Supporting Information

p-Phosphonic acid calix[8]arene assisted dispersion and stabilisation of pea-pod C_{60}@multi-walled carbon nanotubes in water

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Materials and Methods

Pristine fullerene C_{60} (99685-96-8, 99+%, BuckyUSA) and multi-walled carbon nanotubes (773840, 98+%, Sigma Aldrich) were used as received. *p*-Phosphonic acid calix[8]arene was synthesised following the literature procedure.[1] Probe sonication was carried out using a Vibra-Cell™ VCX130 sonicator at 60% amplitude for all samples. Low-speed and high-speed centrifugations were performed using the Orto Alresa Consul 21 and Dynamica Velocity 14R, respectively. Hydrogen (S46965-3, 99.999%, CAC Gas and Instrumentation) was controlled by a Brooks Instrument GF Series Thermal Mass Flow Controller, coupled with Brooks User Software. The hydrogen reduction experiments were carried out at ambient conditions with a flow rate of 20 sccm.

The washed aqueous dispersions were dropped cast onto 200 mesh holey carbon copper grids (#2450-AB, SPI Supplies), and dried in air for TEM characterisations. Philips CM200 TEM operating at 120-200 kV was used for obtaining the TEM and HRTEM data. Image J was used for processing all the TEM images.

Zeta potential analysis was performed using a Malvern Zetasizer Nano series. Measurements for each sample were recorded in triplicate and 20 data acquisitions were recorded in each measurement. All measurements were recorded at 25°C in Malvern disposable clear Folded Capillary Cells.

Raman spectra were acquired using a Witec alpha300R Raman microscope with excitation laser wavelength of 532 nm ($\leq$ 5 mW) at room temperature. The spectra were recorded with an x40 objective (Numerical Aperture 0.60) for each sample with typical integrations times between 10 to 20 seconds with 3 accumulations per spectrum.

S1 Control Experiments in the absence of *p*-phosphonic acid calix[8]arene.

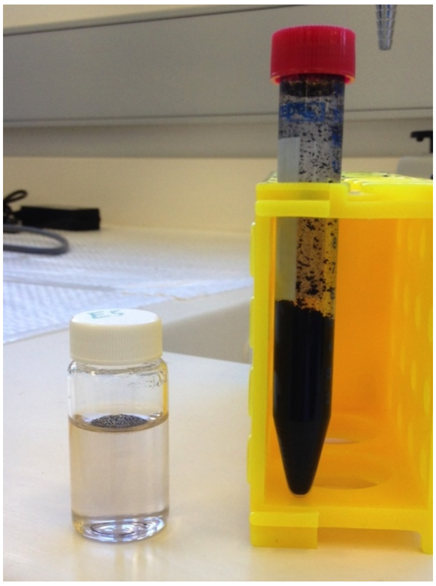

Fig. S1 Photograph of the control experiments where C_{60} (left) and MWCNTs (right) were sonicated in water in the absence of *p*-phosphonic acid calix[8]arene, showing unstable dispersions.

S2 Dispersions after high-speed centrifugation

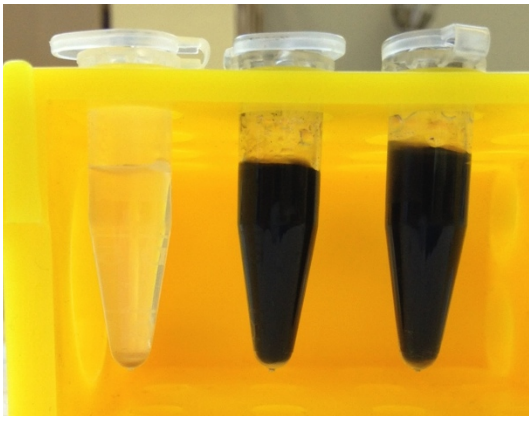

Fig. S2 Photograph of the dispersions of C_{60} (left), MWCNTs (middle) and C_{60}@MWCNTs (right) after high-speed centrifugations.

S3 Additional TEM images on pea-pod C_{60}@MWCNTs

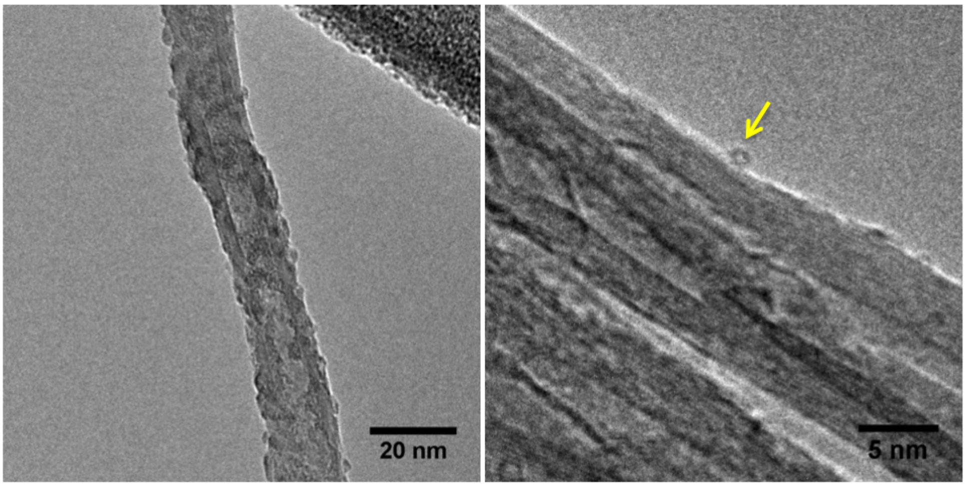

Fig. S3 TEM images of the pea-pod C_{60}@MWCNTs, showing the C_{60} molecules present on the outer surfaces of the MWCNTs.

S4 FT-IR study of C_{60} and *p*-phosphonic acid calix[8]arene in water.

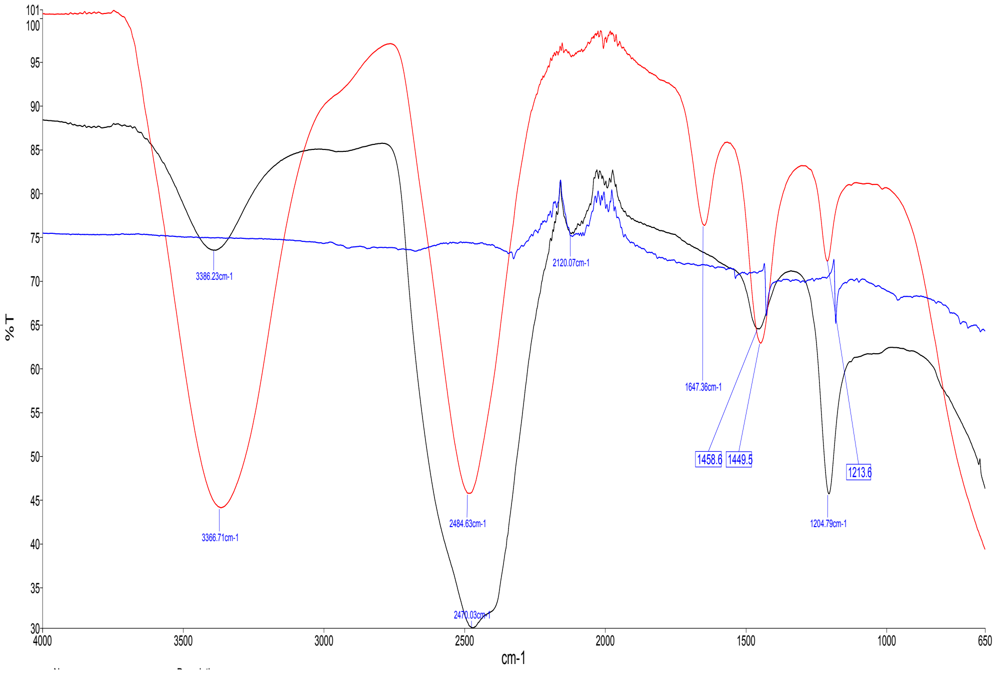

Fig. S4 FT-IR recorded using a Perkin Elmer FTIR instrument. Pure C_{60} is included for comparison, shown as a blue trace. Peaks are shifted, which is consistent with interplay of the fullerene and calixarene molecules, as is a new peak at 1647 cm^{-1}.

Calix[8]arene in water (Black Line)	Calix[8]arene, C_{60} and water (Red Line)
3386 cm^{-1}	3366 cm^{-1}
2470 cm^{-1}	2484 cm^{-1}
-	1647 cm^{-1}
1459 cm^{-1}	1450 cm^{-1}
1205 cm^{-1}	1214 cm^{-1}

S5 UV Visible absorption spectroscopy.

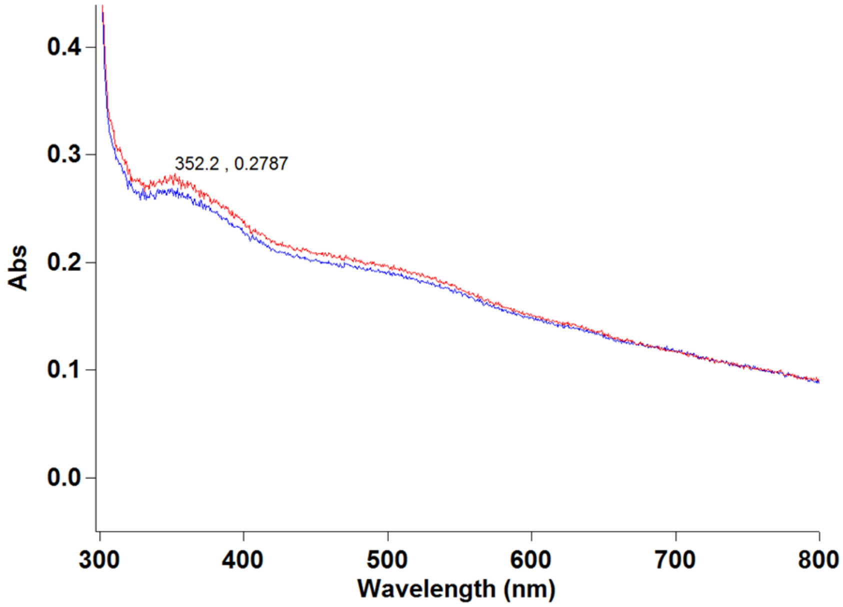

Fig. S5a The UV spectra of *p*-phosphonic acid calixarene stabilised C_{60} in water, with a λ_{max} at 352 nm. The blue and red lines are scans of the same bulk sample.

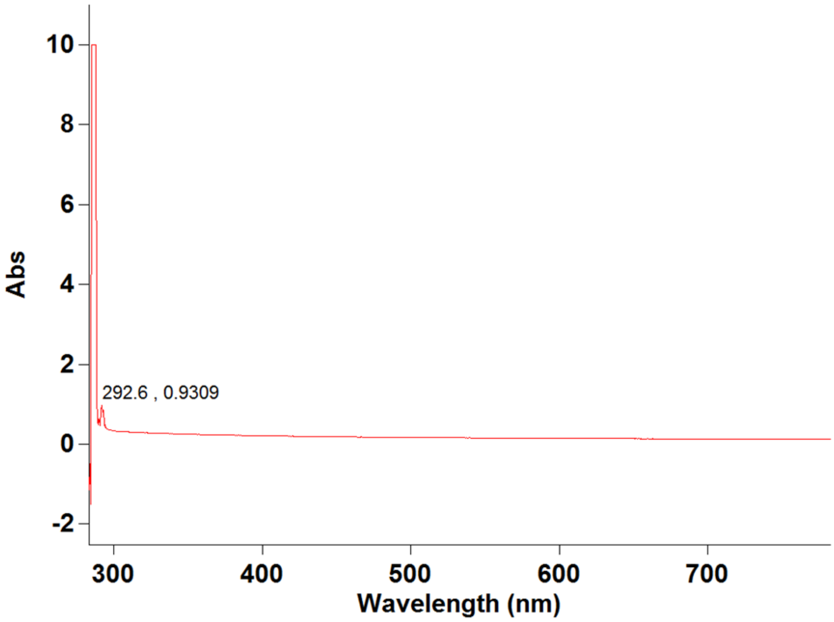

Fig. S5b The UV spectrum of *p*-phosphonic acid calix[8]arene stabilised MWCNTs in water, with a λ_{max} at 293 nm.

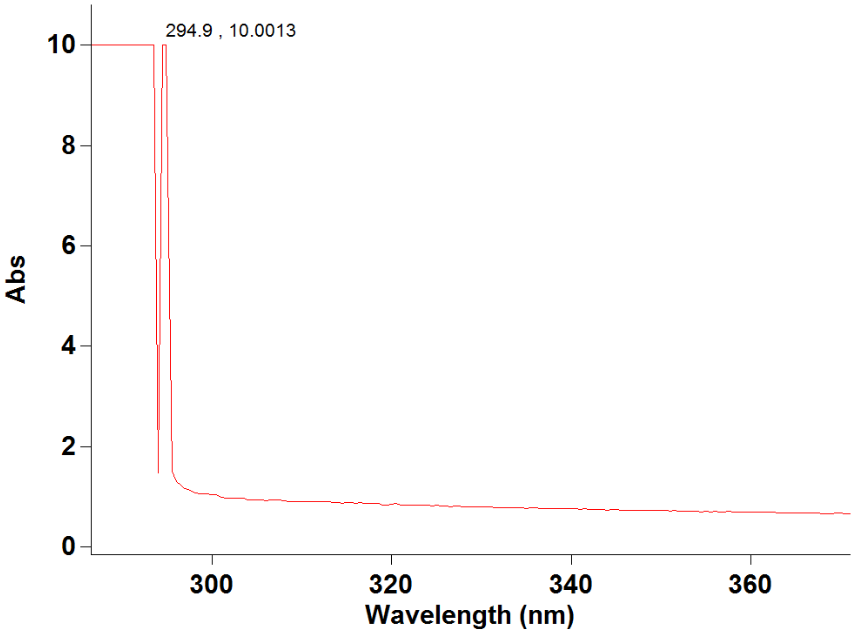

Fig. S5c The UV spectrum of *p*-phosphonic acid calix[8]arene stabilised C_{60}@MWCNTs in water, with a λ_{max} at 295 nm.

S6. ^1H NMR spectroscopy.

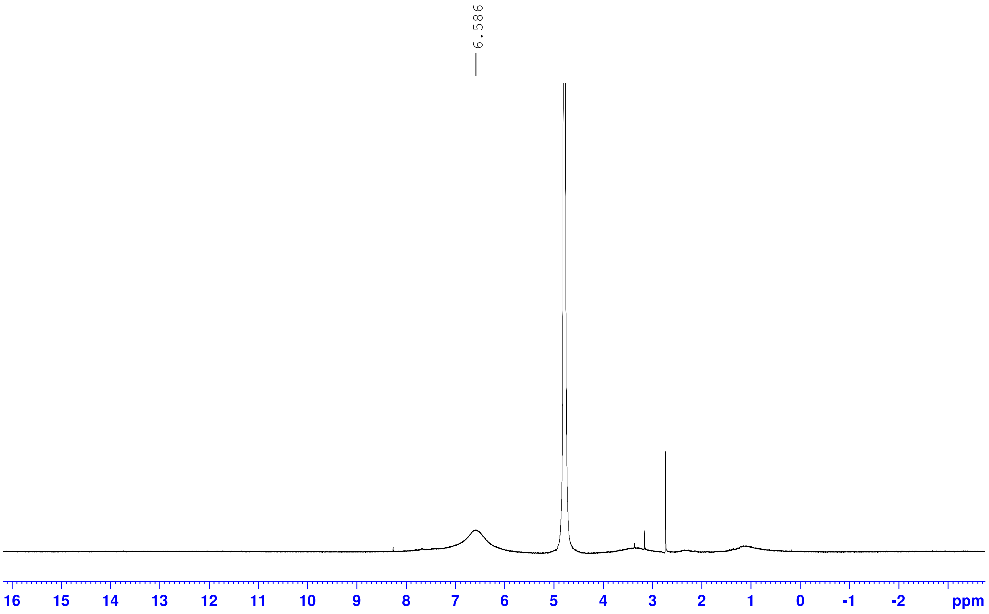

Fig. S6a ^1H NMR spectrum of *p*-phosphonic acid calix[8]arene in D_2O.

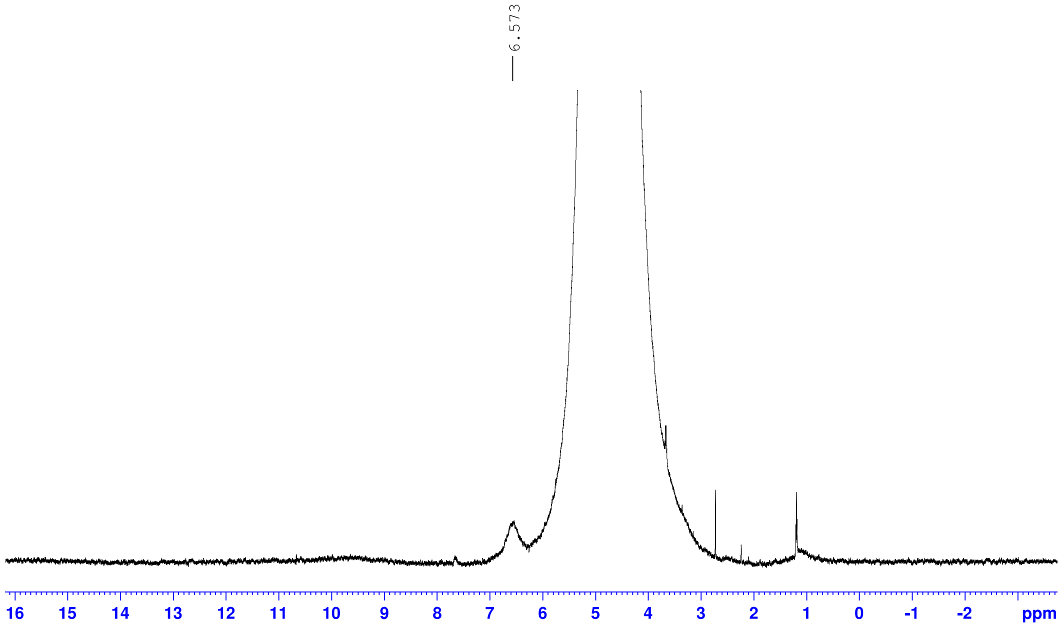

Fig. S6b ${}^{1}H$ NMR of *p*-phosphonic acid calix[8]arene stabilised C_{60} in D_2O

${}^{1}H$ NMR (D_2O, 25.0 °C) were recorded on a 600 MHz Bruker spectrometer. Solvent based NMR was chosen due to the relatively small sample size (2 mg) and the ability to study the system in its native aqueous state. There is a small change in the position of the main calixarene resonance at 6.59 ppm (aryl protons) in introduction of fullerene C_{60} (6.57 ppm). Both the NMR and IR show slight changes, which is commensurate with interplay between the fullerene and calixarene molecules.

The NMR of C_{60} within the calixarene was run using D_1 – 1 and ns-2000, whilst the NMR of just the calix[8]arene was run using D_1 – 1 and ns-300. Elucidation of further peaks as previously reported is not possible in the presence of D_2O, and when looking at limited concentrations, but this was chosen for a direct comparison to be drawn to the synthesis of the material. However, the main peak for the calix[8]arene are still consistent with previously reported NMR spectra.[2]

Reference

1. T. E. Clark, M. Makha, A. N. Sobolev, D. Su, H. Rohrs, M. L. Gross, J. L. Atwood, C. L. Raston, *New J. Chem.*, 2008, **32**, 1478-1483.
2. E. James, P. K. Eggers, A. L. Harvey, S. A. Dunlop, M. Fitzgerald, K. A. Stubbs and C. L. Raston, *Org. Biomol. Chem.*, 2013,**11**, 6108-6112.