Supplemental Information for

Toward a Tunable Synthetic [FeFe] Hydrogenase Mimic: Single-chain Nanoparticles Functionalized With a Single Diiron Cluster

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Supporting Information

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I. Supporting Figures

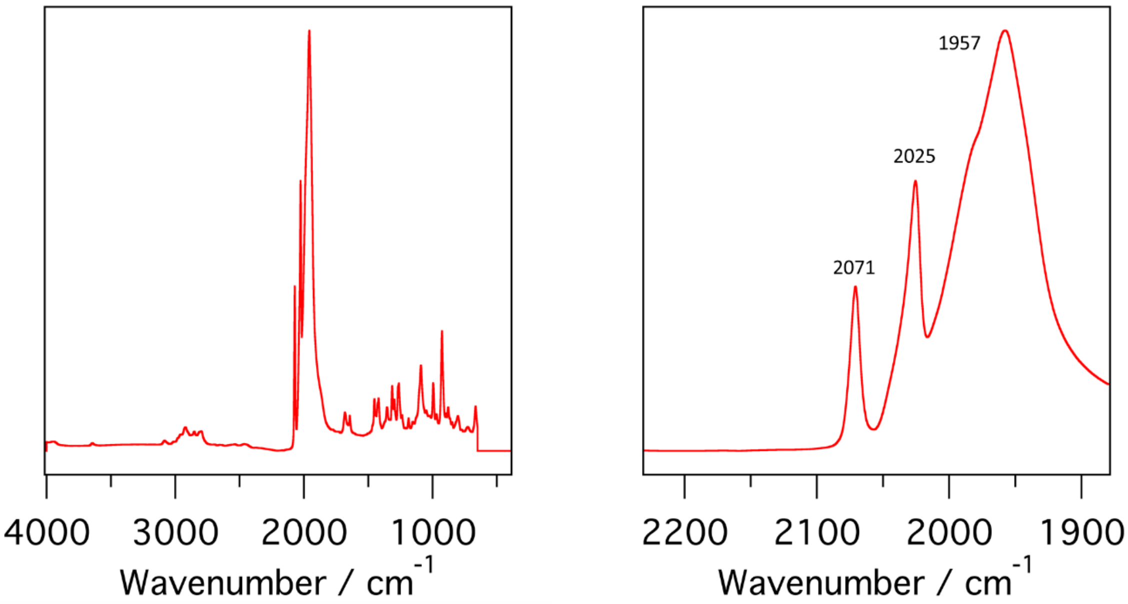


Figure S1. IR spectra of complex **1**.

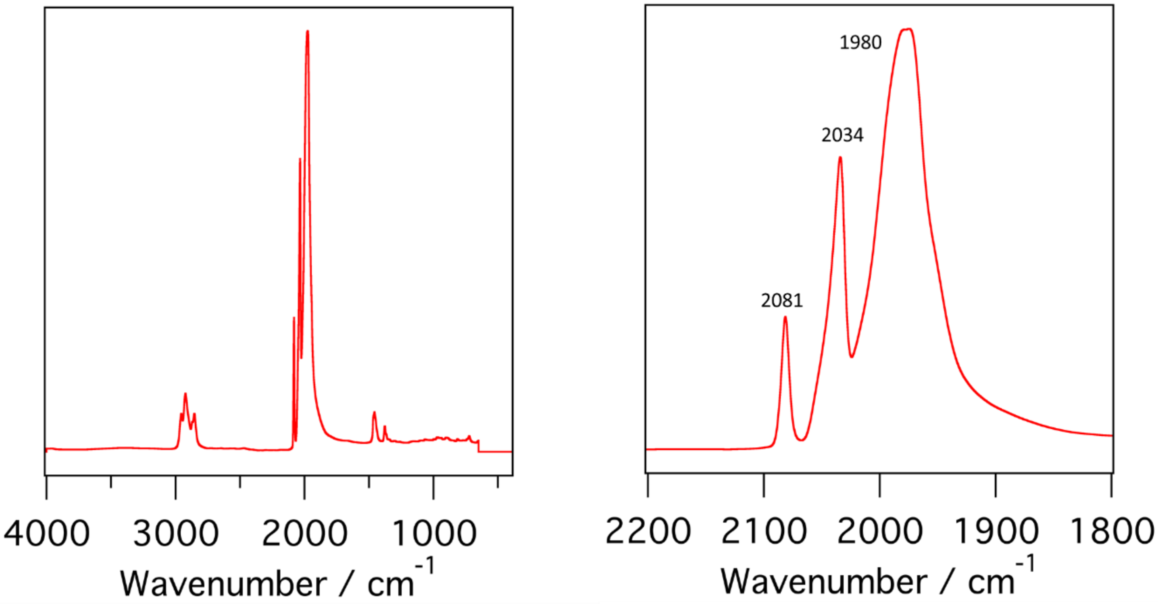


Figure S2. IR spectra of complex **2**.

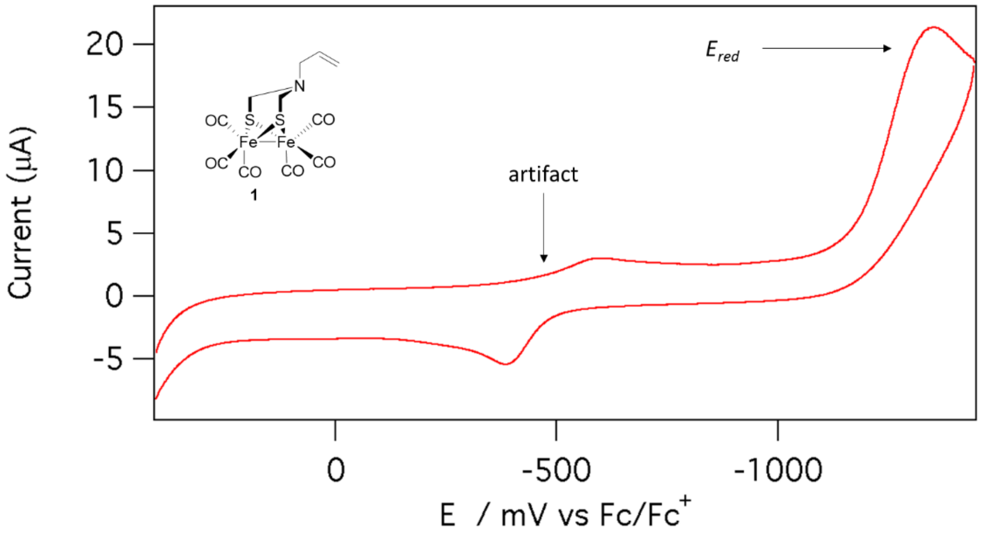


Figure S3. Cyclic voltammogram of complex **1** (E_{red} = -1.35 V). 2.5mM **1**, 0.10 M nBu_4NPF_6 in CH_3CN.

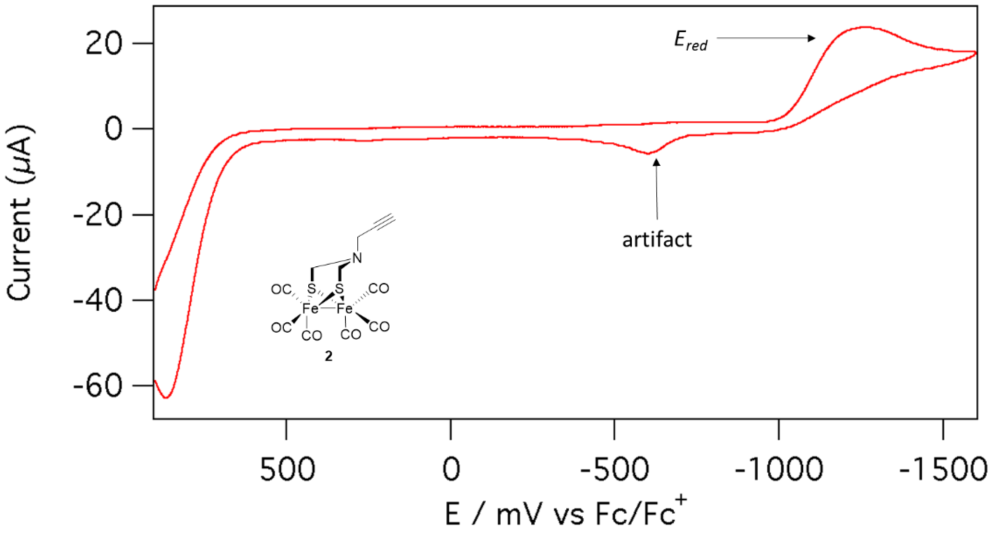


Figure S4. Cyclic voltammogram of complex **2** (E_{red} = -1.36 V). 2.5 mM **2**, 0.10 M nBu_4NPF_6 in CH_3CN.

The artifacts that in **Fig. S3** and **Fig. S4** are unknown. However, it is speculated to possibly be a slight decomposition of the analyte on the working electrode but the low current shows that it may be negligible.

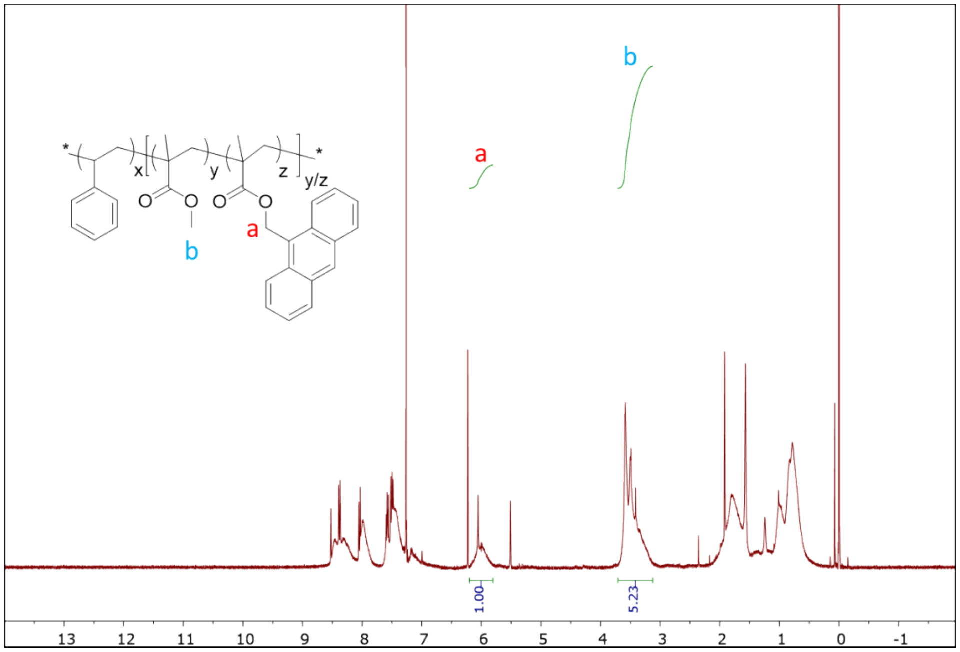
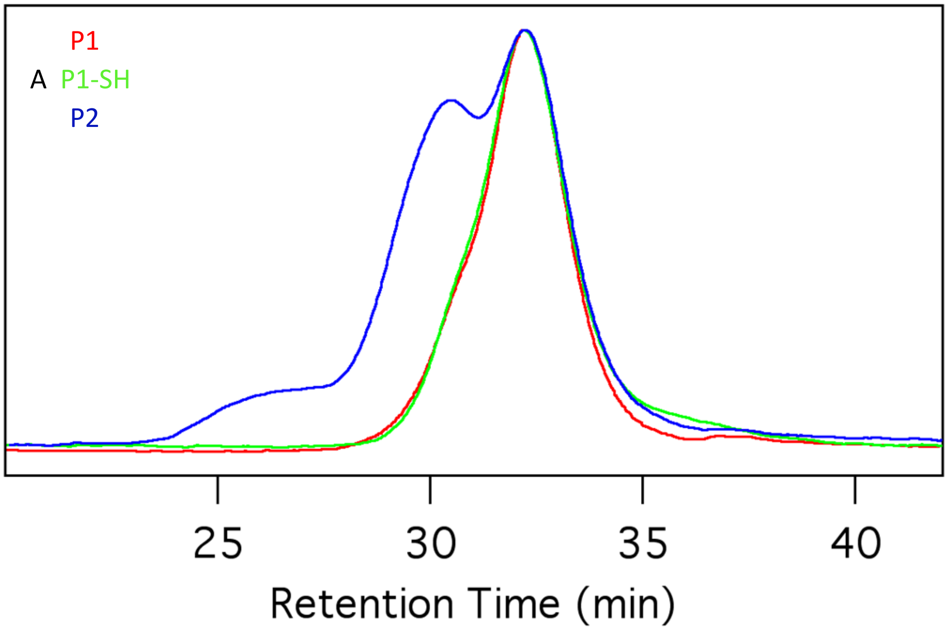


Figure S5. ^{1}H NMR spectrum of PS-*grad*-[(PMMA-*co*-PAMMA)].

The relative composition of AMMA to MMA was determined by:

$$\frac{\dfrac{\int H_a}{\#H_a} * 100\%}{\dfrac{\int H_a}{\#H_a} + \dfrac{\int H_b}{\#H_b}}$$



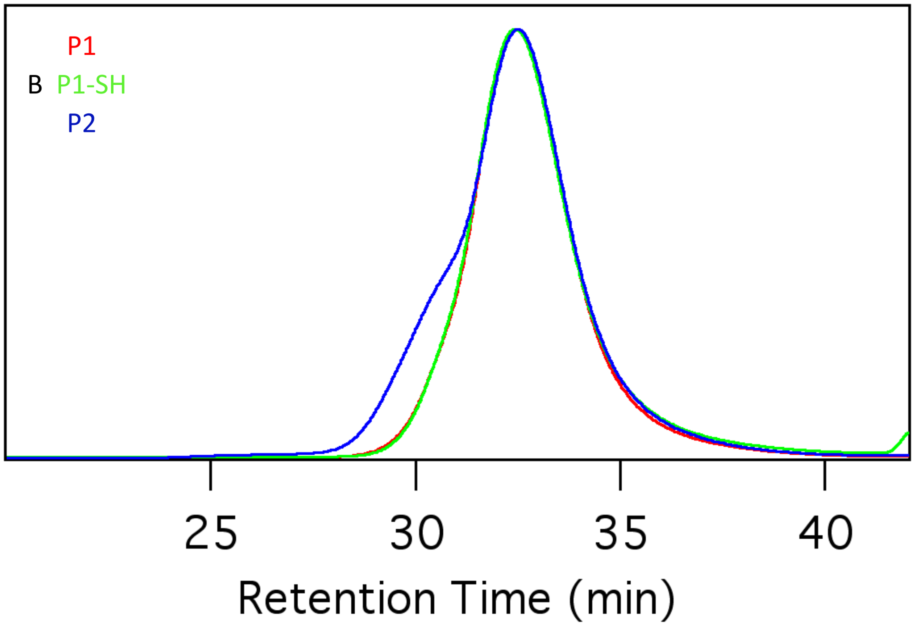


Figure S6. SEC overlay of a) MALS and b) UV traces revealing potential interchain coupling upon covalent attachment of diiron cluster to polymer backbone.

Table S1. Compilation of SEC data.

Sample	Mw (kDa)	Mn (kDa)	PDI	dn/dc (mL/g)	R_h (nm)	η (mL/g)	Conc. (mg/mL)	Inj. Vol. (μL)
P1	35.4	32.8	1.08	**0.135**	3.69	9.79	0.5	50
SCNP1	31.0	28.6	1.08	**0.134**	2.92	5.64	0.5	50
P2*	66.3	63.4	1.05	0.0727	3.65	4.90	0.5	50
SCNP2*	52.1	49.8	1.05	0.0813	3.10	3.81	0.5	50
P2	35.6	34	1.05	**0.135**	3.65	9.13	0.5	50
SCNP2	31.7	30.3	1.05	**0.134**	3.10	6.27	0.5	50
PS	39.6	39.1	1.01	0.160	4.95	19.6	1.0	25
PMMA	27.8	27.1	1.03	0.0815	4.02	15.3	1.0	25
PS-*b*-PMMA	30.0	29.7	1.01	0.100	4.31	17.1	1.0	25

In the main text of this paper we show that absolute molecular mass for **P2** and **SCNP2** calculated from MALS data based on the dn/dc values for **P1** and **SCNP1**. As shown here, the dn/dc for these two materials (**P2*** and **SCNP2***), determined as described in our experimental section, was very different due to absorbance of light by the chromophoric cluster. This leads to the observed discrepancy in the Mw and η.The trend, however, remains consistent.

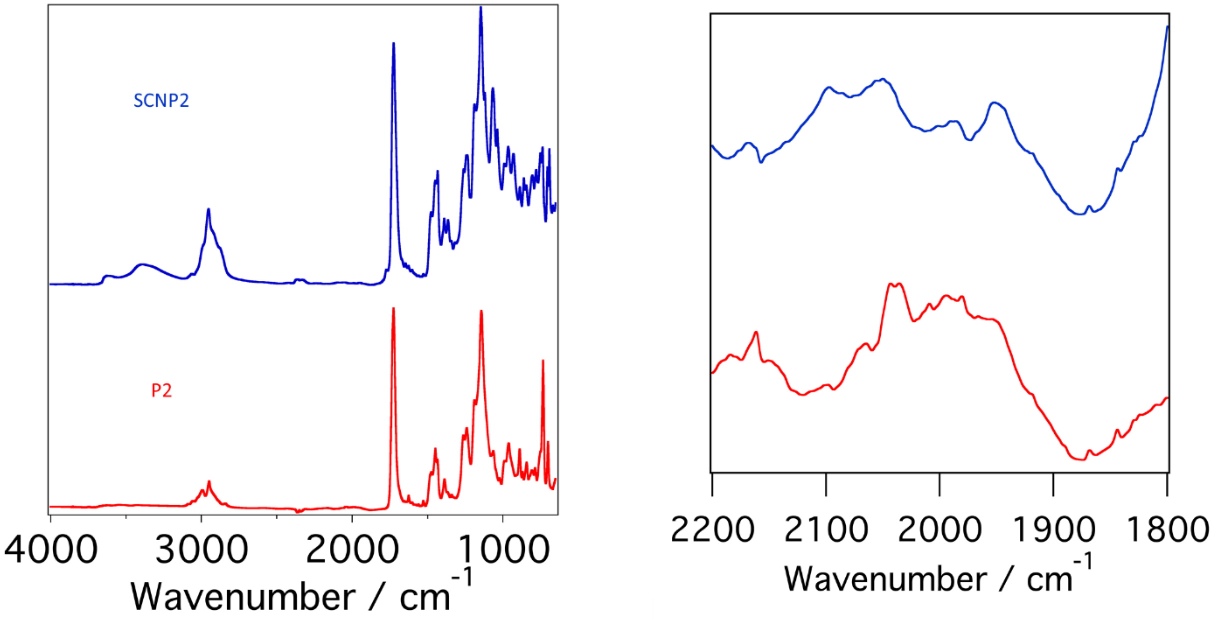


Figure S7. IR spectra of **SCNP2** and **P2**.

II. Crystallographic Data

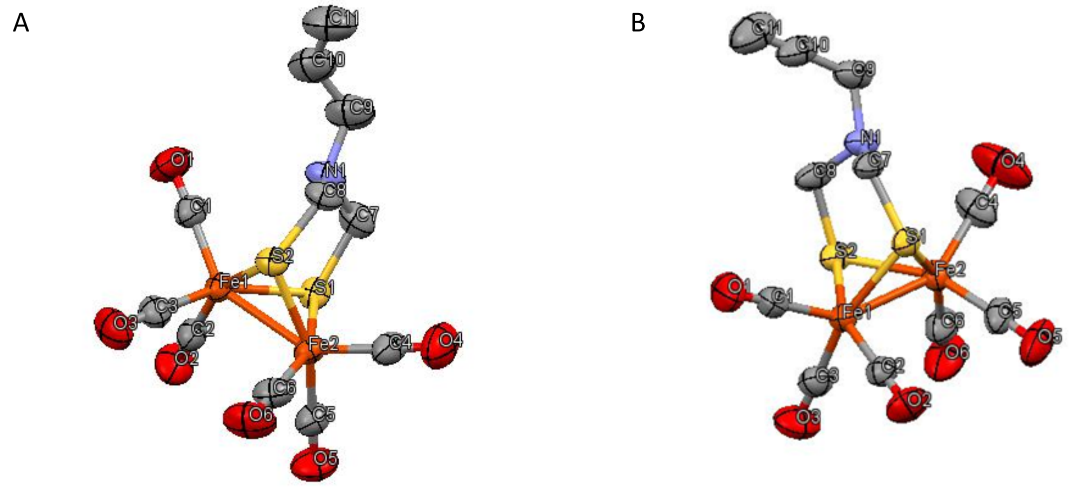


Figure S8. Crystal structures of A) complex **1** and B) complex **2**.

Table S2. Bond lengths of the two $[(\mu\text{-}S_2C_2H_4NR)Fe_2(CO)_6]$ complexes.

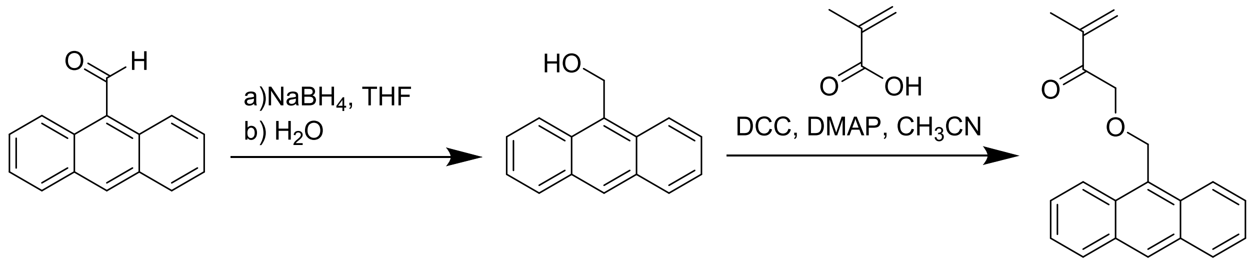
Complex **1**						Complex **2**					
Atom1	Atom2	Length				Atom1	Atom2	Length	Atom1	Atom2	Length
Fe1	Fe2	2.5229(5)	O5	C5	1.135(3)	C1	Fe1	1.789(4)	C8	H8A	0.969
Fe1	S1	2.2527(6)	O6	C6	1.134(3)	C1	O1	1.139(5)	C8	H8B	0.97
Fe1	S2	2.2585(7)	N1	C7	1.437(3)	C2	Fe1	1.795(5)	C8	N1	1.443(4)
Fe1	C1	1.810(3)	N1	C8	1.437(3)	C2	O2	1.135(6)	C8	S2	1.828(4)
Fe1	C2	1.791(3)	N1	C9	1.464(4)	C3	Fe1	1.790(3)	C9	H9A	0.97
Fe1	C3	1.786(3)	C7	H7A	0.97	C3	O3	1.141(4)	C9	H9B	0.969
Fe2	S1	2.2443(7)	C7	H7B	0.97	C4	Fe2	1.794(5)	C9	C10	1.470(6)
Fe2	S2	2.2469(7)	C8	H8A	0.97	C4	O4	1.130(6)	C9	N1	1.471(5)
Fe2	C4	1.793(3)	C8	H8B	0.97	C5	Fe2	1.794(4)	C10	C11	1.162(8)
Fe2	C5	1.795(3)	C9	H9A	0.971	C5	O5	1.136(6)	C11	H11	0.929
Fe2	C6	1.795(3)	C9	H9B	0.97	C6	Fe2	1.793(4)	Fe1	Fe2	2.5101(8)
S1	C7	1.824(3)	C9	C10	1.415(5)	C6	O6	1.133(5)	Fe1	S1	2.2488(9)
S2	C8	1.827(2)	C10	H10	0.93	C7	H7A	0.97	Fe1	S2	2.247(1)
O1	C1	1.132(4)	C10	C11	1.298(6)	C7	H7B	0.97	Fe2	S1	2.255(1)
O2	C2	1.131(3)	C11	H11A	0.929	C7	N1	1.440(5)	Fe2	S2	2.251(1)
O3	C3	1.138(3)	C11	H11B	0.93	C7	S1	1.826(4)			
O4	C4	1.138(4)									

Table S3. Crystallographic parameters for a) complex **1** and b) complex **2**.

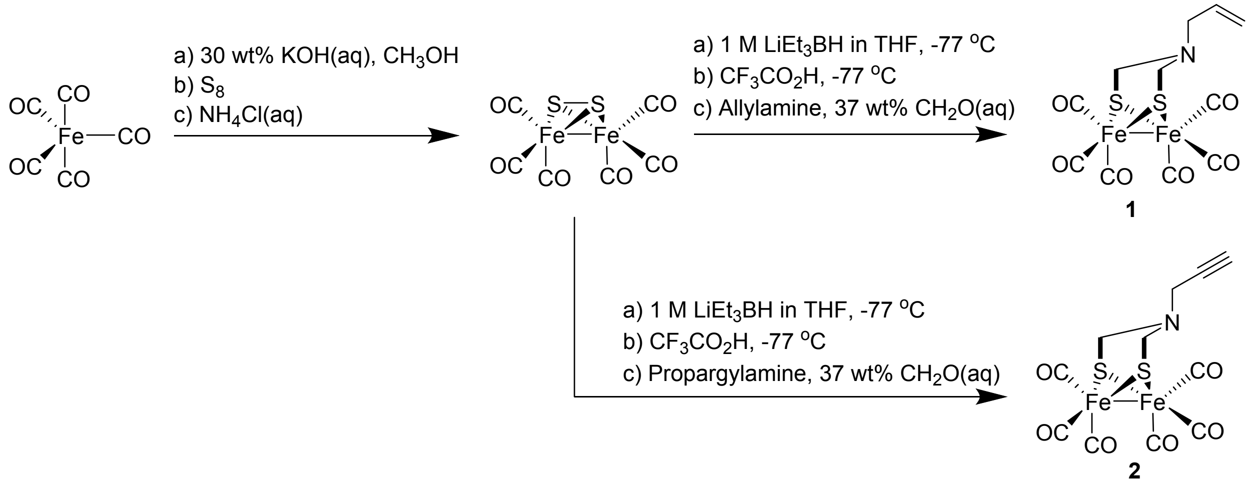
Empirical Formula	$C_{11}H_9Fe_2NO_6S_2$		$C_{11}H_7Fe_2NO_6S_2$	
Formula weight	427.01		425.00	
Temperature	300.15 K		300.15 K	
Wavelength	0.71073 Å		0.71073 Å	
Crystal system	Monoclinic		Triclinic	
Space group	P 1 21/n 1		P-1	
Unit cell dimensions	a = 6.8072(9) Å	α = 90°	a = 9.127(2) Å	α = 102.454(9)°
	b = 18.152(2) Å	β = 90.497(4)°	b = 9.176(2) Å	β = 105.352(9)°
	c = 13.3181(16) Å	γ = 90°	c = 10.453(3) Å	γ = 97.467(9)°
Volume	1645.6(4) Å^3		807.9(4) Å^3	
Z	4		2	
Density (calculated)	1.724 Mg/m^3		1.747 Mg/m^3	
Absorption coefficient	2.040 mm^{-1}		2.077 mm^{-1}	
F(000)	856		424	
Crystal size	0.5 x 0.3 x 0.2 mm^3		0.7 x 0.4 x 0.1 mm^3	
Theta range for data collection	3.059 to 26.442°		2.640 to 25.389°	
Index ranges	-8<=h<=8, -22<=k<=22, -16<=l<=12		-10<=h<=10, -11<=k<=11, -12<=l<=12	
Reflections collected	20710		8396	
Independent reflections	3361 [R(int) = 0.0297]		2923 [R(int) = 0.0389]	
Completeness to theta = 26.000°	99.4 %		92.1%	
Absorption correction	Semi-empirical from equivalents		Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.5622		0.7452 and 0.5053	
Refinement method	Full-matrix least-squares on F^2		Full-matrix least-squares on F2	
Data/restraints/paramaters	3361 / 0 / 199		2923 / 0 / 199	
Goodness-of-fit on F^2	1.043		1.107	
Final R indices [I>2sigma(I)]	R1 = 0.0273, wR2 = 0.0640		R1 = 0.0334, wR2 = 0.0762	
R indices (all data)	R1 = 0.0380, wR2 = 0.0692		R1 = 0.0525, wR2 = 0.0845	
Largest diff. peak and hole	0.586 and -0.331 e.Å-3		0.289 and -0.274 e.Å^{-3}	

III. Outline of Synthetic Schemes

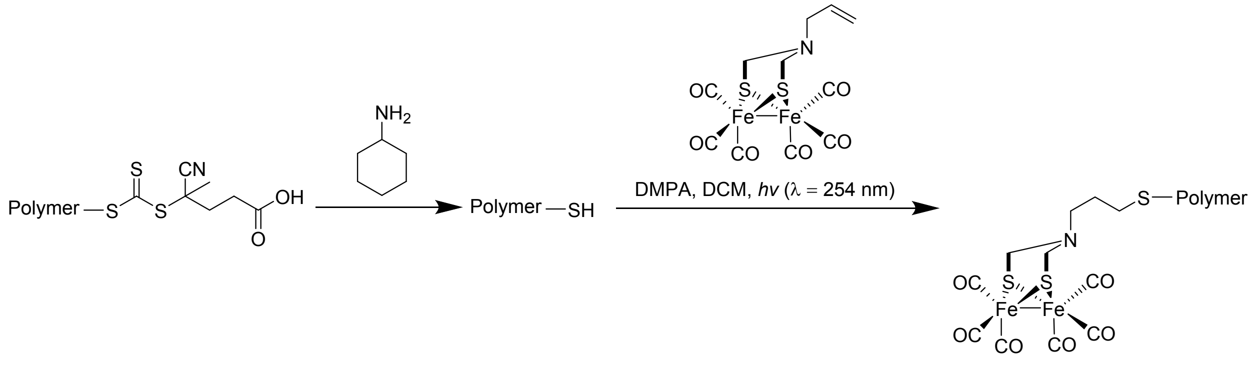
a. Synthesis of 9-AMMA



b. Synthesis of complex 1 and complex 2.



c. Aminolysis of RAFT polymer chains



IV. Experimental Procedures, Spectra, and Chromatograms

Materials

Reagents were obtained from the indicated commercial suppliers and used as received: iron(0) pentacarbonyl (Sigma Aldrich), cyclohexylamine (Sigma Aldrich), dimethylaminopyradine (Sigma Aldrich), methacrylic acid (Sigma Aldrich), N,N'dicyclohexylcarbodiimide (Sigma Aldrich), styrene (Sigma Aldrich), *N*-isopropylacrylamide (Sigma Aldrich), dicyclohexylcarbodiimide (Fisher Scientific), methyl methacrylate (Sigma Aldrich), precipitated sulfur (Fisher Scientific), dichloromethane (Fisher Scientific), hexanes (Fisher Scientific), methanol (Fisher Scientific), tetrahydrofuran (Fisher Scientific), silica gel (230400 mesh) (SiliCycle), azobisisobutyronitrile (Sigma Aldrich), tetrabutylammonium hexafluorophosphate (Sigma Aldrich), allylamine (Sigma Aldrich), propargylamine (Sigma Aldrich), 37 wt% formaldehyde in water (Fisher Scientific), 1 M lithium triethylborohydride (Fisher Scientific), silver(I) nitrate (Fisher Scientific), trifluoroacetic acid (Sigma Aldrich), potassium hydroxide (Sigma Aldrich), chloroform-d (Cambridge Isotope Laboratories), and 4-cyano-4[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (Sigma Aldrich). Dry toluene, acetonitrile, DCM, and THF were obtained from an Innovative Technology solvent purification system model SPS-400-5.

Instrumentation

Instrumentation Photochemical reactions were conducted in a Luzchem photo-reactor CCP-4V equipped with 4 UVA (350 nm centered) and 4 UVC (254 nm centered) lamps. 1H NMR (400 MHz) and 13 C NMR (101 MHz) spectra were recorded on a Varian Associates Mercury 400 spectrometer or Varian Associates Mercury 500. Solvents (CDCl3) contained 0.03% v/v TMS as an internal reference, chemical shifts (δ) are reported in ppm relative to TMS. Peak abbreviations are used as follows: s=singlet, d=doublet, t=triplet, m=multiplet. Size exclusion chromatography (SEC) was performed on a Tosoh EcoSEC dual detection (RI and UV) SEC system coupled to an external Wyatt Technologies miniDAWN Treos multi angle light scattering (MALS) detector and a Wyatt Technologies ViscoStarII differential viscometer. Samples were run in THF at 40 ºC at a flow rate of 0.35 mL/min. The column set was two Tosoh TSKgel SuperMultipore HZ-M columns (4.6x150 mm), one Tosoh TSKgel SuperH3000 column (6x150mm) and one Tosoh TSKgel SuperH4000 column (6x150mm). Increment refractive index values (dn/dc) were calculated online assuming 100% mass recovery (RI as the concentration detector) using the Astra 6 software package (Wyatt Technologies) by selecting the entire trace from analyte peak onset to the onset of the solvent peak or flow marker. This method gave the expected values for polystyrene (dn/dc = .185, Mn = 30k) when applied to a narrow PDI PS standard supplied by Wyatt. Absolute molecular weights and molecular weight distributions were calculated using the Astra 6 software package. Intrinsic viscosity [η] and viscometric hydrodynamic radii (Rh) were calculated from the differential viscometer detector trace and processed using the Astra 6 software. SEC analysis of PNIPAM was carried out in DMF with 0.01 M LiCl running at a flow rate of 1.0 mL/min and 50 ^{o}C. PMMA standards were used for calibration. Sonntek HPLC pump (K-501), Knauer refractive index detector (K-2301), 1 PL gel guard (50 mm x 7.5 mm; length x diameter), 1 PL gel mixed C, 5 µm (300 mm x 7.5 mm; length x diameter), 1 PL gel mixed D, 5 µm (300 mm x 7.5 mm;
length x diameter), and toluene was used as a fluorophore marker. Electrochemical measurements were recorded using a BAS-100W electrochemical potentiostat at a scan rate of 100 mV s^{-1}. A solution of 0.10 M nBu_4NPF_6 in CH_3CN was used as electrolyte, which was degassed by bubbling with dry argon for 15 min before measurement. Cyclic voltammograms were obtained in a three-electrode cell under argon. The working electrode was a glassy carbon disc (diameter 3 mm) successively polished with 3 and 1 lm

diamond pastes and sonicated in ion-free water. The reference electrode was a non-aqueous Ag/Ag$^+$ electrode (0.05 M $AgNO_3$ in CH_3CN) and the counter-electrode was a platinum wire. All potentials are reported relative to the Fc/Fc$^+$ potential. X-ray diffraction data was acquired at room temperature using a Bruker SMART X2S x-ray diffractometer. ATR-IR spectra were acquired from a Thermo Nicolet iS10 FT-IR equipped with a diamond tip.

Experimental

Synthesis of $Fe_2S_2(CO)_6$

The diiron cluster precursor was prepared following the general procedure reported by Rauchfuss.[1] A 500 mL Schlenk flask equipped with a magnetic stir bar was charged 30% wt aqueous potassium hydroxide (20 mL) and methanol (35 mL). The solution was purged under nitrogen and cooled to 0 ^oC. Iron(0) pentacarbonyl (7.5 mL, 56 mmol) was added dropwise and stirred for 3 minutes until the red solution became a homogenous mixture. Elemental sulfur (10.0 g, 39.1 mmol) was added scoopwise with a nitrogen counterflow and turbid black mixture formed. After six minutes of vigorous stirring, 80.0 mL of water, 200 mL of hexanes, and ammonium chloride (25.2 g, 0.471 mol) were added to the solution, which produced $H_2S(g)$. The solution was vigorously stirred for 1.4 hours. The top hexane layer was decanted and the dark aqueous oily phase was extracted with hexanes (x3, 150 mL). The extracts were filtered through a pad of celite, washed with an equivalent volume of water, and then dried over magnesium sulfate. The solution was dried under reduced pressure to yield a dark red solid. The dark red solid was dissolved in hexanes. Two colored bands separated: the first red-orange band was collected and the second maroon band was discarded. The red-orange band was dried to form a bright red solid (1.66 g, 4.84 mmol) in 17% yield. The product was characterized with IR spectroscopy and x-ray crystallography. IR (ATR): ν_{CO} = 2083, 2044, 2007 cm^{-1}.

The condensation of the bridgeheads onto the metal complex was performed using a modified procedure reported by Rauchfuss[1] using allylmine and propargylamine instead of ammonium carbonate.

Synthesis of aadt$Fe_2(CO)_6$

A 100-mL Schlenk flask equipped with a magnetic stir bar was charged with $Fe_2S_2(CO)_6$ (1.00 g, 2.91 mmol) and dissolved in THF (20 mL) to form a bright red solution. The solution was degassed and cooled in a dry ice/acetone bath. 1M $LiEt_3BH$ in THF (6.54 mL, 6.55 mmol) was slowly added dropwise to the Schlenk flask to produce an intensely green solution. After 15 minutes, CF_3CO_2H (0.92 mL, 12.1 mmol) was slowly added dropwise to the Schlenk flask to produce an intensely red solution. After 15 minutes, solution was slowly warmed to room temperature prior to the addition of the allylaminomethylation reagent by cannula transfer. The mixture stirred at room temperature for 16 hours and then concentrated under reduced pressure to a dark red oil. The dark red oil was dissolved in hexanes (ca. 125 mL) and then washed with water and aqueous sodium bicarbonate solution. The extract was dried over $MgSO_4$ and concentrated under reduced pressure to form the crude dark red oily product. The product was dissolved in hexanes and then purified through a column of silica. Three bands were observed eluted in the following order: yellow unreacted $Fe_2S_2(CO)_6$, a purple unknown band, and finally the dark orange band. The dark orange band was concentrated under reduced pressure and the product was dried in vacuo and obtained in 58% yield (0.718 g, 1.78 mmol). Crystals were grown from hexanes. The product was characterized by x-ray crystallography, ^1H NMR and IR spectroscopy. ^1H NMR (500 MHz, CDCl3): δ 3.17 (dt, 2H), 3.32 (s, 4H), 5.11 (dq, 1H), 5.15 (m, 1H), 5.63 (qt, 1H). IR (ATR): ν_{CO} = 2071, 2025, 1957 cm^{-1}.

Preparation of the allylamino methylation reagent

A 100-mL Schlenk flask equipped with a magnetic stir bar was charged with allylamine (0.218 mL, 2.91 mmol) and 50 mL of THF. The solution was degassed prior to the addition of 37% wt aqueous solution of formaldehyde (2.17 mL, 29.1 mmol). The solution was heated at 60 °C for 1 hour and then cooled to room temperature.

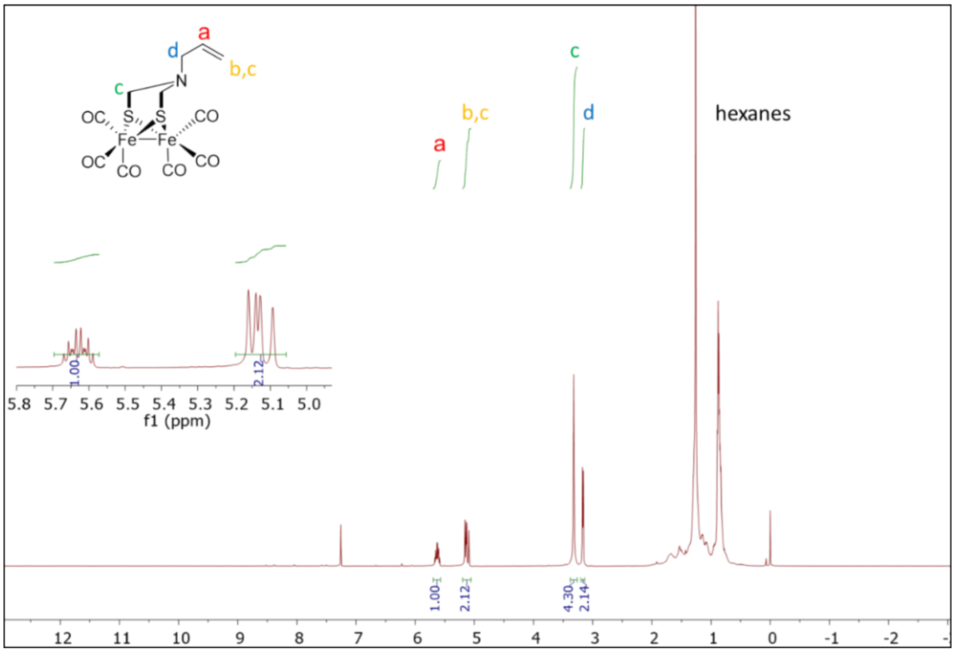


Figure S9. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of complex **1**.

Synthesis of padtFe$_2$(CO)$_6$

Followed same procedure as above but substitute allylamine with propargylamine.

^{1}H NMR (500 MHz, CDCl$_3$): δ 2.29 (s, 1H), 3.22 (s, 4H), 3.34 (s, 2H). IR (ATR): ν_{CO} = 2081, 2034, 1980 cm^{-1}.

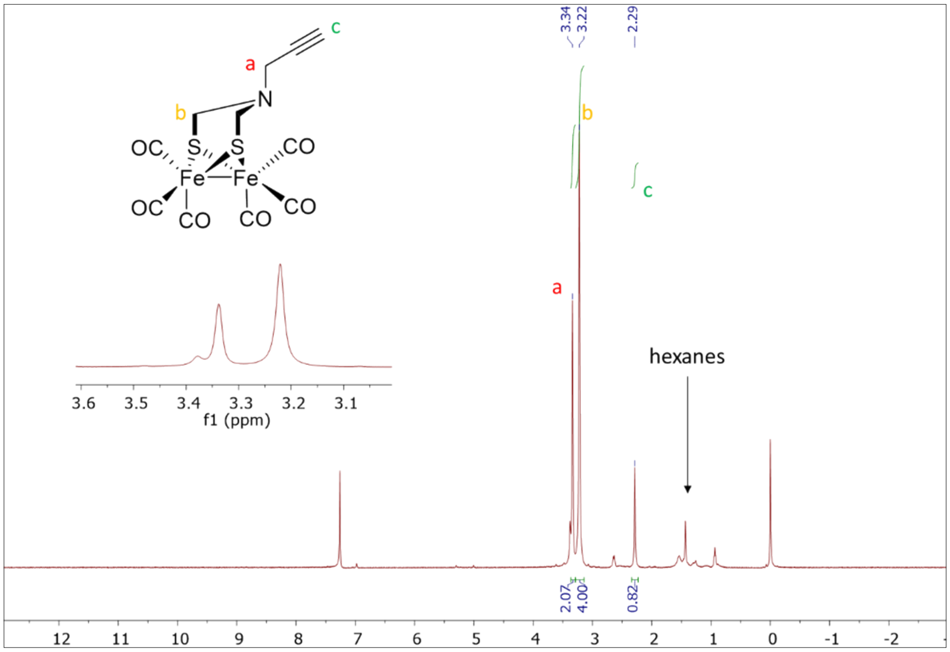


Figure S10. ^{1}H NMR (500 MHz, CDCl$_3$) spectrum of complex **2.**

Synthesis of 9-anthracenemethanol[2]

A 500 mL round bottom flask equipped with a magnetic stir bar was charged with 9-anthraldehyde (10.0 g, 48.7 mmol) and sodium borohydride (1.91 g, 50.5 mmol) and dissolved in 250 mL of dry tetrahydrofuran. The mixture was stirred under ambient conditions for 4 h. The mixture was transferred to a 1 L Erlenmeyer flask and 500 mL of cold water was added to precipitate the product. The yellow powder was collected by vacuum filtration and dried under vacuum. Yield: 8.68 g (87%) ^{1}H NMR (400 MHz, CDCl$_3$: δ 8.47 (t, 1H), 8.42 (dd, 2H), 8.03 (dd, 2H), 7.57 (m, 2H), 7.49 (m, 2H), 5.68 (d, 2H), 1.73 (t, O**H**).

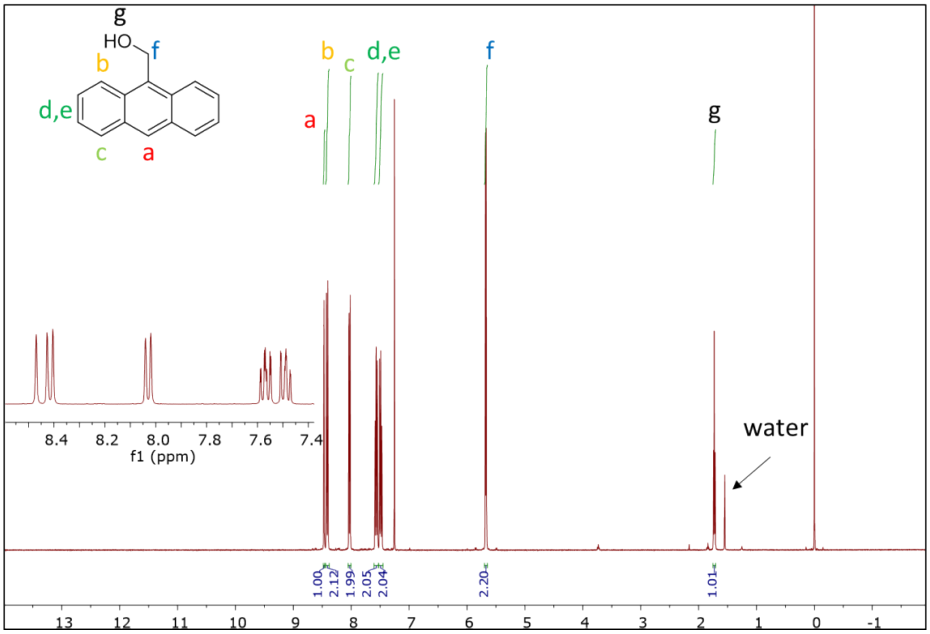


Figure S11. ^1H NMR (400 MHz, CDCl3) spectrum of 9-anthracenemethanol.

Synthesis of 9-anthracenylmethyl methacrylate[2]
A 500 mL Erlenmeyer flask equipped with a magnetic stir bar was charged with 9-anthracenemethanol (5.00 g, 24.0 mmol), dicyclohexylcarbodiimide (9.912 g, 48.0 mmol), and dimethylaminopyridine (0.443 g, 4.53 mmol). A slurry was formed by addition of 50 mL of acetonitrile followed by methacrylic acid (4.15 g, 48.2 mmol). The flask was sealed and allowed to stir at ambient temperature overnight. DCU was separated from the mixture by filtration. The filtrate was concentrated under reduced pressure and the product was separated through a column of silica (9:1 toluene/ethyl acetate). The yellow band was concentrated under reduced pressure and the product was precipitated in ethanol. The yellow solid was collected by vacuum filtration and dried under vacuum. Yield: 5.77 g (88%) ^1H NMR (400 MHz, $CDCl_3$): δ 1.91 (m, 3H), 5.49 (m, 1H), 6.05 (m, 1H), 6.21 (s, 2H), 7.49 (m, 2H), 7.56 (m, 2H), 8.02 (d, 2H), 8.37 (d, 2H), 8.49 (s, 1H).

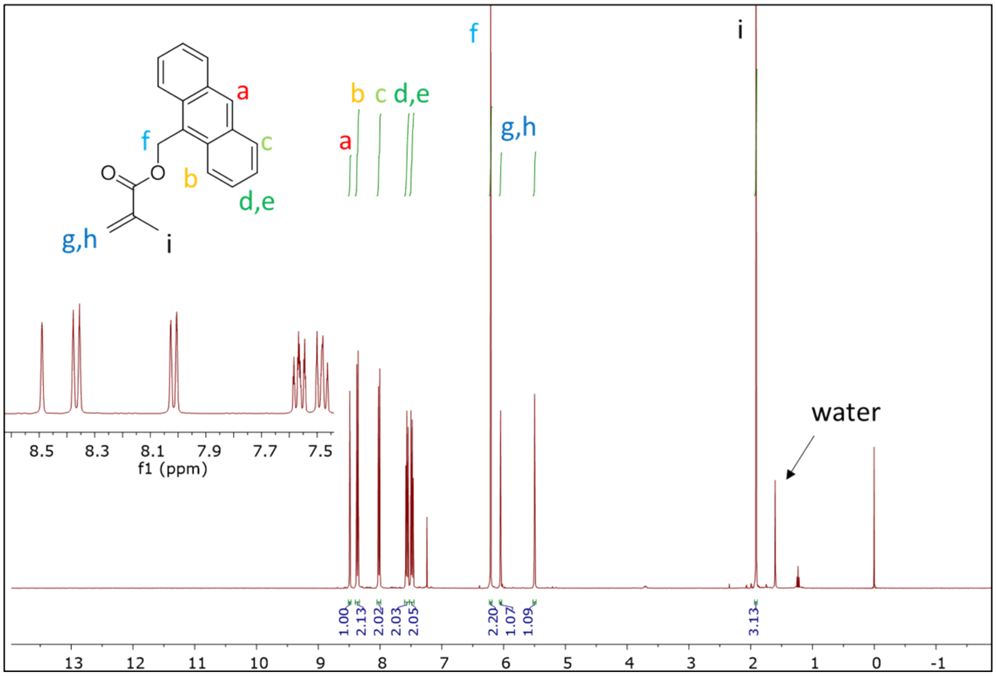


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of AMMA.

RAFT Polymerization of PS-*grad*-(PAMMA-*co*-PMMA)

A 50-mL Schlenk flask equipped with a magnetic stir bar was charged with AIBN (1.09 mg, 6.64×10^{-6} mol), 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (20.2 mg, 5.00×10^{-5} mol), methyl methacrylate (0.771 g, 7.70 mmol), and 9-anthracenylmethyl methacrylate (0.709 g, 2.57 mmol). The contents were dissolved in 2-mL of dry toluene. The Schlenk flask was sealed and degassed by successive freeze-pump-thaw cycles. Polymerization was initiated at 90 °C under nitrogen. After two hours, approximately 0.3 mL of degassed styrene (0.272 g, 2.62 mmol) was added via syringe. Polymerization was quenched 19.5 h later by exposure to ambient air and removal from heat. The polymer was precipitated in cold methanol and isolated by gravity filtration. 0.951 g polymer. M_w = 35.4

kDa, PDI = 1.08, dn/dc = 0.135.

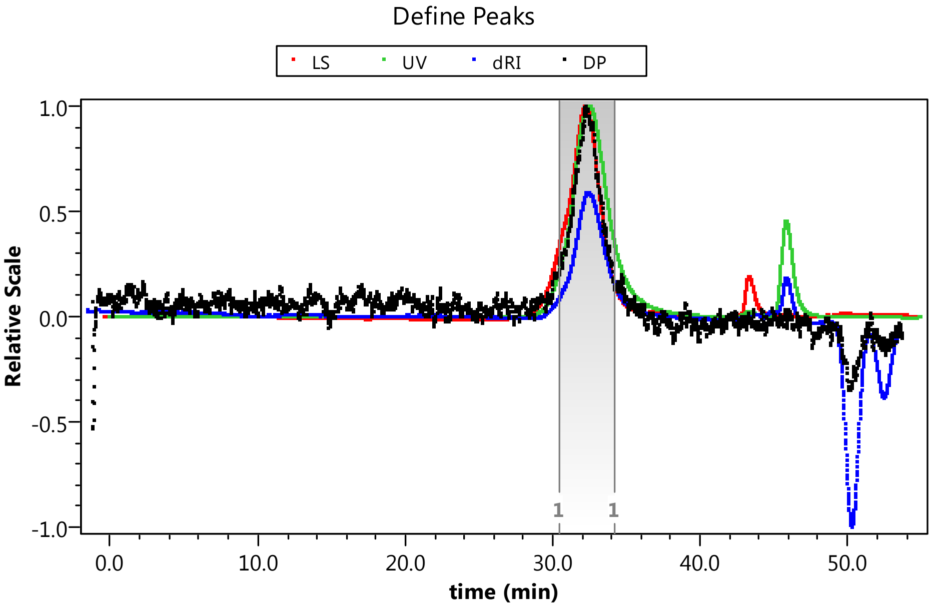


Figure S13. Raw chromatogram of **P1**.

RAFT Polymerization of styrene (PS)

A 50-mL Schlenk flask equipped with a magnetic stir bar was charged with 2.18 mL (1.98 g, 19 mmol) of styrene, 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (16.3 mg, 40.4 µmol), and azoisobutyronitrile (0.657 mg, 4.06 µmol). The solution was degassed by successive freeze-pump-thaw (FPT) cycles. The reaction was initiated by heating at 110 °C for 24 hours. The polymer was precipitated in cold methanol and then dried under vacuum. Yield: 1.424 g. Absolute molecular weight distribution: Mn = 39.1 kDa Mw = 39.7 kDa PDI = 1.01.

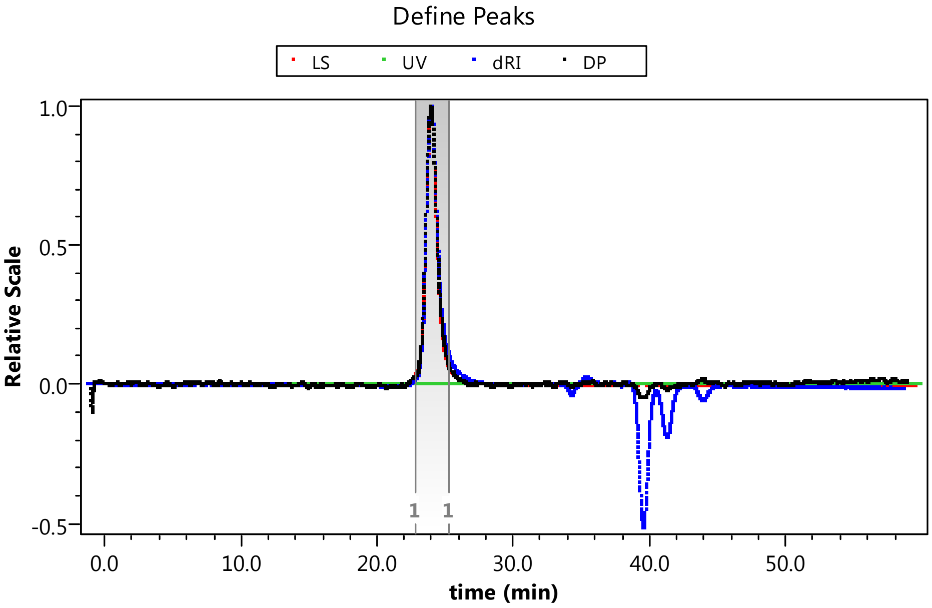


Figure S14. Raw chromatogram of PS.

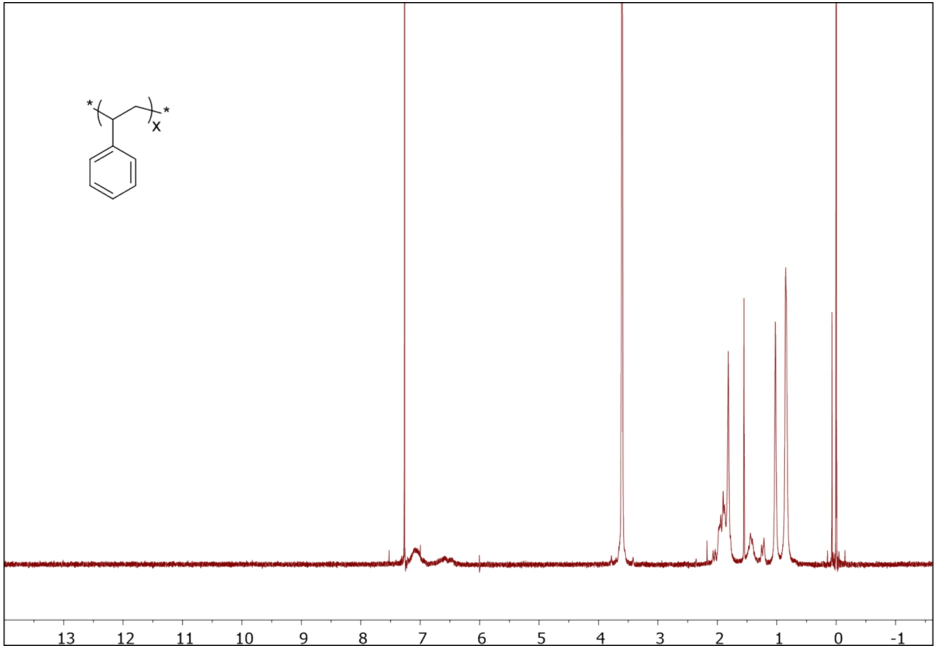


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of PS.

RAFT polymerization of methyl methacrylate (MMA)

A 50-mL Schlenk flask equipped with magnetic stir bar was charged methyl methacrylate (3.95 g, 39.5 mmol), 4-Cyano-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (53.8 mg, 1.33 µmol), azoisobutyronitrile (2.19 mg, 0.133 µmol), and toluene (2.5 mL). The flask was sealed and the solution was degassed by successive (FPT) cycles. The polymerization was performed at 80 °C for twenty hours. PMMA was precipitated in cold hexanes and the yellow beads were collected by filtration. Yield: 2.82 g M_W = 29.0 kDa, dn/dc = 0.082 PDI = 1.05.

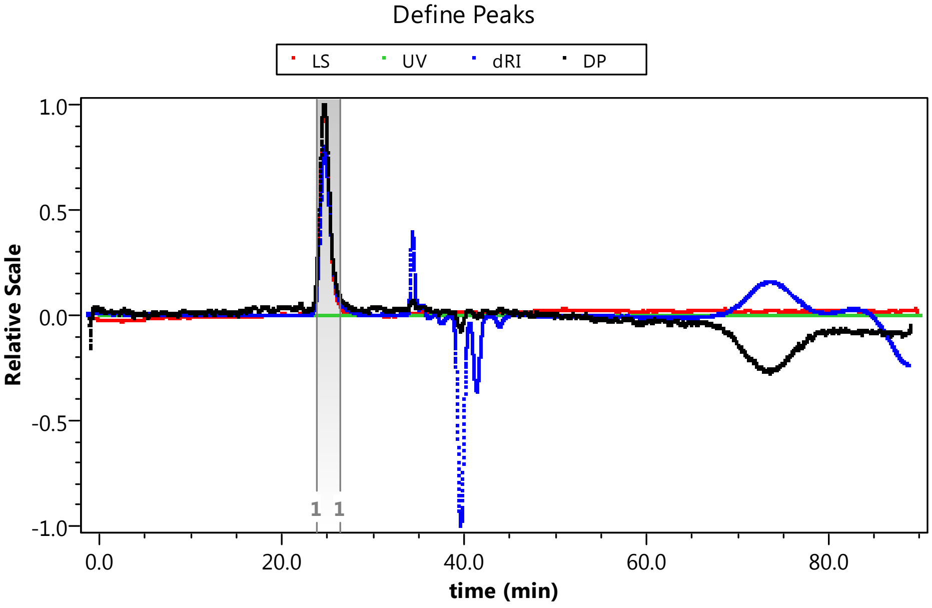


Figure S16. Raw chromatogram of PMMA.

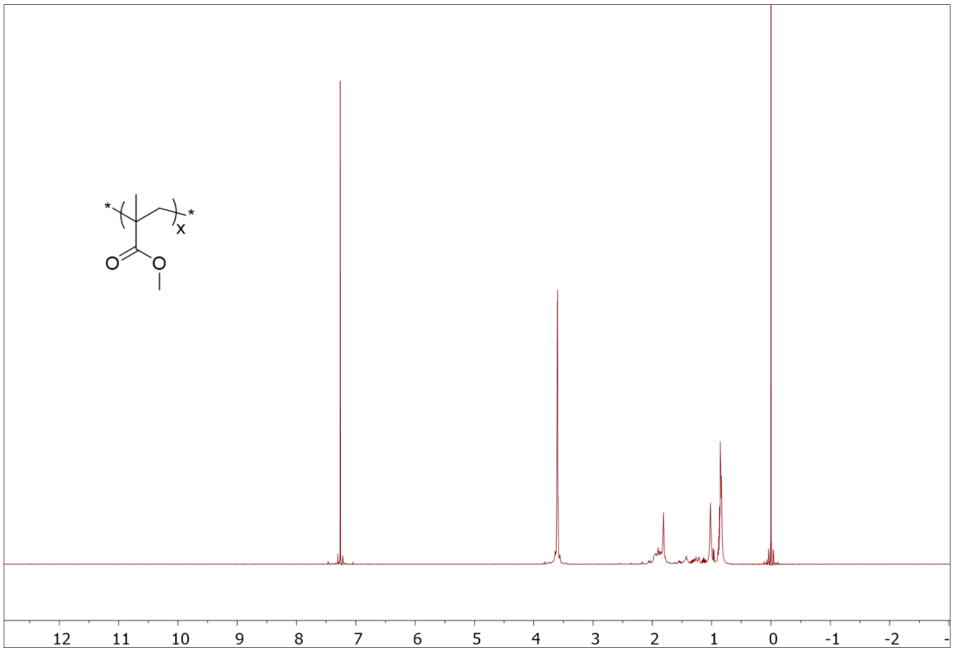


Figure S17. ^{1}H NMR (400 MHz, CDCl$_3$) of PMMA.

RAFT Block Copolymerization of styrene with PMMA

A 50-mL Schlenk flask equipped with a magnetic stir bar was charged with PMMA (0.692 g, 23.9 µmol), and styrene (167 mg, 16.7 mmol). The mixture was dissolved in toluene (1 mL) and the flask was sealed and placed in an ice bath. The solution was degassed by sparging with nitrogen. Polymerization was initiated by heating solution at 80 ^{o}C and stirred for ~20 hours. The polymer was precipitated in cold hexanes and dried in vacuo. Absolute molecular weight distribution: M_W = 30.5 kDa, dn/dc = 0.920 PDI = 1.01.

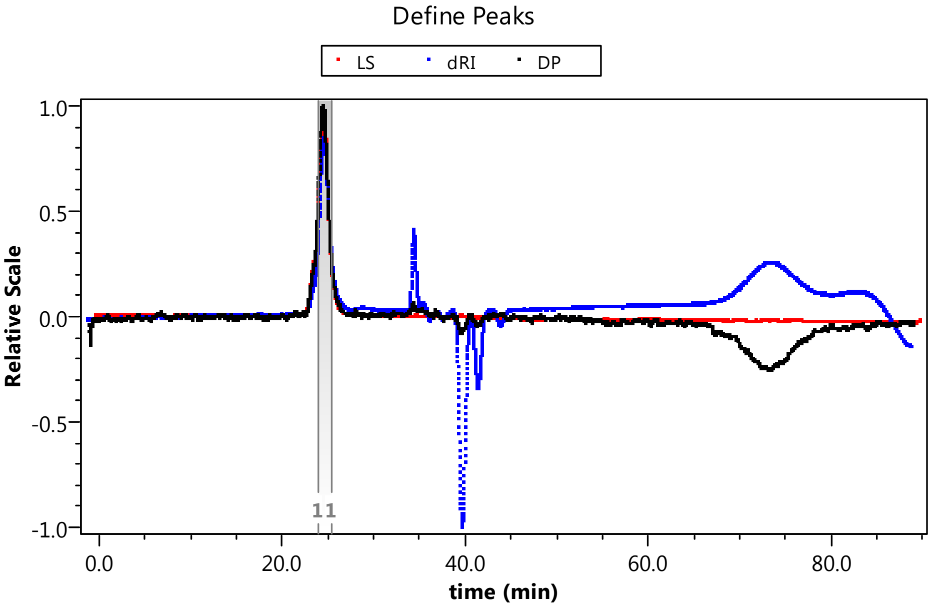


Figure S18. Raw chromatogram of PS-*b*-PMMA.

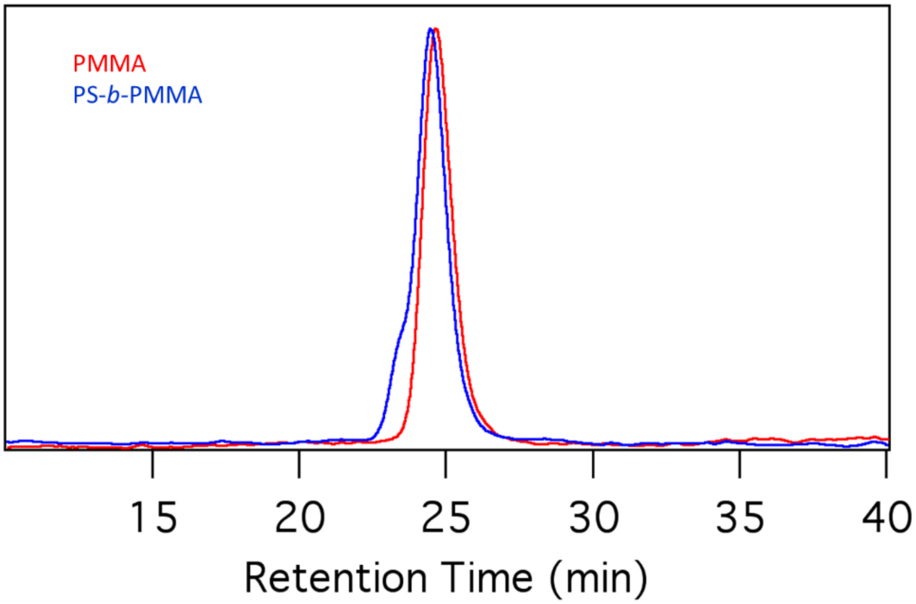


Figure S19. SEC overlay of MALS traces showing addition of styrene units to PMMA.

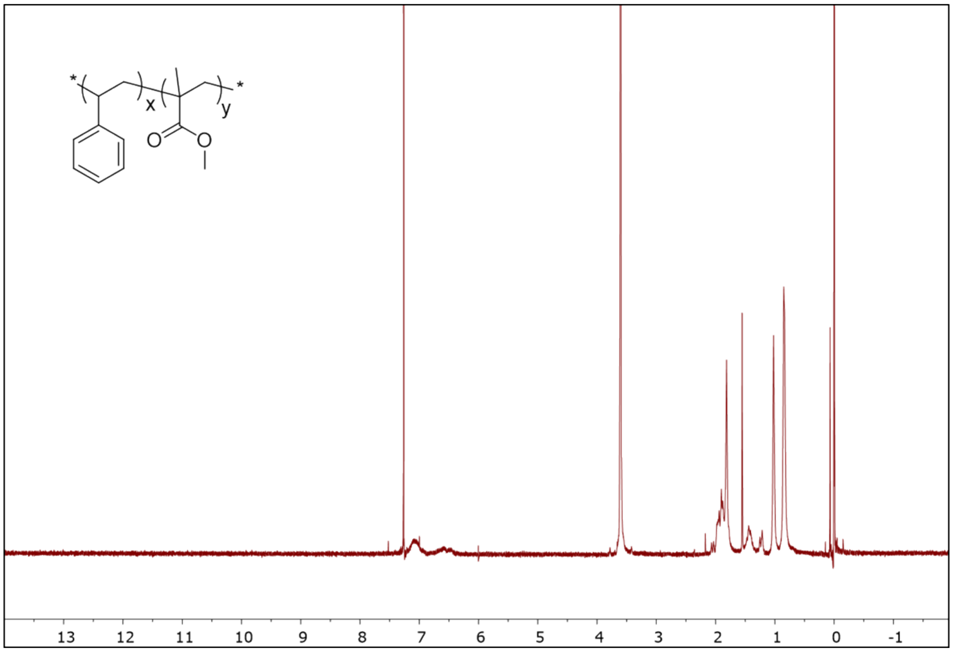


Figure S20. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of PS-*b*-PMMA

RAFT polymerization of N-isopropylacrylamide (NIPAM)

A 50-mL Schlenk flask equipped with a magnetic stir bar was charged with NIPAM (1.00 g, 8.84 mmol), AIBN (0.657 mg, 3.99 µmol), and 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (7.29 mg, 20.0 µmol). The mixture was dissolved in 1.5 mL of dimethylformamide and the flask was sealed. The solution was degassed by successive FPT cycles. Polymerization was initiated by heating the solution at 70 ^{o}C and stirred for 22 hours. PNIPAM was precipitated in cold diethyl ether (ca. 200 mL) and collected onto a filter. Molecular weight information (relative to PMMA standards): Mn = 50.6 kDA, Mw = 59.9 kDa, PDI= 1.18.

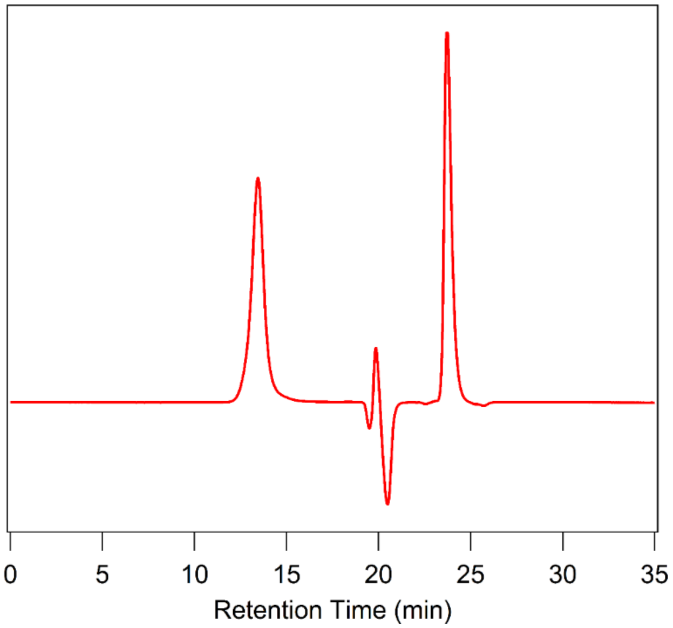


Figure S21. SEC trace of PNIPAM.

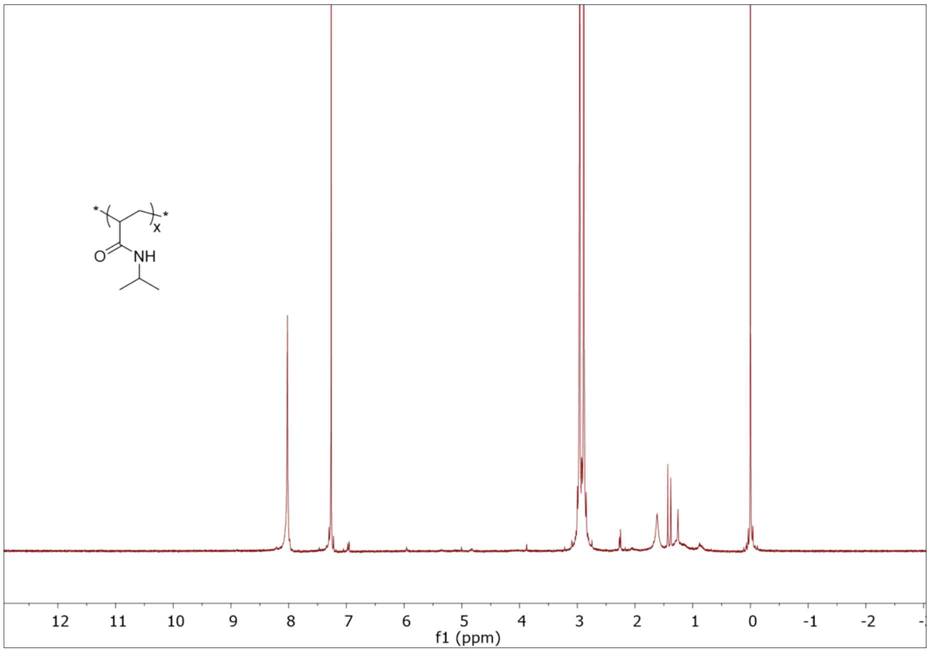


Figure S22. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of PNIPAM.

General aminolysis conditions to cleave end-group from polymers

A 100 mL Schlenk flask equipped with a magnetic stir bar was charged with 100 mg of polymer and purged with N_2(g). The sample was dissolved in an excess of degassed 50% (v/v) cyclohexylamine/THF. The solution was stirred overnight and then concentrated under reduced pressure in a rotary evaporator. The polymer (polymer-SH) was isolated by precipitation in cold methanol.

Preparation of HS-PS-*grad*-(PAMMA-*co*-PMMA) for GPC Analysis

A 100-mL Schlenk flask equipped with a magnetic stir bar was charged with 350 mg of polymer. The flask was purged with N_2(g) before the addition of 6 mL of 50% (v/v) cyclohexylamine/THF. The solution was stirred in the dark for 24 h at ambient temperature. Cyclohexylamine was removed under reduced pressure and the resulting yellow oil was redissolved in 50 mL of degassed THF. An aliquot was transferred to a 100-mL round bottom flask and diluted to 0.5 mg/mL. The flask was sealed and stirred for 24 h. Before GPC analysis, compressed air was gently bubbled into the solution for 2 hours. Additional THF was added to dilute the solution to 0.5 mg/mL. 50 µL of were injected into the GPC instrument.

General "Click" reaction conditions

A 10 mL quartz test tube was charged with 100 mg of polymer-SH, approximately 4 mL of dichloromethane, 2,2'-dimethoxy-2-phenylacetophenone (DMPA), and 100 mg of diiron cluster. The solution was purged with nitrogen and then irradiated in a photoreactor with light centered around 254 nm for 10 minutes. The solution was concentrated under reduced pressure in a rotary evaporated and the polymer-cluster was isolated through precipitation. The polymer-cluster was dissolved and dialyzed (MWCO 6000-8000 Da) in tetrahydrofuran. The solution was concentrated under reduced pressure and the polymer was isolated through precipitation.

Collapse of PS-*grad*-(PAMMA-co-PMMA)

A 0.5 mg/mL polymer stock solution was prepared by dissolving 26.2 mg (8.11 x 10-7 mol) of PS-g-(PAMMA-r-PMMA) in 50 mL of tetrahydrofuran. An aliquot was transferred to a quartz cuvette and a UV-Vis absorbance spectrum was acquired. Photodimerization of the polymer with light entered at 350 nm was monitored by UV-Vis spectroscopy until the absorbance bands between 300-400 nm no longer decreased. The 0.5 mg/mL stock solution was irradiated in a quartz round-bottom flask. Aliquots of the solution were analyzed by SEC with an injection volume of 50 µL.

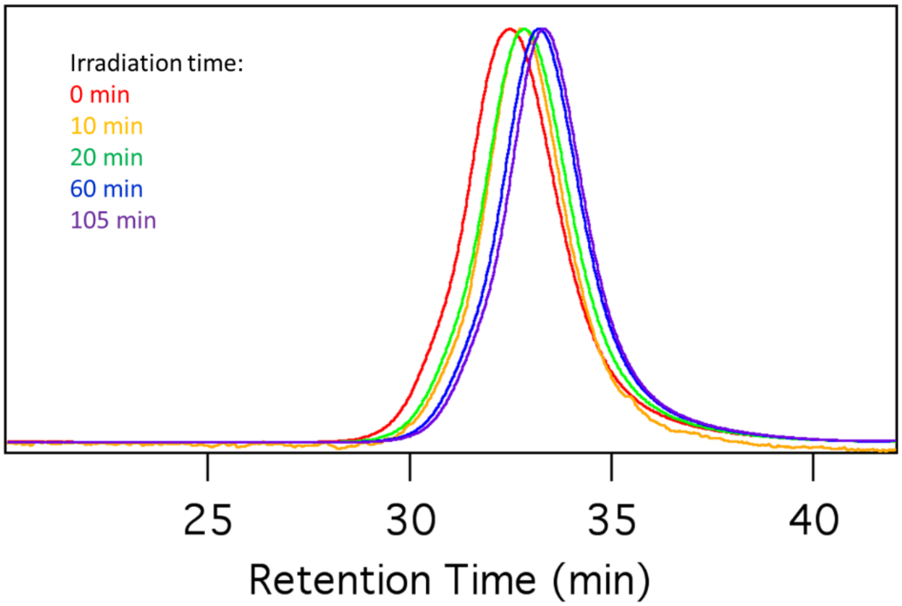


Figure S23. SEC overlay of UV traces showing **SCNP1** formation from **P1**.

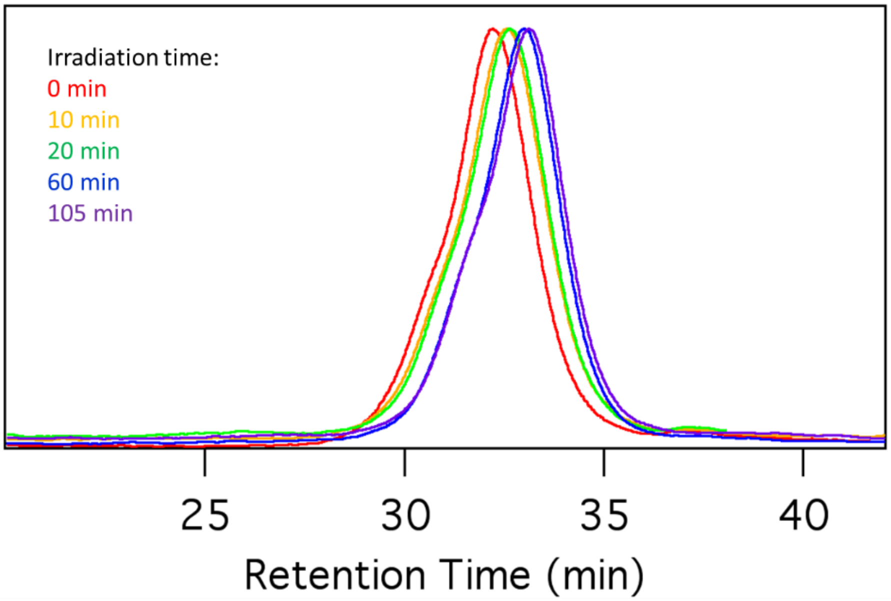


Figure **S24.** SEC overlay of MALS traces showing **SCNP1** formation from **P1**.

V. Statistical Analysis of SCNP2 Formation Chromatograms

Maximum SEC retention times of polymer-bound [(μ-aadt)$Fe_2(CO)_6$], as measured by a UV detector. Three independent samples (0.05 mg/mL) were prepared and the maximum retention time was measured before and after irradiation with λ=350 nm light for 105 min. The mean retention time before irradiation was 32.51 min, with no deviation between samples within the detection limit of the instrument. The mean retention time after radiation was 33.25 min (*SD* = .04 min). The mean retention time after irradiation was about .75 min longer than before irradiation.

UV maximum retention time (min)

Entry	*Before Irradiation*	*After Irradiation*
1	32.51	33.30
2	32.51	33.23
3	32.51	33.23

A paired samples *t* test was performed to assess whether mean retention time differed significantly before and after irradiation. Indeed, the mean retention times differed significantly, *t*(2) = –31.86, *p* = .001.

A similar analysis was performed using SEC data collected on these samples from the MALS detector. As mentioned in the main text, we observe two maxima in the MALS traces. However, we determined that the maximum occurring at lower retention times could be attributed to relatively low-concentration species. Therefore, this analysis was done using the retention times of the maximum at longer retention times.

The mean retention time before irradiation was 32.21 min, with no deviation between samples within the detection limit of the instrument. The mean retention time after radiation was 32.99 min (*SD* = .06 min). The mean retention time after irradiation was about .78 min longer than before irradiation.

Indeed, the mean retention times differed significantly, *t*(2) = –22.51, *p* = .002.

UV maximum retention time (min)

Entry	*Before Irradiation*	*After Irradiation*
1	32.51	33.30
2	32.51	33.23
3	32.51	33.23

VI. Additional Figures

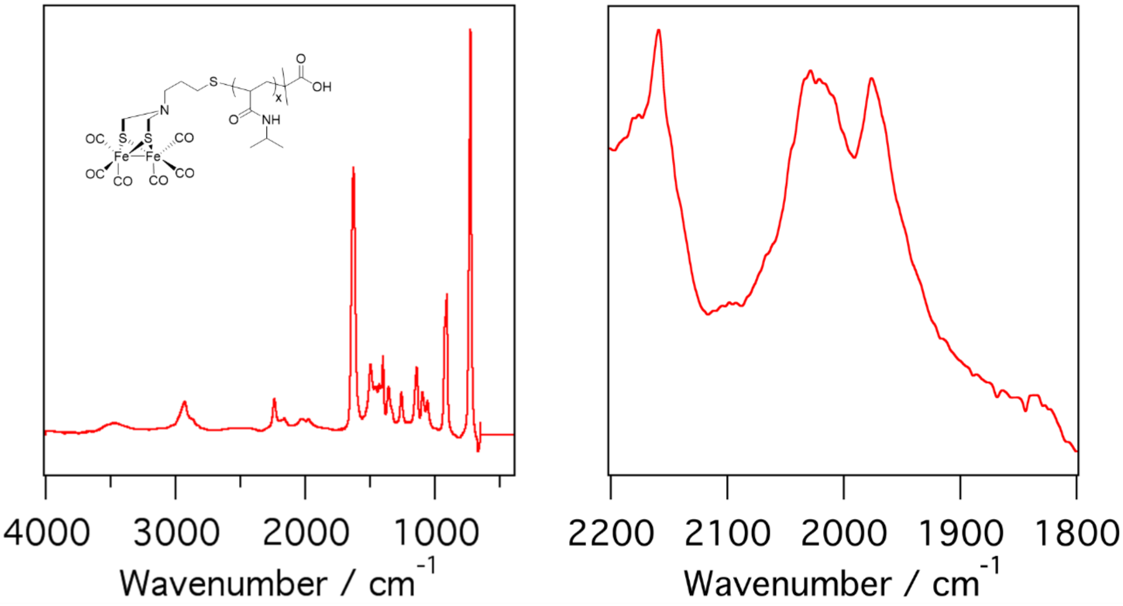


Figure S25. IR spectra of poly(*N*-isopropylacrylamide)-bound aadt$Fe_2(CO)_6$.

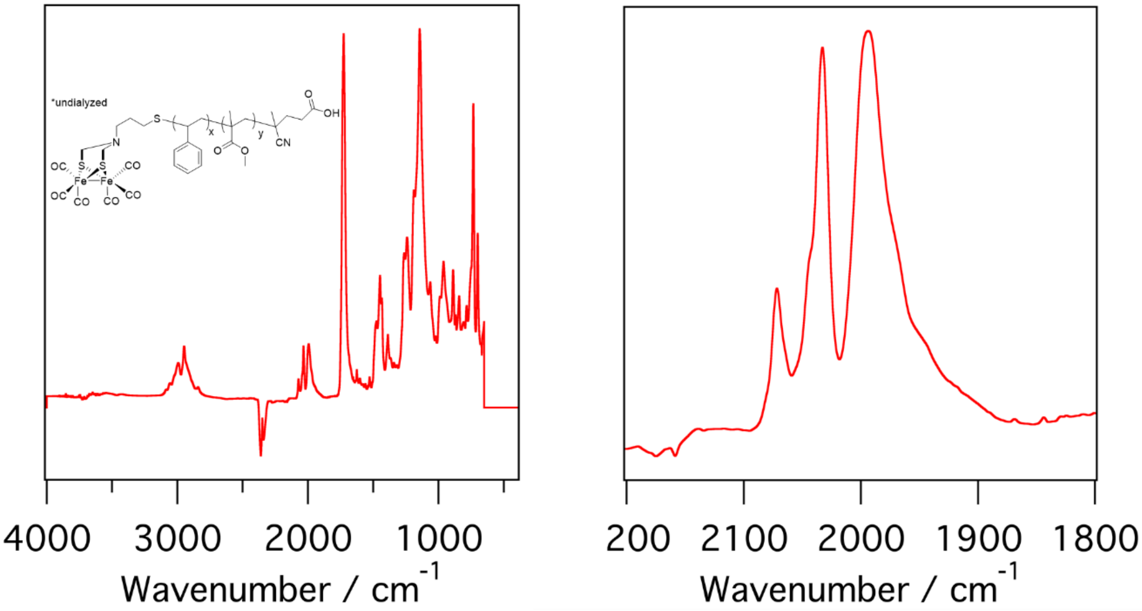


Figure S26. IR spectra of poly(styrene)-*b*-poly(methyl methacrylate)-bound aadt$Fe_2(CO)_6$.

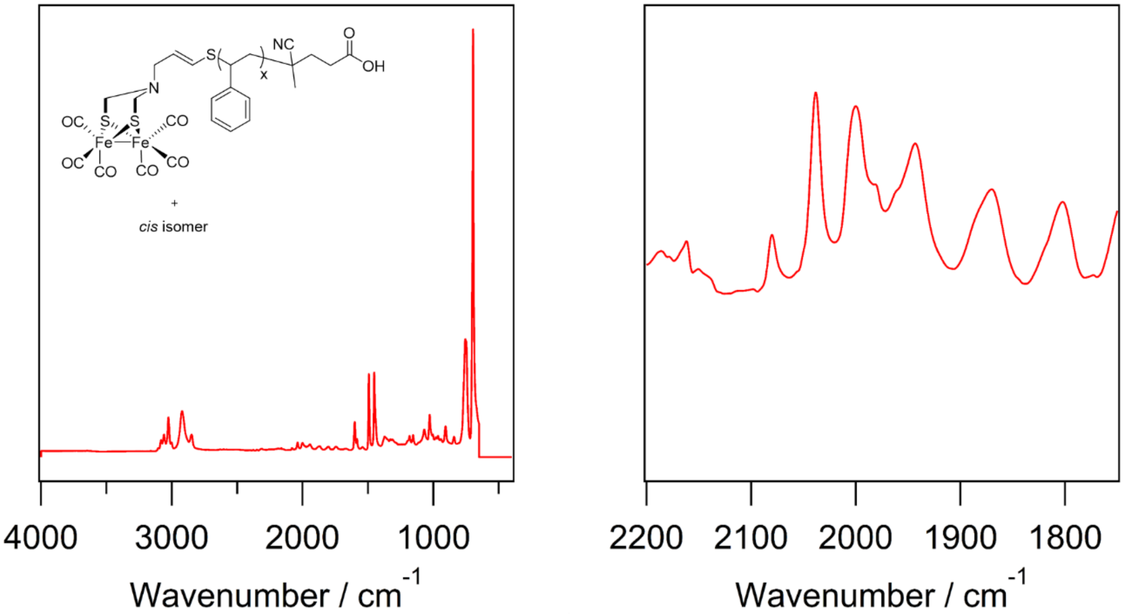


Figure S27. IR spectra of polystyrene-bound complex **2**.

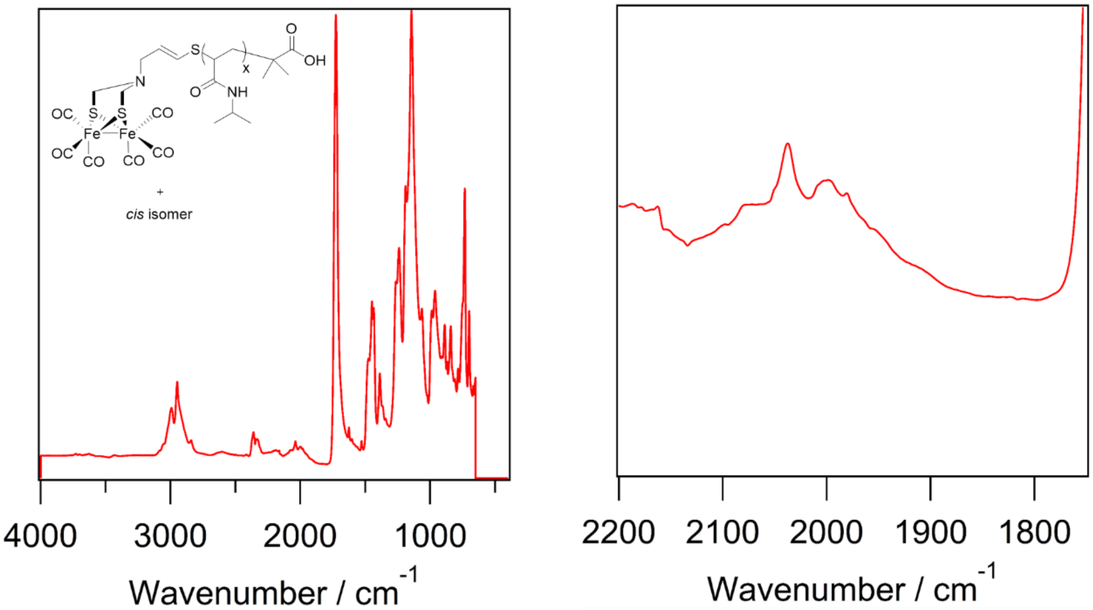


Figure S28. IR spectra of poly(*N*-isopropylacrylamide)-bound complex **2**.

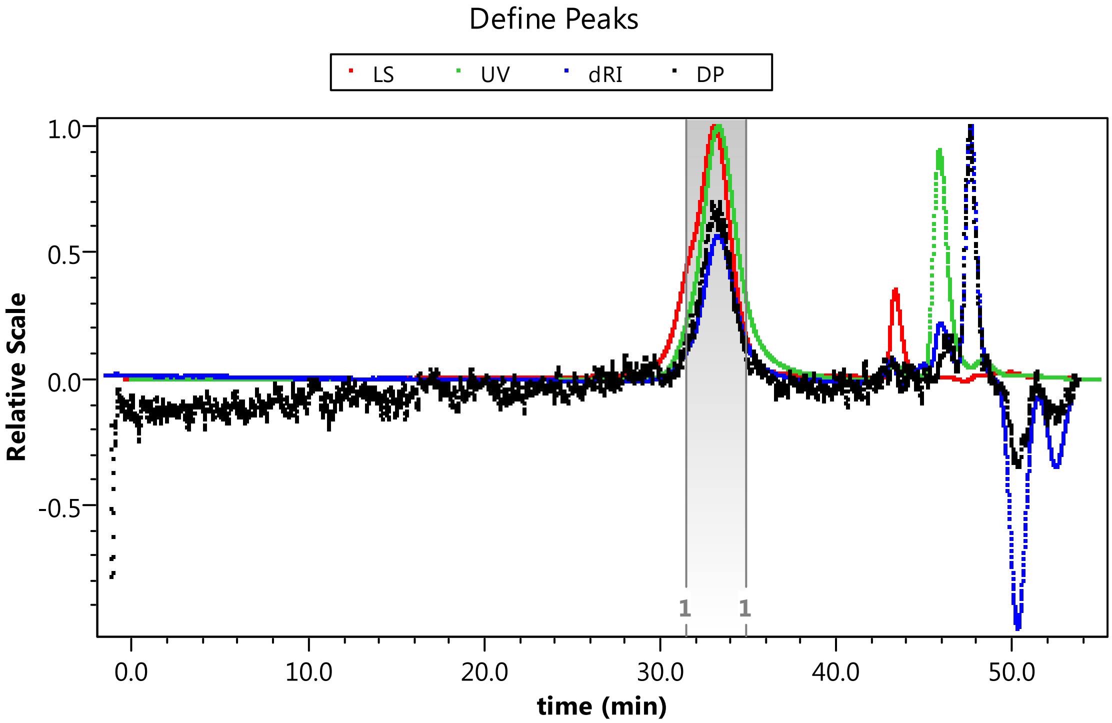


Figure S29. Raw SEC chromatogram of **SCNP1.**

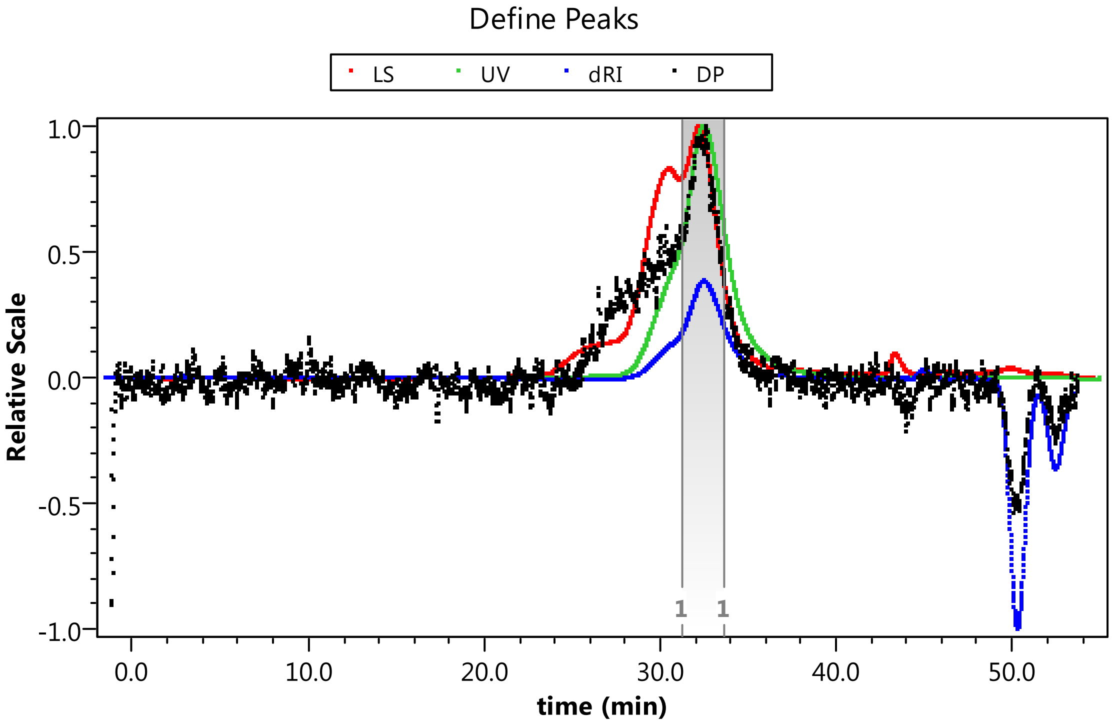


Figure S30. Raw SEC chromatogram of **P2.**

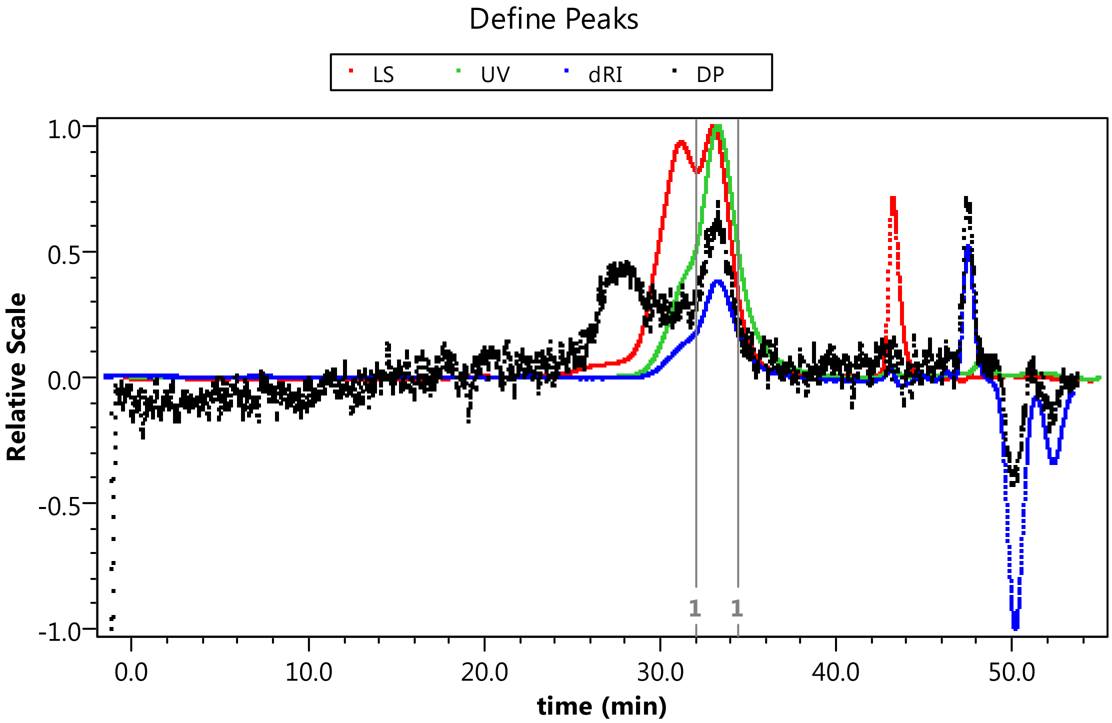


Figure S31. Raw SEC chromatogram of **SCNP2.**

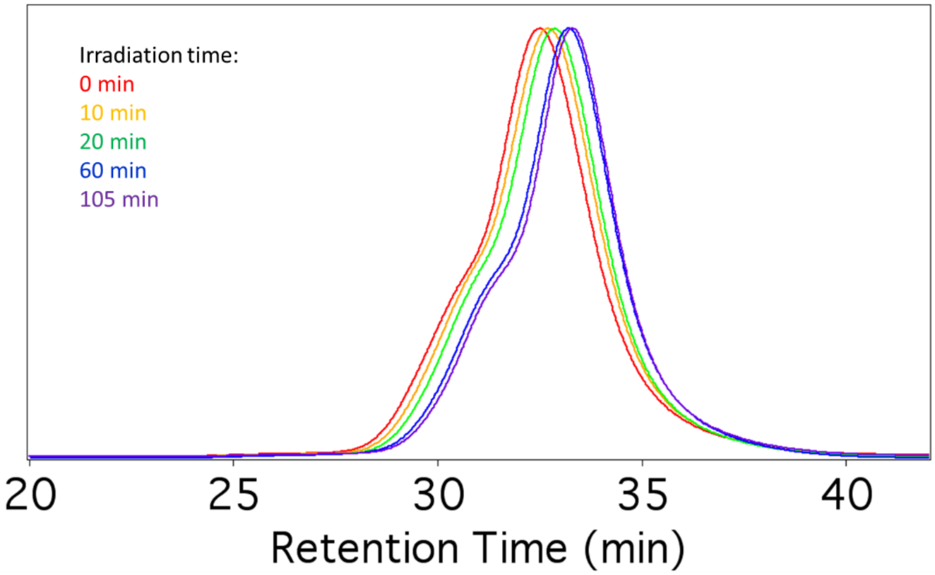


Figure S32. Overlay of UV SEC traces showing **SCNP2** formation from **P2**.

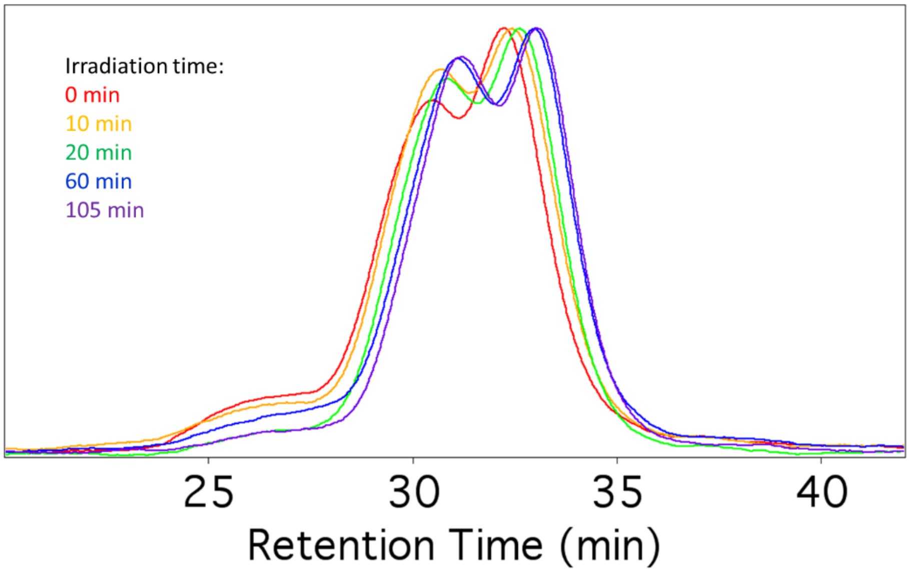


Figure S33. SEC uverlay of MALS traces showing **SCNP2** formation from **P2**.

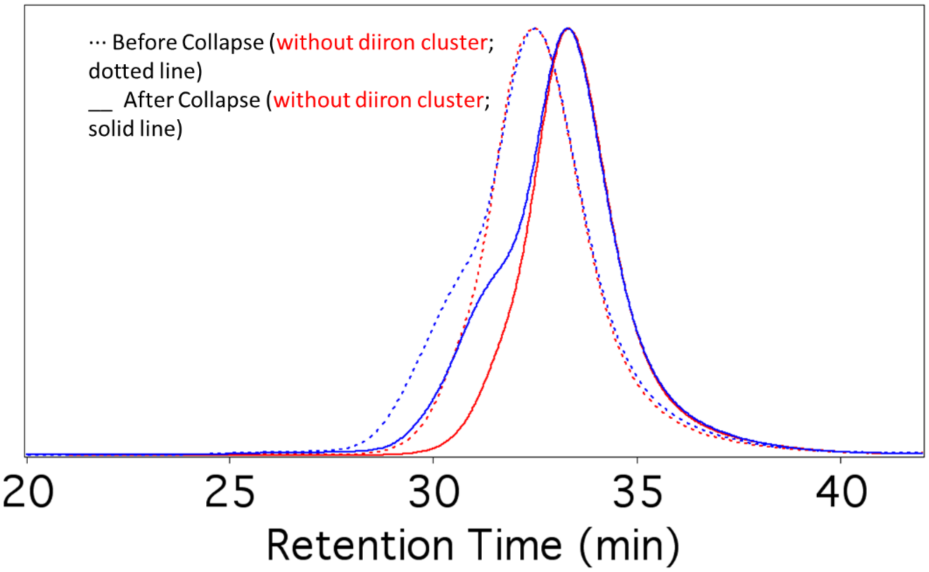


Figure S34. SEC overlay of UV trace showing **SCNP1** and **SCNP2** formation.

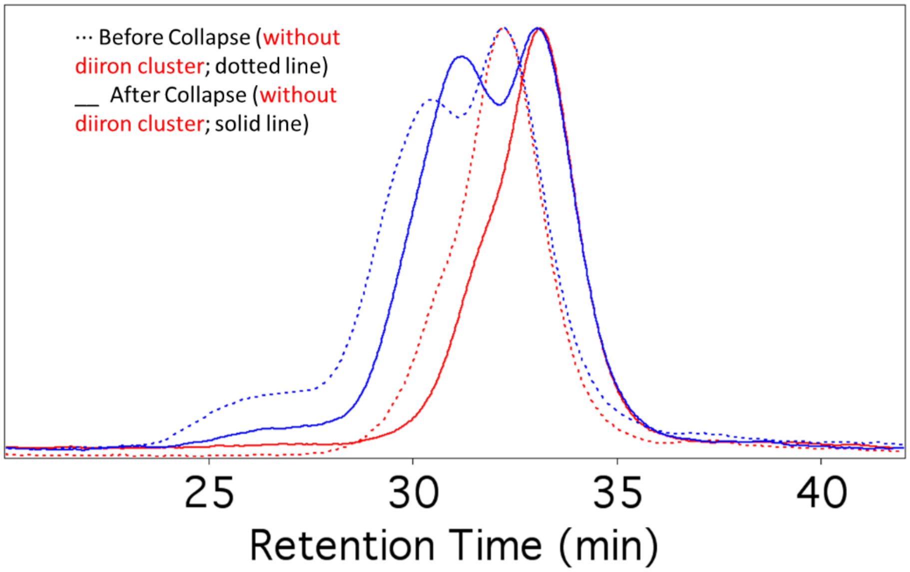


Figure S35. SEC overlay of MALS traces showing **SCNP1** and **SCNP2** formation.

VII. References

1. J. L. Stanley, T. B. Rauchfuss and S. R. Wilson, *Organometallics*, 2007, **26**, 1907-1911.
2. P. G. Frank, B. T. Tuten, A. Prasher, D. Chao and E. B. Berda, *Macromolecular Rapid Communications*, 2014, **35**, 249-253.