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Twin Salphen: Asymmetric Heterodinuclear Complexes $\{\mathrm{M_aM_bL} \mid \mathrm{M_a}, \mathrm{M_b} = \mathrm{Ni, Cu, Zn}\}$ of a Symmetrically Fused Salphen Ligand

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Heterodinuclear complexes of a fully π-conjugated salphen ligand were efficiently synthesized with arbitrary combinations of $\mathrm{Ni^{II}}$, $\mathrm{Cu^{II}}$, and $\mathrm{Zn^{II}}$. The UV—vis spectra of the heterodinuclear complexes were approximately represented by a simple average of the spectra of the corresponding homodinuclear complexes. Systematic analysis of the spectra highlighted weak intracomplex interactions through the π-conjugated system of the ligand.

Introduction

Interest in precisely arranging metal atoms has been growing in connection with the recent development of metal clusters, metal—organic frameworks, various metallo—supramolecular polymers, and other metal-containing materials.[1–4] Metallo—polymers in which metal atoms are directly bound to an organic main chain with extended π-conjugation are of special interest.[5–8] These systems can be expected to show conductivity, redox activity, photoluminescence, magnetism, and other properties originating from electronic communication between the metal atoms mediated by the organic chain. The number of reports highlighting the effects of intracomplex (metal—metal and ligand—metal) interactions on the spectroscopic features of fully π-conjugated oligonuclear salen and salphen complexes has been increasing.[9–12]

As a part of our continuing research exploring various metallo—polyimines, we have studied 2,6-dihydroxynaphthalene-1-carbaldehyde and 2,6-dihydroxynaphthalene-1,5-dicarbaldehyde (**1**) as components of π-conjugated metallo—polysalphens.[13–16] Recently, we synthesized and characterized novel dinuclear salphen complexes with **1** and observed some substantial changes in the spectral profile as compared to the corresponding mononuclear complex; these changes may have originated in the interactions of salphen complexes fused into a π-conjugated system.[16] Phenomena originating in coupling between the metal's d-electrons and the ligand's π-conjugated system can be investigated by means of a complex in which different metals interact with each other through the π-conjugated system. In this report, we describe the preparation and spectroscopic properties of homo- and heterodinuclear complexes of a fully conjugated salphen ligand with arbitrary combinations of $\mathrm{Ni^{II}}$, $\mathrm{Cu^{II}}$, and $\mathrm{Zn^{II}}$ ions.

Experimental Section

General. All chemicals and solvents were purchased from Tokyo Kasei Kogyo (TCI) and used without further purification.

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(1) Abd-El-Aziz, A. S., Carraher, Jr., C. E., Pittman, Jr., C. U., Zeldin, M., Eds. *Macromolecules Containing Metal and Metal-Like Elements. Volume 5 Metal-Coordination Polymers*; John Wiley & Sons, Inc.: Hoboken, NJ, 2005.

(2) Whittell, G. R.; Manners, I. *Adv. Mater.* **2007**, *19*, 3439–3468.

(3) (a) Leung, A. C. W.; Maclachlan, M. J. *J. Inorg.Organomet. Polym. Mater.* **2007**, *17*, 57–89. (b) Leung, A. C. W.; Hui, J. K. −H.; Chong, J. H.; Maclachlan, M. J. *Dalton Trans.* **2009**, 5199–5210.

(4) Hofmeier, H.; Schubert, U. S. *Chem. Commun.* **2005**, 2423–2432.

(5) Hirao, T. *Coord. Chem. Rev.* **2002**, *226*, 81–91.

(6) Holiday, B. J.; Swager, T. M. *Chem. Commun.* **2005**, 23–36.

(7) Pickup, P. G. *J. Mater. Chem.* **1999**, *9*, 1641–1653.

(8) O'Sullivan, T. J.; Djukic, B.; Dube, P. A.; Lemaire, M. T. *Chem. Commun.* **2009**, 1903–1905.

(9) (a) Kleij, A. W. *Eur. J. Inorg. Chem.* **2009**, 193–205. (b) Crreli, S.; Escudero-Adan, E. C.; Benet-Buchholz, J.; Kleij, A. W. *Eur. J. Inorg. Chem.* **2008**, 2863–2873. (c) Escudero-Adan, E. C.; Benet-Buchholz, J.; Kleij, A. W. *Inorg. Chem.* **2007**, *46*, 7265–7267. (d) Wezenberg, S. J.; Kleij, A. W. *Org. Lett.* **2008**, *10*, 3311–3314.

(10) (a) Rotthaus, O.; Thomas, F.; Jarjayes, O.; Philouze, C.; Saint-Aman, E.; Pierre, J.-L. *Chem.—Eur. J.* **2006**, *12*, 6953–6962. (b) Rotthaus, O.; Jarjayes, O.; Philouze, C.; Del Valle, C. P.; Thomas, F. *Chem. Commun.* **2009**, 1792–1800.

(11) (a) Glaser, T.; Heidemeier, M.; Fröhlich, R.; Hildebrandt, P.; Bothe, E.; Bill, E. *Inorg. Chem.* **2005**, *44*, 5467–5482. (b) Theil, H.; von Richthofen, C.-G. F.; Stammler, A.; Bögge, H.; Glaser, T. *Inorg. Chim. Acta* **2008**, *361*, 916–924. (c) Glaser, T.; Heidemeier, M.; Strautmann, J. B. H.; Bögge, H.; Stammler, A.; Krickemeyer, E.; Huenerbein, R.; Grimme, S.; Bothe, E.; Bill, E. *Chem.—Eur. J.* **2005**, *44*, 5467–5482. (d) Glaser, T.; Heidemeier, M.; Krickemeyer, E.; Bögge, H.; Stammler, A.; Fröhlich, R.; Bill, E.; Schnack, J. *Inorg. Chem.* **2009**, *48*, 607–620.

(12) Shimazaki, Y.; Tani, F.; Fukui, K.; Naruta, Y.; Yamauchi, O. *J. Am. Chem. Soc.* **2003**, *125*, 10512–10513. Shimazaki, Y.; Kabe, R.; Huth, S.; Tani, F.; Naruta, Y.; Yamauchi, O. *Inorg. Chem.* **2007**, *46*, 6083–6090.

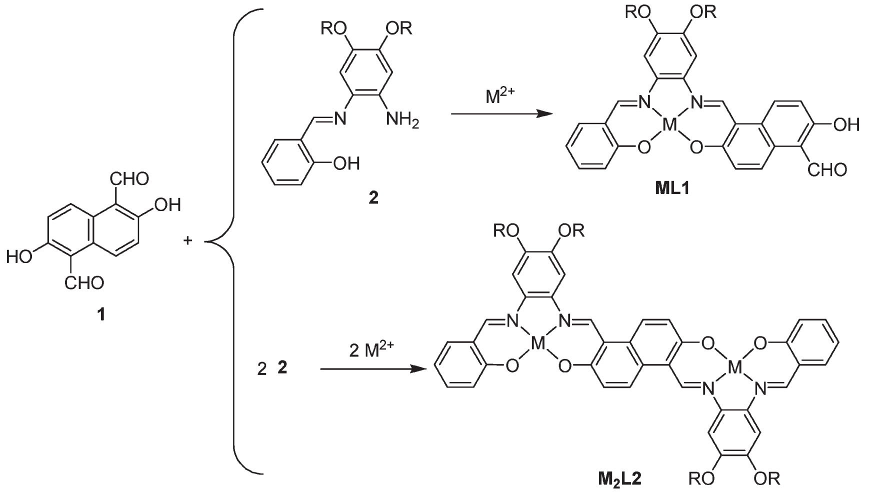
(13) (a) Houjou, H.; Sasaki, T.; Shimizu, Y.; Koshizaki, N.; Kanesato, M. *Adv. Mater.* **2005**, *17*, 606–610. (b) Houjou, H.; Shimizu, Y.; Koshizaki, N.; Kanesato, M. *Adv. Mater.* **2003**, *15*, 1458–1461.

(14) Houjou, H.; Kokubun, M.; Yoshikawa, Y.; Araki, K. *Chem. Lett.* **2009**, *38*, 436–437.

(15) Houjou, H.; Motoyama, T.; Banno, S.; Yoshikawa, I.; Araki, K. *J. Org. Chem.* **2009**, *74*, 520–529.

(16) Houjou, H.; Motoyama, T.; Araki, K. *Eur. J. Inorg. Chem.* **2009**, 533–538.

Scheme 1. Synthesis of **ML1** and **M2L2**



2,6-Dihydroxy-1,5-naphthalenedicarbaldehyde (**1**) and 4,5-didodecyloxy-1,2-phenylenediamine (**3**) were prepared according to the procedure previously reported. UV−vis absorption spectra were measured for a pyridine (spectroscopic grade, 2×10^{-5} M) solution of each solute with a JASCO V-630 spectrophotometer. NMR spectra were recorded on a JEOL JNM-AL400 instrument (400 MHz for ^{1}H). 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.

Synthesis of 2, Monoimine Partial Ligand. Phenylenediamine **3** (954 mg, 2.00 mmol) was dissolved in chloroform (8 mL), to which added was salicylaldehyde (244 mg, 2.00 mmol). To this solution, methanol (8 mL) was added gently so as not to disturb the interface of two solvents. Yellow solid started to separate out near the interface, and was allowed to grow further 24 h. The yellow solid was collected by filtration. Yield: 929 mg (80%). mp: 75−76 °C. IR(KBr): ν = 1612 (C=N), 1205 (ArOH) cm^{-1}. Precise MS(FAB+): m/z = 580.4620 (calcd. for M$^+$ 580.4604). ^{1}H NMR (CDCl$_3$): δ 0.88 (t (6.6 Hz), $-CH_3$, 6H), 1.27−1.56 (m, $-CH_2-$, 36H), 1.80 (m, $-CH_2-$, 4H), 3.83 (s, $-NH_2$, 2H), 3.95 (m, $-OCH_2-$, 4H), 6.37 (s, ArH, 1H), 6.78 (s, ArH, 1H), 6.95 (t (7.5 Hz), ArH, 1H), 7.02 (d (7.8 Hz), ArH, 1H), 7.34 (dd (7.1 Hz, Hz), ArH, 2H), 8.56 (s, $-CH=N-$, 1H), 13.14 (s, $-OH$, 1H). ^{13}C NMR (CDCl$_3$): δ 14.6, 23.1, 26.5, 29.7, 29.8, 29.9, 30.0, 30.1, 30.1, 30.1, 32.2, 69.5, 71.6, 102.5, 106.7, 117.2, 119.5, 120.0, 127.0, 132.1, 132.7, 136.5, 142.5, 150.9, 158.9, 160.7.

Synthesis of Complex Ligand ZnL1. 1 (43 mg, 0.2 mmol) and **2** (117 mg, 0.2 mmol) were dissolved into 10 mL of tetrahydrofuran. To this solution, methanol solution (4 mL) of zinc(II) acetate dihydrate (47 mg, 0.2 mmol) was added, and 3 mL of methanol was added after 3 h to promote precipitation. After 19 h, reddish orange powder was collected by filtration. Yield: 125 mg (74%). IR(KBr): ν = 1638 (C=O), 1614 (C=N), 557 (M−O), 478 (M−N) cm^{-1}. MS(FAB+): m/z = 841.3 (calcd. for M + H$^+$ 841.41). Elemental analysis for $C_{49}H_{64}N_2O_6Zn \cdot H_2O$ (860.45): calcd. C 68.40, H 7.73, N 3.26; found: C 68.46, H 7.88, N 3.31. ^{1}H NMR (CDCl$_3$ with 1 equiv. of 4-dimethylaminopyridine): δ 0.88 (t (7.1 Hz), $-CH_3$, 6H), 1.27−1.44 (m, $-CH_2-$, 32H), 1.53 (m, $-CH_2-$, 4H), 1.90 (m, $-CH_2-$, 4H), 4.09 (t (6.4 Hz), $-OCH_2-$, 2H), 4.14 (t (6.4 Hz), $-OCH_2-$, 2H), 6.56 (dt (1.2 Hz, 7.1 Hz), 1H), 7.07 (d (8.1 Hz), ArH, 1H), 7.08 (s, ArH, 1H), 7.15 (s, ArH, 1H), 7.15 (d (9.0 Hz), ArH, 1H), 7.23−7.31 (m, ArH, 2H), 7.41 (d (9.5 Hz), ArH, 1H), 8.25 (d (9.8 Hz), ArH, 1H), 8.32 (d (9.5 Hz), ArH, 1H), 8.61 (s, $-CH=N-$, 1H), 9.46 (s, $-CH=N-$, 1H), 10.78 (s, $-CHO$, 1H), 12.52 (s, OH, 1H).

Synthesis of Complex Ligand NiL1. 1 (43 mg, 0.2 mmol) and **2** (117 mg, 0.2 mmol) were dissolved into 10 mL of tetrahydrofuran. To this solution, methanol solution (4 mL) of nickel(II) acetate tetrahydrate (52 mg, 0.2 mmol) was added, and 6 mL of methanol was added to promote precipitation. After 24 h, red crystalline solid was collected by filtration. Yield: 140 mg (84%). IR(KBr): ν = 1638 (C=O), 1609 (C=N), 568 (M−O), 459 (M−N) cm^{-1}. MS(FAB+): m/z = 835.6 (calcd. for M + H$^+$ 835.42). Elemental analysis for $C_{49}H_{64}N_2NiO_6$ (835.74): calcd. C 70.42, H 7.72, N 3.35; found: C 70.15, H 7.76, N 3.42. ^{1}H NMR (CDCl$_3$): δ 0.88 (t (6.6 Hz), $-CH_3$, 6H), 1.27−1.44 (m, $-CH_2-$, 32H), 1.53 (m, $-CH_2-$, 4H), 1.89 (m, $-CH_2-$, 4H), 4.06 (t (6.6 Hz), $-OCH_2-$, 2H), 4.11 (t (6.4 Hz), $-OCH_2-$, 2H), 6.69 (t (7.8 Hz), 1H), 7.08 (s, ArH, 1H), 7.11 (s, ArH, 1H), 7.17(d (8.8 Hz), ArH, 1H), 7.24−7.34 (m, Ar, 2H), 7.36 (d (7.8 Hz), ArH, 1H), 7.48 (d (9.8 Hz), ArH, 1H), 7.99 (s, $-CH=N-$, 1H), 8.23 (d (9.8 Hz), ArH, 1H), 8.24 (d (9.5 Hz), ArH, 1H), 8.74 (s, $-CH=N-$, 1H), 10.74 (s, $-CHO$, 1H), 12.53 (s, OH, 1H).

Synthesis of Complex Ligand CuL1. 1 (294 mg, 0.5 mmol) and **2** (109 mg, 0.5 mmol) were dissolved into 15 mL of tetrahydrofuran. To this solution, methanol solution (15 mL) of copper(II) acetate (92 mg, 0.5 mmol) was added, and was left for 15 h to promote precipitation. Reddish brown crystalline solid was collected by filtration. The solid was recrystallized from tetrahydrofuran−methanol. Yield: 264 mg (63%). IR(KBr): ν = 1638 (C=O), 1609 (C=N), 519 (M−O), 446 (M−N) cm^{-1}. MS(FAB+): m/z = 841.2 (calcd. for M + H$^+$ 840.41). Elemental analysis for $C_{49}H_{64}CuN_2O_6 \cdot (H_2O)_{0.5}$ (849.60): calcd. C 69.27, H 7.71, N 3.30; found: C 69.25, H 7.73, N 3.35.

Synthesis of Dinuclear Complex Zn_2L2. 1 (22 mg, 0.1 mmol) and **2** (116 mg, 0.2 mmol) were dissolved into 5 mL of tetrahydrofuran. To this solution, methanol solution (5 mL) of zinc(II) acetate dihydrate (44 mg, 0.2 mmol) was added, and was left for 4 days to promote precipitation. Reddish brown powder was collected by filtration. Yield: 76 mg (52%). IR(KBr): ν = 1609 (C=N), 552 (M−O), 449 (M−N) cm^{-1}. MS(FAB+): m/z = 1468.1 (calcd. for M + H$^+$ 1464.78). Elemental analysis for $C_{86}H_{120}N_4O_8Zn_2 \cdot (H_2O)_2$ (1504.706): calcd. C 68.65, H 8.31, N 3.72; found: C 68.78, H 8.37, N 3.75. ^{1}H NMR (CDCl$_3$ with 2 equiv. of 4-dimethylaminopyridine): δ 0.88 (t (6.6 Hz), $-CH_3$, 12H), 1.27−1.44 (m, $-CH_2-$, 64H), 1.55 (m, $-CH_2-$, 8H), 1.91 (m, $-CH_2-$, 8H), 4.09 (t (6.4 Hz), $-OCH_2-$, 4H), 4.17 (t (6.6 Hz), $-OCH_2-$, 4H), 6.56 (t (7.1 Hz), 2H), 7.08 (d (8.1 Hz), ArH, 2H), 7.09 (s, ArH, 2H), 7.19 (s, ArH, 1H), 7.24−31 (m, ArH, 4H), 8.10 (d (9.6 Hz), ArH, 2H), 8.63 (s, $-CH=N-$, 2H), 9.55 (s, $-CH=N-$, 1H).

Synthesis of Dinuclear Complex Ni_2L2. 1 (22 mg, 0.1 mmol) and **2** (116 mg, 0.2 mmol) were dissolved into 9 mL of chloroform. To this solution, methanol solution (9 mL) of nickel(II) acetate tetrahydrate (50 mg, 0.2 mmol) was added. Further 9 mL

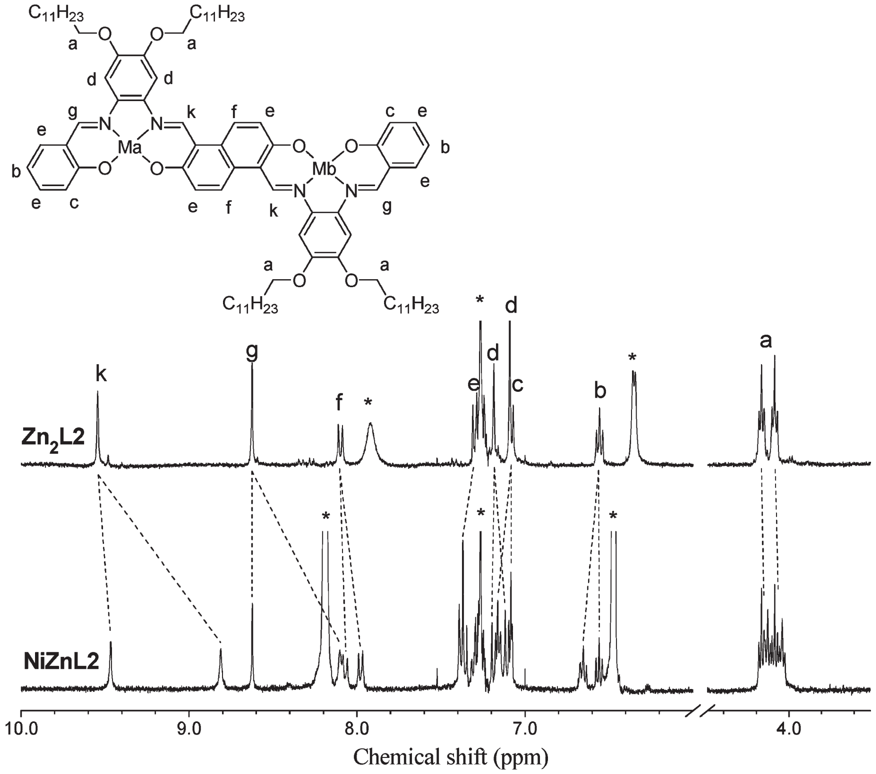
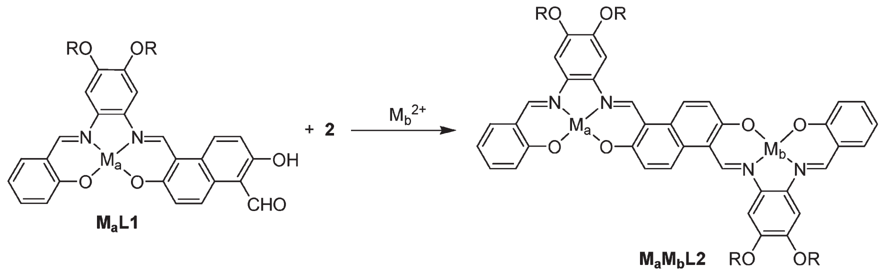


Figure 1. ^{1}H NMR spectra of **Zn$_2$L2** and **NiZnL2** (* denotes signals of chloroform and dimethylaminopyridine).

Scheme 2. Synthesis of Hetero Dinuclear Complex **M$_a$M$_b$L2**



of chloroform was added to the solution, which was refluxed at 60 °C for 14 h to promote precipitation. Dark brown powder was collected by filtration. Yield: 76 mg (52%). IR(KBr): ν = 1604, 1590 (C=N), 568 (M−O), 458 (M−N) cm^{-1}. MS(FAB+): m/z = 1455.2 (calcd. for M + H$^+$ 1453.79). Elemental analysis for $C_{86}H_{120}N_4Ni_2O_8$ (1455.282): calcd. C 70.98, H 8.31, N 3.58; found: C 70.77, H 8.37, N 3.78.

Synthesis of Dinuclear Complex Cu$_2$L2. 1 (22 mg, 0.1 mmol) and **2** (116 mg, 0.2 mmol) were dissolved into 5 mL of tetrahydrofuran. To this solution, methanol solution (5 mL) of copper(II) acetate (38 mg, 0.2 mmol) was added, and was left for 6 h to promote precipitation. Deep purple powder was collected by filtration. Yield: 119 mg (82%). IR(KBr): ν = 1605, 1589 (C=N), 561 (M−O), 448 (M−N) cm^{-1}. MS(FAB+): m/z = 1701.9 (calcd. for M + H$^+$ + 3pyridine 1700.90). Elemental analysis for $C_{86}H_{120}$ $Cu_2N_4O_8$ (1464.987): calcd. C 70.56, H 8.26, N 3.82; found: C 70.32, H 8.23, N 3.77.

Synthesis of Dinuclear Complex NiZnL2. NiL1 (30 mg, 36 μmol) and **2** (21 mg, 36 μmol) were dissolved into 8 mL of chloroform. To this solution, dimethylformamide solution (1 mL) of zinc(II) acetate dihydrate (8.0 mg, 36 μmol) was added, and was stirred at 70 °C. After 18 h, methanol was added to promote precipitation. Dark brown powder was collected by filtration. Yield: 48 mg (91%). IR(KBr): ν = 1606, 1590 (C=N), 556 (M−O), 462 (M−N) cm^{-1}. MS(FAB+): m/z = 1461.4 (calcd. for M + H$^+$ 1459.78). Elemental analysis for $C_{86}H_{120}N_4NiO_8Zn\cdot H_2O$ (1479.994): calcd. C 69.79, H 8.31, N 3.79; found: C 68.69, H 8.41, N 3.67. ^{1}H NMR ($CDCl_3$ with 10 equiv. of 4-dimethylaminopyridine): δ 0.88 (t (7.1 Hz), −CH_3, 12H), 1.27−1.44 (m, −CH_2−, 64H), 1.54 (m, −CH_2−, 8H), 1.89 (m, −CH_2−, 8H), 4.04 (t (6.6 Hz), −OCH_2−, 2H), 4.09 (t (6.6 Hz), −OCH_2−, 2H), 4.13 (t (6.3 Hz), −OCH_2−, 2H), 4.17 (t (6.4 Hz), −OCH_2−, 2H), 6.56 (dt (1.0 Hz, 7.1 Hz), 1H), 6.65 (t (7.5 Hz), 1H), 7.08 (s, ArH, 1H), 7.09 (d (7.6 Hz), ArH, 1H), 7.12 (s, ArH, 1H), 7.15 (d (6.6 Hz), ArH, 1H), 7.17 (d (5.1 Hz), ArH, 1H), 7.20 (s, ArH, 1H), 7.24−32 (m, ArH, 4H), 7.36 (d (9.2 Hz), ArH, 1H), 7.38 (d (9.2 Hz), ArH, 2H), 7.98 (d (9.6 Hz), ArH, 1H), 8.06 (d (10.1 Hz), ArH, 2H), 8.10 (brs, −CH=N−, 1H), 8.62 (s, −CH=N−, 2H), 8.81 (brs, −CH=N−, 1H), 9.47 (s, −CH=N−, 1H).

Synthesis of Dinuclear Complex CuNiL2. CuL1 (42 mg, 50 μmol) and **2** (29 mg, 50 μmol) were dissolved into 8 mL of chloroform. To this solution, dimethylformamide solution (1 mL) of nickel(II) acetate tetrahydrate (12.0 mg, 50 μmol) was added, and was stirred at 70 °C. After 18 h, methanol was added to promote precipitation. Dark brown powder was collected by filtration. Yield: 48 mg (91%). IR(KBr): ν = 1606, 1590 (C=N), 556 (M−O), 462 (M−N) cm^{-1}. MS(FAB+): m/z = 1461.4

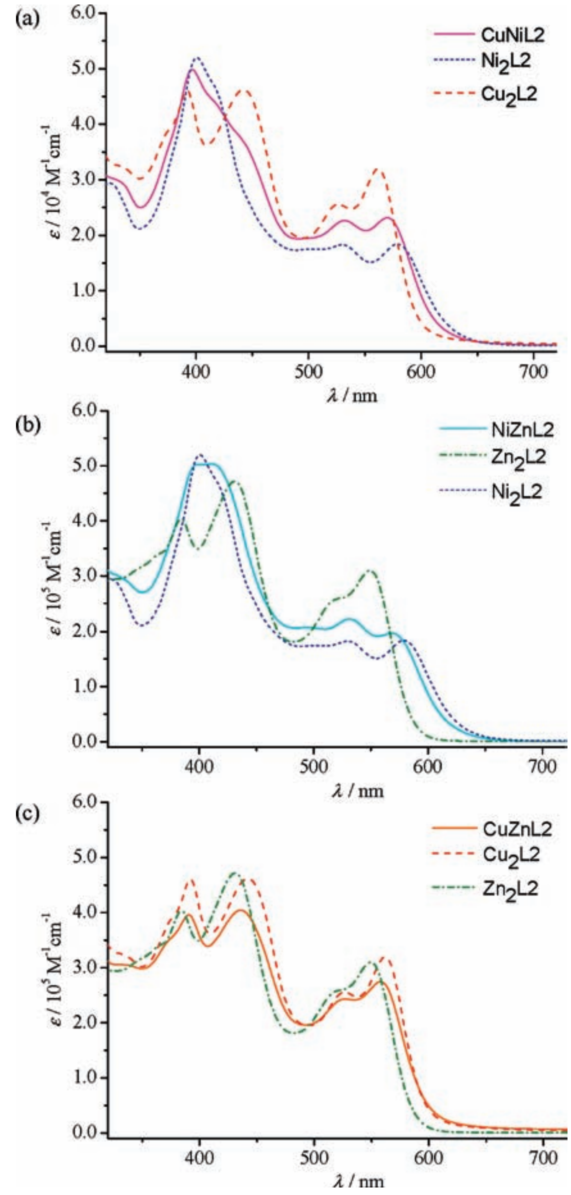


Figure 2. UV−vis spectra of homo- and hetero-dinuclear complexes. Combinations of metals are (a) Cu−Ni, (b) Ni−Zn, (c) Cu−Zn.

(calcd. for M + H$^+$ 1459.78). Elemental analysis for $C_{86}H_{120}N_4NiO_8Zn\cdot H_2O$ (1479.994): calcd. C 69.79, H 8.31, N 3.79; found: C 68.69, H 8.41, N 3.67.

Synthesis of Dinuclear Complex CuZnL2. CuL1 (28 mg, 30 μmol) and **2** (18 mg, 30 μmol) were dissolved into 10 mL of chloroform. To this solution, dimethylformamide solution (1 mL) of bis(pentane-2,4-dionato)zinc(II) (8.3 mg, 32 μmol) was added, and was left for 26 h. The solution was stirred at 60 °C for 11 h, and then diluted with methanol to promote precipitation. Brown−purple powder was collected by filtration. Yield: 36 mg (82%). IR(KBr): ν = 1606, 1589 (C=N), 558 (M−O), 448 (M−N) cm^{-1}. MS(FAB+): m/z = 1465.8 (calcd. for M + H$^+$ 1464.78). Elemental analysis for $C_{86}H_{120}CuN_4O_8Zn\cdot H_2O$ (1484.846): calcd. C 69.56, H 8.28, N 3.77; found: C 69.00, H 8.32, N 3.86.

Results and Discussion

Scheme 1 shows the preparation of mononuclear complex **ML1** and homodinuclear complex **M$_2$L2**. Monoimine half-ligand **2** was synthesized by condensation of salicylaldehyde and 4,5-didodecyloxyphenylene-1,2-diamine in chloroform−methanol. The reaction of **1** with equimolar amounts of both **2** and zinc(II) acetate dihydrate in THF−methanol afforded **ZnL1** in 74% yield. When 2 equivalents of **2** and 2 equivalents of the zinc salt were allowed to react with **1**, dinuclear complex **Zn$_2$L2** was obtained as a red crystalline solid (52%). Similarly, Cu^{II} complexes (**CuL1** and **Cu$_2$L2**) and Ni^{II} complexes (**NiL1** and **Ni$_2$L2**) were synthesized with copper(II) acetate and nickel(II) acetate tetrahydrate, respectively, in 82% and 52% yields. These results show that the condensation of **1** and **2** with concomitant metal binding proceeded efficiently. Mononuclear complexes **M$_a$L1** were employed as intermediates for the preparation of heterodinuclear complexes **M$_a$M$_b$L2**, where M$_a$, M$_b$ = Ni^{II}, Cu^{II}, and Zn^{II} (Scheme 2). The homo- and heterodinuclear complexes were characterized by ^{1}H NMR (if possible), IR, fast atom bombardment mass spectrometry, and elemental analysis.

Figure 1 shows the ^{1}H NMR spectra of **Zn$_2$L2** and **NiZnL2**. As compared to the spectra of **Zn$_2$L2**, that of **NiZnL2** exibits magnetical nonequivalency of oxo-methylene protons (a), aromatic protons (b−f), and imine protons (g and k), which supports the structure of asymmetric hetero dinuclear complex. The enlarged version of this figure and the comparison of the spectra of **ZnL1** and **NiL1** are given in Supporting Information (Figures S1 and S2).

The reaction of **CuL1** with equimolar amounts of **2** and nickel(II) acetate tetrahydrate afforded heterodinuclear complex **CuNiL2** (77%). When the metals were introduced in reverse order, that is, when **NiL1** was allowed to react with equimolar amounts of **2** and copper(II) acetate, we obtained **NiCuL2** (76%), which was confirmed to be identical to **CuNiL2** on the basis of various analytical data. We also confirmed that the stepwise reaction afforded homodinuclear complexes **Cu$_2$L2** and **Ni$_2$L2** when we used the combinations of **CuL1**+copper(II) salt and **NiL1**+nickel(II) salt, respectively.

The UV−vis spectra of **Cu$_2$L2**, **Ni$_2$L2**, and **CuNiL2** measured in pyridine solution (2×10^{-5} M) are compared in Figure 2a. The spectrum of **Ni$_2$L2** showed an intense peak at around 400 nm and moderate absorption in the region of 500−600 nm. In the spectrum of **Cu$_2$L2**, the peak at around 400 nm was split into two peaks, at 392 and 442 nm. These features of the homodinuclear complexes corresponded well to the features of analogous complexes reported previously,[16] where we tentatively assigned the absorption bands at around 350−450 nm to $\pi-\pi^*$-like transitions, whereas the bands at around 500−600 nm were attributed to transitions assuming MLCT-like character. The spectrum of **CuNiL2** had a profile intermediate between the profiles of **Ni$_2$L2** and **Cu$_2$L2**.

We also synthesized heterodinuclear complexes with a combination of Ni^{II} and Zn^{II}. The reaction of **NiL1** with equimolar amounts of **2** and zinc(II) acetate dihydrate afforded heterodinuclear complex **NiZnL2** (91%). However, when the metals were introduced in reverse order, we obtained a considerable amount of **Ni$_2$L2** as a byproduct, in addition to the expected **ZnNiL2** product. This byproduct was likely due to transmetalation at the coordination site of Zn^{II}, which is relatively labile. The spectra of **NiZnL2**, **Zn$_2$L2**, and **Ni$_2$L2** are compared in Figure 2b. As was the case for the Cu−Ni system, the spectra of **NiZnL2** showed a profile intermediate between the profiles of **Ni$_2$L2** and **Zn$_2$L2**, but the profile was much closer to that of the Ni^{II} homodinuclear complex.

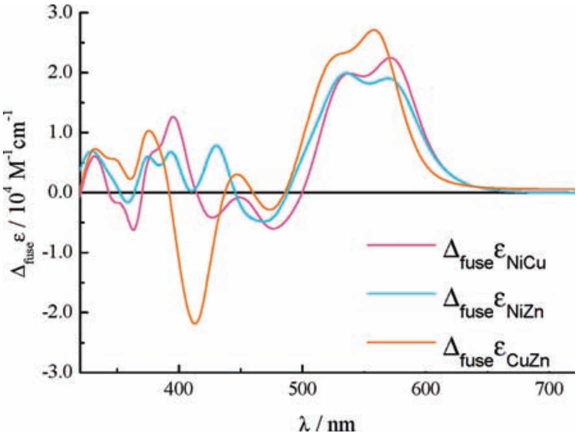


Figure 3. Difference spectra $\Delta_{\mathrm{fuse}}\varepsilon_{\mathrm{MaMb}}$ ($\mathrm{M_a}$, $\mathrm{M_b}$ = Ni, Cu, Zn), obtained by subtracting the spectra of the constitutive mononuclear complexes $\mathbf{M_aL3}$ and $\mathbf{M_bL3}$ from that of $\mathbf{M_aM_bL2}$.

The reaction of **CuL1** with equimolar amounts of **2** and zinc(II) acetate dihydrate did not afford a satisfactory amount of **CuZnL2**. The use of bis(acetylacetonato)zinc(II) as the metal ion source greatly improved both the yield (82%) and the purity. When **ZnL1** was used as the starting material, we obtained a considerable amount of $\mathbf{Cu_2L2}$, again as a result of transmetalation. The spectra of $\mathbf{Zn_2L2}$ and $\mathbf{Cu_2L2}$ were quite similar to each other, in agreement with our previous report,[16] and **CuZnL2** gave a profile intermediate between the profiles of the homodinuclear complexes (Figure 2c).

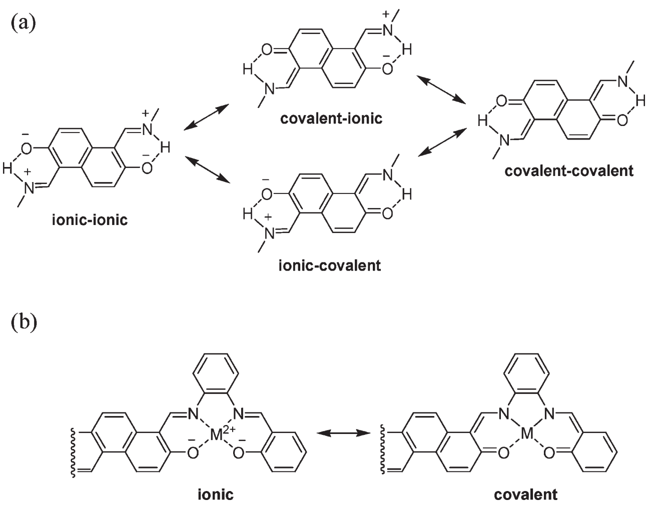
The overall spectral profiles of the heterodinuclear complexes were approximately represented by an arithmetic average of the spectra of the two homodinuclear complexes (with displacement of $<\sim$10% of ε). The relation can be expressed as follows:

$$\varepsilon_{\mathrm{Ma,\,Mb}} = \frac{1}{2}(\varepsilon_{\mathrm{Ma,\,Ma}} + \varepsilon_{\mathrm{Mb,\,Mb}}) = \varepsilon_{\mathrm{Ma}} + \varepsilon_{\mathrm{Mb}} + \Delta_{\mathrm{fuse}}\varepsilon_{\mathrm{MaMb}} \qquad (1)$$

where $\varepsilon_{\mathrm{Ma,Mb}}$ and $\varepsilon_{\mathrm{Ma}}$ are the absorptivites of $\mathbf{M_aM_bL2}$ and $\mathbf{M_aL3}$ ($\mathrm{H_2}$**L3** = *N*,*N′*-disalicylidene-4,5-didodecyloxyphenylenediamine), respectively, and $\Delta_{\mathrm{fuse}}\varepsilon_{\mathrm{MaMb}}$ is an additional term originating from the fusion of π-system. It should be noted that the spectrum of a heterodinuclear complex is *not* represented as a simple sum over the constitutive mononuclear complexes. The difference spectra $\Delta_{\mathrm{fuse}}\varepsilon_{\mathrm{MaMb}}$ for heterometallic system hardly depended on species of metal ions (Figure 3). This observation implies that the intense absorption around 550 nm involves transition(s) innate to naphthalene's π-system, which is slightly perturbed by metal ions. Therefore, the overall spectral tuning is mainly controlled by individual salphen complex moieties.

This result is consistent with our recent study of the spectroscopic properties of **1** and its constitutional isomers.[15] That study suggested that the ground state of **1** can be described as a mixture of covalent and ionic states and that the photophysical properties of **1** are determined by the mixing ratio of the two states. Accordingly, with respect to the effects of intramolecular hydrogen bonding on the adjacent π-system, **1** as well as its derivatives can be represented by the sum of two independent salicylidene moieties. For example, a Schiff base of **1** in enamine form can be represented as in Scheme 3a, and its absorption originates in transitions between covalent-dominant state and ionic-dominant state. Such transition is also interpretable as intramolecular charge transfer between imine group and naphthalene's π-system.

Scheme 3. Resonance Structures of (a) Schiff Base and (b) Salphen Complex Derived from **1**



If we accept the analogy between intramolecular hydrogen bonding and metal chelation, the ground state of the salphen complex moiety can be described as a mixture of ionic- and covalent states (Scheme 3b), and the two salphen-complex units can be treated as if they were independent. As can be seen from Scheme 3, a transition between ionic and covalent states could easily be coupled with a charge transfer transition between metal and ligand. We attribute the absorption band at around 550 nm to such coupled transitions. Although the interaction between the two salphen-complex units was rather weak, changes in the π-electronic state on one side may have affected the other side through changes in charge distribution and/or geometrical parameters. Some properties (acidity, for example) of metal ion may affect such remote interactions, resulting in the small displacement observed for $\Delta_{\mathrm{fuse}}\varepsilon_{\mathrm{MaMb}}$ (Figure 3).

Conclusions

In summary, we synthesized heterodinuclear salphen complexes with fully π-conjugated systems. Dialdehyde **1** efficiently afforded complex ligand **ML1**, which permitted the preparation of heterodinuclear systems with an arbitrary combination of $\mathrm{Ni^{II}}$, $\mathrm{Cu^{II}}$, and $\mathrm{Zn^{II}}$ ions. The UV−vis spectra of the heterodinuclear complexes were approximated by simple superposition of the spectra of the corresponding homodinuclear complexes, and there were relatively small perturbations on terms attributed to the fusion of salphen units. The spectral analysis suggests that the weakness of the intracomplex (metal−ligand−metal) interactions originates in the topology of π-conjugated system. Today, little is known about the photophysical properties of heterometallic d,π-conjugated systems, in spite of the growing interest in their applications in various fields. Our present study provided us with a suitable set of materials to discuss the features of these properties. A systematic study on a series of similar compounds is currently underway in our group.

Supporting Information Available: Some spectral characterization data of the compounds studied. This material is available free of charge via the Internet at http://pubs.acs.org.