Electronic Supplementary Information

Metal Salt Assisted Electrospray Ionization Mass Spectrometry for Soft Ionization of GAP Polymers in Negative Ion Mode

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Table S1. Comparison of the observed peaks in the systems with $NaNO_3$ and related parameters in negative ion mode with variation in applied voltage

condition	$NaNO_3$ or not	series	composition	observed peaks	M_n	M_w	*PDI*
	basic unit		M_1	486, 585, 684, 783, 882, 981, 1080, 1179, 1278, 1377, 1476, 1575, 1674			
-2.5 kV	N-with	A	$[M_1+NO_3]^-$ m/z	647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637	949.1	989.2	1.042
-3.0 kV	N-with	A	$[M_1+NO_3]^-$ m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637, 1736	942.7	997.7	1.058
-3.5 kV	N-with	A	$[M_1+NO_3]^-$ m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637, 1736	979.5	1031.8	1.053
-4.0 kV	N-with	A	$[M_1+NO_3]^-$ m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637, 1736	990.6	1040.6	1.050
	basic unit		M_2	414, 513, 612, 711, 810, 909, 1008, 1107, 1206, 1305, 1404			
-2.5 kV	N-with	B	$[M_2+NO_3]^-$ m/z	575, 674, 773, 872, 971, 1070, 1169, 1268, 1367	810.2	833.2	1.028
-3.0 kV	N-with	B	$[M_2+NO_3]^-$ m/z	476, 575, 674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466	802.6	851.7	1.061
-3.5 kV	N-with	B	$[M_2+NO_3]^-$ m/z	476, 575, 674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466, 1565	812.0	860.4	1.060
-4.0 kV	N-with	B	$[M_2+NO_3]^-$ m/z	476, 575, 674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466, 1565	797.9	841.0	1.054

Note: "N-with" means "negative ion mode and with $NaNO_3$". *A* and *B* mean series *A* and *B* in **Figure 3** in the main text. Due the relative low peak intensity for other series, the M_n, M_w and *PDI* values were not calculated.

Table S2. Comparison of the observed peaks in the systems with $NaNO_3$ and related parameters in negative ion mode with variation in concentration of $NaNO_3$

condition	$NaNO_3$ or not	series	composition	observed peaks	M_n	M_w	*PDI*
	basic unit		M_1	486, 585, 684, 783, 882, 981, 1080, 1179, 1278, 1377, 1476, 1575, 1674			
0 mmol L^{-1}	N-with	A	$[M_1+NO_3]^-$ m/z	548 647, 746, 845, 944, 1043, 1142, 1241	693.1	713.1	1.029
0.1 mmol L^{-1}	N-with	A	$[M_1+NO_3]^-$ m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637	804.8	854.0	1.061
0.5 mmol L^{-1}	N-with	A	$[M_1+NO_3]^-$ m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637, 1736	1010.0	1053.6	1.043
1.0 mmol L^{-1}	N-with	A	$[M_1+NO_3]^-$ m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637, 1736	1042.6	1093.1	1.048
1.5 mmol L^{-1}	N-with	A	$[M_1+NO_3]^-$ m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637,	1027.2	1070.5	1.042
2.0 mmol L^{-1}	N-with	A	$[M_1+NO_3]^-$ m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637,	994.8	1040.9	1.046
3.0 mmol L^{-1}	N-with	A	$[M_1+NO_3]^-$ m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637,	1038.8	1093.2	1.052
5.0 mmol L^{-1}	N-with	A	$[M_1+NO_3]^-$ m/z	548, 647, 746, 845, 944, 1043, 1142, 1241	857.9	889.9	1.037
	basic unit		M_2	414, 513, 612, 711, 810, 909, 1008, 1107, 1206, 1305, 1404			
0 mmol L^{-1}	N-with	B	$[M_2+NO_3]^-$ m/z	575, 674, 773, 872	673.9	687.3	1.020
0.1 mmol L^{-1}	N-with	B	$[M_2+NO_3]^-$ m/z	575, 674, 773, 872, 971, 1070, 1169, 1268	732.4	756.0	1.032
0.5 mmol L^{-1}	N-with	B	$[M_2+NO_3]^-$ m/z	575, 674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466	836.9	874.4	1.045
1.0 mmol L^{-1}	N-with	B	$[M_2+NO_3]^-$ m/z	575, 674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466	823.3	870.8	1.057
1.5 mmol L^{-1}	N-with	B	$[M_2+NO_3]^-$ m/z	575, 674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466	803.4	848.0	1.056
2.0 mmol L^{-1}	N-with	B	$[M_2+NO_3]^-$ m/z	575, 674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466	789.1	834.3	1.057
3.0 mmol L^{-1}	N-with	B	$[M_2+NO_3]^-$ m/z	575, 674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466	798.4	859.9	1.077
5.0 mmol L^{-1}	N-with	B	$[M_2+NO_3]^-$ m/z	575, 674, 773, 872, 971, 1070	718.9	741.9	1.032

Note: "N-with" means "negative ion mode and with $NaNO_3$". *A* and *B* mean series *A* and *B* in **Figure 4** in the main text. Due the relative low peak intensity for other series, the M_n, M_w and *PDI* values were not calculated.

Table S3. Comparison of the observed peaks in the systems with $NaNO_3$ and related parameters in negative ion mode with variation in the types of metal salts

metal salt	$NaNO_3$ or not	series	composition	observed peaks	M_n	M_w	*PDI*
	basic unit		M_1	486, 585, 684, 783, 882, 981, 1080, 1179, 1278, 1377, 1476, 1575, 1674			
$AgNO_3$	N-with	A	$[M_1+NO_3]^-$ m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637, 1736	1014.1	1054.3	1.040
$Mg(NO_3)_2$	N-with	A	$[M_1+NO_3]^-$ m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637, 1736	946.8	997.4	1.053
$Co(NO_3)_2$	N-with	A	$[M_1+NO_3]^-$ m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637	1010.5	1054.3	1.043
$Ni(NO_3)_2$	N-with	A	$[M_1+NO_3]^-$ m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637	894.8	949.1	1.061
$Cu(NO_3)_2$	N-with	A	$[M_1+NO_3]^-$ m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637, 1736	1020.2	1070.8	1.050
$Zn(NO_3)_2$	N-with	A	$[M_1+NO_3]^-$ m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637, 1736	980.2	1032.4	1.053
$Ba(NO_3)_2$	N-with	A	$[M_1+NO_3]^-$ m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637	923.0	968.3	1.049
$Pb(NO_3)_2$	N-with	A	$[M_1+NO_3]^-$ m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637	952.9	997.2	1.046
$Cr(NO_3)_3$	N-with	A	$[M_1+NO_3]^-$ m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637, 1736	1000.2	1048.0	1.048
$Al(NO_3)_3$	N-with	A	$[M_1+NO_3]^-$ m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538	905.5	952.8	1.052
$Fe(NO_3)_3$	N-with	A	$[M_1+NO_3]^-$ m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637	905.7	949.3	1.048
	basic unit		M_2	414, 513, 612, 711, 810, 909, 1008, 1107, 1206, 1305, 1404			
$AgNO_3$	N-with	B	$[M_2+NO_3]^-$ m/z	575, 674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466, 1565	841.7	875.3	1.040
$Mg(NO_3)_2$	N-with	B	$[M_2+NO_3]^-$ m/z	575, 674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466	830.8	867.1	1.044
$Co(NO_3)_2$	N-with	B	$[M_2+NO_3]^-$ m/z	575, 674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466	824.6	868.5	1.053
$Ni(NO_3)_2$	N-with	B	$[M_2+NO_3]^-$ m/z	476, 575, 674, 773, 872, 971, 1070, 1169, 1268, 1367	763.9	801.9	1.050
$Cu(NO_3)_2$	N-with	B	$[M_2+NO_3]^-$ m/z	575, 674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466,	847.1	891.6	1.053
$Zn(NO_3)_2$	N-with	B	$[M_2+NO_3]^-$ m/z	476, 575, 674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466	808.2	854.1	1.057
$Ba(NO_3)_2$	N-with	B	$[M_2+NO_3]^-$ m/z	575, 674, 773, 872, 971, 1070, 1169, 1268, 1367	825.4	858.6	1.040
$Pb(NO_3)_2$	N-with	B	$[M_2+NO_3]^-$ m/z	476, 575, 674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466, 1565	795.1	833.8	1.049
$Cr(NO_3)_3$	N-with	B	$[M_2+NO_3]^-$ m/z	575, 674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466, 1565	854.4	893.1	1.045
$Al(NO_3)_3$	N-with	B	$[M_2+NO_3]^-$ m/z	476, 575, 674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466	753.9	787.5	1.044
$Fe(NO_3)_3$	N-with	B	$[M_2+NO_3]^-$ m/z	575, 674, 773, 872, 971, 1070, 1169, 1268, 1367	779.6	807.1	1.035

Note: "N-with" means "negative ion mode and with $NaNO_3$". *A* and *B* mean series *A* and *B* in **Figure S1** as below. Due the relative low peak intensity for other series, the M_n, M_w and *PDI* values were not calculated.

Table S4. Comparison of the observed peaks in the systems with different salts and related parameters in negative ion modes

salt	with or not	series	composition		observed peaks									M_n	M_w	*PDI*
	basic unit		M_1		486,	585,	684,	783,	882,	981,	1080, 1179, 1278, 1377					
NaF	N-with		$[M_1+F]^-$	m/z	n/a											
NaCl	N-with	C	$[M_1+Cl]^-$	m/z	521,	620,	719,	818,	917,	1016, 1115, 1214, 1313, 1412, 1511, 1610, 1709				986.8	1029.2	1.043
NaBr	N-with	E	$[M_1+Br]^-$	m/z	567,	666,	765,	864,	963,	1062, 1161, 1260, 1359, 1458, 1557, 1656, 1755				1082.1	1126.4	1.041
NaI	N-with	H	$[M_1+I]^-$	m/z		712,	811,	910,	1009,	1108, 1207, 1306, 1405, 1504, 1603, 1702				1065.6	1103.5	1.035
$NaNO_3$	N-with	A	$[M_1+NO_3]^-$	m/z	548,	647,	746,	845,	944,	1043, 1142, 1241, 1340, 1439, 1538, 1637, 1736				968.2	1033.8	1.068
Na_2SO_4	N-with	L	$[M_1+HSO_4]^-$	m/z		682,	781,	880,	979,	1078, 1177, 1276, 1375, 1474, 1573				1028.8	1063.4	1.034
Na_3PO_4	N-with	L	$[M_1+H_2PO_4]^-$	m/z	583,	682,	781,	880,	979,	1078, 1177, 1276				821.6	856.5	1.043
	basic unit		M_2	m/z	414,	513,	612,	711,	810,	909,	1008, 1107, 1206					
NaF	N-with		$[M_2+F]^-$	m/z	n/a											
NaCl	N-with	A	$[M_2+Cl]^-$	m/z		548,	647,	746,	845,	944,	1043, 1142, 1241, 1340, 1439, 1538			816.6	858.0	1.051
NaBr	N-with	D	$[M_2+Br]^-$	m/z		594,	693,	792,	891,	990,	1089, 1188, 1287, 1386, 1485, 1584			900.8	950.5	1.055
NaI	N-with	G	$[M_2+I]^-$	m/z		640,	739,	838,	937,	1036, 1135, 1234, 1333, 1432, 1531				904.0	935.9	1.035
$NaNO_3$	N-with	O	$[M_2+NO_3]^-$	m/z	476,	575,	674,	773,	872,	971,	1070, 1169, 1268, 1367, 1466			805.9	858.9	1.066
Na_2SO_4	N-with	M	$[M_2+HSO_4]^-$	m/z	511,	610,	709,	808,	907,	1006, 1105				810.0	841.6	1.039
Na_3PO_4	N-with	M	$[M_2+H_2PO_4]^-$	m/z	511,	610,	709,	808,	907,	1006				666.6	691.5	1.037
	basic unit		M_3		442,	541,	640,	739								
NaF	N-with		$[M_3+F]^-$	m/z	n/a											
NaCl	N-with	B	$[M_3+Cl]^-$	m/z	477,	576,	675,	774,	873,	972				736.6	759.2	1.031
NaBr	N-with	C	$[M_3+Br]^-$	m/z		622,	721,	820,	919,	1018, 1117, 1216				868.4	905.9	1.043
NaI	N-with	I	$[M_3+I]^-$	m/z		688,	767,	866,	965,					801.7	814.8	1.016
$NaNO_3$	N-with	K	$[M_3+NO_3]^-$	m/z	504,	603,	702,	801						641.4	650.0	1.013
Na_2SO_4	N-with		$[M_3+HSO_4]^-$	m/z	n/a											
Na_3PO_4	N-with	N	$[M_3+NaHPO_4]^-$	m/z			759,	858,	957,	1056, 1155, 1254, 1353, 1452, 1551				1052.2	1083.5	1.030
	basic unit		M_4					756,	855,	954,	1053, 1152, 1251					
NaF	N-with		$[M_4+F]^-$	m/z	n/a											
NaCl	N-with	D	$[M_4+Cl]^-$	m/z					890,	989,	1088, 1187, 1286, 1385, 1484, 1583, 1682			1206.8	1249.5	1.035
NaBr	N-with	F	$[M_4+Br]^-$	m/z					936,	1035, 1134, 1233, 1332, 1431, 1530, 1629, 1728				1292.6	1326.9	1.027
NaI	N-with	J	$[M_4+I]^-$	m/z						1081, 1180, 1279, 1378, 1477, 1576, 1675, 1774				1352.0	1379.3	1.020
$NaNO_3$	N-with	C	$[M_4+NO_3]^-$	m/z	521,	620,	719,	818,	917,	1016, 1115, 1214, 1313, 1412, 1511, 1610, 1709				1052.3	1123.9	1.068
Na_2SO_4	N-with		$[M_4+HSO_4]^-$	m/z	n/a											
Na_3PO_4	N-with		$[M_4+H_2PO_4]^-$	m/z	n/a											

Note: “N-with” means negative ion mode and with related salt, and “n/a” means no related peaks in mass spectrum.

Table S5. Comparison of the observed peaks and related parameters of different GAP samples without and with addition of $NaNO_3$ in negative ion modes with paper spray

sample	with or not	series	composition		observed peaks	M_n	M_w	*PDI*
GAP #2	basic unit		M_1		387, 486, 585, 684, 783, 882, 981, 1080, 1179, 1278, 1377, 1476, 1575, 1674, 1773, 1872			
	N-without	A	$[M_1+NO_3]^-$	m/z	449, 548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637, 1736, 1835, 1934	789.2	881.7	1.117
	N-with	A	$[M_1+NO_3]^-$	m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637, 1736, 1835, 1934	934.2	1033.0	1.106
	basic unit		M_2		513, 612, 711, 810, 909, 1008, 1107, 1206, 1305, 1404, 1503, 1602, 1701, 1800			
	N-without	B	$[M_2+NO_3]^-$	m/z	575, 674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466, 1565, 1664, 1763, 1862	924.9	1028.6	1.112
	N-with	B	$[M_2+NO_3]^-$	m/z	575, 674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466, 1565, 1664, 1763, 1862	957.2	1068.7	1.116
	basic unit		M_3		541, 640, 739, 838, 937, 1036, 1135, 1234, 1333, 1432, 1531, 1630, 1729			
	N-without	C	$[M_3+NO_3]^-$	m/z	603 702, 801, 900, 999, 1098, 1197, 1296	785.9	831.3	1.058
	N-with	C	$[M_3+NO_3]^-$	m/z	603 702, 801, 900, 999, 1098, 1197, 1296, 1395, 1494, 1593, 1692, 1791	1036.4	1116.2	1.077
GAP #3	basic unit		M_1		387, 486, 585, 684, 783, 882, 981, 1080, 1179, 1278, 1377, 1476, 1575, 1674, 1773, 1872			
	N-without	A	$[M_1+NO_3]^-$	m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637, 1736	795.0	869.6	1.094
	N-with	A	$[M_1+NO_3]^-$	m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637, 1736, 1835, 1934	1127.1	1198.2	1.063
	basic unit		M_2		513, 612, 711, 810, 909, 1008, 1107, 1206, 1305, 1404, 1503, 1602, 1701, 1800			
	N-without	B	$[M_2+NO_3]^-$	m/z	575, 674, 773, 872, 971, 1070, 1169, 1268	758.0	790.6	1.043
	N-with	B	$[M_2+NO_3]^-$	m/z	575, 674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466, 1565, 1664, 1763, 1862	1093.0	1163.9	1.065
	basic unit		M_3		541, 640, 739, 838, 937, 1036, 1135, 1234, 1333, 1432, 1531, 1630, 1729			
	N-without	C	$[M_3+NO_3]^-$	m/z	603 702	648.4	652.2	1.006
	N-with	C	$[M_3+NO_3]^-$	m/z	603 702, 801, 900, 999, 1098, 1197, 1296, 1395	929.0	973.2	1.048
	basic unit		M_4		1152, 1251, 1350, 1449, 1548, 1647, 1746, 1845			
	N-without	D	$[M_4+NO_3]^-$	m/z	1214, 1313, 1412, 1511, 1610, 1709, 1808	1426.5	1447.2	1.015
	N-with	D	$[M_4+NO_3]^-$	m/z	1214, 1313, 1412, 1511, 1610, 1709, 1808, 1907	1498.3	1523.9	1.017
GAP #4	basic unit		M_1		387, 486, 585, 684, 783, 882, 981, 1080, 1179, 1278, 1377, 1476, 1575, 1674, 1773, 1872			
	N-without	A	$[M_1+NO_3]^-$	m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637, 1736, 1835	897.7	981.8	1.094
	N-with	A	$[M_1+NO_3]^-$	m/z	548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637, 1736, 1835, 1934	1134.3	1195.0	1.054
	basic unit		M_2		513, 612, 711, 810, 909, 1008, 1107, 1206, 1305, 1404, 1503, 1602, 1701, 1800			
	N-without	B	$[M_2+NO_3]^-$	m/z	575, 674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466, 1565, 1664	962.4	1046.1	1.087
	N-with	B	$[M_2+NO_3]^-$	m/z	575, 674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466, 1565, 1664, 1763, 1862, 1961	1154.1	1241.3	1.076
	basic unit		M_3		541, 640, 739, 838, 937, 1036, 1135, 1234, 1333, 1432, 1531, 1630, 1729			
	N-without	C	$[M_3+NO_3]^-$	m/z	603 702, 801	691.3	699.5	1.012
	N-with	C	$[M_3+NO_3]^-$	m/z	603 702, 801, 900, 999, 1098, 1197, 1296, 1395, 1494, 1593, 1692, 1791	1105.8	1164.0	1.053

Note: "N-without" means negative ion mode and without $NaNO_3$, and "N-with" means negative ion mode and with $NaNO_3$.

Table S6. Comparison of the observed peaks and related parameters of different GAP samples without and with addition of $NaNO_3$ in negative ion modes using nanoESI

sample	with or not	series	composition		observed peaks	M_n	M_w	*PDI*
GAP #1	basic unit		M_1		387, 486, 585, 684, 783, 882, 981, 1080, 1179, 1278, 1377			
	N-without	A	$[M_1+NO_3]^-$	m/z	449, 548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538	839.6	891.4	1.062
	N-without	E	$[M_1+X^*]^-$	m/z	484, 583, 682, 781, 880, 979, 1078, 1177	831.6	864.4	1.039
	N-with	A	$[M_1+NO_3]^-$	m/z	647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637	1079.5	1111.5	1.030
	basic unit		M_2		315, 414, 513, 612, 711, 810, 909, 1008, 1107, 1206, 1305, 1404			
	N-without	B	$[M_2+NO_3]^-$	m/z	674, 773, 872, 971, 1070	883.6	911.2	1.031
	N-without	D	$[M_2+X^*]^-$	m/z	412, 511, 610, 709, 808	615.7	638.7	1.038
	N-with	B	$[M_2+NO_3]^-$	m/z	674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466	938.5	969.0	1.033
	basic unit		M_3		442, 541, 640, 739			
	N-without		$[M_3+NO_3]^-$	m/z	n/a			
	N-with		$[M_3+NO_3]^-$	m/z	n/a			
	basic unit		M_4		558, 657, 756, 855, 954, 1053, 1152, 1251, 1350, 1449			
	N-without	C	$[M_4+NO_3]^-$	m/z	620, 719, 818, 917, 1016, 1115, 1214, 1313, 1412, 1511	941.1	976.8	1.038
	N-with	C	$[M_4+NO_3]^-$	m/z	917, 1016, 1115, 1214, 1313, 1412, 1511, 1610	1225.2	1260.5	1.029
GAP #2	basic unit		M_1		387, 486, 585, 684, 783, 882, 981, 1080, 1179, 1278, 1377, 1476, 1575, 1674, 1773, 1872			
	N-without	A	$[M_1+NO_3]^-$	m/z	449 548, 647, 746, 845, 944, 1043, 1142, 1241	906.9	964.1	1.063
	N-with		$[M_1+NO_3]^-$	m/z	n/a			
	basic unit		M_2		315, 414, 513, 612, 711, 810, 909, 1008, 1107, 1206, 1305, 1404, 1503, 1602, 1701, 1800			
	N-without	D	$[M_2+X^*]^-$	m/z	412, 511, 610, 709, 808, 907, 1006, 1105, 1204, 1303, 1402	817.6	902.6	1.104
	N-with	B	$[M_2+NO_3]^-$	m/z	674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466, 1565, 1664, 1763, 1862	1227.6	1298.3	1.058
	basic unit		M_3		640, 739, 838, 937, 1036, 1135, 1234, 1333, 1432, 1531, 1630, 1729, 1828			
	N-without		$[M_3+NO_3]^-$	m/z	n/a			
	N-with	F	$[M_3+NO_3]^-$	m/z	702, 801, 900, 999, 1098, 1197, 1296, 1395, 1494, 1593, 1692, 1791, 1890	1333.0	1380.1	1.035
	basic unit		M_4		950, 1049, 1148, 1247, 1346, 1445, 1544			
	N-without		$[M_4+NO_3]^-$	m/z	n/a			
	N-with	H	$[M_4+NO_3]^-$	m/z	1012, 1111, 1210, 1309, 1408, 1507, 1606	1312.0	1329.6	1.013
	basic unit		M_5		999, 1098, 1197, 1296, 1395, 1494, 1593, 1692			
	N-without		$[M_5+NO_3]^-$	m/z	n/a			
	N-with	G	$[M_5+NO_3]^-$	m/z	1061, 1160, 1259, 1358, 1457, 1556, 1655, 1754	1324.3	1348.1	1.018
GAP #3	basic unit		M_1		387, 486, 585, 684, 783, 882, 981, 1080, 1179, 1278, 1377, 1476, 1575, 1674, 1773, 1872			
	N-without	A	$[M_1+NO_3]^-$	m/z	746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538	1079.5	1118.6	1.036
	N-with	A	$[M_1+NO_3]^-$	m/z	746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637, 1736, 1835, 1934	1329.4	1382.6	1.040
	basic unit		M_2		315, 414, 513, 612, 711, 810, 909, 1008, 1107, 1206, 1305, 1404, 1503, 1602			
	N-without	D	$[M_2+X^*]^-$	m/z	412, 511, 610, 709, 808, 907, 1006, 1105, 1204, 1303	870.7	917.1	1.053
	N-without	B	$[M_2+NO_3]^-$	m/z	872, 971, 1070, 1169	1027.6	1038.2	1.010
	N-with	B	$[M_2+NO_3]^-$	m/z	674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466, 1565, 1664, 1763, 1862	1109.0	1155.5	1.042
	basic unit		M_3		640, 739, 838, 937, 1036, 1135, 1234, 1333, 1432, 1531, 1630			
	N-without		$[M_3+NO_3]^-$	m/z	n/a			
	N-with	F	$[M_3+NO_3]^-$	m/z	702, 801, 900, 999, 1098, 1197, 1296, 1395	1022.4	1051.0	1.028
GAP #4	basic unit		M_1		387, 486, 585, 684, 783, 882, 981, 1080, 1179, 1278, 1377, 1476, 1575, 1674, 1773, 1872			
	N-without	A	$[M_1+NO_3]^-$	m/z	449, 548, 647, 746, 845, 944, 1043, 1142, 1241, 1340, 1439, 1538, 1637	1119.6	1186.9	1.060
	N-with		$[M_1+NO_3]^-$	m/z	n/a			
	basic unit		M_2		315, 414, 513, 612, 711, 810, 909, 1008, 1107, 1206, 1305, 1404, 1503, 1602			
	N-without	D	$[M_2+X^*]^-$	m/z	412, 511, 610, 709, 808, 907, 1006, 1105, 1204, 1303, 1402	910.1	971.5	1.067
	N-without	B	$[M_2+NO_3]^-$	m/z	872, 971, 1070, 1169, 1268, 1367, 1466	1150.5	1180.6	1.026
	N-with	B	$[M_2+NO_3]^-$	m/z	674, 773, 872, 971, 1070, 1169, 1268, 1367, 1466, 1565, 1664, 1763, 1862	1255.1	1309.0	1.043
	basic unit		M_3		640, 739, 838, 937, 1036, 1135, 1234, 1333, 1432, 1531, 1630, 1729, 1828			
	N-without		$[M_3+NO_3]^-$	m/z	n/a			
	N-with	F	$[M_3+NO_3]^-$	m/z	702, 801, 900, 999, 1098, 1197, 1296, 1395, 1494, 1593, 1692, 1791, 1890	1269.5	1313.0	1.034
	basic unit		M_4		788, 887, 986, 1085, 1184, 1283, 1382, 1481, 1580, 1679, 1778			
	N-without		$[M_4+NO_3]^-$	m/z	n/a			
	N-with	H	$[M_4+NO_3]^-$	m/z	850, 949, 1048, 1147, 1246, 1345, 1444, 1543, 1642, 1741, 1840	1345.7	1378.8	1.025

Note: "N-without" means negative ion mode and without $NaNO_3$, and "N-with" means negative ion mode and with $NaNO_3$; X* is either HSO_4^- or $H_2PO_4^-$; "n/a" means no signal.

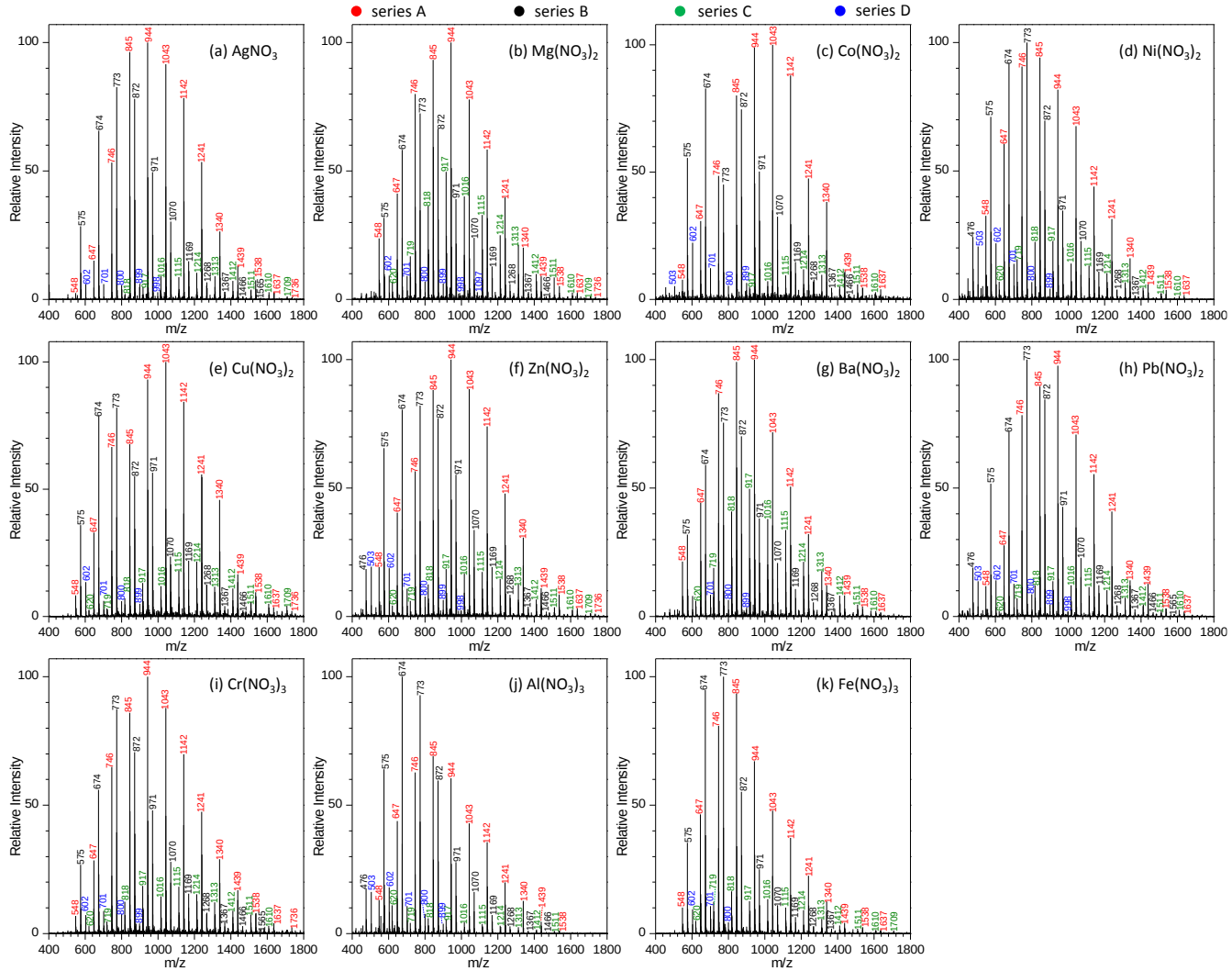

Figure S1. Effect of the type of metal salt on the analysis of 100 μg mL^{-1} GAP #1: **(a)** $AgNO_3$, **(b)** $Mg(NO_3)_2$, **(c)** $Co(NO_3)_2$, **(d)** $Ni(NO_3)_2$, **(e)** $Cu(NO_3)_2$, **(f)** $Zn(NO_3)_2$, **(g)** $Ba(NO_3)_2$, **(h)** $Pb(NO_3)_2$, **(i)** $Cr(NO_3)_3$, **(j)** $Al(NO_3)_3$, and **(k)** $Fe(NO_3)_3$ (sample volume: 25 μL for each spray; applied voltage: -3.5 kV; concentration of each metal salt in GAP #1 solution: 1.0 mmol L^{-1}).

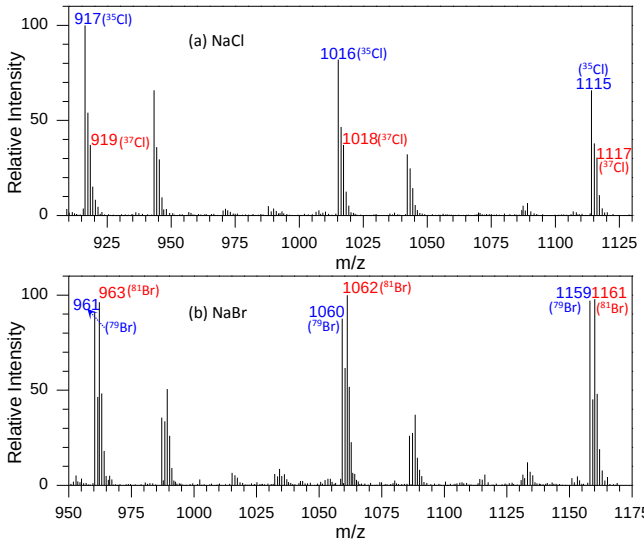

Figure S2. Mass spectra of GAP #1 solution in the presence of (a) NaCl and (b) NaBr (sample volume: 25 μL for each spray; applied voltage: -3.5 kV; concentration of each metal salt in GAP #1 solution: 1.0 mmol L^{-1}).

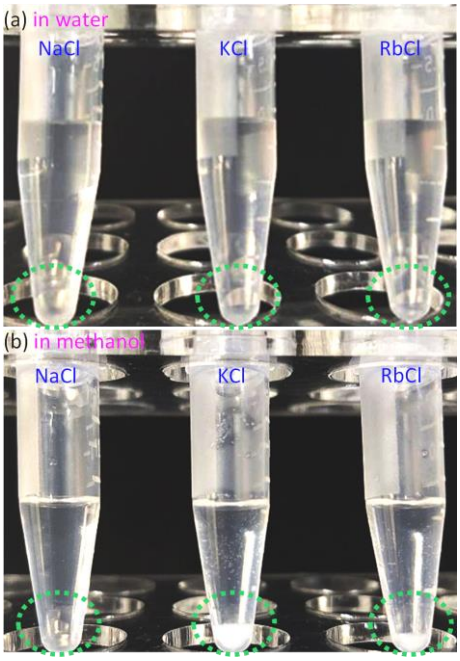

Figure S3. Comparison of the solubility of NaCl, KCl, and RbCl **(a)** in water and **(b)** in methanol (*Note*: For dissolving different salts into water, exactly measured 2.5 mmol of corresponding salts into 1.0 mL deionized water followed by vibration for 5.0 min; for dissolving different salts into methanol, transferred 100 µL of 2.5 mmol mL^{-1} the related aqueous solutions into 900 µL methanol followed by vibration for 5.0 min).

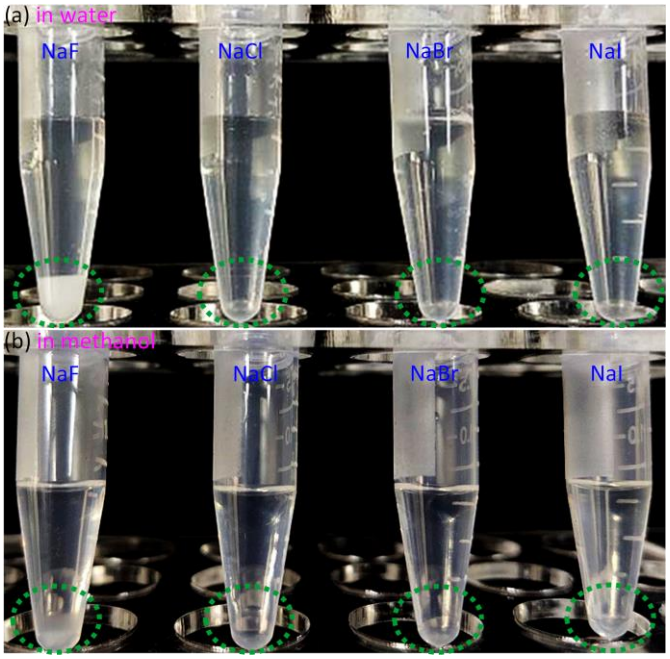

Figure S4. Comparison of the solubility of NaF, NaCl, NaBr, and NaI **(a)** in water and **(b)** in methanol (*Note*: For dissolving different salts into water, exactly measured 2.5 mmol of corresponding salts into 1.0 mL deionized water followed by vibration for 5.0 min; for dissolving different salts into methanol, transferred 100 µL of 2.5 mmol mL^{-1} the related aqueous solutions into 900 µL methanol followed by vibration for 5.0 min).

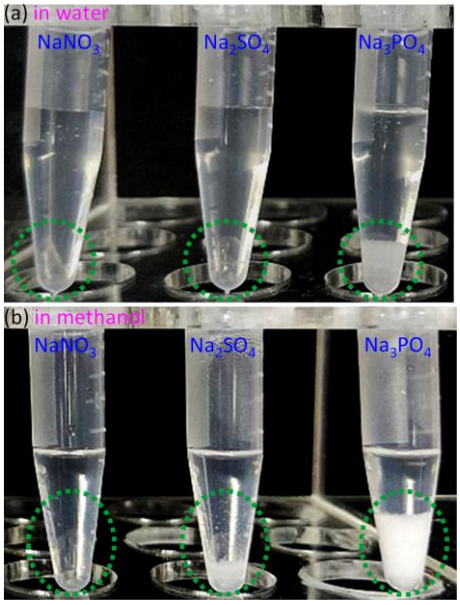

Figure S5. Comparison of the solubility of $NaNO_3$, Na_2SO_4, and Na_3PO_4 **(a)** in water and **(b)** in methanol (*Note*: For dissolving different salts into water, exactly measured 2.5 mmol of corresponding salts into 1.0 mL deionized water followed by vibration for 5.0 min; for dissolving different salts into methanol, transferred 100 µL of 2.5 mmol mL^{-1} the related aqueous solutions into 900 µL methanol followed by vibration for 5.0 min).