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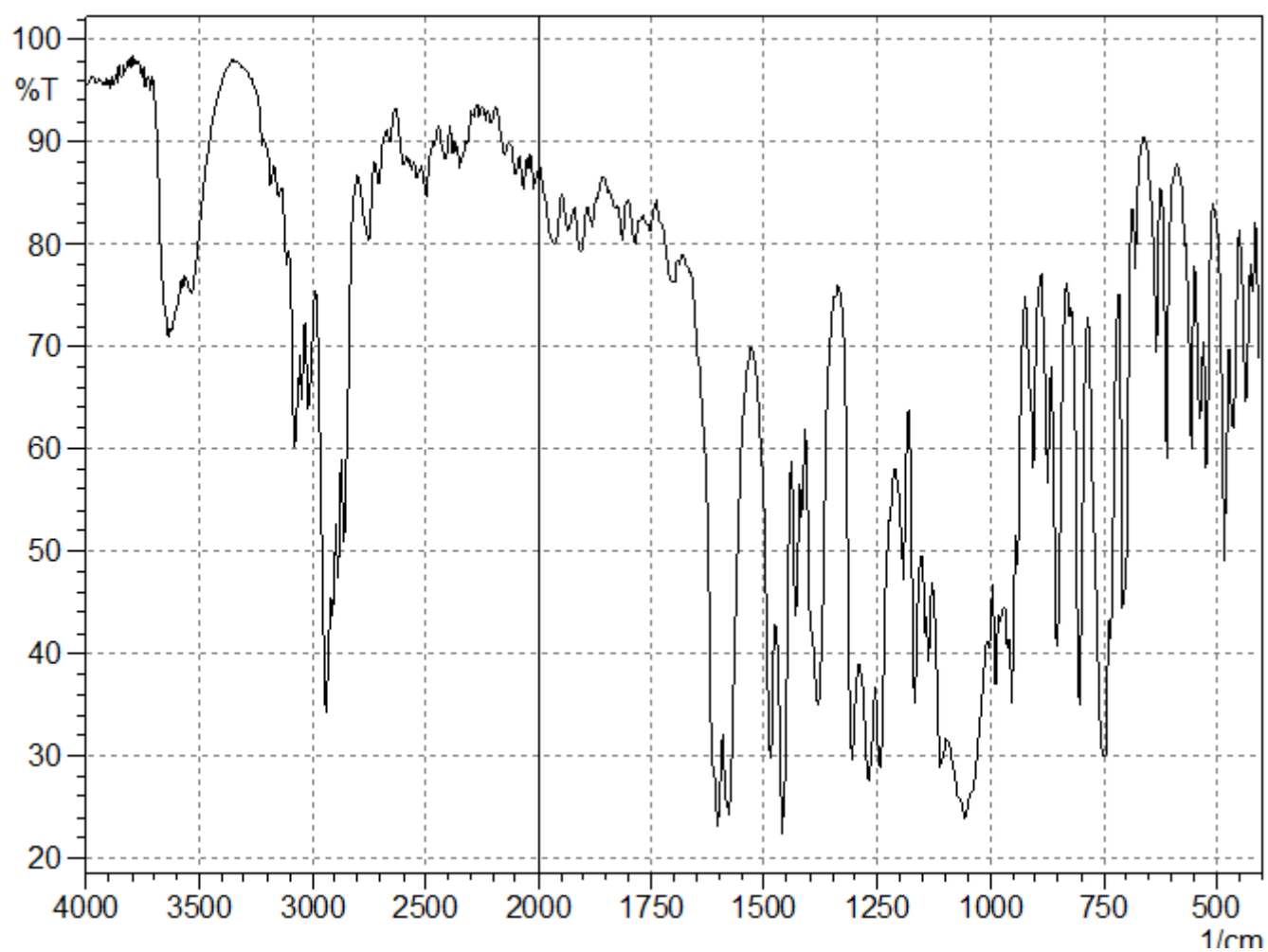


Figure S1. IR spectrum of AgLBF₄

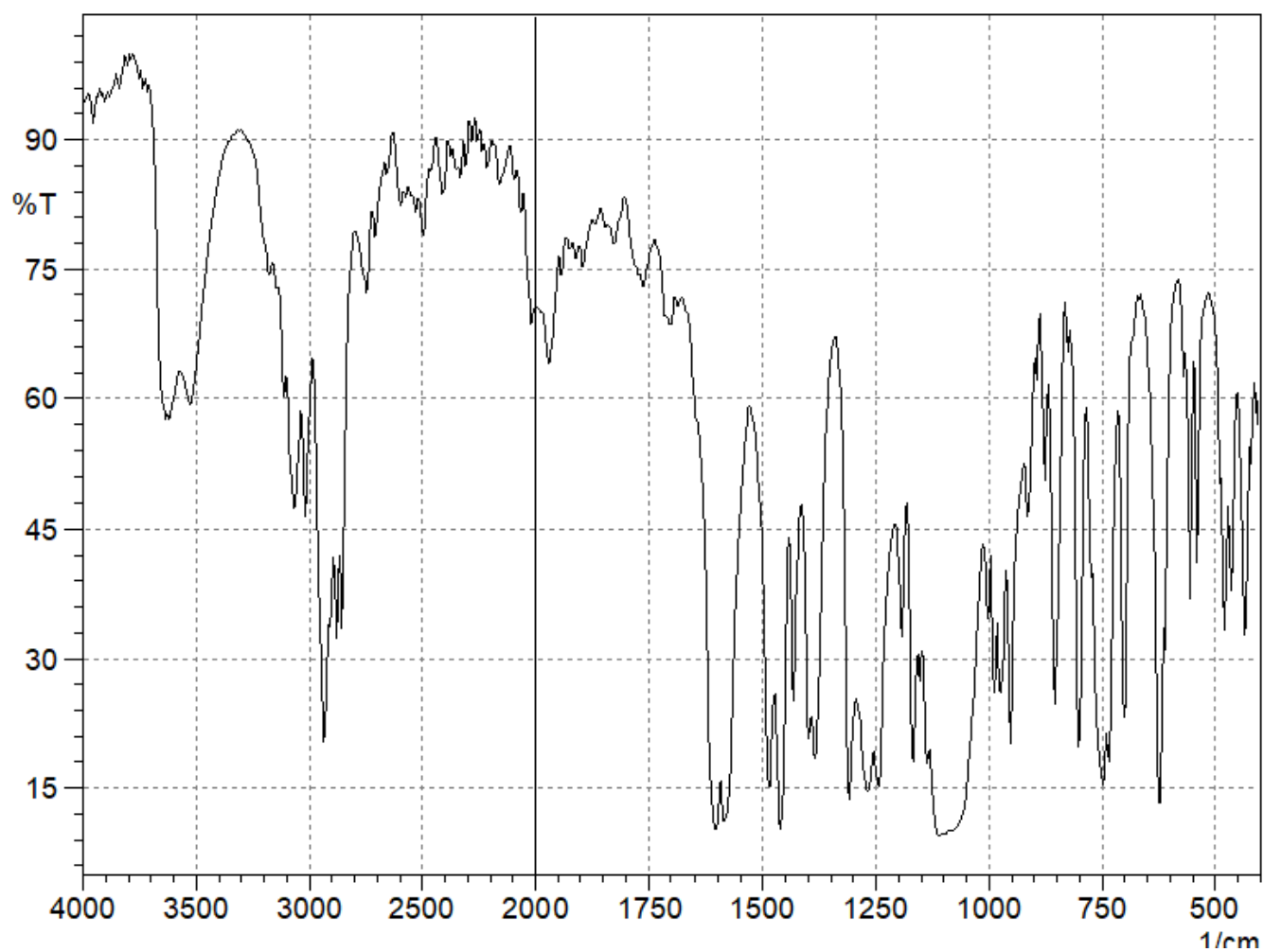


Figure S2. IR spectrum of AgLCIO₄

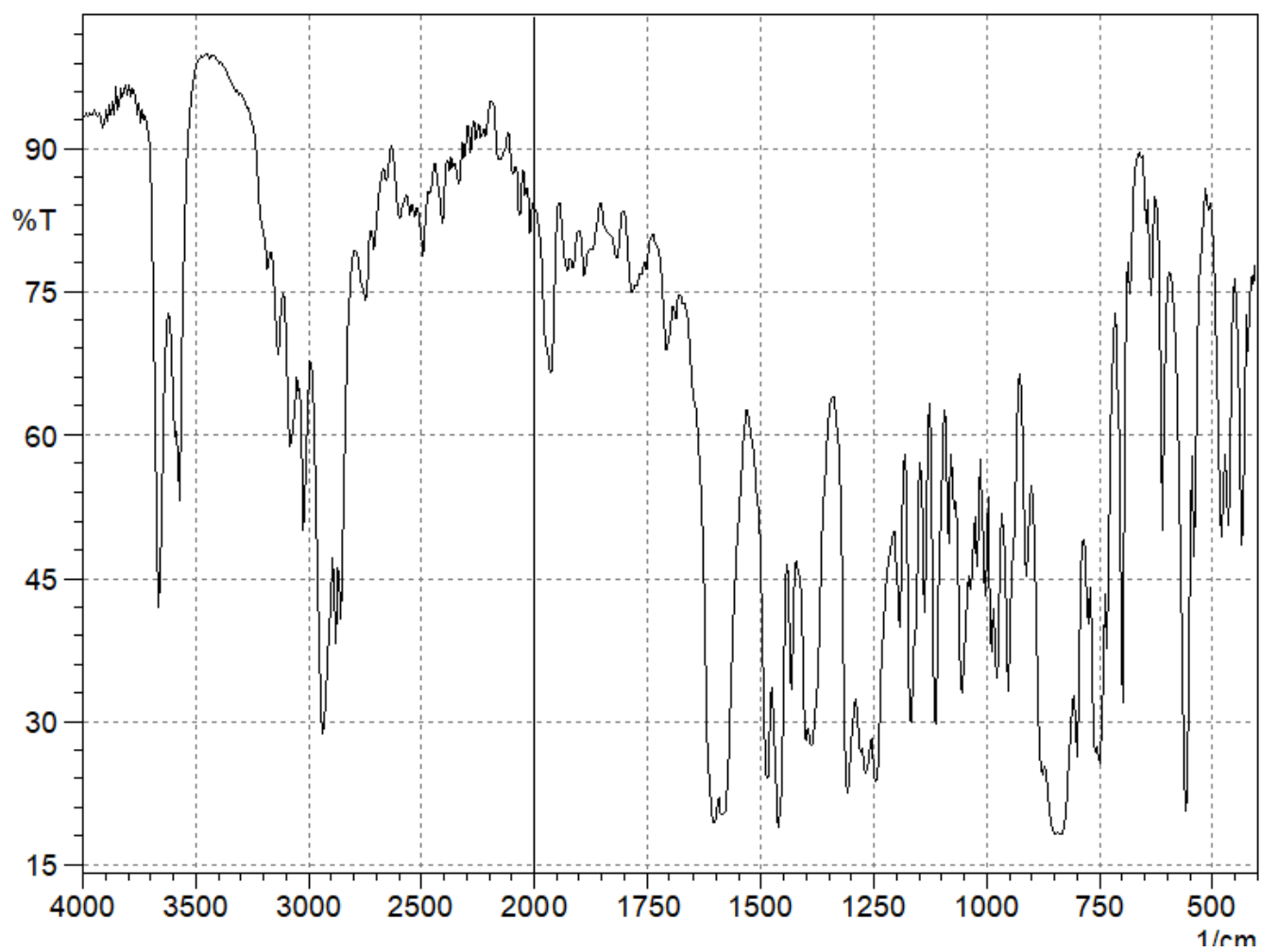


Figure S3. IR spectrum of AgLPF₆

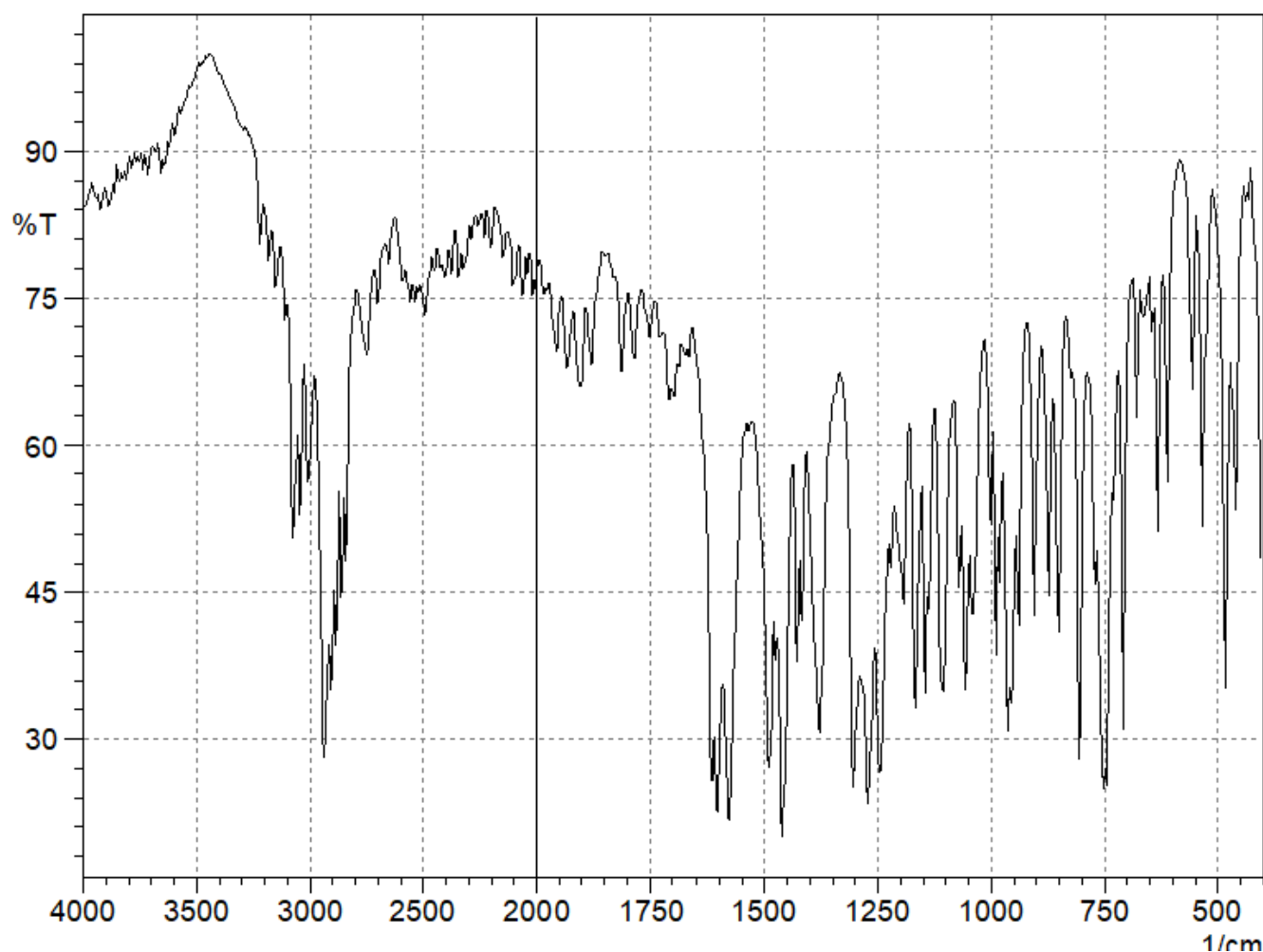


Figure S4. IR spectrum of **AgLSbF₆**

Table S1. Selected interatomic bond distances (Å) and valence angles (°) for compound **AgLCIO₄**

Ag1-N1	2.179(5)	N1-Ag1-N2#1	175.32(19)
Ag1-N2#1	2.182(5)		

Symmetry operations: #1 1-x, -1/2+y, 1/2-z

Table S2. Selected interatomic bond distances (Å) and valence angles (°) for compound **AgLPF₆**

Ag1-N1	2.164(4)	N1-Ag1-N2#1	165.74(16)
Ag1-N2#1	2.166(4)	N3-Ag2-N5	171.81(16)
Ag2-N3	2.150(4)	N6-Ag3-N4#3	173.99(16)
Ag2-N5	2.155(4)		
Ag3-N4#2	2.155(4)		
Ag3-N6	2.151(4)		
Ag2-O7	2.652(1)		

Symmetry operations: #1 -1/2+x, 3/2-y, 1-z; #2 -1+x, +y, +z, #3 -1+x, +y, +z

Table S3. Selected interatomic bond distances (Å) and valence angles (°) for compound **AgLBF₄**

Ag1-N1	2.169(5)	N2#1-Ag1-N1	175.0(2)
Ag1-N2#1	2.168(5)		

Symmetry operations: #1 1-x, 1/2+y, 3/2-z

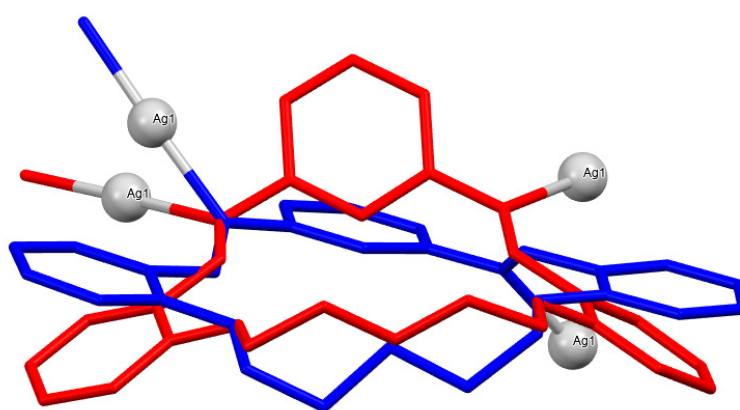
Table S4. Selected interatomic bond distances (Å) and valence angles (°) for compound **AgLSbF₆**

Ag1-N1	2.135(3)	N2#1-Ag1-N1	177.16(13)
Ag1-N2#1	2.129(3)		

Symmetry operations: #1 1/2+x, 3/2-y, -1/2+z

Table S5. Conformational parameters for ligand and silver complexes.

Conformational parameter/Compound	L	AgLClO ₄	AgLPF ₆	AgLBF ₄	AgLSbF ₆
Number of atoms in inner macrocyclic ring	18	18	18	18	18
C-N-Ag-N torsion angle (°)	n.a.	-145, -35	-82, -39 (chain A) 53, 110 (chain B)	147, 33	164, -164
Orientation of donor atoms	N-exo O-endo	N-exo O-endo	N-exo O-endo	N-exo O-endo	N-exo O-endo
Puckering amplitude	1.843(3) Å	2.059(6)	n.a.	2.097(6)	n.a.
Conformation of aliphatic chain	all <i>trans</i>	all <i>trans</i>	all <i>trans</i>	all <i>trans</i>	all <i>trans</i>
Angles between benzene rings (°)	53.16(1), 59.41(1), 56.09(1)	57.69(1), 53.38(1), 66.28(1)	B chain 58.39(1), 52.64(1), 56.54(1) A chain 56.18 (1), 55.21 (1), 52.32 (1)	53.74(1), 58.17(1), 67.38(1)	4.99, 5.13, 6.29

**Figure S5.** Structure overlay of **AgLSbF₆** (blue) and **AgLClO₄** (red)

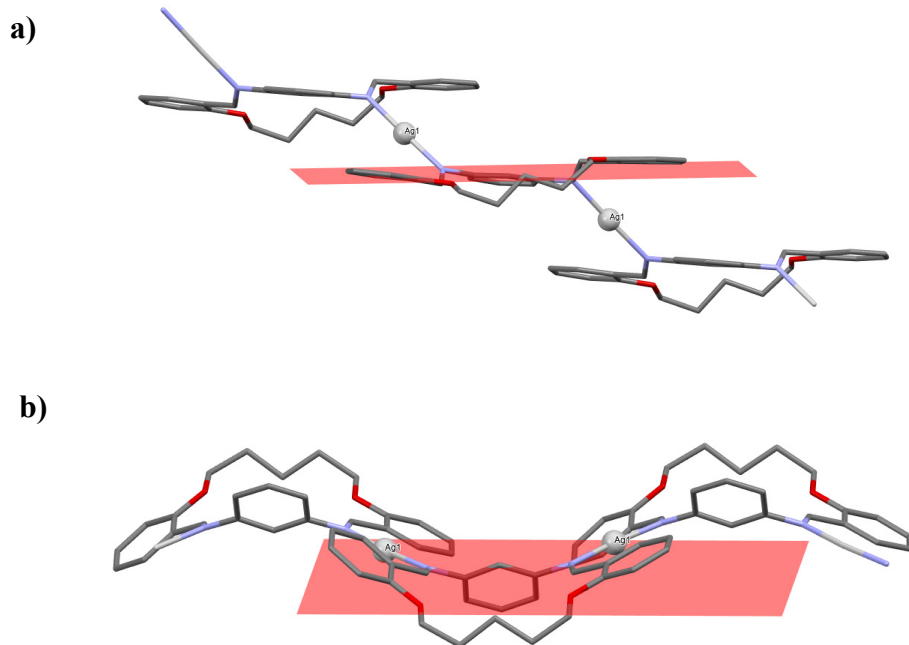


Figure S6. *trans* and *cis* configured polymeric chains in AgLSbF_6 (a) and AgLCIO_4 (b)

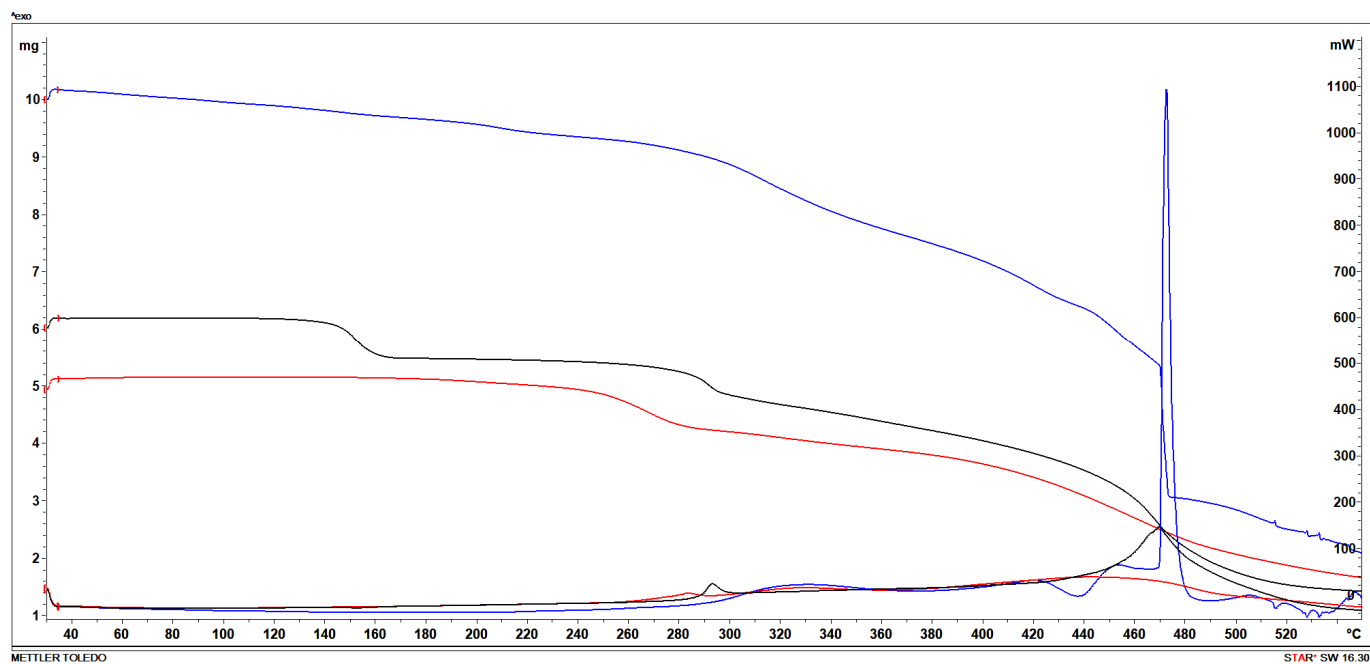


Figure S7. TG and DSC curves of AgLSbF_6 (blue), AgLBF_4 (black) and AgLPF_6