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Title:Bioinspired high-potential porphyrin photoanodes
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Abstract:We report a selection of high-potential porphyrin photoanodes (HPPPs) for use in photoelectrochemical cells (PECs). The anodes consist of bispentafluorophenyl free-base and metallo-porphyrin sensitizers bearing anchoring groups for attachment to metal-oxide surfaces including TiO <inf>2</inf> and SnO<inf>2</inf> nanoparticles. The term "high potential" refers to the relatively large and positive value of the electrochemical reduction potential for the bispentafluorophenyl porphyrin radical cation (P^{˙+} + e⁻ &rarr P) as compared with more conventional nonfluorinated analogues. Photoelectrochemical measurements demonstrate the sensitizers used in these HPPPs extend the absorption of the bare anode well into the visible region. Terahertz spectroscopic studies show the photoexcited dyes are capable of injecting electrons into the conduction band of an underlying metal-oxide with appropriate energetics. The reduction potentials of the resulting photogenerated porphyrin radical cations are relatively high (ranging from ∼1.35 to 1.65 V vs NHE depending on the sensitizer). This is demonstrated by the ability of dye-sensitized solar cells, containing our HPPPs, to use the Br<inf>3</inf>⁻/Br⁻ redox couple as a regenerative electron mediator with superior performance in comparison to results obtained using the lower-potential I<inf>3</inf> ⁻/I⁻ relay. Computational modeling of the structures and equivalent circuits assists in a molecular-based understanding of these systems. Further, the oxidation power of the porphyrin radical cations generated in these bioinspired constructs is similar to that found in the reaction centers of their natural counterpart (photosystem II); thus, HPPPs are promising as components in artificial systems for photochemical water spitting

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