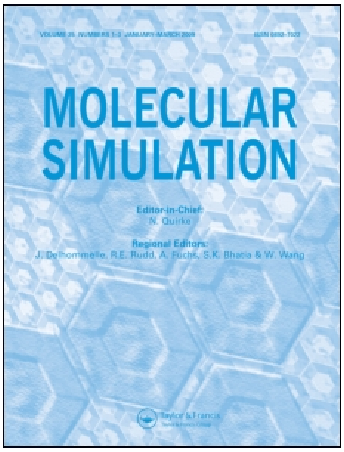

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Theoretical study on phthalocyanine, pyrazinoporphyrazine and their complexation with Mg^{2+} and Zn^{2+}

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We have studied the UV–vis absorption spectra of metal-free phthalocyanine (H_2Pc), metal-free pyrazinoporphyrazine (H_2PyzPz) and their complexes with Mg^{2+} and Zn^{2+} using semiempirical Zerners intermediate neglect of differential overlap and time-dependent density functional theory methods. The predicted absorption spectra of H_2Pc and their complexes are in agreement with a previous experiment report. The calculated results show that the Q band absorption peaks of H_2PyzPz and their complexes are blue-shifted by 40 nm as compared with those of H_2Pc and their complexes, respectively. The frontier molecular orbitals (HOMO and LUMO) of H_2Pc, H_2PyzPz and their metal complexes were investigated as well. The nitrogen atoms in the pyrazine rings stabilise the HOMO more than the LUMO, and the deprotonation of the pyrrole rings induced by the metal coordination destabilises the LUMO more than the HOMO. Because of the increased band gap, the absorption bands of H_2PyzPz and the metal-coordinated compounds are blue-shifted.

Keywords: phthalocyanine; pyrazinoporphyrazine; metal complex; ZINDO; TDDFT; UV–vis absorption spectra

1. Introduction

As one of the most famous scaffolds for blue/green dye and pigment, phthalocyanine (Pc) has been studied over four decades for its photophysical characteristics. Since the spectral assignments of metal-free phthalocyanine (H_2Pc) and its metal complexes in the vapour phase and various solvents by Edwards and Goutermans [1], many significant results for absorption spectra of Pc analogues have been reported [2–7]. In order to predict the absorption parameters precisely, several different theoretical methodologies have so far been proposed [8–14]. Yuan and Chen [15] used the Zerners intermediate neglect of differential overlap (ZINDO)/S method with parameterised $\pi-\pi$ overlap weighting factor and reported excellent agreement between theory and experiment for UV–vis absorption maximum of H_2Pc, MgPc and ZnPc. However, in all optimised structures used for their parameterisation, two pyrrole rings have the asymmetric structure, in which two carbon–nitrogen bonds are different, whereas the other two pyrrole rings have the symmetric structure. It can be assumed that they adopted C_{2h} symmetry for all compounds, although recent X-ray measures have interpreted as D_{2h} and D_{4h} geometry for H_2Pc, MgPc and ZnPc, respectively [16–18]. From a theoretical point of view, a complete study of ZnPc was done by Nemykin et al. [19]. They used the ZINDO/S and time-dependent density functional theory (TDDFT) methods for the prediction of vertical excitation energies and band deconvolution analysis for ZnPc. Although they considered the influence of solvents as well as the amounts of Hartree–Fock exchange involved in the exchange-correlation functional on the calculated vertical excitation energies, their study is limited to only ZnPc.

In contrast to this continuous interest in Pc analogues, pyrazinoporphyrazine (PyzPz), an aza-analogue in which the benzo rings of Pc are substituted by pyrazines, has not been fully explored as a colourant. Gal'pern et al. [20] showed that the longest absorption wavelength of metal-free PyzPz (H_2PyzPz) is blue-shifted with respect to that of H_2Pc. This difference is explained by the electronic structural change due to the aza substitution [21], but detailed investigation on the electronic structure of PyzPz has been rarely reported so far. Moreover, there has been no theoretical study on the frontier molecular orbitals of PyzPz, which are very closely related to the maximum absorption wavelength of the compound.

In this work, we have investigated the electronic structure of H_2Pc, H_2PyzPz and their Mg^{2+} and Zn^{2+} complexes to explain the origin of the blue-shift of H_2PyzPz absorption and to gain an insight into the effects of metals on the spectral properties. Prediction of UV–vis absorption spectra was performed using the semiempirical ZINDO and TDDFT methods. The comparative results of

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H_2Pc, H_2PyzPz and their metal complexes are presented on optimised structures, predicted absorption spectra, electronic structures and frontier molecular orbitals.

2. Theoretical methods

2.1 Geometry optimisation

The structures of H_2Pc, H_2PyzPz and their metal complexes have been optimised by DMol^3 program in the Materials Studio 4.2® package [22], which is based on the quantum mechanical code using DFT. The Perdew, Burke and Ernzerhof exchange-correlation functional [23] was used in the calculations with the double numeric polarisation basis set [24] for all electrons without any special core treatment.

2.2 Prediction of the absorption spectra

Using the fully optimised structures obtained by the geometry optimisation, UV–vis absorption parameters of H_2Pc, H_2PyzPz and their metal complexes were calculated by two different methods, semiempirical ZINDO [25] and TDDFT. These methods have been widely used as reliable methods to predict UV–vis absorption parameters. The 10 highest occupied orbitals and 10 lowest unoccupied orbitals are included in the configuration interaction single calculations using the ZINDO method. This limitation is set up by comparing the calculated peak positions of absorption maxima with experimentally observed ones. All ZINDO and TDDFT calculations were performed by Cerius 2 and NWChem [26] programs, respectively.

3. Results and discussion

3.1 Optimised structures

The molecular structures of H_2Pc, H_2PyzPz and their metal complexes are displayed in Figure 1. The initial structures of the metal-free systems and the metal complexes possess D_{2h} and D_{4h} symmetries, respectively, and this molecular symmetry was employed during the geometry optimisation. The structural parameters of the calculated structures and X-ray crystal structures [16–18] are presented in Table 1. All compounds have similar flat and rigid structures, which agree well with the earlier DFT [13,14] and the experimental results. Even the metal coordination does not cause any significant structural changes. The parameters of ZnPyzPz, which are reported for the first time in this paper, are almost similar to those of MgPyzPz. Absolute energies of all optimised structures and calculated complexation energies of metal complexes are listed in Table 2. The large complexation energies are

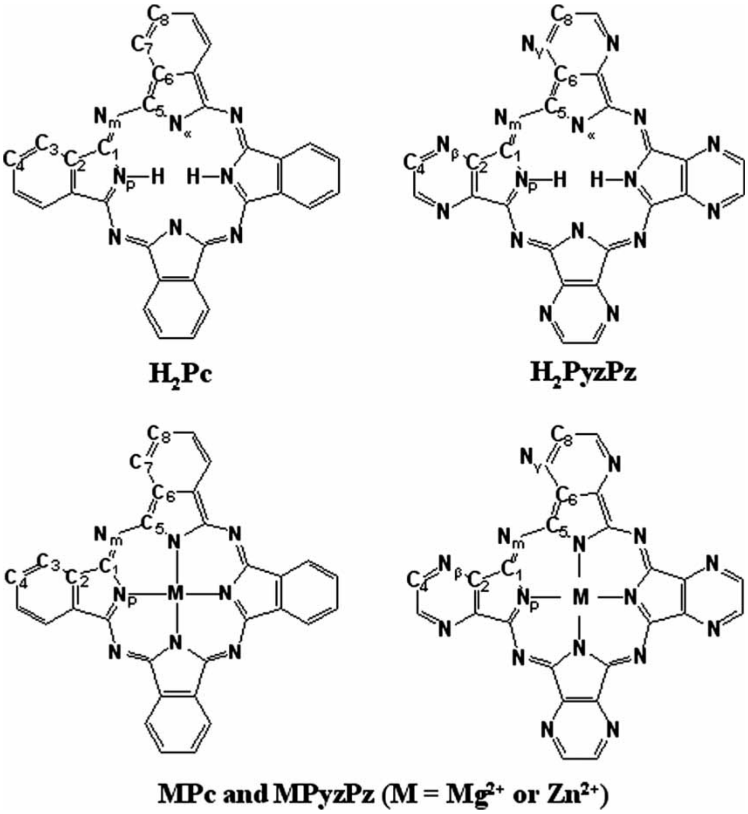

Figure 1. Molecular structures of H_2Pc, H_2PyzPz and their Mg^{2+} and Zn^{2+} complexes.

Table 1. Structural parameters of the calculated structures.

	H_2Pc		MgPc		ZnPc	
	DFT	Exp. [16]	DFT	Exp. [17]	DFT	Exp. [18]
Bond length (Å)						
N_P—H(M)	1.022	0.923	2.009	2.059	2.008	1.980
N_P—C_1	1.382	1.377	1.378	1.372	1.377	1.366
C_1—N_m	1.321	1.326	1.337	1.332	1.335	1.333
N_m—C_5	1.339	1.330				
C_5—N_α	1.370	1.376				
Bond angle (°)						
N_P—C_1—C_2	106.118	108.265	108.445	110.067	108.331	108.808
C_2—C_3—C_4	117.657	117.660	117.779	117.394	117.794	117.561
C_1—N_m—C_5	123.683	121.875	124.662	123.349	124.605	123.034
N_α—C_5—C_6	110.857	109.641				
C_6—C_7—C_8	117.475	117.617				
	H_2PyzPz[a], DFT		$MgPyzPz$[a], DFT		$ZnPyzPz$[a], DFT	
Bond length (Å)						
N_P—H(M)	1.022		2.018		2.016	
N_P—C_1	1.384		1.380		1.379	
C_1—N_m	1.317		1.331		1.329	
N_m—C_5	1.333					
C_5—N_α	1.372					
Bond angle (°)						
N_P—C_1—C_2	105.310		107.708		107.610	
C_2—N_β—C_4	113.296		113.250		113.199	
C_1—N_m—C_5	123.990		124.820		124.755	
N_α—C_5—C_6	110.053					
C_6—N_γ—C_8	112.933					

[a] No experimental data are available.

due to the strong electrostatic interaction between M^{2+} and Pc^{2-} or $PyzPz^{2-}$.

3.2 Predicted absorption spectra

All the calculated absorption parameters are listed in Table 3 with experimental results. In order to investigate the spectral properties of the Pc series (H_2Pc, MgPc and ZnPc) in the vapour phase, we performed the calculations under the vacuum condition. The PyzPz series were also calculated in the same environment for the direct comparison between Pc and PyzPz. In Table 3, the predicted peak positions of the Pc series are compared to experimental ones in the vapour phase, but, to the best of our knowledge, there were no attempts to measure the UV–vis absorption spectrum of the PyzPz series in the vapour phase. The predicted peak positions of the Pc series from the TDDFT calculation are more in agreement with the experimental data for the B band, whereas the ZINDO method is more dependable for predicting the position of the Q band of all compounds except MgPyzPz.

According to Kobayashi and Konami [21], compounds with D_{2h} symmetry such as H_2Pc and H_2PyzPz show the split Q band, whereas compounds with D_{4h} symmetry show no splitting, and this splitting is explained by the symmetry-adapted perturbation method. Experimental results for H_2Pc and H_2PyzPz in Table 3 show the splitting of 63.5 and 57 nm in the Q band, respectively. The ZINDO method predicts the splitting of 42.8 and 23.6 nm for H_2Pc

Table 2. Absolute energies (in Hartree) of all optimised structures and complexation energies (in eV) of metal complexes. Complexation energies (CE) $= E_{\text{complex}} - E^{2-}_{\text{Pc(PyzPz)}} - E^{2+}_{\text{metal}}$.

	H_2Pc −1666.905825	Pc^{2-} in MPc −1665.694633		H_2PyzPz −1795.152556	$PyzPz^{2-}$ in MPyzPz −1793.989444	
		E_{complex}	CE		E_{complex}	CE
Mg^{2+} −199.111798		−1865.833478	−27.95		−1994.075909	−26.52
Zn^{2+} −1778.163128		−3444.990997	−30.84		−3573.232168	−29.38

Table 3. Calculated absorption parameters of H_2Pc, H_2PyzPz and their Mg^{2+} and Zn^{2+} complexes with experimental absorption maxima. For the sake of clarity, some parameters, which have oscillator strength less than 0.01, are excluded.

H_2Pc			MgPc			ZnPc		
TDDFT, nm (f[a])	ZINDO, nm (f)	Exp. [1], nm	TDDFT, nm (f)	ZINDO, nm (f)	Exp. [1], nm	TDDFT, nm (f)	ZINDO, nm (f)	Exp. [1], nm
605.2 (0.83)[b]	724.4 (0.68)	686.0	602.6 (0.42)	680.6 (0.88)	666.0	599.1 (0.42)	678.9 (0.88)	661.0
596.8 (0.44)	681.6 (0.84)	622.5	602.4 (0.42)	680.6 (0.88)	332.0	598.9 (0.42)	678.8 (0.88)	326.5
407.6 (0.06)	364.9 (0.99)	340.0	373.7 (0.01)	347.2 (0.02)	280.3	371.2 (0.01)	345.5 (0.02)	276.1
339.9 (0.13)	356.6 (0.06)	280.0	373.6 (0.01)	347.2 (0.02)		371.0 (0.01)	345.5 (0.02)	239.8
339.8 (0.33)	333.8 (0.11)	270.0	343.4 (0.09)	308.0 (1.55)		341.7 (0.11)	305.2 (1.52)	
336.1 (0.04)	323.0 (1.40)	240.0	343.3 (0.09)	308.0 (1.55)		341.6 (0.11)	305.2 (1.53)	
329.6 (0.92)	298.7 (2.04)		334.3 (0.40)	298.3 (0.64)		333.6 (0.36)	297.3 (0.82)	
324.5 (0.08)	290.0 (0.50)		334.2 (0.40)	298.3 (0.63)		333.6 (0.36)	297.3 (0.81)	
318.6 (0.47)	287.3 (1.13)		327.4 (0.44)	284.6 (1.04)		324.7 (0.41)	284.9 (0.89)	
318.4 (0.12)	287.1 (0.02)		327.4 (0.44)	284.6 (1.04)		324.7 (0.41)	284.9 (0.90)	
304.8 (0.07)	279.5 (0.01)		315.5 (0.13)	254.4 (0.02)		314.2 (0.11)	253.6 (0.02)	
286.9 (0.29)	275.8 (0.12)		315.5 (0.13)	254.4 (0.02)		314.2 (0.11)	253.6 (0.02)	
284.8 (0.15)	273.2 (0.29)		288.1 (0.21)	227.1 (0.36)		287.4 (0.20)	226.5 (0.31)	
252.4 (0.05)	245.8 (0.11)		288.1 (0.21)			287.4 (0.20)		
			241.8 (0.01)			241.9 (0.01)		
			241.8 (0.01)			241.9 (0.01)		

H_2PyzPz			MgPyzPz[b]			ZnPyzPz		
TDDFT, nm (f)	ZINDO, nm (f)	Exp. [27], nm	TDDFT, nm (f)	ZINDO, nm (f)		TDDFT, nm (f)	ZINDO, nm (f)	Exp. [28], nm
564.0 (0.28)	681.3 (0.50)	642.0	563.9 (0.31)	643.9 (0.71)		559.5 (0.32)	642.3 (0.72)	635.0
563.9 (0.31)	657.7 (0.69)	585.0	563.3 (0.31)	643.6 (0.71)		559.4 (0.31)	641.9 (0.72)	580.0
405.4 (0.12)	381.7 (0.03)		371.9 (0.02)	373.2 (0.01)		369.3 (0.02)	371.4 (0.01)	
468.9 (0.01)	378.9 (0.74)		371.7 (0.02)	373.2 (0.01)		369.2 (0.02)	371.4 (0.01)	
349.4 (0.02)	354.4 (0.30)		358.7 (0.01)	316.3 (1.38)		357 (0.02)	314.4 (1.44)	
335.0 (0.01)	318.1 (1.81)		358.6 (0.01)	316.2 (0.92)		356.9 (0.02)	314.4 (1.43)	
329.2 (1.17)	311.6 (2.85)		341.2 (0.01)	316.2 (0.48)		334.6 (0.11)	301.1 (2.03)	
328.9 (0.01)	296.6 (1.32)		337.0 (0.06)	301.2 (2.10)		334.6 (0.11)	300.8 (2.02)	
327.4 (0.15)	288.1 (0.01)		336.7 (0.06)	301.0 (2.09)		327.3 (0.01)	284.3 (0.01)	
319.0 (1.07)	285.7 (0.03)		326.6 (0.01)	268.8 (0.02)		323.6 (1.04)	272.1 (0.02)	
316.9 (0.15)	277.7 (0.09)		325.4 (1.17)			323.6 (1.03)	259.0 (0.01)	
	271.6 (0.01)		325.3 (1.17)			322.4 (0.02)	258.9 (0.01)	

[a] f means oscillator strength.
[b] No experimental data are available.

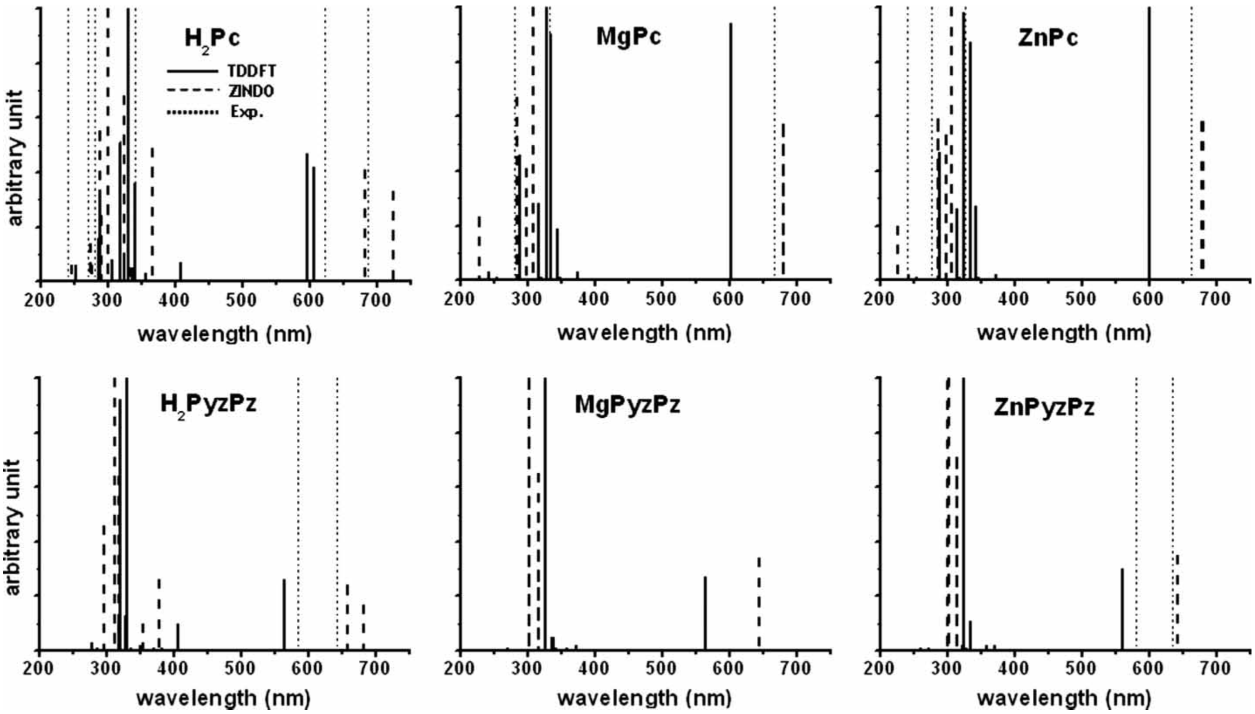

Figure 2. Predicted spectra of H_2Pc, H_2PyzPz and their Mg^{2+} and Zn^{2+} complexes: ZINDO results, dashed lines; TDDFT results, solid lines; experimental results, short dashed lines.

and H_2PyzPz, respectively, but the TDDFT method predicts a smaller splitting of 8.4 nm for only H_2Pc. For clarity, predicted absorption spectra derived from our ZINDO and TDDFT calculation data are displayed in Figure 2. The peak heights were normalised by adjusting the largest peak in each spectrum to the same value. In Figure 2, TDDFT results show no splitting in the Q band for H_2PyzPz clearly.

In order to compare the calculated results, we used the central position between two split peaks in the Q band for H_2Pc and H_2PyzPz. It can be observed that the transition energy values calculated by the ZINDO method are lower than those calculated by TDDFT in the Q band, but, in the B band, both methods show similar results. In the ZINDO results for the Q band, the predicted absorption maxima of H_2Pc, MgPc and ZnPc are located at 703, 680.6 and 678.9 nm, respectively, and those for H_2PyzPz, MgPyzPz and ZnPyzPz are located at 669.5, 643.8 and 642.1 nm, respectively. Experimentally observed peak positions of absorption maxima in the Q band of H_2Pc, MgPc and ZnPc are more similar to the previous results, obtained by parameterisation of $\pi-\pi$ overlap weighting factor, than our results [15,19]. However, our purpose in this study is to investigate the role of pyrazine nitrogen atoms in PyzPz which induce the spectral shift in UV–vis absorption spectra. The ZINDO results confirm the earlier findings on the relative positions of the Q band absorption [13,20]; the Q band of H_2PyzPz and its metal complexes is blue-shifted by about 40 nm compared to that of the corresponding Pc series, and metal complexation causes a blue-shift of the absorption band by about 20 nm. The spectral shift due to the variation of the central metal from Mg^{2+} to Zn^{2+} is very small in both the Pc and PyzPz series. This result is in line with the experimental data as well.

3.3 Electronic structures and frontier molecular orbitals

The electronic transitions corresponding to the two absorption peaks with the largest oscillator strength in the Q band were predicted to be from HOMO to LUMO and LUMO+1 for all calculated systems. In order to explain the spectral differences between the metal and metal-free compounds and between the Pc and PyzPz derivatives, energy levels of these systems were calculated (Table 4). As expected, the metal complexes and the PyzPz series have a larger HOMO–LUMO gap than the metal-free compounds and the Pc series, respectively. Especially for the PyzPz series, the larger HOMO–LUMO gaps are due to the fact that the stabilisation of the HOMO is larger than that of the LUMO. It seems that the nitrogen atoms in the pyrazine rings play an important role in the stabilisation of HOMO.

In order to understand this 'nitrogen effect', frontier molecular orbitals of the Pc and PyzPz derivatives were further examined. All orbitals in Figure 3 are drawn at a default contour level of 0.03 au. As shown in Figure 3, the HOMOs of the PyzPz series are more localised than those

Table 4. Energy levels (in eV) of occupied and unoccupied molecular orbitals.

	H_2Pc	H_2PyzPz	MgPc	MgPyzPz	ZnPc	ZnPyzPz
LUMO+3	−0.925	−2.052	−0.809	−2.013	−0.823	−2.039
LUMO+2	−1.117	−2.280	−1.091	−2.138	−1.095	−2.158
LUMO+1	−2.805	−3.524	−2.769	−3.502	−2.771	−3.505
LUMO	−2.839	−3.611	−2.770	−3.504	−2.773	−3.506
ΔE^{a}	2.139	2.314	2.148	2.348	2.164	2.368
HOMO	−4.978	−5.925	−4.917	−5.851	−4.937	−5.873
HOMO−1	−6.501	−6.909	−6.672	−6.948	−6.697	−6.930
HOMO−2	−6.543	−6.920	−6.727	−7.035	−6.748	−7.053
HOMO−3	−6.806	−7.213	−6.750	−7.036	−6.749	−7.055

[a] ΔE means the energy difference between HOMO and LUMO.

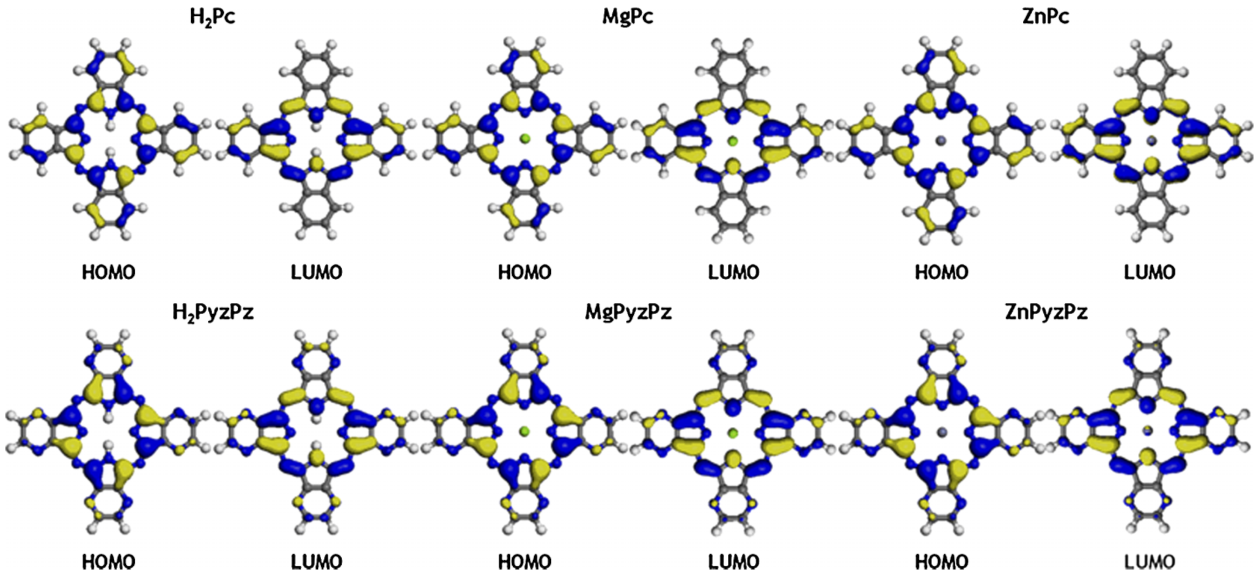

Figure 3. HOMO and LUMO of H_2Pc, H_2PyzPz and their Mg^{2+} and Zn^{2+} complexes. LUMO+1s are not displayed because they have very similar shapes to the corresponding LUMOs.

of the corresponding Pc series around the central region consisting of the pyrrole rings and the nitrogen bridges. The atomic contributions of the pyrazine nitrogen atoms are calculated from the sum of the square of the molecular orbital coefficients of eight pyrazine nitrogen atoms divided by those of all atoms. The contributions to the HOMOs of H_2PyzPz, MgPyzPz and ZnPyzPz are 10.27, 9.99 and 10.19%, respectively (Table 5), and the corresponding contributions to the LUMOs are 8.25, 5.88 and 5.65%. The contributions to the LUMO+1s are almost similar to those of the LUMOs. These findings indicate that the pyrazine nitrogen atoms contribute more to the HOMO than to the LUMO or the LUMO+1. As a result, the nitrogen atoms stabilise the HOMO more than the LUMO or the LUMO+1, and the HOMO–LUMO gap of the PyzPz series becomes larger than that of the corresponding Pc series.

Table 5. Quantitative contribution of nitrogen atoms in the pyrazine rings to HOMO, LUMO and LUMO+1.

	HOMO contribution (%)	LUMO contribution (%)	LUMO+1 contribution (%)
H_2PyzPz	10.27	8.25	4.08
MgPyzPz	9.99	5.88	5.12
ZnPyzPz	10.19	5.65	5.67

The metal coordination also induces an increase in the HOMO–LUMO gap and the absorption band shows a blue-shift (Table 3). In this case, however, the metal coordination destabilises the LUMO more largely than the HOMO (Table 4). In order for a porphyrin ring to coordinate a metal atom, it has to lose two protons and carry a negative formal charge through the conjugated system. Thus, the energy levels of the HOMO and LUMO are higher for the metal complex than the corresponding metal-free compound. Since the deprotonated nitrogen atoms of pyrrole rings are more intensively involved in the LUMO than in the HOMO (Figure 3), the HOMO–LUMO energy gap is increased by the metal coordination.

4. Conclusion

We have studied the absorption spectra of H_2Pc, H_2PyzPz and their Mg^{2+} and Zn^{2+} complexes. In comparison with the results of the TDDFT method, the ZINDO results in this study are in better agreement with the experimental data for the prediction of the Q band position. The calculated results show that because of the larger HOMO–LUMO gap, the Q band of the PyzPz series is blue-shifted by about 40 nm when compared to that of the Pc series. The nitrogen atoms in the pyrazine rings contribute to the stabilisation of the HOMO more than to the stabilisation of the LUMO or the LUMO+1, which results in the increased HOMO–LUMO gap. The metal coordination induces a blue-shift of the absorption by about 20 nm, which results from the increased HOMO–LUMO gap due to the deprotonation of the pyrrole NH protons.

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References

[1] L. Edwards and M. Goutermans, *Porphyrins: XV. Vapor absorption spectra and stability: Phthalocyanines*, J. Mol. Spec. 33 (1970), pp. 292–310.

[2] E. Ough, T. Nyokong, K.A.M. Creber, and M.J. Stillman, *Electrochemistry and spectroscopy of magnesium phthalocyanine. Analysis of the absorption and magnetic circular dichroism spectra*, Inorg. Chem. 27 (1988), pp. 2724-2732.

[3] N. Kobayashi, K. Adachi, and T. Osa, *Some spectroscopic, electrochemical and spectroelectrochemical properties of tetrapyrazinoporphyrazine and its iron and cobalt complexes*, Anal. Sci. 6 (1990), pp. 449–453.

[4] T. Harazono and I. Takagishi, *Solvent effects on electronic states of pthalocyanines*, Bull. Chem. Soc. Jpn. 66 (1993), pp. 1016–1023.

[5] R. Slota and G. Dyrda, *UV photostability of metal phthalocyanines in organic solvents*, Inorg. Chem. 42 (2003), pp. 5743–5750.

[6] K. Bayo, J.C. Mossoyan, and G.V. Ouedraogo, *Preparation and analysis by UV–vis of zinc phthalocyanine complexes*, Spec. Acta Part A 60 (2004), pp. 653–657.

[7] T.M. Mohan and B.N. Achar, *UV–visible spectral study on the stability of lead phthalocyanine complexes*, J. Phys. Chem. Sol. 67 (2006), pp. 2282–2288.

[8] M.G. Cory, H. Hirose, and M.C. Zerner, *Calculated structures and electronic absorption spectroscopy for magnesium phthalocyanine and its anion radical*, Inorg. Chem. 34 (1995), pp. 2969–2979.

[9] J.O. Morley, *Theoretical investigation of the structure and spectra of zinc phthalocyanines*, J. Phys. Chem. 99 (1995), pp. 1928–1934.

[10] A.B.J. Parusel and S. Grimme, *DFT/MRCI calculations on the excited states of porphyrin, hydroporphyrins, tetrazaporphyrins and metalloporphyrins*, J. Por. Phtha. 5 (2001), pp. 225–232.

[11] K.A. Nguyen and R. Pachter, *Ground state electronic structures and spectra of zinc complexes of porphyrin, tetraazaporphyrin, tetrabenzoporphyrin, and phthalocyanine: A density functional theory study*, J. Chem. Phys. 114 (2001), pp. 10757–10767.

[12] G. Ricciardi and A. Rosa, *Ground and excited states of zinc phthalocyanine studied by density functional methods*, J. Phys. Chem. A 105 (2001), pp. 5242–5254.

[13] X. Zhou, A.M. Ren, J.K. Feng, and X.J. Liu, *Theoretical studies on the one- and two-photon absorption of tetrabenzoporphyrins and phthalocyanines*, Can. J. Chem. 82 (2004), pp. 19–26.

[14] Z. Liu, X. Zhang, Y. Zhang, and J. Jiang, *The molecular, electronic structures and IR and Raman spectra of metal-free, N,N0-dideuterio, and magnesium tetra-2,3-pyrazino-porphyrazines: Density functional calculations*, Vib. Spec. 43 (2007), pp. 447–459.

[15] S.F. Yuan and Z.R. Chen, *Study on the prediction of visible absorption maximum of phthalocyanine compounds by semiempirical quantum methods*, J. Phys. Chem. A 109 (2005), pp. 2582–2585.

[16] S. Matsumoto, K. Matsuhama, and J. Mizuguchi, *β Metal free phthalocyanine*, Acta Cryst. C 55 (1999), pp. 131–133.

[17] B. Assmann, G. Ostendorp, G. Lehmann, and H. Homborg, *Magnesium phthalocyanines: Synthesis and properties of halophthalocyaninatomagnesate, $[Mg(X)Pc^{2-}]^{-}$ $(X = F, C1, Br)$; Crystal structure of Bis(tripheny1phosphine)iminiumchloro (phtha1ocyaninato)magnesate acetone solvate*, Z. Anorg. Allg. Chem. 622 (1996), pp. 1085–1090.

[18] W.R. Scheidt and W. Dow, *Molecular stereochemistry of phthalocyanatozinc(II)*, J. Am. Chem. Soc. 99 (1977), pp. 1101–1104.

[19] V.N. Nemykin, R.G. Hadt, R.V. Belosludov, H. Mizuseki, and Y. Kawazoe, *Influence of molecular geometry, exchange-correlation functional, and solvent effects in the modeling of vertical excitation energies in phthalocyanines using time-dependent density functional theory (TDDFT) and polarized continuum model TDDFT methods: Can modern computational chemistry methods explain experimental controversies?,* J. Phys. Chem. A 111 (2007), pp. 12901–12913.

[20] E.G. Gal'pern, E.A. Luk'yanets, and M.G. Gal'pern, *Influence of azasubstitution on the electronic absorption spectra of phthalocyanins*, Russ. Chem. Bull. 9 (1973), pp. 1976–1980.

[21] N. Kobayashi and H. Konami, *Molecular orbitals and electronic spectra of phthalocyanine analogues*, in *Phthalocyanines: Properties and Applications*, C.C. Leznoff and A.B.P. Lever, eds.,Vol. 4, VCH Publishers, New York, NY, 1996, pp. 343–404.

[22] B. Delley, *From molecules to solids with the DMol3 approach*, J. Chem. Phys. 113 (2000), pp. 7756–7764.

[23] J.P. Perdew, K. Burke, and M. Ernzerhof, *Generalized gradient approximation made simple*, Phys. Rev. Lett. 77 (1996), pp. 3865–3868.

[24] B. Delley, *An all-electron numerical method for solving the local density functional for polyatomic molecules*, J. Chem. Phys. 92 (1990), pp. 508–517.

[25] M.C. Zerner, G.H. Loew, R.F. Kirchner, and U.T. Mueller-Westerhoff, *An intermediate neglect of differential overlap technique for spectroscopy of transition-metal complexes. Ferrocene*, J. Am. Chem. Soc. 102 (1980), pp. 589–599.

[26] E.J. Bylaska, W.A. de Jong, K. Kowalski, T.P. Straatsma, M. Valiev, D. Wang, E. Aprà, T.L. Windus, S. Hirata, M.T. Hackler, Y. Zhao, P.-D. Fan, R.J. Harrison, M. Dupuis, D.M.A. Smith, J. Nieplocha, V. Tipparaju, M. Krishnan, A.A. Auer, M. Nooijen, E. Brown, G. Cisneros, G.I. Fann, H. Früchtl, J. Garza, K. Hirao, R. Kendall, J.A. Nichols, K. Tsemekhman, K. Wolinski, J. Anchell, D. Bernholdt, P. Borowski, T. Clark, D. Clerc, H. Dachsel, M. Deegan, K. Dyall, D. Elwood, E. Glendening, M. Gutowski, A. Hess, J. Jaffe, B. Johnson, J. Ju, R. Kobayashi, R. Kutteh, Z. Lin, R. Littlefield, X. Long, B. Meng, T. Nakajima, S. Niu, L. Pollack, M. Rosing, G. Sandrone, M. Stave, H. Taylor, G. Thomas, J. van Lenthe, A. Wong, and Z. Zhang, *NWChem: A Computational Chemistry Package for Parallel Computers*, Version 5.0, Pacific Northwest Laboratory, Richland, WA, 2006.

[27] M.G. Gal'pern and E.A. Luk'yanets, *Phthalocyanines and related compounds. III. Synthesis and electron absorption spectra of some nitrogen-containing heterocyclic analogs of phthalocyanine*, Z. Obs. Khimi. 39 (1969), pp. 2536–2541.

[28] S.V. Kudrevich, M.G. Gal'pern, and J.E. Van Lier, *Octacarboxy substituted tetra(2,3-pyrazino)porphyrazines and their derivatives*, Canadian patent application. (1994), 2133284.