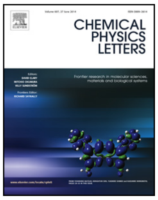
Chemical Physics Letters 635 (2015) 152–156

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett



Two-component relativistic time-dependent density functional theory study on spin-forbidden transitions for metal polypyridyl complexes

Yutaka Imamura[a], Muneaki Kamiya[a,b], Takahito Nakajima[a,*]

[a] RIKEN, Advanced Institute for Computational Science, 7-1-26, Minatojima-minami-machi, Chuo-ku, Kobe, Hyogo 650-0047, Japan
[b] Studies in Regional Environment, Department of Policy Studies, Faculty of Regional Studies, Gifu University, 1-1, Yanagido, Gifu, Gifu 501-1193, Japan

ARTICLE INFO

Article history:
Received 7 May 2015
In final form 12 June 2015
Available online 30 June 2015

ABSTRACT

Spin-forbidden transitions of metal polypyridyl sensitizers are studied by the two-component relativistic time-dependent density functional theory with spin–orbit interaction based on Tamm–Dancoff approximation. The spin-forbidden transitions for a phosphine-coordinated Ru(II), DX1, as well as the modified DX1 complexes whose Ru is replaced with Fe and Os, are calculated. The role of the central metals in spin-forbidden transitions is discussed toward the exploration for new efficient sensitizers.

1. Introduction

Solar energy has attracted attention as a renewable energy source because of the limitation of fossil fuels. Dye-sensitized solar cells (DSCs) exhibit high efficiency among the next-generation photovoltaic sources and become one of the most promising alternatives. Since Grätzel et al. proposed a ruthenium-based molecular DSC [1] and achieved high-energy conversion efficiency [2–5] with Ru complexes such as N719 (*cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylic acid)ruthenium(II)) [2] and black dye (BD) (tri(isothiocyanato)(2,2′;6′,2″-terpyridyl-4,4′,4″-tricarboxylic acid)ruthenium(II)) [4], a number of research groups have worked on DSCs and accumulated technology and knowledge. In spite of extensive efforts for developing new dyes, no rapid and significant increase in the energy conversion efficiency has yet been achieved since 1990s.

Recently, a phosphine-coordinated Ru(II) sensitizer, [*trans*-dichloro-(phenyldimethoxyphosphine)(2,2′;6′,2″-terpyridyl-4,4′,4″-tricarboxylic acid)ruthenium(II)] (DX1) dye [6] has emerged as a promising dye sensitizer because of unique near-infrared absorption by spin-forbidden transition. The advantage of the spin-forbidden transition is to keep the basic structures of conventional efficient dyes and widen the absorption width by introducing spin-forbidden transitions via a slight modification of ligands [6,7]. However, the contribution of the d orbitals that are keys for the spin-forbidden transitions need to be carefully tuned. In fact, the conventional efficient dyes of Ru complexes such as N719 and BD, being the best DSC materials so far, have a relatively small spin–orbit interaction and practically negligible spin-forbidden transitions in terms of the energy conversion efficiency. Therefore, the detailed information toward designing strong spin-forbidden transitions by a theoretical approach would be of essence.

In order to theoretically examine the spin-forbidden transition, quantum chemical methodologies incorporating the spin–orbit interaction are required. The wavefunction-based methodologies with the spin–orbit interaction describe the spin-forbidden transition with a high accuracy, but they also require a high computational cost. On the other hand, density-functional based methodologies [8–10] have been an attractive alternative in terms of a reasonable computational cost and relatively accurate descriptions of ground and excited states. Our group has recently developed two-component relativistic time-dependent density functional theory (2c-TDDFT) with the spin–orbit interaction based on Tamm–Dancoff approximation (TDA) [11,12], which can describe the spin-forbidden transition. The main reasons for choosing TDA are numerical stability [13–15] and simpler formulation [16].

We have investigated in the present study spin-forbidden transitions of the DX1-based complexes by 2c-TDDFT/TDA, which was implemented into the NTChem program [17]. Another group has recently worked on DX1 and other dyes and compared with the experimental spectra [18,19]. The purpose of this study is to focus on spin-forbidden transitions and explore the potential of new dyes with different central metals, which have never been calculated in the previous study [18].

---

* Corresponding author.
E-mail address: nakajima@riken.jp (T. Nakajima).

http://dx.doi.org/10.1016/j.cplett.2015.06.057
0009-2614/

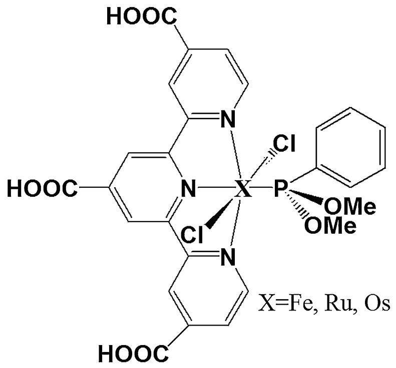


Figure 1. Geometries of DX1-Fe, DX1(-Ru), DX1-Os complexes.

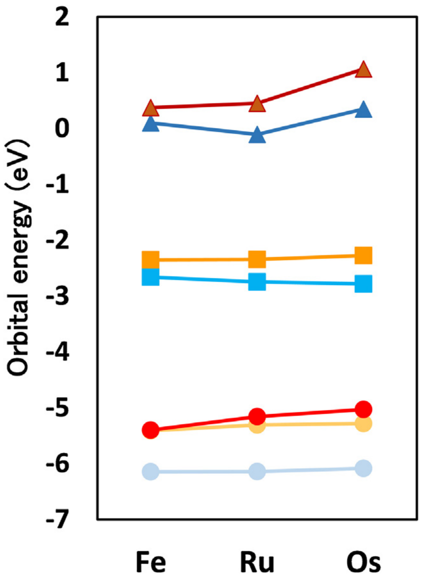


Figure 2. Orbital energies of DX1-Fe, DX1(-Ru), DX1-Os complexes. Circles, squares, and triangles correspond to t_{2g}-type, {LUMO, LUMO+1}, e_g-type orbitals.

2. Computational details

All calculations for excited states were carried out by 2c-TDDFT/TDA with the spin-free and spin-dependent parts of third [20] and first order [21] Douglas–Kroll (DK) Hamiltonians, respectively, which was implemented into NTChem [17]. The screened nucleus spin–orbit approximation was adopted for the spin-dependent part [22]. The basis sets used were Sapporo-DK-DZP for Fe/Ru/Os [23] and cc-pVDZ-DK [24] for the other atoms. The PBE1PBE functional [25], which had been reported to perform well for dyes [26], was adopted for 2c-TDDFT/TDA. The geometries of the DX1-based complexes were optimized using the DL-FIND program [27] by ωB97XD [28] in order to consider van der Waals interaction. The oscillator strengths were estimated according to the formulation of Ref. [29].

3. Results and discussion

In order to examine the role of the central metal, we first analyzed electronic structures of DX1-based complexes whose central metals are Fe, Ru, and Os. Next, we investigated absorption spectra and discussed the potential as DSC materials.

3.1. Electronic structures of DX1-based Fe, Ru and Os complexes

Table 1 shows the orbital energies computed by the scalar and 2c-relativistic DFT for the original DX1 as well as DX1-based Fe and Os complexes (DX1-Fe, DX1-Os) (Figure 1). Since the orbital energies of the scalar and 2c-relativistic DFT are significantly close, only the orbital energies of the scalar relativistic DFT are illustrated in Figure 2. As shown in Ref. [30], the central metal is expected to be able to change the orbital energies.

First, the orbital energies by the scalar relativistic DFT are discussed. Since the DX1-based complexes have a quasi-octahedral symmetry, five d orbitals are split into two groups: The highest occupied molecular orbital (HOMO), HOMO-1, and HOMO-2 belong to the t_{2g}-type orbitals and the lowest unoccupied MO (LUMO)+7 and LUMO+9 belong to e_g-type orbitals. However, Table 1 and Figure 2 demonstrate that the degeneracies of t_{2g}-type and e_g-type orbitals are relatively lifted. As confirmed in Figure 2, the HOMO energies generally increase as the central metal becomes heavier. The other HOMO-1 and HOMO-2 energies do not change significantly. The orbital energies of LUMO and LUMO+1 scarcely change with respect to the central metals. This behavior originates from the distributions of LUMO and LUMO+1 mainly over the terpyridyl ligand, not the metal. e_g orbital energies for DX1-Os are less stable, in comparison to those of the DX1-Fe and DX1 complexes. As predicted from the tendency of the HOMO energies, the gap between HOMO and LUMO decreases in the order of {X = Fe, Ru, Os}, whereas that between HOMO and LUMO+7 (e_g-type orbital) exhibits a mixed behavior, being reflected by the mixed behavior of LUMO+7 orbital energies.

Let us turn to the spin–orbit interaction. The general trend confirmed in the discussion about the orbital energies by the scalar relativistic DFT is virtually applicable to the results of 2c-relativistic DFT. In order to examine more details, the differences in the orbital energies obtained by the scalar and 2c-relativistic DFT are shown in Table 1. The spin–orbit interaction stabilizes HOMO-1 and HOMO-2 and destabilizes HOMO. The influence from the spin–orbit interaction is supposed to be magnified by the quasi-degeneracy in the t_{2g}-type orbitals obtained by the scalar relativistic DFT. These

Table 1
Orbital energies (eV) of DX1-Fe, DX1(-Ru), and DX1-Os by the scalar and 2c-relativistic DFT.

Orbital	Without spin–orbit interaction				With spin–orbit interaction			Difference		
	Type	Fe	Ru	Os[a]	Fe	Ru	Os[a]	Fe	Ru	Os
HOMO-2	t_{2g}	−6.14	−6.14	−6.08	−6.14	−6.15	−6.16	0.00	−0.01	−0.07
HOMO-1	t_{2g}	−5.41	−5.31	−5.28	−5.45	−5.33	−5.39	−0.04	−0.03	−0.11
HOMO	t_{2g}	−5.40	−5.16	−5.03	−5.37	−5.13	−4.94	0.03	0.02	0.09
LUMO	π^*	−2.66	−2.74	−2.78	−2.66	−2.75	−2.78	0.00	0.00	0.00
LUMO+1	π^*	−2.35	−2.34	−2.27	−2.35	−2.34	−2.28	0.00	0.00	0.00
LUMO+7	e_g	0.10	−0.11	0.35	0.09	−0.11	0.36	−0.01	0.00	0.01
LUMO+9	e_g	0.37	0.45	1.06	0.37	0.45	1.04	−0.01	0.00	−0.03
ΔE(HOMO–LUMO)		2.74	2.41	2.25	2.71	2.39	2.16	−0.03	−0.02	−0.09
ΔE(HOMO–LUMO+7)		5.50	5.05	5.38	5.46	5.03	5.30	−0.04	−0.02	−0.08

[a] LUMO+7 and LUMO+9 orbitals for the DX1-Os complex correspond to LUMO+8 and LUMO+10.