Supporting Information

**Figure S1.** Titration of 8.5µM Fe$^{II}$ cytochrome $c_{551}$ with 532 µM Cu$^{II}$ C112D/M121E azurin in 50 mM HEPES, pH 7.0. Generally 3-5 minutes were required after addition and mixing to achieve equilibrium across the pH range in which the titrations were conducted. Titrations were carried out in triplicate at each reported pH.
Figure S2. Plot of calculated $[\text{Fe}^{III}]$ (Eq. 2, main body of text) against volume of $\text{Cu}^{II}$ C112D/M121E azurin in 50 mM HEPES, pH 7.0. The data were fit to Eq. 1 (main body of text) to extract an equilibrium constant. This value was then inserted into the Nernst expression along with $E^{o}_{1/2}$ for cytochrome $c_{551}$ to calculate $E^{o}_{1/2}$ for C112D/M121E azurin. Three such fits were averaged to yield the reported reduction potentials.
Figure S3. X-band EPRs of C112D/M121E azurin. in aqueous 77K glass containing 50 mM buffer.
Figure S4. Active-site region showing the H35-P36 interaction in C112D/M121E azurin at pH 7.0 (2.4 Å, PDBID: 3OQR). 2F_o-F_c maps are contoured at the 1σ level. Nitrogen atoms are blue; oxygen atoms are red.
Table S1. Crystallographic data collection statistics for C112D/M121E azurin at pH 10.0.

<table>
<thead>
<tr>
<th>Space Group</th>
<th>C 2 2 2₁</th>
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<tbody>
<tr>
<td>A</td>
<td>48.422</td>
</tr>
<tr>
<td>B</td>
<td>55.348</td>
</tr>
<tr>
<td>C</td>
<td>95.140</td>
</tr>
<tr>
<td>α</td>
<td>90°</td>
</tr>
<tr>
<td>β</td>
<td>90°</td>
</tr>
<tr>
<td>γ</td>
<td>90°</td>
</tr>
<tr>
<td>Resolution</td>
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<td>Reflections</td>
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<tr>
<td>Completeness</td>
<td>(94.12%)</td>
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<tr>
<td>Multiplicity</td>
<td>2.7 (2.7)</td>
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<tr>
<td>I/sigma</td>
<td>8.2 (4.4)</td>
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<tr>
<td>Rwork</td>
<td>(33.3%)</td>
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<tr>
<td>Rfree</td>
<td>(38.5%)</td>
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<tr>
<td>e.s.u. (work)</td>
<td>1.118 Å</td>
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<tr>
<td>e.s.u. (free)</td>
<td>0.408 Å</td>
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<tr>
<td>B average</td>
<td>52.248 Å²</td>
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Table S2. Donor-atom distances to Cu²⁺ (Å) for C112D/M121E azurin at pH 10.0.

<p>| | |</p>
<table>
<thead>
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<th></th>
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<tbody>
<tr>
<td>O(G45)</td>
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<td>N(H46)</td>
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<td>O₁₂(E121)</td>
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