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

*Corresponding author, FAX +81-78-304-4962

E-mail address: nakajima@riken.jp, Takahito Nakajima

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.

Key words: spin-forbidden transition; two-component relativistic time-dependent density functional theory; DX1; spin-orbit interaction

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, so far being the best DSC materials so far, have a relatively small spin-orbit interaction and practically negligible spin-forbidden transitions in 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].

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 ω B97XD [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 tendencies consequently reduce the gaps between HOMO and LUMO by 0.03, 0.02, and 0.09 eV for the DX1-based Fe, Ru, and Os complexes, respectively. The gaps between HOMO and LUMO+7 are also reduced. Thus, the spin-orbit interaction tends to decrease the gaps and likely lead to the redshifts of excitation energies. In order to examine the effect of spin-orbit interaction, the Mulliken charges [31] of the central metals are listed in Table 2. The charges of central metals are ca. 0.16, 0.16, and 0.32 for Fe, Ru, and Os, respectively. The effect of the spin-orbit interaction is in principle small for Fe and Ru and is relatively large for Os.

3.2 Theoretical absorption spectra of DX1-based Fe, Ru and Os complexes

We have investigated the specific transitions from HOMO (t_{2g}) and HOMO-1 (t_{2g}) to LUMO and LUMO+7 through the 2c-TDDFT/TDA methodology, which is an effective tool for the spin-forbidden transition. For more details about the performance of 2c-TDDFT/TDA, see Appendix, where the calculated absorption spectrum is compared with the experimental one for esterified DX1 complex. The numerical data and absorption spectra are shown in Table 3 and Figure 3, respectively. For DX1, the lowest triply degenerate singlet-triplet transitions from HOMO to LUMO appear at 1.23 eV for the 2c-TDDFT/TDA without the spin-orbit interaction, which is equivalent to the generalized version of TDDFT/TDA. The spin-orbit interaction splits them into lower and higher transition energies: 1.20 and 1.22 eV, respectively. The higher transition has a small oscillator strength, 0.0005. The second lowest triply degenerate singlet-triplet transitions located at 1.34 eV are

assigned to HOMO-1 $\rightarrow$ LUMO. By 2c-TDDFT/TDA calculations with the spin-orbit interaction, a spin-forbidden transition peak appears at 1.30 eV with a strong oscillator strength, 0.0102. The oscillator strengths of the peaks at 1.22 and 1.30 eV are significantly different, as illustrated in Figure 3.

To analyze the difference, we use the quantity of $\langle \Psi_S | H_{SO} | \Psi_T \rangle / (E_S - E_T)$ derived from a simple perturbation theory [6,7], where $\langle \Psi_S | H_{SO} | \Psi_T \rangle$ and $E_S - E_T$ are the spin-orbit interaction between singlet and triplet states and the difference of their total energies. It is noted that all quantities in $\langle \Psi_S | H_{SO} | \Psi_T \rangle / (E_S - E_T)$ are obtained from the 2c-TDDFT/TDA calculations without the spin-orbit interaction. Based on the fact that the spin-orbit interaction can mix two states with different spin multiplicities and spatially different configurations, the lowest singlet-triplet transition of HOMO $\rightarrow$ LUMO at 1.23 eV can basically be mixed with the HOMO-1 $\rightarrow$ LUMO singlet-singlet transition at 1.67 eV, whereas the second lowest singlet-triplet transition of HOMO-1 $\rightarrow$ LUMO at 1.34 eV can basically be mixed with the HOMO $\rightarrow$ LUMO singlet-singlet transition at 1.40 eV. In consideration of the total energy difference of the denominator of $\langle \Psi_S | H_{SO} | \Psi_T \rangle / (E_S - E_T)$, the amplitudes of oscillator strengths can be explained: $E_S - E_T$ are estimated to be 0.44 and 0.06 eV for the HOMO $\rightarrow$ LUMO and HOMO-1 $\rightarrow$ LUMO singlet-triplet transitions, respectively. The other transitions from HOMO and HOMO-1 to π^* orbital range from 1.70 eV to higher energy. The d-d transitions from t_{2g} (HOMO) to e_g (LUMO+7) orbitals start from 2.10 eV. The spin-orbit interaction provides small oscillator strengths for the d-d transitions and cannot be confirmed in the absorption spectrum because the d-d transitions are formally Laporte forbidden.

For DX1-Os, the first and second lowest triply degenerate singlet-triplet transitions assigned to HOMO $\rightarrow$ LUMO excitation are redshifted to be 1.00 and 1.19 eV for the 2c-TDDFT/TDA without spin-orbit interaction, which is consistent with the reduced gap between HOMO and LUMO by the replacement of the central metal as shown in the previous section. This

indicates that DX1-Os can absorb longer wavelength light than DX1. The spin-orbit interaction largely splits the triply degenerate states into two groups. The energy splittings between those states are 0.10 and 0.26 eV for the first and second triply degenerate singlet-triplet transitions, which are significantly larger than the corresponding values of 0.02 and 0.08 eV for DX1. The oscillator strengths of the third and fourth transitions for 2c-TDDFT/TDA with the spin-orbit interaction are 0.0023 and 0.0185, which are larger than the corresponding values of 0.0005 and 0.0102 for DX1. This difference in the oscillator strengths indicates the strong mixing between the singlet and triplet states through the strong spin-orbit interaction. The other peaks ranging below 2.75 eV are all assigned to the metal-to-ligand charge-transfer type transition. The d-d transitions from t_{2g} to e_g do not appear in the energy range up to 2.5 eV of Figure 3. The first lowest d-d transition is located around 2.9 eV. As was pointed out in Ref. [30], the d-d transitions are highly lying. In general, as shown in Figure 3, the shape of the absorption spectrum for DX1-Os is similar to that of DX1, although that of DX1-Os seems to be slightly stretched in comparison with DX1; as a result, relatively low-amplitude region is extended. This tendency might lead to a low incident photon to current conversion efficiency (IPCE).

For DX1-Fe, the first and second lowest singlet-triplet transitions assigned to the main excitation of HOMO to LUMO+7 by 2c-TDDFT/TDA without the spin-orbit interaction appear at 0.57 and 0.92 eV, which are significantly lower than those of DX1 and DX1-Os. Although the gap between the highest t_{2g} (HOMO) and e_g (LUMO+7) orbitals is large, the transition energies are estimated to be low, maybe because of strong d orbital interaction. These transitions have very small oscillator strengths owing to the Laporte forbidden transitions. The corresponding singlet-singlet transition energies are 1.44 and 1.76 eV from HOMO and HOMO-1 to LUMO+7, respectively. The spin-orbit interaction does not affect the transition energies and oscillator strengths. The first and second triply degenerate singlet-triplet transition energies mainly derived from the transitions from HOMO and HOMO-1 to LUMO are 1.47 and 1.55 eV for 2c-TDDFT/TDA without spin-orbit

interaction. The corresponding singlet-singlet transition energies are calculated to be 1.62 and 1.79 eV for HOMO $\rightarrow$ LUMO and HOMO-1 $\rightarrow$ LUMO. The weak spin-orbit interaction from Fe changes transition energies at most within 0.01 – 0.02 eV. In general, the absorption spectrum for DX1-Fe is distinctly different from those of DX1 and DX1-Os; the d-d transitions located in the long wavelength region is a probably main factor for the different shape of the spectra. The above metal-to-ligand charge-transfer type transitions start from approximately 1.6 eV. As is seen in Figure 3, DX1-Fe cannot efficiently absorb long wavelength sunlight, whereas DX1-Os can absorb longer wavelength light and seems to be promising.

4. Concluding remarks

We have investigated the spin-forbidden transitions by 2c-TDDFT/TDA, which was implemented into the quantum chemical program package, NTChem. The potential of spin-forbidden transitions has been discussed with the three DX1-based complexes, i.e., DX1, DX1-Fe, and DX1-Os for the first time. The numerical investigation reveals that the absorption spectrum of DX1-Os is similar to that of DX1, but that of DX1-Fe is different from the others. DX1-Os can absorb a wider-range wavelength light with relatively small oscillator strengths in comparison with DX1, whereas DX1-Fe cannot. This investigation provides information about the roles of transition metals in terms of spin-forbidden transitions, which will be useful for constructing new sensitizers using spin-forbidden transitions.

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Appendix

Theoretical and experimental spectra of esterified DX1 molecule

We have examined the performance of 2c-TDDFT/TDA for the spin-forbidden transition. The esterified DX1 molecule was chosen as a system because the corresponding experimental spectrum was available [6]. The solvent effect was incorporated within the MM molecular mechanics method. The geometry of solvents in the MM region, namely, toluenes were optimized by the MM calculations with OPLSaa potential [32] using TINKER [33]. The excitation energies and oscillator strengths are compared in Table 4 and illustrated in Figure 4 with the experimental results.

Not only spin-allowed but also spin-forbidden peaks assigned to a metal-to-ligand charge-transfer type excitation appear for 2c-TDDFT/TDA with spin-orbit interaction: The lowest peak at ~ 1.36 eV is a spin-forbidden metal-to-ligand charge-transfer type transition. In comparison with the experimental spectrum, it is slightly shifted to lower energy. The other major peaks, i.e., those with relatively large amplitudes, ranging between 1.5 – 3.0 eV, are assigned to metal-to-ligand charge-transfer type and reasonably reproduced with a slight underestimation trend. The effect of the spin-orbit interaction is basically small except for the lowest transition. The d-d transitions appear in the energy range of 2 eV. However, their oscillator strengths are small. The above numerical assessment assures that 2c-TDDFT/TDA can appropriately describe the spin-forbidden transition, which is consistent with the previous studies [18, 19].

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Figure captions

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.

FIGURE 3. Absorption spectra of DX1-Fe, DX1, and DX1-Os by 2c-TDDFT/TDA calculations with and without spin-orbit (SO) interaction. The peaks are illustrated by Lorentzian-type functions with the half bandwidths of 0.12 eV.

FIGURE 4. Absorption spectra of esterified DX1 from experiment and 2c-TDDFT/TDA calculations. The peaks are illustrated by Lorentzian-type functions with the half bandwidths of 0.12 eV.

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.

Table 2 Mulliken charges of central metals of DX1-Fe, DX1(-Ru), and DX1-Os by the scalar and 2c-relativistic DFT.

	Fe	Ru	Os
Without spin-orbit interaction	0.161	0.157	0.314
With spin-orbit interaction	0.159	0.157	0.326
Δ	0.003	0.000	-0.013

Table 3 Excitation energies ΔE (eV) and oscillator strengths f of DX1-Fe, DX1(-Ru), and DX1-Os by 2c-TDDFT/TDA with and without spin-orbit interaction. H and L represent HOMO and LUMO.

System	Without spin-orbit interaction				With spin-orbit interaction		
	ΔE	Spin symmetry	f	Main configuration ^{a)}	ΔE	f	Main configuration ^{a)}
DX1-Fe	0.57	Triplet	0.0000	H-1 -> L+7	0.57	0.0000	H-1 -> L+7, H -> L+7
	0.57	Triplet	0.0000	H-1 -> L+7, H-5 -> L+7	0.57	0.0000	H-1 -> L+7, H -> L+7
	0.57	Triplet	0.0000	H-1 -> L+7	0.57	0.0000	H-1 -> L+7, H -> L+7
	0.92	Triplet	0.0000	H -> L+7	0.92	0.0000	H -> L+7
	0.92	Triplet	0.0000	H -> L+7, H-6 -> L+7	0.92	0.0000	H -> L+7, H -> L
	0.92	Triplet	0.0000	H -> L+7	0.92	0.0000	H -> L+7, H -> L
	1.44	Singlet	0.0000	H-1 -> L+7	1.44	0.0001	H-1 -> L+7, H -> L+7
	1.76	Singlet	0.0002	H -> L+7	1.77	0.0002	H -> L+7
	1.47	Triplet	0.0000	H -> L	1.45	0.0000	H -> L
	1.47	Triplet	0.0000	H -> L	1.45	0.0000	H -> L
	1.47	Triplet	0.0000	H -> L	1.46	0.0006	H -> L
	1.55	Triplet	0.0000	H-1 -> L	1.55	0.0002	H -> L, H-1 -> L
	1.55	Triplet	0.0000	H-1 -> L, H-2 -> L	1.57	0.0000	H-1 -> L
	1.55	Triplet	0.0000	H-1 -> L	1.57	0.0000	H-1 -> L
	1.62	Singlet	0.0113	H-1 -> L	1.64	0.0105	H-1 -> L
	1.79	Singlet	0.0087	H -> L	1.80	0.0083	H -> L, H-1 -> L
DX1	1.23	Triplet	0.0000	H -> L	1.20	0.0000	H -> L
	1.23	Triplet	0.0000	H -> L	1.20	0.0000	H -> L
	1.23	Triplet	0.0000	H -> L	1.22	0.0005	H -> L, H-1 -> L
	1.34	Triplet	0.0000	H-1 -> L	1.30	0.0102	H -> L, H-1 -> L
	1.34	Triplet	0.0000	H-1 -> L	1.38	0.0000	H-1 -> L
	1.34	Triplet	0.0000	H-1 -> L	1.38	0.0000	H-1 -> L
	1.40	Singlet	0.0324	H -> L	1.45	0.0216	H-1 -> L, H -> L
	1.67	Singlet	0.0102	H-1 -> L, H -> L+1	1.67	0.0087	H-1 -> L, H -> L+1
	2.10	Triplet	0.0000	H -> L+7	2.10	0.0019	H -> L+7
	2.10	Triplet	0.0000	H -> L+7	2.10	0.0003	H -> L+7
	2.10	Triplet	0.0000	H -> L+7	2.10	0.0000	H -> L+7
	2.48	Triplet	0.0000	H-1 -> L+7	2.46	0.0002	H-1 -> L+7
	2.48	Triplet	0.0000	H-1 -> L+7	2.49	0.0002	H-1 -> L+7
	2.48	Triplet	0.0000	H-1 -> L+7	2.49	0.0018	H-1 -> L+7
DX1-Os	1.00	Triplet	0.0000	H -> L	0.90	0.0000	H -> L
	1.00	Triplet	0.0000	H -> L	0.90	0.0000	H -> L
	1.00	Triplet	0.0000	H -> L	1.00	0.0023	H -> L
	1.19	Triplet	0.0000	H-1 -> L	1.05	0.0185	H -> L
	1.19	Triplet	0.0000	H-1 -> L	1.31	0.0000	H-1 -> L, H -> L
	1.19	Triplet	0.0000	H-1 -> L	1.31	0.0001	H-1 -> L, H -> L
	1.27	Singlet	0.0478	H -> L	1.44	0.0114	H-1 -> L
	1.62	Singlet	0.0098	H-1 -> L, H -> L+1	1.46	0.0209	H -> L+1
	2.90	Triplet	0.0000	H -> L+8	2.85	0.0438	H -> L+8
	2.90	Triplet	0.0000	H -> L+8	2.91	0.0002	H -> L+8
	2.90	Triplet	0.0000	H -> L+8	2.91	0.0002	H -> L+8

a) The absolute value of configuration coefficients are over 0.3.

Table 4 Excitation energies ΔE (eV) and oscillator strengths f of esterified DX1 by 2c-TDDFT/TDA with spin-orbit interaction. H and L represent HOMO and LUMO.

ΔE	f	Main configuration ^{a)}	Exptl.
1.24	0.0000	H -> L	
1.24	0.0000	H -> L	
1.26	0.0006	H -> L	
1.36	0.0147	H -> L, H-1 -> L	1.45
1.44	0.0000	H-1 -> L	
1.44	0.0000	H-1 -> L	
1.50	0.0215	H-1 -> L	1.61
1.68	0.0000	H -> L+1	
1.68	0.0000	H -> L+1	
1.68	0.0015	H -> L+1	
1.71	0.0111	H-1 -> L, H -> L+1	1.83
1.95	0.0036	H-1 -> L+1	
1.97	0.0000	H-1 -> L+1	
1.97	0.0000	H-1 -> L+1	
2.07	0.0164	H-1 -> L+1	2.08
2.09	0.0011	H -> L+7	
2.10	0.0018	H -> L+7	
2.10	0.0000	H -> L+7	
2.19	0.0239	H -> L+1	2.08

a) The absolute value of configuration coefficients are over 0.3.

Figure

Figure 1

Figure 2

Figure 3

Figure 4

**Spin-
forbidden
Transition**

**New Dye
DX1**