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New olefinic centred binuclear clamshell type phthalocyanines: Design, synthesis, structural characterisation, the stability and the change in the electron cloud at olefine-based symmetrical diphthalonitrile fragment by the combined application of UV–Vis electronic structure and theoretical methods

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ABSTRACT

The olefinic centred Schiff base (**3**) was obtained from the condensation of substituted dialdehyde (**1**) with 2-amino-4-methylphenol (**2**) in a 1:2 ratio. The diphthalonitrile derivative (**5**) was prepared by the reaction of 4-nitrophthalonitrile (**4**) and compound (**3**) in dry dimethylformamide/potassium carbonate. The key product (**5**) was obtained by nucleophilic substitution of an activated nitro group into an aromatic ring. The cyclotetramerization of compound (**5**) with phthalonitrile (**6**) in 1:6.15 ratio gave the expected metal-free phthalocyanine of clamshell type (**7**), and with metal salts of Zn(II), Ni(II), Co(II) and Cu(II) gave metallophthalocyanines of clamshell types (**8–11**), respectively in dimethylaminoethanol/1,8-diazabycyclo[5.4.0]undec-7-ene system. The products were purified by several techniques such as crystallization and preparative thin layer chromatography. The newly prepared compounds were characterised by a combination of elemental analyses, IR, $^1H/^{13}C$ NMR, MS and UV–Vis spectroscopy.

1. Introduction

Phthalocyanines (Pcs), because of their unique properties, have been a popular class of compounds for chemists since their discovery. Pcs have been used in areas such as chemical sensors, semiconductors, liquid crystals, molecular metals, catalysis, non-linear optics and electrochromism [1,2]. Most of the metal ions can bind to the cavity of the Pc macrocycle. So many metallophthalocyanines have been synthesized so far [2–4]. Metallophthalocyanines (MPcs) are important because of their rich redox behaviour and chemical stability [5,6].

While the principle molecules have many useful properties, scientists have attempted considerable effort to achieve novel structures that may show improved or novel characteristics. In this connection binuclear Pcs that have different bridges have been attracted attention [7–10]. Recently, many investigators have been focused on binuclear phthalocyanines linked by only one bridge, called as clamshell [11–15]. Many Pc dimers and multimers that have various kinds of bridges have been reported to date. These dimers and multimers generally show different electrical, electrochemical and spectroscopic properties in proportion to the parent monomers. Solely, there have been few reports on low-symmetry substituted phthalocyanines, mainly because of the difficulties in preparation and purification [16,17]. In addition, in the last few decades scientists have been focused on unsymmetrically substituted phthalocyanines with different substituents at the macrocycle fragment [18]. Such phthalocyanines have interesting characteristics and properties that enable their use as new technical materials in non-linear optics and photosensitisers in the photodynamic therapy of cancer [19–23].

In this study, the synthesis, characterisation and structural investigation of metal-free and metallophthalocyanines of clamshell type, which contain olefinic bridge and schiff base moieties, are described. On the other hand, the substituted diphthalonitrile **5**, because it is the starting material of all pcs and a considerable step compound between the substituted diphenol **3** and functionalised pcs **7–11**, is analysed as part of examination of the role of the most stable conformation in order to have better interpretation of its UV–Vis experimental results, with all possible electron transitions, at density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations.

2. Experimental

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen, using standard Schlenk techniques. All solvents were dried and purified as described by Perin and Armarego [24].

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4,4′-[(2*E*)-but-2-ene-1,4-diylbis(oxy)]bis(3-methoxybenzaldehyde) **1** [25] and 4-nitrophthalonitrile **4** [26] was prepared according to the literature, and 2-amino-4-methyl phenol **2** and phthalonitrile **6** was purchased from Merck. ^{1}H NMR/^{13}C NMR spectra were recorded on a Varian XL-200 NMR spectrophotometer in $CDCl_3$, and chemical shifts were reported (δ) relative to Me_4Si as internal standard. IR spectra were recorded on a Perkin–Elmer Spectrum one FT-IR spectrometer in KBr pellets. The MS spectra were measured with a Micromass Quattro LC/ULTIMA LC–MS/MS spectrometer equipped with chloroform–methanol as solvent. All experiments were performed in the positive ion mode. Elemental analysis were performed on a Costech ECS 4010 instrument; the obtained values agreed with the calculated ones. UV–Vis spectra were recorded by means of a Unicam UV2-100 spectrophotometer, using 1 cm pathlength cuvettes at room temperature. Melting points were measured on an electrothermal apparatus and are uncorrected.

2.1. Synthesis

2.1.1. 2,2′-{(2E)-but-2-ene-1,4-diylbis[oxy(3-methoxy-4,1-phenylene) (E) methylylidene nitrilo]} bis(4-methylphenol) (**3**)

4,4′-[(2*E*)-but-2-ene-1,4-diylbis(oxy)]bis(3-methoxybenzaldehyde) (**1**) (3.92 g, 0.011 mol) and 2-amino-4-methyl phenol **2** (2.71 g, 0.022 mol) were heated under reflux at 160 °C for 3 h with no solvent. The crude product was dissolved in 10 mL DMF and filtered then water was added to the filtrate and precipitate was filtered, washed with hot ethanol and dried over P_2O_5. The precipitated solid was recrystallised from appropriate solvent (DMF/ethanol). Yield: 5.23 g (84%).

Anal. Calc. for $C_{34}H_{34}N_2O_6$: C, 67.41; H, 5.66; N, 4.94. Found: C, 67.35; H, 5.60; N, 4.89%. IR (KBr tablet) ν_{max}/cm^{-1}: 3349 ν(—OH), 3026 ν(Ar-CH), 2914–2881 ν(aliph. CH), 1625–1597 ν(C=C), 1579 ν(CH=N), 1331 δ(—OH), 1271–1225 ν(C—O—C)/(C—N), 1128 δ(C—N), 1028–1009 δ(C—O—C), 981 δ(CH). ^{1}H NMR ($CDCl_3$) (δ: ppm): 12.85 (bs, 2H, OH), 8.57 (s, 2H, CH=N), 7.56 (s, 2H/Ar-H_7), 7.34–7.30 (dd, 2H/Ar-H_{11} *J* = 8.06 and 1.68 Hz), 7.07–6.88 (m, 8H/Ar-$H_{5,4,13,14}$), 6.17 (bs, 2H, =$CH_{olefinic}$), 4.73 (s, 4H, OCH_2), 3.98 (s, 6H, OCH_3), 2.31 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$) (δ: ppm): 163.24 (CH=N), 151.19 (C_8), 147.54 (C_3), 146.21 (C_{15}), 136.79 (C_{10}), 136.18 (C_{12}), 130.11 (C_6), 129.79 (=$CH_{olefinic}$), 126.23 (C_5), 122.73 (C_{13}), 122.40 (C_{11}), 120.52 (C_{14}), 112.71 (C_4), 109.84 (C_7), 68.52 (CH_2), 56.06 (OCH_3), 21.04 (CH_3). MS (ESI) (*m*/*z*): Calculated: 566.24; Found: 566.44 $[M]^+$.

2.1.2. 14,4′-(2,2′-(4,4′-(E)-but-2-ene-1,4-diylbis(oxy)bis(3-methoxy-4,1-phenylene))bis (me-than-1-yl-1-ylidene)bis(azan-1-yl-1-ylidene)bis(4-methyl-2,1-phenylene))bis(oxy) diphthalonitrile (**5**)

To a solution of 4-nitrophthalonitrile **4** (0.0613 g, 0.354 mmol) in dry DMF (15 mL) compound **3** (0.10 g, 0.177 mmol) was added and the temperature was increased up to 55–60 °C. Powdered K_2CO_3 (0.0732 g, 0.531 mmol) was added to the system in eight equal portions at 15 min intervals with efficient stirring and the reaction system was stirred at the same temperature for 5 days. The completeness of the reaction was controlled by thin layer chromatography (TLC) (chloroform). The temperature of the system was lowered to room temperature and poured into ice-water and mixed overnight. The precipitate was filtered and dried in vacuum over P_2O_5 and recrystallised from ethanol to give dark yellow crystalline powder. Yield: 0.099 g (68.3%), m.p.: 184–185 °C.

Anal. Calc. for $C_{50}H_{38}N_6O_6$: C, 73.34; H, 4.68; N, 10.26. Found: C, 73.41; H, 4.74; N, 10.19%. IR (KBr tablet) ν_{max}/cm^{-1}: 3050 ν(Ar-CH), 2923–2853 ν(aliph. CH), 2230 (C≡N), 1624–1599 ν(C=C), 1510 ν(CH=N), 1270–1250 ν(C—O—C)/(C—N), 1112 δ(C—N), 1037–1010 δ(C—O—C), 981 δ(CH). ^{1}H NMR ($CDCl_3$) (δ: ppm): 8.28 (s, 2H, CH=N), 7.68–7.63 (d, 2H/Ar-H_{18}, *J* = 8.39 Hz), 7.43–7.40 (bm, 2H/Ar-H_{21}), 7.26–7.24 (bd, 4H/Ar-$H_{7,11}$), 7.20–7.08 (bd, 6H/Ar-$H_{17,5,4}$), 7.0 (bs, 2H/Ar-H_{14}), 6.87–6.83 (d, 2H/Ar-H_{13}, *J* = 7.72 Hz), 6.12 (bs, 2H/=$CH_{olefinic}$), 4.69 (bs, 4H, OCH_2), 3.81 (s, 6H, OCH_3), 2.42 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$) (δ: ppm): 162.16 (CH=N), 160.65 (C_{16}), 151.27 (C_8), 149.66 (C_{15}), 143.64 (C_3), 137.49 (C_{10}), 135.38 (C_{12}), 134.96 (C_{18}), 130.29 (=$CH_{olefinic}$), 129.23 (C_{13}), 128.34 (C_{21}), 126.61 (C_6), 124.33 (C_{17}), 121.97 (C_{11}), 121.20 (C_5), 120.65 (C_{14}), 117.87 (C_{20}), 115.57 (C≡N), 112.79 (C_4), 109.29 (C_{19}), 107.80 (C_7), 68.57 (CH_2), 56.04 (OCH_3), 21.08 (CH_3). MS (ESI) (*m*/*z*): Calculated: 818.29; Found: 818.79 $[M]^+$.

2.1.3. Binuclear metal-free phthalocyanine of clamshell type (**7**)

The solution of compound **5** (0.20 g, 0.244 mmol), phthalonitrile **6** (0.19 mg, 1.5 mmol) in dry *N*,*N*-dimethylaminoethanol (DMAE) (3 mL) and 1,8-diazabycyclo[5.4.0]undec-7-ene (DBU) (0.037 mL, 0.244 mmol) was heated and stirred in a glass sealed tube at 160 °C for 24 h. Then it was diluted with pure water (ca. 30 mL) and stirred for 12 h. The product was filtered and then washed with water, hot ethanol, diethyl ether and dried in vacuum over P_2O_5. The solid product was chromatographed on preparative silicagel plate (0.5 mm) with chloroform/methanol (5.6:1) as eluents to give dark green product.

Yield: 0.0133 g (3.4%), m.p. >300 °C (decomposition). *Anal.* Calc. for $C_{98}H_{66}N_{18}O_6$: C, 73.95; H, 4.18; N, 15.84. Found: C, 73.75; H, 4.07; N, 14.70%. IR (KBr tablet) ν_{max}/cm^{-1}: 3303 (—NH), 3051 ν(Ar-CH), 2924–2854 ν(aliph. CH), 1617–1600 ν(C=C), 1510 ν(CH=N), 1267–1250 ν(C—O—C)/(C—N), 1118 δ(C—N), 1094 δ (—NH) 1035–1014 δ(C—O—C)/(—NH), 971 δ(CH). ^{1}H NMR ($CDCl_3$) (δ: ppm): 8.34 (s, 2H, CH=N), 7.93–6.69 (bm, 42H/Ar-H), 6.05 (s, 2H/=$CH_{olefinic}$), 4.56 (s, 4H, OCH_2), 3.49 (bs, 6H, OCH_3), 2.49 (s, 6H, CH_3). UV–Vis (chloroform): λ_{max}/nm: [(10^{-5} logε dm^3 mol^{-1} cm^{-1})]: 699 (5.37), 662 (5.32), 641(4.85), 602 (4.73), 339 (5.21), 288 (5.17). MS (ESI) (*m*/*z*): Calculated: 1591.69; Found: 1591.84 $[M]^+$.

2.1.4. The general procedure for synthesis of metallophthalocyanines **8–11**

A mixture of compound **5** (0.15 g, 0.183 mmol), phthalonitrile **6** (0.14 g, 1.124 mmol), related metal salts ($Zn(Ac)_2$ (0.0716 g, 0.390 mmol); $Ni(Ac)_2$ (0.068 g, 0.390 mmol); $CoCl_2$ (0.051 g, 0.390 mmol); $CuCl_2$ (0.053 g, 0.390 mmol)), dry DMAE (3 mL) and 1,8-diazabycyclo[5.4.0]undec-7-ene (DBU) (0.028 mL, 0.183 mmol) was heated and stirred in a glass sealed tube at 160 °C for 24 h. Then it was diluted with pure water (ca. 30 mL) and stirred for 12 h. The product was filtered and then washed with water, hot ethanol, diethyl ether and dried in vacuum over P_2O_5. The solid product was chromatographed on preparative silicagel plate (0.5 mm) with chloroform/methanol (1:17.5) as eluents to give dark green product. The chemical and physical spectral characteristics of these products **8–11** are given below.

*2.1.4.1. Binuclear Zn(II) phthalocyanine of clamshell type (**8**).* Yield: 0.020 g (6.5%), m.p.: >300 °C (decomposition). *Anal.* Calc. for $C_{98}H_{62}N_{18}O_6Zn_2$: C, 68.50; H, 3.64; N, 14.67. Found: C, 68.33; H, 3.41; N, 14.63%. IR (KBr tablet) ν_{max}/cm^{-1}: 3049 ν(Ar-CH), 2924–2846 ν(aliph. CH), 1615–1597 ν(C=C), 1510 ν(CH=N), 1267–1251 ν(C—O—C)/(C—N), 1115 δ(C—N), 1031–1013 δ(C—O—C), 983 δ(CH). ^{1}H NMR ($CDCl_3$) (δ: ppm): 8.25 (bs, 2H, CH=N), 7.90–6.91 (m, 42H/Ar-H), 6.19 (s, 2H/=$CH_{olefinic}$), 4.69 (s, 4H, OCH_2), 3.86 (bs, 6H, OCH_3), 2.38 (s, 6H, CH_3). UV–Vis (chloroform): λ_{max}/nm: [(10^{-5} logε dm^3 mol^{-1} cm^{-1})]: 673 (5.21), 610 (4.61), 346 (5.11), 283 (4.69). MS (ESI) (*m*/*z*): Calculated: 1718.44; Found: 1718.54 $[M]^+$.

*2.1.4.2. Binuclear Ni(II) phthalocyanine of clamshell type (**9**).* Yield: 0.019 g (6.2%), m.p.: >300 °C (decomposition). *Anal.* Calc. for $C_{98}H_{62}N_{18}Ni_2O_6$: C, 69.03; H, 3.67; N, 14.79. Found: C, 69.12; H, 3.74; N, 14.96%. IR (KBr tablet) ν_{max}/cm^{-1}: 3051 ν(Ar-CH), 2925–2854 ν(aliph. CH), 1621–1594 ν(C=C), 1508 ν(CH=N), 1266–1253 ν(C—O—C)/(C—N), 1114 δ(C—N), 1028–1015 δ(C—O—C), 985 δ(CH). ^{1}H NMR (CDCl$_3$) (δ: ppm): 8.23 (bs, 2H, CH=N), 7.89–6.81 (bm, 42H/Ar-H), 6.17 (s, 2H/=CH$_{olefinic}$), 4.74 (s, 4H, OCH$_2$), 3.96 (bs, 6H, OCH$_3$), 2.34 (s, 6H, CH$_3$). UV–Vis (chloroform): λ_{max}/nm: [(10^{-5} logε dm^3 mol^{-1} cm^{-1})]: 672 (5.20), 645 (4.77), 267 (5.18), 246 (5.06). MS (ESI) (*m*/*z*): Calculated: 1705.05; Found: 1705.43 [M]$^+$.

*2.1.4.3. Binuclear Co(II) phthalocyanine of clamshell type (**10**).* Yield: 0.021 g (6.8%), m.p.: >300 °C (decomposition). *Anal.* Calc. for $C_{98}H_{62}Co_2N_{18}O_6$: C, 69.01; H, 3.66; N, 14.78. Found: C, 69.17; H, 3.61; N, 14.63%. IR (KBr tablet) ν_{max}/cm^{-1}: 3049 ν(Ar-CH), 2917–2851 ν(aliph. CH), 1617–1596 ν(C=C), 1511 ν(CH=N), 1281–1257 ν(C—O—C)/(C—N), 1119 δ(C—N), 1035–1016 δ(C—O—C), 981 δ(CH). UV–Vis (chloroform): λ_{max}/nm: [(10^{-5} logε dm^3 mol^{-1} cm^{-1})]: 679 (5.23), 650 (4.78), 310 (5.13), 247 (5.20). MS (ESI) (*m*/*z*): Calculated: 1705.53; Found: 1705.12 [M]$^+$.

*2.1.4.4. Binuclear Cu(II) phthalocyanine of clamshell type (**11**).* Yield: 0.023 g (7.5%), m.p.: >300 °C (decomposition). *Anal.* Calc. for $C_{98}H_{62}Cu_2N_{18}O_6$: C, 68.64; H, 3.64; N, 14.70. Found: C, 68.54; H, 3.81; N, 14.55%. IR (KBr tablet) ν_{max}/cm^{-1}: 3045 ν(Ar-CH), 2926–2862 ν(aliph. CH), 1617–1597 ν(C=C), 1506 ν(CH=N), 1267–1254 ν(C—O—C)/(C—N), 1020 δ(C—N), 1028–1015 δ(C—O—C), 973 δ(CH). UV–Vis (chloroform): λ_{max}/nm: [(10^{-5} logε dm^3 mol^{-1} cm^{-1})]: 679 (5.28), 648 (4.78), 328 (5.13), 231 (5.07). MS (ESI) (*m*/*z*): Calculated: 1714.75; Found: 1714.66 [M]$^+$.

3. Results and discussion

3.1. Methods and spectroscopic characterisation via complementary techniques

The preparation of olefinic centred substituted Schiff bases **3** and **5**, the target binuclear metal-free phthalocyanine **7** and metallophthalocyanines of clamshell type **8, 9, 10** and **11**, is shown in Fig. 1. The structures of novel compounds have been characterised by a combination of ^{1}H/^{13}C NMR, IR, UV–Vis, elemental analysis and MS spectral data.

*3.1.1. Synthesis of precursor **3***

Functionalised olefinic centred Schiff base **3** was synthesized at considerably high temperature with no solvent. The IR spectra were used to identify substituents appearing or disappearing from the periphery of the related compounds. In the IR spectrum of **3**, stretching vibration peaks of NH$_2$ group of reactant **2** at 3344–3321 cm^{-1} and aldehyde group of **1** at 1690 cm^{-1} were not present, and that indicates the amino and aldehyde groups have been converted to Schiff base. In addition, a new band at 1579 cm^{-1} corresponding to imine group of **3** proves the condensation has

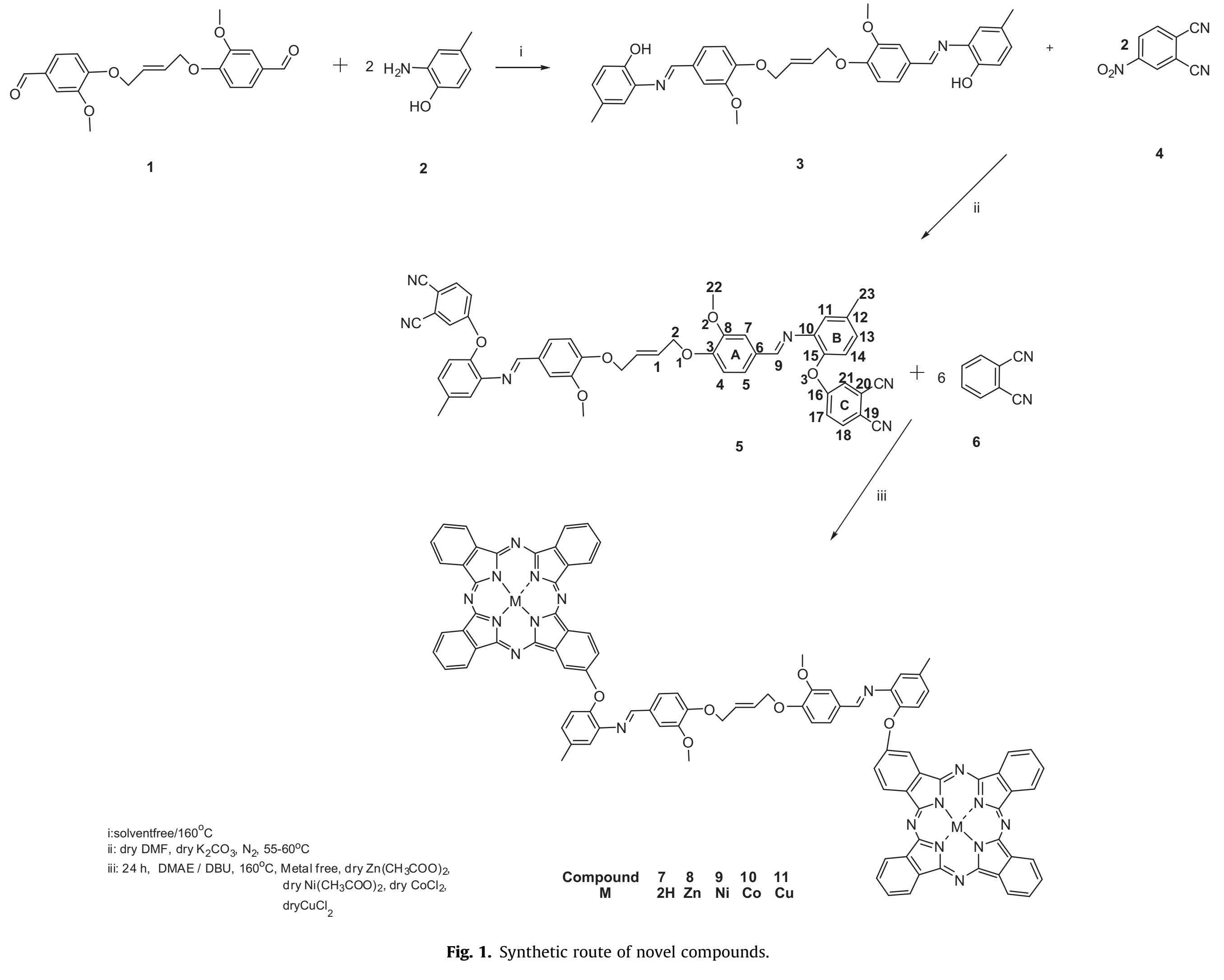


Fig. 1. Synthetic route of novel compounds.

occurred. The rest of the spectrum of **3** was similar those of **1** and **2** involving the characteristic vibrations of aliphatic, olefinic and phenolic groups. ^{1}H NMR spectrum of **3** had many differences from the spectrum of **1** and **2**. The difference between the spectra of **1** and Schiff base **3** has been clearly seen to arise from the absence of aldehyde group at 10.01 ppm. In addition, peaks of the amino group of **2** at 8.01 ppm were not observed in the spectrum of **3** too. Furthermore, D_2O exchangeable phenolic —OH protons and iminic protons of **3** were also observed at 12.85 ppm and 8.57 ppm, respectively. Furthermore, the MS mass spectrum of **3** showed a molecular ion peak at $m/z = 566.44$ $[M]^+$, supporting the proposed formula for this compound.

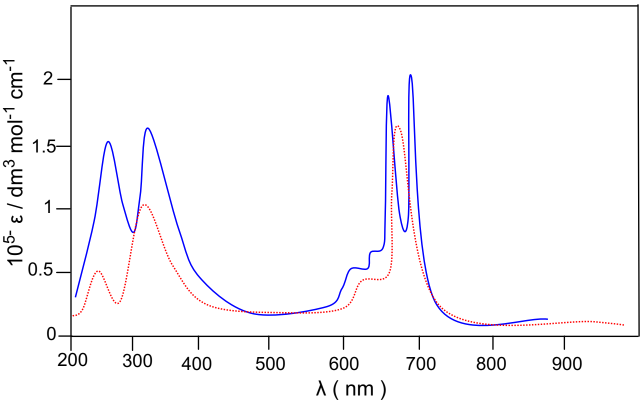


Fig. 2. UV–Vis spectra of compounds **7** (––) and **8** (····) in $CHCl_3$.

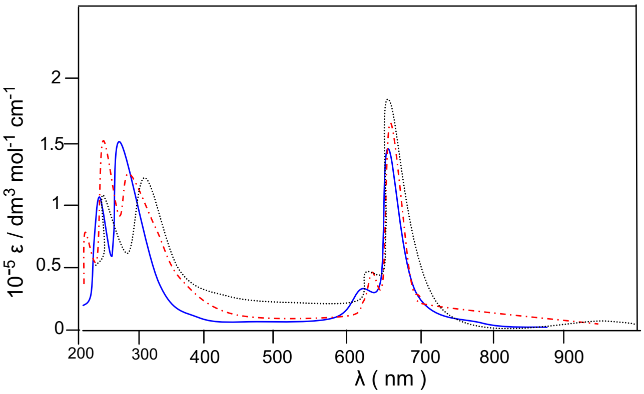


Fig. 3. UV–Vis spectra of compounds **9** (––), **10** (–·–·) and **11** (······) in $CHCl_3$.

*3.1.2. Synthesis of substituted diphthalonitrile **5***

Diphthalonitrile derivative **5** was obtained from the reaction of diphenol derivative **3** with 4-nitrophthalonitrile **4** in dry DMF/dry K_2CO_3 under N_2 atmosphere at 60 °C in schlenk system, for 5 days. This is achieved by base catalysed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile with **3** [27–29]. Spectral investigations for the new product were consistent with the assigned structure. IR spectra, taken with KBr pellets, clearly indicated the formation of compound **5**, by the disappearance of —OH stretching/deformation of **3** at 3349/1331 cm^{-1} and NO_2 stretching of compound **4** at 1519, 1333 cm^{-1} and by the appearance of $C{\equiv}N$ absorption band at 2230 cm^{-1}. Its ^{1}H NMR spectrum, which was taken in chloroform-*d*, was also in good correlation with the structure of the synthesized compound. D_2O exchangeable phenolic —OH at 12.85 ppm disappeared after condensation. Furthermore, in the aromatic region, four doublets at ca. $\delta = 7.68–7.63$ (H_{18}), 7.26–7.24 $(H_{7,11})$, 7.20–7.08 $(H_{4,5,17})$, 6.87–6.83 ppm (H_{13}) and a broad singlet at ca. $\delta = 7.0$ (H_{14}) and broad multiplet at ca. 7.43–7.40 (H_{21}) are observed in the spectrum, respectively. Additionally, ^{1}H NMR spectrum of compound **5** showed five singlets at $\delta = 8.28$ (—CH=N), 6.12 (HC=CH), 4.69 (OCH_2), 3.81 (OCH_3) and 2.42 ppm (CH_3) as expected. The proton-decoupled ^{13}C NMR spectrum indicated the presence of nitrile carbon atoms in compound **5** at 115.57 ppm. In addition, the MS mass spectrum of **5** showed a molecular ion peak at $m/z = 818.79$ $[M]^+$, supporting the proposed formula for this compound.

*3.1.3. Synthesis of metal free **7** and metallophthalocyanines **8–11***

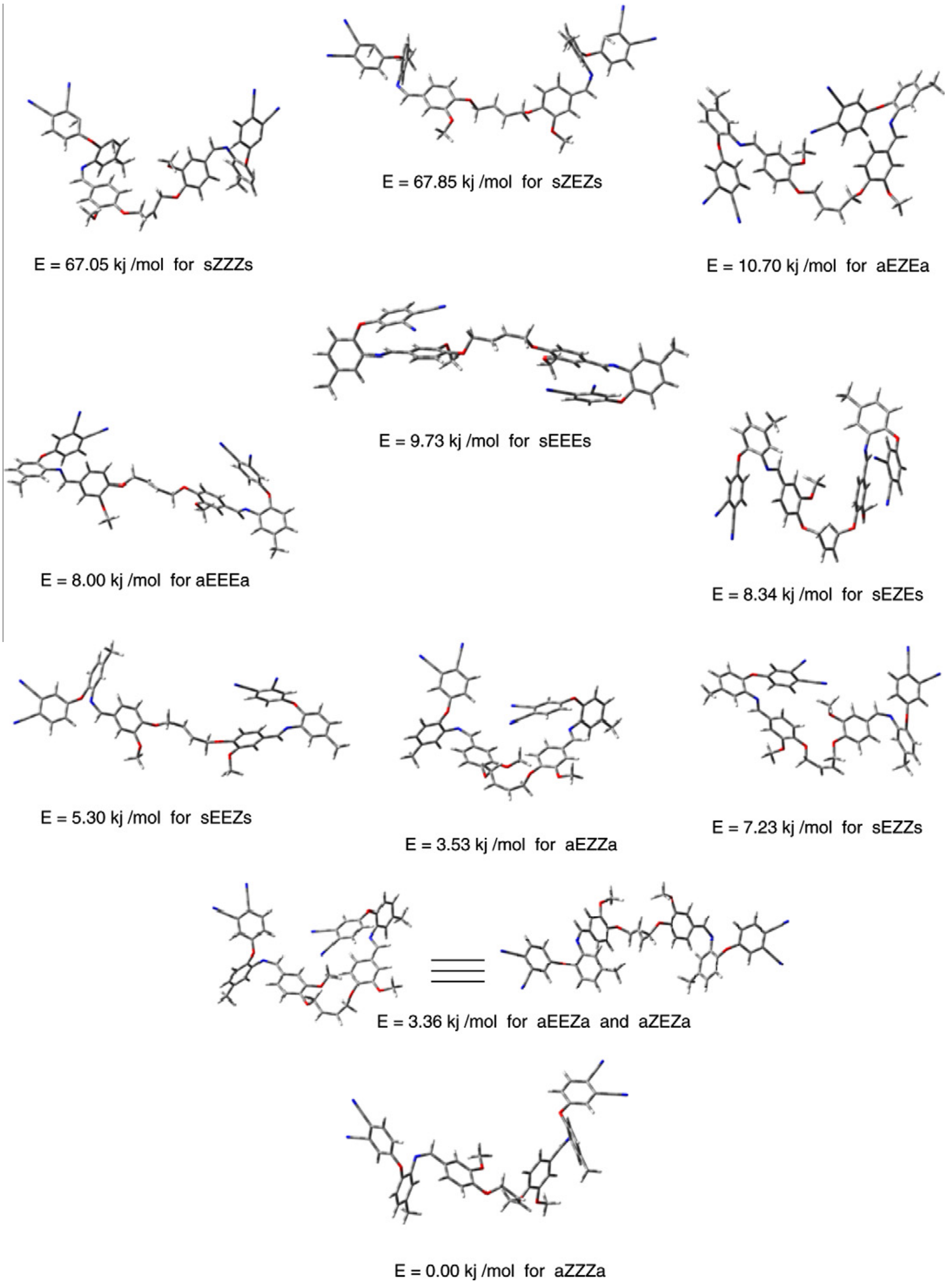
The unsymmetrical metal free phthalocyanine **7** was synthesized by statistical cross-condensation of a 1:6.15 molar ratio of **5** and **6** in DMAE/DBU by heating under reflux for 24 h. In case of metallophthalocyanines, addition to the substituted diphthalonitrile **5** and phthalonitrile **6**, four metal salts, $Zn(CH_3COO)_2$, $Ni(CH_3COO)_2$, $CoCl_2$, $CuCl_2$ were used as templates for the formation of **8, 9, 10** and **11** respectively. It is known that statistical cross-condensation of phthalonitriles gives the mixture of phthalocyanines, however, this method is commonly used for the preparation of different unsymmetrical Pcs [28,29]. Statistical considerations predict that when two phthalonitriles A and B (if they have same reactivity)

Table 1
The spin-allowed singlet–singlet electronic transitions with the TD-DFT method and the assignments of the calculated transitions to the experimental absorption bands of **5** with *aZZZa* conformer (a denotes HOMO, b denotes LUMO and Lp denotes nonbonding).

The most important orbital excitations	Transitions with major/ minor contributions	Oscillator (f)	λ_{exp} (nm)	λ_{calc} (nm)	Character
H−2 → L+1	212 → 216 (6%)	0.071	332	330	$\text{Lp}_{\text{nitrile}}/\text{Lp}_{\text{O1–3}} \rightarrow \sigma^{*}{-}\pi^{*}_{\text{C ring/C}\equiv\text{N/CH=N/O3}}$
H−1 → L	213 → 215 (37%)				$\text{Lp}_{\text{nitrile}}/\text{Lp}_{\text{O1–3}} \rightarrow \sigma^{*}{-}\pi^{*}_{\text{C ring/C}\equiv\text{N/CH=N/O3}}$
^{a}H → L+1	214 → 216 (86%)				$\text{Lp}_{\text{nitrile}}/\text{Lp}_{\text{O1–3}} \rightarrow \sigma^{*}{-}\pi^{*}_{\text{C ring/C}\equiv\text{N/CH=N/O3}}$
H−5 → L	209 → 215 (2%)	0.116	312	319	$\text{Lp}_{\text{azomethine}}/\text{Lp}_{\text{O1–3}} \rightarrow \sigma^{*}{-}\pi^{*}_{\text{C ring/C}\equiv\text{N/CH=N/O3}}$
H−5 → L+2	209 → 217 (4%)				$\text{Lp}_{\text{azomethine}}/\text{Lp}_{\text{O1–3}} \rightarrow \sigma^{*}{-}\pi^{*}_{\text{A ring/C}\equiv\text{N/CH=N/olefinic carbons/O1}}$
H−3 → L	211 → 215 (3%)				$\text{Lp}_{\text{O3}} \rightarrow \sigma^{*}{-}\pi^{*}_{\text{C ring/C}\equiv\text{N/CH=N/O3}}$
H−1 → L+2	213 → 217 (40%)				$\text{Lp}_{\text{nitrile}}/\text{Lp}_{\text{O1–3}} \rightarrow \sigma^{*}{-}\pi^{*}_{\text{A ring/C}\equiv\text{N/CH=N/olefinic carbons/O1}}$
H → ^{b}L	214 → 215 (80%)				$\text{Lp}_{\text{nitrile}}/\text{Lp}_{\text{O1–3}} \rightarrow \sigma^{*}{-}\pi^{*}_{\text{C ring/C}\equiv\text{N/CH=N/O3}}$
H → L+3	214 → 218 (60%)	1.109	287	297	$\text{Lp}_{\text{nitrile}}/\text{Lp}_{\text{O1–3}} \rightarrow \sigma^{*}{-}\pi^{*}_{\text{A ring/C}\equiv\text{N/CH=N/CH2/O1}}$
H−4 → L+3	210 → 218 (2%)	0.098	262	273	$\text{Lp}_{\text{O3}} \rightarrow \sigma^{*}{-}\pi^{*}_{\text{A ring/C}\equiv\text{N/CH=N/CH2/O1}}$
H−2 → L+3	212 → 218 (18%)				$\text{Lp}_{\text{nitrile}}/\text{Lp}_{\text{O1–3}} \rightarrow \sigma^{*}{-}\pi^{*}_{\text{A ring/C}\equiv\text{N/CH=N/CH2/O1}}$
H → L	214 → 215 (20%)				$\text{Lp}_{\text{nitrile}}/\text{Lp}_{\text{O1–3}} \rightarrow \sigma^{*}{-}\pi^{*}_{\text{C ring/C}\equiv\text{N/CH=N/O3}}$
H → L+2	214 → 217 (80%)				$\text{Lp}_{\text{nitrile}}/\text{Lp}_{\text{O1–3}} \rightarrow \sigma^{*}{-}\pi^{*}_{\text{A ring/C}\equiv\text{N/CH=N/olefinic carbons/O1}}$
H−3 → L	211 → 215 (3%)	1.019	239	253	$\text{Lp}_{\text{O3}} \rightarrow \sigma^{*}{-}\pi^{*}_{\text{C ring/C}\equiv\text{N/CH=N/O3}}$
H−3 → L+2	211 → 217 (2%)				$\text{Lp}_{\text{O3}} \rightarrow \sigma^{*}{-}\pi^{*}_{\text{A ring/C}\equiv\text{N/CH=N/olefinic carbons/O1}}$
H−1 → L	213 → 215 (49%)				$\text{Lp}_{\text{nitrile}}/\text{Lp}_{\text{O1–3}} \rightarrow \sigma^{*}{-}\pi^{*}_{\text{C ring/C}\equiv\text{N/CH=N/O3}}$
H−1 → L+2	213 → 217 (40%)				$\text{Lp}_{\text{nitrile}}/\text{Lp}_{\text{O1–3}} \rightarrow \sigma^{*}{-}\pi^{*}_{\text{A ring/C}\equiv\text{N/CH=N/olefinic carbons/O1}}$

react together in the ratio 3:1 will give a mixture of the symmetric Pc (AAAA), and the desired 3:1 Pc (AAAB) and other cross-condensation products [30,31]. Such an approach leads to a mixture of mainly two products, unsubstituted symmetric Pc and desired asymmetric Pc. Chromatographic purification was performed to obtain the desired products. In order to reduce the purification problems we chose phthalonitrile **6** and used excess, because it is known that the solubility of the unsubstituted symmetric Pc in common organic solvents is very low [32]. Therefore, after known classical solvent washings, these unsymmetrical Pcs were isolated by preparative silicagel chromatography plate using chloroform/methanol solvent system. The solubilities of the clamshell type phthalocyanines were good in common organic solvents such as chloroform, ethyl acetate, acetone, tetrahydrofurane and ethanol.

The spectroscopic characterisation of the newly synthesized compounds includes ^{1}H NMR, IR, UV–Vis and mass spectral investigations, and the results are in accordance with the proposed structures. Cyclotetramerization of dinitriles **5** and **6** to Pcs **7**, **8**, **9**, **10** and **11** was confirmed by the disappearance of the sharp C≡N vibration at 2230 cm^{-1} in their IR spectra. The IR spectrum of the metal-free phthalocyanine of clamshell type **7** showed known classical peaks. The peaks at 3303, 1094 and 1035 cm^{-1} are the characteristic metal-free pc —NH stretching and pyrrole ring vibration modes. The rest of the spectrum of **7** was similar



E = 67.05 kj /mol for sZZZs

E = 67.85 kj /mol for sZEZs

E = 10.70 kj /mol for aEZEa

E = 9.73 kj /mol for sEEEs

E = 8.00 kj /mol for aEEEa

E = 8.34 kj /mol for sEZEs

E = 5.30 kj /mol for sEEZs

E = 3.53 kj /mol for aEZZa

E = 7.23 kj /mol for sEZZs

E = 3.36 kj /mol for aEEZa and aZEZa

E = 0.00 kj /mol for aZZZa

Fig. 4. Calculated (B3LYP/6-31G(2d)) relative steric energies of conformations of **5**.

to that of **5**. Thus, it was enough evidence for the formation of metal-free Pc. In the ^{1}H NMR spectrum of compound **7** the typical shielding of inner core protons could not be observed due to the probable strong aggregation. The signals related to aromatic and aliphatic protons in the macrocyclic moieties and phthalocyanine skeleton represent the significant absorbance characteristics of the proposed structure. Furthermore, the MS mass spectrum of compound **7** showed a molecular parent ion peak at $m/z = 1591.84$ $[M]^+$, supporting the proposed formula for this compound. In addition, elemental analysis values was also satisfactory.

The IR spectra of metallophthalocyanines of clamshell type **8–11** were very similar, with the exception of the metal-free phthalocyanine **7** having an —NH stretching band at 3303 cm^{-1} due to the inner core. This band were not present in the spectra of the metallophthalocyanines. The ^{1}H NMR spectra of **10** and **11** could not be determined because of the presence of paramagnetic cobalt and copper atoms [33]. The ^{1}H NMR spectra of the compounds **8** and **9** were almost identical to those of the metal-free phthalocyanine **7**. Although the aggregation behaviour of the asymmetric Pcs is lower than symmetric Pcs, some of the signals of the dyes were broad in their ^{1}H NMR spectrum as a result of the aggregation of phthalocyanine cores at the considerable high concentration used for NMR measurements [34]. In the mass spectra of compounds **8–11**, the parent molecular ion peaks were observed at $m/z = 1718.54$ $[M]^+$ for **8**, 1705.43 $[M]^+$ for **9**, 1705.12 $[M]^+$ for **10** and 1714.66 $[M]^+$ for **11**, these peaks have verified the proposed structures.

3.2. UV–Vis absorption spectra

UV–Vis spectra of phthalocyanines show two well-known bands as a result of $\pi \rightarrow \pi^*$ transitions of the macrocycle moiety. One around ca. 300 nm is called as the "*B*" or Soret band, while the other one at 600–700 nm is called as the "*Q*" band. These two bands are present in all kinds of phthalocyanines. The *Q* band in metal-free phthalocyanine splits due to D_{2h} symmetry [35]. The electronic absorption spectrum of compound **7** in dilute chloroform solution at room temperature is shown in Fig. 2. The *Q* band splits to Q_x and Q_y, as expected [36]. The splitting *Q* band was observed at λ_{max} 699 and 662 nm, indicating the structure with D_{2h} symmetry [36–39].

The UV–Vis absorption spectra of metallophthalocyanines **8–11** in chloroform are very similar, with intense *Q* absorption bands between 679 and 672 nm with shoulders at 650–610 nm (corresponds to degenerate D_{4h} symmetry) and *B* bands at ca. 320 nm. These results were typical for metal complexes of substituted and unsubstituted Pcs with D_{4h} symmetry (Figs. 2 and 3) [35,38–43].

4. Computational details

The input structures of **5** were optimised using with combination of PM3 and RHF/3-21G methods [35,36]. Then the obtained ground-state geometry was optimised in vacuo with the B3LYP/6-31G(2d) method [35,36] and Becke's three-parameter hybrid functional (B3) with the nonlocal Lee–Yang–Parr theoretical correlation (LYP) method [44,45]. The vibrational frequency calculations were performed for all the studied conformations to check the structure stabilities that correspond to the minima in the potential energy surface. All calculations were performed with the GAUSSIAN 03W program package [46]. In calculations, tight converge criteria was used. By allowing that all the parameters could relax, all the calculations converged to optimised geometries, which corresponded to true energy minima. On the basis of the optimised ground state structure, the spectroscopic properties and UV–Vis absorption calculations in vacuum have been carried out by using the time-dependent density functional theory (TD-DFT) at B3LYP level, providing an accurate description of UV–Vis transitions of ligand system. This method was used to compute the 33 singlet → singlet transitions in vacuum. The related transitions are listed in Table 1. To better understanding, the three different benzene rings are abbreviated as A, B and C (Fig. 1).

*4.1. Interpretation of UV–Vis absorption spectrum of **5** via TD-DFT calculations*

We have completed our study also by theoretical calculations. The numbering and structure of the studied compound is illustrated in Fig. 1. The compound **5** can theoretically exist in 12 structural forms as follows [47,48]; *sEEEs, sEEZs, sZEZs, aEEEa, aEEZa, aZEZa, sEZEs, sEZZs, sZZZs, aEZEa, aEZZa, aZZZa* (Fig. 4). The first and fifth letters in the labelling denote the orientation of the methoxy group to the C═C double bond (i.e. in case of s(syn) the methoxy group is oriented towards the C═C double bond or in case of a(anti) the methoxy group is oriented away from the the C═C double bond), the second and fourth letters represent the orientation

Table 2
Selected geometric parameters (bond lengths in Å, bond and dihedral angles in degrees) of the most stable *aZZZa* conformer and the other ones.

	aZZZa Conformer	The other ones
$C_7—C_8$ (in Å)	1.385	between 1.348–1.381
$C_8—O_2$	1.40	1.371–1.399
$C_2—H_{2'}$	1.115	1.097–1.111
$C_6—C_7$	1.399	1.349–1.382
$C_7—H_7$	1.101	1.079–1.099
$C_{22}—H_{22'}$	1.114	1.094–1.10
$C_{22}—H_{22'}$	1.114	1.094–1.10
$C_{11}—C_{12}$	1.394	1.360–1.389
$C_{17}—C_{18}$	1.379	1.357–1.377
$C_{18}—H_{18}$	1.104	1.084–1.102
$C_{18}—C_{19}$	1.396	1.369–1.391
$C_{19}—C_{20}$	1.402	1.376–1.399
$C_{20}—CN$	1.463	1.319–1.411
$O_1—C_3—C_4$ (in °)	120.0	119.83–119.97
$O_1—C_2—H_{2'}$	110.39	108.68–110.0
$O_1—C_2—C_1$	108.86	108.31–108.80
$O_2—C_8—C_3$	116.91	114.57–116.22
$O_2—C_{22}—H_{22'}$	112.23	109.84–111.56
$O_2—C_{22}—H_{22''}$	112.23	109.78–111.54
$N_1—C_{10}—C_{15}$	120.23	118.18–120.21
$C_{19}—C_{20}—C_{20}$	120.43	118.19–120.12
$C_{19}—C_{18}—H_{18}$	119.36	117.39–119.25
$O_3—C_{16}—C_{17}$	118.34	115.39–118.01
$O_3—C_{16}—C_{21}$	124.91	119.97–121.78
$O_1—C_3—C_8—O_2$ (in °)	−4.31	3.99–4.31
$O_2—C_8—C_7—H_7$	0.06	0.05–0.54
$N_1—C_{10}—C_{11}—H_{11}$	5.36	0.04–4.25
$N_2—C_{19'}—C_{19}—C_{18}$	−4.25	−1.11–3.99
$O_3—C_{16}—C_{17}—H_{17}$	2.22	2.11–2.20
$O_3—C_{16}—C_{21}—H_{21}$	−2.71	1.99–2.70

Table 3
Occupancies (*e*) of natural orbitals (NBOs) and interaction energies (kJ/mol) between donor–acceptor NBOs in *aZZZa* conformer calculated at the B3LYP/6-31G(2d) level. Donor → acceptor interaction.

Donor	Acceptor	Energy	Occupancy
$Lp(2)O_1$	$\sigma^*(C_2—H_2)$	26.31	1.923
$Lp(1)O_1$	$\pi^*(C_3—C_8)$	4.90	1.955
$Lp(2)O_2$	$\sigma^*(C_{22}—H_{22})$	25.19	1.857
$Lp(1)O_2$	$\pi^*(C_8—C_7)$	7.10	1.961
$Lp(2)O_3$	$\sigma^*(C_{21}—C_{20})$	42.92	1.848
$Lp(1)O_3$	$\pi^*(C_{16}—C_{17})$	4.99	1.944
$Lp(1)N_1$	$\sigma^*(C_6—C_9)$	4.48	1.972
	$\sigma^*(C10—C11)$	7.17	1.966
$Lp(1)N_2$	$\sigma^*(C_{19}—C_{19'})$	3.28	1.970

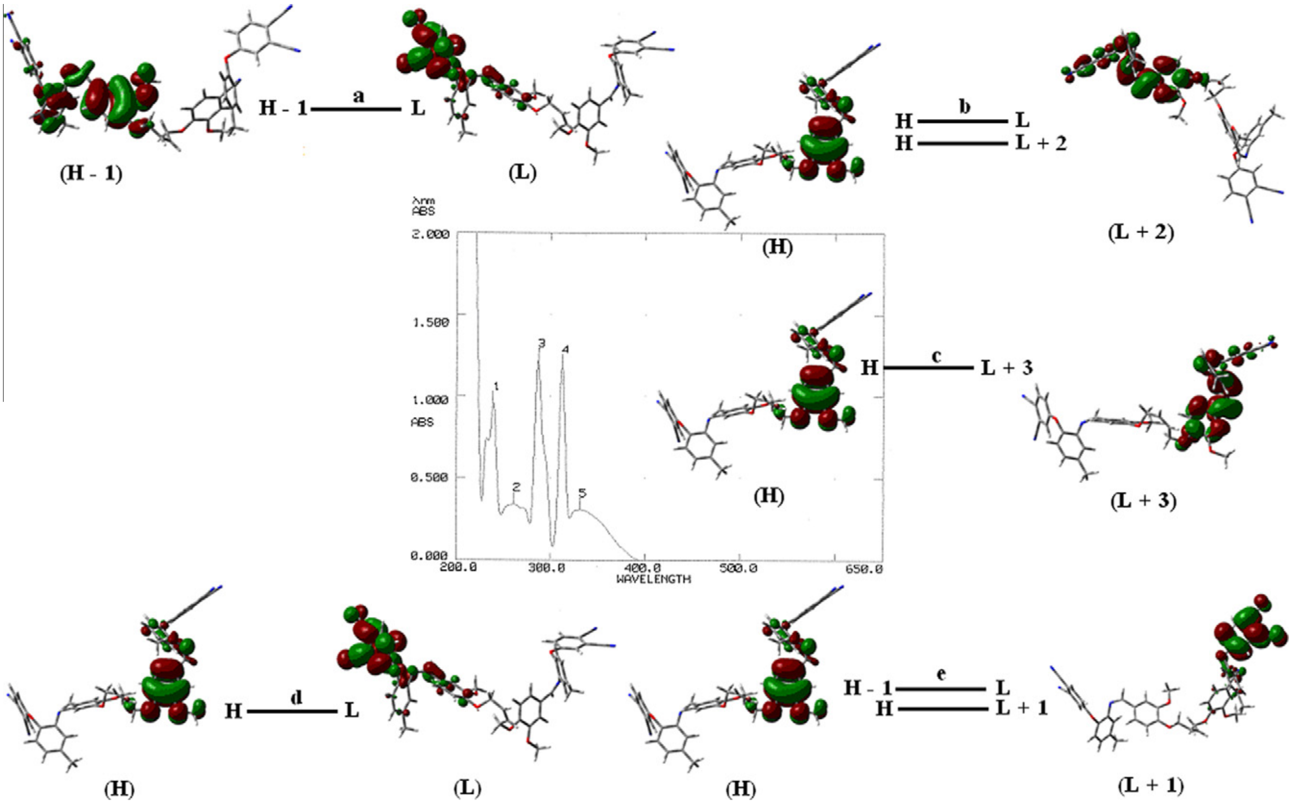


Fig. 5. The calculated transitions corresponding to experimental spectrum of **5** in B3LYP/6-31G(2d) level (TD-DFT). **a** denotes first absorption, **b** denotes second one, **c** denotes third one, **d** denotes fourth one and **e** denotes fifth one.

around CH═N double bond (including $C_6—C_9—N—C_{10}$ dihedral angle), and the third letter corresponds to the variation around the central C═C double bond (including $C_{2'}—C_{1'}—C_1—C_2$ dihedral angle). According to the calculations at DFT level, the energy of *aZZZa* conformer is significantly lower due to the lying at a nearly planar plane of the phenolic oxygen and methoxy group bonded to the olefinic carbons and the possibility of the inclusion of the lone pair/pairs on nitrogen/oxygen frameworks into the conjugation than those other conformers. In this endeavour, the obtained course revealed the hyperconjugation in terms of strong delocalization of the π, σ and lone pair orbitals involved in it.

The term hyperconjugation was introduced by Mulliken to describe the interaction the between a multiple bond and a saturated bond type (first-order hyperconjugation) or between two saturated groups (second-order hyperconjugation) [49,50]. Hyperconjugation can be explained as a stabilizing interaction arising from overlap of an occupied orbital with an adjacent one containing fewer electrons. It endeavours to build π-bond character into bonds having only σ or lone pair character.

For all conformations, the effect of hyperconjugation can be illustrated. Especially, in case of *aZZZa* conformer, while O_1 forms a dihedral angle of −4.31° O_2 donor, O_2 forms a dihedral angle of 0.06° H_7, N_1 forms a dihedral angle of 5.36° H_{11}, N_2 forms a dihedral angle of −4.25° C_{18}, and O_3 forms a dihedral angle of 2.22° $H_{17(21)}$, respectively, the other whole conformers have a value between 0.04 and 4.31 dihedral angles. In that case, hyperconjugation increases $C_8—C_7/C_8—O_2/C_2—H_{2'}$; $C_7—C_6/C_7—H_7C_{22}—H_{22'}/C_{22}—H_{22''}$; $C_{11}—C_{12}$; $C_{18}—C_{19}/C_{19}—C_{20}$; $C_{17}—C_{18}/C_{18}—H_{18}/C_{20}—C_{19}/C_{20}—CN$ bond lengths, and $O_1—C_3—C_4/O_1—C_2—H_{2'}/O_1—C_2—C_1$; $O_2—C_8—C_3/O_2—C_{22}—H_{22'}/O_2—C_{22}—H_{22''}$; $N_1—C_{10}—C_{15}$; $C_{19}—C_{20}—C_{20'}/C_{19}—C_{18}—H_{18}$, and $O_3—C_{16}—C_{17}/O_3—C_{16}—C_{21}$ bond angles, as summarised in Table 2. Besides of these gains, hyperconjugation is also quantified in terms of the second-order perturbation interaction energy obtained from the NBO analysis [51,52], and represents the estimate of the second-order interaction energy ($E^{(2)}$). In this work, we are interested in the interactions between the oxygen/nitrogen lone-pair orbitals as donors and the antibonding $\sigma^*(C_2—H_2)/\pi^*(C_3—C_8)$, $\sigma^*(C_{22}—H_{22})/\pi^*(C_8—C_7)$, $\sigma^*(C_{10}—C_{11})$, $\sigma^*(C_{19}—C_{19'})$, and $\sigma^*(C_{21}—C_{20})/\pi^*(C_{16}—C_{17})$ orbital teams as receptors. The NBO calculations have provided the detailed insight into the nature of the electronic conjugations in the 12 conformers of **5**. The calculated occupancies of natural orbitals and the energies of interactions between the donor and acceptor orbitals in the most stable conformational isomer of **5** are collected in Table 3. As can be seen also from this table, the two lone electron pair orbitals, Lp(1) and Lp(2) on the oxygen atoms O_1, O_2 and O_3, prove a considerable decrease of occupancy from the idealised value of 2.0 e. In *aZZZa*, three hyperconjugative interactions, the donation of electron density from the oxygen (O_1, O_2 and O_3) lone pair orbitals with sp-character, Lp(2)O to a corresponding antibonding orbitals, $\sigma^*(C_2—H_2)$, $\sigma^*(C_{22}—H_{22})$ and $\sigma^*(C_{21}—C_{20})$, are predominant. The calculated $Lp(2)O_1 \rightarrow \sigma^*(C_2—H_2)$, $Lp(2)O_2 \rightarrow \sigma^*(C_{22}—H_{22})$ and $Lp(2)O_3 \rightarrow \sigma^*(C_{21}—C_{20})$ interaction energies are 26.31, 25.29 and 42.92 kcal/mol, respectively. These transitions cause to an increase of occupancies of the antibonding orbitals, $\sigma^*(C_2—H_2)$, $\sigma^*(C_{22}—H_{22})$ and $\sigma^*(C_{21}—C_{20})$, as shown in Table 3. The known fact from the usual interactions summarised above, the *aZZZa* conformer should be the most stable one [53,54].

UV absorption spectrum of **5** was calculated using time-dependent density functional theory (TD-DFT) method based on B3LYP/6-31G(2d) basis set in order to compare with experimental results. This strategy leads to an average discrepancy of 2–12 nm between theoretical and experimental λ_{max} due to several influencing factors, such as solvent effect and intermolecular interaction, etc. DFT calculations were carried out in order to know the geometry of the frontier orbitals of the related compound. According these calculations, the highest occupied molecular orbitals (HOMOs) are mainly localised on the related oxygen atoms, benzene carbons (including A, B and C), C≡N and CH=N groups. Similarly, the lowest unoccupied molecular orbitals (LUMOs) are also centred on the related oxygen atoms, benzene carbons (including A, B and C), CH=N, C≡N, —CH_3 and olefinic carbons with their different contributions.

TD-DFT studies have been very useful in order to assign the electronic absorption transitions of the compounds. The low-energy excitations obtained by this method are in good agreement with the experimental results. According these calculations, the HOMO is composed of the π-bonding $-2p_y + p_z/2p_x + p_y$ orbital teams of the benzene rings– A, B and C, $n\pi_{pz}$ and σ_{px} orbitals of the oxygen atoms O_1, O_2 and O_3, the π_{pz} orbitals of the CH=N and C≡N groups, and p_x orbitals with non-bonding interactions of —CH_3 and —CH_2 groups with small contributions. The HOMO−1 is centred on the same orbital teams with their different density. The HOMO−2 and HOMO−3 are also fragments based on the same orbital teams with their different density. The HOMO−4 and HOMO−5 are located on the $2p_y + p_z/2p_x + p_y$ orbitals with π-symmetry of B and C moieties, π_{pz} orbitals of the CH=N and C≡N groups and similarly related π–p orbitals with same symmetry/energy of the O_2 group with small contributions [35,55].

The LUMO and LUMO+1 are also a set of quasi degenerated orbitals. These orbitals show a predominant character of the C moiety (including $2p_y + p_z$– character), CH=N/C≡N groups (including σ^*—π^* character) and oxygen atom O_3 (including π^*_{pz}-character) combinations. On the other hand, the LUMO+2 is composed of orbital sets with σ^*/π^*-symmetry of the A annular, C≡N/CH=N groups, olefinic carbons C=C and oxygen atom O_1. Similarly, the LUMO+3 has an important contribution of the A ring, CH=N/CH=N groups, —CH_2 and O_1 atoms. The intensity of these transitions has been assessed from the oscillator strength (*f*). All these transitions are of intra-ligand $n(\sigma) \rightarrow \sigma^*$ and $n(\pi) \rightarrow \pi^*$ charge transfer origin (LLCT) transitions [56,57]. The involved orbitals in these transitions are presented in Fig. 5 and the most relevant electronic transitions are present in Table 1.

5. Conclusion

In this paper, we have reported on the preparation of a new type of an olefinic centred metal free and metallophthalocyanines (Zn, Ni, Co and Cu) of clamshell type. In the first stage, substituted Schiff Base analogue was obtained from condensation of **1** and **2** with no solvent. Then, compound **5** was synthesized from a mixture of **3** and **4** (2:1) in the presence of DMF/K_2CO_3 as key structure to give expected pcs. In the final stage, metal free and metallophthalocyanines of clamshell type were synthesized by the interaction of diphthalonitrile **5** with excess of phthalonitrile **6** in DMAE/DBU and corresponding metal salts. The preparations of the new products are supported by elemental analysis, IR, UV–Vis, $^1H/^{13}C$ NMR and mass spectra.

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