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**Metallopolymer-*block*-oligosaccharide
for sub-10 nm microphase separation**

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Experimental

Materials. *sec*-Butyllithium (*sec*-BuLi; Kanto Chemical Co., Inc. (Kanto), 1.00 mol L⁻¹ in cyclohexane, *n*-hexane), CaH₂ (Kanto, >95.0%), dry MeOH (Kanto, >99.8), Palladium 10% on carbon (Pd/C; Tokyo Chemical Industry Co., Ltd (TCI), wetted with *ca.* 55% water), 4-dimethylaminopyridine (DMAP; TCI, >99.0%), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl; TCI, >98.0%), *N,N,N',N',N'*-pentamethyldiethylenetriamine, and copper(I) bromide (CuBr; Sigma-Aldrich Chemicals Co., 99.999% trace metals basis) were purchased from the commercial resources and used as received. Benzyl glycidyl ether (BGE; TCI, >97.0%) was purchased and purified by distillation over CaH₂ under vacuum. EtOH (Kanto, >99.5%) and dry DMF (Kanto, >99.5%, water content, <0.001%) were purchased and used as received. Dry CH₂Cl₂ (Kanto, >99.5%, water content, <0.001%), dry toluene (Kanto, >99.5%, water content, <0.001%) and dry THF (Kanto, >99.5%, water content, <0.001%) were further purified by an MBRAUN MB SPS Compact solvent purification system equipped with two MB-KOL-A columns (for dry CH₂Cl₂), a MB-KOL-C and a MB-KOL-A columns (for dry toluene) or a MB-KOL-A and a MB-KOL-M Type 1 columns (for dry THF), which were directly used for reactions. Vinylferrocene (VFc)¹ and 6-azidohexanoic acid² was synthesized according to reported methods.

Instruments. ¹H NMR (400 MHz) spectra were obtained using a JEOL JNM-ESC 400 instrument at 25 °C. The size exclusion chromatography (SEC) measurements were performed at 40 °C in THF (flow rate, 1.0 mL min⁻¹) using a Jasco high-performance liquid chromatography system (PU-

980 Intelligent HPLC Pump, CO-2065 Plus Intelligent Column Oven, RI-2031 Plus Intelligent RI Detector, and DG-2080-53 Degasser) equipped with a Shodex KF-G guard column (4.6 mm × 10 mm; particle size, 8 μm) and two Shodex KF-804L columns (linear; particle size 7 μm; 8.0 mm × 300 mm; exclusion limit, 4 × 10⁴) or in DMF (flow rate, 0.6 mL min⁻¹; containing 0.01 mol L⁻¹ LiCl) using a JASCO HPLC system (PU-980 Intelligent HPLC Pump, CO-965 Column Oven, RI-930 Intelligent RI Detector, and DG-2080-53 Degasser) equipped with a Shodex KD-G guard column (4.6 mm × 10 mm; particle size, 8 μm), a Shodex Asahipak GF-310 HQ column (linear; particle size, 5 μm; 7.5 mm × 300 mm; exclusion limit, 4 × 10⁴) and a Shodex Asahipak GF-7 M HQ column (linear; particle size, 9 μm; 7.5 mm × 300 mm; exclusion limit, 1.0 × 10⁷). The number-average molecular weight ($M_{n,SEC}$) and dispersity (\mathcal{D}) were calculated based on polystyrene standards. The Fourier transform infrared (FT-IR) spectra were obtained using a PerkinElmer Frontier MIR spectrometer equipped with a single reflection diamond universal attenuated total reflection (ATR) accessory. Differential scanning calorimetry (DSC) experiments were performed using a Hitachi DSC 7000X under nitrogen atmosphere. All the polymer samples were heated to 180 °C, cooled to 30 °C, and heated to 200 °C again at the heating and cooling rates of 10 °C min⁻¹ and 20 °C min⁻¹, respectively.

Atomic force microscopy (AFM). The AFM phase images were obtained using a Molecular Imaging PicoPlus atomic force microscope operating in the tapping mode with a silicon cantilever (Nanoworld AG, NANOSENSORSTM PPP-NCH) having resonant frequency and spring constant of

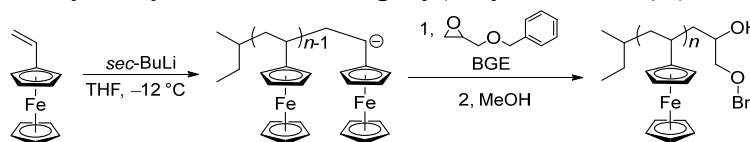
190 kHz and 48 N m^{-1} , respectively. The thin films for the AFM observation were prepared by spin-coating (3000 rpm for 60 s) the polymer solution in DMF (5 wt%) onto a Si substrate with a native oxide layer.

Small angle X-ray scattering (SAXS). The morphology and domain-spacing (d) of the microphase-separated polymer samples were determined by SAXS analysis. The SAXS measurements were performed at the BL-6A beamline of the Photon Factory in the High Energy Accelerator Research Organization (KEK, Tsukuba, Japan) using X-ray beams with $\lambda = 0.15 \text{ nm}$ at room temperature. The scattering data were collected by a 2D detector (a PILATUS3 1M detector (Dectris Ltd.)), where the samples-to-detector distance was set to be 1.5 m. The scattering angle (θ) was calibrated using silver behenate (Nagara Science Co., Ltd) as the standard and derived the scattering vector (q) from Bragg's equation ($q = (4\pi/\lambda)\sin(\theta/2)$). The d value was calculated by $d = 2\pi/q^*$ (q^* is principal scattering peak position.). Before the experiment, the powder samples of the block copolymers (BCPs) was placed in a glass capillary with an inner diameter of 1.5 mm and annealed under vacuum at $180 \text{ }^\circ\text{C}$ for 1 h, which were subjected to the SAXS measurement at room temperature.

Reactive ion etching (RIE). Investigation of etching resistance of homopolymer thin films was performed using Samco RIE-10NRV. The thin film samples of PVFc were prepared by spin-coating (2,000 rpm for 60 s) the polymer solution in toluene (5 wt%) onto Si substrate with a native

oxide layer. The thin film samples of maltotriose were prepared by spin-coating (3,000 rpm for 120 s) the DMF/MeOH (90/10 w/w) solution onto a Si substrate treated with air plasma. The samples of PVFc and MT were etched in O₂ plasma for 5, 10, 20, and 30 s with 80 W applied RF power at 10 Pa and 75 sccm. The film thickness of the samples before and after the etching were measured by ellipsometry (JASCO M-500S) to determine the etching depth.

Synthesis of one ω -end hydroxy-functionalized poly(vinyl ferrocene) (PVFc-OH) ^{1,3,4}

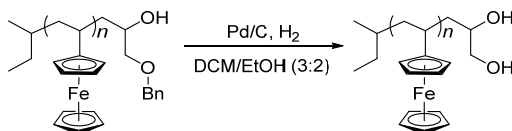


VFc was dissolved in dry toluene and stirred with CaH₂ overnight. After removing the solvent, the solid was purified by sublimation and the purified VFc was stored in the glovebox. In the glovebox, the purified VFc (2.78g, 13.1 mmol) and dry THF (73 mL) were placed in separate Schlenk flasks, then the flasks were sealed with a grease-less valve. After these Schlenk flasks were taken out from the glovebox, a little of *sec*-BuLi was added to the dry THF to completely remove impurities. Then, the dry THF was transferred to the VFc-containing Schlenk flask by trap-to-trap distillation. After cooling to -12 °C, *sec*-BuLi (728 μL, 0.728 mmol as a 1.00 mol L⁻¹ stock solution in cyclohexane, *n*-hexane) was added to the monomer solution to initiate the polymerization under Ar atmosphere. After stirring for 50 min, benzyl glycidyl ether (BGE) was added to the solution. This mixture was stirred for 2 h at -12 °C and an additional overnight at room temperature. Then, a little of dry MeOH was added to the solution, then the mixture was stirred for 2 h. The reaction mixture was reprecipitated into

cold MeOH to give PVFc–OH as a yellow powder. Yield: 1.83 g (65.8%)

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.47–7.22 (m, BGE aromatic), 4.66–3.44 (br, PVFc aromatic –CH), 2.86–0.50 (br, PVFc backbone – CH_2 –CH–)

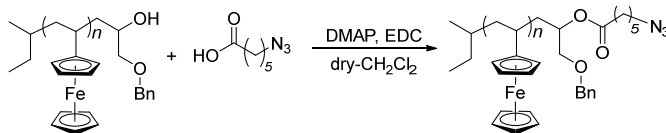
Synthesis of two ω -ends hydroxy-functionalized poly(vinyl ferrocene) (PVFc–(OH) $_2$)^{3,4}



The obtained PVFc–OH (597.4 mg, 187 μmol), Pd/C (59.4 mg), dry CH_2Cl_2 (39 mL), and EtOH (26 mL) were placed in a flask. The flask was filled with H_2 gas and this mixture was stirred for 4 days at room temperature. This reaction mixture was filtered over celite to remove the catalyst, and the solvent was removed under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 and reprecipitated to cold MeOH to give PVFc–(OH) $_2$ as a yellow powder. Yield: 420 mg (72.3%)

^1H NMR (400 MHz, CDCl_3): δ (ppm) 4.64–3.04 (br, PVFc aromatic –CH), 2.75–0.51 (br, PVFc backbone – CH_2 –CH–)

Synthesis of one ω -end azido-functionalized poly(vinylferrocene) (PVFc– N_3)

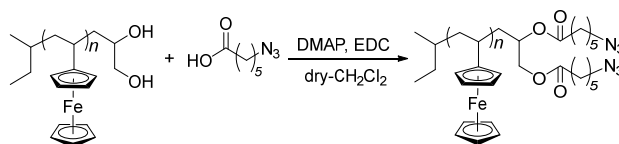


A typical procedure of the synthesis of PVFc– N_3 is as follows (method A): Prior to the reaction, the obtained PVFc–OH was subjected to coevaporation with dry toluene to remove any trace of MeOH. PVFc–OH (604.0 mg, 189 μmol), DMAP (115.8 mg, 948 μmol), EDC \cdot HCl (256.9 mg, 1.34 mmol), 6-azidohexanoic acid (194.9 mg, 1.24 mmol), and dry CH_2Cl_2 (24 mL) were placed in a vial

bottle. After stirring for 5 days at room temperature, the mixture was reprecipitated to cold MeOH, giving PVFc–N₃ as a yellow powder. Yield: 610 mg (96.7%)

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.43–7.20 (m, BGE aromatic), 4.62–3.12 (br, PVFc aromatic –CH), 3.29–3.12 (br, –CH₂N₃). 2.83–0.48 (br, PVFc backbone –CH₂–CH–)

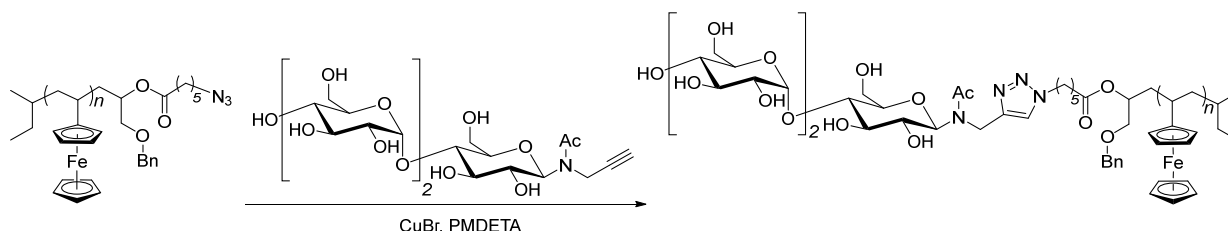
Synthesis of two ω-ends azide-functionalized poly(vinyl ferrocene) (PVFc–(N₃)₂)



Method A was applied for PVFc–(OH)₂ (369.6 mg, 119 μmol), DMAP (128.8 mg, 1.05 mmol), EDC·HCl (261.9 mg, 1.37 mmol), 6-azidohexanoic acid (194.9 mg, 1.24 mmol), and dry CH₂Cl₂ (20 mL) at room temperature for 10 days to give PVFc–(N₃)₂ as a yellow powder. Yield: 340 mg (84.4%)

¹H NMR (400 MHz, CDCl₃): δ (ppm) 4.60–3.10 (br, PVFc aromatic –CH), 3.35–3.17 (br, –CH₂N₃). 2.75–0.51 (br, PVFc backbone –CH₂–CH–)

Synthesis of linear poly(vinyl ferrocene)-*block*-maltotriose (PVFc-*b*-MT)

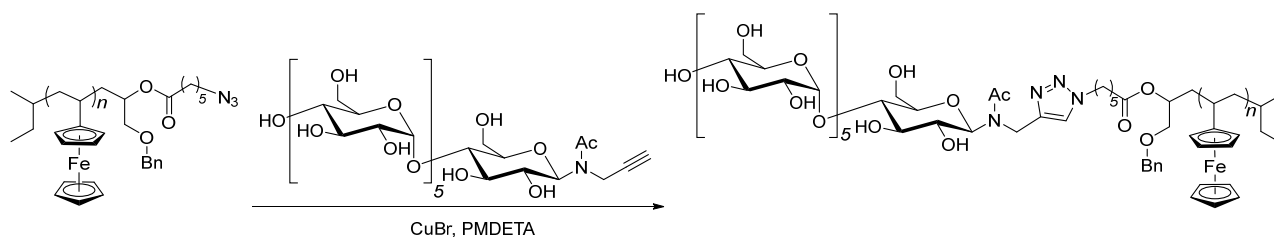


A typical procedure for the click reaction is as follows (Method B): PVFc–N₃ (421.8 mg, 127 μmol), *N*-maltotriosyl-3-acetamido-1-propyne (MT–C≡CH; 96.8 mg, 166 μmol), and CuBr (24.8

mg, 173 μmol) were added in a Schlenk flask. A solution of N,N,N',N',N' -pentamethyldiethylenetriamine (PMDETA; 34.2 μL , 164 μmol) in a mixed solvent of THF (8 mL) and DMF (8 mL) was transferred to the Schlenk flask under Ar atmosphere after degassing by Ar bubbling. After stirring at 60 $^{\circ}\text{C}$ for 3 days, Dowex[®] 50WX2 was added to remove the Cu catalyst. After removing the Dowex by filtration, the solution was reprecipitated to a mixed solvent of acetonitrile and water (acetonitrile/water = 7/3 (v/v)) to give PVFc-*b*-MT as an orange powder. Yield: 430 mg (86.8%)

^1H NMR (400 MHz, DMF- d_7): δ (ppm) 8.34–7.92, 7.75 (rotamers, triazole methine), 7.52–7.22 (br, m, BGE aromatic), 6.06, 5.92–5.52, 5.25–4.56 (sugar protons), 4.85–2.96 (br, PVFc aromatic –CH), 2.95–0.14 (br, PVFc backbone –CH₂–CH–)

Synthesis of linear poly(vinyl ferrocene)-*block*-maltohexaose (PVFc-*b*-MH)

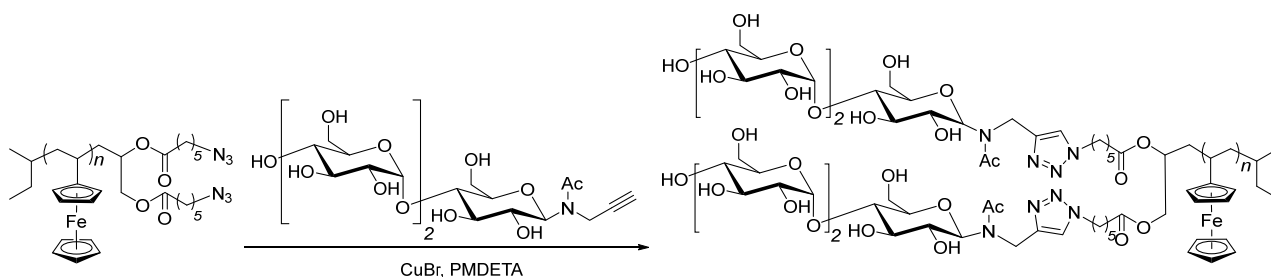


Method B was used applied for PVFc-(N₃)₂ (84.0 mg, 25.2 μmol), *N*-maltohexaosyl-3-acetamido-1-propyne (MH-C≡CH; 37.0 mg, 346 μmol), CuBr (4.8 mg, 33.5 μmol), N,N,N',N',N' -pentamethyldiethylenetriamine (PMDETA; 6.8 μL , 32.8 μmol) in a mixed solvent of THF (5 mL) and DMF (5 mL) at 60 $^{\circ}\text{C}$ for 4 days to give PVFc-*b*-MH as a brown powder. Yield: 50 mg (41%)

^1H NMR (400 MHz, DMF- d_7): δ (ppm) 8.34–8.10, 7.76, 7.71–7.64 (rotamers, triazole methine), 7.52–

7.24 (br, m, BGE aromatic), 6.12–6.05, 6.01–5.54, 5.21–4.58 (sugar protons), 4.81–3.15 (br, PVFc aromatic –CH), 3.14–0.54 (br, PVFc backbone –CH₂–CH–)

Synthesis of miktoarm shape poly(vinyl ferrocene)-*block*-maltotriose (PVFc-*b*-(MT)₂)



Method B was used applied for PVFc-(N₃)₂ (270 mg, 79.9 μmol), *N*-maltotriosyl-3-acetamido-1-propyne (MT-C≡CH; 114.9 mg, 197 μmol), CuBr (28.0 mg, 195 μmol), *N,N,N',N',N'*-pentamethyldiethylenetriamine (PMDETA; 7 μL, 33.5 μmol) in a mixed solvent of THF (8.5 mL) and DMF (8.5 mL) at 60 °C for 4 days to give PVFc-*b*-(MT)₂ as a brown powder. Yield: 300 mg (82.5%)

¹H NMR (400 MHz, DMF-*d*₇) : δ (ppm) 8.34–7.92, 7.7 (rotamers, triazole methine), 7.52–7.22 (br, m, BGE aromatic), 6.07, 5.94–5.56, 5.25–4.57 (sugar protons), 4.85–3.18 (br, PVFc aromatic –CH), 3.16–0.51 (br, PVFc backbone –CH₂–CH–)

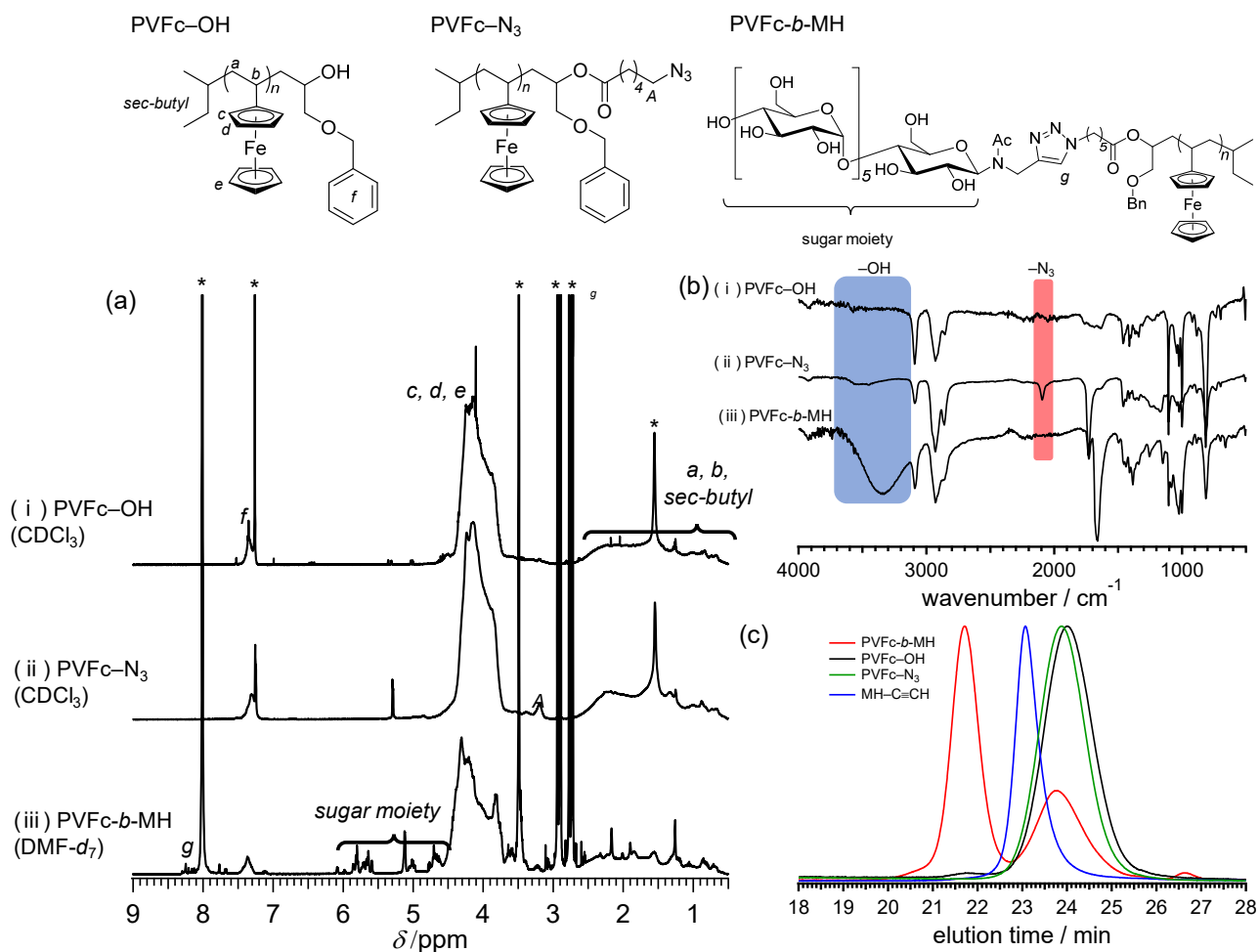


Figure S1. Characterization of PVFc-b-MH. (a) ¹H NMR spectra of PVFc-OH (i) and PVFc-N₃ (ii) in CDCl₃ and PVFc-b-MH (iii) in DMF-*d*₇ (400 MHz). (b) FT-IR spectra of PVFc-OH (i), PVFc-N₃ (ii), and PVFc-b-MH (iii). (c) SEC traces of PVFc-b-MH (red line), PVFc-OH (black line), PVFc-N₃ (green line), and MH-C≡CH (blue line) (eluent, DMF containing 0.01 mol L⁻¹ LiCl; flow rate, 0.60 mL min⁻¹).

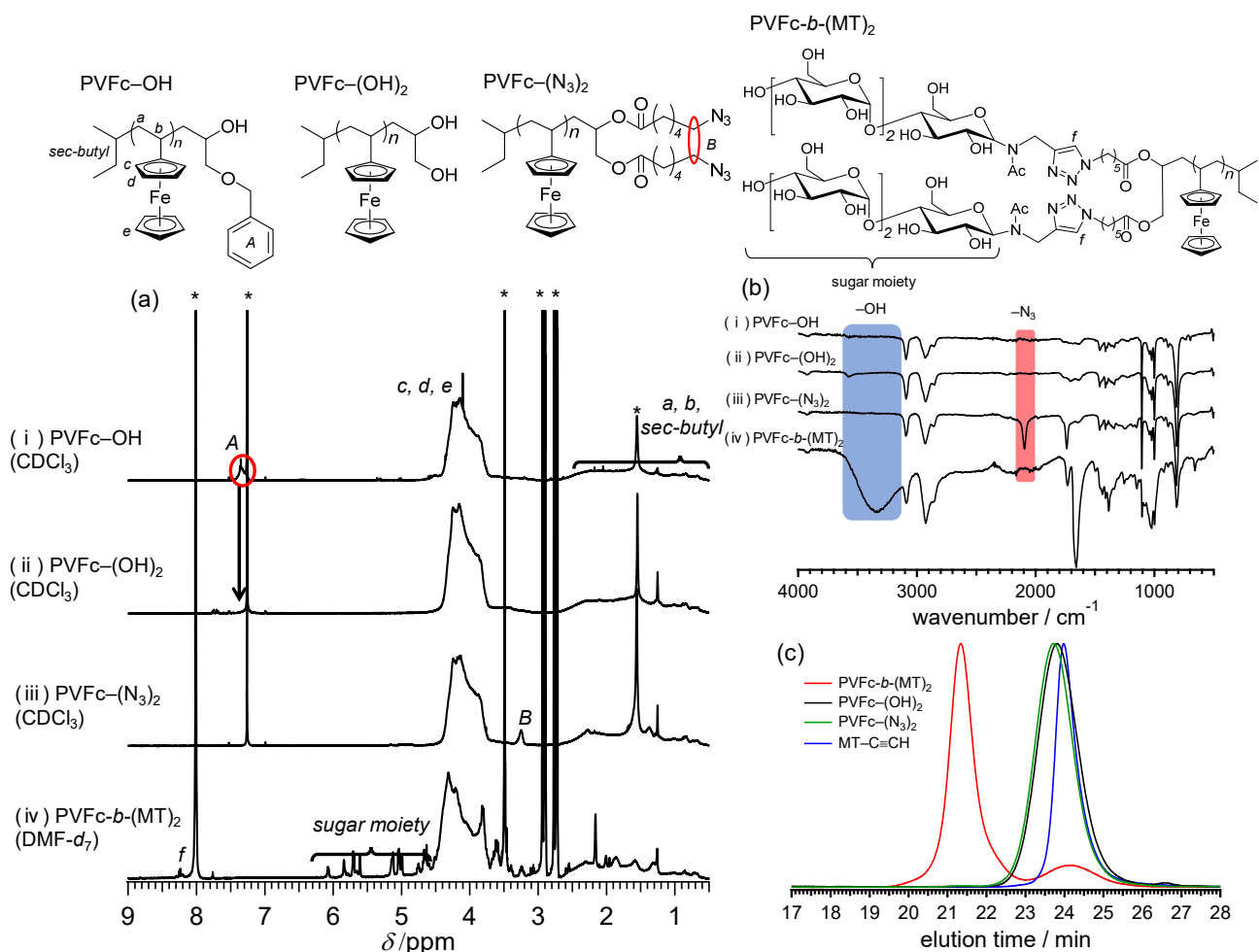


Figure S2. Characterization of PVFc-*b*-(MT)₂. (a) ¹H NMR spectra of PVFc-OH (top), PVFc-(OH)₂ (second from top), PVFc-(N₃)₂ (third from top) in CDCl₃, and PVFc-*b*-(MT)₂ (bottom) in DMF-*d*₇ (400 MHz). (b) FT-IR spectra of PVFc-OH (top), PVFc-(OH)₂ (second from top), PVFc-(N₃)₂ (third from top) and PVFc-*b*-(MT)₂ (bottom). (c) SEC traces of PVFc-*b*-(MT)₂ (red line), PVFc-(OH)₂ (black line), PVFc-(N₃)₂ (green line), and MT-C≡CH (blue line) (eluent, DMF containing 0.01 mol L⁻¹ LiCl; flow rate, 0.60 mL min⁻¹).

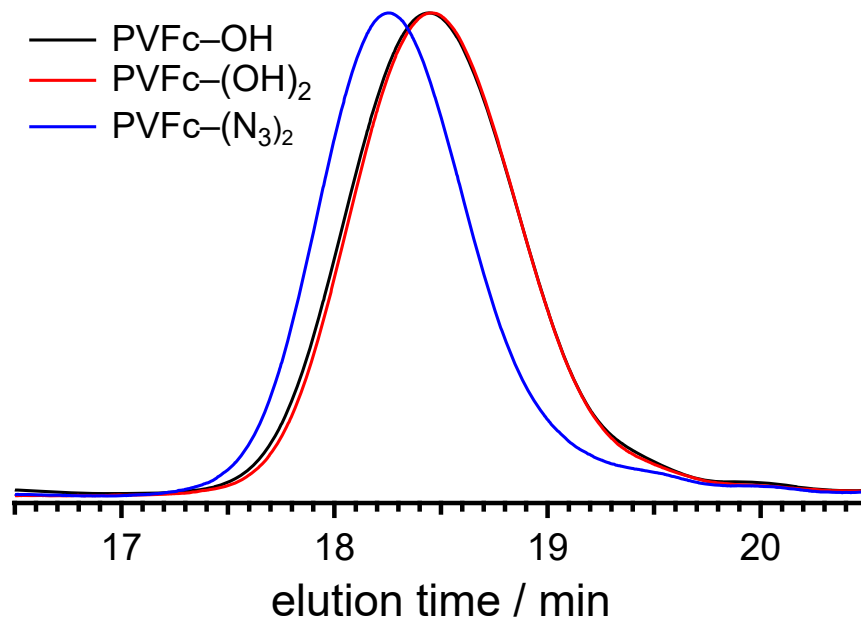


Figure S3. SEC traces of PVFc-OH (black line), PVFc-(OH)₂ (red line) and PVFc-(N₃)₂ (blue line) (eluent, THF; flow rate, 1.0 mL min⁻¹).

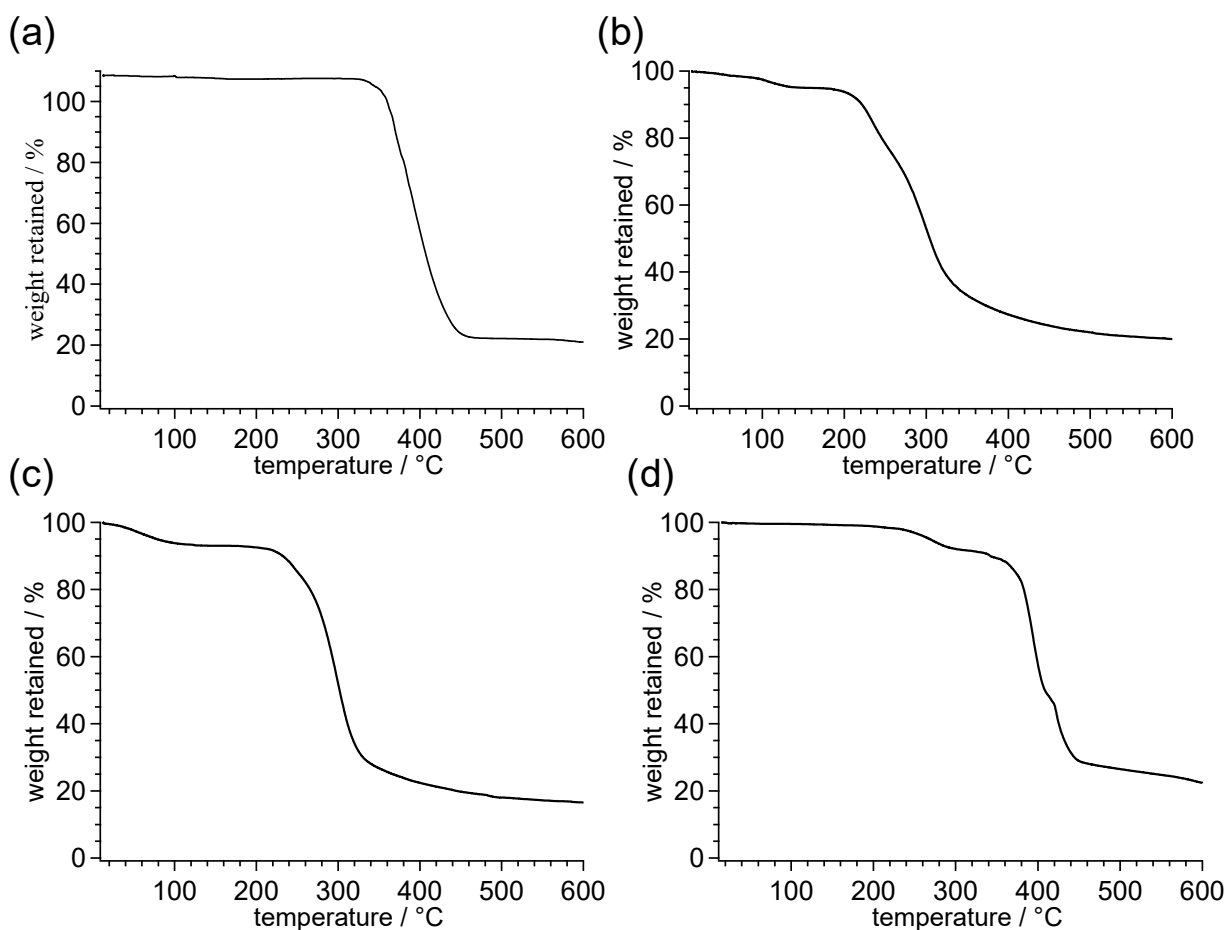
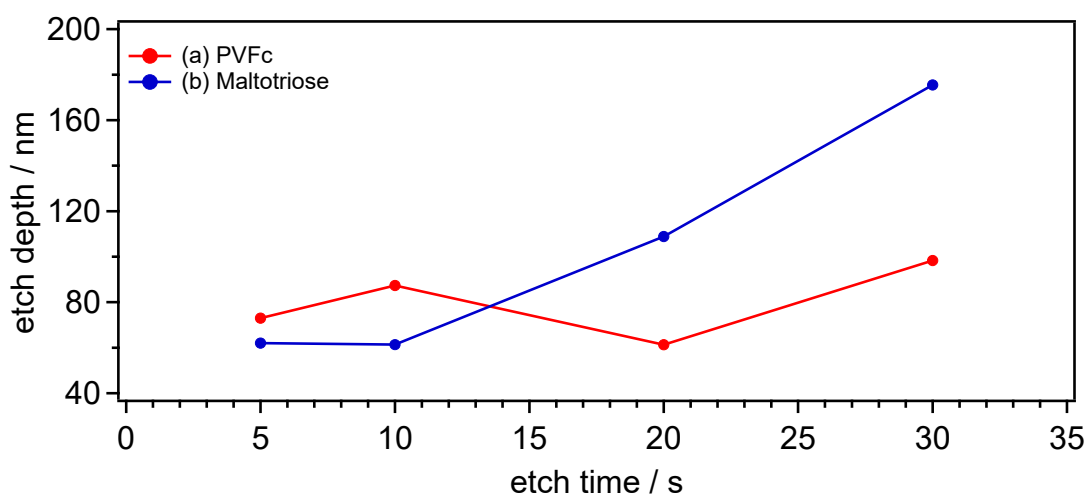
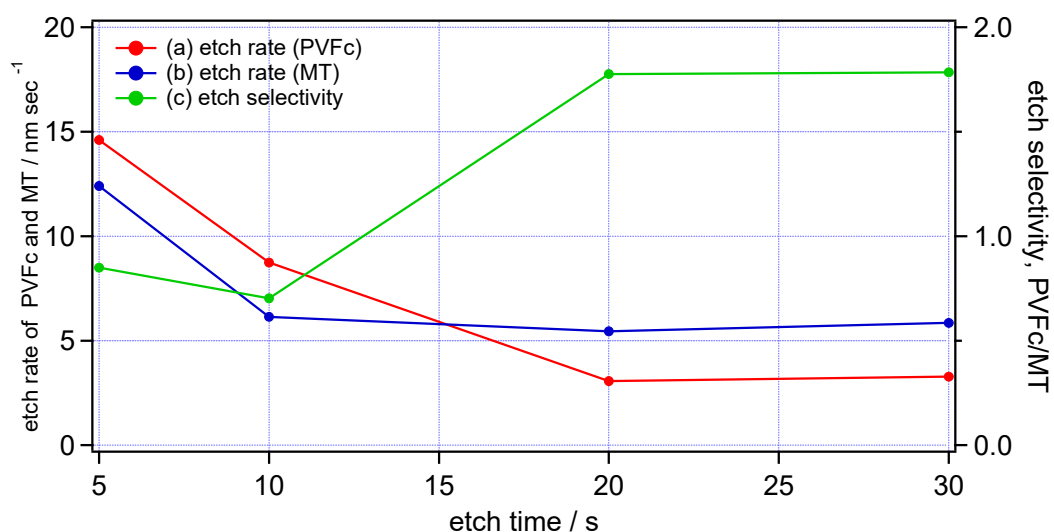


Figure S4. TGA profiles of (a) PVFc-OH, (b) MT-C≡CH, (c) MH-C≡CH, and (d) PVFc-*b*-MT obtained under a nitrogen atmosphere.

Table S1. Results of etching treatments on the PVFc and MT thin films^a

etch time / s ^b	PVFc etch depth / nm	MT etch depth / nm ^b	PVFc etch rate / nm min ^{-1c}	MT etch rate / nm min ^{-1c}	PVFc to MT etch selectivity ^d
5	73.0	62.0	14.6	12.4	0.85
10	87.4	61.4	8.73	6.14	0.70
20	61.3	109	3.07	5.45	1.78
30	98.3	175	3.28	5.85	1.78

^aEtching condition: pressure, 12 Pa; RF power, 80 W; gas flow, 75 sccm; etching gas, O₂

**Figure S5.** Etch profiles of (a) PVFc and (b) MT thin films subjected to an oxygen RIE.**Figure S6.** Etch rates for PVFc (black line) and MT thin films (red line) and etch selectivity between PVFc and MT (blue line) as a function of etch time.

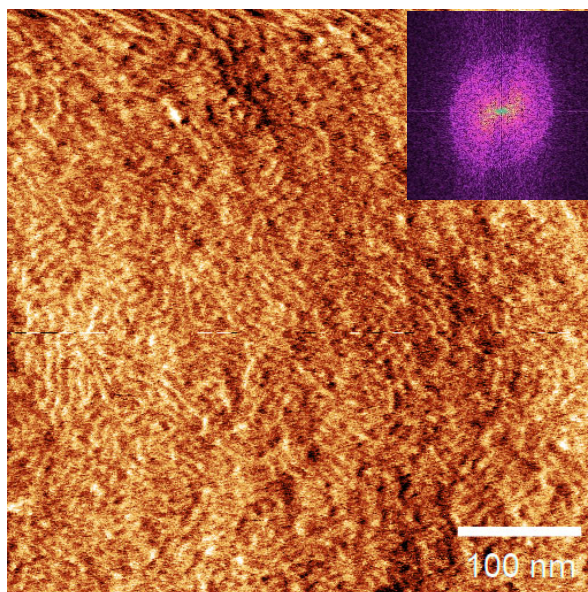


Figure S7. AFM phase image of PVFc-*b*-(MT)₂ thin film. The inset shows the FFT obtained from the phase image. Scale bar is 100 nm.

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