ORGANOMETALLICS

Synthesis of Conjugated Main-Chain Ferrocene-Containing **Polymers through Melt-State Polymerization**

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S Supporting Information

ABSTRACT: Two kinds of conjugated main-chain ferrocene (Fc)-containing polymers, PFcT8 and PFcTP8, were successfully prepared through the facile melt-state polymerization (MSP) of corresponding monomers which combine the Fc motif with thiophene or thiophene-methane groups. The simple, low-cost MSP was chosen as the method, while



thiophene or thiophene-methane groups served as reactive sites for its feature of easy polymerization by a simple heating process. The prepared metallopolymers were characterized by ¹H NMR, FTIR, and photochemical and electrochemical analysis, metal content, and thermal stability. The results show that metallopolymers with a regular backbone and nearly quantitative metal content were obtained. In addition, the metallopolymer PFcTP8 has the smallest optical band gap (absorption edge at 1100 nm) and high thermal stability among reported Fc-containing polymers, which indicates the thiophene-methane-based Fccontaining structure is a good candidate to construct functional polymers through MSP. The low band gap and high thermal stability of prepared conjugated metallopolymers show their potential application in conducting materials with high working temperature.

1. INTRODUCTION

Ferrocene (Fc)-containing polymers have been widely applied in many areas, such as gas storage, 1,2 magnetic materials, 3,4 organic electronics, $^{5-7}$ catalysis, 8,9 sensors, $^{10-13}$ etc., due to their unique sandwich structure and intriguing properties of the Fc group. For example, Fromm et al. have recently reported a mechanically induced metal ion release polymer where Fc was incorporated as an iron ion releasing mechanophore that responds to sonication.¹⁴ Various synthetic pathways, including living and controlled polymerization strategies as well as surface immobilization methodologies,^{15,16} have been developed to prepare main-chain¹⁷ and sidechain¹⁸⁻²⁰ Fc-containing polymers. Poly(vinylferrocene) was the first Fc-containing polymer and was synthesized through free radical polymerization by Arimoto and co-workers in the 1950s.²¹ During the next decades, several controlled and living polymerization methodologies, including the anionic polymerization of vinylferrocene^{22,23} and ring-opening polymerization of norbornene derivatives²⁴ or strained ferrcoenophanes,²⁵ have emerged and enriched the scope of Fc-containing polymers. In order to prepare metallopolymers with a specific morphology or application, some novel methods, including surface-initiated polymerization for surface-decorated Fccontaining polymers,²⁶ an electrostatic layer-by-layer (LbL) deposition technique for functional multilayer polymer films, and self-assembly for nanoparticles^{28,29} or (hydro)gels,^{30,31} have also been developed. For instance, the surface-initiated polymerization of Fc-containing methacrylates can be carried

out in various substrates such as the surface of mesoporous silica,³² organic particles,³³ and cellulose fibers.³⁴

Synthesis of main-chain Fc-containing polymers, in which the Fc motif is integrated into the polymer backbone, is a big challenge due to the necessity of constructing a difunctionalized Fc group in the monomer synthesis step. Moreover, in addition to poly(ferrocenylenevinylene)^{35,36} and polyferrocenylenes,³⁷ there are few reports about conjugated Fccontaining polymers that integrate the Fc into the main chain.^{38,39} Choi and co-workers⁷ have prepared a redox-active main-chain Fc-containing polymer through the palladiumcatalyzed copolymerization of three different components. However, in terms of structure, this method may lead to an irregular structure and poor experimental reproducibility. On the basis of the above research as well as our recent proposal⁴⁰ of preparing a metallopolymer by solid-/melt-state polymerization (S(M)SP), we assume that S(M)SP would be a good choice to prepare a conjugated Fc-containing polymer. Because its only requirement is treating the monomers at an appropriate temperature to promote the reaction, S(M)SP is a solvent-free, catalyst-free, and easy to implement method to prepare polymers. Since it was discovered in the early 1960s,⁴¹ S(M)P has been widely applied in the synthesis of conjugated polythiophene derivatives.²

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Herein, two kinds of Fc-containing monomers, thiophene based (FcT and FcT8) and thiophene methine based (FcTP and FcTP8), have been synthesized and subsequently been subjected to S(M)SP to acquire the polymers. The soluble Fccontaining polymers PFcT8 and PFcTP8 were obtained successfully and were characterized by ¹H NMR, UV–vis, and FTIR spectra, cyclic voltammetry, gel permeation chromatography (GPC), and inductively coupled plasma atomic emission spectrometry (ICP). Due to the high stability of the Fc group and moderate reaction temperature, little degradation occurred in the polymerization process and the metallopolymers were obtained with regular backbones and nearly quantitative metal contents.

2. RESULTS AND DISCUSSION

2.1. Structure and Polymerization Pathway. The disubstituted ferrocene monomers (Scheme 1) were synthe-

Scheme 1. General Synthetic Routes to Disubstituted Ferrocenes



sized according to the reported method,⁴⁹ where the substituents (**RX**) were halogen-substituted thiophene derivatives (**TX** and **T8X**) or thiophene-methine derivatives (**TPX** and **TP8X**). The monomers **FcT** and **FcTP** were designed as models to acquire the structure information on the complexes, whereas the 2-ethylhexyl group was introduced onto **FcT8** and **FcTP8** to improve the solubility of the corresponding metallopolymers.

Single crystals of FcT suitable for single-crystal X-ray analysis were grown in a dichloromethane/diethyl ether mixture. As shown in Figure 1, due to the strong $\pi - \pi$ interaction between the electron-rich thiophene rings, the FcT adopts a cis configuration with two parallel thiophene rings. The shortest and longest atom distances between two thiophene rings are 3.505 and 3.792 Å (Figure 1b),



Figure 1. (a) Crystal structures of **FcT** with thermal ellipsoids drawn at the 30% level. All hydrogen atoms are omitted for clarity. (b) The shortest and longest atom distances as well as the plane angle between two thiophene rings. (c) The shortest intermolecular C–C and Br–Br distances in the **FcT** crystal.

respectively, which are both within the $\pi - \pi$ effect range.⁵⁰ A small plane angle between the two thiophene-determined planes of 5.57° was also observed. The possible polymerization pathway of FcT was proposed from the monomer's crystal structure. As shown in the crystal packing map (Figure 1c), the shortest intermolecular Hal–Hal (Br1–Br2) distance is 4.412 Å and the shortest C1-C10 distance is 5.314 Å, which are longer than those of our previously reported metal complexes⁴⁰ (4.044 Å for Hal-Hal distance and 4.935 Å for C1-C10 distance). However, there is an infinite ...C1-C10-C1-C10... chain in FcT, which means FcT has an far shorter effective Hal-Hal distance of 4.412 Å (6.602 and 6.827 Å in the reported metal complexes), resulting in a lower onset temperature. These results indicate that the possible polymerization pathway of FcT is along the *b* axis and follows the ... C1-C10-C1-C10-··· sequence.

2.2. Characterization of Fc-Containing Polymers. As shown in Scheme 2, the polymers were prepared through melt-state polymerization (MSP) by heating their monomers in a glass tube under a nitrogen atmosphere at a specific temperature (Table 1). The final reaction conditions were

Scheme 2. Synthesis of Ferrocene-Containing Polymers with MSP



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Table 1. Preparation	Details	and	Properties	of	Fc-
Containing Polymers	5				

	PFcT8	PFcTP8
$T_{\text{onset}}^{a} \circ C$	110	80
reaction conditions	122 °C, 24 h	110 °C, 48 h
yield, %	>90	ca. 65
$M_{\rm n}$ of polymer, KDa	7.8	11.6
DP	13	10
dispersity (Đ)	1.01	1.15
calcd Fe content, %	9.32	4.70
tested Fe content, %	8.53	4.46
${}^{a}T_{\text{onset}}$ is determined by the	color change of the	mixture to dark after

heating for 2 h.

optimized by taking a comprehensive consideration of the solubility, molecular weight, and yield of polymer. The reaction rate of FcT8 is slow when the temperature is below 120 °C and is fast and leads to an insoluble polymer when the temperature is raised to 125 °C. The polymer PFcT8 obtained by heating at 122 °C for 24 h has a high yield (>90%) but shows poor solubility. For PFcTP8, a low reaction temperature was needed to ensure a good solubility and avoid degradation, while a long reaction time was applied to improve the yield. After reaction at 110 °C for 48 h, unreacted monomer was first removed by hexane and the final product was extracted by Soxhlet extraction with dichloromethane as solvent. The polymerization temperatures of both Fc-containing polymers are lower than those of our previously reported thiophenemethine based metallopolymers⁴⁰ but higher than those other metal-free polymers with a thiophene-methine structure.⁵

The preparation details and physical properties of metallopolymers are given in Table 1. The molecular weights (M_n) of PFcT8 and PFcTP8 are 7.8 and 11.6 kDa, respectively, corresponding to polymerization degrees (DPs) of 13 and 10 (GPC traces are available in Figure S1). Moreover, the Fe content was confirmed by ICP (Table 1), which shows that ca. 92% and 95% of Fe remain in PFcT8 and PFcTP8, respectively. In our recent work toward preparing metallopolymers with pendant coordination fragments by S(M)SP, 50-70% of the metal was expelled due to the high reaction temperature.⁴⁰ Fortunately, the remaining metal contents of these Fc-containing polymers are higher than those of the previously reported metallopolymers⁴⁰ due to the high stability of Fc and low polymerization temperature. In addition to the stable coordination group (Fc), the thiophene-methane structure bearing a small pendant group is also vital to access high-metal-content metallopolymers by decreasing the reaction temperature. These results indicate that it is possible to acquire a defect-free metallopolymer of almost 100% metal content by S(M)P when a carefully designed monomer is applied.

The structure information on those polymers was first studied by an ¹H NMR analysis. As shown in Figure 2, the Fc-H signals appear at 4.18 ppm for **PFcT8** and 4.41 and 4.64 ppm for **PFcTP8** (marked as 3), whereas the aromatic thiophene proton signals are located at 6.82–7.09 ppm for **PFcTP8** and 6.73 ppm for **PFcT8** (marked as 2). In comparison with **PFcT8**, apart from the phenyl protons appearing at 6.66 ppm (marked as 4), the **PFcTP8** has another new signal at 7.52 ppm (marked as 5), which is characteristic of a quinoid thiophene.⁵² The absence of methenyl-H in **PFcTP8** (Figure 2b) means that the polymer has a regular quinoid structure. In addition, the ratios of Fc-H to thiophene-



Figure 2. ¹H NMR spectra of neutral polymers (a) PFcT8 and (b) PFcTP8. The asterisk denotes the vacuum grease.

H (and phenyl-H) are close to their theoretical values of 1:2 in **PFcTP8** and 1:0.25 in **PFcT8**, which indicates that the structures of the polymers are highly regular.

Their structures were also confirmed by the FTIR spectra. As shown in Figure 3, the broad peaks at ca. 3430 cm^{-1} are ascribed to the -OH groups of water from the air, whereas the peaks at $2835-3000 \text{ cm}^{-1}$ are ascribed to the stretching vibration of C-H in the ferrocene, phenyl rings, and alkyl. The out-of-plane CH bending vibrations from the Cp ring are observed at 1170 and 1023 cm⁻¹.⁵³ The peaks at ca. 815, 1379, and 1457 cm⁻¹ are characteristic of the thiophene ring. In



Figure 3. FTIR absorption spectra of the monomers and metal-lopolymers.

PFcTP8, in addition to the intense peak at 1601 cm⁻¹ that is ascribed to the phenyl group, another new absorption peak around 1657 cm⁻¹ is assigned to the quinoid structure of thiophene.

The UV-vis spectra of monomers and polymers are shown in Figure 4a. The absorption band at 420-550 nm originates



Figure 4. UV-vis spectra of (a) ferrocene-containing monomers and polymers in CH_2Cl_2 and (b) polymers before (PFcT8 and PFcTP8) and after (PFcT8-R and PFcTP8-R) treatment with hydrazine hydrate.

from characteristic d-d electronic transitions of the ferrocenyl groups.⁵⁴ Both of the monomers show an absorption peak around 454 nm, whereas the polymers PFcT8 and PFcTP8, which have extended conjugated backbones, show red-shifted absorptions at around 468 and 502 nm, respectively. The $\pi - \pi^*$ band gap transitions of the polymer are observed around 550-730 nm for PFcT8 and 730-1100 nm for PFcTP8, which show a lower energy gap in comparison to other reported thiophene-based⁴⁰ or Fc-containing metallopolymers.⁵⁵⁻⁵⁷ In addition, due to the existence of the thiophene-methine structure, the polymer PFcTP8 has another new absorption band at 550-730 nm and displays broader spectra in comparison with PFcT8. After treatment with hydrazine hydrate (85% in water/MeOH 1/20, v/v), both of the reduction polymers (PFcT8-R and PFcTP8-R) show lower absorption values but little peak shift in comparison to their freshly made polymers (Figure 4b). When the ratio of polymer to hydrazine hydrate was decreased, the absorption of PFcTP8 decreased at first and ended at a stable value (Figure S3), which is a result of the doping state of these freshly made polymers and the dedoping effect of the hydrazine hydrate.

The electrochemical behaviors were analyzed by cyclic voltammograms (CV); as shown in Figure 5, the redox peaks of the Fc moiety in monomers FcT8 and FcTP8 and polymers PFcT8 and PFcTP8 appear at 0.21, 0.01, 0.13, and 0.09 V, respectively. These assignments were made according to the reported literature⁵⁸ and the reversible/quasi-reversible



Figure 5. Cyclic voltammograms of ferrocene-containing monomers (a) and polymers (b) in CH_2Cl_2 . Conditions: 0.1 M TBAP, scan rate 50 mV/s.

oxidation feature of the Fc moiety. **PFcTP8** has versatile oxidation behavior in comparison to **PFcT8**, such as oxidation peaks at 0.31, 0.6, and 1.2 V, which are assigned to the oxidation of the thiophene-methine structure. The property of multistep irreversible oxidation of **PFcTP8** is similar that of our previously reported poly(thiophene methine) derivatives.^{42,51}

The thermal stabilities of the prepared polymers were investigated by thermogravimetric analysis (TGA), which was recorded in the range of room temperature to 580 °C under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹. As shown in Figure 6, PFcT8 is stable when the temperature is



Figure 6. Thermogravimetric analysis (TGA) of PFcT8 and PFcTP8 measured at a heating rate of 10 $^{\circ}$ C/min under a nitrogen atmosphere.

lower than 254 °C, and a small platform at 254–325 °C that results from further polymerization of polymer is observed. With an increase in the temperature, the weight of **PFcT8** is decreased because of decomposition, and a weight loss of 45% is observed when the temperature is up to 580 °C. The further polymerization platform of **PFcTP8** appears at 185–250 °C, and a gradual weight loss of 10% is observed at 405 °C. In the range of 405–505 °C, **PFcTP8** undergoes a rapid decomposition with 49% weight loss, which is similar to that of some other reported Fc-containing polymers.^{1,59} In comparison with **PFcT8**, **PFcTP8** has a softer backbone and has more alkyl chains, which can cause more serious intermolecular and intramolecular interactions and thus result in a higher decomposition temperature.

3. CONCLUSIONS

A facile method of MSP was successfully applied to the synthesis of conjugated main-chain Fc-containing polymers that integrated the Fc motif with thiophene or thiophenemethane groups, where the thiophene or thiophene-methane groups served as reactive sites for use in S(M)P. The prepared metallopolymers have regular backbones and high metal contents of more than 92%, which prove that bulk polymerization is a good choice to prepare conjugated metallopolymers when a carefully designed monomer is applied. Moreover, these metallopolymers have small band gaps with an absorption edge to 730 and 1100 nm for PFcT8 and PFcTP8, respectively, which are very small among reported Fc-containing polymers as far as we know. The low band gap and high stability of PFcTP8 suggest that the thiophenemethane based Fc-containing structure is an excellent candidate to build functional Fc-containing polymers, which have potential application in conducting materials with high working temperature.

4. EXPERIMENTAL SECTION

The experimental materials, characterization details, and partially synthesis details are available in the Supporting Information.

4.1. Synthesis of TX/T8X. TX and T8X were prepared by a reported method⁶⁰ by iodization of their 2-bromothiopthene derivatives. To a solution of 2-bromothiopthene derivative (20 mmol) in CH₂Cl₂ (50 mL) were added iodine (11.2 mmol) and iodobenzene diacetate (12.2 mmol) at 0 °C. After the mixture was stirred at room temperature for 5 h, 10% aqueous Na₂S₂O₃ was added, and the mixture was extracted with Et₂O. The organic phase was collected and dried over anhydrous Na₂SO₄. After filtration, the organic solvents and iodobenzene were removed by evaporation under reduced pressure. The oil was purified by silica gel column chromatography using petroleum ether as the eluent and further purified by vacuum distillation to give the product (yield 92% for TX and 96% for T8X).

4.2. Synthesis of TPX/TP8X. TPX and **TP8X** were prepared by our previously reported method.⁴⁰ To a mixture of aldehyde (10 mmol) and 2-bromothiophene (40 mmol) dissolved in glacial acetic acid (40 mL) was added a solution of BF₃ (46.7 wt % in Et₂O, 5 mL). After the aldehyde reacted completely (monitored by TLC; a long reaction time leads to polymerization of the product), the brown solution was poured into 100 mL of cooled water and the product was extracted with ethyl acetate. The organic phase was washed with aqueous Na₂CO₃ and dried over anhydrous Na₂SO₄, and the solvent was removed by rotary evaporator. The oil was purified by column chromatography on silica gel.

TPX data were in accord with those in the literature.⁶¹

4.2.1. TP8X: colorless oil, yield 7.95 g, 92%; ¹H NMR (400 MHz, CDCl₃) δ 7.05 (d, J = 8 Hz, 2H), 6.86 (d, J = 8 Hz, 2H), 6.58 (d, J = 4 Hz, 4H), 5.52 (s, 1H, CH), 3.14–3.23 (m, 4H), 1.76–7.78 (m, 2H), 1.26–1.37 (m, 16H), 0.83–0.89 (m, 12H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 149.66, 147.72, 129.36, 128.77, 128.21, 126.09, 112.38, 111.17, 56.46, 47.16, 36.65, 30.69, 28.70, 23.96, 23.28, 14.18, 10.73 ppm; MS (ESI) m/z calculated for C₃₁H₄₃NS₂Br₂ 653.12, found 654.12 (M + H⁺). Anal. Found for C₃₁H₄₃S₂Br₂N: C, 56.79; H, 6.49; N, 2.07. Calcd: C, 56.97; H, 6.63; N, 2.14.

4.3. General Procedure for Syntheses of Disubstituted Ferrocenes. All of the reactions were carried out under Ar₂. In a dry flask containing ferrocene (0.93 g, 5 mmol), dry hexane (10 mL), and tetramethylethylenediamine (TMEDA, 1.34 g, 11.5 mmol) was placed n-BuLi (2.5 M, 4.4 mL, 11 mmol) at 30 °C. After the mixture was stirred at room temperature for 24 h, 1,1'-dilithioferrocene formed as a pale orange precipitate. The solvent was removed, and the precipitate was washed with hexane $(3 \times 8 \text{ mL})$ and dried under reduced pressure. The obtained pale orange powder was dissolved in THF (10 mL) and cooled to -10 °C, and ZnCl₂ (1 M in THF, 11 mL, 11 mmol) was added. After the mixture was stirred at -10 °C for 20 min and then at 30 °C for another 1 h, Pd(PPh₃)₄ (0.29 g, 0.25 mmol) and RX (15 mmol) were added. After it was stirred at room temperature for 2 days, the mixture was poured into 200 mL of brine and extracted with EA. The organic phase was collected and dried over anhydrous Na₂SO₄, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether as eluent.

4.3.1. *FcT*: brick red powder, yield 1.09 g, 43%; ¹H NMR (400 MHz, CDCl₃) δ 6.78 (d, *J* = 4 Hz, 2H), 6.59 (d, *J* = 4 Hz, 2H), 4.41 (d, *J* = 4 Hz, 4H), 4.23 (d, *J* = 4 Hz, 4H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 142.93, 130.13, 122.72, 109.02, 80.98, 70.48, 68.05 ppm (in accord with the literature⁵⁰).

4.3.2. *FcT8*: brick red oil, yield 1.79 g, 49%; ¹H NMR (400 MHz, CDCl₃) δ 6.45 (s, 2H), 4.46 (s, 4H), 4.29 (s, 4H), 2.41 (d, *J* = 4 Hz, 4H), 1.57–1.60 (m, 2H), 1.21–1.34 (m, 16H), 0.86–0.91 (m, 12H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 141.16, 140.48, 124.46, 107.19, 77.22, 70.92, 68.05, 39.86, 33.78, 32.47, 28.79, 25.66, 23.09, 14.18, 10.86 ppm; MS (ESI) *m*/*z* calculated for C₃₄H₄₄S₂Br₂Fe 732.06, found 733.06 (M + H⁺). Anal. Found for C₃₄H₄₄S₂Br₂Fe: C, 55.49; H, 5.98. Calcd: C, 55.75; H, 6.05.

4.3.3. *FcTP*: brick red powder, yield 1.45 g, 34%; ¹H NMR (400 MHz, CDCl₃) δ 7.29–7.36 (m, 10H), 6.90 (d, *J* = 4 Hz, 2H), 6.62 (d, *J* = 4 Hz, 2H), 6.57 (d, *J* = 4 Hz, 2H), 6.49 (d, *J* = 4 Hz, 2H), 5.62 (s, 2H, CH), 4.33 (d, *J* = 4 Hz, 4H), 4.17 (d, *J* = 4 Hz, 4H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 149.15, 143.70, 142.70, 141.40, 129.38, 128.64, 128.29, 127.39, 126.52, 126.28, 121.87, 111.24, 81.27, 70.37, 68.53, 68.51, 47.93 ppm; MS (ESI) *m*/*z* calculated for C₄₀H₂₈S₄Br₂Fe 851.88, found 852.88 (M + H⁺). Anal. Found for C₄₀H₂₈S₄Br₂Fe: C, 56.17; H, 3.26. Calcd: C, 56.35; H, 3.31.

4.3.4. *FcTP8*: brick red oil, stored at -18 °C, yield 1.86 g, 28%; ¹H NMR (400 MHz, CDCl₃) δ 7.09 (d, J = 8.4 Hz, 4H), 6.87 (d, J = 4 Hz, 2H), 6.58–6.63 (m, 8H), 6.51 (d, J = 4 Hz, 2H), 5.51 (s, 2H, CH), 4.34 (d, J = 4 Hz, 4H), 4.15 (d, J = 4 Hz, 4H), 3.14–3.21 (m, 8H), 1.78 (m, 4H), 1.25–1.30 (m, 32H), 0.83–0.90 (m, 24H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 150.69, 147.62, 145.16, 140.93, 129.30, 129.05, 128.83, 126.13, 125.86, 121.88, 112.42, 110.83, 81.54, 70.48, 68.42, 56.47, 47.18, 36.70, 30.70, 28.71, 28.69, 23.97, 23.27, 14.18, 10.74 ppm; MS (ESI) *m/z* calculated for C₇₂H₉₄N₂S₄Br₂Fe 1330.40, found 1331.41 (M + H⁺). Anal. Found for C₇₂H₉₄N₂S₄Br₂Fe: C, 64.61; H, 7.03; N, 2.06. Calcd: C, 64.95; H, 7.12; N, 2.10.

4.4. Synthesis of Metallopolymers. In the general procedure, the metal complex monomer was sealed in a glass tube under a nitrogen atmosphere, and then the glass tube was placed in a muffle furnace and heated at a specific temperature (Table 1). The onset polymerization temperature was determined by the color change of the mixture from brick red to dark after heating for 2 h.

4.4.1. **PFcT8**. After the reaction was completed, the obtained solid was ground to a powder, washed with hexane until the solvent become clean and then washed with methanoland water, and dried under vacuum. **PFcT8** was obtained as a black solid.

4.4.2. **PFCTP8**. After the reaction was completed, the obtained oil was washed with hexane until the solvent become clean and a black solid remained. The precipitate was extracted by Soxhlet extraction with dichloromethane as solvent, the organic phase was collected, and **PFcTP8** was obtained as a black solid after removing the solvent.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.9b00312.

Additional experimental details and supporting figures (PDF)

Accession Codes

CCDC 1903413 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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