Supporting Information for the manuscript:

High current density electrodeposition of cobalt from cobalt(II) liquid metal salts

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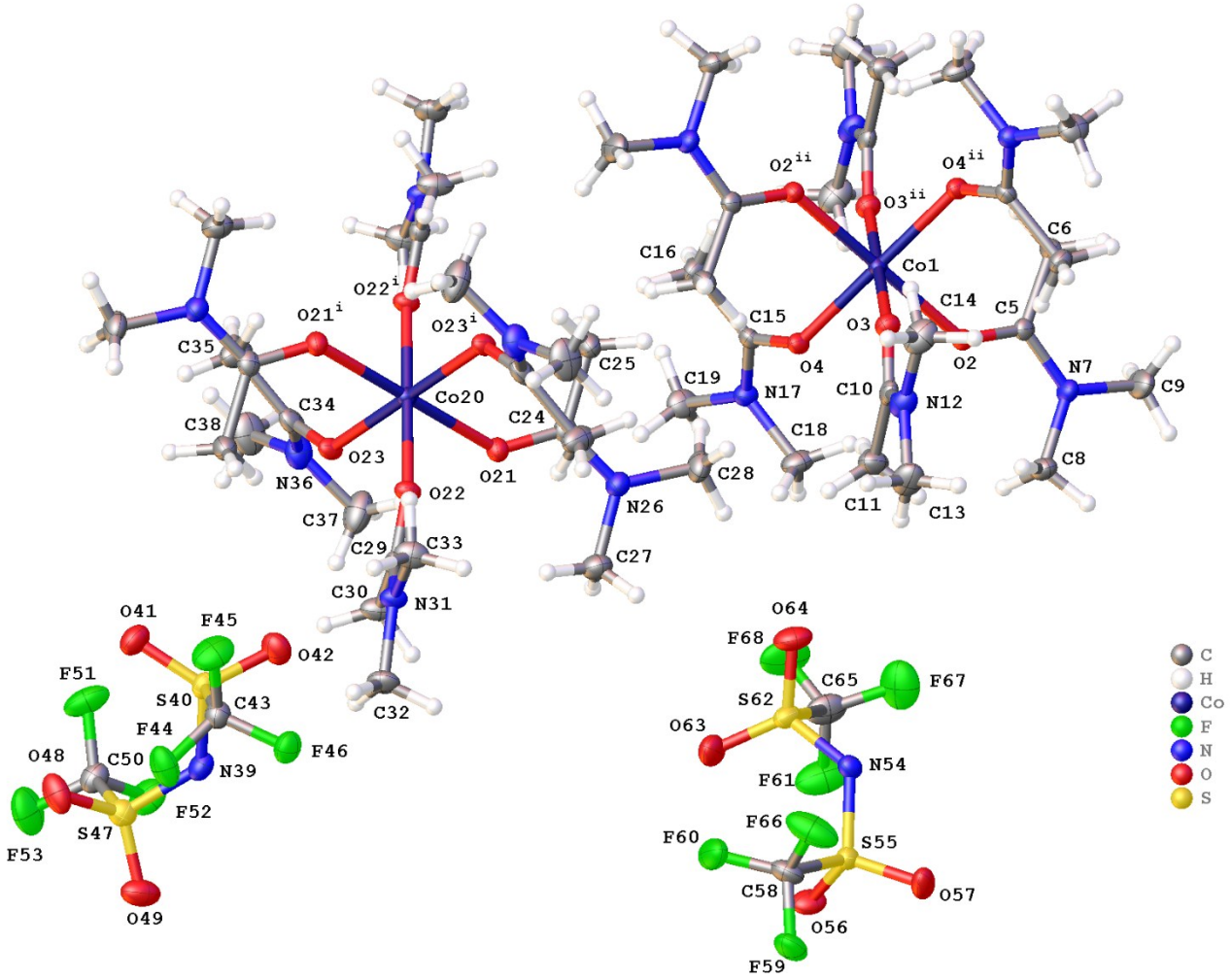

Figure S1: Crystal structure of $[Co(DMAc)_6][Tf_2N]_2$. Symmetry operations: (i) 1-x, -y, 1-z; (ii) 2-x, -y, 1-z. Displacement ellipsoids are drawn at the 50 % probability level.

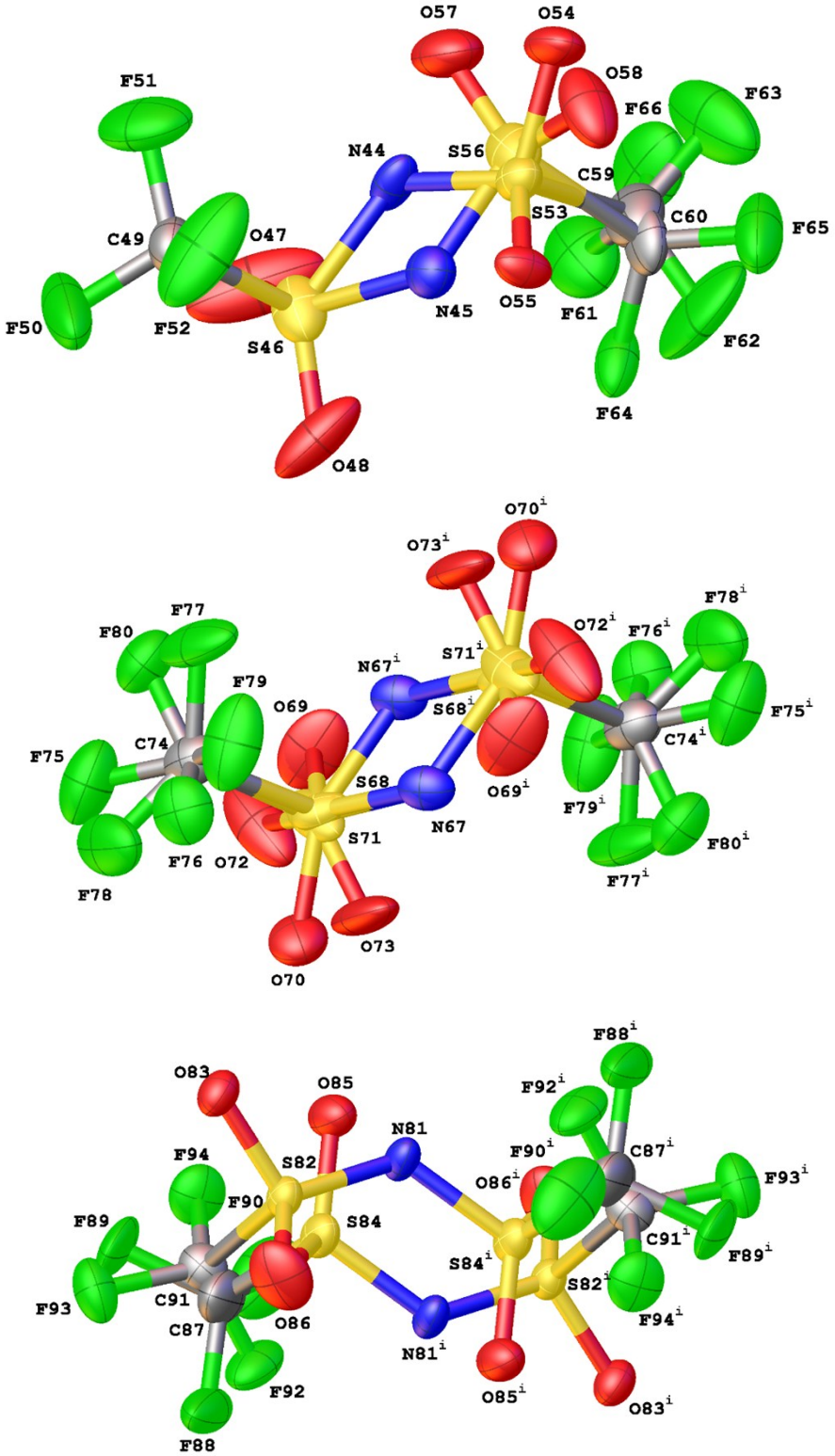

Figure S2: Close-up view of the disorder on the bis(trifluoromethylsulfonyl)imide anions in the crystal structure of $[Co(NMP)_6][Tf_2N]_2$. Symmetry operations: middle: 2-x, 2-y, 1-z; bottom: -x, -y, 2-z. Displacement ellipsoids are drawn at the 50 % probability level.

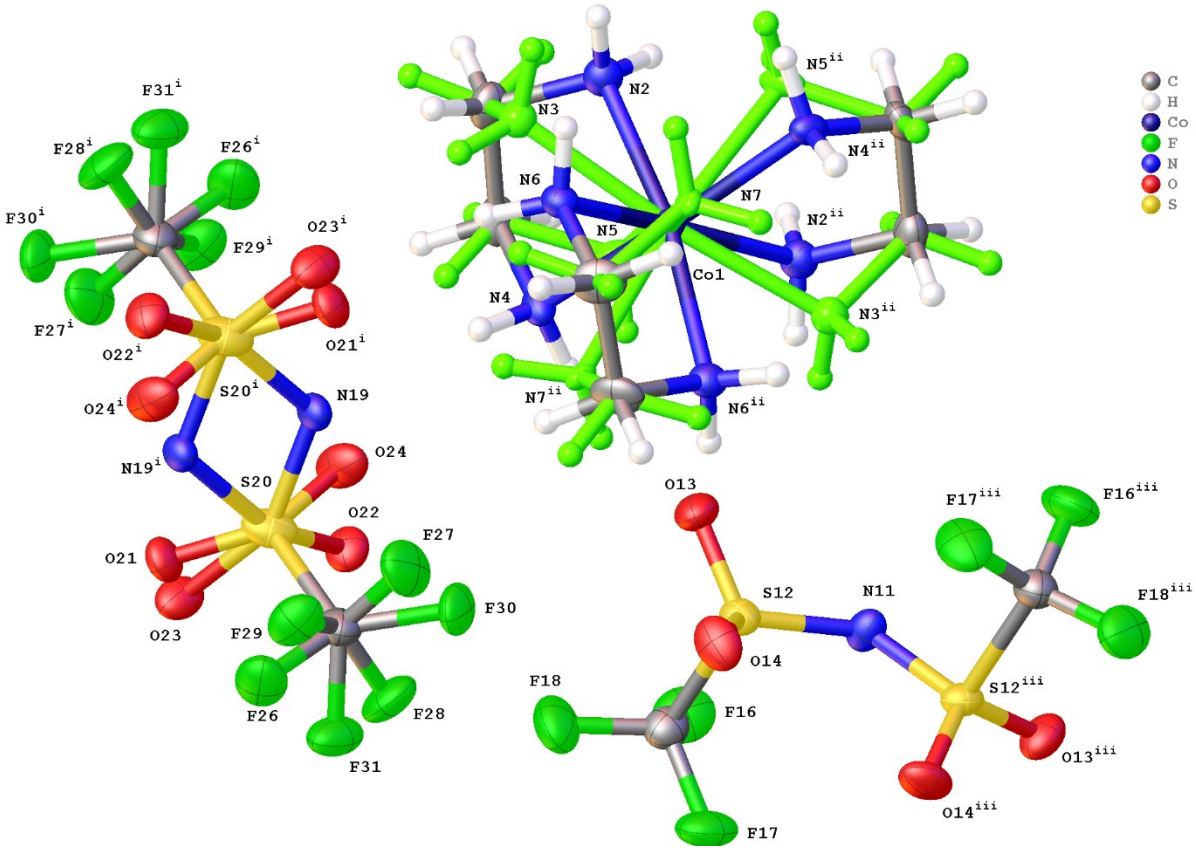

Figure S3: Crystal structure of $[Co(en)_3][Tf_2N]_2$, showing the disorder over two positions of the cation and one bis(trifluoromethylsulfonyl)imide anion. Symmetry operations: (i): -x, -y, 1-z; (iii) 1-x, y, 3/2-z. Displacement ellipsoids are drawn at the 50 % probability level.

Table S1: Interatomic bond lengths and interaction distances for the crystal structures of $[Co(DMSO)_6][Tf_2N]_2$, $[Co(NMP)_6][Tf_2N]_2$ and $[Co(py\text{-}O)_6][Tf_2N]_2$.

Compound	Interaction	Distance (Å)	symmetry operation	Compound	Interaction	Distance (Å)	symmetry operation
$[Co(NMP)_6][Tf_2N]_2$	C10-H10B-O69	3.350(5)	-1+x,y,z	$[Co(py\text{-}O)_6][Tf_2N]_2$	C14-H14-N23	3.461(2)	x,-1+y,z
	C12-H12A-O7	3.215(3)		continued	C15-H15-O2	3.171(2)	x,-1+y,z
	C13-H13A-O2	2.883(3)			C18-H18-O26	3.294(2)	
	C13-H13B-O69	3.227(5)	-1+x,y,z		C20-H20-O32	3.378(2)	1/2-x,1/2+y,1/2-z
	C16-H16B-O54	3.354(5)	x,1+y,z		C21-H21-O32	3.393(2)	-1/2+x,3/2-y,-1/2+z
	C17-H17A-O70	3.295(6)	1-x,2-y,1-z		C22-H22-O3	2.996(2)	1-x,1-y,-z
	C18-H18B-O86	3.269(3)	-x,1-y,1-z				
	C19-H19A-O2	2.841(3)			ring A - ring B	5.1357(10)	x, 1+y, z
	C22-H22A-O83	3.490(4)	1-x,1-y,1-z		ring A - ring C	5.0257(10)	1-x, 1-y, 1-z
	C24-H24A-O55	3.274(4)	1-x,1-y,-z		ring A - ring C	5.5497(10)	1-x, 2-y, -z
	C25-H25A-O4	2.859(4)			ring A - ring A	5.1357(10)	x, -1+y, z
	C29-H29A-O83	3.392(4)	x,y,-1+z		ring A - ring A	5.6201(10)	1-x, 1-y, -z
	C30-H30A-F51	3.298(3)			ring A - ring C	5.1575(10)	x, -1+y, -z
	C31-H31A-O5	2.844(3)			ring A - ring C	5.9237(10)	x, y, z
	C34-H34B-O55	3.121(4)	1-x,1-y,-z		ring A - ring A	5.5498(10)	1-x, 2-y, -z
	C37-H37C-O6	2.849(2)			ring A - ring B	5.1575(10)	x, 1+y, z
	C42-H42A-O4	3.232(3)					
	C43-H43A-O7	2.820(3)			C27-F29-ring A	3.7096(16)	3/2-x, -1/2+y, ½-z
	C43-H43A-O7	2.820(3)			C27-F30-ring B	3.3331(14)	3/2-x, -1/2+y, ½-z
$[Co(py\text{-}O)_6][Tf_2N]_2$	C6-H6-F37	3.214(2)	1/2+x,3/2-y,-1/2+z		C34-F37-ring B	3.3786(13)	1/2-x, -1/2+y, ½-z
	C7-H7-O32	3.454(2)	1/2+x,3/2-y,-1/2+z				
	C10-H10-O26	3.337(2)			S31-O33-ring C	3.2887(15)	½-x, ½+y, ½-z
	C12-H12-O26	3.261(2)					

Table S2: Interatomic bond lengths and interaction distances for the crystal structures of $[Co(DMAc)_6][Tf_2N]_2$, $[Co(en)_3][Tf_2N]_2$ and $[Co(phen)_3][Tf_2N]_2$.

Compound	Interaction	Distance	symmetry operation	Compound	Interaction	Distance	symmetry operation
$[Co(DMAc)_6][Tf_2N]_2$	C6-H6B-O41	3.467(3)	1/2+x,1/2-y,-1/2+z	$[Co(phen)_3][Tf_2N]_2$	C92-H92-F505	3.202(4)	1-x,1/2+y,3/2-z
	C6-H6C-O3	3.228(3)	2-x,-y,1-z	continued	C152-H152-O533	3.045(4)	x,1/2-y,1/2+z
	C6-H6C-O4	3.311(3)	2-x,-y,1-z		C162-H162-O533	3.120(4)	x,1/2-y,1/2+z
	C11-H11B-O4	3.288(3)			C212-H212-O545	3.116(5)	1-x,1/2+y,3/2-z
	C14-H14B-O3	2.706(3)			C222-H222-O466	3.289(5)	
	C25-H25B-O56	3.378(3)	x,-1+y,z		C272-H272-O474	3.383(4)	
	C25-H25C-O23	3.315(4)	1-x,-y,1-z		C292-H292-O535	3.310(4)	
	C27-H27A-O22	2.693(3)			C332-H332-O474	3.397(4)	x,1/2-y,1/2+z
	C28-H28B-O64	3.362(3)			C362-H362-O546	3.293(4)	1-x,-1/2+y,3/2-z
	C30-H30C-O23	3.211(3)			C392-H392-F563	3.171(4)	1-x,1-y,1-z
	C33-H33C-O22	2.690(3)			C647-H647-O543	3.360(5)	
	C35-H35C-F59	3.303(3)	1-x,1-y,1-z		C6#-H5#-ring R	3.828(3)	-x, 1-y, 1-z
	C38-H38A-O49	3.313(4)	x,-1+y,z		C10#-H8#-ring B	3.308(3)	x, y, z
	C38-H38C-O42	3.517(4)	3/2-x,-1/2+y,3/2-z		C21#-H15#-ring Z	3.579(3)	x, y, z
$[Co(en)_3][Tf_2N]_2$	N2-H2A-O13	3.234(4)	-x,y,3/2-z		C46#-H32#-ring N	3.207(3)	x, y, z
	N2-H2B-O14	3.156(3)	-1/2+x,1/2+y,3/2-z		C90#-H60#-ring H	3.518(5)	x, y, z
	N4-H4A-O13	3.140(4)			C75#-F8#-ring Q	4.099(3)	x, 1/2-y, -1/2+z
	N6-H6A-O14	3.316(4)	-x,y,3/2-z		C75#-F9#-ring V	3.980(3)	x, 1/2-y, -1/2+z
$[Co(phen)_3][Tf_2N]_2$	C91-H91-O536	3.313(4)			C78#-F17#-ring P	4.308(4)	1-x, -1/2+y, 3/2-z
	C121-H121-O544	3.197(4)	-x,1-y,1-z		C80#-F24#-ring F	4.685(4)	x, 3/2-y, 1/2+z
	C201-H201-O533	3.163(4)	-x,1/2+y,1/2-z		S2#-O3#-ring D	4.5114(14)	-x, -1/2+y, 1/2-z
	C251-H251-O543	3.020(4)	-x,1-y,-z		S4#-O8#-ring W	4.3072(15)	x, y, z
	C321-H321-O463	3.168(4)			S6#-O11#-ring T	4.2674(14)	x, y, z
	C341-H341-O464	3.186(4)			S7#-O14#-ring I	4.7752(15)	x, y, z
	C341-H341-O463	3.204(4)			S8#-O16#-ring F	4.2898(14)	x, 3/2-y, 1/2+z
	C361-H361-O464	3.225(4)			S8#-O16#-ring K	4.0288(15)	x, 3/2-y, 1/2+z

Table S3: Crystal data and structure refinement details of the crystal structures of $[Co(NMP)_6][Tf_2N]_2$, $[Co(py\text{-}O)_6][Tf_2N]_2$, $[Co(DMAc)_6][Tf_2N]_2$, $[Co(en)_3][Tf_2N]_2$ and $[Co(phen)_3][Tf_2N]_2$.

	$[Co(NMP)_6][Tf_2N]_2$	$[Co(py\text{-}O)_6][Tf_2N]_2$	$[Co(DMAc)_6][Tf_2N]_2$	$[Co(en)_3][Tf_2N]_2$	$[Co(phen)_3][Tf_2N]_2$
Empirical formula	$C_{34}H_{54}CoF_{12}N_8O_{14}S_4$	$C_{34}H_{30}CoF_{12}N_8O_{14}S_4$	$C_{28}H_{54}CoF_{12}N_8O_{14}S_4$	$C_{10}H_{24}CoF_{12}N_8O_8S_4$	$C_{45.25}H_{29.75}CoF_{12}N_8O_8S_4$
Formula weight	1214.02	1189.83	1141.96	799.54	1228.69
Temperature/K	100.00(10)	100.01(10)	100.01(10)	99.98(10)	99.97(11)
Color	pink	pink	pink	pink	pink
Size/mm³	0.2 x 0.2 x 0.15	0.2 x 0.15 x 0.05	0.2 x 0.15 x 0.05	0.2 x 0.1 x 0.05	0.3 x 0.15 x 0.05
Space group	P-1	P21/n	P21/n	Pbcn	P21/c
a/Å	13.2653(5)	12.8271(5)	22.1541(10)	11.2674(6)	18.3290(2)
b/Å	14.2526(6)	8.3492(3)	10.2909(3)	12.6042(5)	23.1050(3)
c/Å	14.3590(5)	22.0771(8)	23.8460(10)	19.7795(8)	23.1472(3)
α/Å	92.887(3)	90	90	90	90
β/Å	100.337(3)	99.636(3)	116.196(6)	90	94.9636(11)
γ/Å	107.217(4)	90	90	90	90
Volume/Å³	2535.52(18)	2331.02(15)	4878.1(4)	2809.0(2)	9765.9(2)
Z	2	2	4	4	8
ρ_{calc} Mg/m³	1.590	1.695	1.555	1.891	1.671
μ/mm^{-1}	0.615	0.667	0.633	1.040	0.632
Wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073
Reflections collected	18375	11281	26709	5978	43524
Independent reflections	10355	4915	10274	2192	20622
R(int)	0.0174	0.0188	0.0242	0.0240	0.0197
R_1 [I≥2σ(I)]	0.0386	0.0289	0.0376	0.0298	0.0484
wR_2 [all data]	0.0909	0.0694	0.0991	0.0702	0.1268

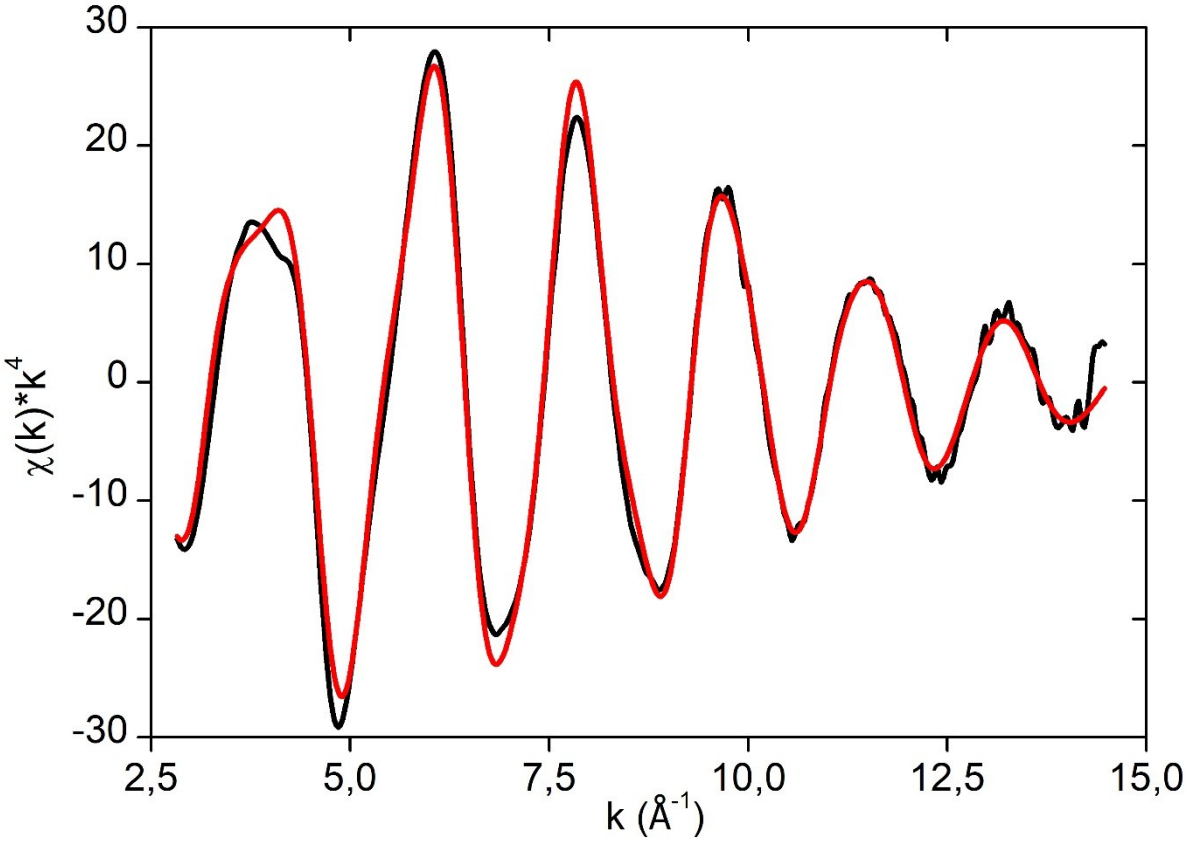

Figure S4: Experimental EXAFS function $\chi(k)*k^4$ (black curve) and fitted model (red curve) of $[Co(DMAc)_6][Tf_2N]_2$ at room temperature.

Table S4: Experimental EXAFS data results and fitting parameters of $[Co(DMAc)_6][Tf_2N]_2$

Temperature	Coordination number	Co-N distance (Å)	Debye Waller factor (Å²)
<RT	6.0(2)	2.075(2)	0.009(1)
RT	5.5(2)	2.059(2)	0.009(1)
80 °C	4.9(2)	2.037(2)	0.010(1)

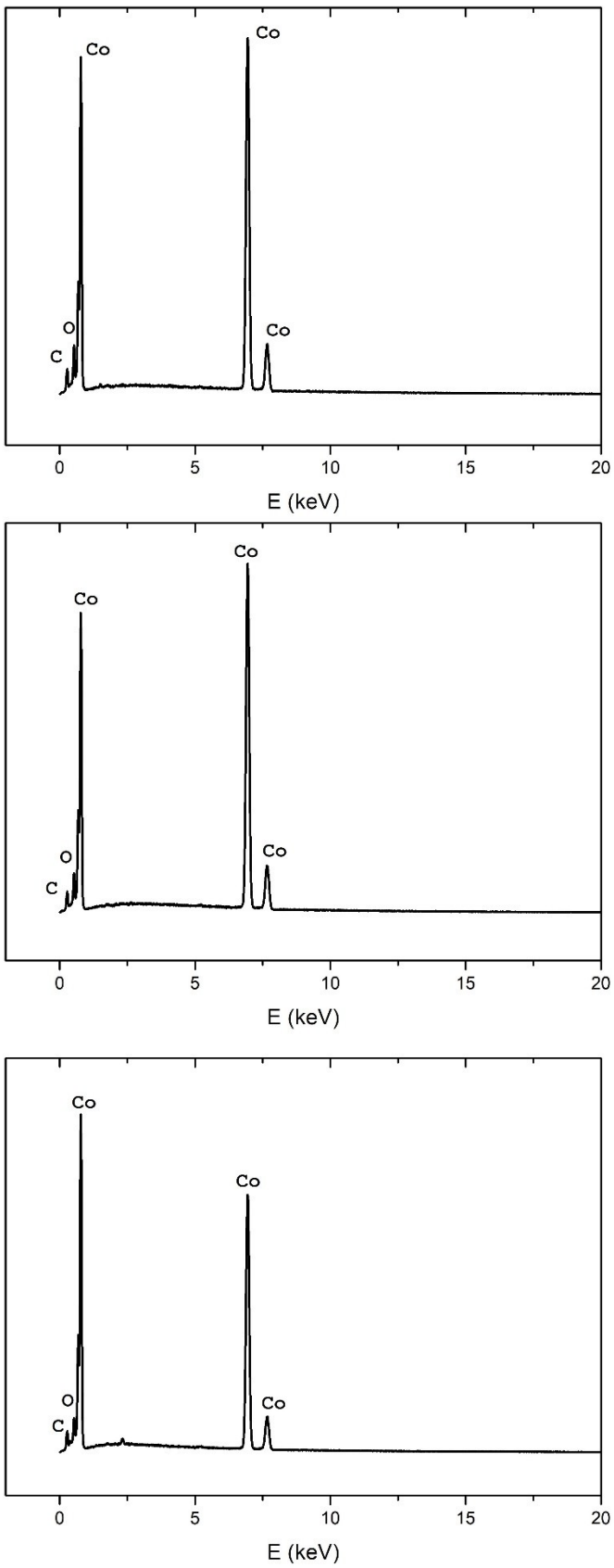

Figure S5: EDX spectra of the deposits, obtained after a galvanic deposition at -1.0 A dm^{-2} for 30 min from $[Co(DMAc)_6][Tf_2N]_2$ (top), $[Co(NMP)_6][Tf_2N]_2$ (middle) and $[Co(DMI)_6][Tf_2N]_2$ (bottom).