## Supporting Informations

## Solvent-mediated crystal-to-crystal transformations from a cationic homometallic metal-organic framework to heterometallic frameworks

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Ag(1)-N(12)	2.187(3)	Cr(1)-O(6)	1.609(2)
Ag(1)-N(2)#1	2.214(3)	Cr(1)-O(7)	1.622(3)
Ag(1)-N(8)#2	2.445(3)	Cr(1)-O(2)	1.792(3)
Ag(1)-Ag(2)#3	3.1396(7)	Cr(2)-O(3)	1.600(3)
Ag(2)-N(7)#2	2.207(3)	Cr(2)-O(4)	1.616(2)
Ag(2)-N(5)	2.235(3)	Cr(2)-O(1)	1.619(3)
Ag(2)-N(11)	2.418(3)	Cr(2)-O(2)	1.785(3)
Ag(2)-O(1)	2.555(3)	Cr(1)-O(5)	1.609(3)
N(12)-Ag(1)-N(2)#1	158.28(10)	N(11)-Ag(2)-Ag(1)#4	108.91(7)
N(12)-Ag(1)-N(8)#2	105.58(10)	O(1)-Ag(2)-Ag(1)#4	130.75(7)
N(2)#1-Ag(1)-N(8)#2	96.10(10)	O(5)-Cr(1)-O(6)	109.08(14)
N(12)-Ag(1)-Ag(2)#3	83.47(8)	O(5)-Cr(1)-O(7)	109.04(14)
N(2)#1-Ag(1)-Ag(2)#3	81.75(8)	O(6)-Cr(1)-O(7)	110.53(14)
N(8)#2-Ag(1)-Ag(2)#3	136.00(7)	O(5)-Cr(1)-O(2)	107.70(13)
N(7)#2-Ag(2)-N(5)	157.79(10)	O(6)-Cr(1)-O(2)	108.64(13)
N(7)#2-Ag(2)-N(11)	108.43(9)	O(7)-Cr(1)-O(2)	111.77(15)
N(5)-Ag(2)-N(11)	93.14(10)	O(3)-Cr(2)-O(4)	109.09(16)
N(7)#2-Ag(2)-O(1)	92.81(10)	O(3)-Cr(2)-O(1)	110.03(17)
N(5)-Ag(2)-O(1)	82.92(10)	O(4)-Cr(2)-O(1)	109.47(15)
N(11)-Ag(2)-O(1)	113.77(9)	O(3)-Cr(2)-O(2)	107.86(15)
N(7)#2-Ag(2)-Ag(1)#4	96.13(7)	O(4)-Cr(2)-O(2)	110.18(13)
N(5)-Ag(2)-Ag(1)#4	71.16(7)	O(1)-Cr(2)-O(2)	110.18(16)

 Table S1 Selected Bond Lengths (Å) and Bond Angles (°) for Complex 1.

Symmetry transformations used to generate equivalent atoms: #1 x-1/4, -y+1/4, z-5/4; #2 - x+3/4, y+1/4, z-1/4; #3 x-1/4, -y+1/4, z-1/4; #4 x+1/4, -y+1/4, z+1/4.

Ag(1)-N(13)	2.255(3)	Cr(1)-O(4)	1.618(4)
Ag(1)-N(7)	2.258(3)	Cr(1)-O(12)	1.620(4)
Ag(1)-N(2)#1	2.469(4)	Cr(1)-O(5)	1.790(4)
Ag(1)-O(8)	2.599(4)	Cr(2)-O(13)	1.597(4)
Ag(2)-N(17)#2	2.196(3)	Cr(2)-O(11)	1.608(3)
Ag(2)-N(17)#3	2.196(3)	Cr(2)-O(3)	1.614(4)
Ag(2)-O(12)#4	2.590(4)	Cr(2)-O(5)	1.783(4)
Ag(2)-O(12)	2.590(4)	Cr(3)-O(9)	1.612(4)
Ag(3)-N(6)	2.178(3)	Cr(3)-O(8)	1.618(4)
Ag(3)-N(10)	2.190(3)	Cr(3)-O(6)	1.621(4)
Ag(3)-Ag(5)	3.3558(6)	Cr(3)-O(14)	1.825(3)
Ag(4)-N(12)	2.248(3)	Cr(4)-O(1)	1.582(5)
Ag(4)-N(8)	2.256(3)	Cr(4)-O(2)	1.583(5)
Ag(4)-N(18)#5	2.534(4)	Cr(4)-O(10)	1.618(3)
Ag(4)-O(10)	2.566(3)	Cr(4)-O(14)	1.799(3)
Ag(5)-N(15)#6	2.189(4)	Cr(1)-O(7)	1.600(4)
Ag(5)-O(14)	2.271(3)	Ag(5)-O(3)	2.481(4)
Ag(5)-O(6)#3	2.474(4)		
N(13)-Ag(1)-N(7)	162.26(14)	O(14)-Ag(5)-Ag(3)	78.75(9)
N(13)-Ag(1)-N(2)#1	93.27(13)	O(6)#3-Ag(5)-Ag(3)	143.56(9)
N(7)-Ag(1)-N(2)#1	92.26(13)	O(3)-Ag(5)-Ag(3)	132.74(10)
N(13)-Ag(1)-O(8)	111.17(14)	O(7)-Cr(1)-O(4)	110.7(2)
N(7)-Ag(1)-O(8)	86.17(14)	O(7)-Cr(1)-O(12)	109.5(2)
N(2)#1-Ag(1)-O(8)	84.00(13)	O(4)-Cr(1)-O(12)	110.8(2)
N(17)#2-Ag(2)-N(17)#3	179.998(2)	O(7)-Cr(1)-O(5)	108.1(2)
N(17)#2-Ag(2)-O(12)#4	86.84(14)	O(4)-Cr(1)-O(5)	107.9(2)
N(17)#3-Ag(2)-O(12)#4	93.16(14)	O(12)-Cr(1)-O(5)	109.8(2)
N(17)#2-Ag(2)-O(12)	93.16(14)	O(13)-Cr(2)-O(11)	109.8(2)
N(17)#3-Ag(2)-O(12)	86.84(14)	O(13)-Cr(2)-O(3)	111.1(2)
O(12)#4-Ag(2)-O(12)	180.00(19)	O(11)-Cr(2)-O(3)	110.3(2)

**Table S2** Selected Bond Lengths (Å) and Bond Angles (°) for Complex 2.

N(6)-Ag(3)-N(10)	172.29(14)	O(13)-Cr(2)-O(5)	107.7(2)
N(6)-Ag(3)-Ag(5)	112.89(10)	O(11)-Cr(2)-O(5)	109.24(19)
N(10)-Ag(3)-Ag(5)	74.18(10)	O(3)-Cr(2)-O(5)	108.7(2)
N(12)-Ag(4)-N(8)	162.68(13)	O(9)-Cr(3)-O(8)	109.6(2)
N(12)-Ag(4)-N(18)#5	94.99(13)	O(9)-Cr(3)-O(6)	111.7(2)
N(8)-Ag(4)-N(18)#5	94.07(13)	O(8)-Cr(3)-O(6)	112.0(2)
N(12)-Ag(4)-O(10)	83.58(12)	O(9)-Cr(3)-O(14)	107.13(18)
N(8)-Ag(4)-O(10)	90.35(13)	O(8)-Cr(3)-O(14)	108.42(18)
N(18)#5-Ag(4)-O(10)	168.56(12)	O(6)-Cr(3)-O(14)	107.78(18)
N(15)#6-Ag(5)-O(14)	148.55(14)	O(1)-Cr(4)-O(2)	109.5(4)
N(15)#6-Ag(5)-O(6)#3	112.89(14)	O(1)-Cr(4)-O(10)	112.4(3)
O(14)-Ag(5)-O(6)#3	88.07(13)	O(2)-Cr(4)-O(10)	111.0(3)
N(15)#6-Ag(5)-O(3)	110.41(15)	O(1)-Cr(4)-O(14)	106.7(2)
O(14)-Ag(5)-O(3)	95.08(13)	O(2)-Cr(4)-O(14)	108.7(3)
O(6)#3-Ag(5)-O(3)	81.77(14)	O(10)-Cr(4)-O(14)	108.39(17)

Symmetry transformations used to generate equivalent atoms: #1 *x*, *y*-1, *z*; #2 *x*-1, *y*, *z*-1; #3 -x+4, -*y*+3, -*z*+3; #4 -*x*+3, -*y*+3, -*z*+2; #5 *x*, *y*, *z*-1; #6 *x*, *y*+1, *z*+1.



Figure S1 Simulate and experimental PXRD patterns of 1.



Figure S2 Simulate and experimental PXRD patterns of 2.



Figure S3 Oscilloscope traces of SHG signals of 1.