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A computational study on Ru complexes with bidentate carboxylate ligands: Insights into the photocurrents of dye-sensitized solar cells

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ABSTRACT

Factors associated with the short-circuit photocurrent densities (J_{sc}) of dye-sensitized solar cells (DSSCs) were investigated using density functional theory (DFT) and time-dependent DFT (TD-DFT). The goal was to explore the origin of the significant variations in the J_{sc} values of tricarboxyterpyridine-Ru(II) complex dyes containing bidentate carboxylate ligands (N^O). These variations in J_{sc} were observed despite the efficient driving force for dye regeneration (ΔG_2) that was estimated by the difference between the redox potential of the dye and the iodine/iodide electrolyte. The change in the orientation of the coordinated 2-pyridinecarboxylate ligand of FT27 (*cis*) weakened its light-harvesting ability at wavelengths longer than 470 nm relative to that of FT28 (*trans*). This change also reduced its ability to inject an electron into the TiO_2 conduction band, while it accelerated the recombination of the injected electrons in the TiO_2 with the oxidized FT27, leading to the lowest J_{sc} among the five tested complexes. The 4-imidazolecarboxylate ligand of FT36 promoted intermolecular interactions with I_2 and enhanced the recombination of the injected electrons in TiO_2 with the I_2 acceptor, leading to poor charge collection and the second-lowest J_{sc} among the five complexes. Conversely, FT12, which contains a 2-quinolinecarboxylate ligand, exhibited the highest J_{sc} due to its superior light-harvesting, injection, and collection abilities. The computational results strongly indicate that the value of ΔG_2 along with other factors such as the light-harvesting, and electron-injection/collection abilities of the dye sensitizer affect the photocurrents of DSSCs.

1. Introduction

Dye-sensitized solar cells (DSSCs) have drawn considerable attention as next-generation solar cells with various shapes, colors, and transparencies. In a DSSC, a wide-band-gap semiconductor (typically TiO_2) is sensitized by a dye, injecting an electron into the TiO_2 conduction band upon illumination (process 1, Fig. 1). The electron diffuses through the mesoporous semiconductor network to the anode and then passes thorough an external load to the cathode, where it reduces an electrolyte. In turn, the electrolyte returns the photo-oxidized dye to its original ground state (regeneration, process 2 in Fig. 1) [1].

The dye sensitizer, which is typically a metal complex or an organic compound, should possess the following characteristics as a crucial component of a DSSC [1,2]. (i) It should have a high molecular extinction coefficient along with an absorption spectrum that spans the entire visible region and ideally the part of the near-infrared (NIR) region. (ii) Anchoring groups such as carboxyl groups should be present to strongly bind the dye onto the TiO_2 surface. (iii) Its lowest unoccupied molecular orbital (LUMO) energy level should be higher than the conduction band edge of TiO_2 for an efficient electron-transfer process between the photo-excited dye and the conduction band of the TiO_2 for electron injection. (iv) Its redox potential, also known as the highest occupied molecular orbital (HOMO) energy level, should be more positive than the redox potential of the electrolyte such as the iodine/iodide redox couple for dye regeneration. (v) The structure should be optimized to avoid unfavorable dye aggregation on the TiO_2 surface. (vi) The dye sensitizer should be photo-, electro-chemically, and thermally stable.

Regarding characteristic (iv), we recently found that the HOMO energy level should be more positive (by approximately 0.3 V *vs.* a saturated calomel electrode (SCE)) than the redox potential of iodine/iodide when Ru(H_3tctpy)(C^N)NCS and Ru(H_3tctpy)(N^O)NCS (tctpy = 4,4',4"-tricarboxy-2,2':6',2"-terpyridine; C^N = cyclometalating ligand; N^O = pyridinecarboxylate and its derivatives) complexes are used as the dye sensitizer. In other words, the energy difference necessary for efficient dye regeneration (ΔG_2, Fig. 1) is 0.3 eV for the above series of Ru complexes [3].

Although the ΔG_2 values of all the tested Ru(H_3tctpy)(N^O)NCS complexes are greater than 0.3 eV, FT27 and FT36 (Scheme 1) exhibit smaller values of incident photon-to-current conversion

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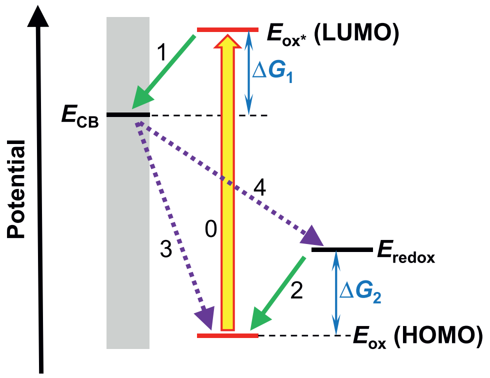


Fig. 1. Simple energy-level diagram for DSSC. Basic electron-transfer processes are indicated by numbers 1–4.

efficiency (IPCE) and short-circuit photocurrent density (J_{sc}) compared to the other complexes (Table 1). These values (IPCE and J_{sc}) are both affected by dye regeneration. The energy difference between the HOMOs of the sensitizer and the redox electrolyte is one of the factors that most significantly influence these values; however, other factors contributing to photocurrent should also be elucidated to improve DSSC performance *via* dye development.

In the present study, we systematically investigated the key parameters determining photocurrent using density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations, which are suitable for the study of large molecular systems such as Ru polypyridyl complexes. The structures of the five Ru(H_3tctpy)(N^O)NCS complexes examined in this study are shown in Scheme 1. FT27 (*cis*) and FT28 (*trans*) are stereoisomers (the relative disposition of the pyridyl group on the 2-pyridinecarboxylate ligand to the central pyridyl group on the tctpy ligand is different for each isomer) [4,5]. FT12 and FT34 are structural isomers possessing quinolinecarboxylate as their N^O ligands. In contrast, the N^O of FT36 consists of a five-membered heterocycle (imidazole). The results of this study are expected to provide guidance for the design of new Ru-complex sensitizers and advance the field of DSSCs.

2. Method

2.1. Theoretical background

The precise J_{sc} value produced by a solar cell in AM 1.5 solar light can be derived by integrating the IPCE spectra over the spectral distribution of the standard AM 1.5 solar photon flux (I_s) [1,6,7]:

$$J_{sc} = \int e\mathrm{IPCE}(\lambda)I_s(\lambda)\mathrm{d}\lambda \quad (1)$$

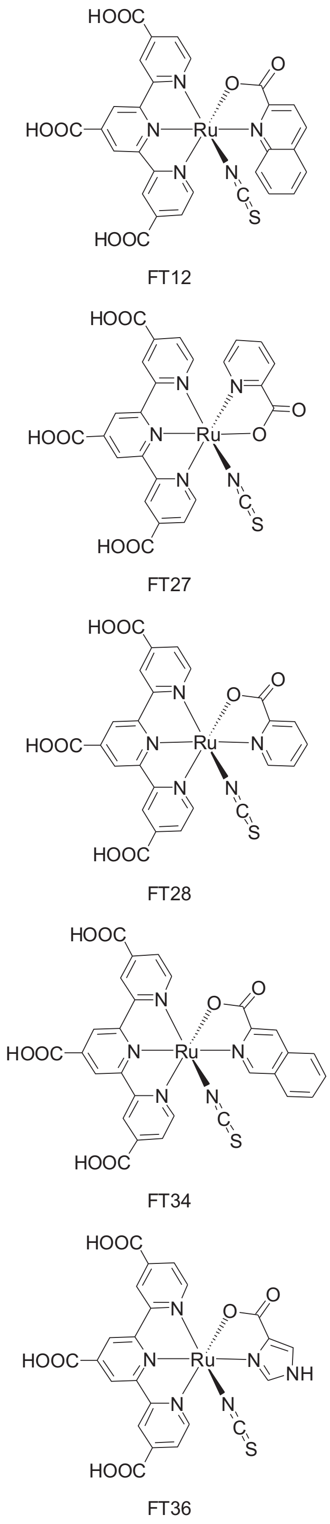
where e is the elementary charge. The IPCE can be obtained from the following equation [1,8]:

$$\mathrm{IPCE}(\lambda) = \mathrm{LHE}(\lambda) \times \Phi_{inj} \times \eta_{reg} \times \eta_{coll} \quad (2)$$

where LHE(λ) is the light-harvesting efficiency at a given wavelength λ, Φ_{inj} is the electron-injection efficiency, η_{reg} is the dye-regeneration efficiency, and η_{coll} denotes the charge-collection efficiency. Therefore, we focused on the effects of LHE, Φ_{inj}, η_{reg}, and η_{coll} on J_{sc}.

2.2. Computational details

The DFT calculations were performed using the Gaussian 09 program at the Research Center for Computational Science, Okazaki, Japan and the Gaussian 09W program on personal computers [9]. Optimizations of the ground state geometry were conducted at the hybrid DFT level using the mPW1PW91 functional, which combines the Perdew-Wang 1991 exchange functional as modified by Adamo and Barone (mPW1) with Perdew and Wang's 1991 gradient-corrected correlation functional (PW91) [10]. This combination improves the well-known deficiency in the long-range behavior of the DFT functional, which is especially important for



Scheme 1. Chemical structures of FT dyes.