

Self-assembled organic donor/acceptor nanojunction arrays

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We have fabricated well-ordered organic donor/acceptor nanojunction arrays comprising *p*-sexiphenyl (6P) and C₆₀ via self-assembly of C₆₀ on the molecular nanotemplate of 6P nanostructures on Ag(111). Our scanning tunneling microscopy measurements show that the preferential trapping of C₆₀ triplets atop 6P single molecule leads to the formation of the C₆₀/6P vertical nanojunctions with well-defined two-dimensional arrangement. Annealing this binary molecular superstructure at 380 K results in the insertion of C₆₀ linear chains between the neighboring 6P nanostructures and thereby the appearance of the periodic C₆₀/6P lateral nanojunction arrays. © 2008 American Institute of Physics. [DOI: 10.1063/1.2920199]

Much recent attention has been devoted to molecular nanodevices, motivated in part by the potential use of single molecule in nanoelectronics.¹ The realization of molecular nanodevices relies on the effective controlling and manipulating the assembly of molecules into highly periodic nanostructure arrays on surfaces with desired functionalities.²⁻⁵ One promising approach to create these nanostructure arrays is the selective coupling of functional molecules at preferential adsorption sites of prepatterned surface nanotemplates.²⁻¹² Organized supramolecular architectures stabilized by noncovalent but directional and selective intermolecular interactions (hydrogen bonding, dipolar coupling, or metal-ligand interactions) represent one fascinating type of surface nanotemplates.^{2-4,12-19} The periodicity or symmetry of these molecular surface nanotemplates can be easily tuned by simply modifying the chemical structures of individual molecules, facilitating the assembling of adsorbed guest molecules into ordered arrays with tunable periodicity.¹²⁻¹⁹ In particular, the direct binding of the acceptor (donor) molecular nanostructures on the nanotemplate exclusively constructed from the donor (acceptor) molecules offers an ease of fabrication of organic donor/acceptor nanojunctions with well-ordered two-dimensional (2D) organization. In this letter, we demonstrate the fabrication of well-ordered organic donor/acceptor nanojunction arrays by adsorbing C₆₀ (acceptor) on the surface nanotemplate of *p*-sexiphenyl (6P, donor) nanostructures on Ag(111), as revealed by low-temperature scanning tunneling microscopy (LT-STM) investigations.

The experiments were conducted in an Omicron LT-STM interfaced to a Nanonis controller (Nanonis, Switzerland).^{16,20} All STM imaging were performed at 77 K. C₆₀ and 6P molecules were sequentially evaporated *in situ* onto the clean Ag(111) held at room temperature (RT) in the growth chamber. In our experiments, 1 ML refers to one full layer of close packed C₆₀ or 6P close packed layer with their conjugated π -plane oriented parallel to substrate surface.

Well-ordered unidirectional 6P nanostructures can be fabricated by the deposition of 1 ML 6P on Ag(111) at RT and subsequent annealing at 380 K for 30 min, as shown in Fig. 1(a), in which each rodlike bright feature represents a single

6P molecule. The width of the 6P monolayer nanostructures is 2.95 ± 0.02 nm, which is very close to the van der Waals length of 6P molecules (2.73 nm).²¹ The periodicity along the 6P molecular nanostructure is 0.70 ± 0.02 nm, as revealed by the line profile in Fig. 1(c). Although the adjacent phenyl units within 6P molecules are twisted in the gas phase or for isolated molecules on metal surfaces²² due to steric hin-

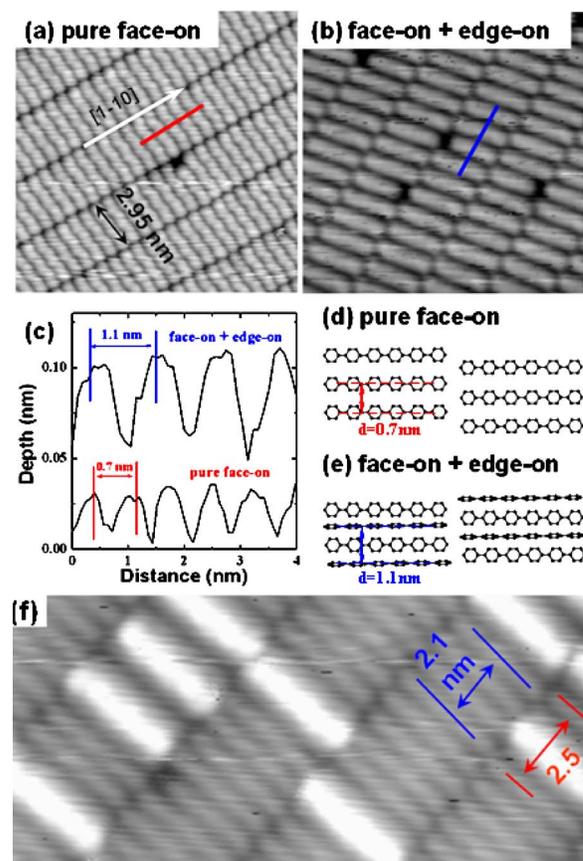


FIG. 1. (Color online) 15×15 nm² STM images of (a) “pure face-on” ($V_{\text{tip}} = +1.8$ V) and (b) “face-on+edge-on” ($V_{\text{tip}} = -3.3$ V) 6P monolayer nanostructure on Ag(111). (c) Corresponding line profiles along the chain direction of both 6P layers. Schematic drawings of molecular structure for (d) pure face-on and (e) face-on+edge-on 6P layers. (f) 15×7 nm² STM image of 0.05 ML 6P on pure face-on 6P monolayer nanostructure on Ag(111) ($V_{\text{tip}} = -1.6$ V), which shows the random insertion of “edge-on” 6P molecules into the pure face-on 6P monolayer.

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drance of the hydrogen atoms of neighboring rings, they become coplanar once they form condensed thin films on solid substrate surfaces or single crystal solids.²³ Therefore, the formation of 6P monolayer nanostripes on Ag(111) in Fig. 1(a) can be understood in terms of self-assembly via side-by-side packing with extended molecular π -planes parallel to the Ag(111) surface, as shown by the schematic in Fig. 1(d) and referred to as the “pure face-on” 6P nanostripe.

Further deposition of 6P can result in the insertion of edge-on 6P molecules into the matrix of the pure face-on 6P nanostripes, where the edge-on represents the configuration of 6P molecules with all their phenyl rings oriented nearly perpendicular to the substrate surface. As shown in Fig. 1(b), a 6P nanostripe array with larger periodicity of 1.1 ± 0.02 nm along the nanostripe packing direction forms after the deposition of 0.3 ML 6P on the pure face-on 6P nanostripes on Ag(111). We propose a model [Fig. 1(e)] involving the alternating arrangement of face-on and edge-on 6P molecules into this 6P nanostripe array, referred to as “face-on+edge-on” 6P nanostripe. Figure 1(f) shows the 15×7 nm² STM image of 0.05 ML 6P on the pure face-on 6P nanostripe array (total 6P coverage is 1.05 ML) with the random insertion of edge-on 6P molecules, where the bright rodlike features represent the edge-on 6P molecules. As highlighted in the right part of the image, the length of three successive face-on 6P has been expanded from the original 2.1 nm ($0.7 \text{ nm} \times 3 = 2.1 \text{ nm}$) to 2.5 nm ($0.7 \text{ nm} \times 2 + 1.1 \text{ nm} = 2.5 \text{ nm}$) after insertion of one edge-on 6P molecule. Similar 6P nanostripe arrays have been observed on Au(111).^{24,25} Such alternating arrangements of face-on and edge-on 6P molecules is reminiscent of the typical herringbone structure commonly observed in 6P single crystal solids, stabilized by the electrostatic force or the quadruple interaction between neighboring face-on and edge-on 6P molecules.²¹

RT adsorption of C₆₀ on the face-on+edge-on 6P nanostripes leads to a unique preferential trapping of C₆₀ triplet atop 6P single molecule. As shown in Fig. 2(a), randomly dispersed C₆₀ triplets form after depositing 0.1 ML C₆₀ on the face-on+edge-on 6P nanostripes with subsequent annealing at 350 K for 30 min. The close-up STM image in Fig. 2(b) clearly reveals the preferential adsorption of C₆₀ triplets atop 6P single molecule. The schematic drawing in the inset in Fig. 2(b) shows the proposed model for the preferential adsorption. Increasing the C₆₀ coverage to 0.5 ML results in a fairly ordered 2D array of C₆₀ triplets, as shown in Fig. 2(c). The corresponding detailed 20 × 20 nm² STM image of the C₆₀ triplet array is displayed in Fig. 2(d). These triplets assemble along the underlying 6P nanostripe packing direction with a separation of about 3.3 nm, as highlighted in Fig. 2(d). We propose that the C₆₀ triplets predominantly nucleate on the edge-on 6P molecules of the 6P nanostripe array. The adsorption on the face-on 6P molecules is likely to be prohibited due to steric hindrance between the adsorbed C₆₀ and the adjacent edge-on 6P molecules. Future experiments with 6P nanostripes of different periodicities will be carried out to verify this hypothesis. As typical donor (6P) and acceptor (C₆₀) molecules, the well-ordered C₆₀ triplet array atop the 6P nanostripes can serve as a novel organic donor/acceptor vertical nanojunction array such as rectifiers, with great potential for future molecular-electronic or nanoelectronic devices.

After annealing the C₆₀/6P vertical nanojunction array (0.5 ML C₆₀ on the face-on+edge-on 6P nanostripe array)

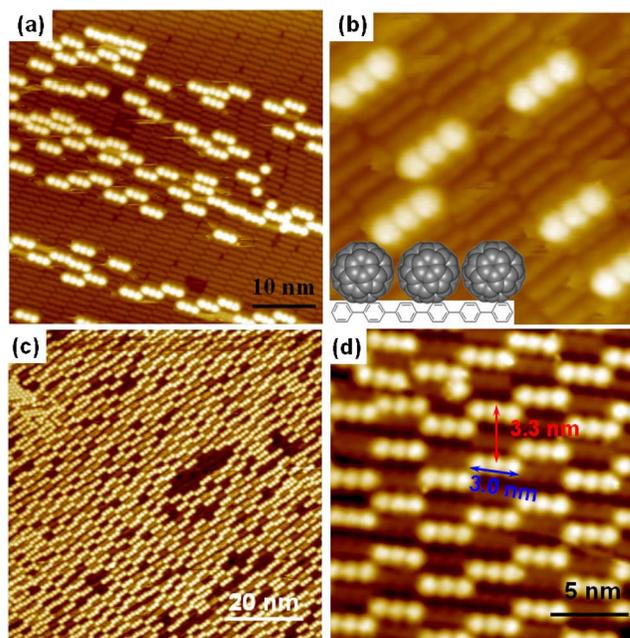


FIG. 2. (Color online) (a) 50×50 nm² STM image of 0.1 ML C₆₀ on “face-on+edge-on” 6P layer on Ag(111) and (b) corresponding 15×15 nm² STM image clearly revealing the preferential adsorption of C₆₀ triplets atop single 6P molecule; the inset in panel (b) shows the proposed model. (c) 80×80 nm² STM images of 0.5 ML C₆₀ on face-on+edge-on 6P layer on Ag(111), showing the formation of a well-ordered vertical C₆₀/6P nanojunction array, and (d) the corresponding detailed 20×20 nm² STM image of panel (c). $V_{\text{tip}} = 1.4$ V for all images.

at 380 K for 30 min, the C₆₀ triplet array is transformed into a highly periodic C₆₀ linear chain array, as shown by the large scale 100×100 nm² STM image in Fig. 3(a). Figure 3(b) shows the corresponding detailed STM image of the C₆₀ linear chain array. It reveals that some rodlike molecules are interposed between the neighboring C₆₀ linear chains, widening the interchain distance. As indicated in Fig. 3(b), the periodicity or the interchain distance is measured to be 3.85 ± 0.02 nm, which is close to the sum of the van der Waals radii of C₆₀ (1.00 nm) and molecular length of 6P

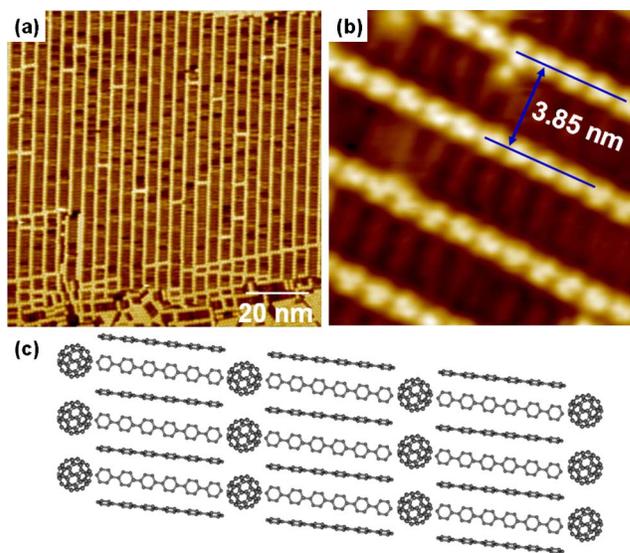


FIG. 3. (Color online) STM images of the lateral C₆₀/6P nanojunction arrays: (a) 100×100 nm² and (b) corresponding detailed 13×13 nm² image ($V_{\text{tip}} = -2.0$ V). (c) Schematic model for the regular superlattice of alternating C₆₀ and 6P linear chains.

(2.95 nm). As such, the interposed rodlike features in Fig. 3(b) are attributed to the 6P molecules. We proposed a model involving the insertion of C₆₀ linear chains into the face-on +edge-on” 6P nanostripe array, as revealed by the schematic drawing in Fig. 3(c). Such highly periodic 2D arrangement of alternating linear chains of C₆₀ (acceptor) and 6P (donor) makes this superlattice an ideal prototype of lateral donor/acceptor nanojunction array for their potential application in organic solar cells.

In conclusion, well-ordered unidirectional 6P nanostripe array has been used as an effective molecular surface nanotemplate to fabricate self-assembled organic donor/acceptor nanojunctions, including periodic C₆₀ triplets preferentially trapped atop 6P single molecule as an organic donor/acceptor vertical nanojunction array and a superlattice of alternating C₆₀ and 6P linear chains as a 2D organic donor/acceptor lateral nanojunction array. These novel organic nanojunction arrays should have promising applications for future molecular-electronic or nanoelectronic devices.

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- ¹C. Joachim and M. A. Ratner, *Proc. Natl. Acad. Sci. U.S.A.* **102**, 8801 (2005).
- ²J. V. Barth, G. Costantini, and K. Kern, *Nature (London)* **437**, 671 (2005).
- ³F. Rosei, *J. Phys.: Condens. Matter* **16**, S1373 (2004).
- ⁴W. Chen and A. T. S. Wee, *J. Phys. D* **40**, 6287 (2007).
- ⁵J. G. Hou, J. L. Yang, H. Q. Wang, Q. X. Li, C. G. Zeng, L. F. Yuan, B. Wang, D. M. Chen, and Q. S. Zhu, *Nature (London)* **409**, 304 (2001).
- ⁶C. G. Zeng, B. Wang, B. Li, H. Q. Wang, and J. G. Hou, *Appl. Phys. Lett.* **79**, 1685 (2001).
- ⁷H. Brune, M. Giovannini, K. Bromann, and K. Kern, *Nature (London)* **394**, 451 (1998).
- ⁸M. Corso, W. Auwärter, M. Muntwiler, A. Tamai, T. Greber, and J. Osterwalder, *Science* **303**, 217 (2004).
- ⁹R. Otero, Y. Naitoh, F. Rosei, P. Jiang, P. Thosttrup, A. Gourdon, E. Laegsgaard, I. Stensgaard, C. Joachim, and F. Besenbacher, *Angew. Chem., Int. Ed.* **43**, 2092 (2004).
- ¹⁰W. Chen, H. Xu, L. Liu, X. Y. Gao, D. C. Qi, G. W. Peng, S. C. Tan, Y. P. Feng, K. P. Loh, and A. T. S. Wee, *Surf. Sci.* **596**, 176 (2005).
- ¹¹N. Néel, J. Kröger, and R. Berndt, *Adv. Mater. (Weinheim, Ger.)* **18**, 174 (2006).
- ¹²D. S. Deak, F. Silly, K. Porfyrakis, and M. R. Castell, *J. Am. Chem. Soc.* **128**, 13976 (2006).
- ¹³J. A. Theobald, N. S. Oxtoby, M. A. Phillips, N. R. Champness, and P. H. Beton, *Nature (London)* **424**, 1029 (2003).
- ¹⁴S. Stepanow, N. Lin, J. V. Barth, and K. Kern, *Chem. Commun. (Cambridge)* **2006**, 2153.
- ¹⁵H. Spillmann, A. Kiebele, M. Stöhr, A. J. Thomas, D. Bonifazi, F. Y. Cheng, and F. Diederich, *Adv. Mater. (Weinheim, Ger.)* **18**, 275 (2006).
- ¹⁶H. L. Zhang, W. Chen, L. Chen, H. Huang, X. S. Wang, J. Yuhara, and A. T. S. Wee, *Small* **3**, 2015 (2007).
- ¹⁷E. Mena-Osteritz and P. Bäuerle, *Adv. Mater. (Weinheim, Ger.)* **18**, 447 (2006).
- ¹⁸B. Xu, C. G. Tao, E. D. Williams, and J. E. Reutt-Robey, *J. Am. Chem. Soc.* **128**, 8493 (2006).
- ¹⁹M. Surin and P. Samori, *Small* **3**, 190 (2007).
- ²⁰W. Chen, H. Huang, S. Chen, L. Chen, H. L. Zhang, X. Y. Gao, and A. T. S. Wee, *Appl. Phys. Lett.* **91**, 114102 (2007).
- ²¹G. Koller, S. Berkebile, M. Oehzelt, P. Puschnig, C. Ambrosch-Draxl, F. P. Netzer, and M. G. Ramsey, *Science* **317**, 351 (2007).
- ²²S. W. Hla, K. F. Braun, B. Wassermann, and K. H. Rieder, *Phys. Rev. Lett.* **93**, 208302 (2004).
- ²³K. N. Baker, A. V. Fratini, T. Resch, H. C. Knachel, W. W. Adams, E. P. Socci, and B. L. Farmer, *Polymer* **34**, 1571 (1993).
- ²⁴C. B. France and B. A. Parkinson, *Appl. Phys. Lett.* **82**, 1194 (2003).
- ²⁵C. B. France, F. A. Frame, and B. A. Parkinson, *Langmuir* **22**, 7507 (2006).