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Supporting Information for

Anion induced structural transformation in silver-(3,6-dimethoxy-1,2,4,5-tetrazine) coordination polymers under mechanochemical conditions

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General Methods All glassware was oven-dried prior to use. Powder X-ray diffraction (PXRD) analysis was performed on a RIGAKU Ultima IV diffractometer using Cu Kα radiation (wavelength 1.541 Å) in focused beam configuration with a continuous scan rate of 3° min^{-1} in the 3-80° range. Simulated PXRD patterns were calculated from single crystal X-ray diffraction data using the Mercury 3.3 program. Elemental analyses were performed on a Thermo Finnigan Flash EA1112 unit. IR spectra were recorded using KBr pellets for solids on a Bruker model Vertex70 spectrometer

Mechanochemical reactions were carried out in a FRITSCH Pulverisette 23 mini-mill model, using 10 ml zircon oxide grinding bowls with 10 mm diameter zirconium oxide milling balls. The reactions were monitored by powder X-ray diffractions.

Materials Silver(I) perchlorate ($AgClO_4$, anhydrous, Alfa Aesar) and Silver(I) trifluoromethanesulfonate ($AgCF_3SO_3$, 98 %, Alfa Aesar) were used as received. 3,6-dimethoxy-1,2,4,5-tetrazine (**dmotz**) was prepared and purified by sublimation following literature procedure previously reported.[1]

Synthesis of $[Ag(dmotz)(CF_3SO_3)]_n$ (1)

$$dmotz + AgCF_3SO_3 \longrightarrow [Ag(dmotz)]_nCF_3SO_3\ (1)$$

A mixture of $Ag(CF_3SO_3)$ (13mg, 0.05 mmol) and dmotz (7 mg, 0.05 mmol) were milled in a zirconium oxide grinding bowl with a zirconium oxide milling ball (10 mm in diameter) in a mini-

mill up to 30 Hz for 5 min. Progress of the reaction was monitored by Powder XRD analysis. Initially pink mixture turned to dark red solid with quantitative yields. The single crystal of **1** was obtained by slow diffusion of diethyl ether to THF solution of **1.**

Synthesis of $[\{Ag(dmotz)_2\}(ClO_4)]_n$ (2)

$$dmotz + AgClO_4 \longrightarrow [Ag(dmotz)_2]_nClO_4\ (2)$$

A mixture of $Ag(ClO_4)$ (20 mg, 0.1 mmol) and dmotz (28 mg, 0.2 mmol) were milled in a zirconium oxide grinding bowl with a zirconium oxide milling ball (10 mm in diameter) in a mini-mill up to 40 Hz for 5 min. Progress of the reaction was monitored by Powder XRD analysis. Initially pale pink mixture turned to bright red solid.

The single crystal of **2** was obtained by vapor diffusion of diethyl ether into CH_2Cl_2 solution of **1.** Elemental analysis for $C_8H_{12}AgClN_8O_8$, calcd. (%): C, 19.55; H, 2.46; N, 22.80. Found (%): C, 19.53; H, 2.42; N, 22.78.

Structural transformation from $[Ag(dmotz)(CF_3SO_3)]_n$ to $[\{Ag(dmotz)_2\}(ClO_4)]_n$

$$[Ag(dmotz)(CF_3SO_3)]_n + dmotz \xrightarrow{NaClO_4} [Ag(dmotz)_2]ClO_4 + NaCF_3SO_3$$

A mixture of compound **1** (40mg, 0.10 mmol), $NaClO_4$ (12mg, 0.10 mmol) and dmotz(14mg, 0.1 mmol) were in a zirconium oxide grinding bowl with a zirconium oxide milling ball (10 mm in diameter) in a mini-mill up to 40 Hz for 5 min.

Single crystal X-ray diffraction analysis of $[Ag(dmotz)(CF_3SO_3)]_n$ (1) A specimen of suitable size and quality was coated with Paratone oil and mounted on a MiTeGen MicroMount©. Reflection data were collected on a Bruker D8 Venture PHOTON 100 area detector diffractometer, with Mo K_α (λ = 0.71073 Å). The full sphere of reflection data was collected as ω and φ scan frames at 0.5°/frame and an exposure time of 10 s/frame. Cell parameters were determined and refined by the APEX2 program.[2] Data reduction was performed using the SAINT software.[3] The data were corrected for Lorentz and polarization effects. Empirical absorption correction was applied using the SADABS program.[4] The structure was solved by direct methods and all nonhydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using the SHELXTL and Olex 2 GUI program.[5] Hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters.

Single crystal X-ray diffraction analysis of $[\{Ag(dmotz)\}(ClO_4)]_n$ (2) A specimen of suitable size and quality was coated with Paratone oil and mounted on a MiTeGen MicroMount©. Reflection data were collected on a Bruker D8 Venture PHOTON 100 area detector diffractometer, with Mo K_α (λ = 0.71073 Å). The full sphere of reflection data was collected as ω and φ scan frames with 1°/frame and an exposure time of 20 s/frame. Cell parameters were determined and refined by the APEX2 program.[2] Data reduction was performed using SAINT software.[3] The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program.[4] The structure was solved by direct methods, and all nonhydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using the SHELXTL and Olex 2 GUI program.[5] Hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters.

Table S1. Crystallographic Data for **$[Ag(dmotz)(CF_3SO_3)]_n$, 1** and **$[Ag(dmotz)_2(CF_3SO_3)]_n$, 2**

	1	**2**
Empirical formula	$C_5H_6AgF_3N_4O_5S$	$C_8H_{12}AgClN_8O_8$
Formula weight	399.07	491.58
Temperature/K	303.5	139.9
Crystal system	Orthorhombic	triclinic
Space group	Aea2	P-1
a/Å	20.8674(13)	7.1463(10)
b/Å	14.9814(10)	7.5474(10)
c/Å	7.6418(4)	7.6047(10)
α/°	90	87.511(5)
β/°	90	88.728(5)
γ/°	90	74.489(5)
Volume/Å^3	2389.0(3)	394.83(9)
Z	8	1
ρ_{calc}mg/mm^3	2.219	2.067
m/mm^{-1}	1.925	1.508
F(000)	1552.0	244.0
Crystal size/mm^3	0.3 × 0.2 × 0.2	0.2 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection	5.438 to 49.96	5.362 to 86.724
Index ranges	$-24 \le h \le 24$, $-17 \le k \le 17$, $-8 \le l \le 9$	$-13 \le h \le 13$, $-14 \le k \le 14$, $-14 \le l \le 14$
Reflections collected	26101	25128
Independent reflections	2018 [R(int) = 0.0193, R(sigma)= 0.0083]	5711 [R_{int} = 0.0503, R_{sigma} = 0.0521]
Data/restraints/parameters	2018/1/175	5711/0/141
Goodness-of-fit on F^2	1.103	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0176, wR_2 = 0.0470	R_1 = 0.0346, wR_2 = 0.0748
Final R indexes [all data]	R_1 = 0.0179 wR_2 = 0.0473	R_1 = 0.0483, wR_2 = 0.0802
Largest diff. peak/hole / e Å^{-3}	0.35/-0.27	0.95/-0.54
Flack parameter	0.002(7)	

Table S2. Bond Distances (Å) in **[Ag(dmotz)$_2$(CF$_3$SO$_3$)]$_n$, 1** [a]

Ag1-N1	2.298(3)	C6-O9	1.317(5)
Ag1-N2[1]	2.378(3)	O7-C8	1.438(6)
Ag1-O13[1]	2.494(6)	O9-C10	1.448(6)
Ag1-O13	2.524(5)	S11-C12	1.805(6)
N1-N2	1.311(5)	S11-O13	1.436(4)
N1-C6	1.337(5)	S11-O14	1.408(4)
N2-Ag1[2]	2.378(3)	S11-O15	1.438(4)
N2-C3	1.341(6)	C12-F16	1.330(7)
C3-N4	1.333(5)	C12-F17	1.324(7)
C3-O7	1.308(6)	C12-F18	1.297(6)
N4-N5	1.313(6)	O13-Ag1[2]	2.494(6)
N5-C6	1.326(5)		

[1]1/2-X,+Y,1/2+Z; [2]1/2-X,+Y,-1/2+Z

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table S3. Bond Angles (deg) in **[Ag(dmotz)$_2$(CF$_3$SO$_3$)]$_n$, 1** [a]

N1-Ag1-N2[1]	120.56(10)	O9-C6-N5	121.3(3)
N1-Ag1-O13	87.71(15)	C3-O7-C8	118.3(4)
N1-Ag1-O13[1]	147.44(12)	C6-O9-C10	117.8(4)
N2[1]-Ag1-O13	89.97(14)	O13-S11-C12	104.6(3)
N2[1]-Ag1-O13[1]	86.72(12)	O13-S11-O15	109.1(3)
O13[1]-Ag1-O13	111.47(17)	O14-S11-C12	103.6(3)
N2-N1-Ag1	121.6(2)	O14-S11-O13	119.0(3)
N2-N1-C6	117.4(3)	O14-S11-O15	114.8(3)
C6-N1-Ag1	120.2(3)	O15-S11-C12	103.9(3)
N1-N2-Ag1[2]	126.4(2)	F16-C12-S11	110.6(4)
N1-N2-C3	117.4(3)	F17-C12-S11	111.6(4)
C3-N2-Ag1[2]	114.1(3)	F17-C12-F16	104.4(6)
N4-C3-N2	124.6(5)	F18-C12-S11	112.2(4)
O7-C3-N2	113.9(3)	F18-C12-F16	107.9(5)
O7-C3-N4	121.5(5)	F18-C12-F17	109.7(6)
N5-N4-C3	117.6(4)	Ag1[2]-O13-Ag1	107.95(14)
N4-N5-C6	117.5(3)	S11-O13-Ag1	147.7(4)
N5-C6-N1	125.1(4)	S11-O13-Ag1[2]	104.1(3)
O9-C6-N1	113.6(4)		

[1]1/2-X,+Y,1/2+Z; [2]1/2-X,+Y,-1/2+Z

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table S4. Bond Distances (Å) in **[Ag(dmotz)$_2$(ClCO$_4$)]$_n$, 2** [a]

Ag1-N1	**2.4593(10)**	**N4-C6^3**	**1.3370(14)**
Ag1-N1^1	**2.4593(10)**	**N5-C6**	**1.3379(14)**
Ag1-N4^1	**2.4341(10)**	**C6-N4^3**	**1.3371(14)**
Ag1-N4	**2.4342(10)**	**C6-O9**	**1.3267(13)**
N1-N2	**1.3160(15)**	**O7-C8**	**1.4439(18)**
N1-C3^2	**1.3366(13)**	**O9-C10**	**1.4433(18)**
N2-C3	**1.3334(14)**	**Cl11-O12**	**1.442(3)**
C3-N1^2	**1.3366(13)**	**Cl11-O13**	**1.369(2)**
C3-O7	**1.3242(15)**	**Cl11-O14**	**1.476(2)**
N4-N5	**1.3197(13)**	**Cl11-O15**	**1.451(2)**

^{1}1/2-X,+Y,1/2+Z; ^{2}1/2-X,+Y,-1/2+Z

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

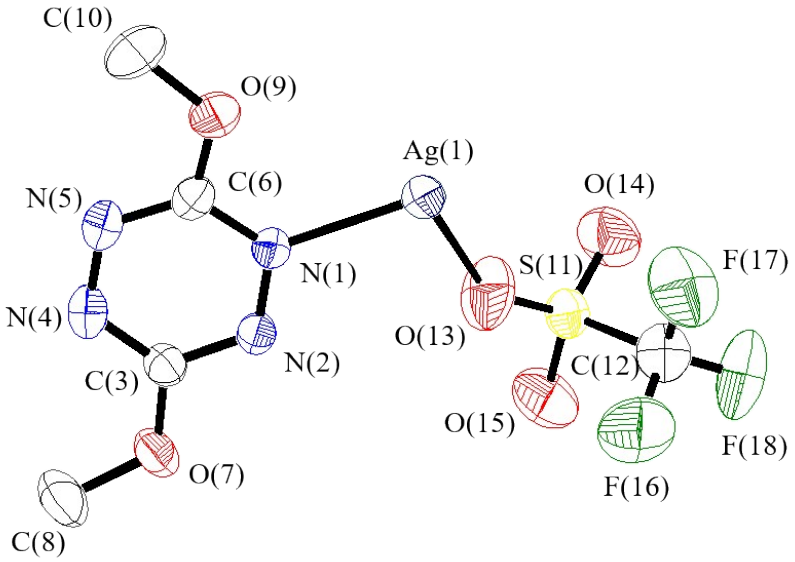
Table S5. Bond Angles (deg) in **[Ag(dmotz)$_2$(Ag(dmotz)$_2$(ClCO$_4$)]$_n$, 2** [a]

N1^1-Ag1-N1	180.00(5)	N5-N4-C6^3	117.92(9)
N4^1-Ag1-N1^1	87.30(3)	C6^3-N4-Ag1	113.48(7)
N4-Ag1-N11	92.70(3)	N4-N5-C6	116.48(9)
N4-Ag1-N1	87.30(3)	N4^3-C6-N5	125.60(9)
N4^1-Ag1-N1	92.70(3)	O9-C6-N4^3	113.52(10)
N4^1-Ag1-N4	180	O9-C6-N5	120.87(10)
N2-N1-Ag1	127.29(6)	C3-O7-C8	117.49(11)
N2-N1-C32	117.61(9)	C6-O9-C10	117.47(11)
C3^2-N1-Ag1	115.08(8)	O12-Cl11-O14	107.79(16)
N1-N2-C3	116.94(9)	O12-Cl11-O15	108.5(2)
N2-C3-N1^2	125.45(11)	O13-Cl11-O12	111.86(19)
O7-C3-N1^2	113.57(10)	O13-Cl11-O14	110.26(17)
O7-C3-N2	120.98(9)	O13-Cl11-O15	112.57(18)
N5-N4-Ag1	128.59(7)	O15-Cl11-O14	105.58(16)

^{1}1/2-X,+Y,1/2+Z; ^{2}1/2-X,+Y,-1/2+Z

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Figure S1. Asymmetric unit of **1** with 50% probability thermal ellipsoids(Up) and packing structure(down).



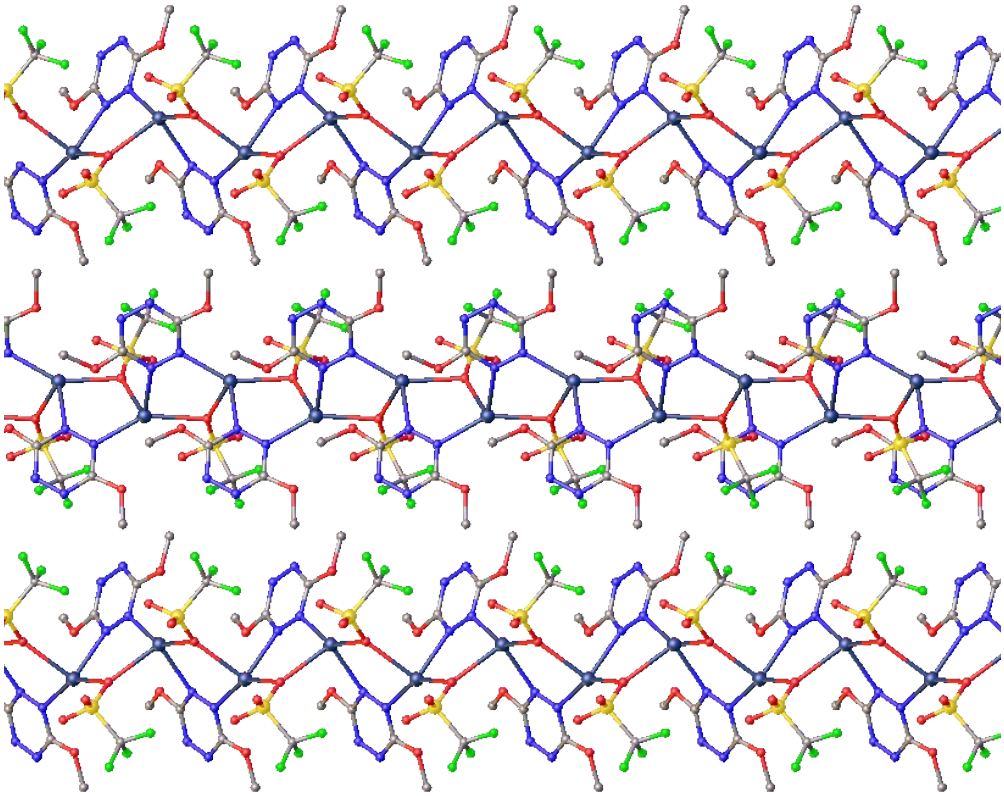


Figure S2. Asymmetric unit of **2** with 50% probability thermal ellipsoids(Up) and packing structure(down).

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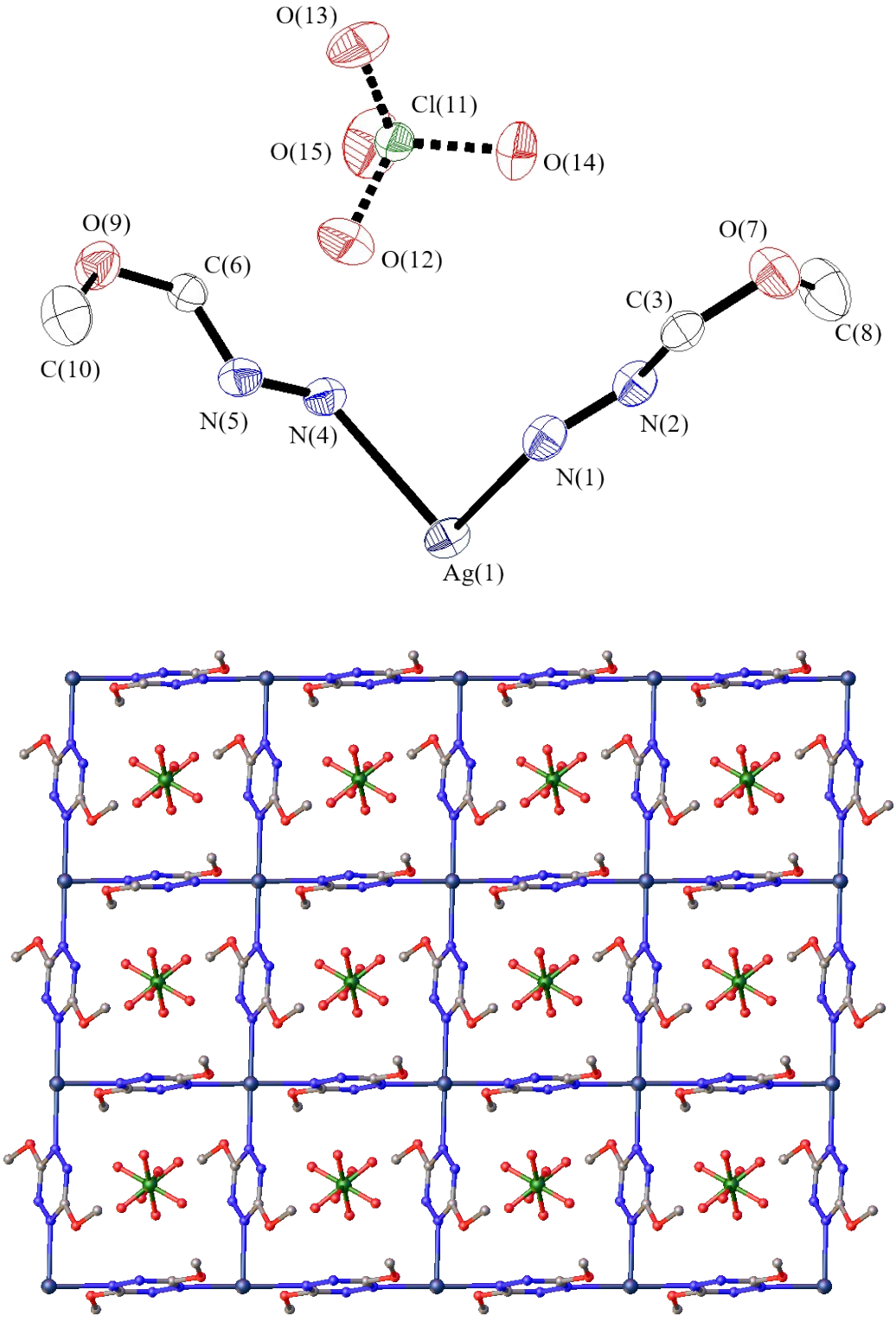
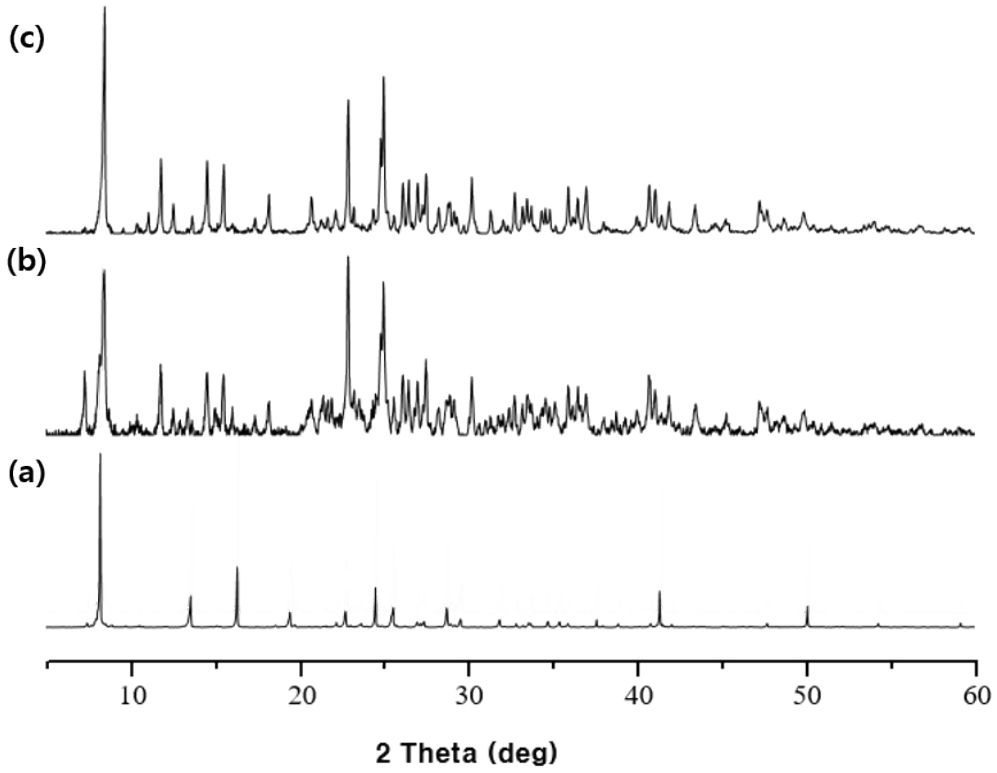
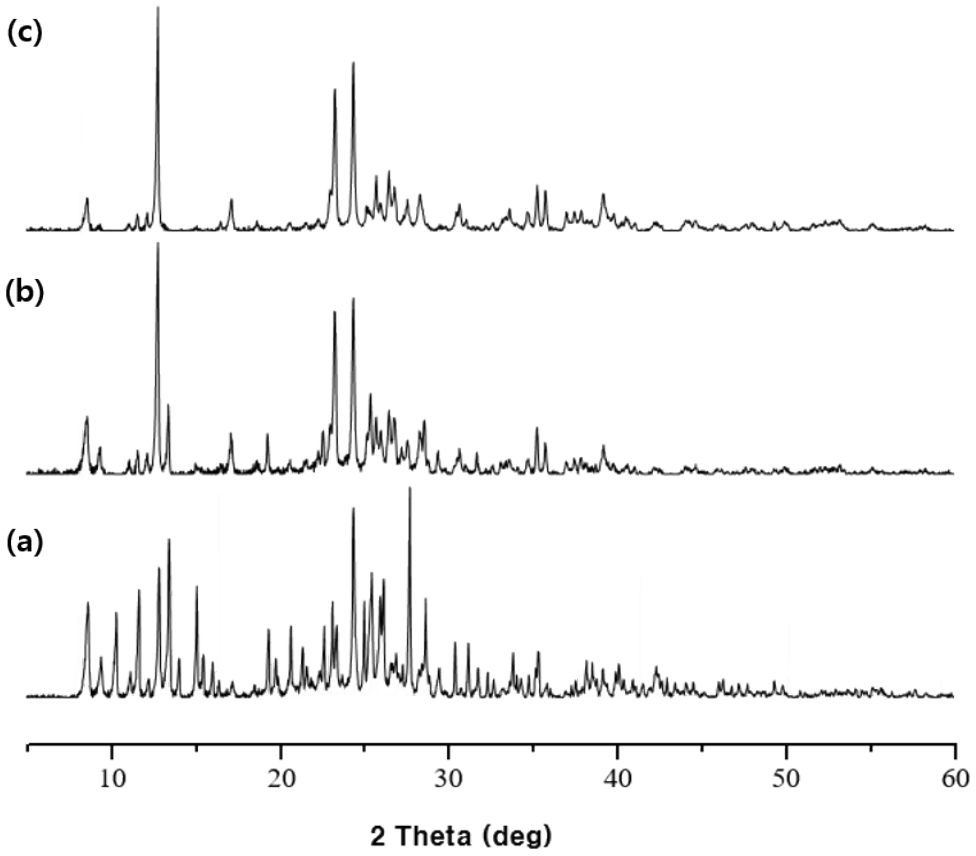


Figure S3. PXRD patterns of the mechanochemical synthesis of $[Ag(dmotz)(CF_3SO_3)]_n$



PXRD patterns of: (a) reaction mixture of $Ag(CF_3SO_3)$ and dmotz; (b) reaction mixture of $Ag(CF_3SO_3)$ and dmotz after 1 min ball milling(30 Hz); (c) reaction mixture of $Ag(CF_3SO_3)$ and dmotz after 2 min ball milling(30 Hz)

Figure S4. PXRD patterns of the mechanochemical synthesis of $[Ag(dmotz)_2(CF_3SO_3)]_n$



PXRD patterns of: (a) reaction mixture of $Ag(ClO_4)$ and dmotz; (b) reaction mixture of $Ag(ClO_4)$ and dmotz after 1 min ball milling(25 Hz); (c) reaction mixture of $Ag(ClO_4)$ and dmotz after 2 min ball milling(25 Hz)

Figure S5. PXRD patterns of with $NaClO_4$, (a) $[\{Ag(dmotz)_2\}(ClO_4)]_n$, (b)$\{Ag(dmotz)_2\}(ClO_4)]_n$, $Na(CF_3SO_3)$ from the reaction of **1** (c) $Na(CF_3SO_3)$ and (d) $[Ag(dmotz)(CF_3SO_3)]_n$.

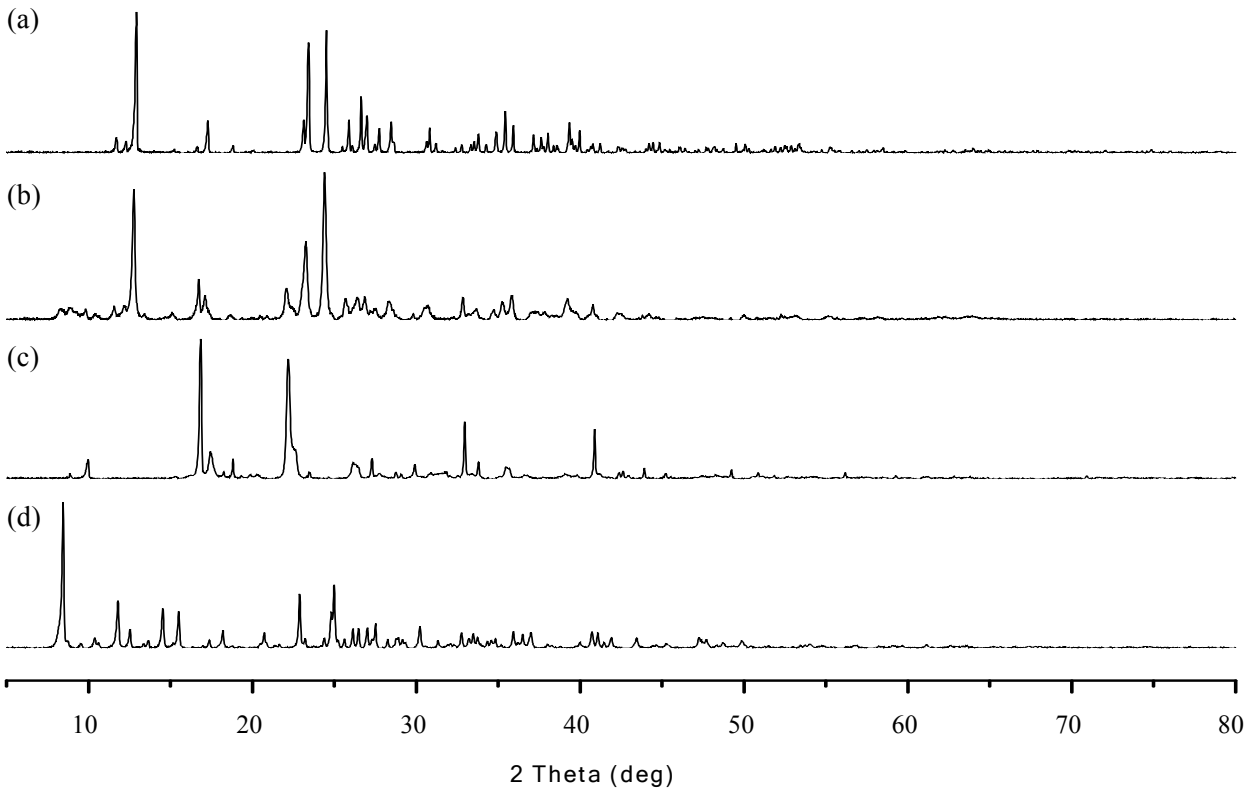
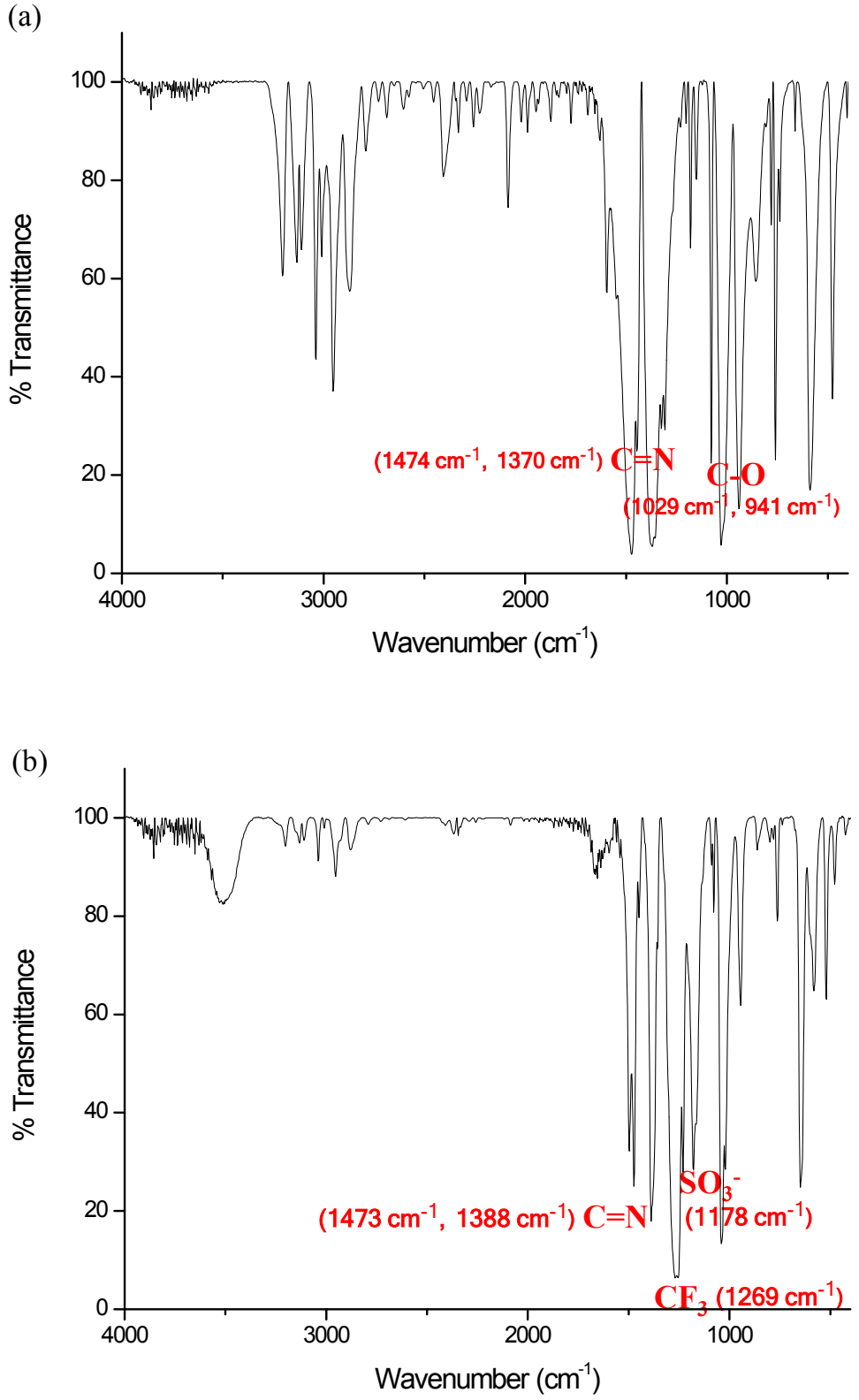
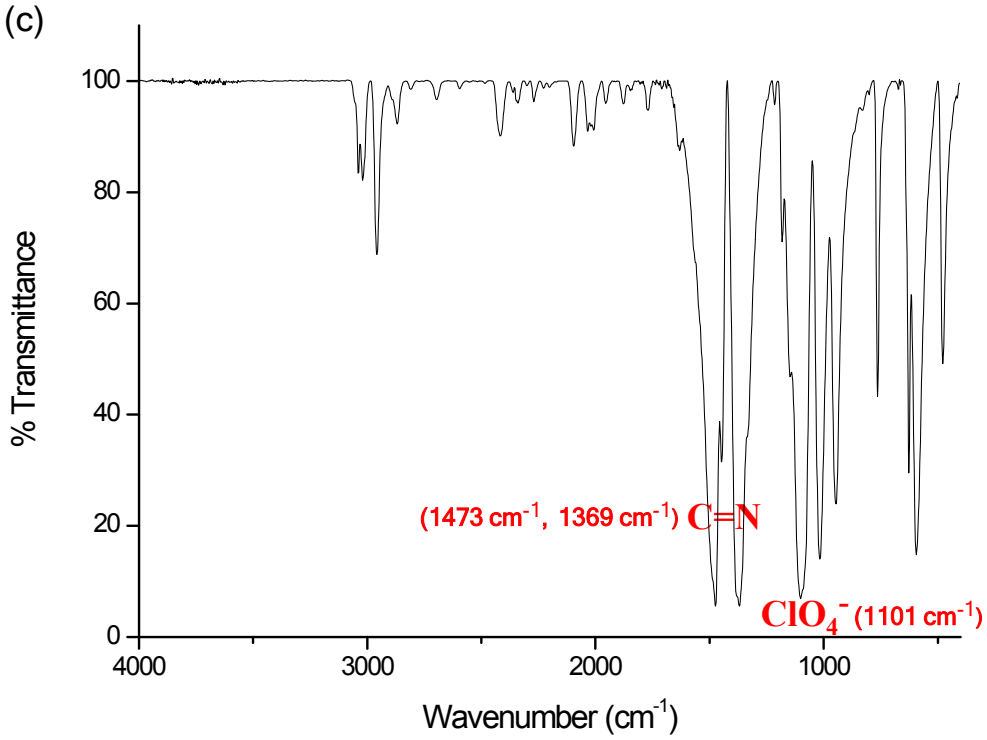


Figure S6. FT-IR spectrum for (a) dmotz, (b) $[Ag(dmotz)(CF_3SO_3)]_n$ and $\{Ag(dmotz)_2\}(ClO_4)]_n$.





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[2] *APEX2 (version 2012.2-0)*, Data collection software, Bruker AXS Inc., Madison, Wiskonsin, (2011).

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