

Highly Efficient Porphyrin-Sensitized Solar Cells

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Recently, a great deal of attention has been devoted to dye-sensitized solar cells (DSSCs) made from mesoporous TiO₂ electrodes owing to the possibility of low-cost production and high power conversion efficiency (η). At present ruthenium polypyridyl complexes have demonstrated to be excellent TiO₂ sensitizers that have achieved the highest η value up to 11.5%. However, their practical application would be impeded substantially considering the limited resources and high cost of ruthenium metal. In this regard, organic dyes without metal or with inexpensive metal have been focused as fascinating sensitizers for DSSCs. To attain highly efficient solar energy conversion, such organic dyes should fulfill the following requirements: i) broad light absorption capability that allows us to collect solar light efficiently in visible and near infrared regions, ii) fast electron injection from the excited dyes to a conduction band (CB) of the TiO₂ electrode, iii) slow charge recombination between the injected electrons and resulting dye cations and/or I₃⁻ in the electrolyte. So far organic dyes composed of various π -conjugative molecules have been explored as potential sensitizers for DSSCs.

Porphyrins are one of the most widely studied sensitizers for DSSCs because of their strong Soret (400–450 nm) and moderate Q bands (550–600 nm). More importantly, the optical, electrochemical, and photophysical properties can be modulated by the peripheral substitutions and/or inner metal complexations. Nevertheless, until recently porphyrins as sensitizers typically disclosed poor cell performances compared with ruthenium polypyridyl complexes as a result of the insufficient light-harvesting ability at around 500 nm as well as >600 nm. Taking into account the fact that the integrated value of molar absorption coefficient of porphyrins as a function of wavenumber over the whole spectrum is much larger than the corresponding value of ruthenium polypyridyl complexes, broadening and red-shift of Soret and Q bands in porphyrins are highly promising to surmount the problem.

Recently we have developed aromatic ring-fused, unsymmetrically π -elongated porphyrins (i.e., naphthalene-fused and quinoxaline-fused porphyrins) that showed broadened, and red-shifted light absorption properties compared to the corresponding porphyrin references, resulting in the η values of 4.1% and 6.3%, respectively. As demonstrated for other sensitizers in DSSCs, introduction of both electron-donating and electron-withdrawing substituents to a core of π system would be appealing for the modulation of the light-

harvesting properties of sensitizers.

In this talk I will present our recent advance in porphyrin-sensitized solar cells.¹⁻⁷ For instance, we have prepared a novel push-pull porphyrin with an electron-donating triaryl amino group at the β, β' -edge through a fused-imidazole group and an electron-withdrawing carboxyquinoxalino anchoring group at the opposite β, β' -edge (ZnPQI) and evaluated the effects of the push-pull structure of ZnPQI on the optical, electrochemical, and photovoltaic properties. ZnPQI showed red-shifted Soret and Q bands relative to reference porphyrin with the only electron-withdrawing group (ZnPQ), demonstrating the improved light-harvesting property of ZnPQI. The optical HOMO-LUMO gap was consistent with that estimated by density functional theory calculations. The ZnPQI-sensitized solar cell exhibited a relatively high power conversion efficiency (η) of 6.8%, which is larger than that of the ZnPQ-sensitized solar cell (η = 6.3%) under the optimized conditions. The short circuit current and fill factor of the ZnPQI-sensitized solar cell are slightly larger than those of the ZnPQ-sensitized solar cell, whereas the open circuit potential of the ZnPQI-sensitized cell is slightly smaller than that of the ZnPQ-sensitized cell, leading to the overall improved cell performance of ZnPQI. Such fundamental information will give us new hints for the rational molecular design of highly efficient dye-sensitized solar cells based on push-pull porphyrins.

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