

# Entrapment of Decanethiol in a Hydrogen-Bonded Bimolecular Template

Luís M. A. Perdigão,<sup>†</sup> Paul A. Staniec,<sup>†</sup> Neil R. Champness,<sup>‡</sup> and Peter H. Beton<sup>\*†</sup>

Schools of Physics & Astronomy and Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, U.K.

Received October 23, 2008. Revised Manuscript Received December 8, 2008

We have used scanning tunneling microscopy to investigate the deposition of 1-decanethiol onto a bimolecular self-assembled network composed of PTCDI (perylene tetracarboxylic diimide) and melamine on a Au(111) surface. A new laterally organized phase in which the pores of a parallelogram bimolecular arrangement trap two decanethiol molecules is identified. Disruption of the hexagonal PTCDI–melamine network arrangement after decanethiol deposition is also observed, providing insights about the interplay between supramolecular and substrate–adsorbate interactions.

## Introduction

Self-assembled monolayers (SAMs) produced by chemisorption of alkanethiol molecules on a Au surface have attracted considerable attention in recent decades.<sup>1–4</sup> SAMs form by the attachment of the sulfur headgroup to a gold atom, and for vapor deposition of alkanethiols, a range of surface phases has been observed and new models for chemisorption have recently been proposed.<sup>5–7</sup> In an alternative approach to the control of molecular organization on surfaces, a number of groups have demonstrated the use of two-dimensional nanoporous arrays to trap diffusing species as a potential route for fabrication of new materials.<sup>8–10</sup> Recently it has been demonstrated by Madueno et al.<sup>11</sup> that these two approaches may be combined using a bimolecular PTCDI–melamine hexagonal network, previously demonstrated as a surface template under vacuum conditions,<sup>8</sup> to control the spatial arrangement of chemisorbed thiolated species in solution-based experiments.<sup>11</sup> These experiments were performed using a Au(111) substrate which, for vacuum preparation, supports several mixed phases of PTCDI and melamine,<sup>12–14</sup> although

only a hexagonal phase is formed under solution conditions. In this paper, we have investigated the deposition of a thiol molecule onto a self-assembled network from the vapor phase under vacuum conditions. We find significant differences in the structures that are stabilized, as compared with solution deposition. These differences are attributed to the adsorption of the alkanethiols parallel rather than near-perpendicular to the surface. Of particular interest is the difference in the adsorption state of the alkanethiols in the cavities of a nanoporous network as compared with the clean Au(111) surface.

Specifically, we have studied the entrapment of 1-decanethiol in the cavities of a bimolecular network composed of perylene tetracarboxylic diimide (PTCDI) and 1,3,5-triazine-2,4,6-triamine (melamine) formed on the Au(111) surface using scanning tunneling microscopy (STM) under ultrahigh vacuum conditions. We find that decanethiol deposition has a disruptive effect on the hexagonal PTCDI–melamine network but that decanethiol may be trapped stably within a network on Au(111) with a parallelogram geometry.

## Experimental Methods

The experiments were conducted under ultrahigh vacuum (UHV) conditions. A 8 × 4 mm gold on mica sample (Agilent) was prepared using standard procedures of Ar sputtering (1 kV, 2 μA) and annealing (500 °C, ~1 h), which result in a clean Au(111) surface. Images of the sample were obtained using an STM which is housed within the UHV chamber and operated in constant current mode at room temperature. Images were processed using the WSxM software (Nanotech Electronica S.L.).<sup>15</sup> PTCDI and melamine were deposited onto a Au(111) surface by sublimation. Postannealing of coadsorbed PTCDI and melamine at 80–100 °C results in coexisting islands of PTCDI and domains of both the parallelogram and hexagonal PTCDI–melamine structures (STM image in Figure 1a). The structure of the parallelogram and hexagonal bimolecular network are given in parts b and c of Figure 1, respectively, following previous reports.<sup>12,13</sup> 1-Decanethiol (Alfa Aesar 96%) was purified by freeze–thaw–pump cycles before dosing onto the substrate. Decanethiol was introduced to the vacuum system through a leak valve during which the pressure rose from a background level of ~1 × 10<sup>-10</sup> to 1.0 × 10<sup>-8</sup> Torr. The sample was at room temperature during decanethiol deposition.

## Results and Discussion

Figure 2a shows an STM image of the surface, after exposing the sample to decanethiol for 60 s. Three regions are observed.

(15) Horcas, I.; Fernandez, R.; Gomez-Rodriguez, J. M.; Colchero, J.; Gomez-Herrero, J.; Baro, A. M. *Rev. Sci. Instrum.* **2007**, *78*, 013705.

\* Corresponding author. Tel: +44 1159515129. E-mail: peter.beton@nottingham.ac.uk.

<sup>†</sup> School of Physics & Astronomy.

<sup>‡</sup> School of Chemistry.

(1) Schreiber, F. *Prog. Surf. Sci.* **2000**, *65*, 151–256.

(2) Poirier, G. E.; Pylant, E. D. *Science* **1996**, *272*, 1145–1148.

(3) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. *Chem. Rev.* **2005**, *105*, 1103–1169.

(4) Poirier, G. E. *Langmuir* **1999**, *15*, 1167–1175.

(5) Maksymovych, P.; Sorescu, D. C.; Yates, J. T. *Phys. Rev. Lett.* **2006**, *97*, 146103.

(6) Mazzarello, R.; Cossaro, A.; Verdini, A.; Rousseau, R.; Casalis, L.; Danisman, M. F.; Floreano, L.; Scandolo, S.; Morgante, A.; Scoles, G. *Phys. Rev. Lett.* **2007**, *98*, 016102.

(7) Yu, M.; Bovet, N.; Satterley, C. J.; Bengio, S.; Lovelock, K. R. J.; Milligan, P. K.; Jones, R. G.; Woodruff, D. P.; Dhanak, V. *Phys. Rev. Lett.* **2006**, *97*, 166102.

(8) Theobald, J. A.; Oxtoby, N. S.; Phillips, M. A.; Champness, N. R.; Beton, P. H. *Nature* **2003**, *424*, 1029–1031.

(9) Stohr, M.; Wahl, M.; Galka, C. H.; Riehm, T.; Jung, T. A.; Gade, L. H. *Angew. Chem., Int. Ed.* **2005**, *44*, 7394–7398.

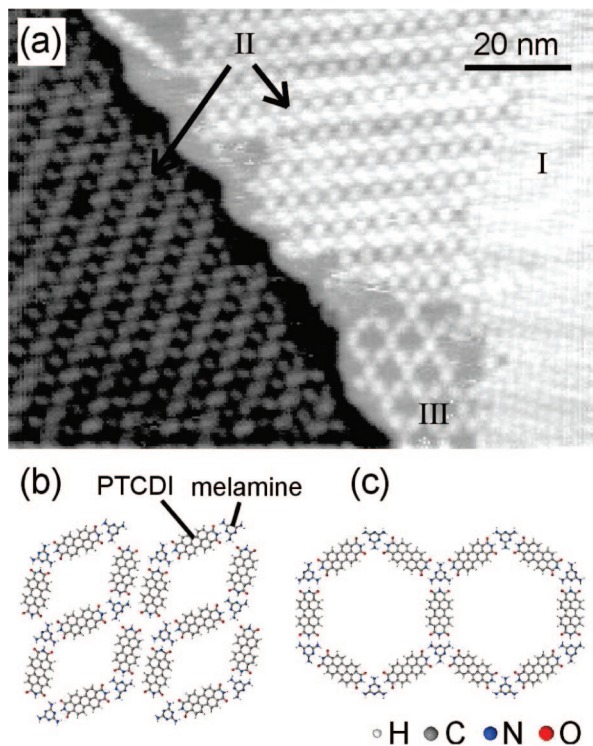
(10) Stepanow, S.; Lingenfelder, M.; Dmitriev, A.; Spillmann, H.; Delvigne, E.; Lin, N.; Deng, X. B.; Cai, C. Z.; Barth, J. V.; Kern, K. *Nat. Mater.* **2004**, *3*, 229–233.

(11) Madueno, R.; Räisänen, M. T.; Silien, C.; Buck, M. *Nature* **2008**, *454*, 618.

(12) Perdigão, L. M. A.; Perkins, E. W.; Ma, J.; Staniec, P. A.; Rogers, B. L.; Champness, N. R.; Beton, P. H. *J. Phys. Chem. B* **2006**, *110*, 12539–12542.

(13) Staniec, P. A.; Perdigão, L. M. A.; Saywell, A.; Champness, N. R.; Beton, P. H. *ChemPhysChem* **2007**, *8*, 2177–2181.

(14) Silly, F.; Shaw, A. Q.; Briggs, G. A. D.; Castell, M. R. *Appl. Phys. Lett.* **2008**, *92*, 023102.

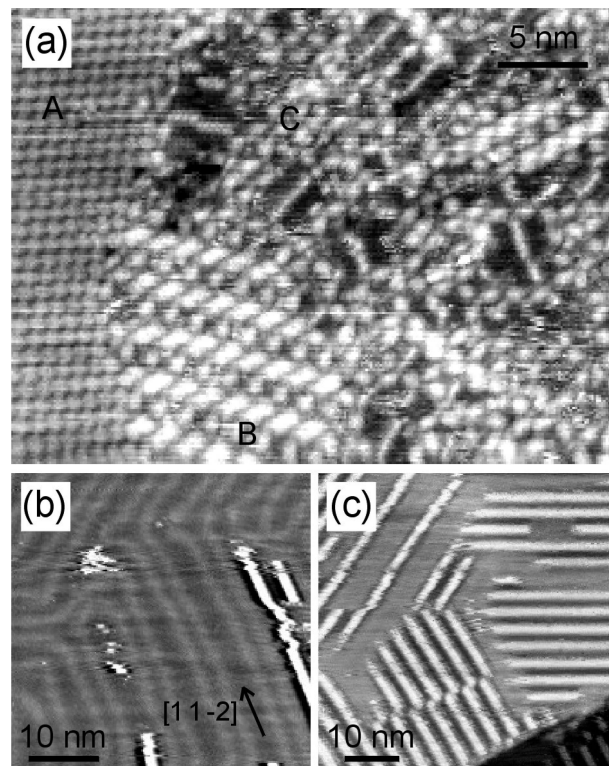


**Figure 1.** (a) STM image ( $-1.8$  V,  $30$  pA) of PTCDI–melamine mixture on Au(111) with three regions identified: I, PTCDI island; II, parallelogram PTCDI–melamine bimolecular arrangement on two distinct terraces; III, PTCDI–melamine hexagonal network. (b) Parallelogram and (c) hexagonal PTCDI–melamine molecular structures.

Region A is an area covered by a close-packed PTCDI island (formed from residual PTCDI that has not interacted with melamine) that appears unaltered following thiol exposure. Region B corresponds to the parallelogram bimolecular network that has survived the exposure to decanethiol. In contrast to the parallelogram phase, no areas of the hexagonal bimolecular arrangements (see Figure 1 and refs 12–14) were present following exposure to decanethiol. However, disordered areas are observed, such as region C, which we attribute to a coexistence of PTCDI, melamine, and decanethiol.

For comparison, two STM images of different exposures of a clean Au(111) surface to decanethiol are shown in Figure 2b,c. At low coverage decanethiol chemisorbs, forming the bright stripes that can be seen in Figure 2b. These stripes are parallel to the  $[1\bar{1}2]$  direction of the Au(111) surface and appear to grow preferentially on face-centered cubic regions of the reconstructed surface.<sup>16</sup> At higher coverages, several parallel lines are observed, corresponding to the  $11 \times \sqrt{3}$  pinstripe structure.<sup>4,17,18</sup> The measured distance between stripes is  $3.5 \pm 0.1$  nm, consistent with previous reports.<sup>17,18</sup> Similar stripes running in three directions can be identified in areas of region C in Figure 2a, supporting our identification of this as a region containing decanethiol. Since the hexagonal PTCDI–melamine arrays are not observed following decanethiol exposure, we attribute areas such as region C to hexagonal arrays that have been disrupted by the formation of the stripe decanethiol phase.

A higher resolution image of the parallelogram PTCDI–melamine network (region B) after decanethiol exposure is shown



**Figure 2.** (a) STM image (sample voltage  $-1.8$  V,  $25$  pA) of PTCDI–melamine on Au(111) after exposure to decanethiol ( $60$  s at  $10^{-8}$  Torr). Region A corresponds to a close-packed PTCDI island, region B to a PTCDI–melamine parallelogram structure, and region C to a disordered PTCDI–melamine–decanethiol region. STM images Au(111) exposed to decanethiol: (b)  $0.06$  ML and imaging parameters,  $-2.3$  V,  $30$  pA; (c)  $0.51$  ML and tunneling conditions,  $-2.0$  V,  $50$  pA, showing elongated parallel stripes attributed to the pin-stripe decanethiol–Au(111) phase.

in Figure 3a. Two parallel lines are resolved inside many of the network cavities. These features were absent prior to thiol exposure and are attributed to two decanethiol molecules lying parallel to each other (see Figure 3b and the molecular arrangement shown in Figure 3c). A detailed observation of the contrast of each of the lines reveals a small bright protrusion at one end. We attribute this feature to the sulfur atom that is associated with a slightly higher density of states within the decanethiol molecule (the calculated HOMO is shown in Figure 3d<sup>19–22</sup> and allows identification of the molecular orientation). These images demonstrate the entrapment and ordering of decanethiol molecules within the hydrogen-bonded host template.

The absence of the hexagonal phase after decanethiol deposition suggests that the parallelogram network is more stable. However, there is also a possibility that the difference could be explained by geometric considerations. Namely, the pore shape of the parallelogram network is compatible with the accommodation of a quasi-close-packed arrangement of decanethiol molecules (Figure 3e). The close-packed nature of this arrangement indicates that van der Waals interactions are significant in stabilizing the trapped molecules. However, a hexagonal cavity is not well

(19) The electronic structure of 1-decanethiol was calculated using DMol<sup>3</sup> molecular density functional quantum mechanical code,<sup>20,21</sup> provided with Accelrys Materials Studio 4.2. The general gradient approximation with the Perdew–Burke–Ernzerhof gradient correction was used.<sup>22</sup> Double numeric plus polarization basis set was employed with no core treatment (all electron).

(20) Delley, B. *J. Chem. Phys.* **1990**, *92*, 508–517.

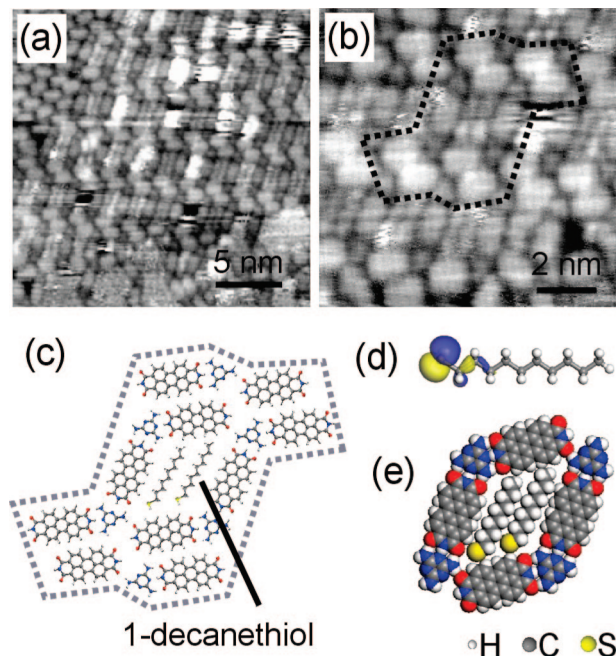
(21) Delley, B. *J. Chem. Phys.* **2000**, *113*, 7756–7764.

(22) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(16) Barth, J. V.; Brune, H.; Ertl, G.; Behm, R. *J. Phys. Rev. B* **1990**, *42*, 9307.

(17) Staub, R.; Toerker, M.; Fritz, T.; Schmitz-Hubsch, T.; Sellam, F.; Leo, K. *Langmuir* **1998**, *14*, 6693–6698.

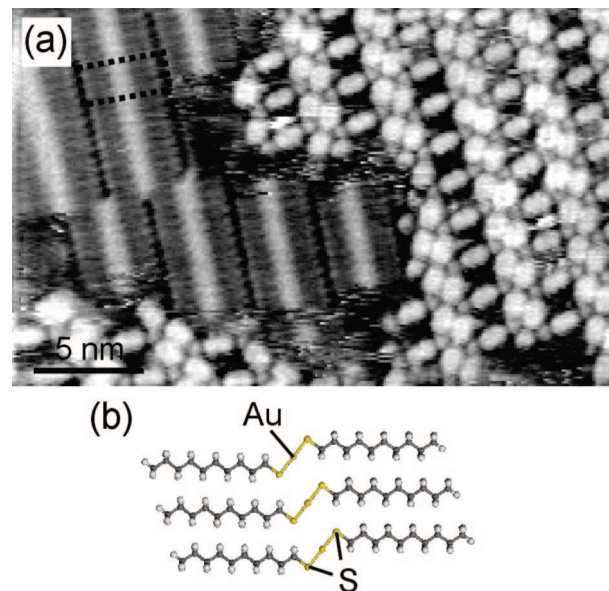
(18) Qian, Y. L.; Yang, G. H.; Yu, J. J.; Jung, T. A.; Liu, G. Y. *Langmuir* **2003**, *19*, 6056–6065.



**Figure 3.** (a) STM image of region B, an area with parallelogram PTCDI–melamine structure after decanethiol deposition. (b) High-resolution image (sample voltage  $-1.5$  V,  $30$  pA) where a molecular cavity containing a twin-parallel stripe has been highlighted with a dashed line. (c) Molecular model of the highlighted region in part b. (d) Molecular structure of 1-decanethiol, with calculated HOMO isosurface represented in blue and yellow (positive and negative signs of the wave function). (e) Same molecular model as in part c but redrawn in space-filling model using van der Waals radius for the atoms, illustrating the close match of the adsorbed decanethiol dimers with the geometry and dimensions of the cavities of the hydrogen-bonded PTCDI–melamine network.

matched geometrically to close-packed decanethiol. In recent studies it has been shown that, under solution conditions, guest molecules may act to stabilize particular supramolecular arrangements, and there are other examples of cooperative intermolecular effects in determining the properties of molecular arrays.<sup>23–32</sup> The present investigation provides an example of differential stabilization and destabilization of coexisting networks by a guest species.

Further exposure of the sample to decanethiol (up to a total exposure time of  $720$  s at  $10^{-8}$  Torr) did not give rise to any significant changes to the morphology shown in Figures 2 and 3. Annealing the sample led to changes in surface structure (see Figure 4a). The decanethiol stripe phase is now clearly observed in the form of rows oriented along the  $[11\bar{2}]$  directions of the Au(111) substrate (Figure 2b,c). The rows are oriented at the expected angle of  $\sim 73^\circ$  to the interlinking PTCDI molecules



**Figure 4.** (a) STM image (sample voltage  $-0.1$  V,  $30$  pA) of PTCDI–melamine–decanethiol on Au(111) sample after heating at  $80$ – $100^\circ\text{C}$  for  $2$  h following exposure at room temperature to decanethiol at  $10^{-8}$  Torr for  $720$  s. (b) Molecular arrangement proposed for the area highlighted in part a.

straddling the double rows of the PTCDI–melamine array.<sup>13</sup> Many ( $\sim 40\%$ ) of the cavities of the network appear unoccupied, indicating that the decanethiol pairs previously trapped in cavities have either desorbed or migrated over the network and become attached to the stripe phase.

The arrangement of decanethiol molecules in the stripe rows is significantly different from those inside the PTCDI–melamine cavities. In particular, the alkane chains fan out either side of a bright central region (width  $\sim 10$  Å). A model for thiol adsorption in this phase, which is based on a covalent linkage between a Au adatom and the S headgroups of two thiol molecules, has recently been proposed.<sup>5,7</sup> Our images of the stripe phase are consistent with this model (see Figure 4b). However, for the trapped thiols, we observe significant differences. First the relative placement of molecules is completely different from that in the stripe phase. Furthermore, the enhanced contrast associated with the S atom of each molecule of the trapped thiol pairs may be clearly resolved as distinct features (see Figure 3b). This shows clearly that the adsorption state of the trapped molecules is different from the thiols in the stripe phase. There is no evidence for Au adatom mediated adsorption for the trapped molecules.

Our results imply that the supramolecular network controls the interaction between trapped molecules and the substrate. The absence, within network cavities, of defects and sources (e.g., terrace steps) of diffusing Au atoms, which play an important role in forming Au–S bonds,<sup>5–7,33</sup> would be expected to locally suppress adatom–thiolate bond formation. Lavrich et al.<sup>34</sup> have shown using temperature-programmed desorption that a fraction of alkanethiols remain in a physisorbed state on clean gold at temperatures  $\sim 425$  K. Furthermore, the measured value ( $0.3$  eV) for the barrier<sup>34</sup> for conversion from physisorption to chemisorption is, in the light of recent results,<sup>5–7</sup> likely to pertain to a Au adatom mediated process that may not be relevant to the trapped thiols. Accordingly, we suggest that the trapped thiols remain in physisorbed states.

(23) Furukawa, S.; Tahara, K.; De Schryver, F. C.; Van der Auweraer, M.; Tobe, Y.; De Feyter, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 2831–2834.

(24) Spillmann, H.; Kiebele, A.; Stöhr, M.; Jung, T. A.; Bonifazi, D.; Cheng, F. Y.; Diederich, F. *Adv. Mater.* **2006**, *18*, 275–279.

(25) Zhang, H. L.; Chen, W.; Chen, L.; Huang, H.; Wang, X. S.; Yuhara, J.; Wee, A. T. S. *Small* **2007**, *3*, 2015–2018.

(26) de Wild, M.; Berner, S.; Suzuki, H.; Yanagi, H.; Schlettwein, D.; Ivan, S.; Baratoff, A.; Guentherodt, H. J.; Jung, T. A. *ChemPhysChem* **2002**, *3*, 881–885.

(27) Palma, C.-A.; Bonini, M.; Llanes-Pallas, A.; Breiner, T.; Prato, M.; Bonifazi, D.; Samorì, P. *Chem. Commun.* **2008**, 5289.

(28) Surin, M.; Samorì, P. *Small* **2007**, *3*, 190.

(29) Nath, K. G.; Ivashenko, O.; MacLeod, J. M.; Miwa, J. A.; Wuest, J. D.; Nanci, A.; Perepichka, D. F.; Rosei, F. *J. Phys. Chem. C* **2007**, *111*, 16996.

(30) MacLeod, J. M.; Ivashenko, O.; Perepichka, D. F.; Rosei, F. *Nanotechnology* **2007**, *18*, 424031.

(31) Nath, K. G.; Ivashenko, O.; Miwa, J. A.; Dang, H.; Wuest, J. D.; Nanci, A.; Perepichka, D. F.; Rosei, F. *J. Am. Chem. Soc.* **2006**, *128*, 4212.

(32) Blunt, M.; Lin, X.; del Carmen, G.-L.; Schröder, M.; Champness, N. R.; Beton, P. H. *Chem. Commun.* **2008**, 2304.

(33) Rzeńnicka, I. I.; Lee, J. S.; Maksymovych, P.; Yates, J. T. *J. Phys. Chem. B* **2005**, *109*, 15992–15996.

(34) Lavrich, D. J.; Wetterer, S. M.; Bernasek, S. L.; Scoles, G. *J. Phys. Chem. B* **1998**, *102*, 3456–3465.

### Conclusions

In conclusion, we have demonstrated entrapment of an alkanethiol in a hydrogen-bonded molecular network. The adsorption of the thiol shows significant differences with recent solution-based experiments.<sup>11</sup> In particular, we observe the destabilization of the hexagonal phase, which does not occur under solution conditions, while the parallelogram phase (not observed for solution deposition) can capture pairs of thiol molecules adsorbed parallel to the surface. Interestingly the thiol selectively disrupts one of the two principal phases of the hydrogen-bonded network. It is also significant that the entrapment of the decanethiol molecules within the hydrogen-bonded template significantly affects the nature of the thiol–Au interaction, showing that the stabilization of molecules within the nonporous

network can influence the adsorbate/substrate interaction. From a technological perspective, the solution-based approach offers many advantages in terms of cost and ease of preparation, while the vacuum-based approach allows access to a wider range of template geometries and leads to an interplay between entrapment and thiol chemisorption. Overall, our work highlights the great potential of combining these two self-assembly routes to form new molecular arrays with controlled molecular organization on the nanometer scale.

**Acknowledgment.** This work was financed by the UK Engineering and Physical Sciences Research Council under the grants GR/S97521/01 and EP/D048761/01.

LA8035314