Polyhedron 38 (2012) 267–274

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis and characterization of metallo phthalocyanines bearing 7-oxy-3-(4-pyridyl)coumarin substituents and their supramolecular structures with vanadyl bis(acetylacetonate)

Aliye Aslı Esenpınar [a], Elif Durmaz [b], Fatma Karaca [c], Mustafa Bulut [b,*]

[a] Kırklareli University, Department of Chemistry, 39100 Kırklareli, Turkey
[b] Marmara University, Faculty of Art and Science, Department of Chemistry, 34722 Kadıkoy, Istanbul, Turkey
[c] Marmara University, Department of Chemical Engineering, 34722 Kadikoy, Istanbul, Turkey

ARTICLE INFO

Article history:
Received 28 December 2011
Accepted 7 March 2012
Available online 23 March 2012

Keywords:
Coumarin (2H-1-benzopyran-2-one)
Cobalt
Phthalocyanines
Vanadyl bis(acetylacetonate)
Zinc

ABSTRACT

The synthesis of novel zinc and cobalt metallo phthalocyanines with four 7-oxy-3-(4-pyridyl)coumarin dye groups on the periphery/non-periphery were prepared by cyclotetramerization of 7-(3,4-dicyanophenoxy)-3-(4-pyridyl)coumarin (**1**)/7-(2,3-dicyanophenoxy)-3-(4-pyridyl)coumarin (**2**) and also a phthalocyanine based on supramolecular structures have been prepared by the ready coordination of pyridine donor sites in 2,9(10),16(17),23(24)-tetrakis[7-oxo-3-(4-pyridyl)coumarin]-phthalocyaninatozinc (**1a**)/1,8(11),15(18),22(25)-tetrakis[7-oxo-3-(4-pyridyl)coumarin]-phthalocyaninatozinc (**2a**) with vanadyl bis(acetylacetonate). The novel chromogenic compounds were characterized by elemental analysis, ^{1}H NMR, Mass spectra, FT-IR and UV–Vis spectral data. The IR-spectra of prepared compounds showed two characteristic intense bands at 1728–1719 cm^{-1} for lactone carbonyl and at 1592 cm^{-1} for the α, β unsaturated doubled bond.

1. Introduction

Coumarins, the 2H-1-benzopyran-2-one derivatives, are one of the most important compounds of natural products and in synthetic organic chemistry. They have been used largely in pharmaceuticals, perfumery, agrochemical industries as starting material or intermediate. They are also used as fluorescent brighteners, efficient laser dyes and as additives in food and cosmetics [1–3]. Several bioactivities of coumarins, such as antibacterial, anticancer, inhibitory of platelet aggregation, inhibitory of steroid 5α-reductase and inhibitory of HIV-1 protease, have also been reported [1,4–6]. Plants are the most important source of coumarins, but extraction from plant is tedious, time consuming and needs sophisticated instrumentation. Many synthetic methods, like Pechmann condensation, Perkin, Reformatsky, Wittig reaction, Knoevenagel condensation and Claisen rearrangement have been investigated for the synthesis of coumarins [7–10].

Phthalocyanines (Pcs) are synthetic substances related to the naturally occurring porphyrins. They consist of a macrocycle made up of four isoindole units linked by aza nitrogen atoms in contrast to the methine carbon atoms in porphyrins [11]. Pcs, which were first developed as pigments, have been found widespread applications in material sciences [12] such as chemical sensors, photocopying machines [13–15], Langmuire Blodgett films [16], solar cells, electrochromism, high energy batteries [17], fibrous assemblies [18], coloring for plastics and metal surfaces and dyestuffs for clothing [19], non-linear optics [20], liquid crystals [21], semiconductors [22], photoconductors, electrochromic displays [23] and gas sensors [12,24]. Apart from their important contributions in materials science, this class of functional dyes also has potential applications in the treatment of a range of cancers, infectious diseases [25], and eye and neurodegenerative diseases [26], most of which are related to the photocytotoxic effects of these compounds.

Unsubstituted Pcs are generally difficult to dissolve in most organic solvents, hence, limiting their further applications. The introduction of substituents not only improves the solubility but also modifies their molecular structure, and therefore, the electrical and optical properties [27]. As a consequence, various kinds of substituents, which appear to be mainly limited to the electron-donating groups such as alkyl, alkoxyl, and alkylthio, have been introduced onto the peripheral/nonperipheral positions of phthalocyanine ligand [28–33]. Phthalocyanines coupled with coumarin moiety exhibit biological activities [34–36].

In this study, phthalocyanines bearing pyridylcoumarin substituents were prepared and their Zn(II), Co(II) metal complexes investigated. The coumarin contain lactone ring, which is involved in the pharmaceutical activity. 7-Hydroxy coumarins allow binding this structure with a Pc by phenoxy bound. This covalent binding

* Corresponding author. Tel.: +90 216 3479641x1370; fax: +90 216 3478783.
E-mail addresses: mustafabulut50@gmail.com, mbulut@marmara.edu.tr (M. Bulut).

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http://dx.doi.org/10.1016/j.poly.2012.03.009

should not affect significantly biological activity of the coumarin moiety. The combined structure and Pc may be a potential candidate molecule in the application of photodynamic therapy [28] and also our choice as a "capping" component was vanadyl bis(acetylacetonate) ($VO(acac)_2$) as this complex has a single empty coordination site and at the same time oxovanadium (VO^{2+}) ions are known to have important biological functions, for example, in the case of diabetes [37].

2. Experimental

Routine IR spectra were recorded on a Shimadzu Fourier Transform FTIR-8300 Infrared Spectrophotometer using KBr pellets, electronic spectra on a Shimadzu UV-1601 UV–Visible Spectrophotometer. ^{1}H NMR spectra were recorded on a Varian 500 MHz spectrometer in DMSO-d_6 for compound. Elemental analysis was performed by the Instrumental Analysis Laboratory of TUBITAK Ankara Test and Analysis Laboratory. Mass spectra were performed on a Bruker Daltonic Autoflex III MALDI–TOF spectrometer. Fluorescence excitation and emission spectra were recorded on a HITACHI F-7000 Fluorescence spectrophotometer using 1 cm pathlength cuvettes at room temperatures.

4-Nitrophthalonitrile [38], 3-nitrophthalonitrile [39] and 7-hydroxy-3-(4-pyridyl)coumarin [40] were synthesized according to the reported procedures. *N*,*N*-dimethylaminoethanole, dimethylsulfoxide (DMSO) and dimethylformamide (DMF) were dried as described by Perrin and Armarego [41] before use. Acetone, ethanol, chloroform ($CHCl_3$), dichloromethane (DCM), *n*-hexane, methanol and tetrahydrofuran (THF) were freshly distilled. 2,4-Dihydroxybenzaldehyde, 4-pyridylacetonitril hydrochloride, pyridine and K_2CO_3 were purchased from Fluka.

2.1. Synthesis of Compounds (**1**,**2**,**1a**–**c**, **2a**–**c**)

2.1.1. 7-(3,4-Dicyanophenoxy)-3-(4-pyridyl)coumarin (**1**) and 7-(2,3-dicyanophenoxy)-3-(4-pyridyl)coumarin (**2**)

7-Hydroxy-3-(4-pyridyl)coumarin (1.00 g, 4.18 mmol) and 4-nitrophthalonitrile (0.723 g, 4.18 mmol) or 3-nitrophthalonitrile (0.723 g, 4.18 mmol) were added successively with stirring to dry DMF (50 ml). After stirring for 15 min, finely ground anhydrous K_2CO_3 (0.865 g, 6.27 mmol)) was added portionwise over 2 h and the mixture was stirred vigorously at room temperature for a further 48 h. Then the reaction mixture was poured into water (150 ml) and the precipitate formed was filtered off, washed with water. The products (**1** and **2**) were synthesized as pure. The compounds are soluble in DMF and DMSO.

Compound **1**: Yield: 1.01 g (72%). m.p.: 280 °C. IR (KBr) γ_{max} (cm^{-1}): 3042–3072 (aryl CH), 2950 (alkyl CH), 2233 (C≡N), 1728 (C=O lactone), 1487 (C=C), 1592 (C=C), 1291 (Ar–O–Ar). ^{1}H NMR (DMSO) δ_H: 7.32 (dd, J = 8.5 ve 2 Hz, 1H), 7.43 (br s, 1H), 7.58 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 4 Hz, 2H), 7.95 (d, J = 8.5 Hz, 2H), 7.99 (t, J = 7.5 Hz, 1H), 8.58 (br s, 1H), 8.73 (br d, J = 4 Hz, 2H). UV–Vis (DMF) λ_{max} ($\log\varepsilon$) (nm) (1×10^{-5}M): 330 (4.15). *Anal.* Calc. for $C_{22}H_{11}N_3O_3$: C, 72.26; H, 3.01; N, 11.49. Found: C, 71.01; H, 2.98; N, 10.51%. Fluorescence data: (EM) 1×10^{-5} M, λ_{em}: 448 nm and (EX) 1×10^{-6} M, λ_{ex}: 336 nm (DMF). MS (MALDI–TOF): m/z 365 $[M]^+$.

Compound **2**: Yield: 1.08 g (72%). m.p.: 290 °C. IR (KBr) γ_{max}(cm^{-1}): 3019–3075 (aryl CH), 2946 (alkyl CH), 2231 (C≡N), 1719 (C=O lactone), 1458 (C=C), 1595 (C=C), 1257 (Ar–O–Ar). ^{1}H NMR (DMSO) δ_H: 7.30 (dd, J = 8.5 ve 2 Hz, 1H), 7.41 (br s, 1H), 7.56 (d, J = 8.5 Hz, 1H), 7.79 (d, J = 4 Hz, 2H), 7.94 (d, J = 8.5 Hz, 2H), 7.98 (t, J = 7.5 Hz, 1H), 8.56 (br s, 1H), 8.70 (br d, J = 4 Hz, 2H). UV–Vis (DMF λ_{max} ($\log\varepsilon$) (nm) (1×10^{-5} M): 321 (4.32). *Anal.* Calc. for $C_{22}H_{11}N_3O_3$: C, 72.26; H, 3.01; N, 11.49. Found: C, 72.09; H, 3.00; N, 11.35%. Fluorescence data: (EM) 1×10^{-5} M, λ_{em}: 418 nm and (EX) 1×10^{-6} M, λ_{ex}: 331 nm (DMF). MS (MALDI–TOF): m/z 365 $[M]^+$.

2.1.2. 2,9(10),16(17),23(24)-Tetrakis[7-oxo-3-(4-pyridyl)coumarin]-phthalocyaninatozinc (**1a**) and 1,8(11),15(18),22(25)-tetrakis[7-oxo-3-(4-pyridyl)coumarin]-phthalocyaninatozinc (**2a**)

7-(3,4-Dicyanophenoxy)-3-(4-pyridyl)coumarin (**1**) (0.10, 0.27 mmol) or 7-(2,3-dicyanophenoxy)-3-(4-pyridyl)coumarin (**2**) (0.10, 0.27 mmol) and $Zn(CH_3COO)_2$ (0.015 g, 0.068 mmol) were heated at 160 °C with dry *N*,*N*-dimethylaminoethanole (2 ml) in a sealed tube with stirring for 24 h. After cooling to room temperature, the reaction mixture was treated with ethanol then filtered off and washed with water to remove unreacted $Zn(CH_3COO)_2$. The crude green products were purified by extraction with first nonpolar solvents such as dichloromethane, chloroform, ethylacetate, tetrahydrofuran and then polar solvents such as acetonitrile, acetone, ethanol, methanol, water (approximately 50 ml of each solvents) and finally purified on silicagel chromatography using DMF as eluent. The compounds (**1a**, **2a**) are soluble in dimethylformamide and dimethylsulfoxide.

Compound **1a**: Yield: 0.06 g (60%). m.p.: >300 °C. IR γ_{max}(cm^{-1}): 3082 (aryl CH), 2850–2925 (alkyl CH), 1724 (C=O lactone), 1471 (C=C), 1602 (C=C), 1265 (Ar–O–Ar). UV–Vis (DMF) λ_{max} ($\log\varepsilon$) (nm) (1×10^{-5} M): 677 (4.16), 335 (4.58). *Anal.* Calc. for $C_{88}H_{44}N_{12}O_{12}Zn$: C, 69.24; H, 2.88; N, 11.01. Found: C, 69.16; H, 2.82; N, 10.98%. Fluorescence data: (EM) 1×10^{-5} M, λ_{em}: 689 nm and (EX) 1×10^{-6} M, λ_{ex}: 646 nm (DMF). MS (MALDI–TOF): m/z 1525 $[M]^+$.

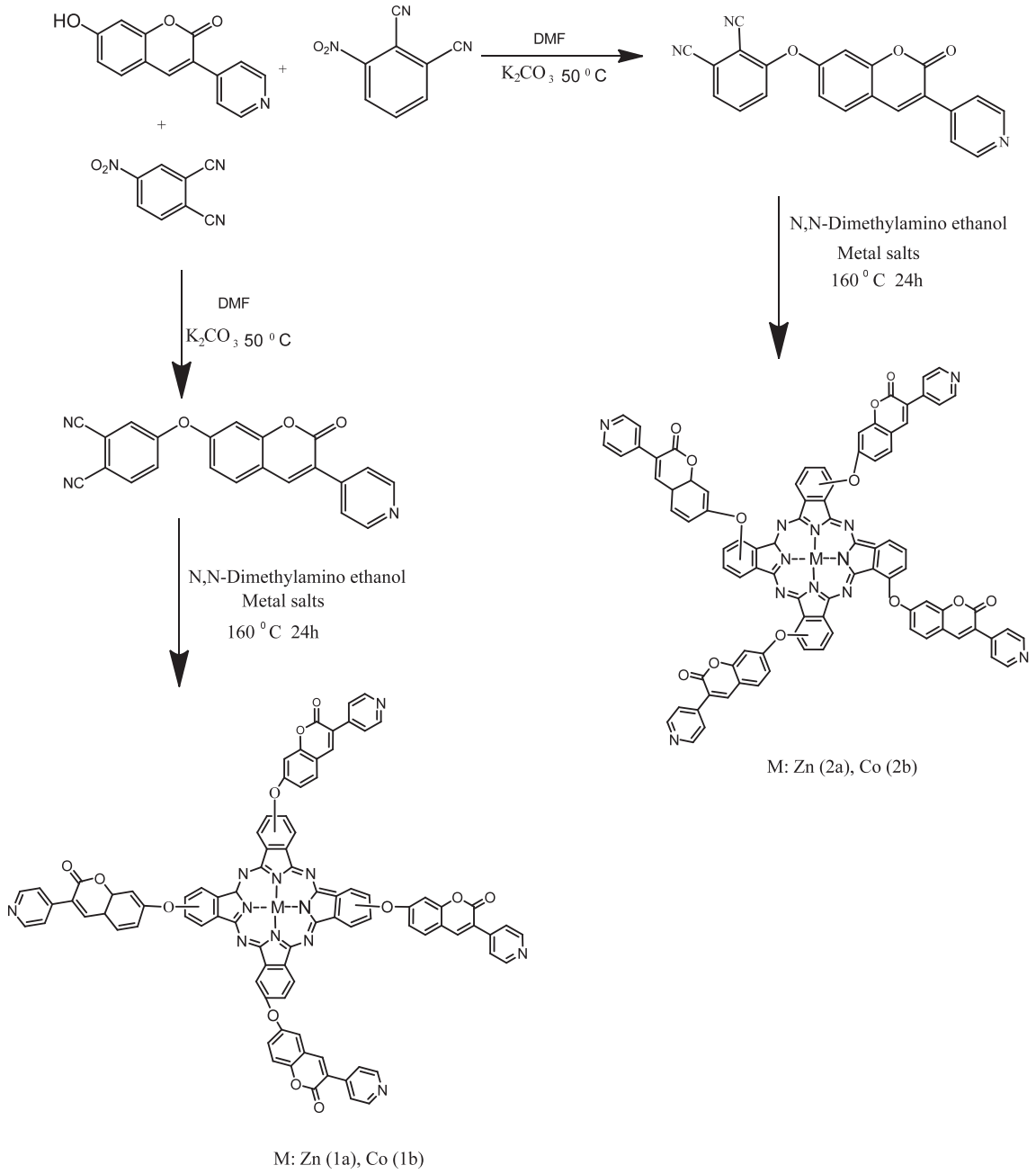
Compound **2a**: Yield: 0.075 g (75%). m.p.: >300 °C. IR γ_{max}(cm^{-1}): 3086 (aryl CH), 2838–2918 (alkyl CH), 1717 (C=O, lactone), 1481 (C=C), 1603 (C=C), 1265 (Ar–O–Ar). UV–Vis (DMF) λ_{max} ($\log\varepsilon$) (nm) (1×10^{-5} M): 689 (4.90), 340 (4.85). *Anal.* Calc. for $C_{88}H_{44}N_{12}O_{12}Zn$: C, 69.24; H, 2.88; N, 11.01. Found: C, 69.22; H, 2.85; N, 11.00%. Fluorescence data: (EM) 1×10^{-5} M, λ_{em}: 704 nm and (EX) 1×10^{-6} M, λ_{ex}: 663 nm (DMF). MS (MALDI–TOF): m/z 1525 $[M]^+$.

2.1.3. 2,9(10),16(17),23(24)-Tetrakis[7-oxo-3-(4-pyridyl)coumarin]-phthalocyaninatocobalt (**1b**) and 1,8(11),15(18),22(25)-tetrakis[7-oxo-3-(4-pyridyl)coumarin]-phthalocyaninatocobalt (**2b**)

7-(3,4-Dicyanophenoxy)-3-(4-pyridyl)coumarin (**1**) (0.10, 0.27 mmol) or 7-(2,3-dicyanophenoxy)-3-(4-pyridyl)coumarin (**2**) (0.10, 0.27 mmol) and $Co(OAc)_2$ (0.017 g, 0.06 mmol) were heated at 160 °C with dry *N*,*N*-dimethylaminoethanole (2 ml) in a sealed tube with stirring for 24 h. After cooling to room temperature, the reaction mixture was treated with ethanol then filtered off and washed with water to remove unreacted $Co(OAc)_2$. The crude green products were purified by extraction with first nonpolar solvents such as dichloromethane, chloroform, ethylacetate, tetrahydrofuran and then polar solvents such as acetonitrile, acetone, ethanol, methanol, water (approximately 50 ml of each solvents) and finally purified on silicagel chromatography using DMF as eluent. The compounds (**1b**, **2b**) are soluble in dimethylformamide and dimethylsulfoxide.

Compound **1b**: Yield: 0.055 g (55%). m.p.: >300 °C. IR γ_{max}(cm^{-1}): 3078 (aryl CH), 2866–2925 (alkyl CH), 1728 (C=O, lactone), 1469 (C=C), 1600 (C=C), 1263 (Ar–O–Ar); UV–Vis (DMF) λ_{max} ($\log\varepsilon$) (nm) (1×10^{-5} M): 686 (4.13), 337 (4.07). *Anal.* Calc. for $C_{88}H_{44}N_{12}O_{12}Co$: C, 69.51; H, 2.89; N, 11.05. Found: C, 69.48; H, 2.87; N, 11.03%. MS (MALDI–TOF): m/z 1519 $[M]^+$.

Compound **2b**: Yield: 0.08 g (80%). m.p.: >300 °C. IR γ_{max}(cm^{-1}): 3078 (aryl CH), 2940 (alkyl CH), 1725 (C=O, lactone), 1471 (C=C), 1609 (C=C), 1267 (Ar–O–Ar). UV–Vis (DMF) λ_{max} ($\log\varepsilon$) (nm) (1×10^{-5} M): 677 (4.52), 333 (4.65). *Anal.* Calc. for $C_{88}H_{44}N_{12}O_{12}Co$: C, 69.51; H, 2.89; N, 11.05. Found: C, 69.50; H, 2.88; N, 11.04%. MS (MALDI–TOF): m/z 1519 $[M]^+$.



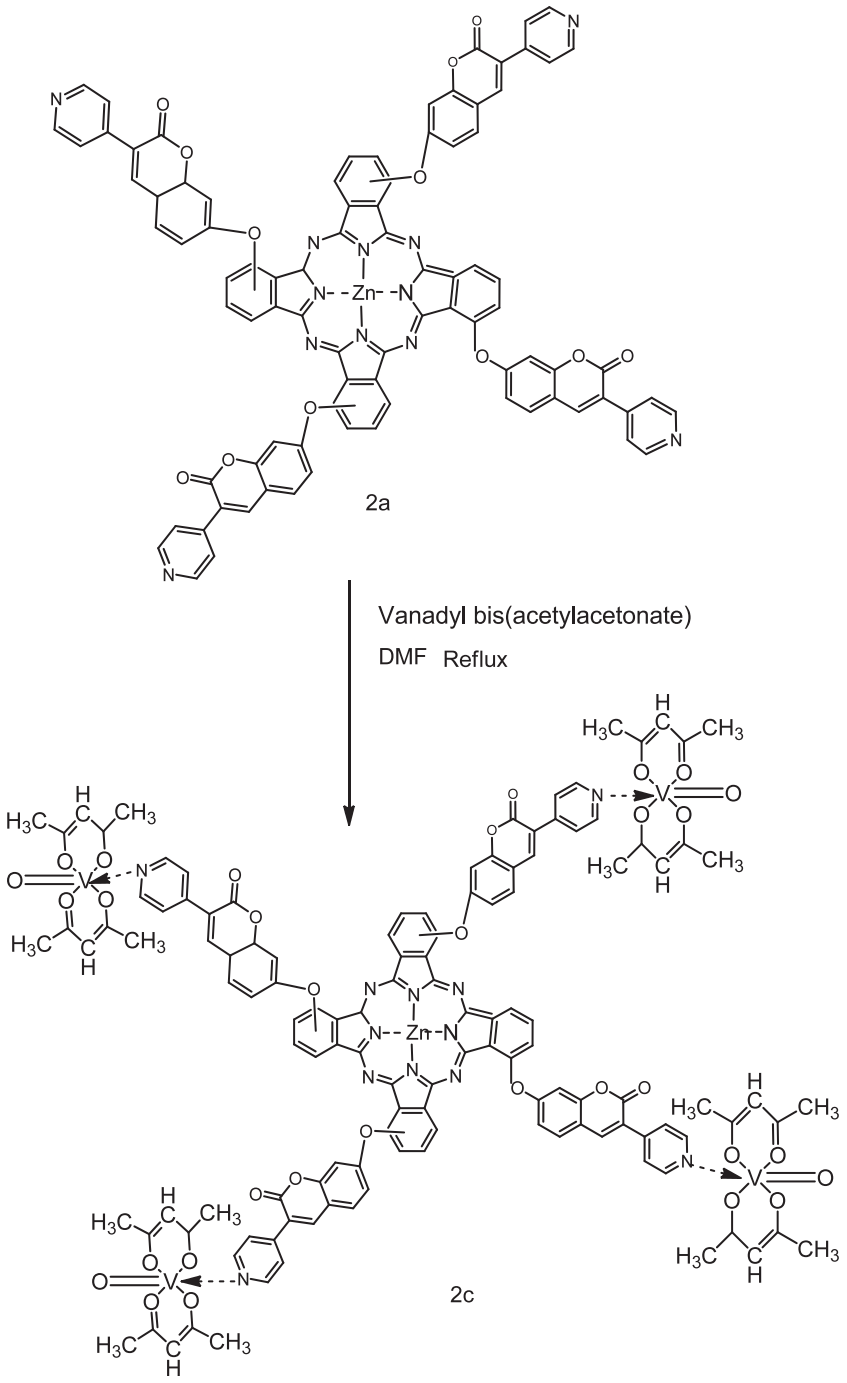
Scheme 1. Synthesis of the starting compounds and metallo phthalocyanines.

*2.1.4. Peripherally (**1c**) and nonperipherally substituted (**2c**) supramolecular phthalocyanines with vanadyl bis(acetylacetonate) [4(VO(acac)$_2$)]ZnPc*

2,9(10),16(17),23(24)-Tetrakis[7-oxo-3-(4-pyridyl)coumarin]-phthalocyaninatozinc (**1a**) (0.1 g, 0.065 mmol) or 1,8(11),15(18), 22(25)-tetrakis[7-oxo-3-(4-pyridyl)coumarin]-phthalocyaninatozinc (**2a**) (0.1 g, 0.065 mmol) and vanadyl bis(acetylacetonate) (0.14 g, 0.52 mmol) were heated in dry DMF (10 ml) with stirring at reflux temperature for 6 h. After cooling to room temperature, the reaction mixture was treated with acetone then filtered off and washed with ethanol to remove unreacted VO(acac)$_2$. The crude green products were purified by extraction with first nonpolar solvents such as dichloromethane, chloroform, ethylacetate, tetrahydrofuran and then polar solvents such as acetonitrile, acetone, ethanol, methanol, water (approximately 50 ml of each solvents) and finally purified on silicagel chromatography using DMF as eluent. The compounds (**1c**, **2c**) are soluble in DMF and DMSO.

Compound **1c**: Yield: 0.048 g (28%). m.p.: >300 °C IR γ_{max}(cm^{-1}): 3072 (aryl CH), 2850–2920 (alkyl CH), 1720 (C=O lactone), 1471 (C=C), 1601 (C=C), 1265 (Ar–O–Ar), 1527 and 1373 (acac), 996 (V=O). UV–Vis (DMF) λ_{max} (log ε) (nm) (1×10^{-5} M): 673 (4.36), 344 (4.43). *Anal.* Calc. for $C_{128}H_{100}O_{32}N_{12}V_4Zn$: C, 59.41; H, 3.86; N, 6.49. Found: C, 59.39; H, 3.85; N, 6.40%. Fluorescence data: (EM) 1×10^{-5} M, λ_{em}: 687 nm and (EX) 1×10^{-6} M, λ_{ex}: 682 nm (DMF). MS (MALDI–TOF): *m*/*z* 2585 [M]$^+$.

Compound **2c**: Yield: 0.075 g (30%). m.p.: >300 °C IR γ_{max}(cm^{-1}): 3080 (aryl CH), 2835–2915 (alkyl CH), 1720 (C=O, lactone), 1482 (C=C), 1607 (C=C), 1266 (Ar–O–Ar), 1528 and 1375 (acac), 995 (V=O). UV–Vis (DMF) λ_{max} (log ε) (nm) (1×10^{-5} M): 685 (5.03), 339 (4.94). *Anal.* Calc. for $C_{128}H_{100}O_{32}N_{12}V_4Zn$: C,



Scheme 2. Synthesis of the nonanuclear supramolecule non-peripheral zinc phthalocyanine.

59.41; H, 3.86; N, 6.49. Found: C, 59.40; H, 3.86; N, 6.45%. Fluorescence data: (EM) 1×10^{-5} M, λ_{em}: 706 nm and (EX) 1×10^{-6} M, λ_{ex}: 695 nm (DMF). MS (MALDI–TOF): m/z 2585 $[M]^+$.

3. Result and discussion

Novel 7-(3,4-dicyanophenoxy)-3-(4-pyridyl)coumarin (**1**)/7-(2,3-dicyanophenoxy)-3-(4-pyridyl)coumarin (**2**) were prepared by a base catalyzed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile/3-nitrophthalonitrile with 7-hydroxy-3-(4-pyridyl)coumarin. The reaction was carried out in a single step synthesis by using K_2CO_3 as the nitro-displacing base at room temperature in dimethylformamide under N_2 atmosphere and the yields were obtained 72% for **1** and **2**. Cyclotetramerization of the phthalonitrile derivative **1** or **2** to the metallo phthalocyanines **1a**,**1b** or **2a**,**2b** were accomplished in 2-*N*,*N*-dimethylaminoethanol (DMAE) at 160 °C in sealed tube. The yields were satisfactory and depended upon the transition metal ion. The tetrasubstituted phthalocyanine products were soluble in DMF and DMSO. The crude green products were purified by extraction with first nonpolar solvents such as dichloromethane, chloroform, ethylacetate, tetrahydrofuran and then polar solvents such as acetonitrile, acetone, ethanol, methanol, water (approximately 50 ml of each solvents) and finally purified on silicagel chromatography using DMF as eluent. Taking into account the ready coordination of $VO(acac)_2$ with pyridine donors, the interaction of this reagent with peripheral and non-peripheral zinc phthalocyanines were performed in DMF at reflux temperature for 6 h. The

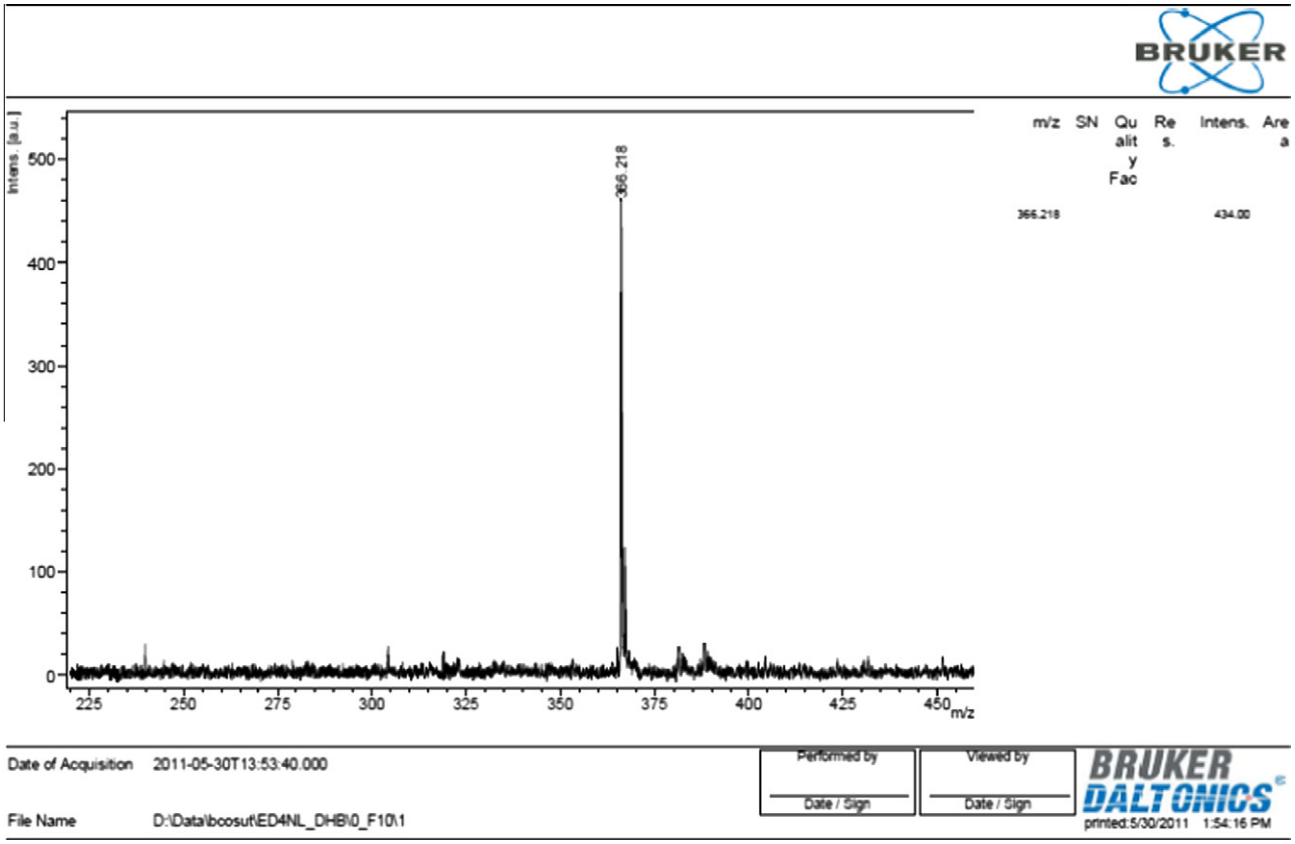


Fig. 1. The positive ion and linear mode MALDI–TOF MS spectrum of 7-(3,4-dicyanophenoxy)-3-(4-pyridyl)coumarin (**1**) (in the presence of 2,5-dihydroxybenzoic acid (DHB) (20 mg/ml in THF) as a matrix) were obtained using nitrogen laser accumulating 50 laser shots.

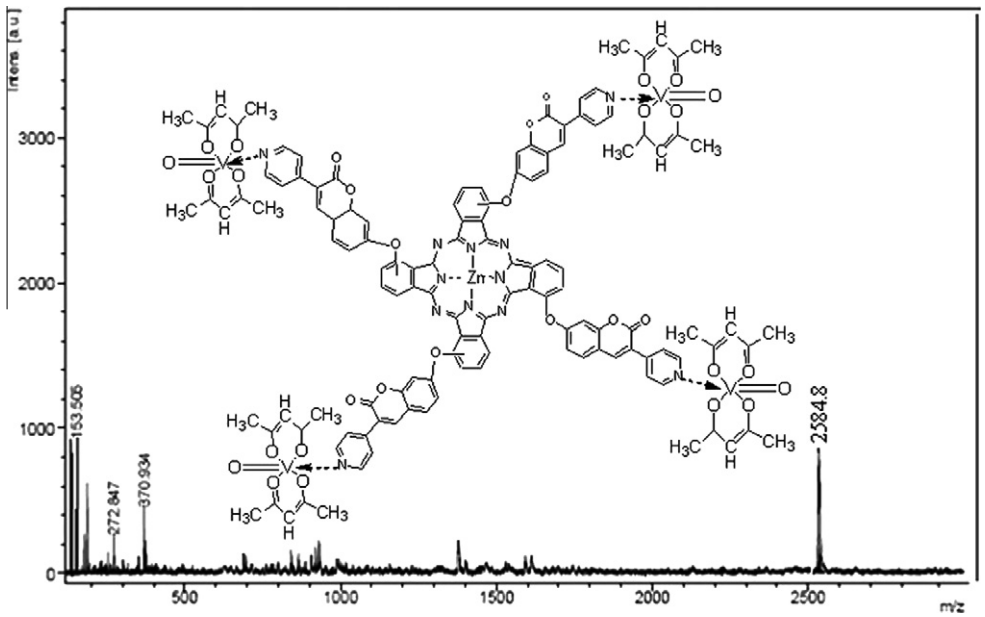


Fig. 2. The positive ion and linear mode MALDI–TOF MS spectrum of supramolecular phthalocyanine (**2c**) (in the presence of 2,5-dihydroxybenzoic acid (DHB) (20 mg/ml in THF) as a matrix) were obtained using nitrogen laser accumulating 50 laser shots.

supramolecular dark green solid products (**1c** and **2c**) were obtained in moderate yield (30%). Characterisation of the products involved a combination of methods including IR-spectra, elemental analysis, UV–Vis, fluorescence and MALDI–TOF spectroscopy.

The novel coumarin-substituted phthalocyanines; **1a**,**1b**/**2a**,**2b** and supramolecular structure (**2c**) from the non-peripheral zinc phthalocyanine (**2a**) were prepared according to the route shown in Schemes 1 and 2.

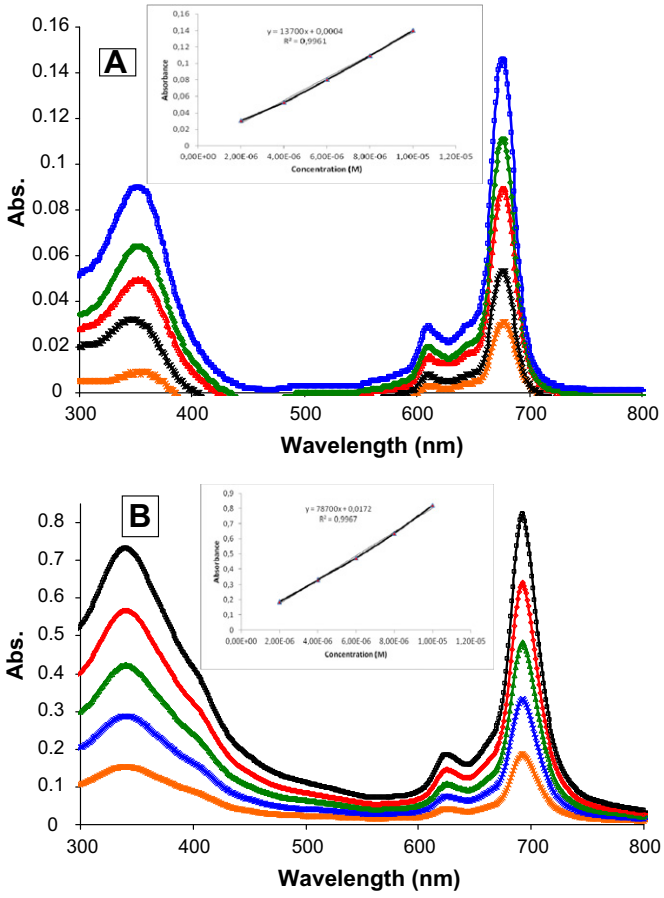


Fig. 3. UV–Vis spectra of **1a** (A) and **2a** (B) in DMF (2×10^{-6} M–1×10^{-5} M).

Spectral data of the newly synthesized compounds are consistent with the proposed structures. Comparison of the IR spectra data clearly indicated the formation of compound **1** and **2**, the appearance of new absorption bands at 2233 cm^{-1}(C≡N) and 1291 cm^{-1}(Ar–O–Ar) for **1**, at 2231 cm^{-1}(C≡N) and 1257 cm^{-1}(Ar–O–Ar) for **2** (the band OH of 7-hydroxy-3-(4-pyridyl)coumarin at 3141 $cm^{-1}$was disappeared in this spectrum). After conversion of the dinitrile derivatives (**1** or **2**) into the phthalocyanines (**1a**,**1b** or **2a**,**2b**), the sharp peak for the C≡N vibration around 2233 cm^{-1} for **1** and 2231 $cm^{-1}$for **2** disappeared. The IR spectra of the metallo phthalocyanine **1a**,**1b**/**2a**,**2b** were very similar. IR data for **1c** and **2c** confirm the presence of a triply bonded terminal oxo ligand (V=O) 995 cm^{-1} and 1373–1527 cm^{-1} (acac).

The ^{1}H NMR spectra of **1** and **2** were almost identical except for small shift; ^{1}H NMR spectrum exhibited lactone protons (C=CH) at 7.43/7.41 ppm (**1**/**2**). The aromatic protons of both compounds appeared at 8.73–7.32/8.70–7.30 ppm (**1**/**2**).

A closed investigation of the mass spectra of the coumarins and phthalocyanines confirmed the proposed structure. In the mass spectra of dicyanophenoxy pyridylcoumarins and metallo phthalocyanines were identified at 365 (**1**/**2**) in Fig. 1 at 1525/1519 (**1a**–**b**) at 1525/1519 (**2a**–**b**), at 2585 (**2c**) in Fig. 2, respectively. The phthalocyanines **1a**/**1b**, **2a**/**2b** and **1c**/**2c** are only soluble in DMF and DMSO.

The coumarins show maximum absorption with single band at 270–310 nm. UV–Vis spectra of **1**/**2** in DMF showed a single band at 330/321 nm.

The phthalocyanines **1a**–**b**/**2a**–**b** show typical electronic spectra with two strong absorption regions, one of them in the UV region at about 300–350 nm (B band) and the other in the visible part of the spectrum around 600–700 nm (Q band). Increasing the concen-

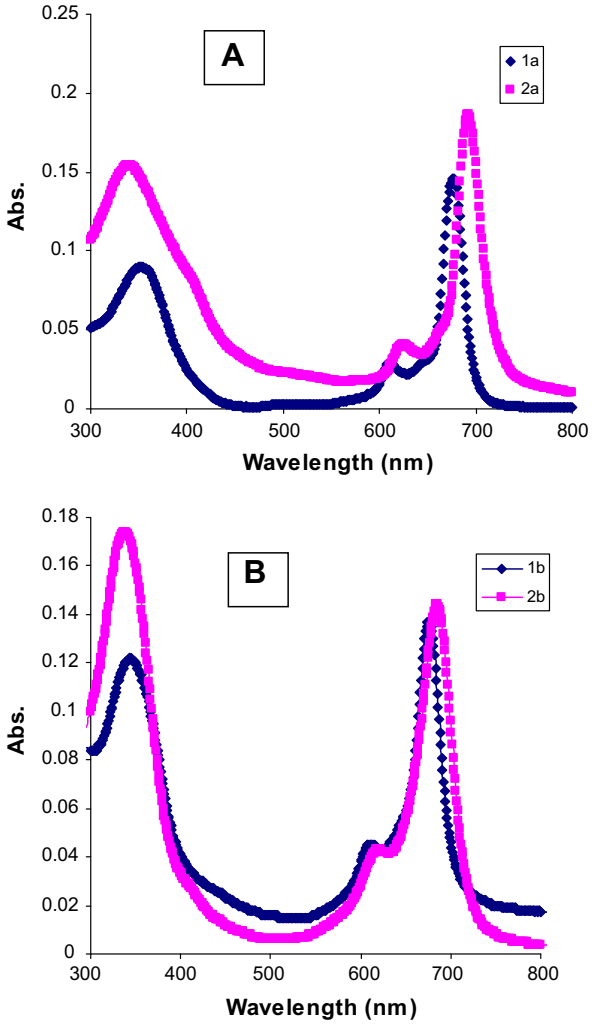


Fig. 4. (A) UV–Vis spectra of **1a** (1×10^{-5} M) as compared with that of **2a** (1×10^{-5} M) in DMF. (B) UV–Vis spectra of **1b** (1×10^{-5} M) as compared with that of **2b** (1×10^{-5} M) in DMF.

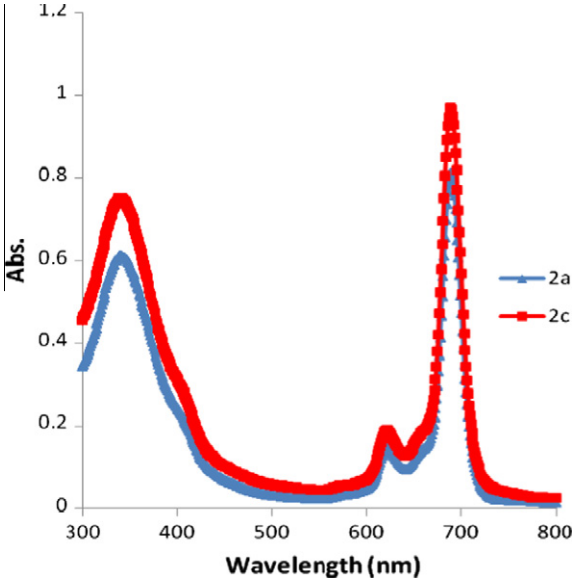


Fig. 5. UV–Vis spectra of **2a** (1×10^{-5} M) as compared with that of **2c** (1×10^{-5} M) in DMF.

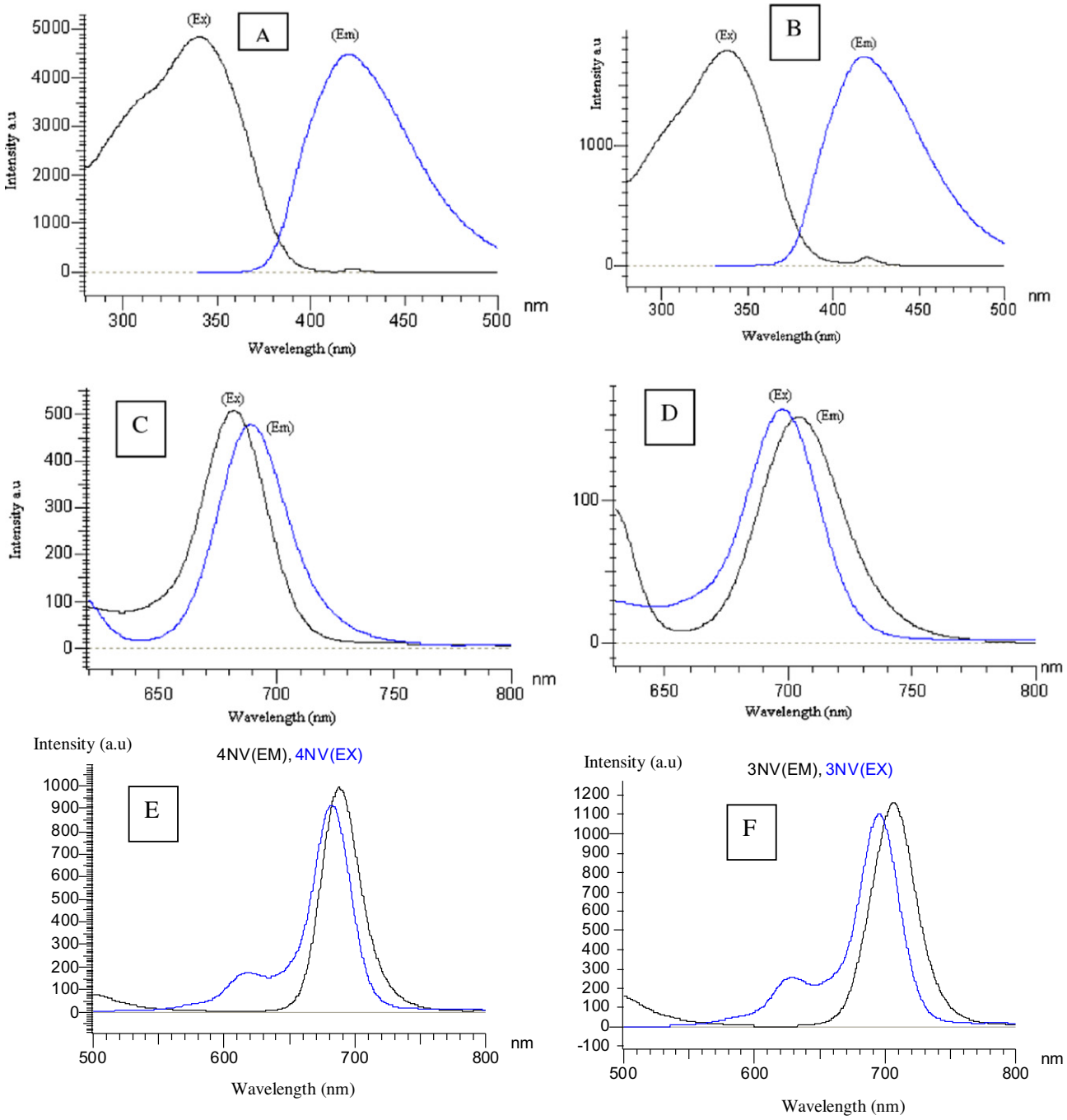


Fig. 6. Fluorescence emission and excitation spectra of **1**–**2** and **1a**, **2a**, **1c**, **2c** in DMF. Excitation wavelength = 336 nm for **1** (A), 331 nm for **2** (B), 646 nm for **1a** (C); 663 nm for **2a** (D); 682 nm for **1c** (E); 695 nm for **2c** (F).

tration leads to aggregation, which is easily observed by the values of the Q bands, which shift to higher energies by a parallel decrease in the molar absorption coefficient. Tetrasubstitution with oxygen bridged groups causes shift (3–18 nm) of the intense Q band to longer wavelengths when compared with the unsubstituted derivatives. A typical spectrum of the zinc metallo phthalocyanines in DMF showed a singlet in the Q band region at 678/693–686/677 nm for **1a**/**2a**–**1b**/**2b** and B band region at 344/333–337/333 nm for **1a**/**2a**–**1b**/**2b** (Fig. 3a and b). UV–Vis spectra of **1a**/**1b** was compared with **2a**/**2b** in Fig. 4. The wavelength of **1a**/**1b**–**2a**/**2b** shifted ~8/~16 nm to lower energies. The vanadyl phthalocyanine (**2c**) shows the expected Q bands a single absorption at around 685 nm. The UV–Vis spectra of supramolecular zinc phthalocyanines as compared with peripheral and non-peripheral zinc phthalocyanines are similar in Fig. 5.

Unsubstituted ZnPc dye is characterized by the band with the maximum at 673 nm as observed in the literature for ZnPc [27]. ZnPc substituted with four pyridylcoumarin moieties show a bathochromic shift of 5 nm for **1a** and 20 nm for **2a**.

Fluorescence emission and excitation spectra for ligands (**1**/**2**) and Pcs (**1a**/**2a**, **1b**/**2b** and **1c**/**2c**) in DMF were shown in Fig. 6. Supramolecular peripheral (**1c**) and non-peripheral (**2c**) zinc phthalocyanines have higher fluorescence intensity than **1a** and **2a** (Table 1). The excitation spectra of the compounds are similar to that of absorption spectra and are mirror images of the fluorescence spectra.

Table 1
The absorption, excitation and emission wavelengths of the compounds.

Compound	B band λ_{max} (nm)	Q band λ_{max} (nm)	log ε	Excitation λ_{Ex} (nm)	Emission λ_{Em} (nm)	Stokes shift Δ_{stokes} (nm)
1	330	–	4.15	336	448	118
2	321	–	4.32	331	418	97
1a	335	677	4.16/4.58	646	689	12
1b	337	686	4.13/4.07	–	–	–
2a	340	689	4.90/4.85	663	704	15
2b	333	677	4.52/4.65	–	–	–
1c	344	673	4.43/4.36	682	687	14
2c	339	685	4.94/5.03	695	706	21

Acknowledgements

We are thankful to the Research Foundation of Marmara University, Commission of Scientific Research Project (BAPKO) FEN-C-YLP-210311-0061.

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