Supplementary Information

An iron-cyclopentadienyl bond cleavage mechanism for the thermal ring-opening polymerization of dicarba[2]ferrocenophanes

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Experimental Details

All reactions were carried out using standard Schlenk line techniques or in an MBraun glove box under dry nitrogen or purified argon. NMR spectra were recorded at ambient temperature on Lambda 300 (^{1}H: 300.5 MHz, ^{13}C: 75.6 MHz), Eclipse 400 (^{1}H: 399.8 MHz, ^{13}C: 100.5 MHz), or Varian 500 (^{1}H: 499.9 MHz, ^{13}C: 125.7 MHz) spectrometers. ^{1}H NMR chemical shifts were referenced to the residual protons of the deuterated solvent (CD_2Cl_2: δ 5.32; $CDCl_3$: δ 7.27); ^{13}C NMR chemical shifts were referenced to residual solvent signals (CD_2Cl_2: δ 54.0; $CDCl_3$: δ 77.0). UV/Vis absorption data were obtained on a Lambda 35 spectrometer employing standard quartz cells (1 cm path length) from 300 to 700 nm with a scan rate of 1 nm s^{-1}. Elemental analyses were carried out by the Laboratory for Microanalysis at the University of Bristol (Model 3000 Euro EA Elemental Analyzer) using V_2O_5 to promote combustion. Mass spectrometry (EI) analyses were carried out on a VG AutoSpec by the Mass Spectrometry Service at the University of Bristol. Silica gel for flash chromatography was purchased from VWR and used as received. Celite 521 was obtained from Sigma-Aldrich and heated to 200 °C for 16 h prior to use. Aluminium oxide (Al_2O_3, activated, neutral, Brockmann I, STD grade, approx. 150 mesh, 58 Å) was purchased from Sigma-Aldrich. Anhydrous $FeCl_2$ was used as received from Strem Chemicals and stored under an atmosphere of dry argon. 6-cyclohexylfulvene and 6-phenylfulvene were prepared by the method of Little and Stone.[1] Flytrap ligands $Li_2[(C_5H_4)_2(CH_2)_2]$,[2] $Li_2[(C_5H_4)_2(CD_2)_2]$,[2] *meso*-$Li_2[(C_5H_4)_2(CHCy)_2]$,[3] and *meso/rac*-$Ca(THF)_2[(\eta^5\text{-}C_5H_4)_2(CHPh)_2]$[4] were prepared according to previously published protocols with the exception that sliced Na metal rather than Na sand was used to prepare the Cy salt. For the preparation of $Li_2\{[C_5H_4]_2[CH(Ph)CH_2]\}$, an adapted synthetic protocol was employed.[2] Yields did not generally exceed 10 % due to predominant formation of the undesired spirocyclic byproduct 1-phenylspiro[2,4]hepta-4,6-diene.

Dicarba[2]ferrocenophane **15**[5] and magnesocene ($MgCp_2$)[6] were prepared according to literature procedures. Polymerization initiator NaCp was prepared via the method reported by Roesky and coworkers, and then purified by precipitating a THF solution of NaCp into dry hexanes.[7]

Thermolysis Experiments

Thermolysis experiments were carried out in a Memert oven fitted with a rocking stage. Samples were sealed in evacuated Pyrex tubes and wrapped in metal mesh as a precaution. Sealed samples should be handled with appropriate heat-proof gloves and face protection.

Photolysis Experiments

Photoirradiation experiments were carried out with Pyrex-glass filtered emission from a 125 W medium-pressure mercury lamp (Photochemical Reactors Ltd.). The emission lines of the mercury lamp were as follows: 577-579, 546, 436, 408-405, 366-365, 334, 313, 302, 297, 289, 280, 270, 265, 254 nm. An ethylene glycol/water bath in conjunction with a thermostat was used to maintain constant temperatures during the photolysis experiments.

Gel Permeation Chromatography (GPC)

Molecular weights of polymers and polydispersity indices ($PDI = M_w / M_n$) of all polymers were obtained by Gel Permeation Chromatography (GPC) using a Viscotek VE 2001 Gel Permeation Chromatograph equipped with automatic sampler, pump, injector, in-line degasser, column oven (30 °C), styrene/divinylbenzene columns with pore sizes of 500 Å and 100,000 Å, and VE 3580 refractometer. THF stabilized with 0.025 % butylated hydroxytoluene (Fisher) was used as the chromatography eluent, at a flow rate of 1.0 mL min^{-1}. Samples were dissolved in the eluent (2 mg mL^{-1}) and filtered (Acrodisc, PTFE membrane, 0.45 μm) before analysis. Calibration of the refractive index detector was performed using polystyrene standards (Viscotek).

MALDI-TOF Mass Spectrometry

MALDI-TOF mass spectra were collected on a 4700 Proteomics Analyzer (Applied Biosystems) equipped with a Nd:Yag laser, operating at 335 nm. Positive ion mass spectra were obtained in linear and reflector mode over a range of *m/z* values. Each spectrum was an accumulation of 10000 laser shots over 50 points on the sample (200 shots/point). Laser intensity was varied. THF solutions of the samples (1 mg mL^{-1}), dithranol (10 mg mL^{-1} THF solution), and sodium trifluoroacetate (1 mg mL^{-1}) were prepared. These were mixed in a 10:10:1 ratio and the resulting solutions were drop-cast by micropipette into sample wells and allowed to evaporate before sample analysis.

Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) studies were carried out using an EG & G model 273A potentiostat linked to a PC using EG&G model 270 Research Electrochemistry software in conjunction with a three-electrode cell or using a BASi Epsilon electrochemical workstation. The working electrode was a glassy carbon disc (3.0 mm diameter), and the auxiliary electrode a platinum wire. The reference electrode was a saturated calomel electrode separated from the test solution by a fine porosity frit and an agar bridge saturated with KCl. Cyclic voltammograms were obtained in dry dichloromethane with 0.1 M NBu_4PF_6 as supporting electrolyte at scan rates of 200 mV s^{-1} and 1 mM in analyte. CVs were referenced to the $[Fe(\eta^5\text{-}C_5H_5)_2]/[Fe(\eta^5\text{-}C_5H_5)_2]^+$ redox couple using $[Fe(\eta^5\text{-}C_5Me_5)_2]$ as an internal standard. The $[Fe(\eta^5\text{-}C_5Me_5)_2]/[Fe(\eta^5\text{-}C_5Me_5)_2]^+$ redox couple was determined to be -540 mV relative to the

$[Fe(\eta^5\text{-}C_5H_5)_2]/[Fe(\eta^5\text{-}C_5H_5)_2]^+$ redox couple in an independent experiment conducted under identical conditions.

Thermal Analysis

DSC analyses were performed on a TA Instruments Q100 coupled to a RCS90 refrigerated cooling system at a heating rate of 10 °C min^{-1}. TGA analyses were performed under a flow of N_2 on a TA Instruments Q100 at a heating rate of 10 ºC min^{-1}. The DSC samples were placed in non-hermetic aluminum pans, and were tared using a XT220A Precisa microbalance prior to analysis. TGA experiments were conducted in Pt pans.

X-ray Structure Determination

Single crystals of ***meso*-13** suitable for X-ray diffraction analysis deposited from a 1:1 THF: hexanes solution of ***meso*-13** at -30 °C. Single crystals of **15** and ***d*$_4$-17** suitable for X-ray diffraction analysis deposited from a 1:4 THF: hexanes solution of **15** or ***d*$_4$-17** respectively, at -40 °C. X-ray diffraction experiments on crystals of ***meso*-13**, **15**, and ***d*$_4$-17** were carried out at 100 K on a Bruker APEX II kappa diffractometer using Mo-K$_\alpha$ radiation (λ = 0.71073 Å). Data collections were performed using a CCD area detector from a single crystal mounted on a glass fiber. Intensities were integrated[8] from several series of exposures measuring 0.5° in ω. Absorption corrections were based on equivalent reflections using SADABS,[9] and structures were refined against all F_o^2 data with hydrogen atoms riding in calculated positions using SHELXTL.[10] Crystal structure and refinement data are given in Table S1.

Synthesis of *meso/rac*-[Fe(η^5-C_5H_4)$_2$(CHPh)$_2$] (*meso/rac*-7)

In a Schlenk flask, *meso/rac*-Ca(THF)$_2$[(η^5-C_5H_4)$_2$(CHPh)$_2$] (2.000 g, 4.060 mmol) was combined with anhydrous $FeCl_2$ (0.515 g, 4.06 mmol) and cooled to -78 °C. 250 mL of freshly distilled THF (Na / benzophenone) was also cooled to -78 °C and added via wide-bore cannula to the flask. The mixture was left to slowly warm to room temperature with stirring for 16 h before it was concentrated to ~ 30 mL and toluene (100 mL) was transferred to the residue. The toluene solution was then passed over a fritted filter containing celite (1” x 1”) giving a clear orange filtrate which was purified further by passing the toluene solution through a short alumina column (6” x 1”). The resulting orange solution was collected and dried *in vacuo* yielding ***meso*/*rac*-7** as an orange powder. Yield = 1.213 g, 82 %. Melting point: 134-136 °C. ^{1}H NMR (399.8 MHz, $CDCl_3$, 25 °C): *rac*-isomer δ = 7.28 - 7.11 (br m, 10H, C_6H_5, overlaps with *meso*-isomer), 5.19-5.17 (m, 2H, η^5-C_5H_4), 4.81-4.79 (m, 2H, η^5-C_5H_4), 4.63 (s, 2H, -C*H*(Ph)-), 4.33-4.30 (m, 2H, η^5-C_5H_4), 3.98-3.95 ppm (m, 2H, η^5-C_5H_4); *meso*-isomer δ = 7.28 - 7.11 (br m, 10H, C_6H_5, overlaps with *rac*-isomer), 5.43 (s, 2H, bridge -C*H*(Ph)-), 4.99-4.95 (m, 2H, η^5-C_5H_4), 4.72-4.69 (m, 2H, η^5-C_5H_4), 4.13-4.10 (m, 2H, η^5-C_5H_4), 4.04-4.02 (m, 2H, η^5-C_5H_4). The ratio of *meso:rac* isomers was determined to be 45:55 by integrating the -C*H*(Ph)- signal from the ^{1}H NMR spectrum of the compound mixture. ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 25 °C): *rac*-isomer δ = 142.7 (C_{ipso} C_6H_5), 128.4, 127.7, 126.7 (C_6H_5), 88.9 (C_{ipso} η^5-C_5H_4), 75.5, 71.7, 69.8, 67.7 (η^5-C_5H_4), 59.1 (-*C*H(Ph)-); *meso*-isomer δ = 141.3 (C_{ipso} η^5-C_6H_5), 129.0, 128.0, 125.7 (C_6H_5), 90.4 (C_{ipso} η^5-C_5H_4), 73.7, 72.2, 69.6, 69.1 (η^5-C_5H_4), 55.3 (-*C*H(Ph)-). UV/Vis (THF): λ_{max} (ε) = 465 nm (390 M^{-1} cm^{-1}). EIMS accurate mass (+ mode): calcd for $^{56}Fe^{12}C_{24}H_{20}$: 364.0914; found 364.0915; fit +0.3 ppm. Elemental analysis Found: C, 79.48; H, 6.03. Calc. for $FeC_{24}H_{20}$: C, 79.13; H, 5.53 %.

Synthesis of ***meso*-[Fe(η^5-C_5H_4)$_2$(CHCy)$_2$] (*meso*-13)**

In a Schlenk flask, $Li_2[(C_5H_4)_2(CHCy)_2]$ (0.881 g, 2.62 mmol) was combined with anhydrous $FeCl_2$ (0.352 g, 2.78 mmol) and cooled to -78 °C. 250 mL of freshly distilled THF (Na / benzophenone) was also cooled to -78 °C and added via a wide-bore cannula to the flask. The mixture was left to slowly warm to room temperature with stirring for 16 h. After removal of the solvent *in vacuo* the brown residue was taken into CH_2Cl_2 and filtered through an alumina column (1" x 5") to give a red solution. The CH_2Cl_2 was removed *in vacuo*, and the residue recrystallized by slow cooling (-30 °C) a saturated 1:1 THF:hexanes solution of ***meso*-13** to yield dark orange-red crystals. Yield = 0.426 g, 43 %. Melting point = 149-151 °C. ^{1}H NMR (300.5 MHz, $CDCl_3$, 25 °C): δ = 4.81-4.80 (m, 2H, η^5-C_5H_4), 4.53-4.52 (m, 2H, η^5-C_5H_4), 3.96-3.94 (m, 4H, η^5-C_5H_4), 3.42-3.36 (m, 2H, -C*H*(Cy)-), 1.99-1.16 (m, 22H, C_6H_{11}) ppm. $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$, 25 °C): δ = 91.26 (C_{ipso} η^5-C_5H_4), 74.2, 71.2, 69.2 and 67.7 (η^5-C_5H_4), 55.7 (-*C*H-bridge), 39.3, 33.9, 31.7, 27.0, 26.9 and 26.6 (C_6H_{11}) ppm. UV/Vis (THF): λ_{max} (ε) = 448 nm (560 $M^{-1}cm^{-1}$). EIMS accurate mass (+ mode): calcd for $^{56}Fe^{12}C_{24}H_{32}$: 376.1853; found 376.1860; fit +1.8 ppm. Elemental analysis Found: C, 77.07; H, 8.57. Calc. for $FeC_{24}H_{32}$: C, 76.59; H, 8.57 %.

Synthesis of {Fe[η^5-C_5H_4]$_2$[CH(Ph)CH_2]} (15)

In a Schlenk flask, $Li_2\{[C_5H_4]_2[CH(Ph)CH_2]\}$ (1.153 g, 4.683 mmol) was combined with anhydrous $FeCl_2$ (0.594 g, 4.68 mmol) and cooled to -78 °C. 250 mL of freshly distilled THF (Na / benzophenone) was also cooled to -78 °C and added via a wide-bore cannula to the flask. The mixture was left to slowly warm to room temperature with stirring for 16 h before it was concentrated to *ca.* 30 mL and treated with toluene (100 mL). The dark orange toluene solution was then concentrated to *ca.* 50 mL before it was passed through a short alumina column (6" x 1") yielding an orange solution. The solvent was removed and the residue sublimed at 80 °C under dynamic vacuum to give **15** as an orange microcrystalline solid, leaving behind a red-brown residue. X-ray quality crystals were grown by slow cooling (-40 °C) a 1:4 THF:hexane solution of **15**. Yield = 0.204 g, 15 %. Melting point = 107-109 °C. ^{1}H NMR (399.8 MHz, $CDCl_3$, 25 °C): δ = 7.39-7.19 (br m, 5H, C_6H_5), 5.05-5.03 (m, 1H, η^5-C_5H_4), 5.00-4.98 (m, 1H, η^5-C_5H_4), 4.82-4.80 (m, 1H, η^5-C_5H_4), 4.72-4.70 (m, 1H, η^5-C_5H_4), 4.67 (d of d, 1H, $^3J_{HH}$ = 12 Hz, $^3J_{HH}$ = 8 Hz, bridge -C*H*(Ph)-), 4.24-4.18 (m, 2H, η^5-C_5H_4), 3.89-3.87 (m, 2H, η^5-C_5H_4), 3.39 (d of d, 1H, $^2J_{HH}$ = 14 Hz, $^3J_{HH}$ = 8 Hz, diastereotopic CH_2), 3.31 ppm (d of d, 1H, $^2J_{HH}$ = 14 Hz, $^3J_{HH}$ = 12 Hz, diastereotopic CH_2). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 143.3 (C_{ipso} η^5-C_6H_5), 128.3, 126.8, 126.2 (C_6H_5), 92.6, 84.5 (C_{ipso} η^5-C_5H_4), 75.7, 75.4, 70.8, 70.3, 69.5, 67.5, 66.8 (C_5H_4), 51.7 (bridge -*C*H(Ph)-), 41.8 ppm (bridge -CH_2-). UV/Vis (THF): λ_{max} (ε) = 469 nm (440 $M^{-1}cm^{-1}$). EIMS accurate mass (+ mode): calcd for $^{56}Fe^{12}C_{18}H_{16}$: 288.0601; found 288.0602; fit +0.3 ppm. Elemental analysis Found: C, 75.45; H, 5.67. Calc. for $FeC_{18}H_{16}$: C, 75.02; H, 5.60 %.

Synthesis of [Fe(η^5-C_5H_4)$_2$(CD_2)$_2$] (*d$_4$*-17)

In a Schlenk flask, $Li_2[(C_5H_4)_2(CD_2)_2]$ (0.900 g, 5.17 mmol) was combined with anhydrous $FeCl_2$ (0.660 g, 5.21 mmol) and cooled to -78 °C. 250 mL of freshly distilled THF (Na / benzophenone) was also cooled to -78 °C and added via a wide-bore cannula to the flask. The mixture was left to slowly warm to room temperature with stirring for 16 h. The solution was then taken to dryness *in vacuo*, and the residues were extracted with 2 x 100 mL dry hexanes which were filtered over Celite leaving a red solution. The solvent was removed and the remaining residue sublimed at RT under dynamic vacuum to give ***d$_4$*-17** as a red crystalline solid, leaving behind a brown residue. X-ray quality crystals were grown by slow cooling (-40 °C) a 1:4 THF:hexane solution of ***d$_4$*-17**. Yield = 1.030 g, 92 %. Melting point: 111-113 °C. ^{1}H NMR (499.9 MHz, CD_2Cl_2, 25 °C): δ = 4.84-4.79 (m, 4H, η^5-C_5H_4), 3.92-

3.88 (m, 4H, η^5-C$_5$*H*$_4$); ^{2}H NMR (76.7 MHz, CH$_2$Cl$_2$, 25 °C): δ 2.93 ppm (s, -C*D*$_2$-). ^{13}C{^{1}H} NMR (125.7 MHz, CD$_2$Cl$_2$, 25 °C): δ = 91.9 (C$_{ipso}$ η^5-*C*$_5$H$_4$), 73.1, 68.6 (η^5-*C*$_5$H$_4$), 33.8 ppm (q, ^{2}J$_{CD}$ = 20 Hz, bridge -*C*D$_2$-). UV/Vis (THF): λ_{max} (ε) = 460 nm (410 M^{-1}cm^{-1}). EIMS accurate mass (+ mode): calcd for ^{56}Fe^{12}C$_{12}$H$_8$D$_4$: 216.0539; found 216.0534; fit -2.5 ppm. Elemental analysis Found: C, 67.19; H, 6.00. Calc. for FeC$_{12}$H$_8$D$_4$ (FeC$_{12}$H$_{12}$): C, 66.96; H, 5.70 % (For the hydrogen elemental analysis studies, the instrument employed does not discriminate between deuterium and hydrogen).

Thermolysis of *meso*-[Fe(η^5-C$_5$H$_4$)$_2$(CHCy)$_2$] (*meso*-13)

A sample of ***meso*-13** (0.197 g, 0.523 mmol) was sealed under vacuum in a Pyrex tube and subsequently heated at 300 °C for 1 h with rocking. The material changed from an orange-red solid to a viscous orange-red oil during thermolysis. The tube and its contents were cooled to room temperature, before the oil was analyzed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum confirmed 93 % conversion of ***meso*-13** to **14**. Purification by chromatography over silica gel (1” x 5”) using hexanes as an eluent yielded **14** as an orange viscous oil. Yield = 0.144 g, 76 %. ^{1}H NMR (499.9 MHz, CDCl$_3$, 25 °C): δ = 5.82 (s, 1H, C*H*=C), 4.20-4.14 (m, 2H, η^5-C$_5$*H*$_4$), 4.12-4.05 (m, 2H, η^5-C$_5$*H*$_4$), 4.02-3.97 (m, 2H, η^5-C$_5$*H*$_4$), 3.97-3.93 (m, 2H, η^5-C$_5$*H*$_4$), 2.37-2.34 (m, 2H, -CH$_2$-), 2.24-2.14 (m, 4H, C$_6$*H*$_{10}$), 1.69-1.52 (m, 11H, C$_6$*H*$_{10}$ and C$_6$*H*$_{11}$), 1.29-1.05 (m, 4H, C$_6$*H*$_{10}$ and C$_6$*H*$_{11}$), 0.90-0.79 ppm (m, 2H, C$_6$*H*$_{10}$ and C$_6$*H*$_{11}$). ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$, 25 °C): δ = 140.7 (=*C*), 118.0 (=*C*H), 87.6, 83.4 (C$_{ipso}$ η^5-*C*$_5$H$_4$), 70.1, 69.4, 68.4, 68.1 (η^5-*C*$_5$H$_4$), 40.1 (-*C*H$_2$-), 37.8, 37.7, 33.3, 30.0, 28.8, 27.8, 26.7, 26.5, 26.3 ppm (*C*$_6$H$_{10}$ and *C*$_6$H$_{11}$). UV/Vis (THF): λ_{max} (ε) = 425 nm (222 M^{-1}cm^{-1}). EIMS accurate mass (+ mode): calcd for ^{56}Fe^{12}C$_{24}$H$_{32}$: 376.1853; found 376.1861; fit +2.0 ppm. Elemental analysis Found: C, 76.37; H, 8.64. Calc. for FeC$_{24}$H$_{32}$: C, 76.59; H, 8.57 %.

Thermolysis of *meso/rac*-[Fe(η^5-C_5H_4)$_2$(CHPh)$_2$] (*meso/rac*-7)

A sample of ***meso*/*rac*-7** (0.250 g, 0.688 mmol) was sealed under vacuum in a Pyrex tube and subsequently heated at 250 °C for 16 hours with rocking to give a free-flowing orange liquid. The liquid was cooled and extracted from the tube using THF. The extract was dried *in vacuo* giving ***rac*-7** as an orange microcrystalline solid. The identity of the isolated ***rac*-7** was confirmed by comparison with a previously published ^{1}H NMR spectrum.[11] Yield = 0.250 g, 100 %. Melting point = 232-234 °C. ^{1}H NMR (399.8 MHz, C_6D_6, 25 °C): δ = 7.28 - 7.11 (br m, 10H, C_6H_5), 5.19-5.17 (m, 2H, η^5-C_5H_4), 4.81-4.79 (m, 2H, η^5-C_5H_4), 4.63 (s, 2H, -CH(Ph)-), 4.33-4.30 (m, 2H, η^5-C_5H_4), 3.98-3.95 ppm (m, 2H, η^5-C_5H_4).

Thermolysis of {Fe[η^5-C_5H_4]$_2$[CH(Ph)CH$_2$]} (15)

Dicarba[2]ferrocenophane **15** (0.150 g, 0.521 mmol) was sealed in an evacuated Pyrex tube and heated at 300 °C for 1 hour. After 10 minutes of heating the sample formed a viscous orange liquid, however, after 50 minutes of heating the tube contained an immobile dark orange solid. The tube was cooled and opened in air before its contents were dissolved in a minimal amount of THF and filtered through cotton wool into rapidly stirring methanol (20 mL) in order to precipitate the polymer that had formed. The precipitate was left to settle and was separated from the non-solvent by centrifugation. This process was repeated twice more to yield **16a** as a beige powder which was subsequently dried *in vacuo* for three days at 40 °C. Yield = 0.038 g, 25 %. ^{1}H NMR (499.9 MHz, CD_2Cl_2, 25 °C): δ = 7.25-6.95 (m br, 5H, C_6H_5), 4.10-3.35 (m br, 9H, η^5-C_5H_4 and bridge -C*H*(Ph)-), 3.10-2.60 ppm (m br, 2H, bridge CH_2). ^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2, 25 °C): δ = 145.8 (C_{ipso} C_6H_5), 128.7, 128.5, 126.6 (br, C_6H_5), 94.5, 87.5 (C_{ipso} η^5-C_5H_4), 70.5, 69.8, 69.0, 68.4 (η^5-C_5H_4), 49.3 (bridge -*C*H(Ph)-), 38.6 ppm (bridge -*C*H$_2$-). UV/Vis (THF): λ_{max} (ε) = 430 nm

(250 $M^{-1}cm^{-1}$). Elemental analysis Found: C, 75.98; H, 5.95. Calc. for $[FeC_{18}H_{16}]_n$: C, 75.02; H, 5.60 %. GPC: M_n = 4,210 g mol^{-1}, M_w = 13,760 g mol^{-1}, PDI = 3.27.

Photocontrolled ROP of {Fe[η^5-C_5H_4]$_2$[CH(Ph)CH_2]} (15)

Low molecular weight sample:

In a glovebox, dicarba[2]ferrocenophane **15** (0.250 g, 0.866 mmol) was combined with 3.85 mL of freshly distilled THF (Na / benzophenone) and 0.11 M sodium cyclopentadienide (NaCp) in THF (315.0 µL, 0.035 mmol). The sample was then irradiated with stirring for 30 h at 20 °C. The living polymer chains were subsequently quenched with a few drops of degassed methanol. The quenched polymer solution was then added to rapidly stirred MeOH (20 mL) in order to precipitate the polymeric species, leaving behind an orange-red solution (unreacted **15**). This process was repeated twice more to yield **16b** as a pale yellow powder which was subsequently dried *in vacuo* for three days at 40 °C. Yield = 0.150 g, 60 %. ^{1}H NMR (499.9 MHz, CD_2Cl_2, 25 °C): δ = 7.25-6.95 (m br, 5H, C_6H_5), 6.45-5.80 (m, 0.2 H, end group-C_5H_5, C*H*=), 4.10-3.35 (m br, 9H, η^5-C_5H_4, η^5-C_5H_5 end group, and bridge -C*H*(Ph)-), 3.10-2.60 ppm (m br, *ca.* 2.5 H, bridge CH_2 and end group-C_5H_5 CH_2). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2, 25 °C): δ = 146.0, 145.9 145.8 (multiple C_{ipso} C_6H_5 environments), 128.7, 128.5, 126.6 (br, C_6H_5), 94.5, 87.4 (C_{ipso} η^5-C_5H_4), 71.0, 70.6, 70.1, 69.9, 69.8, 69.2, 69.1, 69.0, 68.4, 68.2 (multiple η^5-C_5H_4 environments), 49.3, 49.2 (two bridge -*C*H(Ph)- environments), 38.6 ppm (br, bridge CH_2). GPC: M_n = 3,270 g mol^{-1}, M_w = 3,930 g mol^{-1}, PDI = 1.20.

High molecular weight sample:

In a glovebox, dicarba[2]ferrocenophane **15** (0.325 g, 1.13 mmol) was combined with 5.00 mL of freshly distilled THF (Na / benzophenone) and 0.11 M sodium cyclopentadienide

(NaCp) in THF (250.0 μL, 0.028 mmol). The sample was then irradiated with stirring for 168 h at 20 °C. The living polymer chains were subsequently quenched with a few drops of degassed methanol. The quenched polymer solution was then added to rapidly stirred MeOH (20 mL) in order to precipitate the polymeric species, leaving behind a clear and colourless solution. This process was repeated twice more to yield **16c** as a pale yellow powder which was subsequently dried *in vacuo* for 24 h at 40 °C. Yield = 0.286 g, 88 %. ^{1}H NMR (499.9 MHz, CD_2Cl_2, 25 °C): δ = 7.31-6.95 (m br, 5H, $C_6\mathit{H}_5$), 6.45-5.72 (m, 0.1 H, end group-C_5H_5, C*H*=), 4.10-3.25 (m br, 9H, η^5-$C_5\mathit{H}_4$, η^5-$C_5\mathit{H}_5$ end group, and bridge -C*H*(Ph)-), 3.10-2.50 ppm (m br, *ca.* 2.5 H, bridge $C\mathit{H}_2$ and end group-C_5H_5 $C\mathit{H}_2$). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2, 25 °C): δ = 146.0, 145.9 145.8 (multiple C_{ipso} C_6H_5 environments), 128.7, 128.5, 126.6 (br, C_6H_5), 94.5, 87.5 (C_{ipso} η^5-C_5H_4), 70.9, 70.6, 70.5, 70.0, 69.9, 69.8, 69.2, 69.1, 69.0, 68.6, 68.2 (multiple η^5-C_5H_4 environments), 49.3 (bridge -*C*H(Ph)-), 38.7 ppm (br, bridge $\mathit{C}H_2$). GPC: M_n = 8,850 g mol^{-1}, M_w = 10,670 g mol^{-1}, PDI = 1.21.

Thermolysis of $\{Fe[\eta^5\text{-}C_5H_4]_2[CH(Ph)CH_2]\}_n$ (16c) for 1 h

Polyferrocenylethylene **16c** (0.075g, 0.26 mmol) was sealed in an evacuated Pyrex tube and heated at 300 °C for 1 h. The sample became gel-like upon heating, but remained relatively immobile. Upon cooling, the tube was opened in air and its contents extracted with THF. The resulting solution (no insoluble material present) was then filtered into rapidly stirred methanol (20 mL) in order to precipitate the polymer. This process was repeated twice more, isolating the solid by centrifugation each time, to yield **16d** as a pale yellow powder which was subsequently dried *in vacuo* for 48 h at 40 °C. Yield = 0.560 g, 75 %. ^{1}H NMR (499.9 MHz, CD_2Cl_2, 25 °C): δ = 7.25-6.87 (m br, 5H, $C_6\mathit{H}_5$), 4.05-3.27 (m br, 9H, η^5-$C_5\mathit{H}_4$ and bridge -C*H*(Ph)-), 3.05-2.49 ppm (m br, *ca.* 2.5 H, bridge -$C\mathit{H}_2$-). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2, 25 °C): δ = 146.0, 145.9 145.8 (multiple C_{ipso} C_6H_5 environments), 128.7, 128.5, 126.6 (br, C_6H_5), 94.5, 87.5, 87.3 (C_{ipso} η^5-C_5H_4), 70.9, 70.6, 70.5, 70.1, 70.0, 69.8, 69.2, 69.0, 68.5, 68.0 (multiple η^5-C_5H_4 environments), 49.3 (bridge -*C*H(Ph)-), 38.6 ppm (br, bridge CH_2). GPC: M_n = 10,060 g mol^{-1}, M_w = 15,440 g mol^{-1}, PDI = 1.54.

Thermolysis of $\{Fe[\eta^5\text{-}C_5H_4]_2[CH(Ph)CH_2]\}_n$ (16c) for 3 h.

Polyferrocenylethylene **16c** (0.050 g, 0.17 mmol) was sealed in an evacuated Pyrex tube and heated at 300 °C for 3 h. The sample became gel-like upon heating, but remained relatively immobile. Upon cooling, the tube was opened in air and its contents extracted with THF. The resulting solution (no insoluble material present) was then filtered into rapidly stirred methanol (15 mL) in order to precipitate the polymer. This process was repeated twice more, isolating the solid by centrifugation each time, to yield **16e** as a pale yellow powder which was subsequently dried *in vacuo* for 36 h at 40 °C. Yield = 0.042 g, 84 %. ^{1}H NMR (499.9 MHz, CD_2Cl_2, 25 °C): δ = 7.43-6.76 (m br, 5H, C_6H_5), 4.33-3.29 (m br, 9H, η^5-C_5H_4 and bridge -C*H*(Ph)-), 3.21-2.55 ppm (m br, *ca.* 2.5 H, bridge -CH_2-). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2, 25 °C): δ = 145.9 (br, C_{ipso} C_6H_5), 128.7, 128.5, 126.6 (br, C_6H_5), 94.5, 87.5, 87.3 (C_{ipso} η^5-C_5H_4), 71.0, 70.6, 70.5, 70.1, 70.0, 69.9, 69.7, 69.1, 69.0, 68.8, 68.6, 68.5, 68.4, 68.2 (multiple η^5-C_5H_4 environments), 49.3, 49.2 (bridging -*C*H(Ph)- environments), 38.6 ppm (br, bridge CH_2). GPC: M_n = 14,580 g mol^{-1}, M_w = 23,680 g mol^{-1}, PDI = 1.63.

Thermolysis of $\{Fe[\eta^5\text{-}C_5H_4]_2[CH(Ph)CH_2]\}$ (15) and $[Fe(\eta^5\text{-}C_5H_4)_2(CH_2)_2]$ (17)

Dicarba[2]ferrocenophanes **15** (0.200 g, 0.694 mmol) and **17** (0.200 g, 0.943 mmol) were sealed in an evacuated Pyrex tube and heated at 300 °C for 2 h at which time the contents had become immobile. Upon cooling, the tube was opened in air and its soluble contents extracted with THF. The resulting slurry was then filtered to remove insoluble material, into rapidly stirred methanol (20 mL) in order to precipitate the polymer. This process was repeated twice more, isolating the solid polymer by centrifugation each time, to yield **18** as a pale yellow powder which was subsequently dried *in vacuo* for 48 h at 40 °C. Yield = 0.085 g, 21 %. ^{1}H NMR (499.9 MHz, CD_2Cl_2, 25 °C): δ = 7.34-6.97 (m br, 5H, C_6H_5 from **15**), 4.20-3.40 (m br, 18 H, η^5-C_5H_4 from **15** and **17** and -C*H*(Ph)- bridge from **15**), 3.22-2.74 (m br, 2H, -CH_2- bridge from **15**), 2.51 ppm (s, 5H, -CH_2- bridge from **17**). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2, 25 °C): δ = 145.9 (C_{ipso} C_6H_5), 128.7, 128.5, 126.6 (C_6H_5), 94.6 (C_{ipso} η^5-C_5H_4 from **15**), 89.4 (C_{ipso} η^5-C_5H_4 from **17**), 87.4 (C_{ipso} η^5-C_5H_4 from **15**), 70.5, 69.9, 69.5, 69.2, 68.9, 68.3, 68.0 (overlapping η^5-C_5H_4 from **15** and **17**), 49.4 (-*C*H(Ph)- bridge from **15**), 38.6 (-*C*H_2- bridge from **15**), and 31.9 ppm (-*C*H_2- bridge from **17**). GPC: M_n = 6,740 g mol^{-1}, M_w = 33,720 g mol^{-1}, PDI = 5.01.

Thermolysis of $\{Fe[\eta^5\text{-}C_5H_4]_2[CH(Ph)CH_2]\}$ (15) and $[Fe(\eta^5\text{-}C_5H_4)_2(CD_2)_2]$ (*d₄*-17)

Dicarba[2]ferrocenophanes **15** (0.125 g, 0.434 mmol) and ***d₄*-17** (0.125 g, 0.589 mmol) were sealed in an evacuated Pyrex tube and heated at 300 °C for 30 min at which time the contents had become immobile. Upon cooling, the tube was opened in air and its soluble contents extracted with THF. The resulting slurry was then filtered to remove insoluble material, into rapidly stirred methanol (20 mL) in order to precipitate the polymer. This process was repeated thrice more, isolating the solid by centrifugation each time, to yield ***d₄*-18** as a pale yellow powder which was subsequently dried *in vacuo* for 48 h at 40 °C. Yield = 0.065 g, 23 %. The low yield can be partially attributed to the number of precipitation steps employed whereby significant amounts of ***d₄*-18** were lost on laboratory glassware during manipulation. ^{1}H NMR (499.9 MHz, CD_2Cl_2, 25 °C): δ = 7.34-6.97 (m br, 5H, C_6H_5 from **15**), 4.20-3.40 (m br, 18 H, η^5-C_5H_4 from **15** and ***d₄*-17** and -C*H*(Ph)- bridge from **15**), 3.22-2.74 ppm (m br, 2H, CH_2 bridge from **15**). ^{2}H NMR (76.7 MHz, CH_2Cl_2, 25 °C): δ 2.46 ppm (s br, -CD_2-). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2, 25 °C): δ = 145.9 (C_{ipso} C_6H_5), 128.7, 128.5, 126.6

(C_6H_5), 94.6 (C_{ipso} η^5-C_5H_4 from **15**), 89.3 (C_{ipso} η^5-C_5H_4 from ***d₄*-17**), 87.4 (C_{ipso} η^5-C_5H_4 from **15**), 70.5, 69.9, 69.5, 69.2, 68.9, 68.4, 68.0 (overlapping η^5-C_5H_4 from **15** and ***d₄*-17**), 49.4 (-*C*H(Ph)- bridge **15**), 38.5 (-CH_2- bridge from **15**), and 31.6-31.8 ppm (m, -CD_2- bridge from ***d₄*-17**). GPC: M_n = 4,730 g mol^{-1}, M_w = 16,440 g mol^{-1}, PDI = 3.47.

Thermolysis of [Fe(η^5-C_5H_4)$_2$(CH_2)$_2$] (17) and 5 equiv. of MgCp$_2$

A sample of **17** (0.342 g, 1.61 mmol) was combined with MgCp$_2$ (1.242 g, 8.040 mmol, 5 equiv.) and sealed under vacuum in a Pyrex tube. The tube was heated at 300 °C with rocking for 1 hour. After 5 min, the sample melted forming a free-flowing red reaction mixture. No further change in the appearance of the reaction mixture was observed during the heating period. The sample was then allowed to cool, the tube opened under an inert atmosphere and the product extracted in dry and degassed THF (15 mL). The solution was cooled to 0 °C and de-gassed H_2O (15 mL) was added to quench any remaining MgCp$_2$. The THF was removed *in vacuo* and the product extracted into CH_2Cl_2 (3 x 20 mL). The CH_2Cl_2 washings were combined, dried over $MgSO_4$, filtered, and the solvent removed *in vacuo* to yield an orange/yellow crystalline solid. Flash chromatography over silica gel eluted the products as the second band in 40/60 CH_2Cl_2/hexane (R_f = 0.67). Removal of the solvent yielded a mixture of **19a,b** as a yellow crystalline solid. Yield = 0.440 g, 98 %. The identity of isomers (**19a**) and (**19b**) was confirmed by comparison with a previously published ^{1}H NMR spectrum.[12] The ratio of **19a** to **19b** was calculated to be 1:1.3 by comparison of ^{1}H NMR integration data. ^{1}H NMR (400.2 MHz, CD_2Cl_2, 25 °C): δ 6.49-6.46 (m, 1H, pendant-C_5H_5, C*H*=, **19a**), 6.44-6.43 (m, 1H, pendant-C_5H_5, C*H*=, **19a** overlapped with signal from **19b**), 6.44-6.42 (m, 1H, pendant-C_5H_5, C*H*=, **19b** overlapped with signal from **19a**), 6.27-6.25 (m, 1H, pendant-C_5H_5, C*H*=, **19b**), 6.19-6.17 (m, 1H, pendant-C_5H_5, C*H*=, **19b**), 6.05-6.03 (m, 1H, pendant-C_5H_5, C*H*=, **19a**), 4.10 (s, 10H, η^5-C_5H_5, **19a/19b**), 4.10-

4.07 (m br, 4H, η^5-C_5H_4, **19a/19b**), 4.05-4.03 (m br, 4H, η^5-C_5H_4, **19a/19b**), 2.97-2.95 (m br, 2H, pendant-C_5H_5, -CH_2-, **19a**), 2.91-2.90 (m br, 2H, pendant-C_5H_5, -CH_2-, **19b**), 2.66-2.61 (m br, 2H, -CH_2- adjacent to pendant-C_5H_5, **19b**), 2.59-2.57 (m br, 4H, -CH_2-, **19a** overlapped), 2.57-2.54 ppm (m br, 2H, -CH_2- adjacent to η^5-C_5H_5, **19b** overlapped). EIMS accurate mass (+ mode): calcd for $^{56}Fe^{12}C_{17}H_{18}$: 278.0758; found 278.0760; fit +0.8 ppm.

Thermolysis of {Fe[η^5-C_5H_4]$_2$[CH(Ph)CH$_2$]} (15) and 5 equiv. of MgCp$_2$

A sample of **15** (0.100 g, 0.347 mmol) was combined with $MgCp_2$ (0.263 g, 1.74 mmol, 5 equiv.) and sealed under vacuum in a Pyrex tube. The tube was heated at 300 °C for 1 hour with rocking. After 5 min, the sample melted forming a free-flowing red reaction mixture. No further change in the appearance of the reaction mixture was observed during the heating period. The sample was then allowed to cool, the tube opened under an inert atmosphere and the product extracted into dry THF (15 mL). The solution was cooled to 0 °C and de-gassed H_2O (10 mL) was added. The THF was removed *in vacuo* and the product extracted into CH_2Cl_2 (3 x 20 mL). The CH_2Cl_2 washings were combined, dried over $MgSO_4$, filtered and the solvent removed *in vacuo* to yield an orange oil. Flash chromatography over silica gel (9” x 1”) eluted the products as the first band in 18/72 CH_2Cl_2/hexane (R_f = 0.59). Removal of the solvent yielded a mixture of four isomers **20a-d** as an orange oil. Yield = 0.066 g, 54 %. In addition, a large amount of colored material was observed to have a strong interaction with the silica column, possibly as a result of oxidation on the column. Due to overlapping of signals, individual proton resonances could not be distinguished using multinuclear ^1H-^1H, ^1H-^{13}C HMQC spectroscopy at 25 °C. Therefore, the following NMR spectra have been assigned as regions. ^1H NMR (499.9 MHz, CD_2Cl_2, 25 °C): δ 7.28-7.13 (m br, 5H, C_6H_5), 6.43-5.87 (m br, 3H, C*H*=, pendant-C_5H_5), 4.22-3.76 (m, br, 10 H, η^5-C_5H_4 and -C*H*(Ph)- bridge), 3.85-2.68 ppm (m, br, 4H, -CH_2- bridge and -CH_2- pendant-C_5H_5).

^{13}C NMR (125.7 MHz, CD_2Cl_2, 25 °C): δ 153.0, 150.5, 148.3, 146.1, 146.0, 145.8, 145.6, 144.8 (C_{ipso} C_6H_5 and C= pendant-C_5H_5), 135.3, 134.5, 134.3, 133.8, 132.7, 132.5, 131.8, 131.4 (CH= pendant-C_5H_5), 128.8, 128.7, 128.6, 128.4, 128.3, 127.0, 126.7, 126.5 (C_6H_5 and CH= pendant-C_5H_5), 95.0, 94.9, 87.7, 87.6 (C_{ipso} η^5-C_5H_4), 69.8, 69.7, 69.5, 69.4, 69.3, 69.2, 69.1, 69.0, 68.2, 68.1, 67.6, 67.6, 67.5, 67.3, 67.2 (η^5-C_5H_4), 50.5, 49.6, 47.4, 46.4 (-CH(Ph)), 44.2, 43.0, 41.7, 41.7, 38.5, 37.7, 36.8, 36.3 ppm (-CH_2- bridge and -CH_2- pendant-C_5H_5). UV/Vis (THF): λ_{max} = 420 nm (105 M^{-1} cm^{-1}). EIMS accurate mass (+ mode): calcd for $^{56}Fe^{12}C_{23}H_{22}$: 354.1071; found 354.1080; fit +2.6 ppm. Elemental analysis: Found C, 78.27; H, 6.16. Calc. for $FeC_{23}H_{22}$: C, 77.98; H, 6.26 %.

Thermolysis of {Fe[η^5-C_5H_4]$_2$[CH(Ph)CH_2]} (15) and 0.5 equiv. of $MgCp_2$

A sample of **15** (0.180 g, 0.622 mmol) was combined with $MgCp_2$ (0.048 g, 0.31 mmol, 0.5 equiv.) and sealed under vacuum in a Pyrex tube. The tube was heated at 300 °C for 1 hour with rocking. After 5 min, the sample melted forming a free-flowing red reaction mixture. No further change in the appearance of the reaction mixture was observed during the heating period. The sample was then allowed to cool, the tube opened under an inert atmosphere and the product extracted into dry and degassed THF (15 mL). The solution was cooled to 0 °C and de-gassed H_2O (20 mL) was added. The THF was removed *in vacuo* and the product extracted into CH_2Cl_2 (3 x 20 mL). The CH_2Cl_2 washings were combined, dried over $MgSO_4$, filtered and the solvent removed *in vacuo* to yield an orange oil. Flash chromatography over silica gel (9” x 1”) eluted monomeric products **20a-d** as the first band in 15/85 CH_2Cl_2/hexane (R_f = 0.59), dimeric products **20e** as the second band in 35/65 CH_2Cl_2/hexane and trimeric products **20f** as the third band in CH_2Cl_2. The solvent was removed to leave the products as orange oils in the following yields; **20a-d** (0.035 g, 16 %), **20e** (0.023 g, 12 %) and **20f** (0.020 g, 11 %). In addition, a large amount of colored material was observed to have a strong interaction with the silica column, possibly as a result of oxidation on the column. ^{1}H and ^{13}C NMR spectra of **20a-d** were identical to that of samples previously isolated. Analysis of **20e** and **20f** resulted in qualitatively similar ^{1}H and ^{13}C NMR spectra to **20a-d**. We have not completely assigned the ^{1}H and ^{13}C NMR spectra of these products, due to complications arising from the number of isomers present in both **20e** (8 isomers) and **20f** (16 isomers). EIMS (+ mode): calcd for $^{56}Fe^{12}C_{23}H_{22}$ (**20a-d**): 354.0; found 354.2 (45 %); calcd for $^{56}Fe_2{}^{12}C_{41}H_{39}$ (**20e**): 643.4; found 643.2 (87 %); calcd for $^{56}Fe_3{}^{12}C_{59}H_{55}$ (**20f**): 931.6; found 931.2 (38 %).

Table S1 Crystallographic data for ***meso*-13**, **15**, and ***d₄*-17**.

Compound	***meso*-13**	**15**	***d₄*-17**
Color, Habit	red plate	orange block	orange block
Size / mm	0.17 × 0.1 × 0.05	0.32 × 0.17 × 0.17	0.16 × 0.13 × 0.08
Empirical Formula	$C_{24}H_{32}Fe$	$C_{18}H_{16}Fe$	$C_{12}H_8D_4Fe$
MW	376.35	288.16	216.10
Crystal System	triclinic	monoclinic	orthorhombic
Space Group	$P\bar{1}$	$P2_1/c$	*Pbca*
a / Å	9.731(3)	8.2905(9)	7.3925(3)
b / Å	11.057(4)	11.7186(13)	12.3693(6)
c / Å	18.275(5)	13.8485(15)	19.4209(9)
α / °	89.321(18)	90.0	90.0
β / °	76.443(17)	106.910(4)	90.0
γ / °	87.163(19)	90.0	90.0
V / Å^3	1909.2(10)	1287.3(2)	1775.85(14)
Z	4 (Z'=2)	4	8
μ / mm^{-1}	0.793	1.152	1.638
T / K	100	100	100
$\theta_{min,max}$	1.15, 33.64	2.32, 27.57	2.10, 27.56
Completeness	0.999 to θ = 27.50°	0.998 to θ = 27.57°	1.000 to θ = 27.56°
Reflections: total / independent	41476 / 12598	25329 / 2976	17837 / 2048
R_{int}	0.0453	0.0241	0.0250
Final $R1$ and $wR2$	0.0442, 0.1127	0.0283, 0.0737	0.0222, 0.0591
Largest Peak, hole / Å^{-3}	0.472, -0.481	0.983, -0.315	0.320, -0.328
ρ_{calc} / g cm^{-3}	1.309	1.487	1.616

Additional Figures S1-S5

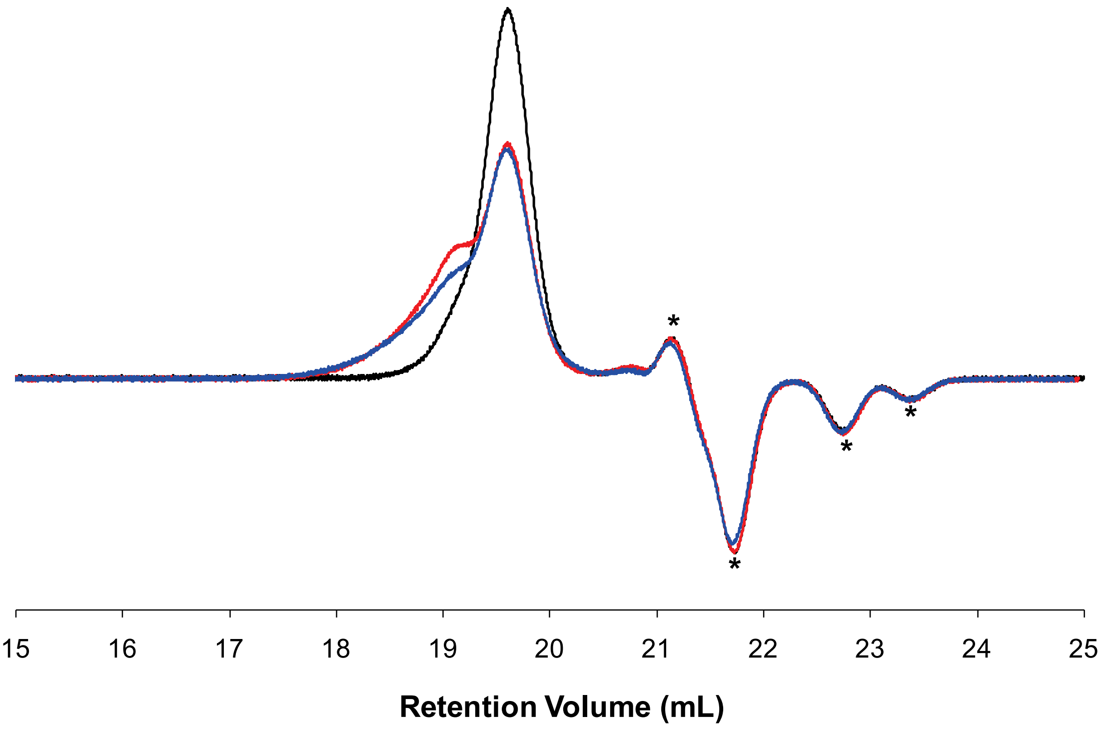

Fig. S1 GPC traces for homopolymer **16c** synthesized via photocontrolled ROP (black), homopolymer **16d** synthesized via thermolysis of **16c** for 1 h at 300 °C (red), and homopolymer **16e** synthesized via thermolysis of **16c** for 3 h at 300 °C (blue). Asterisks donate fluctuations in RI associated with sample injections.

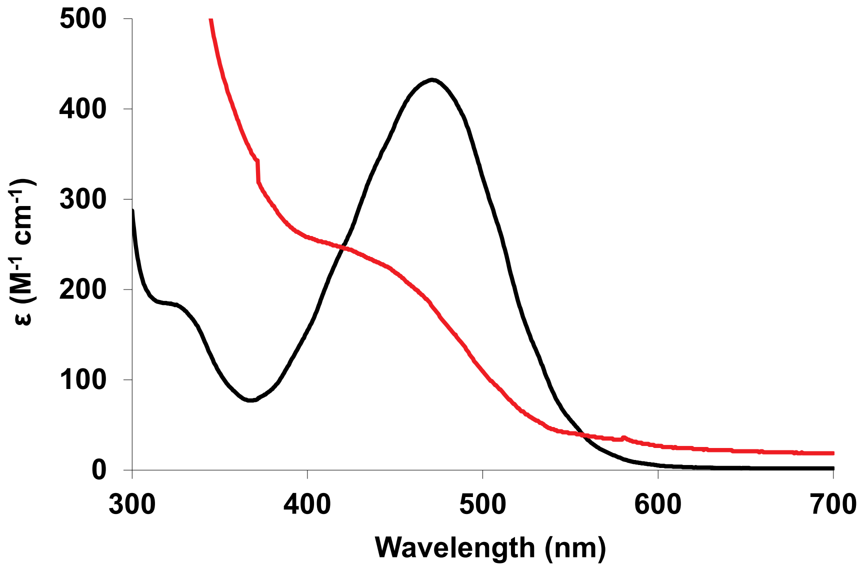

Fig. S2 UV/Vis spectra for **15** (black) and **16a** (red) in THF.

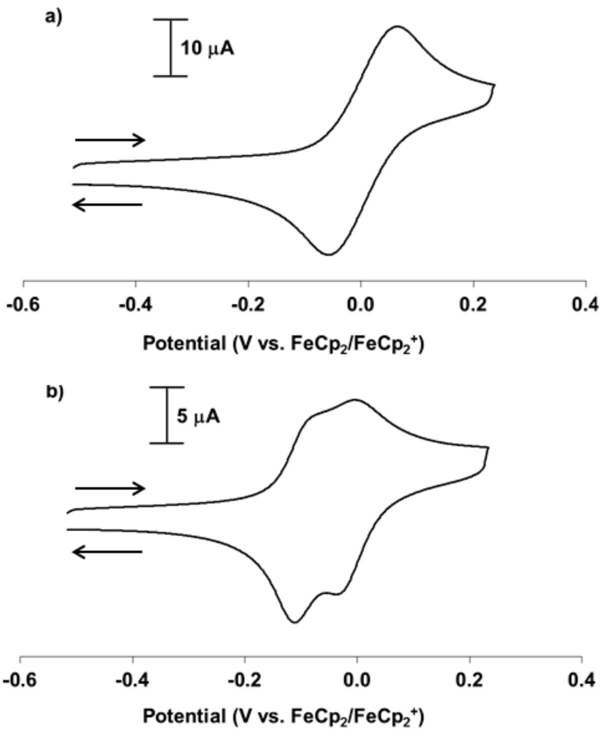

Fig. S3 Cyclic voltammograms of CH_2Cl_2 solutions of a) **15** and b) **16a** (*ca.* 1 mM monomer/repeat unit, 0.1 M nBu_4NPF_6, scan rate = 200 mV s^{-1}) referenced versus the $FeCp_2/FeCp_2^+$ redox couple.

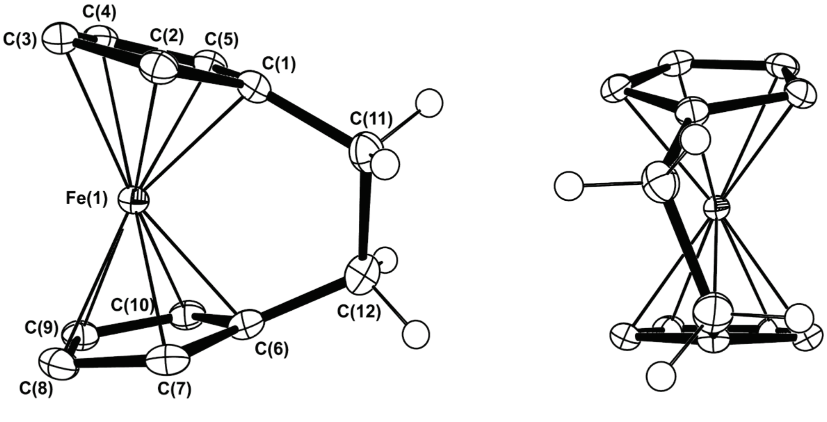

Fig. S4 Solid-state structure of ***d*₄-17**. Thermal ellipsoids shown at 50% probability level. For clarity, only deuterium atoms on the bridging carbons are shown. Selected bond lengths (Å) and angles (deg): C1-C11 = 1.518(2), C11-C12 = 1.551(2), C6-C12 = 1.525(2), C1-C11-C12 = 110.7(1), C6-C12-C11 = 111.1(1).

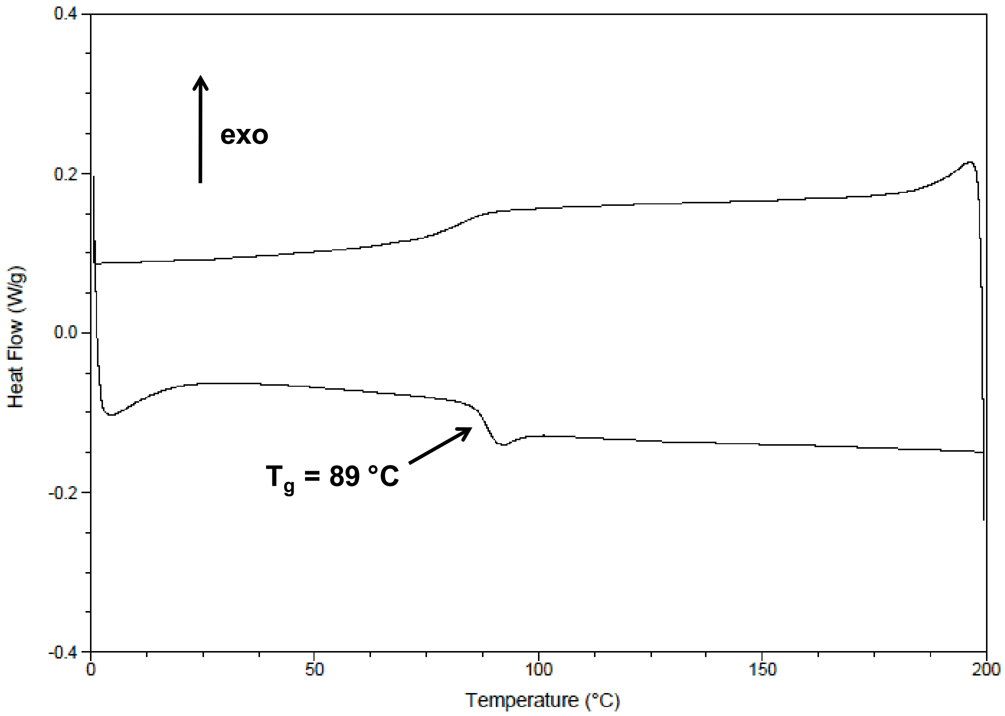

Fig. S5 DSC thermogram of **16a** (6.40 mg) at a scan rate of 10 °C min^{-1}. Only one T_g at *ca.* 89 ºC was observed.

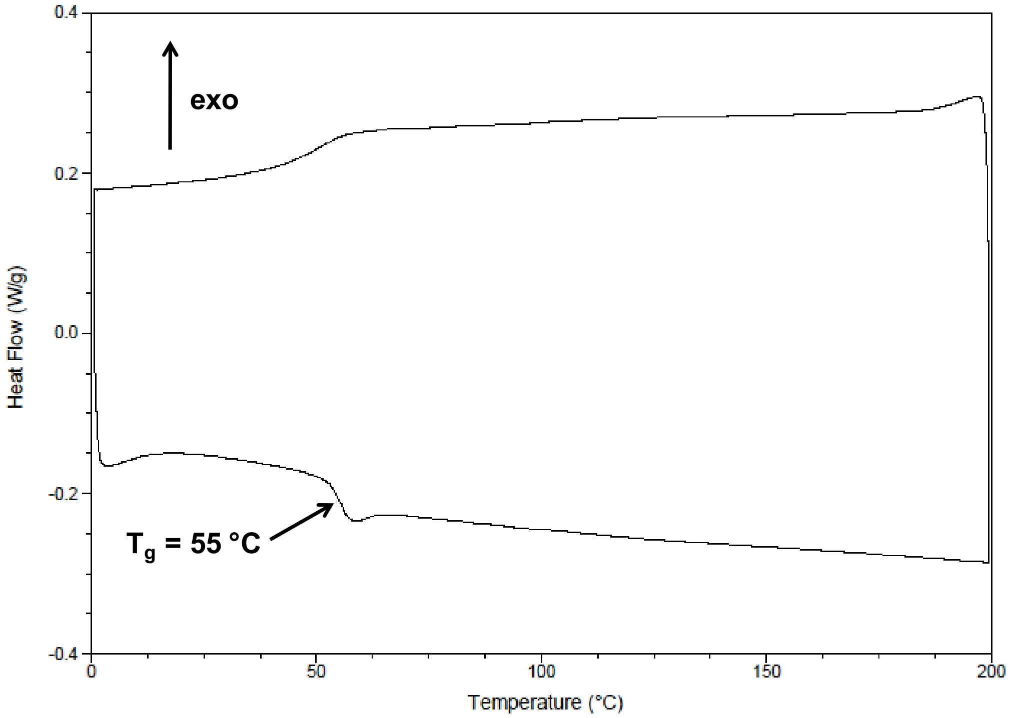

Fig. S6 DSC thermogram of ***d*$_4$-18** (5.20 mg) at a scan rate of 10 °C min^{-1}. Only one T_g at *ca.* 55 ºC was observed.

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