

Supplementary Informations for :

Extended Halogen Bonding between Fully Fluorinated Aromatic Molecules

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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

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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 image¹ 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.

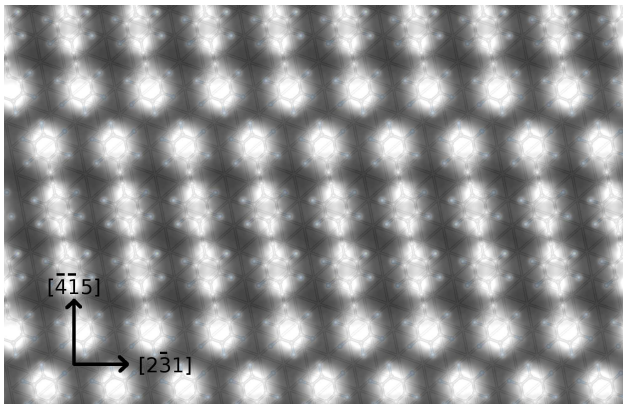


Figure S1: Simulated STM image corresponding to experimental result shown in Fig. 1b. The energetically most favored configuration along with the same parameters as in experiment are used. See text for details.

Tetrafluoromethane

Tetrafluoromethanes (CF_4) were deposited on a clean Ag(111) surface, which stayed in the microscope at 4.8 K. The room temperature CF_4 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.

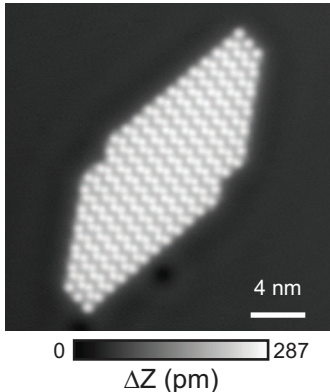


Figure S2: STM topography of the Ag(111) surface partially covered with tetrafluoromethane. Measurement parameters: $V_{\text{tip}} = -200$ mV and $I = 2$ pA.

Molecular electrostatic potential

We show the molecular electrostatic potentials (MEP) calculated on a constant electron density surface (0.001 e/Bohr^3),² for BPEPE and halogen-substituted phenyleneethynylenes ($\text{C}_{30}\text{X}_{18}$, $\text{X}=\text{F}$, Cl , and Br) in Fig. S3. The MEP has positive contributions from the set of nuclei Z_i , located at positions \mathbf{R}_i and a negative contribution from the electrons of density $n(\mathbf{r})$, and is given in atomic units by²

$$V(\mathbf{r}) = \sum_i^{n_{\text{atoms}}} \frac{Z_i}{|\mathbf{R}_i - \mathbf{r}|} - \int \frac{n(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|}. \quad (1)$$

BPEPE has negative MEP at the center, corresponding to an expanded π -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.^{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 σ -hole), the electrostatic interaction in F-F contact is repulsive. While Cl- and Br-substituted phenyleneethynylenes have never been synthesized, we plot their MEP maps for comparison (Fig. S3c,d). σ -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_3X .⁵ Therefore, the electrostatic interaction between the σ -hole and the belt can explain the intermolecular interaction.

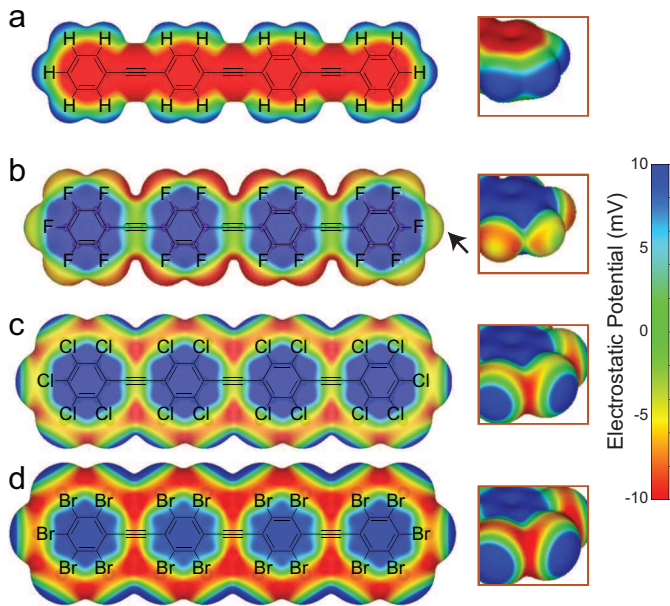


Figure S3: (a) Calculated molecular electrostatic potentials for BPEPE and (b) BPEPE-X18 with X=F, (c) X=Cl, and (d) X=Br. The molecular surface is taken as the iso-density ($0.001 \text{ e}/\text{Bohr}^3$) surface.

Increased negative electrostatic potential by contact

Recent theoretical studies reported that the polarization, induced by the intermolecular interaction in $\text{H}_3\text{C}-\text{Cl} \cdots \text{O}=\text{CH}_2$ ⁶ and $\text{F}_3\text{C}-\text{Cl} \cdots \text{OH}_2$ contacts,⁷ is responsible for generating

the σ hole of Cl, while Cl in the unperturbed molecule has a negative cap (no σ hole). The resultant σ hole induces the halogen bonding.

We investigate the influence of the polarization in the C-F \cdots 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 \cdots O contact, the effect of the polarization is not dominant in our case.

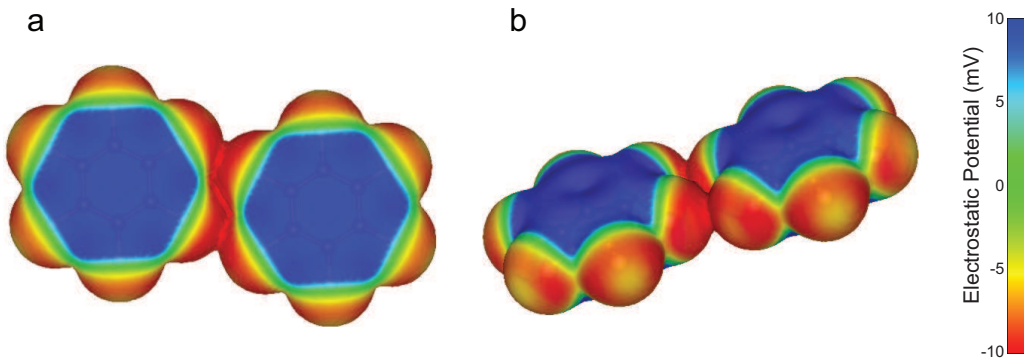


Figure S4: (a) Top view and (b) oblique view of calculated molecular electrostatic potentials for two hexafluorobenzene molecules in contact. The molecular surface is taken as the iso-density (0.001 e/Bohr^3) surface.

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