The structure-property relationships of D-π-A Bodipy dyes for dye-sensitized solar cells

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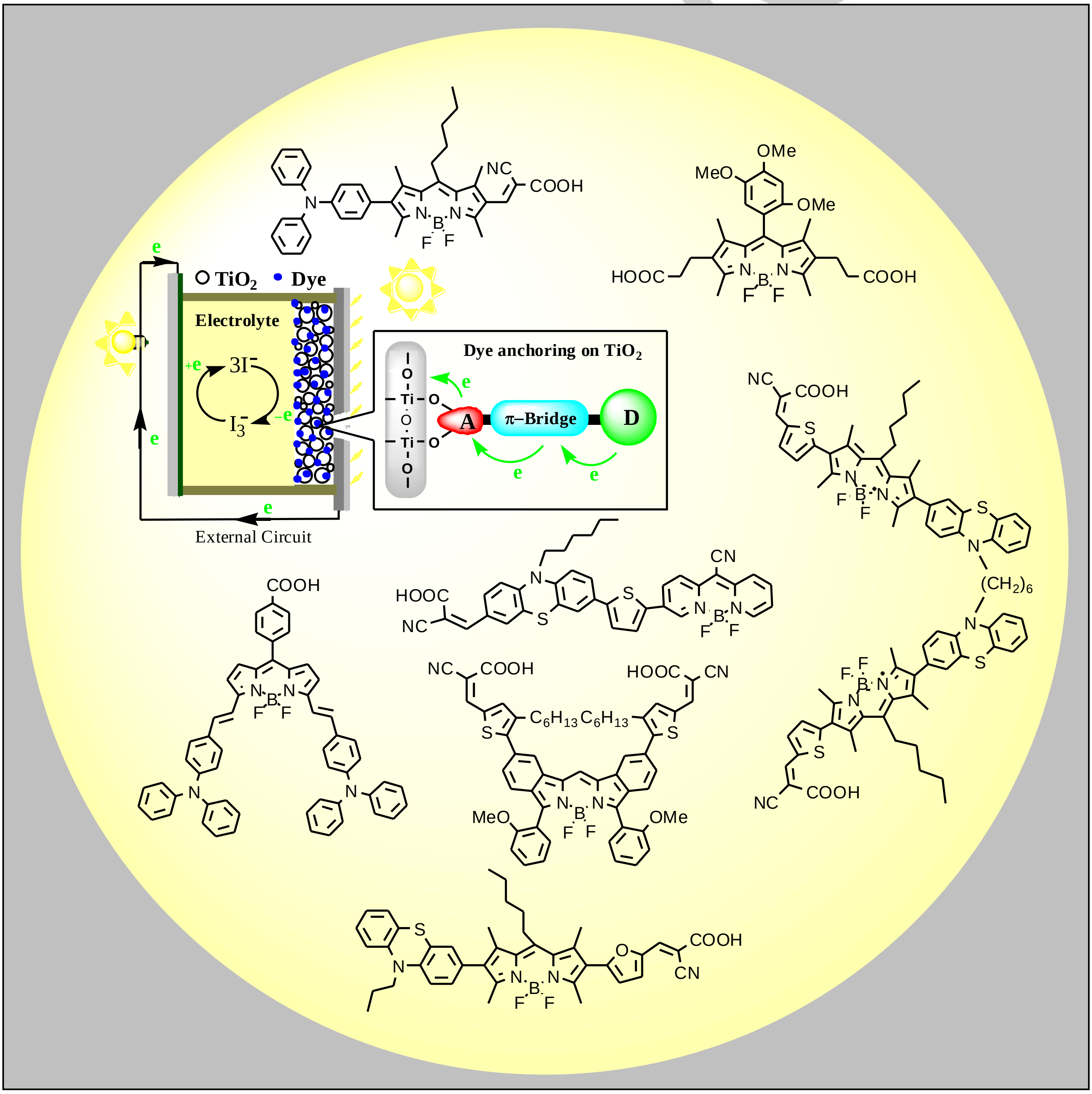
Dedication ((optional))



Abstract: Bodipy dyes have attracted considerable attention as potential photosensitizers in dye-sensitized solar cells (DSSCs) owing to their excellent optical properties and facile structural modification. This account focuses on recent advances in molecular design of D-π-A Bodipy dyes for applications in DSSCs. Special attention has been paid to the structure-property relationships of D-π-A Bodipy dyes for DSSCs. The developmental process in the modified position at Bodipy cores with donor/acceptor was described. The cell devices based on 2,6-modified Bodipy dyes exhibit better photovoltaic performance over the other modified dyes with donor/acceptor. Special consideration has been paid to the correlation between the molecular structure (various donor chromophores, extended units, molecular frameworks and long alkyl group) and physical properties to their performance in DSSCs. These results would give value information and guideline for designing new D-π-A Bodipy dyes for DSSCs.

1. Introduction

The generation of energy is one of the most important scientific and technological challenges in the 21st century. Among several new energy technologies, photovoltaic systems utilizing the sun are one of most promising sustainable energy sources, which have gained more and more attention as alternatives to fossil fuels and nuclear energy. The commercially available solar cells are currently based on inorganic silicon semiconductors, and their energy conversion efficiencies of ca. 15-25% are the highest among various solar cells.[1] However, the demand for high-purity silicon and skilled manufacturing techniques, resulting in a high cost, limits their widespread use in our lives.

Dye-sensitized solar cells (DSSCs) are being intensively investigated as low-cost alternatives to traditional silicon-based solar cells,[2] since Grätzel and co-workers reported high solar cell performances for DSSCs based on a ruthenium(II)-complex dye in 1991.[3] At present, state-of–the-art DSSCs based on the metal-ligand complexes as the active material have overall conversion efficiency (η) up to 13% under standard illumination.[4] However, the class of sensitizers are not so suitable for roof-top/commercial applications mainly because of their limited harvesting capability, expensive ruthenium metal and low durability and requiring careful synthesis and tricky purification steps. On the other hand, the metal-free organic donor-acceptor (D-A) dyes can be prepared rather inexpensively, with desired photophysical and electrochemical properties through suitable molecular design. Moreover, the conversion efficiencies based on metal-free organic dyes are now similar to those of Ru-sensitized solar cells.[5]

Conventional DSSCs basically contain four components: 1) a photoanode with a mesoporous semiconductor metal oxide film, 2) a sensitizer (dye), 3) an electrolyte, and 4) a cathode. In DSSCs, the incoming light is absorbed by the sensitizer, which is anchored to the surface of semiconducting TiO_2 nanocrystals. Charge separation takes place at the interface through photoinduced electron injection from the excited dye into the conduction band (CB) of the TiO_2. The resulting oxidative dye is further regenerated through reduction by the redox couple of the electrolyte, which itself is regenerated at the counterelectrode by electrons through an external circuit. The general operating principle of a DSSC is depicted in Fig. 1.

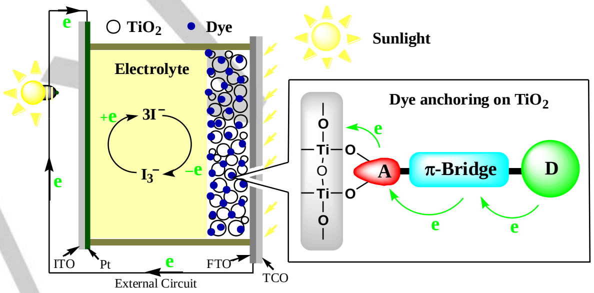


Fig. 1. Fundamental processes in a dye-sensitized solar cell, and the configuration of D-π-A organic dye on the TiO_2 surface.

Various types of organic dye sensitizers for DSSCs have been developed during the last decade, and there has been a gradual accumulation of information about the relationship between the chemical structures and photovoltaic performances of DSSCs. Some general principles to construct an efficient dye and efficient DSSC are as follows: 1) The absorption range of the dye should cover the whole visible and some of the near-infrared region, and its molar extinction coefficient must be as high as possible to enable efficient light harvesting with thinner TiO_2 layers (panchromatic absorption). 2) For efficient electron injection into the anode, the lowest unoccupied molecular orbital (LUMO) of the dye should be localized near the anchoring group (usually a carboxylic or phosphonic acid) and above the conduction band edge of the semiconductor electrode (typically TiO_2, −0.5V vs. NHE), and and the highest occupied molecular orbital (HOMO) of the dye should lie below the energy level of the redox potential of the redox couple in the electrolyte such as I_3^-/I^- redox potential (0.4V vs. NHE), to achieve efficient regeneration of the oxidized dye. 3) To minimize charge recombination between the injected electrons and the resulting oxidized dye, the positive charge resulting after electron injection should be localized on the donor part, which is further away from the TiO_2 surface. 4) The dye should not aggregate on the surface to avoid nonradiative decay of the excited state to the ground state.[6] 5) The periphery of the dye should be hydrophobic to minimize direct contact between the electrolyte and the anode to prevent water-induced desorption of the dye

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