Electronic Supplementary Material

Structure and Vibrational Spectra of Pyridine Solvated Solid Bis(Pyridinesilver(I) Perchlorate, $[Agpy_2ClO_4]\cdot 0.5py$

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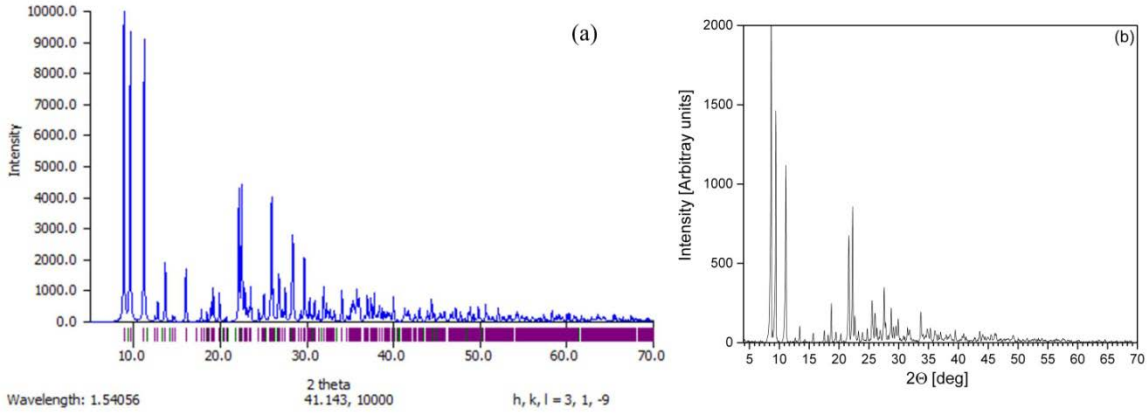


Figure S1. Comparison of the experimental (a) and calculated (from SXRD data) (b) powder XRDs of compound 1.

Table S1. Crystal data and details of the structure determination and refinement of compound **1**.

Empirical formula	$C_{25}H_{25}Ag_2Cl_2N_5O_8$;
Moiety formula	$2(C_{10}H_{10}N_2Ag).2(ClO_4).(C_5\ H_5\ N)$
Formula weight	810.14
Temperature	103(2)K
Radiation and wavelength	Mo-Kα, λ =0.71073Å
Crystal system	monoclinic
Space group	*C* 2/c
Unit cell dimensions	*a* =19.1093(16)Å, *b* =7.7016(8)Å, *c* =20.6915(19)Å
	$\alpha = \gamma = 90°$ $\beta = 105.515(7)°$
Volume	2934.2(5)Å^3
Z	4
Density (calculated)	1.834 Mg/m^3
Absorption coefficient, μ	1.572 mm^{-1}
F(000)	1608
Crystal colour, description	colourless, block
Crystal size	0.5 x 0.3 x 0.3 mm
Absorption correction	multi-scan
Max. and min. transmission	0.717 1.000
θ–range for data collection	$3.141° \leq \theta \leq 27.463°$
Index ranges	$-24 \leq h \leq 24; -9 \leq k \leq 9; -26 \leq l \leq 26$
Reflections collected	58650
Completeness to 2	0.998
Independent reflections	3347 [*R*(int) =0.0305]
Reflections $I>2\sigma(I)$	3257
Refinement method	full-matrix least-squares on F^2
Data / restraints / parameters	3347 /0 /191
Goodness-of-fit on F^2	1.205
Final *R* indices [$I>2\sigma(I)$]	*R*1 =0.0253, *wR*2 =0.0600
R indices (all data)	*R*1 =0.0265, *wR*2 =0.0606
Max. and mean shift/esd	0.001; 0.000
Largest diff. peak and hole	0.916; -0.623 e.Å^{-3}

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) of compound **1**. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	*U*(eq)
Ag1	2127.0(2)	5858.3(2)	4476.1(2)	25(1)
Cl1	3460.7(3)	3826.5(6)	5890.1(2)	20(1)
O1	4166.4(9)	4045(2)	6347.7(9)	32(1)
N1	1328(1)	6107(2)	5037(1)	23(1)
O2	3104(1)	5485(2)	5770(1)	42(1)
N2	2761(1)	5886(2)	3753.8(9)	23(1)
O3	3533(1)	3113(3)	5275(1)	49(1)
N3	5000	7157(4)	7500	37(1)
O4	3032(1)	2669(2)	6173.3(9)	36(1)
C11	764(1)	7201(3)	4832(1)	26(1)
C12	252(1)	7442(3)	5187(1)	30(1)
C13	321(1)	6536(3)	5775(1)	31(1)
C14	898(1)	5399(3)	5987(1)	29(1)
C15	1387(1)	5209(3)	5607(1)	25(1)
C21	3312(1)	4778(3)	3802(1)	27(1)
C22	3702(1)	4689(4)	3327(1)	31(1)
C23	3511(1)	5761(3)	2774(1)	30(1)
C24	2943(1)	6907(4)	2718(1)	32(1)
C25	2588(1)	6941(3)	3220(1)	29(1)
C31	4438(1)	8061(3)	7068(1)	27(1)
C32	4434(1)	9867(3)	7075(1)	31(1)
C33	5000	10770(5)	7500	31(1)

Table S3. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) of compound **1**.

	x	*y*	*z*	*U*(iso)
H11	716	7820	4437	31
H12	-133	8206	5030	36
H13	-14	6686	6025	37
H14	955	4770	6381	35
H15	1771	4434	5749	30
H21	3438	4037	4170	32
H22	4087	3916	3380	37
H23	3760	5712	2445	36
H24	2802	7644	2350	39
H25	2211	7732	3185	34
H31	4064	7459	6773	33
H32	4050	10469	6793	37
H33	5000	11977	7500	37

Table S4. Anisotropic displacement parameters (Å^2 x 10^3) of compound **1**. The anisotropic displacement factor exponent takes the form: -2π^2($h^2a^{*2}U_{11}$ + ... + 2$hka^*b^*U_{12}$).

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ag1	27(1)	28(1)	25(1)	-3(1)	15(1)	-1(1)
Cl1	23(1)	19(1)	20(1)	1(1)	8(1)	2(1)
O1	25(1)	36(1)	32(1)	-2(1)	2(1)	2(1)
N1	22(1)	24(1)	25(1)	-4(1)	10(1)	-3(1)
O2	28(1)	19(1)	77(2)	9(1)	13(1)	6(1)
N2	26(1)	24(1)	21(1)	-3(1)	10(1)	-3(1)
O3	54(1)	68(2)	26(1)	-14(1)	15(1)	-1(1)
N3	35(2)	37(2)	44(2)	0	20(1)	0
O4	38(1)	35(1)	37(1)	9(1)	13(1)	-7(1)
C11	24(1)	25(1)	30(1)	-2(1)	8(1)	-2(1)
C12	24(1)	27(1)	41(1)	-6(1)	11(1)	2(1)
C13	29(1)	32(1)	37(1)	-10(1)	20(1)	-5(1)
C14	31(1)	33(1)	27(1)	-2(1)	14(1)	-6(1)
C15	23(1)	26(1)	29(1)	-1(1)	10(1)	-2(1)
C21	29(1)	28(1)	23(1)	1(1)	9(1)	1(1)
C22	29(1)	36(1)	31(1)	-1(1)	14(1)	6(1)
C23	33(1)	39(1)	22(1)	-5(1)	15(1)	-5(1)
C24	37(1)	40(1)	22(1)	6(1)	12(1)	3(1)
C25	30(1)	31(1)	27(1)	3(1)	11(1)	6(1)
C31	23(1)	31(1)	28(1)	-3(1)	7(1)	-5(1)
C32	28(1)	33(1)	28(1)	6(1)	4(1)	3(1)
C33	34(2)	22(2)	36(2)	0	9(2)	0

Table S5. Bond lengths [Å] in compound **1**.

Ag1-N1	2.158(2)	Ag1-N2	2.161(2)
Cl1-O3	1.426(2)	Cl1-O1	1.435(2)
Cl1-O4	1.437(2)	Cl1-O2	1.438(2)
N1-C11	1.344(3)	N1-C15	1.345(3)
N2-C21	1.337(3)	N2-C25	1.340(3)
N3-C31	1.386(3)	N3-C31#1	1.386(3)
C11-C12	1.383(3)	C12-C13	1.379(4)
C13-C14	1.384(4)	C14-C15	1.382(3)
C21-C22	1.387(3)	C22-C23	1.379(4)
C23-C24	1.379(4)	C24-C25	1.386(3)
C31-C32	1.391(4)	C32-C33	1.386(3)
C33-C32#1	1.386(3)		

Table S6. Bond angles [°] in compound **1**.

N1-Ag1-N2	168.12(7)	O3-Cl1-O1	109.6(1)
O3-Cl1-O4	109.0(1)	O1-Cl1-O4	109.9(1)
O3-Cl1-O2	110.1(1)	O1-Cl1-O2	109.2(1)
O4-Cl1-O2	109.0(1)	C11-N1-C15	118.0(2)
C11-N1-Ag1	120.6(2)	C15-N1-Ag1	121.3(2)
C21-N2-C25	117.7(2)	C21-N2-Ag1	121.2(2)
C25-N2-Ag1	121.0(2)	C31-N3-C31#1	119.7(3)
N1-C11-C12	122.6(2)	C13-C12-C11	119.1(2)
C12-C13-C14	118.6(2)	C15-C14-C13	119.4(2)
N1-C15-C14	122.3(2)	N2-C21-C22	122.7(2)
C23-C22-C21	119.1(2)	C24-C23-C22	118.8(2)
C23-C24-C25	118.8(2)	N2-C25-C24	122.9(2)
N3-C31-C32	120.1(2)	C33-C32-C31	120.1(2)
C32-C33-C32#1	119.7(3)		

Symmetry codes to generate equivalent atoms:

1. [2_656] -x+1,y,-z+1/2+1

Table S7. Molecular geometry of the Agpy2ClO_4 dimer calculated using the M05 functional with LANL2DZ basis set and pseudopotential on Ag and the 6-31G(d,p) basis set on the rest of the atoms

56
scf done: -2805.341856

Ag	0.032981	1.091451	-1.453787
Ag	-0.032885	1.091096	1.454625
N	-2.260144	-1.169590	-1.565627
N	2.327107	-0.989331	-1.605054
N	-2.327047	0.989444	1.605092
N	2.260304	1.169287	1.565206
C	-2.983427	-0.085453	-1.882179
C	-4.374636	-0.101127	-1.908412
C	-5.037112	-1.283093	-1.592404
C	-4.287881	-2.404211	-1.247135
C	-2.901094	-2.302349	-1.242118
C	3.074584	-2.058521	-1.294395
C	4.464864	-2.034890	-1.334734

C	5.101727	-0.854403	-1.704861
C	4.328395	0.261840	-2.009718
C	2.943435	0.152839	-1.945699
C	-2.943992	-0.152347	1.945868
C	-4.329025	-0.260821	2.009036
C	-5.101750	0.855571	1.703166
C	-4.464230	2.035658	1.332914
C	-3.073911	2.058774	1.293444
C	2.900934	2.302393	1.242281
C	4.287696	2.404575	1.247041
C	5.037266	1.283400	1.591394
C	4.375126	0.101069	1.906739
C	2.983907	0.085094	1.880841
O	-0.036684	-1.555862	1.309994
O	0.036473	1.555658	-1.309247
Cl	-0.293455	3.012022	-1.318714
Cl	0.293211 -	3.012242	1.319261
O	1.669656	-3.179540	1.786309
O	0.180021	-3.500775	-0.074646
O	-0.657105	-3.708120	2.174499
O	0.657882	3.708042	-2.172738
O	-0.181923	3.500391	0.075405
O	-1.669334	3.179367	-1.787387
H	2.299843	1.002211	-2.158073
H	-2.430909	0.822870	-2.108113
H	2.431670	-0.823522	2.106296
H	-2.300830	-1.001852	2.159024
H	4.781271	1.206033	-2.290498
H	-4.915583	0.801744	-2.168821
H	-4.782441	-1.204718	2.289943
H	4.916328	-0.801869	2.166392
H	6.185343	-0.803273	-1.749846
H	-6.121708	-1.329198	-1.609828
H	6.121855	1.329744	1.608612
H	-6.185412	0.804839	1.747459
H	5.026389	-2.925997	-1.077035
H	-4.761208	-3.343542	-0.984075
H	4.760733	3.344192	0.984489
H	-5.025274	2.926847	1.074455
H	2.533625	-2.950965	-0.993092
H	-2.274411	-3.145144	-0.961856
H	2.274031	3.145238	0.962668
H	-2.532361	2.950813	0.991966

Table S8. Molecular geometry of the $Agpy2ClO_4$ dimer coordinated by two pyridine ligands at the O_4 atoms, calculated using the M05 functional with LANL2DZ basis set and pseudopotential on Ag and the 6-31G(d,p) basis set on the rest of the atoms

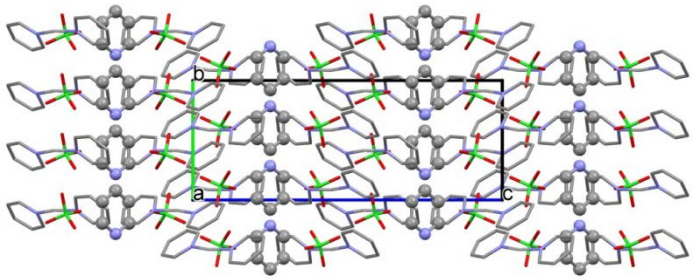
78

scf done: -3301.566349

C	-1.817806	-2.830522	-1.593986

N	-2.293671	-1.589459	-1.405915
C	-3.595382	-1.436971	-1.114556
C	-4.475988	-2.509125	-1.009473
C	-3.979289	-3.792150	-1.218322
C	-2.628379	-3.957010	-1.513883
Ag	-0.946131	0.245378	-1.535626
O	1.114176	-1.505320	-1.387636
Cl	2.578640	-1.721086	-1.279482
O	3.271823	-0.702524	-2.077041
N	0.268614	2.163423	-1.760796
C	1.573811	2.140461	-2.072646
C	2.347820	3.295186	-2.126606
C	1.744796	4.518658	-1.854490
C	0.392620	4.544128	-1.525524
C	-0.306963	3.343600	-1.482610
Ag	0.894794	-0.203707	1.488842
O	-1.135907	1.599624	1.389204
Cl	-2.611351	1.677983	1.252701
O	-3.102682	2.892168	1.889008
N	2.267285	1.637326	1.440439
C	1.808175	2.872251	1.695403
C	2.632922	3.991579	1.677213
C	3.981744	3.826827	1.372986
C	4.461883	2.550613	1.094102
C	3.567725	1.485600	1.141811
N	-0.203976	-2.196244	1.757959
C	0.446875	-3.338650	1.488562
C	-0.159496	-4.585874	1.584996
C	-1.495539	-4.651745	1.969051
C	-2.177224	-3.468714	2.235115
C	-1.495399	-2.261411	2.118198
O	-3.212344	0.487661	1.866815
O	-2.938470	1.698760	-0.191836
O	2.914415	-3.060909	-1.741445
O	2.958375	-1.572923	0.143998
H	-2.000459	-1.316615	2.297857
H	0.746645	2.953962	1.909353
H	-0.754590	-2.909502	-1.800751
H	2.016802	1.167455	-2.267718
H	-3.222723	-3.467436	2.522142
H	2.216155	4.968815	1.894908
H	3.401553	3.222481	-2.370778
H	-2.199084	-4.939666	-1.676482
H	-1.998376	-5.610309	2.054729
H	4.649731	4.682902	1.352844
H	-4.636843	-4.653798	-1.151192
H	2.321283	5.438074	-1.889973
H	0.411009	-5.479673	1.358286
H	5.500114	2.351838	0.841139
H	-5.517225	-2.311610	-0.767958
H	-0.118081	5.472885	-1.297007
H	1.483167	-3.240714	1.180179

H	3.893408	0.473680	0.923469
H	-3.933840	-0.418971	-0.951580
H	-1.356883	3.311634	-1.206614
C	-6.270283	0.286855	0.648898
N	-7.055108	-0.508829	-0.085344
C	-8.079399	0.066573	-0.721287
C	-8.363737	1.428489	-0.657067
C	-7.527895	2.243121	0.103309
C	-6.454507	1.663776	0.771597
H	-5.434596	-0.184989	1.160544
H	-5.762631	2.254024	1.363578
H	-8.708257	-0.593782	-1.317253
H	-9.213008	1.836893	-1.194984
H	-7.708775	3.311776	0.169930
C	6.216616	-0.227784	-0.696207
N	6.992257	0.546425	0.069567
C	8.019529	-0.044103	0.686812
C	8.315509	-1.400113	0.572290
C	7.489589	-2.192243	-0.221913
C	6.413618	-1.596957	-0.871190
H	5.378744	0.254900	-1.193854
H	8.641466	0.598900	1.308606
H	9.166427	-1.821521	1.097437
H	7.680087	-3.255948	-0.329017
H	5.729133	-2.168310	-1.489112



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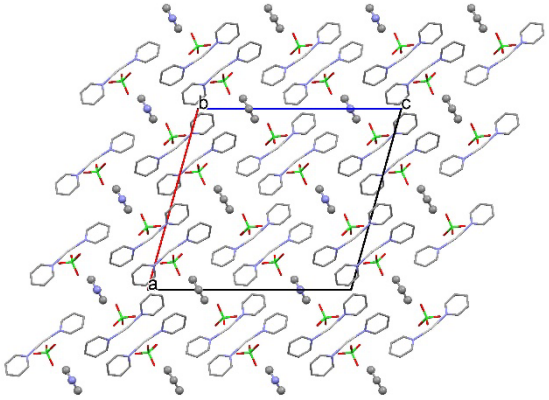
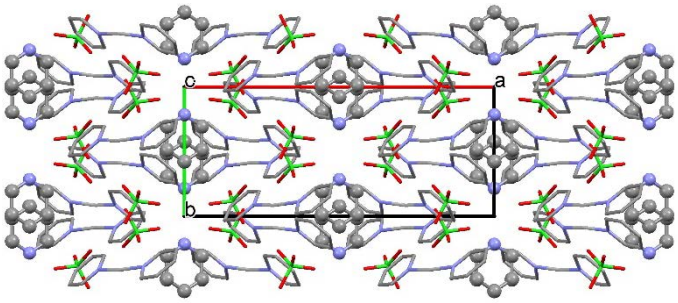


b.,



c.,

Figure S2. The packing arrangement of compound **1** (capped sticks) and the solvent pyridine (ball and stick representation). a., View from the *a* crystallographic axis. b., View from the *b* crystallographic axis. c., View from the *c* crystallographic axis.

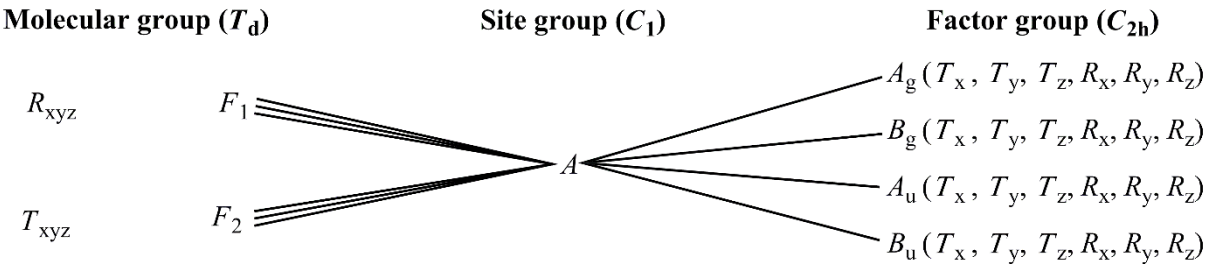


Figure S3. External vibrational modes of perchlorate ion in compound **1.**

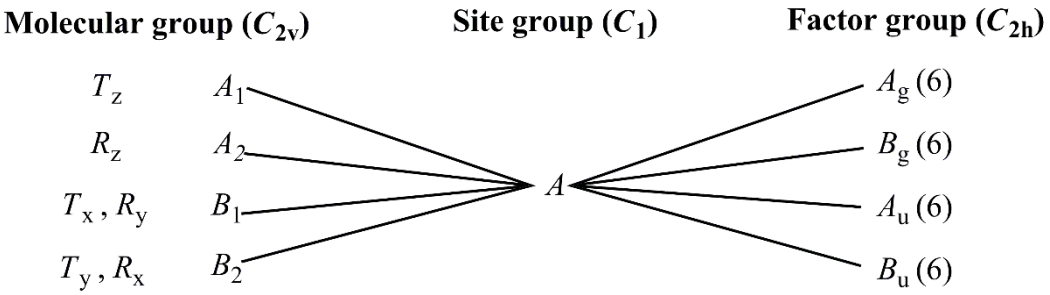


Figure S4. External vibrational modes of pyridines at C1 site (coordinated ones) in compound **1.**

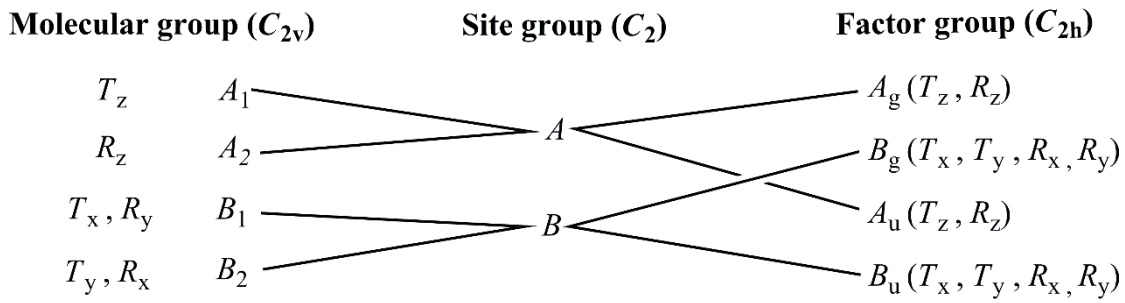


Figure S5. External vibrational modes of pyridine at C2 site (solvate) in compound **1.**

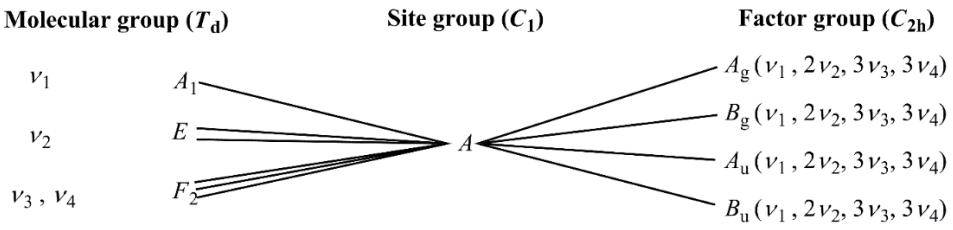


Figure S6. Correlation diagram for perchlorate ion internal modes in compound **1**.

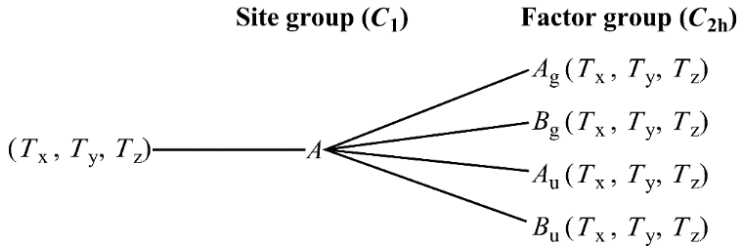
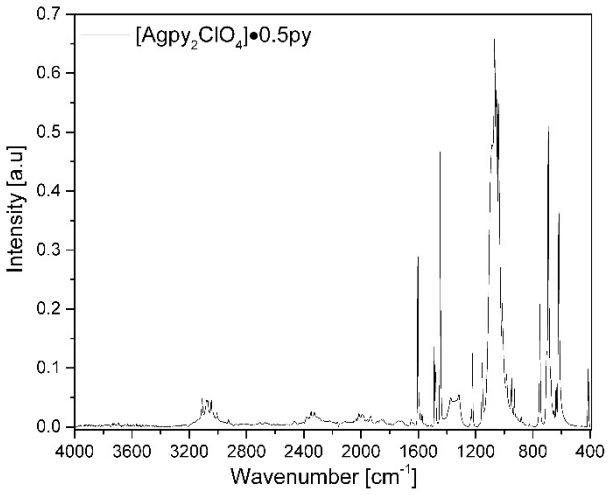
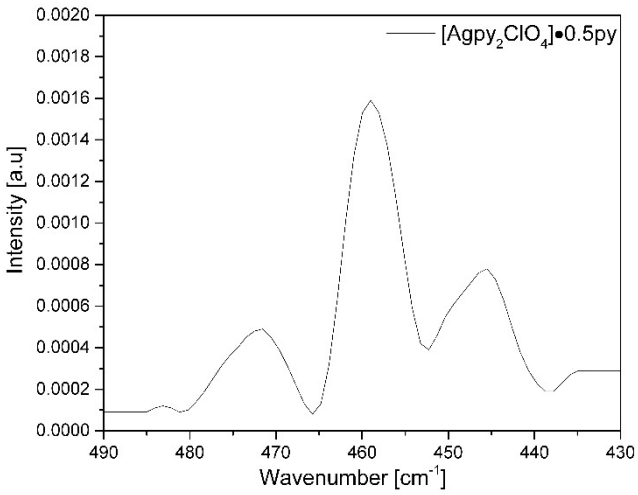


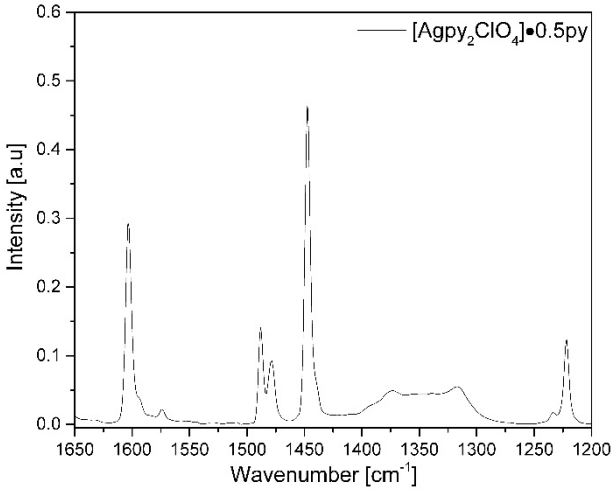
Figure S7. The correlation diagrams for the hindered translations of Ag^+ cations at C_1 sites.


[Agpy2ClO4]•0.5py
Intensity [a.u]
Wavenumber [cm-1]
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
4000
3600
3200
2800
2400
2000
1600
1200
800
400

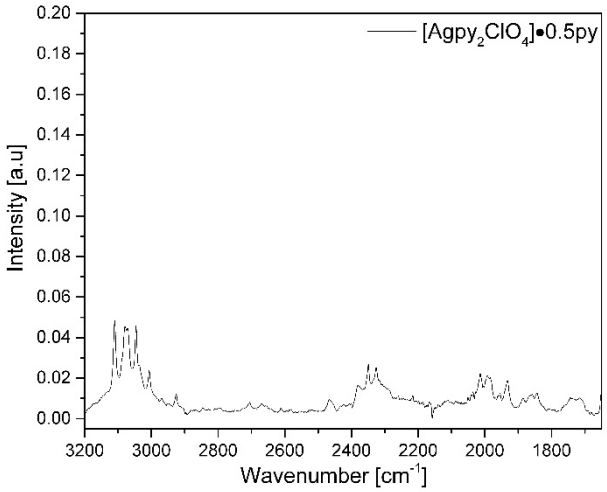
(a)


[Agpy2ClO4]•0.5py
Intensity [a.u]
Wavenumber [cm-1]
0.0000
0.0002
0.0004
0.0006
0.0008
0.0010
0.0012
0.0014
0.0016
0.0018
0.0020
490
480
470
460
450
440
430

(b)

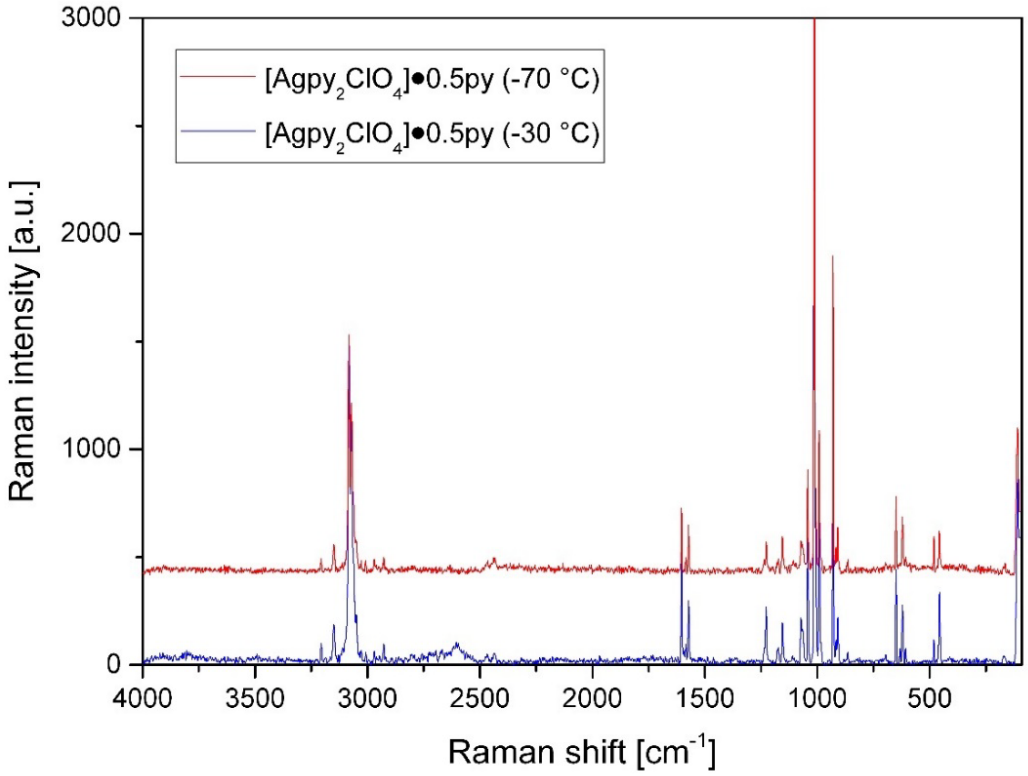


(c)

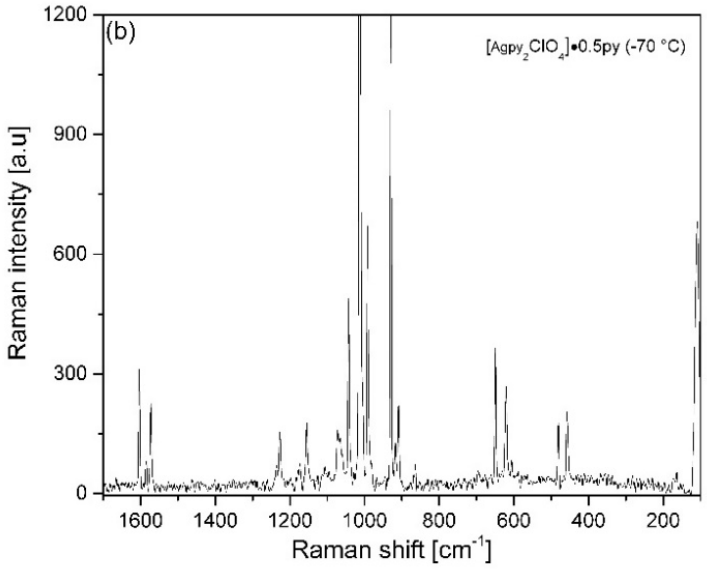


(d)

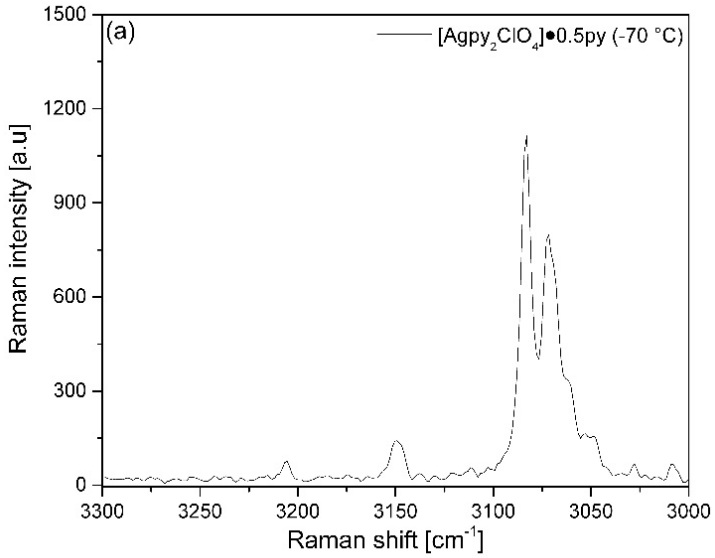
Figure S8. IR spectrum of compound **1** at room temperature between 4000 and 400 cm-1 (a). The enlarged spectrum parts are given between 490 and 430 cm^{-1} (b) and 1650 and 1200 cm^{-1} (c), and 3200 and 1650 cm^{-1} (d).


[Agpy2ClO4]•0.5py (-70 °C)
[Agpy2ClO4]•0.5py (-30 °C)
Raman intensity [a.u.]
Raman shift [cm-1]
3000
2000
1000
0
4000
3500
3000
2500
2000
1500
1000
500

(a)


(b)
[Agpy2ClO4]•0.5py (-70 °C)
Raman intensity [a.u]
Raman shift [cm-1]
1200
900
600
300
0
1600
1400
1200
1000
800
600
400
200

(b)



(c)

Figure S9. Raman spectra of compound **1** between 4000 and 100 cm^{-1} at 243 and 203 K (a). The enlarged spectrum parts recorded at 203 K are given between 1700 and 100 cm^{-1} (b), 3300-3000 cm^{-1} (c).