Electronic Supplementary information

Design and Synthesis of Aniline-Appended P3HT for Single Step Covalent Functionalisation of Carbon Nanotubes

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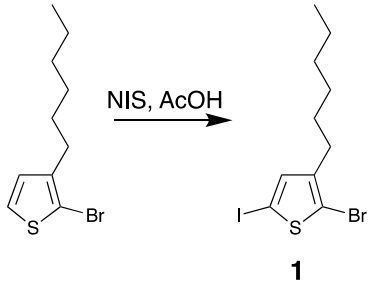
Synthesis of monomer 1



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Scheme S1. Synthesis of 1

Monomer **1** was synthesised by iodation of the commercially available 2-bromo-3-hexylthiophene (Scheme S1)

A solution of 2-bromo-3-hexylthiophene (500 mg, 2.0 mmol) in a $CHCl_3$/AcOH mixture (1/1.6 mL) was stirred at 0°C under Ar and sheltered from light. *N*-Iodosuccinimide (455 mg, 2.0 mmol) was added and the mixture stirred for 2 h at 0°C and for 12 h at 25 °C. The medium is mixed with iced water (10 mL) and extracted with $CHCl_3$. The organic layer is washed with aq. NaOH (0.1 M), with water, dried ($MgSO_4$) and the solvent removed under vacuum. The crude oil is purified by chromatography (SiO_2, cyclohexane) to yield pure **1** as a colorless oil (500 mg, 66% yield):

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.96 (s, 1H, thiophene H4), 2.52 (m, 2H, thiophene-CH_2), 1.57-1.50 (m, 2H, hexyl C2-H_2), 1.48 (m, 2H, hexyl C3-H_2), 1.35-1.26 (m, 4H, hexyl CH_2), 0.88 (t, *J* = 6.8 Hz, 3H, CH_3);

^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 144.4 (thiophene C3), 138.2 (thiophene C4), 111.9 (thiophene C2), 71.1 (thiophene C5), 31.7 (hexyl C4), 29.8 (hexyl C2), 29.3 (hexyl C3), 29.0 (thiophene-CH2), 22.7 (hexyl C5), 14.2 (CH_3);

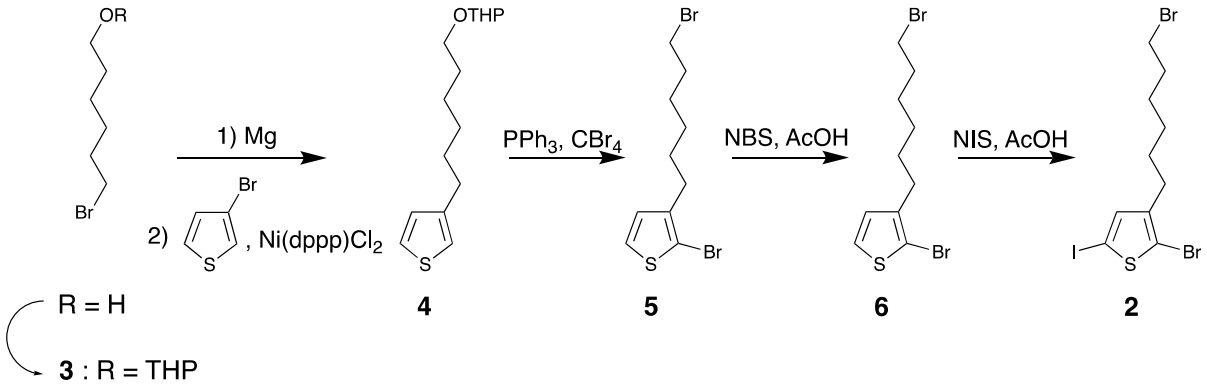
FTIR (ATR diamond) ν (cm^{-1}): 3082 (vw, aromatic νCH), 2953 ($\nu_{as}CH_3$), 2923 ($\nu_{as}CH_2$), 2868, 2854 ($\nu_s CH_2$), 1652 and 1536 (aromatic νCC), 1465 (δCH_2), 1453, 1443, 1403, 1377 (δCH_3), 1354, 1340, 1191, 1095, 995, 975, 909, 826, 724, 650, 580;

MS (ESI): m/z 371.90, 373.84 [M^+ - H];

Anal. calcd. for $C_{10}H_{14}BrIS$: C 32.19, H 3.78; found: C 32.22, H 3.80.

Synthesis of monomer 2.

Monomer **2** was synthesised according with Scheme S2



Scheme S2. Synthesis of monomer 2

2-((6-bromohexyl)oxy) tetrahydro-2*H*-pyran (3): Amberlyst 15® resin (2 g) was suspended in a solution of 6-bromohexanol (10.0 g, 55.3 mmol) in CH_2Cl_2 (125 mL) under Ar. 3,4-dihydro-2H-pyran (6.11 g, 72.6 mmol, 1.3 equiv) was added to the suspension that was stirred for 1 hour at 25 °C. The resin was filtered and the medium evaporated under vacuum. The yellow crude oil was purified by chromatography (SiO_2, EtOAc/C_6H_{12} 1/9) to yield pure **3** as a colorless oil (11.20 g, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.58 (dd, *J* = 4.6, 2.7 Hz, 1H, OCHO), 3.84 (m, 1H, pyran C**H**HO), 3.74 (dt, *J* = 9.6, 6.8 Hz, 1H, CH**H**-OTHP), 3.50 (m, 1H, OC**H**H$(CH_2)_4CH_2Br$), 3.40-3.34 (m, 3H, CH**H**-OTHP + CH_2Br), 1.89-1.33 (m, 14H, CH_2);

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 98.9 (pyran C2), 67.3 (pyran C6), 62.3 (CH_2-O-), 33.9 (CH_2-Br), 32.7 (**C**H_2-CH_2-Br), 30.7 (pyran C3), 29.6 (**C**H_2-CH_2-O-), 27.9 (**C**H_2-$(CH_2)_2$-O-), 25.5 (C**H$_2$**-$(CH_2)_2$-Br), 19.7 (pyran C4);

FTIR (ATR diamond) ν (cm^{-1}): 2937 ($\nu_{as}CH_2$), 2860 (ν_sCH_2), 1453, 1440, 1352, 1322, 1259, 1242, 1200, 1184, 1133, 1118, 1076, 1032, 1021, 987, 904, 868, 814, 729, 645 (νCBr), 634, 632, 626, 620, 616;

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{11}H_{21}BrO_2$, 287.0617; found, 287.0613.

3-(6-(tetrahydro-2*H*-pyran-2-oxy)hexyl)thiophene (4): A suspension of magnesium turnings (110 mg, 2.27 mmol, 1.2 equiv) in dry THF (8 mL) was heated at 50 °C and a few drop of dibromoethane were added. 10% of the total amount of **3** (1 g, 1.89

mmol) was introduced and the medium was refluxed for 2h30. When the mixture darkened and the magnesium reacted, the rest of **4** was added dropwise and the mixture refluxed until most of the magnesium had been consumed. The organomagnesium solution was cooled to 25 °C and kept under Ar. In a separate flask, a solution of bromothiophene (558 mg, 3.44 mmol, 1.1 equiv) and Ni(dppp)Cl_2 (54.5 mg, 100 µmol, 0.03 equiv) in dry THF (4 mL) was heated to 60°C for 30 min. The magnesium bromide solution was added dropwise and heated at reflux for 12 hrs. The reaction was quenched with water and extracted with C_6H_{12}/EtOAc (1/1, 3 × 25 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under vacuum. The crude was purified by chromatography (SiO_2, cyclohexane/EtOAc 95/5) to afford pure **5** as an oil (346 mg, 42% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.23 (dd, *J* = 4.9, 3.0 Hz, 1H, thiophene H5), 6.95 – 6.91 (m, 2H, thiophene H2 and H4), 4.56 (dd, *J* = 4.4, 2.7 Hz, 1H, OCHO), 3.85 (m, 1H, pyran C**H**HO), 3.72 (dt, *J* = 9.6, 6.8 Hz, 1H, C**H**H-OTHP), 3.48 (m, 1H, pyran CH**H**O), 3.37 (dt, *J* = 9.6, 6.6 Hz, 1H, CH**H**-OTHP), 2.61 (t, *J*=7.5 Hz, 2H, thiophen-CH_2), 1.89 – 1.79 (m, 1H, THP C3-**H**H), 1.78-1.48 (m, 9H, CH_2), 1.45-1.30 (m, 4H, CH_2);

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 143.1 (thiophene C3), 128.3 (thiophene C4), 125.1 (thiophene C5), 119.9 (thiophene C2), 98.9 (OCHO), 67.6 (pyran C6), 62.3 (**C**H_2-OTHP), 30.9 30.6 and 30.3 (hexyl C1, C2 and pyran C3), 29.8 (hexyl C5), 29.2 (hexyl C3), 26.2 (hexyl C4), 25.6 (pyranC5), 19.8 (pyranC4);

FTIR (ATR diamond) ν (cm^{-1}): 3100 (aromatic νCH), 2930 ($\nu_{as}CH_2$), 2856 (ν_sCH_2), 1536, 1464, 1453, 1440, 1383, 1364, 1352, 1283,1275, 1259, 1200, 1184, 1135, 1119, 1076, 1064,1030, 1021, 988, 904, 882, 834, 814, 771, 731, 683, 661, 632 (νCBr), 575;

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{24}O_2S$, 291.1389; found, 291.1388;

Anal. calcd for $C_{15}H_{24}O_2S$: C 67.12, H 9.01; found: C 67.09, H 9.17.

3-(6-bromohexyl)thiophene (5): A solution of **5** (995 mg, 3.71 mmol) and CBr_4 (1.726 g, 5.22 mmol, 1.4 equiv) in anhydrous CH_2Cl_2 (50 mL) is cooled to 0°C under Ar. $P(Ph)_3$ (2.741 g, 10.4mmol, 2.4 equiv) was added and the mixture is warmed to 25 °C and stirred for 3 days. The solvent was evaporated in vacuum and the crude is purified by chromatography (SiO_2, EtOAc/C_6H_{12} 2/98) to afford pure **6** as an oil (760 mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.27 (dd, *J* = 4.9 Hz, 3.0 Hz, 1H, thiophene H5), 6.94 (m, 2H, thiophene H2 and H4), 3.43 (t, *J* = 6.8 Hz, 2H, CH_2Br), 2.66 (t, *J* = 7.8 Hz, 2H, thiophene-CH_2), 1.89 (m, 2H, hexyl C5-H_2), 1.67 (p, *J* = 7.7 Hz, 2H, hexyl C2-H_2), 1.53-1.42 (m, 2H, hexyl C4-H_2), 1.41-1.26 (m, 2H, hexyl C3-H_2);

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 143.0 (thiophene C3), 128.3 (thiophene C4), 125.3 (thiophene C5), 120.0 (thiophene C2), 34.1 (CH_2Br), 32.9 (hexyl C5), 30.5 (hexyl C2), 30.3 (hexyl C1), 28.5 (hexyl C3), 28.1 (hexyl C4);

FTIR (ATR diamond) ν (cm^{-1}): 3054 (aromatic νCH), 2928 ($\nu_{as}CH_2$), 2855 (ν_sCH_2), 1536, 1462, 1437, 1410, 1257, 1236, 1152, 1079, 938, 909, 858 and 832, 770, 728 (CH_2rock), 684, 632;

MS (ESI): 246.1, 248.1 [M^+];

Anal. calcd for $C_{10}H_{15}BrS$: C 48.59; H 6.12; found: C 48.26, H 6.12.

2-Bromo-3-(6-bromohexyl)thiophene (6): A solution of **5** (1,00 g, 4.0 mmol, 1 equiv) and AcOH (6mL) in $CHCl_3$ (36 mL) was stirred at 0 °C under Ar. A solution of NBS (721 mg, 4.0 mmol, 1 equiv) in $CHCl_3$ (18 mL) was added in fractions of 5mL spaced by 15 min. After disappearance of **5** (followed by TLC), the solution was neutralised with a 10% NaOH solution, mixed with water (100 mL) and extracted with EtOAc (3 × 40 mL). The organic phases were dried ($MgSO_4$) and concentrated under vacuum. The crude was purified by flash chromatography (cyclohexane) to afford pure **7** as a yellow oil (853 mg, 65% yield):

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.20 (d, *J* = 5.6 Hz, 1H, thiophene H5), 6.80 (d, *J* = 5.6 Hz, 1H,thiophene H4), 3.42 (t, *J* = 6.8 Hz, 2H, CH_2Br), 2.58 (t, *J* = 7.7 Hz, 2H, thiophene -CH_2), 1.87 (p, 2H, *J* = 7.0 Hz, hexyl C5-H_2), 1.61 (p, *J* = 7.7 Hz, 2H, hexyl C2-H_2), 1.48 – 1.44 (m, 2H, hexyl C3-H_2), 1.41 – 1.33 (m, 2H, hexyl C4-H_2);

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.8 (thiophene C3), 128,3 (thiophene C4), 125.4 (thiophene C5), 109.1 (thiophene C2), 34.0 (CH_2Br), 32.9 (hexyl C5), 30.2 (hexyl C2), 29.6 (hexyl C1), 28.4 (hexyl C3), 28.0 (hexyl C4);

FTIR (ATR diamond) ν (cm^{-1}) 3084 (aromatic νCH), 3003, 2938 ($\nu_{as}CH_2$), 2854 (ν_sCH_2), 1655; 1527 (aromatic νCC), 1463, 1435, 1429, 1394, 1338, 1321, 1281, 1236, 1191, 1059, 1008, 992, 955, 895, 860, 828, 727, 691, 644;

MS (EI): 323.9, 325.9 and 327.9 [M^+].

2-Bromo-3-(6-bromohexyl)-5-iodothiophene (2): A solution of **7** (403 mg, 1.23 mmol) and acetic acid (2.7 mL) in $CHCl_3$ (18 mL) was stirred at 0 °C under Ar. N-iodosuccinimide (275 mg, 1.22 mmol, 1 equiv) was added. When **7** was no longer detected by TLC, the mixture was mixed with aq. NaOH (10%, 100 mL) and extracted with CHCl3 (2 x 40 mL). The organic phase was washed with aq. $Na_2S_2O_3$, dried ($MgSO_4$) and evaporated. The crude was chromatographed (SiO_2, eluent cyclohexane) to yield pure **2** as a solid (417 mg, 75 % yield).

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.97 (s, 1H, thiophene H4), 3.42 (t, 2H, *J* = 6.8 Hz, CH_2-Br), 2.55 (t, *J* = 7.6 Hz, 2H, thiophene-CH_2), 1.87 (p, *J* = 7.0 Hz, 2H, hexyl C5-H_2), 1.57 (p, *J* = 7.6 Hz, 2H, hexyl C2-H_2), 1.48 (m, 2H, hexyl C3-H_2), 1.37 (m, 2H, hexyl C4-H_2);

^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 144.0 (thiophene C3), 138.1 (thiophene C4), 112.0 (thiophene C2), 71.3 (thiophene C5), 34.0 (CH_2-Br), 32.8 (hexyl C5), 29.6 (hexyl C2), 29.1 (hexyl C3), 28.3 (hexyl C4), 28.0 (hexyl C1);

FTIR (ATR diamond) ν (cm^{-1}): 3084 (aromatic νCH), 2923 (vasCH_2), 2854 (vasCH_2), 1655, 1527 and 1463 (aromatic νCC), 1435, 1428, 1394, 1338, 1321, 1281, 1236, 1191, 1059, 1008, 992, 955, 895, 860, 828, 727 (methyl rock), 691, 644;

MS (EI): 453.9, 451.9 and 449.9 [M+];

Anal. calcd. for $C_{10}H_{13}Br_2IS$: C 26.57, H 2.90; found: C 26.43; H 3.15.

NMR analysis of the mixtures of monomers

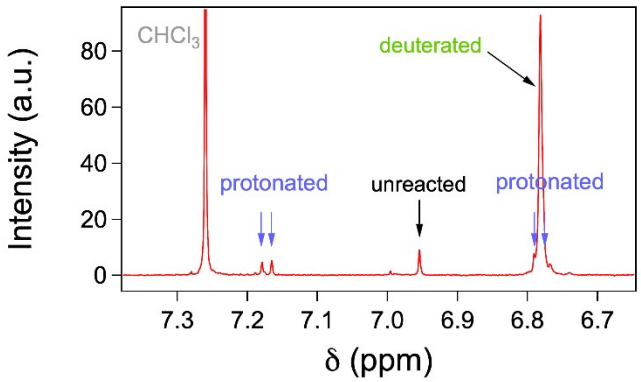


Figure S1. NMR analysis of the mixtures of monomers. The monomers are metallated with *i*-PrMgCl. The observed aliquot has been hydrolysed by CD_3OD.

Determination of copolymer molar mass by SEC

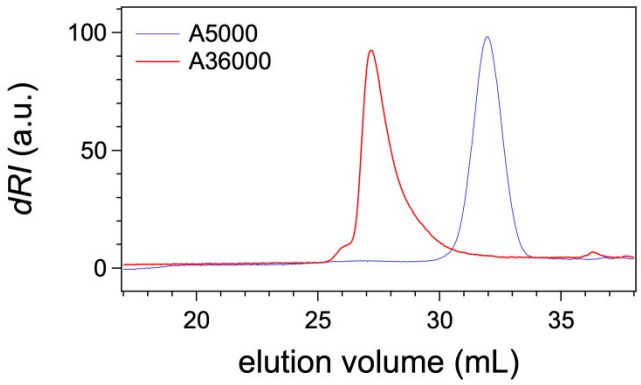


Figure S2. SEC profiles of copolymer A.

Measurement of the rate of incorporation of monomer 2 in polymers.

Mixture of **1** and **2** were polymerised as described above, with feed rates of monomer **2**: 5% 16% and 25%. The amounts were chosen to keep the final OD around 2. During the polymerisation a sample was taken from the reaction before the OD reached 0.2. The sample was hydrolysed with CD_3OD, precipitated in cyclohexane and the brominated monomer ratio in the polymer was measured by NMR. The rate of monomer **2** polymerised is roughly equal to the feed ratio (Figure S2).

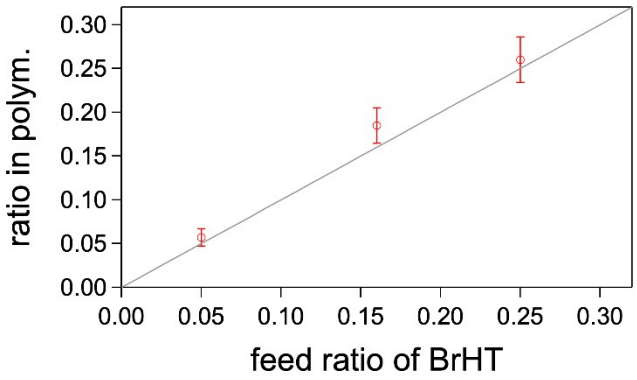


Figure S3. Molar fraction of monomer **2** in the polymer vs molar fraction of the monomer 2 in the feed.

Rate of substitution of the bromine

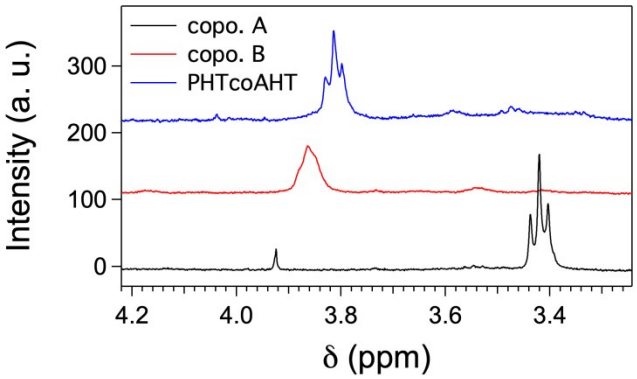


Figure S4. Comparison of the NMR spectra of copolymers A, B and **PHTcoAHT** (M_n = 36000) between 3.2 and 4.3 ppm.

Effect of mass ratio SWNT/PHTcoAHT 5000.

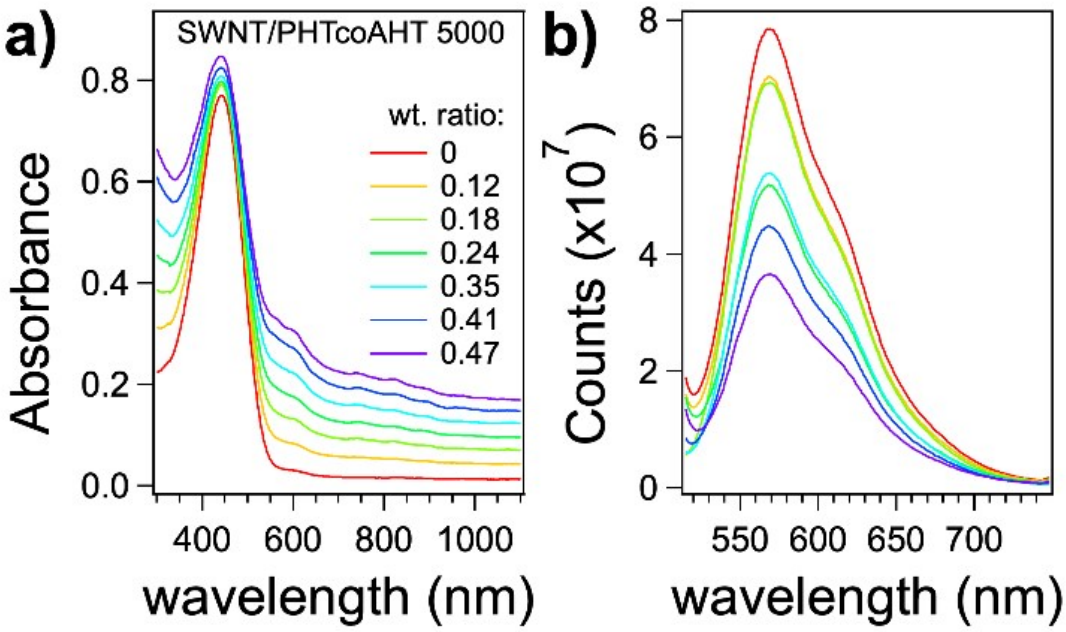


Figure S5: Evolution of the optical absorption (a) and fluorescence spectra (b) of SWNT/**PHTcoAHT 5000** suspensions as a function of wt. ratio.

Behavior of non-covalent nanohybrids in dilute solution

Different amounts of SWNTs mother solution (concentration 420 mg L^{-1}) were added to a solution of **PHTcoAHT** 36000 of concentration 2.8 mg L^{-1} and dispersed by sonication. The obtained solutions were followed by UV-Vis and photoluminescence spectroscopies (in this particular case performed in a square cell of 10 mm). Results are displayed on Figure S6). No aggregation was observed before addition of SWNTs. We observe the same changes as in more concentrated solutions.

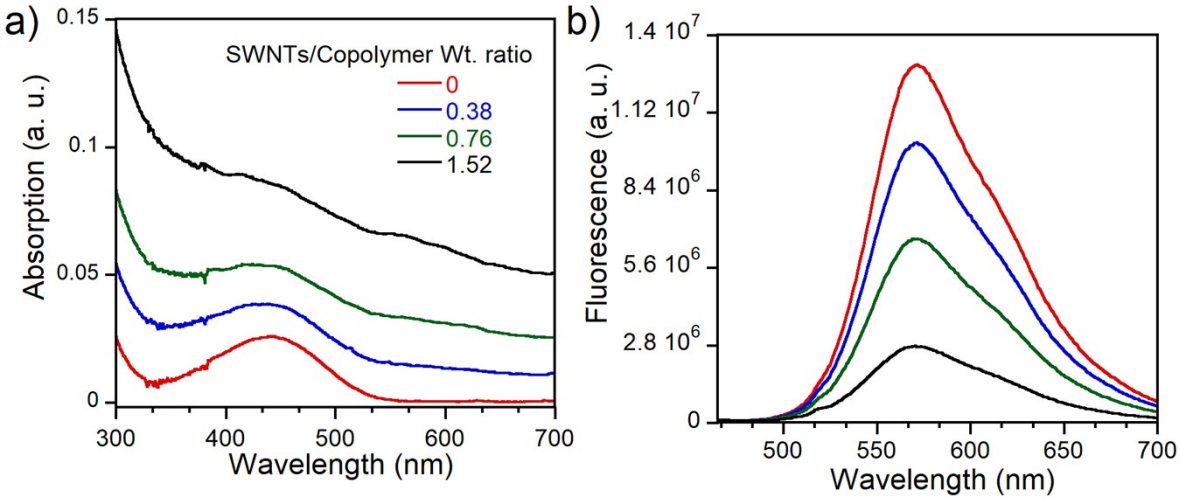


Figure S6: Evolution of the (a) optical absorption and (b) photoluminescence spectra of SWNT/**PHTcoAHT 36000** suspensions as a function of wt. ratio for a diluted copolymer solution.

PL lineshapes of non covalent nanohybrids

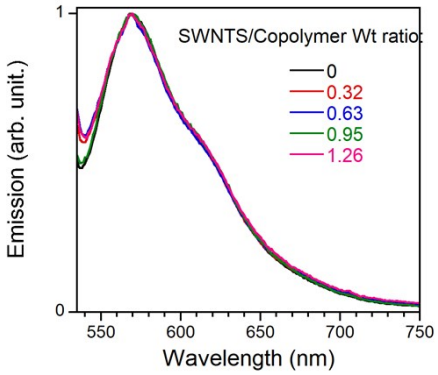


Figure S7: Normalised PL spectra of SWNT/**PHTcoAHT 36000 suspensions as a function of weight ratio**

Solvent extraction method:

A procedure similar to the one described by Schuettford *et al.* (ref. 21) was followed. In a typical experiment, 1.52 mg of SWNTs were added to a solution containing 4.6 mg of copolymer of M_n 36000 g mol^{-1} in 4 mL of THF. The mixture was sonicated for 5 min (tip sonication, 20% of 500W, Fischer Scientific Model FB-505) then centrifuged (25000 g for 80 min). The supernatant was collected. Upon addition of the same volume of toluene to this supernatant, aggregates of nanohybrids form, keeping only free polymer in the solution. The aggregates were separated from the solution through centrifugation (10000 g for 10 min) and then redispersed in toluene by sonicating the sample for 2 min. Reaggregation of the nanohybrids was observed almost immediately after sonication. The procedure of centrifugation and redispersion in toluene was repeated until the supernatant was free of polymer, as observed by the disappearance of the polymer optical absorption peak at 450 nm. The final precipitate is redispersed in THF, giving a final suspension which is stable for a couple of days.

This method seems to be dependent on the polymer molecular weight and no nanohybrids could be obtained through this method for **PHTcoAHT** of M_n = 5200 g mol^{-1}.

Effect of the temperature of Tour's reaction on the suspension of the non-covalent hybrid.

Temperature variation was performed using a Peltier module. To ensure a good thermal contact between the optical cell and the system, a square 10 mm x 10 mm cell was used. The nanohybrids solution was diluted about 100 times to avoid the saturation of the signal and reabsorption effects.

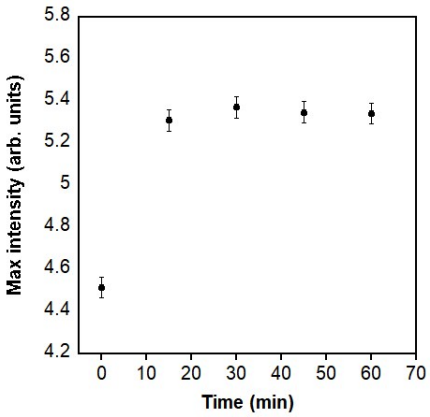


Figure S8: Evolution of the fluorescence intensity measured at the maximum of emission (568 nm) of SWNT/**PHTcoAHT** 36000 at 60°C. The first measurement corresponds to the fluorescence at room temperature.

Effect of isoamyl nitrite on the copolymer.

3.5 mg of **PHTcoAHT 5000** were dissolved in 4 mL of THF. 10 eq of isoamyl nitrite were added to the solution. The mixture was heated to 60 °C for 12 h. The resulting product was precipitated in methanol.

The polymer was recovered by precipitation in methanol. Its molecular mass was analyzed by MALDI-TOF mass spectroscopy (Figure S8). The spectrum shows that the mean molecular mass of the polymer before the reaction is centered at 3400 Da. It does not change significantly after reaction. The chains are therefore not cleaved under the reaction conditions. Moreover, in the same desorption/ionization conditions, the higher masses do not increase significantly, which proves that the reaction does not lead to oxidative coupling of the chains.

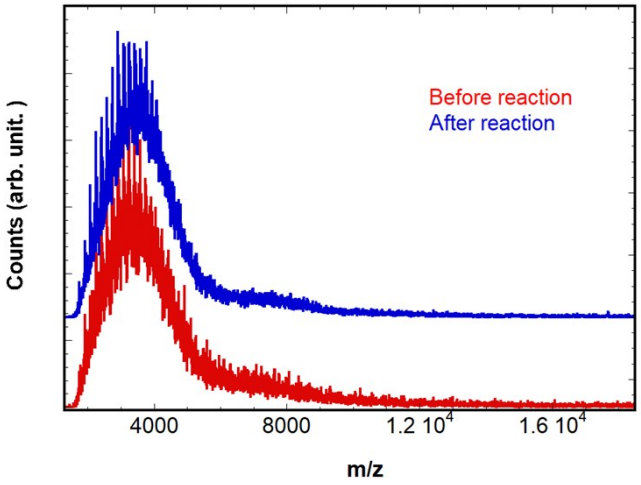


Figure S9: MALDI-TOF MS spectra of **PHTcoAHT 5000** (red) and of the same polymer after 12 h at 60 ° C with *iso*amyl nitrite in THF (blue).

The NMR spectra (not shown) of the crude and the starting polymers show no difference besides of changes in the features related to the aniline group, especially the singlet at 6.99 (thiophene proton) and the massif at 2.81 (thiophene-CH2), with

the same integral ratio. Only the features related to the aniline disappeared: doublets at 6.73 ppm (Ar H2 and H6) and at 6.62 ppm (Ar H3 and H5), the massif at 3.89 corresponding to the $C\mathbf{H_2}$-OC_6H_4-NH_2.

No changes were observed in UV-Vis, fluorescence and Raman (Figure S9) spectra. The resulting polymer was still able to form non-covalent nanohybrids with SWNTs,

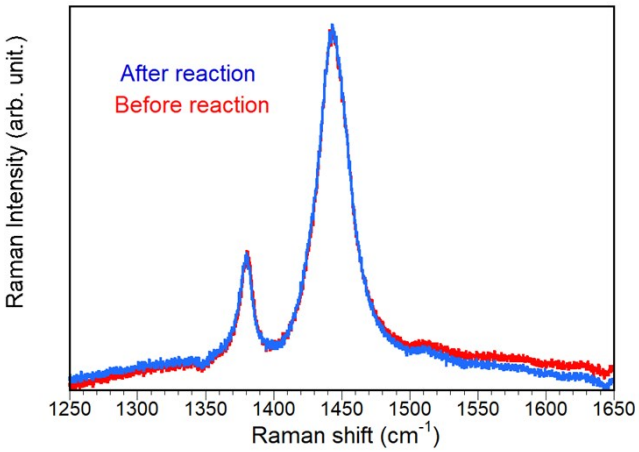


Figure S10: Raman spectra before and after reaction.

In conclusion the side anilines are transformed, but the backbone of the polymer is unaffected by the conditions of Tour's reaction.

Covalent functionalization of SWNTs with PHTcoAHT 5000

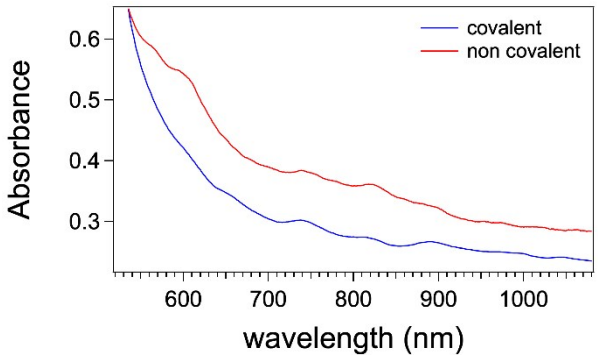


Figure S11: UV-vis spectra of the covalent (blue line left scale), and non-covalent (red line right scale) SWNT/**PHTcoAHT 5000**