Supporting Information

Spontaneous Helical Folding of Bis(Ni-salphen) Complexes in Solution and in Solid-States: Spectroscopic Tracking of Unfolding Process Induced by Na^+ ion

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1. Experimental details for Intermediates and mononuclear complexes

General

All chemicals and solvents were purchased from Tokyo Kasei Kogyo (TCI) or Kanto Chemical Co. and used without further purification. 4,5-Bis-dodecyloxy-benzene-1,2-diamine was prepared according to Rosa, et al. (*Inorg. Synth.*, 2002, **33**, 112-119.). Compound **2a** was prepared according to ref. 24d. The experimental data for intermediates **1b** and **3a** and for mononuclear Ni-salphen complexes are described in the supporting information. Ultraviolet-visible (UV–Vis) absorption spectra were measured for a 2×10^{-5} M chloroform solution of each solute with a JASCO V-630 spectrophotometer. NMR spectra were recorded on a JEOL ECS-400 instrument (400 MHz for ^{1}H) for chloroform-*d* solution unless otherwise noted. IR spectra were recorded with a JEOL FT/IR-420 instrument.

Synthesis

Bis(Ni-salphen) complex, $Ni_2(L^2_{aa})$ (X = H, Y = H)

The mixture of THF (tetrahydrofuran) solution (21 mL) of **1a** (H. Houjou, M. Ito, K. Araki, *Inorg. Chem.*, 2009, **48**, 10703-10707.) (148 mg, 1 mmol), a THF solution (21 mL) of **2a** (580 mg, 0.5 mmol), and methanol solution (42 mL) of nickel(II) acetate tetrahydrate (248 mg, 1 mmol) was left for 24h at room temperature. The reaction mixture was concentrated to a volume of ca. 3/4, resulting in red solid separated out. The solid was collected by filtration, and then recrystallized with chloroform (deuterated)-methanol system. Yield: 217 mg (28%). m.p. 241°C. Anal. $C_{92}H_{128}N_4Ni_2O_8\cdot0.5CDCl_3$ (1595.6): Calcd. C 69.63, H 8.15, N 3.51; Found C 69.72, H 7.91, N 3.24, FAB MS(+) *m*/*z* = 1535.2 (1534.8 calcd. for $M+2H^+$), IR (KBr): ν = 1607 cm^{-1} ($\nu_{C=N}$), ^{1}H NMR: δ = 0.87 (t, $-CH_3$, 6H), 1.27-1.54 (m, $-CH_2-$, 32H), 1.86(m, $-CH_2-$, 4H), 3.28 (s, Ar-CH_2-C-(CH_2), 2H), 3.84 (t, $-OCH_2-$, 2H), 3.92 (t, $-OCH_2-$, 2H), 4.99 (s, $-C(=CH_2)-$, 1H), 6.27 (s, ArH, 1H), 6.48 (t, ArH, 1H), 6.49 (d, ArH, 1H), 6.51 (s, ArH, 1H), 6.58 (t, ArH, 1H), 6.88 (d, ArH and s, -CH=N-, 3H), 6.95 (s, -CH=N-, 1H), 7.20 (t, ArH, 1H), 7.29 (d, ArH, 1H), ^{13}C NMR: δ = 14.3, 22.9, 26.2, 29.3, 29.6, 29.6, 29.8, 29.8, 29.9, 29.9, 32.1, 32.8, 69.2, 70.5, 98.5, 99.3, 111.7, 114.1, 114.6, 119.8, 120.0, 123.2, 131.3, 131.9, 132.8, 133.3, 133.9, 134.8, 136.7, 147.7, 148.7, 150.2, 152.4, 152.4, 164.8, 165.5.

Bis(Ni-salphen) complex, $Ni_2(L^2_{ba})$ (X = 5,6-benzo, Y = H)

The mixture of THF solution (21 mL) of **1b** (315 mg, 0.5 mmol), a THF solution (21 mL) of **2a** (74 mg, 0.25 mmol), and methanol solution (42 mL) of nickel(II) acetate tetrahydrate (124 mg, 0.5 mmol) was stirred for 6h at 70°C. The reaction mixture was concentrated to a volume of ca. 1/2 and kept in a refrigerator (5°C), resulting in red solid separated out. The solid was collected by filtration, and then recrystallized with THF-ethanol system. Yield: 244 mg (60%). m.p. 231°C, Anal. $C_{100}H_{132}N_4Ni_2O_4 \cdot H_2O$ (1653.54): Calcd. C 72.28, H 8.17, N 3.29; Found C 72.28, H 8.10, N 3.29., FAB MS(+) *m*/*z* = 1634.2 (1634.8 calcd. for M+2H$^+$), IR (KBr): ν = 1605 cm^{-1} ($\nu_{C=N}$), ^{1}H NMR: δ = 0.88 (t, -CH_3, 6H), 1.33-1.55 (m, -CH_2-, 32H), 1.89 (m, -CH_2-, 4H), 2.92 (t, -OCH_2-, 2H), 3.37 (s, Ar-CH_2-C-(CH_2), 2H), 4.07 (t, -OCH_2-, 2H), 5.07 (s, -C(=CH_2)-, 1H), 5.98 (s, ArH, 1H), 6.63 (t, ArH, 1H), 6.65 (d, ArH, 1H), 6.72 (s, ArH, 1H), 6.93 (d, ArH, 1H), 7.08 (s, -CH=N-, 1H), 7.27 (t, ArH, 1H), 7.35 (d, ArH, 1H), 7.46 (t, ArH, 1H), 7.56 (d, ArH, 1H) 7.59 (d, ArH 1H), 7.69 (d, ArH, 1H), 7.92 (s, -CH=N-, 1H), ^{13}C NMR: δ = 14.2, 22.7, 25.9, 26.3, 29.1, 29.4, 29.6, 29.7, 29.8, 29.8, 32.0, 32.0, 32.7, 68.1, 70.7, 97.2, 100.1, 110.6, 111.7, 114.4, 118.8, 119.7, 122.3, 125.8, 126.4, 127.3, 128.9, 131.4, 133.2, 133.5, 133.6, 133.6, 136.3, 143.7, 147.6, 148.7, 151.8, 152.2, 164.5, 166.4.

Bis(Ni-salphen) complex, $Ni_2(L^2_{ca})$ (X = 3,5-di-*tert*-butyl, Y = H)

Compound **3a** (121 mg, 0.1 mmol) and 3,5-di-*tert*-butylsalicylaldehyde (47 mg, 0.2 mmol) were dissolved in 2.5 mL of THF, to which ethanol solution (2.5 mL) of nickel(II) acetate tetrahydrate (54 mg, 0.21 mmol) were added, and stirred for 24h at 60°C. To the reaction mixture, 7.5 mL of ethanol was gently poured so as not to disturb the interface. After 24 h, red solid separated out was collected by filtration, and then recrystallized from THF-ethanol system. Yield: 107 mg, 61%, m.p. 106°C, Anal. $C_{108}H_{160}N_4Ni_2O_8$ (1759.83): Calcd. C 73.71, H 9.16, N 3.18; Found C 73.63, H 9.15, N 3.17, FAB MS(+) *m*/*z* = 1758.1 (1758.1 calcd. for M + H$^+$), IR (KBr): ν = 1607 cm^{-1} ($\nu_{C=N}$), ^{1}H NMR: δ = 0.88 (t, -CH_3, 6H), 1.29-1.49 (m, -CH_2-, 32H), 1.31 (s, -C(CH_3)$_3$, 9H), 1.43 (s, -C(CH_3)$_3$, 9H), 1.85 (m, -CH_2-, 2H), 3.55 (s, Ar-CH_2-C-(CH_2), 2H), 4.04(t, -OCH_2-, 4H), 5.04 (s, -C(=CH_2)-, 1H), 6.58 (t, ArH, 1H), 7.03 (s, ArH, 1H), 7.04 (s, ArH, 1H), 7.06 (d, ArH, 1H), 7.16 (d, ArH, 1H), 7.24 (d, ArH, 1H), 7.35 (d, ArH, 1H), 7.86 (s, -CH=N-, 1H), 7.95 (s, -CH=N-, 1H). ^{13}C NMR: δ =14.1, 22.4, 26.0, 26.1, 29.2, 29.2, 29.4, 29.4, 29.6, 29.7, 29.7, 31.3, 31.9, 34.0, 35.6, 35.7, 69.8, 98.8, 98.9, 115.2, 119.3, 119.3, 125.7, 129.7, 130.6, 132.3, 133.6, 136.0, 136.4, 136.5, 140.7, 147.4, 148.8, 149.0, 151.9, 164.0, 164.7.

Bis(Ni-salphen) complex, $Ni_2(L^2_{bb})$ (X = 5,6-benzo, Y = *tert*-butyl)

The mixture of THF solution (2.5 mL) of **1b** (126 mg, 0.2 mmol), a THF solution (21 mL) of **2b**[24b] (40 mg, 0.1 mmol), and methanol solution (5 mL) of nickel(II) acetate tetrahydrate (54 mg, 0.2 mmol) was stirred for 24h at 60°C. The reaction mixture was concentrated to a volume of ca. 3/4, resulting in red solid separated out. The solid was collected by filtration, and then recrystallized with THF-ethanol system. Yield: 105 mg (60%). m.p. 234 °C, Anal. $C_{108}H_{148}N_4Ni_2O_4$ (1747.73): Calcd. C 74.22, H 8.54, N 3.21; Found C 73.95, H 8.49, N 3.09., FAB MS(+) *m*/*z* = 1745.4 (1745.0 calcd. for M), IR (KBr): ν = 1616 cm^{-1} ($\nu_{C=N}$), ^1H NMR: δ = 0.88 (t, -CH_3, 6H), 1.29-1.34 (m, -CH_2-, 32H), 1.55 (s, Ar(OH)-C(CH_3)$_3$, 9H), 1.63 (m, -CH_2-, 2H), 1.88 (m, -CH_2-, 2H), 2.94 (t, -OCH_2-, 2H), 3.34 (s, Ar-CH_2-C-(CH_2), 2H), 4.07 (t, -OCH_2-, 2H), 5.05 (s, -C(=CH_2)-, 1H), 5.99 (s, ArH, 1H), 6.68 (d, ArH, 1H), 6.72 (s, ArH, 1H), 6.82 (d, ArH, 1H), 6.99 (s, -CH=N-, 1H), 7.28 (t, ArH, 1H), 7.45 (d, ArH, 1H), 7.48 (t, ArH, 1H), 7.59 (d, ArH, 1H), 7.69 (d, ArH, 1H), 7.90 (s, -CH=N-, 1H), ^{13}C NMR: δ = 15.2, 23.8, 27.0, 27.3, 30.2, 30.4, 30.5, 30.6, 30.7, 30.8, 30.8, 30.8, 30.8, 30.9, 31.1, 32.5, 33.0, 33.7, 34.9, 69.1, 71.9, 98.3, 101.4, 111.5, 112.5, 119.9, 120.0, 123.3, 127.2, 127.4, 127.8, 128.4, 129.9, 131.8, 133.5, 134.1, 134.3, 136.3, 137.1, 137.7, 144.6, 148.3, 149.8, 153.0, 153.7, 164.3, 167.3.

Imine-amine 1b (X = 5,6-benzo)

4,5-Bis-dodecyloxy-benzene-1,2-diamine (476 mg, 1 mmol) and 2-hydroxy-1-naphthaldehyde (172 mg, 1 mmol) were dissolved in 2 mL of chloroform, which was left for 3h at room temperature. The solution separated out Ocher solid, which was collected by filtration. Yield: 55 %, m.p. 112°C, Anal. $C_{41}H_{62}N_2O_3 \cdot 0.4H_2O$ (638.15): Calcd. C 77.17, H 9.92, N 4.53; Found C 77.45, H 10.02, N 4.53., FAB MS(+) *m*/*z* = 630.2 (630.4calcd. for M^+), IR (KBr): ν = 1604 cm^{-1} ($\nu_{C=N}$), ^1H NMR : δ = 0.88(t, *J* = 4.12 Hz, -$CH_2C\mathit{H}_3$, 6H), 1.25-1.50(m, 32H), 1.82(quint, *J* = 7.32 Hz, -$CH_2C\mathit{H}_2CH_2$-, 4H), 3.87(s, -NH_2, 2H), 3.99(q, -OCH_2CH_2-, *J* = 4.29 Hz, 4H), 6.41(s, 1H), 6.88(s, 1H), 7.19(d, *J* = 9.16 Hz, 1H), 7.37(t, *J* = 7.32 Hz,1H), 7.56(t, *J* = 7.32 Hz,1H), 7.78(d, *J* = 7.44 Hz,1H), 7.84(d, *J* = 8.87 Hz,1H), 8.21(d, *J* = 7.33 Hz,1H), 9.38(s, -C*H*=N-, 1H), 15.36(s, -O*H*, 1H), ^{13}C NMR: δ = ^{13}C NMR: δ = 15.3, 23.9, 27.3, 27.3, 30.4, 30.5, 30.6, 30.7, 30.7, 30.8, 30.9, 30.9, 33.1, 70.9, 71.1, 100.1, 100.3, 112.3, 116.9, 120.1, 121.2, 123.1, 124.1, 125.5, 128.2, 128.8, 130.4, 134.2, 134.6, 135.7, 136.7, 138.5, 147.1, 150.2, 150.8, 153.2, 166.5, 168.3.

Bis(imine-amine) 3a (Y = H)

Compound **2a** (59 mg, 0.2 mmol) and 4,5-Bis-dodecyloxy-benzene-1,2-diamine (200 mg, 0.42 mmol) were dissolved in 1.0 mL ethylacetate, to which three drops of methanol was added. The mixture was left for 3h at room temperature under nitrogen gas atmosphere. Yellow solid separated out was collected by filtration. Yield: 55%, m.p. 111°C, Anal. $C_{78}H_{124}N_4O_6$(1213.84) : Calcd. C 77.18, H 10.28, N 4.62; Found C 76.92, H 10.30, N 4.71, FAB MS(+) *m*/*z* = 1213.0 (1212.9 calcd. for M), IR (KBr): ν = 1607 cm^{-1} ($\nu_{C=N}$), ^{1}H NMR : δ = 0.88(t, *J* = 4.40 Hz, 6H), 1.20-1.50(m, 32H), 1.40-1.47(m, 4H), 1.71-1.80(m, 4H), 3.51(s, Ar-C*H*$_2$-C(=CH_2), 2H), 3.84(s, -N*H*$_2$, 2H), 4.83(s, -C(=C*H*$_2$), 1H), 6.35(s, 1H), 6.77(s, 1H), 6.90(t, *J* = 7.84 Hz, 1H), 7.29(d, *J* = 9.74 Hz, 2H), 8.55(s, -C*H*=N-, 1H), 13.35(s, -O*H*, 1H), ^{13}C NMR: δ = 14.1, 22. 7, 29.3, 29.4, 29.4, 29.5, 29.6, 29.6, 29.6, 29.7, 29.7, 31.9, 35.6, 69.1, 71.2, 76.7, 102.2, 106.4, 112.6, 118.7, 119.3, 126.8, 127.5, 130.1, 133.5, 136.2, 142.2, 146.9, 50.5, 158.7, 158.9.

Ni-salphen complex, Ni (L^1_{aa}) (X = H, Y = H)

The mixture of chloroform solution (23 mL) of **1a** (290 mg, 0.5 mmol), salicylaldehyde (122 mg, 0.5 mmol), and methanol solution(27 mL) of nickel(II) acetate tetrahydrate (299 mg, 0.5 mmol) was left for 24h at room temperature. Red plate crystalline precipitate was collected by filtration. Yield: 201 mg (54%). m.p. 223 °C, Anal. $C_{44}H_{62}N_2NiO_4$ (741.67): Calcd. C 71.25, H 8.44, N 3.78; Found C 71.28, H 8.43, N 3.72., FAB MS(+) *m*/*z* = 741.3 (741.4 calcd. for M+H^+), IR (KBr): ν = 1605 cm^{-1} ($\nu_{C=N}$), ^{1}H NMR: δ = 0.88 (t, -CH_3, 3H), 1.27-1.38 (m, -CH_2-, 6H), 1.50 (m, -CH_2-, 2H), 1.85 (m, -CH_2-, 2H), 4.04 (t, -OCH_2-, 2H), 6.61 (t, ArH, 1H), 7.08 (s, ArH, 1H), 7.16 (d, ArH, 1H), 7.27 (t, ArH, 1H), 7.32 (d, ArH, 1H), 7.97 (s, -CH=N-, 1H), ^{13}C NMR: δ = 14.3, 22.9, 26.2, 29.3, 29.5, 29.6, 29.8, 29.8 29.9, 32.1, 69.9, 98.8, 115.9, 120.1, 122.1, 133.1, 134.8, 136.1, 149.7, 152.4, 165.5.

Ni-salphen complex, Ni (L^1_{ba}) (X = 5,6-benzo, Y = H)

The mixture of THF solution (5 mL) of **1b** (220 mg, 0.38 mmol), salicylaldehyde (46 mg, 0.38 mmol), and methanol solution (5 ml) of nickel(II) acetate tetrahydrate (94 mg, 0.5 mmol) was left for 24 h at room temperature. Red needle was collected by filtration. Yield: 136 mg (45%). m.p. 159 °C, Anal. $C_{48}H_{64}N_2NiO_2 \cdot 0.3H_2O$ (797.13): Calcd. C 72.32, H 8.17, N 3.51; Found C 72.89, H 8.15, N 3.05., FAB MS(+)

m/*z* = 791.1 (791.4 calcd. for $M+H^+$), IR (KBr): ν = 1608 cm^{-1} ($\nu_{C=N}$), ^1H NMR: δ = 0.88 (t, $-CH_3$, 6H), 1.27-1.38 (m, $-CH_2-$, 32H), 1.50 (m, $-CH_2-$, 4H), 1.85 (m, $-CH_2-$, 4H), 4.03 (t, $-OCH_2-$, 2H), 4.10 (t, $-OCH_2-$, 2H), 6.65 (t, ArH, 1H), 7.05 (s, ArH, 1H), 7.15 (d, ArH, 1H), 7.17 (s, ArH, 1H), 7.26 (d, ArH, 1H), 7.28 (d, ArH, 1H), 7.30 (t, ArH, 2H), 7.49 (t, ArH, 1H), 7. 62 (d, ArH, 1H), 7. 67 (d, ArH, 1H), 7.96 (s, -CH=N-, 1H), 7.98 (d, ArH, 1H), 8.83 (s, -CH=N-, 1H). ^{13}C NMR: δ = 15.3, 23.9, 27.2, 27.3, 30.4, 30.5, 30.6, 30.7, 30.7, 30.8, 30.9, 30.9, 33.1, 70.9, 71.1, 100.1, 100.3, 112.3, 116.9, 120.1, 121.2, 123.1, 124.1, 125.5, 128.2, 128.8, 130.4, 134.2, 134.6, 135.7, 136.4, 136.7, 138.5, 147.1, 150.2, 150.8, 153.2, 166.5, 168.3.

Ni-salphen complex, Ni ($L^1{}_{ca}$) (X = 3,5-di-*tert*-butyl, Y = H)

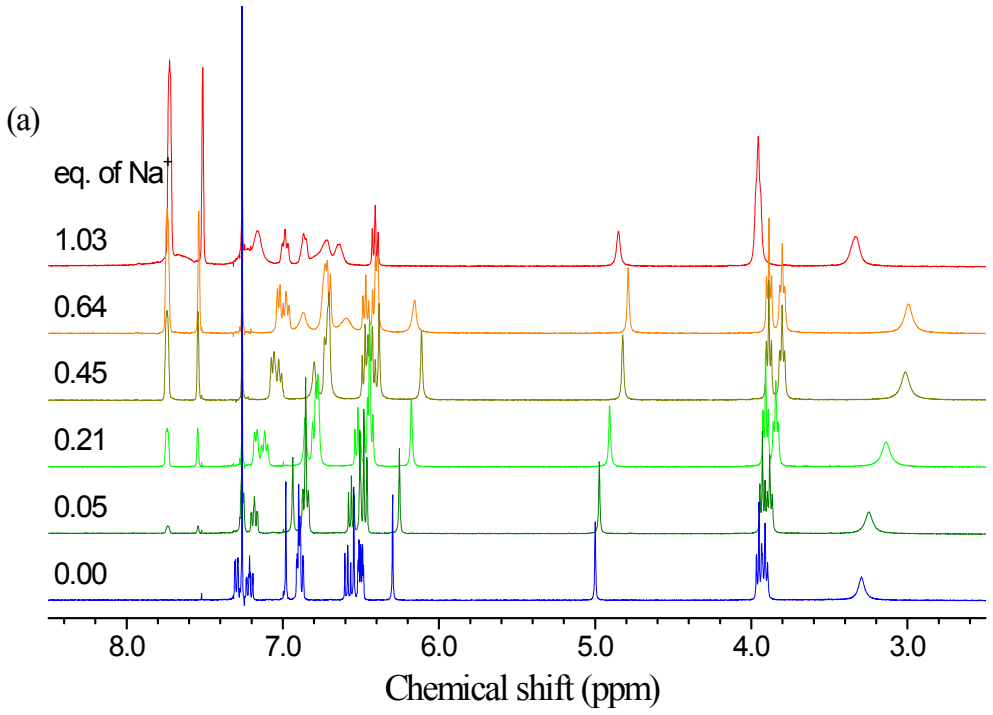
The mixture of THF solution (0.5 mL) of **1a** (58 mg, 0.1 mmol) and 3,5-di-*tert*-butylsalicylaldehyde (23 mg, 0.1 mmol), and methanol solution (0.5 ml) of nickel(II) acetate tetrahydrate (27 mg, 0.11 mmol) was left at for 24h at 60°C. Red precipitate was collected by filtration, and recrystallized from chloroform-methanol system. Yield: 41 mg (48%). m.p. 148 °C, Anal. $C_{52}H_{78}N_2NiO_4 \cdot 0.5H_2O$ (862.89): Calcd. C 72.38, H 9.23, N 3.25; Found C 72.46, H 9.15, N 3.24., FAB MS(+) *m*/*z* = 853.5 (853.54 calcd. for $M+H^+$), IR (KBr): ν = 1607 cm^{-1} ($\nu_{C=N}$), ^1H NMR: δ = 0.88 (t, $-CH_3$, 6H), 1.27-1.38 (m, $-CH_2-$, 32H), 1.31 (s, $-C(CH_3)_3$, 9H), 1.47 (s, $-C(CH_3)_3$, 9H), 1.50 (m, $-CH_2-$, 4H), 1.86 (m, $-CH_2-$, 4H), 4.03 (m, $-OCH_2-$, 4H), 6.59 (t, ArH, 1H), 7.02 (d, ArH, 1H), 7.07 (d, ArH, 1H), 7.08 (s, ArH, 2H), 7.25 (t, ArH, 1H), 7.31 (d, ArH, 1H), 7.36 (d, ArH, 2H), 7.91 (s, -CH=N-, 1H), 7.99 (s, -CH=N-, 1H). ^{13}C NMR: δ = 14.9, 15.0, 23.6, 26.9, 26.9, 30.1, 30.2, 30.3, 30.3, 30.5, 30.5, 30.6, 32.2, 32.8, 34.9, 36.4, 70.6, 70.7, 99.6, 99.8, 116.0, 120.3, 120.9, 122.6, 126.7, 130.8, 133.7, 135.2, 136.6, 137.4, 137.6, 141.6, 149.8, 150.3, 152.5, 153.1, 164.8, 167.3.

Ni-salphen complex, Ni ($L^1{}_{bb}$) (X = 5,6-benzo, Y = *tert*-butyl)

The mixture of THF solution (1.5 mL) of **1b** (35 mg, 0.15 mmol) and 3,5-di-tert-butylsalicylaldehyde (95 mg, 0.1 mmol), and methanol solution(1.5 ml) of nickel(II) acetate tetrahydrate (41 mg, 0.15 mmol) was left for 2h at room temperature. Red solid was collected by filtration, and recrystallized from chloroform-methanol system. Yield: 78 mg(58%). m.p. 220°C, Anal. $C_{56}H_{80}N_2NiO_4$ (903.94): Calcd. C 74.41, H 8.92, N 3.10; Found C 74.41, H 8.93, N 2.99., FAB MS(+) *m*/*z* = 853.5 (853.54 calcd. for

$M+H^+$), IR (KBr): ν = 1604 cm^{-1} ($\nu_{C=N}$), ^1H NMR: δ = 0.88 (t, $-CH_3$, 6H), 1.27-1.41 (m, $-CH_2-$, 32H), 1.33 (s, $-C(CH_3)_3$, 9H), 1.51 (s, $-C(CH_3)_3$, 9H), 1.54 (m, $-CH_2-$, 4H), 1.86 (m, $-CH_2-$, 4H), 4.04 (m, $-OCH_2-$, 4H), 6.95 (s, ArH, 1H), 6.98 (d, ArH, 1H), 7.02 (d, ArH, 1H), 7.19 (s, ArH, 2H), 7.19 (t, ArH, 1H), 7.27 (t, ArH, 1H), 7.39 (d, ArH, 1H), 7.47 (d, ArH, 2H), 7.60 (d, ArH, 2H), 7.74 (s, -CH=N-, 1H), 8.03 (d, ArH, 1H), 8.99 (s, -CH=N-, 1H), ^{13}C NMR: δ = 14.7, 23.3, 26.6 26.7, 29.9, 30.0, 30.1, 30.2, 30.3, 31.9, 32.5, 34.6, 36.15, 70.4, 70.5, 99.4, 99.9, 111.6, 119.5, 120.0, 123.0, 124.6, 126.6, 127.3, 129.4, 130.2, 134.2, 135.0, 136.4, 137.0, 137.6, 141.0, 146.1, 149.6, 152.2, 164.2, 168.2.

2. Figures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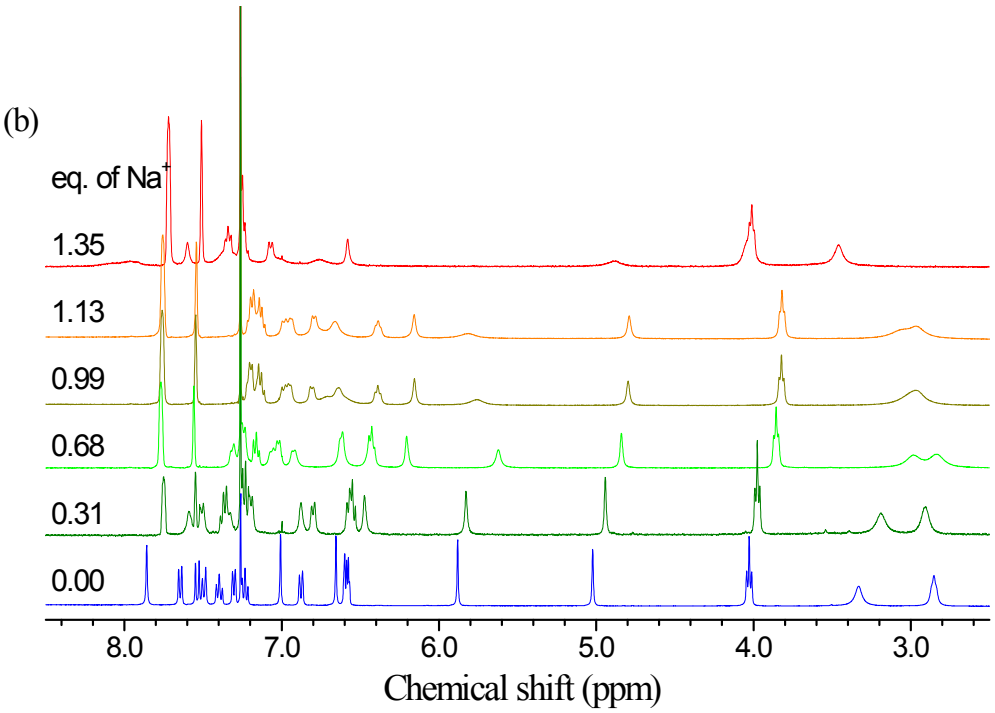
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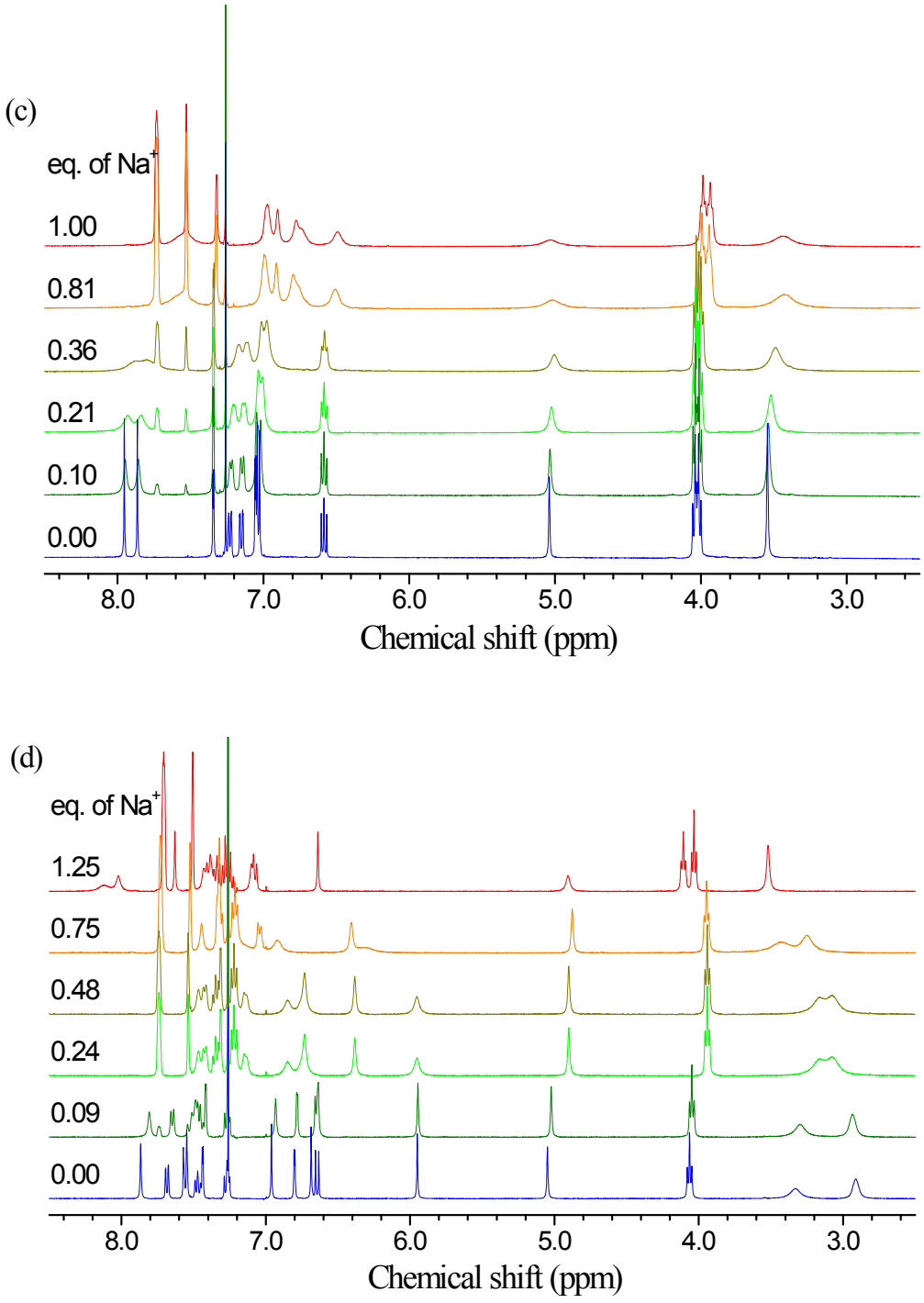


Figure S1 Comparison of ^{1}H NMR spectra of dinuclear Ni complexes with various amounts of Na-TFPB: (a) $Ni_2(L^2_{aa})$, (b) $Ni_2(L^2_{ba})$, (c) $Ni_2(L^2_{ca})$, (d) $Ni2(L^2_{bb})$

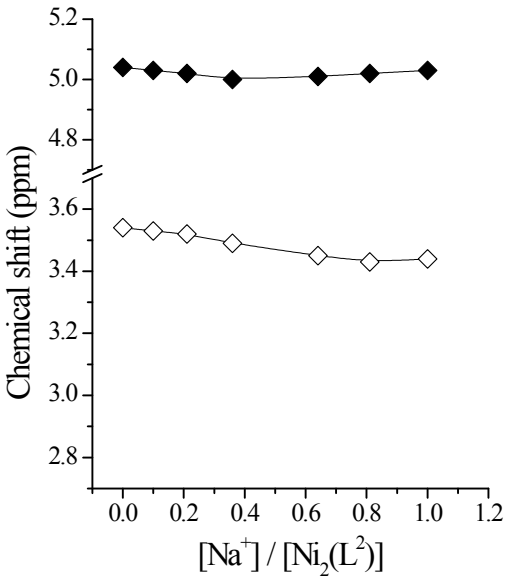


Figure S2 Chemical shift values for H_{ex} (◆) and H_{bn} (◇) of $Ni_2(L^2{}_{ca})$.

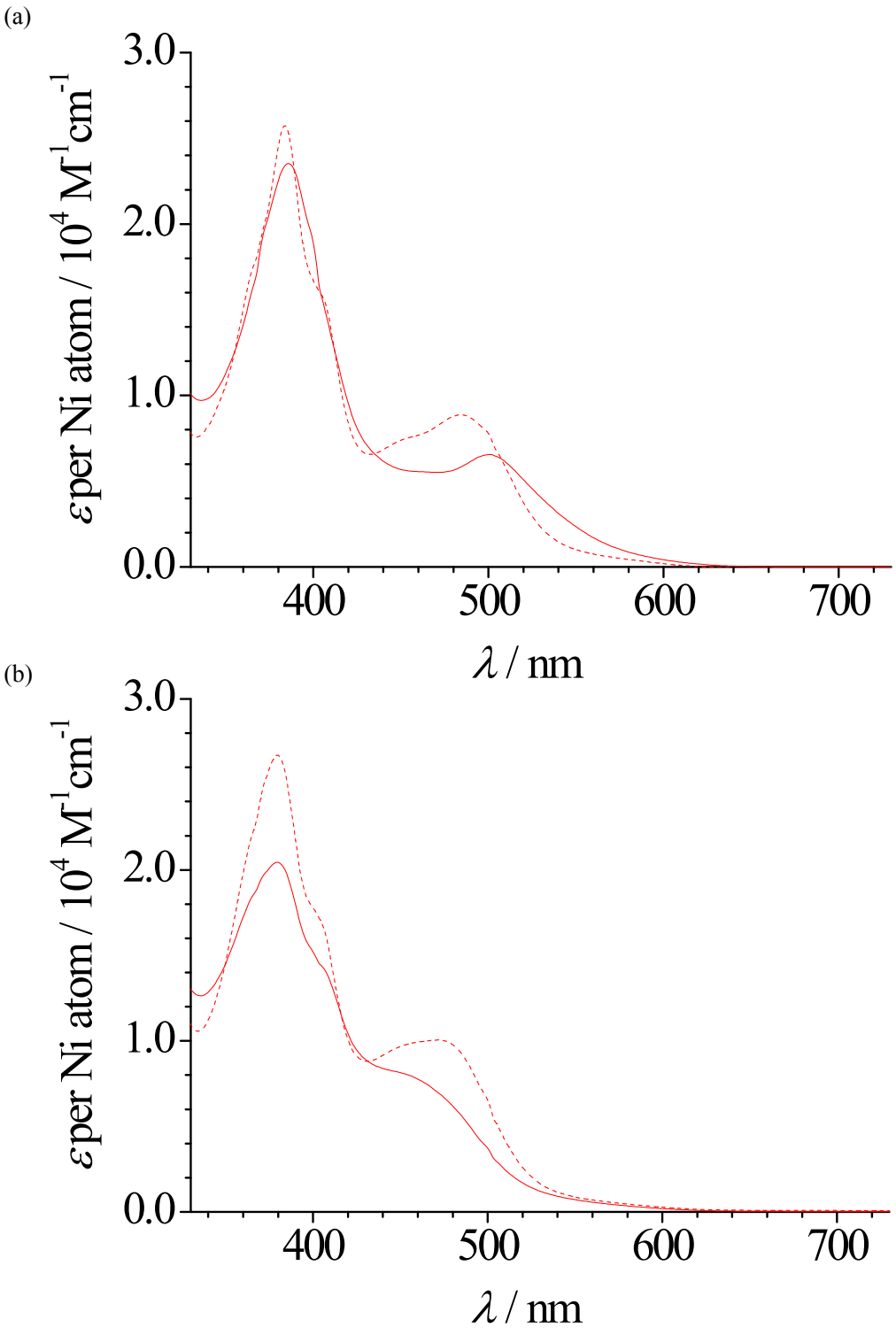


Figure S3 UV-Vis absorption spectra of $Ni_2(L^2_{aa})$ (solid lines) and $Ni(L^1_{aa})$ (dashed lines): (a) no additives, and (b) with Na-TFPB (1.0 eq. per Ni complex moiety).

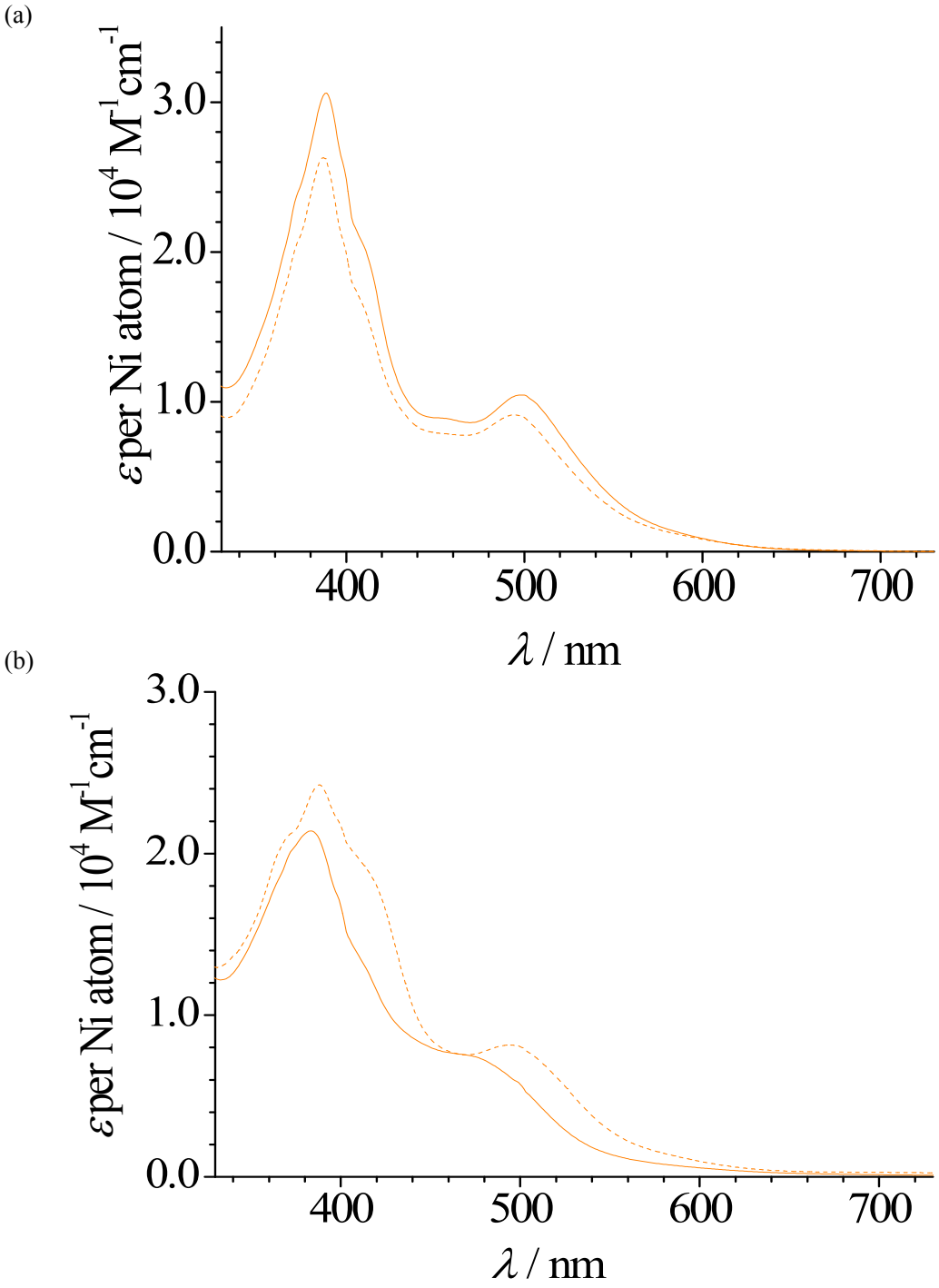


Figure S4 UV-Vis absorption spectra of $Ni_2(L^2_{ca})$ (solid lines) and $Ni(L^1_{ca})$ (dashed lines): (a) no additives, and (b) with Na-TFPB (1.0 eq. per Ni complex moiety).

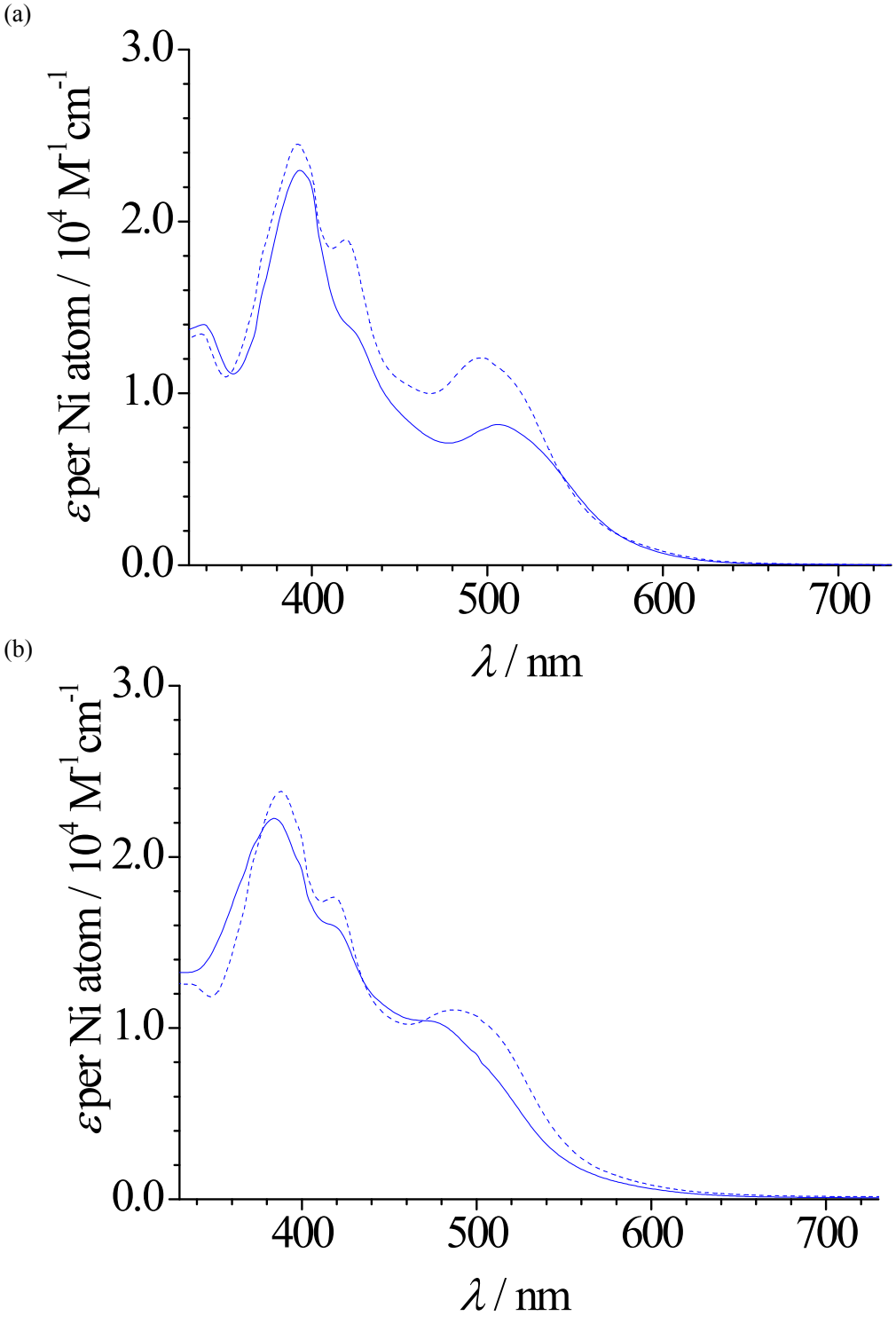


Figure S5 UV-Vis absorption spectra of $Ni_2(L^2_{bb})$ (solid lines) and $Ni(L^1_{bb})$ (dashed lines): (a) no additives, and (b) with Na-TFPB (1.0 eq. per Ni complex moiety).

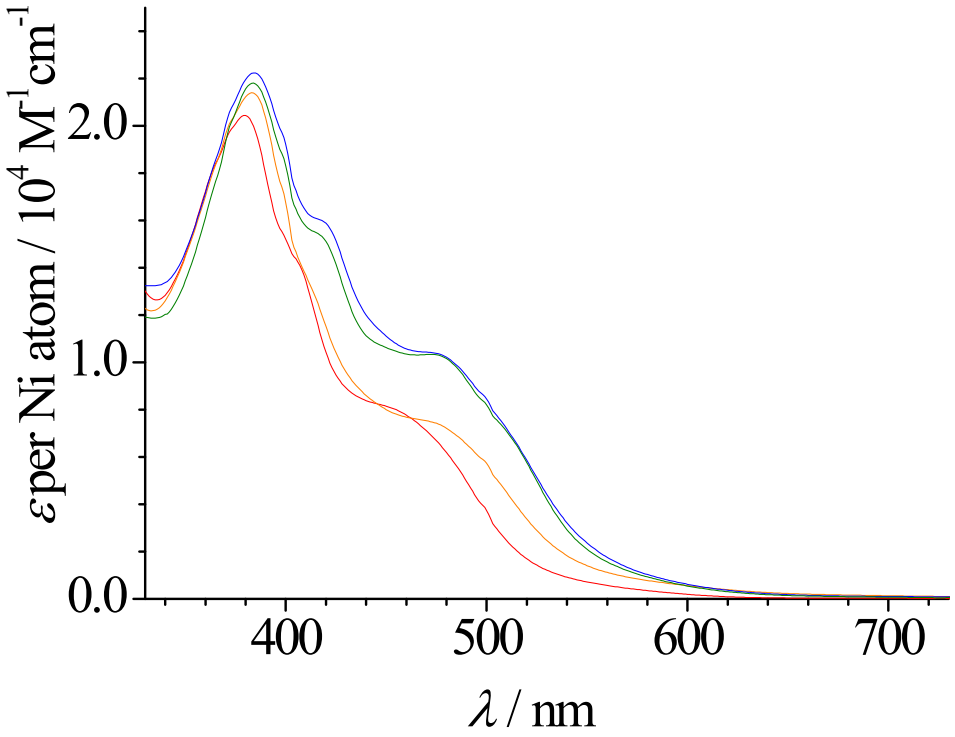
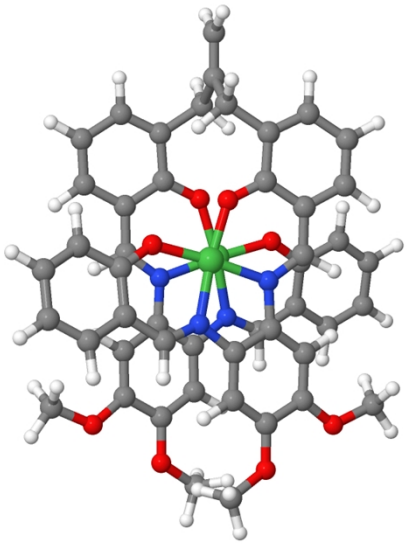


Figure S6 UV-Vis absorption spectra of $Ni_2(L^2_{aa})$ (red), $Ni_2(L^2_{ba})$ (green), $Ni_2(L^2_{ca})$ (orange), and $Ni_2(L^2_{bb})$ (blue) measured in the presence of Na-TFPB.

(a)



(b)

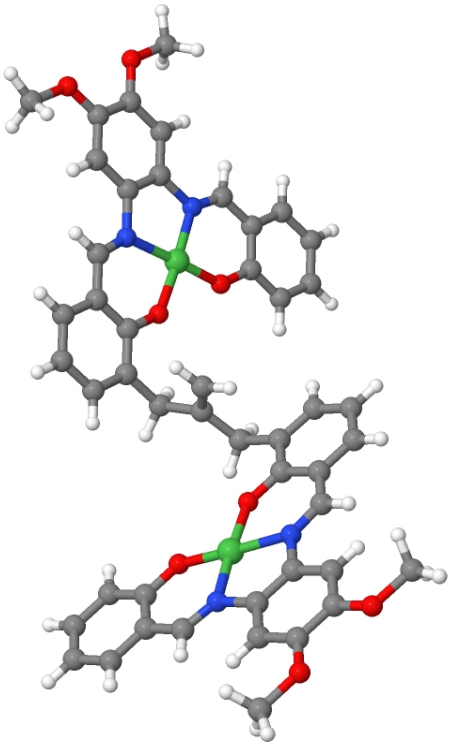


Figure S7 The optimized structure of a model complex $Ni_2(L^2_d)$ in the folded state (a) and unfolded state (b)

3. Table

Table S1 Selected interatomic distances measured from crystal structure of $Ni_2(L^2_{ba})$

Atom pair[a)]	Interatomic distance (Å)	Atom Pair	Interatomic distance (Å)
Ni1-O1	1.842 (4)	O1-C(Ph)	1.301 (7)
Ni1-O4	1.840 (4)	O4-C(Ph)	1.316 (7)
Ni1-N1	1.845 (5)	N1-C(imine)	1.326 (7)
Ni1-N2	1.867 (5)	N2-C(imine)	1.309 (7)
Ni2-O5	1.834 (4)	O5-C(Ph)	1.309 (6)
Ni2-O8	1.860 (4)	O8-C(Ph)	1.315 (6)
Ni2-N3	1.852 (5)	N3-C(imine)	1.310 (7)
Ni2-N4	1.862 (5)	N4-C(imine)	1.317 (7)
Ni1-Ni2	3.217 (2)		

a) The numbering system follows Fig. 2b and the CIF data.