

# Controllable Density of Atomic Bromine in a Two-Dimensional Hydrogen Bond Network

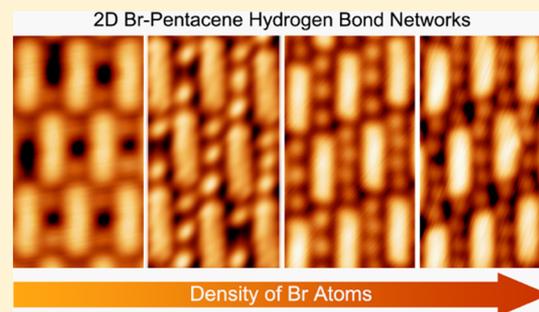
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## Supporting Information

**ABSTRACT:** Using atomic bromine (Br) and pentacene molecules, we successfully constructed and characterized a large-scale Br atom-mediated two-dimensional (2D) organic network on a Ag(111) surface by combining molecular beam epitaxy with scanning tunneling microscopy. The Br atoms form  $-C-H\cdots Br$  hydrogen bonds with pentacene molecules in the network, and the number of Br atoms among pentacene molecules can be tuned from one to five by increasing the pressure or exposure time of hydrogen bromide (HBr) gas. In addition, all of the Br atoms of five 2D organic networks fill themselves in the position of maximum number of hydrogen bonds.



## INTRODUCTION

Nanofabrication based on molecular self-assembly is a key aspect to realizing supramolecular applications in the field of nanoscience and nanotechnology.<sup>1–5</sup> Generally, self-assembly processes rely on the spontaneous and reversible organization of molecular units into ordered structures by noncovalent interactions and can be externally propelled or self-propelled.<sup>6–8</sup> Recently, adatom-mediated self-assembled organic molecule monolayers by either single metal atoms or nonmetal atoms have attracted great interest because of their novel effect on self-assembly processes.<sup>9–13</sup> Although metal atoms can coordinate the self-assembly of monolayers efficiently, the strong metallicity of metal atoms induces electronic states near the Fermi level of the whole system, thus changing the semiconducting properties of two-dimensional (2D) supramolecular architectures.<sup>14–16</sup> In contrast, atomic nonmetal-mediated molecular self-assembly has been proven to be an efficacious way to construct 2D networks and maintain their intrinsic properties owing to the weak electrostatic interaction between nonmetal atoms and organic molecules.<sup>17</sup>

Our previous work has reported on the construction of large-scale, high-quality, and highly ordered 2D chiral networks by Br atoms and  $C_{26}H_{18}$  (DPA) molecules on a Ag(111) surface.<sup>17</sup> However, the networks constructed previously contained a saturation of Br atoms. Studies of 2D hydrogen bond networks with various densities of bromine are lacking. Here, we report a controllable density of atomic Br in hydrogen bond networks formed by Br atoms and pentacene molecules on Ag(111) surfaces at room temperature. All of the Br atoms distribute themselves periodically in the network with

the maximum number of  $-C-H\cdots Br$  hydrogen bonds. By increasing the amount of Br atoms, we achieve a variable density of Br atoms (from one to five per unit cell) among the pentacene molecules.

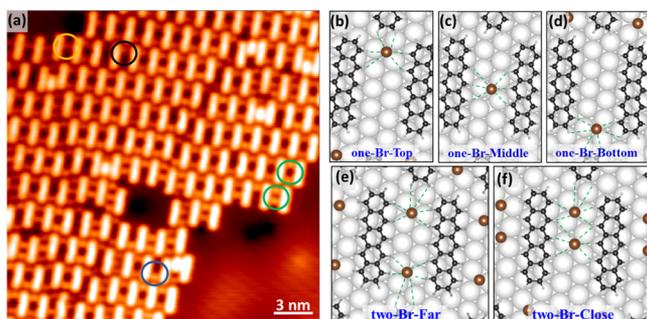
## RESULTS AND DISCUSSION

After the deposition of Br atoms (HBr exposure for 30 min and partial pressure for  $5.0 \times 10^{-6}$  mbar) and pentacene molecules on the Ag(111) surface, we observed a large-scale self-assembled 2D network (Figure 1a). Atomic bromine was introduced by thermal decomposition of HBr gas molecules through a hot filament while the sample surface faced toward the filament at a distance of 5 mm.<sup>17</sup> In Figure 1a, the pentacene molecules are distinguished as rod structures with lengths of 1.38 nm, which is consistent with the theoretic value.<sup>18</sup> Besides the pentacene molecules, there exist many regularly arranged bright dots, which can be assigned to Br atoms originating from the dissociation of HBr gas, according to our previous work.<sup>17</sup> In addition, we find that there are two main Br atom configurations in the whole network. One configuration involves a single Br atom bridging pentacene molecules, as marked by the black circle in Figure 1a. The second configuration involves two Br atoms bridging pentacene molecules, as marked by a green circle in Figure 1a. Interestingly, there appear to be three different configurations when a single Br atom is involved, as marked by the black, blue, and yellow circles in Figure 1a. To

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**Figure 1.** STM image and graphic of pentacene molecules and Br atoms on the Ag(111) surface. Conjunction of two pentacene molecules can be ascribed to variable numbers of Br atoms. (a) STM image showing one and two Br atoms bridging pentacene molecules. Yellow, black, and blue circles mark the three different configurations of a one-Br case. The green circles mark the two different configurations of a two-Br case. (b–d) and (e,f) DFT-optimized structures of one-Br atom and two-Br atom configurations, respectively. All Br atoms reside on the hollow sites. Possible hydrogen bonds between Br and H are marked by the green dashed lines. Scanning parameters:  $V_s = -1.0$  V,  $I_t = 3.0$  nA.

investigate the adsorption structure and adsorption energy of the network, we performed density functional theory (DFT) calculations. Figure 1b–d shows three optimized adsorption structures of a one-Br case on the Ag(111) surface. The result indicates that all Br atoms in the configuration sit on hollow sites of the Ag(111) surface. The distances between the Br atoms and the nearest H atoms in Figure 1b–d are approximately 2.42–2.86 Å, (see Figure S1 for details). According to our previous work, the electronegativity difference between Br and H results in an attractive electrostatic interaction between negatively charged Br atoms and positively charged H atoms, that is,  $-C-H\cdots Br$  hydrogen bonds.<sup>17</sup> More importantly, each Br atom in the Br–pentacene 2D network also forms six hydrogen bonds with pentacene molecules, and six hydrogen bonds are the maximum for the structure. The adsorption energy of three configurations is also calculated, as shown in Table 1. The small difference in energy for the three

**Table 1.** Calculated Adsorption Energies for the One-Br case. The Energy of a One-Br-Top Case is Set to Zero for Better Contrast

configurations	energy difference (meV)
one-Br-top	0
one-Br-middle	−1.47
one-Br-bottom	7.97

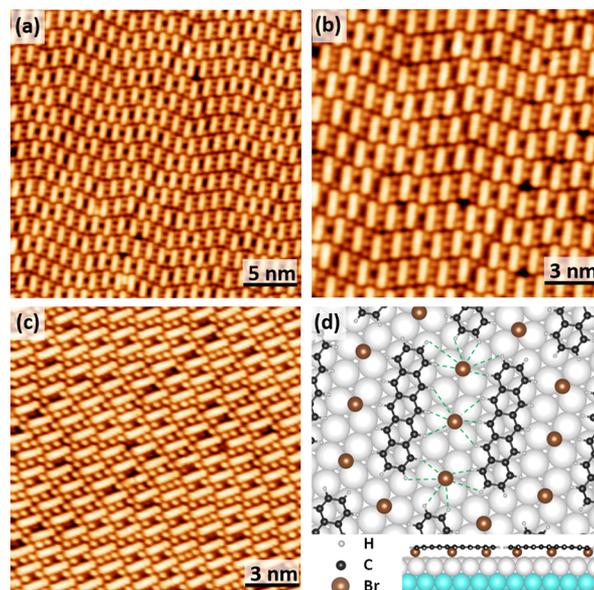
configurations indicates that they can coexist together in the Br–pentacene 2D network, which fits well with the scanning tunneling microscopy (STM) results (Figure 1a). In the case of a two-Br scenario, there are two configurations, as marked by two green circles in Figure 1a. The optimized adsorption models are shown in Figure 1e,f. Similar to the one-Br case, all of the Br atoms sit on the hollow sites of the Ag(111) surface, forming the maximum number of hydrogen bonds with pentacene molecules. The corresponding calculated adsorption energy is shown in Table 2, confirming the possibility of their coexistence.

By increasing the deposition of Br atoms (HBr exposure for 30 min and partial pressure for  $5.0 \times 10^{-6}$  mbar) on the basis

**Table 2.** Calculated Adsorption Energies for the Two-Br case. The Energy of Two-Br-Far Case is Set to Zero for Better Contrast

configurations	energy difference (meV)
two-Br-far	0
two-Br-close	10.34

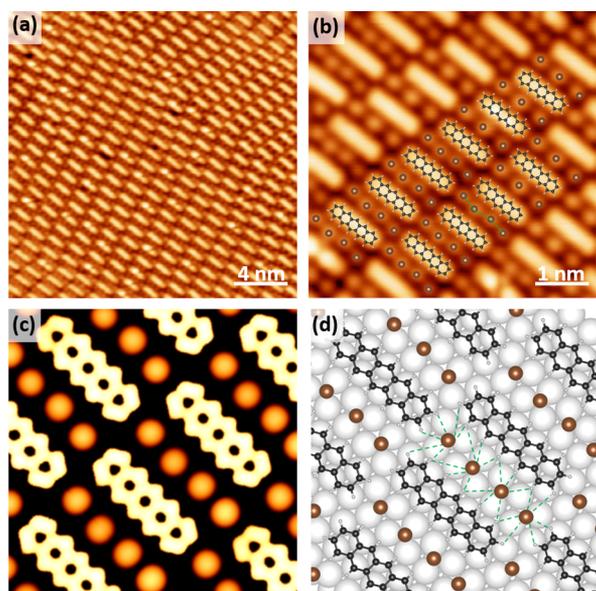
of Figure 1, we can obtain another large-scale and highly ordered 2D organic network, as shown in Figure 2a. Figure



**Figure 2.** STM images and graphic of Br–pentacene networks with two and three Br atoms. (a) Large-area STM image showing two and three Br atoms among pentacene molecules. (b,c) Close-up STM images of two equivalent orientations. (d) Top view and side view of DFT-optimized adsorption configurations. Possible hydrogen bonds between Br and H are marked by the green dashed lines. Scanning parameters: (a)  $V_s = -1.0$  V,  $I_t = 2.0$  nA; (b)  $V_s = -0.1$  V,  $I_t = 3$  nA; and (c)  $V_s = -0.1$  V,  $I_t = 3$  nA.

2b,c shows the high-resolution STM images of two equivalent orientations of a Br–pentacene 2D organic network. In this network, the number of Br atoms among pentacene molecules can increase to two and three. The three Br atoms in the three-Br case have an equally spaced arrangement of  $5.78 \pm 0.05$  Å, as shown in the line profile across the black dashed line in Figure S2, which is very close to 2 times Ag(111) lattice parameter ( $a_{Ag}$ ), that is,  $2 \times a_{Ag}$  ( $2.90$  Å) =  $5.80$  Å. To gain insight into the highly ordered self-assembled 2D organic network, we carried out DFT calculations. Figure 2d shows the optimized adsorption geometry of pentacene molecules and Br atoms on a Ag(111) surface. In the top view (Figure 2d), all Br atoms sit on the hollow sites of Ag(111) surface, and the distance between three equally spaced Br atoms is  $5.80$  Å, which agrees with the experimental results. Furthermore, similar to the one-Br and two-Br cases, each Br atom in the three-Br case forms six hydrogen bonds, as marked by green dashed lines in Figure 2d (3 bromine atoms and 18 hydrogen atoms are involved). With the formation of 18 hydrogen bonds, the three-Br case seems to be the most stable and only one configuration is observed. For the two-Br case, we observed the same adsorption configurations, as shown in Figure 1.

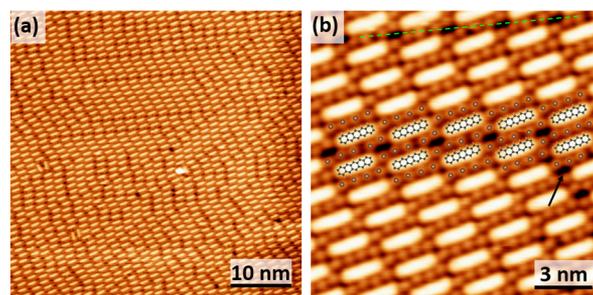
Because the highly ordered self-assembled 2D organic network is stabilized by  $-C-H\cdots Br$  hydrogen bonds, we further explored the effect of larger Br atom density on the 2D network. Figure 3a shows a large-scale and highly ordered 2D



**Figure 3.** STM images and graphic of Br–pentacene 2D networks with three and four Br atoms. (a) Large-area STM image of the four-Br case. (b) Magnified STM image of (a) superimposed with a proposed model (both the three-Br case and four-Br cases are superposed; the brown dots represent Br atoms). (c) Simulated STM image of a four-Br 2D network. (d) DFT-optimized adsorption configuration of (b), where only the four-Br case is taken into consideration. The possible hydrogen bonds between Br and H are marked by the green dashed lines. Scanning parameters: (a)  $V_s = -0.1$  V,  $I_t = 3.0$  nA and (b)  $V_s = -0.1$  V,  $I_t = 2.0$  nA.

network after depositing Br atoms (HBr exposure for 30 min and partial pressure for  $5.0 \times 10^{-6}$  mbar) on the as-obtained sample in Figure 2. A close-up STM image (Figure 3b) shows that there are three and four Br atoms among pentacene molecules. The four Br atoms follow a distorted line arrangement instead of the line arrangement observed in Figure 2, whereas the three-Br case still follows a linear arrangement, as illustrated by the overlaid atomic model in Figure 3b. The distance between two Br atoms in the four-Br case is  $1.186 \pm 0.05$  Å, and the corresponding line profile across the green line is shown in Figure S3. Figure 3d shows the DFT-optimized adsorption configuration of a four-Br network, revealing a distorted linear arrangement of four Br atoms with a distance of 1.184 Å (Figure S3), fitting well with the experimental data (1.186 Å). On the basis of Figure 3d, we obtained a simulated STM image (Figure 3c), which agrees very well with the experimental STM image (Figure 3b). In addition, we found that the occurrence of three or four Br atoms is random in the entire sample. In the four-Br case, all 14 hydrogen atoms in pentacene molecules ( $C_{22}H_{14}$ ) form hydrogen bonds with Br atoms to stabilize the 2D network.<sup>19,20</sup>

When further adding Br atoms (HBr exposure for 30 min and partial pressure for  $5.0 \times 10^{-6}$  mbar) to the 2D network, we observed a different 2D hydrogen bond network, as shown in Figure 4. Besides the four-Br case, five Br atoms appeared among the pentacene molecules. However, due to the fact that



**Figure 4.** STM images of a Br–pentacene 2D network with four and five Br atoms. (a) Large-area STM image of four-Br and five-Br atom cases. The linear distribution of the “black hole” with different orientations can be found. (b) Close-up STM image showing the “black hole”-containing area; the proposed model was superposed along the linear “black hole” area. The dashed green line shows the linear arrangement of the gaps. Scanning parameters: (a)  $V_s = -0.5$  V,  $I_t = 0.9$  nA and (b)  $V_s = -0.5$  V,  $I_t = 1.9$  nA.

the interaction between the Br atoms and Ag(111) substrate is stronger than that between the pentacene molecules and Ag(111) substrate, which can be confirmed by calculated adsorption energies on the Ag(111) substrate ( $-2.05$  eV for one Br atom and  $-1.33$  eV for one pentacene molecule, as shown in Table S2), addition of the fifth Br atom will make the Br–pentacene networks lack registry with the Ag(111) substrate and induce compressive stress to the whole networks. As a result, the gaps among pentacene molecules appear to release the “fifth Br atom” defect strain (indicated by the black arrow in Figure 4b). The gaps themselves form a linear “black hole,” as indicated by the dashed green line in Figure 4b. The fifth Br atoms also form hydrogen bonds with pentacene molecules to stabilize the 2D network. When further adding Br atoms (HBr exposure for 30 min and partial pressure for  $5.0 \times 10^{-6}$  mbar) to the 2D network in Figure 4, we observed a distinct structure with Br atom clusters separated by pentacene molecules, as shown in Figure S4. We attribute this to the fact that more Br atoms will make the 2D network form more gaps because of the strong interaction between the Br atoms and Ag(111) substrate, thus destabilizing the 2D network and forming Br atoms clusters. Therefore, to construct a large-scale and high-quality atomic Br-mediated 2D pentacene network, a reasonable density of Br atoms is crucial.

We have fabricated five types of 2D Br–pentacene networks (one-Br to five-Br) on a Ag(111) surface. Table S1 shows the density of Br atoms for each Br–pentacene network. A larger density of Br atoms means more hydrogen bonds can form, resulting in a relatively more stable 2D network. Therefore, the ranking of network stability is five-Br > four-Br > three-Br > two-Br > one-Br. In this way, we can modulate the network structural changes, from a metastable structure to a stable structure, as well as the density of Br atoms by depositing extra bromine atoms; that is to say, we can selectively control the formation of atomic Br-mediated 2D Br–pentacene networks with different densities of Br atoms.

## CONCLUSIONS

In conclusion, we successfully constructed five large-scale and highly ordered Br atom-mediated 2D organic networks on a Ag(111) surface. Those networks are stabilized by  $-C-H\cdots Br$  hydrogen bonds, and all Br atoms present prefer sites with the maximum number of hydrogen bonds. More importantly, the density of Br atoms in the Br–pentacene configurations can be

well controlled by adjusting the pressure or exposure time of HBr gas during network formation. This work provides a prototype for controllable construction of 2D nonmetal-mediated hydrogen bond networks.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b08964.

Full experimental and calculation details; measured distances in Br–pentacene 2D networks; density of Br atoms for different Br–pentacene networks; STM image for further adding Br atoms in the five-Br case; and calculated adsorption energies for Br atoms and pentacene molecules on Ag(111) substrate (PDF)

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Ciesielski, A.; Palma, C.-A.; Bonini, M.; Samori, P. Towards Supramolecular Engineering of Functional Nanomaterials: Pre-Programming Multi-Component 2D Self-Assembly at Solid-Liquid Interfaces. *Adv. Mater.* **2010**, *22*, 3506–3520.
- (2) Gao, H.-J.; Gao, L. Scanning Tunneling Microscopy of Functional Nanostructures on Solid Surfaces: Manipulation, Self-Assembly, and Applications. *Prog. Surf. Sci.* **2010**, *85*, 28–91.
- (3) Green, J. E.; Choi, J. W.; Boukai, A.; Bunimovich, Y.; Johnston-Halperin, E.; DeIonno, E.; Luo, Y.; Sheriff, B. A.; Xu, K.; Shin, Y. S.; et al. A 160-Kilobit Molecular Electronic Memory Patterned at 10<sup>11</sup> Bits per Square Centimetre. *Nature* **2007**, *445*, 414–417.
- (4) Rosei, F.; Schunack, M.; Naitoh, Y.; Jiang, P.; Gourdon, A.; Laegsgaard, E.; Stensgaard, L.; Joachim, C.; Besenbacher, F. Properties of Large Organic Molecules on Metal Surfaces. *Prog. Surf. Sci.* **2003**, *71*, 95–146.
- (5) Smith, W. F. Self-assembly is ready to roll. *Nat. Nanotechnol.* **2007**, *2*, 77–78.
- (6) Cook, T. R.; Zheng, Y.-R.; Stang, P. J. Metal-Organic Frameworks and Self-Assembled Supramolecular Coordination Complexes: Comparing and Contrasting the Design, Synthesis, and

Functionality of Metal-Organic Materials. *Chem. Rev.* **2013**, *113*, 734–777.

(7) Langner, A.; Tait, S. L.; Lin, N.; Rajadurai, C.; Ruben, M.; Kern, K. Self-Recognition and Self-Selection in Multicomponent Supramolecular Coordination Networks on Surfaces. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 17927–17930.

(8) Stepanow, S.; Lingenfelder, M.; Dmitriev, A.; Spillmann, H.; Delvigne, E.; Lin, N.; Deng, X.; Cai, C.; Barth, J. V.; Kern, K. Steering Molecular Organization and Host-Guest Interactions Using Two-Dimensional Nanoporous Coordination Systems. *Nat. Mater.* **2004**, *3*, 229–233.

(9) Basagni, A.; Ferrighi, L.; Cattelan, M.; Nicolas, L.; Handrup, K.; Vaghi, L.; Papagni, A.; Sedona, F.; Valentin, C. D.; Agnoli, S.; et al. On-Surface Photo-Dissociation of C-Br Bonds: towards Room Temperature Ullmann Coupling. *Chem. Commun.* **2015**, *51*, 12593–12596.

(10) Čechal, J.; Kley, C. S.; Kumagai, T.; Schramm, F.; Ruben, M.; Stepanow, S.; Kern, K. Convergent and Divergent Two-Dimensional Coordination Networks Formed through Substrate-Activated or Quenched Alkynyl Ligation. *Chem. Commun.* **2014**, *50*, 9973–9976.

(11) Langner, A.; Tait, S. L.; Lin, N.; Chandrasekar, R.; Ruben, M.; Kern, K. Ordering and Stabilization of Metal-Organic Coordination Chains by Hierarchical Assembly through Hydrogen Bonding at a Surface. *Angew. Chem., Int. Ed.* **2008**, *47*, 8835–8838.

(12) Schlickum, U.; Klappenberger, F.; Decker, R.; Zoppellaro, G.; Klyatskaya, S.; Ruben, M.; Kern, K.; Brune, H.; Barth, J. V. Surface-Confinement Metal–Organic Nanostructures from Co-Directed Assembly of Linear Terphenyl-dicarbonitrile Linkers on Ag(111). *J. Phys. Chem. C* **2010**, *114*, 15602–15606.

(13) Silly, F. Selecting Two-Dimensional Halogen-Halogen Bonded Self-Assembled 1,3,5-Tris(4-iodophenyl)benzene Porous Nanoarchitectures at the Solid-Liquid Interface. *J. Phys. Chem. C* **2013**, *117*, 20244–20249.

(14) Henningsen, N.; Rurali, R.; Limbach, C.; Drost, R.; Pascual, J. I.; Franke, K. J. Site-Dependent Coordination Bonding in Self-Assembled Metal–Organic Networks. *J. Phys. Chem. Lett.* **2011**, *2*, 55–61.

(15) Hu, X.; Zha, B.; Wu, Y.; Miao, X.; Deng, W. Effects of the Position and Number of Bromine Substituents on the Concentration-Mediated 2D Self-Assembly of Phenanthrene Derivatives. *Phys. Chem. Chem. Phys.* **2016**, *18*, 7208–7215.

(16) Yasuda, S.; Furuya, A.; Murakoshi, K. Control of a Two-Dimensional Molecular Structure by Cooperative Halogen and Hydrogen Bonds. *RSC Adv.* **2014**, *4*, 58567–58572.

(17) Lu, J.; Bao, D.-L.; Dong, H.; Qian, K.; Zhang, S.; Liu, J.; Zhang, Y.; Lin, X.; Du, S.-X.; Hu, W.; et al. Construction of Two-Dimensional Chiral Networks through Atomic Bromine on Surfaces. *J. Phys. Chem. Lett.* **2017**, *8*, 326–331.

(18) Endres, R. G.; Fong, C. Y.; Yang, L. H.; Witte, G.; Wöll, C. Structural and Electronic Properties of Pentacene Molecule and Molecular Pentacene Solid. *Comput. Mater. Sci.* **2004**, *29*, 362–370.

(19) Chung, K.-H.; Kim, H.; Jang, W. J.; Yoon, J. K.; Kahng, S.-J.; Lee, J.; Han, S. Molecular Multistate Systems Formed in Two-Dimensional Porous Networks on Ag(111). *J. Phys. Chem. C* **2013**, *117*, 302–306.

(20) Chung, K.-H.; Park, J.; Kim, K. Y.; Yoon, J. K.; Kim, H.; Han, S.; Kahng, S.-J. Polymorphic Porous Supramolecular Networks Mediated by Halogen Bonds on Ag(111). *Chem. Commun.* **2011**, *47*, 11492–11494.