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Synthesis of fluorine-containing phthalocyanines and investigation of the photophysical and photochemical properties of the metal-free and zinc phthalocyanines

https://doi.org/10.1515/hc-2018-0049
Received March 23, 2018; accepted August 16, 2018; previously published online September 15, 2018

Abstract: 4-(3-(Trifluoromethyl)benzylthio)phthalonitrile (**1**) was synthesized. Metal-free phthalocyanine **2**, zinc(II) phthalocyanine **3** and cobalt(II) phthalocyanine **4** were synthesized starting with dinitrile compound **1**. Photodynamic therapy properties of **2** and **3** were studied.

Keywords: macrocyclic; metal-free phthalocyanine; metallophthalocyanine; photodynamic therapy; phthalocyanine; phthalonitrile.

Introduction

Phthalocyanines (Pc) were discovered for the first time in 1907 by Braun and Tcherniac [1]. This class of compounds has four coordination centers on the square planar geometry. They form structures such as square pyramidal, tetrahedral, and octahedral with metals which prefer a higher number of coordinates and form eight-coordinate sandwich complexes with lanthanides and actinides [2]. Phthalocyanines were mass produced and introduced to the market for the first time in 1935 and now are widely used in electrochromic imaging, staining, catalysis, optical data storage, chemical sensor production and photodynamic therapy (PDT) due to their bright blue or green color, high chemical durability and high light resistance [3]. The important application of phthalocyanines is PDT which provides an option for cancer treatment. It involves intravenous or topical administration of a light-sensitive drug (photosensitizer) to the patient, accumulation of this drug in the tumorous tissue, and then activation of the drug by light exposure to destroy cancer cells [4–8]. Health institutions in many countries including the USA, Germany, Japan, the UK, France, the Netherlands and Canada have approved the use of PDT to treat cancer [9, 10]. In this study, new phthalocyanines H_2Pc (**2**), ZnPc (**3**) and CoPc (**4**) with trifluoromethyl groups in their peripheral positions were synthesized. Photophysical and photochemical properties of compounds **2** and **3** were investigated.

Results and discussion

The synthesis of metal-free phthalocyanine **2**, zinc phthalocyanine **3** and cobalt phthalocyanine **4**, starting with 4-(3-(trifluoromethyl)benzylthio)phthalonitrile (**1**), is shown in Scheme 1. The metal-free phthalocyanine **2** was synthesized by heating a solution of the dinitrile derivative **1** at 160°C for 24 h under a nitrogen atmosphere in n-pentanol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a catalyst. The crude product was purified by column chromatography over silica gel eluting with chloroform to give analytically pure compound **2** in an overall yield of 38%. The C≡N stretching vibration observed at 2230 cm^{-1} for substrate **1** is absent from the IR spectrum of compound **2**, and a new N-H stretching vibration is seen at 3288 cm^{-1}, which is consistent with the formation of phthalocyanine **2** as a result of the cyclotetramerization reaction. In the ^1H NMR spectrum of **2**, the chemical shift of −7.93 for the NH protons in the central phthalocyanine ring is very characteristic for metal-free phthalocyanines. The presence of the molecular ion peak at *m/z* 1274 in the mass spectrum of **2** also supports the proposed structure. In the electronic spectrum of **2** in chloroform, Q bands for π-π^* transitions are observed in the visible region of 615 nm –711 nm (Figure 1). The Soret band is observed at 344 nm. The presence of two strong Q bands around 711 nm with log ε 5.08 nm and 677 nm with log ε 5.09 shows that the monomeric metal-free phthalocyanine **2** has D_{2h} symmetry.

The zinc(II) phthalocyanine **3** was synthesized by the reaction of dinitrile **1** with anhydrous $Zn(CH_3COO)_2$ in the presence of DBU in *N*,*N*-dimethylacetamide (DMAE). The analytically pure product **3** was obtained in 38% yield after

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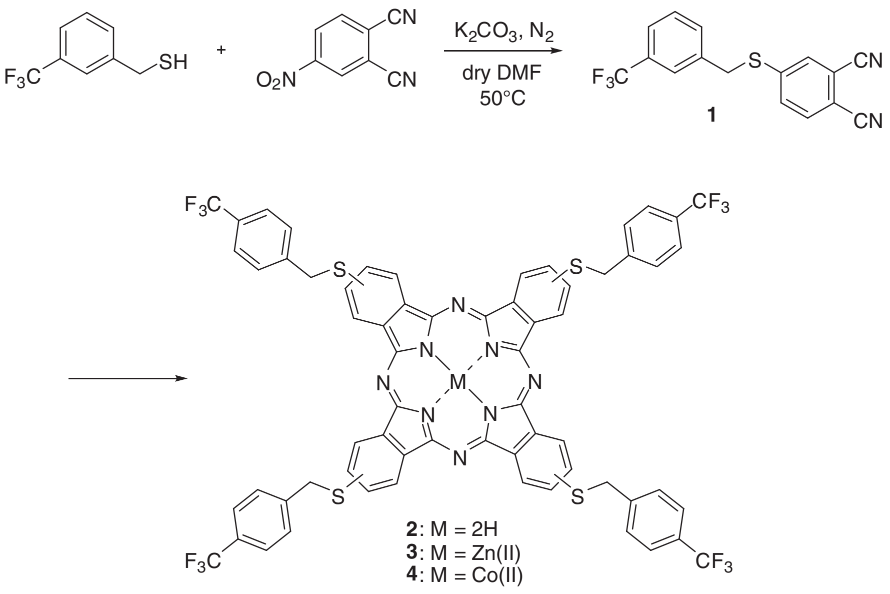

Scheme 1

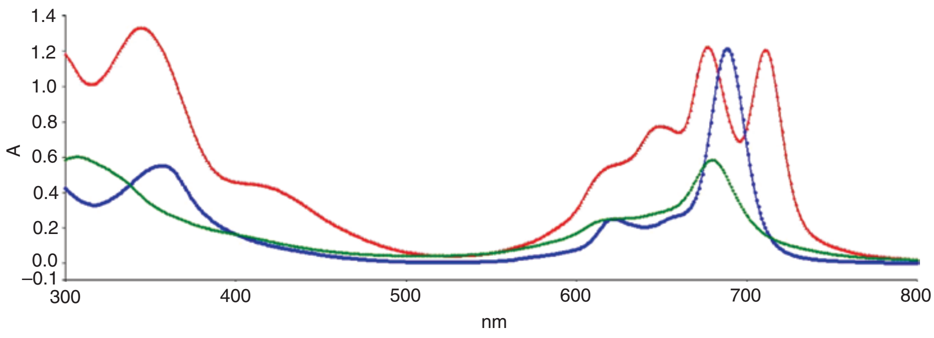

Figure 1 UV-vis spectra of H_2Pc (red), ZnPc (blue) and CoPc (green) complexes.

chromatography. The given structure is fully consistent with the spectral data. In particular, the molecular ion peak at *m/z* 1338 in the mass spectrum supports the proposed structure of the zinc complex. In the UV-vis spectrum of **3** in chloroform (Figure 2), a strong Q absorption band is observed at λ_{max} 688 nm with log ε 5.08 and a shoulder band at 621 nm with log ε 4.39. For metal-containing phthalocyanines, observation of a single Q band indicates a D_{4h} symmetry [11]. The Soret band for **3** is observed at λ_{max} 356 nm (log ε 4.75).

The cobalt(II) phthalocyanine **4** was synthesized in a similar way by treatment of the dinitrile **1** with $CoCl_2$ in DMAE in the presence of DBU. After chromatography, the yield of analytically pure product **4** was 42%. The composition of the complex is fully consistent with the molecular ion peak observed at *m/z* 1331 in the mass spectrum of the compound. In the UV-vis spectrum (Figure 1) of compound **4**, the Q band is observed as a strong absorption band at λ_{max} 679 nm (log ε 4.77) with a weak shoulder band at 614 nm (log ε 4.39).

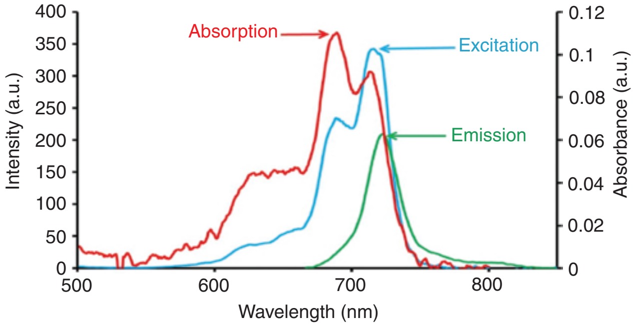

Figure 2 Absorption, fluorescence, emission and excitation spectra of compound **2** in DMSO; excitation wavelength = 723 nm.

Free phthalocyanine **2** and its zinc complex **3** were investigated for the suitability for PDT. Thus, fluorescence quantum yield and lifetime, singlet oxygen production capacity and photodegradation property were examined. For effective photo-sensing, the lifetime of the triplet state must be relatively long. For this purpose, in the PDT, diamagnetic complexes such as zinc or aluminum phthalocyanines are preferred. The copper, cobalt and iron phthalocyanines exhibit shorter triplet lifetimes and lower phototoxicity. Accordingly, the PDT properties of the cobalt derivative **4** was not investigated.

Spectral examination of of H$_2$Pc (**2**) and ZnPc (**3**) in DMSO and DMF showed that these compounds share similar properties (Figures 2–5). These compounds do not undergo degradation during fluorescence studies. The fluorescence emission peaks in DMSO are observed at 723 nm for H$_2$Pc (**2**) and 703 nm for ZnPc (**3**) (Table 1). The fluorescence emission peaks in DMF are observed at 720 nm for H$_2$Pc (**2**) and 699 nm for ZnPc (**3**) (Table 2). The Stokes shift value in DMSO is 10 nm for both compounds. The Stokes shift value in DMF is 8 nm for H$_2$Pc (**2**) and 10 nm for ZnPc (**3**).

The fluorescence lifetime τ_F is the average lifetime (duration) of an excited molecule, and this value is directly related with the fluorescence quantum yield Φ_F. Higher fluorescence lifetime indicates higher fluorescence quantum yield. Any factor that shortens the fluorescence lifetime will reduce the fluorescence quantum yield Φ_F value as well [12, 13]. The fluorescence lifetime τ_F was calculated using the Strickler-Berg equation [14]. The calculations based on fluorescence emission graphs of H$_2$Pc (2) and ZnPc (3) gave the fluorescence quantum yields Φ_F in DMSO of 0.13 and 0.19 for H$_2$Pc (2) and ZnPc (3), respectively, whereas the fluorescence quantum yields Φ_F in DMF were found to be 0.13 and 0.15, respectively. These values are characteristic for phthalocyanine compounds. The natural radiative lifetime τ_o, fluorescence lifetime τ_F and fluorescence constant k_F values for compounds **2** and **3** are listed in Tables 3 and 4.

For singlet oxygen quantum yield measurements, H$_2$Pc (**2**) and ZnPc (**3**) were dissolved in DMSO, and the solutions were treated with 1,3-diphenylisobenzofuran (DPBF) as a quencher. Then, the mixtures were exposed to light with intervals of 5 s to take the UV spectra. The changes in the absorption at 417 nm belonging to DPBF were examined (Figures 6 and 7). As DPBF is a light-sensitive compound, its solutions were prepared in a dark environment.

Photo-degradation of H$_2$Pc (**2**) and ZnPc (**3**) complexes were not observed in the presence of DPBF in the environment designed to remove the singlet oxygen formed during the determination of the singlet oxygen quantum yield Φ_Δ. There was no reduction in the Q band, nor were new bands formed. The Φ_Δ values of H$_2$Pc (**2**) in DMSO and DMF are 0.20 and 0.30, respectively, whereas the respective Φ_Δ

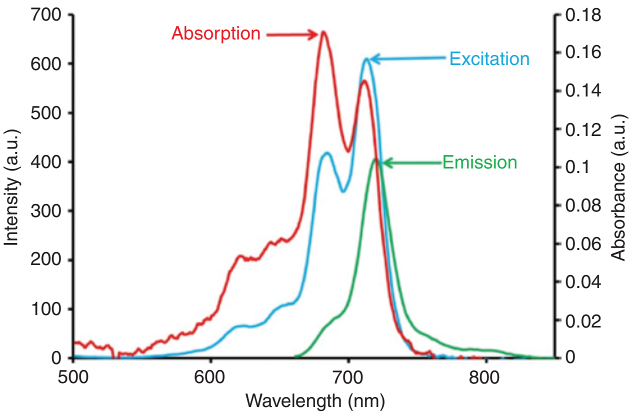

Figure 3 Absorption, fluorescence, emission and excitation spectra of compound **2** in DMF; excitation wavelength = 720 nm.

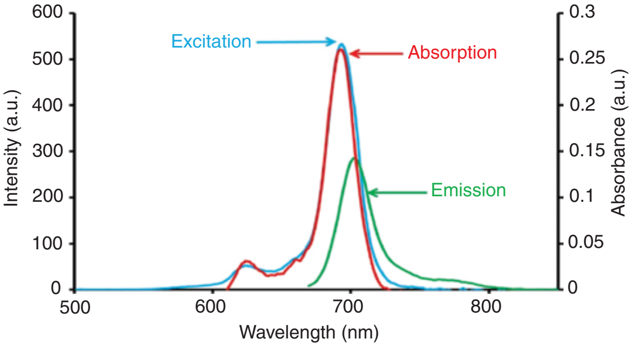

Figure 4 Absorption, fluorescence, emission and excitation spectra of compound **3** in DMSO; excitation wavelength = 703 nm.

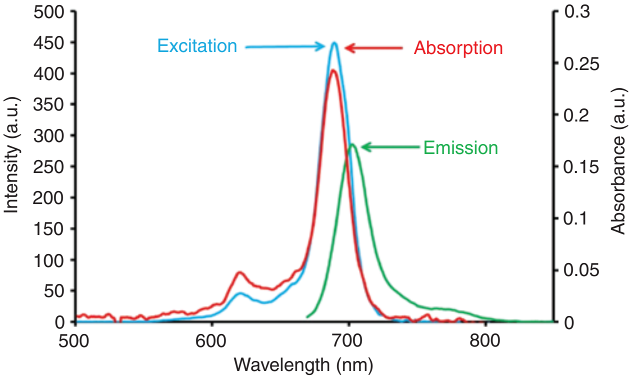

Figure 5 Absorption, fluorescence, emission and excitation spectra of compound **3** in DMF; excitation wavelength = 699 nm.

values of ZnPc (**3**) in DMSO and DMF are 0.78 and 0.81. These values are higher compared to the Φ_Δ value of the standard ZnPc complex ($\Phi_\Delta = 0.67$ in DMSO and $\Phi_\Delta = 0.56$ in DMF [15]). The singlet oxygen quantum yield value Φ_Δ measured for Al, Ga and In phthalocyanines is between 0.27 and 0.90 [16]. The singlet oxygen quantum yields Φ_Δ of

Table 1 Absorption, excitation, and emission data for metal-free phthalocyanine **2** and zinc(II) phthalocyanine **3** in DMSO.

Compound	Q band λ_{max} (nm)	log ε	Excitation λ_{ex} (nm)	Emission λ_{em} (nm)	Stokes shift Δ_{Stokes} (nm)
2	713; 689	4.45; 4.61	714; 688	723	10
3	693	5.12	694	703	10

Table 2 Absorption, excitation, and emission data for unsubstituted and substituted metal-free phthalocyanine **2** and zinc(II) phthalocyanine **3** in DMF.

Compound	Q band λ_{max} (nm)	ε	Excitation λ_{ex} (nm)	Emission λ_{em} (nm)	Stokes shift Δ_{Stokes} (nm)
2	712; 682	4.78; 4.88	713; 684	720	8
3	689	5.12	689	699	10

Table 3 Photophysical and photochemical parameters of metal-free phthalocyanine **2** and zinc(II) phthalocyanine **3** in DMSO.

Compound	Φ_F	τ_F (ns)	$^a k_F$ (s^{-1}) ($\times 10^8$)	τ_0 (ns)	Φ_d ($\times 10^{-3}$)	Φ_Δ
2	0.13	0.54	2.43	4.14	0.32	0.20
3	0.19	0.87	2.17	4.48	0.022	0.78

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

Table 4 Photophysical and photochemical parameters of metal-free phthalocyanine **2** and zinc(II) phthalocyanine **3** in DMF.

Compound	Φ_F	τ_F (ns)	$^b k_F$ (s^{-1}) ($\times 10^8$)	τ_0 (ns)	Φ_d ($\times 10^{-3}$)	Φ_Δ
2	0.13	0.39	3.64	2.76	0.088	0.30
3	0.15	0.41	4.10	2.47	0.30	0.81

H_2Pc (**2**) and ZnPc (**3**) are in the normal range determined for phthalocyanines. This indicates that compounds **2** and **3** can be used in PDT as can other similar compounds.

After dissolving H_2Pc (**2**) and ZnPc (**3**) in DMSO and DMF, the compounds were exposed to light with intervals of 10 min to take their UV spectra, and changes in the Q bands were investigated (Figures 8–11). The light sensitivity of phthalocyanine compounds was determined in this study. Again, this examination of photophysical and photochemical properties of H_2Pc (**2**) and ZnPc (**3**) show that these compounds are suitable photosensitizers for PDT.

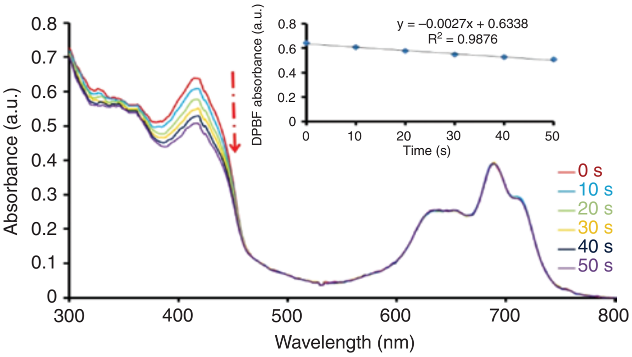

Figure 6 Absorption changes for compound **2** during the determination of singlet oxygen quantum yield (1×10⁻⁵ M in DMSO); inset: plot of DPBF absorbance vs. time.

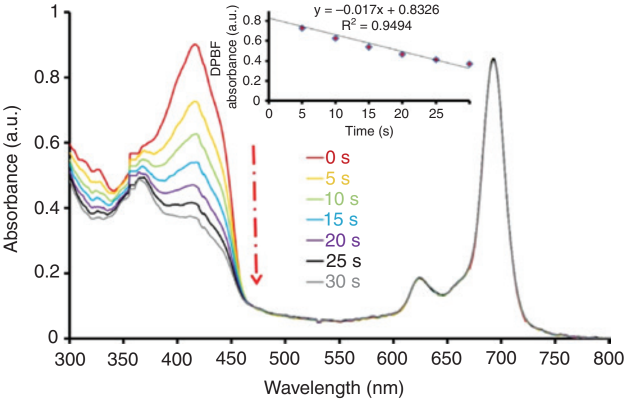

Figure 7 Absorption changes for compound **3** during the determination of singlet oxygen quantum yield (1×10⁻⁵ M in DMSO; inset: plot of DPBF absorbance vs. time.

Experimental

4-Nitrophthalimide, 4-nitrophthalamide and 4-nitrophthalonitrile were synthesized according to the literature [17]. Fourier-transform infrared (FT-IR) spectra were obtained using KBr pellets on a Perkin Elmer 1600 FTIR spectrometer. ^1H NMR spectra were recorded at 400 MHz in $CDCl_3$ using a Varian Mercury spectrometer. UV-vis spectra were taken on a Shimadzu 2101UVPc spectrometer using chloroform as solvent. Mass spectra were recorded using Brucer Microflex LT matrix-assisted laser desorption/ionization- time-of-flight mass spectrometry (MALDI-TOF-MS) and Micromass Quattro liquid chromatography-tandem mass spectrometry (LC-MS/MS) spectrometers. Elemental analyses were recorded using a Leco CHNS-932 apparatus. Fluorescence and emission spectra were recorded on a Varian Eclipse spectrophotometer in 1-cm pathlength cuvettes at room temperature. Photo-irradiations were done using a General Electric quartz line lamp (300 W) for metal-free compound **2** and the zinc-phthalocyanine **3**.

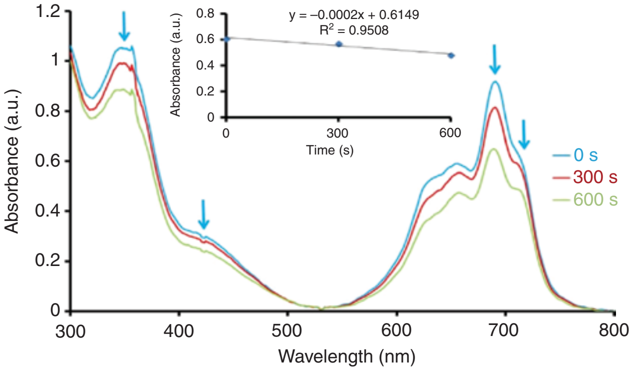

Figure 8 Absorption changes during photodegradation of compound **2** in DMSO showing the disappearance of the Q-band at 10-min intervals; inset: plot of absorbance vs. time.

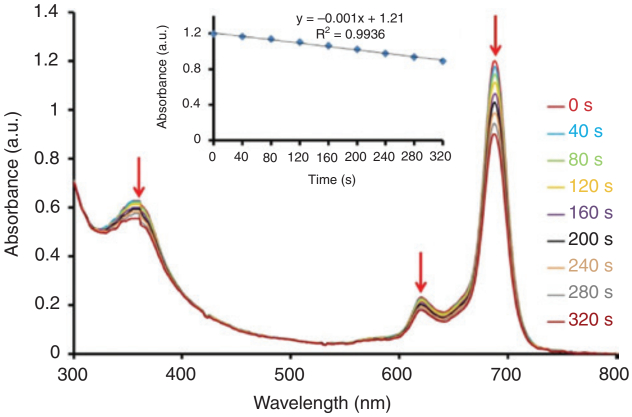

Figure 9 Absorption changes during photodegradation of compound **2** in DMF showing the disappearance of the Q-band at 10-min intervals; inset: plot of absorbance vs. time.

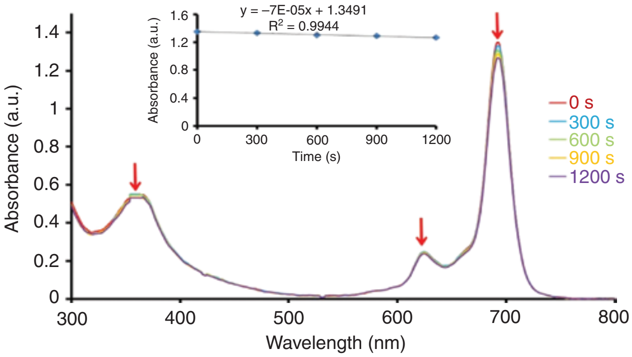

Figure 10 Absorption changes during photodegradation of compound **3** in DMSO showing the disappearance of the Q-band at 10-min intervals; inset: plot of absorbance vs. time.

To filter off IR and UV radiations, a water filter and a Schott (600 nm glass cut off) filter were used. An interference filter (670 nm with a band width of 40 nm) was additionally placed in the light path before the sample. A PowerMax 5100 detector was used to measure the light intensity.

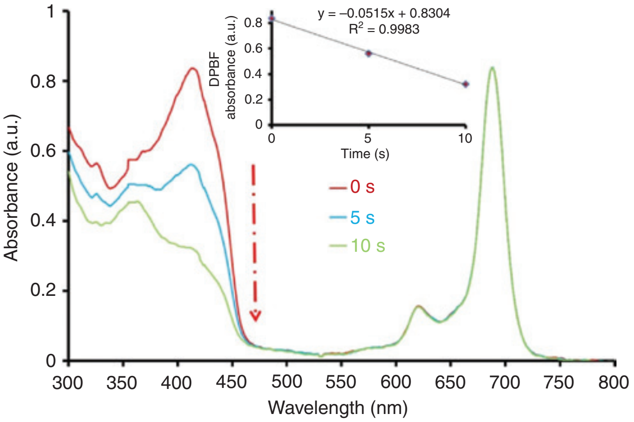

Figure 11 Absorption changes during photodegradation of compound **3** in DMF showing the disappearance of the Q-band at 10-min intervals; inset: plot of absorbance vs. time.

Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_F) were determined by the comparative method using equation (1) [18], where F and F_{Std} are the areas under the fluorescence emission curves

$$\Phi_F = \Phi_{F(std)} \frac{F A_{std} \eta^2}{F_{std} A \eta^2_{std}} \tag{1}$$

of the sample **2** or **3** and the standard, respectively. A and A_{Std} are the relative absorbance of the samples **2** or **3** and standard at the excitation wavelength, respectively. The values η^2 and η^2_{std} are the respective refractive indices of solvents for the sample and standard, respectively. Unsubstituted ZnPc ($\Phi_F = 0.20$) was employed as the standard in DMSO. Natural radiative (τ_0) lifetimes were determined using the Strickler-Berg equation [19]. The fluorescence lifetimes (τ_F) were evaluated using equation (2).

$$\Phi_F = \frac{\tau_F}{\tau_0} \tag{2}$$

Singlet oxygen quantum yields

Determination of the singlet oxygen quantum yields (Φ_Δ) was described in the literature [20]. Equation (3) was employed for the calculation of Φ_Δ values.

$$\Phi_\Delta = \Phi_\Delta^{std} \frac{R \cdot I_{abs}^{std}}{R^{std} \cdot I_{abs}} \tag{3}$$

Photo-degradation quantum yields

Determination of the photo-degradation quantum yield (Φ_d) has been described in the literature [21]. Equation (4) was employed for the calculation of Φ_d values. Φ

$$\Phi_d = \frac{(C_o - C_t)\cdot V \cdot N_A}{I_{abs}\cdot S \cdot t} \tag{4}$$

4-(3-(Trifluoromethyl)benzylthio)phthalonitrile (1)

A mixture of (3-(trifluoromethyl)phenyl)methanethiol (2 mL, 2.59 g, 13.84 mmol), anhydrous DMF (20 mL), and 4-nitrophthalonitrile (2.41 g, 13.84 mmol) was stirred under nitrogen atmosphere at 50°C for 10 min, and then treated with anhydrous K_2CO_3 (0.72 g, 5.28 mmol) in small portions in 2 h. The mixture was stirred at 50°C for 4 days under nitrogen atmosphere, then cooled, poured onto ice (100 g), and stirred for 6 h. The resulting solid was filtered and dried in a vacuum desiccator over P_2O_5. The dried product was subjected to column chromatography over silica gel eluting with hexane/chloroform (3:2) and dried again in the vacuum desiccator; a light-yellow crystalline substance; yield 73%; mp 160–162°C; IR (ν_{max}, cm^{-1}): 3058, 2230, 1236; ^{1}H-NMR: δ 7.62–7.49 (m, 7H, Ar-H), 4.29 (s, 2H, CH_2); MS: *m/z* 318, [M^+]. Anal. Calcd for $C_{16}N_2F_3SH_9$: C, 60.4; N, 8.80; S, 10.06; H, 2.8. Found: C, 60.46; N, 8.86; S, 10.18; H, 2.78.

Metal-free phthalocyanine (2)

A deoxygenated mixture of 4-(3-(trifluoromethyl)benzylthio)phthalonitrile (**1**, 300 mg, 0.94 mmol), *n*-pentanol (5 mL) and three drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in a Schlenk flask under nitrogen atmosphere was stirred at 160°C for 24 h, then cooled and concentrated. The resultant precipitate of product **2** was purified by column chromatography over silica gel eluting with chloroform and dried under reduced pressure; a green solid; yield 38%; mp > 300°C; IR (ν_{max}, cm^{-1}): 3288, 3066, 2918–2849, 1235; ^{1}H NMR: δ −7.93 (s, 2H, N-H), 7.57–7.32 (m, 20H, Ar-H) 7.02–6.59 (m, 8H, Ar-H), 3.96 (s, 8H, CH_2); UV-vis [λ_{max} (nm × 10^{-5}), ε (mol^{-1} cm^{-1})]: 344 (5.13), 615 (4.72), 649 (4.89), 677 (5.09), 711 (5.08); MS: *m/z* 1274, [M^+]. Anal. Calcd for $C_{64}H_{38}N_8S_4F_{12}$: C, 60.28; H, 2.98; N, 8.79; S, 10.04. Found: C, 60.46; H, 2.93; N, 8.82; S, 10.26.

Zinc(II) phthalocyanine (3)

A deoxygenated mixture of4-(3-(trifluoromethyl)benzylthio)phthalonitrile (**1**, 300 mg, 0.94 mmol), 2 mL *N,N*-dimethylacetamide (DMAE, 2 mL), anhydrous $Zn(CH_3COO)_2$ (0.04 g, 0.24 mmol), and three drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in a Schlenk flask under nitrogen atmosphere was stirred at 130°C for 24 h. The green product **3** was purified by column chromatography over silica eluting with chloroform and then dried in a vacuum oven; yield 38%; mp > 300°C; IR (ν_{max}, cm^{-1}): 3060, 2917–2849, 1162; ^{1}H NMR: δ 7.37–7.84 (m, 28H, Ar-H), 4.56 (s, 8H, CH_2); UV-vis [λ_{max} (nm × 10^{-5}), ε (mol^{-1} cm^{-1})]: 356 (4.75), 621 (4.39), 688 (5.08); MS: *m/z* 1338, [M^+]. Anal. Calcd for $C_{64}H_{36}N_8S_4F_{12}Zn$: C, 57.44; H, 2.69; N, 8.37; S, 9.57. Found: C, 57.46; H, 2.57; N, 8.57; S, 9.36.

Cobalt(II) phthalocyanine (4)

A deoxygenated mixture of 4-(3-(trifluoromethyl)benzylthio)phthalonitrile (**1**, 300 mg, 0.94 mmol), DMAE (2 mL), anhydrous $CoCl_2$ (0.031 g, 0.24 mmol), and three drops of DBU in a Schlenk flask under nitrogen atmosphere was stirred at 130°C for 24 h. The crude product was purified by column chromatography over silica gel eluting with chloroform. The resulting green product was dried in a vacuum oven; yield 42%; mp > 300°C; IR (ν_{max}, cm^{-1}): 3044, 2920–2851, 1233; UV-Vis [λ_{max} (nm × 10^{-5}), ε (mol^{-1} cm^{-1})]: 306 (4.78), 624 (4.39), 679 (4.77); MS: *m/z* 1331, [M^+]. Anal. Calcd for $C_{64}H_{36}N_8S_4F_{12}Co$: C, 57.7; H, 2.7; N, 8.41; S, 9.6. Found: C, 57.86; H, 2.45; N, 8.53; S, 9.72.

Acknowledgments: This study was supported by Gümüşhane University Scientific Research Projects Coordination Department, Project Number: 16.A0118.02.01.

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