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Preparation of 1,3-Diphenylselenopheno-tetraazaporphyrinato Ruthenium(II) Bis(4-methylpyridine) by the Reaction of 3,4-Dicyano-2,5-diphenylselenophene and Phthalonitrile: Its Optical and Electrochemical Properties

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ABSTRACT: *2,5-Diphenylselenophene (**2a**) was treated with bromine and then copper(I) cyanide to produce 3,4-dicyano-2,5-diphenylselenophene (**4**). Compound **4** was mixed with phthalonitrile, and the mixture was reacted with ruthenium(III) trichloride and 4-methylpyridine in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in refluxed 2-ethoxyethanol to give 1,3-diphenylselenophenotetraazaporphyrinato ruthenium(II) bis(4-methylpyridine) (**6**). The structure of **6** was determined by ^1H NMR and fast atom bombardment mass spectrometry (FABMS). In the ^1H NMR spectrum, the signals of 4-methylpyridine coordinating to the central ruthenium atom were observed at a higher magnetic field than those of free 4-methylpyridine itself but at a lower magnetic field than those of phthaocyaninato ruthenium(II) bis(4-methylpyridine) (**7**). The ^{77}Se NMR spectrum of **6** showed one singlet peak at $\delta = 759.5$ ppm, which is a lower magnetic field than those of **2a** and **4**. The Q band absorption of **6** ($\lambda_{max} = 660$ nm) lies at a longer wavelength than does that of **7**. Oxidation and reduction potentials of **6** were measured with cyclic voltammetry using $Ag/AgNO_3$ as a reference electrode.* © 2014 Wiley Periodicals, Inc. Heteroatom Chem. 25:428–433, 2014; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21178

INTRODUCTION

Phthalocyanines have been utilized as dyes, pigments, and catalysts for desulfurization of petroleum and posses potential applications in fields of solar cells, organic semiconductors, photodynamic therapy for cancer, and so on [1–3]. As related compounds, tetraazaporphyrins (TAPs), fused with five- or six-membered heterocycles such as thiophene, thiadiazole, selenadiazole, pyridine, and pyradine, have been prepared and reported until now [4–6]. These compounds can be considered as isosteric structures of phthalocyanine. However, while TAPs bearing the pyridine, pyradine, thiadiazole, and selenadiazole rings are stable, the furan, pyrrole, and thiophene derivatives are unstable [4]. Although early attempts to prepare TAPs with four furans, pyrroles, and thiophenes had not given desired products, tetra(2,3-thieno)tetraazaporphyrins whose four thiophene units are linked at the 2,3-positions [2,3-TTTAP] (Fig. 1) were reported as stable derivatives [7].

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Dedicated to Professor Renji Okazaki on the occasion of his 77th birthday.

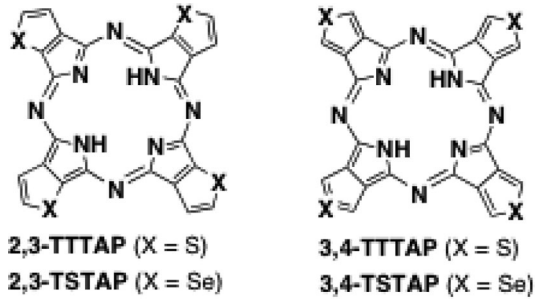
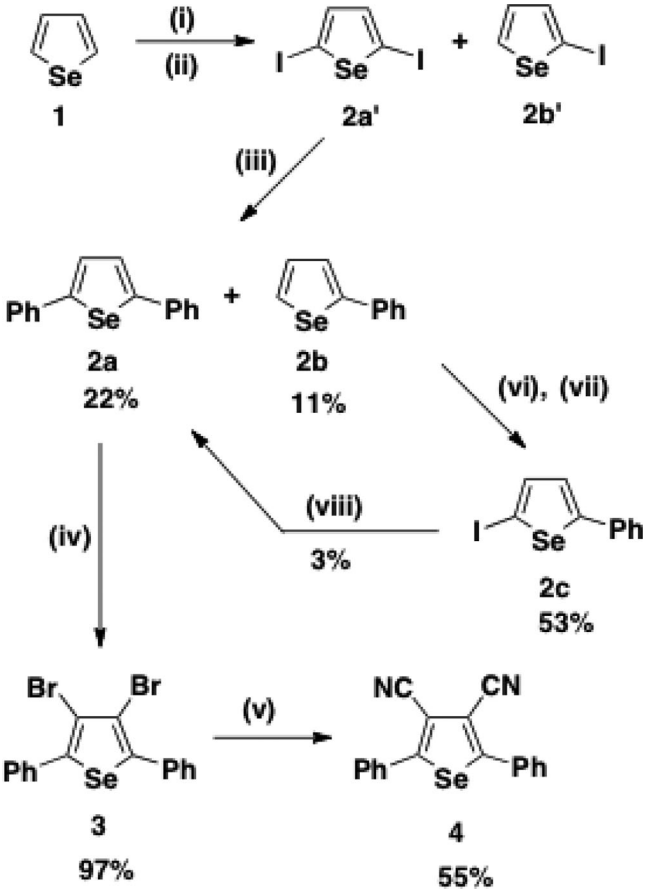


FIGURE 1 TAPs with four chalcogenophenes.

Another thiophene derivative, tetra(3,4-thieno)tetraazaporphyrin, is also acceptable. In this compound, four thiophene units are linked at the 3,4-positions [3,4-TTTAP]; therefore, it is required that one of the thiophene rings contains an unusual tetravalent sulfur atom (Fig. 1) [8, 9]. We recently reported the first structure determination of a ruthenium(II) complex of 3,4-TTTAP having eight phenyl groups on the thiophene rings and two 4-methylpyridines as axial ligands [3,4-TTTAP-Ph8] [8]. Phthalocyaninato ruthenium(II) complexes can link two axial coordinating groups and are stable. These ligands can be applied to estimation of the shielding effect of the TAP ring and can block the aggregation of the planar ring system. There are several reports about TAP derivatives with one thiophene ring linked at the 3,4-positions [10]. Recently, TAPs with four selenophene rings, tetra(2,3-selenopheno)tetraazaporphyrin [2,3-TSTAP] derivatives, which consist of several positional isomers, were first reported by Heeney and co-workers [11]. In contrast, to our knowledge, tetra(3,4-selenopheno)tetraazaporphyrin [3,4-TSTAP] has never been reported yet. To prepare 3,4-TSTAP, 3,4-dicyano-2,5-diphenylselenophene (**4**) was prepared from selenophene via four step reactions and tetramerization of **4** was attempted by a method reported previously [8]. On the other hand, if **4** and phthalonitrile are combined and cyclized, unsymmetrically substituted TAPs can be obtained in a statistical manner. This paper reports the preparation and optical and electrochemical properties of tetraazaporphyrinato ruthenium(II) bis(4-methylpyridine) with the 2,5-diphenylselenophene unit.

RESULTS AND DISCUSSION

A method for preparing 2,5-disubstituted selenophene was reported by Zeni and co-workers [12]. We prepared 2,5-diphenylselenophene (**2a**) with a slightly modified procedure of Zeni's



SCHEME 1 Preparation of 3,4-dicyano-2,5-diphenylthiophene (**4**): (i) *n*-BuLi, TMEDA, Et_2O, –78°C, 1 h; (ii) I_2, rt, 2 h; (iii) $PhB(OH)_2$, $(Ph_3P)_4Pd$, K_3PO_4, toluene, 105°C, 22 h; (iv) Br_2, CH_2Cl_2, 18 h; (v) CuCN/DMF, 150°C, 18 h; (vi) *n*-BuLi, TMEDA, Et_2O, –78°C, 1 h; (vii) I_2, rt, 2 h; (viii) $PhB(OH)_2$, $(AcO)_2Pd$, K_2CO_3, DME, 78°C, 4 h.

method. It was reported that the phenyl groups are effective to stabilize nonclassical thiophene, thieno[3,4-*c*]thiophene [13]. Therefore, we selected the phenyl group as substituents of 3,4-TSTAP. Initially, selenophene (**1**) was lithiated with *n*-butyl lithium in diethyl ether at –78°C in the presence of N,N,N′,N′-tetramethylethylenediamine (TMEDA) and then treated with iodine to produce 2,5-diiodolselenophene (**2a′**) and 2-iodolselenophene (**2b′**) (Scheme 1).

Since we could not separate **2a′** and **2b′** each other by column chromatography, a mixture of them was treated with phenylboronic acid in the presence of tetrakis(triphenylphosphine)-palladium in toluene to give 2,5-diphenylselenophene (**2a**) and 2-phenylselenophene (**2b**) in 22% and 11% yields, respectively. Compounds **2a** and **2b** could be isolated by silica gel column chromatography, and the yields were calculated based on the amount of **1**.

When di(acetoxy)palladium was used as a catalyst, the reaction gave a similar result. Compound **2a** was further treated with bromine in dichloromethane at room temperature for 18 h. The reaction proceeded without any additional catalyst and produced 3,4-dibromo-2,5-diphenylselenophene (**3**) in 97% yield. Finally, **3** was reacted with copper(I) cyanide in DMF at 150°C for 18 h and the reaction gave 3,4-dicyano-2,5-diphenylselenophene (**4**) in 55% yield. On the other hand, **2b** was treated with *n*-butyl lithium and then iodine to give 2-iodo-5-phenylselenophene (**2c**) in 53% yield. Compound **2c** was treated with phenylboronic acid in the presence of di(acetoxy)palladium in 1,2-dimethoxiethane (DME) but the process produced **2a** in low yield.

The preparation of 3,4-TSTAP fused with four 2,5-diphenylselenophene units was attempted by the procedure reported previously [8]. Compound **4** was reacted with ruthenium(III) trichloride and 4-methylpyridine in the presence of DBU in 2-ethoxyethanol at reflux temperature for 48 h. However, we could not obtain 3,4-TSTAP by the reaction. It is expected that if the four selenophenes react at the 3,4-dicyano groups and construct the TAP skeleton, 3,4-TSTAP produced by this treatment has to contain an unusual tetravalent selenium atom in one selenophene ring (Fig. 1). The tetravalent selenium atom is a bonding system similar to the well-known nonclassical selenophene, selenolo[3,4-*c*]selenophene, which was reported to be extremely unstable [14]. Therefore, 3,4-TSTAP would be more unstable than the 2,3-TSTAP derivative reported by Heeney and co-workers [11]. Instead of 3,4-TSTAP, we tried to prepare TAP fused with the several 2,5-diphenylselenophene units; hence, **4** was mixed with phthalonitrile **5** in a 3:1 ratio and the mixture was reacted with ruthenium(III) trichloride, 4-methylpyridine, and DBU in refluxed 2-ethoxyethanol (Scheme 2). The reaction mixture was separated by column chromatography to produce unsymmetrical TAP complex **6** with the 2,5-diphenylselenophene unit and phthalocyanine complex **7** in 1% and 10% yields, respectively. In the reaction, two blue-green colored compounds were obtained together with **6** and **7**. These compounds showed the molecular ion peak at 1212.1 (M^+) by fast atom bombardment mass spectrometry (FABMS) and the Soret and Q band absorption in UV–vis spectra (Fig. 2), suggesting that the two compounds are *adjacent* and *opposite* TAP isomers with two selenophene rings. However, we could not observe clear spectra of these compounds by ^{1}H NMR. In addition, a TAP isomer with three selenophene rings was not detected. When **4** and **5** were mixed in a 1:5 ratio, **6** was obtained in 3% yield. The structure of **6**

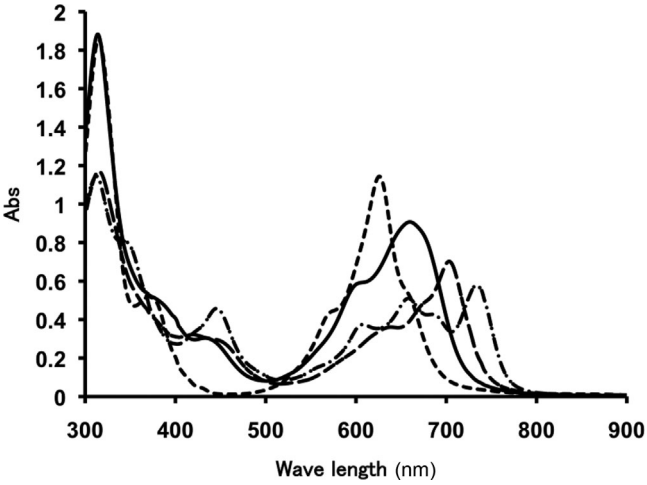


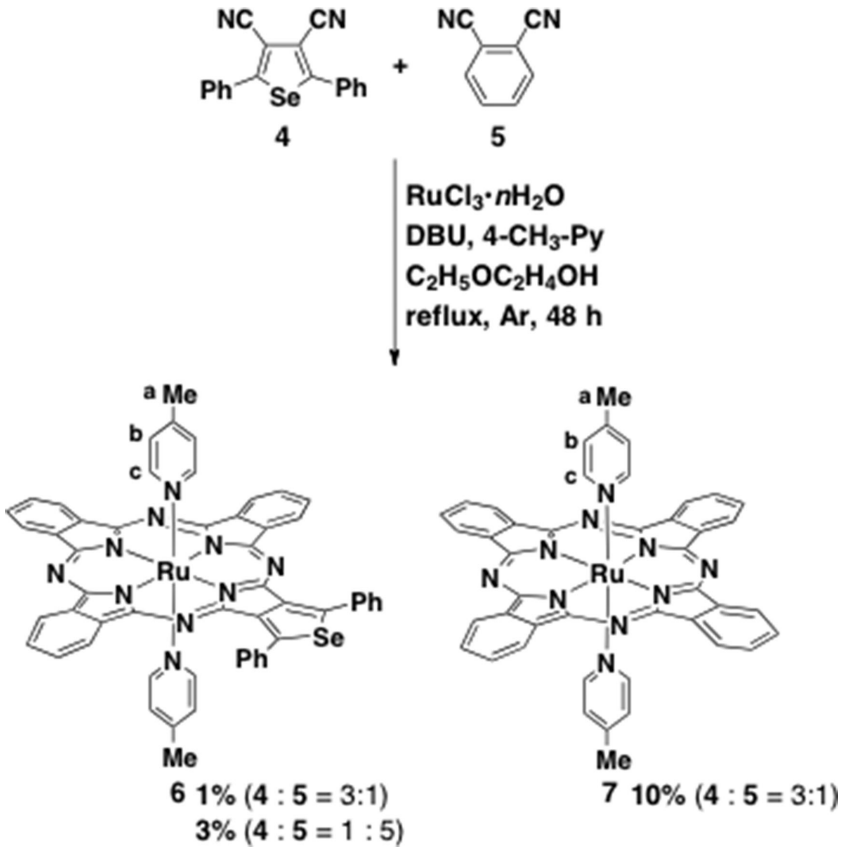
FIGURE 2 UV–vis spectra ($CHCl_3$); solid line: **6**; dotted line: **7**; dashed line and dashed and dotted line: the *adjacent* and *opposite* TAP isomers with two selenophene rings.

TABLE 1 ^{1}H NMR Chemical Shifts of 4-Methylpyridine in the Free and the Coordinated State

	Chemical Shift δ (ppm)		
Compound	*Ha*	*Hb*	*Hc*
3,4-TTTAP-Ph8	1.37	5.46	3.14
6	1.20	5.13	2.49
7	1.15	5.03	2.34
4-Methylpyridine	2.39	7.08	8.45

was determined by ^{1}H NMR and FABMS. FABMS of **6** showed the molecular ion peak at m/z = 1006.1 [M^+] when *m*-nitrobenzyl alcohol was used as a matrix.

In the ^{1}H NMR spectrum of **6**, the protons of the two phenyl groups and peripheral aromatic rings were observed together with those of 4-methyl pyridines as axial ligands, which showed **6** has the unsymmetrical structure. The signals of 4-methylpyridine were observed at δ = 1.20, 2.49, and 5.13 ppm (Table 1). Since the signals of free 4-methylpyridine itself are observed at δ = 2.39, 7.08, and 8.45 ppm, the signals of 4-methylpyridine of **6** are strongly shielded by the magnetic field generated by the TAP ring. There is a report with respect to identification of ^{1}H NMR chemical shifts of four-substituted pyridines in the phthalocyaninato ruthenium(II) complexes [15]. The signals of 4-methylpyridine of **6** were identified based on the report. As reported in our previous paper, **7** and 3,4-TTTAP-Ph8 showed the signals of 4-methylpyridine at δ = 1.15, 2.34, and 5.03 ppm and δ = 1.37, 3.14, and 5.46 ppm, respectively. The ^{1}H NMR chemical shifts of 4-methylpyridine of



SCHEME 2 Preparation of TAP (**6**).

6 appear at a lower magnetic field than do those of **7** and at a higher magnetic field than do those of 3,4-TTTAP-Ph8. The ^{77}Se NMR spectrum of **6** showed one singlet peak at $\delta = 759.5$ ppm, which is a lower magnetic field than those of **2a** ($\delta = 575.2$ ppm), **3** ($\delta = 683.2$ ppm), **4** ($\delta = 675.7$ ppm), and 2,3-TSTAP derivatives ($\delta = 555$ and 558 ppm) [11].

In the UV–vis spectrum measured in chloroform, the Q-band absorption of **6** was observed as a broadened peak at 660 nm ($\log \varepsilon = 5.05$) (Fig. 2). While the absorption of **6** is a lower energy region than that of **7** (626 nm), it is a higher energy area than those of Heeneys' 2,3-TSTAP (701 nm) and 3,4-TTTAP-Ph8 (758 nm). The Q band absorption of the *adjacent and opposite* TAP isomers with two selenophene rings appeared at a lower energy region than did those of **6** and **7**. It is expected that the increase in the number of the selenophene units can heighten the probability of the appearance of the unusual tetravalent selenium atom, which perturbs the π-conjugation system of the macrocycle and influences the Q band absorption. To determine the electrochemical property of **6**, oxidation and reduction potentials were measured by cyclic voltammetry using $Ag/AgNO_3$ as a reference electrode (solvent: CH_2Cl_2, scan rate: 200 mV s^{-1}). In the voltammogram, two reversible oxidation potentials ($E_{1/2} = 0.25$ and 0.92 V) and one irreversible ($E_p = -1.24$ V) and one reversible reduction potentials ($E_{1/2} = -1.64$ V) were observed. It appeared that the first oxidation potential of **6** is slightly lower than that of **7** ($E_{1/2} = 0.37$ V), and the first reduction potential of **6** is higher than that of **7** (–1.66 V).

CONCLUSIONS

The reaction of 3,4-dicyano-2,5-diphenylselenophene (**4**) with phthalonitrile, ruthenium(III) trichloride, and 4-methylpyridine produced TAP **6** with one selenophene ring. The ^{1}H NMR chemical shifts of 4-methylpyridine of **6**, **7**, and 3,4-TTTAP-Ph8 suggest that the diatropic ring current of the TAP ring is weaker in compound **6** than in phthalocyanine **7** but stronger than in 3,4-TTTAP-Ph8. The ^{77}Se NMR signal of **6** was observed at a lower magnetic field than those of **2a**, **3**, **4**, and Heeneys' 2,3-TSTAP, which shows that the selenium atom in the selenophene ring of **6** is strongly deshielded by the

magnetic field generated by the TAP ring. The Q band absorption of **6** is longer wavelength than that of **7** but shorter than those of the 2,3-TSTAP derivatives and 3,4-TTTAP-Ph8.

EXPERIMENTAL

General

NMR spectra were measured with a Bruker Avance 500 III spectrometer. Mass spectra were obtained using a JEOL JMS-700 mass spectrometer. UV–vis spectra were recorded with a Jasco Ubest V-570 spectrophotometer. For IR measurement, a Jasco FT/IR-4200 spectrometer was employed. A Hokuto Denko Co. model HAB-151 apparatus was used to measure oxidation potentials. Bio-beads SX-1 for column chromatography was purchased from Nippon Bio-Rad Laboratories.

Oxidation Potentials

All measurements were performed by cyclic voltammetry, using Ag/0.01 M $AgNO_3$ as a reference electrode, a Pt wire as a counterelectrode, and glassy carbon as a working electrode. A solution of 0.1 M n-Bu_4NClO_4 in CH_2Cl_2 was used as an electrolyte. A scan rate of 200 mV s^{-1} was used for the measurement.

*2,5-Diiodoselenophene (**1**) and 2,5-Diphenylselenophene (**2**)*

2,5-Diiodoselenophene (**1**) and 2,5-Diphenylselenophene (**2**) were prepared by the methods reported previously [12].

*2,5-Diphenyl-3,4-dibromoselenophene (**3**)*

To a solution of **2a** (1.500 g, 5.3 mmol) in CH_2Cl_2 (40 mL), Br_2 (0.6 mL, 11 mmol) was added from A syringe. The solution was stirred at room temperature for 18 h. The aqueous Na_2SO_3 solution was added, and the product was extracted with CH_2Cl_2. The extract was dried over $MgSO_4$, and the solvent was evaporated. The product was purified with column chromatography (Wakogel C-300HG, n-hexane) to give **3** in 97% yield (2.2441 g): Yellow crystals; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (t, 1H, J = 7.5 Hz, p-Ph), 7.45 (t, 2H, J = 7.5 Hz, m-Ph), 7.61 (d, 2H, J = 7.5 Hz, o-Ph); ^{13}C NMR (126 MHz, $CDCl_3$) δ 112.3, 128.4, 128.6, 129.1, 134.7, 142.9; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 683.2; HR-MS Calcd for $C_{16}H_{10}{}^{79}Br_2{}^{80}Se$ = 439.8314. Found (m/z) = 439.8304 (M^+).

*2,5-Diphenyl-3,4-dicyanoselenophene (**4**)*

Compound **3** (1.915 g, 4.0 mmol) and CuCN (1.788 g, 20 mmol) were placed in a glass reactor under Ar. DMF (15 mL) was added and the solution was stirred at 150°C for 18 h. After the reactor was cooled, aqueous $FeCl_3 \cdot 6H_2O$ (5.773 g, 21 mmol) solution (40 mL) was added to the reaction mixture. The solution was stirred at 80°C for 15 min. After cooling the reactor, the reaction mixture was filtered and the residue was dissolved with $CHCl_3$. The $CHCl_3$ solution was dried over $MgSO_4$, and the solvent was evaporated. The product was purified by column chromatography (Wakogel C-300HG, $CHCl_3$) to produce **4** in 55% yield (805.1 mg): Colorless powder; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50–7.54 (m, 6H, Ar-H), 7.71–7.76 (m, 4H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 110.2, 114.1, 128.0, 129.6, 130.9, 131.8, 161.0; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 675.7; IR (KBr) 2224 cm^{-1} (CN); HR-MS Calcd for $C_{18}H_{10}N_2{}^{80}Se$ = 334.0009. Found (m/z) = 334.0014 (M^+).

*2,5-Diphenylselenotetraazaporphyrinato Ruthenium(II) bis(4-Methylpyridine) (**6**)*

Compound **4** (337.5 mg, 1.0 mmol), phthalonitrile (641.1 mg, 5.0 mmol), and $RuCl_3 \cdot nH_2O$ (396.4 mg, 1.5 mmol) were placed in a reactor, and 2-ethoxyethanol (12 mL), DBU (1.8 mL), and 4-methylpyridine (2.2 mL) were added under Ar. The solution was stirred at 135°C for 48 h. After the reactor was cooled, aqueous MeOH was added and the precipitate was filtered. The residue was dissolved in chloroform, and the solution was dried over $MgSO_4$. After the solvent was evaporated, the product was separated by column chromatography (alumina, $CHCl_3$). The product was purified by column chromatography (Wako-gel C-300HG, n-hexane/$CHCl_3$ and Bio-beads SX-1, $CHCl_3$) to produce **6** in 3% (26.4 mg); **6**; green crystals; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20 (s, 6H, –CH_3), 2.32 (d, 4H, J = 6.8 Hz, Py-H), 5.13 (d, 4H, J = 6.8 Hz, Py-H), 7.65 (t, 2H, J = 7.3 Hz, Ar-H), 7.80–7.84 (m, 8H, Ar-H), 7.86–7.91 (m, 2H, Ar-H), 8.85 (d, 2H, Ar-H), 9.01 (d, 4H, J = 7.8 Hz, Ar-H), 9.13 (d, 4H, Ar-H); ^{77}Se-NMR (95 MHz, $CDCl_3$) δ 759.5; FAB-MS (m/s) 1006.1 (M^+).

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