Supporting Information

Should I Stay or Should I Flow? An Exploration of Metallosupramolecular Liquid Crystal Polymers

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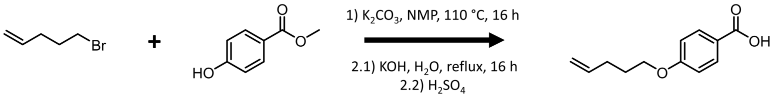
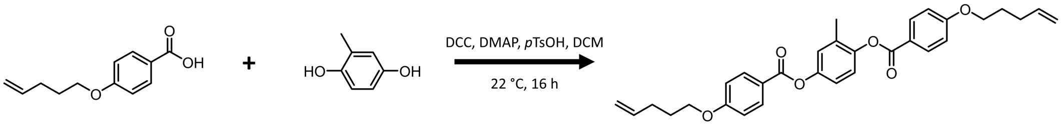
Table of contents:

Materials and Methods:

Potassium carbonate was purchased from Fisher Scientific. 5-Bromo-1-pentene was purchased from Combi-Blocks. All other chemicals were purchased from Millipore-Sigma and were used as received unless noted otherwise. All solvents were purchased from Fisher Scientific and were used as received unless noted otherwise. 2,6-Bis(1H-benzimidazolyl)-4-hydroxypyridine (HOBip) was prepared following literature precedent.[1] Europium tri[bis(trifluoromethylsulfonyl)imide] ($Eu(NTf_2)_3$) was prepared following literature precedent.[2]



4′-(Pent-1-enyloxy)benzoic acid: 4′-(Pent-1-enyloxy)benzoic acid was synthesized using a modified version of previously published procedures.[3,4] 5-bromo-1-pentene (50 g, 0.336 mol, 1 eq), methyl-4-hyroxybenzoate (52.145 g, 0.342 mol, 1.02 eq), potassium carbonate (50.172 g, 0.362 mol, 1.08 eq) were all added to a flask containing N-methyl-2-pyrrolidone (150 mL, 3 vol). The flask was equipped with a condenser, and the reaction mixture was heated to 80°C while stirring. After observing an exotherm in the form of vigorous bubbling the temperature was raised to 110°C where the reaction was allowed to proceed for 16 h. The reaction mixture was then cooled to room temperature and added to a separatory funnel with toluene (300 mL) and water (100 mL). The organic layer was washed three times with water whereafter the solvent was removed under vacuum. To the resulting oil was added 300 mL of 10 wt% aqueous potassium hydroxide solution. The reaction mixture was then heated to 110 °C and allowed to proceed for 16 h with stirring. After cooling to room temperature, the reaction mixture was extracted with ethyl ether (50 mL) three times. The aqueous layer was then diluted with water to a volume of 2 L while stirring whereupon concentrated sulfuric acid (25 mL) was added to adjust the solution to a pH of about 2. As the sulfuric acid is added, white solid began to precipitate from solution until the reaction mixture became a slurry that was difficult to stir magnetically. The solid was removed from the aqueous solution using a Buchner funnel and recrystallized three times in hot ethanol yielding white crystals. (61 g, 88% yield) ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 – 7.97 (m, 2H), 7.00 – 6.88 (m, 2H), 5.98 – 5.74 (m, 1H), 5.17 – 4.94 (m, 2H), 4.04 (t, J = 6.4 Hz, 2H), 2.25 (qd, J = 7.4, 1.4 Hz, 2H), 2.03 – 1.82 (m, 2H).



Liquid crystal monomer (1): Liquid crystal monomer (**1**) was prepared using a previously reported procedure.[5] 4′-(Pent-1-enyloxy)benzoic acid (24.3 g, 0.118 mol, 1.95 eq), an 2-methoxyhydroquinone (8.44 g, 0.060 mol, 1 eq), dicyclohexylcarbodiimide (28.69g, 0.139 mol, 2.4 eq), 4-dimethylaminopyridine (14.050g, 0.115 mol, 1.9 eq), and *p*-toluenesulfonic acid monohydrate (21.88 g, 0.115 mol, 1.9 eq) were added to a flask containing 400 mL of dichloromethane. The reaction mixture was stirred at room temperature (22 °C) for 16 hours. A solid white urea byproduct was then filtered out of the reaction mixture, and the solvent was then removed from the filtrate under vacuum. The remaining solid was then recrystallized three times in hot ethanol to afford white powdery crystals. (44.25 g, 75% yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.04 (m, 4H), 7.22 – 7.04 (m, 3H), 7.04 – 6.92 (m, 4H), 5.96 – 5.77 (m, 2H), 5.17 – 4.97 (m, 4H), 4.07 (td, J = 6.4, 2.0 Hz, 4H), 2.35 – 2.20 (m, 7H), 2.01 – 1.87 (m, 4H).

Alkene functionalized 2,6-bisbenzyimidazolylpyridine (Bip) ligand (3): 5-bromo-1-pentene (5 g, 0.034 mol, 1 eq), 2,6-Bis(1H-benzimidazolyl)-4-hydroxypyridine (HOBip) (12.162 g, 0.034 mol, 1.02 eq), potassium carbonate (5.075 g, 0.037 mol, 1.08 eq) were all added to a flask containing N-methyl-2-pyrrolidone (25 mL, 5 vol). The flask was equipped with a condenser, and the reaction mixture was heated to 80°C while stirring. After observing an exotherm in the form of vigorous bubbling the temperature was raised to 110°C where the reaction was allowed to proceed for 16 h. The reaction mixture was then cooled to room temperature and extracted with toluene (100 mL) and water (25 mL) collecting the organic fraction. The solvent was removed in vacuo and the remaining solid was triturated with hot ethanol and filtered until the filtrate was colorless leaving a light pink fluffy solid. (11.07 g, 77% yield) ^{1}H NMR (500 MHz, CDCl3) δ 7.94 (s, 2H), 7.87 (d, J = 6.3 Hz, 2H), 7.46 (m, 2H), 7.40 – 7.33 (m, 4H), 5.86 (m, 1H), 5.13 – 5.00 (m, 2H), 4.27-4.22 (m, 8H), 2.31 – 2.25 (m, 2H), 1.98 (dt, J = 8.0, 6.5 Hz, 2H).^{13}C NMR (126 MHz, CDCl3) δ 166.67, 151.22, 150.33, 142.63, 137.43, 137.30, 123.64, 122.91, 120.26, 115.77, 111.89, 110.02, 67.87, 32.63, 29.99, 28.20. MALDI-MS: 446.9 ([M]+Na^+).

Bip-terminated telechelate LCP (4): To form the Bip-terminated telechelate LCP with a targeted molecular weight of 10,000 g/mol, **1** (1.032 g, 0.002 mol), 2,2-(ethylenedioxy)diethanethiol (0.281 mL, 0.0017 mol), and a catalytic amount of 2,2-dimethoxy-2-phenylacetophenonec (DMPA) (0.031 g, 0.00012 mol) were added to 3 mL of methylene chloride. The reaction mixture was stirred until all components were well dissolved in solution and then exposed to UV light while stirring (320-390 nm, 60 min, 3 mW cm^{-2}) to initiate the polymerization. A stoichiometric amount of **3** (relative to the thiol chain ends of the polymer) (0.114 g, 0.00027 mol) and a catalytic amount of DMPA (0.0041 g, 0.000016 mol) was dissolved in 1 mL of chloroform and added to the polymer reaction mixture and well mixed. The polymer and ligand reaction mixture was then exposed to UV light (320-390 nm, 600 s, 3 mW cm^{-2}) after which another equivalent of DMPA was then added to the reaction mixture and the UV light exposure was repeated. This telechelate polymer mixture was then precipitated into 100 mL of methanol and placed into a freezer (8 °C) for 2 hours after which the methanol was decanted and the polymer was dried in an oven at 60°C under vacuum for 16 hours.

Metallosupramolecular LCPs (MSLCPs) (4-Zn, 4-Zn+Eu, 4-Eu): MSLCPs were synthesized by adding a stoichiometric amount of **4** with the appropriate metal such that each Bip ligand has a metal binding site. For example, **4-Zn** was prepared via the mixture of a solution of **4** (1.347 g, 0.00013 mol) in 3 mL of chloroform with a solution of zinc di[bis(trifluoromethylsulfonyl)imide] ($Zn(NTf_2)_2$) (0.084 g, 0.00013 mol) dissolved in 1 mL of a 4:1 chloroform:acetonitrile mixture. The resulting mixture was stirred at room temperature until well-mixed and then poured into a PTFE dish and heated to 50°C under ambient conditions for two hours. The dish was then placed in an oven at 60°C under vacuum for 16 hours to remove residual solvent. The resulting material was then collected and melt processed in a hot compression molder (Carver) (130°C, 4 tons, 10 minutes) inside a mold (50 mm x 50 mm x 0.5 mm) to make films of homogeneous thickness for further testing.

Instrumentation:

All nuclear magnetic resonance (NMR) spectra were collected on a Bruker Avance III HD nanobay 400 MHz spectrometer.

All differential scanning calorimetry (DSC) thermograms were collected on a TA Instruments Discovery 2500 differential scanning calorimeter. Experiments were run following a (22/200/-90/200) ramp using heating and cooling rates of 10 °C min^{-1}. All curves shown are from the second heating.

All shear mechanical testing including dynamic temperature ramps and stress relaxation data were collected on TA Instruments ARES-G2 shear rheometer. Shear rheology experiments were performed on discs (diameter = 8 mm, thickness = 0.43 mm)

All tensile mechanical testing of rectangular samples of MSLCPs and stud-pull adhesive joints were collected on a Zwick-Roell zwickiLine Z0.5 materials testing instrument. Tensile tests were performed at 22 °C at a strain rate of 5 mm/min until failure.

All probe-tack testing was performed on a TA Instruments ARES-G2 shear rheometer. Tests were performed at 22 °C on discs (diameter = 8 mm, thickness = 0.43 mm)

All wide-angle x-ray scattering (WAXS) data were collected on a SAXSLAB GANESHA 300XL utilizing a Cu Kα source ($\lambda = 0.154$ nm) at a voltage and power of 40 kV and 40 mA, respectively. Films were affixed to a stage with Kapton tape and shot directly and measured for 5 min at q = 0.05 – 0.25. For the variable temperature studies, samples were sealed inside Kapton tape.

All polarized optical microscopy images were collected on an Leica DM2700P polarized optical microscope equipped with MC170 HD 5 camera.

All gel permeation chromatography (GPC) data were collected on a Shimadzu HPLC LC20-AD outfitted with a Wyatt Optilab T-rEX differential refractive index detector running tetrahydrofuran as the eluent. Samples were prepared at a concentration of 1.5 mg/mL in tetrahydrofuran and passed through a 200 μm syringe filter prior to sample injection. Molecular weights were measured against a calibration curve created from polystyrene standards.

All UV-Vis spectroscopy data was collected on a Shimadzu UV-3600 Plus UV-VIS-NIR spectrophotometer.

All atomic force microscopy (AFM) images were collected using an Asylum Research Cypher ES AFM with BlueDrive. Tapping-mode imaging was performed using Asylum Research FS-1500-AuD cantilevers with resonant frequencies of 1.5 MHz. Images were collected at a scan rate of 4.88 Hz with a 950 mV set point in the repulsive mode (to prevent tip-induced damage of the sample surface). Samples were equilibrated for 15 min at the desired temperature prior to imaging. Images were processed using Gwyddion 2.61. First, a polynomial (3rd degree horizontal, 3rd degree vertical) background was removed before aligning rows via the median method. Using Gwyddion software, any horizontal scars were removed, and samples were colored using the default Gwyddion palette.

WAXS Data Processing

To capture the whole 2D scattering pattern, four individual WAXS patterns are acquired with shifted detector location. Polar transformation is performed to align and average the four scattering patterns. The final scattering pattern is computed by the inverse transformation of the averaged plot. The samples show peak intensity around q = 1.45 ~ 1.5 $Å^{-1}$, indicating an average spacing of d=4.27 Å between the mesogens. To compute the order parameter, the 1D azimuthal data is calculated by integrating the 2D data between q = 0.97 $Å^{-1}$ and q=1.90 $Å^{-1}$. The background is subtracted by a linear fit and the order parameter is calculated by the Kratky method as described previously.

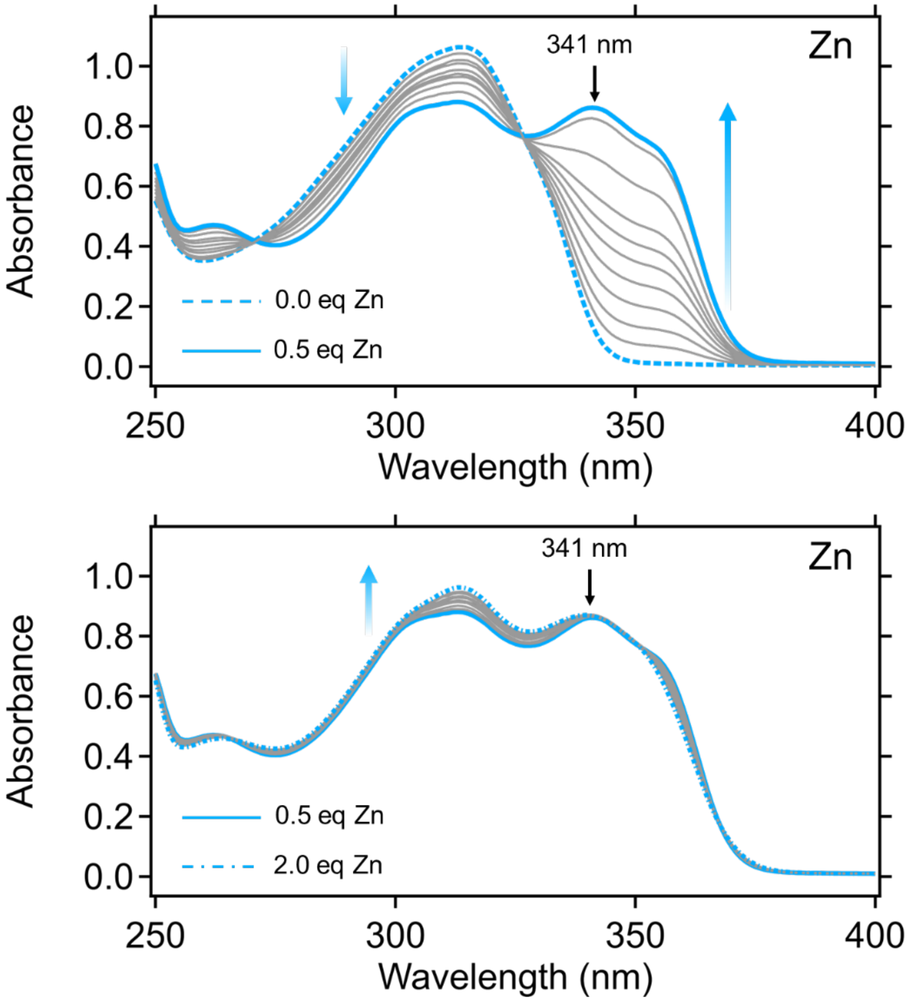


Figure S1: UV-Vis titrations of $Zn(NTf_2)_2$ against **3** from no metal ion to an excess of metal ions.

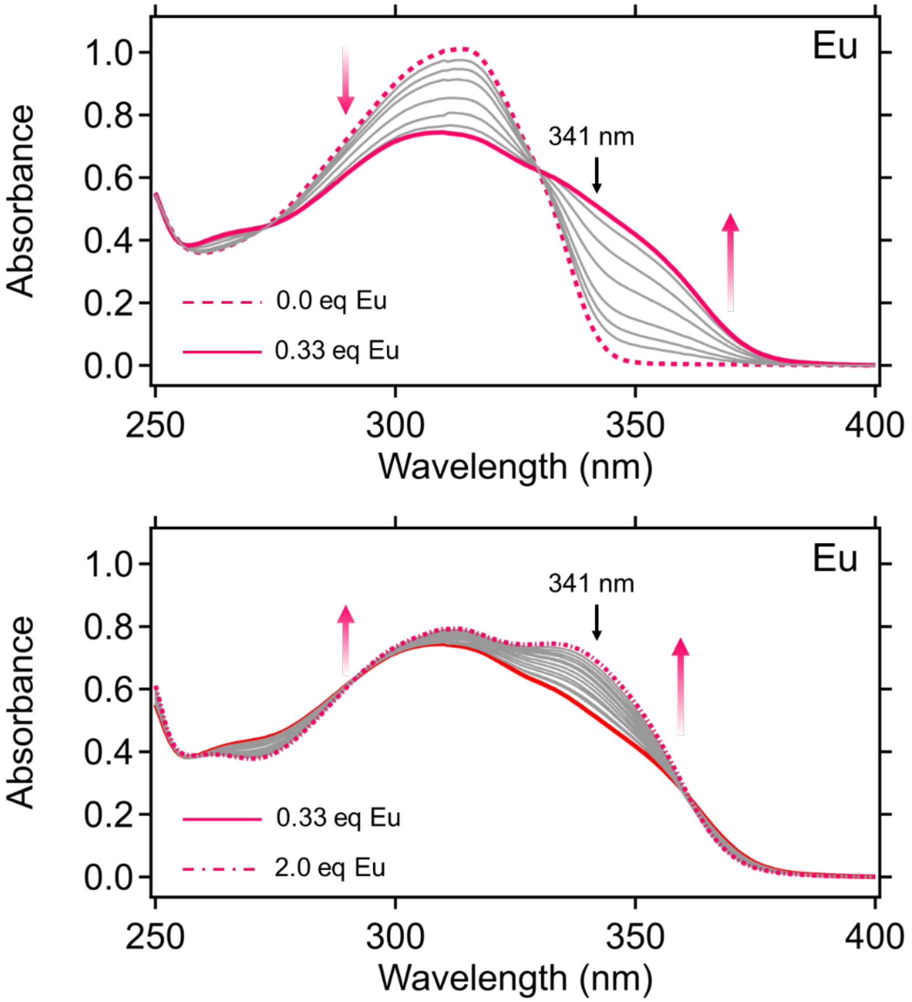


Figure S2: UV-Vis titrations of Eu(NTf$_2$)$_3$ against **3** from no metal ion to an excess of metal ions.

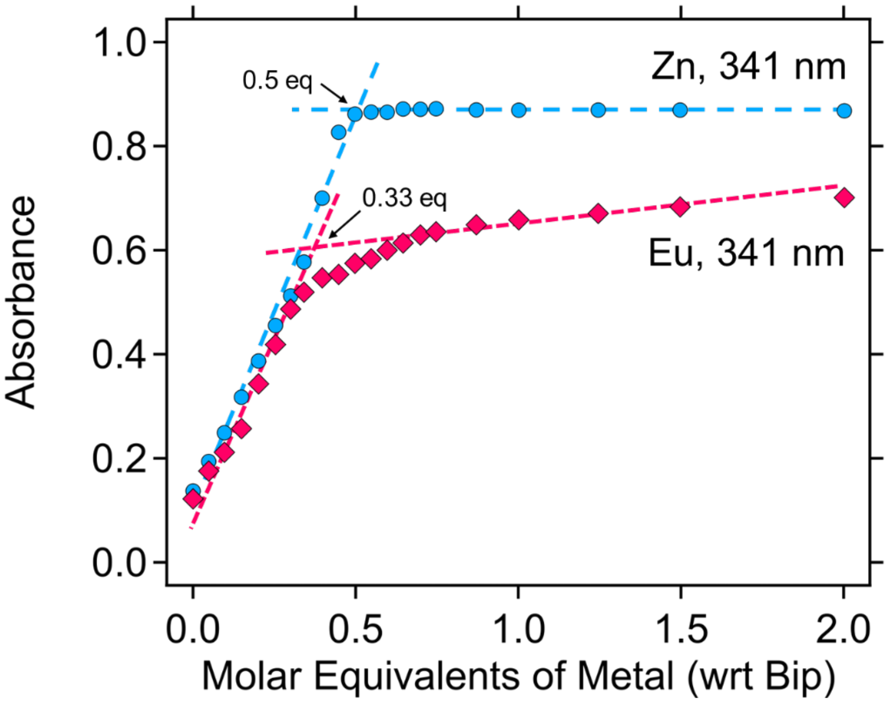


Figure S3: Compiled UV intensity at 341 nm vs molar equivalents of metal ion plots for both the Zn ion and Eu ion titrations

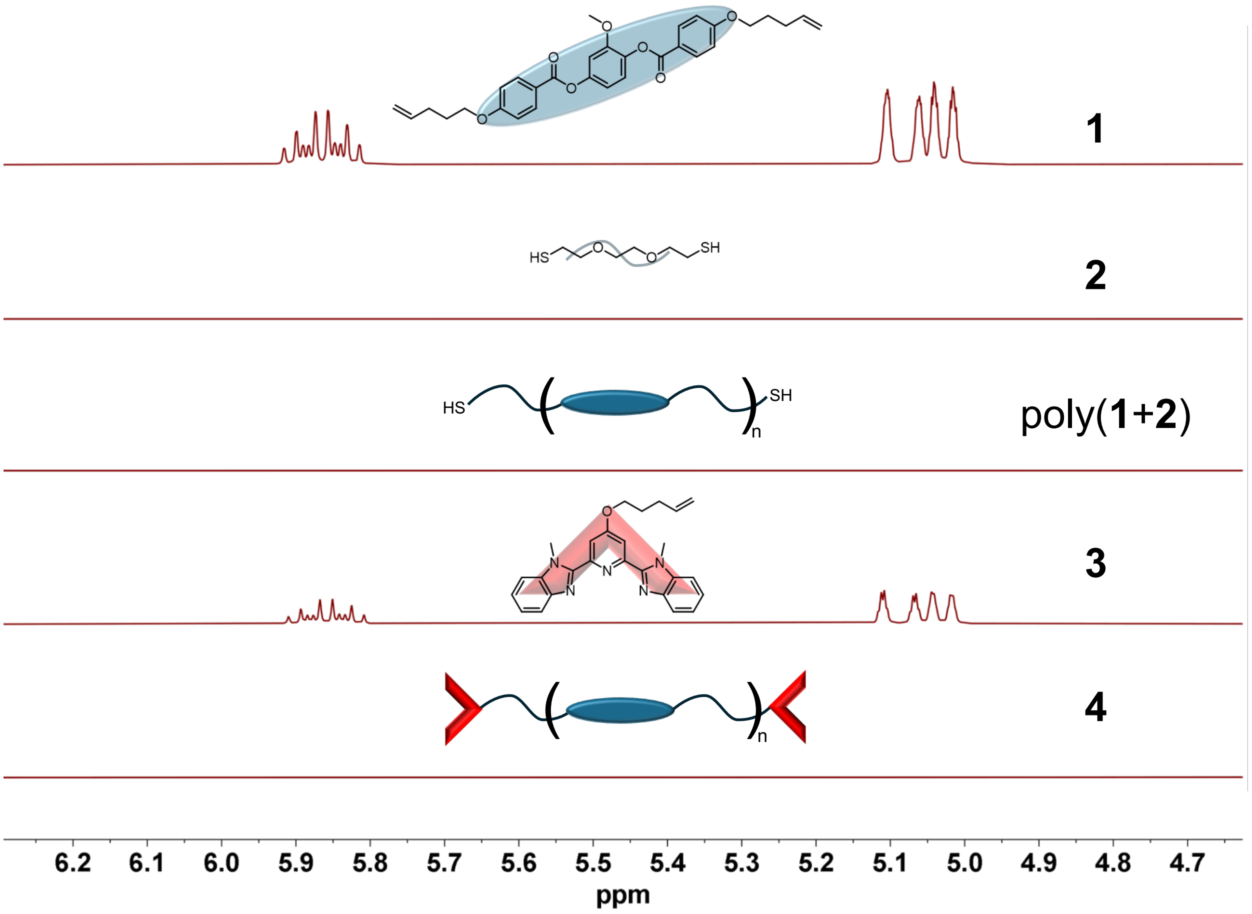


Figure S4: ^{1}H-NMR (CDCl$_3$, 400 MHz, 22 °C) spectra zoomed in on the alkene signals illustrating the disappearance of alkene protons from both the polymerization of **1** and **2** to **poly(1+2)** and the reaction of **poly(1+2)** and **3** to form **4** demonstrating the full conversion of alkene functional groups for these thiol-ene reactions.

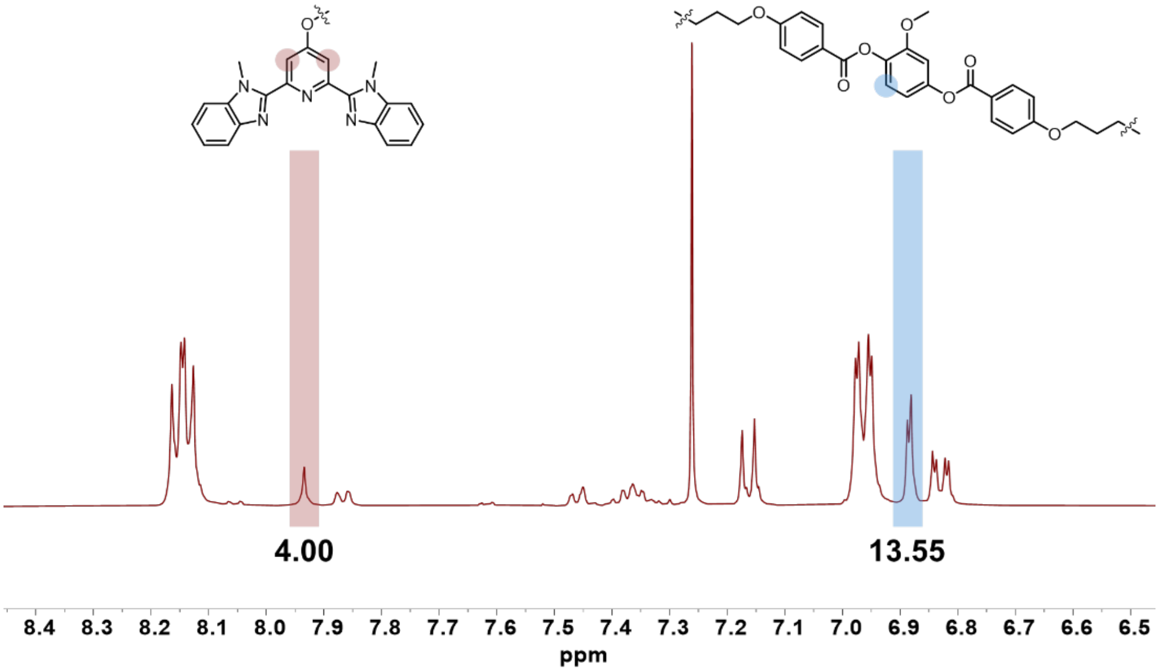


Figure S5: ^{1}H-NMR spectrum (CDCl$_3$, 400 MHz, 22 °C) of the aromatic signals of **4** showing the ratio of chain end protons (left) to repeat unit protons (right)

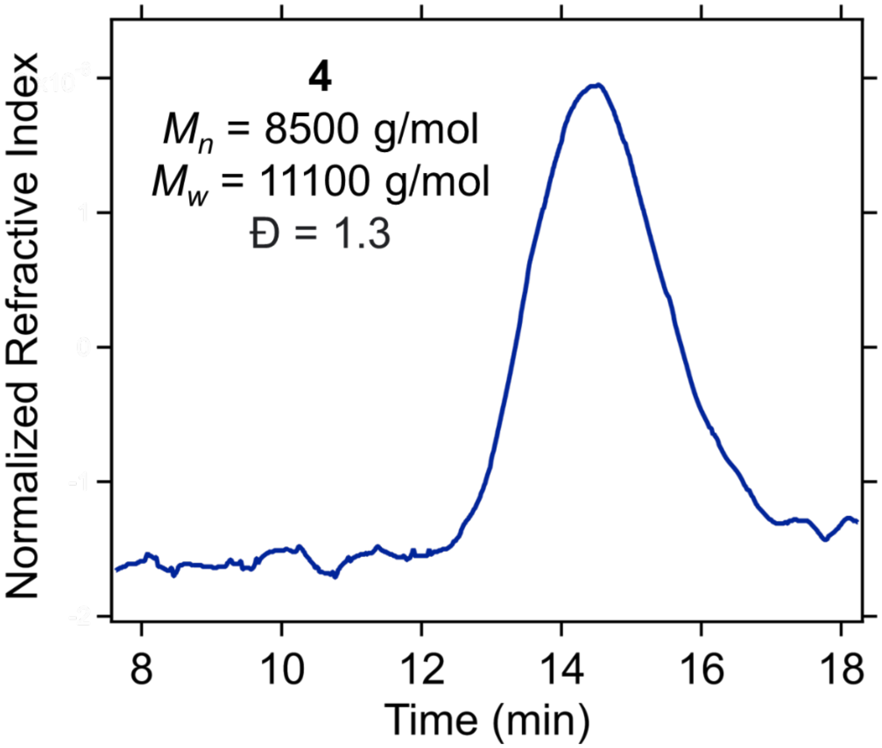


Figure S6: Gel permeation chromatography curve for **4** in tetrahydrofuran with molecular weights calculated against polystyrene standards

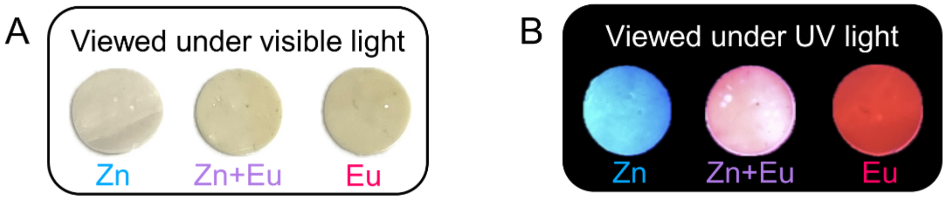


Figure S7: A. Optical images of each of the MSLCP materials; B. Optical images under UV light (365 nm) of each of the MSLCP materials.

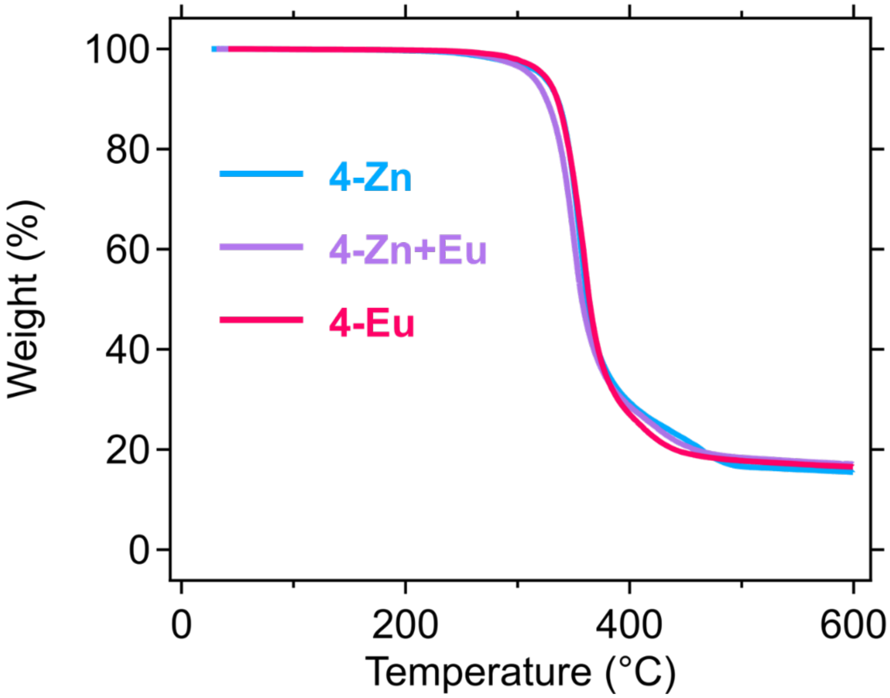


Figure S8: Thermogravimetric analysis of the MSLCP materials performed at a heating rate of 10 °C min^{-1} to 600 °C.

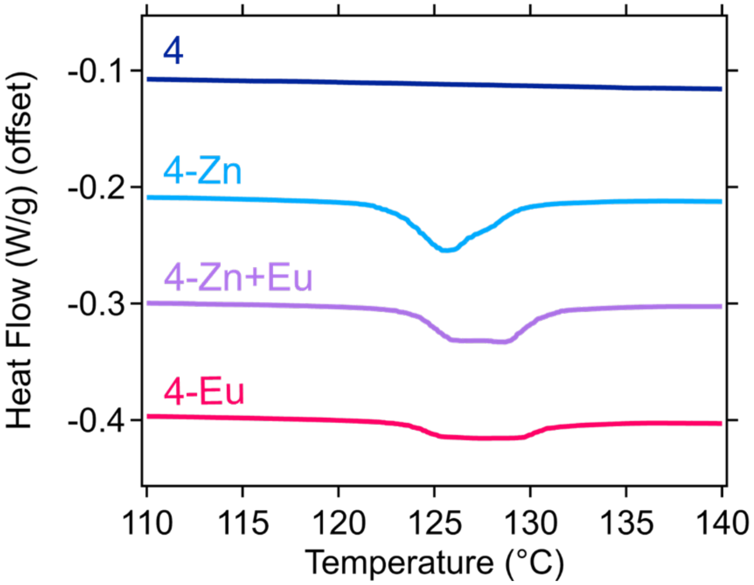


Figure S9: Differential scanning calorimetry heating curve performed at 10 °C min^{-1} zoomed in on T_{UT} showing the bimodal nature the signal.

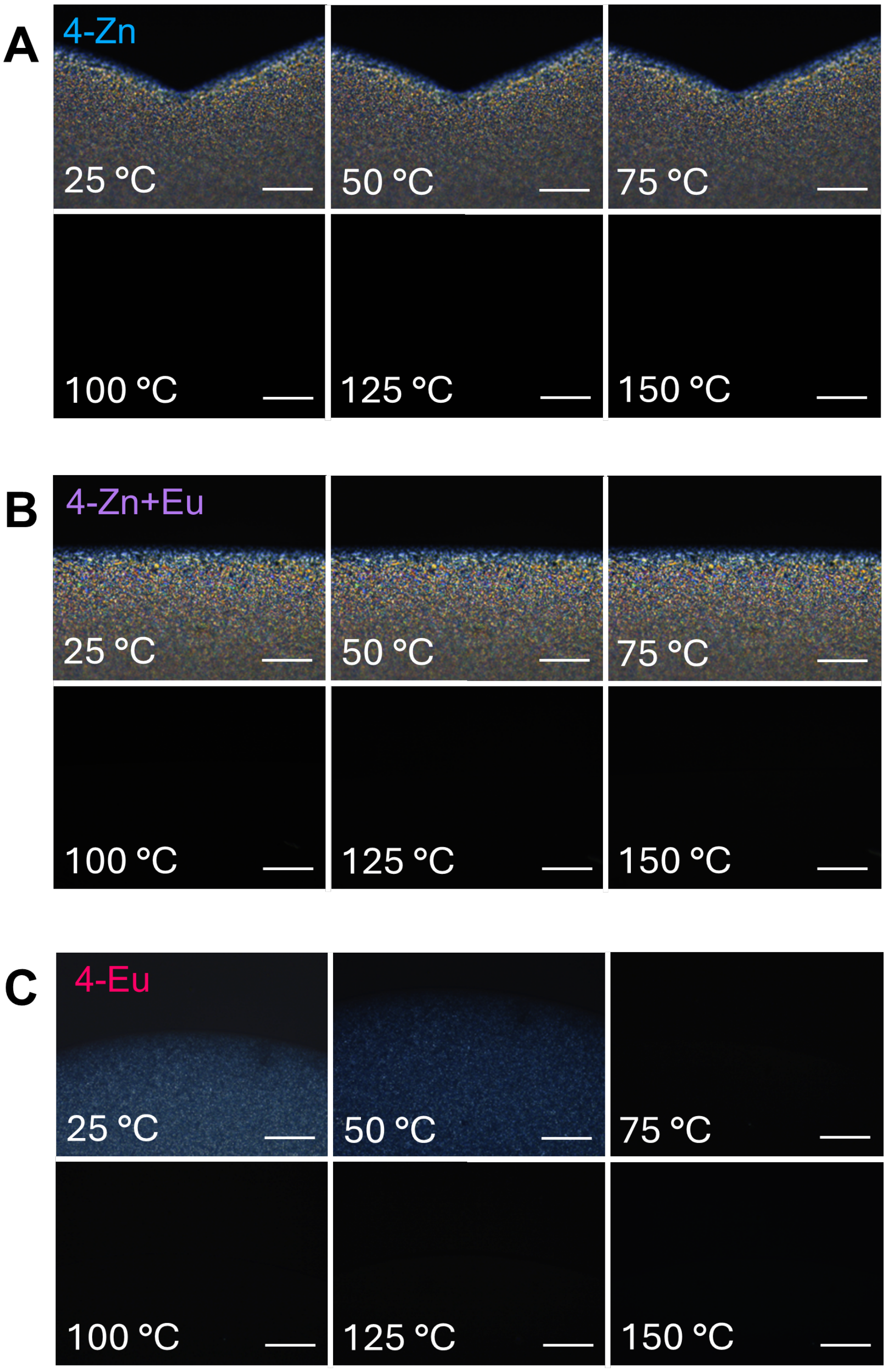


Figure S10: Variable temperature polarized optical microscopy images for: A. **4-Zn**, B. **4-Zn+Eu** and C. **4-Eu**. Scale bar is representative of 50 µm

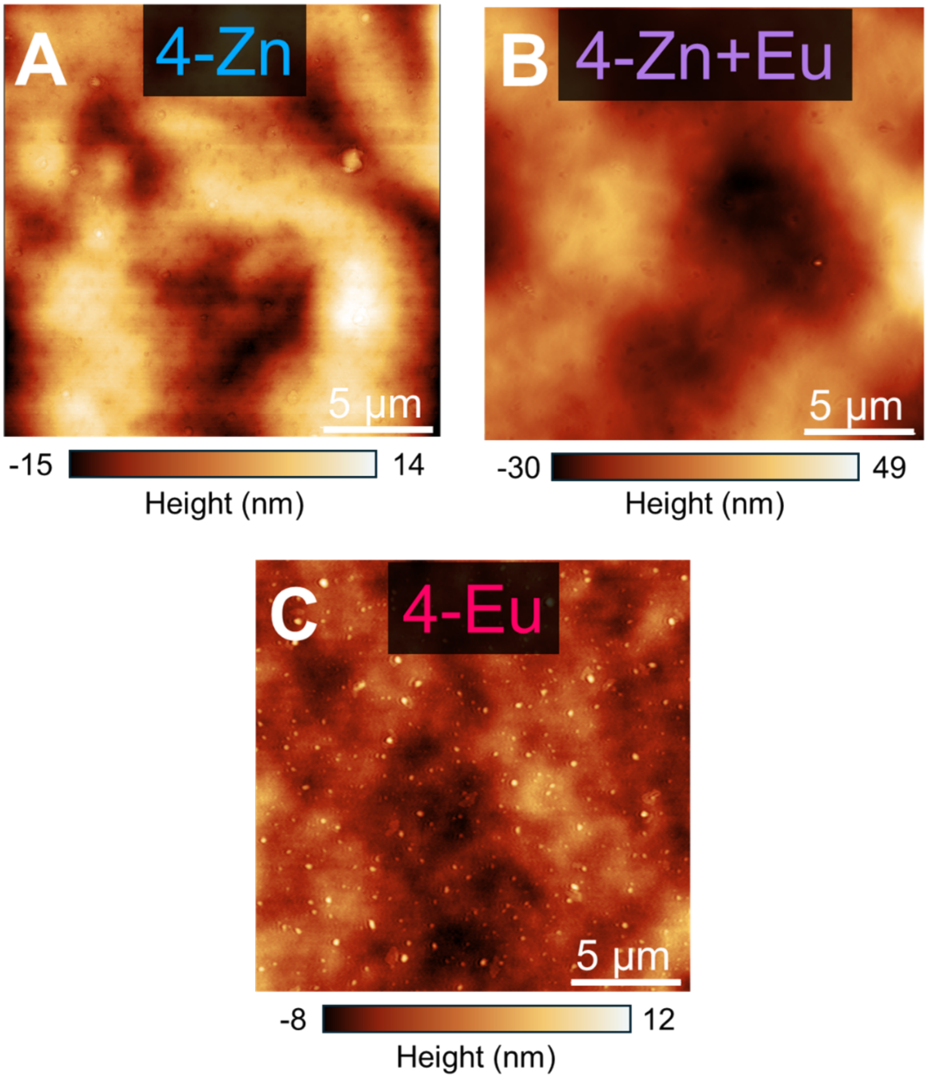


Figure S11: Atomic force microscopy height images for A. **4-Zn**; B. **4-Zn+Eu**; C. **4-Eu**

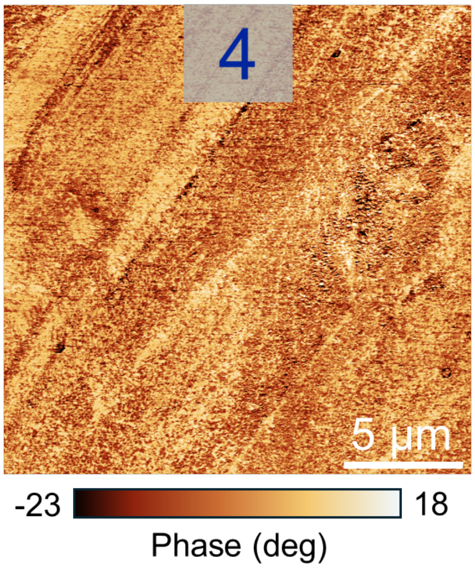


Figure S12: Atomic force microscopy phase image for **4**.

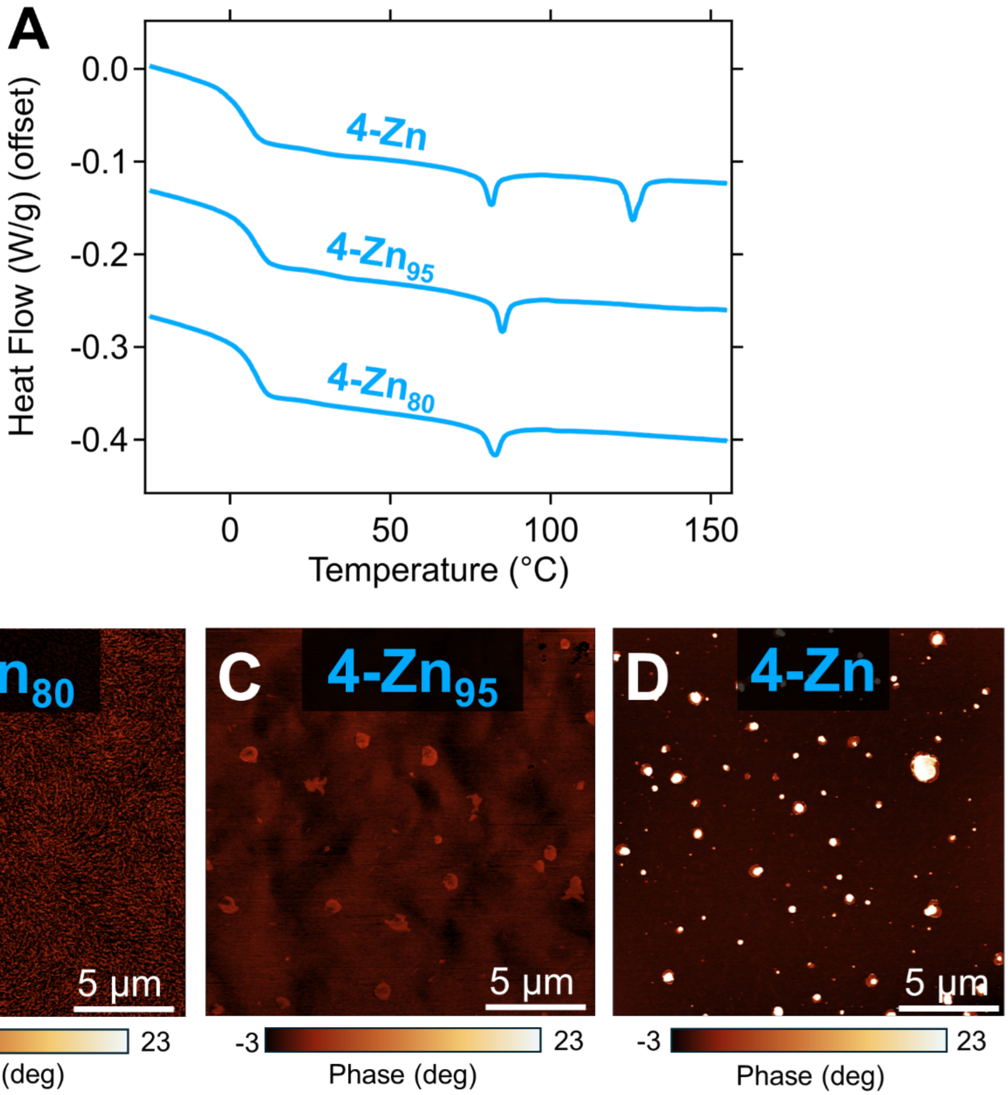


Figure S13: A. Differential scanning calorimetry heating curve performed at 10 °C min^{-1} of **4-Zn**, **4-Zn$_{95}$**, and **4-Zn$_{80}$**, Atomic force microscopy phase images for B. **4-Zn$_{80}$**; C. **4-Zn$_{95}$**; D. **4-Zn**

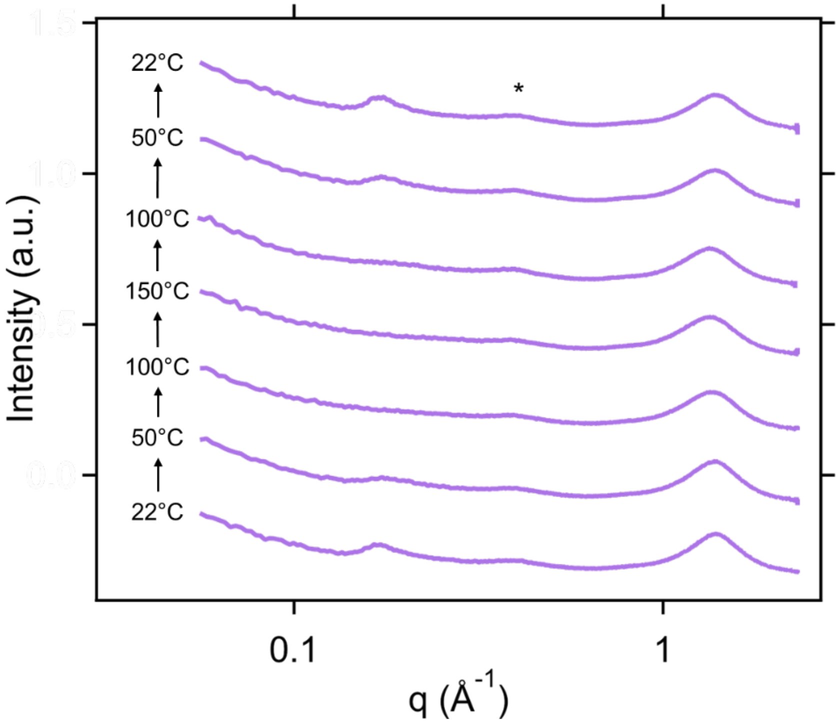


Figure S14: Temperature-dependent wide angle x-ray scattering spectra of **4-Zn+Eu** heated across a range of temperature from 22 °C to 150 °C and back to 22 °C. The feature at q = 0.38 Å^{-1} (d = 16.5 Å) indicated by an asterisk corresponds to the polyimide tape used to seal the samples.

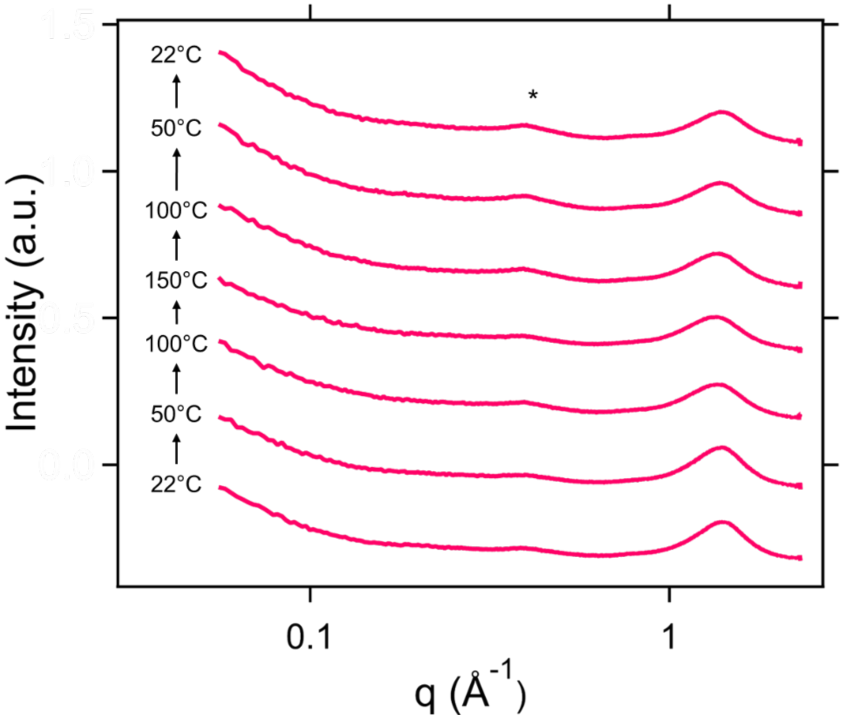


Figure S15: Temperature-dependent wide angle x-ray scattering spectra of **4-Eu** heated across a range of temperature from 22 °C to 150 °C and back to 22 °C. The feature at q = 0.38 Å^{-1} (d = 16.5 Å) indicated by an asterisk corresponds to the polyimide tape used to seal the samples.

References:

[1] P. Froidevaux, J. M. Harrowfield, A. N. Sobolev, **2000**, 4678.

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