

Regulating the stability of 2D crystal structures using an oxidation state-dependent molecular conformation†

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The oxidation state of the phenol-substituted porphyrin TDtBHPP is coupled with its structure so that its 2-electron oxidation leads to a coplanarization of the molecule and a substantial stabilization of its surface self-assembled structures adsorbed at metal substrates.

The 'bottom-up' approach has become popular for assembly of functional molecules with sub-nanometer scale precision^{1–3} being an especially attractive means for fabrication of molecular devices.^{4–6} Porphyrins are implicated as the molecular components of such devices because their high thermal and chemical stabilities allow processing under conditions similar to those used for preparation of conventional solid state electronic components,⁷ highlighting them as promising interfacial materials. In addition, their multiple stable oxidation states⁸ and emissive properties⁹ improve their appeal for such applications. Here we describe work which illustrates that variation in the structure and oxidation state of a porphyrin can also be exploited in the preparation of molecular arrays at metallic surfaces leading to stable assemblies at ambient temperature. Ultimately, this amounts to a synthetic conformational adaptation of the molecules to the metal substrate rather than the passive process where molecules adapt their conformation to the substrate surface upon adsorption.^{10,11} The results present an intriguing and subtle method for controlling the interface assembly processes by variation of the oxidation state of the species for adsorption.

Tetrakis(3,5-di-*t*-butyl-4-hydroxyphenyl)porphyrin (TDtBHPP) contains a tetrapyrrole core substituted at its *meso* positions with four di-*t*-butylphenol substituents. This combination of the porphyrin, well-known for its metal ion chelating ability and characteristic electronic absorption spectrum, with butylated phenol substituents more familiar for their anti-oxidant properties, results in a complex interplay between porphyrin macrocycle and

phenolic substituents and can involve substantial variation in electronic and molecular structure depending on experimental conditions.^{12,13} In particular, two-electron oxidation of the molecule yields a stable compound, Ox(TDtBHPP), whose tetrapyrrole is conformationally similar to a porphyrinogen in the solid state.¹⁴

TDtBHPP has structural characteristics similar to other tetraphenylporphyrin (TPP) derivatives, containing an essentially planar tetrapyrrole macrocycle subtending an angle of 60° with the planes of its phenyl substituents (Fig. 1c, 1e).¹⁵ On the other hand, the 2-electron oxidized and formally non-aromatic derivative Ox(TDtBHPP) has dihedral angles between the planes of the pyrrole groups and least squares plane of the macrocycle even and alternating at ±48° (Fig. 1d, 1f). What is more surprising about this molecule is that the *meso*-substituents are now approximately coplanar with the macrocyclic least squares plane and they are fixed in this configuration by the conjugated π-electron system. This is emphasized by the structures of the highest occupied molecular orbitals (HOMOs) of the porphyrin and oxidized porphyrin (see ESI). Although the HOMO of TDtBHPP is somewhat localized on the tetrapyrrole macrocycle, the HOMO

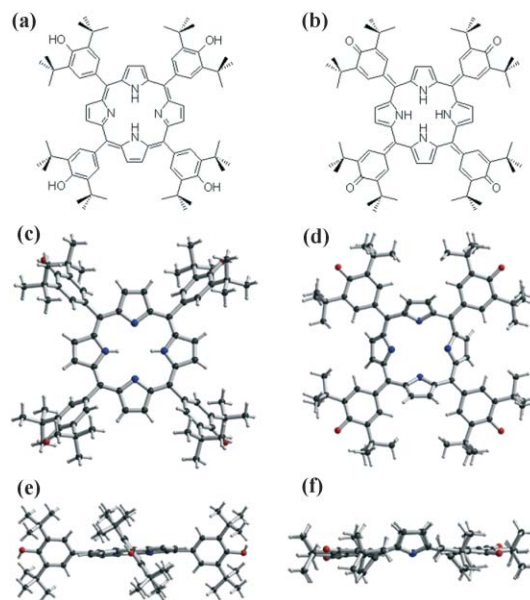


Fig. 1 a) and b) Chemical formulae of TDtBHPP and Ox(TDtBHPP), resp., c) and d) plan views of the molecular structures of TDtBHPP and Ox(TDtBHPP), resp., e) and f) edge-on views of the molecular structures of TDtBHPP and Ox(TDtBHPP), resp.

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for Ox(TDtBHPP) extends over the unsaturated regions of the molecule. For comparison, the calculated structure of the HOMO of the non-phenolic *tetrakis*(3,5-di-*t*-butylphenyl)porphyrin (see ESI) indicates a much smaller contribution from its phenyl substituents. The difference in the electronic structures of TDtBHPP and Ox(TDtBHPP) is reflected in their UV/Vis and fluorescence spectra (see ESI) and their solution state electrochemical properties have been shown to be complementary.¹⁶

TDtBHPP at submonolayer coverage comprises surface-mobile hexagonally-packed domain islands interspersed in a 2D gas phase.¹⁷ At ambient temperature, the hexagonally-packed structure undergoes a transition to the square packed grid motif usually observed for similar TPP molecules adsorbed on metal surfaces of differing symmetry¹⁸ (Fig. 2). The phase transition itself occurs on a timescale of seconds enabling its observation by STM. Square packing is associated with a molecular conformation having a large dihedral angle between the porphyrin macrocyclic plane and the phenyl substituents¹⁹ while hexagonal packing is observed where the dihedral angle is low.²⁰ The presence of electron-donating hydroxyl groups at the periphery of TDtBHPP contributes to the stability of molecular conformations that have an increasing coplanarity between porphyrin and *meso*-substituents so that the structures already proposed for adsorbed TPP molecules²¹ are stabilized by their introduction. Molecular orbital calculations²² indicate that electron density from the phenolic oxygen atoms does indeed contribute to the HOMO of TDtBHPP (ESI). Furthermore, at depressed temperatures, the hexagonal structure is more stable with regard to both surface mobility and phase transition. Therefore, the square packing is associated with a metastable conformation of the molecules. The disc-like shape of the planar conformations of TDtBHPP favours a hexagonal arrangement for optimization of intermolecular van der Waals contacts. Conversely, non-planar conformations optimize the van der Waals contacts between *t*-butyl groups by formation of the square grid structure.¹⁹ The structure at the contacts between molecules with non-planar conformations is mirrored in the crystal structure of TDtBHPP, which contains linear arrays of the porphyrin. The grid structure observed by STM is an extension of these linear arrays into two dimensions and is made possible by nearly orthogonal substitution of the porphyrin with identical

groups. In the crystal, hydrogen bonding by the hydroxyl groups is precluded by their proximity to the bulky *t*-butyl groups and an intermolecular hydrogen–oxygen distance of 2.59 Å is ideal for a van der Waals contact.

Coplanarity of the tetrapyrrole and its substituents can be enhanced by oxidative preprocessing of the molecule. The oxidized form of the porphyrin adsorbed at Cu(111) surfaces with submonolayer coverage shows only one type of surface-immobile hexagonal supramolecular structure at room temperature, and transition to the square phase was not observed (Fig. 3). The lack of mobility in the oxidized form indicates a much stronger molecule–surface interaction. Similarly to the case of the planar conformations of the non-oxidized porphyrin, the increased coplanarity of the oxidized porphyrin increases (doubles) the multiplicity of contacts between *t*-butyl substituents and the metal surface allowing formation of structures that are stable and immobile even at ambient temperatures. It is notable that there can be no possible competing conformations of the molecule, and this is the main factor responsible for improvement of the stability and immobility of the adsorbed structures since all of the *t*-butyl groups can remain in contact with the surface. This enhanced stability of a supramolecular structure adsorbed at a metal surface obtained by increasing the oxidation state of the adsorbed molecule is significant because it permits a new level of control over self-assemblies at metallic interfaces in compounds containing appropriate substituents. In addition, we can obtain stable formations at metallic interfaces without having to resort to the synthesis of much larger molecules for this purpose. Our preprocessing of the porphyrin molecule represents a deliberate reconjugation of the π molecular orbitals over the entire molecule as indicated by structural and physical analyses and molecular orbital calculations. This reconjugation is at the cost of the formal aromaticity of the molecule since the processing requires loss of two π -electrons (and two protons). However, the resulting molecule is stable in this state and forms extended supramolecular arrays on metallic surfaces and at ambient temperatures. The overall conformation of this molecule is remarkably similar to the structure of *tetrakis*(3,5-di-*t*-butylphenyl)porphyrin when adsorbed at metallic substrates, as indicated by STM studies, where porphyrin–phenyl dihedral angles in the range 20–45° have been

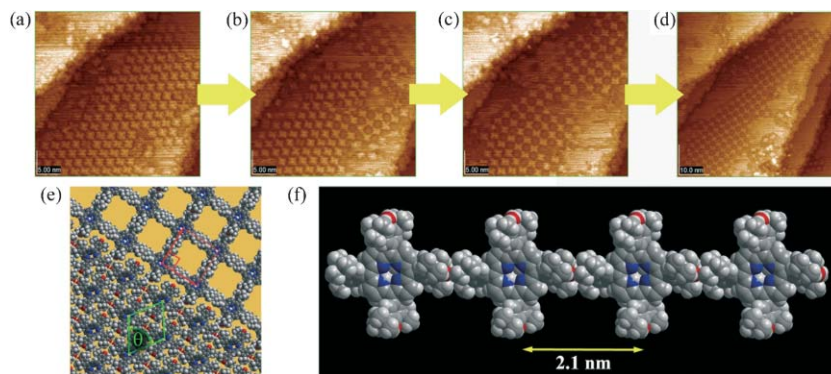


Fig. 2 (a)–(d), A series of STM images, obtained consecutively, of TDtBHPP adsorbed at a Cu(111) surface illustrating the phase transition from hexagonal to square packing of the molecules. For each image: $T = 298$ K, scan area, 35×35 nm² (except (d) 70×70 nm²), scan time 54 s, tunneling current, $I_t = 80$ pA, voltage bias $V_s = +1.0$ V. (e) Model of the packing motifs at the 2D crystal phase boundary based on STM and X-ray crystallographic measurements; $\theta = 68^\circ$. The model illustrates that the phase boundary can exist because of the complementarity of the two structures. (f) 1D chains within the crystal structure of TDtBHPP.¹⁵

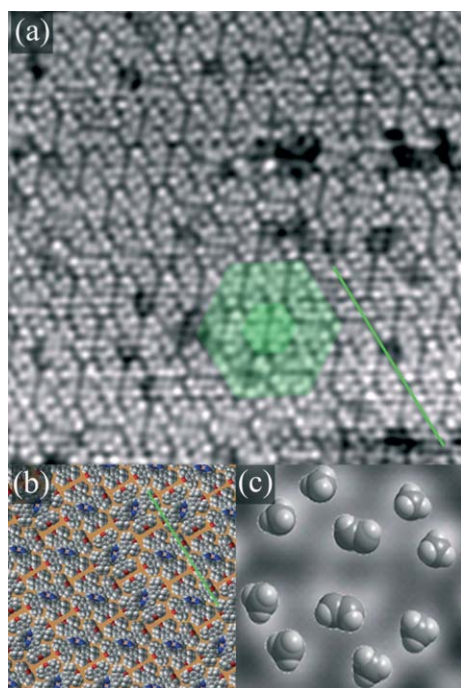


Fig. 3 (a) STM image of Ox(TDtBHPP) adsorbed at a Cu(111) surface illustrating the hexagonal packing at ambient temperature. Green nested hexagons highlight the local packing of the molecules while the green line highlights the *t*-butyl groups which are aligned within the supramolecular structure. Experimental conditions: $T = 298$ K, scan area 24×24 nm², tunneling current $I_t = 75$ pA, voltage bias $V_s = +1.0$ V. The green line is echoed in (b) a model of the 2-dimensional structure of Ox(TDtBHPP). (c) Overlay of the crystallographic space-filling structure of Ox(TDtBHPP) on the STM image of a single molecule of Ox(TDtBHPP) indicating that the molecular conformation is unchanged by adsorption at the Cu(111) surface. Especially notable is the close match of the form held by the *t*-butyl groups.

previously quoted.^{19,20} It is interesting to note that previous attempts to perform scanning tunneling spectroscopy on those molecules resulted in their destruction.¹⁹ We speculate that this is related to an increased propensity for oxidation caused by the severe distortion of the TPP molecules.

Put simply, *tetrakis*(3,5-di-*t*-butylphenyl)porphyrin molecules generally undergo conformational changes in order to occupy the most energetically stable structure for adsorption. Unfortunately, these changes are not favored by the physical structure of the molecule and so several different metastable structures are found.¹⁹ If hydroxyl groups are introduced at the phenyl groups in a position suitable for delocalization of electron density (*i.e.* their *para* or 4-positions) the result is a molecule which can much more easily adopt a coplanar conformation permitting observation of such adsorbed structures at elevated temperatures. If the molecule is fixed in one stable coplanar conformation, as is the case after oxidation of the porphyrin, one form is presented which is, coincidentally, the structure most preferred for adsorption of the molecules at a metallic surface.

We are currently assessing the importance of these findings for metal surface customization using various substituted derivatives of TDtBHPP and Ox(TDtBHPP) and investigating whether this finding can be extended to other molecules suitable for functionalization using 3,5-di-*t*-butyl-4-hydroxyphenyl groups.

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