Inorganic Chemistry Communications 118 (2020) 107998

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

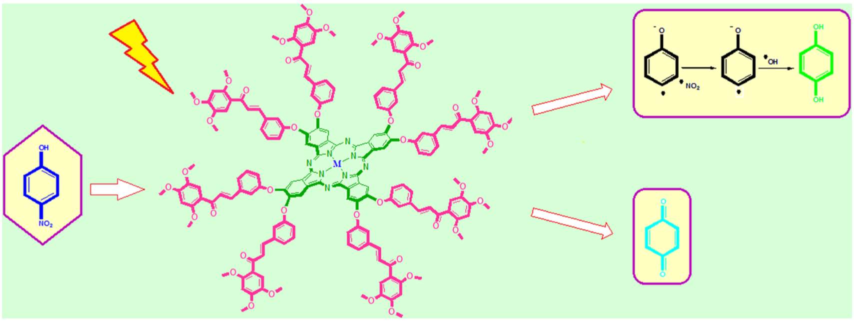
Short communication

Design, syntheses, spectroscopic, aggregation properties of novel peripheral octa-substituted zinc(II), magnesium(II) and lead(II) phthalocyanines and investigation of their photocatalytic properties on the photooxidation of 4-nitrophenol

Halise Yalazan, Kader Tekintas, Vildan Serdaroğlu, Ece Tugba Saka, Nuran Kahriman, Halit Kantekin*

Department of Chemistry, Faculty of Sciences, Karadeniz Technical University, Trabzon, Turkey

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Syntheses
Chalcone
4-nitrophenol
Phthalocyanines
Photodegradation

ABSTRACT

In the present paper, the syntheses, spectroscopic characterization, aggregation behaviours and photocatalytic properties of phthalocyanine compounds were searched. Octa-substituted phthalocyanines (Zn^{II} (***Pc*-Zn**), Mg^{II} (***Pc*-Mg**) and Pb^{II} (***Pc*-Pb**)) with eight peripheral (*E*)-3-(3-hydroxyphenyl)-1-(2,4,5-trimethoxyphenyl)prop-2-en-1-one groups were synthesized by cyclotetramerization. The spectral properties of these compounds were carried out that used widespread spectroscopic techniques. Later on, aggregation properties of synthesized phthalocyanines were examined in polar and apolar solvents. In addition to this, the photocatalytic activities of new synthesized metallophthalocyanines containing various central metal ions (zinc (II), magnesium (II) and lead (II)) were investigated. Three different metal centered phthalocyanines have been prepared for the photodegradation of 4-nitrophenol. In the photodegradation reactions that carried out in the photoreactor for 1 h without using any oxidant, 4-nitrophenol compound was completed with 90% (for Pb^{II} (***Pc*-Pb**)), 56% (for Zn^{II} (***Pc*-Zn**)) and 12% (for Mg^{II} (***Pc*-Mg**)) conversion from toxic species to non-harmful species and unknown intermediates. The turnover numbers were determined as 1500 for Pb^{II} (***Pc*-Pb**), 933 for Zn^{II} (***Pc*-Zn**).

---

* Corresponding author at: Department of Chemistry, Karadeniz Technical University, 61080 Trabzon, Turkey.
E-mail address: halit@ktu.edu.tr (H. Kantekin).

https://doi.org/10.1016/j.inoche.2020.107998
Received 4 April 2020; Received in revised form 21 May 2020; Accepted 2 June 2020
Available online 04 June 2020
1387-7003/ © 2020 Elsevier B.V. All rights reserved.

1. Introduction

Phthalocyanines (Pcs) containing four isoiminoindole units are planar aromatic macrocyclic compounds having 18-π electron system [1]. Because of their unique optical, electronic, structural and catalytic properties, Pcs have been examined comprehensively in recent years [2]. In addition, phthalocyanines have many technological application areas such as photodynamic therapy, catalyst and photocatalytic, liquid crystals, antimicrobial properties, DNA photocleavage and anti-cancer activity [3–9].

Aggregation is an important factor for phthalocyanine compounds, because it prevents the usage of phthalocyanine in many application areas. Two types aggregation is observed in the substituted phthalocyanines. These are called H-aggregation (face-to-face) and J-aggregation (side-to-side) [1,10]. In general, while aggregation ensues in a decrease in intensity of the Q band a new, broader and blue-shifted or red-shifted band is seen to increase in intensity. The H-aggregation is seen a lower wavelength shift in Pcs. On the contrary, the J-aggregation corresponding to red-shifted is observed a higher wavelength shift and is rarely seen in phthalocyanines [11–15]. The insolubility of phthalocyanines in common organic solvents is another important factor. The solubility of phthalocyanines can be enhanced by binding bulky substituents such as crown ether, long chain groups, phenoxy, alkylthio, alkoxy, and alkyl groups on the non-peripheral and peripheral positions to phthalocyanine ring [16–18]. Therefore, methoxylated chalcone group was chosen to hinder the aggregation behavior and to enhance solubility of the Pcs compounds in this work [19].

Chalcones area medically privileged compounds [20]. They are used in many modern applications such as photodynamic therapy, nonlinear optical devices, electrochemistry, biomedical, catalytic and applications. [21–25].

Photocatalysis has been acknowledged as hopeful method for water and air purification and since then, it has been examined comprehensively as an alternative to presently used technologies [26,27]. 4-Nitrophenol (4-NP) is a precedence pollutant listed by the USEPA on account of its great toxicity to the global environment and human health, even at low concentrations [28,29]. Of date, diverse techniques for the degradation of 4-NP from wastewater have been notified such as wet air oxidation degradation, biodegradation and photocatalytic degradation [30,31]. Phthalocyanine compounds become promising candidate as the metal centers as well as nitrogen active sites are responsible for redox reactions that give rise to the pseudo capacitive behavior [32–38].

In our previous studies, we synthesized phthalocyanine compounds peripheral and non-peripheral tetra substituted with methoxylated chalcone group [39,40]. We wondered how substitution different positions of methoxy group on the chalcone skeleton impress photocatalytic properties of phthalocyanine compounds. Hence, in present study, we synthesized nonaggregated, organo-soluble, octa-substituted metallophthalocyanines (Zn^{II} (***Pc*-Zn**), Mg^{II} (***Pc*-Mg**) and Pb^{II} (***Pc*-Pb**)) (see Scheme 1). We have also researched the photocatalytic activities of these new metallophthalocyanines.

2. Experimental

The photodegradation procedure, equipment, the remaining figures and materials were given as Supplementary Information.

2.1. Syntheses

2.1.1. 4,5-bis(3-((E)-3-oxo-3-(2,4,5-trimethoxyphenyl)prop-1-enyl) phenoxy)phthalonitrile (3)

(E)-3-(3-hydroxyphenyl)-1-(2,4,5-trimethoxyphenyl)prop-2-en-1-one (**1**) (1.50 g, 4.77 mmol) and 4,5-dichlorophthalonitrile (**2**) (0.47 g, 2.39 mmol) were dissolved in 10 mL dry dimethylformamide. Then by, finely ground anhydrous K_2CO_3 (1.97 g, 14.30 mmol) was added portion-wise over a period of 30 min to the mixture. The obtained mixture was heated to 55 °C and left to stir for 5 days under the nitrogen stream in a Schlenk system. During the entire reaction, mixture was controlled with TLC used chloroform/ethanol (10:1) solvent system and accordingly, the progress of the reaction was terminated. The mixture was poured into crushed ice and mixed under room conditions for about 1 h. Immediately after, the formed solid precipitates were filtered and dried in vacuo. Purification of the formed solid phthalonitrile was carried out by column chromatography method. In conclusion, title product (**3**) was obtained as yellow solid.

Yield: 74% (1.32 g), solvent of column chromatography: chloroform, m.p: 123–125 °C. FT–IR (ATR), υ_{max} (cm^{-1}): 3075(Ar−H), 2934–2835 (Aliph. C−H), 2228 ($C\equiv N$), 1650, 1573, 1501, 1464, 1437, 1353, 1267, 1207–1142 (Ar−O−Ar), 1075, 972, 858, 787, 753. ^{1}H NMR (400 MHz, DMSO-d_6), (δ:ppm): 7.88–7.83 (d, 2H, =CH−), 7.63 (d, 2H, −CH=), 7.59 (s, 1H, Ar−H), 7.56 (s, 1H, Ar−H), 7.54 (s, 1H, Ar−H), 7.50 (s, 1H, Ar−H), 7.49–7.45 (m, 2H, Ar−H), 7.18–7.15 (m, 2H, Ar−H), 6.79 (s, 2H, Ar−H), 6.77–6.76 (d, 2H, Ar−H), 6.73 (s, 2H, Ar−H), 3.88 (s, 12H, $-O-CH_3$), 3.74 (s, 6H, $-O-CH_3$). MALDI–TOF–MS *m/z*: Calculated: 752.76; Found: 752.725 [M]$^+$.

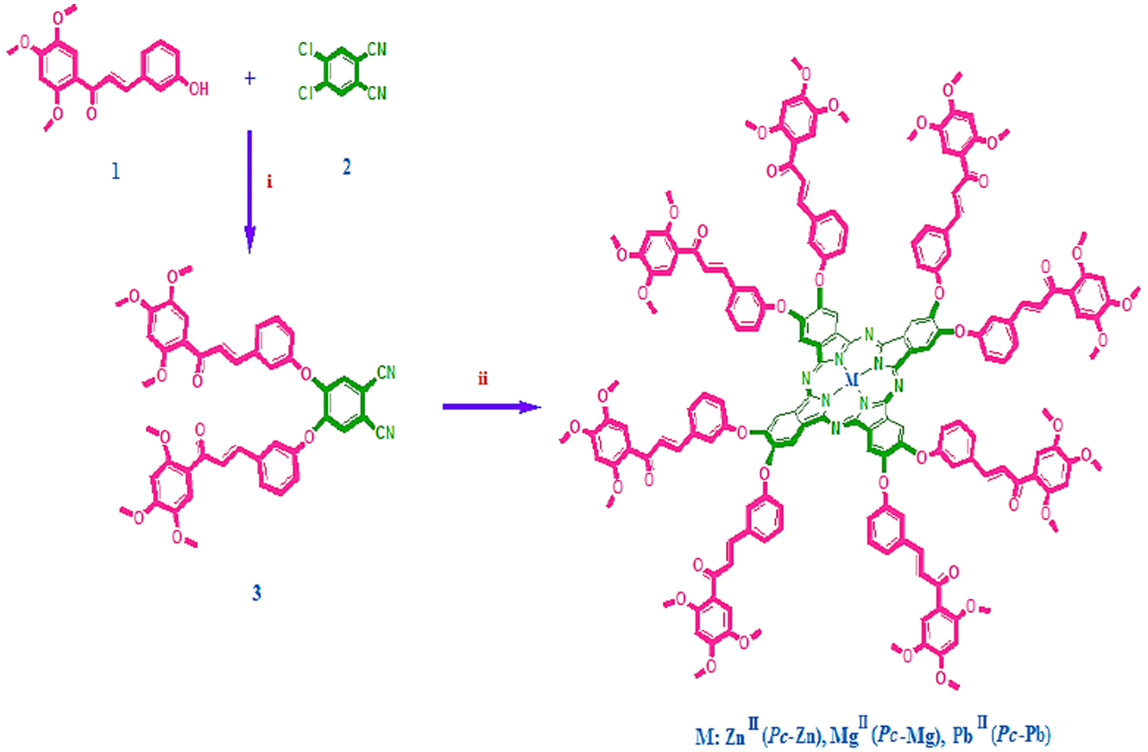
2.1.2. Synthesis method of metallophthalocyanine compounds (*Pc*-Zn,*Pc*-Mg and *Pc*-Pb)

Anhydrous metal salt Zn(OAc)$_2$(12 mg, 0.066 mmol for ***Pc*-Zn**) or MgCl$_2$ (6.32 mg, 0.066 mmol for ***Pc*-Mg**) or Pb(OAc)$_2$ (21 mg, 0.066 mmol for ***Pc*-Pb**) and the phthalonitrile (**3**) (0.1 g, 0.133 mmol) were solved in 3 mL n-amyl alcohol and immediately after, 5 drops DBU for each was attached in mixture. This mixture was heated to boiling point of the solvent in a prevalent Schlenk tube for 22 h under N_2 atmosphere. At the end of this period, the mixture was cooled to room conditions and precipitated by the addition of ethyl alcohol. The precipitated crude product was filtered and purification of the formed solid products (Zn^{II} (***Pc*-Zn**) and Mg^{II} (***Pc*-Mg**)) were carried out by column chromatography method, but Pb^{II} (***Pc*-Pb**) phthalocyanine, till the filtrate was colorless, it was washed with ethyl alcohol and diethyl ether. Finally, Zn^{II} (***Pc*-Zn**) and Mg^{II} (***Pc*-Mg**) metallophthalocyanines were obtained as turquoise blue solids, but Pb^{II} (***Pc*-Pb**) was obtained as grass-green solid.

*2.1.2.1. Zinc(II) phthalocyanine (**Pc-Zn**).* Yield: 80% (41 mg), solvent system of column chromatography: chloroform/ethyl alcohol (50:1), m.p. > 300 °C. FT–IR (ATR), υ_{max} (cm^{-1}): 3066 (Ar−H), 2930–2850 (Aliph. C−H), 1723, 1644, 1578, 1509, 1438, 1267–1207–1176 (Ar−O−Ar), 1085, 974, 875, 787, 746.^{1}H NMR (400 MHz, DMSO-d_6), (δ:ppm): 7.65–7.54 (m, 44H, Ar−H and =CH−), 7.53–7.33 (m, 14H, Ar−H and −CH=), 7.25–7.19 (m, 8H, Ar−H), 6.78–6.58 (m, 6H, Ar−H), 3.66 (s, 18H, $-O-CH_3$), 3.37 (s, 54H, $-O-CH_3$). UV–vis (DMF), λ_{max}, nm (logε): 680 (4.96), 614 (4.30), 354 (4.88). MALDI–TOF–MS *m/z*: Calculated for (***Pc*-Zn**):3076.45; Found:3304.42 [M + DIT + 2H]$^+$.

*2.1.2.2. Magnesium(II) phthalocyanine (**Pc-Mg**).* Yield: 66% (33 mg), solvent system of column chromatography: chloroform/ethyl alcohol (50:2), m.p. > 300 °C. FT–IR (ATR), υ_{max} (cm^{-1}): 3066 (Ar−H), 2930–2851 (Aliph. C−H), 1721, 1604, 1578, 1508, 1438, 1268–1203–1176 (Ar−O−Ar), 1080, 975, 870, 785, 752. ^{1}H NMR (400 MHz, DMSO-d_6), (δ:ppm): 7.94–7.62 (m, 42H, Ar−H and =CH−), 7.54–7.33 (m, 16H, Ar−H and −CH=), 7.28–7.02 (m, 8H, Ar−H), 6.64–6.53 (m, 6H, Ar−H), 3.69 (s, 18H, $-O-CH_3$), 3.37 (s, 54H, $-O-CH_3$). UV–vis (DMF), λ_{max}, nm (logε): 680 (4.79), 613 (4.16), 346 (4.85). MALDI–TOF–MS *m/z*: Calculated for (***Pc*-Mg**): 3035.37; Found:3260.28 [M + DIT–H]$^+$.

*2.1.2.3. Lead(II) phthalocyanine (**Pc-Pb**).* Yield: 87% (46 mg), m.p. > 300 °C. FT–IR (ATR), υ_{max} (cm^{-1}): 3061 (Ar−H), 2931–2842 (Aliph. C−H), 1721, 1647, 1575, 1508, 1437, 1265–1206–1176



Scheme 1. Syntheses of (E)-3-(3-hydroxyphenyl)-1-(2,4,5-trimethoxyphenyl)prop-2-en-1-onesubstituted phthalonitrile (**3**) and metallophthalocyanines (Zn^{II}(***Pc*-Zn**), Mg^{II} (***Pc*-Mg**) and Pb^{II} (***Pc*-Pb**)). Reagents and conditions (i) N_2, K_2CO_3, DMF, 55 °C (ii) N_2, n-amyl alcohol, DBU, $Zn(OAc)_2$, $MgCl_2$, $Pb(OAc)_2$, reflux temperature.

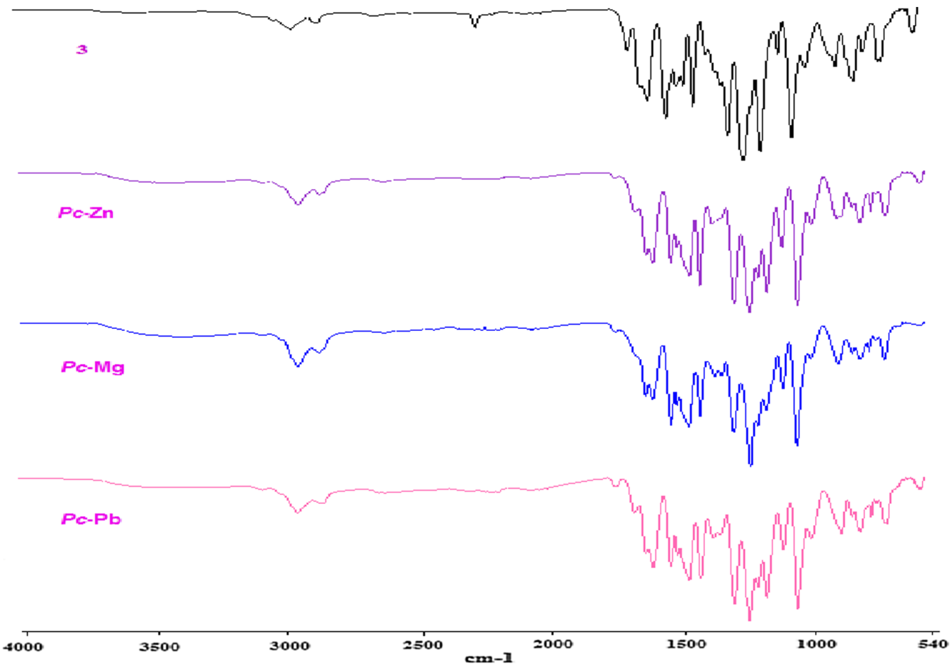


Fig. 1. FT-IR spectrums of phthalonitrile and metallophthalocyanines (Zn^{II} (***Pc*-Zn**), Mg^{II} (***Pc*-Mg**) and Pb^{II} (***Pc*-Pb**)).

(Ar—O—Ar), 1078, 974, 856, 786, 744.^{1}H NMR (400 MHz, DMSO-d_6), (δ:ppm): 7.61–7.55 (m, 46H, Ar—H and =CH—), 7.51–7.30 (m, 12H, Ar—H and —CH=), 7.26–7.09 (m, 8H, Ar—H), 6.71–6.61 (m, 6H, Ar—H), 3.73 (s, 9H, —O—CH_3), 3.67 (s, 9H, —O—CH_3), 3.37 (s, 54H, —O—CH_3). UV–vis (DMF), λ_{max}, nm (logε): 711 (4.57), 642 (3.99), 344 (4.90). MALDI–TOF–MS *m/z*: Calculated for (***Pc*-Pb**): 3218.27; Found: 3412.12 [M + DIT–OCH_3–H]$^+$.

3. Results and discussion

3.1. Syntheses and characterization

Common synthesis route of the obtained phthalonitrile (**3**) and peripheral octa-substituted Zn^{II} (***Pc*-Zn**), Mg^{II} (***Pc*-Mg**) and Pb^{II} (***Pc*-Pb**) phthalocyanines are exhibited in Scheme 1.The phthalonitrile (**3**) was attained by the aromatic nucleophilic substitution reaction of 4,5-dichlorophthalonitrile (**2**) with (E)-3-(3-hydroxyphenyl)-1-(2,4,5-

trimethoxyphenyl)prop-2-en-1-one (**1**) using K_2CO_3 in dry dimethylformamide at 55 °C under N_2 atmosphere for 5 days. Metallophthalocyanines representing the result compounds (Zn^{II} (***Pc*-Zn**), Mg^{II} (***Pc*-Mg**) and Pb^{II} (***Pc*-Pb**)) were accomplished by the cyclotetramerization of phthalonitrile (**3**), in the presence of anhydrous metal salts ($Zn(OAc)_2$, $MgCl_2$, $Pb(OAc)_2$) and DBU in n-amyl alcohol for 22 h. Purification of the obtained metallophthalocyanines was carried out by column chromatography method. These novel MPcs (***Pc*-Zn**, ***Pc*-Mg** and ***Pc*-Pb**) demonstrated good solubility in chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), dimethylformamide (DMF), dimethylsulphoxide (DMSO) and tetrahydrofurane (THF). The structures of phthalonitrile and metallophthalocyanines were proved using spectroscopic techniques such as FT–IR, MALDI–TOF, UV–vis (for phthalocyanines), ^{1}H NMR.

In the IR spectra, the C≡N stretching vibration band of phthalonitrile (**3**) at 2229 cm^{-1} exhibited. Other characteristic vibration bands were demonstrated at 3075 cm^{-1} for aromatic C—H stretching; between 2934 and 2835 cm^{-1} for aliphatic C—H stretching; 1207–1142 cm^{-1} for Ar—O—Ar group stretching (see Fig. 1). When the ^{1}H NMR spectrum taken in DMSO-d_6 were examined, the protons of aromatic ring of phthalonitrile compound (**3**) were exhibited among 7.59–6.73 ppm, methoxy groups protons were observed 3.89–3.88 and 3.74 ppm (see Fig. S1). Also, the mass spectra of phthalonitrile (**3**) was measured by the MALDI–TOF spectral data and molecular ion peak was noticed at *m/z*: 752.725 $[M]^+$ (see Fig. 2).

When the infrared spectra of metal phthalocyanines was examined, characteristic vibration bands were observed at 3066 cm^{-1} (for ***Pc*-Zn**), 3066 cm^{-1} (for ***Pc*-Mg**) and 3061 cm^{-1} (for ***Pc*-Pb**) for aromatic C—H stretching; between 2930 and 2850 cm^{-1} (for ***Pc*-Zn**), 2930–2851 cm^{-1} (for ***Pc*-Mg**) and 2931–2842 cm^{-1} (for ***Pc*-Pb**) for aliphatic C—H stretching; between 1267 and 1207–1176 cm^{-1} (for ***Pc*-Zn**), 1268–1203–1176 cm^{-1} (for ***Pc*-Mg**) and1265–1206–1176 cm^{-1} (for ***Pc*-Pb**) for Ar—O—Ar group stretching (see Fig. 1). The ^{1}H NMR spectra of the obtained Zn^{II} (***Pc*-Zn**), Mg^{II} (***Pc*-Mg**) and Pb^{II} (***Pc*-Pb**) were registered in DMSO-d_6 and also these compounds demonstrated broad absorptions when compared with the of corresponding phthalonitrile derivative **3**. In the ^{1}H NMR spectra, the aromatic protons (Ar—H) and ═CH—/—CH═ bonds were indicated between 7.65 and 6.58 ppm for (***Pc*-Zn**), 7.94–6.53 ppm for (***Pc*-Mg**) and 7.61–6.61 ppm for (***Pc*-Pb**), also methoxy groups protons were showed between 3.66 ppm for (***Pc*-Zn**), 3.69 ppm for (***Pc*-Mg**), 3.73 and 3.67 ppm for (***Pc*-Pb**). The mass spectra of MPcs were measured by the MALDI–TOF spectral data, the molecular ion peaks were observed at *m/z*: 3304.42 $[M+DIT+2H]^+$ for (***Pc*-Zn**), 3260.28 $[M+DIT–H]^+$ for (***Pc*-Mg**) and 3412.12 $[M+DIT—OCH_3—H]^+$ for (***Pc*-Pb**) (see Figs. S2–S4).

The UV–vis spectra of the novel peripheral octa-substituted metallophthalocyanines (***Pc*-Zn**, ***Pc*-Mg** and ***Pc*-Pb**) were recorded at a concentration of 1.0 × 10^{-5} M in DMF. The Q band absorptions of these compounds were observed at 680 nm (logε = 4.96) for ***Pc*-Zn**, 680 nm (logε = 4.79) for ***Pc*-Mg** and 711 nm (logε = 4.57) for ***Pc*-Pb** and lower wavelength vibronic band at 614 nm (logε = 4.30) for ***Pc*-Zn**, 613 nm (logε = 4.16) for ***Pc*-Mg** and 642 nm (logε = 3.39) for ***Pc*-Pb**, respectively. Also, the B–band absorptions were exhibited at 354 nm (logε = 4.88) for ***Pc*-Zn**, 346 nm (logε = 4.85) for ***Pc*-Mg** and 344 nm (logε = 4.90) for ***Pc*-Pb**, respectively in the UV region.

3.2. *Aggregation studies*

In this research paper, the aggregation behaviors of the peripheral octa-substituted MPcs (***Pc*-Zn**, ***Pc*-Mg** and ***Pc*-Pb**) were investigated in various organic solvents such as chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), dimethylformamide (DMF), dimethylsulphoxide (DMSO) and tetrahydrofurane (THF). This study was carried out to select a solvent suitable to photocatalytic study. The absorption intensities of the Q bands did not show significant changes in these solvents. When aggregation studies of these compounds were examined, the Zn^{II}(***Pc*-Zn**), Mg^{II} (***Pc*-Mg**) and Pb^{II} (***Pc*-Pb**) phthalocyanines did not exhibit any aggregation in all studied solvents on account of sharp Q band intensities (see Fig. 3).

The aggregation properties of the MPcs (***Pc*-Zn**, ***Pc*-Mg** and ***Pc*-Pb**) were investigated at different concentrations in DMF (see Fig. 4). When the concentration augmented, the intensity of absorption of the Q band also enhanced and no new band due to the formation of aggregated species in DMF was observed. Beer–Lambert law was implemented for all studied MPcs in the concentrations ranging from 1 μM–10 μM. The studied MPcs (***Pc*-Zn**, ***Pc*-Mg** and***Pc*-Pb**) did not exhibit any aggregation at these concentration ranges in DMF.

3.3. *Catalytic studies*

Photocatalytic properties of Zn^{II}(***Pc*-Zn**), Mg^{II} (***Pc*-Mg**) and Pb^{II} (***Pc*-Pb**) were examined on 4-nitrophenol oxidation by photoreactor

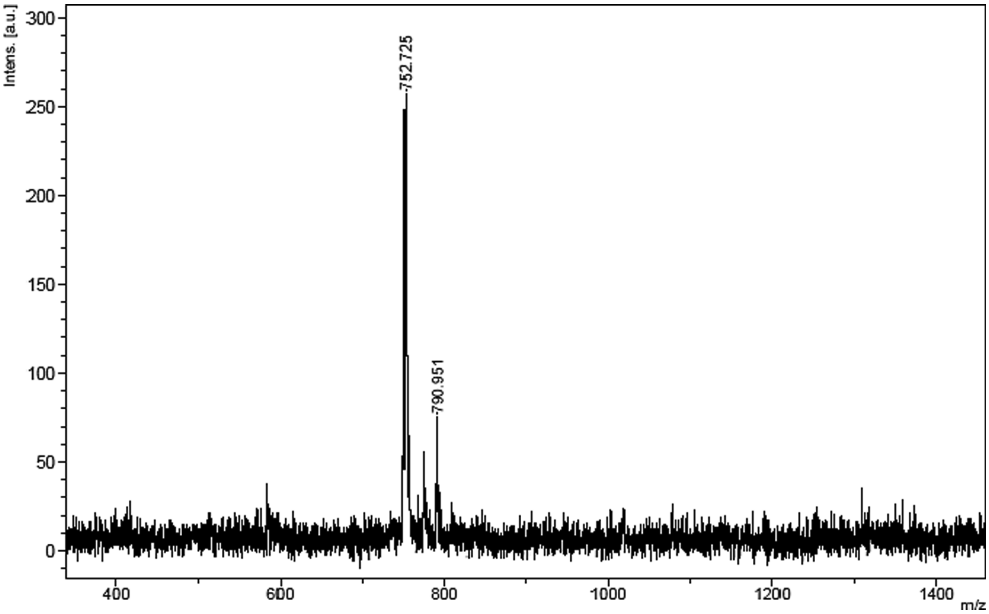


Fig. 2. Mass spectra of phthalonitrile compound (**3**).

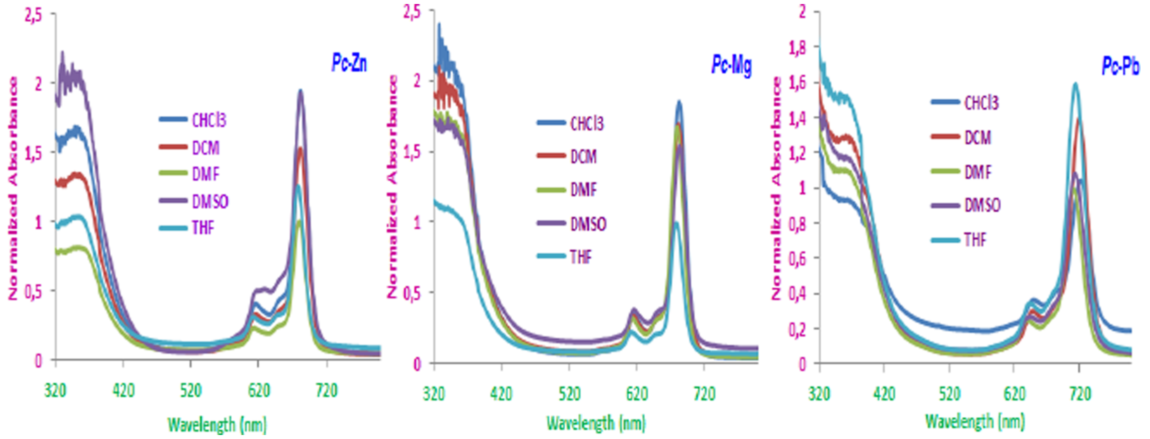


Fig. 3. UV–vis spectrums of metallophthalocyanines (Zn^{II}(***Pc*-Zn**), Mg^{II} (***Pc*-Mg**) and Pb^{II} (***Pc*-Pb**)) in different solvents.

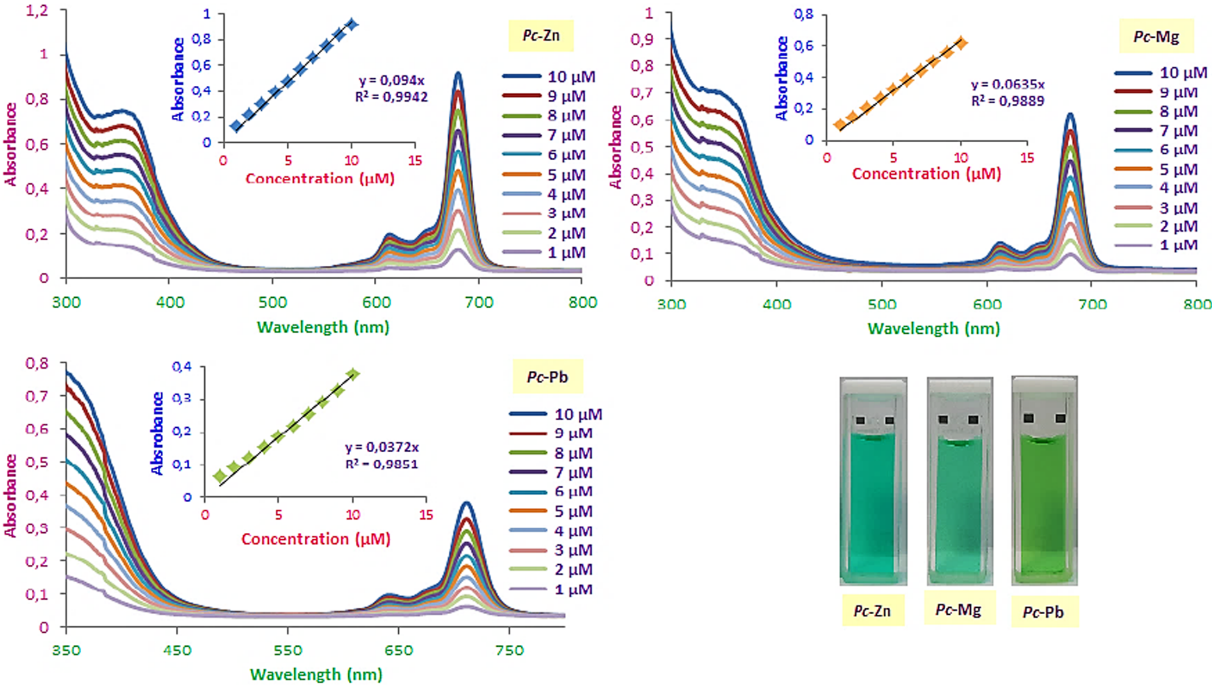


Fig. 4. UV–vis spectrums of metallophthalocyanines (Zn^{II} (***Pc*-Zn**), Mg^{II} (***Pc*-Mg**) and Pb^{II} (***Pc*-Pb**)) in different concentrations.

equipped with 8 pieces 16 W lamps at room temperature. The contents of the samples that are taken from the reaction medium for 60 min were examined by gas chromatography and product conversions were determined as hydroquinone (42% for Pb^{II} (***Pc*-Pb**), 30% for Zn^{II} (***Pc*-Zn**) and 6% for Mg^{II} (***Pc*-Mg**)) and benzoquinone (48% for Pb^{II} (***Pc*-Pb**), 23% for Zn^{II} (***Pc*-Zn**) and 6% for Mg^{II} (***Pc*-Mg**)). According to these results, hydroquinone and benzoquinone were determined as reaction products (see Fig. 5). When the same reactions were repeated at room temperature in the dark, it was determined that the 4-nitrophenol compound did not undergo any oxidation. Moreover, any oxidant was not used during the photooxidation processes.

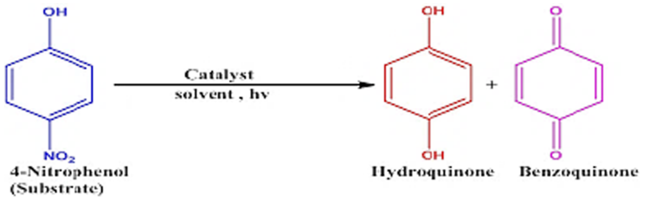


Fig. 5. The oxidation products of 4-nitrophenol.

All reactions for finding optimal conditions of the photooxidation were carried out with different 4-nitrophenol-to-catalysts molar ratios. When the catalyst/substrate ratio was increased from 0.01/2000 to 1/2000, the rate of the reaction increased. In contrast, while the catalytic oxidation was processing from 1/2000 to 50/2000, the conversion fixed to 90% for Pb^{II} (***Pc*-Pb**) and 56% for Zn^{II}(***Pc*-Zn**). Table 1 shows that Pb^{II} (***Pc*-Pb**) is good selectivity (58%) for degradation of 4-nitrophenol with giving hydroquinone (42%) and benzoquinone (48%). Table 1 summarizes all photocatalytic results with selectivity, TON value for Pb^{II} (***Pc*-Pb**) and Zn^{II} (***Pc*-Zn**). At the end of the photoxidation studies, the amount of photodegradation of 4-nitrophenol was determined in the presence of both photocatalysts. For this, the equation given below is used.

$$\mathbf{X_t = C_o - C_t/C_o}$$

In the above equation, X (t) is the molar fraction of 4-nitrophenol, Co, initial concentration and C (t) is the concentration of 4-nitrophenol as a function of illumination time. This equation shows a similar profile

Table 1
Selective oxidation of 4-nitrophenol with catalyst Zn^{II}(***Pc*-Zn**), Mg^{II} (***Pc*-Mg**) and Pb^{II} (***Pc*-Pb**).

4-nitrophenol/Catalyst	Temperature (°C)	Conversion (%)			Selectivity[a] (%)			TON	
		PbPc	ZnPc	MgPc	PbPc	ZnPc	MgPc	PbPc	ZnPc
2000/1	25	90	56	12	53	42	50	1500	933
2000/free	25	10	8	–	48	38	–	166	133
2000/1(in dark)	25	–	–	–	–	–	–	–	–
2000/0.01	25	26	19	8	47	38	–	43,356	31,683
2000/0.1	25	50	30	–	46	36	–	8337	5002
2000/10	25	56	34	–	46	37	–	933	566
2000/50	25	49	26	–	51	45	–	4085	2168

All photocatalytic reaction were done in photoreactor with light.
TON = mole of product / mole of catalyst.
TOF = mole of product / mole of catalyst × time.
Conversion was determined by GC.
Reaction Conditions: solvent 10 mL DMF, 4-nitrophenol (6.22×10^{-3} mol), catalyst (3.73×10^{-6} mol).
[a] = Selectivity of benzoquinone Reaction time = 1 h.

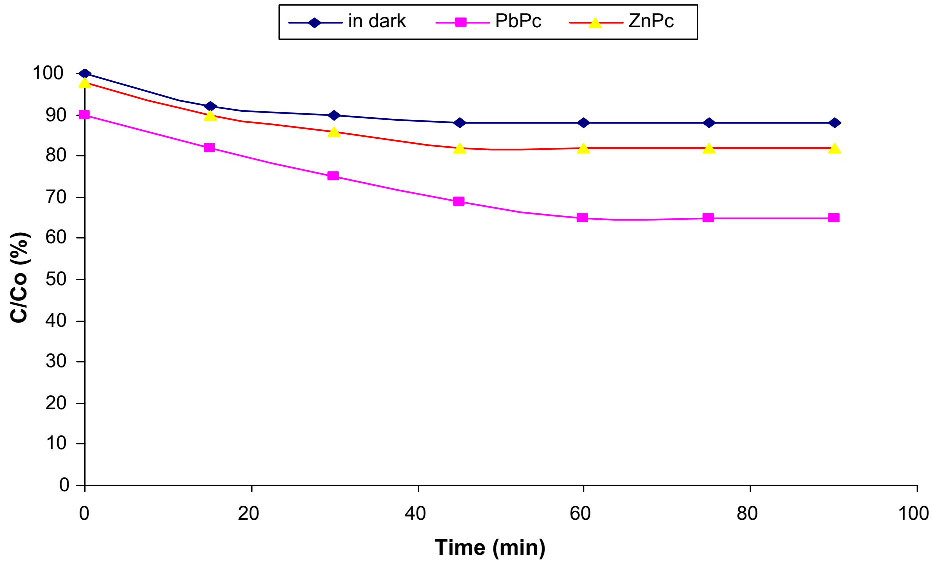


Fig. 6. The photocatalytic oxidation of 4-nitrophenol with near visible light irradiation Pb^{II}(***Pc*-Pb**), Zn^{II} (***Pc*-Zn**) and in dark. (A mixture of 4-nitrophenol (6.22×10^{-3} mol), catalyst (3.73×10^{-6} mol), and solvent (0.01 L) at 1 h.).

to the photocatalytic degradation of other dyes [41,42]. For this purpose, 100 mL of a 0.025 M solution of 4-nitrophenol and 5 mg of solid catalyst were reacted in a photo-reactor under visible light (420 nm) for 1 h. During the photocatalytic reaction, all samples from the reaction medium were diluted with dichloromethane and injected into the GC apparatus. As a result, we observed that most of the 4-nitrophenol was degraded and the rate of degradation was fixed after 60 min. Data on photocatalytic degradation of 4-nitrophenol sensitized with both photocatalysts under visible light are presented in Fig. 6.

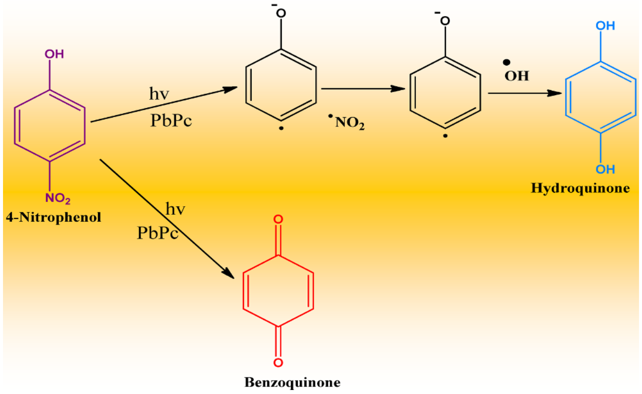


Fig. 7. Mechanism of 4-nitrophenol degradation.

Cobalt (II), iron (II), aluminum (III), copper (II) and metal-free phthalocyanines in which different groups have been substituted for the photoxidation of different pollutants have been studied [43–49]. Nyokong et al. studied the photocatalytic activity of seven octane substituted thio and aryloxy palladium and platinum phthalocyanines in the breakdown of 4-nitrophenol [50]. According to the kinetic studies of this study, two reaction pathways have been identified for the degradation of 4-nitrophenol with phthalocyanine catalyst (see Fig. 7) [51]. In another study by T. Nyokong, quantitative yields of singlet oxygen and photodissection of 4-nitrophenol in the presence of zinc tetrasulfiphthalocyanine ($ZnPcS_4$), zinc octacarboxyphthalocyanine ($ZnPcS4 (COOH)_8$) were investigated [51]. In the light of this literatures ZnPc employees as photocatalyst with 56% product conversion and 42% benzoquinone selectivity. Zn is a divalent atom and may produce singlet oxygen that degrades 4-nitrophenol [51]. On the other hand we focused that metal centered phthalocyanines show good catalytic activities with light for the oxidation of phenols. In the literature, although many studies on the catalytic activities of phthalocyanine [52–57] are available, only a few have examined photooxidation reactions using UV radiation. Table 2 summarizes some of these literature. Our previous

Table 2
Catalytic activities of phthalocyanines in the photooxidation of different organic compounds in some previously reported catalyst.

Catalyst	Substrate	Rxn Time (h)	Rxn Temp. (^oC)	Oxidant	Conv. (%)	Ref.
ZnTsPc[a]	Methyl orange-Orange G	10 min	nr	O_2	Nr	[44]
FePc[b]	Ethyl benzene	9 h	Rt	O_2	> 99	[45]
CoTNPc [c]	Malachite green	30 min	nr	–	99.2	[46]
CoPc[d]	2-mercaptoethanol	2	rt	–	nr[e]	[47]
Metal free Pc[f]	Sülfide ion	1	rt	O_2	70	[48]
CuPc[g]	4-nitrophenol	5	27	–	nr[h]	[49]
CoPc[ı] ZnPc[ı]	4-chlorophenol	3	rt	O_2	99.99 97.05	[50]
SiPc[j]	4-nitrophenol	3	rt	H_2O_2	88.0	[56]

ZnTs-CoFerrite[a] = 2-[5-(phenoxy)-isophthalic acid] 9(10), 16(17), 23(24)-tris (tertbutyl) phthalocyaninato Zn (II).
FePc-POF[b] = four-branched tetra-amine FePc-porous organic framework.
CoTNPc/$SnIn_4S_8$ [c] = Tetranitrocobalt phthalocyanine/ternary chalcogenide.
CoPc[d] = Cobaltphthalocyanine/C_{60}.
Metal free Pc[f] = Metal free phthalocyanine/TiO_2.
CuPc[g] = Copper phthalocyanine/ TiO_2.
CoPc[ı]= 2,9,16,23-tetrakis-(4-carboxyphenylsulphanyl) phthalocyaninato cobalt(II) / TiO_2.
ZnPc[ı]= 2,9,16,23-tetrakis-(4-carboxyphenylsulphanyl) phthalocyaninato zinc (II) / TiO_2.
SiPc[j] = 1-benzylpiperidin-4-oxy substituted silicone phthalocyanine.
nr = not reported.
nr[e] = Turnover number is given as 8.4.
nr[h] = Quantum yield is given as 1.9.

work clearly shows that silicone phthalocyanine employes effective catalyst (88% product conversion) in 4-nitrophenol oxidation with H_2O_2 [3]. But in this study, it is the first time in this field to investigate the photooxidation of 4-nitrophenol using lead phthalocyanine as photocatalyst without any oxygen source in reaction media. The results of photocatalytic experiments can generate promising new research and micro-scale application.

4. Conclusions

In conclusion, present study has explained the syntheses, spectroscopic, aggregation properties and investigation of their photocatalytic properties on the photooxidation of 4-nitrophenol in synthesized MPcs (Zn^{II} (***Pc*-Zn**), Mg^{II} (***Pc*-Mg**) and Pb^{II} (***Pc*-Pb**)).The all novel compounds were identified by general spectroscopic techniques. The effects of concentration and solvent on the aggregation behavior of the new metallophthalocyanine complexes were researched. All novel synthesized MPcs did not exhibit any aggregation in studied common organic solvents and at the concentrations ranging from 1 µM–10 µM. In photodegradation reactions performed without using any oxidant, the 4-nitrophenol compound was completed with 90% (for Pb^{II} (for ***Pc*-Pb**)), 56% (for Zn^{II} (for ***Pc*-Zn**)) and 12% (for Mg^{II} (for ***Pc*-Mg**)) conversion from toxic species to non-harmful species and unknown intermediates.

CRediT authorship contribution statement

Halise Yalazan: Methodology, Investigation, Formal analysis, Validation, Writing - original draft, Writing - review & editing, Visualization. **Kader Tekintas:** Formal analysis. **Vildan Serdaroğlu:** Methodology, Formal analysis. **Ece Tugba Saka:** Investigation, Validation, Writing - original draft, Writing - review & editing. **Nuran Kahriman:** Methodology, Formal analysis. **Halit Kantekin:** Methodology, Resources, Writing - review & editing, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This study was supported by the Research Fund of Karadeniz Technical University.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.inoche.2020.107998.

References

[1] C.C. Leznoff, Phthalocyanines: Properties and Applications vol. 1, VCH Publisher, New York, 1989.
[2] K. Ishii, N. Kobayashi, in: K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, vol. 16, Academic Press/Elsevier, New York, 2003, pp. 1–40 (Chapter 102).
[3] E.T. Saka, H. Yalazan, Z. Bıyıklıoğlu, H. Kantekin, K. Tekintaş, Synthesis, aggregation, photocatalytical and electrochemical properties of axially 1-benzylpiperidin-4-oxy units substituted silicon phthalocyanine, J. Mol. Struct. 1199 (2020) 126994.
[4] A. Aktas Kamiloglu, E.T. Saka, İ. Acar, K. Tekintaş, Synthesis, characterization, and photocatalytic activity of Co(II) and Cu(II) phthalocyanines linked with thiophene–Schiff base substituents for 4-nitrophenol oxidation, J. Coord. Chem. 72 (2019) 2778–2790.
[5] A. Wang, L. Zhou, K. Fang, L. Zhou, Y. Lin, J. Zhou, S. Wei, Synthesis of novel octacationic and non-ionic 1,2-ethanediamine substituted zinc (II) phthalocyanines and their in vitro anti-cancer activity comparison, Eur. J. Med. Chem. 58 (2012) 12–21.
[6] M.A. Idowu, S. Xego, Y. Arslanoglu, J. Mark, E. Antunes, T. Nyokong, Photophysicochemical behaviour and antimicrobial properties of monocarboxy Mg (II) and Al (III) phthalocyanine-magnetite conjugates, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 193 (2018) 407–414.
[7] H. Yalazan, M. Köç, S. Fandaklı, A. Nas, M. Durmuş, H. Kantekin, Synthesis, characterization, and photochemical properties of novel peripherally and non-peripherally tetra substituted zinc(II) and magnesium(II) phthalocyanines containing 4-(1,5-diphenyl-4,5-dihydro-1*H*-pyrazol-3-yl)phenol units, Polyhedron 170 (2019) 576–583.
[8] B. Barut, Ü. Demirbaş, A. Özel, H. Kantekin, Novel water soluble morpholine substituted Zn(II)phthalocyanine: Synthesis, characterization, DNA/BSA binding, DNA photocleavage and topoisomerase I inhibition, Int. J. Biol. Macromol. 105 (2017) 499–508.
[9] Ö. Tüzün Özmen, K. Goksen, A. Demir, M. Durmuş, O. Köysal, Investigation of photoinduced change of dielectric and electrical properties of indium (III) phthalocyanine and fullerene doped nematic liquid crystal, Synth. Met. 162 (2012) 2188–2192.
[10] K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, vol. 15–20, Academic Press, Boston, 2003.
[11] K. Kameyama, M. Morisue, A. Satake, Y. Kobuke, Highly Fluorescent Self-Coordinated Phthalocyanine Dimers[†], Angew. Chem. Int. Ed. 44 (2005) 4763–4766.
[12] J.L. Sesler, J. Jayawickramarajah, A. Gouloumis, G.D. Patnos, T. Torres, D.M. Guldi, Guanosine and fullerene derived de-aggregation of a new phthalocyanine-linked cytidine derivative, Tetrahedron 62 (2006) 2123–2131.
[13] X. Huang, F.Q. Zhao, Z.Y. Li, L. Huang, Y.W. Tang, F. Zhang, C.H. Tung, A novel self-aggregates of phthalocyanine based on Zn–O coordination, Chem. Lett. 36 (2007) 108–115.
[14] X. Huang, F.Q. Zhao, Z.Y. Li, Y.W. Tang, F. Zhang, C.H. Tung, Self-assembled nanowire networks of aryloxy zinc phthalocyanines based on Zn–O coordination, Langmuir 23 (2007) 5167–5172.
[15] M. Morisue, Y. Kobuke, Tandem cofacial stacks of porphyrin–phthalocyaninedyads through complementary coordination, Chem.–A Eur. J. 14 (2008) 4993–5000.
[16] H.E. Alamin Ali, M. Pişkin, S. Altun, M. Durmuş, Z. Odabaş, Synthesis, characterization, photophysical, and photochemical properties of novel zinc(II) and indium (III) phthalocyanines containing 2-phenylphenoxy units, J. Lumin. 173 (2016) 113–119.
[17] P. Zimcik, A. Malkova, L. Hruba, M. Miletin, N. Novakova, Bulky 2,6-diphenylphenylsulfanyl substituents efficiently inhibitaggregation inphthalocyanines and tetrapyrazinoporphyrazines and control their photophysical and electrochemical properties, Dyes Pigm. 136 (2017) 715–723.
[18] B. Ertem, H. Yalazan, Ö. Güngör, G. Sarkı, M. Durmuş, E.T. Saka, H. Kantekin, Synthesis, structural characterization, and investigation on photophysicaland photochemical features of new metallophthalocyanines, J. Lumin. 204 (2018) 464–471.
[19] İ. Acar, T. Arslan, S. Topçu, A. Aktaş, S. Şen, H. Serencam, Synthesis and electrochemistry of metallophthalocyaninesbearing 4-[(2E)-3-(3,4,5-trimethoxyphenyl) prop-2-enoyl]phenoxy groups, J. Organomet. Chem. 752 (2014) 25–29.

[20] C. Zhuang, W. Zhang, C. Sheng, W. Zhang, C. Xing, Z. Miao, Chalcone: a privileged structure in medicinal chemistry, Chem. Rev. 117 (2017) 7762–7810.

[21] Z. Nowakowska, A review of anti-infective and anti-inflammatory chalcones, Eur. J. Med. Chem. 42 (2007) 125–137.

[22] A. Ekbote, P.S. Patil, S.R. Maidur, T.S. Chia, C.K. Quah, Structure and nonlinear optical properties of (E)-1-(4-aminophenyl)-3-(3-chlorophenyl) prop-2-en-1-one: a promising new D-π-A-π-D type chalcone derivative crystal for nonlinear …, J. Mol. Struct. 1129 (2017) 239–247.

[23] E.T. Saka, N. Kahriman, (E)-4-(4-(3-(2-fluoro-5-(trifluoromethyl)phenyl)acryloyl) phen oxy) Substituted Co(II) and Cu(II) phthalocyanines and their catalytic activities on the oxidation of phenols, J. Organomet. Chem. 895 (2019) 48–54.

[24] A. Nas, N. Kahriman, H. Kantekin, N. Yaylı, M. Durmuş, The synthesis of novel unmetallated and metallated phthalocyanines including (*E*)-4-(3-cinnamoylphenoxy) groups at the peripheral positions and photophysicochemical properties of their zinc phthalocyanine derivatives, Dyes Pigm. 99 (2013) 90–98.

[25] G. Sarkı, H. Kantekin, H. Yalazan, N. Kahriman, Z. Biyiklioglu, V. Serdaroğlu, Synthesis, characterization and electrochemical studies of metal-freeand metallophthalocyanines containing two different chalcone units substituted on peripherally positions, J. Mol. Struct. 1196 (2019) 592–603.

[26] A.L. Pruden, D.F. Ollis, Photoassisted heterogeneous catalysis: The degradation of trichloroethylene in water, J. Catal. 82 (1983) 404.

[27] C.Y. Hsiao, C.L. Lee, D.F. Ollis, Heterogeneous photocatalysis: Degradation of dilute solutions of dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4) with illuminated TiO_2 photocatalyst, J. Catal. 82 (1983) 418–423.

[28] Q. Wang, S. Liang, G. Zhang, R. Su, C. Yang, P. Xu, P. Wang, Facile and rapid microwave-assisted preparation of Cu/Fe-AO-PAN fiber for PNP degradation in a photo-Fenton system under visible light irradiationSep, Purif. Technol. 209 (2019) 270–278.

[29] J. Yang, B. Pan, H. Li, S. Liao, D. Zhang, M. Wu, B. Xing, Degradation of *p*-Nitrophenol on Biochars: Role of Persistent Free Radicals, Environ. Sci. Technol. 50 (2015) 694–700.

[30] N.K. Sahoo, K. Pakshirajan, P.K. Ghosh, Appl. Biochem. Batch Biodegradation of Para-Nitrophenol Using Arthrobacter chlorophenolicus A6, Biotechnol. 165 (2011) 1587–1596.

[31] Y.J. Do, J.H. Kim, J.H. Park, S.S. Park, S.S. Hong, C.S. Suh, G.D. Lee, Photocatalytic decomposition of 4-nitrophenol on Ti-containing MCM-41, Catal. Today 101 (2005) 299–305.

[32] K.P. Madhuri, N.S. John, Supercapacitor application of nickel phthalocyanine nanofibres and its composite with reduced graphene oxideAppl, Surf. Sci. 449 (2018) 528–536.

[33] R. Ramachandran, Q. Hu, F. Wang, Z.X. Xu, Synthesis of N-$CuMe_2$Pc nanorods/graphene oxide nanocomposite for symmetric supercapacitor electrodewith excellent cyclic stability, Electrochim. Acta 298 (2019) 770–777.

[34] E.T. Saka, Z. Bıyıklıoğlu, H. Kantekin, Microwave-assisted synthesis and characterization of Co(II) phthalocyanine and investigationof its catalytic activity on 4-nitrophenol oxidation, Turk. J. Chem. 38 (2014) 1166–1173.

[35] E.T. Saka, S. Uzun, Y. Çağlar, Synthesis, Structural Characterization, Catalytic activity on Aerobic Oxidation of novel Co(II) and Fe(II) phthalocyanines and Computational Studies of 4-[2-(2,3 dichlorophenoxy)ethoxy]phthalonitrile, J. Organomet. Chem. 810 (2016) 25–32.

[36] E.T. Saka, Y. Çağlar, New Co(II) and Cu(II) Phthalocyanine Catalysts Reinforced by Long Alkyl Chains for the Degradation of Organic Pollutants, Catal. Lett. 147 (2017) 1471–1477.

[37] A. Aktaş, İ. Acar, E.T. Saka, Z. Bıyıklıoğlu, H. Kantekin, Fluoro functional groups substituted cobalt(II), iron(II) phthalocyanines and their catalytic properties on benzyl alcohol oxidation, J. Incl. Phenom. Macrocycl. Chem. 3–4 (2016) 183–190.

[38] E.T. Saka, G. Sarkı, H. Kantekin, Facile synthesis of highly active Co(II) and Fe(II) phthalocyanine catalysts for aerobic oxidation of phenolic compounds, J. Coord. Chem. 68 (2015) 1132–1141.

[39] H. Kantekin, H. Yalazan, N. Kahriman, B. Ertem, V. Serdaroğlu, M. Pişkin, M. Durmuş, New peripherally and non-peripherally tetra-substituted metal-free, magnesium(II) andzinc(II) phthalocyanine derivatives fused chalcone units: Design, synthesis, spectroscopiccharacterization, photochemistry and photophysics, J. Photochem. Photobiol., A 361 (2018) 1–11.

[40] H. Yalazan, D. Akyüz, V. Serdaroğlu, N. Kahriman, A. Koca, H. Kantekin, Novel peripheral tetra-substituted phthalocyanines containingmethoxylated chalcone group: Synthesis, spectral, electrochemical and spectroelectrochemical properties, J. Organomet. Chem. 912 (2020) 121181.

[41] I. Altın, M. Sokmen, Z. Bıyıklıoglu, Quaternized zinc(II) phthalocyanine-sensitized TiO_2: surfactant-modified sol–gel synthesis, Desalin. Water Treat. 57 (2016) 16196–16207.

[42] R. Bayrak, C. Albay, M. Koç, I. Altın, I. Degirmenci, M. Sokmen, Preparation of Phthalocyanine/TiO2 Nanocomposites for Photocatalytic Removal of Toxic Cr(VI) Ions, Process Saf. Environ. Prot. 102 (2016) 294–302.

[43] S. Mapukata, N. Kobayashi, M. Kimura, T. Nyokong, Asymmetrical and symmetrical zinc phthalocyanine-cobalt ferrite conjugates embedded in electrospun fibers for dual photocatalytic degradation of azo dyes: Methyl Orange and Orange G, J. Photochem. Photobiol., A 379 (2019) 112–122.

[44] W.L. He, C.D. Wu, Incorporation of Fe-phthalocyanines into a porous organic framework for highly efficientphotocatalytic oxidation of arylalkanes, Appl. Catal., B: Environ. 234 (2018) 290–295.

[45] M. Lu, B. Li, Y. Zhang, Q. Liang, X. Li, S. Xu, Z. Li, Facile synthesis and characterization of a cobalt phthalocyanine sensitized, J. Mater. Sci.: Mater. Electron. 29 (2018) 16680–16690.

[46] P. Arunachalam, S. Zhang, T. Abe, M. Komura, T. Iyoda, K. Nagai, Weak visible light (∼mW/cm2) organophotocatalysis for mineralization of amine, thiol and aldehyde by biphasic cobalt phthalocyanine/fullerene nanocomposites prepared by wet process, Appl. Catal., B: Environ. 193 (2016) 240–247.

[47] V. Iliev, D. Tomova, Photocatalytic oxidation of sulfide ion catalyzed by phthalocyanine modified titania, Catal. Commun. 3 (2002) 287–292.

[48] G. Mele, R. Del Sole, G. Vasapollo, E. García-López, L. Palmisano, M. Schiavello, Photocatalytic degradation of 4-nitrophenol in aqueous suspension by using polycrystalline TiO_2 impregnated with functionalized Cu(II)–porphyrin or Cu (II)–phthalocyanine, J. Catal. 217 (2003) 334–342.

[49] Y. Mahmiani, A.M. Sevim, A. Gül, Photocatalytic degradation of 4-chlorophenol under visible light by using TiO_2 catalysts impregnated with Co(II) and Zn(II) phthalocyanine derivatives, J. Photochem. Photobiol., A 321 (2016) 24–32.

[50] T.B. Ogunbayo, E. Antunes, T. Nyokong, Investigation of homogeneous photosensitized oxidation activities of palladium and platinum octasubstituted phthalocyanines: Oxidation of 4-nitrophenol, J. Mol. Catal. A Chem. 334 (2011) 123–129.

[51] E. Marais, R. Klein, E. Antunes, T. Nyokong, Photocatalysis of 4-nitrophenol using zinc phthalocyanine complexes, J. Mol. Catal. A: Chem. 261 (2007) 36–42.

[52] A. Aktas Kamıloglu, I. Acar, Z. Bıyıklıoglu, E.T. Saka, Peripherally tetra-{2-(2,3,5,6-tetrafluorophenoxy)ethoxy} substituted cobalt(II), iron(II) metallophthalocyanines: Synthesis and their electrochemical, catalytic activity studies, J. Organomet. Chem. 828 (2017) 59–67.

[53] A. Aktas Kamıloglu, I. Acar, E.T. Saka, Z. Bıyıklıoglu, Synthesis of polyfluoro substituted Co(II), Fe(II) phthalocyanines and their usage as catalysts for aerobic oxidation of benzyl alcohol, J. Organomet. Chem. 815-816 (2016) 1–7.

[54] V. Cakır, E.T. Saka, Z. Bıyıklıoglu, H. Kantekin, Highly selective oxidation of benzyl alcohol catalyzed by new peripherally tetra-substituted Fe(II) and Co(II) phthalocyanines, Synth. Met. 197 (2014) 233–239.

[55] A. Aktas Kamıloglu, E.T. Saka, Z. Bıyıklıoglu, I. Acar, H. Kantekin, Investigation of catalytic activity of new Co(II) phthalocyanine complexes in cyclohexeneoxidation using different type of oxidants, J. Organomet. Chem. 745–746 (2013) 18–24.

[56] Z. Bıyıklıoglu, E.T. Saka, S. Gökçe, H. Kantekin, Synthesis, characterization and investigation of homogeneous oxidation activities of peripherally tetra-substituted Co(II) and Fe(II) phthalocyanines: Oxidation of cyclohexene, J. Mol. Catal. A: Chem. 378 (2013) 156–163.

[57] E.T. Saka, G. Sarkı, H. Kantekin, A. Koca, Electrochemical, spectroelectrochemical and catalytical properties of new Cu(II) and Co(II)phthalocyanines, Synth. Met. 214 (2016) 82–91.