

Conformation and Packing of Porphyrin Polymer Chains Deposited Using Electrospray on a Gold Surface**

Alex Saywell, Johannes K. Sprafke, Louisa J. Esdaile, Andrew J. Britton, Anna Rienzo, Harry L. Anderson, James N. O'Shea, and Peter H. Beton*

Conjugated porphyrin polymers have stimulated great interest due to their potential applications in nonlinear optics,^[1] light harvesting^[2] and nanoscale charge transport.^[3] As with many other organic materials, interfacial properties are likely to play an important role in their applications in molecular electronics.^[4] However, it has not so far been possible to study these effects due to the difficulty in preparing suitable monolayers, since the relevant polymers and oligomers cannot be sublimed. A question of particular interest relates to the influence of the flexibility of such a large molecule on the ordering within interfacial regions.

We have investigated the adsorption of two oligomers, a porphyrin tetramer (**P4**, $N=4$; see Figure 1 for structural diagrams), a hexamer (**P6**, $N=6$), and a polymer **Pn** ($N=30-50$) on the Au(111) surface using scanning tunneling microscopy (STM). The porphyrin units have long octyloxy side chains to promote solubility in organic solvents. Our experiments are performed at room temperature under ultra-high vacuum (UHV) conditions (base pressure 5×10^{-11} Torr) and we use UHV electrospray deposition (UHV-ESD) to transfer the oligomers and polymers directly from solution onto a surface. In our approach to UHV-ESD,^[5] a volatilized mixture of solvent and solute molecules is produced in atmosphere by electrospray. This mixture enters the UHV system through a small aperture and is passed through a series of differentially pumped chambers, to the Au(111) substrate (for further details see Supporting Information). UHV-ESD and related approaches have been used to introduce nanotubes, fullerenes, dye molecules, and polymers into a UHV environment.^[6,7]

Images acquired after deposition of a sub-monolayer coverage of **P6** (Figure 2) show that, despite their large size, the porphyrin oligomers diffuse on the surface and form

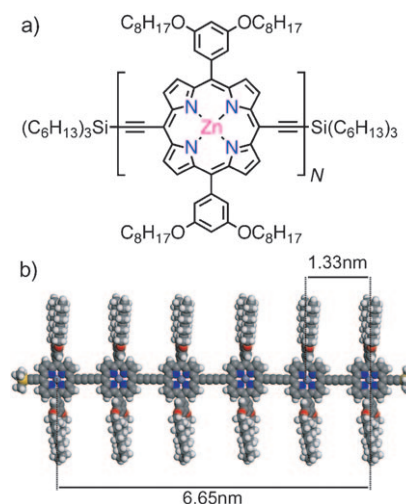


Figure 1. a) Structure of porphyrin oligomers and polymers. b) **P6** molecule with the trihexylsilyl end groups truncated to trimethylsilyl groups for clarity.

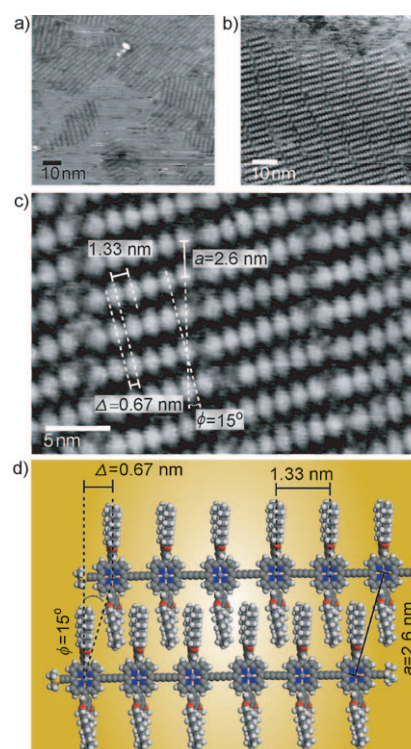


Figure 2. a) STM images of **P6** oligomer on Au(111). b) **P6** domains following annealing at 100°C. c) STM image of a close-packed domain of **P6**. d) Structural model. (STM parameters $V_{\text{sample}} = -1.80$ V, $I_{\text{tunnel}} = 0.03$ nA, for all images.)

[*] A. Saywell, A. J. Britton, A. Rienzo, Dr. J. N. O'Shea, Prof. P. H. Beton
School of Physics & Astronomy, University of Nottingham
Nottingham, NG7 2RD (UK)
E-mail: peter.beton@nottingham.ac.uk

J. K. Sprafke, Dr. L. J. Esdaile, Prof. H. L. Anderson
Department of Chemistry, University of Oxford
Chemistry Research Laboratory
Oxford, OX1 3TA (UK)

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highly ordered islands composed of parallel molecular rows. The porphyrin subunits are clearly resolved with, as expected, six subunits within each **P6** molecule. The measured porphyrin separation within the oligomers, 1.33 ± 0.07 nm, agrees with the value from X-ray crystallography (1.353 nm).^[8] We find no preferred orientation of the rows relative to the Au(111) surface. Annealing at 100 °C causes the **P6** islands to grow and become more ordered (compare Figures 2a,b). Figure 2c is a high-resolution image from which we determine the distance, $a = 2.6 \pm 0.2$ nm, between porphyrins in neighboring molecules and a canting angle, $\phi = 15^\circ$, between the molecular and row axes.

The offset between porphyrin groups in neighboring molecules (see Figure 2), $\Delta = 0.7 \pm 0.1$ nm, is equal, within experimental error, to half the porphyrin spacing, 1.33 nm. This offset is suggestive of an interdigitated arrangement in which the octyl side chains lie perpendicular to the long axis of the molecule and parallel to the gold surface (Figure 2d). This type of interdigitation has previously been shown to be the driving force behind many self-assembled systems.^[9] A similar arrangement is observed when **P4** is deposited on Au(111) (see Supporting Information).

We have used angle-resolved NEXAFS (near edge X-ray absorption fine structure) and XPS (X-ray photoelectron spectroscopy) to show that the plane of the porphyrin subunits is parallel to the substrate and to confirm that Zn atoms remain complexed within the porphyrin (N 1s spectra acquired following UHV-ESD deposition of the **P4** oligomer, for a range of molecular coverages, are shown in Figure 3a). In all cases only one chemical environment is observed,

indicating that all four nitrogen atoms within the porphyrin core are bonded to the zinc (if the Zn were removed to form the porphyrin free base then two chemical environments for the N atoms would be expected). Similarly, Zn 2p XPS spectra (Figure 3b) show only one chemical environment with the expected spin-orbit split pair being observed.^[10]

Angle resolved NEXAFS acquired for a coverage of 5.2 monolayers of **P4** show that the porphyrin cores of the molecule are parallel to the Au(111) surface. This is demonstrated in Figure 3c where the nitrogen 1s NEXAFS shows the growth of the $1s \rightarrow \pi^*$ peak with increasingly grazing angle of incidence. This is consistent with the nitrogen π^* bond being parallel to the surface.^[11] The broad $1s \rightarrow \sigma^*$ peak shows no angular dependence as expected. A multilayer coverage, as considered here, would be expected either to be disordered, which is not consistent with our data, or to grow with the order displayed by the monolayer. The NEXAFS results support the adoption of a planar adsorption of the monolayer in agreement with the topographic height measurements determined with STM.

STM images of the porphyrin polymer, **Pn**, (consisting of, on average, 40 porphyrin subunits as determined by gel permeation chromatography) adsorbed on Au(111) show a co-existence of small quasi-close-packed regions where chains are aligned (similar to, but smaller than the lamella structures formed by polythiophene^[7,12]), and more disordered regions where bends and kinks occur, together with points where polymer chains cross (Figure 4). The porphyrin units are clearly resolved with a spacing of 1.34 ± 0.07 nm, equal to the value observed for oligomers. The average polymer chain

length is 54 nm with a standard deviation of 12 nm, consistent with the expected length of ca. 54 nm for a 40-unit chain. In quasi-close-packed areas we find, prior to annealing, that there is a small variation in the separation of neighboring segments of aligned chains, but after annealing the polymers show an interchain separation of 2.8 ± 0.3 nm.

Individual chains run continuously over step edges and may also bend sharply in a "hairpin" arrangement (Figure 4b). The smallest radius of curvature was found to be 1.3 nm (corresponding to a turn of 180° in 3–4 porphyrin units). Another common feature in the images is the presence of high-contrast regions at the junctions where two polymer chains cross. The apparent height of these cross-over points (P_2 in Figure 3b) is ca. 0.4 nm, roughly twice the measured height of a single polymer chain (ca. 0.2 nm, P_1 in Figure 4b). The angle between the

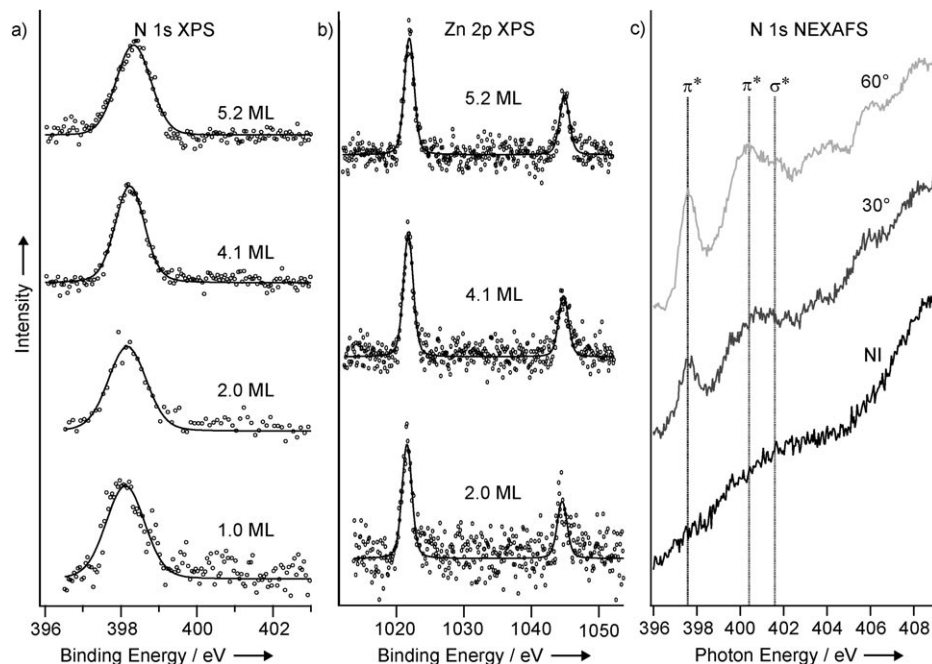


Figure 3. a) N 1s core-level spectrum measured using $h\nu = 500$ eV for a range of coverages. One chemical environment is observed in all cases. ML = monolayer. b) Zn 2p core-level spectrum measured using $h\nu = 1250$ eV. One chemical environment is observed in all cases. c) N 1s NEXAFS spectra. The growth of the $2p \rightarrow \pi^*$ transition with increased grazing angle shows that the porphyrin subunits are lying flat relative to the Au(111) plane. NI = normal incidence. The spectra in (a–c) are vertically offset for clarity.

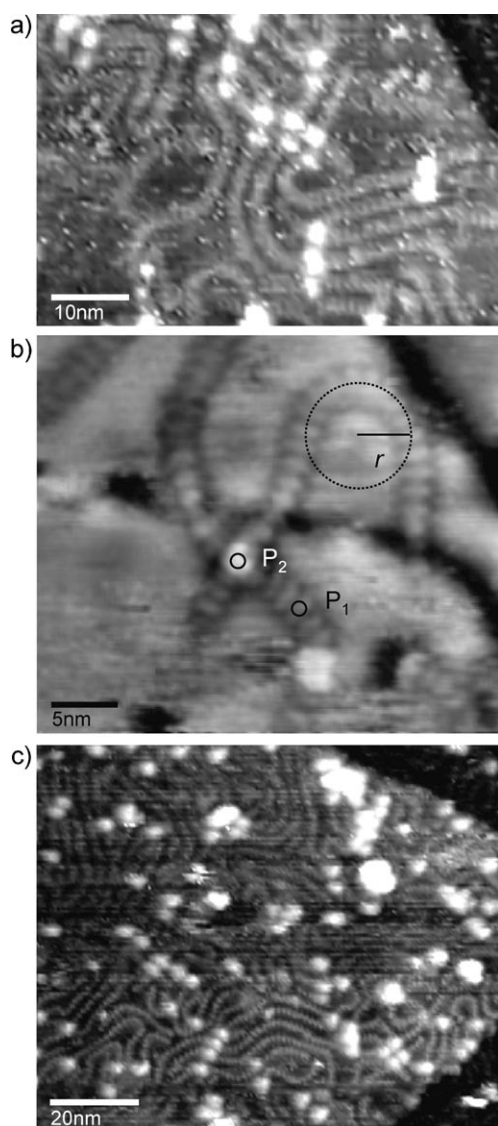


Figure 4. a–c) STM images of the polymer **Pn** on Au(111) ($V_{\text{sample}} = -1.80$ V, $I_{\text{tunnel}} = 0.03$ nA). b) Two **Pn** molecules traverse a step edge, and cross at point P_2 (twice the height of a single strand measured at P_1). A curved chain is shown with its radius of curvature labeled r . c) Large area STM image showing a high-density region of **Pn**. Bright contrast points show crossover points.

axes of two crossing polymers is measured as $91 \pm 9^\circ$, which implies that there is a preferred relative orientation for the overlapping polymer chains, possibly due to interactions between the aryl side groups. The continuous variation in topographic height indicates that polymer chains do not break when crossing.

To determine the influence of chain–chain interactions on polymer flexibility we have performed a statistical analysis of the distance, R , between porphyrin units which are separated by a contour length of L along the polymer chain. L is chosen to be an integer number, N , of porphyrin subunits. Figure 5a shows histograms of the normalized frequency of R for $N = 5, 7, 9$, and 11. For small values of N we observed a sharply peaked distribution with the average value of the end-to-end distance, $R_{\text{av}} \approx L$ (i.e. **Pn** remains straight for short segments)

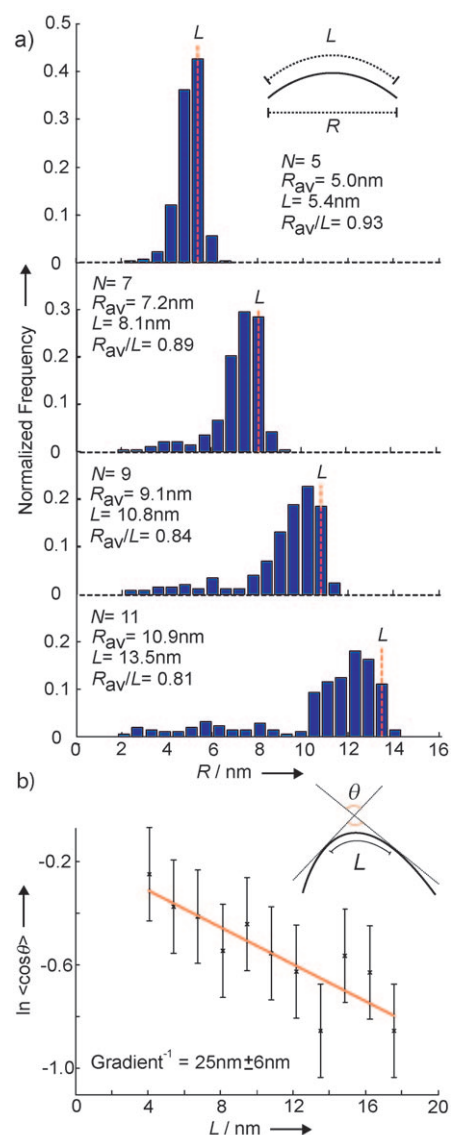


Figure 5. a) Histograms showing the normalized frequency distribution of the end-to-end length R for segments of the polymer chain containing 5, 7, 9, and 11 porphyrin monomer units. b) Plot of $\ln \langle \cos \theta \rangle$.

in agreement with previous studies on **P4** oligomers.^[13] However, we find that for larger values of N the distribution broadens and R_{av} deviates significantly from L . This deviation is due to occurrences of $R \ll L$ arising from chains with “hairpin” bends.

We have determined the angular correlation length, L_c , (i.e. the length over which the chain orientation becomes decorrelated) from the average value of $\cos \theta$, where θ is the angle between two segments of the polymer chain separated by a contour length of L .^[14] The average is taken over all segment pairs with the same contour length separation. It is possible to estimate L_c assuming an exponential dependence^[15] $\langle \cos \theta \rangle = \exp(-L/L_c)$. A plot of $\ln \langle \cos \theta \rangle$ against L shows a linear dependence (Figure 5b), from which we determine $L_c = 25 \pm 6$ nm.

For isolated non-interacting polymers the definition of L_c is equivalent to the persistence length, L_p , a measure of the intrinsic flexibility of a polymer chain^[15] which has been determined in previous scanning probe studies of biopolymers.^[16] For the densely packed porphyrin polymers discussed here the direct equivalence of L_c and L_p does not hold due to interactions with the surface and between neighboring chains, arising, for example, from alkyl chain interdigitation. Nevertheless it is interesting to note that the value of L_c is significantly greater than the value of persistence length previously measured for analogue oligomers in solution ($L_p \approx 19$ nm).^[13] This indicates that polymers adsorbed on surfaces studied here are, on average, straighter than in the solution phase. We attribute this increase to the planar geometry of adsorption of the molecules: in solution, the porphyrins can bend out of plane, whereas on the surface, bending can only occur in the plane of the porphyrins so that deformation is localized in the acetylenic bridges. Interchain interactions are also expected to promote parallel alignment of neighboring chains. This point is consistent with our images which show that sharp bends do not occur in segments in quasi-close-packed regions. The images, supported by the statistical analysis, show that simple models of polymers, such as the wormlike chain (WLC)^[15] model cannot fully account for the arrangement of chains which we observe. In particular the finite frequency of $R \ll L$ in the histograms for the larger values of L in Figure 5a is inconsistent with the WLC model.

Our results highlight the importance of UHV-ESD for the STM imaging of large complex molecules. We have shown that conjugated porphyrin polymers are surprisingly flexible, even when constrained to a two-dimensional surface, and that their conformations and chain-chain crossing geometries are strongly influenced by interchain interactions. Effects of this type are likely to play a critical role in two-dimensional supramolecular organization and must be considered in the design of complex interfaces for applications in sensing and molecular electronics.

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- [1] H. L. Anderson, S. J. Martin, D. D. C. Bradley, *Angew. Chem.* **1994**, *106*, 711–713; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 655–657.

- [2] a) M. H. Chang, M. Hoffmann, H. L. Anderson, L. M. Herz, *J. Am. Chem. Soc.* **2008**, *130*, 10171–10178; b) V. S.-Y. Lin, S. G. DiMaggio, M. J. Therien, *Science* **1994**, *264*, 1105–1111.
- [3] a) G. Sedghi, K. Sawada, L. J. Esdaile, M. Hoffmann, H. L. Anderson, D. Bethell, W. Haiss, S. J. Higgins, R. J. Nichols, *J. Am. Chem. Soc.* **2008**, *130*, 8582–8583; b) M. U. Winters, E. Dahlstedt, H. E. Blades, C. J. Wilson, M. J. Frampton, H. L. Anderson, B. Albinsson, *J. Am. Chem. Soc.* **2007**, *129*, 4291–4297; c) K. Susumu, P. R. Frail, P. J. Angiolillo, M. J. Therien, *J. Am. Chem. Soc.* **2006**, *128*, 8380–8381.
- [4] F. Schreiber, *Prog. Surf. Sci.* **2000**, *65*, 151–256.
- [5] a) A. Saywell, G. Magnano, C. J. Satterley, L. M. A. Perdigão, N. R. Champness, P. H. Beton, J. N. O'Shea, *J. Phys. Chem. C* **2008**, *112*, 7706–7709; b) C. J. Satterley, L. M. A. Perdigão, A. Saywell, G. Magnano, A. Rienzo, L. C. Mayor, V. R. Dhanak, P. H. Beton, J. N. O'Shea, *Nanotechnology* **2007**, *18*, 455304.
- [6] a) H. Suzuki, T. Yamada, T. Kamikado, Y. Okuno, S. Mashiko, *J. Phys. Chem. B* **2005**, *109*, 13296–13300; b) S. Rauschenbach, F. L. Stadler, E. Lunedei, N. Malinowski, S. Koltsov, G. Costantini, K. Kern, *Small* **2006**, *2*, 540–547; c) H. Tanaka, T. Kawai, *Nat. Nanotechnol.* **2009**, *4*, 518–522; d) L. C. Mayor, J. B. Taylor, G. Magnano, A. Rienzo, C. J. Satterley, J. N. O'Shea, J. Schnadt, *J. Chem. Phys.* **2008**, *129*, 114701.
- [7] J. E. Lyon, A. J. Cascio, M. M. Beerbom, R. Schlaf, Y. Zhu, S. A. Jenekhe, *Appl. Phys. Lett.* **2006**, *88*, 222109.
- [8] P. N. Taylor, J. Huuskonen, G. Rumbles, R. T. Aplin, E. Williams, H. L. Anderson, *Chem. Commun.* **1998**, 909–910.
- [9] a) J. A. A. W. Elemans, S. B. Lei, S. De Feyter, *Angew. Chem.* **2009**, *121*, 7434–7469; *Angew. Chem. Int. Ed.* **2009**, *48*, 7298–7332; b) T. Kudernac, S. B. Lei, J. A. A. W. Elemans, S. De Feyter, *Chem. Soc. Rev.* **2009**, *38*, 402–421.
- [10] a) C. S. Gopinath, R. P. Pandian, P. T. Manoharan, *J. Chem. Soc. Dalton Trans.* **1996**, 1255–1259; b) A. Rienzo, L. C. Mayor, G. Magnano, C. J. Satterley, E. Ataman, J. Schnadt, K. Schulte, J. N. O'Shea, *J. Chem. Phys.* **2010**, *132*, 084703.
- [11] J. Stöhr, D. A. Outka, *Phys. Rev. B* **1987**, *36*, 7891–7905.
- [12] a) M. Brun, R. Demadrille, P. Rannou, A. Pron, J. P. Travers, B. Grevin, *Adv. Mater.* **2004**, *16*, 2087–2092; b) E. Mena-Osteritz, A. Meyer, B. Langeveld-Voss, R. A. J. Janssen, E. W. Meijer, P. Bäuerle, *Angew. Chem.* **2000**, *112*, 2791–2796; *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 2679–2684.
- [13] J. E. Lovett, M. Hoffmann, A. Cnossen, A. T. J. Shutter, H. J. Hogben, J. E. Warren, S. I. Pascu, C. W. M. Kay, C. R. Timmel, H. L. Anderson, *J. Am. Chem. Soc.* **2009**, *131*, 13852–13859.
- [14] M. Ullner, C. E. Woodward, *Macromolecules* **2002**, *35*, 1437–1445.
- [15] a) L. D. Landau, E. M. Lifshitz, *Statistical Physics*, Pergamon, London, **1958**; b) G. S. Manning, *Phys. Rev. A* **1986**, *34*, 668–670; c) J. Wilhelm, E. Frey, *Phys. Rev. Lett.* **1996**, *77*, 2581–2584.
- [16] a) C. Rivetti, M. Guthold, C. Bustamante, *J. Mol. Biol.* **1996**, *264*, 919–932; b) P. Samorí, C. Ecker, I. Gossel, P. A. J. de Witte, J. J. L. M. Cornelissen, G. A. Metselaar, M. B. J. Otten, A. E. Rowan, R. J. M. Nolte, J. P. Rabe, *Macromolecules* **2002**, *35*, 5290–5294.