Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers

Perfect encapsulation of a guanidinium ion in a helical trinickel(II) metallocryptand for efficient regulation of the helix inversion rate

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Supplementary Information

Synthesis of ligands and metal complexes

Synthesis of 1,3,5-tris(2-methoxy-4-*tert*-butylphenyl)benzene (3). Under nitrogen atmosphere, a mixture of 1,3,5-tribromobenzene (**1**)[1] (284 mg, 0.902 mmol), boronic acid **2**[2] (754 mg, 3.62 mmol), potassium carbonate (876 mg, 6.34 mmol), tetrakis(triphenylphosphine)palladium(0) (200 mg, 0.173 mmol) in degassed *N*,*N*-dimethylacetamide (9.0 mL), ethanol (1.8 mL), and water (2.4 mL) was prepared. The mixture was heated to reflux for 22 h. After cooling, saturated aqueous solution of sodium hydrogencarbonate (10 mL) was added to the mixture. The organic layer was separated and the aqueous layer was extracted with dichloromethane (10 mL × 5). The combined organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated to dryness. The crude product was purified by column chromatography (silica gel, chloroform) and then recrystallization from chloroform/methanol to yield coupling product **3** (376 mg, 0.653 mmol, 72%) as colorless crystals, mp 194–196 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (s, 27H), 3.81 (s, 9H), 6.94 (d, J = 8.6 Hz, 3H), 7.35 (dd, J = 8.6, 2.6 Hz, 3H), 7.46 (d, J = 2.6 Hz, 3H), 7.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.56 (CH_3), 34.17 (C), 55.51 (CH_3), 110.46 (CH), 124.94 (CH), 128.77 (CH), 129.59 (CH), 130.42 (C), 138.19 (C), 143.28 (C), 154.41 (C). Anal. Calcd for $C_{39}H_{48}O_3$•$0.6H_2O$: C, 81.38; H, 8.62. Found: C, 81.18; H, 8.58.

Synthesis of 3,3',3''-benzene-1,3,5-triyltris(5-*tert*-butyl-2-methoxybenzaldehyde)(4). Under nitrogen atmosphere, *n*-butyllithium (2.66 M in hexane, 3.0 mL, 8.0 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (1.0 mL, 7.5 mmol) were added to a solution of compound **3** (638 mg, 1.11 mmol) in dry diethyl ether (30 mL) at 0 °C. The solution was stirred at room temperature for 12 h. After cooling to 0 °C, *N*,*N*-dimethylformamide (1.1 mL, 14 mmol) was added to the mixture, which was stirred for further 5 h at room temperature. The mixture was then poured onto water (100 mL) and the organic layer was separated. The aqueous layer was extracted with dichloromethane (20 mL × 3). The combined organic layer was dried over anhydrous magnesium sulfate and filtered. After the removal of the solvent under reduced pressure, compound **4** (723 mg, 1.10 mmol, 99%) as colorless crystals, mp 197–200 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (s, 27H), 3.66 (s, 9H), 7.72 (d, J = 2.8 Hz, 3H), 7.85 (s, 3H), 7.92 (d, J = 2.8 Hz, 3H), 10.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.31 (CH_3), 34.73 (C), 62.71 (CH_3), 124.78 (CH), 128.97 (CH), 129.14 (C), 134.62 (CH), 134.77 (C), 138.24 (C), 147.85 (C), 158.69 (C), 190.36 (CHO). Anal. Calcd for $C_{42}H_{48}O_6$•$0.5H_2O$: C, 76.68; H, 7.51. Found: C, 76.80; H, 7.79.

Synthesis of 3,3',3''-benzene-1,3,5-triyltris(5-*tert*-butyl-2-hydroxybenzaldehyde) (5). Under nitrogen atmosphere, boron tribromide (1.0 mL, 11 mmol) was added to a solution of methoxy derivative **4** (765 mg, 1.16 mmol) in distilled dichloromethane (30 mL) at 0 °C. The mixture was stirred at room temperature for 12 h. The mixture was poured onto water (100 mL) and the organic layer was separated. The aqueous layer was extracted with dichloromethane (10 mL × 4)

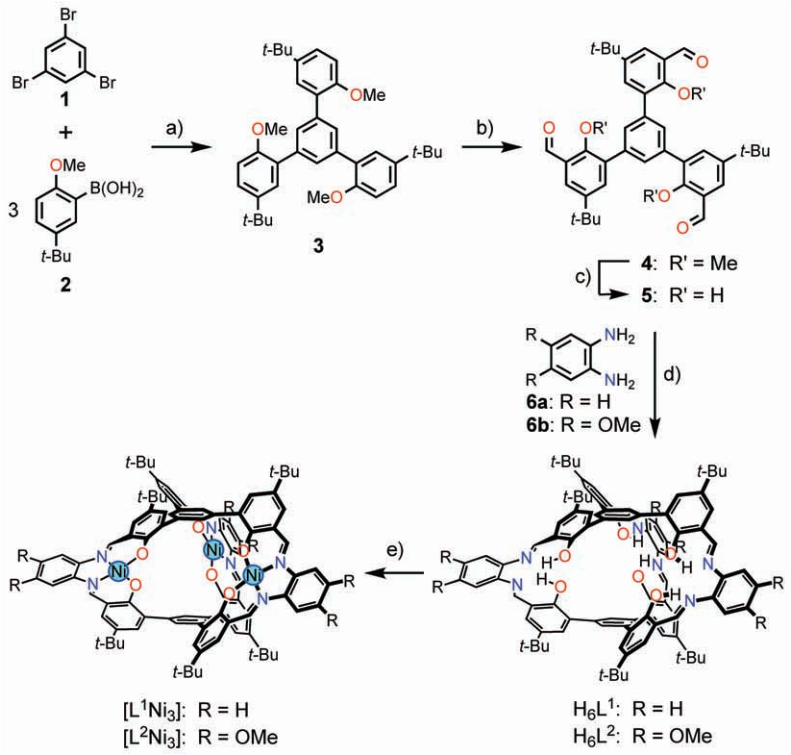
and the combined organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated to dryness. The crude product was recrystallized from chloroform/methanol to yield triol **5** (608 mg, 0.888 mmol, 76%) as colorless crystals, mp 206–209 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (s, 27H), 7.56 (d, J = 3.2 Hz, 3H), 7.77 (d, J = 3.2 Hz, 3H), 7.81 (s, 3H), 9.97 (s, 3H), 11.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.33 (CH_3), 34.25 (C), 120.39 (C), 129.56 (CH), 129.57 (CH), 129.76 (C), 135.99 (CH), 136.86 (C), 142.87 (C), 156.88 (C), 197.04 (CHO). Anal. Calcd for $C_{39}H_{48}O_6$•0.6$CHCl_3$: C, 70.11; H, 6.33.Found: C, 70.19; H, 6.59.

Synthesis of ligand H_6L^1. A solution of compound **5** (226 mg, 0.372 mmol) in dichloromethane (3 mL) and a solution of 1,2-phenylenediamine (**6a**) (60.3 mg, 0.558 mmol) in acetonitrile (3 mL) were mixed. After standing overnight at room temperature, the precipitates were collected on a filter to yield H_6L^1 (157.7 mg, 0.108 mmol, 58%) as yellow crystals, mp > 300 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.26 (s, 54H), 7.29 (br m, 6H), 7.42 (br m, 12H), 7.63 (s, 6H), 7.71 (s, 6H), 8.76 (br s, 6H), 12.90 (br s, 6H). MALDI-TOF MS observed m/z 1467.2 ($[H_6L^1 + K]^+$). Anal. Calcd for $C_{96}H_{96}N_6O_6$•2H_2O: C, 78.66; H, 6.88; N, 5.73. Found C, 79.05; H, 6.93; N, 5.66.

Synthesis of ligand H_6L^2. Under nitrogen atmosphere, a solution of trialdehyde **5** (194 mg, 0.320 mmol) in degassed chloroform (2 mL) was mixed with a solution of diamine **6b**[3] (80.8 mg, 0.480 mmol) in degassed acetonitrile (2 mL). The mixture was heated at 50 °C for 10 h and then kept at room temperature. The formed precipitates were collected by filtration to yield H_6L^2 (160 mg, 0.0924 mmol, 58%) as yellow crystals, mp > 300 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (s, 54H), 3.98 (s, 18H), 6.74 (s, 6H), 7.33 (d, J = 2.4 Hz, 6H), 7.50 (d, J = 2.4 Hz, 6H), 7.95 (s, 6H), 8.59 (s, 6H), 12.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.48 (CH_3), 34.05 (C), 56.39 (CH_3), 102.96 (CH), 119.02 (C), 127.88 (CH), 129.14 (CH), 129.68 (C), 132.35 (CH), 136.83 (C), 137.32 (C), 141.05 (C), 148.55 (C), 156.60 (C), 163.53 (CH). MALDI-TOF MS observed m/z 1632.0 ($[H_6L^2 + Na]^+$). Anal. Calcd for $C_{102}H_{108}N_6O_{12}$•7H_2O: C, 70.57; H, 7.08; N, 4.84. Found: C, 70.70; H, 6.68; N, 4.79.

Synthesis of $[L^1Ni_3]$. A solution of H_6L^1 (28.7 mmol, 0.020 mmol) in DMSO (3 mL) and a solution of nickel(II) acetate tetrahydrate (14.9 mg, 0.060 mmol) were mixed. The mixture was heated at 80 °C for 2 h and then stand overnight at room temperature. The resultant red precipitates were collected on a filter to yield $[L^1Ni_3]$ (20.3 mg, 0.011 mmol, 57%) as red crystals, ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.23 (s, 54H), 7.04 (s, 6H), 7.11 (s, 6H), 7.32–7.35 (m, 6H), 7.53 (s, 6H), 8.13–8.15 (m, 6H), 8.91 (s, 6H). MALDI-TOF MS observed m/z 1621.7 ($[L^1Ni_3 + Na]^+$). Anal. Calcd for $C_{96}H_{90}N_6Ni_3O_6$•2.5DMSO: C, 67.57; H, 5.90; N, 4.68. Found: C, 67.87; H, 5.66; N, 4.93.

Synthesis of [L^2Ni_3]. A solution of H_6L^2 (32.2 mg, 0.020 mmol) in chloroform (1 mL) was mixed with a solution of nickel(II) acetate tetrahydrate (24.9 mg, 0.10 mmol) in DMSO (1 mL) were mixed and the mixture was heated at 50 °C for 8 h and then kept at room temperature. The formed precipitates were collected by filtration to yield [L^2Ni_3] (29.0 mg, 0.014 mol, 72%) as dark red crystals, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (s, 54H), 3.98 (s, 18H), 7.08 (s, 6 H), 7.16 (d, J = 2.6 Hz, 6H), 7.20 (d, J = 2.6 Hz, 6H), 7.47 (s, 6H), 7.99 (s, 6H). MALDI-TOF MS observed m/z 1801.6 ([L^2Ni_3 + Na]$^+$). Anal. Calcd for $C_{102}H_{102}N_6Ni_3O_{12}$•2$CHCl_3$: C, 61.87; H, 5.19; N, 4.16. Found: C, 61.61; H, 5.52; N, 4.26.



Synthesis of ligands H_6L^1, H_6L^2 and trinuclear complexes [L^1Ni_3], [L^2Ni_3]. *Reagents and conditions*, a [$Pd(PPh_3)_4$], K_2CO_3, DMA, EtOH, H_2O, 72%; b (i) *n*-BuLi, TMEDA, Et_2O, (ii) DMF, (iii) H_2O, 99%; c (i) BBr_3, CH_2Cl_2, (ii) H_2O, 76%; d R = H: **6a**, CH_2Cl_2, MeCN, 58%; R = OMe: **6b**, $CHCl_3$, MeCN, 58%; e R = H: $Ni(OAc)_2$, DMSO, 57%; R = OMe: $Ni(OAc)_2$, $CHCl_3$, DMSO, 72%.

References.

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