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Pinning-down molecules in their self-assemblies with multiple weak hydrogen bonds of $C - H \cdots F$ and $C - H \cdots N$

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ABSTRACT

Two-dimensional self-assemblies of four partially fluorinated molecules, 1.4-bis(2,6-difluoropyridin-4yl)benzene, 4,4'-bis(2,6-difluoropyridin-4-yl)-1,1'-biphenyl, 4,4'-bis(2,6-difluoropyridin-4-yl)-1,1':4', 1"-terphenyl and 4,4'-bis(2,6-difluoropyridin-3-yl)-1,1'-biphenyl, involving weak intermolecular C-H···F and C-H···N hydrogen bonds were systematically investigated on Au(111) with lowtemperature scanning tunneling microscopy. The inter-molecular connecting modes and binding sites were closely related to the backbones of the building blocks, i.e., the molecule length determines its binding sites with neighboring molecules in the assemblies while the attaching positions of the N and F atoms dictate its approaching and docking angles. The experimental results demonstrate that multiple weak hydrogen bonds such as $C - H \cdots F$ and $C - H \cdots N$ can be efficiently applied to tune the molecular orientations and the self-assembly structures accordingly.

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12 1. Introduction

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Self-assembled molecular architectures on metal surfaces have attracted great interest due to their structural ordering and abundance, and potential applications in the field of nanotechnology [1-3]. As one of the main driving forces among non-covalent bonding interactions, hydrogen bond (HB) has been extensively exploited to form various assembling patterns owing to its unique properties such as bonding strength, flexibility, directionality and selectivity [3–7]. Compared with their strong counterparts (7-8 kcal/mol) [8-10], weak HBs [11] are usually more flexible in bonding geometries which could be employed to control the orientations of the assembling molecules and hence ultimate assembling structures [12-14].

Weak HBs like $C = H \cdots O$ and $C = H \cdots N$ are frequently utilized to construct two-dimensional (2D) self-assemblies in the past [15–19]. Meanwhile, perfluoro-molecules such as copper hexadecafluorophthalocyanine (F₁₆CuPc), a potential molecular semiconductor serving as an electron acceptor in organic photovoltaic (OPV) devices [20-22] and as an n-type organic semiconducting material in light-emitting diode [23], have received substantial attention due to their extraordinary airstability. Besides the layer thickness, the packing pattern of the F₁₆CuPc molecules governed by weak intermolecular interactions including C-H...F HBs may have great influence in the performance of the OPV devices. In terms of the F₁₆CuPc self-assembly on metallic substrates [20-22], previous research normally focuses on its co-assembly with other p-type organic molecules to form molecular p-n junctions or donor-acceptor pairs [23,24].

While perfluoro-molecules have been generally adopted to prepare organic semiconducting self-assembled membranes [29-32], nano-arrays [33] and networks [34,35] at surfaces, partially fluorinated molecules are less studied in the past. In our previous report [15], we have successfully assembled a whole series of 2D molecular porous networks whose pores possess all possible rotational symmetry, i.e., 2-, 3-, 4- and 6-fold rotations, by using the same building blocks, 4,4'-bis(pyridin-4-yl)-1,1'biphenyl (BPBP) and trimesic acid (TMA). This is achieved by solely

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changing two physical parameters, substrate temperature and coverage ratio of TMA to BPBP. The driving force is the combined strong and weak HB networks formed between TMA and BPBP. Among all possible HBs, the weak ones such as C=O (TMA)···H—C (α - and β -H in the pyridyl group in BPBP) and N(pyridyl)···H—C (pyridyl) play an important role in tuning the final pore symmetry. Therefore, it would be very interesting to explore the assembling behavior of partially fluorinated BPBP derivatives upon substitutions of the α -H in pyridyl with F atoms. The replacing F atoms would accordingly change the acidity of their neighboring H atoms in the pyridyl groups. Such a motivation intrigues the present study of the self-assemblies of 1,4-bis(2,6-difluoropyridin-4-yl) benzene (BDFPB) and its derivatives which can form weak HBs like C—H···F and C—H···N.

As is well known, the structures of the molecular building blocks are of extreme importance in tailoring and engineering the molecular self-assemblies. To do this, several strategies including re-designing the molecular backbones [36–38], introducing additional functional groups [39–42] and changing the number and positions of the substituents [43–46] have been developed, aiming at precisely controlling the assembled architectures on the substrates.

To achieve tuning the 2D molecular self-assembly patterns in a controlled manner, the BPFBP molecule and its three derivatives such as 4,4'-bis(2,6-difluoropyridin-4-yl)-1,1'-biphenyl (BDFPBP), 4,4"-bis(2,6-difluoropyridin-3-yl)-1,1'-biphenyl (BDFPTP) and 4,4'-bis(2,6-difluoropyridin-3-yl)-1,1'-biphenyl (BDFP-3-BP) were deposited onto an atomically flat Au(111) substrate. Their corresponding self-assembly patterns were subsequently scrutinized in detail with scanning tunneling microscopy (STM), a powerful tool to unveiling surface molecular assembling structures at the sub-molecular level. A major experimental observation was that these molecules could be pinned down in their self-assemblies by synergic multiple weak HBs of $C-H\cdots F$ and $C-H\cdots N$.

⁸⁴ 2. Results and discussion

In a previous study [5], a porous honeycomb network was prepared by grouped HBs, exhibiting a much stronger hetero- as opposed to homo-molecular hydrogen bonding between perylene tetra-carboxylic di-imide (PTCDI) and melamine (1,3,5-triazine-2,4,6-triamine) on a silver-terminated silicon surface. Such a honeycomb network contains vertices formed by melamine and straight edges formed by PTCDI. Here, we adopt grouped weak HBs formed by bent F-C-N=C-F and H-C=C-C=C-H in the F-containing molecules to govern the assembling structures.

At the coverage of one monolayer (ML), the BDFPB molecules assembled into a close-packed structure denoted Pattern X (Fig. 1b). In this pattern, one BDFPB molecule perpendicularly approaches to another at the X sites, as marked in the molecular model in Fig. 1a. Such a connection mode is termed as Mode X. Apparently, Pattern X is formed solely via the X mode. One unit cell of this close-packed structure is schematically modelled in Fig. 1d and defined by the cell parameters: $a = (1.2 \pm 0.1)$ nm, $b = (1.8 \pm 0.1)$ nm, and $\alpha = (86 \pm 2)^{\circ}$. Further annealing at 400 K led to partial desorption of the BDFPB molecules (Fig. 1c). However, regardless of the surface coverage decrease or temperature elevation of the sample, Pattern X is the sole structure observed at surface.

Similar to the case of BDFPB, BDFPBP also assembled into a close-packed Pattern X (Fig. 2a) at 1 ML. Two interacting BDFPBP molecules in adjacent rows formed an angle of about $(84 \pm 2)^{\circ}$. It should be pointed out that these two molecules are not strictly perpendicular to each other due to the repulsion interaction of the F atoms in them. Subsequent thermal treatment of the sample led to several new patterns correspondingly labelled as XYI, XYII and Y in Fig. 2b–d. The unit cell parameters for the four assembled patterns are given below: (1) Pattern X, $a = (1.1 \pm 0.1)$ nm, $b = (2.4 \pm 0.1)$ nm, and $\alpha = (89 \pm 2)^{\circ}$; (2) Pattern XYI, $a = (2.1 \pm 0.1)$ nm, $b = (1.9 \pm 0.1)$ nm, and $\alpha = (96 \pm 2)^{\circ}$; (4) Pattern Y, $a = (1.9 \pm 0.1)$ nm, $b = (1.9 \pm 0.1)$ nm, and $\alpha = (93 \pm 2)^{\circ}$. All unit cells are highlighted in the STM images in Fig. 2, and the corresponding schematic models for the patterns are given in Fig. 2e–h.

According to the models given in Fig. 2e–h, two distinct connection modes, namely, X and Y, can be immediately identified. Obviously, each BDFPB molecule possesses four identical X sites. In the Y mode, one BDFPBP molecule perpendicularly approaches another one via the Y sites that bisect the molecule. The distance between the approaching sites for the Y mode and either end of the molecule is about 0.71 nm. Again the repulsion interaction of the F atoms in two connecting BDFPB molecules leads to their docking angle and distance deviations. The proposed molecular models suggest that both $C-H\cdots$ F and $C-H\cdots$ N weak HBs are involved in either X or Y modes.

The close-packed Pattern X is built solely via the X mode (Fig. 2a), and Pattern Y, solely via the Y mode (Fig. 2d). Pattern XY is made possible via a mixture of the X and Y modes. In our experiments, only two large-area ordered XY patterns were observed, namely Pattern XYI (Fig. 2b) and Pattern XYII (Fig. 2c). Both possess different X mode/Y mode ratios. For Pattern XYI, there are six intermolecular binding sites in a unit cell, four of which adopt the X mode to interact with the nearest molecule, while the other two adopt the Y mode (Fig. 2b and f). For Pattern XYII, one unit cell contains four binding sites, two X modes and two Y modes (Fig. 2c). Accordingly, the ratio of X mode to Y mode is 2:1 for Pattern XYI and 1:1 for Pattern XYII, respectively.



Fig. 1. (a) Schematic model of BDFPB, in which the HB acceptor groups and HB donor groups are marked by short lines and arrows. (b–c) STM images of the self-assembled Pattern X at full coverage (b) and after partial desorption (c). The yellow rods highlight the arrangements of BDFPB in within a unit cell, as marked by the black rectangle for eye guidance. (d) Schematic model for Pattern X superimposed onto an enlarged STM image. Imaging conditions: (b–c) bias voltage (V) = 1.5 V, feedback current (I) = 50 pA. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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Fig. 2. Molecular structure of BDFPBP is schematically shown by the model in left panel, and HB acceptor and donor groups are marked by short lines and arrows. STM images of the four assembled patterns: (a) Pattern X, (b) Pattern XYI, (c) Pattern XYII, and (d) Pattern Y. Different connection modes in Patterns XYI and XYII are marked in (c) and (d). (e-h) Schematic models superimposed on enlarged STM images, corresponding to (a-d) respectively. Imaging conditions: (a-d) V=1.5 V, I=50 pA.

As revealed by the STM images, Pattern XYII and Pattern Y are porous molecular networks with rectangular and square pores, and the pore areas are measured to be 0.66 and 0.36 nm^2 , respectively.

As mentioned above, Patterns XYI, XYII and Y were experimentally obtained by thermally annealing of Pattern X. In our experiments, large-area Pattern X appeared at 1 ML. At 450 K, Pattern XYI was formed on the substrate. When the temperature rose up to 460 K, Patterns XYII and Y coexisted at the surface. The domain size of Pattern Y increased with the annealing temperature. Above 500 K, all BDFPBP molecules completely desorbed from the substrate.

For BDFPTP, the increasing number of the phenyl rings in the assembling molecule doubles the number of the identical sites for the Y mode, as depicted by the molecular structural model in Fig. 3. Similar to the densely packed structures of BDFPB and BDFPBP, zigzag-like Pattern X appeared at 1 ML (Fig. 3a). Afterwards, sample annealing resulted in four new structures, namely, XYI. XYII, Y and XYIII (Fig. 3b-e). Among these patterns, Patterns XYI

and XYII are similar to the corresponding patterns achieved with BDFPBP. Due to the elongated molecular backbone, the pore area in Pattern XYII (1.04 nm²) is larger than that in Pattern XYII of BDFPBP.

Pattern XYIII is constructed via mixed X and Y modes at an X mode/Y mode ratio of 1:1. Though being identical to the X/Y ratio for Pattern XYII, the differences between Patterns XYIII and XYII are feasibly noticeable: In Pattern XYII, for a half of the molecules, both ends of an individual molecule are connected to the nearest molecule via the X mode and for the other half, via the Y mode; however, in Pattern XYIII, for all the molecules, one end of an individual molecule interacts with the nearest molecule by the X mode and the other end, by the Y mode. In addition, Pattern XYIII contains two different kinds of pores labelled as A and B in Fig. 3e, and the pore areas were measured to be 1.38 and 0.67 nm², respectively.

The unit cell of each structure is marked in corresponding STM image in Fig. 3, and the unit cell parameters are: (1) Pattern X, $a = (3.0 \pm 0.1)$ nm, $b = (1.1 \pm 0.1)$ nm, and $\alpha = (90 \pm 2)^{\circ}$; (2) Pattern



Fig. 3. Molecular structure of BDFPTP is schematically shown by the model in left panel, and HB acceptor groups and HB donor groups are marked by short lines and arrows. (a -e) STM images of its assembled structures: (a) Pattern X, (b) Pattern XYII, (c) Pattern XYII (d) Pattern Y and (e) Pattern XYIII. (f-j) Schematic models of each assembled patterns respectively. In (e), two different pores are marked as A and B. Imaging conditions: V = 1.5 V, I = 50pA.

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XYI, $a = (2.4 \pm 0.1)$ nm, $b = (2.5 \pm 0.1)$ nm, and $\alpha = (77 \pm 2)^{\circ}$; (3) Pattern XYII, $a = (2.2 \pm 0.1)$ nm, $b = (1.9 \pm 0.1)$ nm, and $\alpha = (88 \pm 2)^{\circ}$; (4) Pattern Y, $a = (2.0 \pm 0.1)$ nm, $b = (2.2 \pm 0.1)$ nm, and $\alpha = (92 \pm 2)^{\circ}$; (5) Pattern XYIII, $a = (3.2 \pm 0.1)$ nm, $b = (3.4 \pm 0.1)$ nm, and $\alpha = (85 \pm 2)^{\circ}$.

All other self-assembled structures were experimentally achieved by thermal treatments of Pattern X for the BDFPTP molecule. At 450 K, the original Pattern X turned into XYI. At 500 K. Patterns XYII and Y became dominant while some small domains of Pattern XYI co-existed. After extended thermal treatment of the sample at 500 K, Pattern Y faded in and became larger and larger at the expense of Pattern XYII. Finally, Pattern XYIII formed after further annealing at 500 K.

According to above-described results, one can straightforward conclude that there are two binding modes in all self-assembled structures for the three molecules studied above. It is the length of the linear molecule that determines the number of the connection sites for different modes. All experimentally observed patterns are formed by the molecules connected by sole X(Y) mode or a mixture of both modes at different ratios.

199 For the BDFPBP molecule, the continuous changes of the 200 assembled structures sequentially occurred during the temperature elevation as follows: Pattern $X \rightarrow$ Pattern $XYI \rightarrow$ Pattern XYI202 $II \rightarrow Pattern Y$. The surface molecular density for Patterns X, XYI, 203 XYII and Y decreased with the annealing temperature, corre-204 spondingly being 0.76, 0.70, 0.62 and 0.55 molecules/nm². The 205 decrease in the surface molecule density can be rationalized by the 206 fact that more and more molecules desorb from the substrate 207 during the annealing process. In another set of experiments, we 208 started from a sample at the sub-monolaver coverage and then 209 added up more and more BDFPBP molecules onto the substrate. As 210 a result, the evolution of the molecularly assembled patterns was 211 inversed with respect to the annealing experiment starting from 212 1 ML. Such a comparison of the above two sets of experiments 213 implies that the structural transformation of the 2D BDFPBP 214 molecular assemblies is solely governed by the surface coverage.

215 For the BDFPTP molecule, warm-up of the substrate gave rise to 216 the sequential pattern change from Pattern X to XYI, then to XYII, Y 217 and finally to XYIII as the molecular density decreased with the 218 substrate temperature. The molecular density for Pattern X, XYI, 219 XYII and XYIII is correspondingly 0.61, 0.51, 0.48, 0.45 and 220 0.37 molecules/nm². All these results suggest again that the surface coverage dictates self-assembled structures for all three 222 molecules.

223 Furthermore, it should be mentioned that in all STM images, the 224 angle between two adjacent weakly-bounded molecules is 225 approximately 90°, but slightly deviates from the right angle 226 due to the repulsing F atoms in involved molecules. Nevertheless, 227 this can still be ascribed to the directional formation of the weak 228 HBs. The "donor line" formed by the C and N atoms at the 229 molecular terminal tends to be parallel to the "acceptor line" 230 composed entirely of the H atoms in the side of the molecules, 231 making the lengths of the intermolecular HBs shortest. To testify 232 this, we designed and synthesized the BDFP-3-BP molecule, and 233 explored its self-assembling behavior on Au(111). Due to the 234 rotational freedom of the σ -bond connecting the pyridyls, BDFP-3-235 BP may have three possible conformations after deposition, 236 labelled as A (blue rod), B (pink rod) and C (red rod) in Fig. 4. 237 It's noticed that, although experimentally captured, Conformation 238 C did not very often appear in the assemblies, possibly due to 239 energy optimization of the assemblies because Conformations A 240 and B in total overtook in their appearance probability and 241 suppressed the occurrence of Conformation C. Nonetheless, 242 Conformation C looks like the half moon and thus can be easily 243 identified in the STM image (red rods in Fig. 4b). Two close-packed 244 structures were experimentally observed on the substrate, as



Fig. 4. (a) Models of three molecular conformations for the BDFP-3-BP molecule at surface, labelled as A, B and C. (b) STM image of the zigzag structure. The black parallelogram marks the unit cell: $a = (1.3 \pm 0.1)$ nm, $b = (1.9 \pm 0.1)$ nm, and $\alpha = (70)$ $\pm 2)^{\circ}$. (c) STM image of triangular structure. The black parallelogram marks the unit cell with parameters: a = (1,7+0,1) nm, b = (4,2+0,1) nm, and $\alpha = (7,3+2)^{\circ}$. (d-e) Proposed models for the assembled structures. Red dashed lines indicate possible HBs. The pink, orange and red rods correspondingly represent Conformation A, B and C. Imaging conditions: (a), V=2.3V, I=30 pA; (b), V=1.6V, I=150 pA. (For interpretation of the references to color in this figure legend and in the text, the reader is referred to the web version of this article.)

shown in Fig. 4b and c. According to the structural symmetry, we can infer that the molecules in Conformation A mingle with those in Conformation B at a ratio of 1:1 in the zigzag structure (Fig. 4b), but in the triangular structure (Fig. 4c), all three molecular conformations are involved and the conformational ratio of A:B:C is 1:1:2. Both self-assembled structures share the similarity that the angle between two interacting molecules is nearly 30°, as expected from our molecular design. Such an orientational arrangement ensures that the "donor line" formed by C and N atoms is parallel to the "acceptor line" including multiple H atoms.

3. Conclusion

In summary, 2D self-assemblies of three partially fluorinated molecules including BDFPB, BDFPBP and BDFPTP via weak C-H···F and C-H···N HBs have been systematically studied on the atomically flat Au(111)-(22 $\times \sqrt{3}$) substrate. The inter-molecular binding sites become abundant as the length of the assembling molecule increases. In comparison with the BDFP-3-BP molecule, the "donor line" involving the F atom and N atom in the molecule endings is attributed to govern that two neighboring and weakly bounded molecules in the assembled structures are perpendicular to each other. For each molecule, various self-assembled structures could be achieved by careful annealing treatments at different temperatures. Our experimental findings demonstrate that by rational design of molecular structures and corresponding weak HBs such as $C-H\cdots F$ and $C-H\cdots N$, the 2D self-assemblies of

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270 semiconducting molecules can be tuned, which may possibly lead 271 to a drastic performance change of the devised molecular devices.

272 4. Experimental

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273 4.1. Molecule syntheses

The molecular models of the fluorinated molecules including BDFPB, BDFPBP, BDFPTP and BDFP-3-BP are schematically shown in Scheme 1. These molecules were not commercially available and hence laboratory-synthesized starting from the precursors of 2,6difluoro-3-iodopyridine (DFIP) and 2,6-difluoro-4-iodopyridine (DFIDP). Such a series of the fluorinated molecules served two aims: (1) The BDFPB, BDFPBP and BDFPTP molecules were designed to study the similarity of and length effect on the final assembling structures; (2) The BDFP-3-BP molecule was designed to explore the orientation effect of the synergic multiple weak HBs of C—H \cdots F and C—H \cdots N at an angle of 60° with respect to its long axial direction, in comparison to the BDFPB, BDFPBP and BDFPTP ones whose grouped $C-H\cdots F$ and $C-H\cdots N$ HBs pointing along their long axial directions.

The synthesized molecules were separated, purified and finally confirmed by ¹H and ¹⁹F nuclear magnetic resonance (NMR), combined gas chromotograph and mass spectroscopy (GC-MS), and melting point (MP) measurements. The synthesis procedures and characterization data of the synthesized precurosors and molecules are listed below.

DFIP: Diisopropylamine (7.0 mL, 50 mmol) and 2,6-difluoropyridine (4.5 mL 50 mmol) were added consecutively to a solution of n-butyllithium (20 mL, 50 mmol, 2.5 mol/L in hexane) in THF (100 mL) and pentane (30 mL) at -78 °C. After 1 h at -78 °C, the mixture was treated with a solution of iodine (13 g, 5.0 mmol) in THF (50 mL) before being washed with 10% aqueous Na₂SO₃ (25 mL). The organic phase was dried and the volatiles evaporated. Crystallization of the residue from pentane afforded the product as colorless crystals (8.0 g, 66%). ¹H NMR (400 MHz, CDCl₃): δ 8.20 (td, 1H, J = 8.1, 7.3), 6.70 (dd, 1H, J = 8.3, 3.0). ¹³C NMR (100 MHz, CDCl₃): 161.9 (dd, J = 248, 13), 160.1 (dd, J = 242, 14), 153.5 (dd, J = 7, 2), 108.2 (dd, J = 35, 6), 69.1 (dd, J = 41, 6).¹⁹F NMR (376 MHz, CDCl₃): δ –69.1, -81.5. GC-MS *m*/*z* calcd. for C₅H₂F₂IN [M⁺]: 241, found: 241. MP: 40-42 °C.

DFIDP: n-Butyllithium (1.66 mL, 4.15 mmol, 2.5 mol/L in hexane) was added dropwise to a solution of diisopropylamine (1.30 mL, 4.15 mmol) in THF (2 mL) at -78 °C. After 25 min 2,6difluoro-3-iodopyridine (1.00 g, 4.15 mmol) in THF (5 mL) was added dropwise into this mixture by cannula. After 12 h at -78 °C, H₂O (0.2 mL, 11 mmol) in THF (2 mL) was added and the mixture was warmed to room temperature during 1 h. The mixture was washed with 10% aqueous Na₂SO₃ (5 mL) and extracted with ethyl acetate $(3 \times 50 \text{ mL})$. The organic extracts were dried (MgSO₄) and concentrated in vacuo. Crystallization from hexane afforded the product as colorless crystals (740 mg, 74%). ¹H NMR (400 MHz, CDCl₃): δ 7.22 (t, 2H,J = 1.2). ¹³C NMR (100 MHz, CDCl₃): 161.1 (dd, *I*=250, 16, 2C), 115.6 (dd, *I*=24, 10, 2C), 110.3. ¹⁹F NMR (376 MHz, CDCl₃): δ –68.1. GC–MS m/z calcd. for C₅H₂F₂IN [M⁺]: 241, found: 241. MP: 78-80°C.

BDFPB: A mixture of 1,4-phenylenediboronic acid (80 mg, 0.48 mmol) and 2,6-difluoro-4-iodopyridine (233 mg, 0.97 mmol) was added to a suspension of Pd (PPh₃)₄ (56 mg, 0.048 mmol) in 1.2-dimethoxyethane (5 mL) and aqueous Na₂CO₃ (1.0 mL, 2 mol/L). The mixture was subsequently maintained at reflux for 14 h. allowed to cool and then poured into H₂O (20 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The organic extracts were dried (MgSO₄), concentrated in vacuo and the residue was purified by column chromatography (CH_2Cl_2 /pentane = 1:9, v/v) to give the product as a white powder (113 mg, 77%). ¹H NMR (400 MHz, CDCl₃): δ 7.77 (s, 4H), 7.07 (s, 4H). ¹⁹F NMR (376 MHz, CDCl₃): δ –67.6. HRMS m/zcalcd. for C₁₆H₈F₄N₂Na [M + Na⁺]: 304.0624, found: 304.0624. MP: 308-310°C.

BDFPBP: A mixture of 4,4-biphenyldiboronic acid (25 mg, 0.10 mmol) and 2,6-difluoro-4-iodopyridine (50 mg, 0.21 mmol) was added to a suspension of Pd (PPh₃)₄ (14 mg, 0.012 mmol) in 1,2-dimethoxyethane (4 mL) and aqueous Na₂CO₃ (0.5 mL, 2 M). The mixture was subsequently maintained at reflux for 14 h, allowed to cool, poured into H₂O (10 mL), and extracted with CH_2Cl_2 (3 × 30 mL). The organic extracts were dried (MgSO₄), concentrated in vacuo, and the residue was purified by column chromatography (CH_2Cl_2 /pentane = 1:9, v/v) to give the product as a white powder (32 mg, 82%). ¹H NMR (400 MHz, DMSO): δ 8.00 (dd, 8H, J=8.5, 38.9), 7.65 (s, 4H). ¹⁹F NMR (376 MHz, CDCl₃): δ-68.6. MALDI-TOF-MS m/z calcd. for C₂₂H₁₂F₄N₂ [M⁺]: 380.094, found: 379.848. MP: 240-242 °C.

BDFPTP: A mixture of 4.4"-dibromo-1.1':4'.1"-terphenvl (200 mg, 0.52 mmol) and (2,6-difluoropyridin-4-yl)boronic acid (164 mg, 1.03 mmol) was added to a solution of $Pd(PPh_3)_4$ (60 mg, 0.052 mmol) in DMF (5 mL) at room temperature. The suspension was stirred and to it was added aqueous Na_2CO_3 (0.5 mL, 2 mol/L). The mixture was subsequently heated to 95 °C for 6 h followed by a filtration of the hot precipitate. The greyish precipitate was washed with H₂O and pentane to furnish the product as a white powder (188 mg, 80%). ¹H NMR (400 MHz, DMSO): δ 8.05 (d, 4H, I = 8.4), 7.93 (d, 4H, J = 8.6,), 7.91 (s, 4H), 7.64 (s, 4H). ¹⁹F NMR (376 MHz, DMSO): δ –69.8. MALDI-TOF-MS *m*/*z* calcd. for C₂₈H₁₆F₄N₂ [M⁺]: 456.125, found: 456.105. MP: 400 °C (decomp.).

BDFP-3-BP: A mixture of 4,4-biphenyldiboronic acid (25 mg, 0.10 mmol) and 2,6-difluoro-3-iodopyridine (50 mg, 0.21 mmol) was added to a suspension of Pd (PPh₃)₄ (14 mg, 0.012 mmol) in 1,2-dimethoxyethane (4 mL) and aqueous Na₂CO₃ (0.5 mL, 2 mol/L). The mixture was subsequently maintained at reflux for 12 h, allowed to cool and then poured into H_2O (10 mL) and 366 extracted with CH_2Cl_2 (3 \times 30 mL). The organic extracts were dried 367 (MgSO₄), concentrated in vacuo and the residue was purified by column chromatography $(CH_2Cl_2/pentane = 1:9, v/v)$ to give the product as a white powder (29 mg, 76%). ¹H NMR (400 MHz, CDCl₃): δ 8.03 (dd, 2H, *I* = 7.9, 17.3), 7.75 (d, 4H, *I* = 8.5), 7.64 (d, 4H, J = 8.4), 6.96 (dd, 2H, J = 2.9, 8.1). ¹⁹F NMR (376 MHz, CDCl₃): δ – 69.8,



Scheme 1. Structural models of the four molecules studied.

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³⁷² -70.8. HRMS m/z calcd. for C₂₂H₁₂F₄N₂Na [M+Na⁺]: 403.0834, found: 403.0837. MP: 193-195 °C.

³⁷⁴ 4.2. Sample preparations and STM imaging

375 All assembly experiments were performed with a UNISOKU 376 scanning tunneling microscopy (STM) at a base pressure 377 $<2 \times 10^{-10}$ Torr. The Au(111) substrate was cleaned by successive 378 cycles of 1 keV Ar⁺ ion sputtering and annealing at 770 K. The W tip 379 used in the experiments was prepared by electrochemical 380 corrosion in 2 mol/L NaOH solution and further cleaned by 381 electron-beam heating up to ~2000K in ultra-high vacuum 382 (UHV) condition. Before their deposition, all molecules were 383 degassed overnight. Afterwards, the BDFPB, BDFPBP, BDFPTP and 384 BDFP-3-BP molecules were separately sublimated from a tantalum 385 boat at 380 K, 450 K, 540 K and 450 K, and accordingly deposited 386 onto the atomically flat Au(111)-(22 $\times \sqrt{3}$) substrate. All STM 387 images were acquired at the temperature of liquid nitrogen.

388 Q2 Uncited references

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