Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Dipole-moment-induced supramolecular assembly of a donor–acceptor-type molecule on a metal surface and in a crystal

W. Nakanishi,[1] Y. Matsushita,[2] M. Takeuchi,[1,3] K. Sagisaka[4]

[1]Molecular Design and Function Group, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 3065-0047, Japan

Email: NAKANISHI.Waka@nims.go.jp

[2]Research Network and Facility Services Division, National Institute for Materials Science (NIMS) 1-2-1 Sengen, Tsukuba, Ibaraki 3065-0047, Japan

[3]Department of Materials Science and Engineering, Faculty of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8577, Japan

[4]Research Center for Advanced Measurement and Characterization, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

Email: SAGISAKA.Keisuke@nims.go.jp

Contents

1. DFT calculation

IBN was optimized at the level of B3LYP/6-31G (d, p) in vacuum.

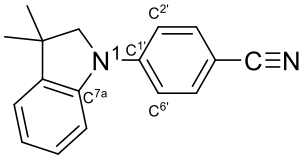

Table S1. Torsion angles ϕ (°) of IBN

	$\lvert\phi_1\rvert$	$\lvert\phi_2\rvert$	Average
Torsion angle	25.0	27.4	26.2

ϕ_1: C^{7a}-N^1-$C^{1'}$-$C^{2'}$; ϕ_2: C^{7a}-N^1-$C^{1'}$-$C^{6'}$

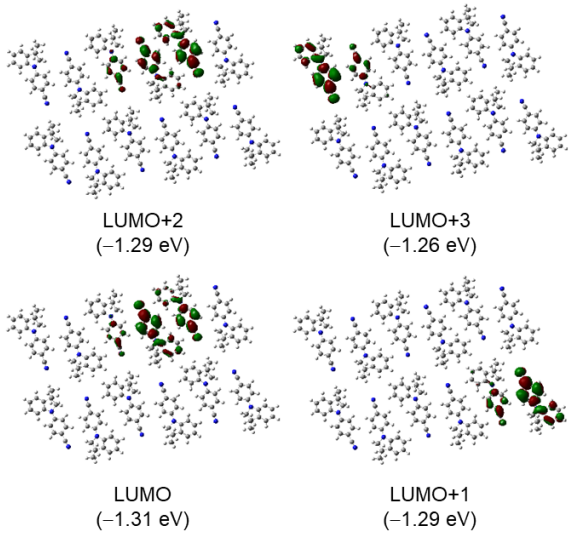

Figure S1. LUMO and higher order molecular orbitals of 12 IBN molecules which have been optimized on the Au(111) surface.

2. X-ray Crystallography

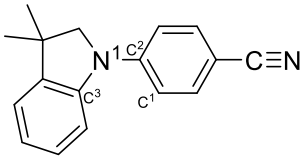

Table S2. Torsion angles ϕ (°) of IBN

	$\lvert\phi_1\rvert$	$\lvert\phi_2\rvert$
IBN 1 (red)	29.2	31.6
IBN 2 (yellow)	30.1	31.5
IBN 3 (green)	23.7	25.6
IBN 4 (blue)	31.1	33.5

ϕ_1: C^{7a}-N^1-$C^{1'}$-$C^{2'}$; ϕ_2: C^{7a}-N^1-$C^{1'}$-$C^{6'}$

(Average = 29.5°)

Colors in brackets are related to the colors in Figure 1(a).

Table S3. Distances (Å) of molecules in anti-parallel pair.

	π... π^1	CN...NC^2
IBN 1 (red)	3.93	3.67
IBN 2 (yellow)	3.93	3.66
IBN 3 (green)	3.88	3.62
IBN 4 (blue)	3.95	3.69

[1] Distance between centroids of cyanobenzene rings in an anti-parallel pair (Average = 3.92 Å).

[2] Distance between CNs (non-bonding C and N/N and C) in anti-parallel pair (Average = 3.66 Å).

Colors in brackets are related to the colors in Figure 1.

3. STM Images

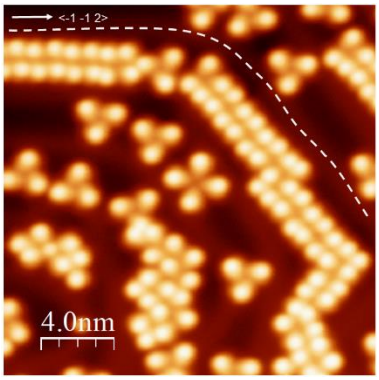

Figure S2. STM image of a liner assembly of IBN on the Au (111). A dashed line is drawn along one of the herringbone patterns. The density of IBN in the image is 0.34 IBN/nm^2. V_s = +1.0 V, I = 10 pA, T = 4.5 K, Image size: 20 × 20 nm^2.

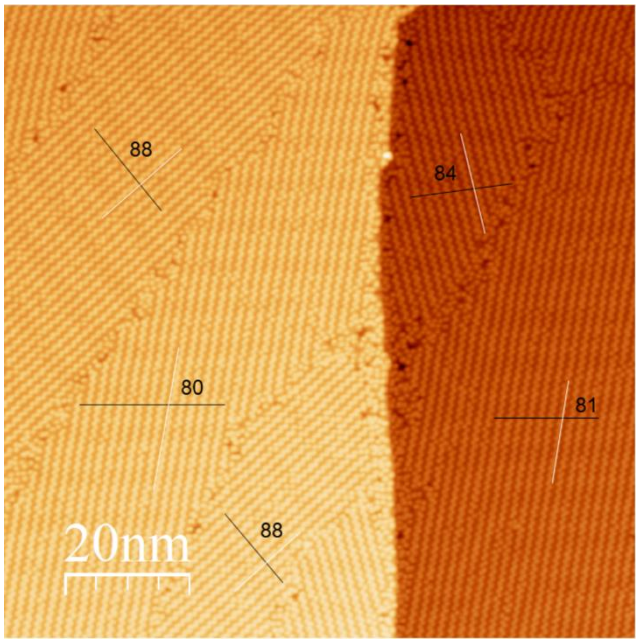

Figure S3. STM image of packed assembly of IBN on the Au(111) (the same as in Figure 2(e). The herringbone reconstruction is visible through the IBN molecules. Black lines denote the orientations of the herringbone patterns in <$\bar{1}\,\bar{1}$ 2> directions and white lines denote the orientations of a grove between two zigzag alignment of IBN. Average angles between black and white lines is 84 ± 4°.

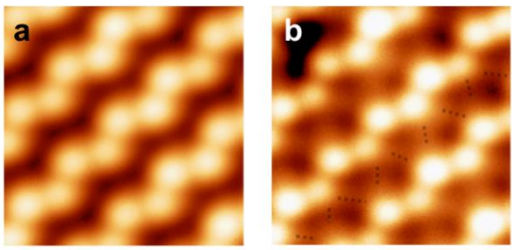

Figure S4. STM images of densely packed IBN on the Au(111) surface. Imaging conditions: (a) V_s = +1.0 V, (b) V_s = +2.8 V, (a), (b) I = 10 pA, T = 4.5 K. Image size: 5 × 5 nm^2. (b) Dotted lines denote a part of lines observed at the high vias voltage (V_s = +2.8 V).

4. MM Calculations

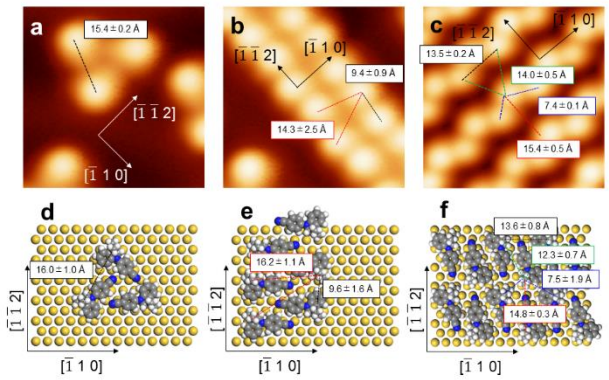

Figure S5. (a)-(c) STM images of self-assembled IBNs on the Au(111) surface as shown in Fig. 3. The distances denoted in the images are average distance (experimental) between the brightest spots of each IBN corresponding to the methyl group. (d)-(f) Structures of (d) trimer, (e) liner, and (f) packed assembly of IBN on an Au(111) surface optimized in MM calculations, the same as in Fig 3. The distances denoted are average distances (simulated) between the methyl groups pointing up. The dotted lines shown in a, b, and c correspond to those with the same color in d, e, and f respectively. Imaging conditions: (a)-(c) $V_s = +1.0$ V, $I = 10$ pA, $T = 4.5$ K. Image size: 5×5 nm^2.