Diblock Metallocopolymers Containing Various Iron Sandwich Complexes:
Living ROMP Synthesis and Selective Reversible Oxidation

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1. General data

Cis-5-norbornene-exo-2,3-dicarboxylic anhydride (95%, NDA), ethyl vinyl ether (99%, EVE) and Grubbs 2nd generation catalyst were purchased from Aldrich, and used directly. Grubbs 3rd generation catalyst 1, s1 chlorocarbonyl ferrocene (FcCOCl), s2 N-[11'-amine-3',6',9'-trioxahendecyl]-cis-5-norbornene-exo-2,3-dicarboximide 5, s2 ferrocene-containing monomer 7, s2 chlorocarbonyl pentamethylferrocene (Fe*COCl), s3 ferrocene-containing monomer 7, s2 chlorocarbonyl mixed-sandwich iron complex [(η^6-C_6Me_6)Fe(η^5-C_5H_4COCl)][PF_6], s4 N-(2-aminoethyl)-cis-5-norbornene-exo-2, 3-dicarboximide 6, s5 and the cationic organoiron monomer 9 were prepared by the method reported in the literatures. All the other chemicals were from commercial sources and used as received. All the solvents used were dried and freshly distilled.

^1H NMR (300, 400 or 600 MHz) and ^13C NMR (50, 75 or 150 MHz) spectra were recorded at 25 °C with a Bruker AC (200, 300, 400 or 600 MHz) spectrometers. All the chemical shifts are reported in parts per million (δ, ppm) with reference to tetramethylsilane (TMS). Mass spectra were recorded using an Applied Biosystems Voyager-DE STR-MALDI-TOF spectrometer. The infrared spectra were recorded on an ATI Mattson Genesis series FT-IR spectrophotometer in the range 400-4000 cm\(^{-1}\). UV-visible absorption spectra were measured with a Perkin-Elmer Lambda 19 UV-vis. spectrometer.

Cyclic voltammetry (CV) measurements was recorded on a PAR 273 potentiostat under nitrogen atmosphere at 20 °C using dry dichloromethane (CH_2Cl_2) or dimethylformamide (DMF) as solvent and [n-Bu_4N][PF_6] 0.1M as supporting electrolyte. The working and counter electrodes were Pt, and the reference electrode was Ag. The internal reference was [FeCp*]_2 (Cp* = η^5-C_5Me_5), and the scan rate was 400 mV.s\(^{-1}\). The Bard-Anson electrochemical method\(^{s7}\) was used to calculate the number of electrons involved in the reduction wave of the copolymers. The experiments were conducted by preparing a known amount of copolymer in dry CH_2Cl_2 or DMF, then a known amount of [FeCp*]_2 in CH_2Cl_2 or DMF was added to the solution. After recording the CV, the intensities of the oxidation waves of the copolymer and the internal reference [FeCp*]_2 were measured. The values were introduced into the Bard-Anson equation\(^{s7}\): n_p = \((i_{dp}/C_p)/(i_{dm}/C_m)\) \((M_p/M_m)^{0.275}\) to provide the final number of transferred electrons (n_p).

Size exclusion chromatography (SEC) measurements were carried out using the PL-GPC 50 plus Integrated GPC system from Polymer laboratories-Varian equipped with refractometric and UV detectors, column oven and integrated degasser. Columns from TOSOH: TSKgel TOSOH, HXL-L (guard column 6.0 mm ID × 4.0 cm L), G4000HXL (7.8 mm ID × 30.0 cm L), G3000HXL (7.8 mm ID × 30.0 cm L), G2000HXL (7.8 mm ID × 30.0 cm L). Flow Marker: TCB (trichlorobenzene, C_6H_5Cl_3), Flow: 1.0 ml/min, Solvent: tetrahydrofuran (THF) from Aldrich, loop: 100 μl.

Abbreviations: Cp = η^5-C_5H_4- (monosubstituted cyclopentadienyl) or η^5-C_5H_5; Fe = ferrocenyln, FeH = ferrocene, Fe* = 1,2,3,4,5-pentamethylferrocenyl; Fe*H = pentamethylferrocene; FbX = [Fe(η^5-C_5H_4-)(η^6-C_6Me_6)][PF_6]; FbHX = [Fe(η^5-C_5H_5)(η^6-C_6Me_6)][PF_6].
2. Synthesis and kinetic study of the ROMP of monomer 7\(^{[s2]}\)

Triethylamine (0.1 mL, 0.72 mmol) was added dropwise at room temperature (r. t.) under nitrogen (N\(_2\)) atmosphere to a suspension of ferrocene carboxylic acid (0.4 g, 1.74 mmol) in dry CH\(_2\)Cl\(_2\) (35 mL). Then, oxalyl chloride (0.75 mL, 8.7 mmol) was added dropwise at 0 °C. The obtained mixture was stirred overnight at r. t. and dried \textit{in vacuo}. The residual red solid of crude chlorocarbonyl ferrocene (FcCOCl) was dissolved in dry CH\(_2\)Cl\(_2\) (15 mL) and added dropwise to a CH\(_2\)Cl\(_2\) solution (20 mL) of 5 (0.2 g, 0.59 mmol) and triethylamine (1.5 mL, 10.7 mmol). The mixture was stirred overnight under N\(_2\) atmosphere at r. t., then washed with saturated NaHCO\(_3\) solution (1 × 100 mL) and distilled water (3 × 100 mL). The organic solution was dried over anhydrous Na\(_2\)SO\(_4\), filtered, and the solvent was removed \textit{in vacuo}. The product 7 was purified by column chromatography with CH\(_2\)Cl\(_2\)/methanol (1% → 20%) as eluent and obtained as a brown sticky oil. Yield: 0.258 g, 79.4%. \(^1\)H NMR (300 MHz, CDCl\(_3\)), \(\delta_{ppm}\) ppm: 6.45 (t, \(J = 9.9\) Hz, 1H, NHCO), 6.25 (t, \(J = 3.6\) Hz, 2H, CH=CH), 4.69 (t, \(J = 3.6\) Hz, 2H, sub. Cp), 4.30 (t, \(J = 3.6\) Hz, 2H, sub. Cp), 4.17 (s, 5H, free Cp), 3.70-3.54 (m, 16H, 4×CH\(_2\)), 3.23 (t, \(J = 3.4\) Hz, 2H, =CH-\(\text{CH}\)), 2.65 (d, \(J = 0.9\) Hz, 2H, CO-CH), 1.45 (d, \(J = 9.9\) Hz, 1H, CH\(_2\)-bridge), 1.32 (d, \(J = 10.0\) Hz, 1H, CH\(_2\)-bridge). \(^{13}\)C NMR (50 MHz, CDCl\(_3\)), \(\delta_{ppm}\): 177.8 (CON), 170.2 (CONH), 137.7 (CH=CH), 70.4, 70.2, 70.1, 70.0, 69.7, 69.6, 68.2 (-OCH\(_2\)CH\(_2\)OCH\(_2\)CH\(_2\)OCH\(_2\)-, sub. Cp and free Cp), 66.8 (-CH\(_2\)NH), 47.7 (CO-CH), 45.1 (=CH-CH), 42.6 (CH\(_2\)-bridge), 39.2 (CH\(_2\)-NCO), 37.7 (-CH\(_2\)CH\(_2\)-NCO). MS (ESI \(m/z\)), calcd. for C\(_{28}\)H\(_{34}\)N\(_2\)O\(_6\)Fe: 550.4; found: 573.2 (M+Na\(^+\)).

**Kinetic study of the ROMP of monomer 7**

A kinetic study was carried out in order to determine the ROMP rate of monomer 7. First, monomer 7 (0.46 g, 0.84 mmol) in 5.0 mL dry CH\(_2\)Cl\(_2\) was added into the solution of Grubbs 3\(^{rd}\) generation catalyst 1 (0.030 g, 0.033 mmol) in 0.5 mL dry CH\(_2\)Cl\(_2\). Then, the obtained reaction mixture was vigorously stirred at r. t. under N\(_2\) atmosphere. At different intervals (5, 15, 30 and 60 minutes, respectively), a 0.5 mL sample of the reaction mixture was taken out, quenched with 0.2 mL of EVE, precipitated by adding 5.0 mL of methanol. The obtained precipitate was washed with methanol (3 × 5 mL), vacuumed and checked for the \(^1\)H NMR spectrum in CDCl\(_3\). All the washing liquors and filtrate were collected, the solvent was removed \textit{in vacuo}, and the \(^1\)H NMR spectrum of the residue was recorded in CDCl\(_3\), too. The monomer conversion was deemed to be 100% when the signal of the olefin protons for monomer 7 at 6.25 ppm disappeared. It was found that the conversion of monomer 7 achieved 100% after 15 minutes stirring.
Figure S1 $^1$H NMR spectrum of monomer 7 in CDCl$_3$.

Figure S2 $^{13}$C NMR spectrum of monomer 7 in CDCl$_3$. 
Figure S3 ESI mass spectrum of monomer 7.

Figure S4 IR spectrum of monomer 7.
3448 cm\(^{-1}\) (\(v_{\text{NH}}\)), 2874 cm\(^{-1}\) (\(v_{\text{CH}_2}\)), 1767 cm\(^{-1}\) (\(v_{\text{C=O}}\)), 1694 cm\(^{-1}\) (\(v_{\text{NC=O}}\)), 1633 cm\(^{-1}\) (\(v_{\text{NHC=O}}\)), 820 cm\(^{-1}\) (\(v_{\text{FeII}}\))
Figure S5 $^1$H NMR spectrum (600 MHz) of homopolymer of 7 in CD$_2$Cl$_2$.

Figure S6 $^1$H NMR spectrum (400 MHz) of homopolymer of 7 in DMSO-$d_6$. 
Figure S7 $^1$H NMR spectrum (300 MHz) in CDCl$_3$ of the ROMP reaction mixture of monomer 7 after 5 minutes stirring. The ROMP of monomer 7 is not complete because the peak at 6.28 ppm for the olefinic protons of monomer 7 is still observed.

Figure S8 $^1$H NMR spectrum (300 MHz) in CDCl$_3$ of the precipitate from the ROMP reaction mixture of monomer 7 after 5 minutes stirring. The precipitate is the purified homopolymer of 7. There is no monomer 7 because no signal at 6.27 ppm or so was observed.
Figure S9 $^1$H NMR spectrum (300 MHz) in CDCl$_3$ of products in filtrate and washing-liquors from the ROMP reaction mixture of monomer 7 after 5 minutes stirring. The ROMP of monomer 7 is not complete because the peaks for monomer 7 were observed.

Figure S10 Enlarged $^1$H NMR spectrum (300 MHz) in CDCl$_3$ of the ROMP reaction mixture of monomer 7 after 10 minutes stirring. The ROMP of monomer 7 is not complete because the small peak at 6.28 ppm for the olefinic protons of monomer 7 is still observed.
Figure S11 ¹H NMR spectrum (300 MHz) in CDCl₃ of products in filtrate and washing liquors from the ROMP reaction mixture of monomer 7 after 15 minutes stirring. The ROMP of monomer 7 is complete because no peak at 6.27 ppm or so for the olefinic protons of monomer 7 was found.
3. Synthesis and kinetic study of the ROMP of monomer 8\[^{[s3]}\]

To a solution of pentamethylferrocene carboxylic acid (0.27 g, 0.90 mmol) in dry CH\(_2\)Cl\(_2\) (40 mL), oxalyl chloride (0.40 mL, 4.5 mmol) was added dropwise at 0 °C under N\(_2\) atmosphere. Then, the mixture was stirred overnight at 20 °C and dried in vacuo. The residual yellow-brown solid of crude chlorocarbonyl pentamethylferrocene was dissolved in dry CH\(_2\)Cl\(_2\) (10 mL) and added dropwise to a CH\(_2\)Cl\(_2\) solution (10 mL) of 5 (0.20 g, 0.59 mmol) and triethylamine (0.83 mL, 5.9 mmol). The obtained mixture was stirred overnight at 20 °C under N\(_2\) atmosphere, then washed with 10% K\(_2\)CO\(_3\) solution (50 mL) and distilled water (2 × 50 mL). The collected organic solution was dried over anhydrous Na\(_2\)SO\(_4\), filtered, and the solvent was removed in vacuo. The product 8 was purified by using column chromatography with CH\(_2\)Cl\(_2\)/methanol (1 : 10 v/v) as eluent and obtained as a red-brown sticky oil (Yield: 0.32 g, 87.2%).

\[^{[s3]}\]H NMR (300 MHz, CDCl\(_3\), 25 °C, TMS), \(\delta\) ppm: 6.23 (t, J = 3.7 Hz, 2H, CH=CH), 6.10 (t, J = 9.2 Hz, 1H, NHCO), 4.1 (t, J = 3.8 Hz, 2H, sub. Cp), 3.83 (t, J = 3.8 Hz, 2H, sub. Cp), 3.70-3.53 (m, 16H, 4×CH\(_2\)CH\(_2\)), 3.20 (t, J = 3.2 Hz, 2H, =CH-C\(_5\)H\(_5\)), 2.62 (d, J = 1.2 Hz, 2H, CO-CH), 1.78 (s, 15H, 5×CH\(_3\)), 1.43 (d, J = 9.8 Hz, 1H, CH\(_2\)-bridge), 1.31 (d, J = 9.8 Hz, 1H, CH\(_2\)-bridge). \(^{13}\)C NMR (75 MHz, CDCl\(_3\), 25 °C, TMS), \(\delta\) ppm: 178.0 (CON), 169.2 (CONH), 137.8 (CH=CH), 81.1 (Cp*) (Cp* =\(\eta^5\)-C\(_5\)Me\(_5\)), 74.4 (sub. Cp), 70.6, 70.2, 70.0 (CH\(_2\) and sub.Cp), 66.9 (−CH\(_2\)NH), 47.8 (CO-CH), 45.3 (=CH-CH), 42.7 (CH\(_2\)-bridge), 39.2 (CH\(_2\)-NCO), 37.7 (−CH\(_2\)CH\(_2\)-NCO), 10.5 (CH\(_3\)). MS (ESI m/z), calcd. for C\(_{33}\)H\(_{44}\)N\(_2\)O\(_6\)Fe: 620.6; found: 643.2 (M+Na\(^+\)).

Kinetic study of the ROMP of monomer 8

A kinetic study was carried out in order to determine the ROMP rate of monomer 8. First, monomer 8 (0.52 g, 0.8384 mmol) in 5.0 mL dry CH\(_2\)Cl\(_2\) was added into the solution of Grubbs 3\(^{rd}\) generation catalyst 1 (0.0297 g, 0.0335 mmol) in 0.5 mL dry CH\(_2\)Cl\(_2\). Then, the obtained reaction mixture was vigorously stirred at r. t. under N\(_2\) atmosphere. At different intervals (10, 15, 30 and 60 minutes, respectively), a 0.5 mL sample of the reaction mixture was taken out, quenched with 0.2 mL of EVE, vacuumed and checked for the \(^{1}\)H NMR spectrum in CDCl\(_3\). The monomer conversion was deemed to be 100% when the signal of the olefin protons for monomer 8 at 6.23 ppm disappeared. It was found that the conversion of monomer 8 achieved 100% after 10 minutes stirring.
Figure S12 $^1$H NMR spectrum of monomer 8 in CDCl$_3$.

Figure S13 $^{13}$C NMR spectrum of monomer 8 in CDCl$_3$. 
Figure S14 ESI mass spectrum of monomer 8.

Figure S15 IR spectrum of monomer 8.
3453 cm$^{-1}$ ($\nu_{\text{NH}}$), 2902 cm$^{-1}$ ($\nu_{\text{CH}_3}$), 1768 cm$^{-1}$ ($\nu_{\text{C=O}}$), 1695 cm$^{-1}$ ($\nu_{\text{NC=O}}$), 1633 cm$^{-1}$ ($\nu_{\text{NHC=O}}$), 817 cm$^{-1}$($\nu_{\text{FeII}}$)
**Figure S16** $^1$H NMR spectrum of homopolymer of 8 in CD$_2$Cl$_2$.

**Figure S17** $^1$H NMR spectrum (300 MHz) in CDCl$_3$ of the ROMP reaction mixture of monomer 8 after 10 minutes stirring. The ROMP of monomer 8 is complete because no peak at 6.23 ppm was observed.
Figure S18: $^1$H NMR spectrum (300 MHz) in CDCl$_3$ of methanol-washed products from the ROMP reaction mixture of monomer 8 after 10 minutes stirring. The product is the purified homopolymer of 8. There is no monomer 8 because no signal at 6.23 ppm was observed.

Figure S19: $^1$H NMR spectrum (300 MHz) in CDCl$_3$ of products in the methanol washing-liquor from the ROMP reaction mixture of monomer 8 after 10 minutes stirring. The ROMP of monomer 8 is complete because no peak at 6.23 ppm for the olefinic protons of monomer 8 was found.
4. Synthesis and kinetic study of the ROMP of monomer 9

The carbonyl mixed-sandwich complex \([\text{Fe}(\eta^6-C_6\text{Me}_6)(\eta^5-C_5\text{H}_4\text{COOH})][\text{PF}_6]\) (0.687 g, 1.46 mmol) was refluxed in 50 mL of SOCl\(_2\) under N\(_2\) atmosphere for 48 h. Then, the excess SOCl\(_2\) was removed using a trap-to-trap system under vacuum, and the resulting orange-red solid, which was the rude product of chlorocarbonyl complex \([\text{Fe}(\eta^6-C_6\text{Me}_6)(\eta^5-C_5\text{H}_4\text{COCl})][\text{PF}_6]\), was dissolved in 40 mL of dry CH\(_2\)Cl\(_2\) under N\(_2\) atmosphere. The mixture of \(N\)-(2-aminoethyl)-cis-5-norbornene-\(\text{exo}\)-2, 3-dicarboximide 6 (0.2 g, 0.97 mmol) and triethylamine (1.4 mL) in dry CH\(_2\)Cl\(_2\) (10 mL) was added dropwise to the above solution, and the obtained mixture was stirred overnight at r. t. under N\(_2\) atmosphere, then dried in vacuo to remove the solvent and excess triethylamine. The residual brown solid was dissolved in 80 mL CH\(_2\)Cl\(_2\), washed with saturated NaHCO\(_3\) solution (3 × 40 mL) and an aqueous solution of HPF\(_6\) (5%, w/w, 1× 40 mL), respectively. The organic layer was separated, dried with anhydrous Na\(_2\)SO\(_4\), filtered, and the solvent was removed under vacuum. The product was purified by precipitating from acetone with diethyl ether (Et\(_2\)O) to yield monomer 9 as a red-brown powder (0.545 g, 85% yield).

1\(^{1}H\) NMR (300 MHz, acetone-\(d_6\)), \(\delta\) ppm: 1.24 (d, \(J = 9.7\) Hz, 1H, CH\(_2\)-bridge), 1.40 (d, \(J = 9.6\) Hz, 1H, CH\(_2\)-bridge), 2.51 (s, 18H, 6×CH\(_3\)), 2.68 (d, \(J = 1.3\) Hz, 2H, CO-CH), 3.12 (t, \(J = 3.2\) Hz, 2H, =CH-C\(_{\text{H}}\)), 3.57-3.63 (m, 2H, CH\(_2\)), 3.66-3.71 (m, 2H, CH\(_2\)), 4.94 (s, 2H, sub. Cp), 5.10 (s, 2H, sub. Cp), 6.30 (t, \(J = 3.6\) Hz, 2H, CH=CH), 7.77 (t, \(J = 9.6\) Hz, 1H, NHCO). 13\(^{13}C\) NMR (75 MHz, acetone-\(d_6\)), \(\delta\) ppm: 178.5 (CON), 164.2 (CONH), 138.5 (CH=CH), 100.3 (\(\eta^6-C_6\text{Me}_6\)), 85.0 (sub. Cp), 81.2 (sub. Cp), 77.2 (sub. Cp), 48.5 (CO-CH), 45.7 (=CH-CH), 43.4 (CH\(_2\)-bridge), 38.6 (CH\(_2\)-NCO), 38.5 (CH\(_2\)-NH-CO), 17.0 (-CH\(_3\)). MS (ESI m/z), calcd. For C\(_{29}\)H\(_{35}\)N\(_2\)O\(_3\)Fe: 515.1991; found: 515.1984 (M\(^+\)).

Kinetic study of the ROMP of monomer 9

A kinetic study was carried out in order to determine the ROMP rate of the cationic organoiron monomer 9. Firstly, monomer 9 (0.454 g, 0.688 mmol) in 4.0 mL dry DMF was added into the solution of Grubbs 3\(^{rd}\) generation catalyst 1 (0.0243 g, 0.0275 mmol) in 0.5 mL dry DMF. Then, the obtained reaction mixture was vigorously stirred at r. t. under N\(_2\) atmosphere. At different intervals (0.5 h, 1 h and 2 h, and overnight (12h), respectively), 0.5 mL of the reaction mixture was taken out, quenched with 0.2 mL of EVE, precipitated by adding 2 mL of Et\(_2\)O. The obtained precipitate was washed with Et\(_2\)O (3 × 2 mL) and then CH\(_2\)Cl\(_2\) (3 × 2 mL). All the washing liquors and filtrate were collected, the solvent was removed in vacuo, and the 1\(^{1}H\) NMR spectrum of the residue was recorded in acetone-\(d_6\). The monomer conversion was deemed to be 100% when the signal of the olefin protons of monomer 9 at 6.30 ppm disappeared. It was found that the conversion of monomer 9 reached 100% only after stirring overnight (i. e. 12 h).
Figure S20 \(^1\)H NMR spectrum of monomer 9 in acetone-\(d_6\).

Figure S21 \(^1\)H NMR spectrum of monomer 9 in CDCl\(_3\).
Figure S22 $^{13}$C NMR spectrum of monomer 9 in acetone-$d_6$.

Figure S23 ESI mass spectrum of monomer 9.
Figure S24 IR spectrum of monomer 9.
3431 cm$^{-1}$ ($\nu$NH), 2985 cm$^{-1}$ ($\nu$CH$_3$), 1769 cm$^{-1}$ ($\nu$C=C), 1698 cm$^{-1}$ ($\nu$NC=O), 1662 cm$^{-1}$ ($\nu$NHC=O), 838 cm$^{-1}$ ($\nu$PF$_6$).

Figure S25 $^1$H NMR spectrum (300 MHz) in acetone-$d_6$ of products in filtrate and washing-liquors from the ROMP reaction mixture of monomer 9 after 1 h stirring. The peak in pink circle corresponds to the olefin protons of monomer 9.
**Figure S26** Enlarged $^1$H NMR spectrum (300 MHz) in acetone-$d_6$ of products in filtrate and washing-liquors from the ROMP reaction mixture of monomer 9 after overnight stirring. No peak was observed at 6.30 ppm. Peaks at 8.41-6.61 probably arise from the protons of catalyst 1 and DMF or/and noise.
5. Diblock copolymer 11

Synthesis
Monomers 7 (36.7 mg, 0.067 mmol) and 9 (44.0 mg, 0.067 mmol) were added into two separate small glass tubes, and dissolved in 0.4 mL and 0.6 mL of dry CH₂Cl₂, respectively. A desired amount of Grubbs catalyst 3rd 1 (2.36 mg, 0.0027 mmol) was added into a small Schlenk flask, flushed with nitrogen, and dissolved in 0.03 mL of dry CH₂Cl₂. First, monomer 7 was transferred to the flask containing the catalyst via a small syringe. The reaction mixture was stirred vigorously for 15 minutes at r. t., after which monomer 9 was added into the flask using a small syringe. The polymerization was allowed to continue for another 10 minutes, and then quenched with 0.2 mL of EVE. The yellow-brown solid polymer 11 was purified by precipitating from CH₂Cl₂ with Et₂O three times and dried in vacuo until constant weight. Yield: 95%. ¹H NMR (300 MHz, CD₂Cl₂), δ ppm: 7.39-7.22 (m, NHCO-(η⁵-C₅H₄)Fe(η⁶-C₆Me₆) and phenyl), 6.51 (broad, 1H, NHCO-Fc), 5.72 and 5.51 (double broad, CH=CH), 4.70 (s, sub. Cp of Fc), 4.32 (s, sub. Cp of Fc), 4.19 (s, free Cp of Fc), 3.61-3.41 (m, CH₂(CH₂OCH₂)₃CH₂ and NCH₂CH₂N), 3.02 (broad, =CH-CH), 2.65 (broad, CO-CH), 2.38 (s, CH₃ of (η⁶-C₆Me₆)), 2.03 (broad, CH=CHCHCH₂).

Kinetic Study
In order to know when the polymerization of the second FbX block finishes, the kinetic study was conducted as following: monomer 7 (0.482 g, 0.876 mmol) in 4 mL dry CH₂Cl₂ was added into the solution of Grubbs catalyst 3rd 1 (0.031 g, 0.035 mmol) in 0.3 mL dry CH₂Cl₂. The reaction mixture was stirred vigorously for 15 minutes at r. t. under N₂ atmosphere. Then, monomer 9 (0.578 g, 0.876 mmol) in 6 mL dry CH₂Cl₂ was added, and after 10, 15, 20, and 30 minutes, respectively, 0.5 mL of samples were taken out, quenched with 0.5 mL of EVE, and vacuumed. The in situ ¹H NMR analysis in CDCl₃ or acetone-d₆ was conducted, and the conversion of monomer 9 was deemed to be 100% when the peak at 6.24 or 6.30 ppm, the signal of olefinic protons for monomer 9, disappeared. Actually, the polymerization of the second block finishes in 10 minutes with 100% monomer conversion.
Figure S27 $^1$H NMR spectrum of diblock copolymer 11 in CD$_2$Cl$_2$.

Figure S28 $^1$H NMR spectrum of diblock copolymer 11 in DMSO-$d_6$.

$^1$H NMR (300 MHz, DMSO-$d_6$), $\delta$ ppm: 8.48 (broad, N$\text{HCO}$-$\left(\eta^5$-$\text{C}_5\text{H}_4\right)$Fe($\eta^6$-$\text{C}_6\text{Me}_6$)), 7.80 (s, N$\text{HCO}$-Fc), 7.41-7.09 (m, phenyl), 5.64 and 5.46 (double broad, CH=CH), 5.05 (broad, sub. Cp of ($\eta^5$-$\text{C}_5\text{H}_4$)Fe($\eta^6$-$\text{C}_6\text{Me}_6$)), 4.86 (broad, sub. Cp of ($\eta^5$-$\text{C}_5\text{H}_4$)Fe($\eta^6$-$\text{C}_6\text{Me}_6$)), 4.78 (s, sub. Cp of Fc), 4.31 (s, free Cp of Fc), 3.46-3.37 (broad, CH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$, H$_2$O and NCH$_2$CH$_2$N), 3.03 (broad, =CH-CH), 2.50 (broad, DMSO and CO-CH), 2.31 (s, CH$_3$ of $\eta^6$-C$_6$Me$_6$), 1.92 (broad, CH=CHCHCH$_3$), 1.45 (broad, CH=CHCHCH$_3$)
Figure S29 $^{13}$C NMR spectrum of diblock copolymer 11 in CD$_2$Cl$_2$.

$^{13}$C NMR (50 MHz, CD$_2$Cl$_2$), δ ppm: 178.1 (CON), 169.9 (CONH), 132.5, 131.758 (C=C), 99.3 ($\eta^6$-C$_6$Me$_6$), 76.4 (free Cp), 70.3, 70.2, 70.0, 69.7, 68.2, 68.9 (CH$_2$ and sub. Cp), 50.9 (CO-CH and =CH-CH), 46.2 (CH$_2$ of cyclopentane), 42.5, 41.4 (CH$_2$-NCO), 39.2, 37.9 (-CH$_2$CH$_2$NCO), 16.6 (CH$_3$ of $\eta^6$-C$_6$Me$_6$).

Figure S30 UV-vis. spectra of diblock copolymer 11, Fe-containing homopolymer of 7 and FbX-containing homopolymer of 9 in CH$_2$Cl$_2$. 

Figure S30 UV-vis. spectra of diblock copolymer 11, Fe-containing homopolymer of 7 and FbX-containing homopolymer of 9 in CH$_2$Cl$_2$. 
Figure S31 MALDI-TOF MS spectrum of diblock copolymer 11. The feed molar ratio of monomers 7 and 9 to 1 is 25 : 25 : 1. (A) is the region of 5000-17000 in the spectrum; and (B) is the enlarged region of the spectrum from 6435 to 8854. The red dotted lines correspond to the difference between molecular peaks of a value of 550 ±1 Da (MW of monomer 7). The blue dotted lines correspond to the difference between molecular peaks of a value of 660 ±1 Da (MW of monomer 9).
Figure S32 IR spectrum of diblock copolymer 11.
3432 cm\(^{-1}\) (NH), 2945 cm\(^{-1}\) (CH\(_3\)), 1771 cm\(^{-1}\) (C=C), 1695 cm\(^{-1}\) (NC=O), 1640 cm\(^{-1}\) (NHC=O), 844 cm\(^{-1}\) (PF\(_6\)).

Figure S33 \(^1\)H NMR spectrum (300 MHz) in CDCl\(_3\) of the ROMP reaction mixture for the synthesis of diblock copolymer 11 after the addition of monomer 9 with 10 minutes stirring. No peak was observed at 6.24 ppm for the olefin protons of monomer 9, namely no monomer 9 was left and the ROMP of 9 is complete.
Figure S34 Enlarged $^1$H NMR spectrum (300 MHz) in acetone-$d_6$ of the ROMP reaction mixture for the synthesis of diblock copolymer 11 after the addition of monomer 9 with 10 minutes stirring. No peak was observed at 6.30 ppm for the olefin protons of monomer 9, namely no monomer 9 was left and the ROMP of 9 is complete.

**Calculation of the polymer degrees of diblock copolymers 11 by $^1$H NMR end-group analysis and errors**

**Table S1** Polymer degree of the first Fc block using the $^1$H NMR spectrum in CD$_2$Cl$_2$ of homopolymer of 7

<table>
<thead>
<tr>
<th>Proton peak</th>
<th>End-phenyl</th>
<th>Amido</th>
<th>olefinic</th>
<th>Sub. Cp</th>
<th>Sub. and free Cp</th>
<th>Methylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$ ppm</td>
<td>7.39-7.16</td>
<td>6.50</td>
<td>5.73 and 5.52</td>
<td>4.70</td>
<td>4.33 and 4.19</td>
<td>3.61-3.52</td>
</tr>
<tr>
<td>Integration</td>
<td>0.21</td>
<td>1.02-1.10</td>
<td>2.11-2.21</td>
<td>2.05-2.14</td>
<td>7.04-7.35</td>
<td>16.62-17.31</td>
</tr>
<tr>
<td>$n_{p2a}$</td>
<td>-</td>
<td>24-26</td>
<td>25-26</td>
<td>24-25</td>
<td>24-25</td>
<td>24-25</td>
</tr>
<tr>
<td>$n_{p2b}$</td>
<td>-</td>
<td>25 ± 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Figure S5 was used for the calculation of the polymer degree of the first Fc block; $^b$ Calculated polymer degrees based on integral of each peak; $^c$ Average polymer degree according to $n_{p2a}$ values.
Table S2 Polymer degree of the first Fc block using the $^1$H NMR spectrum in DMSO-$d_6$ of homopolymer of 7a

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>$\Delta$ppm</td>
<td>7.48-7.23</td>
<td>7.79</td>
<td>5.64 and 5.45</td>
<td>4.78</td>
<td>4.31</td>
<td>4.14</td>
</tr>
<tr>
<td>Integration</td>
<td>0.21</td>
<td>1.01-1.04</td>
<td>2.01-2.15</td>
<td>2.01-2.04</td>
<td>2.04-2.06</td>
<td>4.91-5.02</td>
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<tr>
<td>$n_{p2ab}$</td>
<td>-</td>
<td>24-25</td>
<td>24-26</td>
<td>24-25</td>
<td>24-25</td>
<td>24-24</td>
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<tr>
<td>$n_{p2bc}$</td>
<td></td>
<td></td>
<td></td>
<td>25 ± 1</td>
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</table>

a Figure S6 was used for the calculation of the polymer degree of the first Fc block. b Calculated polymer degrees based on integral of each peak. c Average polymer degree according to $n_{p2a}$ values.

As shown in Table S1 and S2, both the $^1$H NMR end-group analysis in CD$_2$Cl$_2$ and DMSO-$d_6$ provide the value of 25 ± 1 for the polymer degree of the first Fc block. These calculations were conducted by comparing the intensities of the signals of the five protons of the end-phenyl group with those of the characteristic protons in the Fc block. For example, in the $^1$H NMR end-group analysis in CD$_2$Cl$_2$, proton integration for the end-phenyl group (7.39-7.16 ppm) was compared with those of the amide proton (6.50 ppm), olefin protons (5.74 and 5.52 ppm), Cp protons (4.70, 4.33 and 4.19 ppm) and methylene protons (3.61-3.52 ppm), respectively. The obtained values are 24-26, 24-26, 24-25, 24-25 and 24-25, respectively. Thus, the average value of the polymer degree for the first block is 25 ± 1. The error is due to the integration error on each signal.

Table S3 Polymer degree of the second FbX block of copolymer 11a,b.

<table>
<thead>
<tr>
<th>Proton peak</th>
<th>Amido in the first block</th>
<th>Substituted and free Cp in the first block</th>
<th>Amido in the second block</th>
<th>Substituted Cp in the second block</th>
<th>Methyl of C$_6$Me$_6$ in the second block</th>
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<tr>
<td>$\delta$ppm</td>
<td>7.80</td>
<td>4.31 and 4.14</td>
<td>8.48</td>
<td>5.05</td>
<td>2.31</td>
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<tr>
<td>Integration</td>
<td>0.93-1.03</td>
<td>7.04-7.11</td>
<td>0.74-0.81</td>
<td>1.80-1.82</td>
<td>13.1-13.6</td>
</tr>
<tr>
<td>$n_{p2a}$</td>
<td>-</td>
<td>-</td>
<td>17-23c</td>
<td>21-25d</td>
<td>17-20e</td>
</tr>
<tr>
<td>$n_{p2bf}$</td>
<td></td>
<td></td>
<td></td>
<td>21 ± 4</td>
<td></td>
</tr>
</tbody>
</table>

a Figure 1C is used for the calculation of the polymer degree of the second FbX block. b The average polymer degree of 25 ± 1 for the first Fc block is used for the calculation of polymer degree of the second FbX block. c Calculated by comparing the amido proton integrations in the first and second blocks. d Calculated by comparing the amido proton integration in the first block and the substituted Cp proton integration in the second block. e Calculated by comparing the substituted and free Cp proton integration in the first block with the methyl proton integration in the second block. f Average polymer degree for the second block according to $n_{p2a}$ values.

For the second FbX block, the polymer degree is 21 ± 4, as shown in Table S3. The error results
from the following two sides. (1) This analysis is carried out by comparing the integration of characteristic peaks from the first Fc block and the second FbX block. The former is the amido peak at 7.80 ppm with integration of 0.93-1.03 and the substituted and free Cp peaks at 4.31 and 4.14 ppm with the total integration of 7.04-7.11; the latter is the amido peak at 8.48 ppm with the integration of 0.74-0.81, substituted Cp peak at 5.05 ppm with the integration of 1.80-1.82, and the methyl peak of C₆Me₆ at 2.31 ppm with the integration of 13.1-13.6. Obviously, integrations for each peak have errors that result in the corresponding error for the calculated polymer degree of the second block. (2) The above obtained polymer degree of 25 ± 1 for the first Fc block is used for the calculation of the polymer degree for the second FbX block, which also results in a larger error than for the first block. The obtained values are 17-23, 21-25 and 17-20, respectively, and then the average is 21 ± 4.

**Table S4** Redox potentials, chemical \( (i_c/i_a) \) and electrochemical \( (E_{pa}-E_{pc} = \Delta E) \) reversibility data for diblock copolymer 11.

<table>
<thead>
<tr>
<th>Fc redox center</th>
<th>FbX redox center</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{1/2} (\Delta E) ) (V)</td>
<td>( i_c/i_a )</td>
</tr>
<tr>
<td>0.630 (0.010)</td>
<td>1.06</td>
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</table>

**Calculation of polymerization degrees \( (n_{p3}) \) for diblock copolymer 11 by Bard-Anson’s method**

Bard-Anson’s electrochemical equation:\textsuperscript{S6}

\[
n_p = \left( \frac{i_{dp}}{i_{dm}} \right) \frac{C_p}{C_m} \left( \frac{M_p}{M_m} \right)^{0.275}
\]

\( (i_{dp}: \text{intensity of polymer}; \ C_p: \text{concentration of polymer}; \ i_{dm}: \text{intensity of monomer}; \ C_m: \text{concentration of monomer}; \ M_p: \text{molecular weight of polymer}; \ M_m: \text{molecular weight of monomer}).

In this part, the symbol of \( n_{p3} \) is used to stand for the polymerization degree. So,

\[
n_{p3} = \left( \frac{i_{dp}}{i_{dm}} \right) \frac{C_m}{C_p} \left( \frac{M_p}{M_m} \right)^{0.275}
\]

\[
= \left( \frac{i_{dp} C_m}{i_{dm} C_p} \right) \left( \frac{M_p}{M_m} \right)^{0.275}
\]

\[
= \left( \frac{i_{dp} (n_m / v)}{i_{dm} (n_p / v)} \right) \left( \frac{M_p}{M_m} \right)^{0.275} \quad (n_m: \text{mole of monomer}; \ n_p: \text{mole of polymer}; \ v: \text{volume of solution})
\]
Here, we use decamethyferrocene ([FeCp*₂]) as the monomer reference, because (i) it has the same number of electron transferred between its reduced and oxidized forms as that of the monomers 7 and 9, (ii) its redox potential is sufficiently far from that of Fc and FbX redox center in the polymers, which allows a clear distinction of the CV wave of the reference and that of the polymers 11. This leads to calculate the polymerization degrees \( n_{p3} \) of Fc block and the mixed-sandwich FbX block for diblock copolymer 11 by the above equation, and the results are listed in Table S5.

**Table S5** Polymerization degree \( n_{p3} \) for each metalloblock in copolymer 11 calculated using the Bard-Anson electrochemical method.

<table>
<thead>
<tr>
<th></th>
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<th>25 : 25 : 1</th>
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<tbody>
<tr>
<td>([M_7] : [M_9] : [C])^a</td>
<td>(M_m)^b</td>
<td>326.3</td>
</tr>
<tr>
<td>(M_p)^c</td>
<td>30354</td>
<td></td>
</tr>
<tr>
<td>(n_m)^d (mmol)</td>
<td>(3.1 \times 10^{-3})</td>
<td></td>
</tr>
<tr>
<td>(n_p)^e (mmol)</td>
<td>(2.1 \times 10^{-4})</td>
<td></td>
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<tr>
<td>(i_{dm}) (cm)</td>
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<td>Redox centers</td>
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</tr>
<tr>
<td></td>
<td>Fc</td>
<td></td>
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<tr>
<td></td>
<td>FbX</td>
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</tr>
<tr>
<td>(i_{dp}) (cm)</td>
<td>1.6</td>
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<tr>
<td>(n_{p3})^f</td>
<td>28 \pm 3</td>
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<tr>
<td></td>
<td>24 \pm 2</td>
<td></td>
</tr>
</tbody>
</table>

^a [M₇] : [M₉] : [C]: feed molar ratio of monomers 7 and 9 to catalyst 1. ^b Molecular weight of [FeCp*₂]. ^c Molecular weight of polymer calculated by monomer conversion determined by \(^1\)H NMR. ^d \(n_m\): mole of [FeCp*₂] added in the DMF solution of copolymer 11. ^e \(n_p\): mole of polymer 11 added in DMF. ^f \(n_{p3}\): polymerization degree calculated by the above modified Bard-Anson’s equation.
6. Diblock copolymer 13

Synthesis
Monomers 8 (44.4 mg, 0.0716 mmol) and 7 (39.4 mg, 0.0716 mmol) were added into two separate small glass tubes and dissolved in 0.4 mL and 0.3 mL of dry CH₂Cl₂, respectively. A desired amount of Grubbs catalyst 1 (2.53 mg, 0.00286 mmol) was added into a small Schlenk flask, flushed with nitrogen, and dissolved in 0.03 mL of dry CH₂Cl₂. First, monomer 8 was transferred to the flask containing the catalyst via a small syringe. The reaction mixture was stirred vigorously for 10 minutes at r. t., after which monomer 7 was added into the flask using a small syringe. The polymerization was allowed to continue for another 15 minutes, and then quenched with 0.2 mL of EVE. The yellow-brown solid polymer 13 was purified by precipitation from CH₂Cl₂ with methanol five times and dried in vacuo until constant weight. Yield: 94%.

Kinetic Study
In order to know when the polymerization of the second block finishes, the kinetic study was conducted as following: monomer 8 (0.405 g, 0.653 mmol) in 4 mL dry CH₂Cl₂ was added into the solution of Grubbs catalyst 1 (23.1 mg, 0.026 mmol) in 0.3 mL dry CH₂Cl₂. The reaction mixture was stirred vigorously for 10 minutes at r. t. under N₂ atmosphere. Then, monomer 7 (0.359 g, 0.653 mmol) in 3 mL dry CH₂Cl₂ was added, and after 5, 10, 15, 20, 30, 45 and 60 minutes, respectively, 0.5 mL of samples were taken out and quenched with 0.5 mL of EVE. The In situ ¹H NMR analysis in CDCl₃ was conducted, and the conversion of monomer 7 was deemed to be 100% when the peak at 6.26 ppm, the signal of olefinic protons for monomer 7, disappeared. Actually, the polymerization of the second block finishes in 15 minutes with 100% monomer conversion.

Oxidation of copolymer 13 by ferricinium hexafluorophosphate
A freshly prepared solution of ferricinium hexafluorophosphate (3.11 mg, 9.40 × 10⁻³ mmol) in dry CH₂Cl₂ (2.5 mL) was added dropwise to a solution of polymer 13 (10.0 mg, 8.55 × 10⁻³ mmol of Fe*) in dry CH₂Cl₂ (1.5 mL) under nitrogen at 25 °C. The mixture was stirred for 5 min at 25 °C, and then the solvent was removed in vacuo. The blue-green residual solid of crude [Fc*⁺]-containing copolymer 14 was washed with pentane (5 × 5 mL), then dissolved in acetone, precipitated by addition of pentane, and dried in vacuo until constant weight (Yield: 10.8 mg, 96%). IR: ν bar = 3430 (N-H), 2923 (CH₃), 1771 (C=O), 1698 (C=O), 843 (PF₆⁻) cm⁻¹; δ bar = 1655 (N-H) cm⁻¹; UV/Vis (CH₂Cl₂): λmax = 625, 754 nm. The structure was confirmed by reduction to the [Fc*⁺]-containing copolymer.
Reduction by decamethylferrocene of the [Fe*]⁺-containing copolymer 14

A freshly prepared solution of decamethylferrocene (3.2 mg, 9.8 × 10⁻³ mmol) in dry CH₂Cl₂ (2.0 mL) was added dropwise to a solution of copolymer 14 (10.0 mg, 7.605 × 10⁻³ mmol of [Fc*]⁺ hexafluorophosphate) in dry CH₂Cl₂ (5.0 mL) under nitrogen at 25 °C. The mixture was stirred for 5 min at 25 °C, and then the solvent was removed in vacuo. The residual solid was washed five times with methanol (5.0 mL), and the purified Fe*-containing polymer 13 was obtained as a yellow solid (Yield: 8.1 mg, 91%). ¹H NMR (300 MHz, CDCl₃), δ ppm: 7.36-7.17 (m, phenyl and CDCl₃), 6.49 (broad, 1H, NΗCO-Fc), 6.03 (broad, 1H, NΗCO-Fc*), 5.72 and 5.49 (double broad, 4H, 2×CH=CH), 4.71 (s, 2H, sub. Cp of Fc), 4.31 (s, 2H, sub. Cp of Fc), 4.18 (s, 7H, free Cp of Fc and sub. Cp of Fc*), 4.05 (s, 2H, sub. Cp of Fc*), 3.60 (broad, 32H, 2×CH₂(CH₂OCH₂)₃CH₂), 3.23 (broad, =CH-CΗ), 3.01 (broad, CO-CH), 2.66 (broad, CH=CHCH₂H₂), 2.09 (broad, CH=CHCH₂H₂), 1.34 (s, 15H, 5×CH₃). IR: ν bar = 3394 (N-H), 2902 (CH₃), 1771 (C=C), 1701 (C=O), 824 (FeII) cm⁻¹; δ bar = 1637 (N-H) cm⁻¹; UV/Vis (CH₂Cl₂): λ_max = 435 nm.

Figure S35 ¹H NMR spectrum of diblock copolymer 13 in CD₂Cl₂.
¹H NMR (300 MHz, CD₂Cl₂), δ ppm: 7.41-7.27 (m, phenyl), 6.50 (broad, 1H, NΗCO-Fc), 6.14 (broad, 1H, NΗCO-Fc*), 5.72 and 5.51 (double broad, 4H, 2×CH=CH), 4.69 (s, 2H, sub. Cp of Fc), 4.32 (s, 2H, sub. Cp of Fc), 4.18 (s, 7H, free Cp of Fc), 4.12 (s, 2H, sub. Cp of Fc*), 3.87 (s, 2H, sub. Cp of Fc*), 3.59-3.50 (m and broad, 32H, 2×CH₂(CH₂OCH₂)₃CH₂), 3.19 (broad, =CH-CΗ), 3.02 (broad, CO-CH), 2.65 (broad, CH=CHCH₂H₂), 2.04 (broad, CH=CHCH₂H₂), 1.76 (s, 15H, 5×CH₃).
**Figure S36** $^{13}$C NMR spectrum of diblock copolymer 13 in CDCl$_3$.

$^{13}$C NMR (50 MHz, CDCl$_3$), $\delta_{ppm}$: 178.2, 178.1 (CON), 170.2, 169.1 (CONH), 133.4, 131.7 (C=C), 81.8 (Cp*), 71.8, 70.5, 70.3, 70.2, 70.1, 69.8, 69.7, 68.2, (CH$_2$ and sub. Cp), 67.0(-CH$_2$NH), 53.5 (COCH), 51.0, 50.8 (=CHCH), 45.7 (CH$_2$ of cyclopentane), 41.3, 39.3, 39.1 (CH$_2$NCO), 37.7 (CH$_2$CH$_2$NCO), 10.5 (CH$_3$).

**Figure S37** IR spectrum of diblock copolymer 13.

3400 cm$^{-1}$ ($v_{\text{N-H}}$), 2904 cm$^{-1}$ ($v_{\text{CH3}}$), 1771 cm$^{-1}$ ($v_{\text{C=C}}$), 1701 cm$^{-1}$ ($v_{\text{C=O}}$), 1637 cm$^{-1}$ ($\delta_{\text{N-H}}$), 821 cm$^{-1}$ ($v_{\text{FeII}}$).
Figure S38 UV-vis. spectra of diblock copolymer 13, Fc-containing homopolymer of 7 and Fe*-containing homopolymer of 8 in CH₂Cl₂.

MW Averages

<table>
<thead>
<tr>
<th>Peak No</th>
<th>M₀</th>
<th>Mₘ</th>
<th>Mₚ</th>
<th>M_z</th>
<th>M⁺1</th>
<th>Mᵥ</th>
<th>PD</th>
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</table>
Figure S39 SEC curves of the diblock copolymers 13 (A and C) and homopolymer of 8 (B). (A): The feed molar ratio [monomer 8] : [monomer 7] : [catalyst 1] was 25 : 25 : 1; (B): The feed molar ratio [monomer 8] : [catalyst 1] was 50 : 1; (C): The feed molar ratio [monomer 8] : [monomer 7] : [catalyst 1] was 50 : 50 : 1.
Figure S40 MALDI-TOF MS spectrum of diblock copolymer 13.

The feed molar ratio of monomers 8 and 7 to 1 is 25:25:1. (A) is the region of 5000-20000 in the spectrum; and (B) is the enlarge region of the spectrum from 913 to 11560. The red dotted lines are corresponding to the difference between molecular peaks of a value of 620 ±1 Da (MW of monomer 8). The blue dotted lines are corresponding to the difference between molecular peaks of a value of 550 ±1 Da (MW of monomer 7).
Figure S41 $^1$H NMR spectrum in CDCl$_3$ of the ROMP reaction mixture for the synthesis of diblock copolymer 13 after the addition of monomer 7 with 15 minutes stirring. No peak is observed at 6.26 ppm or so for the olefin protons of monomer 7, namely no monomer 7 is left and the ROMP of 7 is complete.

Calculation of the polymer degrees of diblock copolymers 13 by $^1$H NMR end-group analysis and errors

Table S6 Polymer degree of the first Fe* block using the $^1$H NMR spectrum in CD$_2$Cl$_2$ of homopolymer of 8$^a$

<table>
<thead>
<tr>
<th>Proton peak</th>
<th>End-phenyl</th>
<th>Amido</th>
<th>olefinic</th>
<th>Sub. Cp</th>
<th>Substitute d Cp</th>
<th>methylen e</th>
<th>Methyl of C$_5$Me$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$ppm</td>
<td>7.38-7.22</td>
<td>6.16</td>
<td>5.72-5.50</td>
<td>4.13</td>
<td>3.87</td>
<td>3.59-3.50</td>
<td>1.74</td>
</tr>
<tr>
<td>Integ.</td>
<td>0.197</td>
<td>0.96-1.0</td>
<td>2.00-2.04</td>
<td>1.93-2.00</td>
<td>1.86-1.95</td>
<td>15.7-16.3</td>
<td>14.3-14.7</td>
</tr>
<tr>
<td>$n_{p2a}$</td>
<td>-</td>
<td>24-25</td>
<td>25-26</td>
<td>25-25</td>
<td>24-25</td>
<td>25-26</td>
<td>24-25</td>
</tr>
<tr>
<td>$n_{p2b}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>25 ± 1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Figure S16 is used for the calculation of polymer degree of the first Fe* block. $^b$ Calculated polymer degrees based on integral of each peak. $^c$ Average polymer degree according to $n_{p2a}$ values.
As shown in Table S6, the $^1$H NMR end-group analysis in CD$_2$Cl$_2$ provides the value of 25 ± 1 for the polymer degree of the first Fc* block. These calculations were conducted by comparing the intensities of the signals of the five protons of the end-phenyl group with those of characteristic protons in the Fc* block. Namely, the proton integration for end-phenyl group (7.39-7.22 ppm) was compared with those of the amide proton (6.16 ppm), olefin protons (5.72-5.50 ppm), Cp protons (4.13 and 3.87 ppm), methylene protons (3.5-3.50 ppm) and methyl protons of C$_5$Me$_5$ (1.74 ppm), respectively. The obtained values are 24-25, 25-26, 25-25, 24-25, 25-26 and 24-25, respectively. Thus, the average value of the polymer degree for the first block is 25 ± 1. The error is due to the integration error on each signal.

Table S7 Polymer degree of the second Fc block using the $^1$H NMR spectrum in CD$_2$Cl$_2$ of copolymer 13.\textsuperscript{a,b}

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$ ppm</td>
<td>6.139</td>
<td>3.868</td>
<td>6.498</td>
<td>4.692</td>
<td>4.316</td>
</tr>
<tr>
<td>Integration</td>
<td>0.99-1.01</td>
<td>1.99-2.01</td>
<td>1.00-1.01</td>
<td>1.99-2.00</td>
<td>1.98-2.00</td>
</tr>
<tr>
<td>n\textsubscript{p2a}</td>
<td>-</td>
<td>-</td>
<td>24-26\textsuperscript{c}</td>
<td>24-26\textsuperscript{d}</td>
<td>24-26\textsuperscript{d}</td>
</tr>
<tr>
<td>n\textsubscript{p2b}\textsuperscript{e}</td>
<td>25 ± 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Figure S35 is used for the calculation of the polymer degree of the second block. \\
\textsuperscript{b} The average polymer degree of 25 ± 1 for the first Fc* block is used for the calculation of polymer degree of the second Fc block. \\
\textsuperscript{c} Calculated by comparing the amido proton integrations in the first and second blocks. \\
\textsuperscript{d} Calculated by comparing the substituted Cp proton integrations in the first and second blocks. \\
\textsuperscript{e} Average polymer degree for the second block according to the n\textsubscript{p2a} values.

As shown in Table S7, the polymer degree for the second Fc block is 25 ± 1, too, which is equal to that of the first Fc* block. The analysis was carried out by using the above obtained polymer degree of 25 ± 1 for the first Fc* block. The integrations of amido peaks in the first and second blocks, 6.14 ppm with 0.99-1.01 and 6.50 ppm with 1.00-1.01, respectively, were compared, and the value of 24-26 was obtained. Similarly, the integrations of substituted Cp peaks in the first and second blocks were also compared. The former is 1.99-2.01 at 3.87 ppm, and the latter is 1.99-2.00 at 4.69 ppm and 1.98-2.0 at 4.32 ppm, respectively. The obtained corresponding polymer degrees for the second block are 24-26, too. So, the average value is 25 ± 1. Obviously, the used analysis method resulted in a small error.
Table S8 Redox potentials, chemical ($i_c/i_a$) and electrochemical ($E_{pa}-E_{pc} = \Delta E$) reversibility data for the diblock copolymer 13.

<table>
<thead>
<tr>
<th></th>
<th>Fc center</th>
<th></th>
<th>Fc* center</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{1/2}$ (mV)</td>
<td>$\Delta E$ (mV)</td>
<td>$i_c/i_a$</td>
<td>$E_{1/2}$ (mV)</td>
</tr>
<tr>
<td>0.640</td>
<td>0.020</td>
<td>1.10</td>
<td>0.380</td>
</tr>
</tbody>
</table>

Calculation of the polymerization degrees ($n_{p3}$) for the diblock copolymer 13 by Bard-Anson’s method

The following modified Bard-Anson’s empirical electrochemical equation\textsuperscript{87} is used:

$$n_{p3} = \left(\frac{i_{dp}n_m}{i_{dm}n_p}\right)^{0.275} \frac{M_p}{M_m}$$

($i_{dp}$: intensity of polymer; $n_p$: mole of polymer; $i_{dm}$: intensity of monomer; $n_m$: mole of monomer; $M_p$: molecular weight of polymer; $M_m$: molecular weight of monomer).

[FeCp*\textsubscript{2}] was used as the monomer reference. The results of calculated polymerization degrees ($n_{p3}$) of Fc* and Fc blocks for diblock copolymer 13 are listed in Table S9.

Table S9 Polymerization degree ($n_{p3}$) for each metalloblock in copolymer 13 calculated using the Bard-Anson electrochemical method.\textsuperscript{87}

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>[M\textsubscript{8}] : [M\textsubscript{7}] : [C]\textsuperscript{a}</td>
<td>25 : 25 : 1</td>
<td></td>
</tr>
<tr>
<td>$M_m$\textsuperscript{b}</td>
<td>326.3</td>
<td></td>
</tr>
<tr>
<td>$M_p$\textsuperscript{c}</td>
<td>29354</td>
<td></td>
</tr>
<tr>
<td>$n_m$\textsuperscript{d} (mmol)</td>
<td>9.2×10\textsuperscript{-4}</td>
<td></td>
</tr>
<tr>
<td>$n_p$\textsuperscript{e} (mmol)</td>
<td>1.7×10\textsuperscript{-4}</td>
<td></td>
</tr>
<tr>
<td>$i_{dm}$ (cm)</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>Redox centers</td>
<td>Fc*</td>
<td>Fc</td>
</tr>
<tr>
<td>$i_{dp}$ (cm)</td>
<td>2.6</td>
<td>2.7</td>
</tr>
<tr>
<td>$n_{p3}$\textsuperscript{f}</td>
<td>19 ± 2</td>
<td>21 ± 2</td>
</tr>
</tbody>
</table>

\textsuperscript{a} [M\textsubscript{8}] : [M\textsubscript{7}] : [C]: feed molar ratio of monomers 8 and 7 to 1. \textsuperscript{b} Molecular weight of [FeCp*\textsubscript{2}]. \textsuperscript{c} Molecular weight of copolymer 13 calculated by monomer conversion determined by \textsuperscript{1}H NMR. \textsuperscript{d} $n_m$: mole of [FeCp*\textsubscript{2}] added in the CH\textsubscript{2}Cl\textsubscript{2} solution of copolymer 13. \textsuperscript{e} $n_p$: mole of copolymer 13 in CH\textsubscript{2}Cl\textsubscript{2}. \textsuperscript{f} $n_{p3}$: polymerization degree determined by the Bard-Anson’s method.
**Figure S42** IR spectrum of [Fc*]$^+$-containing diblock copolymer 14.
3430 cm$^{-1}$ ($\nu_{\text{N-H}}$), 2923 cm$^{-1}$ ($\nu_{\text{CH}_3}$), 2873 cm$^{-1}$, 1771 cm$^{-1}$ ($\nu_{\text{C=C}}$), 1698 cm$^{-1}$ ($\nu_{\text{C=O}}$), 1655 cm$^{-1}$ ($\delta_{\text{N-H}}$), 1544 cm$^{-1}$, 843 cm$^{-1}$ ($\nu_{\text{PF}_6}$), 558 cm$^{-1}$.

**Figure S43** UV-vis. spectra and pictures of [Fc*]$^+$-containing copolymer 14 and Fe*-containing copolymer 13 in CH$_2$Cl$_2$. 
Figure S44 ¹H NMR spectrum in CDCl₃ of Fe*-containing diblock copolymer 13 prepared by the reduction of [Fe*]⁺-containing copolymer 14.

Figure S45 UV-vis. spectra of Fe*-containing copolymer 13 prepared by the reduction of [Fe*]⁺-containing copolymer 14.
Figure S46 IR spectrum of Fe*-containing copolymer 13 prepared by the reduction of [Fe*]⁺-containing copolymer 14.

3394 cm⁻¹ ($\nu_{\text{N-H}}$), 2902 cm⁻¹ ($\nu_{\text{CH}_3}$), 1771 cm⁻¹ ($\nu_{\text{C=C}}$), 1701 cm⁻¹ ($\nu_{\text{C=O}}$), 1637 cm⁻¹ ($\delta_{\text{N-H}}$), 824 cm⁻¹ ($\nu_{\text{FeII}}$).
7. Diblock copolymer 15

Synthesis

Monomers 8 (27.8 mg, 0.0448 mmol) and 9 (29.6 mg, 0.0448 mmol) were added into two separate small glass tubes, and dissolved in 0.25 mL and 0.4 mL of dry CH$_2$Cl$_2$, respectively. A desired amount of Grubbs catalyst 3rd 1 (1.59 mg, 0.0018 mmol) was added into a small Schlenk flask, flushed with nitrogen, and dissolved in 0.03 mL of dry CH$_2$Cl$_2$. First, monomer 8 was transferred to the flask containing the catalyst via a small syringe. The reaction mixture was stirred vigorously for 10 minutes at r. t., after which monomer 9 was added into the flask using a small syringe. The polymerization was allowed to continue for another 10 minutes, and then quenched with 0.2 mL of EVE. The yellow-brown solid polymer 15 was purified by precipitating from CH$_2$Cl$_2$ with Et$_2$O three times and dried in vacuo until constant weight. Yield: 92%. ^1H NMR (300 MHz, CD$_2$Cl$_2$), δ ppm: 7.42-7.23 (m, NHCO-FbX and phenyl), 6.04 (broad, 1H, NHCO-Fc*), 5.74 and 5.52 (double broad, CH=CH), 4.88 (broad, sub. Cp of FbX), 4.61 (broad, sub. Cp of FbX), 4.17 (broad, sub. Cp of Fc*), 3.59-3.47 (m, CH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$), 3.32 (broad, NCH$_2$CH$_3$N), 3.01 (broad, =CH-C), 2.67 (broad, CO-C), 2.38 (s, CH$_3$ of (η$_6$-C$_6$Me$_6$)), 2.03 (broad, CH=CHCHC$_2$), 1.66 (broad, CH$_3$ of Fc*).

Kinetic Study

In order to know when the polymerization of the second block can finish, the kinetic study was conducted as following: Monomer 8 (0.364 g, 0.587 mmol) in 3 mL dry CH$_2$Cl$_2$ was added into the solution of Grubbs catalyst 3rd 1 (20.8 mg, 0.0235 mmol) in 0.2 mL dry CH$_2$Cl$_2$. The reaction mixture was stirred vigorously for 10 minutes at r. t. under N$_2$ atmosphere. Then, monomer 9 (0.387 g, 0.587 mmol) in 4 mL dry CH$_2$Cl$_2$ was added, and after 10, 15, 20 and 30 minutes, respectively, 0.5 mL of samples were taken out and quenched with 0.5 mL of EVE. The In situ ^1H NMR analysis in acetone-$d_6$ was conducted, and the conversion of monomer 9 was deemed to be 100% when the peak at 6.30 ppm, the signal of olefinic protons for monomer 9, disappeared. Actually, the polymerization of the second block can finish in 10 minutes with 100% monomer conversion.

Oxidation of copolymer 15 by ferricinium hexafluorophosphate

A freshly prepared solution of ferricinium hexafluorophosphate (2.4 mg, 7.3 × 10$^{-3}$ mmol) in dry CH$_2$Cl$_2$ (2.5 mL) was added dropwise to a solution of polymer 15 (8.46 mg, 6.61 × 10$^{-3}$ mmol of PMF) in dry CH$_2$Cl$_2$ (2.5 mL) under nitrogen at 25°C. The mixture was stirred for 5 min at 25°C, and then the solvent was removed in vacuo. The blue-green residual solid of crude [Fc*]$^+$-containing copolymer 16 was washed with pentane (5 × 5 mL), then dissolved in acetone, precipitated by addition of pentane, and dried in vacuo until constant weight (Yield: 8.66 mg, 92%). IR: ν bar = 3432 (N-H), 2922 (CH$_3$), 1771 (C=C), 1696 (C=O), 844 (PF$_6^-$) cm$^{-1}$; δ bar = 1659 (N-H) cm$^{-1}$; UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ = 435, 626, 751 nm. The structure was confirmed by reduction to the Fe*-containing copolymer 15.
Reduction of the \([\text{Fe}^*]\)-containing copolymer 16 by decamethylferrocene

A freshly prepared solution of decamethylferrocene (2.34 mg, \(7.17 \times 10^{-3}\) mmol) in acetone (2.0 mL) was added dropwise to a solution of copolymer 16 (8.5 mg, \(5.97 \times 10^{-3}\) mmol of \([\text{Fe}^*][\text{PF}_6]\)) in acetone (5.0 mL) under nitrogen at 25 °C. The mixture was stirred for 5 min at 25 °C, and then the solvent was removed in vacuo. The residual solid was washed five times with methanol (5.0 mL), and the purified \(\text{Fe}^*\)-containing copolymer 15 was obtained as a yellow solid (Yield: 7.1 mg, 93%). \(^1\)H NMR (300 MHz, CD\(_2\)Cl\(_2\)), \(\delta_{\text{ppm}}\): 7.44-7.24 (m, N\(\text{HCO-FbX}\) and phenyl), 6.02 (broad, 1H, N\(\text{HCO-Fe}^*\)), 5.76 and 5.54 (double broad, CH=CH), 4.90 (broad, sub. Cp of FbX), 4.62 (broad, sub. Cp of FbX), 4.48 (broad, sub. Cp of Fe*), 4.23 (broad, sub. Cp of Fe*), 3.60-3.46 (m, CH\(_2\)(CH\(_2\)OCH\(_2\))\(_3\)CH\(_2\)), 3.30 (broad, NCH\(_2\)CH\(_2\)N), 3.03 (broad, =CH-CH\(_2\)), 2.70 (broad, CO-CH\(_3\)), 2.40 (s, CH\(_3\) of \(\eta^6\)-C\(_6\)Me\(_6\)), 2.05 (s, CH\(_2\) of \(\eta^5\)-C\(_5\)Me\(_5\) and sub. Cp), 1.68 (broad, CH\(_3\) of Fe*). IR: \(\nu_{\text{bar}} = 1642\) (N-H) cm\(^{-1}\); UV/Vis (DCM): \(\lambda_{\text{max}} = 423\) nm.

![Figure S47](image-url)

**Figure S47** \(^{13}\)C NMR spectrum of diblock copolymer 15 in CD\(_2\)Cl\(_2\).

\(^{13}\)C NMR (50 MHz, CD\(_2\)Cl\(_2\)), \(\delta_{\text{ppm}}\): 178.6 (CON), 132.4, 132.3 (C=C), 99.8 (\(\eta^6\)-C\(_6\)Me\(_6\)), 84.4 (\(\eta^5\)-C\(_5\)Me\(_5\) and sub. Cp), 70.8, 70.6, 70.4, 70.3, 67.4 (CH\(_2\) and sub. Cp), 51.3 (CO-CH\(_3\)), 46.8 (=CH-CH\(_3\)), 46.4 (CH\(_2\) of cyclopentane), 39.5, 38.2 (-CH\(_2\)CH\(_2\)-NCO), 17.1 (CH\(_3\) of \(\eta^6\)-C\(_6\)Me\(_6\)), 10.7 (CH\(_3\) of \(\eta^5\)-C\(_5\)Me\(_5\)).
Figure S48 IR spectrum of diblock copolymer 15.
3433 cm$^{-1}$ ($\nu_{N-H}$), 2907 cm$^{-1}$ ($\nu_{CH_3}$), 1771 cm$^{-1}$ ($\nu_{C=C}$), 1701 cm$^{-1}$ ($\nu_{C=O}$), 1638 cm$^{-1}$ ($\delta_{N-H}$), 1541 cm$^{-1}$, 1396 cm$^{-1}$, 845 cm$^{-1}$ ($\nu_{PF_6}$), 733 cm$^{-1}$.

Figure S49 UV-Vis spectra of diblock copolymer 15, Fc*-containing homopolymer of 8, FbX-containing homopolymer of 9 in CH$_2$Cl$_2$. 

S45
Figure S50 MALDI-TOF MS spectrum of diblock copolymer 15. The feed molar ratio of monomers 8 and 9 to 1 is 25 : 25 : 1. (A) is the region of 5000-20000 in the spectrum; and (B) is the enlarged region of the spectrum from 9720 to 12847. The red dotted lines correspond to the difference between molecular peaks of a value of 620 ±1 Da (MW of monomer 8). The pink dotted lines correspond to the difference between molecular peaks of a value of 660 ±1 Da (MW of monomer 9).
Figure S51 ¹H NMR spectrum in acetone-$d_6$ of the ROMP reaction mixture for the synthesis of diblock copolymer 15 after the addition of monomer 9 with 10 minutes stirring. No peak was observed at 6.30 ppm or so for the olefin protons of monomer 9, namely no monomer 9 was left and the ROMP of 9 is complete.

Table S10 Polymer degree of the second FbX block using the ¹H NMR spectrum in CD$_2$Cl$_2$ of copolymer 15.\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Proton peak</th>
<th>Amido in the first block</th>
<th>Sub. Cp in the second block</th>
<th>Sub. Cp in the second block</th>
<th>Methyl of C$_6$Me$_6$ in the second block</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ ppm</td>
<td>6.04</td>
<td>4.88</td>
<td>4.61</td>
<td>2.38</td>
</tr>
<tr>
<td>Integration</td>
<td>1.15-1.19</td>
<td>2.07-2.15</td>
<td>2.03-2.20</td>
<td>17.2-17.6</td>
</tr>
<tr>
<td>$n_{p2a}$</td>
<td>-</td>
<td>21-24\textsuperscript{c}</td>
<td>21-25\textsuperscript{c}</td>
<td>19-22\textsuperscript{d}</td>
</tr>
<tr>
<td>$n_{p2b}$\textsuperscript{e}</td>
<td></td>
<td></td>
<td></td>
<td>22 ± 3</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Figure 3 in the main text was used for the calculation of the polymer degree of the second block. \textsuperscript{b} The average polymer degree of 25 ± 1 for the first Fc* block, as shown in Table S6, was used for the calculation of polymer degree of the second FbX block. \textsuperscript{c} Calculated by comparing the amido proton integration in the first block and the substituted Cp proton integration in the second block. \textsuperscript{d} Calculated by comparing the amido proton integration in the first block and the methyl proton integration of C$_6$Me$_6$ in the second block. \textsuperscript{e} Average polymer degree for the second block according to the $n_{p2a}$ values.
For the second FbX block, the polymer degree is 22 ± 3, as shown in Table S10. The largest error results from the following two sides. (1) This analysis was carried out by comparing the integration of the characteristic peaks of the first Fe* block and the second FbX block. The former is the amido peak at 6.04 ppm with integration of 1.15-1.19; the latter is the substituted Cp peaks at 4.88 ppm with the integration of 2.07-2.15 and 4.61 ppm with the integration of 2.03-2.20, and the methyl peak of C₆Me₆ at 2.38 ppm with the integration of 17.21-17.62. Obviously, integrations for each peak have error that results in the corresponding error for the calculated polymer degree of the second block. (2) The above obtained polymer degree of 25 ± 1 for the first Fe* block is used for the calculation of the polymer degree for the second FbX block, which also results in a larger error than for the first block. The obtained values are 21-24, 21-25 and 19-22, respectively, and then the average is 22 ± 3.

Table S11 Redox potentials, chemical ($i_c/i_a$) and electrochemical ($E_{pa}-E_{pc} = \Delta E$ ) reversibility data for the diblock copolymer 15

<table>
<thead>
<tr>
<th></th>
<th>Fe* center</th>
<th>FbX center</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{1/2}$ (ΔE) (V)</td>
<td>$i_c/i_a$</td>
<td>$E_{1/2}$ (ΔE) (V)</td>
</tr>
<tr>
<td>0.390 (0.02)</td>
<td>1.13</td>
<td>-1.290 (0.07)</td>
</tr>
</tbody>
</table>

Calculation of the polymerization degrees ($n_{p3}$) for diblock copolymer 15 by Bard-Anson’s method

The following modified Bard-Anson’s electrochemical equation is used:

$$n_{p3} = \left( \frac{i_{dp}n_m}{i_{dm}n_p} \right) \left( \frac{M_p}{M_m} \right)^{0.275}$$

($i_{dp}$: intensity of polymer; $n_p$: mole of polymer; $i_{dm}$: intensity of monomer; $n_m$: mole of monomer; $M_p$: molecular weight of polymer; $M_m$: molecular weight of monomer).

[FeCp*₂] was used as the monomer reference. The results of calculated polymerization degrees ($n_{p3}$) of the Fe* and FbX blocks for diblock copolymer 15 are listed in Table S12.
Table S12 Polymerization degree ($n_{p3}$) for each mettallolblock in polymer 15 calculated using the Bard-Anson electrochemical method.

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>$M_m^b$</td>
<td></td>
<td>326.3</td>
</tr>
<tr>
<td>$M_p^c$</td>
<td></td>
<td>32104</td>
</tr>
<tr>
<td>$n_m^d$</td>
<td>(mmol)</td>
<td>9.2×10⁻⁴</td>
</tr>
<tr>
<td>$n_p^e$</td>
<td>(mmol)</td>
<td>1.49×10⁻³</td>
</tr>
<tr>
<td>$i_{dm}$</td>
<td>(cm)</td>
<td>2.5</td>
</tr>
<tr>
<td>Redox center</td>
<td></td>
<td>Fe*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FbX</td>
</tr>
<tr>
<td>$i_{dp}$</td>
<td>(cm)</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.8</td>
</tr>
<tr>
<td>$n_{p1}^f$</td>
<td></td>
<td>20 ± 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21 ± 2</td>
</tr>
</tbody>
</table>

$^a$ [M₈] : [M₉] : [C]: feed molar ratio of monomers 8 and 9 to 1. $^b$ Molecular weight of decamethyferrocene. $^c$ Molecular weight of the copolymer 15 calculated by monomer conversion determined by $^d$ $n_{m}$: mole of [FeCp*₂] added in the DMF solution of the copolymer 15. $^e$ $n_p$: mole of the copolymer 15 in DMF. $^f$ $n_{p1}$: polymerization degree determined by the Bard-Anson method.

Figure S52 IR spectrum of [Fe*]⁺-containing diblock copolymer 16.
3432 cm⁻¹ ($ν_{N-H}$), 2922 cm⁻¹ ($ν_{CH3}$), 1771 cm⁻¹ ($ν_{C=O}$), 1696 cm⁻¹ ($ν_{C=O}$), 1659 cm⁻¹ ($δ_{N-H}$), 1544 cm⁻¹, 1399 cm⁻¹, 844 cm⁻¹ ($ν_{PF6}$), 558 cm⁻¹.
Figure S53 UV-vis. spectrum and picture of [Fc*]⁺-containing copolymer 16 in CH₂Cl₂.

Figure S54 ¹H NMR spectrum in CD₂Cl₂ of Fc*-containing diblock copolymer 15 prepared by the reduction of [Fc*]⁺-containing copolymer 16.
Figure S55 UV-vis. spectrum of Fe*-containing diblock copolymer 15 prepared by the reduction of [Fe*]⁺-containing copolymer 16.

Figure S56 IR spectrum of Fe*-containing diblock copolymer 15 prepared by the reduction of [Fe*]⁺-containing copolymer 16.

3434 cm⁻¹ (νN-H), 2918 cm⁻¹ (νCH₃), 1771 cm⁻¹ (νC=O), 1699 cm⁻¹ (νC=O), 1642 cm⁻¹ (δN-H), 1537 cm⁻¹, 1396 cm⁻¹, 846 cm⁻¹ (νPF₆), 735 cm⁻¹.
8. References


