

## Supporting Information

Synthesis of  $\pi$ -Conjugated Polymers Containing Phosphole Units in the Main Chain by Reaction of an Organometallic Polymer Having Titanacyclopentadiene Unit

Yoshimasa Matsumura<sup>†</sup>, Masahiro Ueda<sup>†</sup>, Katsura Fukuda<sup>†</sup>, Kazuhisa Fukui<sup>‡</sup>, Ichiro Takase<sup>‡</sup>, Hiroki Nishiyama<sup>†</sup>, Shinsuke Inagi<sup>†</sup>, and Ikuyoshi Tomita<sup>† \*</sup>

<sup>†</sup> Interdisciplinary Graduate School of Science and Engineering,  
Tokyo Institute of Technology,  
Nagatsuta-cho 4259-G1-9, Midori-ku, Yokohama 226-8502, JAPAN  
TEL: +81-45-924-5413, FAX: +81-45-924-5489  
e-mail: [tomita@echem.titech.ac.jp](mailto:tomita@echem.titech.ac.jp)

<sup>‡</sup> Central Research Center, Daicel Corporation, Shinzaike 1239, Aboshi-ku,  
Himeji, Hyogo, Japan

## Experimental Details

### General Experimental

$^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECP-300 instrument (300 MHz, 75 MHz, and 121 MHz for  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR respectively). Tetramethylsilane was used as an internal standard for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. Fourier transform infrared (FT-IR) spectra were measured on a Thermo Scientific Nicolet iS10 FT-IR instrument. Gel permeation chromatography (GPC) measurements were performed on a Shimadzu LC-10AS liquid chromatograph equipped with a Shimadzu RID-10A refractive index detector and Tosoh TSK-gel GMHHR-M tandem columns using chloroform ( $\text{CHCl}_3$ ) as an eluent (1 mL/min) at 35 °C. Polystyrene standards were used for calibration. UV-vis absorption spectra were recorded in  $\text{CHCl}_3$  on a Shimadzu UV-3100PC spectrometer. Photoluminescence spectra were recorded in  $\text{CHCl}_3$  on a Shimadzu RF-5300PC spectrometer. Cyclic voltammetric analyses were carried out on a Versa STAT3 (Princeton Applied Research) potentiostat at the scan rate of 50 mV/s. All the measurements were performed in dry acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate at ambient temperature using a three-electrode system, with each solution being purged with  $\text{N}_2$  prior to measurement. The working electrode was a platinum (Pt) disk ( $d = 1.6$  mm, BAS, Japan), the counter electrode was a spiral Pt wire, and the reference electrode was a silver (Ag) wire. Thin films of the polymer (**6**) were prepared on a MIKASA 1H-360S spin coater. Current-voltage characteristics of the polymer (**6**) / p- or n-type silicon wafer were recorded at 25 °C under air on a DC Voltage Current Source/Monitor 6242 (ADC).

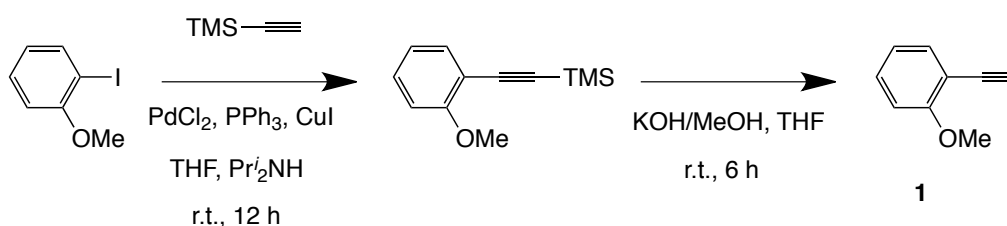
### Materials

Titanium(IV) isopropoxide [ $\text{Ti}(\text{OPr}^i)_4$ ], dichlorophenylphosphine ( $\text{PhPCl}_2$ ), and dichloro-*t*-butylphosphine ( $^t\text{BuPCl}_2$ ) were obtained from Sigma-Aldrich and distilled under reduced pressure. Diethyl ether and tetrahydrofuran (THF)

were dried over sodium benzophenone ketyl and distilled under nitrogen. A diethyl ether solution of isopropylmagnesium chloride ( $\text{Pr}^i\text{MgCl}$ , 1.0 M) was prepared from 2-chloropropane (7.85g, 100 mmol) and magnesium (3.04g, 125 mmol) in diethyl ether (90 mL). Triphenylphosphine was obtained from Sigma-Aldrich and recrystallized from MeOH. The polymerizations, the polymer reactions, and their corresponding model reactions were carried out under argon. p-Type silicon wafer ( $D = 3$  inches,  $\rho = 1\text{-}50\ \Omega\cdot\text{cm}$ , doped by boron) and n-type silicon wafer ( $D = 3$  inches,  $\rho = 1\text{-}50\ \Omega\cdot\text{cm}$ , doped by phosphorous) were obtained from SUMCO.

### Preparation of 2-Ethynylanisole (1)

2-Ethynylanisole (**1**) was prepared by the methods described in reference [1] with slight modifications (Scheme S1).



Scheme S1. Preparation of **1**.

### Synthesis of 2-(Trimethylsilylethynyl)anisole.

To a flask containing 2-iodoanisole (4.68 g, 20.0 mmol),  $\text{PdCl}_2$  (0.071 g, 0.400 mmol),  $\text{PPh}_3$  (0.209 g, 0.800 mmol), and  $\text{CuI}$  (0.076 g, 0.400 mmol) were added THF (50 mL) and diisopropylamine (50 mL) under argon. To this mixture, was added trimethylsilylacetylene (2.36 g, 24.0 mmol) dropwise and the resulting mixture was stirred at ambient temperature for 12 h. Then, the resulting reaction mixture was poured into a saturated ammonium chloride aqueous solution (100 mL). The organic layer was collected and the remaining aqueous phase was extracted three times with hexane (total 100 mL).

After drying the combined organics over  $\text{MgSO}_4$ , the volatile fractions were evaporated and the residue was purified by column chromatography on silica gel (eluent: hexane) to give 2-(trimethylsilylethynyl)anisole in 96% yield (3.92 g, 19.2 mmol) as yellow oil.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 0.27 (s, 9H), 3.88 (s, 3H), 6.85 (d,  $J = 4.9$  Hz, 1H), 6.89 (dd,  $J = 0.8, 7.6$  Hz, 1H), 7.25-7.30 (m, 1H), 7.44 (dd,  $J = 1.6, 7.6$  Hz, 1H).

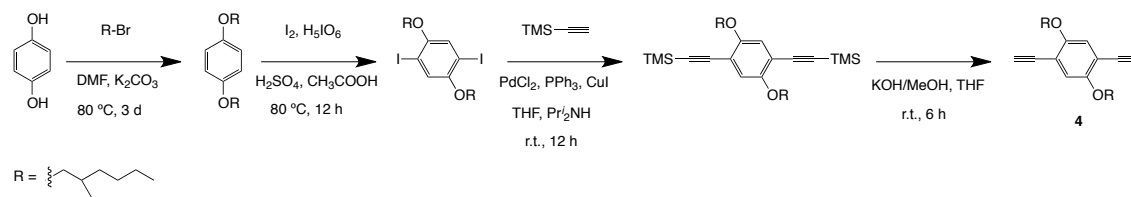
#### Synthesis of 2-Ethynylanisole (**1**).

To a stirred solution of 1.0 M KOH in MeOH (25 mL) were added 2-(trimethylsilylethynyl)anisole (3.92 g, 19.2 mmol) in THF (25 mL) at ambient temperature. After stirring for 6 h at ambient temperature, the reaction mixture was poured into water (100 mL) and neutralized by addition of an aqueous solution of HCl (1.0 M). Then, the mixture was extracted three times with hexane (total 100 mL). After drying the combined organics over  $\text{MgSO}_4$ , the volatile fractions were evaporated and the residue was purified by column chromatography on silica gel (eluent: hexane/dichloromethane, v/v = 9/1) to give 2-ethynylanisole (**1**) in 98% yield (2.49 g, 18.8 mmol) as yellow oil.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 3.36 (s, 1H), 3.86 (s, 3H), 6.85 (d,  $J = 7.4$  Hz, 1H), 6.90 (dd,  $J = 0.8, 7.4$  Hz, 1H), 7.29-7.32 (m, 1H), 7.45 (dd,  $J = 1.7, 7.6$  Hz, 1H).

#### Preparation of Diyne Monomer (**4**)

1,4-Bis(2-ethylhexyloxy)-2,5-diethynylbenzene (**4**) was prepared by the methods described in reference [2] with slight modifications (Scheme S2).



Scheme S2. Preparation of **4**.

#### Synthesis of 1,4-Bis(2-ethylhexyloxy)benzene.

To a *N,N*-dimethylformamide (150 mL) solution of hydroquinone (11.0 g 100 mmol) were added potassium carbonate (78.0 g, 600 mmol) and 2-ethylhexylbromide (52.5 g, 270 mmol) at ambient temperature. The reaction mixture was stirred for 3 days at 80 °C and then cooled to ambient temperature. After addition of water (300 mL), the mixture was extracted three times with hexane (total 200 mL). After drying the combined organics over MgSO<sub>4</sub>, the volatile fractions were evaporated and the residue was purified by column chromatography on silica gel (eluent: hexane) to give 1,4-bis(2-ethylhexyloxy)benzene in 83% yield (27.7 g, 82.8 mmol) as colorless oil.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 0.92-0.98 (12H, —CH<sub>3</sub>), 1.29-1.71 (18 H, —OCH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.81 (d, *J* = 5.8 Hz, 4H, —OCH<sub>2</sub>—), 6.86 (s, C<sub>6</sub>H<sub>4</sub>, 4H).

#### Synthesis of 1,4-Bis(2-ethylhexyloxy)-2,5-diiodobenzene.

A mixture of 1,4-bis(2-ethylhexyloxy)benzene (27.7 g, 82.8 mmol), H<sub>5</sub>IO<sub>6</sub> (10.7 g, 47.1 mmol), I<sub>2</sub> (23.4 g, 92.2 mmol), acetic acid (200 mL), H<sub>2</sub>O (40 mL), and H<sub>2</sub>SO<sub>4</sub> (8.0 mL) was stirred for 12 h at 80 °C and then cooled to ambient temperature. To the resulting mixture, was added an aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (2.0 M) until the brown color of the solution disappeared, and the reaction mixture was extracted three times with hexane (total 200 mL). After drying the combined organics over MgSO<sub>4</sub>, the volatile fractions were evaporated and the residue was purified by column chromatography on silica gel (eluent: hexane) to give 1,4-bis(2-ethylhexyloxy)-2,5-diiodobenzene in 50% yield (24.1 g, 41.1 mmol) as yellow oil.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 0.89-0.96 (12H, —CH<sub>3</sub>), 1.31-1.70 (18H, —OCH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.81 (d, *J* = 5.5 Hz, 4H, —OCH<sub>2</sub>—), 7.16 (s, C<sub>6</sub>H<sub>2</sub>, 2H).

Synthesis of 1,4-Bis(2-ethylhexyloxy)-2,5-bis(2-trimethylsilylethynyl)benzene.

To a flask containing 1,4-bis(2-ethylhexyloxy)-2,5-diiodobenzene (24.1 g, 41.1 mmol), PdCl<sub>2</sub> (0.146 g, 0.822 mmol), PPh<sub>3</sub> (0.430 g, 1.64 mmol), and CuI (0.822 g, 0.215 mmol) were added THF (100 mL) and diisopropylamine (100 mL) under argon. To this mixture was added dropwise trimethylsilylacetylene (9.80 g, 100 mmol) and the resulting reaction mixture was stirred at ambient temperature for 12 h. Then, the resulting reaction mixture was poured into a saturated ammonium chloride aqueous solution (200 mL). The organic layer was collected and the remaining aqueous phase was extracted three times with hexane (total 200 mL). After drying the combined organics over MgSO<sub>4</sub>, the volatile fractions were evaporated and the residue was purified by column chromatography on silica gel (eluent: hexane) to give 1,4-bis(2-ethylhexyloxy)-2,5-bis(2-trimethylsilylethynyl)benzene in 84% yield (18.2 g, 34.6 mmol) as brown oil.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 0.24 (s, 18H, —Si(CH<sub>3</sub>)<sub>3</sub>), 0.88-0.94 (12H, —CH<sub>3</sub>), 1.31-1.74 (18H, —OCH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.77-3.83 (m, 4H, —OCH<sub>2</sub>—), 6.88 (s, 2H, C<sub>6</sub>H<sub>2</sub>).

Synthesis of 1,4-Bis(2-ethylhexyloxy)-2,5-diethynylbenzene (**4**).

To a stirred solution of 1.0 M KOH in MeOH (50 mL) was added 1,4-bis(2-ethylhexyloxy)-2,5-bis(2-trimethylsilylethynyl)benzene (18.2 g, 34.6 mmol) in THF (50 mL) at ambient temperature. After stirring for 6 h at ambient temperature, the reaction mixture was poured into water (100 mL) and neutralized by addition of an aqueous solution of HCl (1.0 M). Then, the mixture was extracted three times with hexane (total 200 mL). After drying the combined organics over MgSO<sub>4</sub>, the volatile fractions were evaporated and the residue was purified by column chromatography on silica gel (eluent: hexane/dichloromethane, v/v = 8/2) to give

1,4-bis(2-ethylhexyloxy)-2,5-diethynylbenzene (**4**) in 96% yield (12.7 g, 33.2 mmol) as pale yellow oil.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 0.88-0.95 (12H,  $-\text{CH}_3$ ), 1.28-1.56 (18H,  $-\text{OCH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 3.31 (s, 2H,  $-\text{C}\equiv\text{CH}$ ), 3.84 (d,  $J = 5.8$  Hz, 4H,  $-\text{OCH}_2-$ ), 6.95 (s, 2H,  $\text{C}_6\text{H}_2$ ).

## Model Reaction

### Synthesis of 2,5-Bis(2-methoxyphenyl)-1-phenylphosphole (**3**)

To a diethyl ether (5.0 mL) solution of **1** (0.132 g, 1.00 mmol) and  $\text{Ti}(\text{OPr}^i)_4$  (0.199 g, 0.700 mmol), was added a diethyl ether solution of  $i\text{PrMgCl}$  (1.0 M, 1.40 mL, 1.40 mmol) at  $-78^\circ\text{C}$  under argon and the mixture was kept stirring at that temperature for 0.5 h and then warmed up to  $-50^\circ\text{C}$ . After stirring at  $-50^\circ\text{C}$  for 12 h,  $\text{PhPCl}_2$  (0.107 g, 0.600 mmol) was added at  $-50^\circ\text{C}$  and the reaction mixture was warmed slowly to ambient temperature for 3 h. Then, the resulting reaction mixture was poured into water (10 mL). The organic layer was collected and the remaining aqueous phase was extracted three times with diethyl ether. After drying the combined organics over  $\text{MgSO}_4$ , the volatile fractions were evaporated and the residue was purified by alumina column chromatography (eluent: hexane) to give **3** in 88% yield (0.163 g, 0.438 mmol) as yellow oil.

**3**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 3.77 (s, 6H), 6.83-6.91 (4H), 7.10-7.16 (5H), 7.29-7.35 (2H), 7.55 (d,  $J = 9.9$  Hz, 2H), 7.62 (d,  $J_{\text{P-H}} = 7.7$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 55.1, 111.3, 120.6, 125.6(d,  $J_{\text{P-H}} = 18.3$  Hz), 127.6, 128.2 (d,  $J_{\text{P-H}} = 8.1$  Hz), 128.5 (d,  $J_{\text{P-H}} = 1.7$  Hz), 128.6 (d,  $J_{\text{P-H}} = 5.7$  Hz), 133.1 (d,  $J_{\text{P-H}} = 8.1$  Hz), 133.4, 133.8 (d,  $J_{\text{P-H}} = 9.8$  Hz), 147.1 (d,  $J_{\text{P-H}} = 4.6$  Hz), 156.1 (d,  $J_{\text{P-H}} = 1.2$  Hz);  $^{31}\text{P}$  NMR (121 MHz,  $\text{CDCl}_3$ ): +14.9; IR (KBr disc,  $\text{cm}^{-1}$ ): 2957, 2930, 2858, 2833, 1595, 1577, 1535, 1500, 1479, 1458, 1433, 1338, 1298, 1263, 1244, 1176, 1114, 1068, 1051, 1022, 972, 935, 858, 800; HR-MS:  $m/z$  calcd for  $\text{C}_{24}\text{H}_{21}\text{O}_2\text{P}$ :

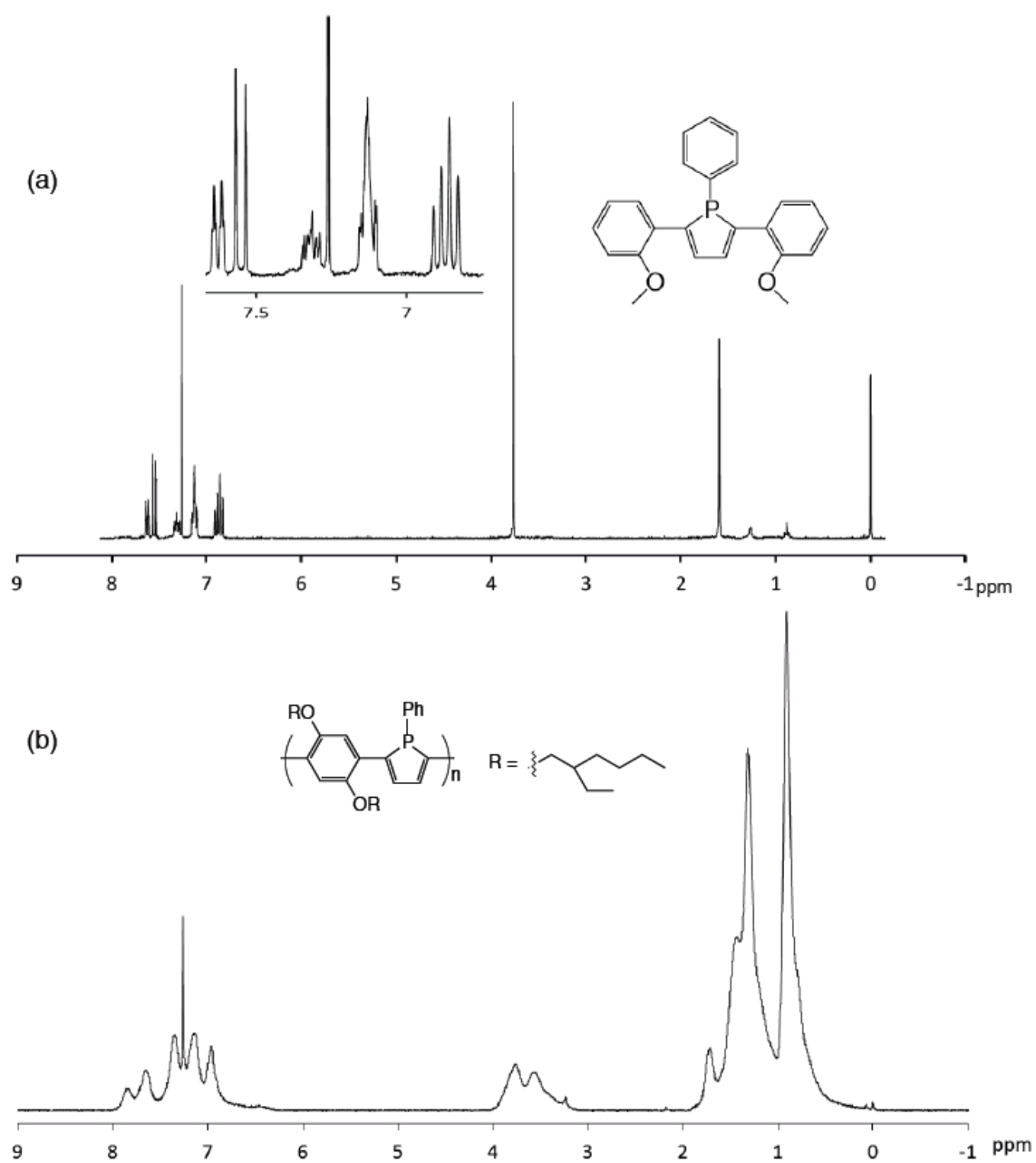
372.1279, Found: 372.1285.

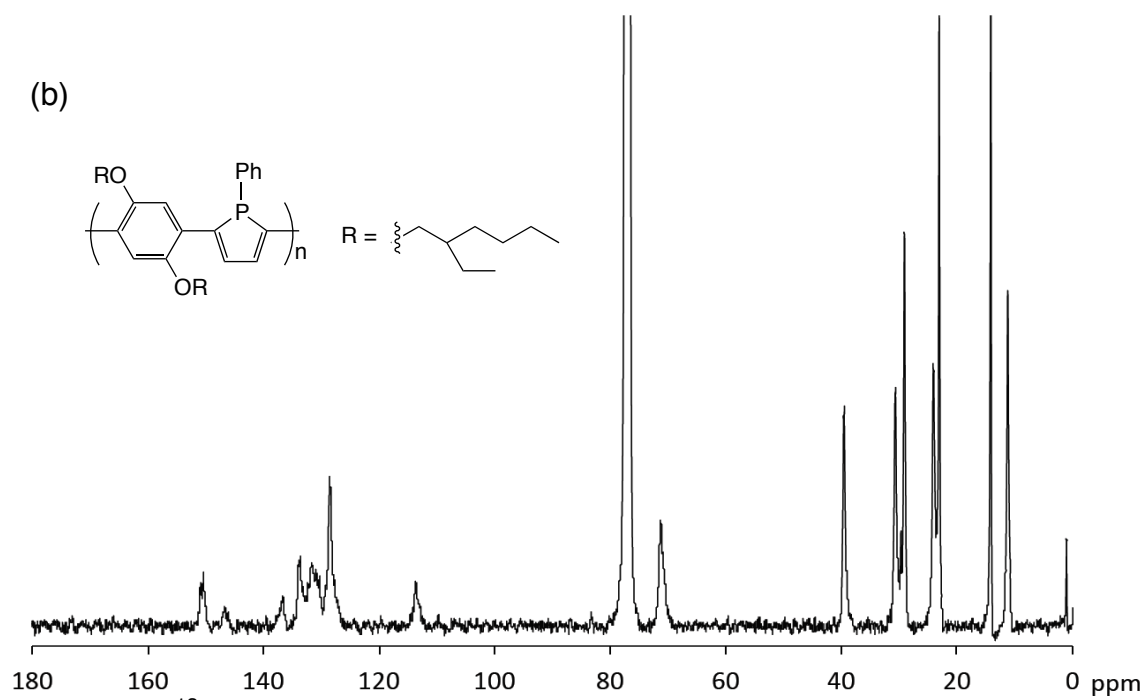
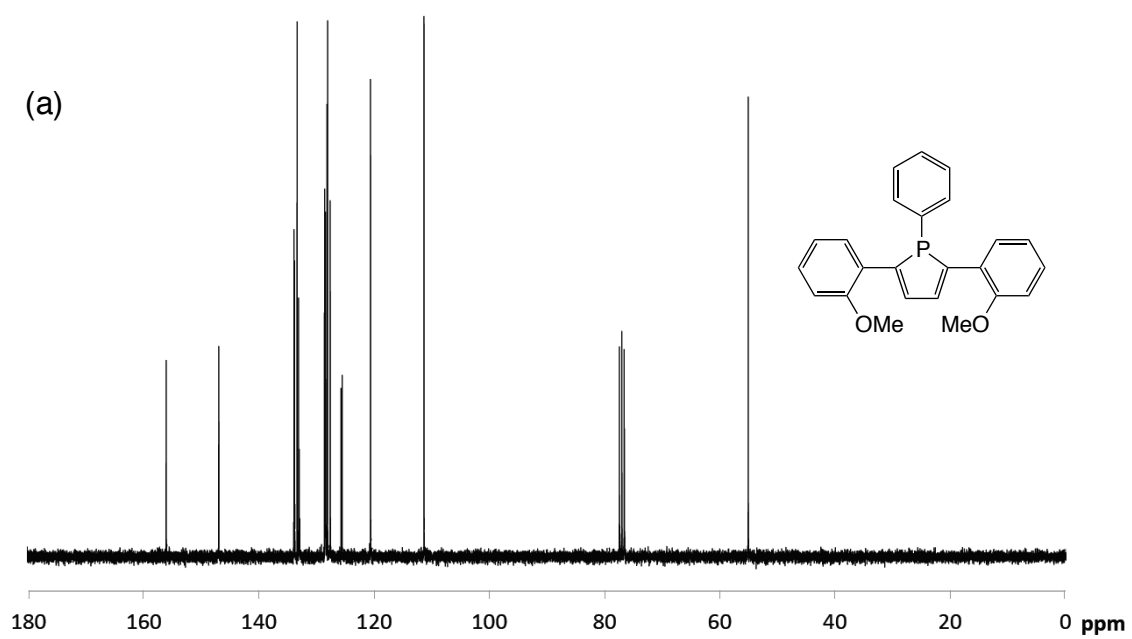
### Synthesis of **6**

To a diethyl ether (20 mL) solution of **4** (0.191 g, 0.500 mmol) and  $\text{Ti}(\text{OPr}^i)_4$  (0.199 g, 0.700 mmol), was added a diethyl ether solution of  $i\text{PrMgCl}$  (1.0 M, 1.4 mL, 1.40 mmol) at  $-78\text{ }^\circ\text{C}$  under argon and the mixture was kept stirring at that temperature for 0.5 h and then warmed up to  $-50\text{ }^\circ\text{C}$ . After stirring at  $-50\text{ }^\circ\text{C}$  for 12 h,  $\text{PhPCl}_2$  (0.107 g, 0.600 mmol) was added at  $-50\text{ }^\circ\text{C}$  and the reaction mixture was warmed slowly to ambient temperature. Then, the resulting reaction mixture was poured into water (10 mL). The organic layer was collected and the remaining aqueous phase was extracted three times with dichloromethane. After drying the combined organics over  $\text{MgSO}_4$ , the volatile fractions were evaporated and the residue was precipitated into hexane to give a 1-phenylphosphole-containing polymer (**6**) in 76% (0.185 g, 0.378 mmol unit).

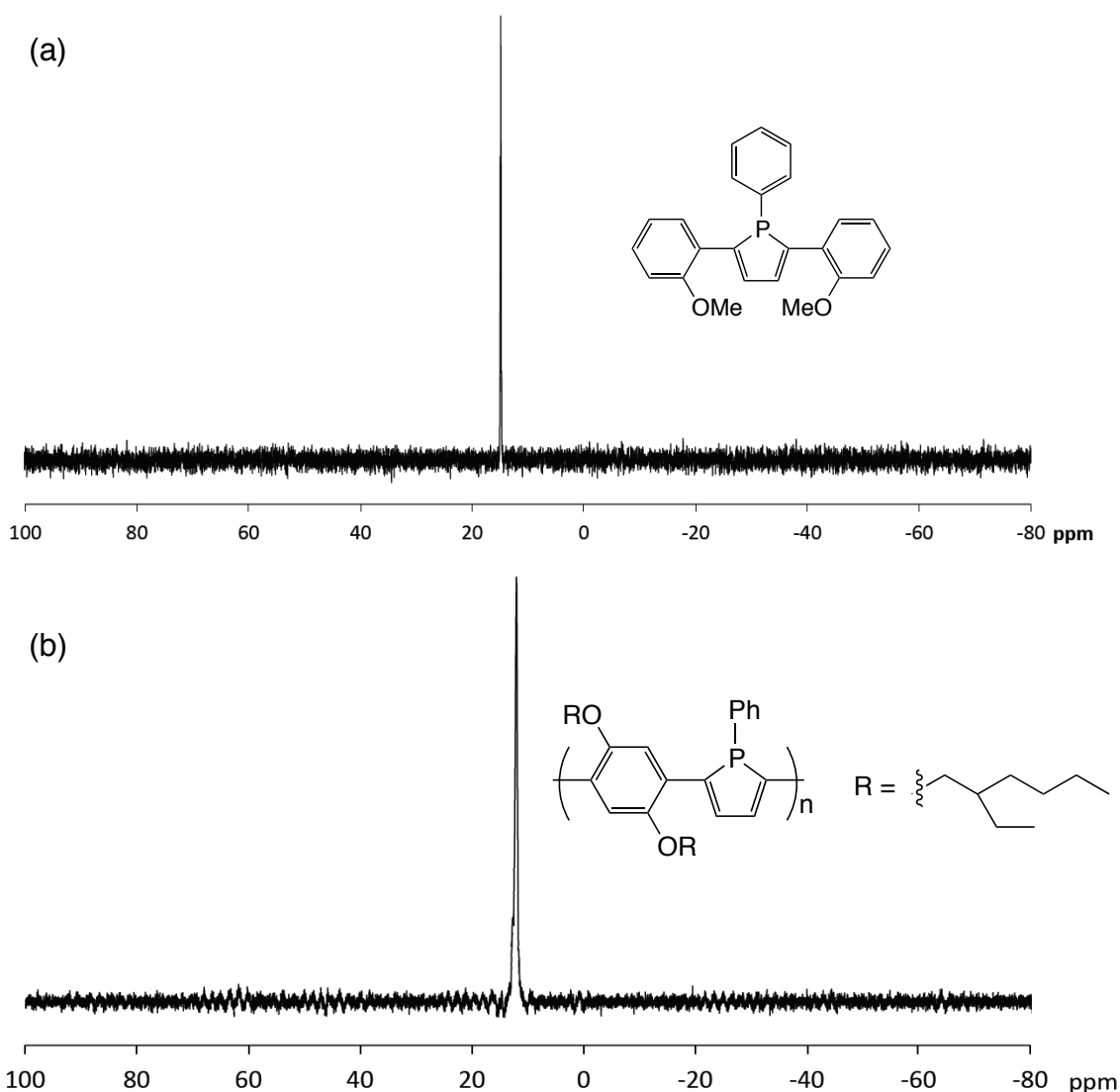
**6**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 0.27-1.93 (30H,  $-\text{OCH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 3.13-3.98 (br, 4H,  $-\text{OCH}_2-$ ), 6.77-7.95 (9H, aromatic);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 11.1, 14.1, 23.1, 24.0, 29.1, 30.6, 39.5, 71.4, 113.5, 127.7, 129.1, 130.2, 132.6, 133.8, 137.2, 146.8, 150.3;  $^{31}\text{P}$  NMR (121 MHz,  $\text{CDCl}_3$ ) +12.0; IR (KBr disc,  $\text{cm}^{-1}$ ): 2962, 2926, 2854, 1637, 1560, 1543, 1508, 1458, 1398, 1261, 1095, 1024, 866, 802.







**Figure S2.**  $^{13}\text{C}$  NMR spectra of **3** (a) and **6** (b).



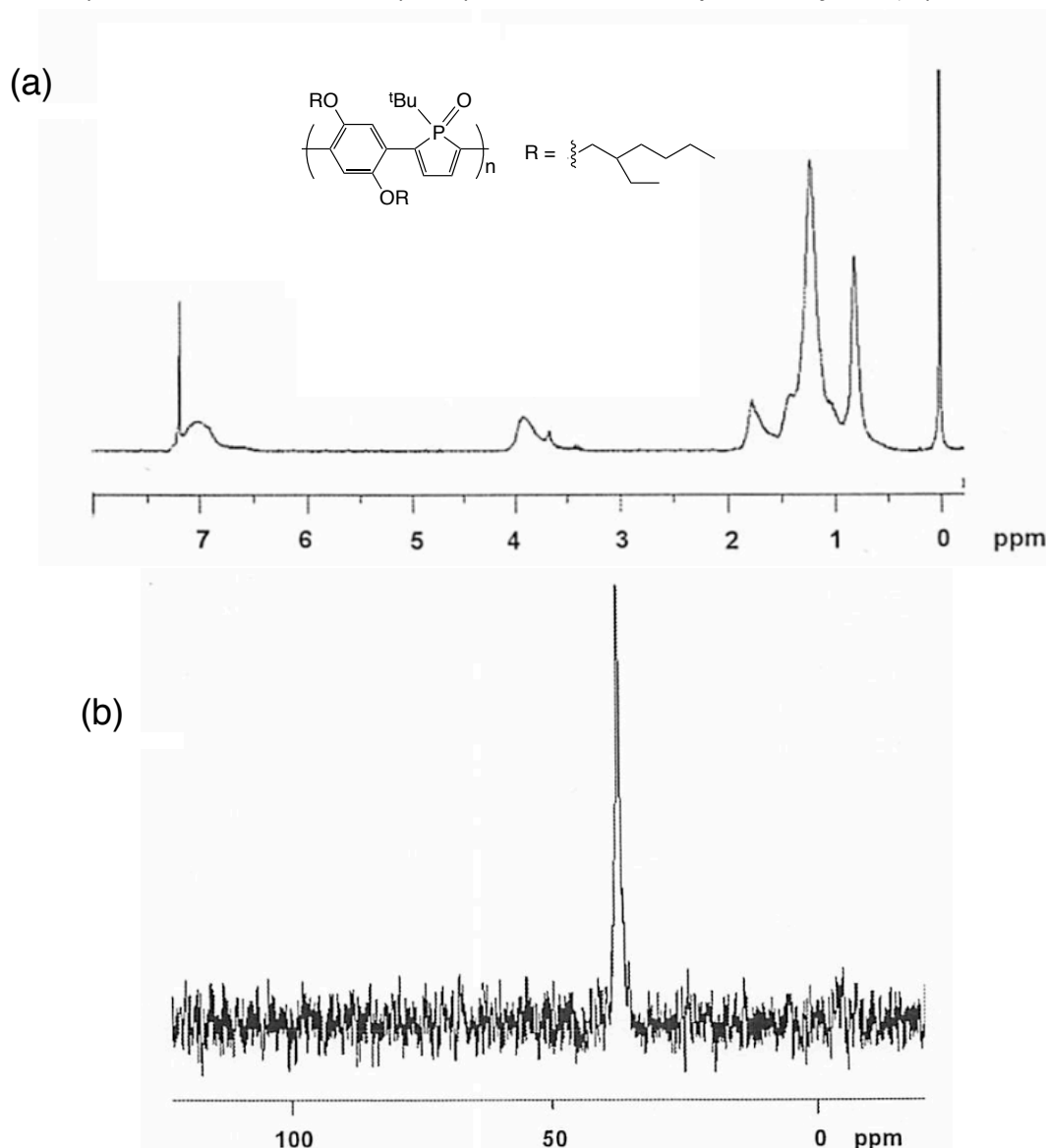
**Figure S3.**  $^{31}\text{P}$  NMR spectra of **3** (a) and **6** (b).

### Synthesis of **7**

To a diethyl ether (20 mL) solution of **4** (0.191 g, 0.500 mmol) and  $\text{Ti}(\text{OPr}^i)_4$  (0.199 g, 0.700 mmol), was added a diethyl ether solution of  $^i\text{PrMgCl}$  (1.0 M, 1.4 mL, 1.40 mmol) at  $-78\text{ }^\circ\text{C}$  under argon and the mixture was kept stirring for 0.5 h at and then warmed up to  $-50\text{ }^\circ\text{C}$ . After stirring at  $-50\text{ }^\circ\text{C}$  for 12 h, a diethyl ether solution of  $^t\text{BuPCl}_2$  (1.0 M, 0.60 mL, 0.600 mmol) was added at  $-50\text{ }^\circ\text{C}$  and the reaction mixture was warmed slowly to ambient temperature. Then, the resulting reaction mixture was poured into water (10 mL). The organic layer was collected and the remaining aqueous phase was extracted three times with dichloromethane. After drying the combined organics over  $\text{MgSO}_4$ , the volatile

fractions were evaporated and the residue was precipitated into MeOH to give a polymer (**7**) in 52% (0.127 g, 0.261 mmol unit). This polymer was found to contain phosphole oxide units as a result of auto-oxidation under ambient conditions as supported by its  $^{31}\text{P}$  NMR spectrum.

**7**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 0.47-0.95 (12H,  $-\text{CH}_3$ ), 0.98-1.86 (27H,  $-\text{OCH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $-\text{PC}(\text{CH}_3)_3$ , 3.68-4.23 (br, 4H,  $-\text{OCH}_2-$ ), 6.62-7.28 (aromatic, 9H);  $^{31}\text{P}$  NMR (121 MHz,  $\text{CDCl}_3$ ): +37.2; IR (KBr disc,  $\text{cm}^{-1}$ ): 3040, 2926, 1597, 1494, 1467, 1417, 1390, 1261, 1201, 1028, 989; UV-vis ( $\text{CHCl}_3$ ): absorption maximum ( $\lambda_{\text{max}}$ ) 445 nm; Photoluminescence ( $\text{CHCl}_3$ ): emission maximum ( $E_{\text{max}}$ ) 547 nm with a quantum yield ( $\Phi$ ) of 0.06.



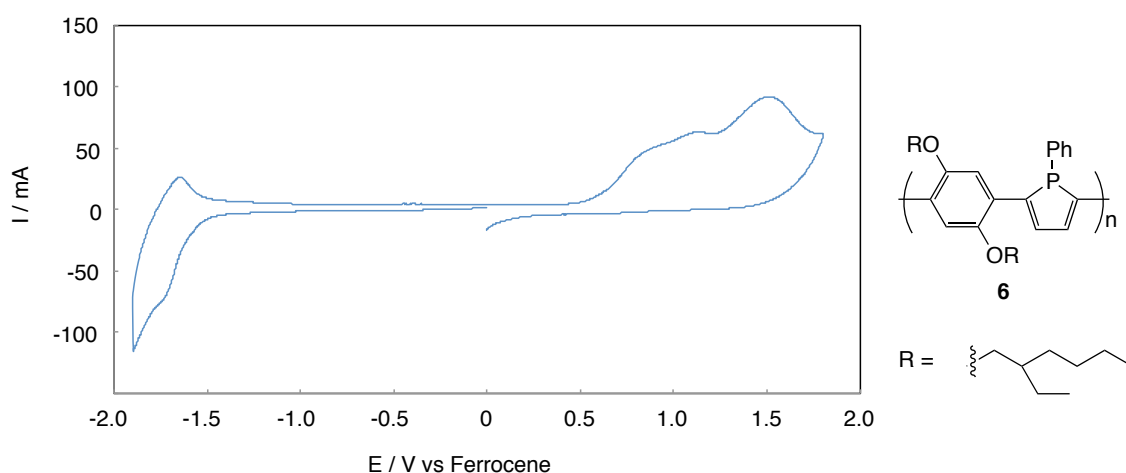
**Figure S4.**  $^1\text{H}$  NMR (a) and  $^{31}\text{P}$  NMR spectra (b) of **7**.

### Cyclic voltammetric (CV) analysis

The onset oxidation potential ( $E_{\text{ox}}$ ) and the reduction potential ( $E_{\text{red}}$ ) of **6** were observed in 0.55 V and -1.52 V (Figure S5). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of **6** were estimated to be -5.35 eV<sup>a</sup> and -3.28 eV<sup>b</sup> from the  $E_{\text{ox}}$  and  $E_{\text{red}}$ .

$$^a\text{HOMO} = -(E_{\text{ox}} + 4.8) \text{ (eV)}.$$

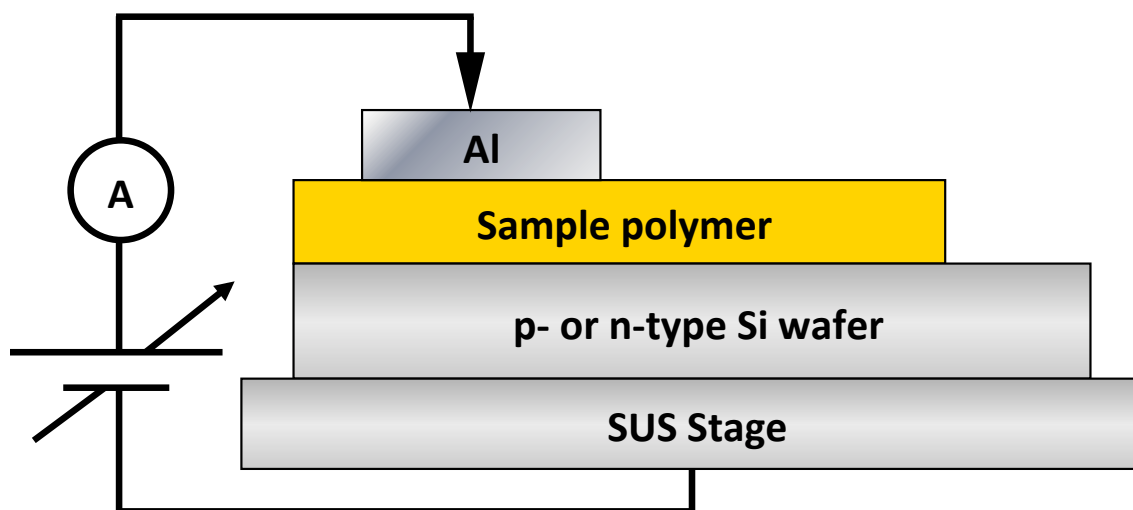
$$^b\text{LUMO} = -(E_{\text{ox}} + 4.8) \text{ (eV)}.$$



**Figure S5.** Cyclic voltammogram of **6** in film on a Pt wire in acetonitrile solution of tetra-*n*-butylammonium hexafluorophosphate (0.10 M), at a sweep rate of 100 mV s<sup>-1</sup>.

### Preparation of Diode Circuits

The phosphole-containing layer was spin-coated (1500 rpm, 20 seconds) from a THF solution of **6** (0.3 wt%, 0.5 mL, filtrated in advance with PTFE filter with pore size of 0.2  $\mu\text{m}$ ) onto n- or p-type silicon wafers, followed by drying at 50 °C for 60 seconds. To complete the diode circuits fabrication, 300 nm thickness aluminium electrode ( $D = 1 \text{ mm}$ ) was successively deposited under vacuum of  $5.0^{-4} \text{ Pa}$  and the silicon materials thus obtained was set onto a stainless (SUS) electrode (Figure S6).



**Figure S6.** Structure of diode circuits.

[1] Huang, Q.; Larock, R. C. *J. Org. Chem.* **2003**, *68*, 980-988.

[2] Egbe, D. A. M.; Roll, C. P.; Birckner, E.; Grummt, U. W.; Stockmann, R.; Klemm, E. *Macromolecules* **2002**, *35*, 3825-3837.