Supporting Information

The Amide Group As Modulator Of Crystalline And Liquid Crystalline Structures In Isocyano-Alkylanilide Silver(I) Complexes.

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Synthesis and characterization of compounds 1 – 12.

Synthesis of the isocyanides

4-CN-C_6H_4-$NHCOCH_3$ **(1).** In a two necked flask were disposed 1g (6.7 mmol) of 4-aminoacetanilide, 5 mL (22.8 mmol) of formic acid and 100 mL of toluene. A Dean-Stark apparatus was connected and the reaction was refluxed until no water drops were observed. The addition of 5 mL of formic acid and refluxing was repeated twice to ensure the complete reaction of the amine. After evaporation, the solid residue was dissolved in ethanol and a little amount of charcoal was added. The mixture was filtered off and the solvent was evaporated. A white solid was obtained in high yields (85-95 %). To obtain the isocyanide, 4-acetanilide-formamide (1 g, 5.6 mmol), dry CH_2Cl_2 (30-40 mL) and NEt_3 (3 mL, 21.2 mmol) were disposed in a two-necked flask under nitrogen atmosphere and then the mixture was cooled into an ice bath. A CH_2Cl_2 solution of triphosgene (1 g, 3.4 mmol) was dropwise added for 30 min. After that, the reaction was maintained for 1 hour maximum. Once checked by TLC that the isocyanide is the main product in the mixture, a little amount of silica for chromatography was added in order to achieve a preliminary purification. After 15 min. stirring, the suspension was filtered off. The solvent was evaporated and the residue was treated with Et_2O or Et_2O/EtOAc 1:1 to separate the isocyanide from the HCl:NEt_3. The solution was further purified by column chromatography though a short pad of silica and using mixtures of Et_2O and EtOAc in increasing rates as eluent. After evaporation of the solvent, the 4-isocyanoacetanilide is obtained as a white yellowish solid which can be recrystallized from diethylether (0.494 g, 55 % yield). ^{1}H-NMR (400 MHz, acetone-d_6) (see Scheme 1 for labels) δ 9.49 (brs, 1H, Hc), 7.75 (d, $J_{AB} + J_{AB'}$ = 8.7 Hz, 2H, Hb), 7.42 (d, $J_{AB} + J_{AB'}$ = 8.7 Hz, 2H, Ha), 2.10 (s, 3H). ^{13}C-NMR (400 MHz,

acetone-d6) δ 168.41 (C=O), 164.17 (CN), 140.56 (C-NH), 126.88 (2CHa), 119.43 (2CHb), 119.35 (C-NC), 23.40 (CH_3). IR (ATR, cm^{-1}) 3302 ν(NH), 2122 ν(CN), 1662 ν(CO), 1540 ν(NCO). Analysis for $C_9H_8N_2O$: Found (calculated) 67.28 % C (67.49), 5.14 % H (5.03), 17.59 % N (17.49).

4-CN-C_6H_4-NHCOC_9H_{19} , **(7)**. The method followed was the same as for **1** but starting from 4-H_2N-C_6H_4-NHCOC_9H_{19} obtained from the corresponding nitro derivative[1] by reduction with metallic Sn. (0.456 g, 62% yield). ^{1}H-NMR (500 MHz, acetone-d_6) (see Scheme 1 for labels) δ 9.37 (brs, 1H, Hc), 7.77(d, $J_{AB} + J_{AB'}$ = 8.9 Hz, 2H, Hb), 7.42(d, $J_{AB} + J_{AB'}$ = 8.8 Hz, 2H, Ha), 2.38(t, J = 7.5 Hz), 2H, CO-CH_2-), 1.66 (m, 2H, -CH_2-), 1.28 (m, 6H, -CH_2-), 0.86 (t, 3H, -CH_3). ^{13}C-NMR (400 MHz, acetone-d6) δ 171.51 (C=O), 164.15 (CN), 140.57 (C-NH), 126.85 (2CHa), 119.50 (2CHb), 119.42 (C-NC), 36.81, 31.67, 29.28, 29.20, 29.09, 29.01, 25.16, 22.39 ($8CH_2$), 14.76 (CH_3). IR (ATR, cm^{-1}) 3304, 3263 ν(NH), 2119 ν(CN), 1672 ν(CO), 1541 ν(NCO). Analysis for $C_{17}H_{24}N_2O$: Found (calculated) 74.98 % C (74.96), 8.51% H (8.88), 10.28% N (10.34).

Synthesis of the complexes .

***[AgX(CNR)] and [Ag(CNR)$_2$]X (R = -C_6H_4-NHCOCH_3, X = NO_3^-, $CF_3SO_3^-$, BF_4^-)* 2 – 6.** To a suspension of AgX (X = NO_3^-, $CF_3SO_3^-$, BF_4^-) (0.5 mmol) in 20 mL of acetone under inert atmosphere and protected from the light, was dropwise added a solution of the corresponding isocyanide (in 1:1 or 1: 2 molar ratio) in acetone (10 mL). Over 24 h of stirring a yellowish suspension appeared. The solvent was removed and the resulting solid washed with acetone (2 × 5 mL) at 0 ºC.

[Ag(NO_3)(4-CN-C_6H_4-NHCOCH_3)], **(2).** White solid, 0.140 g, 85% yield. Colorless single crystals were obtained from a solution in acetone placed under a hexane

[1] Lee, G.-H.; Lim, H. K.; Hah, S. S.; *Bull. Korean Chem. Soc*. **2011**, *32*, 3767-3769.

atmosphere at 4ºC. ^{1}H-NMR (400 MHz, acetone-d_6) (see Scheme 1 for labels) δ 9.64 (brs, 1H, Hc), 7.86 (d, $J_{AB} + J_{AB'}$ = 8.9 Hz, 2H, Hb), 7.72 (d, $J_{AB} + J_{AB'}$ = 8.8 Hz, 2H, Ha), 2.12 (s, 3H). IR (ATR, cm^{-1}) 3302 ν(NH), 2190 ν(CN), 1677 ν(CO), 1522 ν(NCO), 1420, 1307, 1296 (NO_3^-). Analysis for $C_9H_8AgN_3O_4$: Found (calculated) 32.86 % C (32.75), 2.28 % H (2.44), 12.55 % N (12.73).

[Ag(CF_3SO_3)(4-CN-C_6H_4-$NHCOCH_3$)], **(3).** Yellowish solid, 0.115g, 55 % yield. Yellowish crystalline plates were obtained from a solution in acetone placed under a hexane atmosphere at 4ºC. ^{1}H-NMR (400 MHz, acetone-d_6) (see Scheme 1 for labels) δ 9.70 (brs, 1H, Hc), 7.87 (d, $J_{AB} + J_{AB'}$ = 8.9 Hz, 2H, Hb), 7.80 (d, $J_{AB} + J_{AB'}$ = 8.8 Hz, 2H, Ha), 2.13 (s, 3H). IR (ATR, cm^{-1}) 3307 ν(NH), 2198 ν(CN), 1628 ν(CO), 1538 ν(NCO), 1237, 1222 ($CF_3SO_3^-$). Analysis for $C_{10}H_8AgF_3N_2O_4S$: Found (calculated) 28.75 % C (28.80), 1.89 % H (1.93), 6.66 % N (6.72).

[Ag(4-CN-C_6H_4-$NHCOCH_3$)$_2$](NO_3), **(4).** Yellowish solid, 0.184g, 75% yield. Yellowish single crystals were obtained from a solution in DMA placed under a Et_2O atmosphere at 4ºC. ^{1}H-NMR (400 MHz, acetone-d_6) (see Scheme 1 for labels) δ 9.52 (brs, 2H, Hc), 7.81 (d, $J_{AB} + J_{AB'}$ = 8.7 Hz, 4H, Hb), 7.56 (d, $J_{AB} + J_{AB'}$ = 8.7 Hz, 4H, Ha), 2.11 (s, 6H). IR (ATR, cm^{-1}) 3252 ν(NH), 2192 ν(CN), 1688, 1672 ν(CO), 1535 ν(NCO), 1339 (NO_3^-). Analysis for $C_{18}H_{16}AgN_5O_5$: Found (calculated) 43.95 % C (44.10), 3.20 % H (3.29), 14.25 % N (14.27).

[Ag(4-CN-C_6H_4-$NHCOCH_3$)$_2$](CF_3SO_3), **(5)**. Yellowish solid, 0.222 g, 77 % yield. Yellowish single crystals were collected from a solution of 5 in acetone placed under a Et_2O atmosphere at room temperature. ^{1}H-NMR (400 MHz, acetone-d_6) (see Scheme 1 for labels) δ 9.66 (brs, 2H, Hc), 7.87 (d, $J_{AB} + J_{AB'}$ = 9.1 Hz, 4H, Hb), 7.69 (d, $J_{AB} + J_{AB'}$ = 8.9 Hz, 4H, Ha), 2.13 (s, 6H). IR (ATR, cm^{-1}) 3055 ν(NH), 2185 ν(CN), 1678, 1668

ν(CO), 1536 ν(NCO), 1250 ($CF_3SO_3^-$). Analysis for $C_{19}H_{16}AgF_3N_4O_5S$: Found (calculated) 39.59 % C (39.53), 2.81 % H (2.79), 9.58 % N (9.71).

[Ag(4-CN-C_6H_4-NHCOCH_3)$_2$](BF_4), **(6).** Brownish solid, 0.211g, 82 % yield. Brownish single crystals were collected from a solution of **6** in CH_3CN placed under a Et_2O atmosphere at 4ºC. ^{1}H-NMR (400 MHz, acetone-d_6) (see Scheme 1 for labels) δ 9.57 (brs, 2H, Hc), 7.85 (d, $J_{AB} + J_{AB'}$ = 8.8 Hz, 4H, Hb), 7.65 (d, $J_{AB} + J_{AB'}$ = 8.8 Hz, 4H, Ha), 2.12 (s, 6H). IR (ATR, cm^{-1}) 3355 ν(NH), 2190 ν(CN), 1738, 1677 ν(CO), 1535 ν(NCO), 1019 (BF_4^-). Analysis for $C_{18}H_{16}AgBF_4N_4O_2$: Found (calculated) 42.05 % C (41.98), 3.21 % H (3.13), 11.03 % N (10.88).

[Ag(NO$_3$)(CNR)] and [Ag(CNR)$_2$]X (R = -C$_6$H$_4$-NHCOC$_9$H$_{19}$, X = NO$_3^-$, CF$_3$SO$_3^-$, H$_{25}$C$_{12}$SO$_4^-$, BF$_4^-$) **8 – 12.** A solution of the stoichiometric amount of **7** in acetone was added dropwise over 0.5 mmol of a solution of the corresponding silver salt in acetone. The reaction was monitored by IR until there was no evidence of free isocyanide in the solution. The acetone was evaporated and the residue was redisolved in CH_2Cl_2. After filtration through celite, the solution was concentrated and precipitated with hexane.

[Ag(NO$_3$)(4-CN-C$_6$H$_4$-NHCOC$_9$H$_{19}$)], **(8).** White solid, 0.121g, 55 % yield. ^{1}H-NMR (500 MHz, acetone-d_6) (see Scheme 1 for labels) δ 9.53 (brs, 1H, Hc), 7.88 (d, $J_{AB} + J_{AB'}$ =8.6 Hz , 2H, Hb), 7.72 (d, $J_{AB} + J_{AB'}$ = 8.3 Hz, 2H, Ha), 2.41 (t, J = 7.3 Hz, 2H, CO-CH_2-), 1.68 (m, 2H, -CH_2-), 1.29 (m, 6H, -CH_2-), 0.87 (t, J = 6Hz, 3H, -CH_3). IR (ATR, cm^{-1}) 3318 ν(NH), 2199 ν(CN), 1682 ν(CO), 1538 ν(NCO), 1455, 1256 (NO_3^-). Analysis for $C_{17}H_{24}$ AgN_3O_4: Found (experimental) 45.99 % C (46.17), 5.35 % H (5.47), 9.68 % N (9.50).

[Ag(4-CN-C$_6$H$_4$-NHCOC$_9$H$_{19}$)$_2$]NO$_3$ **(9)**. White solid, 0.236 g, 66 % yield. ^{1}H-NMR (500 MHz, acetone-d_6) (see Scheme 1 for labels) δ 9.57 (brs, 2H, Hc), 7.87 (d, J_{AB} +

$J_{AB'}$ = 8.3 Hz, 4H, Hb), 7.66 (d, J_{AB} + $J_{AB'}$ = 7.9 Hz, 4H, Ha), 2.41 (t, J = 7.3 Hz, 4H, CO-CH_2-), 1.67 (m, 4H, -CH_2-), 1.27 (m, 12H, -CH_2-), 0.87 (t, 6H, -CH_3). IR (ATR, cm^{-1}) 3316 ν(NH), 2200 ν(CN), 1674 ν(CO), 1530 ν(NCO), 1375, 1329, 1306 (NO_3^-). Analysis for $C_{34}H_{48}Ag\ N_5O_5$:Found (experimental) 56.97 % C (57.14), 6.65 % H (6.77), 9.90 % N (9.80).

[Ag(4-CN-C_6H_4-NHCOC_9H_{19})$_2$](CF$_3$SO$_3$), **(10)**. White solid, 0.273 g, 68 % yield. ^{1}H-NMR (500 MHz, acetone-d_6) (see Scheme 1 for labels) δ 9.61 (brs, 2H, Hc), 7.90 (d, J_{AB} + $J_{AB'}$ = 8.6 Hz, 4H, Hb), 7.67 (d, J_{AB} + $J_{AB'}$ = 8.5 Hz, 4H, Ha), 2.42 (t, J = 7.4 Hz, 4H, CO-CH_2-), 1.67 (m, 4H, -CH_2-), 1.28 (m, 12H, -CH_2-), 0.87 (t, J = 6.6 Hz, 6H, -CH_3). IR (ATR, cm^{-1}) 3325, 3296 ν(NH), 2200 ν(CN), 1703, 1683 ν(CO), 1538 ν(NCO), 1236 ($CF_3SO_3^-$). Analysis for $C_{35}H_{48}AgF_3N_4O_5S$: Found (experimental) 52.26 % C (52.43), 5.89 % H (6.03), 6.81% N (6.99).

[Ag(4-CN-C_6H_4-NHCOC_9H_{19})$_2$](OSO$_3$C$_{12}$H$_{25}$), **(11)**. White solid, 0.376 g, 82 % yield. ^{1}H-NMR (500 MHz, acetone-d_6) (see Scheme 1 for labels) δ 9.61 (s, 2H, Hc), 7.88 (d, J_{AB} + $J_{AB'}$ = 7.8 Hz, 4H, Hb), 7.63 (d, J_{AB} + $J_{AB'}$ = 8.2 Hz, 4H, Ha), 3.88 (t, 2H, SO_4-CH_2-) 2.42 (t, 4H, CO-CH_2-), 1.68 (m, 4H, -CH_2-), 1.57 (m, 2H, -CH_2-) 1.28 (m, 30H, -CH_2-), 0.87 (t, 9H, -CH_3). IR (ATR, cm^{-1}) 3279 ν(NH), 2196 ν(CN), 1701, 1674 ν(CO), 1534 ν(NCO), 1242, 1192, 1164 ($H_{25}C_{12}SO_4^-$). Analysis for $C_{46}H_{73}AgN_4O_6S$: Found (experimental) 59.97 % C (60.18), 7.86 % H (8.01), 6.04% N (6.10).

[Ag(4-CN-C_6H_4-NHCOC_9H_{19})$_2$]BF$_4$, **(12).** White solid, 0.274 g, 74 % yield. ^{1}H-NMR (500 MHz, acetone-d_6) (see Scheme 1 for labels) δ 9.53 (brs, 2H, Hc), 7.89 (d, J_{AB} + $J_{AB'}$ = 9.0 Hz , 4H, Hb), 7.68 (d, J_{AB} + $J_{AB'}$ = 8.9 Hz, 4H, Ha), 2.41 (t, J = 7.4 Hz, 4H, CO-CH_2-), 1.68 (m, 4H, -CH_2-), 1.29 (m, 12H, -CH_2-), 0.86 (t, 6H, -CH_3). IR (ATR, cm^{-1}) 3337 ν(NH), 2190 ν(CN), 1679 ν(CO), 1532 ν(NCO), 1027 (BF_4^-). Analysis for

$C_{34}H_{48}N_4O_2BF_4Ag$: Found (experimental) 55.17 % C (55.23), 6.40 % H (6.54), 7.46 % N (7.58).

Tables S1 – S5.- Bond distances (Å) and angles (º) for compounds **2** – **6** including ORTEP diagrams and unit cells

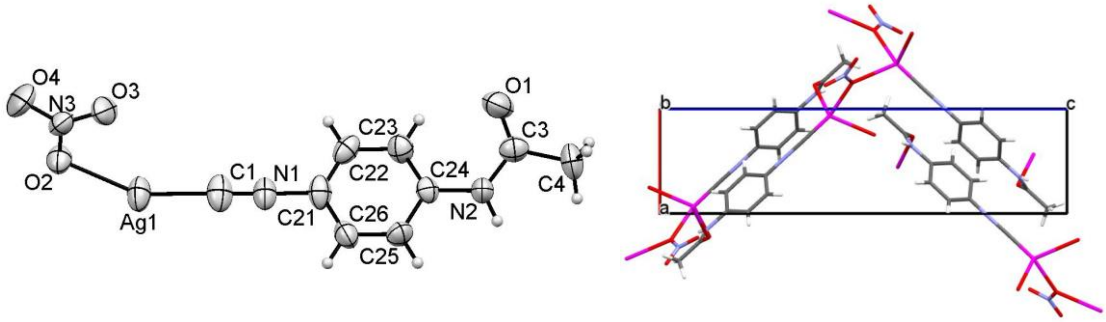


Table S1. Bond lengths [Å] and angles [°] for [Ag(NO_3)(CN-C_6H_4-$NHCOCH_3$)] (**2**).

CCDC 1011688

Ag(1)-C(1)	2.061(7)
Ag(1)-O(2)	2.304(5)
Ag(1)-O(2)#1	2.552(4)
Ag(1)-O(1)#2	2.558(7)
C(1)-N(1)	1.152(8)
N(1)-C(21)	1.411(8)
C(21)-C(22)	1.364(10)
C(21)-C(26)	1.381(9)
C(22)-C(23)	1.387(9)
C(23)-C(24)	1.374(9)
C(24)-C(25)	1.398(9)
C(24)-N(2)	1.405(7)
C(25)-C(26)	1.364(9)
N(2)-C(3)	1.328(9)
C(3)-O(1)	1.205(9)
C(3)-C(4)	1.514(10)
O(1)-Ag(1)#3	2.558(7)
N(3)-O(4)	1.225(7)
N(3)-O(3)	1.230(7)
N(3)-O(2)	1.231(7)

O(2)-Ag(1)#4	2.552(4)
C(1)-Ag(1)-O(2)	150.2(3)
C(1)-Ag(1)-O(2)#1	113.6(2)
O(2)-Ag(1)-O(2)#1	81.43(9)
C(1)-Ag(1)-O(1)#2	104.5(3)
O(2)-Ag(1)-O(1)#2	88.27(19)
O(2)#1-Ag(1)-O(1)#2	118.95(17)
N(1)-C(1)-Ag(1)	178.3(7)
C(1)-N(1)-C(21)	177.8(9)
C(22)-C(21)-C(26)	121.4(6)
C(22)-C(21)-N(1)	119.6(7)
C(26)-C(21)-N(1)	119.0(7)
C(21)-C(22)-C(23)	118.9(6)
C(24)-C(23)-C(22)	120.6(7)
C(23)-C(24)-C(25)	119.4(6)
C(23)-C(24)-N(2)	122.0(6)
C(25)-C(24)-N(2)	118.6(6)
C(26)-C(25)-C(24)	120.0(6)
C(25)-C(26)-C(21)	119.6(7)
C(3)-N(2)-C(24)	127.1(6)
O(1)-C(3)-N(2)	122.8(7)
O(1)-C(3)-C(4)	121.7(8)
N(2)-C(3)-C(4)	115.5(7)
C(3)-O(1)-Ag(1)#3	129.6(5)
O(4)-N(3)-O(3)	121.9(7)
O(4)-N(3)-O(2)	118.8(6)
O(3)-N(3)-O(2)	119.2(6)
N(3)-O(2)-Ag(1)	114.8(4)
N(3)-O(2)-Ag(1)#4	104.0(4)
Ag(1)-O(2)-Ag(1)#4	138.1(2)

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+3/2,-z #2 -x+1,y+1/2,-z+1/2 #3 -x+1,y-1/2,-z+1/2

#4 x+1/2,-y+3/2,-z

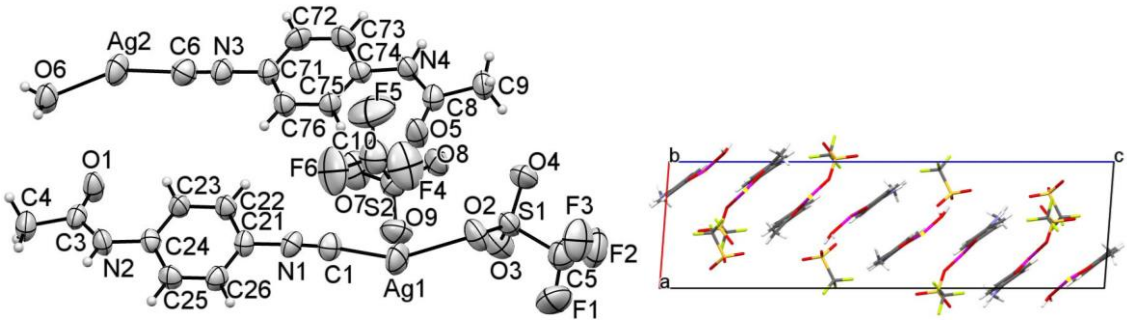


Table S2. Bond lengths [Å] and angles [°] for [Ag(CF_3SO_3)(CN-C_6H_4-$NHCOCH_3$)] (**3**).

CCDC 1011689

Ag(1)-C(1)	2.087(7)
Ag(1)-O(1)#1	2.269(4)
Ag(1)-O(2)	2.390(5)
C(1)-N(1)	1.133(8)
N(1)-C(21)	1.398(8)
C(21)-C(26)	1.358(8)
C(21)-C(22)	1.377(8)
C(22)-C(23)	1.367(8)
C(23)-C(24)	1.392(8)
C(24)-C(25)	1.392(8)
C(24)-N(2)	1.413(7)
C(25)-C(26)	1.367(9)
N(2)-C(3)	1.327(8)
C(3)-O(1)	1.219(8)
C(3)-C(4)	1.491(9)
O(1)-Ag(1)#2	2.269(4)
S(1)-O(4)	1.424(5)
S(1)-O(3)	1.432(5)
S(1)-O(2)	1.448(5)
S(1)-C(5)	1.820(9)
C(5)-F(3)	1.306(10)
C(5)-F(2)	1.309(9)
C(5)-F(1)	1.317(9)
Ag(2)-C(6)	2.047(8)
Ag(2)-O(6)	2.215(6)
Ag(2)-O(5)#2	2.326(4)
C(6)-N(3)	1.138(9)
N(3)-C(71)	1.396(8)

C(71)-C(76)	1.371(9)
C(71)-C(72)	1.372(9)
C(72)-C(73)	1.357(9)
C(73)-C(74)	1.389(8)
C(74)-C(75)	1.394(8)
C(74)-N(4)	1.408(7)
C(75)-C(76)	1.365(8)
N(4)-C(8)	1.337(8)
C(8)-O(5)	1.235(7)
C(8)-C(9)	1.493(9)
O(5)-Ag(2)#1	2.326(4)
S(2)-O(9)	1.415(5)
S(2)-O(8)	1.432(5)
S(2)-O(7)	1.465(6)
S(2)-C(10)	1.786(10)
C(10)-F(6)	1.315(10)
C(10)-F(5)	1.319(11)
C(10)-F(4)	1.339(11)

C(1)-Ag(1)-O(1)#1	137.7(2)
C(1)-Ag(1)-O(2)	145.4(2)
O(1)#1-Ag(1)-O(2)	76.81(17)
N(1)-C(1)-Ag(1)	172.6(6)
C(1)-N(1)-C(21)	176.6(7)
C(26)-C(21)-C(22)	121.3(6)
C(26)-C(21)-N(1)	118.9(6)
C(22)-C(21)-N(1)	119.8(5)
C(23)-C(22)-C(21)	119.9(6)
C(22)-C(23)-C(24)	119.5(6)
C(23)-C(24)-C(25)	119.3(6)
C(23)-C(24)-N(2)	123.5(6)
C(25)-C(24)-N(2)	117.1(5)
C(26)-C(25)-C(24)	120.3(6)
C(21)-C(26)-C(25)	119.6(6)
C(3)-N(2)-C(24)	128.9(5)
O(1)-C(3)-N(2)	121.8(6)
O(1)-C(3)-C(4)	121.3(6)
N(2)-C(3)-C(4)	116.9(6)

C(3)-O(1)-Ag(1)#2	128.0(4)
O(4)-S(1)-O(3)	115.9(3)
O(4)-S(1)-O(2)	114.1(3)
O(3)-S(1)-O(2)	114.6(3)
O(4)-S(1)-C(5)	103.1(4)
O(3)-S(1)-C(5)	102.6(4)
O(2)-S(1)-C(5)	104.4(4)
S(1)-O(2)-Ag(1)	137.9(3)
F(3)-C(5)-F(2)	107.4(7)
F(3)-C(5)-F(1)	109.1(7)
F(2)-C(5)-F(1)	108.3(8)
F(3)-C(5)-S(1)	111.2(6)
F(2)-C(5)-S(1)	109.9(6)
F(1)-C(5)-S(1)	110.8(6)
C(6)-Ag(2)-O(6)	144.5(3)
C(6)-Ag(2)-O(5)#2	132.2(2)
O(6)-Ag(2)-O(5)#2	82.0(2)
N(3)-C(6)-Ag(2)	175.6(7)
C(6)-N(3)-C(71)	179.1(7)
C(76)-C(71)-C(72)	120.2(6)
C(76)-C(71)-N(3)	120.1(6)
C(72)-C(71)-N(3)	119.7(6)
C(73)-C(72)-C(71)	119.8(6)
C(72)-C(73)-C(74)	120.9(6)
C(73)-C(74)-C(75)	118.8(6)
C(73)-C(74)-N(4)	117.3(5)
C(75)-C(74)-N(4)	123.9(5)
C(76)-C(75)-C(74)	119.5(6)
C(75)-C(76)-C(71)	120.8(6)
C(8)-N(4)-C(74)	129.1(5)
O(5)-C(8)-N(4)	122.3(6)
O(5)-C(8)-C(9)	121.9(6)
N(4)-C(8)-C(9)	115.8(6)
C(8)-O(5)-Ag(2)#1	126.2(4)
O(9)-S(2)-O(8)	113.9(3)
O(9)-S(2)-O(7)	116.2(4)
O(8)-S(2)-O(7)	115.2(3)
O(9)-S(2)-C(10)	105.2(4)

O(8)-S(2)-C(10)	103.1(4)
O(7)-S(2)-C(10)	100.7(4)
F(6)-C(10)-F(5)	106.9(9)
F(6)-C(10)-F(4)	110.0(8)
F(5)-C(10)-F(4)	108.5(9)
F(6)-C(10)-S(2)	111.3(7)
F(5)-C(10)-S(2)	110.4(6)
F(4)-C(10)-S(2)	109.7(7)

Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z #2 x,y-1,z

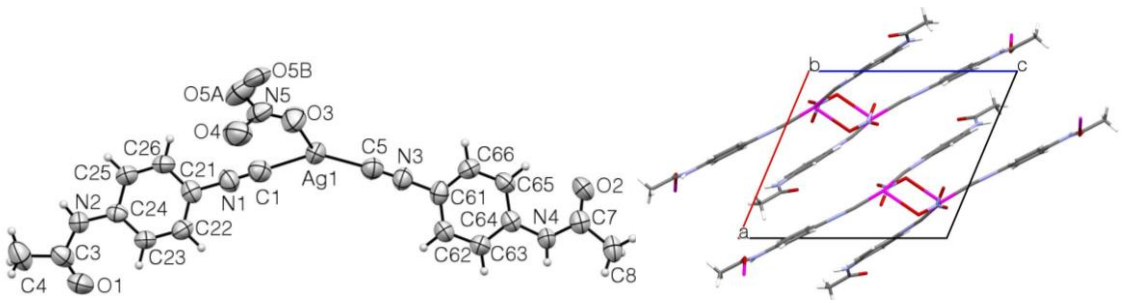


Table S3. Bond lengths [Å] and angles [°] for $[Ag(CN\text{-}C_6H_4\text{-}NHCOCH_3)_2](NO_3)$ (**4**).

CCDC 1011690

Ag(1)-C(5)	2.089(7)
Ag(1)-C(1)	2.103(7)
Ag(1)-O(2)#1	2.446(4)
Ag(1)-O(3)	2.648(5)
C(1)-N(1)	1.138(7)
N(1)-C(21)	1.399(7)
C(21)-C(26)	1.382(7)
C(21)-C(22)	1.386(8)
C(22)-C(23)	1.372(7)
C(23)-C(24)	1.385(7)
C(24)-C(25)	1.385(7)
C(24)-N(2)	1.398(6)
C(25)-C(26)	1.369(7)
N(2)-C(3)	1.362(7)
C(3)-O(1)	1.200(7)
C(3)-C(4)	1.500(8)
C(5)-N(3)	1.143(7)
N(3)-C(61)	1.402(7)
C(61)-C(66)	1.361(7)
C(61)-C(62)	1.372(7)
C(62)-C(63)	1.378(7)
C(63)-C(64)	1.383(7)
C(64)-C(65)	1.384(7)
C(64)-N(4)	1.407(6)
C(65)-C(66)	1.374(7)
N(4)-C(7)	1.345(6)
C(7)-O(2)	1.213(6)
C(7)-C(8)	1.505(7)

O(2)-Ag(1)#2	2.446(4)
N(5)-O(4)	1.208(7)
N(5)-O(3)	1.240(6)
N(5)-O(5B)	1.248(18)
N(5)-O(5A)	1.249(16)

C(5)-Ag(1)-C(1)	146.8(2)
C(5)-Ag(1)-O(2)#1	97.21(18)
C(1)-Ag(1)-O(2)#1	109.59(19)
C(5)-Ag(1)-O(3)	113.2(2)
C(1)-Ag(1)-O(3)	86.4(2)
O(2)#1-Ag(1)-O(3)	90.89(15)
N(1)-C(1)-Ag(1)	173.3(6)
C(1)-N(1)-C(21)	179.0(6)
C(26)-C(21)-C(22)	121.5(5)
C(26)-C(21)-N(1)	119.2(5)
C(22)-C(21)-N(1)	119.3(5)
C(23)-C(22)-C(21)	118.5(5)
C(22)-C(23)-C(24)	121.3(5)
C(23)-C(24)-C(25)	118.6(5)
C(23)-C(24)-N(2)	123.4(5)
C(25)-C(24)-N(2)	118.0(5)
C(26)-C(25)-C(24)	121.5(5)
C(25)-C(26)-C(21)	118.5(5)
C(3)-N(2)-C(24)	128.2(5)
O(1)-C(3)-N(2)	122.5(6)
O(1)-C(3)-C(4)	123.3(6)
N(2)-C(3)-C(4)	114.2(6)
N(3)-C(5)-Ag(1)	174.4(6)
C(5)-N(3)-C(61)	177.5(6)
C(66)-C(61)-C(62)	121.9(5)
C(66)-C(61)-N(3)	120.2(5)
C(62)-C(61)-N(3)	117.9(5)
C(61)-C(62)-C(63)	117.9(5)
C(62)-C(63)-C(64)	121.4(5)
C(63)-C(64)-C(65)	119.2(5)
C(63)-C(64)-N(4)	116.7(5)
C(65)-C(64)-N(4)	124.1(5)

C(66)-C(65)-C(64)	119.6(5)
C(61)-C(66)-C(65)	120.1(5)
C(7)-N(4)-C(64)	127.9(5)
O(2)-C(7)-N(4)	123.0(5)
O(2)-C(7)-C(8)	122.7(5)
N(4)-C(7)-C(8)	114.3(5)
C(7)-O(2)-Ag(1)#2	141.8(4)
O(4)-N(5)-O(3)	121.9(6)
O(4)-N(5)-O(5B)	125.3(9)
O(3)-N(5)-O(5B)	106.2(14)
O(4)-N(5)-O(5A)	105.9(15)
O(3)-N(5)-O(5A)	127.8(10)
O(5B)-N(5)-O(5A)	51.8(7)
N(5)-O(3)-Ag(1)	115.2(4)

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+1/2,z-1/2 #2 x-1/2,-y+1/2,z+1/2

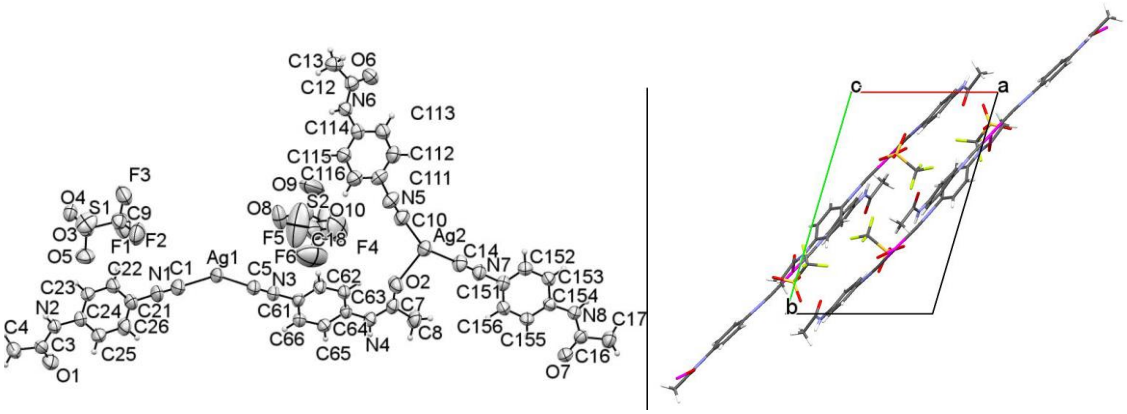


Table S4. Bond lengths [Å] and angles [°] for $[Ag(CN\text{-}C_6H_4\text{-}NHCOCH_3)_2](CF_3SO_3)$ (**5**).

CCDC 1011691

Ag(1)-C(5)	2.095(7)
Ag(1)-C(1)	2.112(8)
Ag(1)-O(7)#1	2.385(5)
C(1)-N(1)	1.125(9)
N(1)-C(21)	1.412(9)
C(21)-C(26)	1.359(11)
C(21)-C(22)	1.365(10)
C(22)-C(23)	1.352(10)
C(23)-C(24)	1.388(10)
C(24)-C(25)	1.382(9)
C(24)-N(2)	1.400(8)
C(25)-C(26)	1.379(11)
N(2)-C(3)	1.346(9)
C(3)-O(1)	1.211(9)
C(3)-C(4)	1.500(10)
C(5)-N(3)	1.131(8)
N(3)-C(61)	1.417(8)
C(61)-C(62)	1.363(10)
C(61)-C(66)	1.372(10)
C(62)-C(63)	1.390(9)
C(63)-C(64)	1.381(9)
C(64)-C(65)	1.366(9)
C(64)-N(4)	1.410(8)
C(65)-C(66)	1.398(9)
N(4)-C(7)	1.336(9)

C(7)-O(2)	1.236(9)
C(7)-C(8)	1.498(9)
O(2)-Ag(2)	2.440(6)
C(9)-F(1)	1.306(11)
C(9)-F(2)	1.321(11)
C(9)-F(3)	1.337(10)
C(9)-S(1)	1.792(9)
S(1)-O(5)	1.424(6)
S(1)-O(4)	1.428(6)
S(1)-O(3)	1.430(7)
Ag(2)-C(10)	2.100(8)
Ag(2)-C(14)	2.102(8)
C(10)-N(5)	1.140(9)
N(5)-C(111)	1.412(9)
C(111)-C(112)	1.356(12)
C(111)-C(116)	1.379(11)
C(112)-C(113)	1.382(11)
C(113)-C(114)	1.382(10)
C(114)-C(115)	1.395(10)
C(114)-N(6)	1.406(9)
C(115)-C(116)	1.376(11)
N(6)-C(12)	1.360(10)
C(12)-O(6)	1.196(9)
C(12)-C(13)	1.493(11)
C(14)-N(7)	1.137(9)
N(7)-C(151)	1.404(9)
C(151)-C(152)	1.361(10)
C(151)-C(156)	1.368(10)
C(152)-C(153)	1.373(10)
C(153)-C(154)	1.402(10)
C(154)-C(155)	1.394(10)
C(154)-N(8)	1.407(8)
C(155)-C(156)	1.376(9)
N(8)-C(16)	1.344(9)
C(16)-O(7)	1.214(9)
C(16)-C(17)	1.507(10)
O(7)-Ag(1)#2	2.385(5)
C(18)-F(5)	1.235(19)

C(18)-F(4)	1.269(13)
C(18)-F(6)	1.363(15)
C(18)-S(2)	1.798(16)
S(2)-O(9)	1.377(9)
S(2)-O(8)	1.404(6)
S(2)-O(10)	1.435(8)

C(5)-Ag(1)-C(1)	144.9(3)
C(5)-Ag(1)-O(7)#1	117.6(2)
C(1)-Ag(1)-O(7)#1	97.2(3)
N(1)-C(1)-Ag(1)	176.9(9)
C(1)-N(1)-C(21)	179.0(9)
C(26)-C(21)-C(22)	121.0(7)
C(26)-C(21)-N(1)	118.4(7)
C(22)-C(21)-N(1)	120.6(7)
C(23)-C(22)-C(21)	119.8(7)
C(22)-C(23)-C(24)	120.9(7)
C(25)-C(24)-C(23)	118.6(6)
C(25)-C(24)-N(2)	124.0(6)
C(23)-C(24)-N(2)	117.4(6)
C(26)-C(25)-C(24)	120.0(7)
C(21)-C(26)-C(25)	119.6(7)
C(3)-N(2)-C(24)	128.0(6)
O(1)-C(3)-N(2)	123.8(7)
O(1)-C(3)-C(4)	122.2(7)
N(2)-C(3)-C(4)	113.9(7)
N(3)-C(5)-Ag(1)	176.5(8)
C(5)-N(3)-C(61)	178.5(8)
C(62)-C(61)-C(66)	122.6(6)
C(62)-C(61)-N(3)	119.0(6)
C(66)-C(61)-N(3)	118.4(6)
C(61)-C(62)-C(63)	119.4(7)
C(64)-C(63)-C(62)	119.6(6)
C(65)-C(64)-C(63)	119.5(6)
C(65)-C(64)-N(4)	117.6(6)
C(63)-C(64)-N(4)	122.8(6)
C(64)-C(65)-C(66)	121.8(7)
C(61)-C(66)-C(65)	117.0(6)

C(7)-N(4)-C(64)	128.8(6)
O(2)-C(7)-N(4)	122.9(6)
O(2)-C(7)-C(8)	121.9(7)
N(4)-C(7)-C(8)	115.2(7)
C(7)-O(2)-Ag(2)	129.2(5)
F(1)-C(9)-F(2)	107.2(8)
F(1)-C(9)-F(3)	107.5(9)
F(2)-C(9)-F(3)	106.1(7)
F(1)-C(9)-S(1)	112.5(6)
F(2)-C(9)-S(1)	112.9(8)
F(3)-C(9)-S(1)	110.3(6)
O(5)-S(1)-O(4)	114.7(4)
O(5)-S(1)-O(3)	114.7(5)
O(4)-S(1)-O(3)	115.3(4)
O(5)-S(1)-C(9)	102.1(4)
O(4)-S(1)-C(9)	103.4(4)
O(3)-S(1)-C(9)	104.3(5)
C(10)-Ag(2)-C(14)	151.3(3)
C(10)-Ag(2)-O(2)	98.4(3)
C(14)-Ag(2)-O(2)	109.4(3)
N(5)-C(10)-Ag(2)	175.6(8)
C(10)-N(5)-C(111)	174.3(9)
C(112)-C(111)-C(116)	121.6(7)
C(112)-C(111)-N(5)	118.1(7)
C(116)-C(111)-N(5)	120.3(8)
C(111)-C(112)-C(113)	120.6(8)
C(114)-C(113)-C(112)	119.4(8)
C(113)-C(114)-C(115)	118.9(7)
C(113)-C(114)-N(6)	123.4(7)
C(115)-C(114)-N(6)	117.7(6)
C(116)-C(115)-C(114)	121.6(7)
C(115)-C(116)-C(111)	117.9(8)
C(12)-N(6)-C(114)	128.5(6)
O(6)-C(12)-N(6)	122.9(8)
O(6)-C(12)-C(13)	122.7(8)
N(6)-C(12)-C(13)	114.3(7)
N(7)-C(14)-Ag(2)	175.7(8)
C(14)-N(7)-C(151)	179.6(8)

C(152)-C(151)-C(156)	121.4(7)
C(152)-C(151)-N(7)	119.2(7)
C(156)-C(151)-N(7)	119.4(7)
C(151)-C(152)-C(153)	119.7(7)
C(152)-C(153)-C(154)	120.2(7)
C(155)-C(154)-C(153)	118.7(6)
C(155)-C(154)-N(8)	124.7(6)
C(153)-C(154)-N(8)	116.5(6)
C(156)-C(155)-C(154)	119.9(6)
C(151)-C(156)-C(155)	119.9(7)
C(16)-N(8)-C(154)	127.6(6)
O(7)-C(16)-N(8)	123.2(7)
O(7)-C(16)-C(17)	122.3(7)
N(8)-C(16)-C(17)	114.5(7)
C(16)-O(7)-Ag(1)#2	130.8(5)
F(5)-C(18)-F(4)	112.6(16)
F(5)-C(18)-F(6)	109.9(15)
F(4)-C(18)-F(6)	104.4(13)
F(5)-C(18)-S(2)	112.0(11)
F(4)-C(18)-S(2)	113.3(12)
F(6)-C(18)-S(2)	103.9(11)
O(9)-S(2)-O(8)	114.3(6)
O(9)-S(2)-O(10)	108.6(8)
O(8)-S(2)-O(10)	119.4(5)
O(9)-S(2)-C(18)	104.0(7)
O(8)-S(2)-C(18)	105.2(5)
O(10)-S(2)-C(18)	103.4(8)

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y+1,z #2 x+1,y-1,z

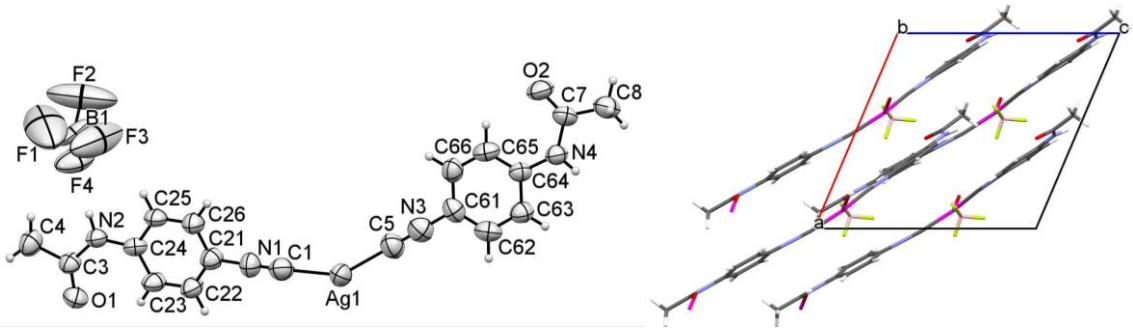


Table S5. Bond lengths [Å] and angles [°] for $[Ag(CN\text{-}C_6H_4\text{-}NHCOCH_3)_2](BF_4)$ (**6**).

CCDC 1011692

Ag(1)-C(5)	2.092(7)
Ag(1)-C(1)	2.094(8)
Ag(1)-O(1)#1	2.444(4)
C(1)-N(1)	1.132(9)
N(1)-C(21)	1.408(8)
C(21)-C(22)	1.370(8)
C(21)-C(26)	1.375(8)
C(22)-C(23)	1.368(8)
C(23)-C(24)	1.387(7)
C(24)-N(2)	1.395(7)
C(24)-C(25)	1.399(8)
C(25)-C(26)	1.353(8)
N(2)-C(3)	1.346(7)
C(3)-O(1)	1.201(6)
C(3)-C(4)	1.522(8)
O(1)-Ag(1)#2	2.444(4)
C(5)-N(3)	1.167(8)
N(3)-C(61)	1.383(8)
C(61)-C(62)	1.377(9)
C(61)-C(66)	1.386(8)
C(62)-C(63)	1.375(9)
C(63)-C(64)	1.390(7)
C(64)-C(65)	1.357(8)
C(64)-N(4)	1.418(7)
C(65)-C(66)	1.368(9)
N(4)-C(7)	1.354(7)
C(7)-O(2)	1.227(7)

C(7)-C(8)	1.495(9)
B(1)-F(1)	1.1132
B(1)-F(3)	1.2456
B(1)-F(4)	1.312(6)
B(1)-F(2)	1.3313

C(5)-Ag(1)-C(1)	146.1(3)
C(5)-Ag(1)-O(1)#1	110.2(2)
C(1)-Ag(1)-O(1)#1	101.5(2)
N(1)-C(1)-Ag(1)	175.2(6)
C(1)-N(1)-C(21)	178.5(6)
C(22)-C(21)-C(26)	120.2(5)
C(22)-C(21)-N(1)	120.4(5)
C(26)-C(21)-N(1)	119.3(5)
C(23)-C(22)-C(21)	120.8(5)
C(22)-C(23)-C(24)	119.6(5)
C(23)-C(24)-N(2)	124.1(5)
C(23)-C(24)-C(25)	118.5(5)
N(2)-C(24)-C(25)	117.3(5)
C(26)-C(25)-C(24)	121.2(5)
C(25)-C(26)-C(21)	119.5(5)
C(3)-N(2)-C(24)	127.6(4)
O(1)-C(3)-N(2)	124.4(5)
O(1)-C(3)-C(4)	122.8(5)
N(2)-C(3)-C(4)	112.8(5)
C(3)-O(1)-Ag(1)#2	146.1(4)
N(3)-C(5)-Ag(1)	176.6(6)
C(5)-N(3)-C(61)	179.6(7)
C(62)-C(61)-N(3)	119.3(5)
C(62)-C(61)-C(66)	120.7(5)
N(3)-C(61)-C(66)	120.0(6)
C(63)-C(62)-C(61)	120.0(5)
C(62)-C(63)-C(64)	118.9(6)
C(65)-C(64)-C(63)	120.4(5)
C(65)-C(64)-N(4)	124.5(5)
C(63)-C(64)-N(4)	115.0(5)
C(64)-C(65)-C(66)	121.3(5)
C(65)-C(66)-C(61)	118.6(5)

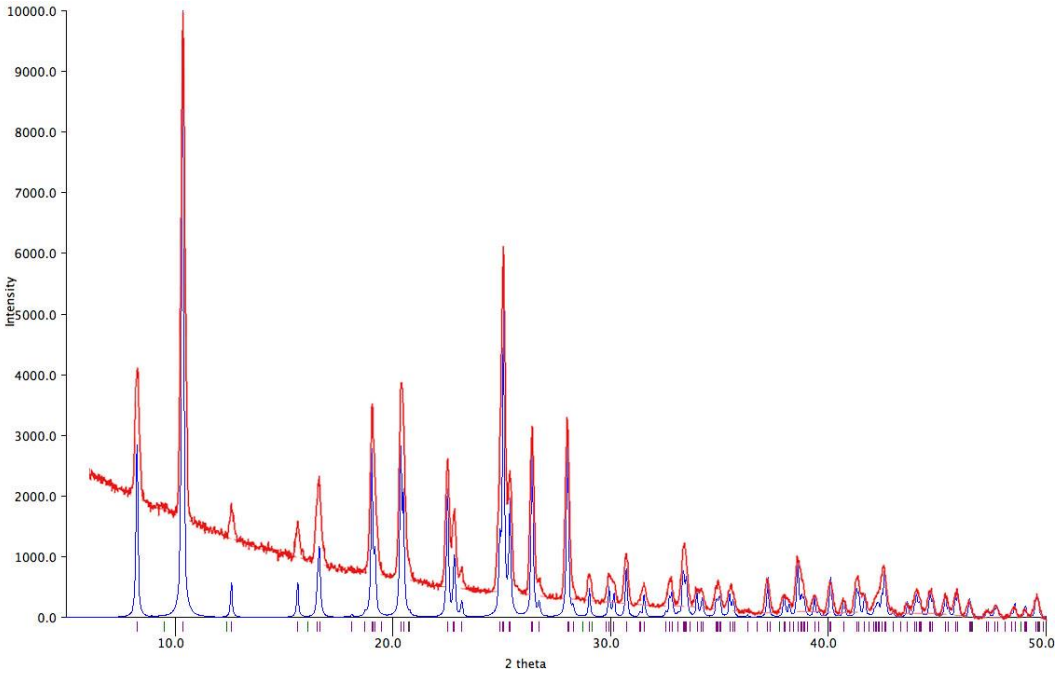
C(7)-N(4)-C(64)	127.9(5)
O(2)-C(7)-N(4)	122.7(6)
O(2)-C(7)-C(8)	122.4(5)
N(4)-C(7)-C(8)	114.9(5)
F(1)-B(1)-F(3)	102.1
F(1)-B(1)-F(4)	117.0(7)
F(3)-B(1)-F(4)	111.0(5)
F(1)-B(1)-F(2)	101.3
F(3)-B(1)-F(2)	109.6
F(4)-B(1)-F(2)	114.8(6)

Symmetry transformations used to generate equivalent atoms:

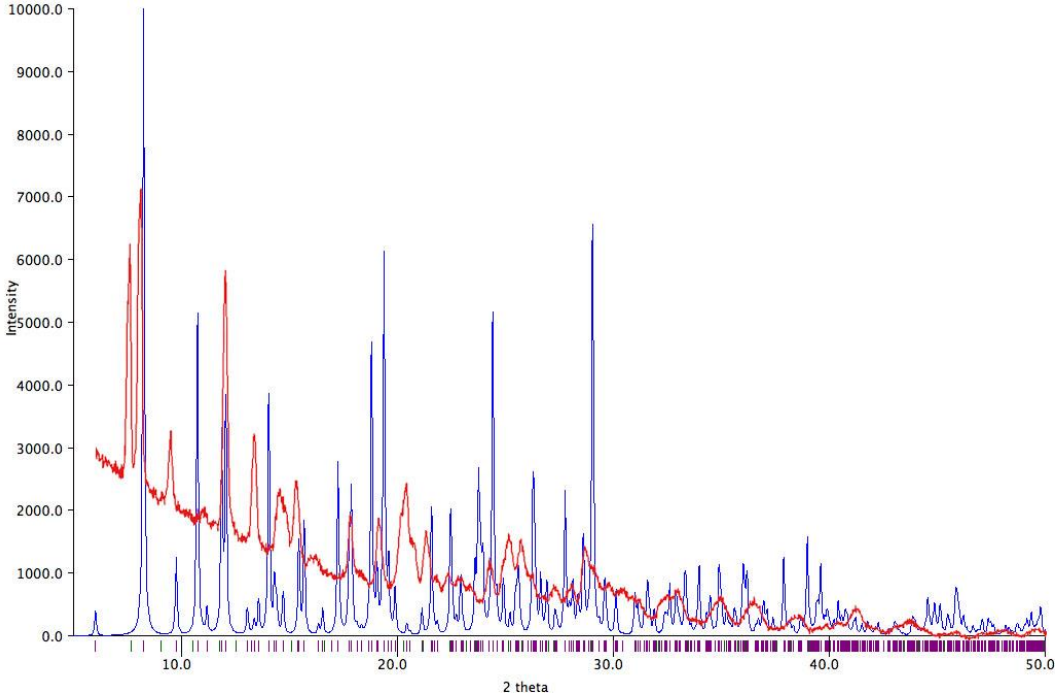
#1 x-1/2,-y+1/2,z+1/2 #2 x+1/2,-y+1/2,z-1/2

Experimental (red) and calculated (blue) Powder X-Ray Diffraction diagrams for complexes 2 – 6

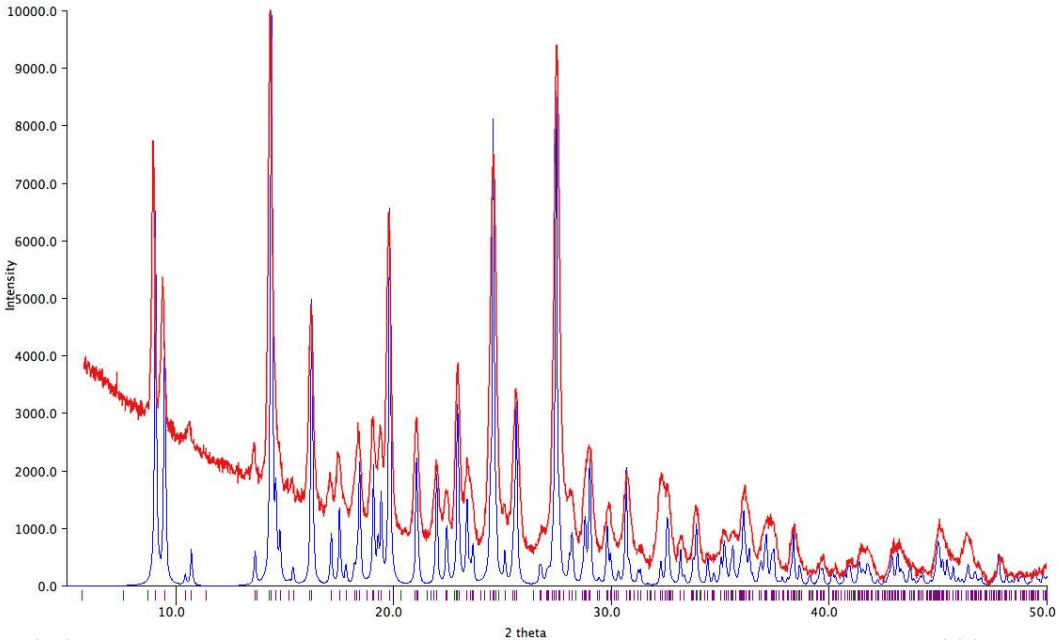
Compound 2



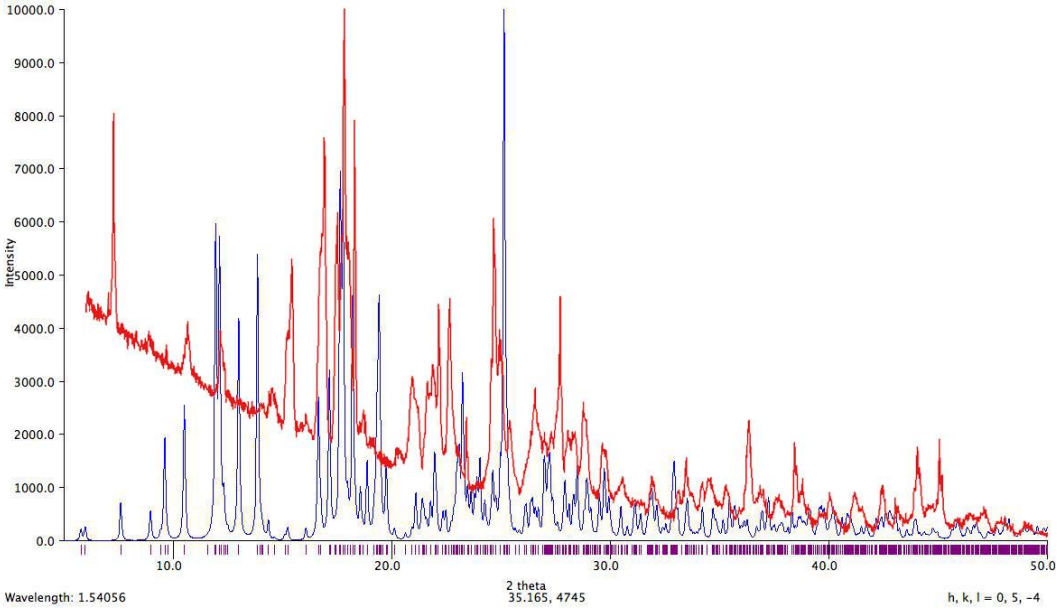
Compound 3



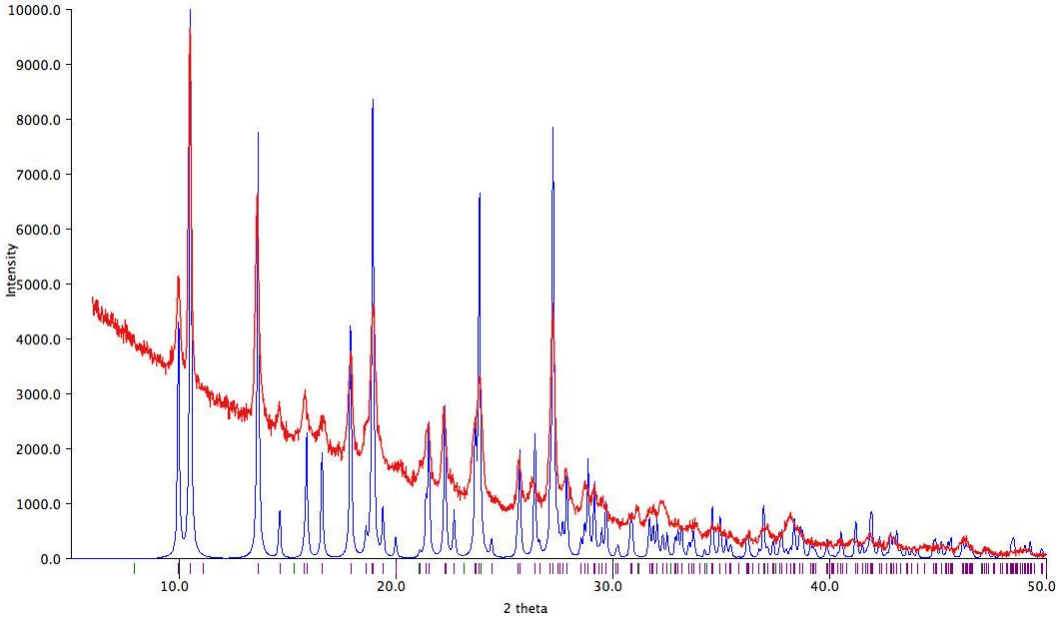
Compound 4



Compound 5



Compound 6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9000.0
8000.0
7000.0
6000.0
5000.0
4000.0
3000.0
2000.0
1000.0
0.0
Intensity
10.0
20.0
30.0
40.0
50.0
2 theta