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Grating of single Lu@C_{82} molecules using supramolecular network†

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Received (in Cambridge, UK) 28th May 2008, Accepted 5th August 2008
First published as an Advance Article on the web 9th September 2008
DOI: 10.1039/b809004a

A supramolecular grating of single Lu@C_{82} molecules was obtained by depositing Lu@C_{82} molecules onto a room temperature PTCDI–melamine network.

The ability of endohedral fullerenes[1] to support discrete quantum states has inspired schemes for using them for quantum technologies.[2] It is not necessary to be able to address each individual fullerene molecule, provided one can make regular arrays.[3] Two-dimensional arrays are entirely suitable for this purpose, and it is possible to use substrate properties[4–10] or supramolecular assembly to create templates for arranging fullerenes on surfaces.[11–22] A combination of PTCDI (3,4,9,10-perylene-tetracarboxylic-diimine) with melamine (1,3,5-triazine-2,4,6-triamine)[23] can produce close packed molecular structures or open molecular networks.[18–20,24] These open structures can serve as a scaffold for ordering fullerene clusters.[11,19] However the challenge still consists in discovering the right conditions to obtain the long range and stable formation of single functionalized molecules on metal surfaces at room temperature. Metallofullerenes are model functionalized molecules; they have different electronic and geometrical properties from empty fullerene cages, and the cages are generally larger.

We have therefore studied the ordering of single Lu@C_{82} on Au(111) at room temperature using a PTCDI and melamine supramolecular network. We observed, using scanning tunneling microscopy (STM), that deposition of Lu@C_{82} onto a PTCDI–melamine of parallelogram cavities leads to the trapping of single Lu@C_{82}, forming a long-range grating of single Lu@C_{82}. This supramolecular network is stable at room temperature. In comparison we observed that Lu@C_{82} deposited on bare Au(111) leads to the formation of multilayer islands with close-packed structures.

The substrates were Au(111) films grown on mica. The samples were introduced into the ultrahigh vacuum (UHV) chamber of a STM (JEOL JSTM4500S) operating at a pressure of 10^{-8} Pa. Etched tungsten tips were used to obtain constant current images at room temperature with a bias voltage applied to the sample. The Au(111) surfaces were sputtered with argon ions and annealed in UHV at 600 °C, typically for 30 min. Lu@C_{82} (Fig. 1a) and PTCDI (Fig. 1b) molecules were sublimated at 550 °C and melamine (Fig. 1c) at 100 °C. STM images have been processed and analyzed with FABVIEWER.[25]

Fig. 2a shows the molecular superstructure formed after deposition of PTCDI and melamine on Au(111) followed by post annealing at 150 °C for 10 h. PTCDI molecules appear brighter than melamine molecules, suggesting they are more conducting. The network is composed of a succession of double rows of PTCDI–melamine, connected to neighbouring rows through PTCDI molecules arranged like the rungs of a ladder. The PTCDI molecules are connected to the melamine molecules of the row through three hydrogen bonds, two O···H–N bonds and one N–H···N. Inside the double row, PTCDI molecules are connected to each other through two O···H–N hydrogen bonds, and melamine molecules are connected on one side to a PTCDI molecule through three hydrogen bonds, and to another PTCDI of the row through a single hydrogen bond (O···H–N bond). The third side of each melamine molecule is connected to a rung PTCDI molecule. The unit cell of the PTCDI–melamine network is shown in Fig. 2b; it is not rectangular but has a parallelogram shape with 2.7 nm and 2.0 nm lattice constant. We observed that the angle between the unit cell axes may vary between 80–90°, indicating that the network has some flexibility. The PTCDI : melamine ratio in this molecular structure is 3 : 2. This supramolecular network is stable at room temperature.

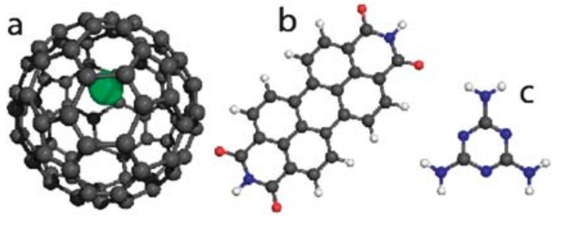

Fig. 1 Scheme of molecules. Gray balls represent carbon atoms, red balls are oxygen atoms, white balls are hydrogen atoms, blue balls are nitrogen atoms and the green ball is the lutetium atom. (a) Lu@C_{82}. X-ray structural analysis of Metal@C_{82} suggests that the metal atom should be close to one of the hexagons on the C_{82} surface.[29] (b) PTCDI (3,4,9,10-perylene-tetracarboxylic-diimine). (c) Melamine (1,3,5-triazine-2,4,6-triamine).

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† Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/b809004a

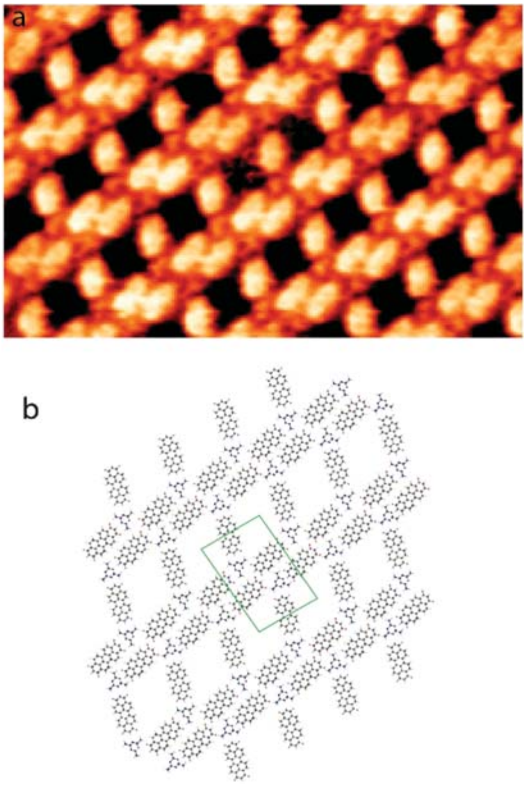

Fig. 2 (a) STM image of a mixed PTCDI and melamine parallelogram domain on a Au(111) surface, 16 × 10 nm^2, $V_s = -1.8$ V, $I_t = 0.4$ nA. (b) Model of the supramolecular PTCDI–melamine parallelogram unit cell.

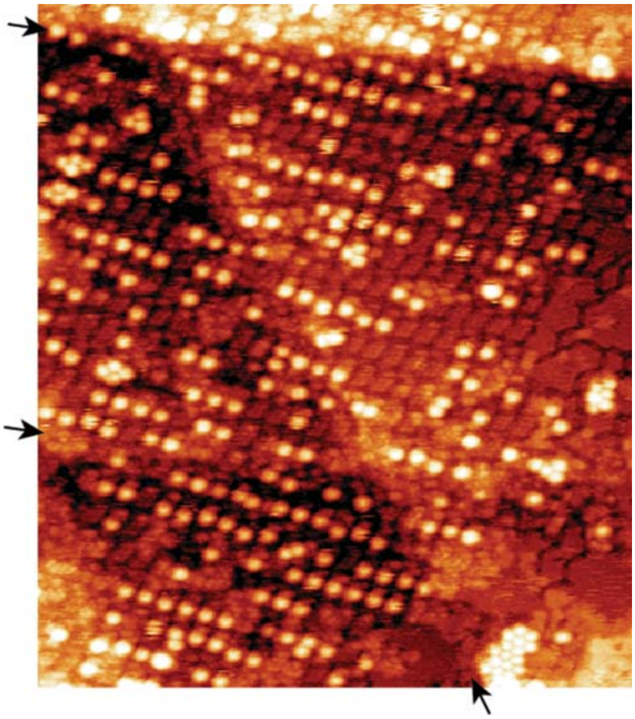

Fig. 3 STM image of a PTCDI–melamine–Lu@C$_{82}$ domain on a Au(111) surface (53 × 60 nm^2; $V_s = -1.8$ V, $I_t = 0.3$ nA). Gold step edges are highlighted by arrows.

Fig. 3 shows the surface after deposition of Lu@C$_{82}$ molecules onto the room temperature PTCDI–melamine supramolecular template. The Lu@C$_{82}$ molecules are not close-packed but form rows on the surface on top of the PTCDI–melamine supramolecular network. Fig. 3 shows that Au step edges, highlighted by arrows, do not break the molecular ordering. The STM image shows that Lu@C$_{82}$ molecules are preferentially located between the rows of single PTCDI molecules, in the empty pores of the supramolecular network, generally with one Lu@C$_{82}$ molecule in each pore.

Further deposition of Lu@C$_{82}$ molecules leads to filling of the supramolecular pores of the network and long range ordering of Lu@C$_{82}$ molecules, Fig. 4. Defects in the PTCDI–melamine supramolecular network perturb the long range ordering of the Lu@C$_{82}$ molecules. In Fig. 4 the Lu@C$_{82}$ molecules have some freedom about where to sit in each PTCDI–melamine pore, implying that the pore size is bigger than the trapped C$_{82}$ fullerene.

Fig. 5 shows the surface after deposition of Lu@C$_{82}$ molecules onto a room temperature bare Au(111) gold surface. The molecules form close-packed domains on the surface. The molecule separation is 1.15 nm. Some molecules appear brighter on large molecular domains, Fig. 5a, indicating the beginning of the growth of the second Lu@C$_{82}$ monolayer. A high resolution STM image of the Lu@C$_{82}$ island, Fig. 5b, shows defects appearing in the first and second layers, with a few single Lu@C$_{82}$ missing in the layer. The C$_{82}$ cages have C_{2v} symmetry and are not perfectly spherical. This probably explains why defects appear in the close-packed Lu@C$_{82}$ layers. These defects in the first Lu@C$_{82}$ layer may serve as nucleation sites for the second layer.

A PTCDI–melamine supramolecular network on an Au(111) surface can thus be used as a template for arrays of single Lu@C$_{82}$ molecules. The long-range PTCDI–melamine supramolecular network forms parallelogram cavities that trap single metallofullerene molecules, forming a lattice of single Lu@C$_{82}$. This is different from the way that C$_{70}$ molecules form dimers in the same template.[19] The small increase in fullerene cage dimensions induced by the presence of 12 more carbon atoms in C$_{82}$ in comparison to C$_{70}$ is sufficient to allow the trapping of one single fullerene in the PTCDI–melamine supramolecular network pores.

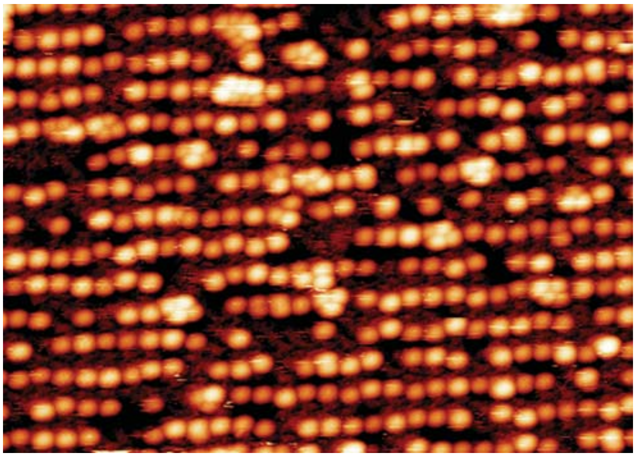

Fig. 4 STM image of PTCDI–melamine–Lu@C$_{82}$ network on a Au(111) surface (55 × 40 nm^2; $V_s = -1.8$ V, $I_t = 0.1$ nA).

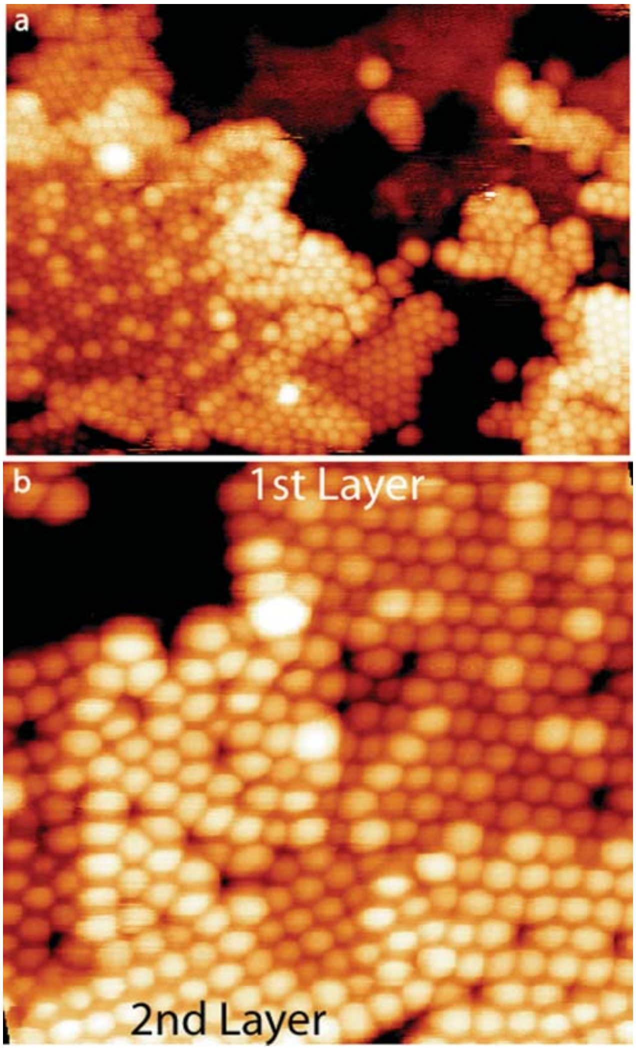

Fig. 5 (a) STM image of Lu@C_{82} domain on a Au(111) surface (43 × 31 nm^2; $V_s = -1.8$ V, $I_t = 0.1$ nA). (b) Detailed image of the domain (20 × 20 nm^2; $V_s = -1.8$ V, $I_t = 0.1$ nA). Molecules form multilayer islands. Molecules of the first layer are darker than those of the second layer in (b).

Lu@C_{82} molecules serve as a paradigm for other metallofullerenes which have spin and optical properties which may be useful for quantum technologies.[26] The ordering is not broken by gold monoatomic steps. In contrast Lu@C_{82} on bare Au(111) forms close-packed multilayer islands. In this way long range assembly of single metallofullerene architectures on metal surfaces, stable at room temperature, can be achieved using supramolecular structures. The ability to control the long-range ordering of fullerenes using supramolecular networks opens new possibilities for the development of devices based on functionalized fullerene molecules.[27,28]

The authors thank the EPSRC (EP/D048761/1 and GR/S15808/01) for funding, C. Spencer (JEOL UK) for valuable technical support, and P. Beton for helpful discussions.

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