

Tunability of Supramolecular Kagome Lattices of Magnetic Phthalocyanines Using Graphene-Based Moiré Patterns as Templates

Jinhai Mao, Haigang Zhang, Yuhang Jiang, Yi Pan, Min Gao, Wende Xiao, and H.-J. Gao*

Institute of Physics, Chinese Academy of Sciences, 100190 Beijing, China

Received June 15, 2009; E-mail: hjgao@aphy.iphy.ac.cn

A Kagome lattice is a two-dimensional (2D) pattern composed of interlaced triangles whose lattice points have four neighboring points each.¹ As the most geometrically frustrated magnetic system, the Kagome lattice has long been a toolkit for theorists,² but molecular Kagome lattices are very rare. To date, only a few organic Kagome lattices have been fabricated on surfaces through metal–organic coordination or supramolecular self-assembly of specific molecules including groups with special functions.³

Phthalocyanines (Pc's) are a family of highly stable molecules with a single metal ion in the central position of a macrocycle consisting of alternating carbon and nitrogen atoms (Figure 1a inset). Depending on the central metal ion, Pc molecules take various spin configurations, so they can be viewed as tunable single-molecule magnets.^{4–7} As a 2D honeycomb lattice of sp²-bonded carbon atoms, graphene has attracted great interest because of its novel properties and potential applications.⁸ Recently, we synthesized a highly ordered graphene monolayer (MG) on a Ru(0001) substrate.⁹ The lattice mismatch between MG and the Ru(0001) surface results in the formation of a regular moiré pattern,⁹ which might serve as a desirable template for fabrication of unique nanoarchitectures.¹⁰ However, no 2D organic Kagome lattice on graphene has been reported to date.

Herein, we report on the template-directed formation of supramolecular Kagome lattices of Pc molecules on epitaxial MG. Taking advantage of the inhomogeneous moiré pattern of MG epitaxy on Ru(0001), we observed the formation of regular Kagome lattices that duplicate the lattice of the moiré pattern of MG. Varying the central metal ion of the Pc molecule affords Kagome lattices with tunable molecular spins, providing ideal 2D model systems for studying spin frustration.

Prior to the deposition of Pc molecules, highly ordered single-crystal MG was grown on an atomically cleaned Ru(0001) surface via chemical vapor deposition (see the Supporting Information). Scanning tunneling microscopy (STM) of the as-prepared MG revealed a hexagonal moiré pattern composed of atop, fcc, and hcp regions^{9,10a} having different apparent heights, suggesting different properties for molecular adsorption.¹⁰ After vapor deposition of ~0.75 monolayer (ML) of iron(II) Pc (FePc) on MG at room temperature (RT), we observed by STM at a sample temperature of ~5 K complete coverage of MG with regular hexagonal open networks (Figure 1a) that show a pore-to-pore distance of ~3 nm, precisely matching the lattice constant of the moiré pattern of the as-prepared MG on Ru(0001).⁹ Despite the presence of Ru(0001) terraces with a typical width of several hundred nanometers, the open networks of FePc illustrate an identical lattice orientation on different terraces. Since MG epitaxy on Ru(0001) yields a continuous single crystal with a lateral size on the millimeter scale,⁹ the fact that the open networks of FePc follow the periodicity of the moiré pattern of MG highlights the key role that the MG template plays in the self-organization of FePc molecules.

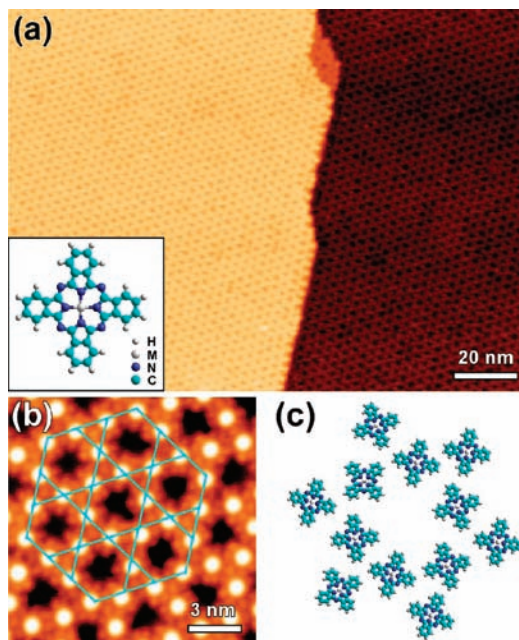


Figure 1. STM images obtained after RT deposition of 0.75 ML of FePc on MG/Ru(0001). (a) Overview image showing identical orientations of the Kagome lattice of FePc across steps of the Ru(0001) substrate. The structural model of Pc is shown in the inset. (b) Details of the Kagome lattice of FePc. A trihexagonal tiling is highlighted. The unit cell of the Kagome lattice is marked with blue lines. (c) Structural model of the Kagome lattice showing molecular orientation disorder.

Images of high magnification (Figure 1b and Figure S2 in the Supporting Information) demonstrate that the FePc molecules of the open networks occupy both the fcc and hcp regions of MG, leaving the atop regions entirely empty. Each FePc molecule is imaged as four dim lobes around a central bright spot, consistent with the molecular geometry. Each molecule is attached to four neighboring molecules, whereas three molecules form a three-branch joint, thus constructing a Kagome lattice. The distinct geometric features of a 2D Kagome lattice, namely, a semiregular trihexagonal uniform tiling, can be clearly seen after straight lines are drawn across the molecular central ions, as illustrated in Figure 1b. It is noteworthy that the Kagome lattice of FePc illustrates a molecular orientation disorder, as shown in Figure 1b. This behavior might originate from the weak, less-specific van der Waals interactions between FePc molecules, in contrast to the directional hydrogen bonds or metal–organic coordination that can guide molecular connection during the formation of Kagome lattices with ordered molecular orientation arrangements.³ The structural model of the Kagome lattice of FePc on MG is shown in Figure 1c.

The formation of open networks with the Kagome lattice on the moiré pattern of epitaxial MG on Ru(0001) was also observed for other Pc molecules, such as metal-free Pc (H₂Pc) and nickel(II) Pc

(NiPc), as shown in Figure 2. The self-assembly of Pc molecules on flat graphite and single-crystal metal surfaces has been intensely explored in the past decade. In most cases, Pc molecules are densely packed into 2D islands and overlayers, for instance, on graphite,^{11,12} Au(111),^{12,13} Ag(111), and Cu(111) surfaces.¹⁴ The formation of unique Kagome lattices of various Pc molecules on the moiré pattern of MG on Ru(0001) again demonstrates that the MG template plays a key role in the self-organization of Pc molecules. For the large Pc derivative (t-Bu)₄-ZnPc on MG, which has four *tert*-butyl spacers, a distorted Kagome lattice with slight local disorder was observed (Figure S3 in the Supporting Information), suggesting that the moiré pattern is highly selective with respect to the molecular size in forming ordered Kagome lattice.

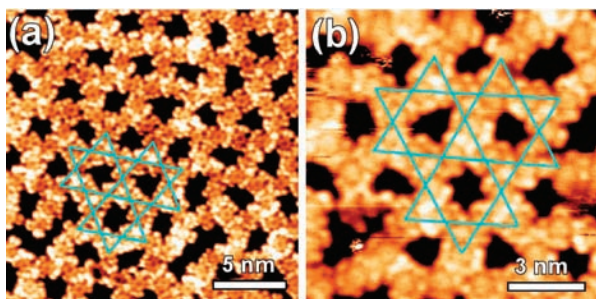


Figure 2. STM images of Kagome lattices of (a) H₂Pc and (b) NiPc molecules on MG/Ru(0001).

Usually, Pc molecules appear as featureless cross-shaped structures in STM images after direct adsorption on metal substrates^{4,5,12–14} Interestingly, submolecular-resolution STM images (Figures 1b and 2) revealing the molecular orbitals of Pc can be routinely imaged after Pc adsorption on MG, akin to the direct STM imaging of individual molecular orbitals of pentacene on NaCl(100) films and naphthalocyanine on aluminum oxide films,^{15,16} which suggests that MG can act as a buffer layer and efficiently decouple the Pc molecules from the metal substrate, preserving the intrinsic electronic properties of the molecules. This is highly desirable for investigating spin properties of Kagome lattices, as it is known that electronic coupling between Pc molecules and the metal substrates upon which they directly lie can lead to complete or partial quenching of the molecular spins.^{4,6}

It has been shown that the corrugations and lattice constants of the moiré patterns of epitaxial MG can be tuned by the underlying metal substrates,^{9,10a,17} which in turn might result in fine tailoring of the lattice constant of the Kagome lattices of Pc molecules. The possibility of tuning the molecular spins of Pc molecules and the lattice constant of the Kagome lattices, in combination with the decoupling of the magnetic molecules from the metal substrates by MG, makes the template-guided supramolecular Kagome lattices of magnetic Pc molecules on epitaxial MG excellent model systems for studying spin frustration. Investigation of the magnetic properties of such Kagome lattices is underway.

In summary, we have used STM to investigate the self-assembly of magnetic Pc molecules on epitaxial MG at the submolecular level. The formation of regular Kagome lattices that follow the lattice of the moiré pattern of MG demonstrates that MG can act as a wonderful template for fabrication of unique nanoarchitectures with remarkable properties. Varying the central metal ion of the Pc molecules potentially can afford Kagome lattices with tunable

molecular spins, providing ideal 2D model systems for studying frustration physics.

Acknowledgment. We are grateful to Y. L. Wang, H. M. Guo, and S. X. Du for helpful discussions. Financial support from the National Basic Research Program of China (973 Program Project 2009CB929103 and 2006CB921305), the National Natural Science Foundation of China, and the Chinese Academy of Sciences is gratefully acknowledged.

Supporting Information Available: Preparation of epitaxial MG on Ru(0001), details of STM experiments, and STM images of selective FePc adsorption on MG and the distorted Kagome lattices of (t-Bu)₄-ZnPc. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Syözi, I. *Prog. Theor. Phys.* **1951**, *6*, 306.
- (2) (a) Atwood, J. L. *Nat. Mater.* **2002**, *1*, 91. (b) Mekata, M. *Phys. Today* **2003**, *56*, 12.
- (3) (a) Furukawa, S.; Uji-i, H.; Tahara, K.; Ichikawa, T.; Sonoda, M.; De Schryver, F. C.; Tobe, Y.; De Feyter, S. *J. Am. Chem. Soc.* **2006**, *128*, 3502. (b) Tahara, K.; Furukawa, S.; Uji-i, H.; Uchino, T.; Ichikawa, T.; Zhang, J.; Mamdouh, W.; Sonoda, M.; De Schryver, F. C.; De Feyter, S.; Tobe, Y. *J. Am. Chem. Soc.* **2006**, *128*, 16613. (c) Zhou, H.; Dang, H.; Yi, J.-H.; Nanci, A.; Rochefort, A.; Wuest, J. D. *J. Am. Chem. Soc.* **2007**, *129*, 13774. (d) Schlickum, U.; Decker, R.; Klappenberger, F.; Zoppellaro, G.; Klyatskaya, S.; Auwärter, W.; Neppi, S.; Kern, K.; Brune, H.; Ruben, M.; Barth, J. V. *J. Am. Chem. Soc.* **2008**, *130*, 11778. (e) Shi, Z.; Lin, N. *J. Am. Chem. Soc.* **2009**, *131*, 5376.
- (4) Zhao, A.; Li, Q.; Chen, L.; Xiang, H.; Wang, W.; Pan, S.; Wang, B.; Xiao, X.; Yang, J.; Hou, J. G.; Zhu, Q. *Science* **2005**, *309*, 1542.
- (5) (a) Gao, L.; Ji, W.; Hu, Y. B.; Cheng, Z. H.; Deng, Z. T.; Liu, Q.; Jiang, N.; Lin, X.; Guo, W.; Du, S. X.; Hofer, W.; Xie, X. C.; Gao, H.-J. *Phys. Rev. Lett.* **2007**, *99*, 106402. (b) Gao, L.; Liu, Q.; Zhang, Y. Y.; Jiang, N.; Zhang, H. G.; Cheng, Z. H.; Qiu, W. F.; Du, S. X.; Liu, Y. Q.; Hofer, W. A.; Gao, H.-J. *Phys. Rev. Lett.* **2008**, *101*, 197209.
- (6) Fu, Y.-S.; Ji, S.-H.; Chen, X.; Ma, X.-C.; Wu, R.; Wang, C.-C.; Duan, W.-H.; Qiu, X.-H.; Sun, B.; Zhang, P.; Jia, J.-F.; Xue, Q.-K. *Phys. Rev. Lett.* **2007**, *99*, 256601.
- (7) Wang, J.; Shi, Y.; Cao, J.; Wu, R. *Appl. Phys. Lett.* **2009**, *94*, 122502.
- (8) For a recent review, see: Castro Neto, A. H.; Guinea, F.; Peres, N. M. R.; Novoselov, K. S.; Geim, A. K. *Rev. Mod. Phys.* **2009**, *81*, 109, and references therein.
- (9) (a) Pan, Y.; Shi, D.-X.; Gao, H.-J. *Chin. Phys.* **2007**, *16*, 3151. (b) Pan, Y.; Zhang, H.; Shi, D.; Sun, J.; Du, S.; Liu, F.; Gao, H.-J. *Adv. Mater.* **2009**, *21*, 2777.
- (10) (a) N'Diaye, A. T.; Bleikamp, S.; Feibelman, P. J.; Michely, T. *Phys. Rev. Lett.* **2006**, *97*, 215501. (b) Xiao, W.; Ruffieux, P.; Ait-Mansour, K.; Gröning, O.; Palotas, K.; Hofer, W. A.; Gröning, P.; Fasel, R. *J. Phys. Chem. B* **2006**, *110*, 21394.
- (11) (a) Ahlund, J.; Schnadt, J.; Nilson, K.; Göthelid, E.; Schiessling, J.; Besenbacher, F.; Mårtensson, N.; Puglia, C. *J. Chem. Phys.* **2007**, *601*, 3661. (b) Nilson, K.; Ahlund, J.; Brena, B.; Göthelid, E.; Schiessling, J.; Mårtensson, N.; Puglia, C. *J. Chem. Phys.* **2007**, *127*, 114702. (c) Liu, A.-Z.; Lei, S.-B. *Surf. Interface Anal.* **2007**, *39*, 33. (d) Gopakumar, T. G.; Lackinger, M.; Hackert, M.; Müller, F.; Hietschold, M. *J. Phys. Chem. B* **2004**, *108*, 7839.
- (12) Walzer, K.; Hietschold, M. *Surf. Sci.* **2001**, *471*, 1.
- (13) (a) Lu, X.; Hipps, K. W.; Wang, X. D.; Mazur, U. *J. Am. Chem. Soc.* **1996**, *118*, 7197. (b) Lu, X.; Hipps, K. W. *J. Phys. Chem. B* **1997**, *101*, 5391. (c) Cheng, Z. H.; Gao, L.; Deng, Z. T.; Jiang, N.; Liu, Q.; Shi, D. X.; Du, S. X.; Guo, H. M.; Gao, H.-J. *J. Phys. Chem. C* **2007**, *111*, 9240.
- (14) (a) Koudia, M.; Abel, M.; Maurel, C.; Bliet, A.; Catalin, D.; Mossoyan, M.; Mossoyan, J.-C.; Porte, L. *J. Phys. Chem. B* **2006**, *110*, 10058. (b) Scarfato, A.; Chang, S.-H.; Kuck, S.; Brede, J.; Hoffmann, G.; Wiessendanger, R. *Surf. Sci.* **2008**, *602*, 677. (c) Bai, Y.; Buchner, F.; Wendahl, M. T.; Kellner, I.; Bayer, A.; Steinrück, H.-P.; Marbach, H.; Gottfried, J. M. *J. Phys. Chem. C* **2008**, *112*, 6087. (d) Lackinger, M.; Hietschold, M. *Surf. Sci.* **2002**, *520*, L619. (e) Karacuban, H.; Lange, M.; Schaffert, J.; Weingart, O.; Wagner, Th.; Möller, R. *Surf. Sci.* **2009**, *603*, L39. (f) Wang, Y.; Kröger, J.; Berndt, R.; Hofer, W. *Angew. Chem., Int. Ed.* **2009**, *48*, 1261.
- (15) Repp, J.; Meyer, G.; Stojković, S. M.; Gourdon, A.; Joachim, C. *Phys. Rev. Lett.* **2005**, *94*, 026803.
- (16) Ogawa, N.; Mikaelian, G.; Ho, W. *Phys. Rev. Lett.* **2007**, *98*, 166103.
- (17) Preobrajenski, A. B.; Ng, M. L.; Vinogradov, A. S.; Mårtensson, N. *Phys. Rev. B* **2008**, *78*, 073401.

JA904907Z