1. Supplementary Information

Table S1: Harmonic vibrational frequencies used in the RRKM modeling of $[PMMA_n][DAA+mH]^{+m}$ complexes

	Harmonic vibrational frequencies (cm^{-1})
Monomer modes	17, 90, 113, 117, 129, 192, 222, 267, 306, 444, 549, 604, 781, 816, 847, 852, 954, 979, 1007, 1012, 1015, 1075, 1123, 1133, 1140, 1141, 1148, 1150, 1150, 1154, 1179, 1188, 1194, 1281, 1700, 2498, 2540, 2541, 2543, 2546, 2553, 2560, 2615, 2618, 2618
Complex modes	13, 19, **21**, 27, 36, 43
Diaminobutane($1H^+$) modes	59, 69, 109, 163, 163, 245, 372, 404, 550, 759, 816, 874, 919, 1019, 1058, 1073, 1143, 1185, 1200, 1213, 1220, 1223, 1254, 1264, 1319, 1330, 1344, 1356, 1365, 1382, 1391, 1399, 1402, 1469, 1638, 1646, 1654, 1728, 2963, 2977, 3012, 3025, 3035, 3044, 3079, 3099, 3216, 3223, 3351, 3435, 3475,
Diaminohexane($1H^+$) modes	38, 45, 83, 95, 95, 115, 164, 236, 239, 309, 406, 528, 544, 748, 774, 825, 900, 934, 978, 1037, 1056, 1074, 1163, 1181, 1183, 1197, 1204, 1208, 1226, 1228, 1229, 1252, 1257, 1264, 1303, 1328, 1336, 1348, 1360, 1373, 1382, 1387, 1396, 1404, 1405, 1407, 1436, 1469, 1638, 1646, 1654, 1731, 2963, 2978, 3003, 3016, 3025, 3030, 3039, 3047, 3075, 3084, 3096, 3104, 3217, 3224, 3351, 3427, 3470,
Diaminodecane($1H^+$) modes	18, 24, 44, 45, 59, 77, 89, 103, 112, 116, 118, 164, 212, 214, 233, 322, 400, 433, 516, 540, 571, 740, 750, 767 794, 833, 882, 934, 970, 983, 1023, 1049, 1056, 1075, 1167, 1176, 1179, 1188, 1191, 1197, 1203, 1207, 1208, 1213, 1221, 1223, 1232, 1234, 1235, 1235, 1248, 1264, 1267, 1269, 1288, 1311, 1325, 1332, 1350, 1350, 1365, 1376, 1383, 1387, 1395, 1401, 1403, 1404, 1406, 1408, 1409, 1410, 1426, 1447, 1456, 1469, 1638, 1647, 1655, 1732, 2963, 2979, 3000, 3004, 3010, 3018, 3025, 3026, 3032, 3038, 3041, 3048, 3074, 3077, 3082, 3088, 3094, 3100, 3104, 3107, 3217, 3225, 3352, 3421, 3466,
Diaminobutane($2H^+$) modes	62, 80, 113, 164, 167, 169, 367, 404, 546, 760, 817, 919, 1017, 1053, 1062, 1069, 1181, 1192, 1215, 1217, 1222, 1238, 1261, 1262, 1271, 1275, 1331, 1351, 1366, 1385, 1387, 1397, 1411, 1424, 1639, 1639, 1643, 1644, 1648, 1648, 2948, 2949, 2999, 3013, 3013, 3020, 3068, 3084, 3180, 3180, 3195, 3196, 3326, 3328
Diaminohexane($2H^+$) modes	44, 50, 87, 99, 99, 118, 164, 166, 239, 307, 402, 526, 539, 750, 776, 825, 899, 976, 1033, 1049, 1058, 1068, 1178, 1181, 1197, 1198, 1199, 1207, 1227, 1229, 1239, 1240, 1253, 1269, 1269, 1270, 1313, 1338, 1355, 1368, 1382, 1390, 1392, 1397, 1398, 1404, 1413, 1436, 1643, 1643, 1644, 1644, 1649, 1649, 2957, 2957, 2999, 3010, 3020, 3020, 3023, 3034, 3071, 3078, 3089, 3099, 3200, 3200, 3207, 3207, 3338, 3339
Diaminodecane($2H^+$) modes	24, 25, 46, 50, 59, 80, 90, 106, 114, 117, 120, 164, 164, 212, 212, 320, 396, 431, 510, 540, 569, 742, 753, 769, 796, 833, 881, 932, 979, 1018, 1044, 1055, 1057, 1058, 1174, 1178, 1180, 1185, 1188, 1202, 1203, 1203, 1204, 1211, 1219, 1221, 1225, 1234, 1234, 1235, 1246, 1254, 1266, 1266, 1266, 1272, 1294, 1315, 1333, 1346, 1359, 1369, 1382, 1387, 1390, 1395, 1396, 1399, 1400, 1405, 1405, 1407, 1408, 1421, 1441, 1451, 1641, 1641, 1645, 1645, 1653, 1653, 2961, 2961, 3000, 3003, 3009, 3016, 3023, 3023, 3024, 3030, 3036, 3041, 3073, 3075, 3079, 3085, 3091, 3097, 3102, 3106, 3214, 3214, 3215, 3215, 3347, 3347

Table S2: Summary of m/z for non-covalent complexes between [$PMMA_n$] and cationizing agent

DAA	$[PMMA_n][DAA+1H]^{+1}$*(Da)*	$[PMMA_n][DAA+2H]^{+2}$*(Da)*
Diaminobutane	91.12+ (100.05)**n**	46.05+ (50.03)**n**
Diaminohexane	119.15+ (100.05)**n**	59.58+ (50.03)**n**
Diaminodecane	175.22+ (100.05)**n**	88.11+ (50.03)**n**

Table S3: RRKM calculated E_0, $\Delta S^{\ddagger}$ and α of $[PMMA_n][DAA+1H]^{+1}$ complexes

	$[PMMA_n][DAB+1H]^{1+}$			$[PMMA_n][DAH+1H]^{1+}$			$[PMMA_n][DAD+1H]^{1+}$		
n	**E_0 (eV)**	**$\Delta S^{\ddagger}$ J $K^{-1}mol^{-1}$**	**α K eV^{-1}**	**E_0(eV)**	**$\Delta S^{\ddagger}$ J $K^{-1}mol^{-1}$**	**α K eV^{-1}**	**E_0(eV)**	**$\Delta S^{\ddagger}$ J $K^{-1}mol^{-1}$**	**α K eV^{-1}**
7	0.81±0.02	-63±7	421±16	0.91±0.01	-67±7	444±25	0.87±0.01	-73±3	458±13
8	0.85±0.01	-52±6	380±14	1.01±0.01	-30±5	336±9	1.03±0.01	-32±4	378±10
9	0.96±0.02	-27±7	348±13	1.13±0.02	-24±10	351±22	1.02±0.01	-35±4	357±11
10	1.01±0.01	-1±4	291±5	1.1±0.01	-10±4	281±5	1.1±0.03	-15±10	319±17
11	1.11±0.02	16±9	284±12	1.21±0.02	0±11	297±18	1.18±0.02	-3±6	317±7
12	1.15±0.02	26±4	232±7	1.32±0.01	22±5	278±8	1.22±0.01	26±6	250±9
13	1.3±0.01	48±9	254±6	1.31±0.02	42±8	236±9	1.31±0.03	34±10	262±11
14	1.35±0.02	76±7	214±9	1.40±0.03	43±7	255±10	1.36±0.02	62±5	211±13
15	1.43±0.03	99±2	190±11	1.38±0.04	70±11	209±6	1.43±0.01	80±2	195±10

Table S4: RRKM calculated E_0, $\Delta S^{\ddagger}$ and α of $[PMMA_n][DAA+2H]^{+2}$ complexes

	$[PMMA_n][DAB+2H]^{2+}$			$[PMMA_n][DAH+2H]^{2+}$			$[PMMA_n][DAD+2H]^{2+}$		
n	**E_0(eV)**	**$\Delta S^{\ddagger}$ J $K^{-1}mol^{-1}$**	**α K eV^{-1}**	**E_0(eV)**	**$\Delta S^{\ddagger}$ J $K^{-1}mol^{-1}$**	**α K eV^{-1}**	**E_0(eV)**	**$\Delta S^{\ddagger}$ J $K^{-1}mol^{-1}$**	**α K eV^{-1}**
8	0.63±0.01	-90±5	395±27	0.94±0.02	-77±5	428±30	1.22±0.03	-62±11	410±24
9	0.78±0.01	-56±4	348±12	1.32±0.02	0±9	378±14	1.43±0.02	-20±14	352±32
10	1.02±0.02	10±7	269±7	1.46±0.02	45±7	301±9	1.64±0.02	14±13	360±25
11	1.35±0.04	44±13	328±13	1.53±0.03	48±9	303±9	1.76±0.03	40±11	325±17
12	1.47±0.05	94±14	279±14	1.76±0.06	80±18	300±16	1.89±0.05	75±16	313±18
13	1.66±0.05	133±15	257±7	1.82±0.04	105±10	264±6	1.97±0.07	104±23	278±19
14	1.67±0.06	173±14	194±3	1.95±0.04	128±13	246±9	2.17±0.07	153±20	251±10
15	1.77±0.02	223±6	184±4	1.99±0.03	229±8	205±15	2.17±0.02	173±6	224±23