Excited-state absorption for zinc phthalocyanine from linear-response time-dependent density functional theory

Chunrui Wang,^1 Junfeng Shao,^1 Fei Chen^1 and Xiaowei Sheng^1,*^2

The mechanism for zinc phthalocyanine (ZnPc) showing optical-limiting character is related to the first singlet excited-state absorption (ESA). Two distinct band peaks in this ESA spectrum (1.97 eV and 2.56 eV) were observed in experiments. However, the origin of the absorption is not well understood. In the present work, we perform accurate quantum mechanical calculations and analysis of the absorption of ZnPc in the first singlet excited state. It is found that the transitions of $S_1 \rightarrow S_2$ and $S_1 \rightarrow S_24$ are the origin of the first and second band peaks, respectively. Charge transfer character is observed between the edges and central parts of ZnPc for those two transitions, but occurs in opposite directions. It is gratifying to note that the absorption can be modified smoothly through the substitution of nitrogen atoms in ZnPc with methylene or benzene rings. The aggregation phenomenon is also investigated with ZnPc dimers. The present calculations show that the absorptions of two ZnPc molecules with cofacially stacked and slightly shifted cofacially stacked configurations both result in an obvious blueshift compared with the zinc phthalocyanine monomer. The present observations may be utilized in tuning the optical-limiting character of ZnPc.

Metallophthalocyanines as typical organic compounds have received lots of attention in this field.^6,13–19^ Zinc phthalocyanine (ZnPc) as a metallophthalocyanine has attracted the greatest interest. The absorption spectra of ZnPc in the ground state and excited states have been well studied in experiments. One of the most recent experimental measurements of the GSA and ESA was conducted by Savolainen et al. They recorded the spectrally resolved pump–probe data of zinc phthalocyanine on time scales ranging from femtoseconds to nanoseconds. Two distinct bands peaking at 1.85 eV and 3.59 eV were observed in the GSA. In addition, it was found that the main bands of the first singlet excited state absorption are centered at 1.97 eV and 2.56 eV.

Theoretically, the absorption spectrum of ZnPc in the ground state has also been investigated extensively. Ricciardi et al. afforded an accurate description of the electronic spectrum of ZnPc in the ground state. Theisen et al. studied the absorption spectra for seven derivatives of ZnPc in the ground state. Yanagisawa et al. and Ueno et al. investigated the effect of molecularly stacked aggregation on the ground state absorption spectra. However, theoretical investigation of the ESA for ZnPc has been less explored. This is mainly attributed to the fact that the developed quantum chemical methods to study ESA are limited and immature. As far as we know, the first and only theoretical prediction of the ESA for ZnPc was reported by Fischer et al. They performed real-time time-dependent density functional theory (RT-TD-DFT) calculations for ZnPc in the first singlet excited state. The predicted band peaks overestimated...
the transition energies by 0.27 eV and 0.28 eV, respectively, compared with the experimental measurement. Although the spectral band of the ESA for ZnPc has been qualitatively predicted with the RT-TDDFT method, accurate quantum mechanical calculations and analysis of the absorption are still required to fully characterize the ESA.

Most recently, we found that the oscillator strengths for the transition between two excited states can be well described with the excited state wavefunctions approximated by a linear combination of singly excited configurations built from the Kohn–Sham orbitals. The computational cost of this method scales as $N^4$, which is much cheaper compared with the QR-TDDFT method. This method was applied to ZnPc and it was shown that the predicted band peaks of ZnPc in the first singlet excited state are in excellent agreement with the experimental measurements. According to this observation, we afford an accurate quantum mechanical analysis for the absorption of ZnPc in the first singlet excited state. The manuscript is organized as follows: the methods used to

Fig. 1 Geometry of ZnPc optimized at BHandHLYP/6-31G(d,p) level in the ground state. White, grey and blue spheres represent hydrogen, carbon and nitrogen atoms, respectively.

Fig. 2 Simulated absorption spectrum for ZnPc in the first singlet excited state ($S_1$), which is in good agreement with the experimental results. The red dashed lines are the two peaks of the spectrum observed in the experiment.
estimate the ESA are described in the next section; the results are reported and discussed in the Results and discussions section; then, the paper closes with the Conclusions section.

II. Methods and computational details

The ESA of ZnPc, modified ZnPc and ZnPc dimers were simulated by using our recently proposed method. This method is based on the assumption that the excited state wavefunction can be well approximated by a linear combination of singly excited configurations built from the Kohn–Sham orbitals. The linear expansion coefficients are obtained by projecting the linear response orbitals on the Kohn–Sham orbitals. The transition energies are obtained from linear-response time-dependent density functional theory (LR-TDDFT). For validation and a more elaborate explanation of this method we refer to ref. 27.

The structure of the ground state ZnPc geometry was optimized with the BHandHLYP functional with the 6-31G(d,p) basis set. The basis set and the functional used here have been calibrated in ref. 27. The spectra are described using the calculated oscillator strengths and the excitation energies broadened with the Gaussian function (FWHM = 0.4 eV). The ESA simulations were done in DMSO solvent with the polarizable continuum model (PCM), which is consistent with the experimental measurements. Geometry optimization was

<table>
<thead>
<tr>
<th>Transition</th>
<th>Excitation energy (eV)</th>
<th>Oscillator strength</th>
</tr>
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<tbody>
<tr>
<td>S₁ → S₃</td>
<td>1.9104</td>
<td>0.5806</td>
</tr>
<tr>
<td>S₁ → S₁₀</td>
<td>2.2271</td>
<td>0.2998</td>
</tr>
<tr>
<td>S₁ → S₁₃</td>
<td>2.3620</td>
<td>0.2394</td>
</tr>
<tr>
<td>S₁ → S₁₄</td>
<td>2.6179</td>
<td>0.3569</td>
</tr>
<tr>
<td>S₁ → S₂₇</td>
<td>2.8180</td>
<td>0.2263</td>
</tr>
</tbody>
</table>

Fig. 3  Natural transition orbital analysis for the S₀ → S₁ transition and S₀ → S₃ transition. (a) S₀ → S₁ transition: the weighting of this pair of NTOs (HONTO → LUNTO) is 96.2%. (b) S₀ → S₃ transition: the weighting of this pair of NTOs (HONTO → LUNTO) is 93.4%.
done by using the Gaussian 09 package. A modified GAMESS-US package was used to preform the LR-TDDFT and ESA simulations. The natural transition orbital analysis and calculations of the electron density difference between the two singlet excited states were done using the wavefunction analysis program Multiwfn.

III. Results and discussions

A. First singlet excited state absorption of ZnPc

The geometry of ZnPc is shown in Fig. 1. The calculated first singlet excited state absorption spectrum (black solid line) is shown in Fig. 2, together with the experimental results (red dashed lines). The present theoretical predicted peak positions of the ESA spectrum in Fig. 2 are 1.97 eV and 2.53 eV. Our calculations underestimate the transition energies by only 0.03 eV for the second peak, compared with the experimental measurement. We also note that Fischer et al. reported RT-TDDFT results for the present system. The predicted two band peaks based on the RT-TDDFT calculations overestimated the transition energies by 0.27 eV and 0.28 eV, respectively, compared with the experimental measurement. More detailed discussions of the ESA calculated from RT-TDDFT can be found in ref. 31.

Table 1 lists the first five strong transitions of the theoretical prediction of ESA. It is clearly seen that $S_1 \rightarrow S_3$ is the main contribution to the first band peak. $S_1 \rightarrow S_{10}, S_1 \rightarrow S_{13}, S_1 \rightarrow S_{24}$ and $S_1 \rightarrow S_{27}$ all make considerable contributions to the second band peak.

![Figure 4](https://example.com/figure4.png)

**Fig. 4** Natural transition orbital analysis for the $S_0 \rightarrow S_{24}$ transition. (a) The weighting of this pair of NTOs (HONTO → LUNTO) is 48.7%. (b) The weighting of this pair of NTOs (HONTO-1 → LUNTO+1) is 48.7%.
Fig. 5  Electron density difference of ZnPc for $S_1 \rightarrow S_3$ and $S_1 \rightarrow S_{24}$ transitions. Blue and green regions show a decrease and increase of electron density, respectively. The wavefunction analysis program Multiwfn\textsuperscript{30} was used for this analysis. The isosurface values are fixed to $0.0005\, \text{Å}^{-3}$. (a) $S_1 \rightarrow S_3$, $\Delta \rho = \rho_3(r) - \rho_1(r)$; (b) $S_1 \rightarrow S_{24}$, $\Delta \rho = \rho_{24}(r) - \rho_1(r)$.

Fig. 6  Geometry of modified ZnPc optimized at the BHandHLYP/6-31G(d,p) level in the ground state. White, grey and blue spheres represent hydrogen, carbon and nitrogen atoms, respectively. (a) ZnTBTTrAP, (b) ZnTBP, (c) ZnMPTBTrAP, (d) ZnTbtransDAP.
B. First singlet excited state absorption of modified ZnPc

It is well known that the optical properties of phthalocyanine-based materials can be tuned through chemical modifications.

Here we investigated four types of chemical modification for ZnPc (zinc tetrabenzo[tetrazaporphyrin, ZnTBTAP; zinc tetrabenzoophorpyrin, ZnPBP; zinc monophenyltetrabenzo[tetrazaporphyrin, ZnMPTTPAP; zinc diphenyltetrabenzo[diaza]porphyrin, ZnDPTbTrAP). These molecules were reported by Theisen et al.24 A diagram of the modified ZnPc molecules is shown in Fig. 6. These chemical modifications are simply replacing N atoms in ZnPc with C–H or C–C6H5 units. ZnTBTAP and ZnMPTTPAP are obtained by replacing one nitrogen atom in ZnPc with C–H and C–C6H5, respectively. ZnPBP is obtained by replacing four nitrogen atoms in ZnPc with C–H units. ZnDPTbTrAP is obtained by replacing two nitrogen atoms in ZnPc with C–C6H5 units.

The calculated absorption spectra for ZnTBTAP, ZnPBP, ZnMPTTPAP and ZnDPTbTrAP in the first singlet excited state, together with the ESA of ZnPc (black solid line), are shown in Fig. 7. For molecules ZnTBTAP and ZnPBP, only one nitrogen atom in ZnPc is replaced by C–H and C–C6H5, respectively. The positions of the two absorption band peaks of ZnTBTAP and ZnPBP are closer compared with those of ZnPc. These two band peaks merge into one band peak for ZnPBP and ZnDPTbTrAP. It is also noted that the absorptions of these modified ZnPc molecules for the transition energies between 2.0 eV and 2.5 eV are enhanced compared with that of ZnPc. Consequently, the absorption spectrum of ZnPc can be modified smoothly by replacing nitrogen atoms in ZnPc with C–H or C–C6H5. These observations may be utilized in the field of searching for enhanced optical limiting materials.32 It should also be mentioned that the observed charge transfer characters of the transitions between the excited states for these modified ZnPc molecules are similar to those of ZnPc. Charge transfer also occurs between the edges and central parts.

Fig. 7 Comparison of the absorption spectra of ZnPc and modified ZnPc in the first singlet excited state (S1). The spectra are described using the calculated oscillator strengths and excitation energies broadened with the Gaussian function (FWHM = 0.4 eV).
of modified ZnPc. This is expected, as the structure of ZnPc is not totally destroyed with the present modifications.

C. First singlet excited state absorption of ZnPc dimers

It is well known that phthalocyanines in solution systems and doped in solid substrates possess aggregated states, such as dimers, which seriously affect the optical-limiting effect. Here we investigated two configurations of ZnPc dimers. In one, the two ZnPc molecules are cofacially stacked. In the other configuration the two ZnPc molecules are cofacially stacked but with a slight shift. The distance between the two ZnPc molecules is fixed to 3.3 Å. Two ZnPc molecules are slipped 5.4 Å along the molecular axes in the second configuration. These configurations were reported by Yanagisawa et al. Fig. 8 presents diagrams of these configurations. Top view (left side) and side view (right side) are both shown for these two configurations. In order to investigate the effect of molecular stacking on the absorption spectra, the ZnPc dimer structures are not optimized but the monomer geometry is optimized.

Fig. 9 shows the calculated absorption spectra for the ZnPc dimers with two different configurations in the first singlet excited state. For comparison, the absorption spectrum of the

![Fig. 8 Geometry of ZnPc dimers. White, grey and blue spheres represent hydrogen, carbon and nitrogen atoms, respectively (left: top view; right: side view). (a) Cofacially-stacked dimer, (b) slightly shifted cofacially-stacked dimer.](image-url)
ZnPc monomer in the first singlet excited state is also included in Fig. 9 (red solid line). It is found that the band peaks of the ZnPc dimers are blueshifted compared with those of the ZnPc monomer. In addition, the blueshift depends on the geometrical overlap between the two ZnPc molecules. The ZnPc dimer with a complete overlapped configuration results in a larger blueshift compared with the configuration with partial overlap between the two monomers. Similar results were also observed by Yanagisawa et al. for ZnPc in the ground state. It was shown that the absorption spectra of ZnPc dimers with configurations (a) and (b) in the ground state both result in blueshift. In addition, the blueshift of the absorption spectrum for the ZnPc dimer with configuration (a) in the ground state is also larger compared with that for configuration (b). This was attributed to the fact that configurations (a) and (b) are typical H-aggregates. Dipolar coupling between the two ZnPc molecules results in the blueshift of the absorption band. The present paper shows that this is also true for the first singlet excited state absorption. According to Kasha’s transition dipole–dipole interaction model, it means that the excitations for the first singlet excited state absorption bands may also come from the monomer transition dipoles being arranged side-by-side.

IV. Conclusions

In the present paper, the absorption spectra of ZnPc, modified ZnPc and ZnPc dimers in the first singlet excited state were simulated. The predicted absorption band peaks for ZnPc are in excellent agreement with experimental measurements. It is shown that the \( S_1 \rightarrow S_3 \) and \( S_1 \rightarrow S_{24} \) transitions, respectively, are the dominant contributions to the experimentally observed two band peaks. The excited states \( S_1 \) and \( S_3 \) can be well characterized by a single electronic transition from the highest occupied natural transition orbital (HONTO) to the lowest unoccupied natural transition orbital. In contrast, the dominant transitions for the higher excited state \( S_{24} \) are HONTO → LUNTO and HONTO→1 → LUNTO+1. The NTO analysis, together with the calculations of electron density difference between the two excitations, reveals that the transitions \( S_1 \rightarrow S_3 \) and \( S_1 \rightarrow S_{24} \) both show charge transfer character but with different charge transfer directions. It is also shown that the absorption of ZnPc in the first singlet excited state can be tuned through chemical modification of the nitrogen atoms in ZnPc. The calculated absorption spectra of ZnPc dimers indicate that the aggregation of ZnPc may result in a blueshift of the absorption. These observations are useful for tuning the optical-limiting window of ZnPc.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References