Electronic Supplementary Information

Microwave assisted covalent functionalization of C_{60}@SWCNT peapods

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General

Steady-state absorption spectroscopy. The electronic absorption spectra were recorded on a Perkin Elmer (Lambda 19) UV-Vis-NIR spectrophotometer.

Attenuated-total-reflectance infrared spectroscopy. Mid-infrared spectra in the region 550-4000 cm^{-1} were obtained on a Fourier Transform IR spectrometer (Equinox 55 from Bruker Optics) equipped with a single reflection diamond ATR accessory (DuraSamp1IR II by SensIR Technologies). A drop of the solution was placed on the diamond surface, followed by evaporation of the solvent, in a stream of nitrogen, before recording the spectrum. Typically, 100 scans were acquired at 4 cm^{-1} resolution.

Raman spectroscopy. Micro-Raman scattering measurements were performed at room temperature in the backscattering geometry using a RENISHAW inVia Raman microscope equipped with a CCD camera and a Leica microscope. A 2400 lines mm^{-1} grating was used for all measurements, providing a spectral resolution of ± 1 cm^{-1}. As an excitation source the Ar^+ laser (514 nm with less than 0.5 mW laser power) was used. Measurements were taken with 60 seconds of exposure times at varying numbers of accumulations. The laser spot was focused on the sample surface using a long working distance 50x objective. Raman spectra were collected on numerous spots on the sample and recorded with Peltier cooled CCD camera. The intensity ratio I_D/I_G was obtained by taking the peak intensities following any baseline corrections. The data were collected and analyzed with Renishaw Wire and Origin software.

Photoluminescence spectroscopy. PL measurements were performed by using Shimadzu NIR-PL system with an IR-enhanced InGaAs detector (Princeton instruments OMA-V2.2) and tunable Ti-Sapphire Laser (Spectra physics 3900S). The slit width for emission was 10 nm and scan steps were 5 nm and 2 nm for excitation and emission, respectively. Raw data, 1000-2200 nm for emission and 700-1060 nm for excitation, were corrected for wavelength–dependent instrumental factors and excitation laser intensities. Samples were dispersed in D_2O with 1 wt% sodium dodecylbenzene sulfonate (SDBS) by using tip–type sonicator (SONICS VCX500, operated at 200 W for 10 minute), and then centrifuged at 127600 g for 2.5 hour. After centrifugation, supernatant was collected for measurement.

Thermogravimetric analysis. The thermogravimetric analysis was performed using a TGA Q500 V20.2 Build 27 instrument by TA in an inert atmosphere of nitrogen. In a typical experiment 1 mg of the material was placed in the sample pan and the temperature was equilibrated at 40 ^oC. Subsequently, the temperature was increased to 900 ^oC with a rate of 10 ^oC min^{-1} and the weight changes were recorded as a function of temperature.

Specimen preparation. The C_{60}@SWCNT peapod specimen was dispersed in n-hexane and then fixed on a copper TEM grid coated with holey carbon film. Several drops of the aryl-functionalized C_{60}@SWCNTs solution were placed on a copper TEM grid coated with holey carbon film.

TEM analysis. TEM observations were carried out using a JEM-2010F (JEOL) equipped with a CEOS post specimen spherical aberration corrector (C_s corrector) operating at 120 kV.

Electrochemistry analysis. Electrochemistry studies were performed using a standard three-electrode cell. Platinum guaze (52mesh, 99.9%) was used as a counter electrode and Pt disk (1.6 mm diameter) as a working electrode (BASi). Silver/silver nitrate (Ag/$AgNO_3$ 0.1 M in acetonitrile) was used as a reference electrode. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$; 98%) was used as electrolyte and was recrystallized three times from acetone and was dried in a vacuum at 100 °C. Before each experiment the cell was purged with high purity N_2 for 5 minutes. Before the start of the measurement the inert gas was turned to "blanket mode". Measurements were recorded using an EG&G Princeton Applied Research potensiostat/galvanostat Model 2273 connected to a personal computer running PowerSuite software. The working electrode was cleaned before each experiment through polishing using a cloth and 6, 3 and 1μm diamond pastes. The Ag/$AgNO_3$ electrode was calibrated before each experiment by running cyclic voltammetry on ferrocene. The potential values obtained versus Ag/$AgNO_3$ were converted versus saturated calomel electrode (SCE) using ferrocene. All DPV reduction runs were carried out using pulse height 0.05 V, pulse width 100 ms, step height 2 mV and step time 200 ms. DPV oxidation run was carried out using pulse height 0.025 V, pulse width 100 ms, step height 2 mV and step time 110 ms. Electrochemistry of fullerene was carried out in $TBAPF_6$ 0.1M in (o-DCB):acetonitrile (5:1), Blank experiment of a mixture of aryl functionalized SWCNTs and C_{60} was run in $TBAPF_6$ 0.1M in a mixture of o-DCB:acetonitrile (5:1) and DMF. All peapod experiments were carried out in $TBAPF_6$ 0.1M in DMF.

Microwave-assisted reactions. For the microwave synthesis, a CEM Discover microwave reactor (frequency = 2.45 GHz, P_{max} = 300 W) with internal infra-red pyrometer and pressure control system was used. The microwave reactions were carried out in a 10 mL capacity glass vessel with self-sealing septa, specially designed for operation in the microwave apparatus. Magnetic stirring was provided to assure complete mixing of the reactants, which irradiated under appropriate power and time.

Synthesis of C_{60}@SWCNT peapods. The arc-SWCNTs (Meijo Arc APJ-type, Meijo Nano Carbon Co. Ltd) were heated at 350 °C for 30 minutes in air to remove the most of amorphous carbon and other carbon materials which coats catalyst metal particles. The as-obtained SWCNTs were treated in methanol solution of sodium hydroxide for 30 minute and washed by propanol-2 for several times. The remaining metal particles were washed by hydrochloric acid and heated at 600°C for 2 hours in vacuum. To open the cap of SWCNTs, purified arc-SWCNTs were heated at 500°C for 30 minutes in air. The treated SWCNTs and fullerenes were sealed under vacuum ($\sim 1 \times 10^{-4}$ Pa) in a quartz tube and heated at 600 °C for 24 hours. The obtained nanopeapods were washed extensively with toluene to remove the fullerenes adsorbed on the outside of the walls.

Microwave-assisted synthesis of aryl-functionalized C_{60}@SWCNT peapods. In a typical experiment, 5 mg C_{60}@SWCNTs and 150 mg (0.41 mmol) of tert-butyl 2-(2-(2-(4-aminobenzamido) ethoxy)ethoxy)ethylcarbamate were added in the microwave glass vessel and flushed with nitrogen. Then, 70 µL (61,0 mg, 0,52 mmol) of isoamyl nitrite were added and the vessel was tapped with the sealing septa and placed in the microwave reactor. The initial power was 10 W, the preselected temperature was set at 160 °C and the reaction time at 30 min. Under these conditions, the temperature raised up to 137 °C and the pressure in the tubes up to 88 psi. After completion of the reaction time, the crude material was suspended in DMF, filtered through PTFE membrane filter (0.2 µm), washed with DMF (100 mL), methanol (100 mL) and dichloromethane (100 mL) and dried in a vacuum oven at 60 °C overnight.

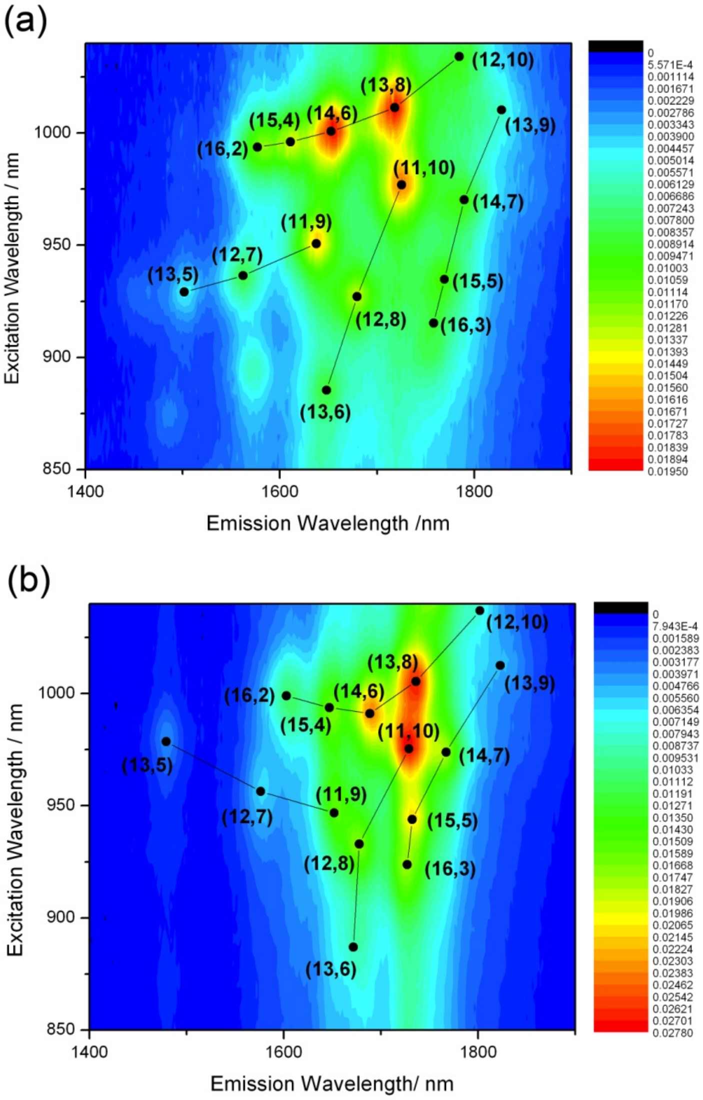

Fig. S1. 2D PL contour maps of (a) SWCNTs and (b) C_{60}@SWCNT peapods. The PL maxima on the map are seen in the second interbands (E_{22}) excitation region (λ_{22} = 850 – 1050 nm) and the first interbands (E_{11}) emission region (λ_{11} = 1400 – 1900 nm) of SWCNTs with 1.3 – 1.5 nm in diameter. The observed peaks can be assigned to specific (n, m) SWCNTs. The filling ratio was estimated from the relative intensity of the PL peaks of (13, 5) peapods and the original SWCNTs (Fig. S1(b)).

Table S1. Conditions for microwave-assisted aryl functionalization of SWNTs.[a]

Method	Power (Watts)	Run Time (Minutes)	Weight loss (%)	Carbons per 1 functional group
A	50	15	19.1	122
B	5	25	17.3	138
C	10	15	27.1	77
D	10	30	32.5	60
Conventional Heating	—	1080	24.4	89

Evaluation of Raman spectroscopy results and TGA data (Supporting Information, Fig. S2-S3), let us conclude on Method D – that is, microwave irradiation with continuous power of 10W for 30 min. – as optimum.

[a] The ratio SWNTs / aniline / isoamyl nitrite is 5 mg / 150 mg / 61 mg and kept the same in all experiments.

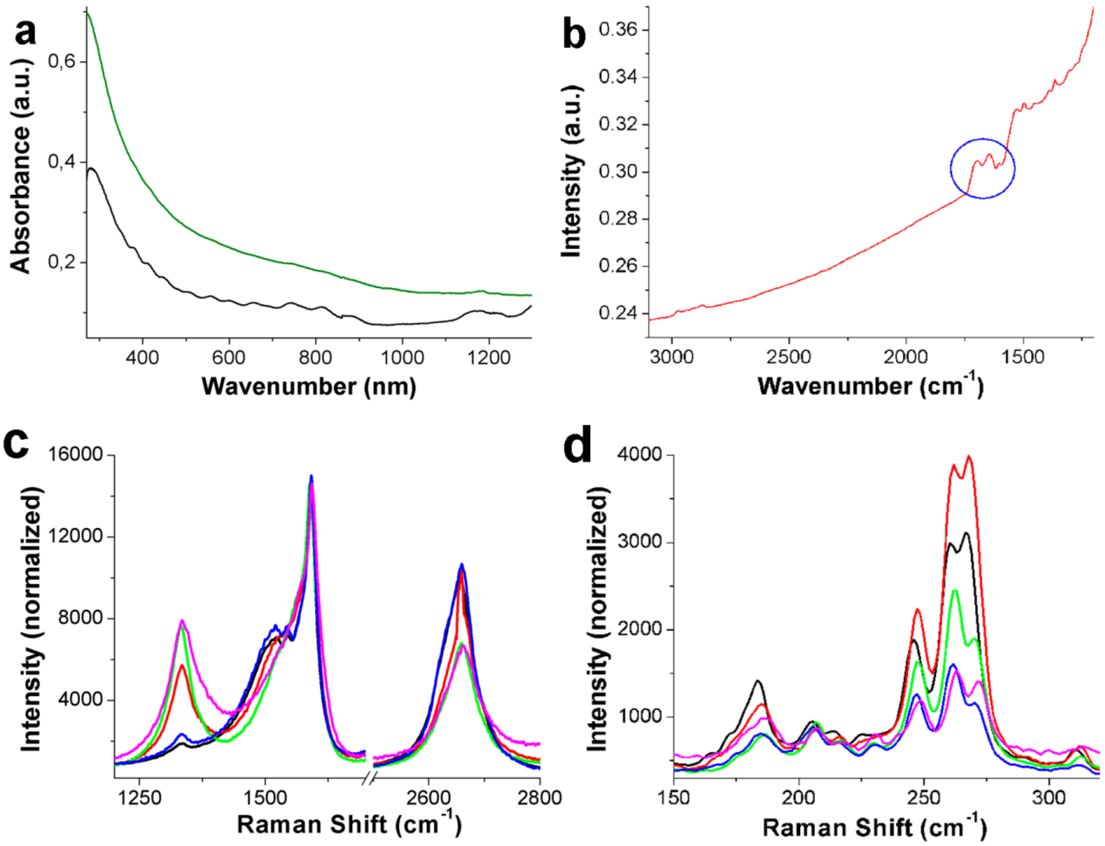

Fig. S2. a) UV-Vis spectra of pristine SWNTs (black) and microwave-assisted aryl-functionalized SWNTs, b) ATR-IR spectra of microwave-assisted aryl-functionalized SWNTs, c) High frequencies and d) low frequencies Raman spectra of pristine SWNTs (black) and microwave-assisted aryl-functionalized SWNTs via method A (red), B (green) and D (purple). Raman spectra of material obtained from blank experiment via method D using only SWNTs (blue).

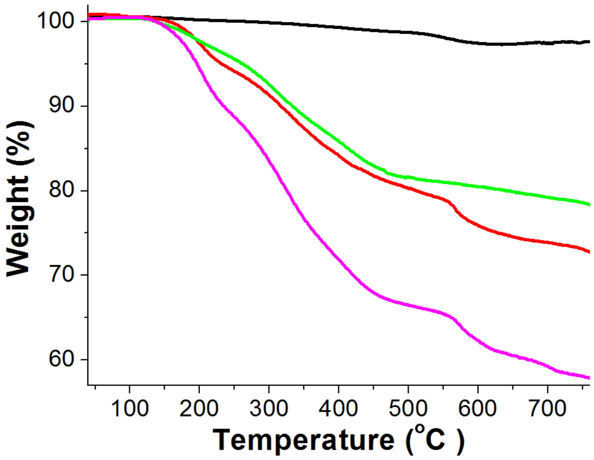

Fig. S3. Thermogravimetric analysis of pristine SWNTs (black) and microwave-assisted aryl-SWNTs produced via method A (red), B (green) and D (purple).

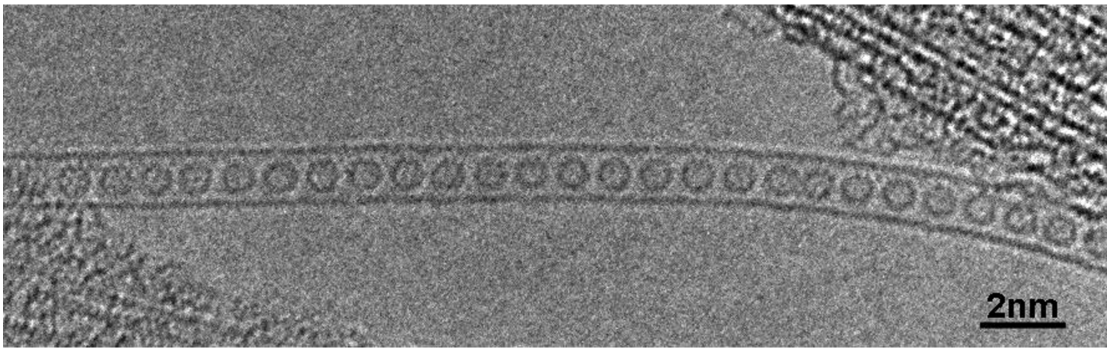

Fig. S4. Representative HRTEM image of intact C_{60}@SWCNT peapods indicating the absence of any soft material on the outer surface.

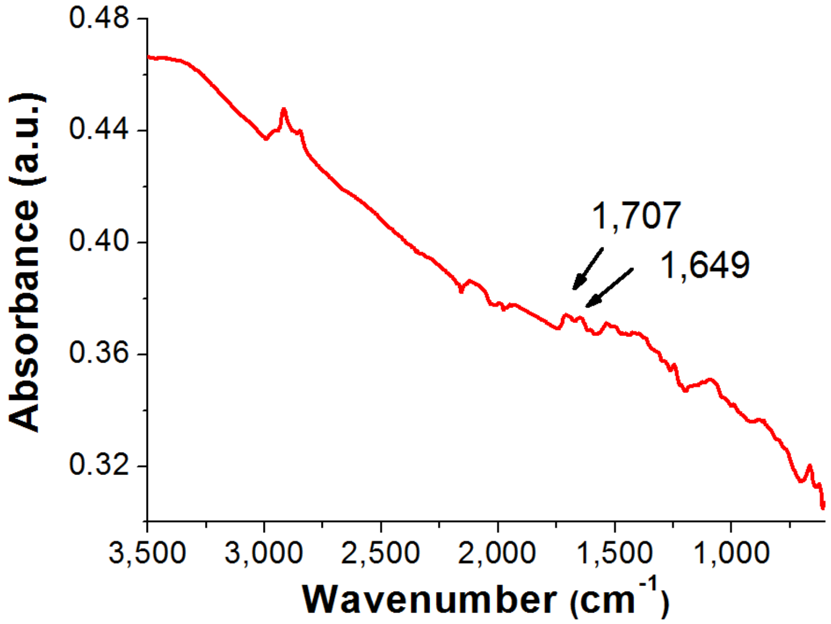

Fig. S5. Attenuated-total-reflectance infra-red (ATR-IR) spectrum of aryl-functionalized C_{60}@SWCNT peapods.

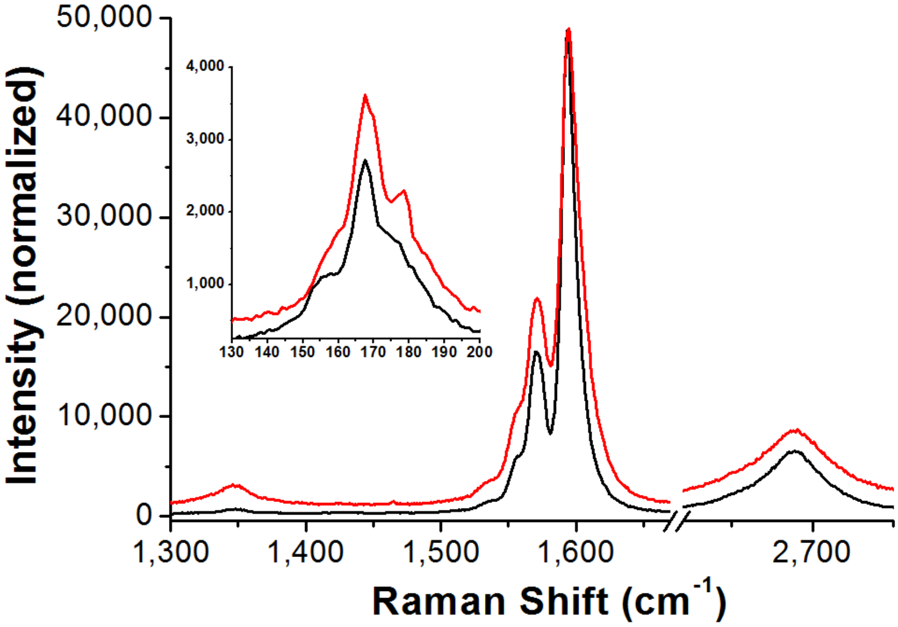

Fig. S6. Raman spectra of pristine C_{60}@SWCNT (black) and aryl-functionalized C_{60}@SWCNT peapods (red), obtained with λ_{exc} = 514 nm. Inset: Radial breathing mode (RBM) region.

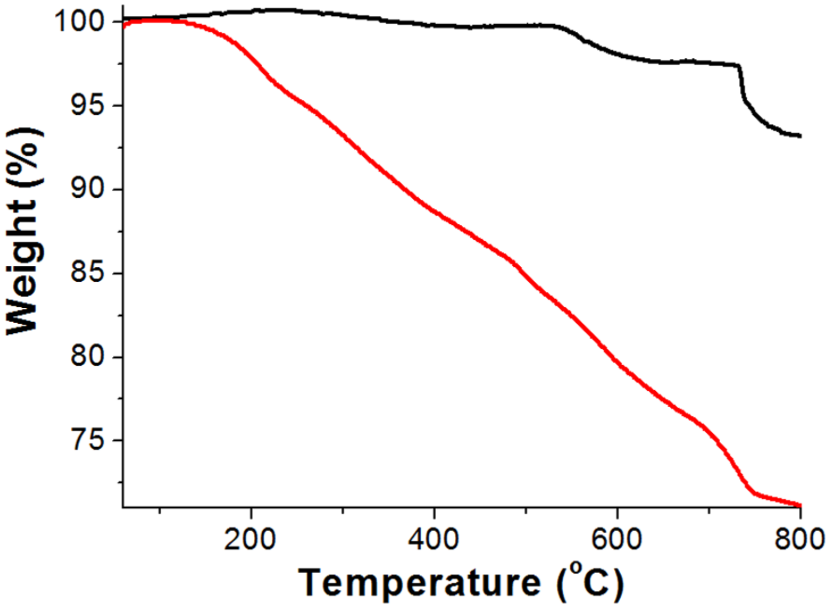

Fig. S7. Thermographs of pristine C_{60}@SWCNT peapods (black), and aryl-functionalized C_{60}@SWCNT peapods (red), obtained under inert atmosphere.