Highly stable electron-shuttling processes mediated by *in situ* deposited phenoxazin

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Phenoxazin as well as quinone are widespread electron mediators in nature. The electron shuttling process of quinone is well studied while phenoxazin is not. Here, a model phenoxazin (resazurin, RZ) was examined as an electron mediator in a bioelectrochemical system with *Shewanella oneidensis* MR-1. The presence of RZ substantially enhanced the current generation, which is similar with the well-known quinone mediators. However, the current in BES with RZ was almost unaffected, even after replacing the medium with a new solution without RZ. The results from scanning electron microscopy, fluorescence microscopy and UV-visible spectroscopy suggested that, resorufin (RR), as an intermediate product in RZ reduction, was *in situ* deposited on the electrode, and it could stabilize the electron shuttling efficiency. Electrochemical characterization further confirmed that oxidation from dihydroresorufin to RR on the electrode was the key step in the deposition process, which was suggested to be a dominant mechanism for stabilizing the electron-shuttling efficiency by phenoxazin. Since the solubilities of chemicals are commonly affected by changes in redox states in natural environments, this *in situ* deposition mechanism might contribute significantly to the widespread natural electron shuttling processes. This study reveales a novel electron shuttling mechanism of phenoxazin and provides a new insight into the interaction between microbe and solid electron acceptor from a molecular scale.

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