## **Supporting Online Material**



**Supplementary Figure 1a:** Overlay of NMR <sup>1</sup>H-<sup>15</sup>N correlation (HSQC) spectra of Ag(I)-<sup>15</sup>N-CusF (black) and Ag(I)-<sup>15</sup>N-CusF mixed 1:1 with unlabeled apo-CusB (red).



**Supplementary Figure 1b:** Overlay of NMR <sup>1</sup>H-<sup>15</sup>N correlation (HSQC) spectra of apo-<sup>15</sup>N-CusF (black) and apo-<sup>15</sup>N-CusF mixed 1:1 with unlabeled Ag(I)-CusB (red).



**Supplementary Figure 1c:** Overlay of NMR <sup>1</sup>H-<sup>15</sup>N correlation (HSQC) spectra of apo-<sup>15</sup>N-CusF (black) and apo-<sup>15</sup>N-CusF mixed 1:1 with unlabeled apo-CusB (red).



Supplementary Figure 1d: Overlay of NMR <sup>1</sup>H-<sup>15</sup>N correlation (HSQC) spectra of Ag(I)-<sup>2</sup>H/<sup>15</sup>N/<sup>13</sup>C-CusF (black) and Ag(I)-<sup>2</sup>H/<sup>15</sup>N/<sup>13</sup>C-CusF mixed 1:1 with unlabeled Ag(I)-CusB (red).



**Supplementary Figure 1e:** Overlay of NMR <sup>1</sup>H-<sup>15</sup>N correlation (HSQC) spectra of apo-<sup>2</sup>H/<sup>15</sup>N/<sup>13</sup>C-CusF mixed 1:1 with unlabeled Ag(I)-CusB (black) and Ag(I)-<sup>2</sup>H/<sup>15</sup>N/<sup>13</sup>C-CusF mixed 1:1 with unlabeled apo-CusB (red).



**Supplementary Figure 2:** Silver-stained SDS-PAGE gel of cross-linking experiment shows bands for CusF, CusB and CusF/CusB cross-linked (XL) product. The higher molecular weight band was not analyzed, but is likely to be CusB/CusB cross-linked product.



**Supplementary Figure 3**: Tandem MS spectrum of cross-linked product with precursor ion m/z 1135.55. The cross-link includes CusF<sub>31-50</sub> with cross-link at K31 and CusB<sub>27-55</sub> with cross-link at K29. Fragment ions are labeled in the spectrum and fragmentation is displayed within the peptide sequence.



**Supplementary Figure 4**: Plot of CusF residue number and corresponding  $T_1$  value for Ag(I)-<sup>15</sup>N-CusF (gray circles) and <sup>15</sup>N-CusF/CusB/Ag(I) (black squares).

## Supplementary Online Table 1: Resonance assignments determined from analysis of

HNCA spectra for Ag(I)-<sup>2</sup>H/<sup>15</sup>N/<sup>13</sup>C-CusF mixed 1:1 with unlabeled apo-CusB.

| <u>Residue</u> | <u>δ<sub>NH</sub></u> | $\underline{\delta}_{\underline{N}}$ | <u>δCα<sup>i</sup></u> |
|----------------|-----------------------|--------------------------------------|------------------------|
| 6E             | 8.49275               | 122.5018                             | 56.47457               |
| 7T             | 8.26277               | 115.4705                             | 61.74765               |
| 8M             | 8.4478                | 122.9705                             | 55.5168                |
| 9S             | 8.33686               | 116.8767                             | 58.36967               |
| 10E            | 8.41608               | 122.5018                             | 56.27221               |
| 11A            | 8.25474               | 124.3768                             | 52.46899               |
| 12Q            | 8.32442               | 120.6268                             | 53.44429               |
| 13P            |                       |                                      | 62.588                 |
| 14Q            | 8.42738               | 121.0955                             | 55.27034               |
| 15V            | 8.16498               | 124.3768                             | 62.07455               |
| 16I            | 8.96183               | 131.4081                             | 59.79852               |
| 17S            | 7.86479               | 120.6268                             | 56.7041                |
| 18A            | 8.5789                | 125.7831                             | 51.26845               |
| 19T            | 8.53867               | 110.7829                             | 59.5325                |
| 20G            | 8.6903                | 105.6266                             | 46.63033               |
| 21V            | 8.3804                | 119.2205                             | 59.81185               |
| 22V            | 8.84888               | 126.7206                             | 63.88682               |
| 23K            | 9.26281               | 128.5956                             | 54.39915               |
| 24G            | 7.63005               | 107.0329                             | 45.89091               |
| 25I            | 8.60224               | 122.5018                             | 61.59469               |
| 26D            | 8.39431               | 126.7206                             | 52.19548               |
| 27L            | 9.04383               | 123.9081                             | 57.01584               |
| 28E            | 8.48357               | 119.6893                             | 59.0323                |
| 29S            | 7.74482               | 112.6579                             | 58.25966               |
| 30K            | 7.72931               | 116.408                              | 56.86069               |
| 31K            | 8.019                 | 115.4705                             | 53.605                 |
| 32I            |                       | В                                    |                        |
| 33T            | 9.17771               | 126.7206                             | 62.55053               |
| 34I            | 9.34                  | 127.6581                             | 59.977                 |
| 35H            | 8.95728               | 128.1269                             | 54.76841               |
| 36H            |                       | В                                    |                        |
| 37D            | 8.328                 | 119.6893                             | 55.983                 |
| 38P            |                       | NA                                   |                        |
| 391            |                       |                                      | 59.73818               |
| 40A            | 8.92561               | 131.4081                             | 55.36799               |
| 41A            | 8.85796               | 117.8142                             | 55.26718               |
| 42V            | 6.28276               | 132.8144                             | 59.02288               |
| 43N            | 7.73773               | 118.283                              | 54.55283               |
| 44W            | 7.96928               | 115.0017                             | 51.96832               |
| 45P            | 0.05150               | 116 0565                             | FC (0000               |
| 46E            | 8.2/1/8               | 116.8767                             | 56.69308               |
| 4/M            | 0.0(077               | B                                    | (0.000                 |
| 481            | 8.20277               | 115.4705                             | 02.239                 |

| 49M | 8.80321 | 126.2518 | 53.69383 |
|-----|---------|----------|----------|
| 50R |         | В        |          |
| 51F |         | В        |          |
| 52T | 9.181   | 119.2205 | 63.565   |
| 53I | 8.454   | 127.1893 | 61.133   |
| 54T | 9.21194 | 119.6893 | 59.36871 |
| 55P |         |          | 64.31309 |
| 56Q | 7.86762 | 112.6579 | 55.86752 |
| 57T | 7.87334 | 119.6893 | 64.21452 |
| 58K | 8.29194 | 129.0644 | 55.50365 |
| 59M | 8.44682 | 123.9081 | 54.46067 |
| 60S | 7.55086 | 117.3455 | 57.50151 |
| 61E | 8.30971 | 120.158  | 57.44827 |
| 62I | 7.79808 | 122.9705 | 59.05087 |
| 63K | 9.00488 | 122.5018 | 54.12352 |
| 64T | 8.37837 | 115.9392 | 64.96511 |
| 65G | 9.06618 | 115.0017 | 43.80994 |
| 66D | 7.97819 | 121.0955 | 55.59249 |
| 67K | 8.6106  | 122.9705 | 55.75205 |
| 68V | 9.17466 | 115.0017 | 58.52899 |
| 69A | 8.85898 | 122.9705 | 51.08045 |
| 70F | 8.85177 | 119.6893 | 55.50198 |
| 71N | 8.16751 | 116.8767 | 51.75296 |
| 72F | 9.72575 | 121.0955 | 55.98593 |
| 73V | 8.7866  | 115.4705 | 59.41405 |
| 74Q |         | В        |          |
| 75Q |         | В        |          |
| 76G |         | NA       |          |
| 77N |         | NA       |          |
| 78L | 8.1728  | 121.5643 | 54.32381 |
| 79S | 8.48498 | 119.6893 | 57.59637 |
| 80L | 9.61768 | 125.7831 | 54.36187 |
| 81L | 9.3951  | 125.3143 | 55.97789 |
| 82Q | 9.94899 | 127.1893 | 56.79122 |
| 83D | 7.88993 | 115.0017 | 53.45918 |
| 84I | 7.9026  | 115.4705 | 60.52825 |
| 85K | 8.65974 | 124.3768 | 54.55943 |
| 86V | 8.5393  | 121.5643 | 63.07316 |
| 87S | 8.84282 | 122.9705 | 57.39588 |
| 88Q | 8.04068 | 128.1269 | 55.95192 |

## NA: Not assigned B: Broadened beyond detection