



OPEN

SUBJECT AREAS:

TWO-DIMENSIONAL
MATERIALS

CROSS-COUPLING REACTIONS

SCANNING PROBE
MICROSCOPY

SELF-ASSEMBLY

Polymerization or Cyclic Dimerization: Solvent Dependent Homo-Coupling of Terminal Alkynes at HOPG Surface

Xuemei Zhang*, Lingyan Liao*, Shuai Wang, Fangyun Hu, Chen Wang & Qingdao Zeng

CAS Key Laboratory of Standardization and Measurement for Nanotechnology, National Centre for Nanoscience and Technology, No. 11 Zhongguancun Bei yitiao Beijing 100190, China.

Received
11 July 2013Accepted
6 January 2014Published
28 January 2014

Correspondence and
requests for materials
should be addressed to
Q.D.Z. (zengqd@
nanocr.cn) or C.W.
(wangch@nanocr.cn)

* These authors
contributed equally to
this work.

Surface reactivity has become one of the most important issues in surface chemistry over the past few years. In this work, we, for the first time, have investigated the homo-coupling of a special terminal alkyne derivative on the highly oriented pyrolytic graphite (HOPG) surface. Using scanning tunneling microscopy (STM) technique, we have found that such coupling reaction seriously depends on the supramolecular assembly of the monomer on the studied substrate, whereas the latter appears an obvious solvent effect. As a result, the reaction in our system undergoes polymerization and cyclic dimerization process in 1-phenyloctane and 1,2,4-trichlorobenzene, respectively. That is to say, the solvent effect can be extended from the two-dimensional (2D) supramolecular self-assembly to surface chemical reactions, and the selective homo-coupling has been successfully achieved at the solid/liquid interface.

Nanotechnology in the lab research has been one of the most challenging work during the last two decades. In order to realize the ultimate goal of creating novel functional materials, the methods for the precise mutual arrangement of the individual molecules need to be increasingly developed. One of the most promising approaches to date is the “bottom-up” strategy or molecular self-assembly^{1,2}. Under this principle, there has been tremendous progress in the engineering of high ordered molecular architectures over the past few years^{3–7}. The supramolecular architectures are usually formed through the intermolecular weak non-covalent forces including the hydrogen bonding, π - π stacking, electrostatic interactions, metal-ligand coordination and van der Waals interactions between molecules^{8–12}. In recent years, covalent chemical bonding has flourished as a new strategy to prepare novel two-dimensional (2D) functional structures at the surface. It has also been well demonstrated that the 2D supramolecular structures produced by covalent bonding are superior in thermal stability as compared to those formed by non-covalent interactions, because of the relative stronger chemical bonds between the building blocks^{13–18}. Notably, most studies have been performed on clean metallic surfaces using well-defined ultrahigh-vacuum (UHV) conditions. For instance, various higher-molecular-weight hydrocarbons resulting from C-H bond activation and direct C-C coupling reactions have been achieved at appropriate metal surfaces under UHV conditions^{19–24}. Apparently, the metallic surfaces possess good catalytic activity, whereas some unfavorable reactions under ambient conditions can be initiated at the surface under UHV conditions, which offers scientists many opportunities to manufacture newfashioned structures and materials. However, such condition makes it extremely difficult to simulate the real reactions in solution and to explore the mechanisms of chemical reactions afterwards. Therefore, one has to carefully choose the reactants and reactions from the very beginning in order to eliminate the solvent effects. In fact, as in this work, the surface carbon-carbon coupling in a solution environment can also be feasible though such study was surprisingly rare until now.

Solvent effects on the organic chemical reactions have been widely investigated by self-consistent reaction field (SCRF) theory^{25,26}. On the other hand, revealed by scanning tunneling microscopy (STM) technique, solvent has also been affirmed as an important factor in controlling and tuning the 2D surface molecular self-assembled progress as well as structures, which makes the supramolecular self-assembly at the solid/liquid interface more available and diverse^{27–30}. Herein, utilizing the obviously solvent-induced supramolecular self-assembly, we, for the first time, obtain the selective surface Glaser coupling on a highly oriented pyrolytic graphite (HOPG) surface which is commercially available at an affordable price and highly stable in air. As a result, the solvent effects on the supramolecular chemistry have been extended from the 2D crystal engineering to surface reactivity.



Results

With a long alkoxy chains and two terminal alkynes, the monomer (5-(dodecyloxy)-N1,N3-di(prop-2-ynyl)isophthalamide, named DPIA, Fig. 1) for Glaser coupling was designed and synthesized (see the supplementary information). To better describe the assembled structures afterward, we divided a DPIA molecule into three parts, and named the two amide-connected terminal alkyne groups as antenna, the benzene ring as head, and the long alkoxy chain as tail. Before performing the surface Glaser coupling, we firstly investigated the self-assembled structures of DPIA in two types of solvents with opposite polarity. Figs. 2(a) and 3(a) displayed the physisorbed monolayers of DPIA at the 1-phenyloctane/HOPG and 1,2,4-trichlorobenzene/HOPG interface, respectively. Clearly, though periodic and ordered structures can be observed in these two solvents, the DPIA organized two totally different supramolecular patterns. In other words, the self-assembly of DPIA molecules at graphite surface appears significant solvent effects.

At the 1-phenyloctane/HOPG interface, the DPIA molecules assembled into the lamellar structure with alternating dark and light bands, as shown in Fig. 2(a). With a measured width (d_1) of 0.7 nm, the bright bands should be attributed to the head and the antenna parts, due to their higher tunneling efficiency. And the remaining alkyloxy chains of DPIA co-assembled with the adsorbed 1-phenyloctane molecules (marked by the green dotted circles), which can be found in the dark bands. Because of the weak interactions between the antenna part and the substrate, the assembled structures along the bright bands seemed to be confused and disordered. Fortunately, the distinct organization of alkoxy chains can help us constructing a tentative molecular model. As presented in Fig. 2(b), the long chains of DPIA molecules in two neighboring lamellae were interdigitated, but the terminal alkyne groups of adjacent monomers were parallel to each other along the bright bands, forming a reversed shoulder-to-shoulder organization.

However, DPIA assembled into a close-packed structure with bright feature can be clearly observed in 1,2,4-trichlorobenzene

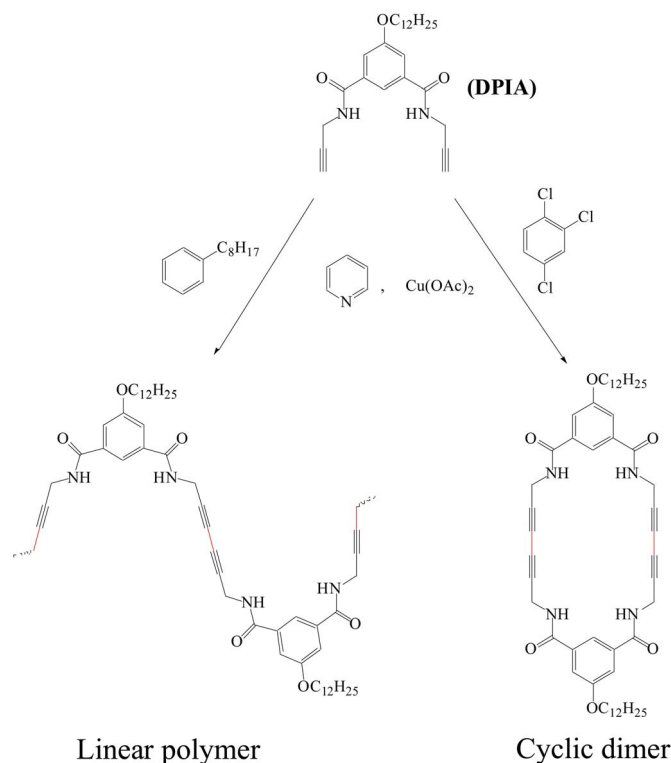


Figure 1 | The two coupling models of DPIA in 1-phenyloctane (left) and 1,2,4-trichlorobenzene (TCB) (right).

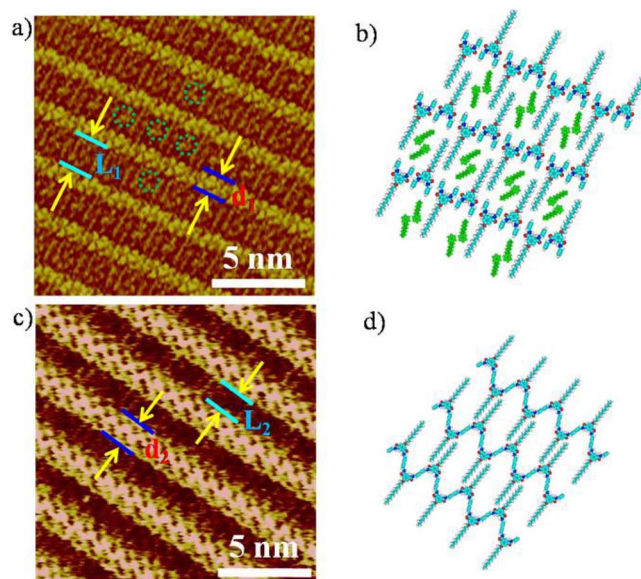


Figure 2 | (a) STM images of the self-assembled structures of the monomer DPIA at 1-phenyloctane/HOPG interface. $I_{\text{set}} = 258.1$ pA, $V_{\text{bias}} = 720$ mV. (b) A suggested molecular model corresponding to the observed structure in (a), and the green parts represent the 1-phenyloctane molecules. The green parts represent the co-adsorbed 1-phenyloctane molecules. (c) STM images of the self-assembled structures after treatment of the DPIA-covered HOPG surface. $I_{\text{set}} = 258.1$ pA, $V_{\text{bias}} = 680.5$ mV. (d) A tentative molecular model for the observed structure in (c).

(TCB) (Fig. 3(a)). Separated by the blind ditch (indicated by the colored arrows), the self-assembled structures showed row characteristics. In each row, two DPIA molecules formed into a dimer through the van der Waals interaction of their interdigitated alkoxy

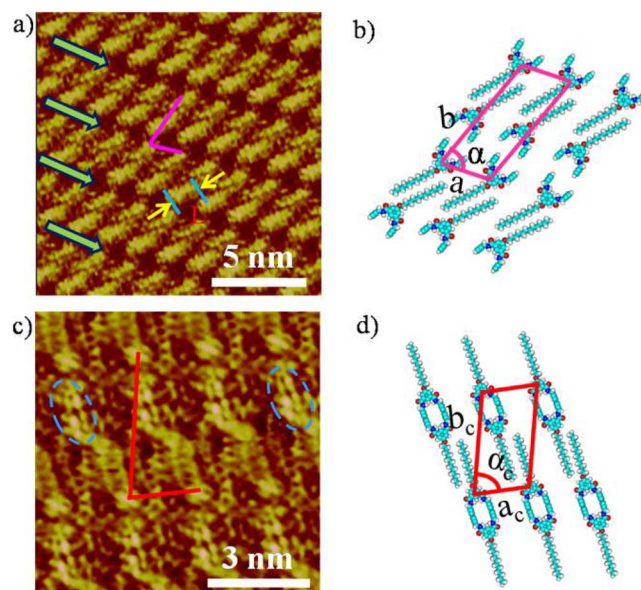


Figure 3 | (a) STM images of the self-assembled structures of the monomer DPIA at TCB/HOPG interface. $I_{\text{set}} = 300$ pA, $V_{\text{bias}} = 600$ mV. (b) A suggested molecular model corresponding to the observed structure in (a), the unit cell parameters are: $a_1 = 2.0 \pm 0.1$ nm, $b_1 = 4.0 \pm 0.1$ nm, and $\alpha_1 = (78 \pm 1)^\circ$. (c) STM images of the self-assembled structures after treatment of the DPIA-covered HOPG surface. $I_{\text{set}} = 300$ pA, $V_{\text{bias}} = 625$ mV. (d) A tentative molecular model for the observed structure in (c), the unit cell parameters are: $a_c = 2.3 \pm 0.1$ nm, $b_c = 4.2 \pm 0.1$ nm, and $\alpha_c = (71 \pm 2)^\circ$.



chains. Different from that in 1-phenyloctane, each bright dot (with the length (L) of 1.1 nm) in TCB should be ascribed to the antenna and the head as well as partial alkoxy chain of an individual DPIA molecule. Moreover, the spots nearby the colored arrows seemed bigger, which may correspond to the terminal alkyne groups. That is to say, at the HOPG/TCB interface, the terminal alkyne groups in adjacent rows organized into a face-to-face conformation as displayed in Fig. 3(b).

Since the Glaser coupling can be initiated under suitable conditions, such as in solution^{31–33} and at surface^{34–36}, the direct covalent coupling of the terminal alkyne derivative in our system will occur after the subsequent treatment of these two DPIA-covered HOPG surfaces (see the method section). Therefore, new compounds will be produced, leading to the structural transformation and formation of novel 2D supramolecular structures.

As shown in Figs. 2(c) and 3(c), the original lamellar structure of DPIA in 1-phenyloctane transformed into the extended zigzag polymers, while the close-packed structure in TCB has been replaced by the cyclic dimer (indicated by the blue dotted circles in Fig. 3(c)). It is obvious that the DPIA molecules underwent a polymerization and cyclic dimerization coupling route in 1-phenyloctane and TCB, respectively (Fig. 1), which were also proved by the attenuated total reflectance (ATR) Fourier-transform infrared (FT-IR) experiment. As presented in Fig. 4, there appeared an IR spectrum peak at 3294 cm^{-1} (blue curve), which was assigned to be the typical stretching vibration of alkyne $\text{C}\equiv\text{H}$, when using 1-phenyloctane as the solvent. However, this spectrum cannot be found in the case of the structure synthesized at 1,2,4-trichlorobenzene/HOPG interface (green curve), that is to say, there was nearly no $\text{C}\equiv\text{H}$ sign in the structure of final product synthesized at TCB/HOPG interface. So it can be confirmed that the product at TCB/HOPG surface may almost be cyclic dimers, but that at 1-phenyloctane/HOPG interface may mainly be linear polymers.

Discussion

In general, the chemical reactions result from the collisions between molecules. Compared with the free movement in solution phase, the molecules adsorbed on a solid surface are usually limited within the

two dimensions. Nevertheless, such surface confinement can promote some unique reaction pathways²³. For our system, the translational and rotational motion of molecules was ensured on the HOPG surface with poor reactivity, and the selective coupling reaction should be dominated by the solvent-dependent supramolecular self-assembly of the monomer precursors. Upon addition of the pyridine solution containing $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$ into the well-ordered structures on graphite, the terminal alkynes group coordinated with the copper ions to form a metal-organic complex, and followed by the deprotonation of the complex with the help of pyridine³². As a result, two terminal alkyne groups of the two closest DPIA precursors produced a new diacetylene unit with C-C coupling.

In 1-phenyloctane, the terminal alkyne groups of the nearest DPIA molecules organized in a shoulder-to-shoulder pattern. Therefore, the best strategy for coupling was linear polymerization along the bright band, and one DPIA molecule in this case only need tune itself in a short distance (less than 0.1 nm). Eventually, the DPIA monomers fabricated the extended zigzag polymers. After polymerization, the width (d) of the bright bands of the structure at the 1-phenyloctane/HOPG interface became wider (from $d_1 = 0.7\text{ nm}$ to $d_2 = 1.2\text{ nm}$), while the dark lamellae became shorter (from $L_1 = 2.0\text{ nm}$ to $L_2 = 1.4\text{ nm}$). On the other hand, since the terminal alkynes groups of the nearest DPIA molecules displayed a face-to-face model at TCB/HOPG interface, the proper coupling way for the monomer was cyclic dimerization to form a cyclic diacetylene. Notably, after reaction in TCB, the periodic distances along a and b directions (Fig. 3(d)) were measured to be both expanded (0.3 nm for a , and 0.2 nm for b), which may result from the movement of the terminal alkynes and also the alkyl chains of DPIA molecules (Fig. 3(d)) in the reaction process.

However, it should be noted that not all solvents were suitable to the coupling reaction of this terminal alkynes derivative on HOPG, because of the solubility of reactors and catalyst. At the same time, both the polymers and the cyclic dimers can only be obtained at the presence of pyridine and copper salt, that is to say, the homo-coupling of terminal alkyne resulted from the synergetic effect of the metal-ligand coordination and deprotonation. Besides, similarly to the on-surface polymerization of a linear alkane²³, we found such

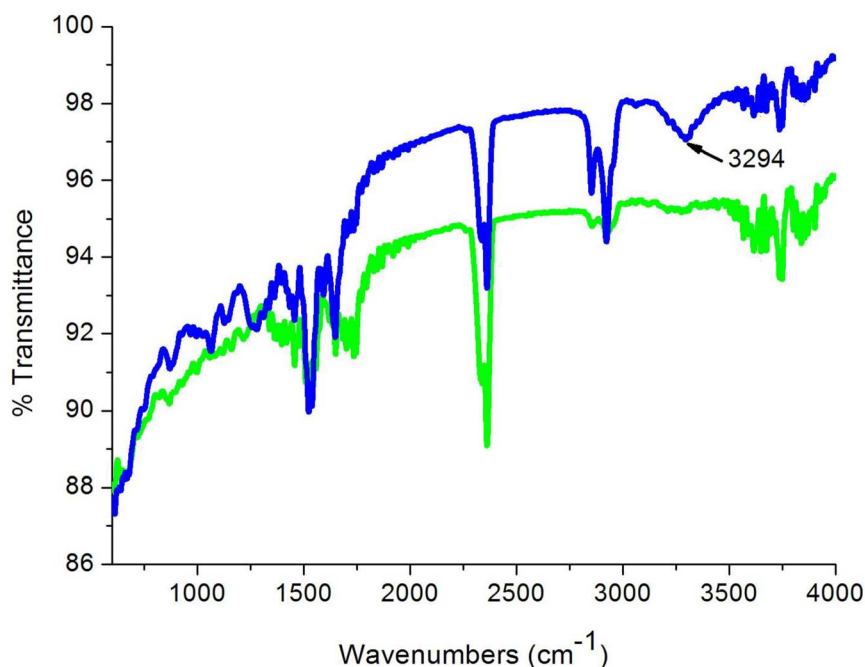


Figure 4 | ATR-FTIR spectra in the $4000\text{--}600\text{ cm}^{-1}$ region of the product synthesized at 1-phenyloctane/HOPG interface (blue curve) and TCB/HOPG interface (green curve).



ordered polymers and cyclic dimers can only be synthesized through the direct chemical coupling on graphite surface. The product synthesized in solution phase was a mixture of dimer, trimer, tetramer and pentamer (see supplementary information), and it cannot form well-ordered nanostructure on graphite surface¹². Though no information of the product by ex-situ method was probed on HOPG, it can demonstrate that the above-mentioned linear polymerization and cyclic dimerization indeed happened on surface rather than in solution, whereas the surface reaction was still an unaccountable problem until now.

In summary, the controllable and selective Glaser-coupling of a special terminal alkynes derivative was successfully realized at the HOPG/liquid interface. It has been confirmed that such selective coupling reaction resulted from the solvent-regulated 2D supramolecular assembly of the monomer precursors. In 1-phenyloctane, the monomers assembled into well-ordered lamellar structures with a reversed shoulder-to-shoulder conformation of their terminal alkynes groups. But in TCB, the precursors assembled into close-packed structures with a face-to-face organization of the terminal alkynes. As a result, the monomer underwent the polymerization and dimerization in 1-phenyloctane and TCB, respectively, after suitable treatment of the monomer-covered HOPG surfaces. Thus it can be concluded that the solvent effect on supramolecular chemistry can be delivered from 2D self-assembly to surface reactivity. Needless to say, this work provided a new strategy for functionalizing surfaces, and importantly it opened up a road from the controllable supramolecular crystal engineering to the selective chemical reactions on surface, which is of importance in supramolecular chemistry and nanotechnology.

Methods

STM measurements were performed with a Nanoscope IIIa (Bruker, USA) under atmosphere conditions. Cu(OAc)₂·H₂O (Acros company) and the solvent mentioned ((1-phenyloctane, pyridine and 1,2,4-trichlorobenzene, TCI company) were used without further purification. The STM images presented were acquired in constant current mode using a mechanically formed Pt/Ir (80/20) tip. All STM images provided were raw data without any treatment except for the flattening procession and the drift was calibrated using the underlying graphite lattice as a reference. The specific tunneling conditions including tunneling current (*I*_{set}) and sample bias (*V*_s) are given in the corresponding figure captions. The molecular models were built with a HyperChem software package. Prior to imaging, the monomer DP1A was dissolved in 1-phenyloctane or 1,2,4-trichlorobenzene (TCB) with the concentration less than 10⁻⁴ M. A droplet (0.4 μL) of solution was applied into a freshly cleaved highly oriented pyrolytic graphite (HOPG) (grade ZYB, NTMDT, Russia) surface. The sample was immediately annealed at 60°C for 15 minutes, then the STM tip was immersed in solution, and images were recorded at the liquid-solid interface. After imaging the assembled structure of the sample by STM, a drop of pyridine (0.6 μL) containing Cu(OAc)₂·H₂O (10⁻³ g/L) was added into this HOPG surface, the content of copper salt used in each surface sample is about 0.6 × 10⁻⁹ g. It should be noted that pyridine in our experiment is not only a catalytic but also a good solvent for the copper salt. Then, the samples were again annealed at 60°C for 1 h. After that, the reacted samples were washed with the ethanol and again investigated by STM at the liquid/solid interface. One thing we should mention is that we add some pure solvent (1-phenyloctane or TCB) onto the reacted samples when doing STM investigation, in order to keep liquid/solid interface. When finishing STM investigation, we performed the infrared spectra to characterize the structure difference in the on-surface synthesized product using these two solvents. Infrared spectra were obtained in the 4000–600 cm⁻¹ range using a Varian 3100 Fourier-transform infrared (FT-IR) instrument equipped with an attenuated total reflectance (ATR) attachment.

- Barth, J. V., Costantini, G. & Kern, K. Engineering atomic and molecular nanostructures at surfaces. *Nature* **437**, 671–679 (2005).
- Whitesides, G. M. & Grzybowski, B. Self-assembly at all scales. *Science* **295**, 2418–2421 (2002).
- Yang, Y. L. & Wang, C. Hierarchical construction of self-assembled low-dimensional molecular architectures observed by using scanning tunneling microscopy. *Chem. Soc. Rev.* **38**, 2576–2589 (2009).
- Furukawa, S. & De Feyter, S. Two-dimensional crystal engineering at the liquid-solid interface. *Top. Curr. Chem.* **287**, 87–133 (2009).
- Lei, S. B. *et al.* One Building Block, two different supramolecular surface-confined patterns: concentration in control at the solid-liquid interface. *Angew. Chem. Int. Ed.* **47**, 2964–2968 (2008).
- Zhang, X. M., Zeng, Q. D. & Wang, C. Molecular templates and nano-reactors: twodimensional hydrogen bonded supramolecular networks on solid/liquid interfaces. *RSC Adv.* **3**, 11351–11366 (2013).
- Barth, J. V. Molecular architectonic on metal surfaces. *Annu. Rev. Phys. Chem.* **58**, 375–407 (2007).
- Bishop, K. J. M., Wilmer, C. E., Soh, S. & Grzybowski, B. A. Nanoscale forces and their uses in self-assembly. *Small* **5**, 1600–1630 (2009).
- Zhang, X. M. *et al.* Triphenylene substituted pyrene derivative: synthesis and single molecule investigation. *J. Phys. Chem. C* **117**, 307–312 (2013).
- Xu, L., Miao, X. R., Ying, X. & Deng, W. L. Two-dimensional self-assembled molecular structures formed by the competition of van der waals forces and dipole-dipole interactions. *J. Phys. Chem. C* **116**, 1061–1069 (2012).
- Zhang, X. M. *et al.* One plus two: supramolecular coordination in a nano-reactor on surface. *Sci. Rep.* **2**, 742 (2012).
- Xu, R. L., Yang, L. & Lei, S. B. Self-assembly of conjugated oligomers and polymers at the interface: structure and properties. *Nanoscale* **4**, 4399–4415 (2012).
- Zhang, X. M. *et al.* Photo-induced polymerization and isomerization on the surface observed by scanning tunneling microscopy. *J. Phys. Chem. C* **116**, 8950–8955 (2012).
- Lafferentz, L. *et al.* Controlling on-surface polymerization by hierarchical and substrate-directed growth. *Nat. Chem.* **4**, 215–220 (2012).
- Champhess, N. R. Surface chemistry: making the right connections. *Nat. Chem.* **4**, 149–150 (2012).
- Zhang, X. M., Zeng, Q. D. & Wang, C. On-surface single molecule synthesis chemistry: a promising bottom-up approach towards functional surfaces. *Nanoscale* **5**, 8269–8287 (2013).
- Zheng, Y. B., Kiraly, B., Cheunkar, S., Huang, T. J. & Weiss, P. S. Incident-angle-modulated molecular plasmonic switches: a case of weak exciton-plasmon coupling. *Nano Lett.* **11**, 2061–2065 (2011).
- Li, Y. B. *et al.* Transformation of self-assembled structure by the addition of active reactant. *J. Phys. Chem. C* **115**, 6540–6544 (2011).
- Gourdon, A. On-surface covalent coupling in ultrahigh vacuum. *Angew. Chem. Int. Ed.* **47**, 6950–6953 (2008).
- Kanuru, V. K. *et al.* Sonogashira coupling on an extended gold surface in vacuo: reaction of phenylacetylene with iodobenzene on Au(111). *J. Am. Chem. Soc.* **132**, 8081–8086 (2010).
- Lafferentz, L. *et al.* Conductance of a Single Conjugated Polymer as a Continuous Function of Its Length. *Science* **323**, 1193–1197 (2009).
- Saywell, A., Schwarz, J., Hecht, S. & Grill, L. Polymerization on stepped surfaces: alignment of polymers and identification of catalytic sites. *Angew. Chem. Int. Ed.* **51**, 5096–5100 (2012).
- Zhong, D. *et al.* Linear alkane polymerization on a gold surface. *Science* **334**, 213–216 (2011).
- Chen, X., Engle, K. M., Wang, D. H. & Yu, J. Q. Palladium(II)-catalyzed C–H activation/C–C cross-coupling reactions: versatility and practicality. *Angew. Chem. Int. Ed.* **48**, 5094–5115 (2009).
- Farina, V., Krishnan, B., Marshall, D. R. & Roth, G. P. Palladium-catalyzed coupling of arylstannanes with organic sulfonates: a comprehensive study. *J. Org. Chem.* **58**, 5434–5444 (1993).
- Wiberg, K. B., Rablen, P. R., Rusch, D. J. & Keith, T. A. Amides. 3. Experimental and theoretical studies of the effect of the medium on the rotational barriers for n,n-dimethylformamide and n,n-dimethylacetamide. *J. Am. Chem. Soc.* **117**, 4261–4270 (1995).
- Mamdouh, W. *et al.* Solvent controlled self-assembly at the liquid/solid interface revealed by STM. *J. Am. Chem. Soc.* **128**, 317–325 (2006).
- Yang, Y. L. & Wang, C. Solvent effects on two-dimensional molecular self-assemblies investigated by using scanning tunneling microscopy. *Curr. Opin. Colloid Interface Sci.* **14**, 135–147 (2009).
- Shen, Y. T. *et al.* A foldamer at the liquid/graphite interface: the effect of interfacial interactions, solvent, concentration and temperature. *Chem. Eur. J.* **17**, 7061–7068 (2011).
- Zhang, X. M. *et al.* Solvent dependent supramolecular self-assembly and surface reversal of a modified porphyrin. *Phys. Chem. Chem. Phys.* **15**, 12510–12515 (2013).
- Xu, Y. W. *et al.* Thermal reaction of a columnar assembled diacetylene macrocycle. *J. Am. Chem. Soc.* **132**, 5334–5335 (2010).
- Stefani, H. A., Guarezemini, A. S. & Cella, R. Homocoupling reactions of alkynes, alkenes and alkyl compounds. *Tetrahedron* **66**, 7871–7918 (2010).
- Siemens, P., Livingston, R. C. & Diederich, F. Acetylenic coupling: a powerful tool in molecular construction. *Angew. Chem. Int. Ed.* **39**, 2632–2657 (2000).
- Zhang, Y. Q. *et al.* Homo-coupling of terminal alkynes on a noble metal surface. *Nat. Commun.* **3**, 1286 (2012).
- Gao, H. Y. *et al.* Glaser coupling at metal surfaces. *Angew. Chem. Int. Ed.* **52**, 4024–4028 (2013).
- Li, Q. *et al.* Self-organized and Cu-coordinated surface linear polymerization. *Sci. Rep.* **3**, 2102 (2013).

Acknowledgments

This work was supported by the National Basic Research Program of China (Nos. 2011CB932303, 2013CB934200). And the National Natural Science Foundation of China (Nos. 21073048, 51173031, 91127043) is also gratefully acknowledged.



Author contributions

Q.D.Z. and C.W. contributed to the conception and design of the experiments, analysis of the data and revise the paper. L.Y.L. carried out the synthetic experiments. S.W. constructed the molecular models. F.Y.H. optimized the experimental parameters. X.M.Z. designed and carried out the STM experiments, analyzed the data and wrote the paper.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Zhang, X.M. *et al.* Polymerization or Cyclic Dimerization: Solvent Dependent Homo-Coupling of Terminal Alkynes at HOPG Surface. *Sci. Rep.* **4**, 3899; DOI:10.1038/srep03899 (2014).



This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivs 3.0 Unported license. To view a copy of this license, visit <http://creativecommons.org/licenses/by-nc-nd/3.0>