Supplementary Information for

Fabrication of 2D Extended CoCrystal on Au(111) Surface via I···$O_{aldehyde}$ Halogen Bond

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1. Experimental Section

2,2'-bipyridyl-5,5'-dialdehyde (BPyDA), 4,4"-p-terphenyldicarboxaldehyde (TPDA), and 1,4-diiodotetrafluorobenzene (DITFB) were purchased from Alfa Aesar and were used as received. STM experiments were performed on ultra-high vacuum scanning tunneling microscope (UHV-STM) (Unisoku Co., Ltd., Japan). The pressure of the preparation chamber and the STM chamber is about 2×10^{-10} Torr and 8×10^{-11} Torr respectively. The Au(111) single crystal was purchased from Mateck Company (Germany). Before deposition of the molecular adlayer, the Au(111) single crystal was cleaned by cycling Ar^+ sputtering and annealing. A self-made tantalum boats (The tantalum foil was purchased from Alfa Aesar.) was used as simple evaporator for evaporation of the molecules. The molecular adlayer was deposited on cold Au(111) surface whose temperature is about 130 K. All STM images were recorded at 78 K under constant current model and shown without further process except for flatten. The tunneling conditions were shown in the figure caption. All of the structural models are built in Material studio and optimized using the Forcite package based on the universal force field.

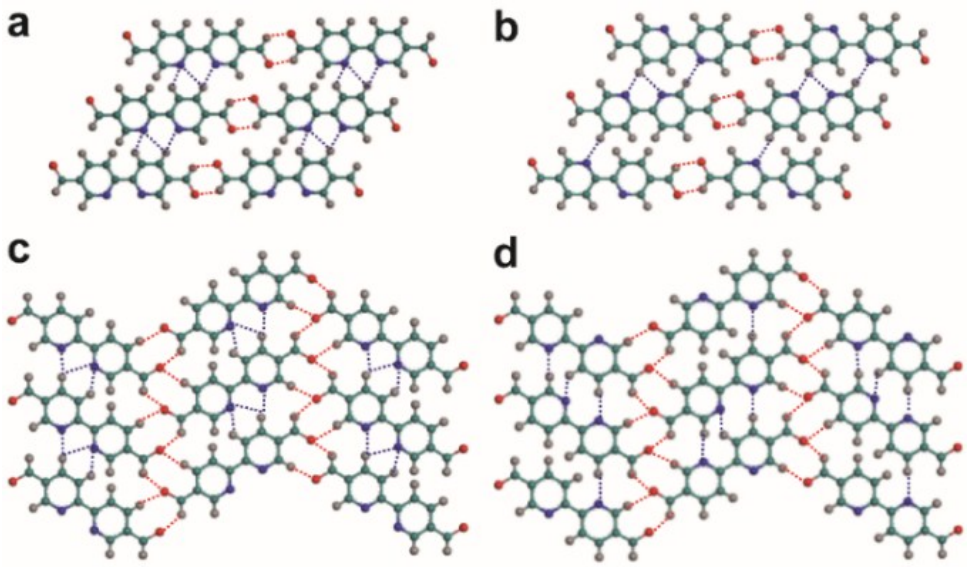

Figure S1. Possible molecular models of structure Ⅰ (a, b) and structure Ⅱ (c, d) in the BPyDA adlayer. In Fig. S1a and S1c, all of the BPyDA molecules adopt cis-configuration. In Fig. S1b and Fig. S1d, the trans-BPyDA and cis-BPyDA arrange alternatively within the molecular row.

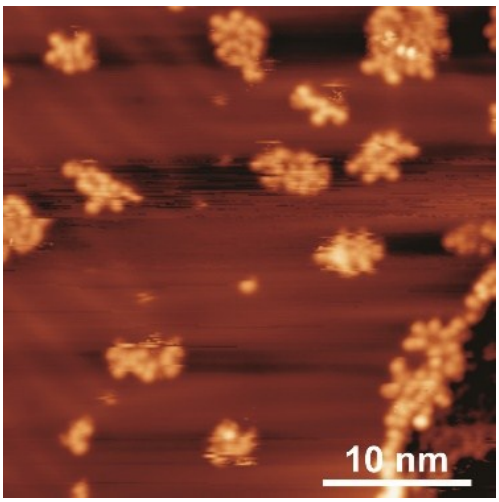

Figure S2. STM image of the disordered aggregations of DITFB deposited on cold Au(111) surface (about 130 K). Tunneling conditions: V_{bias} = 200 mV, I = 30 pA.

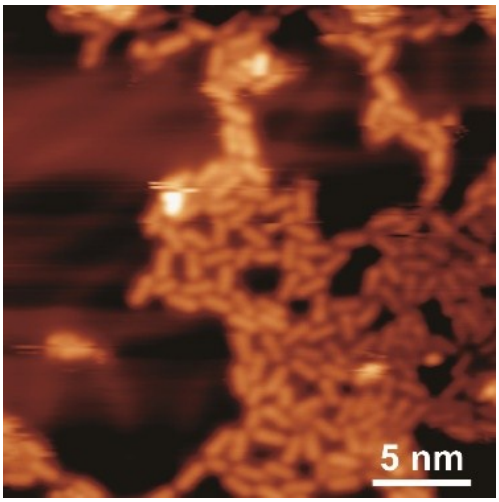

Figure S3. STM image of the TPDA adlayer deposited on cold Au(111) surface (about 130 K). Tunneling conditions: V_{bias} = 1000 mV, I = 30 pA.

Table 1. Summary of the 2D crystallization of the aldehyde compounds and their mixing behaviour with DITFB on Au(111) surface.

Building blocks	2D crystal[a]	Unit cell parameters			Intermolecular interactions	
		a (nm)	b (nm)	α (°)	within the row	between the rows
BPyDA		1.4 ± 0.1	0.7 ± 0.1	60 ± 2	N···H–C	C–H···$O_{aldehyde}$
		2.4 ± 0.1	0.7 ± 0.1	90 ± 2	N···H–C	C–H···$O_{aldehyde}$
BPyDA + DITFB		2.3± 0.1	0.7 ± 0.1	55 ± 2	N···H–C F···H–C F···F	I···$O_{aldehyde}$
TPDA	Disordered aggregations	–	–	–	–	–
TPDA + DITFB		2.7 ± 0.1	1.4 ± 0.1	75 ± 2	F···H–C	I···$O_{aldehyde}$

[a] The orange sticks represent the ditopic aldehyde compounds, and the green sticks represent DITFB.