rd
Br···H	6	8	0	6	7	3	2	2	4	2.5
O···H	2	2	0	0	1	0	0	0	0	0
Br···Br	2	6	2	0	4	0	1	2	2	0
Br···O	0	4	0	2	2	0	0	0	1	0

[a]: The bond lengths in DBA-I are measured based on the tentative structural model.

2) STM simulation of the structures DBA·Na-II, DBA·Cs-I and -II.

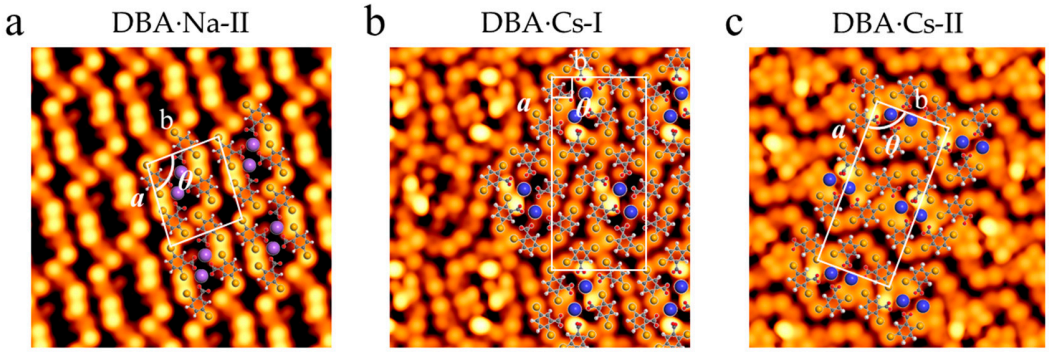

Figure S1. STM simulation of DBA·Na-II, DBA·Cs-I and DBA·Cs-II. Simulated STM images are covered with the corresponding atomic structural models. The white frames show the unit cells used in DFT calculations. The parameters of the unit cells (*a*, *b* and *θ*) are (a) 1.80 nm, 1.60 nm, 94°; (b) 4.04 nm, 2.00 nm, 90°; and (**c**) 3.54 nm, 1.61 nm, 90.4°. The energy range for STM simulations is from −1.0 eV to the Fermi level, which is comparable with the bias voltages in the STM experiments (−1.2 ~ −0.5 V).

3) The reversible structural conversion of DBA·Cs-I and -II.

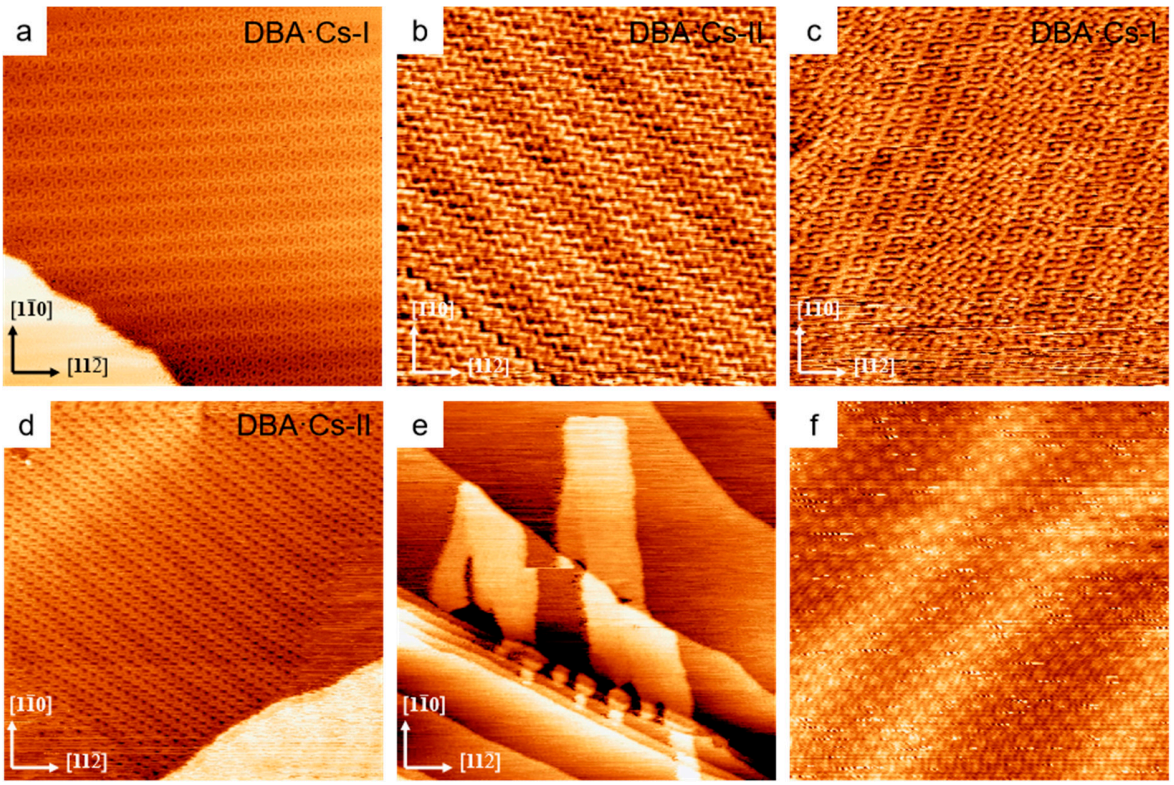

Figure S2. STM results of the reversible structural conversion of DBA·Cs-I and -II. (a) The pure phase of DBA·Cs-I after a codeposition of DBA (0.6 ML) with CsCl (0.16 ML) (50 × 50 nm; U = −1.2 V, I = 200 pA). (b) An STM image of the sample acquired after a post-deposition of CsCl (0.09 ML) (28 × 28nm; U = −1.2 V, I = 50 pA). (c) An STM overview of the sample after a post-deposition of DBA (0.3 ML) (30 × 30 nm; U = −2.6 V, I = 200 pA). (d) An STM overview of the sample after a 450 K-annealing (62 × 62 nm; U = −1.2 V, I = 50 pA). (e) A typical CsCl bilayer structure on Au(111) (300 × 300 nm; U = −0.6 V, I = 50 pA). (f) The atomic-resolution of the CsCl bilayer (10 × 10 nm; U = −1.6 V, I =50 pA), measuring the lattice constant of 4.8 Å. 1 ML of DBA refers to a full coverage of the DBA-I structure on the surface. 1 ML of CsCl refers to a full coverage of the CsCl bilayer on the surface.