Electronic supplementary materials for the paper

Intermolecular Non-Covalent Interactions In The Organic Perrhenates Crystal Structures: From Theory To Practice

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Single-Crystal X-ray analysis

Table S1. Crystal data and structure refinement for **1**-**5**.

Identification code	**1**	**2a**	**2b**	**3**	**4**	**5**
Organic fragment	3,5-Dimethylpyrazolium	3-Methylpyrazolium	3-Methylpyrazolium	Picoliniu m	Piperidinium	Pyrrolidinium
CCDC number	2384438	2384443	2384441	2384445	2384437	2384446
Empirical formula	$C_5H_{10}N_2O_4Re$	$C_4H_7N_2O_4Re$	$C_4H_7N_2O_4Re$	$C_{12}H_{11}N_2O_8Re$	$C_5H_{12}NO_4Re$	$C_4H_{10}NO_4Re$
Formula weight	348.35	333.32	333.32	497.43	336.36	322.33
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	orthorhombic	monoclinic	triclinic	monoclinic	triclinic	monoclinic
Space group	Pnma	$P2_1/c$	P-1	$P2_1/c$	P1	$P2_1/c$
a/Å	12.086(2)	5.4022(3)	7.0126(9)	10.7017(9)	5.807(2)	5.4974(3)
b/Å	8.5629(14)	14.7984(9)	8.0573(10)	11.3642(9)	6.087(2)	8.7838(6)
c/Å	8.3490(13)	9.4457(6)	14.2499(17)	12.4987(11)	6.157(2)	15.4679(10)
α/°	90	90	99.816(5)	90	95.814(11)	90
β/°	90	94.184(3)	91.370(5)	106.006(3)	94.570(11)	96.576(3)
γ/°	90	90	93.454(5)	90	100.825(11)	90
Volume/Å^3	864.1(2)	753.11(8)	791.45(17)	1461.1(2)	211.57(12)	742.00(8)
Z	4	4	4	4	1	4
ρ_{calc}g/cm^3	2.678	2.940	2.797	2.261	2.640	2.885
μ/mm^{-1}	14.042	16.104	15.324	8.362	14.328	16.335
F(000)	644.0	608.0	608.0	944.0	156.0	592.0
Crystal size/mm^3	0.13 × 0.06 × 0.04	0.07 × 0.04 × 0.03	0.16 × 0.08 × 0.06	0.1 × 0.07 × 0.06	0.08 × 0.05 × 0.04	0.16 × 0.12 × 0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	8.254 to 59.986	8.654 to 60	8.3 to 50	8.194 to 59.998	8.904 to 59.998	8.648 to 64.996
Index ranges	-16 ≤ h ≤ 16, -12 ≤ k ≤ 11, -11 ≤ l ≤ 11	-7 ≤ h ≤ 7, -20 ≤ k ≤ 20, -13 ≤ l ≤ 13	-8 ≤ h ≤ 8, -9 ≤ k ≤ 9, -16 ≤ l ≤ 16	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17	-8 ≤ h ≤ 8, -8 ≤ k ≤ 8, -8 ≤ l ≤ 8	-8 ≤ h ≤ 8, -13 ≤ k ≤ 13, -23 ≤ l ≤ 23
Reflections collected	14162	22667	9853	25068	4129	39441
Independent reflections	1326 [R_{int} =	2192 [R_{int} =	2772 [R_{int} =	4241 [R_{int} =	2042 [R_{int} =	2684 [R_{int} =

	0.0852, R_{sigma} = 0.0422]	0.0857, R_{sigma} = 0.0403]	0.0742, R_{sigma} = 0.0769]	0.1143, R_{sigma} = 0.0899]	0.0248, R_{sigma} = 0.0453]	0.0418, R_{sigma} = 0.0162]
Data/restraints/parameters	1326/0/65	2192/0/108	2772/0/202	4241/3/218	2042/3/96	2684/0/98
Goodness-of-fit on F^2	1.064	1.060	1.031	1.005	1.011	1.293
Final R indexes [I>=2σ (I)]	R_1 = 0.0274, wR_2 = 0.0531	R_1 = 0.0293, wR_2 = 0.0545	R_1 = 0.0464, wR_2 = 0.0929	R_1 = 0.0438, wR_2 = 0.0764	R_1 = 0.0187, wR_2 = 0.0333	R_1 = 0.0197, wR_2 = 0.0388
Final R indexes [all data]	R_1 = 0.0376, wR_2 = 0.0566	R_1 = 0.0429, wR_2 = 0.0597	R_1 = 0.0661, wR_2 = 0.1002	R_1 = 0.0723, wR_2 = 0.0871	R_1 = 0.0187, wR_2 = 0.0333	R_1 = 0.0218, wR_2 = 0.0392
Largest diff. peak/hole / e $Å^{-3}$	1.06/-1.32	1.79/-1.83	1.50/-1.33	1.03/-1.35	0.86/-0.92	1.74/-2.36
Flack parameter					0.07(2)	

Table S2. Crystal data and structure refinement for **6-10**.

Identification code	**6**	**7**	**8**	**9**	**10**
Organic fragment	Pyrazinium	Triazolium	Pyrimidinium	Pyridaziniu m	Piperaziniu m
CCDC number	2384444	2384439	2384442	2252646	2384440
Empirical formula	$C_4H_5N_2O_4Re$	$C_2H_4N_3O_4Re$	$C_4H_5N_2O_4Re$	$C_4H_5N_2O_4Re$	$C_4H_{12}N_2O_8Re_2$
Formula weight	331.30	320.28	331.30	331.30	588.56
Temperature/K	100(2)	100(2)	100.15	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/m$	$P2_1/c$	$P2_1/m$	P-1
a/Å	5.8384(5)	5.1704(2)	9.8128(3)	5.3382(3)	6.2945(4)
b/Å	8.7977(7)	12.0115(6)	9.7587(3)	12.9726(8)	7.3292(4)
c/Å	14.3012(12)	9.9500(5)	7.4027(2)	10.5955(7)	7.3349(4)
α/°	90	90	90	90	115.398(2)
β/°	99.293(2)	94.583(1)	101.976(1)	101.710(2)	107.627(2)
γ/°	90	90	90	90	90.178(2)
Volume/$Å^3$	724.93(10)	615.96(5)	693.45(4)	718.47(8)	287.83(3)
Z	4	4	4	4	1
$\rho_{calc}g/cm^3$	3.036	3.454	3.173	3.063	3.395
μ/mm^{-1}	16.729	19.686	17.488	16.879	21.038
F(000)	600.0	576.0	600.0	600.0	264.0
Crystal size/mm^3	0.08 × 0.08 × 0.06	0.2 × 0.14 × 0.13	0.15 × 0.11 × 0.1	0.13 × 0.1 × 0.1	0.08 × 0.06 × 0.04
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	8.456 to 59.998	8.218 to 59.982	8.354 to 69.972	8.406 to 64.996	8.538 to 59.996
Index ranges	$-8 \le h \le 7$, $-12 \le k \le 12$, $-20 \le l \le 20$	$-7 \le h \le 7$, $-16 \le k \le 16$, $-11 \le l \le 13$	$-15 \le h \le 15$, $-15 \le k \le 15$, $-11 \le l \le 11$	$-8 \le h \le 8$, $-19 \le k \le 19$, $-16 \le l \le 16$	$-8 \le h \le 8$, $-10 \le k \le 10$, $-10 \le l \le 10$

Reflections collected	7861	10224	37290	16953	5275
Independent reflections	2094 [R_{int} = 0.0401, R_{sigma} = 0.0403]	1867 [R_{int} = 0.0444, R_{sigma} = 0.0303]	3041 [R_{int} = 0.0385, R_{sigma} = 0.0168]	2681 [R_{int} = 0.0375, R_{sigma} = 0.0238]	1664 [R_{int} = 0.0315, R_{sigma} = 0.0393]
Data/restraints/parameters	2094/0/104	1867/1/107	3041/1/104	2681/0/113	1664/0/80
Goodness-of-fit on F^2	1.061	1.163	1.093	1.074	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0269, wR_2 = 0.0526	R_1 = 0.0208, wR_2 = 0.0488	R_1 = 0.0143, wR_2 = 0.0299	R_1 = 0.0154, wR_2 = 0.0302	R_1 = 0.0218, wR_2 = 0.0358
Final R indexes [all data]	R_1 = 0.0347, wR_2 = 0.0549	R_1 = 0.0223, wR_2 = 0.0495	R_1 = 0.0171, wR_2 = 0.0305	R_1 = 0.0199, wR_2 = 0.0311	R_1 = 0.0249, wR_2 = 0.0367
Largest diff. peak/hole / e $Å^{-3}$	1.37/-1.32	1.87/-1.51	1.19/-1.01	1.12/-1.24	1.03/-1.19

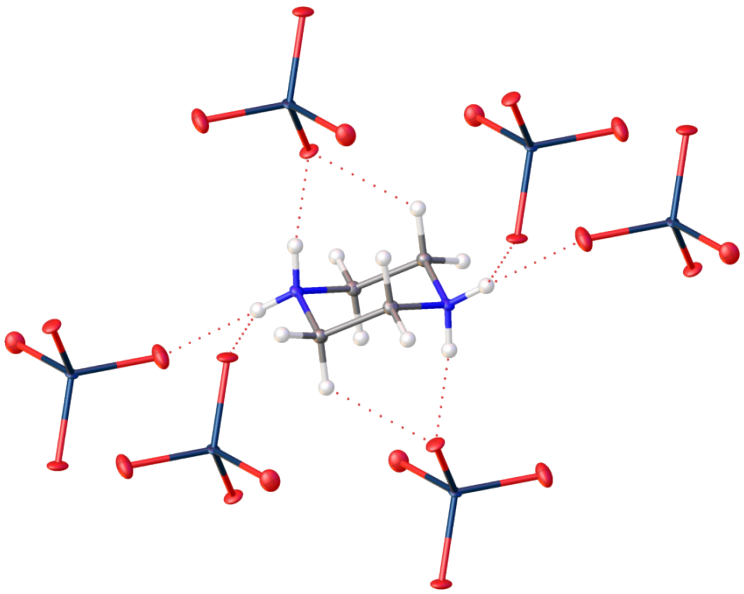

Figure S1. Fragment of the hydrogen bond system of structure **10**.

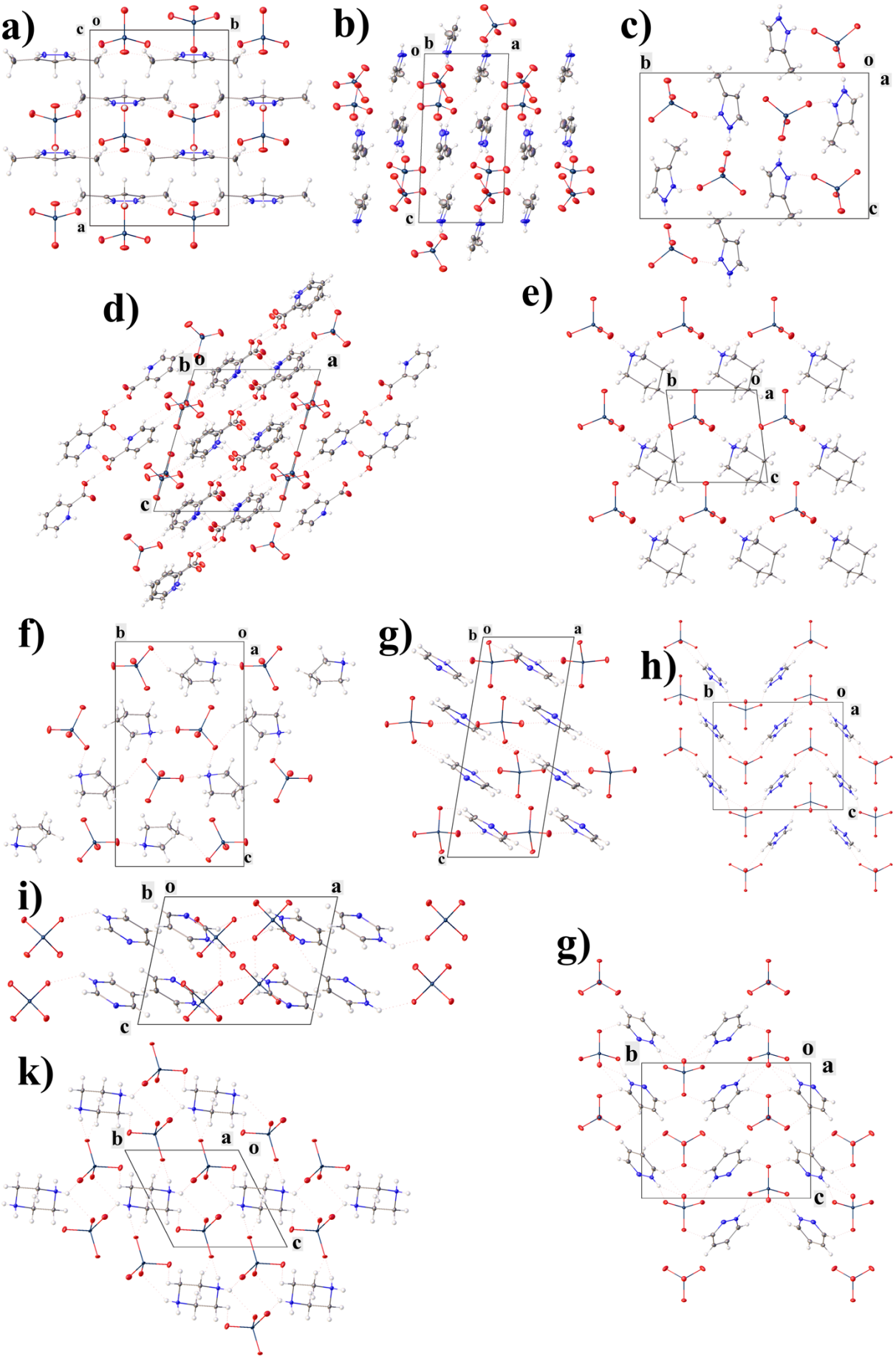

Figure S2. Crystal packing of **1** - **10** (a-k) showing cationic and anionic layers.

Table S3. Parameters of π-stacking interactions in **2a**.

Ring 1	Ring 2	Angle	Centroid-centroid distance	Shift distance
C15N11N12C13C14	C15N11N12C13C14 (-X,2-Y,1-Z)	0.000	3.657	1.231
	C15N11N12C13C14 (1-X,2-Y,1-Z)	0.000	3.613	1.691
C15N11N12C13C14	C15N11N12C13C14 (1-X,3-Y,2-Z)	0.000	3.623	1.434

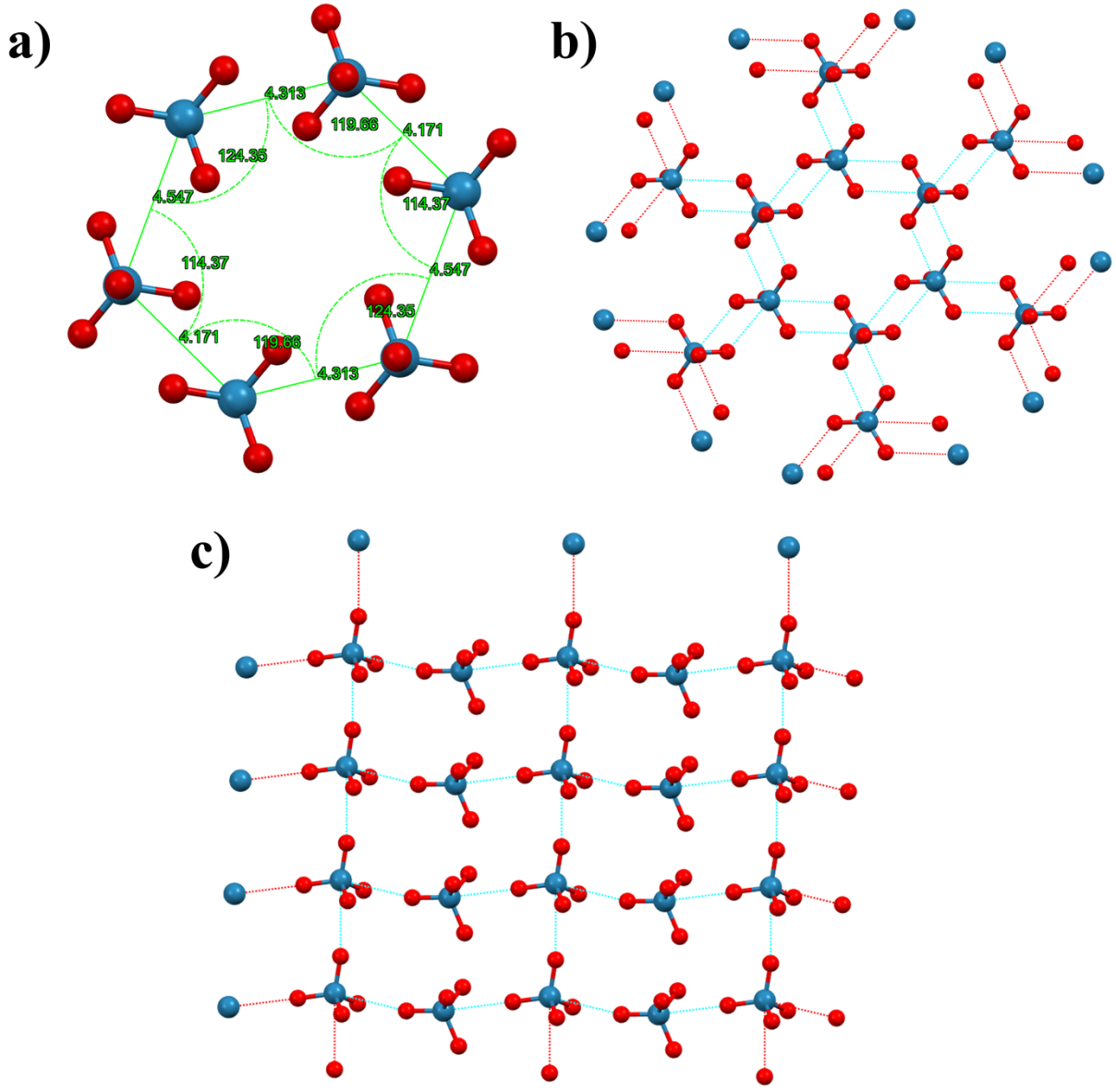

Figure S3. An elementary unit of a 2D network in **10** with distances and angles (a) and a fragment of a 2D anion network in **10** (b) and **7** (c).

Powder X-ray diffraction (pXRD)

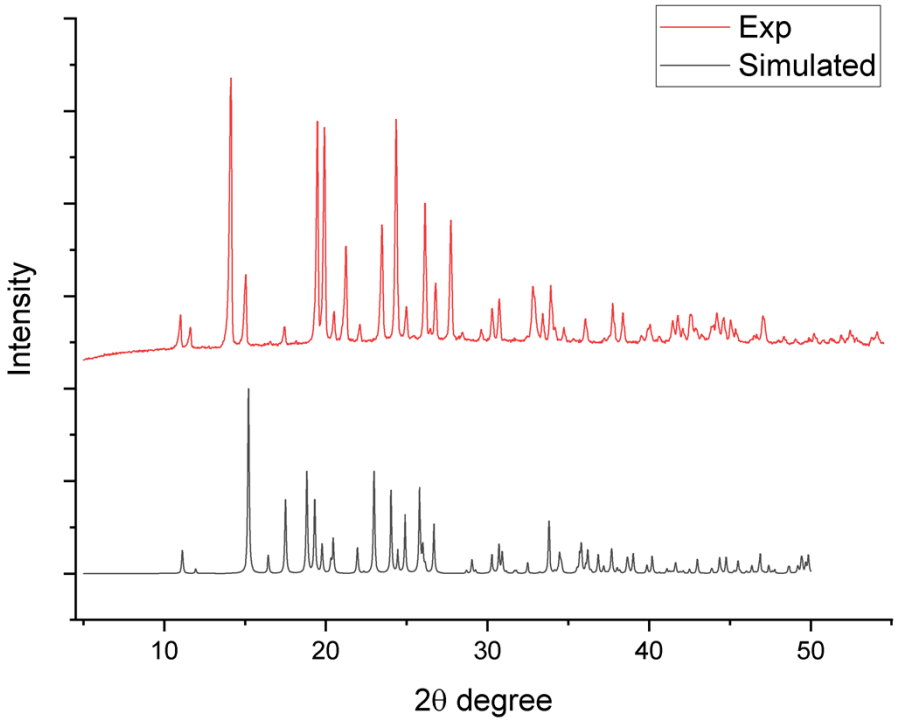

Figure S4. Experimental and theoretical X-ray phase patterns of dimethylpyrazolium perrhenate (compound **1**)

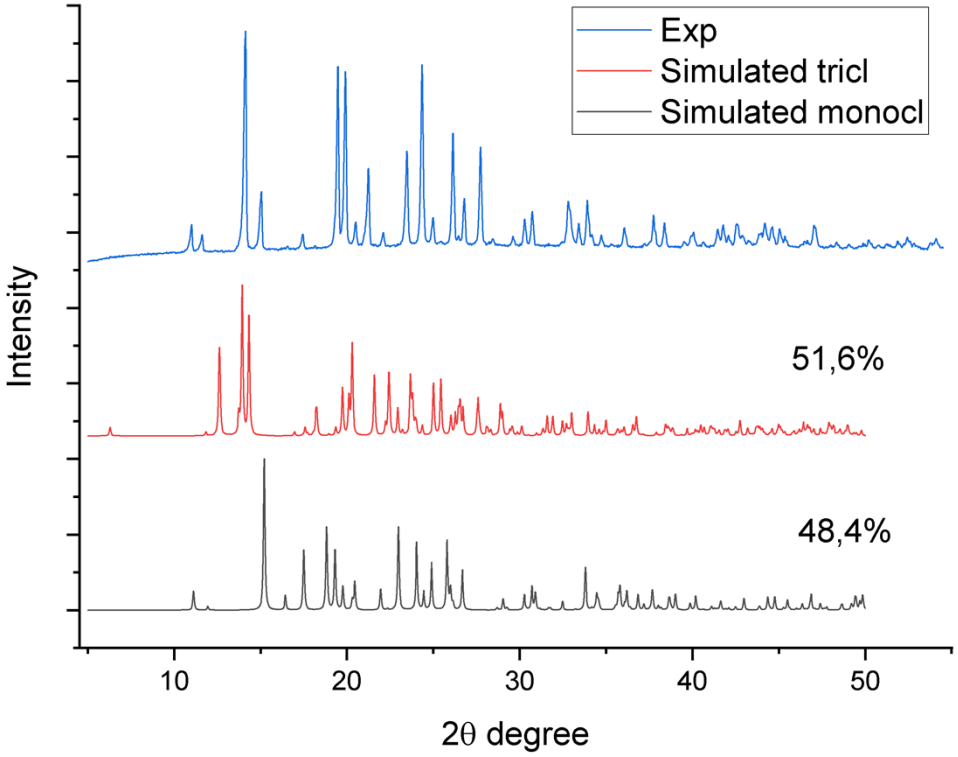

Figure S5. Experimental and theoretical X-ray phase patterns of 3-methylpyrazolium perrhenate (compound **2**) with the percentage content of each phase.

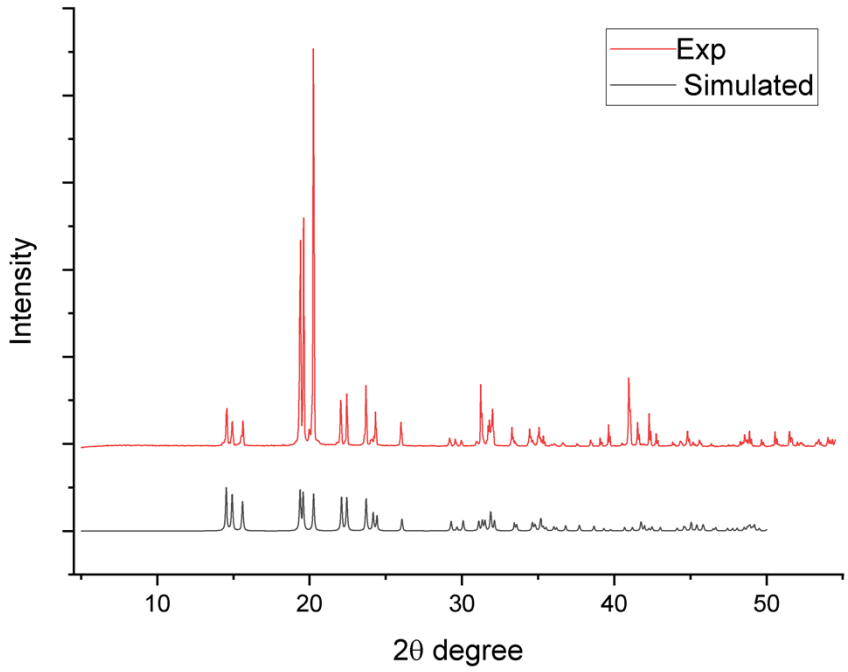

Figure S6. Experimental and theoretical X-ray phase patterns of picolinium perrhenate (compound **3**)

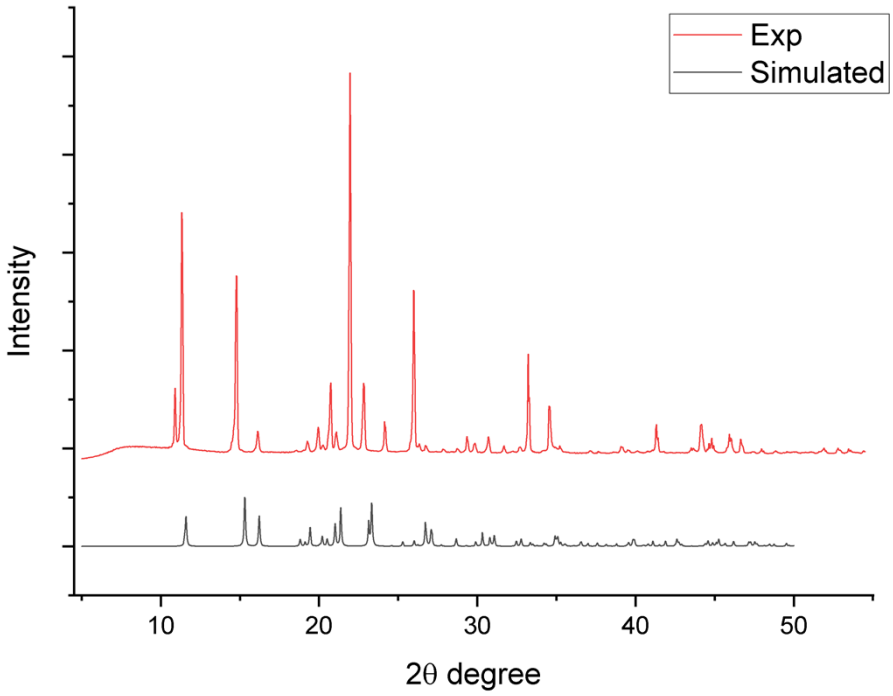

Figure S7. Experimental and theoretical X-ray phase patterns of piperidinium perrhenate (compound **4**)

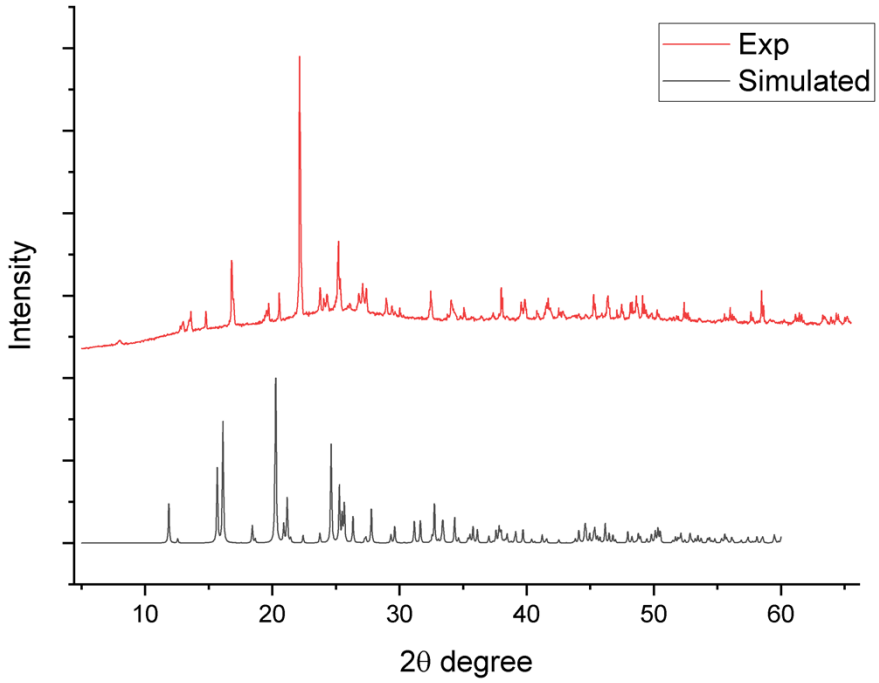

Figure S8. Experimental and theoretical X-ray phase patterns of pyrrolidinium perrhenate (compound **5**)

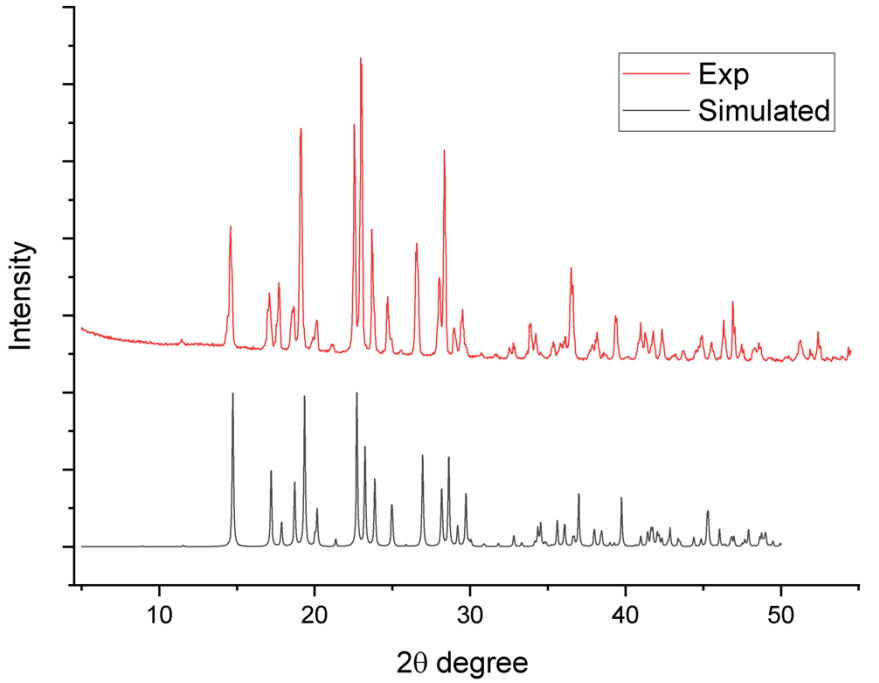

Figure S9. Experimental and theoretical X-ray phase patterns of pyrazinium perrhenate (compound **6**)

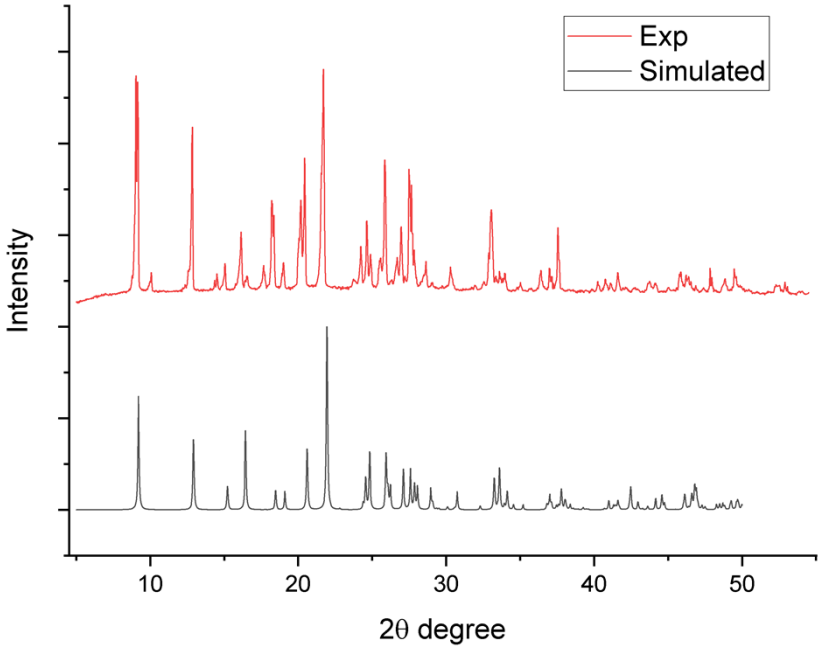

Figure S10. Experimental and theoretical X-ray phase patterns of triazolium perrhenate (compound **7**)

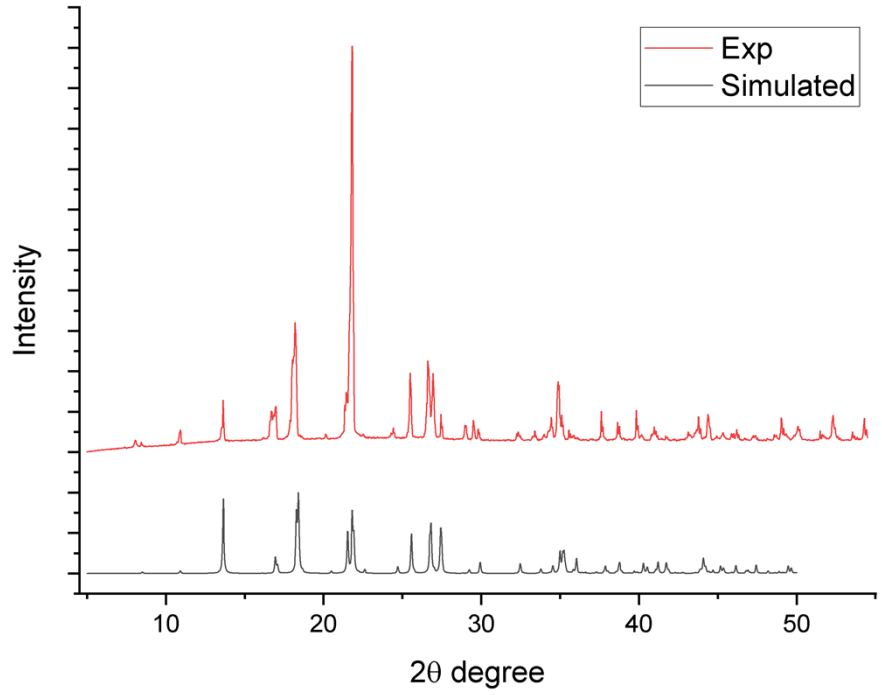

Figure S11. Experimental and theoretical X-ray phase patterns of pyrimidinium perrhenate (compound **8**)

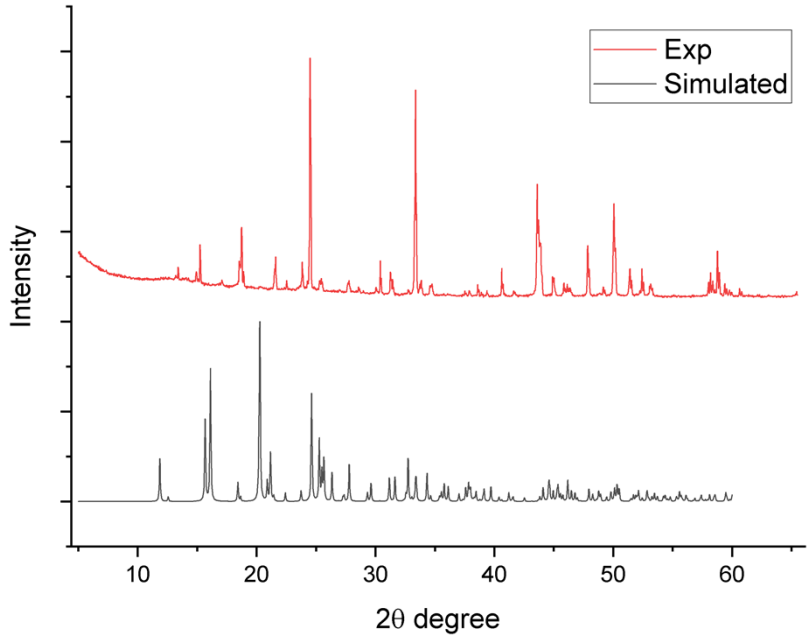

Figure S12. Experimental and theoretical X-ray phase patterns of pyridazinium perrhenate (compound **9**)

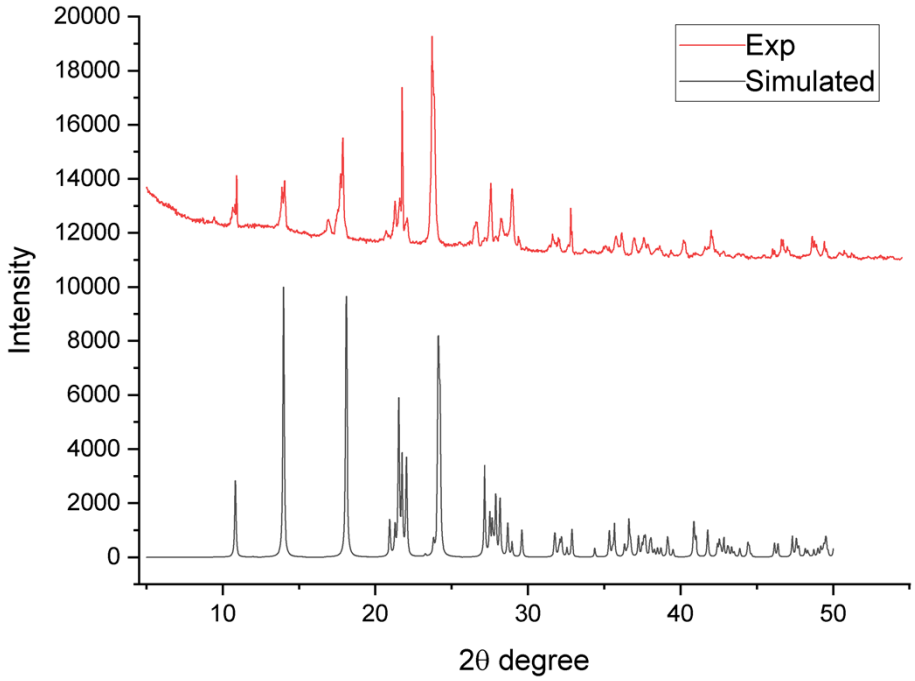

Figure S13. Experimental and theoretical X-ray phase patterns of piperazinium perrhenate (compound **10**)

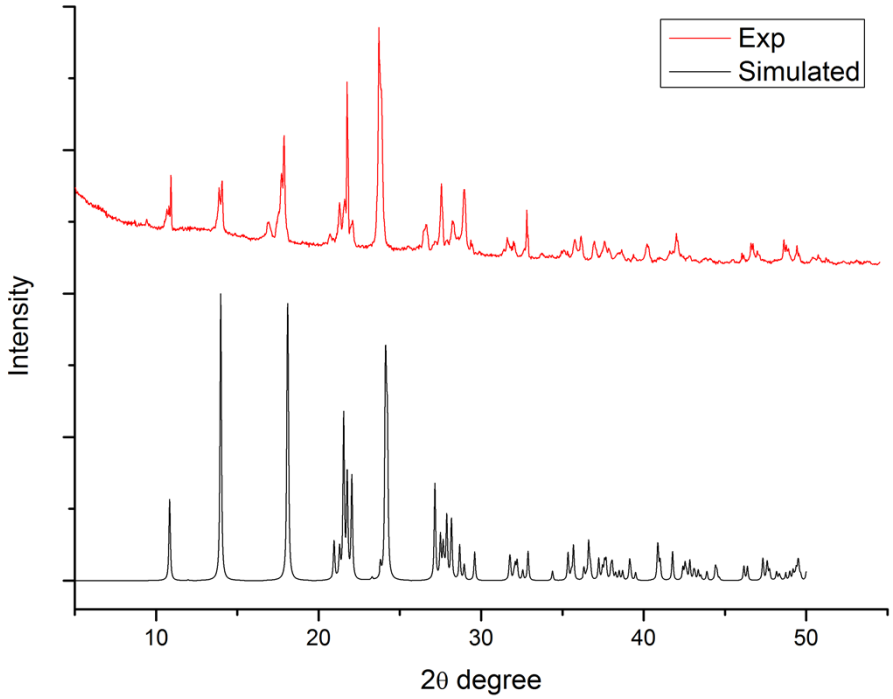

Figure S14. Experimental and theoretical X-ray phase patterns of guanidinium perrhenate (compound **11**)

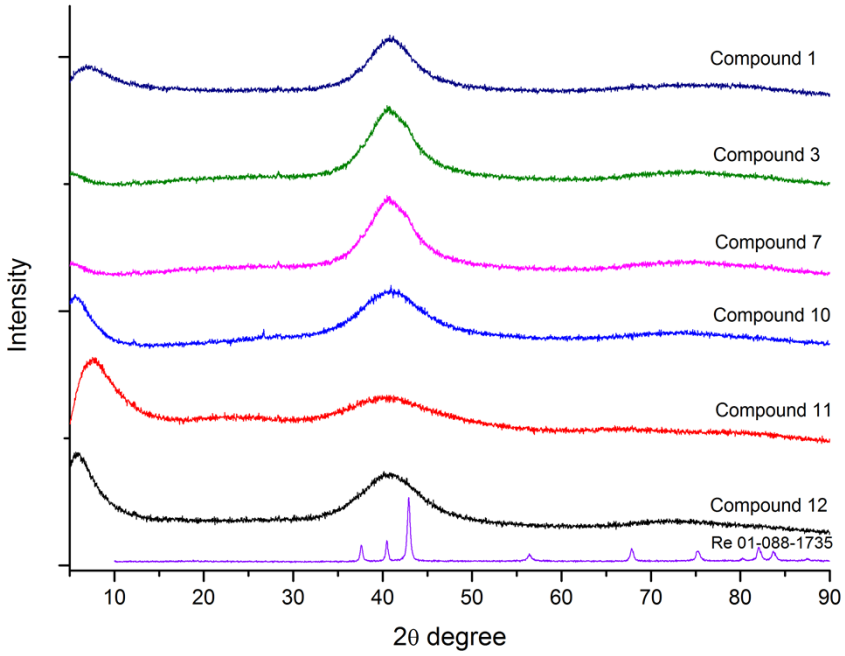

Figure S15. X-ray phase analysis of thermal decomposition products of compounds **1**, **3**, **7**, **10**, **11**, **12** in comparison with metallic rhenium.

MALDI-ToF

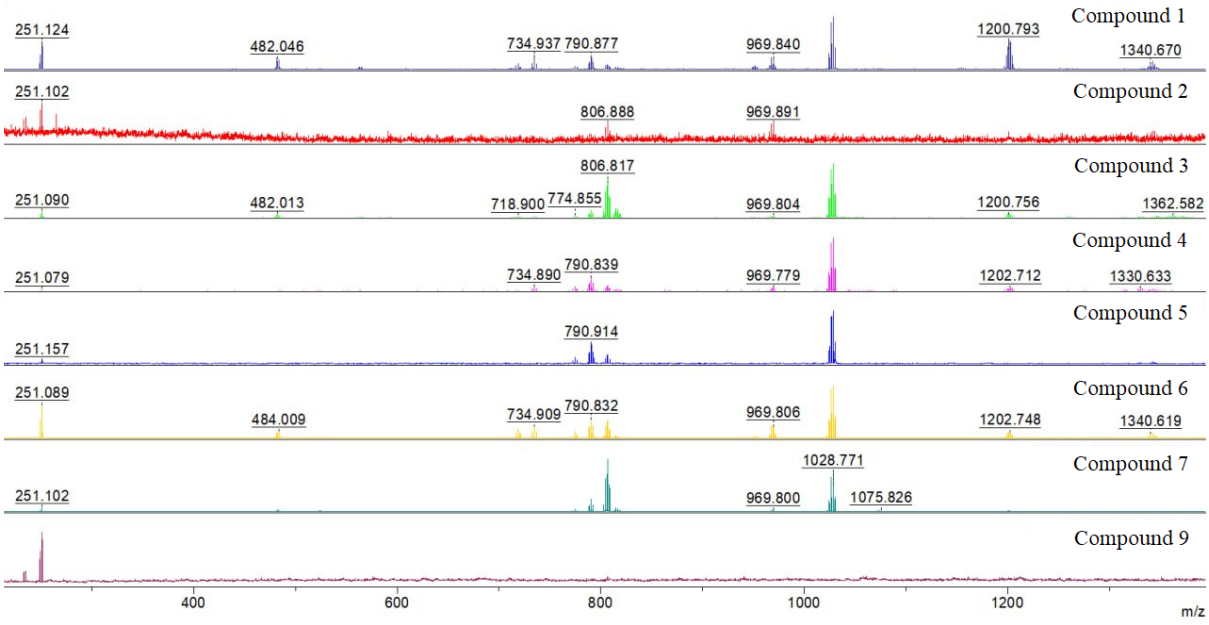

Figure S16. MALDI spectrometry of compounds **1**-**7** and **9** obtained for anions in reflex