Sapphyrin Derivatives

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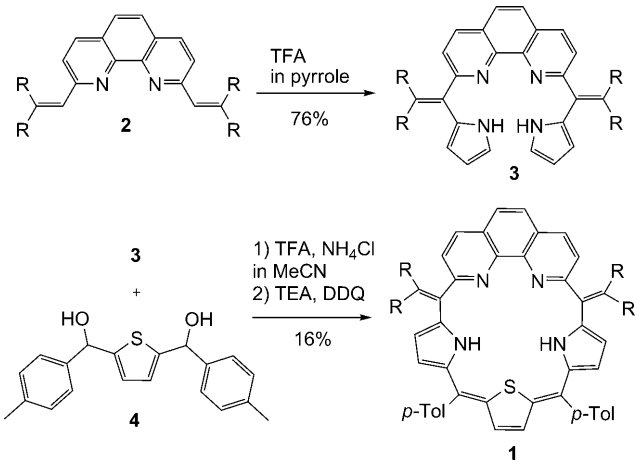
# Protonation-Induced Formation of a Stable Singlet Biradicaloid Derived from a Modified Sapphyrin Analogue**

*Masatoshi Ishida, Satoru Karasawa, Hidemitsu Uno, Fumito Tani, and Yoshinori Naruta**

Development of novel functional molecules, whose magnetic properties can be altered by external perturbations such as photoirradiation, electrochemical reaction, temperature, and chemical treatment, have been the subject of much interest with regard to their potential applications in construction of molecular devices and switches.[1] Among these external stimuli, the protonation process provides a general and reversible means for unique switching phenomena.[2] However, the process of protonation-induced magnetization is poorly understood, because of a limited number of examples on the generation of high-spin molecules (e.g. biradical compounds[3]) by protonation.[4] During the development of these perspectives, the protonation-induced alteration of the macrocyclic π conjugation in porphyrin analogues[5] bearing *meso* exocyclic double bonds have been reported. This has inspired us to synthesize new porphyrin analogues.

Sapphyrin derivatives belong to the family of porphyrinoids which consists of a further expanded 22π-conjugated pentapyrrolic macrocycle. Such compounds have been studied for their potential applications as anion binding agents,[6] photosensitizers for photodynamic therapy (PDT),[7] medicinal drugs,[8] and optical materials.[9] Owing to their intriguing properties, a diverse range of modified sapphyrin analogues has been synthesized by replacing the components of the macrocyclic skeleton of sapphyrin.[10] Such modifications have produced remarkable perturbations of molecular conformations, spectroscopic properties, as well as alterations of metal–ion and/or anion binding properties. In this study, we have synthesized and characterized a novel 1,10-phenanthroline-embedded sapphyrin analogue (**1**) bearing *meso* alkylidenyl double bonds. Unprecedentedly, we have found that the protonated form of **1** exhibits singlet biradicaloid character, while the related pyriporphyrins,[5a,11] which incorporated a pyridine unit in their macrocycles, only gave the corresponding protonated derivatives upon addition of an acid.

The sapphyrin analogue **1** was synthesized by the "4+1" condensation strategy of the 1,10-phenanthroline-containing tetrapyrrane analogue **3** with thiophene carbinol **4** (Scheme 1). The tetrapyrrane **3** was obtained by trifluoroacetic acid (TFA) catalyzed condensation of 1,10-phenanthroline bisvinyl derivatives **2** in an excess amount of freshly distilled pyrrole and provided a pale yellowish solid in 76% yield. In the final cyclization step, **3** was treated with **4** in MeCN in the presence of TFA and $NH_4Cl$, neutralized with triethylamine (TEA), and oxidized with 2,3-dichloro-5,6-dicyano1,4-benzoquinone (DDQ), and afforded the desired sapphyrin analogue **1** as a purple solid in 16% yield. In this cyclization reaction, neutralization with TEA is essential to obtain the desired compound **1** before oxidation with DDQ. When DDQ was added to the reaction mixture without neutralization with TEA, the yield of **1** decreased to 3%. The formation of **1** was confirmed by NMR and high-resolution fast atom bombardament (FAB) mass spectroscopic experiments, as well as elemental analysis. The $^1$H NMR spectrum of **1** does not exhibit evidence of macrocyclic π-conjugation. Both the β-pyrrolic and thiophenic protons resonate in the typical alkene proton range and the inner pyrrolic NH resonances are significantly shifted downfield to $\delta = 8.83$ ppm (Figure S1a in the Supporting Information). This interruption of full conjugation is caused by the presence of stable exocyclic double bonds at the *meso* positions.




***Scheme 1.*** Synthesis of **1**. R = COOEt, Tol = tolyl.

The crystal structure[12] of **1** exhibits severe distortion of the macrocycle with significant bending at the *meso*-exo

[*] Dr. M. Ishida, Prof. Dr. F. Tani, Prof. Dr. Y. Naruta
Institute for Materials Chemistry and Engineering
Kyushu University, Fukuoka, 812-8581 (Japan)
Fax: (+89) 92-642-2731
E-mail: naruta@ms.ifoc.kyushu-u.ac.jp
Prof. Dr. S. Karasawa
Graduate School of Pharmaceutical Sciences
Kyushu University, Fukuoka, 812-8582 (Japan)
Prof. Dr. H. Uno
Graduate School of Science and Engineering
Ehime University, Matsuyama, 790-8577 (Japan)

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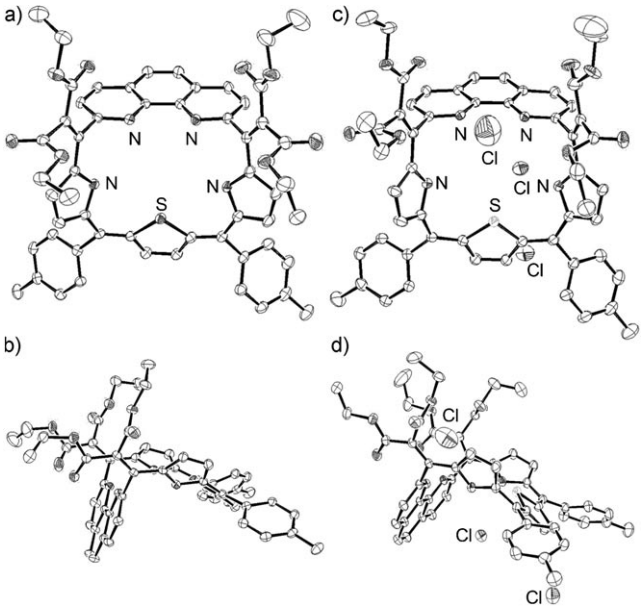


***Figure 1.*** ORTEP plots of **1**·($CHCl_3$)·(hexane) and **1·3 HCl**·2 (MeOH)·5 ($H_2O$). Top views; a) and c) and side views; b) and d) are shown, respectively. Thermal ellipsoids are shown at the 50% probability level. Cocrystallized solvent molecules and hydrogen atoms are omitted for clarity.

double bond positions (Figure 1 a and b and Figure S2a in the Supporting Information). The 1,10-phenanthroline moiety lies essentially perpendicular to the tripyrrane plane and each of the pyrrole rings, which are connected through the *meso* carbon atoms of the double bond, are slightly inclined toward the inside of the cavity.

During the reaction of **1** with TFA in $CHCl_3$ the clear solution changes from purple to brown. The changes in the near-infrared (NIR) region of the UV/Vis absorption spectrum, which accompanies this color change, include the appearance of a broad band extending to 1400 nm as well as a characteristic absorption at 766 nm (Figure 2). The emergence of the absorption at 766 nm implies that the protonation-induced alteration of the macrocyclic π-conjugation

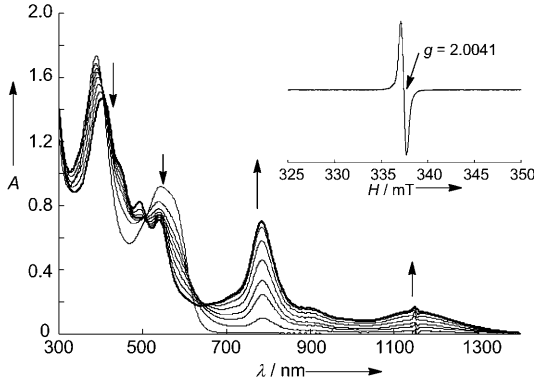


***Figure 2.*** UV/VIS-NIR spectroscopic change of **1** upon titration with TFA in $CHCl_3$ ([**1**] = $4\times10^{-5}$ M). The arrows show the increase of acid concentration (up to [TFA] = 0.2 M). Inset shows the solid ESR spectrum of **1·3 TFA** at room temperature.

pathway is similar to that of the corresponding porphyrin analogue.[5] Similar features of the UV/Vis-NIR absorption spectrum are observed for the protonated **1** upon addition of trichloroacetic acid (TCA). This outcome suggests that the presence of the acid does not affect the formation of this protonated species of **1** (Figure S3 in the Supporting Information). To characterize the structure of the protonated form of **1** in detail, the $^1$H NMR spectrum was measured in $CDCl_3$/TFA (100:1, v/v; Figure S1b in the Supporting Information). However, the protonated form of **1** does not exhibit clear signals in the $^1$H NMR spectrum. Subsequently, we obtained single crystals of the protonated form of **1**, which were prepared using concentrated aqueous HCl, and successfully characterized the structure[12] by X-ray crystallographic analysis (Figure 1 c and d and Figure S2b in the Supporting Information). Two chloride anions are located near the nitrogen atoms of the 1,10-phenanthroline moiety and one of the pyrrole groups. This arrangement implies that the chloride anions are involved in intermolecular hydrogen bonds with the NH groups of the 1,10-phenanthroline and pyrrole units, respectively. Another chloride anion is located within the complicated hydrogen-bonding network constructed by the cocrystallized solvent molecules (Figure S4 in the Supporting Information). This result indicates that the hydrochloric acid complex of **1** has a tricationic form (**1·3 HCl**), which is consistent with the elemental analyses of the other acid salts of TFA (**1·3 TFA**) and TCA (**1·3 TCA**) prepared by the same procedure. Importantly, the π-conjugation system of the macrocycle in **1·3 HCl** seems to be altered upon protonation as evident by the bond lengths and $C_\alpha$-N-$C_\alpha$ bond angles of pyrrole rings without overall structral change. There are significant similarities between the conjugative pathway in **1·3 HCl** and that of the protonated thia-*p*-benziporphyrin species (Figure S5 in the Supporting Information).[13] Furthermore, **1·3 HCl** is in the oxidized state during the protonation process as evidenced by our structural data (see below).

To our surprise, each of the ESR spectra of the isolated solids of **1·3 TFA**, **1·3 TCA**, and **1·3 HCl** at room temperature exhibit a relatively broad signal centered at $g = 2.004$ for all the salts (Figure 2 and Figure S6 in the Supporting Information). These results indicate that an organic radical-like species has been generated upon protonation. The intensity of the ESR signal of **1·3 TFA** in solution was also observed with a lower spin concentration (Figure S7 in the Supporting Information), and did not change after standing for 24 hours under ambient conditions in the solid state. This outcome indicates that the product is a highly stable radical species even in the presence of air and moisture.

To gain further insights into this protonated species of **1**, the temperature-dependent magnetic susceptibility of **1·3 TCA**, which is thermally more stable than **1·3 TFA**,[14] was measured over the range of 4–400 K (Figure 3). The $\chi_p T$ value of **1·3 TCA** was found to be quite small at room temperature relative to the corresponding value of 0.375 emu K mol$^{-1}$ for the general monoradical species. Although the $\chi_p T$ value below 250 K was almost zero, the value gradually increased upon warming from 250 K and reached 0.115 emu K mol$^{-1}$ at 400 K. The thermal reversibility

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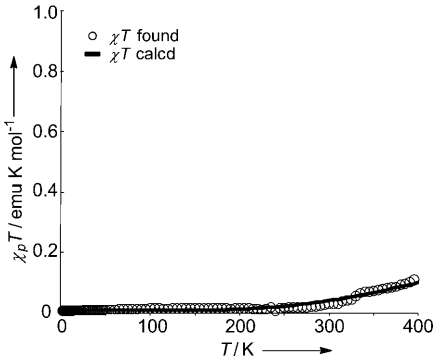
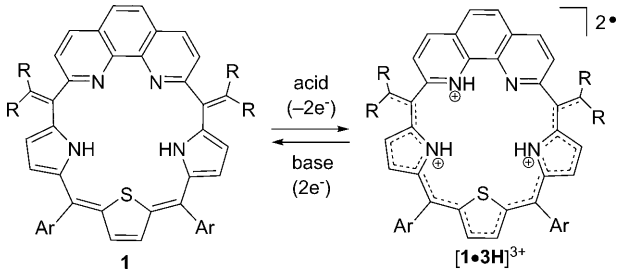



***Figure 3.*** Temperature-dependent SQUID magnetic susceptibility of **1·3TCA.** The measured data is plotted as open circles, and the fitting curve is drawn using the Bleaney–Bowers equation with $g = 2.0040$.




***Scheme 2.*** Conversion between closed-shell **1** and singlet biradicaloid of $[\mathbf{1{\cdot}3H}]^{3+}$. R = COOEt, Ar = *p*-tolyl.

of this sample of **1·TCA** is reproducible. Taking into consideration the various spectroscopic results, the protonated **1·3TCA** has a singlet biradicaloid electronic structure[15] in its ground state with a singlet and triplet energy gap of $J_{S\text{-}T} = -470\ cm^{-1}$ calculated from the Bleaney–Bowers equation.[16] Such a large value is due to the strong antiferromagnetic intramolecular coupling interaction between two unpaired electrons. According to the spin alteration rule, such exchange coupling could depend upon the topology and conformation of the coupling pathway connecting the radicals. These trends are in agreement with the larger negative *J* value observed in our proposed model (Figure S9 in the Supporting Information).[17]

The redox potentials of **1·3TFA** were measured by cyclic voltammetry and differential pulse voltammetry in a solution of TFA/$CH_2Cl_2$ (1:100, v/v; Figure S10 and Table S1 in the Supporting Information). The measurements for **1·3TFA** indicate two quasireversible oxidation waves at 0.02 and 0.18 V (vs, $Fc/Fc^+$), respectively and one irreversible reduction wave at −0.62 V. The HOMO–LUMO energy gap of **1·3TFA** is estimated to be 0.64 V, which is much smaller than that for the original **1** (1.81 V). Thus, **1·3TFA** possesses frontier orbitals with a nonbonding molecular orbital character arising from a weak perturbation between singly occupied molecular orbitals and the frontier orbitals of the tripyrrane conjugated system. **1·3TFA** does not exhibit fluorescence emission, presumably because its low-lying electronic states in the NIR region play an important role in relaxation of the excitation-energy processes. This outcome is consistent with the characteristics of the biradicaloid of biscorrole[15i] and the monoradical of [26]hexaphyrin[18] (Figure S11 in the Supporting Information).

The reaction of **1** with acid provides the oxidized tricationic form of **1** ($[\mathbf{1{\cdot}3H}]^{3+}$), which is defined as a singlet biradicaloid (Scheme 2). With regard to the mechanism of formation, Lee and co-workers[5] have reported that the protonation occurs at the α carbon of the diethyl malonyl groups to provide the fully π-conjugated species, which is obtained for similar porphyrin analogues upon addition of acid. This α protonation is expected to occur for our sapphyrin analogue **1**, which includes a similar heterotripyrrin conjugated moiety. However, we could not characterize the corresponding species under the present conditions, presumably because the subsequent oxidation reaction to form $[\mathbf{1{\cdot}3H}]^{3+}$ is accompanied by steric interactions with the *meso* substituents. The redox-active π-conjugated tripyrrin unit can adopt two oxidation states along with alterations of the π system, which are similar to the conversion from [20π]isophlorin into [18π]porphyrin as a dicationic species by oxidation with acids (Scheme S1 in the Supporting Information).[19,20] Consequently, $[\mathbf{1{\cdot}3H}]^{3+}$ could be identified as an oxidized form upon addition of acid. Evidently, the direct treatment of **1** with oxidants such as DDQ or cerium ammonium nitrate without the addition of acid does not generate the biradicaloid. This result implies that the protonation crucially contributes to the formation of $[\mathbf{1{\cdot}3H}]^{3+}$ (Figure S13 in the Supporting Information).[21]

Considering that expanded quinoidal oligothiophenes[15d,g] with terminal dicyanomethylene groups have singlet biradicaloid character in the ground state, it is reasonable to conclude that the π-conjugated form of $[\mathbf{1{\cdot}3H}]^{3+}$ could be represented by the resonance of the closed-shell quinoid Kekulé structure and the biradicaloid form (Scheme S2 in the Supporting Information). The switchable tripyrrin subunit of $[\mathbf{1{\cdot}3H}]^{3+}$ might be a thermodynamically more favorable singlet biradical form relative to the singlet Kekulé structure. The triplet biradical form of $[\mathbf{1{\cdot}3H}]^{3+}$ is proposed to be in thermal equilibrium with a singlet state, which was assumed to exist on the basis of the temperature dependence of the magnetic susceptibility and the ESR activity energetically populated at room temperature.[22] The high stability of the singlet biradicaloid in $[\mathbf{1{\cdot}3H}]^{3+}$ may be rationalized by delocalization of the unpaired electrons over the extensive π-conjugated system. In addition, it was found that this structural combination of the embedded 1,10-phenanthroline unit with the thiatripyrrin conjugation in **1** is critical for the formation of a singlet biradicaloid of $[\mathbf{1{\cdot}3H}]^{3+}$ upon addition of acids (Figure S15 in the Supporting Information). Finally, the neutrization of the biradicaloid $[\mathbf{1{\cdot}3H}]^{3+}$ by TEA gave the original **1** in 48 % yield, which implies the redox conversion of the open-shell $[\mathbf{1{\cdot}3H}]^{3+}$ into the closed-shell **1**.

In summary, we have synthesized and characterized a novel 1,10-phenanthroline-embedded sapphyrin analogue **1** bearing *meso* alkylidenyl double bonds. Interestingly, protonation of the sapphyrin **1** by acid reagents resulted in an unprecedented, stable biradicaloid species, which was characterized by various spectroscopic methods as well as electro-

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chemical and magnetic susceptibility measurements. The mechanism of formation of a stable biradicaloid of the sapphyrin-related macrocycle induced by the protonation process is also quite interesting from the point of view of fundamental physical organic chemistry. This acid-triggered conversion from closed-shell molecules into biradicaloid species provides a significant opportunity for development of functional molecular magnetic materials.

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[12] Crystallographic data for **1**: $C_{64}H_{67}O_9N_4Cl_3S$, $M_w = 1174.67$, purple, triclinic, Space Group $P\bar{1}$, $a = 13.904(4)$, $b = 13.881(4)$, $c = 16.313(5)$ Å, $\alpha = 87.34(2)$, $\beta = 96.58(2)$, $\gamma = 102.77(2)°$, $V = 3049.7(15)$ Å$^3$, $Z = 2$, $D_{calcd} = 1.279$ g cm$^{-3}$, $F_{000} = 1236.00$, $R_1$ $(I > 2.00\sigma(I)) = 0.0710$, $_wR_2$ (All data) $= 0.1845$, GOF $= 1.023$. Crystallographic data for **1·3HCl**: $C_{58}H_{72}Cl_3N_4O_{14}S$, $M_w = 1180.69$, brown, triclinic, space group, $P\bar{1}$, $a = 12.635(3)$, $b = 14.945(4)$, $c = 17.703(5)$ Å, $\alpha = 98.107(13)$, $\beta = 107.022(12)$, $\gamma = 105.122(15)°$, $V = 3032.6(15)$ Å$^3$, $Z = 2$, $R_1$ $(I > 2.00\sigma(I)) = 0.0890$, $R_w$ (all data) $= 0.2486$, GOF $= 1.336$ CCDC 758900 (**1**) and 758901 (**1·3HCl**) 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.

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