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カテコールが配位したチタンフタロシアニン錯体による
チタニアフタロシアニン二次元構造の制御

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Controlling sublayer structure of titanyl phthalocyanines with
adsorbed catechol-liganded titanium phthalocyanines

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[Introduction] Axial substitution of metal phthalocyanines (Pcs) shows adsorbed structures that are different and more complex than for the metal free compound.^{1,2} In this report, we contrast the structures of titanyl phthalocyanine (TiOPc) and titanium phthalocyanine axially bounded to a catechol ligand (TiPcat), as shown in Figure 1, at the interface between graphite and octylbenzene solution.

[Experimental Section] Highly oriented pyrolytic graphite (10 mm × 10 mm by 1 mm thick) was purchased from SPI Supplies. TiOPc was obtained from Aldrich (40,455-1, CAS 26201-32-1) and used without further purification. TiPcat was synthesized according to a modified procedure reported earlier.^{3,4} More details on the synthesis are reported elsewhere.⁵ Pcs were dissolved in chloroform. A 6 μl droplet of the prepared chloroform solution then was put on a freshly cleaved graphite substrate. The amount of Pcs deposited on each substrate was controlled by the number of droplets and the concentration of the solution. Typically, two droplets (~11 μl total) of a 1.6 μM solution were used to prepare a near-monolayer on regions of the substrate. This corresponds to an average coverage of 0.54 molecules/nm². In the case of binary adsorption, each species was 0.8 μM with an equal molar mixture in solution. The droplets spread out onto an approximately circular

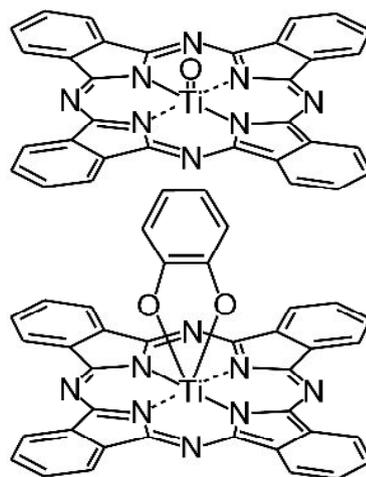


Figure 1: Structural model of titanylphthalocyanine (TiOPc upper) and titanium phthalocyanine with a catechol ligand (TiPcat, lower).

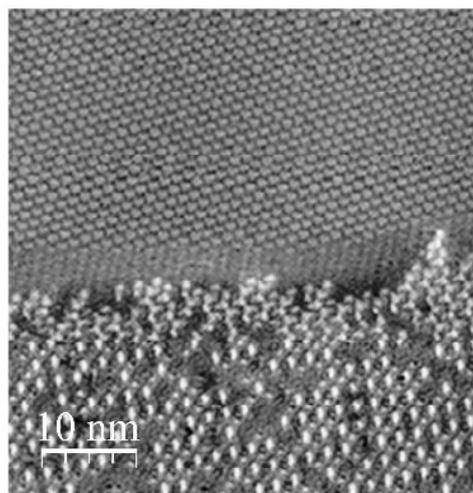


Figure 2: STM image of TiOPc (upper domain) and TiPcat on TiOPc layer (lower domain).

region at *ca.* 5 mm diameter. The deposited sample then was dried under Ar gas flow for 3 minutes. Finally, a droplet of *n*-octylbenzene (Alfa Aesar L03086, CAS 2189-60-8) was put on the sample surface. The surface was imaged through the octylbenzene layer in order to obtain stable STM images. It is noted that STM imaging without using *n*-octylbenzene is possible but very difficult. With dried samples, the Pcs on the sample surface frequently stick onto the scanning STM tip, causing unstable imaging. Moreover, for molecular coverage in excess of a monolayer, or less than 0.7 monolayer, one obtains unstable images because of Pc movement during the scan.

[Results and Discussion] Figure 2 shows the scanning tunneling microscope (STM) image at 1:1 molar mixture of TiOPc and TiPcat. The upper domain is a TiOPc monolayer with a hexagonal structure. The lower domain consists of TiPcat molecules adsorbed on an underlying TiOPc monolayer but the outermost TiPcat molecules formed a square-like structure. As shown in the STM image, co-adsorption of TiOPc and TiPcat forms bilayer structure with TiOPc molecules in the first layer and TiPcat in the second layer. The structure of the TiOPc sub layer changed into a rectangular structure and the TiPcat molecules sit on the hollow site of the TiOPc sub layer, which was confirmed with the images as shown in Figure 3. Another image with a different tip condition (Figure 4) showed the orientation of outermost TiPcat molecules with the catechol ligand up. This adsorbate mediation of surface structure is a useful phenomenon to control two dimensional structure where the fraction of an outermost layer converts the under layer structure.

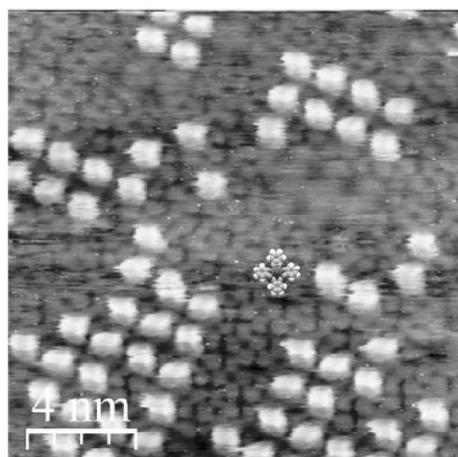


Figure 3: STM image of TiPcat on TiOPc layer. TiOPc molecular model is imposed in the image.

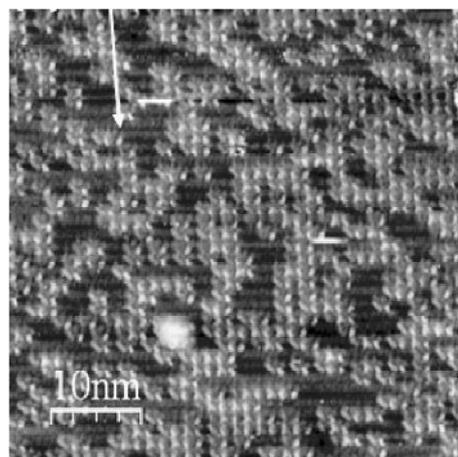


Figure 4: STM images of TiPcat on TiOPc monolayer on graphite. The $[11\bar{2}0]$ directions of the substrate graphite is shown with an arrow.

- 1) S. Kera, A. Abduaini, M. Aoki, K.K. Okudaira, N. Ueno, Y. Harada, Y. Shirota, and T. Tsuzuki, *J. Elec. Spec. Relat. Phenom.* **88-91**, 885 (1998).
- 2) U. Mazur, K.W. Hipps, and S.L. Riechers, *J. Phys. Chem. C*, **112**, 20347 (2008).
- 3) M. Barthel and M. Hanack, *J. Porph. Phthal.* **4**, 635 (2000)
- 4) M. Barthel, D. Dini, S. Vagin, and M. Hanack, *Eur. J. Org. Chem.* 3756 (2002).
- 5) T. Takami, A. Clark, R. Caldwell, U. Mazur, and K.W. Hipps, *Langmuir*, DOI:10.1021/la1020127 (2010).