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A Quantum-Chemistry Study of Novel Copper- and Cobalt-Complex Based Redox Mediators for Dye-Sensitized Solar Cells

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Abstract—Novel redox mediators are necessary in order to increase the efficiency and lifetime of dye-sensitized solar cells. In this work, complex copper and cobalt ions with phenanthroline and bipyridine ligands are studied in the quantum chemical aspect. New complexes with cyano bipyridine derivatives are studied. The redox potentials of the complexes and inner sphere reorganization energies are calculated.

Keywords: dye sensitized solar cells,, photoelectrochemical solar cells, redox mediators, copper metal complexes, cobalt metal complexes, quantum chemistry, density functional method.

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INTRODUCTION

One promising method for creating cheap and efficient solar cells is the development of photoelectrochemical solar cells (PSCs). These are also called dye sensitized cells or Grátzel cells. The number of scientific publications in the PSC field is growing exponentially; in recent years, according to the WEB of Science, it exceeds 1000 works per year. The first efficient PSCs were demonstrated more than 20 years ago by B. O'Regan and M. Grátzel [1]. At present, the efficiency of the best PSC samples is reported to exceed 12% [2]; the efficiency of certified samples reaches 11% [3].

The main PSC components (Fig. 1) are a wide-bandgap nanocrystalline highly porous semiconductor on whose surface a thin (nominally monomolecular) layer of a photosensitizer is deposited and an electrolyte that fills the semiconductor pores and contains a redox pair (the redox mediator). The light is absorbed mainly by the photosensitizer (usually, an organic dye) that injects a photoexcited electron into the nanocrystalline semiconductor (usually, titanium dioxide). Electrons injected into the conduction band of the semiconductor (E_c) diffuse on the percolating nanoparticles of the semiconductor and reach the anode. At the same time, a hole on the photosensitizer, to which

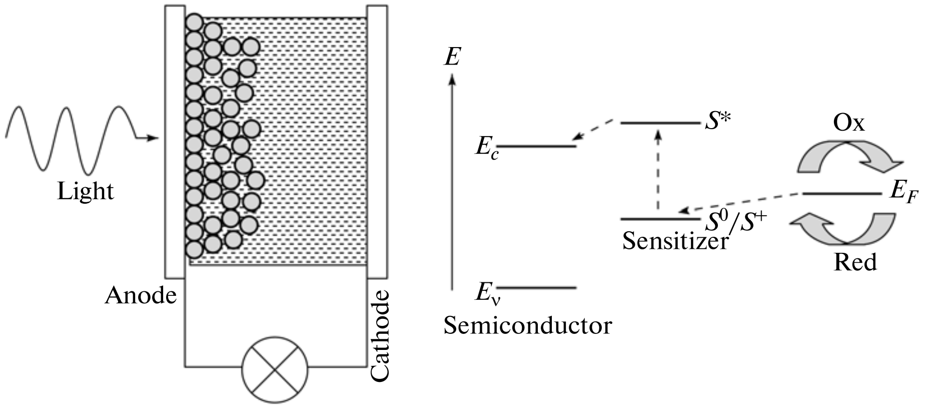


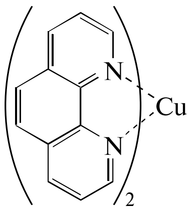
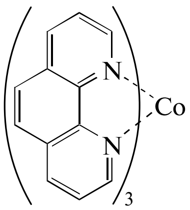
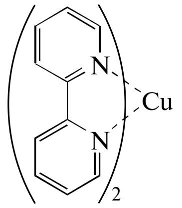
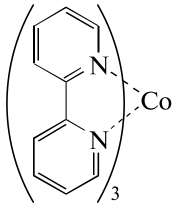
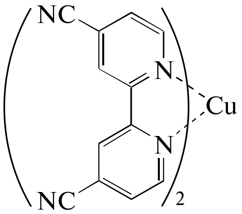
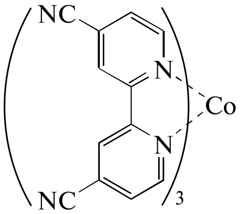
Fig. 1. The scheme and the energy diagram of PSC. Wide bandgap semiconductor nanoparticles covered with a photosensitizer (circles) are deposited on the anode; the PSC is filled with an electrolyte (hatching). E_c and E_v are the energies of the conduction band and of the valence band of the semiconductor, respectively; S^0, S^*, and S' are the ground, photoexcited, and oxidized states of the photosensitizer; and E_F is the Fermi level of the redox mediator. The dashed arrows show electron transitions. The undulated arrows illustrate the diffusion of the Ox (Red) form of the mediator to the cathode (to the nanoparticles).

the S^+ state corresponds, is injected onto the redox mediator, i.e., an oxidized form of the mediator (Ox) is created. The form diffuses to the cathode and is reduced there (Red). Until very recently, the iodide redox mediator (including the iodide/triiodide (I^-/I_3^-) redox pair) served as a standard mediator and led to the highest PSC efficiency [4]. However, the iodide redox mediator has some disadvantages, among which are its fixed Fermi level position and high corrosiveness. Indeed, the PSC efficiency significantly depends on the Fermi level position of the redox mediator (E_F). One the one hand, the difference between the energy level of the S^+ state of the photosensitizer ($E(S^+)$) and E_F must ensure an efficient injection of a hole to the redox mediator. On the other hand, the lower the energy, E_F, is, the higher the maximum possible PSC voltage is, which is determined by the difference $E_c - E_F$ (Fig. 1). Therefore, there is a need for redox mediators whose Fermi level can be varied to reach the minimally necessary difference $E_F - E(S^+)$ for a given type of a photosensitizer.

Complex metal ion based redox mediators for PSCs are under intensive development [5]. They permit one to tune the redox potential of the mediator by varying the ligand type and by modifying their chemical structure. An increase in the solvability of complex ions is also possible because their high solvability is important for the successful operation of PSCs [4]. The most advantageous metal complex redox mediators for PSCs were obtained on Co^{2+}/Co^{3+} ions [6]. We note that a record-breaking efficiency was obtained on PSC samples using a cobalt ion based mediator [2]. Copper ion based redox mediators are also considered as promising ones [5]; they are known as efficient centers for electron transfer in various chemical and biological reactions [7]. The first redox mediators for copper complex based PSCs were studied in 2005 [8]. Recently, 7% efficiency was reached in a PSC using a Cu^{1+}/Cu^{2+} based redox mediator [9]. Thus, copper- and cobalt-based metal complex redox mediators are a promising alternative to the traditional iodine-based redox mediator.

In this work, a quantum chemical study of copper and cobalt metal complex ions with bipyridine and phenanthroline based ligands was performed. Recent studies demonstrate that metal complexes with ligands of this type are promising for PSCs [5]. Metal complexes with ligands that are modified by cyano groups are studied for the first time in this work. Such a modification permits one to lower E_F (Fig. 1), which is necessary to increase the working PSC voltage. The structural formulas of the studied complexes are presented in Table 1.

Table 1. The structural formulas of the studied copper and cobalt complexes

Ligand	Copper	Cobalt
Phenan-throline		
Bipyridine		
Dicyano bipyridine		

1. INVESTIGATION TECHNIQUE

The geometries of ions were optimized by the density functional method using the generalized gradient-corrected functional of the PBE type [10]. The calculations involved a three-exponential basis set containing polarization functions (TZ2P). The electrons of the inner atomic shells were modeled by the ECP-SBKJC effective core potentials [11–13]. The calculations were carried out using the Priroda program [14].

2. RESULTS AND DISCUSSION

Electron-transfer processes in which a redox pair in a PSC takes part are commonly considered in the context of the Born–Oppenheimer approximation, i.e., electron transitions are supposed to proceed under a constant geometry of complex ions. Therefore, the processes of electron transfer ($\longrightarrow$) and of corresponding relaxation $\Rightarrow$) can be denoted by the following schemes:

$$\text{Red} - \text{e} \longrightarrow \text{Ox}^* \Rightarrow \text{Ox},$$

$$\text{Ox} + \text{e} \longrightarrow \text{Red}^* \Rightarrow \text{Red},$$

where Red/Ox is the state of the reduced (oxidized) form of a complex ion and Ox* and Red* are the states of the complex ion under the geometry of the Red and Ox states, respectively. Figure 2 illustrates that these four characteristic states appear in processes of redox pair operation in a PSC.

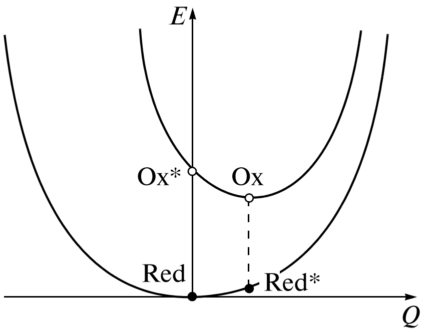


Fig. 2. A Schematic image of the energy surfaces of the studied complexes as functions of the geometry (the Q coordinate) in the Red and Ox states.

The complexes of copper were calculated for the one- and two-charge states of copper ions ($Cu^{1+/2+}$) and complexes of cobalt were calculated for two- and three-charge states of cobalt ions ($Co^{2+/3+}$). The results of the calculations are summarized in Table 2, which presents energies of the Red and Ox states of metal complex ions, as well as the energies of the states that form in the process of electron transfer under a constant geometry of the Red* and Ox* complex. The difference of energies E(Ox) – E(Red) corresponds to the redox potential that determines the Fermi level position of the redox pair with respect to the vacuum level with a zero energy. As follows from Table 2, E(Ox) – E(Red) varies in the range from 9 to 12 eV for all the studied complexes.

One can see that the redox potentials for all the studied copper complexes are smaller than those for cobalt complexes. At the same time, variation of redox potentials is insignificant when phenanthroline ligands are replaced by nonsubstituted bipyridine ones; this is less than 0.2 eV for both cobalt and copper complexes. This corresponds to the experimental data for cobalt complexes, for which the obtained difference between the redox potentials was less than 0.1 eV [1]. Note a significant increase in the redox potential when passing to cyano substituted ligands; for example, for copper and cobalt complexes, this difference is about 1 eV.

The efficient operation of a PSC from a redox mediator requires an efficient injection of a hole onto a photoexcited dye and as low as possible efficient inverse transfer of an electron from the dye or from the wide bandgap semiconductor to the redox mediator (recombination). The efficiency of these processes is determined by many parameters, among which the difference between the Gibbs energies of the initial and final states and the reorganization energy are of significant importance. The aforementioned processes of electron transfer are usually analyzed in the context of the Marcus model. The injection of a hole to the dye is supposed to occur in the "normal" region of the Marcus model; as for the recombination, it can occur both in the "normal" and in the "inverted" region [16]. Here, the reorganization energy of the redox mediator is of significant importance for the rates of these reactions. This is why the energies of inner sphere reorganization of complexes in the Red and Ox states were calculated in this work: $\lambda(\mathrm{Ox}) = E(\mathrm{Ox}^*) - E(\mathrm{Ox})$ and $\lambda(\mathrm{Red}) = E(\mathrm{Red}^*) - E(\mathrm{Red})$ (see Fig. 2). As follows from Table 2, λ(Red) varies in the range from 0.37 to 0.44 eV for all the studied complexes; at the same time, λ(Ox) is visibly larger and varies within the range of 0.52–0.65 eV. Note that the energy of inner sphere reorganization is not large and is about 5% of the redox potential. This is quite expectable because the type of the geometry of both the types of the complexes is similar in the Red and Ox states, which is verified by the performed calculations. It is reasonable to attribute the higher reorganization energy of complexes in the Ox state to the larger charge of the ion.

Table 2. The calculated energies of metal complex ions. The data are presented in eV with respect to the corresponding Red form. The energies of the calculated states are illustrated in Fig. 2

Redox pair	Red		Red*		λ(Red)	Ox		Ox*		λ(Ox)
	au	eV	au	eV	eV	au	eV	au	eV	eV
$Cu(phen)_2^{1+/2+}$	–381.9379	0	–381.9244	0.37	0.37	–381.6035	9.10	–381.5845	9.62	0.52
$Cu(bpy)_2^{1+/2+}$	–359.1967	0	–359.1811	0.42	0.42	–358.8602	9.16	–358.8380	9.76	0.60
$Cu((CN)_2bpy)_2^{1+/2+}$	–419.1279	0	–419.1127	0.41	0.41	–418.7550	10.15	–418.7350	10.69	0.54
$Co(phen)_3^{2+/3+}$	–423.1942	0	–423.1777	0.45	0.45	–422.8017	10.68	–422.7815	11.23	0.55
$Co(bpy)_3^{2+/3+}$	–389.0791	0	–389.0630	0.44	0.44	–388.6802	10.86	–388.6601	11.40	0.54
$Co((CN)_2bpy)_3^{2+/3+}$	–478.9383	0	–478.9234	0.41	0.41	–478.5014	11.89	–478.4816	12.43	0.54

We note that the performed calculations do not take the effect of outer sphere reorganization of redox mediators into account, i.e., the solvation effect in the solvent. The solvation effect can strongly change the calculated values of the redox potential. For example, the characteristic experimental values of redox potentials of copper and cobalt complexes obtained in electrochemical studies are of about 5 eV. Nevertheless, these calculations are useful for choosing and optimizing the properties of new redox mediators for PSCs.

CONCLUSIONS

A quantum chemical study was carried out for promising copper and cobalt ion complexes with bipyridine and phenanthroline based ligands, as well as with new acceptor ligands on the basis of bipyridine and phenanthroline cyano derivatives. The redox potentials of the complexes and inner sphere reorganization energies were calculated.

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