Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers. This journal is © the Partner Organisations 2018

Supplementary Information

On-surface synthesis of grephene clusters from a Z-bar-linkage precursor with quaterphenyl branches

Zhen Xu, Takahiro Kojima, Wanyu Wang, Kabya Kaushik, Alex Saliniemi, Nakae Takahiro and Hiroshi Sakaguchi*

Institute of Advanced Energy, Kyoto University, Uji, 611-0011 Kyoto, Japan *Correspondence to: sakaguchi@iae.kyoto-u.ac.jp

Table of Contents

Materials and Methods	3
Compounds	3
Two-zone chemical vapor deposition (2Z-CVD)	3
Au(111) substrates	4
STM measurements	4
Raman spectra	4
Calculations	4
Figures	5
NMR charts	7
References	8

Materials and Methods

Compounds

Synthesis of precursor

5,5'-Dibromo-2,2'-diiodo-1,1'-biphenyl¹ and [1,1':4',1"-terphenyl]-4-ylboronic acid² was prepared according to the literature. The other commercially available reagents were used as received, unless otherwise stated.

All manipulations were performed under N₂ atmosphere using standard Schlenk techniques. NMR spectra were recorded with JEOL JNM-ECA600 (600 MHz for ¹H, 150 MHz for ¹³C) instruments. NMR spectra were reported in parts per million from internal tetramethylsilane (δ 0.00 ppm for chloroform-d) or residual solvent (δ 7.26 ppm for chloroform-d) for ¹H NMR, and from the solvent carbon (δ 77.00 ppm for chloroform-d) for ¹³C NMR. Thin-layer chromatography (TLC) and column chromatography were performed on Art. 5554 (Merck KGaA) and Silica Gel 60N (Kanto Chemical Co.), respectively. Gel permeation chromatography (GPC) was performed on a LC-Forte system (YMC Co. Ltd.) with JAIGEL 1HR and 2HR polystyrene columns (eluent: CHCl₃, flow: 10 mL/min).

4''',5''''-Dibromo-1,1':4',1'':4'',1''':2''',1'''':2'''',1'''':4''''',1'''''-octiphenyl: (1)



Firstly, [1,1':4',1"-terphenyl]-4-ylboronic acid (194.5 mg, 0.7095 mmol, 4 equiv.) and KOH (79.6 mg, 1.4187 mmol, 8 equiv.) were added into a solution of 5,5'-dibromo-2,2'-diiodo-1,1'-biphenyl (100 mg, 0.1774 mmol, 1 equiv.) in nitrobenzene (10 mL) and H₂O (5 mL). Secondly, Pd(PPh₃)₄ (20.49 mg, 0.01774 mmol, 0.1 equiv.) was added into the solution after degassing. Thirdly, the mixture was heated to 70 °C for 7 h under N₂ atmosphere. After cooling to room temperature, the reaction mixture was diluted with chloroform, and the organic layer was collected, washed with brine (50 mL), dried with Na₂SO₄, and concentrated in vacuo. Then, the catalyst was removed by passing through a short silica gel pad. Finally, the resulting solid was purified by GPC and recrystallized using toluene affording the title compound (24.5 mg, 18%) as a white powder. ¹H NMR (600 MHz, 20 °C, CDCl₃) δ 7.71 (d, *J* = 1.98 Hz, 2H), 7.67 (d, *J* = 8.28, 4H), 7.63 (d, *J* = 6.78 Hz, 8H), 7.52 (dd, *J* = 2.04, 7.8 Hz, 2H), 7.46 (t, *J* = 7.56 Hz, 4H), 7.36 (t, *J* = 7.02 Hz, 2H), 7.28 (d, *J* = 8.16 Hz, 4H), 7.05 (d, *J* = 8.22 Hz, 2H), 6.56 (d, *J* = 8.16 Hz, 4H); ¹³C NMR (150 MHz, 20 °C, CDCl₃) δ 140.71, 140.65, 140.35, 139.63, 139.60, 138.73, 138.51, 134.13, 131.58, 131.30, 129.41, 128.92, 127.65, 127.49, 127.34, 127.12, 126.31, 121.46. Figure S4 shows NMR spectra.

Two-zone chemical vapor deposition (2Z-CVD)

The 2Z-CVD system is composed of a quartz tube (ϕ 26 mm, length 86 cm) as the reactor, a rotary pump which can evacuate the system to below 7 × 10⁻⁴ Torr, a two-zone electric furnace with

temperature controllers, an Ar gas flow system with a mass-flow controller, and a mantle heater for precursor sublimation. Ar gas was fed into the quartz tube at a flow rate of 500 sccm, resulting in a vacuum of 1 Torr. Before the CVD process, the quartz tube was annealed at 1000 °C for 20 min to remove impurities that can deactivate precursor radicals. The precursor (20 μ g, prepared by casting 200 μ L of precursor solution, 0.1 mg/mL in toluene) in a quartz boat was placed in the quartz tube before zone 1. An Au(111)-deposited mica substrate was placed in zone 2 of the quartz tube. The CVD process was conducted in two sequential steps: firstly, zone 1 (the path of the precursors) and zone 2 were heated to 350 and 250 °C, respectively, and the precursors were sublimated using the mantle heater by heating to 350 °C for 15 min. Finally, to anneal the sample, the temperature of zone 2 was increased stepwise to the final temperature.

Au(111) substrates

Substrates consisting of Au(111) on mica were prepared by using an electron-beam vacuumdeposition system. Evaporated Au atoms were deposited onto a mica substrate that was pre-heated to 350 °C under a vacuum of 2×10^{-8} Torr. Deposition was performed at a rate of 0.5 Å s⁻¹, with a final thickness of 30 nm.

STM measurements

STM measurements were performed with a current-constant mode using a commercial instrument (PicoSPM; Keysight Technologies Inc., formerly Molecular Imaging) under Ar atmosphere at room temperature.³ All STM images were acquired at a tip bias of 0.2 V with a constant current of 5–20 pA. An electrochemically etched Pt-Ir (80:20) wire was used as the STM tip.

Raman spectra

Raman spectroscopy was performed using a laser Raman microscope (LV-RAM500/532; Lambda Vision Inc.) with a 532 nm laser. A laser power of 70 mW was used, with an exposure time of 10 seconds and a 10 time averaging.

Calculations

Calculations were performed using the Materials Studio software suite (BIOVIA Inc.). Adsorption conformations of precursor 1 biradicals on Au(111) calculated by quantum mechanics/molecular mechanics (QM/MM) approach were performed according to our previous publication.⁴

Geometry optimization of biradical form of precursor 1

Quantum mechanics/molecular mechanics (QM/MM) with the QMERA module were used to calculate the optimized geometries of the biradical forms of R_{uu} , R_{ud} and R_{dd} adsorbed on Au(111). The input structures were generated by the modification of optimized structures of DPSP.⁴ The QM/MM calculations can treat organic molecule radicals on metal surface with electronic interaction at the QM level, the exterior metal surface treated at the MM level. The unit cell was expanded by the insertion of MM level metal surface in order to avoid intermolecular interactions. In this work, the precursor biradicals on Au(111) showed the lowest C_1 symmetry; thus, a small periodic unit cell with high symmetry cannot be constructed. Optimized conformations and the corresponding formation energies can be obtained by employing the QM/MM approach.

A unit cell (46.14 × 39.96 × 51.19 Å) with three-layered Au(111) was used to minimize intermolecular interactions. Input geometries of the conformers R_{uu} , R_{ud} and R_{dd} and the underneath two Au layers (154 atoms) were treated at the QM level. At the same time, the other Au atoms (614 atoms) were treated at the MM level. The QMERA module was used to perform QM/MM calculations on the periodic system. Spin-unrestricted DFT calculations were carried out with the DMol³ program^{5,6} using the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) functional as the electron exchange and correlation functional⁷ in combination with the DND basis set (ver. 4.4) and effective core potential for Au. For the MM region, the GULP program was employed with the ReaxFF 6.0 force field. QM/MM interactions were handled by mechanical embedding. In the QMERA implementation, the QM and MM interfaces were handled by ChemShell.⁸ Table S1 shows the optimized conformations of R_{uu} , R_{ud} and R_{dd} in the singlet and triplet states, as well as the corresponding formation energies.

Figures



Fig. S1 Large scale STM images of 2Z-CVD grown samples from 20 μ g of the precursor DBOP at 250 °C (a), 400 °C (b), 450 °C (c), and 500 °C (d).



Fig. S2 (a) STM image of sample annealed at 400 °C with overlaid chemical structures, (b) crosssectional analysis along the dotted line in (a), (c) illustration of theoretical periodic distances with and without metal-organic bonds formation.



Fig. S3 Top views of the hindrance effect of the bimolecular reactions between heterochiral (a) and homochiral (b) precursors. The red benzene rings of the precursor in the space-filling models point toward the Au(111) surface, the radical-carbon is denoted by a light blue color.

Table S1 Formation energy of conformers of the biradical form of DBOP on Au(111) at the optimized geometry calculated by QM/MM approach. Colors of the benzene rings in the space-filling models of the precursor indicate the relative heights from the Au(111) surface; red, pointing toward the surface; blue, away from the surface.

Geometry	(R _{uu})	(R _{ud})	(R _{dd})
Δ <i>E</i> _f (singlet) (Kcal/mol)			
	172.70	35.31	0.00
Δ <i>E</i> _f (triplet) (Kcal/mol)	172.70	36.91	0.62
	1/2./0	20.91	0.02



Fig. S4 NMR spectra of DBOP in CDCl₃. (a) ¹H NMR; (b) ¹³C NMR.

References

- 1. K. L. Chan, S. E. Watkins, C. S. Mak, M. J. McKiernan, C. R. Towns, S. I. Pascu and A. B. Holmes, *Chem. Commun.*, 2005, 5766-5768.
- 2. I. Yamaguchi, K. Goto and M. Sato, *Macromolecules*, 2009, **42**, 7836-7845.
- 3. H. Sakaguchi, H. Matsumura, H. Gong and A. M. Abouelwafa, *Science*, 2005, **310**, 1002-1006.
- 4. H. Sakaguchi, S. Song, T. Kojima and T. Nakae, *Nat. Chem.*, 2017, **9**, 57-63.
- 5. B. Delley, J. Chem. Phys., 1990, **92**, 508-517.
- 6. B. Delley, J. Chem. Phys., 2000, **113**, 7756-7764.
- 7. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- P. Sherwood, A. H. de Vries, M. F. Guest, G. Schreckenbach, C. R. A. Catlow, S. A. French, A. A. Sokol, S. T. Bromley, W. Thiel, A. J. Turner, S. Billeter, F. Terstegen, S. Thiel, J. Kendrick, S. C. Rogers, J. Casci, M. Watson, F. King, E. Karlsen, M. Sjøvoll, A. Fahmi, A. Schäfer and C. Lennartz, *J. Mol. Struct: Theochem*, 2003, **632**, 1-28.