Bacterial Microcompartment Shell Biohybrids: Photophysics and Light-Driven Electron Transfer of Ruthenium Photosensitizers in Confinement

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Bacterial microcompartments (BMCs) are self-assembling, selectively permeable protein shells that encapsulate enzymes to enhance the catalytic efficiency of segments of metabolic pathways through means of confinement. The modular nature of BMC shells' structure and assembly enables programming of shell permeability and underscores their promise in biotechnology engineering efforts for applications in industry, medicine, and clean energy. Realizing this potential requires methods for encapsulation of abiotic molecules, which have been developed here for the first time. We report *in vitro* cargo loading of BMC shells with ruthenium photosensitizers (RuPS) by two approaches–one involving site-specific covalent labelling and the other driven by diffusion, requiring no specific interactions between cargo molecules and shell proteins. The shells retain the encapsulated RuPS cargo over one week without egress, denoting the impressive structural stability of these biohybrid constructs. The photophysical properties of the RuPS(II)* excited state are responsive to confinement within BMC shell's unique interior microenvironment, but overall activity as photosensitive electron donor is maintained. This study is an important foundation for further work that will converge biological BMC architecture with synthetic chemistry to facilitate biohybrid photocatalysis.

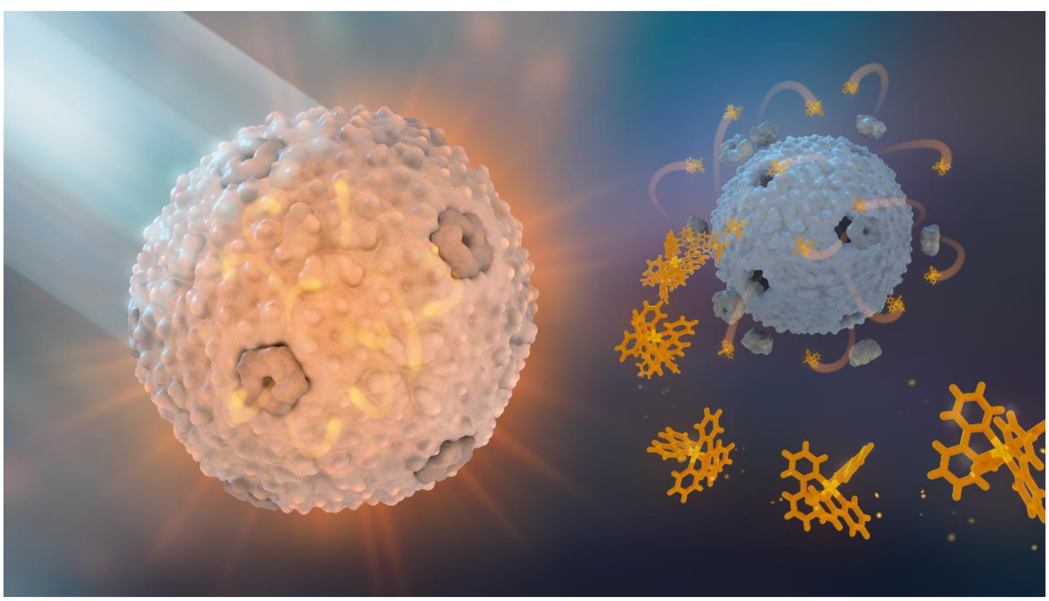

Figure. 1. Scheme for abiotic cargo loading of a BMC shell with ruthenium photosensitizers.