Supplementary Material (ESI) for Chemical Communications

Supporting Information

Highly efficient regulation of cation recognition and promotion of self-assembly by metalation of macrocyclic bis(N_2O_2) ligand with nickel(II)

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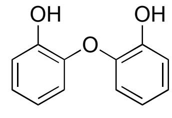
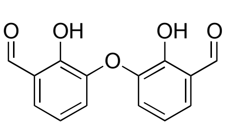
Synthesis of Macrocyclic Ligand 1 and Metallohost 2

General Procedures. All experiments were carried out in air unless otherwise noted. Commercial chloroform, methanol, and dehydrated tetrahydrofuran (THF) were used without purification. All chemicals were of reagent grade and were used as received. Column chromatography was performed with Kanto Chemical silica gel 60N (spherical, neutral). Melting points were determined on a Yanaco melting point apparatus and not corrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX400 spectrometer (400 and 100 MHz). Mass spectra (electrospray ionization, positive mode) were recorded on an Applied Biosystems QStar Pulsar *i* spectrometer.



3

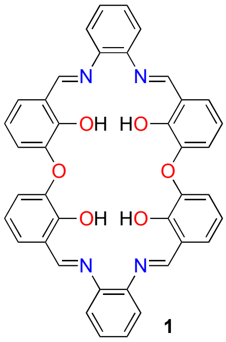
Synthesis of 2,2'-oxydiphenol (3). Under nitrogen atmosphere, *n*-bulyllithium (2.6 M in hexane, 19.8 mL, 52 mmol) was slowly added to a solution of diphenyl ether (4.00 g, 23.5 mmol) in THF (15.0 mL) at room temperature. After the addition of *N,N,N',N'*-tetramethylethylenediamine (7.8 mL, 52 mmol), the mixture was stirred for 18 h at room temperature. Trimethyl borate (10.4 mL, 92 mmol) was added and the mixture was stirred for further 5 h. A solution of potassium hydroxide (3.6 g) and 30% hydrogen peroxide (9 mL) in water (30 mL) was then added to the mixture, which was further stirred overnight at room temperature. After the acidification with 2 M HCl, the mixture was extracted with chloroform, dried over anhydrous magnesium sulfate, filtered, and concentrated to dryness. The residue was recrystallized from chloforom/hexane to give diol **3** (3.36 g, 71%) as colorless crystals, mp 120–121 °C (lit[1] 122–123 °C), ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.56 (s, 2H), 6.84-6.87 (m, 4H), 7.05-7.07 (m, 4H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 116.5, 118.1, 120.9, 125.0, 143.3, 146.9. Anal. Calcd for C$_{12}$H$_{10}$O$_3$: C, 71.28; H, 4.98. Found: C, 71.36; H, 5.07.



4

Synthesis of 3,3'-oxybis(2-hydroxybenzaldehyde) (4). A solution of *N*-bromosuccinimide (1.072 g, 6.0 mmol) in dichloromethane (18.0 mL) was added dropwise over a period of 30 min to a stirred solution of 2,2'-oxydiphenol (**3**) (608 mg, 3.0 mmol) and diisopropylamine (0.84 mL, 6.0 mmol) in dichloromethane (4 mL) at –50 °C. After the mixture was stirred for 30 min at –50 °C, the solution was acidified with 2 M hydrochloric acid. The mixture was extracted with chloroform and the organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated to dryness. The crude dibromide was then treated with sodium hydride (60% in oil, 512.1 mg, 13 mmol) in tetrahydrofuran (18 mL) under nitrogen atmosphere. The mixture was stirred for 1 h at room temperature, the solution was cooled to –78 °C and *n*-bulyllithium (2.6 M in hexane, 2.7 mL, 7.0 mmol) was added. After the mixture was stirred for 30 min *N,N*-dimethylformamide (1.5 mL, 19 mmol) was added and the resulting suspension was stirred for further 2.5 h at –78 °C. The mixture was warmed to room temperature, acidified with 2 M hydrochloric acid, and extracted with chloroform. The organic layer was washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated to dryness. The residue was subjected to column chromatography on silica gel (eluent, 1.5% ethyl acetate/chloroform) to afford dialdehyde **4** (217 mg, 28%) as pale yellow crystals, mp 110–111 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (t, J = 7.8 Hz, 2H), 7.19 (dd, J = 7.8, 1.3 Hz, 2H), 7.39 (dd, J = 7.8, 1.3 Hz, 2H), 9.96 (s, 2H), 11.13 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 119.7, 121.9, 125.7, 128.5, 144.5, 152.5, 196.3. Anal. Calcd for $C_{14}H_{10}O_5 \bullet 0.25H_2O$: C, 64.00; H, 4.03. Found: C, 64,21; H, 4.10.

Synthesis of macrocyclic ligand 1. A solution of dialdehyde **4** (71.6 mg, 0.28 mmol) in acetonitrile (4 mL) was added to a solution of 1,2-phenylenediamine (29.9 mg, 0.28 mmol) in acetonitrile (4 mL). After the mixture was allowed to stand overnight at room temperature, the precipitates were collected to give ligand **1** (65.6 mg, 64%) as orange crystals, ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.92 (t, J = 7.9 Hz, 4H), 7.04 (dd, J = 7.9, 1.4 Hz, 4H), 7.43 (dd, J = 7.9, 1.4 Hz, 4H), 7.44–7.53 (m, 8H), 8.97 (s, 4H), 13.52 (s, 4H). ESI-MS m/z 661.2 [**1** + H]$^+$. Anal. Calcd for $C_{40}H_{28}N_4O_6 \bullet 1.5MeCN \bullet H_2O$: C, 69.77; H, 4.70; N, 10.41. Found C, 69.44; H, 4.81; N, 10.37.



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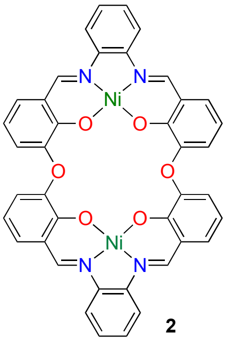
Synthesis of metallohost 2. A solution of ligand **1** (80.8 mg, 0.11 mmol) in dimethyl sulfoxide/acetonitrile (1:1, 8 mL) was added to a solution of nickel(II) acetate tetrahydrate (52.2 mg, 0.21 mmol) in dimethyl sulfoxide (2.0 mL). After the solution was heated at 60 °C, the mixture was allowed to stand for 2 d. The precipitates were collected to afford metallohost **2** (90.4 mg, 93%) as dark brown crystals, ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.61 (t, J = 7.7 Hz, 4H), 7.26 (d, J = 7.7 Hz, 4H), 7.34–7.40 (m, 8H), 8.13–8.16 (m, 4H), 8.97 (brs, 4H). ESI-MS m/z 387.0 [**2** + 2H]$^{2+}$, 773.0 [**2** + H]$^+$. Anal. Calcd for $C_{40}H_{24}N_4O_6Ni_2 \bullet 2DMSO$: C, 56.81; H, 3.90; N, 6.02. Found: C, 57.24; H, 3.93; N, 6.15.



2

[1] D. E. Kime and J. K. Norymberski, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1048–1052.