

Supporting Information

Synthesis of a functionalized and photodegradable fluorene-based polymer for aqueous SWNT dispersion

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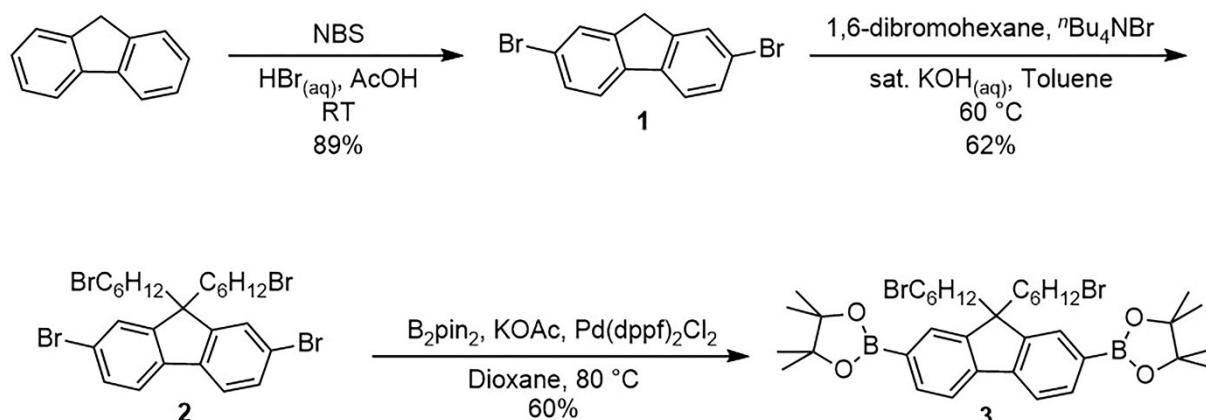
Experimental

General

Raw HiPco SWNTs were purchased from NanoIntegris (batch #HR37-0878) and used without further purification. All reagents were purchased from commercial chemical suppliers and used as received. Flash chromatography was performed using a CombiflashRF200 by Teledyne ISCO. Unless otherwise noted, compounds were monitored using a variable wavelength detector at 254 nm. Solvent amounts used for gradient or isocratic elution were reported in column volumes (CV). Columns were prepared in Biotage® SNAP KP-Sil cartridges using 40 – 63 μm silica or 25 – 40 μm silica purchased from Silicycle. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded at 25°C on a Bruker Avance 600 MHz instrument and shift-referenced to the residual solvent resonance. The polymer molecular weight and the dispersity were analyzed (relative to polystyrene standards) via GPC using a Waters 2695 Separations Module equipped with a Waters 2414 refractive index detector and a TSKgel SuperH2M-N with 3 μm particle diameter. THF with 2% acetonitrile was used as the eluent at a flow rate of 0.3 mL/min. Photoirradiation of the samples was performed in a home-built UV reactor equipped with two 25W lamps exhibiting emission at 365 nm. HPLC analysis was performed using a Waters Alliance 2695 separations module equipped with a 150 \times 46 mm Phenomenex Kinetex column (2.6 μm particle size) at 35 °C and a Waters 2487 Dual wavelengths absorbance detector. 5% of acetonitrile in water was used as the eluent at a flow rate of 1.23 mL/min. All Sonication was performed using a QSonica Q700 Sonicator equipped with a 13 mm probe. The amplitude of the probe was 60 μm and the sonication power was 30 Watts. Centrifugation of the polymer-SWNT samples was performed using a Beckman Coulter Allegra X-22 centrifuge. UV-Vis-NIR absorption spectra were recorded on a Cary 5000 spectrometer in dual beam mode,

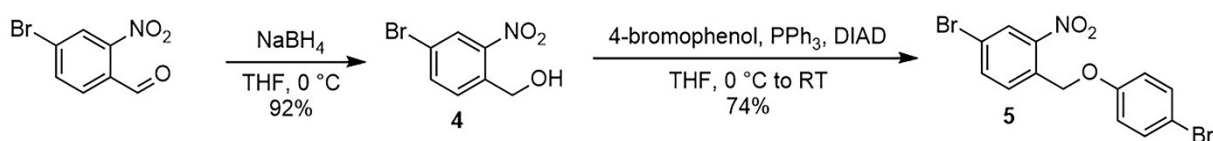
using matched 10 mm quartz cuvettes. Raman spectra were collected with a Renishaw InVia Laser Raman spectrometer, using two different excitation lasers: a 500 mW HeNe Renishaw laser (633 nm, 1800 L/mm grating); and a 300 mW Renishaw laser (785 nm, 1200 L/mm grating). Raman samples were drop-cast onto freshly cleaned silicon wafers and allowed to air-dry at room temperature. Thermogravimetric analysis was performed on a Mettler Toledo TGA/DSC 3+, and all measurements were conducted under an argon atmosphere. The TGA plots in Figure 5.4 were obtained by heating the sample to 100 °C for 5 minutes to drive off water, followed by heating to 800 °C (10 °C per min).

Synthetic procedures



Scheme S1 Synthesis of monomer **3**.

Compounds **1**, **2** and **3** were synthesized following literature procedures.¹



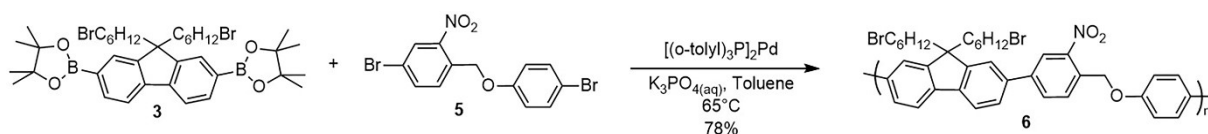
Scheme S2. Synthesis of monomer **5**.

(4-bromo-2-nitrophenyl)methanol (**5**)² (adapted from reference 2)

A 50 mL round bottom flask equipped with a stir bar was charged with 4-bromo-2-nitrobenzaldehyde (0.75 g, 3.3 mmol) in 11 mL of dry THF. NaBH₄ (0.25 g, 6.5 mmol) was added portionwise and the solution was stirred at 0 °C for 1h30 min, quenched with water (10 mL) and extracted with Et₂O (3 x 20 mL). The organic phases were combined, dried over MgSO₄ and concentrated *in vacuo*. The crude product was purified by flash chromatography (Hex/EtOAc 0% to 50%) to afford compound **4** as a light yellow powder (0.7 g, 92%). ¹H-NMR (600 MHz; CDCl₃): δ 8.25 (d, *J* = 2.0 Hz, 1H), 7.80 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 1H), 4.96 (d, *J* = 6.3 Hz, 2H), 2.36 (t, *J* = 6.4 Hz, 1H).

4-bromo-1-((4-bromophenoxy)methyl)-2-nitrobenzene (**5**)² (Adapted from reference 2)

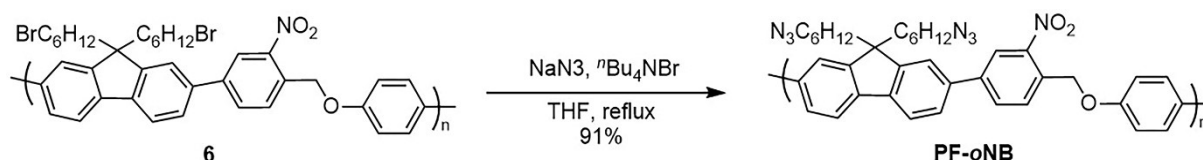
The reaction was performed in the absence of light. A 50 mL round bottom flask equipped with a stir bar was charged with **4** (0.5 g, 2.2 mmol), 4-bromophenol (0.45 g, 2.6 mmol) and triphenylphosphine (0.68 g, 2.6 mmol) in 17 mL of dry THF. The solution was stirred at 0 °C and diisopropyl azodicarboxylate (0.53 g, 2.6 mmol) was added dropwise within 10 min. The reaction was stirred overnight and concentrated *in vacuo*. The crude mixture was purified by flash chromatography (Hex/ DCM, 0% to 50%) to give compound **5** (0.62 g, 74%). ¹H-NMR (600 MHz; CDCl₃): δ 8.32 (d, *J* = 2.0 Hz, 1H), 7.81 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.42-7.40 (m, 2H), 6.88-6.85 (m, 2H), 5.40 (s, 2H).



Scheme S3. Synthesis of copolymer **6**.

Copolymer (6)

A 100 mL Schlenk tube equipped with a magnetic stir bar was charged with **3** (0.38 g, 0.52 mmol), **5** (0.20 g, 0.52 mmol), toluene (10.3 mL) and 3M $K_3PO_4(aq)$ (10.3 mL). The biphasic mixture was degassed by three freeze-pump-thaw cycles, then, while frozen under liquid nitrogen, $[(o\text{-tolyl})_3P]_2Pd$ (18 mg, 26 μ mol) was added under a positive pressure of nitrogen. The Schlenk tube was evacuated and backfilled with nitrogen four times, and the reaction mixture was vigorously stirred at 65°C for 6h. The phases were allowed to separate, and the organic layer was isolated and filtered through a single plug of celite and neutral alumina. The plug was thoroughly washed with THF and the filtrate was concentrated *in vacuo*. The crude polymer was precipitated into MeOH (~ 200 mL) and then filtered to afford **PF-oNB** as a yellow solid (0.3 g, 78%). $^1H\text{-NMR}$ (600 MHz; $CDCl_3$): δ 8.51-8.44 (m, 1H), 8.06-7.97 (m, 2H), 7.89-7.49 (m, 8H), 7.18-7.07 (m, 2H), 5.69-5.55 (m, 2H), 3.35-3.20 (m, 4H), 2.16-1.98 (m, 4H), 1.74-1.60 (m, 4H), 1.29-1.03 (m, 8H), 0.79-0.59 (m, 4H).

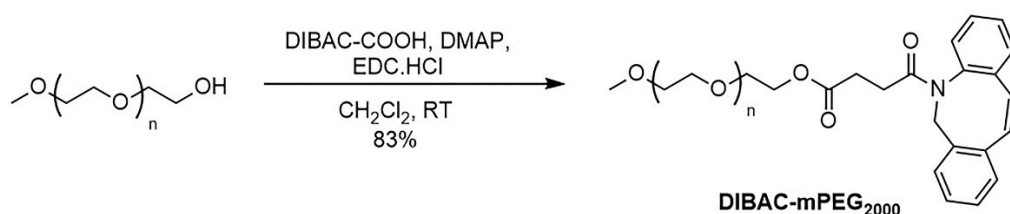


Scheme S4. Synthesis of **PF-oNB**.

PF-oNB

A 100 mL round bottom flask equipped with a magnetic stir bar and a reflux condenser was charged with **6** (0.29 g, 0.4 mmol), NaN_3 (0.26 g, 4.0 mmol), nBu_4NBr (0.26 g, 4.0 mmol), and THF (40 mL). The reaction mixture was heated to reflux for 12 h. The reaction mixture was filtered through an alumina plug, concentrated *in vacuo*, precipitated into MeOH (~ 200 mL)

and filtered to afford **PF-*o*NB** as a yellow solid (0.23 g, 91%). ¹H-NMR (600 MHz; CDCl₃): δ 8.50-8.46 (m, 1H), 8.05-7.97 (m, 2H), 7.89-7.49 (m, 8H), 7.18-7.10 (m, 2H), 5.66-5.53 (m, 2H), 3.13-3.08 (m, 4H), 2.12-2.00 (m, 4H), 1.57-1.51 (m, 4H), 1.43-1.35 (m, 4H), 1.14-1.04 (m, 8H), 0.77-0.64 (m, 4H).



Scheme S5. Synthesis of **DIBAC-mPEG₂₀₀₀**.

DIBAC-COOH was synthesized following literature procedures.³

DIBAC-mPEG₂₀₀₀

A 20 mL glass vial equipped with a stir bar was charged with poly(ethylene glycol) monomethyl ether (mPEG₂₀₀₀-OH) (100 mg, 50 μmol), DIBAC-COOH (46 mg, 200 μmol), 4-dimethylaminopyridine (3 mg, 25 μmol) in 1 mL of DCM. To the solution, N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC-HCl) (34 mg, 175 μmol) was added and the reaction was stirred at RT for 12h. The reaction mixture was diluted with ~ 5 mL of DCM, precipitated into 100 mL of 1:1 Hexanes/Et₂O and washed with cold Et₂O (3 x 20 mL). ¹H-NMR (600 MHz; DMSO-d₆): δ 7.68-7.65 (m, 1H), 7.62-7.61 (m, 1H), 7.53-7.45 (m, 3H), 7.40-7.33 (m, 1H), 7.30 (dd, *J* = 7.4, 1.3 Hz, 1H), 5.05-5.02 (m, 1H), 4.03-3.91 (m, 2H), 3.64-3.60 (m, 4H), 3.49 (m, 160H), 3.42 (m, 3H), 3.24 (s, 3H), 2.66-2.61 (m, 2H), 2.44-2.35 (m, 2H), 2.34-2.25 (m, 2H), 1.89-1.77 (m, 2H), 1.78-1.73 (m, 2H). ¹³C-NMR (151 MHz; DMSO-d₆): δ 172.0,

170.5, 151.4, 148.3, 132.4, 129.6, 128.9, 128.2, 128.0, 127.7, 126.8, 125.1, 122.5, 121.5, 114.3, 108.0, 71.3, 69.6, 68.1, 63.2, 58.0, 54.9, 29.1, 28.8.

PF-*o*NB-mPEG₂₀₀₀

A 100 mL round bottom flask equipped with a stir bar was charged with **PF-*o*NB** (14 mg, 21 μ mol) and **DIBAC-mPEG₂₀₀₀** (100 mg, 43 μ mol) in 21 mL of THF. The solvent was evaporated using a stream of N₂. The polymer was then precipitated into a mixture of 1:1 Hex/Et₂O (100 mL) to afford **PF-*o*NB-mPEG₂₀₀₀** (100 mg, 90%). ¹H-NMR (600 MHz; DMSO-d₆): δ 8.66-8.34 (m, 1H), 8.29-8.08 (m, 2H), 8.04-7.77 (m, 2H), 7.77-6.99 (m, 16H), 5.99-5.65 (m, 2H), 5.65-5.36 (m, 2H), 4.50-4.23 (m, 2H), 4.23-3.88 (m, 8H), 3.38-3.23 (m, 204H), 2.31-2.06 (m, 12H), 2.10-1.94 (m, 4H), 1.94-1.68 (m, 4H), 1.57-1.17 (m, 12H), 1.17-0.71 (m, 8H), 0.69-0.41 (m, 4H).

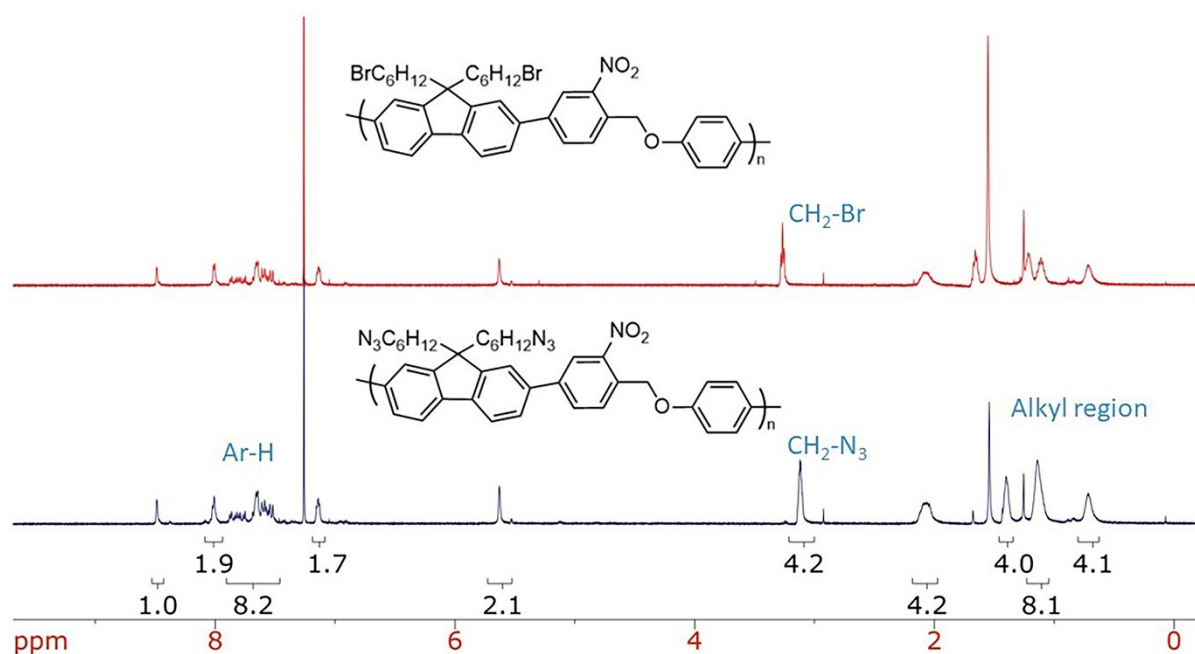


Figure S1. ¹H-NMR overlay of copolymer **6** (red) and **PF-*o*NB** (blue).

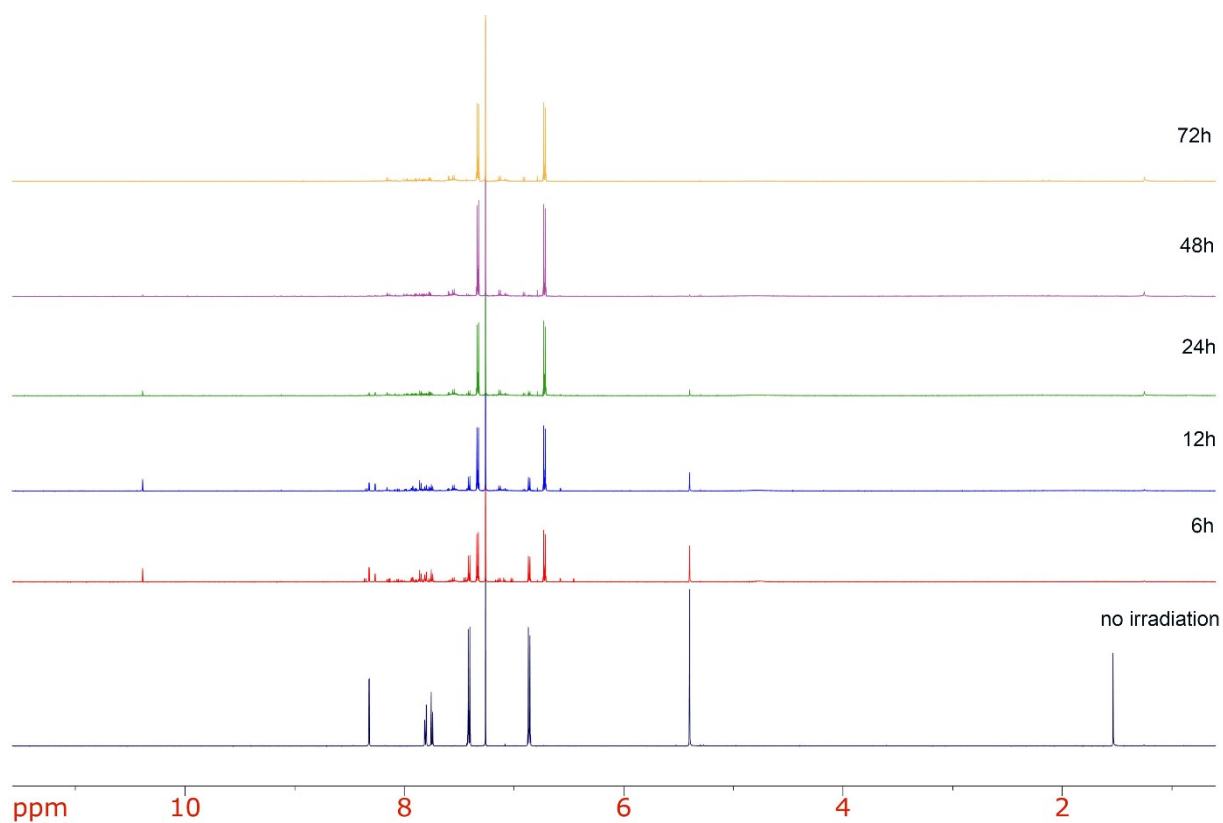


Figure S2. Full ^1H -NMR spectra overlay of monomer **5** in CDCl_3 upon irradiation at 365 nm for 72 h.

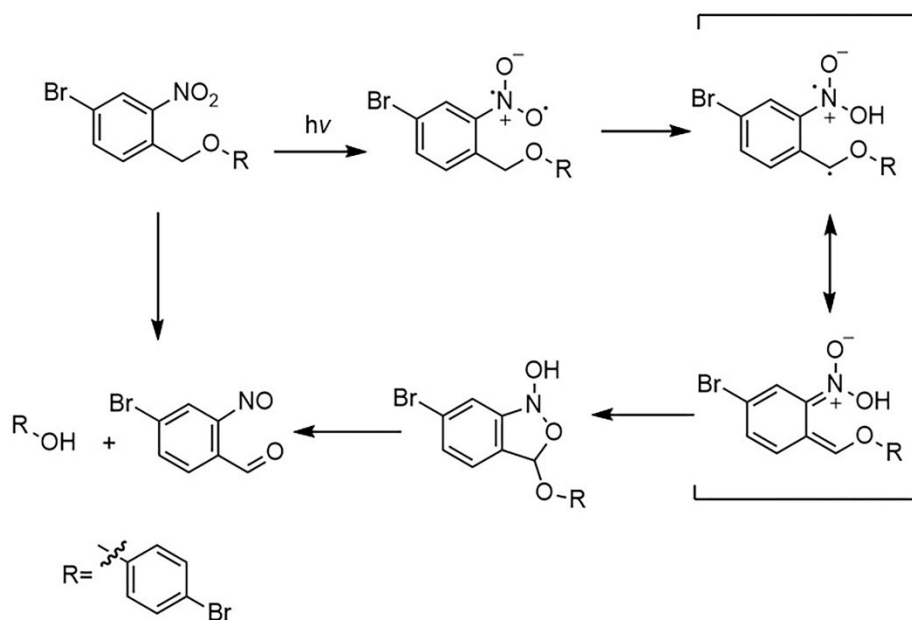


Figure S3. Photoisomerization mechanism of monomer **5**. Inspiration for this figure is adopted from reference 4.⁴

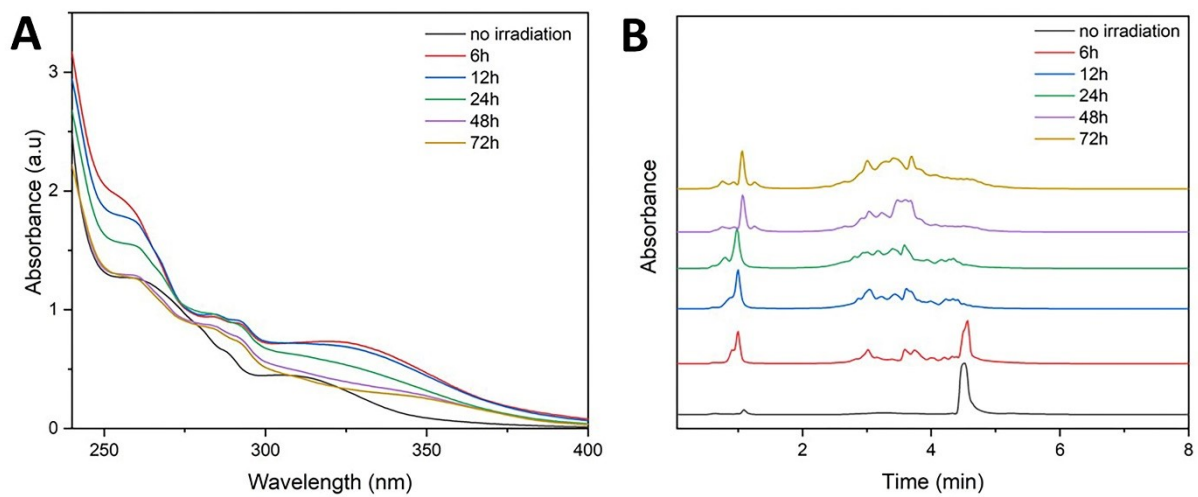


Figure S4. A) UV-Vis absorption spectral overlay of monomer **5** in THF (0.1 mg/mL) upon irradiation at 365 nm for 72 h and B) HPLC chromatogram overlay of monomer **5** upon irradiation at 365 nm for 72 h.

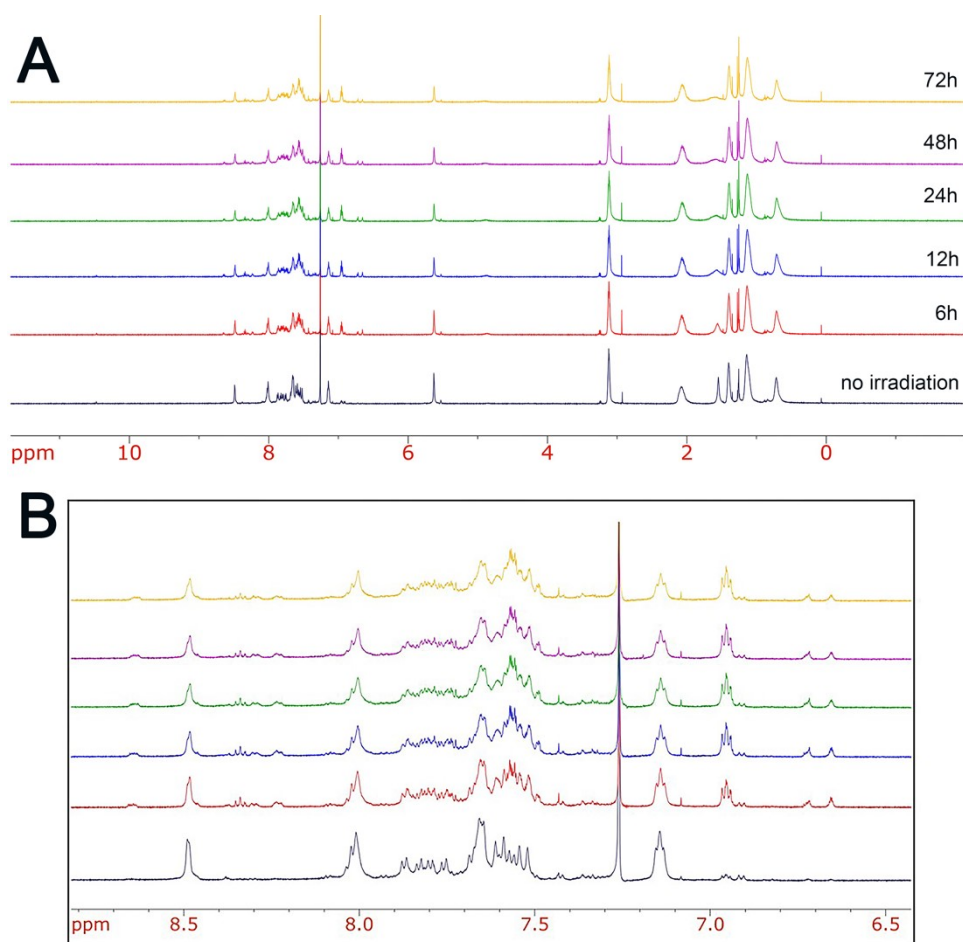


Figure S5. ^1H -NMR spectral overlay of **PF-oNB** in CDCl_3 upon irradiation at 365 nm for 72 h A) shows the full spectra and B) shows the aromatic region from 6.5 to 9 ppm.

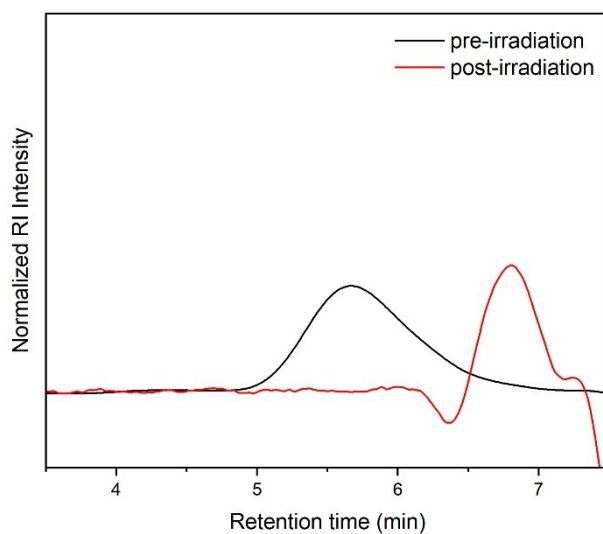


Figure S6. GPC trace of **PF-oNB** pre- (black) and post-irradiation (red) at 365 nm.

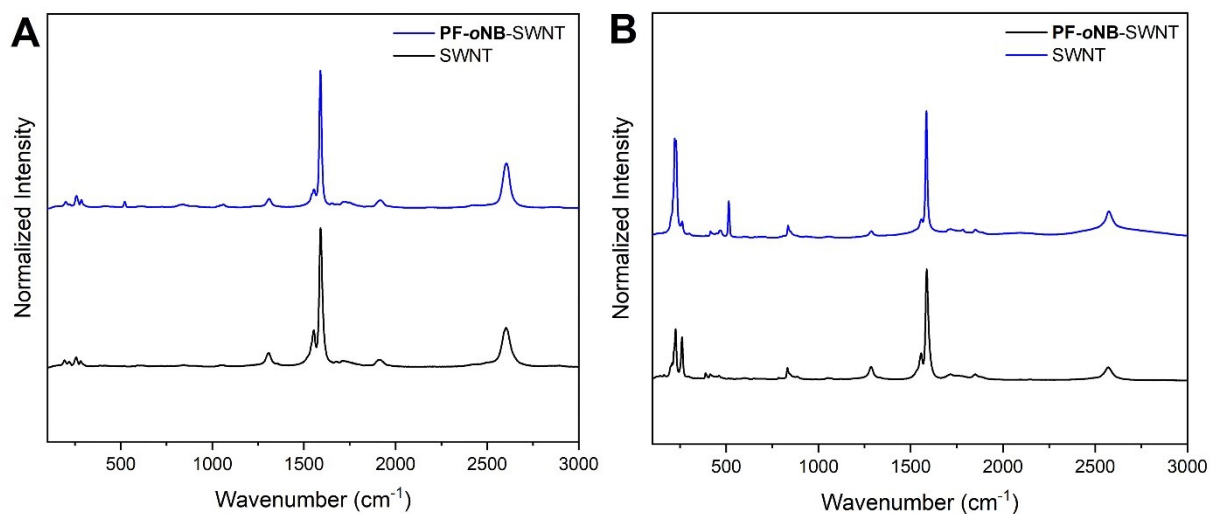


Figure S7. Full Raman spectra for HipCo **PF-oNB** -SWNT samples at A) $\lambda_{\text{ex}} = 633$ nm, B) $\lambda_{\text{ex}} = 785$ nm. All the spectra were normalized at ~ 1590 cm⁻¹.

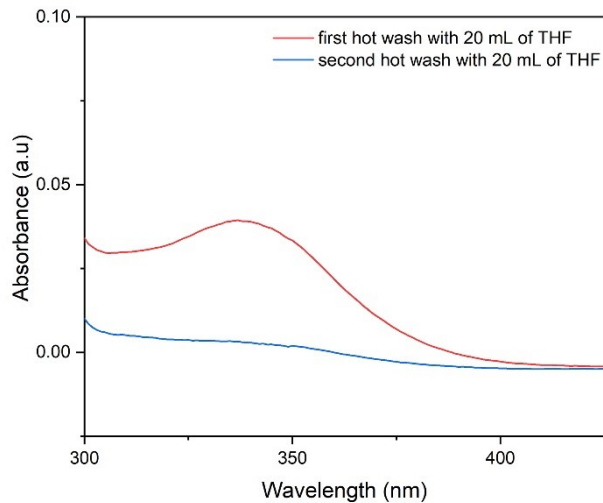


Figure S8. UV-Vis absorption spectral overlay of washing step of the SWNT residues with boiling THF post-irradiation.

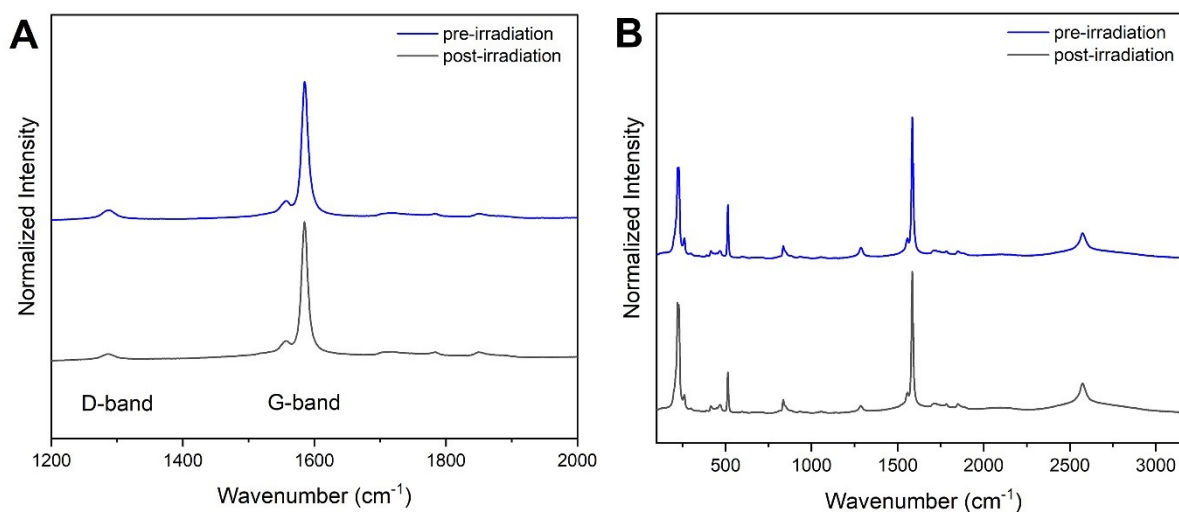


Figure S9. Raman spectra for HipCo **PF-oNB** -SWNT samples at $\lambda_{\text{ex}} = 785$ nm pre- and post-irradiation showing A) the G- and D-band and B) the full spectra. All the spectra were normalized at ~ 1590 cm⁻¹.

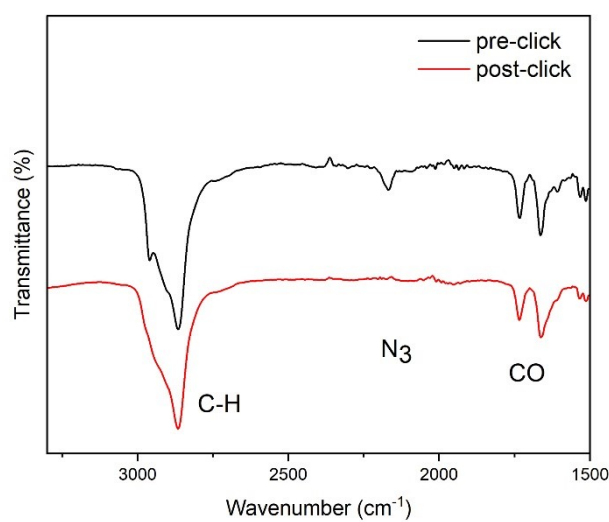


Figure S10. Overlay of FT-IR spectra of the SPACC reaction between **PF-oNB** and **DIBAC-mPEG₂₀₀₀**.

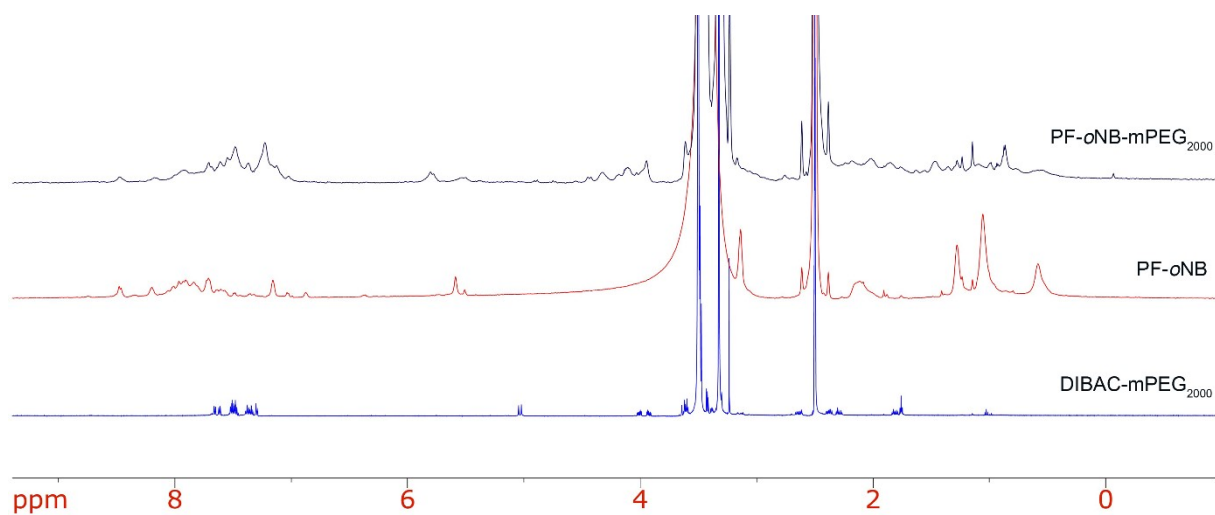


Figure S11. Overlay of $^1\text{H-NMR}$ spectra of PF-oNB, DIBAC-mPEG₂₀₀₀ and PF-oNB-mPEG₂₀₀₀ in DMSO-d₆.

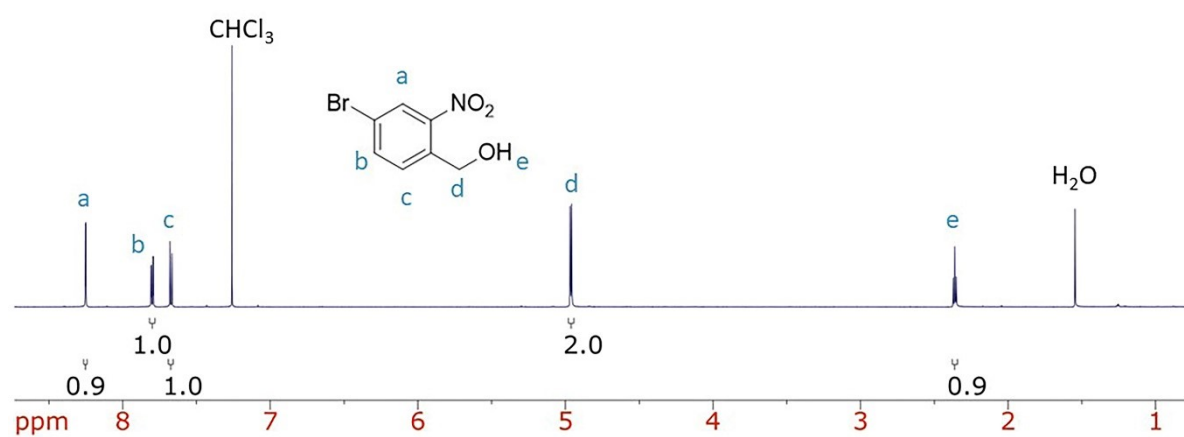


Figure S12. $^1\text{H-NMR}$ spectrum of compound **4** in CDCl_3 .

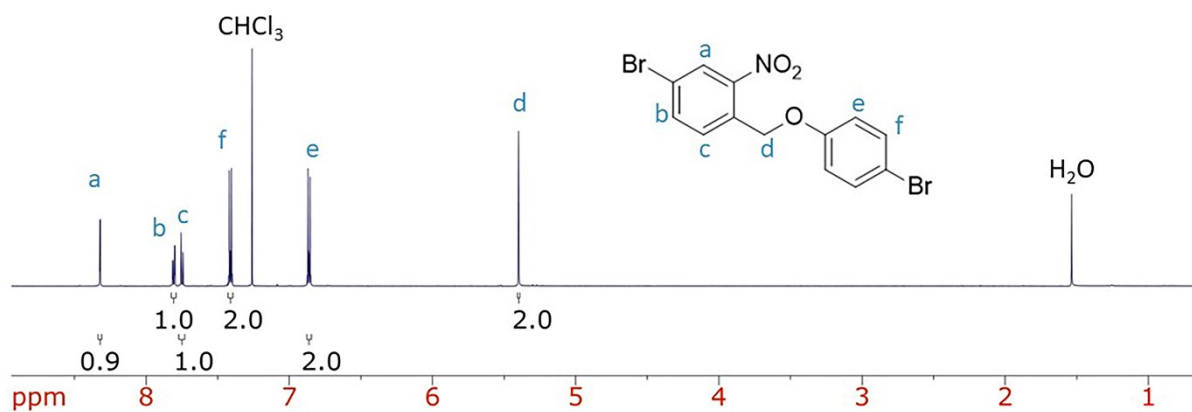


Figure S13. $^1\text{H-NMR}$ spectrum of monomer **5** in CDCl_3 .

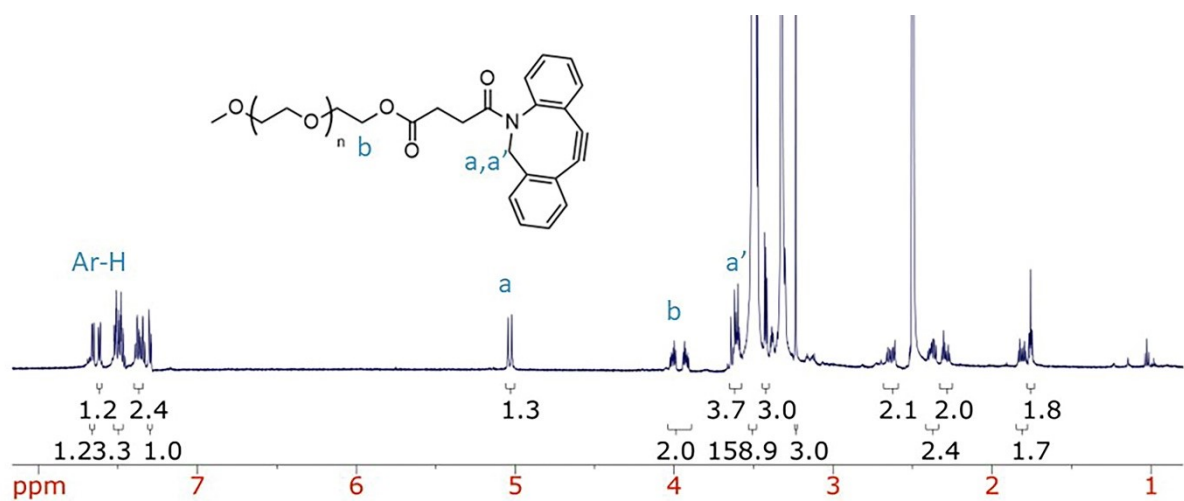


Figure S14a. $^1\text{H-NMR}$ spectrum of **DIBAC-mPEG**₂₀₀₀ in DMSO-d_6 .

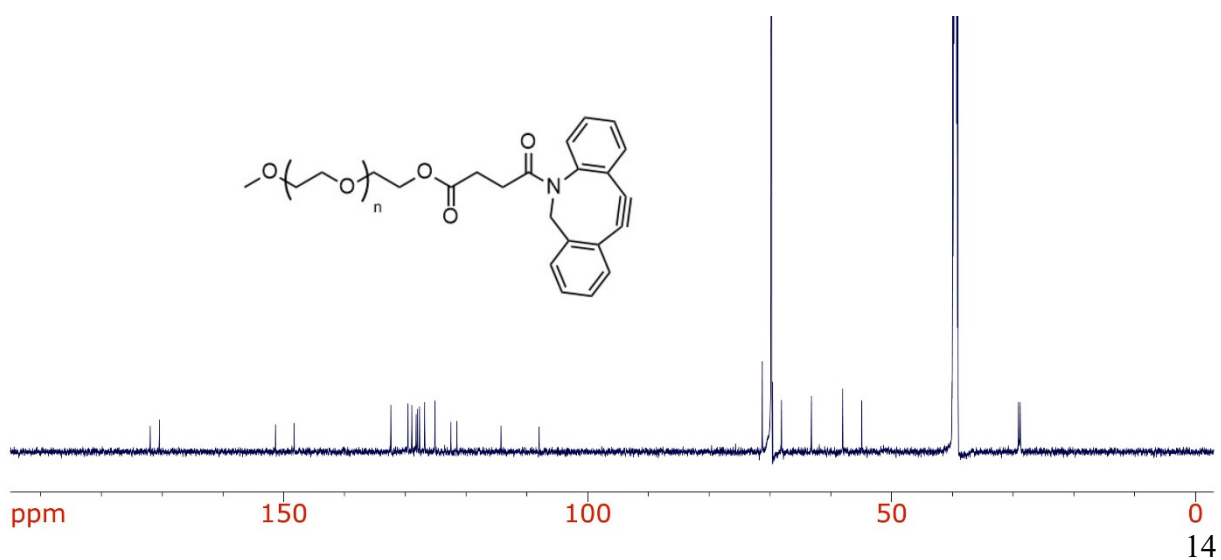


Figure S14b. ^{13}C -NMR spectrum of **DIBAC-mPEG₂₀₀₀** in DMSO-d_6 .

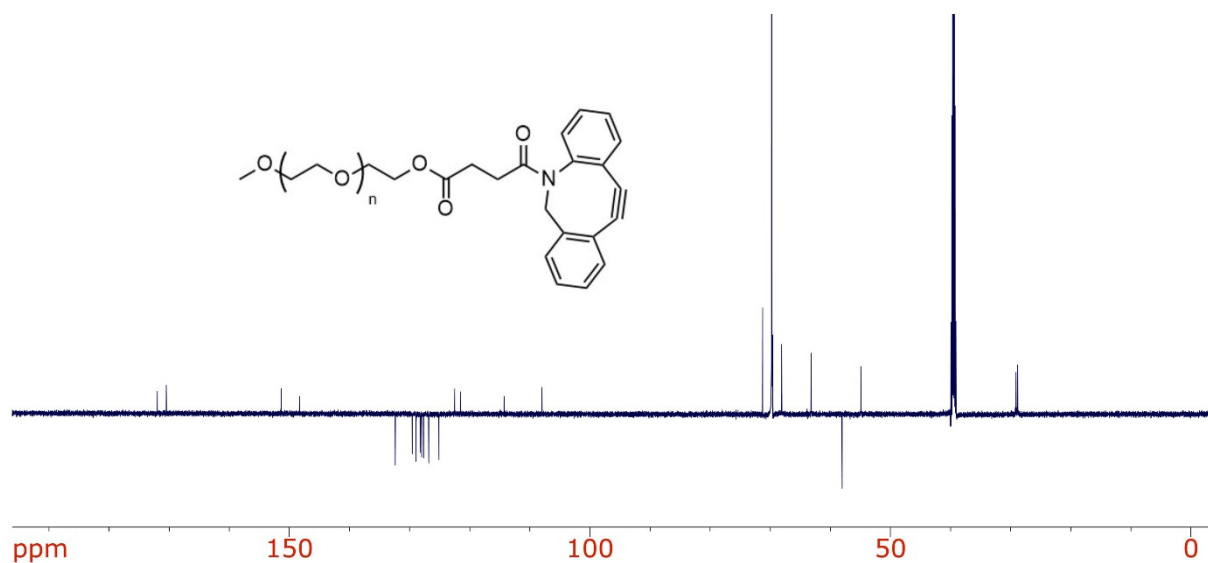


Figure S14c. DEPTq-135 NMR spectrum of **DIBAC-mPEG₂₀₀₀** in DMSO-d_6 .

References

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2. Lemasson, F., Tittmann, J., Hennrich, F., Stürzl, N., Malik, S., Kappes, M. M., Mayor, M. *Chem. Commun.*, 2011, **47**, 7428–7430.
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4. Zhao, H., Sterner, E. S., Coughlin, E. B., Theato, P. *Macromolecules*, 2012, **45**, 1723–1736.