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# Spectrum of copper phthalocyanine: Experiments and semi-empirical quantum chemical calculations

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## Abstract

We investigate the spectrum of copper phthalocyanine (CuPc) both experimentally and theoretically, which is a potential laser protective organic absorbing dye. The observed visible absorption maximum is located at 658 nm, which corresponds to  $a_{1u} \rightarrow e_g$  electronic transition. We then theoretically investigate the electronic spectrum of CuPc. By setting OWF $_{\pi-\pi}$  ( $\pi-\pi$  overlap weighting factor, one of the adjustable parameters in the ZINDO/S method) at 0.522, the visible absorption maximum of CuPc is precisely calculated using the ZINDO/S method. The result shows that the calculated visible absorption maximum is well consistent with the experimental value. Finally, we discuss the validity and applicability of Yuan's calculation formula [J. Phys. Chem. A 109 (2005) 2582], and investigate the new relationship between OWF $_{\pi-\pi}$  and molecular structural parameters for the other metal phthalocyanine series.  
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**Keywords:** Copper phthalocyanine; Visible absorption maximum; Laser protection

## 1. Introduction

Nowadays, the requirements of laser protection increase daily with the wide applications of laser in military and industry [1]. The most objects that laser attacks are eyes and photo-electricity devices of the weapon. Therefore, it is very important and significant to study the laser protective materials to protect eyes and photo-electricity devices. At present, the laser protection wavelength mainly transfers from visible band to near infrared band [2]. Considering the possibility of technology and economy, the organic absorbing dyes are the most potential laser protective materials. Some of the most important technical requirements for laser protective dyes are as follows: sharp absorption bands at specific wavelengths corresponding to

laser emission, excellent lightfastness, robust thermal and chemical stability, high optical density and scotopic luminous transmission [3].

The phthalocyanine (Pc) compounds are of excellent stability which lead to their widespread use as colorants in the chemical industry, catalysts for the electrochemical reduction of oxygen, anti-cancer agents, optical data storage organic semiconductors for gas sensor, low-dimensional conducting materials, and infrared dyes for laser technology [4–8]. Many applications of Pc compounds are interrelated tightly with their spectral properties; so it is very significant to study the spectrum of Pc compounds.

In recent years, using quantum theory to calculate the absorption spectrum of dyes has been attracted great interests. Some semi-empirical methods, such as AM1 [9], MNDO [10] and PM3 [11] have been used to calculate the structure and spectrum of Pc's. Ab initio [12] and DFT [13–15] calculations also have been carried out to study Pc's electronic spectrum, but the agreement with the experiment is not satisfactory. The ZINDO/S method is

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developed from intermediate neglect of differential overlap (INDO) method, two adjustable parameters, i.e.,  $\sigma$ – $\sigma$  overlap weighting factor (simplified as  $\text{OWF}_{\sigma-\sigma}$ ) and  $\pi$ – $\pi$  overlap weighting factor (simplified as  $\text{OWF}_{\pi-\pi}$ ) are introduced to ZINDO/S. Adjusting the parameters provides a mechanism to adjust the relative contributions of  $\sigma$  vs  $\pi$  bonding. Therefore, the value of  $\text{OWF}_{\pi-\pi}$  could be considered as a measurement of the extent of  $\pi$ -electron delocalization [16]. Based on this idea, Yuan and Chen [17] have concluded a formula to precisely calculate the visible absorption maximum of metal Pc compounds by ZINDO/S method.

CuPc is one of the most important colorants and widely used in industry. In this paper, we investigate the spectrum of CuPc both experimentally and theoretically, to discuss its possibility to be used as a potential infrared dye for laser protective technology. Moreover, we discuss the validity and applicability of Yuan's calculation formula, and investigate the new relationship between  $\text{OWF}_{\pi-\pi}$  and molecular structural parameters for the metal phthalocyanine series whose total electron number is odd.

## 2. Experimental and computational details

The molecular structure of CuPc is shown in Fig. 1. CuPc was dissolved in tetrahydrofuran (THF) solvent. The concentration of the solution was  $1.69 \times 10^{-6}$  M. The visible spectrum was recorded with HITACHI U-3310 Spectrophotometer using 5 mm pathlength cuvette at room temperature.

All semi-empirical quantum-chemical computations were performed with the HyperChem 7.0 computer program. Firstly, the skeleton of CuPc was constructed. Then the “Model Build” conformation was used as the initial one for spatial structure optimization. The spatial structure was further optimized using the PM3 method. In the PM3 method, RHF was used, and in SCF controls, the accelerate convergence was selected and the convergence limit was set as 0.01. In the optimization calculation, the

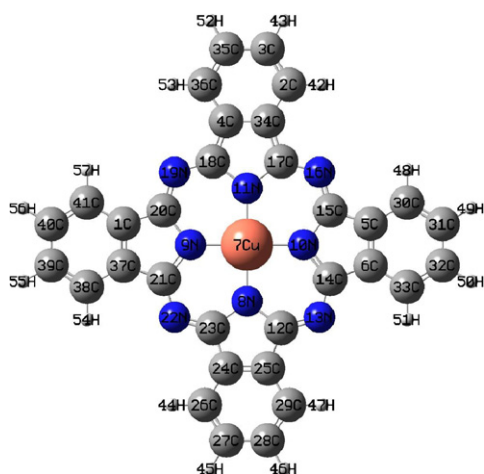


Fig. 1. The structure of copper phthalocyanine.

algorithm of Polak–Ribiere (conjugated gradient) was adopted, and as termination condition, the RMS gradient was set as 0.01. Based on the optimized spatial structure, the electronic spectrum was then calculated by the ZINDO/S method. For the ZINDO/S method,  $\text{OWF}_{\sigma-\sigma}$  ( $\sigma$ – $\sigma$  overlap weighting factor) is set at 1.267 (as the default value). An appropriate value of  $\text{OWF}_{\pi-\pi}$  ( $\pi$ – $\pi$  overlap weighting factor) needs to be sought so that the calculated visible absorption maximum could coincide with that observed.

## 3. Results and discussion

### 3.1. The observed visible absorption spectrum

Fig. 2 shows the visible spectrum of CuPc solution. As seen in Fig. 2, there is an intense and sharp absorption peak at 658 nm with a small shoulder at 597 nm, and there is almost no absorption during the band of 400–600 nm, which is suitable to be used as a potential infrared dye for laser protective technology. Interestingly, the maximum absorption peak of CuPc's vapor absorption spectrum is also located at 658 nm [18]. The absorption spectrum can be well elucidated with the energy levels diagram of metal Pc [19], which is shown in Fig. 3, where MLCT indicates metal to ligand charge transfer transition, LMCT indicates ligand to metal charge transfer transition. For Pc's, there are two permitted electronic transition from  $\pi$  to  $\pi^*$ , namely, the well-known Q-band and B-band originate from  $a_{1u}$  to  $e_g$  and  $a_{2u}$  to  $e_g$ , respectively. The MLCT, LMCT and other mixed charge transfers also can influence the Q-band and B-band.

### 3.2. The calculated visible absorption maximum

In order to further study the absorption spectrum of CuPc, we calculate the electronic spectrum with the ZINDO/S method. In HyperChem, the default value of

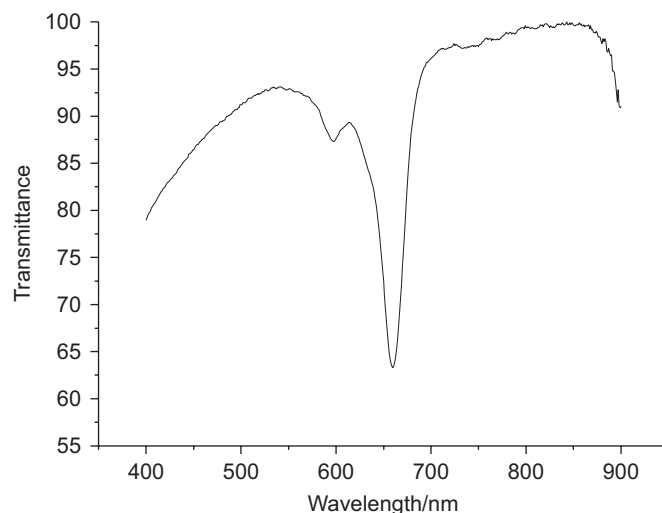


Fig. 2. The measured absorption spectrum of CuPc.

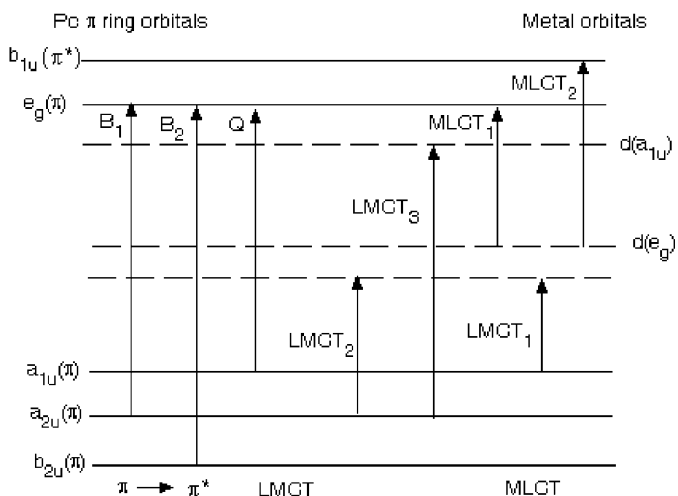


Fig. 3. Energy levels in a typical phthalocyanine with the metal orbitals.

Table 1

Values of  $OWF_{\pi-\pi}$  and the corresponding calculated results of CuPc

$OWF_{\pi-\pi}$	$\lambda_1^a$ (nm)	$f_1^b$	$\lambda_2^a$ (nm)	$f_2^b$	$\lambda_{max}$
0.540	635.87	0.651	595.03	0.528	635.87
0.530	648.11	0.502	607.43	0.466	648.11
0.524	653.67	0.641	615.49	0.468	653.67
0.523	654.70	0.608	613.10	0.451	654.70
0.522	657.94	0.609	613.92	0.499	657.94
0.521	659.30	0.615	618.00	0.459	659.30
0.520	665.63	0.446	618.75	0.444	665.63
0.510	675.25	0.505	628.83	0.420	675.25
0.507	676.63	0.533	629.43	0.402	676.63
0.504	680.57	0.600	635.12	0.419	680.57
0.500	684.48	0.554	637.35	0.393	684.48
0.490	696.47	0.567	649.86	0.384	696.47

<sup>a</sup>Only those in visible region with higher  $f$  value are given.

<sup>b</sup>Oscillator strength.

$OWF_{\sigma-\sigma}$  and  $OWF_{\pi-\pi}$  are 1.267 and 0.585, respectively. By setting  $OWF_{\pi-\pi}$  at this value, the calculated visible absorption maximum is 592.7 nm, which greatly deviates from the experimental result of 658 nm. Considering the variety of molecular structure and the complexity of molecular conformation, the extent of  $\pi$ -electron delocalization is different for different molecules. Yuan et al. [17] has concluded a relationship between  $OWF_{\pi-\pi}$  and molecular structural parameters to predict the absorption maximum of Pc compounds, which is as follows:

$$OWF_{\pi-\pi} = 0.58126 + 0.04562ANC1 + 0.03839X, \quad (1)$$

where ANC1 is the average net charge on coordinate bonded nitrogens,  $X$  is the electronegativity value of central atom. According to our molecular structure calculation, the value of ANC1 and  $X$  is  $-0.3031275$  and  $0.388101$ , respectively. According to formula (1), the value of  $OWF_{\pi-\pi}$  is 0.582, and the calculated visible absorption maximum is 601.92 nm, which also greatly deviates from the experimental result of 658 nm. Thus, the formula (1) cannot be applied to the whole Pc compounds. Formula (1) is concluded from the absorption maximum calculations of  $H_2Pc$ ,  $ZnPc$ ,  $MgPc$ ,  $FePc$  and  $NiPc$ . It is found that each total electron number of these Pc's is even, and the spin multiplicity is 1, which is odd. While the total electron number of CuPc is odd, and the spin multiplicity is 2, which is even. So formula (1) cannot apply to precisely calculate the absorption maximum of this series whose total electron number is odd like CuPc. A new relationship between  $OWF_{\pi-\pi}$  and molecular structural parameters for this series needs to be investigated.

In comparison with the observed visible absorption maximum, the appropriate value of  $OWF_{\pi-\pi}$  should be used in the ZINDO/S method, and the corresponding calculated results are shown in Table 1. It can be seen that when  $OWF_{\pi-\pi} = 0.522$ , the calculated absorption maximum of 657.94 nm is close to the experimental value, the difference is only 0.06 nm. It can be noticed that the

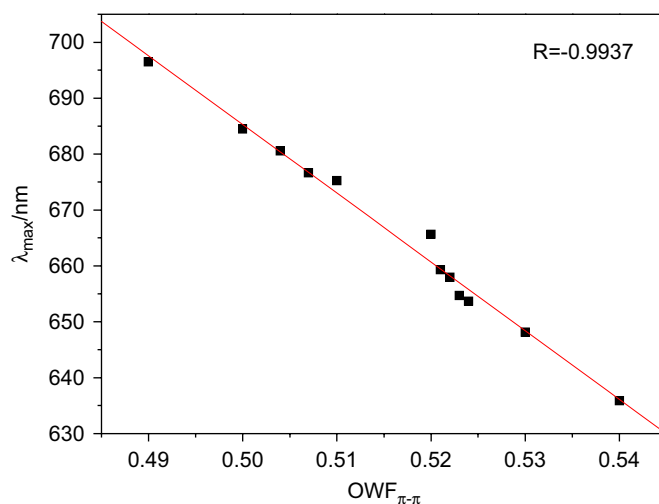


Fig. 4. The relationship between  $OWF_{\pi-\pi}$  and  $\lambda_{max}$  of CuPc.

absorption maximum splits into two peaks, namely,  $\lambda_1$  and  $\lambda_2$ , and the two maxima is somewhat too large ( $> 38$  nm). Therefore, the maximum with higher strength, namely  $\lambda_1$ , should be used to reflect the absorption maximum. The splitting of Q-band results from the splitting of doubly degenerated molecular orbital  $e_g$  (LUMO, the lowest unoccupied molecular orbital). The molecular orbital  $e_g$  splits into two orbitals  $e_g^H$  and  $e_g^L$ . The energy of  $e_g^H$  is higher than that of  $e_g$ , and the energy of  $e_g^L$  is lower than that of  $e_g$ . Accordingly, the electronic transition from  $a_{1u}$  (HOMO, the highest occupied molecular orbital) to  $e_g^L$  and  $e_g^H$  forms a strong absorptive peak and a comparative weak one.

The method of stepwise multiple linear regression is used in order to reveal the relationship between  $OWF_{\pi-\pi}$  and  $\lambda_{max}$ . It can be seen from Fig. 4 that they are in well linear relationship ( $R = -0.9937$ ).  $\lambda_{max}$  decreases with the decreasing of  $OWF_{\pi-\pi}$ . It is because that  $OWF_{\pi-\pi}$  is considered as a measurement of the extent of  $\pi$ -electron delocalization. As  $OWF_{\pi-\pi}$  decreasing, the extent of

$\pi$ -electron delocalization increases, and the extent of molecular conjugation increases. That is, electron clouds transfer from the molecular center to the around, which results in the increasing of the electron cloud density of nitrogen atoms, so the visible absorption maximum shifts to longer wavelength.

Moreover, the electronic spectrum for CoPc, whose total electron number is odd, is similarly calculated by ZINDO/S method. By using formula (1) the calculated  $\lambda_{\max}$  is 408.1 nm, which greatly deviates from the experimental result of 657 nm [18]. So by adjusting  $\text{OWF}_{\pi-\pi}$  newly, which are shown in Table 2, when  $\text{OWF}_{\pi-\pi} = 0.793$ , the calculated absorption maximum of 656.85 nm is close to the experimental value of 657 nm, the difference is only 0.15 nm. Similarly, the absorption maximum splits into two peaks, but differently, the two maxima are nearly overlapped. The smallest difference is 0.1 nm and the greatest difference is 8.58 nm. So a weighting average is defined to reflect the absorption maximum as follows [17]:

$$\lambda_{\max} = (\lambda_1 f_1 + \lambda_2 f_2) / (f_1 + f_2), \quad (2)$$

where  $\lambda_1$  and  $\lambda_2$  are wavelengths of the two maxima,  $f_1$  and  $f_2$  are the corresponding oscillator strengths. The method

Table 2  
Values of  $\text{OWF}_{\pi-\pi}$  and the corresponding calculated results of CoPc

$\text{OWF}_{\pi-\pi}$	$\lambda_1^a$ (nm)	$f_1^b$	$\lambda_2^a$ (nm)	$f_2^b$	$\lambda_{\max}$
0.620	757.68	0.220	749.10	0.193	753.67
0.720	707.13	0.290	703.60	0.280	705.40
0.785	661.41	0.331	661.30	0.332	661.35
0.790	658.30	0.335	658.20	0.335	658.23
0.792	657.30	0.337	657.20	0.337	657.25
0.793	656.90	0.338	656.80	0.338	656.85
0.795	655.80	0.339	655.70	0.340	655.70
0.800	652.78	0.343	652.50	0.254	652.66
0.810	647.88	0.353	645.90	0.347	651.36
0.820	642.14	0.359	640.80	0.359	641.47

<sup>a</sup>Only those in visible region with higher  $f$  value are given.

<sup>b</sup>Oscillator strength.

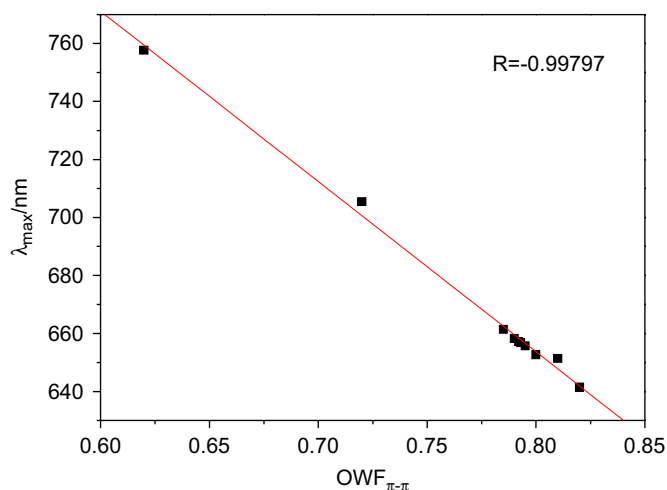


Fig. 5. The relationship between  $\text{OWF}_{\pi-\pi}$  and  $\lambda_{\max}$  of CoPc.

of stepwise multiple linear regression is also used in order to reveal the relationship between  $\text{OWF}_{\pi-\pi}$  and  $\lambda_{\max}$ . As shown in Fig. 5, they are in well linear relationship ( $R = -0.99797$ ).  $\lambda_{\max}$  decreases with the decreasing of  $\text{OWF}_{\pi-\pi}$  which has the similar result of CuPc.

#### 4. Conclusions

In summary, we measured the absorption spectrum of CoPc and calculated its electronic spectrum by the ZINDO/S method. The results show that there is an intense and sharp absorption in the near infrared band, and weak absorptions in most visible bands, which meets the requirements of laser protection. Moreover, we discussed the validity and applicability of Yuan's calculation formula, and investigated the new relationship between  $\text{OWF}_{\pi-\pi}$  and molecular structural parameters for the metal phthalocyanine series whose total electron number are odd. It is a good complementary to investigate the whole Pc compounds' relationship between  $\text{OWF}_{\pi-\pi}$  and molecular structural parameters, which is significant to study the spectral properties and applications of Pc compounds.

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