

**SUPPLEMENTAL MATERIAL**

**Radical Induced Disulfide Bond Cleavage within Peptides via  
Ultraviolet Irradiation of an Electrospray Plume**

Craig A. Stinson and Yu Xia\*

Department of Chemistry, Purdue University, West Lafayette, IN, 47907-2084, USA

Address reprint requests to:

Dr. Yu Xia

Department of Chemistry

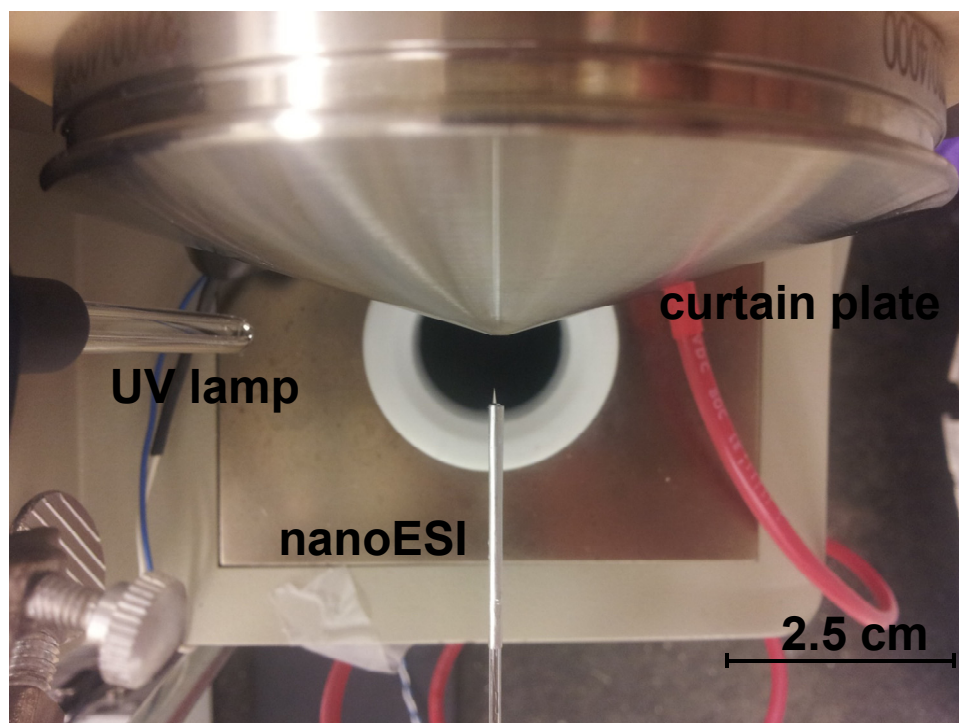
Purdue University

West Lafayette, IN, USA 47907-2084

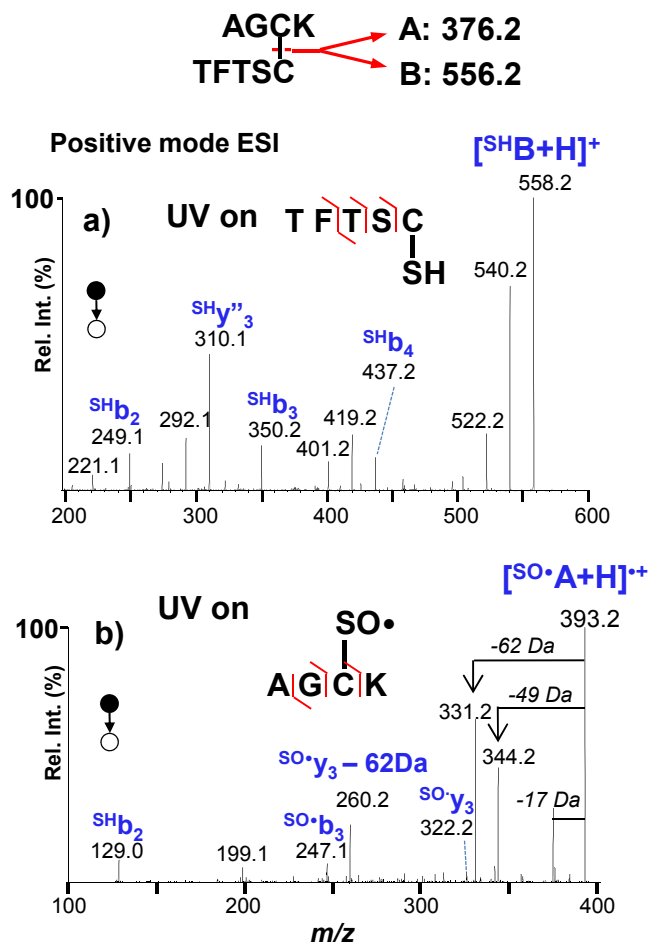
Phone: (765) 494-1142

Fax: (765) 494-9421

E-mail: [yxia@purdue.edu](mailto:yxia@purdue.edu)

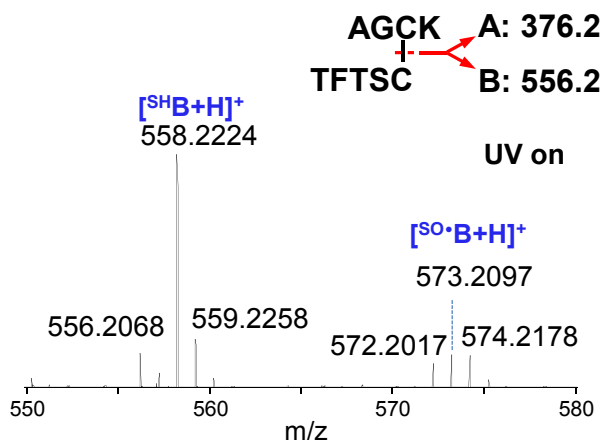


**Fig. S1:** Photograph of the setup showing the UV lamp relative to the nanoESI source.

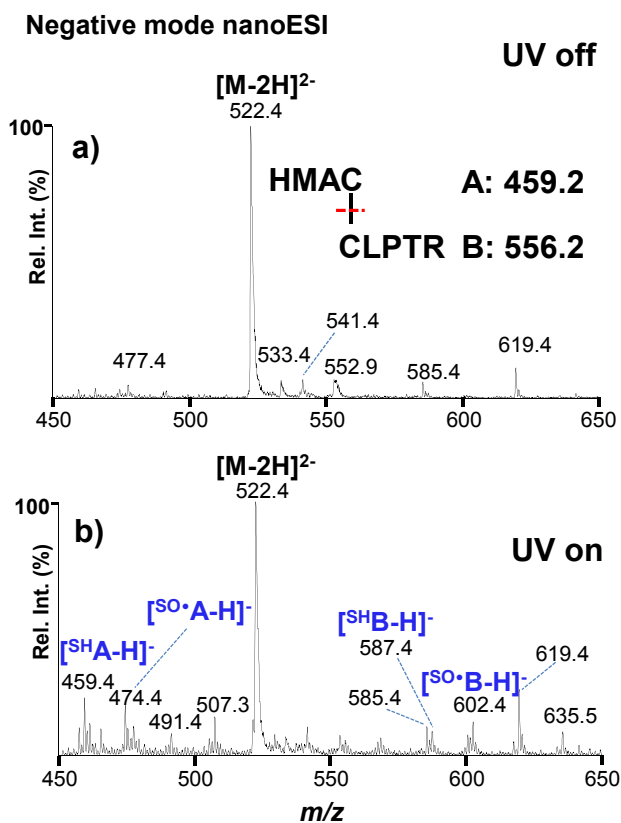


**Fig. S2:** MS<sup>2</sup> CID spectra of radical reaction products of interchain linked disulfide Peptide 2.

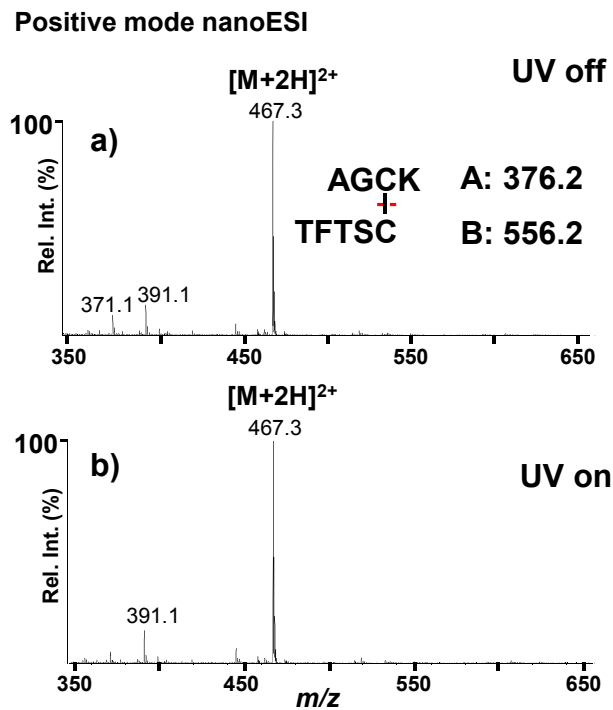
(a) Beam-type CID (CE 25 V) of [<sup>SH</sup>B+H]<sup>+</sup>. (b) Ion trap CID of [<sup>SO</sup>•A+H]<sup>+</sup>.



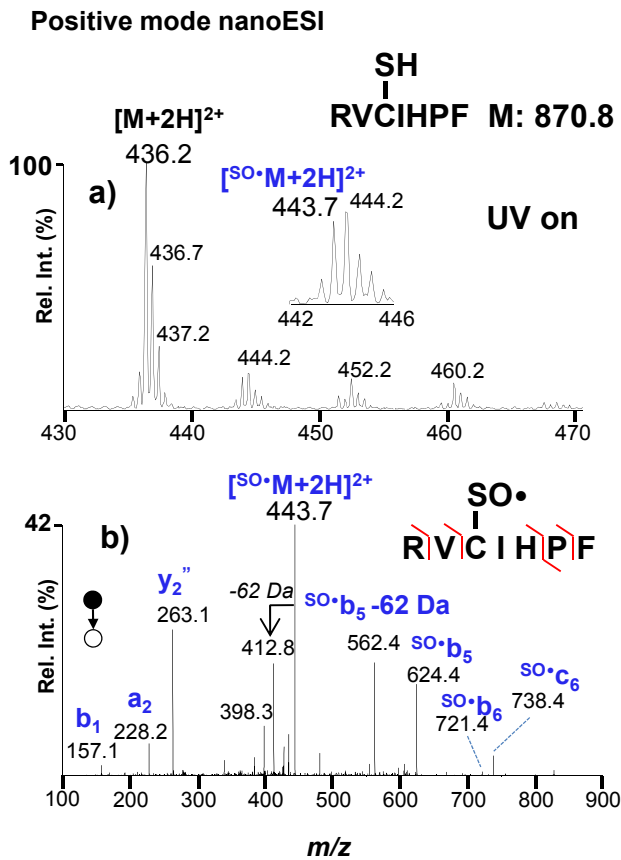
**Fig. S3:** Accurate mass measurement spectra of B-chain radical reaction products of Peptide 2.



**Fig. S4:** (a)  $\text{MS}^1$  negative mode nanoESI of Peptide 4 before UV. (b)  $\text{MS}^1$  of Peptide 4 with the lamp on.



**Fig. S5:** positive mode nanoESI experiments with Peptide 2 when applying 185 nm filtered UV lamp. (a) MS<sup>1</sup> before application of the filtered lamp. (b) MS<sup>1</sup> when the lamp is on.



**Fig. S6:** Optimized sulfenyl radical reaction products for Peptide 6. (a)  $MS^1$  with the lamp on.

(b) Ion trap CID of  $[^{SO\bullet}M+2H]^{2+}$ .

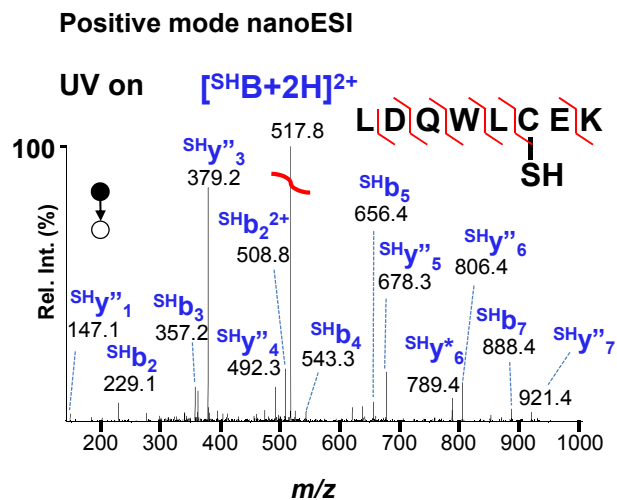


Fig. S7: Beam-type CID (CE 25 V) of  $[\text{SHB}+2\text{H}]^{2+}$  from Peptide 3.