

Supporting Information for
The Inner-Sphere Electron Transfer Single Iodide
Mechanism for Dye-Regeneration in
Dye-Sensitized Solar Cells

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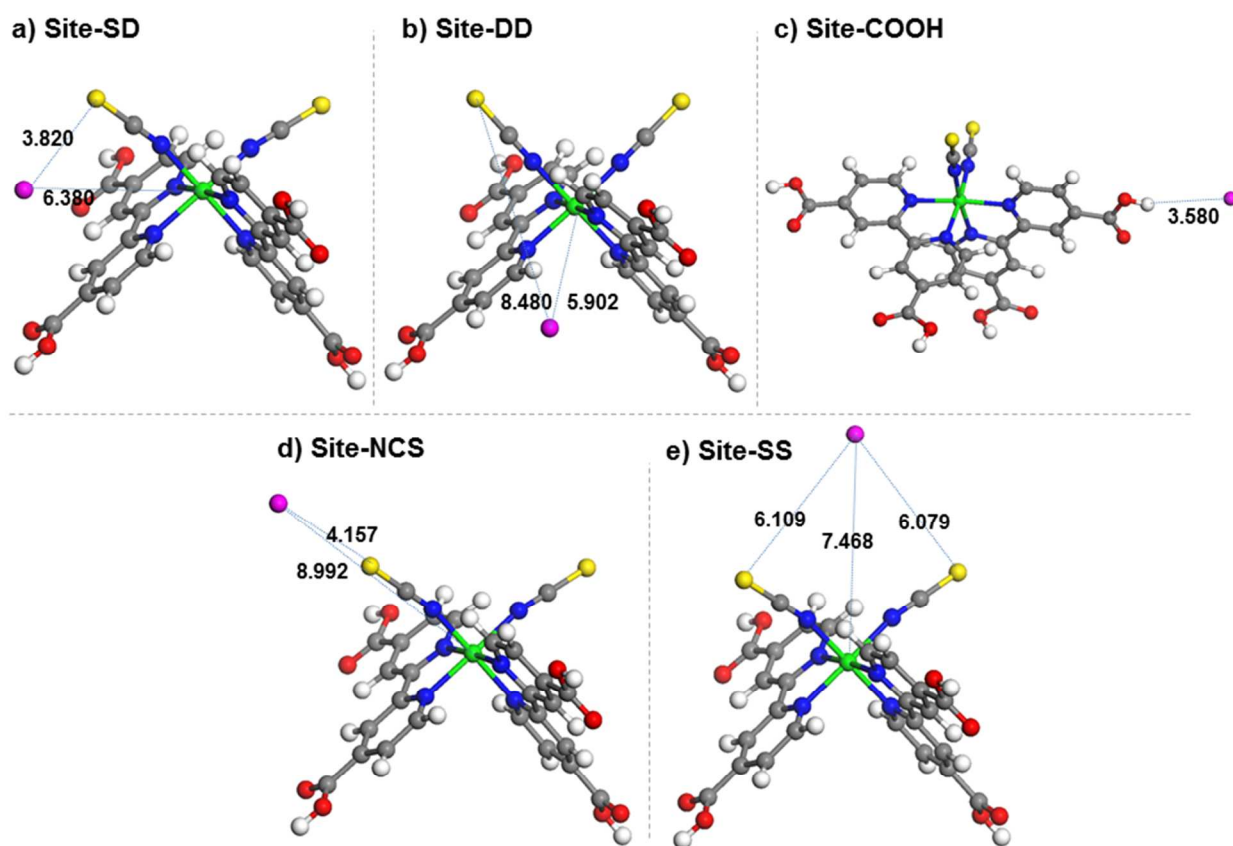


Figure S1 Initial structure of five distinct sites of ($D^+\cdots I$) complex;

- a) Site-SD : starts with I^- located in between the NCS ligand and dicarboxylic-bipyridine (dcB) ligand of D^+ ,
- b) Site-DD : starts with I^- located in between two dicarboxylic-bipyridine ligands of D^+ ,
- c) Site-COOH : starts with I^- located near the carboxylic group of one dicarboxylic-bipyridine ligand of D^+ .
- d) Site-NCS : starts with I^- located linearly along one of the NCS ligands of D^+ ,
- e) Site-SS : starts with I^- located in between the two NCS ligands of D^+

Color description: magenta: I^- , red: O (oxygen), blue: N (nitrogen), grey: C (carbon), white: H (hydrogen), green: Ru (ruthenium), yellow: S (sulfur)

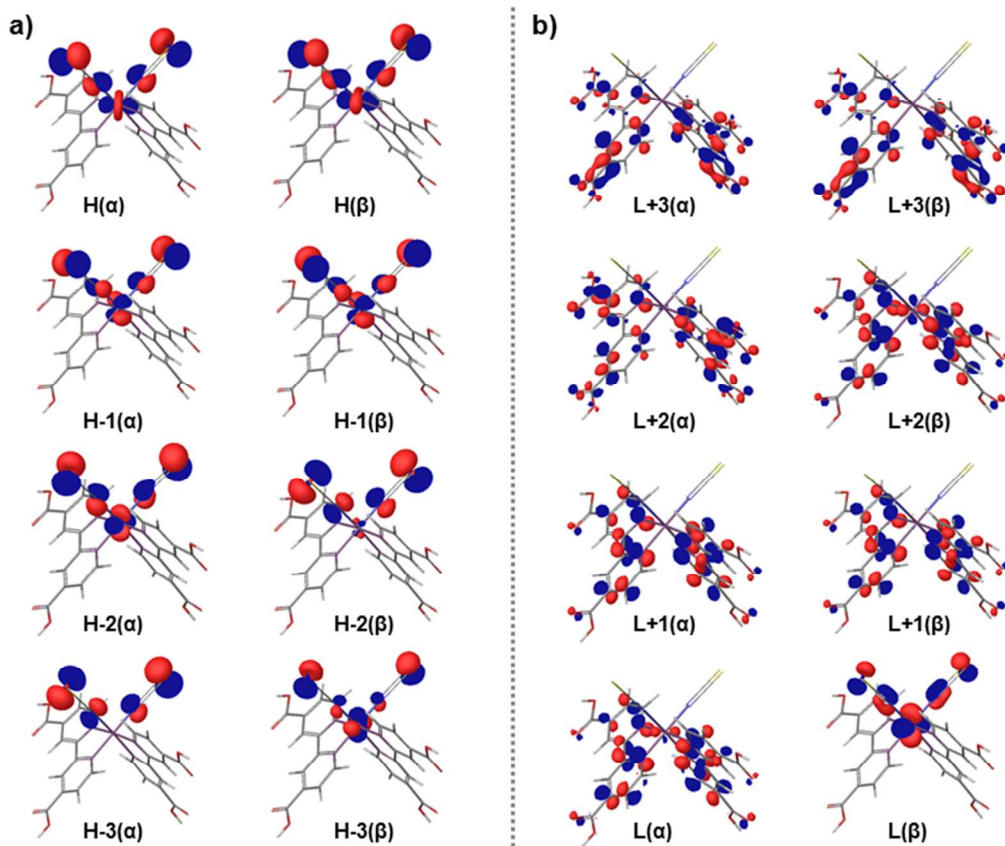


Figure S2 The molecular orbitals of oxidized dye (D^+) in acetonitrile (AN). a) HOMOs b) LUMOs. LUMO (beta phase) shows that the hole state is delocalized over the two NCS ligands and the Ru d_{xy} .

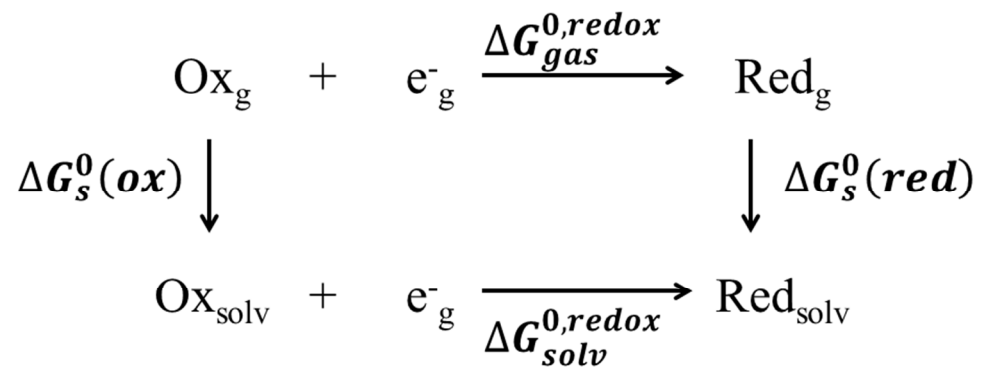


Figure S3 The Born-Haber cycle used to derive the standard reduction potential of iodine related species and dye molecule.

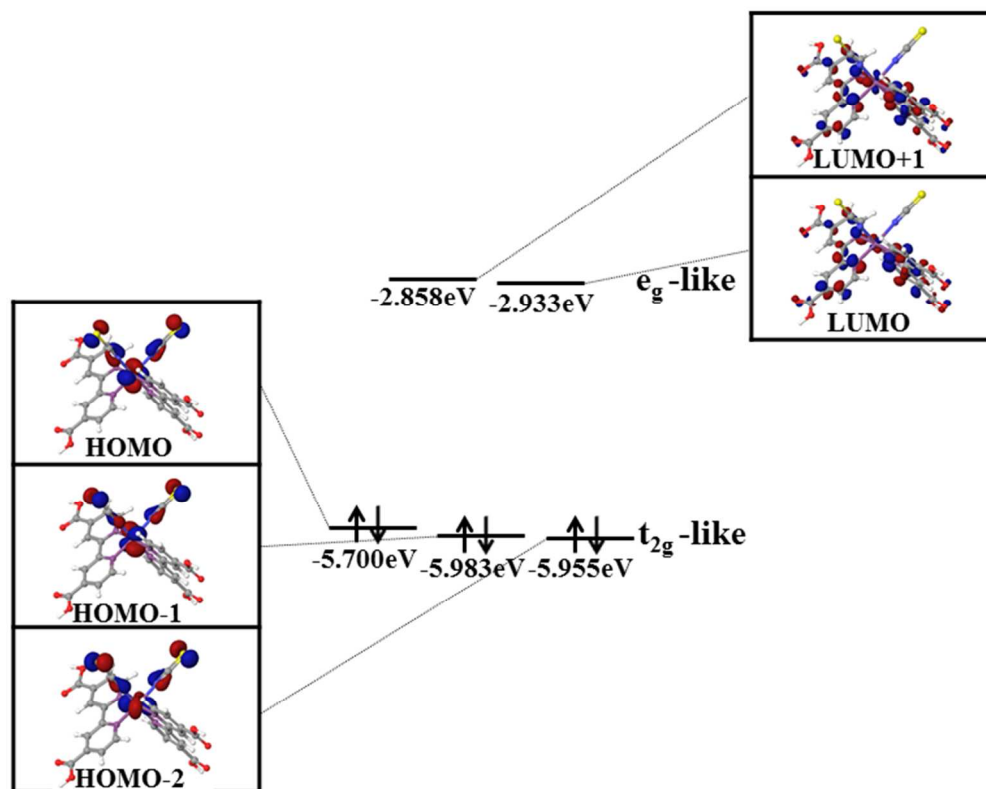


Figure S4 Ru atom is hexa-coordinated by 1) two nitrogen atoms of NCS ligands and 2) four nitrogen atoms of dicarboxylic-bipyridine (dcb) ligands; thus, we can consider that it has a pseudo-octahedral electronic geometry, although the Ru-N distances are not exactly identical to each other. This symmetry breaking leads to the frontier molecular orbital (MO) diagram shown in the figure, where HOMO, HOMO-1, and HOMO-2 have comparable energy eigenvalues and LUMO and LUMO+1 have comparable energy eigenvalues. Thus, we consider the three HOMO's as " t_{2g} -like orbitals", and two LUMO's as " e_g -like orbitals" even though the degeneracy is somewhat broken.

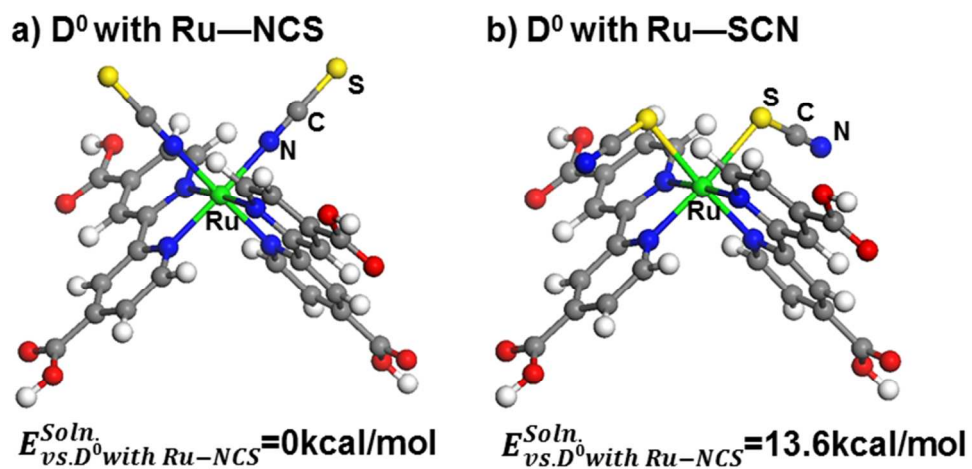


Figure S5 The N3 dye ($\text{Ru}(\text{dcb})_2(\text{NCS})_2$) has a) N-bonded (Ru-NCS) isomer and b) S-bonded (Ru-SCN) isomer. N-bonded (Ru-NCS) isomer is 13.6 kcal/mol stable than S-bonded (Ru-SCN) isomer in acetonitrile (AN). This calculation is performed using PBF built in Jaguar software. We used B3LYP with the basis set of LACVP** and 6-311++G** for sulfur.

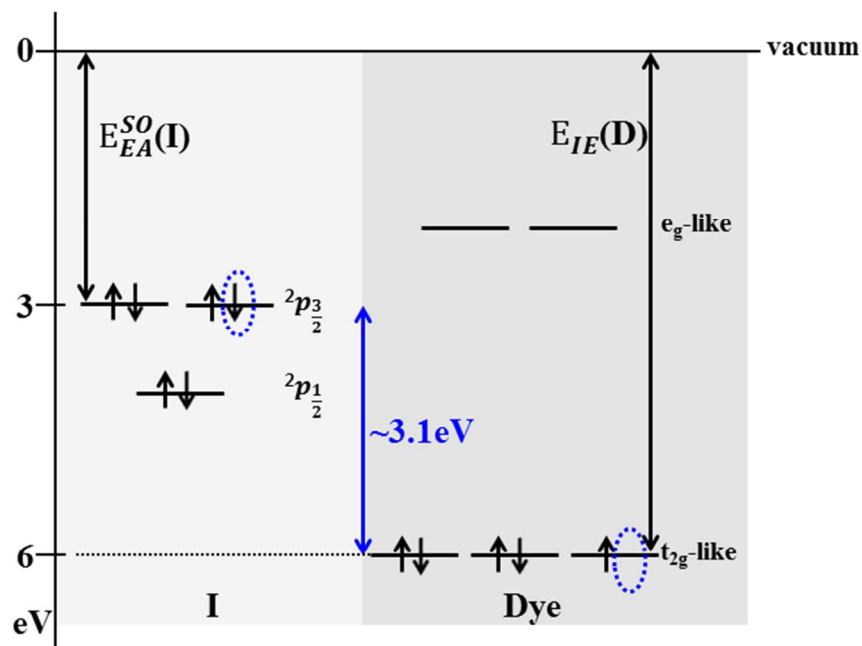


Figure S6 The diagram referenced to the vacuum state. From the spin-orbit corrected electron affinity (E_{EA}^{SO}) of I we consider that p -orbital of I is located at -3.0 eV, and from the ionization potential (E_{IE}) of D, we consider that the t_{2g} -like hole state of D^+ is located at -6.1 eV, both referenced to the vacuum state. The large energy separation between electron donating and accepting orbitals (3.1 eV) would be expected to yield a fast charge transfer. Indeed the QM shows that a delocalized hole state over the iodide and dye molecule forms as they are complexed.

Table S1 Solvation energy ΔG_s° of I^- and I_3^- calculated using PBF built in Jaguar software. We used B3LYP with the basis set of aug-cc-pVTZ-pp. We modified the van der Waal's (vdW) radius of I (r_{vdW}^I) from 2.25 (Jaguar default value) to 2.73Å to reproduce the experimental ΔG_s° . (Unit : kcal/mol)

	$r_{vdW}^I = 2.25$	$r_{vdW}^I = 2.73$	Exp. ¹
I^-	-61.945	-55.198	-55.900
I_3^-	-40.264	-37.359	-38.400

Table S2 The electron affinity of I, I₂, and I₃ based on B3LYP with various basis sets; aug-cc-pVDZ-pp, aug-cc-pVTZ-pp and aug-cc-pVQZ-pp proposed by T. H. Dunning²⁻⁵. We found that the aug-cc-pVTZ-pp level produces comparable accuracy with aug-cc-pVQZ-pp level calculation. (Unit: eV)

	aug-cc-pVDZ-pp	aug-cc-pVTZ-pp	aug-cc-pVQZ-pp
I	3.356	3.302	3.306
I ₂	2.953	2.760	2.747
I ₃	4.631	4.579	4.582

Table S3 Standard reduction potential, E^0 vs SHE(standard hydrogen electrode) (unit: V). We convert our calculated results referenced to ferrocene electrode (Fc^+/Fc) to values referenced to SHE by adding 0.624 V.⁶ The amount of spin-orbit (SO) correction is quantified based on the difference of electron affinities between SO-DFT and SO free DFT using the NWchem software because SO-DFT is not available in the Jaguar package. Solvation energy contributions are estimated from Jaguar PBF calculations. We note that the spin-orbit (SO) corrected calculations were performed for all iodine containing species.

	NWchem ^a	NWchem ^b	Jaguar ^c	Exp.
SO	w/o	w/	w/o	
$E^0(\text{I}^-/\text{I})$	1.397	1.107	1.471	1.224 ⁷
$E^0(\text{I}_2/\text{I}_2^{\cdot-})$	0.429	0.391	0.438	0.314
$E^0(\text{I}_3^-/\text{I}_2^{\cdot-}, \text{I}^-)$	0.035	-0.054	-0.015	-0.086 ⁸
$E^0(\text{I}_2^{\cdot-}/\text{I})$	0.632	0.597	0.623	0.784 ⁸
$E^0(\text{I}_3^-/\text{I})$	0.333	0.271	0.304	0.354 ⁹
$E^0(\text{I}_2/\text{I})$	0.531	0.494	0.530	0.554 ⁹
$E^0(\text{D}^+/\text{D}^0)$	1.037 ^d	-	1.035 ^e	1.094 ¹⁰

^aSO-free DFT using NWchem package, Functional: B3LYP (combined with VWN5), Basis set: aug-cc-pVTZ-pp, Solvation Energy Contribution: (non-self-consistent manner) PBF coupled with Jaguar SO-free B3LYP, aug-cc-pVTZ-pp calculation.

^bSO-DFT using NWchem package, Functional: B3LYP (combined with VWN5), Basis set: aug-cc-pVTZ-pp, Solvation Energy Contribution: (non-self-consistent manner) PBF coupled with Jaguar SO-free B3LYP, aug-cc-pVTZ-pp calculation.

^cSO-free DFT using Jaguar package, Functional: B3LYP (combined with VWN3), Basis set: aug-cc-pVTZ-pp, Solvation Energy Contribution: self-consistent manner.

^dSO-free DFT using NWchem package, functional:B3LYP(combined with VWN5), Basis set: LANL2DZ, Solvation Energy Contribution: (non-self-consistent manner) PBF coupled with Jaguar SO-free B3YP, LACVP++** calculation

^eSO-free DFT using Jaguar package, Functional: B3LYP(combined with VWN3), Basis set: LACVP++** calculation, Solvation Energy Contribution: self-consistent manner.

Table S4 DFT calculations of the reduction potential of (Fc⁺/Fc), using LACVP** the basis set. Ionization energy and solvation energy difference of (Fc⁺/Fc) well match with the experimental result, inferring that there is a minimal systematic error imposed in the reference electrode calculation. (Unit : eV)

	B3LYP	Ref.
$E^0(\text{Fc}^+/\text{Fc})$	5.034	-
Ionization energy	7.014	6.82±0.08 ¹¹
Solvation energy difference ($G_{\text{solv}}^{\text{Fc}^+} - G_{\text{solv}}^{\text{Fc}}$)	1.98	1.91 ¹²

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