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Preparation and Characterization of Nonclassical Tetraazaporphyrin, Bis(4-methylpyridine)[1,3,5,7,9,11,13,15-octaphenyltetra(3,4-thieno)tetraazaporphyrinato]ruthenium(II)

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The tetramerization reaction of 2,5-diphenyl-3,4-dicyanothiophene (**2**) proceeded on treatment with ruthenium(III) trichloride, DBU, and 4-methylpyridine in 2-ethoxyethanol at 135 °C to give bis(4-methylpyridine)[1,3,5,7,9,11,13,15-octaphenyltetra(3,4-thieno)tetraazaporphyrinato]ruthenium(II) (**3**). Because the structure of this product cannot be represented by a usual bonding system, this molecule has to contain an unusual tetravalent sulfur atom in one of the four thiophene rings. In the ^{1}H NMR spectrum of the product, signals from 4-methylpyridine coordinated to the central ruthenium atom showed an upfield shift. The structure of **3** was determined by X-ray crystallography, which revealed that **3** has four thiophene units linked at their 3,4-positions to the tetraazaporphyrin scaffold. Four pairs of phenyl groups are in close proximity and are sterically congested, which causes the four thiophene rings to deviate from the mean plane of the central four pyrrole nitrogen atoms. The UV/Vis spectrum of **3** shows a Q-band absorption at λ_{max} = 758 nm. In the MCD spectrum of **3**, dispersion-type absorptions (Faraday *A* term) are observed at 746 and 776 nm. The MCD spectra suggest that the two LUMOs of **3** could be degenerate even though its structure deviates from D_{4h} symmetry. The electrochemical properties of **3** were examined by cyclic voltammetry with $Ag/AgNO_3$ as the reference electrode. The optimized structure and the NMR shielding constants of a simplified model molecule were calculated by using density functional theory.

Introduction

Tetraazaporphyrins and related compounds have actual and potential applications in the fields of sensors, catalysts, field-effect transistors, dye-sensitized solar cells, photodynamic therapy for cancer, among others .[1,2] The characteristics of these compounds can be adjusted by introducing several heteroatoms and substituents,[3] linking axial ligands to the central metal atom,[4] and connecting them to other dye components.[5] The π-conjugation system of these molecules has also been extended.[6,7] In a related study, we recently reported the preparation, structural determination, and optical and electrochemical properties of octaethyloctakis(benzylthio)phthalocyanine and octaoctyltetrakis(trithiolo)phthalocyanine and their derivatives.[8]

On the other hand, it is known that tetraazaporphyrins fused to four five-membered heterocycles such as furans, pyrroles, and thiophenes are extremely unstable, although these compounds can be considered as isosteric structures of phthalocyanine.[9] Despite many early attempts to prepare tetraazaporphyrins with four five-membered heterocycles, up to now only tetra(2,3-thieno)tetraazaporphyrin (2,3-TTTAP) bearing four thiophene units linked at their 2,3-positions and several related compounds have been reported as stable derivatives.[10,11] However, if the four five-membered heterocycles are linked at their 3,4-positions to the tetraazaporphyrin skeleton, their structures cannot be represented by a usual bonding system. It is expected that tetra(3,4-thieno)tetraazaporphyrin (3,4-TTTAP) contains an unusual tetravalent sulfur atom in one thiophene ring[12] and hence this molecule is more stable than the corresponding furan and pyrrole derivatives. This tetravalent sulfur atom has a similar bonding arrangement to the well-known nonclassical thiophene, thieno[3,4-*c*]thiophene (3,4-TT; Figure 1).[13]

Although the synthesis of 3,4-TTTAP was described in 1995, no characterization data were reported in the literature.[14] Furthermore, Cook and Jafari-Fini reported that 3,4-TTTAP with eight octyl groups could not be obtained at all by the reaction of 2,5-dioctyl-3,4-dicyanothiophene with lithium alkoxide.[11b] In addition, it is known that

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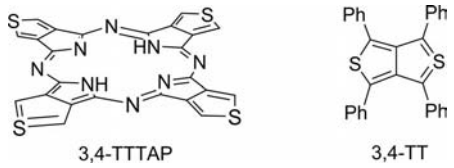


Figure 1. Structures of tetra(3,4-thieno)tetraazaporphyrin and tetraphenylthieno[3,4-*c*]thiophene.

thieno[3,4-*c*]thiophene can be stabilized by introducing several kinds of substituents. According to Cava,[13a] Yoneda,[13c] and Nakayama[13d] and their co-workers, phenyl, alkylthio, and thienyl groups are effective in stabilizing the thieno[3,4-*c*]thiophene scaffold and they isolated the respective molecules as single crystals and determined their structures by X-ray crystallography. Therefore the preparation of a 3,4-TTTAP derivative and a study of its structure and optical and electrochemical properties could be of considerable interest.

It was planned to introduce eight phenyl groups onto the four thiophene rings in an attempt to stabilize and isolate 3,4-TTTAP. Thus, 2,5-diphenyl-3,4-dicyanothiophene (**2**) was prepared and its tetramerization examined. In addition, we selected ruthenium as the central metal atom of 3,4-TTTAP and chose 4-methylpyridine to be the axial ligands. This paper reports the preparation, structural determination, and optical and electrochemical properties of the unprecedented 3,4-TTTAP complex, the tetrathieno-fused bis(4-methylpyridine)[1,3,5,7,9,11,13,15-octaphenyltetraazaporphyrinato]ruthenium(II) **3** with a nonclassical bonding system.

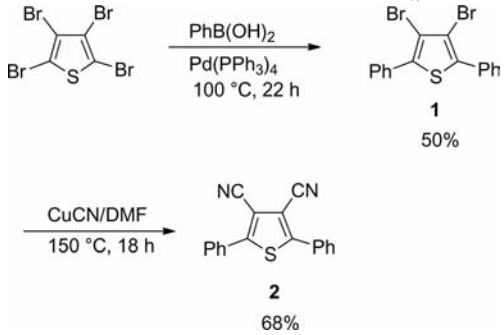
Results and Discussion

Preparation and Structural Determination of 3

To prepare **2** as a precursor of 3,4-TTTAP, 2,5-diphenyl-3,4-dibromothiophene (**1**) was synthesized in 50% yield from 2,3,4,5-tetrabromothiophene and phenylboronic acid by the Suzuki–Miyaura coupling reaction (Scheme 1).[15] Compound **1** was then treated with copper(I) cyanide in DMF at 150 °C for 18 h to give **2** in 68% yield.[16] In addition, 3,4-dicyanothiophene,[17] 2,3-dicyanothiophene,[11a] and 2,5-dimethyl-3,4-dicyanothiophene[11a] were prepared in yields of 28, 20, and 62%, respectively, from the corresponding dibromothiophene by similar procedures.

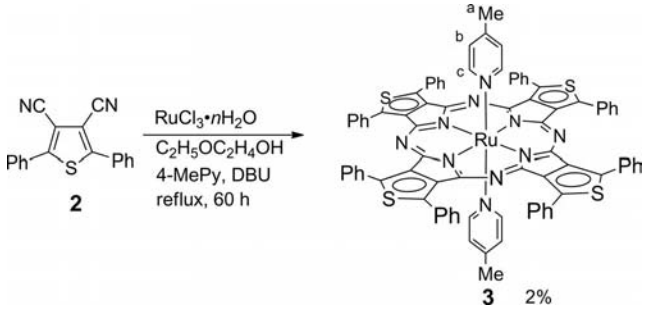
The tetramerization of **2** was attempted with lithium alkoxide in *n*-hexanol following a commonly used procedure for the construction of sterically congested phthalocyanines. Although the solution gradually turned dark green as expected, we could not obtain the desired product by this process. Therefore we tried to introduce a ruthenium atom into the central hole of 3,4-TTTAP and two 4-methylpyridines as axial ligands.

There are many reports for the preparation of the skeletal framework of bis(4-methylpyridine)phthalocyaninatoruthenium(II) (**5**).[18,19] We used a slightly modified procedure. A solution of ruthenium(III) trichloride in 2-ethoxyethanol



Scheme 1. Preparation of 2,5-diphenyl-3,4-dicyanothiophene (**2**).

was heated at reflux until the mixture turned dark blue. Compound **2** was then added along with DBU in the presence of 4-methylpyridine and hydroquinone and the mixture was heated at reflux for 60 h. Then work-up and purification by column chromatography using activated alumina and bio-beads were performed and **3** was obtained as a dark-green solid in 2% yield (Scheme 2). We next attempted to prepare unsubstituted and octamethylated 3,4-TTTAP from 3,4-dicyanothiophene and 2,5-dimethyl-3,4-dicyanothiophene, respectively. However, we were not able to obtain the corresponding tetraazaporphyrins in either case.



Scheme 2. Preparation of **3** by treatment of **2** with $RuCl_3 \cdot nH_2O$, 4-methylpyridine, and DBU in ethoxyethanol at reflux for 60 h.

To determine the structure of **3**, FAB-MS was employed with *m*-nitrobenzyl alcohol as the matrix, which showed the molecular ion peak at m/z = 1432.2 ($[M]^+$). The two axial ligands maintained their coordination to the ruthenium atom under the ionization conditions, which is in contrast to the phthalocyanine derivatives reported previously.[19e] In the ^{1}H NMR spectrum measured at 25 °C in [D]chloroform, the phenyl groups were observed as two broad signals arising from the *ortho* protons and the *meta* and *para* protons with a 2:3 integral ratio, which indicates that free rotation of the phenyl groups was obstructed by steric hindrance from the neighboring phenyl groups. The signals for 4-methylpyridine coordinated to the central ruthenium atom are observed at δ = 1.37, 3.14, and 5.46 ppm (Table 1), which are at a higher magnetic field than those of uncoordinated 4-methylpyridine (δ = 2.39, 8.45, and 7.08 ppm, respectively). This indicates that 4-methylpyridine linked to the central ruthenium atom is strongly affected by the magnetic shielding of the tetraazaporphyrin ring. The ^{1}H NMR

chemical shifts of 4-substituted pyridines coordinated to phthalocyaninatoruthenium(II) complexes have been reported by McDonagh and co-workers.[19e]

Table 1. ^{1}H NMR chemical shifts of the 4-methylpyridines in **3**, **4**, and **5**.

Compounds	Chemical shifts [ppm]		
	a	b	c
3	1.37	5.46	3.14
4	1.26	5.21	2.71
5	1.15	5.02	2.33
4-Methylpyridine	2.39	7.08	8.45

As a reference compound, the tetrathieno-fused bis(4-methylpyridine)tetraazaporphyrinatoruthenium(II) **4** was prepared from 2,3-dicyanothiophene in an extremely low yield. Compound **4** is a mixture of several positional isomers of thiophene rings, as shown in Figure 2. Bis(4-methylpyridine)phthalocyaninatoruthenium(II) (**5**) was also synthesized according to the method reported by Sun and co-workers.[19d] In the ^{1}H NMR spectrum of **5**, the signals for 4-methylpyridine were observed at δ = 1.15, 2.33, and 5.02 ppm (Table 1). Because the mixture **4** shows ^{1}H NMR signals at δ = 1.26, 2.71, and 5.21 ppm, the shielding effect of the isomers should be similar. Interestingly, the upfield shift of the resonances of 4-methylpyridine decrease in the order **5** > **4** > **3**. It seems that the magnetic shielding effect in **3** is weaker than in **4** and **5**, which suggests that the large π-electron ring system of tetraazaporphyrin is disturbed in **3** compared with in **4** and **5** by the steric repulsion of the eight phenyl groups and/or the unusual bonding system in the one thiophene ring.

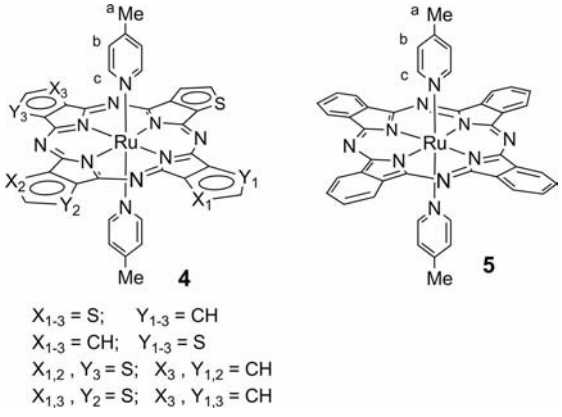


Figure 2. Compounds **4** and **5** were prepared from 2,3-dicyanothiophene and phthalonitrile, respectively.

X-ray Crystallographic Analysis

Recrystallization of **3** from chloroform and methanol produced small single crystals. X-ray crystallographic analysis showed that **3** has a monoclinic form and the space group is $P2_1/n$ (#14) with parameters a = 11.5476 (8), b = 18.4177 (16), c = 16.9028 (15) Å, and β = 92.878 (3)°. It appears that the unit cell consists of two molecules of **3**. The final goodness of fit and the R factor are GOF = 1.070 and R_1 = 0.0920. As described by Sun and co-workers, the scaffold of the phthalocyanine complex **5** lies in a plane except for the two 4-methylpyridine ligands.[19d] The ORTEP drawing in Figure 3a reveals that **3** contains the tetraazaporphyrin skeleton with four thiophene units fused at the 3,4-positions to the macrocycle; the central ruthenium(II) atom is hexa-coordinated. Four pairs of phenyl groups are in close proximity and should exert strong steric repulsion between them. Apparently, the scaffold of the 3,4-TTTAP in **3** deviates from the mean plane of the central four pyrrole nitrogen atoms (4N plane) and the complex has a C_2 axis of symmetry through the N_1 and N_1* atoms (Figure 3, b). Thus, the thiophenes in the molecule have two types of structures. The pairs of phenyl groups that are close are sterically congested and directed above and below the 4N plane. The sulfur atoms of the S_1 and S_1* thiophenes are 0.691 Å from the 4N plane. In addition, the distortion forces the S_2 and S_2* thiophene rings to twist relative to the 4N plane. On the other hand, although the thiophene rings are clearly deformed by the steric repulsion between the eight phenyl groups, the deviation of the inner tetraazaporphyrin skeleton from the 4N plane is not large.

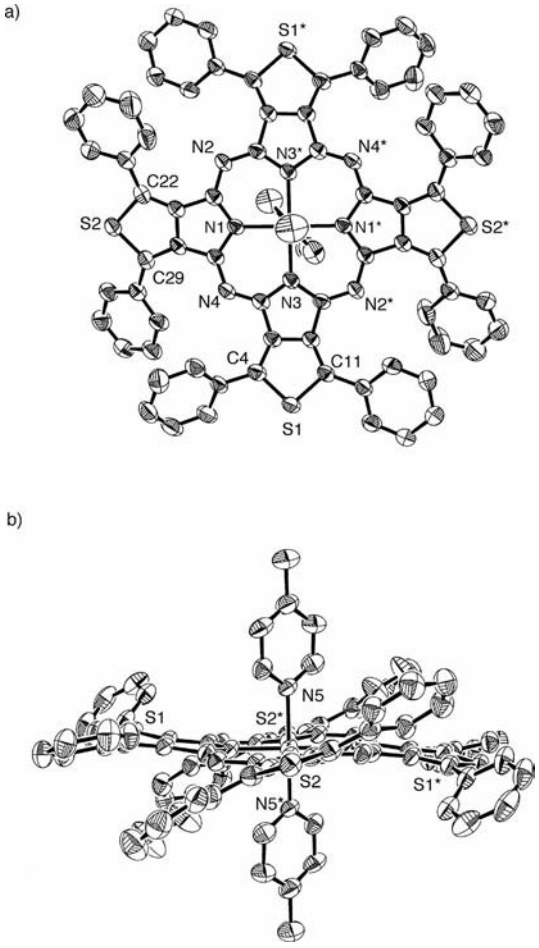


Figure 3. ORTEP drawing of **3**: a) top view from the axial direction and b) side view from the S2 atom. For clarity, all hydrogen atoms and chloroform have been omitted.

It has been reported that octaphenylated phthalocyanines[20a–20c] and tetraphenylporphyrins with a 20π electron system[20d] are highly deformed and their structures are described as saddle-shaped. However, although **3** has a distorted structure, the skeleton of **3** is not saddle-shaped. The S_1 atom is above the 4N plane and the S_1* atom is below it. Thus, **3** has a chair-like form. The observed maximum deviation of **3** (0.691 Å) is smaller than that of deformed phthalocyanines (ca. 1.03 Å)[14] and highly disordered porphyrins (ca. 0.7–1.4 Å).[21] The lengths of the Ru–N bonds in **3** are 2.010(5) (Ru–N1, eq), 2.015(6) (Ru–N3, eq), and 2.095 (6) Å (Ru–N5, ax). The axial Ru–N bond of **3** is slightly shorter than the axial Ru–N bonds of **5** (2.101 Å).[19d] The S–C bond lengths of **3** are 1.745(6) (S1–C4), 1.743(7) (S1–C11), 1.759(7) (S2–C22), and 1.740(7) Å (S2–C29) (see the Supporting Information), which are longer than those of tetraphenylthieno[3,4-*c*]thiophene (1.706 Å)[8b] and thiophene (1.714 Å).[22] These results suggest that the four sulfur atoms of the thiophene rings of **3** do not strongly interact with the π-conjugation system of tetraazaporphyrin.

Optical and Electrochemical Properties

The UV/Vis absorption and magnetic circular dichroism (MCD) spectra of **3** were recorded in chloroform and are shown in Figure 4. The UV/Vis spectrum shows the Q-band absorption at 758 nm. Compounds **4** and **5** show Soret band absorptions at 313 and 315 nm and Q-band absorptions at 608 and 626 nm, respectively (see Figure 5 and the Supporting Information). The Q-band absorption of **3** is observed at a longer wavelength than those of **4** and **5**. It has been reported that the Q-band absorptions of phthalocyanines with substituents at the α positions are at longer wavelengths than those of unsubstituted phthalocyanines or phthalocyanines with substituents at the β positions.[23] The phenyl groups of **3** could affect the Q-band absorption similarly to the α substituents of phthalocyanine. In the MCD spectrum of **4**, dispersion-type absorptions (Faraday *A* term) are observed at 602 and 613 nm for the Q-band absorption and at 312 and 339 nm for the Soret band absorption, which essentially originate from the electron transition from the HOMO and next-HOMO to the degenerate two LUMOs. Compound **5** shows dispersion-type MCD absorptions (Faraday *A* term) at 610 and 634 nm for the Q-band absorption and at 307 and 336 nm for the Soret band absorption, which suggests that the structure of **5** has D_{4h} symmetry and the two LUMOs are degenerate. The MCD curve corresponding to the Q-band absorption of **3** consists of Faraday *A*-term-like dispersed absorptions at 746 and 776 nm (Figure 4). This could indicate that the two LUMOs

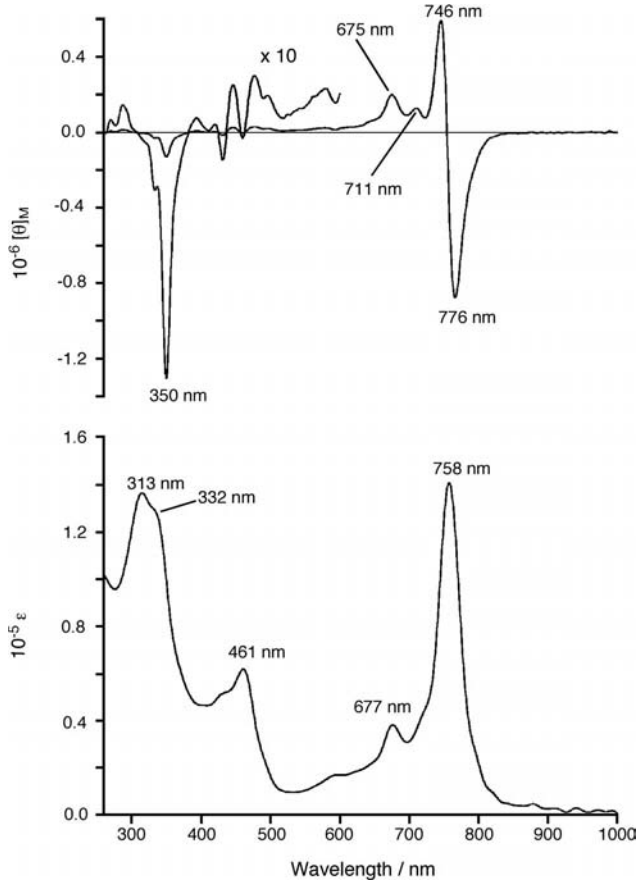


Figure 4. UV/Vis absorption and MCD spectra of **3** recorded in chloroform.

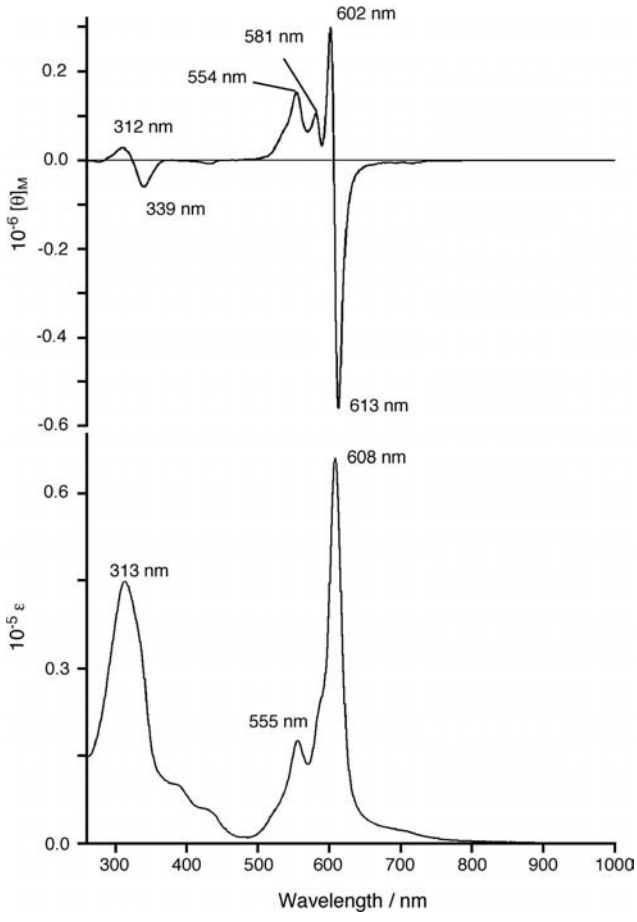


Figure 5. UV/Vis absorption and MCD spectra of **4** recorded in chloroform.

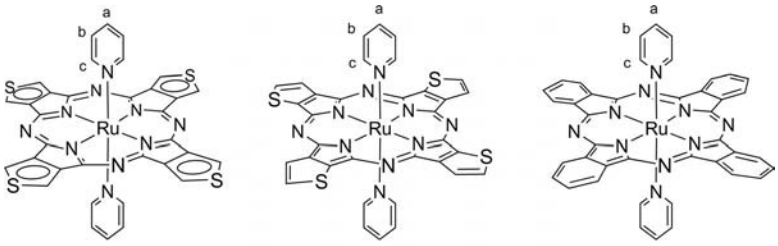


Figure 6. Structures of **3A**, **4A**, and **5A**.

almost retain their degeneracy although the structure of **3** deviates from D_{4h} symmetry. It is unclear why **3** does not show a dispersion-type absorption for the Soret band absorption.

The redox potentials of **3** and **5** were measured by cyclic voltammetry using $Ag/AgNO_3$ as a reference electrode (solvent: CH_2Cl_2). The redox potential of the ferrocene/ferrocenium couple was observed at $E_{1/2}$ = 0.09 V without correction using this apparatus. The voltammogram of **3** shows two reversible couples ($E_{1/2}$ = 0.29 and 0.50 V) for the oxidation potentials and one irreversible peak (E_p = –1.35 V) for the reduction potential (scan rate: 200 mV/s). In contrast, **5** shows one reversible oxidation potential ($E_{1/2}$ = 0.36 V) and one reversible reduction potential ($E_{1/2}$ = –1.67 V; scan rate: 100 mV/s). It seems that the four thiophene rings cause the reduction potentials of **3** to shift to the anodic side compared with **5** whereas they cause the oxidation potential to shift to the cathodic side.

Theoretical Study

To obtain further information about 3,4-TTTAP, the optimized structures and the NMR shielding constants of simplified model compounds **3A**, **4A**, and **5A** were calculated by using density functional theory (DFT; Figure 6). To simplify the calculations, all the methyl groups of **3**, **4**, and **5** and the eight phenyl groups of **3** were omitted. Because **4** is a mixture of several isomers, optimization was performed for one of them. The structures of these compounds were optimized using the Gaussian 03 program at the B3LYP/LANL2DZ level for Ru and at the B3LYP/6-31G(d,p) level for C, H, N, and S, which produced a completely planar form for each tetraazaporphyrin skeleton.[24] Because the optimized structure of **3A** has D_{4h} symmetry, the tetravalent sulfur atom of **3A** would be delocalized onto all the thiophene rings. Although the structure of **3** deviates from the 4N plane of tetraazaporphyrin, the 3,4-TTTAP of **3A** is planar. This could indicate that the deformation of **3** arises from the steric hindrance of the eight phenyl groups. The partial bond lengths of the optimized structures of **3A**, **4A**, and **5A** are presented in the Supporting Information. The lengths of the Ru–N bonds of **3A** are 2.036 (eq) and 2.156 Å (ax) and the S–C bond lengths of **3A** are 1.741 Å. The axial Ru–N bond of **3A** is slightly shorter than that of **5A** (2.157 Å), whereas the equatorial Ru–N bond of **3A** is longer than that of **5A** (2.022 Å).

The shielding constants of **3A**, **4A**, and **5A** were then calculated by using the same basis sets. The calculated ^{1}H NMR chemical shifts of pyridine protons are presented in Table 2. The chemical shifts were calculated to be at a higher magnetic field than the usual aromatic region. In addition, the results show that the signal for proton c is observed at a higher magnetic field than that of proton b. Apparently, the shift in the chemical shifts of pyridine to a higher magnetic field decreases in the order **5A** > **4A** > **3A**, which is a similar result to that observed for 4-methylpyridine in **3**, **4**, and **5**. In these model compounds, the magnetic shielding effect of **3A** is weaker than that of **4A** and **5A**. These results suggest that the π-electron ring system of tetraazaporphyrin in **3** is affected more by the unusual bonding system than by the steric repulsion of the eight phenyl groups, with the tetravalent sulfur atom delocalized on to all the thiophene rings.

Table 2. ^{1}H NMR chemical shifts of pyridine of **3A**, **4A**, and **5A**.

Compounds	Chemical shifts [ppm]		
	a	b	c
3A	6.062	5.352	2.941
4A	5.970	5.259	2.852
5A	5.841	5.099	2.577

Conclusions

We have prepared the novel and sterically congested complex **3** with a nonclassical thiophene unit. In the ^{1}H NMR spectra, the upfield shifts of the pyridine resonances decrease in the order **5** > **4** > **3**. The large π-electron ring system of tetraazaporphyrin is disturbed in **3** compared with those of **4** and **5**. X-ray crystallographic analysis clearly shows that **3** has four thiophene units annelated at the 3,4-positions. The thiophene rings in the molecule have two different types of structure as a result of the steric repulsion between four pairs of neighboring phenyl groups, which are in close proximity. In addition, the four sulfur atoms of the thiophene rings of **3** do not strongly interact with the π-conjugation system of the tetraazaporphyrin. Although the four thiophene rings are distorted by the steric repulsion between the eight phenyl groups, the deviation of the tetraazaporphyrin skeleton from planarity is not large. The MCD spectra of **3** shows a Faraday *A* term typical of the Q-band absorption, which suggests that the two

LUMOs of **3** could maintain their degenerate states although the molecular structure deviates from D_{4h} symmetry. Molecular orbital calculations using DFT showed that the tetravalent sulfur atom of **3A** would be delocalized on to all the thiophene rings, which suggests that the π-conjugation system of **3** is weakened more by the unusual bonding system than by the steric repulsion of the eight phenyl groups.

Experimental Section

General: NMR spectra were recorded with Bruker AVANCE 500, III, AC 400 spectrometers. Mass spectra were obtained by 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. A Rigaku Saturn 70 CCD detector system with VariMax Mo Optic at Kyoto University was used for X-ray crystallographic analysis. Magnetic circular dichroism (MCD) measurements were made at Tohoku University with a JASCO J-725 spectrodichrometer equipped with a JASCO electromagnet that produced magnetic fields of up to 1.09 T with parallel and antiparallel fields. Its magnetic magnitude is expressed in terms of molar ellipticity per tesla $[\theta]_M/10^4$ deg mol^{-1} dm^3 cm^{-1} T^{-1}. Bio-beads (SX-1) for column chromatography were purchased from Nippon Bio-Rad Laboratories.

Oxidation Potentials: All measurements were performed by cyclic voltammetry using $Ag/AgNO_3$ (0.01 mol dm^{-3}) as the reference electrode, glassy carbon as the working electrode, and Pt as the counter electrode (scan rate: 100 and 200 mV s^{-1}). A solution of nBu$_4$NClO$_4$ in CH_2Cl_2 (0.1 mol dm^{-3}) was used as electrolyte.

2,5-Diphenyl-3,4-dibromothiophene (1): Tetrabromothiophene (8.0 g, 20 mmol) was placed in a glass reactor and toluene (80 mL) and tetrakis(triphenylphosphane)palladium(0) (1.38 g, 1.19 mmol) were added. The solution was stirred at room temperature for 1 h and then phenylboronic acid (5.28 g, 40.8 mmol) and K_3PO_4 were added. Water (20 mL) was then added and the solution was heated at reflux for 22 h. Afterwards, the reactor was cooled, a large amount of toluene was added, and the solution was dried with $MgSO_4$. After filtration and evaporation, the pale-yellow solid obtained was purified by column chromatography (Wakogel C-300HG, hexane) to produce **1** in 50% yield (3.96 g). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.38–7.49 (m, 6 H, ArH), 7.63–7.86 (m, 4 H, ArH) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, TMS): δ = 112.3, 128.6, 128.8, 129.0, 132.8, 138.1 ppm. MS: m/z = 394.0 [M]$^+$.

2,5-Diphenyl-3,4-dicyanothiophene (2): Compound **1** (3.96 g, 10 mmol) and CuCN (7.18 g, 80 mmol) were placed in a glass reactor under Ar. DMF (20 mL) was added to the reactor and the solution was stirred at 150 °C for 18 h. Afterwards, the reactor was cooled, $FeCl_3 \cdot 6H_2O$ (21.6 g, 80 mmol) was added, and the solution was stirred at 80 °C for 10 min. After cooling, water was added to the reactor and the solution was filtered. The residue was washed with water. The product was extracted from the residue with $CHCl_3$ and the solvent was evaporated. The pale-yellow solid obtained was purified by column chromatography (Wakogel C-300HG, hexane/$CHCl_3$ = 1:1) to produce **2** as a colorless powder in 68% yield (1.97 g), m.p. 182–183 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.52–7.57 (m, 6 H, ArH), 7.77–7.82 (m, 4 H, ArH) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, TMS): δ = 108.5, 113.0, 127.7, 129.6, 129.7, 131.0, 153.2 ppm. IR (KBr): $\tilde{\nu}$ = 2223 (CN) cm^{-1}. HRMS (EI): calcd. for $C_{18}H_{10}N_2S$ [M]$^+$ 286.0565; found 286.0562.

Tetrathieno-Fused Bis(4-methylpyridine)[1,3,5,7,9,11,13,15-octaphenyltetraazaporphyrinato]ruthenium(II) Complex 3: $RuCl_3$ (52 mg, 0.25 mmol) was placed in a glass reactor under Ar. 2-Ethoxyethanol (5 mL) was added and the solution was heated at reflux until it turned blue. Compound **2** (288 mg, 1 mmol), hydroquinone (21 mg, 0.2 mmol), DBU (0.6 mL), and 4-methylpyridine (0.8 mL) were added and the solution was heated at reflux for 60 h. Afterwards, the reactor was cooled, MeOH and water were added, and the green precipitate was filtered and dried. The residue was dissolved in $CHCl_3$ and the solution was filtered. After evaporation of the solvent, the product was purified by column chromatography (activated alumina, $CHCl_3$, and then bio-beads, $CHCl_3$) to produce **3** as green crystals ($CHCl_3$/MeOH) in 2% yield (5.8 mg), m.p. >300 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.37 (s, 6 H, CH_3), 3.14 (d, $^4J_{H,H}$ = 6.4 Hz, 4 H, py-H), 5.46 (d, $^4J_{H,H}$ = 6.4 Hz, 4 H, py-H), 6.81–7.19 (m, 24 H, ArH), 7.97–8.64 (m, 16 H, ArH) ppm. MS (FAB): m/z = 1432.2 [M]$^+$.

Crystal data for **3**: $C_{86}H_{56}Cl_6N_{10}RuS_4$, F(000) = 1704, crystal size 0.12 mm × 0.05 mm × 0.01 mm, Mo-K_α (λ = 0.71073 Å), T = 103(2) K, monoclinic, $P2_1/n$ (#14), a = 11.5476(8), b = 18.4177(16), c = 16.9028(15) Å, β = 92.878(3)°, V = 3590.4(5) Å^3, Z = 2, D(calcd.) = 1.546 Mg/m^3, absorption coefficient = 0.616 mm^{-1}, θ = 2.19–25.50°, reflections collected = 30045, independent reflections = 6641 [R(int) = 0.0703], data/restraints/parameters = 6641/0/487, GOF on F^2 = 1.070, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0920, wR_2 = 0.2545, R indices (all data): R_1 = 0.1129, wR_2 = 0.2758, largest diff. peak and hole 1.246 and –1.577 e Å^{-3}.

CCDC-796148 contains the supplementary crystallographic data fort this paper. These data can be obtained free for charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3,4-Dicyanothiophene[17] and 3,4-Dicyano-2,5-dimethylthiophene:[11a] These compounds were prepared from the corresponding 3,4-dibromothiophene derivatives by procedures described in the literature.

2,3-Dicyanothiophene: 2,3-Dicyanothiophene was prepared from 2,3-dibromothiophene and CuCN by a procedure similar to that described above; yield 27%. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.40 (d, $^4J_{H,H}$ = 5.2 Hz, 1 H, Ar-H), 7.74 (d, $^4J_{H,H}$ = 5.2 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, TMS): δ = 110.8, 111.9, 118.2, 119.5, 129.8, 133.6 ppm.

Tetrathieno-Fused Bis(4-methylpyridine)tetraazaporphyrinatoruthenium(II) Complex 4: Complex **4** was prepared from 2,3-dicyanothiophene by a procedure similar to that described above; yield trace; m.p. >300 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.28 (s, 6 H, CH_3), 2.71 (d, $^4J_{H,H}$ = 4.9 Hz, 4 H, py-H), 5.21 (d, $^4J_{H,H}$ = 4.9 Hz, 4 H, py-H), 7.72–7.78 (m, 4 H, ArH), 8.15–8.20 (m, 4 H, ArH) ppm. MS (FAB): m/z = 824.03 [M]$^+$.

Computational Methods: All calculations were performed by using the Gaussian 03 program package.[24] The structure optimizations and shielding constant calculations for **3A**, **4A**, and **5A** were carried out by using DFT at the B3LYP/LANL2DZ level for Ru and at the B3LYP/6-31G(d,p) level for C, H, N, and S.

Supporting Information (see footnote on the first page of this article): Partial bond lengths and deviations of the thiophene rings of **3**, UV/Vis and MCD spectra of **5** recorded in chloroform, and partial bond lengths of the calculated structures of **3A**, **4A**, and **5A**.

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