

Supporting information file

Switching Intermolecular Interactions by Confinement in Carbon Nanotubes

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TEM images of **1**@SWNT

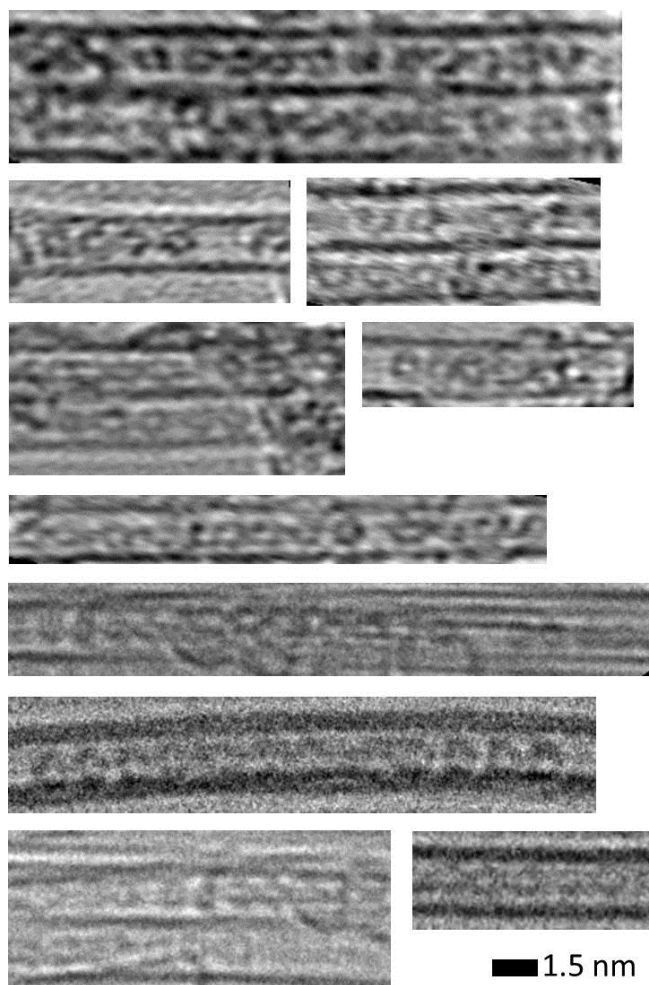


Figure S1. Several examples of HRTEM images of **1**@SWNT illustrating the high filling rates and tight packing of molecules of **1** within the nanotube channels.

Experimental details

Fullerene **1** was prepared according to the previously reported method.¹

Black, block shaped single crystals suitable for X-ray diffraction were grown by slow diffusion of diethyl ether vapour into a carbon disulphide solution of **1** over the course of a few weeks.

Crystal Data. **1**, C₈₁H₂₀N, *M* = 1006.98, orthorhombic, *a* = 15.499(2) Å, *b* = 27.568(4) Å, *c* = 9.7851(15) Å, $\alpha = \beta = \gamma = 90^\circ$, *V* = 4181.1(11) Å³, *T* = 100(2) K, space group *Cmc*2₁ (no. 36), *Z* = 4, $\rho_{calc.}$ = 1.600 mg/mm³, $\lambda(\text{CuK}\alpha)$ = 1.54 Å, $\mu(\text{CuK}\alpha)$ = 0.714 mm⁻¹, 18720 reflections collected, 3786 unique (*R*_{int} = 0.0478) which were used in all calculations. The final *wR*₂ was 0.1088 (all data) and *R*₁ was 0.0408 (>2 σ (*I*)). Crystal data set was collected on a Rigaku Saturn944+ (2x2 bin mode) diffractometer. The structure was solved using OLEX2² with the ShelXS³ structure solution programme using Direct Methods and refined with the ShelXL³ refinement package using least squares minimisation.

Encapsulation of **1** into carbon nanotubes:

Purified SWNT (3 mg) (NanoCarbLab, *d*_{NT} = 1.39 nm) were heated in air at 520 °C for 15 minutes. A three-fold excess of **1** (9 mg) was dispersed in toluene (1 mL) using ultrasound to form a super-saturated solution. Freshly annealed nanotubes were then added to the fullerene suspension and the resultant mixture heated at 80 °C for 8 hours under Ar. The mixture was filtered and sequentially washed with toluene (20 mL) and then n-hexane (20 mL), and the precipitate consisting of **1**@SWNT dried in air.

TEM conditions and image analysis:

HRTEM analysis was performed on a JEOL2100 field emission gun transmission electron microscope. The imaging conditions were carefully tuned by lowering the accelerating voltage of the microscope to 100 kV and reducing the beam current density to a minimum to reduce the e-beam damage on specimen. The **1**@SWNT sample (0.1 mg) was dispersed in iso-propanol (2 mL) using ultrasound and drop-cast onto a lacey carbon film coated TEM copper grid. TEM image simulations were performed using a custom-made programme (MUSLI code).⁴

Computational methods:

Molecular mechanics simulations were performed by the NAMD program⁵ which has been successfully used for fullerene–nanotube interaction studies previously^{6–8} using the CHARMM27 force field. Lennard-Jones potential parameters for the carbon atoms situated in the cage of the functionalised fullerene **1** and the (10,10)SWNT were taken from reference 9 for this study. Conventional Lennard-Jones parameters from the CHARMM27 force field were employed for the other atoms of functionalised fullerene **1**. The partial atomic charges of functionalised fullerene **1** were obtained using the QEq technique originally developed by Rappé and Goddard.¹⁰ The (10,10)SWNT was treated as neutral.

The binding energy calculated for C₆₀ molecule inside a (10,10)SWNT calculated by the above method is in good agreement with the experimentally measured value for C₆₀ encapsulation.¹¹ However, an energetic barrier to encapsulation was not observed in our study due to the fact that our calculations use an improved nanotube model which allows bond stretching and angle bending

of the carbon framework during fullerene encapsulation, while the rigid nanotube used for the simulations in reference 9 did not.

This allowed the potential energy profile along the reaction coordinate for both fullerene first (blue) and trityl group first encapsulation (red) to be calculated, see Fig S2.

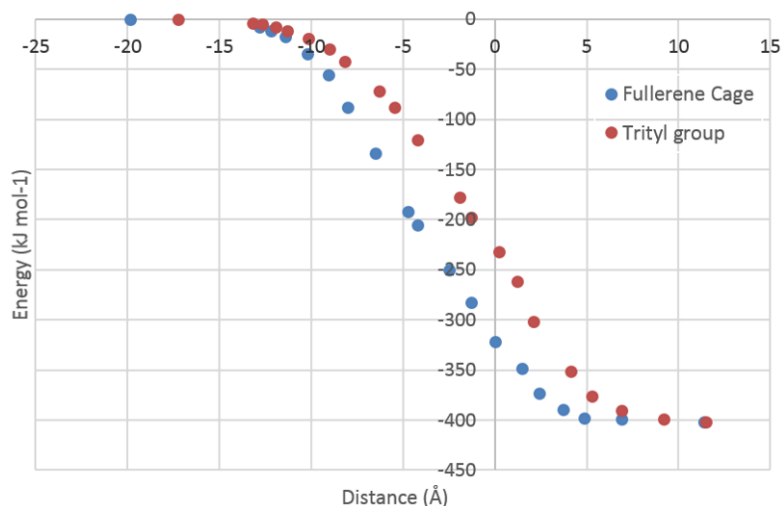


Figure S2 . The potential energy profiles for encapsulation of **1** into a (10,10)SWNT for two different orientations: fullerene cage first (blue) and trityl group first (red). The entrance of the (10,10)SWNT is at distance = 0.

The simulation snapshots obtained for the three different orientations of pairs of **1** within (10,10)SWNT are shown below, Fig S3. Fullerenes cages and trityl groups are shown as Van der Waals spheres.

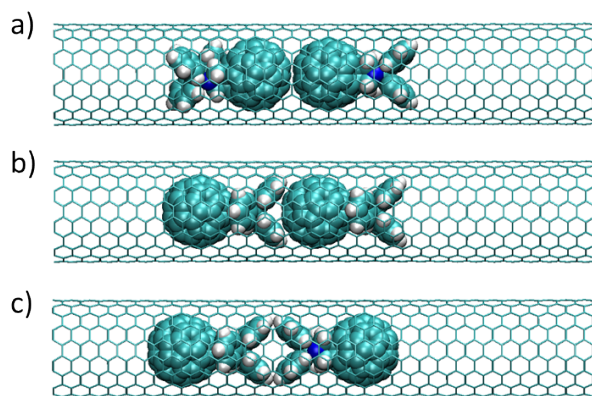


Figure S3 . Simulation snapshots obtained for a), fullerene-to-fullerene, b), fullerene-to-trityl, and c), trityl-to-trityl orientations within (10,10)SWNT

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