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Computational study of the geometry and electronic structure of triazolephthalocyanines

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Semiempirical molecular orbital methods were used to simulate the molecular structure and electronic spectra of a series of triazolephthalocyanines (Tpcs). All molecular studies are in agreement with an aromatic macrocycle where a hypothetical substitution on both triazole and *meso* nitrogens of the core causes a partial breakdown in the Gouterman's four level model. Minor effects are predicted for the substitution in the isoindole subunit.

Comparison between the experimental and theoretical UV–VIS spectra of different metal substituted triazolephthalocyanines is also made.

Introduction

The search for advanced materials with potential technological applicability, especially in the optoelectronic and photonic fields, has activated interest in phthalocyanines[1,2] and related compounds. These azaporphyrin systems are considered as targets in materials science not only because of their unique physical and chemical properties, such as chemical versatility, thermal stability,[3] semiconductor behaviour[1] and intense nonlinear-optical responses,[4–7] but also because of their intrinsic capability to self-assemble providing supramolecular devices.[8–12]

Most of the specific properties of phthalocyanine-like compounds are founded on the aromatic character, the π-electron distribution and the macrocyclic skeleton structure of the Pc-core. Therefore, the development of theoretical calculations for these macrocycles is of great interest to elucidate their molecular geometry and electronic based parameters such as redox potentials, electronic conductivity properties, optical absorptions, *etc.*

Many theoretical studies have been carried out on several phthalocyanine compounds,[13–17] such as metal-free phthalocyanine, various extended conjugation analogues,[18,19] and metal phthalocyanines.[20–22] Different calculation methodologies have been reported and these studies have proved to be useful in both explaining and predicting experimental data for phthalocyanine derivatives.

Although theoretical studies on symmetrical phthalocyanines are quite well documented, there are few reports on non-centrosymmetrical phthalocyanines and Pc analogues.[23,24] Pc analogues are core-modified phthalocyanines where one or two benzo-fused rings have been replaced by another heteroaromatic system. The theoretical study of these core-modified macrocycles is of great interest since this change significantly modifies the electronic structure of the Pc macrocycle, clearing the path to understanding the nature of aromaticity in these systems and to allow the computer design of azaporphyrin-based new materials.

As a consequence of the interest of our group in the theoretical understanding of phthalocyanine related systems, the molecular electronic analysis of different subphthalocyanines has been reported recently.[25] MNDO calculations on the triazolehemiporphyrazine[26] (Thp), a four-unit macrocycle which bears two opposite-faced isoindole units and two 1,2,4-triazole moieties all bound through aza bridges, explained why it was impossible to obtain the aromatic triazolehemiporphyrazines which was owing to the antiaromatic character of the triazolinediimine substructure.

Recently, we have focused our interest on triazolephthalocyanines (Tpc),[27,28] isoelectronic core-modified phthalocyanines in which one isoindole ring has been formally replaced by a 1,2,4-triazole subunit. These compounds can be synthesised by two synthetic approaches: a statistical procedure useful to prepare triazolephthalocyanines with the same substitution pattern in the three isoindole subunits,[29] and a stepwise route,[30] that allows the synthesis of Tpcs with a differently substituted isoindole opposite to the triazole moiety. These unsymmetrical macrocycles have shown comparable properties with phthalocyanines; they are able to be organised in Langmuir–Blodgett films[31,32] and have shown liquid-crystal behaviour,[33] high conductivity measurements,[34] important second and third non-linear optical properties,[35] and high thermal stability.[3]

Previous Tpc theoretical studies have been reported on the metal free triazolephthalocyanine.[36] The geometry optimization that was carried out using a semiempirical AM1 method showed that the macrocycle should be visualised as an 18 π-carbon-nitrogen macrocycle with peripheral N–N and benzene moieties. The electronic structure was calculated at the HF *ab initio* 3-21G level. However, there were no experimental data available to compare with the theoretical results.

The comparison of experimental and computational data is a good way to check the validity of the theoretical calculations, and also experimental data, especially absorption data can be predicted. It opens the way to a more effective design of triazolephthalocyanine materials based on required properties assisted by computer tools.

In this article, a theoretical chemistry study, based on semiempirical molecular orbital calculations on triazolephthalocyanines has been carried out. A comparative study of the results yielded by spectroscopic calculation methods and

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experimental absorption spectra of Tpc compounds[28,30–32] is also reported.

Experimental

Computational methods

Geometry optimizations were carried out using the AM1,[37] MNDO-PM3[38] and MNDO/d[39,40] semi-empirical methods as implemented in the Unichem 4.1 package, and the ZINDO[41] semi-empirical method as implemented in the Hyperchem 3.1 package. All structures were fully optimised at the Hartree–Fock level; for nickel(II) and metal-free compounds the restricted Hartree–Fock (RHF) approximation was applied, while the unrestricted approximation (UHF) was applied on copper compounds, due to their open-shell configuration.

AM1, MNDO-PM3, MNDO and ZINDO methods have been used to optimise the geometry of the free macrocycle **1a**, **2a**, **3a**, **4a**, **5a**, **6a** (Fig. 1). For metal compounds (**1b,c**, **2b,c**, **3b,c**), AM1, MNDO-PM3 and MNDO methods could not be applied since Ni and Cu metals are not parameterised. Consequently, for nickel and copper triazolephthalocyanines the ZINDO method is the only semiempirical method available.

Spectroscopic calculations were performed with the ZINDO/S method implemented in the Hyperchem package.

Results and discussion

Molecular geometries

The optimised molecular structure of one of the Tpcs (**1b**), which is representative of all studied compounds, is shown in Fig. 2.

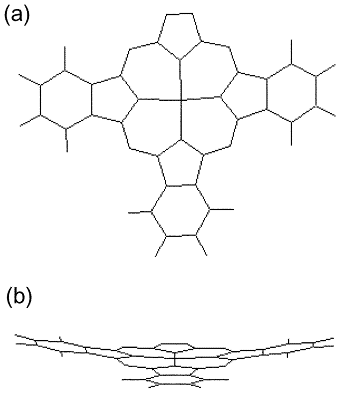
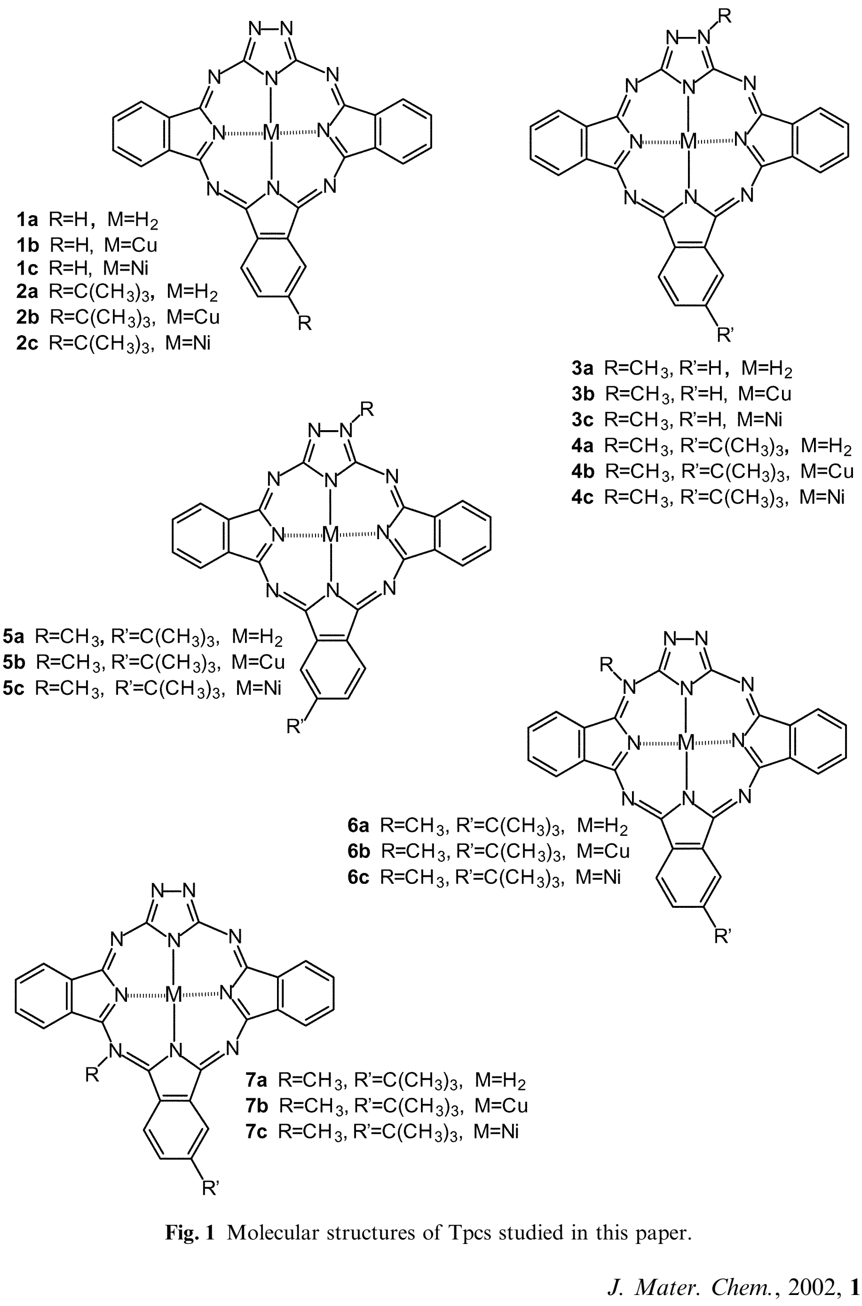


Fig. 2 Optimized geometry of copper Tpc (**1b**). (a) *z*-axis view; (b) *x*-axis view.



1a R=H, M=H_2
1b R=H, M=Cu
1c R=H, M=Ni
2a R=$C(CH_3)_3$, M=H_2
2b R=$C(CH_3)_3$, M=Cu
2c R=$C(CH_3)_3$, M=Ni

3a R=CH_3, R'=H, M=H_2
3b R=CH_3, R'=H, M=Cu
3c R=CH_3, R'=H, M=Ni
4a R=CH_3, R'=$C(CH_3)_3$, M=H_2
4b R=CH_3, R'=$C(CH_3)_3$, M=Cu
4c R=CH_3, R'=$C(CH_3)_3$, M=Ni

5a R=CH_3, R'=$C(CH_3)_3$, M=H_2
5b R=CH_3, R'=$C(CH_3)_3$, M=Cu
5c R=CH_3, R'=$C(CH_3)_3$, M=Ni

6a R=CH_3, R'=$C(CH_3)_3$, M=H_2
6b R=CH_3, R'=$C(CH_3)_3$, M=Cu
6c R=CH_3, R'=$C(CH_3)_3$, M=Ni

7a R=CH_3, R'=$C(CH_3)_3$, M=H_2
7b R=CH_3, R'=$C(CH_3)_3$, M=Cu
7c R=CH_3, R'=$C(CH_3)_3$, M=Ni

Fig. 1 Molecular structures of Tpcs studied in this paper.

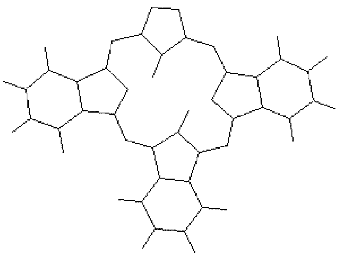


Fig. 3 Metal-free Tpc (**1a**) optimized structure using the ZINDO method.

Attempts to find an out-of-plane minimum were unsuccessful. The optimised structure of the free macrocycle **1a** using both AM1 and PM3 methods showed a planar structure. However, the planarity of the macrocycle is not complete when the ZINDO method is applied, the Tpc core adopts a slightly pyramidal configuration of the four heterocyclic moieties (Fig. 2b). This kind of pyramidal configuration has been described in porphyrin systems that have large metallic atoms in a macrocyclic cavity.[42–47]

Optimization of the metal-free Tpc (**1a**) by the ZINDO method resulted in an in-plane distortion of the macrocycle caused by the shortening of the N–N distance on the core, which is due to a hydrogen bond-type interaction, forming a kind of bridge between the nitrogens (Fig. 3). This result can be justified considering an intermediate structure of the two possible tautomeric positions adopted by the inner hydrogens. Compound **4a** does not present such distortion.

Considering that ZINDO is the only method that allowed the optimisation of all structures, the following macrocyclic structures discussed were all analyzed by the ZINDO method.

The comparison of the different substituted triazolephthalocyanines showed that substitutions in the Tpc ring destabilize the molecule, the smallest effect was observed with the *tert*-butyl addition to the isoindole (**2a**), followed by methylation in the triazole ring (**4a**) and methylation in the *meso* nitrogens (**6a** and **7a**). This effect has also been observed on Cu and Ni derivatives.

The analysis of bond distances in the inner macrocycle (d = 1.32–1.37 Å, 1.35 Å) is close to the estimated distances for 1.5 C–N and 1.5 C–C bonds. This result, together with the planarity of the system and the existence of Hückel number of resonant electrons, are the criteria which establish the aromaticity of the triazolephthalocyanine.

The N–N distance in the triazole ring is *ca.* 1.25 Å, close to the estimated N–N distance for a double bond. This result is similar to the distance calculated for thiazolehemiporphyrazines,[26] which are non-aromatic species due to the unstability caused by the presence of two triazole moieties, while Tpcs have just one triazole unit.

Formal methylation at the triazole and *meso* nitrogens causes distinguishable changes in the macrocycle parameters. These changes are caused by the enlargement of the bond distances in the region of substitution due to the electron donating effect of the methyl. However, addition of the *tert*-butyl group to the isoindole moiety of the macrocycle does not cause such a significant effect to the macrocycle geometrical parameters due to the more remote position occupied in the core.

Table 1 presents a selection of some of the more relevant geometrical parameters of compounds **1a**, **1b** and **1c**. Only copper Tpc (**1b**) has significant variations relative to metal-free Tpc in the triazole moiety bond lengths, the C–N distance is enlarged and N–N bond is shortened, with a higher double bond character (1.26 Å). Geometrical parameters of the macrocycle and triazole moieties of nickel Tpc are similar to the metal-free Tpc where C–metal distances are slightly higher in copper Tpc than nickel Tpc.

Another interesting result is the high dipolar moment calculated for these compounds (Table 2) – which is in agreement with some experimental data in related triazolephthalocyanines.[35]

The analysis of the Mulliken charges obtained from ZINDO structures (Table 3) indicates that the positive charge upon methylation in the triazole and *meso* nitrogen seems to be distributed over the macrocycle carbons and over the nitrogen to which the methyl group is attached (from the table, it can be verified that the charge in the triazole and *meso* nitrogens varies from around −0.18 when it is unsubstituted, to around zero when it is methylated). With metal Tpcs, in addition to this effect, the charge over the metal is increased, together with a slight decrease in the charge of the metal-bonded nitrogens.

Table 1 Selected geometrical parameters of compounds **1a**, **1b**, **1c**

Compound	C–N (triazole) /Å	N–N (triazole) /Å	C–Metal (mean dist.) /Å
1a	1.36	1.30	—
1b	1.41	1.26	1.93
1c	1.36	1.30	1.89

Table 2 Calculated dipolar moments of **2b** and **2c**

	Theoretical $\mu^{(0)}$ (D)		
Compound	AM1	MNDO	ZINDO
1a	7.54	8.61	
1b		6.78	
2a	12.28		
2b		6.98	6.90
2c			13.18
4a	3.34		
4b		2.17	
5a	4.17		
5b		3.31	
6a	9.39		

Table 3 Mulliken charges over some of the key-positions in Tpcs

	Compound								
	1a	**4a**	**6a**	**1b**	**4b**	**6b**	**1c**	**4c**	**6c**
Central atom	0.29	0.32	0.31	−0.41	−0.05	0.35	−0.11	0.00	−0.06
Triazole N	−0.19	−0.22	−0.17	−0.12	−0.22	0.00	−0.18	−0.22	−0.16
	−0.19	0.05[a]	−0.20	−0.13	−0.06[a]	−0.19	−0.18	−0.06[a]	−0.18
Meso N	−0.25	−0.31	−0.03[a]	−0.26	−0.29	0.06[a]	−0.22	−0.29	0.00
Metal-bonded N	—	—	—	−0.17	−0.20	−0.17	−0.18	−0.21	−0.19
				−0.18	−0.23	−0.19	−0.18	−0.23	−0.19
				−0.19	−0.23	−0.20	−0.19	−0.24	−0.22
				−0.19	−0.21	−0.32	−0.22	−0.24	−0.22

[a] Substituted atom

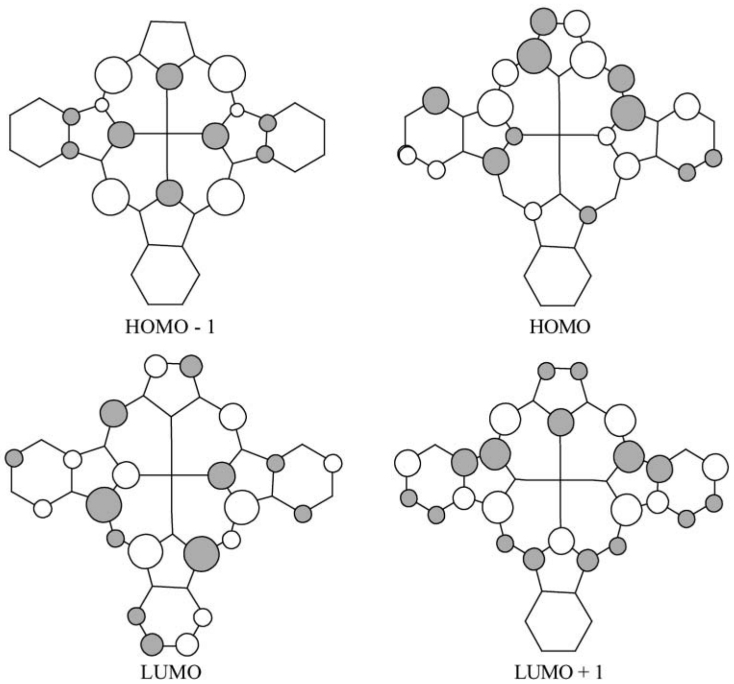


Fig. 4 Frontier orbitals in triazolephthalocyanines.

Analysis of molecular orbitals

The frontier orbitals of the metal-free unsubstituted Tpc (compound **1a**), minimised by ZINDO/s, are shown in Fig. 4. It can be seen that the HOMO and LUMO orbitals have a_2 symmetry, and the HOMO-1 and LUMO+1 are b_1 type.

Nickel Tpc has the same frontier orbitals as the metal-free analog, while copper Tpc, due to the open-shell configuration, has a different distribution – the singly occupied molecular orbital of copper Tpc corresponds to the LUMO of the metal-free and nickel analogs. Thus, the HOMO-1 and HOMO orbitals of copper Tpc have a_2 symmetry, the LUMO is b_1 type, and the LUMO+1, which is a *d*-type orbital, has a_1 symmetry.

The Gouterman's four level model, which predicts that these four frontier orbitals are separated by a gap of 1.5 to 3.0 eV from the others, is partially broken in these triazolephthalocyanines. As in the previously studied subphthalocyanines,[25] the HOMO-1 is split from the HOMO and is very close to the HOMO-2 (see Fig. 5).

This phenomenon was previously studied by *ab initio* calculations[25] and seems to be related to the presence of the *meso* nitrogens. The *meso*-nitrogens contribute to a large extent to the HOMO-1 orbital (Fig. 4), and are responsible for the stabilization of HOMO-1. The LUMO and LUMO+1 energy levels are in agreement with the Gouterman's model.

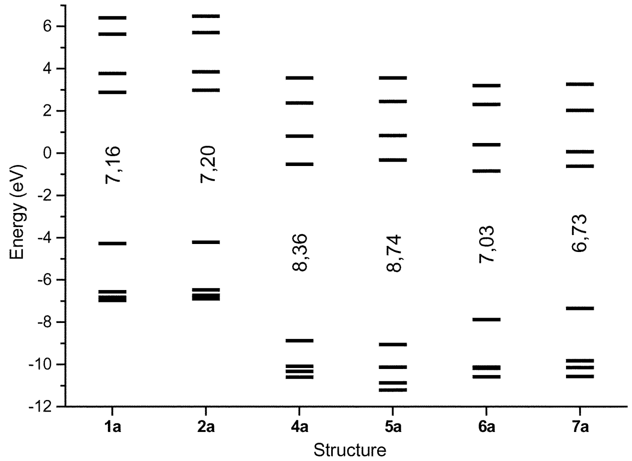


Fig. 5 Frontier orbital energy levels of metal-free triazolephthalocyanines.

The substitution effects on the orbital energies are also depicted in Fig. 5. The *tert*-butyl addition does not cause any significant changes in the energy profile, since the frontier orbitals have no contributions from the substituted carbon, except for the LUMO, which is slightly unstabilised. Methyl substitution in the triazole nitrogens seems to affect the HOMO orbital significantly, stabilizing it in relation to the unsubstituted Tpc. A possible reason for this effect is that the substitution produces a better distribution of the electronic density in the π system in the HOMO orbital – it is distributed over a higher number of atoms (Fig. 6), improving the stability of the bonds.

The "upper" *meso*-nitrogens (closer to the triazole) in compound **6a** also contribute to the HOMO orbital (see Fig. 6), but methylation in this position does not affect the orbital energy significantly – only a small stabilization of the HOMO orbital is perceived. Compound **7a** (substituted in the "lower" nitrogen – further away from the triazole), on the other hand makes no contribution to the HOMO – thus, the orbital shape and the frontier orbitals energy profile is similar to that of the unsubstituted compound (**1a**).

Electronic spectra

Some of the ZINDO calculated electronic spectra of the Tpc's with their most important transitions and the corresponding experimental spectra[28–30] are shown in Fig. 7.

The spectrum analysis of copper Tpc compounds were more restricted than for nickel and H_2, since the transitions cannot be identified in the program output for open-shell configurations. This fact also seems to be responsible for a remarkable difference between the energy levels of the unsubstituted structure and the *tert*-butyl substituted one. A difference of 0.39 eV in the HOMO–LUMO gap is found between these compounds.

Experimental UV–VIS results show a pattern similar to the theoretical spectrum for compounds **2c** and **2b** (Figs. 7a and 7b respectively), even though the peaks do not match exactly. According to the calculations, for all the compounds, the two

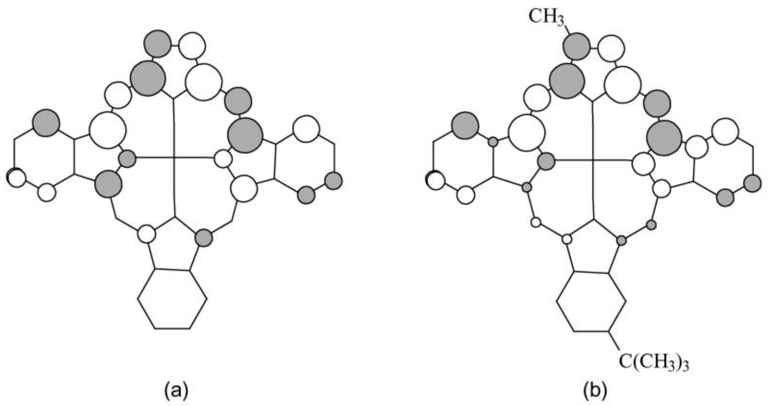


Fig. 6 HOMO orbitals of compounds **1a** (a) and **5a** (b).

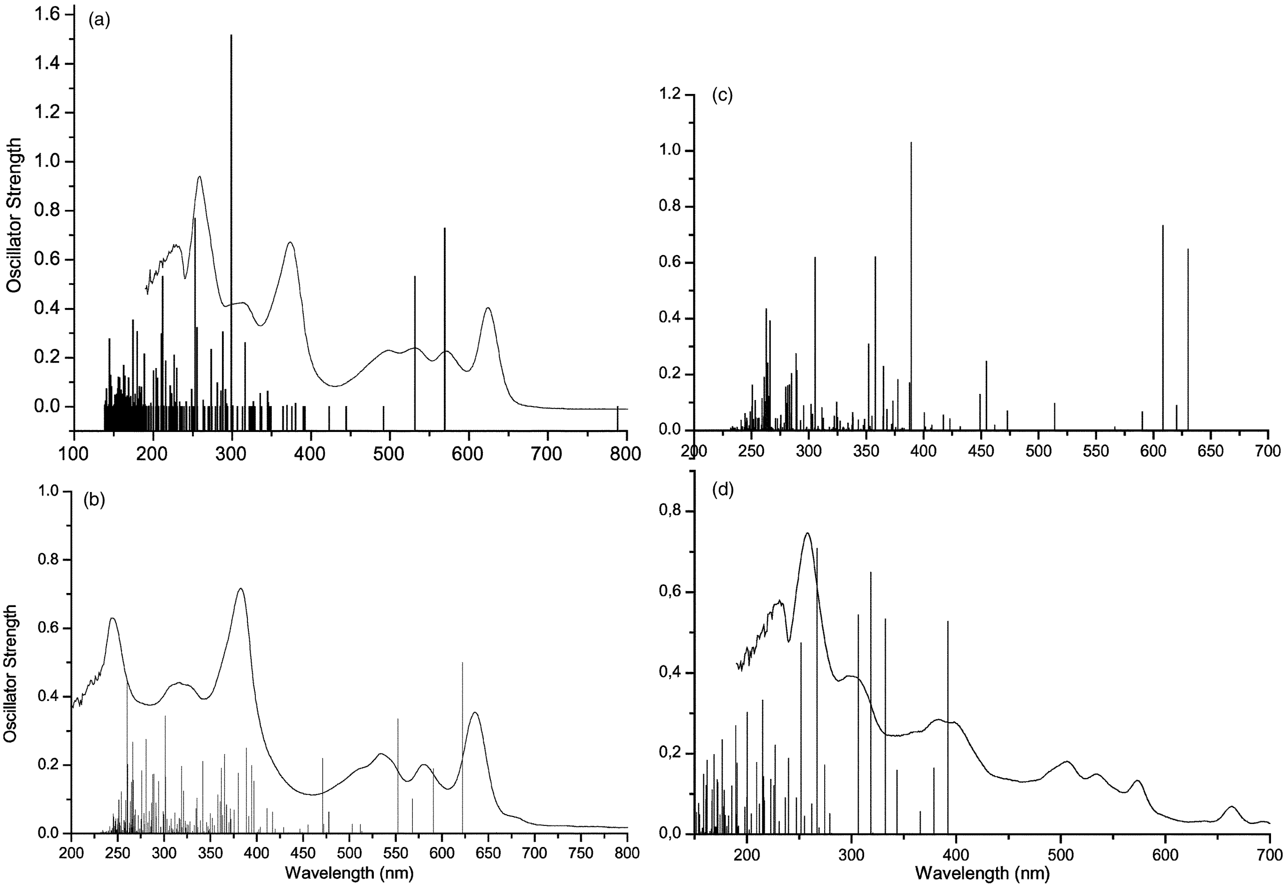


Fig. 7 Calculated and experimental electronic spectra of compounds **2c** (a); **2b** (b); **1b** (c) and **3c** (d).

peaks that appear in the visible region (500–700 nm) are attributed to the HOMO → LUMO (higher wavelength) and HOMO → LUMO+1 (shorter wavelength). The most intense group of signals in the UV region, which appears around 300 and 400 nm, is attributed to transitions from inner valence orbitals to the LUMO orbital, usually with contributions of more than one transition. Other transitions in the UV region (below 300–400) are not identifiable as a pattern between all the structures.

While the theoretical spectrum of compound **2c** (Fig. 7a) just shows two bands on the visible region, four bands can be observed on the experimental one. However, copper Tpc **2b** spectrum (Fig. 7b) presents more similarities in this region since the calculated spectrum also has four transitions in this range.

Comparison between Cu and Ni Tpcs **1b** and **1c** is not possible due to the insolubility of these substances in low polar solvents.

The effect of substitution in the isoindole moiety can be analysed by comparison of theoretical spectra of **1b** and **2b** (Figs. 7c and 7b respectively). The addition of the *tert*-butyl substituent does not change the electronic spectra significantly, only a variation of relative intensity and an increase of distance between bands is observed in the visible region. This trend may indicate a loss of resolution in this zone of the spectrum by increasing the number of substituents in the isoindole unit. This effect has already been found experimentally within triazolephthalocyanines with donor substituents such as $OC_{12}H_{25}$ and a higher number of donor substituents.[35]

The addition of the methyl group in the triazole subunit (**3c**) causes the appearance of a high number of intense peaks in the UV region (from 200 to 300 nm). The comparison of compounds **3c** (590 nm) and **2c** (690 nm) also shows a strong hypsochromic shift of the HOMO → LUMO and HOMO → LUMO+1 transitions from the visible 500–700 nm to the UV

350–400 nm region (Figs. 7d and 7a respectively). This fact has also been observed experimentally.[28]

Summary and conclusions

This report presents a theoretical analysis, by means of quantum mechanical semiempirical calculations, of a series of molecular properties of triazolephthalocyanines, where the influence of the central metal and alkyl substituents in different positions of the structure has been studied. The results clearly indicate that *tert*-butyl group substitution in the isoindole has minor effects overall on the molecular properties. The addition of methyl groups to the nitrogens of the triazole moiety and to the *meso*-nitrogens of the macrocycle causes a partial breakdown in the Gouterman's four level model – a splitting between the HOMO and HOMO-1 energies is observed. As expected, there are some differences between the electronic spectra of metal-free and metallated Tpcs. However, the spectra of metallated Tpcs seem to be less susceptible to changes upon alkyl substitutions than those from metal-free Tpcs. Experimental UV–VIS spectra of Tpcs are compared to the electronically calculated spectra showing a similar pattern. These results are of interest for the design of new triazolephthalocyanines with appropriate features, useful for the preparation of molecular materials.

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