

A Theoretical Study on Photosensitizers of Solar-energy Cell: Transition Metal Carboxyphthalocyanine Complexes

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Keywords: Carboxyphthalocyanine Photosensitizer; DSSC; Electronic spectra; TD-DFT

Abstract. Transition metal phthalocyanine complexes have been applied in the dye-sensitized solar cells (DSSCs), owing to their high absorbance coefficient in red-light region, good thermodynamic stability and facile synthesis. Structures of carboxyphthalocyanine complexes containing zinc, cadmium and mercury were optimized using the B3LYP functional. The M-N distances (M = Zn, Cd and Hg) were calculated to be 2.03, 2.12 and 2.16 Å, respectively. On the basis of these geometries, the electronic spectra in ethanol were predicted at the time-dependent density functional theory (TD-DFT) level. It was shown that the variation of Zn→Cd→Hg changes the transition nature of lower-energy absorption, but slightly affects the excitation energies. In addition, the effects of basis sets (Lan2DZ and SDD), solvent-effect models (PCM and CPCM) and solvents (ethanol and methanol) on absorption spectra were discussed in detail.

Introduction

Since 1991[1], the dye-sensitized solar cells (DSSCs) have been intensely investigated as possible low-cost alternatives to conventional solid-state photovoltaic devices. So far, the 11% conversion efficiency of solar to electric power for DSSC has been achieved[2]. The photosensitizer is the most important part in DSSCs, absorbing sunlight to form its excited state and then injecting the photo-generated electron into conductor band of semiconductor electrode[3]. The polypyridyl Ru(II)-type dye is one of the most successful sensitizers applied in DSSCs[4]. Owing to its expensive cost and low utilization for the red part of sunlight, there is a quest for other transition metal complex sensitizers that achieve effective harnessing of the low-energy sunlight[5]. Up to now, special attention has devoted to the phthalocyanine complex with metal ions such as Zn(II), Cd(II) and Hg(II) [6]. Their photophysical, electrochemical and excited-state properties have been extensively studied in experiments. Besides a large amount of experimental exploration, theoretical studies are helpful to understanding their electronic properties, ensuring the improvement for the overall conversion efficiency of DSSC. In this work, we theoretically explored a series of carboxyphthalocyanine complexes containing Zn(II), Cd(II) and Hg(II) center ions. Their structures in the ground states were optimized, and related electronic structures and spectroscopic properties were discussed in detail.

Computational details

In the study, we optimized three carboxyphthalocyanine complexes with zinc(II), cadmium(II) and mercury(II) center ions, labeled as **Zncpc**, **Cdcpc** and **Hgcpc**, using the B3LYP functional. Up to now, the electronic spectroscopy of a similar zinc complex[6] has been reported, but the information about their crystal structures is not available. On the basis of the optimized structures, the time-dependent density functional theory (TD-DFT) was performed to calculate absorption spectra of complexes. As indicated in our previous studies[7-8], many factors affect the electronic spectra. Different solvent-effect models (PCM and CPCM), solvents (ethanol and methanol) and basis sets (SDD and LanL2DZ, belonging to small core effective core potentials) were used in the calculations. All the calculations were accomplished using the *Gaussian03* program package[9].

Results and discussion

Geometry Structures. Accurate functional, suitable basis sets and relativistic approximation will present a reasonable description of sensitizer's structure, especially for the ground state. In Table 1, we summarized the optimized geometry parameters of **Zncpc**, **Cdcpc** and **Hgcpc** in the ground state. The optimized structures were depicted in Fig. 1.

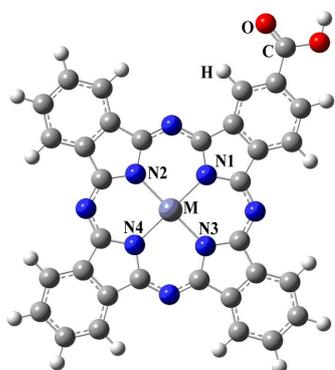


Fig. 1 Structures of Zn, Cd and Hg carboxyphthalocyanine complexes

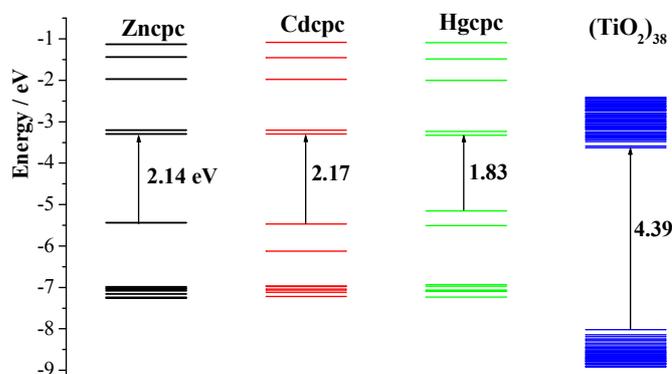


Fig. 2 Diagrams of frontier molecular orbitals of complexes in ethanol under the TD-B3LYP/PCM calculations.

In the ground state, all the Zn-N bond lengths of **Zncpc** were calculated between 2.023 and 2.026 Å, where the Zn-N bond close to the carboxyl group is a bit longer. Similar cases were found in the calculations on **Cdcpc** and **Hgcpc**. Due to lanthanum contraction, the calculated Cd-N and Hg-N are relatively close, corresponding to 2.118 and 2.162 (mean values), respectively. Additionally, the d^{10} metal center is square-planar coordination, with 90° N1-M-N2 angle and 180° N1-M-N4 one.

Table 1. Optimized geometry parameters of complexes (Distances in Å and angles in $^\circ$)

Parameters	Zncpc	Cdcpc	Hgcpc
M-N1	2.026	2.119	2.163
M-N2	2.025	2.118	2.161
M-N3	2.023	2.117	2.161
M-N4	2.024	2.118	2.162
N1-M-N2	90.0	90.0	90.0
N1-M-N4	180.0	180.0	180.0

Electronic Structures. Analysis on the electronic structures of **Zncpc**, **Cdcpc** and **Hgcpc** in the ethanol solution indicates that most frontier molecular orbitals are phthalocyanine-based characters. Zinc complex has the ligand-based composition for all the orbitals. Replacement of Zn with heavier Cd and Hg metals results in the change of orbital compositions. The HOMO-1, for example, has only 0.4% metal composition for the Zinc sensitizer, while those of Cadmium and Mercury counterparts possess about 14.5% and 21.5% metal contribution, respectively. LUMO+2 is quite similar for the carboxylic group contribution. The contribution of -COOH to LUMO+2 in the Cd and Hg sensitizers is about 20% more than that (0.8%) in Zinc sensitizer. In addition, the electronic structures of **Zncpc**, **Cdcpc** and **Hgcpc** are different from those of the reported famous Ru(II) polypyridine complexes, which feature the antibonding combination of $d(\text{Ru})$ and $\pi(\text{NCS})$ characters for the higher-energy occupied orbitals, and the $\pi^*(\text{polypyridine})$ for the lower-energy unoccupied orbitals.

A schematic orbital energy diagram of the investigated carboxyphthalocyanine complexes in solution was depicted in Fig. 2. The HOMO energy of **Zncpc** complex was calculated to be at -3.30 eV, and the HOMOs of other complexes were kept unchanged, ranging from -3.30 to -3.32 eV. The LUMOs energies are -5.44, -5.47 and -5.15 eV for **Zncpc**, **Cdcpc** and **Hgcpc**, respectively. There is only a

relative apparent stabilization of 0.32 eV from cadmium complex to mercury one due to the relativistic effect of heavy mercury metal. At the B3LYP/LanL2DZ theory level, we calculated the energetics of anatase cluster (TiO₂)₃₈ in solution, showing HOMO (-8.01 eV) and LUMO (-3.62 eV). In the thermodynamic point of view, it is possible to inject electron from the excited states of currently investigated carboxyphthalocyanine dyes into the conduction band of TiO₂ semiconductor.

Electronic Spectra. To improve the conversion efficiency of light into electricity, exploration on absorption spectra of the sensitizer is of importance. The electronic absorptions of **Zncpc**, **Cdcpc** and **Hgcpc** in ethanol were obtained by the TD-DFT/PCM calculations. In Table 2, the transition energies (eV / nm) and oscillator strengths (*f*) of selected absorptions were listed. We have simulated their absorption spectra in Fig. 3 using the Gaussian function.

Table 2. Calculated absorptions in ethanol at the TD-DFT(B3LYP)/PCM level

	λ (nm)	E (eV)	Oscillator Strength (<i>f</i>)	Configurations	CI coefficient > 0.2
Zncpc	634	1.96	0.621	HOMO→LUMO	0.621
	610	2.03	0.543	HOMO→LUMO+1	0.621
Cdcpc	627	1.98	0.642	HOMO→LUMO	0.623
	620	2.00	0.000	HOMO-1→LUMO	0.697
	603	2.06	0.560	HOMO→LUMO+1	0.622
	598	2.07	0.000	HOMO-1→LUMO+1	0.698
	401	3.09	0.044	HOMO→LUMO+2	0.657
Hgcpc	622	1.99	0.647	HOMO-1→LUMO	0.625
	599	2.07	0.566	HOMO-1→LUMO+1	0.625
	398	3.12	0.042	HOMO-1→LUMO+2	0.656

For **Zncpc**, two peaks were found in the simulated spectra in Fig. 3. The lower-energy peak is located between 1.96-2.03 eV. Two transitions from the HOMO→LUMO/LUMO+1 configurations form the band as shown in Table 2. Analysis on electronic structures demonstrates the band is $\pi \rightarrow \pi^*$ transition property around phthalocyanine ligand. The 3.40-3.80 eV transitions generate a strong absorption peak, which is still a ligand-based character. Like **Zncpc**, other two chromophores display similar general pattern for absorption spectra (Fig. 3), but the variation of Zn→Cd→Hg results in a slight

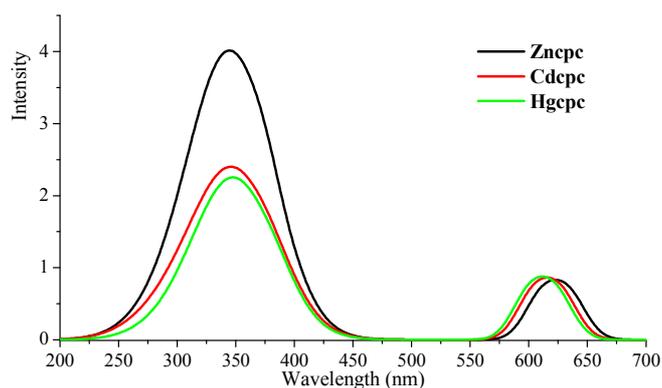


Fig. 3 Simulated absorption spectra of transition metal carboxyphthalocyanine complexes under the calculations of the TD-B3LYP method, PCM model and SDD basis sets

blueshift of the lower-energy absorption band. **Cdcpc** has the ligand-based lower-energy absorption band. Its absorption transitions contributed by HOMO-1 that is featured with 14.5% Cd composition, such as 2.00 eV (620 nm) and 2.07 eV (598 nm), can not be observed for they are spin-forbidden with zero of oscillator strength. As indicated earlier, the LUMO+2 in **Cdcpc** has 21.7% contribution of carboxylic group. So there is apparent phthalocyanine→COOH charge transfer in the 3.09 eV (401 nm) absorption transition (Table 2). Although, **Hgcpc** has similar absorption energies to those of its zinc and cadmium counterparts, its lower-energy peak has very different characters. The 1.99-2.07

absorption band comes from HOMO-1→LUMO/LUMO+1 configurations, where the HOMO-1 has 21.5% Hg composition. Therefore, we attributed the lower-energy absorption band to the combined characters of MLCT (metal-to-ligand charge transfer) and ILCT (intraligand charge transfer).

In this work, we took **Hgcp** as an example to examine the effects of basis sets, solvent-effect models and solvents on electronic spectra. The basis sets of LanL2DZ and SDD, the PCM and CPCM models, and the methanol and ethanol solvents were used in the TD-DFT calculations. It was shown that such variation does not change the nature of absorption transitions, and affects absorption excitation energies slightly.

Summary

The structures and spectroscopic properties of **Mcp** (M = Zn, Cd and Hg) were investigated by DFT and TD-DFT methods. Our calculations show that the zinc chromophore displays phthalocyanine-based characters for all the orbitals, whereas there are metal participation in the occupied orbitals and the carboxylic group contribution to the unoccupied orbitals for the cadmium and mercury complexes.

The electronic spectra in ethanol were obtained under the TD-DFT/PCM calculations. Two types of absorption bands were found with the featured characters of MLCT/ILCT and ILCT for **Hgcp**, and only ILCT is responsible for absorptions of **Zncp** and **Cdcp**. In addition, our study revealed that different basis sets, solvent-effect models and solvents has a slight effect on the electronic spectra of complexes.

Acknowledgments

This work is the Natural Science Foundation of China (No. 20703015, 30901136), the Program for New Century Excellent Talents of Common Universities of Heilongjiang Province of China (No. 1154-NCET-010), the Key Project of Chinese Ministry of Education (No. 211048), the Scientific Research Foundation for the Postdoctoral Fellow of Heilongjiang Province (2010) and the Special Fund from the Central Collegiate Basic Scientific Research Bursary (No. DL11CB07).

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10.4028/www.scientific.net/AMR.415-417

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10.4028/www.scientific.net/AMR.415-417.1287