Comparative study on the interactions of sulfide and iodine mediators with a dye in p-type dye-sensitized solar cells

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ABSTRACT

The intermolecular interactions of a typical triphenylamine-based push-pull dye (P1) with three sulfide species T_3^-, T_2, and $T_2^- \cdot$ and with the iodine species I_3^-, I_2, and $I_2^- \cdot$ were investigated by means of density functional theory. The reduced form of P1 interacts with both T_3^- (I_3^-) and $T_2^- \cdot$ ($I_2^- \cdot$) through reductive cleavage of the S−S (I−I) bond, whereas T_2 (I_2) interactions involving single-electron transfer occur without S−S (I−I) bond breakage. Therefore, regeneration with a thiolate–disulfide redox couple (as well as with iodide–triiodide) proceeds by three different mechanisms: by interaction with T_3^- (I_3^-) via the transient intermediate complex $T_2^- \cdot \cdots P1 \cdots T^-$ ($I_2^- \cdot \cdots P1 \cdots I^-$) to give $T_2^- \cdot$ ($I_2^- \cdot$) and T^- (I^-); by interaction with T_2 (I_2) via $P1 \cdots T_2^-$ ($P1 \cdots I_2^-$) to give $T_2^- \cdot$ ($I_2^- \cdot$); or by interaction with $T_2^- \cdot$ ($I_2^- \cdot$) via $T^- \cdots P1 \cdots T^-$ ($I^- \cdots P1 \cdots I^-$) to give two T^- (I^-) moieties. The P1–$T_2^- \cdot$ complexes have far fewer configurations, and the $T_2^- \cdot$ species are much farther away from the semiconductor surface than are the $I_2^- \cdot$ species in P1–$I_2^- \cdot$. This suggests that recombination of injected holes with electron donors in the thiolate–disulfide electrolyte is suppressed relative to that in iodide–triiodide, leading to a greater than expected increase in the open-circuit photovoltage for a p-type dye-sensitized solar cell.

1. Introduction

Dye-sensitized solar cells (DSSCs) based on the concept of photosensitization of wide-band-gap oxide semiconductors have attracted a great deal of attention over the last three decades because of their potential to realize solar cells of the next-generation that have various colors, shapes, and transparencies. Most of the research and development effort has been devoted to n-type DSSCs based on TiO$_2$ semiconductors, which have a confirmed cell efficiency (η) of only 12% under global AM 1.5 spectrum illumination [1]. To reach an η similar to that of conventional crystalline silicon cells (about 20%), we require a p-type DSSC. A tandem device pairing a TiO$_2$-based photoanode with a photocathode such as a NiO or Cu(I)-based delafossite (pn-type DSSC) [2] could, theoretically, have an η value in excess of 40% [3]. Because p-type DSSCs have not been well studied, such devices are difficult to realize at present.

A basic p-type DSSC consists of three fundamental components: a sensitized photocathode, an anode (counter electrode), and an electrolyte solution. The photocathode is typically that molecules of an organic dye or a metal complex sensitizer are adsorbed on a nanostructured semiconductor film with transparent conductive oxide (TCO) glass. The anode is a platinized TCO glass, and the electrolyte solution contains an iodide–triiodide redox couple. Photoexcitation of the dye

sensitizer leads to the formation of its excited state, which decays by hole injection into the valence band of the p-type semiconductor to form a charge-separated state. A redox shuttle then reacts with the photoreduced sensitizer, regenerating it and transporting an electron to the anode, where it is delivered to the external electric circuit [2,3]. Simultaneously with these forward pathways, backward reactions occur, such as recombination of the injected hole in the semiconductor with an electron donor in the electrolyte; these result in a decrease in the performance of the DSSC [2].

Iodide–triiodide has been generally used as the redox shuttle in the electrolyte solutions of both n- and p-type DSSCs. However, alternative redox couples have recently been developed [4] to overcome some of the drawbacks of the iodide–triiodide system, such as its limited open-circuit photovoltage (V_{oc}), concomitant corrosion of the electrode metals, and an undesired dark color that results in absorption of some of the incident sunlight, decreasing the photocurrent [5]. Consequently, organic sulfur redox couples, which have a noncorrosive and transparent nature, have attracted attention as promising alternative mediators. In 2010, Wang et al. presented a new thiolate–disulfide redox couple (Fig. 1a and b) with an η value of more than 6% in an n-type DSSC due to its intrinsic characteristics such as rapid regeneration, slow recombination, and rapid mass transport [6]. In p-type DSSCs, a combination of the thiolate–disulfide electrolyte with the benchmark dye 4-
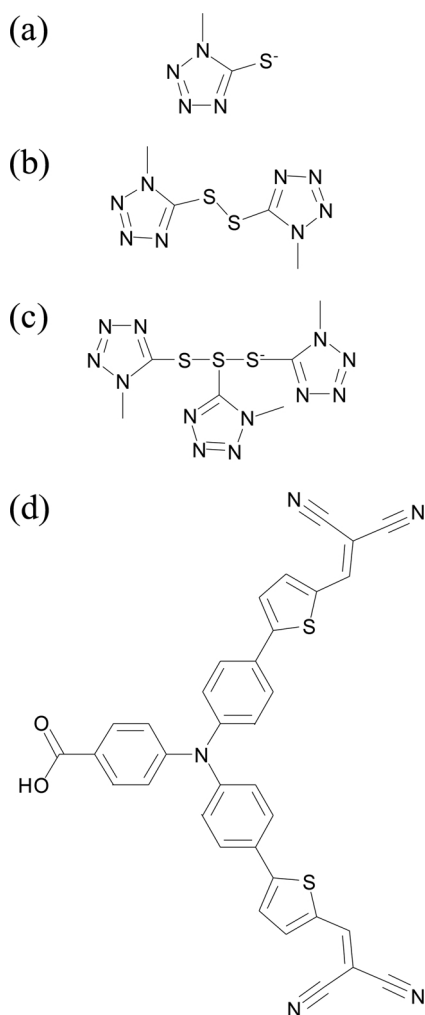
(a)

(b)

(c)

(d)

Fig. 1. Chemical structures of (a) T^-, (b) T_2, (c) T_3^-, and (d) P1.

(bis-{4-[5-(2,2-dicyano-vinyl)-thiophen-2-yl]-phenyl}-amino)-benzoic acid (P1; Fig. 1d) and a delafossite $CuCrO_2$ photocathode has been shown to have an η that is more than three times that attainable by using iodide–triiodide [7].

The mechanisms of regeneration and of recombination of the thiolate–disulfide mediator in n-type DSSCs have been elucidated by examining the intermolecular interactions between thiolate anions and an oxidized Ru complex sensitizer [8]; however, the mechanisms of intermolecular interactions of sulfide species with the reduced dye and of the subsequent dye-regeneration process through the thiolate–disulfide redox couple in p-type DSSCs remain unknown. This is surprising, because the regeneration of the dye sensitizer is a central function in DSSCs [9]. In the case of p-type DSSCs, regeneration mechanisms mediated by iodide–triiodide have been proposed [10,11], but the recombination reaction facilitated by the sensitizer through interaction between the dye and the iodine species or the sulfide species [12] has yet to be investigated. Consequently, to achieve a better understanding and to enhance the performance of p-type DSSCs in terms of both the dye and electrolyte, it is necessary to clarify the mechanism of regeneration by a redox mediator other than iodide–triiodide and the mechanisms of recombination induced by various redox mediators.

Here, we focus on the intermolecular interactions of a thiolate–disulfide redox couple consisting of 1-methyl-*1H*-tetrazole-5-thiolate (T^-; Fig. 1a) and bis(1-methyl-*1H*-tetrazol-5-yl)-disulfide (T_2; Fig. 1b) [6,7,13], as well as those of the iodide–triiodide redox couple, with the typical push–pull dye P1, in which one electron-donor (D) triphenyla-mine (TPA) group and two electron-acceptor (A)

methylenemalononitrile groups are covalently linked through π-conjugated thiophene bridges (π) [2,14]. We use quantum-chemical calculations at the density functional theory (DFT) level to elucidate the mechanisms of regeneration and recombination for the p-type organic dye with the thiolate–disulfide mediator and with the iodide–triiodide mediator. Our findings have implications in the design of dye–electrolyte structures and they should permit an improvement in the performance of p-type DSSCs by promoting regeneration and suppressing recombination.

2. Computational details

The DFT calculations were performed by using Gaussian 16 software at the Research Center for Computational Science, Okazaki, Japan, and by Gaussian 16 W on personal computers [15]. The ground-state geometry was optimized at the hybrid DFT level by 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) [16]. This combination ameliorates the well-known deficiency in the long-range behavior of the DFT functional, which is especially important for investigations of noncovalent intermolecular interactions such as hydrogen bonds or halogen bonds [16–18]. The DGDZVP basis set [19,20], which provides appropriate results for intermolecular halogen-bond structures involving iodine atom [21], was adopted in all systems. Frequency calculations were performed to confirm the optimized structures with no imaginary frequencies, corresponding to the real minima on the entire potential energy surface. The solvent effects of acetonitrile (dielectric constant = 35.688) were modeled by using a conductor-like polarizable continuum model (C-PCM) [22] within the self-consistent reaction field theory.

To calculate the atomic charges and the spin densities, Mulliken population analysis [23] and natural population analysis (NPA) [24] were conducted on the optimized geometries at the same level. Mulliken analysis divides overlap populations equally between the two atoms of a bond, and therefore has the advantage of simplicity; however, its results tend to vary with the basis set employed, and it yields unnatural values in some cases. The NPA method is based on the construction of orthonormal natural atomic orbitals and is noted for the much lower sensitivity of atomic charge to basis set [25].

3. Results

3.1. Structures of reduced dye isomers

On the basis of a previous report [14], we considered four conformational isomers (conformers) of dye P1 differing in the directions of the S atoms in the two thiophene rings: **1**, **2**, **3**, and **4**. After the injection of a hole, P1 becomes $P1^-$ with a single negative charge in the ground doublet electronic spin state. Fig. S1 depicts the optimized geometries of the $P1^-$ species 1^-, 2^-, 3^-, and 4^-. The dihedral angles of about 18° between the D moiety and the thiophene rings, such as C22–C30–C36–S39 for **1** and **3** (in agreement with previous computational results [26]), narrow to around 4° on becoming $P1^-$ species.

Fig. S2 shows the spin densities corresponding to the optimized geometries in Fig. S1. Irrespective of the conformation, the unpaired electron is delocalized over the entire molecule apart from the terminal carboxyl group. This suggests that regeneration by an electrolyte oxidant can occur at any point within the $P1^-$ molecule other than the anchor portion that interacts with the semiconductor surface.

3.2. Structures of interactions with T_3^- and I_3^-

According to the literature [6,13,27], the T_3^- electron acceptor (Figs. 1 and S3), formed by charge-transfer complexation between T^- and T_2, is present in the thiolate–disulfide electrolyte solution. The