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SUPPLEMENTARY INFORMATION

Peripherally, non-peripherally and axially pyrazoline-fused phthalocyanines: Synthesis, aggregation behaviour and fluorescence, singlet oxygen generation and photodegradation studies

Halise Yalazan[a], Halit Kantekin[a,*], Mahmut Durmuş[b]

[a]*Karadeniz Technical University, Department of Chemistry, Faculty of Sciences, Trabzon, Türkiye*

[b]*Gebze Technical University, Department of Chemistry, Gebze, 41400, Kocaeli, Türkiye*

[*] Author for correspondence: Dr. Halit KANTEKİN, Department of Chemistry, Karadeniz Technical University, 61080 Trabzon, Turkey Tel: 00 90 462 377 25 89 Fax: 00 90 462 325 31 96 E-mail: halit@ktu.edu.tr

1.1. Materials and Equipments

All used chemicals were of reagent grade quality. 1,3-diphenylisobenzofuran (DPBF) and metal salts were purchased from Fluka or Merck and used as received. The used solvents and metal salts were purchased from Merck and Sigma Aldrich used as received.

All reactions were carried out under dry and oxygen free nitrogen atmosphere using Schlenk system. Infrared spectra were recorded on a Perkin Elmer 1600 FT–IR Spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Ascent 400 Mhz NMR spectrometer $CDCI_3$, DMSO-d_6 and chemical shifts were reported (δ) relative to Me_4Si (tetramethylsilane) as internal standard. Mass spectra were measured on a MALDI-TOF spectrometer. Optical spectra in the UV–Vis region were recorded with a Perkin Elmer Lambda 25 spectrophotometer and a Shimadzu 2101 UV/vis spectrophotometer. Melting points were measured by an Electrothermal apparatus.

Photo-irradiations were done using a General Electric quartz line lamp (300W). 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 or 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 MAX5100 (Molelectron detector incorporated) power meter.

2. Photophysical and Photochemical Parameters

2.1. Photophysical parameters

2.1.1. Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_F) of newly synthesized phthalocyanines were determined by the comparative method using equation 1 [1-2],

$$\phi_F = \phi_{F(Std)} \frac{F}{F_{Std}} . \frac{A_{Std}}{A} . \qquad (1)$$

where F and F_{Std} are the areas under the fluorescence emission curves of the samples and the standard, respectively. A and A_{Std} are the respective absorbances of the samples and standard at the excitation wavelengths, respectively. Unsubstituted ZnPc (in DMSO) ($\Phi_F = 0.20$) [3] was employed as the standard. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

Fluorescence lifetimes were measure using a time correlated single photon counting setup (TCSPc). The natural radiative lifetimes (τ_0) were evaluated using equation 2.

$$\tau_0 = \frac{\tau_f}{\phi_f}$$

2.2. Photochemical parameters

2.2.1. Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_Δ) determinations were carried out using the experimental set-up described in literature [4-6]. Typically, a 3 mL portion of the respective novel phthalocyanines solutions (C:1x10^{-5}M) containing the singlet oxygen quencher were irradiated in the Q band region with the photo-irradiation set-up described in Refs. [4-6]. Singlet oxygen quantum yields (Φ_Δ) were determined in air using the relative method with unsubstituted ZnPc as reference in DMSO. DPBF was used as a chemical quencher for singlet oxygen determination and equation 3 was employed for the calculations:

$$\phi_\Delta = \phi_\Delta^{Std} \frac{R.I_{abs}^{Std}}{R^{Std}.I_{abs}} \tag{3}$$

where ϕ_Δ^{Std} is the singlet oxygen quantum yield for the standard ZnPc (ϕ_Δ^{Std} = 0.67 in DMSO) [7]. R and R_{Std} are the DPBF photobleaching rates in the presence of the respective samples and standard, respectively. I_{abs} and I_{abs}^{Std} are the rates of light absorption by the samples and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen, the concentration of quencher was lowered to ~3×10^{-5} mol dm^{-3} [8]. Solutions of sensitizer containing DPBF was prepared in the dark and irradiated in the Q band region using the set-up described in literature [4-6]. A decreasing at 417 nm was monitored for the absorption of DPBF. The light intensity 6.60×10^{15} photons s^{-1} cm^{-2} was used for Φ_Δ determinations.

2.2.2. Photodegradation quantum yields

Photodegradation quantum yield (Φ_d) determination of studied novel phthalocyanines were carried out using the experimental set-up described in literature [4-6]. Photodegradation quantum yields of complexes were determined using equation 4,

$$\phi_d = \frac{(C_0 - C_t).V.N_A}{I_{abs}.S.t} \tag{4}$$

where C_0 and C_t are the concentrations of the samples before and after irradiation, respectively, V is the reaction volume, N_A is the Avogadro's constant, S is the irradiated cell area and t is the irradiation time, I_{abs} is the overlap integral of the radiation source light intensity and the absorption of the samples.

References

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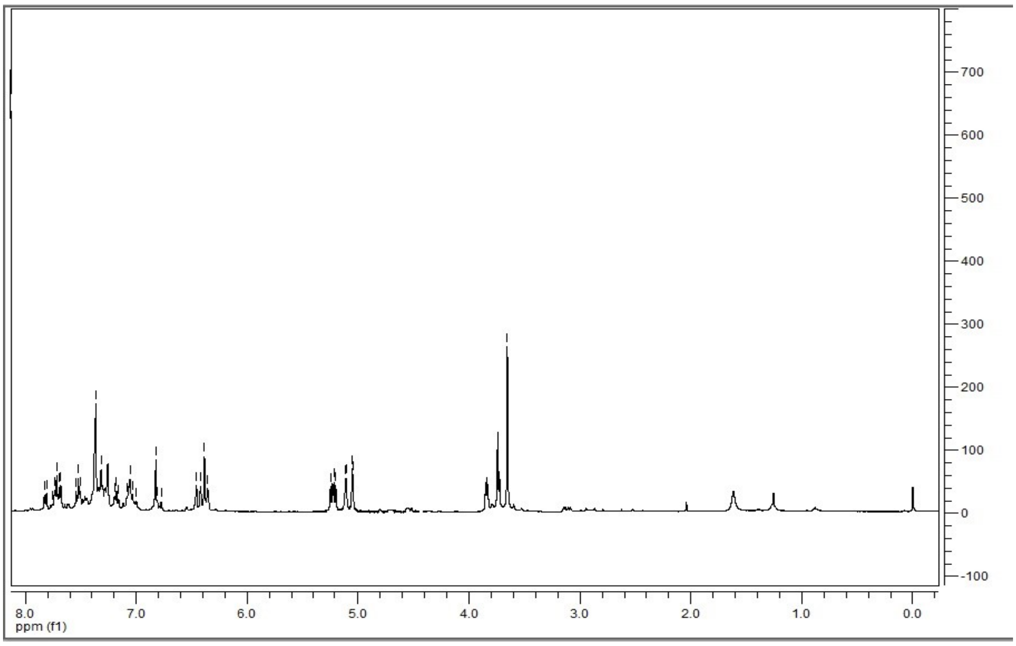

Fig. S1: ^{1}H NMR spectrum of **HY-CN**^{p}

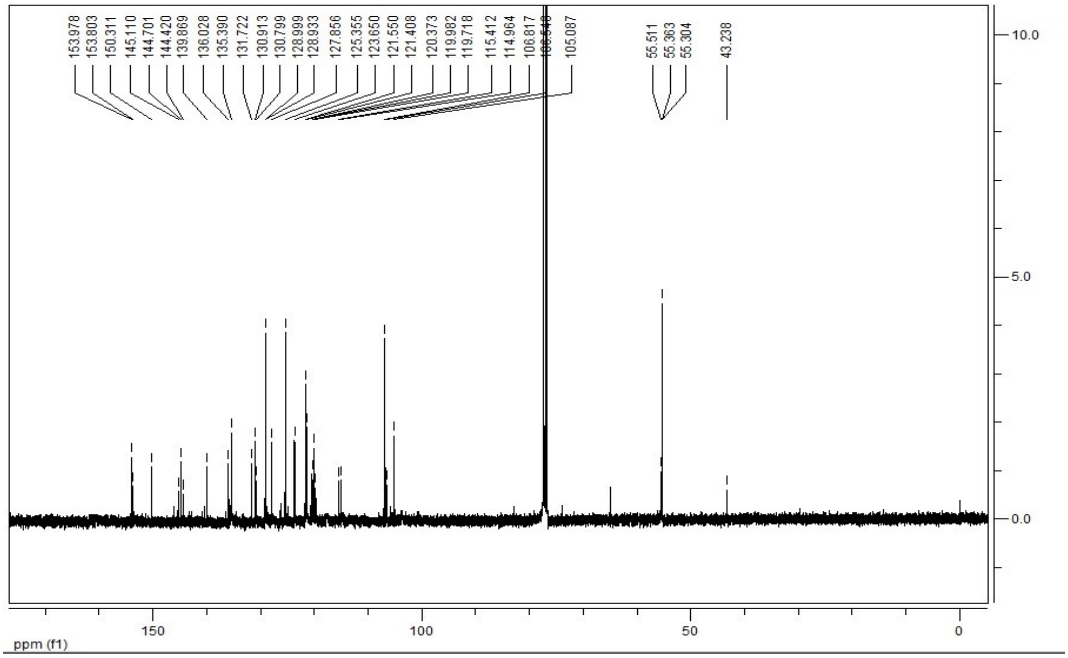

Fig. S2: ^{13}C NMR spectrum of **HY-CN**^{p}