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Effects of coumarin substituents on the photophysical properties of newly synthesised phthalocyanine derivatives

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In this study, synthesis of new ligands, 8-hydroxy-3-[*p*-(3′,4′-dicyanophenoxy)-phenyl]coumarin and 8-hexyloxy-3-[*p*-(3′,4′-dicyanophenoxy)-phenyl]coumarin, and their phthalocyanines, 2,9,16,23-tetrakis[8-hexyloxy-3-(4-oxyphenyl)coumarin]-metal-free and metallophthalocyanines {M[Pc(OBzCou)$_4$] (M = 2H, Zn(II), Co(II); Bz: benzene; Cou: coumarin)} were synthesised. The novel chromogenic compounds were characterised by elemental analysis: ^{1}H NMR, ^{13}C NMR, MALDI-TOF, IR and UV–vis spectral data. The effect of coumarin substituents on the photophysical properties of metal-free (H_2Pc) and zinc phthalocyanines (ZnPc) derivatives has been examined. Spectrophotometric measurements revealed that coumarin-substituted ZnPc derivatives were in the unaggregated form, whereas those of H_2Pc species were in aggregated form. It means that substitution of coumarin derivative prevents the cluster formation in the presence of zinc ion in the centre of Pc.

Keywords: phthalocyanines; fluorescence; coumarin derivatives; aggregation; cobalt; zinc

Introduction

Phthalocyanines exhibit excellent chemical and photochemical properties, but poor fluorescent properties (*1–3*). An approach to the problem in the spectrofluorometry that measures emission and excitation intensities of a fluorescent molecule was the introduction of metal-chelating groups into fluorescent dyes with the aim of forming derivatives that would undergo changes in the fluorescence intensity and/or wavelength upon formation of metal complexes (*3–5*). Detection of various metal ions is therefore crucial in biological as well as electronic areas and there are numerous detection techniques in use today (*6*). The benefits of phthalocyanines (Pcs) in terms of technological applications are beyond question, such as sensing elements in chemical sensors, photoconducting agents in photocopying machines and carrier generation materials in near-IR (*7–10*). Although several thousands of phthalocyanine complexes have been synthesised and tested so far for technological applications since the discovery of phthalocyanine, many important properties have, however, been extensively studied for their low solubility in most organic solvents and their aggregation (*11*). It is well known that their physicochemical properties can be fine-tuned by changing the metal and/or nature of the substituents on the periphery of the Pcs (*12*, *13*). On the other hand, the family of the functional phthalocyanines has been an interesting target for the chemists for the development of further chemical reactions on the phthalocyanine complexes (*14*, *15*). Therefore, in this paper, we have in particular combined functional coumarins (2H-1-benzopyran-2-one) with phthalocyanines as a single compound via synthetic methodology to form soluble phthalocyanine-bearing coumarin derivative as a fluorescence probe. The experimental results demonstrate that introduction of coumarin derivatives into the peripheral ring of phthalocyanines enhances the fluorescence property of phthalocyanines. Phthalocyanines coupled with the coumarin moiety may exhibit biological activities, and after the cleavage of the lactone ring of the peripheral 2H-1-benzopyran-2-one (coumarin) in the phthalocyanine, the solubility can also be increased (*16*).

In this study, metal-free and metallophthalocyanine derivatives, {M[Pc(OBzCou)$_4$] (M = 2H, Zn(II), Co(II))}, containing 8-hexyloxy-3-(4-oxyphenyl)coumarin and the cleavage of the lactone ring of the peripheral 2H-1-benzopyran-2-one (coumarin) in metal-free and zinc(II) phthalocyanines were studied with respect to the effects on the photophysical properties of phthalocyanines. The effect of substituents on the fluorescence spectra of Pcs was also reported.

Results and discussion

8-Hydroxy-3-[*p*-(3′,4′-dicyanophenoxy)-phenyl]coumarin (**1**) and 8-hexyloxy-3-[*p*-(3′,4′-dicyanophenoxy)-phenyl]-coumarin (**2**) were obtained according to the literature procedure (*16*). While metal-free (**3**) was obtained in the presence of 1,8-diazabicyclo-[5,4,0]-undec-7-ene (DBU)

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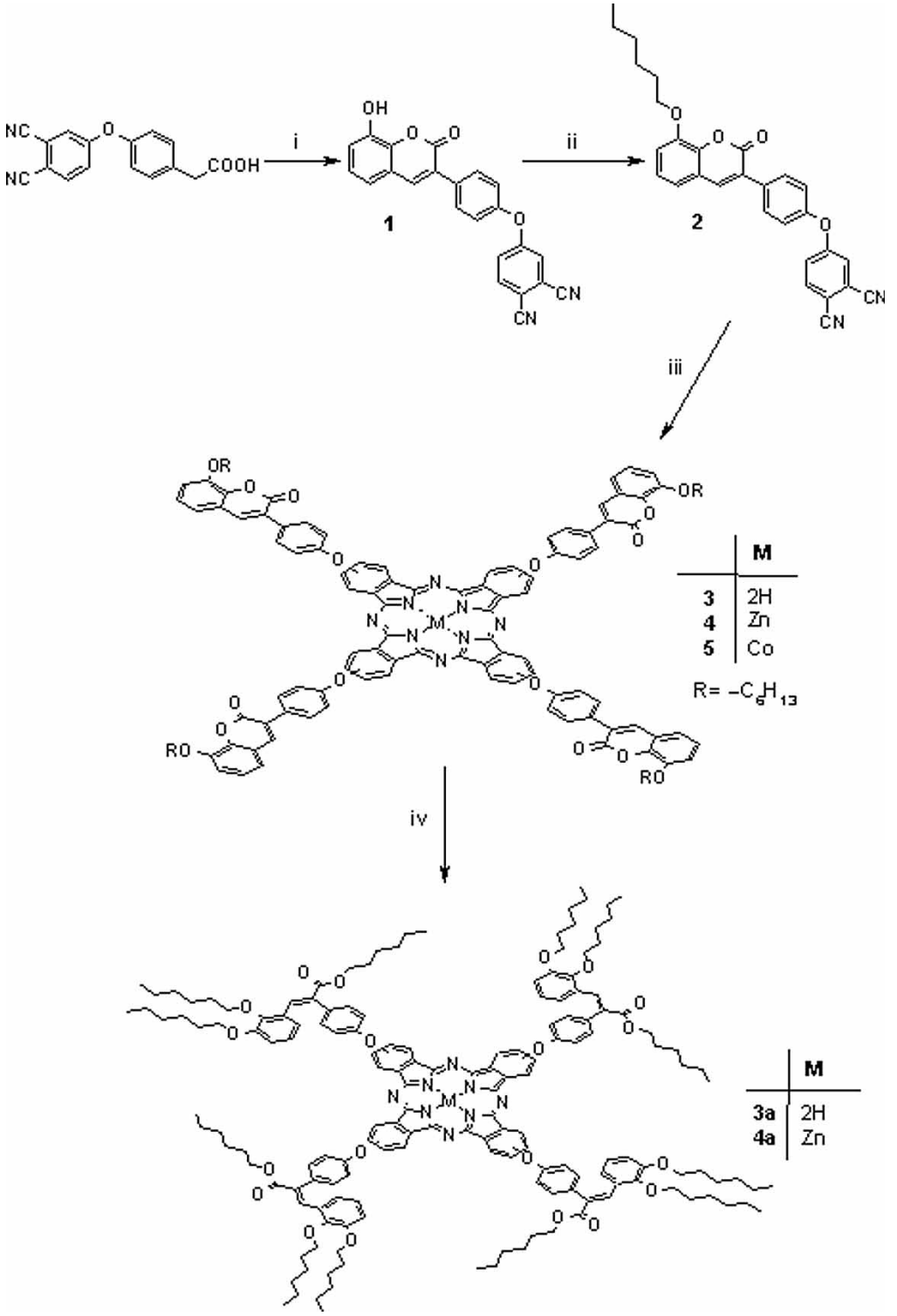
in anhydrous 2-(dimethylamino)-ethanol solvent, metallophthalocyanines (**4** and **5**) bearing fluorescence coumarin were accomplished by heating a mixture of 8-hexyloxy-3-[*p*-(3′,4′-dicyanophenoxy)-phenyl]coumarin with anhydrous $Zn(O_2CMe)_2$ salts and $CoCl_2$ at *ca.* 180°C under N_2 atmosphere in the presence of DBU in hexanol (Scheme 1).



Scheme 1. Synthetic route of **3**–**5**, {M[Pc(OBzCou)$_4$] (M = 2H, Zn(II), Co(II))} and their lactone ring-opening complexes (**3a**, **4a**). (i) 2,3-Dihydroxybenzaldehyde, $(Ac)_2O$, NaOAc, 160–170°C; HCl, MeOH. (ii) $C_6H_{13}Br$, K_2CO_3, DMF, 80–90°C. (iii) and (iv) *N*,*N*-dimethylaminoethanol, DBU and anhydrous $Zn(O_2CMe)_2$, $CoCl_2$ and DBU. Li, *n*-hexanol, bromohexane, 24 h.

In addition, the lactone rings of 2,9,16,23-tetrakis[8-hexyloxy-3-(4-oxyphenyl)coumarin]metal-free phthalocyanine (**3**) and 2,9,16,23-tetrakis[8-hexyloxy-3-(4-oxyphenyl)coumarin]phthalocyaninatozinc(II) (**4**) were opened and the hydroxyl groups released were hexylated. The yields of **3**–**5** were rather low (33% for **3**, 73% for **4** and 42% for **5**). The structure of phthalocyanines (**3**–**5**) was verified by FT-IR, ^{1}H NMR, UV–vis and MALDI-TOF MS spectroscopic methods, as well as by elemental analysis. All the analytical and spectral data are consistent with the predicted structures. Conversion of the 8-hexyloxy-3-[*p*-(3′,4′-dicyanophenoxy)-phenyl]coumarin to the phthalocyanines (**3**–**5**) was confirmed by the disappearance of the sharp —C≡N vibration at 2230 cm^{-1} in compound **2** and appearance of the strong C=O (lactone) at *ca.* 1701 as well as the others (Ar-H and Aliph-H together with Ar-O-Ar band) in Pcs. However, ester stretching bands in the FT-IR spectrum of **3a** and **4a** at *ca.* 1710 cm^{-1} are the evidence for the formation of **3a** and **4a**.

The ^{1}H NMR spectra of compounds **3**–**4** are somewhat broader than the corresponding signals in the starting dinitrile derivative. This broadening is likely due to chemical exchange caused by aggregation–disaggregation equilibria and the fact that the product obtained in these reactions is a mixture of positional isomers that are expected to show chemical shifts that differ slightly from each other (*11*, *13*). The inner NH protons of **3** and **3a** were also identified in the ^{1}H NMR spectrum with a broad chemical shift between $\delta = -3.47$ and -3.48 ppm, respectively, as a consequence of the 18 π-electron systems of the planar molecule and this signal disappears on deuterium oxide exchange (*11*, *16*). The other resonances related to aliphatic and aromatic (OCH_2, CH_2, CH_3 and Ar-H) protons in the ^{1}H NMR spectra **3** and **3a** are similar to each other except esteric protons. The ^{1}H NMR spectrum of **3a** and **4a** indicated characteristic aromatic (Bz_1, Bz_2 and Bz_3) at 8.40–6.78 and 8.36–6.82, ethylenic protons at 6.63 and 6.70 and aliphatic ester protons at 4.30–4.00, 4.30–4.02 ppm, respectively. The signals belonging to aromatic protons in the downfield of the spectrum in **3**, **3a**, **4** and **4a** are broader than the aliphatic ones in the high field of the spectrum.

While divalent **4** and **4a** gave a single Q-band of high intensity due to a single π–π* transition as expected as a result of this D_{4h} symmetry, **3** and **3a** exhibited splitted Q-band as a result of D_{2h} symmetry with shoulders at slightly higher energy side of the Q-band for each phthalocyanine in addition to B-bands in UV region (*17*, *18*). The Q-band absorptions in the DMSO of **3**, **4** and **5** were observed at 703, 675 (Qx and Qy), 683 and 669 nm, respectively, with shoulders at slightly higher energy side of the Q-band for each phthalocyanine (Figure 1). The B-bands are broad due to the superimposition of the B1- and B2-bands in the 330–350 nm region in the case of compounds **3**–**5** (*19*, *20*).

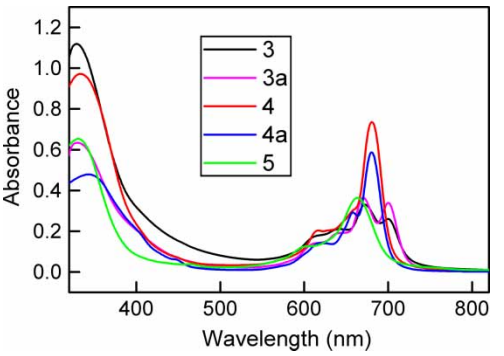


Figure 1. UV–vis spectra of **3**, **3a**, **4**, **4a** and **5**.

Protonated molecular ion peak for **3** (2,5-dihydroxybenzoic acid, DHB) was observed at 1858 Da for the monoisotopic masses of the elements in compound **3** (H_2Pc) with the other isotopic peaks (between 1857 and 1460 with about 1 Da mass differences). It was mainly resulted from the isotopic distribution of carbon, which was exactly overlapped with the mass of the ligand calculated theoretically from the elemental composition (*13*, *14*). The mass spectra of compound **3a** also confirmed the proposed structures giving MS (MALDI-TOF, DHB as matrix) at *m/z*: 2603.43 $[M+H]^+$. The protonated molecular ion peaks were identified at *m/z*: 1922.09 $[M+H]^+$ for **4** at *m/z*: 2666.34 $[M+H]^+$ for **4a** and at *m/z*: 1915.07 $[M]^+$ for **5** by using DHB as matrix in MS MALDI-TOF. Following the protonated molecular ion peak, a peak group was observed at 38 Da mass higher than the protonated molecular ion peak group. This peak is resulted from the potassium adduct to the neutral molecule of **4** (Figure 2).

Fluorescence measurements

The excitation spectra of phthalocyanine derivatives with coumarin substituents were obtained at 460 and 730 nm emission wavelengths (Figure 3). The spectra at low-wavelength regions belong to coumarin substituents since the contribution of Pc is negligible (*21*, *22*). As shown in Figure 3, the coumarin substituent exhibits high excitation intensity alone and excitation maximum wavelength at 340 nm. Maximum wavelength of coumarin moiety that bound to Pc core shifts to 1, 4, 3 and 5 nm blue region for **3**, **3a**, **4** and **4a**, respectively. On the other hand, drastic diminishes at excitation intensities were observed in the case of **4** and **4a** species. This shows that chemically treated coumarin moiety, which has a ring-opened structure, has restricted conjugation structure causing a decrease in excitation intensity (*23*). When monitoring the emission at 730 nm, the excitation spectra (at high-wavelength regions) of coumarin-substituted **3**–**4** were obtained (Figure 3). It was observed that the excitation spectra of **3** and **3a** closely match the absorption spectra

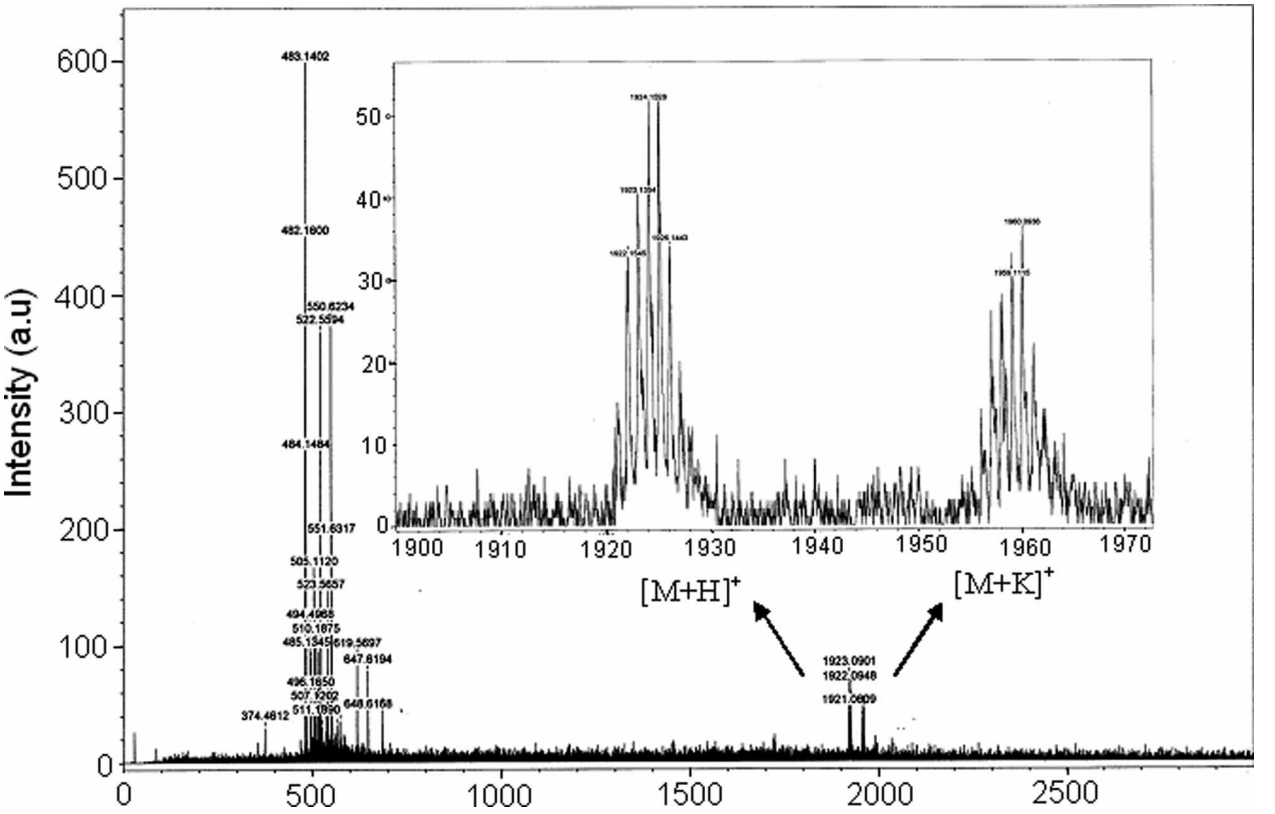


Figure 2. Positive ion and reflectron mode MALDI-MS spectrum of **4** (in DHB as matrix). Inset: spectrum shows expanded molecular mass region of **4**.

from 450 to 730 nm. This indicates the presence of a single species and that the energy-transfer process is nearly quantitative. This also shows that **4** and **4a** are essentially in the non-aggregated form in this concentration (*24*). Whereas excitation spectra of coumarin-substituted **3** and **3a** are not nearly identical with their ground-state absorption spectra, showing that these Pc derivatives are in the aggregated form in this media (*25*, *26*). Fluorescence excitation and emission spectra of compound **5** were excluded since cobalt ion in the centre of Pc almost quenched the fluorescence intensity of Pc derivative.

Figure 4 shows the fluorescence emission spectra of coumarin moiety and Pc derivatives containing coumarin substitutes in DMSO at room temperature upon excitation at 390 nm. Emissions observed at 480 nm are almost exclusively from coumarin-substituent bound to Pc core since unsubstituted Pc does not exhibit any fluorescence emission (data not shown) in this excitation wavelength. Spectrofluorimeter shows secondary harmonic emission at the wavelength of 680 nm when excitation wavelength of 340 nm used where coumarin moiety has maximum excitation intensity. Therefore, excitation wavelength was chosen as 390 nm to eliminate this emission and also to obtain emissions from both the coumarin moiety and the Pc core. As shown in Figure 4, emission intensity of coumarin moiety is less than that of Pc derivatives because of low excitation intensity at this excitation wavelength. Whereas coumarin moiety shows higher emission intensity compared with the Pc derivatives when it was excited at 340 nm (spectra not shown). This shows that the fluorescence intensity from the peripherally bonded coumarin derivatives is decreased because of inner filter effect of Pc core causing to radiative energy transfer. The decrease

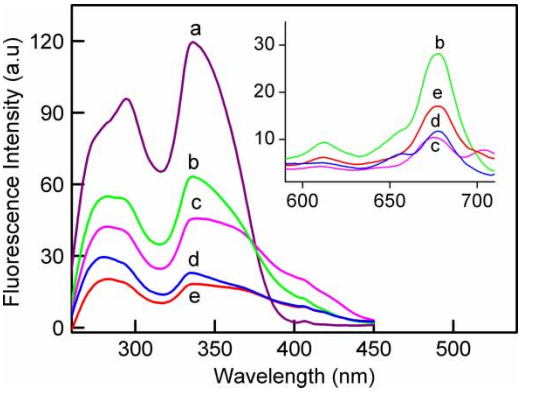


Figure 3. Excitation spectra of coumarin-substituent alone (a), **3** (b), **3a** (c), **4** (d) and **4a** (e) in DMSO. Inset: excitation spectra were recorded for emission at 460 and 730 nm.

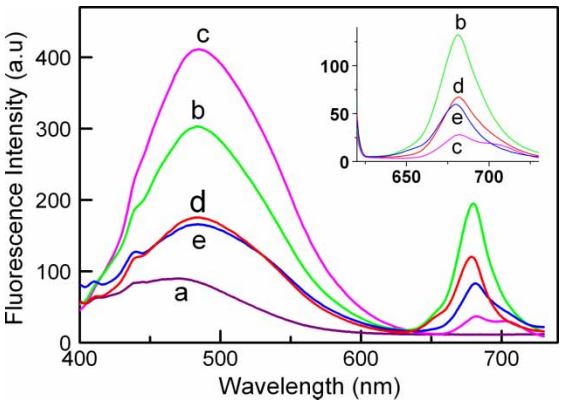


Figure 4. Emission spectra of coumarin-substituent alone (a), **3** (b), **3a** (c), **4** (d) and **4a** (e) in DMSO (emission excited at 390 nm). Inset: emissions obtained for excitation at 620 nm.

in emission is more intense in the case of **3**, since **4** core gives poorer spectral overlap compared with that of metal-free core (*27*, *28*). On the other hand, decrease in the emission intensity of coumarin derivative, which was chemically treated, is more pronounced because of the degradation of aromatic structure of coumarin moiety. The spectra of Pc derivatives containing coumarin moiety show Stokes shifts, indicating very little molecular rearrangement in the excited state. The emission maximum for coumarin moiety is blue shifted (by 15 nm) compared with coumarin-containing Pc derivatives, indicating that there are intramolecular interactions causing excited-state degeneracy as a result of molecular rearrangement (*29*, *30*).

The fluorescence emissions at higher wavelength occur exclusively from the Pc moiety (Figure 4, right spectra). As shown in Figure 4, zinc phthalocyanine (ZnPc) species with same coumarin moieties exhibit more intense emission than those of metal-free species and there is no spectral shift in the emission wavelengths. When the steady-state fluorescence spectra of coumarin-substituted Pcs with Zn and metal-free performed in DMSO upon excitation at 620 nm Q-band vibrations, same emission spectra around 680 nm were obtained (Figure 4, inset). This shows that there is no spectral shift effect of coumarin derivatives on the fluorescence emission from S1 singlet excited state of the Pc core with or without metal ion. On the other hand, decrease in the emission of Pc core with the different type of appended coumarin derivatives suggests that the Pc core excited state rapidly decays through radiationless conversion to the ground state (*31*, *32*).

As a conclusion, we have synthesised novel Pc derivatives possessing the axial 8-hexyloxy-3-(4-oxyphenyl)coumarin and the cleavage of the lactone ring of coumarin substituent. These substituents enhance the solubility of Pc derivatives and inhibit the aggregation. Spectrophotometric measurements revealed that ZnPc derivatives, which have coumarin derivatives and cleavage of its lactone ring, are in the unaggregated form, whereas H_2Pc species possessing the same substituents are in the aggregated form. This shows that not only the substitution of coumarin derivatives effects the aggregate formation, but also zinc ion in the centre of Pc prevents the cluster formation. On the other hand, derivatives of the coumarin units produced emission from them and also from Pc core upon specific excitation. It was concluded that the derivatives of coumarin units decay by two pathways: either by direct luminescence giving rise to the band at $\lambda_{max} = 485$ nm or by energy transfer to the Pc core, leading to red emission at $\lambda_{max} = 680$ nm.

Experimental

Tetrahydrofuran, chloroform ($CHCl_3$), Zn $(O_2CCH_3)_2$, $CoCl_2$, DBU and 4-nitro-1,2-dicyanobenzene were purchased from Merck (Darmstadt, Germany) and Alfa Aesar (Karlsruhe, Germany), and used as received. All other reagents were obtained from Aldrich Chemical Co. (Milwaukee, WI, USA) and used without purification. The purity of the products was tested in each step by thin layer chromatography. Routine IR spectra were recorded on a Shimadzu Fourier Transform FT-IR-8300 Infrared Spectrophotometer using KBr pellets, and electronic spectra on a Shimadzu UV-1601 UV–vis Spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 spectrometer instrument using tetramethylsilane as an internal reference at Sakarya University. Elemental analysis was performed by the Instrumental Analysis Laboratory of TUBITAK Ankara Test and Analysis Laboratory. Mass spectra were performed on a Bruker Autoflex III mass spectrometer. Fluorescence excitation and emission spectra were recorded on a Jasco FP-750 spectrofluorimeter. Emission and excitation spectra at 5 nm bandpass in both excitation and detection paths were measured in the DMSO solution containing 10 μM concentration of phthalocyanine derivatives.

8-Hydroxy-3-[p-(3′,4′-dicyanophenoxy)-phenyl]-coumarin (1)

A mixture of 2,3-dihydroxybenzaldehyde (0.99 g, 7.19 mmol), *p*-(3,4-dicyanophenoxy)-phenylacetic acid (2.00 g, 7.19 mmol), anhydrous acetic anhydride (20 ml) and sodium acetate (2.95 g, 36 mmol) was heated and stirred at reflux temperature in a sealed glass tube for 6 h under N_2. After cooling to room temperature, water was added and the mixture stirred for one night. The resulting solid 8-acetoxy-3-[*p*-(3′,4′-dicyanophenoxy)-phenyl]-coumarin was filtered, washed with water and dried. The crude product 8-acetoxy-3-[*p*-(3′,4′-dicyanophenoxy)-phenyl]coumarin was suspended in methanol. A 10% HCl was added to make pH 3.0 and the mixture was heated

and stirred at 60°C for 4 h under N_2. At the end of the reaction, the resulting powder 8-hydroxy-3-[*p*-(3′,4′-dicyanophenoxy)-phenyl]coumarin was filtered, washed with water and dried. It was purified on silica gel column chromatography with $CHCl_3$ as an eluent.

Yield: 1.45 g (53%); mp 265–267°C. IR ν (cm^{-1}): 3387 (OH), 3074–3044 (Ar-H), 2916–2851 (alkyl-CH), 2237 (—C≡N), 1709 (C═O lactone), 1616 (C═C), 1589–1485 (Ar-C═C), 1258 (Ar-O-Ar). ^{1}H NMR (DMSO-d_6) δ: 9.82 (Ar-OH, 1H, deuterium exchangeable), 8.24 (Bz_1; dd, 1H, *meta* to CN; H2), 8.10 (d, isomer, 1H, *ortho* to CN; H3), 7.88 (d, 1H, *ortho* to CN, phenyl H2), 7.77 (s, 1H, *meta* to lactone, Cou-H), 7.41 (Bz_2; dd, 4H, Ar-H), 7.23 (d, 1H, *meta* to Cou-OH), 7.01 (dd, 1H, *ortho* to Cou-OH), 6.90 (d, 1H, *ortho* to Cou-OH). ^{13}C NMR (300 MHz, δ, DMSO-d_6): 162.3 (Ar-C═O), 161.4 (Ar-H, *ortho* to Ar-OH), 145.6, 142.0 (Cou), 140.8 (Bz_1), 137.9 (Bz_2), 135.5, 134.3, 133.2, 130.7, 127.3 (Bz), 127.2, 125.4 (Cou), 123.5, 123.1, 116.6 (Bz_1), 115.5, 115.0, 114.3, 40.4 (DMSO) ppm. Anal. calcd for $C_{23}H_{12}N_2O_4$ (380 g/mol): C, 72.63; H, 3.16; N, 7.37. Found: C, 72.50; H, 3.35; N, 7.34. UV–vis (DMF): λ_{max} (nm) (log ε): 324 (4.84), 382 (3.77 coumarin).

8-Hexyloxy-3-[p-(3′,4′-dicyanophenoxy)-phenyl]-coumarin (2)

8-Hydroxy-3-[*p*-(3′,4′-dicyanophenoxy)-phenyl]coumarin **1** (1.30 g, 3.42 mmol) and 1-bromohexane (0.57 g, 3.42 mmol) were dissolved in dry DMF (40 ml), and K_2CO_3 (0.47 g, 3.42 mmol) and tetrabutylammonium bromide (0.02 g, excess) as catalyst were added. After refluxing for 4 days under N_2, the reaction mixture was poured into ice-cold water and acidified with aqueous HCl solution. The precipitate formed was filtered, washed with water and the crude product dried. It was purified on silica gel column chromatography with $CHCl_3$ as an eluent.

Yield: 1.35 g (85.0%); mp 108–109°C. IR ν (cm^{-1}): 3067–3051 (Ar-H), 2939–2851 (alkyl-CH), 2230 (—C≡N), 1720 (C═O lactone), 1605 (C═C), 1593–1481 (Ar-C═C), 1277 (Ar-O-Ar), 1245–1169 (Ar-O—C). ^{1}H NMR (DMSO-d_6) δ: 8.25 (Bz_1; dd, 1H, *meta* to CN; H2), 8.14 (d, isomer, 1H, *ortho* to CN; H3), 7.88 (d, 1H, *ortho* to CN, phenyl H2), 7.82 (s, 1H, *meta* to lactone, Cou-H), 7.45 (Bz_2; dd, 4H, Ar-H), 7.32 (d, 1H, *meta* to Cou-OR), 7.26 (dd, 1H, *ortho* to Cou-OR), 7.20 (d, 1H, *ortho* to Cou-OR), 3.96 (t, OCH_2—, 2H), 1.76–1.68 (m, —OCH_2CH_2—), 1.44–1.20 (m, $CH_2CH_2CH_2CH_3$), 0.92 (t, CH_3). ^{13}C NMR (300 MHz, δ, DMSO-d_6): 162.6 (Ar-C═O), 160.1 (Ar-H, *ortho* to Ar-OH), 144.4, 140.2 (Cou), 140.0 (Bz_1), 135.9 (Bz_2), 134.5, 133.5, 130.1, 129.7 (Bz), 127.3, 125.2 (Cou), 124.6, 123.5, 116.7 (Bz_1), 115.8, 115.4, 113.8, 67.6 (CH_2O—), 40.41 (DMSO), 28.8 ($CH_2CH_2CH_3$), 28.2 (OCH_2CH_2), 25.4 ($OCH_2CH_2CH_2$), 22.8 (CH_3CH_2), 14.8 (CH_3) ppm. Anal. calcd for $C_{29}H_{24}N_2O_4$ (464 g/mol): C, 75.00; H, 5.17; N, 6.03. Found: C, 74.56; H, 5.01; N, 5.77; UV–vis ($CHCl_3$): λ_{max} (nm) (log ε): 326 (3.76).

2,9,16,23-Tetrakis[8-hexyloxy-3-(4-oxyphenyl)-coumarin]metal-free phthalocyanine (3)

Compound **2** (0.10 g, 0.22 mmol) and anhydrous 2-(dimethylamino)-ethanol (1.0 ml) were refluxed with stirring for 48 h in a sealed glass tube under N_2. After cooling to room temperature, methanol (2 ml) was added in order to precipitate the product. The green product was filtered and washed with water, MeOH, CH_3CN, EtOH, acetone, ethyl acetate and diethyl ether, and dried.

Yield: 0.033 g (33%); mp > 300°C. IR ν (cm^{-1}): 3298 (N—H), 3051–3036 (Ar-H), 2924–2866 (alkyl-CH), 1709 (C═O lactone), 1601 (C═C), 1504–1469 (Ar-C═C), 1269–1234 (Ar-O-Ar), 1169–1095 (Ar-O—C). ^{1}H NMR (DMSO-d_6) δ: 8.42–7.50 (Bz_1 vs. Bz_2; br, 28H), 7.40–6.67 (br, 16H, Bz_1; Bz_3), 3.96 (t, OCH_2—, 8H), 1.78–1.72 (m, —OCH_2CH_2—, 8H), 1.44–1.22 (m, $CH_2CH_2CH_2CH_3$, 24H), 0.96 (t, CH_3, 12H), −3.47 (s, br, NH, inner). Anal. calcd for $C_{116}H_{98}N_8O_{16}$ (1858 g/mol): C, 74.92; H, 5.27; N, 6.03. Found: C, 74.32; H, 5.22; N, 5.68; UV–vis (DMSO): λ_{max} (nm) (log ε): 336 (5.26), 642 (4.76), 675 (4.88), 703 (4.77). MS MALDI-TOF, DHB as matrix *m/z*: 1858.6 $[M+H]^+$.

2,9,16,23-Tetrakis[(E)-hexyl-3-(2,3-bis(hexyloxy)phenyl-2-(4-oxyphenyl)acrylate) phthalocyanine]metal-free phthalocyanine (3a)

To a solution of 2,9,16,23-tetrakis[8-hexyloxy-3-(4-oxyphenyl)coumarin]-phthalocyanine (**3**) (0.025 g, 0.0135 mmol) in dry DMF (5 ml), hexanol (7 ml) and lithium metal (0.0012 g, 0.17 mmol) were added. The mixture was refluxed for 24 h, and then it was cooled to room temperature. 1-Bromohexane (0.3 ml) was added to the reaction mixture and it was heated at 50°C for 3 days under N_2. After cooling to room temperature, the mixture was treated with 2 M HCl under ice. The precipitate was collected by filtration, washed with H_2O, MeOH, EtOH, CH_3CN, acetone, ethyl acetate and diethyl ether, and dried.

Yield: 0.005 g (15%); mp > 300°C. IR ν (cm^{-1}): 3290 (N—H), 3067–3044 (Ar-H), 2932–2866 (alkyl-CH), 1720 (C═O ester), 1597 (C═C), 1504–1474 (Ar-C═C), 1269–1234 (Ar-O-Ar), 1165–1096 (Ar-O—C). ^{1}H NMR (DMSO-d_6) δ: 8.40–7.22 (Bz_1 vs. Bz_2; br, 28H), 7.50–6.78 (br, 12H, Bz_1; Bz_3), 6.63 (s, 4H, —C═CH—), 4.30–4.00 (t, $OCOCH_2$, 8H), 3.96–3.70 (t, OCH_2—, 16H), 1.80–1.60 (m, —OCH_2CH_2—, 24H), 1.43–1.24 (m, $CH_2CH_2CH_2CH_3$, 72H), 0.94 (t, CH_3, 36H), −3.48 (s, br, NH, inner, 2H) ppm. Anal. calcd for $C_{164}H_{202}N_8O_{20}$ (2602 g/mol): C, 75.63; H, 7.76; N, 4.30. Found: C, 74.77; H, 7.28; N, 4.18; UV–vis (DMSO): λ_{max} (nm) (log ε): 291

(4.78), 330 (4.79), 639 (sh, 4.21), 680 (4.33), 704 (4.15). MS (MALDI-TOF, DHB as matrix) *m/z*: 2603.43 $[M+H]^+$.

2,9,16,23-Tetrakis[8-hexyloxy-3-(4-oxyphenyl)-coumarin]phthalocyaninatozinc(II) (4)

A mixture of compound **2** (0.10 g, 0.215 mmol), DBU (0.07 cm^3, 0.04 mmol) and Zn $(AcO)_2$ (0.012 g, 0.055 mmol) in hexanol (1.0 cm^3) was heated and stirred at 170°C for 18 h under N_2. The resulting green mixture was cooled to room temperature and then methanol (3 ml) was added in order to precipitate the product. The product was filtered and washed with water, methanol, acetonitrile, ethanol, acetone, ethyl acetate and diethyl ether, and dried.

Yield: 0.076 g (73%); mp > 300°C. IR ν (cm^{-1}): 3067–3044 (Ar-H), 2924–2843 (alkyl-CH), 1720 (C═O lactone), 1601 (C═C), 1500–1358 (Ar-C═C), 1269–1234 (Ar-O-Ar), 1173–1096 (Ar-O—C). ^{1}H NMR (DMSO-d_6) δ: 8.33–7.24 (Bz_1 vs. Bz_2; br, 28H), 7.30–6.62 (br, 16H, Bz_1; Bz_3), 3.95 (t, OCH_2—, 8H), 1.74–1.68 (m, —OCH_2CH_2—, 8H), 1.45–1.25 (m, $CH_2CH_2CH_2CH_3$, 24H), 0.96 (t, CH_3, 12H). Anal. calcd for $C_{116}H_{96}N_8O_{16}Zn$ (1921 g/mol): C, 72.46; H, 4.99; N, 5.83. Found: C, 72.22; H, 5.29; N, 5.55; UV–vis (DMSO): λ_{max} (nm) (log ε): 337 (4.66), 621 (sh, 3.96), 683 (4.56). MS (MALDI-TOF; DHB as matrix) *m/z*: 1922.09 $[M+H]^+$, 1960.09 $[M+K]^+$.

*2,9,16,23-Tetrakis[(***E***)-hexyl-3-(2,3-bis(hexyloxy)phenyl-2-(4-oxyphenyl)acrylate)]-phthalocyaninatozinc(II) (4a)*

To a solution of 2,9,16,23-tetrakis[8-hexyloxy-3-(4-oxyphenyl)coumarin]phthalocyaninatozinc(II) (**4**) (0.030 g, 0.0135 mmol) in dry DMF (5 ml), hexanol (5 ml) and lithium metal (0.0012 g, 0.171 mmol) were added. The mixture was refluxed for 24 h, and then it was cooled to room temperature. 1-Bromohexane (0.3 ml) was added to the reaction mixture and it was heated at 50°C for 3 days under N_2. After cooling to room temperature, the mixture was treated with 2 M HCl under ice. The precipitate was collected by filtration, washed with water, methanol, acetonitrile, ethanol, acetone, ethyl acetate and diethyl ether, and dried.

Yield: 0.005 g (12%); mp > 300°C. IR ν (cm^{-1}): 3036–3059 (Ar-H), 2932–2858 (alkyl-CH), 1720 (C═O ester), 1601 (C═C), 1504–1466 (Ar-C═C), 1269–1234 (Ar-O-Ar), 1161–1096 (Ar-O—C). ^{1}H NMR (DMSO-d_6) δ: 8.36–7.69 (Bz_1 vs. Bz_2; br, 28H), 7.60–6.82 (br, 12H, Bz_1; Bz_3), 6.70 (s, 4H, —C═CH—), 4.30–4.02 (t, $OCOCH_2$, 8H), 3.92 (t, OCH_2—, 16H), 1.84–1.53 (m, superimposed, br, —OCH_2CH_2—, 24H), 1.44–1.20 (m, br, $CH_2CH_2CH_2CH_3$, 72H), 0.94 (t, CH_3, 36H) ppm. Anal. calcd for $C_{164}H_{200}N_8O_{20}Zn$ (2665 g/mol): C, 73.85; H, 7.51; N, 4.20. Found: C, 73.43; H, 7.41; N, 4.05; UV–vis (DMSO): λ_{max} (nm) (log ε): 349 (4.80), 621 (sh, 4.27), 660 (sh, 4.59), 682 (4.90). MS (MALDI-TOF, DHB as matrix) *m/z*: 2666.34 $[M+H]^+$.

2,9,16,23-Tetrakis[8-hexyloxy-3-(4-oxyphenyl)coumarin]-phthalocyaninatocobalt(II) (5)

A mixture of compound **2** (0.10 g, 0.215 mmol), DBU (0.07 ml, 0.04 mmol) and $CoCl_2$ (0.0134 g, 0.054 mmol) in hexanol (1.5 ml) was heated and stirred at 170°C for 24 h under N_2. The resulting green mixture was cooled to room temperature and then methanol (2 ml) was added in order to precipitate the product. The product was filtered and washed with water, methanol, acetonitrile, ethanol, acetone, ethyl acetate and diethyl ether, and dried.

Yield: 0.043 g (42%); mp > 300°C. IR ν (cm^{-1}): 3067–3036 (Ar-H), 2916–2866 (alkyl-CH), 1720 (C═O lactone), 1601 (C═C), 1504–1469 (Ar-C═C), 1323–1234 (Ar-O-Ar), 1169–1096 (Ar-O—C). Anal. calcd for $C_{116}H_{96}N_8O_{16}Co$ (1915 g/mol): C, 72.69; H, 5.01; N, 5.85. Found: C, 72.22; H, 5.14; N, 5.38; UV–vis (DMSO): λ_{max} (nm) (log ε): 335 (4.47), 606 (3,77), 669 (4.23). MS (MALDI-TOF, DHB as matrix) *m/z*: 1915.07 $[M]^+$.

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