Supporting Information

Metallohosts with a Heart of Carbon

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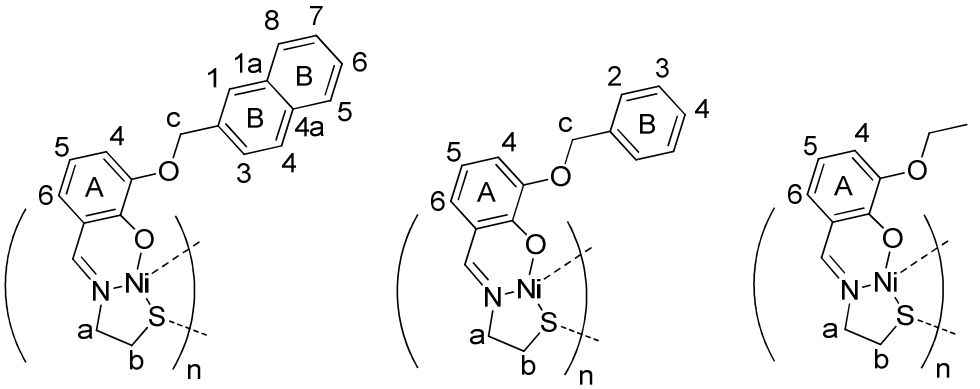
General experimental

^{1}H and ^{13}C NMR spectra were recorded on Bruker AvanceIII 600 with BBFO+SP probehead, DRX-500 and DRX-400 NMR spectrometers; chemical shifts are referenced to residual solvent peaks (TMS = δ 0 ppm). Absorption spectra were recorded on a Varian-Cary 5000 spectrophotometer. A Shimadzu FTIR-8400S spectrophotometer was used to record IR spectra with solid samples using a Golden Gate diamond ATR accessory. Biosystems Voyager DE PRO and Bruker esquire 3000plus mass spectrometers were used to record the MALDI-TOF and ESI mass spectra.



1 **2** **3**

Scheme S1: Atom numbering for NMR spectroscopic assignments in compounds **1-3**.

Experimental section

2-Hydroxy-3-(naphthalen-2-ylmethoxy)benzaldehyde

A solution of 2,3-dihydroxybenzaldehyde (1.93 g, 0.014 mol) in DMSO (7 cm^3) was added to a suspension of NaH (1.39 g, 0.035 mol, 60% in mineral oil) in DMSO (15 cm^3) at room temperature under N_2. The mixture was stirred for 1 h and then a solution of 2-(bromomethyl)naphthalene (3.08 g, 0.014 mol) in DMSO (5 cm^3) was added. The reaction mixture was stirred at room temperature for 40 h, and was then poured into distilled water (80 cm^3) and extracted with $CHCl_3$ (2 × 20 cm^3). The aqueous layer was acidified with 6 M HCl to adjust the pH to ≈4 and was again extracted with $CHCl_3$ (3 × 40 cm^3). The combined $CHCl_3$ extracts were washed with 1 M HCl (2 × 40 cm^3), and dried over Na_2SO_4, filtered and concentrated to give brown solid, which was purified by flash column chromatography on silica gel (n-hexanes/ethyl acetate, 19:1, v/v). 2-Hydroxy-3-(naphthalen-2-ylmethoxy)benzaldehyde was isolated as a pale-yellow solid (1.56 mg, 40.0%). M.p.: 113-114°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm 11.13 (s, 1H, $H^{C\underline{H}=O}$), 9.90 (s, 1H, H^{OH}), 7.87 (s, 1H, H^{B1}), 7.85 (d, J = 8.5 Hz, 1H, H^{B4}), 7.82 (m, overlapping, 2H, H^{B5+B8}), 7.55 (dd, 1H, J = 8.4, 1.2 Hz, 1H, H^{B3}), 7.47 (m, overlapping, 2H, H^{B6+B7}), 7.16 (m, 2H, H^{A6+A4}), 6.86 (t, J =

7.9 Hz, 1H, H^{A5}), 5.35 (s, 2H, H^{c}). ^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm 196.8 ($C^{\underline{C}H=O}$), 152.6 (C^{A2}), 147.4 (C^{A3}), 134.2 (C^{B2}), 133.5 ($C^{B1a/B4a}$), 133.3 ($C^{B1a/B4a}$), 128.7 (C^{B4}), 128.2 ($C^{B5/B8}$), 128.0 ($C^{B5/B8}$), 126.5 (C^{B1}), 126.5 ($C^{B6/B7}$), 126.4 ($C^{B6/B7}$), 125.6 (C^{A6}), 125.3 (C^{B3}), 121.4 (C^{A4}), 121.3 (C^{A1}), 119.7 (C^{A5}), 71.8 (C^{c}). UV/VIS λ_{max}/nm (1.0×10^{-5} mol dm^{-3}, CH_2Cl_2) 229 (ε / 10^3 dm^3 mol^{-1} cm^{-1} 94.0), 267 (19.0), 350 (3.50). IR (solid, cm^{-1}): 2832w, 1659s, 1580w, 1457s, 1388m, 1375m, 1308w, 1270m, 1244s, 1217s, 1165m, 1124w, 1092w, 1056m, 965s, 950m, 894w, 866s, 846w, 824s, 791s, 756s, 731s, 716s, 653s. ESI-MS (MeOH) *m/z* 579.1 $[2M + Na]^+$ (calc. 579.2), 301.1 $[M + Na]^+$ (base peak, calc. 301.1). Elemental analysis calcd. (%) for $C_{18}H_{14}O_3$: C 77.68, H 5.07; found C 77.29, H 5.00.

1·CH_2Cl_2: 2-Hydroxy-3-(naphthalen-2-ylmethoxy)benzaldehyde (139 mg, 0.50 mmol) and 2-aminoethanethiol (38.5 mg, 0.50 mmol) were dissolved in CH_2Cl_2/CH_3OH (14 cm^3, v/v, 1:6). Solid $NiCl_2·6H_2O$ (118 mg, 0.50 mmol) was added while the mixture was stirred at room temperature. Et_3N (50.1 mg, 0.50 mmol) was added dropwise. The resulting suspension was stirred for 1 hour, then filtered. The pale-brown solid was washed with MeOH and dried in the air. Yield: 90.0 mg, 45.8%. ^1H NMR (500 MHz, $CDCl_3$) δ / ppm 7.83 (m, 12H, $H^{B5+B8+B4+B1}$), 7.53 (m, 6H, H^{B6+B7}), 7.45 (d, J = 8.1 Hz, 3H, H^{B3}), 6.74 (br, 3H, H^{A4}), 6.48 (s, 3H, $H^{C\underline{H}=N}$), 6.42 (br, 6H, H^{A5+A6}), 4.96 (s, 6H, H^{c}), 2.84 (br, 6H, H^{a}), 1.34 (br, 6H, H^{b}). ^{13}C NMR (126 MHz, $CDCl_3$) δ/ ppm 159.6 ($C^{\underline{C}H=N}$), 154.4 (C^{A2}), 150.7 (C^{A3}), 134.8 (C^{B2}), 133.3 ($C^{B1a/B4a}$), 133.2 ($C^{B1a/B4a}$), 128.26 (C^{B1}), 128.17 ($C^{B5/B8}$), 128.14 ($C^{B5/B8}$), 127.95 (C^{B4}), 127.2 (C^{B3}), 126.62 ($C^{B6/B7}$), 126.56 ($C^{B6/B7}$), 124.3 (C^{A6}), 119.8 (C^{A1}), 113.7 (C^{A5}), 113.3 (C^{A4}), 70.9 (C^{c}), 70.0 (C^{a}), 24.5 (C^{b}). ^1H NMR (600 MHz, 1,2-$C_6D_4Cl_2$) δ/ ppm 7.77 (m, 12H, H^{B5+B8}), 7.74 (d, J = 8.4 Hz, 3H, H^{B4}), 7.67 (s, 3H, H^{B1}), 7.46 (m, 3H, H^{B6+B7}), 7.37 (d, J = 8.0 Hz, 3H, H^{B3}), 6.71 (d, J = 7.0 Hz, 3H, H^{A4}), 6.48 (t, J = 7.6 Hz, 3H, H^{A5}), 6.43 (d, J = 7.6 Hz, 3H, H^{A6}), 6.29 (s, 3H, $H^{C\underline{H}=N}$), 4.81 (s, 6H, H^{c}), 2.65 (br, 6H, H^{a}), 1.28 (m, 6H, H^{b}). ^{13}C

NMR (151 MHz, 1,2-$C_6D_4Cl_2$) δ/ ppm 159.3 ($C^{\underline{C}H=N}$), 154.3 (C^{A2}), 150.7 (C^{A3}), 134.7 (C^{B2}), 133.4 (C^{B1a}), 133.3 (C^{B4a}), 128.5 (C^{B1}), 128.2 (C^{B4}), 128.1 (C^{B8}), 127.9 (C^{B5}), 126.52 (C^{B7}), 126.47 (C^{B6}), 126.3 (C^{B3}), 124.2 (C^{A6}), 119.7 (C^{A1}), 113.9 (C^{A5}), 112.8 (C^{A4}), 70.6 (C^{c}), 70.2 (C^{a}), 24.3 (C^{b}). UV/VIS λ_{max}/nm (1.0×10^{-5} mol dm^{-3}, CH_2Cl_2) 230 (ε / 10^3 dm^3 mol^{-1} cm^{-1} 188), 268 (74.6), 379 (14.1), 513sh (1.30), 616 (0.400). IR (solid, cm^{-1}): 1652m, 1609s, 1557w, 1539w, 1507w, 1465s, 1446s, 1326m, 1228s, 1208s, 1171m, 1073w, 949w, 854m, 809m, 738s, 668s. MALDI-TOF MS (NOBA): *m/z* 1181.1 $[M]^+$ (calc. 1181.1), 788.4 $[Ni_2L_2]$ (base peak, calc. 788.1). Elemental analysis calcd. (%) for $C_{60}H_{51}N_3Ni_3O_6S_3 \cdot CH_2Cl_2$: C 57.81, H 4.22, N 3.32; found C 58.04, H 4.20, N 3.40.

2$\cdot$**CH_2Cl_2**: The procedure was as for **1**, but using 3-(benzyloxy)-2-hydroxybenzaldehyde (228 mg, 1.00 mmol), 2-aminoethanethiol (77.0 mg, 1.00 mmol) and $NiCl_2 \cdot 6H_2O$ (236 mg, 1.00 mmol). Brown crystals of **2**$\cdot CH_2Cl_2$ were isolated after 5 days. Yield: 170 mg, 45.7%. Compound **2** (dissolved crystalline **2**$\cdot CH_2Cl_2$): ^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm major component: 7.35 (m, overlapping with minor component, 5H, H^B), 7.12 (s, 1H, $H^{N=CH}$), 6.72 (d, J = 7.4 Hz, 1H, H^{A4}), 6.68 (d, J = 7.9 Hz, 1H, H^{A6}), 6.43 (t, J = 7.6 Hz, 1H, H^{A5}), 4.82 (s, overlapping with minor component, 2H, H^c), 3.12 (br, 2H, H^a), 1.45 (br, overlapping with minor component, 2H, H^b); minor component: 7.66 (s, 1H, $H^{N=CH}$), 7.35 (m, overlapping with major component, 5H, H^B), 6.83 (d, J = 7.6 Hz, 2H, H^{A4+A6}), 6.48 (t, J = 7.5 Hz, 1H, H^{A5}), 4.82 (s, overlapping with major component, 2H, H^c), 3.36 (m, 2H, H^{a1+a2}), 2.57 (m, 1H, $H^{b1/b2}$), 1.45 (br, overlapping with major component, 1H, $H^{b1/b2}$); ^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm major component: 159.7 ($C^{N=CH}$), 154.4 (C^{A2}), 150.5 (C^{A3}), 137.3 (C^{B1}), 129.2 (C^{B2}), 128.6 (C^{B3}), 128.4 (C^{B4}), 124.2 (C^{A6}), 119.8 (C^{A1}), 113.8 (C^{A5}), 113.4 (C^{A4}), 70.7 (C^c), 70.4 (C^a), 24.7 (C^b); minor component: 160.7 ($C^{N=CH}$), 155.4 (C^{A2}), 150.2 (C^{A3}), 137.3 (C^{B1}), 129.2 (C^{B2}), 128.6 (C^{B3}), 128.4 (C^{B4}), 125.8 (C^{A6}), 119.5 (C^{A1}), 117.5 (C^{A4}), 113.9

(C^{A5}), 70.7 (C^{c}), 69.0 (C^{a}), 27.4 (C^{b}). UV/VIS λ_{max}/nm (1.0×10^{-5} mol dm^{-3}, C_6H_5Cl) 291sh (ε / 10^3 dm^3 mol^{-1} cm^{-1} 38.8), 345sh (16.7), 378 (16.2), 515 (2.25), 623sh (0.48). IR (solid, cm^{-1}): 2912w, 1603s, 1539m, 1464s, 1447s, 1393w, 1331s, 1242s, 1226s, 1173m, 1106w, 1070m, 996m, 959w, 945w, 864w, 848s, 729s. MALDI-TOF MS (NOBA): 1034.0 $[M + H]^+$ (calc. 1032.1), 688.8 $[Ni_2L_2 + H]^+$ (base peak, calc. 687.0). ESI-MS (CH_2Cl_2/MeOH): *m/z* 1397.3 $[Ni_4L_4 + Na]^+$ (calc. 1397.1), 1054.3 $[M + Na]^+$ (calc. 1054.0), 1031.3 $[M + H]^+$ (calc. 1032.1), 709.3 $[Ni_2L_2 + Na]^+$ (base peak, calc. 709.0). Elemental analysis calcd. (%) for $C_{48}H_{45}N_3Ni_3O_{16}S_3 \cdot CH_2Cl_2$: C 52.68, H 4.24, N 3.76; found C 52.93, H 4.04, N 4.00%.

2(3)·CH_2Cl_2: The procedure was as for **1**, but using 3-ethoxy-2-hydroxybenzaldehyde (166 mg, 1.00 mmol), 2-aminoethanethiol (77.0 mg, 1.00 mmol) and $NiCl_2 \cdot 6H_2O$ (236 mg, 1.00 mmol). Slow evaporation of the filtrate at room temperature over 1 week resulted in the formation of brown block-like crystals which were separated by filtration, washed with MeOH and dried in air. Yield: 130 mg, 44.3%. Compound **3** (dissolved crystalline 2(**3**)·CH_2Cl_2): ^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm major component: 7.62 (s, 1H, $H^{N=CH}$), 6.72 (dd, J = 8.0, 1.4 Hz, 1H, H^{A6}), 6.64 (dd, J = 7.6, 1.3 Hz, 1H, H^{A4}), 6.43 (t, J = 7.8 Hz, 1H, H^{A5}), 3.88 (overlapping m, 4H, $H^{CH_2(Et)+a}$), 1.85 (br, 2H, H^{b}), 1.35 (t, J = 6.9 Hz, 3H, $H^{CH_3(Et)}$); minor component: 7.67 (s, 1H, $H^{N=CH}$), 6.79 (dd, J = 8.0, 1.4 Hz, 1H, H^{A6}), 6.75 (dd, J = 7.6, 1.4 Hz, 1H, H^{A4}), 6.47 (t, J = 7.8 Hz, 1H, H^{A5}), 3.95 (m, 2H, $H^{CH_2(Et)}$), 3.76 (m, 2H, H^{a1+a2}), 2.64 (m, 1H, $H^{b1/b2}$), 1.69 (m, 1H, $H^{b1/b2}$), 1.34 (t, J = 6.9 Hz, 3H, $H^{CH_3(Et)}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm major component: 160.1 ($C^{N=CH}$), 154.3 (C^{A2}), 150.6 (C^{A3}), 123.9 (C^{A6}), 119.5 (C^{A1}), 114.0 (C^{A5}), 113.2 (C^{A4}), 68.9 (C^{a}), 63.5 ($C^{CH_2(Et)}$), 24.9 (C^{b}), 15.3 ($C^{CH_3(Et)}$); minor component: 160.6 ($C^{N=CH}$), 155.4 (C^{A2}), 150.8 (C^{A3}), 124.8 (C^{A6}), 119.5 (C^{A1}), 115.6 (C^{A4}), 114.3 (C^{A5}), 70.6 (C^{a}), 64.0 ($C^{CH_2(Et)}$), 26.7 (C^{b}), 15.3 ($C^{CH_3(Et)}$). UV/VIS λ_{max}/nm (1.0×10^{-5} mol dm^{-3}, C_6H_5Cl) 291sh (ε/10^3 dm^3 mol^{-1} cm^{-1} 43.9), 343sh (18.7), 381

(21.8), 416 (19.5), 514 (3.31), 624sh (0.893). IR (solid, cm^{-1}): 2970w, 2909w, 1606s, 1540m, 1464s, 1449s, 1436m, 1391w, 1330s, 1242s, 1228s, 1175w, 1115w, 1077m, 1024w, 948s, 842m, 728s. MALDI-TOF MS (NOBA): 845.1 $[M + H]^+$ (calc. 846.0), 562.5 $[Ni_2L_2+ H]^+$ (base peak, calc. 563.0). ESI-MS (CH_2Cl_2) 1149.2 $[Ni_4L_4+ Na]^+$ (calc. 1149.0), 1126.2 $[Ni_4L_4+ H]^+$ (calc. 1127.0), 868.4 $[M + Na]^+$ (calc. 868.0), 845.2 $[M + H]^+$ (calc. 846.0), 585.1 $[Ni_2L_2+ Na]^+$ (base peak, calc. 585.0), 564.1 $[Ni_2L_2+ H]^+$ (calc. 563.0). Elemental analysis calcd. (%) for $C_{33}H_{39}N_3Ni_3O_6S_3 \cdot 0.5CH_2Cl_2$: C 45.29, H 4.54, N 4.73; found C 45.33, H 4.41, N 4.82%.

$1 \cdot C_{60} \cdot 0.5(1,2\text{-}Cl_2C_6H_4) \cdot Et_2O$: Crystalline 2(**1**)$\cdot CH_2Cl_2$ (12.6 mg, 10.0 μmol) was dissolved in 1,2-$Cl_2C_6H_4/CH_2Cl_2$ (2.0 cm^3, 4:1, v/v), and C_{60} (7.20 mg, 10.0 μmol) was added to the solution. The solid dissolved after sonication in an ultrasonic bath for 5 min. The reaction mixture was filtered, and Et_2O was allowed to diffuse into the filtrate. Over three days black plates of **1**$\cdot C_{60} \cdot 0.5(1,2\text{-}Cl_2C_6H_4) \cdot Et_2O$ were obtained (13.2 mg, 69.5%). IR (solid, cm^{-1}): 1605s, 1541m, 1463s, 1447s, 1328s, 1273w, 1240m, 1226s, 1178w, 1107w, 1073m, 991w, 950w, 900w, 867w, 818m, 795m, 732s. Elemental analysis calcd. (%) for $C_{120}H_{51}N_3Ni_3O_6S_3 \cdot 0.2(1,2\text{-}Cl_2C_6H_4)$: C 75.33, H 2.70, N 2.17; found C 75.67, H 2.57, N 1.98.

$2(2) \cdot C_{60} \cdot 1,2\text{-}Cl_2C_6H_4 \cdot 0.25H_2O$: The method was as above, starting with crystalline **2**$\cdot CH_2Cl_2$ (10.3 mg, 9.22 μmol). The product was isolated as black plates (7.60 mg, 60.0%). IR (solid, cm^{-1}): 2907w, 1609s, 1839m, 1464s, 1447s, 1387m, 1331s, 1270w, 1246s, 1228s, 1205w, 1174m, 1116w, 1080m, 1069m, 1027w, 995m, 945m, 898w, 868w, 845s, 738s, 729s**.** Elemental analysis calcd. (%) for $C_{156}H_{90}N_6Ni_6O_{12}S_6 \cdot C_6H_4Cl_2 \cdot 0.25H_2O$: C 66.26, H 3.24, N 2.86; found C 66.15, H 3.13, N 2.65%.

2(3)·C_{60}·CH_2Cl_2: The method was as above, starting with crystalline 2(**3**)·CH_2Cl_2 (8.85 mg, 5.00 μmol). The product was isolated as black blocks (8.90 mg, 71.5%). IR (solid, cm^{-1}): 3060w, 2908w, 2866w, 1608s, 1540m, 1463s, 1450s, 1330s, 1275w, 1243s, 1227s, 1182m, 1173m, 1107w, 1072m, 1032w, 993m, 864s, 840s, 737s, 728s. Elemental analysis calcd. (%) for $C_{66}H_{78}N_6Ni_6O_{12}S_6 \cdot C_{60} \cdot CH_2Cl_2$: C 61.08, H 3.23, N 3.36; found C 61.32, H 3.13, N 3.24%.

Crystallography

Data were collected on a Stoe IPDS or Bruker-Nonius KappaAPEX diffractometer. The data reduction, solution and refinement used Stoe IPDS [1] or Bruker[2] software, and SHELXL97.[3] ORTEP figures were drawn using Ortep-3 for Windows.[4] Structures were analysed using Mercury v. 2.3.[5,6]

2(1)·CH_2Cl_2: $C_{121}H_{104}Cl_2N_6Ni_6O_{12}S_6$, M = 2449.62, black block, rhombohedral, space group R–3, $a = b$ = 20.479(3), c = 21.481(4) Å, U = 7802(2) $Å^3$, Z = 3, D_c = 1.564 Mg m^{-3}, μ(Mo-K_α) = 1.305 mm^{-1}, T = 173 K. Total 39038 reflections, 3078 unique, R_{int} = 0.1443. Refinement of 2696 reflections (259 parameters) with $I > 2\sigma(I)$ converged at final $R1$ = 0.0492 ($R1$ all data = 0.0579), $wR2$ = 0.1090 ($wR2$ all data = 0.1129), gof = 1.156.

2·CH_2Cl_2: $C_{49}H_{47}Cl_2N_3Ni_3O_6S_3$, M = 1117.08, black plate, monoclinic, space group $P2_1/c$, a = 15.661(3), b = 18.078(3), c = 18.236(3) Å, β = 115.008(12)°, U = 4678.9(15) $Å^3$, Z = 4, D_c = 1.586 Mg m^{-3}, μ(Mo-K_α) = 1.497 mm^{-1}, T = 173 K. Total 86319 reflections, 10736 unique, R_{int} = 0.0707. Refinement of 10007 reflections (595 parameters) with $I > 2\sigma(I)$ converged at final $R1$ = 0.0344 ($R1$ all data = 0.0375), $wR2$ = 0.0855 ($wR2$ all data = 0.0873), gof = 1.117.

2(3)·CH_2Cl_2: $C_{67}H_{80}Cl_2N_6Ni_6O_{12}S_6$, M = 1776.83, brown prism, monoclinic, space group $P2_1/c$, a = 17.1563(10), b = 16.5850(8), c = 24.7229(14) Å, β = 90.326(3)°, U = 7034.5(7) Å^3, Z = 4, D_c = 1.678 Mg m^{-3}, μ(Mo-K$_\alpha$) = 1.893 mm^{-1}, T = 123 K. Total 87397 reflections, 16154 unique, R_{int} = 0.0425. Refinement of 12111 reflections (908 parameters) with $I > 2\sigma(I)$ converged at final $R1$ = 0.0352 ($R1$ all data = 0.0650), $wR2$ = 0.1043 ($wR2$ all data = 0.1474), gof = 1.142.

1·C_{60}·0.5(1,2-$Cl_2C_6H_4$)·Et_2O: $C_{127}H_{63}ClN_3Ni_3O_7S_3$, M = 2050.54, black plate, monoclinic, space group $C2/c$, a = 46.302(6), b = 13.8507(10), c = 27.326(3) Å, β = 98.033(9)°, U = 17352(3) Å^3, Z = 8, D_c = 1.570 Mg m^{-3}, μ(Mo-K$_\alpha$) = 0.819 mm^{-1}, T = 173 K. Total 106200 reflections, 18018 unique, R_{int} = 0.1355. Refinement of 14202 reflections (1299 parameters) with $I > 2\sigma(I)$ converged at final $R1$ = 0.0648 ($R1$ all data = 0.0844), $wR2$ = 0.1546 ($wR2$ all data = 0.1671), gof = 1.060.

2(2)·C_{60}·1,2-$Cl_2C_6H_4$·0.25H_2O: $C_{162}H_{94.50}Cl_2N_6Ni_6O_{12.25}S_6$, M = 2936.40, black plate, triclinic, space group P–1, a = 13.2134(15), b = 16.8326(17), c = 27.248(3) Å, α = 92.936(2), β = 94.129(2), γ = 94.028(2)°, U = 6020.0(11) Å^3, Z = 2, D_c = 1.620 Mg m^{-3}, μ(Mo-K$_\alpha$) = 1.143 mm^{-1}, T = 123 K. Total 107293 reflections, 30466 unique, R_{int} = 0.0824. Refinement of 17799 reflections (1846 parameters) with $I > 2\sigma(I)$ converged at final $R1$ = 0.0560 ($R1$ all data = 0.1285), $wR2$ = 0.1463 ($wR2$ all data = 0.2119), gof = 1.064.

2(3)·C_{60}·CH_2Cl_2: $C_{127}H_{80}Cl_2N_6Ni_6O_{12}S_6$, M = 2497.76, black block, trigonal, space group $P31c$, $a = b$ = 18.551(3), c = 16.155(3) Å, U = 4814.5(13) Å^3, Z = 2, D_c = 1.723 Mg m^{-3}, μ(Mo-K$_\alpha$) = 1.412 mm^{-1}, T = 173 K. Total 81838 reflections, 7362 unique, R_{int} = 0.0714.

Refinement of 7006 reflections (484 parameters) with $I > 2\sigma(I)$ converged at final $R1$ = 0.0444 ($R1$ all data = 0.0471), $wR2$ = 0.1127 ($wR2$ all data = 0.1145), gof = 1.106.

Pulsed-field gradient spin-echo (PGSE) spectroscopy: The experimental details are similar to those detailed previously by us.[7]

NMR titration of 1 with C_{60} in 1,2-$Cl_2C_6D_4$: Compound **1** (19.8 mg, 1.68×10^{-2} mmol) was dissolved in 1,2-$Cl_2C_6D_4$ (4.0 mL). The sample was split into 10 equal portions (400 μL) in 10 NMR tubes. To each was added, respectively, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 μL of 2.54×10^{-2} mol dm^{-3} solution of C_{60} in of 1,2-$Cl_2C_6D_4$ (1.0 mL) then neat 1,2-$Cl_2C_6D_4$ was added to each tube to give a total volume of 500 μL for each sample. TMS was added to each tube as an internal standard. The ^{1}H NMR spectrum was recorded for each sample. The sample containing 100 μL of 2.54×10^{-2} mol dm^{-3} solution of C_{60} (corresponding to 1 : 1 molar equivalents of **1** : C_{60}) was then taken, and to it was added 0.75 equivalents C_{60} (0.92 mg) and (after 15 minutes sonication) the ^{1}H NMR spectrum was recorded. This last procedure was repeated to give solutions with 3.0, 4.5, 6.0, 7.5 equivalents of C_{60} with respect to **1**.

K_d was obtained by non-linear two-parameter fitting of the induced changes in chemical shifts $\Delta\delta_{obs}$ to the following equation:

$$\Delta\delta_{obs} = (\delta_{cplx} - \delta_{free}) \times {}^1/_2[(k + 1 + x_{C_{60}}) - \{(k + 1 + x_{C_{60}})^2 - 4x_{C_{60}}\}^{1/2}]$$

where: x_{C60} is the molar ratio of fullerene to **1**

k is K_d / [**1**]

δ_{free} is the chemical shift of pure **1** in the absence of C_{60}

δ_{cplx} is the hypothetical chemical shift of the 1:1 host–guest complex

Table S1: Titration data: chemical shift differences for each proton, labeled as in Scheme S1.

	H Δδ/ ppm										
Equiv of C_{60}	$H^{CH=N}$	H^{A4}	H^{A5}	H^{A6}	H^{B1}	H^{B3}	H^{B4}	H^{B5}	H^{B6}	H^{B7}	H^{B8}
0	0 (δ6.29 ppm)	0 (δ6.71 ppm)	0 (δ6.48 ppm)	0 (δ6.43 ppm)	0 (δ7.67 ppm)	0 (δ7.37 ppm)	0 (δ7.74 ppm)	0 (δ7.76 ppm)	0 (δ7.45 ppm)	0 (δ7.48 ppm)	0 (δ7.77 ppm)
0.15	–0.031	0.002	0.005	–0.007	0.009	0.007	0.005	0.006	0.006	0.009	0.007
0.30	–0.056	0.003	0.008	–0.012	0.016	0.011	0.008	0.011	0.009	0.015	0.012
0.45	–0.078	0.004	0.011	–0.018	0.023	0.014	0.013	0.015	0.012	0.021	0.016
0.60	–0.100	0.005	0.015	–0.022	0.028	0.020	0.016	0.020	0.016	0.028	0.021
0.75	–0.119	0.006	0.018	–0.026	0.033	0.023	0.019	0.023	0.019	0.033	0.025
0.90	–0.130	0.006	0.019	–0.029	0.038	0.024	0.020	0.024	0.021	0.036	0.030
1.05	–0.144	0.007	0.021	–0.033	0.042	0.027	0.022	0.027	0.023	0.041	0.034
1.20	–0.155	0.007	0.023	–0.034	0.044	0.029	0.025	0.027	0.024	0.043	0.037
1.36	–0.166	0.007	0.025	–0.038	0.047	0.032	0.026	0.029	0.026	0.047	0.040
1.50	–0.174	0.008	0.026	–0.040	0.050	0.033	0.027	0.030	0.028	0.049	0.043
2.27	–0.205	0.010	0.031	–0.046	0.060	0.040	0.034	0.035	0.033	0.059	0.052
3.03	–0.222	0.010	0.034	–0.050	0.065	0.043	0.037	0.036	0.035	0.064	0.057
4.54	–0.257	0.012	0.039	–0.058	0.076	0.051	0.043	0.042	0.041	0.074	0.068
6.05	–0.268	0.013	0.042	–0.060	0.081	0.055	0.046	0.044	0.044	0.079	0.073
7.56	–0.278	0.013	0.043	–0.062	0.085	0.057	0.048	0.046	0.045	0.082	0.076

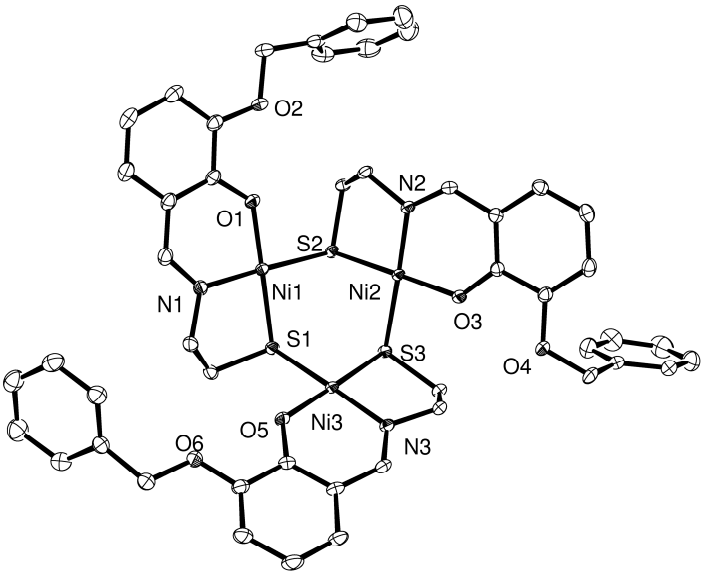


Fig. S1 Structure of **2** in **2**·CH_2Cl_2 with ellipsoids plotted at the 40% probability level; H atoms omitted.

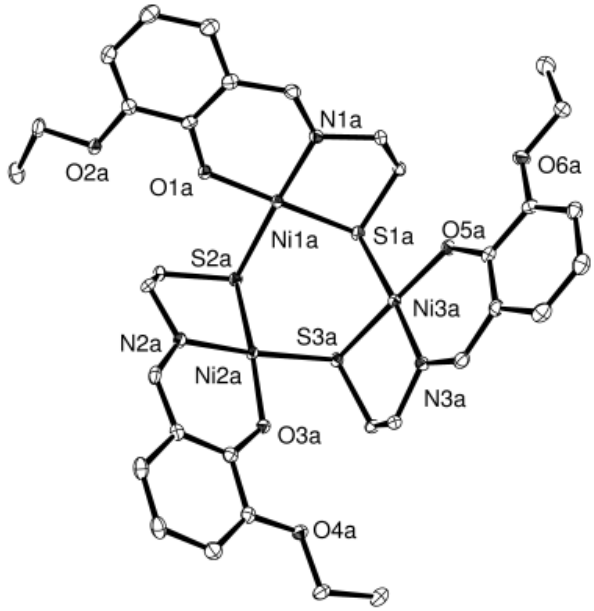


Fig. S2 Structure of one of the two independent molecules of **3** in 2(**3**)·CH_2Cl_2 with ellipsoids plotted at the 40% probability level; H atoms omitted.

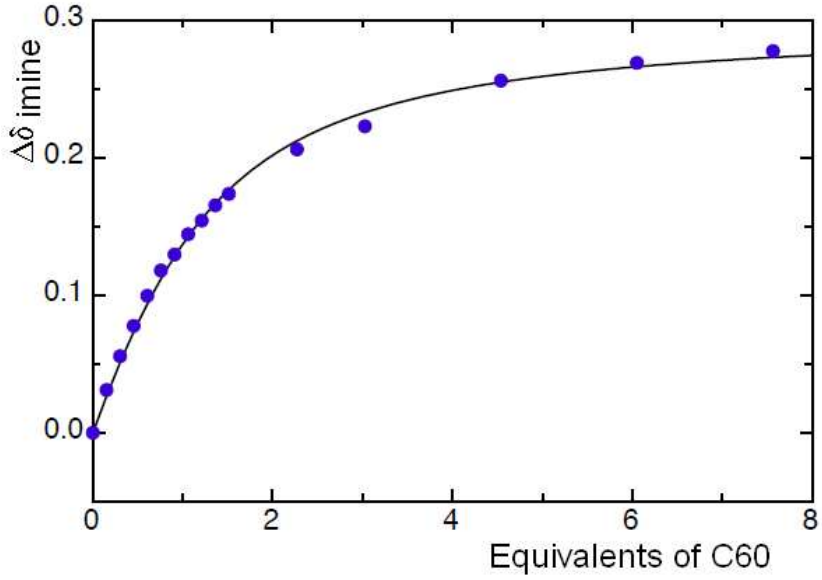


Fig. S3 Titration curve of $\Delta\delta_{imine}$ against equivalents of C_{60} added to one equivalent of **1**.

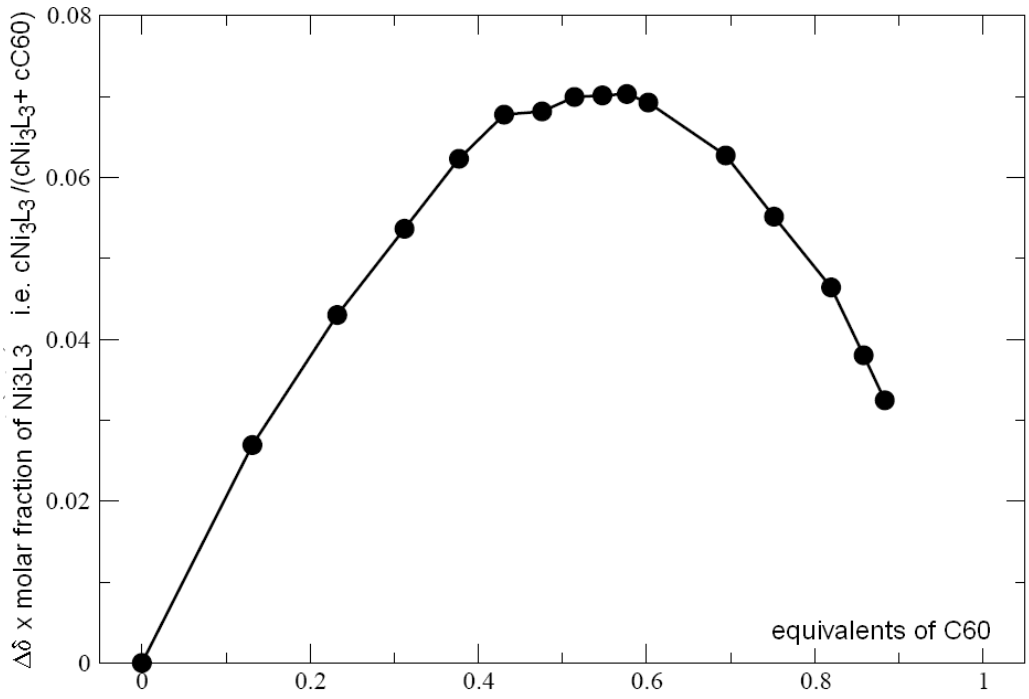


Fig. S4 Job's plot for the formation of host–guest complex between **1** and C_{60} in 1,2-$Cl_2C_6D_4$.

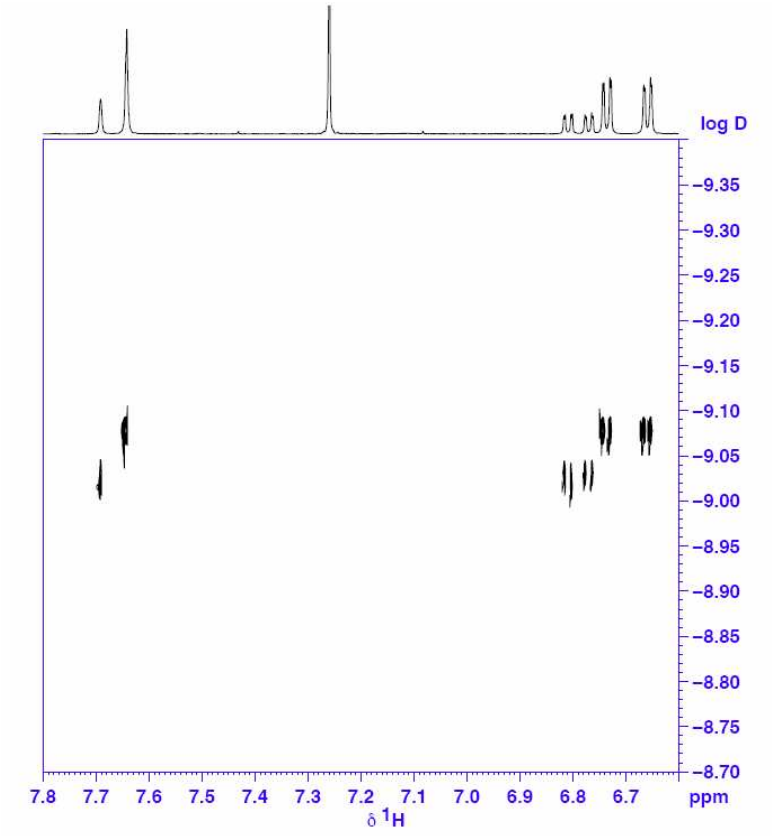


Fig. S5 ^{1}H DOSY-type plot (600 MHz, $CDCl_3$) of the two solution components of **3**.

[1] Stoe & Cie, IPDS software v 1.26, Stoe & Cie, Darmstadt, Germany, 1996.

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[7] See for example: E. C. Constable, G. Zhang, C. E. Housecroft, J. A. Zampese, *CrystEngComm* 2010, **12**, 3724-3732.