DOI: 10.1002/asia.201000822

A Vanadium Porphyrin with Temperature-Dependent Phase Transformation: Synthesis, Crystal Structures, Supramolecular Motifs and Properties

Wentong Chen,[a, b] Tomoyoshi Suenobu,[a] and Shunichi Fukuzumi*[c]

Abstract: A vanadium porphyrin, V(O)TMeOPP (**1**; TMeOPP = 5, 10, 15, 20-tetrakis(4-methoxyphenyl)-21H, 23H-porphyrin), has been synthesized by solvothermal reactions and characterized by single-crystal X-ray diffractions at room temperature and low temperature to reveal two different structures **1R** and **1L**, respectively. Both **1R** and **1L** crystallized in the orthorhombic system, but their space groups were different: *Pbca* and $Pca2_1$ for **1R** and **1L**, respectively. The cell parameters of *a*, *b*, and *c* were different and the cell volume of **1R** was larger than that of **1L** by circa 200 Å^3. **1R** and **1L** were characteristic of an isolated motif with a five-coordinate vanadium(IV) ion and a saddle-distorted nonplanar porphyrin macrocycle. Molecules of **1R** were interconnected through hydrogen-bonding interactions to yield a 3D framework; whilst for the low-temperature phase **1L**, there were more hydrogen-bonding interactions that link the molecules to construct a more-complex 3D supramolecular network. In a solution of acetone, the title compound exhibited purple and green colors at room temperature and low temperature, respectively, which is unprecedented for vanadium porphyrins. The spectral data of UV/Vis, FT-IR, and MALDI-TOF-MS of **1R** and **1L** are reported together with the electrochemical data.

Keywords: phase transformation · porphyrins · saddle distortion · supramolecular chemistry · vanadium

Introduction

In recent years, the phase transformations of compounds have attracted increasing interest owing to their application in forming well-defined nano-sized apparatus and functional supramolecules at the molecular level.[1–9] In general, a phase transformation of a compound would take place when the compound is stimulated by a proper stimulus from outside, such as heat, pressure, optical, electronic, or magnetic field and so forth. Until now, many compounds that display phase transformations have been documented, among which, many are inorganic compounds, such as $Cu_{12}Sb_4S_{13}$,[10] $Ba_{4-x}Sr_xNaSb_3O_{12}$,[11] $SrZrO_3$,[12,13] $Ba_2Bi_2O_6$,[14] Sr_2CoWO_6,[15,16] $LaSeTe_2$[17] and so on. However, organic compounds that show phase transformations are relatively rare.[18,19]

Porphyrins are one of the most-widely studied chemical systems owing to their plentiful properties, and the crucial roles they play in nature, such as in green leaves and red blood cells, have been discovered for many years, as well as their applications in optics, catalysis, magnetism, medicine, solar-energy conversion, conductive materials and so forth.[20–31] The coordination of a metal ion at the center of a porphyrin ring, as well as the substitution of the periphery of a porphyrin ring by suitable organic groups, provides various programming elements for the design of novel porphyrin compounds. Therefore, extensive efforts have been devoted to preparing a variety of metalloporphyrin compounds that bear reformative characteristics that may have possible practical applications.[32–36] However, to the best of our knowledge, there are no reports of metalloporphyrins with phase transformations. Among various metalloporphyrins, vanadium porphyrins merit special attention because they

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[a] Dr. W. Chen, Dr. T. Suenobu
Department of Material and Life Science
Graduate School of Engineering
Osaka University, Suita
SORST (Japan) Science Technology Agency
Osaka 565-0871 (Japan)
Fax: (+81) 6-6879-7370

[b] Dr. W. Chen
School of Chemistry and Chemical Engineering
Jinggangshan University
Ji'an, Jiangxi 343009 (China)

[c] Prof. S. Fukuzumi
Department of Bioinspired Science
Ewha Womans University
Seoul 120-750 (Korea)

Supporting information for this article, including X-ray crystallographic files in CIF format for **1**, IR spectra, MALDI-TOF-MS spectra, UV/Vis absorption spectra, and photos, is available on the WWW under http://dx.doi.org/10.1002/asia.201000822.

are known as a new class of anti-HIV agents.[37] Compared with other vanadium complexes as potential therapeutics,[38,39] vanadium porphyrins are stable and seldom become demetalated.

Herein, we report the synthesis, X-ray crystal structures, and properties of V(O)TMeOPP (**1**), which displays temperature-controlled phase transformation. V(O)TMeOPP was characterized in detail by single-crystal X-ray diffraction, elemental analysis, UV/Vis, FT-IR, MALDI-TOF-MS, and electrochemical techniques, such as cyclic voltammetry (CV) and differential pulse voltammetry (DPV).

It should be pointed out that compound **1** exhibits different supramolecular motifs, **1R** and **1L**, at room temperature and low temperature, respectively. Such a temperature-dependent change in the supramolecular motif has rarely been observed.[40] It is also noteworthy that compound **1** showed purple and green colors at room temperature and low temperature, respectively.

Results and Discussion

General Characterization

The IR spectra of the title compound exhibit similar characteristics to TMeOPP and the bands mainly appeared in the range of 700–1600 cm^{-1} (see the Supporting Information, Figure S1). The IR spectra of the free base of TMeOPP showed two bands at $\nu \sim 3319$ and $\nu \sim 965$ cm^{-1}, corresponding to the ν_{N-H} and δ_{N-H} vibrations of the pyrrole rings, respectively. However, in the IR spectra of **1** these two bands vanished owing to the deprotonation and the metalation of the pyrrole rings. These results provide evidence for the conversion of the free-based porphyrin into a metalloporphyrin. The strong peak at around 1005 cm^{-1} can be assigned to the V=O stretch.

For **1**, MALDI-TOF-MS analysis in chloroform (matrix: CHCA; reflectron mode) showed a molecular ion peak, which was in good agreement with the corresponding calculated exact mass number (see the Supporting Information, Figure S2). This result implies that compound **1** retained its structure in solution as in the solid state.

Abstract in Chinese:

摘要：通过溶剂热法合成了一个钒卟啉化合物 V(O)TMeOPP (**1**) (TMeOPP = 5, 10, 15, 20-四(4-甲氧基苯基)-21H, 23H-卟啉)。对该化合物进行的单晶 X-射线衍射结构表征揭示出它具有室温和低温下的两种不同的晶体结构 **1R** 和 **1L**。**1R** 和 **1L** 结晶于正交晶系，但是它们具有不同的空间群：分别是 *Pbca* 和 $Pca2_1$。此外它们的晶胞参数也不同，而且 **1R** 的晶胞体积比 **1L** 大了大约 200 $Å^3$。**1R** 和 **1L** 都是孤立的结构，其中的钒(IV)都是五配位的，卟啉大环都是鞍状扭曲的非平面构型。**1R** 中分子通过氢键相互联结构成三维框架，而低温相 **1L** 中通过更多的氢键相互联结构成更复杂的三维超分子框架。在丙酮中，标题化合物室温下显示紫色，而低温下呈现绿色。这在钒卟啉中是首次发现。本文中我们还报道了该化合物的紫外-可见吸收光谱、红外光谱、质谱和电化学性质等。

Crystal Structures of V(O)TMeOPP (1): Room-Temperature Phase (1R)

The molecular structure of **1R** is depicted in Figure 1 (ORTEP). X-ray diffraction analysis reveals that compound **1R** consists of one neutral V(O)TMeOPP molecule and crystallizes in the space group *Pbca*. All crystallographically independent atoms are in general positions. The vanadium(IV) ion is bound by four nitrogen atoms and one oxygen atom to form a five-coordinate square pyramid. The bond lengths from the vanadium ion (at the center of a saddle-distorted nonplanar porphyrin macrocycle) to the pyrrole nitrogens are within 2.043(2)–2.082(2) Å in **1R**, which is comparable with that found in the literature.[43] The bond length between the vanadium and oxygen atoms is 1.582(1) Å, normal for a V=O double bond and comparable with those reported.[44] Bond-valence calculations indicate that the vanadium ion is in the +4 oxidation state [V(1): 4.041].[45] The porphyrin macrocycle in **1R** displays a saddle conformation and the four pyrrole rings appreciably distort in an alternant fashion either upward and downward with respect to the mean plane of the saddle-like porphyrin core. The displacement of the four pyrrole nitrogen atoms are within ±0.008 Å from their mean N4 plane. The dihedral angles between the planes of the four pyrrole rings distorted in the same direction with respect to the N4 plane are 19.47° and 25.57°. The dihedral angles between the neigh-

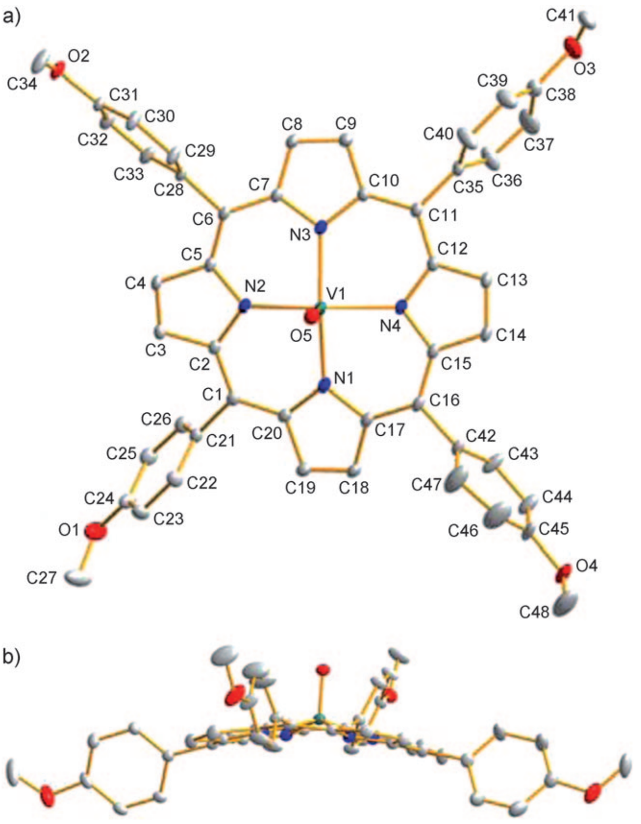

Figure 1. ORTEP drawing of **1R** with 10% thermal ellipsoids. Hydrogen atoms were omitted for clarity. a) perspective view; b) side view.

boring pyrrole rings are 17.00°, 12.10°, 21.32°, and 12.65°. With respect to the N4 plane, which may represent the mean plane of the porphyrin core, the twisted angles of the aryl rings are 78.74°, 70.49°, 68.09°, and 110.21°. In **1R**, some C−H···π and C−H···O interactions link the molecules to construct a 3D supramolecular network (Figure 2).

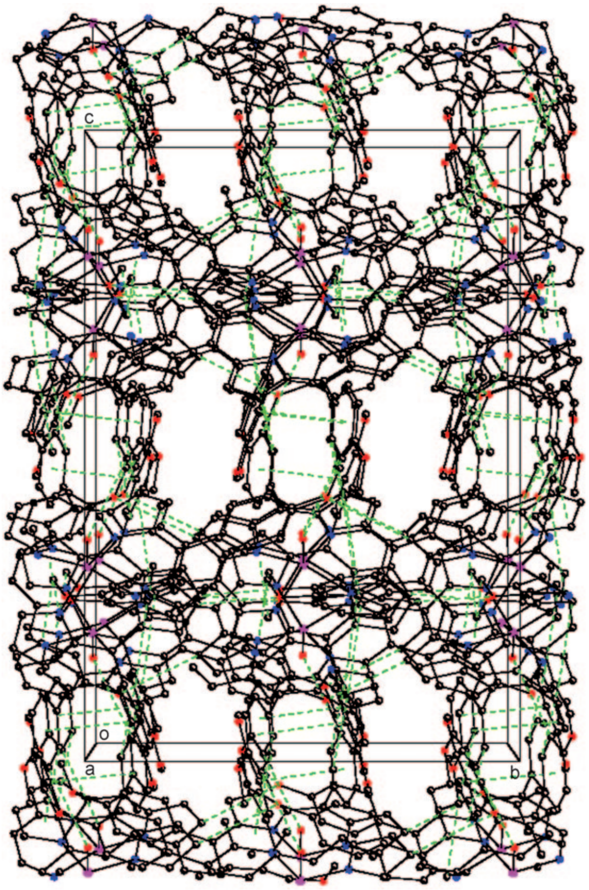

Figure 2. Packing diagram of **1R** with the dashed lines representing hydrogen-bonding interactions. Geometry of represented hydrogen-bonding interactions: C(22)-H(22A)···C_g(1) with $d_{C\cdots Cg}=3.634(3)$ Å and $\measuredangle(\mathrm{DHA})=134.46°$; C(33)-H(33A)···$C_g$(1) with $d_{C\cdots Cg}=3.517(3)$ Å and $\measuredangle(\mathrm{DHA})=118.18°$; C(34)-H(34B)···$C_g$(2) with $d_{C\cdots Cg}=3.516(4)$ Å and $\measuredangle(\mathrm{DHA})=134.23°$; C(39)-H(39A)···$C_g$(3) with $d_{C\cdots Cg}=3.780(4)$ Å and $\measuredangle(\mathrm{DHA})=113.54°$; C(4)-H(4A)···O(4) 3.353(3) Å and $\measuredangle(\mathrm{DHA})=146°$; C(14)-H(14A)···O(2) 3.227(3) Å and $\measuredangle(\mathrm{DHA})=150°$; C(23)-H(23A)···O(5) 3.267(3) Å and $\measuredangle(\mathrm{DHA})=151°$ [C_g(1), C_g(2) and C_g(3) stand for the centers of the gravity of the rings N1(C17-C20), N3(C7-C10) and C21-C26, respectively]. V: magenta; O: red; N: blue; C: gray.

Low-Temperature Phase (1L)

Low temperature X-ray diffraction analysis shows that compound **1L** (Figure 3) crystallizes in the space group $Pca2_1$, which differs from that of **1R** (*Pbca*). There are two crystallographic independent vanadium ions in the crystal structure of **1L**. Each vanadium ion is located at the center of the porphyrin macrocycle and coordinated by four nitrogen atoms and one oxygen atom to yield a square pyramid. The V−N bond lengths range from 2.038(3) to 2.091(3) Å with an average value of 2.066(3) Å, which is close to that of **1R** [2.063(2) Å] and comparable to that found in the literature.[43] The V=O bond lengths are 1.593(2) and 1.594(3) Å, approximately 0.01 Å longer than that of **1R**. The dihedral angles between the porphyrin macrocycle and the mean planes of the aryl rings are in a wide range of 55.24°–117.35°. The assignment of the oxidation states for the vanadium atoms is consistent with the electronic charge, and was confirmed by bond valence sum calculations. The BVS values for the crystallographically independent vanadium atoms, V(1) and V(2), are 3.970 and 3.965, respectively, thereby indicating that the oxidation state for each vanadium atom is +4.[45] The porphyrin macrocycles in **1L** show a saddle conformation and the pyrrole nitrogen atoms exhibit displacements of ±0.012 Å from their mean N4 plane. With respect to the N4 plane, the dihedral angles between the planes of the pyrrole rings (that are distorted in the same direction) are in the range 18.72°–22.08°. In comparison with **1R**, **1L** has more C−H···π and C-H···O interactions, which allow **1L** to form a more-complex 3D supramolecular framework (Figure 4). It should be pointed out that the supramolecular motifs of **1R** and **1L** differ greatly when they viewed along the same direction, for instance, along the *a* axis in Figure 2 and 4.

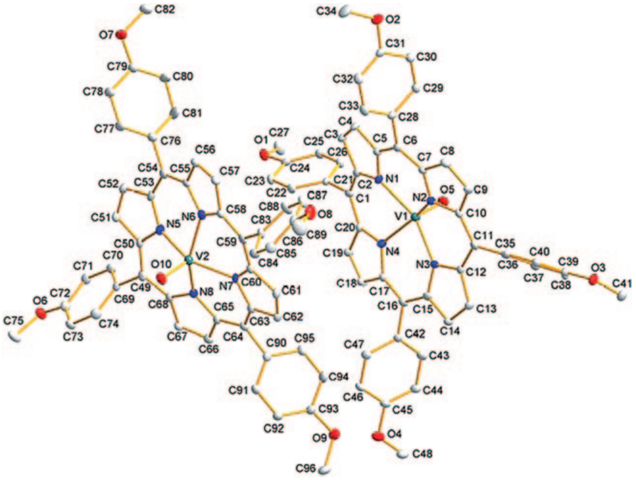

Figure 3. ORTEP of **1L** with thermal ellipsoids set at the 20 % probability level. Hydrogen atoms were omitted for clarity.

UV/Vis Absorption Spectroscopy

According to Gouterman's four-orbitals model,[46] metalloporphyrins generally show two types of strong absorption bands: strong Soret bands (B bands) at around 400 nm with an absorption coefficient $\varepsilon \sim 10^5\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$, and several weaker Q bands at around 450–650 nm with $\varepsilon \sim 10^3\text{-}10^4\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$. The UV/Vis absorption spectra for compound **1** and free-based TMeOPP are given in the Supporting Information, Figure S3 and S4, respectively. The B and Q bands for free-based TMeOPP are observed at 422, 454, 519, 556, 595, and 649 nm ($\varepsilon_{422\ \mathrm{nm}}=7.82\times10^5\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$). The B band of compound **1** appears at 427 nm ($\varepsilon=7.51\times10^5\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$), which is

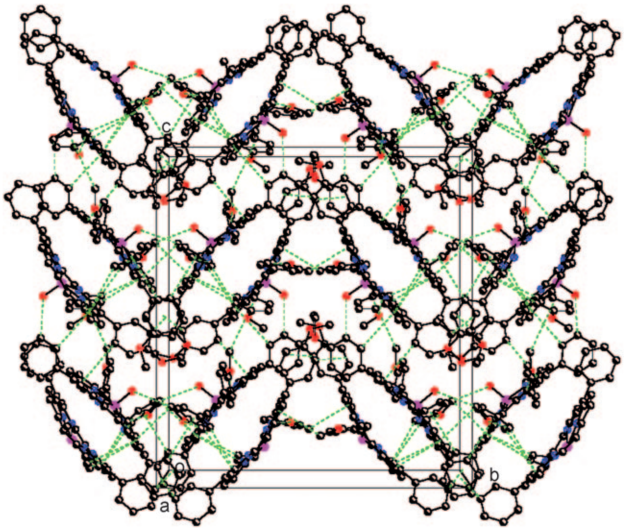

Figure 4. Packing diagram of **1L** with the dashed lines representing hydrogen bonding interactions. Geometry of represented hydrogen bonding interactions: C(27)-H(27C)$\cdots$$C_g$(1) with $d_{C\cdots Cg}=3.545(5)$ Å and $\measuredangle$(DHA)=118.31°; C(87)-H(87A)$\cdots$$C_g$(1) with $d_{C\cdots Cg}=3.661(4)$ Å and $\measuredangle$(DHA)=128.89°; C(88)-H(88A)$\cdots$$C_g$(1) with $d_{C\cdots Cg}=3.761(4)$ Å and $\measuredangle$(DHA)=122.97°; C(77)-H(77A)$\cdots$$C_g$(2) with $d_{C\cdots Cg}=3.530(4)$ Å and $\measuredangle$(DHA)=136.44°; C(22)-H(22A)$\cdots$$C_g$(3) with $d_{C\cdots Cg}=3.833(4)$ Å and $\measuredangle$(DHA)=125.23°; C(23)-H(23A)$\cdots$$C_g$(3) with $d_{C\cdots Cg}=3.853(4)$ Å and $\measuredangle$(DHA)=121.93°; C(43)-H(43A)$\cdots$$C_g$(3) with $d_{C\cdots Cg}=3.612(4)$ Å and $\measuredangle$(DHA)=125.91°; C(75)-H(75A)$\cdots$$C_g$(4) with $d_{C\cdots Cg}=3.436(4)$ Å and $\measuredangle$(DHA)=89.60°; C(75)-H(75C)$\cdots$$C_g$(4) with $d_{C\cdots Cg}=3.436(4)$ Å and $\measuredangle$(DHA)=132.46°; C(29)-H(29A)$\cdots$$C_g$(5) with $d_{C\cdots Cg}=3.574(4)$ Å and $\measuredangle$(DHA)=158.90°; C(92)-H(92A)$\cdots$$C_g$(6) with $d_{C\cdots Cg}=3.541(4)$ Å and $\measuredangle$(DHA)=128.96°; C(41)-H(41C)$\cdots$$C_g$(7) with $d_{C\cdots Cg}=3.788(4)$ Å and $\measuredangle$(DHA)=127.05°; C(9)-H(9A)$\cdots$O(1) 3.203(4) Å and $\measuredangle$(DHA)=145°; C(19)-H(19A)$\cdots$O(3) 3.318(4) Å and $\measuredangle$(DHA)=142°; C(27)-H(27C)$\cdots$O(5) 3.340(5) Å and $\measuredangle$(DHA)=152°; C(61)-H(61A)$\cdots$O(6) 3.215(4) Å and $\measuredangle$(DHA)=148°; C(51)-H(51A)$\cdots$O(8) 3.341(4) Å and $\measuredangle$(DHA)=142°; C(44)-H(44A)$\cdots$O(10) 3.207(4) Å and $\measuredangle$(DHA)=154°. [C_g(1), C_g(2), C_g(3), C_g(4), C_g(5), C_g(6), and C_g(7) stand for the centers of the gravity of the rings N1(C2-C5), N3(C12-C15), N6(C55-C58), N8(C65-C68), C21-C26, C42-C47, and C83-C88, respectively.] V: magenta; O: red; N: blue; C: gray.

red-shifted by 5 nm compared with that of TMeOPP. Compound **1** has only two Q bands, at 550 and 590 nm, as compared with five Q bands in the free-based TMeOPP. This difference is ascribed to an increase in the molecular symmetry, resulting from the metalation of the free-based TMeOPP. The absorption coefficient of the B band for metalloporphyrin **1** is circa $10^5\,\text{M}^{-1}\,\text{cm}^{-1}$, which is in good agreement with the conclusion drawn by Gouterman.[46] The ε values of the B bands for compound **1** and free-based TMeOPP are similar, thus indicating that the metalation of a porphyrin hardly affects the absorption coefficient.

Electrochemical Studies

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements (benzonitrile solvent, room temperature, 0.1 M $TBAPF_6$) were performed for **1** and free-based TMeOPP to investigate their redox properties (Figure 5). Hitherto, the electrochemistry of many vanadyl porphyrins has been researched by several groups.[47] In general, each vanadyl porphyrin undergoes two reactions at the porphyrin π-ring system, yielding a π-anion and a dianion upon reduction and a π-cation and a dication upon oxidation. Similarly, as shown in Figure 5 a, slow sweep CV of **1** exhibits two quasi-reversible waves ($E_{1/2}=0.63$ and 0.90 V), which are close to the values of DPV (0.62 and 0.88 V). Besides these two quasi-reversible waves, there are two successive and well-defined anodic waves (−0.46 and −0.91 V), but no corresponding cathodic bands are observed on the inversed scan. Unlike **1**, the CV of free-based TMeOPP is characterized by two oxidation peaks at 0.50 V and 0.71 V and a reversible redox couple ($E_{1/2}=-1.54$ V), which are close to the values of DPV (0.47, 0.66, −1.55 V), as shown in Figure 5 b. It should be pointed out that the potentials of free-based TMeOPP are negatively shifted compared to those of **1**. The difference in the electrochemical properties between free-based TMeOPP and metalloporphyrins **1** is probably due to the metalation effect.

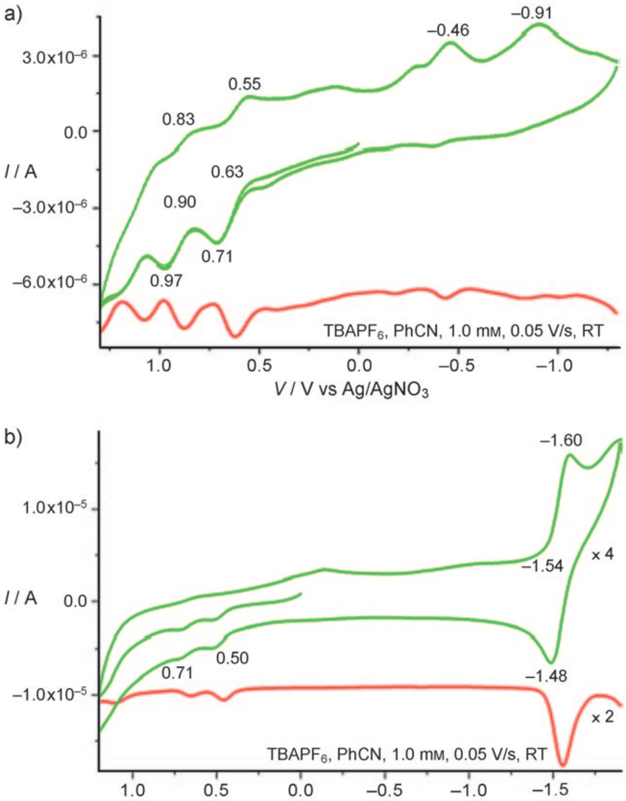

Figure 5. CV and DPV profiles for a) **1**, and b) free-based TMeOPP under an argon atmosphere.

Experimental Section

Measurements

Elemental analyses of carbon, hydrogen, and nitrogen were carried out on an Elementar Vario EL III microanalyser. The infrared spectra were recorded on a Thermo Nicolet NEXUS 870 FT-IR spectrophotometer over the frequency range 4000–400 cm^{-1} (KBr pellet). The UV/Vis absorption spectrosa were recorded at room temperature on a computer-controlled Hewlett Packard 8453 UV/Vis spectrophotometer equipped with 89090 A Peltier temperature controller with the wavelength range of 190–1100 nm. Matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectra were measured on a Kratos Compact MALDI I (Shimadzu).

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed at 298 K using a BAS 100W electrochemical analyzer in a deaerated solvent containing 0.1 M TBAPF$_6$ (tetra-*n*-butylammonium hexafluorophosphate) as a supporting electrolyte. A conventional three-electrode cell was used with a platinum working electrode and a platinum wire as a counter electrode. The measured potentials were recorded with respect to Ag/AgNO$_3$ (1.0×10^{-2} M). All electrochemical measurements were carried out under an atmospheric pressure of argon.

Syntheses

All reactants of analytical reagent grade were obtained commercially and used without further purification. The title compound was prepared by mixing VCl$_3$ (0.1 mmol, 15.7 mg), TMeOPP (0.1 mmol, 73.5 mg), and 10 mL ethanol in a 23 mL Teflon-lined stainless-steel autoclave and heating the mixture at 453 K for 4 days. After slowly cooling the mixture to room temperature at 6 K/h, purple crystals suitable for X-ray analysis were obtained. The yield was 20% (based on vanadium). Anal. Calcd. for $C_{48}H_{36}N_4O_5V$: C 72.02, H 4.50, N 7.00. Found: C 72.12, H 4.82, N 7.06. Fourier transform IR (KBr): $\tilde{\nu}=2996$(w), 2928(w), 2834(w), 2359(w), 1606(s), 1512(s), 1460(m), 1440(m), 1340(s), 1288(s), 1246(vs), 1173(vs), 1105(m), 1073(w), 1037(m), 1005(vs), 849(m), 807(s), 729(m), 666(m) and 635 cm^{-1}(w) (Figure S1). *m*/*z* (MALDI-TOF-MS in CHCl$_3$; matrix: CHCA, that is, α-cyano-4-hydroxycinnamic acid) 799.42 ($C_{48}H_{36}N_4O_5V$ requires 799.21). See the Supporting Information, Figure S2.

X-ray Crystallographic Studies

The X-ray intensity data sets were collected for the same single crystal at two different temperatures (123 and 293 K) on a Rigaku AFC-8 X-ray diffractometer with graphite monochromated Mo$_{K\alpha}$ radiation ($\lambda=0.71073$ Å) using a ω-scan technique. CrystalClear software was used for data reduction and empirical absorption corrections.[41] The structures were solved by direct methods using the Siemens SHELXTL Version 5 package crystallographic software.[42] The difference Fourier maps based on these atomic positions yielded the other non-hydrogen atoms. The positions of the hydrogen atoms were generated theoretically, being allowed to ride on their respective parent atoms, and were included in the structure-factor calculations with assigned isotropic thermal parameters. The structures were refined using a full-matrix least-squares refinement on F^2. All atoms except for hydrogen atoms were refined anisotropically. The summary of crystallographic data and structure analysis is given in Table 1. The selected bond lengths and bond angles are listed in Table 2.

CCDC 772465 (**1L**) and CCDC 772466 (**1R**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal parameters for **1** measured at room temperature (**1R**) and low temperature (**1L**).

Compound	**1R**	**1L**
formula	$C_{48}H_{36}N_4O_5V$	$C_{48}H_{36}N_4O_5V$
Fw	799.75	799.75
color	purple	purple
crystal size/mm3	0.46 0.21 0.17	0.46 0.21 0.17
crystal system	orthorhombic	orthorhombic
space group	*Pbca*	$Pca2_1$
a [Å]	22.387(6)	15.633(3)
b [Å]	15.572(8)	21.429(1)
c [Å]	22.677(8)	23.068(2)
V [Å^3]	7905(6)	7728(2)
Z	8	8
$2\theta_{max}$ [°]	50	50
reflections collected	47581	43252
independent, observed reflections	6843, 5929	12819, 7610
(R_{int})	(0.0435)	(0.2337)
$d_{calcd.}$ [g cm^{-3}]	1.344	1.375
μ(mm^{-1})	0.305	0.312
F(000)	3320	3320
*R*1, *wR*2	0.0968, 0.2486	0.0802, 0.1538
S	0.967	0.868
largest and mean Δ/σ	0.001, 0	0.001, 0
$\Delta\rho$(max, min) (e/Å^3)	1.144, −0.584	0.536, −0.775

Table 2. Selected bond lengths (Å) and bond angles (°).

Compound **1R**			
V(1)-O(5)	1.582(1)	O(5)-V(1)-N(3)	103.37(7)
V(1)-N(1)	2.082(2)	O(5)-V(1)-N(4)	103.99(6)
V(1)-N(2)	2.072(2)	N(2)-V(1)-N(1)	86.07(6)
V(1)-N(3)	2.043(2)	N(3)-V(1)-N(1)	151.64(6)
V(1)-N(4)	2.053(2)	N(3)-V(1)-N(2)	86.09(6)
		N(3)-V(1)-N(4)	87.80(6)
O(5)-V(1)-N(1)	104.99(7)	N(4)-V(1)-N(1)	85.86(6)
O(5)-V(1)-N(2)	105.29(6)	N(4)-V(1)-N(2)	150.71(6)
Compound 1L			
V(1)-O(5)	1.593(2)	N(1)-V(1)-N(3)	152.3(1)
V(1)-N(1)	2.059(3)	N(1)-V(1)-N(4)	85.8(1)
V(1)-N(2)	2.064(3)	N(2)-V(1)-N(3)	85.9(1)
V(1)-N(3)	2.067(2)	N(2)-V(1)-N(4)	151.0(1)
V(1)-N(4)	2.075(3)	N(3)-V(1)-N(4)	86.5(1)
V(2)-O(10)	1.594(3)	O(10)-V(2)-N(5)	104.7(1)
V(2)-N(5)	2.073(3)	O(10)-V(2)-N(6)	105.6(1)
V(2)-N(6)	2.091(3)	O(10)-V(2)-N(7)	104.3(1)
V(2)-N(7)	2.063(3)	O(10)-V(2)-N(8)	102.7(1)
V(2)-N(8)	2.038(3)	N(5)-V(2)-N(6)	86.7(1)
O(5)-V(1)-N(1)	102.4(1)	N(7)-V(2)-N(5)	151.0(1)
O(5)-V(1)-N(2)	104.7(1)	N(7)-V(2)-N(6)	85.5(1)
O(5)-V(1)-N(3)	105.3(1)	N(8)-V(2)-N(5)	86.6(1)
O(5)-V(1)-N(4)	104.3(1)	N(8)-V(2)-N(6)	151.8(1)
N(1)-V(1)-N(2)	88.1(1)	N(8)-V(2)-N(7)	87.2(1)

Conclusions

In conclusion, we have synthesized a vanadium porphyrin, V(O)TMeOPP, by using a solvothermal method, whose crystal structures at room temperature and low temperature were compared by using the same single-crystal. The compound has been characterized by X-ray structural analysis, UV/Vis, FT-IR, MALDI-TOF-MS, and CV/DPV. V(O)TMeOPP showed purple and green colors at room temperature and low temperature (see the Supporting Information, Figure S5), respectively, which is unprecedented for vanadium porphyrins. Future research in our laboratory will focus on other vanadium porphyrins, to gain new insights into the synthesis, crystal structure, and properties, as well as the relationship among them.

Acknowledgements

This work was supported by KOSEF/MEST through WCU project (R31-2008-000-10010-0), a Grant-in-Aid (No. 19205019), and the Global COE program, “the Global Education and Research Center for Bio-Environmental Chemistry” from the Ministry of Education, Culture, Sports, Science and Technology.

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Received: November 16, 2010