Supporting Information

Reinforcement of polyimine covalent adaptable networks with mechanically interlocked derivatives of SWNTs.

*Ion Isasti, Silvia Miranda, David M. Jiménez, Sylwya Parzyszek, Natalia Martín Sabanés, Henrik Pedersen and Emilio M. Pérez**

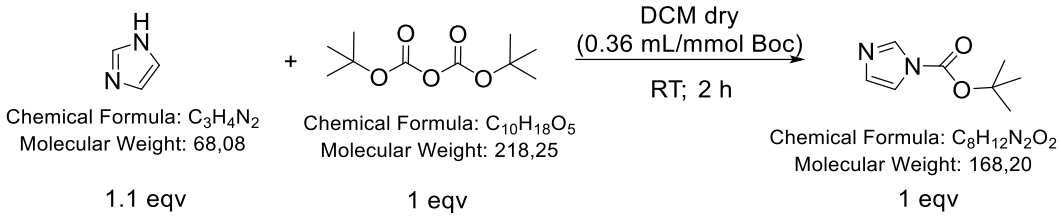
General synthetic procedures

All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under inert atmosphere. Analytical thin layer chromatography (TLC) was performed on precoated silica gel on aluminum cards (0.25 mm thick, with fluorescent indicator 254 nm) and observed under UV light. NMR spectra were recorded on a BrukerAvance 400 (^{1}H: 400 MHz; ^{13}C: 101 MHz) spectrometer at 298 K using partially deuterated solvents as internal standards, unless otherwise stated. Spectra of the synthesized compounds were assigned with the aid of both DEPT and 2D NMR experiments (COSY, HMQC or HMBC). Coupling constants (*J*) are expressed in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet; br = broad; d = doublet; t = triplet; m = multiplet. High-Resolution Mass Spectroscopy (HRMS) was obtained using both Atmospheric-Pressure Chemical Ionization (APCI) and Electrospray Ionization (ESI) on a MAXIS II (Bruker) spectrometer, Matrix-Assisted Laser Desorption Ionization (MALDI-TOF) on a VS AutoSpec spectrometer, both coupled to a time-of-flight (TOF) instrument and time-of-flight mass spectrometry coupled to a Gas Chromatograph with Electron Ionization (GCEI) on a GCT Agilent Technologies 6890N. UV-Vis spectroscopy was performed on a Cary 50 UV-Visible spectrophotometer. Fourier-transform infrared spectroscopy with attenuated total reflection (FT-ATR-IR) was performed on a Bruker ALPHA FTIR spectrometer. Thermogravimetric analyses (TGA) were performed using a TA Instruments TGAQ500. The TGA method was set to perform a first equilibration at 50 °C during 15 min followed by a ramp of 10 °C/min under air or N_2 from 100 to 1000 °C. Raman measurements and optical images were performed using a commercial confocal

Raman microscope (Senterra II, Bruker). A NTEGRA ACADEMIA instrument was used to obtain images of the MINTs. For image processing and measuring the heights of the SWNTs, the Gwyddion software was used.

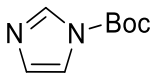
Synthesis of diamino U-shaped molecule

*** STEP 1:**



$(Boc)_2O$ was added over the imidazole solution in dry DCM. The reaction mixture was stirred at room temperature for 2 hours. Then, the crude was washed with water, the organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo to obtain imidazole-Boc, white solid, with 99 % yield.[1]

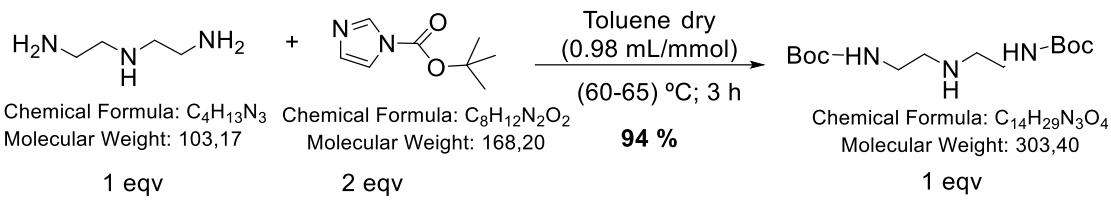
N-Boc Imidazole:



^1H MMR (300MHz, ***CDCl₃***) δ (ppm): 7.97(s, 1H, H_{Ar}), 7.27 (s, 1H, H_{Ar}), 6.31 (s, 1H, H_{Ar}), 1.51 (s, 9H, 3x-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 147.1 (C=O), 137.0 (C_{Ar}), 130.2 (C_{Ar}), 117.1 (C_{Ar}), 85.5 ($C_{q\text{-}Boc}$), 27.8 (3x-CH_3).

*** STEP 2:**

SMA_SP2

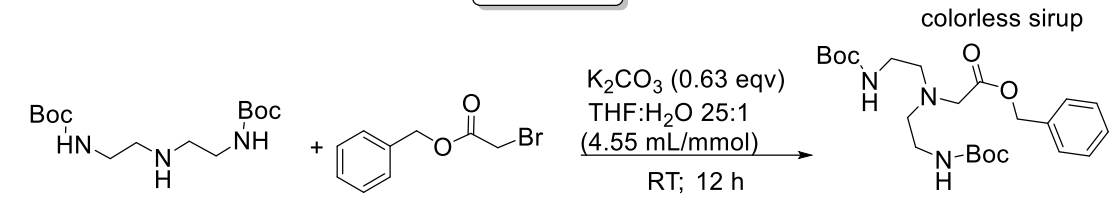


Diethylenetriamine was added over the imidazole-Boc solution in dry toluene. The crude was stirred at (60-65) °C for 3 hours. Then, the solvent was removed in vacuo, and

the crude was extracted with DCM (3x) and washed with water. The organic phase was dried over anhydrous Na_2SO_4 and filtrated; DCM was removed in vacuo to give the desired product. Yield: **94** %.

*** STEP 3:**

SMA_SP3



Chemical Formula: $C_{14}H_{29}N_3O_4$
Molecular Weight: 303,40
1 eqv

Chemical Formula: $C_9H_9BrO_2$
Molecular Weight: 229,07
1.5 equv

Chemical Formula: $C_{23}H_{37}N_3O_6$
Molecular Weight: 451,56
1 eqv

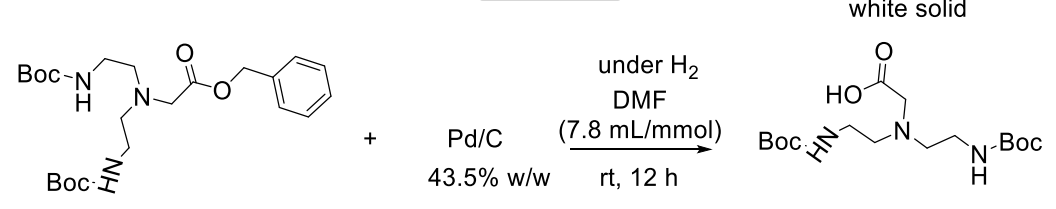
A solution of SMA_SP2 (1 equiv) in 3 ml/mmol of THF-H_2O (25:1) was treated with a solution of Benzyl bromoacetate (1.45 equiv) and K_2CO_3 (0.63 equiv) in 1.5 ml/mmol of THF-H_2O (25: 1) and stirred at rt for 12 h. The solution was concentrated to 5 ml by rotary evaporation, loaded on a silica gel column and eluted with ethyl acetate-hexane (2:98) until all Benzyl bromoacetate was removed. The product was then eluted with 100% ethyl acetate. Removal of all solvent by rotary evaporation left the desired product. Yield **(86%).**[2]

^{1}H NMR (400 MHz, D_2O) δ (ppm): 7.36 (m, 5H), 5.15 (s, 2H), 3.43 (s, 2H), 3.15 (t, 4H), 2.74 (t, 4H), 1.45 (s, 18H).

^{1}H NMR (400 MHz, ***$(CD_3)_2CO$***) δ (ppm): 7.46 – 7.28 (m, 5H, H_{Ar}), 5.89 (s, 2H, 2x-NH), 5.16 (s, 2H, -OCH_2-), 3.53 (s, 2H, -NCH_2-C=O), 3.12 (q, J = 6.1 Hz, 4H, 2x-NCH_2-), 2.76 (t, J = 6.1 Hz, 4H, 2x-NCH_2-), 1.41 (s, 18H, 6x-CH_3).

*** STEP 4:**

SMA_SP4



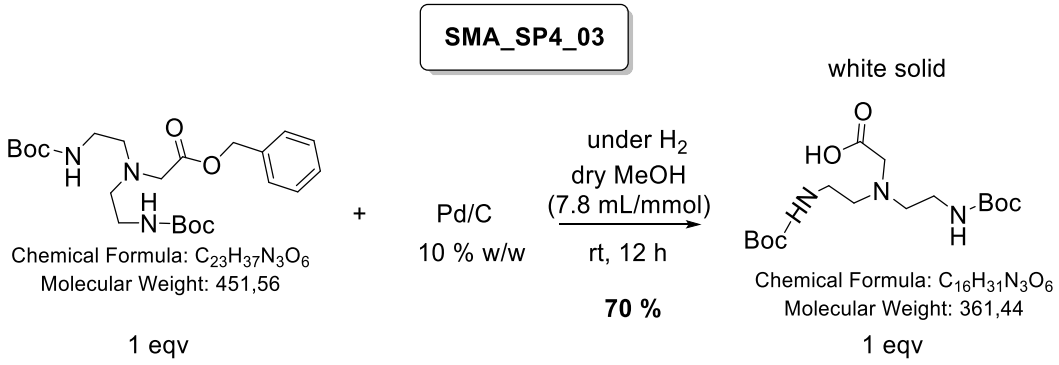
Chemical Formula: $C_{23}H_{37}N_3O_6$
Molecular Weight: 451,56
1 eqv

Chemical Formula: $C_{16}H_{31}N_3O_6$
Molecular Weight: 361,44
1 eqv

SMA_SP3 (**1 equiv**) was dissolved in of DMF (6.5 mL/mmol). Pd/C (43.5% w/w) was added in an additional of DMF (1.3 mL/mmol). The mixture was stirred for 12 h under H_2 and then filtered through Celite, which was washed with methanol. The solvent was removed by rotary evaporation to yield an off-white solid. The solid was dissolved in a small volume of methanol and was crystallized by addition of diethyl ether. The solid obtained was washed with diethyl ether and air dried to give aminoacid with **30% yield**. (To me: 30 %)[2]

^{1}H NMR (400 MHz, ***CDCl$_3$***) δ (ppm): 3.80 (s, 2H), 3.51 (t, 4H), 3.41 (t, 4H), 1.47 (s, 18H).

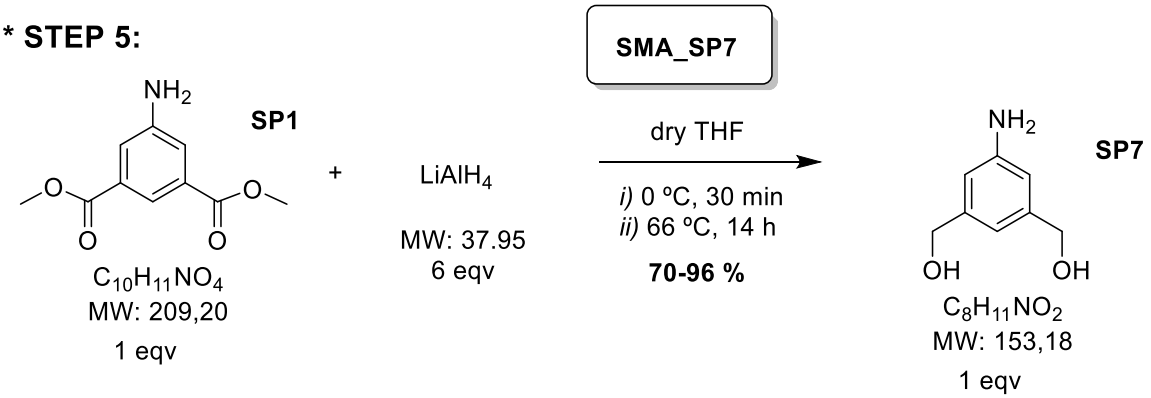
When the reaction is carried out on a large scale, DMF is very difficult to completely eliminate. Therefore DMF was changed to MeOH, as described in the following reaction.



SMA_SP3 (1 equiv) was dissolved in dry MeOH (7.8 mL/mmol). Pd/C (10 % w/w) was added. The mixture was stirred for 12 h under H_2 and then filtered through silica gel, which was washed with methanol/$CHCl_3$. The solvent was removed by rotary evaporation to yield an off-white solid. The solid was dissolved in a small volume of methanol and was crystallized by addition of diethyl ether. The solid obtained was washed with diethyl ether and air dried to give aminoacid with **70-89 %** yield.

^{1}H NMR (400 MHz, ***CDCl$_3$***) δ (ppm): 5.29 (s, 2H, 2x-NH), 3.37 (s, 2H, -NCH_2-C=O), 3.27 (br q, J = 6.0 Hz, 4H, 2x-NCH_2-), 2.80 (br t, J = 6.0 Hz, 4H, 2x-NCH_2-), 1.45 (s, 18H, 6x-CH_3).

*** STEP 5:**

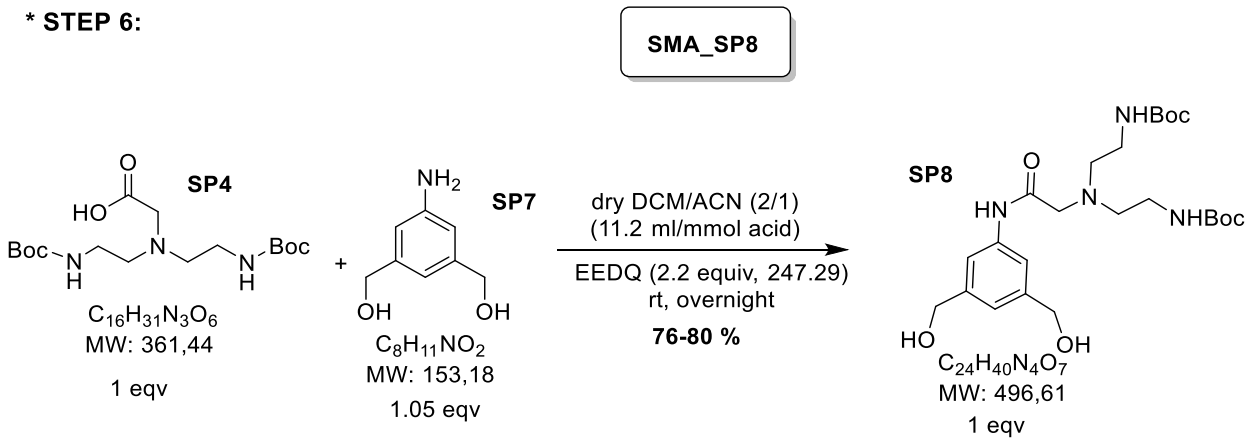


5-aminoisophathalic acid dimethyl ester (**SP1**) (2 g, 9.56 mmol) in dry THF (20 mL, 2.09 mL/mmol) was slowly added into a THF (100 mL, 10.5 mL/mmol) slurry of $LiAlH_4$ (2.17 g, 57.36 mmol) at 0 °C with vigorous stirring. After stirring at 0 °C for 30 minutes, the mixture was allowed to reflux for 14 hours.[3]

At which point it was cooled at 0 °C, ethyl acetate (20 mL, 2.09 mL/mmol) was then added into the grayist mixture under vigorous stirring to quench excess $LiAlH_4$ and ca. H_2O (15 mL, 1.6 mL/mmol) was then added to hydrolyze the alumina salt. A color change from grayist to green and then yellowish were observed. After stirring for another 1 hour, the resulting slurry was filtered through a pad of silica gel using a coarse frit and washed with several portions of THF (3 x 100 mL, 10.5 mL/mmol). Solvent removal of the combined filtrate and washing afforded a yellow-brownish crude compound **SP7**. Further purification was achieved by recrystallization from THF/Hex; 1.4 g, 96 % Yield

^{1}H NMR (**THF-d$_8$**): δ = 6.58 (1H, s, H_{Ar}), 6.53 (2H, s, H_{Ar}), 4.47 (4H, d, *J* = 5.7 Hz, OCH2), 4.40 (2H, br, OH), 3.93 (2H, t, *J* = 5.85 Hz, NH_2).

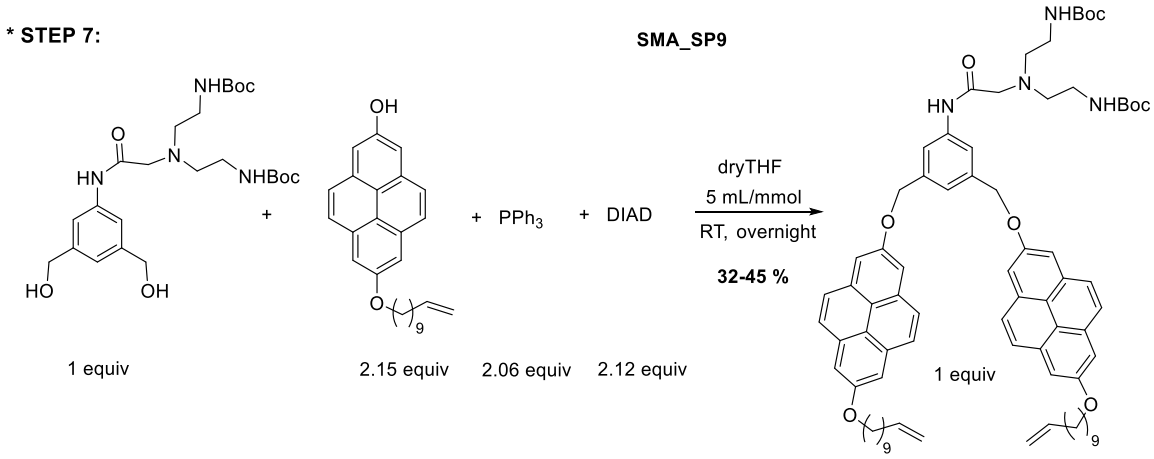
*** STEP 6:**



Carboxylic acid **SP4** (209 mg, 0.578 mmol) and Amine **SP7** (93 mg, 0.607 mmol) were suspended in anhydrous DCM/CH_3CN (2:1) (11.2 ml/mmol acid) at room temperature under Ar atmosphere. EEDQ (143 mg, 0.578 mmol) was added into the mixture and the reaction was stirred at room temperature overnight. After, the solvent was removal in vacuo. NH_4Cl saturated solution was added and the crude was extracted with 3x DCM. The organic layer was washed with brine. Lastly, the organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated. The crude product was purification by column chromatography (DCM/MeOH as eluyent, from 98/2 to 96/4). The desired product was obtained with **76 % yield** (220 mg).

^{1}H NMR (400 MHz, **$CDCl_3$**) δ = 9.36 (s, 1H, HN_{amide}), 7.42 (s, 2H, H_{Ar}), 7.04 (s, 1H, H_{Ar}), 5.50 (s, 2H, , HN_{amine}), 4.53 (s, 4H, OCH_2), 3.36 – 3.03 (m, 6H, OC-CH_2-N, 2xNCH_2), 2.63 (s, 4H, NCH_2), 1.36 (s, 18H, $CH_{3,Boc}$).

^{1}H NMR (400 MHz, **Acetone**) δ = 9.43 (s, 1H, HN_{amide}), 7.61 (s, 2H, H_{Ar}), 7.10 (s, 1H, H_{Ar}), 6.16 (s, 2H, HN_{amine}), 4.59 (t, J = 6.0 Hz, 4H, OCH_2), 4.13 (br-q, J = 5.0 Hz, 2H, O=C-CH_2-N), 3.24 (dd, J = 12.0, 6.0 Hz, 4H, NCH_2), 2.70 (t, J = 5.8 Hz,4H, NCH_2), 1.38 (s, 18H, $CH_{3,Boc}$).



DIAD (1.02 g, 5.04 mmol, 2.12 equiv) was slowly added to a stirred solution of Compound **SMA_SP8** (1.17 g, 2.35 mmol, 1 equiv), monoalkylated pyrene (1.96 g, 5.04 mmol, 2.15 equiv) and Ph_3P (1.27 g, 4.84 mmol, 2.06 equiv) in dry THF (12 mL, 5 mL/mmol) at 0ºC. The mixture was left stirring at 0 ºC for 30 min. Then, the reaction was warmed at room temperature and left stirring overnight. THF was removed under reduced pressure. Et_2O (25 mL/mmol) and NaOH 10 % (50 mL/mmol) were added. The mixture was stirred at room temperature for 1 hr. The aqueous phase was extracted three times

with Et_2O (25 mL/mmol). The organic phase was washed with water and then with brine. The organic phase was dried with Na_2SO_4 anh. The solvent was evaporated in vacuum. The brown crude was recrystallized with diethyl ether/hexane. A cream solid obtained was washed with a little amount of cool diethyl ether and air dried to give the desired product with 40-53 % yield.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.49 (s, 1H, NH_{amida}), 7.94 – 7.82 (m, 10H, 8H_{pyr}, 2H_{Ar}), 7.72 (s, 4H_{pyr}), 7.67 (s, 4H_{pyr}), 7.54 (s, 1H_{Ar}), 5.82 (ddt, J = 16.9, 10.2, 6.7 Hz, 2H, 2xHC=), 5.36 (s, 4H, 2xOCH_2), 5.12 – 4.82 (m, 6H, 2x$NH_{uretano}$, 2xH_2C=), 4.24 (t, J = 6.6 Hz, 4H, 2xOCH_{2_chain}), 3.30 (s, 2H, O=C-CH_2-N), 3.26 (dd, J = 11.3, 5.8 Hz, 4H, 2xNCH_2), 2.68 (t, J = 5.5 Hz, 4H, 2xNCH_2), 2.05 (dd, J = 14.3, 6.8 Hz, 4H, 2xCH_{2_chain}), 1.98 – 1.86 (m, 4H, 2xCH_{2_chain}), 1.64 – 1.48 (m, 10H, 5xCH_{2_chain}), 1.47 – 1.22 (m, 32H, 7xCH_{2_chain}, 6xCH_{3_boc}).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.8 (C=O_{amida}), 156.9 (C=O_{boc}), 156.3 (C=O_{boc}), 139.4 (2xHC=, 2C), 138.6 (1Cq_{Ar}), 131.7 (Cq_{pyr}), 131.6 (Cq_{pyr}), 127.6 (4C_{pyr}), 127.5 (4C_{pyr}), 122.4 (1C_{Ar}), 120.4 (Cq_{pyr}), 120.1 (Cq_{pyr}), 118.7 (2C_{Ar}), 114.3 (2xH_2C=, 2C), 111.7 (4C_{pyr}), 111.5 (4C_{pyr}), 79.9 (1Cq_{boc}), 77.2 (1Cq_{boc}), 70.4 (2xOCH_2, 2C), 68.7 (2xOCH_{2_chain}, 2C), 60.4 (O=C-$\underline{C}H_2$-N, 1C), 55.9 (2xNCH_2, 2C) , 38.9 (2xNCH_2, 2C), 33.9 (2xOCH_{2_chain}, 2C), 29.7 (2xOCH_{2_chain}, 2C), 29.6 (3xOCH_{2_chain}, 3C), 29.3 (2xOCH_{2_chain}, 2C), 29.1 (2xOCH_{2_chain}, 2C), 28.5 (6xCH_{3_boc}, 6C), 26.3 (5xOCH_{2_chain}, 5C).

MALDI: calculated for [$C_{78}H_{96}N_4NaO_9$] = 1,255.7075; found: 1,255.7070

Synthesis of MINTs:

This procedure is adapted from our previous work.[6] Tuball-SWNTs (Tuball SWNTs 01RW03, ø = 1.6±0.4 nm, 20 mg) were dispersed in tetrachloroethane (TCE, 20 mL, 1 mg SWNT/mL TCE) by sonication in a bath sonicator (at 20 °C for 15 min). To this dispersion, the Diamino-Boc U-shape was added (20 mg, 1 mg U-shape/mg SWNTs). The mixture was degassed with N_2 and Grubbs second generation catalyst was added (1.0 equiv with respect to the U-shape molecule). The reaction was stirred for 72 h at room temperature. After this time, the suspension was filtered through a 0.2 μm-pore size polytetrafluoroethylene (PTFE) membrane. The solid obtained was removed from the

filter and washed with dichloromethane employing 10 min sonication. This cleaning procedure was repeated three times, until the filtration solvent was completely colourless. A final wash with Et_2O was performed and the product was dried in oven at 135 °C overnight.

Alternatively, a mechanochemical synthetic method was also explored:

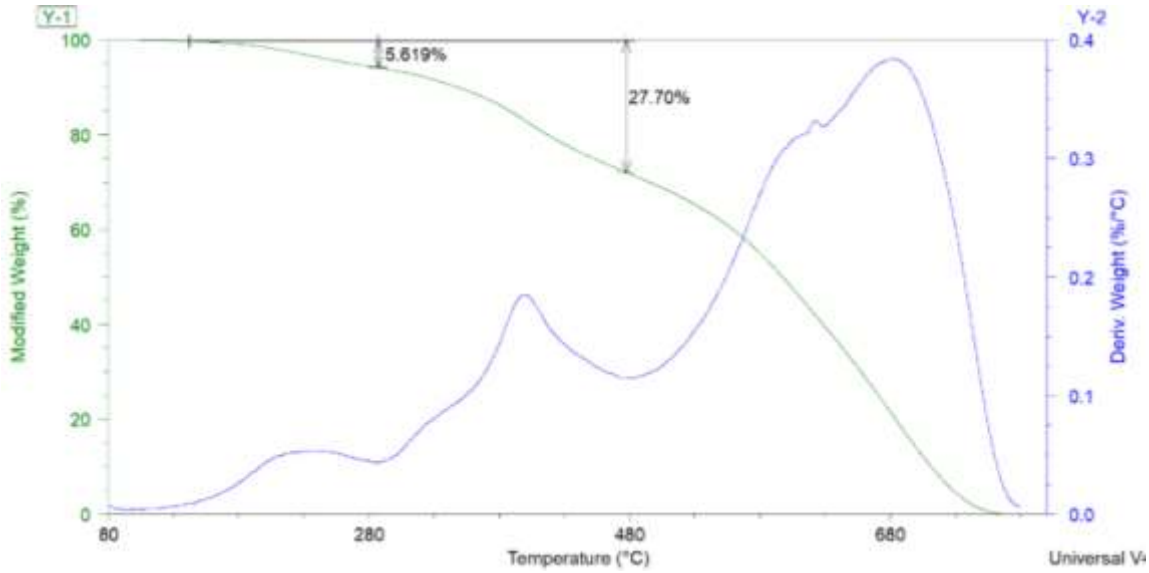
In a 20 mL-size stainless steel ball mill reactor, Tuball SWNTs (150 mg), U-shape (150 mg, 1 mg/1 mg CNTs) and 2ndgen. Grubbs catalyst (0.5 mol %) were added. The reactor was charged with five stainless steel balls. The powders were milled for 10 min at 500 rpm in an air atmosphere. After this time, the reactor content was recovered.

Dichloromethane was added and the reaction mixture was filtered through a PTFE membrane of 0.2μm pore size. The filter cake was collected and was re-dispersed in dichloromethane in a round-bottom flask by bath sonication for 10 min. The sample was filtered again through a PTFE membrane of 0.2μmpore size. This cleaning procedure was repeated three times, until the filtration solvent was completely colourless. A final wash with Et_2O was performed and the product was dried in oven at 135 °C for 3 hours.

Characterization of MINTs:

Thermogravimetric analysis (TGA) of the sample was employed in order to quantify the degree of functionalization. Both TGAs show a weight loss in the range 130-480 ºC (see derivative curve) that corresponds to around 27.7 % of the total weight for the sample obtained after performing the reaction in TCE (Figure S1, a) and 27.4% of the total weight of the sample obtained after performing the mechanochemistry method (Figure S1, b). In this range, there is always a small weight loss between 130-280 ºC, corresponding to approximately 5 % of the weight of the Boc group. The derivative of data curves shows a single peak between 300-480 ºC for the macrocycle decomposition, suggesting the absence of U-shape oligomers adsorbed onto the SWNT wall.[7]

a)



b)

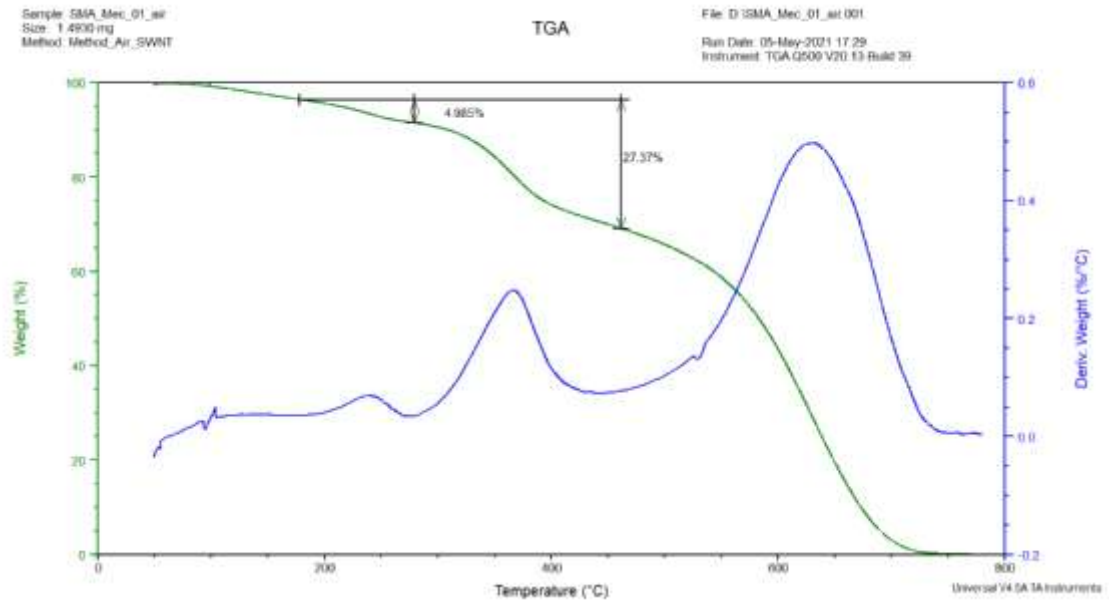


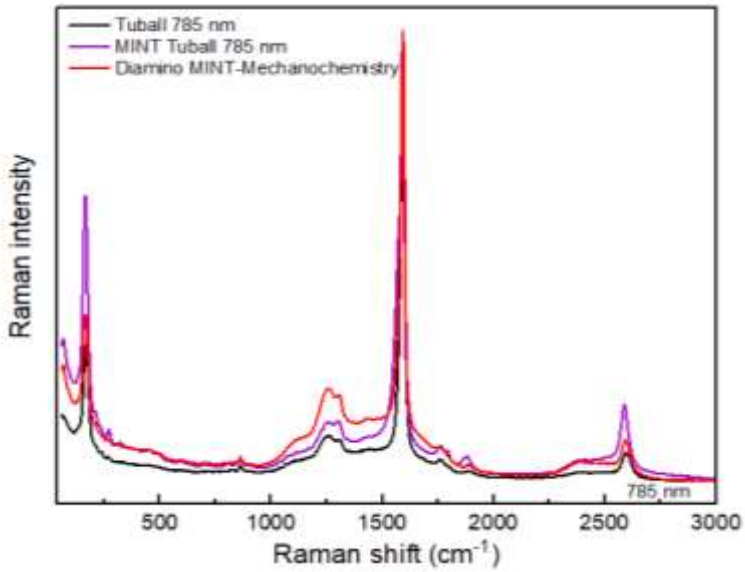
Figure S1. *a) TGA (Air, 10 ºC·min-1) of MINTs synthesized in TCE b) TGA (Air, 10 ºC·min-1) of MINTs synthesized by mechanochemistry.*

Raman spectroscopy was performed in the powder samples of the initial SWNTs and the MINTs samples obtained in TCE (see Figure S2). In addition, Raman spectra of PI-SWNT, PI-daMINT and PI-ctrlMINT composites at different strain levels were acquired. For each sample, 15 spectra were taken at different sample locations for each strain value

using 785 nm excitation wavelength, 1 mW power and 30 seconds acquisition. Figure S3 a-c shows the average spectra where the characteristic Raman modes of CNTs are resolved. The radial breathing modes (RBM) are related to the movement of carbon atoms in the radial direction, the G mode is an in-plane stretching of the sp2 atoms and the 2D band is an overtone of the disorder-induced D band. We fitted each individual spectrum with Lorentzian functions (1 lorentzian for RBM, 2 lorentzian in the G region for G- and G+ modes and 1 lorenzian for the 2D mode) using an automatic peak fitting routine.[8]

The strain-dependent Raman shift of the G+ and 2D modes has been used as an indicator of the load transfer between the polymer matrix and SWNTs.[9-11] We observe a downshift of the G and 2D modes for the 3 samples upon strain increase (Figure S3 d-e). This is a consequence of an elongation of carbon-carbon bonds in the tubes and a decrease of force constant under tensile strain, indicating an effective load transfer to the tubes. The total shift of the 2D band (PI-daMINT > PI-ctrlMINT > PI-SWNT) informs on the load transfer efficiency (higher shift implies better load transfer) and confirms the reinforcement capabilities reported in the main text (TS and YM values obtained under mechanical tests).[12, 13]

a)



b)

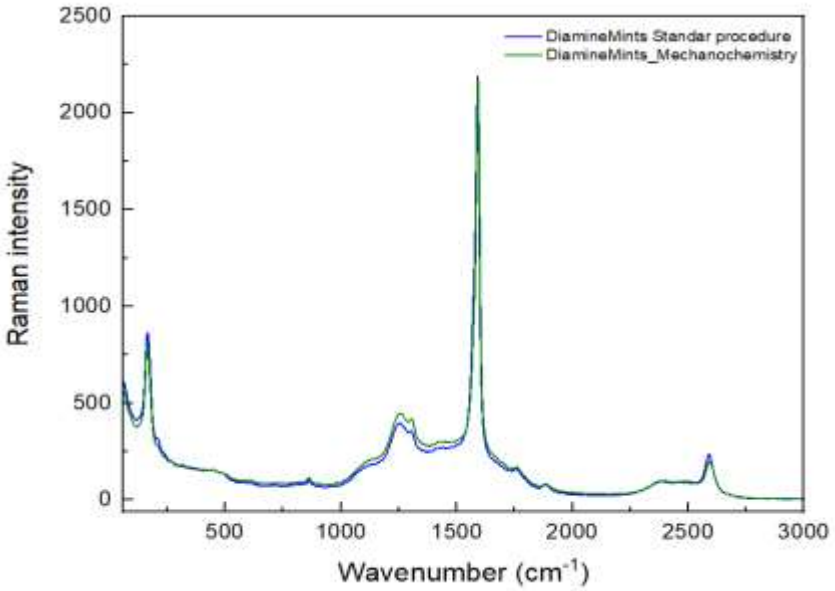
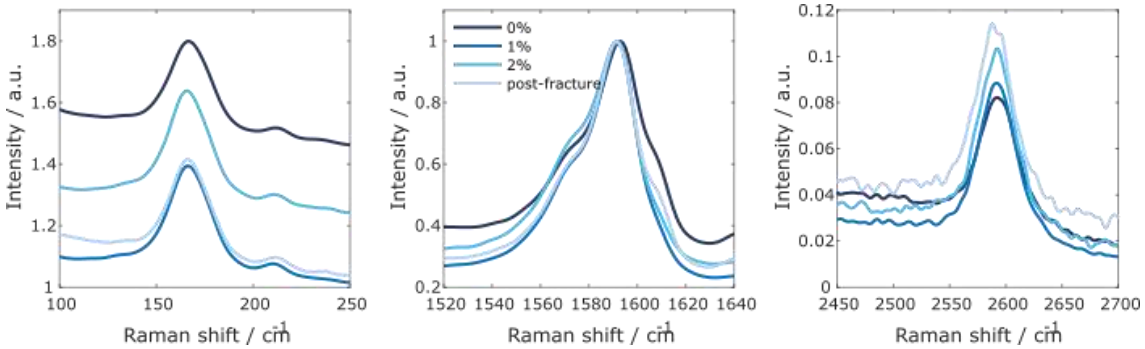
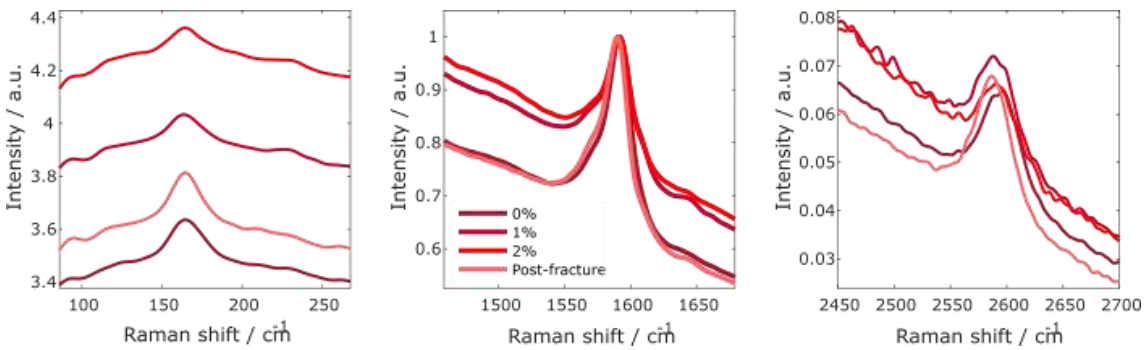


Figure S2. *a) Raman spectra of MINTs synthesized by mechanochemistry (red line), SWNTs (black line) and control standard-Mints (purple line). b) Raman spectra of MINTs synthesized in TCE (blue line) and MINTs synthesized by mechanochemistry (green line).*

a)



b)



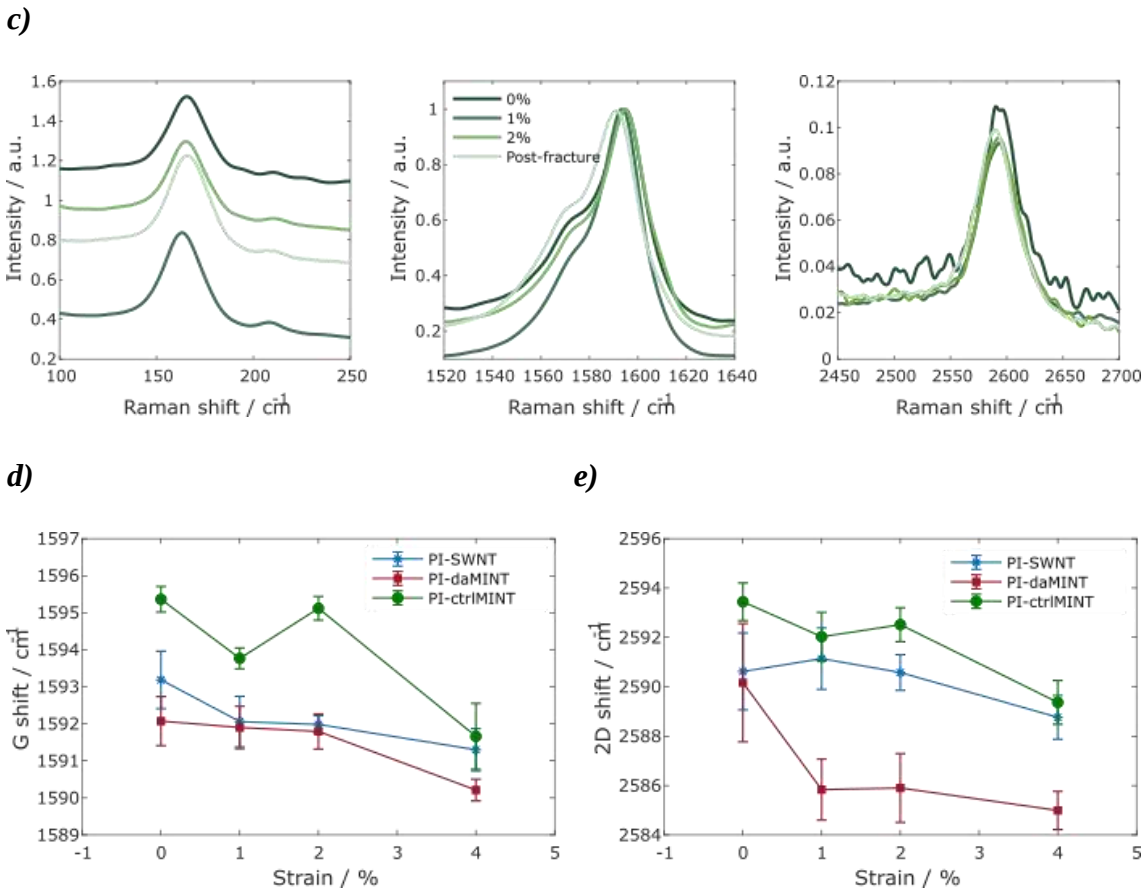
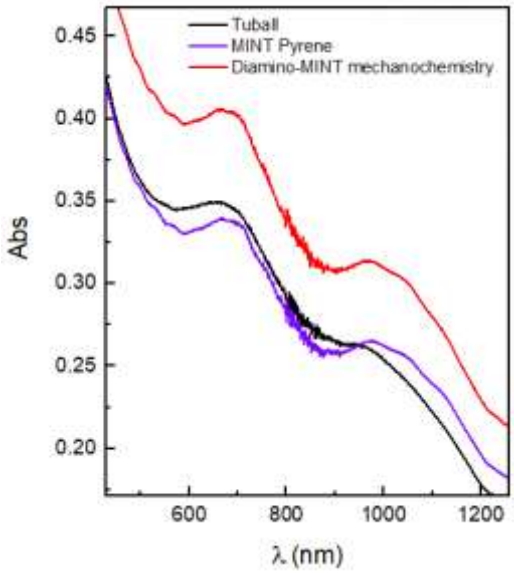


Figure S3. *Average Raman spectra at different strain levels for (a) PI-SWNT, (b) PI-daMINT and (c) PI-ctrlMINT, zoomed at the characteristic RBM (left), G modes (middle) and 2D modes (right). Each spectrum corresponds to the average of 15 spectra acquired at different sample positions. Corresponding strain dependent Raman shifts of the (d) G+ mode and (e) 2D mode for PI-SWNT (blue), PI-daMINT (red) and PI-ctrlMINT (green).*

UV-Vis spectra

a)



b)

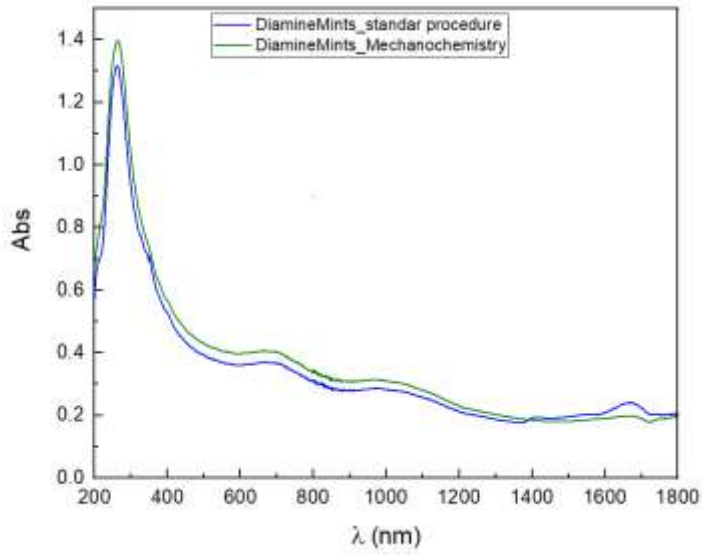
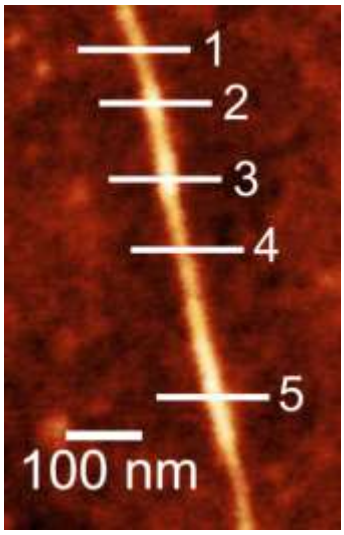
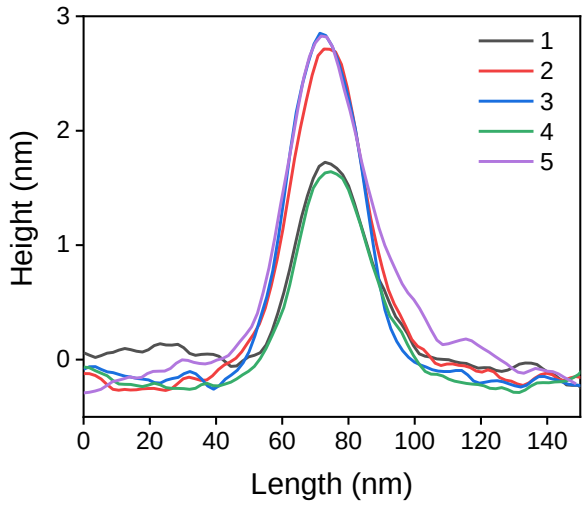
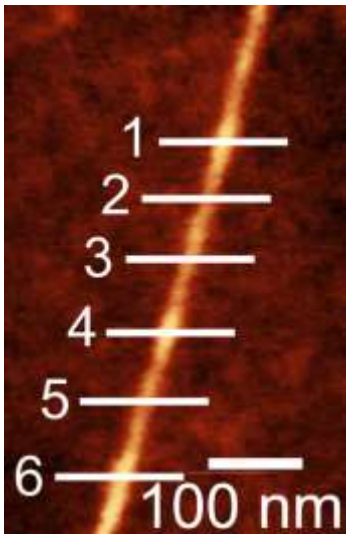


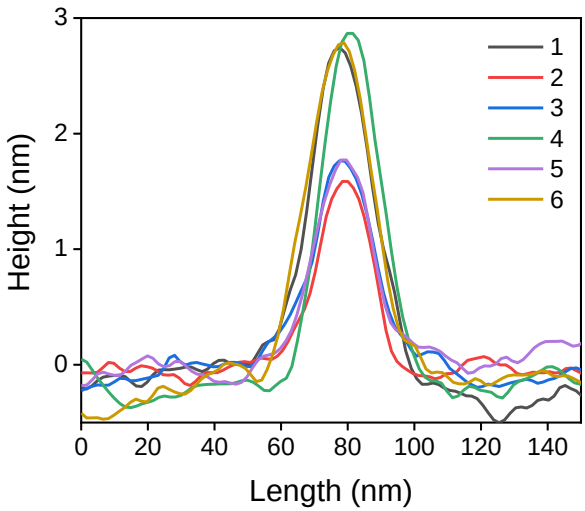
Figure S4. *a) UV-VIs spectra of the supernatants obtained after sonicating MINTs synthesized by mechanochemistry (red line), SWNTs (black line) and control standard-Mints (purple line). b) UV-VIs spectra of the supernatants obtained after sonicating MINTs synthesized in TCE (blue line) and MINTs synthesized by mechanochemistry (green line).*

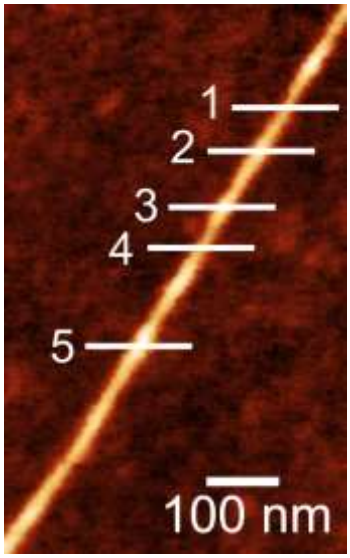
Atomic Force Microscopy:











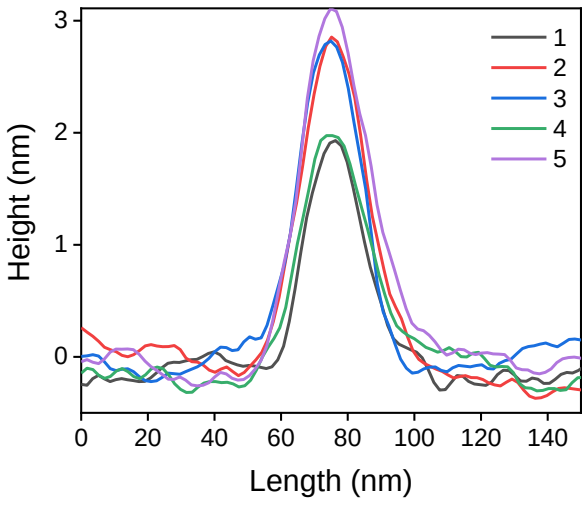


Figure S5. *AFM images and graphic profiles of da-MINTs deposited on mica.*

Reaction between diamino U-shaped molecule and TPA:

Diamino U-shape (58.8 mg, 0.053 mmol), TPA (14.24 mg, 0.106 mmol) and two drops of triethylamine were added to a stainless steel ball mill reactor and the sample milled and analyzed by FTIR after different reaction times. The results clearly show the growth of the characteristic imine IR band (1638 cm^{-1}) with reaction time.

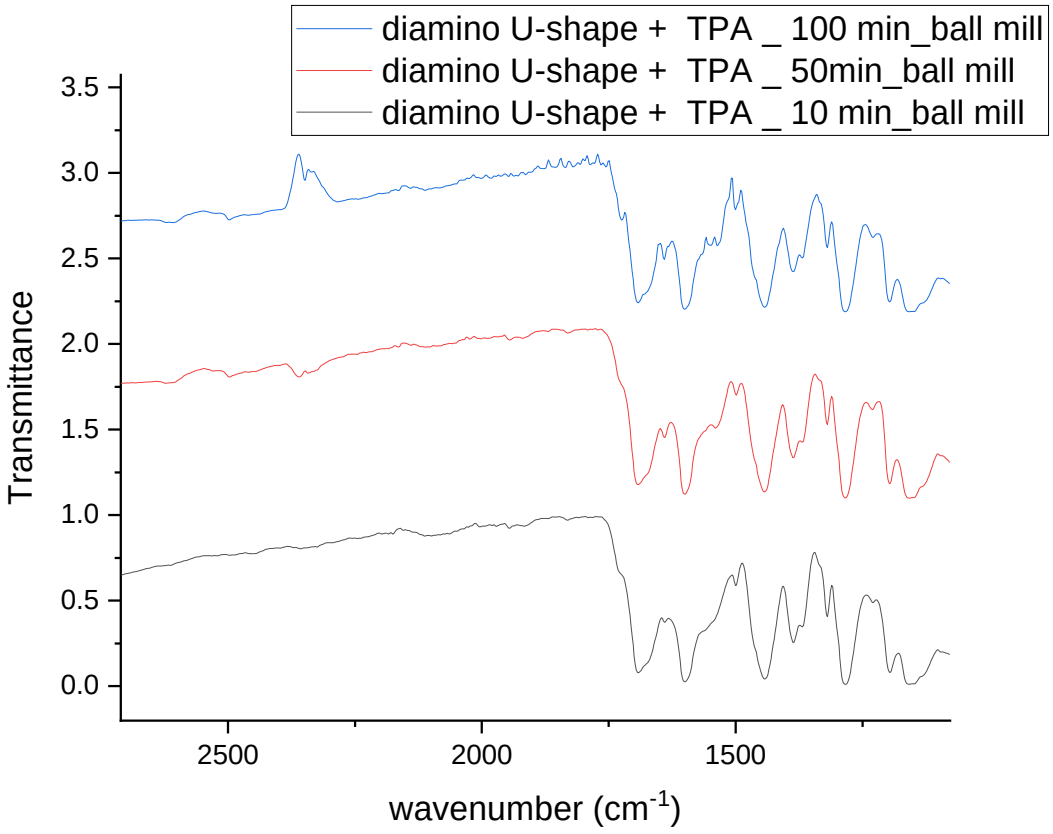


Figure S6. *FTIR spectra of the mixture of diamino U-shape and TPA after different reaction times in the ball mil, showing the growth of the imine band stretch (dashed lines).*

Recycling of the composites of polyimines with MINTs:

To demonstrate the recyclability of the polyimines with MINTs, several experiments were conducted.

1. All the pieces of the samples from the tensile test were gathered and pressed for 15 minutes at 130 ºC to obtain a new film, which was then cut into three dog bones with the dimensions described previously to perform a tensile test.

Table S1. *Young's modulus and tensile strength values for each of the composites after the recycling process.*

Neat		Y. M (MPa)	T.S. (MPa)
	1	1883.31	27.32
	2	1480.76	33.63
	3	1531.41	38.59
Mean		1631.83	33.18
Standard deviation		219.26	5.65
1% SWNT PI		Y. M (MPa)	T.S. (MPa)
	1	1678.07	41.64
	2	1918.21	38.63
	3	1429.28	39.68
Mean		1675.18	39.99
Standard deviation		244.48	1.53
1% **MINT** PI		Y. M (MPa)	T.S. (MPa)
	1	3111.78	62.6
	2	3077.87	60.26
	3	3188.53	57.40
Mean		3126.06	60.07
Standard deviation		56.70	2.61

2. A single dog bone specimen of 1% diamino MINTs-PI was measured in a tensile test and recycled three times with heat for re-measurement. An ASTM D638 TYPE V dog

bone mold with a thickness of 0.30 mm was used to ensure that the recycled specimen retained the same shape after each recycling process.

Table S2. *Young's modulus and tensile strength values for PI-daMINTs composite depending on number of recycling steps.*

Thermal recycling	**YM (MPa)**	**TS (Mpa)**
not recycled	2960.02	69.89
recycled 1	2945.93	73.66
recycled 2	2960.99	70.63
recycled 3	2938.39	72.67

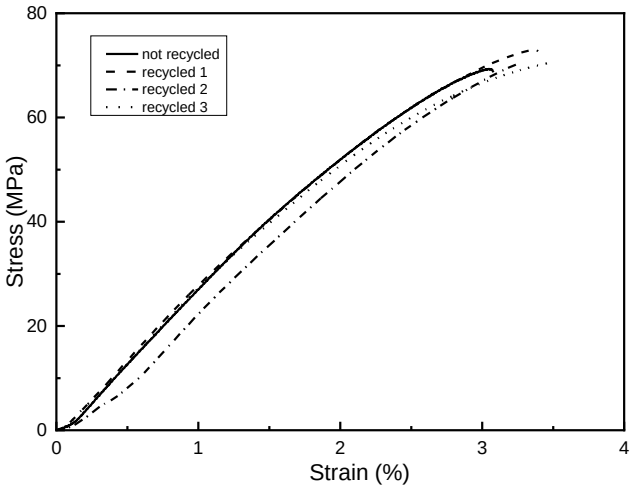


Figure S7. *Representative stress-strain curves for the PI-daMINTs after 0 (solid line), 1 (dashed line), 2 (dash-dotted line) and 3 (dotted line) recycling steps.*

A different recycling process approach was carried out by depolymerizing the polyimine composite with 1% diamino MINTs by combining small pieces of dog bone and covering them with an excess of propylamine (20 ml). This mixture was heated to 40 degrees Celsius under reflux and stirred magnetically for thirty minutes to accelerate the

depolymerization process. After this process, the solid had completely dissolved, and the resulting liquid mixture was poured into a Teflon container and left on a hot plate overnight to evaporate the propylamine. The resulting solid was polymerized again using a hot press for one hour at 75 ºC, one hour at 85 ºC, and three hours at 105 ºC. The obtained film was reformed using an ASTM D638 TYPE V dog bone mold with a thickness of 0.30 mm for measurement in the tensile test.

Table S3. *Young's modulus and tensile strength values for PI-daMINTs composite after chemical recycling*

Chemical recycling	**YM (MPa)**	**TS (Mpa)**
not recycled	3100.9	65.3
recycled 1	3123.63	59.7

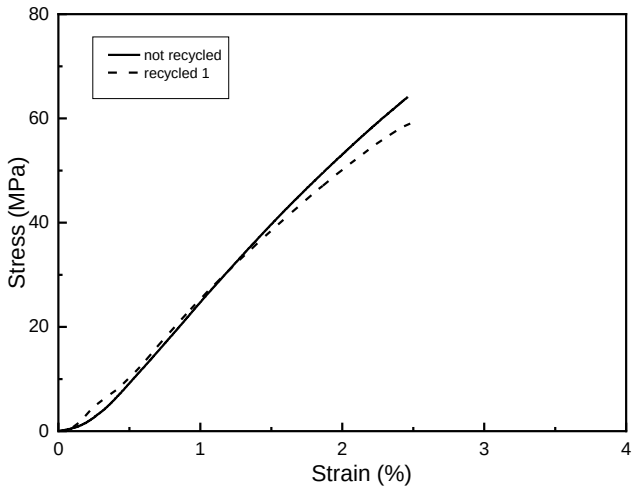


Figure S8. *Representative stress-strain curves for the PI-daMINTs composite after chemical recycling*

We have added two more composites to the initial tensile curves: 0.1 wt. % diamino MINTs and 1 wt. % Standard MINTs. Three dog bone specimens were also tested for

each type of sample. The graph shows the results of the dog bones with the highest tensile strength.

Table S4. *Young's modulus and tensile strength values for pristine SWNTs and different MINT species*

	YM (MPa)	TS
1% wt.Standard MINTs	2430.36±188.84	47.51±4.41
0.1wt. diamino MINTs	2545.48± 39.58	70.3 ± 1.41

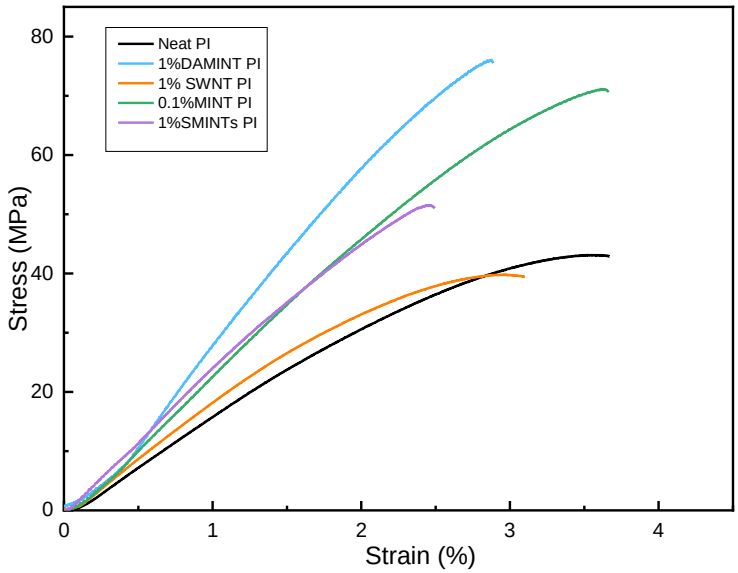


Figure S9. *Representative stress-strain curves for pristine SWNTs and different MINT species*

At a concentration of 0.1% diamino MINTs, the Young's modulus decreases, but there are no significant changes in tensile strength. With the Standard MINTs, there is an improvement compared to the neat and Tuball, but the results are worse than with the diamino.

Supplementary references:

[1] *Ramdahl, T., Bonge-Hansen, H. T., Ryan, O. B., Larsen, Å., Herstad, G., Sandberg, M., ... & Cuthbertson, A. S., Bioorg. and Medicinal Chem. Lett.* ***2016,*** *26 (17), 4318-4321.*

[2] *Ndinguri, M. W., Fronczek, F. R., Marzilli, P. A., Crowe, W. E., Hammer, R. P., & Marzilli, L. G., Inorganica Chimica Acta* ***2010****, 363, 1796–1804.*

[3] *Yu, K., Sommer, W., Richardson, J. M., Weck, M., & Jones, C. W., Adv. Synth. Catal.* ***2005,*** *347, 161, 171.*

[4] *Patent: Manami US2016/82114,* ***2016****, A1 (DCM/MeOH).*

[5] *Fletcher, S. Organic Chemistry Frontiers* ***2015****, 2(6), 739-752.*

[6] *Villalva, J., Rapakousiou, A., Monclús, M. A., Fernández Blázquez, J. P., de la Vega, J., Naranjo, A., ... & Pérez, E., ACS Nano* ***2023****, 17(17), 16565-16572.*

[7] *de Juan, A., Mar Bernal, M., & Pérez, E. M., ChemPlusChem* ***2015****, 80(7), 1153-1157.*

[8] *Sabanés, N. M., Eaton, M. D., Moreno-Da Silva, S., Naranjo, A., & Pérez, E. M. Nanoscale* ***2024,*** *16(4), 2048-2059.*

[9] *Wang, S., Liang, R., Wang, B., & Zhang, C., Chemical Physics Letters* ***2008****, 457(4-6), 371-375.*

[10] *Mu, M., Osswald, S., Gogotsi, Y., & Winey, K. I., Nanotechnology* ***2009****, 20(33), 335703.*

[11] *Papageorgiou, D. G., Li, Z., Liu, M., Kinloch, I. A., & Young, R. J., Nanoscale* ***2020****, 12(4), 2228-2267.*

[12] *Deng, L., Eichhorn, S. J., Kao, C. C., & Young, R. J., ACS applied materials & interfaces* ***2011****, 3(2), 433-440.*

[13] *Young, R. J., Deng, L., Wafy, T. Z., & Kinloch, I. A., Journal of materials science* ***2016****, 51, 344-352.*