Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPORTING INFORMATION

Functionalization of Polyfluorene-Wrapped Carbon Nanotubes via Copper-Mediated Azide-Alkyne Cycloaddition

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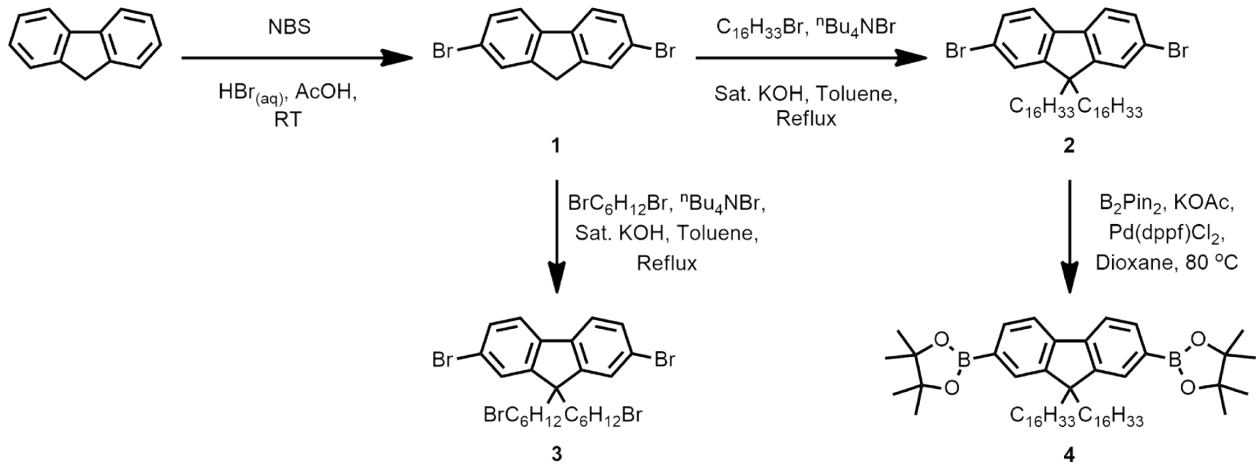
Experimental

General

Raw HiPCO SWNTs were purchased from NanoIntegris (batch #HR27-104, 10 wt % in anhydrous EtOH) and used without further purification. Reagents were purchased from commercial suppliers and used as received. Monomethyl ether polyethylene glycol (mPEG) was purchased from Fluka. Flash chromatography was performed using an IntelliFlash 280 system from Analogix. 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. NMR was performed on a Bruker Avance 600 MHz or 700 MHz instrument and shift-referenced to the residual solvent resonance. Polymer molecular weights and dispersities were analyzed (relative to polystyrene standards) via GPC using a Waters 2695 Separations Module equipped with a Waters 2414 refractive index detector and a Jordi Fluorinated DVB mixed bed column in series with a Jordi Fluorinated DVB 10^5 Å pore size column. THF with 2% acetonitrile was used as the eluent at a flow rate of 2.0 mL/min. Sonication was performed in a Branson Ultrasonic B2800 bath sonicator. Centrifugation of the polymer-SWNT samples was performed using a Beckman Coulter Allegra X-22 centrifuge. Infrared spectra were recorded using a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with a Smart iTX attenuated total reflectance (ATR) sample analyzer. UV-Vis-NIR spectra were recorded on a Cary 5000 spectrometer in dual beam mode, using matching 10 mm quartz cuvettes. Slit widths for both excitation and emission were set to 10 nm band-pass, and correction factor files were applied to account for instrument variations. Raman spectra were collected using a Renishaw InVia Laser Raman spectrometer with a 500 mW HeNe Renishaw laser (633 nm, 1800 L/mm grating). Laser intensity was set to 1% for the 633 nm excitation wavelength for the polymer-SWNT samples. X-ray photoelectron spectroscopy

(XPS) survey spectra were collected using a K-Alpha X-ray photoelectron spectrometer system from Thermo Scientific.



Scheme S1. Synthesis of monomers **3** and **4**.

Synthetic Procedures

2,7-dibromofluorene (1) (adapted from reference 1)

A round bottom flask equipped with a stir bar was charged with fluorene (33.2 g, 200 mmol), NBS (89.0 g, 500 mmol) and acetic acid (400 mL). While the mixture was stirring, conc. HBr (10 mL) was slowly added and then the reaction mixture was stirred at RT for 1.5 h. Water (200 mL) was added and the resulting suspension was filtered and washed with water to obtain an orange-white solid. The solid was recrystallized from a 1.5:1 v/v mixture of EtOH:acetone (~1.8 L total volume), and the mother liquor was recrystallized again from the same solvent mixture (~1.5 L total volume). The crops were combined to afford **1** (41.2 g, 64%) as a white solid. ^{1}H-NMR (600 MHz; $CDCl_3$): δ 7.67 (d, J = 1.1 Hz, 2H), 7.61 (d, J = 8.1 Hz, 2H), 7.51 (dd, J = 8.1, 1.8 Hz, 2H), 3.88 (s, 2H).

2,7-dibromo-9,9-dihexadecylfluorene (2) (adapted from reference 2)

A round bottom flask equipped with a stir bar was charged with **1** (2.7 g, 8.3 mmol), 1-bromohexadecane (6.36 g, 20.8 mmol), ^{n}Bu$_4$NBr (537 mg, 1.7 mmol), toluene (16.6 mL), and sat. $KOH_{(aq)}$ (16.6 mL). The reaction mixture was heated to 60 °C and stirred vigorously for 1 h under a nitrogen atmosphere. The biphasic mixture was allowed to separate and the organic layer was isolated. The aqueous phase was

extracted twice with diethyl ether (2 x 20 mL) and the organic extracts were combined and concentrated *in vacuo* to obtain a viscous green oil. The crude product was purified by flash chromatography (100 g column, 100% hexanes over 10 CV) to afford **2** as a white solid (5.19 g, 81%). ^{1}H-NMR (600 MHz; $CDCl_3$): δ 7.51 (d, J = 8.0 Hz, 1H), 7.46-7.43 (m, 2H), 1.92-1.88 (m, 2H), 1.24-1.03 (m, 26H), 0.88 (t, J = 7.0 Hz, 3H), 0.59-0.57 (m, 2H).

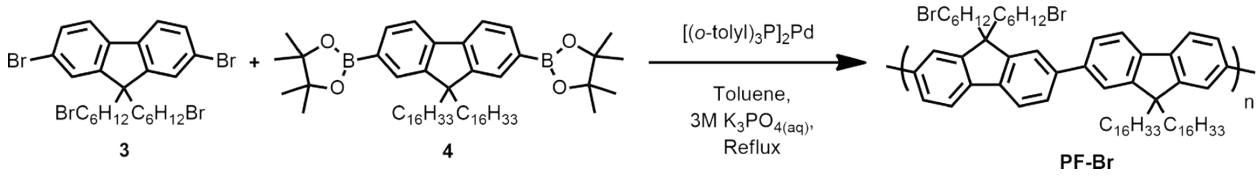
2,7-dibromo-9,9-bis(6-bromohexyl)fluorene (3) (adapted from reference 1)

A round bottom flask equipped with a stir bar was charged with **1** (5 g, 15.4 mmol), 1,6-dibromohexane (37.7 g, 154 mmol), toluene (31 mL), and sat. KOH (31 mL). ^{n}Bu_4NBr (1.0 g, 3.1 mmol) was then added and the reaction mixture was heated to 60 °C and stirred vigorously for 1 h under a nitrogen atmosphere. The biphasic mixture was allowed to separate, and the organic layer was isolated. The aqueous phase was extracted twice with diethyl ether (2 x 120 mL) and the organic extracts were combined and concentrated *in vacuo* to obtain a viscous green oil. Excess 1,6-dibromohexane was removed using vacuum distillation (1 mbar, 115 °C) to obtain a viscous yellow oil. The crude mixture was purified by flash chromatography (100 g column, 0 to 20% CH_2Cl_2 in hexanes over 10 CV) to obtain a white solid containing two spots by TLC. The crude product was recrystallized from MeOH (~250 mL) to afford **3** as a white solid (4.4 g, 44%). ^{1}H-NMR (600 MHz; $CDCl_3$): δ 7.53-7.52 (m, 1H), 7.47-7.43 (m, 2H), 3.31-3.28 (t, 2H), 1.94-1.91 (m, 2H), 1.68-1.66 (m, 2H), 1.22-1.19 (m, 2H), 1.10-1.07 (m, 2H), 0.60-0.57 (m, 2H).

2,2'-(9,9-dihexadecylfluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**4**) (adapted from reference 2)

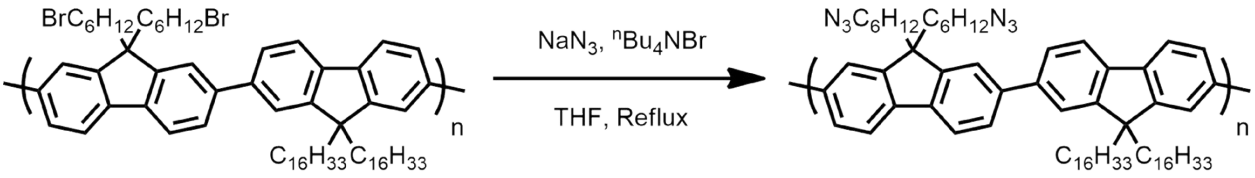
A round bottom flask equipped with a stir bar was charged with **2** (5.2 g, 6.7 mmol), B_2Pin_2 (3.76 g, 14.8 mmol), KOAc (1.98 g, 20.2 mmol), and dioxane (28 mL). $Pd(dppf)_2Cl_2$ (165 mg, 202 μmol) was added and then the reaction mixture was stirred at 80 °C for 12 h. The reaction mixture was partitioned with water and extracted thrice with Et_2O. The organic extracts were combined and dry loaded onto silica (9.9

g). The crude product was purified by flash chromatography (100 g column, 0 to 70% CH_2Cl_2 in hexanes over 10 CV) to afford **3** as a white solid (4.88 g, 63%). ^{1}H-NMR (600 MHz; $CDCl_3$): δ 7.80 (d, J = 7.5 Hz, 1H), 7.74-7.71 (m, 2H), 2.00-1.97 (m, 2H), 1.39 (s, 12H), 1.24-0.99 (m, 26H), 0.87 (t, J = 7.0 Hz, 3H), 0.55-0.53 (m, 2H).



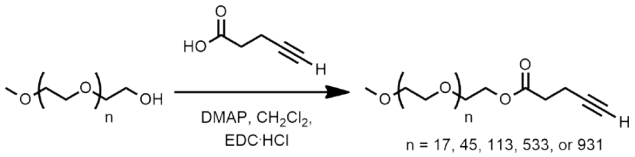
Poly(dihexadecylfluorene-*alt*-bis(bromohexyl)fluorene) (PF-Br)

A Schlenk tube equipped with a stir bar was charged with **3** (447.7 mg, 0.69 mmol), **4** (597 mg, 0.69 mmol), toluene (4.9 mL), and 3M $K_3PO_{4(aq)}$ (4.9 mL). The biphasic mixture was degassed by three freeze-pump-thaw cycles, then, while frozen under liquid nitrogen, [(*o*-tol)$_3$P]$_2$Pd (18 mg, 2.5 μmol) 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 80 °C for 12 h. 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 flow-through was concentrated *in vacuo*. The crude polymer was precipitated into MeOH (~300 mL) and then filtered to afford **PF-Br** as a yellow solid (478 mg, 63%). ^{1}H-NMR (700 MHz; $CDCl_3$): δ 7.85-7.83 (m, 4H), 7.73-7.68 (m, 8H), 3.30 (t, 4H), 2.17-2.11 (m, 4H), 1.72-1.69 (m, 4H), 1.30-1.13 (m, 60H), 0.87 (t, 6H). GPC: M_n = 125.3 kDa, Đ = 3.34.



Poly(dihexadecylfluorene-*alt*-bis(azidohexyl)fluorene) (PF-N_3)

A round bottom flask equipped with a stir bar and reflux condenser was charged with **PF-Br** (400 mg, 0.36 mmol), NaN_3 (236 mg, 3.6 mmol), $^nBu_4NBr$ (234 mg, 0.73 mmol), and THF (60 mL) and the reaction mixture was heated to reflux for 12 h. The reaction mixture was filtered through an alumina plug and washed thoroughly with THF, then the solution was concentrated *in vacuo* and precipitated into MeOH (~200 mL) to afford **PF-N_3** as a yellow solid (328 mg, 86%). ^{1}H-NMR (700 MHz; $CDCl_3$): δ 7.86-7.84 (m, 4H), 7.71-7.68 (m, 8H), 3.15 (t, 4H), 2.21-2.08 (m, 4H), 1.45-1.42 (m, 4H), 1.29-1.14 (m, 60H), 0.87 (t, 6H).



mPEG$_x$-alkyne syntheses adapted from Ref 3.

mPEG$_{750}$-alkyne. A glass vial equipped with a stir bar was charged with mPEG$_{750}$-OH (1 g, 1.3 mmol), 4-pentynoic acid (392 mg, 4 mmol), 4-dimethylaminopyridine (37 mg, 300 μmol), and CH_2Cl_2 (2 mL). To the solution *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (EDC·HCl) (767 mg, 4 mmol) was added, and the reaction mixture was stirred for 12 h at RT. The reaction mixture was purified by flash chromatography (25 g, 5 CV CH_2Cl_2 followed by 0 → 7% MeOH in CH_2Cl_2 over 10 CV) and fractions were stained with Dragendorff reagent to identify pure fractions. Pure fractions were combined and solvent was removed *in vacuo* to afford **mPEG$_{750}$-alkyne** as a yellow liquid (885 mg, 80%). ^{1}H-NMR (700 MHz; $CDCl_3$): δ 4.26 (dd, J = 5.3, 4.3 Hz, 2H), 3.71-3.54 (m, 62H), 3.38 (s, 3H), 2.62-2.58 (m, 2H), 2.53-2.51 (m, 2H), 1.99 (t, J = 8.3, 2.6 Hz, 1H). ^{13}C NMR (176 MHz; $CDCl_3$): δ 175.4, 171.9, 70.7, 64.0, 59.2, 33.4, 33.0, 14.5.

mPEG$_{2000}$-alkyne. A glass vial equipped with a stir bar was charged with mPEG$_{2000}$-OH (1 g, 0.5 mmol), 4-pentynoic acid (147 mg, 1.5 mmol), 4-dimethylaminopyridine (15 mg, 130 μmol), and CH_2Cl_2 (2 mL). Mild sonication was used to fully dissolve the mPEG$_{2000}$-OH. To the solution EDC·HCl (288 mg, 1.5 mmol) was added, and the reaction mixture was stirred for 12 h at RT. The reaction mixture was precipitated into 1:1 Et_2O:hexanes (~100 mL). The precipitate was collected on a Hirsch funnel, then washed with Et_2O (3 x 20 mL), ice cold EtOH (6 x 50 mL), and Et_2O (3 x 20 mL), followed by drying *in vacuo* to afford **mPEG$_{2000}$-alkyne** as a fine white powder (796 mg, 77%). ^{1}H-NMR (700 MHz; $CDCl_3$): δ 4.26 (t, J = 4.8 Hz, 2H), 3.76-3.51 (m, 145H), 3.38 (s, 3H), 2.60-2.57 (t, J = 7.1 Hz, 2H), 2.52-2.49 (m, 2H), 1.98 (t, J = 2.6 Hz, 1H). ^{13}C NMR (176 MHz; $CDCl_3$): δ 171.8, 72.0, 70.6, 69.2, 63.9, 59.1, 33.4, 14.4.

mPEG$_{5000}$-alkyne. A glass vial equipped with a stir bar was charged with mPEG$_{5000}$-OH (1 g, 0.2 mmol), 4-pentynoic acid (59 mg, 0.6 mmol), 4-dimethylaminopyridine (6 mg, 50 μmol), and CH_2Cl_2 (2 mL). Mild sonication was used to fully dissolve the mPEG$_{5000}$-OH. To the solution EDC·HCl (115 mg, 0.6 mmol) was added, and the reaction mixture was stirred for 12 h at RT. The reaction mixture was precipitated into 1:1 Et_2O:hexanes (~100 mL). The precipitate was collected on a Hirsch funnel, then washed with Et_2O (3 x 20 mL), ice cold EtOH (6 x 50 mL), and Et_2O (3 x 20 mL), followed by drying *in vacuo* to afford **mPEG$_{5000}$-alkyne** as a fine white powder (852 mg, 84%). ^{1}H-NMR (700 MHz; $CDCl_3$): δ 4.27-4.25 (dd, J = 5.5, 4.2 Hz, 2H), 3.76-3.51 (m, 418H), 3.38 (s, 3H), 2.60-2.57 (m, 2H), 2.52-2.49 (m, 2H), 1.98 (t, J = 2.6 Hz, 1H). ^{13}C NMR (176 MHz; $CDCl_3$): δ 171.8, 70.7, 63.9, 59.1, 33.4, 14.4.

$mPEG_{23500}$-alkyne. A glass vial equipped with a stir bar was charged with $mPEG_{23500}$-OH (1 g, 43 μmol), 4-pentynoic acid (13 mg, 128 μmol), 4-dimethylaminopyridine (1.3 mg, 11 μmol), and CH_2Cl_2 (2 mL). Mild sonication was used to fully dissolve the $mPEG_{23500}$-OH. To the solution EDC·HCl (25 mg, 128 μmol) was added, and the reaction mixture was stirred for 12 h at RT. The reaction mixture was precipitated into 1:1 Et_2O:hexanes (~100 mL). The precipitate was collected on a Hirsch funnel, then washed with Et_2O (3 x 20 mL), ice cold EtOH (6 x 50 mL), and Et_2O (3 x 20 mL), followed by drying *in vacuo* to afford **$mPEG_{23500}$-alkyne** as a fine white powder (610 mg, 60%). ^{1}H-NMR (700 MHz; $CDCl_3$): δ 4.26 (dd, J = 5.5, 4.2 Hz, 2H), 3.76-3.51 (m, 1970H), 3.38 (s, 3H), 2.61-2.57 (m, 2H), 2.52-2.49 (m, 2H), 1.98 (t, J = 2.6 Hz, 1H). ^{13}C NMR (176 MHz; $CDCl_3$): δ 70.7.

$mPEG_{41000}$-alkyne. A glass vial equipped with a stir bar was charged with $mPEG_{41000}$-OH (1 g, 24 μmol), 4-pentynoic acid (7 mg, 72 μmol), 4-dimethylaminopyridine (0.7 mg, 6 μmol), and CH_2Cl_2 (2 mL). Mild sonication was used to fully dissolve the $mPEG_{41000}$-OH. To the solution EDC·HCl (14 mg, 72 μmol) was added, and the reaction mixture was stirred for 12 h at RT. The reaction mixture was precipitated into 1:1 Et_2O:hexanes (~100 mL). The precipitate was collected on a Hirsch funnel, then washed with Et_2O (3 x 20 mL), ice cold EtOH (6 x 50 mL), and Et_2O (3 x 20 mL), followed by drying *in vacuo* to afford **$mPEG_{41000}$-alkyne** as a fine white powder (664 mg, 67%). ^{1}H-NMR (700 MHz; $CDCl_3$): δ 4.26 (dd, J = 5.5, 4.2 Hz, 2H), 3.76-3.51 (m, 3660H), 3.38 (s, 3H), 2.61-2.57 (m, 2H), 2.52-2.49 (m, 2H), 1.98 (t, J = 2.6 Hz, 1H). ^{13}C NMR (176 MHz; $CDCl_3$): δ 70.7.

Dragendorff reagent (adapted from Ref 4). To an Erlenmeyer flask (250 mL) bismuth oxynitrate (800 mg, 2.6 mmol), glacial acetic acid (1 mL), and distilled water (99 mL) were added. The reagents were gently agitated, and then potassium iodide (2 g, 12.0 mmol) was added. The suspension was mixed

thoroughly and then filtered through a Buchner funnel to remove reddish-orange precipitate. The reddish-orange solution was used as isolated and stored under ambient conditions in a thin layer chromatography jar wrapped in aluminum foil.

CuAAC procedure for Cu source screening. A glass vial was charged with **PF-N_3** (5 mg, 4.9 μmol) and 2.05 equivalents of phenylacetylene (0.9 mg, 0.75 μmol). To the reaction mixture, 1 mg of Cu source [CuCl, CuBr, CuI, or Cu(OAc)] and 10 equivalents of Hunig's base (^{i}Pr$_2$EtN) with respect to the Cu source (52 – 100 μmol) were added. In the case of Cu(0) wire, 2 inches of 0.5 mm diameter wire (surface area of ~80 mm^2) was wrapped around the stir bar and 9% v/v of Hünig's base (670 μL) was added. The reaction mixtures were stirred at 60 °C, and reaction progress was monitored by IR spectroscopy for the disappearance of the azide stretch at ~2090 cm^{-1}. The % conversion (if the azide stretch remained after 12 h) was estimated by determining the relative peak intensity of the azide stretch (~2090 cm^{-1}) to the C-H stretch (~2870 cm^{-1}) at t = 0 h and t = 12 h. Using the *Peak Area Tool* from the OMNIC software provided with the IR spectrometer, the C-H and azide stretch of each respective IR spectrum was integrated at t = 0 h and t = 12 h. The integration values for the N_3 stretches were normalized to the C-H stretches at each respective time point, and % conversion could thus be calculated as per Eq. 1:

$$\%\ conversion = [1 - \frac{\frac{I_{N_3,12h}}{I_{C-H,12h}}}{\frac{I_{N_3,0h}}{I_{C-H,0h}}}]x100\% \qquad (1)$$

Where I is the integration value for the respective IR stretch at a specific time.

CuAAC procedure for PF-N_3-SWNT and phenylacetylene. A glass vial was charged with 500 μL of **PF-N_3**-SWNT and 2.05 equivalents of phenylacetylene (0.9 mg, 0.75 μmol). Equivalents were calculated by determining the polymer concentration in solution (based on the SWNT dispersion protocol),

calculating the mass of polymer present, and then using the molecular weight of the repeat unit to determine the number of moles of azide moiety (two per repeat unit). To the reaction mixture, 1 mg of Cu(OAc) and 10 equivalents of Hunig's base with respect to Cu(OAc) (10.6 mg, 82 μmol) were added. The reaction mixture was stirred at RT or 60 °C, and reaction progress was monitored by IR spectroscopy for the disappearance of the azide stretch at ~2090 cm^{-1}.

CuAAC procedure for PF-N_3-SWNT and mPEG$_x$-alkyne. A glass vial was charged with 1.6 mL of **PF-N_3**-SWNT dispersion and 2.05 equivalents of mPEG$_x$-alkyne (2.4 μmol). Equivalents were calculated by determining the polymer concentration in solution (based on the SWNT dispersion protocol), calculating the mass of polymer present, and then using the molecular weight of the repeat unit to determine the number of moles of azide moiety (two per repeat unit). To the reaction mixture, 1 mg of Cu(OAc) and 10 equivalents of Hünig's base with respect to Cu(OAc) (10.6 mg, 82 μmol) were added. The reaction mixture was stirred at RT and reaction progress was monitored by IR spectroscopy for the disappearance of the azide stretch at ~2090 cm^{-1}. Solvent was removed *in vacuo*, then D_2O (3.2 mL) was added and mild sonication was used to re-disperse the solid polymer-SWNT complex into solution. The resulting polymer-SWNT dispersions were characterized by UV-Vis-NIR spectroscopy.

Control reactions between PF-N_3-SWNT and mPEG$_{5000}$-alkyne. The following recipe was used, where a single ingredient [either Hünig's base, Cu(OAc), or mPEG$_{5000}$-alkyne] was omitted, per control reaction. A glass vial was charged with 200 μL of **PF-N_3**-SWNT dispersion and two equivalents of mPEG$_{5000}$-alkyne (1.5 mg, 0.3 μmol). Equivalents were calculated by determining the polymer concentration in solution (based on the SWNT dispersion protocol), calculating the mass of polymer present, and then using the molecular weight of the repeat unit to determine the number of moles of azide moiety (two per repeat unit). To the reaction mixture, 0.5 mg of Cu(OAc) and 10 equivalents of Hünig's

base with respect to Cu(OAc) (5.3 mg, 41 μmol) were added. The reaction mixture was stirred at RT for 12 h and reaction progress was monitored by IR spectroscopy for the disappearance of the azide stretch at ~2090 cm^{-1} (see Figure S2 below).

Preparation of XPS samples. The pre-CuAAC sample was prepared by filtering **PF-N_3**-SWNT dispersion (5 mL) through a Teflon membrane (0.2 μm pore diameter) and washing with CH_2Cl_2 (15 mL). The post-CuAAC sample was prepared by filtering **PF-N_3-phenylacetylene**-SWNT dispersion (using the same procedure as outlined above with Cu(OAc), on a 5 mL scale) through a Teflon membrane (0.2 μm pore diameter) and washing with CH_2Cl_2 (15 mL).

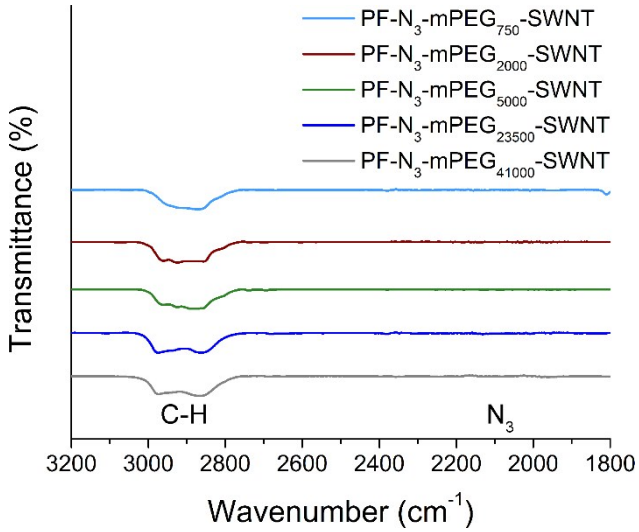


Figure S1. FT-IR overlay of the reaction between the **PF-N_3**-SWNT complex and $mPEG_x$-alkyne (x = 0.75, 2.0, 5.0, 23.5, or 41 kDa) using Hünig's base and Cu(OAc) at RT after stirring for 12 h.

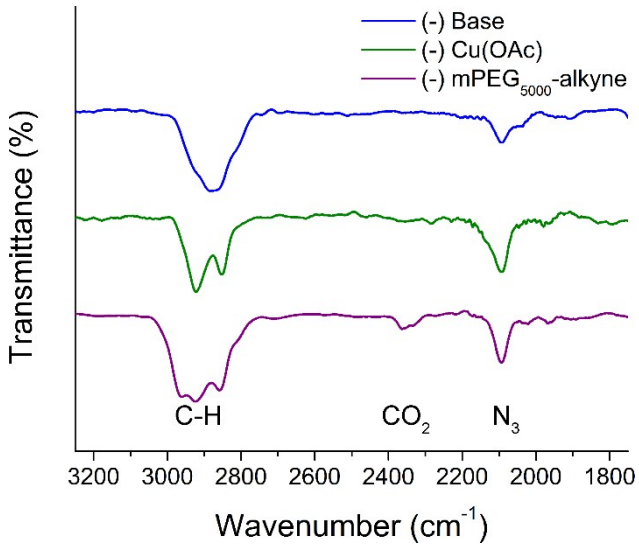


Figure S2. FT-IR overlay of the control reactions between the **PF-N_3**-SWNT complex and $mPEG_{5000}$-alkyne using Hünig's base and Cu(OAc) at RT after stirring for 12 h.

Table S1. Atomic %s of C, N, O, Cu, and Fe for **PF-N_3**-SWNT Bucky Paper Pre- and Post-CuAAC With Phenylacetylene Using Hünig's Base and Cu(OAc)

Element	Pre-CuAAC (%)	Post-CuAAC (%)
C	95.66	89.87
N	0.57	2.85
O	3.71	4.88
Cu	0.00	2.27
Fe	0.06	0.13

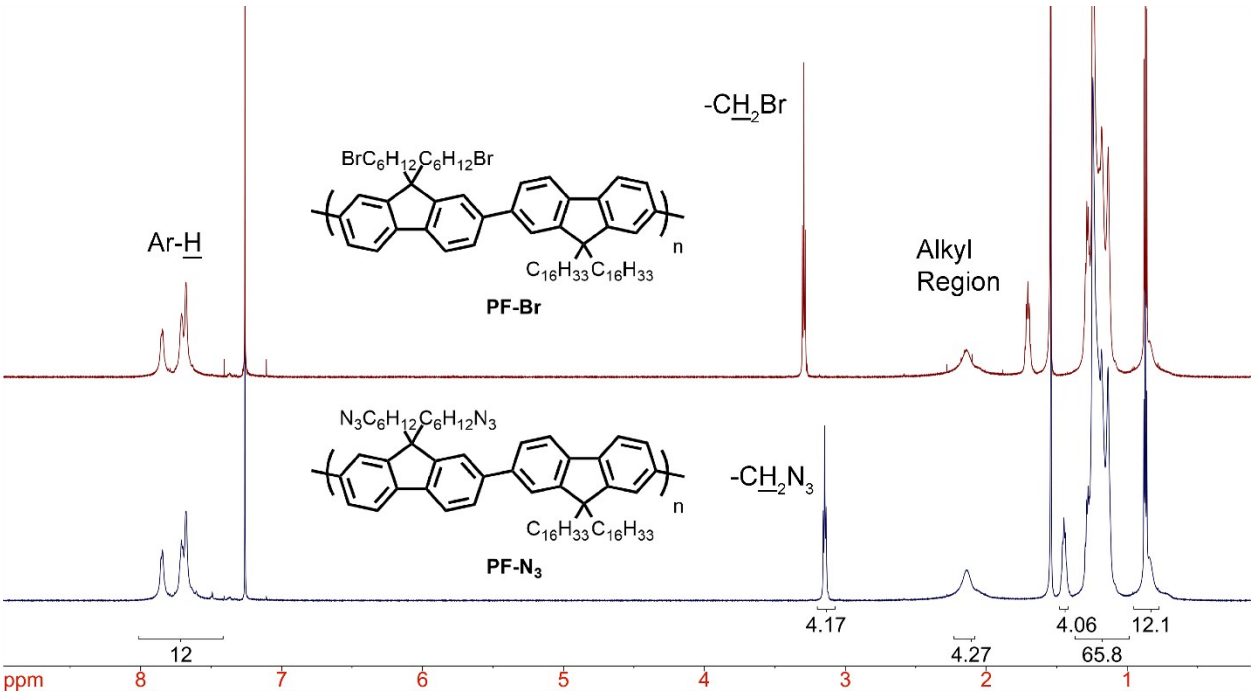


Figure S3. ^{1}H NMR overlay of (a) **PF-Br** (red) and (b) **PF-N_3** (blue).

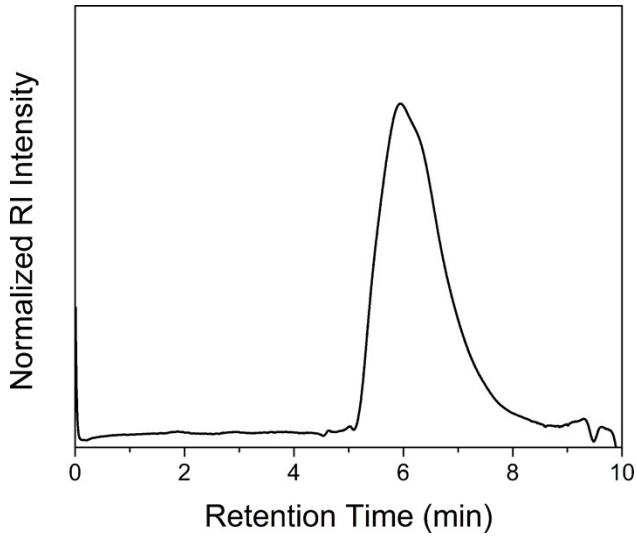


Figure S4. GPC trace of **PF-Br**.

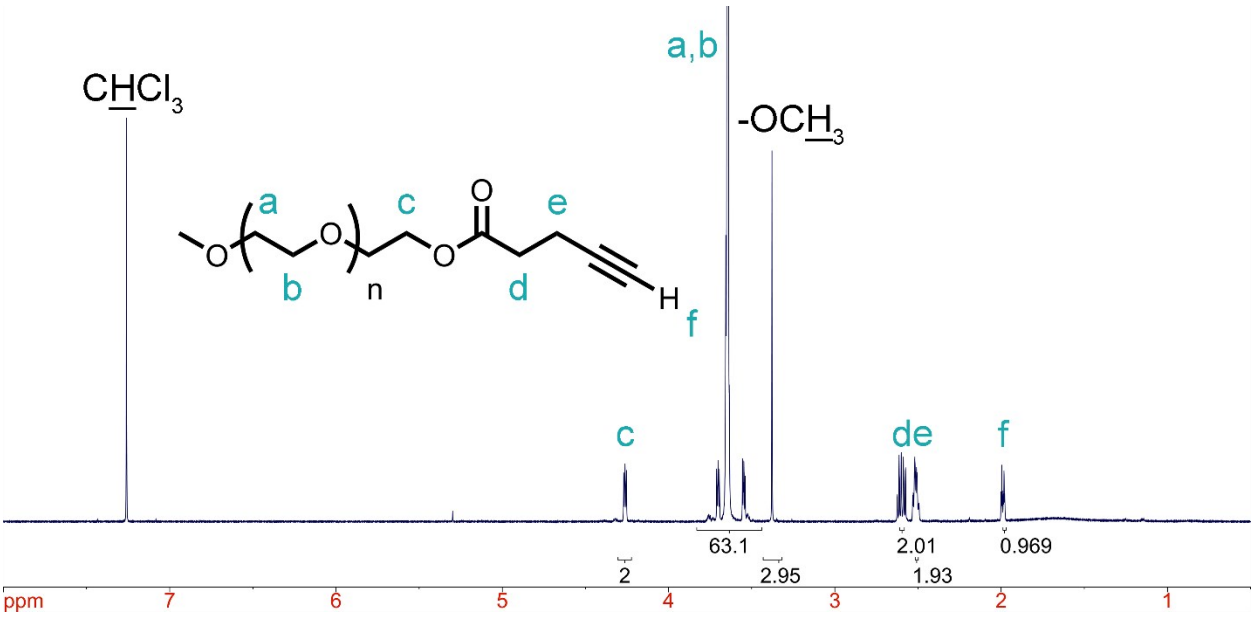


Figure S5. ^{1}H NMR spectrum of mPEG$_{750}$-alkyne.

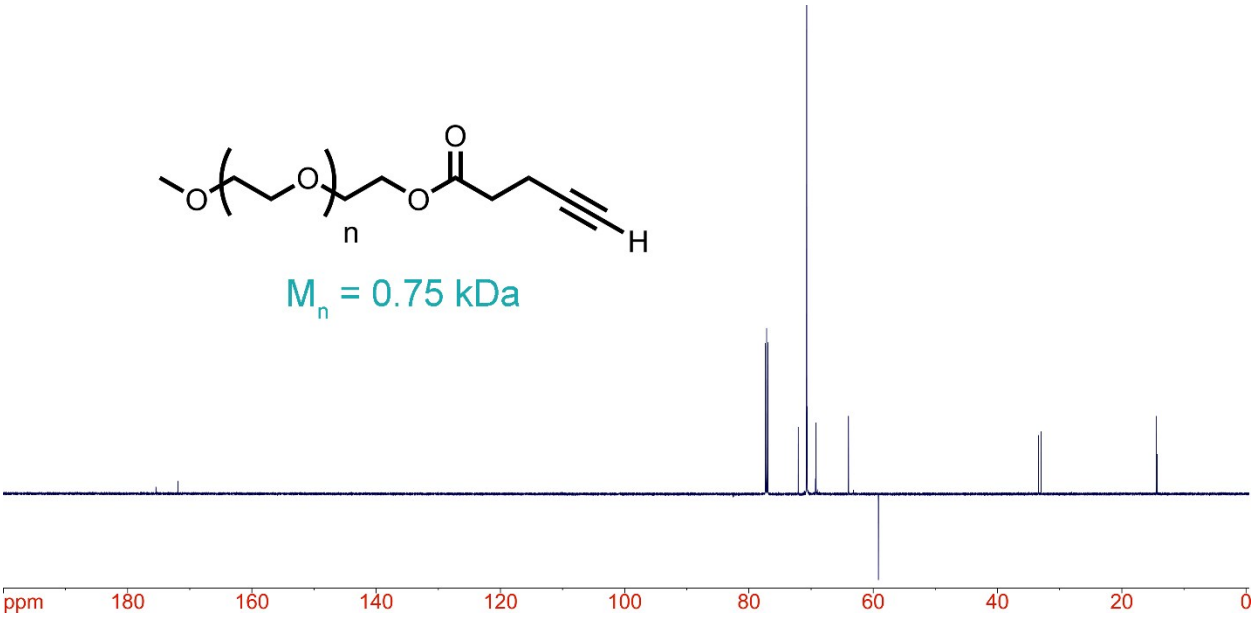


Figure S6. DEPTq spectrum of mPEG$_{750}$-alkyne in $CDCl_3$.

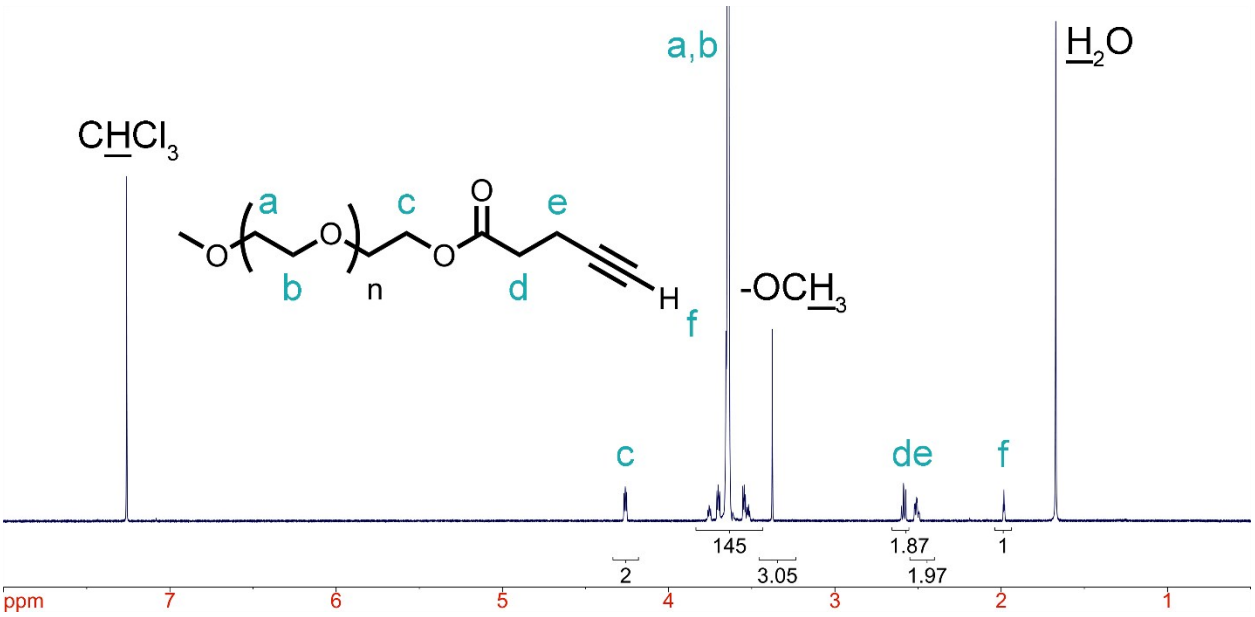


Figure S7. ^{1}H NMR spectrum of mPEG$_{2000}$-alkyne.

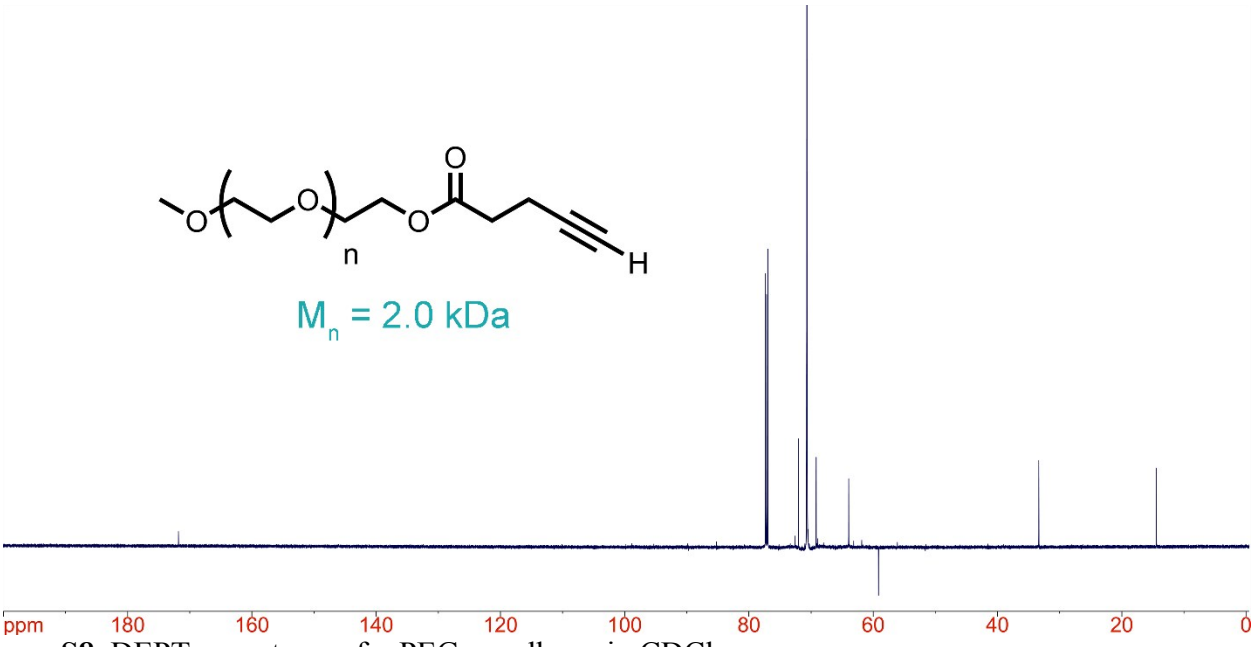


Figure S8. DEPTq spectrum of mPEG$_{2000}$-alkyne in $CDCl_3$.

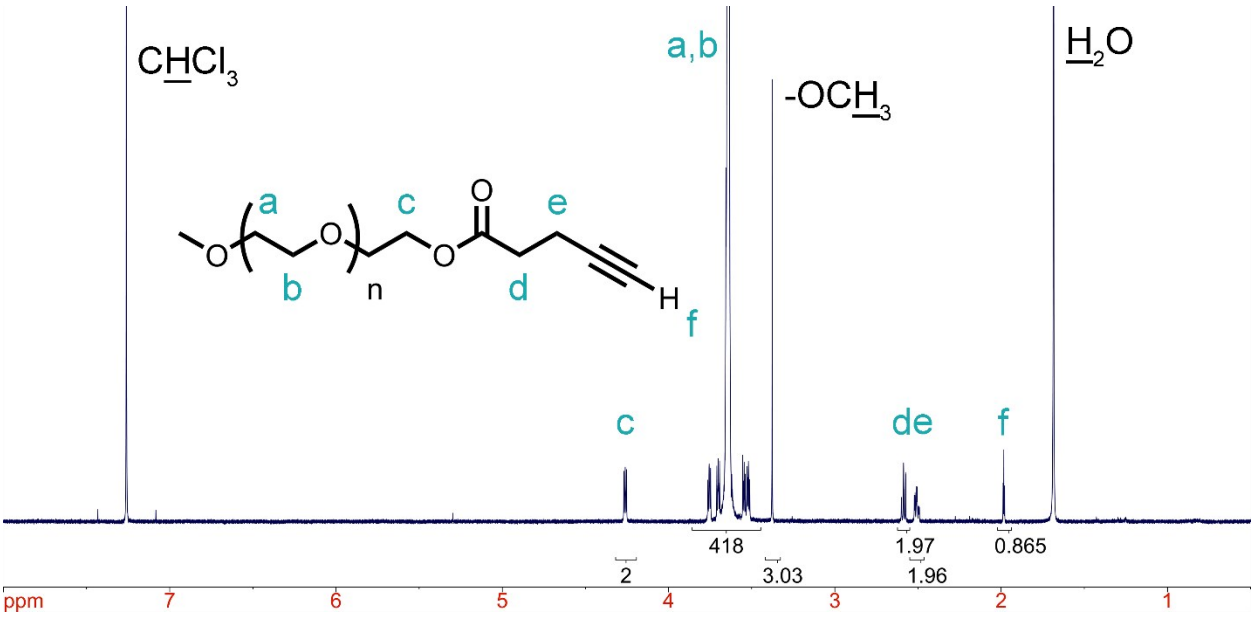


Figure S9. ^{1}H NMR spectrum of mPEG$_{5000}$-alkyne.

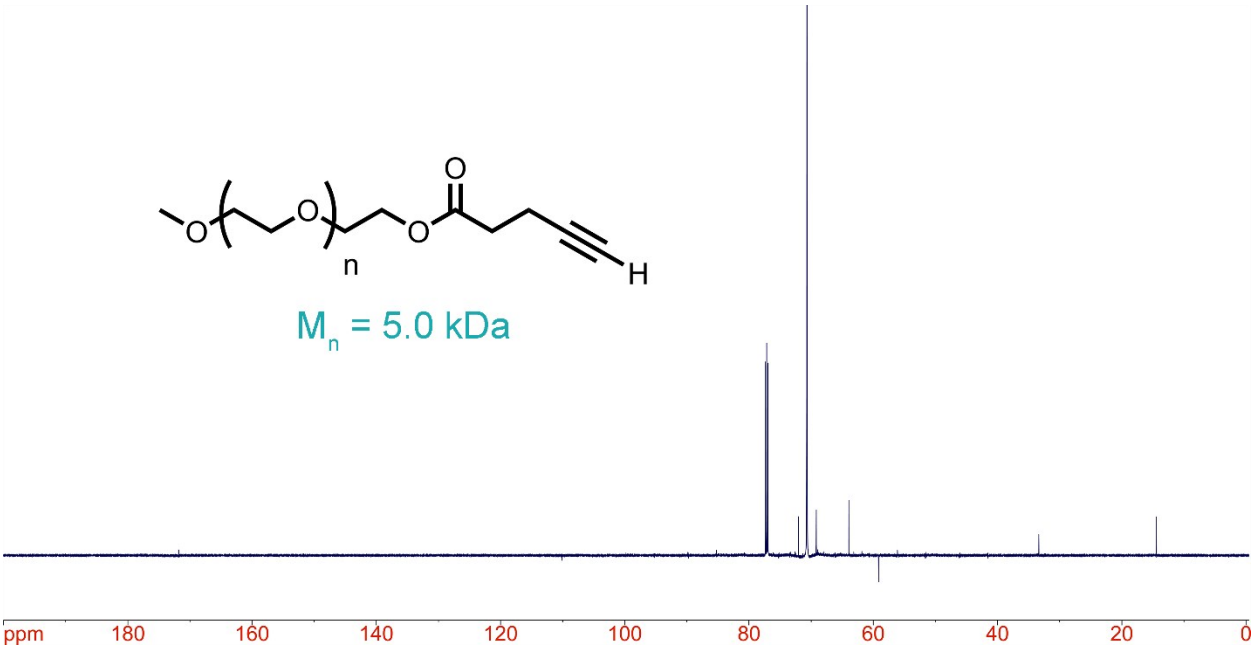


Figure S10. DEPTq spectrum of mPEG$_{5000}$-alkyne in $CDCl_3$.

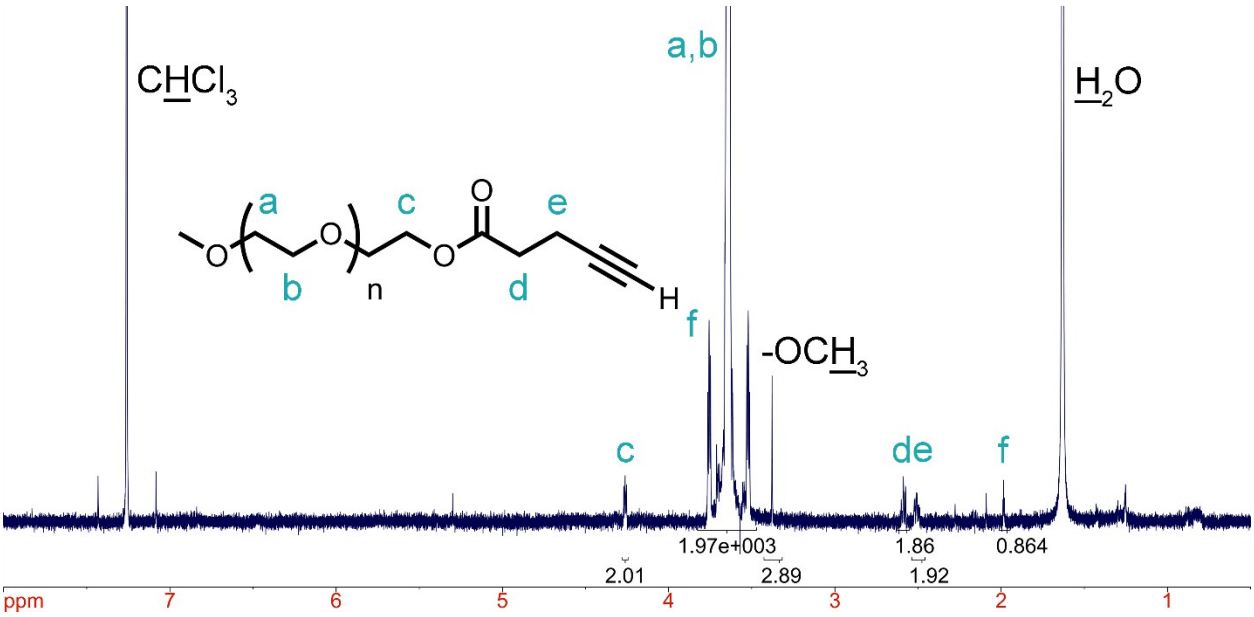


Figure S11. ^{1}H NMR spectrum of $mPEG_{23500}$-alkyne.

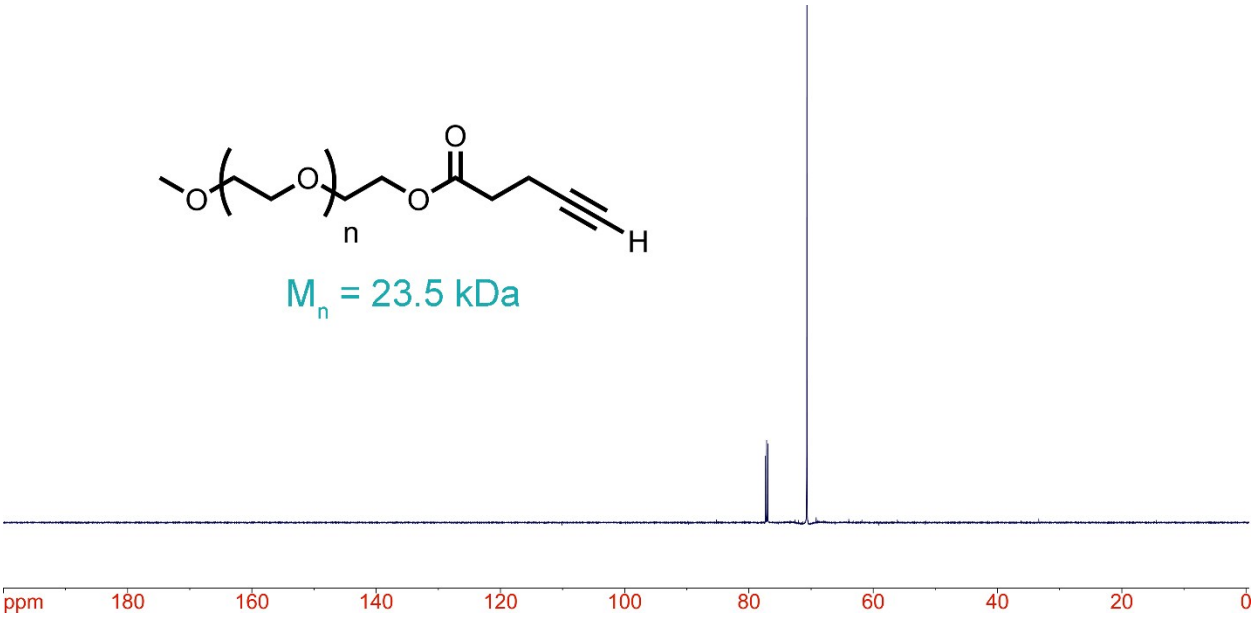


Figure S12. DEPTq spectrum of $mPEG_{23500}$-alkyne in $CDCl_3$.

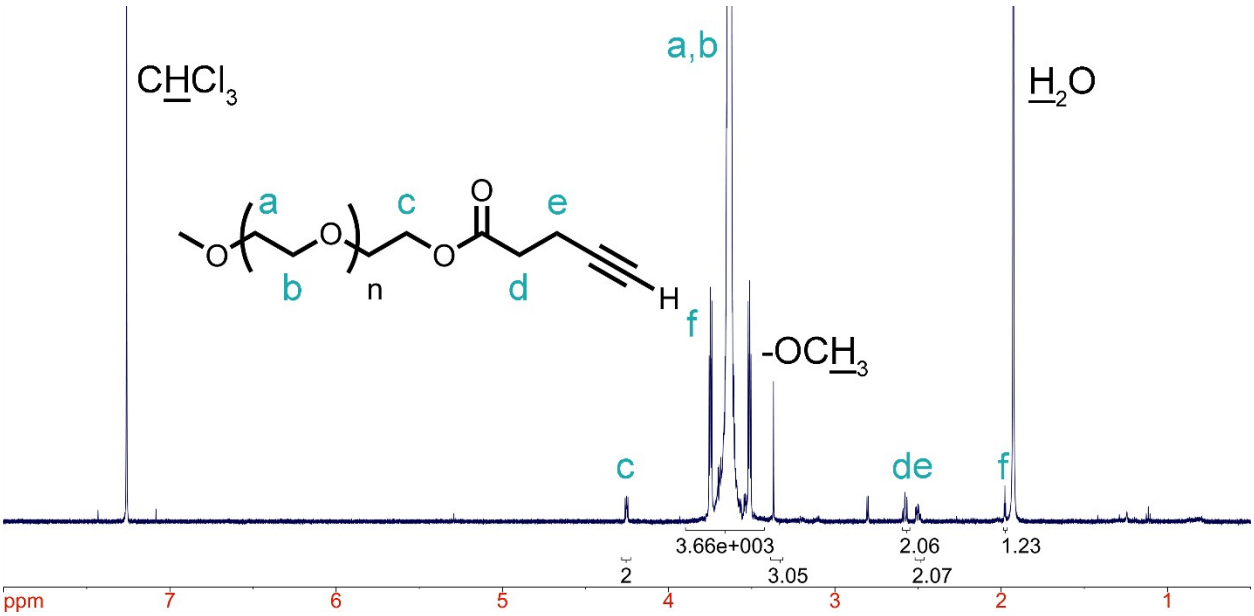


Figure S13. ^{1}H NMR spectrum of mPEG$_{41000}$-alkyne.

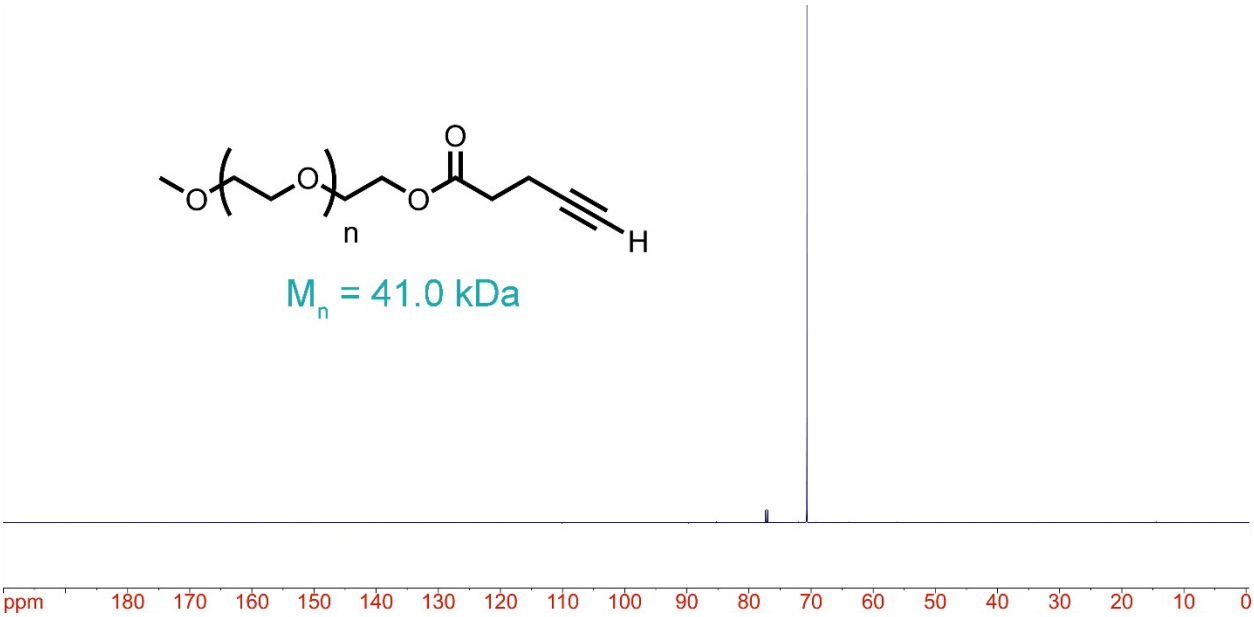


Figure S14. DEPTq spectrum of mPEG$_{41000}$-alkyne in $CDCl_3$.

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