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Metal complexes of 5,15-porphyrinquinones: Systematic study of crystal structure, electronic structure, and Lewis acidity

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Abstract: We conducted the first systematic study on the synthesis, structure, and properties of various divalent metal complexes (Ni^{II}, Cu^{II}, Zn^{II}, Pd^{II}, Pt^{II}, and Pb^{II}) of 5,15-porphyringuinone (PQ, a guinone compound of porphyrin) for diversifying the chemistry of traditional quinone-metal complexes. Similar to electron-accepting nature of PQ, the metal complexes studied here also exhibit it. Ni^{II}, Pd^{II}, and Pt^{II} complexes favor face-to-face stacked structures in the crystals, thus inducing effective Pt^{II} - Pt^{II} interaction, which has not been observed in the porphyrin analogues to date. Ultraviolet-visible (UV-vis) absorption spectra of the metal complexes vary widely depending on the metal ion, and owing to the effective d(metal)- π (PQ) coupling in their molecular orbitals. Quantitative analyses of the axial ligation on the central metal ions (Ni^{II} and Cu^{II}) revealed significantly larger binding constants than those of the porphyrin analogues, indicating significant enhancement of their Lewis acidities due to the strong electron-withdrawing nature of PQ.

can bind the metal ion to their center. In fact, Mg^{II}, ^[3] Mn^{III}, ^[4] Fe^{III}, ^[5] Ni^{II, [6-8]} Zn^{II}, ^[3,8-12] and TI^{III} ^[3] complexes have been reported to date. Although these metal complexes are also expected to have characteristics typical of guinone-metal complexes, the properties of those complexes have not been adequately explored except for Fe^{III,[5]} Ni^{II,[6,7]}, and Zn^{II [9-12]} complexes, or the complexes with analogous ligands.^[13,14] For example, Ni^{II}-PQ complexes exhibit axial ligation of two pyridine ligands and the corresponding diamagnetic-to-paramagnetic change.^[6,7] This feature is induced by the strong electron-withdrawing nature of the PQ ligand, and is thus not observed in typical porphyrin analogues like tetraphenylporphyrin.^[15-21] However, quantitative analyses of this axial ligation on Ni^{II}-PQ complexes have not yet been explored while that on Zn^{II}-PQ reported by Sanders revealed its 100-times higher binding constant than that of the corresponding porphyrin.^[9]

Introduction

Quinones are one of the oxidized nonaromatic form of aromatic compounds and an important class of π -conjugated organic compounds.^[1] Typically, quinones are strong electron acceptors and are readily converted to dihydroxyarenes via reversible and stepwise 2e reduction. According to coordination chemistry, this redox behavior has drawn considerable research attention lately because quinones (typically *o*-quinones) are representative redox-non-innocent ligands, which have strong capacities to electronically communicate with metal ions.^[2]

Porphyrinquinones (PQs), which are also called dioxoporphodimethenes or dioxoporphyrins, are one of the quinone compounds of 18π -aromatic porphyrins (Figure 1a). PQs have two representative structural isomers: 5,15-PQ and 5,10-PQ, both of which were first synthesized in 1973 by oxidizing octaethylporphyrin with TI^{III}(OCOCF₃)₃.^[3] Like porphyrins, PQs

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Figure 1. (a) Chemical structures of porphyrin and two representative isomers of porphyrinquinones (PQs). (b) Chemical structure of [M^{II}(PQ1)].

Recently, we reported the facile preparation of 10,20-diaryl-5,15-PQ (2H-PQ1, Figure 1b) through the oxidation of the corresponding 5,15-diarylporphyrin by PhI(OAc)₂, and its efficient conversion to 10,20-diaryl-5,15-dialkoxyporphyrin.^[22] As a result, we obtained a large amount of PQ1, allowing for their systematic study along that of relevant compounds. Herein, we report the first systematic study of the synthesis, structure, and properties of a series of divalent metal complexes of porphyrinquinone [M^{II}(PQ1)] (M = Ni, Cu Zn, Pd, Pt and Pb). We also quantitatively study the axial ligation of [Ni^{II}(PQ1)] and [Cu^{II}(PQ1)].

Results and Discussion

Syntheses

The metal complexes [M^{II}(PQ1)] (M = Ni, Cu Zn, Pd, Pt, and Pb) were obtained almost quantitatively through the same method as that of the preparation of the porphyrin analogues (Table 1). Each complex was characterized by APCI HR-MS, NMR (for diamagnetic complexes), and elemental analysis. All obtained complexes were stable under ambient conditions.

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Table 1. Synthetic condition of the metalation reactions of 2H-PQ1 and the product yields for [M ^{II} (PQ1)].					
М	metal salt (equiv)	solvent	temp / °C	time / h	yield / %
Ni	Ni ^{II} (acac) ₂ (5)	Toluene	reflux	3	93
Cu	Cu ^{II} (OAc) ₂ ·(H ₂ O) (5)	CHCl₃/MeOH (10:1)	r.t.	1	90
Zn	Zn ^{II} (OAc) ₂ ·(H ₂ O) ₂ (5)	CHCl₃/MeOH (10:1)	r.t.	1	quant
Pd	Pd ^{II} (OAc) ₂ (1.5)	CHCl₃/MeOH (10:1)	r.t.	0.5	98
Pt	Pt ^{II} Cl ₂ (PhCN) ₂ (2)	PhCl	reflux	3	quant
Pb	Pb ^{II} (OAc) ₂ ·(H ₂ O) ₃ (10)	CHCl₃/MeOH (10:1)	r.t.	1.5	95

¹H NMR analyses

In the ¹H NMR spectra of the obtained diamagnetic complexes (M = Ni, Zn, Pd, Pt, and Pb), two doublet signals assigned for β -protons of the PQ1 ligand were observed within the range of 7.4 to 6.5 ppm. These are characteristic to nonaromatic quinone compounds.

In the reported Pb^{II} porphyrin complexes, Pb^{II} ion is situated off center from the mean plane of the macrocycles because of its large ion radius.^[23,24] This translates to reduced symmetry of the complexes, resulting in the splitting of the NMR signals of the aryl substituents, which are orthogonal to the porphyrin plane. This behavior was also observed in the ¹H NMR signals for 'Bu protons and Ar_o protons of [Pb^{II}(PQ1)].

X-ray Crystallography

The molecular structures of [M^{II}(PQ1)] (M = Ni, Cu Zn, Pd, and Pt) were successfully elucidated by the X-ray diffraction measurements but suitable crystals of [Pb^{II}(PQ1)] were not obtained. Selected crystallographic and structural data are summarized in Tables S1 and 2, respectively.





Figure 2. Crystal structure of [Ni^{II}(PQ1)] (C = black, H = white, N = blue, O = red, and Ni = green). Thermal ellipsoids are drawn at 40% probability level. Two crystallographically independent molecules with similar structural parameters are found in the asymmetric unit, and only one molecule (Molecule *A*) is illustrated. (a) Top view, (b) side view, (c) top and (d) side views of the dimeric structure. *t*-Butyl groups on the phenyl groups are omitted for clarity.

The C_{meso}=O bond lengths in all compounds are within the range of those of the typical C=O double bonds, and C_{meso}-C_α bond lengths are considerably longer than those of the C-C bonds in the macrocycles. These are typical of the nonaromatic quinoidal compounds. Notable structural features are 1) group-8-metal complexes exhibited considerably ruffled conformations and formed π -stacked dimers (Figures 2, and S1–S4), which are found in the crystals of 2H-PQ1^[22]; and 2) for [Cu^{II}(PQ1)] and [Zn^{II}(PQ1)], both or one carbonyl oxygen atom were coordinated to the central metal of the neighboring molecules to form the 1D-chains successively (Figure 3).

[Ni^{II}(PQ1)] and [Pd^{II}(PQ1)] crystallized in the orthorhombic *lbca* space group with almost the same crystallographic parameters while [Pt^{II}(PQ1)] crystallized in the orthorhombic crystal system with the *Pccn* space group. The crystals of Ni^{II} and Pd^{II} contained two crystallographically independent but structurally similar molecules (*A* and *B*) in the asymmetric unit.

[Ni^{II}(PQ1)] exhibited severely ruffled conformations with a mean deviation of 0.40 Å from the 24-atom mean plane (Figure S7). This is typically observed in the Ni^{II} porphyrins because of the small ion radii of the Ni^{II} ion. It is worth noting that [Pd^{II}(PQ1)] and [Pt^{II}(PQ1)] also exhibit considerably ruffled conformation whereas the conformation of typical Pd^{II} and Pt^{II} porphyrins is almost planar. The geometry-optimized structures of [Pd^{II}(PQ)] and [Pd^{II}(PQ)] according to the density functional theory (DFT) calculation (*vide infra*) exhibit relatively more planar conformation.

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Table 2. Selected structural data for the structure of [M ^{II} (PQ1)]								
M ^{II}	Ni A	Ni B	Cu	Zn	Pd A	Pd B	Pt	2H ^[b]
O=C _{meso} / Å	1.237(4), 1.234(4)	1.227(4), 1.232(4)	1.242(5)	1.229(5), 1.251(5)	1.218(9), 1.237(9)	1.228(9), 1.248(9)	1.228(6), 1.240(7)	1.231(5)
(C _{meso} –C _α) _{av} / Å	1.453	1.461	1.463	1.467	1.463	1.461	1.462	
(M–N) _{av} / Å	1.925	1.927	2.021	2.072	2.019	2.009	2.027	
conformation	ruffle	ruffle	planar	dome	ruffle	ruffle	ruffle	planar
mpd / Å ^[a]	0.40	0.41	0.06	0.05	0.31	0.32	0.22	0.08

[a] Mean plane deviation defined by 24 core atoms. [b] Data from reference [22].

Therefore, this deformation may be attributable to intermolecular interactions.

In the crystals, Ni^{II}, Pd^{II}, and Pt^{II} complexes formed π -stacked dimers (Figures 2c and 2d), whose selected structural data are summarized in Table S3. The two molecules in the dimer are twisted against the M–M axis by approximately 66° with respect to each other. The distances between two metal centers are ca. 3.2–3.5 Å. It is worth noting that the Pt^{II}–Pt^{II} distances for [Pt^{II}(PQ1)] (3.3618(6) Å) is shorter than twice the van der Waals radius of Pt^{II} ion (ca. 3.5 Å). This indicates Pt^{II}–Pt^{II} electronic interaction,^[25,26] which is not observed in the Pt^{II} porphyrins probably because of the strong π repulsion between the porphyrins. As far as we know, these are the first Pt^{II} complexes with porphyrinoid ligands to exhibit Pt^{II}–Pt^{III} interaction.

In the crystal of $[Zn^{II}(PQ1)]$, one of the oxygen atoms of the PQ1 is coordinated to the Zn^{II} ion of the other molecule to form 1D zigzag-chains (Figure 3a). The dihedral angle between two neighboring PQ1 macrocycles is 88°. Due to the axial coordination, the Zn ion is placed 0.32 Å above the PQ plane (Figure S7g), and the PQ macrocycle is slightly dome-distorted, but almost planar (mpd; 0.05).

On the other hand, $[Cu^{II}(PQ1)]$ forms partially stacked 1D chains in the crystal (Figure 3b). Unlike $[Zn^{II}(PQ1)]$, the two neighboring molecules are in a perfectly parallel orientation. The two oxygen atoms of PQ1 are placed above the almost planar mean plane, defined by the 24 core atoms of the PQ ligand (Figure S7f), and close to the Cu^{II} ion of other molecules. The Cu^{II}...O distance (2.878 Å) is slightly larger than the typical bond length between the axial ligand and the Cu^{II} ion in the Cu^{II}-porphyrin complexes.^[27–31] The C=O bond length (1.242(5) Å) is larger than those of the other complexes (M= 2H, Ni, Pd, and Pt). These results suggest an associative interaction between the oxygen atom in the PQ ligand and the Cu^{II} ion.





Figure 3. 1D chains of (a) $[Zn^{II}(PQ1)]$ and (b) $[Cu^{II}(PQ1)]$ in the crystals (C = black, H = white, N = blue, O = red, Zn = purple, and Cu = brown). Thermal ellipsoids are drawn at 40% probability level. Solvated molecules and *t*-butyl groups on the phenyl groups are omitted for clarity.

Electrochemistry

Cyclic voltammograms and half-wave potentials of $[M^{II}(PQ1)]$ determined through cyclic voltammetry are shown in Figure 4 and Table 3, respectively. The PQ1 ligand and all the metal complexes yield one irreversible oxidation wave and two reversible reduction waves in CH₂Cl₂ containing 0.1 M TBAPF₆. Both oxidation and reduction potentials for $[M^{II}(PQ1)]$ are significantly higher than those of the corresponding porphyrin complexes, which clearly indicates the strong electron-accepting nature of $[M^{II}(PQ1)]$. Both first and second reduction potentials exhibited relationships that were almost linear with Pauling's electronegativity of the central metal ions, as is the case with porphyrin analogues^[32] (Figure 5). It is worth noting that both first and second reduction potentials of $[Ni^{II}(PQ1)]$ are slightly abnormal. This may reflect its large saddle distortion of $[Ni^{II}(PQ1)]$ as described in the crystallography section.



 $\label{eq:Figure 4. Cyclic voltammogram of [M^{II}(PQ1)] in CH_2Cl_2 containing 0.1 M \\ TBAPF_6. M = (a) 2H,^{[22]} (b) Ni, (c) Cu, (d) Zn, (e) Pd, (f) Pt, and (g) Pb.$

Table 3. Half-wave	potentials	s (V vs.	Fc/Fc ⁺)	of [M ^{II} (PQ1)]	in CH ₂ Cl ₂
containing 0.1 M	TBAPF ₆ .	Potentia	ls were	determined	by cyclic
voltammetry.					

М	E_{Red2}	E _{Red1}	Eox	E _{Red1} - E _{Red2}
2H ^[a]	-1.24	-0.89	(1.18) ^[c]	0.35
Ni	-1.19	-0.69	(0.96) ^[c]	0.50
Cu	-1.23	-0.76	(0.95) ^[c]	0.47
Zn ^[b]	-1.50	-0.98	(1.14) ^[c]	0.52
Pd	-1.08	-0.66	(1.16) ^[c]	0.42
Pt	-0.97	-0.58	(1.04) ^[c]	0.39
Pb	-1.39	-0.90	(0.92) ^[c]	0.49

[a] Data from reference [22]. [b] To dissolve the complex completely, the measurement was performed in CH_2Cl_2 -pyridine (99:1). [c] Irreversible peak.





Figure 5. Plot of the first (black circle) and second (blue triangle) reduction potentials versus Pauling's electronegativity of the central metal ion (M) for $[M^{II}(PQ1)]$.

Spectroscopic Properties

[M^{II}(PQ1)], except for [Pd^{II}(PQ1)], yield a brown color in solution while [Pd^{II}(PQ1)] yield a green color (Figure 6). UV–vis absorption spectra of [M^{II}(PQ1)] in toluene are shown in Figure 7. All [M^{II}(PQ1)] have roughly three absorption bands: at ca. 400–500 nm (band I), at ca. 500–600 nm (band II), and at ca. 600– and quite weak with Log(ϵ) ca. 2~3 (band III). The shape and intensity of each band strongly depend on the central metal. For band II, only Pd^{II} have significantly broad and split bands while those of the others are sharp. This is the main cause of the difference in the color of [Pd^{II}(PQ1)]. For band III, Log(ϵ) of Ni^{II} and Pt^{II} is considerably higher than those of the others.



Figure 6. Photographs of the solution of $[M^{II}(PQ1)]$ in toluene. M = (a) Cu, (b) Ni, (c) Pd, and (d) Pt.

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Figure 7. UV-vis absorption spectra of [M^{II}(PQ1)] in toluene. M = (a) 2H, $^{[22]}$ (b) Ni, (c) Cu, (d) Zn, (e) Pd, (f) Pt, and (g) Pb.

Theoretical calculation

To gain further insight into the electronic state and physical properties of [M^{II}(PQ)], DFT calculations were performed. For simplicity, all *t*-butyl groups on the aryl substituents were removed from the model structures to allow calculation ([M^{II}(PQ1')]). Obtained molecular orbital (MO) energy diagrams are shown in Figure 8. For group-8 element complexes (M = Ni, Pd, and Pt), the orbital energies of HOMO-2 and HOMO-3 are quite different from the those of the rest; and are generated by mixing PQ π -orbitals, which correspond to HOMO-4 and HOMO-5 of [Zn^{II}(PQ1')], with metal d_{yz} or d_{zx} orbitals (Figures 9 and S10–S16). Time-dependent density functional theory (TDDFT) calculation suggests that the contribution of these orbitals to electronic transitions is the dominant factor affecting the characteristic colors and absorption spectra of group-8-element complexes (Tables S5–S10, and Figures S17–S22).



Figure 8. MO Energy diagram of [M^{II}(PQ1')]. Blue: ligand-centered MOs, red: metal-centered MOs (dz^2), green: mixed MOs.



Figure 9. Selected MO of [Pd^{II}(PQ1')] and [Zn^{II}(PQ1')].

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The order of the orbital energy of HOMO and LUMO is approximately consistent with those of the experimental redox potentials except for [Pb^{II}(PQ)], which may be due to the incomplete treatment of the relativistic effects.

Axial coordination behavior of [Ni^{II}(PQ1)]

Nickel(II) complexes of porphyrins with electron-withdrawing substituents undergo axial ligand coordination, which induces a change in the spin state from S = 0 (diamagnetic) to S = 1(paramagnetic).^[16-21,33] In other word, electron-withdrawing substituents enhances the Lewis acidity of the central nickel ion. Due to the strong electron accepting character of PQ ligand, their nickel complexes are expected to have strong ligation, and this was qualitatively examined in the previous study using pyridine as an axial ligand.^{[6][7]} We conducted quantitative analyses of the axial ligand coordination behavior of [Ni^{II}(PQ1)] (Scheme 1). Strong axial coordination behavior of [Ni^{II}(PQ1)] was indicated by the difference in color and UV-vis absorption spectra in the presence/absence of axial ligand. A solution [Ni^{II}(PQ1)] in toluene displayed brown color whereas that in toluene/pyridine (3:1) displayed red color (Figure 10 inset). UV-vis absorption spectra of [Ni^{II}(PQ1)] in both solvents are shown in Figure 10. The shape of both spectra was guite similar with that of the reported analog in CH₂Cl₂ and pyridine.^[6] Two sharp bands at 450 nm and 526 nm and a severely broadened peak around 650 nm were observed in toluene whereas the characteristic broad peak disappeared along with the new peak at 580 nm with a shoulder at 525 nm.





UV-vis absorption spectra of [Ni^{II}(PQ1)] in various solvents were measured and are shown in Figure S23. Those in 1methylimidazole/toluene (1:26), DMF, THF, and MeOH/toluene (1:3) are similar with that in toluene/pyridine, indicating the axial coordination of these solvents. It is worth noting that the axial coordination of these oxygen-based ligands is quite rare in the case of Ni-porphyrins.^[33] On the other hand, that in acetone is similar to that in toluene, indicating no axial coordination of acetone. That in acetonitrile/toluene (3:1) shows both characteristic peaks, indicating that both 4-coordinate and 6-coordinate species exist in this condition.

NMR studies clearly indicate a change in the spin state of Ni^{II} ion upon axial ligand coordination.^[34-37] In the ¹H NMR spectrum of [Ni^{II}(PQ1)] in CDCI₃, all proton signals for [Ni^{II}(PQ1)] were observed within the range of typical diamagnetic compounds (Figure 12a); e.g., two doublet signals assigned for β protons of PQ ligand were observed at 6.58 and 6.25 ppm. On the other hand, the ¹H NMR spectrum of [Ni^{II}(PQ1)] in CDCl₃/pvridine-d₅ (1:1) showed two significantly broadened and downfield-shifted signals for β protons of PQ1 ligand around 50 ppm (Figure 2b). That strongly indicates the formation of the paramagnetic nature of the 6-coordinated complex [Ni^{II}(PQ1)(pyridine- d_5)₂]. Thus, we identified a paramagnetic susceptibility (χ_m) and an effective magnetic moment (μ_{eff}) of [Ni^{II}(PQ1)(pyridine- d_5)₂] in CDCl₃/pyridine-d₅ (1:1) at 298 K through the Evans NMR method.^[38-42] The obtained values of χ_m and μ_{eff} were 3.25×10⁻³ emu mol⁻¹ and 2.79 $\mu_{\rm B}$, respectively. These values are within the range observed for 6-coordinate paramagnetic Nill complexes (S = 1).



Figure 11. ¹H NMR spectra (500 MHz, 298 K) of [Ni^{II}(PQ1)] in (a) CDCl₃ (4-coordinate, diamagnetic), and (b) CDCl₃/[D₅]pyridine (1:1) (6-coordinate, paramagnetic). * solvent signals.

Direct evidence of axial coordination was obtained from X-ray structural analyses. Although Balch reported the crystal structures of OEP analogues, the relative orientation of the two oxo substituents could not be ascertained because of the disorder of the macrocycle.^[6] This resulted in uncertainty in their structural information such as bond lengths.

Slow diffusion of methanol vapor into a solution of [Ni^{II}(PQ1)] in 4-picoline (4-methylpyridine) afforded a single crystal, and X-

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ray analysis for this crystal revealed the nondisordered structure of the 6-coordinate complexes, $[Ni^{II}(PQ1)(4\text{-picoline})_2]$ (Figure 12). The PQ1 ligand is almost planar with an average mean Ni–N_{PQ1} bond length of 2.07 Å and a mean deviation from the mean plane of 0.07 Å.



Figure 12. Crystal structure of $[Ni^{II}(PQ1)(4-picoline)_2]$ (C = black, H = white, N = blue, O = red, and Ni = green). Thermal ellipsoids are drawn at 40% probability level.



Figure 13. (a) UV-vis spectral change of [Ni^{II}(PQ1)] upon the addition of pyridine (0–80 mM) in toluene at 298 K. (b) Titration curve of [Ni^{II}(PQ1)] with pyridine monitored at 659 nm. The solid line represents the best fitting curve.

To determine the binding constants between [Ni^{II}(PQ1)] and axial ligand L (L = pyridine, 1-methylimidazole), UV-vis titration experiments were carried out. Change in the UV-vis spectrum of

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[Ni^{II}(PQ1)] in toluene upon a titration with pyridine at 298 K is shown in Figure 13a. There are no clear isosbestic points, implying the formation of a 5-coordinated complex as an intermediate product (Scheme 1). Thus, nonlinear curve fitting was performed using the change in the absorption at 659 nm to determine the first and second binding constants, K_1 and K_2 (Figure 13b). To determine the binding constants successfully, we assumed that the 5-coordinate and 6-coordinate complexes have the same value in ε at 659 nm as similar manners with porphyrin analogues.^[19,20] K_1 and K_2 were determined to be 78 ± 2 M⁻¹ and $(4.1 \pm 0.2) \times 10^2$ M⁻¹, and thus $\beta (= K_1 \times K_2)$ value is determined to be (3.2 \pm 0.2) \times 10 4 $M^{-2}.$ The results of titration with 1methylimidazole are shown in Figure S24. In a similar manner, K_1 , K_2 , and β values between [Ni^{II}(PQ1)] and 1-methylimidazole were also determined to be $(3.3 \pm 0.2) \times 10^4$ M⁻¹, $(6.9 \pm 0.7) \times 10^4$ M⁻¹, and (2.2 \pm 0.4) \times 107 $M^{-2},$ respectively. Table 4 summarizes binding constants for [Ni^{II}(PQ1)] and the representative Ni^{II} porphyrin analogues.^[16,17,20] Those values are significantly higher than those of Ni-porphyrins. These results clearly indicate the stronger Lewis acidity of nickel ion incorporated in the electron deficient porphyringuinone ligand.

Table 4. Binding constants for $[M^{II}(PQ1)]$ (M = Ni and Cu) and the representative Ni porphyrin analogues.

Compd. ^[a]	Ligand [[]	<i>K</i> ₁ / M ⁻¹	<i>K</i> ₂ / M ⁻¹	β / M ⁻²
[Ni(PQ1)]	ру	78±2	(4.1±0.2) ×10 ²	(3.2±0.2) ×10 ⁴
[Ni(TFPP)] ^[c]	ру	8.2	22.4	1.8×10 ²
[Ni(TMAFPP)] ^[d]	ру	33±5	50±10	1.7×10 ³
[Ni(PQ1)]	Melm	(3.3±0.2) ×10 ⁴	(6.9±0.7) ×10 ⁴	(2.2±0.4) ×10 ⁷
[Ni(TMAFPP)] ^[d]	Melm	(5.5±0.5) ×10 ²	(1.1±0.2) ×10 ²	3.9×10 ⁵
[Ni(TPP)] ^[e]	pyrro	1.08	3.79	4.09
[Cu(PQ1)]	ру	13.2±0.4	4.1±0.4	55±5
[Cu(PQ1)]	Melm	181±4	12±2	(2.1±0.4)×10 ³
[Cu(TPP)] ^[f]	ру	0.05±0.02	_	-

[a] TFPP = tetrakis(pentafluorophenyl)porphyrinato, TMAFPP = tetrakis(4-(trimethylammonium)-2,3,5,6-tetrafluorophenyl)porphyrinato, TPP = tetraphenylporphyrinato. [b] py = pyridine, MeIm = 1-methylimidazole, pyrro=pyrrolidine. [c] Data from reference [20]. In [D₈]toluene. [d] Data from reference [16]. In CH₃CN. [e] Data from reference [17]. In CH₂Cl₂. [f] Data from reference [27]. In benzene. Only formation of the 5-coordinated complex is considered.

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Axial coordination behavior of [Cu^{II}(PQ1)]

The results of [Ni^{II}(PQ1)] prompted us to evaluate the axial coordination behavior of a copper(II) complex [Cu^{II}(PQ1)] because the 5- or 6-coordinate Cu(II) porphyrin complexes are still rare owing to their significantly lower binding constants compared to Ni^{II}.^[27-31]

UV-vis titration experiments with pyridine and 1methylimidazole were carried out for [Cull(PQ1)] (Figures 14 and S25). The spectrum of [Cu^{II}(PQ1)] in the absence of pyridine exhibits peaks at 568 nm and 458 nm. Upon the addition of pyridine, a new peak is attained at a relatively shorter wavelength. Initially, an unsuccessful attempt at curve fitting of the spectral changes, assuming the 5-coordinate complex as the sole product, was made because this assumption was generally applied for the reported analyses of the Cu^{II} porphyrin complexes. There are no clear isosbestic points at the late-stage of titration, implying the formation of a 6-coordinated complex via the intermediate 5coordinated complex. By assuming 5- and 6-coordinate complexes similar with the case of [Nill(PQ1)], the spectral changes were fitted appropriately. Therefore, we concluded that the 6-coordinated complex was the final product, even though the inconsistent X-ray diffraction study described below. The obtained K_1, K_2 , and β values are summarized in Table 4. These values are lower than those of [Ni^{II}(PQ1)], but significantly higher than that of Cu^{II}-tetraphenylporphyrin with pyridine (0.05 \pm 0.02 M⁻¹, only considering 5-coordinated complexes).[27-31]



Figure 14. (a) UV-vis spectral change of $[Cu^{II}(PQ1)]$ upon the addition of pyridine (0–0.78 M) in toluene at 298 K. (b) Titration curve of $[Ni^{II}(PQ1)]$ with pyridine monitored at 554 nm.

A single crystal of $[Cu^{II}(PQ1)]$ grown in the presence of 4picoline was analyzed through X-ray diffractometry. The revealed structure was not a 6-, but a 5-coordinated structure, i.e., $[Cu^{II}(PQ1)(4-picoline)]$. The crystal contained two crystallographically independent molecules in the asymmetric unit (Figure 15 and S8). The conformation of A is saddle shaped while that of B is ruffled. The coordination environment around Cu ions is similar between A and B; the bond length of Cu–N_{picoline} is ca. 0.34 Å longer than that of Cu–N_{PQ1}. Contrary to the Ni analogue, the difference between the bond lengths of Cu–N_{PQ1} for 4-coordinated and 5-coordinated complexes was quite small. In the crystal, A and B are stacked to form a dimeric structure, which is observed in the crystals of [M^{III}(PQ1)] (M = 2H, Ni, Pd, and Pt) as shown above. These results suggest that the driving force of the dimerization of PQ macrocycles is considerably strong. This and the small K_2 value of [Cu^{III}(PQ1)] may be the main factor influencing crystallization as a 5-coordinated, and not a 6-coordinated complex.



Figure 15. (a) Top, and (b) side views of crystal structure of [Cu^{II}(PQ1)(4-picoline)] (C = black, H = white, N = blue, O = red, Cu = brown). Thermal ellipsoids are drawn at 40% probability level. Two crystallographically independent molecules are found in the asymmetric unit, and only one molecule (Molecule *A*) is illustrated.

Conclusions

Varieties of divalent metal complexes of 5,15-porphyrinquinone [M^{II}(PQ1)] were almost quantitatively synthesized. In the crystals, the complexes tend to form stacked dimers (M = Ni, Pd, and Pt) or 1D-infinite chains via the coordination of the oxygen atom of the ligand to the central metal ions (M = Cu and Zn). The dimerization effectively induces Pt^{II}-Pt^{II} interaction, which has not been observed in the porphyrin analogues to date. The high reduction potentials of [M^{II}(PQ1)] indicate their strong electron accepting nature. UV-vis absorption spectra of the complexes vary widely depending on the metal ion. Especially, longer absorption bands of the complexes with d⁸ metal ions are quite different from one another and from those of the other metal complexes. Theoretical studies suggest that this is caused by the effective d- π coupling in the MO of the complexes. The strong electron-withdrawing nature of PQ enhances the Lewis acidity of the central metal ions, thus inducing the significantly strong axial ligation of the various ligands on the central metals. We anticipate that the revealed basic properties of the metal-PQ complexes could contribute to the new design of catalysts or advanced

materials. For this purpose, we are currently performing further experiments to reveal the catalytic or redox-non-innocent behavior of the complexes.

Experimental Section

Instrumentation and Materials

The porphyrinquinone ligand (2H-PQ1) was synthesized using the procedure developed by our group.^[22] Toluene, CH₂Cl₂, pyridine, and 1methylimidazole were distilled from CaH2. All the other chemicals were of reagent grades and used without further purification. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 plates. Flash column chromatography was performed using silica gel 60N (spherical. neutral, 40-50 µm). All NMR spectral data were recorded on a Bruker AV-500 (500 MHz) spectrometer. These data were collected at ambient temperature (25 °C) unless otherwise noted. ¹H NMR spectra were internally referenced to tetramethylsilane as a standard. ¹³C NMR spectra were internally referenced to solvent signals (δ = 77.0 ppm for CDCl₃). ESI HRMS data were measured on a Bruker micrOTOF II. APCI HRMS data were measured on a Bruker micrOTOF II equipped with the DirectProbe assembly. IR spectral data were recorded on a PerkinElmer Spectrum Two spectrometer equipped with an ATR unit. UV-Vis spectral data were recorded on a HITACHI U-3500 spectrometer or Shimadzu UV-3600 spectrometer. Melting points were determined on a Yanaco MP-S3 melting point apparatus. Cyclic voltammetry (CV) measurements were carried out using ALS 650C electrochemical analyzer in argon-saturated CH2Cl2 solutions containing 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte at ambient temperature (298 K). A conventional three-electrode cell was used with a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. Ferrocene was used as the internal standard in all electrochemical experiments.

[Ni^{II}(PQ1)]

A mixture of 2H-PQ1 (81.3 mg, 0.11 mmol) and Ni(acac)₂ (146.1 mg, 0.57 mmol) in toluene (5 mL) was refluxed for 3 h. The reaction mixture was directly poured on top of a silica gel column packed with CHCI₃, then eluted with CHCl₃. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica gel, hexane: $CH_2CI_2 = 1:1$), and then recrystallized from toluene-octane to give [Ni^{II}(PQ1)] as dark brown microcrystals (87.1 mg, 0.01 mmol, 93%). Spectral data were consistent with the previously reported data.^[8] $R_f = 0.15$ (hexane/CH₂Cl₂ 1:1); m.p.: >300 °C; ¹H NMR (500 MHz, CDCl₃) δ = 7.50 (t, J = 1.7 Hz, 2H, H_{Ar-p}), 7.16 (d, J = 1.7 Hz, 4H, ArH_{Ar-o}), 6.58 (d, J = 4.6Hz, 4H, H_{β}), 6.25 (d, J = 4.6 Hz, 4H, H_{β}), 1.34 ppm (s, 36H, *t*-Bu); ¹³C NMR (125 MHz, CDCl₃) δ = 179.4 (Cq), 155.5 (Cq), 152.3 (Cq), 150.5 (Cq), 142.3 (Cq), 134.8 (Cq), 133.6 (CH), 124.0 (CH), 123.7 (CH), 120.9 (CH), 34.9 (Cq), 31.4 ppm (CH₃); IR (ATR): v~ = 3112, 2961, 2866, 1623, 1558, 1554, 1490, 1394, 1346, 1327, 1267, 1235, 1206, 1052, 1018, 976, 899, 851, 839, 828, 808, 759, 727, 716, 563, 499, 443 cm⁻¹; UV/Vis (toluene): λ_{max} (Log ε) = 321 (4.34), 363 (4.39), 450 (4.82), 526 nm (4.24); HRMS(APCI): m/z calcd for C48H51N4O2Ni: 773.3360 ([M+H]+), found 773.3366; elemental analysis calcd (%) for C48H50N4O2Ni: C, 74.52; H, 6.51; N, 7.24; found: C, 74.60; H, 6.48; N, 7.15.

[Cu^{II}(PQ1)]

A mixture of 2H-PQ1 (28.7 mg, 0.040 mmol) and Cu(OAc) $_2$ ·H $_2$ O (40.4 mg, 0.20 mmol) in CHCl $_3$ (2 mL) and MeOH (0.2 mL) was stirred at room

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temperature for 1 h. The reaction mixture was directly poured on top of a basic alumina column packed with CHCl₃, then eluted with CHCl₃. The solvent was removed under reduced pressure. The crude product was recrystallized from toluene–octane to give [Cu^{II}(PQ1)] as dark red microcrystals (28.2 mg, 0.036 mmol, 90%). m.p.: >300 °C; IR (ATR): v[~] = 2960, 2904, 2867, 1592, 1552, 1490, 1393, 1349, 1320, 1264, 1232, 1206, 1054, 1015, 969, 897, 851, 832, 811, 760, 727, 714, 587, 492, 452, 421 cm⁻¹; UV/Vis (toluene): λ_{max} (Log*x*) = 309 (4.42), 365 (4.50), 421 (4.49), 458 (4.51), 529 (4.08), 568 nm (4.67); HRMS(APCI): *m/z* calcd for C4₈H₅₁N₄O₂Cu: 778.3303 ([M+H]⁺), found 778.3293; elemental analysis calcd (%) for C4₄B₅₀N₄O₂Cu: C, 74.06; H, 6.47; N, 7.20; found: C, 73.99; H, 6.47; N, 7.10.

[Zn^{II}(PQ1)]

A mixture of 2H-PQ1 (28.6 mg, 0.040 mmol) and Zn(OAc)₂·2H₂O (44.0 mg, 0.20 mmol) in CHCl₃ (2 mL) and MeOH (0.2 mL) was stirred at room temperature for 1 h. The reaction mixture was directly poured on top of a basic alumina column packed with CHCl₃, then eluted with CHCl₃. The solvent was removed under reduced pressure to give [ZnII(PQ1)] as dark red powder (31.53 mg, 0.040 mmol, quant.). The product was further recrystallized from butyronitrile-toluene to give [ZnII(PQ1)] (PrCN) as dark red microcrystals (23.6 mg, 0.027 mmol, 68%). m.p.: >300 °C; ¹H NMR (500 MHz, CDCl₃) δ = 7.43 (br, 2H, H_{Ar-p}), 7.08 (d, J = 1.5 Hz, 4H, H_{Ar-o}), 7.04 (d, J = 4.4 Hz, 4H, H_{β}), 6.23 (d, J = 4.4 Hz, 4H, H_{β}), 1.22 ppm (s, 36H, t-Bu); ¹³C NMR (125 MHz, CDCl₃/[D₅]pyridine (19:1)) δ = 177.6 (Cq), 157.7 (Cq), 156.2 (Cq), 149.7 (Cq), 146.6 (Cq), 137.6 (Cq), 133.4 (CH), 124.6 (CH), 122.9 (CH), 121.2 (CH), 34.7 (Cq), 31.3 ppm (CH₃); IR (ATR): v~ = 2958, 2904, 2870, 1592, 1528, 1496, 1480, 1395, 1347, 1313, 1246, 1225, 1201, 1052, 1007, 964, 896, 852, 832, 808, 760, 727, 582, 562, 488, 452, 409 cm⁻¹; UV/Vis (toluene/pyridine (99:1)): λ_{max} (Log ε) = 357 (4.59), 453 (4.86), 505 (4.21), 542 nm (4.86); HRMS(APCI): m/z calcd for C₄₈H₅₁N₄O₂Zn: 779.3298 ([M+H]⁺), found 779.3285; elemental analysis calcd (%) for C48H50N4O2Zn (C4H7N): C, 73.53; H, 6.76; N, 8.24; found: C, 73.54; H, 6.89; N, 8.19.

[Pd^{II}(PQ1)]

A mixture of 2H-PQ1 (35.6 mg, 0.050 mmol) and Pd(OAc)₂ (16.5 mg, 0.075 mmol) in CHCl3 (2.5 mL) and MeOH (0.25 mL) was stirred at room temperature for 25 min. The reaction mixture was directly poured on top of a silica gel column packed with CHCl₃, then eluted with CHCl₃. The solvent was removed under reduced pressure to give [Pd^{II}(PQ1)] as green powder (40.4 mg, 0.049 mmol, 98%). Analytically pure product was obtained by the recrystallization from hot toluene-hexane. $R_{\rm f} = 0.26$ (hexane/toluene 1:1); m.p.: >300 °C; ¹H NMR (500 MHz, CDCl₃) δ = 7.51 (t, J = 1.7 Hz, 2H, H_{Ar-p} , 7.19 (d, J = 1.7 Hz, 4H, Ar H_{Ar-o}), 6.93 (d, J = 4.7 Hz, 4H, H_{β}), 6.36 (d, J = 4.7 Hz, 4H, H_{β}), 1.35 ppm (s, 36H, t-Bu); ¹³C NMR (125 MHz, CDCl₃) δ = 176.7 (Cq), 155.8 (Cq), 150.5 (Cq), 150.0 (Cq), 140.4 (Cq), 136.2 (Cq), 133.7 (CH), 124.8 (CH), 123.1 (CH), 121.6 (CH), 35.0 (Cq), 31.4 ppm (CH₃); IR (ATR): v~ = 3108, 2962, 2866, 1611, 1542, 1476, 1394, 1349, 1342, 1271, 1234, 1205, 1052, 1023, 986, 899, 850, 839, 827, 809, 758, 725, 565, 507, 453, 438 cm⁻¹; UV/Vis (toluene): λ_{max} (Log ε) = 323 (4.37), 365 (4.34), 441 (4.79), 576 (3.99), 618 nm (4.16); HRMS(APCI): m/z calcd for C48H51N4O2Pd: 821.3058 ([M+H]+), found 821.3052; elemental analysis calcd (%) for C₄₈H₅₀N₄O₂Pd: C, 70.19; H, 6.14; N, 6.82; found: C, 70.45; H, 6.21; N, 6.60.

[Pt^{II}(PQ1)]

Synthesis of [Pt^{II}(PQ1)] was performed as a similar manner with the facile synthesis of Pt^{II}-porphyrin analogues reported by us.^[43] A mixture of 2H-PQ1 (14.2 mg, 0.020 mmol) and PtCl₂(PhCN)₂ (18.6 mg, 0.040 mmol) in

chlorobenzene (0.5 mL) was refluxed for 3 h. The solvent was removed under reduced pressure, and the crude product was purified by chromatography (silicagel, hexane:CH2Cl2=2:1). The solvent was removed under reduced pressure to give $[Pt^{II}(PQ1)]$ as black microcrystals (18.1 mg, 0.020 mmol, quant.). Analytically pure product was obtained by the recrystallization from hot toluene-hexane. $R_{\rm f} = 0.13$ (hexane/CH₂Cl₂ 1:1); m.p.: >300 °C; ¹H NMR (500 MHz, CDCl₃) δ = 7.49 (t, J = 1.8 Hz, 2H, H_{Ar}-_p), 7.22 (d, J = 1.8 Hz, 4H, Ar H_{Ar-o}), 6.86 (d, J = 4.7 Hz, 4H, H_{β}), 6.28 (d, J= 4.7 Hz, 4H, H_{β}), 1.35 ppm (s, 36H, *t*-Bu); ¹³C NMR (125 MHz, CDCl₃) δ = 176.1 (Cq), 156.0 (Cq), 151.2 (Cq), 150.1 (Cq), 139.4 (Cq), 135.9 (Cq), 133.9 (CH), 124.6 (CH), 123.1 (CH), 121.0 (CH), 35.0 (Cq), 31.4 (CH₃); IR (ATR): v~ = 3107, 2962, 2866, 1615, 1543, 1475, 1349, 1337, 1271, 1234, 1205, 1051, 1024, 982, 899, 849, 839, 827, 809, 759, 726, 564, 497, 452, 439 cm⁻¹; UV/Vis (toluene): λ_{max} (Log ε) = 366 (4.33), 438 (4.72), 499 (3.90), 535 nm (4.51); HRMS(APCI): m/z calcd for C48H51N4O2Pt: 910.3658 ([M+H]⁺), found 910.3675; elemental analysis calcd (%) for C₄₈H₅₀N₄O₂Pt: C, 63.35; H, 5.54; N, 6.16; found: C, 63.43; H, 5.57; N, 6.12.

[Pb^{II}(PQ1)]

A mixture of 2H-PQ1 (28.7 mg, 0.040 mmol) and Pb(OAc)₂·3H₂O (151.5 mg, 0.40 mmol) in CHCl₃ (2 mL) and MeOH (0.2 mL) was stirred at room temperature for 90 min. The reaction mixture was directly poured on top of a basic alumina column packed with CHCl₃, then eluted with CHCl₃. The solvent was removed under reduced pressure, and then recrystallized from toluene-hexane to give [Pbll(PQ1)] as dark brown microcrystals (35.2 mg, 0.038 mmol, 95%). Analytically pure product was obtained by the recrystallization from hot toluene-hexane. m.p.: >300 °C; ¹H NMR (500 MHz, C₆D₆) δ = 7.68 (t, J = 1.6 Hz, 2H, H_{Ar-p}), 7.60 (brs, 2H, ArH_{Ar-o}), 7.56 $(d, J = 4.3 \text{ Hz}, 4\text{H}, H_{\beta})$, 7.48 (brs, 2H, Ar H_{Ar-o}), 6.78 (d, $J = 4.3 \text{ Hz}, 4\text{H}, H_{\beta}$), 1.38 (s, 18H, *t*-Bu), 1.35 ppm (s, 18H, *t*-Bu); ¹³C NMR (125 MHz, CDCl₃) δ = 177.3 (Cq), 157.2 (Cq), 157.0 (Cq), 150.1 (Cq), 149.9 (Cq), 144.9 (Cq), 137.5 (Cq), 135.0 (CH), 125.2 (CH), 124.8 (CH), 123.3 (CH), 122.4 (CH), 35.0 (Cq), 31.5 ppm (CH₃); IR (ATR): v~ = 2955, 2906, 2869, 1578, 1536, 1513, 1506, 1461, 1394, 1339, 1331, 1293, 1239, 1231, 1224, 1058, 1051, 1000, 958, 843, 834, 810, 760, 737, 725, 566, 483, 448, 403 cm⁻¹; UV/Vis (toluene): λ_{max} (Log ε) = 360 (4.52), 472 (4.91), 507 (4.14), 544 nm (4.74); HRMS(APCI): m/z calcd for C48H51N4O2Pb: 923.3779 ([M+H]+), found 923.3759; elemental analysis calcd (%) for C48H50N4O2Pb: C, 62.52; H, 5.47; N, 6.08; found: C, 62.82; H, 5.62; N, 5.90.

X-Ray crystal structure determinations

Single crystals of [Ni^{II}(PQ1)] were grown by the vapor diffusion of hexane into its benzene solution. Single crystals of [Cu^{II}(PQ1)] were grown by the vapor diffusion of acetonitrile into its chloroform solution. Single crystals of [Zn^{II}(PQ1)] were grown by the vapor diffusion of acetone into its chloroform solution. Single crystals of [Pd^{II}(PQ1)] were grown by the vapor diffusion of hexane into its chloroform solution. Single crystals of [Pd^{II}(PQ1)] were grown by the vapor diffusion of hexane into its chloroform solution. Single crystals of [Pd^{II}(PQ1)] were grown by the vapor diffusion of hexane into its toluene solution. Single crystals of [Ni^{II}(PQ1)] were grown by the vapor diffusion of methanol into its 4-picoline solution. Single crystals of [Cu^{II}(PQ1)] were grown by the vapor diffusion of hexane into its 4-picoline solution.

Single-crystal X-ray diffraction data for [Cu^{II}(PQ1)] were collected on a Rigaku XtaLab P200 diffractometer using multi-layer mirror monochromated Mo-K α radiation ($\lambda = 0.71075$ Å) by the ω scan mode. The crystal was cooled by a stream of cooled N₂ gas. Data were collected and processed using CrystalClear (Rigaku). The data were corrected for Lorentz and polarization effects, and empirical absorption correction was applied.

Single-crystal X-ray diffraction data for the rest were collected on a Bruker Smart APEX CCD diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) by the ω scan mode. The crystal was cooled by a stream of cooled N₂ gas. The program SAINT was used for integration of the diffraction profiles. Empirical absorption corrections were applied by using the SADABS program.

The structures were solved by direct methods $(SHELXS97)^{[44]}$ or $SHELXT^{[45]}$ program and refined by full-matrix least-squares calculations on P^2 (SHELXL2014).^[46] All non-hydrogen atoms were modeled anisotropically. Hydrogen atoms were fixed at calculated positions and refined with a riding model. A summary of the crystallographic data is given in Tables S1 and S2. CCDC 1989954 ([Ni^{II}(PQ1)]), 1989949 ([Cu^{II}(PQ1)]), 1989952 ([Zn^{II}(PQ1)]), 1989953 ([Pd^{II}(PQ1)]), 1989955 ([Pt^{II}(PQ1)]), 1989951 ([Ni^{II}(PQ1)(4-picoline)₂]), and 1989950 ([Cu^{II}(PQ1)(4-picoline)₂]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Determination of binding constants for [Ni^{II}(PQ1)]

First, 1.81 mg (2.34 µmol) of [Ni^{II}(PQ1)] was dissolved in 20 mL of toluene. Then 3 mL of the solution was placed in a 1 cm quartz cell, and 3 µL of a toluene solution of pyridine (0.40 M) or 1-methylimidazole (2.5 mM) was added into the solution via a micro-syringe. The resultant solution was stirred for 3 min at room temperature. UV–vis spectra were recorded at room temperature after each addition. The changes in absorption at 659 nm as a function of the concentration of the axial ligand were plotted. The first and second binding constants (K_1 and K_2) were determined by a nonlinear curve fitting based on the following equation.

$$\Delta A = \frac{\Delta \varepsilon_1 K_1 [L]_0 [P]_0 + \Delta \varepsilon_2 K_1 K_2 [L]_0^2 [P]_0}{1 + K_1 [L]_0 + K_1 K_2 [L]_0^2}$$

where ΔA is differential absorbance $(A - A_0)$, and $\Delta \varepsilon$ is the difference between the molar extinction coefficient of $[Ni^{II}(PQ1)(L)_2]$ and that of $[Ni^{II}(PQ1)]$.

Evans measurements

The magnetic susceptibility of [Ni^{II}(PQ1)(pyridine- d_5)₂] in CDCl₃/pyridine- d_5 (1:1) solution was determined through the Evans method^[38–42] using TMS as the reference. To do so, 3.00 mg of [Ni^{II}(PQ1)] was dissolved in 0.5 mL of CDCl₃/pyridine- d_5 (1:1) containing 1% TMS. In a special coaxial tube, the resultant solution was placed in the outer tube and the same solvent was placed in the inner tube. ¹H NMR spectra were recorded at 298 K on a Bruker AV-500 (500.13 MHz) spectrometer. The separation of a TMS peak from the inner and outer tubes (Δv) was determined to be 60.7 Hz. The molar magnetic susceptibility, χ_M is calculated using the appropriate equation for a superconducting magnet:

$\chi^{\text{para}}M=1000 \Delta v / v_0 S_f c - \chi^{\text{dia}}M$

where ν_{0} is the spectrometer frequency (500.13 \times 10⁶ Hz), Sr is the shape factor of the magnet (4π/3 for a cylindrical sample in a superconducting magnet), c is the molar concentration of [Ni^{II}(PQ1)(pyridine-d_5)2] (7.76 \times 10⁻³ mol L⁻¹), and $\chi^{dia}{}_{M}$ is the diamagnetic contribution of the complex. The $\chi^{dia}{}_{M}$ value is roughly estimated using Pascal's constants.^[47]

Computational Details

For simplicity, all *t*-butyl groups on the phenyl rings were removed from the model structures (PQ1'). Geometries of all models were optimized by the DFT method at the Becke, three-parameter, Lee-Yang-Parr (B3LYP) exchange-correlation functional. Stuttgart RSC 1997 ECP and the

associated basis set (SDD)^[48] were used for the metal atoms, and the 6-311+G(d,p) basis set was used for the other light atoms. To confirm that the optimized geometries were not in saddle points but in stable points, frequency calculations without scaling were performed. None of the geometry-optimized structures gave imaginary frequencies. Excitation energies and oscillator strengths were computed with the time-dependent density functional theory (TDDFT) method, in which the solvent effect of toluene was included by the PCM method. All calculations were carried out using the Gaussian 09 program package (Rev. E01).^[49]

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Keywords: Lewis acids • Metal-metal interactions • Porphyrinoids • Quinones • Transition metals

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Aimed at the expansion of the chemistry of quinone-metal complexes, the systematic study of divalent metal complexes of 5,15-porphyrinquinone revealed their strong electron-accepting nature and metal-metal interaction (for Pt), effective $d(metal)-\pi(ligand)$ coupling in their molecular orbital, and their great enhancement of the Lewis acidity of the central metals.

Ken-ichi Yamashita,* Daisuke Hirano, Ken-ichi Sugiura*

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Metal complexes of 5,15porphyrinquinones: Systematic study of crystal structure, electronic structure, and Lewis acidity