



Some Properties of an Unmetalled Phthalocyanine Obtained by Chance at Low Temperature

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Abstract: A novel tetrasubstituted metal-free phthalocyanine bearing phthalonitrile groups on the peripheral positions was synthesized accidentally by the cyclotetramerization reaction of the 4,4'-(1,3-phenylenebis(oxy))diphthalonitrile. For photodynamic therapy (PDT) application, photophysical properties including fluorescence quantum yield (Φ_F), fluorescence lifetime (τ_F), triplet state lifetime (τ_T), and triplet quantum yield (Φ_T) and photochemical properties including singlet oxygen quantum yield (Φ_{Δ}) and photodegradation quantum yield (Φ_d) as well as magnetic circular dichroism (MCD) properties were described. The Φ_T of the phthalocyanine was 0.81. The obtained lifetime (τ_T) was 40 μ s for metal-free Pc.

Keywords: Metal-free phthalocyanine, singlet oxygen quantum yield, magnetic circular dichroism.

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INTRODUCTION

Phthalocyanines (Pcs) are macrocyclic compounds that consist of 4 pyrrolic subunits. The first synthesis of a Pc was found by accident in 1907, and it involves with low yield the reaction of o-cyanobenzamide in refluxing ethanol (1). However, nowadays a substituted phthalonitrile can be easily prepared by many different routes. Substituted Pcs can be formed from these phthalonitriles. The most commonly used method for the synthesis of Pc is cyclotetramerization of the phthalonitrile to form a Pc. A Pc offers 16 possible sites for peripheral and non-peripheral substitutions and a central cavity with metal ions and this makes them useful compounds in different fields and them are applied as dye, catalysis in a wide range of areas (2,3) non-linear optics (4), Langmuir-Blodgett thin films (5,6), chemical sensors (7), as photosensitizers in PDT (8-11) and as photocatalysts (12-14). On the other hand, ball-type structures of Pcs were first obtained as a new class of compound by Zefirova

in 2002 (15,16) and both Pcs and their ball-type derivatives (BPcs) have gained significance in a number of fields including their use as photosensitizers in photodynamic therapy (PDT) of cancer (17-20). In this study, a metal-free phthalocyanine, which was obtained accidentally during a reaction between 4-nitrophthalonitrile and resorcinol (1,3-dihydroxybenzene), was investigated photo-physico-chemical behaviors and MCD properties.

EXPERIMENTAL SECTION

Materials and methods

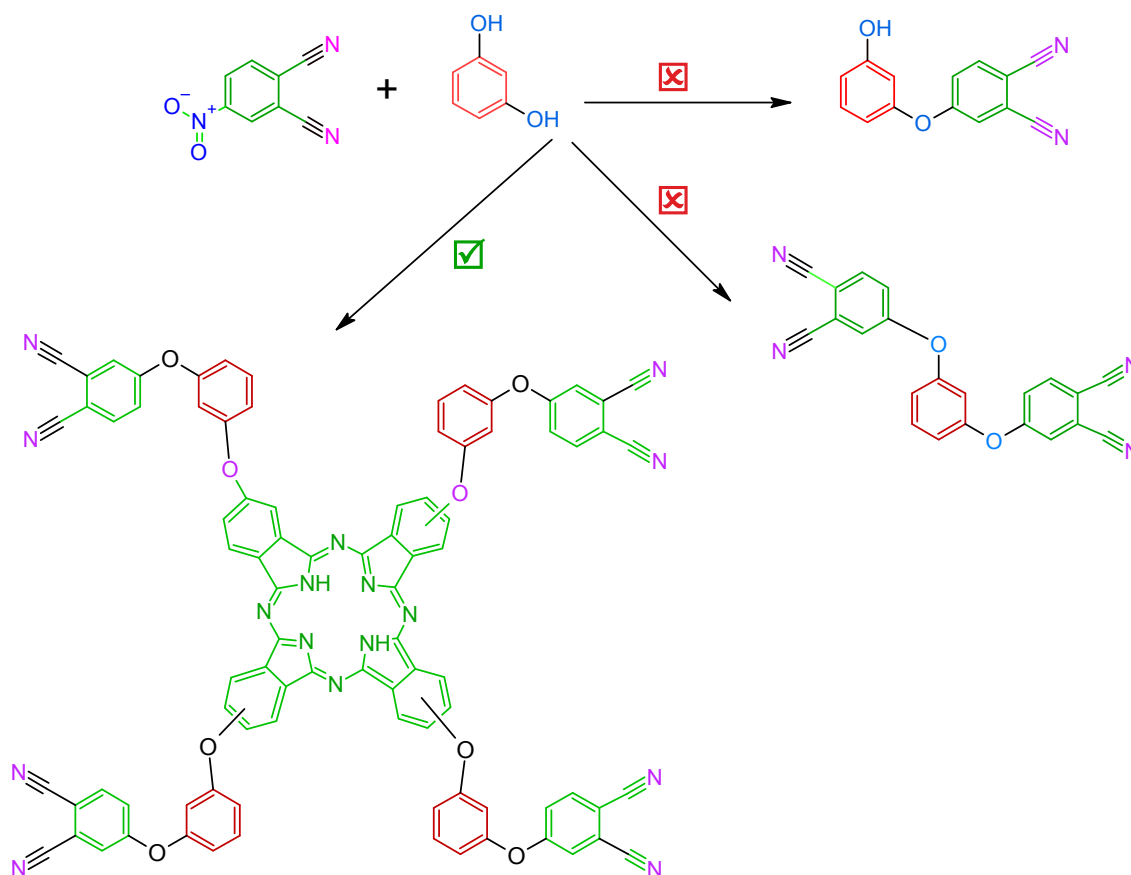
All equipments and chemicals that were used during all experimental and measurements are the same as the paper published earlier in the literature. The photophysical and photochemical properties of metal-free Pc were performed according to methods previously described in the literature (19,20).

Synthesis

Synthesis of 2(3), 9(10), 16(17), 23(24)-tetrakis(4-(3-oxyphenoxy) phthalocyanine (**5**):

Compound **2** (1.272 g, 11.54 mmol) was dissolved in dry DMSO (25 mL) and compound 1 (3.98 g, 23.08 mmol) was added under inert atmosphere. To this reaction mixture finely ground anhydrous potassium carbonate (4.00 g, 28.94 mmol) was added. The color of the mixture changed to the green from light brown while it was continued stirring at the end of 5 days at 70 °C. after a total of 6 days of stirring at this temperature, the entire green reaction mixture was then poured onto cracked ice to produce a precipitate, and the precipitate was washed sequentially with ethanol

and methanol resulting in the formation of a pure green precipitate. Finally, it was purified by silica gel column chromatography using gradient of chloroform, tetrahydrofuran as eluent and metal-free Pc was obtained as a green powder which has mp > 350 °C and is soluble in THF, DMSO, and DMF. Yield 0.069 g. UV-Vis (DMSO): λ_{\max}/nm : 700, 668, 334. IR (ATR): ($\mu_{\max}/\text{cm}^{-1}$), 3296 (Ar-CH), 2238 (CN), 1717 (CO), 1596 (C=C), 1121/1083 (C-O-C). $^1\text{H-NMR}$ (DMSO- d_6): δ , ppm: 7.85–7.00 (40H, Ar-H). Anal. calcd. for $\text{C}_{88}\text{H}_{42}\text{N}_{16}\text{O}_8$: C, 72.82; H, 2.92; N, 15.44, found: C, 72.79; H, 2.88; N, 15.45 %. MALDI-TOF-MS: m/z calcd. 1451.4, found 1453.5 $[\text{M}+2\text{H}]^+$.



Scheme 1. Synthetic pathway for metal-free phthalocyanine (**5**): DMSO, 6 days, K_2CO_3 .

RESULTS AND DISCUSSION**Synthesis and spectroscopic characterization**

A reaction of 4,4'-(1,3-phenylenebis(oxy))diphthalonitrile (**3**) was started for the synthesis of the one which was intended for a BPc (Scheme 1). At the end of the fifth day, a green color was observed in the reaction tube. Metal-free phthalocyanine was obtained accidentally during a reaction which it give two possible products (**3** and **4**) between 4-

nitrophthalonitrile and resorcinol at low temperature. This showed that compound **3** gave quickly metal-free Pc (**5**) by self-condensation; it means that compound **5** occurred unexpectedly under the experimental conditions (21). So, compound **3** was not isolated and characterized (22).

After purification, the novel tetrakis (4-(3-oxyphenoxy) substituted Pc (**5**) was characterized by a handful of common spectroscopic techniques,

including FTIR, ^1H NMR, MALDI-TOF MS and UV-Vis, along with elemental analysis.

FT-IR spectrum of the H_2Pc was obtained with ATR and the spectrum showed $\text{-C}\equiv\text{N}$ stretching at 2238 cm^{-1} . this value confirmed that compound **5** contains cyano end groups as determined by FT-IR spectroscopy. Aromatic C-H at 3296 cm^{-1} , aromatic C=C 1596 cm^{-1} and C-O-C vibrations at $1121/1083\text{ cm}^{-1}$ were observed. The ^1H NMR spectrum of (**5**) showed a multiplicity between 7.85 – 7.00 ppm in deuterated DMSO as the solvent. The inner core protons could not be observed. This may be due to the strong aggregation between the Pc rings. MALDI-TOF result showed the molecular peak of the compound **5** at m/z 1292.57, and also elemental analysis supported compound **5**.

The electronic absorption spectra for Pcs is generally characterized by two bands. One of both,

the Q band is found in the longer wavelengths around 600-700 nm region were responsible for the green color of this complex. The other that are referred to as the B (Soret band). Figure 1 show the typical strong absorption bands. These transitions were assigned to $\pi\text{-}\pi^*$ transition between bonding and antibonding molecular orbitals. In the case of metal-free phthalocyanine, this band generally split into at two components. The B band is located at the shorter wavelengths around 300-400 nm region. B band arises mainly from the π to π^* transition. The Q band results from $\pi \rightarrow \pi^*$ transition that involves a_{1u} to e_g and the Soret band result from the $\pi \rightarrow \pi^*$ transition that involves a_{2u} or b_{2u} to e_g . The non-degenerated e_g level leads to the observed split Q band in the UV-vis spectra for H_2Pc . On the other word, the splitting of the Q band is due to the splitting in the e_g level. In the spectrum of compound **5**, a loss was observed in the geometrically induced splitting between the Q_x and Q_y components (23).

Table 1: Photophysical and photochemical data of the Pc.

Compound	λ_{Abs}	λ_{Ems}	λ_{Exc}	λ_{Stokes}	Φ_{F}	Φ_{T}	Φ_{Δ}	$\tau_{\text{T}}(\text{ns})$	$\tau_{\text{T}}(\mu\text{s})$	$\Phi_{\text{d}}(\times 10^{-6})$
H₂Pc	668/700	709	701	9	0.06	0.81	0.19	4.65	40	1.959

MCD is used as an optical technique for the detection of the electronic structure of both ground and excited states (24). MCD can give information on the relative size of the ΔHOMO and ΔLUMO . Figure 1 shows the absorption and MCD spectra of compound **5** dissolved in DMSO. When the optical activity of compound **5** was investigated, a slight deviation was observed because its Q band showed less splitting, improved which this is attributed to its low symmetry as C_{2v} is isomer. The B_0 term appeared +320 nm and -370 nm. Faraday A term showed positive and negative sign since the excited state is orbitally degenerated. In the MCD spectrum, it was observed as a negative sign at -662 nm and -691nm.

Figure 2 shows the absorption, emission, and excitation spectra of compound **5** in DMSO. The spectral data are listed in Table 1. Fluorescence emission peaks was observed at 709 nm for **5**. The fluorescence quantum yield (Φ_{F}) value is 0.06 which is predicted for aggregated Pcs. Table 1 also shows Φ_{T} , Φ_{d} , τ_{F} and τ_{T} values of **5**. The high triplet state quantum yield value (Φ_{T}) is 0.81. The Φ_{T} value suggests more efficient intersystem crossing (ISC), corresponding to low Φ_{F} values. The values of compound **5** are 0.75 for ISC, 4.65 ns for fluorescence lifetime and 40 μs for triplet lifetime. A triplet decay curve of change in

absorbance (ΔA) versus time in seconds is obtained from the experiment and from this the triplet lifetime can be determined as shown in Figure 3. All this data may indicate metal-free structure including aggregations.

Figure 4 shows spectral changes obtained during photolysis of complexes with increasing time from 0 to 140 seconds in the presence of DPBF and the results are summarized in Table 1. DPBF degradation of the complexes **5** at 414 nm was monitored with UV-Vis spectrophotometry. There were no changes in the Q band intensities during these determinations, which is indicative of the fact that compound **5** is not degraded during singlet oxygen studies. The Φ_{Δ} value is 0.19. Although high triplet oxygen quantum yields of the phthalocyanine complex, accompany high singlet oxygen quantum yield, the compound gave a lower value of singlet oxygen quantum yield. This can be due to aggregation.

The photodegradation quantum yield value (Φ_{d}) of compound **5** was obtained by decrease in the intensities of the Q band under irradiation with increasing time from 0 to 60 minutes and the Φ_{d} was found as 1.959×10^{-6} . This result showed that the Pc is of high stability in DMSO (Figure 5).

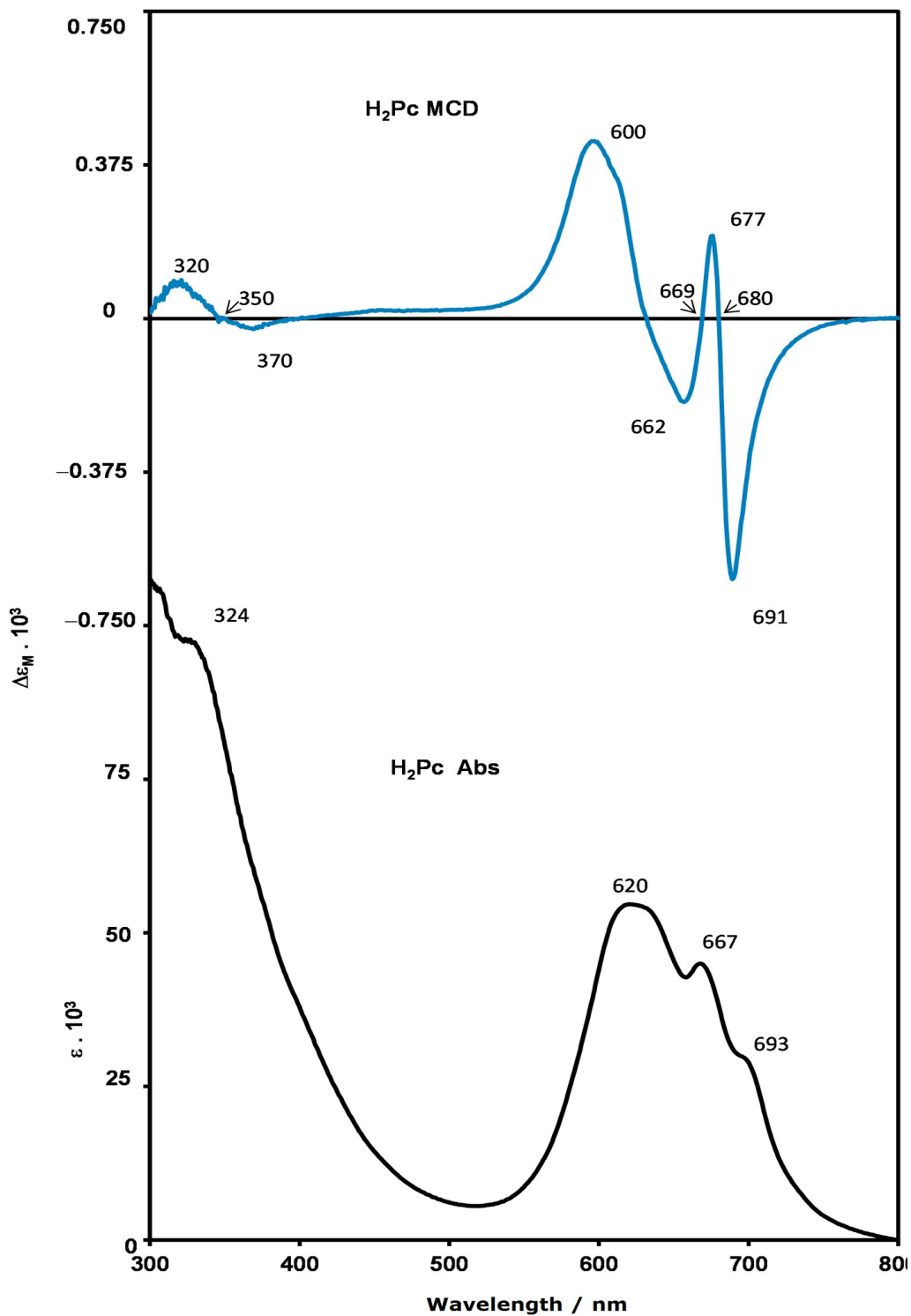


Figure 1. MCD (top) and UV-Vis (bottom) spectra for metal-free Pc.

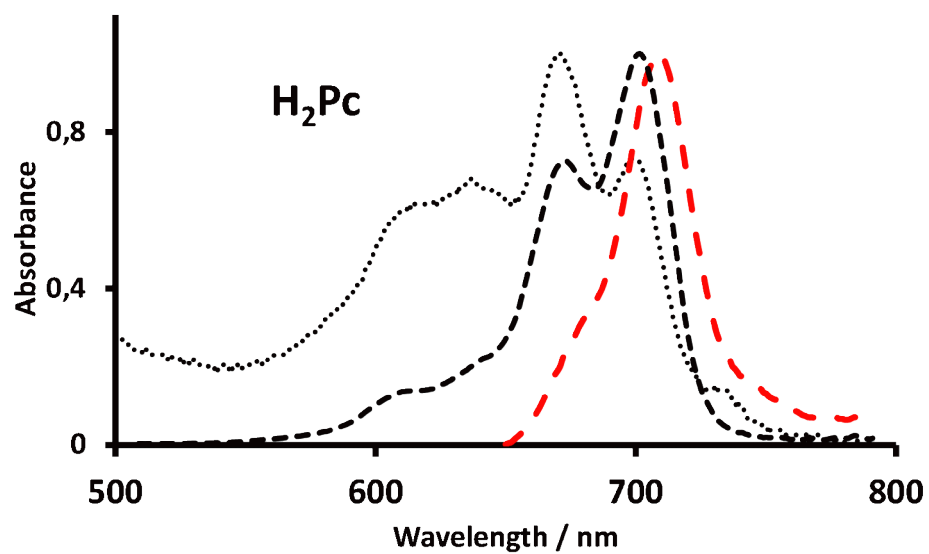


Figure 2. Absorption round dot line (black), excitation square dot line (black), and emission spectra dash line (red) of compound **5** $\lambda_{exc} = 606$ nm.

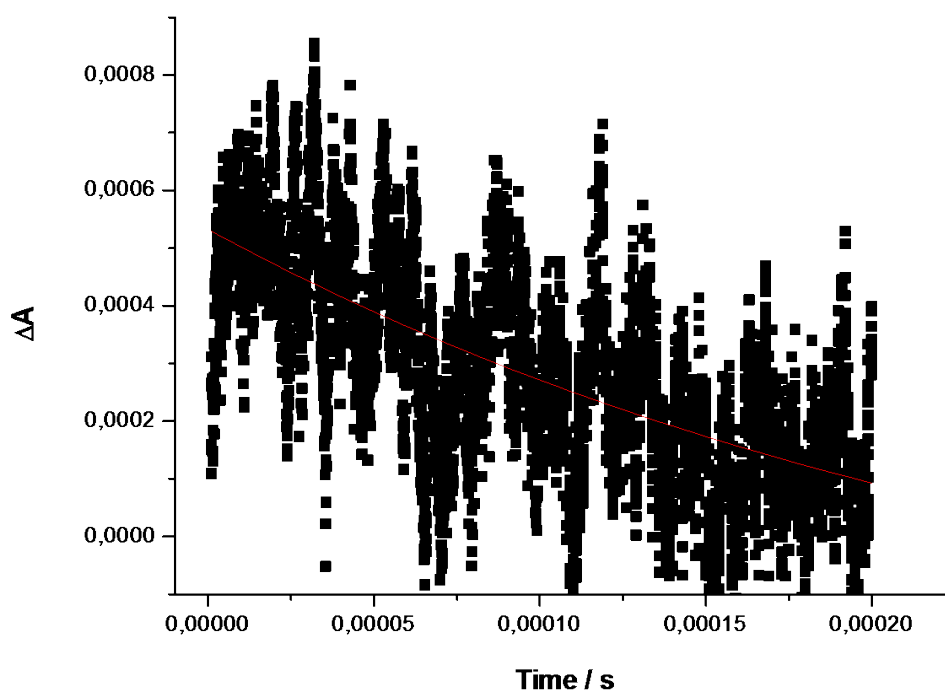


Figure 3. Triplet absorption decay curve for metal-free Pc.

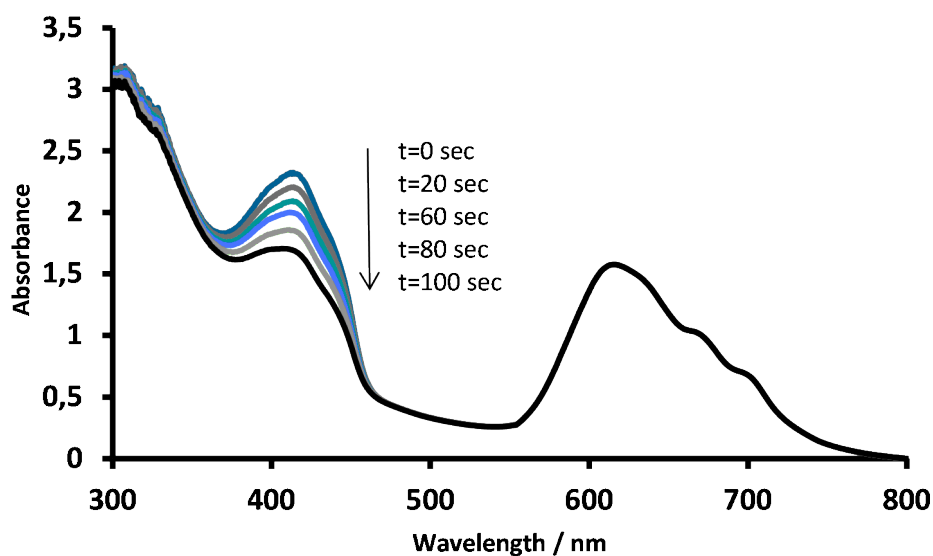


Figure 4. Time-dependent photobleaching of DPBF absorption in the presence of metal-free Pc in DMSO.

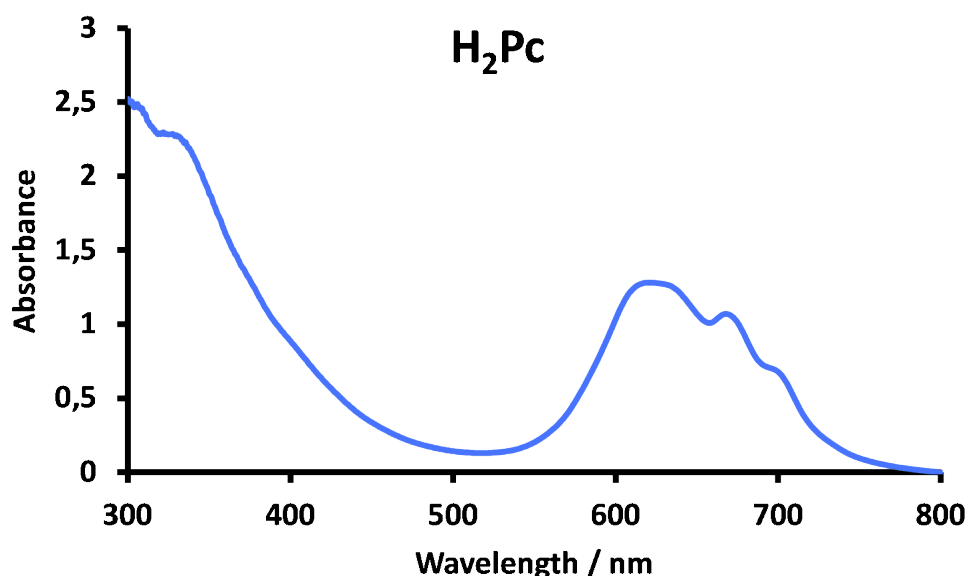


Figure 5: The spectra of photodegradation for metal-free Pc in DMSO.

CONCLUSION

β -substituted metal-free phthalocyanine which was obtained accidentally at 70 °C in DMSO was obtained. The molecules have high photostabilities. The photophysical behavior was found suitable for photodynamic therapy activity of the unmetallated phthalocyanine. The reaction is rapid enough to proceed at very low temperatures for phthalocyanine formation. Unfortunately, formation of side products leads to low yields. The Q band of metal free Pc displays a slight deviation showing less splitting, attributed to lower symmetry as well as is also attributed to aggregation.

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