

Bioinspired Electro-Photoswitchable Grippers: Radical Control of Molecular Machinery

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Molecular grippers feature a binary conformational switch in response to external stimuli that results in reversible encapsulation of smaller molecules. This behavior makes them applicable as delivery systems, sensors, elements in nanorobotics, and memory devices.^[1,2] However, the control of molecular machinery by physical stimuli, such as voltage or light, is a prerequisite to their application.^[2] We therefore developed electro-photoswitchable molecular grippers based on resorcin[4]arene cavitand platforms equipped with quinone (Q) walls that were inspired by the role of semiquinones (SQ) in natural photosynthesis (Figure 1).^[2,3] The SQ state was generated electrochemically, via cyclic voltammetry, and photochemically, by using $[\text{Ru}(\text{bpy})_3]^{2+}$ as a photocatalyst. The properties were studied by UV-Vis spectroelectrochemistry, EPR, and transient absorption spectroscopy, in conjunction with DFT calculations.^[2,3] It was shown that these systems adopt an open conformation in the oxidized Q state until redox interconversion to the paramagnetic SQ radical anion provides the stabilization of the closed form through hydrogen bonding.^[3] Their tunable magnetic properties and enhanced binding affinities, along with remarkable reversibility and responsiveness to electrical and electromagnetic stimuli, set the stage for a new generation of artificial molecular machines and devices based on this switching concept in the future.

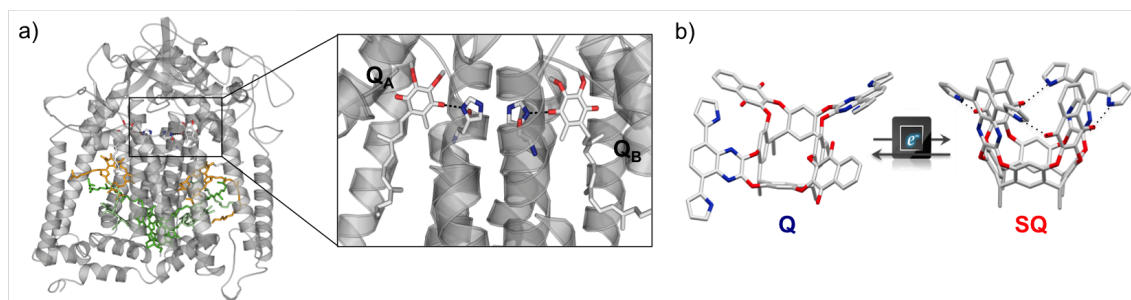


Figure 1. Schematic representation of the (a) photosynthetic reaction center of *Rb. sphaeroides* (PDB 1DV3) that inspired the design of (b) electro-photoswitchable molecular grippers.

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