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Research Article

Practical synthesis, characterization and photo-physical properties of metallophthalocyanines bearing benzhydryloxy substituents

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ABSTRACT

The aim of present study is to make practical synthesis of benzhydryloxy substituted phthalocyanines with high solubility. Therefore, the synthesis and characterization of benzhydryloxy substituted zinc and magnesium of phthalocyanines were performed. The characterization of the new compounds was clarirified by spectra such as IR, NMR, UV and Mass spectra. Furthermore, fluorescence and aggregation behaviors of these new compounds were investigated. It was seen to be obtained the compounds more economically with the method used.

Keywords: Phthalocyanine, practical synthesis, characterization, aggregation.

Benzhidriloksi substituentlerini taşıyan metalloftalosiyaninlerin pratik sentezi, karakterizasyonu ve foto-fiziksel özellikleri

ÖZ

Bu çalışmanın amacı, yüksek çözünürlüğe sahip benzhidriloksi substitue ftalosiyaninlerin pratik sentezini yapmaktadır. Bu nedenle, ftalosiyaninlerin benzhidrilksi substitueli çinko ve magnezyum sentezi ve karakterizasyonu gerçekleştirmiştir. Yeni bileşiklerin karakterizasyonu, IR, NMR, UV ve Kütle spektrumları gibi spektrumlarla açıklandı. Ayrıca, bu yeni bileşiklerin floresan ve agregasyon davranışları araştırıldı. Kullanılan yöntemle bileşiklerin daha ekonomik olarak elde edildiği görüldü.

Anahtar Kelimeler: Ftalosiyanin, pratik sentez, karakterizasyon, agregasyon.

1. INTRODUCTION

Phthalocyanines (Pcs) are known to have been synthesized since a century. In addition to being used as dyes and pigments, they are also being used in different areas.[1-2] Some of these areas can be listed as liquid crystals[3], catalysts[4], chemical sensors[5], photovoltaic[6], data storage[7], semiconductors[8], light-emitting diodes[9], solar cell[10], nonlinear optic material[11] and sensor for photodynamic therapy.[12] Innovations are added these areas depending on technological developments. At the beginning of the factors that limit the use of phthalocyanines in these areas lies low resolution and aggregating.[13] Many studies with regard solubility of phthalocyanines are present in the literature.[14-16] Factors that inhibit solubility are obstacles to other applications. For compounds of phthalocyanine, determining the behavior of aggregation also gives an idea of solubility.[17] Aggregation also inhibits the solubility of phthalocyanine compounds.[18] Thus aggregated phthalocyanine compounds are ineffective as photosensitizers. Soluble and non-aggregated phthalocyanines are also needed to obtaine applicable photophysical data.[19] As a result, phthalocyanine compounds are prevented from effectively using the optical and redox properties.[20] An important way to prevent this is to choose appropriate groups for peripheral and non-peripheral positions.[21]

In this study, we reported the synthesis and the characterization of new metallo phthalocyanines substituted with benzhydryloxy peripheral units. The reasons for choosing this functional group are that the bulky and Pcs core enhance the solubility in organic solvents and control the aggregation behavior in different concentrations. At same time, a significant advantage of these compounds is that they can dissolve in a wide range of solvent environments.

2. MATERIALS AND METHODS

2.1. Materials

Zinc(II) chloride ($ZnCl_2$), magnesium (II) chloride ($MgCl_2$), potassium carbonate (K_2CO_3), ethanol, methanol, ethyl acetate, acetonitrile, chloroform ($CHCl_3$), dichlormathane (CH_2Cl_2), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO) were purchased from Merck and Sigma. The solvents were purified according to standard procedure[22] and stored over molecular sieves (4 Å). All reactions were carried out under dry nitrogen atmosphere. Melting points were measured on an electro-thermal apparatus. Electronic spectra were recorded on a Hitachi U-2900 Spectrophotometer (Van YYU, Central Laboratory, Turkey). Routine FT-IR spectra were recorded on a Thermo Scientific FT-IR (ATR sampling accessory) spectrophotometer (Van YYU, Central Laboratory, Turkey). ^1H NMR spectra were recorded on an Agilent 400 MHz spectrometer (Van YYU, Central Laboratory, Turkey) with tetramethylsilane as internal standard. Mass spectra were recorded on a MALDI (matrix assisted laser desorption ionization) BRUKER Microflex LT.

2.2. Method

2.2.1. 4-(benzhydryloxy)phthalonitrile (3)

A mixture of diphenyl methanol **1** (0.532 g, 2.89 mmol) and 4-nitrophthalonitrile **2** (0.500 g, 2.89 mmol) in 15 mL dimethylformamide (DMF) was stirred at room temperature under nitrogen atmosphere. After stirring for 15 min, K_2CO_3 (1.27 g, 9.2 mmol) was added into the mixture over a period of 2 h. The reaction mixture was further stirred for 48 h, and then poured into cold water (150 mL) and stirred again. The precipitate was filtered, washed with water to neutralize, and then dried. The residue was recrystallized from ethanol. The product is soluble in ethyl acetate, acetonitrile, $CHCl_3$, CH_2Cl_2, dichloroethane, benzene, THF, DMF and DMSO. Yield; 0.40 g (45 %). Mp: 158-160ºC. FT-IR spectrum (cm^{-1}): 3109, 3059, 3039 (Ar-CH), 2900 (CH), 2225 (CN), 1593, 1566, 1492, 1454, 1354, 1414, 1311, 1253, 1207, 1161, 1087, 1006, 879, 702. ^1H NMR (400 MHz, DMSO-d_6) δ ppm: 8.02, 8.00, 7.84, 7.47, 7.46, 7.36, 7.34, 7.29, 7.27, 6.83, 1.73.

2.2.2. 2, 10, 16, 24 – Tetrakis(benzhydryloxy phthalocyaninato) Zinc (II) (4)

A mixture of 4-(benzhydryloxy) phthalonitrile **3** (0.100 g) and $ZnCl_2$ (0.020 g) was powdered in a quartz crucible and heated in a sealed glass tube for 5 min under nitrogen at 270 ºC. After cooling to room temperature, the product was washed with water, and was filtered. Then, the product washed with hexane, benzene and toluene again. The product was purified by column chromatography on silica with an eluent of THF. The product is soluble in CH_2Cl_2, dichloroethane, ethanol, methanol, $CHCl_3$, propanol, butanol, ethyl acetate, DMF, THF, and DMSO. The yield was 0.048 g (46 %). UV-Vis (THF) λmax (log ε: 680 (5.22), 614 (4.71), 350 (5.08). FT-IR spectrum (cm^{-1}): 3059, 2920, 1604, 1485, 1450, 1400, 1350, 1242, 1095, 1037, 941, 879, 744. MALDI-TOF MS: m/z $[M]^+$ calcd. for $C_{84}H_{56}N_8O_4Zn$: 1306.77; found $[M]^+$:1306.79.

2.2.3. 2, 10, 16, 24 – Tetrakis (benzhydryloxy phthalocyaninato) Mg (II) (5)

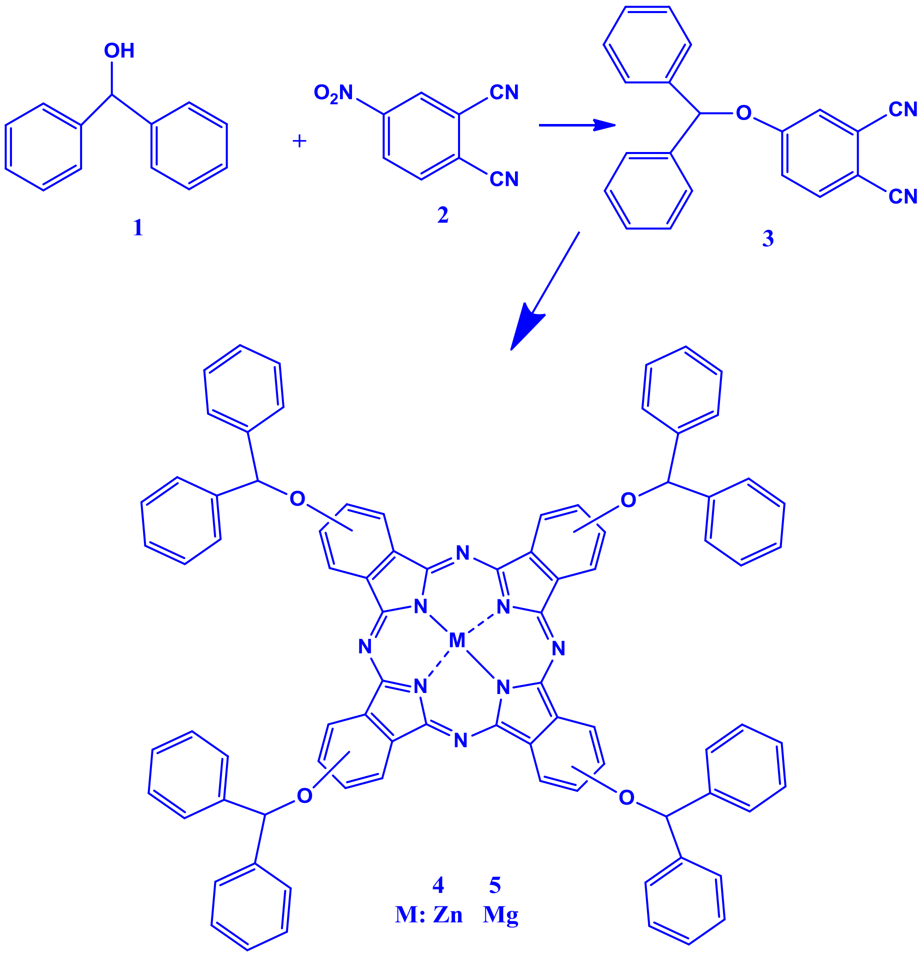
A mixture of 4-(benzhydryloxy) phthalonitrile **3** (0.100 g) and $MgCl_2$ (0.020 g) was powdered in a quartz crucible and heated in a sealed glass tube for 5 min under nitrogen at 270 ºC. After cooling to room temperature, the product was washed with water, and was filtered. Then, the product washed with hexane, benzene, and toluene and diethyl ether again. The product is soluble in CH_2Cl_2, dichloroethane, ethanol, methanol, $CHCl_3$, propanol, butanol, ethyl acetate, DMF, THF, and DMSO. The yield was 0.032 g (31 %). UV-Vis (THF) λmax (log ε: 690(5.25), 622(4.74), 354(4.98). FT-IR spectrum (cm^{-1}):3024,2924,1600,1492,1450,1338,1261,1095,1026,906, 802,756. MALDI-TOF MS: m/z $[M]^+$ calcd. for $C_{84}H_{56}MgN_8O_4$: 1265.70; found $[M]^+$:1265.17.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization

The synthetic recipe and the formulas of the 4-(benzhydryloxy) phthalonitrile (**3**) and metallophthalocyanines (**4-5**) are shown in Scheme 1. Synthesis of 4 - (benzhydryloxy) phthalonitrile (**3**) was carried out in a similar way to our previous studies. Diphenyl methanol **2** and 4-nitrophthalonitrile **1** were added the reaction mixture in the presence of potassium carbonate to obtain the phthalonitrile derivative. The reaction was completed at room temperature under a nitrogen atmosphere for 48 hours. The phthalocyanines (**4-5**) were prepared by the reaction of 4-(benzhydryloxy) phthalonitrile (**3**) with $ZnCl_2$, $MgCl_2$ under N_2 atmosphere. Spectra such as UV, IR, NMR and mass spectra were used in the elucidation of the structure of the newly prepared compounds.

Novel phthalocyanines (**4-5**) were purified by column chromatography after pre-purification (solvent washing). This purification is not to separate the isomers, but is for obtaining of the appropriate isomer mixtures. In the literature, such compounds are given as molecular symmetry as C_{4h}, C_{2v}, C_s, and D_{2h}. It is often not necessary to purify these isomers. If the separation of the isomers is necessary, different chromatographic methods can be used.[23] New phthalocyanines are easy soluble in ordinary organic solvents such as chloroform, dichloroethane, dichloromethane, tetrahydrofurane, dimethylformamide, dimethyl sulfoxide, ethanol, methanol, propanol, butanol, ethyl acetate. The high solubility of these compounds of phthalocyanine gives advantages in terms of applications.



Scheme 1. The route for the synthesis of compounds **3-5**.

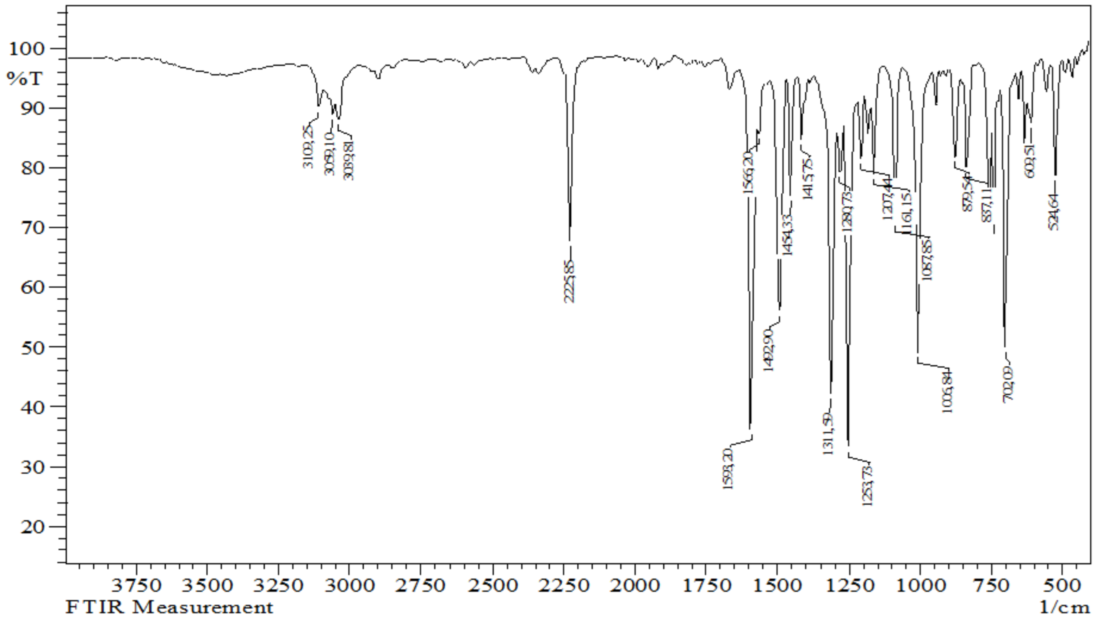


Figure 1. FT-IR spectrum of 4-(benzhydryloxy) phthalonitrile **3**.

The IR spectrum gives information on the nitrile peak, which is regarded as a significant difference between phthalonitrile derivatives, and phthalocyanine compounds. This peak reveals the structural difference. It is not found in compounds of 2225(-CN) cm^{-1} band phthalocyanine in 4- (benzhydryloxy) phthalonitrile compound. This confirms what is expected for the compounds. The FT-IR spectrum of compound **3** is shown in Figure 1. The complex compound **4** gives IR vibration bands at 702, 879, 1006, 1087, 1253(C-O-C), 1454-1492, and 1598(C=C) cm^{-1}. These data support what is expected. The Compound **5** shows similar bands except minor shift values.

The NMR spectrum used to elucidate the structure of organic compounds gives important information. The ^1H NMR spectrum of the 4- (benzhydryloxy) phthalonitrile compound having an organic structure in DMSO-d_6 gives the aromatic and aliphatic protons as 8.02, 8.00, 7.84, 7.47, 7.46, 7.36, 7.34, 7.29, 7.27, 6.83 (Ar-H), 1.73 ppm, respectively. Compounds **4** and **5** show slight shifts relative to the starting material. Complex **4** compound gives aromatic at 7.45, 7.29, 7.18, 7.06, 6.86, 6.62 (Ar–H) and aliphatic peaks at 1.37 ppm. Complex **5** shows 7.65, 7.31, 7.18, 6.86, 6.62, and 1.35 peaks.

The mass spectra of the compounds of phthalocyanine confirm the structures of the compounds. The 1306.79 ion peak value obtained for zinc phthalocyanine is equivalent to the calculated mass of 1306.77. This confirms the expected complex structure. A similar phenomenon has also been observed for the compound of magnesium phthalocyanine. It corresponds to the value of 1265.17 which is calculated at 1265.70 value.

3.2. Photophysical study

UV spectral studies provide some characteristic information by electronic structure of phthalocyanine compounds. One of them is the characteristic Q and B bands. These bands are basic indicators for molecular structure. At the same time, these bands provide information on whether or not the structural metal of the composite is connected. Absorption, excitation, and emission spectra play an important role in determining the structure and the photophysical properties of the compound when evaluated together. The tetrahydrofuran solvent was used for the spectral work. The π-π* transitions of Q and B bands of the synthesized phthalocyanine compounds are in accordance with the literature.[23] The numerical values of the UV absorption bands are given experimental limitations. Some parameters present that affect the void space between HOMO and LUMO for phthalocyanine compounds. This value gives information about whether phthalocyanine compound can be used as semiconductor or photosensor.[24] Current studies show that compounds of phthalocyanine are useful in the case of reddish absorption bands to be used as photosensors. When a compound meets these requirements, it can provide a potential to be used therapeutically.[25] The values for the phthalocyanine compounds have been obtained at values of 680 and 690 nm which are much higher than the assumed value of 650 nm.

Aggregation studies for **4-5** compounds of phthalocyanine were carried out in THF. Aggregation studies for **4-5** compounds of phthalocyanine were carried out in THF. Absorption values were read in the UV spectrum against the increase of the amount of substance in the range of $5.74x10^{-6}$M - $3.22x10^{-5}$ M concentration. The aggregation studies of compounds **4** and **5** are given in Figures 2 and 3, respectively. Aggregation studies show that these compounds are well suited to the Beer-Lambert law. These compounds are solubilized not only in THF, but also in solvents such as CH_2Cl_2, dichloroethane, ethanol, methanol, $CHCl_3$, propanol, butanol, ethyl acetate, DMF, and DMSO. Both non- aggregation and high resolution give advantages for applications.

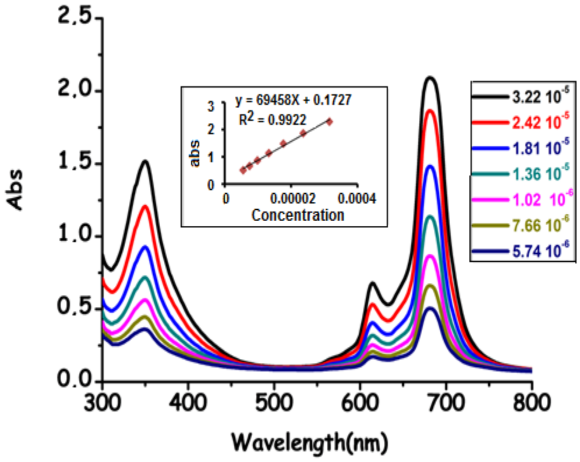


Figure 2. Aggregation study of compound **4** in THF (Concentrations: $3.22.10^{-5}$, $2.42.10^{-5}$, $1.81.10^{-5}$, $1.36.10^{-5}$, $1.02.10^{-6}$, $7.66.10^{-6}$, $5.74.10^{-6}$ M).

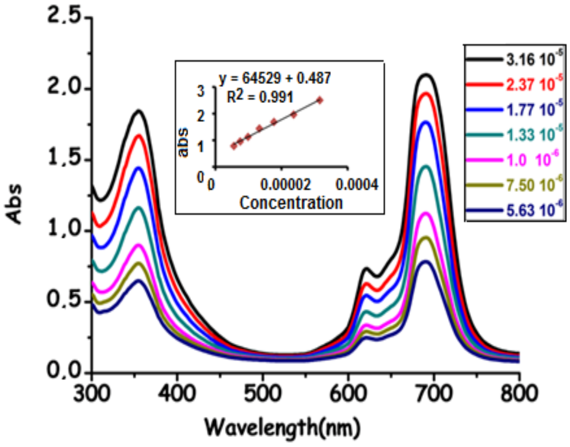


Figure 3. Aggregation study of compound **5** in THF (Concentrations: $3.16.10^{-5}$, $2.37.10^{-5}$, $1.77.10^{-5}$, $1.33.10^{-5}$, $1.0.10^{-6}$, $7.50.10^{-6}$, $5.63.10^{-6}$ M).

As is known, fluorescence substances have an increasing interest day by day. This is why some of these materials are widely used. They are used in many applications such as DNA, sensors and many technological applications. The absorption, excitation and emission spectra for phthalocyanines **4** and **5** are shown in Figures 4 and 5. The Stoke's shifts are consistent with available data in the literature.[26-27] Phthalocyanines are often obtained with sophisticated processes with low yields. Often the resolution is not as good as desired. For this reason, the synthesis of phthalocyanines which are easily designed and have high solubility is economically important.

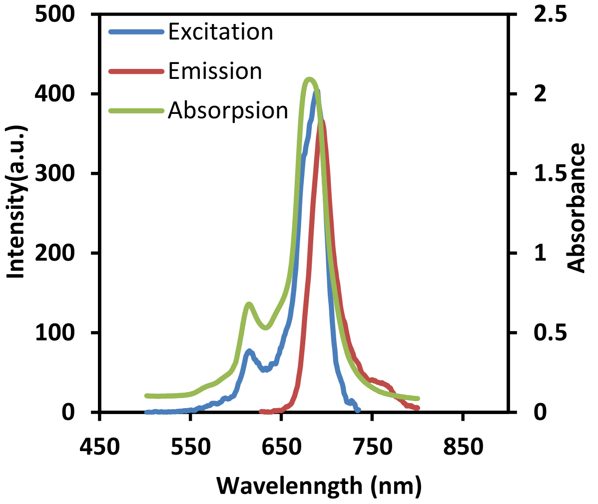


Figure 4. Electronic absorption, excitation and emission spectra of compound 5 in THF (Excitation wavelength = 693 nm).

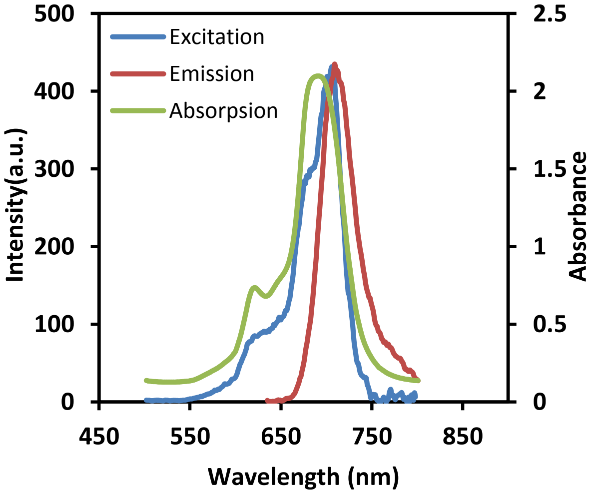


Figure 5. Electronic absorption, excitation and emission spectra of compound 6 in THF (Excitation wavelength = 647 nm).

4. CONCLUSIONS

Zinc (II) and magnesium (II) phthalocyanines (**4-5**) bearing benzhydryloxy groups were synthesized for the first time *via* the cyclotetramerisation reaction of new 4-(benzhydryloxy) phthalonitrile (**3**) in the presence of corresponding metal salt. New compounds were characterized by spectroscopic data (^{1}H NMR, MALDI-TOF, IR, and UV-vis). All the studied metal (II) phthalocyanines are soluble in most solvents chloroform, dichloroethane, dichloromethane, tetrahydrofurane, dimethylformamide, dimethyl sulfoxide, ethanol, methanol, propanol, butanol, ethyl acetate. These phthalocyanines have a significant advantage in solubility in a large number of solvents. In addition, these compounds may have potential for use in different areas due to their fluorescence, non-aggregation, and high-resolution properties.

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Conflict of Interest

Authors declare that there is no a conflict of interest with any person, institute, company, etc.

REFERENCES

1. McKeown, N.B. *Phthalocyanine Materials: Synthesis, Structure and Function*, Cambridge University Press, Cambridge, 1998.

2. Leznoff, C.C.; Lever, A.B.P. Eds. *Phthalocyanines: Properties and Applications*, vol. 4, VCH, New York, 1989.

3. Garland, A.D.; Chambrier, I.; Cammidge, A.N.; Cook, M.J. *Tetrahedron* **2015,** 71, 7310-7314.

4. Lianga, Q.; Zhanga, M.; Liub, C.; Xua, S.; Li, Z. *Appl. Catal. A.* **2016,** 519,107–115.

5. Shi, J.; Luan, L.; Fang, W.; Zhao, T.; Liu, W.; Cui, D. *Sens. Actuators B.* **2014,** 204, 218–223.

6. Sánchez-Díaz, A.; Pacios, R.; Muñecas, U.; Torres, T.; Palomares, E. *Org. Electron.* **2011,** 12: 329– 335.

7. Lile, J.R.D.; Heine, T.; Zhou, S. *Comp. Mater. Sci.* **2017,** 129, 24–36.

8. Shao, X.; Wang, S:; Li, X.; Su, Z.; Chen, Y.; Xiao, Y. *Dyes Pigments* **2016**, 132, 378-386.

9. Deng, Z.; Lü, Z.; Chen, Y.; Yin, Y.; Zou, Y.; Xiao, J.; Wang, Y. *Solid State Electron*. **2013,** 89, 22–25.

10. Ma, D.; Pan, S.; Zhang, T.; Huang, B.; Xie, S.; Yang, H.; Peng, Y. *Dyes Pigments* **2016,** 127,78-86.

11. Sekhosana, K.E.; Nyokong, T. *J. Mol. Struct*. **2016,** 1117,140-146.

12. Wang, A.; Gui, L.; Lu, S.; Zhou, L.; Zhou, J.; Wei, S. *Dyes Pigments*. **2016,** 126, 239-250.

13. Erdoğmus, A.; Arıcı, M. *J. Fluorine Chem*. **2014**, 166, 127–133.

14. Ağırtaş, M.S. *Dyes Pigments*. **2008**, 79, 247-51.

15. Ağırtaş, M.S. *Inorg. Chim. Acta* **2007,** 360, 2499–502.

16. Bandera, Y.; Burdette, M.K.; Shetzline, J.A.; Jenkins, R.; Creager, S.E.; Foulger, S.H. *Dyes Pigments* **2016,** 125, 72-79.

17. Palewska, K.; Sworakowski, J.; Lipinski, J. *Opt. Mater.* **2012,** 34, 1717–1724.

18. Chen, J.; Zhang, T.; Wang, S.; Hu, R.; Li, S.; Ma, J.S.; Yang, G. *Spectrochim. Acta A*. **2015,** 149, 426–433.

19. Nyokong, T., Antunes, E. *Photochemical and Photophysical Properties of Metallophthalocyanines. Handbook of Porphyrin Science*, 2010, pp. 247-357.

20. Claessens, C.G.; Hahn, U.; Torres, T. *Chem. Rec*. **2008**, 8, 75-97.

21. Tillo, A.; Stolarska, M.; Kryjewski, M.; Popenda, L.; Sobotta, L.; Jurga, S.; Mielcarek, J.; Goslinski, T. *Dyes Pigments* **2016,** 127, 110-115.

22. Armarego, W.L.F.; Chai, C.L.L. *Purification of laboratory Chemicals*, 7nd ed., Butterwordh-Heinemann, Oxford, 2013.

23. Saka, E.T.; Kobak, R.Z.U.; Alp, H.; Sarkı, G.; Koca, A.; Kantekin, H. *Synthetic Met.* **2016,** 217, 295–303.

24. Fukuda, T.; Kobayashi, N. In: Kadish KM, Smith KM, Guilard R, editors. Handbook of porphyrin science with applications to chemistry, physics, materials science, engineering, biology and medicine, Singapore: World Scientific Publishing Co. Pte. Ltd, vol. 9, 2010.

25. Mehraban, N.; Freeman, H.S. *Materials* **2015**, 8, 4421-4456.

26. Saka, E.T.; Durmuş, M.; Kantekin, H. *J. Organomet. Chem*. **2011,** 696, 913-924.

27. İşçi, Ü.; Beyreis, M.; Tortik, N.; Topal, S.Z.; Glueck, M.; Ahsen, V.; Dumoulina, F.; Kiesslich, T.; Plaetzer, K. *Photodiagn. Photodyn.* 2016, 13, 40–47.

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