

Synthesis, characterization, and photophysical and photochemical properties of 3-(4-phenyloxy)coumarin containing metallo- and metal-free phthalocyanines

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Received: 29.05.2014 • Accepted: 08.08.2014 • Published Online: 24.11.2014 • Printed: 22.12.2014

Abstract: The synthesis of novel zinc, cobalt, indium, and metal-free phthalocyanines carrying four 3-(4-phenyloxy)coumarins in the periphery/nonperiphery were prepared by cyclotetramerization of 3-[4-(3,4-dicyanophenoxy)phenyl]coumarin (**2**)/3-[4-(2,3-dicyanophenoxy)phenyl]coumarin (**3**). The novel chromogenic compounds were characterized by elemental analysis, ¹H NMR, mass spectra, F-IR, and UV-vis spectral data. The effects of the coumarin units on the zinc, indium, and metal-free phthalocyanine complexes (**2a/3a**, **2c/3c**, **2d/3d**) were also investigated.

Key words: Coumarin (2*H*-chromen-2-one), benzocoumarin, phthalocyanine, fluorescence quenching, singlet oxygen, quantum yield

1. Introduction

Coumarins are naturally occurring benzopyrone derivatives. They have been used largely in the pharmaceuticals, perfumery, and agrochemical industries as starting materials or intermediates. They are also used as fluorescent brighteners, as efficient laser dyes, and as additives in food and cosmetics.^{1–3} The natural and synthetic coumarins attract great attention due to their wide range of biological properties, including anticancer,⁴ anti-HIV,⁵ anti-inflammatory,⁶ and antibacterial⁷ activities. Plants are the most important source of coumarins, but extraction from plants is tedious and time consuming and needs sophisticated instrumentation. Many synthetic methods, like Pechmann condensation; Perkin, Reformatsky, and Wittig reactions; Knoevenagel condensation; and Claisen rearrangement have been investigated for the synthesis of coumarins.^{8–10}

Phthalocyanines (Pcs) were discovered in 1928¹¹ and from then on these synthetic analogues of the naturally occurring porphyrins have been the subject of extensive research in many different fields.¹² Pcs are planar aromatic macrocycles consisting of 4 isoindole units presenting an 18 π -electron aromatic cloud delocalized over an arrangement of alternated carbon and nitrogen atoms. Pcs, remarkably robust and versatile compounds first developed as industrial pigment, have been applied in a wide range of areas such as photovoltaic devices,¹³ catalysts,¹⁴ gas sensors,^{15,16} electrochromic displays,¹⁷ and photodynamic therapy (PDT) agents.^{18,19} These properties may be modulated by central metals and a huge variety of substitutions attached to the Pc cores.^{20,21} Photodynamic cancer therapy (PDT) has been developed over the last century because of its potential usage in the treatment of some cancers. PDT uses a photosensitizing agent (PS) that is introduced followed by illumination using light of a specific intensity and wavelength to activate the particular

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PS agent. Metallophthalocyanines have been used as photosensitizing agents for photodynamic therapy due to their intense absorption in the visible region.^{22–27}

In this study, we aimed to synthesize and investigate the photophysical (fluorescence quantum yields and lifetimes) and photochemical (singlet oxygen generation and photodegradation) properties of zinc, indium, and metal-free phthalocyanine complexes substituted with 3-(4-phenyloxy)coumarin as potential PDT agents. These properties, especially singlet oxygen generation, are very important for PDT of cancer.

This work also explores the effects of ring substitutions on the fluorescence quenching of zinc, indium, and metal-free phthalocyanines by 1,4-benzoquinone (BQ) using the similar literature.²⁴

2. Results and discussion

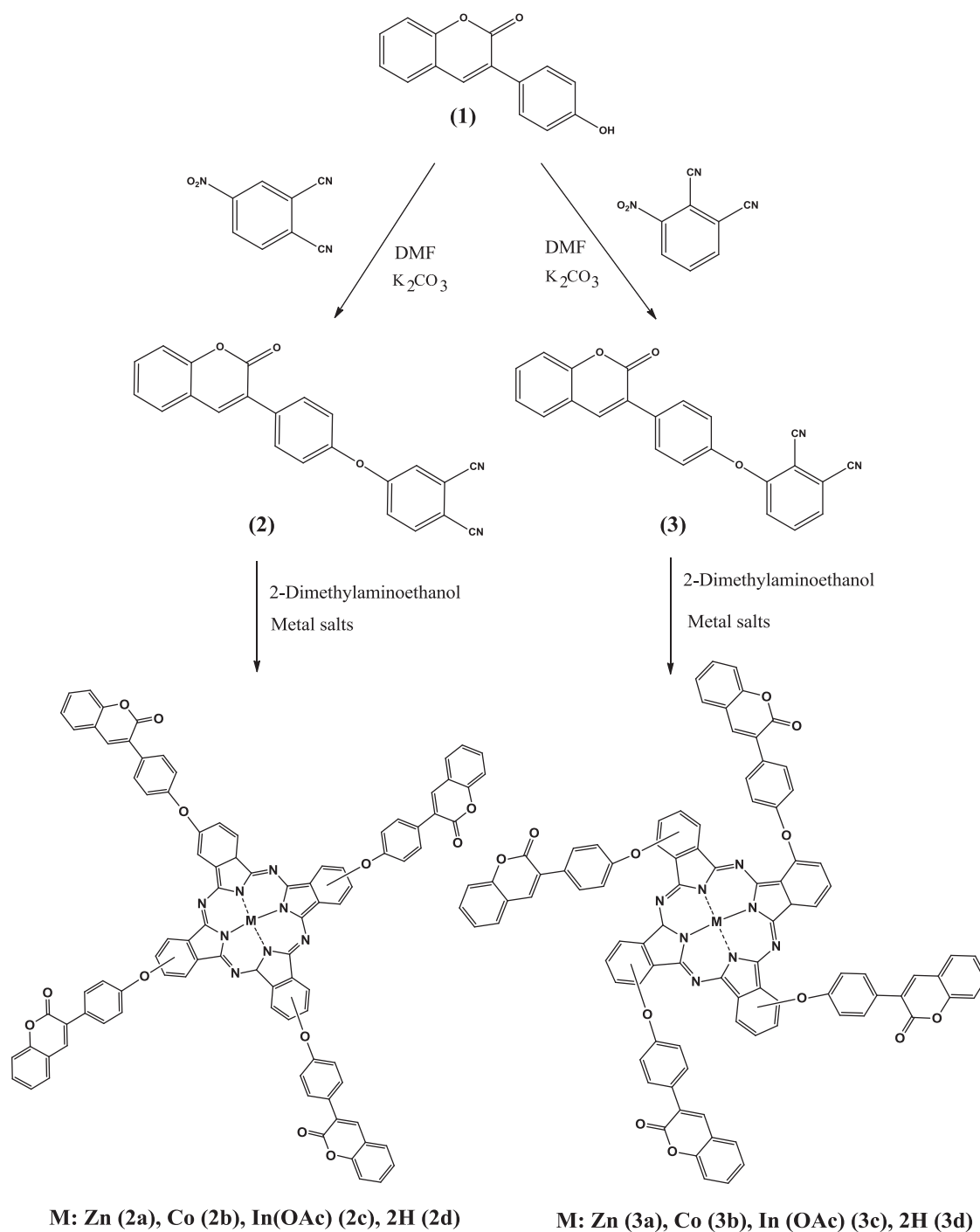
2.1. Synthesis and characterization

3-(4-Phenyloxy)coumarin (**1**) and 4-nitrophthalonitrile or 3-nitrophthalonitrile were added successively with stirring to dry DMF. After stirring for 15 min, finely ground anhydrous K_2CO_3 was added portionwise over 2 h and the mixture was stirred vigorously at room temperature for a further 48 h. The crude products (**2** and **3**) were purified by column chromatography over silica gel using $CHCl_3$ as eluent (Scheme). The metal-free and metallo-Pc complexes show good solubility in solvents such as DMF and DMSO. The novel compounds were characterized by elemental analysis FT-IR, 1H NMR, and MALDI-MS spectroscopy.

The IR spectra showed 4 vibration peaks at ca. $3108\text{--}3042\text{ cm}^{-1}$ / 3100 cm^{-1} for compound **2/3** due to the aromatic C–H stretching band. The characteristic vibrational peaks of the carbonyl (C=O) appeared in the region $1720/1700\text{ cm}^{-1}$ (for **2** and **3**). The vibration peaks corresponding to the C–O–C ether chain appeared in the range $1234/1256\text{ cm}^{-1}$ (**2/3**). The characteristic $C\equiv N$ peaks were also seen at 2222 cm^{-1} for compound **2** and 2223 cm^{-1} for compound **3**.

The 1H NMR spectra showed the expected peak resonances and peak integrals due to the protons of 3-[4-(3,4-dicyanophenyloxy)phenyl]coumarin (**2**) and 3-[4-(2,3-dicyanophenyloxy)phenyl]coumarin (**3**) in $DMSO-d_6$. The 1H NMR spectra of **2** and **3** showed a characteristic singlet peak for vinylic protons at δ 8.20 ppm. In addition, the chemical shifts of the aromatic protons were observed at 7.85–7.30 ppm for compound **2** and 8.01–7.20 ppm for compound **3** as doublets, respectively.

2(3), 9(10), 16(17), 23(24)-Tetrakis[3-(4-phenyloxy)phenyl]coumarin phthalocyaninato zinc (II) (**2a**)/1(3), 8(11), 15(18), 22(25)-tetrakis[3-(4-phenyloxy)phenyl]coumarin phthalocyaninato zinc (II) (**3a**), 2(3), 9(10), 16(17), 23(24)-tetrakis[3-(4-phenyloxy)phenyl]coumarin phthalocyaninato cobalt (II) (**2b**)/1(3), 8(11), 15(18), 22(25)-tetrakis[3-(4-phenyloxy)phenyl]coumarin phthalocyaninato cobalt(II) (**3b**), 2(3), 9(10), 16(17), 23(24)-tetrakis[3-(4-phenyloxy)phenyl]coumarin phthalocyaninato indium(III)acetate (**2c**)/1(3), 8(11), 15(18), 22(25)-tetrakis[3-(4-phenyloxy)phenyl]coumarin phthalocyaninato indium(III) acetate (**3c**) and 2(3), 9(10), 16(17), 23(24) tetrakis[3-(4-phenyloxy)phenyl]coumarin phthalocyanine (**2d**)/1(3), 8(11), 15(18), 22(25)-tetrakis[3-(4-phenyloxy)phenyl]coumarin phthalocyanine (**3d**) complexes were prepared by cyclotetramerization of novel 3-[4-(3,4-dicyanophenyloxy)phenyl]coumarin (**2**) and 3-[4-(2,3-dicyanophenyloxy)phenyl]coumarin (**3**), respectively. Cyclotetramerization of the dinitril compounds (**2** and **3**) to the ZnPc, CoPc, In(OAc)Pc, and metal-free complexes (**2a–2d/3a–3d**) was confirmed by the disappearance of the sharp $C\equiv N$ vibration at 2222 and 2223 cm^{-1} for compounds **2** and **3**, respectively. The IR spectra showed characteristic vibrational peaks at $3100/3050/3070/3075/3100\text{--}3050/3085/3060/3080\text{ cm}^{-1}$ for complexes **2a/3a/2b/3b/2c/3c/2d/3d** to aro-



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

matic C–H stretching frequency. The characteristic vibrational peaks of the carbonyl groups (C=O) appeared at $1740\text{ cm}^{-1}/1720\text{ cm}^{-1}$ for complexes **2a/3a**, at $1712\text{ cm}^{-1}/1710\text{ cm}^{-1}$ for complexes **2b/3b**, at $1715\text{ cm}^{-1}/1729\text{ cm}^{-1}$ for complexes **2c/3c**, and at $1708\text{ cm}^{-1}/1712\text{ cm}^{-1}$ for complexes **2d/3d**, respectively. The vibrational peaks were observed at $\sim 1200\text{--}1250\text{ cm}^{-1}$ for all complexes corresponding to C–O–C ether chains.

The mass spectra of complexes **2** and **3** confirmed the proposed structure. Figures 1 and 2 show the mass spectral study by the MALDI-TOF technique on the newly synthesized phthalocyanine complexes (**2a** and **3a**) identified at m/z : 1523 $[M]^+$ /1524 $[M + 1]^+$ in the presence of 2,5-dihydroxybenzoic acid (DHB) (20 mg/mL in DMF) as a matrix.

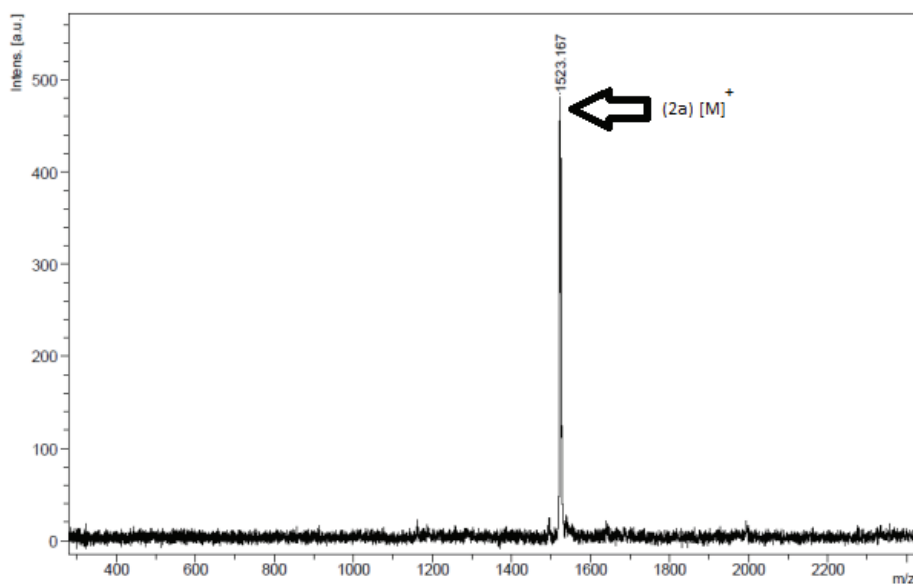


Figure 1. The positive ion and linear mode MALDI-TOF MS spectrum of 2(3), 9(10), 16(17), 23(24)-tetrakis[3-(4-phenoxy)phenyl]coumarin phthalocyaninato zinc(II) (**2a**) (20 mg/mL in DMF) were obtained using a nitrogen laser accumulating 50 laser shots.

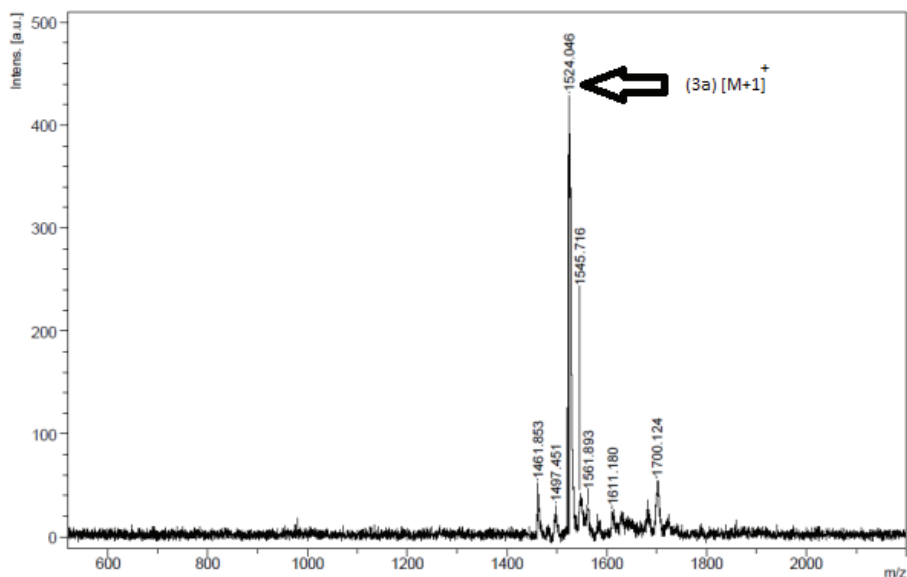


Figure 2. The positive ion and linear mode MALDI-TOF MS spectrum of 1(3), 8(11), 15(18), 22(25)-tetrakis[3-(4-phenoxy) phenyl] coumarin phthalocyaninato zinc(II) (**3a**) (20 mg/mL in DMF) were obtained using a nitrogen laser accumulating 50 laser shots.

2.2. UV-visible electronic absorption spectra

The ground state electronic spectra of the compounds showed characteristic absorption bands in the Q band region at 677/690 nm for **2a/3a**, 699/686 nm for **2b/3b**, 693/690 nm for **2c/3c**, and 699/685 nm for **2d/3d** in DMF. The B band region was observed around 346/334 nm for **2a/3a**, 338/333 nm for **2b/3b**, 338/334 nm for **2c/3c**, and 331/340 nm for **2d/3d** in DMF (Table 1). Theoretical knowledge about the UV-vis spectrum is given in the literature.^{24–28} Figure 3A shows a bathochromic shift of 4 nm for compound **2a**, with 5 nm for compound **2b** in Figure 3B, 3 nm for compound **2c** in Figure 3C, 5 nm for compound **2d** in Figure 3D, 17 nm for compound **3a** in Figure 3E, 15 nm for compound **3b** in Figure 3F, 12 nm for compound **3c** in Figure 3G, and 10 nm for compound **3d** in Figure 3H.

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

Compound	B band λ_{\max} (nm)	Q band λ_{\max} (nm)	$\log \varepsilon$	Excitation λ_{Em} (nm)	Emission λ_{Em} (nm)	Stokes shift Δ_{stokes} (nm)
2	309	-	4.98/-	-	432	123
3	320	-	5.01/-	-	441	121
2a	346	677	4.86/5.17	682	690	13
2b	338	699	5.00/4.06	-	-	-
2c	338	693	5.00/4.78	698	700	7
2d	331	699	5.38/4.06	703	708	9
3a	334	690	4.9/5.24	696	704	14
3b	333	686	5.25/5.41	-	-	-
3c	348	691	5.06/4.84	700	703	12
3d	338	715	4.74/4.59	717	723	8

The differences of UV-vis spectral changes between peripheral and nonperipheral positions are investigated with atomic and molecular orbital theory in the literatures.^{24–31}

2.3. Photophysical measurements (fluorescence quantum yields and lifetimes)

Fluorescence emission spectra were recorded for compounds **2a/3a**, **2c/3c**, and **2d/3d** in DMF for zinc Pc, indium Pc, and metal-free complexes. The emission peaks were observed at 690/704 nm for **2a/3a**, 703 nm for **2c** and **3c**, and 708/723 nm for **2d/3d** (Table 1). The excitation spectra of all the Pc complexes (**2a/3a**, **2c/3c**, and **2d/3d**) are similar to the absorption spectra, and they are mirror images of the fluorescence emission spectra. Figures 4A–4D show the absorption, fluorescence emission, and excitation spectra for zinc and indium complexes (**2a/3a** and **2c/3c**), respectively, in DMF.

The fluorescence quantum yields (Φ_F) of the studied zinc Pc, indium Pc, and metal-free complexes are given in Table 2. The Φ_F values of peripherally and nonperipherally substituted zinc Pc and indium Pc complexes were similar and typical of MPc complexes in DMF. The Φ_F values of the substituted zinc Pc, indium Pc, and metal-free complexes (**2a/3a**, **2c/3c**, **2d/3d**) are lower compared to unsubstituted zinc Pc complex.

Lifetimes of fluorescence (τ_F) are calculated using the literature.^{24–27} A good correlation was found for the experimentally and theoretically determined fluorescence lifetimes for the phthalocyanine molecules as is the case in this work for **2a/3a**, **2c/3c**, and **2d/3d** in DMF solution. While τ_F and natural radiative lifetime (τ_0) values of peripherally and nonperipherally substituted zinc, indium, and metal-free phthalocyanine complexes were lower than the τ_F and τ_0 values of unsubstituted ZnPc complex in DMF. The rate constants for fluorescence

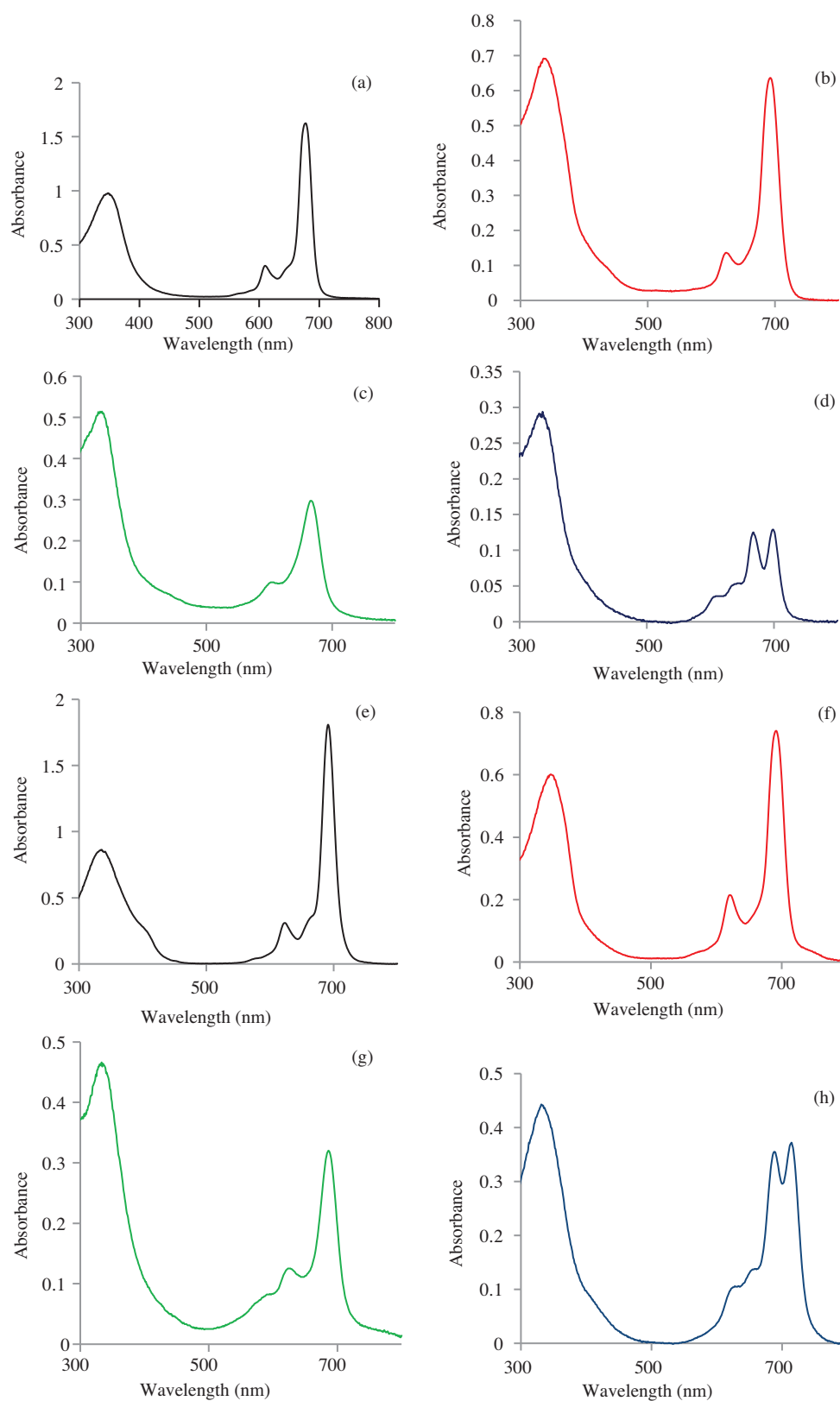


Figure 3. UV-vis spectra of metal-free and metallo-Pcs (A: **2a**, B: **2b**, C: **2c**, D: **2d**, E: **3a**, F: **3b**, G: **3c**, H: **3d**) in DMF (1.10^{-5} M).

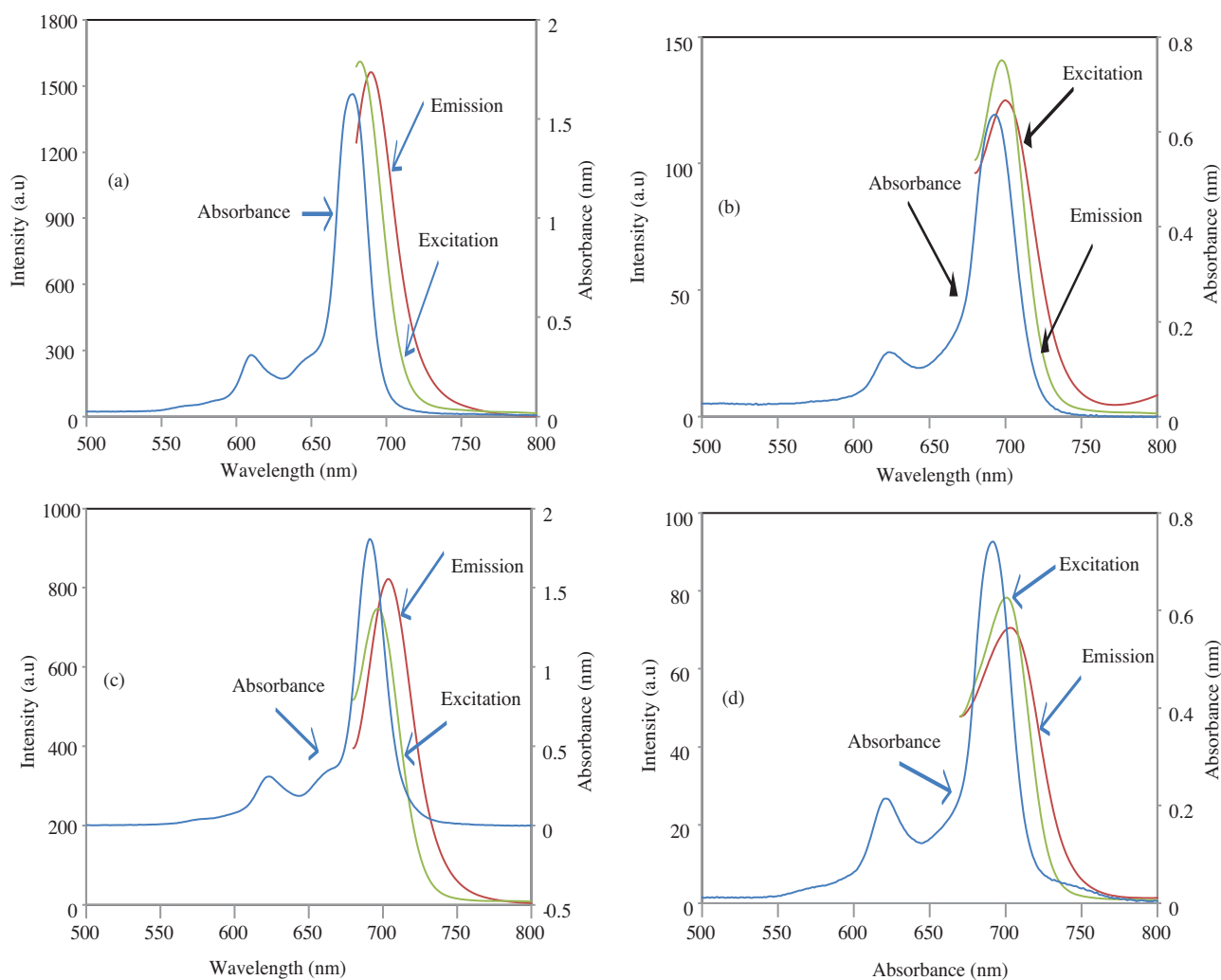


Figure 4. Fluorescence absorption, emission, and excitation spectra of A: **2a**, B: **2c**, C: **3a**, and D: **3c** in DMF. Excitation wavelength = 682 nm for **2a**, 698 nm for **2c**, 696 nm for **3a**, 700 nm for **3c**.

Table 2. Photophysical and photochemical parameters and fluorescence quenching data of unsubstituted and substituted phthalocyanine complexes in DMF.

Compound	Φ_F	Φ_Δ	Φ_d	τ_F (ns)	τ_0 (ns)	$^a k_F$ (s^{-1}) ($\times 10^8$)	K_{SV} (M^{-1})	$k_q/10^{10}$ ($M^{-1} s^{-1}$)
2a	0.0266	0.968	3.2×10^{-4}	0.247	0.247	0.10	2.49	0.1
2b	-	-	-	-	-	-	-	-
2c	0.0072	0.668	1.88×10^{-4}	0.154	0.154	0.046	5.50	0.35
2d	0.08	0.408	7.83×10^{-5}	0.255	0.255	0.015	8.75	1.0
3a	0.0153	0.632	8.67×10^{-5}	0.136	0.136	0.11	4.76	0.35
3b	-	-	-	-	-	-	-	-
3c	0.0042	0.747	3.68×10^{-4}	0.071	0.071	0.059	5.46	0.6
3d	0.0091	0.513	1.51×10^{-4}	0.174	0.174	0.052	4.51	0.259
ZnPc ⁴³	0.17 ⁴³	0.56 ⁴³	$(2.3 \times 10^{-5})^{43}$	1.03 ⁴³	6.80	1.47	31.90	2.61

^a k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$.

(k_F) of tetra-substituted Pc complexes (**2a/3a**, **2c/3c**, and **2d/3d**) were lower than for unsubstituted ZnPc complex in DMF.

2.4. Photochemical measurements (singlet oxygen generation)

Theoretical information is given about photochemical measurements (singlet oxygen generation) in the literature.^{24–27,32}

In this study, the singlet oxygen quantum yield values of the tetra-substituted zinc, indium, and metal-free phthalocyanines (**2a/3a**, **2c/3c**, and **2d/3d**) were determined in DMF by chemical method using diphenylisobenzofuran (DPBF) as a singlet oxygen quencher as in the literature.²⁴ The decreasing of the absorbances of DPBF at 417 nm under the appropriate light irradiation at 5-s intervals was monitored using UV-vis spectrometer. No changes were observed in the Q band intensities of the studied phthalocyanines during the FD determinations, indicating that the studied phthalocyanine compounds were not degraded under light irradiation (30 V) during singlet oxygen determinations.^{24–27} Figures 5A–5C show singlet oxygen quantum yield respectively for complexes **2a**, **2c**, **3a**, and **3c** in DMF. The Φ_{Δ} values of **2a/3a** and **2c/3c** complexes are higher when compared to unsubstituted ZnPc in DMF.

2.5. Photodegradation studies

Theoretical information is given about photodegradation measurements in the literature.^{24–27,32}

Stable zinc phthalocyanine complexes show Φ_d values as low as 10^{-6} and for unstable molecules values of the order of 10^{-3} have been reported.^{24–27,33} It seems that all synthesized Pc complexes (**2a/3a**, **2c/3c**, and **2d/3d**) also show similar Φ_d values and stability to the known zinc phthalocyanine complexes. The Φ_d values of the peripherally and nonperipherally substituted zinc Pc complexes are higher than those of the unsubstituted ZnPc in DMF. Figures 6A–6D show absorption changes during the photodegradation studies for complexes **2a**, **2c**, **3a**, and **3c** in DMF.

2.6. Fluorescence quenching studies by 1,4-benzoquinone (BQ)

The fluorescence quenching of zinc phthalocyanine complexes by 1,4-benzoquinone (BQ) was similar to the literature.^{24–27} Figures 7A and 7B show the quenching of complex **2a** and **3a** by BQ in DMF solution. The slope of the plots shown in the inset of Figures 7A and 7B gave the K_{SV} values, listed in Table 2. The K_{SV} values of the peripherally and nonperipherally substituted Pc complexes (**2a/3a**, **2c/3c**, and **2d/3d**) were lower than those of the unsubstituted ZnPc. The substitution with coumarin groups seems to decrease the K_{SV} values of the complexes in DMF. The bimolecular quenching constant (k_q) values of the substituted zinc, indium, and metal-free phthalocyanine complexes (**2a/3a**, **2c/3c**, and **2d/3d**) were also lower than those for the unsubstituted ZnPc, but generally substitution with coumarin groups seems to decrease the k_q values of the complexes.

3. Conclusion

The photophysical and photochemical properties of the peripherally and nonperipherally tetra-substituted zinc, indium, and metal-free Pc complexes (**2a/3a**, **2c/3c**, and **2d/3d**) in DMF were described for comparison. In solutions, the absorption spectra showed monomeric behavior evidenced by a single (narrow) Q band for **2a/3a** and **2c/3c** in DMF but metal-free Pc complex **2d/3d** gives a doublet Q band as a result of the D_{2h} symmetry.

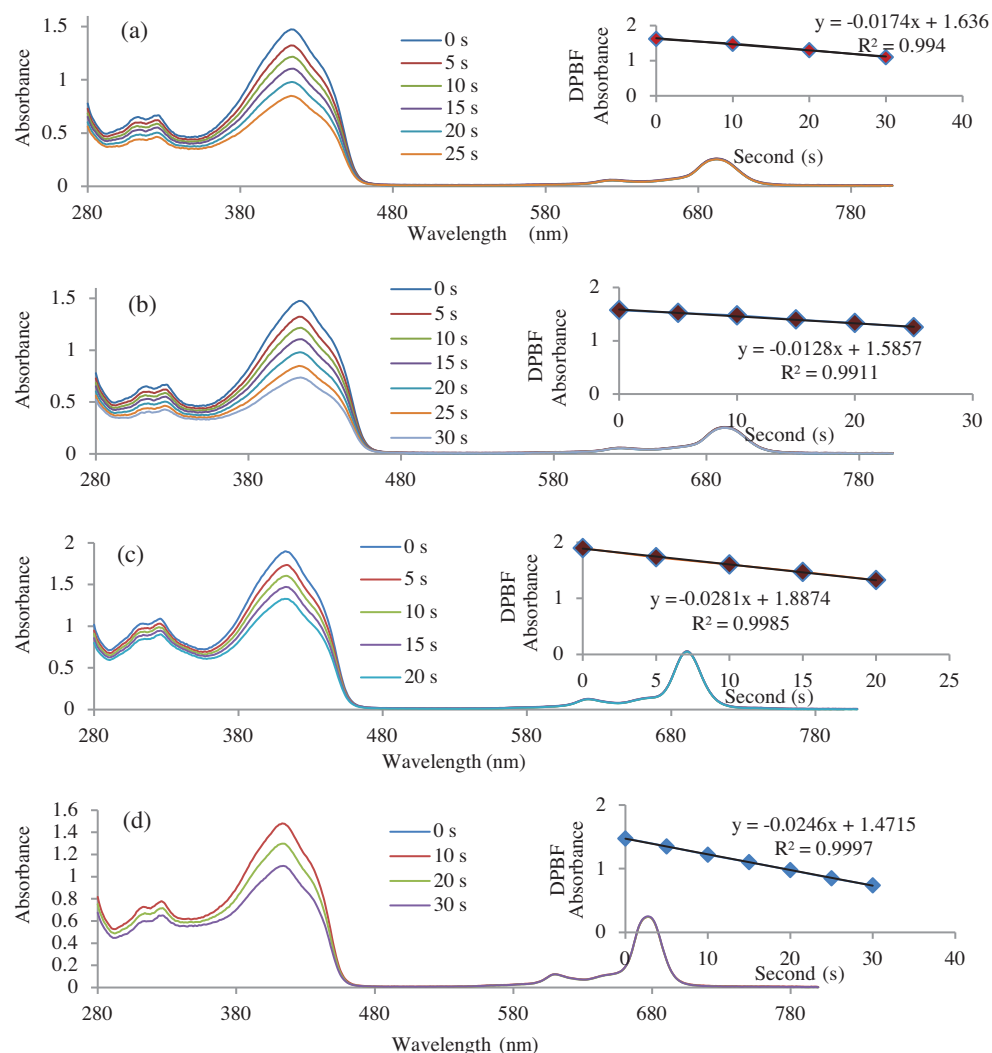


Figure 5. A typical spectrum for the determination of singlet oxygen quantum yield. These determinations were for A: **2a**, B: **2c**, C: **3a**, D: **3c** in DMF at a concentration of 1×10^{-5} M. (Inset: Plot of DPBF absorbance versus time).

The 3-(4-phenyloxy)coumarin substituted Pc complexes (**2a/3a**, **2c/3c**, and **2d/3d**) have enough singlet oxygen quantum yields (Φ_{Δ}) for photocatalytic reactions, but peripherally substituted zinc Pc has very high singlet oxygen quantum yields for application in PDT. The peripherally and nonperipherally tetra-substituted Pc complexes show similar Φ_d value and stabilities of these complexes.^{24–27} The peripherally and nonperipherally tetra-substituted complexes (**2a/3a**, **2c/3c**, and **2d/3d**) showed lower K_{sv} and k_q values when compared to the unsubstituted ZnPc in DMF solution in the fluorescence quenching studies by BQ.

4. Experimental

4.1. Materials

Unsubstituted zinc(II) phthalocyanine (ZnPc) and 1,3-diphenylisobenzofuran (DPBF) were purchased from Aldrich. 2-Hydroxybenzaldehyde and potassium carbonate (K_2CO_3) was purchased from Fluka. P-Hydroxyphenylacetic acid was purchased from Sigma Aldrich. N,N-dimethylaminoethanol (DMAE), sodium carbonate

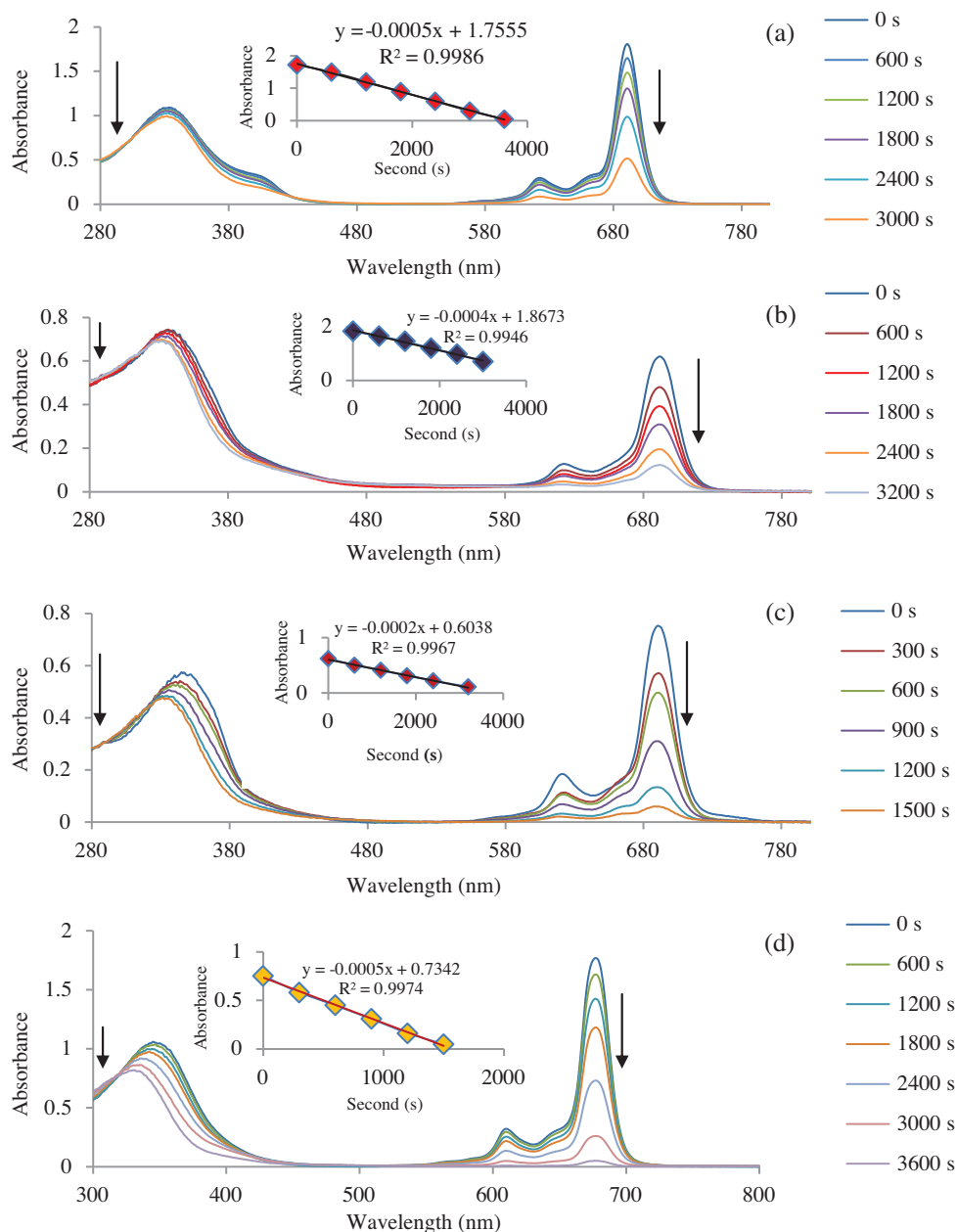


Figure 6. Absorption changes during the photodegradation studies of the Pc compounds **A: 2a**/**B: 3a** and **C: 2c**/**D: 3c** in DMF showing the disappearance of the Q band at 10-min intervals. (Inset: Plot of absorbance versus time). A 300-W general electric quartz line lamp was used as a light source. Power density was 18 mW/cm^2 and energy used was 100 W.

(Na_2CO_3), calcium chloride (CaCl_2), zinc acetate ($\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$), cobalt acetate ($\text{Co}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$), and indium acetate ($\text{In}(\text{OAc})_3$) were purchased from Acros. Dimethylsulfoxide (DMSO), dimethylformamide (DMF) and acetic anhydride were dried as described by Perrin and Armarego³⁴ before use. Methanol, n-hexane, chloroform (CHCl_3), dichloromethane (DCM), tetrahydrofuran (THF), acetone, and ethanol were freshly distilled. 4-Nitrophthalonitrile,³⁵ 3-nitrophthalonitrile,³⁶ and 3-(4-phenoxy)coumarin³⁷ were synthesized according to the reported procedures.

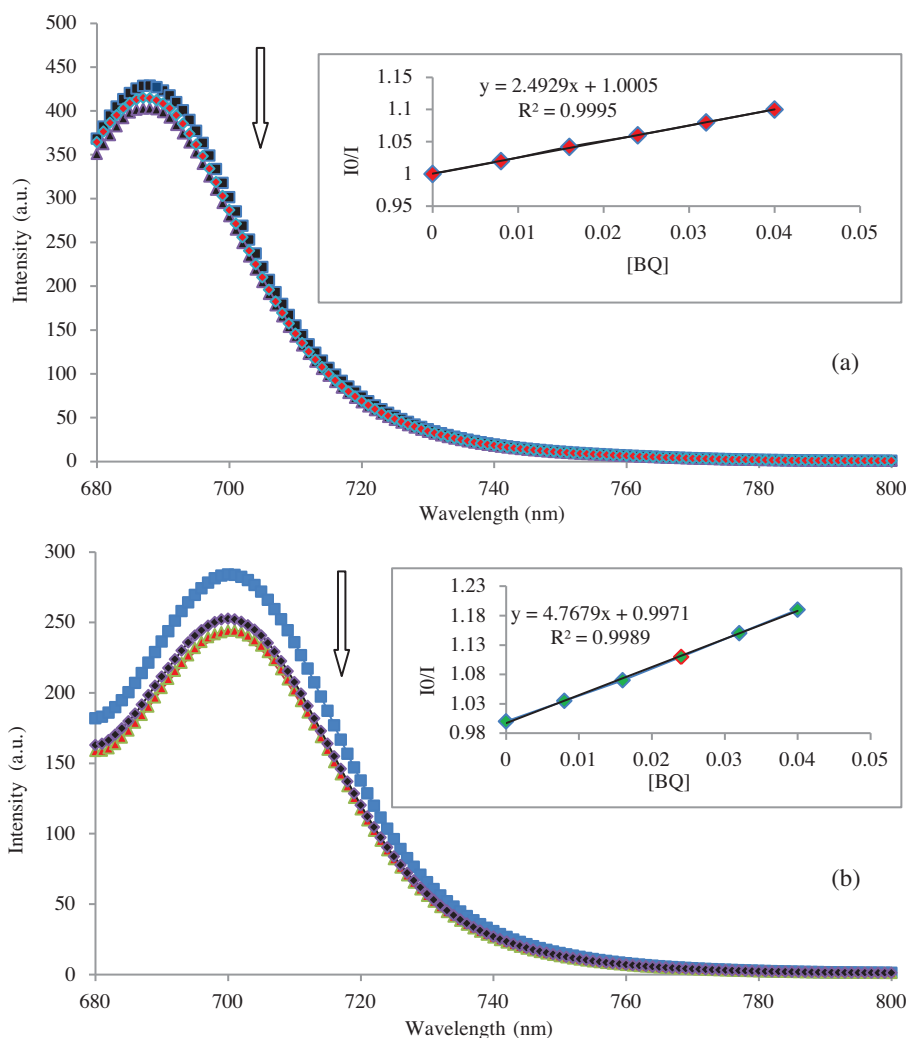


Figure 7. Fluorescence emission spectral changes and Stern–Volmer plots for 1,4-benzoquinone (BQ) quenching of A: **2a** and B: **3a** (1.00×10^{-5} M) on addition of different concentrations of BQ in DMSO. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 M.

4.2. Equipment

The IR spectra were recorded on a PerkinElmer 100 FT-IR using KBr pellets. ^1H NMR spectra were recorded on a Varian 500 MHz spectrometer in DMSO- d_6 for compounds **1** and **2**. Mass spectra were performed on a Bruker Daltonics Autoflex III MALDI-TOF spectrometer. Absorption spectra in the UV-visible region were recorded with a Shimadzu 2450 UV spectrophotometer. Fluorescence excitation and emission spectra were recorded on a HITACHI F-7000 Fluorescence spectrophotometer using 1-cm pathlength cuvettes at room temperatures. The studies of photo-irradiations were done as described in the literature.²⁴

4.3. Photophysical parameters

4.3.1. Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_F) and lifetimes (τ_F) (**2a/3a**, **2c/3c**, and **2d/3d**) were determined by the comparative method in the literature.^{24–27}

4.4. Photochemical parameters

4.4.1. Singlet oxygen quantum yields

Singlet oxygen quantum yields (Φ_{Δ}) of the samples (**2a/3a**, **2c/3c**, and **2d/3d**) were determined in DMF by using the photo-irradiation set-up described in the literature.^{24–27,38}

4.4.2. Photodegradation quantum yields

Determination of photodegradation quantum yields (Φ_d) was carried out as previously described in the literature.^{24–27,38}

4.4.3. Fluorescence quenching by 1,4-benzoquinone (BQ)

Fluorescence quenching experiments on the substituted zinc, indium, and metal-free phthalocyanine complexes (**2a/3a**, **2c/3c**, and **2d/3d**) were carried out by the addition of different concentrations of BQ to a fixed concentration of the complexes (**2a/3a**, **2c/3c**, and **2d/3d**) as reported in the literature.^{24–27,39–42}

4.5. Synthesis

4.5.1. Synthesis of 3-(4-phenoxy)coumarin (1)

A mixture of 2-hydroxybenzaldehyde (salicylaldehyde) (2.00 g, 16.37 mmol), *p*-hydroxyphenyl acetic acid (2.43 g, 16.37 mmol), dry sodium acetate (5.25 g, 65.48 mmol), and anhydrous dry acetic anhydride (15 mL) was heated and stirred at 160–170 °C in a sealed glass tube for 8 h under nitrogen. After cooling to room temperature, water was added and the mixture was stirred overnight. The resulting solid, 3-(4-acetoxyphenyl)phenyl coumarin, was filtered, washed with water, and dried. The crude product was suspended in methanol. Then 10% HCl was added to adjust pH to 3 and the ensuing mixture was heated and stirred at 90 °C for 120 h under nitrogen. The resulting solid, 3-(4-phenoxy)phenyl coumarin, was filtered, washed with water, and dried. The slightly brown products were purified by silica gel column chromatography using CHCl_3 as eluent.³⁷

4.5.2. Synthesis of 3-[4-(3,4-dicyanophenoxy)phenyl] coumarin (2) and 3-[4-(2,3-dicyanophenoxy)phenyl] coumarin (3)

3-(4-Phenoxy)coumarin (0.50 g, 2.09 mmol) and 4-nitrophthalonitrile (0.36 g, 2.09 mmol) or 3-nitrophthalonitrile (0.36 g, 2.09 mmol) were added successively with stirring to dry DMF (15–20 mL). After stirring for 15 min, finely ground anhydrous K_2CO_3 (0.8665 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 and washed with water. Column chromatography of the crude products (silica gel 60, Merck) with chloroform gave pure compounds. The compounds are soluble in ethanol, methanol, THF, CHCl_3 , CH_2Cl_2 , DMF, and DMSO.

Compound 2: Yield: 0.62 g (83%). mp: 220–230 °C. IR $\nu(\text{cm}^{-1})$: 3108–3042 (Ar–CH), 1720 (C=O lactone), 1590 (Ar C=C), 1234 (Ar–O–C). ¹H NMR (d_6 -DMSO, 500 MHz, δ ppm): 7.32 (d, $J = 8.0$ Hz, 1H, Ar-H₁), 7.30 (d, $J = 8.0$ Hz, 1H, Ar-H₂), 8.20 (s, 1H, vinylic H₃), 7.85 (d, 1H, Ar-H₄), 7.80 (d, $J = 8.0$ Hz, 1H, Ar-H₅), 7.45 (d, $J = 8.0$ Hz, 1H, Ar-H₆), 7.60 (dd, $J = 8.0$ Hz, $J = 3.0$ Hz, 2H, Ar-H₇), 7.70 (d, $J = 8.0$ Hz, 1H, Ar-H₈). UV-vis λ_{max} (nm) (log ϵ) (DMF) (1.10×10^{-5} M): 309 nm (4.98). Anal. calcd. for

$C_{23}H_{12}N_2O_3$: C 75.82; H 3.29; N 7.69; O 13.18%. Found: C 75.12; H 3.12; N 7.01; O 13.15%. Fluorescence data: (EM) 1.10^{-5} M, λ_{em} : 432 nm (DMF). MS (MALDI-TOF): m/z 364 [M]⁺.

Compound 3: Yield: 0.60 g (80%). mp: 200–220 °C. IR ν (cm^{-1}): 3100 (Ar-CH), 2968–2930 (aliphatic CH), 2223 (C \equiv N), 1700 (C=O lactone), 1584 (Ar C=C), 1256 (Ar-O-C). ¹H NMR (d_6 -DMSO, 500 MHz, δ ppm): 7.40 (d, J = 8.0 Hz, 1H, Ar-H₁), 7.30 (d, ortho J = 8.0 Hz, meta, J = 3.0 Hz, 2H, Ar-H₂), 7.20 (d, ortho J = 8.0 Hz, 1H, Ar-H₃), 7.40 (d, ortho, J = 8.0 Hz, 1H, Ar-H₄), 8.20 (s, 1H, vinylic H₅), 7.70 (d, ortho J = 8.0 Hz, 1H, Ar-H₆), 7.60 (dd, ortho J = 8.0 Hz, J = 3.0 Hz, 2H, Ar-H₇), 8.01 (d, ortho J = 8.0 Hz, 1H, Ar-H₈), 7.85 (d, ortho J = 8.0 Hz, 1H, Ar-H₉), 7.80 (d, ortho J = 8.0 Hz, 1H, Ar-H₁₀). UV-vis λ_{max} (nm) (log ϵ) (DMF) (1.10^{-5} M): 320 nm (5.01). Anal. calcd. for $C_{23}H_{12}N_2O_3$: C 75.82; H 3.29; N 7.69; O 13.18%. Found: C 75.12; H 3.12; N 7.01; O 13.15%. Fluorescence data: (EM) 1.10^{-5} M, λ_{em} : 441 nm (DMF). MS (MALDI-TOF): m/z 364 [M]⁺.

4.6. General procedure for the metallo-phthalocyanines

A mixture of **2** or **3** (0.100 g, 0.72 mmol) and metal salts $Zn(AcO)_2 \cdot 2H_2O$ (0.04 g, 0.06 mmol), $Co(AcO)_2 \cdot 4H_2O$ (0.04 g, 0.072 mmol), and $In(OAc)_3$ (0.04 g, 0.13 mmol) in dry 2-dimethylaminoethanol (DMAE) (1.5 mL) was refluxed with stirring for 24 h under nitrogen atmosphere at 160–170 °C. At room temperature, methanol (5 mL) was added to precipitate the product.^{24–27} The resulting product was filtered and washed with water, methanol, ethanol, acetonitrile, ethyl acetate, acetone, acetic acid, and diethylether. The resulting products were purified by column chromatography on silica gel with $CHCl_3$ as eluent.

4.6.1. Synthesis of **2(3)**, **9(10)**, **16(17)**, **23(24)**-Tetrakis[3-(4-phenyloxy)phenyl] coumarinphthalocyaninato zinc(II) (**2a**) and **1(3)**, **8(11)**, **15(18)**, **22(25)**-tetrakis[3-(4-phenyloxy)phenyl] coumarin phthalocyaninato zinc(II) (**3a**)

Compound 2a: Yield: 0.05 g (50%). mp: >300 °C. IR γ_{max} (cm^{-1}): 3100 (Ar-CH), 1740 (C=O lactone), 1595 (C=C), 1222 (Ar-O-C). UV-vis (DMF) λ_{max} (log ϵ) (nm) ($1.2 \cdot 10^{-5}$ M): 346 (log ϵ = 4.86), 677 (log ϵ = 5.17); Fluorescence data: (EM) 1.10^{-5} M, λ_{em} : 690 nm and (EX) 1.10^{-5} M, λ_{ex} : 682 nm (DMF). MS (MALDI-TOF) (2,5-dihydroxybenzoic acid as matrix): m/z 1523.167 [M]⁺.

Compound 3a: Yield: 0.04 g (40%). mp: >300 °C. IR γ_{max} (cm^{-1}): 3050 (Ar-CH), 1720 (C=O lactone), 1591 (C=C), 1220 (Ar-O-C). UV-vis (DMF) λ_{max} (log ϵ) (nm) ($1.2 \cdot 10^{-5}$ M): 334 (log ϵ = 4.91), 690 (log ϵ = 5.24); Anal. Calc. for $C_{95}H_{62}N_8O_{12}Zn$: C, 72.47; H, 3.94; N, 7.12%. Found: C, 72.41; H, 3.90; N, 7.10%. Fluorescence data: (EM) 1.10^{-5} M, λ_{em} : 704 nm and (EX) 1.10^{-5} M, λ_{ex} : 696 nm (DMF). MS (MALDI-TOF) (2,5-dihydroxybenzoic acid as matrix): m/z 1524.04 [M + 1]⁺.

4.6.2. **2(3)**, **9(10)**, **16(17)**, **23(24)**-Tetrakis[3-(4-phenyloxy)phenyl]coumarin phthalocyaninato cobalt(II) (**2b**) and **1(3)**, **8(11)**, **15(18)**, **22(25)**-tetrakis [3-(4-phenyloxy) phenyl]coumarin phthalocyaninato cobalt(II) (**3b**)

Compound 2b: Yield: 0.03 g (35%). mp: >300 °C. IR γ_{max} (cm^{-1}): 3070 (Ar-CH), 1712 (C=O lactone), 1591 (C=C), 1212 (Ar-O-C). UV-vis (DMF) λ_{max} (log ϵ) (nm) ($1.2 \cdot 10^{-5}$ M): 338 (log ϵ = 5.00), 699 (log ϵ = 4.06); Anal. Calc. for $C_{95}H_{62}CoN_8O_{12}$: C, 72.77; H, 3.95; N, 7.14%. Found: C, 72.76; H, 3.92; N, 7.14%. MS (MALDI-TOF) (2,5-dihydroxybenzoic acid as matrix): m/z 1517 [M]⁺.

Compound 3b: Yield: 0.03 g (30%). mp: >300 °C. IR γ_{\max} (cm⁻¹): 3075 (Ar-CH), 1710 (C=O lactone), 1590 (C=C), 1230 (Ar-O-C). UV-vis (DMF) λ_{\max} (log ϵ) (nm) (1.2.10⁻⁵ M): 333 (log ϵ = 5.25), 686 (log ϵ = 5.41); Anal. Calc. for C₉₅H₆₂CoN₈O₁₂: C, 72.77; H, 3.95; N, 7.14%. Found: C, 72.77; H, 3.93; N, 7.12%. MS (MALDI-TOF) (2,5-dihydroxybenzoic acid as matrix): m/z 1517 [M]⁺.

4.6.3. 2(3), 9(10), 16(17), 23(24)-Tetrakis[3-(4-phenyloxy)phenyl]coumarin phthalocyaninatoindium(III) acetate (2c) and 1(3), 8(11), 15(18), 22(25)-tetrakis[3-(4-phenoxy) phenyl]coumarin phthalocyaninato indium(III) acetate (3c)

Compound 2c: Yield: 0.01 g (15%). mp: >300 °C. IR γ_{\max} (cm⁻¹): 3100–3050 (Ar-CH), 1715 (C=O lactone), 1593 (C=C), 1210 (Ar-O-C). UV-vis (DMF) λ_{\max} (log ϵ) (nm) (1.2.10⁻⁵ M): 338 (log ϵ = 5.00), 693 (log ϵ = 4.78); Anal. Calc. for C₉₇H₆₅InN₈O₁₄: C, 69.22; H, 4.13; N, 6.66%. Found: C, 69.20; H, 4.11; N, 6.65%. Fluorescence data: (EM) 1.10⁻⁵ M, λ_{em} : 703 nm and (EX) 1.10⁻⁵ M, λ_{ex} : 700 nm (DMF). MS (MALDI-TOF) (2,5-dihydroxybenzoic acid as matrix): m/z 1631.82 [M]⁺.

Compound 3c: Yield: 0.015 g (15%). mp: >300 °C. IR γ_{\max} (cm⁻¹): 3085 (Ar-CH), 1729 (C=O lactone), 1595 (C=C), 1212 (Ar-O-C). UV-vis (DMF) λ_{\max} (log ϵ) (nm) (1.2.10⁻⁵ M): 334 (log ϵ = 4.91), 690 (log ϵ = 5.24); Anal. Calc. for C₉₇H₆₅InN₈O₁₄: C, 69.22; H, 4.13; N, 6.66%. Found: C, 69.22; H, 4.13; N, 6.66%. Fluorescence data: (EM) 1.10⁻⁵ M, λ_{em} : 703 nm and (EX) 1.10⁻⁵ M, λ_{ex} : 700 nm (DMF). MS (MALDI-TOF) (2,5-dihydroxybenzoic acid as matrix): m/z 1631.82 [M]⁺.

4.7. General procedure for the metal-free phthalocyanines

A mixture of **2** or **3** (0.100 g, 0.72 mmol) in dry 2-dimethylaminoethanol (DMAE) (1.5 mL) was refluxed with stirring for 24 h under nitrogen atmosphere at 160–170 °C. At room temperature, methanol (5 mL) was added to precipitate the product. The resulting product was filtered and washed with water, methanol, ethanol, acetonitrile, ethyl acetate, acetone, acetic acid, and diethylether. The resulting products were purified by column chromatography on silica gel with CHCl₃ as eluent.

4.7.1. 2(3), 9(10), 16(17), 23(24)-Tetrakis[3-(4-phenyloxy)phenyl]coumarin phthalocyanine (2d) and 1(3), 8(11), 15(18), 22(25)-tetrakis[3-(4-phenyloxy)phenyl]coumarin phthalocyanine (3d)

Compound 2d: Yield: 0.03 g (30%). mp: >300 °C. IR γ_{\max} (cm⁻¹): 3060 (Ar-CH), 1708 (C=O lactone), 1590 (C=C), 1210 (Ar-O-C). UV-vis (DMF) λ_{\max} (log ϵ) (nm) (1.2.10⁻⁵ M): 331 (log ϵ = 5.38), 699 (log ϵ = 4.06); Anal. Calc. for C₉₅H₆₆N₈O₁₂: C, 75.41; H, 4.36; N, 7.40%. Found: C, 75.40; H, 4.30; N, 7.25%. Fluorescence data: (EM) 1.10⁻⁵ M, λ_{em} : 708 nm and (EX) 1.10⁻⁵ M, λ_{ex} : 703 nm (DMF). MS (MALDI-TOF) (2,5-dihydroxybenzoic acid as matrix): m/z 1460 [M]⁺.

Compound 3d: Yield: 0.025 g (25%). mp: >300 °C. IR γ_{\max} (cm⁻¹): 3080 (Ar-CH), 1712 (C=O lactone), 1595 (C=C), 1220 (Ar-O-C). UV-vis (DMF) λ_{\max} (log ϵ) (nm) (1.2.10⁻⁵ M): 340 (log ϵ = 4.82), 685 (log ϵ = 4.95); Anal. Calc. for C₉₅H₆₆N₈O₁₂: C, 75.41; H, 4.36; N, 7.40%. Found: C, 75.36; H, 4.31; N, 7.30%. Fluorescence data: (EM) 1.10⁻⁵ M, λ_{em} : 723 nm and (EX) 1.10⁻⁵ M, λ_{ex} : 717 nm (DMF). MS (MALDI-TOF) (2,5-dihydroxybenzoic acid as matrix): m/z 1460 [M]⁺.

Acknowledgement

We are thankful to the Research Foundation of Marmara University, Commission of Scientific Research (BAPKO), Project: FEN-C-YLP-150513-0182.

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