

Supporting information

Sliding Windows in Ion Mobility (SWIM): a New Approach to Increase the Resolving Power in Trapped Ion Mobility-Mass Spectrometry Hyphenated with Chromatography

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Table S1: A list of the POP standards investigated in this study, along with their experimentally measured $^{TIMS}CCS_{N_2}$, is available in the attached file "Table S1".

Table S2: GC-APCI source parameters.

Transfer line temperature	300°C
Source temperature	300°C
End plate offset	-500 V
Capillary	-4500 V
Corona	+1000 nA
Nebulizer	2.4 Bar
Dry gas	1.5 L/min
Dry temperature	175°C

Table S3: TIMS parameters.

		Standard mode	SWIM mode	UHR mode
Accumulation time (duty cycle %)		20 ms (5.71%)		
Ramp time (spectra rate)		350 ms (2.81 Hz)		
Accumulation range		Same as analysis range		
Analysis range	1/K ₀	0.6 – 1.0 1/K ₀ $\Delta 1/K_0 = 0.40$	Variable (cfr. Table S6) $\Delta 1/K_0 = 0.11$	Variable (cfr. Table S7) $\Delta 1/K_0 = 0.03$
	Elution voltage	71.7 – 122.4 V $\Delta V_{ramp} = 51 V$	Variable $\Delta V_{ramp} = 14 V$	Variable $\Delta V_{ramp} = 3.5 V$
Scan speed βv		145 V/s	40 V/s	10 V/s
Tunnel pressure	Entrance (P1)	2.40 mBar		
	Exit (P2)	0.84 mBar		
	ΔP	1.56 mbar		
IM cell temperature		Not available		
RF voltage		250 V _{pp}		
Transfer voltages	D1	- 20 V		
	D2	- 120 V		
	D3	50 V		
	D4	20 V		
	D5	0 V		
	D6	100 V		

Table S4: qTOF parameters.

Funnel 2 RF	200 V _{pp}
Multipole RF	200 V _{pp}

Collision RF	1000 V _{pp}
Quadrupole energy	8 eV
Collision cell energy	8 eV
Collision cell in	190 V
Transfert time	60 μs
Prepulse storage	9 μs

Table S5: Polysiloxanes ions used for mass calibration in the range 100 - 1000 m/z.

Formula	m/z
[C ₆ H ₁₉ Si ₃ O ₃] ⁺	223.0636
[C ₇ H ₂₁ Si ₄ O ₄] ⁺	281.0511
[C ₉ H ₂₇ Si ₅ O ₅] ⁺	355.0699
[C ₁₁ H ₃₃ Si ₆ O ₆] ⁺	429.0887
[C ₁₃ H ₃₉ Si ₇ O ₇] ⁺	503.1075
[C ₁₉ H ₄₃ Si ₇ O ₆] ⁺	563.1439
[C ₂₁ H ₄₉ Si ₈ O ₇] ⁺	637.1627
[C ₂₃ H ₅₅ Si ₉ O ₈] ⁺	711.1815
[C ₂₉ H ₅₉ Si ₉ O ₇] ⁺	771.2179
[C ₃₁ H ₆₅ Si ₁₀ O ₈] ⁺	845.2367
[C ₃₃ H ₇₁ Si ₁₁ O ₉] ⁺	919.2554

Table S6: Optimized ion mobility windows for the 174 POPs in SWIM mode.

IM windows	RT segments (sec)	Analysis range (K ₀)	Analysis range (1/K ₀)
1	0 – 400	1.67 – 1.41	0.60 – 0.71
2	400 - 525	1.59 – 1.35	0.63 – 0.74
3	525 - 651	1.45 – 1.25	0.69 – 0.80
4	641 - 704	1.41 – 1.22	0.71 – 0.82
5	704 - 748	1.37 – 1.19	0.73 – 0.84
6	748 - 796	1.35 – 1.18	0.74 – 0.85
7	796 - 805	1.33 – 1.16	0.75 – 0.86
8	805 - 815	1.32 – 1.15	0.76 – 0.87
9	815 - 822	1.37 – 1.19	0.73 – 0.84
10	822 - 856	1.33 – 1.16	0.75 – 0.86
11	856 - 888	1.32 – 1.15	0.76 – 0.87
12	888 - 920	1.28 – 1.12	0.78 – 0.89
13	920 - 948	1.30 – 1.14	0.77 – 0.88
14	948 - 979	1.28 – 1.12	0.78 – 0.89
15	979 - 1020	1.23 – 1.09	0.81 – 0.92
16	1020 - 1030	1.25 – 1.10	0.80 – 0.91
17	1030 - 1140	1.23 – 1.09	0.81 – 0.92
18	1140 - 1276	1.18 – 1.04	0.85 – 0.96
19	1276 - 2280	1.12 – 1.00	0.89 – 1.00

Table S7: IM ranges used in UHR TIMS mode for the analysis of the isomeric pair mixtures.

Mixtures	Analysis range (K ₀)	Analysis range (1/K ₀)
DiCB 4 & DiCB 10	1.54 – 1.47	0.65 – 0.68
TriCB 28 & TriCB 31	1.45 – 1.39	0.69 – 0.72
TeCB 66 & TeCB 70	1.37– 1.32	0.73 – 0.76
PeCB 90 & PeCB 101	1.33 – 1.28	0.75 – 0.78
HxCB 153 & HxCB 168	1.27 – 1.22	0.79 – 0.82
HxCB 138 & HxCB 158	1.27 – 1.22	0.79 – 0.82
HpCB 180 & HpCB 193	1.22 – 1.18	0.82 – 0.85
1,2,3,4,7,8-HxCDF & 1,2,3,6,7,8-HxCDF	1.28 – 1.23	0.78 – 0.81
1,2,3,4,7,8-HxCDD & 1,2,3,6,7,8-HxCDD	1.23 – 1.19	0.81 – 0.84
1,2,3,4,7,8-HxBDD & 1,2,3,6,7,8-HxBDD	1.12 – 1.09	0.89 – 0.92
8-Br-2,3,4-Cl-Dibenzofuran & 3-br-2,7,8-Cl-Dibenzofuran	1.35 – 1.30	0.74 – 0.77

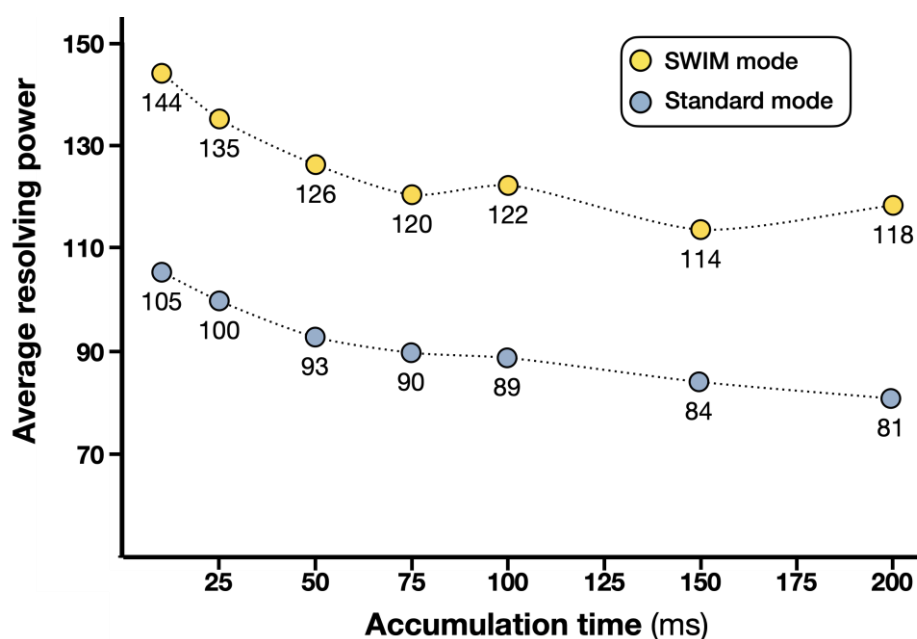


Figure S1 - Average ion mobility resolving power of POPs (n=174) in standard (light blue dots) and SWIM (yellow dots) modes as a function of accumulation time. In both modes, R_p decreased significantly from 10 to 75 ms due to space charge effects. A value of 20 ms was chosen in this work as a best compromise between resolving power and signal intensity.

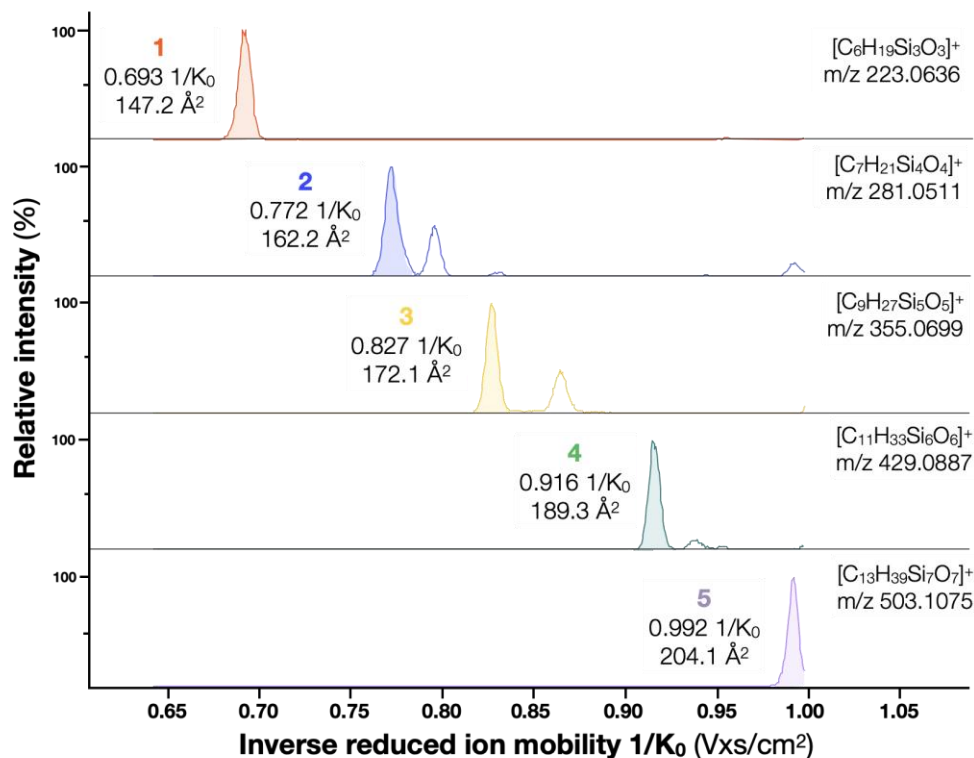


Figure S2 - Listed ion mobility spectra of the five Polysiloxane ions used as internal IM calibrants. The reported CCS values were determined based on the calibration curve shown in Figure S3.

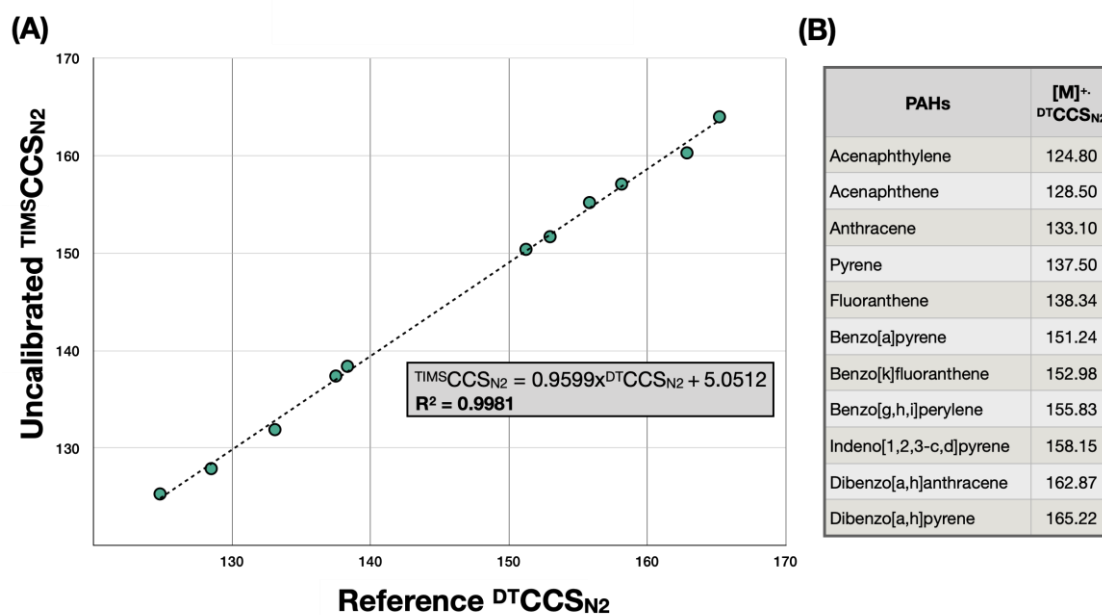


Figure S3 – (A) Experimentally measured $TIMS\text{CCS}_{N_2}$ of the radical molecular ion of 11 PAHs vs their corresponding reference $DTCCS_{N_2}$. The dotted linear regression curve was used as a calibration curve to assign the CCS values to the Polysiloxanes ions in Figure S2. (B) Reference $DTCCS_{N_2}$ of radical PAH ions taken from ref. [1].

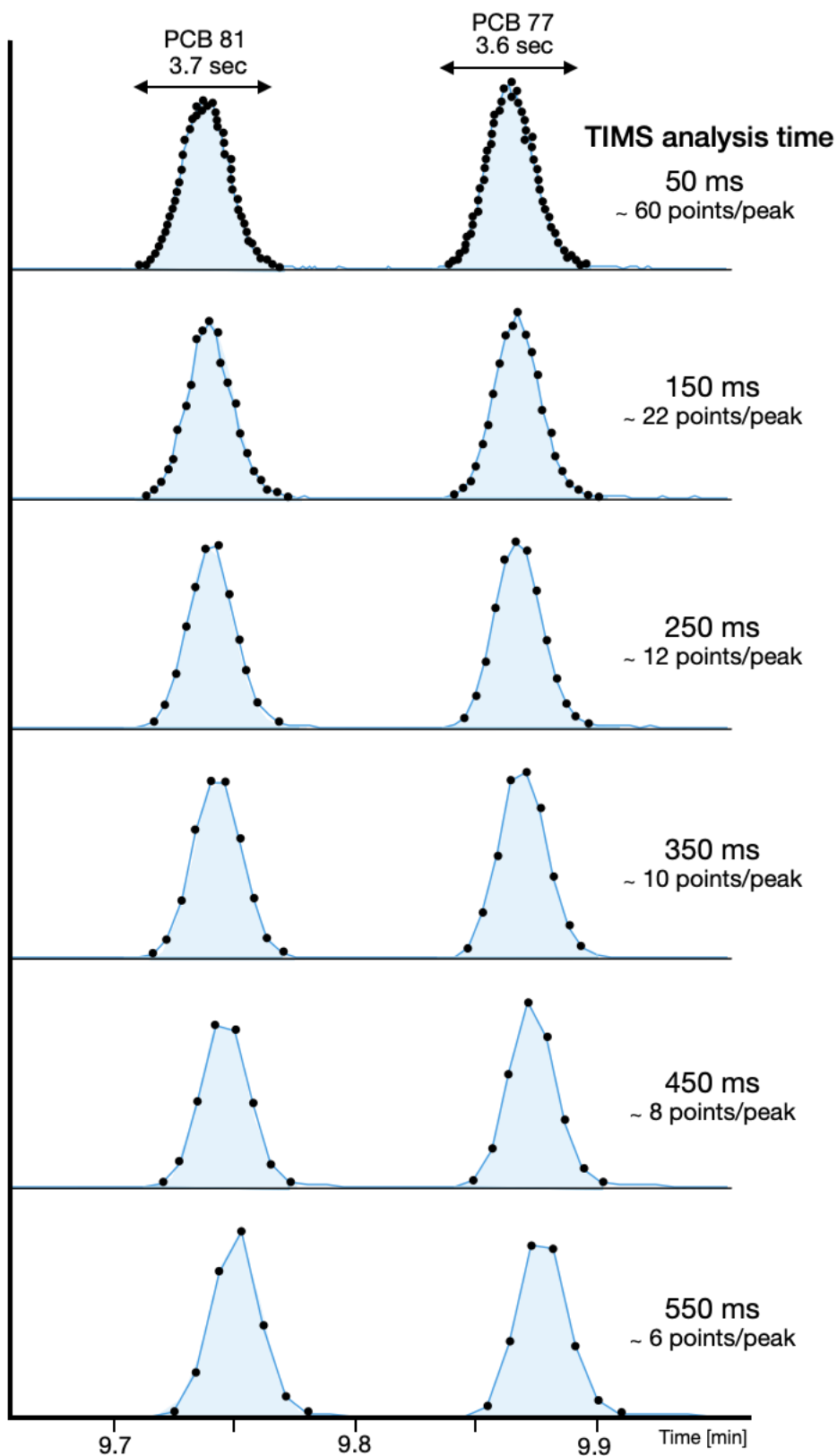


Figure S4 – Variation of the chromatographic sampling rate of two tetra PCBs (77 and 81) as a function of the TIMS analysis time. Each black point corresponds to a single TIMS separation.

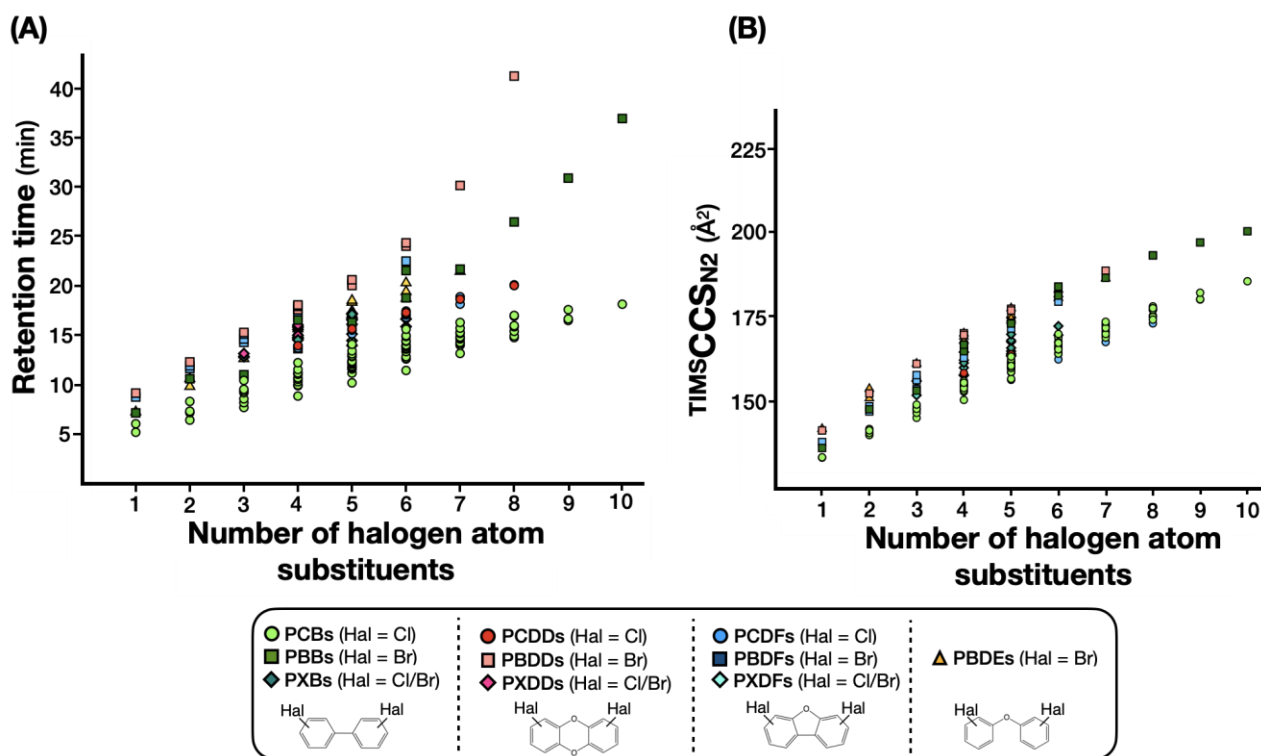


Figure S4 – Relationship between halogenation degree and GC retention time (A) and CCS (B). For a given type of POP, we observe an overall increase in both retention times and CCS with increasing number of halogen substituents, due to the concomitant increase in boiling point and molecular size, respectively.

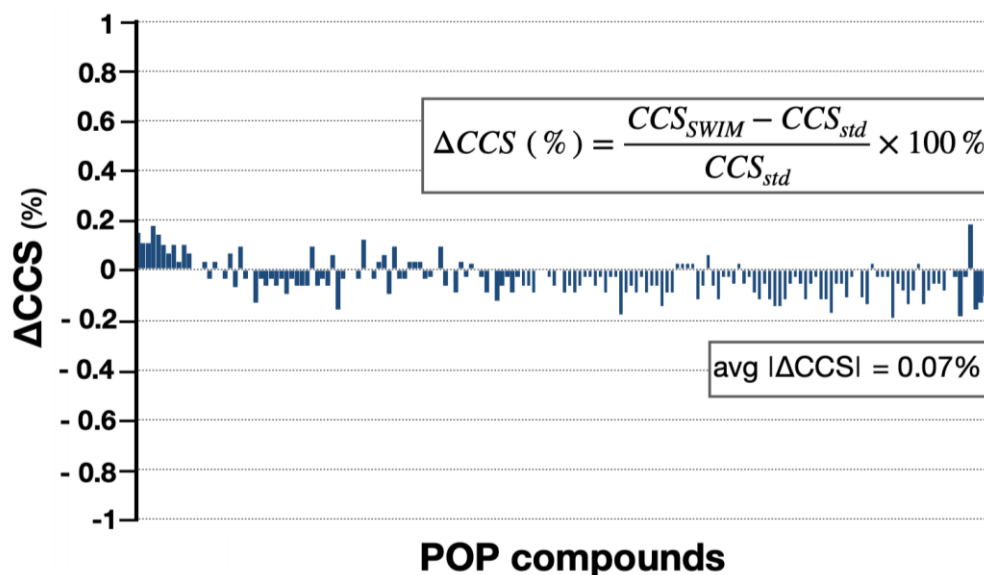


Figure S5 – Percentage difference in the measured CCS of the 174 POP standards between the standard and the SWIM mode.

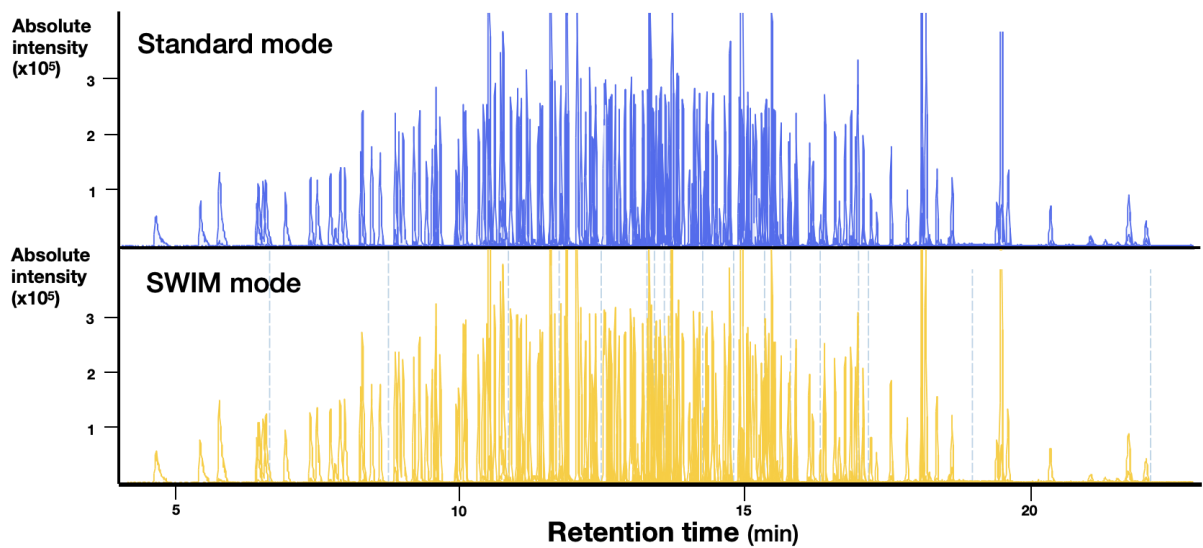
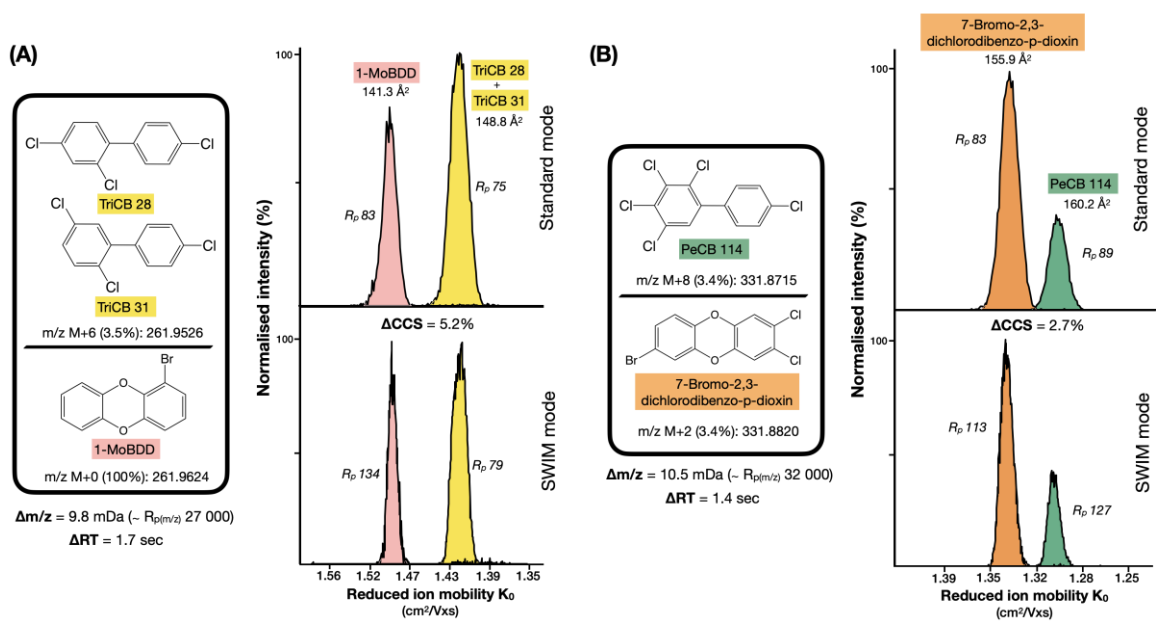
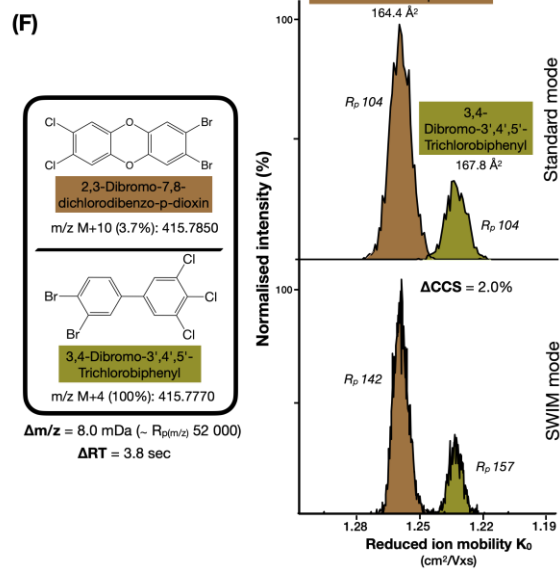
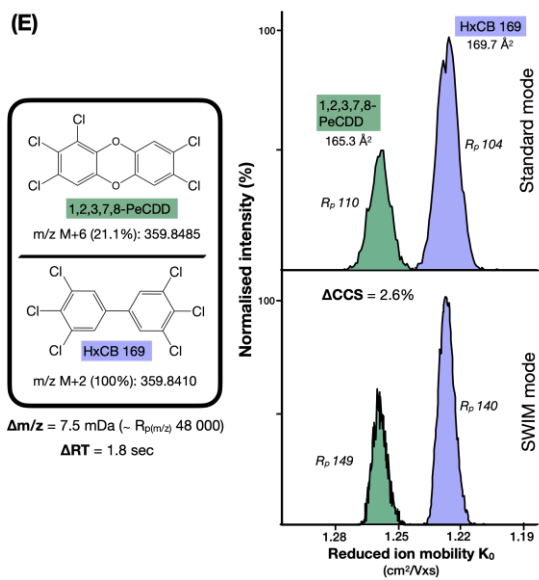
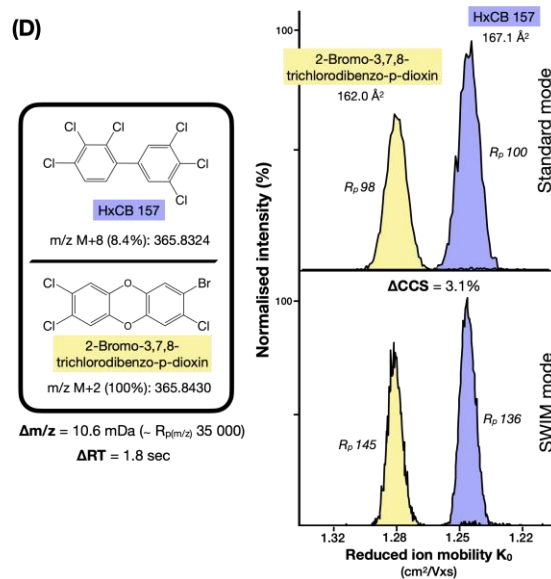
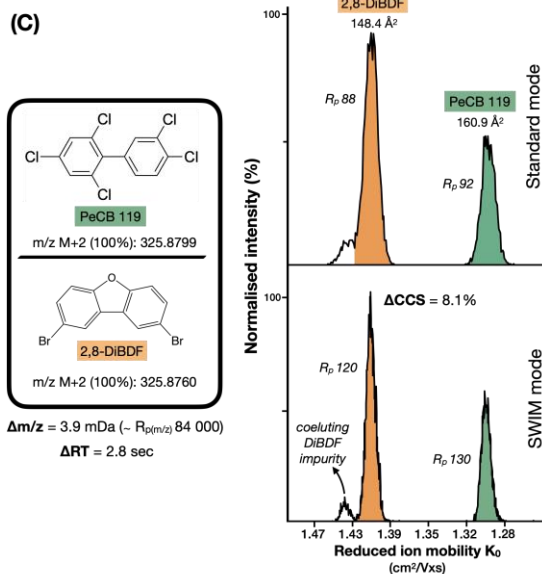


Figure S6 – Overlaid extracted ion chromatograms of POPs in standard (upper chromatogram) and SWIM (lower chromatogram) modes. Overall, signal intensity is of the same order of magnitude in both modes.





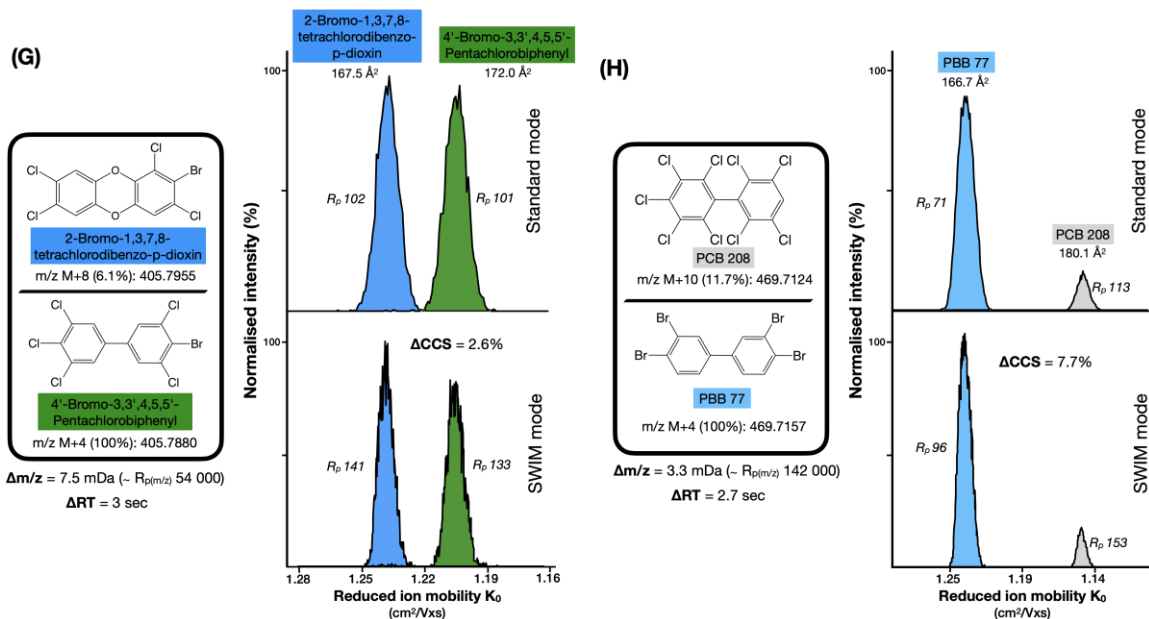
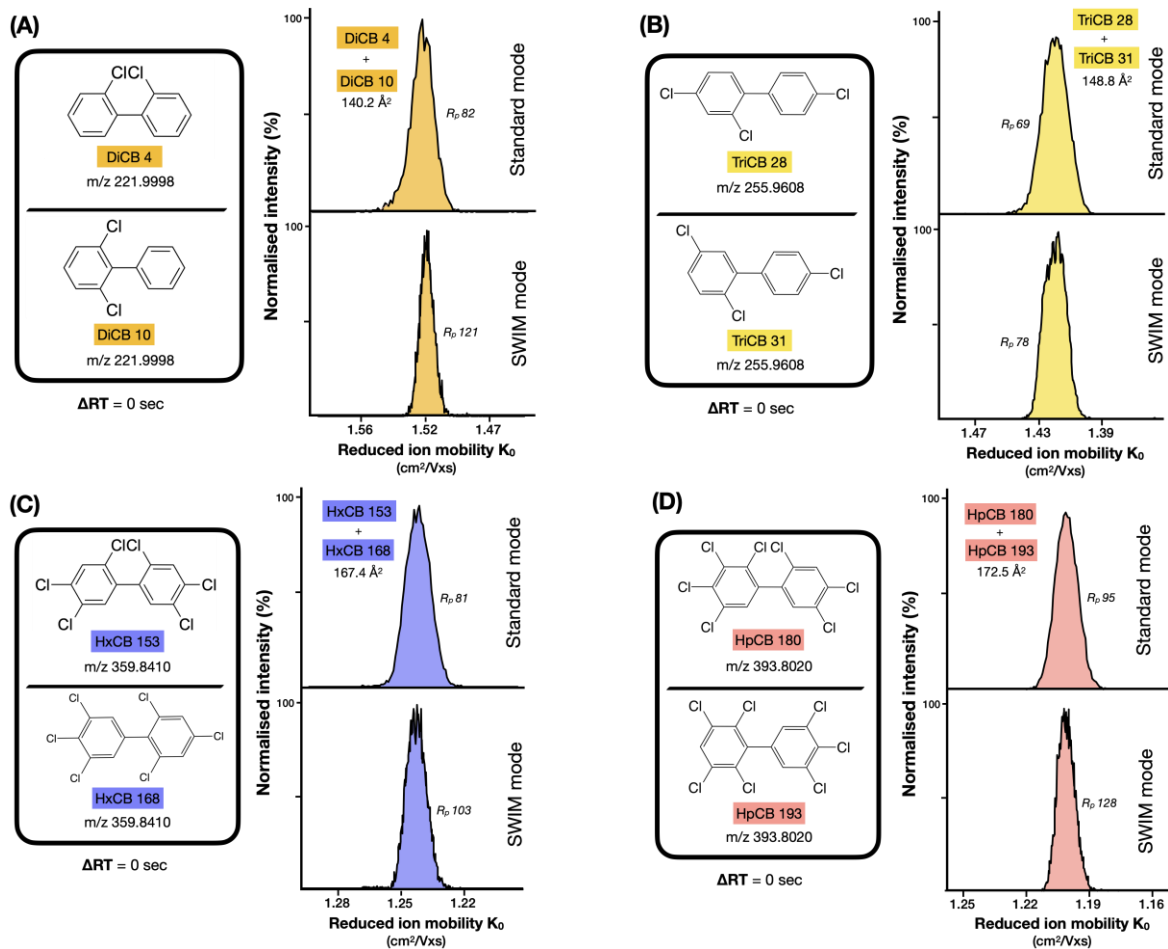
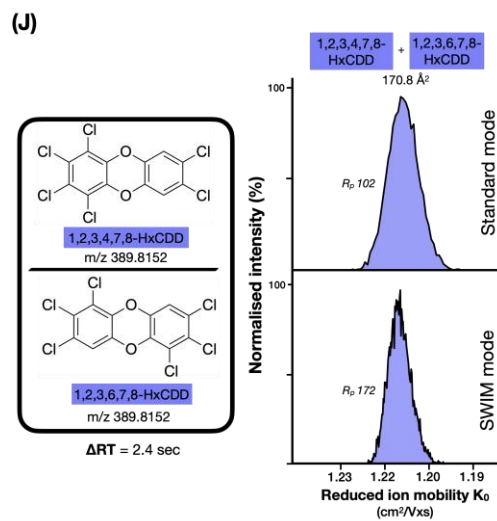
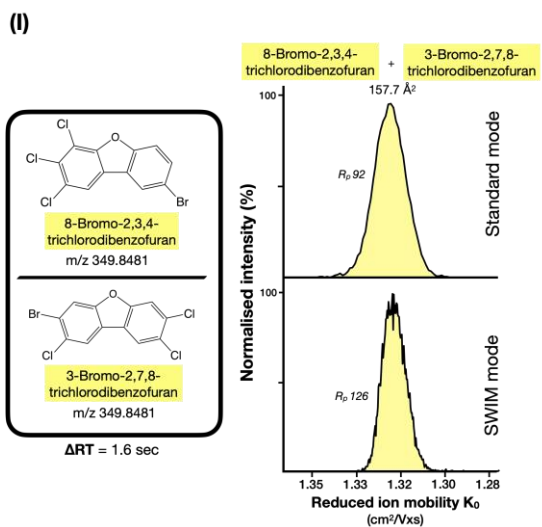
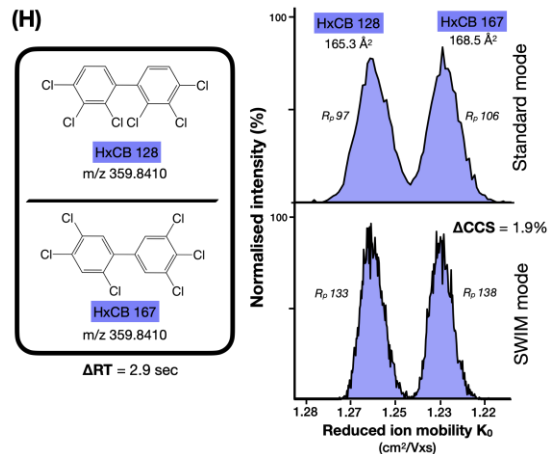
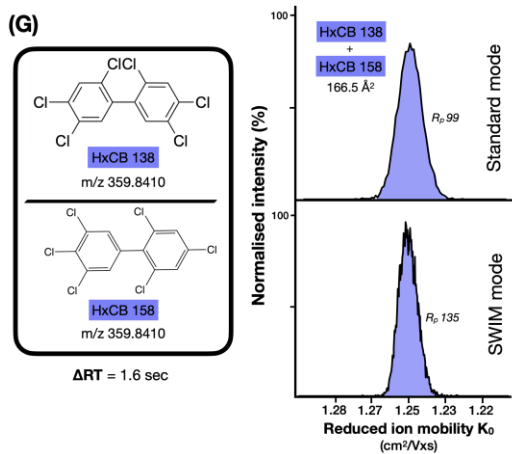
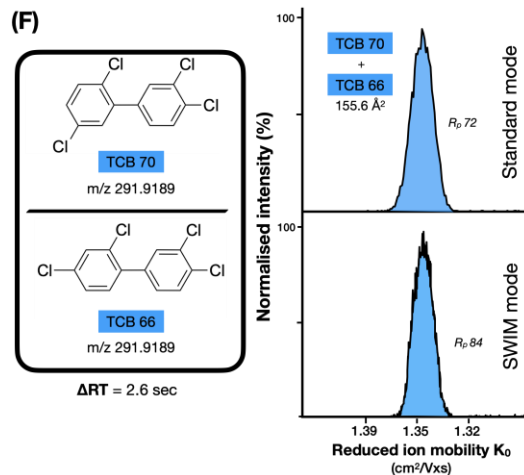
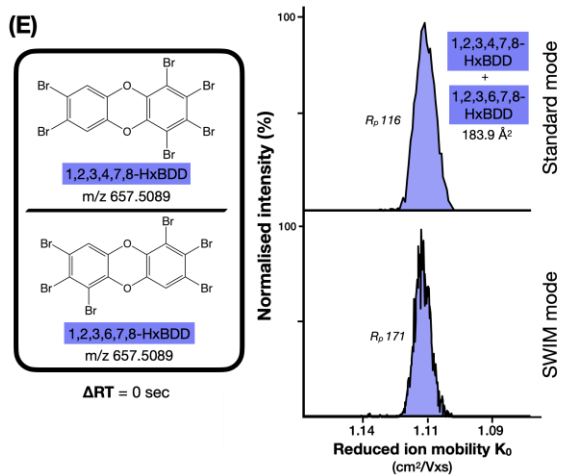


Figure S7 (A-H) – Ion mobility spectra (in both standard and SWIM modes) of critical isobaric coelutions (defined here as $\Delta m/z < 11$ mDa and $\Delta RT < 4$ sec, where $\Delta m/z$ is the mass difference between the interfering M+X isotopologues and ΔRT is the GC elution time difference between the apexes of the respective chromatographic peaks). The minimum mass resolving power ($R_{p(m/z)}$) required to resolve the two signal in the m/z dimension is specified in each case, along with the ion mobility resolving power (R_p), CCS values and % difference in CCS.





(K)

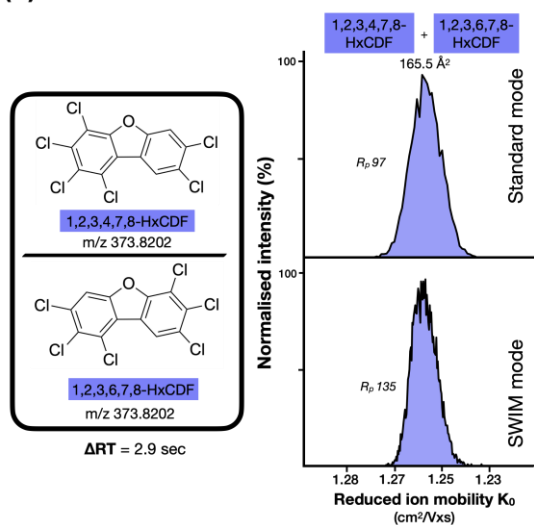
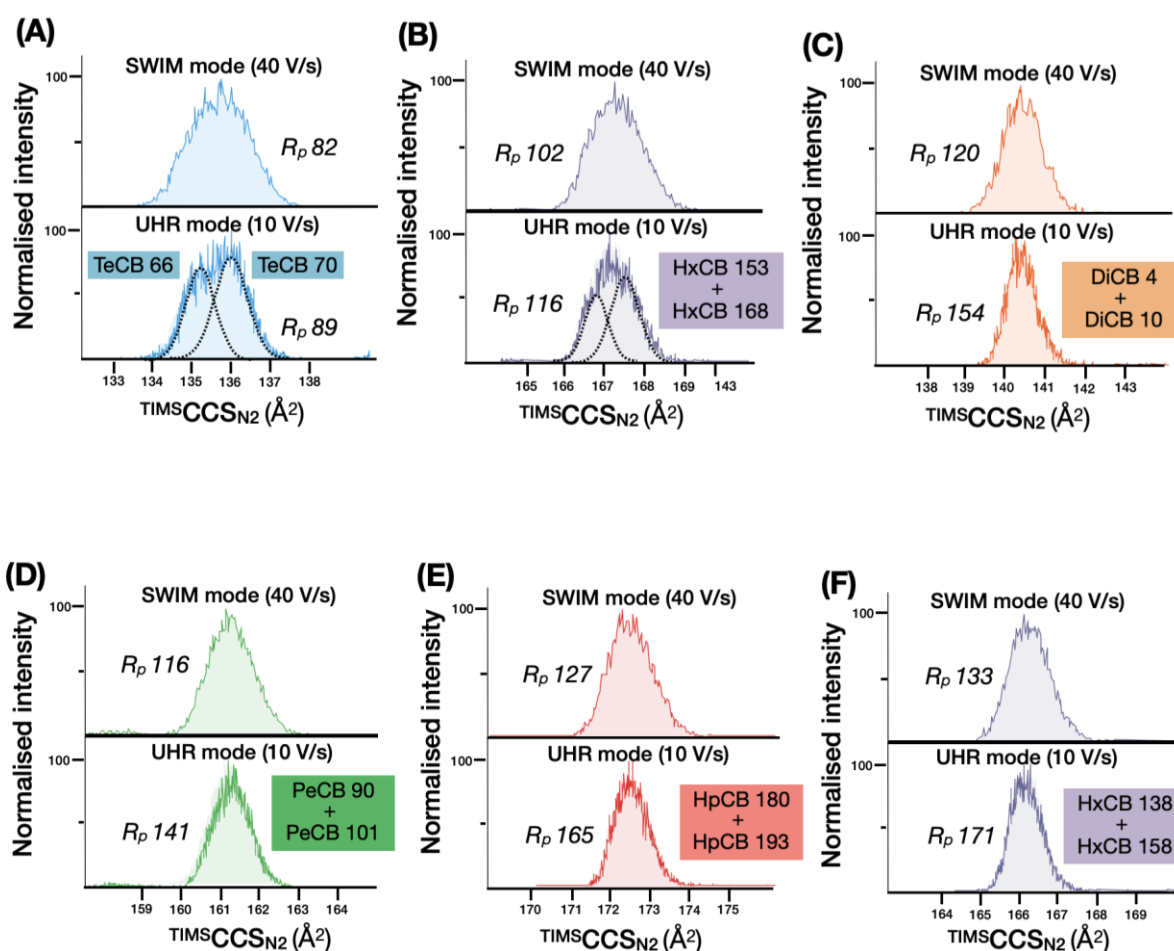


Figure S8 – Ion mobility spectra (in both standard and SWIM modes) of perfectly coeluting (A-E, $\Delta RT = 0$ sec) and partially coeluting isomers (E-K, $\Delta RT < 4$ sec, where ΔRT is the GC elution time difference between the apexes of the respective chromatographic peaks). The ion mobility resolving power (R_p), CCS values and % difference in CCS is specified in each case.



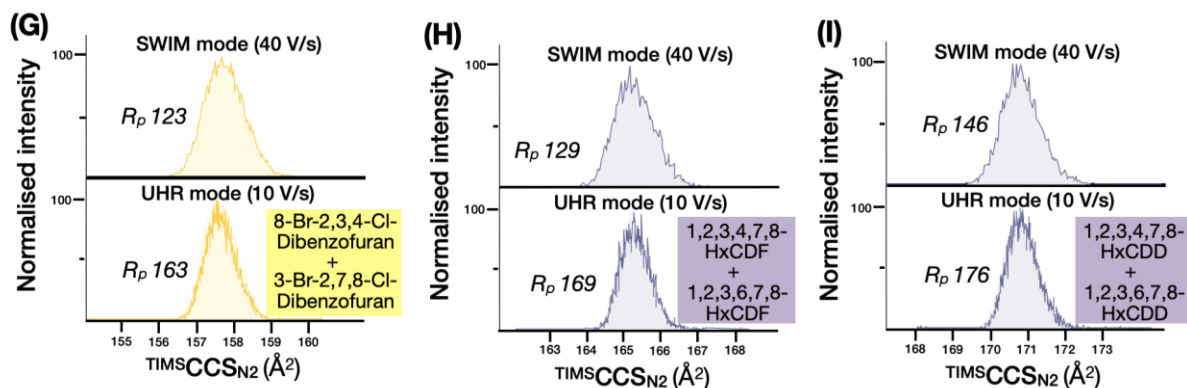


Figure S9 - Ion mobility spectra of the other GC (partially) coeluting isomeric pairs acquired in UHR mode.

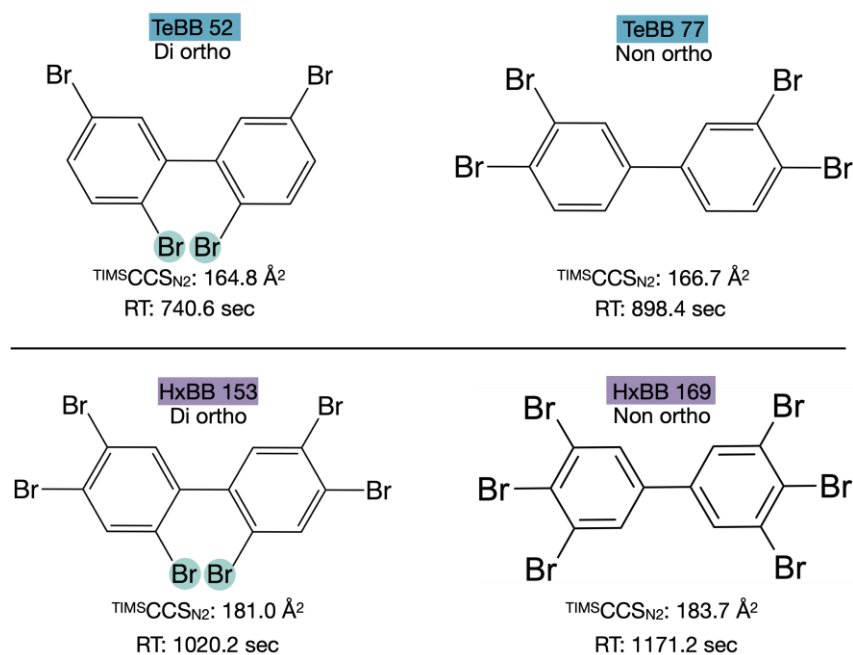


Figure S10 – CCS and GC retention time comparison of two polybrominated biphenyls (PBBs) isomeric pairs with different extent of ortho substitution. Both retention time and CCS increase with decreasing ortho substitution degree.

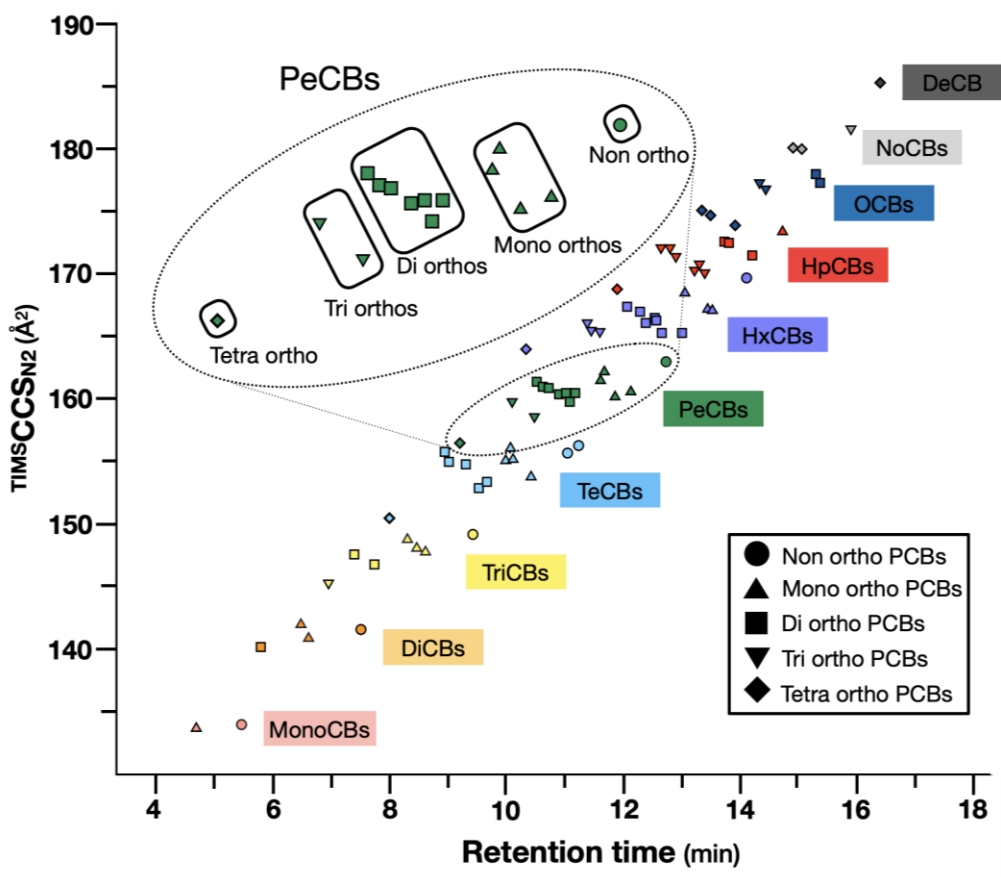
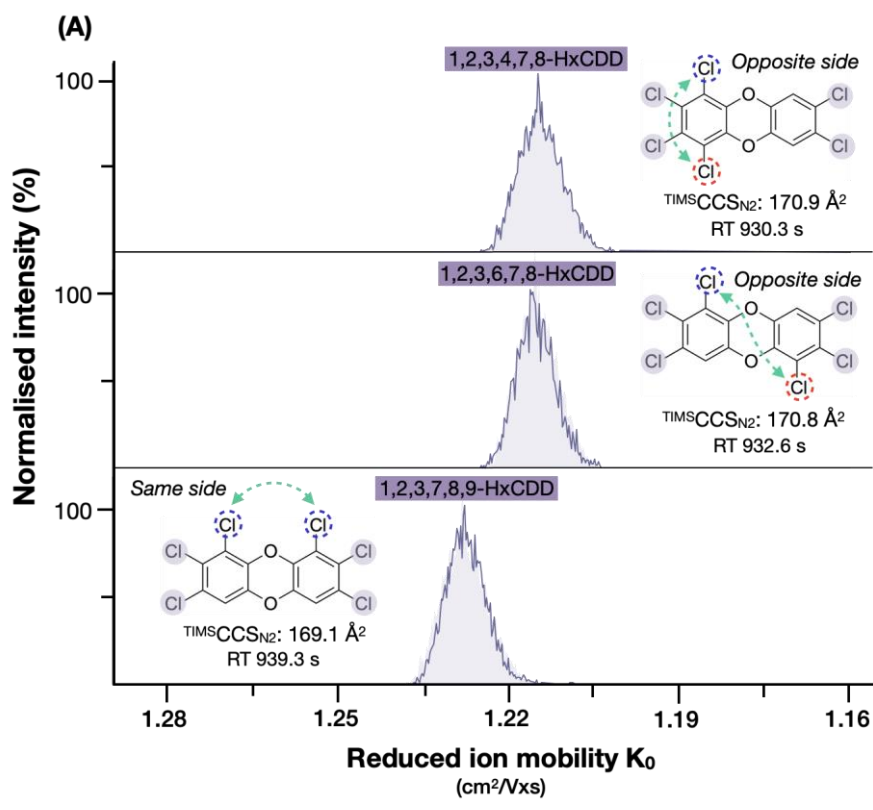


Figure S11 – Retention time versus CCS of PCBs ($n=82$). Color and shape respectively refer to halogenation and ortho substitution degree of the PCBs. The inset is a close-up view of the data of penta chloro substituted biphenyls (PeCBs).



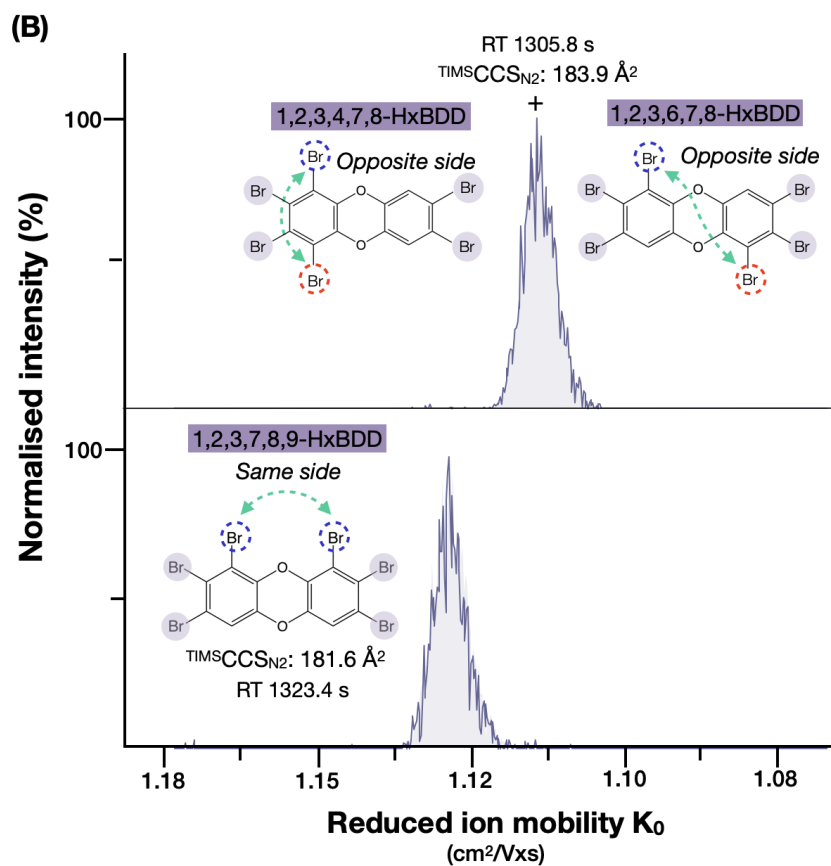
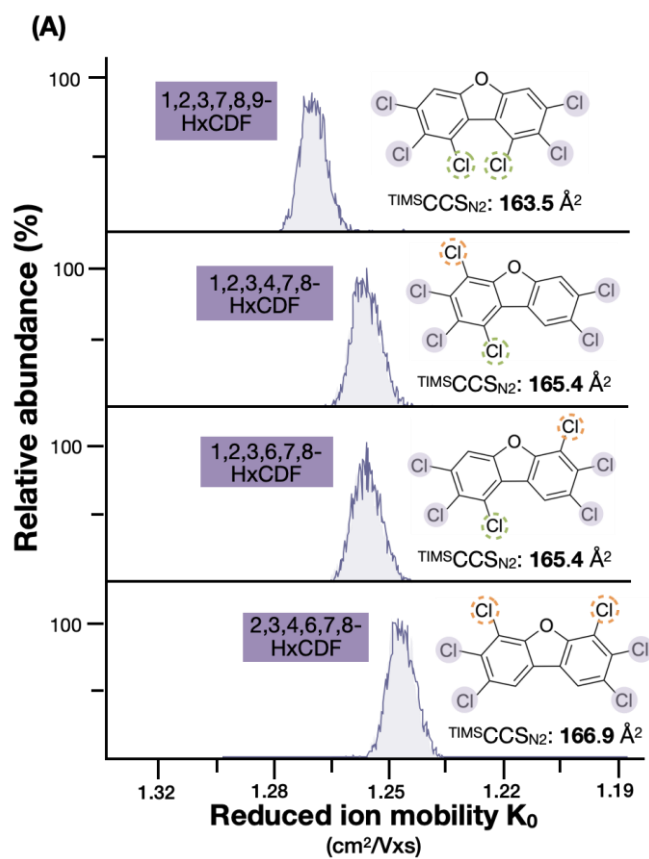


Figure S12 – Ion mobility spectra of hexa substituted 2,3,7,8-PCDDs (A) and 2,3,7,8-PBDDs (B).



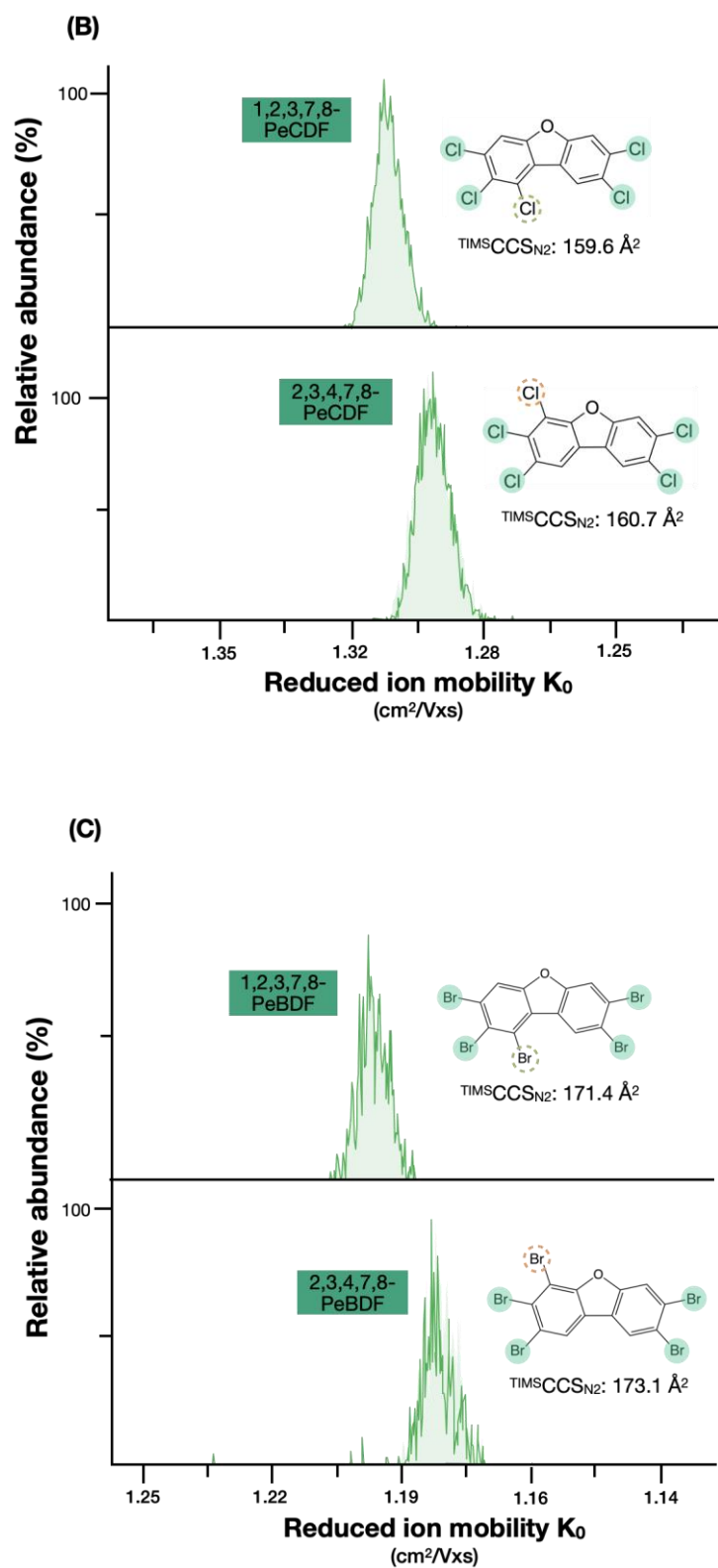


Figure S13 - Ion mobility spectra of hexa substituted 2,3,7,8-PCDFs (**A**), penta substituted 2,3,7,8-PCDFs (**B**) and penta substituted 2,3,7,8-PBDFs (**C**). Extra halogen atoms that are on the same side of the dibenzo furan moiety as the oxygen atom (positions 4 and 6) are circled in orange, while those on the opposite side (positions 1 and 9) are circled in green.

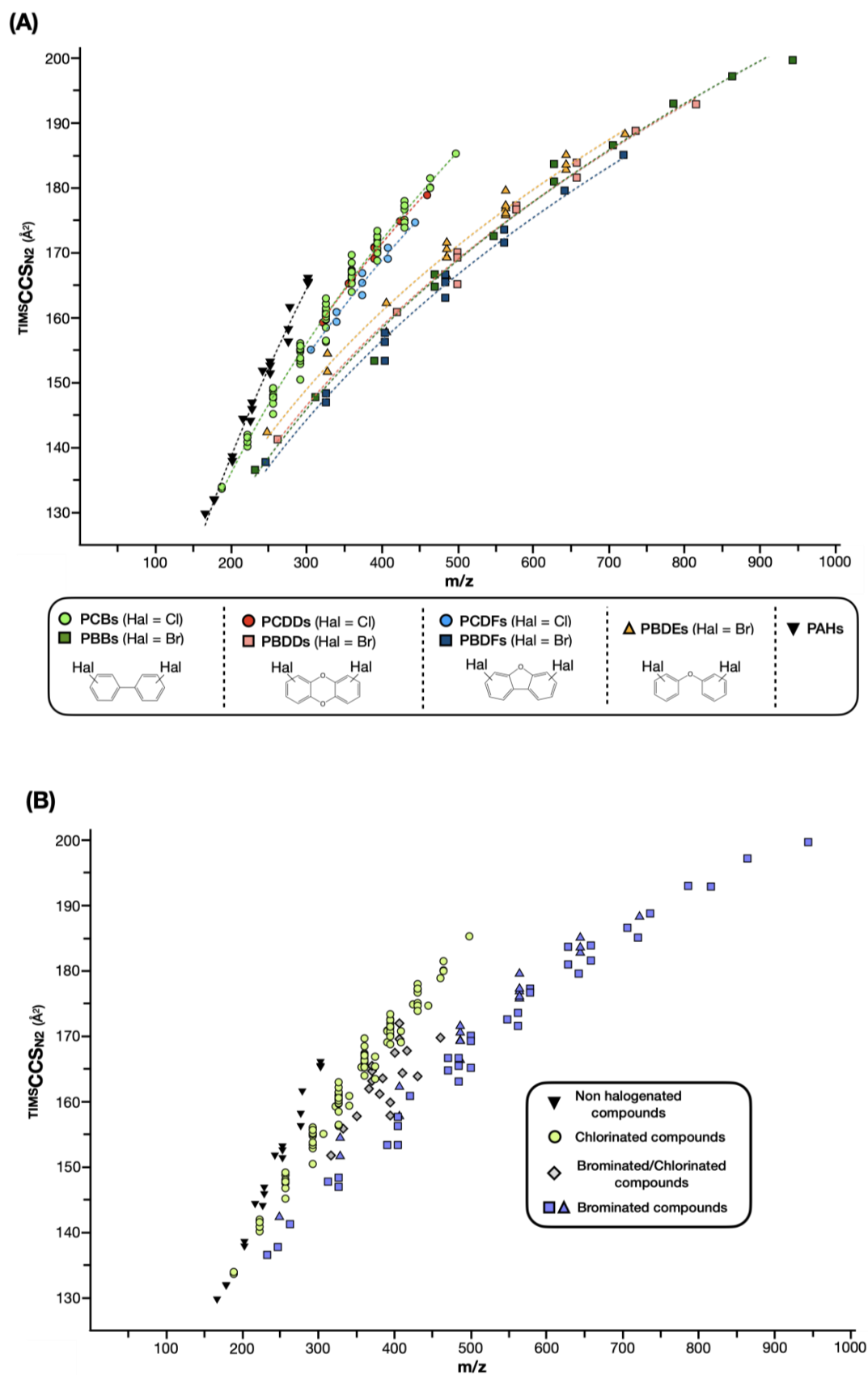
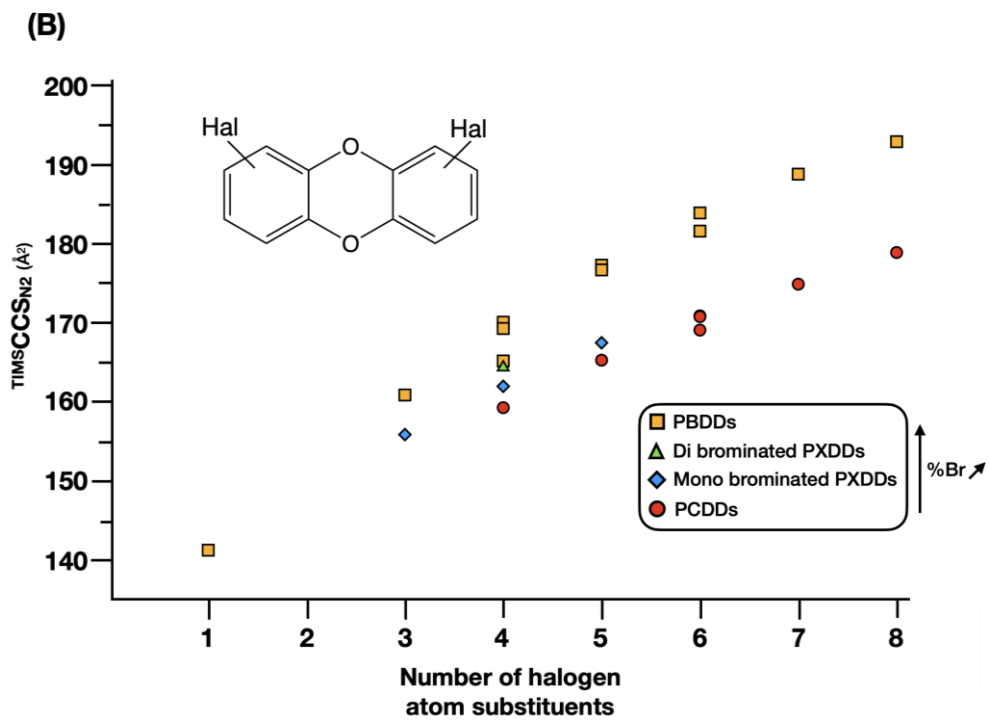
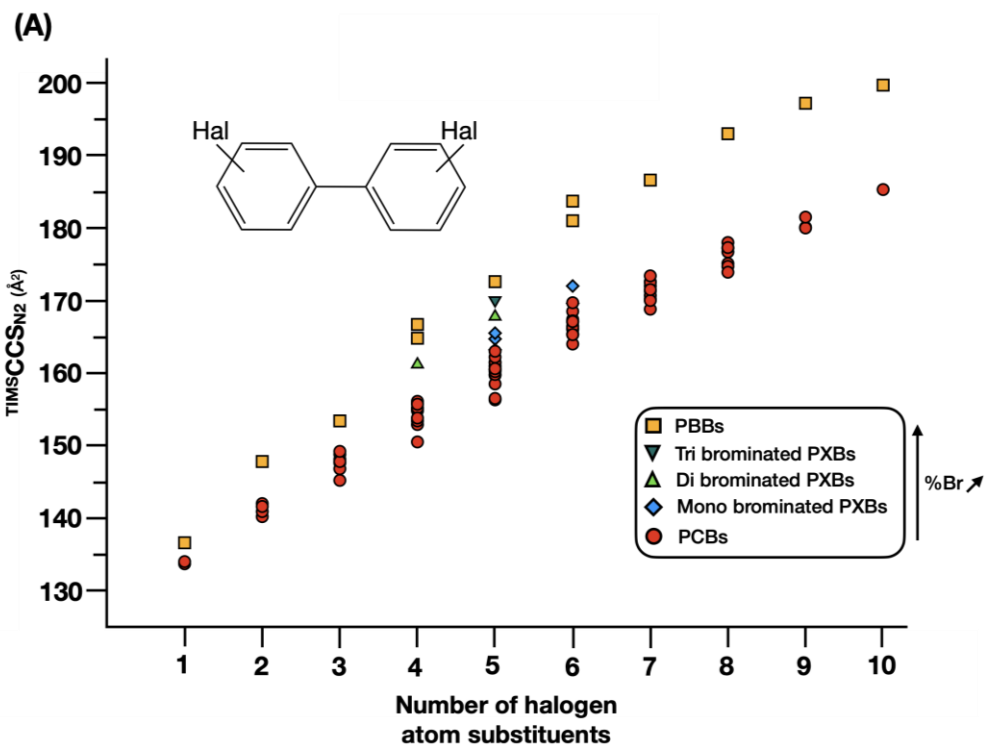


Figure S14 – CCS vs m/z plots of the different POP classes analysed in this work. Panel (A) represents the data as a function of the different classes of POPs. Data were fitted with power trendlines (except for the classes of mixed brominated-chlorinated POPs due to the lower number of data points). Panel (B) represents the same data as a function of halogenation type.



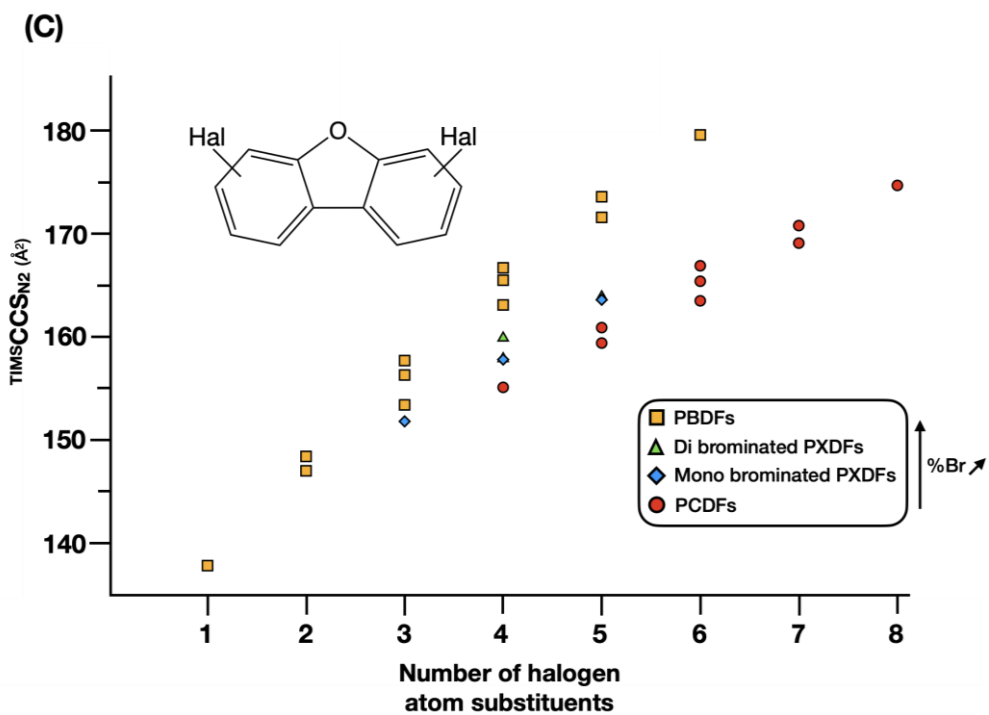
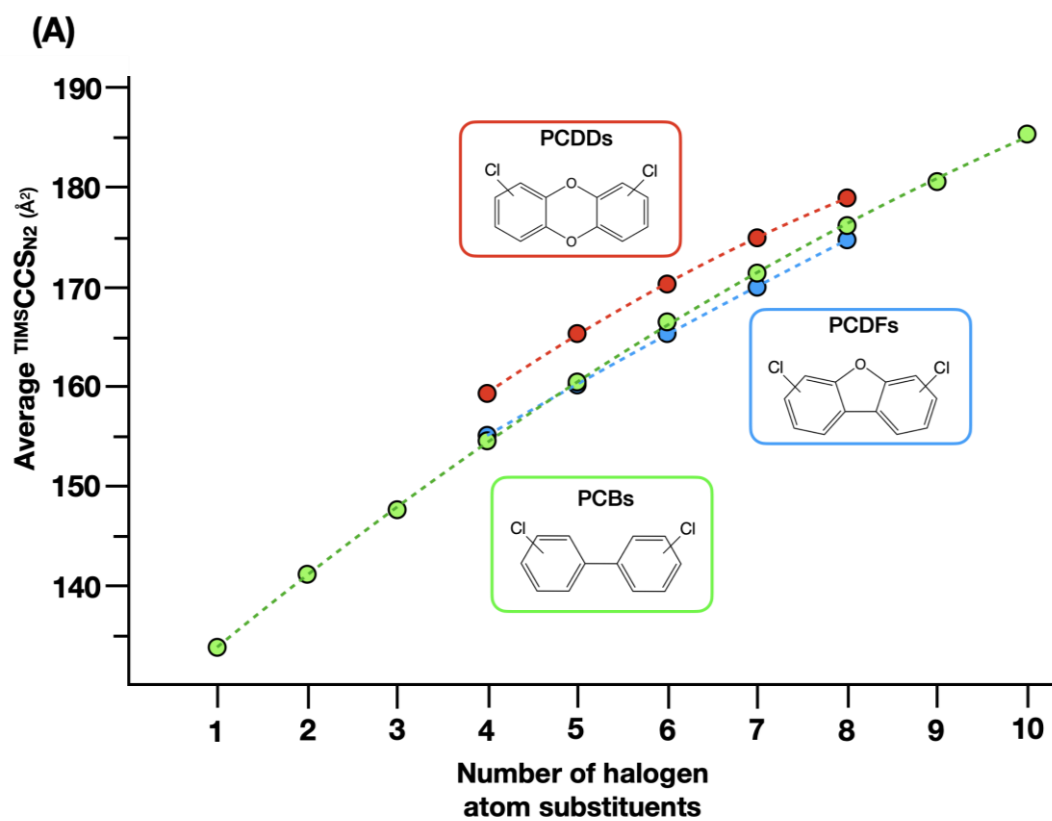


Figure S15 – CCS vs halogenation degree plots for the different classes of halogenated biphenyls (A), halogenated dibenzo-p-dioxins (B) and halogenated dibenzofurans (C).



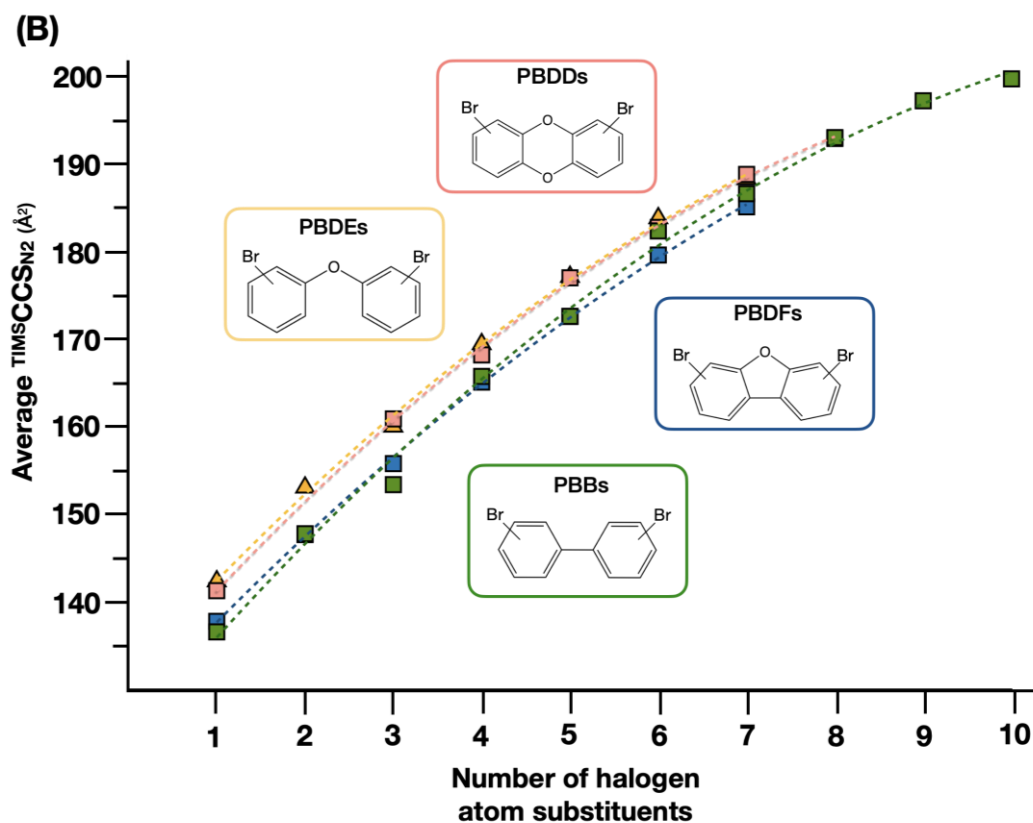


Figure S16 – Average $TIMS\text{CCS}_{N_2}$ of chlorinated (A) and brominated (B) POPs classes per halogenation degree. Data were fitted with a second order polynomial regression (dotted curves).

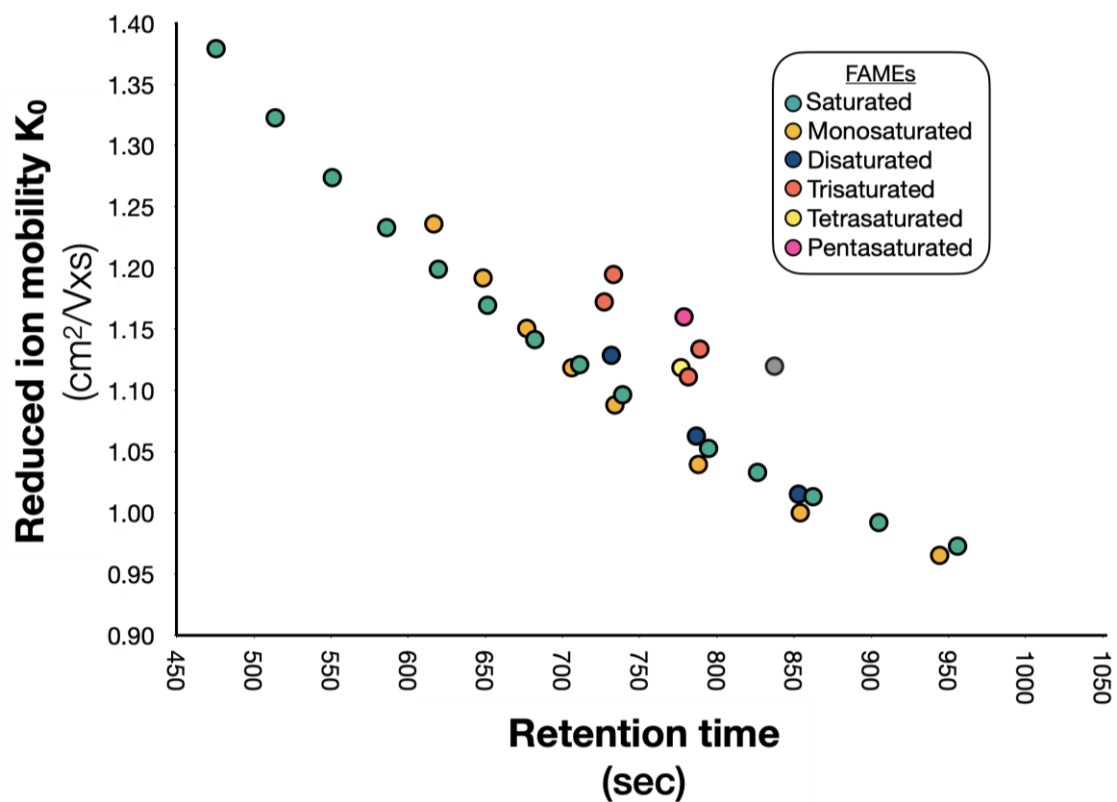


Figure S18 – Reduced ion mobility vs retention time plot of a mixture of saturated and (poly)unsaturated fatty acid methyl esters (FAMES) from C11 to C25 analyzed by GC-TIMS-MS.

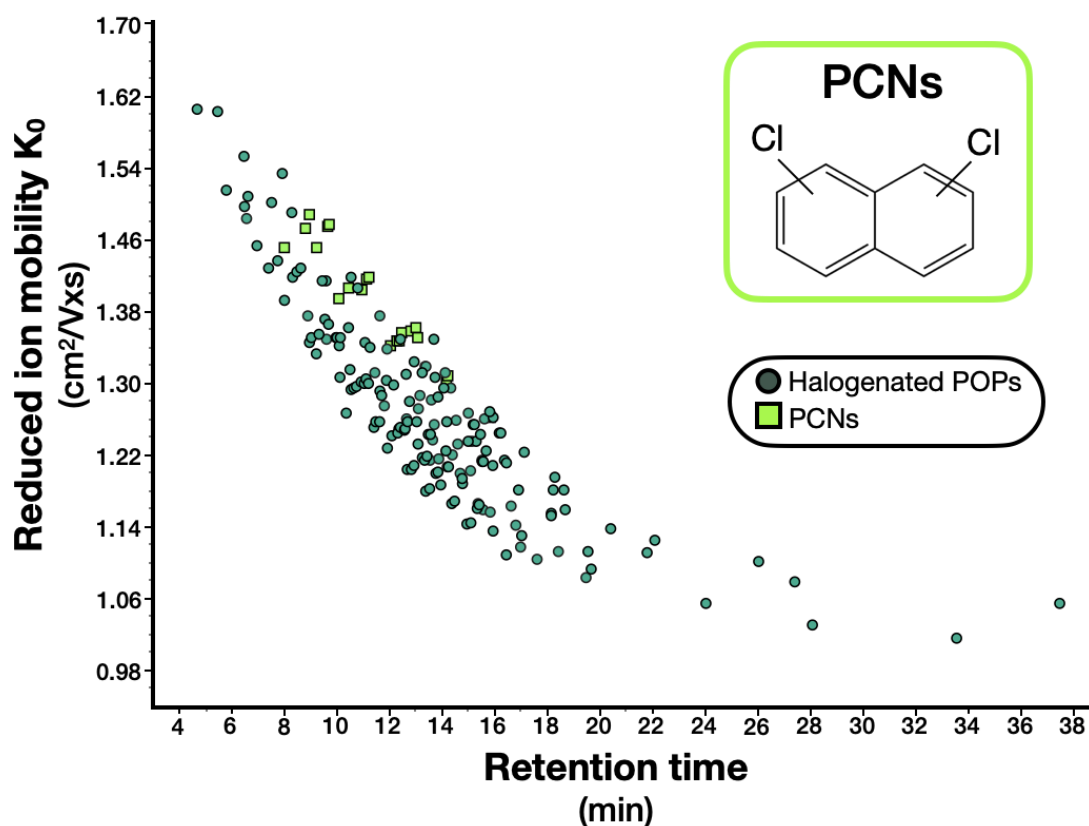


Figure S19 – Reduced ion mobility vs retention time plot of the PCNs and the other 174 halogenated POPs from Figure 1.

Reference

(1) Zheng, X.; Dupuis, K. T.; Aly, N. A.; Zhou, Y.; Smith, F. B.; Tang, K.; Smith, R. D.; Baker, E. S. Utilizing Ion Mobility Spectrometry and Mass Spectrometry for the Analysis of Polycyclic Aromatic Hydrocarbons, Polychlorinated Biphenyls, Polybrominated Diphenyl Ethers and Their Metabolites. *Anal. Chim. Acta* **2018**, *1037*, 265–273. <https://doi.org/10.1016/j.aca.2018.02.054>.