Dyes and Pigments 92 (2012) 954–960

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

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

Synthesis and photophysical properties phthalocyanine–pyrene dyads[☆]

İbrahim Özçeşmeci[a], Ali Gelir[b], Ahmet Gül[a,*]

[a] Department of Chemistry, Technical University of Istanbul, Maslak 34469, Istanbul, Turkey
[b] Department of Physics, Technical University of Istanbul, Maslak 34469, Istanbul, Turkey

ARTICLE INFO

Article history:
Received 27 May 2011
Received in revised form
9 August 2011
Accepted 21 August 2011
Available online 8 September 2011

Keywords:
Phthalocyanine
Pyrene
Antenna effect
Energy transfer
Fluorescence
Synthesis

ABSTRACT

Metal-free, zinc (II) and nickel(II) phthalocyanines (**3**–**5**) with a 1-pyrenylmethoxy substituent on each benzo group were prepared from 4-(1-pyrenylmethoxy)phthalonitrile (**2**). The new compounds have been characterized by elemental analyses, IR, UV/vis, mass and ^{1}H NMR spectroscopy. The electronic spectra exhibit an intense π–π^* transition of pyrene unit identity together with characteristic Q and B bands of the phthalocyanine core. The energy transfer to phthalocyanine core and radiative decays of the pyrene emission and phthalocyanine core were examined. Energy transfer through methoxy bridges has been confirmed by ultraviolet irradiation of pyrene antenna leading to red light emission in **3** and **4**.

1. Introduction

Phthalocyanines (Pcs) with planar or nearly planar structures have an extended network of π-electrons. Because of their special electronic and optical properties and good processibility, substituted phthalocyanines have established themselves in many applied fields such as active materials for organic electronics [1], gas sensors [2], photovoltaic cells [3], electrochromic devices [4] nonlinear optics [5], photodynamic reagents for cancer therapy [6] and electrocatalytic reagents [7]. Their high thermal and chemical stability, well defined optical absorption, semiconducting and photoconducting properties, ability to coordinate a large variety of central atoms and the ease of their preparation add to their broad applicability [8]. It is well known that the electrochemical and spectroscopic properties of phthalocyanine derivatives can be tuned by varying the central metal atom, changing the size of the π-conjugation, or alternating the type, number, and positions of the substituents on the macrocycle ligands [9–12].

Despite the considerable use of individual Pc as chromophores, multichromophoric systems where Pc are covalently linked to other electro or photoactive units such as organic moieties that have fluorescent nature are of great interest. These systems can also serve as models for the study of energy and electron-transfer processes in artificial photosynthetic systems. Organic materials that absorb at various wavelengths of visible light and fluorescence with high efficiency are good candidates for organic photoelectronic devices such as photosensitizing solar cells [13] and organic light emitting diodes [14].

Phthalocyanines exhibit excellent chemical and photochemical properties, but poor fluorescent properties [15]. The interaction of a fluorescence probe with a phthalocyanine core may change the fluorescent characteristics of the aromatic structure. For example, it may be the binding process where fluorescent probe bind chemically or physically to the phthalocyanine molecules, thereby causing a shift in their fluorescence spectra or a change in the fluorescence intensity [16,17]. On the other hand, pyrene (Py) and its derivatives, having a high quantum yield and lifetime (0.65 and 410 ns, respectively, in ethanol at 293 K), have been used as valuable molecular probes for fluorescence spectroscopy. Its fluorescence emission spectrum is very sensitive to the solvent polarity, so Py has been used as a probe to determine solvent environments. This is due to its excited state having a different, non-planar structure than the ground state [18].

As an energy transfer process, "Antenna effect", where the fluorescent moiety has been attached directly to the unsaturated macrocycle or fused to it, has been frequently used, but the combination of these two functionalities through saturated groups as in the case of Pc derivatives is rather rare [19,20].

[☆] Dedicated to Professor Michael Hanack on the occasion of his 80th birthday.

[*] Corresponding authors. Tel.: +90 212 285 68 27; fax: +90 212 285 63 86.
E-mail address: ahmetg@itu.edu.tr (A. Gül).

0143-7208/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2011.08.013

The aim of the present work was to synthesize a series of metallo and metal-free phthalocyanines functionalized with peripheral 1-pyrenylmethoxy substituents and to explore the energy transfer between the Py units and the macrocyclic core. Py has been chosen as a substituent for this study as it is a thermally very stable unit which can act as an antenna to harvest and transfer energy efficiently to longer wavelength emitters in blends or composite structures [21]. Here we report the consequence of 1-pyrenylmethoxy substituent on the intensity of the fluorescence emission spectra of metal-free and zinc Pcs as well as its effect on energy transfer to phthalocyanine core.

2. Experimental

2.1. Equipments and materials

IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrometer, electronic spectra on a Scinco Neosys-2000 double-beam ultraviolet–visible (UV–vis) spectrophotometer using 1 cm path length cuvettes at room temperature. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Centre. ^{1}H NMR spectra were recorded on a Bruker 250 MHz spectrometer using TMS as internal reference. Mass spectra were performed on Ultima Fourier Transform and Varian 711 mass spectrometer. Fluorescence excitation and emission spectra were recorded by using Varian Cary Eclipse Fluorescence Spectrophotometer. All reagents and solvents were of reagent grade quality obtained from commercial suppliers. All solvents were dried and purified according to [22]. The homogeneity of the products was tested in each step by TLC (SiO_2). 4-nitrophthalonitrile was prepared according to a reported procedure [23]. 1-pyrenylmethanol (**1**) was prepared according to a reported procedure [24].

2.2. Synthesis

*2.2.1. 4-(1-pyrenylmethoxy)phthalonitrile (**2**)*

4-Nitrophthalonitrile (0.173 g, 1.0 mmol) and 1-pyrenylmethanol (**1**) (0.232 g, 1.0 mmol) were added successively with stirring to dry DMSO (10 ml). After they were dissolved, anhydrous K_2CO_3 (0.5 g, 3.5 mmol) was added portion wise over 2 h and the mixture was stirred vigorously at room temperature for further 24 h. Then, the reaction mass was poured into cold water (50 ml) and the precipitate formed was filtered off, washed successively first with water, then with cold hexane, and then with cold diethyl ether and dried *in vacuo*. Yield: 235 mg (65.6%); m.p. 194 °C. IR, υ (cm^{-1}): 3081–3043 (Ar–H), 2918 (alkyl-CH), 2229 (C≡N), 1251 (C–O–C); ^{1}H NMR (d-DMSO):8.34–7.67 (br, 12H, Ar–H), 5.90 (br s, 8H, OCH_2) UV–Vis λ_{max} (nm) (log ε) in THF: 345 (4.60), 329 (4.44), 275 (4.72), 266 (4.53); Anal. calcd. for $C_{25}H_{14}N_2O$; C, 83.78; H, 3.94; N, 7.82; found: C, 83.92; H, 3.86; N, 7.65%; MS: *m*/*z* 358.22 [M]$^+$.

*2.2.2. Tetra(1-pyrenylmethoxy)phthalocyanine (**3**)*

A mixture 0.5 mmol (0.179 g) of 4-(1-pyrenylmethoxy)phthalonitrile (**2**) and 1.0 mmol of lithium metal in 1.5 ml of pentanol was heated and stirred at 142 °C for 2 h under N_2 in a sealed tube. The resulting green suspension was cooled to ambient temperature. After that, reaction mass was dissolved in 1 ml DMF and poured into 100 ml ice-water mixture with the addition 4 ml conc HCl. In this mixture Li_2Pc formed was converted into H_2Pc. The precipitate formed was filtered off and the crude product was subsequently treated with boiling acetone, ethanol, hexane and then dried *in vacuo*. Purification of the product was accomplished by column chromatography on silica gel first with ethanol then with THF as eluent. Yield: 46 mg (25.7%); m.p. > 200 °C. IR υ (cm^{-1}): 3264 (–NH), 3042 (Ar–H), 2948 (alkyl-CH), 1215 (C–O–C); ^{1}H NMR (d-DMSO): 8.24–7.33 (br, 48H, Ar–H), 5.90 (br s, 8H, OCH_2), –4.05 (bs, 2H, –NH); UV–Vis λ_{max} (nm) (log ε) in THF: 726 (5.14), 694 (5.13), 341 (5.27), 326 (5.18), 282 (5.13), 269 (4.95); Anal. calcd. for $C_{100}H_{58}N_8O_4$; C, 83.66; H, 4.07; N, 7.81; found: C, 83.82; H, 4.16; N, 7.68%. MS: *m*/*z* 1435.24 [M]$^+$.

*2.2.3. Tetra(1-pyrenylmethoxy)phthalocyaninatozinc (II) (**4**)*

A mixture 0.5 mmol (0.179 g) of 4-(1-pyrenylmethoxy)phthalonitrile (**2**) and 0.125 mmol (0.023 g) of anhydrous $Zn(OAc)_2$ with 2 drop DBU in 1.5 ml hexanol was heated and stirred at 160 °C for 6 h under N_2 in a sealed tube. After cooling to room temperature, the suspension was dissolved in 1 ml DMF and poured into 150 ml ice-water mixture. After that, precipitated green–blue solid was filtered off. The precipitate was first refluxed in chloroform and then washed subsequently with ethanol and acetone and then dried *in vacuo*. Purification of the product was accomplished by column chromatography on silica gel first with ethanol then with THF as the eluent. Yield: 52 mg (27.8%); m.p. > 200 °C. IR υ (cm^{-1}): 3037 (Ar–H), 2952 (alkyl –CH), 1215 (C–O–C); ^{1}H NMR (d-DMSO): 8.24–7.71 (br, 48H, Ar–H), 5.95 (br s, 8H, OCH_2); UV–Vis λ_{max} (nm) (log ε) in THF: 679 (5.21), 346 (5.39), 331 (5.27), 282 (5.16), 268 (4.97); Anal. calcd. for $C_{100}H_{56}N_8O_4Zn$; C, 80.13; H, 3.77; N, 7.48; found: C, 80.22; H, 3.68; N, 7.54%. MS: *m*/*z* 1497.98 [M]$^+$.

*2.2.4. Tetra(1-pyrenylmethoxy)phthalocyaninatonickel (II) (**5**)*

A mixture 0.5 mmol (0.179 g) of 4-(1-pyrenylmethoxy)phthalonitrile (**2**) and 0.125 mmol (0.016 g) of anhydrous $NiCl_2$ with 2 drop DBU in 1.5 ml hexanol was heated and stirred at 160 °C for 6 h under N_2 in a sealed tube. After cooling to room temperature, the suspension was dissolved in 1 ml DMF and poured into 150 ml ice-water mixture. After that, precipitated green–blue solid was filtered off. The precipitate was first refluxed in chloroform and then washed subsequently with ethanol and acetone and then dried *in vacuo*. Purification of the product was accomplished by column chromatography on silica gel first with ethanol then with THF as the eluent. Yield: 55 mg (29.6%); m.p. > 200 °C. IR υ (cm^{-1}): 3032 (Ar–H), 2948 (alkyl –CH), 1219 (C–O–C); ^{1}H NMR (d-DMSO): 8.09–7.63 (br, 48H, Ar–H), 5.85 (br s, 8H, OCH_2); UV–Vis λ_{max} (nm) (log ε) in THF: 684 (5.15), 347 (5.32), 332 (5.14), 283 (5.13), 269 (4.94); Anal. calcd. for $C_{100}H_{56}N_8NiO_4$; C, 80.13; H, 3.78; N, 7.51; found: C, 80.31; H, 3.62; N, 7.64%. MS: *m*/*z* 1493.28 [M+1]$^+$.

2.3. Fluorescence studies

Comparative method was used to determine the quantum yields of the compounds (**3** and **4**) as described in [18]. In this method, the quantum yield of a compound is determined by using a standard which has similar fluorescence properties as the compound has. Also at least 5 samples of the standard and the compound with different concentrations must be prepared to be able to carry out the relation between the absorbance and the fluorescence emission. All measurements of the standard and the compound must be performed at the same environmental conditions with the same instrumental settings.

The quantum yield of a compound according to comparative method is given by Eq. (1):

$$\Phi_{F,C} = \frac{\text{slope}(A_c - I_c)}{\text{slope}(A_{\text{std}} - I_{\text{std}})} \frac{n_c^2}{n_{\text{std}}^2} \Phi_{F,\text{std}} \tag{1}$$

where $\Phi_{F,C}$ and $\Phi_{F,\text{std}}$ are the quantum yields of the compound and the standard, n_c and n_{std} are the refractive indices of the solution of the compound and the standard, slope ($A_c - I_c$) and slope ($A_{\text{std}} - I_{\text{std}}$) are the slopes of the graphs plotted between the integrals of the fluorescence spectra and the absorbances for the compound and the standard at different concentrations, respectively.

In this paper Rhodamine-101 (**S**) was used as standard which has excitation and emission peaks at 369 nm and 586 nm, respectively, and has quantum yield, $\Phi_F = 1$ in ethanol [18]. These wavelengths are in the region of the wavelengths of the compounds (**3**) ($\lambda_{exc} = 347$ nm, $\lambda_{em} = 728$ nm) and (**4**) ($\lambda_{exc} = 347$ nm, $\lambda_{em} = 691$ nm) studied in this work. 5 different concentrations of (**3**), (**4**) and (**S**) ranging between 10^{-6} M and 10^{-7} M were used and all measurements were performed at 20 °C. The refractive indices of (**3**), (**4**) and (**S**) are 1.464, 1.457 and 1.364, respectively.

Excitation energy transfer or resonance energy transfer (RET) occurred from Py units of **3** and **4** to H_2Pc core of **3** and ZnPc core of **4**. This energy transfer from donor (Py units) to acceptor (H_2Pc and ZnPc core of **3** and **4**) studies was determined according to the Förster theory by accumulating both the donor and acceptor [25]. Transfer efficiency, ε_T, from donor to acceptor is given by

$$\varepsilon_T = \frac{\Delta I_A}{I_D \Phi_A} \tag{2}$$

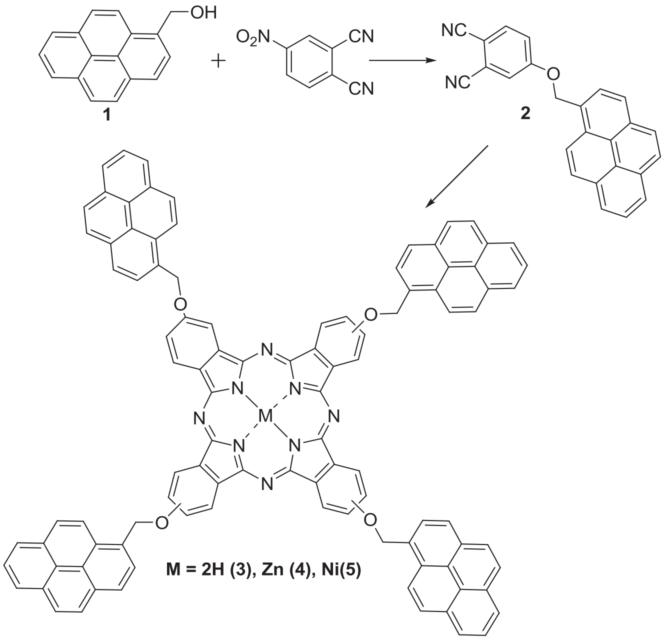
where ΔI_A is the increase in the integral of the fluorescence emission spectra of the acceptor upon binding of donor to acceptor, I_D is the integral of fluorescence spectrum of the donor before binding to the acceptor and Φ_A is the quantum yield of the acceptor in the absence the acceptor.

3. Results and discussions

The starting point for novel phthalocyanine structures with four Py units bound to the periphery is through base-catalysed aromatic nitro displacement of 4-nitrophthalonitrile with **1** in DMSO; K_2CO_3 was used as the base for this nucleophilic aromatic displacement [26,27]. This reaction has been used in the preparation of a variety of ether or thioether-substituted phthalonitriles [28–30]. The solid product **2** was obtained in a yield of 65.6%.

Conversion of **2** into phthalocyanine was accomplished through the usual cyclotetramerization reaction in the presence of a reductant and/or metal salt, i.e., lithium was used to obtain the metal-free derivative **3**, while the metal salt [$Zn(OAc)_2$, $NiCl_2$] and a suitable solvent, such as hexanol were required for the metal phthalocyanines **4** and **5** (Scheme 1). This procedure yields a mixture of four geometric isomers with a 1-pyrenylmethoxy group at the 2- or 3- position of each benzo-ring in the phthalocyanine molecule. These phthalocyanines are soluble to a certain extent in donor solvents such as DMSO, DMF and THF. Characterization of the products involved combination of elemental analysis and spectroscopic data (UV–Vis, FT-IR, ^{1}H NMR, and Mass spectroscopy). Spectral investigations for all these products were consistent with the assigned structures.

In the IR spectrum of dinitrile compound **2**, aromatic C–H and C≡N stretching vibrations appeared at 3081–3043 cm^{-1} and 2229 cm^{-1}, respectively. This sharp C≡N peak disappeared in the IR spectra of the phthalocyanines. In addition, the characteristic vibrations of the aromatic C–H and aromatic C–O–C were observed at 1598 and 1251 cm^{-1}, respectively. ^{1}H NMR spectrum of **2** exhibited the aliphatic CH_2 protons as a singlet at $\delta = 6.02$ ppm and the aromatic protons at around $\delta = 7.67$–8.34 ppm. In the mass spectra of **2** the presence of the characteristic molecular ion peaks at $m/z = 358.22$ $[M]^+$ confirmed the proposed structure.



Scheme 1. Synthesis of 1-pyrenylmethoxy substituted phthalocyanines.

The ^{1}H NMR spectra of compounds **3**–**5** 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 which are expected to show chemical shifts that differ slightly from each other. The inner NH protons of **3** were also identified in the ^{1}H NMR spectra with a broad chemical shift, $\delta = -4.05$ ppm as a consequence of the 18 π-electron system of the planar molecule. ^{1}H NMR spectra of **3**–**5** exhibited the aliphatic CH_2 protons as a singlet peaks at around $\delta = 5.85$–5.95 ppm and the aromatic protons as a broad peaks at around $\delta = 7.33$–8.24 ppm. In the mass spectra of **3**–**5** the presence of the characteristic molecular ion peaks at $m/z = 1435.24$ $[M]^+$ for **3**, m/z 1497.98 $[M]^+$ for **4** and m/z 1493.28 $[M+1]^+$ for **5** confirmed the proposed structures.

Electronic absorption spectra of compounds **3**–**5** combine the spectral features of both the phthalocyanines and the Py (Fig. 1). The absorption spectrum of Py units is dominated by two intense bands of similar intensity around 345 nm and 275 nm as observed

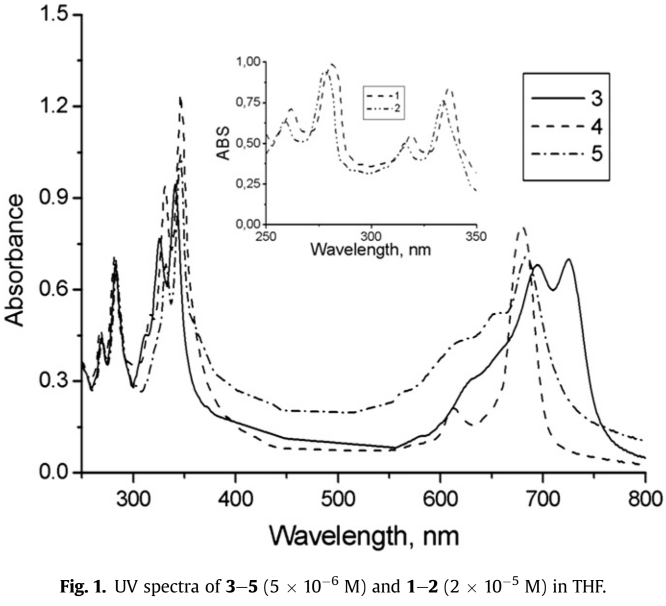


Fig. 1. UV spectra of **3**–**5** (5×10^{-6} M) and **1**–**2** (2×10^{-5} M) in THF.

in the spectra of compounds **1** and **2**; after conversion into phthalocyanine, on the other hand, electron absorption spectra of compounds **3**–**5** have intense absorbtion around 345 nm due to the overlap of phthalocyanine Soret band and the absorption of Py units. Visible part of the spectrum around 600–700 nm (Q-band) attributed to the π–π^* transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc^{-2} ring. Metallophthalocyanine **4** and **5** showed intense single Q-band absorptions at 679 nm for **4** and 684 nm for **5**, while metal-free phthalocyanine **3** showed the expected Q-band splitting around 694 nm and 726 nm as a result of D_{2h} symmetry. An apparent difference between the Q-band absorption spectra of **4** and **5** is rather broad absorbances in the higher energy side of the spectrum in nickel compound which might be due to higher planarity and lower tendency to axial coordination of the solvents [31,32].

Increasing the concentration leads to aggregation, which is easily observed by the values of the Q-bands, which shift to higher energies [33] by a parallel decrease in the molar absorption coefficient. The aggregation behaviour of the phthalocyanine complexes (**3**–**5**) were also investigated at different concentrations in THF (Fig. 2). In THF, as the concentration was increased, the intensity of absorption of the Q-band also increased and no new bands (normally blue shifted) due to the aggregated species were observed for the all phthalocyanine complexes (**3**–**5**). In addition, apparent molar extinction coefficient of samples **3**–**5** in this concentration range (2.0×10^{-5}–6.125×10^{-7} M) remained almost constant as expected from Beer–Lambert law as seen in Fig. 2. It indicates the presence of mainly a pure monomeric form [34]. It is generally accepted that addition of a surfactant, e.g. Triton X, leads decomposition of aggregates. In order to verify this phenomena, electronic spectra of the Pcs **3**–**5** were taken also after addition of Triton X to the solutions (Fig. 3). The results indicate no appreciable aggregation which can be decomposed by the addition of Triton X. Changes in the absorbance values are only those which correspond to lowering of the concentrations. By evaluating these observations, it can clearly be concluded that the phthalocyanine derivatives (**3**–**5**) did not show aggregation behaviour in THF at the concentration range studied.

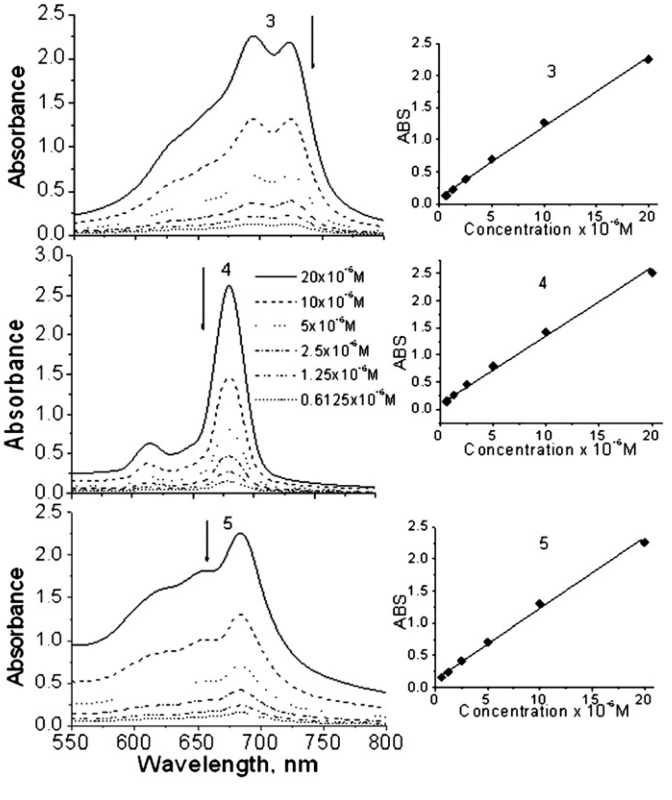


Fig. 2. Absorption spectra at different concentrations and Lambert–Beer law plots of **3**–**5** in THF.

Fluorescence emission spectra of **1**, **S**, **3** and **4** were represented in Fig. 4. Since the fluorescence quantum yield (Φ_F) of **5** is predictably low (<0.01) due to the open-shell nature of the

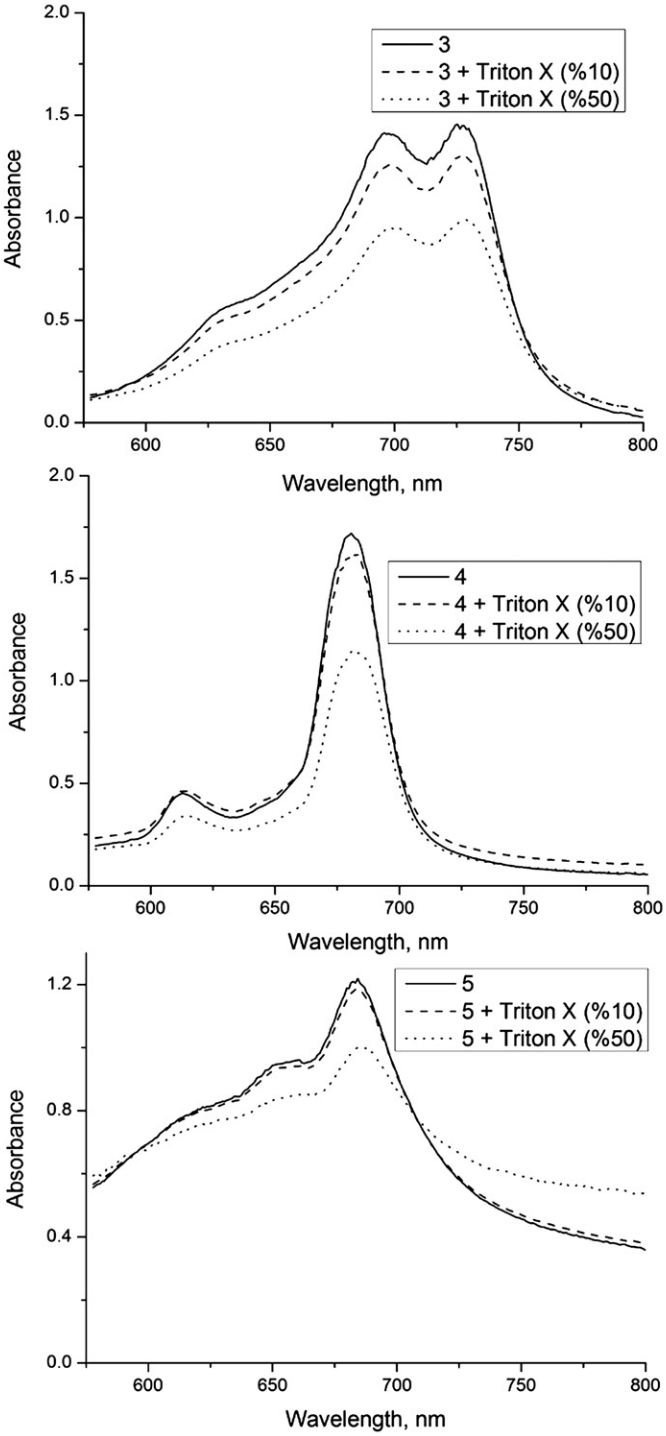


Fig. 3. Absorption spectral changes for **3**–**5** upon the addition of Triton X.

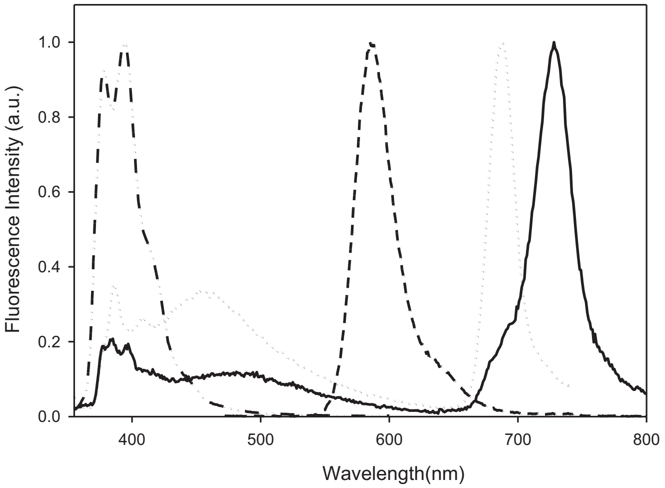


Fig. 4. Fluorescence emission spectra of samples **3** (———), **4** (·········), **1** (·· - ·· - ·· -) in THF and **S** (- - - -) in ethanol. The concentration of each sample is 2 × 10^{-7} M. The excitation wavelengths are around 345 nm for samples **3**, **4** and **1** and 369 nm for **S**.

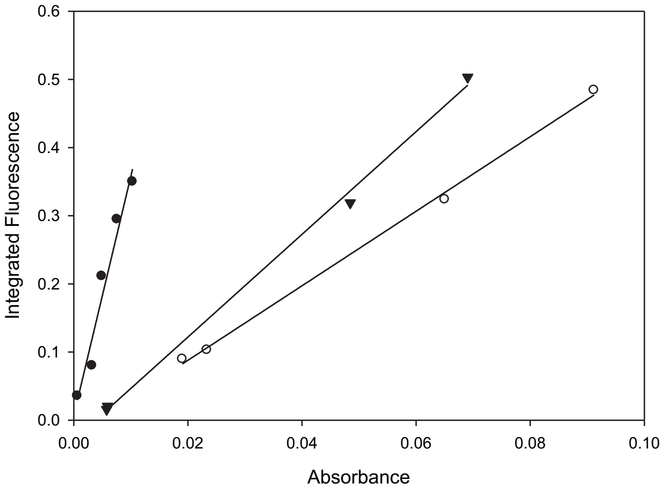


Fig. 5. Integrals of fluorescence spectra versus absorbances at different concentrations for the samples **S** (●), **3** (○) and **4** (▼).

complexes [35], it was not included in this figure. As seen from this figure that **3** and **4** have characteristic emission peaks of both Pcs (728 nm and 688 nm) and Py (394 nm and 378 nm). By comparing the emission spectra of **3** and **4**, it can be concluded that the binding of Zn into the cavity of Pc caused a blue shift from 728 nm to 688 nm in the emission spectrum [36]. Another important point in this figure is the excimer emission [18] at around 465 nm appeared in the fluorescence spectra of **3** and **4** which is not observable in the fluorescence spectrum of **1**. This excimer emission shows that in both phthalocyanine complexes (**3** and **4**) the Py units around Pc core come close enough to each other so as to make an excimer energy level. One of the reasons to observe such an excimer emission may be the aggregation of phthalocyanine complexes (**3** or **4**), but it has been clearly shown and discussed in detail in the previous paragraphs that the phthalocyanine complexes (**3** or **4**) do not aggregate in THF (Fig. 2). By eliminating the aggregation probability, it may be concluded that the excimer energy level is the intrinsic property of **3** and **4** meaning that the Py units around Pc core are close enough to each other to form excimer energy level. This excimer energy level may also be an indicator of the success of the synthesis of complexes **3** and **4**.

The integrals of the fluorescence spectra of **S**, **3** and **4** with respect to absorbances for different concentrations are given in Fig. 5. By using the slopes of the plots in this figure and Eq. (1), the quantum yields of **3** and **4** were calculated as 0.18 and 0.25, respectively. It was recently shown by Bartelmess et al. [36] that binding a Py unit to ZnPc as substituent does not change the quantum yield of ZnPc. In this reference only one Py unit was bonded to ZnPc as substituent and the quantum yield of ZnPc with and without Py was determined as 0.27. In our study four Py units were bonded to ZnPc and the quantum yield was calculated as 0.25. It can be concluded from this comparison that substituting ZnPc with Py units does not change the quantum yield considerably. However, the situation for H_2Pc is different than ZnPc. It was shown in [36] and in this paper that upon binding Py units to H_2Pc as substituents, the quantum yield decreases depending on the number of the substituents. In [34], after binding one Py unit, the quantum yield decreased to 0.28 from 0.34 and here in this paper it decreased to 0.18 after binding four Py units as substituents. It can be clearly concluded that substituting H_2Pc with Py units changes the quantum yield considerably.

In Fig. 6 the excitation spectra of **3**, **4** and the emission spectrum of **1** were represented together. A considerable overlap between the emission spectrum of **1** and the excitation spectra of **3** and **4** is observed in this figure. This overlap is a clear evidence of the energy transfer from Py units to the Pc core of **3** and **4** after covalently binding of **1** as substituents to Pc [18,37].

Fig. 7 shows the fluorescence spectra of 2 × 10^{-7} M **3** and a mixture of 8 × 10^{-7} M **1** and 2 × 10^{-7} M H_2Pc (tetra(acetoxyethylthio) phthalocyanine) [38]. The latter has been preferred as a similar Pc derivative without pyrenyl substituents. It is clearly seen in this figure that the fluorescence emission intensity of the free **1** is bigger than that of the covalently bound pyrenyl groups in **3**. Since the distance between **1** and H_2Pc molecules in the mixture solution is sufficiently long, **1** cannot transfer its excitation energy to H_2Pc. However, after covalently binding of **1** to H_2Pc to produce **3** by the mechanism described in Scheme 1, the fluorescence emission of bound **1** (Py units of **3**) decreased considerably and a red-shift from 717 nm to 728 nm occurred in the fluorescence emission of H_2Pc core of **3**. This decrease in the fluorescence emission intensity of Py units of **3** can be considered as an indication of the excitation energy transfer from Py units in **3** to the Pc core of **3** as suggested before due to the overlap between the emission

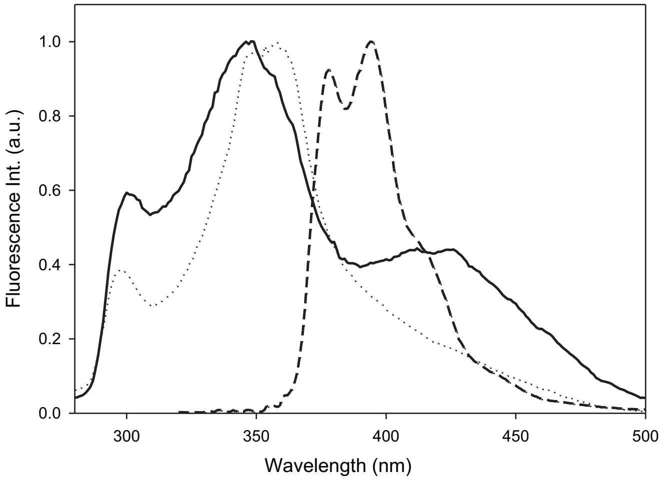


Fig. 6. Fluorescence excitation spectra of samples **3** (———), **4** (·········), and the fluorescence emission spectrum of **1** (- - - -) in THF. The concentration of each sample is 2 × 10^{-7} M. The excitation wavelength for **1** is 345 nm.

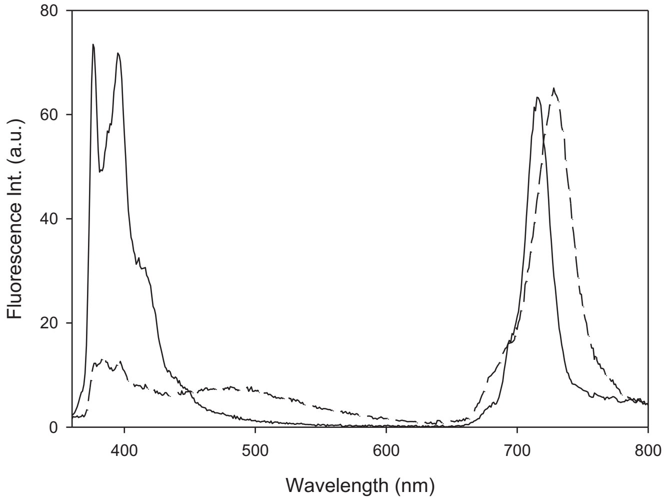


Fig. 7. Fluorescence emission spectra of 2 × 10^{-7} M sample **3** (- - - -) and mixture of 8 × 10^{-7} M **1** and 2 × 10^{-7} M H_2Pc (Tetra(acetoxyethylthio) phthalocyanine) in THF. The excitation wavelength is 345 nm for each sample.

spectrum of **1** and the excitation spectrum of **3** in Fig. 6. In addition to this decrease, an increase in the fluorescence emission of H_2Pc core of **3** is expected. But this was not observed in Fig. 7. This may be due to the lower quantum yield of **3**, $\Phi_F = 0.18$, in comparison with the quantum yield of unconjugated H_2Pc, $\Phi_F = 0.34$ [36].

The fluorescence spectra of 2 × 10^{-7} M **4** and the mixture of 8 × 10^{-7} M **1** and 2 × 10^{-7} M ZnPc (tetra(acetoxyethylthio) zinc(II) phthalocyanine without Py units) [38] are represented in Fig. 8. The results obtained from the fluorescence spectrum of **4** are very similar to the results obtained for **3** (Fig. 7). As observed in **3**, after covalently binding of **1** to ZnPc, the fluorescence emission intensity of Py units of **4** decreased considerably. As mentioned in the above paragraph that this decrease in the fluorescence emission of Py units of **4** indicates that the energy of the excited Py units in **4** is transferred to the ZnPc core of **4**. In addition to this decrease, an increase in the fluorescence emission of ZnPc core of **4** was also observed.

By using the data in Figs. 7 and 8 and Eq. (2), the energy transfer efficiency from Py units to H_2Pc core of **3** and ZnPc core of **4** were calculated as 0.64 and 0.66, respectively. Such high energy transfer efficiency values can be explained by the stable absorption energy levels of both the donor and the acceptors. As seen in Fig. 1 that the absorption spectra of the donor and the acceptors did not change considerably before and after conjugation.

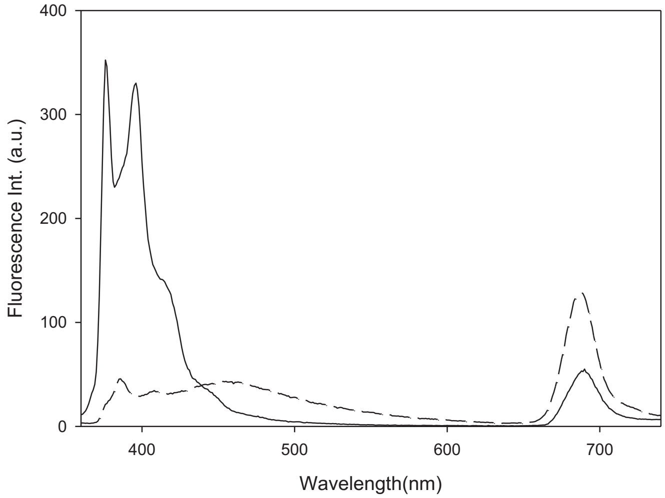


Fig. 8. Fluorescence emission spectra of 2 × 10^{-7} M sample **4** (- - - -) and the mixture of 8 × 10^{-7} M **1** and 2 × 10^{-7} M ZnPc (Tetra(acetoxyethylthio) zinc(II)phthalocyanine) in THF. The excitation wavelength is 345 nm for each sample.

4. Conclusion

In summary, we have synthesized and characterized new phthalocyanines bearing four 1-pyrenylmethoxy pendant arms peripherally. These phthalocyanines emit essentially red light after selective ultraviolet or visible irradiation. In the case of ultraviolet irradiation, these systems comprising central phthalocyanines linked to peripheral photon-harvesting pyrene moieties have been shown to act as efficient antennas. Since the absorption energy levels were not affected upon binding, efficient energy transfers were calculated. Also it was concluded that binding of Py units to ZnPc did not change the quantum yield of ZnPc while it changed the quantum efficiency of H_2Pc considerably.

Acknowledgement

This work was supported by the Research Fund of the Technical University of Istanbul.

References

[1] Schuster C, Kraus M, Opitz A, Brütting W, Eckern U. Transport properties of copper phthalocyanine based organic electronic devices. Eur Phys J Spec Top 2010;180:117–34.
[2] Sadaokap Y, Göpel TA, Jones W. Fast NO_2 detection at room temperature with optimized lead phthalocyanine thin-film structures. Sens Actuators B 1990;1: 148–53.
[3] Waltera MG, Rudineb AB, Wamser CC. Porphyrins and phthalocyanines in solar photovoltaic cells. J Porphyrins Phthalocyanines 2010;14:759–92.
[4] Lin CL, Lee CC, Ho KC. Spectroelectrochemical studies of manganese phthalocyanine thin films for applications in electrochromic devices. J Electroanalytical Chem 2002;524–525:81–9.
[5] Hanack M, Dini D, Vagin M, Barthel S. Conjugated macrocycles as active materials in nonlinear optical processes: optical limiting effect with phthalocyanines and related compounds. Chem Rec 2002;2:129–48.
[6] Ali H, Lier JE. Metal complexes as photo- and radiosensitizers. Chem Rev 1999; 99:2379–450.
[7] Lever ABP, Hempstead MR, Leznoff CC, Liu W, Melnik M, Nevin WA, et al. Recent studies in phthalocyanine chemistry. Pure Appl Chem 1986;58: 1467–76.
[8] Dini D, Hanack M. In: Kadish KM, Smith KM, Guilard R, editors. The porphyrin handbook, vol. 17. Amsterdam: Elsevier Science; 2003. p. 1–36.
[9] Özçeşmeci M, Özçeşmeci İ, Hamuryudan E. Synthesis and characterization of new polyfluorinated dendrimeric phthalocyanines. Polyhedron 2010;29(13): 2710–5.
[10] Özçeşmeci İ, Güner S, Okur Aİ, Gül A. Tetranuclear supramolecular structures containing phthalocyanine cores. J Porphyrins Phthalocyanines 2007;11: 531–6.
[11] Bayır ZA. Synthesis and characterization of novel soluble octa-cationic phthalocyanines. Dyes Pigm 2005;65:235–42.
[12] Selçukoğlu M, Hamuryudan E. Novel phthalocyanines with pentafluorobenzyloxy-substituents. Dyes Pigm 2007;74:17–20.
[13] Barker CA, Findlay KS, Bettington S, Batsanov AS, Perepichka IF, Bryce MR, et al. Synthesis of new axially-disubstituted silicon-phthalocyanine derivatives: optical and structural characterisation. Tetrahedron 2006;62:9433–9.
[14] Hagfeldt A, Grätzel M. Molecular photovoltaics. Acc Chem Res 2000;33: 269–77.
[15] Liu MO, Tai CH, Teh Hu A. The fluorescent and photoelectric conversion properties of phthalocyanine–perylene tetracarboxylic complexes. J Photochem Photobiol A 2004;165:193–200.
[16] Kaya D, Pekcan O, Yılmaz Y. Direct test of the critical exponents at the sol-gel transition. Phys Rev E Stat. Nonlinear Soft Matter Phys 2004;69. 016117-(10).
[17] Frahn MS, Abellon RD, Jager WF, Luthjens LH, Warman JM. Synthesis and characterization of a new fluorogenic probe molecule *N*-(1-pyrene)methacrylamide for monitoring radiation-induced polymerization. Nucl Instrum Methods Phys Res. Sect B 2001;185:241–7.
[18] Valeur B. Molecular fluorescence principles and applications. Germany: Weinheim: Wiley-VCH; 2002.
[19] Berera R, Stokkum IHM, Kodis K, Keirstead AE, Pillai E, Herrero C, et al. Energy transfer, excited-state deactivation, and exciplex formation in artificial

caroteno-phthalocyanine light-harvesting antennas. J Phys Chem B 2007;111: 6868–77.
[20] Ng DKP. Dendritic phthalocyanines: synthesis, photophysical properties, and aggregation behavior. C R Chim 2003;6:903–10.
[21] Sheng N, Zhu P, Ma C, Jiang J. The synthesis, spectroscopy, electrochemistry and photophysical properties of novel, sandwich europium (III) complexes with a porphyrin ligand bearing four pyrenyl groups in meso-positions. Dyes Pigm 2009;81:91–6.
[22] Perin DD, Armarego WLF, Perin DR. Purification of laboratory chemicals. 2nd ed. New York: Pergamon Press; 1985.
[23] Young JG, Onyebuagu W. Synthesis and characterization of di-disubstituted phthalocyanines. J Org Chem 1990;55:2155–9.
[24] Yoshioka N, Andoh C, Kubo K, Igarashi T, Sakurai T. Competitive occurrence of homolytic N–O and heterolytic C–O bond cleavage in excited-state 1-(arylmethyloxy)-2-pyridones. J Chem Soc. Perkin Trans 2001;2:1927–32.
[25] Durmus M, Chen JY, Zhao ZX, Nyokong T. Energy transfer in zinc porphyrin–phthalocyanine heterotrimer and heterononamer studied by fluorescence resonance energy transfer (FRET). Spectrochim Acta Part A 2008;70:42–9.
[26] Yenilmez HY, Özçeşmeci İ, Okur Aİ, Gül A. Synthesis and characterization of metal-free and metallo phthalocyanines with four pendant naphthoxy-substituents. Polyhedron 2004;23:787–91.
[27] Gelir A, Yılmaz İ, Yılmaz Y. In situ monitoring of the synthesis of a pyranine-substituted phthalonitrile derivative via the steady-state fluorescence technique. J Phys Chem B 2007;111:478–84.
[28] Kalkan A, Koca A, Bayır ZA. Unsymmetrical phthalocyanines with alkynyl substituents. Polyhedron 2004;23:3155–62.
[29] Özçeşmeci M, Hamuryudan E. The synthesis and characterization of functionalized polyfluorinated phthalocyanines. Dyes Pigm 2008;77:457–61.
[30] Sesalan BŞ, Koca A, Gül A. Water soluble novel phthalocyanines containing dodeca-amino groups. Dyes Pigm 2008;79:259–64.
[31] Adebayo AI, Nyokong T. Synthesis, spectroscopic and electrochemical properties of manganese, nickel and iron octakis-(2-diethylaminoethanethiol)-phthalocyanine. Polyhedron 2009;28:2831–8.
[32] Gök Y, Kantekin H, Kılıçaslan MB, Alp H. Synthesis and characterization of new metal-free and nickel(II) phthalocyanines containing tetraazatrioxa macrotricyclic moieties. Dyes Pigm 2007;74:692–8.
[33] Snow AW. In: Kadish KM, Smith KM, Guilard R, editors. The porphyrin handbook-phthalocyanines: properties and materials, vol. 17. Amsterdam: Elsevier Science; 2003. p. 129–76.
[34] Lyubimtsev A, Iqbala Z, Cruciusa G, Syrbub S, Taraymovich ES, Ziegler T, et al. Aggregation behavior and UV–vis spectra of tetra- and octaglycosylated zinc phthalocyanines. J Porphyrins Phthalocyanines 2011;15:39–46.
[35] Ogunbayo TB, Ogunsipe A, Nyokong T. The syntheses, characterization and fluorescence spectra of novel, octakis(alkylthio-phthalocyanato) nickel(II) and palladium(II) complexes. Dyes Pigm 2008;79:259–64.
[36] Bartelmess J, Ballesteros B, Torre G, Kiessling D, Campidelli S, Prato M, et al. Phthalocyanine–pyrene conjugates: a powerful approach toward carbon nanotube solar cells. J Am Chem Soc 2010;132:16202–11.
[37] Lakowicz JR. Principles of fluorescence spectroscopy. 3rd ed. Berlin: Springer; 2006.
[38] Özçeşmeci İ, Okur Aİ, Gül A. New phthalocyanines bearing tetra(hydroxyethylthio) functionalities. Dyes Pigm 2007;75:761–5.