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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Theoretical Insight into Novel Zinc Di-Corrole Dye with Excellent Photoelectronic Properties for Solar Cells

Chun Zhu,*^a and Jin-Xia Liang*^b

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Zinc di-corrole dye (**Zn-cor** dye), which has been constructed by substitution of Ga of Ga di-corrole dye (**Ga-cor** dye) with zinc, has been characterized having a strong light harvesting ability by density functional theory calculations. And charge has been significantly separated in its excited states. It is worthy of note that inserting different central metals can adjust the optical and charge-transfer properties of this kind of dyes, which are quite promising for fabrication of the high performance dye-sensitized solar cells. Based on the first-principles calculations, possible mechanisms for direct electron injections from the adsorbed dye to TiO₂ have been discussed with analyses the band structure and DOS of **Zn-cor** dye-TiO₂ system.

1 Introduction

As O'Regan and Grätzel reported their pathbreaking work in 1991¹, Dye -sensitized solar cells (DSCs), which is an economical and environmentally friendly photoelectric device compared to silicon-based photoelectric conversion device, have attracted increasing interest. In the past few decades, the theoretical and experimental scientists have made a great of efforts to improve the power conversion efficiency (PCE) of DSCs,²⁻³¹ from exploring new and efficient dyes,^{2-16,27-31} modifying the semiconductor structure¹⁷⁻²⁰ to optimizing the electrolyte composition,²¹⁻²³ as well as exploiting different photoactive working electrodes and counter electrodes.²⁴ Among these factors, the dyes with wide absorption band and high absorption efficiency play a crucial role responsible for the performance improvement of DSCs. Over the past decades, scientists have explored a variety of dyes to DSCs, involving metal complexes, porphyrins, phthalocyanines as well as metal-free organic dyes.³² Among these dyes, the performance of the ruthenium sensitizer with efficient light-harvesting, incorporating an electron-rich hexylthio-terminal chain and in conjunction with iodide/triiodide redox couple, were excellent, and its PCE is higher than 11%.³³⁻³⁵

On the other hand, the research on porphyrin dyes playing an important role in nature photosynthesis have made rapid progress in solar cells applications in recent years, and the new PCE record of 12.3% has been reached for the porphyrin-based solar cells in combination with the cobalt-based redox electrolyte.³ The corrole,^{25,36} of which structure is very similar to porphyrin, just its two pyrrole rings connecting directly, demonstrate novel photophysical properties compared with porphyrin, such as lower oxidation potentials, larger Stokes shift, and relatively more intense absorption in the red light region.³⁷ However, few researches have focused on the corrole-based dyes in DSCs.

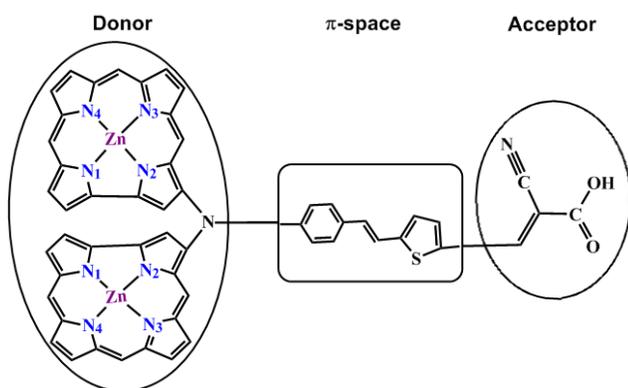
Walker etc. have reported their research that the corrole-sensitized TiO₂ solar cells were found to have relatively low PCEs.³⁸

Recently, we designed a novel type of corrole-based dyes with the unique Ga di-corrole structure (**Ga-cor**),³⁹ which exhibits strong light harvesting ability and excellent charge separation properties. And its optical and electronic properties can be well modulated by incorporation different metals. Moreover, their adsorbed TiO₂ systems demonstrate excellent efficiency of charge transference from dye to semiconductor. In order to further improve PCE of corrole-based DSCs, enrich the knowledge about corrole dyes and expand their application, herein, new zinc di-corrole dye (**Zn-cor**) have been designed by substitution Ga of **Ga-cor** with Zn. Their optical and electronic properties were studied by extensive DFT calculations. The effect of structure on properties of the dye was discussed. Furthermore, their interactions with TiO₂ was explored and plausible electron injection mechanisms have been suggested.

2 Computational details

The optical and electronic properties of the isolated dye molecules were studied by using Gaussian 09 package. The B3LYP^{40,41} hybrid functional in combination with the all-electron 6-31G(d) basis set⁴² was used in DFT calculations. The structures of dyes were full optimized without any symmetry constraints. And frequencies were computed to access the nature of stationary points on the potential-surfaces. The continuum solvation model of SMD⁴³ was use to evaluate the solvent effects. Acetonitrile was considered to be a solvent by analogy to the general experimental medium. Time-dependent density functional theory (TD-DFT) with CAM-B3LYP^{44,45} exchange-correlation functional was used to compute vertical excitation energies based on the optimized structures by B3LYP.

The TiO₂ nano-particle in DSCs was model by the two-



Scheme 1 Unique **Zn-cor** dye consisting of the zinc di-corrole (donor), different π -space bridge-conjugated groups, and the cyanoacrylate group (acceptor)

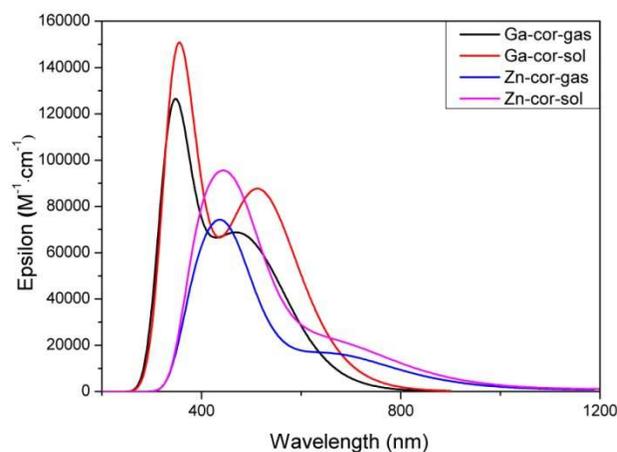


Fig. 2 Calculated UV-Vis spectra of **Ga-cor** and **Zn-cor** in the gas phase and in acetonitrile, respectively

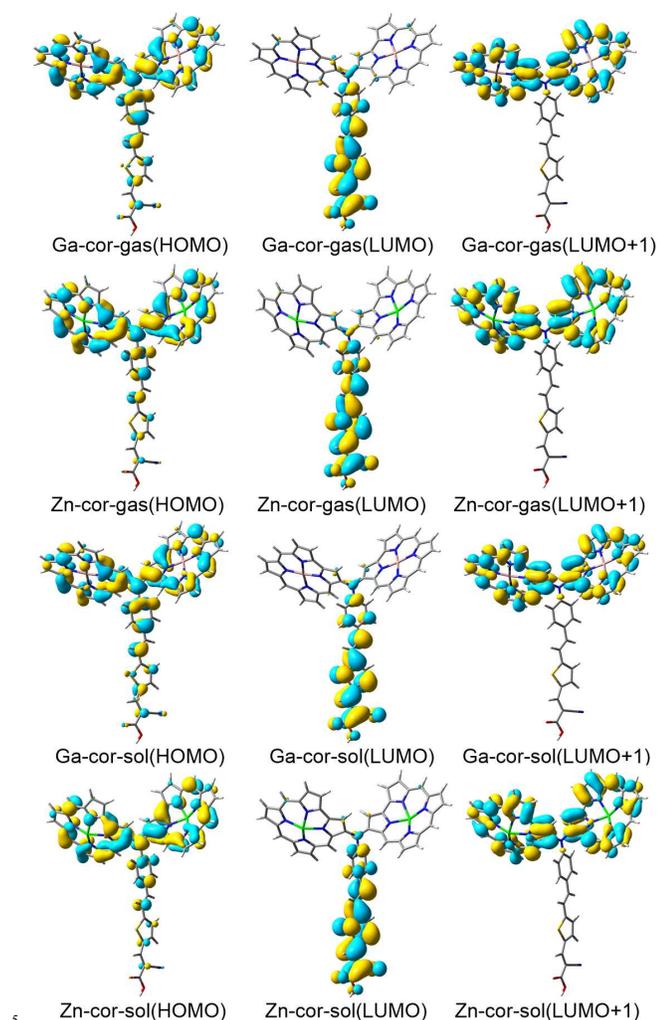


Fig. 1 Optimized structures and selected molecular orbitals of **Ga-cor** and **Zn-cor** in the gas and solution

dimensional slab model of TiO_2 nanostructure obtained by
 10 appropriately cutting the most stable anatase TiO_2 (101) surface.

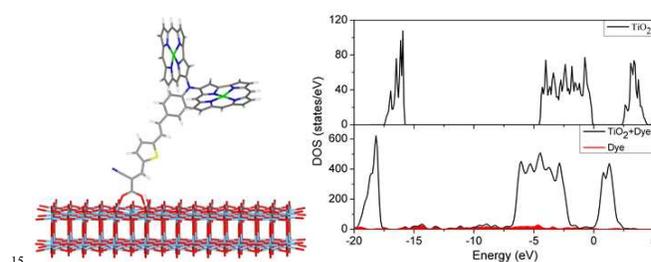


Fig. 3 (a) Optimized structure of **Zn-cor**/ TiO_2 system with the dye **Zn-cor** adsorbed on the surface of TiO_2 semiconductor nano-material; (b) The total density of states (DOS) of bare TiO_2 (on the top) and the total DOS and partial density of states (PDOS) of **Zn-cor**/ TiO_2 system (at the bottom)

Calculations of the structural and electronic properties for the periodic systems with and without the adsorbed sensitizer were performed by using the plane-wave technique implemented in
 25 Vienna ab initio simulation package (VASP).^{46,47}

The exchange-correction potential was described by generalized gradient approximation (GGA) with the PBE functional⁴⁸ in all calculations. The projector augmented wave (PAW) method⁴⁹ was employed to describe the electron-ion interaction and the cutoff energy was set to 380 eV. The conjugated gradient method was used to optimize all atomic positions with the converging tolerance of 0.02 eV/Å for the force on all atoms. The 2D periodic boundary conditions are employed along the growth direction of the slab TiO_2 nanostructure. A vacuum distance >8 Å
 30 was set to keep the negligible interaction between layer nanostructures in the adjacent cells. Monkhost pack meshes of Gamma point were used for the geometry optimization. The $2 \times 2 \times 1$ and $11 \times 11 \times 1$ Γ -centered k -point meshes were used in the density of states (DOS) integral for the periodic systems with and
 35 without the adsorbed dye, respectively. The Brillouin zone was sampled by 44 k -point and 20 k -point by using the line-mode to calculate their electronic band structures.

3 Results and discussion

3.1 Electronic and optical properties of free **Zn-cor** dyes

Cite this: DOI: 10.1039/c0xx00000x

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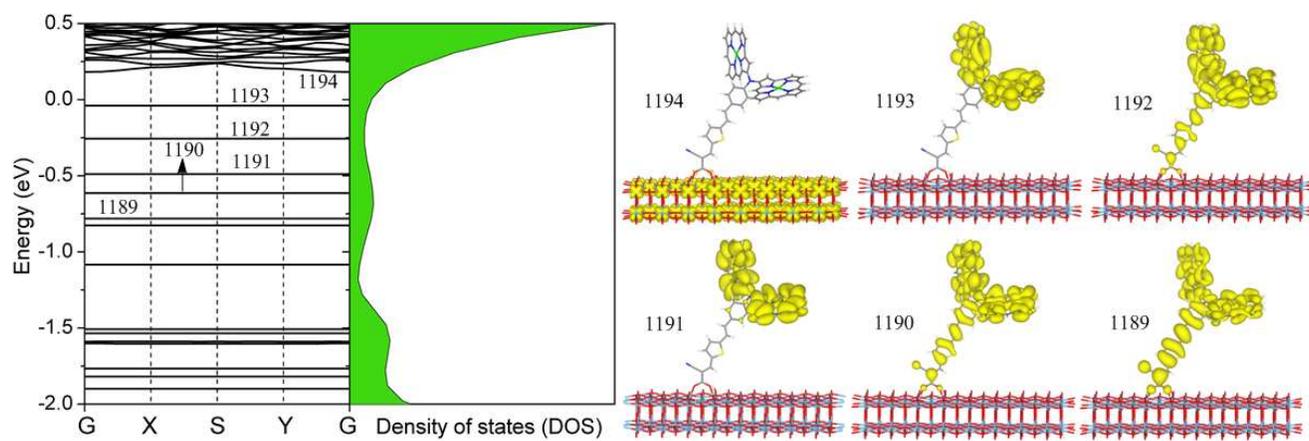


Fig. 4 The band structures and the density of states of the **Zn-cor**/TiO₂ system (on the right), the selected occupied molecular orbitals of **Zn-cor** in the ground state (at the bottom) and the partial charge densities (isovalue 0.0004 au) for the Gamma point of the 1189-1194 bands corresponding to the identified band structures, respectively

Table 1 HOMO-LUMO Energy gaps (E_g in eV), transition energies (λ), selected excited states and corresponding bands and oscillator strength (f) for **Ga-cor** and **Zn-cor** dyes in the gas phase and solvent

Molecular	$-E_{\text{HOMO}}$	$-E_{\text{LUMO}}$	E_g	$\lambda/\text{nm}(\text{ev})$	Excited state	f	LHE	ΔG_{inject} (eV)
Ga-cor-gas	4.72	2.66	2.06	541 (2.29)	231→233	0.4201	0.62	-1.57
				524(2.36)	231→232	0.5363		
				454(2.73)	(H)231→232(L)	0.9792		
				407(3.05)	231→233	0.3683		
Ga-cor-sol	4.72	2.78	1.94	548(2.26)	231→233	0.5294	0.70	-1.54
				538(2.31)	(H)231→232(L)	0.9414		
				474(2.61)	231→232	0.8506		
				410(3.03)	231→233	0.4296		
Zn-cor-gas	5.66	1.79	3.87	465(2.67)	(H)241A→242A(L)	0.7789	0.83	-1.01
				680(1.82)	241A→243A 237B→240B	0.2002		
Zn-cor-sol	5.57	1.82	3.75	485(2.55)	(H)241A→242A(L)	0.6786	0.79	-0.98
				480(2.58)	(H)241A→242A(L)	0.3391		

Similar to our previous unique Ga di-corrole dyes,³⁹ here **Zn-cor** dye was constructed by using the phenylamino moiety as the electron donor, of which hydrogen atoms were substituted by Zn-corrole rings, and the cyanoacry acid as the electron acceptor, as shown in Scheme 1. Their frontier molecular orbitals are displayed in Figure 1 and the predicted UV-vis spectra in the gas phase and in acetonitrile are shown in Figure 2. As Figure 1 displays, their highest-occupied molecular orbitals (HOMOs) are mainly distributed over the donor of dyes and the lowest-unoccupied molecular orbitals (LUMOs) are basically spread over the bridge-anchor moiety of dyes, indicating the significant charge separation between their HOMO and LUMO.

There are two quasi-porphyrin characteristic absorption bands in visible region in the predicted UV-vis spectra of **Zn-cor** dye,

corresponding to the Soret and Q bands, respectively, as shown in Figure 2 and Table 1. Furthermore, the **Zn-cor** dye exhibits the stronger absorptions in acetonitrile solution with respect to the gas phase as found in the **Ga-cor** dye.³⁹ In comparison with **Ga-cor** dyes,³⁹ the absorptions in the visible region of **Zn-cor** dye is red shift (shown in Figure 2). As seen from Table 1, the largest oscillator strength (f) 0.7789 and 0.6786 for **Zn-cor** in gas phase and in acetonitrile respectively, both of which are correspond to the excited electron from HOMO to LUMO, showing that these spectroscopic features are very favorable for the dyes to harvest the solar energy in practical application of DSCs.

In addition, short-circuit current density (J_{SC}) is another crucial factor to improve the PCE of DSCs, which is mainly determined by the light harvesting efficiency (LHE) and the electron injection

efficiency (Φ_{inject}) closely related to the driving force (ΔG_{inject}) of the electron injection, where LHE can be computed by the relationship: $LHE=1-10^{-f}$,⁵⁰ where f is the absorbance of the dye at the maximum wavelength, and ΔG_{inject} can be computed by Katoh's equation,⁵¹ respectively. And Table 1 lists the predicted orbital energies, transition energies, and factors accounting for the performance improvement of DSCs.

As Table 1 shows, in comparison with the **Ga-cor** dye,³⁹ **Zn-cor** dye have relatively small ΔG_{inject} . However, with the introduction of zinc metal center, LHE of the **Zn-cor** dye increases significantly indicating that the introduction of zinc metal center will enhance the light absorption.

3.2 Electronic properties of the Zn-cor dye-TiO₂ system

Adsorption of Zn-cor dye on the TiO₂ surface. In order to evaluate the performance of the **Zn-cor** dye adsorbed on TiO₂ substrate for DSCs, the interaction between the novel sensitizer and the TiO₂ nano-particle is further investigated. Here the most probably adsorption mode, following with previous investigations,^{52,53} the bridged-bidentate coordination with the deprotonated form for its cyanoacrylic acid anchoring group, has been researched. The optimized structure of the **Zn-cor** adsorbed TiO₂ system is shown in Figure 3a, where the dye molecule is bound to the TiO₂ surface by bidentatively chelating model, in which its two oxygen atoms connect with two titanium atoms on the TiO₂ (101) surface, and the proton is transferred to the oxygen atom on the surface of TiO₂ near the adsorbed position. The internal geometrical parameters of **Zn-cor** dye slightly vary, except for the anchoring group before and after adsorption on the surface of TiO₂, demonstrating the overall rigidity of the backbone of the **Zn-cor** dye. The average distances of Ti–O (2.18 Å) between the carboxylic oxygen atoms of the **Zn-cor** dye and the Ti atoms on the (101) surface of TiO₂ in the chelate configuration are very similar to that (2.19 Å) of **Ga-cor** dye,³⁹ and the bonds are comparable to the Ti–O distance (1.973 Å) in the bulk TiO₂, revealing the strong interaction between the **Zn-cor** dye and the TiO₂ surface.

Energy band structure and density of states. The density of states (DOS) of the bare TiO₂, the total DOS and the **Zn-cor** partial DOS (PDOS) of the **Zn-cor**/TiO₂ system are computed and provided in Figure 3b on the basis of the optimized structure to further investigate the electronic coupling strength between the **Zn-cor** dye and TiO₂ semiconductor. As Figure 4 shows, some new π -occupied levels on the top of the TiO₂ valence band are introduced owing to the **Zn-cor** adsorption compared with the DOS of bare TiO₂, which are corresponding to the linear band structures, illustrating that the molecular orbitals of **Zn-cor** dye entirely account for these new levels. It is worthy of note that there are the broad surface valence bands and conduction bands with a relatively large band gap (2.64 eV by PBE and 3.86 eV by HSE06) in bare TiO₂ model and the PDOS of **Zn-cor** dye strongly overlap with the valence bands and the higher energy conduction bands of the TiO₂ semiconductor over a wide range of energies. Thus the top of the valence band of the **Zn-cor**/TiO₂ system arise from the new π -occupied levels of **Zn-cor** dye. As the pure functional GGA-PBE generally underestimates the band gap remarkably, following previous study,³⁹ the band gap is corrected by the hybrid functional HSE06 calculation, which can predict relatively accurate band gap,^{54,55}. The increment of 1.22

eV is incorporated into the underestimated gaps.³⁹ Accordingly, the corrected band gap of the dye-TiO₂ system is 1.36 eV.

Electronic injection mechanism. Further comparison of the partial charge densities at Gamma (G) point of bands of the **Zn-cor**/TiO₂ system and the molecular orbitals of the free **Zn-cor** dye, as shown in Figure 4, shows that the partial charge density of the highest valence band 1193 at G point of the **Zn-cor**/TiO₂ system is very similar to the HOMO orbital, suggesting that the band mainly comes from the contribution of the HOMO of pure **Zn-cor** dye. On the contrary, the lowest unoccupied band 1194 of the **Zn-cor**/TiO₂ system basically origins from Ti(3d) of the substrate TiO₂ conduction band. Therefore, it is possible that the photoexcited electrons can transfer from HOMO in the ground-state **Zn-cor** dye into the conduction band if this direct electronic excitation is accessible.

4 Conclusions

Based on the precious study, the **Zn-cor** dye has been designed with zinc substitution for Ga of **Ga-cor** dye, which exhibits strong light harvesting ability in broad visible region. And there is excellent charge separation between its donor and acceptor moieties in its excited state. Moreover, calculations show that the electronic and photoelectronic properties of these metal di-corrole dyes can well be modulated by incorporating different center metals. On the basis of analyses of band structures and DOS of the **Zn-cor** dye-TiO₂ system, possible mechanisms for direct electron injections were proposed. The present theoretical studies further enrich the knowledge to design the metal di-corrole-based dye for DSCs.

Acknowledgment. This work was supported by the Spring Plan of Ministry of Education of China (No. Z142005), the Research Fund for the Doctoral Program of Guizhou University of China (No. X131052), Science Foundation of Guizhou Province of China (No. [2012]2151). We acknowledge simulating discussions with Z. Cao and thank the computational resources assistance by the State Key Laboratory of Physical Chemistry of Solid Surfaces (Xiamen University).

Notes and references

^a School of Chemistry and Chemical Engineering, Guizhou University, Guizhou 550025, China. Fax: +86-851-3625867; E-mail: czhu2014@163.com

^b Guizhou Provincial Key Laboratory of Computational Nano-Material Science, Guizhou Normal College, Guiyang, 550018, China. E-mail: liangjx2009@163.com

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