Supporting Information for

Homochiral Metal-Organic Frameworks Based on Transition Metal Bisphosphonates

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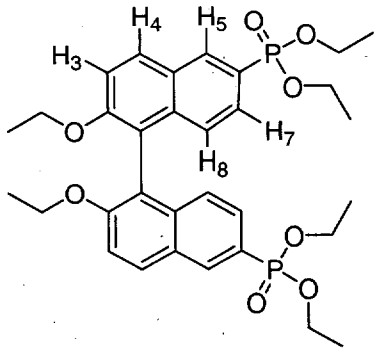
Experimental

Synthesis of (*R*)-2,2'-diethoxy-1,1'-binaphthalene-6,6'-bisphosphonic acid, (L-H_4). 60g (0.210 mol) of 1,1'-bi-2-naphthol was dissolved in 1.2 L of CH_2Cl_2 under N_2. The solution was cooled to -78° and 29 mL of Br_2 was added dropwise at -78°C. After the addition of Br_2, the mixture was allowed to stir at -78°C for an additional 30 minutes and then allowed to warm to room temperature. The mixture was then cooled to 0°C and quenched with a solution of 50 g of $NaHSO_3$ in 200 mL of H_2O. The mixture was extracted with CH_2Cl_2/H_2O three times. The organic layer was removed, dried over $MgSO_4$ and concentrated to dryness to afford pure 6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthalene (Yield: 93g, 99.9%). Spectroscopic data are identical to those reported in literature.[8]

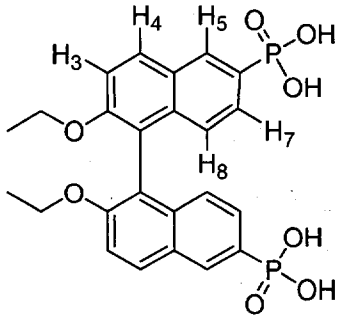
A mixture of 6,6,-dibromo-2,2'-dihydroxy-1,1'-binaphthlene (40g, 90 mmol), bromoethane (40 mL, 536 mmol), K_2CO_3 (48g, 348 mmol), and NaI (0.65g, 4.2 mmol) was dissolved in 200 mL of anhydrous acetone and refluxed for 3 days under N_2. The acetone was

removed in vacuo and the residue was extracted with CH_2Cl_2/H_2O. The organic layer was removed, dried over $MgSO_4$ and concentrated dry to afford pure 6,6'-dibromo-2,2'-dihyroxy-1,1'-binaphthalene (Yield: 45g, 99%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.00 (d, J = 1.8 Hz, 2H, H_5), 7.84 (d, J = 9.0 Hz, 2H, H_3), 7.42 (d, J = 9.6 Hz , 2H, H_4), 7.26 (dd, J = 9.1 Hz , J = 1.8 Hz, 2H, H_7), 6.95 (d, J = 9.6 Hz, 2H, H_8), 4.05 (m, 4H, OCH_2CH_3), 1.06 (t, J = 6.9 Hz, OCH_2CH_3).



A mixture of (*R*)-6,6'-dibromo-2,2'-diethoxy -1,1'-binaphthalene (14g, 24.1 mmol) and diethyl phosphite (8.97g, 65 mmol) in 100 mL of anhydrous toluene and 10 mL of distilled triethylamine was refluxed under nitrogen in the presence of tetrakis(triphenylphosphine)palladium (0.9g, 0.78 mmol) for 48 hours. Organic volatiles were removed under reduced pressure, and the residue dissolved in 250 ml of ethyl acetate and washed twice with 100 mL of deionized water. The organic layer was dried over $MgSO_4$ and evaporated to dryness. Silica gel chromatography eluting with a mixture of hexanes and acetone (2:1 v/v) afforded 11.16g of pure (*R*)-tetraethyl-2,2'-diethoxy-1,1'-binaphthalene-6,6-diphosphonate (67% yield). $[\alpha]^{25}_D$= -2.07° (*c* = 2.32, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, 2H, $^3J_{H\text{-}P}$ = 15.6 Hz, H_5), 8.06 (d, 2H, $^3J_{H\text{-}H}$ = 8.6 Hz, H_3), 7.50 (d, 2H, $^3J_{H\text{-}H}$ = 8.6 Hz, H_4), 7.46 (dd, 2H, $^3J_{H\text{-}H}$ = 8.6 Hz, $^3J_{H\text{-}P}$ = 1.6 Hz, H_7), 7.16 (dd, 2H, $^3J_{H\text{-}H}$ = 8.6 Hz, $^4J_{H\text{-}P}$ = 3.9 Hz, H_8), 4.15 (m, 4H, O-CH_2CH_3), 4.1 (m, 8H, PO-CH_2CH_3), 1.33 (dt, 12H, $^2J_{H\text{-}H}$ = 7.03 Hz, $^4J_{H\text{-}P}$ = 2.3 Hz, PO-CH_2CH_3), 1.09 (t, 6H, $^3J_{H\text{-}H}$ = 6.6 Hz, O-CH_2CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 49.0 (s). ^{13}C NMR ($CDCl_3$): δ 156.3 (s, C_2), 136.0 (d, $^4J_{C\text{-}P}$ = 2.3 Hz, C_9), 134.5 (d, $^2J_{C\text{-}P}$ = 9.9 Hz, C_5), 130.9 (s, C_4), 128.1 (d, $^3J_{C\text{-}P}$ = 16.8 Hz, C_{10}), 126.9 (d, $^2J_{C\text{-}P}$ = 10.7 Hz, C_7), 125.8 (d, $^3J_{C\text{-}P}$ = 13.7 Hz, C_8), 122.6 (d, $^1J_{C\text{-}P}$ = 190 Hz, C_6),

119.6 (s, C_1), 116.0 (s, C_3), 65.0 (s, OCH_2CH_3), 62.3 (d, $^2J_{C\text{-}P}$ = 3.1 Hz, $POCH_2CH_3$), 16.5 (d, $^3J_{C\text{-}P}$ = 6.1 Hz, $POCH_2CH_3$), 15.0 (s, OCH_2CH_3).



A mixture of (*R*)-diethyl-2,2'-diethoxy-1,1'-binaphthalene-6,6-diphosphonate (1.6g , 2.61 mmol) and trimethylsilyl bromide (2.1g, 14 mmol) in 50 mL of distilled methylene chloride was stirred under nitrogen at room temperature. After 24 hours, the volatiles were removed under reduced pressure and methanol was added (50 mL) was added to the residue. The solution was then removed under reduced pressure to give 1.282g of pure (*R*)-2,2'-diethoxy-1,1'-binaphthalene-6,6'-bisphosphonic acid (98% yield). $[\alpha]^{25}_D$= 12.5° (*c*=2, MeOH); ^{1}H NMR (400 MHz, CD_3OH) δ 8.38 (d, 2H, $^3J_{H\text{-}P}$ = 15.3 Hz, H_5), 8.07 (d, 2H, $^3J_{H\text{-}H}$ = 9.2 Hz, H_3), 7.60 (d, 2H, $^3J_{H\text{-}H}$ = 9.2 Hz, H_4), 7.48 (dd, 2H, $^3J_{H\text{-}H}$ = 8.6 Hz, $^3J_{H\text{-}P}$ = 9.7 Hz, H_7), 7.06 (dd, 2H, $^3J_{H\text{-}H}$ = 8.6 Hz, $^4J_{H\text{-}P}$ = 3.05 Hz, H_8), 4.06 (q, 4H, $^3J_{H\text{-}H}$ = 6.7 Hz, O-CH_2CH$_3$), 1.01 (t, 6H, $^3J_{H\text{-}H}$ = 6.7 Hz, O-CH$_2$CH_3). ^{31}P{^{1}H} NMR (CD_3OH): δ 46.5 (s). ^{13}C {^{1}H} NMR (CD_3OH): δ 156.3 (s, C_2), 135.5 (d, $^4J_{C\text{-}P}$ = 2.3 Hz, C_9), 132.6 (d, $^2J_{C\text{-}P}$ = 9.9 Hz, C_5), 130.6 (s, C_4), 128.2 (d, $^3J_{C\text{-}P}$ = 16.0 Hz, C_{10}), 126.3 (d, $^2J_{C\text{-}P}$ = 10.7 Hz, C_7), 125.8 (d, $^1J_{C\text{-}P}$ = 189 Hz, C_6), 125.1 (d, $^3J_{C\text{-}P}$ = 13.7 Hz, C_8) 119.4 (s, C_1), 115.8 (s, C_3), 64.7 (s, OCH_2CH_3), 14.1 (s, OCH_2CH_3). The *(S)*-enantiomer of **L-H$_4$** was synthesized using the identical protocol. As expected, similar yields and identical spectroscopic data were obtained.

Table S1. Selected distances (Å) and bond angles (degrees) for **1-5**.

1

Mn1—O5c	2.074(5)	O5c—Mn1—O1b	92.2(2)	O3—Mn1—O4a	98.5(2)
Mn1—O1b	2.136(6)	O5c—Mn1—O3	87.4(2)	O5c—Mn1—O7	120.7(2)
Mn1—O3	2.124(5)	O1b—Mn1—O3	172.3(2)	O1b—Mn1—O7	88.9(2)
Mn1—O4a	2.181(5)	O5c—Mn1—O4a	101.5(2)	O3—Mn1—O7	84.7(2)
Mn1—O7	2.165(5)	O1b—Mn1—O4a	89.1(2)	O4a—Mn1—O7	137.8(2)

2

Co2—O8	1.937(5)	Co1—O13	2.093(2)
Co2—O1b	1.974(1)	Co1—O6	2.067(1)
Co2—O12a	1.950(1)	Co1—O14	2.191(4)
Co2—O5	1.935(1)	Co1—O9d	2.061(1)
Co1—O15	2.171(1)	Co1—O2c	2.108(4)

O12a—Co2—O1b	108.75(1)
O1b—Co2—O8	113.65(1)
O8—Co2—O5	113.36(1)
O12a—Co2—O1a	108.75(1)
O1b—Co2—O8	113.65(1)
O8—Co2—O5	113.36(1)
O5—Co2—O1b	104.29(1)
O12b—Co2—O8	113.14(1)
O5—Co2— O5	102.74(1)
Co2—O1b O12a	104.29(1)
O12a—Co2—O8	113.14(1)
O5—Co2—O8	113.36(1)
O12a—Co2—O5	102.74(1)
O8—Co2—O12a	113.14(1)
O15—Co1—O9d	87.11(1)
O9d—Co1—O6	95.51(1)
O6—Co1—O13	91.80(1)
O13—Co1—O15	85.48(1)
O15—Co1—O6	177.24(1)
O2c—Co1—O14	173.88(1)
O14—Co1—O9d	83.99(1)
O14—Co1—O13	87.38(1)
O14—Co1—O6	86.29(1)
O14—Co1—O15	93.11(1)
O2c—Co1—O9d	98.41(1)
O2c—Co1—O6	87.87(1)

3

Ni1—O1	1.989(4)	Ni1—O10	2.083(4)
Ni1—O6A	2.005(3)	Ni1—O12	2.085(4)
Ni1—O9	2.082(4)	Ni1—O11	2.093(4)

O1—Ni1—O6a	97.35(1)
O1—Ni1—O9	90.24(2)
O6a—Ni1—O9	91.60(1)
O1—Ni1—O10	171.7(2)
O6a—Ni1—O10	90.37(2)
O9—Ni1—O10	86.44(2)
O1—Ni1—O12	95.68(2)
O6a—Ni1—O12	96.23(2)
O9—Ni1—O12	169.49(2)
O10—Ni1—O12	86.52(2)
O1—Ni1—O11	88.08(2)
O6a—Ni1—O11	174.04(2)
O9—Ni1—O11	85.89(1)
O10—Ni1—O11	84.09(2)
O12—Ni1—O11	85.64(2)

4

Cu1—O6a	1.919(5)	Cu1—O4	1.910(5)
Cu1—O2b	1.908(5)	Cu1—O1	1.920(5)

O6—Cu1—O2b	92.0(3)
O6—Cu1—O4c	173.2(3)
O2—Cu1—O4c	89.8(2)
O6—Cu1—O1	88.6(3)
O2—Cu1—O1	166.1(2)
O4—Cu1—O1	91.2(2)

5

Zn1-N1	2.065(7)	O5B-Zn1-O2	104.33(19)
Zn1-N2	2.001(11)	O5B-Zn1-O1a	109.14(19)
Zn1-O5b	1.922(5)	O2-Zn1-O1a	116.18(17)
Zn1-O1a	1.951(4)	O5B-Zn1-N2	93.35(40)
Zn1-O2	1.933(4)	O2-Zn1-N2	121.36(35)
Zn2-O3a	1.959(5)	O1A-Zn1-N2	109.17(32)
Zn2-O4d	1.928(7)	O5B-Zn1-N1	121.42(28)
Zn2-O4c	1.928(7)	O2-Zn1-N1	100.04(25)
Zn2-O3	1.959(5)	O1A-Zn1-N1	106.02(26)
P1-O2	1.524(5)	N2-Zn1-N1	30.28(38)
P1-O1	1.544(5)	O4D-Zn2-O4C	115.53(26)
P1-O3	1.504(6)	O4d-Zn2-O3	112.70(23)
P2-O6	1.571(5)	O4c-Zn2-O3	102.73(22)
P2-O4	1.485(6)	O4-Zn2-O3a	102.73(22)

P2-O5	1.503(5)	O4c-Zn2-O3a	112.70(23)

[a] Symmetry Codes: For **1**: a = 1-x, 0.5+y, 2.5-z; b = 0.5+x, 1.5-y, 2-z. For **2**: a = -1+x, y, -1+z.; b = x, y, -1+z; c = 1-x, 0.5+y, 3-z.; d = 1-x, 0.5+y, 2-z. For **3**: A = 0.5-x, 1-y, -0.5+z. For **4**: a = 2-x, -0.5+y, 0.5-z; b = -0.5+x, 0.5-y, -z; c = 2.5-x, 1-y, -0.5+z. For **5**: a = -x, y, 2-z; b = 0.5-x, 0.5+y, 2-z; c = -0.5+x, -0.5+y, z; d = 0.5-x, -0.5+y, 2-z.

Fig S1. Thermogravimetric analysis curves of compounds **1-5**. Curves have been manually offset for clarity.