



Novel lanthanide metallophthalocyanines bearing iodine group and their singlet oxygen generation ability

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Abstract: In this study, five novel mono rare earth metallo phthalocyanine derivatives (**1a-e**) were synthesized by cyclotetramerization of 4-iodophthalonitrile and corresponding metal salts. These novel compounds were characterized by FT-IR, elemental analyses, UV-Vis, and MALDI-TOF spectral data. Moreover, the ability of singlet oxygen generation and aggregation behavior of these phthalocyanines were investigated in dimethyl sulfoxide using UV-Vis spectroscopy. Gadolinium metallo phthalocyanine has the best singlet oxygen quantum yield and it can be a potential candidate for the photodynamic therapy (PDT) of cancer.

Keywords: Phthalocyanine, Iodine, Lanthanide, Singlet Oxygen.

Submitted: December 16, 2021. **Accepted:** May 13, 2022.

Cite this: Köksoy B. Novel lanthanide metallophthalocyanines bearing iodine group and their singlet oxygen generation ability. JOTCSA. 2022;9(3):741-50.

DOI: <https://doi.org/10.18596/jotcsa.1037664>.

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INTRODUCTION

Phthalocyanine compounds (Pcs) and their derivatives are a family of aromatic molecules which are delocalized with an 18- π electron system and they have been comprehensively studied in many areas as chemical sensors (1, 2), liquid crystals (3), solar cell applications (4, 5), photodynamic therapy (PDT) (6-8) and catalysts (9). In recent years, they have been used as a photosensitizer in photodynamic therapy (PDT) because of their high singlet oxygen generation ability and good photostability (10, 11). The main problem of phthalocyanines is poor solubility in common organic solvents. To overcome this problem, it can be decorated with some non-polar/polar groups on the Pc core (12, 13). Another disadvantage of these compounds is called "aggregation" which means they stack on each other in the solvent and affect the photochemical properties. Also, Pc aggregation

is another limitation in their applications which drastically decreases their fluorescence quantum yields, shortens their triplet state lifetime, and reduces their photosensitizing efficiency, especially in aqueous media.

Peripheral substitution of the macrocyclic ring with halogen groups leads to phthalocyanine products which are soluble in common organic solvents (14). Moreover, it is anticipated that the introduction of halogen/ester groups into a moiety of phthalocyanine compound will induce high solubility in organic solvents and improved photosensitizer activity of Pcs for PDT (15-19).

For phthalocyanine photosensitizers, the metal atom is very important to singlet oxygen generation and PDT applications, incorporating zinc(II), indium(III), aluminum(III), gallium(III), and silicon(IV) (20, 21). On the other hand, the number of phthalocyanines

including lanthanide metals in the literature is rare for PDT applications.

Phthalocyanines containing lanthanide series metal atoms have been studied by scientists for a long time. Double-decker and triple-decker phthalocyanines containing lutetium or europium metals were synthesized and various applications were studied (22-23). Additionally, the synthesis of homoleptic and heteroleptic complexes containing rare earth elements is also available in the literature (24-25). It has been reported that rare earth element phthalocyanine complexes are used in electrochromic materials (22) liquid crystal (26), nonlinear optics (25) and optoelectronic materials applications.

According to this information, the aim of this study is to synthesize and characterize novel phthalocyanines containing lanthanide metal atoms (Eu, Sm, Gd, Tb, Dy) and bearing iodine groups that may have high production of singlet oxygen.

EXPERIMENTAL

General Information

1,3-diphenylisobenzofuran (DPBF), 4-iodophthalonitrile, Ln(OAc)₃ metal salts, and other chemicals/reagents were purchased from Aldrich. All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers.

FT-IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer. Positive ion and linear mode MALDI-TOF-MS of Pcs were obtained in 1,8,9-anthracenetriol (DIT) as a MALDI matrix using nitrogen laser accumulating 50 laser shots using Bruker Microflex LT MALDI-TOF mass spectrometer. Absorption spectra in the UV-visible region were recorded with a Shimadzu 2101 UV-Vis spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm path length cuvettes at room temperature.

Photo-irradiations were done using a General Electric quartz line lamp (300 W). A 600 nm glass cut-off filter (Schott) was used to filter off ultraviolet and low wavelength visible parts of the spectrum. A water filter was also used to filter off infrared radiations. An interference filter (Intor, 670 nm with a bandwidth 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

Synthesis

All lanthanide series metallo-phthalocyanines were synthesized from 4-iodophthalonitrile and Ln(OAc)₃ metal salts in n-pentanol/DBU solvent-base system at reflux. Phthalocyanine compounds (**1a-e**) including iodine groups were recovered in pure form with column chromatography using dichloromethane-ethanol as eluent. All these phthalocyanine derivatives were fully characterized by spectroscopic methods such as FT-IR, UV-Vis, fluorescence, MALDI-TOF, and elemental analyses as well.

General synthesis of mono-phthalocyanine derivatives (**1a-e**)

4-Iodophthalonitrile (0.1 g, 0.393 mmol) and lanthanide metal salt (50 mg, 0.075 mmol samarium(III) acetate monohydrate for SmPc; 50 mg 0.076 mmol europium (III) acetate monohydrate for EuPc; 50 mg, 0.074 mmol gadolinium(III) acetate monohydrate for GdPc; 50 mg, 0.074 mmol terbium (III) acetate monohydrate for TbPc; and 50 mg, 0.073 mmol dysprosium(III) acetate monohydrate for DyPc) were stirred and heated in sealed tubes at reflux temperature in 24 h. After one day, the greenish solutions were poured into 50 mL of hot methanol. The greenish precipitates were centrifuged and washed several times with hot water, ethyl acetate, and diethyl ether, and then all mono-Pcs were separated by column chromatography on silica gel using dichloromethane-ethanol as eluent, and final products were dried in the vacuum.

2(3),9(10),16(17),23(24)- Tetra(iodo)phthalocyaninatosamarium (III) acetate (**1a**)

Yield: 35 mg (29%), Chemical Formula: C₃₄H₁₅N₈O₂I₄Sm, FT-IR(ATR), $\nu_{\max}/\text{cm}^{-1}$: 3090-3059 (Aromatic-CH), 2949-2854 (Aliphatic-CH), 1716 (C=O, acetate), 1583-1491 (C=C), 818 (Ar-I), UV-Vis (DMSO): λ_{\max} nm (log ϵ): 356 (4.93), 616 (4.36), 684 (5.08), Anal. Calc. for C₃₄H₁₅N₈O₂I₄Sm, C: 33.32, H: 1.23, N: 9.14%, Found: C: 33.28; H: 1.19, N: 9.11%; MS(MALDI-TOF) (DHB): 1166.13 (M-OAc)⁺, 1320.61 (M-OAc+DHB)⁺.

2(3),9(10),16(17),23(24)- Tetra(iodo)phthalocyaninatoeuropium (III) acetate (**1b**)

Yield: 30 mg (24.8%), Chemical Formula: C₃₄H₁₅N₈O₂I₄Eu, FT-IR(ATR), $\nu_{\max}/\text{cm}^{-1}$: 3088-3057 (Aromatic-CH), 2949-2851 (Aliphatic-CH), 1718 (C=O, acetate), 1585-1490 (C=C), 819

(Ar-I), UV-Vis (DMSO): λ_{\max} nm (log ϵ): 346 (4.86), 617 (4.35), 684 (5.11) Anal. Calc. for $C_{34}H_{15}N_8O_2I_4Eu$, C: 33.28, H: 1.23, N: 9.13%, Found: C: 33.22; H: 1.21, N: 9.12%, MS(MALDI-TOF) (DHB): 1168.23 (M-OAc)⁺, 1322.55 (M-OAc+DHB)⁺.

*2(3),9(10),16(17),23(24)-
Tetra(iodo)phthalocyaninatogadolinium (III)
acetate (1c)*

Yield: 42 mg (34.6%), Chemical Formula: $C_{34}H_{15}N_8O_2I_4Gd$, FT-IR(ATR), ν_{\max}/cm^{-1} : 3089-3058 (Aromatic-CH), 2948-2854 (Aliphatic-CH), 1719 (C=O, acetate), 1581-1488 (C=C), 820 (Ar-I), UV-vis (DMSO): λ_{\max} nm (log ϵ): 356 (4.80), 617 (4.36), 685 (5.11), Anal. Calc. for $C_{34}H_{15}N_8O_2I_4Gd$, C: 33.14, H: 1.23, N: 9.09%, Found: C: 33.12; H: 1.20, N: 9.05%, MS(MALDI-TOF) (DHB): 1173.44 (M-OAc)⁺, 1327.33 (M-OAc+DHB)⁺.

*2(3),9(10),16(17),23(24)-
Tetra(iodo)phthalocyaninatoterbium (III)
acetate (1d)*

Yield: 39 mg (32.1%), Chemical Formula: $C_{34}H_{15}N_8O_2I_4Tb$, FT-IR(ATR), ν_{\max}/cm^{-1} : 3088-3059 (Aromatic-CH), 2947-2852 (Aliphatic-CH), 1719 (C=O, acetate), 1580-1491 (C=C), 821 (Ar-I), UV-Vis (DMSO): λ_{\max} nm (log ϵ): 352 (4.95), 619 (4.42), 686 (5.11), Anal. Calc. for $C_{34}H_{15}N_8O_2I_4Tb$, C: 33.09, H: 1.23, N: 9.08%, Found: C: 33.01; H: 1.17, N: 9.04%, MS(MALDI-TOF) (DHB): 1175.22 (M+H-OAc)⁺, 1329.19 (M+H-OAc+DHB)⁺.

*2(3),9(10),16(17),23(24)-
Tetra(iodo)phthalocyaninatodysprosium (III)
acetate (1e)*

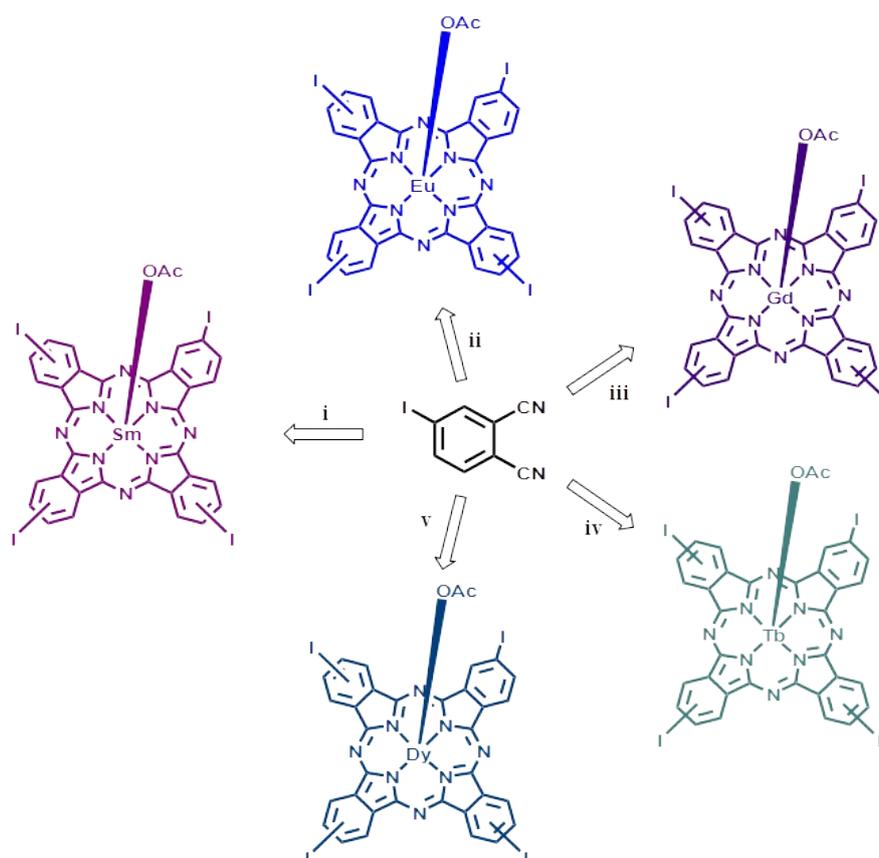
Yield: 33 mg (27.1%), Chemical Formula: $C_{34}H_{15}N_8O_2I_4Dy$, FT-IR(ATR), ν_{\max}/cm^{-1} : 3089-3061 (Aromatic-CH), 2949-2853 (Aliphatic-CH), 1720 (C=O, acetate), 1584-1488 (C=C), 820 (Ar-I), UV-Vis (DMSO): λ_{\max} nm (log ϵ): 356 (4.79), 617 (4.38), 686 (5.10). Anal. Calc. for $C_{34}H_{15}N_8O_2I_4Dy$, C: 33.00, H: 1.22, N: 9.05%, Found: C: 32.98; H: 1.18, N: 9.03%, MS(MALDI-TOF) (DHB): 1178.45 (M-OAc)⁺, 1332.67 (M-OAc+DHB)⁺.

RESULT AND DISCUSSION

The synthetic pathway of novel lanthanide series phthalocyanines was figured out in Scheme 1. The final products were obtained by 4-iodophthalonitrile and corresponding $Ln(OAc)_3$ metal salts with catalytic amount DBU in the solvent of n-pentanol. All synthesized phthalocyanines were characterized by using various spectroscopic characterization techniques such as ground state electronic spectra, FT-IR, MALDI-TOF, and elemental analysis. The obtained results from these techniques are compatible with the proposed structures for all the newly prepared compounds.

CHARACTERIZATION

The vibrational peak appeared at 2230 cm^{-1} for 4-iodophthalonitrile was disappeared in the FT-IR spectra of metallophthalocyanines **1a-e** as expected. This is an important clue concerning the formation of the phthalocyanine macrocycle from the corresponding phthalonitriles. The typical carbonyl (acetate group) vibration was observed in the range of 1720-1716 cm^{-1} for all metallophthalocyanines (**1a-e**). The aromatic-CH and aliphatic-CH stretching peaks for all synthesized phthalocyanines were appeared between 3090-3057 cm^{-1} and 2949-2852 cm^{-1} regions, respectively. Also, other typical bands Ar-C=C and Ar-I were monitored at 1585-1488 cm^{-1} , 821-818 for novel lanthanide(III) phthalocyanines. The MALDI-TOF spectra of **1a-e** were recorded using a 2,5-dihydroxybenzoic acid matrix and given in Figure-1. All the lanthanide(III) phthalocyanine compounds showed (M⁺-OAc) and (M⁺-OAc+DHB) peaks. The values of molecular ion peaks (*m/z*) were monitored at 1166.13 and 1320.61 Da for **1a**, 1168.23, and 1322.55 Da for **1b**, 1173.44 and 1327.33 Da for **1c**, 1175.22 and 1329.19 Da for **1d**, 1178.45 and 1332.67 Da for **1e**.



i) $\text{Sm}(\text{OAc})_3$, 1-pentanol, DBU, reflux, 12 h ii) $\text{Eu}(\text{OAc})_3$, 1-pentanol, DBU, reflux, 14 h, iii) $\text{Gd}(\text{OAc})_3$, 1-pentanol, DBU, reflux, 10 h, iv) $\text{Tb}(\text{OAc})_3$, 1-pentanol, DBU, reflux, 12 h, v) $\text{Dy}(\text{OAc})_3$, 1-pentanol, DBU, reflux, 14 h.

Scheme 1: Synthetic route of mono lanthanide metallophthalocyanines (**1a-e**).

UV-Vis and Aggregation

For the phthalocyanine macrocycles, there are two main transitions known as $\pi-\pi^*$ in the UV-Vis spectrum. These transitions named as Q and B band are generally found at 300-450 nm and 650-850 nm, respectively. In this work, synthesized metallo-phthalocyanine derivatives exhibited a sharp-single Q band at the range of 684-686 nm in the DMSO solvent. Also, B bands of these phthalocyanines were observed within the range of 346-356 nm. Aggregation is a phenomenon that occurs when two or more compounds stack on top of each other, encountered in macrocyclic structures or planar compounds with n electrons. Whereas this

phenomenon is an advantage in applications such as energy transfer, it is a disadvantage in healthcare applications such as PDT. For this reason, it is important data that the photosensitizer to be used in PDT applications does not show aggregation.

In this study, the aggregation attitudes of all lanthanide phthalocyanines including iodine atom (**1a-e**) were examined at 2-12 μM in DMSO (Figure-2). The Beer-Lambert law was fitted for studied phthalocyanines (**1a-e**) at 12 to 2 μM concentration range and there was no aggregation behavior of these lanthanide metallophthalocyanines in DMSO.

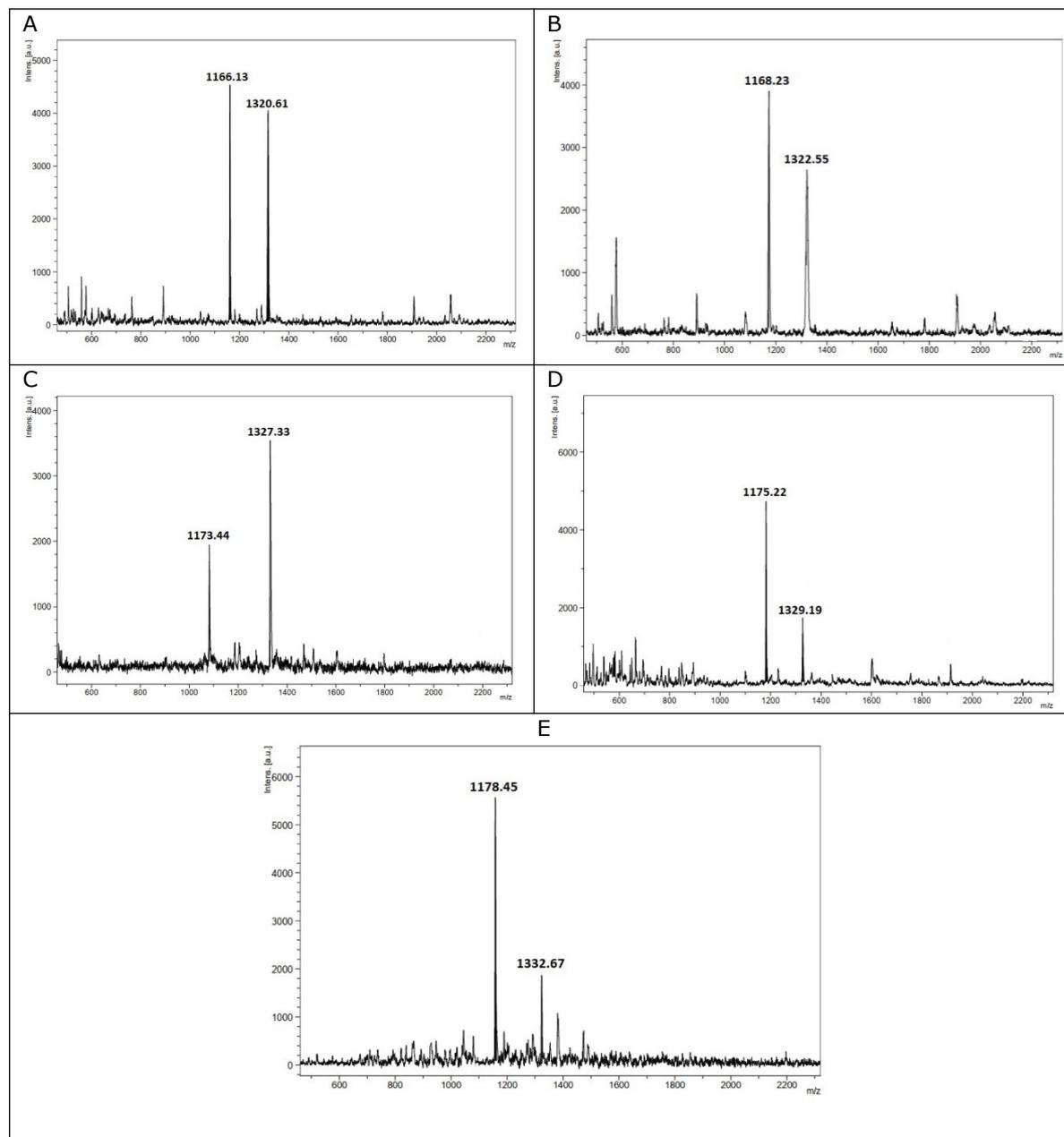


Figure 1: Maldi-TOF mass spectra of synthesized lanthanide metallophthalocyanines using DHB as a matrix (A: compound **1a**, B: compound **1b**, C: compound **1c**, D: compound **1d**, E: compound **1e**).

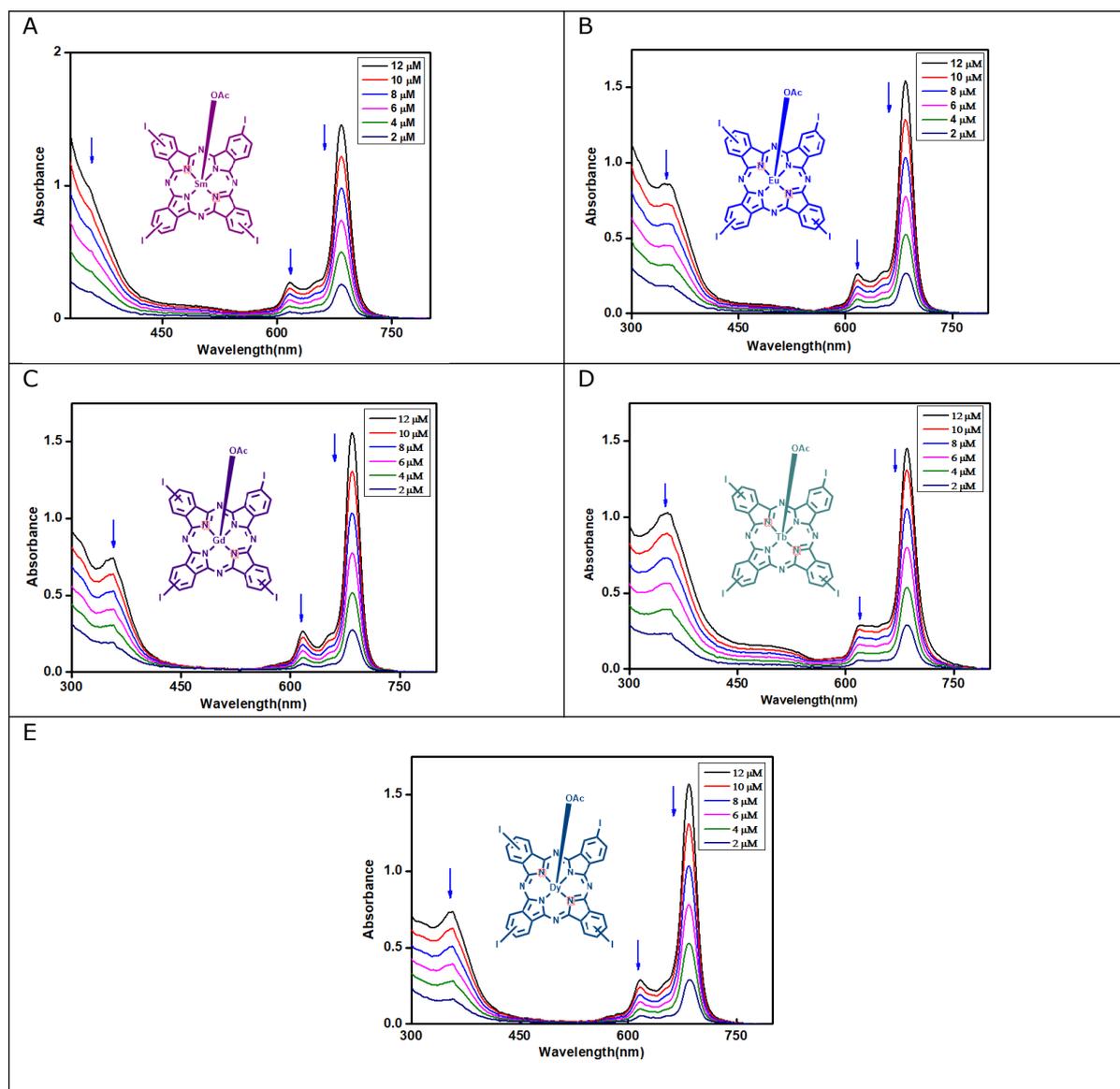


Figure 2: UV-Vis spectra of lanthanide metallophthalocyanines (**1a-e**) in DMSO at different concentration (2-12 ppm) (A: compound **1a**, B: compound **1b**, C: compound **1c**, D: compound **1d**, E: compound **1e**).

Singlet Oxygen Generation

Photodynamic therapy (PDT) which is based on the destruction of cancer cells by singlet oxygen, is a new treatment for cancer disease. This process consists of three important basic stones, "light, oxygen, and photosensitizer". It is believed that during photosensitization, the electrons of the photosensitizer are excited by the light and pass to the triplet state (intercrossing systems) and transfer their energy to molecular oxygen for occurring the singlet

oxygen. These reactive types of oxygen which are called "singlet oxygen" kill the cancer cells.

The Φ_{Δ} for compound (**1a-e**) were studied and calculated in DMSO by a chemical method using 1,3-diphenylisobenzofuran (DPBF) as a quencher. The decreasing of DPBF at 417 nm was observed using a UV-Vis spectrophotometer. The Φ_{Δ} value of compound **1a-e** was found lower than standard zinc (II) (StdZnPc) except compound **1c** in DMSO as given in Figure 3.

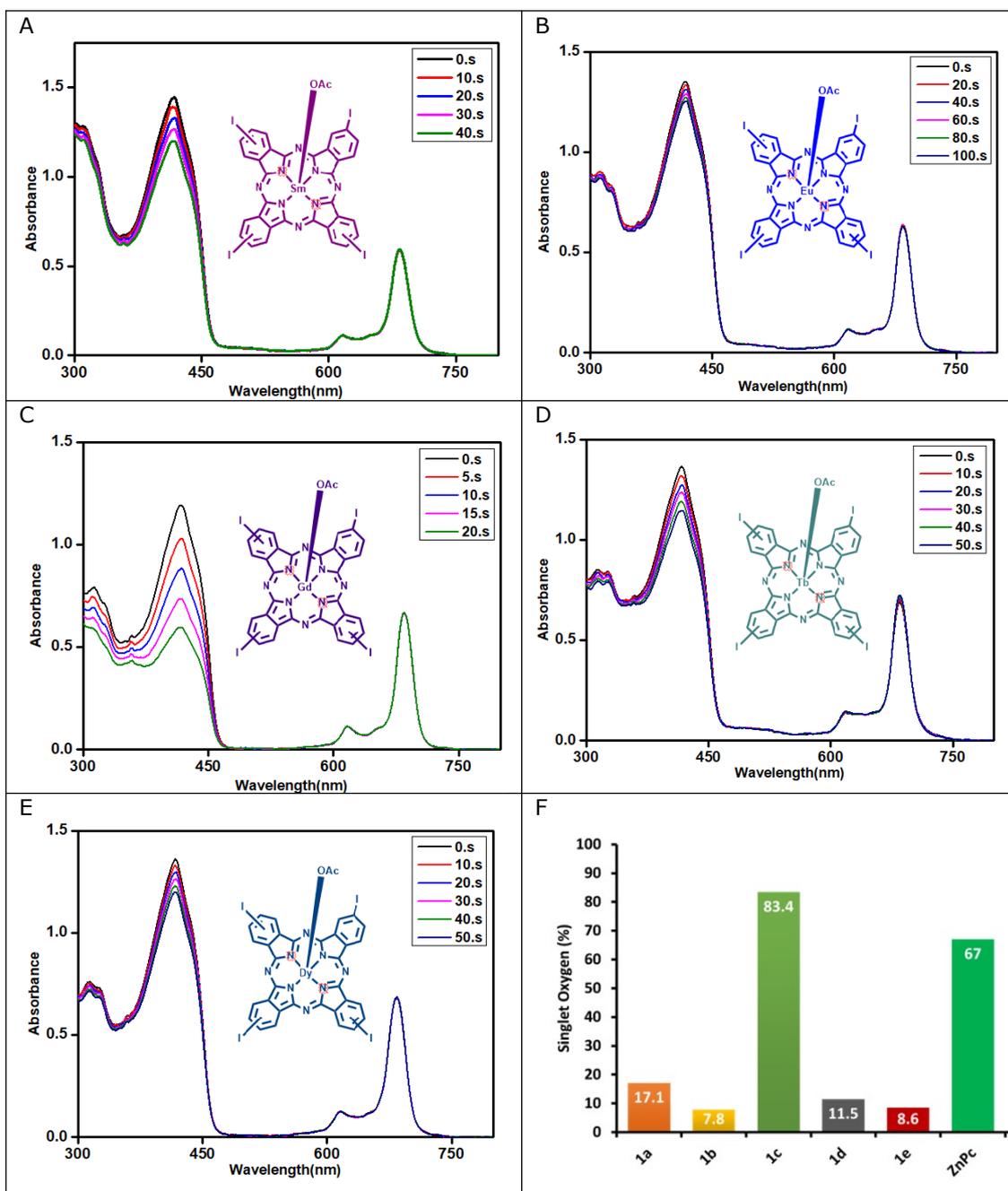


Figure 3: The absorption spectral changes during the determination of singlet oxygen quantum yields. This determination was for all compounds (**1a-e**) in DMSO at a concentration of 1×10^{-5} M (A: compound **1a**, B: compound **1b**, C: compound **1c**, D: compound **1d**, E: compound **1e**) and bar graphic of singlet oxygen quantum yields of synthesized mono lanthanide metallophthalocyanines (F).

Normally, singlet oxygen quantum yields of photosensitizers containing heavy atoms such as bromine or iodine are higher than other types. However, the metal atom in the center of the phthalocyanine nucleus has a great effect

on the electrons that pass into the triplet level. As seen in this study, the singlet oxygen values of compounds **1a**, **1b**, **1d**, and **1e**, which contain metals from the lanthanide series in their center, were measured low despite the

presence of iodine in their structure. The tetraiodophthalocyanine derivative containing only gadolinium metal in its center produced singlet oxygen much better than both its own species and the standard zinc(II) phthalocyanine derivative. The reason for this can be related to the spherically symmetrical property of gadolinium metal, which has similar examples in the literature (27, 28).

ACKNOWLEDGMENT

Synthesis and measurements were performed at Gebze Technical University, and I want to thank Prof. Dr. Mahmut DURMUS.

CONCLUSION

As a result, the singlet oxygen generation properties of five phthalocyanine building block compounds with lanthanide series metal atom in its center and iodine as heavy atom in its peripheral position were investigated in this study. It was determined that the gadolinium phthalocyanine derivative produced the highest singlet oxygen obtained from the macrocyclic phthalocyanine compounds. The singlet oxygen quantum yields of the other four phthalocyanine derivatives were quite low. It has also been observed that these compounds did not produce fluorescence due to both the heavy atom effect and the effect of the metal atoms in the center.

The important part of the study in terms of literature is that these compounds can easily be modified with important reactions using different catalysts. Important and useful reactions such as Sonogashira, Suzuki, and Heck cross-coupling reactions can be performed over the iodine atom in the peripheral position, and the physical and chemical properties of these phthalocyanines can be changed as desired. In addition, gadolinium phthalocyanine compound, which has the highest singlet oxygen quantum yield, can be made a more effective photosensitizer candidate by attaching it with water-soluble groups, which is especially important for PDT, and a potential PDT agent.

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