Supplementary information

Core functionalization of polydiacetylene micelles by "click" reaction.

Emmanuel Contal, Andrey Klymchenko, Yves Mély, Stéphane Meunier, Alain Wagner

Content:

General Methods

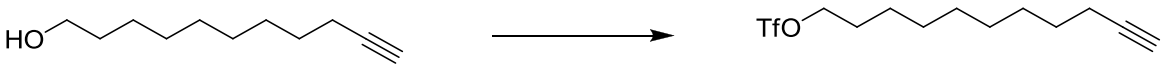
All reactions were carried out in a flame dried glassware under an argon atmosphere with dry solvents, under anhydrous conditions unless otherwise indicated. Solvents for reactions were dried using a dry solvent station GT S100. All reactions were controlled by analytical thin-layer chromatography using Merck pre-coated silica gel plates with F254 indicator. Visualization was accomplished by UV light (254 nm), cerium sulfate or vanillin stains. Yields refer to chromatographically and spectroscopically pure compounds, unless ortherwise indicated. Purifications by column chromatography were carried out using Merck silicagel Si 60 (0.040-0.063). ^{1}H NMR and ^{13}C NMR were recorded on a Bruker DPX-200 (200 MHz ^{1}H NMR, 50MHz ^{13}C NMR), Brucker Advance 300 (300 MHz ^{1}H NMR, 75MHz ^{13}C NMR) and Brucker Advance 400 (400 MHz ^{1}H NMR, 100MHz ^{13}C NMR) . Chemical shift values (δ) are reported in ppm (residual chloroform δ = 7.26 ppm for ^{1}H; residual chloroform δ = 77.16 ppm for ^{13}C, residual methanol δ = 3.31 ppm for ^{1}H; residual methanol δ = 49.00 ppm for ^{13}C). The proton spectra are reported as follows δ (multiplicity, number of protons, coupling constant *J*). Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and etc. Infra-red spectra were recorded with a Nicolet 380 FT-IR apparatus. High resolution mass spectra were recorded with an Agilent Q-Tof 6520 apparatus equipped with a positive ESI source. Melting points (Mp) were recorded with a Stuart Scientific SMP3 apparatus.

All reagents were purchased from Sigma-Aldrich, ABCR, Alfa-Aesar, and Acros.

The TEM images were done using a Philips CM 120 microscope. The size of samples was determined by dynamic light scattering using a Nano-ZS (Malvern Instruments). The absorption spectra were observed using a Shimadzu UV-1800 spectrophotometer. Fluorescence spectra were recorded on a Jobin-Yvon Fluorolog (Longjumeau, France) spectrofluorometer. Electrophoresis was realized on agarose gel (1% w/vol) in TAE (Tris/Acetate/EDTA) buffer. After migration (100V, 45 min), the gel was revealed using an UV-lamp (254nm).

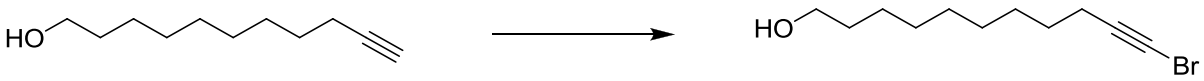
General procedures and analytical datas

undec-10-yn-1-yl trifluoromethanesulfonate 5 :



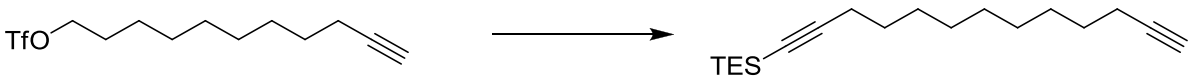
To a cold (0°C) stirred solution of 10-undecyn-1-ol (5.0 g, 29.8 mmol, 1.0 eq) in dichloromethane (120 mL), was added pyridine (2.63 mL, 1.1 eq) followed by triflic anhydride (6.50 mL, 1,3 eq). The reaction was stirred at 0°C for 2h then diluted with cyclohexane (100 mL) and filtered through a celite pad. The concentrated filtrate was purified by flash chromatography on silica gel using dichloromethane as eluent to yield **5** (8.3 g, 92%) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.53 (t, 2H, *J* = 6.6 Hz), 2.19 (td, 2H, *J* = 5.4 Hz, 2.7 Hz), 1.94 (t, 1H, *J* = 2.7 Hz), 1.83 (q, 2H, *J* = 6.6 Hz), 1.57-1.25 (m, 12H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ =118.8, 84.7, 77.8, 68.2, 29.3, 29.0, 28.9, 28.7, 28.5, 25.1, 18.5 ppm. IR (neat): ν = 3308, 2932, 2858, 1412, 1246, 1205, 1146, 935, 616; MS (ESI, *m/z*): 169.2 $[M\text{-}OTf]^+$.

11-bromoundec-10-yn-1-ol 6 :



To a stirred solution of 10-undecyn-1-ol (5.0 g, 29.8 mmol, 1.0 eq) in dry acetone (100 mL) was added $AgNO_3$ (300 mg, 0.1 eq) and N-bromosuccinimide (5.80 g, 1.1 eq). The resulting mixture was stirred overnight at room temperature. Water (50 mL) and diethyl ether (100 mL) were added and the organic layer was separated. The aqueous layer was extracted with diethyl ether (2*50 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography on silica gel using cyclohexane/ethyl acetate (70/30) as eluent to yield **6** (9.13 g, 90%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.61 (t, 2H, *J* = 6.6 Hz), 2.18 (t, 2H, *J* = 6.9 Hz), 1.65-1.40 (m, 4H), 1.40-1.18 (m, 10H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 80.5, 63.0, 37.6, 32.8, 29.5, 29.4, 29.1, 28.8, 28.3, 25.8, 19.7 ppm. IR (neat): ν = 3329, 2927, 2855, 1464, 1057; HRMS (ESI, *m/z*): calcd. for $C_{11}H_{19}BrO$ $[M+H]^+$: 247.0697; found: 247, 0671.

triethyl(trideca-1,12-diyn-1-yl)silane 7 :

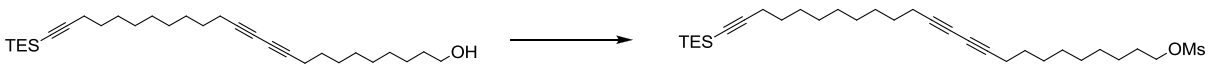


To a cold (-78°C) stirred solution of triethylsilylacetylene (4.58 mL, 25.62 mmol, 1.0 eq) in dry THF (160 mL) was added *n*-BuLi 1.41M in hexane (20.0 mL, 22.80 mmol, 0.89 eq). The solution was stirred at room temperature for 1h. After the solution was cooled back to –78°C, a solution of triflate **5** (7.00 g, 21.26 mmol, 0.83 eq) in THF (30 mL) was slowly added. The solution was allowed to warm to room temperature overnight. Then, the reaction was quenched with brine (100 mL) and ethyl acetate was added. The aqueous layer was extracted with ethyl acetate (3*200 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude was purified by flash chromatography on silica gel using cyclohexane/ethyl acetate (98/2) as eluent to yield **7** (5.01 g, 74%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (m, 4H), 1.93 (t, 1H, *J* = 2.7 Hz), 1.60-1.18 (m, 14H), 0.98 (t, 9H, *J* = 7.9 Hz), 0.56 (q, 6H, *J* = 7.9 Hz) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 108.9, 84.8, 81.2, 68.2, 29.5, 29.3, 29.1, 28.8, 28.6, 20.0, 18.2, 7.6, 4.7 ppm. IR (neat): ν = 3313, 2931, 2874, 2856, 2171, 1459, 1236, 1016, 722.

24-(triethylsilyl)tetracosa-10,12,23-triyn-1-ol 8 :

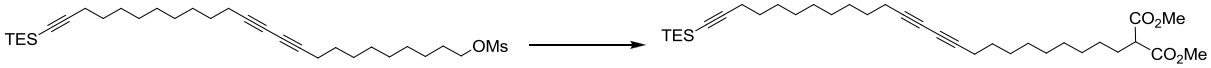
To a stirred solution of terminal alkyne **7** (2.70 g, 9.30 mmol, 1.0 eq) in a mixture of methanol and ethylamine (70% in water) 1/1 (100 mL), in darkness was added copper chloride (100 mg, 0.01 eq). Then, hydroxylamine hydrochloride (190 mg, 0.02 eq) was added and the blue dark solution became yellow. After that, the bromo-alkyne **6** (2.52 g, 1.1 eq) was added and the solution was stirred at room temperature for 4h. Then, the reaction was quenched with brine (100 mL) and the organic layer separated. The aqueous layer was extracted with ethyl acetate (3*200 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography on silica gel using cyclohexane/ethyl acetate (4/1) as eluent to yield **8** (2.42 g, 55%) as a yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.64 (t, 2H, *J* = 6.6 Hz), 2.23 (m, 6H), 1.60-1.25 (m, 28H), 1.00 (t, 9H, *J* = 7.7 Hz), 0.59 (q, 6H, *J* = 7.7 Hz) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 108.9, 100.7, 77.8, 65.4, 63.1, 32.9, 29.5, 29.4, 29.1, 28.9, 28.8, 28.4, 25.8, 19.9, 19.3, 7.6, 4.7 ppm. IR (neat): ν = 3337, 2927, 2854, 2170, 1458, 1017, 725; HRMS (ESI, *m/z*): calcd. for $C_{30}H_{52}OSi$ $[M+H]^+$: 457.3865; found: 457.3860.

24-(triethylsilyl)tetracosa-10,12,23-triyn-1-yl methanesulfonate 9 :



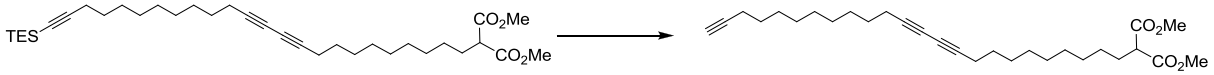
In darkness, to a stirred solution of alcohol **8** (2.36 g, 5.17 mmol, 1.0 eq) in dry THF (30 mL), were added triethylamine (1.7 mL, 6.20 mmol, 1.2 eq) and methanesulfonyl chloride (0.51 mL, 6.20 mmol, 1.2 eq). The solution was stirred at room temperature for 1h. Then, the reaction was quenched with a solution of potassium carbonate (10 mL) and water (30 mL). The aqueous layer was extracted with ethyl acetate (3*50 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography on silica gel using dichloromethane as eluent to yield **9** (2.48 g, 90%) as a yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.22 (t, 2H, *J* = 6.4 Hz), 3.01 (s, 3H), 2.24 (m, 6H), 1.76 (quint, 2H, *J* = 6.5 Hz), 1.64-1.25 (m, 26H), 1.00 (t, 9H, *J* = 7.7 Hz), 0.59 (q, 6H, J = 7.7 Hz) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 108.8, 81.4, 77.5, 77.4, 70.2, 65.4, 65.4, 37.3, 29.3, 29.2, 29.0, 28.9, 28.8, 28.7, 28.7, 28.4, 28.3, 25.4, 19.8, 19.2, 7.5, 4.6 ppm. IR (neat): ν = 2929, 2855, 2170, 1460, 1356, 1176, 1017, 971, 948, 819, 724; HRMS (ESI, *m/z*): calcd. for $C_{31}H_{54}O_3SSi$ $[M+Na]^+$: 557,3455; found: 557.3453.

dimethyl [24-(triethylsilyl)tetracosa-10,12,23-triyn-1-yl]malonate 10 :



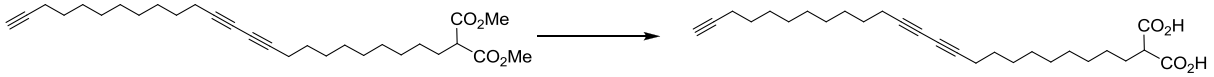
In darkness, to a stirred suspension of NaH (60% in oil) (225 mg, 4.94 mmol, 1.1 eq) in dry THF (30 mL), was added a solution of **9** (2.40 g, 4.49 mmol, 1.0 eq) in dry THF (10 mL) during 1h. The reaction mixture was stirred for 1h at room temperature and then at reflux for 24h. The solution was cooled to room temperature and quenched with HCl 1M (10 mL). The aqueous layer was extracted with ethyl acetate (3*50mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography on silica gel using cyclohexane/ethyl acetate (95/5) as eluent to yield **10** (2.23 g, 85%) as a yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.73 (s, 6H), 3.35 (t, 1H, *J* = 7.6 Hz), 2.23 (m, 6H), 1.88 (m, 2H), 1.66-1.25 (m, 26H), 0.98 (t, 9H, *J* = 7.8 Hz), 0.56 (q, 6H, J = 7.8 Hz) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 178.1, 77.4, 65.4, 52.5, 51.8, 29.5, 29.4, 29.3, 29.1, 29.0, 28.9, 28.8, 28.5, 27.4, 20.0, 19.3, 7.6, 4.7 ppm. IR (neat): ν = 2928, 2855, 5170, 1736, 1458, 1434, 1234, 1153, 1017, 909, 729; HRMS (ESI, *m/z*): calcd. for $C_{35}H_{58}O_4Si$ $[M+Na]^+$: 593.3997; found: 593.3992.

dimethyl tetracosa-10,12,23-triyn-1-ylmalonate 11 :



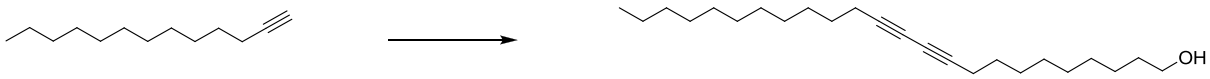
In darkness, to a stirred solution of **10** (1.50 g, 3.04 mmol, 1.0 eq) in THF (50 mL), was added tetrabutylammonium fluoride 1.0 M in hexane (4.51 mL, 4.56 mmol, 1.5 eq). The reaction mixture was stirred for 4h at room temperature and quenched with water (20 mL). The aqueous layer was extracted with ethyl acetate (3*50 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography on silica gel using cyclohexane/ethyl acetate (90/10) as eluent to yield **11** (1.15 g, 80%) as a white solid. Mp: 31-32°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.73 (s, 6H), 3.34 (t, 1H, *J* = 7.4 Hz), 2.23 (m, 6H), 1.92 (m, 3H), 1.67-1.25 (m, 26H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.1, 77.6, 68.2, 68.1, 65.4, 51.7, 29.5, 29.4, 29.3, 29.1, 29.0, 28.9, 28.8, 28.5, 27.4, 19.3, 18.5 ppm. IR (neat): ν = 3304, 2922, 2853, 1737, 1463, 1435, 1344, 1244, 1156, 1017; HRMS (ESI, *m/z*): calcd. for $C_{29}H_{44}O_4$ $[M+H]^+$: 495, 2871; found: 495, 2873.

tetracosa-10,12,23-triyn-1-ylmalonic acid 1 :



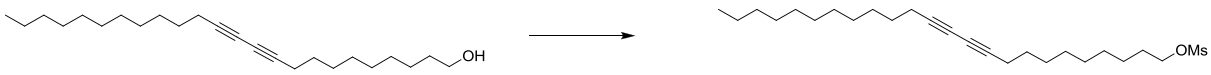
In darkness, to a stirred solution of **11** (200 mg, 0.44 mmol, 1.0 eq) in a mixture of THF and methanol (1/1) (2 mL), wad added an aqueous solution of lithium hydroxide 1M (0.52 mL, 1.32 mmol, 3.0 eq) is added. The reaction mixture was stirred for 24h at room temperature and quenched with HCl 1M (1 mL). The aqueous layer was extracted with ethyl acetate (3*5 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The product **1** (188 mg, 95%) was obtained as a white solid. Mp: 94-96°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.47 (t, 1H, *J* = 7.4 Hz), 2.23 (m, 6H), 1.93 (m, 3H), 1.66-1.25 (m, 28H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.2, 77.7, 68.2, 65.4, 51.7, 29.6, 29.4, 29.2, 28.9, 28.8, 28.6, 28.4, 27.5, 19.3, 18.5 ppm. IR (neat): ν = 3283, 2918, 2848, 1715, 1693, 1463, 1429, 1293, 1211, 917, 723, 270; HRMS (*m/z*): calcd. for $C_{27}H_{40}O_4$ [ESI, $M+H]^+$: 429.3004; found: 429.3000.

Tetracosa-10,12-diyn-1-ol 12 :



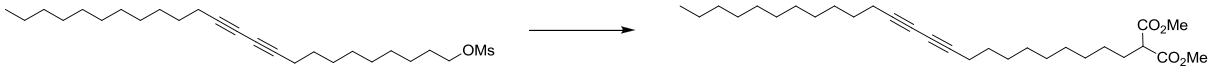
To a stirred solution of terminal alkyne (4.74 g, 26.70 mmol, 1.0 eq) in a mixture of methanol and ethylamine (70% in water) 1/1 (200 mL), in darkness was added copper chloride (220 mg, 0.01 eq). Then, hydroxylamine hydrochloride (420 mg, 0.02 eq) was added: the blue dark solution became yellow. After that, bromo-alkyne **6** (6.0 g, 23.76 mmol, 0.89 eq) was added and the solution was stirred at room temperature for 4h. Then, the reaction was quenched with brine (200 mL) and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (3*400 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography on silica gel using cyclohexane/ethyl acetate (4/1) as eluent to yield **12** (4.42 g, 53%) as a white solid. Mp: 55-56°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.63 (t, 2H, J = 6.6 Hz), 2.23 (t, 4H, J = 6.6 Hz), 1.58-1.25 (m, 32H), 0.87 (t, 3H, J = 6.6 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 77.7, 65.4, 65.4, 63.2, 32.9, 32.0, 29.7, 29.6, 29.5, 29.5, 29.2, 29.1, 29.0, 28.9, 28.5, 25.8, 22.8, 19.3, 14.2 ppm. IR (neat): ν = 3407, 3337, 2916, 2849, 1467, 1414, 1351, 1059, 1044, 1013, 981, 718, 615; HRMS (ESI, *m/z*): calcd. for $C_{24}H_{42}O$ $[M+H]^+$: 347.3314; found: 347.3309.

Tetracosa-10,12-diyn-1-yl methanesulfonate 13 :



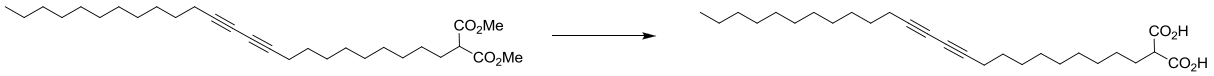
In darkness, to a stirred solution of **12** (4.42 g, 12.75 mmol, 1.0 eq) in dry THF (100 mL), were added triethylamine (4.3 mL, 15.3 mmol, 1.2 eq) and methanesulfonyl chloride (1.29 mL, 15.3 mmol, 1.2 eq). The solution was stirred at room temperature for 1h and quenched with a solution of potassium carbonate (50 mL) and water (100 mL). The aqueous layer was extracted with ethyl acetate (3*150 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography on silica gel using dichloromethane as eluent to yield **13** (5.17 g, 95%) as a white solid. Mp: 51-52°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.22 (t, 2H, J = 6.6 Hz), 2.99 (s, 3H), 2.23 (t, 4H, J = 6.8 Hz), 1.74 (q, 2H, J = 6.7 Hz), 1.55-1.25 (m, 30H), 0.87 (t, 3H, J = 6.7 Hz) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 77.7, 77.5, 70.3, 65.4, 65.3, 37.5, 32.0, 29.7, 29.6, 29.4, 29.3, 29.2, 29.0, 29.0, 28.9, 28.5, 28.4, 25.5, 22.8, 19.3, 14.2 ppm. IR (neat): ν = 2916, 2850, 1470, 1330, 1164, 999, 962, 849, 745, 717, 543; HRMS (ESI, *m/z*): calcd. for $C_{25}H_{44}O_3S$ $[M+K]^+$: 464.2676; found: 464.2681.

Dimethyl tetracosa-10,12-diyn-1-ylmalonate 14 :



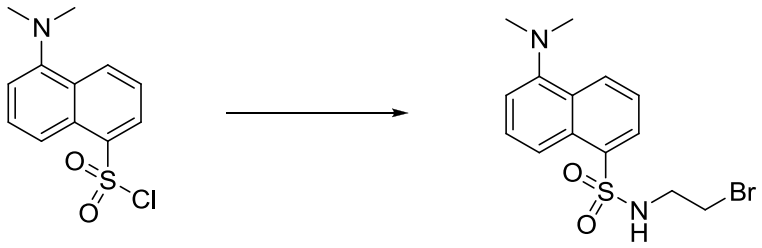
In darkness, to a stirred suspension of NaH (60% in oil) (682 mg, 13.39 mmol, 1.1 eq) in dry THF (100 mL), was added a solution of **13** (5.17 g, 12.17 mmol, 1.0 eq) in dry THF (20 mL) during 1h. The reaction mixture was stirred for 1h at room temperature and then at reflux for 24h. The solution was cooled to room temperature and quenched with HCl 1M (30 mL). The aqueous layer was extracted with ethyl acetate (3*150mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography on silica gel using cyclohexane/ethyl acetate (95/5) as eluent to yield **14** (4.26 g, 76%) as a white solid. Mp: 36-37°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.73 (s, 6H), 3.35 (t, 1H, *J* = 7.6 Hz), 2.23 (t, 4H, *J* = 6.9 Hz), 1.90 (m, 2H), 1.56-1.25 (m, 32H), 0.88 (t, 3H, *J* = 6.6 Hz) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.1, 77.7, 65.4, 65.4, 52.5, 51.8, 32.0, 29.7, 29.6, 29.4, 29.4, 29.3, 29.2, 29.1, 29.0, 28.5, 27.4, 22.8, 19.3, 14.2 ppm. IR (neat): ν = 2914, 2849, 1754, 1732, 1471, 1438, 1338, 1296,1268, 1242, 1214, 1191, 1152, 1127, 1007, 1022, 956, 715; HRMS (ESI, *m/z*): calcd. for $C_{29}H_{48}O_4$ $[M+K]^+$: 499, 3190; found: 499.3191.

Tetracosa-10,12-diyn-1-ylmalonic acid 2 :



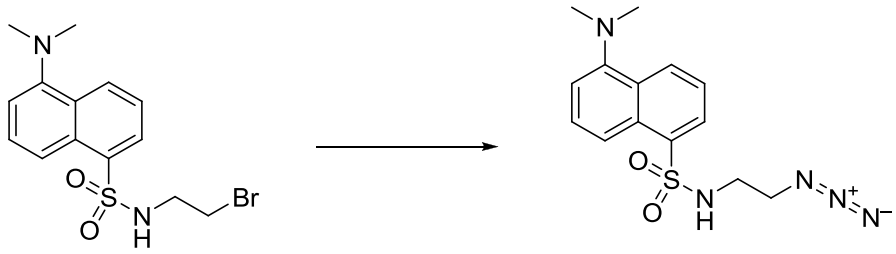
In darkness, to a stirred solution of **14** (200 mg, 0.43 mmol, 1.0 eq) in a mixture of THF and methanol (1/1) (2 mL), wad added an aqueous solution of lithium hydroxide 1M (0.52 mL, 1.29 mmol, 3.0 eq) is added. The reaction mixture was stirred for 24h at room temperature and quenched with HCl 1M (1 mL). The aqueous layer was extracted with ethyl acetate (3*5 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The product **2** (191 mg, 98%) was obtained as a white solid. Mp: 106-108°C. RMN: ^{1}H NMR (400 MHz, MeOD): δ = 3.28 (t, 1H, *J* = 7.2 Hz), 2.24 (t, 4H, *J* = 6.8 Hz), 1.83 (m, 2H), 1.53-1.25 (m, 32H), 0.90 (t, 3H, *J* = 6.4 Hz) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 173.3, 77.8, 66.4, 53.0, 33.1, 30.7, 30.6, 30.5, 30.4, 30.3, 30.1, 30.1, 29.9, 29.5, 28.5, 23.7, 19.7, 14.4 ppm. IR (neat): ν = 2913, 2849, 2359, 2341, 1720, 1699, 1469, 1417, 1301, 1266, 933, 717, 670; HRMS (ESI, *m/z*): calcd. for $C_{27}H_{44}O_4$ $[M+H]^+$: 433.3317; found: 433, 3319.

***N*-(2-bromoethyl)-5-(dimethylamino)naphthalene-1-sulfonamide 15 :**



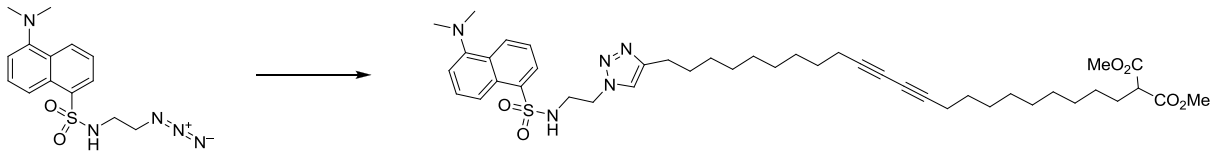
In darkness, to a stirred solution of dansyl chloride (4.00 g, 14.82 mmol, 1.0 eq) in dioxane (80 mL), were added bromoethylamine bromohydride (3.33g, 16.30 mmol, 1.1 eq) and triethylamine (4.96 mL, 32.60 mmol, 2.2 eq). The reaction mixture was stirred for 24h at room temperature and then filtered and concentrated. The crude product was purified by flash chromatography on silica gel using dichloromethane as eluent to yield **15** (4.57 g, 86%) as a yellow solid. Mp: 117-119°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.56 (d, 1H, J = 8.7 Hz), 8.26 (m, 2H), 7.55 (m, 2H), 7.19 (d, 1H, J = 7.8 Hz), 5.34 (t, 1H, J = 6.1 Hz), 3.30 (m, 4H), 2.88 (s, 6H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 152.2, 134.6, 130.9, 130.0, 129.6, 128.7, 123.2, 118.7, 115.5, 45.5, 44.7, 31.7 ppm. IR (neat): ν = 3290, 2923, 2831, 2787, 1573, 1453, 1407, 1312, 1231, 1201, 1138, 1073, 945, 786, 982, 622, 587; HRMS (ESI, *m/z*): calcd. for $C_{14}H_{17}BrN_2O_2S$ $[M+H]^+$: 379.0089 ; found: 379.0086.

***N*-(2-azidoethyl)-5-(dimethylamino)naphthalene-1-sulfonamide :**



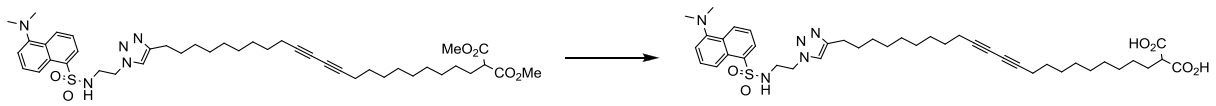
In darkness, to a stirred solution of **15** (4.57 g, 12.8 mmol) in DMF (400 mL), was added sodium azide (2.50g, 38.4 mmol, 3.0 eq). The reaction mixture was stirred for 24h at 80°C and then concentrated under vacuum. The crude product was purified by flash chromatography on silica gel using dichloromethane as eluent to yield **3** (3.64 g, 89%) as a yellow-green oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.58 (d, 1H, J = 8.4 Hz), 8.29 (m, 2H), 7.61 (m, 2H), 7.22 (d, 1H, J = 7.5 Hz), 5.09 (t, 1H, J = 6.6 Hz), 3.32 (t, 2H, J = 5.4 Hz), 3.10 (t, 2H, J = 6.0 Hz), 2.89 (s, 6H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 152.4, 135.1, 131.0, 130.3, 129.9, 128.9, 123.6, 119.1, 115.7, 51.3, 45.8, 42.8 ppm. IR (neat): ν = 2943, 2870, 2833, 2104, 1588, 1574, 1456, 1408, 1321, 1161, 1144, 1093, 1074, 945, 190, 625, 571; HRMS (ESI, *m/z*): calcd. for $C_{14}H_{17}N_5O_2S$ $[M+K]^+$: 358.0735 ; found: 358.0735.

dimethyl (22-{1-[2-({[5-(dimethylamino)-1-naphthyl]sulfonyl}amino)ethyl]-1*H*-1,2,3-triazol-4-yl}docosa-10,12-diyn-1-yl)malonate 16 :



In darkness, to a stirred solution of dansyl azide **3** (68 mg, 0.21 mmol, 1.0 eq) in a 1/1 *tert*-butanol/water mixture (4 mL), were added **11** (100 mg, 0.21 mmol, 1.0 eq), sodium ascorbate (8.4 mg, 0.2 eq) and $CuSO_4$, $5H_2O$ (5.3 mg, 0.1 eq). The reaction mixture was stirred under micro-waves irradiation for 10 minutes at 80°C and then concentrated under vacuum. The crude product was purified by flash chromatography on silica gel using dichloromethane/ethyl acetate (9/1) as eluent to yield **16** (143 mg, 85%) as a pale yellow solid. Mp: 71-73°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (d, 1H, *J* = 8.0 Hz), 8.26 (m, 2H), 7.55 (t, 2H, *J* = 7.2 Hz), 7.21 (d, 1H, *J* = 7.6 Hz), 5.62 (bs, 1H), 4.36 (m, 2H), 3.76 (s, 6H), 3.45 (m, 2H), 3.37 (t, 1H, *J* = 7.6 Hz), 2.91 (s, 6H), 2.62 (m, 2H), 2.24 (t, 4H, *J* = 6.0 Hz), 1.91 (m, 2H), 1.62 (m, 2H), 1.52 (m, 2H), 1.40-1.15 (m, 24H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 146.5, 134.7, 130.8, 130.7, 129.9, 129.7, 129.6, 128.7, 123.4, 122.1, 115.6, 77.7, 65.4, 52.6, 51.9, 50.1, 45.6, 42.9, 42.8, 29.5, 29.4, 29.4, 29.3, 29.2, 29.1, 29.0, 28.5, 27.4, 25.7, 19.3 ppm. IR (neat): ν = 2926, 2854, 1735, 1574, 1456, 1435, 1328, 1201, 1144, 1103, 1060, 914, 791, 742, 623; HRMS (ESI, *m/z*): calcd. for $C_{43}H_{61}N_5O_6S$ $[M+H]^+$: 776.4415 ; found: 776.4413.

(22-{1-[2-({[5-(dimethylamino)-1-naphthyl]sulfonyl}amino)ethyl]-1*H*-1,2,3-triazol-4-yl}docosa-10,12-diyn-1-yl)malonic acid 4 :



In darkness, to a stirred solution of **16** (105 mg, 0.14 mmol, 1.0 eq) in a mixture of THF and methanol (1/1) (2 mL), was added an aqueous solution of lithium hydroxide 1M (1.0 mL, 0.98 mmol, 7 eq). The reaction mixture was stirred for 48h at room temperature and quenched with HCl 1M (1 mL). The aqueous layer was extracted with ethyl acetate (3*5 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The product **4** (95 mg, 95%) was obtained as a yellow-green oil. ^{1}H NMR (400 MHz, MeOD): δ = 8.42 (d, 1H, *J* = 8.4 Hz), 8.13 (d, 1H, *J* = 8.8 Hz), 8.05 (d, 1H, *J* = 6.0 Hz), 7.44 (td, 2H, *J* = 2.8 Hz, *J* = 8.4 Hz), 7.21 (s, 1H), 7.12 (d, 1H, *J* = 7.6 Hz), 4.91 (s, 1H), 4.24 (t, 2H, *J* = 5.6 Hz), 3.25 (3.25, 2H, *J* = 6.0 Hz), 3.21 (m, 1H), 2.74 (s, 6H), 2.40 (t, 2H, *J* = 7.6 Hz), 2.11 (m, 4H), 1.74 (m, 4H), 1.40-1.15 (m, 28H) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 173.3, 153.1, 149.0, 136.7, 131.5, 131.2, 130.8, 130.2, 129.4, 124.5, 123.7, 120.6, 120.5, 116.6, 78.2, 66.7, 51.0, 46.0, 43.8, 30.6, 30.5, 30.4, 30.3, 30.2, 30.1, 30.0, 29.6, 28.5, 26.3, 19.9 ppm. IR (neat): ν = 3325, 2928, 2855, 1716, 1574, 1457, 1326, 1231, 1161, 1143, 1119, 1060, 974, 790, 623; HRMS (ESI, *m/z*): calcd. for $C_{41}H_{57}N_5O_6S$ $[M+Na]^+$: 770,3922 ; found: 770,3918.

Polymerization of micelles:

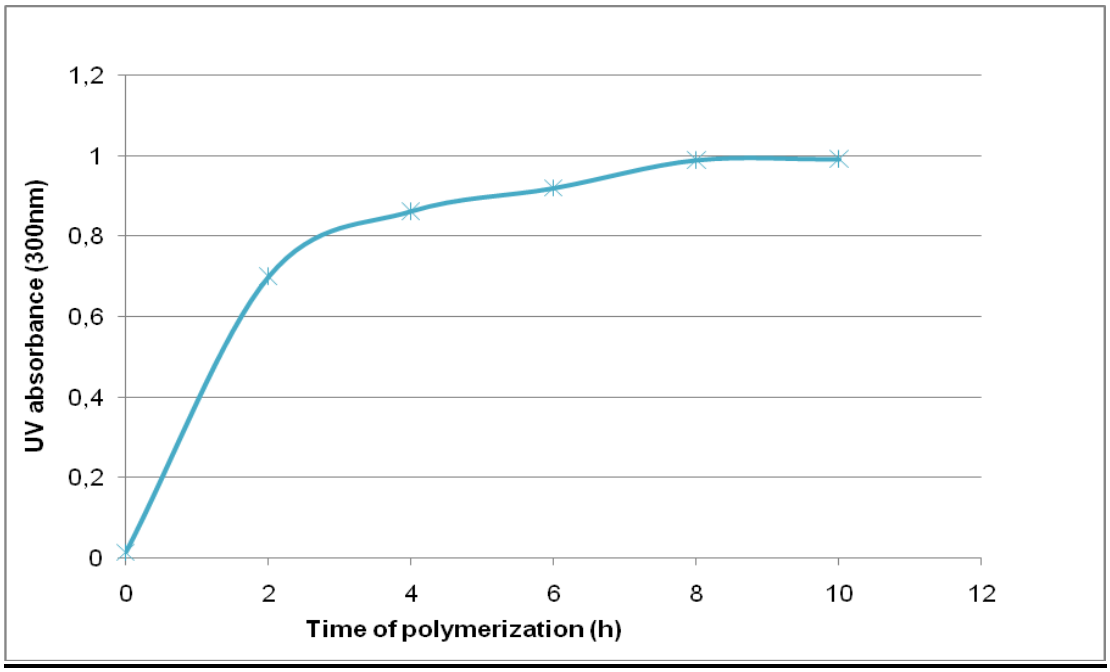
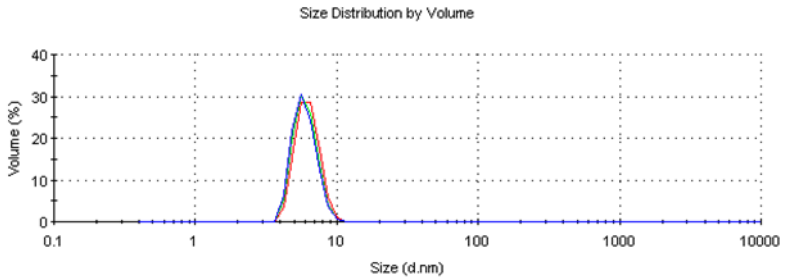
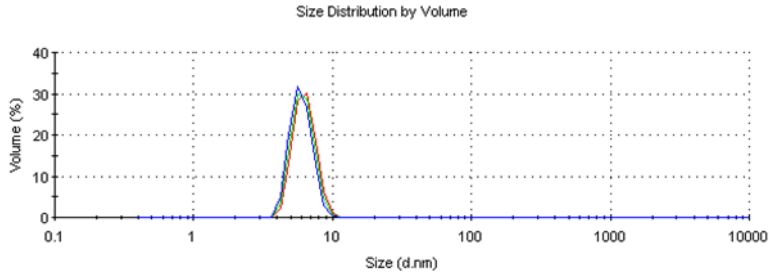


Figure S1- Kinetics of polymerization of micelles of lipid 1 by UV absorbance at 300nm

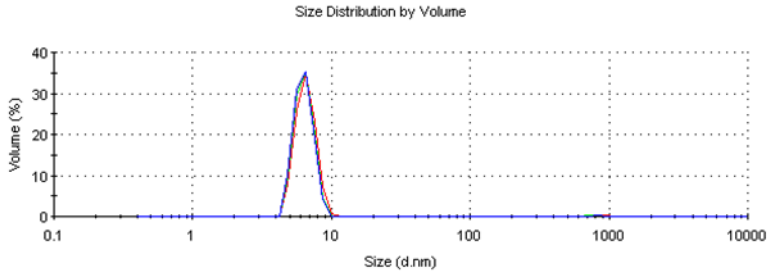
DLS measurements :



a)



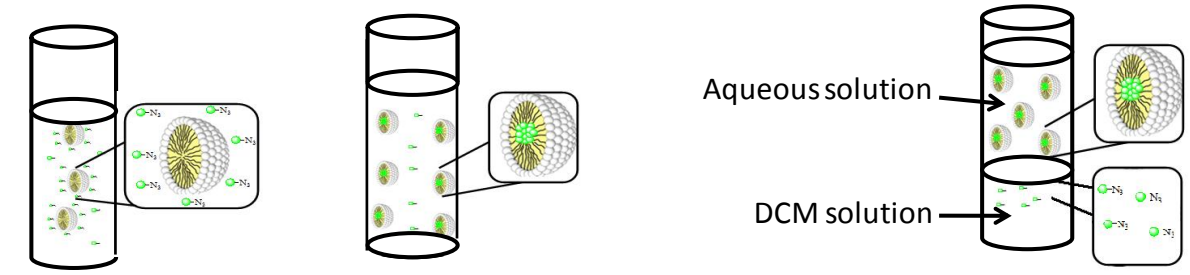
b)



c)

Figure S3: DLS measurements of micelles from lipid 2: a) before polymerization; b) after polymerization; c) after reaction

UV titration of dansyl 3:



a) Before reaction in the *tert*-butanol/Tris mixture

b) After reaction in the *tert*-butanol/Tris mixture

c) After treatment

Figure S4 : Protocol used for the titration of free dansyl 3. After labelling, a fixed volume of DCM was added to the solution and the organic layer was separated. The free dansyl 3 in the organic layer was titrated by UV-spectroscopy

Table S1: UV-titration at 330 nm of the free dansyl.

% of dansyl **3** used	% of dansyl **3** recovered in the DCM solution
80	12.0
60	0.9
40	0.5
20	0.1
10	0.0
2	0.0

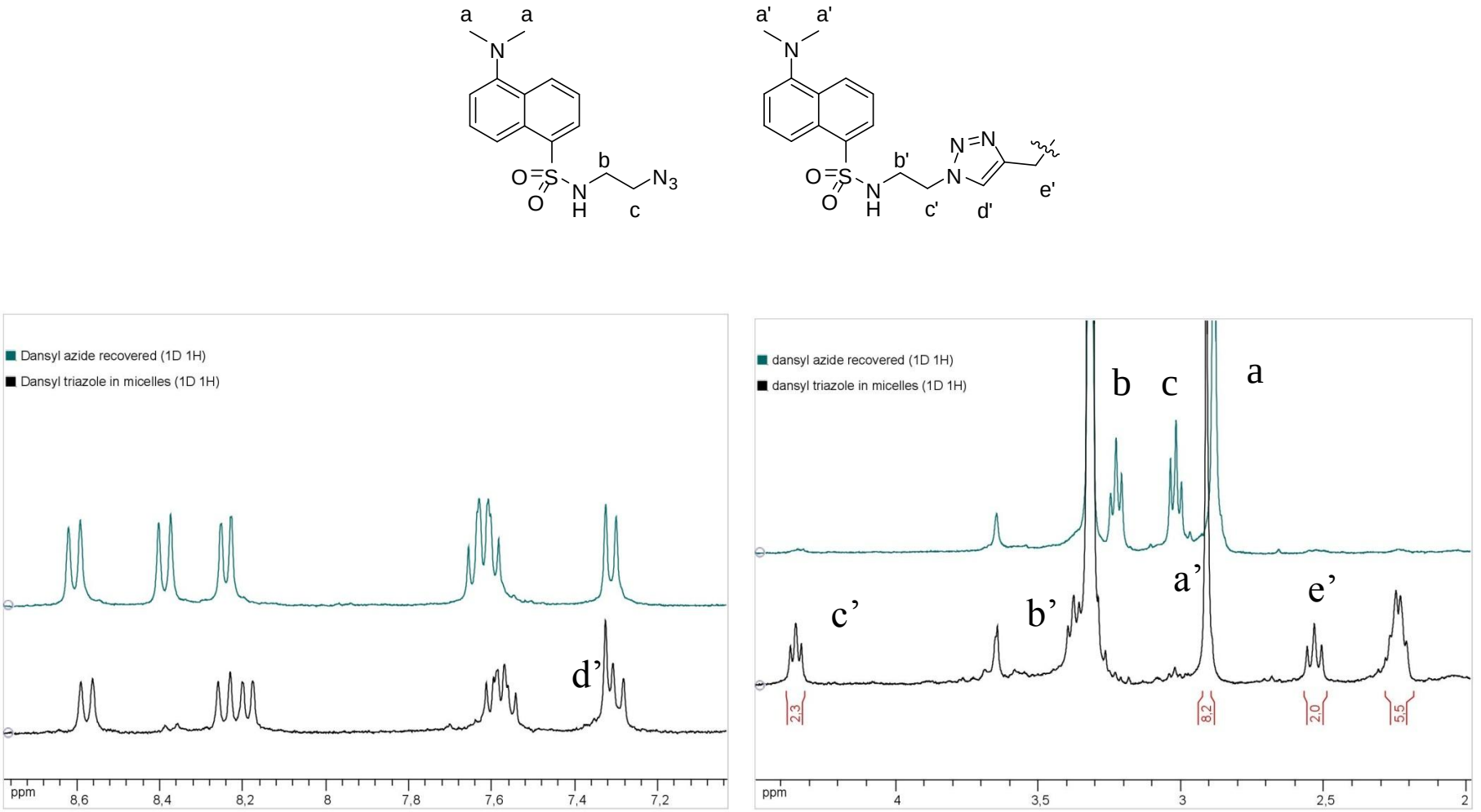


Figure S5: ^{1}H NMR of micelles containing dansyl grafted in the aqueous solution and dansyl azide 3 recovered in the DCM solution.

The ^{1}H NMR of the organic layer indicated the presence of dansyl azide 3 and the ^{1}H NMR of micelles in the aqueous layer showed the presence of grafted dansyl to micelles

Fluorescence spectra :

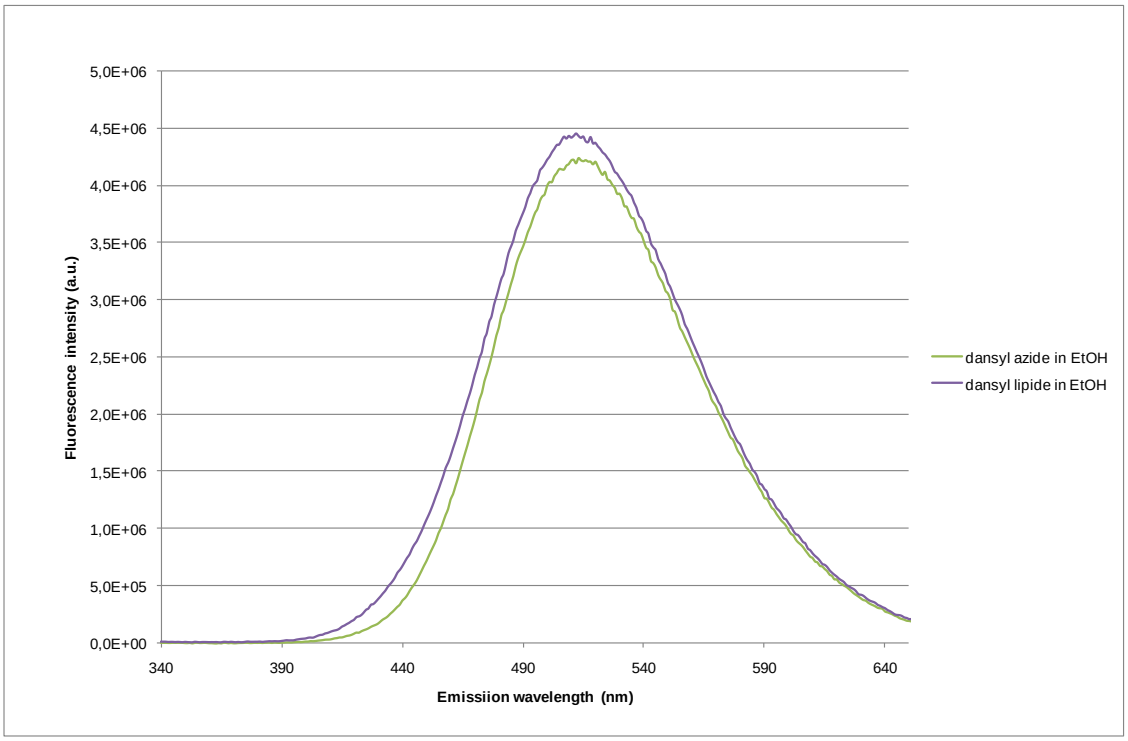


Figure S7 – Fluorescence of dansyl azide 3 and molecule 4 in EtOH – λexc = 330 nm