PHYSICAL REVIEW B **79**, 245404 (2009)

Density functional theory study of the iron-based porphyrin haem(b) on the Si(111):H surface

Alex M. P. Sena, Veronika Brázdová, and David R. Bowler
Department of Physics and Astronomy, London Centre for Nanotechnology, Materials Simulation Laboratory,
University College London, Gower Street, London WC1E 6BT, United Kingdom

(Received 23 January 2009; published 4 June 2009)

Iron porphyrins, of which the biological molecule haem(b) is a derivative, have shown potential for use in molecular electronics. Understanding the influence of a surface on a molecules electronic properties is an important step in the assessment of its potential for use in nanoscale devices. Here, a density functional study of haem(b) on the Si(111):H surface has been performed in order to investigate the effect of the molecule-substrate interaction on the electronic structure of haem and provide valuable guidance to current experimental work on this and other like systems. The molecule is found to weakly physisorb onto the surface in a planar conformation at a distance of 3.24 Å with a binding energy of 0.42 eV. Creation of a defect in the hydrogen layer of the surface is found to allow the adsorption to strengthen with the binding energy increasing to 0.54 eV and the separation decreasing to 3.05 Å. Simulated STM images indicate that the molecule should be visible on the surface and retain its conjugated charge distribution.

DOI: 10.1103/PhysRevB.79.245404 PACS number(s): 68.43.Bc, 71.15.Mb

I. INTRODUCTION

Driven by the ever decreasing size of computer devices, efforts to construct nanoscale electronic components (e.g., transistors, switches, wires) have intensified. The field of molecular electronics[1] aims to build these components using small molecules, often taken from biological systems. Porphyrins are ring-shaped carbon-nitrogen-based aromatic molecules that have attracted a lot of attention with regard to molecular electronics. This is due to their ability to facilitate a number of complex biological processes such as photosynthesis, respiration, and oxygen transport.[2] Porphyrins can take on such a wide range of roles thanks to the ability to control their chemistry by either functionalizing them with various side chains or varying their central metal atom. This makes them very attractive from a molecular electronics stand point. There have been many attempts to create demonstration devices using porphyrins with investigations into switches,[3] nanowires,[4] sensors,[5] spintronic devices,[6] information storage[7] or processing, and light-harvesting[8] systems, having all been performed. In almost all such cases, devices built using porphyrin derivatives require some means of providing structure to support the active molecules and hold them in place. A common way of providing this is to deposit them on a substrate. The interaction between the molecule and surface then becomes very important to characterize as it can have a large effect on the molecule's electronic properties and greatly impact its potential use. The electronic interaction between a molecule and a substrate can be studied using *ab initio* electronic-structure calculations. These give detailed information on the ground-state geometry, charge and spin distributions, and can also provide simulated scanning-tunneling microscopy and spectroscopy (STM/S) images for comparison with experiment. Of the many electronic structure methods, density functional theory (DFT) (Refs. 9 and 10) is one of the most widely used. Its capacity to simulate relatively large systems ($\simeq 500$ atoms) at acceptable speed and accuracy has made it the most popular choice for investigating large biological systems quantum mechanically.

The porphyrins found in biological systems often possess various side chains, which tailor their chemistry to a particular role. For example, the molecule haem(b), Fig. 1(a), is an iron-coordinated porphyrin derivative which plays an active role in the proteins haemoglobin and cytochrome(c).[11]

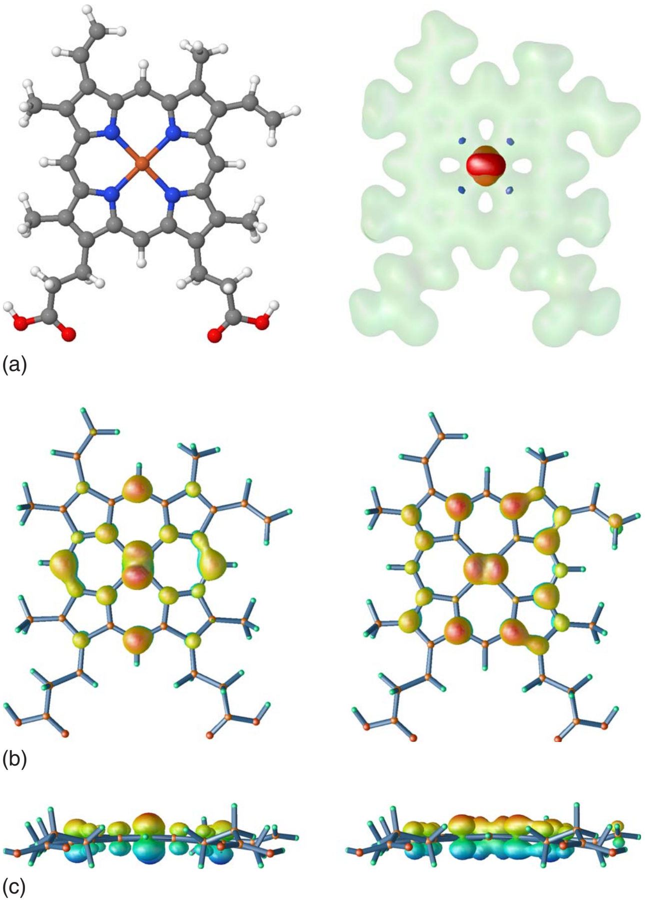

FIG. 1. (Color online) Equilibrium structure, charge, and spin densities for the isolated haem(b) molecule. All isosurfaces are plotted at 0.01 e^{-} Å^{-3}.

Haem's ability to facilitate electron transfer in these systems has seen it investigated as a potential molecular wire.[12,13] Other investigations have looked at providing structure to groups of haems using amyloid fibrils[14] with the eventual aim of incorporating haem(b) into a conducting nanostructure. The interest in haem has resulted in extensive theoretical characterization being performed of both the molecule in isolation[15] and in dimer pairs.[16] Indeed, iron porphyrins in general have been found to have very promising properties and have been the subject of many prototype molecular-electronic devices.[17,6] As a consequence, their properties on surfaces such as Ag(111) (Ref. 18) and Au(111) (Ref. 17) have been studied and their coupling to magnetic substrates also investigated.[19] There has also been much work investigating which methods are best used to address these systems, in particular with regard to producing the correct spin-state energetics.[20] There has so far, however, been no work studying the haem molecule on the semi-conducting Si(111):H hydrogen-terminated substrate. Studying the molecule on this particular surface is of interest for a number of reasons. First, the surface's (1×1) reconstruction makes it easy to model computationally. Simulations of small pieces of surface can be performed without worrying about the failure to reproduce large-scale reconstructions, such as the (7×7) present in the clean Si(111) surface, affecting the energy greatly. Second, the surface is easy to prepare and handle experimentally as its passivated surface prevents impurities from binding strongly to the surface. This should enable contact with future experimental work, an important consideration when performing computational studies. Finally, the surface offers the interesting possibility to tune the interaction between the molecule and the substrate by removing individual hydrogen atoms from the surface. That is, switching parts of the surface from passivated to activated, using lithography as in Refs. 21 and 22. Varying the interaction between the molecule and the substrate allows the electronic properties of the system to be changed and also offers possible routes to easier assembly of device structures.

With the above in mind, a DFT study of haem(b) on the Si(111):H surface is performed to characterize the electronic structure and binding when haem is on this substrate. First, the haem is studied in the gas phase to provide an accurate structure for adsorption onto the surface with results for the DFT and DFT+U methods being compared. The haem is then adsorbed onto the Si(111):H surface and its interaction with the surface is studied via spin-density plots and simulated STM images. Finally, a defect is created in the surface's hydrogen layer and the haem adsorbed over this defect. The change in the binding and interaction that the defect causes is described and explained.

II. METHODS

Spin-polarized Kohn-Sham DFT calculations were performed using the periodic plane-wave pseudopotential code VASP.[23,24] The projector augmented wave method[25] was used with a plane-wave cutoff of 325 eV. The exchange-correlation functional used was GGA-PW91.[26] All calculations were performed at the Gamma point. The electronic-convergence tolerance was 1×10^{-6} eV and simulations ran until the force on each atom was less than 0.01 eV Å^{-1}. The Si(111):H surface was modeled using a (1×1) reconstructed six-layer slab with the bottom two layers held fixed in the bulk positions and both surfaces passivated with hydrogen. For the adsorption simulations, the unit cell was $23\times20\times38$ Å^3, which always left at least a 16 Å vacuum gap between the adsorbed haem and the next periodic-slab image. To check convergence, higher-accuracy calculations were performed with a 450 eV cutoff and $2\times2\times1$ k points. The energy difference between the $2\mu_B$ and $0\mu_B$ spin states of the haem was found to be converged within 0.01 eV and the energy difference between the normal and defective surfaces within 0.005 eV.

Simulated STM images were created with the program BSKAN,[27] working in the Tersoff-Hamann[28] approximation. Bias voltages of ±1.5 V were used to image empty and filled states. Binding energies were calculated using the following formula while keeping all the relevant computational parameters constant:

$$\Delta E_{\text{Bind}} = E_{\text{IsolatedHaem}} + E_{\text{CleanSurface}} - E_{\text{Complex}}. \tag{1}$$

Recent work[15,29] has found that iron porphyrins must often be treated using the DFT+U (Refs. 30 and 31) method to correctly describe the iron atom's tightly localized d electrons and produce the correct magnetic ground state. All calculations were performed using both conventional DFT and the DFT+U method as formulated by Dudarev.[32] Coulomb and exchange parameters of $U=4$ eV and $J=1$ eV were used as recommended for iron porphyrins in Ref. 15. To avoid repetition, predominantly DFT+U calculations are presented with the differences and improvements over using conventional DFT, highlighted when necessary.

III. RESULTS

A. Isolated haem

To produce an accurate structure for adsorption onto the surface, the haem was first studied in the gas phase. The equilibrium structure, charge, and spin isosurfaces from a conventional DFT calculation are shown in Fig. 1(a). The haem remained planar with an Fe-N bond length of 1.99 Å agreeing well with Ref. 20. The haem was found to have a magnetic moment of $\mu=2\mu_B$ arising from the polarization of the iron atom's $3d$ electrons. This is in agreement with Ref. 20 and other systems where the iron atom is fourfold coordinated such as an iron tetraphenyl porphyrin.[15] The density of states, Fig. 2, shows a separation in energy between the spin-up and spin-down components of the d electrons close to the Fermi energy. The spin-down (minority) channel is expected to be conducting and the spin-up (majority) channel insulating, thus resulting in a spin-polarized transport profile. The highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) charge plots in Fig. 1(b) are spread across the porphyrin ring but also have a large component on the central iron atom.

DFT+U calculations were performed as described in Sec. II and in this case led to the same $\mu=2\mu_B$ ground state as

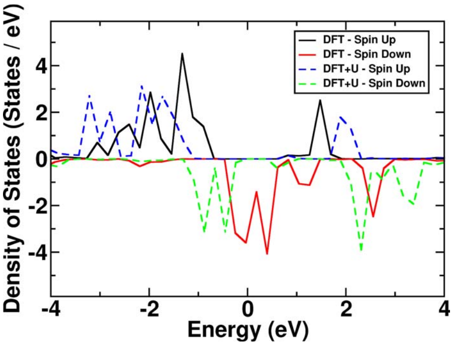

FIG. 2. (Color online) Density of states for the d orbitals of the isolated haem molecule, shown for DFT and DFT+U simulations. The DFT+U method is clearly seen to shift the filled/empty states down/up in energy. In the DFT+U case the presence of four occupied spin-up orbitals and two occupied spin-down orbitals, can be seen clearly. These give the molecule its overall $\mu=2\mu_B$ magnetic moment.

conventional DFT and gave a very similar equilibrium geometry. The density of states is altered, as shown in Fig. 2, with the occupied (unoccupied) d states being dragged down (up) in energy. The reason for this is seen[31] from the differential of the DFT+U energy expression

$$E = E^{\mathrm{GGA}} - \frac{1}{2}UN(N-1) + \frac{1}{2}U\sum_{i\neq j} n_i n_j \tag{2}$$

with respect to the orbital occupation n_i, which gives the eigenvalue energy

$$\epsilon_i = \frac{\partial E}{\partial n_i} = \epsilon_{\mathrm{GGA}} + U\left(\frac{1}{2} - n_i\right). \tag{3}$$

Thus occupied d orbitals with $n_i=1$ are at a lower energy than in conventional DFT. This is enough to change the ground state of the haem from metallic to insulating, though the spin components are still separated in energy.

Previous work[15,29] has ascertained that the DFT+U method best reproduces the system's electronic structure and this is reflected in the clearer density-of-states energy levels produced by the method here. Having characterized the isolated haem molecule, this gas-phase equilibrium structure is now adsorbed onto the Si(111):H surface and the interaction between substrate and molecule is investigated.

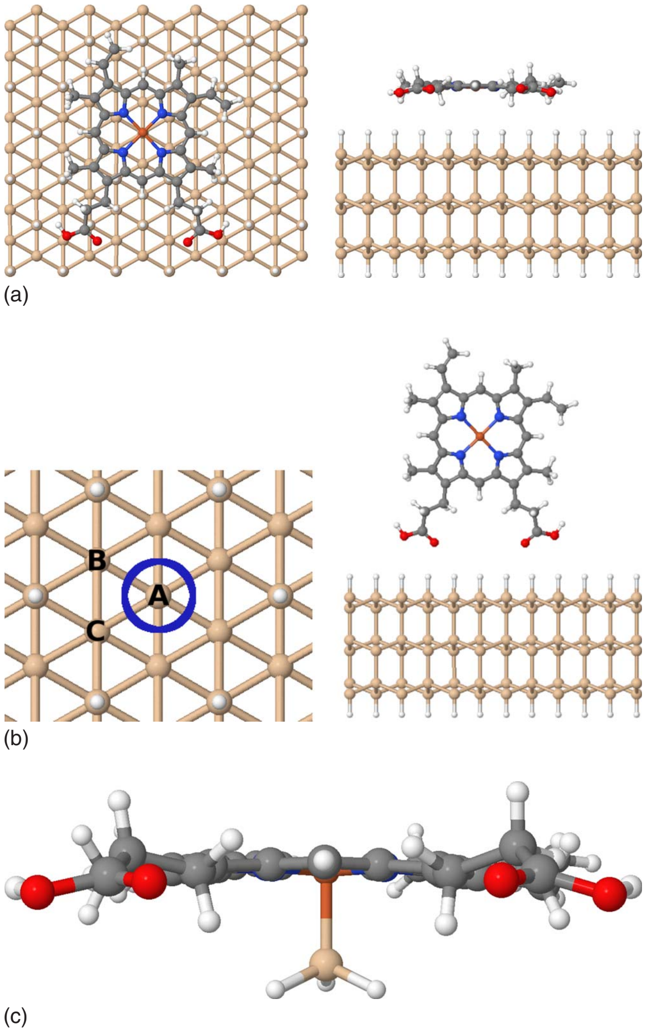

FIG. 3. (Color online) The different adsorption geometries used in the simulations.

B. Perfect H surface

Previous experimental and theoretical studies have shown that isolated planar molecules such as haem, prefer to adsorb flat onto a surface.[18] Thus the haem was first adsorbed in this manner over the three surface sites, as shown in Fig. 3(a), using the DFT+U method. It was found to weakly physisorb in all cases. The most favorable adsorption was over site A, when the haem's iron atom was centered directly over a surface hydrogen atom. This site had a binding energy of 0.42 eV and an equilibrium separation from the surface hydrogen plane of 3.25 Å, broadly agreeing with previous investigations of planar iron porphyrin adsorption performed on Au(111).[17] The other adsorption sites, B and C, were marginally less well bound. The molecule was found to have almost complete rotational freedom on the surface. A rotation of 45° about an axis perpendicular to the surface plane and through the iron atom cost less than 10 meV. To ensure the haem was as well bound as it could be, it was forced closer to the surface, around 2.00 Å from the hydrogen plane. This however, resulted in a very high energy and the molecule soon relaxed away back to its equilibrium separation. The binding curve, created by fixing the iron atom at certain distances from the surface, is shown as the dashed line in Fig. 4.

To check whether planar adsorption was the most favorable conformation, simulations with the haem in a standing configuration, as shown in Fig. 3(b), were also performed. Simulations were carried out at different facial separations (i.e., distance in a direction perpendicular to the plane of the haem molecule) by changing the cell size in that direction. In all cases the standing conformation was found to be less well bound than the planar conformations with a maximum binding energy of 0.114 eV at a facial separation of 13 Å. Tilting the haem toward the surface by 30° slightly increased the binding to 0.118 eV. This indicates that haem should bind to

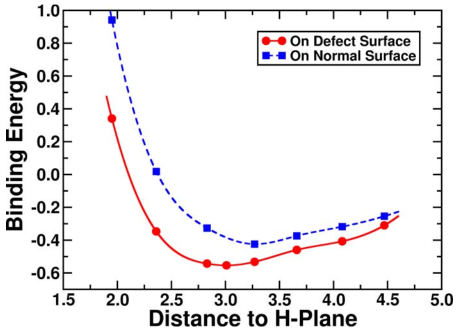

FIG. 4. (Color online) Graph showing the change in binding energy with height from surface for planar adsorption of haem on a perfect and defective Si(111):H surface. Line through points is a cubic spline intended only as a guide to the eyes.

the Si(111):H surface in a planar conformation. The results for haem on the perfect surface are summarized in Table I. The planar adsorption over site *A* is now studied in more detail.

When over site *A* the molecule retained its moment of $\mu = 2\mu_B$ and its density of states was only mildly perturbed from that of the gas phase. There was no charge transfer or substrate polarization. Population analysis, taken using a number of different Wigner-Seitz radii, always showed that the charge associated with the central iron atom remained practically unchanged between the isolated and on surface cases. Along with the small binding energy, this indicates that the interaction between molecule and substrate is due only to weak dispersive force with no covalent-bonding component. There is likely to be a larger van der Waals dispersive component to the binding energy, which is not correctly described in DFT approaches.[33] Simulated STM images of the planar adsorption, shown in Fig. 5, were created to provide a link with future experimental work. They are diffuse, broadly reflect the shape of the isolated molecule's HOMO/LUMO and exhibit a noticeable symmetry change between filled and empty states. The even contrast of the charge distribution around the porphyrin ring suggests that the molecule retains its π-conjugated aromatic charge distribution when on the surface. These images show that the haem should be visible in STM experiments and clearly distinguishable from the substrate.

TABLE I. Summary of results for the different haem-substrate adsorption conformations.

Configuration		Separation[a] (Å)	Moment (μ_B)	Binding (eV)
Surface	Site			
Perfect	Site *A*	3.246	2.000	0.424
	Site *B*	3.504	2.000	0.317
	Site *C*	3.438	2.000	0.361
	Standing	8.679	2.000	0.114
	Tilted	8.421	2.000	0.119
Defect	Fe centered	3.056	3.001	0.543
	N centered	3.089	2.275	0.418
	C centered	3.200	2.292	0.367
	R centered	3.153	3.000	0.457

[a] Distance from the central iron atom to upper hydrogen plane of surface.

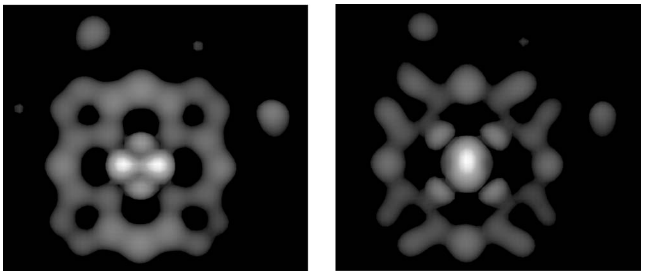

FIG. 5. Simulated STM image of haem on the perfect Si(111):H surface. Bias voltage ±1.5 V. Left: filled states. Right: empty states. Isosurface of 0.003 $e^- Å^{-3}$.

However, recent attempts to image haem at room temperatures have not been possible due to the molecules reactivity as well as its high mobility on the Si(111):H surface.[34] Previous studies[21,35] have shown that it is possible to create favorable binding sites for molecules on hydrogen-passivated surfaces by creating defects in the hydrogen layer. Phthalocyanines were found to weakly physisorb on the hydrogen-terminated surface. But when hydrogen atoms were removed from the surface to create dangling bonds, the phthalocyanines were found to bind to these very strongly. It may be possible to pin the haem to the surface and alleviate the problem of high mobility in the same way. In Sec. III, a defect is created in the Si(111):H hydrogen layer and the interaction between the resulting defective surface and the haem investigated.

C. Defective H surface

A defect was created in the hydrogen layer by removing the hydrogen atom from above site *A*, as shown in Fig. 3(b). The haem was adsorbed in a planar manner with its iron atom directly over this defect. It was found to adsorb more strongly than on the perfect surface with a binding energy of 0.543 eV. The equilibrium separation to the hydrogen plane was found to reduce to 3.06 Å, which was 0.25 Å closer to the surface than previously. The binding curve is shown as the solid line in Fig. 4. Simulations were also performed with other atoms of the haem, such as one of the nitrogen atoms or a carbon atom in one of the loose side chains, centered over the defect. These gave less well-bound structures at slightly larger separations. A summary of the results obtained is shown in Table I. The adsorption with the iron atom centered over the defect is now considered in detail. This is the most interesting conformation, as the useful properties of a porphyrin system often originate from the charge and spin state of its central metal atom. The interaction between the iron and the dangling bond is therefore important to characterize.

With the iron atom centered over the defect, the simulation cell's magnetic moment was $3\mu_B$ with $2\mu_B$ coming from the haem and $1\mu_B$ from polarization of the exposed silicon's

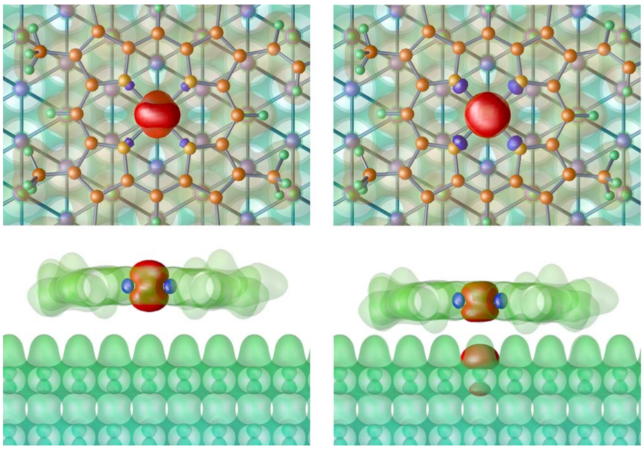

FIG. 6. (Color online) Left: spin distribution for haem on the perfect Si(111):H surface. Right: for haem on defect Si(111):H surface. There is a clear difference in the spin distribution around the iron atom, although both have a magnetic moment of $2\mu_B$.

dangling bond. The spin distribution around the iron atom was found to change slightly as shown in Fig. 6. The density of states was also slightly altered, although the main features, such as the separation in energy of spin-up and spin-down components, were again preserved. The change in spin distribution is reflected by a change in the appearance of the central iron atom in the filled states STM image of Fig. 7 compared with Fig. 5.

The increase in binding energy and change in spin distribution when the haem is on this defect surface is indicative of some interaction between the dangling $2p_z$ orbital of the underlying silicon and the orbitals of the iron atom. Studies of analogous systems, such as nitrogen atoms on Cu(100) saw the nitrogen $2p_z$ orbitals hybridizing with the copper $3d_{r^2-z^2}$.[36] However, here the effects of the haem-substrate interaction are fairly undramatic. The molecule is still only physisorbed and remains too far away from the surface for a covalent bond to form between the iron and exposed silicon atom. This is due to the presence of the other surface hydrogen atoms. These would force the molecule to distort in an unfavorable way if it approached too close to the surface. The energy cost of bending the inner porphyrin ring out of its natural planar conformation and breaking the aromatic electronic structure, may be far greater than the energy gained from binding with the silicon atom.

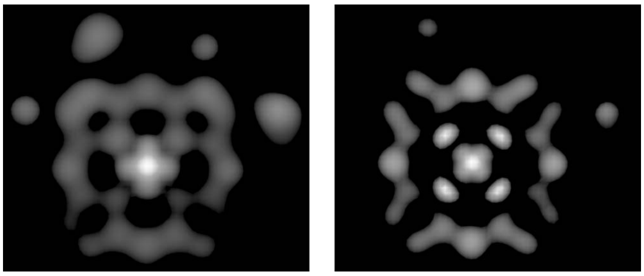

FIG. 7. Simulated STM image of haem on the defective Si(111):H surface. Bias voltage ±1.5 V. Left: filled states, right: empty states. Isosurface of 0.002 $e^- Å^{-3}$.

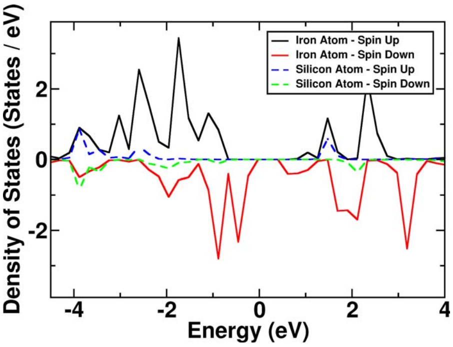

FIG. 8. (Color online) Density of states of the iron atom and the silicon atom for an SiH_3-[Haem] complex.

To investigate the silicon-iron binding in the absence of the obtrusive surface hydrogens, simulations were performed of just an SiH_3-[Haem] complex, Fig. 3(c). It was found to form a bond with binding energy 1.243 eV and length 2.33 Å using the DFT+U method. In this case, the magnetic moment of the system became $1\mu_B$. There was some charge transfer from the silicon atom creating an extra spin-down occupation on the iron atom at −2 eV as shown in Fig. 8. This reduces the magnetic moment of the complex to $1\mu_B$. It is now clear that when on the defect surface, the haem did not get close enough for this hybridization to occur fully. However, studies of similarly planar phthalocyanines[22] have found that the central metal atom can displace itself out of the plane of the molecule. This may allow the central metal atom to get closer to the surface.

Simulations were performed with the iron atom moved out of the plane of the porphyrin ring toward the surface so that it bound with the silicon. However, these structures were less stable and the iron atom soon relaxed back into the plane of the porphyrin ring. It may be important to include the occupied $4s$ orbitals of the iron atom as valence electrons in the pseudopotential as these also contribute to the sigma bonding with the $2p_z$ orbital below. However, calculations with these pseudopotentials could not be accurately converged for this system. Previous studies[22] found a second stable conformation for the phthalocyanines on a defective surface. In these, the dangling bond from the surface hybridized with the aromatic structure of a benzene ring in the phthalocyanines. This tethered the molecule in place but allowed it to rotate around the bond. Similar simulations were performed here; the dangling bond was centered under one of the six-membered Fe-C-N rings (R centered in Table I). However, the binding energy was found to be similar to previous case with the iron atom centered over the defect. This may be due to the absence of sufficient charge delocalization around the Fe-C-N ring.

Although the haem did not bind covalently to the defective surface, the dangling bond caused an increase in binding strength and interaction. Even stronger binding could be achieved by removing a number of hydrogens from the same area of the surface, instead of just one. This stronger binding energy could help hold the molecule still for room-temperature STM imaging. In addition, being able to pin molecules in position is important if nanoscale-patterned electronic devices are to be created from the molecules on the surface.[35]

IV. CONCLUSION

Iron porphyrins and in particular haem, are an important class of molecules with potential molecular-electronic applications. A DFT study of haem(b) on the Si(111):H surface has been performed in order to characterize the effect of the substrate on haem's electronic structure and to search for a solution to current difficulties faced when imaging iron-based porphyrins with STMs at room temperature on this surface.

The haem was first characterized in the gas phase. Using conventional DFT, the density of states of the isolated molecule was found to be metallic for one spin component and insulating for the other. However, this was no longer the case when using the DFT+U method, which is known to be more accurate for some transition-metal porphyrins. In both cases there was a separation in energy of the spin-up and spin-down components close to the Fermi level. The molecule was then studied on the Si(111):H surface. It was found to weakly physisorb in a planar conformation onto the surface with an adsorption energy of 0.42 eV. Its gas-phase magnetic moment and density of states were almost unchanged. Simulated STM images showed the haem to be visible on the surface and distinguishable from the substrate. A strong difference between the filled and empty states was seen. The creation of a defect in the surface hydrogen layer directly below the molecule allowed the haem to move 0.25 Å closer to the surface and stronger adsorption to occur. When the iron atom was centered over the exposed silicon-dangling bond the binding energy was 0.54 eV. However, there was still no strong covalent bonding between the molecule and the substrate with the haem remaining over 3.00 Å away from the surface. The remaining surface hydrogens forced the haem to distort if it was moved closer to the surface. This is energetically unfavorable as the energy cost of breaking the aromatic structure of the porphyrin is far greater than that gained from forming an Fe-Si bond. Moving the iron atom out of the porphyrin plane to bind it with the surface was also not energetically favorable.

The removal of individual hydrogen atoms from a semiconductor surface is possible using voltage pulses from an STM tip and has been performed previously with for phthalocyanines on Si(001):H (Ref. 35) and on Si(111):H.[22] By creating multiple defects which allow haem to bind more strongly with the surface in certain sites, patterns of molecules such as long chains, could be created which may have the potential to act as a functional nanostructure. The task of creating a device which is both easily assembled and possesses useful electronic properties, however, remains a huge challenge.

ACKNOWLEDGMENTS

A.M.P.S. and V.B. are funded by the IRC in nanotechnology. D.R.B. is funded by the Royal Society. The authors thank Colm Durkin and Sigrid Weigelt for useful discussions.

---

[1] A. Nitzan and M. Ratner, Science **300**, 1384 (2003).

[2] *The Porphyrins*, edited by D. Dolphin (Academic, New York, 1978), Vols. I–VII.

[3] J. Barth, G. Costantini, and K. Kern, Nature (London) **437**, 671 (2005).

[4] K. Tagami, M. Tsukada, T. Matsumoto, and T. Kawai, Phys. Rev. B **67**, 245324 (2003).

[5] H. Nakanishi, M. David, E. Dy, R. Tanaka, and H. Kasai, J. Phys.: Condens. Matter **19**, 365234 (2007).

[6] H. Wende, M. Bernien, J. Luo, C. Sorg, N. Ponpandian, J. Kurde, J. Miguel, M. Piantek, X. Xu, P. H. Eckhold, W. Kuch, K. Baberschke, P. M. Panchmatia, B. Sanyal, P. M. Oppeneer, and O. Eriksson, Nature Mater. **6**, 516 (2007).

[7] C. Carcel, J. Laha, R. Loewo, P. Thamyongkit, K.-H. Schweikart, V. Misra, D. Bocian, and J. Lindsey, J. Org. Chem. **69**, 6739 (2004).

[8] H. Imahori, H. Norieda, H. Yamada, Y. Nishimura, I. Yamazaki, Y. Sakata, and S. Fukuzumi, J. Am. Chem. Soc. **123**, 100 (2001).

[9] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[10] W. Kohn and L. Sham, Phys. Rev. **140**, A1133 (1965).

[11] J. P. Collman, R. Boulatov, C. J. Sunderland, and L. Fu, Chem. Rev. (Washington, D.C.) **104**, 561 (2004).

[12] M. P. Johansson, M. R. A. Blomberg, D. Sundholm, and M. Wikstrom, Biochim. Biophys. Acta **1553**, 183 (2002).

[13] D. Smith, K. Rosso, M. Dupuis, M. Valiev, and T. Straatsma, J. Phys. Chem. B **110**, 15582 (2006).

[14] A. Baldwin, R. Bader, J. Christodoulou, C. MacPhee, C. Dobson, and P. Barker, J. Am. Chem. Soc. **128**, 2162 (2006).

[15] D. Scherlis, M. Cococcioni, P. Sit, and N. Marzari, J. Phys. Chem. B **111**, 7384 (2007).

[16] D. Khvostichenko, Q.-Z. Yang, and R. Boulatov, Angew. Chem. **46**, 8368 (2007).

[17] K. Leung, B. Rempe, P. Schultz, E. Sproviero, V. Batista, M. Chandross, and C. Medforth, J. Am. Chem. Soc. **128**, 3659 (2006).

[18] L. Zotti, G. Teobaldi, W. Hofer, W. Auwarter, A. Weber-Bargioni, and J. Barth, Surf. Sci. **601**, 2409 (2007).

[19] M. Bernien, J. Miguel, C. Weis, M. E. Ali, J. Kurde, B. Krumme, P. M. Panchmatia, B. Sanyal, M. Piantek, P. Srivastava, K. Baberschke, P. M. Oppeneer, O. Eriksson, W. Kuch, and H. Wende, Phys. Rev. Lett. **102**, 047202 (2009).

[20] P. Panchmatia, B. Sanyal, and P. Oppeneer, *Ab Initio Calculations of the Electronic Structure and Magnetism of Iron Porphyrin-Type Molecules: A Benchmarking Study* (Springer, Berlin, 2007).

[21] M. Hersam, N. Guisinger, and J. Lyding, Nanotechnology **11**, 70 (2000).

[22] N. Papageorgiou, E. Salomon, T. Angot, L.-M. Layet, L. Giovanelli, and G. Le Lay, Prog. Surf. Sci. **77**, 139 (2004).

[23] G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11169 (1996).

[24] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).

[25] P. E. Blochl, Phys. Rev. B **50**, 17953 (1994).

[26] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R.

Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[27] W. Hofer and J. Redinger, Surf. Sci. **447**, 51 (2000).

[28] W. Hofer and J. Redinger, Prog. Surf. Sci. **71**, 147 (2003).

[29] P. Panchmatia, B. Sanyal, and P. Oppeneer, Chem. Phys. **343**, 47 (2008).

[30] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991).

[31] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyzyk, and G. A. Sawatzky, Phys. Rev. B **48**, 16929 (1993).

[32] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B **57**, 1505 (1998).

[33] A. Ruzsinszky, J. Perdew, and I. Csonka, J. Phys. Chem. A **109**, 11015 (2005).

[34] S. Weigelt and C. Durkan, private communication, 2008.

[35] M. C. Hersam, J. Lee, N. P. Guisinger, and J. W. Lyding, Superlattices Microstruct. **27**, 583 (2000).

[36] A. Nilsson, L. Pettersson, and J. Norskov, *Chemical Bonding at Surfaces and Interfaces* (Elsevier, New York, 2007), pp. 72–74.