

**Design of Spin-Forbidden Transitions for Polypyridyl Metal
Complexes by Relativistic Time-dependent Density Functional Theory
Including Spin-orbit Interaction**

Shohei Kanno, Yutaka Imamura,* Masahiko Hada

Department of Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo,
Japan

*Corresponding author

E-mail address: yimamura@tmu.ac.jp, Yutaka Imamura

Part 1 : Frontier orbitals of DX1-Fe-X (X = Cl, Br and I)

The contributions of the atomic orbitals for frontier orbitals of DX1-Fe-X (X = Cl, Br and I) are given in Table S1. The occupied frontier orbitals are composed of Fe t_{2g} and halogen p orbitals, which is similar to the case of the DX1-based dyes. The similar tendency that the contributions of atomic orbitals increase for halogen p molecular orbitals as the halogen atomic number increases, is confirmed.

Table S1 Characters of frontier orbitals of DX1-Fe-X (X = Cl, Br and I).

Molecules	Orbital	Fe character	Halogen character
DX1-Fe-Cl	HOMO	d_{xz} :68%	p_x :24%
	HOMO-1	d_{yz} :66%	p_y :27%
	LUMO	d_{yz} :2%, d_{xz} :1%	p_z :2%
	LUMO+1	d_{xz} :2%	0%
DX1-Fe-Br	HOMO	d_{yz} :21%, d_{xz} :34%	p_x :22%, p_y :7%
	HOMO-1	d_{yz} :33%, d_{xz} :25%	p_x :14%, p_y :24%
	LUMO	d_{yz} :2%, d_{xz} :1%	p_z :3%
	LUMO+1	d_{xz} :2%	0%
DX1-Fe-I	HOMO	d_{yz} :25%, d_{xz} :5%	p_x :10%, p_y :57%
	HOMO-1	d_{yz} :5%, d_{xz} :33%	p_x :50%, p_y :10%
	LUMO	d_{yz} :2%, d_{xz} :1%	p_z :5%
	LUMO+1	d_{xz} :2%	0%

Part 2 : The assignments of the absorption peaks of DX1-Fe-X (X = Cl, Br and I)

Fig. S1 and Table S2 show the assignments of the absorption peaks of DX1-Fe-X (X = Cl, Br and I). For all dyes, four excited states calculated by SR-TDDFT in the long wavelength region, i.e., two singlet excited states S_3 (HOMO \rightarrow LUMO) and S_4 (HOMO-1 \rightarrow LUMO) and two triplet excited states T_7 (HOMO \rightarrow LUMO) and T_8 (HOMO-1 \rightarrow LUMO) are involved in the low-lying excited states obtained by SO-TDDFT. The absorption peaks of S_3 , S_4 , T_7 and T_8 appear at 2.10, 2.32, 1.98 and 2.04 eV with $f = 0.031$, 0.029, 0.000 and 0.000 for DX1-Fe-Cl, whereas the same peaks for DX1-Ru-Br appear at 2.08, 2.26, 1.96 and 2.02 eV with $f = 0.025$, 0.023, 0.000 and 0.000 and for DX1-Ru-I appear at 2.09, 2.23, 2.00 and 2.06 eV with $f = 0.021$, 0.013, 0.000 and 0.000.

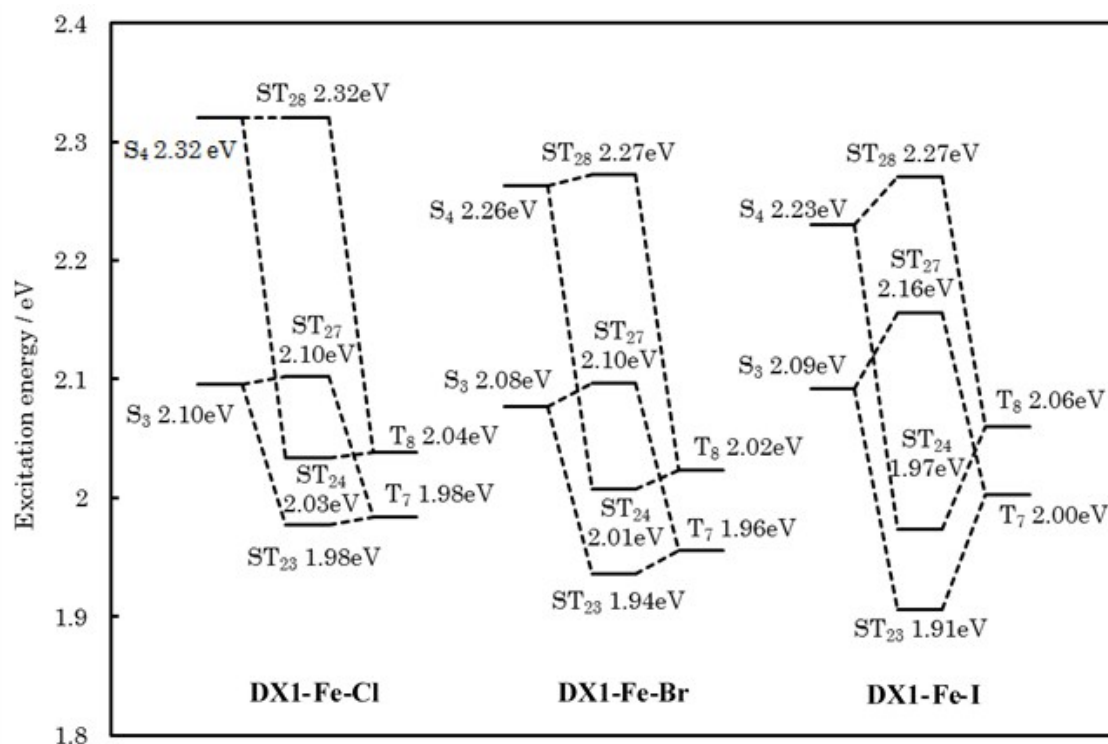


Fig. S1 Excitation energies of DX1-Fe-X (X = Cl, Br, and I) in acetonitrile solution. In respective molecules, excited states obtained by SR-TDDFT and SO-TDDFT are given left, right and center, respectively.

Table S2 Assignments of absorption spectra of DX1-Fe-X (X = Cl, Br, and I) calculated by SO-TDDFT and SR-TDDFT. Excitation energies, oscillator strengths, and contributions of SR states in states calculated by SO-TDDFT are given, respectively.

Molecules	Perturbative SOC transitions				SR transition contributions								
	States	(eV)	f	(%)	States	(eV)	f	Compositions					
DX1-Fe-Cl	ST ₂₃	1.98	0.001	5	S ₃	2.10	0.031	64%	HOMO→LUMO				
								29%	HOMO-1→LUMO				
				95	T ₇	1.98	0.000	65%	HOMO→LUMO				
								30%	HOMO-1→LUMO				
					ST ₂₄	2.03	0.001	1	S ₄	2.32	0.029	58%	HOMO-1→LUMO
												26%	HOMO→LUMO
	96	T ₈	2.04	0.000	65%	HOMO-1→LUMO							
					31%	HOMO→LUMO							
		ST ₂₇	2.10	0.028	93	S ₃	2.10	0.031	64%	HOMO→LUMO			
									29%	HOMO-1→LUMO			
	4				T ₇	1.98	0.000	65%	HOMO→LUMO				
								30%	HOMO-1→LUMO				
ST ₂₈					2.32	0.028	98	S ₄	2.32	0.029	58%	HOMO-1→LUMO	
											26%	HOMO→LUMO	
	1	T ₈	2.04	0.000			65%	HOMO-1→LUMO					
							31%	HOMO→LUMO					
		ST ₂₃	1.94	0.003			12	S ₃	2.08	0.025	12%	HOMO→LUMO	
											79%	HOMO-1→LUMO	

				87	T ₇	1.96	0.000	91%	HOMO→LUMO
								0%	HOMO-1→LUMO
	ST ₂₄	2.01	0.002	5	S ₄	2.26	0.023	77%	HOMO-1→LUMO
								11%	HOMO→LUMO
				92	T ₈	2.02	0.000	1%	HOMO-1→LUMO
								95%	HOMO→LUMO
	ST ₂₇	2.10	0.021	85	S ₃	2.08	0.025	12%	HOMO→LUMO
								79%	HOMO-1→LUMO
				11	T ₇	1.96	0.000	91%	HOMO→LUMO
								0%	HOMO-1→LUMO
	ST ₂₈	2.27	0.022	94	S ₄	2.26	0.023	77%	HOMO-1→LUMO
								11%	HOMO→LUMO
				5	T ₈	2.02	0.000	1%	HOMO-1→LUMO
								95%	HOMO→LUMO
DX1-Fe-I	ST ₂₃	1.91	0.006	29	S ₃	2.09	0.021	2%	HOMO→LUMO
								78%	HOMO-1→LUMO
				66	T ₇	2.00	0.000	73%	HOMO→LUMO
								17%	HOMO-1→LUMO
	ST ₂₄	1.97	0.004	25	S ₄	2.23	0.013	1%	HOMO-1→LUMO
								91%	HOMO→LUMO
				70	T ₈	2.06	0.000	74%	HOMO-1→LUMO
								17%	HOMO→LUMO
	ST ₂₇	2.16	0.014	67	S ₃	2.09	0.021	2%	HOMO→LUMO
								78%	HOMO-1→LUMO

			26	T ₇	2.00	0.000	73%	HOMO→LUMO
							17%	HOMO-1→LUMO
ST ₂₈	2.27	0.009	67	S ₄	2.23	0.013	1%	HOMO-1→LUMO
							91%	HOMO→LUMO
			24	T ₈	2.06	0.000	74%	HOMO-1→LUMO
							17%	HOMO→LUMO

Part 3 : Comparison of the scalar TDDFT, TDDFT based on perturbation of spin-orbit and full two-component TDDFT

Fig. S2 shows the absorption spectra of DX1-Ru-I having the largest SO matrix elements, calculated by scalar relativistic theory (called SR-TDDFT in this paper), perturbation theory (SO-TDDFT) and full two-component theory. SO-TDDFT can perturbatively estimate the effect of SOI, and the differences of excitation energies between SO-TDDFT and full two-component TDDFT are estimated to be within 0.03 eV. On the other hand, SR-TDDFT cannot reproduce spin-forbidden peaks in the long wavelength region as can be confirmed in the absorption spectra obtained by SO-TDDFT and full two-component TDDFT.

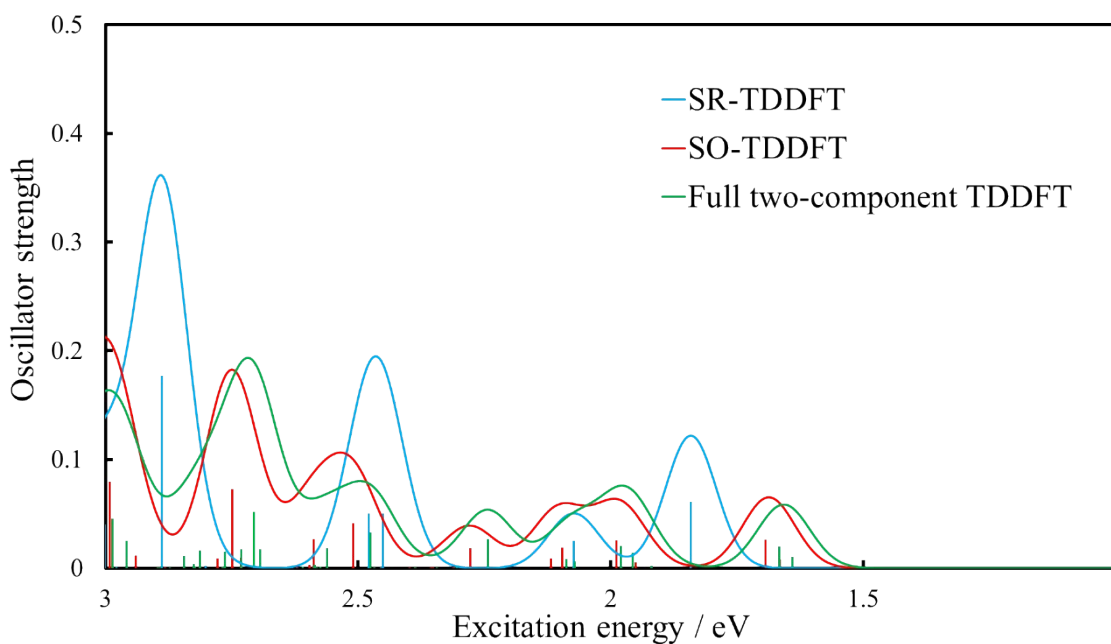


Fig. S2 Absorption spectra of DX1-Ru-I in acetonitrile solution calculated by SR-TDDFT (blue line), SO-TDDFT (red line) and full two-component theory (green line). All spectra are interpolated using Gaussian functions with $\sigma = 0.05$ eV.