Electronic Supplementary Material (ESI) for Nanoscale.
This journal is © The Royal Society of Chemistry 2016

Supporting Information

The mechanical bond on carbon nanotubes: diameter-selective functionalization and effects on physical properties.

Emiliano Martínez-Periñán, Alberto de Juan, Yann Pouillon, Christoph Schierl, Volker Strauss, Nazario Martín, Ángel Rubio, Dirk M. Guldi, Encarnación Lorenzo, and Emilio M. Pérez

1. Synthesis.

General. All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230-240 mesh, or Scharlau 60, 230-240 mesh). Analytical thin layer chromatographies (TLC) were performed using aluminium-coated Merck Kieselgel 60 F254 plates. NMR spectra were recorded on a Bruker Avance 400 (1 H: 400 MHz; 13C: 100 MHz), spectrometers at 298 K, unless otherwise stated, using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad. Electrospray ionization mass spectrometry (ESI-MS) and Matrix-assisted Laser desorption ionization (coupled to a Time-Of-Flight analyzer) experiments (MALDI-TOF) were recorded on a HP1100MSD spectrometer and a Bruker REFLEX spectrometer, respectively. Thermogravimetric analyses (TGA) were performed using a TA Instruments TGAQ500 with a ramp of 10 °C/min under air from 100 to 1000 °C.

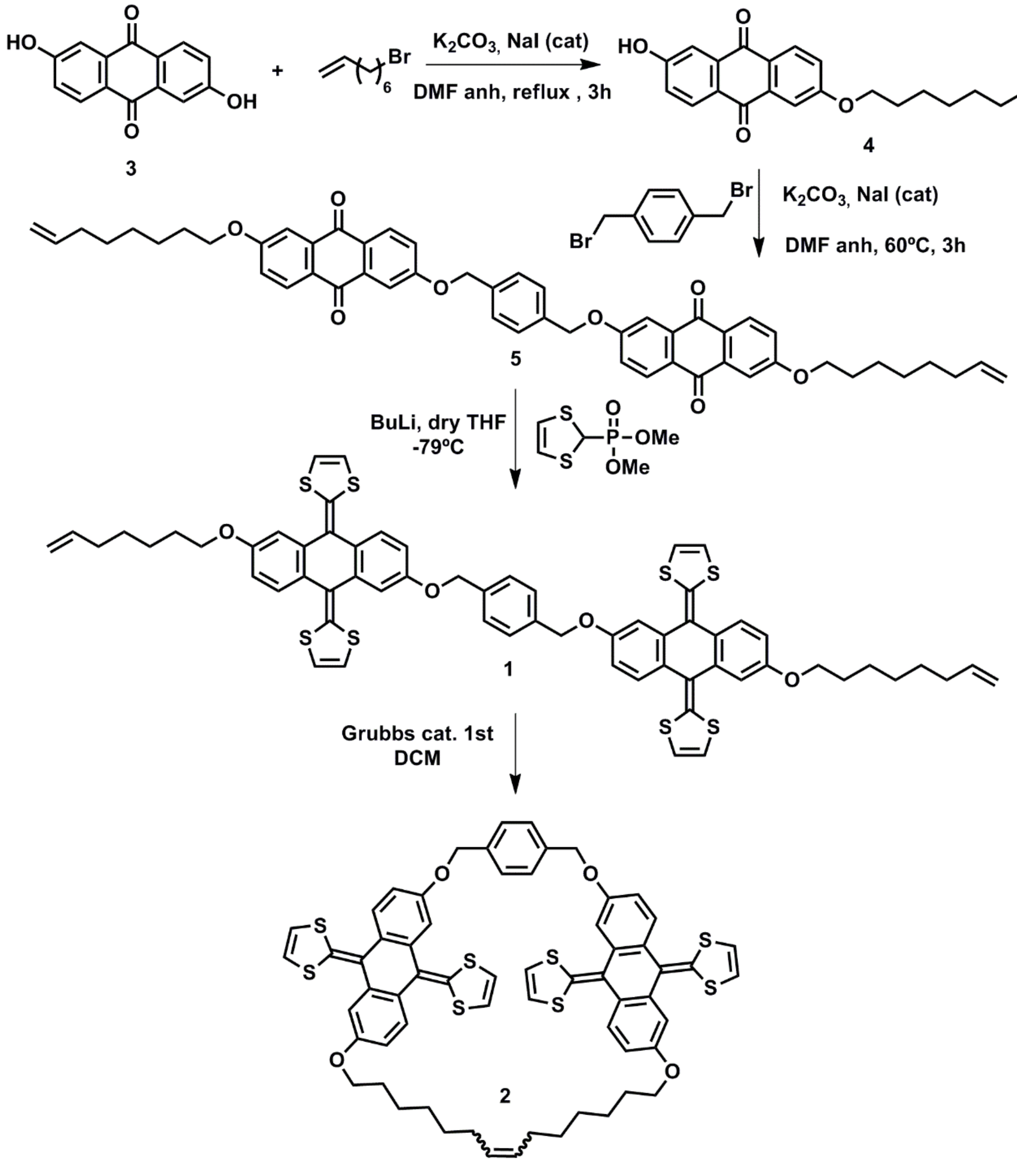

Figure S1. Synthetic scheme towards **1** and **2**.

Compounds **1** and **2** were synthetized following the Figure S1 as described in *J. Am. Chem. Soc*. 2011, **133**, 3184-3190. The spectroscopic properties of the target molecules and intermediates match with the description carried out in that work.

General procedure for SWNTs purification.

50 mg of (6,5)- enriched SWNTs were suspended in 34 mL of 35% HCl, and sonicated for 10 min. The mixture was poured in 100 mL of miliQ water and filtered through a polycarbonate membrane of 0.2 μm pore size. The solid was washed with water until neutral pH, with diethyl-ether to remove water and then dried in an oven at 350^0C for 30 min.

General procedure for MINTs synthesis.

20 mg of purified (6,5)-enriched SWNTs were suspended in 20 mL of tetrachloroethane (TCE) through sonication (10 min.) and mixed with linear precursor **1** (10 mg, 0.0087 mmol, 1 equiv.). The mixture was bubbled with N_2 flow for 30 min and Grubb's 2nd generation catalyst (7.4 mg, 0.0087 mmol, 1 equiv.) was added at room temperature and stirred for 72 hours. After this time, the suspension was filtered through a PTFE membrane of 0.2 μm pore size, and the solid washed profusely with dichloromethane (DCM). The solid was re-suspended in 20 mL of DCM through sonication for 10 min. and filtered through a PTFE membrane of 0.2 μm pore size again. This washing procedure was repeated three times. The degree of functionalization, 32% load in organic material was determined by thermogravimetric analysis (TGA, fig. S2).

General procedure for control experiments.

10 mg of purified (6,5)- enriched SWNTs were suspended in 10 mL of TCE through sonication bath (10 min.) and mixed with compound **1** or **2** (5 mg, 0.0043 mmol) at room temperature for 72 hours. After this time, the suspension was filtered through a PTFE membrane of 0.2 μm pore size, and the solid washed profusely with DCM. The solid was re-suspended in 20 mL of DCM through sonication for 10 min. and filtered through a PTFE membrane of 0.2 μm pore size again. This washing procedure was repeated three times. The figure S3 shows a little bit amount of organic material (around

9% in weight loss) link to the nanotubes. Also, the temperature at organic material burn is different.

Stability tests for MINTs.

4 mg of MINTs were suspended in 10 mL of TCE by sonication for 10 min. and then heated to reflux (bp = 146^{0}C) for 30 min. The suspension was filtered through a PTFE membrane of 0.2 μm pore size, and the solid washed profusely with DCM. No de-threading was observed by TGA (fig S2).

The macrocycles can be removed by heating under air. 2 mg of MINTs were heated at 370ºC for 30 min in an oven. All organic material was removed (fig. S4).

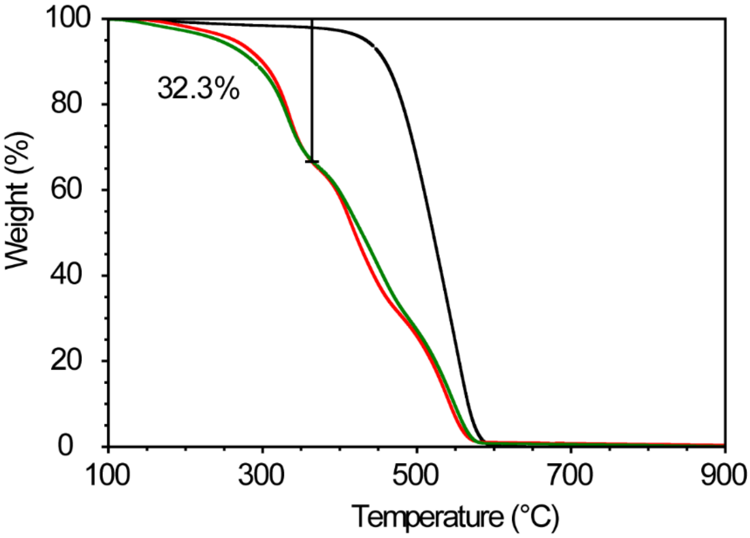

Figure S2. Thermogravimetric analysis in air (10º/min) of (6,5)-enriched SWNTs (black), MINT$_{(6,5)}$-**2** (red). and MINTs after reflux in TCE (green).

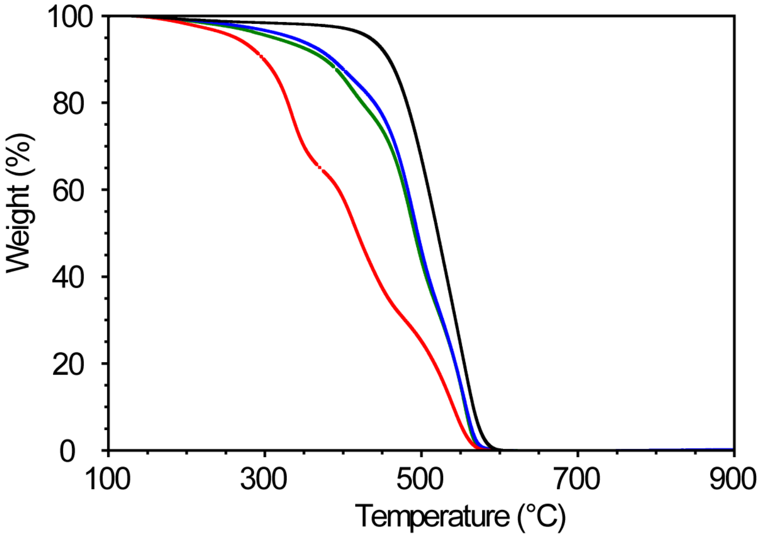

Figure S3. Thermogravimetric analysis in air (10º/min) of (6,5)-enriched SWNTs (black), MINT$_{(6,5)}$-**2** (red), control experiments (6,5)-enriched SWNTs + **1** (green) and (6,5)-enriched SWNTs + **2** (blue).

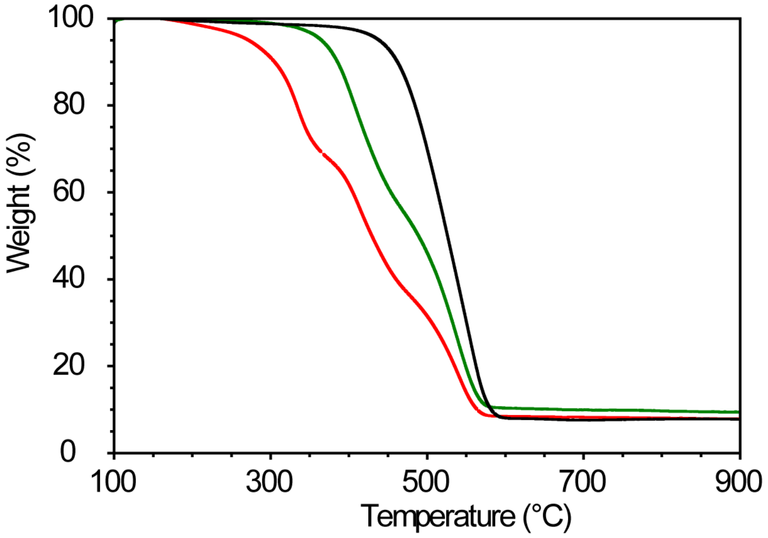

Figure S4. Thermogravimetric analysis in air (10º/min) of (6,5)-enriched SWNTs (black), MINT$_{(6,5)}$-**2** (red). and MINTs after heat at 370ºC for 30 min (green)

2 Microscopic characterization.

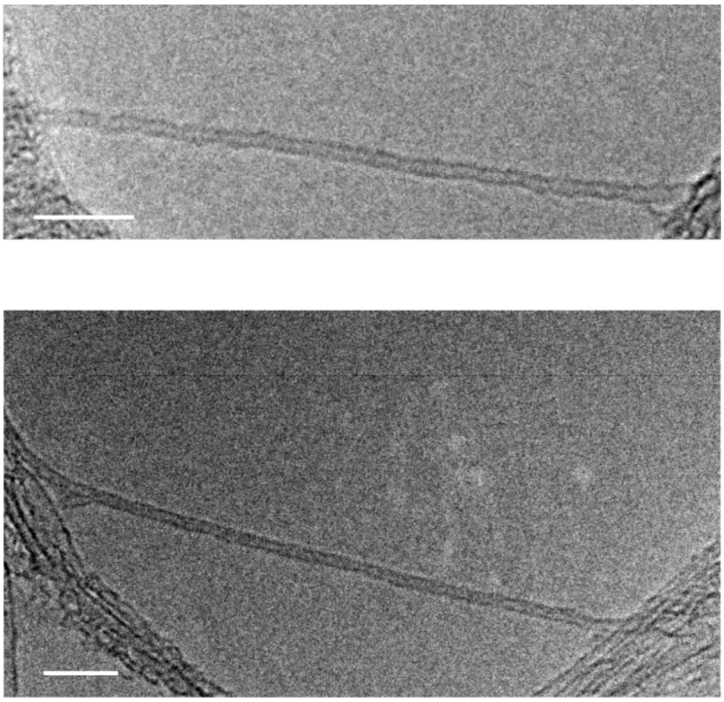

Figure S5. Transmission electron microscopy photograph of pristine (6,5)-enriched SWNTs. Scale bars are 5 nm.

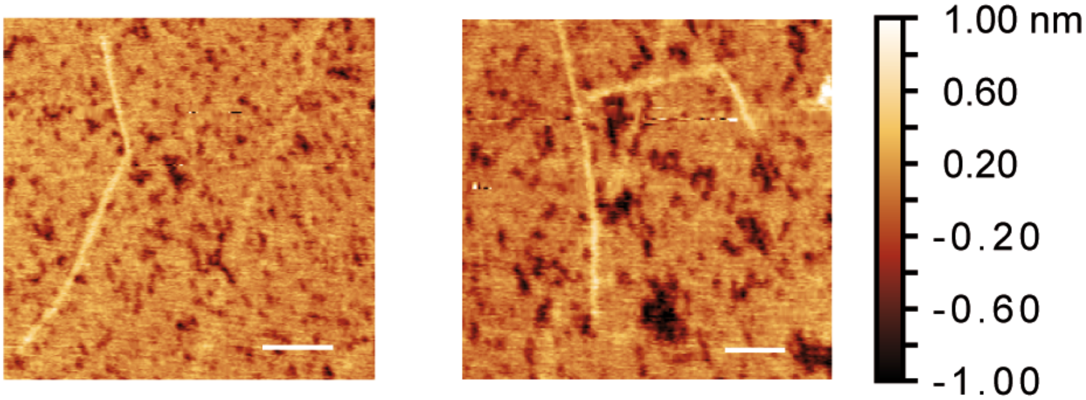

Figure S6. AFM topographic images of pristine (6,5)-enriched SWNTs. Scale bars are 100 nm.

3 Electronic characterization.

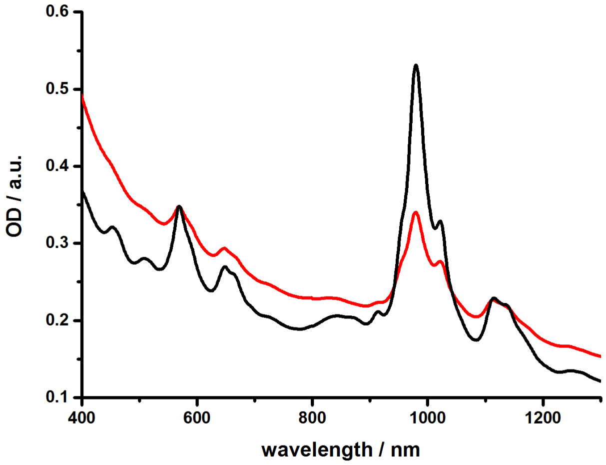

Figure S7. As-obtained absorption spectra of (6,5)-enriched-SWNTs (black) and MINT$_{(6,5)}$-**2** (red) in D_2O/SDBS (1 wt%) at room temperature.

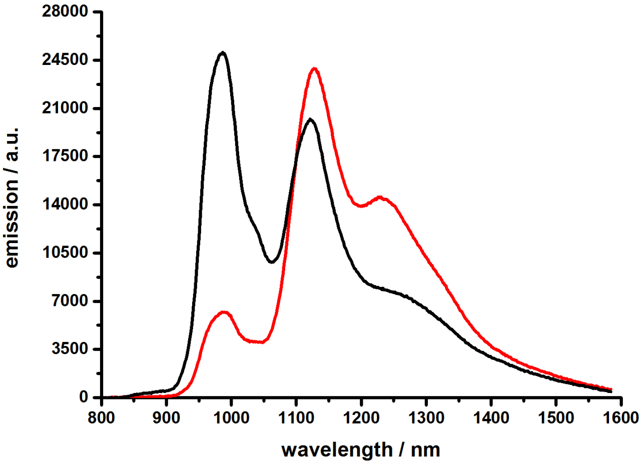

Figure S8. Fluorescence spectra of (6,5)-enriched – SWNTs (black) and MINT$_{(6,5)}$-**2** (red) in D_2O/SDBS (1wt%) at excitation wavelengths of 570 nm.

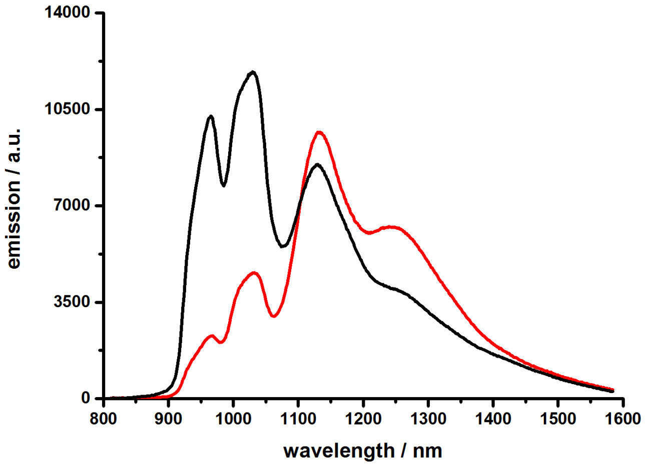

Figure S9. Fluorescence spectra of (6,5)-enriched – SWNTs (black) and MINT$_{(6,5)}$-**2** (red) in D_2O/SDBS (1wt%) at excitation wavelengths of 650 nm.

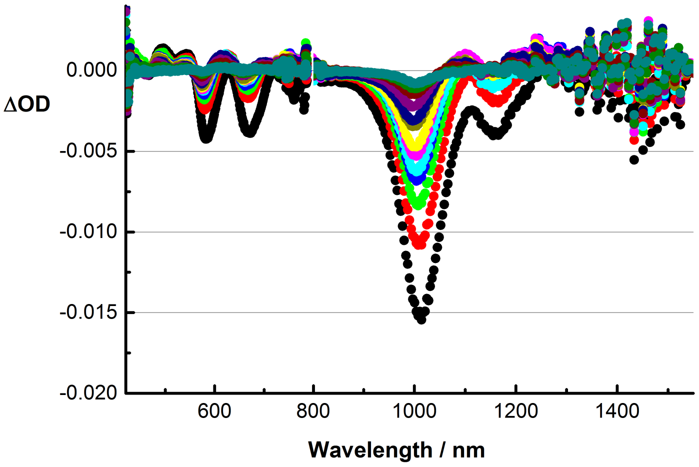

Figure S10. Differential absorption spectra obtained upon femtosecond pump probe experiments (λ_{ex} = 387 nm) of (6,5) SWNTs in SDS/D_2O (1wt%) with several time delays between 0.5 and 500 ps at room temperature.

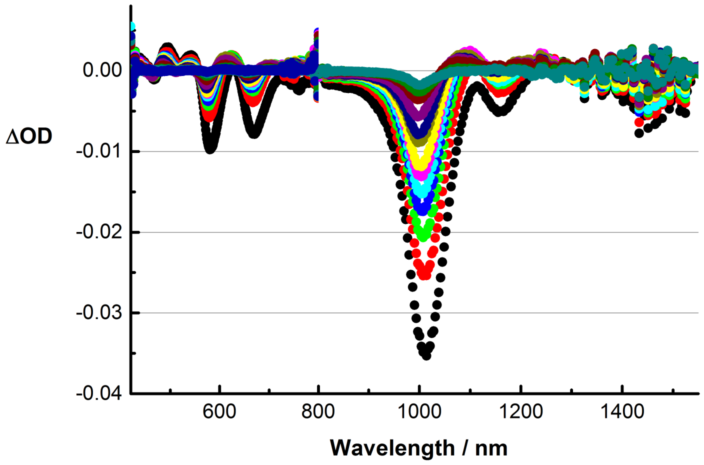

Figure S11. Differential absorption spectra obtained upon femtosecond pump probe experiments (λ_{ex} = 387 nm) of MINT$_{(6,5)}$-**2** in SDS/D_2O (1wt%) with several time delays between 0.5 and 500 ps at room temperature.

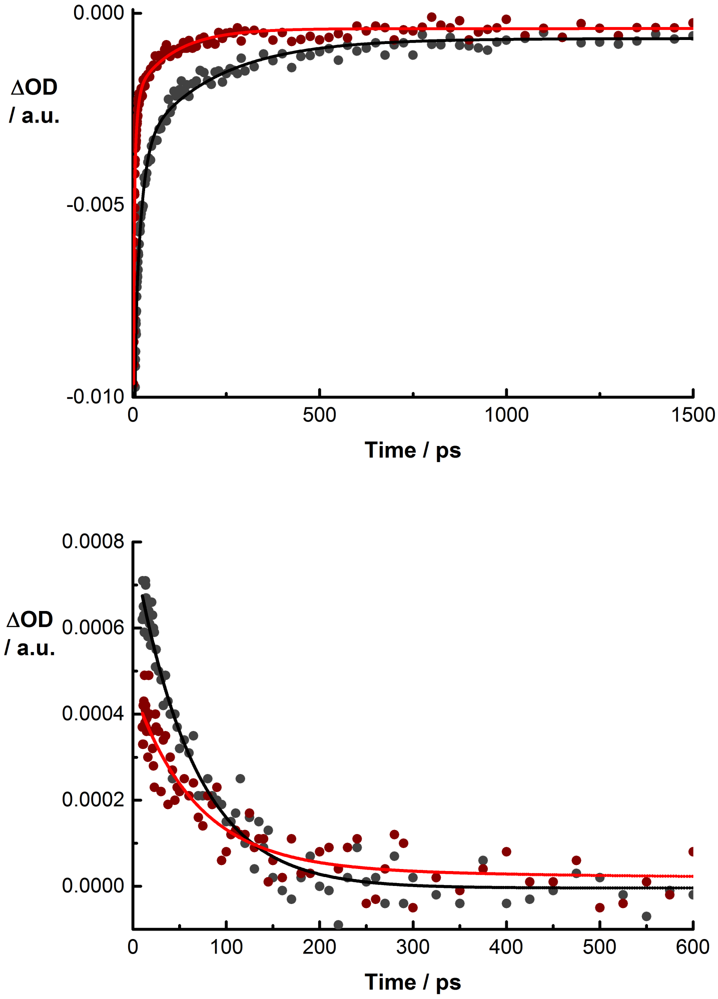

Figure S12. Upper part – Time absorption profiles of SWNTs (black) and MINT$_{(6,5)}$-**2** (red) SDS/D_2O (1wt%) at 1000 nm monitoring the excited state decay. Lower part – Time absorption profiles of SWNTs (black) and MINT$_{(6,5)}$-**2** (red) at 700 nm monitoring the excited state decay.

4 Electrochemical characterization.

Materials. N,N- Dimethylformamide (99.8%) (DMF), Tetrabutylammonium perchlorate (TBAP) specific for electrochemical measures were purchase from Sigma-Aldrich.

Electrochemical studies were carried out with a potentiostat Autolab PGSTAT128N (EcoChemie, NL) using the software package GPES 4.9 (General Purpose Elec. Experiments). All measurements were performed in a homemade single compartment three electrodes electrochemical cell. Glassy Carbon (GC) electrodes (0.07 cm^2 Ø with an electrochemical area of 0.1 cm^2) from CH Instruments were used as working electrodes and Pt wire as counter electrode. Specific calomel electrode, 1M LiCl for organic media from Radiometer Analytical was used as reference electrode.

Rotating disk-ring electrode (RRDE) measurements were carried out using a bipotentiostat CHI900B (CH Instruments) and a Glassy Carbon disk/platinum ring RRDE electrode from PINE. A modulated speed rotator from PINE Instruments was used and measures were carried out in a commercial electrochemical cell adapted to rotating disc electrodes.

Preparation of samples for measurements.

For solution electrochemical experiments and coefficient diffusion measures 0.34 mg/ml of MINTs were suspended in 0.1M TBAP/DMF. At purified (6,5)- enriched-SWNTs + compound **1** or **2** measurements 0.34 mg/ml of non-modified SWCNT were suspended at 0.16 mg compound **1** or **2**/ml 0.1M TBAP/DMF solution. At compound **1** or **2** measurements 0.16 mg/ml were dissolve in 0.1M TBAP/DMF. For solution electrochemical experiments we use 5 ml of these suspensions for carried the measures. In the case of coefficient diffusion measures we use 15 ml of each suspensions.

For drop casting deposition experiments we prepared the same solution proportions and the same solvent DMF but without using TBAP. 5 μL of these suspensions were deposited onto Glassy Carbon disc electrode and dried at ambient conditions. We measures the different electrodes immersed in 5 ml 0.1M TBAP/DMF.

Cyclic Voltammetry (CV) measures: In the CV electrochemical measures we have scan the potential between -0.2 to 0.6 V at different scan rates.

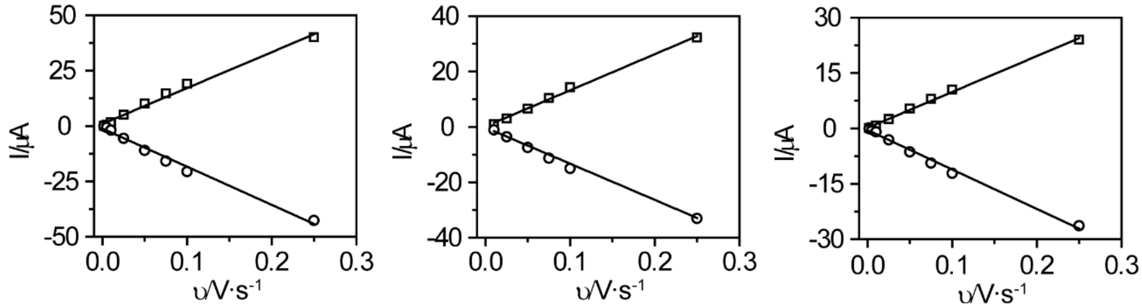

Figure S13. Oxidation (○) and reduction (□) peak current intensity *vs.* potential scan rate of (6,5)-enriched-SWNTs + **1**, (6,5)-enriched-SWNTs + **2**, and MINT$_{(6,5)}$-**2**; on GC electrodes from left to right.

In the case of drop casting electrodes, we have carried out an intensive scan rate study in order to obtain the necessary data to performed a Laviron's plot (peak potential (E_p) vs. log scan rate (ν)), from the linear region we can determine the heterogeneous electron transfer rate constant K_{ET}, which is a kinetic constant of the electrochemical process, and the transfer coefficient α, which is a measure of the symmetry of the energy barrier of the redox reaction. Ideally, α = 0.5 for all overpotentials, however in many cases α deviates from 0.5. Therefore, determination of α is crucial to finding k_{ET}.

Laviron's equation:

$$E_p = E^0 + \frac{RT}{\alpha nF} - \frac{RT}{\alpha nF}\ln \nu$$

Where α is the cathodic electron transfer coefficient, n is the number of electrons, T is the temperature (293 K here), R the gas constant (8.314 $JK^{-1}mol^{-1}$) and F the Faraday constant (96,485 C mol^{-1}).

Diffusion coefficient determination

The diffusion coefficient (D) was determined by the method reported by Chatenet et al. basic on the transit-time technique on platinum-glassy carbon rotating ring-disk electrodes (RRDEs). A potential step of +0.4 V was first applied to the ring from the open-circuit potential to a potential at which the electroactive species is consumed at the ring–solution interface. After the ring current had reached its steady-state value (which was attained within a few seconds), the same potential step is applied to the disk for 2 seconds. The induced lack of electroactive species created at the disk reaches the ring after a so-called transit time, t_s [s], related to the electrode rotational speed, ω [rpm], the diffusion coefficient of the electroactive species, D [cm^2/s], K [s/rpm] constant, and the solution kinematic viscosity, ν [cm^2/s], according to the equation:

$$t_s = [K\,(\nu/D)^{1/3}]/\omega$$

K only depends on the electrode dimensions, and for an ideal RRDE, with an absolutely concentric ring and disk electrodes and a perfectly smooth surface, K [s/rpm] is given by the equation:

$$K = 43.1\times[\log(r_{\text{inner ring}}/\ r_{\text{outer disk}})]^{2/3}$$

From this equation a value of 4.428 for the RRDE used ($r_{\text{outer disk}}$ = 4.6 mm, $r_{\text{inner ring}}$ = 5.0 mm) was calculated. Since the experiments were carried out in DMF, the value of kinematic viscosity was 0.00912 (cm^2/s).

5 Calculations.

Chirality	Diameter (nm)	SWNT (kJ/mol)	**2** (kJ/mol)	SWNT+**2** (kJ/mol)	Eb (kJ/mol)	Eb (kcal/mol)	atoms	SWNT units	Experiment
(06,05)	0.747	22187.8	1257.98	23278.9	-166.88	-39.88	492	1	1
(07,05)	0.818	25371.9	1393.75	26650.2	-115.45	-27.59	564	1	1
(07,06)	0.882	28621.9	1623.22	30201.7	-43.42	-10.38	636	1	1
(07,07)	0.949	17715.3	2004.53	19773.6	53.77	12.85	408	10	0
(08,03)	0.771	23386.1	2385.71	25608.4	-163.41	-39.05	516	1	1
(08,04)	0.829	25732.5	1431.74	27063.2	-101.04	-24.14	576	4	1
(08,05)	0.889	20375.7	1680.19	22026.3	-29.59	-7.07	472	2	0
(08,06)	0.953	18072.3	2274.04	20394.5	48.16	11.51	424	1	0
(08,07)	1.018	35958.6	2536.91	38655.1	159.59	38.13	804	1	0
(09,04)	0.903	29614.1	1721.28	31319.3	-16.08	-3.84	660	1	0
(09,05)	0.962	32656.3	2077.26	34811.8	78.24	18.7	732	1	1
(09,06)	1.024	25378.9	2581.46	28131.4	171.04	40.87	584	2	0
(10,03)	0.923	30784.5	1829.08	32629.1	15.52	3.71	684	1	0
(10,04)	0.978	18374.7	2215.21	20690	100.09	23.92	440	3	0
(11,01)	0.903	29928.6	1721.48	31640.6	-9.48	-2.27	660	1	0
(11,02)	0.949	22214.1	2005.85	24275.3	55.35	13.23	520	2	0
(11,03)	1	34933.4	2352.45	37423.8	137.95	32.96	780	1	0
(12,00)	0.94	19663.2	1982.17	21682.4	37.03	8.85	512	8	0
(12,01)	0.981	34022.4	2186.92	36310.5	101.18	24.18	756	1	0
(12,02)	1.027	19477.1	2569.93	22225.4	178.37	42.62	472	1	0
(13,00)	1.018	15686	2513.31	18364.6	165.29	39.5	440	6	0
(14,00)	1.096	13878.5	3297.63	17458.2	282.07	67.4	408	5	0
(15,00)	1.175	14586.9	4287.28	19286.5	412.32	98.52	428	5	0
(16,00)	1.253	15310.6	5444.58	21307.1	551.92	131.88	448	5	0
(17,00)	1.331	16046.9	6804.44	23566.6	715.26	170.91	468	5	0

(18,00)	1.409	13984.1	8361.71	23245.3	899.49	214.93	488	5	0
(19,00)	1.488	13712.9	13383.7	37602.5	10505.9	2510.37	508	5	0
(20,00)	1.566	14435.3	Breaks	Breaks	N/D	N/D	528	5	0

Table S1. Interaction energies of a series of SWNTs with macrocycle **2**.