Extended Halogen Bonding between Fully Fluorinated Aromatic Molecules

Shigeki Kawai,†,‡ Ali Sadeghi,†,§ Feng Xu,† Lifen Peng,† Akihiro Orita,† Junzo Otera,‡ Stefan Goedecker,† and Ernst Meyer†

†Department of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland, ‡PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi 332-0012, Japan, §Department of Physics, Shahid Beheshti University, Evin, 19839 Tehran, Iran, and †Department of Applied Chemistry, Okayama University of Science, 1-1 Ridai-cho, Kita-ku, Okayama 700-0005, Japan

ABSTRACT Halogen bonding is a noncovalent interaction where an electrophilic cap on a halogen atom, the so-called σ-hole, attracts a nucleophilic site on an adjacent molecule. The polarizability of halogens relates to the strength of the σ-hole, and accordingly the halogen–halogen distance becomes shorter in the order of Cl, Br, and I. Fully fluoro-substituted aromatic molecules, on the contrary, are generally believed not to form halogen bonds due to the absence of a σ-hole. Here, we study atomic-scale in-plane F–F contacts with high-resolution force microscopy. Our ab initio calculations show that the attractive dispersion forces can overcome the electrostatic repulsion between the fluorine atoms, while the anisotropic distribution of the negative electrostatic potential leads the directional bond and even changes the gap. The coexistence of these two competing forces results in the formation of a “windmill” structure, containing three C–F···F bonds among neighboring molecules. While the σ-hole is absent, the scheme of the C–F···F bonding has a high similarity to halogen bonding.

KEYWORDS: intermolecular interaction, chemical structure, F–F contact, halogen bonding, atomic force microscopy
of the $\sigma$-hole. Since the belt of the halogen atom still has a negative electrostatic potential, the $\sigma$-hole can also bind to the belt of the halogen atom in an adjacent molecule, forming the halogen···halogen bond. However, fluorine has the strongest electronegativity and a low polarizability, so that it usually has no $\sigma$-hole. The $\sigma$-hole is strongly affected by the electron-attracting power, and so, for instance, the cyano moiety behind the C–F bond in FCN$^{23}$ and the oxygen in hypofluorite$^{24}$ can induce a $\sigma$-hole. However, if the electron extraction is not strong enough, F has an intrinsic negative electrostatic potential. Simple fluoro-substituted hydrocarbons, such as C$_6$F$_6$ and CF$_4$, are categorized as the latter case. Thus, the halogen bond in such molecules is rarely seen in analyses of crystal structure databases and the stronger C···F···$\pi$ interaction generally dominates.$^{25,26}$ Therefore, analyses of bulk crystal structures cannot reveal the F···F contact. Since, however, the freedom of molecules on a surface is restricted, the in-plane intermolecular interaction at the F···F contact can readily be investigated.

Here, we present clear evidence that an anisotropically distributed negative electrostatic potential around a fluorine atom in a fluoro-substituted aromatic molecule together with a large dispersion force induces a highly directional bonding and gives rise to a well-ordered supramolecular structure on a Ag(111) surface at low temperature. The angle and distance of the bond conformation are directly observed by high-resolution atomic force microscopy (AFM). Furthermore, density functional theory (DFT) calculations show quantitatively the strengths of the competing electrostatic and dispersion forces. This bond has a high similarity to halogen···halogen bonding.

RESULTS AND DISCUSSION

In our experiment, nonsubstituted phenyleneethynylene (bis(4-phenylethynyl)phenylethynylene, BPEPE, Figure 1a) and fully fluoro-substituted phenyleneethynylene (bis(2,3,5,6-tetrafluoro-4-(2,3,4,5,6-pentafluorophenylethynyl)phenylethynylene, BPEPE-F18, Figure 1b) were deposited on a clean Ag(111) surface. Their conformations were analyzed

Figure 1. (a, b) Chemical structures of phenyleneethynlenes (BPEPE) and the fully fluoro-substituted phenyleneethynlenes molecule (BPEPE-F18). (c) STM topography of the Ag(111) surface deposited only with BPEPE (0.25 ML). (d) Frequency shift $\Delta f$ map in a close view. (e) STM topography of the surface with BPEPE (0.12 ML) and a lesser amount of BPEPE-F18 (0.08 ML). (f) Corresponding $\Delta f$ map, measured at constant height. (g) STM topography of the surface with BPEPE (0.35 ML) and an excess amount of BPEPE-F18 (0.50 ML). (h) Corresponding $\Delta f$ map, measured at constant height. Measurement parameters: $V_{tip} = 200$ mV and $I = 10$ pA in (c) and $V_{tip} = 200$ mV and $I = 2$ pA in (e) and (g) for STM measurements. $V_{tip} = 0$ mV and $A = 60$ pm for all AFM measurements.
with scanning tunneling microscopy (STM) and AFM at 4.8 K under ultrahigh-vacuum condition.

(Co-)deposition of Non- and Fluoro-substituted Molecules. In order to inspect the intermolecular interactions in the hydrogen–hydrogen contact, we first deposited the nonsubstituted phenyleneethynylene (BPEPE) on a clean Ag(111) surface. In the case of a submonolayer, the molecules have no ordered structure and are individually and randomly adsorbed along six equivalent directions of the Ag(111) surface (Figure 1c). This is due to the fact that the repulsive electrostatic interaction between two molecules is dominating as previously observed with hexa-peri-hexabenzocoronene on Au(111) and free-base porphine on Ag(111). Since long-range molecular orbitals usually affect the STM contrast, a detailed chemical structure can be hard to achieve. Therefore, in order to perform high-resolution imaging, we used AFM, which senses the total electron density of the sample surface. With a CO-terminated tip close to the surface, the chemical structure of molecules can even directly be resolved in the frequency shift map of an oscillating force sensor.

We attempted to image the chemical structure of BPEPE with AFM, but it was laterally moved by the tip–sample interaction before the tip approaches the repulsive region (Figure 1d). This result indicates the small corrugation amplitude of potential on the Ag(111) surface. Therefore, resolving the chemical structure was not possible.

Consequently, we co-deposited excess BPEPE and, to a lesser extent, BPEPE-F18. Figure 1d shows the STM topography. At the left-hand side, the residual BPEPEs are adsorbed individually, as observed in Figure 1c. We observed a well-ordered supramolecular structure at the right-hand side. The brighter and darker contrasts correspond to BPEPE-F18 and BPEPE, respectively. The two kinds of molecules are alternatively aligned, and the weak C–F⋯F–H hydrogen bonding (attractive interaction) is responsible for the assembly. Since the supramolecular structure increases the stability of the individual molecule, the molecules were no longer manipulated by the CO-terminated tip with a conventional tip–sample separation for imaging chemical structures of molecules (Figure 1f). Due to the effect of the tilting CO molecule, the benzenes of BPEPE are observed as distorted and larger. In contrast, due to the different extents of their π-electrons, the fluorobenzenes are observed smaller and brighter. Although the actual positions of the atomic cores in the molecule cannot be imaged directly, the atomic-scale arrangements of BPEPE and BPEPE-F18 are clearly observed. In addition to the C–F⋯F–H hydrogen bonding, C–F⋯F–C bondings are also observed as indicated with arrows. Next, we co-deposited BPEPE and excess BPEPE-F18. A well-ordered molecular film was again observed (Figure 1g), but in this case, no residual BPEPE nor BPEPE-F18 was observed on the terrace because all BPEPE and BPEPE-F18 are incorporated into the self-assembly by C–F⋯F–H hydrogen bonding. Further, the number of C–F⋯F–C bondings in the supramolecular structure increases (Figure 1h), yet it is not conclusive evidence for whether C–F⋯F–C bondings increase the stability of the supramolecular structure or not.

Apparent Intermolecular Bond. We observed an interesting bond-like feature in the C–F⋯F–C contact. Zhang et al. reported in 2013 that the hydrogen bondings can be resolved by a CO-functionalized tip of AFM, similar to the intramolecular covalent bonds. The explanation put forward in their article is that the partially covalent nature of the hydrogen bond increases the electron density, and hence the bond site has a stronger Pauli repulsion. More recently Hapala et al. claimed that the increased electron density is not sufficient for the contrast; rather the landscape of the potential energy in the adjacent atoms is responsible. Thus, they claimed that sharp apparent intermolecular bonds should not be interpreted as true hydrogen bonds. Very recently, the conclusive study to support the argument of Hapala et al. was presented via the experimental and theoretical studies of hydrogen bonding. Nevertheless, since our F⋯F intermolecular interaction is purely of electrostatic nature, the increased electron density is absent. For this reason, it is ideal to examine the topic. Figure 2a shows the conformations of BPEPE and BPEPE-F18 (Figure 1h repeated for convenience). In order to emphasize the contrast, we applied Laplace filtering to the image (Figure 2b). The different orders of intramolecular bond are clearly visible. In addition, we observe the intermolecular bonds in the F⋯F contact. Figure 2c and d show the magnified views of the Δf and corresponding Laplace filtered image, respectively. Although no shared electron exists in the C–F⋯F–C contact (as calculated in Figure 4b), apparent intermolecular bonds are clearly observed. This is an indirect evidence that the observed bond-like feature does not relate to any intramolecular bond, but rather the tilting of the CO molecule on the tip by the landscape of the potential, as reported by Hapala et al. and Hämäläinen et al.

Atomic-Scale Imaging of Organic Fluorine Contact. In order to investigate the C–F⋯F–C interaction, we deposited only BPEPE-F18. In contrast to BPEPE, a well-ordered supramolecular assembly was formed with BPEPE-F18 (Figure 3a), indicating that C–F⋯F–C bonding observed in Figure 1h is attractive. The structure grew in the [231] direction, and its domain extended on the terrace of Ag(111) up to 100 nm × 100 nm. The inset shows the close-up view of the molecules. The four observed protrusions in the STM topography correspond to the benzene rings; the two rings at the ends appear higher than the central two at an applied bias voltage of −200 mV.
Figure 3b shows the frequency shift map of the film, obtained with a CO tip. In contrast to the STM topography, all four benzene rings appear with almost the same contrast, which implies that the molecule lies flat on the surface. The molecular axis is an almost perfect straight line, even though the phenyleneethynylene array is somewhat flexible. Therefore, the difference in the apparent height in the STM topography (Figure 3a) is associated with the orbitals localized on the pentafluorobenzene moieties (Supporting Information). Since no other structure of assembly was observed, this conformation would be energetically the most stable. Our interest was immediately focused on the intermolecular interactions. In order to obtain a higher signal-to-noise ratio, the image was mesh-averaged over the unit cell. Then, the area indicated by a square box in Figure 3b was magnified (Figure 3c). The hexagonal benzene rings and the C–F bonds are clearly observed.

As described above, since the apparent intermolecular bond is subject to the complex imaging mechanism (tilting CO tip and the potential landscape), it is not trivial to assign the bond length and angle directly from the observed AFM image. Further, the effect of the CO tip tilt is sensitive enough to detect the bond order and extended electronic cloud. In other words, the actual positions of atomic cores cannot be measured directly from the AFM image. Therefore, we first assigned the chemical structure of the molecule with the known dimension of BPEPE-F18 (Figure 1b, length: 20.60 Å, C–F: 1.34 Å, and C–F: 1.39 Å) to the observed molecule and then analyzed the bond length and angle. As indicated with broken white lines (Figure 3d), each C–F bond points to a fluorine atom.
in the adjacent molecule, which results in highly directional C–F⋯F bonds (∼180 deg). Furthermore, the angles between the C–F⋯F bonds are approximately 120 deg, resulting in the formation of an inverted “windmill” structure. All F–F contacts in Figure 3d have almost the same bond lengths and angles. Similar directional bondings in the X⋯C0 contacts (X = Cl, Br, and I) have been reported, where the lengths of the halogen bonds are shorter than the sum of the van der Waals (vdW) radii due to the halogen halogen bonding. However, in the present case, the measured F⋯F bond length (broken white lines) is at least 300 pm, i.e., slightly larger than twice the vdW radius of a fluorine atom (i.e., 294 pm), indicating the coexistence of a repulsive interaction. This large distance is a clear evidence that this bond differs from the typical halogen halogen bonding observed before. A similarly packed structure was also observed with tetrafluoromethane (Supporting Information).

Electrostatic Potential Analysis. First, we attempted to understand the mechanism of the directional C–F⋯F bonding, based on the commonly used electrostatic potential analysis. Figure 4a shows the calculated molecular electrostatic potential (MEP) of BPEPE-F18 on a constant electron density surface (0.001 eBohr⁻³). Because of the high electronegativity of fluorine, BPEPE-F18 has a positive MEP at the center of benzenes, enabling it to serve as an electron-accepting material such as an n-type semiconductor, while on the outer shell of BPEPE-F18 the MEP turns negative. In a detailed inspection (right panel of Figure 4a), the MEP on the fluorine atom varies and the cap has the least negative value. However, since no positive part appears (no σ-hole), the electrostatic interaction in the F–F contact is always repulsive. Therefore, the analysis in terms of the electrostatic potential is not sufficient to explain the observed directional C–F⋯F bonding in contrast to the case of other heavier halogen atoms such as Cl and Br (Supporting Information).

Next, we performed a series of extensive periodic DFT calculations, including both the molecules and the substrate. We used the PBE functional together with empirical vdW corrections, which is widely used for this kind of analysis (for details, see the Methods section). Figure 4b depicts the relaxed conformation of BPEPE-F18 in the molecular film on the Ag(111) surface. Since the conformation of the supramolecular structure is commensurate with the substrate lattice, the centers of the pentafluorobenzene moieties are
The rotation angle \( \theta = 0 \) corresponds to the shown configuration, i.e., C–F···F along a straight line. The inset illustrates that the \( \pi \)-electronic density surface (0.005 au) remains angle-independent over carbon atoms in both C6H6 (left) and C6F6 (right).

Analysis of Directional Halogen Bond. To investigate the directionality of the bond in detail, two isolated hexafluorobenzenes (HFBs) are considered. After the relaxation of the isolated HFBs, one of the HFBs is rigidly rotated around its normal axis (the C6 axis) while the other one is kept at the equilibrium distance (see inset of Figure 5a), the vdW energy varies only slightly. This can be explained in terms of the very low polarizability of fluorine, while the electron clouds made from the carbon \( \pi \)-orbitals of each HFB are polarizable and therefore have strong vdW interactions. Since the spatial distribution of the \( \pi \)-cloud is nearly independent of the rotation angle (see inset of Figure 5b), the vdW energy changes only marginally when \( \theta \) is varied. On this basis, we argue that the deep minimum of the energy versus \( \theta \) curve, i.e., the high directionality of the C–F···F bond, originates from the F–F electrostatic interactions. Likewise in the commonly known X–X halogen bonding (X = Cl, Br), the energy minimum occurs when the three atoms in C–F···F are positioned on a straight line, i.e., when the cap of one F points toward the belt of the other one. Note that the strong electron attraction of the halogenated carbon atom, as evidenced by the less negative potential at the cap of fluorine, plays a crucial role, whereas the intrinsically strong electrostatic repulsion between two spherically symmetric F\(^{-}\) ions prevents bonding (the Coulomb interaction is repulsive).
repulsion between two F⁻ separated by 3.1 Å is 108 kcal/mol (4.7 eV); from DFT it is 99 kcal/mol (4.3 eV). The influence of the less negative cap can be seen via the different C–F⋯F bond lengths. The electron attraction of the halogenated carbon atom along the molecular axis is stronger than others due to the imbalanced charge distribution, so that the F cap has the least negative potential compared to the other F caps, as shown in Figure 4a. Thus, the length of the C–F⋯F bond along the molecular axis is the smallest due to the smaller electrostatic repulsion. In order to investigate this influence, the geometrical details of the molecular structure, based on our DFT calculations, is presented in Figure 6. We found that the C–F bonds vary, depending on the molecular site, while the C–C bond length is almost constant (139 pm). This is due to the fact that the electron attraction by the halogenated carbon atom is tuned by the imbalance of the charge distribution in the pentafluorobenzene moiety. This strong electron attraction of the C–F bond along the molecular axis results in the least negative potential at the F cap (Supporting Information). Therefore, the electrostatic repulsion in the C–F⋯F contact along the molecular axis becomes smaller, so that the bond length (307 pm) becomes longer compared to the others (321 pm).

This delicate balance of competing electrostatic and vdW forces gives rise to the C–F⋯F bond. This bond has a high similarity to the halogen–halogen bonding but is weaker than the others since the σ-hole is absent. Further, through the inspection of Figures 1 and 3, the C–F⋯F⋯C bond is weaker than the weak C–F⋯H hydrogen bond; otherwise a condensed BPEPE-F18 domain would have appeared in Figure 1g. This observation is in good agreement with the calculation. The total cohesive energy in two hexafluorobenzenes is −1.06 kcal/mol (−46 meV, Figure 5b). This contact is composed of two C–F⋯F⋯C halogen bondings and so that each energy is approximately −0.53 kcal/mol (−23 meV), which is half of that of the C–F⋯H⋯C hydrogen bonding (−1.08 kcal/mol (−47 meV)). Thus, C–F⋯H⋯C hydrogen bonding is more preferential in the compounds as found in the crystal analysis.46 The existence of the C–F⋯F bond can experimentally also be deduced from the fact that the nonsubstituted molecules do not self-assemble because the dispersion interaction is not strong enough to overcome the electrostatic repulsion.

Finally, we address the charge transfer between organic molecules and a metallic substrate, which can induce significant change on the electrostatic interaction between adjacent molecules. To this aim, the Bader definition41 was employed to determine the splitting border between the molecules and substrate. The charges, transferred to each of the non-
F-substituted molecules, turn out to be $-0.12$ and $-0.63$ e, respectively. Since vdW interactions are directly related to the molecular polarizability, the extra charge would strengthen or weaken the vdW interactions at the end. Therefore, we calculated the molecular polarizability for both neutral and charged free molecules along the molecule axis ($\alpha_{xx}$). We obtained $\alpha_{xx} = 1432$ and $\alpha_{xx} = 1585$ for the nonsubstituted molecule and neutral F-substituted molecules in atomic units, respectively. Once the above-mentioned fractional charges are added to the molecules, those values increase by 28% and 32%, respectively. Therefore, one expects that the vdW attraction becomes even stronger than that predicted by the empirical method of Grimme for neutral molecules, which helps to condense BPEPE-F18. However, the increased vdW forces is still not strong enough to condense BPEPE as previously discussed in refs 27 and 28.

CONCLUSION

In summary, we reported an atomic-scale fluorine homocountact of fully fluoro-substituted aromatic molecules, which induces a two-dimensional supramolecular structure on the Ag(111) surface. The complex chemical structure is directly revealed by high-resolution atomic force microscopy, clearly showing that the directional bonding exists in an organic fluorine contact. The dispersion force takes the major part in the attraction, but the driving force of the directional bonding is due to the anisotropically distributed electrostatic potential around the fluorine atoms. The geometrical conformations of the molecule on the substrate, obtained by dispersion-corrected density functional calculations, are in perfect agreement with the experimentally observed structures. Furthermore, the contributions from each of the two competing interactions to the cohesive energy of the layer were calculated. Our system illustrates well that dispersion forces can play a decisive role in the formation of ordered supramolecular structures. Our interpretation can be applied to the previously observed fluoro-substituted molecular film by scanning tunneling microscopy with submolecular resolution and the in-plane molecular interaction of $\pi$-stacked perfluoropentacene. The reported C–F···F bonding has a high similarity to halogen—halogen bonding in terms of the directionality and influence of the anisotropically distributed electrostatic potential on F and can be categorized as halogen–halogen bonding.

METHODS

AFM Measurements. All measurements were performed with a commercially available Omicron low-temperature STM/AFM system, operating in ultrahigh vacuum at 4.8 K. We used a tuning fork with a chemically etched tungsten tip as a force sensor. The resonance frequency and the mechanical quality factor are 24,803.5 Hz and 18,648, respectively. The high stiffness of 1800 N/m realizes a stable operation with a small amplitude of 60 pm, which was calibrated by the current control method. The small-amplitude operation enhances the detection sensitivity to the short-range tip–sample interaction, and hence the spatial resolution can be improved. The frequency shift, caused by the tip–sample interaction, was detected with a commercially available digital phase-locked loop (Nanonis: OC-4 and Zurich Instruments: HF2-Li and HF2-PLL). In order to avoid cross-talk between the STM and AFM detection lines, the tungsten tip was electrically decoupled to the detection line of the tuning fork sensor oscillation with a separate Au wire. In the measurement, no significant correlation between the energy dissipation and tunneling current signals was detected. For the STM measurement, the bias voltage was applied to the tip while the sample was electrically grounded. The tip apex was ex situ sharpened by milling with a focused ion beam. The tip radius was less than 10 nm. A clean silver tip was in situ prepared by indenting the Ag sample surface and applying a pulse bias voltage between the tip and sample several times. For AFM, the tip apex was terminated with a CO molecule, which was picked up from the surface. A clean Ag(111) surface was in situ prepared by repeated cycles of standard Ar$^+$ sputtering ($3 \times 10^{-6}$ mbar, 1000 eV, and 15 min) and annealing at 480 °C. The typical width of the Ag(111) terrace was more than 200 nm. In this experiment, we used bis(2,3,5,6-tetrafluoro-4-(2,3,4,5,6-pentafluorophenylethynyl)phenylethylene, BPEPE-F18) and bis(4-phenylethynyl)phenylethylene (BPEPE). BPEPE-F18 and BPEPE were deposited on the surfaces from crucibles of Krudsen cell, heated at 145 °C after degassing at 100 °C for several days. The substrate was kept at room temperature. Measured images were analyzed using the WSxM software.

Theoretical Calculations. The periodic $ab$ initio calculations were carried out within the generalized gradient approximation of DFT using the VASP code. For the molecules, we used the BigDFT code using a wavelet basis set with a grid spacing of 0.17 Bohr and HGH pseudopotential. As valence electrons of C, F, and Ag, we considered the $2s^22p^2$, $2s^22p^5$, and $3s^14d^{10}$ electrons, respectively. The wave functions were expanded using a plane-wave basis with a kinetic energy cutoff of 400 eV. The core electrons were eliminated using the projector-augmented wave (PAW) method. Dispersion effects were treated with the DFT-D2 method of Grimme, where the C$_2$ parameters were set to 24.67, 1.75, 0.75, and 0.14 and R$_0$ to 1.639, 1.452, 1.287, and 1.001 for Ag, C, F, and H atoms, respectively. The Ag(111) surface was modeled by a four-layer slab of 112 atoms in total. An orthorhombic supercell (0.775 x 2.68 x 2.2 nm$^3$) was used; the lateral edges (along [011] and [110]) coincide with the lattice vectors of the molecular layer, while the third one (along [111]) was chosen such that a vacuum not thinner than 1.2 nm separates the repeated images of the Ag slab. Two atomic layers at the bottom were kept frozen in their bulk position, while all other atoms were allowed to relax until the force on each atom became smaller than 0.02 eV/Å. The reciprocal space was sampled using a 4 x 2 x 1 k-mesh. For visualizing the atomic structures, V_Sim and VESTA were used.

Conflict of Interest: The authors declare no competing financial interest.

Acknowledgment: This work was supported in part by the Japan Science and Technology Agency (JST) “Precursory Research for Embryonic Science and Technology (PRESTO)” for the project “Molecular technology and creation of new function”, by the Swiss National Science Foundation, by the NCCR “Nanoscale Science” of the Swiss National Science Foundation, by a matching fund subsidy for private universities from the Ministry of Education, Culture, Sports, Science and Technology, Japan, by the Japan Society for the Promotion of Science (JSPS) through its “Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program)”, and by...


25. Hamalainen, S. K.; van der Heijden, N.; van der Lit, J.; den Hartog, S.; Lijferhof, P.; Swart, I. Intermolecular Contrast in...

Supplementary Informations for :
Extended Halogen Bonding between Fully
Fluorinated Aromatic Molecules

Shigeki Kawai,*†‡ Ali Sadeghi,† Feng Xu,¶ Lifen Peng,¶ Akihiro Orita,¶ Junzo Otera,¶ Stefan Goedecker,§ and Ernst Meyer§

Department of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland., PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Japan, Department of Applied Chemistry, Okayama University of Science, 1-1 Ridai-cho, Kita-ku, Okayama, 700-0005, Japan., and Department of Physics, University of Basel, Klingbergstrasse 82, 4056 Basel, Switzerland

E-mail: shigeki.kawai@unibas.ch
Phone: +41 (0)61 267 3730. Fax: +41 (0)61 267 3784

Scanning tunneling microscopy image contrast

In the STM topography shown in Fig. 3a of the main text, two terminal rings of the molecule appear higher than the central two in the middle. In contrast, both AFM image and the calculated geometry with DFT reveal that the molecule is almost flat on the substrate. This

*To whom correspondence should be addressed
†Department of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland.
‡PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Japan
¶Department of Applied Chemistry, Okayama University of Science, 1-1 Ridai-cho, Kita-ku, Okayama, 700-0005, Japan.
§Department of Physics, University of Basel, Klingbergstrasse 82, 4056 Basel, Switzerland
discrepancy is discussed here.

AFM senses the total electron density and hence the observed frequency shift map directly corresponds to the chemical structure of the probed sample. Contrary, STM senses the local density of the electronic states (LDOS) close to the Fermi level of the sample. To simulate the STM image with the tip biased at -200 mV, we plot the LDOS within an energy window of width 200 meV from the Fermi energy for the most favored relaxed configuration (Fig. S1). In the terminal rings whose adsorption sites are different from those of the central rings, the LDOS is extended largely over all benzene carbons, while in the central rings, the LDOS is localized at carbons connecting to the acetylene moieties. This calculation explains the apparent height difference seen in the STM topography in Fig. 3a.

Figure S1: Simulated STM image corresponding to experimental result shown in Fig. 1b. The energetically most favored configuration along with the same parameters as in experiment are used. See text for details.

Tetrafluoromethane

Tetrafluoromethanes (CF₄) were deposited on a clean Ag(111) surface, which stayed in the microscope at 4.8 K. The room temperature CF₄ gas was introduced via the needle gas valve and the partial pressure of the microscope chamber was approximately 5×10⁻⁸ mbar. Then, the radiation shutter of the microscope was open for 1 min. The temperature of the sample
was increased up to 8 K by the radiation. After the temperature of the sample reached to 4.8 K, the surface was scanned. We observed a well-ordered structure on the surface (Fig. S2). This is another evidence that fluoro-substituted molecules can be assembled by the similar scheme to the halogen bonding.

![STM topography](image)

Figure S2: STM topography of the Ag(111) surface partially covered with tetrafluoromethane. Measurement parameters: $V_{\text{tip}} = -200$ mV and $I = 2$ pA.

**Molecular electrostatic potential**

We show the molecular electrostatic potentials (MEP) calculated on a constant electron density surface (0.001 e/Bohr³), for BPEPE and halogen-substituted phenyleneethynlenes ($C_{30}X_{18}$, X=F, Cl, and Br) in Fig. S3. The MEP has positive contributions from the set of nuclei $Z_i$, located at positions $R_i$, and a negative contribution from the electrons of density $n(r)$, and is given in atomic units by

$$V(r) = \sum_{i}^{n_{\text{atoms}}} \frac{Z_i}{|R_i - r|} - \int \frac{n(r')dr'}{|r' - r|}. \quad (1)$$

BPEPE has negative MEP at the center, corresponding to an expanded $\pi$-system, and positive MEP on the outer shell (Fig. S3a). Because of the positive MEP on hydrogens, the H-H contact underwent repulsive electrostatic interaction as observed in Fig. 1c. BPEPE-F18 has
an inversed electron density distribution due to the electron-withdrawing property of fluorine (Fig. S3b) and acts as an electron-accepting material.\textsuperscript{3,4} As discussed in the main text, the MEP on the fluorine atom varies and the cap has the least negative value. However, since no positive part appears (no $\sigma$-hole), the electrostatic interaction in F-F contact is repulsive. While Cl- and Br-substituted phenyleneethynlenes have never been synthesized, we plot their MEP maps for comparison (Fig. S3c,d). $\sigma$-holes appear both on the Cl and Br atom surfaces and their intensity increases by the size of the halogen atom, which is consistent with the previous calculation for CF\textsubscript{3}X.\textsuperscript{5} Therefore, the electrostatic interaction between the $\sigma$-hole and the belt can explain the intermolecular interaction.

Figure S3: (a) Calculated molecular electrostatic potentials for BPEPE and (b) BPEPE-X18 with X=F, (c) X=Cl, and (d) X=Br. The molecular surface is taken as the iso-density (0.001 e/Bohr\textsuperscript{3}) surface.

**Increased negative electrostatic potential by contact**

Recent theoretical studies reported that the polarization, induced by the intermolecular interaction in H\textsubscript{3}C-Cl $\cdots$ O=CH\textsubscript{2}\textsuperscript{6} and F\textsubscript{3}C-Cl $\cdots$ OH\textsubscript{2} contacts,\textsuperscript{7} is responsible for generating
the $\sigma$ hole of Cl, while Cl in the unperturbed molecule has a negative cap (no $\sigma$ hole). The resultant $\sigma$ hole induces the halogen bonding.

We investigate the influence of the polarization in the C-F···F-C contact. Figure S4 shows the top and side views of the molecular electrostatic potential of two hexafluorobenzene molecules in contact. The calculation was performed with the same method, describe in the main text for Fig. 5. We found that the cap of F becomes more negative due to the fact that the electrons are repelled from the negative potentials in the molecular contact. Thus, contrary to the C-Cl···O contact, the effect of the polarization is not dominant in our case.

![Image](b.png)

Figure S4: (a) Top view and (b) oblique view of calculated molecular electrostatic potentials for two hexafluorobenzene molecules in contact. The molecular surface is taken as the isodensity (0.001 e/Bohr$^3$) surface.

References


