

Supporting information

Organometallic Macromolecules with Piano Stool Coordination Repeat Units: Chain Configuration and Stimulated Solution Behaviour

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Materials and Instrumentation

All experiments were performed under dry nitrogen atmosphere using either standard Schlenk techniques or a glovebox unless otherwise indicated. THF was freshly distilled under nitrogen from Na/benzophenone. Hexane was degassed with dry nitrogen. Toluene was dried with molecular sieves before use. Sodium (Na), 1-bromo-3-chloropropane, potassium (K) were purchased from Sigma-Aldrich. Cyclopentadienyl iron dicarbonyl dimer (Fp₂) were purchased from Strem Chemicals Inc. Chlorodiphenylphosphine was purchased from Tokyo Chemical Industry (TCI). Benzophenone was purchased from Fisher Scientific. All chemicals were used as received unless otherwise indicated.

¹H, ³¹P NMR spectra were obtained on a Bruker Avance 300 (¹H NMR: 300 MHz, ³¹P NMR: 120 MHz) spectrometer at ambient temperature using appropriate solvents. NMR samples were prepared under dry nitrogen atmosphere unless otherwise indicated.

Fourier transform infrared spectroscopies (FT-IR) were recorded using a Perkin Elmer Spectrum RX I FT-IR system. The samples were ground with KBr and then pressed into transparent pellet.

Molecular weights and molecular weight distributions, M_w/M_n , were characterized using GPC analysis at room temperature with THF as eluent at a flow rate of 1.0 mL/min. The Viscotek GPC max unit used was equipped with a VE 2001 GPC, three PolyAnalytik organic mixed bed columns, PAS-103-L, PAS-104-L, and PAS-105-L, with dimension of 8 mm (ID) × 300 mm (L) each and a Viscotek triple detector array, including refractive index, viscosity, and dual-angle light scattering detectors.

UV absorption spectra for the samples with four different concentrations in DCM were conducted on a Varian (Carey 100 Bio) UV visible spectrophotometer using a quartz cuvette with a path length of 1 cm. DCM was used as the blank. Absorption intensities at wavelength of 350 nm were plotted against the solution concentrations, leading to a straight line. The molar extinction coefficient was determined from the slope of the line.

Turbidity measurements were performed on a Varian (Carey 100 Bio) UV visible spectrophotometer equipped with a temperature controller. The heating program started at 25 °C at a constant rate of 1.0 °C/min, followed by cooling back to 25 °C at the same rate. The wavelength was fixed at 600 nm. The transmittance curve was obtained by plotting the transmittance as a function of temperature. The inflection point in the transmittance curve was taken as the cloud point; this point was graphically determined by the maximum of the first derivative of the heating or cooling curve.

Synthesis of FpP

A solution of Ph₂PCH₂CH₂CH₂Cl (1.01 g, 3.8 × 10⁻³ mol) in THF (5 mL) was added to an orange suspension of FpK (1.00 g, 4.6 × 10⁻³ mol) in THF (25 mL) at 0 °C. The reaction flask was wrapped in aluminum foil to shield it from light. The mixture was

stirred at room temperature for 2 h. THF was then removed under vacuum. Degassed hexane was subsequently added to dissolve the crude product, while the KCl precipitated from the solution. The supernatant was transferred using a cannula into another Schlenk flask. After removing the solvent, an oil-like crude product was obtained. The oil was dissolved in a minimum amount of hexane/DCM (4: 1, v/v) and filtered on a short silica gel column to remove the Fp dimer which formed during the reaction. The bright yellow solution was collected and the solvents were subsequently removed under vacuum, giving a bright yellow powder. Yield: 1.1 g (60%) ^1H NMR (DMSO- d_6): 7.35 (t, 4 H, ortho- C_6H_5), 7.32 ppm (m, 6 H, para, meta- C_6H_5), 4.87 ppm (s, 5H, C_5H_5), 2.07 ppm (2H, PCH_2), 1.46 ppm (4H, FeCH_2CH_2).

Polymerization of FpP

The polymerization of FpP was carried out in bulk at elevated temperature without or with DMSO (5% by weight). After the polymerization the crude product was dissolved in a minimum amount of THF and precipitated in hexane. The precipitate was collected by filtration and dried in vacuum at room temperature overnight. The resulting polymer was a bright yellow powder. ^1H NMR (DMSO- d_6): 7.8-7.1 ppm (b, 10H, C_6H_5), 4.4-4.2 ppm (b, 5H, C_5H_5), 2.78-2.60 ppm (b, 1H, COCH_2), 2.47-2.17 ppm (b, 1H, COCH_2), 2.13-1.89 ppm (b, 2H, CH_2P), and 1.32-0.74 ppm (b, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), ^{31}P NMR (DMSO- d_6): 73.2 ppm (main chain coordinated phosphorus), 35 ppm (chain end oxidized phosphorus) ^{13}C NMR (DMSO- d_6): 20 ppm ($\text{CH}_2\text{CH}_2\text{CH}_2$), 29 ppm (CH_2PPh_2), 65 ppm ($\text{CH}_2\text{C}=\text{O}$), 84 ppm, 86 ppm (C_5H_5), 127 ppm, 128 ppm, 129 ppm, 130 ppm, 132 ppm (C_6H_5), 274 ppm ($\text{CH}_2\text{C}=\text{O}$), 220 ppm ($\text{C}\equiv\text{O}$) IR: 1910 cm^{-1} (terminal carbonyl groups), 1600 cm^{-1} (migrated carbonyl groups) All the polymers obtained from different conditions have the same NMR and IR spectra. In ^1H NMR, the integration ratio for each peak is the same for the polymers produced from different conditions.

Migration insertion reaction between PFpP and hexanyldiphenylphosphine ($\text{Ph}_2\text{PC6}$)

20 mg PFpP (DP = 7) was dissolved in 4 mL of DMSO in a NMR tube and the solution was heated to 50 °C in the presence of one equivalent of $\text{Ph}_2\text{P}(\text{CH}_2)_5\text{CH}_3$. The reaction mixture was analyzed by ^{31}P NMR before and after heating for 44 h. After this time the reaction solution was precipitated in hexane, yielding a yellow powder; the powder was collected by centrifugation and dried under vacuum overnight. The resulting product was then characterized by ^{31}P NMR, ^1H NMR and FT-IR. ^{31}P NMR (DMSO- d_6): 73.6 ppm; ^1H NMR (DMSO- d_6): 7.8-7.1 ppm (b, 10H, C_6H_5), 4.3 ppm (b, 5H, C_5H_5), 2.8-2.60 ppm (b, 1H, COCH_2), 2.47-1.87 ppm (b, 1H, COCH_2), 2.47-1.87 ppm (b, 2H, CH_2P), 2.47-1.87 ppm (b, 2H, $\text{CH}_2\text{PPh}_2(\text{CH}_2)_5\text{CH}_3$), 1.35-0.87 ppm (b, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.35-0.87 ppm (b, 2H, $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 0.87-0.63 ppm (b, 3H, $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$) ^{13}C NMR (DMSO- d_6) 13.7 ppm ($\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{PPh}_2$), 21.7 ppm ($\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{PPh}_2$), 30.5 ppm ($\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{PPh}_2$), 65 ppm ($\text{CH}_2\text{C}=\text{O}$), 20 ppm ($\text{CH}_2\text{CH}_2\text{CH}_2$), 29 ppm (CH_2PPh_2), 84 ppm, 86 ppm (C_5H_5), 127 ppm, 128 ppm, 129

ppm, 130 ppm, 132 ppm (C_6H_5), 274 ppm ($CH_2C=O$), 220 ppm ($C\equiv O$) IR: 1910 cm^{-1} (terminal carbonyl groups), 1600 cm^{-1} (migrated carbonyl groups)

Density functional theory calculations

Gaussian 9 Inc. revC1 was used for the Density Functional Theory (DFT) of the monomer, dimer and trimer species, using the LanL2DZ basis set and the LSDA method. Zero point energy (ZPE) calculations found no imaginary frequencies and therefore confirmed that all the structures were in a local minimum. The larger oligomeric systems, containing 5, 6, and 11 Fp units were modeled using a PM6 semi-empirical method and a single point energy calculation was undertaken.

Reaction of PFpP with FpMe

The reactivity of the phosphine end group in PFpP was investigated. The PFpP oligomer (20 mg) and FpMe (5 equivalents vs. PFpP) were dissolved in 4 mL of $DMSO-d_6$ in an NMR tube and the solution was heated at $50\text{ }^\circ\text{C}$. FpMe was prepared according to literature.^[1] The reaction mixture was analyzed by ^1H NMR before and after heating for 3 days.

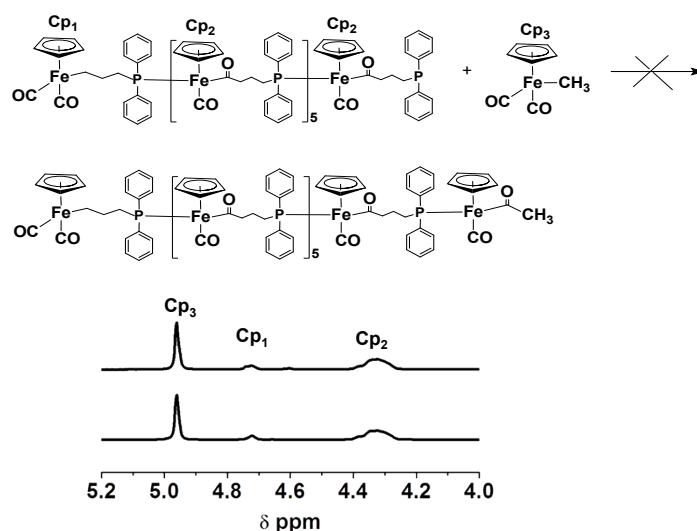


Figure S1. ^1H NMR of PFpP $DMSO-d_6$ solution in the presence of FpMe before (above) and after (below) heating at $50\text{ }^\circ\text{C}$.

The chemical shift at 4.95 ppm (Cp_3) represents the Cp ring in FpMe, the resonance signals for the chain end and main chain Cp ring appear at 4.72 ppm (Cp_1) and 4.3 ppm (Cp_2), respectively. The integration ratio for these three peaks remains the same after heating, indicating that no MIR occurred for both the Fp end group and FpMe.

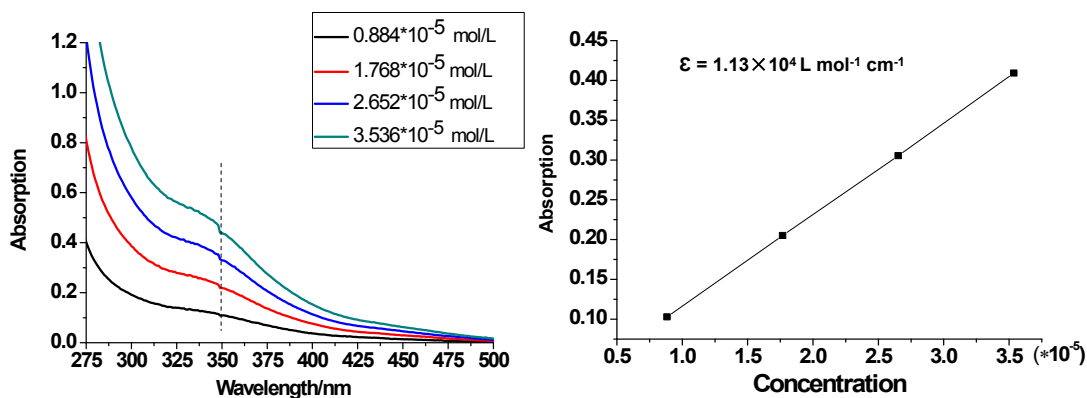


Figure S2. UV absorption spectra for PFpP in DCM (left) and plot of the absorption at 350 nm as a function of solution concentration (right).

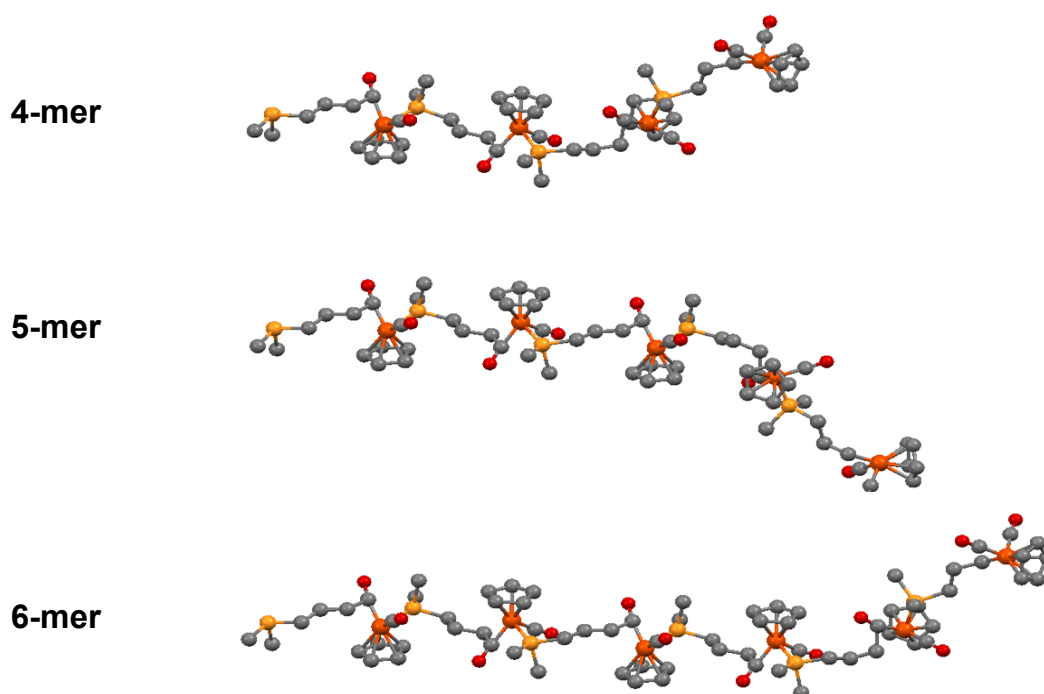


Figure S3. Side view of simulated PFpP for 4-, 5-, and 6-mers.

Table S1. Comparison of the bond lengths for Fe-coordinated bonds in simulated PFpP with those in small molecule Fp acyl derivatives.

Bond distances [\AA]	$\text{CpFe(CO)(PPhRR')C(O)R'}$		DP=5	DP=6	DP=11
	R = Ph; R' = Bu ^[2]	R = Me; R' = Me ^[3]			
Fe-P	2.198	2.180	2.11	2.11	2.11
Fe-CO	1.723	1.725	1.69	1.69	1.69
Fe-COR	1.992	1.948	1.83	1.83	1.83

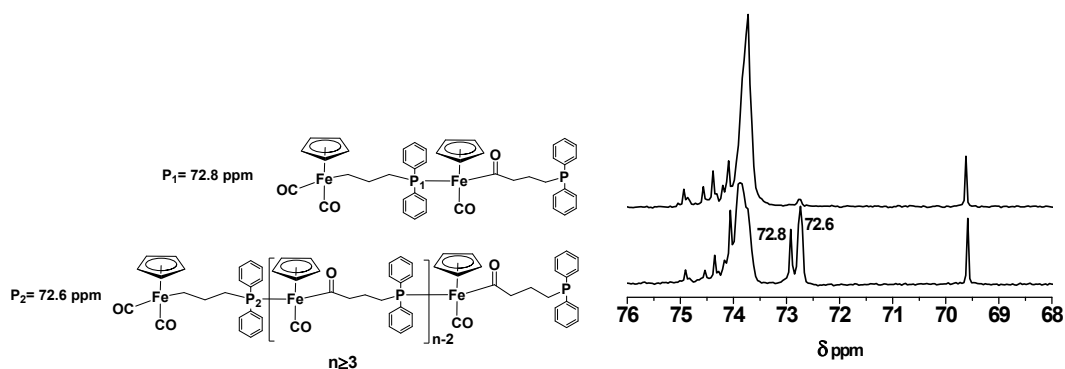


Figure S4. ^{31}P NMR for the PFpP crude products produced from MIP of FpP at 105 °C (above) and 70 °C (below) in bulk.

The peak at 72.8 ppm in Figure S4 is assigned to the coordinated phosphorus in the FpP dimer. For the oligomer with $\text{DP} > 2$, this peak appears at 72.6 ppm.^[4] As shown in Figure S3, the disappearance of the peak at 72.8 ppm and the decreased intensity of the peak at 72.6 ppm suggests that step-growth reaction of the FpP dimers and other oligomers with DP larger than 2 are both enhanced at higher temperature.

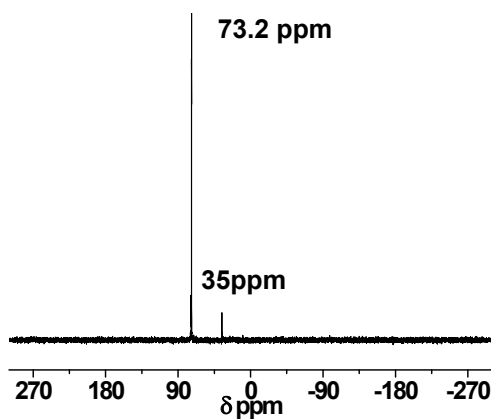


Figure S5. ^{31}P NMR for PFpP produced from MIP of FpP at 105 °C in the presence of DMSO. The polymer was obtained after four successive precipitations from THF solutions into hexane.

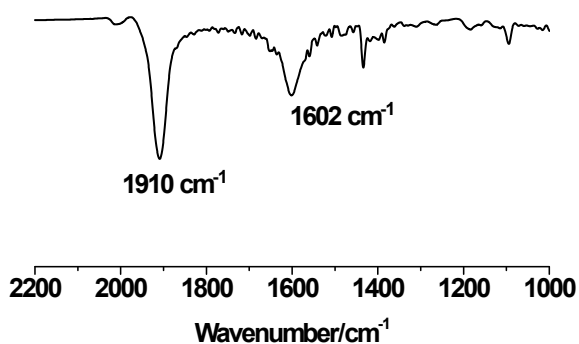


Figure S6. FT-IR of PFpP produced from MIP of FpP at 105 °C in the presence of DMSO.

The presence of the two peaks at 1910 cm⁻¹ and 1602 cm⁻¹ indicates there is no CO loss for the PFpP produced from 105 °C in the presence of DMSO.

References

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