Supporting Information for

Modification of DNA-Templated Conductive Polymer Nanowires via Click Chemistry

Jennifer Hannant, Joseph H. Hedley, Jonathan Pate, Adam Walli, Said A. F. Al-Said, Miguel Galindo, Bernard A. Connolly, Benjamin R. Horrocks, Andrew Houlton and Andrew R. Pike

Materials and Methods

Materials. Lambda DNA was purchased from New England Biolabs. All other reagents were purchased from Sigma Aldrich and used as received unless otherwise stated. NMR was performed on a 300MHz Bruker Spectrospin WM 300 WB spectrometer and mass spectra were measured on a Waters Micromass LCT Premier mass spectrometer.

AFM images of CT-DNA and λ-DNA templated nanowires

Tapping mode AFM images were acquired in air using a Dimension Nanoscope V system (Veeco Inc.) with NanoProbe tips (Veeco Inc.). The cantilever was 200–250 μm long, with 1–5 N m^{-1} spring constant and 252 kHz resonant frequency.

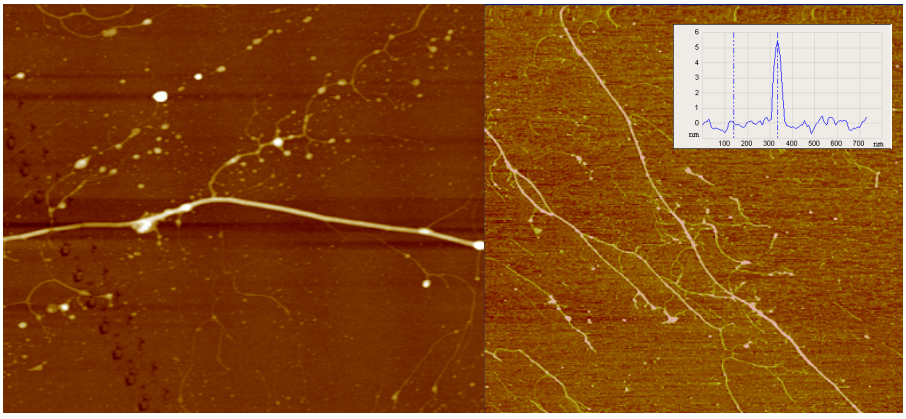

Figure S1. Tapping AFM image of **poly-2** DNA hybrid nanowires. Left, λ–DNA, 7μm scan size, 45 nm height scale. Right, CT-DNA, 10 μm scan size, 10 nm height scale, and inset shows a typical height cross section of the nanowire.

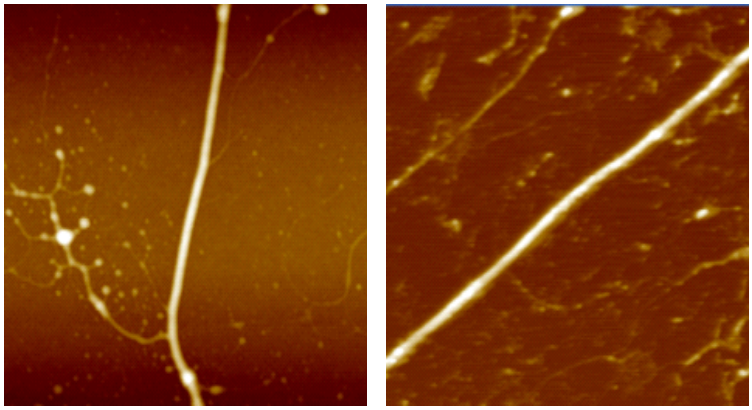

Figure S2. Tapping AFM image of **poly-2** DNA hybrid nanowires before and after click treatment. Left, before click, 4μm scan size, 15 nm height scale. Right, after click treatment, 7 μm scan size, 50 nm height scale.

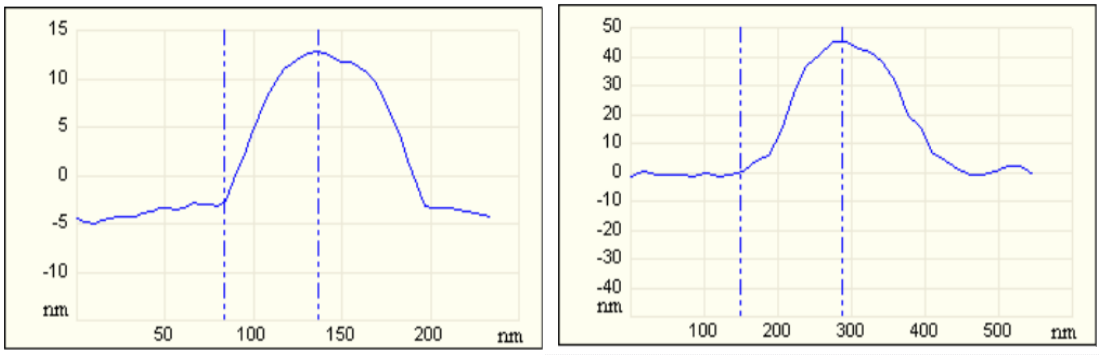

Figure S3. Cross section (height) of **poly-2** DNA hybrid nanowires before and after click treatment, as seen if Figure S2. Left, before click and right, after click.

Note: In **Figure S2** and **Figure S3** the images and heights shown are not of the same wire before and after treatment but typical of each type of nanowire

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IR spectra

IR spectra were recorded on a Varian 800 FT-IR, 256 scans at 4 nm resolution.

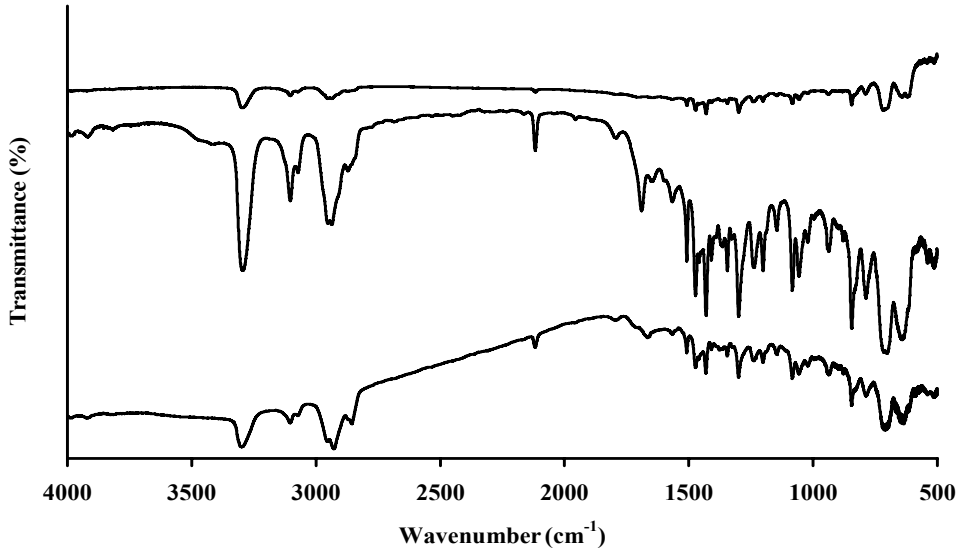


Figure S4. IR spectra of **2**(top) **poly-2** (middle) and **poly-2**/DNA hybrid (bottom)

IR after "click" reaction:

In addition to the observations stated in the text characteristic absorptions bands at 1720 cm^{-1} (triazole ring vibration), 1100-1150 cm^{-1} (triazole breathing mode) and 965-945 cm^{-1} (C-N stretch) indicate that the cycloaddition has been successfully achieved.

Table S1 Selected bands in **poly-2**/DNA and DNA spectra and their assignments.

Wavenumber (cm^{-1}) in DNA	Wavenumber (cm^{-1}) in poly-2/DNA	Assignment
1065	1061	[(a)]C-O deoxyribose stretch / PO_2^- symmetric stretch
1223	1203	PO_2^- asymmetric stretch
1331	1347	C-N stretch of thymine and adenine
1408	1432	CH, N-H deformation, C-N stretch
1531	1509	in plane vibrations of cytosine and guanine
1585	1574	[(b)]C=N guanine and adenine C7=N stretches
1658, 1705	1674, 1723	C=O strectch of pyrimidine bases

(a) This broad peak, centered at 1065 cm^{-1} in the samples measured in this work, comprises several unresolved components. These have previously been assigned to the symmetric stretch of the phosphate and the vibrations associated with the phosphodiester linkage of the DNA backbone.

(b) Another broad peak which includes unresolved contributions from several C=N stretching vibrations of the nucleobases. The broad absorption due to bending modes of bound water also contributes in this region of the spectrum.

References for assignment of DNA FTIR spectral features.

[S1] Ouameur, A. A.; TajmirRiahi, H.A. *J. Biol. Chem.* 2004, *279*, 42041.

[S2] Alex, S.; P. Dupuis, P. *Inorganica Chimica Acta* 1989, *157*, 271.

[S3] Dovbeshko, G. I.; Gridina, N. Y.; Kruglova, E. B.; Pashchuk, O. P. *Talanta* 2000, *53*, 233.

EFM of conductive poly-2/DNA nanowires (Enlarged copy of Figure 3)

The lift height was 60 nm, the tip resonant frequency was about 74 kHz, spring constant = 2.8 N m^{-1} and the quality factor = 260. The tip was grounded and a dc bias was applied to the Si chip (Si(100), p++, doping density 10^{21} cm^{-3}, 200 nm-thick oxide.

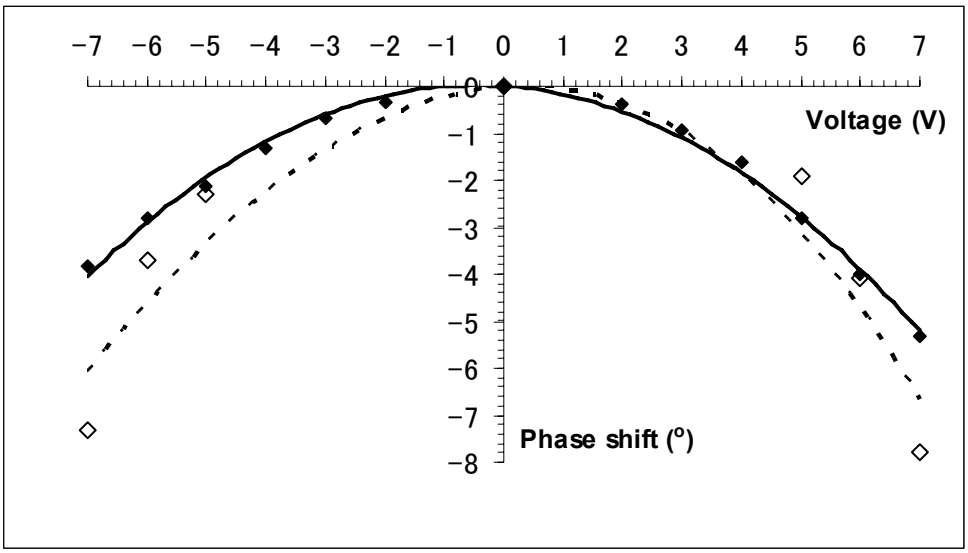


Figure S5. Parabolic dependence of phase shift on bias for voltages between -7 and +7 V for **poly-2**/DNA hybrid nanowires before (solid points and line) and after click modification with dansyl azide (hollow points and dashed line).

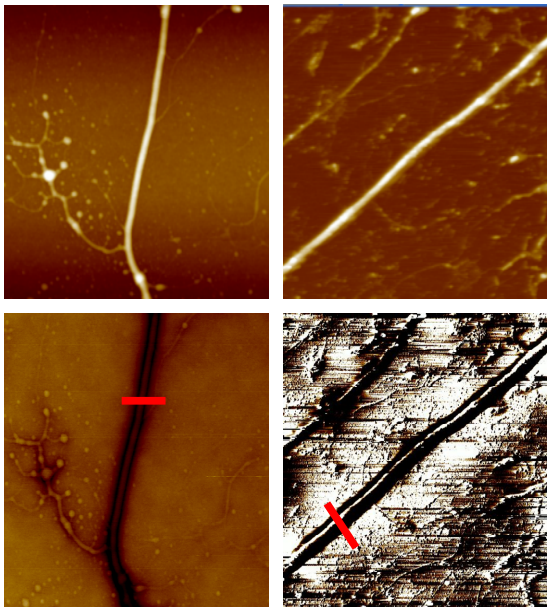


Figure S6.Tapping mode AFM (top) and EFM (at +7 V bias voltage) (bottom) images of **poly-2**/DNA hybrid nanowires before (left) and after (right) modification with danzyl azide. The red line in each lower image indicates the point of measurement across the nanowire for the phase change data shown in Figure S5.

Preparation of SiO_2 wafers for AFM/EFM and FTIR

N doped Si <111> wafers were sequentially cleaned using a cotton bud soaked in acetone, propanol and finally water. The wafers were then soaked in a solution of SDS and water (0.01g in 100 mL) and heated to 50 ºC for 20 minutes after which, the wafers were sonicated in nanopure water for 10 minutes. Following a further rinse they were dried using a nitrogen stream and the wafer was placed in 'piranha solution' (4:1, H_2SO_4:H_2O_2) for 1 hour, rinsed again with nanopure water and then dried in an oven for 15 minutes. Surface modification to provide a hydrophobic surface for AFM/EFM was achieved through exposure to TMS for 10 minutes, typically giving contact angles between 60° and 70°. This range of contact angles is for optimal combing of polymer/DNA nanowires (ref 22 in text).

For EFM the Si wafers have a 220nm thick oxide layer. A piece of silicon <100>was diced into chips approximately 1 cm^{-1} cm. The chips were degreased in a series of solvents (trichloroethylene, acetone, isopropanol) and dipped into 40% aqueous solution of HF to remove the native oxide. Chips were then placed in a furnace at 1000 °C with an oxygen flow of 80mL min^{-1} for 5 h. This procedure produces an oxide layer of about 200nm thickness as determined by a spectrometric thin film analyser (Filmetrics F40).

General procedure for DNA-templated synthesis of hybrid polymers on SiO_2

Typically, a 0.1 M solution of monomer (**2)** in DMF (1 mL) was added to an aqueous mixture of CT-DNA, 40 μg mL^{-1} (1 mL) and 0.5 M $MgCl_2$ (1 mL). 0.1 M aqueous $FeCl_3$ (1 mL) as an oxidant was added. The solution was stirred for 30 minutes at room temperature in darkness. A silicon chip, prepared as above, was deposited in the reaction mixture and left for 8 hours. The chip was removed, dried in a vacuum oven (25 $^{\circ}C$) rinsed with nanopure water and dried again.

General procedure for 'Click' chemistry of DNA/pentnyl hybrid polymers on SiO_2

The silicon chip **poly-2**/DNA hybrids was suspended in a solution of water:*tert*-butyl alcohol (2:1, 30 mL) containing sodium ascorbate (0.03g, 0.15 mmol), copper (II) sulphate (4.72 mg, 0.03 mmol) and 3-azido propanol (0.3g, 2.95 mmol). The mixture was stirred gently in darkness for 8 hours. The chip was washed with excess of nanopure water and dried in a vacuum oven (25 $^{\circ}$C).

The above two procedures were replicated to monitor the polymerisation of **2** and the subsequent reaction of **poly-2** with 3-azido propanol by IR. The conditions were kept the same except that DNA or $MgCl_2$ were not included during the oxidative polymerisation step.

Fluorescence images:

Fluorescence images were collected on an Axioplan 2 microscope (Zeiss) using Axiovision Viewer 3 software (Zeiss). The fluorescence was excited using the light from a Hg lamp passed through a 300-400 nm band-pass filter with a maximum transmission of 65% at 365 nm. The emitted light was separated from scattered light using a long pass filter with a cut-off at 420 nm.

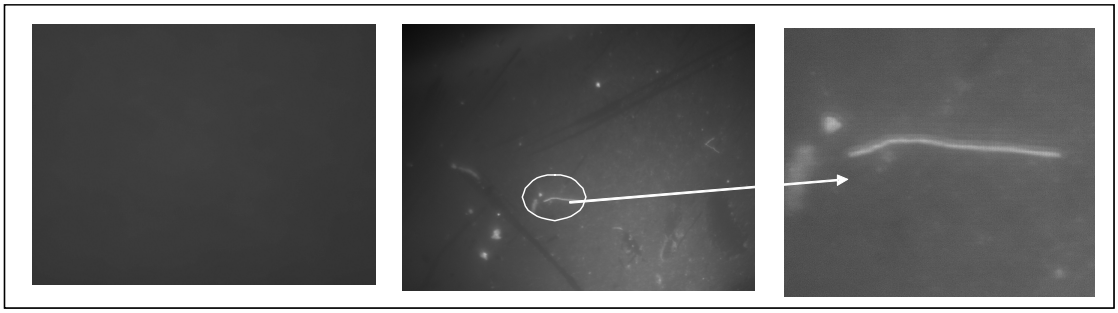
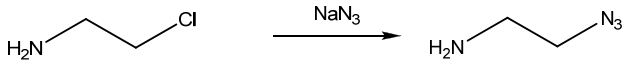


Figure S7. Fluorescence images of pre-click, left, and post-click (centre and right,) modified **poly-2** / DNA hybrid wires with dansyl azide. The width of the images is 170 μm (left and centre), and 20 μm (right)

Synthetic procedures

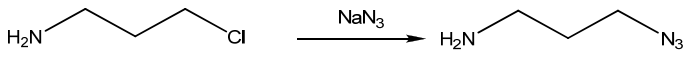
Synthesis of 2-azido-1-ethylamine



To a solution of 2-chloroethylamine hydrochloride (490 mg, 4.3 mmol) in water (5 mL) was added sodium azide (837 mg, 12.9 mmol) and the reaction mixture was heated to 80 °C for 15 h. The solution was basified with solid potassium hydroxide and extracted with diethyl ether (3 × 10 mL). The organic layer was concentrated to give 371 mg (99%) of a volatile colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$, δ): **3.35** (t, *J* = 5.7 Hz, 2H; CH_2), **2.96-2.78** (m, 2H; CH_2), **1.39-1.00** ppm (m, 2H; NH_2).

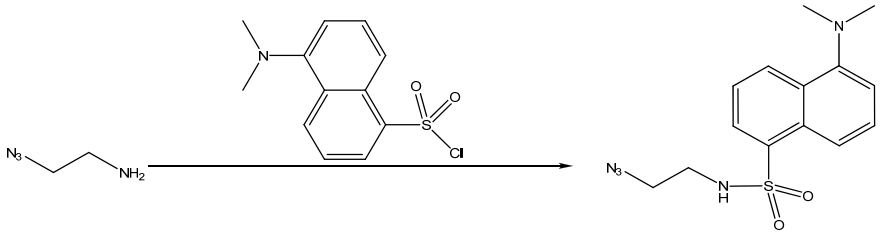
Synthesis of 3-azido-1-propylamine



To a solution of 3-chloropropyl-1-amine hydrochloride (1.53 g, 11.5 mmol) in water (15 mL) was added sodium azide (2.25 g, 34.6 mmol) and the reaction mixture was heated to 80 °C for 15 h. The solution was basified with solid potassium hydroxide and extracted with diethyl ether (3 × 25 mL), the organic layer was washed with water (10 mL) and brine (10 mL) and then concentrated to give 1.15 g (98%) of a volatile colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$, δ): **3.36** (t, *J* = 6.7 Hz, 2H; CH_2), **2.79** ppm (t, *J* = 6.8 Hz, 2H; CH_2), **1.72** (quin (tt), *J* = 6.8, 6.8 Hz, 2H; CH_2), **1.45** ppm (s_{br}, 2H; NH_2).

Synthesis of 2-azido-1-*N*-dansylethylamine

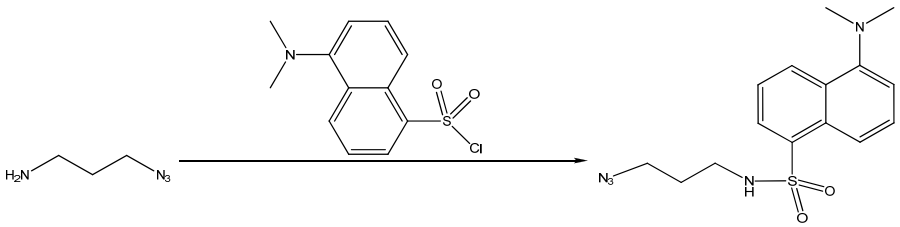


To a solution of 2-azido-1-ethylamine (371 mg, 4.31 mmol) in dichloromethane (7 mL) was added dansyl chloride (225 mg, 840 μmol), and the reaction mixture was stirred for 2 h. The solvent was removed in vacuo and the oily residue was extracted four times with small amounts of a hot mixture of 25% ethyl acetate in hexane. The extract was purified by column chromatography (25% ethyl acetate/hexane) to afford 209 mg (75%) of a glowing-yellow oil.

R_f 0.17 (25% EtOAc/hexane).

^{1}H NMR (300 MHz, $CDCl_3$, δ): **8.57** (d, J = 8.4 Hz, 1H; Ar H), **8.28-8.22** (m, 1H; Ar H), **7.60** (dd, J = 8.6, 7.7 Hz, 1H; Ar H), **7.53** (dd, J = 8.5, 7.4 Hz, 1H; Ar H), **7.21** (d, J = 7.7 Hz, 1H; Ar H), **4.94** (t, J = 6.4 Hz, 1H; NH), **3.34-3.28** (m, 2H; CH_2), **3.11-2.99** (m, 2H; CH_2), **2.89** ppm (s, 6H; CH_3).

Synthesis of 3-azido-1-*N*-dansylpropylamine



To a solution of 3-azido-1-propylamine (1.15 g, 11.5 mmol) in dichloromethane (20 mL) was added dansyl chloride (676 mg, 2.5 mmol), and the reaction mixture was stirred for 2 h. The solvent was removed in vacuo and the oily residue was extracted four times with small amounts of a hot mixture of 25% ethyl acetate in hexane. The extract was purified by column chromatography (25% ethyl acetate/hexane) to afford 759 mg (91%) of a glowing-yellow oil.

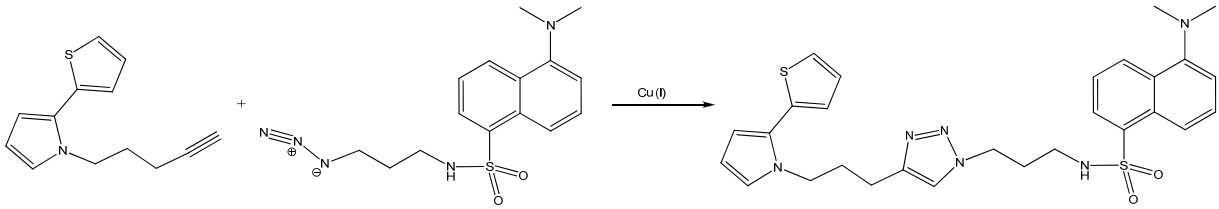
R_f 0.17 (25% EtOAc/hexane).

^{1}H NMR (300 MHz, $CDCl_3$, δ): **8.56** (d, *J* = 8.53 Hz, 1H; Ar H), **8.28-8.23** (m, 2H, Ar H), **7.58** (dd, *J* = 8.6, 7.7 Hz, 1H; Ar H), **7.54** (dd, *J* = 8.5, 7.4 Hz, 1H; Ar H), **7.20** (d, *J* = 7.6 Hz, 1H; Ar H), **4.88** (t, *J* = 6.2 Hz, 1H; NH), **3.27** (t, *J* = 6.4 Hz, 2H; CH_2), 2.97 (q (td), *J* = 6.4, 6.4 Hz, 2H; CH_2), **2.89** (s, 6H; CH_3), **1.65** ppm (quin (tt), *J* = 6.4, 6.4 Hz, 2H; CH_2).

^{13}C NMR (75 MHz, $CDCl_3$, δ): 152.39 (C_{Ar}), 135.10 (C_{Ar}), 130.65 (C_{Ar}), 130.33 (C_{Ar}), 129.88 (C_{Ar}), 129.71 (C_{Ar}), 128.47 (C_{Ar}), 123.18 (C_{Ar}), 118.85 (C_{Ar}), 115.46 (C_{Ar}), 48.98 (CH_2), 45.39 (CH_3), 40.98 (CH_2), 29.09 ppm (CH_2).

HRMS (ESI, m/z): **[M + Na]**$^+$ calcd for $C_{15}H_{19}N_5NaO_2S$, 356.1157; found, 356.1133. **[2M + Na]**$^+$ calcd for $(C_{15}H_{19}N_5O_2S)_2Na$, 689.2416; found, 689.2346. **[3M + Na]**$^+$ calcd for $(C_{15}H_{19}N_5O_2S)_3Na$, 1022.3676; found, 1022.3586. **[4M + Na]**$^+$ calcd for $(C_{15}H_{19}N_5O_2S)_4Na$, 1355.4935; found, 1355.4905.

Synthesis of 5-(dimethylamino)-*N*-(3-(4-(3-(2-(thiophen-2-yl)-1H-pyrrol-1-yl)propyl)-1*H*-1,2,3-triazol-1-yl)propyl)naphthalene-1-sulfonamide



3-Azido-1-*N*-dansylpropylamine (77.0 mg, 230 μmol) and 1-(pent-4-ynyl)-2-(thiophen-2-yl)-1*H*-pyrrole (50.0 mg, 230 μmol) were suspended in a 1:1 mixture of water and *tert*-butyl alcohol (1 mL). Freshly prepared aqueous 1 M sodium ascorbate solution (25 μL, 25.0 μmol) was added, followed by copper (II) sulphate pentahydrate (1.70 mg, 7.00 μmol, in 40 μL water). The mixture was stirred vigorously in a small capped vial over night. The solvent was decanted and the residue washed with water (3 × 1 mL) and dried in vacuo to afford 111.0 mg (88%) of a green oil.

^{1}H NMR (300 MHz, $CDCl_3$, δ): **8.52** (d, *J* = 8.4 Hz, 1H; Ar H), **8.26** (d, *J* = 8.6 Hz, 1H; Ar H), **8.18** (d, *J* = 7.2 Hz, 1H; Ar H), **7.55** (t, *J* = 8.1 Hz, 1H; Ar H), **7.48** (t, *J* = 7.9 Hz; Ar H), **7.23** (d, *J* = 5.1 Hz, 1H; triazole H), **7.17** (d, *J* = 7.5 Hz, 1H; Ar H), **7.07-6.83** (m, 3H; pyrrolyl thiophene H), **6.76** (s, 1H; pyrrolyl thiophene H), **6.28** (s, 1H; pyrrolyl thiophene H), **6.19-6.14** (m, 1H; pyrrolyl thiophene H), **5.36-5.27** (m, 1H; NH), **4.28** (t, *J* = 6.1 Hz, 2H; CH_2), **4.04** (t, *J* = 6.9 Hz, 2H; CH_2), **2.87** (s, 6H; CH_3), **2.84-2.78** (m, 2H; CH_2), **2.60** (t, *J* = 7.0 Hz, 2H; CH_2), **2.10-1.93** ppm (m, 4H; CH_2).

^{13}C NMR (75 MHz, $CDCl_3$, δ): 152.55 (C_{Ar}), 135.37 (C_{Ar}), 135.17 (C_{Ar}), 130.85 (C_{Ar}), 130.44 (C_{Ar}), 129.97 (C_{Ar}), 129.82 (C_{Ar}), 129.69 (C_{Ar}), 128.75 (C_{Ar}), 127.38 (C_{Ar}), 126.63 (C_{Ar}), 125.76 (C_{Ar}), 124.96 (C_{Ar}), 123.32 (C_{Ar}), 123.03 (C_{Ar}), 121.42 (C_{Ar}), 118.93 (C_{Ar}), 115.65 (C_{Ar}), 110.92 (C_{Ar}), 108.38 (C_{Ar}), 47.08 (NCH_2), 46.85 (NCH_2), 45.52 (NCH_3), 40.42 (NCH_2), 31.00 (CH_2), 30.51 (CH_2), 22.88 ppm (CH_2).

HRMS (ESI, m/z): **[M + Na]**$^+$ calcd for $C_{28}H_{32}N_6NaO_2S_2$, 571.1926; found, 571.2050. **[2M + Na]**$^+$ calcd for $C_{56}H_{64}N_{12}NaO_4S_4$, 1119.3949; found, 1119.4232.