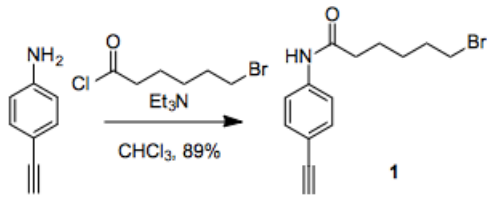
Supporting information for Supramolecular Helix-Helix Block Copolymers

Materials and Methods

All reagents were purchased from Acros Organics, Sigma-Aldrich, or Alfa Aesar and used without further purification unless otherwise noted. Methacryloyl chloride was distilled prior to use. 4,4′-Azobis(4-cyanovaleric acid) (ACVA) was recrystallized from MeOH. NMR spectra were recorded using a Bruker AV-400 (^{1}H: 400.1 MHz; ^{13}C: 100.6 MHz, ^{31}P: 162 MHz) and AV-600 (^{1}H: 600 MHz, ^{13}C: 150 MHz) spectrometer. Chemical shifts are shown in ppm and referenced to TMS. Mass spectra of samples in acetonitrile were acquired with an Agilent 6224 Accurate-Mass TOF/LC/MS Spectrometer. Gel-permeation chromatograms (GPC) were obtained from a Shimadzu pump coupled to a Shimadzu UV detector with THF as the mobile phase. The flow rate was 1 mL/min on an American Polymer Standards column set (100, 1000, 100,000 Å, linear mixed bed). The GPC was calibrated using poly(styrene) standards and carried out at 25 °C. M_w, M_n, and $Đ$ represent weight-average molecular weight, number-

average molecular weight, and dispersity, respectively. X-ray diffraction data was collected on a Bruker D8 DISCOVER GADDS microdiffractometer equipped with a VÅNTEC-2000 area detector. X-rays generated with sealed Cu tube was monochromated by a graphite crystal and collimated by a 0.5 mm MONOCAP (λ = 1.54178 Å). Matrix-assisted light desorption ionization time-of-flight (MALDI-TOF) data was recorded on a Bruker UtrafleXtreme using *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malonitrile (DCTB) as the matrix. The sample was prepared using a layer-by-layer approach.[1] IR spectra were obtained ob a Nicolet 6700 FTIR using attenuated total reflectance (ATR) mode. Circular dichroism spectra were collected using an Aviv stopped flow CD Spectropolarimeter Model 202SF (Lakewood, NJ). The spectra were obtained using a 2-mm path length quartz cell in $CHCl_3$.

Synthesis of Palladium (II) initiator and precursor molecules.



Scheme S1. Synthesis of Compound **1**.

6-bromo-*N*-(4-ethynylphenyl)hexanamide, compound **1.** A flask containing 4-ethynylaniline (0.663 g, 5.66 mmol) was evacuated and purged with N_2, charged with 50 mL dry, distilled chloroform and submerged in an icebath to cool to 0 ºC. Triethylamine (1.18 mL, 8.49 mmol) was added dropwise followed by 6-hexanoylchloride (1.04 mL, 6.79 mmol). After 14 hours, the reaction was diluted with dichloromethane (100 mL) and washed with diluted HCl (3x 100 mL) followed by brine (2x 80 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The purified compound was obtained after column chromatography gradient elution on SiO_2 with DCM/Et_3N (99.5/0.5) increasing to 10% MeOH/DCM. Yellow solid, 1.48 g (89 %). ^{1}H NMR (400 MHz; $CDCl_3$, δ ppm): 7.46 (q, J = 9.8, 4H), 7.26 (d, J = 6.3, 1H), 3.42 (t, J = 6.7, 2H), 3.04 (s, 1H), 2.38 (t, J = 7.4, 2H), 1.90 (t, J = 7.5, 2H), 1.76 (s, 2H), 1.53 (s, 2H). ^{13}C NMR (600 MHz; $CDCl_3$, δ ppm): 24.7 27.8, 32.5, 33.7, 37.5, 117.8, 119.5, 133.02, 138.4, 171.3. FT-IR (ATR, cm^{-1}): 3278 (alkyne $\nu_{C\text{-}H}$), 3302 ($\nu_{N\text{-}H}$), 2104 ($\nu_{C\text{-}C}$, alkyne), 1660 ($\nu_{C=O}$, amide).

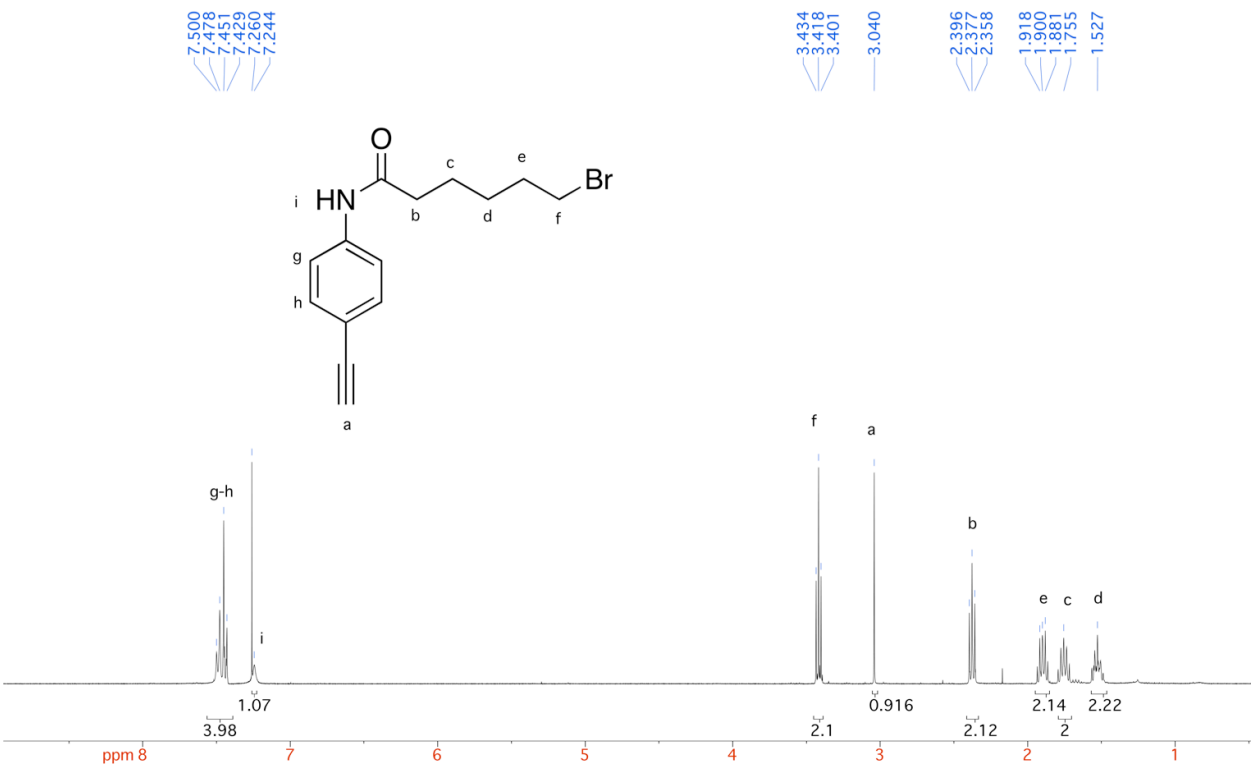


Figure S1. ^{1}H NMR spectrum of compound **1** (400 MHz, $CDCl_3$).

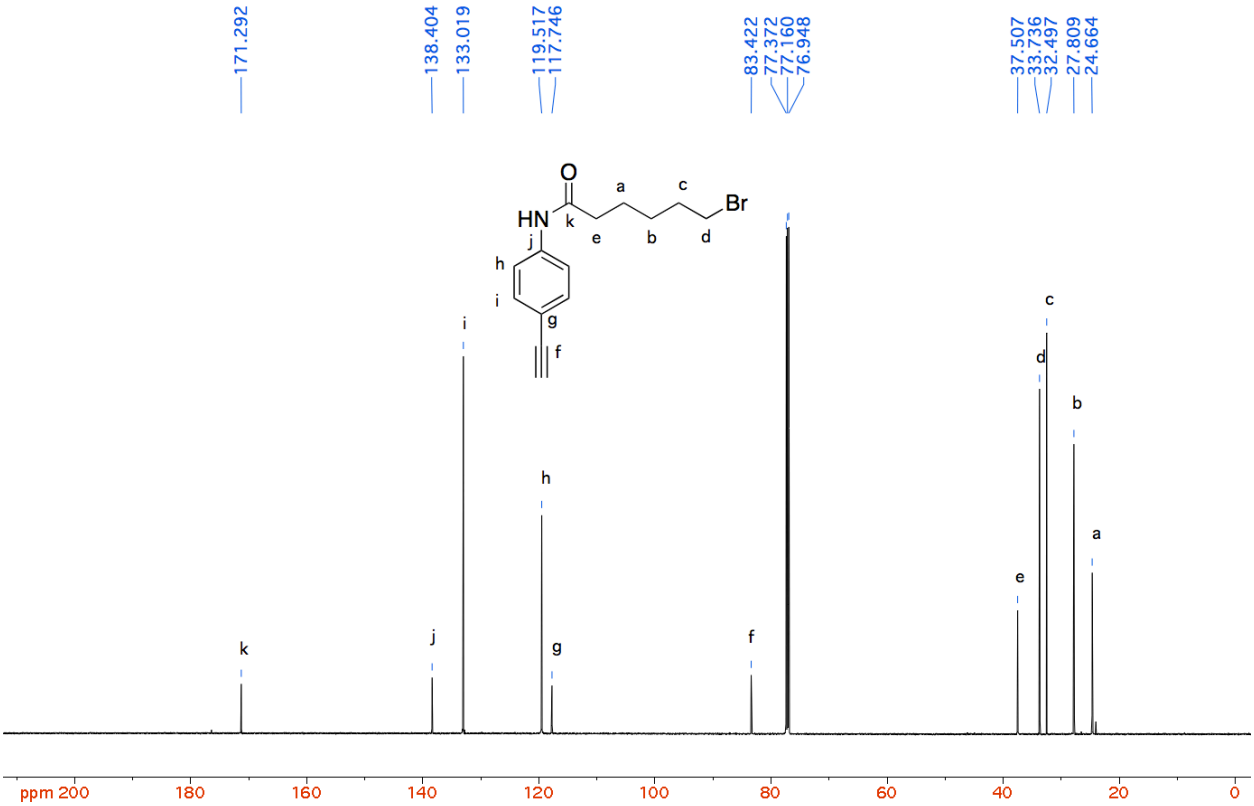
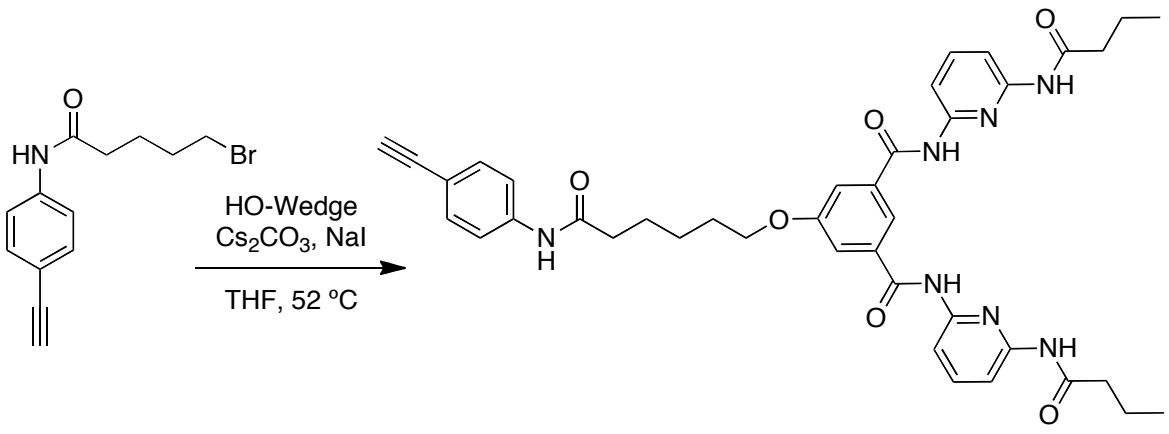


Figure S2. ^{13}C NMR spectrum of compound **1** (125 MHz, $CDCl_3$).



Scheme S2. Synthesis of compound **2**.

6-(*N*^{1},*N*^{3}-bis(6-butyramidopyridin-2-yl)-5-hydroxyisophthalamide)-N-(4-ethynyl)hexanamide, compound **2.** Hamilton Wedge receptor (HO-Wedge) was synthesized by a reported procedure.[2] A flask and reflux condenser were evacuated and purged with N_2 and charged with HO-Wedge (0.350 g, 0.694 mmol), Cs_2CO_3 (0.452 g, 1.39 mmol), and catalytic NaI. The solids were dissolved in 12 mL dry, distilled THF. In a separate flask, 6-bromo-N-(4-ethynyl)hexamide (0.220 g, 0.75 mmol) was dissolved in 6 mL dry, distilled THF and added dropwise to the stirred solution of HO-Wedge and base. The reaction was heated to reflux at 52 ºC and stirred for 42 hours. The reaction was removed from heat and filtered to remove solids. The filtrate was diluted with EtOAC (100mL) and washed with brine (3x 50mL). The organic portion was dried over Na_2SO_4 and solvent was removed by reduced pressure. The product was purified by column chromatography with 7% MeOH/DCM as the eluent. The product stains red with vanillin, Rf = 0.55 (MeOH/DCM, 7/93). Pale yellow solid, 0.449 g (90 %). ^1H NMR (400 MHz; $CDCl_3$, δ ppm): 8.70 (s, 2H), 8.40 (s, 2H), 8.27 (s, 1H), 7.92-7.83 (m, 6H), 7.64 (t, *J*= 8.1, 2H), 7.57 (d, *J*= 8.6, 2H), 7.39 (t, *J*= 8.6, 4H), 3.79 (t, *J*= 5.9, 2H), 3.02 (s, 1H), 2.36 (t, *J*= 7.4, 7H), 1.73 (dd, *J*= 14.9, 7.4, 7H), 1.62 (s, 2H), 1.38 (s, 2H), 1.25 (s, 2H), 0.98 (t, *J*= 7.4, 7H) ^{13}C NMR (125 MHz; $CDCl_3$, δ ppm): 13.9, 19.0, 25.2, 25.7, 28.6, 37.6, 39.6, 68.3, 83.5, 109.8, 110.5, 117.2, 117.7, 119.5, 133.0, 135.9, 138.8, 140.8,

149.4, 150.1, 159.7, 164.4, 172.0, 172.4. FT-IR (ATR, cm^{-1}): 2106 (ν_{C-C}, alkyne), 1667 ($\nu_{C=O}$, amide), 3293 (ν_{N-H}). HRMS-ESI: $M_{theoretical}$=717.327482, M_{sample}=717.327952, ΔM=0.47 mmass units (0.65 ppm), $C_{40}H_{43}N_7O_6$, (M+).

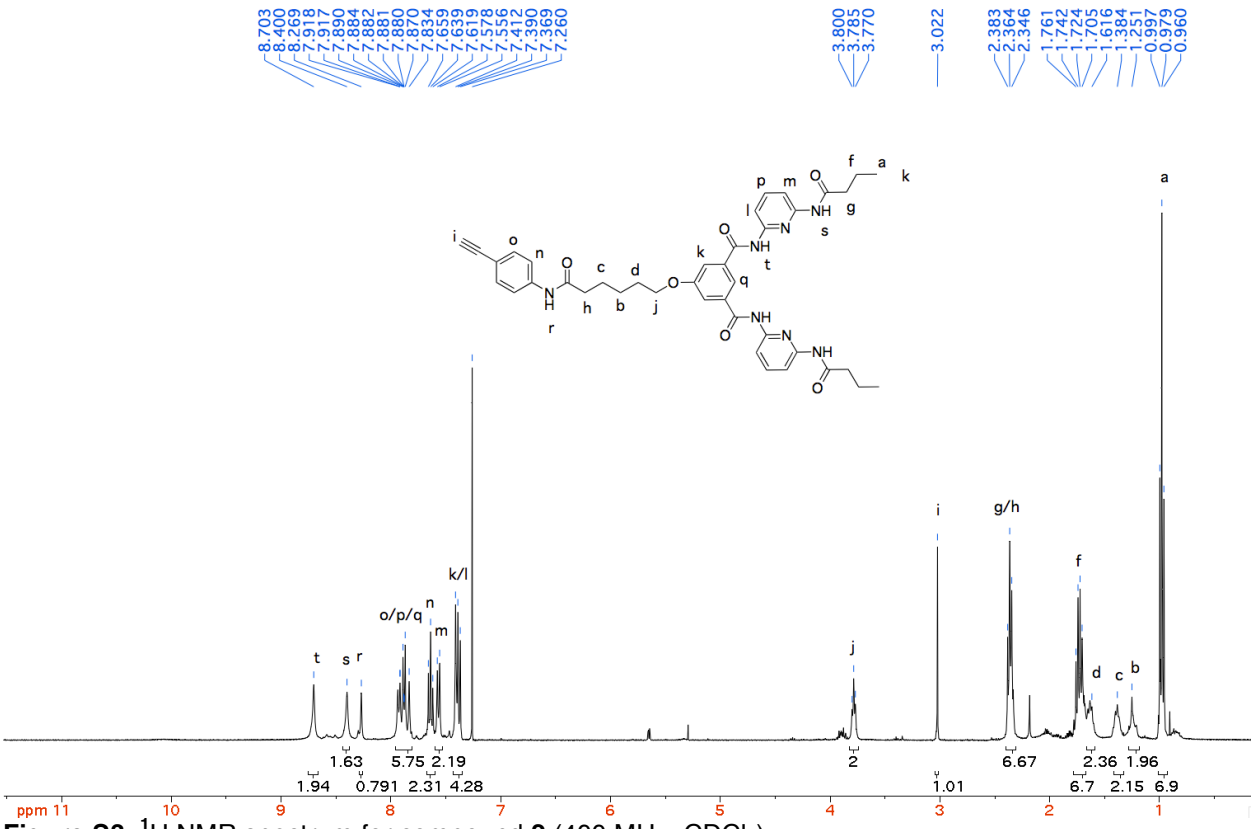


Figure S3. ^{1}H NMR spectrum for compound **2** (400 MHz, $CDCl_3$).

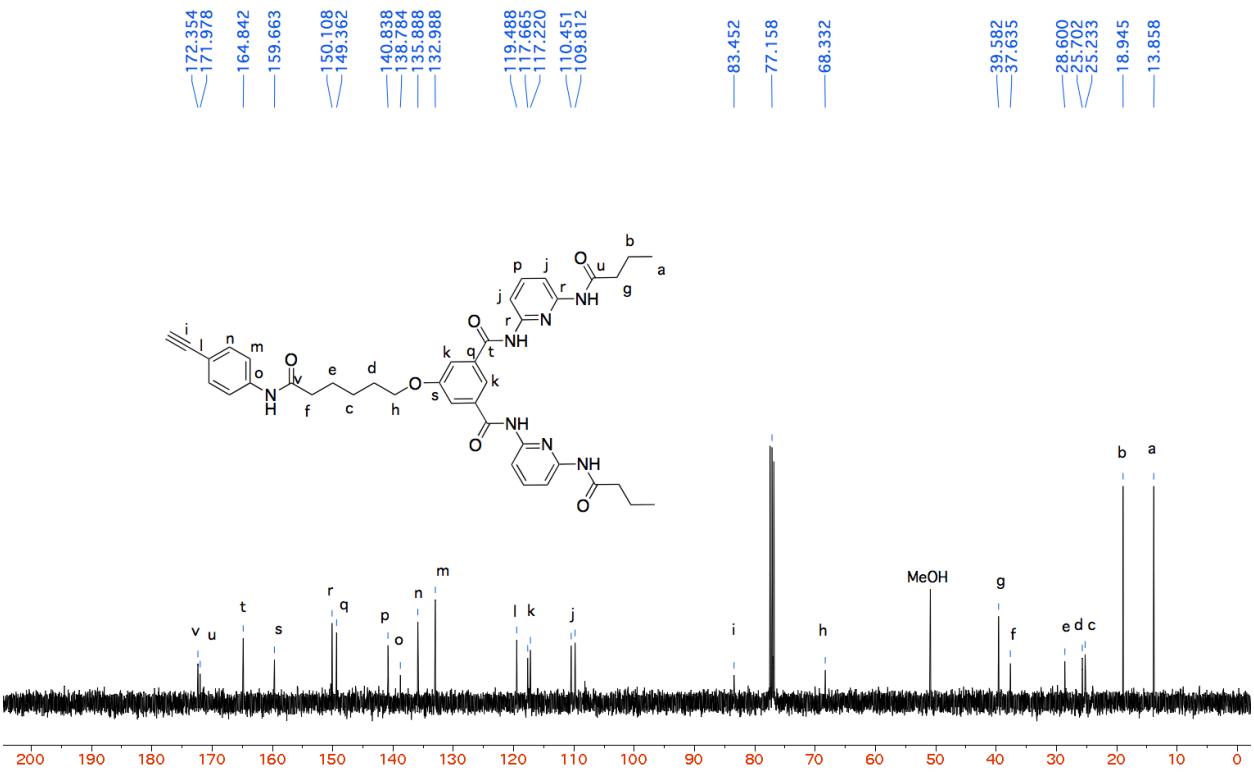
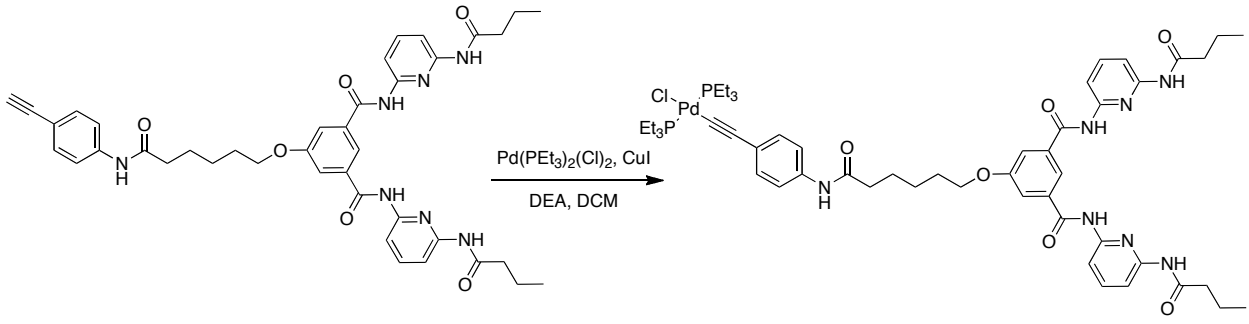


Figure S4. ^{13}C NMR spectrum for compound **2** (150 MHz, $CDCl_3$).



Scheme S3. Synthesis of **HW-Pd**.

Hamilton Wedge functionalized chloro-bis-(triethylphosphine)-4-ethynylphenyl palladium(II), HW-Pd. Hamilton Wedge functionalized 4-ethynylphenyl (0.200 g, 0.279 mmol), dichlor-bis(triethylphosphine) palladium(II) (0.120 g, 0.289 mmol), and CuI (3.6 mg, 0.019 mmol) were added to a flask purged with Ar. The solids were dissolved in 20 mL distilled DCM and 5 mL diethylamine was added. After stirring for 15 hours, the solvent was removed and the residue was purified by column chromatography with

MeOH/DCM (5/95). Pale yellow solid, 0.187 g (61%). ^{1}H NMR (600 MHz; $CDCl_3$, δ ppm): 8.84 (s, 1H), 8.48 (s, 1H), 8.21 (s, 1H), 7.87 (s, 5H), 7.67 (d, J= 8.1, 2H), 7.47 (d, J= 10, 2H), 7.42 (s, 2H), 7.16 (d, J= 8.5, 2H), 3.80 (s, 2H), 2.37 (d, J= 7.6, 7H), 2.21 (m, 2H), 1.95 (tt, J= 8.2,14H), 1.73 (dd, J= 14.8, 7.4, 7H), 1.64 (s, 3H), 1.40 (s, 2H), 1.30-1.25 (m, 2H), 1.20-1.15 (m, 23H), 0.99 (t, J= 7.2, 8H). ^{13}C NMR (150 MHz; $CDCl_3$, δ ppm): 8.5, 13.9, 15.5, 18.9, 25.3, 25.7, 28.6, 29.4, 37.7, 39.5, 68.3, 94.8, 109.7, 110.4, 117.3, 117.7, 119.7, 123.8, 131.3, 135.8, 136.0, 140.8 149.4, 150.9, 159.6, 164.8 171.7, 172.3. ^{31} P NMR (161 MHz; $CDCl_3$, δ ppm): 17.98. FT-IR (ATR, cm^{-1}): 2117 (ν_{C-C}, alkyne), 1668 ($\nu_{C=O}$, amide), 3294 (ν_{NH}).

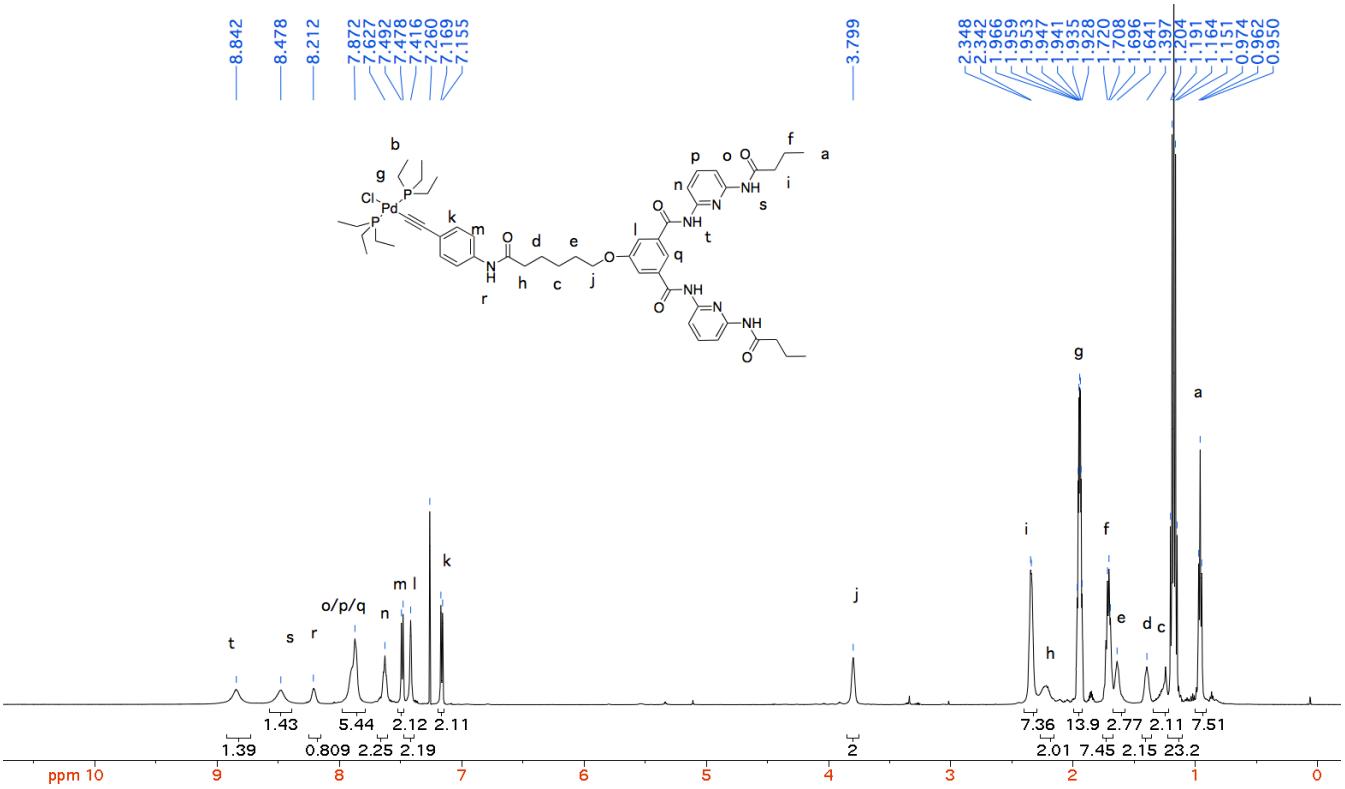


Figure S5. ^{1}H NMR spectrum for **HW-Pd** (600 MHz, $CDCl_3$).

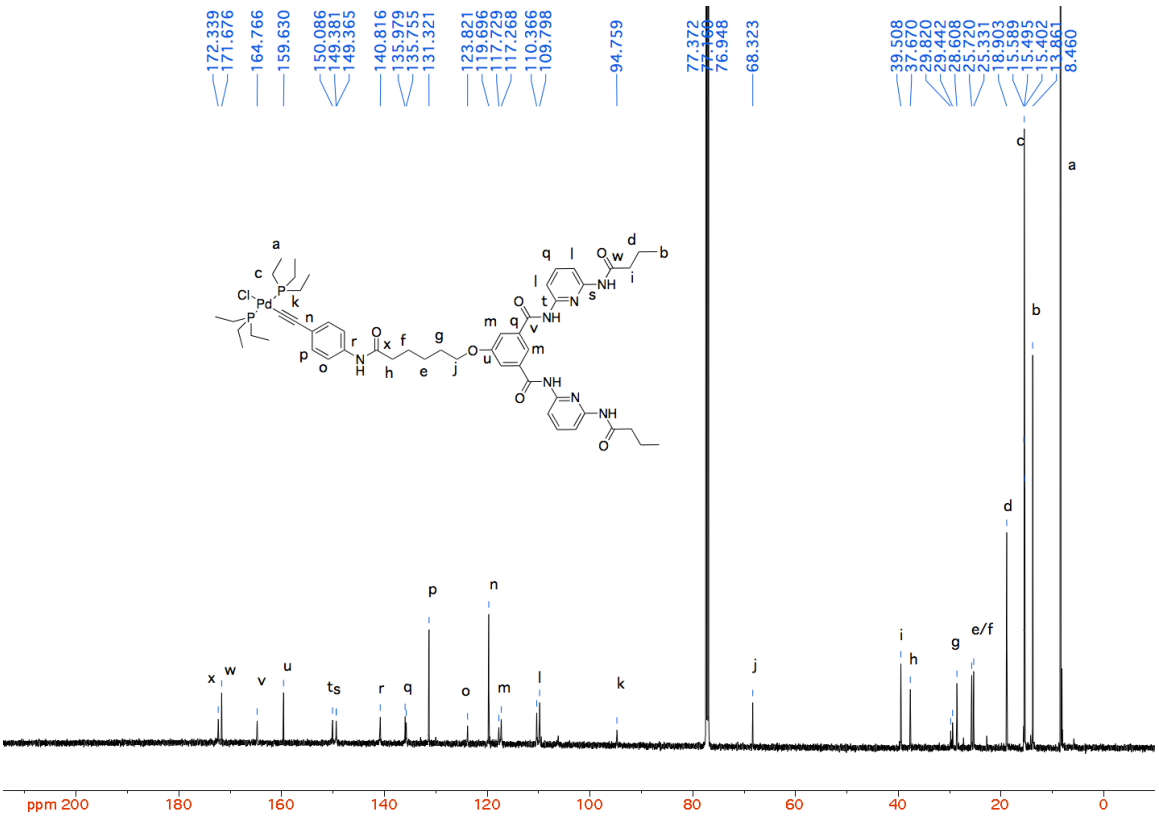


Figure S6. ^{13}C NMR spectrum for **HW-Pd** (150 MHz, $CDCl_3$).

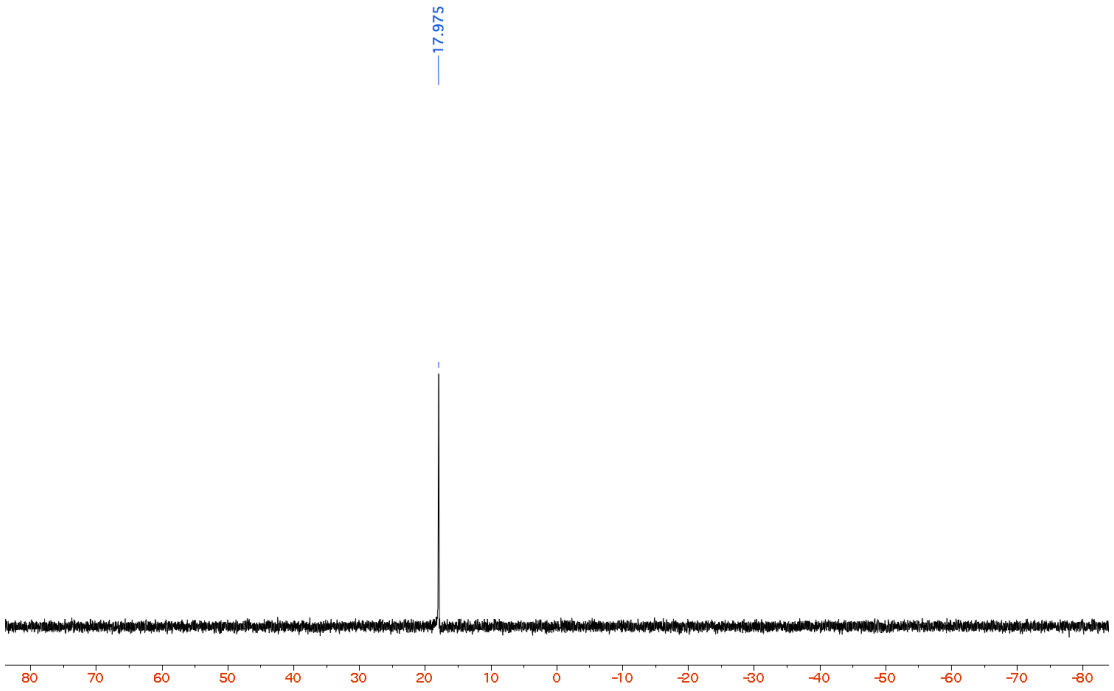


Figure S7. ^{31}P NMR spectrum for **HW-Pd** (161 MHz, $CDCl_3$).

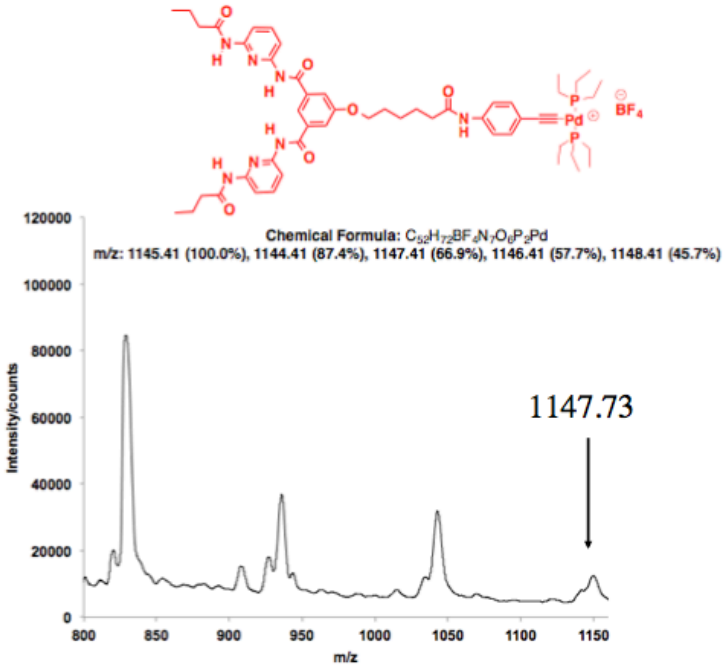


Figure S8. MALDI-TOF spectrum of **HW-Pd**.

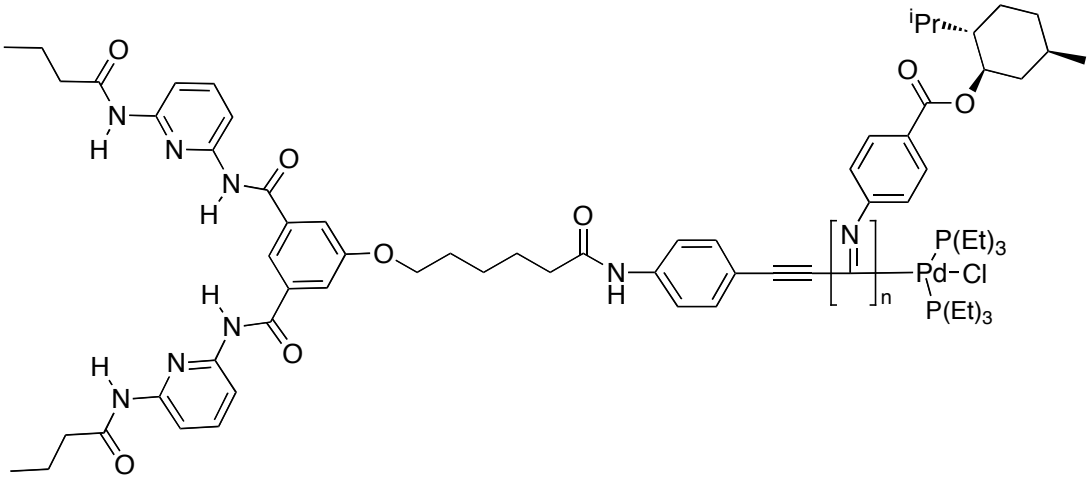


Figure S9. Structure of **HW-Poly-1**.

Typical Polymerization for HW-Poly. In a Schlenk tube purged with argon, monomer (157.48 mg, 37 mmol) was dissolved in 2.25 mL dry, distilled THF and degassed via freeze-pump-thaw. Initiator (16.74

mg, 0.015 mmol) was dissolved in 0.4 mL and added to monomer mixture. The reaction was heated to 55 ºC for 6 hours, whereupon the polymerization mixture was precipitated into 50 mL MeOH/H_2O (3:1). The brown solids were further purified via dialysis in DCM by using 3500 MWCO dialysis tubing. After 24 hours, the contents of the dialysis tubing were precipitated into cold MeOH and the polymer was obtained after centrifugation. Brown solid, HW-Poly-1: 0.130 g, M_n=13100, *Đ*=1.36 (SEC, THF), HW-Poly-2: 0.82g, M_n= 9000, *Đ*=1.38 (SEC, THF).

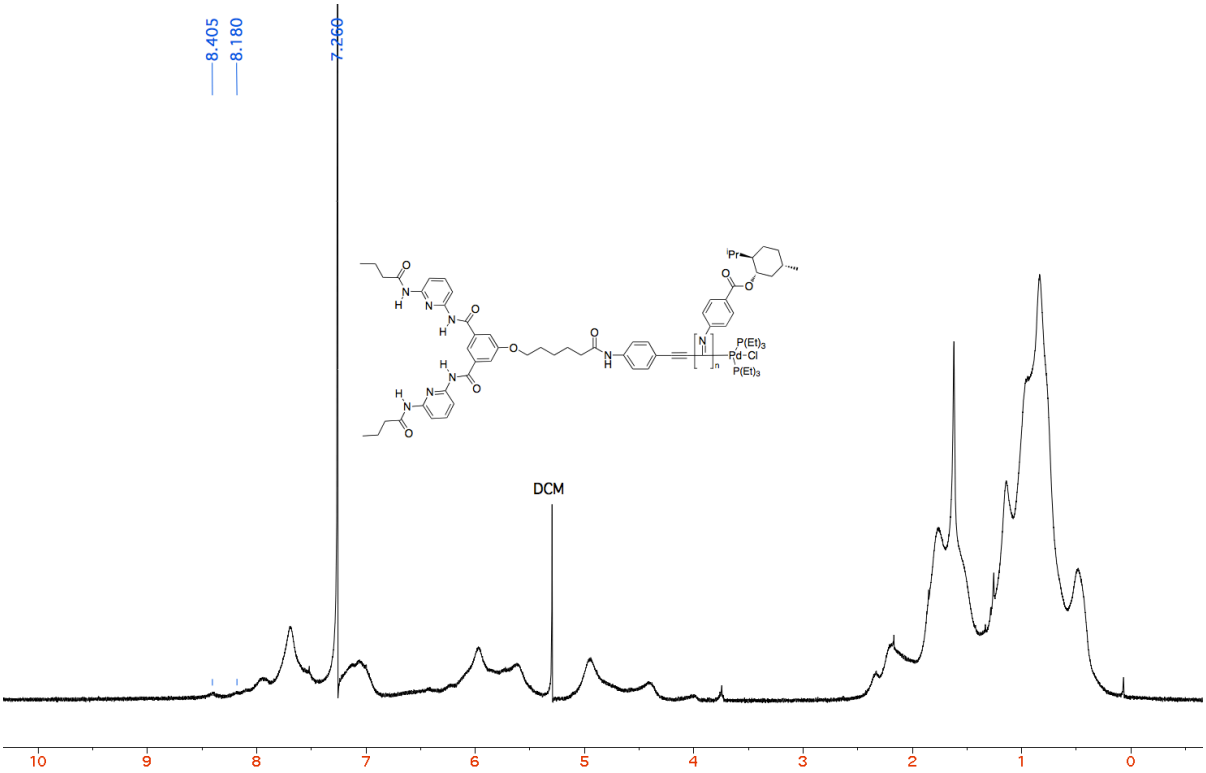


Figure S10. ^{1}H NMR spectrum for **HW-Poly-1** featuring HW N–H signals at *δ* 8.4 and 8.2 ppm (400 MHz, $CDCl_3$).

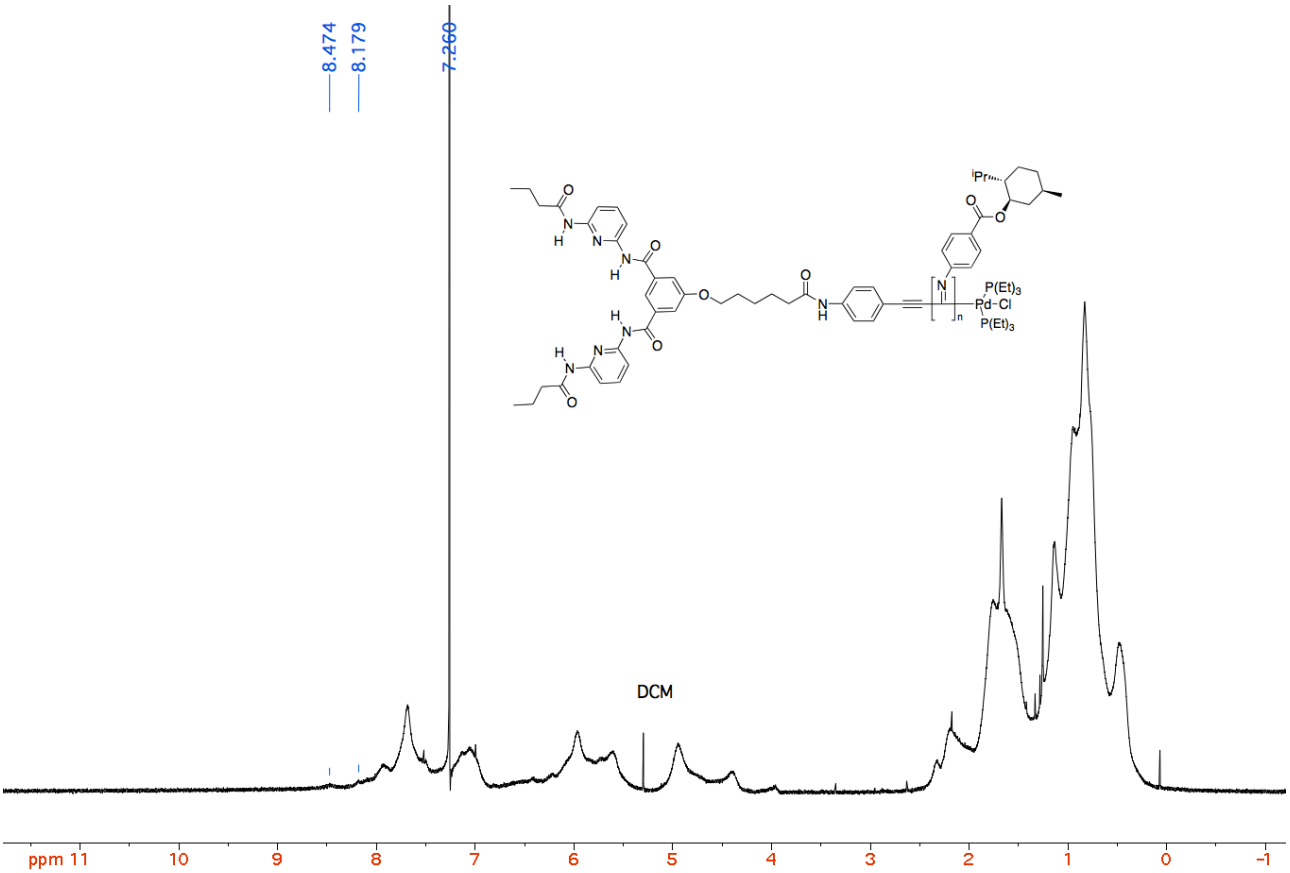
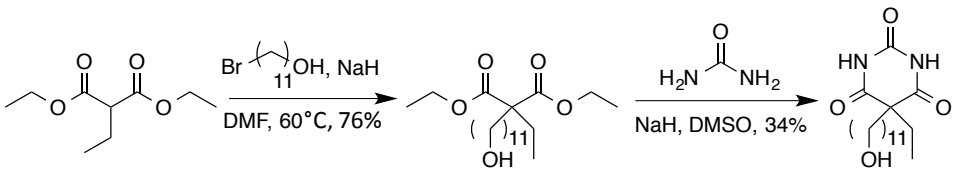


Figure S11. ^{1}H NMR spectrum for **HW-Poly-2** featuring HW N–H signals at δ 8.5 and 8.2 ppm (400 MHz, $CDCl_3$).

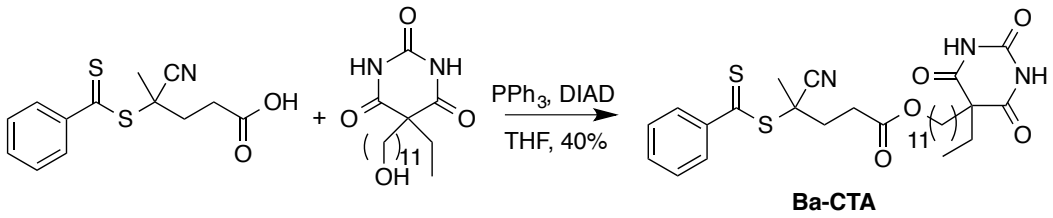
Synthesis of RAFT Ba-CTA and precursor molecules.



Scheme S4. Synthesis of compounds **3** and **4**.

Diethyl 2-ethyl-2-(11-hydroxyundecyl)malonate, compound **3.** Synthesized according to literature procedure.[3]

5-Ethyl-5-(11-hydroxyundecyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione, compound **4.** Synthesized according to literature procedure.[3]



Scheme S5. Synthesis of RAFT **Ba-CTA**.

11-(5-ethyl-2,4,6-trioxohexahydropyrimidin-5-yl)undecyl4-cyano-4-((phenylcarbonothioyl)thio)pentanoate, Ba-CTA. PPh_3 (0.289 g, 1.1 mmol) was dissolved in freshly distilled THF (40 mL) in a three-neck flask under argon and placed over an ice bath. DIAD (0.224 g, 1.1 mmol) added dropwise and stirred until the solution became cloudy indicating formation of the betaine complex. 4-Cyano-4-((phenylcarbonothioyl)thio)pentanoic acid (CPADB) (0.243 g, 0.871 mmol) was dissolved in THF (10 mL) was added to the cloudy solution dropwise. The solution became clear upon deprotonation of the carboxylic acid. Compound **4**[3] (0.316 g, 0.968 mmol) in THF (10 mL) was added to the mixture dropwise. The solution was stirred for 12 hours at room temperature and then diluted with DCM (100 mL). The organic phase was washed with water (2 x 150 mL). The organic layer was dried over magnesium sulfate and concentrated. The crude product was purified on neutral alumina using MeOH/DCM (5/95) to afford a bright pink viscous oil. Yield 202 mg, (40%). (^{1}H NMR (400 MHz; $CDCl_3$, δ ppm): δ 8.44 (s, 2H), 7.92-7.89 (m, 2H), 7.58-7.54 (m, 1H), 7.41-7.37 (m, 2H), 4.10 (t, J = 6.78 Hz, 2H), 2.73-2.60 (m, 3H), 2.47-2.40 (m, 1H), 2.03 (q, J = 7.41 Hz, 2H), 1.99-1.94 (m, 4H), 1.66-1.61 (m, 3H), 1.25 (d, 18H), 0.88 (t, J = 7.43 Hz, 3H) ^{13}C NMR (150 MHz, CDCl3): 222.6, 172.8, 172.0, 148.9, 144.7, 133.3, 128.9, 126.9, 118.7, 65.5, 57.6, 45.9, 38.9, 33.7, 32.7, 30.0, 29.5, 29.4, 29.3, 29.2, 28.7, 26.0, 25.3, 24.3, 9.7. ESI-MS $(M+Na)^+$ $C_{30}H_{41}N_3O_5S_2$, theoretical: 587.25, experimental: 587.26.

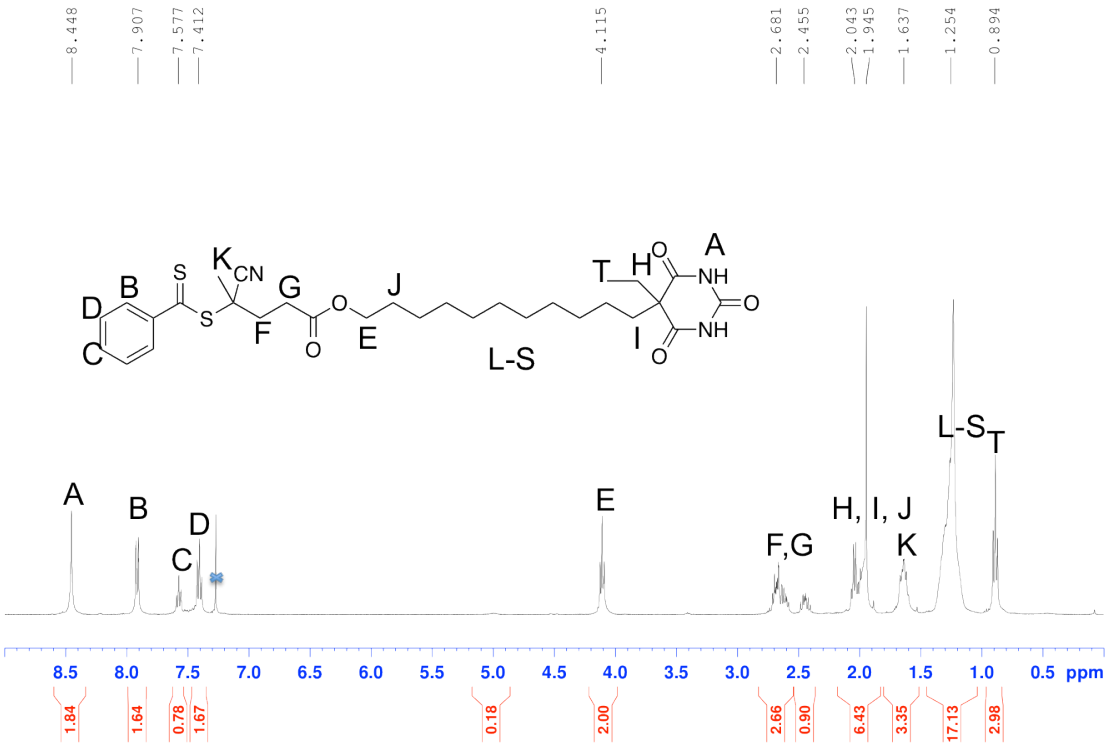


Figure S12. ^{1}H NMR spectrum for **Ba-CTA** (600 MHz, $CDCl_3$).

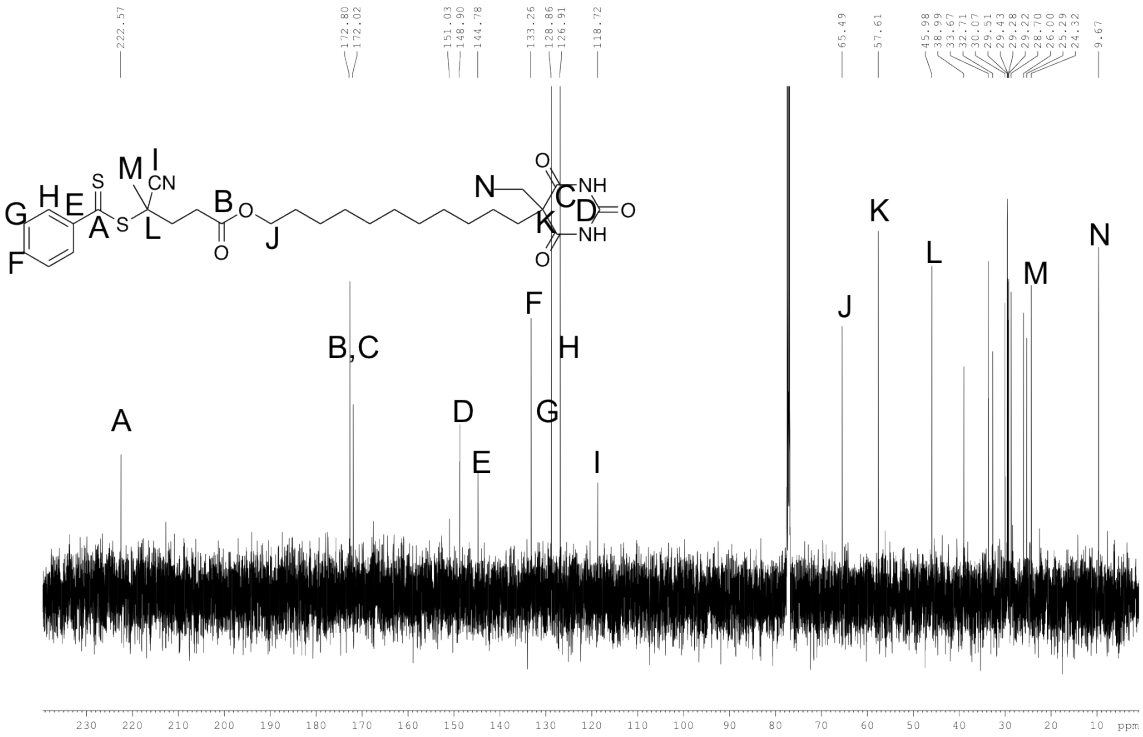


Figure S13. ^{13}C NMR spectrum for **Ba-CTA** (150 MHz, $CDCl_3$).

General Polymerization Procedure for RAFT.

The desired amounts of monomer, Ba-CTA, ACVA and anhydrous THF were placed in a Schlenk flask. The typically molar ratio was 100:1:0.1, [M]:[CTA]:[I], respectively. The freeze-pump-thaw method was employed over five cycles and the flask was backfilled with argon. The polymerization mixture was heated to 60°C and quenched in liquid nitrogen after approximately 12-18 hours. Crude polymers were purified via precipitation in cold MeOH three times.

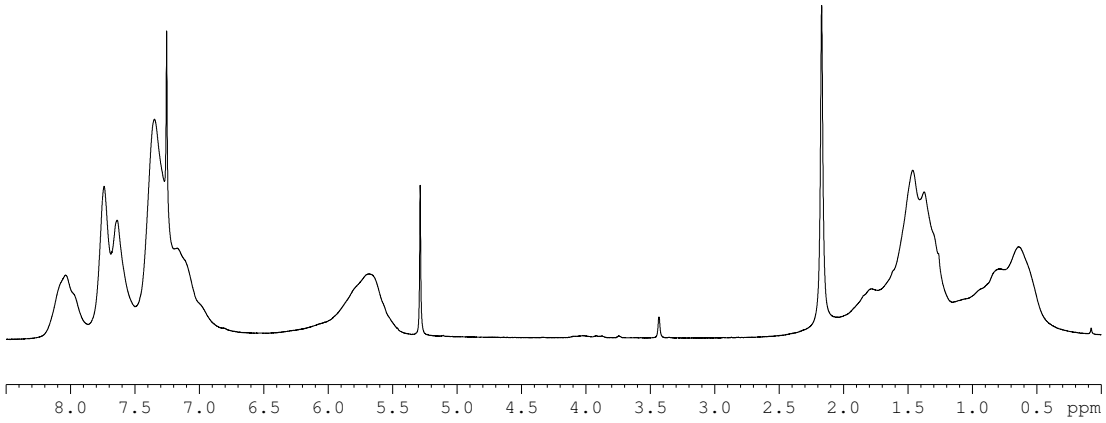


Figure S14. ^{1}H NMR spectrum for **Ba-Poly-3** (600 MHz, $CDCl_3$).

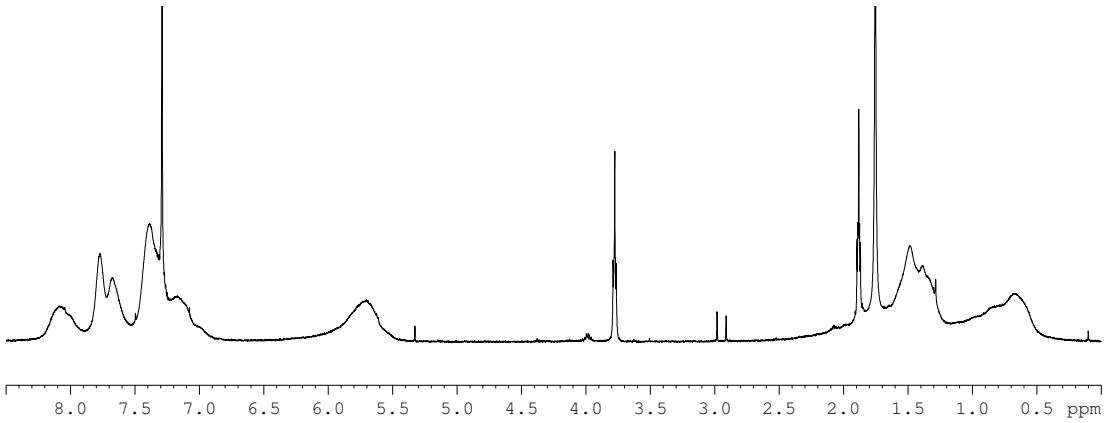


Figure S15. ^{1}H NMR spectrum for **Ba-Poly-4** (600 MHz, $CDCl_3$).

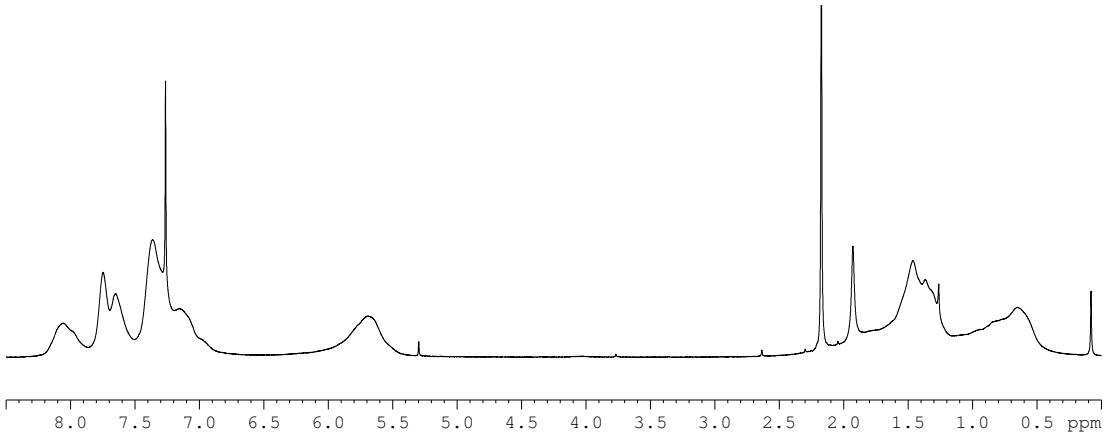


Figure S16. ^{1}H NMR spectrum for **Ba-Poly-5** (600 MHz, $CDCl_3$).

SEC Profiles of Homopolymers.

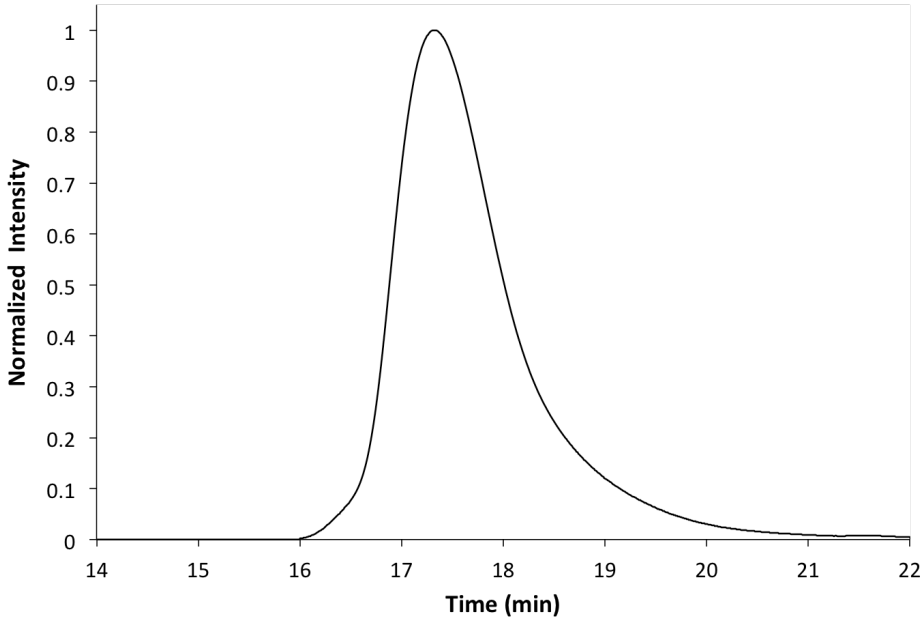


Figure S17. Normalized GPC trace for **HW-Poly-1** (M_n = 13100, $Đ$ = 1.36, SEC, THF).

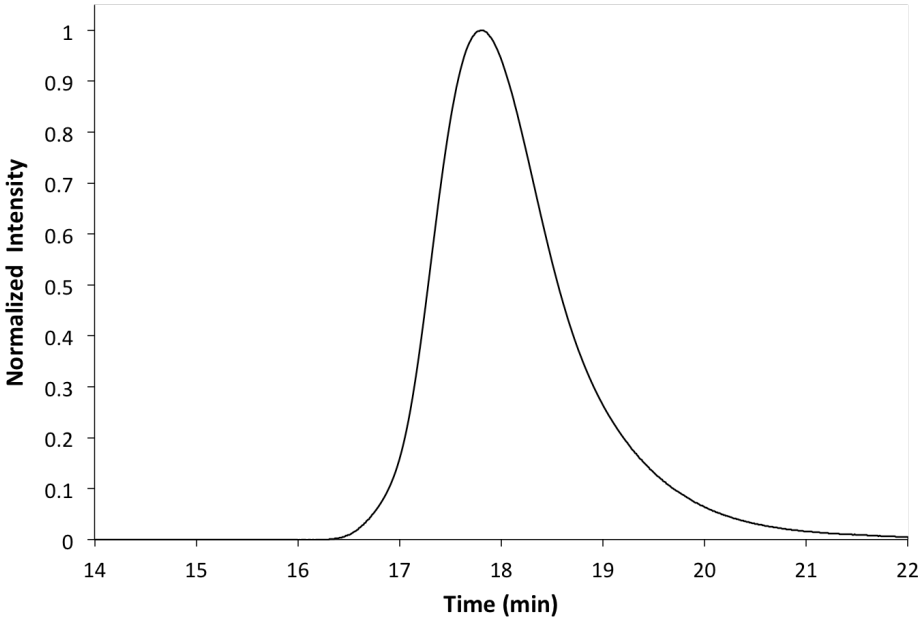


Figure S18. Normalized GPC trace for **HW-Poly-2** (M_n = 9000, $Đ$ = 1.38, SEC, THF).

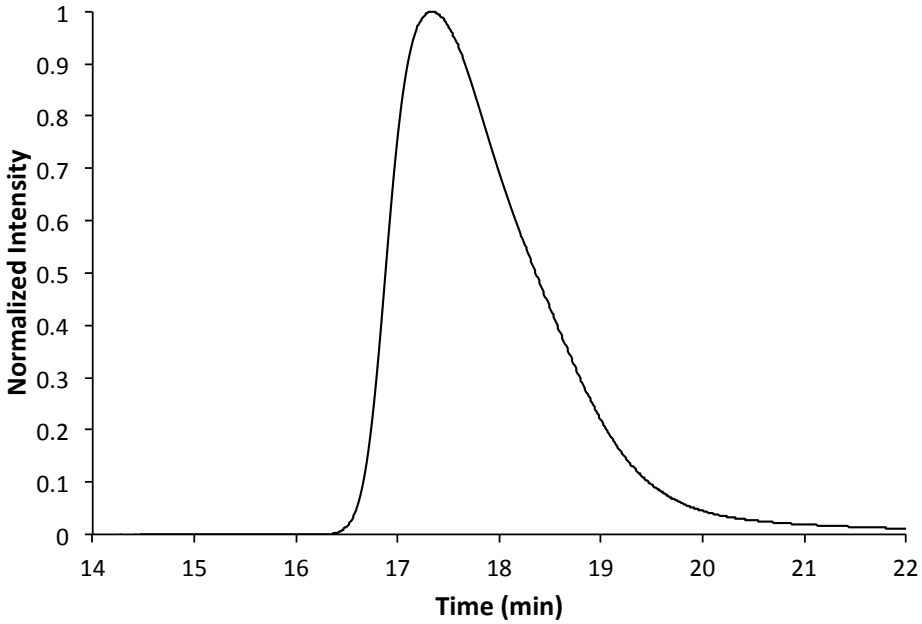


Figure S19. Normalized GPC trace for **Ba-Poly-3** (M_n = 13100, $Đ$ = 1.25, SEC, THF).

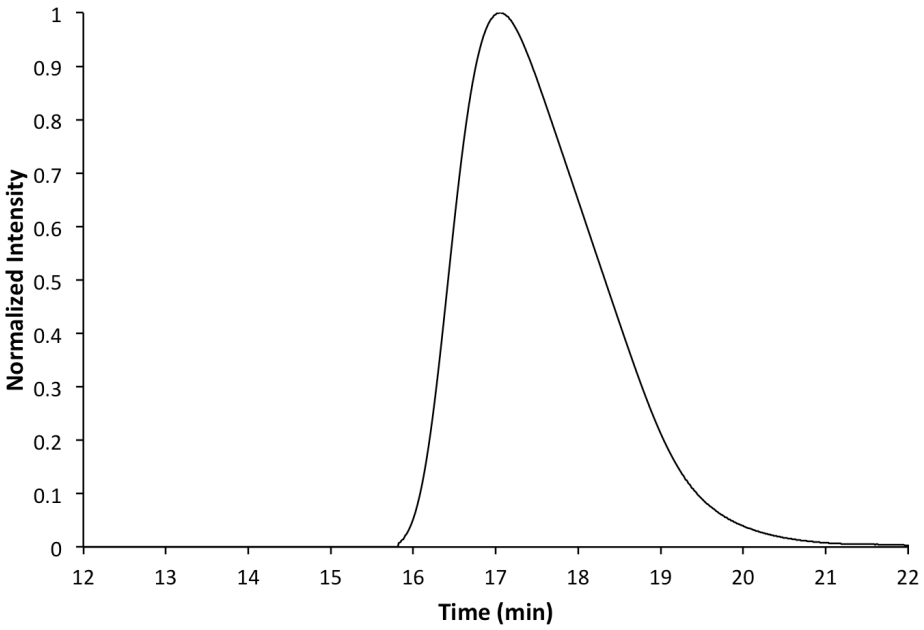


Figure S20. Normalized GPC trace for **Ba-Poly-4** (M_n = 14900, $Đ$ = 1.49, SEC, THF).

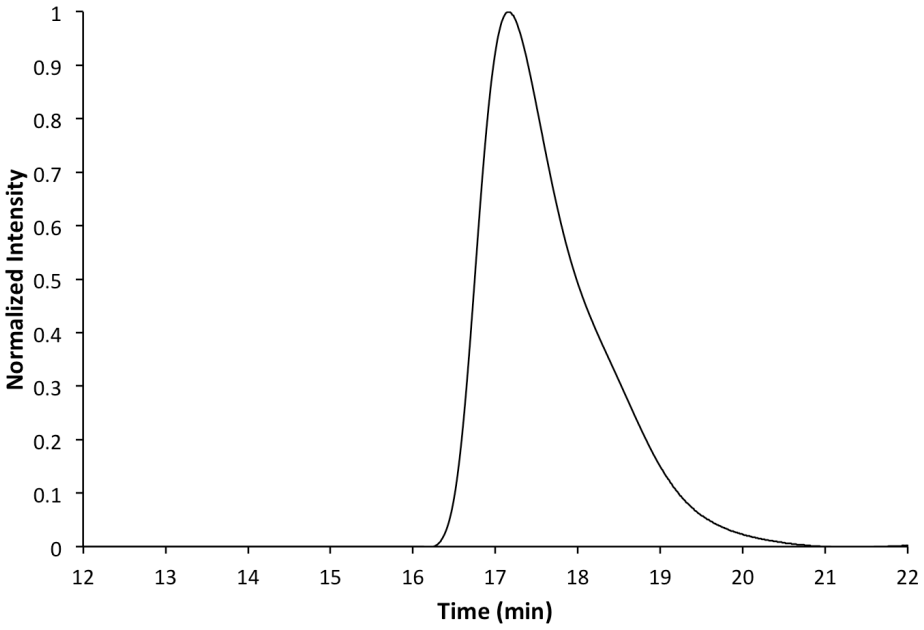


Figure S21. Normalized GPC trace for **Ba-Poly-5** (M_n = 14700, $Đ$ = 1.38, SEC, THF).

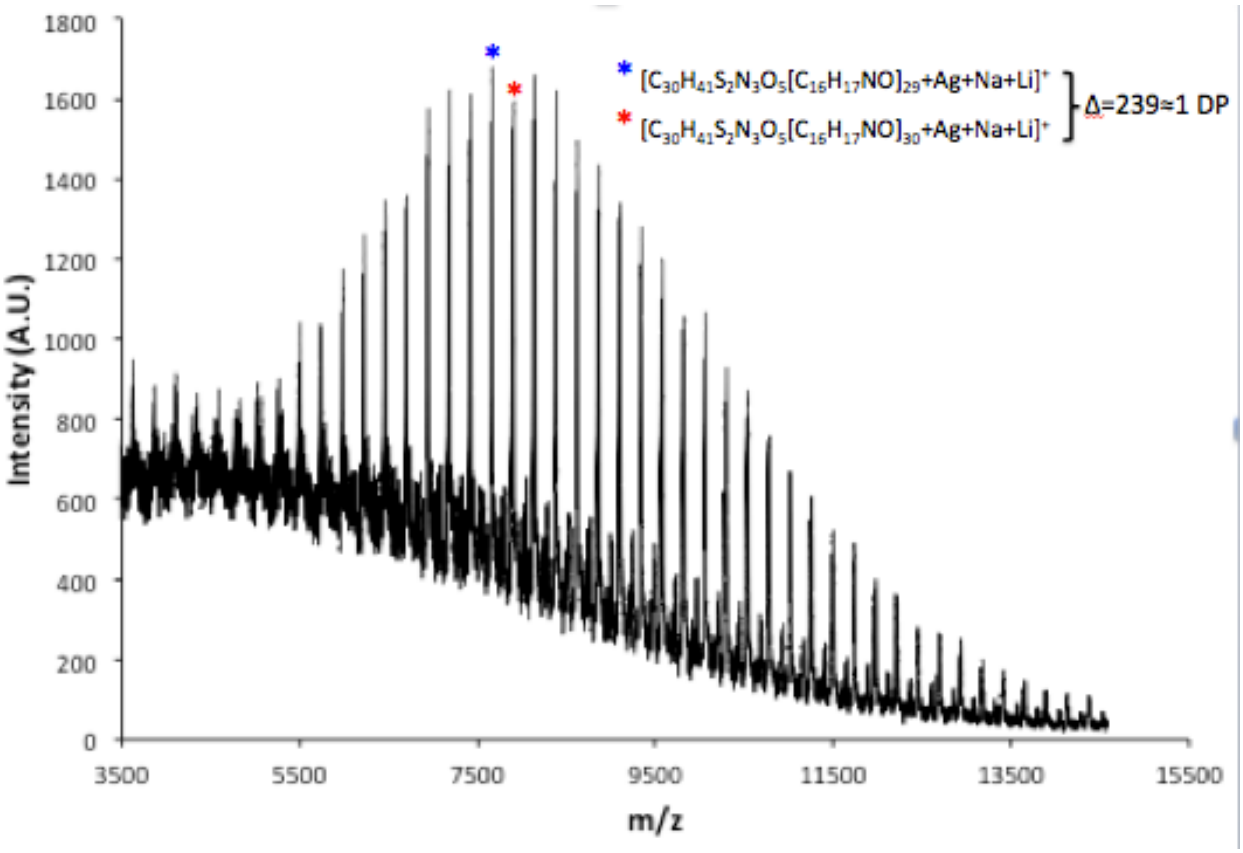


Figure S22. MALDI-TOF mass spectrum (full spectrum) of **Ba-Poly-6**.

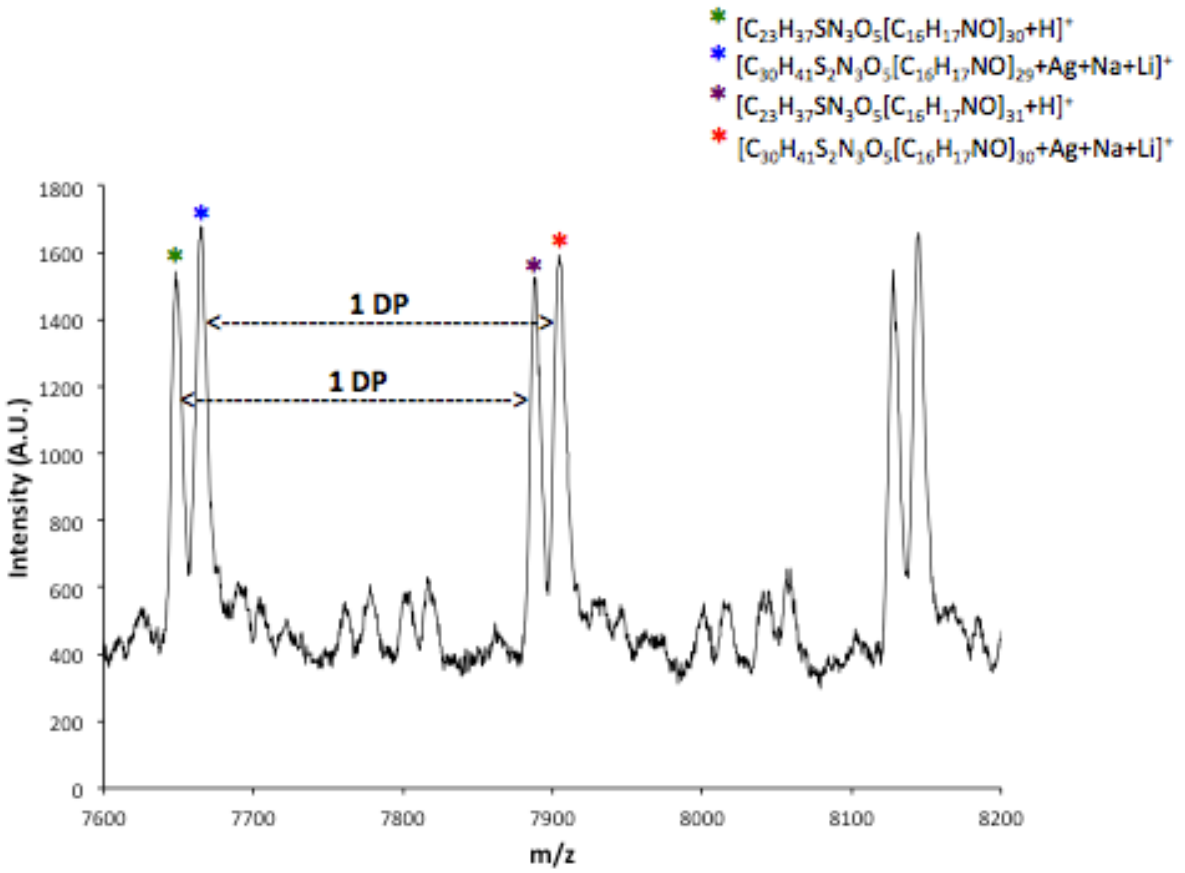


Figure S23. MALDI-TOF mass spectrum (expansion) of **Ba-Poly-6**.

A relatively low molecular weight polymer ($M_n \approx 5000$, $Đ = 1.2$,THF GPC) was synthesized in order to assess chain functionalization of the poly(NEMAM) with Ba by MALDI-TOF. The mass spectrum of Ba-Poly was observed in linear mode and the sample was ionized using 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as matrix and AgTFA and/or LiTFA as a cationization agent. The polymer solution and the salt were premixed in a ratio of 100:10:1 (dry-droplet method). The MALDI-TOF spectrum showed a charged main series with the signals of greatest intensity indicative of a DP≈29-31 containing the Ba end-group. A second, relatively intense, minor series correlated to the mass of a Ba-functionalized polymer with fragmentations of the labile C-S (thioester) bond, which has been reported in other RAFT-generated polymers. The observed isotope patterns of the main and relatively minor species differ by the molecular weight of 1 DP or the mass of the monomer (Figure S23). Based on this evidence we conclude that the poly(NEMAM) polymers resulting from RAFT using Ba-CTA are

functionalized with high end-group fidelity, despite the poor resolution of the Ba protons observed by ^{1}H NMR spectroscopy.

NMR Titration Studies with HW-Poly(Isocyanide)s and Ba-poly(NEMAM)

Table 1. Characterization and details of polymers used for small molecule **sBa** and **sHW** ^{1}H NMR spectroscopy and ITC.

Polymer	M_n[a] (g/mol)	$Đ$[a]	Monomer
Ba-Poly-6	5000	1.21	(*R*)-NEMAM
HW-Poly-3	4900	1.37	(+)-Menthol

[a] The Mn and Mw/Mn (*Đ)* were determined by SEC in THF using poly(styrene) standards.

Titration of **HW-Poly-3** with small molecule Ba (**sBa**)

HW-polymer was titrated with a small molecule Ba analogue (**sBa**) to observe the change in chemical shift of the HW N–H amide protons upon complexation with the Ba N–H imide protons via ^{1}H NMR spectroscopy. **HW-Poly-3** (8.54 mg) was dissolved in 500 μL of deuterated $CDCl_3$ and the resulting solution was transferred to an NMR tube. A stock solution containing **sBa** was prepared. Aliquots of this solution were added to the HW-Poly-3 solution in variable stoichiometric ratios (0.2, 0.3, 0.4, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, and 2.0 mole equivalents, respectively) to induce self-assembly between the complementary recognition units. The ^{1}H NMR experiment was continued until no significant change in the chemical shift was observed in the ^{1}H NMR spectra. The shifts of the N–H protons from the HW moiety were used to calculate the association constant (K_a = 2.0 x 10^4 M^{-1})**.**

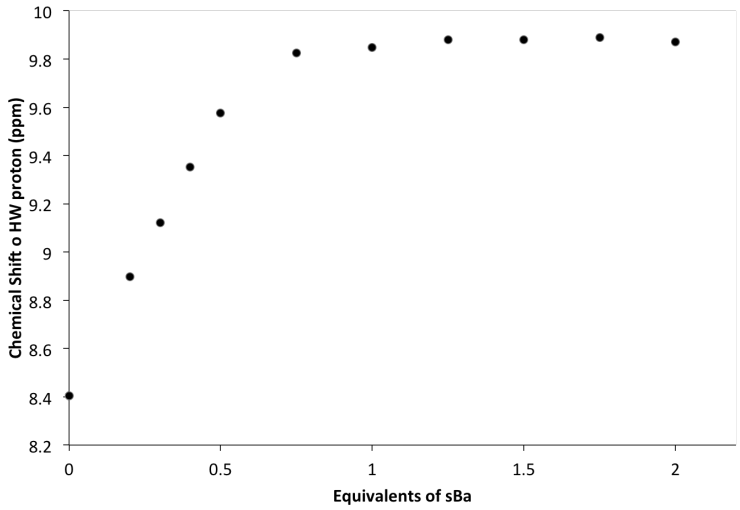


Figure S24. Chemical Shifts of the amide proton of **HW-Poly-3** upon hydrogen bonding as a function of equivalents of **sBa.** The concentration of **HW-Poly-3** was kept constant at 2.02 mM.

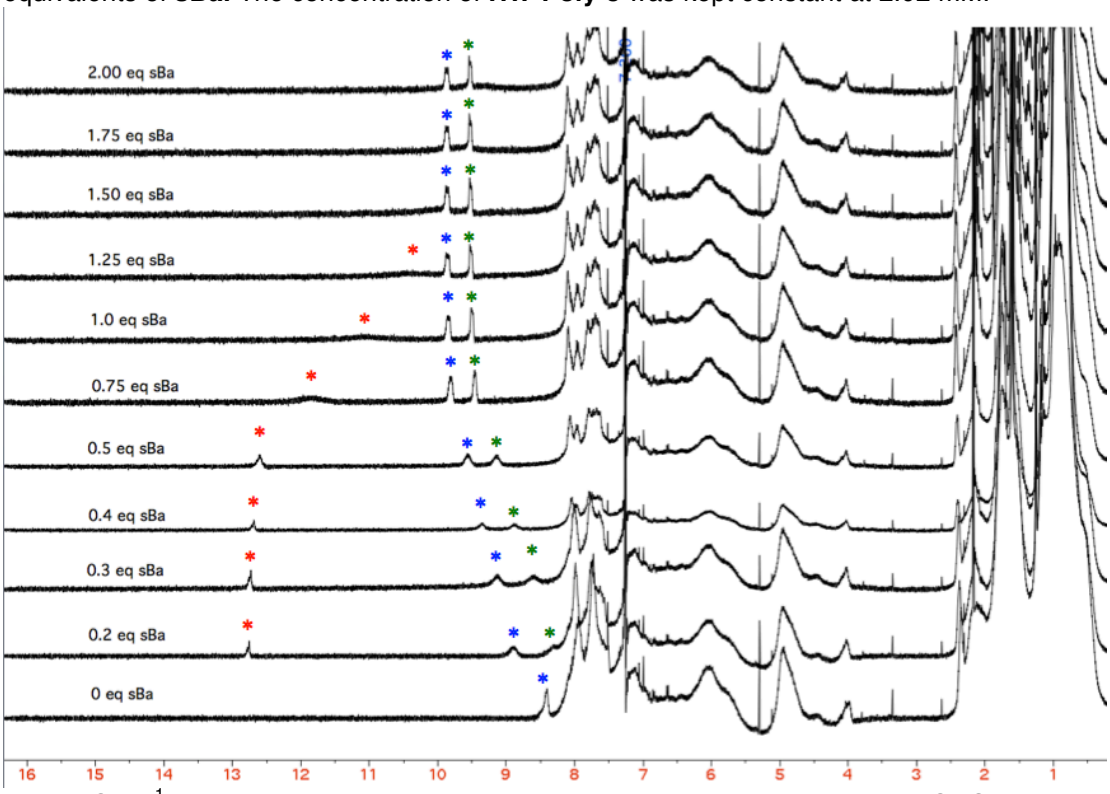


Figure S25. ^{1}H NMR spectral overlay of the titration of **HW-Poly-3** with **sBa** in $CDCl_3$ showing the hydrogen bonding proton resonances of the HW protons moving downfield and the Ba proton moving upfield and broadening as more equivalents are added.

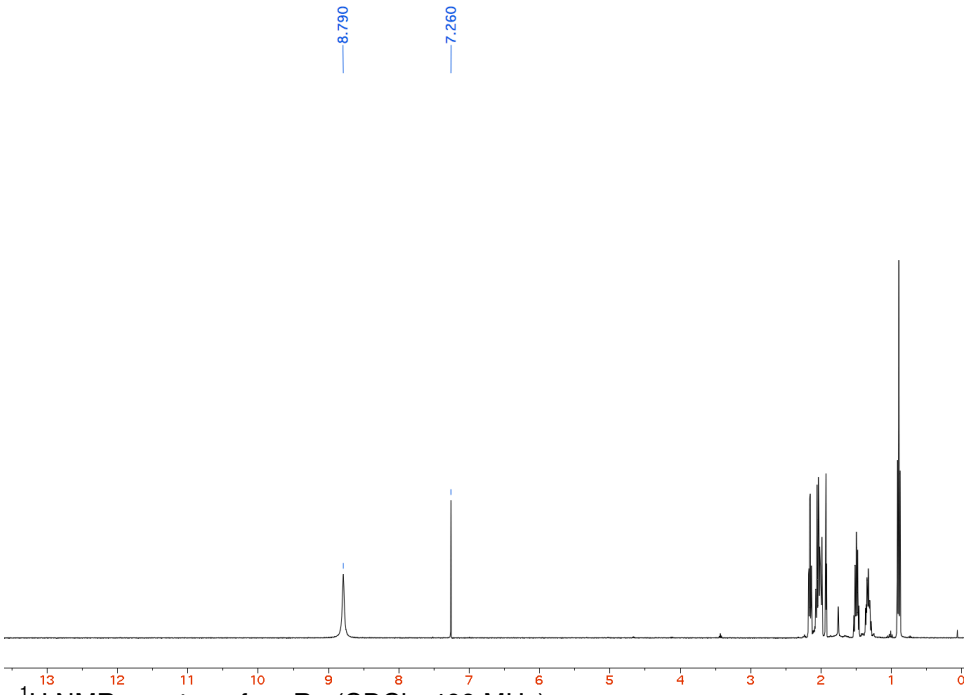


Figure S26. ^{1}H NMR spectrum for **sBa** ($CDCl_3$, 400 MHz).

Titration of Ba-Poly-6 with small molecule **HW (sHW)**

Ba-Polymer was titrated with a small molecule HW analogue (**sHW**) to observe the change in chemical shift of the Ba N–H imide protons upon complexation with the HW N–H amide protons by ^{1}H NMR spectroscopy. **Ba-Poly-6** (17 mg) was dissolved in 500 μL of deuterated $CDCl_3$ and the resulting solution was transferred to an NMR tube. A stock solution containing **sHW** was prepared. Aliquots of this solution were added to the **Ba-Poly-6** solution in variable stoichiometric ratios (0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, and 2.0 mole equivalents, respectively) to induce self-assembly between the complementary recognition units. The ^{1}H NMR experiment was continued until no significant change in the chemical shift was observed in the ^{1}H NMR spectra. The shifts of the N–H protons from the Ba moiety were used to calculate the association constant (K_a = 2.0 x 10^4 M^{-1}).

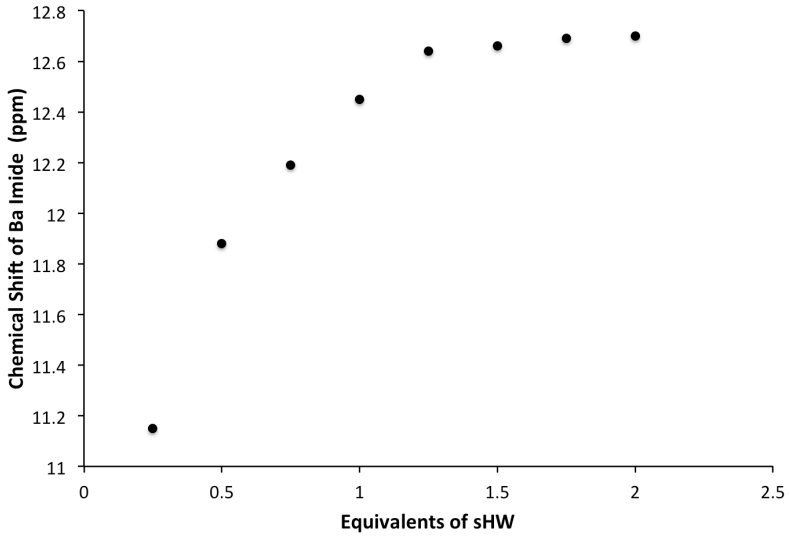


Figure S27. Chemical shifts of the imide protons of **Ba-Poly-6** upon hydrogen bonding as a function of equivalents of **sHW.** The concentration of **Ba-Poly-6** was kept constant at 2.04 mM.

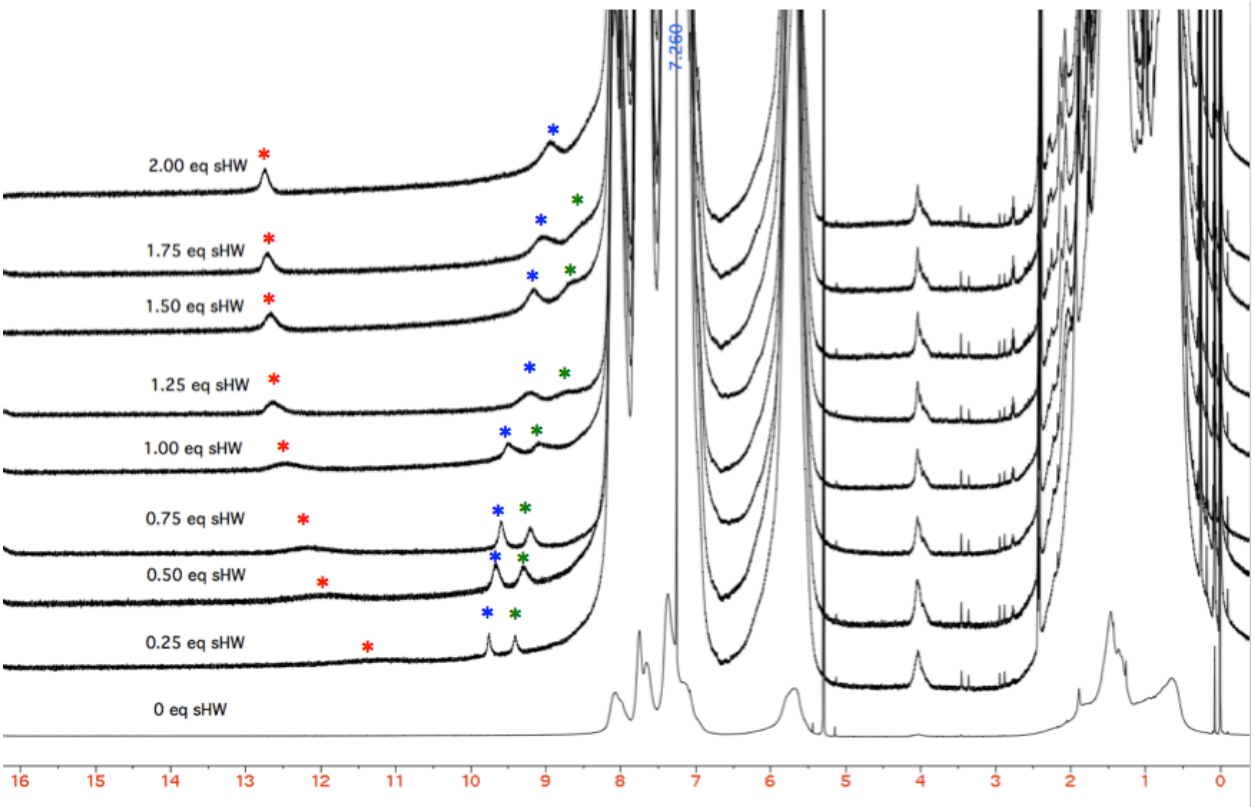


Figure S28. ^{1}H NMR spectral overlay of the titration of **Ba-Poly-6** with **sHW** in $CDCl_3$ showing the hydrogen bonding proton resonances of the HW protons moving upfield and the Ba proton moving downfield as more equivalents were added.

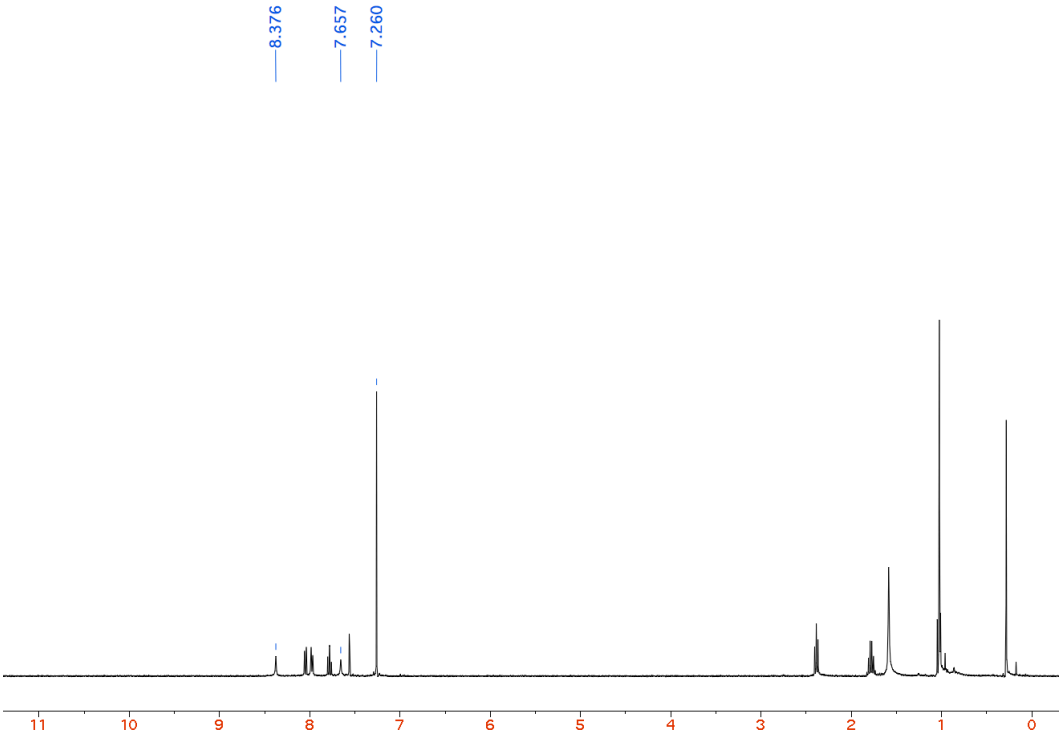


Figure S29. ^{1}H NMR spectrum for **sHW** ($CDCl_3$, 400 MHz).

Titration of HW-Poly with Ba-Poly

HW-Poly-2 (8.1 mg) was dissolved in 500 µL of $CDCl_3$ and the resulting solution was transferred into an NMR tube. A stock solution of **Ba-Poly-4** was prepared to deliver molar equivalent ratios (0.2, 0.3, 0.4, 0.5, 0.75, 1, 1.25, 1.50, and 1.75 equiv., respectively) in 20 μL aliquots to induce self-assembly between the complementary recognition units. The ^{1}H NMR experiment was continued until no significant change in chemical shift was observed in the ^{1}H NMR spectra. The association constant, K_a = 9.97 x 10^3 M^{-1}, was calculated by reported methods[4] by observing the downfield N–H proton shifts of the HW amide group with respect to the molar equivalents of Ba-Poly added.

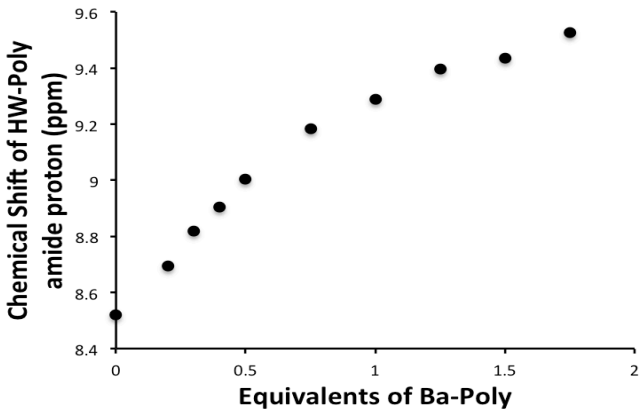


Figure S30. Change in chemical shift of the amide protons of the **HW-Poly-2** upon hydrogen bonding as a function of equivalents of **Ba-Poly-4**. The concentration of **HW-Poly-2** was kept constant at 1.191 mM.

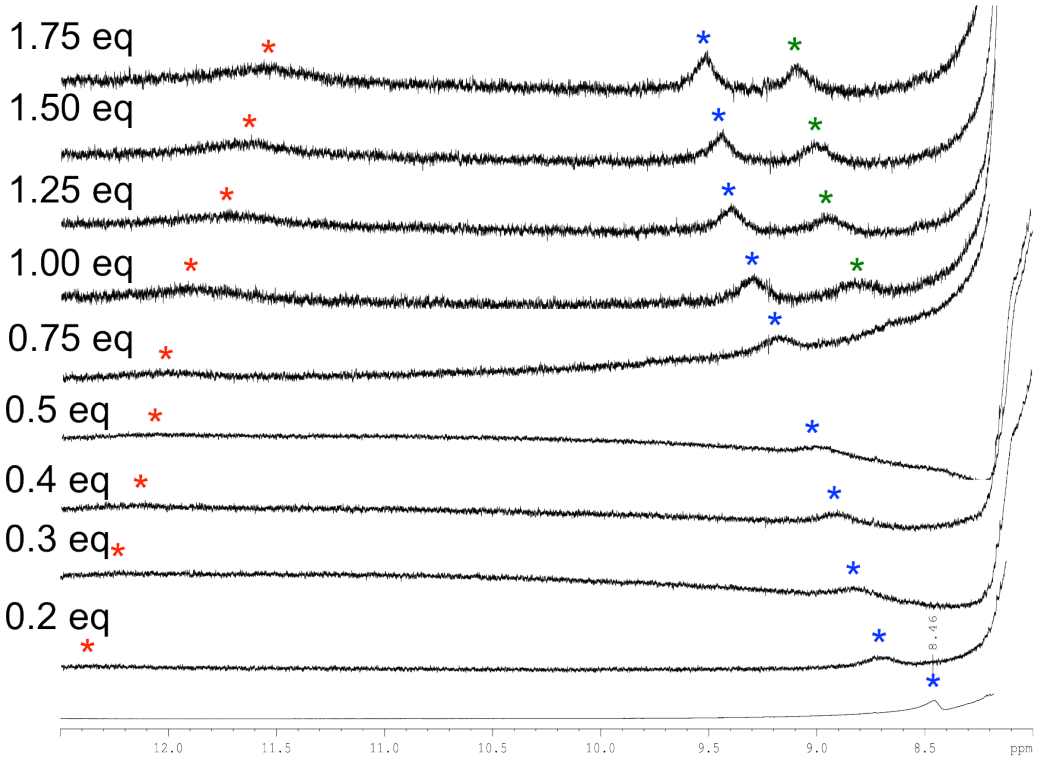


Figure S31. A representative overlay of the ^{1}H NMR spectra obtained when **HW-Poly-2** is titrated with **Ba-Poly-4** in $CDCl_3$ at 25 ºC showing the shift in hydrogen bonding proton resonances of the HW protons (* and *) on **HW-Poly-2** and the Ba protons (*) of **Ba-Poly-4** upon the addition of varying molar equivalents of **Ba-Poly-4.**

Titration of Ba-Poly with HW-Poly

Ba-Poly-3 (12.9 mg) was dissolved in 500 µL of deuterated solvent and the resulting solution was transferred into an NMR tube. **HW-Poly-1** was added to the solution in variable stoichiometric ratios (0.2,

0.3, 0.4, 0.5, 0.75, 1, 1.25, 1.50, and 2 equiv., respectively) to induce self-assembly between the complementary recognition units. The ^{1}H NMR experiment was continued until no significant change in chemical shift was observed in the ^{1}H NMR spectra. The shifts of the N–H protons on the Ba moiety were observed to calculate the association constant (K_a = 9.0 x 10^3 M^{-1}).

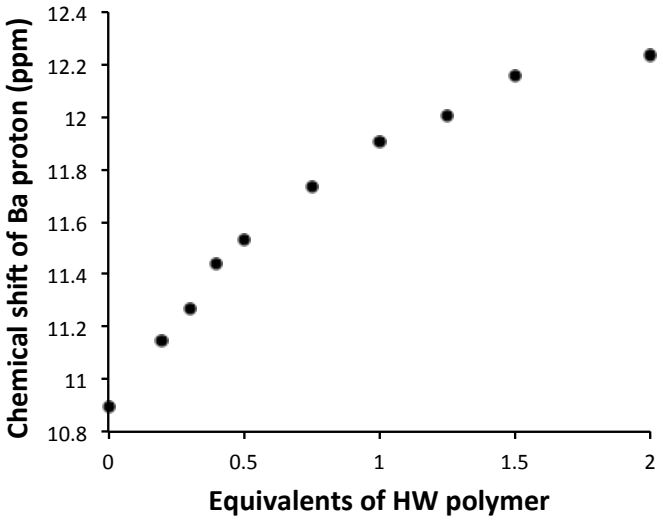


Figure S32. Change in the chemical shifts of the amide proton of the **Ba-Poly-3** upon hydrogen bonding as a function of equivalents of **HW-Poly-1.** The concentration of **Ba-Poly-3** was kept constant at 1.11 mM.

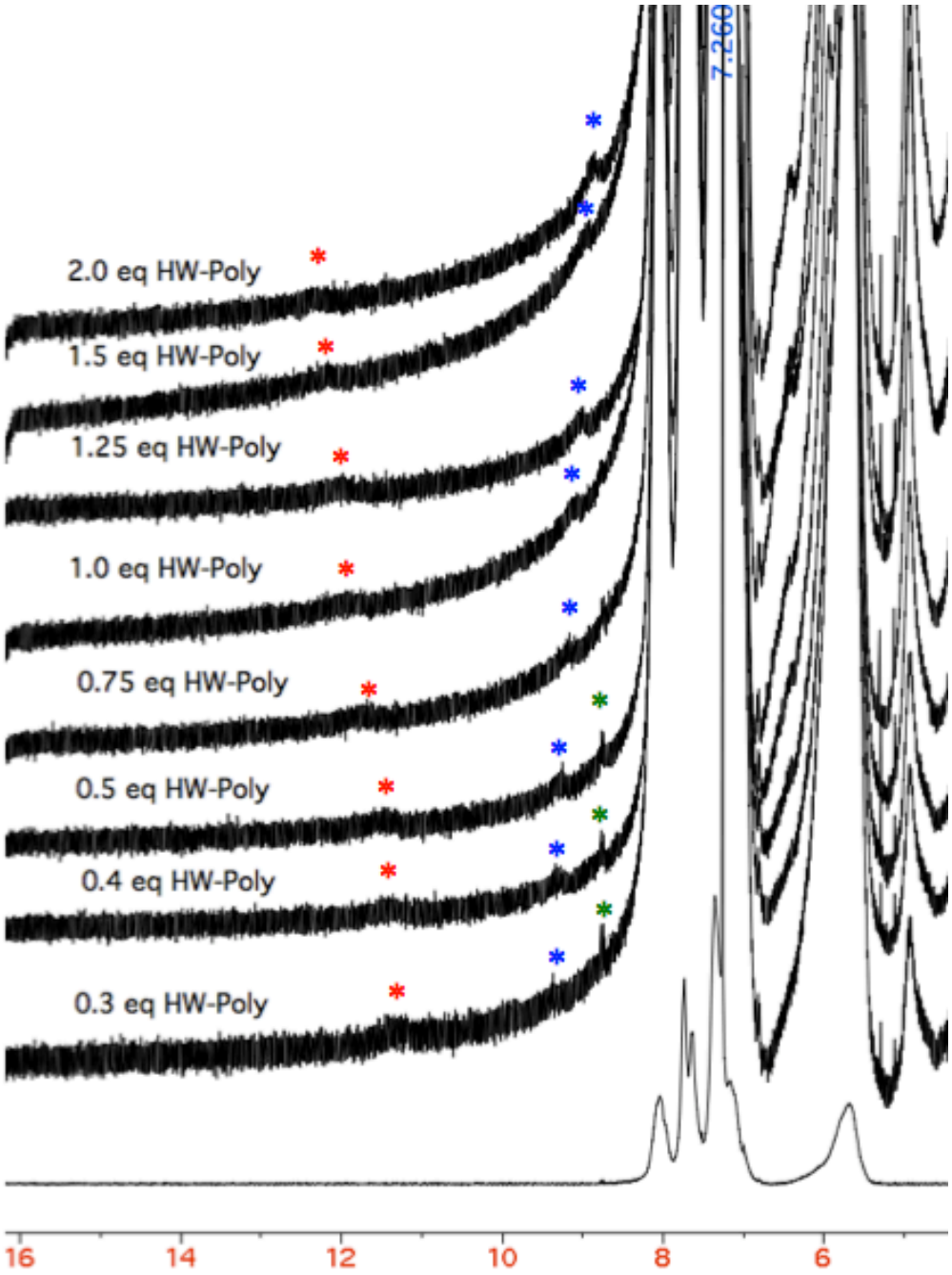


Figure S33. ^{1}H NMR spectral overlay in $CDCl_3$ showing the shift in hydrogen bonding proton resonances of the HW protons (* and *)on **HW-Poly-1** and the Ba protons (*) of **Ba-Poly-3** upon the addition of varying molar equivalents of **HW-Poly-1.**

Nano Isothermal Titration Calorimetry Experiments

For all ITC experiments, HPLC grade chloroform was distilled and degassed prior to use. All samples were carefully loaded into the sample cell or syringe with care to prevent air bubble formation. Each

experiment was performed in triplicate and corrected by applying the baseline from a blank prepared by the titration of chloroform into the host polymer. All titrations were performed at 25 ºC with 300 RPM spinning, 2.5 μL injection volume, 300 seconds between injections, with a preliminary baseline equilibration period ≤1200 seconds. After data acquisition and baseline corrections, K_a values were calculated with NanoAnalyze software by applying the Indpendent model with n=1.0.

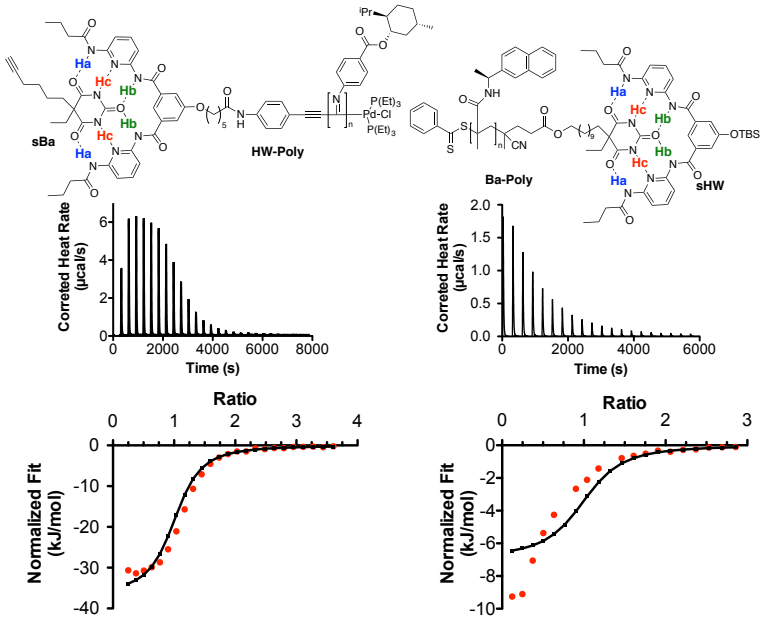


Figure S34. Representative small molecule titrations for HW-Poly with sBA (left) and Ba-Poly with sHW (right).

Titration of HW-Poly with sBa.

A 1.0 mM solution of **HW-Poly-3** was prepared (M_n = 5000 g/mol, 1.74 mg/350 μL) in distilled, degassed chloroform and was loaded into the sample cell. A 5 mM solution of **sBa** was prepared (M_w = 236.27 g/mol, 59 μg/50 μL) and was loaded into the syringe for titration. After three trials, the K_a's were calculated by the NanoAnalyze software to be 1.713 x 10^4, 2.069 x 10^4, and 2.813 x 10^4 M^{-1}, respectively. The average K_a was 2.2 x10^4 M^{-1}.

Titration of Ba-Poly with sHW

A 1.0 mM solution of **Ba-Poly-6** was prepared (M_n = 4100 g/mol, 1.446 mg/350 μL) in distilled, degased chloroform and was loaded into the sample cell. An 8 mM solution of **sHW** was prepared (M_w= 619.83 g/mol, 247.93 μg/50 μL) and was loaded into the syringe for titration. After three trials, the K_a's were

calculated by the NanoAnalyze software to be 1.753 x 10^4, 7.354 x 10^3, and 1.031 x 10^4 M^{-1}, respectively. The average K_a was 1.2 x10^4 M^{-1}.

Titration of HW-Poly with Ba-Poly for ITC

A 0.65 mM solution of **HW-Poly** was prepared in distilled, degased chloroform and was loaded into the sample cell. A 4.5 mM solution of **Ba-Poly** was prepapred and loaded into the syringe. The weight of the polymer and heavy organic solvent in the 50 μL syringe resulted in small droplets of polymer solution forming at the syringe tip prior to loading into the calorimeter. Care was given to avoid the premature leaking of titrant into the host solution, however it is possible that this occurred after the calorimeter was loaded and prior to data acquisition. After three trials, the K_a's were calculated by the NanoAnalyze software to be 2.184 x 10^2, 1.599 x 10^2, and 2.417 x 10^2 M^{-1}, respectively. The average K_a was 2.1 x10^2 M^{-1}.

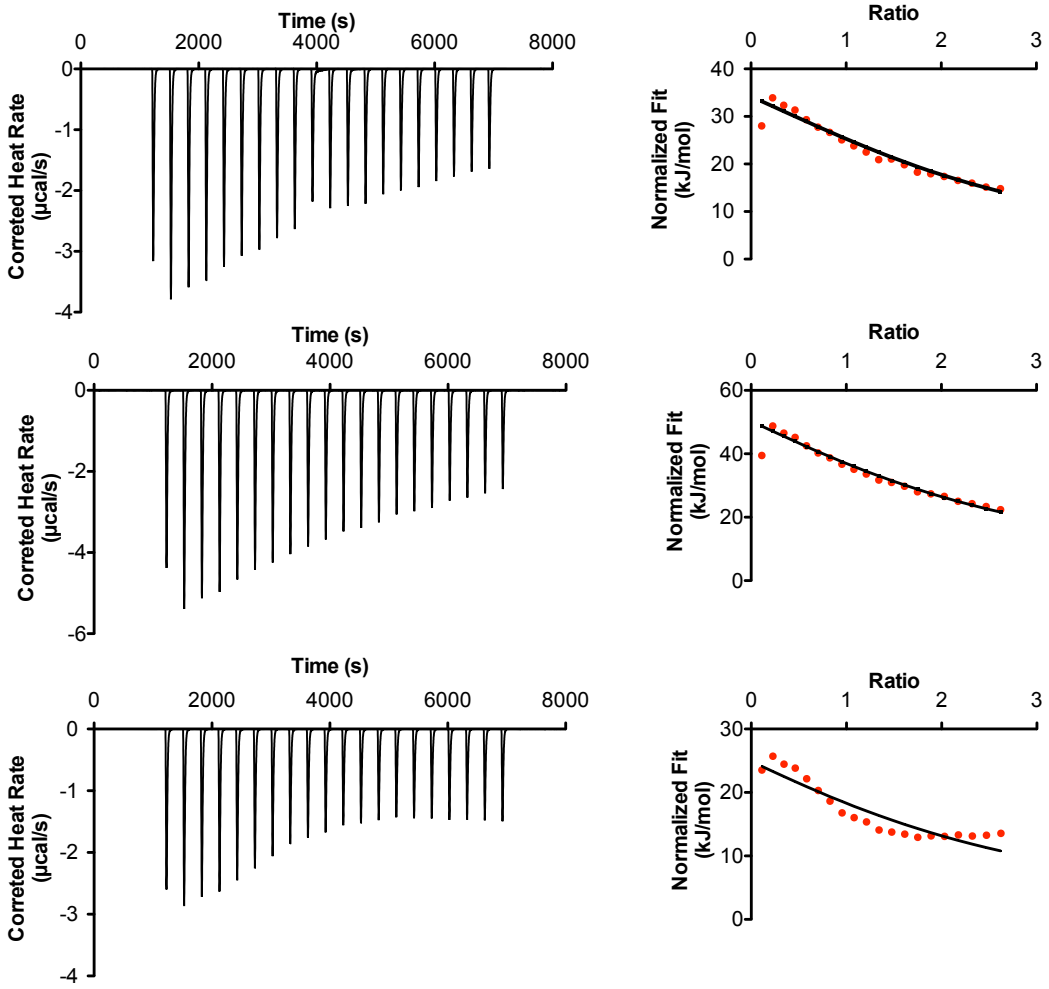


Figure S35. ITC binding isotherms and plots of the normalized fit for the titration of **HW-Poly** with **Ba-Poly** performed over three trials.

Table S2. Calcuated K_a values for the trials displayed in **Figure S35.**

Trial	Calculated K_a (M^{-1})
Top	2.184×10^2
Middle	1.599×10^2
Bottom	2.417×10^2

Circular Dichroism Studies

Table S3. Molar circular dichroism values at various wavelengths observed in the homopolymers of HW-Poly and Ba-Poly and comparison to the observed values for the 1:1 mixture.

Sample	Concentration	$\Delta\varepsilon_{364}$	$\Delta\varepsilon_{283}$	$\Delta\varepsilon_{249}$	$\Delta\varepsilon_{236}$
HW-Poly-1	3.75 μM	–4.04	–0.89	+8.48	–2.99

Ba-Poly-5	3.75 μM	+0.03	–1.06	–0.12	–2.84
Sum of Signals (Theoretical Δε)		–4.07	–1.95	+8.36	+0.15
Observed Δε	3.75 μM	–4.22	–2.03	+8.63	+0.69

Table S3 displays the molar circular dichroism (Δε) for the homopolymers, **HW-Poly-1** and **Ba-Poly-5**. Listed are the molar circular dichroism values at two characteristic wavelengths for each polymer. In each case, the theoretical molar circular dichroism was considered the sum of the contributions from each of the homopolymers. When compared to the observed molar CD, each chromophore exhibited a molar CD within range of the error for each wavelength as determined by a calibration curve prepared for each homopolymer (See S26-S29).

^{1}H-NMR Analysis of Assembled Polymers in Racemic Mixture

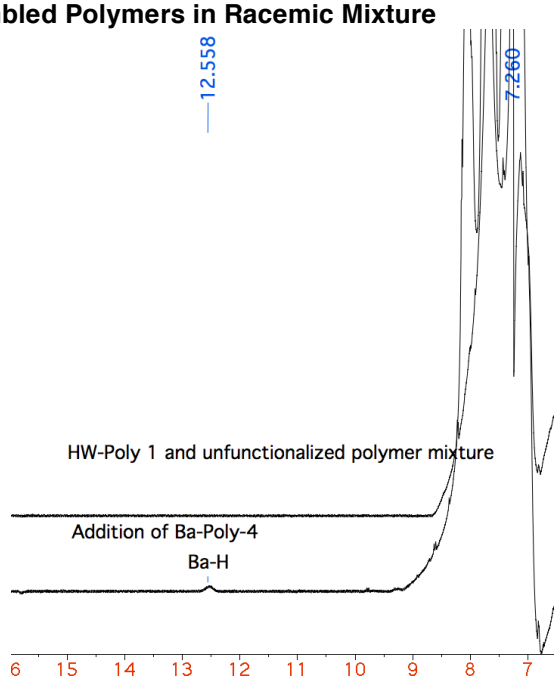


Figure S36. ^{1}H NMR spectrum overlay of the pseudo-racemic polymer mixture (top) and the equimolar (1:1) addition of **Ba-Poly-4** (bottom) in $CDCl_3$ (600 MHz).

CD and UV-Vis Calibration Curves

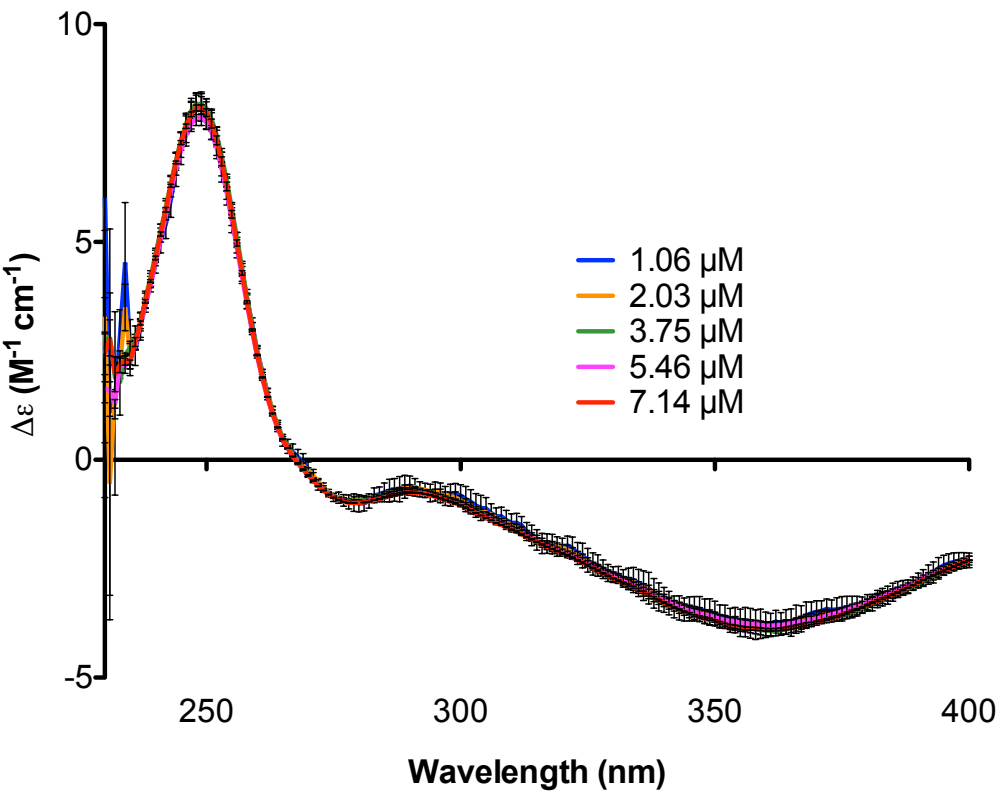


Figure S37. Overlay of CD chromatograms for **HW-Poly-1** at concentrations 1.00 μM, 2.03 μM, 3.75 μM, 5.46 μM, and 7.14 μM performed in triplicate and plotted with error bars (SEM).

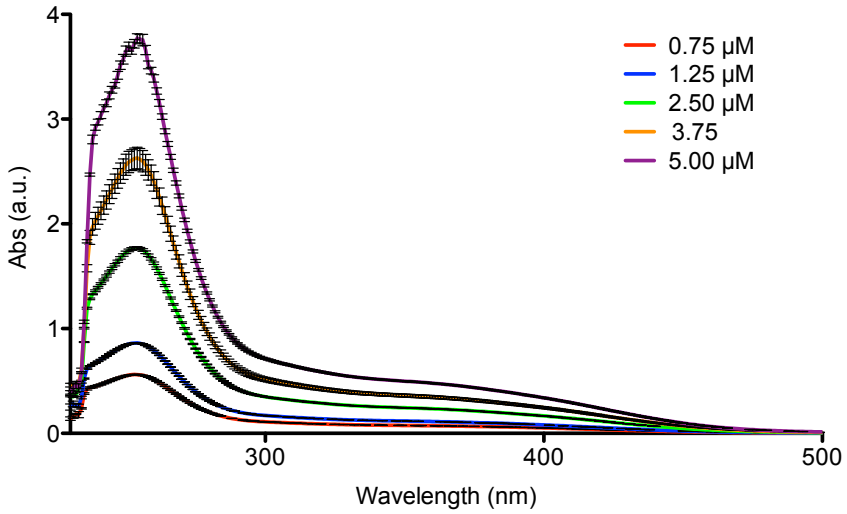


Figure S38. Overlay of UV chromatograms for **HW-Poly-1** at concentrations 0.75 μM, 1.25 μM, 2.50 μM, 3.75 μM, 5.00 μM performed in triplicate and plotted with error bars (SEM).

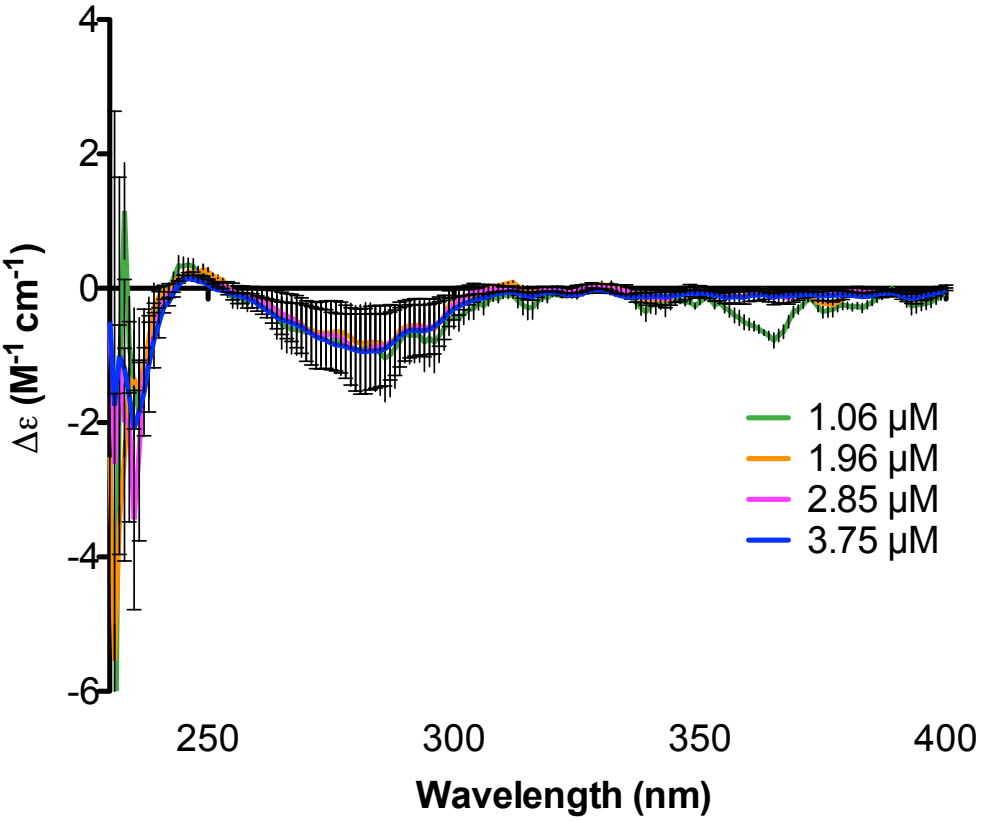


Figure S39. Overlay of CD chromatograms for **Ba-Poly-5** at concentrations 1.06 μM, 1.96 μM, 2.85 μM, 3.75 μM performed in triplicate and plotted with error bars (SEM).

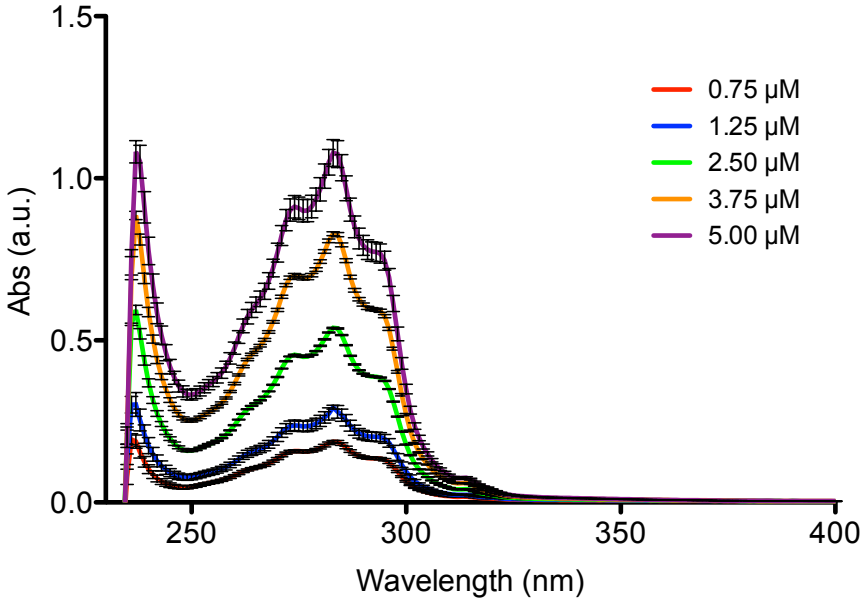


Figure S40. Overlay of UV chromatograms of **Ba-Poly-5** at concentrations, 0.75 μM, 1.25 μM, 2.50 μM, 3.75 μM, 5.00 μM performed in triplicate and plotted with error bars (SEM).

IR Spectra for Homopolymers and 1:1 Polymer Mixture

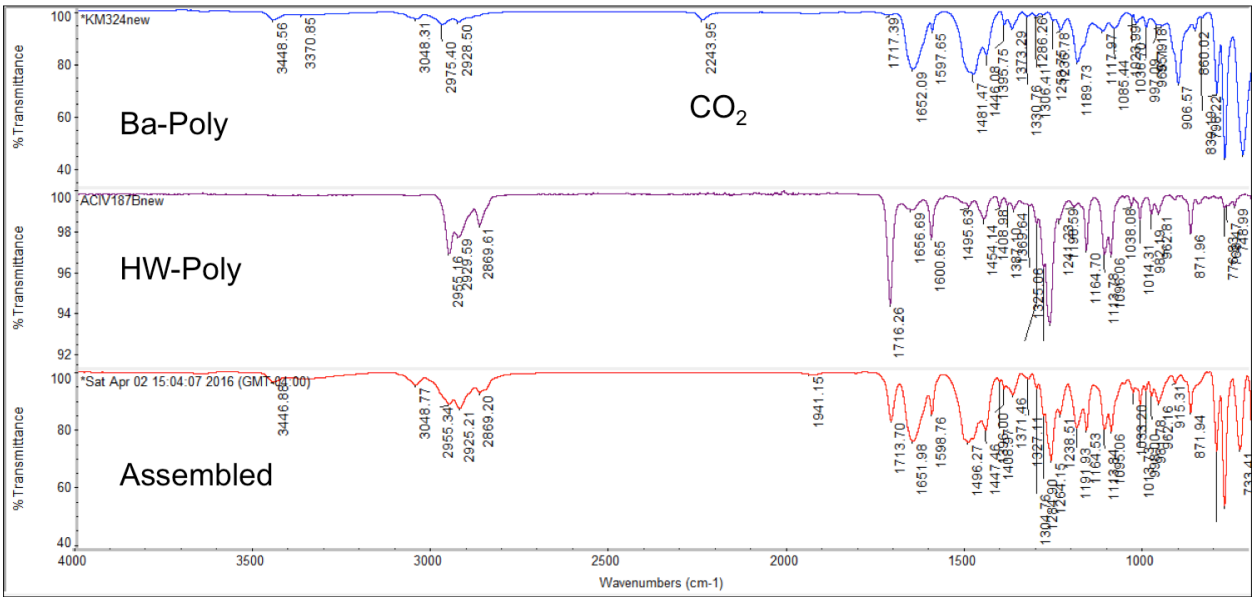


Figure S41. Stacked FT-IR spectra of **Ba-Poly-3** and **HW-Poly-1** before and after assembly in chloroform.

Miscellaneous.

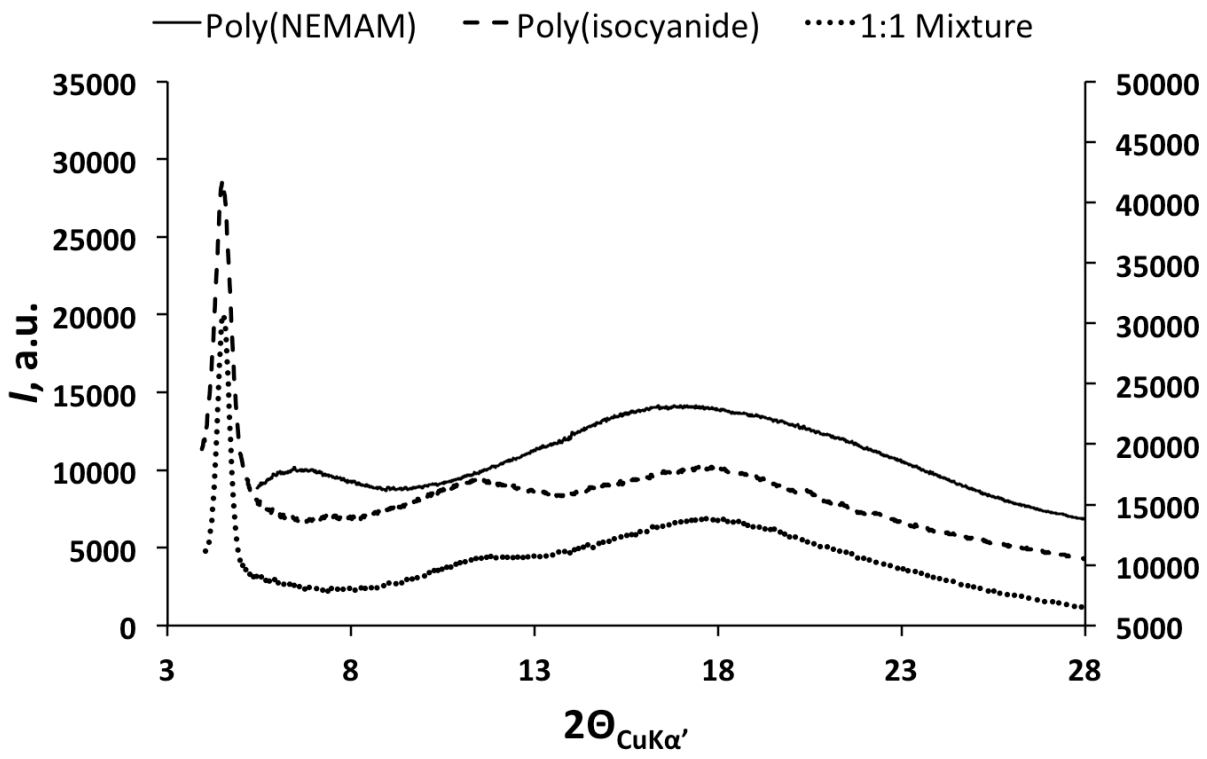


Figure S42. WAXS diffraction patterns for unfunctionalized Poly(NEMAM) (left axis), Poly(isocyanide) (left axis), and a solution-prepared 1:1 Mixture of both polymers(right axis).

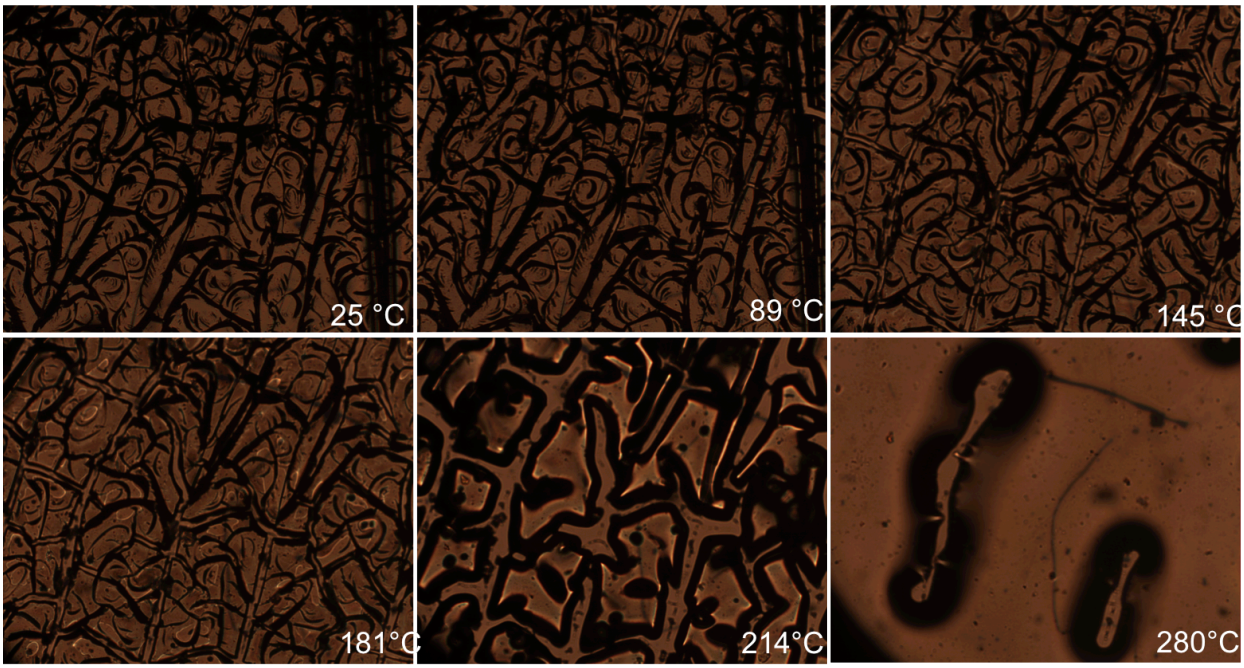


Figure S43. Optical micrographs of **Ba-Poly-3** upon heating displaying large melting-point range.

Although no thermal transition was detected by DSC for any of the polymers, by optical microscopy, **Ba-Poly-3** shows a gradual melt between approximately 80-280 °C, with relatively rapid melting between 202-225 °C. The large melting-point range is indicative of an amorphous material. The sample was heated at 10 °C/min.

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