Supporting Information

The continuous-flow cycloaddition of azomethine ylides to carbon nanotubes

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1. Instruments, materials and methods

Carbon nanotubes suppliers. Single-walled carbon nanotubes (SWNTs) were purchased from NanoCarblab (SWNT purity: 70 – 80 wt%, diameter: 1.2 - 1.4 nm, length: 1 - 5 μm), double-walled carbon nanotubes (DWNTs) were provided by Cheap Tubes Inc (CNT purity > 90 wt%, DWNT purity > 60 wt%, outer diameter: 2 - 4 nm, length: 5 - 30 μm). Multi-walled carbon nanotubes (MWNTs) were purchased from Sigma Aldrich (MWNT purity > 90 wt%, outer diameter 10 – 15 nm, inner diameter: 2 – 6 nm, length: 0.1 – 10 μm) were used as received. 2-(2-(2-Methoxyethoxy)ethoxy)acetaldehyde **2** was synthesized according to a literature procedure.[1] Ethyl 2-(benzylamino)acetate **1** was purchased by Sigma Aldrich and used as received. All solvents were purchased from Sigma Aldrich and purified by distillation under reduced pressure. Dispersions of CNTs were achieved using the Sonicator 3000 (Misonix) with the following pulse parameters: time on = 3 sec, time off = 3 sec, power level = 5 (15-20 watt). The sonicated solutions were centrifuged with an IEC CL10 centrifuge (Thermo electron corporation) at 3500 rpm for 3 minutes. Absorption spectra of nanotube samples, dispersed in air-equilibrated solvent, were registered with a Varian Cary 5000 spectrophotometer, at room temperature, between 280 and 1400 nm, data interval = 0.5 nm, scan rate = 300 nm/min, SBW = 2 nm. DLS measurements of nanotube samples dispersed in air-equilibrated NMP were performed with a Zetasizer Nano S (Malvern Instruments) at 20 °C setting 20 runs of 10 seconds for each measurement. Raman spectra of carbon nanotubes, drop-casted on pre-cleaned glass micro slides (Corning) and annealed at 100°C, were recorded with an Invia Renishaw Raman microspectrometer (50× objective) using the 633 nm laser line of an He–Ne laser at room temperature with a low laser power. Thermogravimetric analyses (TGA) of CNT samples, precipitated by adding cyclohexane and dried at 80 °C at 0.2 mbar overnight, were carried out with a TA SDT 2960 TGA under nitrogen from 100 °C to 1000 °C with a heating rate of 20 °C/min.

Continuous-flow functionalisation of CNTs. The flow reactions were carried out in a PTFE (polytetrafluoroethylene) tubing (O.D. = 1.58 mm, I.D. = 0.8 mm, total volume = 2 ml, Supelco, Item no. 58696-U) coiled and immersed into an oil bath, set to 140 ºC, for 400 cm of effective length (Figure S1). A

Rheodyne valve was used to inject a stock dispersion of CNTs and reagents **1** and **2**, in the selected solvent, to the main flow line through a sample loop (I.D. = 2.0 mm, volume = 10 ml, length = 80 cm). The main flow was set to 4 ml/h by a HPLC pump (Model KP-12-01S by Flom, Japan). The reactor outlet was connected to a mechanical back-pressure regulator (S series Metering Valve, Swagelok) set to 25 psi. The reagents, before loading, were kept under vigorous magnetic stirring.

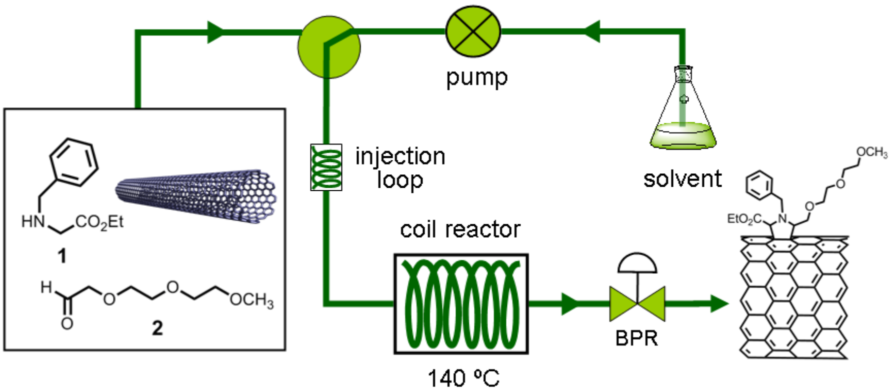


Fig. S1 The continuous-flow synthesis of functionalised CNTs.

The 2.0 ml total volume of the reactor coil corresponds to a residence time of 30 min with a flow rate of 4.0 ml/h. The first reaction mixture was recycled for further two runs by adding fresh aldehyde and aminoacid at each cycle (Table S1 and Table S2) for a total residence time of 90 minutes and an overall processing time of 7.5 hours. The final mixture was then centrifuged at 3500 rpm for 3 minutes, the supernatant was removed and the black residue washed with toluene (5 × 7 ml). The residual carbon material was dried under vacuum (0.2 mbar) at 80 °C for 4 h and weighted. Aliquots of soluble CNT material were extracted from the crude sample by means of sonication/centrifugation cycles. For the extractions, 2.0 ml of NMP were added to the CNT material, followed by 1 minute sonication (see above for sonicator parameters). The resulting dispersion was centrifuged again at 3500 rpm for 3 min, and the supernatant characterized by UV-Vis spectroscopy and DLS analysis immediately after centrifugation. Each DLS measurement was averaged over 20 runs (10 s per run). It is worth noting that the less soluble fractions gave DLS data poorly reproducible for the presence of large aggregates. Therefore, only DLS data for the first five extracts, in the solvents indicated in Table S1 and Table S2, were considered. The distribution of particle sizes was obtained by plotting the number size distribution provided by correlograms taken with the software program by Malvern (see above). Raman spectra were taken on samples prepared by drop casting the solutions, previously subjected to DLS measurements, on glass micro slides. In order to produce smooth CNT layers and reproducible Raman spectra, the drop-casted samples were annealed at 100 °C. TGA was used to estimate the degree of functionalisation corresponding to the number of functional groups introduced per atom of carbon on the nanotube sidewalls (see section 4). In order to do that, the CNT samples corresponding to the most soluble fractions (the first one for each reaction solvent) were precipitated from NMP by adding methanol (5 ml) and the solid was washed with methanol (2 x 5 ml). The residue was dried under vacuum (0.2 mbar) at 80 °C for 2h and was analyzed in a thermogravimeter under nitrogen from room temperature to 1000 °C with a heating rate of 20 °C/min.

Table S1 Flow synthesis of functionalised SWNTs.

Solvent	**SWNTs**/mg (mmol of C)	**1**/mg (mmol)	**2**/mg (mmol)	functionalised **SWNTs**/mg[a]	degree of functionalisation of **SWNTs** from 1st extract[b]
DMF	9.7 (0.81)	70 (0.36) 73 (0.38) 65 (0.34)	59 (0.36) 62 (0.38) 63 (0.39)	9.2	1.4 %
NMP	11.1 (0.92)	75 (0.39) 72 (0.37) 67 (0.35)	60 (0.37) 55 (0.34) 62 (0.38)	10.9	1.4 %
NCP	10.0 (0.83)	70 (0.36) 78 (0.40) 64 (0.34)	57 (0.35) 60 (0.37) 57 (0.35)	10.3	2.2 %

[a] Functionalised SWNTs recovered after collecting all extracts, evaporation of solvent and drying in vacuo.

[b] Fraction of functionalised SWNTs carbon atoms.

Table S2 Flow synthesis of functionalised DWNTs and MWNTs in NMP.

	CNTs/mg (mmol of C)	**1**/mg (mmol)	**2**/mg (mmol)	functionalised **CNTs**/mg[a]
DWNTs	10.1 (0.84)	33 (0.17) 36 (0.19) 33 (0.17)	28 (0.16) 25 (0.14) 31 (0.18)	9.1
MWNTs	11.3 (0.94)	38 (0.20) 45 (0.23) 40 (0.21)	30 (0.17) 35 (0.20) 41 (0.23)	10.8

[a] Functionalised SWNTs recovered after collecting all extracts, evaporation of solvent and drying in vacuo.

Functionalisation of SWNTs in flask.[2] A dispersion of SWNTs in the selected solvent (Table S3), containing glycine derivative **1** and aldehyde **2**, was heated to 140 ºC for 72 h in a 25 ml flask under vigorous stirring. Fresh ylide precursors were added every 24 h to compensate thermal degradation. Then the mixture was centrifuged (3500 rpm for 3 min), the supernatant discarded and the black solid residue washed with toluene (5 x 7 ml). The functionalised carbon material was dried under vacuum (0.2 mbar) at 80 °C for 4 h and weighted. Aliquots of soluble carbonaceous material were extracted from the crude SWNT sample by means of sonication/centrifugation cycles as described above.

Table S3 Flask synthesis of functionalised SWNTs.

Solvent	**SWNTs**/mg (mmol of C)	**1**/mg (mmol)	**2**/mg (mmol)	functionalised **SWNTs**/mg[a]	degree of functionalisation of **SWNTs** from 1st extract[b]
DMF	8.1 (0.67)	74 (0.38) 78 (0.40 69 (0.36)	65 (0.40) 63 (0.39) 68 (0.42)	10.1	1.2%
NMP	10.5 (0.87)	74 (0.38) 69 (0.36) 70 (0.36)	58 (0.36) 61 (0.38) 61 (0.38)	10.2	1.0%
NCP	9.7 (0.81)	75 (0.39) 70 (0.36) 74 (0.38)	64 (0.39) 58 (0.36) 58 (0.36)	9.9	1.8%

[a] Functionalised SWNTs recovered after collecting all extracts, evaporation of solvent and drying in vacuo.

[b] Fraction of functionalised SWNTs carbon atoms.

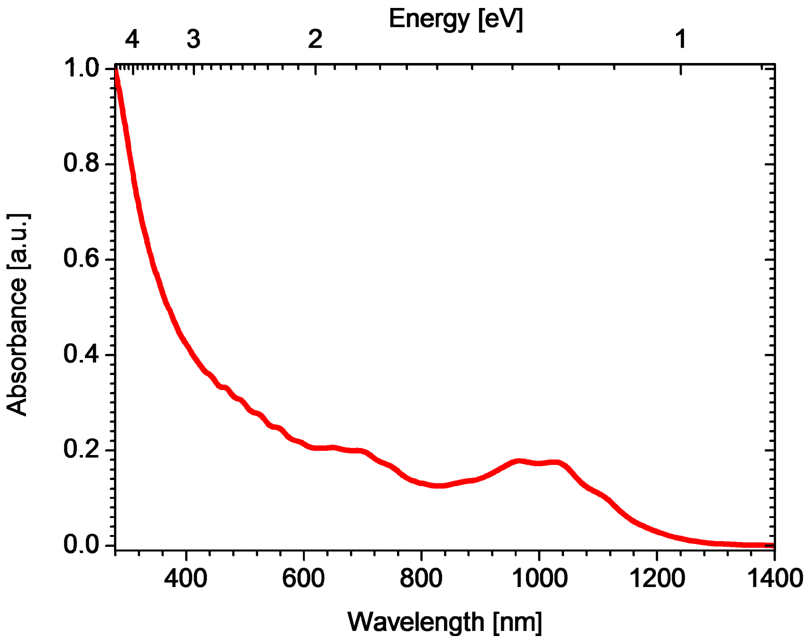
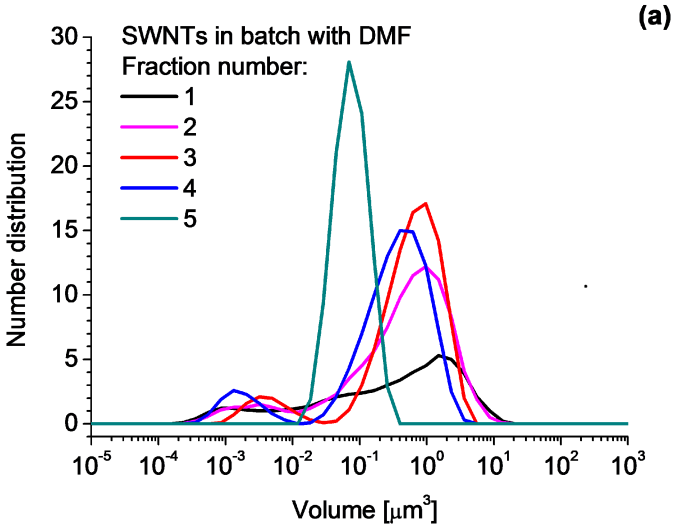
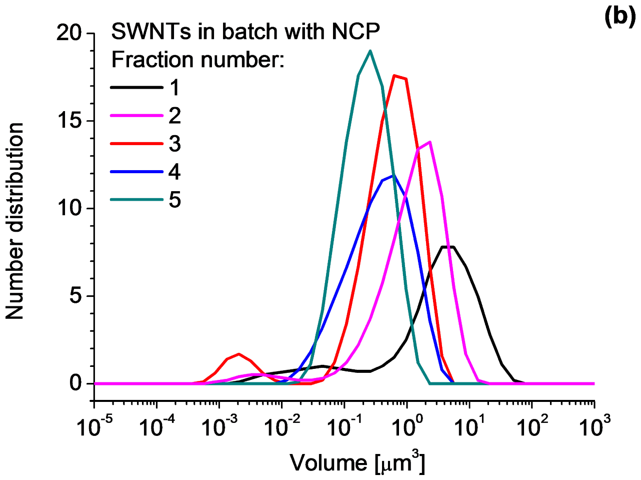
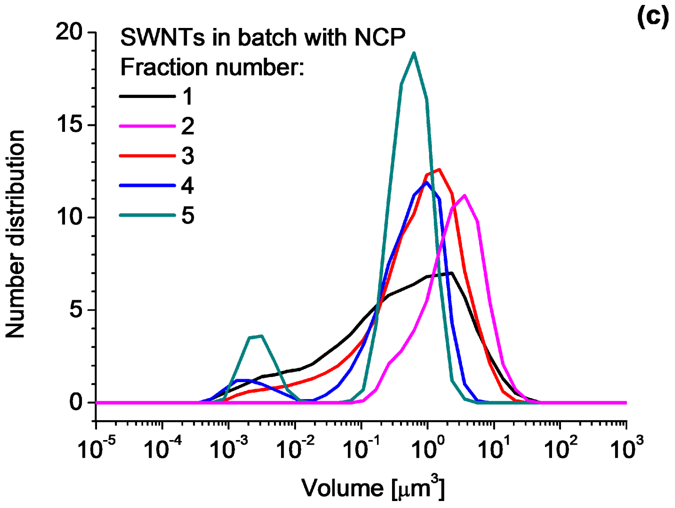


Fig. S2. Representative absorption spectrum of SWNTs in air-equilibrated DMF.

2. Dynamic light scattering (DLS) measurements







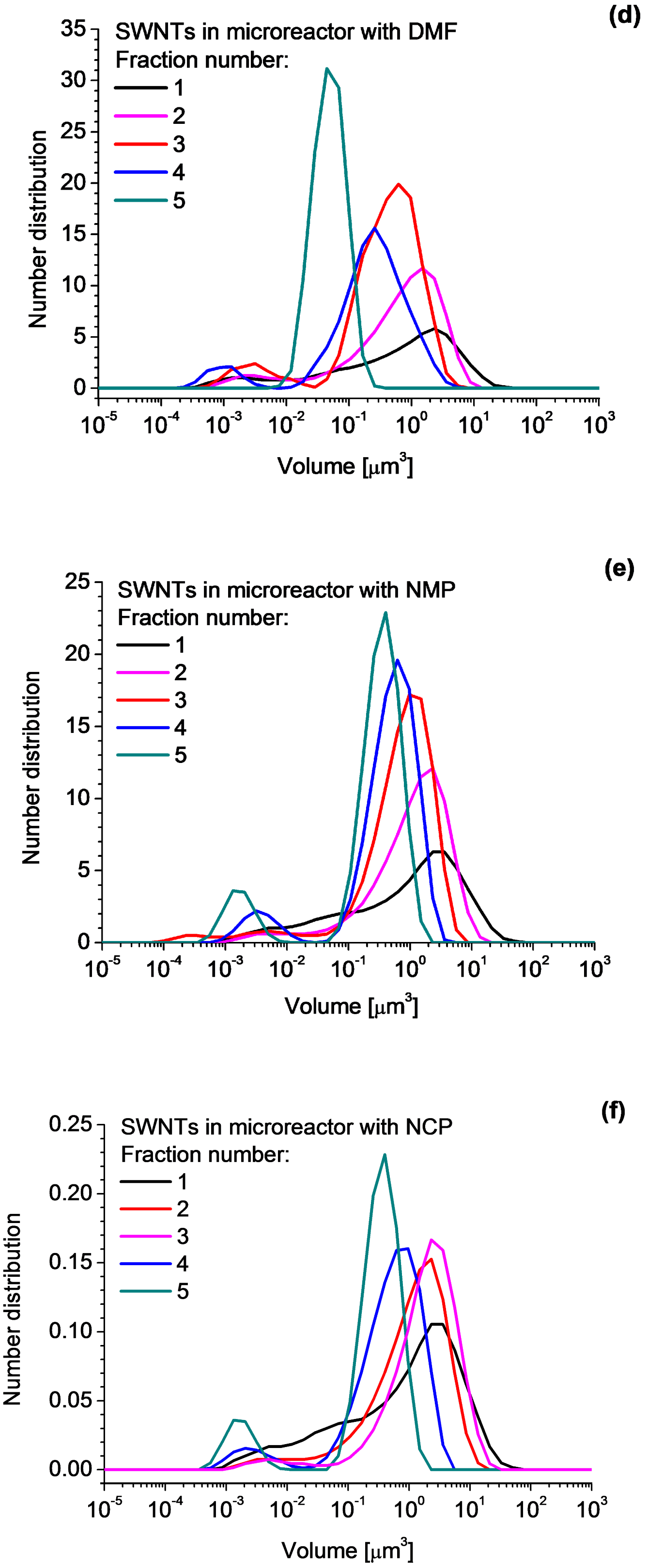
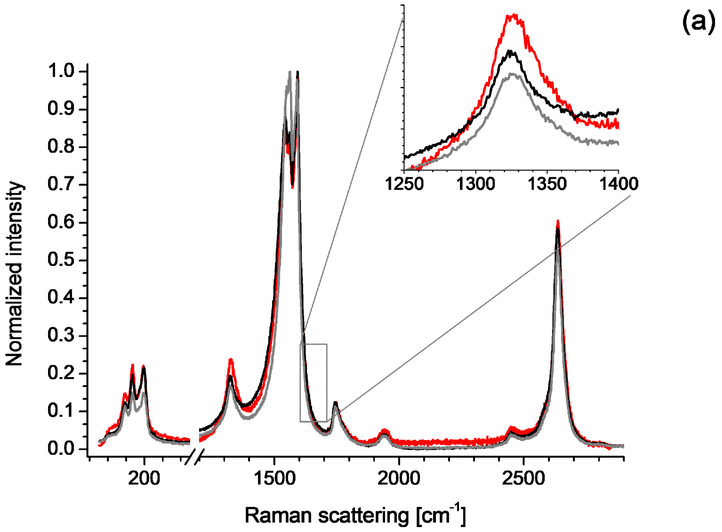
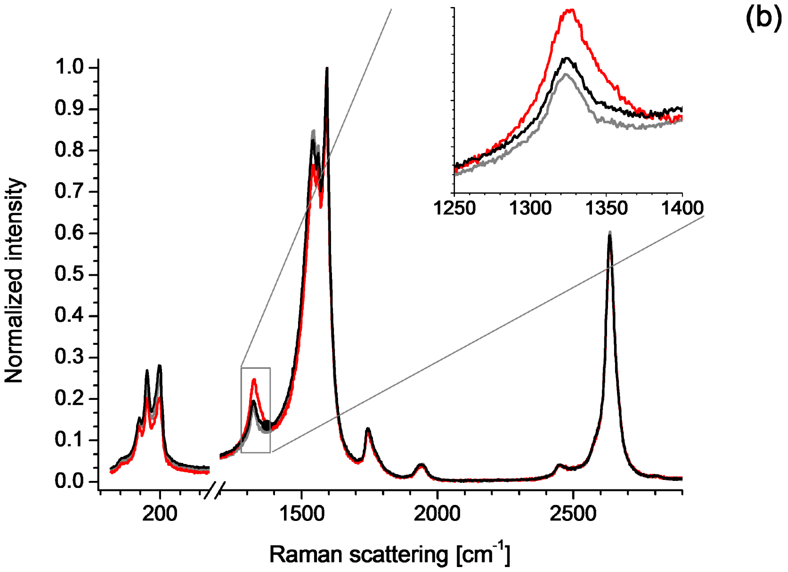
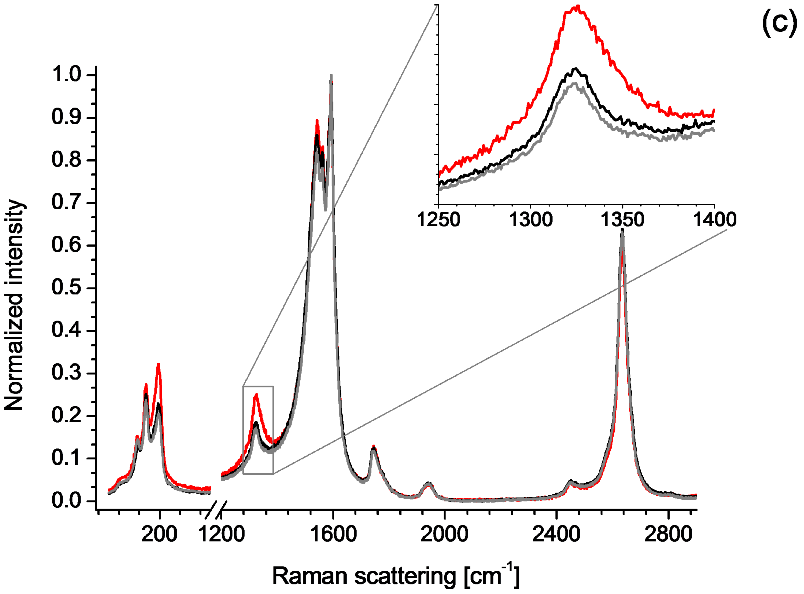


Fig. S3. DLS number distributions for SWNT derivatives present in the NMP extracts (5 x 2 ml) of the first five fractions of experiments run in batch and flow with DMF, NMP and NCP as solvent.

3. Raman spectra of functionalised SWNTs







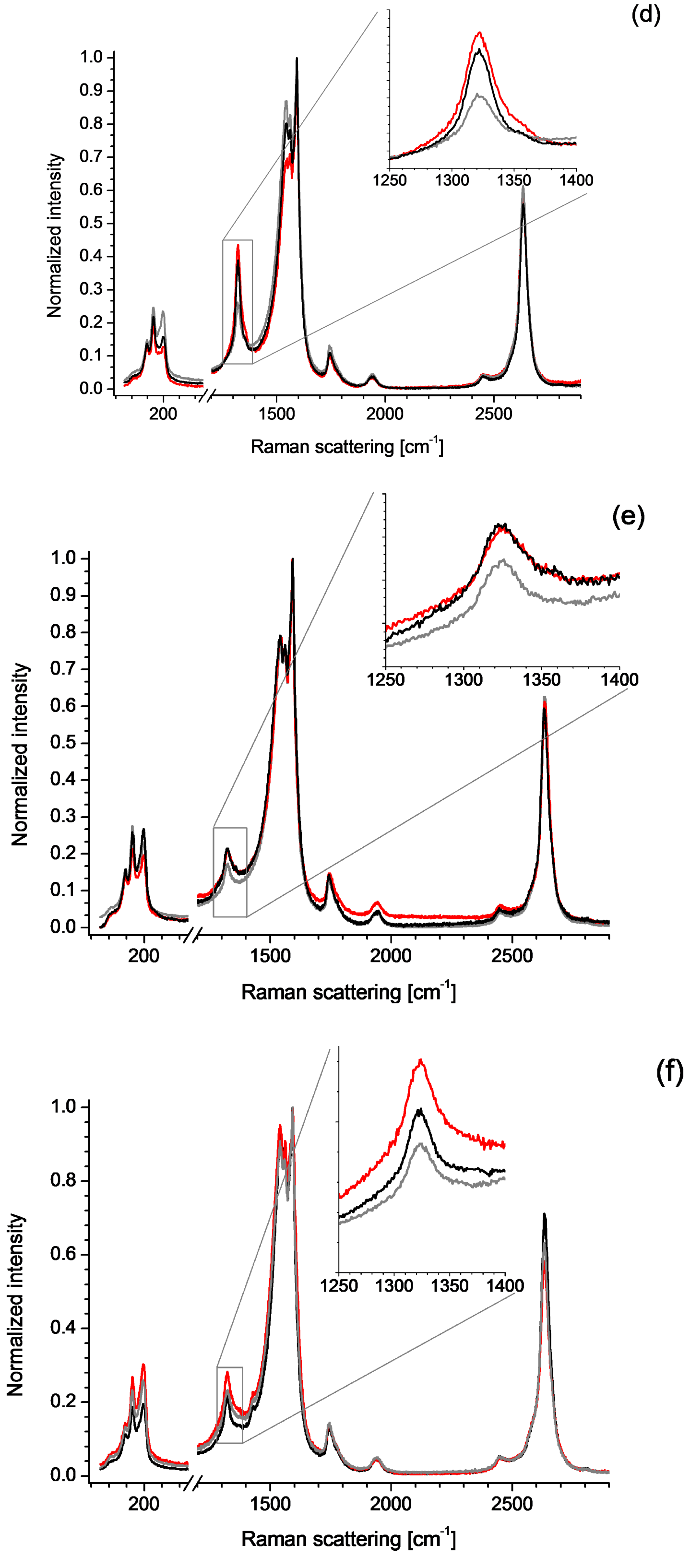


Fig. S4. Raman spectra of pristine (gray) and functionalised SWNTs in the first (red line) and third (black line) NMP extracts from the synthesis carried out in batch using (a) DMF, (b) NMP, and (c) NCP as solvent, and in flow using (d) DMF, (e) NMP, and (f) NCP. The inset highlights the behavior of the D band.

4. Degree of SWNTs functionalisation

In Tables S1-S3 we expressed the degree of SWNTs functionalisation as the fraction of functionalised CNT atoms. We assume that the weight loss (TGA) between 200 °C and 600 °C is entirely due to the thermal decomposition of pyrrolidine moieties ($MW_{FG} = 265.17$). The moles of CNT carbon atoms (mol_C) are:

$$mol_C = P_{SWNT,600} / MW_C$$

where $P_{SWNT,600}$ is the residual weight at 600°C (TGA) and MW_C is molecular weight of C. The moles of functional groups (mol_{FG}) are given by the difference between the residual weight at 200 °C and the residual weight at 600°C divided by the molar weight of the pyrrolidine moiety.

$$mol_{FG} = (P_{SWNT,200} - P_{SWNT,600})/MW_{FG}$$

The degree of functionalisation is calculated by dividing mol_{FG} by the number of available reactive sites (C=C bonds = half the moles of CNT carbon atoms):

$$\% = \frac{mol_{FG}}{mol_C/2}$$

Since TGA was performed on the first extracted fractions for each synthetic procedure (hence the most soluble ones) the reported values correspond to the maximum degree of functionalisation .

References

1. J. Carlise, R. Kriegel, W. Rees Jr, M. Weck, *J. Org. Chem.* **2005,** *70*, 5550-5560.

2. V. Georgakilas, K. Kordatos, M. Prato, D. M. Guldi, M. Holzinger, A. Hirsch, *J. Am. Chem. Soc.* **2002,** *124*, 760-761.