

REGULAR ARTICLE

Incorporation of Thiadiazole Derivatives as π -Spacer to Construct Efficient Metal-free Organic Dye Sensitizers for Dye-sensitized Solar Cells: A Theoretical Study

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Abstract: Based on theoretical calculations, we studied four triphenylamine (TPA)-based dyes (namely D1-D4) incorporating electron-deficient thiadiazole derivatives as the π -spacer for the applications in dye-sensitized solar cells (DSSCs). The effects of the electron-deficient units on the spectra and electrochemical properties have been investigated by the combination of density functional tight-binding (DFTB), density functional theory (DFT), and time-dependent DFT (TDDFT) approaches. Compared with the model compound D0, which adopts a phenylene unit as the π -spacer, D1-D4 dyes display remarkably enhanced spectral responses in the red portion of the solar spectrum and possess desirable energetic properties once anchored on TiO₂ surface. The newly constructed dyes D2, D3, and D4 demonstrate desirable energetic and spectroscopic parameters, and may lead to efficient metal-free organic dye sensitizers for DSSCs.

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1 Introduction

Dye sensitized solar cells (DSSCs) are currently receiving significant attention as a low-cost and high-efficiency alternative to inorganic semiconductor-based photovoltaic devices for the conversion of sunlight into electricity [1-4]. The DSSCs are made of three parts: (i) a wide band gap semiconductor (usually TiO_2) deposited on a translucent conducting substrate; (ii) an anchored molecular sensitizer; and (iii) a redox electrolyte (usually I^-/I_3^-). Photosensitizers have been investigated to play a significant role for efficient DSSCs. Ruthenium photosensitizers have shown very impressive solar-to-electric power conversion efficiencies exceeding 11% under standard illumination [5, 6]. Taking account of the limited Ru resource and the environmental issues, metal-free organic dyes have attracted increasing interest as the substitute for the Ru complexes in recent years, owing to their crucial advantages including the flexibility in tailoring their molecular structures, high molar extinction coefficients, and low cost [7]. Recently, novel organic dyes based coumarin, perylene, triphenylamine (TPA), indoline, squaraine, and other organic units have been studied for applications in DSSCs [8-12]. Especially, TPA-based organic dyes, with TPA derivatives and the cyanoacetic acid moiety as electron donor and electron acceptor units, respectively, have displayed prominent light-to-electrical energy conversion efficiencies reaching 10% in DSSCs [12]. The TPA group with a sizable steric hindrance is expected to greatly confine the cationic charge from the TiO_2 surface and prevent unfavorable dye aggregation at the TiO_2 surface. The structural modifications of TPA-based organic dyes have been investigated intensively [7,13-16]. Most of the efficient organic sensitizers are made of the donor-(π -spacer)-acceptor (D- π -A) system. Using sensitizers with high molar extinction coefficients that extend throughout the visible and into the near-IR regions is desirable for efficient solar to energy conversion. Organic sensitizers with long π -conjugations had been demonstrated to augment the molar extinction coefficients and enhance panchromatic light harvesting, thus giving desirable DSSC efficiency and stability [12,15,17,18].

For organic sensitizers, one of the main drawbacks remains the sharp and narrow absorption bands in the visible region, which impairs the light-harvesting capabilities. One effective method to lower the highest occupied molecular orbital (HOMO)-the lowest unoccupied molecular orbital (LUMO) gap is by lifting the energy of HOMO while at the same time maintain the suitable LUMO energy level. For example, Wang group has reported that adding one electron-rich 3,4-ethylenedioxythiophene unit in organic dye C217 results in a evident 0.18 eV lift of the HOMO, compared to dye C206, thus narrowing the HOMO and LUMO gap and enhancing the extinction coefficients [12]. Another effective method to lower the HOMO-LUMO gap is by lowering the LUMO orbitals and meanwhile maintains the low