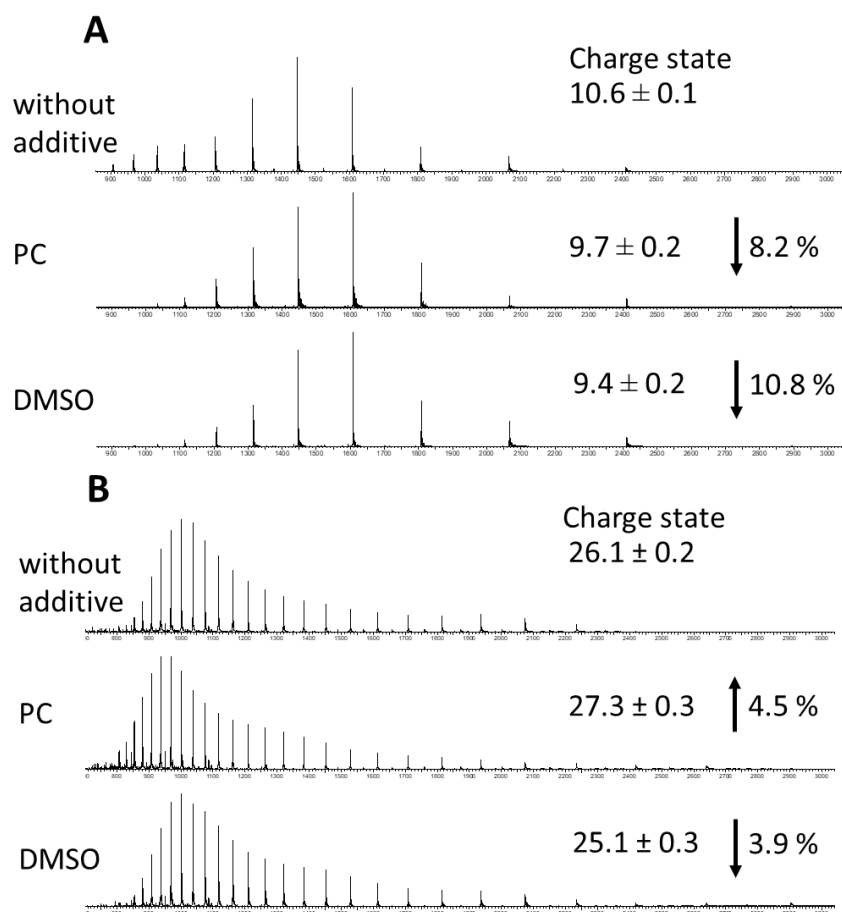


## Supplementary Information to: Charge site manipulation to enhance top-down fragmentation efficiency

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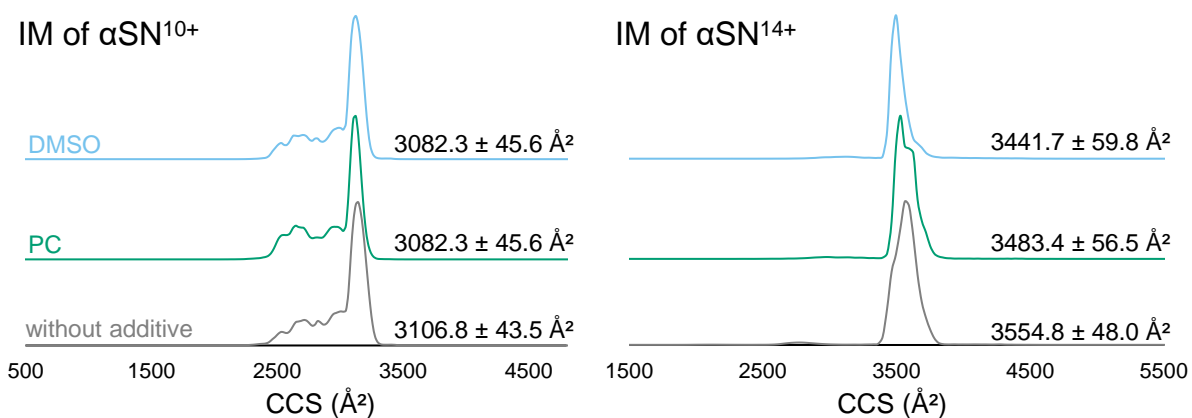
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### 1. Influence of the additives on the overall charge state

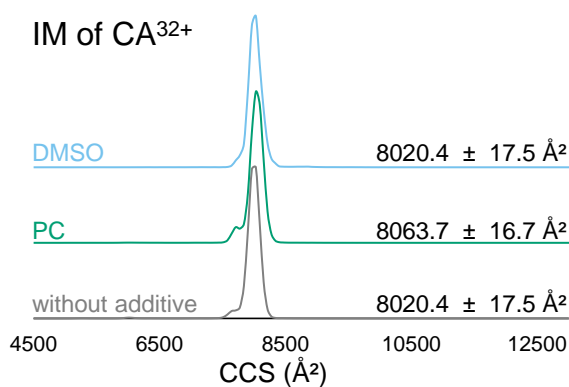


**Supplementary Figure 1:** Example spectra showing the overall charge state distribution with different solution conditions of (A)  $\alpha$ SN and (B) CA. The intensity-weighted average charge states are displayed on the right, and the reported standard deviations were calculated from triplicate measurements.

## 2. Influence of the additives on the CCS values



Supplementary Figure 2: CCS distribution of charge states 10+ and 14+ of  $\alpha\text{SN}$ .



Supplementary Figure 3: CCS distribution of charge states 32+ of CA.

## 3. Physicochemical properties of the used solvents

Supplementary Table 1: Comparison of the properties of the used solvents

Solvent	Boiling point (°C)	Dielectric constant (at 20°C)	Proticity	Structure	Molecular weight (g/mol)
Methanol	65	32.7	protic	$\text{H}_3\text{C}-\text{OH}$	32.0
Water	100	80.1	protic	$\text{H}-\text{O}-\text{H}$	18.0
DMSO	189	46.7	aprotic	$\text{H}_3\text{C}-\text{S}(\text{CH}_3)-\text{O}$	78.1
Propylene carbonate	242	64.9	aprotic	$\text{H}_3\text{C}-\text{C}(\text{O})_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$	102.1

4. Raw relative intensities and their standard deviations for the cleavage sites (data used to generate Figures 2, 4B, and 5B of the main text)

Note: all values are multiplied by a factor of  $10^6$  for better readability.

**Supplementary Table 2A: aSN<sup>14+</sup>**

Cleavage site	additive free sample		PC		DMSO	
	Average intensity	Standard deviation	Average intensity	Standard deviation	Average intensity	Standard deviation
107	137.10	36.09	97.74	23.31	64.63	39.18
114	28.10	8.80	202.56	22.52	130.85	43.99
115	6.46	2.16	431.00	42.18	388.16	74.63
117	176.29	35.29	128.87	9.56	62.21	11.72
119	135.29	40.96	372.11	36.57	202.44	47.97
128	158.13	37.96	137.01	15.32	48.03	14.88
137	142.83	20.73	1725.74	346.07	424.16	124.53
138	1236.18	226.68	1065.46	22.57	485.86	103.17

**Supplementary Table 2B: aSN<sup>10+</sup>**

Cleavage site	additive free sample		PC		DMSO	
	Average intensity	Standard deviation	Average intensity	Standard deviation	Average intensity	Standard deviation
15	98.93	28.11	73.58	8.78	61.21	2.98
49	152.25	26.31	136.05	13.73	26.08	1.87
66	193.45	36.05	1065.28	112.63	833.73	48.61
83	16.55	1.34	102.52	7.78	89.92	4.07
107	73.79	15.85	337.07	32.57	313.61	18.95
119	125.56	17.27	905.48	127.36	785.67	39.97
137	234.90	27.63	316.26	28.85	252.61	15.04

**Supplementary Table 2C: CA<sup>32+</sup>**

Cleavage site	additive free sample		PC		DMSO	
	Average intensity	Standard deviation	Average intensity	Standard deviation	Average intensity	Standard deviation
40	323	19.2	241	27	250	8.93
68	52.3	4.61	61.9	5.48	65.7	7.26
184	33.1	1.7	58	10.7	31.7	3.36
192	74.5	4.37	231	7.98	168	13.4
193	662	13.8	926	50.1	688	61.8
197	41	4.88	56	0.789	41	1.73
198	62.9	4.3	84.5	4.77	68.9	4.23
213	123	10.3	90.3	7.05	80	9.36
235	1669	43.1	1514	80.5	1076	9.85