

Invited paper

Interaction between disulfide/thiolate mediators and ruthenium complex in dye-sensitized solar cells



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ABSTRACT

The intermolecular interactions of thiolate anions and disulfide molecules as disulfide/thiolate (T_2/T^- , S_2/S^-) redox couples with a Ru bipyridyl complex (Z907) are investigated using density functional theory. **T** and **S** are 1-methyl-1*H*-tetrazole-5-thiolate and 2-methyl-5-trifluoromethyl-2*H*-1,2,4-triazole-3-thiolate, respectively. Similar to the typical reductant I^- , the S atoms of thiolate anions interact with the oxidized Z907 ($Z907^+$) via the terminal S atoms of the isothiocyanate (NCS) ligands. However, nearly 40% of the atomic charge and spin still remain after complexation. If a second thiolate anion, as well as I^- , is considered, the atomic charge and spin are transferred completely. The distances of the formed S—S bonds for the $Z907^+$ —two anions species correspond to isolated dithiolate radicals. These results suggest that $Z907^+$ can be completely regenerated by two thiolate anions via a two-step mechanism rather than by only one thiolate anion through a one-step mechanism as previously suggested. Unlike the I_2 molecule, the unbound $Z907$ –disulfide complex structure supports the slower recombination process with the disulfide/thiolate electrolyte compared with the I_3^-/I^- system in dye-sensitized solar cells.

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1. Introduction

Dye-sensitized solar cells (DSSC) consist of three fundamental components: a sensitized photoanode, a cathode, and an electrolyte solution. The photoanode is typically a metal complex or an organic dye-sensitized nanocrystalline TiO_2 film on a transparent conductive oxide (TCO) glass. The cathode is a platinized TCO glass, and the electrolyte solution contains a redox couple. When irradiated with light, the dye in the ground state absorbs a photon and reaches an excited state. The photoexcited dye then injects an electron into the TiO_2 conduction band. The injected electron diffuses through the TiO_2 layer into the TCO glass, passing the external load to the cathode, where it reduces the electrolyte. Finally, the reduced electrolyte returns the photo-oxidized dye to its original ground state (regeneration). In addition to these forward electron-transfer pathways, backward reactions occur simultaneously, e.g., recombination of injected electrons in the TiO_2 with acceptors in the electrolyte solution. This results in the degradation of performance of DSSC.

To date, I_3^-/I^- has been widely used as the redox couple in the electrolyte solution, reaching the highest confirmed solar energy conversion efficiency (η) of nearly 12% under the global AM 1.5 spectrum [1]. However, alternative redox couples have been

recently developed [2] in order to overcome some of the I_3^-/I^- system drawbacks, such as limited open-circuit photovoltage (V_{oc}), concomitant corrosion of the electrode metals, and an undesired dark color that absorbs some of the irradiating sunlight that decreases the photocurrent [3]. Notably, organic sulfur redox couples with noncorrosive and transparent nature have drawn attention as promising alternative mediators. In 2010, Wang and coworkers presented a new disulfide/thiolate redox couple (Fig. 1a and b) with a η value above 6% due to the intrinsic characteristics such as rapid dye regeneration, very slow charge-recombination, and fast mass transport [4]. Following this landmark paper, a number of thiolate-based electrolytes have been studied aiming to improve the V_{oc} because of the ease of modification of the molecules and the related redox potentials [5–8]. Simultaneously, various cathode materials have been examined [5–16] because the typical Pt cathode shows poor electrocatalytic activity with the disulfide/thiolate electrolyte, which lowers the fill factor (ff) of DSSC [4,17].

The regeneration reaction of the disulfide/thiolate redox couple by the cathode has also been studied [9,17], but the regeneration mechanism of the oxidized dye through the disulfide/thiolate mediator has yet to be elucidated. Although the interactions of the oxidized dye with the iodide species, which are closely associated with the regeneration mechanism, have been experimentally [18,19] and theoretically [20,21] investigated, the intermolecular interactions between the oxidized dye and the thiolate species

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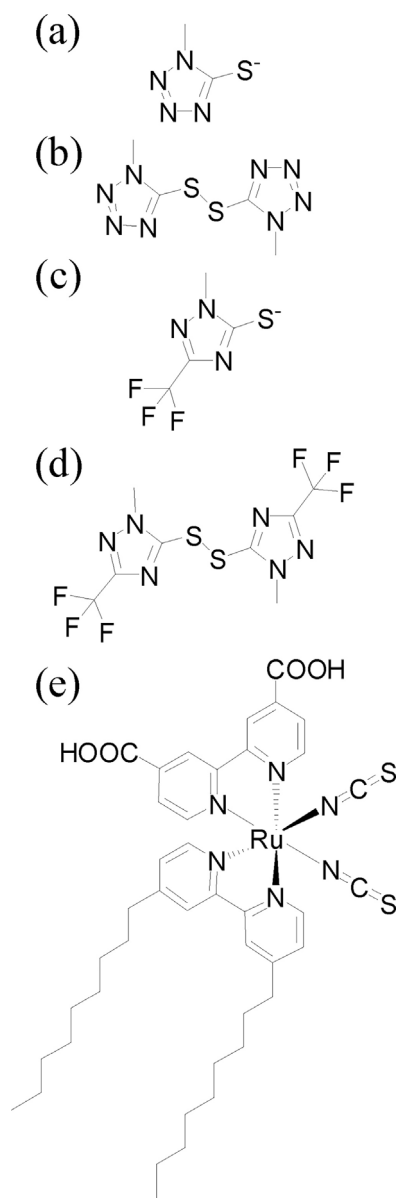


Fig. 1. Chemical structures of (a) T^- , (b) T_2 , (c) S^- , (d) S_2 , and (e) Z907.

remain unknown. The lack of studies is very surprising because the regeneration of oxidized dye is a key function of DSSCs [22]. Additionally, Wang et al. believe that the properties of the disulfide/thiolate redox couple, such as the molecular structure and size, may influence the interfacial charge-recombination [23], but evidence to support that belief is still missing. To enhance the DSSCs' performance using disulfide/thiolate electrolytes, both the dye regeneration and recombination mechanisms must be investigated.

Here, we focus on the intermolecular interactions of the disulfide/thiolate redox mediators bis(1-methyl-1H-tetrazol-5-yl)-disulfide/1-methyl-1H-tetrazole-5-thiolate (T_2/T^- , Fig. 1a and b) [4,6] and 3,3'-dithiobis(2-methyl-5-trifluoromethyl-2H-1,2,4-triazole)/2-methyl-5-trifluoromethyl-2H-1,2,4-triazole-3-thiolate (S_2/S^- , Fig. 1c and d) [6] with the sensitizer Ru(4,4'-dicarboxy-2,2'-bipyridine)(4,4'-dinonyl-2,2'-bipyridine)(NCS)₂ (Z907, Fig. 1e) [4,11] using quantum chemical calculations at the density functional theory (DFT) level. The regeneration and the

recombination mechanism for the Ru dye by disulfide/thiolate mediator are discussed based on the DFT results compared with that of the typical I_3^-/I^- redox system (Fig. S1). The findings in this study have implications in the design of dye/electrolyte structures and should improve DSSCs' performance by promoting regeneration and suppressing recombination.

2. Computational details

DFT calculations were performed using Gaussian 16 software at the Research Center for Computational Science, Okazaki, Japan, and Gaussian 16W in personal computers [24]. 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 the Perdew and Wang's 1991 gradient-corrected correlation functional (PW91) [25]. This combination improves the well-known deficiency in the long-range behavior of the DFT functional, which is especially important for investigations on noncovalent intermolecular interactions [25–27]. The DGDZVP basis set [28,29] was used for all systems; it provides appropriate results for the intermolecular halogen bond structures [30]. Frequency calculations were performed to confirm the optimized structures with no imaginary frequencies, corresponding to real minima on the entire potential energy surface. The solvent effects of acetonitrile (dielectric constant = 35.688), which has been experimentally used as a solvent for DSSCs' electrolyte solutions [4,6,11], were modeled using a conductor-like polarizable continuum model (C-PCM) [31] within the self-consistent reaction field theory.

To calculate the atomic charges and the spin densities, Hirshfeld population analysis [32], Mulliken population analysis [33], and natural population analysis (NPA) [34,35] were conducted on the optimized geometries at the same level.

3. Results and discussion

3.1. Structures of thiolate and disulfide species

Fig. 2 depicts the optimized geometries of the thiolate and disulfide species. For disulfide T_2 (Fig. 1b), two formally identical thiotetrazole moieties interconnected via a disulfide bridge are rotated relative to each other around the S–S line, where the torsion angle of C1–S1–S2–C3 is 86.8°. The H2···N8 distance, 2.539 Å, is smaller than the net van der Waals radii of the binding atoms (2.75 Å) [36], indicating intramolecular hydrogen bonding. The distances for the S1–S2 bond (2.076 Å) and the angles for the C1–S1–S2 and C3–S2–S1 bonds (102.0°) are in good agreement with previous X-ray results [37]. For S_2 (Fig. 1d), the S1–S2 bond distance (2.097 Å), the C1–S1–S2 and C5–S2–S1 bond angles (101.7°), and the C1–S1–S2–C5 torsion angle (86.5°) closely resemble T_2 , but the intramolecular hydrogen bond is not observed due to the C8 trifluoromethyl group. This could account for the smaller bond energy, over 1 kcal mol⁻¹, for S_2 than for T_2 . Compared with that of the disulfide molecules, the S1–S2 bond distances for the dithiolate radicals ($T_2^{\cdot-}$ and $S_2^{\cdot-}$) are over 0.7 Å longer. The H2···N8 distance of the intramolecular hydrogen bond for $T_2^{\cdot-}$ is also larger than that of T_2 . The torsion angles of C1–S1–S2–C3 for $T_2^{\cdot-}$ and C1–S1–S2–C5 for $S_2^{\cdot-}$ are around 104°, which is broader than those of T_2 and S_2 .

According to the literature [4,38], a T_3^- charge transfer complex seems to exist in the disulfide/thiolate redox electrolyte solution because T^- and T_2 are colorless, but their mixture is pale yellow; however, the structure of this complex remains unknown. We also optimized the geometries of T_3^- and S_3^- species in the singlet electronic spin state. Three thiolates connect to one another via the

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