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Synthesis and physicochemical properties of some 5,15-diarylporphyrin derivatives

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Abstract

Several derivatives of *meso*-5,15-diarylporpyrins (**1**–**4**) and their metal complexes were prepared and their physicochemical properties were studied. Their magnetic properties were characterized by SQUID magnetometer. The temperature dependence of the molar magnetic susceptibility of the copper and vanadyl complex of 5,15-diphenylporphyrin (**1-Cu**, **1-VO**) obeyed the Curie law and were almost identical with those of corresponding *meso*-tetraphenyl derivatives. In addition to the magnetic properties of disubstituted porphyrins, the properties of Langmuir film of *meso*-disubstituted porphyrins **2-H$_2$** were investigated by π–A isotherms and visible absorption spectra.

Keywords: Molecular-based magnetism; Diaryl porphyrin; Magnetic property; Monolayer

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1. Introduction

Transition metal complexes of porphyrin have been widely used in the field of molecular magnetism as paramagnetic spin units for polymer pendant groups [1] and ion radical centers [2] as well as electron-donor component for charge-transfer complexes [3,4]. For this architecture, conventional 5,10,15,20-tetraphenylporphyrins and 2,3,7,8,12,13,17,18-octaethylporphyrins are commonly used, while other skeletons are rarely used. We have been interested in the chemistry of 5,15-diarylporphyrins because of their unique structures. 5,15-Diphenylporphyrin itself was originally reported by Treibs and Häberle [5], however, the synthetic chemistry of 5,15-diarylporphyrins was not developed because starting 2,2′-dipyrromethane needed multi-step synthesis. After Wang and Bruce devised convenient and simple synthetic routes of dipyrromethane [6], the synthetic feasibility for chemical modification of *meso*-10,20-positions attracted synthetic chemists to 5,15-diarylporphyrins [7]. In addition, the absence of two *meso*-substituents in *trans* positions is expected to drive close contact between π-systems. Recently, Bond et al. reported the crystal structures of a series of diarylporphyrins [8]. According to their report, offset π–π interactions were often observed in diarylporphyrin crystals. These features are expected to provide unique electronic characteristics. We have already reported the disubstituted porphyrin derivatives as an intermediate of tetrasubstituted ones exhibiting self-organization in solution induced by intermolecular hydrogen bonding and metal coordination [9]. The physicochemical properties of disubstituted porphyrins themselves have not been studied in detail. In the present paper, the copper and vanadyl complexes of 5,15-diphenylporphyrin (**1-Cu**, **1-VO**) were prepared (Chart 1). Their magnetic properties were characterized by ESR and SQUID magnetometer.

While there have been a lot of studies on LB films of tetrasubstituted porphyrins, those of *meso*-disubstituted ones have not been reported [10]. In addition to the magnetic properties of disubstituted porphyrins, the properties of LB films of *meso*-disubstituted porphyrins **2-H$_2$** (Chart 1) and *meso*-tetrasubstituted porphyrin **3-H$_2$** were investigated by π–A isotherms and visible absorption spectra.

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2. Experimental

2.1. Synthesis

5,15-Diphenylporphyrin **1-H$_2$** was synthesized using a condensation reaction [11]. 5,15-Diphenylporphinatocopper(II)(**1-Cu**) was prepared using the standard acetate method [12]. Yield, 82%. M.p.: $>300\ ^\circ C$. *Anal.* Calc. for $C_{32}H_{20}CuN_4 \cdot H_2O$, C, 70.90; H, 4.09; N, 10.34, Found: C, 71.05; H, 4.21; N, 9.83.

Oxo(5,15-Diphenylporphinato)vanadium(IV) (**1-VO**) was prepared according to Walker et al. [13]. Yield, 86%. M.p.: $>300\ ^\circ C$. *Anal.* Calc. for $C_{32}H_{20}N_4OV \cdot 3/2H_2O$, C, 69.31; H, 4.18; N, 10.10, Found: C, 69.73; H, 3.72; N, 10.08.

5-(Pyridine-4-yl)-15-(4-*n*-octyloxyphenyl)porphyrin **2-H$_2$** was synthesized from the condensation of dipyrromethane and 4-*n*-octyloxybenzaldehyde and 4-pyridinecarboxaldehyde followed by DDQ oxidation [11]. Yield, 10%. M.p. 295 °C. ^1H NMR (300 MHz, $CDCl_3$), δ 10.35 (s, 2H, *meso*-CH), 9.45 (d, 2H, pyrrole–H_β, $J = 4.8$ Hz) 9.42 (d, 2H, pyrrole–H_β, $J = 4.5$ Hz), 9.15 (d, 2H, pyrrole–H_β, $J = 4.5$ Hz), 9.09 (dd, 2H, pyridine–CH, $J = 5.9$, 1.5 Hz), 9.04 (d, 2H, pyrrole–H_β, $J = 4.8$ Hz), 8.24 (dd, 2H, pyridine–CH, $J = 6.0$, 1.4 Hz), 8.18 (dd, 2H, phenyl–CH, $J = 8.7$, 2.1 Hz), 7.35 (dd, 2H, phenyl–CH, $J = 8.7$, 2.0 Hz), 4.29 (t, 2H, octyl–C_1 CH_2, $J = 6.6$ Hz), 2.02 (m, 2H, octyl–C_2 CH_2), 1.38–1.70 (m, 10H, octyl–C_{3-7} CH_2), 0.96 (t, 3H, octyl–C_8 CH_3), -3.13 (br s, 2H, inner-NH). *Anal.* Calc. for $C_{39}H_{37}N_5O \cdot 1/2H_2O$, C, 77.97; H, 6.38; N, 11.66, Found: C, 77.85; H, 6.16; N, 11.58.

5-(Pyridine-4-yl)-10,15,20-tris(4-*n*-octyloxyphenyl)-porphyrin **3-H$_2$** was synthesized by the condensation of pyrrole and 4-*n*-octyloxybenzlaldehyde and 4-pyridinecarboxaldehyde followed by DDQ oxidation [11]. Yield, about 1%. M.p.: 255 °C, ^1H NMR (300 MHz, $CDCl_3$), δ 9.01 (dd, 2H, pyridine–CH, $J = 4.4$, 1.7 Hz), 8.91 (d, 2H, pyrrole–H_β, $J = 4.9$ Hz) 8.88 (s, 4H, pyrrole–H_β), 8.77 (d, 2H, pyrrole–H_β, $J = 4.9$ Hz), 8.16 (dd, 2H, pyridine–CH, $J = 4.4$, 1.7 Hz), 8.09 (m, 6H, phenyl–CH), 7.27 (m, 6H, phenyl–CH), 4.23 (t, 6H, octyl–C_1 CH_2, $J = 6.5$ Hz), 1.97 (m, 2H, octyl–C_2 CH_2), 1.30–1.70 (m, 30H, octyl–C_{3-7} CH_2), 0.94 (m, 9H, octyl–C_8 CH_3), -2.78 (br s, 2H, inner–NH), *Anal.* Calc. for $C_{67}H_{77}N_5O_3 \cdot 1/2H_2O$, C, 79.52; H, 7.72; N, 6.94, Found: C, 79.52; H, 7.78; N, 6.48.

5,10,15,20-Tetraphenylporphyrin **4-H$_2$** was synthesized by the condensation of pyrrole and benzaldehyde using the conventional Adler's method [14]. 5,10,15,20-Tetraphenylporphinatocopper(II) (**4-Cu**) was prepared using the standard acetate method [12]. *Anal.* Calc. for $C_{44}H_{28}CuN_4 \cdot H_2O$, C, 76.12; H, 4.36; N, 8.07; Found: C, 76.25; H, 4.21; N, 8.09.

Oxo(5,10,15,20-tetraphenylporphinato)vanadium(IV) (**4-VO**) was prepared according to Walker et al. [13]. *Anal.* Calc. for $C_{44}H_{28}N_4OV \cdot 1/2H_2O$, C, 76.74; H, 4.24; N, 8.14; Found: C, 76.45; H, 4.18; N, 8.08.

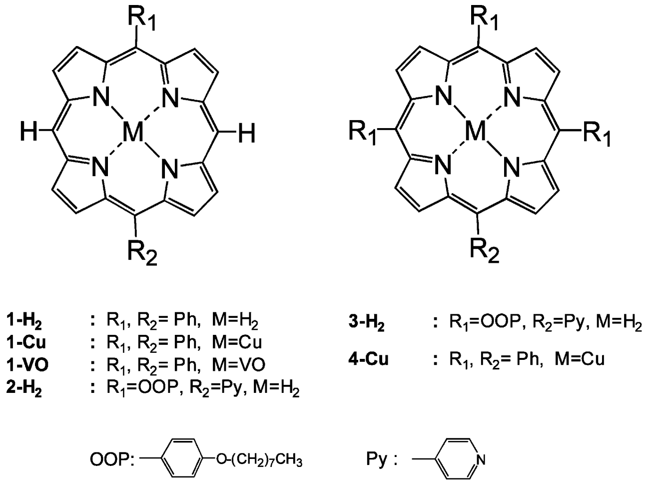

Chart 1.

2.2. Measurements

ESR spectra were recorded on a JEOL JES-RE3X spectrometer. Magnetic susceptibilities were measured using a Quantum Design MPMS-5 SQUID susceptometer at the field strength of 0.5 T in the temperature range of 1.8–300 K. In addition to correcting for the diamagnetic contribution from the sample holder, core diamagnetic corrections of 311.1×10^{-6}, 314.6×10^{-6}, 409.3×10^{-6}, and 402.4×10^{-6} emu mol^{-1} were used for **1-Cu**, **1-VO**, **4-Cu**, and **4-VO**, respectively [15].

Monolayers were formed by spreading the chloroform solution of porphyrins onto pure water subphase using microsyringe at 10 °C. After spreading, the monolayer was allowed to equilibrate, then compressed at a rate of 760 mm^2 min^{-1}. The concentration of porphyrin solution was adjusted to 1.0 mg ml^{-1}. Surface pressure and area (π–A) isotherms were recorded on a NL-LB-MWC trough (Japan Laser Electronics Lab. Co., Japan). The visible absorption spectra of monolayers were measured at air–water interface using a fiber optic probe IMUC 7000 (Otsuka Electronics Co., Japan). The solution UV–vis spectra were recorded with a V-570 spectrometer (Jasco Co., Japan).

3. Results and discussion

3.1. Magnetic properties of *meso*-disubstituted metalloporphyrins

ESR measurement on **1-Cu** in benzene solution at room temperature was carried out. The ESR spectrum showed typical hyperfine splitting for copper complexes. Compared with **4-Cu**, no significant difference was observed. ESR measurement on **1-VO** in benzene solution was carried out in the same way, showing also typical vanadium hyperfine splitting. These results indicate that the magnetic environments for metal ions in disubstituted porphyrin cores are almost identical with those of tetrasubstituted porphyrin cores in solution.

The values of μ_{eff} of **1-Cu** and **4-Cu** at 300 K were 1.58 and 1.69 B.M., respectively. These values correspond to paramagnetic $S = 1/2$ systems. The temperature dependence of χ_{m} and χ_{m}^{-1} for **1-Cu** are shown in Fig. 1. The straight lines for χ_{m}^{-1} vs. T plot pass through the near origin, indicating that χ_{m} obeys the Curie law and that almost no interaction occurs between the unpaired electrons of Cu(II). In μ_{eff} vs. T plots for **1-Cu** and **4-Cu** the values of μ_{eff} were virtually constant at relatively high temperature, indicating that the isolated doublet state were predominant for **1-Cu** and **4-Cu** (Fig. 2). The μ_{eff} values slightly decrease at low temperatures (< 20 K) for both porphyrins, indicating the occurrence of weak antiferromagnetic interaction between spins. These results agree with the antiferromagnetic interaction reported for TPP-Cu at very low temperature [16].

The values of μ_{eff} of **1-VO** and **4-VO** at 300 K were 1.57 and 1.58 B.M., respectively. These values correspond to paramagnetic $S = 1/2$ systems. The temperature dependence of χ_{m} and χ_{m}^{-1} for **1-VO** are shown in Fig. 3. The straight lines for χ_{m}^{-1} vs. T pass through the origin, and the μ_{eff} value is virtually constant independent of temperature in Fig. 4, indicating that χ_{m} obeys the Curie law and that no interaction occurs between the unpaired electrons in **1-VO** or **4-VO**.

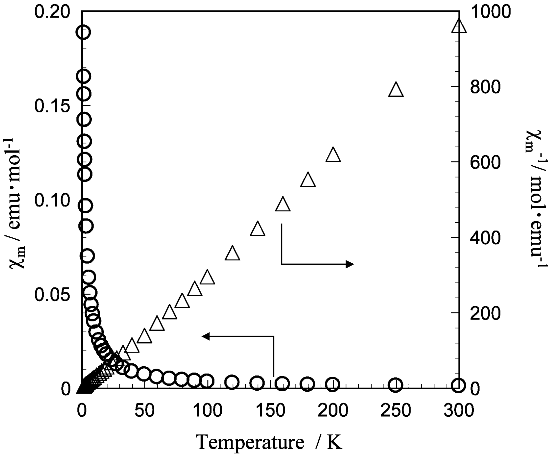

Fig. 1. Temperature dependences of χ_{m} (○) and χ_{m}^{-1} (△) for **1-Cu**.

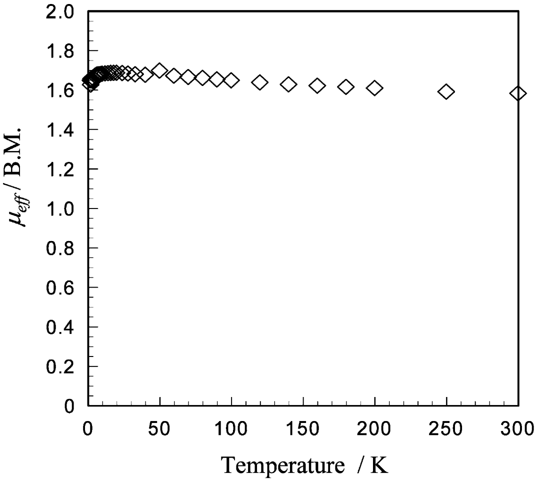

Fig. 2. Temperature dependence of μ_{eff} for **1-Cu**.

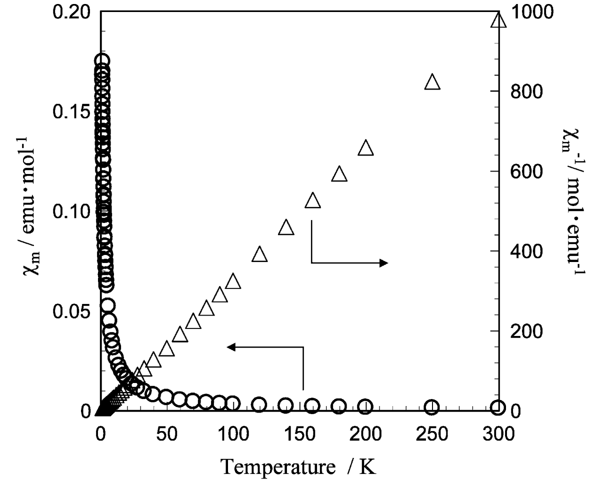

Fig. 3. Temperature dependences of χ_{m} (○) and χ_{m}^{-1} (△) for **1-VO**.

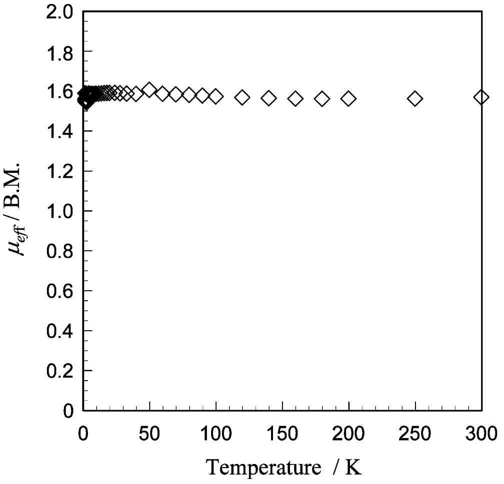

Fig. 4. Temperature dependence of μ_{eff} for **1-VO**.

The effects of the reduction of the number of the substituents were not observed on ESR and SQUID measurements. The results of SQUID measurements imply that magnetic interaction through π–π interaction did not occur in the crystals. This is because the overlap of the magnetic orbital of the metal center of adjacent molecule might be small. According to Bond et al. [8], the typical offset face-to-face π-stacking interactions are not observed for some diarylporphyrins. Instead the phenyl substituents are involved in edge-to-face interactions with adjacent porphyrins. Similar interactions are commonly observed in tetraphenylporphyrins [17]. These derivatives have the interplanar separations of approximately 0.4 nm, considerably greater than those in a typical π-stacked structure (~ 0.34 nm). X-ray analysis for **1-Cu** and **1-VO** will reveal these points.

3.2. *Monolayer of meso-disubstituted porphyrin*

2-H$_2$ and **3-H$_2$** formed stable monolayers at air–water interface, whose π–A isotherms are shown in Fig. 5. The observed mean molecular areas for **2-H$_2$** and **3-H$_2$** are 0.6 and 1.2 nm^2, respectively. This difference implies that the reduction of steric hindrance could induce the π–π interaction. For simple tetraarylporphyrins the expected mean molecular areas of LB films would be about 0.9 nm^2 if the porphyrin rings lie vertical to the aqueous surface and about 2.3 nm^2 when the porphyrin rings lie parallel based on crystal structural data or CPK models [18,19]. In case of 5,15-diarylporphyrins, the expected value would be about 0.4 nm^2 for vertical packing, and about 1.6 nm^2 for parallel packing [8]. The obtained values are relatively small, indicating that porphyrin macrocycles have a nearly perpendicular orientation on the water surface, or are partially overlapped. Figs. 6 and 7 show the in situ visible absorption spectra of porphyrin monolayers. Compared with chloroform solution, the Soret bands of **2-H$_2$** and **3-H$_2$** in monolayers are red shifted by about 38 and 15 nm, respectively, which assigned to the formation of J-type association. According to the exciton model developed by Kasha et al., the magnitude of shift is sensitive for the center-to-center distance of two adjacent chromophores ($\Delta E \propto r^{-3}$) [20]. The magnitude of shift in **2-H$_2$** is larger than that of **3-H$_2$**, implying that the center-to-center distance becomes shorter enhancing the interaction between porphyrin π-conjugated planes.

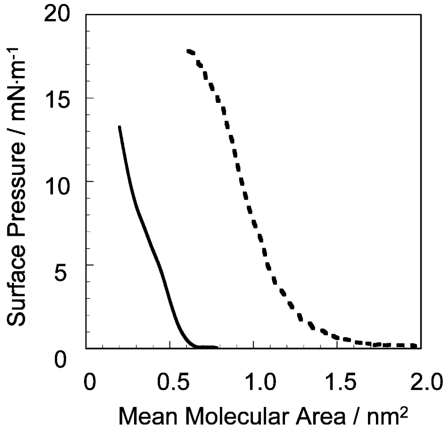

Fig. 5. π–A isotherms of **2-H$_2$** (solid line) and **3-H$_2$** (dotted line) on pure water subphase at 10 °C.

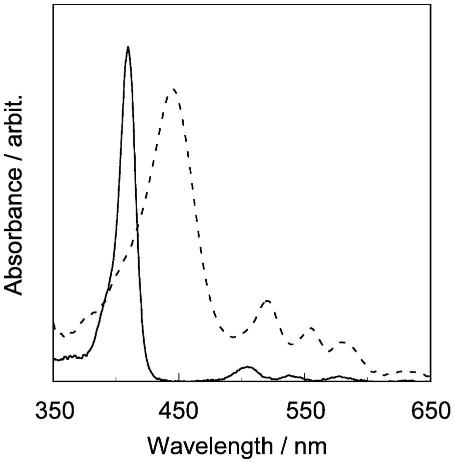

Fig. 6. Visible absorption spectra of monolayer state (solid line) and chloroform solution state (dotted line) for **2-H$_2$**.

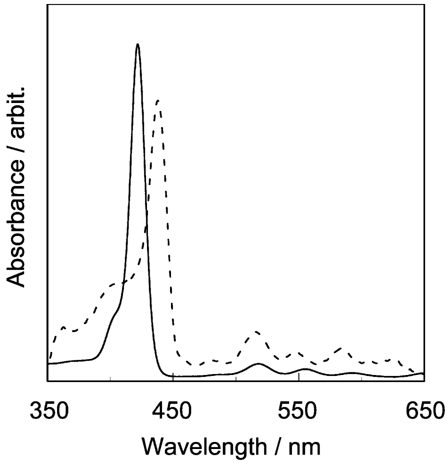

Fig. 7. Visible absorption spectra of monolayer state (solid line) and chloroform solution state (dotted line) for **3-H$_2$**.

4. Conclusions

meso-Disubstituted metalloporphyrins (**1-Cu**, **1-VO**) exhibited isolated doublet state and there were no significant differences compared with corresponding *meso*-tetrasubstituted porphyrins. The influence of π–π interaction was not observed for magnetic properties. Amphiphilic disubstituted porphyrin **2-H$_2$** formed stable monolayer, that showed a large red shift pattern in the visible absorption spectrum at air–water interface compared with the solution state, indicating that the reduction of steric hindrance leads to relatively strong exciton interaction between porphyrin macrocycles.

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