# Supporting Information

## Enhancing Mass Analysis of Ultra-High Molecular Weight Polystyrene: A Comparative Study of Copper and Silver Salts with MALDI Mass Spectrometry

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Table S1 The experimental conditions used to obtain different polystyrene mass spectra using MALDI LIT-MS

| Experimental Parameters | | Polystyrene | | | |
|---|---|---|---|---|---|
| | | PS210k | PS650k | PS900k | PS2M |
| **Q1** | **RF Frequency *f* (kHz)** | 201 | 82 | 82 | 51 |
| | **RF Amplitude $kV_{p-p}$** | 1.5 | 1 | 1.4 | 1.2 |
| | **LMCO (Dalton)** | 26769 | 107226 | 150116 | 332636 |
| **LIT** | **RF Frequency *f* (kHz), Start** | 70433 | 39843 | 32539 | 23004 |
| | **RF Frequency *f* (kHz), End** | 16266 | 10649 | 10649 | 7274 |
| | **RF Amplitude $V_{p-p}$** | 560 | 560 | 560 | 560 |
| | **Auxiliary AC $V_{p-p}$** | 54 | 72 | 84 | 84 |
| | **LMCO (Dalton)** | 32k | 100k | 150k | 300k |
| | **Cooling time (ms)** | 800 | 800 | 800 | 800 |
| | **Scanning time (ms)** | 500 | 500 | 500 | 500 |

Table S2 The molecular weight data measured using MALDI LIT-MS for a variety of UHMW PS standards and cationization reagents.

| **PS** | **MALDI LIT-MS** | **gel permeation chromatography (GPC)*** | | | | **Light scattering$** |
|---|---|---|---|---|---|---|
| | **Molecular Weight (Da)** | **Molecular Weight (Da)** | | | **PDI=** $\frac{M_w}{M_n}$ | **Molecular Weight (Da)** |
| | **$M_w$ (At peak center)** | **$M_n$** | **$M_w$** | **$M_p$** | | **$M_w$** |
| PS210k | 240,056 | 211,400 | 213,600 | 218,500 | ≤1.01 | 211600 |
| PS650k | 606,178 | 617,600 | 649,400 | 648,800 | ≤1.06 | 670,000 |
| PS900k | 945,500 | 892,000 | 942,000 | 949,000 | ≤1.10 | 929,000 |
| PS2M | 2,006,169 | 1,524,000 | 1,971,000 | 2,161,000 | ≤1.30 | 1,971,000 |

* Molecular weight measured using gel permeation chromatography by supplier.

$ Molecular weight measured using Light scattering method by supplier.

$M_p$ = molecular weight of the highest peak

Table S3 Polystyrene concentrations used to optimize the concentration ratio of PS : matrix : cationization salt using DCTB matrix (0.1 M) and $AgNO_3$ salt (0.15 M) at fixed concentration.

The red-colored numbers represent the best concentration condition for each PS standard which resulted in the highest signal intensity.

| **Serial No.** | **Polystyrene molar concentration (M)** | | |
|---|---|---|---|
| | PS210k | PS650k | PS900k |
| 1 | 1.0E-05 | 1.0E-06 | 1.0E-07 |
| **2** | **5.0E-05** | 5.0E-06 | 5.0E-07 |
| 3 | 1.5E-04 | **1.0E-05** | 1.0E-06 |
| 4 | 5.0E-04 | 5.0E-05 | **5.0E-06** |
| 5 | | 1.0E-04 | 1.0E-05 |

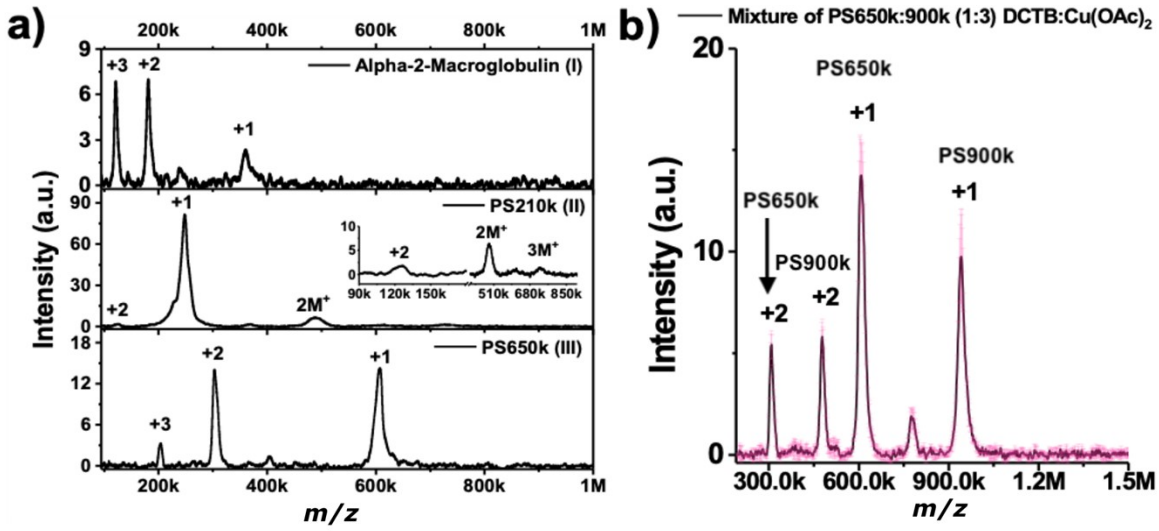


Figure S1 a) Mass spectrum of I) alpha-2-macroglobulin acquired with SA matrix and mass spectra of II) PS210k, and III) PS650k obtained with a DCTB matrix and $Cu(OAc)_2$ salt. All mass spectra were acquired at similar ion trapping and experimental conditions. b) Mass spectra of PS650k and PS900k mixture with the mixing ratio of 1:3 obtained with a DCTB matrix and $Cu(OAc)_2$ salt.

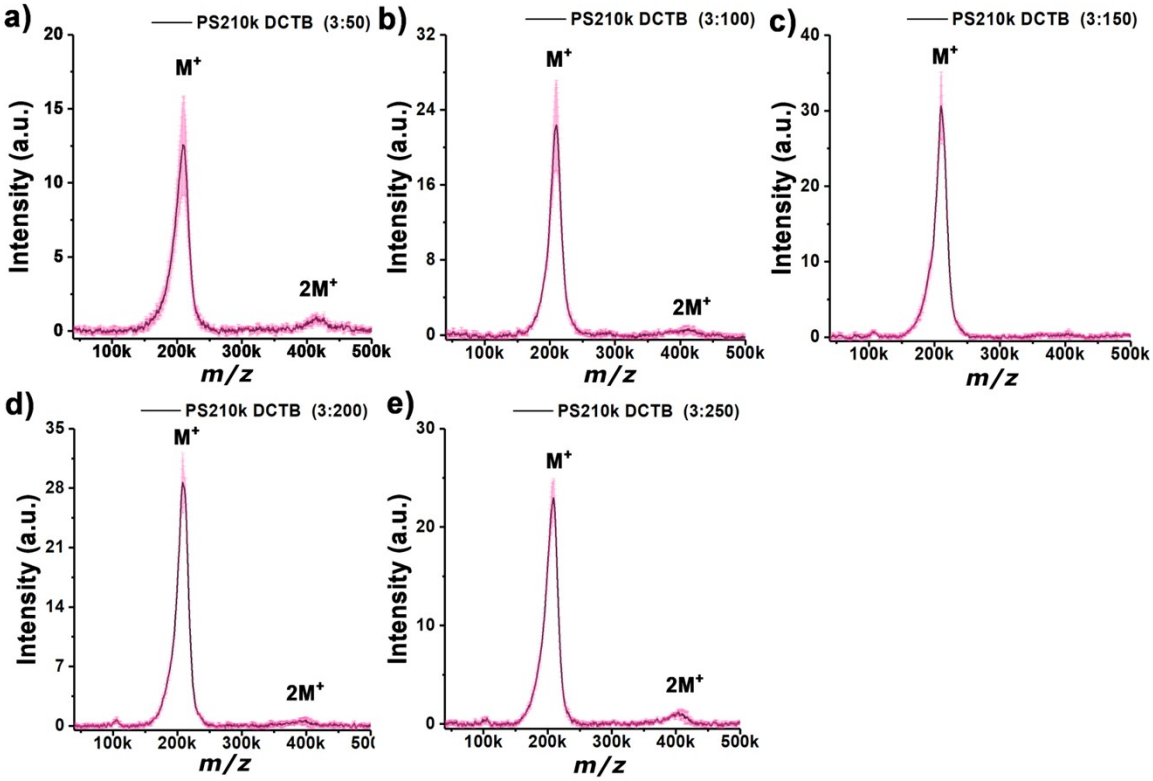

Figure S2 Mass spectra of PS210k obtained using DCTB matrix with PS : matrix concentration (v/v) ratios of a) 3:50, b) 3:100, c) 3:150, d) 3:200, and e) 3:250.

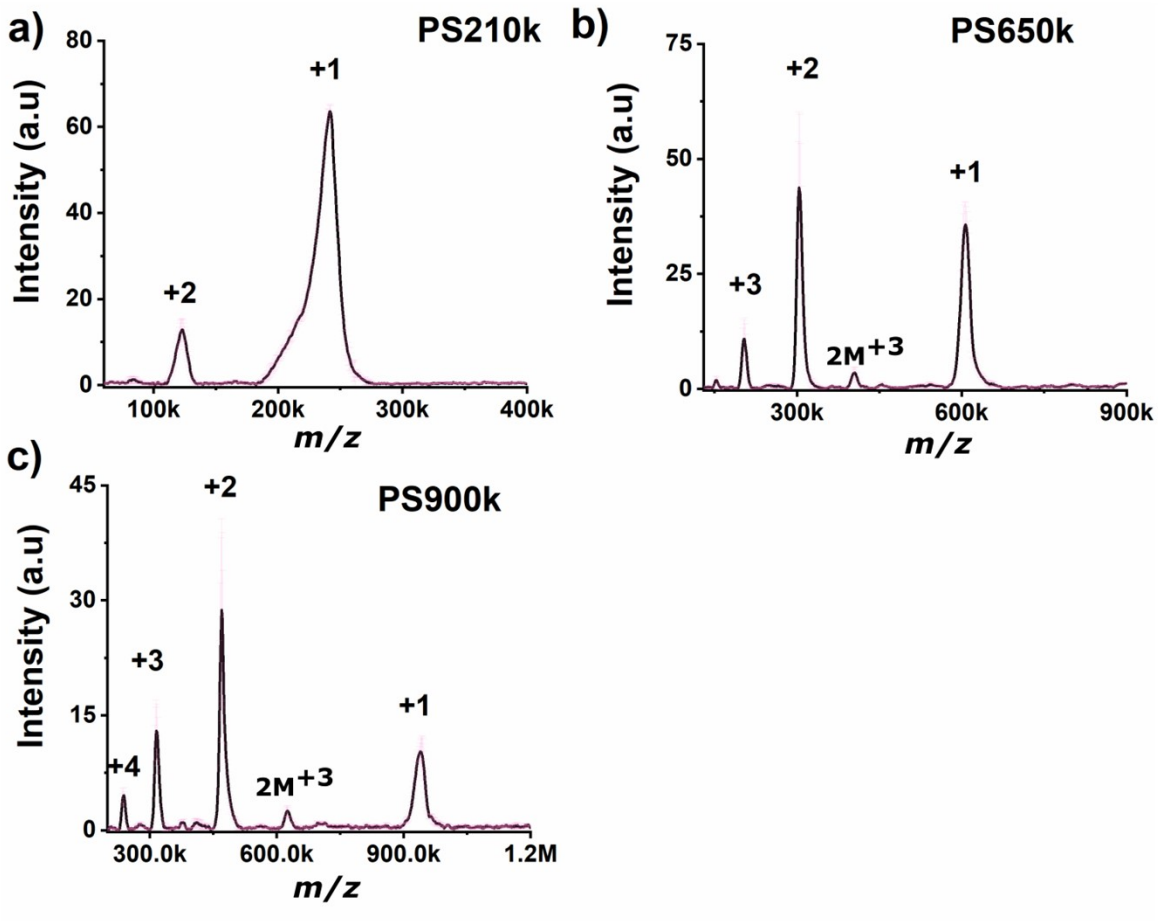


Figure S3 Mass spectra of a) PS210k, b) PS650k, and c) PS900k obtained with a DCTB matrix and $AgNO_3$ salt at the optimized ratio of PS: matrix: $AgNO_3$ concentration conditions listed in Table 1.

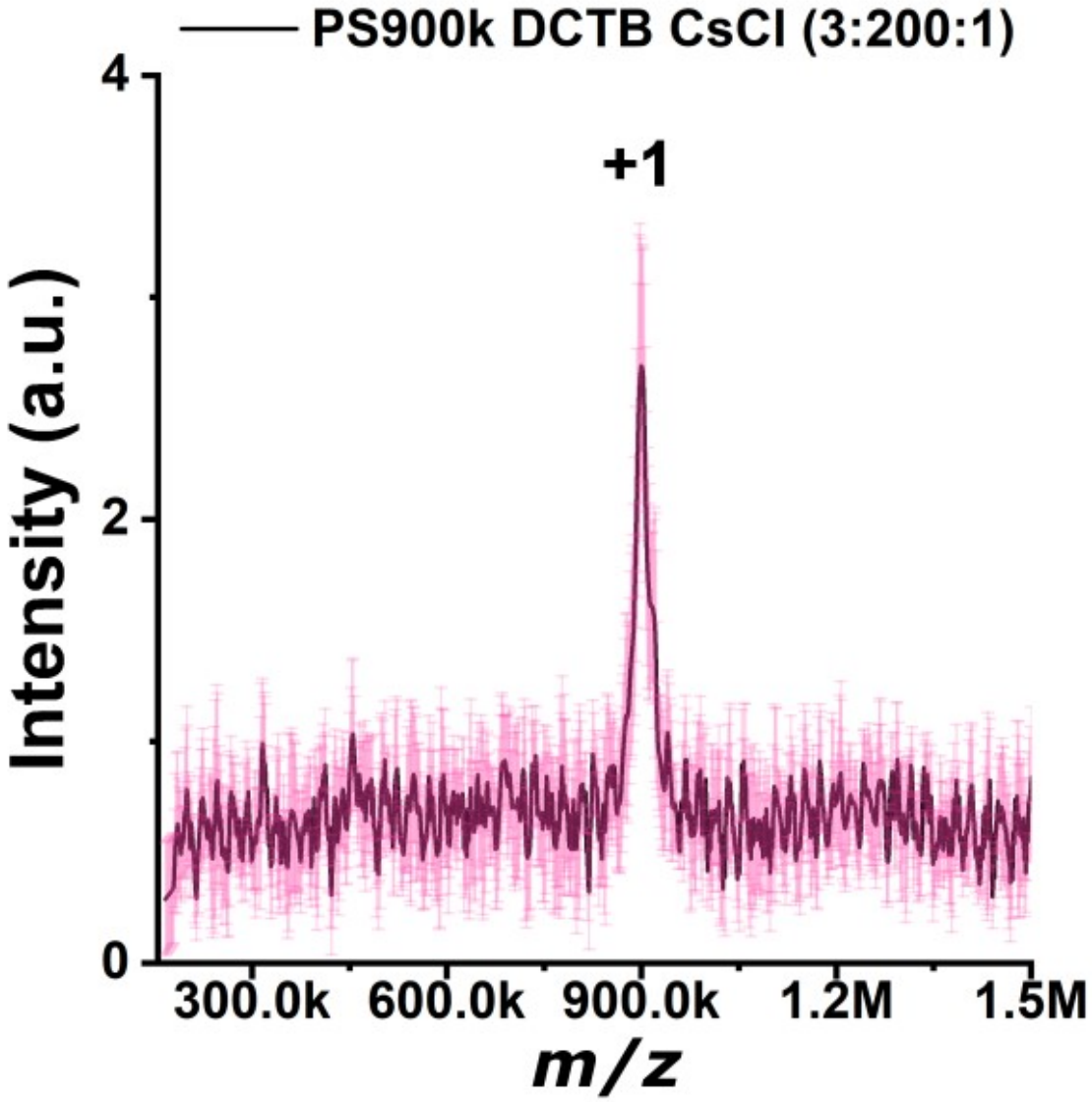


Figure S4 Mass spectra of PS900k obtained with a DCTB matrix using CsCl salt.

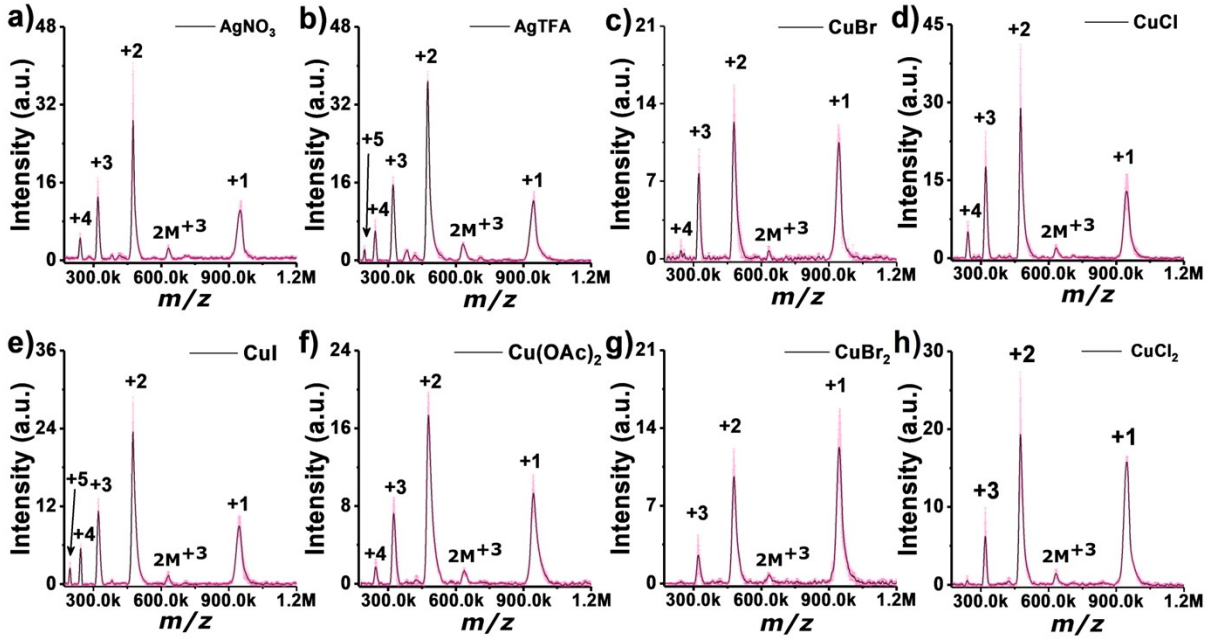


Figure S5 Mass spectra of PS900k obtained with a DCTB matrix using various cationizing reagents with a) AgTFA, b) $AgNO_3$, c) CuI, d) CuBr, e) CuCl, f) $CuBr_2$, g) $CuCl_2$, and h) $Cu(OAc)_2$. The optimal ratio of PS : matrix : cationizing reagent was 3:200:1 (v/v/v).

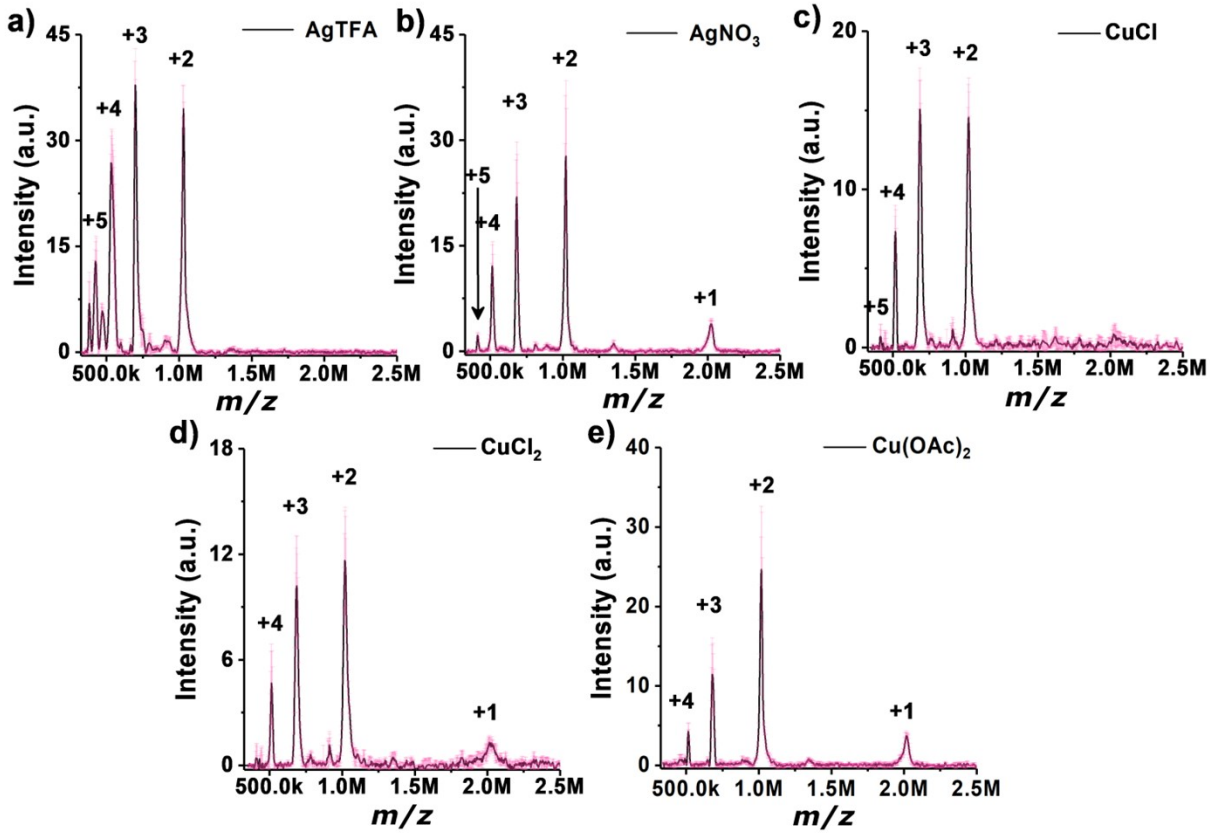


Figure S6 Mass spectra of PS2M obtained with a DCTB matrix using cationizing reagents with a) AgTFA, b) $AgNO_3$, c) CuCl, d) $CuCl_2$, and e) $Cu(OAc)_2$. The optimal ratio of PS : matrix : cationizing reagent was 3:200:1 (v/v/v).

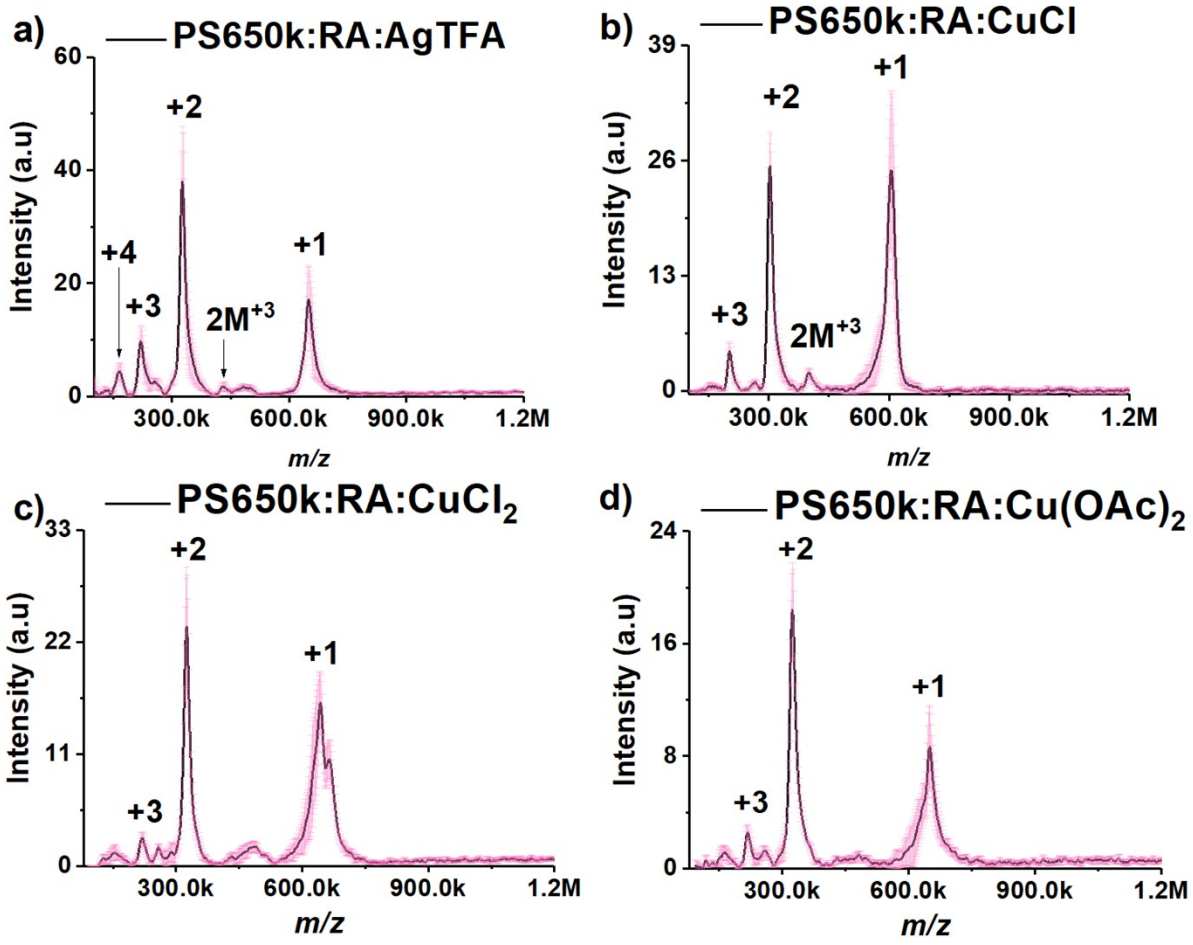


Figure S7 Mass spectra of PS650k obtained with a RA matrix using various cationizing reagents with a) AgTFA, b) CuCl, c) $CuCl_2$, and d) $Cu(OAc)_2$. The optimal ratio of PS : matrix : cationizing reagent was 3:200:1 (v/v/v).

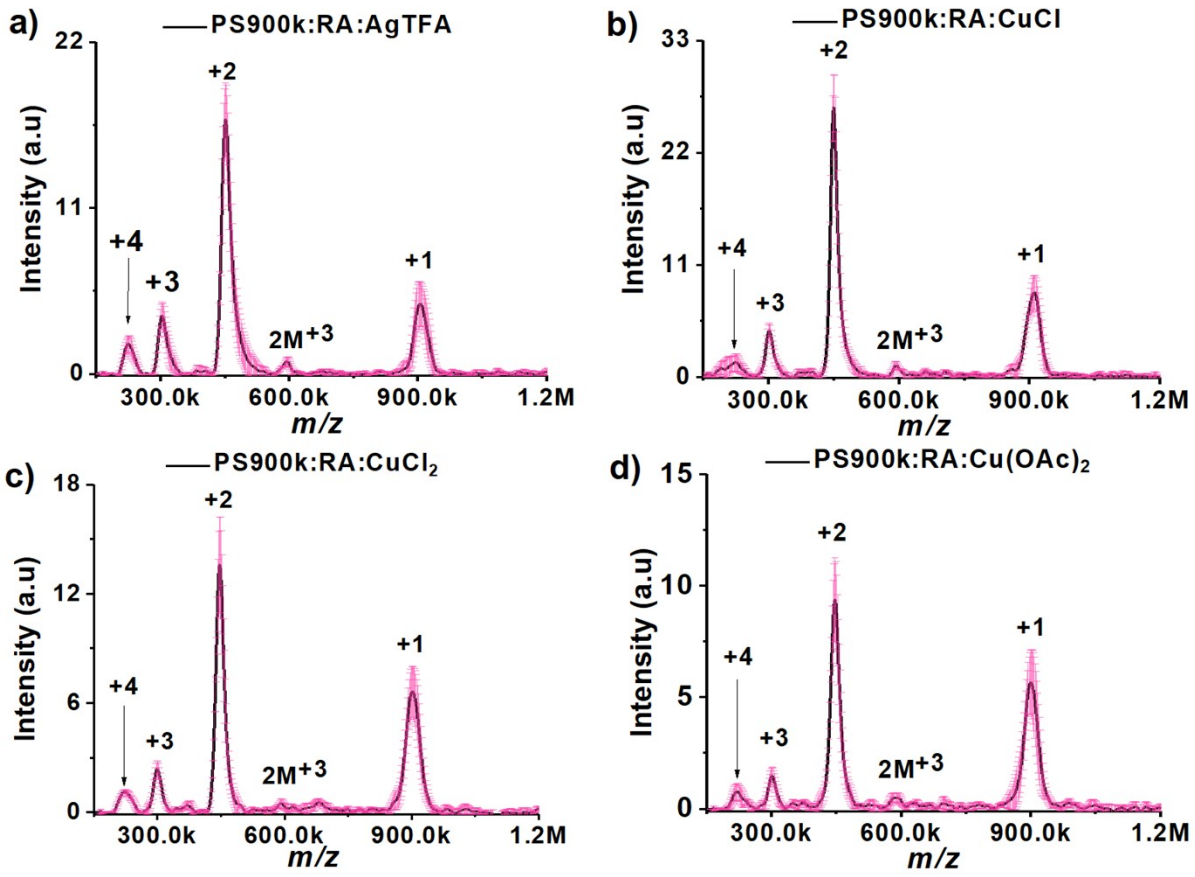


Figure S8 Mass spectra of PS900k obtained with a RA matrix using various cationizing reagents with a) AgTFA, b) CuCl, c) $CuCl_2$, and d) $Cu(OAc)_2$. The optimal ratio of PS : matrix : cationizing reagent was 3:200:1 (v/v/v).

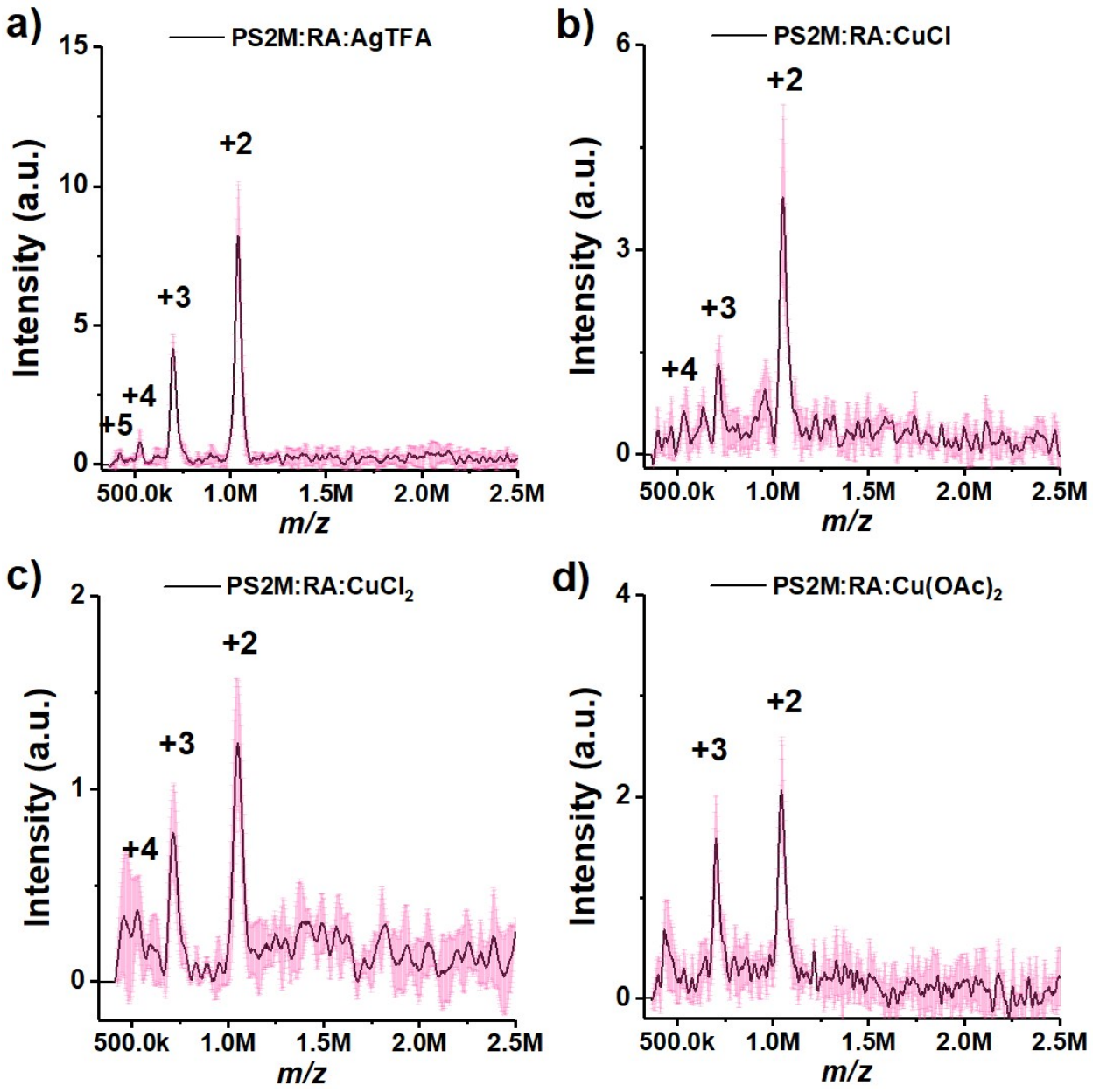


Figure S9 Mass spectra of PS2M obtained with a RA matrix using various cationizing reagents with a) AgTFA, b) CuCl, c) $CuCl_2$, and d) $Cu(OAc)_2$. The optimal ratio of PS : matrix : cationizing reagent was 3:200:2 (v/v/v).