Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information for the manuscript: Cobalt(II) containing liquid metal salts for electrodeposition of cobalt and electrochemical nanoparticle formation

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1 Synthesis

1.1 $Co(Tf_2N)_2 \cdot 6H_2O$

A solution of cobalt(II) carbonate (2.737 g, 23.01 mmol) and hydrogen bistriflimide (80 wt% aqueous solution) (12.50 g, 35.57 mmol) in H_2O (50 mL) was stirred at room temperature until the pH was neutral. CO_2 was released during the reaction. The remaining solids were filtered off and the excess of solvent was removed on a rotary evaporator after which the product was dried overnight at 50 °C on a vacuum line to yield $[Co(H_2O)_6][Tf_2N]_2$ as a pink crystalline solid (yield 13.05 g; 78 %). FTIR (ATR, ν_{max}/cm^{-1}): 3492 (H_2O), 1636, 1348 (SO_2), 1312 (SO_2), 1196 (CF_3), 1129 (SO_2), 1038 (SNS), 799 (CS), 770 (SNS), 746 (CF_3), 614 (SO_2), 570 (CF_3), 511 (CF_3). CHN found (calculated for $C_4H_{12}CoF_{12}N_2O_{14}S_4$): C 6.64 (6.61) %, H 1.89 (1.66) %, N 3.76 (3.85) %.

1.2 $[Co(MeIm)_6][Tf_2N]_2$

A solution of $Co(Tf_2N)_2 \cdot 6H_2O$ (1.00 g, 1.38 mmol) and *N*-methylimidazole (0.68 g, 8.32 mmol) in ethanol (25 mL) was stirred for 5 min at room temperature. The excess of ethanol was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a pale pink solid product (yield 1.46 g; 95 %). Melting point: 137 °C. FTIR (ATR, ν_{max}/cm^{-1}): 3140 (CH), 2968 (CH), 1532 (ring), 1519 (ring), 1425 (ring), 1349 (SO_2), 1332 (ring), 1287 (CH), 1174 (CF_3), 1139 (SO_2), 1107 (ring), 1088 (CH), 1052 (SNS), 937 (ring), 830 (CH), 791 (CS), 755 (CH), 744 (CF_3), 662 (ring), 609 (ring), 569 (CF_3), 513 (CF_3), 409 (SO_2). CHN found (calculated for $C_{28}H_{36}CoF_{12}N_{14}O_8S_4$): C 30.28 (30.25) %, H 3.43 (3.26) %, N 17.40 (17.64) %.

1.3 $[Co(EtIm)_6][Tf_2N]_2$

A solution of $Co(Tf_2N)_2 \cdot 6H_2O$ (1.00 g, 1.38 mmol) and *N*-ethylimidazole (0.80 g, 8.32 mmol) in ethanol (25 mL) was stirred for 5 min at room temperature. The excess of ethanol was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a pale pink solid product (yield 1.68 g; 99 %). Melting point: 83 °C. FTIR (ATR, ν_{max}/cm^{-1}): 3139 (CH), 2984 (CH), 1522 (ring), 1470 (ring), 1457 (ring), 1405 (ring), 1345 (SO_2), 1321 (ring), 1289 (CH), 1232 (CF_3), 1144 (SO_2), 1132 (SO_2), 1113 (ring), 1093 (CH), 1059 (SNS), 1034, 964, 933 (ring), 843 (CH), 788 (CS), 761, 752 (CH), 741 (CF_3), 665 (ring), 651 (ring), 620 (ring), 597, 570 (CF_3), 529 (CF_3), 505 (CF_3), 443 (CF_3). CHN found (calculated for $C_{34}H_{52}CoF_{12}N_{14}O_{10}S_4$): C 33.11 (33.15) %, H 4.45 (4.25) %, N 15.99 (15.92) %.

1.4 $[Co(PrIm)_6][Tf_2N]_2$

A solution of $Co(Tf_2N)_2 \cdot 6H_2O$ (1.00 g, 1.38 mmol) and *N*-propylimidazole (0.92 g, 8.32 mmol) in ethanol (25 mL) was stirred for 5 min at room temperature. The excess of ethanol was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a pale pink solid product (yield 1.73 g; 98 %). Melting point: 32 °C. FTIR (ATR, ν_{max}/cm^{-1}): 3136 (CH), 2970 (CH), 2942 (CH), 2883 (CH), 1525 (ring), 1514 (ring), 1460 (ring), 1405 (ring), 1341 (SO_2), 1330 (ring), 1283 (CH), 1229 (CF_3), 1180 (CF_3), 1133 (SO_2), 1105 (ring), 1087 (CH), 1060 (SNS), 937 (ring), 901, 855, 844 (CH), 826, 788 (CS), 760 (CH), 739 (CF_3), 665 (ring), 652 (ring), 633 (ring), 596, 569 (CF_3), 505 (CF_3), 438, 405 (SO_2). CHN found (calculated for $C_{40}H_{60}CoF_{12}N_{14}O_8S_4$): C 37.32 (37.53) %, H 3.64 (3.91) %, N 15.23 (15.32) %.

1.5 $[Co(BuIm)_6][Tf_2N]_2$

A solution of $Co(Tf_2N)_2{\cdot}6H_2O$ (1.00 g, 1.38 mmol) and *N*-butylimidazole (1.04 g, 8.32 mmol) in ethanol (25 mL) was stirred for 5 min at room temperature. The excess of ethanol was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a pale pink solid product (yield 99 %). Melting point: 60 °C. FTIR (ATR, ν_{max}/cm^{-1}): 3132 (CH), 2964 (CH), 2937 (CH), 2879 (CH), 1516 (ring), 1464 (ring), 1349 (SO_2), 1333 (ring), 1280 (CH), 1226 (CF_3), 1189 (CF_3), 1139 (SO_2), 1108 (ring), 1093 (CH), 1051 (SNS), 1034 (SNS), 937 (ring), 830 (CH), 792 (CS), 762 (CH), 736 (CF_3), 664 (ring), 609, 569 (CF_3), 513 (CF_3), 409 (SO_2). CHN found (calculated for $C_{46}H_{72}CoF_{12}N_{14}O_8S_4$): C 40.26 (40.50) %, H 5.13 (5.32) %, N 14.29 (14.37) %.

1.6 $[Co(PeIm)_6][Tf_2N]_2$

A solution of $Co(Tf_2N)_2{\cdot}6H_2O$ (1.00 g, 1.38 mmol) and *N*-pentylimidazole (1.2 g, 8.32 mmol) in ethanol (25 mL) was stirred for 5 min at room temperature. The excess of ethanol was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a pale pink solid product (yield 1.93 g; 97 %). Melting point: 56 °C. FTIR (ATR, ν_{max}/cm^{-1}): 3133 (CH), 2957 (CH), 2935 (CH), 2867 (CH), 1524 (ring), 1469 (ring), 1351 (SO_2), 1338 (ring), 1286 (CH), 1226 (CF_3), 1193 (CF_3), 1180 (CF_3), 1140 (SO_2), 1107 (ring), 1086 (CH), 1054 (SNS), 936 (ring), 834 (CH), 793 (CS), 764 (CH), 733 (CF_3), 664 (ring), 615, 568 (CF_3), 513 (CF_3), 408 (SO_2). CHN found (calculated for $C_{52}H_{84}CoF_{12}N_{14}O_8S_4$): C 43.19 (43.12) %, H 5.16 (5.35) %, N 13.54 (13.54) %.

1.7 $[Co(HeIm)_6][Tf_2N]_2$

A solution of $Co(Tf_2N)_2{\cdot}6H_2O$ (1.00 g, 1.38 mmol) and *N*-hexylimidazole (1.27 g, 8.32 mmol) in ethanol (25 mL) was stirred for 5 min at room temperature. The excess of ethanol was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a pink undercooled liquid (yield 2.09 g; 99 %). Melting point: 27 °C. FTIR (ATR, ν_{max}/cm^{-1}): 3133 (CH), 2957 (CH), 2932 (CH), 2861 (CH), 1516 (ring), 1457 (ring), 1350 (SO_2), 1333 (ring), 1284 (CH), 1229 (CF_3), 1180 (CF_3), 1134 (SO_2), 1108 (ring), 1088 (CH), 1056 (SNS), 937 (ring), 827 (CH), 787 (CS), 738 (CF_3), 664 (ring), 615, 600, 569 (CF_3), 511 (CF_3), 406 (SO_2). CHN found (calculated for $C_{58}H_{96}CoF_{12}N_{14}O_8S_4$): C 45.44 (45.45) %, H 5.66 (5.93) %, N 12.95 (12.79) %.

1.8 $[Co(HpIm)_6][Tf_2N]_2$

A solution of $Co(Tf_2N)_2{\cdot}6H_2O$ (1.00 g, 1.38 mmol) and *N*-heptylimidazole (1.39 g, 8.32 mmol) in ethanol (25 mL) was stirred for 5 min at room temperature. The excess of ethanol was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a pink undercooled liquid (yield 2.23 g; 100 %). Melting point: 26 °C. FTIR (ATR, ν_{max}/cm^{-1}): 3133 (CH), 2929 (CH), 2859 (CH), 1516 (ring), 1458 (ring), 1350 (SO_2), 1333 (ring), 1289 (CH), 1228 (CF_3), 1182 (CF_3), 1137 (SO_2), 1107 (ring), 1088 (CH), 1057 (SNS), 937 (ring), 827 (CH), 787 (CS), 739 (CF_3), 665 (ring), 615, 600, 570 (CF_3), 512 (CF_3). CHN found (calculated for $C_{64}H_{108}CoF_{12}N_{14}O_8S_4$): C 47.75 (47.54) %, H 6.78 (6.73) %, N 12.31 (12.13) %.

1.9 $[Co(OcIm)_6][Tf_2N]_2$

A solution of $Co(Tf_2N)_2{\cdot}6H_2O$ (1.00 g, 1.38 mmol) and *N*-octylimidazole (1.50 g, 8.32 mmol) in ethanol (25 mL) was stirred for 5 min at room temperature. The excess of ethanol was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a pink undercooled liquid (yield 2.32 g; 99 %). Melting point: 23 °C. FTIR (ATR, ν_{max}/cm^{-1}): 3134 (CH), 2928 (CH), 2858 (CH), 1588 (ring), 1516

(ring), 1458 (ring), 1350 (SO_2), 1333 (ring), 1285 (CH), 1228 (CF_3), 1181 (CF_3), 1137 (SO_2), 1108 (ring), 1088 (CH), 1056 (SNS), 937 (ring), 828 (CH), 786 (CS), 761, 739 (CF_3), 665 (ring), 615, 600, 570 (CF_3), 511 (CF_3). CHN found (calculated for $C_{70}H_{120}CoF_{12}N_{14}O_8S_4$): C 49.71 (49.73) %, H 7.58 (7.31) %, N 11.74 (11.53) %.

1.10 $[Co(NoIm)_6][Tf_2N]_2$

A solution of $Co(Tf_2N)_2{\cdot}6H_2O$ (1.00 g, 1.38 mmol) and *N*-nonylimidazole (1.61 g, 8.32 mmol) in ethanol (25 mL) was stirred for 5 min at room temperature. The excess of ethanol was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a pale pink solid product (yield 2.44 g; 99 %). Melting point: 29 °C. FTIR (ATR, ν_{max}/cm^{-1}): 3132 (CH), 2957 (CH), 2925 (CH), 2856 (CH), 1514 (ring), 1457 (ring), 1350 (SO_2), 1333 (ring), 1286 (CH), 1230 (CF_3), 1187 (CF_3), 1140 (SO_2), 1108 (ring), 1090 (CH), 1054 (SNS), 938 (ring), 830 (CH), 788 (CS), 762, 738 (CF_3), 665 (ring), 614, 569 (CF_3), 513 (CF_3), 408 (SO_2). CHN found (calculated for $C_{76}H_{132}CoF_{12}N_{14}O_8S_4$): C 51.30 (51.13) %, H 7.90 (7.65) %, N 10.80 (10.98) %.

1.11 $[Co(DeIm)_6][Tf_2N]_2$

A solution of $Co(Tf_2N)_2{\cdot}6H_2O$ (1.00 g, 1.38 mmol) and *N*-decylimidazole (1.73 g, 8.32 mmol) in ethanol (25 mL) was stirred for 5 min at room temperature. The excess of ethanol was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a pale pink solid product (yield 2.45 g; 95 %). Melting point: 41 °C. FTIR (ATR, ν_{max}/cm^{-1}): 3133 (CH), 2957 (CH), 2925 (CH), 2855 (CH), 1514 (ring), 1457 (ring), 1350 (SO_2), 1333 (ring), 1288 (CH), 1230 (CF_3), 1190 (CF_3), 1141 (SO_2), 1108 (ring), 1090 (CH), 1054 (SNS), 938 (ring), 831 (CH), 818 (CH), 789 (CS), 762, 738 (CF_3), 664 (ring), 613, 569 (CF_3), 513 (CF_3), 408 (SO_2). CHN found (calculated for $C_{82}H_{144}CoF_{12}N_{14}O_8S_4$): C 52.98 (52.69) %, H 8.32 (8.06) %, N 10.28 (10.49) %.

1.12 $[Co(UnIm)_6][Tf_2N]_2$

A solution of $Co(Tf_2N)_2{\cdot}6H_2O$ (1.00 g, 1.38 mmol) and *N*-undecylimidazole (1.86 g, 8.32 mmol) in ethanol (25 mL) was stirred for 5 min at room temperature. The excess of ethanol was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a pale pink solid product (yield 2.70 g; 100 %). Melting point: 43 °C. FTIR (ATR, ν_{max}/cm^{-1}): 3132 (CH), 2957 (CH), 2923 (CH), 2854 (CH), 1514 (ring), 1457 (ring), 1350 (SO_2), 1333 (ring), 1287 (CH), 1231 (CF_3), 1198 (CF_3), 1141 (SO_2), 1108 (ring), 1091 (CH), 1054 (SNS), 938 (ring), 831 (CH), 817 (CH), 789 (CS), 762, 738 (CF_3), 665 (ring), 614, 569 (CF_3), 514 (CF_3), 410 (SO_2). CHN found (calculated for $C_{88}H_{156}CoF_{12}N_{14}O_8S_4$): C 54.47 (54.21) %, H 8.55 (8.25) %, N 9.82 (10.04) %.

1.13 $[Co(DoIm)_6][Tf_2N]_2$

A solution of $Co(Tf_2N)_2{\cdot}6H_2O$ (1.00 g, 1.38 mmol) and *N*-dodecylimidazole (1.96 g, 8.32 mmol) in ethanol (25 mL) was stirred for 5 min at room temperature. The excess of ethanol was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a pale pink solid product (yield 2.78 g; 99 %). Melting point: 43 °C. FTIR (ATR, ν_{max}/cm^{-1}): 3132 (CH), 2925 (CH), 2854 (CH), 1514 (ring), 1457 (ring), 1350 (SO_2), 1332 (ring), 1288 (CH), 1230 (CF_3), 1188 (CF_3), 1140 (SO_2), 1108 (ring), 1091 (CH), 1055 (SNS), 938 (ring), 818 (CH), 788 (CS), 762, 738 (CF_3), 664 (ring), 615, 569 (CF_3), 513 (CF_3), 409 (SO_2). CHN found (calculated for $C_{94}H_{168}CoF_{12}N_{14}O_8S_4$): C 55.75 (55.51) %, H 8.85 (8.51) %, N 9.41 (9.62) %.

1.14 $Co(Tf_2N)_2 \cdot 6H_2O$

A solution of cobalt(II) carbonate (9.85 g, 82.809 mmol) and methanesulfonate (14.99 g, 152.86 mmol) in H_2O (50 mL) was stirred at room temperature until the pH was neutral. CO_2 was released during the reaction. The remaining solids were filtered off and the excess of solvent was removed on a rotary evaporator after which the product was dried overnight at 50 °C on a vacuum line to yield $[Co(H_2O)_6][OMs]_2$ as a pink crystalline solid (yield 24.55 g; 83 %). FTIR (ATR, ν_{max}/cm^{-1}): 3536 (H_2O)), 3375 (H_2O), 3041 (CH_3), 1624 (H_2O), 1430 (CH_3), 1331 (CH_3), 1213 (SO_3), 1149, 1052 (SO_3), 978 (CH_3), 786 (CS), 691, 566, 537, 516, 420 (SO_3). CHN found (calculated for $C_2H_{18}CoO_{12}S_2$): C: 6.44 (6.72) %, H 4.98 (5.08) %, N 0.01 (0.00) %.

1.15 $[Co(MeIm)_6][OMs]_2$

A solution of $Co(OMs)_2 \cdot 6H_2O$ (0.50 g, 1.41 mmol) and *N*-methylimidazole (0.71 g, 8.59 mmol) in ethanol (25 mL) was stirred for 5 min at room temperature. The excess of ethanol was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a pale pink solid product (yield 1.04 g; 100 %). Melting point: 190 °C. FTIR (ATR, ν_{max}/cm^{-1}): 3117 (CH), 3010 (CH), 2934 (CH), 1636, 1531 (ring), 1517 (ring), 1483 (ring), 1456 (ring), 1422 (ring), 1373 (SO_2), 1334 (ring), 1318, 1288 (CH), 1196, 1089 (CH), 1036 (SO_2), 938 (ring), 863, 829 (CH), 763 (CH), 743, 662 (ring), 620 (ring), 550, 531, 522. CHN found (calculated for $C_{26}H_{42}CoN_{12}O_6S_2$): C 42.21 (42.10) %, H 5.78 (5.71) %, N 22.64 (22.66) %.

1.16 $[Co(EtIm)_6][OMs]_2$

A solution of $Co(OMs)_2 \cdot 6H_2O$ (0.50 g, 1.41 mmol) and *N*-ethylimidazole (0.81 g, 8.59 mmol) in ethanol (25 mL) was stirred for 5 min at room temperature. The excess of ethanol was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a pale pink solid product (yield 1.16 g; 100 %). Melting point: 131 °C. FTIR (ATR, ν_{max}/cm^{-1}): 3118 (CH), 2979 (CH), 1736, 1653, 1517, 1449 (ring), 1385 (SO_2), 1356 (ring), 1321, 1290 (CH), 1197 (CH), 1091 (CH), 1038 (SO_2), 959 (ring), 937(ring), 869, 831, 764 (CH), 743, 663 (ring), 623 (ring), 550, 523. CHN found (calculated for $C_{32}H_{54}CoN_{12}O_6S_2$): C 46.42 (46.54) %, H 6.51 (6.59) %, N 20.54 (20.35) %.

1.17 $[Co(PrIm)_6][OMs]_2$

A solution of $Co(OMs)_2 \cdot 6H_2O$ (0.50 g, 1.41 mmol) and *N*-propylimidazole (0.92 g, 8.59 mmol) in ethanol (25 mL) was stirred for 5 min at room temperature. The excess of ethanol was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a pale pink solid product (yield 1.28 g; 100 %). Melting point: 116 °C. FTIR (ATR, ν_{max}/cm^{-1}): 3119 (CH), 2964 (CH), 2877 (CH), 1636, 1519 (ring), 1457 (ring), 1420 (ring), 1386 (SO−2), 1321, 1290 (C-H), 1190, 1089 (CH), 1038 (SO_2), 938 (ring), 902, 865, 826 (CH), 800 (CH), 763 (CH), 663 (ring), 622 (ring), 549, 522. CHN found (calculated for $C_{38}H_{66}CoN_{12}O_6S_2$): C 50.21 (50.15) %, H 7.36 (7.31) %, N 18.52 (18.47) %. Viscosity at 80 °C: 126 mPa s.

1.18 $[Co(BuIm)_6][OMs]_2$

A solution of $Co(OMs)_2 \cdot 6H_2O$ (0.50 g, 1.41 mmol) and *N*-butylimidazole (1.05 g, 8.59 mmol) in ethanol (25 mL) was stirred for 5 min at room temperature. The excess of ethanol was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a pale pink solid product (yield 1.40 g; 100 %). Melting point: 130 °C. FTIR (ATR, ν_{max}/cm^{-1}): 3122 (CH), 2958 (CH), 2932 (CH), 2873 (CH), 1636, 1518 (ring), 1458 (ring), 1420 (ring), 1376 (SO_3), 1323, 1305, 1284 (CH), 1228,

1184, 1115, 1091 (CH), 1041 (SO_3), 937 (ring), 862, 827 (CH), 765 (CH), 736, 665 (ring), 628 (ring), 551, 522, 434. CHN found (calculated for $C_{44}H_{78}CoN_{12}O_6S_2$): C 53.09 (53.15) %, H 7.86 (7.91) %, N 16.94 (16.91) %.

1.19 $[Co(PeIm)_6][OMs]_2$

A solution of $Co(OMs)_2{\cdot}6H_2O$ (0.50 g, 1.41 mmol) and *N*-pentylimidazole (1.20 g, 8.59 mmol) in ethanol (25 mL) was stirred for 5 min at room temperature. The excess of ethanol was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a pale pink solid product (yield 1.52 g; 100 %). Melting point: 114 °C. FTIR (ATR, ν_{max}/cm^{-1}): 3121 (CH), 2959 (CH), 2931 (CH), 2862 (CH), 1624, 1516 (ring), 1468 (ring), 1456 (ring), 1420 (ring), 1408, 1377 (SO_3), 1295 (CH), 1231, 1203, 1108, 1089 (CH), 1040 (SO_3), 997, 938 (ring), 854, 833 (CH), 766 (CH), 733, 665 (ring), 632 (ring), 549, 523, 490. CHN found (calculated for $C_{50}H_{90}CoN_{12}O_6S_2$): C 55.72 (55.69) %, H 8.49 (8.41) %, N 15.67 (15.59) %.

1.20 $[Co(HeIm)_6][OMs]_2$

A solution of $Co(OMs)_2{\cdot}6H_2O$ (0.50 g, 1.41 mmol) and *N*-hexylimidazole (1.29 g, 8.59 mmol) in ethanol (25 mL) was stirred for 5 min at room temperature. The excess of ethanol was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a pale pink solid product (yield 1.64 g; 100 %). Melting point: 130 °C. FTIR (ATR, ν_{max}/cm^{-1}): 3121 (CH), 2956 (CH), 2927 (CH), 2858 (CH), 1636, 1520 (ring), 1459 (ring), 1408, 1378 (SO_3), 1321, 1288 (CH), 1225, 1187, 1110, 1092 (CH), 1048 (SO_3), 1039, 938 (ring), 871, 828 (CH), 764 (CH), 734, 665 (ring), 632 (ring), 549, 521. CHN found (calculated for $C_{56}H_{102}CoN_{12}O_6S_2$): C 57.93 (57.86) %, H 8.97 (8.84) %, N 14.54 (14.46) %. Viscosity at 80 °C: 68 mPa s.

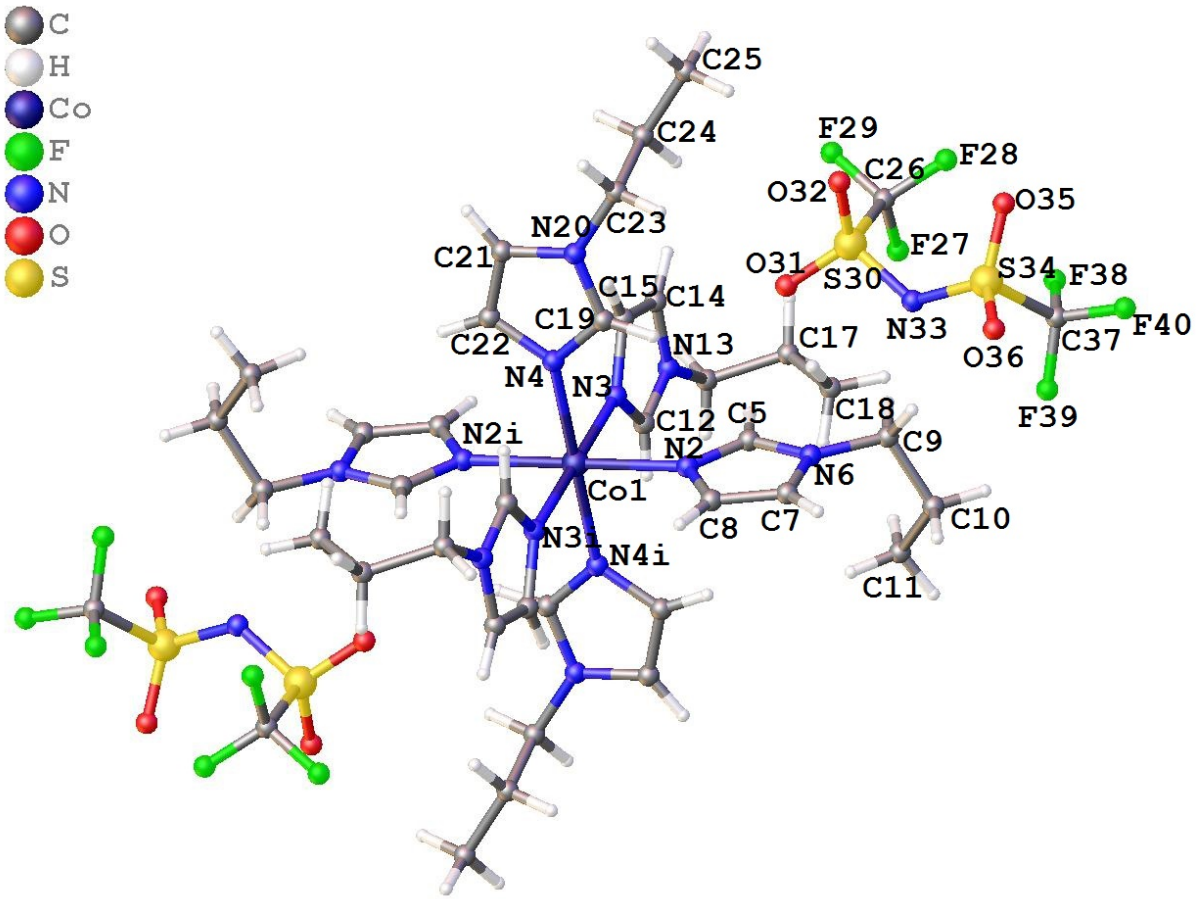

Figure 1 Crystal structure of $[Co(PrIm)_6][Tf_2N]_2$. Symmetry code: (i) 2-x, -y, 1-z.

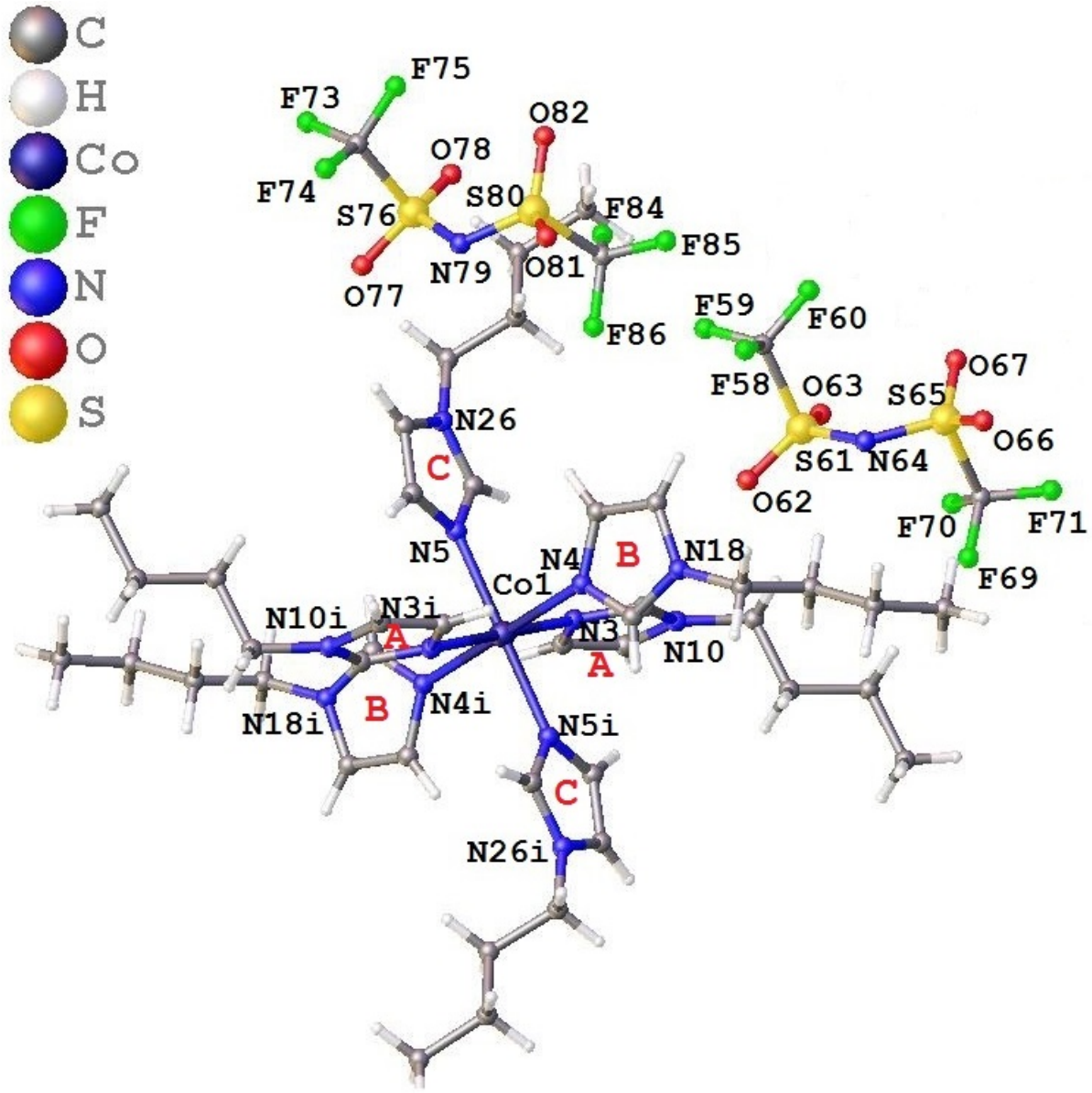

Figure 2 Crystal structure of $[Co(BuIm)_6][Tf_2N]_2$. Symmetry code: (i) -x, 1-y, 1-z.

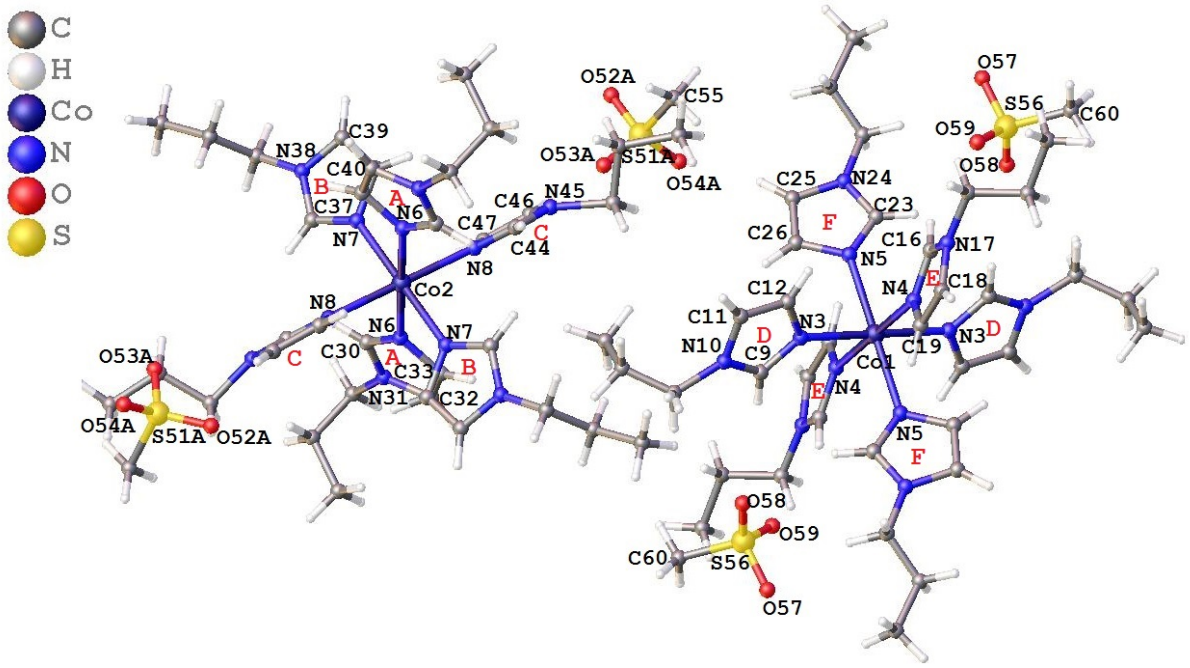

Figure 3 Crystal structure of $[Co(PrIm)_6][OMs]_2$. Symmetry code: (i) 1-x, 1-z, 1-z.

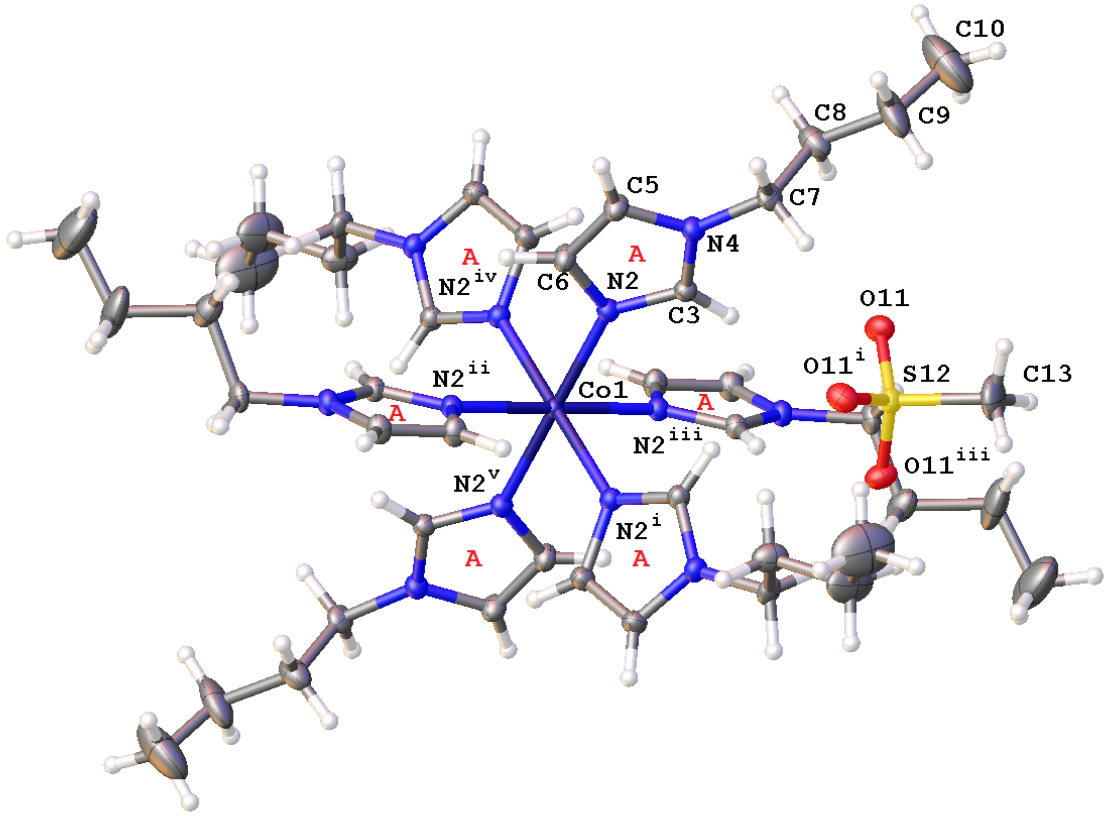

Figure 4 Crystal structure of $[Co(BuIm)_6][OMs]_2$. Symmetry codes: (i) 2-x+y, 1-x, z (ii) 1-y, -1+x, z (iii) 1+y, 1-x+y, 2-z (iv) 2-x, -y, 2-z (v) x-y, -1+x, 2-z

Table 1 Crystal data and structure refinement for the structures of $[Co(EtIm)_6][Tf_2N]_2$, $[Co(PrIm)_6][Tf_2N]_2$, $[Co(BuIm)_6][Tf_2N]_2$, $[Co(EtIm)_6][OMs]_2$, $[Co(PrIm)_6][OMs]_2$ and $[Co(BuIm)_6][OMs]_2$

Compound	$[Co(EtIm)_6][Tf_2N]_2$	$[Co(PrIm)_6][Tf_2N]_2$	$[Co(BuIm)_6][Tf_2N]_2$	$[Co(EtIm)_6][OMs]_2$	$[Co(PrIm)_6][OMs]_2$	$[Co(BuIm)_6][OMs]_2$
Empirical formula	$C_{34}H_{48}Co F_{12}N_{14}O_8S_4$	$C_{40}H_{60}Co F_{12}N_{14}O_8S_4$	$C_{46}H_{71}Co F_{12}N_{14}O_8S_4$	$C_{48}H_{81}Co_{15} N_{18}O_9S_3$	$C_{38}H_{66}Co N_{12}O_6S_2$	$C_{44}H_{78}Co N_{12}O_6S_2$
Formula weight	1196.03	1280.19	1363.33	1238.88	910.07	994.23
Temperature/K	100(2)	100(2)	100(2)	99.9(2)	250.01(10)	100(2)
Color	pink	pink	pink	pink	pink	pink
Size/mm^3	0.19 x 0.14 x 0.1	0.19 x 0.16 x 0.15	0.16 x 0.09 x 0.08	0.40 x 0.08 x 0.07	0.24 x 0.12 x 0.12	0.24 x 0.15 x 0.04
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Trigonal
Space group	$P2_1/c$ (no.14)	$P2_1/c$ (no.14)	$P\bar{1}$ (no.2)	$P2_1/c$ (no.14)	$P\bar{1}$ (no.2)	$R\bar{3}$ (no.148)
a/Å	11.0532(5)	11.15538(16)	9.6957(3)	23.6765(7)	8.8446(3)	13.4995(7)
b/Å	11.1257(5)	12.3581(3)	17.4965(6)	12.9804(4)	15.7075(6)	13.4995(7)
c/Å	20.1637(10)	21.4046(3)	18.8465(6)	21.7673(7)	17.6599(7)	25.8633(14)
α/°	90	90	88.258(3)	90	88.763(3)	90
β/°	98.154(5)	101.7361(15)	89.339(3)	112.358(4)	80.229(3)	90
γ/°	90	90	80.363(3)	90	85.243(3)	120
Volume/$Å^3$	2454.6(2)	2889.14(9)	3150.49(19)	6186.8(4)	2409.44(16)	4081.8(5)
Z	2	2	2	4	2	3
ρ_{calc} / $Mg.m^{-3}$	1.618	1.472	1.437	1.330	1.254	1.213
μ/mm^{-1}	0.628	0.539	0.499	0.573	0.497	0.445
Wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Reflections collected	10709	12615	24409	28716	19415	6466
Independent refl.	5012	5886	12848	12644	9822	1863
R(int)	0.0460	0.0302	0.0181	0.0217	0.0204	0.0160
R_1 [$I \geq 2\theta(I)$]	0.0305	0.0624	0.0352	0.0368	0.0621	0.0441
wR_2 [all data]	0.0717	0.0648	0.0844	0.0921	0.1852	0.1176
$\delta\rho_{max,min}$/e Å − 3	0.43/-0.43	0.39/-0.33	0.85/-0.42	1.23/-0.56	0.76/-0.50	1.44/-0.45

Table 2 Non-classical hydrogen bonds C-H···X and C-H··· π in $[Co(EtIm)_6][Tf_2N]_2$ and $[Co(PrIm)_6][Tf_2N]_2$. Labels of atoms and planes as shown in Figures 2 and S1.

Compound	Interaction	Distance (Å)	Symmetry Operation
$[Co(EtIm)_6][Tf_2N]_2$	C8-H8···ring B	3.6108(19)	x, y, z
	C10-H10B···ring A	3.499(2)	1-x, 1-y, 1-z
	C14-H14···ring C	3.6169(19)	x, y, z
	C20-H20···ring A	3.4036(19	-x, 1-y, -z
	S31-O32···ring B	3.9875(16)	-x, 1-y, -x
	S31-O33···ring C	3.4930(14)	x, 1/2-y, -1/2+z
	C5-H5···O32	3.236(2)	x, y, z
	C11-H11···O29	3.362(2)	-x, 1-y, -z
	C14-H14···O33	3.386(2)	x, 1/2-y, 1/2+z
	C19-H19···O29	3.297(2)	-x, -y, -z
$[Co(PrIm)_6][Tf_2N]_2$	C5-H5···ring B	3.6584(15)	x, y, z
	C15-H15···ring C	3.5912(16)	x, y, z
	C22-H22···ring A	3.7115(16)	2-x, -y, 1-z
	S30-O31···ring A	3.5378(13)	x, y, z
	S30-O32···ring C	3.3158(12)	1-x, -y, 1-z
	C7-H7···O36	3.352(2)	1-x, 1-y, 1-z
	C9-H9A···O32	3.513(2)	x, y, z
	C12-H12···O32	3.1855(19)	1+x, y, z
	C12-H12···N4	3.1450(17	2-x, -y, 1-z
	C14-H14···O35	3.3804(18)	1-x, -1/2+y, 1/2-z
	C19-H19···O31	3.3718(17)	x, y, z

Table 3 Non-classical hydrogen bonds C-H···X and C-H··· π in $[Co(BuIm)_6][Tf_2N]_2$. Labels of atoms and planes as shown in Figure S2.

Compound	Interaction	Distance (Å)	Symmetry Operation
$[Co(BuIm)_6][Tf_2N]_2$	ring B - ring B	4.1947(11)	1-x, 1-y, 1-z
	ring E - ring E	4.3267(11)	1-x, -y, -z
	C20-H20···ring C	3.559(2)	x, y, z
	C28-H28···ring A	3.470(2)	-x, 1-y, 1-z
	C44-H44···ring D	3.353(2)	x, y, z
	C49-H49···ring E	3.633(2)	x, y, z
	S61-O62···ring B	3.649(2)	x, y, z
	S65-O67···ring E	3.5627(16)	x, y, z
	S80-O81···ring C	3.3810(17)	1+x, y, z
	C17-H17···O81	3.299(2)	1-x, 1-y, 1-z
	C27-H27···O77	3.223(3)	x, y, z
	C30-H30B···F84	3.391(2)	x, y, z
	C35-H35···O82	3.288(2)	x, -1+y, z
	C37-H37B···O77	3.277(2)	1+x, -1+y, z
	C41-H41···O78	3.332(2)	1-x, 1-y, -z
	C45-H45B···O78	3.364(3)	1-x, 1-y, -z
	C51-H51···O63	3.368(2)	1+x, y, z

Table 4 Non-classical hydrogen bonds C-H···X and C-H··· π in $[Co(EtIm)_6][OMs]_2$. Labels of atoms and planes as shown in Figure 3.

Compound	Interaction	Distance (Å)	Symmetry Operation
$[Co(EtIm)_6][OMs]_2$	C27-H27···ring E	3.454(2)	x, y, z
	C33-H33···ring C	3.570(2)	x, y, z
	C35-H35C···ring B	3.753(3)	1-x, 1/2+y, 1/2-z
	C39-H39···ring A	3.640(2)	x, y, z
	C51-H51···ring H	3.675(2)	1-x, 1/2+y, 1/2-z
	C57-H57···ring I	3.635(2)	x, y, z
	C12-H12···O72	3.086(3)	1-x, -1/2+y, 1/2-z
	C17-H17A···O78	3.280(3)	1-x, -1/2+y, 1/2-z
	C18-H18···O72	3.361(3)	1-x, -1/2+y, 1/2-z
	C20-H20···O67	3.371(3)	1-x, -1/2+y, 1/2-z
	C24-H24···O72	3.317(3)	1-x, 1/2+y, 1/2-z
	C26-H26···O69	3.179(3)	x, y, z
	C27-H27···N7	3.063(3)	
	C28-H28A···74	3.348(3)	1-x, -1/2+y, 1/2-z
	C30-H30···O68	3.326(3)	1-x, 1-y, 1-z
	C32-H32···O74	3.320(3)	x, y, z
	C38-H38···O73	3.211(3)	1-x, 1-y, 1-z
	C46-H46A···O78	3.232(3)	1-x, 1/2+y, 1/2-z
	C50-H50···O77	3.285(3)	2-x, 1-y, 1-z
	C50-H50···O78	3.431(3)	2-x, 1-y, 1-z
	C54-H54···O79	3.129(3)	x, 1/2-y, 1/2+z
	C58-H58A···O77A	3.392(10)	x, 1/2-y, 1/2+z
	C62-H62···O72	3.335(3)	x, 3/2-y, 1/2+z
	C64-H64A···O73	3.215(3)	x, 3/2-y, 1/2+z
	C64-H64B···O77	3.263(3)	2-x, 1/2+y, 3/2-z
	C75-H75B···O68	3.318(3)	x, 1/2-y, -1/2+z

Table 5 Non-classical hydrogen bonds C-H···X and C-H··· π in $[Co(PrIm)_6][OMs]_2$ and $[Co(BuIm)_6][OMs]_2$. Labels of atoms and planes as shown in Figures S3 and S4.

Compound	Interaction	Distance (Å)	Symmetry Operation
$[Co(PrIm)_6][OMs]_2$	C13-H13···ring C	3.692(11)	x, y, z
	C19-H19···ring F	3.470(4)	1-x, 4-y, 1-z
	C16-H16···O59	3.167(6)	x, y, z
	C18-H18···O58	3.291(6)	1+x, y, z
	C20-H20B···O59	3.293(6)	x, y, z
	C25-H25···O54	3.314(5)	x, y, z
	C30-H30···O52	3.136(8)	1-x, 2-y, -z
	C37-H37···O52	3.248(9)	1+x, y, z
	C39-H39···O57	3.172(7)	1+x, 1+y, z
	C41-H41A···O53	3.366(10)	1+x, y, z
	C44-H44···O52	3.370(11)	1+x, y, z
	C44-H44···O52A	3.082(10)	x, y, z
	C46-H46···O53A	3.190(10)	
	C49-H49A···O53	3.361(12)	x, y, z
$[Co(BuIm)_6][OMs]_2$	C3-H3···O11	3.293(3)	x, y, z
	C5-H5···O11	3.225(3)	2/3+x-y, -4/3+x, 5/3-z