Reactive Polythiophenes with Zincke Salt Structure: Synthesis, Polymer Reactions, and Chemical Properties

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ABSTRACT: Polythiophenes with reactive Zincke salt structure, such as PThThPy⁺DNP(CI⁻)Th, were synthesized by the oxidation polymerization of 3'-(4-*N*-(2,4-dinitrophenyl)pyridinium chloride)-2,2':5',2"-terthiophene (ThThPy⁺DNP(CI⁻)Th) with iron(III) chloride or copper(II) trifluoromethanesulfonate. The reaction of PThThPy⁺DNP(CI⁻)Th with R-NH₂ (R = *n*-hexyl (Hex) and phenyl (Ph)) substituted the 2,4-dinitrophenyl group into the R group with the elimination of 2,4-dinitroaniline to yield PThThPy⁺R(CI⁻)Th. Similarly, model compounds, ThThPy⁺R(CI⁻)Th (R = Hex and Ph), were also synthesized. In contrast to the photoluminescent ThThPy⁺R(CI⁻)Th, and

ThThPy⁺**R(CI⁻)Th** showed no photoluminescence because their internal pyridinium rings acted as quenchers. Cyclic voltammetry measurements suggested that **PThThPy**⁺**DNP(CI⁻)Th** received an electrochemical reduction of the pyridinium and 2,4-dinitrophenyl groups and oxidation of the polymer backbone. **PThThPy**⁺**DNP(CI⁻)Th** was electrically conductive ($\rho = 2.0 \times 10^{-6} \text{ S cm}^{-1}$) in the non-doped state. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: conjugated polymers; electrochemistry; reactive polythiophene; Zincke salt

INTRODUCTION Poly(thiophene-2,5-diyl)s (PThs) have been extensively studied because of their interesting chemical properties and practical applications.¹⁻⁴ PRThs with substituents (R) on the thiophene ring have attracted considerable attention because they exhibit high solubility in organic solvents and have unique solid-state structures.5-35 For example, regioregular PRThs (where R is a long alkyl chain) cause π -stacking between the polymer chains to form ordered structures in the solid state or in films, which results in high electric conductivity and carrier ion mobility.^{32,33} These properties allow the use of PRThs for the development of electroluminescence, field-effect transistors, and solar cell devices. Furthermore, PRThs (R = $(CH_2)_mSO_3H$) with an alkylsulfonic acid group exhibit a self-doping nature.³⁶⁻⁴⁰ These characteristic properties of PRThs depend on the structure of the side chain groups. In other words, the chemical properties of PRThs can be easily modulated by changing the side chain group. To obtain PRThs, the corresponding RTh monomers should be synthesized and polymerized. Usually, such reactions require transition-metal complex catalysts. The use of transition-metal complexes is a disadvantage in terms of cost, safety, and environmental concerns. In this study, we designed reactive PRThs that can be converted into various PR'Ths derivatives through simple polymer reactions without the use of transition-metal complexes.

It is well known that N-(2,4-dinitrophenyl)pyridinium chlorides, the so-called Zincke salts, react with primary amines to vield *N*-substituted pyridinium compounds.^{41–49} Recently, we reported the synthesis of various Zincke salts, and some of them were used as starting materials for the synthesis of functional aromatic compounds and π -conjugated polymers.^{50–58} Based on these reports, PRThs ($R = Py^+DNP(Cl^-)$, where Py^+ = pyridinium, and DNP = 2,4-dinitrophenyl) with a reactive N-(2,4-dinitrophenyl)pyridinium chloride unit bonded to the Th ring are promising materials as reactive PRThs. In this study, 3'-(4-N-(2,4-dinitrophenyl)pyridinium chloride)-2,2':5',2"-terthiophene (**ThThPy**⁺**DNP(Cl**⁻**)Th**) was synthesized as a monomer and polymerized with iron (III) chloride or copper(II) trifluoromethanesulfonate. The resulting **PThThPy⁺DNP(Cl⁻)Th** reacted with both aromatic and aliphatic amines (R—NH₂) to yield **PThThPy⁺R(Cl⁻)Th**. This reactivity promises to offer high synthetic flexibility for the generation of a large number of PTh derivatives.

Herein, we report the synthesis of **ThThPy**⁺**DNP(Cl**⁻)**Th**, **PThThPy**⁺**DNP(Cl**⁻)**Th**, and **PThThPy**⁺**R(Cl**⁻)**Th** (R = n-hexyl (Hex) and phenyl (Ph)) through the polymer reactions and their optical, electrochemical, and electric properties. In addition, the model compounds **ThThPy**⁺**R(Cl**⁻)**Th** (R =Hex and Ph) and a polymer without a Zincke structure,

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PThThPyTh, were synthesized for comparison with the corresponding **PThThPy**⁺**R(Cl⁻)Th**. This is the first report on the synthesis, chemical properties, and polymer reactions of PThs with a reactive Zincke salt structure.

EXPERIMENTAL

General

Solvents were dried, distilled, and stored under nitrogen. 2,5-Di(2-thienyl)-3-bromothiophene and 4-(3-thienyl)pyridine were synthesized according to the reported manner.⁵⁹ Other reagents were purchased and used without further purification. Reactions were carried out with standard Schlenk techniques under nitrogen.

IR and NMR spectra were recorded on a JASCO FT/IR-660 PLUS spectrophotometer with a KBr pellet and JEOL AL-400 and ECX-500 spectrometers, respectively. Elemental analysis was conducted on a Yanagimoto MT-5 CHN corder. Gel permeation chromatography (GPC) analyses were carried out by a Toso HLC 8020 with polystyrene gel columns (TSKgel G2000H_{HR} and TSKgel GMH_{HR}-M) using a N,N-dimethylformamide (DMF) solution of LiBr (0.006 M) as an eluent with RI and UV detectors. UV-vis and photoluminescence (PL) spectra were obtained by a JASCO V-560 spectrometer and a JASCO FP-6200, respectively. Quantum yields were calculated by using a diluted ethanol solution of 7-dimethylamino-4methylcoumarin as the standard. Cyclic voltammetry was performed in a dimethyl sulfoxide (DMSO) solution containing 0.10 M [Et₄N]BF₄ with a Hokuto Denko HSV-110. Electric conductivity measurements were conducted on the molded pellets of the polymers by an Advantest R8340A ultra high resistance meter with a two-probe method.

Synthesis of ThThPyTh

2,5-Di(2-thienyl)-3-bromothiophene (1.33 g, 4.1 mmol) and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (0.83 g, 4.1 mmol) were dissolved in 15 mL of dry THF under N₂. $K_2CO_3(aq)$ (2.0 M, 6 mL; N_2 bubbled before use) and $Pd(PPh_3)_4$ (0.47 g, 0.41 mmol) were added to the solution. After the mixture was refluxed for 60 h, the precipitate from the reaction solution was removed by filtration and the solvent of the filtrate was removed under vacuum. The resulting solid was purified by silica gel column chromatography (eluent = $CHCl_3$). The solvent was removed by evaporation, a resulting solid was recrystallized from chloroform, and dried in vacuo to give ThThPyTh as a yellow crystal (0.50 g, 38%). ¹H NMR (400 MHz, DMSO- d_6 , δ , ppm): 8.46 (d, J = 6.0Hz, 2H), 7.37-7.39 (m, 2H), 7.25-7.27 (m, 4H), 7.00 (dd, J = 3.6 and 5.0 Hz, 1H), 6.98 (d, I = 7.2 Hz, 1H), 6.94 (dd, I =3.6 and 5.4 Hz, 1H). ¹³C NMR (125 MHz, DMSO- d_6 , δ , ppm): 150.0, 143.6, 136.8, 136.5, 136.2, 134.4, 131.8, 128.0, 127.6, 127.4, 126.7, 125.7, 125.1, 124.3, 123.8. Calcd for $C_{17}H_{11}NS_3$: C, 62.73; H, 3.41; N, 4.30. Found: C, 62.32; H, 3.67; N, 4.31.

Synthesis of ThThPy⁺DNP(Cl⁻)Th

ThThPyTh (0.53 g, 1.5 mmol) and 1-chloro-2,4-dinitrophenylbenzene (0.30 g, 1.5 mmol) were dissolved in dry ethanol (50 mL). After the reaction solution was refluxed for 39 h, the solvent was removed by evaporation. The resulting solid was washed with acetone, collected by filtration, and dried under vacuum to give ThThPy⁺DNP(Cl⁻)Th as a reddish orange powder (0.17 g). The solvent of the filtrate was removed by evaporation. The resulting solid was washed with acetone, collected by filtration, and dried under vacuum to give **ThThPy⁺DNP(Cl⁻)Th** (0.11 g). After the filtration was further refluxed for 12 h, the solvent was removed by evaporation. The resulting solid was recrystallized from chloroform, collected by filtration, and dried under vacuum to give ThThPy⁺DNP(Cl⁻)Th (0.14 g). The total yield of ThThPy⁺DNP(Cl⁻)Th was 85%. ¹H NMR (400 MHz, DMSO d_{6i} , δ_{i} , ppm): 9.29 (d, J = 6.8 Hz, 2H), 9.13 (d, J = 2.4 Hz, 1H), 8.98 (dd, J = 2.4 and 8.8 Hz, 1H), 8.43 (d, J = 8.8 Hz, 1H), 8.39 (d, J = 6.8 Hz, 2H), 7.81 (s, 1H), 7.82 (d, J = 4.8Hz, 1H), 7.67 (d, J = 4.8 Hz, 1H), 7.52 (d, J = 2.4 Hz, 1H), 7.33 (d, J = 2.4 Hz, 1H), 7.18-7.22 (m, 2H). ¹³C NMR (100 MHz, DMSO-d₆, δ, ppm): 153.0, 149.1, 145.7, 143.2, 138.5, 137.5, 136.6, 134.4, 133.0, 132.0, 131.9, 130.2, 129.9, 129.4, 128.9, 128.7, 127.3, 126.5, 126.0, 125.8, 121.5. Calcd for C₂₃H₁₄ClN₃O₄S₃ · 1.2H₂O: C, 50.26; H, 3.01; N, 7.65. Found: C, 50.14; H, 3.11; N, 7.34.

Synthesis of ThPy⁺DNP(Cl⁻)

ThPy⁺**DNP(Cl⁻)** was synthesized by the reaction of **ThPy** with 1-chloro-2,4-dinitrophenylbenzene in a similar manner.

Data of ThPy⁺DNP(Cl⁻)

Yield = 57%. ¹H NMR (400 MHz, DMSO- d_6 , δ , ppm): 9.32 (d, J = 6.4 Hz, 2H), 9.14 (d, J = 2.4 Hz, 1H), 9.01 (d, J = 2.0 Hz, 1H), 8.98 (dd, J = 2.8 and 8.8 Hz, 1H), 8.75 (d, J = 6.8 Hz, 1H), 8.42 (d, J = 8.4 Hz, 1H), 8.09 (dd, J = 1.4 and 5.2 Hz, 1H), 7.95 (dd, J = 2.8 and 5.2 Hz, 1H). ¹³C NMR (125 MHz, DMSO- d_6 , δ , ppm): 151.4, 149.0, 145.8, 143.2, 138.5, 135.7, 133.4, 132.1, 130.2, 129.8, 126.7, 123.0, 121.4. Calcd for C₁₅H₁₀ClN₃O₄S · H₂O: C, 47.19; H, 3.17; N, 11.01. Found: C, 47.50; H, 3.21; N, 11.36.

Synthesis of PThThPy⁺DNP(Cl⁻)Th-a

ThThPy⁺**DNP(Cl⁻)Th** (0.24 g, 0.50 mmol) and FeCl₃ (0.32 g, 2.0 mmol) were dissolved in dry acetonitrile (25 mL). After the reaction solution was stirred in an ice bath for 62 h, the solvent was removed by evaporation. The resulting solid was extracted with acetone and the solvent was removed by evaporation. The resulting solid was extracted with acetone and the solvent was removed by evaporation. The resulting solid was washed with water, diethyl ether, and chloroform until the filtrate became colorless and dried under vacuum to give **PThThPy**⁺**DNP(Cl⁻)Th-a** as a black powder (0.11 g, 43%). ¹H NMR (500 MHz, DMSO-*d*₆, *δ*, ppm): 9.32–9.49 (2H), 9.13 (1H), 9.00 (1H), 8.32–8.52 (3H), 7.98 (0.55H), 7.86 (0.11H), 7.84 (0.45H), 7.65 (0.11H), 7.57 (1H), 7.49 (1H), 7.35 (1H), 7.22 (1H). Calcd for C₂₃H₁₂ClN₃O₄S₃ · 1.5H₂O: C, 49.95; H, 2.73; N, 7.60. Found: C, 50.21; H, 3.03; N, 7.99.

Synthesis of PThThPy⁺DNP(Cl⁻)Th-b

 $PThThPy^+DNP(Cl^-)Th-b$ was synthesized at 20 °C in a similar manner.

Data of PThThPy⁺DNP(Cl⁻)Th-b

Yield = 64%. ¹H NMR (500 MHz, DMSO- d_6 , δ , ppm): 9.33– 9.50 (2H), 9.14 (1H), 9.00 (1H), 8.33–8.54 (3H), 8.00



SCHEME 1 Synthesis of monomers.

(0.55H), 7.90 (0.26H), 7.84 (0.45H), 7.68 (0.26H), 7.57 (1H), 7.50 (1H), 7.36 (1H), 7.22 (1H). Calcd for $C_{23}H_{12}ClN_3O_4S_3$ · 1.5H₂O: C, 49.95; H, 2.73; N, 7.60. Found: C, 49.53; H, 2.65; N, 7.51.

Synthesis of PThThPy⁺DNP(Cl⁻)Th-c

ThThPy⁺**DNP(Cl⁻)Th** (0.30 g, 0.57 mmol) and Cu(CF₃SO₃)₂ (0.82 g, 2.3 mmol) were dissolved in dry acetonitrile (25 mL). After the reaction solution was stirred in an ice bath for 60 h, the resulting precipitate was filtered off. The solvent of the filtrate was removed by evaporation and resulting solid was washed with acetonitrile until the filtrate became colorless. The acetonitrile insoluble part was collected by filtration and dried under vacuum to give **PThThPy**⁺**DNP(Cl⁻)Th-c** as a black powder (0.23 g, 79%). ¹H NMR (500 MHz, DMSO-*d*₆, δ , ppm): 9.49 (0.35H), 9.35 (1.65H), 9.14 (1H), 9.01 (d, *J* = 8.5 Hz, 1H), 8.45-8.57 (3H), 7.17-8.21 (5H). Calcd for C₂₃H₁₂ClN₃O₄S₃ · H₂O: C, 50.78; H, 2.59; N, 7.72. Found: C, 50.53; H, 2.18; N, 8.15.

Synthesis of PThThPy⁺DNP(Cl⁻)Th-d

PThThPy⁺DNP(Cl⁻)Th-d was synthesized at 20 °C in a similar manner.

Data of PThThPy⁺DNP(Cl⁻)Th-d

Yield = 58%. ¹H NMR (500 MHz, DMSO- d_6 , δ , ppm): 9.51 (1H), 9.36 (1H), 9.15 (1H), 9.02 (1H), 8.46–8.57 (3H), 7.24–7.97 (5H). Calcd for C₂₃H₁₂ClN₃O₄S₃ · H₂O: C, 50.78; H, 2.59; N, 7.72. Found: C, 50.33; H, 2.20; N, 7.29.

Synthesis of PThThPy⁺Ph(Cl⁻)Th

After a DMSO (2 mL) solution of **PThThPy**⁺**Ph(Cl⁻)Th** (40 mg, 0.076 mmol) and aniline (0.011 g, 0.11 mmol) was stirred at 90 °C for 12 h, the solvent was removed under vacuum. The resulting solid was washed with acetone, collected by filtration, and dried under vacuum to give **PThThPy**⁺**Ph(Cl⁻)Th** as a black powder (0.019 g, 56%). ¹H NMR (500 MHz, DMSO- d_6 , δ , ppm): 9.50 (0.6H), 9.36 (1.4H), 8.38–8.44 (2H), 8.00 (1H), 7.90 (2H), 7.76 (3H), 7.20–7.56 (4H). Calcd for C₂₃H₁₄ClNS₃ · 1.2H₂O: C, 60.36; H, 3.61; N, 3.06. Found: C, 60.45; H, 3.39; N, 2.87.

Synthesis of PThThPy⁺Hex(Cl⁻)Th

PThThPy⁺**Hex(Cl**⁻**)Th** was synthesized in a similar manner.

Data of PThThPy⁺Hex(Cl⁻)Th

Yield = 85%. ¹H NMR (500 MHz, DMSO- d_6 , δ , ppm): 9.23 (0.3H), 9.08 (1.7H), 8.24–8.32 (2H), 7.11–7.82 (5H), 4.67 (0.55H), 4.58 (1.45H), 1.93 (2H), 1.29 (6H), 0.85 (3H). Calcd for C₂₃H₂₂ClNS₃ · H₂O: C, 59.78; H, 5.24; N, 3.03. Found: C, 59.65; H, 4.90; N, 2.88.

Synthesis of ThThPy⁺Ph(Cl⁻)Th

After an ethanol (20 mL) solution of **ThThPy**⁺**Ph(Cl⁻)Th** (0.10 g, 0.19 mmol) and aniline (25 mg, 0.28 mmol) was refluxed for 12 h, the solvent was removed by evaporation. The resulting solid was washed with water and chloroform, collected by filtration, and dried under vacuum to give **ThThPy**⁺**Ph(Cl⁻)Th** as an orange powder (19 mg, 56%). ¹H NMR (400 MHz, DMSO- d_6 , δ , ppm): 9.30 (d, J = 7.2 Hz, 2H), 8.27 (d, J = 6.8 Hz, 2H), 7.88–7.90 (m, 2H), 7.86 (s, 1H), 7.81 (d, J = 4.8 Hz, 1H), 7.74–7.76 (m, 3H), 7.68 (d, J = 5.2 Hz, 1H), 7.51 (d, J = 3.6 Hz, 1H), 7.34 (d, J = 2.8 Hz, 1H), 7.18–7.21 (m, 2H). ¹³C NMR (125 MHz, DMSO- d_6 , δ , ppm): 151.1, 144.6, 142.3, 137.3, 135.8, 134.5, 133.0, 131.9, 131.2, 130.2, 129.7, 129.4, 128.9, 128.7, 127.2, 126.6, 126.1, 125.7, 124.6. Calcd for C₂₃H₁₆ClNS₃ · 0.3H₂O: C, 62.30; H, 3.77; N, 3.16. Found: C, 62.50; H, 3.79; N, 2.81.

Synthesis of ThThPy⁺Hex(Cl⁻)Th

After an EtOH (3 mL) solution of **ThThPy**⁺**Ph(Cl⁻)Th** (0.10 g, 0.19 mmol) and *n*-hexylamine (29 mg, 0.28 mmol) was refluxed for 12 h, the solvent was removed by evaporation. The resulting paste was washed with cold ether, collected by filtration, and dried under vacuum to give **ThThPy**⁺**Hex(Cl⁻)Th** as a yellow powder (55 mg, 65%). ¹H NMR (400 MHz, DMSO-*d*₆, δ , ppm): 9.03 (d, *J* = 6.4 Hz, 2H), 8.13 (d, *J* = 6.8 Hz, 2H), 7.74–7.76 (m, 2H), 7.65 (d, *J* = 5.2 Hz, 1H), 7.47 (d, *J* = 3.2 Hz, 1H), 7.26 (d, *J* = 3.2 Hz, 1H), 7.15–7.18 (m, 2H), 4.54 (t, *J* = 7.6 Hz, 2H), 1.91 (m, 2H), 1.28 (s, 6H), 0.87 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (125 MHz, DMSO-*d*₆, δ , ppm): 150.2, 144.5, 137.0, 134.7, 134.4, 133.3, 131.9, 129.3, 129.0, 128.6, 128.5, 127.0, 126.9, 125.9, 125.5, 60.0, 30.4, 24.9, 21.7, 13.7. Calcd for C₂₃H₂₄ClNS₃ · 0.2H₂O: C, 61.43; H, 5.47; N, 3.11. Found: C, 61.34; H, 5.31; N, 2.89.





SCHEME 2 Synthesis of PThThPy⁺DNP(Cl⁻)Th and PThThPyTh.

RESULTS AND DISCUSSION

Synthesis

The monomers, 3-(4-*N*-(2,4-dinitrophenyl)pyridinium chloride)thiophene (**ThPy**⁺**DNP(Cl**⁻)) and **ThThDNP(Cl**⁻)**Th**, were synthesized through the reaction of 4-(3-thienyl)pyridine (**ThPy**) and 4'-(4-pyridyl)-2,2':5',2"-terthiophene (**ThThPyTh**), which were synthesized by Pd-catalyzed coupling reactions, with 1-chloro-2,4-dinitrobenzene (Scheme 1).

PThPy⁺DNP(Cl⁻) could not be obtained from either oxidative polymerizations by treating **ThPy⁺DNP(Cl⁻**) with FeCl₃ or by applying positive potential. This result can be possibly attributed to the presence of an electron-withdrawing Py⁺DNP group bonded to the thiophene ring. On treating ThThPy⁺DNP(Cl⁻)Th with FeCl₃ at 0 °C and 20 °C yielded PThThPy⁺DNP(Cl⁻)Th-a and PThThPy⁺DNP(Cl⁻)Th-b in 43% and 64% vields, respectively [Scheme 2(a)]. The lower yield of **PThThPy⁺DNP(Cl⁻)Th-a** is similar to that reported for PHexTh obtained from the oxidation polymerization of 3-hexylthiophene with FeCl₃ at 0 °C that is lower than that at room temperature.⁵⁸ PThThPy⁺DNP(Cl⁻)Th-c and **PThThPy⁺DNP(Cl⁻)Th-d** were obtained by treating **ThThPy**⁺**DNP(Cl**⁻**)Th** with copper(II) trifluoromethanesulfonate at 0 °C and 20 °C in 79% and 58% yields, respectively [Scheme 2(a)]. PThThPyTh was synthesized using the same procedure with FeCl₃ to compare the chemical properties with **PThThPy⁺DNP(Cl⁻)Th** [Scheme 2(b)].

PThThPy⁺**DNP(Cl**⁻)**Th-c** was converted to **PThThPy**⁺-**R(Cl**⁻)**Th** (R = Ph and Hex) by reaction with R—NH₂ in refluxing ethanol (Scheme 3). Model compounds **ThThPy**⁺**R(Cl**⁻)**Th** (R = Ph and Hex) were synthesized by the analogous reactions of **ThThPy**⁺**DNP(Cl**⁻)**Th** with

 $R\mathrm{--}N\mathrm{H}_2$ (Scheme 4). The synthesis results are summarized in Table 1.

PThThPy⁺DNP(Cl⁻)Th-a, PThThPy⁺DNP(Cl⁻)Th-b, PThThPy⁺-DNP(Cl⁻)Th-c, PThThPy⁺DNP(Cl⁻)Th-d, and PThThPy⁺R(Cl⁻)-**Th** (R = Ph and Hex) were soluble in polar organic solvents such as DMF and DMSO, but were insoluble in non-polar organic solvents such as chloroform and toluene. These solubilities are in contrast to those of PRThs (R = alkyl chain) that are soluble in non-polar organic solvents such as chloroform and toluene but insoluble in polar organic solvents. The difference in solubility is attributed to the presence of the polar Py^+DNP pendant group in $PThThPy^+$ -**DNP(Cl⁻)Th**. On the other hand, **PThThPyTh** was partly soluble in DMF and DMSO probably due to its structural rigidity. However, UV-vis and PL measurements of the DMSO solution component of PThThPyTh were possible (vide infra). The monomers and model compounds were soluble in water and organic solvents such as chloroform, DMF, and DMSO.

The M_n and M_w values of the obtained polymers were determined by GPC measurements and are summarized in Table 1. The M_n values of the DMF solutions of **PThThPy**⁺**DNP(CI**⁻)**Th-a**, **PThThPy**⁺**DNP(CI**⁻)**Th-b**, **PTh-ThPy**⁺**DNP(CI**⁻)**Th-c**, and **PThThPy**⁺**DNP(CI**⁻)**Th-d** were 5,690, 3,190, 5,820, and 2,660, respectively. The higher M_n values of **PThThPy**⁺**DNP(CI**⁻)**Th-a** and **PThThPy**⁺-**DNP(CI**⁻)**Th-c** as compared with **PThThPy**⁺**DNP(CI**⁻)**Th-b** and **PThThPy**⁺**DNP(CI**⁻)**Th-d** correspond to a previous report that the M_n value of PHexTh obtained from the oxidation polymerization of 3-hexylthiophene at 0 °C is higher than that obtained at room temperature.⁶⁰



SCHEME 3 Polymer reactions of PThThPy⁺DNP(Cl⁻)Th with amines.



SCHEME 4 Synthesis of model compounds.

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TABLE 1 Synthesis Results and Chemical Properties of the Obtained Polymers and Model Compounds

	Yield (%)	M ^{n a}	Mw ^a	Absorption/ nm ^d	λem/ nm ^f	Oxidation potential/V (vs. Ag ⁺ /Ag) ^g	Reduction potential/ V (vs. Ag ⁺ /Ag) ^g	electric conductivity/ Scm ^{-1h}
PThThPy ⁺ DNP(CI ⁻)Th-a	43	5,690	6,450	436 (4.08)		0.72	-0.81, -1.98, -2.24	2.1×10^{-6}
PThThPy ⁺ DNP(CI ⁻)Th-b	64	3,190	3,230	426 (3.99)		0.82	-0.84, -2.20	$2.0 imes 10^{-6}$
PThThPy ⁺ DNP(CI ⁻)Th-c	79	5,820	6,190	440 (4.12)		0.67	-0.95, -1.78, -2.25	$2.1 imes 10^{-6}$
PThThPy ⁺ DNP(CI ⁻)Th-d	58	2,660	3,040	440 (4.11)		0.69	-0.87, -1.80, -2.25	$2.1 imes 10^{-6}$
PThThPy ⁺ Hex(CI ⁻)Th	85	٩	٩	458 (4.03)		0.63	-1.32, -1.72, -2.23	
PThThPy ⁺ Ph(Cl ⁻)Th	56	٩	٩	436 (4.15)		0.63	-1.21, -2.10	
РТҺТҺРуТҺ	51	3,820 ^c	3,960°	463 (4.10) ^e	570 (0.10) ^e			$8.5 imes 10^{-7}$
ThThPy ⁺ DNP(Cl ⁻)Th	85			317 (4.50), 427 (3.69)		0.83	-0.84, -2.14, -2.38	
ThThPy ⁺ Hex(CI ⁻)Th	65			305 (4.30), 400 (3.70)		0.77	-0.84, -1.93, -2.38	
ThThPy ⁺ Ph(Cl ⁻)Th	56			315 (4.51), 417 (3.67)		0.72	-0.88, -2.29	
тһТһРуТһ	38			354 (4.49)	481 (0.09)	0.94	-2.40	
^a Determined by GPC (vs. polyst	yrene standaro	ds).						

^b Not measured. ^c DMF soluble part.

^d In DMSO. log svalues were shown in the parenthesis. ^e DMSO soluble part. ^f In DMSO. Quantum yields of photoluminescence were shown in parenthesis. ^g Measured by cyclic voltammetry in a DMSO solution of [Et4N]BF4 (0.10 M). ^h Measured using a two-probe method.



FIGURE 1 IR spectra of (a) $ThThPy^+DNP(CI^-)Th$, (b) $PThThPy^+DNP(CI^-)Th$, (c) $PThThPy^+Ph(CI^-)Th$, and (d) $PThThPy^+Hex(CI^-)Th$.

The reduced viscosities (η_{sp}/c) of **PThThPy⁺DNP(Cl⁻)Th-a** and **PThThPy⁺DNP(Cl⁻)Th-b** in DMSO were 0.13 and 0.10 g^{-1} dL (c = 0.10 g dL⁻¹), respectively. The η_{sp}/c values of the polymers in DMSO increased when their concentration cwas reduced. The η_{sp}/c value of **PThThPy⁺DNP(Cl⁻)Th-a** changes from 0.13 g⁻¹ dL (c = 0.10 g dL⁻¹) to 0.57 g⁻¹ dL (c = 0.056 g dL⁻¹) through to a value of 0.32 g⁻¹ dL (c =0.070 g dL⁻¹). These results suggest that the polymers behave as polymeric electrolytes in dilute solutions.⁶¹

IR and ¹H NMR Spectra

Figure 1 shows the IR spectra of ThThPy⁺DNP(Cl⁻)Th, PThThPy⁺DNP(Cl⁻)Th-a, PThThPy⁺Ph(Cl⁻)Th, and PTh-ThPy⁺Hex(Cl⁻)Th.

The absorption peaks corresponding to the symmetric and asymmetric stretching vibrations of the NO₂ groups were observed at 1342 cm⁻¹ and 1543 cm⁻¹ in the IR spectra of **ThThPy⁺DNP(Cl⁻)Th** and **PThThPy⁺DNP(Cl⁻)Th-a**, respectively. The IR spectrum of **ThThPy⁺DNP(Cl⁻)Th** showed an absorption peak corresponding to the out-of-plane bending vibrations of the thiophene rings at 835 cm⁻¹. The decrease in absorption corresponding to the out-of-plane bending vibrations of the thiophene rings in the IR

spectrum of **PThThPy**⁺**DNP(Cl⁻)Th-a** was attributed to polymerization at the thiophene rings. Absorption corresponding to the symmetric and asymmetric stretching vibrations of the NO₂ groups disappeared in the IR spectra of **PThThPy**⁺**Ph(Cl⁻)Th** and **PThThPy**⁺**Hex(Cl⁻)Th**. Furthermore, instead of the stretching vibrations corresponding to the NO₂ group, new absorption peaks corresponding to the stretching vibration of the C–H bonds of the hexyl group appears at 2862 cm⁻¹, 2931 cm⁻¹, and 2954 cm⁻¹ in the IR spectrum of **PThThPy**⁺**Hex(Cl⁻)Th**. The presence of peaks corresponding to v(O-H) around 3400 cm⁻¹ in the IR spectra of the polymers suggests that they contain hydrated water molecule(s). This view is supported by the elemental analysis.

Figure 2 shows the ¹H NMR spectra of **ThThPy**⁺**DNP(Cl⁻)Th**, **PThThPy**⁺**DNP(Cl⁻)Th-a**, **PThThPy**⁺**DNP**(**Cl⁻)Th-b**, and **PThThPy**⁺**DNP(Cl⁻)Th-c** in DMSO- d_6 . The peak assignments are indicated in the figure. The peaks corresponding to the DNP protons (H⁸-H¹⁰) of the polymers are observed at almost the same positions as those of the monomer. However, the two peaks corresponding to the proton (H³) of the thiophene ring bonded to the Py⁺(DNP)Cl⁻ group are observed at δ 7.85 and 8.00 in the ¹H NMR spectra of **PThThPy**⁺**DNP(Cl⁻)Th-a** and **PThThPy**⁺**DNP-(Cl⁻)Th-b**. This observation is attributed to the presence of the head-to-tail (HT) and head-to-head (HH) linkages in the main chain (Chart 1).

It has been reported that poly(3-alkylthiophene-2,5-diyl)s obtained from the oxidation polymerization with FeCl₃ exhibit several peaks corresponding to the thiophene proton in the HT and HH linkages.^{13,60} The amount of HT and HH linkages in **PThThPy⁺DNP(Cl⁻)Th-a** and **PThThPy⁺DNP-**(Cl⁻)Th-b were estimated to be 0.45:0.55 and 0.55:0.45, respectively, from the integral ratio of the peaks at δ 7.85 and 8.00. The peaks corresponding to the terminal protons $(H^5 \text{ and } H^{5''})$ decreased in the ¹H NMR spectra of PThThPy⁺DNP(Cl⁻)Th-a and PThThPy⁺DNP(Cl⁻)Th-b. The peaks at δ 7.68 and 7.90 in the ¹H NMR spectra of PThThPy⁺DNP(Cl⁻)Th-a and PThThPy⁺DNP(Cl⁻)Th-b are assigned to the terminal protons of the polymers. The peak integral ratio between the protons corresponding to the polymer main chain and the terminal protons suggests that the degree of polymerization (DP) values of PThThPy⁺DNP(Cl⁻)Th-a and PThThPy⁺DNP(Cl⁻)Th-b are 9 and 4, respectively. The molecular weights of **PThThPy⁺DNP(Cl⁻)Th-a** and **PThThPy⁺DNP(Cl⁻)Th-b** calculated from the DP values are 4,590 and 2,040, respectively. These values are largely consistent with the $M_{\rm n}$ values determined by GPC. The ¹H NMR spectra of PThThPy⁺DNP(Cl⁻)Th-c and PThThPy⁺DNP(Cl⁻)Th-d exhibited complex signals corresponding to the thiophene protons. The DP values of **PThThPy⁺DNP(Cl⁻)Th-c** and **PThThPy⁺DNP(Cl⁻)Th-d** could not be determined from their ¹H NMR spectra because the peaks corresponding to the terminal thiophene protons were ambiguous. However, the content of the HT and HH linkages in **PThThPy⁺DNP(Cl⁻)Th-c** could be estimated from the ¹H



FIGURE 2 ¹H NMR spectra of (a) **ThThPy**⁺**DNP(CI**⁻)**Th**, (b) **PThThPy**⁺**DNP(CI**⁻)**Th-a**, (c) **PThThPy**⁺**DNP(CI**⁻)**Th-b**, and (d) **PThThPy**⁺**DNP(CI**⁻)**Th-c** in DMSO- d_6 . The peaks with an asterisk in (b) and (c) correspond to the terminal protons.

NMR spectra of $PThThPy^+R(Cl^-)Th$ (R = Ph and Hex) as described below.

Figure 3 shows the ¹H NMR spectra with peak assignments of **ThThPy**⁺**Ph(Cl**⁻)**Th**, **ThThPy**⁺**Hex(Cl**⁻)**Th**, **PTh-ThPy**⁺**Ph(Cl**⁻)**Th**, and **PThThPy**⁺**Hex(Cl**⁻)**Th** in DMSO-*d*₆. The peaks corresponding to the DNP protons are not present in the ¹H NMR spectra of **ThThPy**⁺**Ph(Cl**⁻)**Th**, **ThThPy**⁺-**Hex(Cl**⁻)**Th**, **PThThPy**⁺**Ph(Cl**⁻)**Th**, and **PThThPy**⁺-**Hex(Cl**⁻)**Th**. This suggests that the polymer reaction of



CHART 1 HT and HT linkages in the PRTh main chain.

PThThPy⁺**DNP(Cl**⁻)**Th** with aniline or *n*-hexylamine proceeded to completion. The observation that the peak corresponding to the β-protons of the pyridinium ring of **ThThPy**⁺**Ph(Cl**⁻)**Th** and **ThThPy**⁺**Hex(Cl**⁻)**Th** shifted to the upper magnetic field positions by 0.13 ppm and 0.49 ppm, respectively, as compared with those of **ThThPy**⁺**DNP(Cl**⁻)**Th** is attributed to the displacement of the DNP group in **ThThPy**⁺**Ph(Cl**⁻)**Th** and **ThThPy**⁺**Hex(Cl**⁻)**Th** with phenyl and hexyl groups, respectively. The



FIGURE 3 ¹H NMR spectra of **ThThPy**⁺**Ph(CI**⁻)**Th**, **ThThPy**⁺**Hex(CI**⁻)**Th**, **PThThPy**⁺**Ph(CI**⁻)**Th**, and **PThThPy**⁺**Hex(CI**⁻)**Th** in DMSO- d_{6} .

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FIGURE 4 UV-vis spectra of ThThPy⁺DNP(Cl⁻)Th, PThThPy⁺-DNP(Cl⁻)Th-a, PThThPy⁺DNP(Cl⁻)Th-b, and PThThPy⁺DNP-(Cl⁻)Th-c in DMSO.

larger shift of **ThThPy⁺Hex(Cl⁻)Th** as compared with **ThThPy⁺Ph(Cl⁻)Th** is because of the presence of the electron-donating hexyl group in **ThThPy⁺Hex(Cl⁻)Th**. The new peaks corresponding to the phenyl group of **PThThPy**⁺-**Ph(Cl⁻)Th** were observed at δ 7.76 and 7.90, whereas those of the hexyl group of **PThThPy⁺Hex(Cl⁻)Th** were observed at δ 4.67, 4.58, 1.93, 1.29, and 0.85. These peak positions are comparable to those of the corresponding model compounds. The peak integral ratios between the phenyl or hexyl protons and the main chain protons suggest reaction completion of the polymer reactions. The observation that PThThPy+-Ph(Cl⁻)Th and PThThPy⁺Hex(Cl⁻)Th exhibited the two peaks corresponding to the protons at the 2-position of the pyridinium ring and the α -position of the hexyl group suggests that the polymers contain HT and HH linkages in the main chain. It has been reported that poly(3-alkylthiophene-2,5-diyl)s synthesized by the oxidative polymerization with FeCl₃ contain HT and HH linkages in the main chain. The ¹H NMR peak corresponding to the α -methylene protons in the HH linkage is 0.24 ppm upfield of the HT linkage.⁶⁰ The content of the HT and HH linkages of **PThThPy⁺DNP(Cl⁻)Th-c** could not be determined because of the unresolved ¹H NMR spectrum. However, the content of the HT and HH linkages in PThThPy⁺Hex(Cl⁻)Th are estimated at 1:2.3 from the peak integral ratio of the α -methylene protons at δ 4.67 and 4.58 in the ¹H NMR spectrum of **PThThPy**⁺**Hex(Cl⁻)Th**. This value is consistent with the content of the HT and HH linkages in **PThThPy⁺Ph(Cl⁻)Th** (HT/HH = 1:2.3) estimated from the integral ratio of the ¹H NMR peaks at δ 9.50 and 9.36.

UV-Vis and Photoluminescence Spectra

Optical data are summarized in Table 1. Figure 4 shows the UV-vis spectra of the DMSO solutions of ThThPy⁺-DNP(Cl⁻)Th, PThThPy⁺DNP(Cl⁻)Th-a, PThThPy⁺DNP-(Cl⁻)Th-b, and PThThPy⁺DNP(Cl⁻)Th-c.

The absorption peaks corresponding to the π - π * transition of **PThThPy**⁺**DNP(Cl⁻)Th-a** ($\lambda_{max} = 436$ nm), **PThThPy**⁺**DNP(Cl⁻)Th-b** ($\lambda_{max} = 426$ nm), and **PThThPy**⁺**DNP(Cl⁻)Th-**

c ($\lambda_{max} = 440$ nm) were observed at a longer wavelength than that of **ThThPy**⁺**DNP(Cl**⁻)**Th** ($\lambda_{max} = 324$ nm), suggesting that the π -conjugation system was expanded along the polymer chain. The λ_{max} values of **PThThPy**⁺**DNP(Cl**⁻)**Ths** are comparable to those of poly(3-alkylthiophene)s ($\lambda_{max} =$ 430–450 nm) synthesized by oxidative polymerization with FeCl₃.^{8,60} The resulting λ_{max} value of **PThThPy**⁺**DNP(Cl**⁻)**Th-a** was larger than that of **PThThPy**⁺**DNP(Cl**⁻)**Th-b** and corresponds to the fact that the DP value of **PThThPy**⁺**DNP(Cl**⁻)**Th-b**. **The** larger λ_{max} value of **PThThPy**⁺**Ph(Cl**⁻)**Th-c** ($\lambda_{max} = 442$ nm) as compared with those of **PTh-ThPy**⁺**Ph(Cl**⁻)**Th** ($\lambda_{max} = 433$ nm) suggests that the π -conjugation system was expanded to the nitro groups in **PTh-ThPy**⁺**DNP(Cl**⁻)**Th-c**.

ThThPyTh and PThThPyTh were photoluminescent in solution. The emission peak position of PThThPyTh ($\lambda_{em} = 570$ nm) was higher than that of **ThThPyTh** ($\lambda_{em} = 481$ nm). These observations are consistent with the results that the λ_{\max} value of **PThThPyTh** was larger than that of ThThPyTh. The PL peak of the polymer appears at the onset position of its absorption band, which is typical of photoluminescent aromatic compounds. The quantum yields (Φ values) of the PL of ThThPyTh and PThThPyTh were 0.10 and 0.09, respectively. On the other hand, ThThPy⁺-DNP(Cl⁻)Th, PThThPy⁺DNP(Cl⁻)Th-a, PThThPy⁺DNP-(Cl⁻)Th-b, PThThPy⁺DNP(Cl⁻)Th-c, PThThPy⁺DNP(Cl⁻)-**Th-d**, and **PThThPy⁺R(Cl⁻)Th** (R = Ph and Hex) did not show PL because of the presence of the pyridinium rings. It has been reported that pyridinium salts quench the PL of photoluminescent π -conjugated polymers.⁶²

Cyclic Voltammograms

Figure 5 shows the cyclic voltammograms of PThThPy⁺-DNP(Cl⁻)Th-a and ThThPy⁺DNP(Cl⁻)Th in a DMSO solution containing [Et₄N]BF₄ (0.10 M). **PThThPy⁺DNP(Cl⁻)Th**a and ThThPy⁺DNP(Cl⁻)Th exhibited a peak at 0.72 V (vs. Ag^+/Ag) and 0.83 V (vs. Ag^+/Ag) corresponding to the electrochemical oxidation of the thiophene rings, respectively. The observation that the oxidation potential of **PThThPy**⁺-DNP(Cl⁻)Th-c is more negative than that of ThThPy⁺DNP-(Cl⁻)Th is attributed to the expanded π -conjugation system of PThThPy⁺DNP(Cl⁻)Th-a. PThThPy⁺Ph(Cl⁻)Th and **PThThPy⁺Hex(Cl⁻)Th** exhibited electrochemical oxidation peaks of the thiophene rings at more negative potentials (E_a = 0.63 V and 0.63 V vs. Ag⁺/Ag, respectively) than **PThThPy**⁺**Ph(Cl⁻)Th-c**. These observations can be explained by the absence of an electron-withdrawing nitro group in **PThThPy⁺Ph(Cl⁻)Th** and the presence of an electron-donating hexyl group in **PThThPy⁺Hex(Cl⁻)Th**. **ThThPy⁺DNP(Cl⁻)Th** exhibited peaks corresponding to the electrochemical reduction of the nitro groups and the benzene and pyridinium rings at -0.84 V (vs. Ag⁺/Ag), -2.14 V (vs. Ag⁺/Ag), and –2.38 V (vs. Ag⁺/Ag), respectively. **PThThPy⁺DNP(Cl⁻)Th-a** exhibited peaks corresponding to the electrochemical reduction of the nitro groups as well as benzene and pyridinium rings at -0.81 V (vs. Ag⁺/Ag), -1.98V (vs. Ag^+/Ag), and -2.24 V (vs. Ag^+/Ag), respectively. The

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FIGURE 5 Cyclic voltammograms of **PThThPy**⁺**DNP(CI**⁻)**Th-a** and **ThThPy**⁺**DNP(CI**⁻)**Th** in a DMSO solution containing $[Et_4N]BF_4$ (0.10 M). Scan rate was 50 mV s⁻¹.

observation that the electrochemical reduction peak potentials of **PThThPy**⁺**DNP(Cl⁻)Th-a** are more positive than those of **ThThPy**⁺**DNP(Cl⁻)Th** is attributed to the expanded π -conjugation system of **PThThPy**⁺**DNP(Cl⁻)Th-a**. The fact that the reduction potentials of **PThThPy**⁺**Hex(Cl⁻)Th** were observed at more negative positions as compared with those of **PThThPy**⁺**DNP(Cl⁻)Th** is attributed to the presence of the electron-donating hexyl group in **PThThPy**⁺**Hex(Cl⁻)Th**. Any electrochromism was not observed on the polymers obtained in this study.

Electrical Conductivity

The electrical conductivities (σ) of **PThThPy**⁺**DNP(Cl**⁻**)Th-a**, PThThPy⁺DNP(Cl⁻)Th-b, PThThPy⁺DNP(Cl⁻)Th-c, PTh-**ThPy⁺DNP(Cl⁻)Th-d**, and **PThThPhTh** under nitrogen were 2.1 × 10⁻⁶ S cm⁻¹, 2.0 × 10⁻⁶ S cm⁻¹, 2.1 × 10⁻⁶ S cm⁻¹, 2.1 × 10⁻⁶ S cm⁻¹, 2.1 × 10⁻⁶ S cm⁻¹, and 8.5 × 10⁻⁷ S cm⁻¹, respectively. The higher σ value for **PThThPy**⁺**DNP(Cl**⁻)**Th-a** as compared with **PThThPhTh** supports the assumption that the self-doping via electron transfer from the polymer backbone to the electron-withdrawing Py^+DNP group occurs in **PThThPy⁺DNP(Cl⁻)Th-a**. It has been reported that PThs with nitro side group(s) exhibit a self-doping nature because the nitro group(s) induce an effective charge delocalization.⁶² The electrical conductivities of **PThThPy⁺DNP(Cl⁻)Th** polymers were considerably smaller than that of the electrochemically synthesized PThThTh ($\sigma = 10^{-3}$ to 10^{-2} S cm^{-1}).^{61,62} The origin of the lower conductivity appears to be the ring twisting along the polymer backbone, which was induced by the steric hindrance of the bulky **Py⁺DNP(Cl⁻)** group.

CONCLUSIONS

Polythiophenes with a reactive Zincke salt $(Py^+DNP(Cl^-))$ structure, such as **PThThPy⁺DNP(Cl⁻)Th**, were obtained from oxidation polymerizations. The reaction of PThThPy⁺-**DNP(Cl⁻)Th** with aromatic and aliphatic amines (R–NH₂; R = phenyl and n-hexyl) resulted in the substitution of the 2,4-dinitrophenyl (DNP) group into the R group to yield **PThThPy⁺R(Cl⁻)Th**. The UV-vis measurements suggested that **PThThPy⁺DNP(Cl⁻)Th** had an expanded π -conjugation system along the polymer main chain. The pyridinium group of **PThThPy⁺DNP(Cl⁻)Th** acted as a quencher for photoluminescence. PThThPy⁺DNP(Cl⁻)Th and PThThPy⁺-R(Cl⁻)Th received both electrochemical oxidation and reduction reactions. PThThPy⁺DNP(Cl⁻)Th exhibited semi-conductive electrical properties in a non-doped state. The results suggest that the methodology developed in this study has a lot of potential as a fucntionalization tool for a large number of PTh derivatives.

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