Electronic Supplementary Information

Thermoelectric thiophene dendrimers with large Seebeck coefficients

Kota Oki,[a] Shohei Horike,*[a,b,c] Mana Yamaguchi,[a] Chikayo Takechi,[a] Yasuko Koshiba,[a] Tatsuya Fukushima,[a] Atsunori Mori,[a,d] and Kenji Ishida*[a,d]

[a]Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan.

[b]Nanomaterials Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba 305-8565, Japan.

[c]PRESTO, Japan Science and Technology Agency, Kawaguchi 332-0012, Japan.

[d]Research Center for Membrane and Film Technology, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan.

Table of contents

I. Materials

Table S1. Used chemicals for dendrimer synthesis, doping, and film preparation.

Chemical (IUPAC name)	Supplier	Purity
Oxolane	Kanto chemical, Tokyo, Japan	99.5%
Trichloromethane	Nakalai Tesque, Kyoto, Japan	99%
Dichloro($^2H_2$)methane	Nakalai Tesque, Kyoto, Japan	99%
Diethyl ether	Nakalai Tesque, Kyoto, Japan	>98%
Hexane	Wako, Osaka, Japan	95%
dichloromethane	Wako, Osaka, Japan	99.995%
Sodium sulfate	Nakalai Tesque, Kyoto, Japan	98.5%
Copper(Ⅱ) chloride	Nakalai Tesque, Kyoto, Japan	99.97%
1,3,5-Tribromobenzene	Wako, Osaka, Japan	98%
Ammonium Chloride	Nakalai Tesque, Kyoto, Japan	98.5%
[1,3-bis(2,6-diisopropylphenyl)imidazolidene](3-chloropyridyl)palladium(II) dichloride	Sigma Aldrich Japan, Tokyo, Japan	-
2,2,6,6-Tetramethylpiperidinylmagnesium chloride lithium chloride complex solution	Sigma Aldrich Japan, Tokyo, Japan	1.0 M in THF,Toluene

II. Synthesis of dendron and dendrimers

7T. A thiophene dendron (7T) has been synthesized by a reported method [1].

Ph-$(7T)_3$. Under nitrogen atmosphere, 7T (459.1 mg, 0.5 mmol) and 2,2,6,6-tetramethylpiperidinylmagnesium chloride lithium chloride complex solution (TMPMgCl·LiCl) (1 mL, 1.0 mmol) dissolved in oxolane (4.5 mL) were stirred at room temperature for 3 hours. Under nitrogen atmosphere, 1,3-bis(2,6-diisopropylphenyl) imidazolidene (3-chloropyridyl) palladium (II) dichloride (1.9 mg, 2.79 μmol) and 1,3,5-tribromobenzene (44.07 mg, 0.14 mmol) were added to the mixture, and then stirred at 60 °C for 24 hours. The reaction was terminated by the addition of sat. aqueous ammonium chloride. The organic materials were extracted with diethyl ether and the organic layer was dried over anhydrous sodium chloride. Removal of the solvent under reduced pressure left a crude solid, which was subjected to column chromatography on silica gel to afford Ph-$(7T)_3$ in 90 % yield.

14T. Under nitrogen atmosphere, 7T (1.37 g, 1.5 mmol) and TMPMgCl·LiCl (1 mL, 1.0 mmol) dissolved in oxolane (4.5 mL) were stirred at room temperature for 3 hours. Under oxygen atmosphere, copper (II) chloride was added to the mixture, and then stirred at room temperature for 24 hours. The terminating, rinsing and extracting procedure were the same as Ph-$(7T)_3$ to afford 14T in 53 % yield.

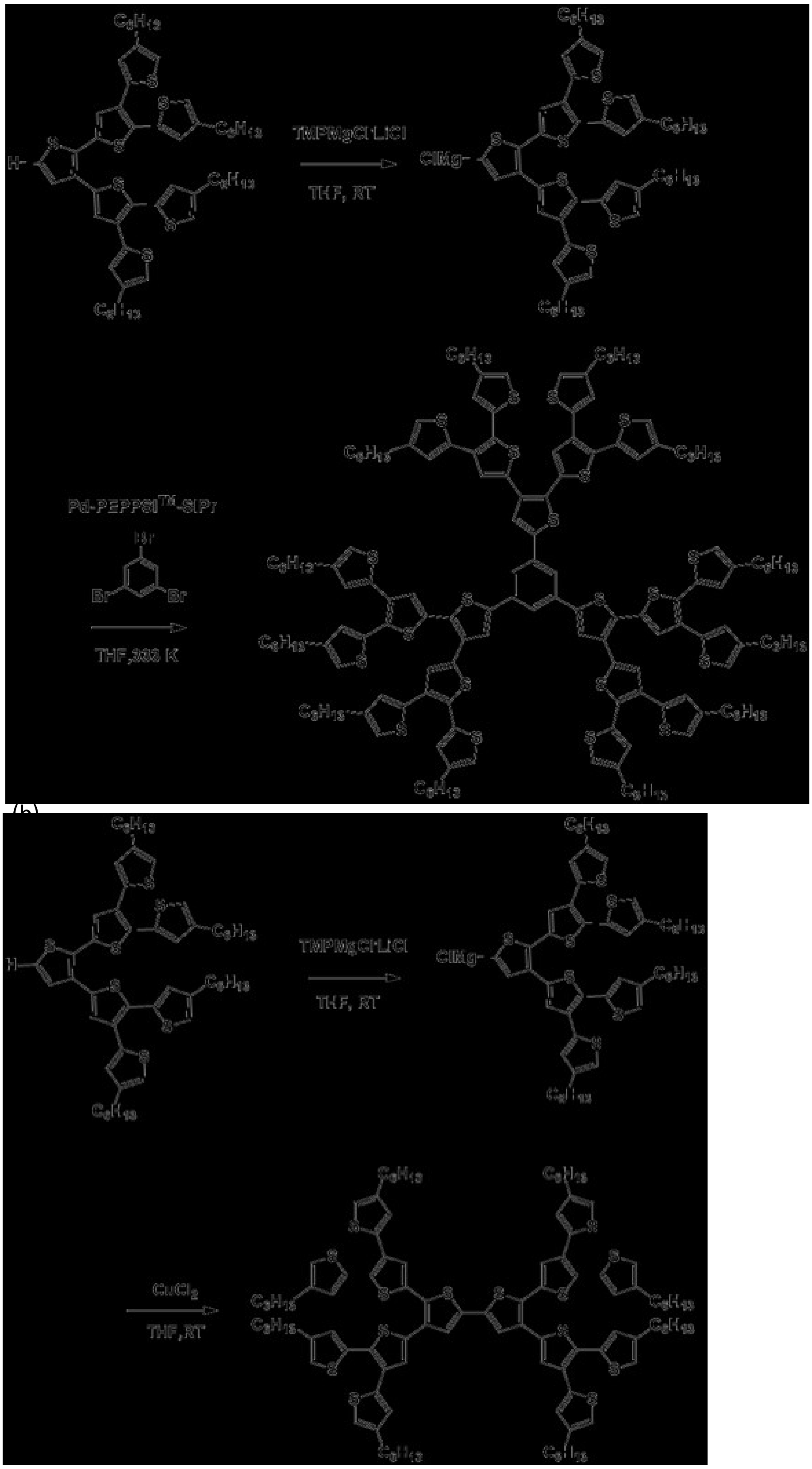


Figure S1. Synthesis procedures of (a) Ph-$(7T)_3$ and (b) 14T.

III. Nuclear magnetic resonance data

Ph-(7T)$_3$: ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.77 (s, 3H), 7.52 (s, 3H), 7.33 (s, 3H), 7.30 (s, 3H), 7.01 (d, J = 0.9 Hz, 3H), 7.00 (d, J = 1.2 Hz, 3H), 6.94 (br s, 6H), 6.88 (br s, 6H), 6.85–6.86 (br m, 6H), 2.55 (t, J = 5.7 Hz, 24H), 1.58 (m, 24H), 1.29 (m, 72H), 0.86-0.90 (m, 36H)
14T: ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.28 (s, 4H), 7.00 (d, J = 0.9 Hz, 2H), 6.99 (d, J = 1.2 Hz, 2H), 6.93 (s, 4H), 6.88 (s, 4H), 6.86 (s, 2H), 6.85 (s, 2H), 2.55 (t, J = 5.7 Hz, 16H), 1.58 (br m, 16H), 1.30 (br m, 48H), 0.88 (t, J = 5.0 Hz, 24H)

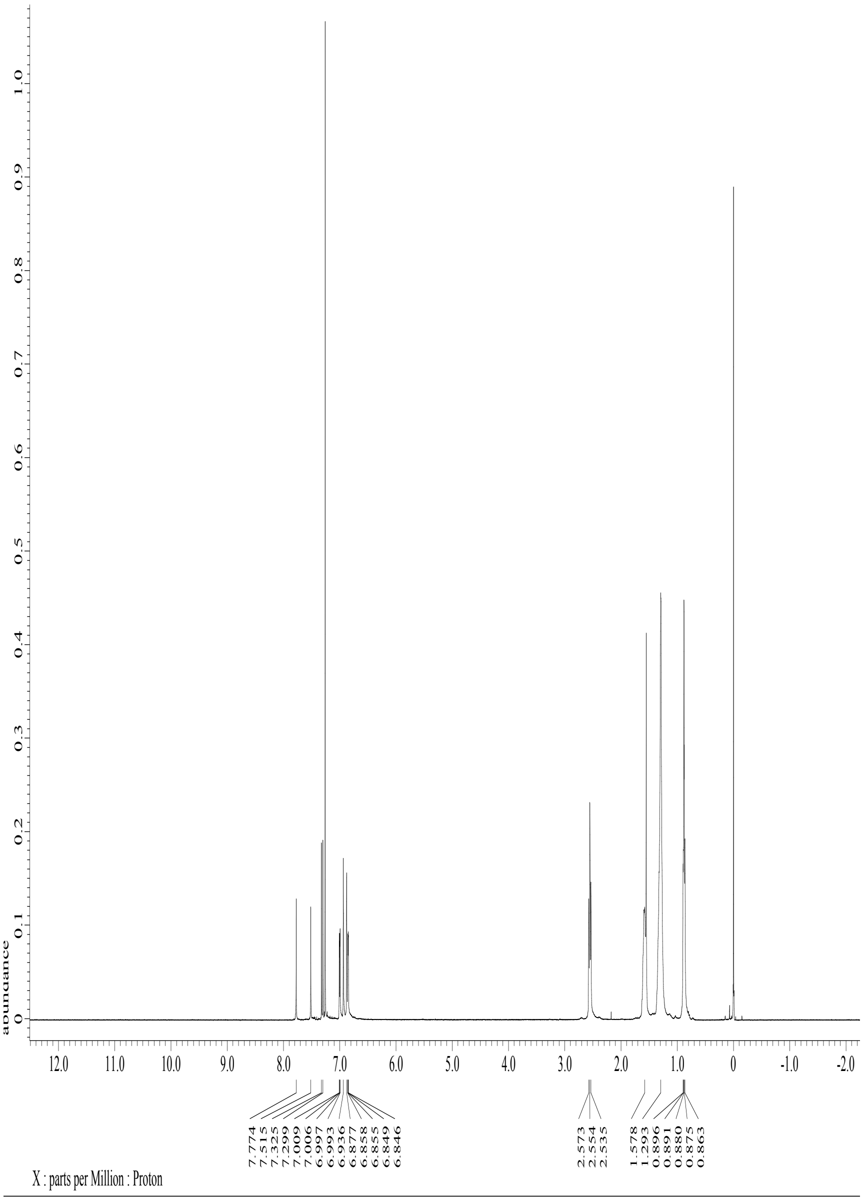


Figure S2. ^{1}H NMR (400 MHz, CDCl$_3$) data of Ph-(7T)$_3$.

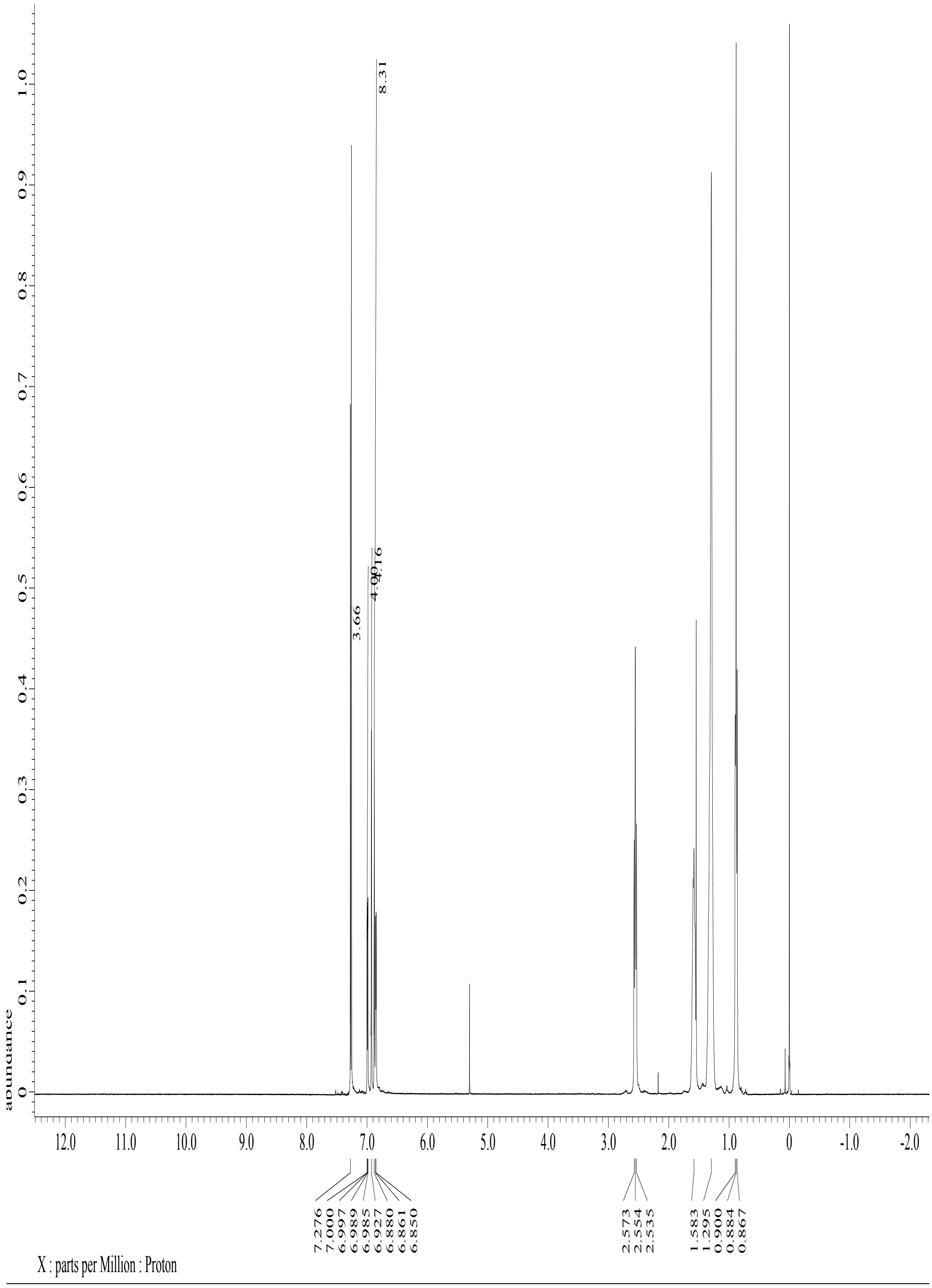
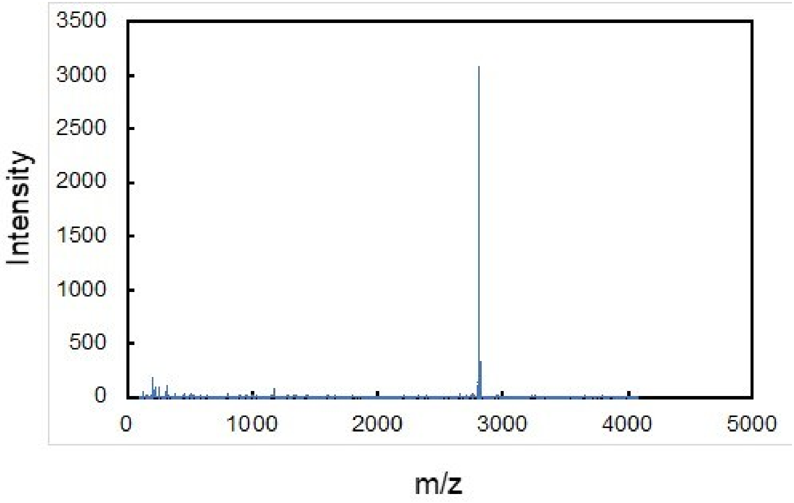


Figure S3. ^{1}H NMR (400 MHz, CDCl$_3$) data of 14T.

IV. MALDI-TOF-MS spectra

(a)



(b)

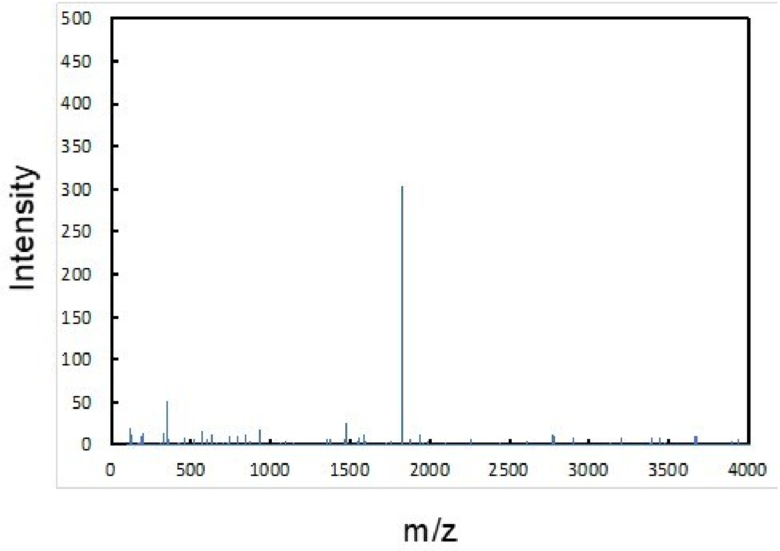


Figure S4. MALDI-TOF-MS spectra of (a) Ph-$(7T)_3$ and (b) 14T. Sharp peaks appear at around m/z = 2812 for Ph$(7T)_3$ and 1823 and 1824 for 14T. Molecular weight of each compound is 2808 and 1822.

V. Four-terminal resistance properties

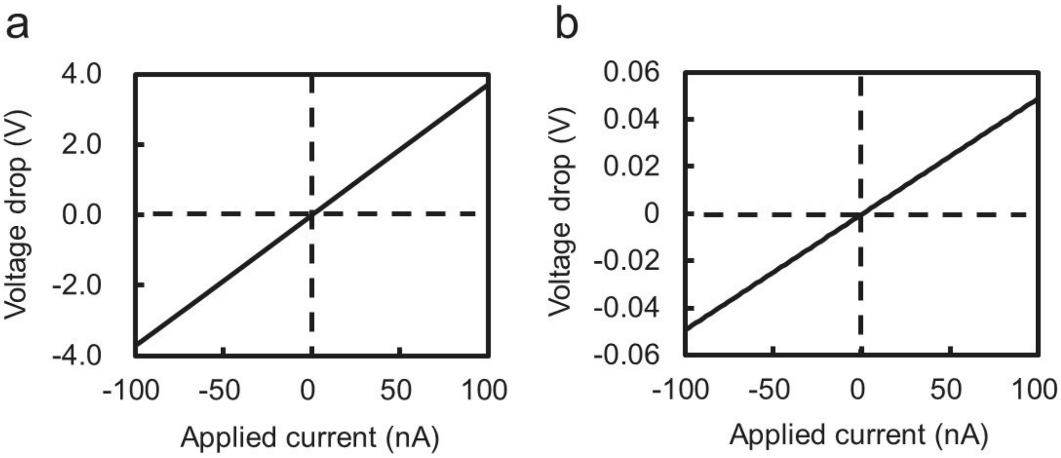
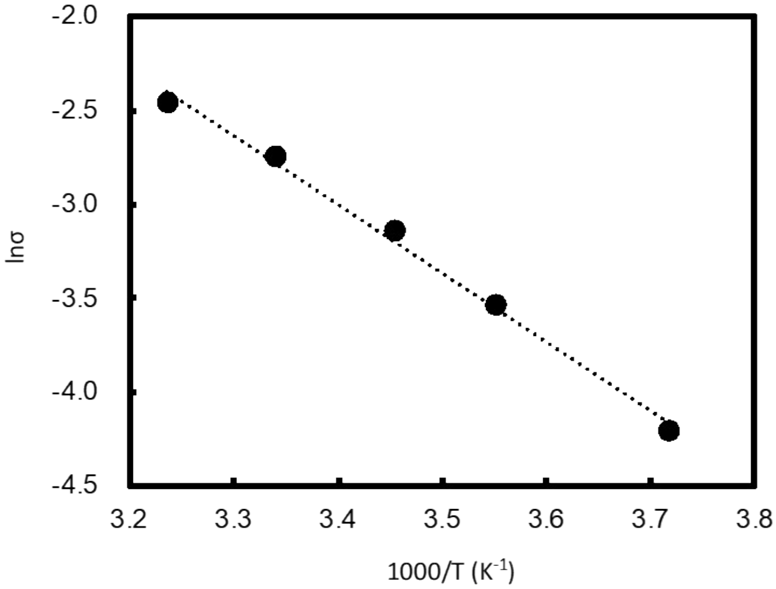


Figure S5. Voltage drop–applied current properties of (a) Ph-(7T)$_3$ and (b) 14T films doped with $FeCl_3$ measured by four-terminal method.

VI. Temperature dependence of electrical conductivity

(a)



(b)

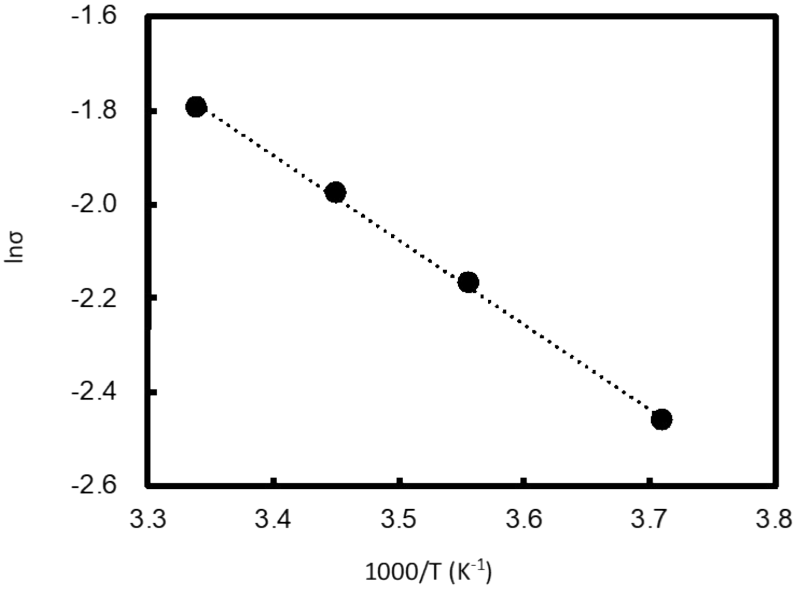
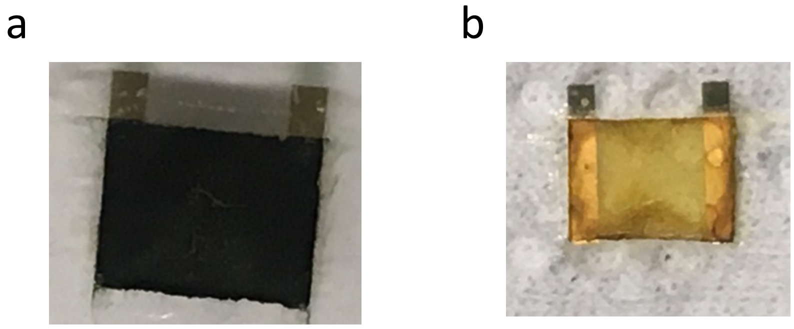


Figure S6. Arrhenius plots of electrical conductivity of (a) Ph-$(7T)_3$ and (b) 14T doped film.

VII. Dedoping property



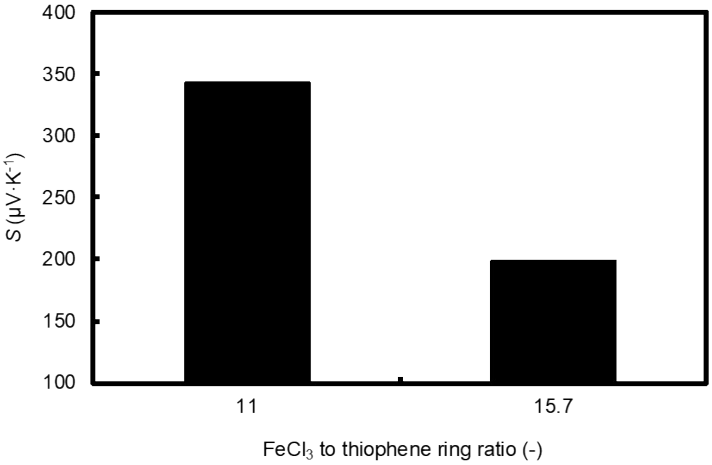
Doped 14T

Dedoped 14T

Figure S7. Photographs of the doped 14T film. (a) Immediately after film preparation and (b) after dedoped.

VIII. Doping level dependence of Seebeck coefficient

(a)



(b)

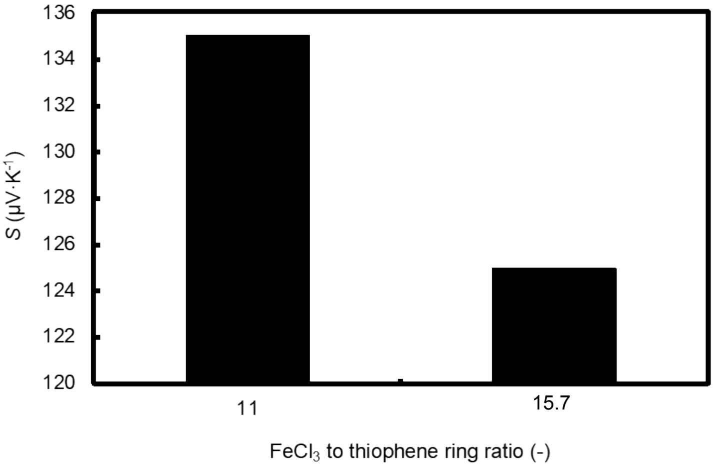


Figure S8. Doping level dependences of the Seebeck coefficients of (a) Ph-$(7T)_3$ and (b) 14T films. In this study, the doping level was controlled by changing the molar ratio (the number) of $FeCl_3$ to the thiophene rings of the dendrimers. The Seebeck coefficients decreased by increasing the doping level. In general, higher density of charge carriers decreases the Seebeck coefficient. Therefore, it is implied that the increased amount of $FeCl_3$ injected larger amount of charge carriers to the dendrimer molecules.

IX. Reference

[1] Tanaka *et al.*, *Chem. Eur. J.* **19**, 1658 (2013).