How molecules accommodate a 2D crystal lattice mismatch: an unusual 'mixed' conformation of tetraphenylporphyrin

Jonathan P. Hill,*ac Yutaka Wakayamab and Katsuhiko Arigac

Received 23rd June 2006, Accepted 28th July 2006 First published as an Advance Article on the web 8th August 2006 DOI: 10.1039/b608935f

Tetraphenylporphyrin molecules adopt unusual unsymmetrical conformations in order to achieve perfect order at the region between differing 2-D crystal phases.

The behaviour of molecules when adsorbed at metallic surfaces is of importance for their potential use as components in electronic devices.^{1,2} From this point of view, porphyrinic molecules have been subjected to intense scrutiny because of their high chemical and thermal stabilities,³ multiple stable oxidation states⁴ and synthetic flexibility in relation to their adsorbed structures.⁵ In particular, scanning tunneling microscopy (STM) studies of porphyrins substituted with 3,5-di-tbutylphenyl groups (i.e. 5,10,15,20-tetrakis(3,5-di-t-butylphenyl)porphyrin, TDtBPP, Scheme 1) have illustrated that the physical shape of the molecule strongly influences their properties⁶ and their supramolecular arrangement at metallic surfaces.⁷ These features help to determine the use of TDtBPP and similar molecular species as interfacial or electronic materials or in single molecule devices. The lessons learnt from the study of TDtBPP molecules can be transferred, to some extent, to other molecular systems containing similar substituents attached to large aromatic moieties.

The term 'lattice mismatch' is more commonly used in solid state chemistry where it is applied to differences in lattice parameters between inorganic materials especially in epitaxially-grown thin film multilayer systems.⁸ It is important since it can have a serious effect on the performance of devices prepared in this way although the effect is not always deleterious.⁹ In this work we have used the term to describe the mismatch between lattice parameters of 2-D molecular monolayer self-assemblies. We found that molecules of a particular compound can exist in a variety of self-assembled structures when adsorbed at a metal surface and, while this in itself is not unique, the mechanisms by which the molecules' different self-assemblies compensate for the incommensurateness of lattice parameters of their 2-D crystal structures are remarkable.

At the outset of this work, we sought to study the supramolecular and conformational adaptation of a TDtBPP derivative when adsorbed at the Cu(111) surface. In this case, TDtBPP is substituted with hydroxyl groups in the *para* positions of its phenyl substituents giving 5,10,15,20-tetrakis(3,5-di-*t*-butyl-4-hydroxyphenyl) porphyrin, TDtBHPP, †as depicted in Scheme 1.

While the effects of variation of the functional groups at the periphery of the porphyrin molecule on its 2-D crystal structure are relatively well appreciated,⁵ the more subtle influence of electron-donating groups at the periphery of the molecule on the molecular structure and hence on its self-assembled structures has not been investigated in any depth.¹⁰ For this reason, we selected TDtBHPP in which electron-donating hydroxyl groups are ostensibly prevented from intermolecular interactions by positioning between bulky t-butyl groups, while delocalization of electron density over the molecule is permitted by virtue of their substituent 4-position. This is of importance because changes in the molecular structure upon adsorption may enhance or reduce the electronic communication between the meso-substituents and the porphyrin macrocycle depending on the intermolecular packing and molecule-surface interactions. In addition, the presence of the electron-donating groups influences the surface assembly of these molecules by lowering the barrier to rotation at the bond between the porphyrin macrocycle and its phenyl substituents thus improving the stability of conformations with small dihedral angles at this position.

Within its crystals, the phenyl substituents of TDtBHPP subtend a dihedral angle of 60° ,¹¹ and it is the variation of this angle, together with alterations to the conformation of the tetrapyrrole macrocycle, that are significant in relation to structure and properties of these molecules when adsorbed at a metal surface.

Fig. 1a shows the TDtBHPP molecules at submonolayer coverage. Initial aggregation occurs predominantly at substrate step edges. Subsequently, domains are formed whose structure



Scheme 1 Chemical structures of 5,10,15,20-tetrakis(3,5-di-*t*-butyl phenyl)porphyrin, TDtBPP, and 5,10,15,20-tetrakis(3,5-di-*t*-butyl-4-hydroxyphenyl)porphyrin, TDtBHPP.

^a International Center for Young Scientists, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan. E-mail: Jonathan.Hill@nims.go.jp; Tel: +81 29 860 4832

^b Nanomaterials Assembly Group, National Institute for Materials Science, 1-1 Naniki, Tsukuba, Ibaraki, 305-0044, Japan

^c Supermolecules Group, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan



Fig. 1 STM imaging of TDtBHPP at submonolayer coverage. (a) 180 nm \times 180 nm, $I_t = 100$ pA, $V_s = +1.0$ V, (b) 70 nm \times 70 nm, $I_t = 80$ pA, $V_s = +1.2$ V. Regions containing a new packing motif are indicated by yellow arrows.

is similar to those already reported for this type of molecule.¹² That is, a hexagonally packed formation where the porphyrin molecules adopt a conformation in which the phenyl substituent groups and tetrapyrrole macrocycle approach coplanarity as depicted in the left hand side of Fig. 2c. In STM images, this conformation is composed of eight bright spots, corresponding to the t-butyl groups, surrounding two parallel oblong protrusions, which are due to the β -positions of opposing pyrrole rings. Only these β -positions can be observed since rotation of the phenyl substituents to a low dihedral angle (in response to surface adsorption) causes distortion of the tetrapyrrole core to a saddle shape (see Fig. 2d). A notable feature emerging from this is a dark line (between the two parallel protrusions) and this can be used to observe the relative orientation of the molecules within a surface-adsorbed structure.¹² Apart from the more common hexagonal structure, an unusual and previously unreported structural motif is present and is indicated in Fig. 1b. Fig. 2a shows the higher magnification topography of the commonly observed hexagonal packing structure while Fig. 2b shows that of another site revealing the internal structure of the new domain type.

Further inspection reveals several interesting features of the structure. First, the TDtBHPP molecules are arranged in a distorted square packing. In the assembly depicted, there is an additional but slight irregularity in the structure, which may be due to the small size of this 2-D domain. Second, the aforementioned saddle deformation of the porphyrin macrocycle, caused by a low dihedral angle between phenyl groups and macrocycle, results in a dark line within the topography of these molecules. Most commonly the orientation of this dark line is not ordered until annealing has been applied.¹² Orientation of the molecules with respect to the macrocyclic saddling (and resulting dark lines) is uniform within the unusual assembly with the 'saddle line' coinciding with a mirror plane of the deformed TDtBHPP molecule. This uniformity is a direct result of the conformation of the meso-phenyl substituents and is due to steric factors as illustrated. In Fig. 2d, the molecular plan view contains mauve arrows which indicate the direction of movement of t-butyl groups when the phenyl groups twist away from perpendicularity in the case of the TDtBHPP molecules involved in the unusual packing motif (i.e. towards alternating \pm dihedral angles).



Fig. 2 STM image of (a) hexagonally packed TDtBHPP molecules, 20 nm \times 20 nm, $I_t = 80$ pA, $V_s = +1.0$ V, and (b) the unusual packing arrangement for TDtBHPP, 20 nm \times 20 nm, $I_t = 80$ pA, $V_s = +1.0$ V. Green octagons highlight the hexagonal packing while, for the unusual packing, blue and red shapes highlight the interior and exterior conformations, respectively, (c) (and (d)) Colored symbols used to denote the respective molecular conformations of TDtBHPP formed at the Cu(111) surface. (d) Model of the molecular conformation involved at the interior of the novel 2-D assembly. Note, that the alternate twisting of the phenyl substituents permits a larger aspect ratio and introduces a mirror symmetry plane as indicated (dotted line). The mirror plane coincides with the dark line appearing between the bright contrast of opposing β -pyrrole positions. In the plan view, mauve shaded areas represent the parts of the molecule observable in the STM image. Blue and red arrows in the side view indicate the phenyl group rotation and points of steric interaction between *t*-butyl and β -pyrrole positions, respectively.

However, the most remarkable feature of this supramolecular phase is an apparent 'mixed' conformation of the molecules at the periphery of the assembly. That is, phenyl substituents of molecules at the assembly exterior more closely approach coplanarity with the molecular mean plane (and therefore approach a parallel arrangement relative to the surface) while those involved within the assembly are constrained against this. Using our own model and also based on previous estimates, which used the aspect ratio of individual molecules to assign dihedral angles,⁷ we assigned a value of approximately 45° for molecules involved in the novel packing motif. However, their large aspect ratio also indicates alternating dihedral angles of $\pm 45^{\circ}$. Molecules with apparent 'mixed' conformations at the fringes of the assembly cannot be assessed using this rationale. For those molecules, phenyl substituents at the interior of the assembly are likely to have similar dihedral angles (*i.e.* $\sim 45^{\circ}$) while those at the exterior appear to have much smaller dihedral angles between them and the porphyrin macrocycle. The substituents at the periphery of the assembly present STM topographies akin to those bearing angles of 10° - 20° .



Fig. 3 STM image of the structure at the interface between the new phase and the common hexagonal phase of TDtBHPP, 35 nm \times 35 nm, $I_t = 80$ pA, $V_s = \pm 1.0$ V. Yellow arrows indicate the phase boundary. Molecules of differing geometry are highlighted: green (approximately planar), red (mixed conformation) and blue (denotes $\pm 45^{\circ}$ conformation).

One significant feature of the substituent mixed conformation of the porphyrin molecule is that it further permits its assemblies to exist in contact with other supramolecular assemblies (of differing domain structure) and this is illustrated by the STM image in Fig. 3. The boundary region is characterized by a highly ordered structure, which is due solely to the existence of the mixed molecular conformation of TDtBHPP. No dynamic processes were observed within this supramolecular assembly although the phase boundary region suggests that a transition



Fig. 4 Model of the interface structure. L.H.S.: molecular models, space filling representations of the three non-identical molecular conformations and their relationships with the STM images and designated colored symbol (a), symmetrical, phenyl substituent dihedral angle = $10^{\circ}-20^{\circ}$, (b) conformationally unsymmetrical TDtBHPP, (c) phenyl substituent dihedral angle = $\pm 45^{\circ}$. R.H.S.: (d) packing model. The yellow ladder denotes the respective 2D unit cell edges with $\theta_1 = 65^{\circ}$, $\theta_2 = 78^{\circ}$.



Fig. 5 Model of the interlocking hexagonal/square packing in the 2-D crystal structure of TDtBHPP on Cu(111).¹¹ Yellow grid indicates the smooth transformation of the 2-D unit cell from square to trigonal symmetry.

could occur and a lesser change in the assembly structure would be required than in a previous case where an actual phase transition was observed using STM.¹¹ A model of the packing of the domain is shown in Fig. 4 together with space-filling representations of the three differing molecular conformations present. In Fig. 4 the yellow grid represents the 2D unit cells and reveals a transformation from hexagonal (trigonal) to a quasisquare packed structure. This transformation is smooth because of mediation by the mixed conformation molecules at the phase boundary.

Well structured crystal–crystal interfaces in 2D self-assemblies are rare and non-matched or disordered areas are usually observed in inter-domain regions even between domains of identical structure. One important example where the interface between non-identical 2D crystal phases was observed also involves the TDtBHPP molecule.¹¹ In that case, square and hexagonal phases can be interlocked because of an accidental 'lattice match' between square grid and hexagonal packing motifs, as shown in Fig. 5.

TDtBHPP molecules within each phase of that surface selfassembly maintain a consistent conformation with regard to the orientation of the *meso*-phenyl substituents. In the present case, a lattice match between two non-identical phases is not achieved by an interlock but by the creation of a conformationally unsymmetrical molecule, which exists at the interface between two differing domain structures.

The uniquely substituted TPP molecules serve to compensate for differences in molecular structure between the two nonidentical self assemblies. It has been previously observed that a single molecular species can give rise to differing domain structures during individual experiments. In particular, TDtBPP can form enantiopure domains of chiral conformers because of a symmetrical, concerted twisting of the *meso*-phenyl In summary, we have observed new conformations of phenyl groups in tetraphenylporphyrin and their effect on the packing of the supramolecular structure of the TDtBHPP molecules. Furthermore, spontaneous formation of a mixed conformer of TDtBHPP has been obtained. Now, TDtBHPP molecules have been shown to form not only interlocked 2D lattice interfaces¹¹ but also an arrangement where the difference between the lattices of two 2D crystal structures is compensated for by the existence of an unsymmetrical molecular conformation. Our current motivation for studying such a phenomenon lies in the possibility that, with the knowledge gained from its analysis we may 'engineer' similar features into molecular species for adsorption. Ultimately, this may result in perfectly crystalline heterogeneous molecular monolayers whose structure and physical properties should be of substantial interest.

Acknowledgements

The authors are grateful for support received from the Special Coordination Funds for Promoting Science and Technology from MEXT, Japan through an ICYS Fellowship (J. P. H.).

References

† 5,10,15,20-Tetrakis(3,5-di-*t*-butyl-4-hydroxyphenyl)porphyrin was prepared as previously reported using the Adler modification of the Rothemund synthesis whereby pyrrole was condensed with 3,5-di-*t*butyl-4-hydroxybenzaldehyde in refluxing propionic acid.¹⁴ After cooling, the resulting porphyrinic precipitate was filtered then purified by column chromatography followed by recrystallization from dichloromethane/methanol. The purple microcrystalline solid was dried *in vacuo* before use in STM experiments. Atomically clean single crystals of Cu(111) used as substrates were prepared by Ar⁺ sputtering and annealing (700 K) cycles. Sub-monolayer coverage of the substrate was obtained by sublimation for 10 min at 320 °C from a Knudsen cell to the metal substrate over an intervening distance of 30 cm in ultrahigh vacuum (1×10^{-8} Pa), followed by characterization using STM (JEOL Ltd., SPM-4500X) at 150 K using an electrochemically etched tungsten tip. The tunneling current, I_t , and voltage, V_s , were 80–100 pA and +1.0 V, respectively, and are noted in the respective figure captions.

- (a) C. Joachim, J. K. Gimzewski and A. Aviram, *Nature*, 2000, 408, 541–548; (b) J. K. Gimzewski and C. Joachim, *Science*, 1999, 283, 1683–1688.
- (a) J. A. Theobald, N. S. Oxtoby, M. A. Phillips, N. R. Champness and P. H. Beton, *Nature*, 2003, **424**, 1029; (b) P. Samori, A. Fechtenkötter, F. Jäckel, T. Böhme, K. Müllen and J. Rabe, *J. Am. Chem. Soc.*, 2001, **123**, 11462.
- 3 Z. Liu, A. M. Yasseri, J. S. Lindsey and D. F. Bocian, *Science*, 2003, **302**, 1543–1545.
- 4 K. M. Kadish, G. Royal and E. van Caemelbecke, in *The Porphy*rin Handbook, ed. K. M. Kadish, K. M. Smith and R. Guilard, 1999, Academic Press, vol. 8.
- 5 T. Yokoyama, S. Yokoyama, T. Kamikado, Y. Okuno and S. Mashiko, *Nature*, 2001, **413**, 619.
- 6 F. Moresco, G. Meyer, K.-H. Rieder, H. Tang, A. Gourdon and C. Joachim, *Surf. Sci.*, 2002, **499**, 94–102.
- 7 T. A. Jung, R. R. Schittler and J. K. Gimzewski, *Nature*, 1997, **386**, 696–698.
- 8 (a) F. C. Frank and J. H. van der Merwe, Proc. R. Soc. London, Ser. A, 1949, 198, 216; (b) J. H. van der Merwe, in Single Crystal Films, ed. M. H. Francombe and H. Sato, Pergamon, New York, 1964, p. 139.
- 9 (a) K. Mistry, M. Armstrong, C. Auth, S. Cea, T. Coan, T. Ghani, T. Hoffmann, A. Murthy, J. Sandford, R. Shaheed, K. Zawadzki, K. Zhang, S. Thompson and M. Bohr, *Symp. VLSI Tech. Dig.*, 2004, 50–51; (b) M. L. Lee and E. A. Fitzgerald, *J. Appl. Phys.*, 2003, **94**, 2590–2596.
- 10 For one significant example of discotics substituted with a variety of functional groups and assembled at surfaces see S. Ito, M. Wehmeier, J. D. Brand, C. Kübel, R. Epsch, J. P. Rabe and K. Müllen, *Chem.-Eur. J.*, 2000, 6, 4329.
- 11 J. P. Hill, Y. Wakayama, W. Schmitt, T. Tsuruoka, T. Nakanishi, M. L. Zandler, A. L. McCarty, F. D'Souza, L. R. Milgrom and K. Ariga, *Chem. Commun.*, 2006, 2330–2332.
- 12 T. Yokoyama, S. Yokoyama, T. Kamikado and S. Mashiko, J. Chem. Phys., 2001, 115, 3814–3818.
- 13 T. Sekiguchi, Y. Wakayama, S. Yokoyama, T. Kamikado and S. Mashiko, *Thin Solid Films*, 2004, 464/465, 393–397.
- 14 A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, J. Org. Chem., 1967, 32, 476.