Atomic–molecular superlattices

Andrew A. R. Watt,*[a] Mark R. Sambrook,[a] Kyriakos Porfyrakis,[a] Brendon W. Lovett,[a] Hassane El Mkami,[b] Graham M. Smith[b] and G. Andrew D. Briggs[a]

Received (in Cambridge, UK) 16th February 2006, Accepted 17th March 2006
First published as an Advance Article on the web 31st March 2006
DOI: 10.1039/b602307j

In this communication we demonstrate a directly-bonded crystalline fullerene superlattice and show that the incorporation of spin-active N@C_{60} endohedral fullerenes is readily achieved to give an atomic–molecular hybrid spin-active superlattice material.

The assembly of ordered arrays of molecular scale structures is key to designing new materials for quantum nanotechnology. Such arrays could be used to build spintronic architectures for quantum and classical computation,[1] or quantum measurement[2] based on cellular automata. A particularly promising carrier of quantum information is the electron spin associated with a nitrogen atom encapsulated inside a C_{60} molecule (N@C_{60}).[3,4] It has an extremely long coherence time and is straightforwardly manipulated using microwave spin resonance.[5] To date, ensemble measurements of N@C_{60} solutions and one-dimensional arrays of N@C_{60} molecules inside single-walled carbon nanotubes (SWNTs) have been reported;[6] however, higher-dimensional structures have yet to be achieved. Superlattices, in which control over both chemical composition and the placement of components is achieved, provide attractive arrays for the distribution of quantum information over significant distances. Numerous inorganic-based superlattices have been produced from a wide range of inorganic nanoparticles, with structural control *via* the steric interactions of organic templates.[7]

The polymerisation of fullerene molecules to give two-dimensional structures *via* photo-irradiation[8] and high temperature or pressure[9,10] is well known. However, these harsh conditions are detrimental to the survival of incarcerated nitrogen atoms in N@C_{60} endohedral fullerene.[11] Using C_{60} and N@C_{60} as building blocks and short chain bis-amine linkers, the spontaneous formation of fullerene-based superlattices is achieved *via* a one pot reaction method. Mild reaction conditions allow for the retention of the incarcerated nitrogen atoms, thus giving rise to a spin-active ordered array.

The highly facile reaction of fullerenes with a wide range of primary amines is well understood, proceeding *via* a charge-transfer state to give the general species C_{60}H–NH–R (where R = alkyl chain).[12] Fullerene superlattices were found to be formed in a single step reaction using a 0.05% N@C_{60}/C_{60} toluene solution, prepared according to literature procedures,[13] and 10 equivalents of ethylenediamine. The latter was selected due to its propensity to form inter- over intra-fullerene bonds as a result of its short amine–amine separation. The reaction was found to proceed readily at room temperature under ultraviolet irradiation (254 nm, 30 min), and a colour change from the characteristic purple of C_{60} to yellow, typical of functionalised fullerene cages, was observed (Fig. 1(a) and Fig. 1(b)).

Samples for transmission electron microscopy (TEM) were prepared by filtering dilute solutions through a 0.45 μm PTFE filter and dropping onto ultra-thin amorphous carbon supports. A JEOL 4000EX TEM operating at 100 kV was used to image the structures. Electron spin resonance (ESR) measurements were performed at room temperature using an X-Band Bruker Elexsys E580 spectrometer. Care was taken to ensure that spectra were not modulation-limited and that samples had the same concentration of C_{60}.

To understand the nature of the material formed, high resolution transmission electron microscopy (HRTEM) of dilute solutions dried onto amorphous carbon supports was used. At low magnification, polymeric sheets were observed (Fig. 1(c)), and at higher magnification, a graphene-like lattice structure could be determined (Fig. 2(a)). Plotting the pixel intensity as a function of distance along the line perpendicular to the lattice gives an average lattice spacing of 0.4 ± 0.02 nm (Fig. 2(b)). This is smaller than the predicted unit cell, determined from a simple molecular structure (Fig. 3). This indicates that the area we are observing is relatively thick, with a crystalline structure in three dimensions that gives rise to the lattice projection we see here. It is also likely that upon solvent evaporation, the fullerene–amine structure folds up due to the flexible ethylene linker.

In selected areas of the same sample, individual fullerene molecules can be resolved, as shown in Fig. 4a, and the unit spacing can be determined as approximately that expected from

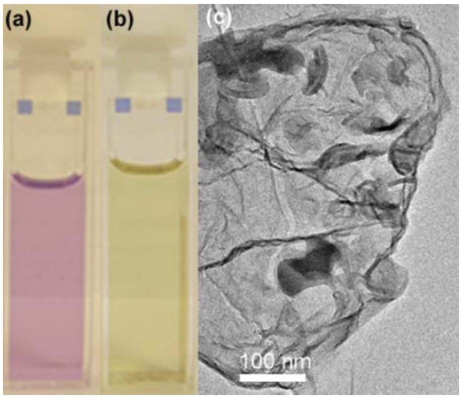

Fig. 1 C_{60} solutions (a) before and (b) after multiple bis-amine functionalisation. (c) TEM image of polymeric C_{60} superlattice.

---

[a] *Department of Materials, Oxford University, Oxford, UK OX1 3PH. E-mail: andrew.watt@materials.ox.ac.uk; Tel: +44 (0)1865 273790*
[b] *School of Physics and Astronomy, University of St. Andrews, St. Andrews, UK KY16 9SS*

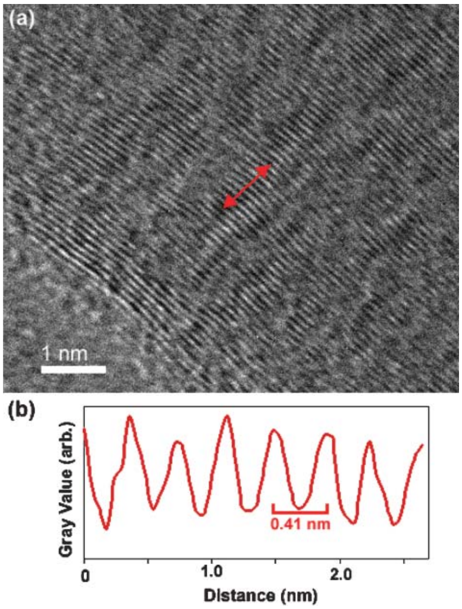

Fig. 2 (a) HRTEM image of the lattice structure of the C_{60} superlattice. (b) Pixel intensity plot with distance along the red-arrowed line.

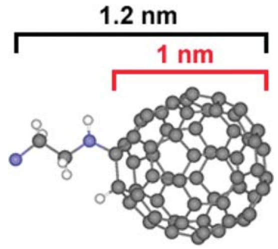

Fig. 3 Schematic representation of a superlattice unit cell (grey—carbon, blue—nitrogen, white—hydrogen).

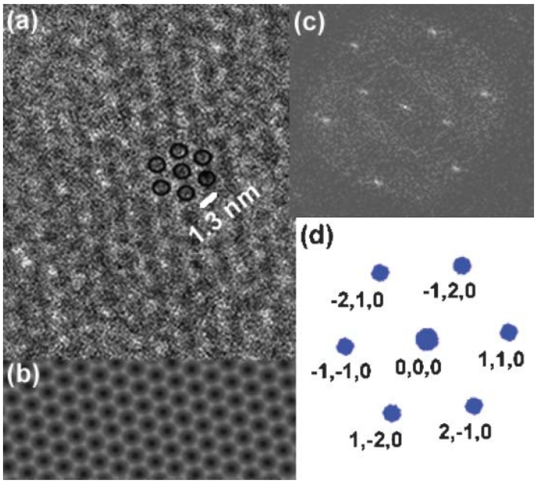

Fig. 4 (a) HRTEM image of individual fullerenes in the superlattice showing the rhombohedral structure. (b) Simulation of a rhombohedral carbon structure with space group (*R*-3*m*) looking along the [001] zone axis. (c) A two-dimensional FFT of (a). (d) Kinematic electron diffraction simulation of a rhombohedral carbon structure with space group (*R*-3*m*) looking along the [001] zone axis.

the schematic shown in Fig. 3. Closer examination of the image reveals a rhombohedral fullerene structure.[9] Images simulated using the Bloch wave approach[14] for a rhombohedral carbon structure with space group (*R*-3*m*) agree closely with the experimental observations (Fig. 4(b)).

A two-dimensional fast Fourier transformation (FFT) of the experimentally-determined structure is shown in Fig. 4(c). The outer ring of the diffraction pattern matches well with that generated from a kinematic electron diffraction simulation along the [001] axis (Fig. 2d). The inner ring indicates that there is a degree of long-range order across the sample.

ESR measurements of toluene solutions of the $N@C_{60}/C_{60}$ taken directly from the reaction mixture (C_{60} concentration = 0.006 mol dm^{-3}) indicate approximately complete retention of the incarcerated nitrogen atom (Fig. 5). The increase in the nitrogen spin linewidth from 0.06 G in $N@C_{60}$ to 0.13 G in the superlattice is postulated to be a result of the modification of the fullerene cage symmetry and the corresponding interaction with the encapsulated atomic nitrogen. The calculated *g*-values for both the control and superlattice solutions is 2.006 ± 0.0005. Importantly, these initial observations indicate that remarkably little perturbation of the fullerene cage environment, in which the nitrogen atom is incarcerated, occurs upon superlattice formation.

In conclusion, we have shown the spontaneous formation of a crystalline organic fullerene species and short bis-amine linkers. Despite the lack of control over the number and position of the amine functionalisation of the fullerene cages, a highly ordered structure is readily obtained. The ease with which this methodology can be implemented indicates great potential for further control over the final lattice structure. Even though flexible linkers were employed, the short fullerene–fullerene spacing indicates the possible presence of π–π stacking interactions between neighbouring fullerenes, and thus the possibility for good electronic transport exists. This is exciting, considering the recent observation of the quantum hall effect in graphene.[15] By employing a simple and mild methodology, the problem of endohedral nitrogen loss through thermal or optical pathways has been overcome.

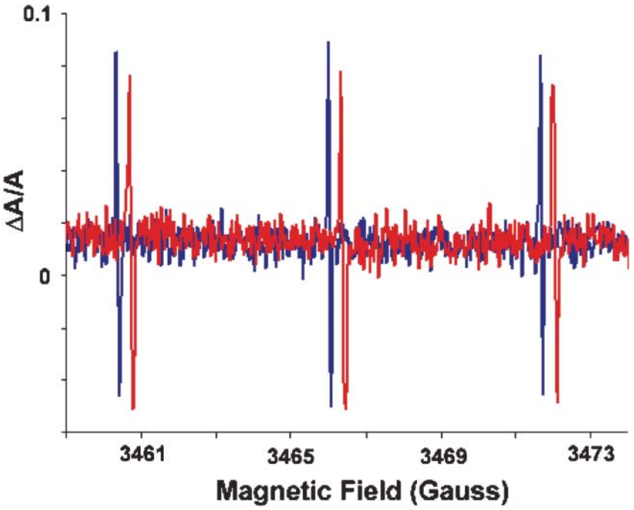

Fig. 5 Electron spin resonance of pristine $N@C_{60}/C_{60}$ (0.05% N) (blue) and the $N@C_{60}/C_{60}$ superlattice (red).

These results are a significant step towards low-dimensional atomic–molecular arrays for fullerene-based quantum information processing.

We thank Simon Benjamin, Sarah Haigh, Angus Kirkland and John Morton for discussions. This research is part of the QIP IRC http://www.qipirc.org (GR/S82176/01). GADB is supported by an EPSRC Professorial Research Fellowship (GR/S15808/01).

Notes and references

1 S. C. Benjamin and N. F. Johnson, *Phys. Rev. A*, 1999, **60**, 4334.
2 C. A. Perez-Delgado, M. Mosca, P. Cappellaro and D. G. Cory, http://lanl.arxiv.org/abs/quant-ph/0601054.
3 W. Harneit, *Phys. Rev. A*, 2002, **65**, 032322.
4 D. Suter and K. Lim, *Phys. Rev. A*, 2002, **65**, 052309.
5 J. J. L. Morton, A. M. Tyryshkin, A. Ardavan, S. C. Benjamin, K. Porfyrakis, S. A. Lyon and G. A. D. Briggs, *Nat. Phys.*, 2006, **2**, 40–43.
6 B. Corzilius, A. Gembus, N. Weiden and K.-P. Dinse, *AIP Conf. Proc.*, 2005, **786**, 317.
7 E. V. Shevchenko, D. V. Talapin, N. A. Kotov, S. O'Brien and C. B. Murray, *Nature*, 2006, **439**, 55.
8 A. M. Rao, P. Zhou, K.-A. Wang, G. T. Hager, J. M. Holden, Y. Wang, W.-T. Lee, X.-X. Bi, P. C. Eklund, D. S. Cornett, M. A. Duncan and I. J. Amster, *Science*, 1993, **259**, 955.
9 N. Núñez-Regueiro, L. Marques, J.-L. Hodeau, O. Béthoux and M. Perroux, *Phys. Rev. Lett.*, 1995, **74**, 278.
10 Y. Iwasa, T. Arima, R. M. Fleming, T. Siegrist, O. Zhou, R. C. Haddon, L. J. Rothberg, K. B. Lyons, H. L. Carter, A. F. Hebard, R. Tycko, G. Debbagh, J. J. Krajewski, G. A. Thomas and T. Yagi, *Science*, 1995, **264**, 1570.
11 M. Waiblinger, K. Lips, W. Harneit, A. Weidinger, E. Dietal and A. Hirsch, *Phys. Rev. B*, 2001, **63**, 045421; M. Waiblinger, K. Lips, W. Harneit, A. Weidinger, E. Dietal and A. Hirsch, *Phys. Rev. B*, 2001, **64**, 159901 (E).
12 A. S. D. Sandayaka, Y. Araki, C. Luo, M. Fujitsuka and O. Ito, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 1113.
13 M. Kanai, K. Porfyrakis, G. A. D. Briggs and T. J. S. Dennis, *Chem. Commun.*, 2004, 2, 210.
14 J. M. Zuo and J. C. Mabon, *WebEMAPS software*, University of Illinois, Urbana-Champaign, USA, http://emaps.mrl.uiuc.edu/.
15 Y. Zhang, Y.-W. Tan, H. L. Stormer and P. Kim, *Nature*, 2005, **438**, 201.