Surface science

Topology of two-dimensional C_{60} domains

Two-dimensional systems possess a unique topological ordering that is not found in either three- or one-dimensional systems[1]. Using high-resolution scanning tunnelling microscopy, we show here that a 60-carbon-atom (C_{60}) array on a self-assembled monolayer of an alkylthiol forms an ideal two-dimensional system which has another novel topological order originating from the orientational degrees of freedom. At a temperature of 5 K, the two-dimensional C_{60} forms a domain structure in which the correlation function of the molecular orientation within a domain is constant anywhere (so every C_{60} has the same orientation) but changes abruptly at domain boundaries. Remarkably, the positional order and the bond-orientational order are both fully preserved across domain boundaries.

The self-assembled monolayer substrate was prepared using a standard procedure[2] and transferred into an ultra-high-vacuum and low-temperature scanning tunnelling microscope (STM) chamber where a submonolayer of C_{60} was then thermally evaporated onto the substrate. The STM images show that the C_{60} molecules form close-packed hexagonal arrays, with a nearest-neighbour distance of 10 Å (ref. 3). At room temperature, molecules at the edge of an array can detach readily and diffuse to another part of the same array or to other nearby arrays. Each C_{60} displays a smooth hemispherical protrusion, suggesting that the C_{60} molecules are rotating freely at this temperature. This contrasts with C_{60} adsorbed on metal or semiconductor surfaces, when the molecular rotation is frozen even at room temperature owing to strong binding of C_{60} on the substrate[4].

At 77 K, the C_{60} molecule appears as a hemisphere, a tilted doughnut, or an asymmetric dumb-bell, each being consistent with a rotating pattern around a fixed axis. When the sample is cooled down to 5 K, all C_{60} molecules in the STM image (Fig. 1a) start to reveal an identical internal fine structure that closely matches the well-known cage structure (stick model in Fig. 1b). To our knowledge, this is the first time that the C_{60} native cage structure has been seen in the STM.

From the evolution of C_{60} internal patterns with decreasing temperature, we conclude that there is an ordered rotational motion of the two-dimensional C_{60} array, as in the case of bulk C_{60}, except that the two-dimensional rotationally ordered phase persists down to 77 K (already 13 K below the bulk freezing temperature[3]). Unlike the orientation-related glassy phase in bulk C_{60}, these two-dimensional C_{60} arrays form orientationally ordered domains at 5 K. These observations, together with the fact that the C_{60} molecules are not in an epitaxial (or commensurate) arrangement with respect to the self-assembled monolayer (the lattice of the underlying monolayer has a rectangular unit cell of 9.994 × 8.655 Å, containing four alkythiol molecules; see ref. 5, for example), are indicative of a very weak interaction between the C_{60} and the alkylthiol.

Figure 1a (inset) shows a simulated STM image of a C_{60} structure obtained by integrating the electron density of states on a C_{60} from the Fermi level to the bias voltage[6]. The C_{60} orientation is tuned for the best agreement between the simulation and the experiment. The final molecule orientation has an edge atom facing towards the substrate and can be specified by the azimuthal ($\theta = 1.5°$) and polar ($\phi = 0.6°$) rotation, as defined in Fig. 1b. This remarkable conformity between simulation and experiment allows us confidently to identify C_{60} domains with different molecular orientations.

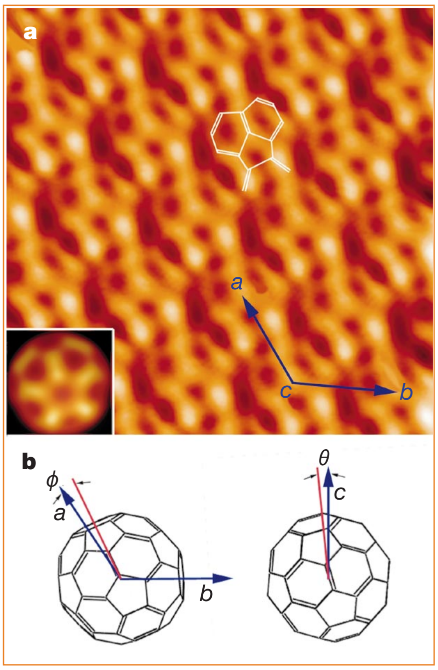

Figure 1 The native cage structure of C_{60} molecules, seen using a scanning tunnelling microscope (STM). **a,** STM image (35 × 35 Å) of a C_{60} lattice taken at 5 K with −2.0 V sample bias. Detailed internal features of the C_{60} molecule are evident that closely resemble the C_{60} cage structure and match the theoretical simulation shown in the inset. **b,** Top view (left) and side view (right) of a stick model outlining the C_{60} orientations obtained by simulation. The *c*-axis points out of the image.

Although most of the C_{60} arrays feature a single orientation, we have also observed a single array consisting of domains of two different orientations (Fig. 2a), in which the boundary separates two distinguishable domains by their internal features. Comparison with our simulation results enabled us to identify these two orientations as those shown in Fig. 2b. Apart from the two different molecular orientations, there is no positional defect at the domain boundary and the entire C_{60} array maintains the perfect translation symmetry for the centres of the C_{60}. Although the two orientation domains are quite stable, we found that the domain boundary fluctuates in time, especially when the tip is brought closer to the surface. No domain boundaries are found in the adjacent self-assembled monolayer substrate that can be correlated to the C_{60} domains.

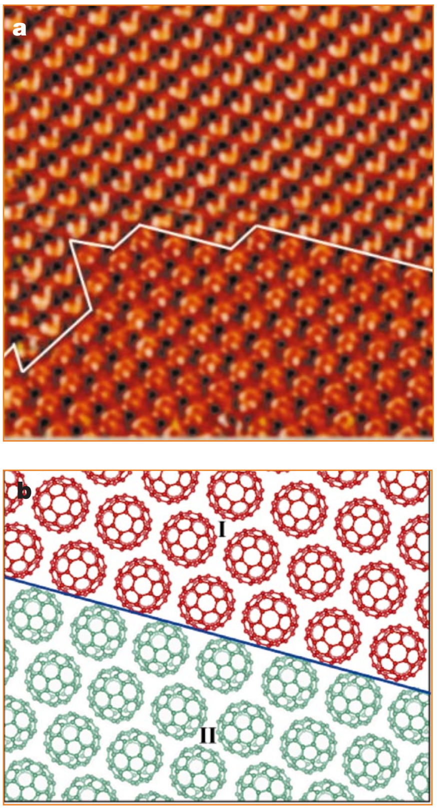

Figure 2 Domain boundary of a two-dimensional C_{60} array. **a,** STM image (100 × 100 Å) of two molecular orientational domains and the domain boundaries. Both the positional order and bond-orientational order are fully preserved and no defect exists along the domain boundaries. **b,** Representation of the two molecular orientations derived by comparison with the theoretically simulated images.

A C_{60} molecule consists of 60 single and 30 double carbon bonds. There is a small charge deficiency between the single bonds and a charge excess on the double bonds. Thus the intermolecular potential contains, in addition to the van der Waals potential, a small bond-to-bond Coulomb energy dependent on relative molecule orientations[7]. The latter results in a variation of the domain energy by about 0.1 eV per molecule, roughly one tenth of the binding energy of a C_{60} in a two-dimensional close-packed array (Y.J. *et al.*, unpublished results).

This large energy-scale difference is probably responsible for the preservation of the positional and bond-orientational

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order across the domain boundary, even though most of the boundary structures yield positive boundary energy of around $0.01\ \text{eV}\ \text{Å}^{-1}$. The fact that C_{60} forms orientationally ordered domains suggests that the magnitude of the domain energy variation sets the upper bound of the rotational barrier due to the monolayer substrate. However, an absence of positional and bond-orientational domain walls, such as those in noble gases adsorbed on graphite[8], implies that the lateral variation of the substrate fields is much smaller than the C_{60} intermolecular potential. We conclude that the novel topological order observed here must be an intrinsic property of a two-dimensional system.

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Neurology

Self-recognition and the right hemisphere

Although monkeys can perceive complex stimuli such as faces[1], only the higher apes are capable of recognizing their own face in a mirror[2]. Here we show that in humans the right hemisphere of the brain seems to be preferentially involved in self-face recognition. Our findings indicate that neural substrates of the right hemisphere may selectively participate in processes linked to self-awareness.

We first studied a group of patients undergoing the intracarotid amobarbital (Wada) test. The Wada test involves anaesthetization (that is, inactivation) of one cerebral hemisphere in order to provide information regarding cerebral dominance for language and other cognitive phenomena. Five right-handed (left hemisphere is language-dominant) patients, who were undergoing Wada tests for evaluation for surgery to treat epilepsy, were shown pictures of faces generated by morphing the picture of a famous person with the patient's own face (Fig. 1). Patients were instructed to remember the picture presented. Different pictures were presented during selective anaesthesia of the right and the left hemispheres.

After recovery from anaesthesia, patients were given a forced-choice task in which they had to choose the picture of the face that they had been shown. The two choices were the pictures from which the morphed image had been generated (self and famous), although neither choice had actually been presented during anaesthesia. Following anaesthesia of the left hemisphere, all five patients selected the 'self' face as the one they thought had been presented; however, after anaesthesia of the right hemisphere, four out of the five selected the famous face. These results suggest that the anterior right hemisphere may be critically engaged in detecting the self face.

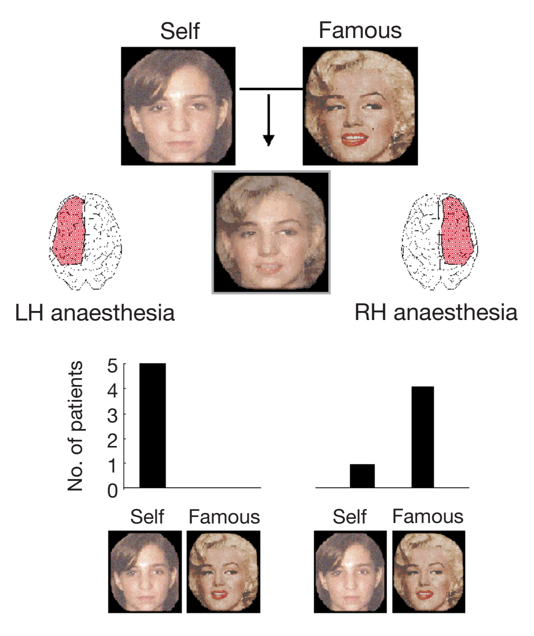

Figure 1 Five patients (a real patient is not shown) were presented with a picture showing a morph of a face that was composed of their own face and a famous face during the time when either the right or the left hemisphere of their brain was anaesthetized. Following anaesthesia of the left hemisphere (LH), patients selected the 'self' face as having been shown to them (5/5); after anaesthesia of the right hemisphere (RH), patients selected the famous face as the one they had viewed (4/5). In a second experiment with 10 normal subjects (results not shown), transcranial magnetic stimulation was delivered to the motor cortex of the RH or LH during self–famous or familiar–famous morph display. The amplitude of the resulting motor-evoked potentials (MEPs) was significantly greater for the RH than for the LH during presentation of self morphs ($M = 1.26$ mV and $M = 1.02$ mV; s.e., 0.09, respectively) and the former (RH, self morph) was also significantly greater than the MEP amplitude from both hemispheres during presentation of familiar morphs (RH, familiar: $M = 1.04$ mV, s.e., 0.07; LH, familiar: $M = 1.03$ mV, s.e., 0.08).

To find out whether a similar effect operates in normal subjects, we presented morphed photographs to ten volunteers (instructed to attend to the photographs) and delivered transcranial magnetic stimulation to the motor cortex of the left or right hemisphere at random times (100–450 ms) during picture presentation. We measured the amplitude of the motor-evoked potentials induced by this stimulation in the contralateral first dorsal interosseous muscle as an indicator of the amount of activation of each hemisphere[3] during exposure to pictures morphing their own or a familiar face with that of a famous person.

We found that there was a significant association ($P < 0.05$) between subjects' hemisphere activation and their exposure to the 'self' and 'familiar' conditions. Post-hoc Bonferroni tests revealed that motor-evoked potentials were significantly greater from the right hemisphere while subjects viewed pictures containing elements of their own face than for all other conditions.

Some people can suffer from neglect or misidentification of their own extremities (a condition known as asomatopagnosia) after damage[4] to or anaesthetization[5] of the right hemisphere. It is also known that patients with lesions to the right frontotemporal cortex may experience a cognitive detachment from self[6]. This recently evolved network includes prefrontal regions of the brain and demonstrates a high degree of lateralization[7] in humans and apes, but not in monkeys. It is conceivable that a right-hemisphere network gives rise to self-awareness, which may be a hallmark of higher-order consciousness[8].

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