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Synthesis and Photophysical Properties of A_3B-type Unsymmetrically Substituted Anthracene-based Zinc(II)phthalocyanine

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Abstract: A novel unsymmetrical zinc(II) phthalocyanine (ZnPc) (**3**) with an alkynyl functional group was prepared by an efficient mixed statistical condensation of 4-((4-ethynylbenzyl)oxy)phthalonitrile (**1**) and 4-(4-tertbutylphenoxy)phthalonitrile (**2**). FTIR, ^{1}H NMR, UV-Vis, elemental analysis, and MALDI-TOF were used to characterize this new compound. Working with different concentrations, the compound's aggregation properties were investigated and concluded that no aggregation tendency has been observed in the studied concentration range (1.0×10^{-6} M to 1.2×10^{-5} M). Fluorescent quantum yields and lifetimes of the compound were studied and found to be 0.09 and 0.57 ns, respectively. As a fluorescent quencher, 1,4-benzoquinone was used in the experiments at differing concentrations in tetrahydrofuran. The kq values showed a close follow-up to the diffusion control limits, around 10^{11} s^{-1} and they seem to agree with Einstein-Smoluchowski's approximation for bimolecular, diffusion-control-including, interactions. For the new compound, the K_{SV} value was calculated as 27.55, which is lower than that of unsubstituted ZnPc. The fluorescence of the studied compound **3** was effectively quenched by 1,4-benzoquinone.

Keywords: Zinc, anthracene, phthalocyanine, fluorescence, characterization.

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INTRODUCTION

Phthalocyanines, also referred to as Pcs, are tetrabenzo-containing tetraazaporphyrin macrocycles, famous for their high stability, flexibility, coordination, and fine spectroscopic behavior (1). Photodynamic therapy, optical data storage, reversed saturable absorbers, and solar screens are phthalocyanines' chief important high technological applications (2). Thanks to their π-electron conjugation, Pcs can readily undergo electron transfer reactions (3). There are two main substitution patterns for Pcs: Peripheral (2, 9(10), 16(17), 23(24)) and non-peripheral (1, 8(11), 15(18), 22(25)) and these patterns allow for greater solubility in organic solvents, thereby increasing the spectral behaviors and applications (4-8). To synthesize substituted Pcs, a reaction called cyclotetramerization must be exercised, and substituted phthalonitriles will give way to substituted phthalocyanines. The substitution of phthalonitriles with hydroxyl, amine, azide or alkynyl functional groups is preferable (9-12).

Second-order nonlinear optics (13), photodynamic therapy of cancer (14), liquid crystals (15), Langmuir-Blodgett (LB) film formation (16), and solar cells (17,18) are popular uses of unsymmetrical phthalocyanines. When there are two different types of substituents on the Pc molecule, multiple properties like enhanced solubility and reactivity on one or two points of the macrocycle are possible, thereby a better control over the molecule is gained (19). Although there are numerous methods to prepare symmetrically substituted Pcs, the number of methods for unsymmetrically Pcs are fairly limited (20). The simplest technique to prepare a unsymmetrically substituted Pc is to conduct a statistically mixed condensation of two different phthalonitriles. The main drawback of this method is the hardship to isolate the targeted Pc in a mixture of differently substituted Pcs; all of them have similar physical and chemical properties. An alternative to the method above was proposed by Leznoff and Hall (21). This method comprises of an insoluble polymer with a diiminoisoindoline or phthalonitrile attached to it. A differently substituted phthalonitrile is introduced to the medium and the two are reacted, and the symmetrical phthalocyanine is isolated from the medium, then, as the last step, the non-substituted phthalocyanine is released from the polymeric backbone. A yet another method to prepare unsymmetrical Pcs has been described by Kobayashi and his coworkers (22, 23). In this method, a sub-phthalocyanine undergoes ring expansion in the presence of a different phthalonitrile and a unsymmetrical Pc is obtained.

Photovoltaics, molecular transistors, light-emitting devices, and other molecular electronic applications (24, 25) use organic materials, which are capable of absorbing various wavelengths of visible light and fluorescence highly efficiently. Since Pcs highly absorb in the Soret band of ultraviolet spectrum (about 300-400 nm), they are considered as efficient energy acceptors and they provide the required overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor. As a donor group in this study, we have chosen anthracene unit because it is very stable thermally and can act as an antenna to harvest and transfer energy in an efficient manner to longer wavelength emission in blends or composites (26).

The poor solubility of Pcs in common organic solvents (like chlorinated solvents, ethers, and water) hamper the uses of them. If the Pc molecule is decorated with alkyl, alkoxy, alkylsulfanyl, or bulky groups at the peripheral, non-peripheral or axial positions, the solubility increases drastically (27, 28). Aggregation, in general, is the bringing together of molecules in dimers or higher oligomers in solution and aggregates present their hydrophobic part (at the center) as a group. The extended π system (29, 30) is responsible for aggregation. It hampers solubility in many solvents, reduces nonlinear optical properties drastically, and detrimental for photosensitization in photodynamic therapy (31). In Pcs, aggregation is frequently encountered at a concentration as low as 1×10^{-5} M, but if bulky groups are introduced into the molecule, aggregation rate diminishes considerably.

In this work, we have reacted two different phthalonitriles to obtain a novel, A_3B type, unsymmetrical zinc phthalocyanine with peripheral substitution of three anthracene-9-methoxy and one ethynylbenzyloxy groups. Not only have the anthracene groups the ability to harvest light but also they provide better solubility in organic solvents due to their bulky nature. With the aid of mono alkynyl group, this novel zinc(II)phthalocyanine can be modified further by using well known techniques such as Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition (better known as the “click chemistry”) or Sonogashira carbon-carbon cross-coupling reactions that leads to expand the application field of this novel complex. The new compound was dissolved in volumetric flasks at different concentrations to see if it undergoes aggregation, by recording the UV-Vis spectrum. The fluorescent quantum yields and lifetimes were tabulated for the new compound by conducting the experiment in tetrahydrofuran. We have found out that 1,4-benzoquinone is an efficient fluorescent quencher in tetrahydrofuran for the Pc molecule we have prepared.

EXPERIMENTAL SECTION

Materials and methods

Fourier transform infrared spectra were collected with a Perkin-Elmer Spectrum One spectrometer by using a universal attenuated total reflectance (ATR) module in the 600-4000 cm^{-1} range. A Scinco SD 1000 single-beam UV-Vis spectrophotometer was utilized to record the UV-Vis spectra of the compounds in 1 cm path length cuvettes at room temperature. A Perkin-Elmer LS55 fluorescence spectrophotometer was used to obtain fluorescence spectra. Proton NMR spectra were obtained with an Agilent VNMRS 500 MHz spectrometer, employing tetramethylsilane (TMS) as the internal reference. Elemental analyses were obtained in the Instrumental Analysis Laboratory of TUBITAK Marmara Research Center. A Bruker Microflex MALDI-TOF/MS mass spectrometer was used to record the mass spectra of the required compounds. Reagent grade chemicals and solvents were used and procured from commercial suppliers. At each reaction step, we have tested the reaction’s status and the purity of the compounds by running thin layer chromatography (TLC) on silica. All reactions were run in nitrogen atmosphere and the solvents we used were dried over molecular sieves. The two phthalonitriles we have used, namely 4-hex-5-ynyloxy-phthalonitrile (**1**) and 4-anthracen-9-ylmethoxy)phthalonitrile (**2**), were synthesized by referring to the reported procedures (32, 33).

Synthesis

*Synthesis of 9(10), 16(17), 23(24)-tris-(4-anthracen-9-ylmethoxy)-2(3)-(4-hex-5-ynyloxy) phthalocyaninatozinc (II) (**3**):*

0.045 g (0.20 mmol) of **1**, 0.201 g (0.60 mmol) of **2**, and 0.050 g (0.27 mmol) zinc acetate were charged into a screw-capped tube and immersed into an oil bath, 3 mL of 2-dimethylaminoethanol was added and the temperature of the reaction was raised to 145 °C and sustained for 24 h. After this step, the obtained greenish product was cooled to room temperature, and precipitated by pouring into 3:1 (v/v) water/methanol mixture, then filtered. Hot methanol, n-hexane, and acetone were used to wash the crude product until there were no yellowish-brown impurities observed, then dried in an oven at 110 °C. The dried greenish compound was chromatographed on a silica-loaded glass column with ethyl acetate – n-hexane (3:1, v/v) as eluent.

Solubility: Soluble in tetrahydrofuran, chloroform, dichloromethane, dimethylsulfoxide, and dimethylformamide. Yield: 0.059 g, (23 %). FT-IR (υ_{max}/cm^{-1}): 3289 (H-C≡), 3052 (Ar-C-H), 2927-2861 (Aliph. -C-H), 2210 (C≡C), 1601, 1446, 1387, 1315, 1226 1088, 993, 881, 826, 730. UV-Vis λ_{max} (nm) THF: 339, 351, 367, 387, 678. ^{1}H-NMR (500 MHz, $CDCl_3$): δ, ppm: 8.34-7.18 (39H, m, Ar-H), 4.28 (6H, s, Ar-C**H_2**-O-), 4.11 (2H, t, -C**H_2**-O-), 2.28 (1H, t, -C≡C**H**), 1.74 (2H, m, -C**H_2**-C≡CH), 1.44 (2H, m, -CH_2), 1.27 (2H, m, -CH_2). Anal. Calc. for $C_{83}H_{54}N_8O_4Zn$ (1292,78 g/mol) %: C, 77.11; H, 4.21; N, 8.67 Found: C, 77.42; H, 4.01; N, 8.96. MALDI-TOF MS: *m/z* 1292.57 $[M]^+$.

Photophysical parameters

Fluorescence quantum yields and lifetimes:

To determine the fluorescent quantum yields (Φ_F) comparatively, Equation 1 below was employed, with ZnPc in DMF as the standard compound (Φ_F = 0.17) (34,35):

$$\Phi_F = \Phi_{F(Std)} \frac{F A_{Std}\, \eta^2}{F_{Std}\, A\, \eta_{Std}^2} \qquad \text{(Eq. 1)}$$

F and F_{std} are the areas calculated under the fluorescence curves of the phthalocyanine (**3**) and the unsubstituted phthalocyanine, respectively. A and A_{std} are absorbances of substituted and unsubstituted phthalocyanines, respectively. Normally they are about 0.04 and 0.05 for all solvents. η and η_{std} are the refractive indices of the solvents used. The standard and sample were excited at the same wavelength.

Fluorescent lifetime (τ_F) is the average time of the molecule residing at the excited state before fluorescing. These data were calculated with the Strickler-Berg equation, which was readily available in the PhotoChemCad software. Fluorescent quantum yield and fluorescent lifetime (τ_F) are directly proportional values. For the calculation of natural radiative lifetime (τ_0), Equation 2 was employed (36):

$$\Phi_F = \frac{\tau F}{\tau o} \qquad \text{(Eq. 2)}$$

1,4-benzoquinone-mediated fluorescent quenching:

When increasing amounts of 1,4-benzoquinone (BQ) were added into the solutions of zinc phthalocyanine at a fixed concentration, we observed fluorescent quenching; the concentrations of BQ at each step were 0.008, 0.016, 0.024, 0.032, 0.040, and 0.048 M. A transfer of energy occurs between BQ which is the quencher and ZnPc which is the fluorophore. The fluorescence spectra at each increment of BQ were recorded and by utilizing the Stern-Volmer (SV) equation given below (see Equation 3), the changes in fluorescent intensity concerning the BQ concentration (37).

Stern-Volmer (SV) equation, which is given below, was used to find the Stern-Volmer constant (K_{SV}) from a graph and this is the product of bimolecular quenching constant (k_q) and τ_F (see Equation 4) (35). In Equation 3, I_0 and I are the fluorescent intensities of the fluorophore in the absence and presence of quencher, respectively. [BQ] is the concentration of the quencher.

$$\frac{I_0}{I} = 1 + K_{SV}[BQ] \qquad \text{(Eq. 3)}$$

$$K_{SV} = k_q \times \tau_F \qquad \text{(Eq. 4)}$$

The ratios of I_0 / I against [BQ] were plotted and K_{SV} was determined from the slope of the line.

RESULTS AND DISCUSSION

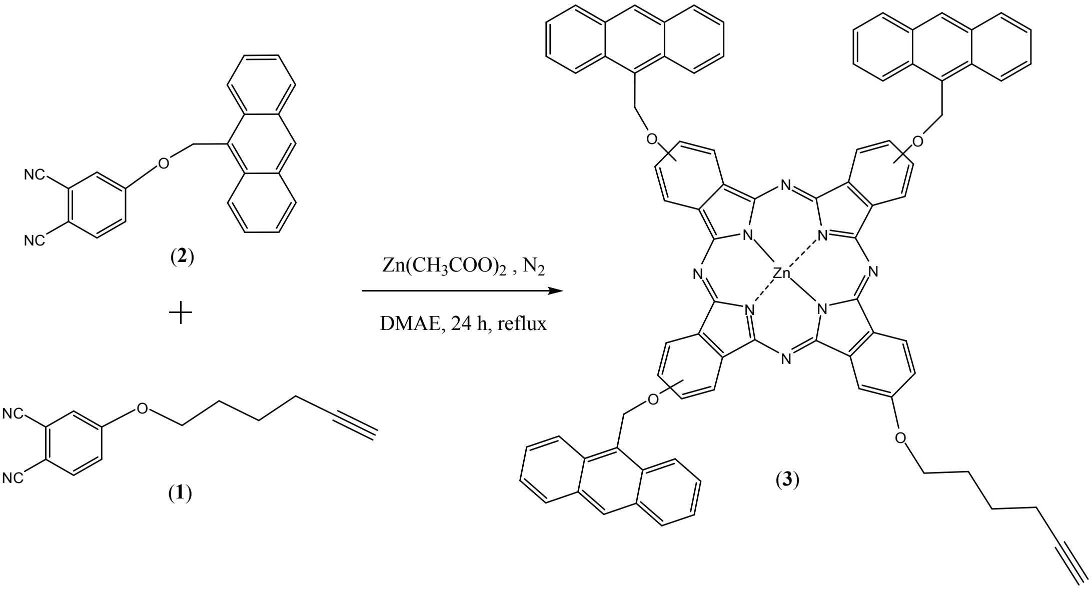
Synthesis and spectroscopic characterization

Scheme 1 indicates the synthetic work of the targeted unsymmetrical ZnPc (**3**). The two phthalocyanine precursors leading to the unsymmetrical phthalocyanine were 4-hex-5-ylnyloxyphthalonitrile (**1**) and 4-(anthracene-9-ylmethoxy)phthalonitrile (**2**). The two precursors were synthesized with a base-catalyzed nucleophilic aromatic nitro displacement (at the ipso position) of 4-nitrophthalonitrile with 5-hexyn-1-ol and anthracene-9-ylmethanol (32,33). As a nitro-displacement base, potassium carbonate was used and the synthesis was completed in a single step at 40 °C for (**1**) and room temperature for (**2**). The solvent of choice was dimethylformamide and the reaction flask's atmosphere was maintained with nitrogen.

When a mixture of two phthalocyanine precursors, A and B, considered to have equal reactivity, are reacted in a 3:1 ratio will yield an isomeric mixture of phthalocyanines of A_4 (33%), A_3B (44%) and other cross-condensation products (27%) (20,38). If the solubilities of the phthalocyanine precursors are very different, the final purification of the targeted phthalocyanine will be a very easy one.

The targeted phthalocyaninatozinc(II) compound was synthesized with the cyclotetramerization of three equivalents of dinitrile (**2**) and one equivalent of dinitrile derivative (**1**), in the presence of 2-dimethylaminoethanol as the solvent and zinc acetate as the metal source, at 145 °C under nitrogen. Several other molar ratios were tried to see if the reaction yield increases, but 3:1 ratio of (**1**):(**2**) was found to be the best one (see Scheme 1). In the work-up, the crude product was subjected to column chromatography over silica, the eluent being the 3:1 v/v mixture of ethyl acetate / n-hexane. The first fraction was symmetrical A_4 as compared with authentic samples shown by TLC. The second fraction was the targeted A_3B one (**3**), a bright green solid obtained with a 23% yield.

The new compound (**3**) was characterized by a series of spectral analysis methods, including FT-IR, ^{1}H NMR, MALDI-TOF MS and UV-Vis, along with elemental analysis. The results showed that they are in accordance with proposed structures.



Scheme 1. Synthesis of the unsymmetrical zinc(II)phthalocyanine.

The FT-IR spectrum of (**3**) showed that anthracene and alkyl moieties appeared at expected positions, but C≡N stretching disappeared after cyclotetramerization, which is also an expected outcome. The alkynyl proton H-C≡, aromatic C-H, aliphatic C-H, C≡C, aromatic C=C and C–O–C vibrations were observed at 3289, 3052, 2927-2861, 2210, 1601-1446 and 1226 cm^{-1}, respectively. The ^{1}H NMR spectrum of (**3**) showed a multiplicity between δ 8.34 – 7.18 ppm in deuterated chloroform as the solvent. The methylene protons situated between the etheric oxygen bonded Pc core and anthracenyl group had a chemical shift of δ 4.28 ppm as a singlet. The other methylene group between the etheric oxygen and the hexynyl group showed a chemical shift of δ 4.11 ppm as a triplet. Also, the alkynyl proton H-C≡ and the aliphatic CH_2 protons belonging to the hexynyl chain were spotted at δ 2.28 ppm (triplet) and δ 1.74-1.27 ppm (multiplet), respectively. Also, the assignment of the product to a 3:1 combination of the reactants was made based on elemental analysis and mass spectral data results confirming the proposed structures. Elemental analysis confirmed the 3:1 molar ratio and MALDI-TOF showed the molecular peak of the expected compound (**3**) at m/z 1292.57 (see Figure 1).

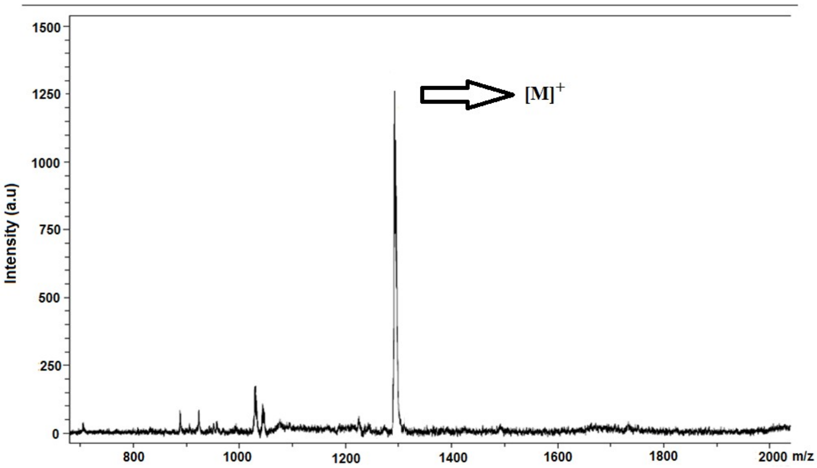


Figure 1. MALDI-TOF Mass spectrum of targeted zinc(II) phthalocyanine.

All phthalocyanines' electronic spectra feature two intense π – π* transitions. The first one is Soret (or B) band, located around 300 and 400 nm, and the second one is the Q band, located around 600-700 nm. The tetrahydrofuran solution, compound (**3**) showed B and Q bands at 339 and 678 nm, respectively (see Figure 2). Since anthracene is also a UV-active entity, its peaks were also spotted at 351, 367, and 387 nm (see Figure 2). Owing to the presence of anthracenyl group, the B band's intensity is as much as that of the Q band. There are reports in the literature, mentioning of an overlap between phthalocyanine's B band and anthracene moiety's absorption at 350 nm (27).

Phthalocyanine aggregation has been the subject of numerous studies. The extended flat aromatic structure of phthalocyanines leads to attractive π-π* stacking, thereby forming aggregates starting from monomers to higher order complex structures. Generally, there is a hypsochromic shift of the aggregate owing to the cooperative interaction among the transition dipole moments of the molecules. This leads to a broadening of the Q band and reducing its intensity. In general, concentration, temperature, substituents, the nature of solvents and the metal ion residing at the inner core are chief factors affecting the phenomenon of aggregation. Since aggregated species are photo-inactive, aggregation is not a desired outcome in phthalocyanines. In polar media like water, the problem is very significant; water tends to self-associate and repels the hydrophobic π system, forming aggregates. In our work, aggregation behaviors of the metallophthalocyanines were investigated in tetrahydrofuran, by recording the absorption at different concentrations; the reason for selection of THF as the solvent is the high solubility of the complexes in this solvent. At the higher energy side of the strong Q band, we have observed weak peaks at 610-630 nm in the electronic spectra. Studying the absorption values for a series of concentrations is a method to see if the system shows aggregation. We have studied a wide range of concentrations (1.0×10^{-6} M to 1.2×10^{-5} M) and absorbance values in Q band maxima showed a linear change (obedience to Lambert-Beer's law) with respect to the increasing concentration for the monomeric species. We can conclude that no aggregation tendency has been observed for our target compound (**3**) in studied concentration range (Figure 2).

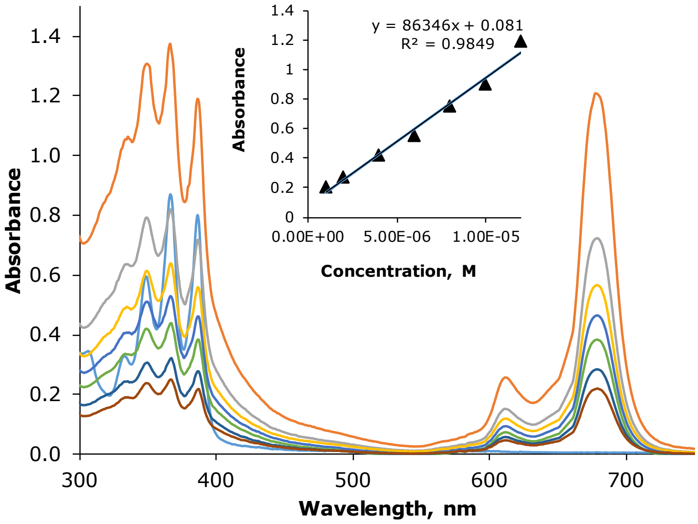


Figure 2. Electronic absorption spectra observed on the increase in the concentration of the compound (**3**) in THF. Inset: Beer–Lambert's plot for (**3**) in THF. The range of concentrations: 1.0 x 10^{-6} M to 1.2 x10^{-5} M).

Measurements of fluorescence and fluorescent quenching studies of compound (**3**) were carried out in tetrahydrofuran, with an excitation of the Q band at 611 nm. Figure 3 shows the fluorescent emission, excitation, and absorption spectra of (**3**) in THF. 697 nm was the peak fluorescent emission value of compound (**3**) and the Stokes' shift was 19 nm, which was within the expected range of 15-20 nm (11). The excitation spectrum and the absorption spectrum are similar to each other and they are mirror images of the fluorescent spectra for compound (**3**) in tetrahydrofuran. This indicates that the nuclear configurations of the ground and excited states have a similarity and excitation does not affect this (39).

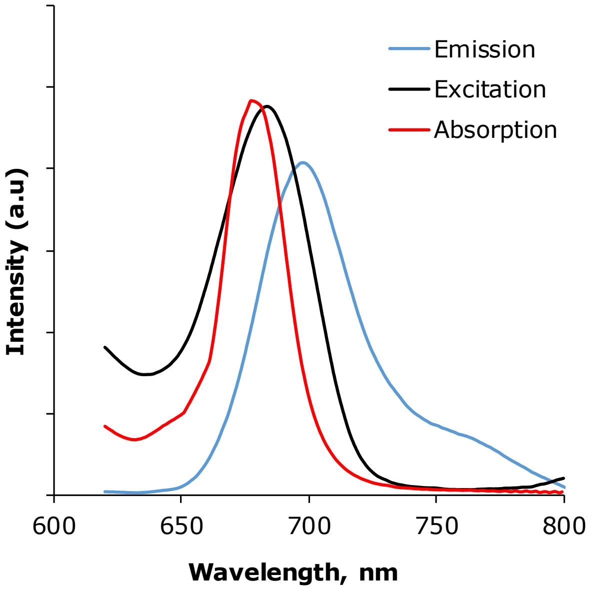


Figure 3. Absorption and fluorescence (excitation and emission) spectra of (**3**) in tetrahydrofuran, excitation wavelength = 611 nm.

Solutions prepared with THF were employed to find the fluorescent quantum yield (ΦF) of (**3**). As Equation 1 states, the comparative method is used to calculate the fluorescent quantum yield (ΦF). Unsubstituted zinc phthalocyanine was used as a standard compound, and its solution in dimethylformamide had ΦF of 0.17 (35), and the wavelength to excite the sample and standard compounds was the same. The fluorescent quantum yield for (**3**) was found 0.09. In THF solution, the ΦF value for compound (**3**) was lower than that of the unsubstituted ZnPc (ΦF = 0.25) (40) and this value is recognized as a typical one for Pc compounds (see Table 1).

τ_F, also known as the fluorescent lifetime, is the average time of a fluorophore which stays at the excited state before fluorescing and fluorescent quantum yield is very close to this value. This means that if the fluorescent lifetime is long, the quantum yield is also high. Intersystem crossing, internal conversions, and such others will cause a reduction of the fluorophore's fluorescent lifetime, thereby causing a reduction in the quantum yield. The fluorescent lifetime is thereby determined by the nature and the surroundings of a compound. To calculate the fluorescent lifetime, Strickler-Berg equation (see Equation 2) is used. Compound **3**'s τF value was calculated was 0.57 ns, which is lower than that of unsubstituted ZnPc in tetrahydrofuran (40), and this has a meaning that there is more quenching after substitution around the periphery.

Natural radiative lifetimes (τ_o) and fluorescent rate constant (k_F) values are shown in Table 1. In THF solution, k_F value of compound (**3**) is higher than the unsubstituted ZnPc solution.

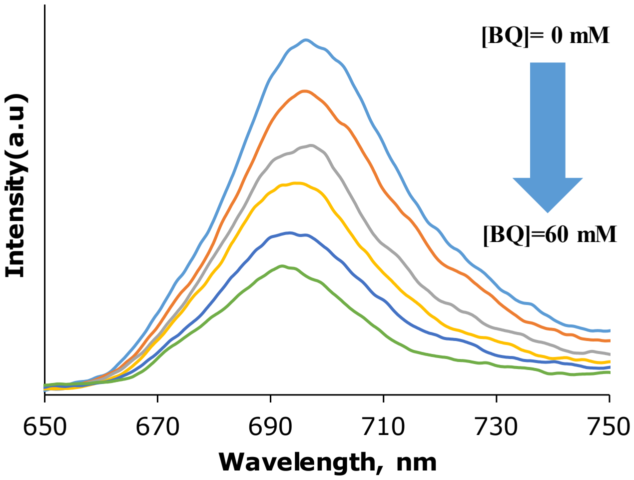


Figure 4. Spectral changes of fluorescent emission for (**3**) (1.50×10^{-6} M) on the addition of increasing amounts of 1,4-benzoquinone in THF. The concentrations of BQ: 0 mM, 12 mM, 24 mM, 36 mM, 48 mM, 60 mM.

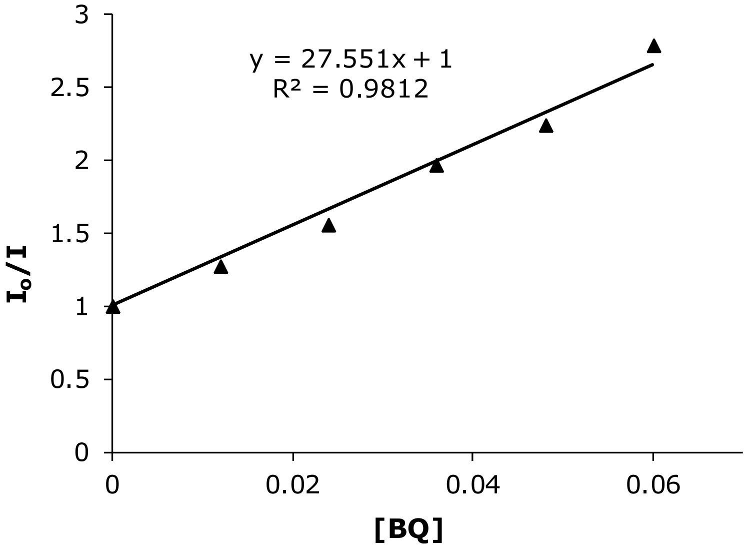


Figure 5. Stern-Volmer plots for benzoquinone (BQ) quenching of compound (**3**) (1.50×10^{-6} M) in THF. The concentrations of BQ: 0 mM, 12 mM, 24 mM, 36 mM, 48 mM, 60 mM.)

Compound (**3**) is quenched by 1,4-benzoquinone in tetrahydrofuran, obeying Stern-Volmer kinetics; it is also in parallel with the diffusion-controlled bimolecular reactions. Figure 4 shows that compound (**3**) has fluorescent emission spectral changes with increasing BQ concentration in THF.

Using an increased concentration of BQ, fluorescent intensity of compound (**3**) shows a decline. The Stern-Volmer plot of compound (**3**) shows a linear behavior, indicating a quenching mechanism with diffusion control (Figure 5). From Figure 5, the K_{SV} value is found from the slope of the plot and shown in Table 1, which also shows the bimolecular quenching constant (kq) for 1,4-benzoquinone-induced quenching of compound (**3**) in THF. The kq values showed a close follow-up to the diffusion control limits, around 10^{11} s^{-1} (see Table 1) and they seem to be in agreement with Einstein-Smoluchowski's approximation for bimolecular, diffusion-control-including, interactions (41). For compound (**3**), the K_{SV} value is 27.55, which is lower than that of unsubstituted ZnPc in THF (40).

CONCLUSION

In this work, we have co-cyclotetramerized anthracene-9-methoxy- and ethynylbenzyloxy-containing phthalonitriles in 3:1 ratio to yield the A_3B-type unsymmetrical zinc phthalocyanine in a statistical condensation route. After the full characterization of compound (**3**), aggregation behavior, photophysics, and photochemistry of it were studied and the data were compiled in Table 1, along with ZnPc (unsubstituted) as a standard compound. Photophysical fluorescence of compound (**3**) was investigated in THF solution. It shows that compound (**3**) has a lower fluorescent quantum yield and shorter lifetime than the unsubstituted counterpart. In tetrahydrofuran solution, compound (**3**) was effectively quenched by 1,4-benzoquinone and Stern-Volmer kinetics were shown.

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REFERENCES

1. McKeown NB. Phthalocyanine materials: synthesis, structure, and function. Cambridge, U.K.; New York: Cambridge University Press; 1998. 193 p. (Chemistry of solid state materials).

2. Gregory P. Industrial applications of phthalocyanines. Journal of Porphyrins and Phthalocyanines. 2000;4(4):432–7.

3. Bekaroğlu Ö. Structure and Bonding. In: Functional Phthalocyanine Molecular Materials. Berlin, Heidelberg: Springer-Verlag; 2010. p. 105.

4. Sevim AM, Arıkan S, Koca A, Gül A. Synthesis and spectroelectrochemistry of new phthalocyanines with ester functionalities. Dyes and Pigments. 2012 Mar;92(3):1114–21.

5. Sevim AM, Ilgün C, Gül A. Preparation of heterogeneous phthalocyanine catalysts by cotton fabric dyeing. Dyes and Pigments. 2011 May;89(2):162–8.

6. Arslanoglu Y, Mertsevim A, Hamuryudan E, Gul A. Near-IR absorbing phthalocyanines. Dyes and Pigments. 2006;68(2–3):129–32.

7. Sevim AM. Synthesis and characterization of Zn and Co monocarboxy-phthalocyanines and investigation of their photocatalytic efficiency as TiO2 composites. Journal of Organometallic Chemistry. 2017 Mar;832:18–26.

8. Akkurt B, Hamuryudan E. Enhancement of solubility via esterification: Synthesis and characterization of octakis (ester)-substituted phthalocyanines. Dyes and Pigments. 2008 Nov;79(2):153–8.

9. Quinton D, Antunes E, Griveau S, Nyokong T, Bedioui F. Cyclic voltammetry and spectroelectrochemistry of a novel manganese phthalocyanine substituted with hexynyl groups. Inorganic Chemistry Communications. 2011 Jan;14(1):330–2.

10. Chen X, Thomas J, Gangopadhyay P, Norwood RA, Peyghambarian N, McGrath DV. Modification of Symmetrically Substituted Phthalocyanines Using Click Chemistry: Phthalocyanine Nanostructures by Nanoimprint Lithography. J Am Chem Soc. 2009 Sep 30;131(38):13840–3.

11. Sevim AM, Özçeşmeci İ, Gül A. Synthesis and photophysical properties of a novel ethynyl zinc(II) phthalocyanine and its functionalized derivative with click chemistry. J Porphyrins Phthalocyanines. 2013 Jun;17(06n07):540–7.

12. Akkurt B, Koca A, Hamuryudan E. Synthesis, in situ spectroelectrochemistry and in situ electrocolorimetry of electrochromic octakis(chloroethylsulfanyl) phthalocyaninatomanganese(iii) chloride. New J Chem. 2009;33(11):2248.

13. O'Flaherty SM, Hold SV, Cook MJ, Torres T, Chen Y, Hanack M, et al. Molecular Engineering of Peripherally And Axially Modified Phthalocyanines for Optical Limiting and Nonlinear Optics. Adv Mater. 2003 Jan 3;15(1):19–32.

14. Allen CM, Sharman WM, Van Lier JE. Current status of phthalocyanines in the photodynamic therapy of cancer. J Porphyrins Phthalocyanines. 2001 Feb;05(02):161–9.

15. Iino H, Hanna J, Bushby RJ, Movaghar B, Whitaker BJ, Cook MJ. Very high time-of-flight mobility in the columnar phases of a discotic liquid crystal. Appl Phys Lett. 2005 Sep 26;87(13):132102.

16. Cook MJ, McKeown NB, Simmons JM, Thomson AJ, Daniel MF, Harrison KJ, et al. Spectroscopic and X-ray diffraction study of Langmuir–Blodgett films of some 1,4,8,11,15,18-hexaalkyl-22,25-bis(carboxypropyl)phthalocyanines. J Mater Chem. 1991;1(1):121–7.

17. O'Regan BC, López-Duarte I, Martínez-Díaz MV, Forneli A, Albero J, Morandeira A, et al. Catalysis of Recombination and Its Limitation on Open Circuit Voltage

for Dye Sensitized Photovoltaic Cells Using Phthalocyanine Dyes. J Am Chem Soc. 2008 Mar;130(10):2906–7.

18. Bartelmess J, Ballesteros B, de la Torre G, Kiessling D, Campidelli S, Prato M, et al. Phthalocyanine−Pyrene Conjugates: A Powerful Approach toward Carbon Nanotube Solar Cells. J Am Chem Soc. 2010 Nov 17;132(45):16202–11.

19. Kobayashi N, Miwa H, Nemykin VN. Adjacent versus Opposite Type Di-Aromatic Ring-Fused Phthalocyanine Derivatives: Synthesis, Spectroscopy, Electrochemistry, and Molecular Orbital Calculations. J Am Chem Soc. 2002 Jul;124(27):8007–20.

20. de la Torre G, Claessens C, Torres T. Phthalocyanines: The Need for Selective Synthetic Approaches. European Journal of Organic Chemistry. 2000;2000(16):2821–30.

21. Leznoff CC, Hall TW. The synthesis of a soluble, unsymmetrical phthalocyanine on a polymer support. Tetrahedron Letters. 1982 Jan;23(30):3023–6.

22. Kobayashi N, Kondo R, Nakajima S, Osa T. New route to unsymmetrical phthalocyanine analogs by the use of structurally distorted subphthalocyanines. J Am Chem Soc. 1990 Dec;112(26):9640–1.

23. Dabak S, Gül A, Bekaroğlu Ö. Hexakis(alkylthio)-Substituted Unsymmetrical Phthalocyanines. Chem Ber. 1994 Oct;127(10):2009–12.

24. Zhou J, Mi J, Zhu R, Li B, Qian S. Ultrafast excitation relaxation in titanylphthalocyanine thin film. Optical Materials. 2004 Dec;27(3):377–82.

25. de la Torre G, Claessens CG, Torres T. Phthalocyanines: old dyes, new materials. Putting color in nanotechnology. Chem Commun. 2007;(20):2000–15.

26. Zhang G, Zhang D, Guo X, Zhu D. A New Redox-Fluorescence Switch Based on a Triad with Tetrathiafulvalene and Anthracene Units. Org Lett. 2004 Apr;6(8):1209–12.

27. Sevim AM, Arıkan S, Özçeşmeci İ, Gül A. Photophysical properties of anthracenylmethyloxycarbonylmethylsulfanyl-phthalocyanines. Synthetic Metals. 2013 Nov;183:1–7.

28. Coşkun NY, Ödevci Ö, Yalçın SM, Gül A. Synthesis, Absorption and Fluorescence Spectral Investigation of Porphyrazines with Eight 9-Anthracenecarboxy Esters. Main Group Metal Chemistry [Internet]. 2007 Jan [cited 2019 Oct 11];30(2–3). Available from: https://www.degruyter.com/view/j/mgmc.2007.30.2-3/mgmc.2007.30.2-3.83/mgmc.2007.30.2-3.83.xml

29. Snow A. Phthalocyanine Aggregation. In: The Porphyrin Handbook [Internet]. Amsterdam: Elsevier; 2003. p. 129–76. Available from: https://www.sciencedirect.com/book/9780080923918/the-porphyrin-handbook

30. Wiggins M, Flom S, Shirk J, Pong R, Lepkowicz R, Ranade A. Abstract Papers American Chemical Society. Vol. 228. Washington: American Chemical Society (ACS); 2004.

31. Zoller P, Walsh DJ. Standard pressure-volume-temperature data for polymers. Lancaster, PA: Technomic Pub. Co; 1995. 412 p.

32. Bankole O, Britton J, Nyokong T. Photophysical and non-linear optical behavior of novel tetra alkynyl terminated indium phthalocyanines: Effects of the carbon chain length. Polyhedron. 2015;88:73–80.

33. Kahouecha M, Hrizb K, Touaitia S, Bassem J. New anthracene-based-phtalocyanine semi-conducting materials: Synthesis and optoelectronic properties. Materials Research Bulletin. 2016;75:144–54.

34. Masilela N, Nyokong T. The synthesis and fluorescence behaviour of new unsymmetrically mono-functionalized carboxy Ge, Ti and Sn phthalocyanines. Dyes and Pigments. 2011;91(2):164–9.

35. Durmuş M, Nyokong T. Photophysicochemical and fluorescence quenching studies of benzyloxyphenoxy-substituted zinc phthalocyanines. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2008 Apr;69(4):1170–7.

36. Du H, Fuh R, Li J, Corkan L, Lindsey J. PhotochemCAD: A Computer-Aided Design and Research Tool in Photochemistry. Photochemistry and Photobiology. 1998;68:141–8.

37. Rose J. Advanced Physico-Chemical Experiments. London: Sir Isaac Pitman & Sons Ltd; 1964. 257 p.

38. Bakboord J, Cook M, Hamuryudan E. Non-uniformly substituted phthalocyanines and related compounds: alkylated tribenzo-imidazolo [4, 5]-porphyrazines. Journal of Porphyrins and Phthalocyanines. 2000 Aug;4(5):510–7.

39. Zorlu Y, Dumoulin F, Durmuş M, Ahsen V. Comparative studies of photophysical and photochemical properties of solketal substituted platinum (II) and zinc (II) phthalocyanine sets. Tetrahedron. 2010;66(17):3248–58.

40. Saka E, Durmuş M, Kantekin H. Solvent and central metal effects on the photophysical and photochemical properties of 4-benzyloxybenzoxy substituted phthalocyanines. J Organomet Chem. 2011;696:913–24.

41. Gümrükcü G, Karaoglan G, Erdoğmuş A, Gül A, Avcıata U. A novel phthalocyanine conjugated with four salicylideneimino complexes: Photophysics and fluorescence quenching studies. Dyes Pigm. 2012;95:280–9.

Table 1. Photophysical and photochemical parameters along with fluorescent quenching data of (**3**) and unsubstituted ZnPc complexes in THF.

Complex	λ_{max}(nm)	Excitation λ_{max}(nm)	Emission λ_{max}(nm)	Stokes‛ shift Δ_{stokes}(nm)	Φ_F	τ_F, ns	τ_o, ns	k_F, s^{-1} ($x10^8$)	K_{SV}, M^{-1}	k_q, s^{-1}($x10^{11}$)
3	678	611	697	19	0.09	0.57	6.33	1.58	27.55	0.48
ZnPc[a]	667	667	672	5	0.25	2.72	10.9	0.92	48.48	1.78

a= Reference 40.