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Synthesis and Spectroscopic Properties of 5-Amino-1,3,4-Thiadiazole Substituted Zinc(II) Phthalocyanine Compound

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Abstract. Thiadiazole substituted phthalonitrile **1** was prepared by a nucleophilic displacement reaction of 4-nitrophthalonitrile with 5-Amino-1,3,4-thiadiazole-2-thiole. Thiadiazole tetrasubstituted zinc(II) monophthalocyanine **2** was synthesized by tetramerization of compound **1**. The new compounds were characterized by ^{1}H-NMR, UV-vis and IR spectra. Aggregation behavior of compound **2** was investigated both in different solvents ($CHCl_3$, DMF, DMSO) and in different concentrations. The fluorescence properties of compound **2** were also studied.

Keywords: Phthalocyanine, thiadiazole, aggregation, zinc.

5-Amino-1,3,4-Tiyadiazol Sübstitüye Çinko(II) Ftalosiyanin Bileşiğinin Sentezi ve Spektroskopik Özellikleri

Özet. Tiyadiazol sübstitüye ftalonitril **1**, 5-Amino-l, 3,4-tiyadiazol-2-tiyol ile 4-nitroftalonitrilin nükleofilik yer değiştirme reaksiyonu ile hazırlandı. Bileşik **1**’in tetramerizasyonu ile tiyadiazol tetrasübstitüye çinko(II) monoftalosiyanin **2** sentezlendi. Yeni bileşikler, ^{1}H-NMR, UV-vis ve IR spektrumları ile karakterize edildi. Bileşik **2**'nin agregasyon davranışı hem farklı çözücülerde ($CHCl_3$, DMF, DMSO) hem de farklı konsantrasyonlarda araştırılmıştır. Bileşik **2**'nin floresans özellikleri de incelenmiştir.

Anahtar Kelimeler: Ftalosiyanin, tiyadiazol, agregasyon, çinko.

1. INTRODUCTION

Organic solar cells, which are clean and renewable energy sources, have attracted attention as a promising technology in many areas. In recent years, academic studies have been intensely continuing to produce new organic molecules that may be active in this area. It is very important to achieve high energy efficiency in organic solar cells [1-4]. For this reason, the organic material to be used must be highly active in this area.

Metal phthalocyanines are organic materials of p-type semiconductors and have been widely preferred in applications such as gas sensing, non-linear optic, OFET. Phthalocyanines are also attention in organic solar cell applications due to their photo- and thermal stabilities, the controllable redox potentials, intense absorption at high wavelength in UV-visible and near IR region and semiconducting properties [5,6]. These properties of phthalocyanines were strongly affected by the metal ion in the cavity and by the nature, number and position of substituent [4,7,8]. It is desirable that phthalocyanines do not

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aggregation as they will degrade energy efficiency in organic solar cell applications [4]. In addition, it is important to examine the fluorescence properties of phthalocyanines in order to explain the energy and electron transfer processes. In these applications, it is desirable to be high of fluorescence quantum yield calculated from the fluorescence emission spectra of the compounds [9,10]. It has been observed in the literature that perovskite organic solar cells using phthalocyanine derivatives have reached energy efficiency of up to 17.5% [11].

On the other hand, 1,3,4-thiadiazoles being chemically and biologically active molecules, are on important classes of heterocyclic compounds. 1,3,4-Thiadiazole has electron poor nature and good electron-accepting ability. In this respect, they show interesting optical, electronic and chemical properties [12]. Many studies have shown that 1,3,4-thiadiazole derivatives have a very high potential for use in organic solar cell applications [1,13-15]. It has been observed in the literature that in the organic solar cell applications of 1,3,4-thiadiazole derivative compounds can reach up to 13% energy efficiency [1].

It is believed that the new organic compound obtained as a result of the combination of these two active groups is expected to have a high usability potential for organic solar cell applications.

2. EXPERIMENTAL

2.1. Materials and instruments

All reactions were carried out under argon atmosphere. All solvents were dried by molecular sieves or proper methods [16]. 4-nitrophthalonitrile was prepared according to the literature [17]. IR spectra were recorded on a PerkinElmer Spectrum100 FT-IR Spectrometer using ATR. UV-vis spectra were recorded on a Shimadzu UV-1800 UV-vis spectrophotometer. ^{1}H-NMR spectra were obtained by using JEOL Resonance ECZ400S 400 MHz spectrometer. Melting points are determined with an Electrothermal 9100 digital melting point apparatus.

2.2. Synthesis of compounds

4-(5-amino-1,3,4-thiadiazole-2-thio)phthalonitrile (**1**)

4-nitrophthalonitrile (1000 mg, 5.8 mmol) and 5-Amino-1,3,4-thiadiazole-2-thiole (773 mg, 5.8 mmol) were dissolved in anhydrous DMF (30 mL) at room temperature. To the solution in DMF was added the anhydrous potassium carbonate (2400 mg, 17.4 mmol) over period of 2h with efficient stirring. The reaction mixture was stirred at 60°C for 72h. The reaction was controlled by TLC. Then the mixture was poured into water (300 mL) and the precipitate was filtered off, washed with water and dried. The crude product was purified by column chromatography on silica gel using $CHCl_3$ and diethyl ether (30:10). The yellow solid was soluble in acetone, $CHCl_3$, THF, DMF and DMSO. Yield 550 mg (37%). Mp: 197°C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25°C): δ= 9.8 (s, 2H, N-H); 8.8 (d, 1H, Ar-H); 8.6 (d, 1H, Ar-H); 8.5 (d, 1H, Ar-H). IR (ATR) υ (cm^{-1}) 2973; 2848; 2234; 1582; 1507; 1480; 1385; 1276; 1073; 762.

Thiadiazole tetrasubstituted zinc(II) phthalocyanine (**2**)

Mixtures of **1** (100.0 mg, 0.38 mmol) and $Zn(OAc)_2$ (5.4 mg, 0.10 mmol) in pentanol (3 mL) was heated at 180°C at the presence of 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) for 24h. After cooling, the green product mixture was precipitated by MeOH and filtered off. The green solid was washed with MeOH and dried. The crude product was purified by column chromatography on silica gel using $CHCl_3$. The dark green solid was soluble in $CHCl_3$, THF, DMF and DMSO. Yield 35.0 mg (32%). Mp: >300°C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): δ= 10.2 (s, 8H, N-H); 9.1-8.7 (br m, 12H, Pc Ar-H). UV-Vis ($CHCl_3$) λ_{max}/nm (log ε, dm^3 mol^{-1} cm^{-1}) 681 (5.15), 618 (4.55), 352 (4.84). IR (ATR) υ (cm^{-1}) 3024; 2928; 2865; 1643; 1584; 1489; 1443; 1320; 1205; 1063; 767.

3. RESULTS AND DISCUSSIONS

3.1. Synthesis and characterization

The synthesis route for the compounds **1**, **2** are shown in Figure 1. The compound **1** was synthesized by the reaction of 4-nitrophthalonitrile and 5-Amino-1,3,4-thiadiazole-2-thiole in the presence of K_2CO_3. The zinc(II) phthalocyanine **2** was synthesized by heating of compound **1** with $Zn(OAc)_2$ in pentanol at the presence DBU, respectively. UV-vis, ^{1}H-NMR, IR spectra results of starting compound **1** and phthalocyanine compound **2** were confirmed the proposed structure of the new compounds.

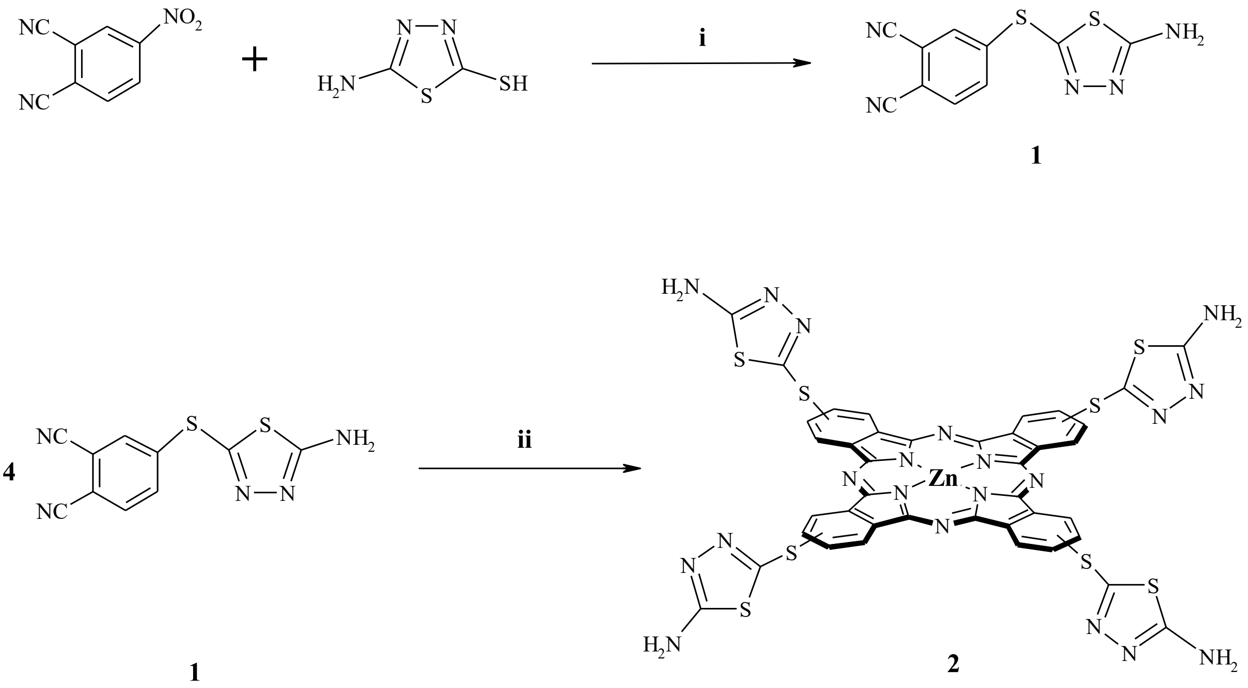

Figure 1. Synthesis of compounds **1**, **2**. (i) K_2CO_3, DMF; (ii) $Zn(OAc)_2$, DBU, pentanol.

The characteristic vibration band of the -C≡N group appeared at 2234 cm^{-1} in the IR spectra of **1**, it disappeared after conversion to zinc(II) phthalocyanine **2**. In the ^{1}H-NMR spectrum of compound **1** which was taken in $CDCl_3$ at room temperature, the aromatic protons appeared at between 8.8 ppm-8.5 ppm, and $-NH_2$ proton appeared at 9.8 ppm. $-NH_2$ peak disappeared with D_2O exchange. The spectrum of the compound **2** was showed phthalocyanine aromatic protons at between 9.1 ppm-8.7 ppm. The $-NH_2$ protons at compound **2** appeared at 10.2 ppm which disappeared with D_2O exchange. The UV-vis spectra of compound **2** in $CHCl_3$ showed typical absorptions between 600-700 nm in the Q band region. The UV-Vis spectra of compound **2** give characteristic Q-band absorption for the metallophthalocyanines a peak at 681 nm. In addition, B-band of compound **2** appeared at 352 nm [18,19].

3.2. Aggregation behaviors

Phthalocyanines aggregate due to electronic interactions between rings of two or more molecules [20]. Aggregation is dependent on the concentration, metal ions, nature of the solvent, nature of substituent and temperature. In many cases, the spectra in the Q-band region show the effects of aggregation, typically a blue shift and broadening of the maximum absorbance [20-22]. In this study, the aggregation behaviors of compound **2** were investigated in $CHCl_3$, DMF and DMSO. Compound **2** did not show an aggregation in these solvents (Figure 2). The aggregation behavior of compound **2** was also investigated at different concentration in DMSO, DMF and $CHCl_3$ (Figure 3). There is no aggregation of compound **2** at different concentrations.

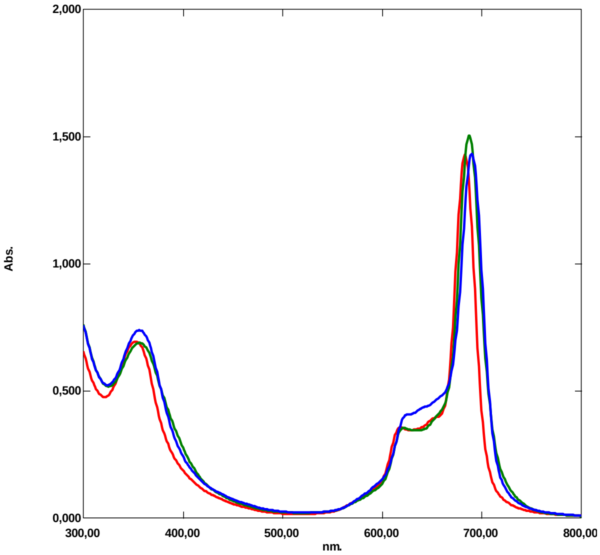

Figure 2. UV-Vis spectra of compound **2** in $CHCl_3$ (-), DMF (-), DMSO (-).

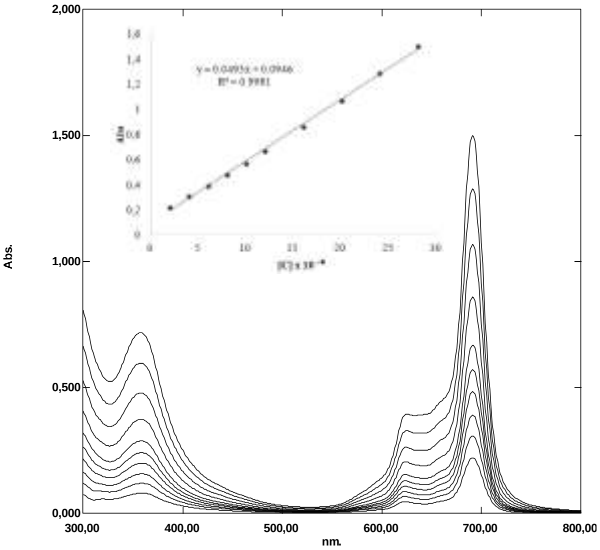

Figure 3. UV-Vis spectra of compound **2** in different concentrations at DMSO (the concentration is decreasing at from top to bottom).

3.3. Fluorescence properties

Figure 4 shows the fluorescence emission and excitation spectra for compound **2**. In DMSO, the excitation and the absorption spectrum of compound **2** are similar and these spectra are mirror images of the emission spectrum [23].

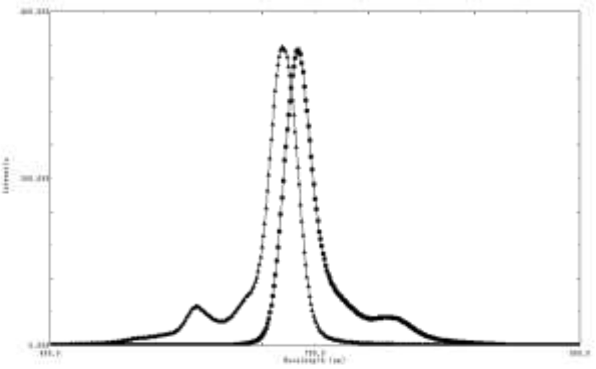

Figure 4. Excitation (▲) and emission (■) spectra of compound **2** in DMSO.

Table 1. Spectral data for compound **2** in DMSO.

Compound	Q-band λ (nm)	Excitation λ (nm)	Emission λ (nm)	Stokes shift Δ_{stokes} (nm)	Φ_F
2	681	682	692	11	0.24
* Φ_F of unsubstituted ZnPc is 0.18 in DMSO [23,24].					

The fluorescence quantum yield of compound **2** was determined by a comparative method in equation 1 [23,25,26].

$$\Phi_F = \Phi_F(\mathrm{Std}) \frac{F A_{\mathrm{Std}} \eta^2}{F_{\mathrm{Std}} A \eta_{\mathrm{Std}}^2} \qquad (1)$$

Where, F and F_{Std} are the areas under the fluorescence emission curves of the compound **2** and the standard, respectively. A and A_{Std} are the absorbance of the samples and standard at the excitation wavelength, respectively, η and η_{Std} are the refractive indexes of solvents used for compound **2** and standard, respectively. Unsubstituted ZnPc was used as standard (Φ_F = 0.18 in DMSO) [23,27].

The stokes shift and fluorescence quantum yield for compound **2** are similar to that of typical metallophthalocyanines [28]. The fluorescence quantum yield for compound **2** is higher than the fluorescence quantum yield of unsubstituted ZnPc (Table 1).

4. CONCLUSIONS

Thiadiazole tetrasubstituted zinc(II) monophthalocyanine **2** synthesized and characterized. The effect of solvent and concentration on the aggregation behavior of compound **2** were investigated. It did not show aggregation. The fluorescence properties of compound **2** were also studied and the fluorescence quantum yield calculated. The fluorescence quantum yield (0.24 in DMSO) of thiadiazole substituted zinc(II) phthalocyanine **2** was observed to be higher than the fluorescence quantum yield (0.18 in DMSO) of the unsubstituted zinc(II) phthalocyanine used as standard. It can be said that the substituted group contributes to the energy and electron transfer. According to the results obtained, it can be said that compound **2** has the potential to be used in organic solar cells.

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REFERENCES

[1]. Xu X., Yu T., Bi Z., Ma W., Li Y., Peng Q., Realizing Over 13% Efficiency in Green-Solvent-Processed Nonfullerene Organic Solar Cells Enabled by 1,3,4-Thiadiazole-Based Wide-Bandgap Copolymers, Adv. Mater., 30 (2018) 1703973.

[2]. Bagher A.M., Introduction to Organic Solar Cells, Sustain. Energy, 2 (2014) 85-90.

[3]. Peng Y., Zhang L., Cheng N., Andrew T.L., ITO-Free Transparent Organic Solar Cell with Distributed Bragg Reflector for Solar HarvestingWindows, Energies, 10 (2017) 707-720.

[4]. Li X., Wang H., Wu H., Phthalocyanines and Their Analogs Applied in Dye-Sensitized Solar Cell, Structure and Bonding, 135 (2010) 229-274.

[5]. Leznoff C.C., Lever A.B.P. Phthalocyanines: properties and applications. vols. 2-4. Cambridge: VCH Publishers, 1989, 1993, 1996.

[6]. McKeown N.B., Phthalocyanine materials. Synthesis, structure and function. Cambridge: Cambridge University Press, 1998.

[7]. Altın Ş., Dumludağ F., Oruç Ç., Altındal A., Influence of humidity on kinetics of xylene adsorption onto ball-type hexanuclear metallophthalocyanine thin film, Microelectron. Eng., 134 (2015) 7-13.

[8]. Shi J., Luan L., Fang W., Zhao T., Liu W., Cui D., High-sensitive low-temperature NO_2 sensor based on Zn (II) phthalocyanine with liquid crystalline properties, Sensor. Actuat. B-Chem., 204 (2014) 218-223.

[9]. Özceşmeci İ., Gelir A., Gül A., Synthesis and photophysical properties phthalocyanineepyrene dyads, Dyes Pigments, 92 (2012) 954-960.

[10]. Sevim A.M., Arıkan S., Özçeşmeci İ., Gül A., Photophysical properties ofanthracenylmethyloxycarbonylmethylsulfanyl-phthalocyanines, Synthetic Met., 183 (2013) 1-7.

[11]. Cho K.T., Trukhina O., Roldán-Carmona C., Ince M., Gratia P., Grancini G., Gao P., Marszalek T., Pisula W., Reddy P.Y., Torres T., Nazeeruddin M.K., Molecularly Engineered Phthalocyanines as Hole-Transporting Materials in Perovskite Solar Cells Reaching Power Conversion Efficiency of 17.5%, Adv. Energy Mater., 7 (2017) 1601733.

[12]. Hu Y., Li C.Y., Wang X.M., Yang Y.H., Zhu H.L., 1,3,4-Thiadiazole: Synthesis, Reactions, and Applications in Medicinal, Agricultural, and Materials Chemistry, Chem. Rev., 114 (2014) 5572-5610.

[13]. Thompson B.C. and Frechet J.M.J., Polymer–Fullerene Composite Solar Cells, Angew. Chem. Int. Edit., 47 (2008) 58-77.

[14]. Tian H., Yu Z., Hagfeldt A., Kloo L., Sun L., Organic Redox Couples and Organic Counter Electrode for Efficient Organic Dye-Sensitized Solar Cells, J. Am. Chem. Soc., 133 (2011) 9413-9422.

[15]. Pang H., Skabara P.J., Crouch D.J., Duffy W., Heeney M., McCulloch I., Coles S.J., Horton P.N., Hursthouse M.B., Structural and Electronic Effects of 1,3,4-Thiadiazole Units Incorporated into Polythiophene Chains, Macromolecules, 40 (2007) 6585-6593.

[16]. Armarego W.L.F., Chai C.L.L., Purificaiton of Laboratory Chemicals. Fifth ed. Tokyo: Butterworth/Heinemann, 2003.

[17]. Wöhrle D., Eskes M., Shigehara K., Yamada A., A Simple Synthesis of 4,5-Disubstituted 1,2-Dicyanobenzenes and 2,3,9,10,16,17,23,24-Octasubstituted Phthalocyanines, Synthesis, 2 (1993) 194-196.

[18]. Yabaş E., Sülü M., Saydam S., Dumludağ F., Salih B., Bekaroğlu Ö., Synthesis, characterization and investigation of electrical and electrochemical properties of imidazole substituted phthalocyanines, Inorg. Chim. Acta, 365 (2011) 340-348.

[19]. Yabaş E., Sülü M., Dumludağ F., Salih B., Bekaroğlu Ö., Imidazole octasubstituted novel mono and double-decker phthalocyanines: Synthesis, characterization, electrical and gas sensing properties, Polyhedron, 153 (2018) 51-63.

[20]. Nyokong T., Effects of substituents on the photochemical and photophysical properties of main group metal phthalocyanines, Coord. Chem. Rev., 251 (2007) 1707-1722.

[21]. Nyokong T., Electronic Spectral and Electrochemical Behavior of Near Infrared Absorbing Metallophthalocyanines, Structure and Bonding, 135 (2010) 45-88.

[22]. Leznoff C.C., Lever A.B.P., Phthalocyanines Properties and Applications. Vol.1. Cambridge: VCH Publisher, 1989.

[23]. Durmuş M., Nyokong T., Photophysicochemical and fluorescence quenching studies of benzyloxyphenoxy-substituted zinc phthalocyanines, Spectrochim. Acta A, 69 (2008) 1170-1177.

[24]. Ogunsipe A., Nyokong T., Effects of substituents and solvents on the photochemical properties of zinc phthalocyanine complexes and their protonated derivatives, J. Mol. Struct., 689 (2004) 89-97.

[25]. Fery-Forgues S., Lavabre D., Are Fluorescence Quantum Yields So Tricky to Measure? A Demonstration Using Familiar Stationery Products, J. Chem. Educ., 76 (1999) 1260-1264.

[26]. Maree D., Nyokong T., Suhling K., Phillips D., Effects of axial ligands on the photophysical properties of silicon octaphenoxyphthalocyanine, J. Porphyr. Phthalocya., 6 (2002) 373-376.

[27]. Jacques P., Braun A.M., Laser Flash Photolysis of Phthalocyanines in Solution and Microemulsion, Helv. Chim. Acta, 64 (1981) 1800-1806.

[28]. Durmuş M., Nyokong T., Synthesis and solvent effects on the electronic absorption and fluorescence spectral properties of substituted zinc phthalocyanines, Polyhedron, 26 (2007) 2767-2776.