SUPPLEMENTARY INFORMATION

Synthesis and characterization of novel 7-oxy-3-ethyl-6-hexyl-4-methylcoumarin substituted metallo phthalocyanines and investigation of their photophysical and photochemical properties.

Mücahit Özdemir,a Begümhan Karapınar,a Bahattin Yalçın,*a Ümit Salan,a Mahmut Durmuşb and Mustafa Bulut*a

a. Marmara University, Department of Chemistry, 34722 Kadıköy, Istanbul, Turkey. E-mail: byalcin@marmara.edu.tr, mbulut@marmara.edu.tr, mozdemir17@marun.edu.tr, usalan@marmara.edu.tr, begumhankarapinar@gmail.com
b. Gebze Technical University, Department of Chemistry, 41400 Gebze, Kocaeli, Turkey. E-mail: durmus@gtu.edu.tr

1. Experimental

1.1. Materials

All chemicals used were of reagent grade quality. 3-Nitrophthalonitrile, 4-nitrophthalonitrile, 4,5-dichlorophthalonitrile, 7-hydroxy-3-ethyl-6-hexyl-4-methylcoumarin (1) and its phthalonitrile derivatives (2-5) were synthesized and purified according to the methods described previously in literature respectively.1-3 4-Hexylresorcinol, ethyl 2-ethylacetoacetate, 1,3-diphenylisobenzofuran (DPBF) and metal salts were purchased from Sigma-Aldrich and used as received. The solvents were purified, dried and stored over 4Å molecular sieves. All reactions were carried out under high purity N₂ atmosphere unless otherwise noted. The Pc compounds (6a-9b) were purified successively by washing with hot acetic acid, water, ethanol and acetonitrile in the Soxhlet apparatus. Column chromatography was performed on silica gel 60 (0.040-0.063 mm) for a proper purification. Melting points of the Pc compounds were found to be higher than 300°C. The homogeneity of the products was tested in each step by thin layer chromatography (TLC Silica gel 60 F254).

1.2. Equipment

IR spectra were recorded on a Perkin Elmer Spectrum One fourier transform infrared spectrophotometer. 1H-NMR spectra were recorded on a Bruker Avance III 500 MHz Three channel NMR spectrometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TUBITAK, Marmara Research Centre. Mass spectra were recorded on the Bruker microflex LT MALDI-TOF Mass Spectrometer equipped with a nitrogen UV-Laser operating at 337 nm using the 2,5-dihydroxybenzoicacid (DHB) and dithranol (DIT) matrix. Optical spectra in the UV-vis region were recorded with a Shimadzu 2450 UV-vis spectrophotometer. Fluorescence lifetimes were measured using a time correlated single photon counting setup (TCSPC) (Horiba Fluorolog 3 equipment.) Fluorescence excitation and emission spectra were recorded on the Hitachi F-7000 spectrofluorometer using 1 cm path length cuvette at room temperature. Photo-irradiations were done using an Osram optic halogen lamp (300W-120V). A 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiations respectively. An interference filter (Intor, 670 nm and 700 nm with a band width of 40 nm) was additionally placed in the light path before the sample. Light intensities were measured with a POWER MAX PM5100 laser (Molectron detector incorporated) power meter. Thermal properties of phthalocyanines were examined by Thermal Gravimetric Analysis (TGA) using a Perkin-Elmer Thermogravimetric analyzer STA6000 model. TGA curves of the phthalocyanines were obtained in the 30-750°C temperature range with heating rate of 10°C/min under air and N₂ atmospheres. Phase change properties and phase transitions of phthalocyanines were examined by Pyris Diamond differential scanning calorimeter (DSC). DSC analysis was run from 0°C to 80 with 5°C/min heating and cooling rates under N₂ at 25 ml/min.

1.3. Photophysical Parameters

1.3.1. Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (ΦF) were determined by the comparative method using equation 1.4-5

\[ \Phi_F = \frac{F \times A_{std} \times \eta^2}{F_{std} \times A \times \eta_{std}^2} \]

eq. (1)
where $F$ and $F_{std}$ are the areas under the fluorescence emission curves of the samples (6a-9b) and the standard (Unsubstituted ZnPc), respectively. $\tilde{A}$ and $\tilde{A}_{std}$ are the relative absorbance of the samples and standard at the excitation wavelength, respectively. $\eta^2$ and $\eta_{std}^2$ are the refractive indices of solvents for the sample and standard, respectively.

Unsubstituted ZnPc (in DMF) ($\Phi_F = 0.170$) was employed as the standard. Both the sample and standard were excited at the same wavelength. The absorbance of the solutions was ranged between 0.10 and 0.12 at the excitation wavelength.

Fluorescence lifetimes $\tau_F$ were measured using a time correlated single photon counting setup (TCSPC). The natural radiative lifetimes ($\tau^0$) were evaluated using equation 2.

$$\tau^0 = \frac{\tau_F}{\Phi_F}$$

**eq. (2)**

### 1.4. Photochemical Parameters

#### 1.4.1. Singlet oxygen quantum yields

Singlet oxygen quantum yield ($\Phi_{\Delta}$) determinations were carried out using the experimental set-up described in literature. Typically, a 3 mL portion of the respective unsubstituted, peripherally, non-peripherally tetra-substituted and octa-substituted Zn(II) Pc and In(III) CICp solutions (concentration = $1 \times 10^{-5}$ M) containing the singlet oxygen quencher was irradiated in the Q band region with the photo-irradiation set-up described in the reference. $\Phi_{\Delta}$ values were determined in air using the relative method with unsubstituted ZnPc (in DMF) as references. Diphenylisobenzofuran (DPBF) was used as chemical quencher for singlet oxygen in DMF. The $\Phi_{\Delta}$ values of the studied Pc complexes were calculated using equation 3:

$$\Phi_{\Delta} = \frac{\Phi_{\Delta}^{std} \times I_{abs}^{std}}{R \times I_{abs}}$$

**eq. (3)**

where $\Phi_{\Delta}^{std}$ is the singlet oxygen quantum yield for the standard. Unsubstituted ZnPc ($\Phi_{\Delta} = 0.56$ in DMF) was used as standard. $R$ and $R_{std}$ are the DPBF photobleaching rates in the presence of the respective samples (6a-9b and Unsubs. ZnPc) and standard, respectively. $I_{abs}$ and $I_{abs}^{std}$ are the rates of light absorption by the samples and standards, respectively $I_{abs}$ was determined by using equation 4.

$$I_{abs} = \frac{\alpha \times S \times I}{N_A}$$

**eq. (4)**

$N_A$ is the Avogadro’s constant, $S$ is the irradiated cell area, $\alpha$ is the irradiation time and $I_{abs}$ is the overlap integral of the radiation source light intensity and the absorption of the samples (6a-9b and Unsubs. ZnPc).

To avoid chain reactions induced by DPBF in the presence of singlet oxygen, the concentration of quenchers (DPBF) was lowered to $\sim 3 \times 10^{-5}$ M. Solutions of sensitizer (concentration = $1 \times 10^{-5}$) containing DPBF were prepared in the dark and irradiated in the Q band region using the setup described in literature. DPBF degradation at 417 nm was monitored. The light intensity used for $\Phi_{\Delta}$ determinations was found to be $6.60 \times 10^{15}$ photons s$^{-1}$ cm$^{-2}$.

#### 1.4.2. Photodegradation quantum yields

Photodegradation quantum yield ($\Phi_d$) determinations were carried out using the experimental set-up described in literature. Photodegradation quantum yields were determined using equation 5,

$$\Phi_d = \frac{(C_0 - C_t) \times V \times N_A}{I_{abs} \times S \times t}$$

**eq. (5)**

where $C_0$ and $C_t$ are the samples (Unsubs. ZnPc, 6a-9b) concentrations before and after irradiation respectively, $V$ is the reaction volume, $N_A$ is the Avogadro’s constant, $S$ is the irradiated cell area, $t$ is the irradiation time and $I_{abs}$ is the overlap integral of the radiation source.
light intensity and the absorption of the samples (6a-9b and Unsubs. ZnPc). A light intensity of 2.15×10^{16} photons s^{-1} cm^{-2} was employed for \( \Phi_d \) determinations.

1.4.3. Fluorescence quenching by benzoquinone or potassium iodide (BQ or KI)

Fluorescence quenching experiments on the substituted ZnPc (6a-9a) were carried out by the addition of different concentrations of quencher [BQ] or [KI] to a fixed concentration of the complexes, and the concentrations of quencher in the resulting mixtures were 0, 0.008, 0.016, 0.024, 0.032 and 0.040 M. The fluorescence spectra of substituted ZnPc (6a-9a) at each quencher concentration were recorded, and the changes in fluorescence intensity related to quencher concentration by the Stern–Volmer equation\(^{12} \) (equation 6):

\[
\frac{I_0}{I} = 1 + K_{sv}[\text{Quencher concentration}]
\]

where \( I_0 \) and \( I \) are the fluorescence intensities of fluorophore in the absence and presence of quencher, respectively, [BQ] or [KI] is the concentration of the quencher, and \( K_{sv} \) is the Stern–Volmer constant, and is the product of the bimolecular quenching constant \( (k_q) \) and the fluorescence lifetime \( \tau_F \), i.e.

\[
K_{sv} = k_q \times \tau_F
\]

The ratios \( \frac{I_0}{I} \) were calculated and plotted against [BQ] or [KI] according to equation 6, and \( K_{sv} \) determined from the slope.

**Fig. S1.** Photophysical and photochemical measurement process.
2. References


### Table S1. The specific IR bands of the compounds (1-5, 6a-9b and unsubs. ZnPc, InPc)

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<th>The Compounds</th>
<th>Aromatic –O–H</th>
<th>Aromatic –C–H</th>
<th>Aliphatic –C–H</th>
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Fig. S2. The IR spectra of the compounds (1-5, 6a-9a, 6b-9b).
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<th>$\lambda^\text{B}^\text{max}$ (log $\varepsilon$)</th>
<th>$\lambda^\text{Shoulder}^\text{max}$ (log $\varepsilon$)</th>
<th>$\lambda^\text{Aggregation}^\text{max}$ (log $\varepsilon$)</th>
<th>$\lambda^\text{em}^\text{max}$ (nm)</th>
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**Fig. S3.** Emission spectra of compound 7a in different solvents.
**Fig. S4.** Positive ion in reflectron mode MALDI-TOF mass spectrum of compound 7a were obtained in dithranol (DIT).

**Fig. S5.** Positive ion in reflectron mode MALDI-TOF mass spectrum of compound 8a were obtained in dithranol (DIT).

**Fig. S6.** Positive ion in reflectron mode MALDI-TOF mass spectrum of compound 9a were obtained in dithranol (DIT).
Fig. S7. $^1$H NMR spectrum of compound 1.
Fig. S8. $^1$H NMR spectrum of compound 2.
Fig. S9. $^1$H NMR spectrum of compound 6a.
Fig. S10. TGA and DSC curves of compound 6b.

Fig. S11. a) UV-vis spectrums of 6b in different solvents. b) UV-vis spectrums of 7b in different solvents.
**Fig. S12.** Absorption spectra of indium phthalocyanine complexes (6b-9b) in DMF.

**Fig. S13.** a) Aggregation behaviors of 8b in DMF at different concentrations. b) Aggregation behaviors of 7a in DMF at different concentrations.
Fig. S14. a) Absorption spectra of 6a in DMSO and Triton X-100. Concentration $\sim 1 \times 10^{-5}$ M. b) Absorption spectra of 7a in dichloromethane and $K_2CO_3 + CH_2Cl_2$ solution. Concentration $\sim 1 \times 10^{-5}$ M.
Fig. S15. a) Normalized absorption, emission and excitation spectra for compounds 8a in DMF. b) Normalized absorption, emission and excitation spectra for compounds 9a in DMF.
Fig. S16. Time correlated single photon counting (TCSPC) trace for compound 7a, 8a and 9a in DMF with residuals. $\lambda_{\text{Ex}} = 661$ nm for 7a, $\lambda_{\text{Ex}} = 650$ nm for 8a and $\lambda_{\text{Ex}} = 644$ nm for 9a.
Fig. S17. a) A typical spectra for the determination of singlet oxygen quantum yield of 8a, in DMF at 1×10⁻⁵ M (inset: plots of DPBF absorbance versus time). b) A typical spectra for the determination of singlet oxygen quantum yield of 9b, in DMF at 1×10⁻⁵ M (inset: plots of DPBF absorbance versus time).
Fig. S18. a) The photodegradation of compounds 8b in DMF showing the disappearance of the Q-band at eight minutes intervals. b) The photodegradation of compounds 6b in DMF showing the disappearance of the Q-band at ten minutes intervals.
Fig. S19. a) Fluorescence emission spectral changes of compound 8a on addition of different concentrations of BQ in DMF. b) Fluorescence emission spectral changes of compound 9a on addition of different concentrations of KI in DMF. Concentration \( \sim 1 \times 10^{-6} \) M.
Fig. S20 a) Stern-Volmer plots for 1,4-benzoquinone (BQ) quenching of 6a, 7a, 8a and 9a, concentration: $\sim1\times10^{-6}$ M in DMF. b) Stern-Volmer plots for potassium iodide (KI) quenching of 6a, 7a, 8a and 9a, concentration: $\sim1\times10^{-6}$ M in DMF. [BQ] and [KI] concentration = 0, 0.008, 0.016, 0.024, 0.032, 0.040 M.