## SUPPORTING INFORMATION

## Structural Characterization of Native Proteins and Protein Complexes by Electron Ionization Dissociation-Mass Spectrometry

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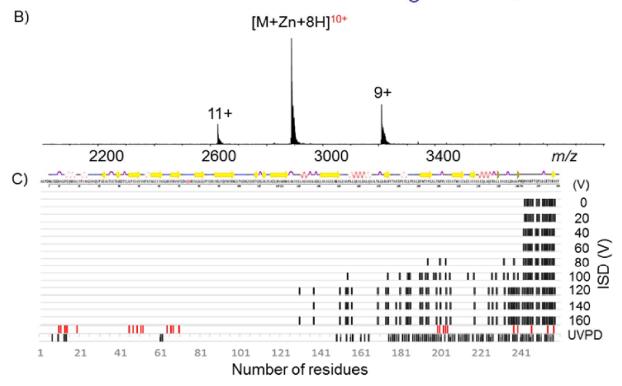
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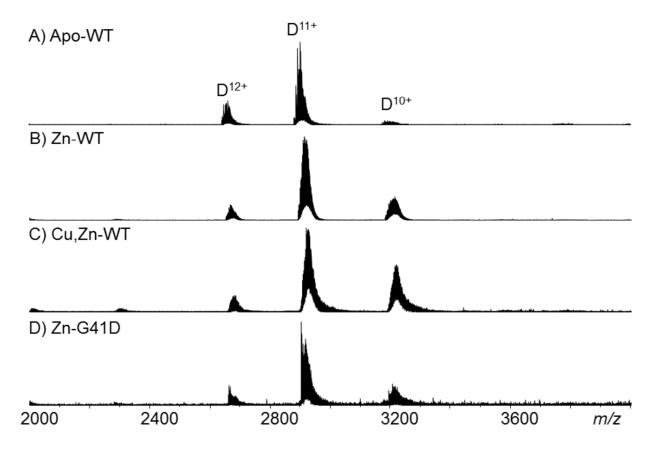
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ASPDWGYDD KNGPEQWSKL YPIANGNNQS PVDIKTSETK HDTSLKPISV SYNPATAKEI INVGHSFHVN FEDNDNRSVL KGGPFSDSYR LFQFHFHWGS TNEHGSEHTV DGVKYSAELH VAHWNSAKYS SLAEAASKAD GLAVIGVLMK VGEANPKLQK VLDALQAIKT KGKRAPFTNF DPSTLLPSSL DFWTYPGSLT HPPLYESVTW IICKESISVS SEQLAQFRSL LSNVEGDNAV PMQHNNRPTQ PLKGRTVRAS F



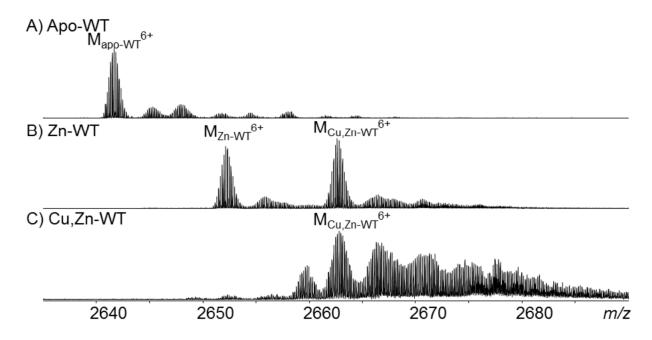
**Figure S-1.** (A) Sequence of HCA-1. (B) Full ESI mass spectrum of HCA-1. (C) Plot of backbone cleavage sites of HCA-I with different dissociation conditions; the plots for ISD-EID are shown at the top and the plot for UVPD shown at the bottom. Black bars show ions from the C-terminal region (x, y, and z) and red bars represent ions from the N-terminal region (a, b, and c).



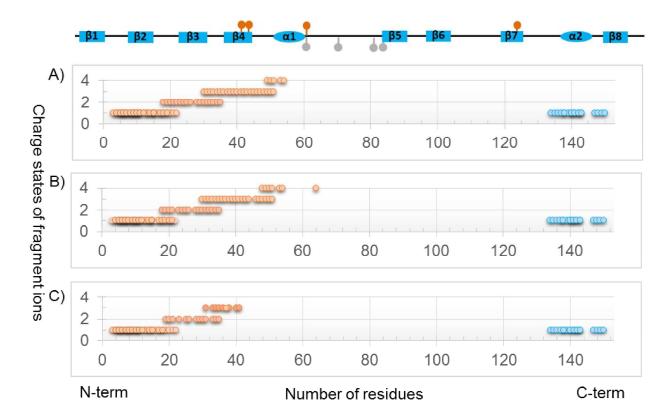
**Figure S-2.** Full ESI mass spectra of SOD1 dimers. (A) apo-WT, (B) Zn-WT, (C) Cu,Zn-WT, and (D) Zn-G41D.

ATKAVCVLK GDGPVQGIIN FEQKESNGPV KVWGSIKGLT EGLHGFHVHE FGDNTAGCTS AGPHFNPLSR KHGGPKDEER HVGDLGNVTA DKDGVADVSI EDSVISLSGD HCIIGRTLVV HEKADDLGKG GNEESTKTGN AGSRLACGVI GIAQ

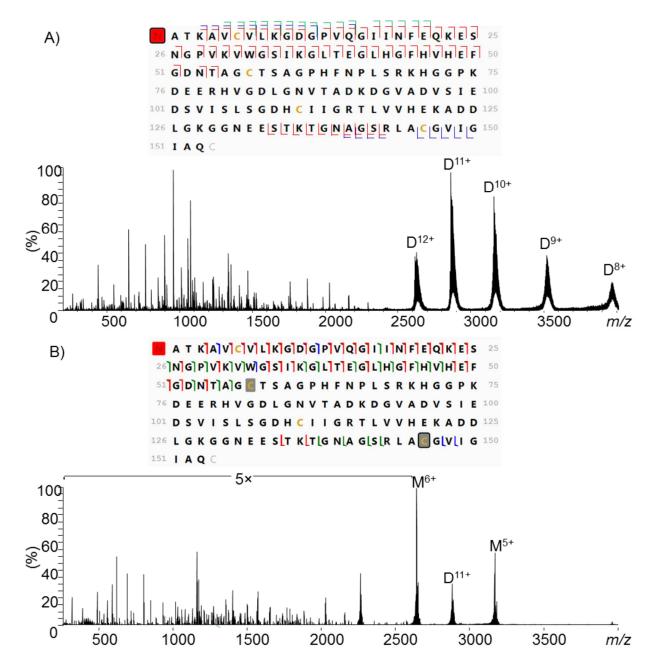
**Figure S-3.** Sequence of human SOD1. Copper-binding sites are indicated in orange, zinc-binding sites are in grey, and the disulfide bond is in green.



**Figure S-4.** The metal-binding states of SOD1s; (A) apo-WT, (B) Zn-WT, and (C) Cu,Zn-WT. M represents SOD1 monomer. ISD was applied to remove salt adducts and to dissociate dimers into monomers for a clearer view of the metal-binding states.



**Figure S-5**. Plot of backbone cleavage sites with respect to the charge states of fragment ions for different forms of WT-SOD1 dimer: (A) apo-WT, (B) Zn-WT, and (C) Cu/Zn-WT. The fragment ions from the N-terminal region are labelled in orange dots and the fragments from the C-terminal region are in cyan dots.



**Figure S-6.** (A) EID spectrum of apo-WT SOD1 dimer with the backbone cleavage map shown at the top. (B) UVPD spectrum of apo-WT SOD1 dimer with the backbone cleavage map shown at the top. The c/z-type ions are in red, b/y-type ions in blue, and a/x-type ions in green.