

Supporting Information

Star Polymers Composed Entirely of Amino Acid Building Blocks: A Route towards Stereospecific, Biodegradable and Hierarchically Functionalized Stars

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MATERIALS AND METHODS.

Materials. Z-L-Lys(Z)-OH (Bachem), L-cystine (Aldrich), hexamethyldisilazane (HMDS) (99.9 %, Aldrich), benzyl chloroformate (95 %, Aldrich), sodium bicarbonate (NaHCO_3) (99 %, Ajax Fine Chemical), magnesium sulfate (MgSO_4) (> 98 %, Scharlau), phosphorus pentachloride (PCl_5) (> 99 %, Merck), dithiothreitol (DTT) (> 99 %, A.G. Scientific), 3-bromopropanol (97 %, Aldrich), sodium azide (> 99.5 %, BioUltra), tetrabutylammonium hydrogen sulfate (TBAHS) (> 99 %, Aldrich), γ -Oxo-1-pyrenebutyric acid (Aldrich), potassium hydroxide (KOH) (> 85 %, Biolab), N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDCI) (> 98 %, Fluka), 4-(dimethylamino)pyridine (DMAP) (99 %, Aldrich), pirarubicin (> 95 %, Aldrich), propargylamine (98 %, Aldrich), aminomethylpyrene hydrochloride (95 %, Aldrich), propylamine (Merck), copper(I) bromide (CuBr) (98 %, Aldrich), N,N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA) (98 %, Fluka), hydrobromic acid (33 % in acetic acid) (Aldrich), trifluoroacetic acid (TFA) (98 %, Aldrich), hydrochloric acid (37 %, Scharlau), lithium bromide (99 %, Aldrich), tetrahydrofuran (THF) (99.9 %, Scharlau) and N,N-dimethylformamide (DMF) (anhyd., Aldrich) were used as received. n-Hexane, ethyl acetate, dimethylsulfoxide (DMSO), chloroform and methanol were purchased from Chem-Supply and used as received. 1,4-Dioxane (Fluka) and diethyl ether (Chem-Supply) were used to make binary solvent (2:3 v/v) and dried for 48 hours prior to use over 3 Å molecular sieves. Acetonitrile (HPLC grade, B&J) was stored over 3 Å molecular sieves. Dichloromethane (Chem-Supply, 99.5 %) was distilled from CaH_2 . Milli-Q water (18.2 M Ω .cm) was obtained from a Millipore Synergy Water System. Acetone- d_6 (99.9 %), DMSO- d_6 (99.9 %), and DMF- d_7 (99.5 %), D_2O (99.9 %) were purchased from Cambridge Isotope and used as received.

Instrumentation. GPC analysis was performed on a Shimadzu liquid chromatography system fitted with a Wyatt DAWN Treos LS detector ($\lambda = 658 \text{ nm}$), a Shimadzu RID-10 refractometer ($\lambda = 633 \text{ nm}$), and a Shimadzu SPD-20A UV-Vis detector, using three identical PLgel columns (5 μm , MIXED-C) in series and HPLC grade DMF with 0.05 M LiBr (70 °C, 1 mL/min) as the mobile. Astra software (Wyatt Technology Corp.) was used to determine the molecular weight characteristics using known dn/dc values for PZLL in DMF ($dn/dc_{\text{PZLL}} = 0.101 \text{ mL/g}$ (25 °C)). The dn/dc values of densely branched CCS polymers and linear polymers of the same

monomeric constitution have been reported to be comparable;¹ thus, the dn/dc of linear PZLL was used to determine the molecular weights of the CCS polymers. ¹H NMR spectroscopy was performed using Varian Unity400 (400 MHz) spectrometer using the deuterated solvent as reference and a sample concentration of around 20 mg/ml. DLS measurements were performed on a Malvern high performance particle sizer (HPPS) with a He-Ne laser (633 nm) at an angle of 173° and a temperature of 25 ± 0.1 °C, initial sample concentrations of 10 mg/ml in DMF were used then serial dilutions were performed until stable spectra were obtained. All sample solutions were filtered using 0.45 µm filters. UV-Vis spectrophotometry was performed on a Shimadzu UV-2101PC spectrometer using quartz cuvettes with a 1 cm path length. TEM was conducted using carbon-coated grids stained with uranyl acetate (5.0 wt% in DMF or DMSO). Optical rotation measurements were conducted on JASCO DIP-1000 digital polarimeter using a 10 cm microcell and samples dissolved in DMF (10 mg/mL). Fluorescence spectrophotometry was performed on FluoroLog Jobin Yvon using quartz cuvettes with a 1 cm path length.

Synthesis of Z-L-Lysine-NCA (lysine NCA).² Z-L-Lys(Z)-OH (20.0 g, 48.2 mmol) was added to 1,4-dioxane:diethyl ether mixture (2:3 v/v, 80 mL) and cooled to 0 °C in a sealed flask. PCl₅ (15.1 g, 32.1 mmol) was added and the mixture was stirred for 30 min. After removal of the solvent *in vacuo* the resulting residue was azeotroped with acetonitrile (3 × 20 mL) to afford a waxy solid that was recrystallized from ethyl acetate:*n*-hexane (1:1 v/v, 3 × 50 mL). Isolation via filtration and drying *in vacuo* (0.1 mbar) yielded the lysine NCA derivative as a white solid, 10.0 g (67 %); ¹H NMR (400 MHz, *d*₆-DMSO) δ_H 1.22-1.45 (*m*, 4H, 2 CH₂), 1.60-1.77 (*m*, 4H, 2 CH₂), 2.98 (*q*, 2H, *J* = 6.0 Hz, CH₂N), 4.42 (*t*, 1H, *J* = 6.0 Hz, CHN), 5.00 (*s*, 2H, CH₂O), 7.25-7.38 (*m*, 5H, 5 ArH), 9.10 (*br s*, 2H, 2 NH) ppm; ¹³C NMR (100 MHz, *d*₆-DMSO) δ_C 21.5 (CH₂), 28.7 (CH₂), 30.6 (CH₂), 56.9 (CHN), 65.0 (CH₂N), 127.6 (3 ArCH), 128.2 (2 ArCH), 137.1 (ArCC), 151.8 (NHCO₂), 156.0 (NHCO₂), 171.5 (CHCO₂) ppm.

Synthesis of di-Z-L-Cystine ((Z-Cys-OH)₂).³ L-Cystine (4.0 g, 16.6 mmol), sodium bicarbonate (15.0 g, 17.9 mmol) and benzyl chloroformate (4.23 g, 24.9 mmol) were added to

(1) H. Gao, N. V. Tsarevsky, K. Matyjaszewski, *Macromolecules* **2005**, 38, 9018 – 9027

(2) Yuki, H. *Nippon Kagaku Zasshi* **1956**, 77, 44 – 51.

(3) C. Gravel, D. Lapierre, J. Lavelle, J. W. Keillor. *Can. J. Chem.* **2007**, 85, 164–174.

MilliQ water (525 mL). The mixture was stirred rapidly at 0 °C for 2 h and then at 25 °C for 16 h. The mixture was extracted with ethyl acetate (3 × 150 mL) and the combined organic extracts were dried (MgSO₄), filtered and concentrated *in vacuo* to yield an oily yellow residue. Hot chloroform (60 °C) was added to afford a homogenous solution, which upon cooling yielded a precipitate. Filtration and drying (0.1 mbar) afforded (Z-Cys-OH)₂ as a white solid, 5.8 g (72.5 %); ¹H NMR (400 MHz, d₆-Acetone) δ_H 3.09 (*dd*, 4H, *J* = 9.2 Hz, 4.1 Hz, 2 SCH₂), 4.57 (*m*, 2H, 2 CHN), 5.10 (*s*, 4H, 2 CH₂O), 6.78 (*s*, 2H, 2 NHC), 7.27-7.36 (*m*, 10H, 10 ArH) ppm; ¹³C NMR (100 MHz, d₆-Acetone) δ_C 42.0 (2 SCH₂), 55.2 (2 CHN), 67.9 (2 CH₂O), 129.6 (6 ArCH), 130.14 (4 ArCH), 138.9 (2 ArCC), 157.9 (2 NHCO₂), 173.1 (2 CO₂H) ppm.

Synthesis of L-Cystine NCA (cystine NCA). (Z-Cys-OH)₂ (2.0 g, 3.9 mmol) was dissolved in 1,4-dioxane:diethyl ether mixture (2:3 v/v, 20 mL). PCl₅ (15.1 g, 32.1 mmol) was added and the mixture was stirred for 30 min at 25 °C. After removal of the solvent *in vacuo* the resulting residue was azeotroped with acetonitrile (3 × 10 mL) and then precipitated into anhydrous dichloromethane (50 mL) under argon. After stirring at 25 °C for 16 h to remove excess PCl₅, the precipitate was isolated via filtration and dried *in vacuo* (0.1 mbar) to afford the cystine NCA as an off white solid, 0.80 g (70 %); ¹H NMR (400 MHz, d₆-Acetone) δ_H 3.09 (*dd*, 4H, *J* = 9.2 Hz, 4.1 Hz, 2 SCH₂), 4.57 (*m*, 2H, 2 CHN), 8.17 (*s*, 2H, 2 NHC) ppm; ¹³C NMR (100 MHz, d₆-Acetone) δ_C 41.4 (2 SCH₂), 58.9 (2 CHN), 67.9 (2 CH₂O), 153.4 (2 NHCO₂), 171.4 (2 CHCO₂) ppm.

General Procedure for Synthesis of PZLL_{arm}PLC_{core} CCS Polymers 1. Lysine NCA was dissolved in anhydrous DMF (100 mg/mL) in a flame-dried, argon purged two-necked flask. HMDS (M/I ratio varied depending on desired MW) was added and the mixture was stirred at room temperature until the NCA conversion reached *ca.* 80 %, as determined by ¹H NMR. To this PZLL solution was added cystine NCA, and the mixture was stirred for a further 6 hours. The resulting CCS polymer could either be isolated via precipitation into water:methanol (1:1 v/v, 10 times the volume of DMF) or core-functionalised via the addition of primary amines. Different MW star polymers were prepared by variation of the MI MW and cross-linker to MI ratio.

Synthesis of CCS 1a. Starting from lysine NCA (200 mg, 0.654 mmol) and HMDS (M/I = 40, 3.41 μ L, 16.4 μ mol), PZLL (M_w = 15.0 kDa, PDI = 1.09, d_h = 10.8 nm) was obtained after 7 h. Addition of cystine NCA (Cross-linker/MI = 35, 170 mg, 0.582 mmol) afforded after 6 h PZLL_{arm}PLC_{core} CCS polymer **1a** (M_w = 523 kDa, PDI = 1.63, $f \approx 21$, d_h = 74 nm). Precipitation of the polymer solution into water:methanol (1:1, 20 mL) followed by isolation via centrifugation and drying (0.1 mbar) afford **1a** (M_w = 1440 kDa, PDI = 1.33, $f \approx 66$, d_h = 180 nm) as a pale yellow solid, 0.257 g (89 %).

Preparation of Organogels via Degradation of PZLL_{arm}PLC_{core} CCS Polymer 1a. CCS polymer **1a** (M_w = 1140 kDa, 100 mg, 87.7 μ mol) was dissolved in degassed DMF (1.0 mL) and a 10 times excess of DTT (135 mg, 877 μ mol) with respect to the disulfide cross-links was added. After stirring for 2 hours under argon the resulting P(ZZL-*b*-LC) copolymer (M_w = 34.4 kDa, PDI = 1.69, d_h = 10.4 nm) was either exposed to the atmosphere and allowed to stand or sonicated. In both cases gelation occurred rapidly within minutes.

Synthesis of Aminomethylpyrene (AMP). Aminomethylpyrene hydrochloride (0.400 g, 1.49 mmol) was dissolved in DMSO (10 mL) and KOH pellets (25 equiv., 2.09 g, 37.3 mmol) were added. The mixture was stirred in a sealed flask for 16 h at room temperature and then filtered. The filtrate was added under rapid stirring to 0.05 M NaHCO₃ (120 mL). The resulting precipitate was collected by filtration, washed with 0.05 M NaHCO₃ (10 mL) and MilliQ water (2 $\times$ 20 mL), and dried *in vacuo* (0.1 mbar) to afford the neutralized AMP as a pale yellow solid, 0.312 g (91 %); ¹H NMR (400 MHz, *d*₆-DMSO) δ_H 4.43 (*br s*, 2H, NH₂), 4.85 (*s*, 2H, CH₂), 8.00-8.39 (*s*, 9H, 9ArH) ppm. ¹³C NMR (100 MHz, *d*₆-DMSO) δ_C 43.4 (CH₂N), 123.6 (ArCH), 124.4 (ArCH), 125.1 (ArCC), 125.3 (2ArCH), 125.4 (ArCC), 126.3 (ArCH), 126.6 (ArCH), 127.1 (ArCH), 127.7 (ArCH), 127.9 (ArCH), 128.1 (ArCC), 130.0 (ArCC), 130.7 (ArCC), 131.2 (ArCC), 137.7 (ArCC) ppm. UV-vis (DMF): ϵ (λ = 344 nm) = 39881 M⁻¹ cm⁻¹.

Synthesis of 3-azidopropanol.⁴ NaN₃ (2.81 g, 43.2 mmol) and TBAHS (85.0 mg, 0.250 mmol) were dissolved in MilliQ water (40 mL). 3-Bromopropanol (1.95 mL, 21.6 mmol) was then added and the mixture was stirred at 80 °C for 24 hours, followed by a further 12 hours at

(4) B. G. De Geest, W. Van Camp, F. E. Du Prez, S. C. De Smedt, J. Demeester, W. E. Hennink, *Chem. Commun.* **2008**, 190-192.

25 °C. The mixture was extracted with diethyl ether (3 × 75 mL) and the organic extracts were combined, dried (MgSO₄), filtered and concentrated *in vacuo* (0.1 mbar) to yield a transparent oil, 1.78 g (82 %). ¹H NMR (400 MHz, CDCl₃) δ_H 1.82 (*quin*, 2H, *J* = 6.6 Hz, CH₂), 1.91 (*br s*, 1H, OH), 3.44 (*t*, 2H, *J* = 6.6 Hz, CH₂N), 3.74 (*t*, 2H, *J* = 6.6 Hz, CH₂O) ppm.

Synthesis of 3-azidopropyl 4-oxo-4-(pyren-4-yl) butanoate. γ-Oxo-1-pyrenebutyric acid (1.20 g, 3.97 mmol), EDCI (0.837 g, 4.37 mmol), DMAP (97.0 mg, 794 μmol) and anhydrous dichloromethane (24 mL) were added into a round bottom flask under argon. After the reagents had completely dissolved, 3-azidopropanol (0.385 mL, 3.97 mmol) was added and the mixture was stirred at 30 °C for 40 hours. The reaction mixture was then washed with 0.05 M HCl (3 × 100 mL), dried (MgSO₄), filtered and the filtrate concentrated *in vacuo* (0.1 mbar) to yield a dark brown solid. The compound was purified via column chromatography (20:80 hexane:DCM). The desired compound (*R_f* = 0.06) was dissolved in dichloromethane (30 mL), dried (MgSO₄), filtered and concentrated *in vacuo* (0.1 mbar, 50 °C) to yield a dark brown solid, 0.90 g (56 %); ¹H NMR (400 MHz, CDCl₃, TMS) δ_H 1.92 (*quin*, 2H, *J* = 6.4 Hz, CH₂), 2.90 (*t*, 2H, *J* = 6.4 Hz, CH₂CO₂), 3.39 (*t*, 2H, *J* = 6.4 Hz, CH₂N), 3.53 (*t*, 2H, *J* = 6.4 Hz, CH₂CO), 4.23 (*t*, 2H, *J* = 6.4 Hz, CH₂O), 8.00–8.05 (*m*, 2H, 2ArH), 8.13–8.23 (*m*, 5H, 5 ArH), 8.38 (*d*, 1H, *J* = 8.0 Hz, ArH), 8.91 (*d*, 1H, *J* = 9.6 Hz, ArH) ppm; UV-vis (DMF): ε (λ = 353 nm) = 26878 M⁻¹ cm⁻¹.

General Procedure for Core-functionalisation of PZLL_{arm}PLC_{core} CCS Polymers. The CCS polymers **1** were directly core-functionalised prior to isolation from their reaction solutions. Thus, primary amine (PA, PGA or AMP) dissolved in anhydrous DMF (15 mL) was added directly to the CCS polymer solution to give a final star concentration of *ca.* 0.01-0.02 mg/mL. After a period of time stirring under argon the reaction solution was concentrated *in vacuo* to *ca.* 1.0 mL and precipitated into diethyl ether (30 mL). The residue was isolated via centrifugation, redissolved in DMF (2 mL) and precipitated into ethyl acetate (30 mL); this step was repeated 3 times and the residue dried *in vacuo* (0.1 mbar) to afford the core-functionalised CCS polymers **2** as pale brown solids.

Core-functionalisation with PA. PA (0.217 mL, 2.66 mmol) in DMF was added to a solution of CCS polymer **1b** ($M_w = 596$ kDa, PDI = 1.65, 0.155 mg/mL, 1 mL) and stirred for 10 min to afford, after isolation, CCS polymer **2_{PA}** ($M_w = 494$ kDa, PDI = 1.73).

Core-functionalisation with PGA. PGA (0.565 mL, 5.31 mmol) in DMF was added to a solution of CCS polymer **1b** ($M_w = 596$ kDa, PDI = 1.65, 0.155 mg/mL, 2 mL) and stirred for 3 h to afford, after isolation, CCS polymer **2_{PGA}** ($M_w = 704$ kDa, PDI = 1.69).

Core-functionalisation with AMP. AMP (1.42 g, 6.15 mmol) in DMF was added to a solution of CCS polymer **1c** ($M_w = 832$ kDa, PDI = 1.98, 0.155 mg/mL, 2 mL) and stirred for 3 h to afford, after isolation, CCS polymer **2_{AMP}** ($M_w = 1028$ kDa, PDI = 2.25).

Click Functionalisation of CCS Polymer 2_{PGA} with Azidopyrene. CCS polymer **2_{PGA}** ($M_w = 704.3$ kDa, 74.6 mg, 0.124 μ mol), PMDETA (6.08 μ L, 29.1 μ mol) and 3-azidopropyl 4-oxo-4-(pyren-4-yl) butanoate (67.3 mg, 0.175 mmol) were dissolved in anhydrous DMF (4 mL) under argon. Argon was bubbled through the solution for 30 min and then CuBr (4.18 mg, 29.1 μ mol) was added and the reaction stirred at room temperature for 72 h. The reaction solution was passed through a column of basic alumina, concentrated *in vacuo* to ca. 2 mL and precipitated into ethyl acetate (30 mL). The residue was isolated via centrifugation, redissolved in DMF (2 mL) and precipitated into ethyl acetate (30 mL); this step was repeated 3 times and the residue dried *in vacuo* (0.1 mbar) to afford the pyrene core-functionalised star polymer as a black solid ($M_w = 1190$ kDa, PDI = 2.03). UV-vis analysis provided a pyrene loading of 117 mol/mol star.

General Procedure for Synthesis of PLL_{arm}PLC_{core} CCS Polymers 3. PZLL_{arm}PLC_{core} CCS polymers **2** were dissolved in TFA (200 mg/mL) and 33 % HBr in acetic acid was then added (20 mL/g of star). After stirring for 30 min at room temperature the mixture was precipitated into diethyl ether (10 times the reaction volume). The residue was isolated via centrifugation, redissolved in water (2 mL) and precipitated into tetrahydrofuran (30 mL); this step was repeated 3 times and the residue dried *in vacuo* (0.1 mbar) to afford PLL_{arm}PLC_{core} CCS polymers **3** as off-white solids. ¹H NMR spectroscopic analysis confirmed that the Cbz protecting groups had been almost completely removed. Regardless of the core-functionality of

the CCS polymers **3** all of the ^1H NMR spectra were similar, showing only resonances corresponding to the PLL arms; as anticipated, the reduced segmental mobility of the cross-linked core leads to the broadening and complete disappearance of the core resonances.⁵

Encapsulation Studies. Pirarubicin was encapsulated by the CCS polymer **3**_{AMP} via a biphasic extraction method. 300 μL of pirarubicin in dichloromethane (1 mg/mL) and 300 μL star **3**_{AMP} in MilliQ water (0.1 mg/mL) were placed in a vial to afford a biphasic mixture. After stirring at 1200 rpm for 24 h the mixture was allowed to phase separate and the concentration of pirarubicin in the organic phase was measured via the UV-Vis spectroscopy. This allowed for the amount of encapsulated pirarubicin to be calculated (pirarubicin UV-vis (dichloromethane): $\epsilon(\lambda = 482 \text{ nm}) = 13600 \text{ M}^{-1} \text{ cm}^{-1}$). Control experiments performed under identical conditions but using core unfunctionalised star **3** revealed no transfer of the pirarubicin into the aqueous phase.

(5) a) M. Sawamoto, K. Y. Baek, M. Kamigaito, *Macromolecules* **2001**, 34, 215 – 221; b) J. T. Wiltshire, G. G. Qiao, *Macromolecules* **2006**, 39, 4828 – 4285.

SUPPORTING FIGURES

Table S1. Characterization of CCS Polymers

Polymer	M_w MI ^a (kDa)	PDI MI ^a	[CL]/[MI]	Rxn Time (h)	M_w Star ^a (kDa)	PDI ^a Star	X_{CL} ^b (%)	f ^c
1a	15.0	1.09	35	6	523*	1.69	100	21
1b	13.8	1.10	35	6	596*	1.65	100	26
1c	12.4	1.06	35	16	832*	1.98	100	40

^a Determined via GPC; $dn/dc_{PZLL} = 0.101$ mL/g (70 °C).

^b Determined via ¹H NMR spectroscopy.

^c Estimation based upon % core of star MW = 40 %, as deduced by the following calculations;

Sample calculation:

The calculation of f for **1a** is outlined below and based upon the following assumptions: (i) lysine NCA conversion prior to addition of cross-linker = 83 % (as determined by ¹H NMR spectroscopy analysis); (ii) Since no lysine NCA was detected via ¹H NMR spectroscopy after star formation (6 h) it is presumed that the remaining 17 % is incorporated into the core; (iii) Similarly, no cystine NCA could be detected indicating its complete inclusion into the star core.

- PZLL $MW_{(GPC)} = 15.0$ kDa (*ca.* 83 % lysine NCA conversion); therefore, at 100 % lysine NCA conversion, $MW_{(theor.)} = 18.1$ kDa.
- Thus, mass of lysine that contributes towards the core per MI = 3.1 kDa (i.e. 18.1 kDa – 15.0 kDa).
- $[CL]/[MI] = 35$, therefore, mass of cystine (based upon repeat unit) per MI = 7.1 kDa.
- For every MI (i.e. arm) mass contribution towards core = 10.2 kDa = 3.1 kDa + 7.1 kDa.
- Thus, % core = $(10.2 \text{ kDa} / (15.0 \text{ kDa} + 10.2 \text{ kDa})) \times 100 \% = 40 \%$.

Therefore, number of arm, $f = (523 \text{ kDa} \times 0.6_{(arm \text{ fraction})}) / 15.0 \text{ kDa} \approx 21$.

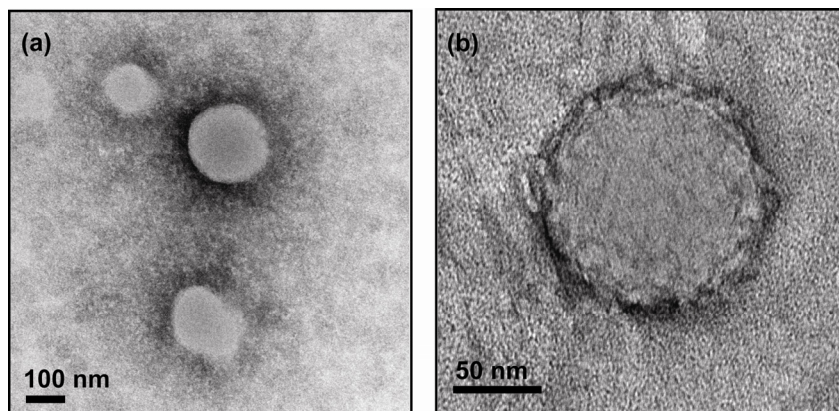


Figure S1. TEM images of (a) star **1a** cast from DMF and (b) star **2_{AMP}** cast from DMSO.

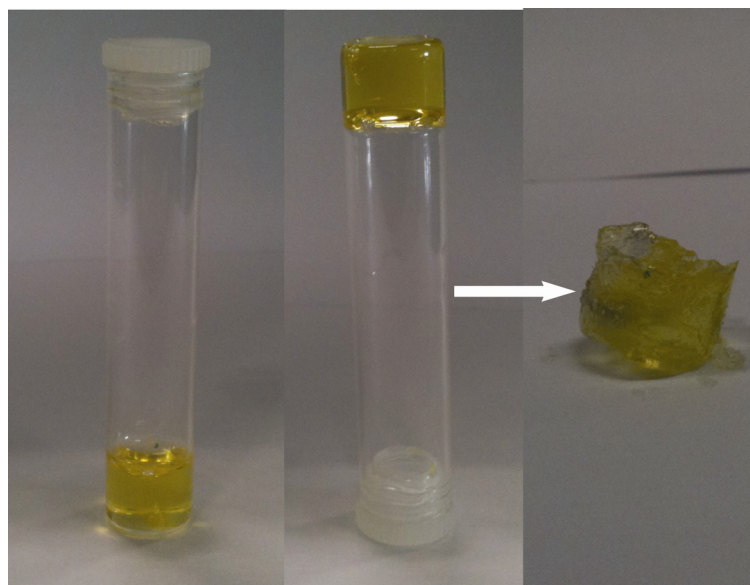


Figure S2. Organogel formed after DTT cleavage of **1a** to form P(ZLL-*b*-LC), followed by sonication induced gelation.

Fluorescence Quantum Yield Determination

The quantum yields of fluorescently labeled CCS **2**_{AMP} and the pure AMP were determined using fluorescein as reference with a known quantum yield ($\Phi_R = 0.95$ at $\lambda_{em} = 496$ nm in 0.1 M NaOH).⁶ The fluorescence quantum yield was calculated by using **equation 1**.^{6,7}

$$\Phi_F = \frac{I}{I_R} \left(\frac{1 - 10^{-A_R}}{1 - 10^{-A}} \right) \frac{n^2}{n_R^2} \quad (1)$$

where Φ_F is the quantum yield of the unknown, I is the integral area under the fluorescence emission curve, A is the UV-visible absorbance, and n is the refractive index ($n_{H_2O} = 1.333$; $n_{DMSO} = 1.479$). The R subscript refers to the reference (i.e., fluorescein).

Four different concentrations of fluorescein in 0.1 M NaOH were prepared and the absorption and emission spectra were measured (**Figure S3a** and **b**, respectively). Integration of the emission spectra gave peak areas, which were then used in **equation 1** to calculate quantum yield of free AMP and **2**_{AMP}.

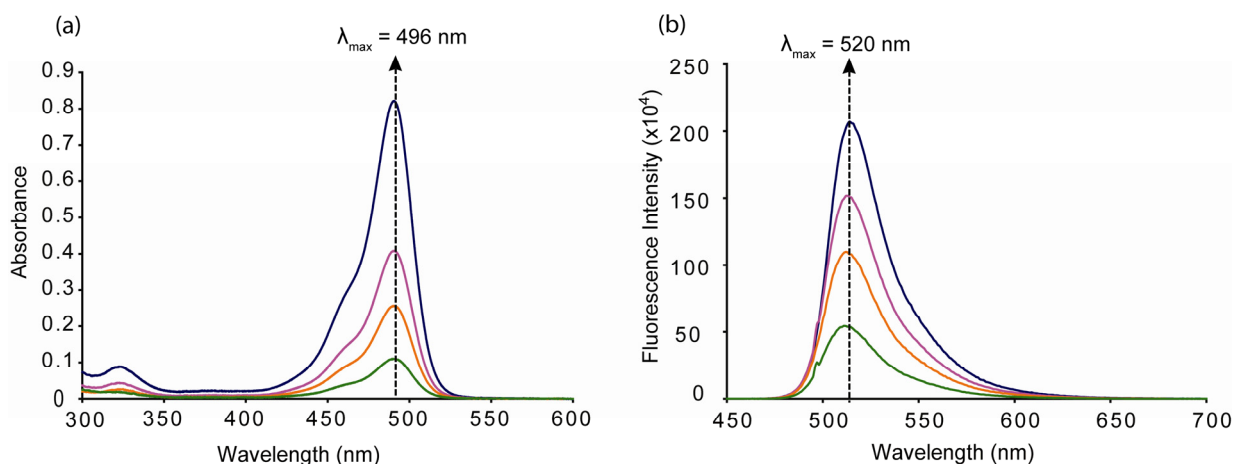


Figure S3. (a) UV-visible absorption and (b) fluorescence emission spectra for different concentration fluorescein solutions in 0.1 M NaOH.

- (6) J.R. Lakowicz, **1999**, Principles of Fluorescence Spectroscopy, 2nd Ed., Kluwer Academic/Plenum Publishers: New York.
(7) M. Spiniello, A. Blencowe, G. G. Qiao, *J. Polym. Sci. Polym. Chem.*, **2008**, 46, 2422.

Based upon the absorption and emission spectra of free AMP (**Figure S4a and b**, respectively) the quantum yield of free AMP in DMSO was determined to be 0.180.

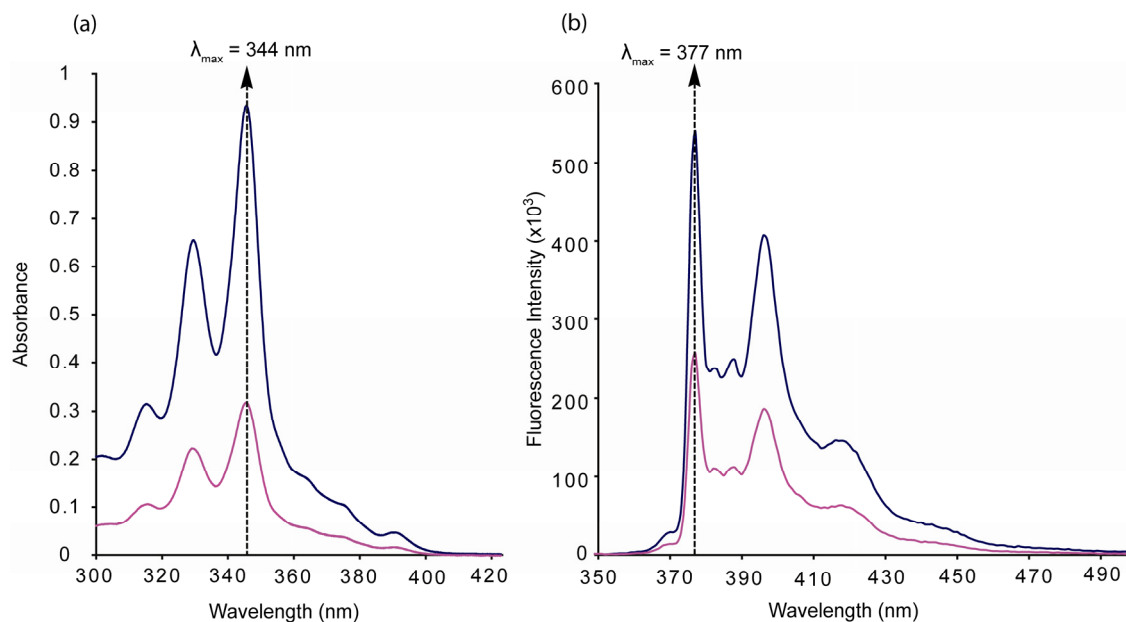


Figure S4. (a) UV-visible absorption and (b) fluorescence emission spectra for solutions of pure AMP in DMSO.

From the absorption and emission spectra of star **2_{AMP}** (**Figure S5a and b**, respectively) the quantum yield was calculated to be 0.083.

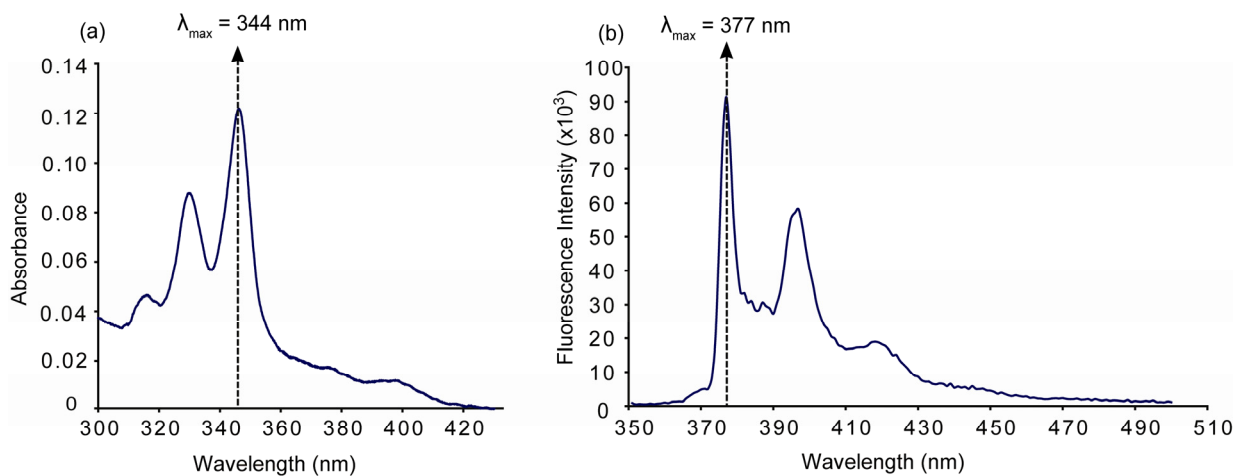


Figure S5. (a) UV-visible absorption and (b) fluorescence emission spectra for solutions of star **2_{AMP}** in DMSO.