Chapter5

Quantum chemical calculation of ZnCl$_2$ substituted Phthalocyanine for dye sensitized solar cells applications

5.1 The geometric structure

The optimized geometry of the ZnCl$_2$ substituted phthalocyanine is shown in Figure 5.1, and the bond lengths, bond angles and dihedral angles are listed in Table 5.1. Since the crystal structure of the exact title compound is not available till now, the optimized structure can be only be compared with other similar systems for which the crystal structures have been solved. From the theoretical values we can find that most of the optimized bond lengths, bond angles and dihedral angles.

5.2 Electronic structures and charges

Natural Bond Orbital (NBO) analysis was performed in order to analyze the charge populations of the dye Zinc dichloride substituted phthalocyanine. The frontier molecular orbitals (MO) energies and corresponding density of state of the dye ZnCl$_2$ substituted phthalocyanine is shown in Figure 5.2.

The HOMO–LUMO gap of the dye ZnCl$_2$ substituted phthalocyanine in vacuum is 1.82 eV.

Figure 5.1 Optimized Geometry structure of the ZnCl$_2$ substituted phthalocyanine.

Table 5.1 Selected bond lengths (in Å), bond angles (in degree) and dihedral angles (in degree) of the dye $ZnCl_2$ substituted phthalocyanines

Parameters	B3LYP/6-311++G(d-p)
Bond length	(Å)
Cl1-Zn3	2.1608
Cl2-Zn3	2.162
Zn3-N4	1.8354
Zn3-N5	1.8261
Bond Angle (in degree)	(˚)
Cl1-Zn3-Cl2	89.8427
Cl1-Zn3-N4	101.0388
Cl1-Zn3-N5	103.4841
Cl2- Zn3-N4	100.9817
Cl2- Zn3-N5	103.4634
N4- Zn3-N5	145.1404
Zn3-N4-C12	126.4465
Zn3-N4-C13	126.4817
C12-N4-C13	105.7328
Zn3-N5-C14	125.8811
Zn3-N5-C15	125.8447
Dihedral Angles (in degree)	(˚)
Cl1-Zn3-N4-C12	36.467
Cl1- Zn3-N4-C13	-128.4037
Cl2- Zn3-N4-C12	128.4731
Cl1- Zn3-N5-C14	126.6113
Cl1- Zn3-N5-C15	-33.5718

Cl2- Si3-N5-C14	33.487
Zn3-N4-C12-N6	38.5803
Zn3-N4-C12-C16	-148.9143
C13-N4-C12-N6	-154.0127
Zn3-N4-C13-N7	-38.5958
Zn3-N4-C13-C17	148.9097
C12-N4-C13-N7	154.003
Zn3-N5-C14-N8	36.5896
Zn3-N5-C14-C18	-152.3012
C15-N5-C14-N8	-160.0171
Zn3-N5-C15-N9	-36.61
Zn3-N5-C15-C19	152.3068

While the calculated HOMO and LUMO energies of the bare $Ti_{38}O_{76}$ cluster as a model for nanocrystalline are -6.55 and -2.77eV, respectively, resulting in a HOMO–LUMO gap of 3.78 eV, the lowest transition is reduced to 3.20 eV according to TDDFT, and this value is slightly smaller than typical band gap of TiO_2 nanoparticles with nm size [1]. Furthermore, the HOMO, LUMO and HOMO–LUMO gap of $(TiO_2)_{60}$ cluster is -7.52, -2.97, and 4.55 eV (B3LYP/VDZ), respectively [2]. Taking into account of the cluster size effects and the calculated HOMO, LUMO, HOMO–LUMO gap of the dye $ZnCl_2$ substituted phthalocyanine, $Ti_{38}O_{76}$ and $(TiO_2)_{60}$ clusters, we can find that the HOMO energies of these dyes fall within the TiO_2 gap. The above data also reveal the interfacial electron transfer between semiconductor TiO_2 electrode and the dye sensitizer $ZnCl_2$ substituted phthalocyanine is

electron injection processes from excited dye to the semiconductor conduction band. This is a kind of typical interfacial electron transfer reaction.
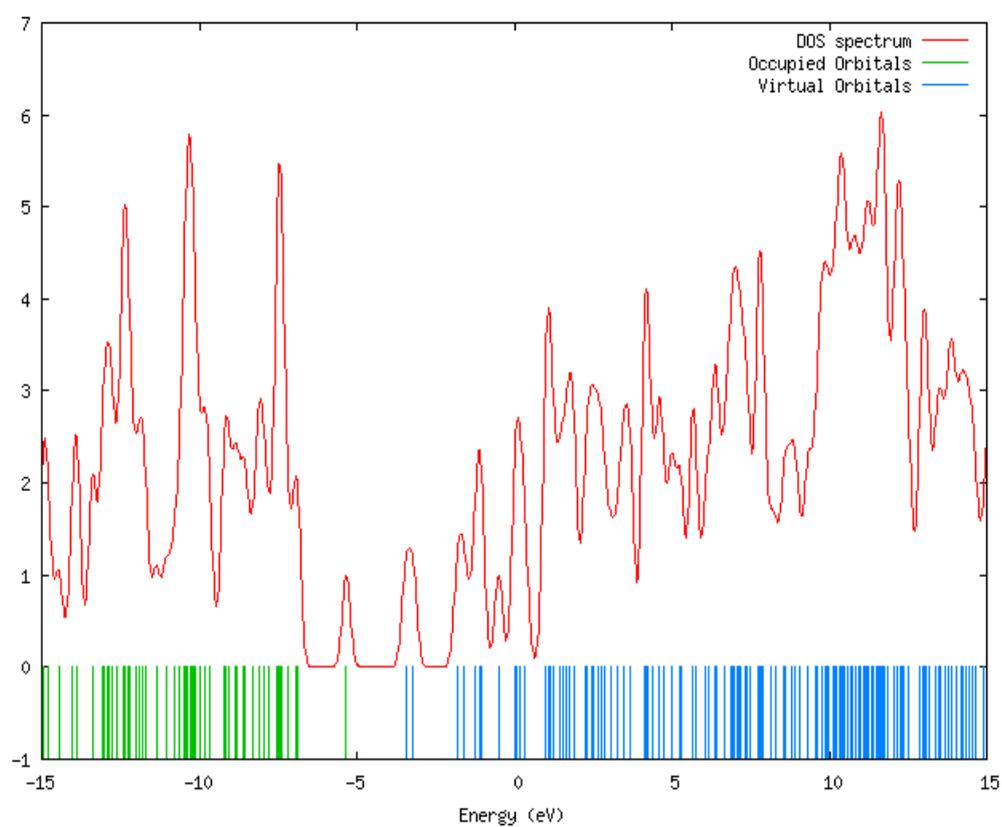

Figure 5.2 The frontier molecular orbital energies and corresponding density of state (DOS) spectrum of the dye $ZnCl_2$ substituted phthalocyanine.

5.3 IR and Raman frequencies

Figure 5.3 and 5.4 shows the calculated IR and Raman spectra of $ZnCl_2$ substituted phthalocyanine respectively. In our study we have followed scaling factors B3LYP/6-311++G(d,p).
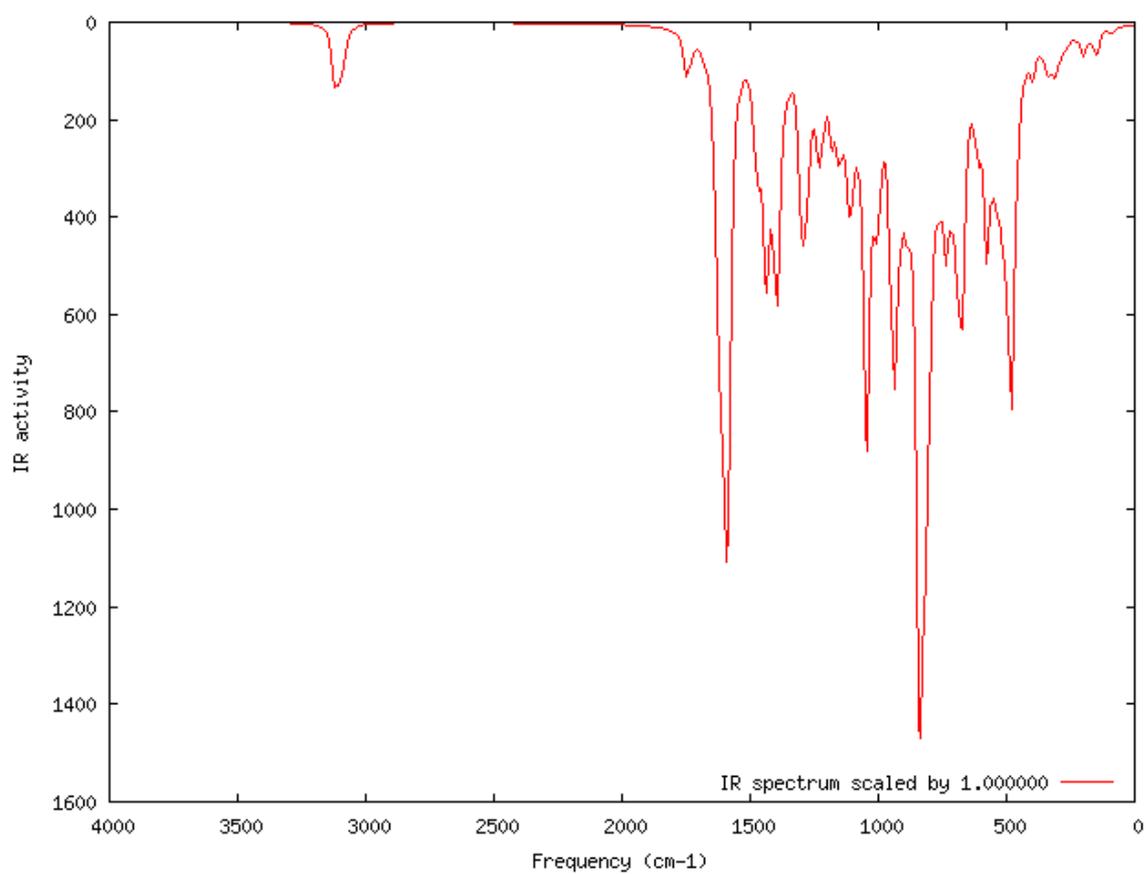

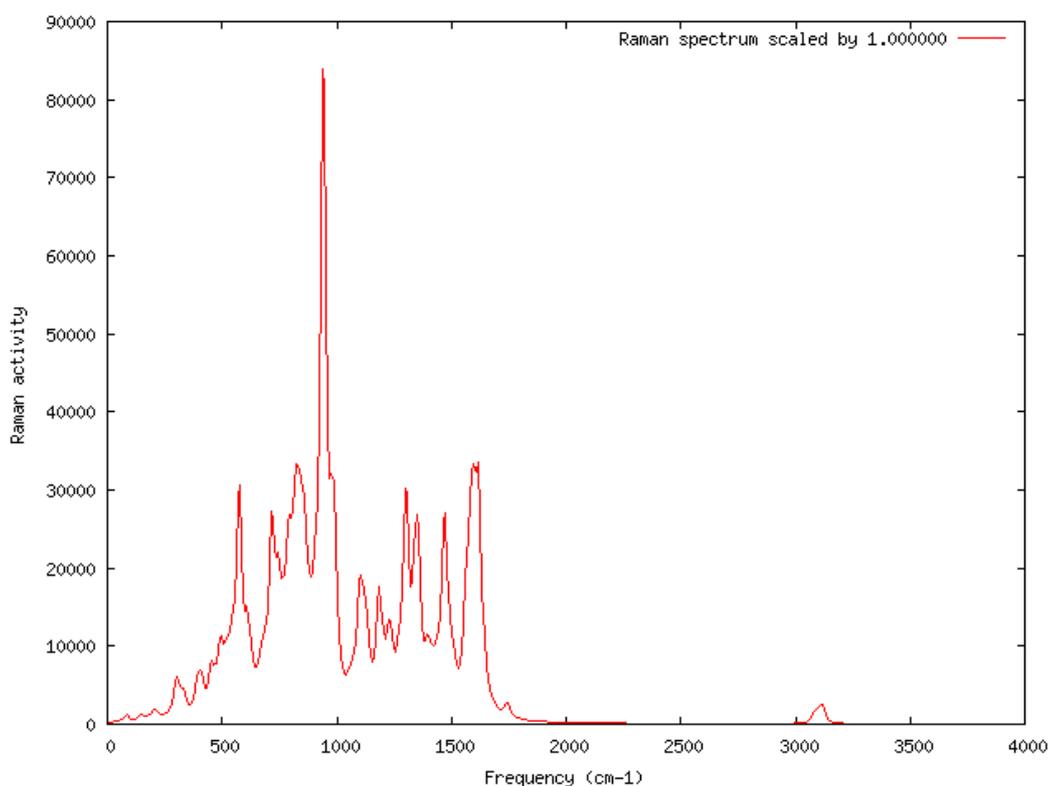Figure 5.3 Calculated FT-IR spectra of $ZnCl_2$ substituted phthalocyanine.

Figure 5.4 Calculated Raman spectra of $ZnCl_2$ substituted phthalocyanine.

5.4 Polarizability and hyperpolarizability

Polarizabilities and hyperpolarizabilities characterize the response of a system in an applied electric field [3]. They determine not only the strength of molecular interactions (long-range intermolecular induction, dispersion forces, etc.) as well as the cross sections of different scattering and collision processes, but also the nonlinear optical properties (NLO) of the system [4,5]. It has been found that the dye sensitizer hemicyanine system, which has high NLO property, usually possesses high photoelectric conversion

performance. In order to investigate the relationships among photocurrent generation, molecular structures and NLO, the polarizabilities and hyperpolarizabilities of $ZnCl_2$ substituted phthalocyanine was calculated. The polarizabilities and hyperpolarizabilities could be computed via finite field (FF) method, sum-over state (SOS) method based on TDDFT, and coupled-perturbed HF (CPHF) method. However, the use of FF, SOS, and CPHF methods with large sized basis sets for $ZnCl_2$ substituted phthalocyanine is too expensive. Here, the polarizability and the first hyperpolarizabilities are computed as a numerical derivative of the dipole moment using B3LYP/6-311++G(d,p). The definitions [4,5] for the isotropic polarizability is

$$\alpha = \frac{1}{3}\left(\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ}\right) \quad (5.1)$$

The polarizability anisotropy invariant is

$$\Delta\alpha = \left[\frac{\left(\alpha_{XX} - \alpha_{YY}\right)^2 + \left(\alpha_{YY} - \alpha_{ZZ}\right)^2 + \left(\alpha_{ZZ} - \alpha_{XX}\right)^2}{2}\right]^{\frac{1}{2}} \quad (5.2)$$

and the average hyperpolarizability is

$$\beta_{\&} = \frac{1}{5}\left(\beta_{iiZ} + \beta_{iZi} + \beta_{Zii}\right) \quad (5.3)$$

Where, α_{XX}, α_{YY}, and α_{ZZ} are tensor components of polarizability; β_{iiZ}, β_{iZi}, and β_{Zii} (i from X to Z) are tensor components of hyperpolarizability.

Table 5.2 Polarizability (α) of the dye $ZnCl_2$ substituted phthalocyanine (in a.u.).

α_{xx}	α_{xy}	α_{yy}	α_{xz}	α_{yz}	α_{zz}	α	$\Delta\alpha$
-231.35	0.0006	-218.25	-0.0249	-1.3619	-261.51	242.03	66.006

Table 5.3 Hyperpolarizability (β) of the dye $ZnCl_2$ substituted phthalocyanine (in a.u.).

β_{xxx}	β_{xxy}	β_{xyy}	β_{yyy}	β_{xxz}	β_{xyz}	β_{yyz}	β_{xzz}	β_{yzz}	β_{zzz}	β_{ii}
0.076	-1.812	0.0351	-38.40	-93.91	-0.025	51.75	-0.060	-3.456	-3.207	27.81

Tables 5.2 and 5.3 list the values of the polarizabilities and hyperpolarizabilities of the dye $ZnCl_2$ substituted phthalocyanine. In addition to the individual tensor components of the polarizabilties and the first hyperpolarizabilities, the isotropic polarizability, polarizability anisotropy invariant and hyperpolarizability are also calculated. The calculated isotropic polarizability of $ZnCl_2$ substituted phthalocyanine is 242.03 a.u. However, the calculated isotropic polarizability of JK16, JK17, dye 1, dye 2, D5, DST and DSS is 759.9, 1015.5, 694.7, 785.7, 510.6, 611.2 and 802.9 a.u., respectively [6,7]. The above data indicate that the donor-conjugate pi bridge-acceptor (D-π-A) chain-like dyes have stronger response for external electric field. Whereas, for dye sensitizers D5, DST, DSS, JK16, JK17, dye 1 and dye 2, on the basis of the published photo-to-current conversion efficiencies, the similarity and the difference of geometries, and the calculated isotropic polarizabilities, it is found that the longer the length of the conjugate bridge in similar dyes, the larger the polarizability of the dye molecule, and the lower the photo-to-current conversion efficiency.

This may be due to the fact that the longer conjugate-π-bridge enlarged the delocalization of electrons, thus it enhanced the response of the external field, but the enlarged delocalization may be not favorable to generate charge separated state effectively. So it induces the lower photo-to-current conversion efficiency.

138

5.5 Electronic Absorption Spectra and Sensitized Mechanism

In order to understand the electronic transitions of $ZnCl_2$ substituted phthalocyanine, TDDFT calculations on electronic absorption spectra in vacuum were performed, and the results are shown in Figure 5.5. It is observed that, for $ZnCl_2$ substituted phthalocyanine, the absorption in the visible region is much weaker than that in the UV region. The calculated results have a red-shift with experimental results. The results of TDDFT have an appreciable red-shift, and the degree of red-shift in solvent is more significant than that in vacuum. The discrepancy between experimental and solvent effects in TDDFT calculations may result from two aspects. The first aspect is smaller gap of materials which induces smaller excited energies. The other is solvent effects. Experimental measurements of electronic absorptions are usually performed in solution. Solvent, especially polar solvent, could affect the geometry and electronic structure as well as the properties of molecules through the long-range interaction between solute molecule and solvent molecule. For these reasons it is more difficult to make the TDDFT calculation is consistent with quantitatively. Though the discrepancy exists, the TDDFT calculations are capable of describing the spectral features of $ZnCl_2$ substituted phthalocyanine because of the agreement of line shape and relative strength as compared with the experimental and calculated values.
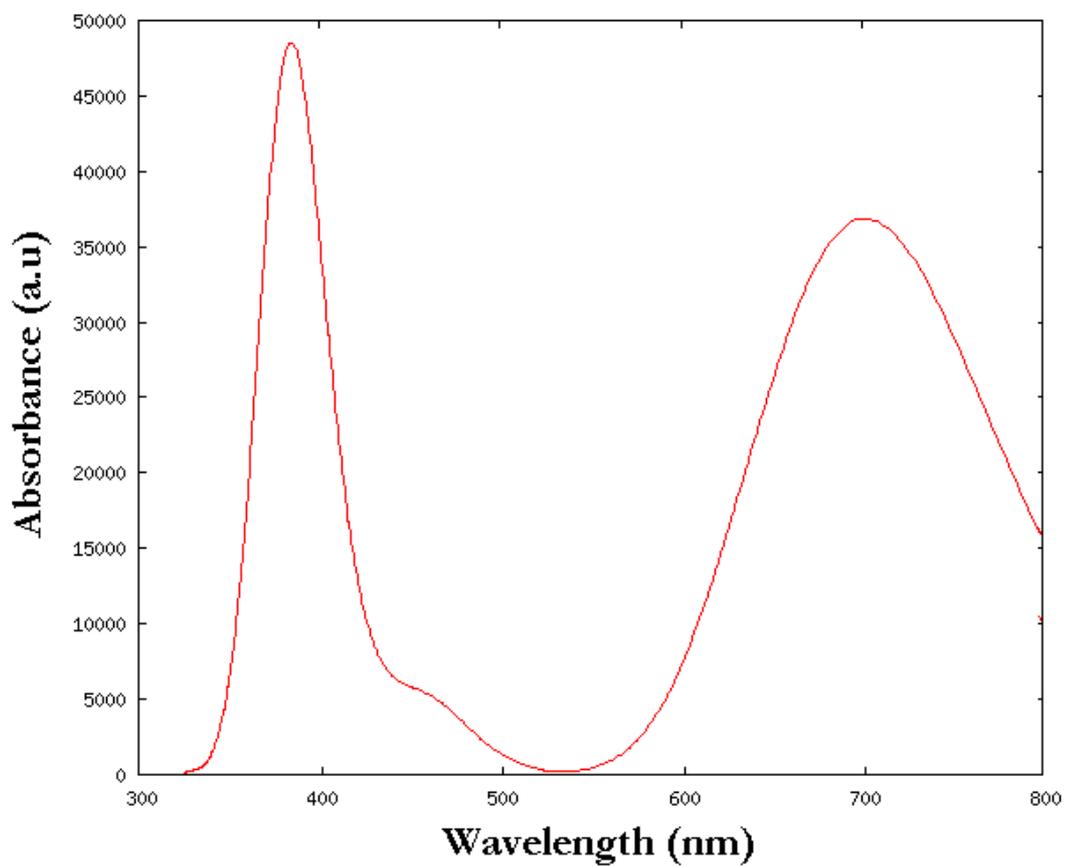
Figure 5.5 Calculated UV/Vis spectra of Zinc dichloride substituted phthalocyanine.

The HOMO-LUMO gap of $ZnCl_2$ substituted phthalocyanine in acetonitrile at B3LYP/6-311++G(d,p) theory level is smaller than that in vacuum. This fact indicates that the solvent effects stabilize the frontier orbitals of $ZnCl_2$ substituted phthalocyanine. So it induces the smaller intensities and red-shift of the absorption as compared with that in vacuum.

In order to obtain the microscopic information about the electronic transitions, the corresponding MO properties are checked. The absorption in visible and near-UV region is the most important region for photo-to-current conversion, so only the 20 lowest singlet/singlet transitions of the absorption band in visible and near-UV region for $ZnCl_2$ substituted phthalocyanine is listed in Table 5.4. The data of Table 5.4 and Figure 5.5 are based on the 6-311++G(d,p) results with solvent effects involved.

Table 5.4 Computed excitation energies, electronic transition configurations and oscillator strengths (f) for the optical transitions with f > 0.01 of the absorption bands in visible and near- UV region for the dye $ZnCl_2$ substituted Phthalocyanine

| State	Configurations composition (corresponding transition orbitals)	Excitation energy (eV/nm)	Oscillator strength (f)
1	-0.11094 (151 →158) -0.11371 (154 →158) 0.59483 (156 →157)	1.7676 eV / 701.41 nm	f=0.3220
2	0.12947 (153 →157) 0.17562 (154 →157) 0.61189 (156 →158)	1.9230 eV / 644.73 nm	f=0.2506
3	0.69455 (155 →157)	2.7805 eV / 445.90 nm	f=0.0013
4	0.18589 (153 →157) 0.64914 (154 →157)	2.8610 eV / 433.36 nm	f=0.0636
5	0.67294 (156 →159)	3.0585 eV / 405.37 nm	f=0.0081

6	-0.10566 (149 →158) 0.67247 (155 →158)	3.1214 eV / 397.20 nm	f=0.0023
7	-0.18940 (153 →158) 0.63238 (154 →158)	3.2406 eV / 382.60 nm	f=0.0356
8	-0.28058 (151 →157) 0.45485 (153 →157) 0.41903 (156 →160)	3.2467 eV / 381.88 nm	f=0.0617
9	0.41426 (150 →157) 0.37786 (151 →157) -0.10130 (152 →158) 0.36431 (156 →160)	3.3778 eV / 367.05 nm	f=0.0066
10	0.13395 (147 →157) 0.32174 (149 →157) 0.12531 (151 →158) 0.56069 (152 →157) -0.13023 (153 →158)	3.3824 eV / 366.55 nm	f=0.0221

11	0.48844 (149 →157) -0.11694 (150 →158) -0.24616 (151 →158) -0.19474 (152 →157) 0.33173 (153 →158)	3.4040 eV / 364.23 nm	f=0.0047
12	-0.10529 (146 →157) -0.10145 (147 →157) -0.31421 (149 →157) -0.14649 (150 →158) -0.17916 (151 →158) 0.28748 (152 →157) 0.39749 (153 →158) 0.15125 (154 →158) 0.17300 (156 →161)	3.4446 eV / 359.94 nm	f=0.0122
13	0.16851 (148 →157) 0.32837 (151 →157)	3.4467 eV / 359.72 nm	f=0.4623

	0.43476 (153 →157)		
	-0.27780 (156 →160)		
14	0.49376 (146 →157) 0.27812 (147 →157) -0.19100 (148 →158) -0.30820 (150 →158) -0.11210 (151 →158)	3.5168 eV / 352.54 nm	f=0.0015
15	0.16998 (147 →158) 0.29151 (148 →157) 0.45106 (150 →157) -0.28879 (151 →157) 0.21851 (152 →158) -0.16308 (156 →160)	3.5324 eV / 351.00 nm	f=0.0565
16	-0.34518 (146 →157) 0.37661 (147 →157) -0.15123 (149 →157)	3.5424 eV / 350.00 nm	f=0.0180

	-0.26380 (150 →158)		
	0.15070 (151 →158)		
	-0.30889 (156 →161)		
17	-0.25994 (146 →157) -0.16555 (147 →157) -0.29426 (148 →158) -0.26585 (150 →158) -0.11443 (152 →157) -0.25503 (153 →158)	3.5643 eV / 347.85 nm	f=0.0193
18	0.53331 (148 →157) 0.26954 (149 →158) -0.23729 (150 →157) 0.13616 (156 →160)	3.5859 eV / 345.76 nm	f=0.0256
19	0.41592 (147 →157) 0.26847 (148 →158) 0.17897 (150 →158)	3.6374 eV / 340.86 nm	f=0.0460

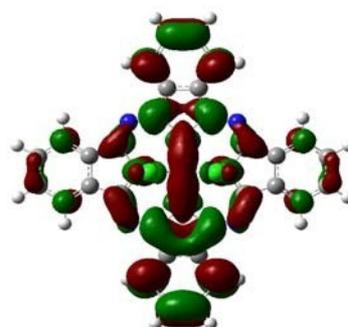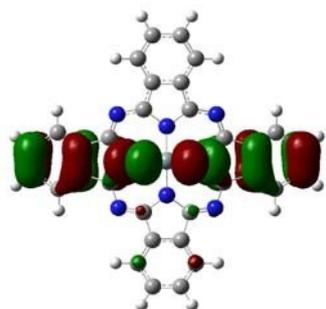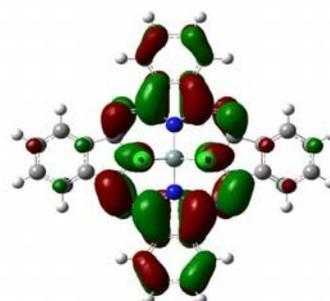|			
	-0.11750 (151 →158) 0.37550 (156 →161)		
20	0.10343 (144 →157) -0.21360 (146 →158) -0.28929 (147 →158) -0.33913 (149 →158) -0.10277 (150 →157 0.36630 (152 →158) 0.24289 (156 →163)	3.7076 eV / 334.41 nm	f=0.0041
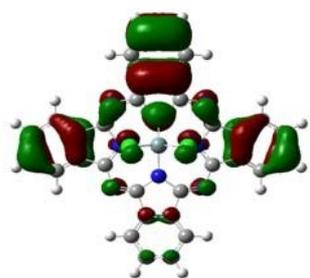
HOMO-3 (-7.19 eV)
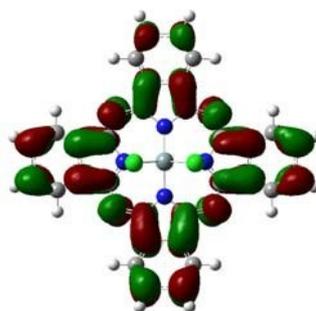
LUMO+3 (-1.59 eV)
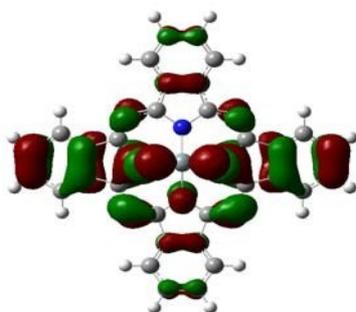
HOMO-2 (-6.93eV)

LUMO+2 (-1.79 eV)

HOMO-1 (-6.89eV)

LUMO+1 (-3.20 eV)

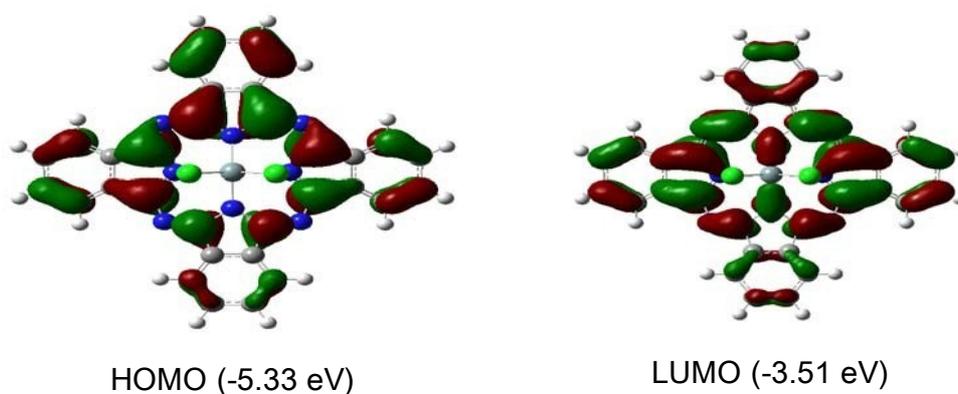HOMO (-5.33 eV)   LUMO (-3.51 eV)

Figure 5.6 Isodensity plot (isodensity contour = 0.02 a.u.) of the frontier orbitals of ZnCl$_2$ substituted phthalocyanines and corresponding orbital energy.

This indicates that the transitions are photoinduced charge transfer processes, thus the excitations generate charge separated states, which should favour the electron injection from the excited dye to semiconductor surface.

The solar energy to electricity conversion efficiency (η) under AM 1.5 white-light irradiation can be obtained from the following formula:

$$\eta(\%) = \frac{J_{SC}[mAcm^{-2}]V_{OC}[V]ff}{I_0[mWcm^{-2}]} \times 100 \qquad (5.4)$$

Where I$_0$ is the photon flux, J$_{sc}$ is the short-circuit photocurrent density, and V$_{oc}$ is the open-circuit photovoltage, and ff represents the fill factor [8]. At

present, the J_{sc}, the V_{oc}, and the ff are only obtained by experiment, the relationship among these quantities and the electronic structure of dye is still unknown. The analytical relationship between V_{oc} and E_{LUMO} may exist. According to the sensitized mechanism (electron injected from the excited dyes to the semiconductor conduction band) and single electron and single state approximation, there is an energy relationship:

$$eV_{oc} = E_{LUMO} - E_{CB} \qquad (5.5)$$

Where, E_{CB} is the energy of the semiconductor's conduction band edge. So the Voc may be obtained applying the following formula:

$$V_{oc} = \frac{(E_{LUMO} - E_{CB})}{e} \qquad (5.6)$$

It induces that the higher the E_{LUMO}, the larger the V_{oc}. The results of organic dye sensitizer JK16 and JK17 [7], D-ST and D-SS also proved the tendency [9] (JK16: LUMO = -2.73 eV, V_{oc} = 0.74 V; JK17: LUMO = -2.87 eV, V_{oc} = 0.67 V; D-SS: LUMO = -2.91 eV, V_{oc} = 0.70 V; D-ST: LUMO = -2.83 eV, V_{oc} = 0.73 V). Certainly, this formula expects further test by experiment and theoretical calculation. The J_{sc} is determined by two processes, one is the rate of electron injection from the excited dyes to the conduction band of semiconductor, and the other is the rate of redox between the excited dyes and electrolyte. Electrolyte effect on the redox processes is very complex, and it is not taken into account in the present

calculations. This indicates that most of excited states of $ZnCl_2$ substituted phthalocyanine have larger absorption coefficient, and then with shorter lifetime for the excited states, so it results in the higher electron injection rate which leads to the larger Jsc of $ZnCl_2$ substituted phthalocyanine. On the basis of above analysis, it is clear that the $ZnCl_2$ substituted phthalocyanine has better performance in DSSC.

References

[1]   M. K. Nazeeruddin, F. De Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S.Ito, B. Takeru, M. Gratzel, J. Am. Chem. Soc. 2005, 127, 16835.

[2]   M. J. Lundqvist, M. Nilsing, P. Persson, S. Lunell, Int. J. Quantum Chem. 2006, 106, 3214.

[3]   C. R. Zhang, H. S. Chen, and G. H. Wang, Chem. Res. Chin. U. 2004, 20, 640.

[4]   Y. Sun, X. Chen, L. Sun, X. Guo, W. Lu, Chem. Phys. Lett. 2003, 381, 397.

[5]   O. Christiansen, J. Gauss, J. F. Stanton, Chem. Phys. Lett. 1999, 305, 147.

[6]   Z. S. Wang, Y. Y. Huang, C. H. Huang, J. Zheng, H.M. Cheng, S. J. Tian, Synth. Met. 2000, 14, 201.

[7]   C. R. Zhang, Y. Z. Wu, Y. H. Chen, H. S. Chen, Acta Phys. Chim. Sin. 2009, 25, 53.

[8]   K. Hara, T. Sato, R. Katoh, A. Furube, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H.Sugihara, H. Arakawa, J. Phys. Chem. B. 2003, 107, 597.

[9]   C.R. Zhang, Z.J. Liu, Y.H. Chen, H.S. Chen, Y.Z. Wu, L.H. Yuan, J. Mol. Struct. 2009, 899, 86.