Electronic Supplementary Material (ESI) for Dalton Transactions

Electronic supporting information

High current density electrodeposition of silver from silver-containing liquid metal salts with pyridine-*N*-oxide ligands

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Table S1: Selected bond lengths and interatomic distances in the crystal structures of α-[Ag(py-O)$_3$][Tf$_2$N], β-[Ag(py-O)$_3$][Tf$_2$N], [Ag$_3$(py-O)$_8$][OTf]$_3$, [Ag(py-O)$_2$][OMs] and [Ag(py-O)$_2$][NO$_3$].

Compound	Ag-O	Distance (Å)	Ag-Ag	Distance (Å)	Compound	Ag-O	Distance (Å)	Ag-Ag	Distance (Å)
α-[Ag(py-O)$_3$][Tf$_2$N]	Ag1 - O7	2.455(4)	Ag1 - Ag2	3.247(1)	[Ag$_3$(py-O)$_8$][OTf]$_3$	Ag1 - O1	2.271(3)	Ag1 - Ag2	3.2915(5)
	Ag1 - O8	2.490(4)	Ag2 - Ag3	3.1054(8)		Ag1 - O8	2.599(3)	Ag2 - Ag3	3.3210(5)
	Ag2 - O8	2.444(4)	Ag3 - Ag4	3.2004(8)		Ag1 - O15	2.477(3)		
	Ag2 - O9	2.489(3)	Ag4 - Ag1	3.0244(7)		Ag1 - O22	2.459(3)		
	Ag3 - O9	2.494(3)	Ag5 - Ag6	3.2300(8)		Ag1 - O29	2.409(3)		
	Ag3 - O10	2.449(3)	Ag5 - Ag6	3.0586(8)		Ag2 - O8	2.478(3)		
	Ag4 - O7	2.527(4)				Ag2 - O15	2.559(3)		
	Ag4 - O10	2.451(3)				Ag2 - O22	2.448(3)		
	Ag5 - O11	2.463(3)				Ag2 - O43	2.413(3)		
	Ag5 - O12	2.499(3)				Ag2 - O36	2.488(3)		
	Ag6 - O11	2.461(3)				Ag2 - O43	2.413(3)		
	Ag6 - O12	2.491(3)				Ag3 - O15	2.444(3)		
β-[Ag(py-O)$_3$][Tf$_2$N]	Ag1 - O1	2.4842(2)	Ag1 - Ag2	3.1508(3)		Ag3 - O29	2.556(4)		
	Ag2 - O1	2.4722(2)	Ag2 - Ag3	3.1598(4)		Ag3 - O36	2.333(3)		
	Ag2 - O2	2.4905(2)	Ag3 - Ag4	3.2238(4)		Ag3 - O43	2.632(3)		
	Ag3 - O2	2.4748(2)	Ag4 - Ag5	3.0803(4)		Ag3 - O50	2.248(3)		
	Ag3 - O3	2.4665(2)	Ag5 - Ag6	3.0522(4)	[Ag(py-O)$_3$][OTf]	Ag1 - O2	2.4621(1)	Ag1 - Ag1	3.0191(2)
	Ag4 - O3	2.4490(2)	Ag6 - Ag7	3.1935(4)		Ag1 - O2	2.5117(1)		
	Ag4 - O4	2.4918(2)	Ag7 - Ag8	3.1039(4)		Ag1 - O3	2.3651(1)		
	Ag5 - O4	2.4806(2)	Ag8 - Ag9	3.0418(4)		Ag1 - O4	2.3957(1)		
	Ag5 - O5	2.513(2)	Ag9 - Ag10	3.2032(3)		Ag1 - O4i	2.4892(1)		
	Ag6 - O5	2.490(2)	Ag10 - Ag9	3.2036(3)	[Ag(py-O)$_2$][OMs]	Ag1 - O2	2.4108(2)		
	Ag6 - O6	2.4587(2)				Ag1 - O3	2.3386(1)		
	Ag7 - O6	2.4762(2)				Ag1 - O3	2.3430(1)		
	Ag7 - O7	2.4898(2)				Ag1 - O4	2.4961(1)		
	Ag8 - O7	2.4893(2)				Ag1 - O4	2.5828(1)		
	Ag8 - O8	2.4799(2)			[Ag(py-O)$_2$][NO$_3$]	Ag1 - O2	2.5225(1)		
	Ag9 - O8	2.4900(2)				Ag1 - O2	2.3228(1)		
	Ag9 - O9	2.4664(2)				Ag1 - O3	2.2958(1)		
	Ag10 - O9	2.4698(2)				Ag1 - O4	2.5193(1)		
						Ag1 - O5	2.4253(1)		

Table S2: π-π interactions for the different compounds. The lettering of the planes is presented in the respective figures of the compounds.

Compound	Planes	Angle (°)	centroid-centroid distance (Å)	shift (Å)
α-[Ag(py-O)$_3$][Tf$_2$N]	A-B ^{i}	4.3	3.608	1.474
β-[Ag(py-O)$_3$][Tf$_2$N]	A-Q ^{ii}	4.0	3.714	1.753
	B-C ^{iii}	8.0	3.583	1.121
	E-F ^{iv}	4.8	3.788	2.052
	F-G ^{v}	2.5	3.649	1.580
	G-H ^{vi}	5.0	3.891	2.101
	I-J ^{vii}	1.9	3.870	1.923
	J-K ^{viii}	3.7	3.668	1.621
	K-L ^{ix}	5.0	3.802	1.879
	N-O ^{x}	9.2	3.575	1.459
[Ag$_3$(py-O)$_8$][OTf]$_3$	A-B ^{xi}	6.3	3.883	2.219
	C-F ^{xii}	3.1	3.606	1.071
	C-F ^{xiii}	3.1	3.778	1.911
	D-G ^{xiv}	9.4	3.503	0.940
	D-G$_i$ ^{xv}	9.4	3.715	1.228
	E-H ^{xvi}	2.6	3.693	1.598
[Ag(py-O)$_3$][OTf]	A-C ^{xvii}	15.7	3.799	1.797
	B-C ^{xviii}	13.8	3.714	0.812
[Ag(py-O)$_2$][OMs]	A-A ^{xix}	0	3.804	1.969
	A-B ^{xx}	9.0	3.533	0.995
[Ag(py-O)$_2$][NO$_3$]	A-B ^{xxi}	2.8	3.668	1.671

Symmetry operations:

i	1-x. +x-y. +z	*xiii*	+x. +y. +z
ii	+y-x, 1-x, 1+z	*xiv*	-1+x. +y. +z
iii	+x, +y, +z	*xv*	+x. +y. +z
iv	+x, +y, +z	*xvi*	+x. +y. +z
v	+x, +y, +z	*xvii*	3/4-y. 1/4+x. 1/4+z
vi	+y-x, 1-x, +z	*xviii*	-1/4+y. 3/4-x. -1/4+z
vii	+y-x, 1-x, +z	*xix*	2-x. 2-y. -z
viii	1-y, 1+x, +z	*xx*	+x. +y. +z
ix	+y-x, 1-x, +z	*xxi*	-x. 1-y. 1-z
x	+x, +y, +z		
xi	+x. +y. +z		
xii	-1+x. +y. +z		

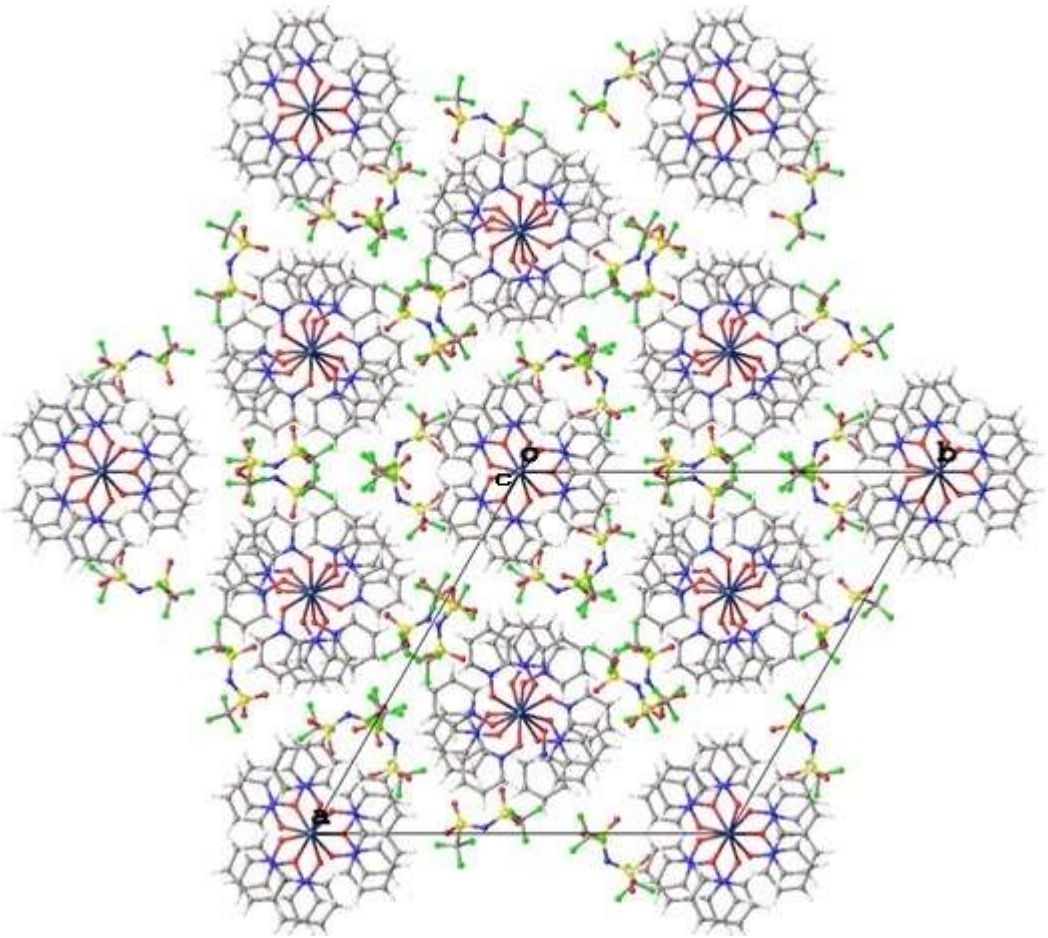

Figure S1: View along the *c* axis of the packing in the crystal structure of α-[Ag(py-O)$_3$][Tf$_2$N] showing the two different [Ag(py-O)$_3$]$_\infty$ chains with the bis(trifluoromethanesulfonyl)imide anions in between. Disorder of the anions is omitted for clarity.

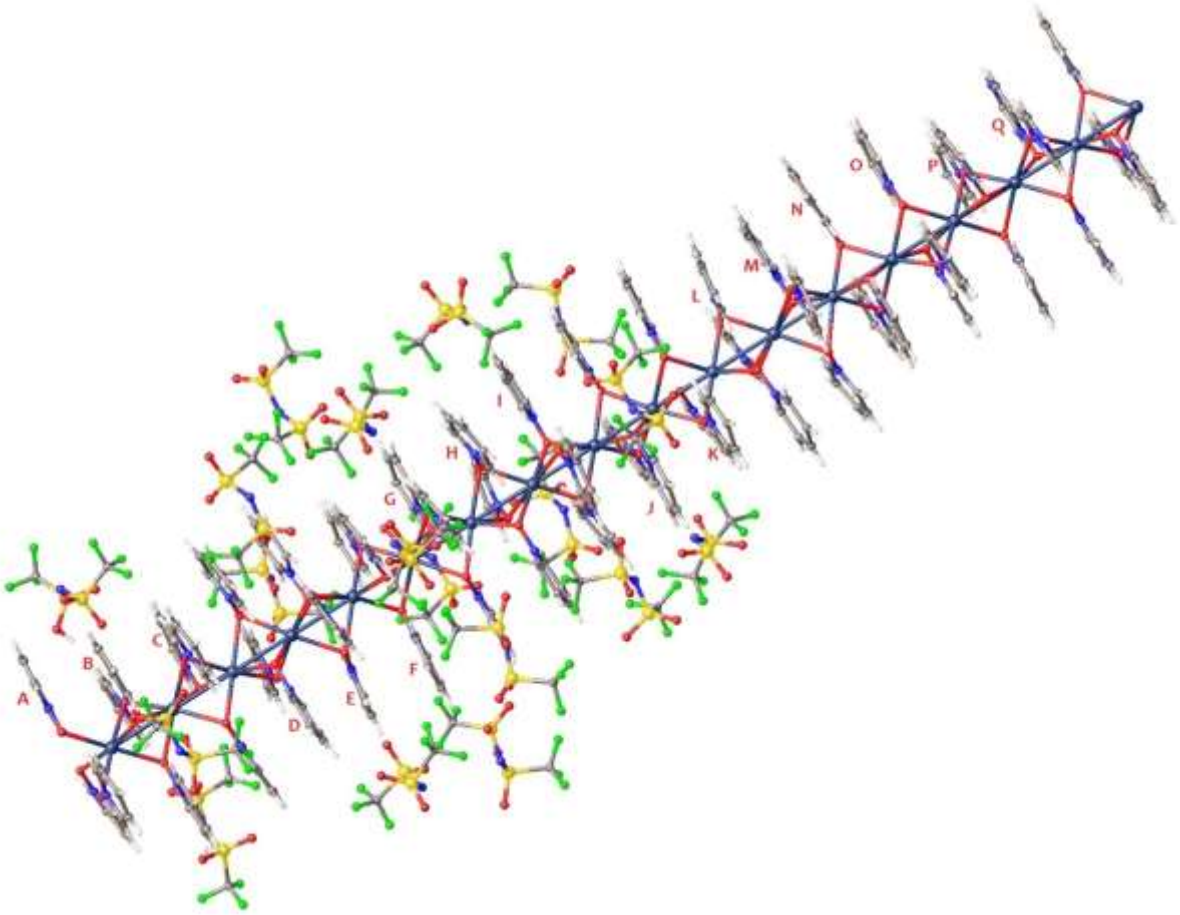

Figure S2: View of the crystal structure of β-[Ag(py-O)$_3$][Tf$_2$N] showing the Ag···Ag interactions. Disorder of the anions is omitted for clarity.

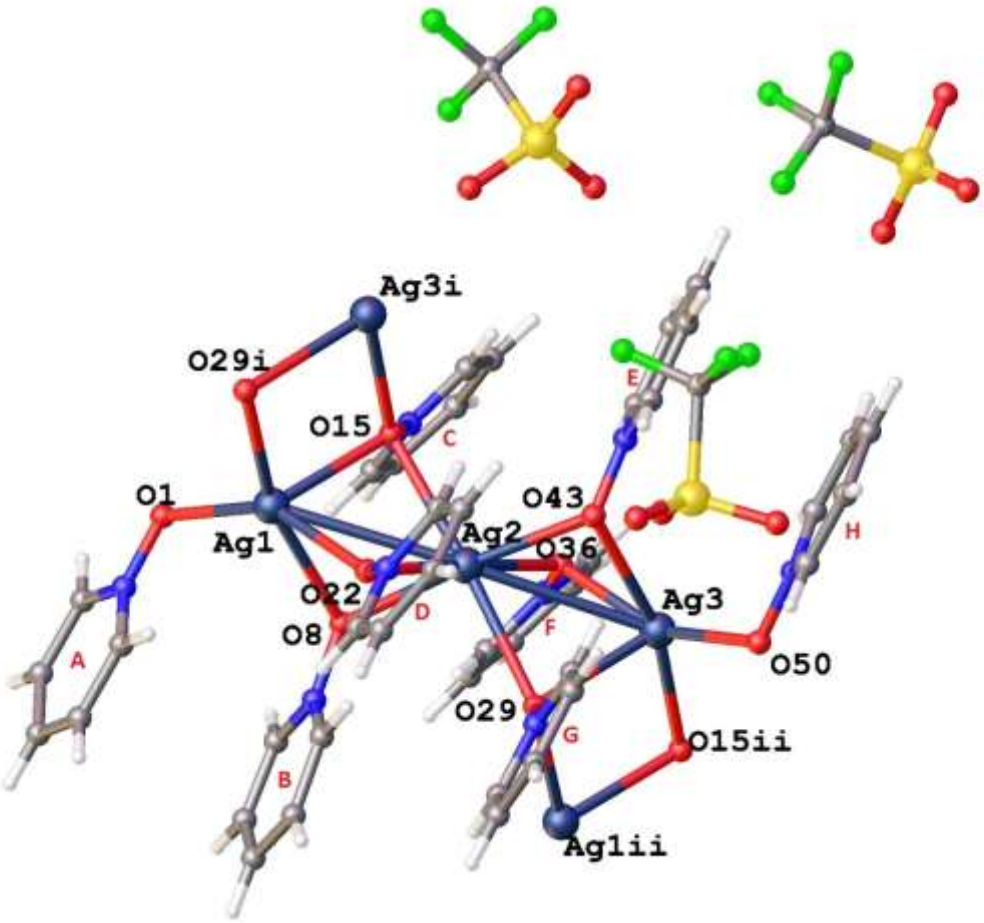

Figure S3: View of the crystal structure of $[Ag_3(py\text{-}O)_8][OTf]_3$ showing the coordination environment of the silver centres and the bridging nature of the py-O ligands. (symmetry codes: i 1-x, y, z; ii 1+x, y, z).

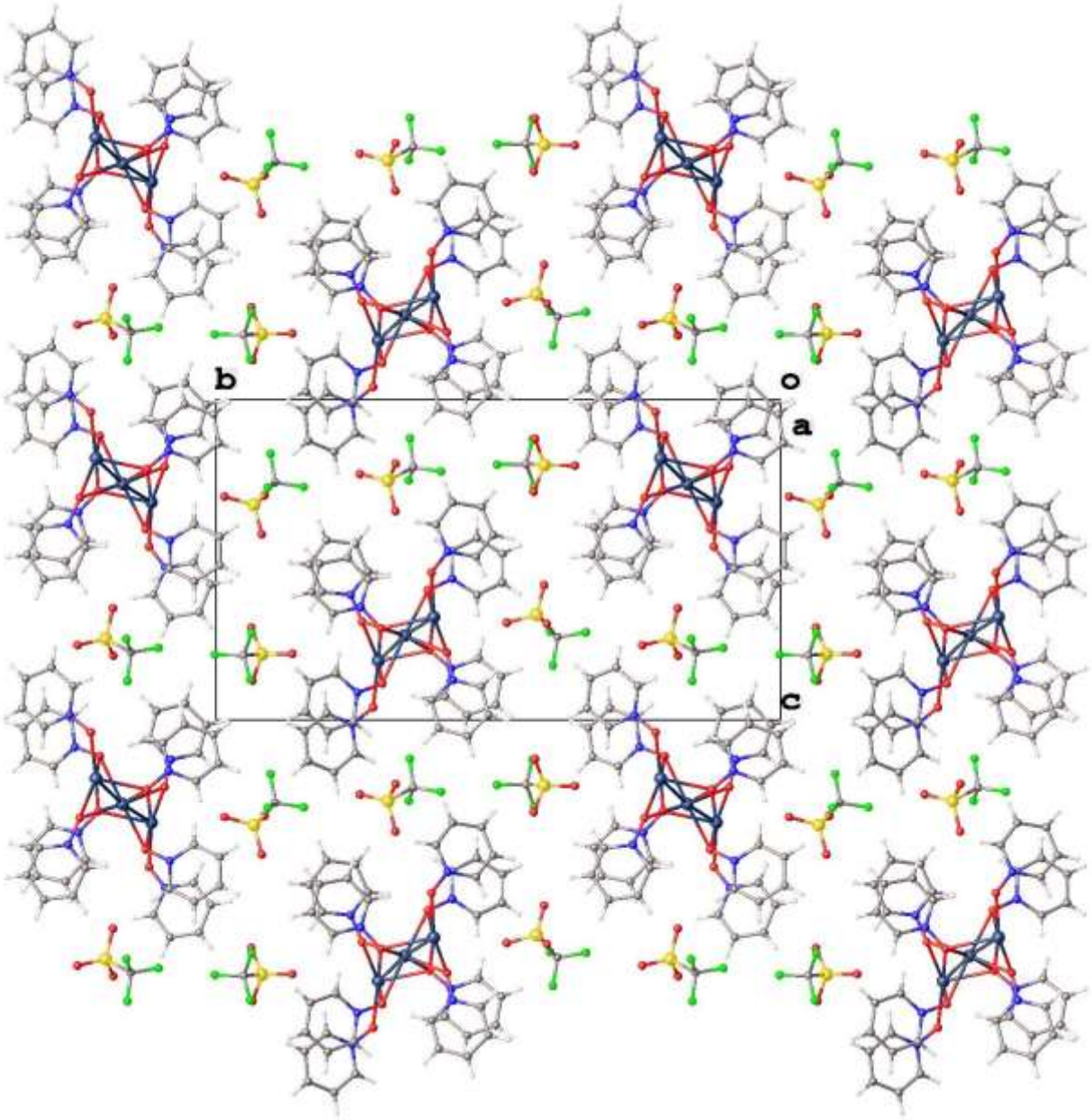

Figure S4: View of the packing in the crystal structure of $[Ag_3(py\text{-}O)_8][OTf]_3$ showing the π-π interactions and the packing of the chains and uncoordinated OTf anions.

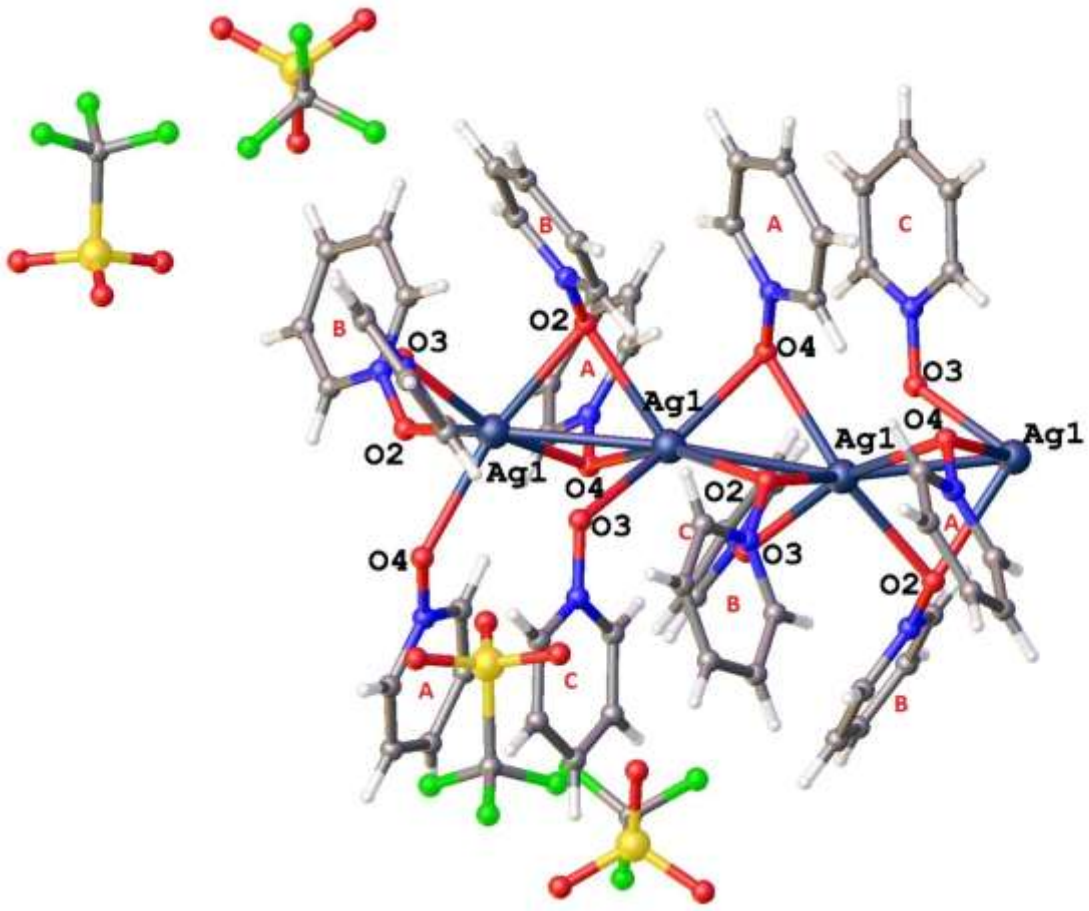

Figure S5: View of the crystal structure of $[Ag(py\text{-}O)_3][OTf]$ showing the Ag···Ag interactions and bridging py-O ligands.

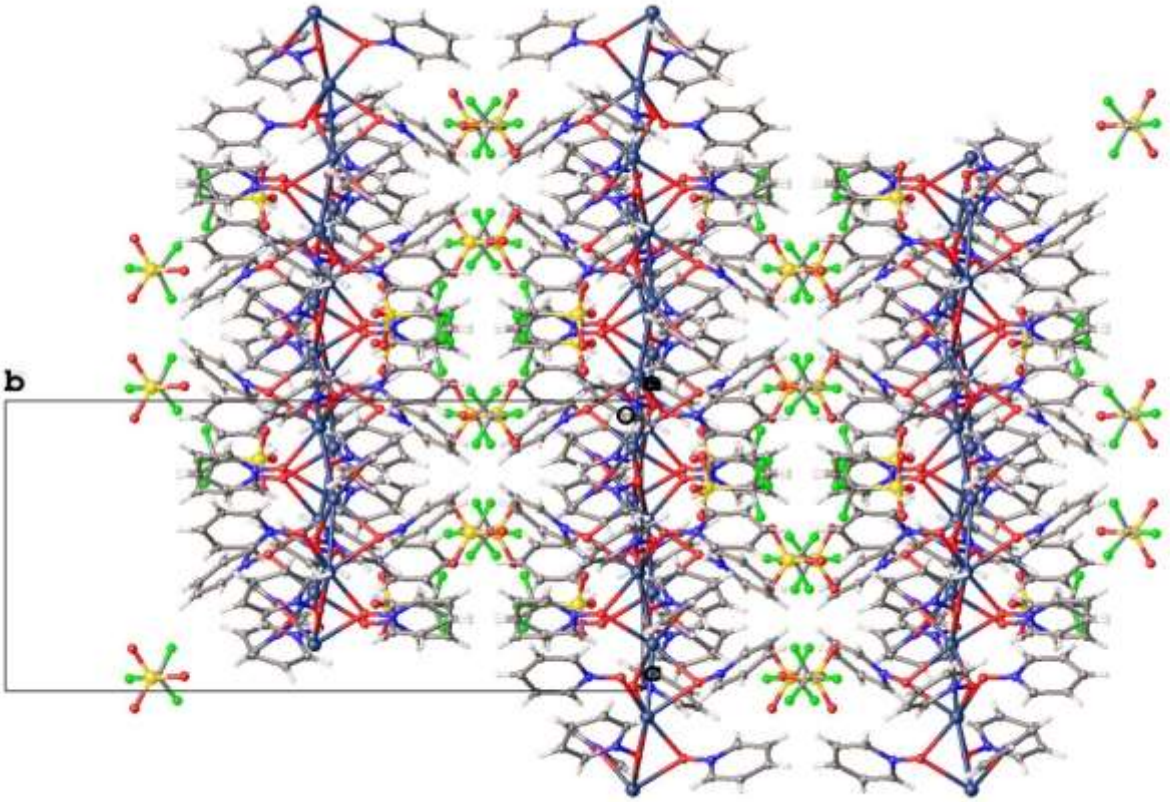

Figure S6: View of the packing of the $[Ag(py\text{-}O)_3]_\infty$ moieties and anions in the structure of $[Ag(py\text{-}O)_3][OTf]$.

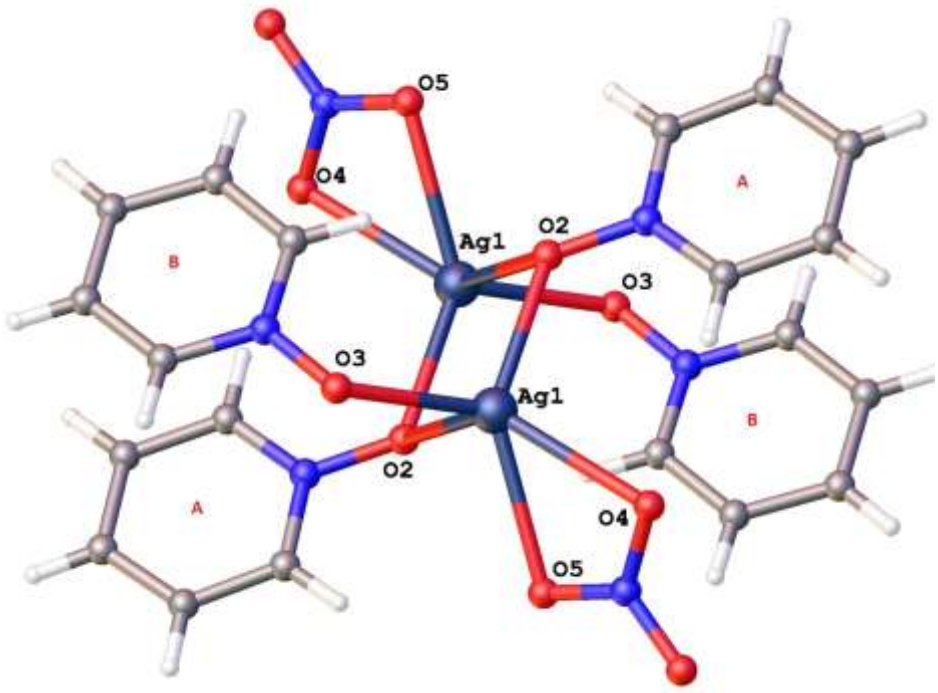

Figure S7: View of the crystal structure of $[Ag(py\text{-}O)_2][NO_3]$ showing dimeric $[Ag_2(py\text{-}O)_4(NO_3)_2]$ moiety formed.

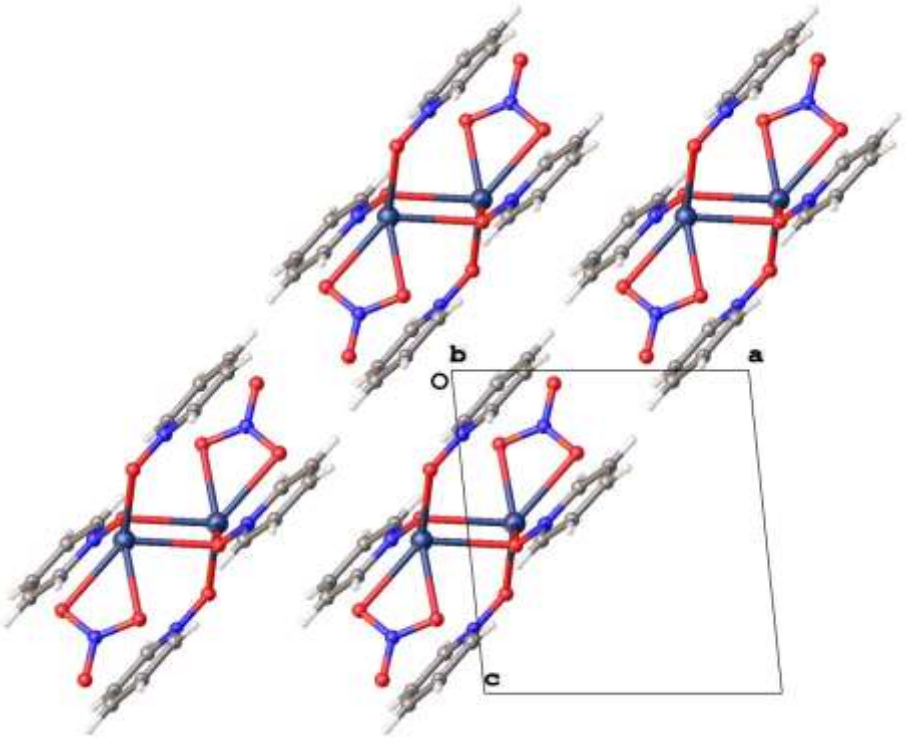

Figure S8: View of the packing in the crystal structure of $[Ag(py\text{-}O)_2][NO_3$.

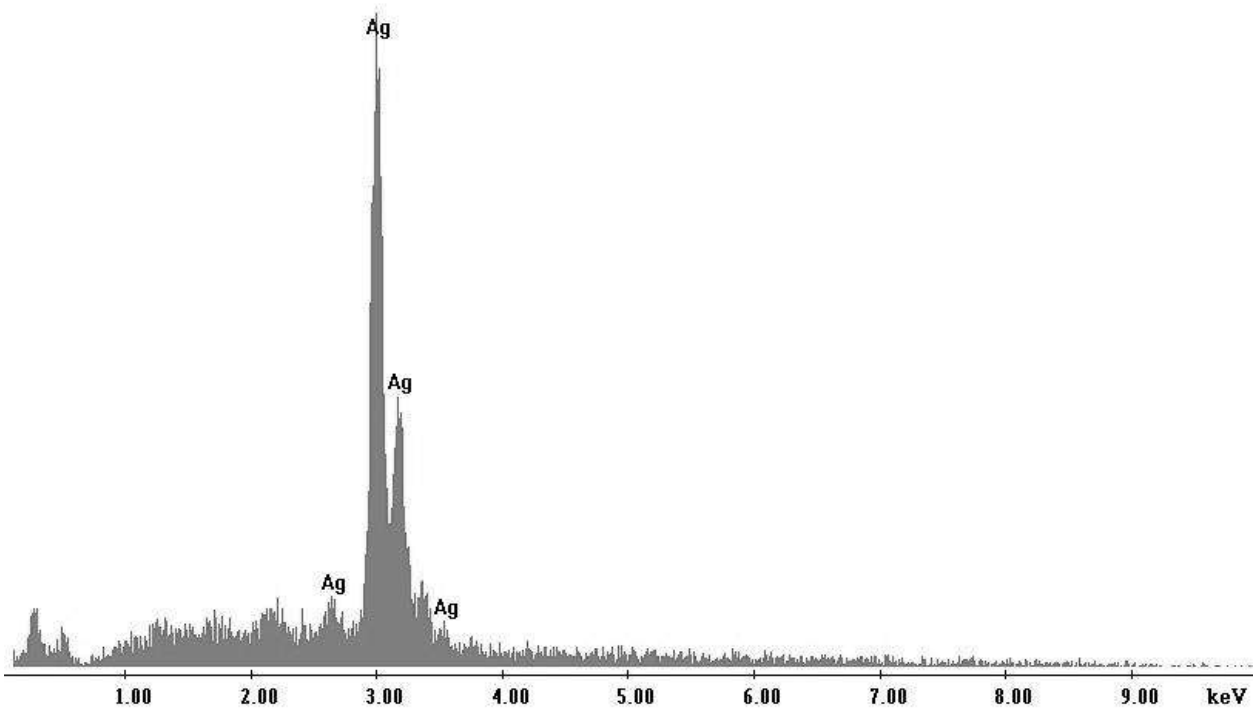

Figure S9: EDX spectrum of a silver deposit of $[Ag(pyO)_3][NO_3]$ plated at -1.0 A dm^{-2} for 60 seconds at 90°C showing only peaks of silver, indicating that the gold substrate is completely covered and the deposits are pure silver.