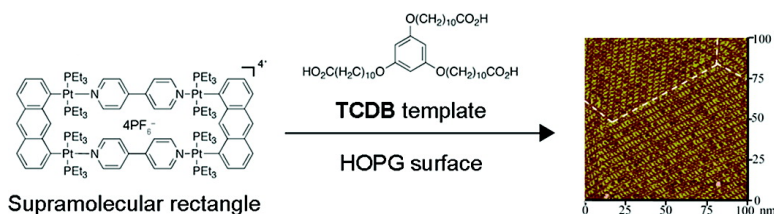


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Control of Supramolecular Rectangle Self-Assembly with a Molecular Template

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With the goal of fabricating functional materials in accordance with the so-called “bottom-up” strategy¹ comes the necessity to be able to rationally design and control molecular structure at the nanoscale. Self-assembly² and self-organization,³ which benefit from the facile formation of thermodynamically stable structures under mild conditions, have emerged as powerful tools for achieving this goal. Exhibiting control over the assembly of molecules on surfaces⁴ is especially desirable given that, when compared to the solution phase, surface-confined molecular assemblies display much greater coherence in their orientation, structure, and, ultimately, function. Previous studies have shown⁴ that both intermolecular and molecule–substrate interactions govern self-assembly processes on solid surfaces. Fine-tuning of the chemical and/or physical properties that influence these interactions can allow for control over structure and molecular distribution of molecules self-assembled on surfaces.

We have previously reported⁵ the coordination-driven self-assembly of several supramolecular rectangles, squares, and three-dimensional cages of varying shapes and sizes. These high-symmetry polygons^{5a} and polyhedra^{5b,c} have well-defined molecular architectures and are part of a new class of metal-containing supramolecular structures⁶ with promising magnetic, photophysical, and electronic properties. Earlier studies⁷ investigated the self-assembly of nanoscale supramolecular rectangles (Figure 1a) on Au(111) and highly oriented pyrolytic graphite (HOPG) surfaces and revealed surprisingly different results: a well-defined adlayer was obtained on Au(111) while a disordered adlayer was observed on HOPG. Understanding the factors that control self-assembly of these supramolecules on solid substrates is a vital prerequisite to understand and explore their potential materials applications. In an effort to exert control over the self-assembly of supramolecular rectangles on HOPG, we have employed a molecular template to trap and distribute them. With this strategy, the disorder previously observed on HOPG has been successfully regulated into an ordered self-assembly with monodispersity.

Herein, we report the regulation of supramolecular self-assembly using a triple-armed amphiphile, 1,3,5-tris(10-carboxydecyloxy)-benzene (TCDB, Figure 1a), as a molecular template. TCDB is a derivative of trimesic acid and can form two-dimensional networks on HOPG with well-defined nanoscale cavities.⁸ The coadsorption of organic molecules such as coronene and decacyclene into these cavities has been previously reported.⁸ Using TCDB as a template, nanoscale supramolecular rectangles can be well distributed and monodispersed on a HOPG surface. To the best of our knowledge, there have been no previous reports on the regulation and monodispersity of metallomacrocyclic supramolecules in 2D networks. This approach provides a new method for the facile fabrication of low-dimensionality functional materials incorporating novel supramolecular architectures.

The supramolecular rectangle⁹ and TCDB⁸ were synthesized according to literature procedures. A drop of an ethanol (Acros Organics) solution containing TCDB ($<10^{-4}$ M), rectangle ($<10^{-4}$ M), and a TCDB/rectangle mixture (1:3) was each directly deposited onto freshly cleaved, atomically flat HOPG surfaces. STM experi-

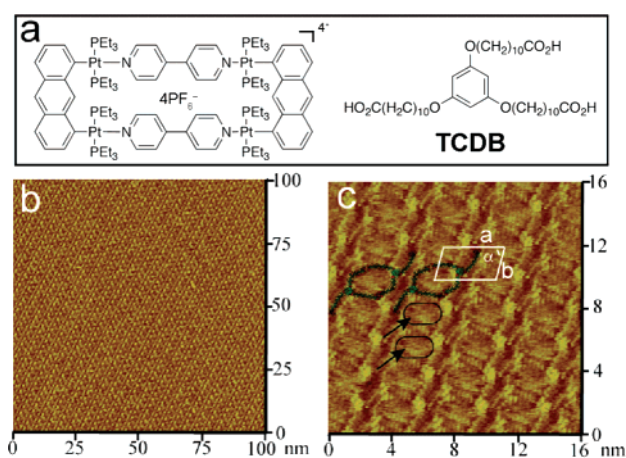


Figure 1. Chemical structures (a) of the supramolecular rectangle and TCDB; large-scale (b) and high-resolution (c) STM images of the TCDB molecules adsorbed on HOPG. The imaging conditions were $E_{\text{bias}} = 655$ mV, $I_{\text{tip}} = 620$ pA.

ments were carried out under ambient air at room temperature on a Nanoscope III STM with mechanically cut Pt/Ir tips. All STM images presented here were recorded with the constant current mode and represented without further processing.

The structure of the molecular template was first confirmed by STM. Figure 1b is a large-scale STM image of the TCDB adlayer acquired on HOPG. It is clear that a uniform and well-ordered adlayer of TCDB has been prepared, the structural details of which are revealed by the high-resolution STM image (Figure 1c). Each TCDB molecule can be recognized as one bright spot, the benzene core, and three chains, the carboxydecyloxy “arms,” consistent with previous results.⁸ An important structural feature in the image is the existence of quasi-rectangular cavities, indicated by ovals, formed by intermolecular hydrogen bonds between carboxyl functionalities of adjacent arms. As measured with STM, the size of the cavity is about 2.4×1.3 nm (± 0.2 nm). A unit cell for the adlayer is outlined in Figure 1c with $a = 4.3 \pm 0.1$ nm, $b = 2.2 \pm 0.1$ nm, and $\alpha = 75 \pm 2^\circ$. Superimposed in Figure 1c is a schematic molecular model of the hydrogen-bound, self-assembled network.

Upon depositing a drop of ethanol solution containing the supramolecular rectangle on a HOPG surface at varying concentrations, a disordered adlayer was seen by STM (Figure S2). Given the similar dimensions of the supramolecular rectangles⁹ (2.1×1.2 nm) and the cavities formed with TCDB monolayers, a TCDB/rectangle mixture was prepared to explore the possibility of using TCDB to template the self-assembly of the supramolecular rectangles on HOPG. The resulting adlayer was investigated by STM.

An ethanol solution containing a TCDB/rectangle mixture (1:3) was deposited on a HOPG surface; a large-scale STM image of the mixed adlayer is shown in Figure 2a. In contrast to the disordered adsorption of supramolecular rectangles obtained without TCDB (Figure S2), a well-ordered assembly is obtained. Several domains, indicated by dashed lines, can be seen in the image with

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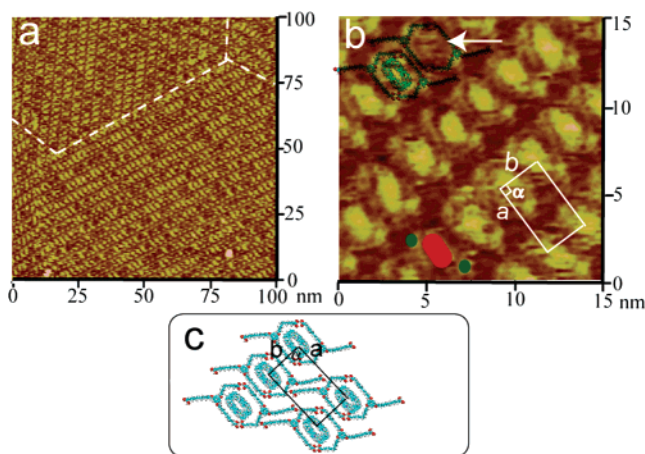


Figure 2. Large-scale (a) and high-resolution (b) STM images of the supramolecular rectangle pattern adsorbed on HOPG in a TCDB template. The imaging conditions were $E_{\text{bias}} = 600$ mV, $I_{\text{tip}} = 712$ pA. (c) Proposed structural model for the ordered adlayer.

extending molecular rows. A similar molecular arrangement exists in each domain. The appearance of the adlayer is different from both the pure TCDB adlayer and the pure rectangle adlayer. An important feature is the appearance of well-dispersed, bright, elongated ovals. The dark vacancies in the TCDB adlayer have disappeared, suggesting that the rectangles are entrapped in the molecular template, thus forming the ordered assembly. A high-resolution STM image is shown in Figure 2b, and the details of the entrapped molecules are clearly visible. The bright ovals measure 2.1×1.2 nm, consistent with the size of the supramolecular rectangles. Therefore, each bright oval corresponds to an entrapped supramolecular rectangle, indicated as a red oval in Figure 2b. Two small bright spots marked by green circles can also be observed around each oval, which correspond to the benzene cores of TCDB.⁸ Occasionally a defect where a rectangle is missing is found, as indicated by an arrow (Figure 2b). The similarity between the defect and the TCDB template (Figure 1c) can be seen, further indicating the entrapment of rectangles within the other cavities. Schematic representations of a rectangle and molecular template are superimposed in Figure 2b. On the basis of symmetry and intermolecular distance, a unit cell is superimposed on the image in Figure 2b with $a = 4.5 \pm 0.1$ nm, $b = 2.4 \pm 0.1$ nm, and $\alpha = 90 \pm 2^\circ$. The unit cell parameters closely resemble those of the TCDB networks in Figure 1c. It is important to note, however, that the angle α is changed from 75° to 90° to accommodate the entrapped rectangles. A structural model for the adlayer is proposed (Figure 2c) in good agreement with the STM results.

The successful self-assembly of supramolecular rectangles on a HOPG surface is achieved because of the complementarity between structural parameters of the TCDB adlayer and the rectangles themselves. TCDB's alkyl chains determine the size of the adlayer cavities and are able to promote the entrapment of molecules within the cavity of the TCDB template through stabilizing van der Waals interactions.⁸ No additional noncovalent interactions could be observed between TCDB and the rectangle in solution-phase studies (Figure S5–S7). The long alkyl chains of TCDB allow it to form a 2D structure with tetragonal cavities, which differ from related triply symmetric benzoic acid templates that form honeycomb networks.¹⁰ The flexibility of the chains enables the TCDB template to undergo minor structural changes without disrupting its underlying stability, such as the change in α from 75° to 90° to accommodate the entrapped rectangles. The mechanism of assembly is believed to involve formation of the TCDB adlayer followed by

entrapment of the rectangles. Experiments carried out in the presence of phenyloctane support this conclusion. The combination of geometric parameters and intermolecular and molecule–surface interactions promotes the template-directed self-assembly and monodispersion of supramolecular rectangles on a HOPG surface.

To explore the scope of this method we introduced a supramolecular square^{5b} (2.2×2.2 nm) to the TCDB template. However, all TCDB cavities were found to be empty, and phase separation (Figure S3) was observed between the supramolecular square and the template. This observation further highlights the importance of the geometric, spatial, and intermolecular interactions that govern assembly. It is likely that the design of a molecular template that maximizes structural complementarity and thermodynamic stability of a template/square mixture will facilitate self-organization and monodispersion, resulting in a new array with an ordered structure.

In summary, we have successfully controlled the self-assembly and monodispersion of a well-ordered array of supramolecular rectangles on HOPG using a TCDB template. STM images reveal the details of the regulated organization. Although supramolecular rectangles do not form a well-ordered adlayer on a HOPG surface alone, the TCDB template enables the self-organization of a new desirable supramolecular structure to be achieved. This method provides a facile approach to surface modification and the fabrication of 2D assemblies. Further studies on these and related systems are underway.

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Supporting Information Available: Complete refs 4d and 10b, supramolecule chemical structures, STM images, deposition procedures, and solution NMR studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Seeman, N. C.; Belcher, A. M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 6451. (b) Balzani, V.; Credi, A.; Venturi, M. *Chem.–Eur. J.* **2002**, *8*, 5524.
- (2) (a) Lindsey, J. S. *New J. Chem.* **1991**, *15*, 153. (b) Philp, D.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154. (c) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705.
- (3) (a) Orr, G. W.; Barbour, L. T.; Atwood, J. L. *Science* **1999**, *285*, 1049. (b) Storhoff, J. J.; Mirkin, C. A. *Chem. Rev.* **1999**, *99*, 1849. (c) Lehn, J.-M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4763. (d) Lehn, J.-M. *Science*, **2002**, *295*, 2400.
- (4) (a) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533. (b) Whitesides, G. M.; Boncheva, M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4769. (c) Hipps, K. W.; Scudiero, L.; Barlow, D. E.; Cooke, M. P., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 2126. (d) Stepanow, S.; et al. *Nat. Mater.* **2004**, *3*, 229. (e) De Feyter, S.; De Schryver, F. C. *J. Phys. Chem. B* **2005**, *109*, 4290. (f) Wan, L. J. *Acc. Chem. Res.* **2006**, *39*, 334.
- (5) (a) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502. (b) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (c) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972.
- (6) (a) Schwab, P. F. H.; Levin, M. D.; Michl, J. *Chem. Rev.* **1999**, *99*, 1863. (b) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022. (c) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759. (d) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 369. (e) Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2005**, *38*, 349.
- (7) (a) Gong, J. R.; Wan, L. J.; Yuan, Q. H.; Bai, C. L.; Jude, H.; Stang, P. J. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 971. (b) Yuan, Q. H.; Wan, L. J.; Jude, H.; Stang, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 16279.
- (8) Lu, J.; Lei, S. B.; Zeng, Q. D.; Kang, S. Z.; Wang, C.; Wan, L. J.; Bai, C. L. *J. Phys. Chem. B* **2004**, *108*, 5161.
- (9) Kuehl, C. J.; Huang, S. D.; Stang, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 9634.
- (10) (a) Griessl, S.; Lackinger, M.; Edelwirth, M.; Hietschold, M.; Heckl, W. M. *Single Mol.* **2002**, *3*, 25. (b) Ruben, M.; et al. *J. Am. Chem. Soc.* **2006**, *128*, 15644. (c) Griessl, S. J. H.; Lackinger, M.; Jamitzky, F.; Markert, T.; Hietschold, M.; Heckl, W. M. *J. Phys. Chem. B* **2004**, *108*, 11556.

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