Electronic Supplementary Information for Dalton Transactions
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Supplementary Information:

Characterization data of compounds

2b: Yield 53%. M. P. 96–98 ^{o}C. R (KBr): 3143, 3093, 2966, 2940, 2880, 1770, 1714, 1626, 1563, 1449, 1428, 1392, 1360, 1231, 1190, 1162, 1120, 1086, 1044, 1006, 930, 883, 841, 805, 776, 723, 676, 653, 605, 528 cm^{-1}. ^{1}H NMR (250 MHz, D_2O): δ 0.82–0.88 (t, J = 7.3 Hz, 3H, ImN-$(CH_2)_3$-CH_3), 1.09–1.24 (m, 2H, ImN-$(CH_2)_2$-CH_2-CH_3), 1.71–1.83 (m, 2H, ImN-CH_2-CH_2-CH_2-CH_3), 4.16–4.22 (m, 4H, PhtN-CH_2-CH_2-NIm and ImN-CH_2-$(CH_2)_2$-CH_3), 4.56–4.61 (t, J = 5.5 Hz, 2H, PhtN-CH_2-CH_2-NIm), 7.54–7.56 (m, 1H, 1 × C*H* arom.), 7.64–7.66 (m, 1H, 1 × C*H* arom.), 7.88 (s, 4H, 4 × C*H* arom.), 8.89 (s, 1H, 1 × C*H* arom.) ppm. ^{13}C NMR (63 MHz, D_2O): δ 12.93, 18.82, 31.53, 38.21, 48.28, 49.74, 123.14, 123.23, 123.92, 130.87, 135.48, 135.96, 169.67 ppm. ESI MS: In positive mode peaks at m/z 299.1 (21%, $[C_{17}H_{20}N_3O_2+1]^+$), 298.1 (100%, $[C_{17}H_{20}N_3O_2]^+$) a.m.u. and in negative mode m/z 78.9 (82%, $[^{79}Br]^-$) and 80.8 (100%, $[^{81}Br]^-$) a.m.u.

3b: Yield 94%. M. P.: 127–129 ^{o}C. IR (KBr): 3153, 3099, 2968, 2936, 2877, 1776, 1712, 1617, 1569, 1466, 1427, 1399, 1365, 1170, 1124, 1088, 1049, 1011, 935, 842, 756, 722, 649, 609, 558, 530 cm^{-1}. ^{1}H NMR (250 MHz, DMSO d_6): δ 0.80–0.86 (t, J = 7.4 Hz, 3H, ImN-$(CH_2)_3$-CH_3), 1.08–1.23 (m, 2H, ImN-$(CH_2)_2$-CH_2-CH_3), 1.62–1.73 (m, 2H, ImN-CH_2-CH_2-CH_2-CH_3), 3.99–4.04 (t, J = 5.3 Hz, 2H, PhtN-CH_2-CH_2-NIm), 4.08–4.14 (t, J = 6.8 Hz, 2H, ImN-CH_2-$(CH_2)_2$-CH_3), 4.40–4.45 (t, J = 5.3 Hz, 2H, PhtN-CH_2-CH_2-NIm), 7.74–7.75 (m, 1H, 1 × C*H* arom.), 7.85–7.88 (m, 5H, 5 × C*H* arom.), 9.23 (s, 1H, 1 × C*H* arom.) ppm. ^{13}C NMR (63 MHz, DMSO d_6): δ 13.18, 18.41, 31.28, 37.96, 47.99, 48.53, 122.55, 123.02, 123.14, 131.46, 134.52, 136.50, 167.56 ppm. ^{31}P NMR (101 MHz, acetone d_6): -159.95 to -117.88 ppm (septet). ^{19}F NMR (235 MHz, acetone d_6): -67.90 to -64.88 ppm (doublet). ESI MS: In positive mode peaks at m/z 299.1 (20%, $[C_{17}H_{20}N_3O_2+1]^+$), 298.1 (100%, $[C_{17}H_{20}N_3O_2]^+$) a.m.u. and in negative mode peak at m/z 144.7 (100%, $[PF_6]^-$) a.m.u.

4b: Yield 96%. IR (Neat): 3645, 3590, 3398, 3336, 3161, 3116, 2967, 2935, 2875, 1603, 1566, 1452, 1361, 1333, 1252, 1171, 1088, 1035, 833, 747, 649, 559 cm^{-1}. ^{1}H NMR (250 MHz, DMSO d_6): δ 0.88–0.94 (t, J = 7.4 Hz, 3H, ImN-$(CH_2)_3$-CH_3), 1.21–1.35 (m, 2H, ImN-$(CH_2)_2$-CH_2-CH_3), 1.73–1.93 (m, 4H (2H are D_2O exchangeable), ImN-CH_2-CH_2-CH_2-CH_3 and ImN-CH_2-CH_2-NH_2), 2.90–2.95 (t, J = 5.5 Hz, 2H, ImN-CH_2-CH_2-NH_2), 4.08–4.19 (m, 4H, ImN-CH_2-CH_2-NH_2 and ImN-CH_2-$(CH_2)_2$-CH_3), 7.71–7.73 (m, 2H, 2 × C*H* arom.), 9.10 (s, 1H, 1 × C*H* arom.) ppm. ^{13}C NMR (63 MHz, DMSO d_6): δ 13.22, 18.80, 31.32, 41.16, 48.56, 52.01, 122.09, 122.65, 136.18 ppm. ^{31}P NMR (101 MHz, DMSO d_6): -159.95 to -117.87 ppm (septet). ^{19}F NMR (235 MHz, DMSO d_6): -67.98 to -64.97 ppm (doublet). ESI MS: In positive mode peaks at m/z 169.1 (16%, $[C_9H_{18}N_3+1]^+$), 168.1 (100%, $[C_9H_{18}N_3]^+$) a.m.u. and in negative mode peak at m/z 144.7 (100%, $[PF_6]^-$) a.m.u.

5b: Yield 40%. Melting point: 68–70 ^{o}C. IR (KBr): 3159, 2981, 2936, 2874, 1746, 1720, 1557, 1467, 1371, 1333, 1288, 1229, 1154, 1072, 1035, 1002, 979, 839, 748, 656 cm^{-1}.

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^{1}H NMR (250 MHz, $CDCl_3$): δ 0.94–0.99 (t, J = 7.3 Hz, 3H, ImN-$(CH_2)_3$-CH_3), 1.26–1.44 (m, 20H, ImN-$(CH_2)_2$-CH_2-CH_3 and -N(CH_2COOC(CH_3)$_3$)$_2$), 1.84–1.96 (m, 2H, ImN-CH_2-CH_2-CH_2-CH_3), 3.09–3.13 (m, 2H, ImN-CH_2-CH_2-N(CH_2COOC(CH_3)$_3$)$_2$), 3.35 (s, 4H, ImN-CH_2-CH_2-N(CH_2COOC(CH_3)$_3$)$_2$), 4.13–4.22 (m, 4H, ImN-CH_2-CH_2-N(CH_2COOC(CH_3)$_3$)$_2$ and ImN-CH_2-$(CH_2)_2$-CH_3), 7.23–7.24 (m, 1H, 1 × CH arom.), 7.58–7.59 (m, 1H, 1 × CH arom.), 9.09 (s, 1H, 1 × CH arom.) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ 13.33, 19.40, 28.07, 31.70, 48.05, 49.76, 54.37, 56.52, 81.72, 121.15, 123.36, 136.59, 170.49 ppm. ^{31}P NMR (101 MHz, $CDCl_3$): -164.90 to -122.76 ppm (septet). ^{19}F NMR (235 MHz, $CDCl_3$): -74.85 to -71.83 ppm (doublet). ESI MS: In positive mode peaks at m/z 397.2 (24%, $[C_9H_{18}N_3+1]^+$), 396.2 (100%, $[C_9H_{18}N_3]^+$) a.m.u. and in negative mode peak at m/z 144.7 (100%, $[PF_6]^-$) a.m.u.

6b: M=Cu: ESI MS: In positive mode peaks at m/z 628.0 ($[C_{26}H_{40}N_6O_8Cu+1]^+$, ^{63}Cu), 629.1 ($[C_{26}H_{40}N_6O_8Cu+2]^+$, ^{63}Cu), 630.1 ($[C_{26}H_{40}N_6O_8Cu+1]^+$, ^{65}Cu), 631.1 ($[C_{26}H_{40}N_6O_8Cu+2]^+$, ^{65}Cu) other peak at 284.1 ($C_{13}H_{20}N_3O_4$+2) a.m.u. M=Ni: ESI MS: In positive mode peaks at m/z 623.0 ($[C_{26}H_{40}N_6O_8Ni+1]^+$, ^{58}Ni), 624.1 ($[C_{26}H_{40}N_6O_8Ni+2]^+$, ^{58}Ni), 625.0 ($[C_{26}H_{40}N_6O_8Ni+1]^+$, ^{60}Ni), 626.0 ($[C_{26}H_{40}N_6O_8Ni+2]^+$, ^{60}Ni) other peak at 284.1 ($C_{13}H_{20}N_3O_4$+2) a.m.u. M = Co: In positive mode peaks at m/z 623.1 ($[C_{26}H_{40}N_6O_8Co]^+$, ^{59}Co), 624.0 ($[C_{26}H_{40}N_6O_8Co+1]^+$, ^{59}Co), 625.0 ($[C_{26}H_{40}N_6O_8Co+2]^+$, ^{59}Co) other peak at 284.1 ($C_{13}H_{20}N_3O_4$+2) a.m.u.

11b: Yield: 84%, M. P. 129–131 ^{o}C. IR (KBr) 3162, 3130, 3051, 2954, 2928, 2871, 2856, 1779, 1766, 1712, 1610, 1565, 1463, 1433, 1413, 1387, 1348, 1311, 1284, 1254, 1237, 1191, 1171, 1140, 1108, 1090, 1073, 1041, 971 cm^{-1}. ^{1}H NMR (250 MHz, DMSO d_6): δ 0.83–0.89 (t, J = 6.8 Hz, 3H, ImN-$(CH_2)_5$-CH_3), 1.27 (bs, 6H, ImN-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3), 1.73–1.84 (m, 2H, ImN-CH_2-CH_2-$(CH_2)_3$-CH_3), 2.13–2.24 (m, 2H, ImN-CH_2-CH_2-CH_2-NPht), 3.59–3.64 (t, J = 6.4 Hz, 2H, ImN-CH_2-$(CH_2)_4$-CH_3), 4.14–4.20 (t, J = 7.3 Hz, 2H, ImN-CH_2-CH_2-CH_2-NPht), 4.22–4.28 (t, J = 7.3 Hz, 2H, ImN-CH_2-CH_2-CH_2-NPht), 7.81–7.82 (m, 2H, 2 × CH arom.), 7.83–7.91 (m, 4H, 4 × CH arom.), 9.21 (s, 1H, 1 × CH arom.) ppm. ^{13}C NMR (63 MHz, D_2O): δ 13.54, 22.07, 25.28, 28.14, 29.40, 30.61, 34.81, 47.36, 49.95, 122.52, 122.88, 123.55, 131.09, 135.15, 135.72, 170.14 ppm. ESI MS: In positive mode peaks at m/z 341.2 (20%, $[C_{20}H_{26}N_3O_2+1]^+$) and 340.2 (100%, $[C_{20}H_{26}N_3O_2]^+$) a.m.u. and in negative mode peaks at m/z 79.0 (79%, $[^{79}Br]^-$) and 80.9 (100%, $[^{81}Br]^-$) a.m.u.

12b: Yield: 95%. M. P.: 77–79 ^{o}C. IR (KBr) 3163, 3122, 2957, 2936, 2862, 1862, 1770, 1718, 1614, 1568, 1468, 1439, 1412, 1387, 1346, 1307, 1289, 1237, 1221, 1192, 1171, 1142, 1111, 1090, 1073, 1044, 970 cm^{-1}. ^{1}H NMR (250 MHz, DMSO d_6): δ 0.84–0.89 (t, J = 6.6 Hz, 3H, ImN-$(CH_2)_5$-CH_3), 1.27 (bs, 6H, ImN-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3), 1.74–1.85 (m, 2H, ImN-CH_2-CH_2-$(CH_2)_3$-CH_3), 2.14–2.25 (m, 2H, ImN-CH_2-CH_2-CH_2-NPht), 3.60–3.65 (t, J = 6.3 Hz, 2H, ImN-CH_2-$(CH_2)_4$-CH_3), 4.13–4.19 (t, J = 7.1 Hz, 2H, ImN-CH_2-CH_2-CH_2-NPht), 4.22–4.28 (t, J = 7.3 Hz, 2H, ImN-CH_2-CH_2-CH_2-NPht), 7.78–7.81 (m, 2H, 2 × CH arom.), 7.83–7.92 (m, 4H, 4 × CH arom.), 9.15 (s, 1H, 1 × CH arom.) ppm. ^{13}C NMR (63 MHz, CD_3CN): δ 14.29, 23.13, 26.41, 29.82, 30.49, 31.80, 35.32, 48.24, 50.73, 123.52, 123.58, 124.01, 133.16, 135.39, 136.57, 169.52 ppm. ^{31}P NMR (101 MHz, DMSO d_6): -159.97 to -117.87 ppm (septet). ^{19}F NMR (235 MHz,

DMSO d_6): -67.92 to -64.90 ppm (doublet). ESI MS: In positive mode peaks at m/z 341.2 (21%, $[C_{20}H_{26}N_3O_2+1]^+$) and 340.2 (100%, $[C_{20}H_{26}N_3O_2]^+$) a.m.u. and in negative mode peak at m/z 144.7 (100%, $[PF_6]^-$) a.m.u.

13b: Yield: 96%. IR (Neat): 3390, 3164, 3118, 2959, 2933, 2862, 1645, 1567, 1468, 1380, 1247, 1165, 1111, 1053, 841, 776, 740 cm^{-1}. ^1H NMR (250 MHz, DMSO d_6): δ 0.84–0.89 (t, J = 6.8 Hz, 3H, ImN-$(CH_2)_5$-CH_3), 1.27 (bs, 6H, ImN-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3), 1.75–1.93 (m, 4H, ImN-CH_2-CH_2-$(CH_2)_3$-CH_3 and ImN-CH_2-CH_2-CH_2-NH_2), 2.36 (bs, 2H, D_2O exchangeable, ImN-CH_2-CH_2-CH_2-NH_2), 2.53–2.58 (t, J = 6.6 Hz, 2H, ImN-CH_2-CH_2-CH_2-NH_2), 4.13–4.19 (t, J = 7.1 Hz, 2H, ImN-CH_2-$(CH_2)_4$-CH_3) 4.22–4.27 (t, J = 6.9 Hz, 2H, ImN-CH_2-CH_2-CH_2-NH_2), 7.76–7.77 (m, 2H, 2 × CH arom.), 9.17 (s, 1H, 1 × CH arom.) ppm. ^{13}C NMR (63 MHz, DMSO d_6): δ 13.76, 21.87, 25.15, 29.24, 30.52, 32.45, 37.75, 46.70, 48.91, 122.41, 122.50, 136.04 ppm. ^{31}P NMR (101 MHz, DMSO d_6): -159.97 to -117.87 ppm (septet). ^{19}F NMR (235 MHz, DMSO d_6): -67.96 to -64.94 ppm (doublet). ESI MS: In positive mode peaks at m/z 211.1 (14%, $[C_{12}H_{24}N_3+1]^+$) and 210.1 (100%, $[C_{12}H_{24}N_3]^+$) a.m.u. and in negative mode peak at m/z 144.7 (100%, $[PF_6]^-$) a.m.u.

14b: Yield: 49%. IR (Neat): 3156, 3117, 2976, 2934, 2872, 1731, 1595, 1566, 1458, 1394, 1369, 1225, 1160, 1082, 1034, 983, 938, 916, 839, 753, 740 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 0.84–0.90 (t, J = 6.5 Hz, 3H, ImN-$(CH_2)_5$-CH_3), 1.32 (bs, 4H, ImN-$(CH_2)_3$-CH_2-CH_2-CH_3), 1.45–1.49 (m, 20H, -N(CH_2COOC(CH_3)$_3$)$_2$ and ImN-$(CH_2)_2$-CH_2-$(CH_2)_2$-CH_3), 1.86–2.05 (m, 4H, ImN-CH_2-CH_2-$(CH_2)_3$-CH_3 and ImN-CH_2-CH_2-CH_2-N(CH_2COOC(CH_3)$_3$)$_2$), 2.69–2.74 (t, J = 6.0 Hz, 2H, ImN-CH_2-CH_2-CH_2-N(CH_2COOC(CH_3)$_3$)$_2$), 3.30 (s, 4H, ImN-CH_2-CH_2-CH_2-N(CH_2COOC(CH_3)$_3$)$_2$), 4.14–4.20 (t, J = 7.4 Hz, 2H, ImN-CH_2-$(CH_2)_4$-CH_3), 4.36–4.41 (t, J = 6.1 Hz, 2H, ImN-CH_2-CH_2-CH_2-N(CH_2COOC(CH_3)$_3$)$_2$), 7.37 (s, 1H, 1 × CH arom.), 7.48 (s, 1H, 1 × CH arom.), 8.88 (s, 1H, 1 × CH arom.) ppm. ^{13}C NMR (63 MHz, acetone d_6): δ 14.16, 22.96, 26.43, 28.16, 28.26, 30.46, 31.74, 48.30, 50.41, 51.01, 56.14, 81.29, 123.18, 123.46, 137.36, 171.12 ppm. ^{31}P NMR (101 MHz, $CDCl_3$): -164.91 to -122.76 ppm (septet). ^{19}F NMR (235 MHz, $CDCl_3$): -74.76 to -71.74 ppm (doublet). ESI MS: In positive mode peaks at m/z 439.3 (25%, $[C_{24}H_{44}N_3O_4+1]^+$) and 438.3 (100%, $[C_{24}H_{44}N_3O_4]^+$) a.m.u. and in negative mode peak at m/z 144.7 (100%, $[PF_6]^-$) a.m.u.

15b: ESI MS: In positive mode peaks at 712.3 ($[C_{32}H_{52}N_6O_8Cu+1]^+$, ^{63}Cu), 713.3 ($[C_{32}H_{52}N_6O_8Cu+2]^+$, ^{63}Cu), 714.3 ($[C_{32}H_{52}N_6O_8Cu+1]^+$, ^{65}Cu), 715.3 ($[C_{32}H_{52}N_6O_8Cu+2]^+$, ^{65}Cu).

11c: Yield: 83%. M. P.: 133–135 ^oC. IR (KBr): 3160, 3130, 3053, 2954, 2924, 2854, 1779, 1766, 1712, 1611, 1564, 1464, 1433, 1413, 1387, 1348, 1311, 1284, 1253, 1238, 1190, 1174, 1140, 1108, 1090, 1073, 1041, 971 cm^{-1}. ^1H NMR (250 MHz, DMSO d_6): δ 0.82–0.87 (t, J = 6.3 Hz, 3H, ImN-$(CH_2)_7$-CH_3), 1.25 (bs, 10H, ImN-$(CH_2)_2$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3), 1.73–1.84 (m, 2H, ImN-CH_2-CH_2-$(CH_2)_5$-CH_3), 2.13–2.24 (m, 2H, ImN-CH_2-CH_2-CH_2-NPht), 3.59–3.64 (t, J = 6.4 Hz, 2H, ImN-CH_2-$(CH_2)_6$-CH_3), 4.13–4.18 (t, J = 7.3 Hz, 2H, ImN-CH_2-CH_2-CH_2-NPht), 4.21–4.27 (t, J = 7.3 Hz, 2H, ImN-CH_2-CH_2-CH_2-NPht), 7.79–7.80 (m, 2H, 2 × CH arom.), 7.83–7.91 (m, 4H, 4 × CH

arom.), 9.18 (s, 1H, 1 × C*H* arom.) ppm. ^{13}C NMR (63 MHz, DMSO d_6): δ 13.89, 22.04, 25.45, 28.33, 28.47, 28.58, 29.34, 31.13, 34.28, 46.53, 48.79, 122.35, 122.45, 122.99, 131.62, 134.40, 136.19, 167.95 ppm. ESI MS: In positive mode peaks at m/z 369.2 (23%, $[C_{22}H_{30}N_3O_2+1]^+$) and 368.2 (100%, $[C_{22}H_{30}N_3O_2]^+$) a.m.u. and in negative mode peak at m/z 79.0 (86%, $[^{79}Br]^-$) and 80.9 (100%, $[^{81}Br]^-$) a.m.u.

12c: Yield: 94%. M. P.: 93–95 ^{o}C. IR (KBr): 3164, 3109, 2924, 2857, 1770, 1718, 1615, 1568, 1469, 1441, 1412, 1387, 1345, 1289, 1238, 1220, 1192, 1171, 1143, 1111, 1090, 1074, 1044, 971, 837 cm^{-1}. ^{1}H NMR (250 MHz, DMSO d_6): δ 0.82–0.87 (t, J = 6.5 Hz, 3H, ImN-$(CH_2)_7$-CH_3), 1.25 (bs, 10H, ImN-$(CH_2)_2$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3), 1.76–1.84 (m, 2H, ImN-CH_2-CH_2-$(CH_2)_5$-CH_3), 2.13–2.24 (m, 2H, ImN-CH_2-CH_2-CH_2-NPht), 3.60–3.65 (t, J = 6.4 Hz, 2H, ImN-CH_2-$(CH_2)_6$-CH_3), 4.13–4.18 (t, J = 7.1 Hz, 2H, ImN-CH_2-CH_2-CH_2-NPht), 4.21–4.27 (t, J = 7.3 Hz, 2H, ImN-CH_2-CH_2-CH_2-NPht), 7.79–7.80 (m, 2H, 2 × C*H* arom.), 7.83–7.91 (m, 4H, 4 × C*H* arom.), 9.16 (s, 1H, 1 × C*H* arom.) ppm. ^{13}C NMR (63 MHz, DMSO d_6): δ 13.94, 22.11, 25.51, 28.37, 28.52, 28.58, 29.33, 31.19, 34.31, 46.64, 48.91, 122.43, 122.45, 123.06, 131.75, 134.44, 136.19, 168.06 ppm. ^{31}P NMR (101 MHz, DMSO d_6): -159.97 to -117.87 ppm (septet). ^{19}F NMR (235 MHz, DMSO d_6): -67.91 to -64.89 ppm (doublet). ESI MS: In positive mode peaks at m/z 369.2 (22%, $[C_{22}H_{30}N_3O_2+1]^+$) and 368.2 (100%, $[C_{22}H_{30}N_3O_2]^+$) a.m.u. and in negative mode peak at m/z 144.7 (100%, $[PF_6]^-$) a.m.u.

13c: Yield: 95%. IR (Neat): 3390, 3164, 3118, 2929, 2858, 1646, 1567, 1468, 1366, 1247, 1165, 1111, 1063, 1022, 840, 774, 740 cm^{-1}. ^{1}H NMR (250 MHz, DMSO d_6): δ 0.83–0.88 (t, J = 6.5 Hz, 3H, ImN-$(CH_2)_7$-CH_3), 1.25 (bs, 10H, ImN-$(CH_2)_2$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3), 1.74–1.90 (m, 6H, ImN-CH_2-CH_2-$(CH_2)_5$-CH_3, ImN-CH_2-CH_2-CH_2-NH_2 and ImN-CH_2-CH_2-CH_2-NH_2, two protons D_2O exchangeable), 2.50–2.55 (t, J = 6.4 Hz, 2H, ImN-CH_2-CH_2-CH_2-NH_2), 4.12–4.18 (t, J = 7.1 Hz, 2H, ImN-CH_2-$(CH_2)_6$-CH_3), 4.20–4.26 (t, J = 7.0 Hz, 2H, ImN-CH_2-CH_2-CH_2-NH_2), 7.77–7.78 (m, 2H, 2 × C*H* arom.), 9.16 (s, 1H, 1 × C*H* arom.) ppm. ^{13}C NMR (63 MHz, DMSO d_6): δ 13.96, 22.12, 25.54, 28.36, 28.53, 29.34, 31.21, 32.76, 37.85, 46.72, 48.91, 122.43, 122.55, 136.08 ppm. ^{31}P NMR (101 MHz, DMSOd_6): -159.99 to -117.88 ppm (septet). ^{19}F NMR (235 MHz, DMSOd_6): -67.92 to -64.90 ppm (doublet). ESI MS: In positive mode peaks at m/z 239.2 (15%, $[C_{14}H_{28}N_3+1]^+$) and 238.2 (100%, $[C_{14}H_{28}N_3]^+$) a.m.u. and in negative mode peak at m/z 144.7(100%, $[PF_6]^-$) a.m.u.

14c: Yield: 55%. IR (Neat): 3160, 3117, 2931, 2859, 1733, 1566, 1458, 1394, 1369, 1225, 1159, 1083, 1033, 982, 938, 916, 841, 753, 740 cm^{-1}. ^{1}H NMR (250 MHz, CD_3CN): δ 0.84–0.89 (t, J = 6.1 Hz, 3H, ImN-$(CH_2)_7$-CH_3), 1.27–1.29 (m, 8H, ImN-$(CH_2)_3$-CH_2-CH_2-CH_2-CH_2-CH_3), 1.42–1.46 (m, 20H, -N(CH_2COOC(CH_3)$_3$)$_2$ and ImN-$(CH_2)_2$-CH_2-$(CH_2)_4$-CH_3), 1.76–1.97 (m, 4H, ImN-CH_2-CH_2-$(CH_2)_5$-CH_3 and ImN-CH_2-CH_2-CH_2-N(CH_2COOC(CH_3)$_3$)$_2$), 2.62–2.67 (t, J = 6.1 Hz, 2H, ImN-CH_2-CH_2-CH_2-N(CH_2COOC(CH_3)$_3$)$_2$), 3.27 (s, 4H, ImN-CH_2-CH_2-CH_2-N(CH_2COOC(CH_3)$_3$)$_2$), 4.06–4.12 (t, J = 7.4 Hz, 2H, ImN-CH_2-$(CH_2)_6$-CH_3), 4.23–4.28 (t, J = 6.6 Hz, 2H, ImN-CH_2-CH_2-CH_2-N(CH_2COOC(CH_3)$_3$)$_2$), 7.34–7.35 (m, 1H, 1 × C*H* arom.), 7.40–7.41 (s, 1H, 1 × C*H* arom.), 8.65 (s, 1H, 1 × C*H* arom.) ppm. ^{13}C NMR (63 MHz, CD_3CN): δ 14.41, 23.34, 26.79, 28.21, 28.41, 29.60, 29.77, 30.50, 32.46, 48.42, 50.61, 51.24, 56.50, 81.80,

123.22, 123.52, 137.14, 171.57 ppm. ^{31}P NMR (101 MHz, $CDCl_3$): -164.95 to -122.79 ppm (septet). ^{19}F NMR (235 MHz, $CDCl_3$): -74.94 to -71.91 ppm (doublet). ESI MS: In positive mode peaks at m/z 467.3 (27%, $[C_{26}H_{48}N_3O_4+1]^+$) and 466.3 (100%, $[C_{26}H_{48}N_3O_4]^+$) a.m.u. and in negative mode peak at m/z 144.7 (100%, $[PF_6]^-$) a.m.u.

15c: ESI MS: In positive mode peaks at 768.3 ($[C_{36}H_{60}N_6O_8Cu+1]^+$, ^{63}Cu), 769.3 ($[C_{36}H_{60}N_6O_8Cu+2]^+$, ^{63}Cu), 770.3 ($[C_{36}H_{60}N_6O_8Cu+1]^+$, ^{65}Cu), 771.3 ($[C_{36}H_{60}N_6O_8Cu+2]^+$, ^{65}Cu) a.m.u.

11d: Yield: 84%. M. P.: 134–136 ^{o}C. IR (KBr): 3158, 3131, 3054, 2954, 2919, 2852, 1766, 1712, 1611, 1566, 1464, 1433, 1413, 1387, 1348, 1284, 1238, 1190, 1173, 1141, 1109, 1090, 1073, 1041, 971 cm^{-1}. ^{1}H NMR (250 MHz, DMSO d_6): δ 0.81–0.86 (t, J = 6.5 Hz, 3H, ImN-$(CH_2)_9$-CH_3), 1.23 (bs, 14H, ImN-$(CH_2)_2$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3), 1.73–1.84 (m, 2H, ImN-CH_2-CH_2-$(CH_2)_7$-CH_3), 2.13–2.24 (m, 2H, ImN-CH_2-CH_2-CH_2-NPht), 3.59–3.64 (t, J = 6.4 Hz, 2H, ImN-CH_2-$(CH_2)_8$-CH_3), 4.13–4.19 (t, J = 7.0 Hz, 2H, ImN-CH_2-CH_2-CH_2-NPht), 4.22–4.28 (t, J = 7.3 Hz, 2H, ImN-CH_2-CH_2-CH_2-NPht), 7.80–7.81 (m, 2H, 2 × CH arom.), 7.83–7.91 (m, 4H, 4 × CH arom.), 9.20 (s, 1H, 1 × CH arom.) ppm. ^{13}C NMR (63 MHz, DMSO d_6): δ 13.83, 21.99, 25.39, 28.30, 28.50, 28.58, 28.74, 28.79, 29.25, 31.18, 34.24, 46.51, 48.78, 122.31, 122.40, 122.95, 131.61, 134.35, 136.15, 167.89 ppm. ESI MS: In positive mode peaks at m/z 397.1 (23%, $[C_{24}H_{34}N_3O_2+1]^+$) and 396.3 (100%, $[C_{24}H_{34}N_3O_2]^+$)a.m.u. and in negative mode peak at m/z 79.1 (86%, $[^{79}Br]^-$) and 81.0 (100%, $[^{81}Br]^-$) a.m.u.

12d: Yield: 94%. M. P.: 104–106 ^{o}C. IR (KBr): 3164, 3116, 2922, 2854, 1770, 1717, 1615, 1569, 1469, 1441, 1412, 1387, 1345, 1289, 1239, 1192, 1172, 1144, 1111, 1074, 1044, 971, 838 cm^{-1}. ^{1}H NMR (250 MHz, DMSO d_6): δ 0.82–0.87 (t, J = 6.4 Hz, 3H, ImN-$(CH_2)_9$-CH_3), 1.23 (bs, 14H, ImN-$(CH_2)_2$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3), 1.78–1.83 (m, 2H, ImN-CH_2-CH_2-$(CH_2)_7$-CH_3), 2.15–2.26 (m, 2H, ImN-CH_2-CH_2-CH_2-NPht), 3.61–3.66 (t, J = 6.4 Hz, 2H, ImN-CH_2-$(CH_2)_8$-CH_3), 4.14–4.20 (t, J = 7.1 Hz, 2H, ImN-CH_2-CH_2-CH_2-NPht), 4.23–4.29 (t, J = 7.3 Hz, 2H, ImN-CH_2-CH_2-CH_2-NPht), 7.79–7.81 (m, 2H, 2 × CH arom.), 7.84–7.91 (m, 4H, 4 × CH arom.), 9.16 (s, 1H, 1 × CH arom.) ppm. ^{13}C NMR (63 MHz, DMSO d_6): δ 13.86, 22.06, 25.45, 28.35, 28.52, 28.66, 28.79, 28.86, 29.27, 31.26, 34.26, 46.62, 48.91, 122.38, 122.41, 123.00, 131.70, 134.37, 136.15, 167.97 ppm. ^{31}P NMR (101 MHz, DMSOd_6): -160.23 to -118.14 ppm (septet). ^{19}F NMR (235 MHz, DMSOd_6): -68.24 to -65.22 ppm (doublet). ESI MS: In positive mode peaks at m/z 397.1 (24%, $[C_{24}H_{34}N_3O_2+1]^+$) and 396.3 (100%, $[C_{24}H_{34}N_3O_2]^+$) a.m.u. and in negative mode peak at m/z 144.7 (100%, $[PF_6]^-$) a.m.u.

13d: Yield: 98%. IR (Neat): 3165, 2928, 2859, 1568, 1462, 1367, 1166, 1106, 841 cm^{-1}. ^{1}H NMR (250 MHz, CD_3CN): δ 0.85–0.90 (t, J = 6.1 Hz, 3H, ImN-$(CH_2)_9$-CH_3), 1.27 (bs, 14H, ImN-$(CH_2)_2$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3), 1.77–1.96 (m, 4H, ImN-CH_2-CH_2-$(CH_2)_7$-CH_3 and ImN-CH_2-CH_2-CH_2-NH_2), 2.43 (bs, 2H, ImN-CH_2-CH_2-CH_2-NH_2), 2.72 (bs, 2H, D_2O exchangeable, ImN-CH_2-CH_2-CH_2-NH_2), 4.09–4.15 (t, J = 7.4 Hz, 2H, ImN-CH_2-$(CH_2)_8$-CH_3), 4.22–4.27 (t, J = 7.0 Hz, 2H, ImN-CH_2-CH_2-CH_2-NH_2), 7.40–7.43 (m, 2H, 2 × CH arom.), 8.53 (s, 1H, 1 × CH arom.) ppm. ^{13}C NMR (63 MHz, CD_3CN): δ 14.23, 22.41, 25.81, 28.66, 28.98, 29.13, 29.20, 29.60, 31.61, 32.79, 38.04,

46.99, 49.19, 122.73, 122.82, 136.36 ppm. ^{31}P NMR (101 MHz, DMSO d_6): -160.21 to -118.12 ppm (septet). ^{19}F NMR (235 MHz, DMSO d_6): -68.19 to -65.18 ppm (doublet). ESI MS: In positive mode peaks at m/z 267.1 (18%, $[C_{16}H_{32}N_3+1]^+$) and 266.2 (100%, $[C_{16}H_{32}N_3]^+$) a.m.u. and in negative mode peak at m/z 144.9 (100%, $[PF_6]^-$) a.m.u.

14d: Yield: 62%. IR (Neat): 3155, 3116, 2926, 2856, 1735, 1565, 1458, 1394, 1368, 1224, 1159, 1082, 983, 938, 916, 839 cm^{-1}. ^{1}H NMR (250 MHz, CD_3CN): δ 0.85–0.91 (t, J = 6.4 Hz, 3H, ImN-$(CH_2)_9$-CH_3), 1.28 (bs, 12H, ImN-$(CH_2)_3$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3), 1.44 (bs, 20H, -N(CH_2COOC(CH_3)$_3$)$_2$ and ImN-$(CH_2)_2$-CH_2-$(CH_2)_6$-CH_3), 1.82–2.00 (m, 4H, ImN-CH_2-CH_2-$(CH_2)_7$-CH_3 and ImN-CH_2-CH_2-CH_2-N(CH_2COOC(CH_3)$_3$)$_2$), 2.65–2.70 (t, J = 6.3 Hz, 2H, ImN-CH_2-CH_2-CH_2-N(CH_2COOC(CH_3)$_3$)$_2$), 3.30 (s, 4H, ImN-CH_2-CH_2-CH_2-N(CH_2COOC(CH_3)$_3$)$_2$), 4.09–4.15 (t, J = 7.4 Hz, 2H, ImN-CH_2-$(CH_2)_8$-CH_3), 4.25–4.31 (t, J = 6.5 Hz, 2H, ImN-CH_2-CH_2-CH_2-N(CH_2COOC(CH_3)$_3$)$_2$), 7.37–7.38 (m, 1H, 1 × CH arom.), 7.43–7.44 (m, 1H, 1 × CH arom.), 8.69 (s, 1H, 1 × CH arom.) ppm. ^{13}C NMR (63 MHz, CD_3CN): δ 14.50, 23.42, 26.80, 28.17, 28.44, 29.65, 30.03, 30.12, 30.23, 30.51, 32.65, 48.40, 50.60, 51.27, 56.47, 81.83, 123.22, 123.51, 137.14, 171.48 ppm. ^{31}P NMR (101 MHz, $CDCl_3$): -164.86 to -122.72 ppm (septet). ^{19}F NMR (235 MHz, $CDCl_3$): -74.61 to -71.59 ppm (doublet). ESI MS: In positive mode peaks at m/z 495.3 (25%, $[C_{28}H_{52}N_3O_4+1]^+$) and 494.5 (25%, $[C_{28}H_{52}N_3O_4]^+$) a.m.u. and in negative mode peak at m/z 144.7 (100%, $[PF_6]^-$) a.m.u.

15d: ESI MS: For copper complex: In positive mode peaks at 824.4 ($[C_{40}H_{68}N_6O_8Cu+1]^+$, ^{63}Cu), 825.4 ($[C_{40}H_{68}N_6O_8Cu+2]^+$, ^{63}Cu), 826.4 ($[C_{40}H_{68}N_6O_8Cu+1]^+$, ^{65}Cu), 827.4 ($[C_{40}H_{68}N_6O_8Cu+2]^+$, ^{65}Cu) a.m.u. For nickel complex: In positive mode peaks at 819.5 ($[C_{40}H_{68}N_6O_8Ni+1]^+$, ^{58}Ni), 820.4 ($[C_{40}H_{68}N_6O_8Ni+2]^+$, ^{58}Ni), 821.4 ($[C_{40}H_{68}N_6O_8Ni+1]^+$, ^{60}Ni), 822.4 ($[C_{40}H_{68}N_6O_8Ni+2]^+$, ^{60}Ni) a.m.u. For the cobalt complex: In positive mode peaks at 819.7 ($[C_{40}H_{68}N_6O_8Co]^+$, ^{59}Co), 820.5 ($[C_{40}H_{68}N_6O_8Co+1]^+$, ^{59}Co), 821.4 ($[C_{40}H_{68}N_6O_8Co+2]^+$, ^{59}Co) a.m.u.

Supplementary information on ICP-MS

Reagents

Ultra pure water with the sensitivity of 18MΩ was used during all stages of the complex formation and workup procedures. The ultra pure water was obtained by reverse osmosis (Milli-RO 12 Plus, Millipore water purification system) followed by water deionization (Sybron/Barnstead filtration unit). All the solutions aspirated in the torch were 1% (v/v) with respect to trace metal grade HNO_3. Trifluoroacetic acid, CF_3COOH (reagent plus, Aldrich Chemical Company) had purity of 99%. Dichloromethane, CH_2Cl_2 (HPLC grade, Caledon Laboratories) had 99.8% purity, Copper(II) chloride dihydrate, $CuCl_2.2H_2O$ (ACS reagent, Sigma-Aldrich Chemical Company) had 99% purity, 1-butanol (Caledon Laboratories) had 99.6% purity and NH_3 (28% aq. solution, reagent grade, Caledon Laboratories) was used for the preparation of 10% solution.

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Instrumentation

The Thermoelemental VG PQ ExCell (Thermo Electron) ICP-MS was used for the Cu analysis. Samples were weighted using a TR-104 Balance (Denver Instrument Company), with readability 0.1 mg, maximum weighing capacity 110 g, linearity 0.2 mg and repeatability ±0.1 mg. The glassware used for the ICP-MS analysis was pre-rinsed three times with 10% HNO_3 (trace metal grade, Fischer Scientific) followed by rinsing with ultra pure water and the sample vials were pre-rinsed with the respective sample solutions.

ICP-MS Acquisition Parameters

Instrument detector	Simultaneous
Dynamic range of Cu	0.3-200 ppb
Acquisition mode	Continuous peak jump
Number of sweeps	100
Dwell time	30 ns
Channels per mass	1
Acquisition duration	13.00 s
Channel spacing	0.02 a.m.u.
Main scan region	^{63}Cu (62.92 a.m.u.)

Preparation of the stock solutions

A 1% trace metal grade aq. HNO_3 solution was prepared by diluting 14.93 cm^3 of 67% HNO_3 to 1000 cm^3 using ultra pure water. A 2500 ppm solution of Cu(II) was prepared by dissolving 1.6767 g of $CuCl_2.2H_2O$ in 250 cm^3 of 1% solution of trace metal grade HNO_3, from which a 250 ppm solution of Cu(II) was prepared by diluting 25 cm^3 to 250 cm^3 with 1% HNO_3 solution. A 10% solution of aq. NH_3 was prepared by diluting 35.71 cm^3 of 28% aq. NH_3 solution to 100 cm^3 using ultra pure water.

Preparation of the sample solutions

The ligand dieters were prepared and characterized by the method documented earlier. The deprotection of the diesters was achieved by using trifluoroacetic acid in dichloromethane. To a suitable amount of diester (2.2 equiv.), in a round bottom flask, was added dichloromethane and trifluoroacetic acid (220 equiv.) such that the dichloromethane solution is 50% (v/v) with respect to trifluoroacetic acid and the resulting mixture was stirred at room temperature for 24 h. The contents of the reaction mixture were then evaporated at the reduced pressure to get rid of dichloromethane and excess trifluoroacetic acid. To this was added the 250 ppm solution of Cu(II) (1 equiv.) and the resulting solution was stirred well for 5 min to assure homogeneity. To this was added a 10% solution of ammonia (374 equiv.) and the resulting reaction mixture was stirred again for 5 min. The concentrations of the solutions are such that for any sample preparation, upon combination of Cu (II) solution with the ligand solution and subsequent treatment with 10% ammonia, a solution which is 200 ppm with respect to Cu(II) was

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generated. 1-Butanol was added to the solution of the complex and the mixture was stirred vigorously for 5 min. The volume of 1-butanol is exactly equal to the net volume of the solution. Finally, the contents are transferred to the separating funnel and the extraction was repeated. After the separation of the two layers, the appropriate quantity of aqueous solution was carefully transferred (using pipette) to a volumetric flask (100 cm^3), treated with appropriate quantity of 67% HNO_3 solution (374 equiv.) and finally diluted to 100 cm^3 using 1% HNO_3. The precise quantities of all the reagents and solutions for each sample preparation are shown below:

Sample C_n / Reagents/solutions	Sample C_4	Sample C_6	Sample C_8	Sample C_{10}
Amount of diester ligand	0.1513 g	0.0531 g	0.0744 g	0.0829 g
Amount/volume of CF_3COOH	3.108 g 2.10 cm^3	1.038 g 0.70 cm^3	1.388 g 0.94 cm^3	1.479 g 1.00 cm^3
Amount/volume of CH_2Cl_2	2.10 cm^3	0.70 cm^3	0.94 cm^3	1.00 cm^3
Volume of 250 ppm Cu (II) solution	31.50 cm^3	10.52 cm^3	14.07 cm^3	14.99 cm^3
Volume of 10% NH_3 solution	7.88 cm^3	2.63 cm^3	3.52 cm^3	3.75 cm^3
Volume of 1-butanol	39.38 cm^3	13.15 cm^3	17.59 cm^3	18.74 cm^3
Volume of aqueous Cu(II) solution transferred using pipette	35.0 cm^3	11.5 cm^3	15.5 cm^3	14.0 cm^3
Volume of 67% HNO_3 added	4.36 cm^3	1.45 cm^3	1.95 cm^3	2.07 cm^3
Final volume of the sample solution	100 cm^3	100 cm^3	100 cm^3	100 cm^3
Expected maximum concentration of Cu(II) assuming zero extraction	70 ppm	23 ppm	31 ppm	28 ppm

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efficiency

Preparation of the blank solutions for samples

The deprotection of the diesters was achieved by using trifluoroacetic acid in dichloromethane. To a suitable amount of diester (2.2 equiv.), in the round bottom flask, was added dichloromethane and trifluoroacetic acid (220 equiv.) such that the dichloromethane solution is 50% (v/v) with respect to trifluoroacetic acid and the resulting mixture was stirred at room temperature for 24 h. The contents of the reaction mixture were then evaporated at the reduced pressure to get rid of dichloromethane and excess trifluoroacetic acid. To this was added a solution of 1% HNO_3 (volume equivalent to the volume of 250 ppm Cu(II) solution added for the sample solution preparation) and the resulting solution was stirred well for 5 min to assure homogeneity. To this was added a 10% solution of ammonia (374 equiv.) and the resulting reaction mixture was stirred again for 5 min. 1-Butanol was added to the solution of the complex and the mixture was stirred vigorously for 5 min. The volume of 1-butanol is exactly equal to the net volume of the solution. Finally, the contents were transferred to the separating funnel and the extraction is repeated. After the separation of the two layers, the appropriate quantity of aqueous solution was carefully transferred (using pipette) to a volumetric flask (100 cm^3), treated with appropriate quantity of 67% HNO_3 solution (374 equiv.) and finally diluted to 100 cm^3 using 1% HNO_3. The precise quantities of all the reagents and solutions for each sample preparation are shown below:

Blank for the sample C_n / Reagents/solutions	Blank C_4	Blank C_6	Blank C_8	Blank C_{10}
Amount of diester ligand	0.1513 g	0.0531 g	0.0744 g	0.0829 g
Amount/volume of CF_3COOH	3.108 g 2.10 cm^3	1.038 g 0.70 cm^3	1.388 g 0.94 cm^3	1.479 g 1.00 cm^3
Amount/volume of CH_2Cl_2	2.10 cm^3	0.70 cm^3	0.94 cm^3	1.00 cm^3
Volume of 1% HNO_3 solution	31.50 cm^3	10.52 cm^3	14.07 cm^3	14.99 cm^3
Volume of 10% NH_3 solution	7.88 cm^3	2.63 cm^3	3.52 cm^3	3.75 cm^3
Volume of 1-butanol	39.38 cm^3	13.15 cm^3	17.59 cm^3	18.74 cm^3

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Volume of solution transferred	35.0 cm^3	11.5 cm^3	15.5 cm^3	14.0 cm^3
Volume of 67% HNO_3 added	4.36 cm^3	1.45 cm^3	1.95 cm^3	2.07 cm^3
Final volume of the sample solution	100 cm^3	100 cm^3	100 cm^3	100 cm^3

Preparation of the Cu (II) control solutions

To an appropriate volume of 250 ppm Cu(II) solution (1 equiv.) (exactly the same volume that has been used for the preparation of the respective sample) was added a 10% solution of ammonia (374 equiv.) and the resulting reaction mixture was stirred for 5 min. 1-Butanol was added to the solution of the complex and the mixture was stirred vigorously for 5 min. The volume of 1-butanol is exactly equal to the net volume of the solution. Finally, the contents are transferred to the separating funnel and the extraction was repeated. After the separation of the two layers, the appropriate quantity of aqueous solution was carefully transferred (using pipette) to a volumetric flask (100 cm^3), treated with appropriate quantity of 67% HNO_3 solution (374 equiv.) and finally diluted to 100 cm^3 using 1% HNO_3. The precise quantities of all the reagents and solutions for each preparation of control solution are shown below:

Control C_n / Reagents/solutions	Control C_4	Control C_6	Control C_8	Control C_{10}
Volume of 250 ppm Cu (II) solution	31.50 cm^3	10.52 cm^3	14.07 cm^3	14.99 cm^3
Volume of 10% NH_3 solution	7.88 cm^3	2.63 cm^3	3.52 cm^3	3.75 cm^3
Volume of 1-butanol	39.38 cm^3	13.15 cm^3	17.59 cm^3	18.74 cm^3
Volume of aqueous Cu(II) solution transferred	35.0 cm^3	11.5 cm^3	15.5 cm^3	14.0 cm^3
Volume of 67% HNO_3 added	4.36 cm^3	1.45 cm^3	1.95 cm^3	2.07 cm^3
Final volume of the	100 cm^3	100 cm^3	100 cm^3	100 cm^3

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sample solution

Preparation of the blanks for Cu (II) control solutions

To an appropriate volume of 1% HNO_3 (exactly the same volume that corresponds to the volume of 250 ppm solution of Cu(II) used for the preparation of the individual control and sample solutions) was added a 10% solution of ammonia (exactly the same volume that corresponds to the preparation of the individual control and sample solutions, 374 equiv.) and the resulting reaction mixture was stirred for 5 min. 1-Butanol was added to the solution and the mixture was stirred vigorously for 5 min. The volume of 1-butanol is exactly equal to the net volume of the resulting aqueous solution. Finally, the contents were transferred to the separating funnel and the extraction was repeated. After the separation of two layers, the appropriate quantity of aqueous solution was carefully transferred (using pipette) to a volumetric flask (100 cm^3), treated with appropriate quantity of 67% HNO_3 solution (374 equiv.) and finally diluted to 100 cm^3 using 1% HNO_3. The precise quantities of all the reagents and solutions for each blank solution preparation are shown below:

Blank for the Control C_n / Reagents/solutions	Control C_4	Control C_6	Control C_8	Control C_{10}
Volume of 1% HNO_3	31.50 cm^3	10.52 cm^3	14.07 cm^3	14.99 cm^3
Volume of 10% NH_3 solution	7.88 cm^3	2.63 cm^3	3.52 cm^3	3.75 cm^3
Volume of 1-butanol	39.38 cm^3	13.15 cm^3	17.59 cm^3	18.74 cm^3
Volume of solution transferred	35.0 cm^3	11.5 cm^3	15.5 cm^3	14.0 cm^3
Volume of 67% HNO_3 added	4.36 cm^3	1.45 cm^3	1.95 cm^3	2.07 cm^3
Final volume of the sample solution	100 cm^3	100 cm^3	100 cm^3	100 cm^3

ICP-MS analysis

^{63}Cu isotope was used for the analysis as it offers the advantage of good natural abundance (69.0900%) and was also found to be free from the interferences offered by the polyatomic ions under the conditions of analysis.

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ICP-MS optimization

The ICP-MS was tuned and optimized for maximum sensitivity and stability with a ^{115}In solution which has the concentration of 1 μg dm^{-3}. The short term stability test was performed to ensure that the ICP-MS measurements were repeatable on a short tem basis. The test used the standard solution containing 1 μg dm^{-3} each of ^{7}Li, ^{9}Be, ^{59}Co, ^{60}Ni, ^{115}In, ^{138}Ba, ^{156}Ce, ^{209}Bi and ^{238}U. Each respective standard was acquired ten times for the duration of one min per acquisition; hence each test lasted for 10 min. The percentage relative standard deviation (%RSD) for the multielemental standard in the range between ^{7}Li and ^{238}U was acceptable at less than 2% RSD. The tuning parameters were optimized to maintain the ratio of Ba^{2+}/Ba^{+} and CeO^{+}/Ce^{+} to less than 5%.

Calibration

The 0.3, 0.5, 1.0, 5.0, 10.0, 50.0, 100, 200 ppb solutions that were required for the preparation of calibration curve were prepared by appropriate dilution of the 250 ppm Cu(II) solution. As the ICP-MS analysis was run over a period of time on different days, a calibration curve of Cu(II) standards was generated on every occasion. Each calibration curve was generated from Cu(II) standards having the concentrations: 0.3, 0.5, 1.0, 5.0, 10.0, 50.0, 100, 200 ppb. A typical equation for the curve is given by: signal intensity = 13312 [Cu] + 28944. The calibration curve was forced through the blank. The ICP-MS software (PlasmaLab) automatically calculated the concentration of all samples using the calibration curve equation, taking in to account any dilutions that may have been performed. The limit of detection (LOD) for Cu(II) was determined to be 0.004 ppt and the limit of quantification (LOQ) is 0.012 ppt.

Sample Analysis

The sample and control solutions being highly concentrated were diluted 560 times before using them for the analysis. Triplicate measurements were obtained for each sample and control and the average value was accepted. The signal intensities were measured against the respective blanks in all the cases. The validity of the calibration curve was verified by analysis of a 50 ppb standard after each sample and control solution. The dilution and the blank corrected concentration of Cu(II) in the different sample and control solutions are indicated below:

C_n	Concentration of Cu(II) in sample solution (*a*)	Concentration of Cu(II) in control solution (*b*)	Expected maximum concentration of Cu(II) assuming zero extraction efficiency (*c*)	K_n (*a*/*b*)
C_4	69 ppm	70 ppm	70 ppm	0.986

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C_6	15 ppm	23 ppm	23 ppm	0.652
C_8	6 ppm	31 ppm	31 ppm	0.194
C_{10}	2 ppm	28 ppm	28 ppm	0.071

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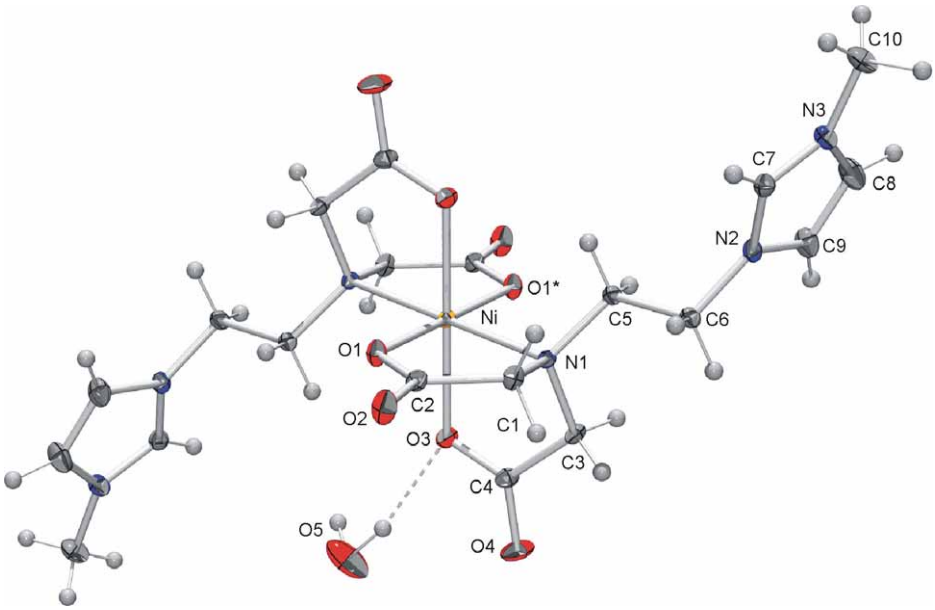

Ortep representation of the compound 6a – Ni Complex.

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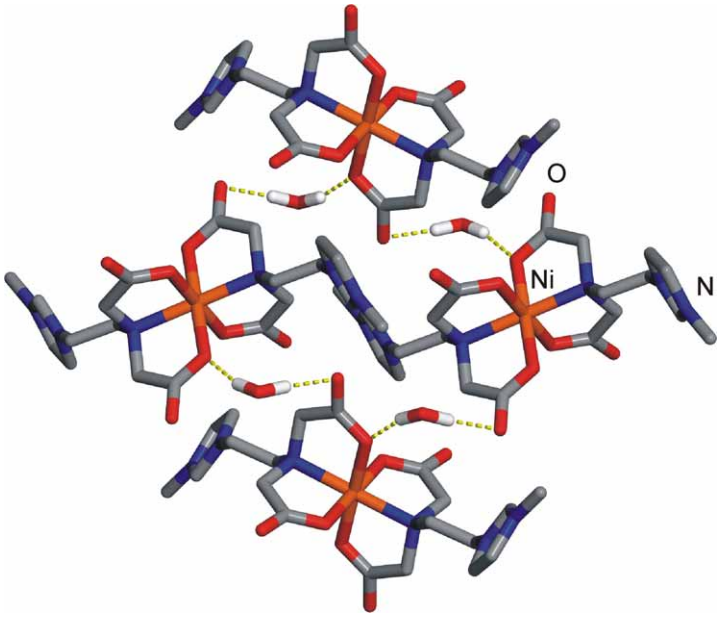

A wireframe representation of a hydrogen-bonded eight-membered ring in the crystal structure of the compound 6a – Ni Complex.

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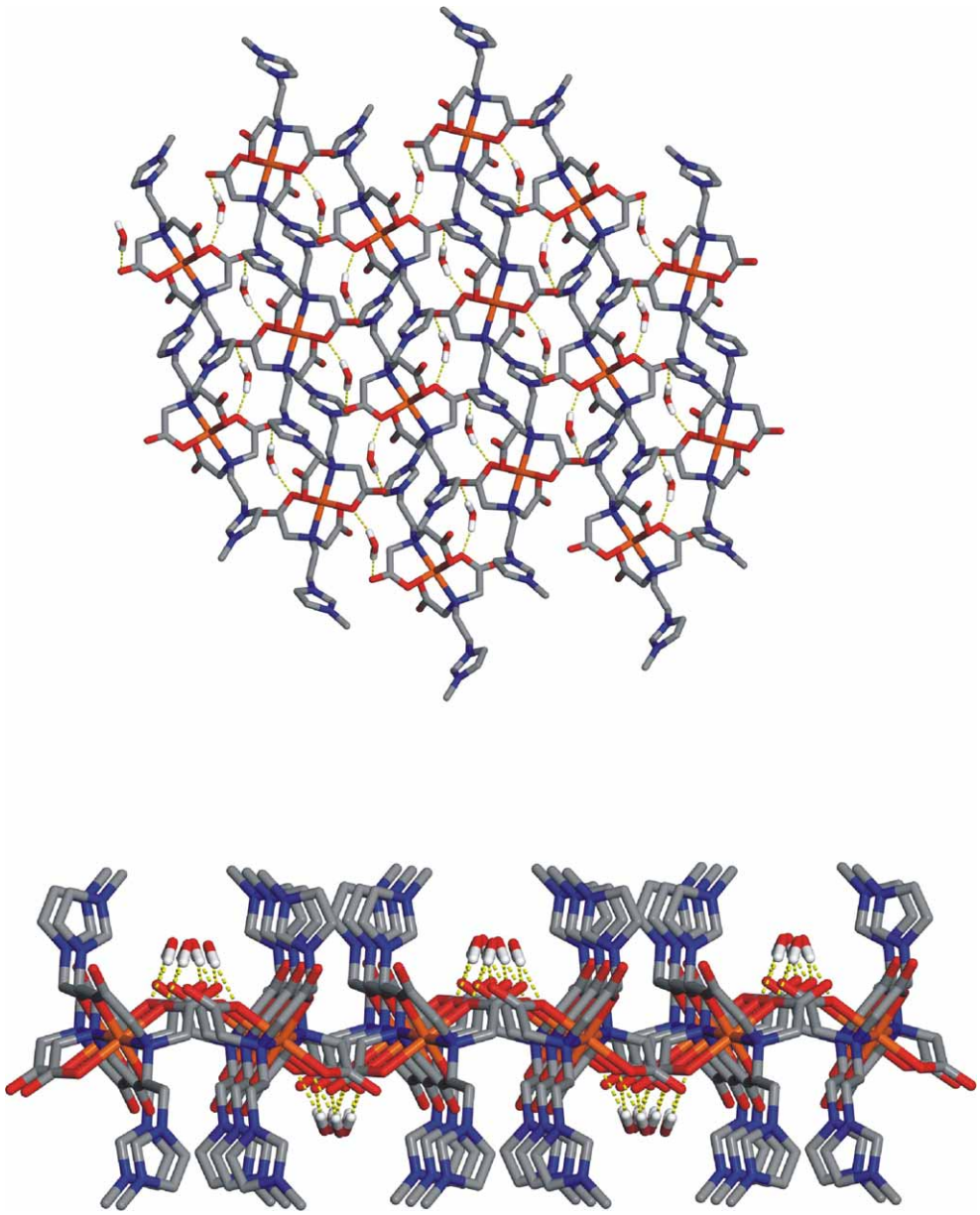

A wireframe representation of a hydrogen-bonded molecular layer in the crystal structure of the compound 6a – Ni Complex.

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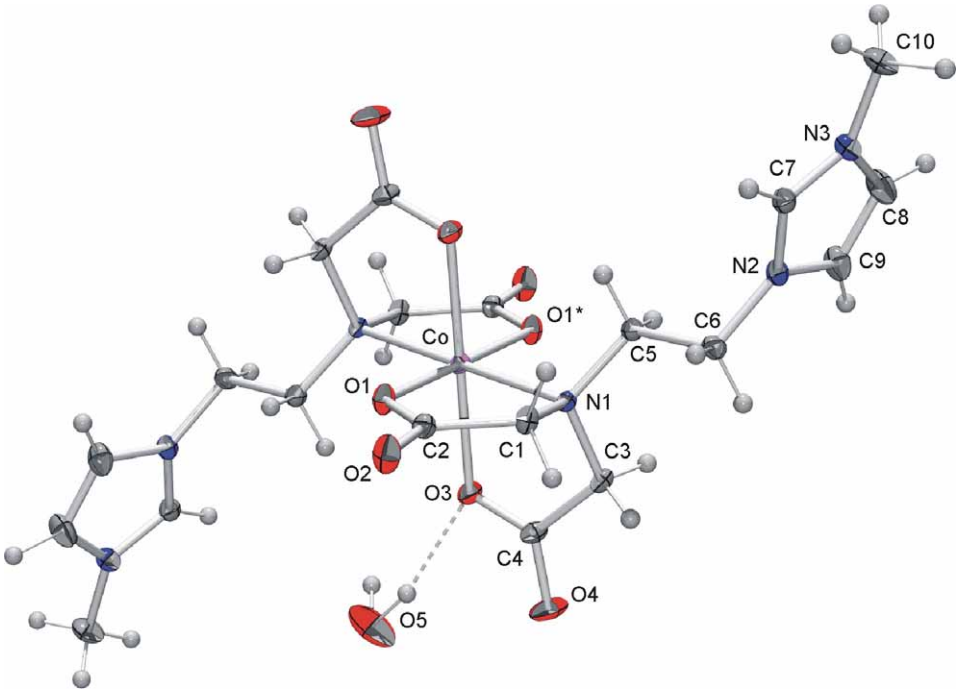
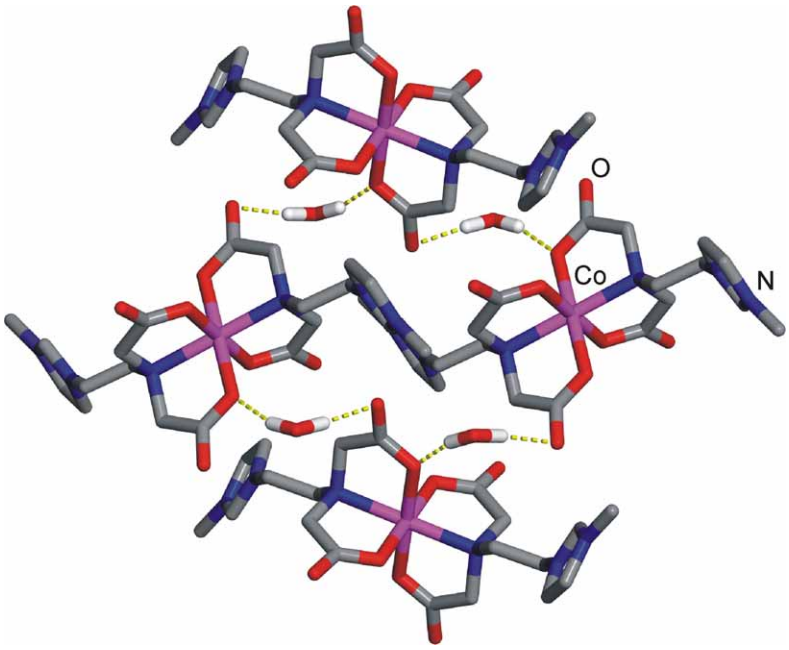


Ortep representation of the compound 6a – Co Complex.



A wireframe representation of a hydrogen-bonded eight-membered ring in the crystal structure of the compound 6a – Co Complex.

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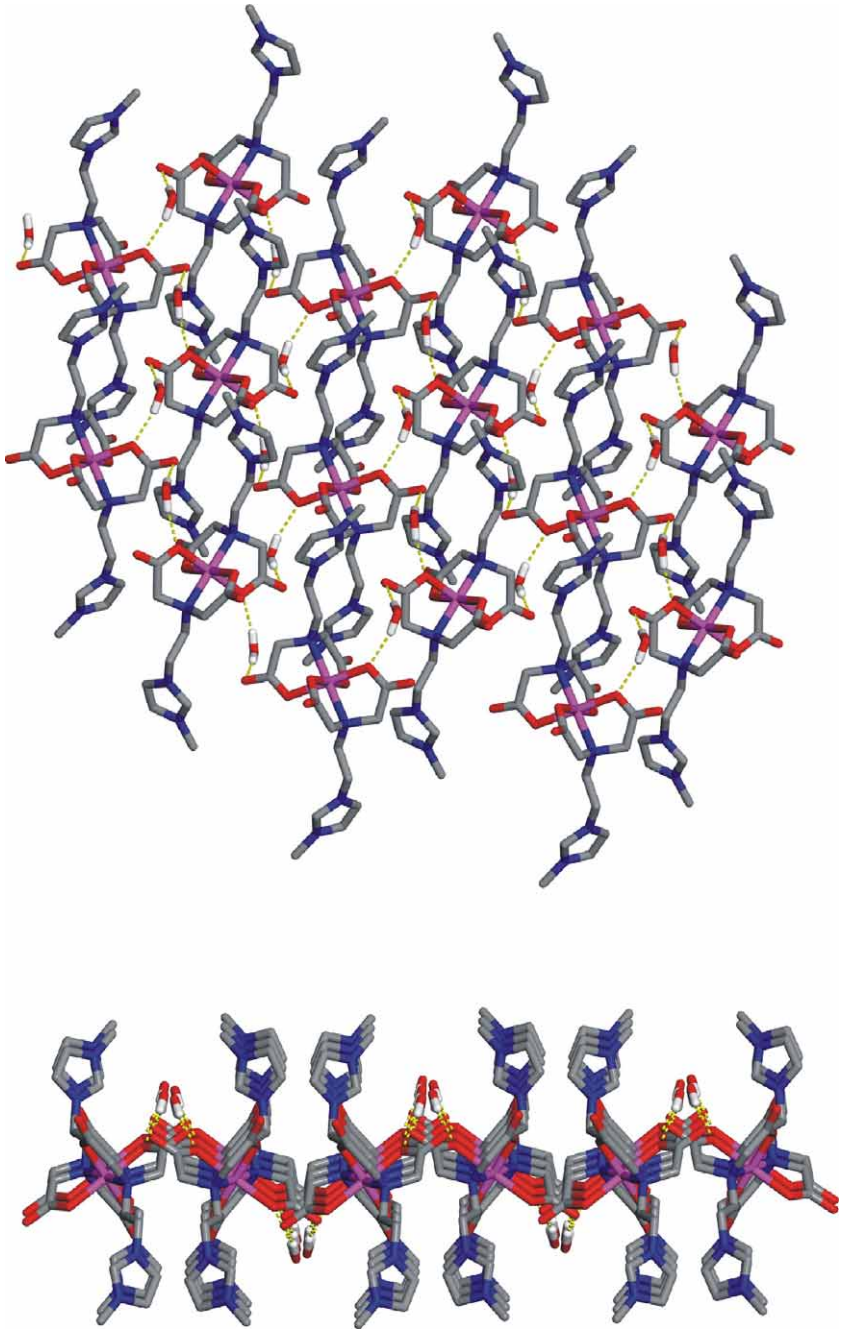

A wireframe representation of a hydrogen-bonded molecular layer in the crystal structure of the compound 6a – Co Complex.