Polymorphic Porous Supramolecular Networks Mediated by Halogen Bonds on Ag(111)

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Experimental Section

All STM experiments were performed using a home-built STM housed in an ultrahigh vacuum(UHV) chamber with a base pressure below 7×10^{-11} torr. An Ag(111) single crystal was cleaned by several cycles of Ne-ion sputtering and annealing at 800 K. The surface cleanliness was checked using an STM observation of a flat Ag(111) surface. Commercially available 4,4''-Dibromo-p-terphenyl (DBTP) (Tokyo Chemical Industry, Japan) was thermally evaporated onto the Ag(111) surface at submonolayer coverage from an alumina-coated crucible, keeping the substrate temperature at 150K. The DBTP molecules were degassed for several hours prior to deposition. The molecular flux was about 0.11 /nm^2 · min. An average molecular density was 0.33 per nm^2. The prepared sample was transferred to the STM and cooled down to 80K. The Pt-Rh alloy tip was used as an STM probe.

Theoretical Calculations

We performed density-functional calculations using the VASP code [1, 2]. Interaction between ions and electrons was approximated by the projector-augmented wave (PAW) potential.[3] A generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was used to describe the exchange correlations between electrons.[4] The energy cutoff for the plane wave basis was set to 500 eV. The lattice parameters and molecular geometries were very similar to those based on the PBE functional. To describe non-bonding interactions between the molecules, especially of the van der Waals type, an empirical correction scheme proposed by Grimme et al. was adopted.[5] The energy and electrostatic potential for the isolated molecules were obtained using a $25 \times 15 \times 10$ Å^3 supercell. A simulation cell containing two (square network), four (rectangular network), and five (hexagonal network) DBTP molecules was adopted to describe the periodic structure, respectively. The height of the simulation box perpendicular to the molecule plane was fixed at 10 Å, while the lateral cell parameters were optimized such that the residual stress was reduced under 1 kbar.

Electrostatic potential

The electrostatic potential were calculated using DFT methods based on the generalized gradient approximation (GGA)[4] and mapped on the isosurfaces of 0.003 e Bohr^{-3}. H atoms (in red) have positive electrostatic potential, and Br atoms have both positive and negative (in blue) regions with cylindrical symmetry about the axis of the covalent bond.

Summarized computed interatomic distances and angles

(a)
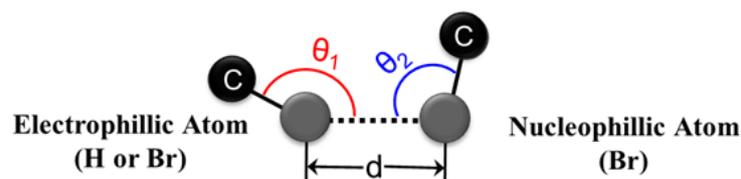
(b)

Intermolecular Bonding	Bonding distance (nm)							Sum of the Van der Waals Radii (nm)
	Square	Rectangle	Hexagonal					
H...Br	0.30	0.29	0.34	0.34	0.34	0.40	0.48	0.30
Br...Br	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37

(c)

Intermolecular Bonding	Bonding Angle (°)							Median of θ in references (°)	
	Square	Rectangle	Hexagonal						
H...Br	150	151	143	143	147	143	144	150	θ_1
	121	121	115	115	135	114	124	120	θ_2
Br...Br	172	173	165	165	167	165	177	180	θ_1
	98	97	105	105	118	106	135	90	θ_2

Figure S1. (a) Definition of the intermolecular bond distance, angle θ_1 around an electrophillic atom, and angle θ_2 around a nucleophillic atom. (b) Summarized Computed interatomic distances for Br···H and Br···Br bonds. The sums of the van der Waals radii are marked in right side of table. (c) Computed θ_1 (red) and θ_2 (blue) for two intermolecular bonds in square, rectangular, and hexagonal structures and corresponding medians from references.

  Computed θ_1 and θ_2 are shown for each bond in Fig. S1(c). The values of θ_1 around electrophillic atoms (Br and H) were close to 180° and 150°, respectively, and the values of θ_2 around nucleophillic atoms (Br) were close to 120° and 90° in Br···H and Br···Br, respectively. These results are consistent with reported medians [6-12] and are explained by the distribution of electrostatic potentials at the H and Br atoms. However, in the three-molecule windmill, the observed θ_2 angles of two Br···Br bonds are significantly larger than 120°. Two DBTP molecules of three-molecule windmills have 90° angle such that the third molecule has no choice but to make the larger 120° angles.

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