

## STABLE ALIGNMENT OF TAUTOMERS AT ROOM TEMPERATURE IN PORPHYRIN 2-D LAYERS

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A major challenge in molecular electronics is to develop logic devices based on a truly intramolecular switching mechanism. Recently, a new type of molecular device has been proposed where the switching characteristic is mediated by the bistability in the position of the two hydrogen atoms which can occupy different, energetically equivalent positions (tautomerization) in the inner cavity of porphyrins and naphthalocyanines. Up to now, such a reaction has only been exploited at low temperatures and induced or detected through atomic scale manipulation. In addition, the unpredictability of the tautomer orientation currently excludes molecular interconnection to functional electronic circuits. Here, we provide full evidence that, following a newly proposed growth strategy, 2-D layers of metal-free tetraphenylporphyrins (H<sub>2</sub>TPP) show frozen tautomerization even at room temperature on macroscopic domains, with the H atoms aligned along a direction settled *a priori*. We ascribe this behavior to the buckling of the molecule, anchored to the substrate, which removes the degeneracy between the two tautomer alignments. On this basis we are able to propose a new way to exploit uniaxially oriented H<sub>2</sub>TPP tautomers in a first elementary logic device.

## 1. Introduction

Porphyrins and porphyrinic compounds are used as building blocks in organic electronic devices, such as switches,<sup>[1,2]</sup> memories,<sup>[3]</sup> spectroscopic markers,<sup>[4]</sup> solar cells,<sup>[5]</sup> sensors,<sup>[6]</sup> tailored molecular catalysts,<sup>[7]</sup> engineered molecular nanostructures<sup>[8]</sup> or molecular spintronics devices.<sup>[9,10]</sup> Many of the works reported in the literature address large areas of self-assembled monolayers of porphyrinoids, and therefore are not able to clarify whether the observed properties directly stem from the nanoscale local environment at the molecular level rather than from supramolecular phenomena.

Research targeting the internal physico-chemical processes of porphyrins aims instead at clarifying and possibly exploiting single molecule properties. The building block molecule to synthesize more complex porphyrinic compounds is tetraphenyl-porphyrin (H<sub>2</sub>TPP), a free-base porphyrin with two central hydrogen atoms, bonded to an opposite couple of the four available nitrogen atoms. At RT, the two hydrogen atoms readily transfer between the two pairs of opposite nitrogens, both in solution and in solid crystal structures.<sup>[11]</sup> This chemical reaction is known as tautomerization<sup>[2, 12]</sup> and has been extensively studied<sup>[13]</sup> since it can play a fundamental role in complex structures like DNA<sup>[14]</sup> and represents a stable charge storing mechanism in a variety of phenomena, possibly even for electronic applications.<sup>[3]</sup>

Both the environment<sup>[15]</sup> and the porphyrin crystal structure<sup>[16]</sup> can deeply influence the tautomerization rate. In general, below 240 K the hydrogen atoms are frozen in one of the two tautomeric forms.<sup>[12, 17]</sup> Due to the uniaxial symmetry of the proton arrangement in the inner cavity of the molecule, a frozen tautomer should induce in the molecule anisotropic electronic and optical properties.<sup>[18]</sup> However, detailed understanding of tautomerization is far from being complete. In particular, there is still a lack of knowledge regarding the influence of the tautomers in the physical properties of 2-D single layer domains of free base porphyrins. The reasons are: i) an apparent impossibility to obtain a pure H<sub>2</sub>TPP 2-D phase on a substrate

without the simultaneous growth of 3-D crystals; ii) the expected coexistence of the two energetically equivalent tautomeric forms on the surface even when tautomerization is frozen, which excludes the possibility to address single tautomers and eventually compare experimental data with theoretical predictions;<sup>[18]</sup> iii) the unpredictability of the tautomer orientation when molecules are deposited on a substrate, which prevents/hinders the interconnection of molecules to functional electronic circuits and precludes the practical realization of devices that have been theoretically predicted.<sup>[19]</sup> These facts represent severe drawbacks in view of possible applications of tautomers in next generation organic electronics.

In this work, we discuss the significant example of a purely 2-D H<sub>2</sub>TPP phase, grown on highly oriented pyrolytic graphite (HOPG) and constituted of domains in which just a single, stable and ordered tautomeric form is observed at RT. Indeed, the preferential alignment of tautomers, which can be chosen *a priori* by a specific exfoliation procedure of the HOPG, makes the overall optical properties of the porphyrin layer anisotropic, as pointed out by measuring the anisotropic reflectivity of macroscopic samples. Then, by exposing the H<sub>2</sub>TPP to vapors of hydrochloric acid (HCl), two more H-atoms can be added in the inner cavity of the original porphyrin, obtaining the di-acid H<sub>4</sub>TPP molecule, characterized by an isotropic optical response in the B-band region.<sup>[20]</sup> We can switch back from the di-acid H<sub>4</sub>TPP to the H<sub>2</sub>TPP molecule by applying a heat pulse, while optically reading the state-flip by using polarized light. A subsequent exposure to HCl vapors generates the di-acid H<sub>4</sub>TPP again, without any evidence of ageing effects neither on the physical properties of the molecules nor on their switching ability (see the Supplementary material ). Porphyrins can thus be viewed as a logic system that can be switched between two different, well-separated and stable states by addition and removal of H-atoms from their inner cavity, a completely new strategy that does not require a physical tautomer rotation,<sup>[1, 2, 19]</sup> but simply relies on their quenching. This

opens the route to applications of porphyrins as memory units based on a single and stable alignment of the porphyrin tautomers at RT, and represents a first logic device.

## 2. Main text

In our study, H<sub>2</sub>TPP has been deposited on HOPG by organic molecular beam epitaxy (OMBE). Being conductive and optically isotropic, HOPG represents an ideal substrate for our experimental studies, which include scanning tunneling microscopy (STM) and reflectance anisotropy spectroscopy (RAS). In addition, as compared to metals, HOPG is suitable for organic molecule deposition and represents a bio-compatible substrate that avoids strong interaction between the molecules and the substrate itself. The growth of free-base porphyrins on metal surfaces may in fact induce spontaneous metalation of the inner cavity of the molecules affecting their conformation and functionality. Conversely, semiconductor surfaces undergo considerable reconstructions leaving unsaturated dangling-bonds, which can interact with porphyrins and quench molecular mobility across the surface.

**Fig. 1**, panel a, shows the surface morphology of a nominal 0.5 Å-thick film of H<sub>2</sub>TPP, acquired by atomic force microscopy (AFM). A few steps separating large terraces of flat graphite can be observed in the image. They are aligned almost orthogonally to the direction along which HOPG was exfoliated in order to obtain a clean surface. As expected, many crystals (few nanometers in height) are also visible in the image. This 3-D phase coexists with a 2-D phase (wetting layer), as indeed shown by the phase contrast image in Fig. 1, panel b, where different regions are observed in the background displaying a clearly different contrast, thus indicating the presence of two chemically dissimilar surfaces. Here we attribute the yellow regions to the bare HOPG surface, whereas the blue ones represent the H<sub>2</sub>TPP wetting layer, having a thickness below 1 nm (see cross-sectional profile of Fig. 1-a). When the sample is exposed to vapors of hydrochloric acid, to obtain the di-acid H<sub>4</sub>TPP, the surface morphology dramatically changes (see Fig. 1, panel c). Just a few islands remain visible while

the 2-D phase is still covering the graphite substrate, as indicated by the corresponding phase contrast image (Fig. 1, panel d). Afterwards, subsequent HCl cycles do not disrupt the 2-D phase, their only effect being a further reduction of the density of 3-D crystals.

In order to determine the molecular arrangement in this 2-D phase, the sample has been analyzed by STM. **Fig. 2** presents our data acquired at RT; in particular, panel a, reports a single domain of the 2-D phase. The image clearly shows that the molecules are organized in a square lattice, with a spacing of  $(1.48 \pm 0.04)$  nm, which is not compatible with the hexagonal symmetry of the substrate: this suggests that the molecule-molecule interactions are stronger than those between each porphyrin and the graphite surface. These findings are in agreement both with recent theoretical calculations<sup>[21]</sup> and with experimental observation of H<sub>2</sub>TPP aggregates on metallic substrates and in different environments.<sup>[22-24]</sup> The square lattice is almost parallel to the exfoliation direction, suggesting that such an alignment could be influenced by the presence of surface steps created in the HOPG surface during exfoliation (see Fig. 1).

At the single molecule level, the tunneling current shows oblate corrugation maxima (in red in the image) that closely resemble the one observed over a single porphyrin molecule and reported in Reference 2. In that work, the authors demonstrate that the corrugation maximum is associated with the presence of a frozen H<sub>2</sub>TPP tautomer at 6 K.

In addition, we point out that all the molecules in the domain shown in Fig. 2 are oriented along the same direction, as evidenced in panel b, where we report the STM profiles of porphyrin molecules measured along the  $\alpha$  and  $\beta$  orthogonal directions. We can thus conclude that not only is tautomerization suppressed at RT, but that stable and well-defined tautomers are organized with long-range order across the entire porphyrin domain, resulting in a spontaneous symmetry breaking leading to uniaxial anisotropy. All tautomers are aligned

along the direction (labeled as  $\beta$ ) parallel to the graphite surface steps obtained after exfoliation.

The ordered assembling of tautomers inside a porphyrin domain and their freezing at RT can be better understood through simulations of H<sub>2</sub>TPP adsorption on HOPG using *ab initio* density functional theory (DFT). A periodic array of molecules in an unrelaxed geometry were placed about 3.5 Å above a double layer of graphene, assuming a molecular coverage and packing geometry consistent with that seen in the experimental STM image (Fig. 2). Upon relaxation, the H<sub>2</sub>TPP becomes moderately distorted with respect to the initial planar structure: the four external phenyl rings bend upwards thereby inducing a curvature (saddle shape) of the central aromatic ring [**Fig. 3** panel c]. Due to the lowering of symmetry induced by the molecule/substrate interaction, energetic degeneracy between H<sub>2</sub>TPP tautomers [these *trans* configurations, termed *T1* and *T2*, are shown in Fig. 3 (c)] is broken. The *T1* tautomer -its internal N-H bonds being bent towards the substrate- is found to be more energetically favored by about 50 meV/molecule (i.e., 2kT at RT). Notably, the porphyrin skeleton is very similar for both tautomers. We then simulate the constant current STM image of the most stable tautomer (*T1*) for a bias of 0.4 eV. The result is reported in Fig. 3 (a), alongside the STM signal profiles in (b). Elongation of the signal clearly coincides with the direction of the tautomer axis; this is also true for the other tautomer (as shown in the Supporting Information), i.e., independent of the buckling axis of the internal ring. The tautomerization process was then studied for the full physisorbed system using the climbing-image nudged-elastic-band (NEB) method through the minimization of a set of 13 intermediate images. The results, shown in Fig. 3 (c), demonstrate that tautomerization is a step-wise process involving the transfer of one proton at a time and passing through a metastable intermediate *cis* configuration such that the two hydrogens occupy neighbouring nitrogen sites. Both reaction barrier heights and *trans-cis* differences are slightly larger (few tens of meV) to those of the

free molecule in the gas phase according on our calculations and other reports on free-base porphyrin<sup>[25]</sup> and naphthalocyanin<sup>[26]</sup> in confirmation of previous experimental suggestions.<sup>[2]</sup>

Our theoretical simulations thus demonstrate that the 2-D porphyrin domain can be thought in terms of a discrete system of tautomers, where each molecule is characterized by one of two distinct states ( $T1$  or  $T2$ ). The energy barrier between  $T2$  and  $T1$  is above the thermal energy at RT. Such a discrete system can be thus fully described within a two-dimensional Ising model<sup>[27]</sup> over a square lattice. A well known property of such a model is that symmetry is spontaneously broken below a critical finite temperature below which the system displays long-range order in very close agreement with our STM analysis.

Tautomer alignment should induce anisotropy in the electronic and optical properties of the porphyrin domain.<sup>[18]</sup> In order to verify this statement, a home-made high sensitivity RAS apparatus has been set up.<sup>[28-30]</sup> Our RAS apparatus can detect a normalized reflectivity difference of about  $\Delta R/R = 2 \times 10^{-6}$  between the intensities of light reflected by the sample when the probe beam has two orthogonal directions of the linear polarization, with respect to the mean intensity of the light. In **Fig. 4** we summarize the most important RAS spectra, acquired both on  $H_2TPP$  and  $H_4TPP$  films on HOPG. As a consequence of the  $C_3$  symmetry of the HOPG surface, the anisotropy spectrum of clean graphite is an optimal RAS reference (dashed line), which means that HOPG shows, within experimental accuracy, a perfectly isotropic optical response in the 400 to 480 nm wavelength range. After sublimation of  $H_2TPP$  in the OMBE chamber, the RAS spectrum (open dots) displays a maximum ( $\Delta R = R_\alpha - R_\beta$ ) for linearly polarized electric fields aligned along the  $\alpha$  and  $\beta$  directions (see Fig. 2, panel a). The sharp peak at 434 nm is consistent with the B-band characteristic of the optical spectrum of  $H_2TPP$ .<sup>[31]</sup> This peak is measured on the sample that shows the morphology reported in Fig. 1, panel a. Exposure of porphyrins to HCl vapors (protonation) dramatically changes the film morphology (Fig. 1, panel c) and induces the formation of di-acid  $H_4TPP$  molecules. The

RAS signal, acquired after sample protonation, is dramatically changed (dash-dotted line), being reduced in intensity and without any clearly peaked structure. We thus verify that the di-acid H<sub>4</sub>TPP film is, from the optical point of view, substantially isotropic.<sup>[20]</sup> Sample flash heating at 60 °C recovers the optical anisotropic spectrum (full squares in Fig. 4), in stark contrast to the irreversibility of the morphological evolution, which shows a permanent degradation of the 3-D porphyrin crystals.

Important conclusions can be deduced from these results. i) The RAS signal arises only from the 2-D porphyrin phase,<sup>[32]</sup> which is the only stable and persistent phase across the HCl-exposure/annealing cycles of the organic film. ii) The maximum RAS signal of the 2-D phase is acquired when the electric fields are aligned perpendicular or parallel to the tautomer direction (labeled  $\alpha$  and  $\beta$  in Fig. 2, panel a). We thus deduce that the RAS signal strictly originates from the existence of porphyrin domains, characterized by a common and stable orientation of tautomers, which breaks the isotropic square symmetry of the overall porphyrin layer. This conclusion is in perfect agreement with the STM topography of the 2-D domain (Fig. 2) and it is also fully supported by the disappearance of optical anisotropy observed following protonation. A similar role played by tautomers in determining the anisotropic optical response of H<sub>2</sub>TPP molecules has been recently described in a theoretical work,<sup>[18]</sup> the results of which can be now compared to the experimental spectra. iii) From an optical point of view, porphyrin protonation (exposure to HCl vapors) and deprotonation (annealing at 60 °C) processes are completely reversible. Each of the spectra measured after tens of cycles performed on our sample are perfectly superimposable onto the red line of Fig. 4,<sup>[32]</sup> meaning that, while removing two H atoms from the di-acid H<sub>4</sub>TPP molecule, the two remaining hydrogen atoms still align along the very same direction. The reproducibility of the tautomer alignment across protonation-deprotonation cycles implies that long-range order emerges from the intervention of porphyrin-HOPG interactions, which remove the degeneracy between

the two equivalent tautomeric forms within the same porphyrin domain and from domain to domain, forcing the anisotropy axis to always align in the same direction (associated with steps at the graphite surface). As a proof, when graphite is exfoliated along a different direction, the RAS signal maximum is detected after a proper sample rotation, which makes the RAS electric fields align again along the new exfoliation direction.

The optical reversibility of the protonation-deprotonation cycles allows us to consider the H<sub>2</sub>TPP and the di-acid H<sub>4</sub>TPP molecules as two different *states* of the same system (1 and 0 states, respectively). The experimental procedure described above indicates how to switch from one state to the other by protonation/deprotonation and how to read the 1 or 0 states using polarized optical spectroscopy. Both processes -driving the tautomerization and reading the logic state- occur on a macroscopic scale. **Fig. 5** shows a few switching cycles<sup>[32]</sup> of our sample between the two states, thus acting as 1/0 logic levels. We have not observed any sign of degradation of the stored information encoded in this way over the investigated time scale (several days).

This example thus represents a first demonstration of the possibility of exploiting tautomer alignment in RT functional devices.

### 3. Conclusions

In this work, we describe a new growth strategy to obtain a pure 2-D layer of H<sub>2</sub>TPP on HOPG. We find that the organic layer is structured in domains, characterized by porphyrins showing their inner H atoms (tautomer) aligned along a direction settled *a priori*, as a consequence of the substrate preparation procedure (graphite exfoliation). This represents the first evidence of ordered domains of frozen tautomers at room temperature.

On this basis we are able to propose a new way to exploit uniaxially oriented H<sub>2</sub>TPP tautomers in a first optically-readable logic device.

#### 4. Experimental

$\alpha$ -degree highly-oriented pyrolytic graphite (HOPG from Optigraph®) has been used as a substrate. 10x10 mm<sup>2</sup> HOPG substrate has been exfoliated with adhesive tape before each experiment. H<sub>2</sub>TPP molecules (Sigma Aldrich, purity  $\geq 99\%$ ) were deposited on HOPG via organic molecular beam epitaxy (OMBE) (base pressure during sublimation:  $2 \times 10^{-7}$  mbar). During growth, a degassed quartz crucible has been held at 550 K, while the HOPG has been always kept at RT. The atomic force microscopy (AFM) images have been collected by a Multimode Nanoscope V (Bruker®) in intermittent contact mode operation. All the scanning tunneling microscopy (STM by Omicron®) images were recorded in constant-current mode at RT, using an electrochemically etched tungsten tip. A high sensitivity home-made reflection anisotropy spectroscopy (RAS) apparatus, with a light spot diameter of about 1 mm, has been used to collect optical spectra in the energy range 2.6÷3.1 eV (400÷480 nm). The integration time of each single experimental point is 100 ms.

DFT calculations were performed using a plane-wave basis set and soft pseudo-potentials together with a van der Waals corrected PBE exchange-correlation functional as implemented in the quantum-ESPRESSO code [34]. Repeated images perpendicular to the graphene plane were separated by a vacuum region of 10 Å. Structural relaxations used a force component threshold of 30meV/Å. STM images were computed from the local density of states using the Tersoff-Hamann approximation. A single k-point was used throughout.

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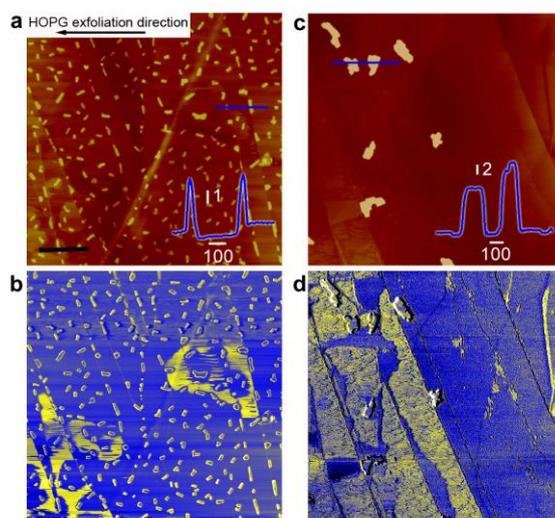
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**Any Additional Author notes:** G.B. and M.C. contributed equally to this work.

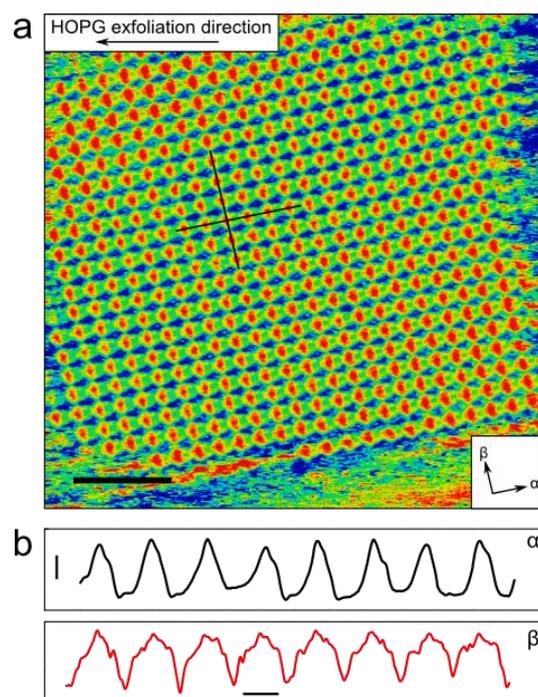
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- \_[33] The switching time between 0 and 1 states is shorter than the reverse process, since the former is influenced by the heat capacity of the Peltier junction used here to heat the sample and to the finite heat conductivity across the Peltier-graphite junction. A faster state flip would be achieved by a different heating of the sample, e.g. by using a laser beam.
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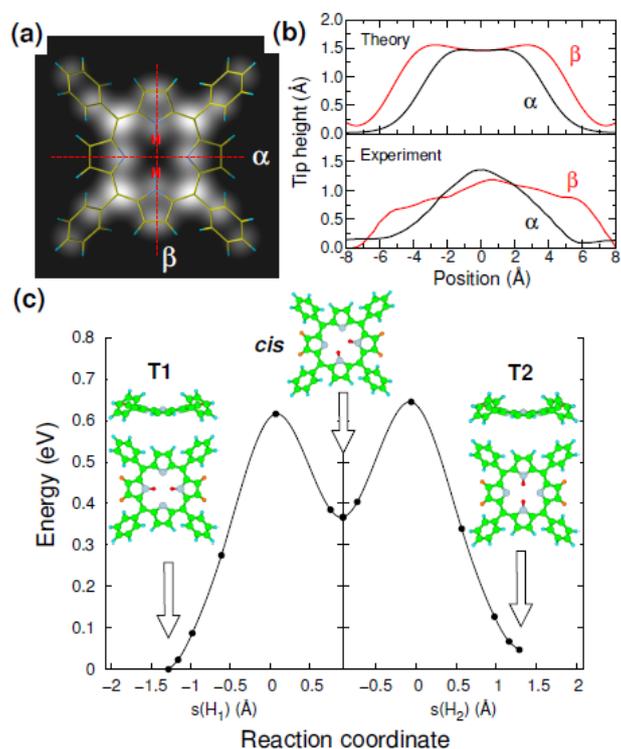


**Figure 1. AFM surface morphology of H<sub>2</sub>TPP films.** **a**, a 0.5 Å-thick film immediately after sublimation in vacuum. Scale bar on the bottom left is 600 nm. The HOPG exfoliation direction is also reported. **c**, the same film in **a** after exposure to HCl vapors. **b** and **d**, phase contrast images of the regions in **a** and **c**, respectively, showing the presence of two chemically different surfaces in the background. Cross-sectional profiles taken along the blue segments are reported on the bottom-right of **a** and **c**. Numbers next to the scale bars, close to the profile, are nanometer units.

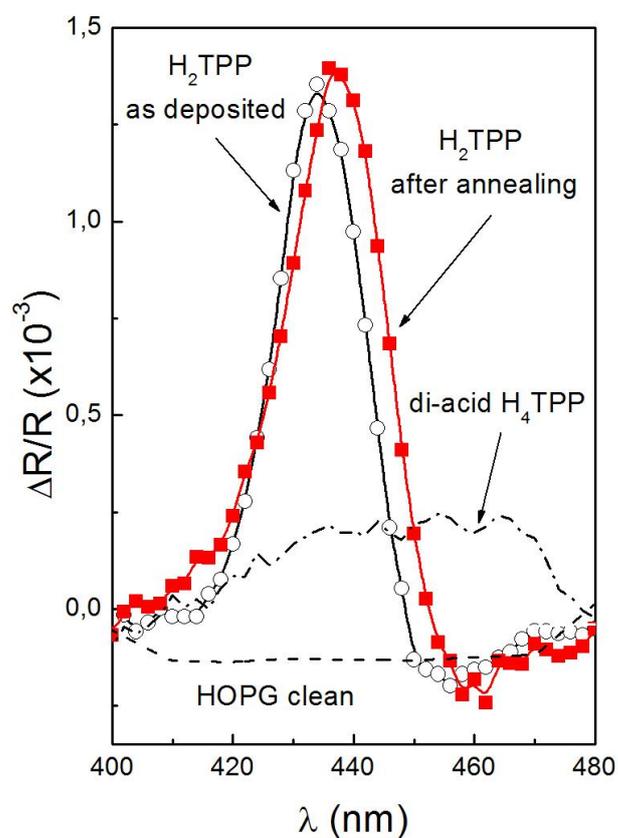


**Figure 2. Structure of a H<sub>2</sub>TPP 2D domain on HOPG.** **a**, 36x36 nm<sup>2</sup> STM image showing the arrangement of molecules in a square unit cell. The enhancement of signal modulation of the tunneling current, visible in the centre of each porphyrin molecule (red), is due to a uniaxial alignment of the inner H-atoms of the molecules composing the domain ( $V_{\text{bias}} = 0.4$  V,  $I_{\text{tunnel}} = 50$  pA). The HOPG exfoliation direction is also indicated. The reported scale bar (bottom left) is 7 nm-long. **b**, STM signal profiles acquired along the  $\alpha$  and  $\beta$  directions, respectively. The vertical and the horizontal scale bars are 50 pm and 1 nm, respectively. The STM scan direction is nearly parallel with respect to the exfoliation one. Data have been acquired at RT.

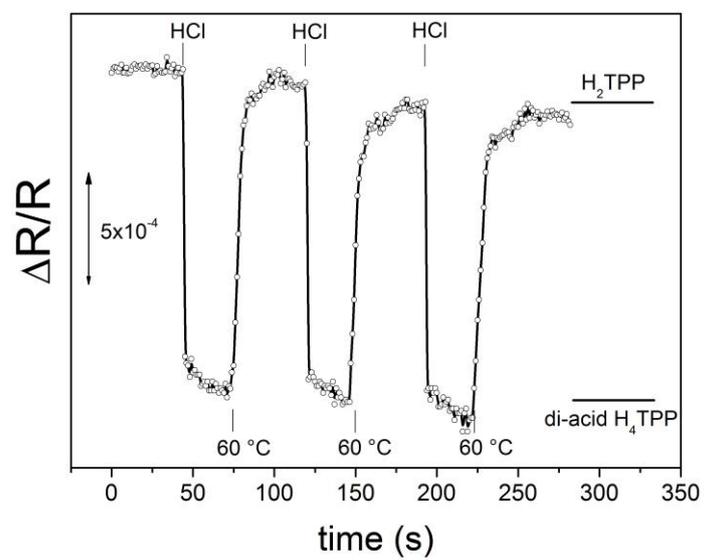
*Inset:* the free-base H<sub>2</sub>TPP molecule with two hydrogen atoms (red spheres) in the inner cavity of the molecule. In this picture, the tautomer is frozen along the  $\beta$  direction. The molecule occupies a square surface with sides of about 12.2 Å.



**Figure 3. Theoretical simulations:** **a**, simulated constant-current STM image of H2TPP adsorbed on graphite. The molecular backbone is superimposed as a guide to the eye. **b**, simulated and measured STM profiles along the two molecular axes  $\alpha$  and  $\beta$ . **c**, computed energy profile for the stepwise tautomerization process, along a path between *trans* configurations T1 and T2 with intermediate metastable *cis*-like state. Reaction coordinate  $s$  is defined as  $s = d_1 - d_2$  where  $d_1$  and  $d_2$  are the two N-H distances relevant to each proton transfer. Upward tilted pyrrole groups are indicated by the orange colored H atoms [N.B. the inner red hydrogens are tilted differently].



**Figure 4. Optical anisotropy of H<sub>2</sub>TPP films on HOPG.** The black line (open circles) is the RAS spectrum acquired immediately after H<sub>2</sub>TPP growth in vacuum. The dash-dotted line spectrum is acquired after the exposure of the porphyrin films to HCl vapors (di-acid H<sub>4</sub>TPP). The red line (full squares) is measured on the sample after exposure to HCl vapors and subsequent heating at 60 °C. The same indistinguishable spectrum is observed after each film exposure plus recovery by heating. The dashed black line is the reference RAS signal of clean HOPG.

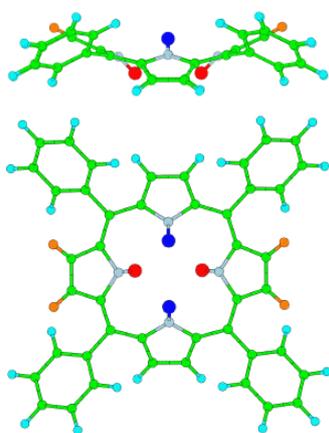


**Figure 5. Protonation-deprotonation cycles.** Switching between the  $H_2TPP$  and di-acid  $H_4TPP$  states is reported as monitored by the RAS signal during several cycles of HCl exposure and 60 °C heating.

### Supporting Information.

Protonation: the optical switch illustrated in this work is intimately related to the fact that the induced change in the atomic structure, following exposure of the H<sub>2</sub>TPP/graphite system to HCl, is a reversible process. We therefore used a theoretical/computational methodology similar to that described in the text and methods section to investigate the effect of adding two protons to the macrocyclic ring.

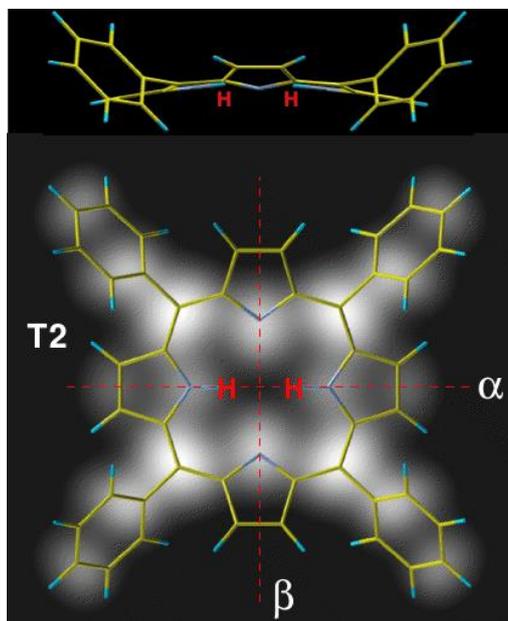
As reported in Fig. 1S, the calculations clearly demonstrate that the final protonated molecular phase exhibits a strongly distorted central ring: the original two H atoms (red balls in Fig. 1S) are tilted further downwards (below the molecular plane) while the added protons (blue dots in Fig. 1S) bond to the other two central nitrogen atoms and point upward, away from the surface. This result clearly supports the idea that the deprotonation process involves breaking the latter H-N bonds allowing the system to revert to the original H<sub>2</sub>TPP atomic structure.



**Figure 1S:** side view (top panel) and top view (bottom panel) of the di-acid H<sub>4</sub>TPP molecule. Upwardly tilted pyrrole groups are indicated by orange colored H atoms. The two hydrogens already present in the H<sub>2</sub>TPP molecule are shown in red, while the two added protons are shown in blue.

Regarding the STM sensitivity to tautomer direction, **Fig. 2S** shows the calculated constant STM image for the less stable tautomer T2. The calculation clearly shows that the elongation

of the STM profile follows the direction of the two N-H bonds, and not the curvature of the molecule after adsorption, called here T2.



**Figure 2S:** simulated constant-current STM image for the T2 tautomer. Similarly to Figure 3A in the text, the molecular backbone is superimposed as a guide to the eye.