Supporting Information

Resistive and Capacitive γ-Ray Dosimeters based on Triggered Depolymerization in Carbon Nanotube Composites

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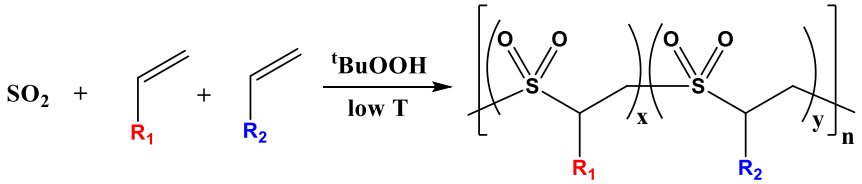
Contents

General Methods and Instrumentation

All chemicals were purchased from Sigma-Aldrich and were used as received, except for sulfur dioxide, which was purchased from Airgas. 6,5-chirality enriched SWCNTs were acquired from Sigma-Aldrich. Unless stated otherwise, all reactions were performed under an oxygen-free atmosphere of argon. Graduated flasks were used for polymerization reactions with condensed sulfur dioxide. NMR spectra were obtained on a Bruker Avance (400 MHz). ATR-FTIR spectra were obtained using a Thermo Scientific Nicolet 6700 FTIR with a Ge crystal for ATR. Polymer molecular weights were determined at room temperature on a HP series 1100 GPC system in THF at 1.0 mL/min (0.5 mg/mL sample concentrations), approximate molecular weights were estimated using a polystyrene calibration standard. UV-Vis-NIR absorption spectra were obtained using an Agilent Cary 5000 spectrophotometer. Raman spectra were collected using a Horiba LabRAM HR800 Raman spectrometer. X-ray photoelectron spectroscopy (XPS) was performed with a PHI Versaprobe II XPS spectrometer.

Polymer Synthesis & Characterization

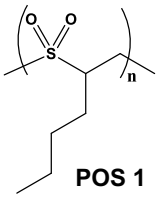
General Polymer Synthesis



The general synthesis of poly (olefin sulfone)s has been reported previously and was carried out following literature procedures. In brief, a typical polymerization procedure was carried out as follows: Sulfur dioxide was condensed into a graduated vessel at - 78 °C. After transferring the reaction vessel into a - 45 °C acetone/dry ice bath, the olefin monomer(s) were added in the desired ratio and the solution was stirred for 15 min. Then, *tert*-butyl hydroperoxide (5-6 M in decane) was added to the solution. The polymerization was allowed to proceed at - 45°C for 2 h. The polymerization was stopped by pouring the reaction mixture into cold methanol. After reaching RT, the solvent was evaporated and the resulting powder was redissolved, reprecipitated and washed three times before the polymer was dried under vacuum overnight. The synthesis of **POS 1**, **POS 2**, **POS 3**, and **POS 7** has been described previously and the characterization of these polymers was consistent with the previous reports.[1]

Synthetic Procedures

POS 1: *Poly (1-hexene sulfone)*

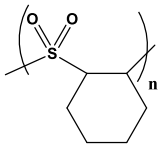


POS 1

Polymerization was carried out with 1-hexene (1 eq., 10.0 mmol, 0.84 g), SO_2 (10 eq., 100 mmol, 5.0 mL), and ^{t}BuOOH (2 mol % at 5.5 M in decane, 0.2 mmol, 25 μL), yielding **POS 1** as white solid (1.45 g, 98 %).

^{1}H-NMR (400 MHz, $CDCl_3$) δ = 3.8 (2 H, br), 3.4 (1 H, br), 2.1 (1 H, br), 1.9 (1 H, br), 1.4 (4 H, br), 0.9 (3 H, br *t*); ^{13}C-NMR (151 MHz, $CDCl_3$) δ = 57.1, 49.8, 28.3, 27.9, 22.5, 13.7; GPC (THF): M_n = 84 kDa, M_w = 191 kDa, PDI = 2.28; FT-IR (ATR): $\tilde{\nu}_{max}$ = 2960, 2872, 1309, 1126, 715; TGA: T_{decomp}= 246 °C.

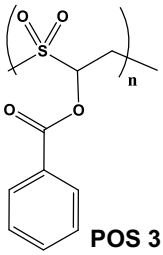
POS 2: *Poly (cyclohexene sulfone)*



POS 2

Polymerization was carried out with cyclohexene (1 eq., 10.0 mmol, 0.82 g), SO_2 (10 eq., 100 mmol, 5.0 mL), and ^{t}BuOOH (2 mol % at 5.5 M in decane, 0.2 mmol, 25 μL), yielding **POS 2** as white solid (1.10 g, 76 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 4.0 (2 H, br), 2.2 (4 H, br), 1.7 (4 H, br *d*); ^{13}C-NMR (151 MHz, $CDCl_3$) δ = 53.1, 22.6, 19.9; GPC (THF): M_n = 26 kDa, M_w = 58 kDa, PDI = 2.23; FT-IR (ATR): $\tilde{\nu}_{max}$ = 2943, 2862, 1458, 1302, 1120; TGA: T_{decomp}= 232 °C.

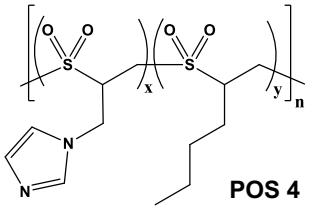
POS 3: *Poly (vinyl benzoate sulfone)*



POS 3

Polymerization was carried out with freshly distilled vinyl benzoate (1 eq., 10.0 mmol, 1.48 g), SO_2 (10 eq., 100 mmol, 5.0 mL), and ^{t}BuOOH (2 mol % at 5.5 M in decane, 0.2 mmol, 25 μL), yielding **POS 3** as yellowish solid (1.29 g, 61 %). ^{1}H-NMR (400 MHz, THF) δ = 8.1 (2 H, br), 7.6 (1 H, br), 7.4 (2 H, br), 6.8 (1 H, br), 4.2 (2 H, br); ^{13}C-NMR (151 MHz, THF) δ = 163.8, 134.0, 132.3, 130.3, 129.5, 128.4, 128.0, 80.1, 48.9; GPC (THF): M_n = 53 kDa, M_w = 115 kDa, PDI = 2.17; FT-IR (ATR): $\tilde{\nu}_{max}$ = 3012, 2914, 2321, 2304, 1748, 1321, 1249, 1105, 1083, 708; TGA: T_{decomp}= 188 °C.

POS 4: *Poly (1-hexene sulfone)-co-(1-allylimidazole sulfone)*

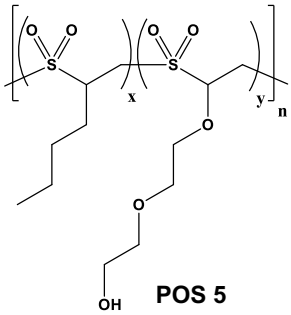


POS 4

Polymerization was carried out with 1-hexene (0.66 eq., 6.6 mmol, 0.55 g), freshly distilled 1-allyimidazole (0.33 eq., 3.3 mmol, 0.36 g), SO_2 (10 eq., 100 mmol, 5.0 mL), and ^{t}BuOOH (2 mol % at 5.5 M

in decane, 0.2 mmol, 25 μL), yielding **POS 4** with a x/y ratio of 1.0/9.8 (X_x. X_y were determined by comparison of the integration of the ^{1}H-NMR signal at 8.9 ppm - 1 H from repeat unit x - and at 0.9 ppm – 3H from repeat unit y) as white solid (1.17 g, 78 %). ^{1}H-NMR (400 MHz, DMF) δ = 8.9 (1 H, br), 7.7 (1 H, br), 7.6 (1 H, br), 6.2 (1 H, br *m*), 5.4 (2 H, br *m*), 5.0 (2 H, br *d*), 4.2 (1 H, br), 4.0 (1 H, br), 3.8 (1 H, br), 2.1 (2 H, br *d*), 1.6 (2 H, br), 1.4 (2 H, br), 0.9 (3 H, br); ^{13}C-NMR (151 MHz, DMF) δ =136.5, 132.9, 122.9, 121.5, 119.1, 57.1, 50.4, 49.1, 27.9, 22.4, 13.4; GPC (THF): M_n = 60 kDa, M_w = 135 kDa, PDI = 2.25; FT-IR (ATR): $\tilde{\nu}_{max}$ =3092, 2928, 2847, 1484, 1314, 1119, 716, 702; TGA: T_{decomp}= 148 °C.

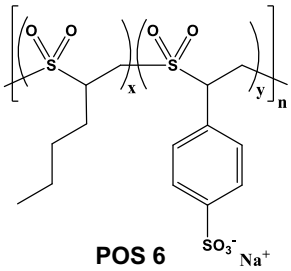
POS 5: *Poly (1-hexene sulfone)-co-(di(ethylene glycol) vinyl ether sulfone)*



POS 5

Polymerization was carried out with 1-hexene (0.33 eq., 3.3 mmol, 0.28 g), di(ethylene glycol) vinyl ether (0.66 eq., 6.6 mmol, 0.88 g), SO_2 (10 eq., 100 mmol, 5.0 mL), and ^{t}BuOOH (2 mol % at 5.5 M in decane, 0.2 mmol, 25 μL), yielding **POS 5** with a x/y ratio of 2.6/1.0 (X_x. X_y were determined by comparison of the integration of the ^{1}H-NMR signal at 8.9 ppm - 9 H from repeat unit x and 1 H from repeat unit y - and at 0.9 ppm – 3H from repeat unit y) as white solid (1.08 g, 59 %). ^{1}H-NMR (400 MHz, DMF) δ = 6.9 (1 H, br), 3.9 (4 H, br *m*), 3.53 (10 H, br *m*), 2.1 (1 H, br), 1.9 (1 H, br), 1.6 (2 H, br), 1.4 (2 H, br), 0.9 (3 H, br *t*); ^{13}C-NMR (151 MHz, DMF) δ = 151.7, 137.1, 127.8, 124.9, 72.9, 61.3, 57.1, 49.3, 34.1, 29.7, 27.8, 22.5, 20.4, 13.2; GPC (THF): M_n = 49 kDa, M_w = 122 kDa, PDI = 2.49; FT-IR (ATR): $\tilde{\nu}_{max}$ = 3408, 2945, 2858, 1421, 1302, 1110, 1073; TGA: T_{decomp}= 156 °C.

POS 6: *Poly (1-hexene sulfone)-co-(sodium 4-vinylbenzenesulfonate sulfone)*

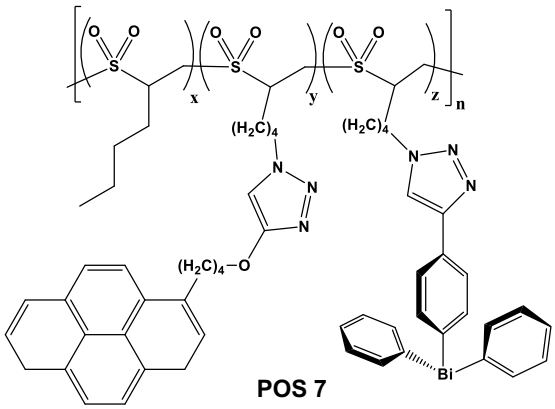


POS 6

Polymerization was carried out with 1-hexene (0.5 eq., 5.0 mmol, 0.28 g), di(ethylene glycol) vinyl ether (0.5 eq., 5.0 mmol, 0.88 g), SO_2 (10 eq., 100 mmol, 5.0 mL), and ^{t}BuOOH (2 mol % at 5.5 M in decane, 0.2 mmol, 25 μL), **POS 6**, poly (1-hexene sulfone)-co-(sodium 4-vinylbenzenesulfonate sulfone), yielding

POS 6 with an approximate x/y ratio of 3.1/1.0 (X_x. X_y were determined by the ratio of mass loss in TGA above (sodium 4-vinylbenzenesulfonate) and below (1-hexene) 300 °C) as white solid with limited solubility (3.18 g, 75 %). The Mol. Wt. of the polymer was determined using DLS in a mixture of DMF and H_2O: M_n = 44 kDa, M_w = 99 kDa, PDI = 2.24; FT-IR (ATR): $\tilde{\nu}_{max}$ = 3410, 2948, 2861, 1409, 1294, 1112; T_{decomp}= 262 °C.

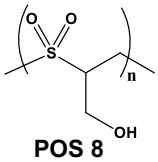
POS 7:



POS 7

The synthesis of POS 7 involved multiple steps and was carried out as described in our previous publication.[1a]

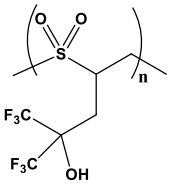
POS 8: *Poly (allyl alcohol sulfone)*



POS 8

Polymerization was carried out with allyl alcohol (1.0 eq., 10.0 mmol, 0.58 g), SO_2 (10 eq., 100 mmol, 5.0 mL), and ^{t}BuOOH (2 mol % at 5.5 M in decane, 0.2 mmol, 25 μL), yielding **POS 8** as a white solid (0.81 g, 66 %). The Mol. Wt. of the polymer was determined by DLS: M_n = 35 kDa, M_w = 66 kDa, PDI = 1.89; FT-IR (ATR): $\tilde{\nu}_{max}$ = 3484, 2987, 1302, 1119, 1067, 752; T_{decomp}= 273 °C.

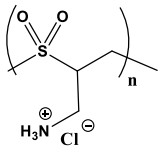
POS 9: *Poly (2-allyl hexafluoroisopropanol sulfone)*



POS 9

Polymerization was carried out with 2-allyl hexafluoroisopropanol (1.0 eq., 10.0 mmol, 2.08 g), SO_2 (10 eq., 100 mmol, 5.0 mL), and ^{t}BuOOH (2 mol % at 5.5 M in decane, 0.2 mmol, 25 μL), yielding **POS 9** as a white solid (2.47 g, 91 %). ^{1}H-NMR (400 MHz, THF) δ = 7.9 (1 H, br), 4.2 (2 H, br *m*), 3.9 (1 H, br *d*), 2.9 (1 H, br), 2.7 (1 H, br); ^{13}C-NMR (151 MHz, THF) δ = 122.7, 120.0, 117.0, 52.8, 49.7, 26.4; ^{19}F-NMR (376 MHz, THF) = -79.7; GPC (THF): M_n = 173 kDa, M_w = 339 kDa, PDI = 1.96; FT-IR (ATR): $\tilde{\nu}_{max}$ = 3280, 1306, 1228, 1131; TGA: T_{decomp}= 182 °C.

POS 10: *Poly (allylamine hydrochloride sulfone)*



POS 10

Polymerization was carried out with allylamine hydrochloride (1 eq., 10.0 mmol, 0.94 g), SO_2 (10 eq., 100 mmol, 5.0 mL), and ^{t}BuOOH (2 mol % at 5.5 M in decane, 0.2 mmol, 25 μL), yielding **POS 10** as yellowish solid (1.36 g, 86 %). GPC (THF): M_n = 37 kDa, M_w = 71 kDa, PDI = 1.89; FT-IR (ATR): $\tilde{\nu}_{max}$ = 2942, 1597, 1505, 1308, 1128; TGA: T_{decomp}= 182 °C.

NMR-Spectra

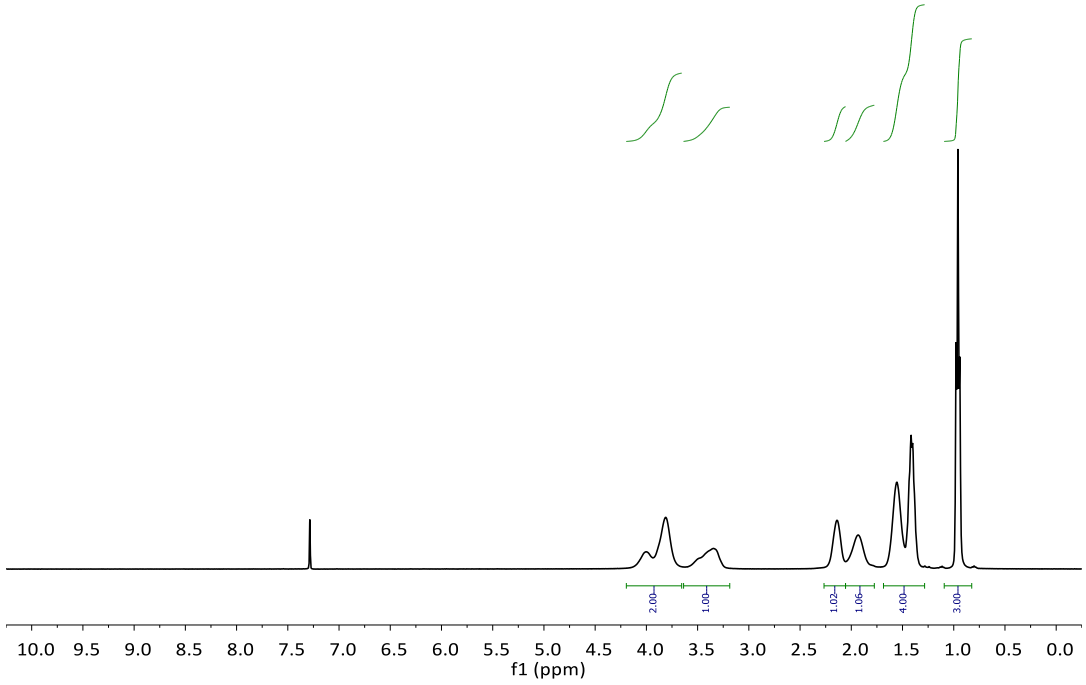


Figure S1. ^{1}H-NMR POS 1.

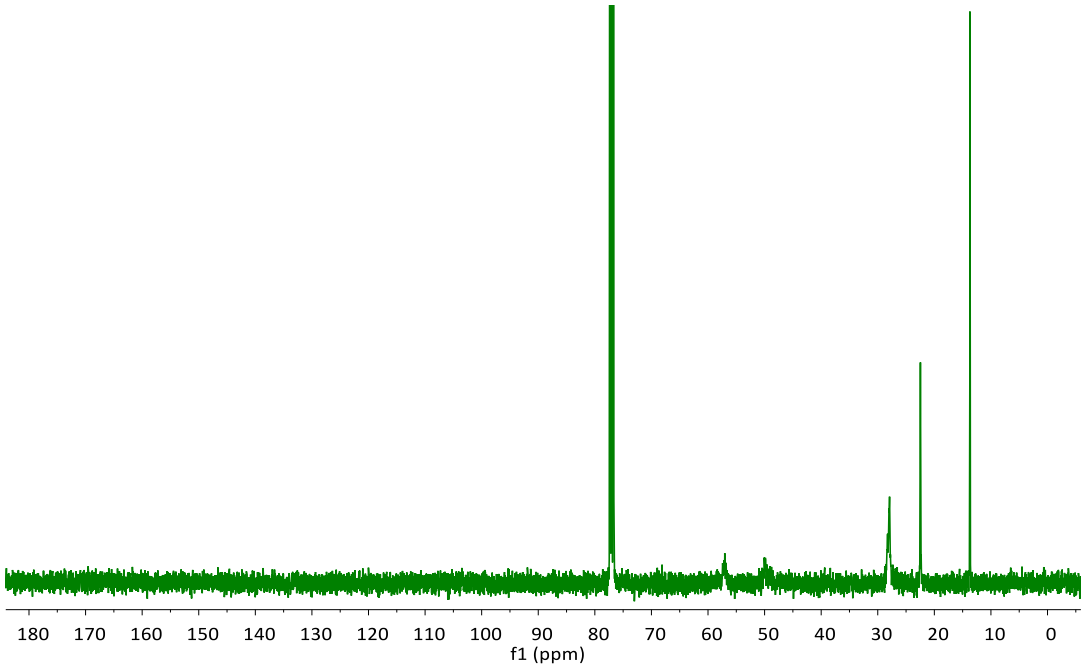


Figure S2. ^{13}C-NMR POS 1.

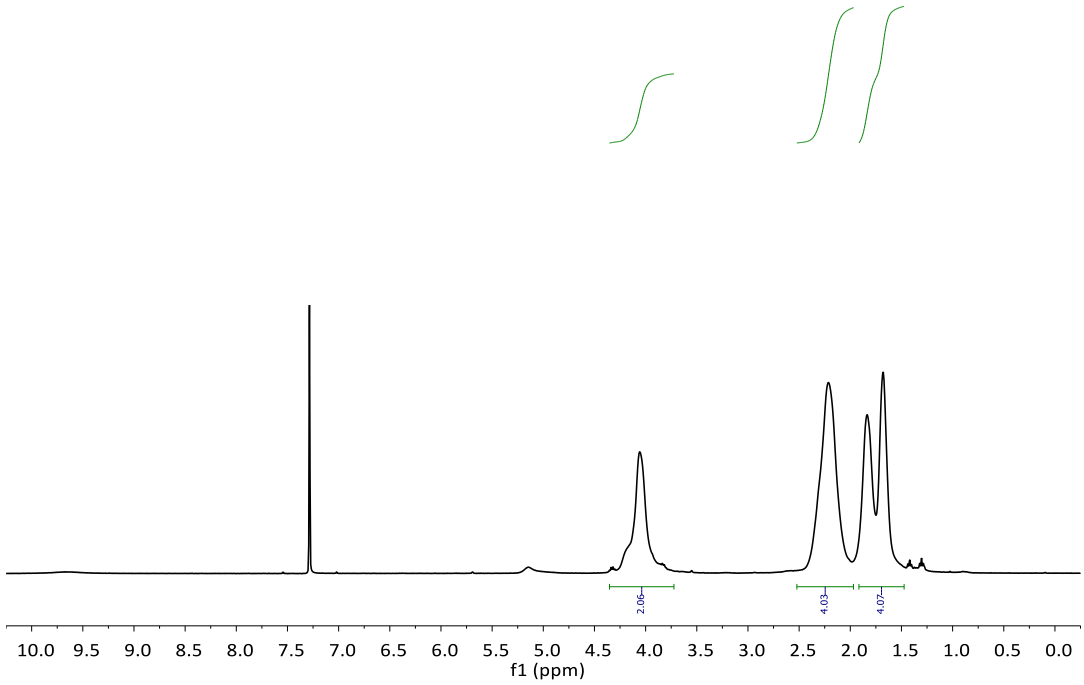


Figure S3. ^{1}H-NMR POS 2.

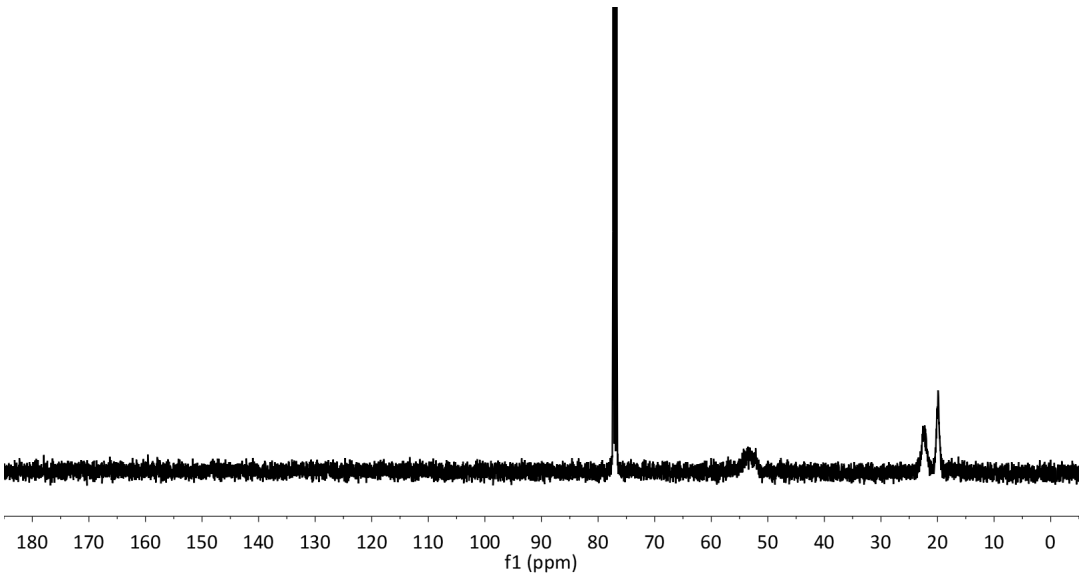


Figure S4. ^{13}C-NMR POS 2.

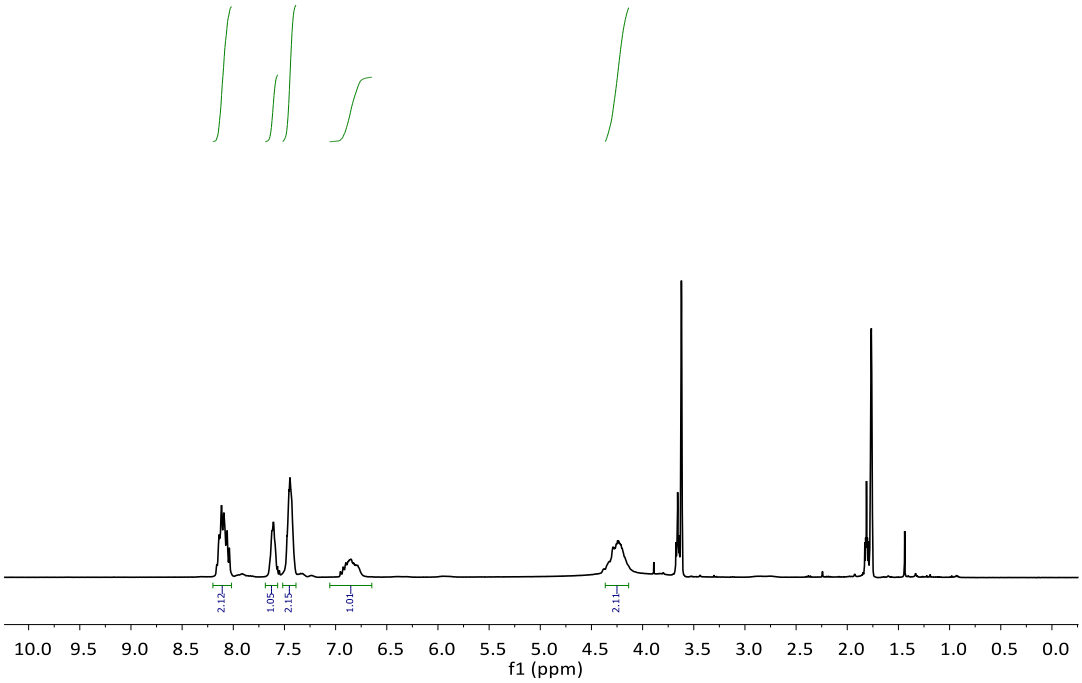


Figure S5. ^{1}H-NMR POS 3.

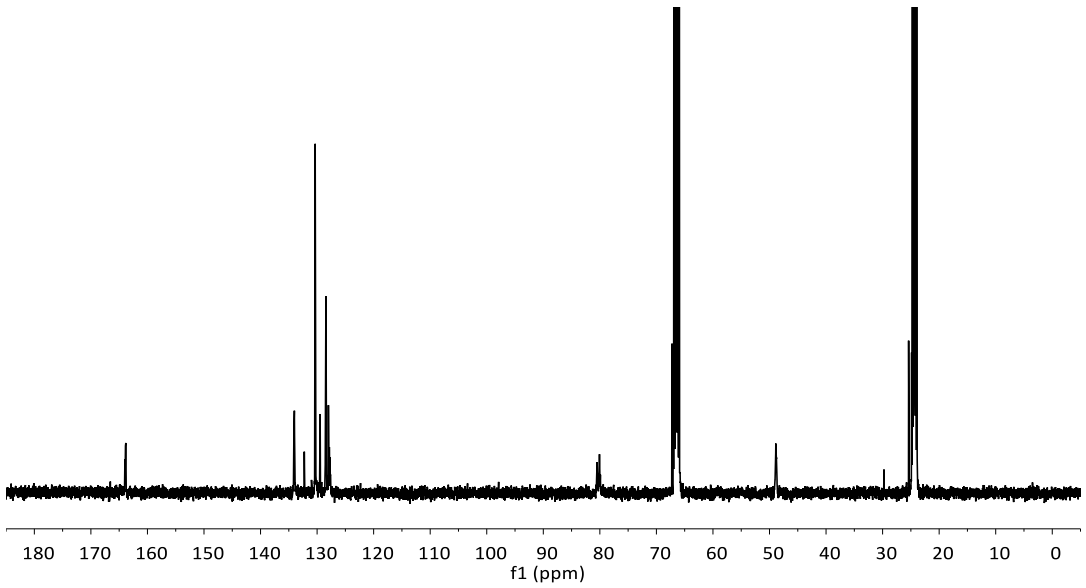


Figure S6. ^{13}C-NMR POS 3.

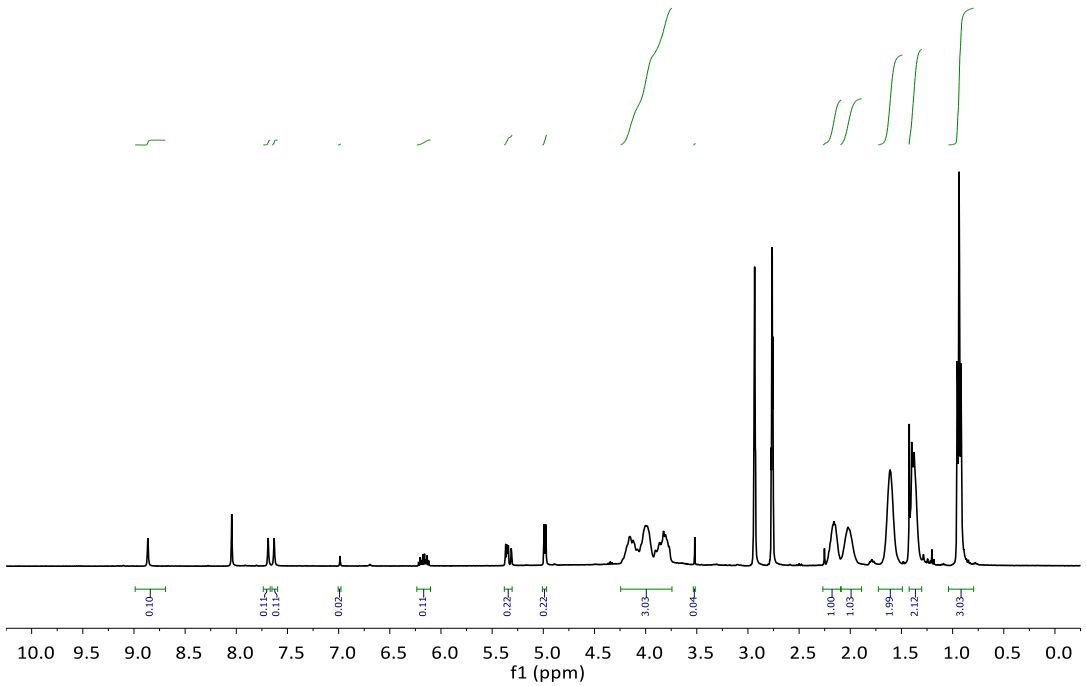


Figure S7. ^{1}H-NMR POS 4.

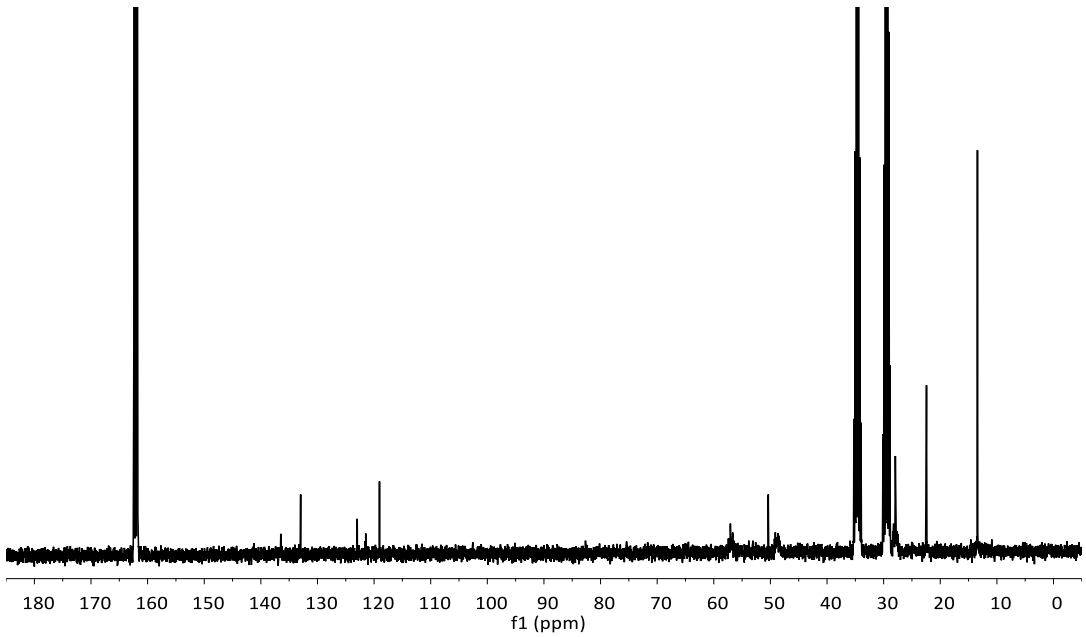


Figure S8. ^{13}C-NMR POS 4.

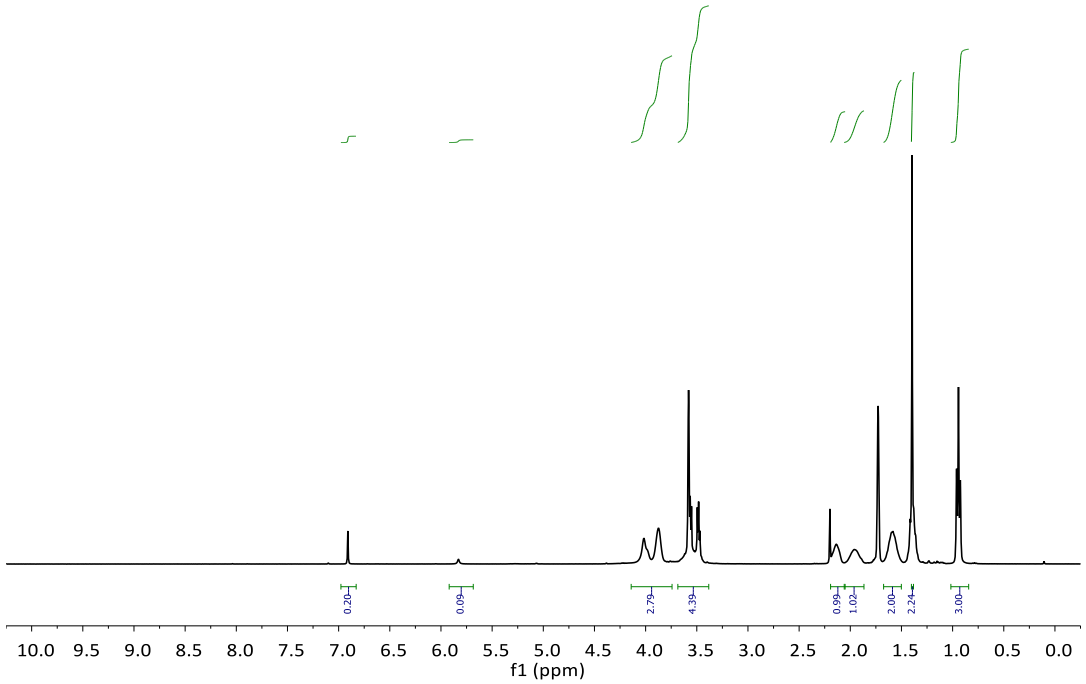


Figure S9. ^{1}H-NMR POS 5.

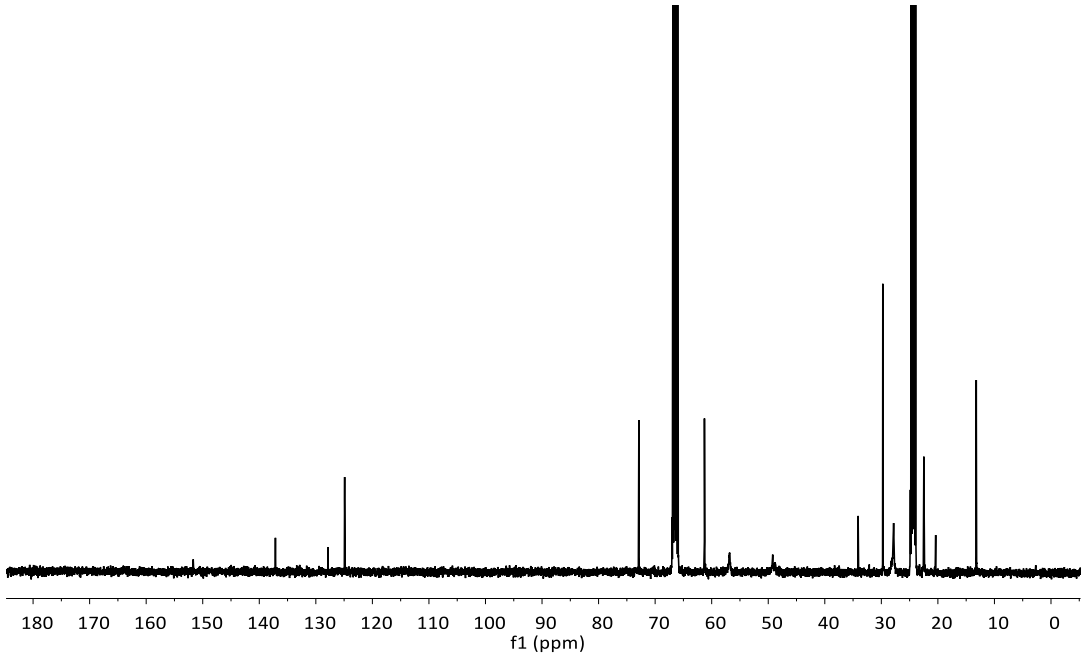


Figure S10. ^{13}C-NMR POS 5.

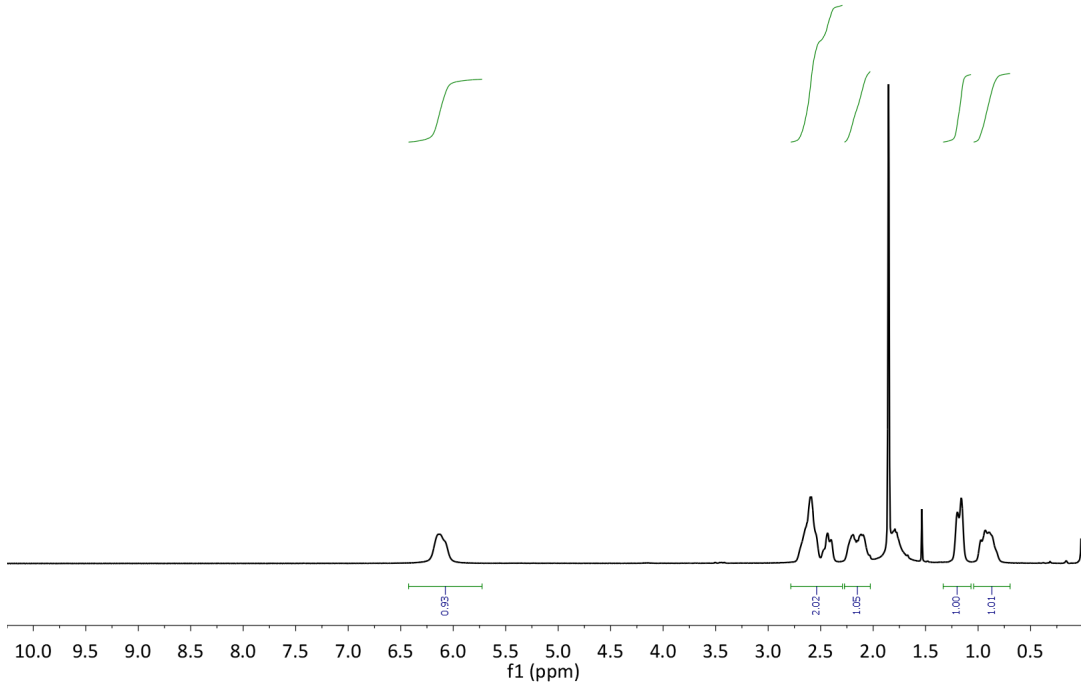


Figure S11. ^{1}H-NMR POS 9.

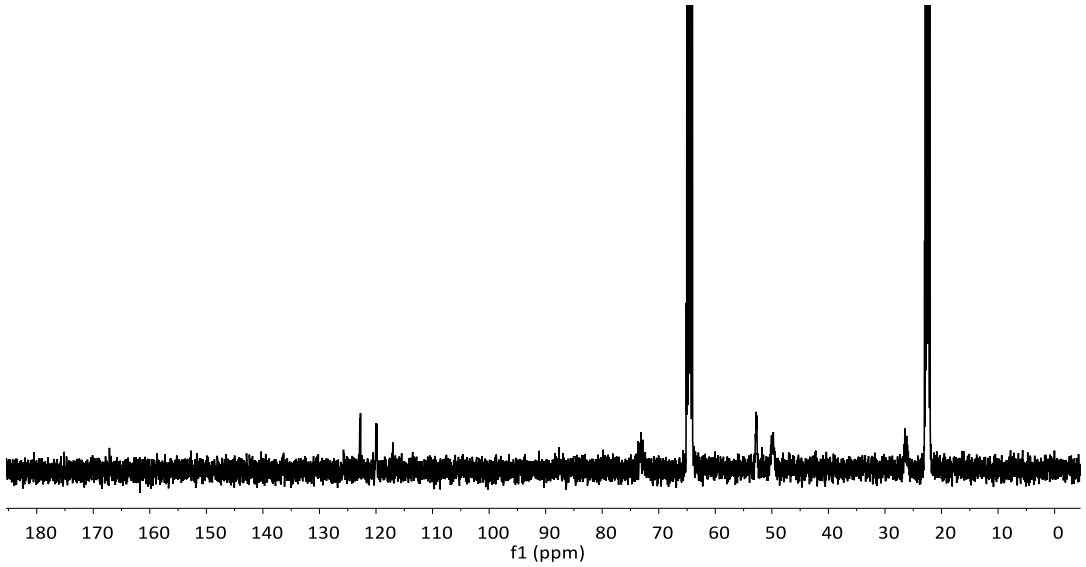


Figure S12. ^{13}C-NMR POS 9.

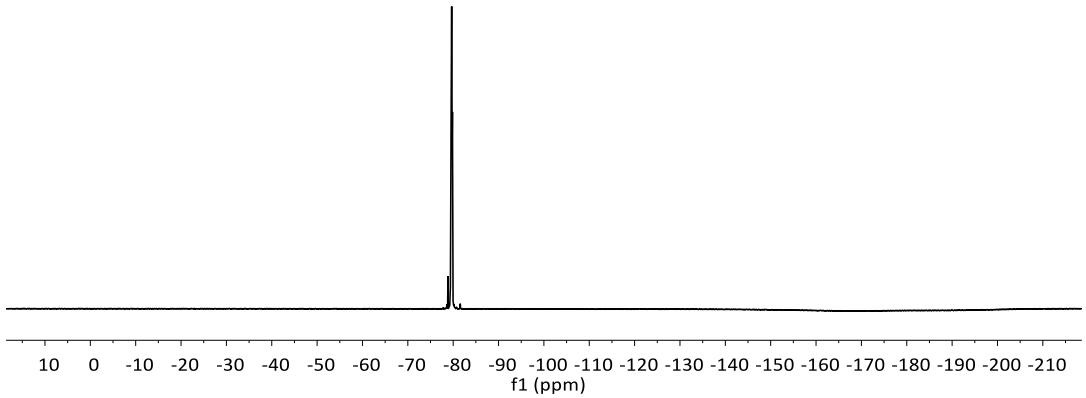


Figure S13. ^{19}F-NMR POS 9.

FT-IR-Spectra POSs 1-10

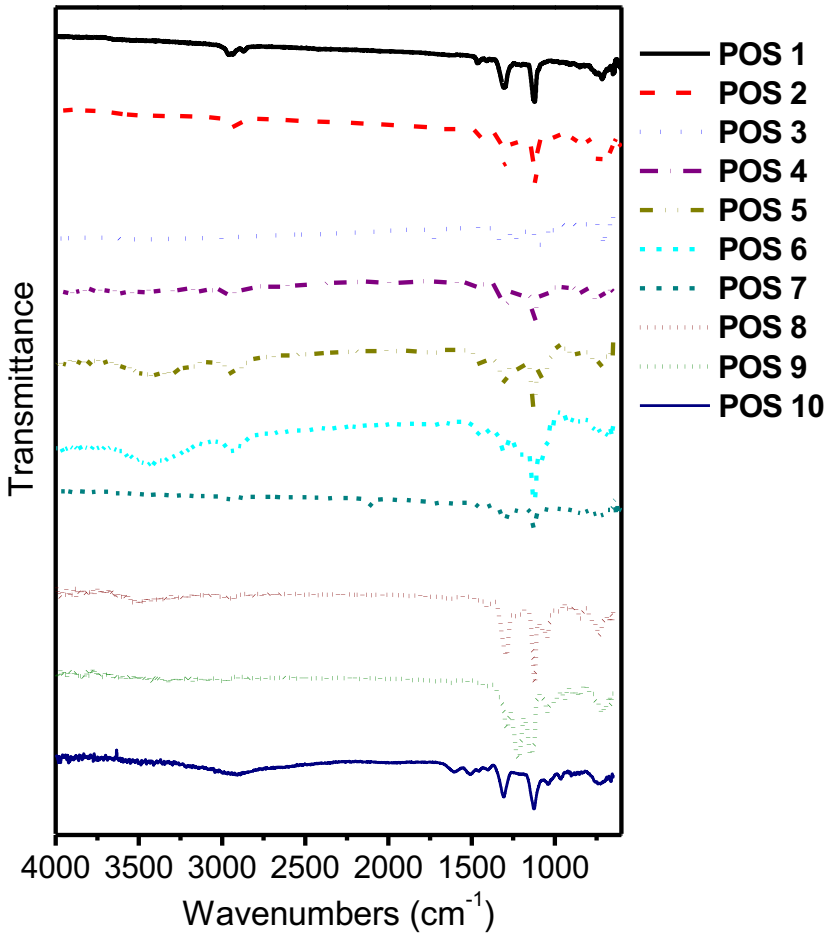


Figure S14. FT-IR spectra of Poly(olefin sulfone)s 1-10.

TGA curves POSs 1-10

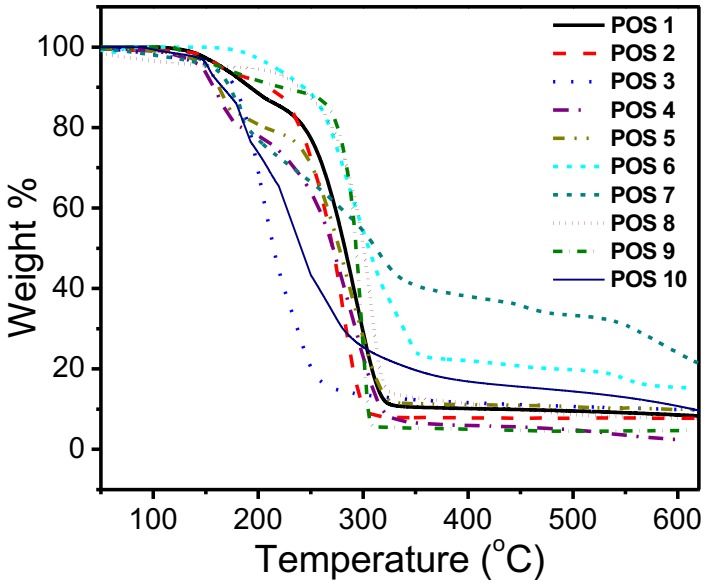


Figure S15. TGA weight loss curves of poly(olefin sulfone)s 1-10.

Functionalization of SWCNTs

The non-covalent functionalization of SWCNTs was accomplished by addition of 3.00 mg pyrene tetrasulfonate to an aqueous dispersion of SWCNTs prior to the coating with POS 10. The covalent attachment of pyridyl-units to the SWCNT sidewalls was accomplished by means of in-situ diazonium chemistry according to procedures described previously.[2] This fast and simple functionalization sequence yielded *f*-SWCNTs which was evidenced by Raman microscopy, UV-Vis-NIR spectroscopy, as well as X-ray photoelectron spectroscopy (XPS). In the Raman spectra, the increased relative intensity of the D-band to the G-band intensity provided evidence of the successful covalent surface functionalization.

Raman-spectra of pristine and functionalized SWCNTs

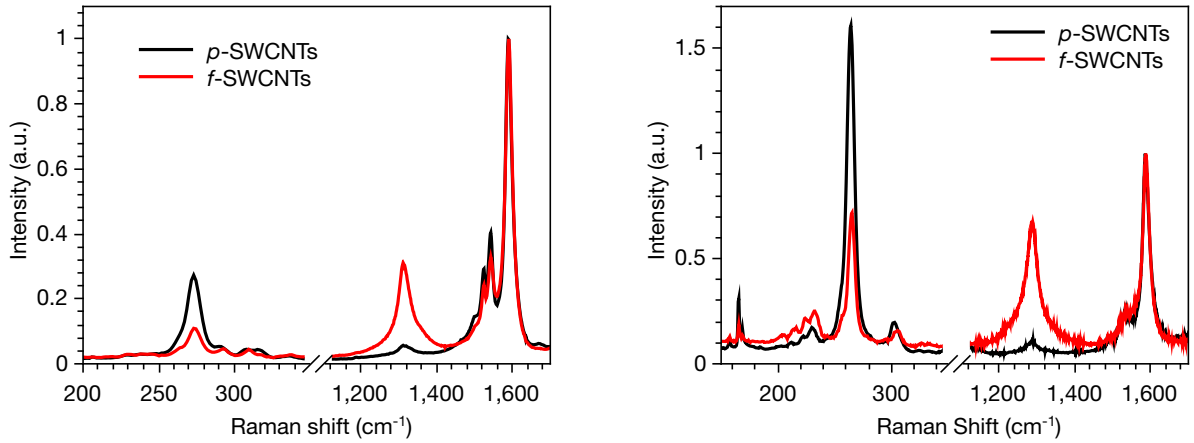


Figure S16. Raman spectra of *p*-SWCNTs and *f*-SWCNTs measured with 532 nm excitation (left) and 785 nm excitation (right).

XPS spectra of pristine and functionalized SWCNTs

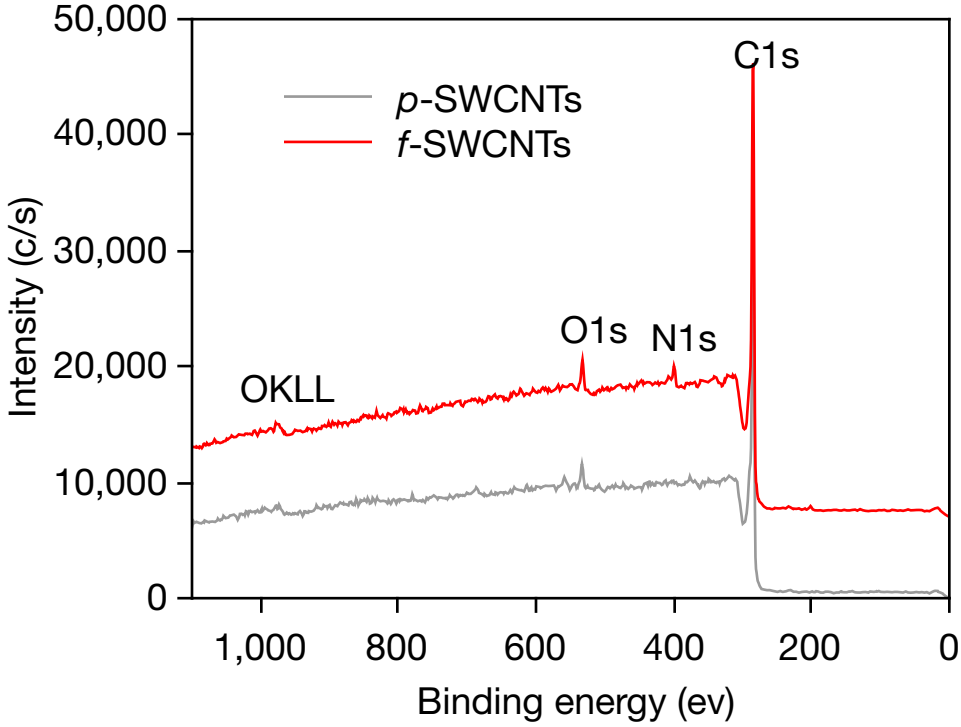


Figure S17. XPS spectra of pristine (*p*) and functionalized *(f)* SWCNTs.

Preparation of POS-SWCNT Dispersions

To a solution of POS (10 mg) in N,N-dimethylformamide or water (5 mL), SWCNTs (1 mg) were added and the resulting mixture was sonicated for 1 h in an ultrasonic bath (Branson, 3510) chilled with ice and then allowed to reach room temperature. Subsequently, the suspension was centrifuged for 30 min at 15,000 rpm and allowed to stand overnight undisturbed. The isolated supernatant was directly used for the device fabrication via spray coating or dropcasting unless otherwise indicated. For UV-Vis-NIR absorption spectroscopy, the isolated supernatant was further diluted.

Fabrication of γ-Ray Sensor Devices

For the preparation of resistive γ-ray sensor devices, glass slides (VWR Microscope Slides) were cleaned by sonication in acetone for 5 min followed by UV-ozone treatment using a UVO cleaner (Jelight Company Inc., Model 42) for 20 min. A 10 nm layer of chromium (99.99%, R.D. Mathis) and a subsequent 100 nm layer of gold (99.99%, R.D. Mathis) were deposited through a custom stainless steel mask using a thermal evaporator (Angstrom Engineering). The gap between one pair of gold electrodes was 1.0 mm. The desired amount of POS-SWCNT dispersion was loaded into an airbrush (Revolution BR, Iwata) and manually spray-coated on the gap of gold electrode pairs through a homemade transparency film (CG3700, 3M) mask. In order to prevent unwanted nozzle drips and over-wetting on the substrate surface, which resulted in non-uniform deposition of composites, the dispersion was sprayed intermittently multiple times with an injection rate of about 40 µL/min at a distance of 10 cm from the substrate placed on a 90 ^{o}C hot plate under N_2 carrier gas of 2 bar pressure. After the spraying process, the resulting substrate was thermally annealed at 90 ^{o}C for 2h. The sheet resistance of POS-SWCNT composite films before, during, and after γ-irradiation was measured using a Keithley 2400 source meter or a Keithley 2000 multimeter. For a read-out of the capacitance change of POS-SWCNT composites upon irradiation a SC-200 sensor chip platform provided by Seacoast Inc. was used. The sensor chips were coated via micro-pipetting the POS-SWCNT dispersions directly on top of the sensor chips. The capacitance change of POS-SWCNT composites deposited on Seacoast SC-200 sensor chips was recorded using the software SC-200 Series Data Logger.

γ-Irradiation

A Gammacell irradiator 'Gammacell 200' with a ^{60}Co source was used for γ-irradiation of both, the resistive and capacitive devices. Typically, devices were irradiated for 10 min to achieve a radiation dose of approximately $50 \cdot 10^3$ rad.

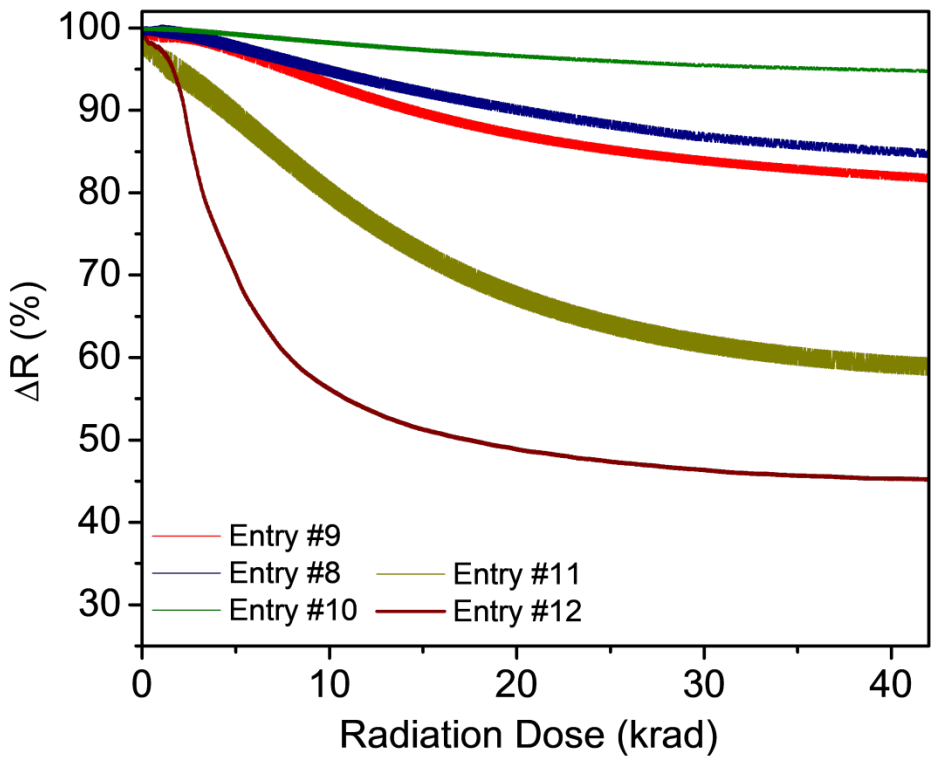


Figure S18. Real-time resistance changes of POS-SWCNT nanocomposites #8-#12 during γ-ray irradiation (see Table 1 for POS-SWCNT composites #8, #9, #10, #11, and #12).

References

1. (a) Lobez, J. M.; Swager, T. M., Radiation detection: Resistivity responses in functional poly (olefin sulfone)/carbon nanotube composites. *Angewandte Chemie International Edition* **2010,** *49* (1), 95-98; (b) Lee, O. P.; Lopez Hernandez, H.; Moore, J. S., Tunable Thermal Degradation of Poly (vinyl butyl carbonate sulfone) s via Side-Chain Branching. *ACS Macro Letters* **2015,** *4* (7), 665-668; (c) Bowmer, T. N.; O'donnell, J. H., Radiation degradation of poly (olefin Sulfone) s: a volatile product study. *Journal of Macromolecular Science—Chemistry* **1982,** *17* (2), 243-263; (d) Possanza Casey, C. M.; Moore, J. S., Base-Triggered Degradation of Poly (vinyl ester sulfone) s with Tunable Sensitivity. *ACS Macro Letters* **2016,** *5* (11), 1257-1260.

2. (a) Bosch, S.; Zeininger, L.; Hauke, F.; Hirsch, A., A Supramolecular Approach for the Facile Solubilization and Separation of Covalently Functionalized Single-Walled Carbon Nanotubes. *Chemistry-A European Journal* **2014,** *20* (9), 2537-2541; (b) Savagatrup, S.; Schroeder, V.; He, X.; Lin, S.; He, M.; Yassine, O.; Salama, K. N.; Zhang, X. X.; Swager, T. M., Bio-Inspired Carbon Monoxide Sensors with Voltage-Activated Sensitivity. *Angewandte Chemie International Edition* **2017,** *56* (45), 14066-14070.