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Electronic Spectra of Mono- and Dinuclear Complexes of Fully π-Conjugated salphen Ligands Synthesized by Using 2,6-Dihydroxynaphthalene Carbaldehydes

Hirohiko Houjou,*[a] Takatoshi Motoyama,[a] and Koji Araki[a]

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A series of mono- and dinuclear zinc(II), copper(II), nickel(II), and iron(III) complexes of novel salphen ligands were synthesized and spectroscopically characterized. The mononuclear ligand (H_2L^1) was synthesized from 2,6-dihydroxynaphthalene-1-carbaldehyde and an *o*-phenylenediamine; the dinuclear ligand (H_4L^2), which was not isolated, contains a 2,6-dihydroxynaphthalene-1,5-dicarbaldimine linkage that enables extended π-conjugation over two salphen units. By means of a controlled sequence of condensation reactions, the constituents were built into either mono- ([ML^1]) or dinuclear complexes ([M_2L^2]). The UV/Vis spectra of the [M_2L^2] complexes exhibited absorbances that were approximately twice as intense as those of the [ML^1] complexes, as well as a 30–50-nm bathochromic shift and considerable extension of the low-energy absorption edge relative to the spectrum of [ML^1]. The spectra of the complexes showed markedly intensified peaks in various regions, depending on M, which implies that the effects of extension of π-conjugation were due to more than simple additivity.

Introduction

Interest in precisely arranging metal atoms has been growing in connection with the recent development of metal cluster chemistry, the coordination space that results from metal–organic frameworks, and various metallosupramolecular polymers and other metal-containing materials.[1–4] Among metallopolymers, systems in which metal atoms are directly bound to an organic main chain with an extended π-conjugated system are of special interest.[5–7] They can be expected to show specific properties, such as conductivity, redox activity, photoluminescence, and magnetism, that originate from electronic communication between the metal atoms mediated by the organic part. The imine linkage is a promising candidate for the construction of such systems. Of various metallopolyimines, those with salen (*N*,*N*′-disalicylideneethylenediamine) and salphen (*N*,*N*′-disalicylidene-*o*-phenylenediamine) ligands have a long history and have been used in various functional materials.[8–13] In addition, electrolytic polymerization of Ni–salen complexes is interesting methodology for the fabrication of conductive films, although the mechanism of conduction (e.g., by an intrachain or interchain carrier path) is still controversial.[14–16] Clarification of the physicochemical properties of such d_π, p_π-conjugated metallopolysalen and polysalphen compounds requires the preparation and analysis of well-defined oligonuclear complexes. However, there have been few reports[17] highlighting the effects of intracomplex (metal–metal and ligand–metal) interactions on the spectroscopic features of fully π-conjugated oligonuclear salen and salphen complexes.

As a part of our continuing works of exploring various metallopolyimines,[18] we studied carbaldehyde **1** and dicarbaldehyde **2** as a component of π-conjugated metallopolysalphen. When these compounds are used as a ligand for a metal complex, the electronic state of the metal couples with that of the π system of the ligand, affording such interesting phenomena as metalloaromaticity[19] and valence tautomerism.[20–22] Previously, dioximato complexes of copper and nickel were prepared from **2**, and these compounds exhibit semiconducting performance for electronic functional materials.[23] Despite such promising results, the literature contains surprisingly few other studies of **1** and **2**. Condensation of **2** with diamines would lead to a new class of polynuclear salen and salphens applicable to the preparation of organic electronic device materials. As a primary step toward accomplishing this goal, we synthesized and characterized novel mono- and dinuclear salphen complexes with **1** and **2**. We will describe some interesting spectroscopic features that may have originated in the interactions of salphen complexes fused into a π-conjugated system.

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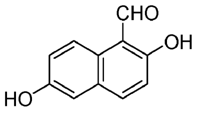
[a] Institute of Industrial Science, University of Tokyo,
4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan
E-mail: houjou@iis.u-tokyo.ac.jp



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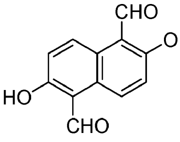

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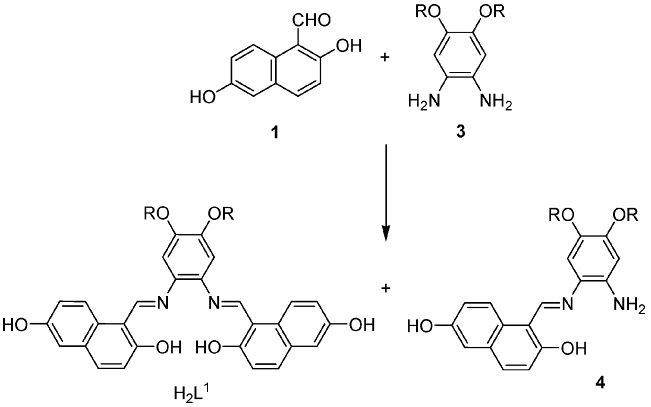
Results and Discussion

Synthesis of Ligands

Monoaldehyde **1**,[24] dialdehyde **2**,[25] and diamine **3** (R = $C_{12}H_{25}$)[26] were prepared according to previously reported methods. Scheme 1 shows the preparation of mononuclear ligand H_2L^1 and monoimine half-ligand **4**. The reaction of diamine **3** with **1** (2.2 equiv.) afforded reddish purple and orange crystalline solids, which were identified as H_2L^1 and **4**, respectively. The relatively low yield (≈30%) of H_2L^1 suggests that the second of the two condensation reactions was slow and that **4** separated out before the reaction was complete. A similar reaction carried out under ethanol-rich conditions afforded mostly **4** (>70%). The reaction of equal amounts of **1** and **3** afforded mainly **4**, but the yield was lower, owing to contamination of the product by unreacted **3**. The "partial ligand" **4** was then utilized as either a constituent of mono- or dinuclear complexes.

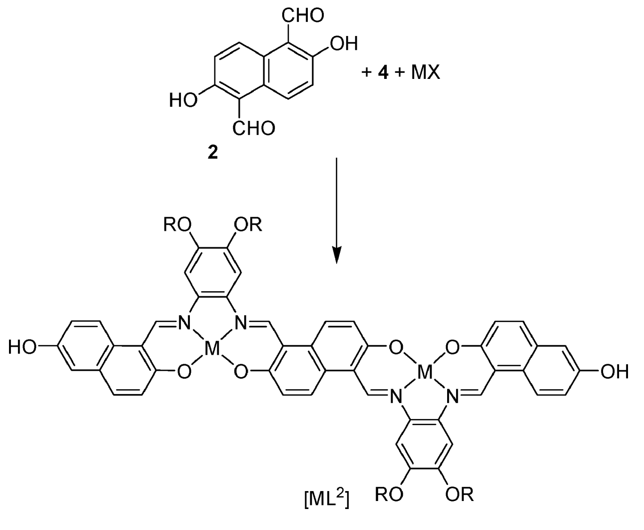


Scheme 1.

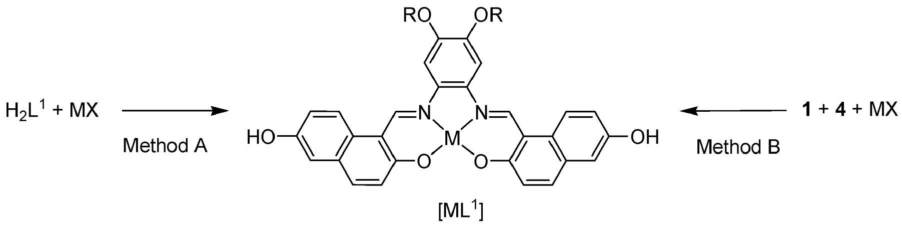
Synthesis of Mono- and Dinuclear Complexes

Mononuclear complexes $[ML^1]$, where M = Zn^{II}, Cu^{II}, Ni^{II}, or Fe^{III}, were synthesized by one of two methods (A and B, Scheme 2). Method A used H_2L^1 as a reactant, and method B involved the condensation of **1** and **4** with concomitant metal binding. The products obtained by means of the two methods were identical to each other, and method A afforded a slightly higher yield than method B. The complexes were identified as $[ZnL^1]$, $[CuL^1]$, $[NiL^1]$, and $[FeL^1Cl]$ by IR spectroscopy, fast atom bombardment mass spectrometry [MS (FAB)], and elemental analysis. The Zn and Ni complexes were analyzed by ^1H NMR spectroscopy ([D_5]pyridine). The NMR signals of the nickel complex were slightly broadened probably due to the coordination of pyridine molecule(s) in the axial position. The IR spectra showed a strong peak at 1601–1607 cm^{-1}, which was assigned to the C=N stretch vibration. The ν_{M-O} and ν_{M-N} bands appeared at 556–584 cm^{-1} and 419–421 cm^{-1}, respectively, in agreement with the values reported for analogous salphen complexes.[27–30] The overall profiles of $[CuL^1]$ and $[NiL^1]$ were similar, as were those of $[ZnL^1]$ and $[FeL^1Cl]$, which suggests that the coordination geometries of the complexes were similar, that is, square planar (Cu and Ni) or square pyramidal (Zn and Fe).

Homodinuclear complexes $[M_2L^2]$ were synthesized as shown in Scheme 3. Although we attempted to synthesize the dinuclear ligand H_4L^2 from **4** and **2** by varying the reaction parameters, such as the solvent ratio, we were unable to isolate H_4L^2. Therefore, we utilized the condensation reaction of **2** and **4** with concomitant metal binding (similar to method B in Scheme 2) to prepare the dinuclear complexes. A similar protocol was utilized to obtain some double salen and nonsymmetric salen complexes.[31,32]



Scheme 3.



Scheme 2.

The complexes were obtained in moderate yields and identified as [Zn_2L^2], [Cu_2L^2], [Ni_2L^2], and [$Fe_2L^2Cl_2$] by IR spectroscopy, MS (FAB), and elemental analysis. The ^{1}H NMR spectrum ([D_5]pyridine) of the Zn complex gave a set of identifiable peaks, whereas the spectrum of the Ni complex showed a series of significantly broad signals, which is again attributable to the coordination of pyridine molecule(s). The IR spectra showed stretching bands for C=N, M–O, and M–N in the regions expected for the estimated structure, and again there was similarity between the profiles of [Cu_2L^2] and [Ni_2L^2], and between those of [Zn_2L^2] and [$Fe_2L^2Cl_2$].

UV/Vis Spectra

The electronic absorption spectra in the ultraviolet/visible (UV/Vis) region were measured for each of the mono- and dinuclear complexes (pyridine, 1×10^{-4} M). The spectra of [ZnL^1] and [Zn_2L^2] were generally similar to each other, although the absorbance of [Zn_2L^2] was about 1.5–2 times as intense as that of [ZnL^1] (Figure 1a). The peaks (with ε in parentheses) of [Zn_2L^2] at 461 nm (53600 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) and 531 nm (30300 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) were substantially bathochromically shifted relative to the corresponding peaks of [ZnL^1] at 447 nm (41900 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) and 503 nm (23100 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$). The prominent peak at 558 nm (31800 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) for [$Zn_2L^2$] might correspond to the shoulder at 536 nm (16800 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) for [$ZnL^1$]. In contrast, the peaks for [Zn_2L^2] at shorter wavelengths (<400 nm) were almost unchanged or were slightly hypsochromically shifted relative to those of [ZnL^1].

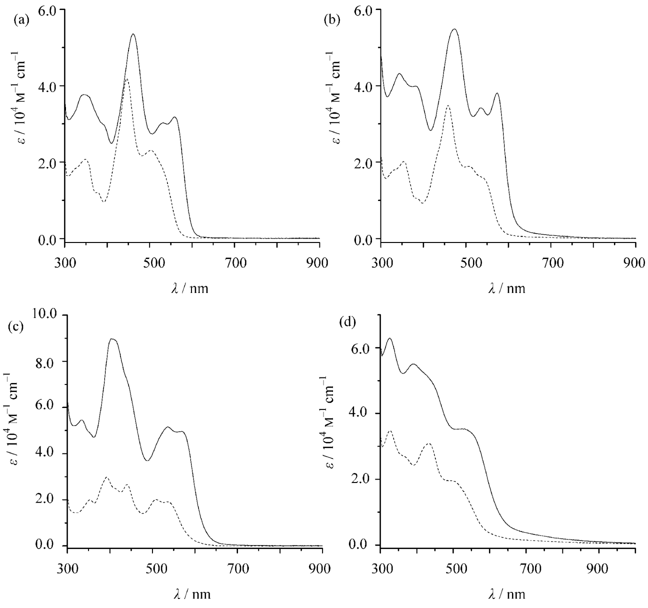


Figure 1. UV/Vis spectra of (a) [ZnL^1] and [Zn_2L^2], (b) [CuL^1] and [Cu_2L^2], (c) [NiL^1] and [Ni_2L^2], and (d) [FeL^1Cl] and [$Fe_2L^2Cl_2$]. The mononuclear ([ML^1]) and dinuclear complexes ([M_2L^2]) are denoted by dashed lines and solid lines, respectively.

The spectra of [CuL^1] and [Cu_2L^2] (Figure 1b) are similar to those of [ZnL^1] and [Zn_2L^2], respectively, and again the absorption of the latter was nearly twice as intense as that of the former. The peaks of [Cu_2L^2] at 474 nm (54900 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) and 536 nm (34200 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) were bathochromically shifted relative to the corresponding peaks of [CuL^1] at 458 nm (34900 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) and 506 nm (19000 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$), respectively; the shoulder at 543 nm (15,700 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) in the spectrum of [$CuL^1$] might correspond to the sharp peak at 574 nm (38,100 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) in the spectrum of [$Cu_2L^2$]. Notably, the spectrum of [Cu_2L^2] exhibited a sharper peak at the long-wavelength edge of the spectrum, as compared to the spectrum of [Zn_2L^2]. The d–d transition of Cu^{II} complexes is normally observed at around 600–700 nm, but the corresponding peak was ambiguous for [CuL^1] and [Cu_2L^2], because the peak overlapped substantially with the onset of the absorption.

Similarly, in the spectra of [NiL^1] and [Ni_2L^2] (Figure 1c), the absorbance of the dinuclear complex was more than twice that of the mononuclear complex. Intensification of the peak in the region of 380–480 nm was significant, and hence, the profiles of the two complexes differed considerably. The peak for [NiL^1] at 440 nm (26600 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) might correspond to the shoulder observed for [Ni_2L^2] at 440 nm (72000 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$). In the longer-wavelength region, the peaks for [Ni_2L^2] at 536 nm (51500 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) and 569 nm (49600 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) were bathochromically shifted relative to the corresponding peaks for [NiL^1] at 509 nm (20000 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) and 534 nm (19200 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$), respectively. In contrast to the Cu and Zn complexes, the Ni complexes did not exhibit sharpening of the peaks at the lower-energy edge of the spectrum. The d–d transitions for both Ni complexes were expected to appear at around 500–600 nm, but again they were obscured by an intense absorption.

We should note a possibility that the coordination of pyridine molecule(s) on [NiL^1] and [Ni_2L^2] causes the difference in the UV/Vis spectra. The NMR spectroscopic results showed more broadened signals for [Ni_2L^2] relative to those for [NiL^1], implying that there is a difference in affinity to pyridine molecules. However, because the molecular environment of the coordination sites is similar, the difference in line broadening is expected to arise from a kinetic effect. Namely, during a rapid exchange of the pyridine ligand, the more coordination sites a complex has, the longer period the molecule spends in octahedral coordination responsible for paramagnetism. Therefore, as far as we measure steady-state UV/Vis absorption, we can neglect the effects of solvent coordination. Moreover, the difference in coordination geometry mainly affects the relative energy levels of the $d_{x^2-y^2}$ and d_{xy} orbitals, which were not likely to have been involved in the transition of the region of 400–450 nm. It should rather be taken into account that the absorption of this region is influenced by the change in π-conjugated system of salicylidene groups.[27,28]

The spectra of mono- and dinuclear Fe^{III} complexes are shown in Figure 1d. Although the spectra were measured in pyridine solution, we assume that the two iron complexes are present as inner-sphere type [FeL^1Cl] and [$Fe_2L^2Cl_2$] as identified in the solid state, as the spectra of similarly prepared complex [Fe(salphen)Cl] in chloroform, less polar and noncoordinative, gave quite a similar absorption profile to that of [FeL^1Cl]. Further, the similarity between the spectra of the mono- and dinuclear complexes suggests that they had similar coordination environments. The spectra of the Fe^{III} complexes were markedly broadened relative to those of Zn^{II}, Cu^{II}, and Ni^{II} and the low-energy onset was extended toward 800–900 nm. The extension was more prominent for the dinuclear system. The absorption of [$Fe_2L^2Cl_2$] was nearly double that of [FeL^1Cl]. The peak for [$Fe_2L^2Cl_2$] at 534 nm (35200 $M^{-1}cm^{-1}$) was bathochromically shifted relative to the corresponding peak for [FeL^1Cl] at 498 nm (19600 $M^{-1}cm^{-1}$), and the peak at 434 nm (30900 $M^{-1}cm^{-1}$) in the spectrum of [FeL^1Cl] may correspond to the shoulder at 442 nm (49600 $M^{-1}cm^{-1}$) in the spectrum of [$Fe_2L^2Cl_2$]. As was observed for the Ni complexes, the peak at around 380 nm was markedly more intense for the dinuclear system than for the mononuclear system.

Comparison of the spectra of the mononuclear complexes with the spectra of analogous complexes without the 6-hydroxy group on the naphthalene ring[27–30] suggests that the 6-hydroxy group was responsible for about 30–50 nm of redshift, owing to its electron-donating character; the overall profiles remained similar. Furthermore, with regard to the Ni complexes, there was no drastic difference between the profiles of salphen and *N*,*N′*-bis(2-hydroxynaphthylmethyl-1-ene)-*o*-phenylenediamine, except for a redshift of ca. 10 nm for the latter.[27,28] Therefore, we interpret the absorption profile of the dinuclear complexes as the sum of the contributions from each salphen moiety.

Definitively assigning the spectra for d_π,p_π-conjugated systems such as salphen complexes is intrinsically difficult. Because the π(ligand) and π*(ligand) orbitals and the d_π(metal) orbitals mix to form new π(metal + ligand) and π*(metal + ligand) orbitals, the transitions between them cannot be unambiguously characterized as either metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer.[19] In view of the level of the d orbitals of the first transition metals, the lowest-energy transition (500–600 nm) of [ZnL^1] was MLCT-like, and the second-lowest transition (400–500 nm) had ligand-center π–π* transition-like character. Therefore, the overall redshift of the spectra implies a lowering of the π* level as well as an elevation of the d_π level.

Notably, the changes in absorbance resulting from the fusion of the salphen unit differed from peak to peak, although the similarity of the overall profiles suggests that each peak corresponded to a similar transition for the mono- and dinuclear systems. The changes in the spectra may not have only originated from the extension of π conjugation. Recently, suggestive examples were reported by Glaser et al. in studies of Ni, Cu, and V complexes with a phloroglucinol-based triple salen.[33] Compared to a "single" salen complex with C_{2v} symmetry, a triple salen complex with C_{3h} symmetry shows a marked increase in absorbance in the region of 330–380 nm, which is attributable to the π–π* transition of the terminal and central benzene rings, whose transition moment is enhanced by the reduction in the local symmetry of the salen unit. In our case, the intensification of the absorption peak may have arisen from the change in transition moment due to the change in symmetry from C_{2v} (mononuclear complex) to C_{2h} (dinuclear complex). According to Glaser et al.[33] such a change in electronic absorption spectra can be interpreted in terms of the strong electronic communication between the π molecular orbitals of salen units.

Conclusions

We synthesized several mono- and dinuclear complexes of novel π-conjugated salphen ligands. The absorption peaks of the dinuclear complexes were markedly redshifted relative to the peaks of the mononuclear complexes, and there were additional spectral changes beyond simple additivity. For Zn^{II} and Cu^{II}, the dinuclear system showed a steep onset at the low-energy edge of the spectrum. For Ni^{II} and Fe^{III}, the peak at around 380 nm was more intense for the dinuclear system than for the mononuclear one. Notably, the absorption edge of the dinuclear system was extended toward the near-infrared region. These changes in optical properties are potentially advantageous for applications to optical and optoelectronics materials. Further studies on the mechanism of the spectral changes and on the fabrication of polynuclear system are in progress.

Experimental Section

General: All chemicals and solvents were purchased from Tokyo Kasei Kogyo (TCI) and used without further purification. Monoaldehyde **1**[24] and phenylenediamine **3**[26] were prepared according to literature procedures. Dialdehyde **2** was prepared by the route of Kuriakose,[25] which was improved by us.[34] UV/Vis absorption spectra were measured for a pyridine (spectroscopic grade, 1×10^{-4} M) solution of each solute with a JASCO V-630 spectrophotometer. NMR spectra were recorded with a JEOL JNM-AL400 instrument (400 MHz for ^1H). IR spectra were recorded with a Shimadzu FTIR-8700 instrument. Melting points were determined with an optical microscope equipped with a Linkam LK-600 temperature-variable stage; the heating rate was 2 $K\,min^{-1}$.

H_2L^1: Monoaldehyde **1** (207 mg, 1.1 mmol) was dissolved in thf (4 mL), and the solution was added to a thf/methanol solution (1:1, 5 mL) of diamine **3** (239 mg, 0.5 mmol). After 12 h, methanol was added to promote precipitation. The product was filtered, then washed with methanol, and obtained as a reddish purple crystalline solid. Yield: 139 mg (34%). M.p. 244–246 °C. IR (KBr): $\tilde{\nu}$ = 3365 (ν_{O-H}), 1611 ($\nu_{C=N}$) cm^{-1}. MS (FAB+): *m/z* = 817.8 $[M + H]^+$. $C_{52}H_{68}N_2O_6$ (817.08): calcd. C 76.44, H 8.39, N 3.43; found C 76.15, H 8.40, N 3.41. ^1H NMR ([D_6]DMSO): δ = 0.85 (t, ^1J = 7.3 Hz, 6 H, CH_3), 1.20–1.40 (m, 32 H, -CH_2-), 1.42–1.51 (m, 4 H, -CH_2-), 1.73–1.80 (m, 4 H, -CH_2-), 4.15 (t, ^1J = 5.9 Hz, 4 H, -CH_2O-), 7.01 (d, ^1J = 9.2 Hz, 2 H, Ar*H*), 7.10–7.12 (m, 4 H, Ar*H*), 7.38 (s, 2 H, Ar*H*), 7.76 (d, ^1J = 9.3 Hz, 2 H, Ar*H*), 8.39 (d, ^1J = 9.7 Hz, 2 H, Ar*H*), 9.54 (br., 2 H, ArO*H*), 9.56 (s, 2 H, -C*H*=N-), 15.05 (br., 2 H, ArO*H*) ppm.

Partial Ligand 4: Monoaldehyde **1** (753 mg, 4.0 mmol) was dissolved in thf/ethanol (1:4, 25 mL), and the solution was added to a thf/ethanol solution (4:3, 35 mL) of diamine **3** (954 mg, 2.0 mmol). After 12 h, the mixture was concentrated in vacuo; then, methanol (30 mL) was added to promote precipitation. The product was obtained as an orange crystalline solid. Yield: 946 mg (73%). M.p. 140–142 °C. IR (KBr): ṽ = 3192 ($\nu_{\text{O–H}}$), 1607 ($\nu_{\text{C=N}}$) cm^{-1}. MS (FAB+): *m/z* = 647.5 [M + H]$^+$. $C_{41}H_{62}N_2O_4{\cdot}0.5H_2O$ (655.93): calcd. C 75.07, H 9.68, N 4.27; found C 74.84, H 9.71, N 4.30. ^{1}H NMR ([D$_6$]DMSO): δ = 0.85 (t, ^1J = 6.6 Hz, 6 H, C*H*$_3$), 1.19–1.38 (m, 32 H, -C*H*$_2$-), 1.40–1.48 (m, 4 H, -C*H*$_2$-), 1.64–1.74 (m, 4 H, -C*H*$_2$-), 3.90 (t, ^1J = 6.3 Hz, 2 H, -C*H*$_2$O-), 3.95 (t, ^1J = 6.4 Hz, 2 H, -C*H*$_2$O-), 4.76 (s, 2 H, ArN*H*$_2$), 6.50 (s, 1 H, Ar*H*), 7.04 (d, ^1J = 9.1 Hz, 1 H, Ar*H*), 7.10–7.13 (m, 2 H, Ar*H*), 7.22 (s, 1 H, Ar*H*), 7.72 (d, ^1J = 9.1 Hz, 1 H, Ar*H*), 8.41 (d, ^1J = 8.8 Hz, 1 H, Ar*H*), 9.49 (s, 1 H, -C*H*=N-), 15.43 (s, 1 H, ArO*H*) ppm.

[ZnL^1]: To a solution of H_2L^1 (40.9 mg, 0.05 mmol) dissolved in thf (5 mL) was dropwise added a methanol solution (1 mL) of zinc acetate dihydrate (12.1 mg, 0.055 mmol). After 18 h, methanol (6 mL) was added, and the mixture was then concentrated in vacuo until a solid precipitated. The product was obtained as a reddish purple crystalline solid. Yield: 38 mg (86%). IR (KBr): ṽ = 3368 ($\nu_{\text{O–H}}$), 1607 ($\nu_{\text{C=N}}$), 566 ($\nu_{\text{M–O}}$), 419 ($\nu_{\text{M–N}}$) cm^{-1}. MS (FAB+): *m/z* = 879.6 [M + H]$^+$. $C_{52}H_{66}N_2O_6Zn{\cdot}2H_2O$ (916.49): calcd. C 68.15, H 7.70, N 3.06; found C 68.18, H 7.44, N 3.00. ^{1}H NMR ([D$_6$]DMSO): δ = 0.85 (t, ^1J = 6.5 Hz, 6 H, C*H*$_3$), 1.20–1.42 (m, 32 H, -C*H*$_2$-), 1.48–1.56 (m, 4 H, -C*H*$_2$-), 1.75–1.83 (m, 4 H, -C*H*$_2$-), 4.20 (t, ^1J = 6.0 Hz, 4 H, -C*H*$_2$O-), 6.92 (d, ^1J = 9.1 Hz, 2 H, Ar*H*), 6.99 (s, 2 H, Ar*H*), 7.03 (d, ^1J = 8.9 Hz, 2 H, Ar*H*), 7.56 (s, 2 H, Ar*H*), 7.59 (d, ^1J = 9.3 Hz, 2 H, Ar*H*), 8.29 (d, ^1J = 9.3 Hz, 2 H, Ar*H*), 9.23 (s, 2 H, -C*H*=N-), 9.58 (s, 2 H, ArO*H*) ppm.

[CuL^1]: To a solution of H_2L^1 (40.9 mg, 0.05 mmol) dissolved in thf (2 mL) was dropwise added a methanol solution (2 mL) of anhydrous copper(II) acetate (10.0 mg, 0.055 mmol). An additional amount of methanol (1 mL) was added, and the mixture was allowed to stand for 16 h, by which time a solid had precipitated. The product was obtained as a dark-purple crystalline solid. Yield: 45 mg (100%). IR (KBr): ṽ = 3352 ($\nu_{\text{O–H}}$), 1605 ($\nu_{\text{C=N}}$), 569 ($\nu_{\text{M–O}}$), 419 ($\nu_{\text{M–N}}$) cm^{-1}. MS (FAB+): *m/z* = 878.5 [M + H]$^+$, 900.7 [M + Na]$^+$. $C_{52}H_{66}CuN_2O_6{\cdot}H_2O$ (896.63): calcd. C 69.65, H 7.64, N 3.12; found C 69.38, H 7.64, N 3.15.

[NiL^1]: To a solution of H_2L^1 (40.9 mg, 0.05 mmol) dissolved in thf (5 mL) was dropwise added a methanol solution (1 mL) of nickel(II) acetate tetrahydrate (13.7 mg, 0.055 mmol). The product immediately precipitated as a purple crystalline solid. Yield: 41 mg (94%). IR (KBr): ṽ = 3354 ($\nu_{\text{O–H}}$), 1605 ($\nu_{\text{C=N}}$), 581 ($\nu_{\text{M–O}}$), 421 ($\nu_{\text{M–N}}$) cm^{-1}. MS (FAB+): *m/z* = 873.7 [M + H]$^+$, 895.7 [M + Na]$^+$. $C_{52}H_{66}N_2NiO_6{\cdot}H_2O$ (891.77): calcd. C 70.03, H 7.69, N 3.14; found C 69.85, H 7.54, N 3.16. ^{1}H NMR ([D$_6$]DMSO): δ = 0.84 (t, ^1J = 6.3 Hz, 6 H, C*H*$_3$), 1.20–1.40 (m, 32 H, -C*H*$_2$-), 1.45–1.54 (m, 4 H, -C*H*$_2$-), 1.73–1.80 (m, 4 H, -C*H*$_2$-), 4.18 (t, ^1J = 6.8 Hz, 4 H, -C*H*$_2$O-), 7.04 (d, ^1J = 9.1 Hz, 2 H, Ar*H*), 7.08 (s, 2 H, Ar*H*), 7.10 (d, ^1J = 8.9 Hz, 2 H, Ar*H*), 7.64 (d, ^1J = 9.2 Hz, 2 H, Ar*H*), 7.80 (s, 2 H, Ar*H*), 8.38 (d, ^1J = 8.5 Hz, 2 H, Ar*H*), 9.06 (s, 2 H, -C*H*=N-), 9.44 (s, 2 H, ArO*H*) ppm.

[FeL^{1}Cl]: To a solution of H_2L^1 (40.9 mg, 0.05 mmol) dissolved in thf (2 mL) was dropwise added a methanol solution (1 mL) of iron(III) chloride hexahydrate (14.9 mg, 0.055 mmol). Triethylamine (5 µL) was added, and the mixture was allowed to stand for 18 h. After the addition of methanol (6 mL) and concentration by evaporation, the product precipitated as a dark-brown crystalline solid. Yield: 29 mg (64%). IR (KBr): ṽ = 3366 ($\nu_{\text{O–H}}$), 1601 ($\nu_{\text{C=N}}$), 584 ($\nu_{\text{M–O}}$), 419 ($\nu_{\text{M–N}}$) cm^{-1}. MS (FAB+): *m/z* = 870.6 [M – Cl]$^+$, 905.6 [M]$^+$. $C_{52}H_{66}ClFeN_2O_6{\cdot}H_2O$ (924.38): calcd. C 67.56, H 7.41, N 3.03; found C 67.44, H 6.83, N 2.80.

[Zn$_2$L^2]: To a solution of ligand **4** (129.4 mg, 0.2 mmol) dissolved in thf (5 mL) was added a thf solution (5 mL) of **2** (21.6 mg, 0.1 mmol). After the solution turned reddish brown, a methanol solution (3 mL) of zinc acetate dihydrate (48.3 mg, 0.22 mmol) was added dropwise. After 4 h, the mixture gave a precipitate, which was collected by filtration and washed with methanol. Reddish purple crystalline solid. Yield: 127.6 mg (80%). IR (KBr): ṽ = 3384 ($\nu_{\text{O–H}}$), 1607 ($\nu_{\text{C=N}}$), 569 ($\nu_{\text{M–O}}$), 415 ($\nu_{\text{M–N}}$) cm^{-1}. MS (FAB+): *m/z* = 1599.7 [M + H]$^+$. $C_{94}H_{124}N_4O_{10}Zn_2{\cdot}4H_2O$ (1672.82): calcd. C 67.49, H 7.95, N 3.35; found C 67.38, H 7.46, N 3.48. ^{1}H NMR ([D$_5$]pyridine): δ = 0.89 (t, ^1J = 6.6 Hz, 12 H, C*H*$_3$), 1.20–1.39 (m, 72 H, -C*H*$_2$-), 1.48–1.58 (m, 8 H, -C*H*$_2$-), 1.77–1.87 (m, 8 H, -C*H*$_2$-), 4.18 (t, ^1J = 6.4 Hz, 4 H, -C*H*$_2$O-), 4.22 (t, ^1J = 6.3 Hz, 4 H, -C*H*$_2$O-), 7.48 (d, ^1J = 9.3 Hz, 2 H, Ar*H*), 7.51 (d, ^1J = 9.2 Hz, 2 H, Ar*H*), 7.56 (s, 2 H, Ar*H*), 7.77 (d, ^1J = 9.5 Hz, 2 H, Ar*H*), 7.85 (s, 2 H, Ar*H*), 7.92 (s, 2 H, Ar*H*), 8.65 (d, ^1J = 9.3 Hz, 2 H, Ar*H*), 8.74 (d, 2 H, Ar*H*), 8.83 (d, ^1J = 9.3 Hz, 2 H, Ar*H*), 10.16 (s, 2 H, -C*H*=N-), 10.20 (s, 2 H, -C*H*=N-), 11.44 (s, 2 H, ArO*H*) ppm.

[Cu$_2$L^2]: To a solution of ligand **4** (129.4 mg, 0.2 mmol) dissolved in thf (5 mL) was added a thf solution (5 mL) of **2** (21.6 mg, 0.1 mmol). After the solution turned reddish brown, a methanol/thf solution (1:3, 8 mL) of anhydrous copper(II) acetate (40.0 mg, 0.22 mmol) was added dropwise. After 11 h the mixture gave a precipitate, which was collected by filtration and washed with methanol. Dark-purple crystalline solid. Yield: 137.5 mg (86%). IR (KBr): ṽ = 3378 ($\nu_{\text{O–H}}$), 1605 ($\nu_{\text{C=N}}$), 571 ($\nu_{\text{M–O}}$), 421 ($\nu_{\text{M–N}}$) cm^{-1}. MS (FAB+): *m/z* = 1596.9 [M + H]$^+$. $C_{94}H_{124}Cu_2N_4O_{10}{\cdot}2H_2O$ (1633.10): calcd. C 69.13, H 7.90, N 3.43; found C 68.92, H 7.81, N 3.35.

[Ni$_2$L^2]: To a solution of ligand **4** (129.4 mg, 0.2 mmol) dissolved in thf (5 mL) was added a thf solution (5 mL) of **2** (21.6 mg, 0.1 mmol). After the solution turned reddish brown, a methanol solution (5 mL) of nickel(II) acetate tetrahydrate (54.7 mg, 0.22 mmol) was added dropwise. After 12 h the mixture gave a precipitate, which was collected by filtration and washed with methanol. Reddish purple crystalline solid. Yield: 132.2 mg (83%). IR (KBr): ṽ = 3354 ($\nu_{\text{O–H}}$), 1603 ($\nu_{\text{C=N}}$), 550 ($\nu_{\text{M–O}}$), 424 ($\nu_{\text{M–N}}$) cm^{-1}. MS (FAB+): *m/z* = 1585.4 [M + H]$^+$. $C_{94}H_{124}N_4Ni_2O_{10}{\cdot}3H_2O$ (1641.40): calcd. C 68.78, H 7.98, N 3.41; found C 69.15, H 7.79, N 3.41.

[Fe$_2$L^{2}Cl$_2$]: To a solution of ligand **4** (64.7 mg, 0.1 mmol) dissolved in thf (3 mL) was added a thf solution (4 mL) of **2** (10.8 mg, 0.05 mmol). After the solution turned reddish brown, a methanol solution (2 mL) of iron(III) chloride hexahydrate (29.7 mg, 0.11 mmol) was added dropwise. Triethylamine (10 µL) was added, and the mixture was allowed to stand for 16 h. The resulting precipitate was collected by filtration and washed with methanol. Black crystalline solid. Yield: 33.0 mg (40%). IR (KBr): ṽ = 3414 ($\nu_{\text{O–H}}$), 1599 ($\nu_{\text{C=N}}$), 573 ($\nu_{\text{M–O}}$), 417 ($\nu_{\text{M–N}}$) cm^{-1}. MS (FAB+): *m/z* = 1580.7 [M – 2Cl]$^+$. $C_{94}H_{124}Cl_2Fe_2N_4O_{10}{\cdot}2H_2O$ (1688.60): calcd. C 66.86, H 7.64, N 3.32; found C 66.70, H 7.09, N 3.45.

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[34] Synthesis of **2**: 1,5-Bis(dimethylaminomethyl)-2,6-dihydroxynaphthalene (**4**) was prepared according to ref.[25] To a solution of Mannich base **4** (6.60 g, 24 mmol) dissolved in aqueous acetic acid (81 vol.-%, 148 mL) was added hexamethylenetetramine (9.45 g, 67.5 mmol). The mixture was stirred at 130 °C for 4 h. After the mixture cooled to room temperature, the precipitate was collected by filtration and washed with methanol. For details, see: H. Houjou, T. Motoyama, S. Banno, I. Yoshikawa, K. Araki, *J. Org. Chem.*, in press.

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