Supporting Information

Topochemical Polymerization in Self-assembled Rodlike Micelles of Bisurea Bolaamphiphiles

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Materials: Solvents used in synthesis were reagent grade. CH_2Cl_2, $CHCl_3$, Et_3N and Pyridine were distilled from CaH_2. All PEO derivatives were dried in vacuum over P_2O_5 during at least 12 h. The reagents 11-aminoundecanoic acid, poly(ethylene glycol)-monomethyl ether (M_n = 350), pyrene, 5-hexynoic acid and 6-heptynoic acid were purchased from Aldrich, Fluka, or Acros and were used without additional purification. 11-Aminoundecanoyl-(poly(ethylene glycol)-monomethylether)-ester[1] and 11-Aminohexanoyl-(poly(ethylene glycol)-monomethylether)-ester were prepared according to literature procedures.

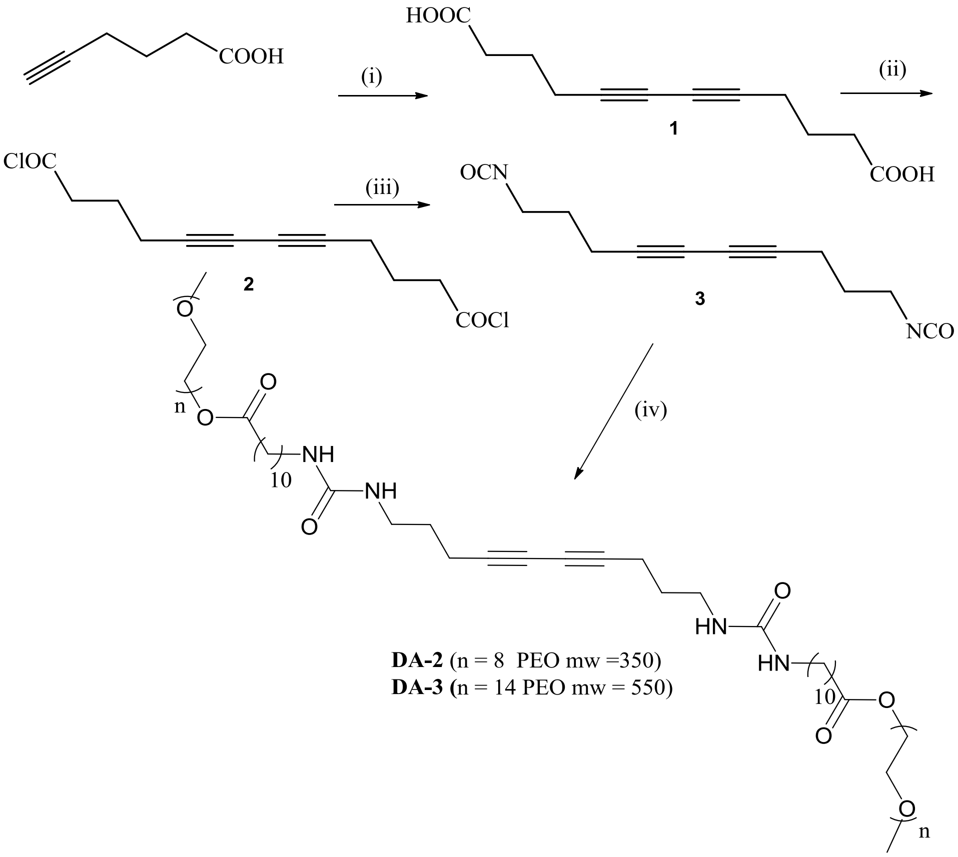
General Methods: NMR spectra were acquired on a 400 MHz Varian Mercury Vx (400 MHz for ^{1}H-NMR, 100 MHz for ^{13}C-NMR). Proton and carbon chemical shifts are reported in ppm downfield of tetramethylsilane using the resonance of the deuterated solvent as internal standard. Splitting patterns are designated as singlet (*s*), doublet (*d*), triplet (*t*) and multiplet (*m*). Infrared spectra were measured on a Perkin Elmer 1600FT-IR. Matrix assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF) was performed on a Perseptive DE PRO Voyager MALDI-TOF mass spectrometer using α-cyano-4-hydroxycinnamic acid as the calibration matrix. Fluorescence spectra were recorded on an Edinburgh Instrument FS920 double-monochromator spectrometer with a Peltier-cooled red-sensitive photomultiplier.

Samples for cryogenic transmission electron microscopy (cryo-TEM) were prepared in a 'Vitrobot' instrument4 (PC controlled vitrification robot, patent applied, Frederik et al 2002, patent licensed to FEI) at room temperature and a relative humidity >95%. In the preparation chamber of the 'Vitrobot' 3 μl sample was applied on a Quantifoil grid (R 2/2, Quantifoil Micro Tools GmbH; freshly glow discharged just prior to use), excess liquid was blotted away and the thin film thus formed was shot (acceleration about 3 g) into liquid ethane. The vitrified film was transferred to a cryoholder (Gatan 626) and observed at -170 °C in a Technai microscope operating at 120 kV. Micrographs were taken at low dose conditions.

Synthesis of Bisurea based Bolaamphiphiles:

Bisurea-DA Synthesis:

The general synthetic strategy towards the triblock amphiphiles is outlined in Scheme S1, S2 and S3. The oxidative coupling of 5-hexynoic acid with CuCl yielded 5,7-dodecadiynedioic acid which was converted to the 5,7-dodecadiynedioic acid chloride with oxalyl chloride. The acid chloride via a Curtius rearrangement yielded the 1,10-Diisocyanatodeca-4,6-diyne which was attached the amine functionality of PEG derivative.



DA-2 (n = 8 PEO mw =350)
DA-3 (n = 14 PEO mw = 550)

Scheme S1: *Synthesis of the triblock bolaamphiphile; (i)NH_4Cl, CuCl, O_2, water, 60 ^oC, 2h, 65%; (ii) (a) NaOH, EtOH, THF, 5 min, RT; (b) $(COCl)_2$, Et_2O, DMF (cat), 2h, RT; (iii) NaN_3, CH_3CN, 65 ^oC, 1h, 50%; (iv)PEG-$OOC(CH_2)_{10}NH_3Cl$, Et_3N, CH_2Cl_2, RT, 65-70%.*

5,7-Dodecadiynedioic Acid (1). A suspension of copper(I) chloride (2.63 g, 26.6 mmol) and ammonium chloride (4.78 g, 89.3 mmol) in 14 mL water was added to a solution of 5-hexynoic acid (1 g, 8.92 mmol) in 14 mL of water. The green reaction mixture was heated to 60 °C, and air was bubbled through the solution while stirring vigorously for 2 h. The reaction mixture was quenched with 20 mL of concentrated hydrochloric acid, and the resulting precipitate was collected by suction filtration immediately, washed with a 1/1 mixture of hydrochloric acid/water, and recrystallized from a water/methanol mixture (2/8), resulting in white crystals of compound **1** (650 g, 65%). ^{1}H NMR (400 MHz, CD_3OD): δ: 2.43 (t, 4H, C=OC*H*2), 2.35 (t, 4H, CH_2-C), 1.81 (m, 4H, CH_2-CH_2-CH_2). ^{13}C NMR (100 MHz, CD_3OD): δ: 175.3 (*C*=O), 75.7 (CH_2-*C*), 65.3 (*C*-*C*), 32.2 (C=O-*C*H_2), 23.5 (CH_2-*C*H_2-CH_2), 17.7 (*C*H_2-C).

5,7-Dodecadiynedioic Acid Dichloride (2). 5,7-Dodecadiynedioic acid (730 mg, 3.3 mmol) was dissolved in an ethanol/tetrahydrofuran (5 mL/5 mL) mixture. To this solution was added an ethanolic NaOH solution (262 mg, 6.57 mmol) at room temperature. Immediate precipitation was observed. After stirring for 5 min the solvent was evaporated in rotavapor and in vacuum, and the residue was dried under vacuum for 5 h. The residue was dissolved in 10 mL of dry ether and 1 drop of dry DMF and was cooled to 0 °C. At this temperature oxalyl chloride (2.5 mL, 32 mmol) was added, and the solution was stirred for 2 h. The resulting suspension was filtered, and the filtrate was evaporated to dryness, resulting in 0.86 g of compound **2**, which was used in the next step without purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ: 3.05 (t, 4H, O=CCH_2), 2.40 (t, 4H, CH_2-C), 1.92 (m, 4H, CH_2C$H_2$$CH_2$). FT-IR (cm^{-1}): 2945, 1793.

1,10-Diisocyanatodeca-4,6-diyne (3). To 5,7-dodecadiynedioic acid dichloride (870 g, 3.3 mmol) in dry acetonitrile (15 mL) was added sodium azide (472 mg, 7.3 mmol) with stirring under an argon atmosphere. The reaction mixture was heated to 65 °C. N_2 started to evolve. After the nitrogen evolution had become negligible (1 h), a white solid was filtered off, and the filtrate was purified by distillation. The diisocyanate (**3**) was collected as a colorless oil (0.35 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 3.45 (t, 4H, O=C=N-CH_2), 2.39 (t, 4H, CH_2-C), 1.80 (m, 4H, CH_2C$H_2$$CH_2$). ^{13}C NMR(100 MHz, $CDCl_3$): δ 122.4 (O=*C*=N), 79.4 (CH_2-*C*), 65.9 (*C*-*C*), 42.2 (N-*C*H_2), 31.8 (CH_2-*C*H_2-CH_2), 13.7 (C-*C*H_2). FT-IR (cm^{-1}): 2959, 2253(-N=C=Ostr).

UD10U-350 (DA-2). A solution of 11-aminoundecanoyl-(poly(ethylene glycol)-monomethylether)-ester (550 mg, 0.91 mmol) and triethylamine (91 mg, 0.91 mmol) in 2 ml dichloromethane was added to 1,10-diisocyanatodeca-4,6-diyne (94 mg, 0.43 mmol) 2 ml dichloromethane and stirred overnight. The solution was concentrated and the product was purified using column chromatography (silica gel, $CHCl_3$/Methanol 19:1 v/v). Finally, precipitation from diethyl ether yielded 0.85 g (68%) of the product **(DA-2)** as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.82, 4.69 (bs, 4H, N*H*), 4.22 (t, 4H, ^3J(H,H) = 4.0 Hz, CH_2OCO), 3.71-3.54 (m, 52H, OCH_2), 3.38 (s, 6H, OCH_3), 3.30-3.26 (m, 4H, CH_2N), 3.18-3.14 (m, 4H, CH_2N), 2.31 (t, 4H, ^3J(H,H) = 4 Hz, CH_2CO), 1.74-1.68 (m, 4H, CH_2C), 1.63-1.58 (m, 4H, CH_2CH_2NH), 1.47-1.32 (m, 4H, CH_2CH_2CO), 1.28 (bs, 24H, CH_2).

^{13}C-NMR (100 MHz, $CDCl_3$, T=295K): δ =173.85, 158.55, 71.90, 70.53, 69.17, 65.89, 63.35, 58.99, 40.45, 40.38, 39.21, 39.04, 34.17, 30.32, 30.27, 29.45, 29.42, 29.28, 29.18, 29.15, 29.02, 28.77, 28.70, 26.91, 26.87, 24.86, 16.65. FT-IR (cm^{-1}): 3335, 2921, 2852, 1731, 1615, 1579, 1468.

GPC (THF; PS standards): M_n = 1707 g/mol, PDI = 1.10.

MALDI-TOF [M+Na+] = 1373.74 ± n*44 (calcd: 1373.88 ± n*44).

UD10U-550 (DA-3). A solution of 11-aminoundecanoyl-(poly(ethylene glycol)-monomethylether)-ester (700 mg, 0.85 mmol) and triethylamine (91 mg, 0.90 mmol) in 2 ml dichloromethane was added to 1,10-Diisocyanatodeca-4,6-diyne (88 mg, 0.41 mmol) 2 ml dichloromethane and stirred overnight. The solution was concentrated and the product was purified using column chromatography (silica gel, $CHCl_3$/Methanol 19:1 v/v). Finally, precipitation from diethyl ether yielded 1.05 g (58%) of the product **(DA-3)** as a white solid.

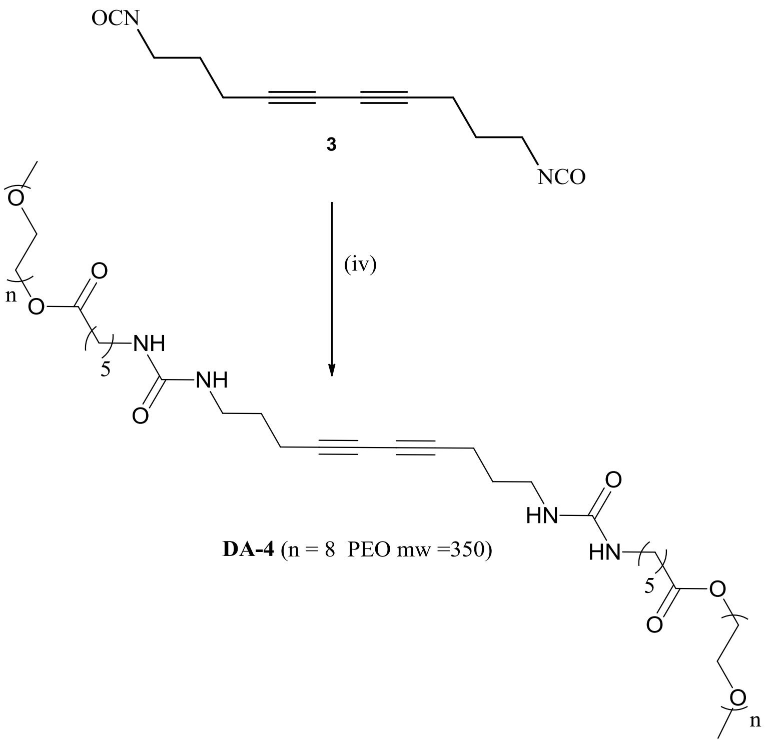
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.81, 4.69 (bs, 4H, N*H*), 4.22 (t, 4H, ^3J(H,H) = 4.0 Hz, CH_2OCO), 3.82-3.49 (m, 92H, OCH_2), 3.38 (s, 6H, OCH_3), 3.31-3.26 (m, 4H, CH_2N), 3.16-3.11 (m, 4H, CH_2N), 2.31 (t, 4H, ^3J(H,H) = 4 Hz, CH_2CO), 1.73-1.69 (m, 4H, CH_2C), 1.63-1.59 (m, 4H, CH_2CH_2NH), 1.49-1.31 (m, 4H, CH_2CH_2CO), 1.27 (bs, 24H, CH_2).

^{13}C-NMR (100 MHz, $CDCl_3$, T=295K): δ = 173.84, 158.43, 72.57, 71.91, 70.54, 69.17, 65.88, 63.35, 61.70, 59.00, 40.46, 39.26, 34.17, 30.27, 29.41, 29.27, 29.14, 29.02, 28.79, 26.86, 24.85, 16.67.

FT-IR (cm^{-1}): 3337, 2921, 2865, 1732, 1615, 1579, 1466.

GPC (THF; PS standards): M_n = 2654 g/mol, PDI = 1.04.

MALDI-TOF [M+Na+] = 1815.11 ± n*44 (calcd: 1815.14 ± n*44).



Scheme S2: *Synthesis of the triblock bolaamphiphile (**DA-4**) with caproic acid spacer; (i)PEG-OOC(CH_2)$_5$$NH_3Cl$, Et_3N, CH_2Cl_2, RT, 65-70%.*

Caproic-UD10U-350 (DA-4). A solution of 11-aminohexanoyl-(poly(ethylene glycol)-monomethylether)-ester (1.38 g, 2.78 mmol) and triethylamine (280 mg, 2.78 mmol) in 2 ml dichloromethane was added to 1,10-Diisocyanatodeca-4,6-diyne (285 mg, 1.32 mmol) 2 ml dichloromethane and stirred overnight. The solution was concentrated and the product was purified using column chromatography (silica gel, $CHCl_3$/Methanol 19:1 v/v). Finally, precipitation from diethyl ether yielded 1.05 g (66%) of the product **(DA-4)** as a white solid.

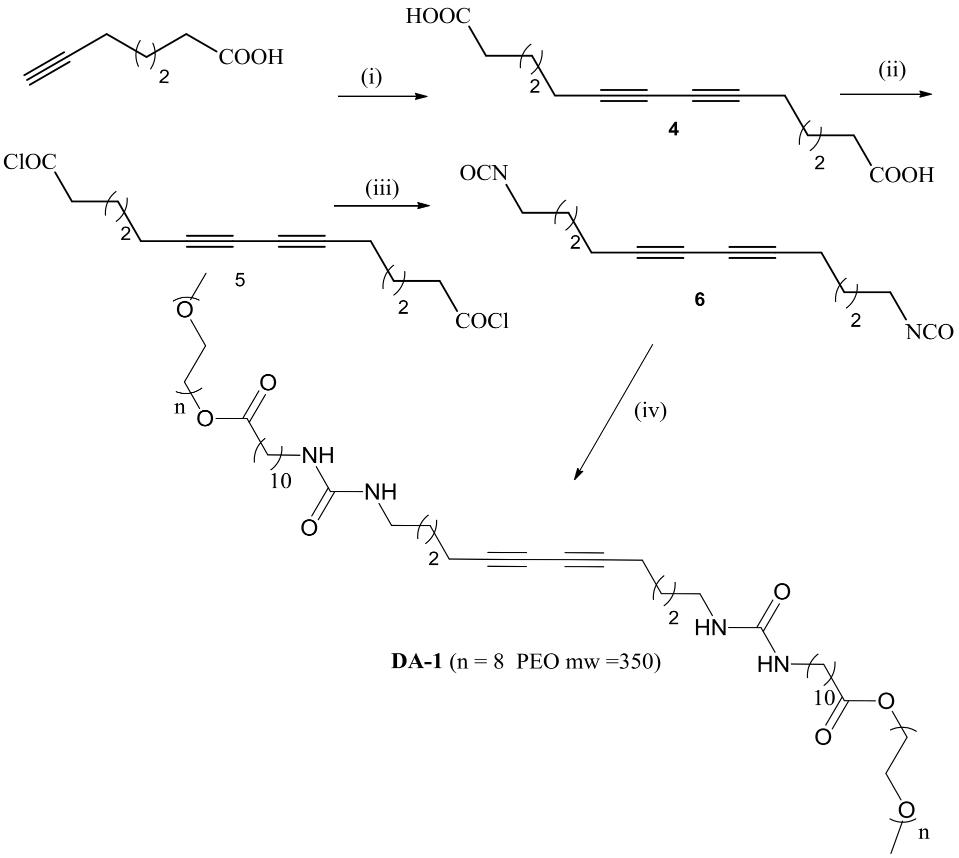
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.82, 4.77 (bs, 4H, N*H*), 4.23 (t, 4H, ^3J(H,H) = 4.0 Hz, CH_2OCO), 3.71-3.54 (m, 60H, OCH_2), 3.38 (s, 6H, OCH_3), 3.28-3.24 (m, 4H, CH_2N), 3.14-3.18 (m, 4H, CH_2N), 2.33 (t, 4H, ^3J(H,H) = 7 Hz, CH_2CO), 1.74-1.61 (m, 8H, CH_2C, $NHCH_2CH_2CH_2CH_2CH_2C$=O), 1.54-1.46 (m, 4H, CH_2CH_2NH), 1.40-1.34 (m, 4H, CH_2CH_2CO).

^{13}C-NMR (100 MHz, DMSO-*d*6, T=295K): δ = 173.63, 158.80, 71.89, 70.55, 70.52, 70.47, 70.44, 69.15, 65.87, 63.30, 59.00, 39.96, 39.04, 34.03, 29.89, 28.86, 26.27, 24.55, 16.62.

FT-IR (cm^{-1}): 3335, 2921, 2852, 1732, 1614, 1580, 1468.

GPC (THF; PS standards): M_n = 1628 g/mol, PDI = 1.03.

MALDI-TOF [M+Na+] = 1233.68 ± n*44 (calcd: 1233.73 ± n*44).



Scheme 3: *Synthesis of the triblock bolaamphiphile* **DA-1***; (i)NH_4Cl, CuCl, O_2, water, 60 °C, 2h, 65%; (ii) (a) NaOH, EtOH, THF, 5 min, RT; (b) $(COCl)_2$, Et_2O, DMF (cat), 2h, RT; (iii) NaN_3, CH_3CN, 65 °C, 1h, 85%; (iv)PEG-OOC$(CH_2)_{10}NH_3Cl$, Et_3N, CH_2Cl_2, RT, 65-70%.*

6,8-Tetradecadiynedioic Acid (4). A suspension of copper(I) chloride (2.63 g, 26.5 mmol) and ammonium chloride (4.78 g, 89.3 mol) in 14 mL water was added to a solution of 5-heptynoic acid (1.12 g, 8.9 mmol) in 14 mL of water. The green reaction mixture was heated to 60 °C, and air was bubbled through the solution while stirring vigorously for 2 h. The reaction mixture was quenched with 20 mL of concentrated hydrochloric acid, and the resulting precipitate was collected by suction filtration immediately, washed with a 1/1 mixture of hydrochloric acid/water, and recrystallized from a water/methanol mixture (2/8), resulting in white crystals (600 g, 65%). ^{1}H NMR (400 MHz, CD_3OD): δ: 2.33-2.26 (m, 8H, C=OCH_2, CH_2-C), 1.69 (dt, 4H, CH_2-CH_2C=O), 1.54 (dt, 4H, CH_2-CH_2-C). FT-IR (cm^{-1}): 3036, 2950, 1699.

6,8-Tetradecadiynedioic Acid Dichloride (5). 6,8-Tetradecadiynedioic acid (772 mg, 3.1 mmol) was dissolved in an ethanol/tetrahydrofuran (5 mL/5 mL) mixture. To this solution was added an ethanolic NaOH solution (247 mg, 6.17 mmol) at room temperature. Immediate precipitation was observed. After stirring for 5 min the solvent was evaporated and the residue was dried under vacuum for 5 h. The residue was dissolved in 10 mL of dry ether and 1 drop of dry DMF and was cooled to 0 °C. At this temperature oxalyl chloride (2.5 mL, 32 mmol) was added, and the solution was stirred for 2 h. The resulting suspension was filtered, and the filtrate was evaporated to dryness, resulting in 0.86 g of compound **7**, which was used in the next step without purification. FT-IR (cm^{-1}): 2939, 1790.

1,12-Diisocyanatodeca-4,6-diyne (6). To 6,8-tetradecadiynedioic acid dichloride (870 g, 3.3 mmol) in dry acetonitrile (15 mL) was added sodium azide (440 mg, 6.8 mmol) with stirring under an argon atmosphere. The reaction mixture was heated to 65 °C. N_2 started to evolve. After the nitrogen evolution had become negligible (1 h), a white solid was filtered off, and the filtrate was purified by distillation. The diisocyanate was collected as a colorless oil (0.45 g, 55%). ^{1}H NMR (200 MHz, $CDCl_3$): δ: 3.35 (t, 4H, O=C=N-CH_2), 2.32 (t, 4H, CH_2-C), 1.75-1.70 (m, 4H, $CH_2CH_2CH_2N$), 1.65-1.59 (m, 4H, CH_2CH_2C=O). FT-IR (cm^{-1}): 2950, 2257 (-N=C=O stretch).

UD12U-350 (DA-1). A solution of 11-aminoundecanoyl-(poly(ethylene glycol)-monomethylether)-ester (1 g, 1.65 mmol) and triethylamine (0.27 ml, 1.97 mmol) in 2 ml dichloromethane was added to 1,10-Diisocyanatodeca-4,6-diyne (194 mg, 0.787 mmol) 2 ml dichloromethane and stirred overnight. The solution was concentrated and the product was purified using column chromatography (silica gel, $CHCl_3$/Methanol 19:1 v/v). Finally, precipitation from diethyl ether yielded 0.7 g (62%) of the product **(DA-1)** as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.60 (bs, 4H, N*H*), 4.22 (t, 4H, ^3J(H,H) = 4.0 Hz, CH_2OCO), 3.71-3.54 (m, 52H, OCH_2), 3.37 (s, 6H, OCH_3), 3.18-3.12 (m, 8H, CH_2N), 2.31 (t, 4H, ^3J(H,H) = 4 Hz, CH_2CO), 1.63-1.57 (m, 8H, CH_2C & CH_2CH$_2$NH), 1.45-1.38 (m, 4H, CH_2CH$_2$CO), 1.28 (bs, 24H, CH_2).

^{13}C-NMR (100 MHz, DMSO-*d*6, T=295K): δ = 173.98, 158.37, 71.90, 70.55, 69.18, 65.75, 63.48, 59.00, 40.54, 39.82, 34.18, 30.19, 29.46, 29.40, 29.26, 29.14, 29.02, 18.92.

FT-IR (cm^{-1}): 3326, 2922, 2852, 1732, 1613, 1578, 1458.

GPC (THF; PS standards): M_n = 1939 g/mol, PDI = 1.03.

MALDI-TOF [M+Na+] = 1373.74 ± n*44 (calcd: 1373.88 ± n*44).

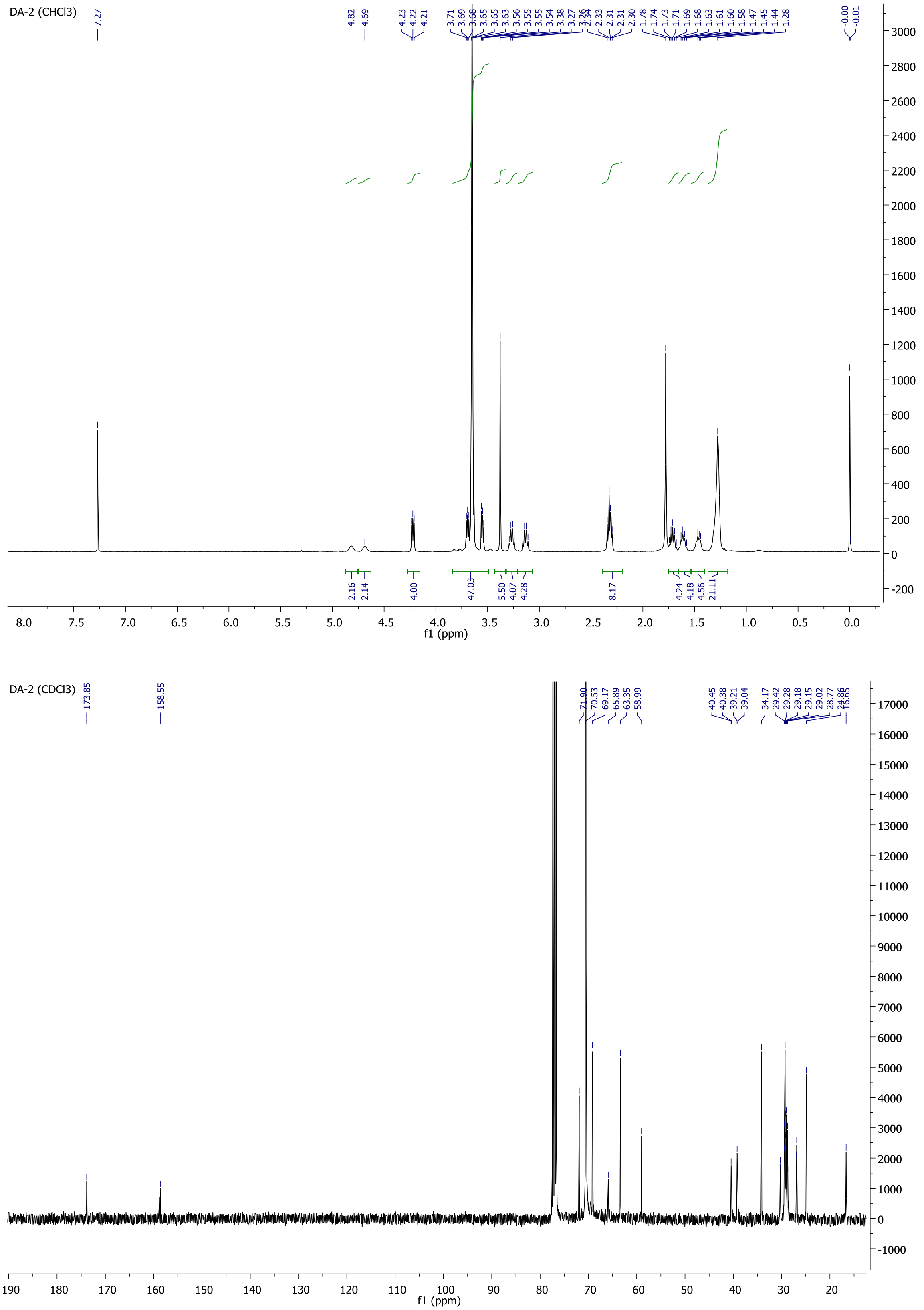
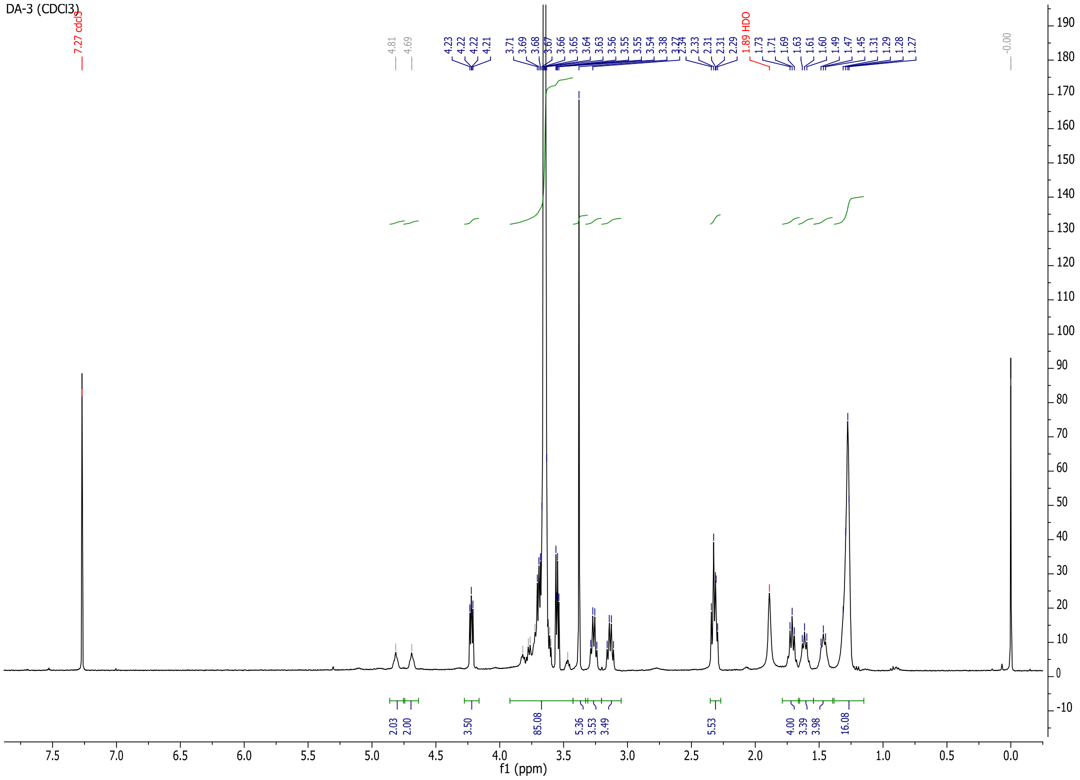


Figure S1. ^{1}H NMR and ^{13}C NMR of **DA-2** in $CDCl_3$.



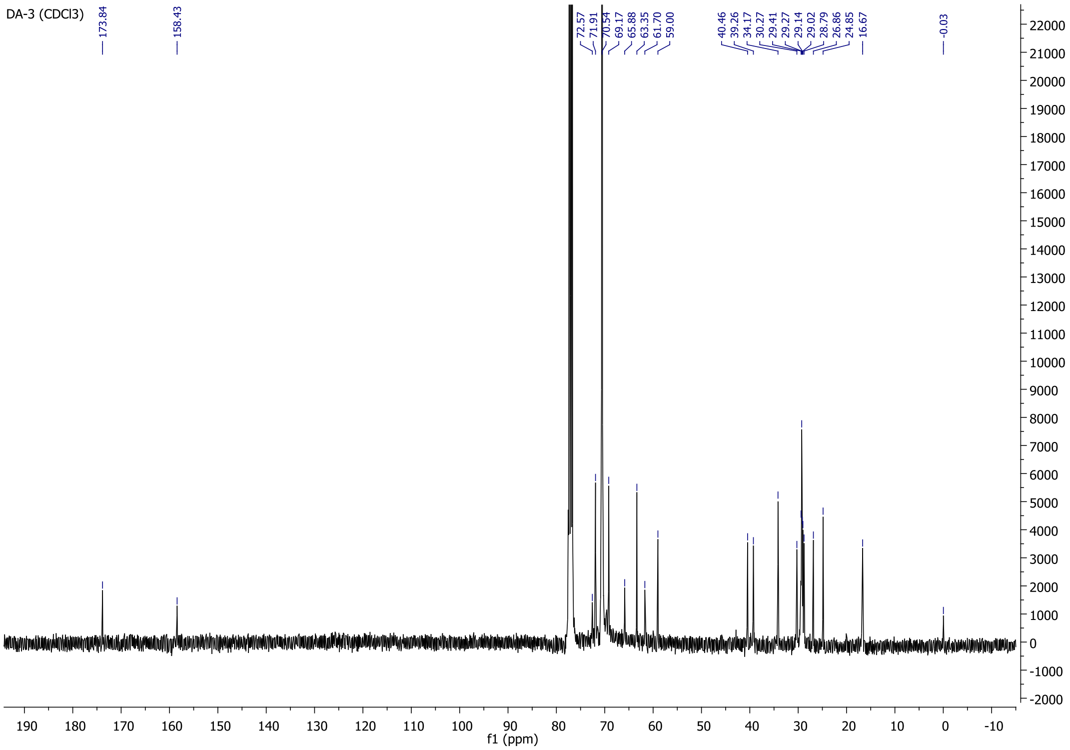


Figure S2. ^{1}H NMR and ^{13}C NMR of **DA-3** in CDCl$_3$.

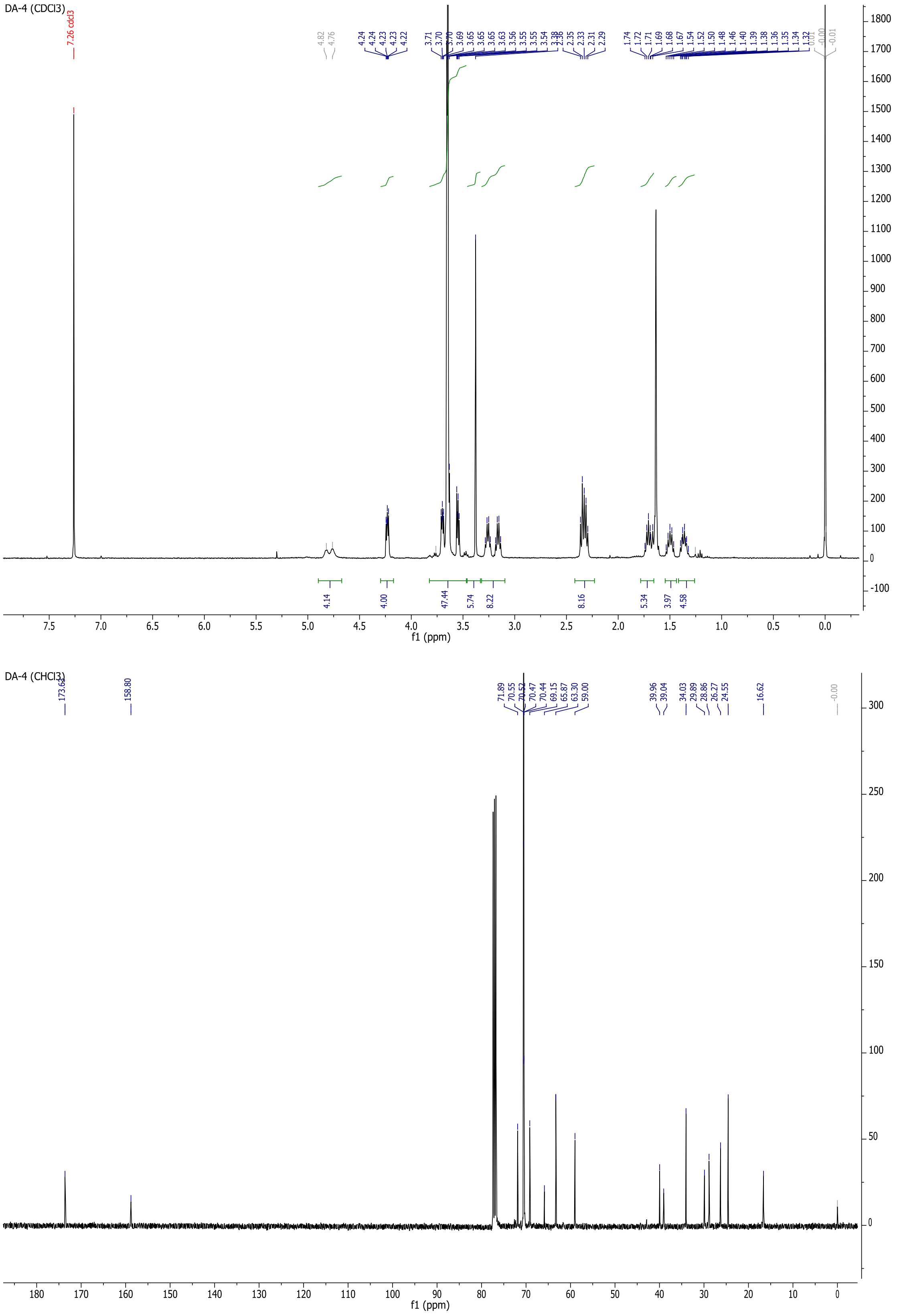


Figure S3. ^{1}H NMR and ^{13}C NMR of **DA-4** in CDCl$_3$.

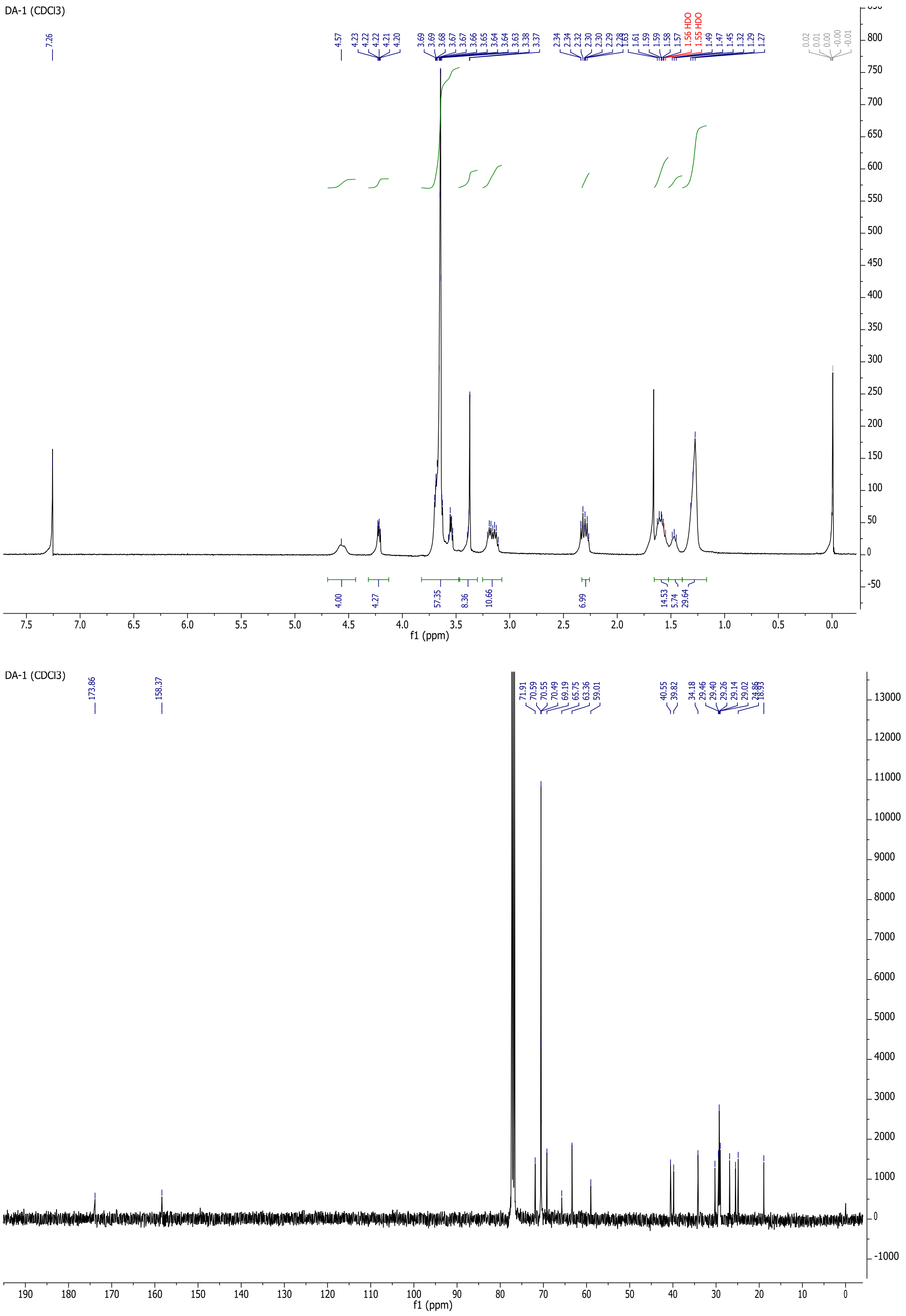


Figure S4. ^{1}H NMR and ^{13}C NMR of **DA-1** in $CDCl_3$**.**

Measurement of critical micellar concentration (cmc) of the diacetylene bolaamphiphiles:

For determination of critical micelle concentration of the bolaamphiphiles, pyrene was used as a fluorescence probe. Pyrene emission spectra of aqueous solutions of bolaamphiphiles containing different concentrations was recorded and ratio of intensities of peak 1 and peak 3 (I1/I3) was plotted versus logarithm of concentration.[1] The cmc is taken as the concentration at which the ratio starts to decrease.

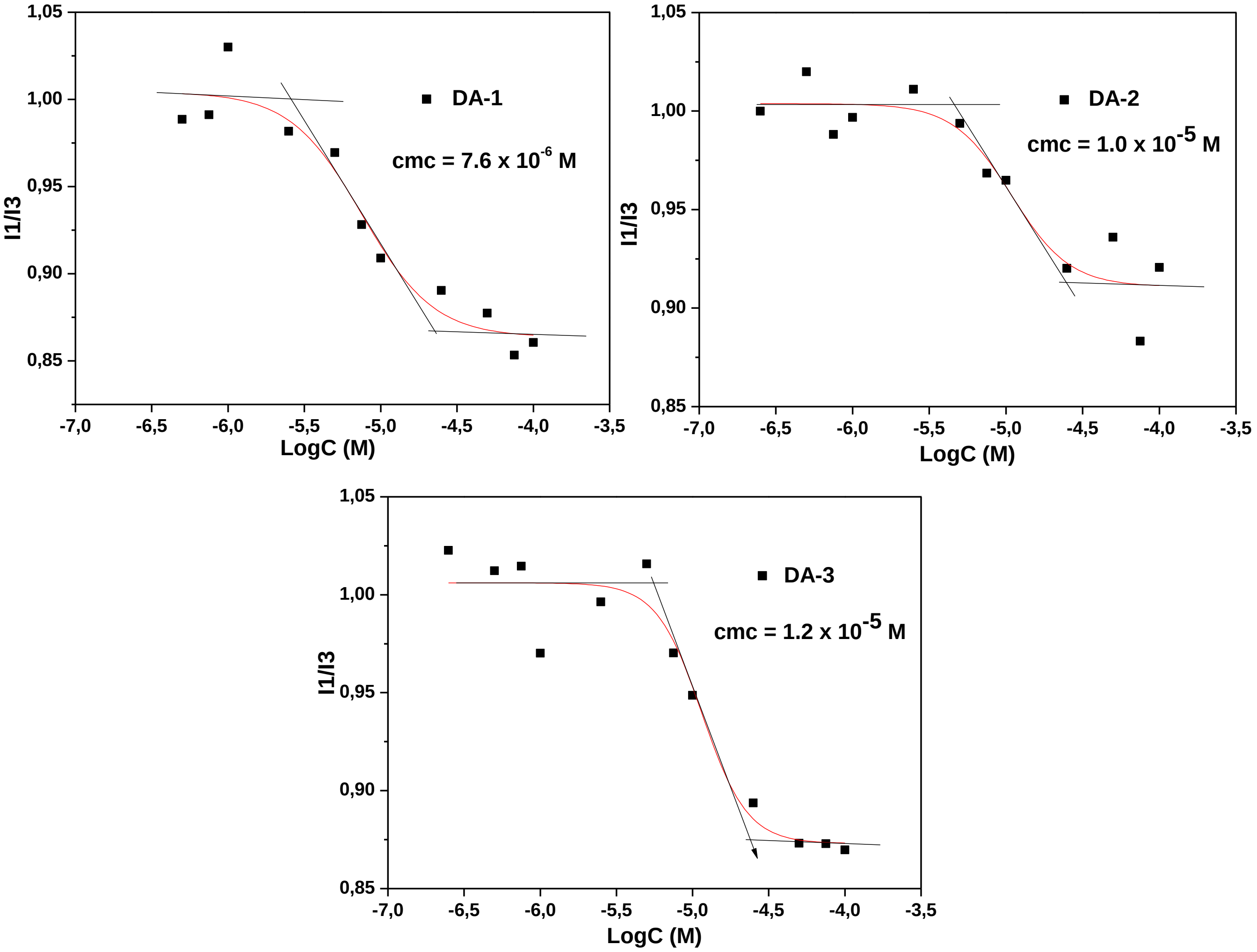


Figure S5. Determination of critical micelle concentration of DA-**1**, DA-**2**, DA-**3** using pyrene as a fluorescence probe. Ratio of intensities of peak 1 and peak 3 (I1/I3) *vs* concentration; The cmc is taken as the concentration at which the ratio starts to decrease.

Cryo-TEM:

The sample vitrification procedure was carried out using an automated vitrification robot (FEI Vitrobot™ Mark III). CryoTEM grids, R2/2 Quantifoil Jena grids, were purchased from Quantifoil Micro Tools GmbH. Prior to the vitrification procedure (3 μL aliquots, 4 s blotting time, -2 mm blotting offset, 100 % relative humidity) the grids were surface plasma treated using a Cressington 208 carbon coater operating at 5 mA for 40 s. The cryo-TEM experiments were performed on a FEI Technai 20, type Sphera (www.cryotem.nl). The Technai 20 is equipped with a LaB_6 filament operating at 200 kV and the images were recorded using a 1k x 1k Gatan CCD camera.

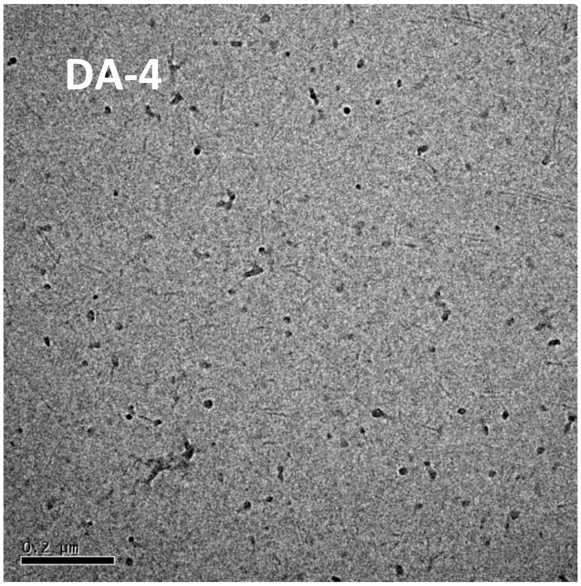


Figure S6. Cryo-TEM image of 1 mM of DA-**4** in water**.**

UV-Vis Spectra:

At elevated temperature: The UV cuvette was heated to with a thermostat in the carrousel. The carrousel was fitted with eight 8W hitachi lamp of wavelength 254 nm. For 15 min irradiation, 1 mM PDA-**1** shows a pronounced blue band (675 nm) over purple band (619 nm) while PDA-**2** shows predominance of 680 nm over 627 and 540 nm peaks.

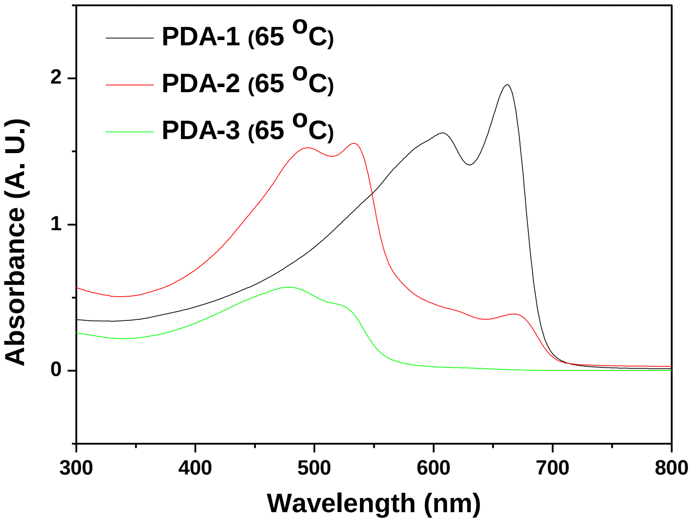


Figure S7. UV-vis spectra of bolaamphilphiles irradiated at elevated temperature (65 °C).

Solid film: 1 mM $CHCl_3$ solution of the bolamphiphiles were drop casted on the quartz plates and solvent was evaporated on air before they were exposed to irradiation.

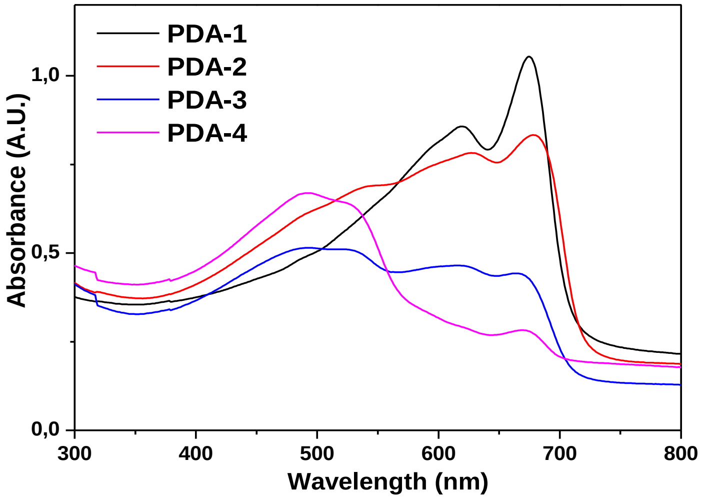


Figure S8. UV-vis spectra of bolaamphilphiles irradiated in solid film.

Thermochromism: The conjugated backbone is sensitive to changes in side chain organization. Thus, the optical properties of PDA can be modified by changing the temperature. UV-vis measurement was performed with heating and cooling back the UV cuvette with peltier. For PDA-**1**, a semi-reversible change was observed while for PDA-**2** and PDA-**3** irreversible changes were obtained.

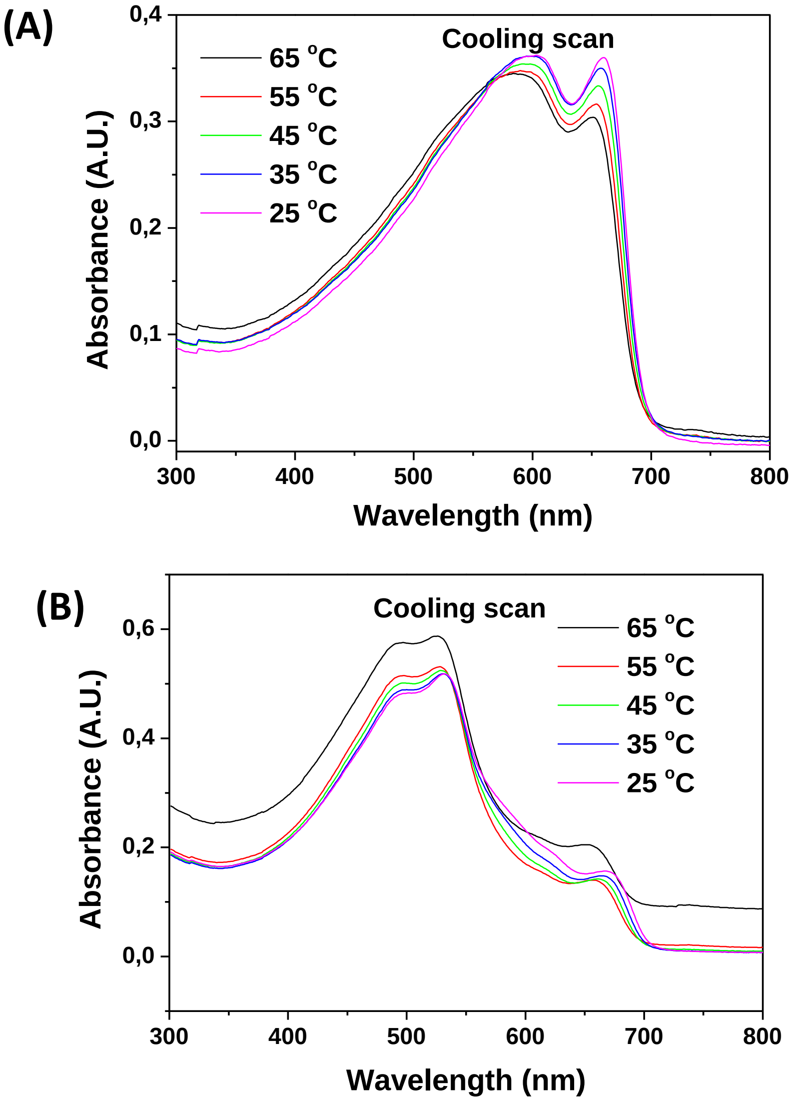


Figure S9. Thermochromism behaviors (cooling scan) of (A) PDA-**1** and (B) PDA-**2** in water.

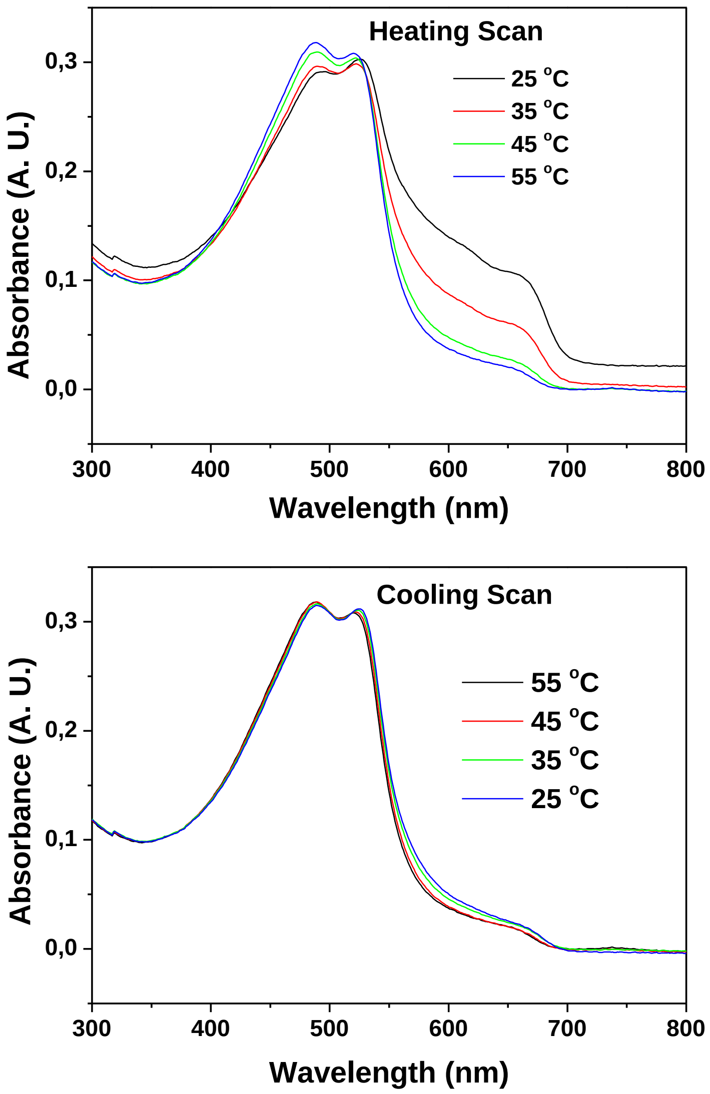


Figure S10. Thermochromism behaviors, (A) heating scan and (B) cooling scan of PDA-**3** in water showing an irreversible thermochromism behavior.

Solvatochromism: The UV-vis spectra of PDA solution were recorded. Then water was evaporated and PDAs were taken in a thermodynamically good solvent like chloroform and spectra were recorded. Then the solvent was evaporated and the PDAs were re-dispersed in water.

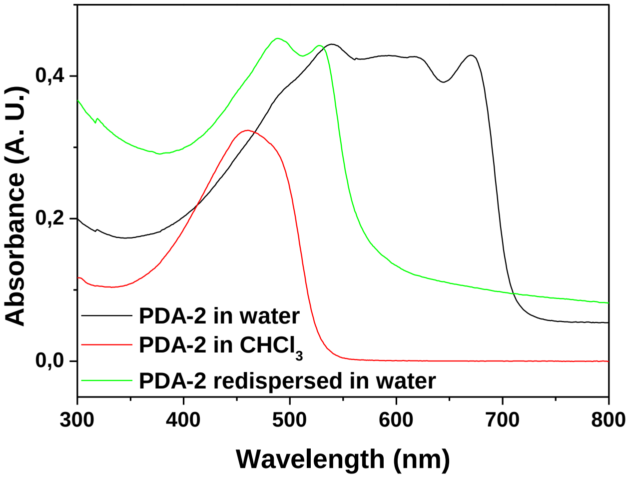


Figure S11. Solvatochromism behaviors of PDA-**2** in water and chloroform.

For PDA-**2** in chloroform, it showed yellow solution. However after re-dispersing in water it gave red solution (540 nm) and does not revert back to blue and purple bands. This is an example of irreversible solvatochromism.

Resonance Raman Scattering:

Raman spectra were recorded with a Jobin-Yvon T64000 triple stage spectrograph. The laser line at 632.8 nm of a CVI Melles Griot HeNe laser was used as exciting source. The intensity of Raman-active C=C (~1450 cm^{-1}) and C≡C (2100 cm^{-1}) bond stretching vibrations associated with the conjugated backbone is strongly enhanced because of low-lying electronic transitions associated with the conjugated backbone. All the diacetylene show very week Raman scattering; however, irradiation UV light produced the conjugated polymer backbone with very high intensity of RRS signals. While the unpolymerized DA rods showed Raman-active C=C and C≡C bond stretching vibrations at 1453 and 2100 cm^{-1}, the polymerized rods showed a remarkable decrease in wavenumber (~15 cm^{-1}) due to the extent of conjugation. The Raman bands at 1440 and 2083 cm^{-1} correspond to characteristic carbon-carbon double bond and triple bond. The peaks at 1220, 1083 are assigned to bending vibrations of the double and triple bond respectively.

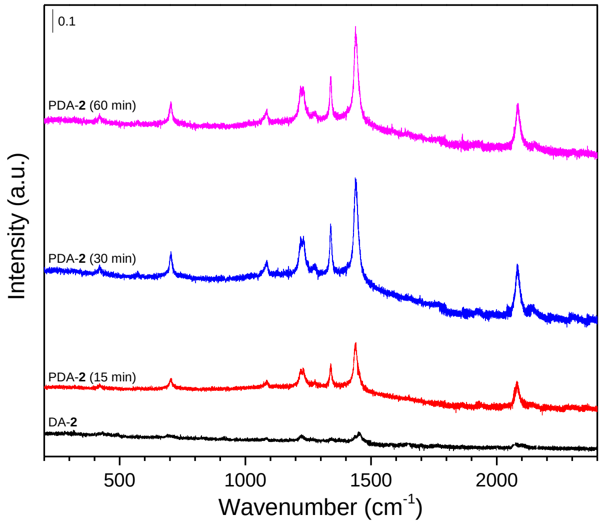


Figure S12: Raman scattering of DA-**2** and PDA-**2** with different irradiation time.

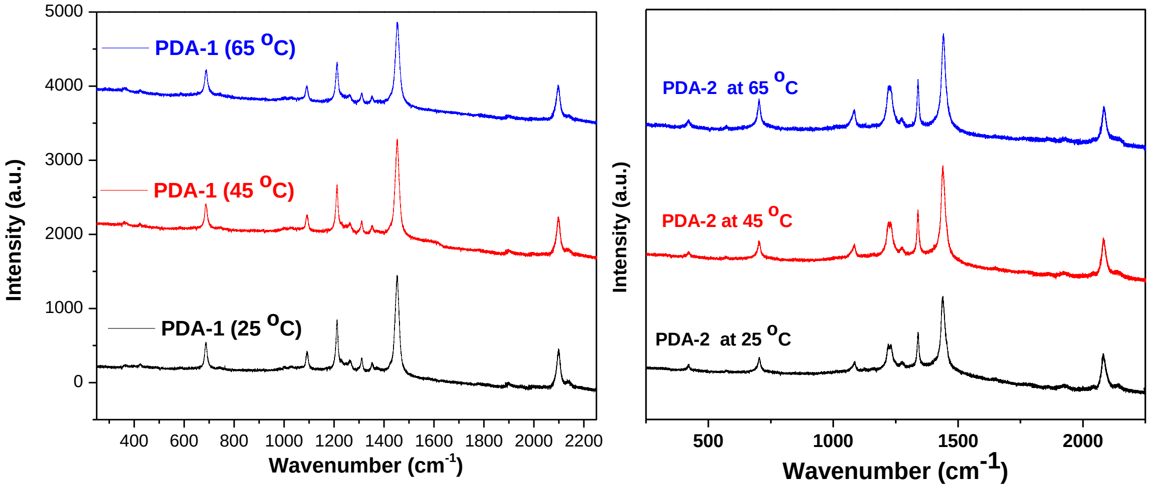


Figure S13: Temperature dependent Raman scatterings of (A) PDA-**1** and (B) PDA-**2**.

Photon correlation spectroscopy (PCS)

Static (SLS) and dynamic light scattering (DLS) experiments were performed over a wide time range t = 10^{-7} - 10 s and angular range from 20 ° to 150 °, while the corresponding scattering vector were in the range of q = 5 x 10^{-3} – 2.5 x 10^{-2} nm^{-1}. For the light scattering measurements, a commercially available set up from ALV GmbH was used, consisting of a goniometer and an ALV-5000 multiple-tau full digital correlator. The light source was a He-Ne laser operating at 633 nm. All measurements were carried out at temperature T = 20 °C.

For the preparation of the samples, dust free dispersions were obtained by filtration only the solvent – chloroform - through PTFE membrane with a pore size of 20 nm (Millipore) directly into cylindrical silica glass cuvettes (Hellma, inner diameter 10 mm) containing known amount of the polymer as powder. The empty cuvettes were cleaned in advance, with acetone and with the solvent in order to remove any containing traces of dust.

The Mw of the PDA-**2** and PDA-**3** was obtained from the SLS experiments at low concentrations using the Zimn equation:

$$\frac{K^{*}c}{R(q,c)} = \frac{1}{M_w\, P(q)} + 2A_2c$$

Where $R(q,c)$ is the excess Rayleigh ratio of the solution as a function of the wavevector q and concentration c and it is directly proportional to the intensity of the scattered light in excess of the light scattered by the pure solvent. c is the solute concentration. M_w is the weight-averaged solute molar mass. A_2 is the second virial coefficient in the virial expansion of the osmotic pressure and $P(q)$ is the form factor which describes the angular dependence of the scattered light. For measurements, performed at low angle and infinite dilution, we assume $P(q) = 1$.

K^* is the constant which equals to $K^* = 4\pi^2(dn/dc)^2 n_0^2/N_a l_0^4$.

N_a is Avogadro's number, n_0 is the index of refraction of the solvent and l_0 is the vacuum wavelength of the laser.

For obtaining the *dn/dc* values of PDA-**2** and PDA-**3** in solution, measurements were performed at MPIP Mainz, where chloroform solutions of PDA-**2** and PDA-**3** were prepared at different concentrations c = 0.5 – 5 g/L and their refractive index was determined using scanning Michelson interferometer equipped with 633 nm laser. The refractive index has a linear dependence with the polymer concentrations. With a linear fit through 0.0 the *dn/dc* values for the polymer solutions were determined.

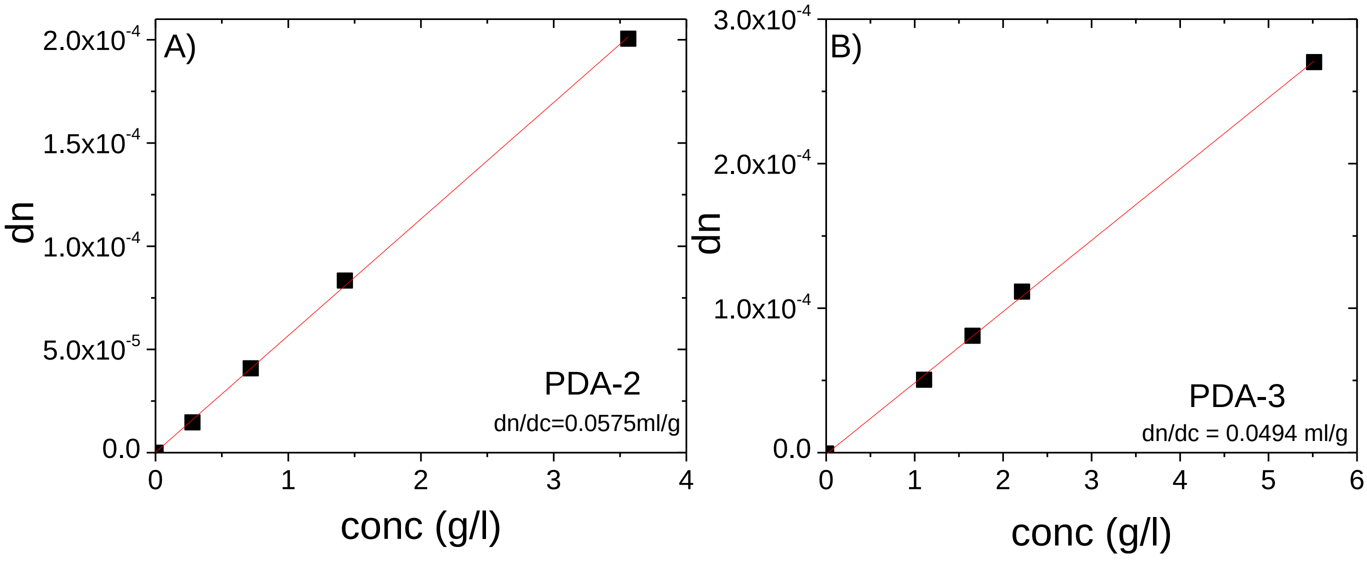


Figure S14: Plot of refractive index vs. concentration for (A) PDA-**2** and (B) PDA-**3**.

Reference:

1. Kalyanasundaram K., Thomas, J. K., *J. Am. Chem. Soc*. **1977**, 99, 2039.