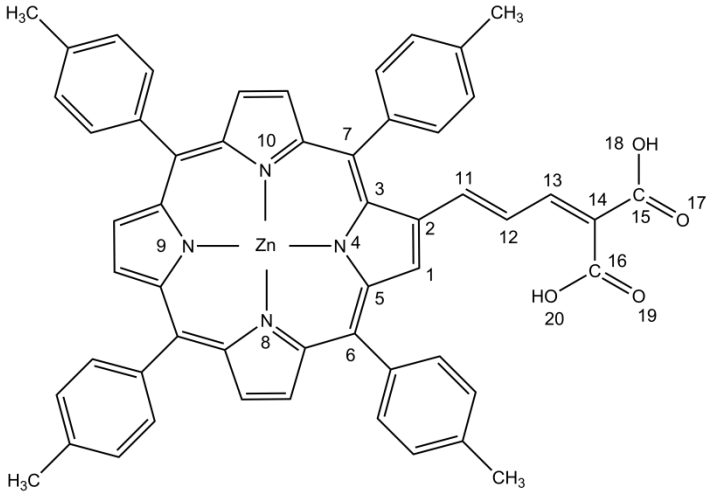
Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

A DFT Study of Regeneration Process of Zinc Porphyrin Analogues for Dye-Sensitized Solar Cells

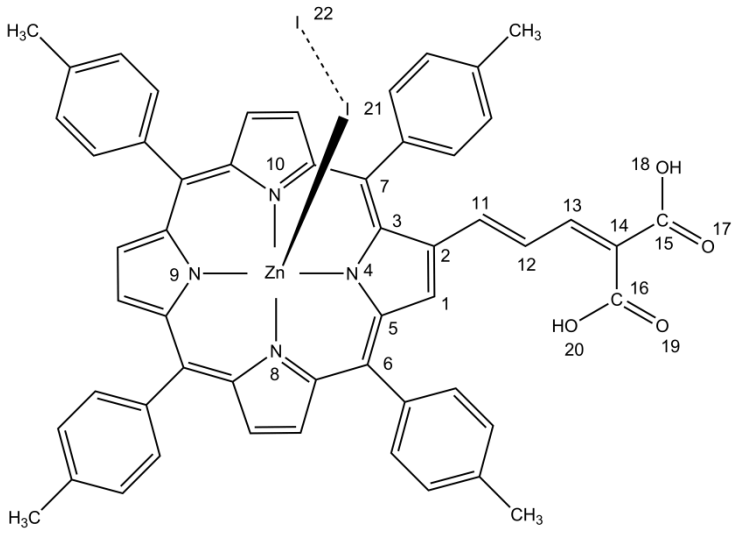
Table S1. Geometric parameters (in Å and °) of Zinc Tetraarylporphyrin Malonic Acid and its cationic state calculated at different methods.



Zinc porphyrin	B3LYP	MPW1K	BP86	BLYP	CAM-B3LYP
r(Zn-N4)	2.086	2.062	2.095	2.105	2.071
r(Zn-N8)	2.064	2.042	2.073	2.082	2.052
r(Zn-N19)	2.075	2.052	2.083	2.093	2.062
r(Zn-N10)	2.059	2.038	2.067	2.076	2.048
α(C3-N4-C5)	107.9	107.7	107.6	107.8	107.8
α(N4-C3-C2)	108.9	109.1	109.1	108.8	108.9
α(N4-Zn-N8)	90.6	90.6	90.6	90.6	90.6
α(C2-C11-C12-C13)	179.6	178.6	179.2	179.9	179.9
α(C13-C14-C15-O17)	-163.9	-164.0	-164.6	-164.1	-163.6
α(C13-C14-C15-O18)	14.2	14.0	13.5	14.1	14.6
α(C13-C14-C16-O19)	-145.2	-143.1	-146.6	-146.9	-144.4
α(C13-C14-C16-C20)	33.8	35.8	32.3	32.2	34.6

Zinc porphyrin Cation	B3LYP	MPW1K	BP86	BLYP	CAM-B3LYP
r(Zn-N4)	2.087	2.067	2.092	2.103	2.075
r(Zn-N8)	2.073	2.051	2.081	2.091	2.061
r(Zn-N19)	2.082	2.061	2.089	2.099	2.071
r(Zn-N10)	2.066	2.046	2.073	2.083	2.055
α(C3-N4-C5)	107.2	107.0	107.0	107.2	107.1
α(N4-C3-C2)	109.4	109.7	109.6	109.2	109.2
α(N4-Zn-N8)	90.5	90.5	90.5	90.5	90.5
α(C2-C11-C12-C13)	-179.7	179.1	178.6	-179.4	-179.3
α(C13-C14-C15-O17)	-161.6	-162.3	-162.8	-161.4	-161.3
α(C13-C14-C15-O18)	16.6	15.7	15.1	16.7	16.9
α(C13-C14-C16-O19)	-138.9	-137.4	-136.8	-138.7	-139.9
α(C13-C14-C16-C20)	39.9	41.3	41.9	40.1	39.0

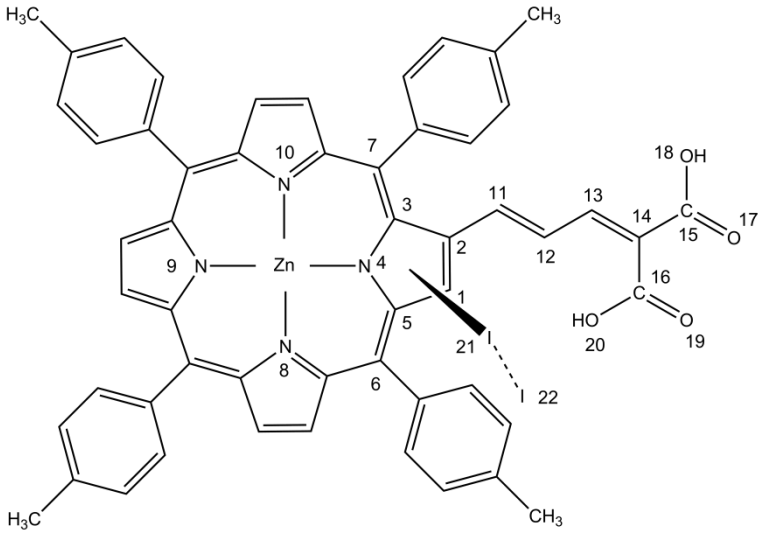
Table S2. Geometric parameters (in Å and °) of $DyeI_{Zn}$ and $DyeI_{Zn}$-I intermediates calculated at different methods.



$DyeI_{Zn}$ intermediate	B3LYP	MPW1K	BP86	BLYP	CAM-B3LYP
r(Zn-N4)	2.155	2.132	2.151	2.164	2.144
r(Zn-N8)	2.149	2.129	2.147	2.159	2.140
r(Zn-N9)	2.149	2.130	2.149	2.162	2.143
r(Zn-N10)	2.135	2.117	2.135	2.147	2.127
r(Zn-I21)	2.769	2.699	2.789	2.836	2.723
α(N4-Zn-I21)	105.1	105.4	105.6	105.7	105.6
α(C3-N4-C5)	107.4	107.2	107.2	107.4	107.3
α(N4-C3-C2)	109.6	109.9	109.8	109.5	109.7
α(N4-Zn-N8)	86.6	86.7	87.1	87.0	86.5
α(C2-C11-C12-C13)	-179.7	179.0	179.9	-179.1	-179.6
α(C13-C14-C15-O17)	-162.7	-163.0	-163.5	-162.9	-162.3
α(C13-C14-C15-O18)	15.5	15.0	14.6	15.3	15.9
α(C13-C14-C16-O19)	-145.8	-145.8	-147.1	-147.4	-145.3
α(C13-C14-C16-O20)	33.2	35.1	31.9	31.7	33.8

$DyeI_{Zn}$-I intermediate	B3LYP	MPW1K	BP86	BLYP	CAM-B3LYP
r(Zn-N4)	2.120	2.093	2.130	2.143	2.104
r(Zn-N8)	2.109	2.085	2.121	2.131	2.094
r(Zn-N9)	2.124	2.098	2.136	2.146	2.106
r(Zn-N10)	2.103	2.079	2.114	2.124	2.088
r(Zn-I21)	3.044	2.963	2.986	3.061	3.012
r(I21-I22)	3.440	3.334	3.431	3.509	3.374
α(Zn-I21-I22)	103.6	101.9	103.1	103.1	101.57
α(C3-N4-C5)	108.0	107.9	107.7	107.9	107.9
α(N4-C3-C2)	109.0	109.2	109.3	109.0	109.1
α(N4-Zn-N8)	88.6	88.7	88.4	88.4	88.7
α(C2-C11-C12-C13)	179.8	178.4	179.5	179.5	179.8
α(C13-C14-C15-O17)	-1645.0	-164.7	-166.1	-165.6	-164.2
α(C13-C14-C15-O18)	13.3	13.4	12.2	12.8	14.0
α(C13-C14-C16-O19)	-153.9	-151.2	-156.1	-156.1	-152.3
α(C13-C14-C16-C20)	25.4	26.9	23.1	23.2	27.0

Table S3. Geometric parameters (in Å and °) of $DyeI_{Py}$ and $DyeI_{Py}$-I intermediates calculated at different methods.

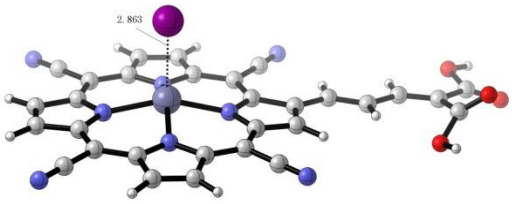


$DyeI_{Py}$ intermediate	B3LYP	MPW1K	BP86	BLYP	CAM-B3LYP
r(Zn-N4)	2.088	2.068	2.099	2.101	2.075
r(Zn-N8)	2.062	2.040	2.069	2.082	2.050
r(Zn-N9)	2.075	2.051	2.083	2.096	2.061
r(Zn-N10)	2.060	2.038	2.068	2.080	2.048
r(Zn-I21)	5.709	5.549	5.709	5.854	5.650
r(N4-I21)	4.144	3.954	4.079	4.310	4.127
α(C3-N4-C5)	108.3	108.4	108.2	108.1	108.2
α(N4-C3-C2)	109.2	109.4	109.4	109.2	109.2
α(N4-Zn-N8)	90.6	90.6	90.6	90.7	90.6
α(N4-I21-C5)	18.7	19.3	19.0	18.3	19.2
α(C1-I21-C2)	23.4	24.7	24.4	22.7	23.7
α(C2-C11-C12-C13)	179.4	178.8	178.6	179.5	179.8
α(C13-C14-C15-O17)	-163.0	-163.3	-163.8	-162.8	-163.0
α(C13-C14-C15-O18)	15.1	14.7	14.2	15.3	15.1
α(C13-C14-C16-O19)	-142.2	-141.0	-141.5	-142.4	-142.6
α(C13-C14-C16-C20)	36.7	37.8	37.1	36.3	36.3

$Dye I_{Py}$-I intermediate	B3LYP	MPW1K	BP86	BLYP	CAM-B3LYP
r(Zn-N4)	2.079	2.055	2.088	2.098	2.064
r(Zn-N8)	2.064	2.042	2.072	2.082	2.052
r(Zn-N9)	2.081	2.057	2.089	2.098	2.068
r(Zn-N10)	2.062	2.041	2.071	2.080	2.050
r(I21-I22)	3.446	3.343	3.438	3.514	3.380
r(Zn-I21)	8.301	8.147	9.034	9.018	10.265
r(Zn-I22)	10.391	10.262	10.546	10.754	8.229
α(C3-N4-C5)	107.6	107.5	107.3	107.6	107.6
α(N4-C3-C2)	109.0	109.3	109.3	109.0	109.1
α(N4-Zn-N8)	90.7	90.7	90.7	90.7	90.7
α(C2-C11-C12-C13)	178.7	177.6	178.5	179.5	178.9
α(C13-C14-C15-O17)	-159.8	-159.9	-160.9	-160.1	-159.7
α(C13-C14-C15-O18)	18.2	18.0	16.9	17.9	18.3
α(C13-C14-C16-O19)	-143.9	-143.6	-142.2	-142.9	-144.2
α(C13-C14-C16-C20)	34.8	35.2	36.1	35.6	34.8

Figure S1. The molecular structures of $Zn^{+}I^{-}$ intermediates for porphyrin analogues

The distance of the Zn and I are shown (Å). (B3LYP)



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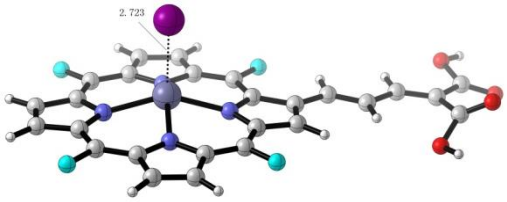

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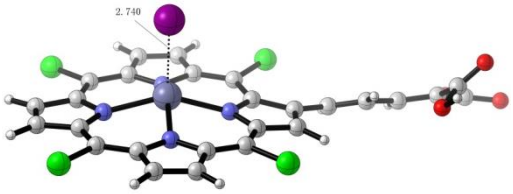

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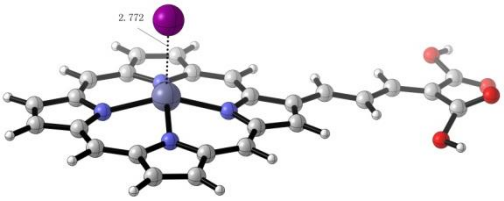

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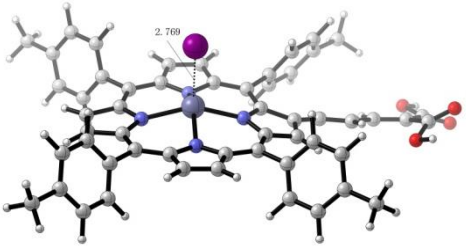

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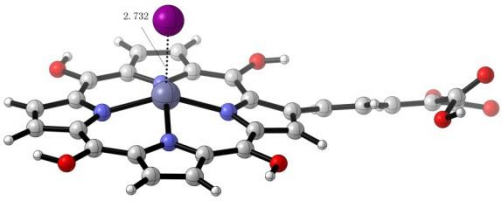

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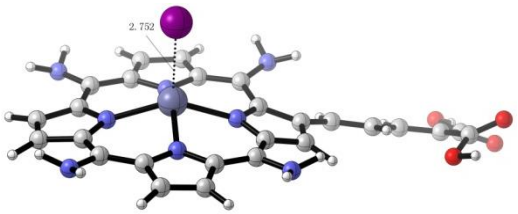
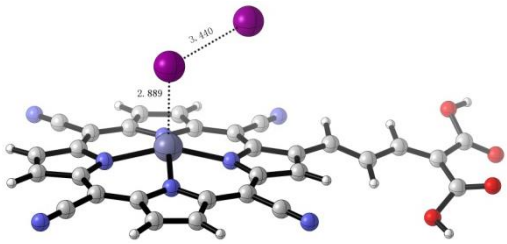


Por-NH_2

Color scheme: Zn, purple; N, blue; H, white; O, red; F, light blue; Cl, green; I, purple red.

Fig S2. The molecular structures of $DyeI_{Zn}$ intermediates for porphyrin analogues
The distance of the Zn-I and I-I are shown (Å). (B3LYP)



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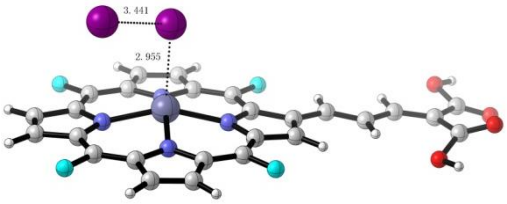

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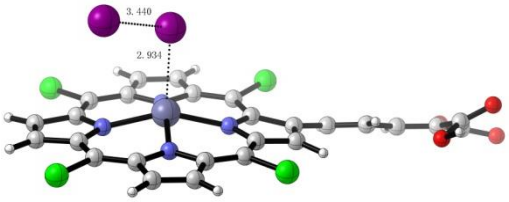

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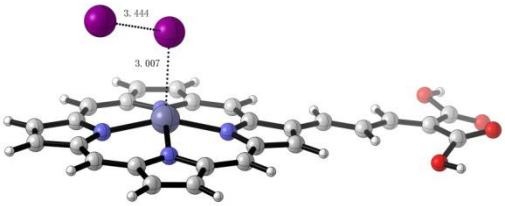
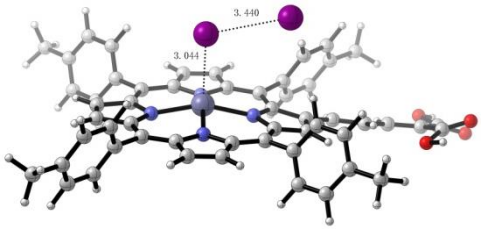
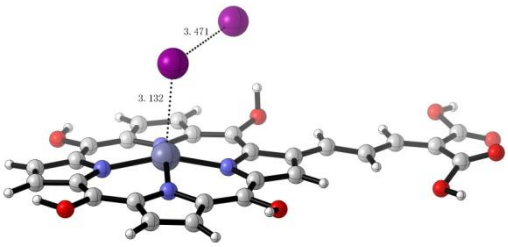


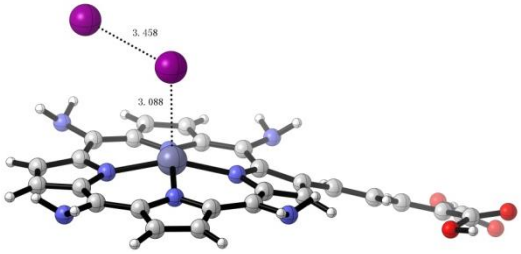
Por-H



Por-$PhCH_3$



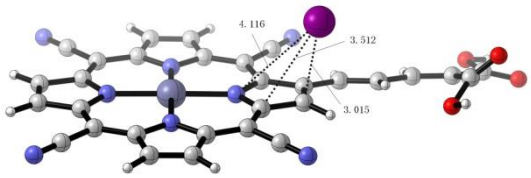
Por-OH



Por-NH_2

Color scheme: Zn, purple; N, blue; H, white; O, red; F, light blue; Cl, green; I, purple red.

Fig S3. The molecular structures of $DyeI_{Py}$ intermediates for zinc porphyrin analogues. The distance of the I-N and C-I are shown (Å). (B3LYP)



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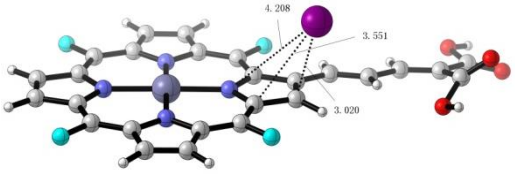
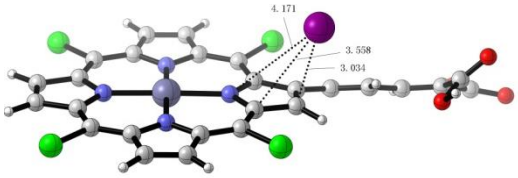


Por-F



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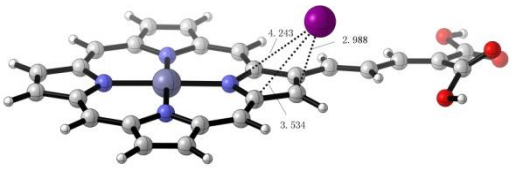

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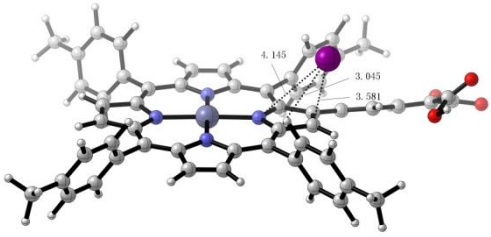
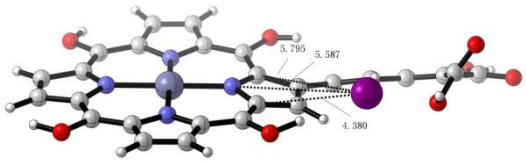
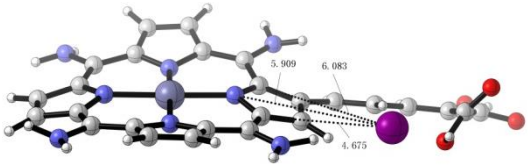


Por-$PhCH_3$



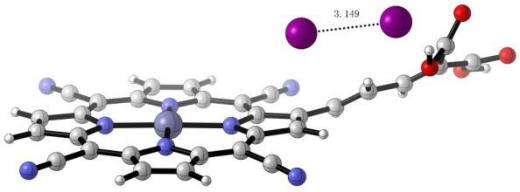
Por-OH



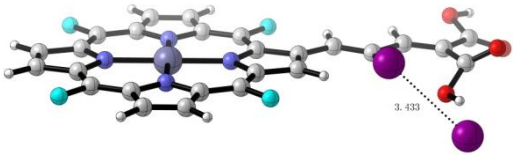
Por-NH_2

Color scheme: Zn, purple; N, blue; H, white; O, red; F, light blue; Cl, green; I, purple red.

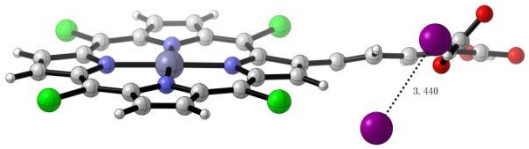
Fig S4. The molecular structures of $DyeI_{Py}$-I intermediates for zinc porphyrin analogues. The distance of the I-I are shown (Å) (B3LYP)



Por-CN



Por-F



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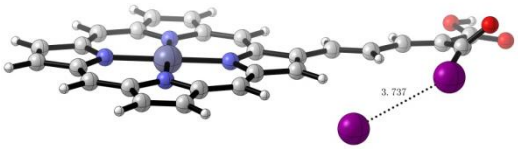
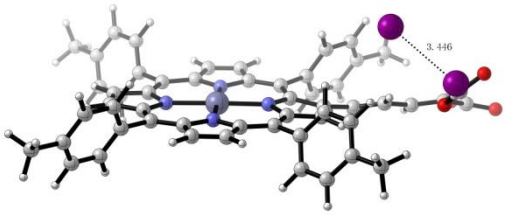
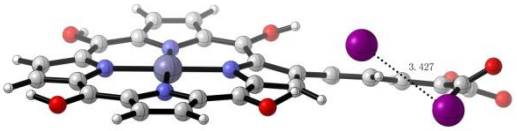


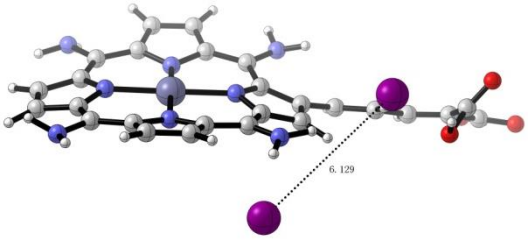
Por-H



Por-$PhCH_3$



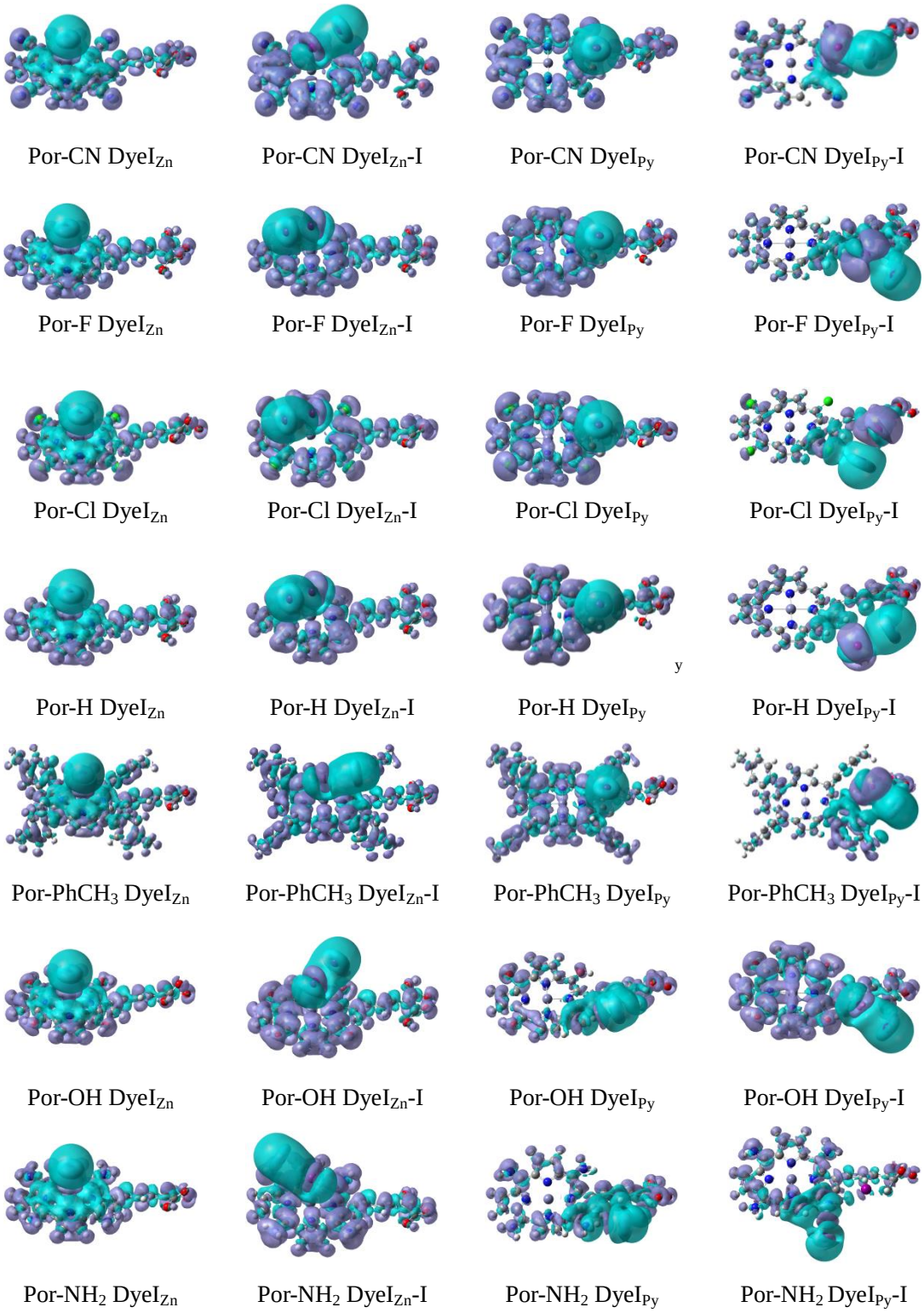
Por-OH



Por-NH_2

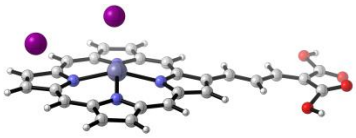
Color scheme: Zn, purple; N, blue; H, white; O, red; F, light blue; Cl, green; I, purple red.

Fig S5. The charge density difference (Δρ) of intermediates for zinc porphyrins analogues, the blue section highlights the loss of charge density and the purple section highlights the addition of charge density. (CAM-B3LYP)

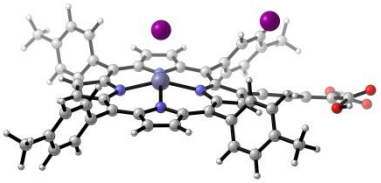


Color scheme: Zn, purple; N, blue; H, white; O, red; F, light blue; Cl, green; I, purple red.

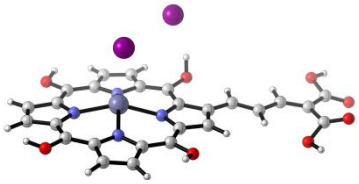
Fig S6. The structures of transition states for the formation of $DyeI_{Zn}$-I and $DyeI_{Py}$-I intermediates in the regneration for Cl-, H-, $PhCH_3$- and OH-substituted porphyrins (B3LYP)



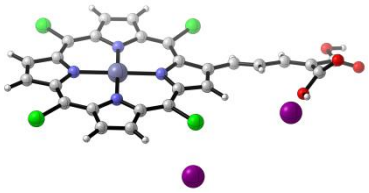
Por-H



Por-$PhCH_3$



Por-OH



Por-Cl

The calculation of free energy of electron injection for the zinc porphyrins

In this paper, the free energy for electron injection was calculated to evaluate the injection properties of zinc porphyrin analogues. The free energy of electron injection was calculated by the following equation[1, 2] (1):

$$\Delta G^{inject} = E_{OX}^{dye^*} - E_{CB}^{SC} \quad (1)$$

The E_{CB}^{SC} =4.0eV for TiO_2.

$E_{OX}^{dye^*}$ is the oxidation of the excited state dye and it can be calculated by two models. The first is the electron injection model that happens from the unrelaxed excited state. In this case, the oxidation of excited state $E_{OX}^{dye^*}$ is computed by the equation (2):

$$E_{OX}^{dye^*} = E_{OX}^{dye} - \lambda_{\max}^{(1)} \quad (2)$$

Here, E_{OX}^{dye} is the oxidation of the dye and $\lambda_{\max}^{(1)}$ is the first intense absorption band. The strong absorption band around 400nm is used for $\lambda_{\max}^{(1)}$. Note that, in zinc porphyrins, the absorption of Q (500-600) band exists but it is very weak. The second electron injection model is that the injection happens from the relaxed excited state. The $E_{OX}^{dye^*}$ is computed by:

$$E_{OX}^{dye^*} = E_{OX}^{dye} - E_{0-0}^{dye} \quad (3)$$

E_{0-0}^{dye} is the difference between the ground state and the relaxed excited state. It is expressed as:

$$E_{0-0}^{dye} = \lambda_{\max}^{(1)} - E_{S_1}^{reorg} \quad (4)$$

$$E_{S_1}^{reorg} = E_{S_1}(Q_{S_0}) - E_{S1}(Q_{S_1}) = E_{S_0}(Q_{S_0}) + \Delta E_{S_1} - E_{S1}(Q_{S_1}) \quad (5)$$

Q_{S_0} and Q_{S_1} are the stable structures of the ground state and excited state. In this paper, the E_{0-0}^{dye} can be computed directly and the $E_{OX}^{dye^*}$ is computed using equation (3). The ΔG^{inject} using these two models are both calculated (Table S8). The optimization of ground and excite states are computed with CAM-B3LYP, the basis set is 6-31g* for C, H, O, N, F and Cl, the Lanl2dz for Zn atom.

Table S4 The free energy of electron injection (eV)

Scheme	E_{OX}^{dye}	$\lambda_{\max}^{(1)}$	f	E_{0-0}^{dye}	E_{CB}^{SC}	ΔG^{inject} (unrelaxed)	ΔG^{inject} (relaxed)
Por-CN	7.409	3.424	1.017	3.397	4.0	-0.015	0.011
Por-F	6.464	3.248	1.888	3.188	4.0	-0.784	-0.724
Por-Cl	6.727	3.279	1.748	3.448	4.0	-0.552	-0.721
Por-H	6.406	3.270	1.806	3.136	4.0	-0.864	-0.730
Por-OH	5.547	3.244	1.259	2.903	4.0	-1.697	-1.356
Por-NH_2	4.603	3.179	1.547	2.523	4.0	-2.576	-1.920

References

1 J. Preat, C. Michaus, D. Jacquemin and E. A. Perpete, *J. Phys. Chem. C*, 2009, **113,** 16821.

2 R. Kathoh, A. Furube, T. Yoshihara and K. Hara, *J. Phys. Chem. B*, 2004, **108,** 4818.