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Preparation, Optical and Electrochemical Properties, and Molecular Orbital Calculations of Tetraazaporphyrinato Ruthenium (II) Bis(4-methylpyridine) Fused with One to Four Diphenylthiophene Units

Takeshi Kimura,^{a*} Naoko Murakami,^a Eiichi Suzuki,^b Taniyuki Furuyama,^c Tsukasa Nakahodo,^d Hisashi Fujihara,^d and Nagao Kobayashi^c.*

^aCenter for Instrumental Analysis, Iwate University, Morioka 020-8551, Japan

^bDepartment of Chemistry and Bioengineering, Faculty of Engineering, Iwate University, Morioka, 020-8551, Japan

^cDepartment of Chemistry, Graduated School of Science, Tohoku University, Sendai 980-8578, Japan

^dDepartment of Applied Chemistry, Kinki University, Higashi-Osaka 577-8502, Japan

(T. Kimura) E-mail: kimura@iwate-u.ac.jp; FAX: +81-19-621-6858

(N. Kobayshi) E-mail: nagaok@m.tohoku.ac.jp; FAX: +81-268-21-5499

Abstract

2,5-Diphenyl-3,4-dicyanothiophene (1) and phthalonitrile (2) were mixed and treated with ruthenium (III) trichloride, 4-methylpyridine, and DBU in 2-ethoxyethanol at 135 °C, to produce low-symmetrical tetraazaporphyrins (TAPs) (3), (4), (5), and (6) with one to three thiophene rings. Two thiophene-annelated tetraazaporphyrins were isolated as *opposite* and *adjacent* isomers 4 and 5. The structure of **3** was determined by X-ray crystallography, showing that the thiophene ring linked at the 3,4-positions on the tetraazaporphyrin scaffold deviates from the mean plane of the four central pyrrole nitrogen atoms (N1-N3-N5-N7). Optical and electrochemical properties of the products were examined by UV-vis and magnetic circular dichroism (MCD) spectroscopy, together with cyclic voltammetry. In the ¹H NMR spectra, the signals of 4-methylpyridine coordinating to the central ruthenium atom appeared at a higher magnetic field than those of uncoordinated 4-methylpyridine itself due to the shielding effect of the TAP ring. Increasing the number of

fused thiophene rings resulted in 1) lower magnetic field shifts of the signals of axially coordinated 4-methylpyridine in the ¹H NMR spectra, 2) lower energy shifts of the Q band absorption in the UV-vis spectra, and 3) decreasing (cathodic shift) of the first oxidation potentials. The structures of simplified model compounds were optimized using the DFT method with the Gaussian 09 program at the B3LYP/LANL2DZ level for the Ru atom and the B3LYP/6-31G (d, p) level for the C, H, N, and S atoms. The optimized structures were utilized to calculate the NMR shielding constants, the HOMO and LUMO orbital energies, and the electronic absorption spectra.

Keywords: ruthenium, phthalocyanine, thiophene, magnetic circular dichroism, electrochemistry, molecular orbital calculations

1. Introduction

As seen on going from normal porphyrins to chlorophylls, modification of the porphyrin periphery often significantly alters the properties of porphyrinoids. In order to detect this change, tetraazaporphyrins (TAPs) and tetrabenzotetraazaporphyrins, conventionally called phthalocyanines (Pcs), have been quite often utilized, since the forbidden character of the longest-wavelength band (the so-called Q band) is weakened, so that the change is relatively easily detectable spectroscopically. From this respect, we have decided in this work to prepare low-symmetry TAPs fused with varying numbers of thiophene units, and have compared their properties with those of TAPs and Pcs. We considered that the fusion of heteroatom-containing thiophene further facilitates or enhances the changes in properties, so that the knowledge obtained in this work may help to understand the properties of porphyrinoids.

Low-symmetry TAPs are known to exhibit not only intriguing spectroscopic properties but also unique properties in nonlinear optics and molecular devices which are different from those of symmetrical species [1-10]. To prepare low-symmetrical Pcs, an acceptable method is by substitution of one to four peripheral benzene rings with five- or six-membered heterocycles [11-27]. For example, TAPs linked with thiadiazole [14-16], selenadiazole [17-20], pyridine [21-23], and pyrazine rings [24-27] have been prepared, and their stability and optical and electrochemical properties examined. On the other hand, it is known that TAPs fused with furan, pyrrole, and thiophene at their 3,4-positions are extremely unstable, although the related derivatives

linked with thiophene and selenophene rings at their 2,3-positions are stable [28-34]. These results were explained by considering that, in fusing four thiophene rings to TAP through their 3,4-positions, one of the thiophene rings must contain a ring system with an unusual tetravalent sulfur atom in the conjugated structures. In the course of our work on several symmetrical and unsymmetrical Pcs [35-39], we recently succeeded in preparing TAP **7** with four diphenylthiophene units which were fused via the 3,4-positions to the central macrocycle [40,41]. If benzene units of Pc are substituted by one to four thiophene rings, it is expected that both the Q band in the absorption spectra and the shielding effect in the NMR spectra will be affected by the substitution [42-46].

On the other hand, many ruthenium complexes have been utilized to promote drag development [48] and it was reported that some Ru (II) Pc derivatives with two axial ligands have potential for application to the photodynamic therapy of cancer [47]. Two axial ligands, coordinated to the central metal atom, can be used as a probe to assess the shielding effect of the TAP ring, can prevent aggregation of the planar π -conjugated ring system, and can solubilize the macrocycles for aqueous solvents [47]. In addition, metallated Pcs and related complexes have been applied to biological catalysts [49-51]. To prepare low-symmetrical TAPs with two axial ligands, we performed a statistical condensation reaction using two phthalonitrile derivatives [52-54]; thus, 2,5-diphenyl-3,4-dicyanothiophene (1) was mixed with phthalonitrile (2), and the mixture treated with ruthenium (III) trichloride and 4-methylpyridine in the presence of DBU [55,56]. This paper reports the preparation and optical and electrochemical properties of low-symmetrical tetraazaporphyrinatoruthenium (II) bis(4-methylpyridine) fused with one to three diphenylthiophene units (3-6), together with those of analogous symmetrical derivatives (7,8) [40,41].

2. Experimental

2.1. Instrumentation

NMR spectra were measured with a Bruker AVANCE 500 III spectrometer and a Bruker AC 400 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 and reduction potentials. Magnetic circular dichroism (MCD) measurements were made with a JASCO J-725 spectrodichrometer equipped with a JASCO electromagnet that produced magnetic fields of up to 1.03 T with parallel and antiparallel fields. Its magnetic magnitude was expressed in terms of molar ellipticity per tesla [θ] M/10⁴ deg M⁻¹ cm⁻¹ T⁻¹. Bio-beads (SX-1) for column chromatography were purchased from Nippon Bio-Rad Laboratories.

2.2. Synthesis

2.2.1. 2,5-Diphenyl-3,4-dicyanothiophene (1)

2,5-Diphenyl-3,4-dicyanothiophene (1) was prepared by the method reported previously [40,55].

2.2.2. Preparation of low-symmetrical tetraazaporphyrin derivatives (3)-(6).

Into a 50 mL reactor, diphenyldicyanothiophene (1) (571.4 mg, 2 mmol), phthalonitrile (2) (256.0 mg, 2 mmol), and RuCl₃•nH₂O (261.5 mg, 1 mmol) were placed under Ar [56]. To this mixture, 2-ethoxyethanol (8 mL), DBU (1.2 mL), and 4-methylpyridine (1.4 mL) were added, and the mixture reacted under reflux for 48 h. After the reactor was cooled, aqueous MeOH was added, and the precipitate was collected by filtration. The residue was dissolved in CHCl₃ and dried After the solvent was evaporated, the product was purified by column over MgSO₄. chromatography (Wako-gel C-300HG, hexane : chloroform = 2 : 3; Bio-Beads SX-1, chloroform), to produce 3 in 2%, 4 in 1%, 5 in 2%, and 6 (trace); 3: green crystals; ¹H NMR (500 MHz, CDCl₃) δ 1.20 (s, 6H, CH₃), 2.47 (d, 4H, J = 6.8 Hz, Py-H), 5.12 (d, 4H, J = 6.8 Hz, Py-H), 7.64 (t, 2H, J = 7.4 Hz, Ar-H), 7.83-7.91 (m, 10H, Ar-H), 8.9-8.99 (m, 2H, Ar-H), 9.10-9.19 (m, 4H, Ar-H), 9.26 (d, 4H, J = 7.3 Hz, Ar-H); ¹³C NMR (126 MHz, CDCl₃) δ 19.5, 120.9, 121.1, 121.2, 123.6, 127.4, 127.6, 127.7, 128.5, 128.8, 129.6, 133.5, 135.7, 140.0, 140.5, 140.7, 141.2, 141.7, 142.1, 142.6, 143.3, 145.1, 149.1; HR-FAB-MS calcd for $C_{54}H_{36}N_{10}RuS = 958.1889$. Found (m/z) 958.1884 (M⁺); crystal data: $C_{54}H_{36}N_{10}RuS$; F(000) = 1960; crystal size 0.620 mm × 0.420 mm × 0.090 mm; MoKa $(\lambda = 0.71075 \text{ Å}); T = -173 \pm 1 \text{ °C}; \text{ monoclinic}; P2_1/c (\#14); a = 10.4754(10) \text{ Å}, b = 21.224(2) (16)$ Å, c = 20.3281(19) Å, $\beta = 102.3076(13)^{\circ}$; V = 4415.6 (7) Å³; Z = 4; D (calcd) = 1.441 g/cm^{3} ; μ (MoK α) = 4.541 cm⁻¹; reflections collected = 41193; unique = 8518 [*R*(int) = 0.0884]; Reflection/Parameter Ratio = 14.27; GOF = 1.056; final R indices $[I > 2\sigma(I)] R_1 = 0.1062$, w $R_2 =$

0.2682; max and min diff. peaks = 2.00 and -1.22 eÅ^{-3} ; **4**: green crystals; ¹H NMR (500 MHz, CDCl₃) $\delta 1.25$ (s, 6H, CH₃), 2.60 (d, 4H, J = 6.8 Hz, Py-H), 5.21 (d, 4H, J = 6.8 Hz, Py-H), 7.64 (t, 4H, J = 7.3 Hz, Ar-H), 7.82-7.88 (m, 12H, Ar-H), 8.94-8.99 (m, 4H, Ar-H), 9.27 (d, 8H, J = 7.3 Hz, Ar-H); HR-FAB-MS calcd for C₆₄H₄₂N₁₀RuS₂ = 1116.2079. Found (*m*/*z*) 1116.2055 (M⁺); **5**: green crystals; ¹H NMR (500 MHz, CDCl₃) $\delta 1.25$ (s, 6H, CH₃), 2.67 (d, 4H, J = 6.8 Hz, Py-H), 5.23 (d, 4H, J = 6.8 Hz, Py-H), 7.03 (dd, 4H, J = 8.0, 7.4 Hz, Ar-H), 7.14 (t, 2H, J = 7.4 Hz, Ar-H), 7.64 (t, 2H, J = 7.4 Hz, Ar-H), 7.85 (dd, 4H, J = 8.0, 7.4 Hz, Ar-H), 7.87-7.91 (m, 4H, Ar-H), 8.39 (dd, 4H, J = 8.0, 1.0 Hz, Ar-H), 8.96-9.03 (m, 2H, Ar-H), 9.14-9.20 (m, 2H, Ar-H), 9.22 (dd, 4H, J = 8.0, 1.0 Hz, Ar-H); HR-FAB-MS calcd for C₆₄H₄₂N₁₀RuS₂ = 1116.2079. Found (m/z) 1116.2094 (M⁺); **6**: green crystals; ¹H NMR (500 MHz, CDCl₃) $\delta 1.26$ (s, 6H, CH₃), 2.87 (d, 4H, J = 6.8 Hz, Py-H), 5.34 (d, 4H, J = 6.8 Hz, Py-H), 6.96-7.14 (br, 12H, Ar-H), 7.74-7.92 (br, 6H, Ar-H), 8.18-8.43 (br, 10H, Ar-H), 8.99-9.28 (br, 6H, Ar-H); HR-FAB-MS calcd for C₇₄H₄₈N₁₀RuS₃ = 1274.2269. Found (m/z) 1274.2210 (M⁺).

2.2.3. Tetraazaporphyrin (7) and phthalocyanine (8)

Tetraazaporphyrin (**7**) and phthalocyanine (**8**) were prepared by the method reported previously [40,56]; **7**: ¹H NMR (500 MHz, CDCl₃) δ 1.52 (s, 6H, CH₃), 3.62 (d, 4H, *J* = 6.9 Hz, Py-H), 5.69 (d, 4H, *J* = 6.9 Hz, Py-H), 7.30-7.77 (m, 20H, Ar-H), 8.00-8.28 (m, 22H, Ar-H); **8**: ¹H NMR (500 MHz, CDCl₃) δ 1.15 (s, 6H, CH₃), 2.34 (d, 4H, *J* = 6.7 Hz, Py-H), 5.03 (d, 4H, *J* = 6.7 Hz, Py-H), 7.84-7.90 (m, 8H, Ar-H), 9.08-9.16 (m, 8H, Ar-H).

2.3. X-Ray crystallography

A dark-green platelet crystal of $C_{54}H_{36}N_{10}RuS$ having approximate dimensions of $0.620 \times 0.420 \times$ 0.090 mm was mounted in a loop. All measurements were made on a Rigaku Saturn70 diffractometer using graphite monochromated Mo $K\alpha$ ($\lambda = 0.71075$ Å) radiation [Voltage (50 kV) and Current (60 mA)]. The data were collected at a temperature of -173 ± 1 °C to a maximum 2θ value of 55.0°. The crystal-to-detector distance was 75.00 mm. Readout was performed in the 0.140 mm pixel mode, and a total of 1440 oscillation images were collected. A sweep of data was done using ω scans from -120.0 to 60.0° in 0.50° step, at $\chi = 45.0^{\circ}$ and $\phi = 0.0^{\circ}$. The The detector swing angle was -30.00° . A second sweep was exposure rate was 90.0 [sec/deg]. performed using ω scans from -120.0 to 60.0° in 0.50° step, at $\chi = 45.0^{\circ}$ and $\phi = 90.0^{\circ}$. The

exposure rate was 90.0 [sec/deg]. The detector swing angle was -30.00° . Another sweep was performed using ω scans from -120.0 to 60.0° in 0.50° step, at $\chi = 45.0^{\circ}$ and $\phi = 180.0^{\circ}$. The exposure rate was 90.0 [sec/deg]. The detector swing angle was -30.00° . Another sweep was performed using ω scans from -120.0 to 60.0° in 0.50° step, at $\chi = 45.0^{\circ}$ and $\phi = 270.0^{\circ}$. The exposure rate was 90.0 [sec/deg]. The detector swing angle was -30.00° .

The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL2013; Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre: the deposition number is CCDC 1042057. The data can be obtained free for charge from CCDC via www.ccdc.cam.ac.uk/data_request/cif.

2.4. Oxidation potentials

All measurements were performed by cyclic voltammetry, using Ag/0.01 M AgNO₃ as a reference electrode. A solution of 0.1 M n-Bu₄NClO₄ in CH₂Cl₂ was used as an electrolyte. A scan rate of 200 mVs⁻¹ was used for measurement.

2.5. Computational Methods

All calculations for **3a**, **4a**, **5a**, **6a**, **7a**, and **8** were performed at the DFT level, by means of the hybrid Becke3LYP (B3LYP) functional as implemented in Gaussian 09 [57]. Ru atoms were described using the LANL2DZ. The 6-31G* basis set was used for the other atoms. Geometry optimization, NMR shielding constants, molecular orbital energies and time-dependent density functional theory (TDDFT) calculations were performed at the same level.

3. Results and Discussion

As a starting compound, **1** was prepared by treatment of tetrabromothiophene with phenylboronic acid according to the Suzuki-Miyaura coupling reaction, and then with copper (I) cyanide in DMF [55].

To prepare TAPs fused with one to four diphenylthiophene units, 1 was mixed with 2 in a 1:1 ratio, and the mixture reacted with ruthenium (III) trichloride and 4-methylpyridine in the presence

of DBU in 2-ethoxyethanol under reflux for 48 h (Scheme 1) [56]. The products were separated by column chromatography using silica gel and Bio-Beads (SX-1), to give three low-symmetrical TAPs **3**, **4**, and **5** in 2, 1, and 2% yield, respectively. In addition, while we could obtain TAP **6** containing three thiophene rings in a trace amount, compound **7** was not produced by this reaction. The *adjacent* and *opposite* isomers **4** and **5** bearing two thiophenes could be easily isolated by column chromatography. When a mixture of **1** and **2** (1 : 5 ratio) was treated similarly as described above, compound **3** was obtained as a major product: **3** (4%), **4** (1%), and **5** (1%).

The structures of the products were determined by ¹H NMR spectroscopy, fast atom bombardment mass spectrometry (FAB-MS), and UV-vis spectroscopy. In the HR-FAB-MS spectra using *m*-nitrobenzyl alcohol as a matrix, the corresponding molecular ion peaks were observed for the respective compounds; **3**: m/z = 958.1884 (M⁺), **4**: m/z = 1116.2055 (M⁺), **5**: m/z =1116.2094 (M⁺), and **6**: m/z = 1274.2210 (M⁺). Two axial ligands of the products did not cleave their coordination bond with the ruthenium atom under the ionization condition [47].

Recrystallization of **3** from chloroform and methanol produced single crystals. However, we could not obtain sufficient diffraction spots on the higher angle side by usual measurement of crystals of suitable size at -173 + 1 °C. Based on the measurement results, it was expected that the crystals contain the mosaicity; since the chloroform molecules in the crystals gradually vaporized, the arranged molecules may go slightly out of order and, as a result, the crystals are partially changed to the mosaic crystals. After many trials seeking a suitable crystal, we found that larger-sized crystals showed diffraction spots on the higher angle side in addition to the lower angle side. Therefore, a slightly large crystal was used for the data collection, but the measurement required a longer distance between the crystal and the CCD detector; hence, we changed the distance from 45 mm to 75 mm. In addition, to obtain strong diffraction spots on the higher angle side, the measurement required a longer exposure time than the normal method, as shown in the Experimental Section. As a result, X-ray crystallographic analysis showed that 3 has a monoclinic form with a space group of $P2_1/c$ (#14), a = 10.4754(10) Å, b = 21.224(2) Å, c =20.3281(19) Å, $\beta = 102.3076(13)^{\circ}$. The unit cell consists of four molecules of **3**, and the final goodness of fit and R factor were GOF = 1.056 and $R_1 = 0.1062 [I > 2.00\sigma(I)]$. As described by Sun and coworkers, the scaffold of the Pc complex 8 has an essentially planar form except for

two 4-methylpyridine ligands [56]. As shown in Figure 1, the ORTEP drawing reveals that the central ruthenium (II) atom is six-coordinate, and 3 contains a skeleton of TAP with a thiophene unit which is fused to the macrocycle at the 3,4-positions. It seems that there is no steric congestion with respect to the phenyl groups in the molecular structure. However, the thiophene ring linked to the TAP scaffold deviates from the mean plane of the four central pyrrole nitrogen atoms (N1-N3-N5-N7). In compound 3, while the angle between the plane (C17-C2-C3-C18) in the thiophene ring and the central mean plane (N1-N3-N5-N7) is 15.81°, the angle between the plane (C17-S1-C18) in the thiophene ring and the central mean plane is 13.77°. The part (C17-S1-C18) of the thiophene ring of **3** is the *exo* conformation. In contrast, the angle formed by the plane (C1-C2-C3-C4) in the thiophene ring and the central mean plane (N1-N2-N1*-N2*) in 7 is 10.29° and that between the plane (C1-S1-C4) in the thiophene ring and the central mean plane is 11.15° as shown in Supplemental data [40]. The deviation of the thiophene ring from the central mean plane is larger in 3 than in 7. It is expected that the sulfur atom of the thiophene rings of **3** may weakly interact with the π -conjugation system. Although the thiophene rings of 7 (S2-C7-C8-C9-C10) are deformed from the mean plane of the four central pyrrole nitrogen atoms, the two benzene rings of 3 (C6-C19-C20-C21-C22-C7 and C14-C27-C28-C29-C30-C15) are slightly twisted from the central mean plane.

The S-C bond distances of **3** are 1.745 (10) Å (S1-C17) and 1.749 (8) Å (S1-C18), which are similar to those of **7** [1.747 Å (mean)], but longer than those of tetraphenylthieno[3,4-*c*]thiophene [1.706 Å (mean)] and thiophene [1.714 Å (mean)] (Table 1) [42,58]. The C-C bond distances of the thiophene ring in **3** are 1.377 (11) Å (C2-C17), 1.349 (13) Å (C3-C18), and 1.450 (12) Å (C2-C3), and are similar to those of **7** [1.381 Å (C1-C2) and 1.425 Å (C2-C3)]. In the crystal, the lengths of the two axial (ax) bonds of **3** are slightly different, while the equatorial (eq) Ru-N7 bond is somewhat longer than those of other equatorial Ru-N bonds. The axial Ru-N bond of **7** is slightly shorter than the axial Ru-N bonds of **3** (a mean value, 2.103 Å) and **8** (2.101 Å) (Table 2). While the lengths of the Ru-N bonds of **7** are 2.013 Å (Ru-N, eq) and 2.095 Å (Ru-N, ax), those of **3** are 1.990 (7) Å (Ru-N1 eq), 1.990 (7) Å (Ru-N3, eq), 1.991 (7) Å (Ru-N5, eq), 2.011 (7) Å (Ru-N7, eq), 2.117 (7) Å (Ru-N9, ax), and 2.089 (6) Å (Ru-N10, ax).

The ¹H NMR spectra of the products showed the signals of phenyl and peripheral benzo

protons, which suggests that compounds 3, 4, 5, and 6 have low-spin d^6 structures. As reported in a previous paper [40], the signals for axially coordinated 4-methylpyridine were observed at $\delta =$ 1.37, 3.14, and 5.46 ppm for **7** and $\delta = 1.15$, 2.34, and 5.03 ppm for **8**. The shielding effect of the TAPs can more strongly affect H_c protons than H_a and H_b protons. While the signals for 4-methylpyridine of **7** and **8** are shielded by the magnetic field of the TAP ring, from the above δ values, it appears that the ring current of TAP is stronger in 8 than in 7. Interestingly, the extent of the higher magnetic field shift of 3-8 depends on the number of fused thiophene and benzene Thus, an increasing number of thiophene rings (decreasing number of benzene rings (Table 2). rings) produced a lower magnetic field shift of the signals of 4-methylpyridine. The order of the higher magnetic field shifts is 8 > 3 > 4 > 5 > 6 > 7. The chemical shifts of the 4-methylpyridine in the opposite isomer 4 were observed at a slightly higher magnetic field than those of the adjacent isomer 5.

Electronic absorption spectra of the products were measured in chloroform, and the absorption wavelengths and molar extinction coefficients determined (Figure. 2). The spectra showed Soret bands at around 310–320 nm and Q bands at around 620–760 nm. In the UV-vis spectra of the TAP and Pc derivatives, it is known that the differences between the Q_{x00} and Q_{y00} absorption are strongly affected by the symmetry of the π -conjugation system [59].

While 7 and 8 are D_{4h} in symmetry, 3, 4, 5, and 6 have lower symmetry. Compounds 7 and 8 showed slightly broadened Q-bands at $\lambda_{max} = 758$ nm ($\varepsilon = 1.13 \times 10^5$) and 626 nm ($\varepsilon = 75,000$), respectively [40]. Although no absorption data of substituent-free RuTAP has been reported, since most of the substituent-free transition metal TAPs show the Q bands at 575-585 nm [60], the effect of the four diphenylthiophene units of 7 can be considered to amount to ca. 180 nm (ca. 4000 cm⁻¹). Compound 8 showed dispersion-type MCD absorption (Faraday *A*-term) at 610 and 634 nm corresponding to the Q band absorption and 307 and 336 nm for the Soret band absorption [40]. The MCD curve corresponding to the Q band absorption of 7 consisted of Faraday *A*-term-like dispersion curve at 746 and 776 nm. The result indicates that the two LUMOs of 7 are practically degenerate, although the central TAP is deformed from the planar structure due to repulsion between the eight phenyl groups [40].

As shown in Figure 3, compounds 3, 4, 5, and 6 showed broadened, split Q-bands, with ε

values as follows: **3**: $\lambda_{\text{max}} = 663 \text{ nm} (\varepsilon = 69,000)$, **4**: $\lambda_{\text{max}} = 683 \text{ nm} (\varepsilon = 63,000)$ and 721 nm ($\varepsilon = 62,000$), **5**: $\lambda_{\text{max}} = 699 \text{ nm} (\varepsilon = 77,000)$, and **6**: $\lambda_{\text{max}} = 720 \text{ nm} (\varepsilon = 82,000)$ and 736 nm ($\varepsilon = 80,000$). In the Q-band region of low-symmetrical TAP derivatives **3**, **4**, **5**, and **6**, unequal troughs and peaks appeared in the MCD spectra, corresponding to the peak and shoulder of the Q band absorption. These are Faraday *B* MCD terms which generally appear when there is no degeneracy in both the ground (HOMO and HOMO–1) and excited states of the TAPs (*vide infra*) [61,62]. From the minus-to-plus change in MCD sign in ascending energy, it is expected that the energy difference between the HOMO and HOMO–1 is larger than that between the LUMO and LUMO+1 [63].

In the MCD spectrum of 3, a peak and trough are observed at 599 and 680 nm associated with the absorption peaks at 601 and 663 nm, respectively. However, their energy difference is too large to assign them to Q_{x00} and Q_{v00} bands. It was previously reported that in Pc derivatives having a similar π -conjugation system, the energy difference between the Q_{x00} and Q_{x01} absorption is roughly constant, being about 1040–1160 cm⁻¹ (ΔQ_{x00} – $Q_{x01} = 40-45$ nm) [64,65]. Therefore, in the MCD spectrum of **3**, it is inferred that the peak of Q_{v00} may overlie the trough of Q_{x01} . In addition, we can observe a shoulder at around 620 nm in the MCD spectrum. Based on this consideration, the Q_{y00} absorption of 3 can be approximately estimated to lie at around 660 nm in the MCD spectrum. Compound **6** showed two peaks at 736 and 720 nm (energy difference = ca. 300 cm⁻¹), and from the change in MCD sign, these two peaks can be safely assigned to Q_{x00} and In assigning the absorption of 4, the most important aspect is the assignment of a Q_{v00} bands. peak at 683 and a shoulder at 658 nm. Since the energy difference between the 721 nm peak (Q_{x00}) and this peak and shoulder is ca. 770 and 1330 cm⁻¹, respectively, the 683 nm peak can be assigned to the Q_{v00} band. The UV-vis spectrum of 5 showed a peak and shoulder at around 699 and 680 nm, respectively, in the Q band region. Since the MCD exhibits a trough and peak at 714 and 673 nm, the absorption peak and shoulder may correspond to Q_{x00} and Q_{v00} bands.

To determine the electrochemical properties of tetraazaporphyrins **3**, **4**, **5**, **6**, and **7**, their oxidation and reduction potentials were measured by cyclic voltammetry using Ag/AgNO₃ as a reference electrode (solvent: CH₂Cl₂): cyclic voltammograms are shown in Supplemental data. As shown in Table 3, two reversible oxidation potentials ($E_{1/2} = 0.25$ and 0.92 V) and one reversible

reduction potential ($E_{1/2} = -1.64$ V) were observed for monothieno derivative **3**. For the TAPs with two thiophene rings, three reversible oxidation potentials ($E_{1/2} = 0.14$, 0.81, and 1.15 V) and one reversible and one irreversible reduction potential ($E_{1/2} = -1.40$ V and $E_p = -1.65$ V) were observed for the *opposite* derivative **4**, while three reversible oxidation potentials ($E_{1/2} = 0.13$, 0.50, and 0.78 V) and one irreversible and one reversible reduction potential ($E_p = -1.35$ V and $E_{1/2} = -1.71$ V) were found for the *adjacent* derivative **5**. Compound **6** shows three reversible oxidation potentials ($E_{1/2} = 0.03$, 0.64, and 1.13 V) and one irreversible and one reversible and one reversible and one reversible and reduction potentials ($E_p = -1.14$ V and $E_{1/2} = -1.76$ V). The oxidation and reduction potentials of **7** and **8** are shown in Table 3 [40].

Figure 4-A shows the relationship between the wave number of the Q band absorption $[(Q_{x00}+Q_{y00})/2 \text{ cm}^{-1}]$ in the UV-vis and MCD spectra and the chemical shift of the 4-methylpyridine of tetraazaporphyrins in the ¹H NMR spectra. Interestingly, increasing the number of thiophene rings caused lower magnetic field shifts of the chemical shifts of the 4-methylpyridines and lower energy shifts of the Q band absorption. At the same time, increasing the number of thiophene rings lowered the first oxidation potential and raised the HOMO levels (*vide infra*), which correlated with a decrease in the energy of the Q band absorption (Figure 4-B).

Since it is important to obtain further information about TAPs with one to four thiophene units, the optimized structures, NMR shielding constants, and electronic absorption spectra were calculated using the density functional theoretical (DFT) method. To simplify the calculations, all of the phenyl groups of 3, 4, 5, 6 and 7 were substituted with protons, where 3a, 4a, 5a, 6a, and 7a represent the corresponding structures of calculated model compounds containing protons instead of the phenyl groups. It should be noted that in these model compounds, the Q band absorption is observed at higher energy than the measured spectra because the Q band absorption of α -substituted Pc occurs at lower energy than that of unsubstituted Pc [66]; for example, the energy difference between zinc complexes of unsubstituted Pc and α -octa(butylthio) Pc is about 110 nm. The structures of **3a**, **4a**, **5a**, **6a**, **7a**, and **8** were optimized using the Gaussian 09 program at the B3LYP/LANL2DZ level for Ru and the B3LYP/6-31G (d, p) level for C, H, N, and S [57]. The optimized structures showed that the TAP rings of 3a-8 take completely planar forms. In the optimized structures, the thiophene rings of the compounds **3a**–**7a** are similar in structure (Table 1).

The partial structural parameters of **3a–8** are shown in Table 1 and 2, together with those of **3**, **7**, and **8** determined by X-ray analysis. Furthermore, to estimate the transition energies of the electronic absorption spectra, the TDDFT method was used by adopting similar basic functions.

Since the ¹H NMR spectra were obtained, the ruthenium (II) complexes **3–8** with six electrons in the 4*d* orbitals appear to be low spin complexes. In the ¹H NMR spectra (Table 2), the calculated chemical shifts of 4-methylpyridine for all of the model compounds **3a–8** showed a higher magnetic field shift than those for uncoordinated 4-methylpyridine, the results of which are similar to the experimental data. The methyl signals in the ¹H NMR spectra of **3–8** were observed at a slightly lower magnetic field than those of calculated species **3a–8**. It appears that the degree of the higher magnetic field shifts of the model compounds may depend on the number of thiophene rings. Thus, increasing the number of the thiophene rings could produce a lower magnetic field shift of the signals of 4-methylpyridine in both the experimental and calculated data. In addition, the chemical shifts of 4-methylpyridine in the *opposite* isomer **4** were observed at a slightly higher magnetic field than those of the *adjacent* isomer **5**.

The calculated absorption spectra are shown in Figure 5, with the transition energies, oscillator strengths *f*, and configurations summarized in Table 4. Although the calculated wavelengths of the Q band absorption for 3a-8 obtained by this method are shorter than those of the measured absorption, the order of the absorption wavelength and the splitting of the Q band due to the number of the thiophene rings in the calculated spectra are nicely related to the experimentally-measured spectra [65,67]. In both spectra, the Q band absorption shifts to longer wavelength in the order 8 < 3a < 4a < 5a < 6a < 7a. The splitting of the Q band absorption of 3a, 4a, and 6a is larger than for 5a and 7a, while compound 4a shows the largest split width.

In general, the Q band absorption of Pc derivatives with a D_{4h} point group can be explained qualitatively using a four orbital model including the HOMO (denoted as a_{1u}), HOMO–1 (a_{2u}) and degenerate LUMO (e_{gx}), and LUMO+1 (e_{gy}) [68]. Figures 6 and 7 show the frontier molecular orbitals and energies for TAP derivatives **3a**–**8**. Actually, in the compounds **3a**–**8**, the HOMO–1 orbitals are different from the a_{2u} orbitals. It appears that, while the two LUMOs of **7a** and **8** are energetically degenerate, those of **3a**, **4a**, and **6a** have different energies. In contrast, although the structure of the *adjacent* isomer **5a** is close to C_{2v} , the energy levels of the two LUMOs are very

similar. With increasing number of thiophene rings, the HOMO is destabilized, consistent with the observed decrease (cathodic shift) of the 1st oxidation potentials (Figure 4B). In the case of **3a**, **4a**, and **6a**, with lowering of the molecular symmetry by increasing the number of thiophene rings, the e_g LUMOs split into two non-degenerate orbitals, so that both the Q and Soret bands split Figure 6 shows the frontier molecular orbitals of TAP derivatives 3a-8. into two bands. Since compounds 7a and 8 belong to the D_{4h} point group, the HOMO orbitals of these compounds have Although the symmetry of the TAP rings of **3a–6a** is lowered from D_{4h} due to the a_{1u} symmetry. substitution of the benzene ring with one to three thiophene rings, the molecular orbital symmetry of these compounds is similar to that of 7a and 8 with the exception of compound 5a. While the HOMO-1 and HOMO-2 orbitals of 7a and 8 are degenerate, and hence the symmetries of these orbitals are e_{gx} and e_{gy} , it appears that the HOMO-3 has b_{1u} symmetry. In addition, the two LUMOs of these compounds are degenerate, so that they are e_{gx} and e_{gy} in symmetry. On the other hand, we could assign the a_{2u} orbitals of 8 and 7a as the HOMO-6 (184) and HOMO-9 orbitals (185) (Table 4) and the related orbitals of 3a, 4a, 5a, and 6a are determined as the HOMO-7 (184), the HOMO-8 (184), HOMO-8 (184), and HOMO-9 orbitals (184), respectively (Supplemental data).

The main electronic configuration of the Q_{x00} band of 3a, 4a, 6a, 7a, and 8 is the HOMO-LUMO transition, whereby the ratios are 90% in 3a, 98% in 4a, 97% in 6a, 97% in 7a, and 94% in 8 (Table 4). On the other hand, the Q_{y00} band mainly consists of the HOMO–LUMO+1 electronic configuration, in which the ratios are 77% in 3a, 94% in 4a, 88% in 6a, 97% in 7a, and 92% in 8, respectively. These calculated results are consistent with the qualitative interpretation obtained with the four orbital model. The orbitals of the HOMO-1, HOMO-2, and HOMO-3 orbitals of 3a-8 may be related to the MLCT bands between the Soret and the Q bands. In contrast, for 5a, the contributions of HOMO-LUMO, HOMO-LUMO+1, and HOMO+1-LUMO+1 transitions are mixed in the electronic configurations of both the Q_{x00} and Q_{y00} bands, while a contribution of the transition from HOMO+2-LUMO is present and affects the Q band absorption. Therefore, it is clear that the electronic structure of the Q band state of 5a is different from those of the other compounds. On the other hand, although the contribution from the HOMO-7 (184) orbital of 3a in the electronic transition is smaller than those of 4a: HOMO-8 (184), 5a: HOMO-8

(184), **6a**: HOMO–9 (184), **7a**: a_{2u} , HOMO–9 (185), and **8**: a_{2u} , HOMO–6 (184) (Table 4), these transitions could be related to the Soret band absorption in the absorption spectra.

4. Conclusions

TAPs with thiophene rings obtained from Low-symmetrical one to three were 2,5-diphenyl-3,4-dicyanothiophene (1), phthalonitrile (2), ruthenium (III) trichloride, and The X-ray crystallography for 3 showed that the thiophene ring linked at the 4-methylpyridine. 3,4-positions on the tetraazaporphyrin scaffold deviates from the mean plane of the four central In the ¹H NMR spectra of the products, the chemical shifts of axially pyrrole nitrogen atoms. coordinated 4-methylpyridine were affected by the number of peripheral thiophene units, and increasing the number of thiophene rings produced a lower magnetic field shift of the signals. This is a similar phenomenon to that observed on going from TAP to Pc, and further to naphthalocyanine and anthracocyanine, where the ring current of the macrocycle decreases with increasing electron-donating ability of the fused unit [2,6,65-67,69]. The optical and electrochemical properties were examined by UV-vis and MCD spectroscopy, and cyclic voltammetry, clearly showing that the number of thiophene units influences the Q band absorptions and oxidation potentials. Thus, increasing the number of thiophene rings cathodically shifted the first oxidation potential, which correlates well with the red-shifted Q band position. The structures of simplified model compounds were optimized using the DFT method with the Gaussian Although the calculated wavelengths of the Q band absorption for **3a–8** obtained by 09 program. this method appear at shorter wavelength than those experimentally measured, the wavelengths and splitting of the Q band absorption due to the number and position of the fused thiophene rings correlate well with the calculated results.

Abbreviations

B3LYP Becke 3-parameter, Lee, Yang, and Parr
CCD Charge Coupled Device
DBU 1,8-diazabicyclo[5.4.0]undec-7ene
D (calcd) density (calculated)

- DFT density functional theory
- DMF dimethylformamide
- Fc ferrocene

GOF goodness of fit

- HOMO highest occupied molecular orbital
- HR-FAB-MS high-resolution fast atom bombardment mass spectrometry
- LANL2DZ Los Alamos National Laboratory 2 double zeta
- LUMO lowest unoccupied molecular orbital
- MCD magnetic circular dichroism
- NMR nuclear magnetic resonance
- ORTEP Oak Ridge thermal ellipsoid plotting program
- Pc phthalocyanine
- TAP tetraazaporphyrin
- TDDFT time-dependent density functional theory
- MLCT Metal to Ligand Charge Transfer

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Highlight

• Low-symmetrical tetraazaporphyrins (TAPs) with one to three thiophene rings were prepared by the reaction of 2,5-Diphenyl-3,4-dicyanothiophene, phthalonitrile, ruthenium (III) trichloride, and 4-methylpyridine.

• Optical and electrochemical properties of the products were examined by UV-vis and magnetic circular dichroism (MCD) spectroscopy, together with cyclic voltammetry.

• Increasing the number of fused thiophene rings resulted in 1) lower magnetic field shifts of the signals of 4-methylpyridine in the ¹H NMR spectra, 2) lower energy shifts of the Q band absorption in the UV-vis spectra, and 3) decreasing of the first oxidation potentials.

• The optimized structures were utilized to calculate the NMR shielding constants, the HOMO and LUMO orbital energies, and the electronic absorption spectra.





Figure 1. ORTEP drawing of **3**, A) side view from the N7 atom, B) top view from the axial direction,



Figure 2. UV-vis spectra of TAP derivatives **3–8** measured in chloroform.



derivatives measured in chloroform; A) 3, B) 4, C) 5, and D) 6.



Figure 4. Correlation between absorption peaks $[(Q_{x00}+Q_{y00})/2 \text{ cm}^{-1}]$ and A) ¹H NMR chemical shifts of 4-methylpyridine, B) first oxidation potentials (blue box) and calculated 1st HOMO energies (red circle).



Figure 5. Calculated transition energies and oscillator strengths f for TAP derivatives **3a**-**8**.



Figure 6. Frontier molecular orbitals of TAP derivatives **3a–8**.



Figure 7. Frontier molecular orbital energies of TAP derivatives 3–8.

Figure Caption

Figure 1. ORTEP drawing of 3, A) side view from the N7 atom, B) top view from the axial direction.

Figure 2. UV-vis spectra of TAP derivatives **3–8** measured in chloroform.

Figure 3. UV-vis and MCD spectra of TAP derivatives measured in chloroform; A) **3**, B) **4**, C) **5**, and D) **6**.

Figure 4. Correlation between absorption peaks $[(Q_{x00}+Q_{y00})/2 \text{ cm}^{-1}]$ and A) ¹H NMR chemical shifts of 4-methylpyridine, B) first oxidation potentials (blue box) and calculated 1st HOMO energies (red circle).

Figure 5. Calculated transition energies and oscillator strengths *f* for TAP derivatives **3a–8**.

Figure 6. Frontier molecular orbitals of TAP derivatives 3a-8.

Figure 7. Frontier molecular orbital energies of TAP derivatives 3–8.

S C	Mean bond distances (Å)									
$C_{\gamma} C_{\beta}$	S-Ca		Cα-C β		Cļ	3-Сү	eq-Ru-N			
					4	2				
Compd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.		
8	-	-	-	-	1.400	1.414	1.981	2.021		
3 (a)	1.747	1.743	1.363	1.367	1.450	1.437	1.996	2.025		
4(a)	-	1.743	-	1.367		1.437	-	2.028		
5(a)	-	1.744	-	1.367	-	1.437	-	2.028		
6(a)	-	1.743	-	1.368	-	1.437	-	2.031		
7(a)	1.747	1.742	1.381	1.368	1.425	1.437	2.013	2.035		

Table 1. Partial bond distances of tetraazaporphyrins **3–8**.

Calculated bond distances for **3a**, **4a**, **5a**, **6a**, **7a**, and **8** were obtained by the DFT method (*vide infra*). To simplify the calculations, all of the phenyl groups of **3**, **4**, **5**, **6**, and **7** were substituted with protons.

	Chemical shift δ (ppm)						Bond ler	ngths (Å)	
Compd.	H_a		H _b			He		ax-Ru-N	
	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	
8	1.15	1.069	2.34	2.495	5.03	5.124	2.101	2.163	
3 (a)	1.20	1.107	2.47	2.570	5.12	5.182	2.103	2.162	
4 (a)	1.25	1.144	2.60	2.626	5.21	5.238	-	2.162	
5(a)	1.25	1.151	2.67	2.667	5.23	5.249	-	2.163	
6(a)	1.31	1.186	2.87	2.732	5.34	5.305	-	2.162	
7 (a)	1.37	1.223	3.14	2.789	5.46	5.361	2.095	2.162	
4-MePy	2.39	-	8.45	-	7.08	-	-	-	

Table 2. ¹H NMR chemical shifts of 4-methylpyridine and ax-Ru-N bond lengths.

4-MePy: 4-methylpyridine; Calculated chemical shifts and ax-Ru-N (Å) for **3a**, **4a**, **5a**, **6a**, **7a**, and **8** were obtained by the DFT method (*vide infra*). To simplify the calculations, all of the phenyl groups of **3**, **4**, **5**, **6**, and **7** were substituted with protons.

		E	1/2 V vs Fc/Fc	+	9	ΔE obs	Q band	ΔE calcd
Compd.	2nd	1st	1st	2nd	3rd	eV	nm	eV
	Redn	Redn	Oxid	Oxid	Oxid			
8		-1.66	0.37			2.03	630	1.97
3		-1.64	0.25	0.92		1.89	663	1.87
4	-1.65 ^a	-1.40	0.14	0.81	1.15	1.54	683	1.82
5	-1.71	-1.35 ^a	0.13	0.50	0.78	1.48	699	1.77
6	-1.76	-1.14 ^a	0.03	0.64	1.14	1.17	720	1.72
7	-1.38	-1.21 ^a	-0.12	0.48	1.05	1.09	758	1.64

Table 3 Oxidation and reduction potentials of tetraazaporphyrins.

The oxidation and reduction potentials of them were measured by cyclic voltammetry using Ag/AgNO₃ as a reference electrode, Pt as a counter electrode, and glassy carbon as a working electrode (solvent: CH_2Cl_2 , scan rate: 200 mVs⁻¹); ^airreversible; ΔE obs = 1st Oxid – 1st Redn.

Energy (nm)	f	Configuration
8 (Th0)		
567	0.48	$190 \to 191 \ (94\%)$
567	0.48	$190 \to 192 \ (92\%)$
363	0.24	$188 \rightarrow 194 (48\%) 189 \rightarrow 193 (48\%)$
315	0.37	$178 \rightarrow 191\; (36\%)\; 184 \rightarrow 191\; (13\%)\; 186 \rightarrow 191\; (12\%)\; 189 \rightarrow 196\; (15\%)$
315	0.37	$178 \rightarrow 192\; (36\%)\; 184 \rightarrow 192\; (13\%)\; 186 \rightarrow 192\; (12\%)\; 188 \rightarrow 196\; (15\%)$
313	0.21	$178 \rightarrow 191 \ (54\%) \ 181 \rightarrow 192 \ (11\%) \ 189 \rightarrow 198 \ (11\%)$
313	0.21	$178 \rightarrow 192 \ (54\%) \ 181 \rightarrow 191 \ (11\%) \ 188 \rightarrow 198 \ (11\%)$
308	0.17	$181 \rightarrow 192 \ (38\%) \ 186 \rightarrow 191 \ (14\%) \ 189 \rightarrow 198 \ (20\%)$
308	0.17	$181 \rightarrow 191 \; (38\%) \; 186 \rightarrow 192 \; (14\%) \; 188 \rightarrow 198 \; (20\%)$
305	0.33	$181 \rightarrow 192 \ (16\%) \ 189 \rightarrow 198 \ (48\%) \ 190 \rightarrow 200 \ (23\%)$
305	0.34	$181 \rightarrow 191 \ (16\%) \ 188 \rightarrow 198 \ (48\%) \ 190 \rightarrow 101 \ (23\%)$
288	0.53	$189 \to 199 \ (90\%)$
288	0.53	$188 \to 199 \ (90\%)$
3a (Th1)		
591	0.46	$191 \to 192 \ (90\%)$
554	0.39	$188 \to 192 \ (14\%) \ 191 \to 193 \ (77\%)$
361	0.23	$189 \to 194~(43\%)~189 \to 195~(25\%)~190 \to 194~(10\%)~190 \to 195~(18\%)$
321	0.15	$186 \rightarrow 193 \ (29\%) \ 189 \rightarrow 197 \ (57\%)$
316	0.18	$179 \rightarrow 192 \ (65\%) \ 184 \rightarrow 192 \ (4\%)$
314	0.36	$179 \rightarrow 192 \ (17\%) \ 182 \rightarrow 192 \ (33\%) \ 184 \rightarrow 192 \ (8\%) \ 187 \rightarrow 192 \ (14\%)$
311	0.38	$182 \to 192~(50\%)~184 \to 192~(5\%)~187 \to 192~(10\%)$
307	0.34	$189 \rightarrow 199 \ (39\%) \ 189 \rightarrow 200 \ (37\%)$
297	0.43	$178 \rightarrow 192 \ (21\%) \ 180 \rightarrow 193 \ (21\%) \ 190 \rightarrow 199 \ (10\%) \ 190 \rightarrow 200 \ (22\%)$
297	0.24	$178 \rightarrow 192 \ (54\%) \ 184 \rightarrow 193 \ (3\%) \ 190 \rightarrow 200 \ (12\%)$
293	0.25	$180 \rightarrow 193 \ (38\%) \ 188 \rightarrow 203 \ (31\%) \ 190 \rightarrow 200 \ (11\%)$
287	0.18	$176 \rightarrow 193 \ (30\%) \ 190 \rightarrow 201 \ (56\%)$
281	0.15	$189 \rightarrow 201 \ (60\%) \ 190 \rightarrow 202 \ (28\%)$
4a (Th2op)		
620	0.50	$192 \to 193 \ (98\%)$
544	0.42	$192 \to 194 \; (94\%)$
358	0.21	$190 \rightarrow 195 \ (83\%) \ 191 \rightarrow 196 \ (14\%)$
345	0.13	$186 \rightarrow 193 \ (20\%) \ 190 \rightarrow 197 \ (69\%)$
329	0.13	$185 \to 193 \ (92\%)$
324	0.17	$186 \to 193~(34\%)~187 \to 193~(14\%)~191 \to 199~(22\%)~192 \to 203~(16\%)$
310	0.97	$184 \to 193\;(10\%)\;187 \to 193\;(17\%)\;190 \to 197\;(10\%)\;191 \to 199\;(36\%)$
305	0.23	190 → 201 (75%)
291	1.23	$184 \to 194~(14\%)~187 \to 194~(13\%)~191 \to 202~(50\%)$

Table 4. Calculated transition energies, oscillator strengths f, and configurations.

Excited states with energy less than 4.5 eV, f greater than 0.10, and contribution greater than 10% are shown (except for **3a**).

5a (Th2ad)			
600	0.11	$190 \rightarrow 193 \ (41\%) \ 191 \rightarrow 194 \ (26\%) \ 192 \rightarrow 193 \ (31\%)$	
578	0.45	$192 \to 194 \ (95\%)$	
576	0.34	$191 \to 194 \ (25\%) \ 192 \to 193 \ (63\%)$	
360	0.24	$190 \rightarrow 195 \ (45\%) \ 191 \rightarrow 196 \ (49\%)$	
306	0.37	$182 \to 194~(12\%)~183 \to 193~(24\%)~189 \to 204~(19\%)~190 \to 201~(14\%)$	
304	0.23	$183 \to 193~(22\%)~184 \to 193~(24\%)~188 \to 193~(16\%)~191 \to 199~(11\%)$	
303	0.27	$183 \rightarrow 194 \ (47\%) \ 190 \rightarrow 199 \ (26\%)$	
302	0.72	$183 \to 194~(32\%)~188 \to 194~(13\%)~190 \to 199~(18\%)$	
280	0.17	$190 \to 203 \ (79\%)$	
277	0.21	$190 \rightarrow 202 \ (18\%) \ 191 \rightarrow 203 \ (66\%)$	
6a (Th3)			
608	0.47	$193 \to 194 \ (97\%)$	
568	0.41	$193 \to 195 \ (88\%)$	
358	0.21	$191 \to 198~(61\%)~192 \to 197~(24\%)$	
355	0.14	$192 \rightarrow 196~(69\%)~193 \rightarrow 200~(17\%)$	
351	0.15	$191 \to 196~(75\%)~191 \to 198~(10\%)$	
318	0.13	$188 \rightarrow 195 \ (45\%) \ 191 \rightarrow 199 \ (32\%)$	
312	0.15	$181 \to 194~(12\%)~186 \to 194~(31\%)~187 \to 194~(18\%)~188 \to 195~(14\%)$	
309	0.13	$181 \to 194 \ (58\%) \ 191 \to 199 \ (13\%)$	
302	0.41	$183 \rightarrow 194 \ (45\%) \ 184 \rightarrow 194 \ (22\%)$	
296	0.19	$191 \rightarrow 200 \ (53\%) \ 191 \rightarrow 203 \ (18\%)$	
296	0.12	$179 \rightarrow 194 \ (59\%) \ 192 \rightarrow 203 \ (21\%)$	
296	0.53	$184 \rightarrow 195~(53\%)~187 \rightarrow 195~(13\%)$	
295	0.21	$179 \to 194~(16\%)~183 \to 194~(11\%)~192 \to 193~(55\%)$	
278	0.17	$183 \to 195 \ (16\%) \ 192 \to 204 \ (67\%)$	
7a (Th4)			
599	0.44	$194 \to 195 \ (97\%)$	
599	0.44	$194 \to 196 \ (97\%)$	
358	0.25	$192 \rightarrow 199 \ (48\%) \ 193 \rightarrow 198 \ (48\%)$	
357	0.19	$193 \rightarrow 197 \ (82\%) \ 194 \rightarrow 202 \ (10\%)$	
357	0.19	$192 \rightarrow 197 \ (82\%) \ 194 \rightarrow 201 \ (2\%)$	
323	0.15	$187 \to 195 \ (19\%) \ 190 \to 196 \ (40\%) \ 193 \to 200 \ (24\%)$	
323	0.15	$187 \to 196 \ (19\%) \ 190 \to 195 \ (40\%) \ 192 \to 200 \ (24\%)$	
310	0.33	$190 \rightarrow 196 \ (22\%) \ 193 \rightarrow 200 \ (67\%)$	
310	0.33	$190 \rightarrow 195 \ (22\%) \ 192 \rightarrow 200 \ (67\%)$	
303	0.20	$182 \to 195 \ (19\%) \ 186 \to 195 \ (42\%) \ 187 \to 195 \ (31\%)$	
303	0.20	$182 \to 196 \ (19\%) \ 186 \to 196 \ (42\%) \ 187 \to 196 \ (31\%)$	
295	0.49	$185 \to 195 \ (83\%)$	
295	0.49	$185 \to 196 \ (83\%)$	
283	0.18	193 → 205 (93%)	
283	0.18	182 → 205 (93%)	

Table 4. Calculated transition energies, oscillator strengths *f*, and configurations (continued).

Excited states with energy less than 4.5 eV, f greater than 0.10, and contribution greater than 10% are shown.

Caption to Tables

Table 1. Partial bond distances of tetraazaporphyrins **3–8**.

Calculated bond distances for **3a**, **4a**, **5a**, **6a**, **7a**, and **8** were obtained by the DFT method (*vide infra*). To simplify the calculations, all of the phenyl groups of **3**, **4**, **5**, **6** and **7**, were substituted with protons.

Table 2. ¹H NMR chemical shifts of 4-methylpyridine and ax-Ru-N bond lengths.

4-MePy: 4-methylpyridine; Calculated chemical shifts and ax-Ru-N (Å) for **3a**, **4a**, **5a**, **6a**, **7a**, and **8** were obtained by the DFT method (*vide infra*). To simplify the calculations, all of the phenyl groups of **3**, **4**, **5**, **6** and **7** were substituted with protons.

Table 3. Oxidation and reduction potentials of tetraazaporphyrins.

The oxidation and reduction potentials were measured by cyclic voltammetry using Ag/AgNO₃ as a reference electrode, Pt as a counter electrode, and glassy carbon as a working electrode (solvent: CH_2Cl_2 , scan rate: 200 mVs⁻¹); ^airreversible; ΔE obs = 1st Oxid – 1st Redn.

Table 4. Calculated transition energies, oscillator strengths f, and configurations. Excited states with energy less than 4.0 eV, f greater than 0.10, and contribution greater than 10% are shown.

Graphical Abstract (Figure)



Ruthenium complexes of diphenylthiophene-fused low-symmetrical phthalocyanine analogues have been synthesized and characterized and their optical and electrochemical properties examined by electronic absorption, magnetic circular dichrosm spectroscopy, and redox potential measurements. These properties were interpreted by the help of molecular orbital (MO) calculations.

