SUPPORTING INFORMATION

The control of supramolecular rectangle self-assembly with a molecular template

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I. Chemical structures and sizes of the supramolecular rectangle and square.

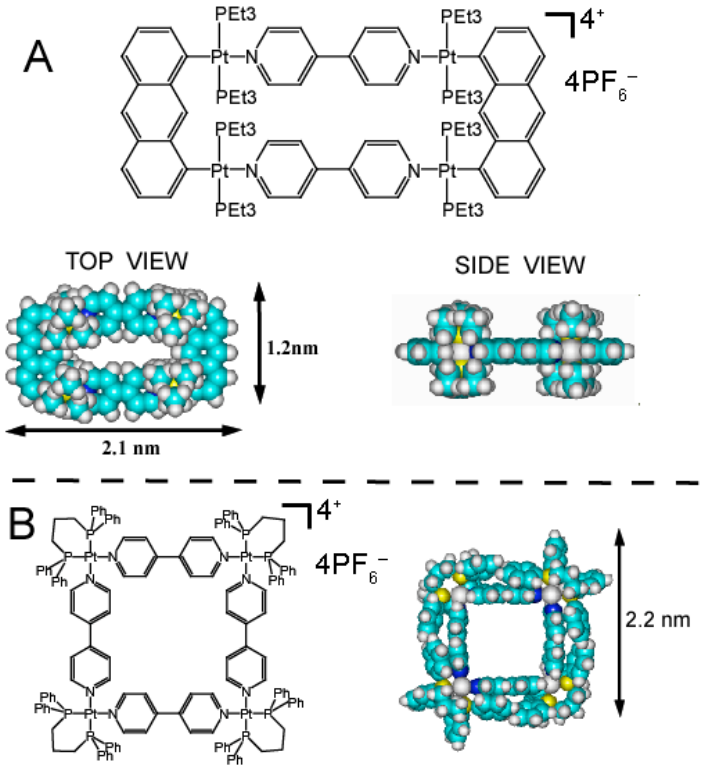

Figure S1. Chemical structures and space-filling/ball-and-stick models of the (A) supramolecular rectangle and (B) supramolecular square.

II. Sample preparation and supplemental STM images.

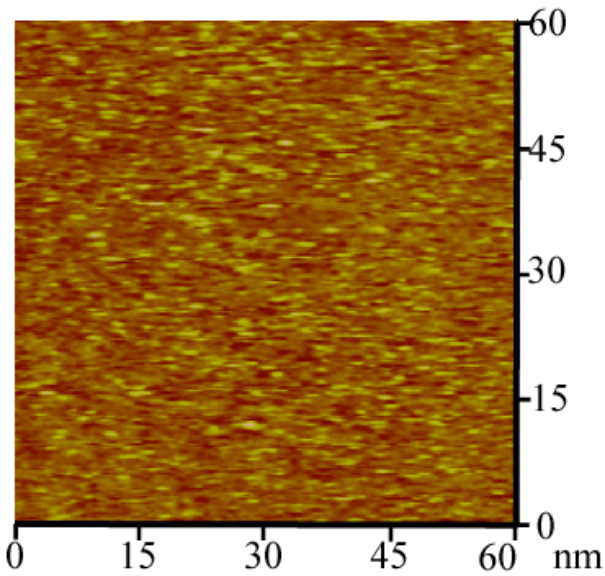

Figure S2. A disordered adlayer of the supramolecular rectangle adsorbed on HOPG

(1) Procedure 1: A drop of ethanol solution containing only TCDB was deposited on

HOPG, resulting in the self-assembly in Figure 1 of the paper. However, when a drop of ethanol solution containing only rectangle was deposited on HOPG, the disordered adlayer shown in Figure S2 was observed.

(2) Procedure 2: A drop of ethanol solution containing TCDB and rectangle was deposited on HOPG, resulting the self-assembly in Figure 2 of the paper.

(3) Procedure 3: After a TCDB adlayer was achieved on HOPG by procedure (1), a drop of ethanol solution containing rectangles was added on the surface modified by TCDB. However, no template-regulated organization was observed. The TCDB template became unclear and clusters could be seen on HOPG or template surface. In this case the previously formed well-ordered TCDB molecules were re-dissolved upon addition of ethanol solvent containing the supramolecular rectangle. However, the TCDB molecules and rectangles could not mix well in the short time before evaporation of the ethanol solvent, resulting in a disordered adlayer.

(4) Procedure 4: In order to understand the formation of the template-regulated rectangle organization, we carried out an experiment by placing a drop of phenyloctane solution containing both TCDB and rectangle. The phenyloctane solvent was present throughout the whole STM experiment. An ordered TCDB template was clearly observed in the phenyloctane solution and is shown in Figure S3, indicating a preferred adsorption of TCDB. The high resolution STM image (not shown here) showed the same structure of TCDB adlayer on HOPG prepared by procedure 1. In Figure S3, the adlayer is composed of only TCDB although several bright spots can be seen on the adlayer and clusters exist in the TCDB domain boundary. We imaged the surface for at least 40 min. No rectangle could be observed in the TCDB template. However, when the substrate was annealed at 100 °C for 30 min., the phenyloctane solvent was completely evaporated. Then we acquired STM images again on the same surface as that in Figure S3. Figure S4a and S4b are a large-scale STM image and a high resolution STM image, respectively. The images clearly show the existence of

rectangle in the TCDB template. From these results we came to the following conclusion: when a solution containing TCDB and rectangle is deposited on HOPG, the TCDB first forms an organized adlayer. Following adlayer formation, and driven by dispersion forces between the guest molecule and host template, rectangles are then entrapped in the cavities of TCDB template.

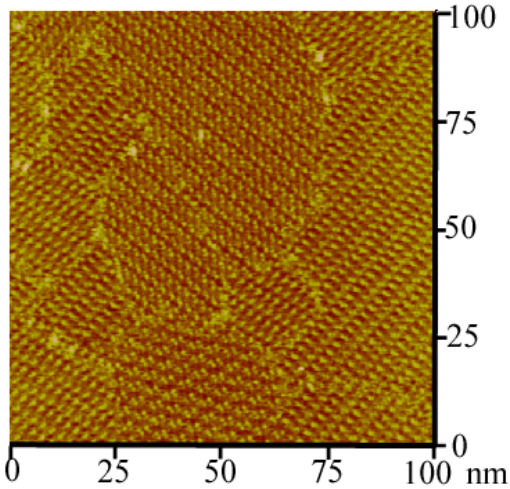

Figure S3 TCDB layer in phenyloctane before annealing

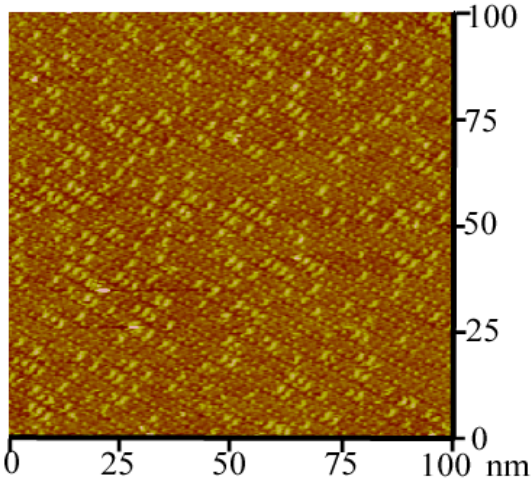

Figure S4a Rectangles on TCDB template

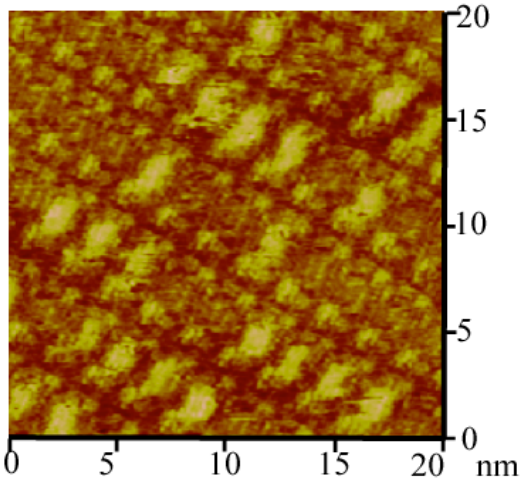

Figure S4b Rectangles on TCDB template

III. ^{1}H and ^{31}P NMR solution studies of TCDB and supramolecular rectangle

^{1}H and ^{31}P NMR spectroscopic studies were undertaken to investigate what interaction(s), if any, exist between the TCDB template molecule and the supramolecular rectangle in solution. Three separate solutions (all in a 2:1 mixture of CD_3OD/CD_3CN) were prepared: (1) a 2.7 mM solution of the supramolecular rectangle; (2) a 2.7 mM solution of the TCDB template; and (3) a 2.7 mM solution of a 1:1 mixture of supramolecular rectangle and TCDB template. The resulting spectra showed no significant interaction between the template molecule and the supramolecular rectangles in solution, as evidenced by the fact that no signals associated with TCDB or the rectangle displayed any shifts in their ^{1}H NMR spectra (Figures S5 and S6) or ^{31}P spectra (Figure S7) upon mixing.

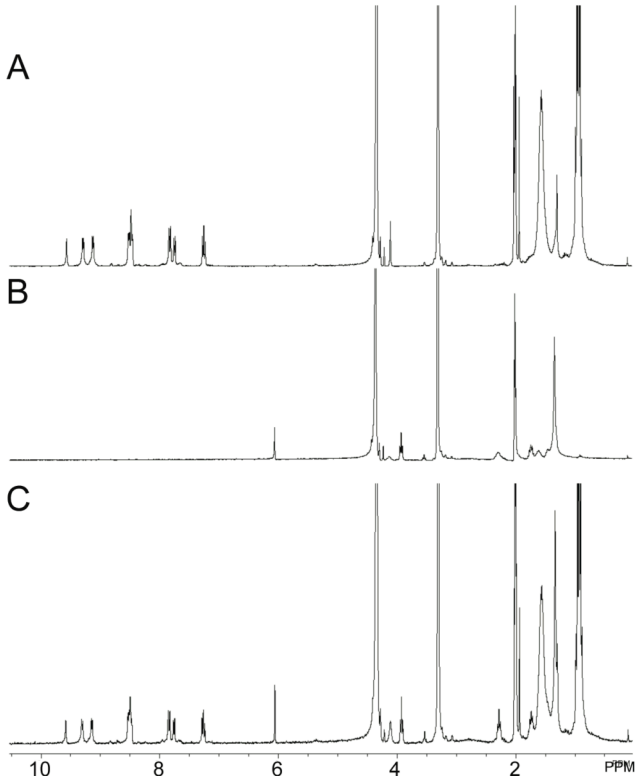

Figure S5. ^{1}H NMR spectra (2:1 CD_3OD/CD_3CN) of (A) supramolecular rectangle, (b) TCDB, and (C) a 1:1 mixture of TCDB and rectangle showing no observable shifts in proton signals associated with either compound.

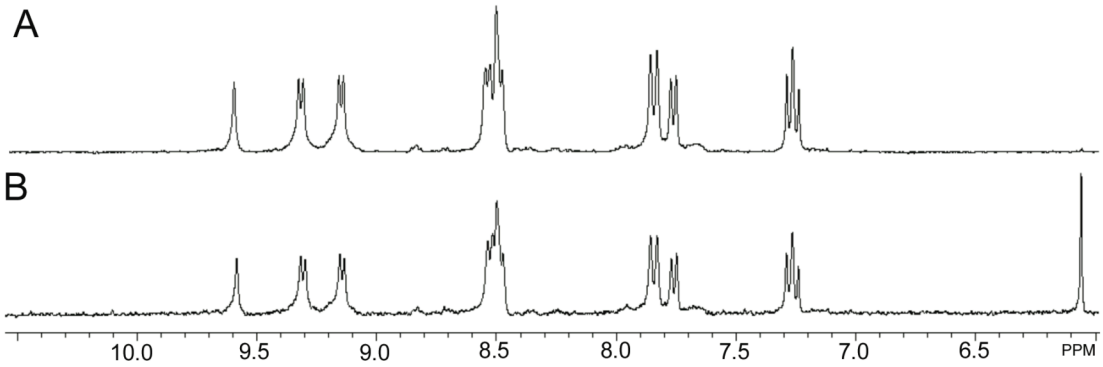

Figure S6. Expanded view of the aromatic section of the ^{1}H NMR spectra from Figure S5 of (A) the supramolecular rectangle and (B) the 1:1 mixture of rectangle and TCDB.

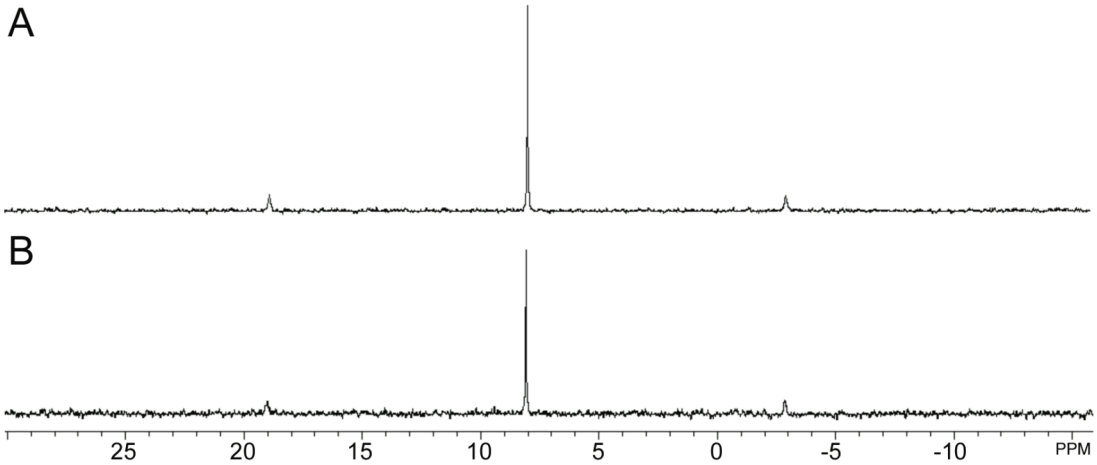

Figure S7. ^{31}P NMR spectra (2:1 CD_3OD/CD_3CN) of (A) supramolecular rectangle and (B) a 1:1 mixture of the rectangle and TCDB displaying no observable shift in the phosphorous signal upon mixing.

IV. Supramolecular squares.

When a drop of ethanol solution containing TCDB and square was deposited on HOPG a phase separation is observed in the adlayer as shown in Figure S8.

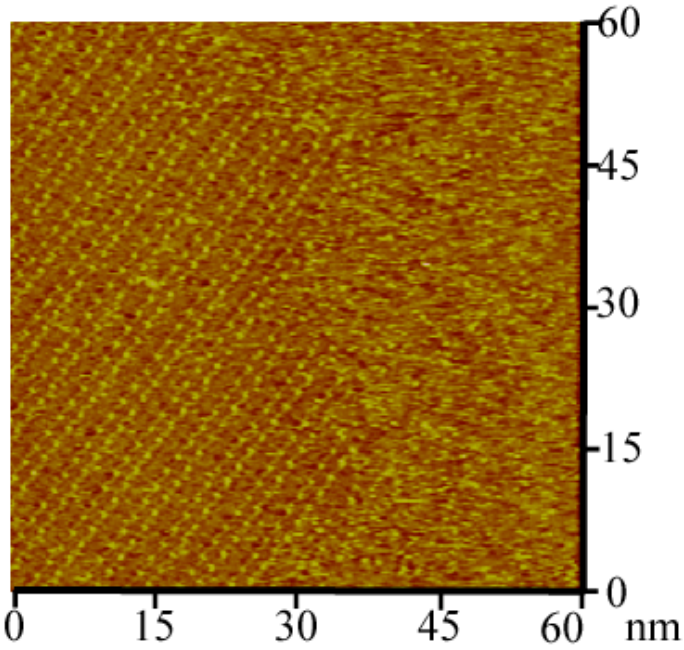

Figure S8. Phase separation between supramolecular square and TCDB. On the left part of this image is a well-ordered adlayer of TCDB, while on the right part is a disordered adlayer of supramolecular square.

To understand the geometric effect of TCDB on the dispersion of square molecules, we also carried out STM experiment in phenyloctane. A drop of phenyloctane solution containing TCDB and square was deposited on HOPG. The phenyloctane solvent persisted throughout the STM experiment. An ordered TCDB template identical to that shown in Figure 1 was observed in the phenyloctane solution, indicating a preferred adsorption of TCDB. Figure S9a is the STM image showing the TCDB template without the appearance of square. However, after annealing the sample at 100 °C for 30 min., the STM image in Figure S9b was acquired. Although the TCDB template is partially seen, no dispersion of square molecules can be observed. Intriguingly, disordered domain and clusters in domain boundaries appear in Figure S9b. This image is consistent with that in Figure S8 of the supporting information in previous version. The results demonstrate the importance of geometric parameters when templating the self-assembly of such metallacycles onto a TCDB adlayer. The disordered domains and clusters corresponded to square molecules or the co-existence of square and TCDB. The squares may also sit on the top of TCDB template.

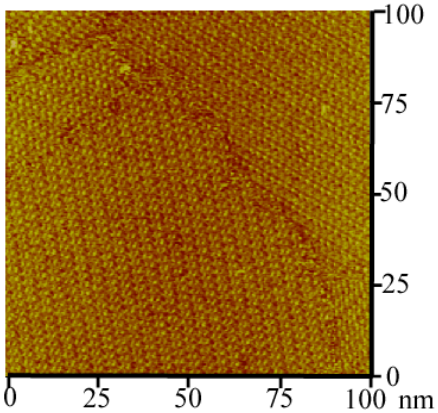

Figure 9a TCDB layer in phenyloctane before annealing

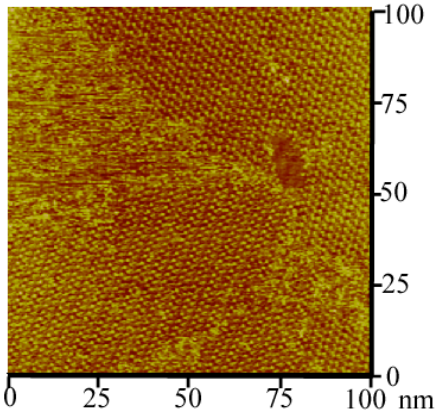

Figure 9b Disordered domain in phenyloctane after annealing

V. Complete author lists for references 4(d) and 10(b).

4. (d) Stepanow, S.; Lingenfelder, M.; Dmitriev, A.; Spillmann, H.; Delvigne, E.; Lin, N.; Deng, X. B.; Cai, C. Z.; Barth, J. V.; Kern, K. *Nature Mater.* **2004**, *3*, 229.

10. (b) Ruben, M.; Payer, D.; Landa, A.; Comisso, A.; Gattinoni, C.; Lin, N.; Collin, J. P.; Sauvage, J. P.; De Vita, A.; Kern, K. *J. Am. Chem. Soc.* **2006**, *128*, 15644.