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The new tetrasubstituted metallophthalocyanines bearing four Schiff bases on the periphery: Synthesis, spectroscopic properties, and investigation of the effect of various central metals on aggregation properties

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Abstract

In the present study, new Schiff base compound (Z)-4-((quinolin-2-ylmethyleneamino)methyl)phenol (3) and phthalonitrile derivative (Z)-4-(4-((quinolin-2-ylmethyleneamino)methyl)phenoxy)phthalonitrile (4) were synthesized in the first step. Then, zinc (II) (Pc-5), cobalt (II) (Pc-6) and copper (II) (Pc-7) phthalocyanines containing Schiff base group including quinoline on peripheral positions were synthesized. All new compounds were characterized by general spectroscopic techniques. Aggregation properties of the obtained metallophthalocyanines were researched in polar and apolar solvents.

Keywords: Aggregation, metallophthalocyanine, phthalocyanine, Schiff base, quinoline

1. Introduction

Phthalocyanine complexes (Pcs) exhibit amazing physical and chemical properties. Phthalocyanines (Pcs) are versatile and stable aromatic macrocycles, they can also add a large number of metallic and non-metallic ions to the ring core. Due to the electronic and optical properties of Pcs, they have a great number of application areas. The most important disadvantage of unsubstituted Pcs is their poor solubility in prevalent polar and apolar solvents. Therefore, the solubility properties of Pcs are important for their usability in many applications. The solubility properties of phthalocyanines can be increased by adding long-chain alkyl, alkoxy, alkylthio, and bulky groups at the peripheral positions [1-5].

Aggregation is an important event for phthalocyanine complexes. Two types of aggregation are observed in the substituted phthalocyanines. These are called H-aggregation (face-to-face) and J-aggregation (side-to-side) [1,2]. In general, while phthalocyanine aggregation ensues a decrease in intensity of the Q band corresponding to the monomeric species, a new, broader, and blue-shifted band with increasing intensity is seen. The H-aggregation corresponding to blue-shifted is seen as a lower wavelength shift in Pcs. On the contrary, the J-aggregation corresponding to red-shifted is observed as a higher wavelength shift and is rarely seen in phthalocyanines [6-10].

Alkaloids containing nitrogen atoms are compounds that exhibit natural biological activity [11,12]. The quinolines are an important hetero-ring alkaloid obtained from coal tar and Cinchona (Quina) tree. Due to quinoline rings in its structures, these compounds show wide biological activity such as anti-malaria, anti-bacterial, anti-fungal, antitumor, anti-asthma, anti-inflammatory, and HIV replication inhibitor [13-22]. Many quinolines are ligands used in coordination chemistry as a N or O atom donor for chelating with metals [23-26].

Schiff base compounds formed with azo and azomethine groups are called azo-containing Schiff bases. These compounds are usually synthesized by condensation of an azo aldehyde with primary amine

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[27]. Schiff bases play an important role in the development of organic synthesis and coordination chemistry. Their complexes in the literature are generally formed by transition metals [28].

As seen in the literature, there are few studies on the effect of aggregation properties of phthalocyanines containing quinoline. In our previous studies, we synthesized phthalocyanine compounds peripheral tetra substituted containing a quinoline group [29-31]. We wondered how different quinoline groups on the Schiff base impress aggregation properties of phthalocyanine compounds. In this work, we have planned to prepare phthalocyanine compounds containing substituted (*Z*)-4-((quinolin-2-ylmethyleneamino)-methyl)phenol as substituents on peripheral positions and investigated their aggregation properties. We used 2-quinolinecarboxaldehyde (1) and 4-hydroxybenzylamine (2) compounds during the synthesis of the Schiff base compound because the long-chain and bulky groups increase the solubility of phthalocyanine compounds. The solubility of phthalocyanines is important for their applications.

In the present study, the synthesis, characterization, spectroscopic and aggregation properties of zinc (II) (Pc-5), cobalt (II) (Pc-6) and copper (II) (Pc-7) phthalocyanines bearing four (*Z*)-4-((quinolin-2-ylmethyleneamino)methyl)phenol groups at the peripheral positions are investigated (Scheme 1). These phthalocyanine complexes exhibited good solubility in many organic solvents such as diethyl ether, DCM, ethyl acetate, THF, chloroform, DMF, and DMSO. As a result, the influence on aggregation properties of diverse central metal ions (zinc (II), cobalt (II), and copper (II)) in new phthalocyanine complexes was researched in many organic solvents.

2. Experimental

2.1. Synthesis

2.1.1. (Z)-4-((quinolin-2-ylmethyleneamino)methyl) phenol (3)

1.00 g (6.36 mmol) of 2-quinolinecarboxaldehyde (**1**) and 0.78 g (6.36 mmol) of 4-hydroxybenzylamine (**2**) were mixed in the methanol in a round-bottomed flask. Then, 15 drops of glacial acetic acid was added to the reaction mixture. This mixture was stirred under nitrogen atmosphere at reflux temperature for 48 h. At the end of this period, the reaction mixture was cooled and removed under vacuum. The resulting crude product was extracted with water:chloroform (20:20 v/v). The organic phase was dried with $MgSO_4$, filtered and evaporated. The purification of the product was made by column chromatography on silica gel with chloroform: ethanol (50:1 v/v) solvent system. In conclusion, (*Z*)-4-((quinolin-2-ylmethyleneamino)-methyl)phenol(the Schiff base derivative) **(3)** was attained as orange solid product. Yield: 0.70 g (42%), m.p: 91-94 °C. FT-IR (ATR), υ_{max} (cm^{-1}): 3059 (O-H), 3009 (Ar-H), 2921-2850 (Aliph. C-H), 1681, 1615, 1596, 1503, 1450, 1426, 1376, 1237, 1143, 1101, 938, 827, 752.^1H NMR ($CDCl_3$), (δ:ppm): 8.22-8.18 (m, 4H, Ar-H), 8.04 (m, 1H, Ar-H), 7.84-7.73 (m, 3H, Ar-H), 7.55 (s, 1H, CH=N),7.00 (s, 1H, OH), 6.78(d, 1H, Ar-H), 6.63 (d, 1H, Ar-H), 3.34 (s, 2H, -N-CH_2) ^{13}C NMR ($CDCl_3$), (δ:ppm):155.77 (imine carbon), 153.81,152.88, 151.05, 150.21, 149.77, 147.77, 145.81, 136.41, 136.10, 129.70, 128.44, 121.79, 120.54, 115.33, 115.08, 58.48 (N-CH_2) MS (ES^+) *m*/z: Calculated: 262.31; Found: 263.22 $[M+H]^+$.

2.1.2. (Z)-4-(4-((quinolin-2-ylmethyleneamino)methyl) phenoxy)phthalonitrile (4)

The Schiff base derivative (**3**) (0.70 g, 2.67 mmol) and 4-nitrophthalonitrile (0.46 g, 2.67 mmol) were dissolved in dry DMF (15 mL) in a two-necked round-bottomed flask. After stirring for 30 min at 50 °C, anhydrous potassium carbonate (1.11g, 8.01 mmol) was added in reaction ingredient with small portions. The reaction mixture was monitored by TLC and stirred at 55 °C for 112 h under N_2 atmosphere. At the end of this period, this mixture was poured into ice-water and stirred at room temperature. The obtained crude product filtered and washed with ethyl alcohol and hexane, then dried in a vacuum desiccator. The purification of the product was made by column chromatography on silica gel with chloroform:ethanol (50:5 v/v) solvent system. Consequently, the phthalonitrile derivative (**4**) was obtained as straw yellow solid product. Yield: 0.64 g (62%), m.p: 137-140 °C. FT-IR (ATR), υ_{max} (cm^{-1}): 3044 (Ar-H), 2919-2851 (Aliph. C-H), 2231 (C≡N), 1675, 1617, 1592, 1562, 1484, 1423, 1377, 1278, 1248, 1208, 1167, 1088, 1015, 950, 830, 756. ^1H NMR ($CDCl_3$), (δ:ppm): 8.30-8.27 (m, 1H, Ar-H), 8.18 (d, 1H, Ar-H), 8.08 (m, 1H, Ar-H), 8.00 (m, 2H, Ar-H), 7.91-7.86 (m, 2H, Ar-H), 7.59-7.46 (m, 2H, Ar-H and CH=N), 7.05 (m, 3H, Ar-H), 6.72 (d, 2H, Ar-H), 3.45 (s, 2H, N-CH_2) ^{13}C NMR ($CDCl_3$), (δ:ppm): 161.71, 158.02, 152.10, 147.82, 140.41, 136.89, 136.07, 135.26, 134.96, 129.96, 129.56, 129.37, 129.18, 127.20, 126.96, 125.75, 123.83, 121.71, 120.29-120.21 (C≡N), 117.50, 115.35, 114.96, 108.64, 58.49 (N-CH_2) MS (ES^+) *m*/z: Calculated: 388.42; Found: 388.08 $[M]^+$.

2.1.3. *General synthesis of metallophthalocyanines* (***Pc* 5-7**)

The phthalonitrile compound (4) (0.15 g, 0.386 mmol) and anhydrous metal salts [$Zn(OAc)_2$ (35 mg, 0.193 mmol) (for the complex ***Pc*-5**), $CoCl_2$ (25 mg, 0.193 mmol) (for the complex ***Pc*-6**) and CuCl2 (26 mg, 0.193 mmol) (for the complex ***Pc*-7**)] were dissolved in n-amyl alcohol (3 mL) and immediately after6 drops of DBU were added. The reaction mixtures were heated and stirred at 140 °C in a standard Schlenk tube under a nitrogen atmosphere for 20 h. After cooling to room temperature, green reaction mixtures were precipitated by adding ethanol. The obtained green solid products were stirred in ethyl alcohol under the N_2 atmosphere at reflux temperature overnight. Then, this mixture was filtered off, washed with ethanol and diethyl ether, and then dried in a vacuum desiccator. Finally, all metallophthalocyanine complexes (***Pc* 5-7**) were obtained as green solids.

2.1.3.1. *Zinc (II) Phthalocyanine* (***Pc*-5**)

Yield: 34 mg (22%), m.p.>300 ºC. FT-IR (ATR), υ_{max} (cm^{-1}): 3060 (Ar-H), 2922-2852 (Aliph. C-H), 1645, 1596, 1504, 1467, 1389, 1318, 1261, 1229, 1164, 1088, 982, 943, 834, 759. ^1H NMR ($CDCl_3$), (δ:ppm): 7.19 (m, 44H, Ar-H), 3.41 (m, 8H, N-CH_2)UV-vis (THF), λ_{max}, nm (logε): 677 (4.44), 611 (3.91), 351 (4.47). MALDI-TOF-MS *m/z*: Calculated: 1619.08; Found: 1642.08 $[M+Na]^+$.

2.1.3.2. *Cobalt (II) Phthalocyanine* (***Pc*-6**)

Yield: 22 mg (14%), m.p.>300 ºC. FT-IR (ATR), υ_{max} (cm^{-1}): 3060 (Ar-H), 2919-2850 (Aliph. C-H), 1597, 1504, 1466, 1406, 1329, 1262, 1230, 1093, 1057, 1015, 956, 872, 828, 753, 662. UV-vis (THF), λ_{max}, nm (logε): 665 (4.38), 606 (4.03), 339 (4.67). MALDI-TOF-MS *m/z*: Calculated: 1612.63; Found: 1635.63 $[M+Na]^+$.

2.1.3.3. *Copper (II) Phthalocyanine* (***Pc*-7**)

Yield: 38 mg (24%), m.p.>300 ºC. FT-IR (ATR), υ_{max} (cm^{-1}): 3059 (Ar-H), 2919-2850 (Aliph. C-H), 1646, 1596, 1504, 1464, 1376, 1318, 1266, 1232, 1156, 1091, 1052, 1016, 983, 950, 873, 827, 747 UV-vis (THF), λ_{max}, nm (logε):677 (4.66), 611 (4.15), 347 (4.66). MALDI-TOF-MS*m/z*: Calculated: 1617.25; Found: 1640.25 $[M+Na]^+$.

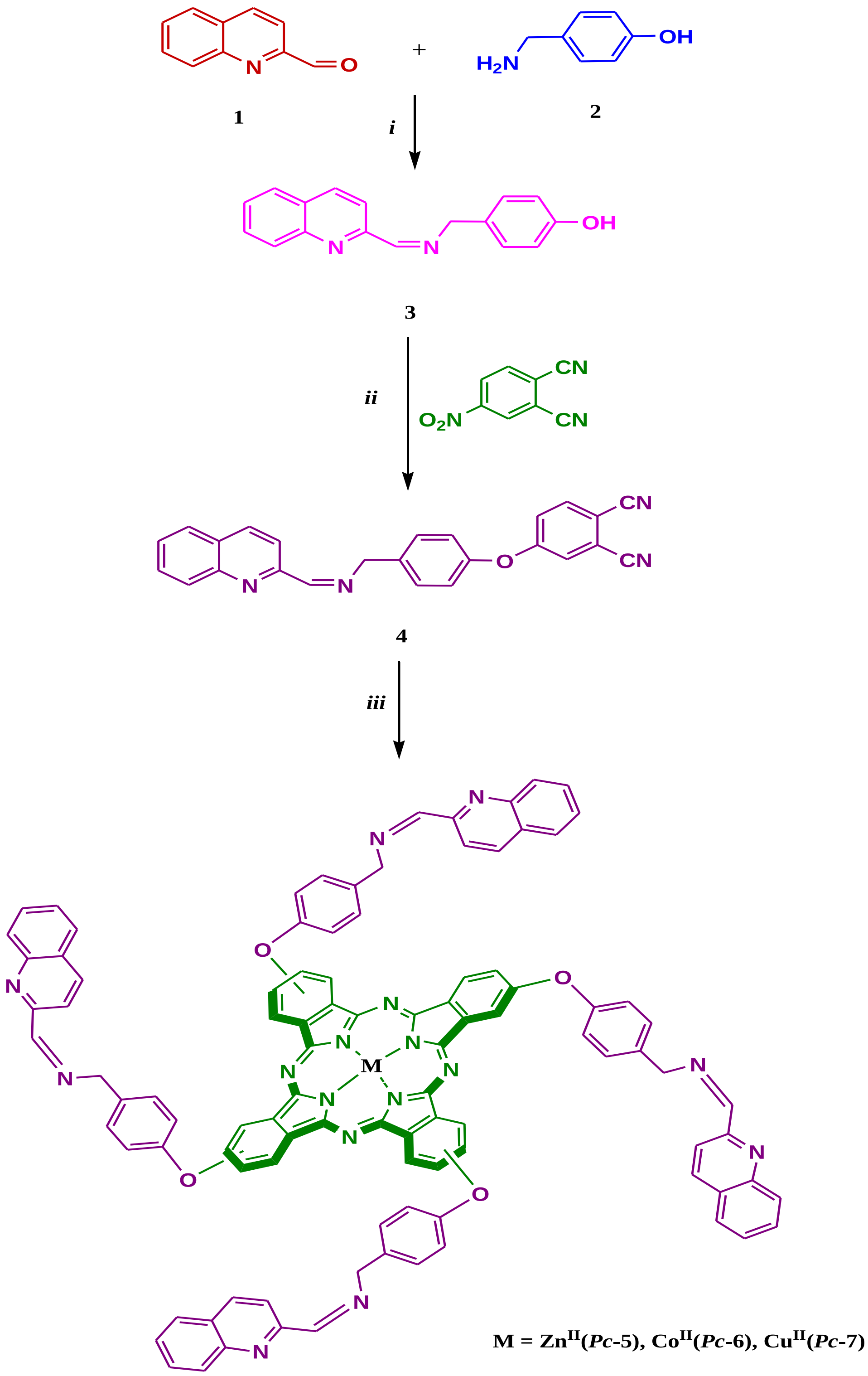
3. Results and discussion

3.1. Synthesis and characterization

The synthesis scheme of all compounds was shown in Scheme 1. The Schiff base derivative (*Z*)-4-((quinolin-2-ylmethyleneamino)methyl)phenol (**3**) and phthalonitrile derivative (*Z*)-4-(4-((quinolin-2-ylmethyleneamino) methyl) phenoxy) phthalonitrile (**4**) were synthesized in the first step. Afterward zinc (II) (***Pc*-5**), cobalt (II) (***Pc*-6**), and copper (II) (***Pc*-7**) phthalocyanines containing Schiff base were synthesized at peripheral positions. 2-quinolinecarboxaldehyde (**1**) and 4-hydroxybenzylamine (**2**) were treated with the glacial acetic acid in the methanol led to (*Z*)-4-((quinolin-2-ylmethyleneamino) methyl) phenol (**3**). The phthalonitrile (**4**) was acquired by the aromatic nucleophilic substitution reaction of 4-nitrophthalonitrile with (*Z*)-4-((quinolin-2-ylmethyleneamino)methyl)phenol (**3**) using K_2CO_3 as the base in dry DMF. This reaction was performed at 55 °C under N_2 atmosphere for 112 h. Subsequently, the metallophthalocyanines zinc (II) (***Pc*-5**), cobalt (II) (***Pc*-6**) and copper (II) (***Pc*-7**) phthalocyanines were accomplished by the cyclotetramerization of phthalonitrile in the presence of anhydrous metal salts ($Zn(OAc)_2$, $CoCl_2$ and $CuCl_2$) in n-amyl alcohol and in the presence of DBU for 20 h. The structures of the new compounds were approved using UV-vis (for the metallophthalocyanines), FT-IR (all new compounds), ^1H NMR (except (***Pc*-6**) and (***Pc*-7**)), ^{13}C NMR and LC-MS/MS (for the compounds **3** and **4**), MALDI-TOF mass spectral data (for all the MPcs). The obtained data are consistent with the expected structures as indicated in Section 2.

Some opinions about the structures of the products were obtained with the comparison of FT-IR spectra. In the IR spectrum of Schiff base derivative (**3**) stretching vibrations of OH group at 3059 cm^{-1} appeared and this value, in the IR spectrum of phthalonitrile derivative (**4**) disappeared. The dinitrile derivative (**4**) exhibited the characteristic C≡N stretching vibrations at 2231 cm^{-1}. Other characteristic vibration bands were observed at 3009 cm^{-1} (for the compound **3**) and 3044 cm^{-1} (for the compound **4**) for aromatic C-H stretching; between 2921-2850 cm^{-1} (for the compound **3**) and between 2919-2851 cm^{-1} (for the compound **4**) for aliphatic C-H stretching.

The ^1H NMR spectra of Schiff base derivative (**3**) and dicyano compound (**4**) were recorded in $CDCl_3$. In the ^1H NMR spectra of phthalonitrile (**4**), the signal OH group belonging to Schiff base derivative (**3**) disappeared as predicted after the conversion of this compound. In the ^1H NMR spectra of Schiff base derivative (**3**) and dicyano compound (**4**), the aromatic protons were observed among 8.20-6.59 ppm (for the compound **3**) and 8.30-6.65 ppm (for the compound **4**). The ^{13}C NMR spectra of the dinitrile compound demonstrated that the nitrile group of carbon atoms was observed between 120.29-120.21 ppm (for **4**). The mass spectra of Schiff base derivative (**3**) and dicyano compound (**4**) were measured by the LC-MS/MS spectral data and molecular ion peaks were specified at *m*/*z*: 263.22 [M+H]$^+$, 388.08 [M]$^+$ respectively (Fig. 1).



Scheme 1. Synthesis of Schiff base compound (**3**), phthalonitrile derivative (**4**) and metallophthalocyanines (***Pc*-5**, ***Pc*-6** and ***Pc*-7**). Reagents and conditions (i) Methanol, glacial acetic acid, reflux temperature, N_2; (ii) N_2, K_2CO_3, DMF, 55°C; (iii) N_2, n-amyl alcohol, DBU, $Zn(OAc)_2$, $CoCl_2$ and $CuCl_2$, 140°C.

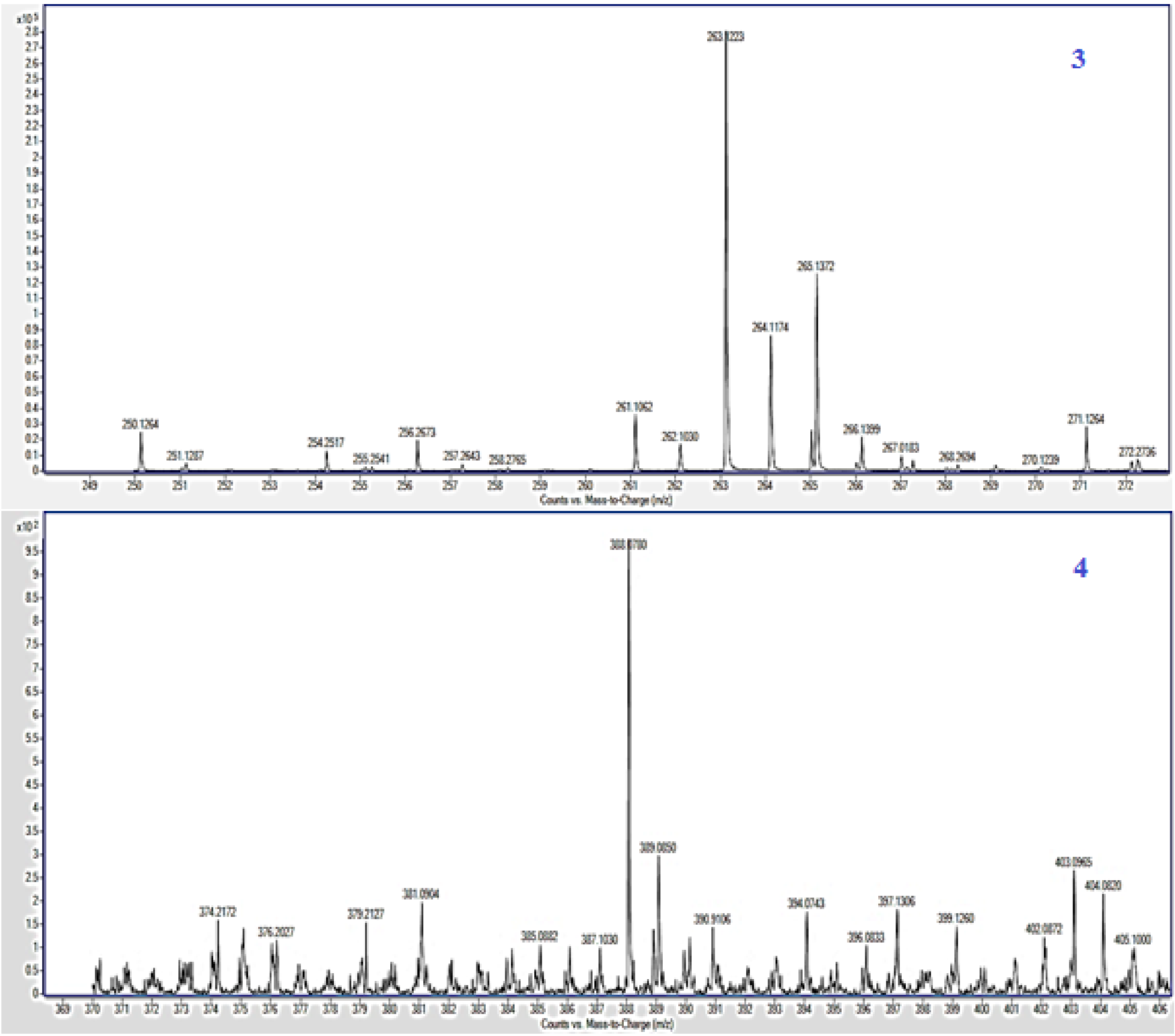


Figure 1. Mass spectra of the compounds 3 and 4.

In the FT-IR spectra of metallophthalocyanines, vibration bands were observed at 3060 cm^{-1} (for the complexes ***Pc*-5** and ***Pc*-6**) and 3059 cm^{-1} (for the complex ***Pc*-7**) for aromatic C-H stretching; between 2922-2852 cm^{-1} (for the complex ***Pc*-5**), 2919-2850 cm^{-1} (for the complexes ***Pc*-6** and ***Pc*-7**) for aliphatic C-H stretching. The ^{1}H NMR spectra of the synthesized phthalocyanine complex (***Pc*-5)** was recorded in CDCl$_3$ and this MPc complex exhibited broad chemical shift when compared with that of corresponding Schiff base derivative (**3**) and dicyano compound (**4**). In the ^{1}H NMR spectra of MPc complex (***Pc*-5**), the aromatic protons were observed at 7.19 ppm (for the complex ***Pc*-5**). In the mass spectra of phthalocyanine complexes acquired by the MALDI-TOF technique, the molecular ion peaks were observed at m/z: 1642.08 [M+Na]$^+$ for ***Pc*-5**, 1635.63 [M+Na]$^+$ for ***Pc*-6** and 1640.25 [M+Na]$^+$ for ***Pc*-7**.

The UV-vis spectra of the synthesized all new peripheral zinc (II) (***Pc*-5**), cobalt (II) (***Pc*-6**) and copper (II) (***Pc*-7**) phthalocyanines were registered in THF at a concentration of 1.0 x 10^{-5} M. All of the obtained phthalocyanine complexes (***Pc*-5**, ***Pc*-6**, and ***Pc*-7**) exhibited a spectrum similar to non-aggregated Pcs. The UV-vis spectra of peripheral zinc (II) (***Pc*-5**), cobalt (II) (***Pc*-6**) and copper (II) (***Pc*-7**) phthalocyanines exhibited sharp and intense absorption band belonging the typical Q-bands at 677 nm ($\log\varepsilon$ = 4.44) for ***Pc*-5**, 665 nm ($\log\varepsilon$ = 4.38) for ***Pc*-6** and 677 nm ($\log\varepsilon$ = 4.66) for ***Pc*-7** with a lower wavelength vibronic band at 611 nm ($\log\varepsilon$ = 3.91) for ***Pc*-5**, 606 nm ($\log\varepsilon$ = 4.03) for ***Pc*-6** and 611 nm ($\log\varepsilon$ = 4.15) for ***Pc*-7**.The B-band absorptions for these complexes were exhibited at 351 nm ($\log\varepsilon$ = 4.47) for ***Pc*-5**, 339 nm ($\log\varepsilon$ = 4.67) for ***Pc*-6** and 347 nm ($\log\varepsilon$ = 4.66) for ***Pc*-7**.

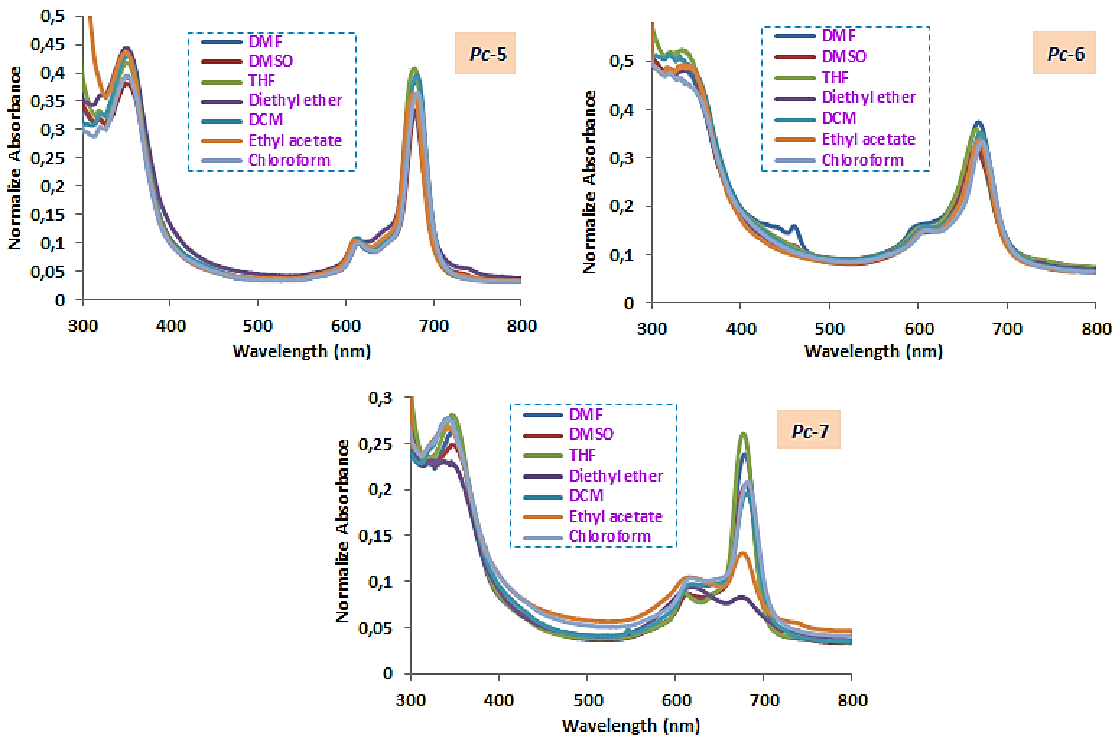


Figure 2. The ground state electronic absorption spectra of ***Pc*-5**, ***Pc*-6**, and ***Pc*-7** in different solvents.

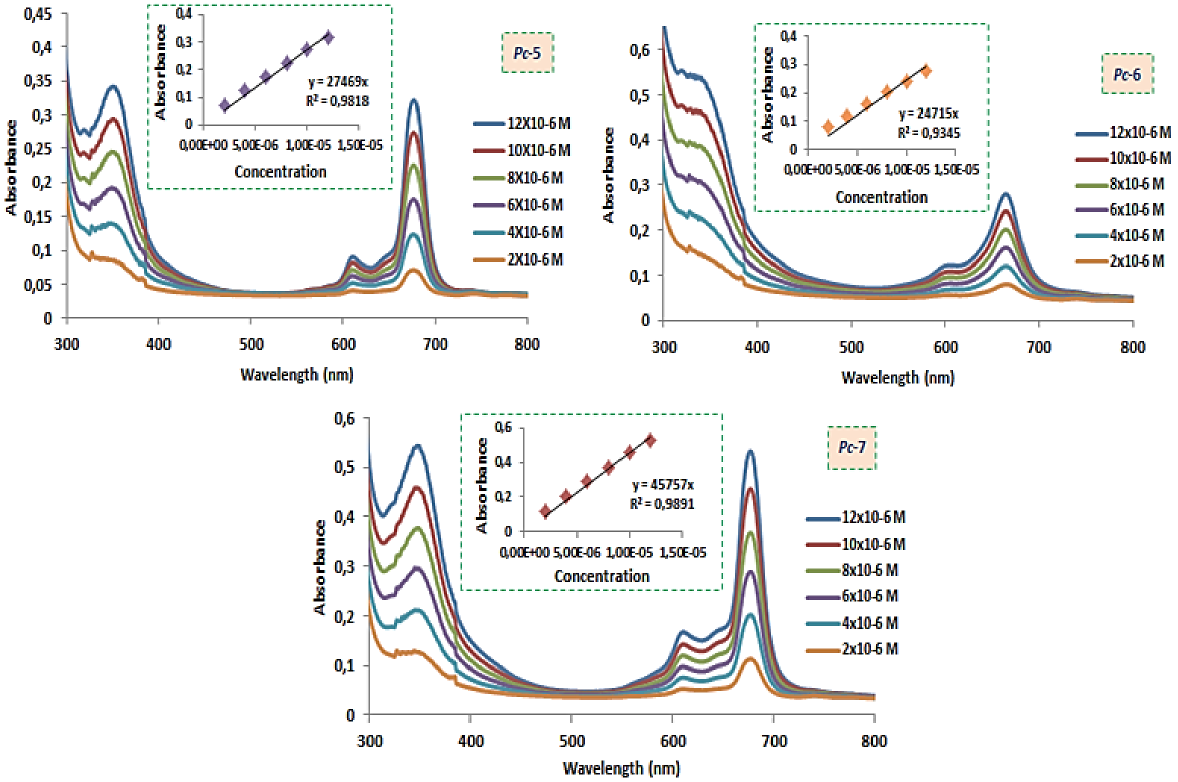


Figure 3. The ground state electronic absorption spectra of *Pc*-5, *Pc*-6 and *Pc*-7 in THF at different concentrations (2.0×10−6 to 12×10−6 M).

3.2. Aggregation studies

Aggregation is a co-planar association of macrocyclic rings and forms the assembly of monomers to dimers and higher-order aggregates. When the molecules aggregate, new bands come out in the absorption spectra. The reason is the formation of aggregation when the intermolecular attraction force between phthalocyanine molecules is stronger than the Pc-solvent association [32,33]. Pcs have a high aggregation affinity on account of the interactions between their 18-π electron systems, which decreases their solubility property in many solvents and seriously affect their areas of usage. The aggregation behavior of MPcs depends on the nature of the temperature, the concentration-nature of the solvent, the substituents, and the complexed metal ion [34, 35].

In this paper, the aggregation behaviors of the peripheral tetra substituted zinc (II) (***Pc*-5**), cobalt (II) (***Pc*-6**) and copper (II) (***Pc*-7**) phthalocyanines were researched in various solvents such as DMF, DMSO, THF, diethyl ether, DCM, ethyl acetate and chloroform to select an appropriate solvent for the usage of their in many applications (Fig. 2). The absorption intensities of Q bands showed significant changes by these solvents. If we look at the aggregation studies, the zinc (II) (***Pc*-5**) phthalocyanine did not exhibit any aggregation in all studied solvents on account of sharp Q band intensities. Also, the cobalt (II) (***Pc*-6**) phthalocyanine exhibited aggregation (H-aggregation) in DMSO and ethyl acetate, however, it did not demonstrate any aggregation in the other studied solvents. In addition to these, Q band of the copper (II) (***Pc*-7**) phthalocyanine considerably reduced in diethyl ether and ethyl acetate and it exhibited aggregation (H-aggregation) in these two solvents.

The aggregation behaviors of the MPcs (***Pc*-5**, ***Pc*-6**, and ***Pc*-7**) were examined at different concentrations in THF (Fig. 3). When the concentration increased, the absorption intensity of the Q band also increased and a new band due to the formation of aggregated species in THF was not observed. Beer-Lambert law was applied for all studied MPcs in the concentrations ranging from 2.0×10^{-6} to 12×10^{-6} M. The studied MPcs (***Pc*-5**, ***Pc*-6**, and ***Pc*-7**) did not exhibit any aggregation at these concentration ranges in THF.

4. Conclusion

In conclusion, the present study has been explained the synthesis, spectroscopic properties, and investigation of the effect on aggregation properties of various central metal ions in synthesized MPcs. The Schiff base derivative (*Z*)-4-((quinolin-2-ylmethyleneamino)methyl)phenol (**3**), phthalonitrile derivative (*Z*)-4-(4-((quinolin-2-ylmethyleneamino)methyl)phenoxy) phthalonitrile (**4**) and peripheral tetra substituted zinc (II) (***Pc*-5**), cobalt (II) (***Pc*-6**), and copper (II) (***Pc*-7**) phthalocyanines were synthesized for the first time. The all new compounds were identified by general spectroscopic techniques. Because the aggregation and solubility of phthalocyanines are important for their applications, we used 4-hydroxybenzylamine (**2**) containing long chain and 2-quinolinecarboxaldehyde (**1**) including bulky group. Thus, metallophthalocyanine complexes exhibited good solubility in many organic solvents such as diethyl ether, DCM, ethyl acetate, THF, chloroform, DMF, and DMSO. The effects of concentration and solvent on the aggregation behavior of the new metallophthalocyanine complexes were researched. The effects of solvent on the aggregation behavior were investigated for MPcs (***Pc*-5**, ***Pc*-6**, and ***Pc*-7**) in diethyl ether, DCM, ethyl acetate, THF, chloroform, DMF, and DMSO. All synthesized MPcs did not exhibit aggregation in chloroform, THF, and DCM. Besides, the effects of concentration on the aggregation behavior were examined for MPcs (***Pc*-5**, ***Pc*-6**, and ***Pc*-7**) in THF. The all studied MPcs did not demonstrate any aggregation in the concentrations ranging from 2.0×10^{-6} to 12×10^{-6} M.

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References

[1] C.C. Leznoff, A.B.P. Lever, Phthalocyanines: Properties and Applications, 1989, New York, VCH Publishers.

[2] K. Kadish, K.M. Smith, R. (Eds.) Guilard, The Porphyrin Handbook, 2003, Boston, Academic Press.

[3] N.B. McKeown, Phthalocyanine materials synthesis, structure and function, 1998, Cambridge University Press.

[4] B. Ertem, H. Yalazan, Ö. Güngör, G. Sarkı, M. Durmuş, E.T. Saka, H.Kantekin, Synthesis, structural characterization, and investigation on photophysical and photochemical features of new metallophthalocyanines, J Lumin, 204, 2018, 464-471.

[5] H. Kantekin, E.T. Saka, B. Ertem, M.N. Mısır, H. Yalazan, G. Sarkı, New peripherally tetra-[trans-3,7-dimethyl-2,6-octadien-1-ol] substituted metallophthalocyanines: Synthesis, characterization and catalytic activity studies on the oxidation of phenolic compounds, J Coord Chem,71(1), 2018, 164-182.

[6] K. Kameyama, M. Morisue, A. Satake, Y. Kobuke, Highly fluorescent self-coordinated phthalocyanine dimers, Angew Chem Int Edit, 44, 2005, 4763-4766.

[7] 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.

[8] 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.

[9] 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.

[10] M. Morisue, Y. Kobuke, Tandem cofacial stacks of porphyrin-phthalocyanine dyads through complementary coordination, Chem-Eur J, 14, 2008, 4993-5000.

[11] H. Manfred, Alkaloids: Nature's curse or blessing, Verlag Helvetica Chimica Acta, 2002, Zürich, Switzerland and, Weinheim, Germany, Wiley-VCH,

[12] C.Y. Poon, P. Chiu, A synthesis of the tetracyclic carboskeleton of isaindigotidione. Tetrahedron Lett, 45, 2004, 2985-2988.

[13] S. Ökten, O. Çakmak, Ş. Tekin, The structure activity relationship (SAR) study of 6,8-disubstituted quinoline derivatives as anti cancer agents, Turk J Clin Lab, 8(4), 2017, 152-159.

[14] I. Jacquemond-Collet, F. Benoit-Vical, A. Valentin, E. Stanislas, M. Mallié, I. Fourasté, Antiplasmodial and cytotoxic activity of galipinine and other tetrahydroquinolines from Galipea officinalis, Planta Med, 68 (1), 2002, 68-69.

[15] K.C. Fang, Y.L. Chen, J. Sheu, T.C. Wang, C.C. Tzeng, Synthesis, antibacterial, and cytotoxic evaluation of certain 7-substituted norfloxacin derivatives, J Med Chem, 43, 20, 2000, 3809-3812.

[16] P. Palit, P. Paira, A. Hazra, S. Banerjee, A.D. Gupta, S.G. Dastidar, N.B. Mondal, Phase transfer catalyzed synthesis of bisquinolines: Antileishmanial activity in experimental visceral leishmaniasis and in vitro antibacterial evaluation, Eur J Med Chem, 44, 2009, 845-853.

[17] B. Podeszwa, H. Niedbala, J. Polanski, R. Musiol, D. Tabak, J. Finster, K. Serafin, M. Milczarek, J. Wietrzyk, S. Boryczka, W. Mol, J. Jampilek, J. Dohnal, D.S. Kalinowski, Dolezal, D.R. Richardson, Investigating the antiproliferative activity of quinoline-5,8-diones and styrylquinolinecarboxylic acids on tumor cell lines, Bioorg Med Chem Lett, 17, 2007, 6138-6141.

[18] R. Musiol, J. Jampilek, V. Buchta, L. Silva, H. Niedbala, B. Podeszwa, A. Palka, K. Majerz-Maniecka, B. Oleksyn, J. Polanski, Antifungal properties of new series of quinoline derivatives, Bioorg Med Chem, 14, 2006, 3592-3598.

[19] S. Ökten, O. Çakmak, R. Erenler, Ö.Y. Şahin, Ş. Tekin, Simple and convenient preparation of novel 6,8-disubstituted quinoline derivatives and their promising anticancer activities, Turk J Chem, 37, 2013, 896-908.

[20] S. Ökten, Ö.Y. Şahin, Ş. Tekin, O. Çakmak, In vitro antiproliferative/ cytotoxic activity of novel quinoline compound SO-18 against various cancer cell lines, J Biotechn, 185S, 2014, S37-S125.

[21] F. Zouhiri, M. Danet, C. Benard, M. Normand-Bayle, J-F. Mouscadet, H. Leh, C.M. Thomas, G. Mbemba, J. D'Angelo, D. Desmaele, HIV-1 replication inhibitors of the styrylquinoline class: Introduction of an additional carboxyl group at the C-5 position of the quinoline, Tetrahedron Lett, 46, 2005, 2201-2205.

[22] A. Şahin, O. Çakmak, İ. Demirtaş, S. Ökten, A. Tutar, Efficent and selective synthesis of quinoline derivatives, Tetrahedron, 64, 2008, 10068-10074.

[23] S. Broch, B. Aboab, F. Anizon, P. Moreau, Synthesis and in vitro antiproliferative activities of quinoline derivatives, Eur J Med Chem, 45, 2010, 1657-1662.

[24] J.E. Nycz, M. Szala, G.J. Malecki, M. Nowak, J. Kusz, Synthesis, spectroscopy and computational studies of selected hydroxyquinolines and their analogues, Spectrochim Acta A, 117, 2014, 351-359.

[25] B. Machura, J. Milek, J. Kusz, J. Nycz, D. Tabak, Reactivity of oxorhenium(V) complexes towards quinoline carboxylic acids. X-ray structure of [ReOCl2(hquin-7-COOH)(PPh_3)]·OPPh3, [ReOBr_2(hquin-7-COOH)(PPh3)] and [ReOX_2(hmquin-7-COOH)(PPh_3)]. DFT and TD-DFT calculations for [ReOCl_2(hquin-7-COOH)(PPh_3)], Polyhedron, 27, 2008, 1121-1130.

[26] S.D. Lytton, B. Mester, I. Dayan, H. Glickstein, J. Libman, A. Shanzer, Z.I. Cabantchik, Mode of action of iron (III) chelators as antimalarials: I. Membrane permeation properties and cytotoxic activity, Blood, 81, 1993, 214-221.

[27] Z. Rezvani, L.R. Ahar, K. Nejati, S.M. Seyedahmadian, Syntheses, characterization and liquid crystalline properties of new bis[5-((4-''alkoxyphenyl)azo)-N-(''alkyl) salicylaldiminato]copper (II) and nickel (II) complex homologs, Acta Chim Slov, 51, 2004, 675- 686.

[28] P. Sen, S.Z. Yildiz, M. Tuna, M. Canlica, Preparation of aldehyde substituted phthalocyanines with improved yield and their use for Schiff base metal complex formation, J Organomet Chem, 769, 2014, 38-45.

[29] Z. Bıyıklıoglu, M. Durmuş, H. Kantekin, Synthesis, photophysical and photochemical properties of quinoline substituted zinc (II) phthalocyanines and their quaternized derivatives, J Photoch Photobiol A, 211, 2010, 32-41.

[30] A. Nas, Ü. Demirbaş, M. Pişkin, M. Durmuş, H. Kantekin, The photophysical and photochemical properties of new unmetallated and metallated phthalocyanines bearing four 5-chloroquinolin-8-yloxy substituents on peripheral sites, J Lumin, 145, 2014, 635-642.

[31] A.A. Kamiloglu, İ. Acar, Z. Bıyıklıoglu, Synthesis and electrochemical properties of new metal-free and metallophthalocyanines bearing 2,6-dimethylquinoline-4-yl derivatives, Polyhedron, 137, 2017, 10-16.

[32] S. Altun, A.R. Özkaya, M. Bulut, Peripheral octa-substituted metal-free, cobalt (II) and zinc (II) phthalocyanines bearing coumarin and chloro groups: Synthesis, characterization, spectral and electrochemical properties, Polyhedron, 48, 2012, 31-42.

[33] A.W. Snow, Phthalocyanine aggregation, in: K. Kadish, R. Guilard, K.M. Smith, The Porphyrin Handbook, Phthalocyanines: Properties and Materials, 17, 2003, Amsterdam, Academic Press.

[34] H. Enkelkamp, R.J.M. Nolte, Molecular materials based on crown ether functionalized phthalocyanines, J Porphyr Phthalocya, 4, 2000, 454-459.

[35] D.D. Dominguez, A.W. Snow, J.S. Shirk, R.S. Pong, Polyethyleneoxide-capped phthalocyanines: limiting phthalocyanine aggregation to dimer formation, J Porphyr Phthalocya, 5, 2001, 582-592.