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Synthesis and photophysical properties of a novel ethynyl zinc(II) phthalocyanine and its functionalized derivative with click chemistry

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Dedicated to Professor Özer Bekaroğlu on the occasion of his 80th birthday

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ABSTRACT: The synthesis of novel, symmetrical zinc(II) phthalocyanine (ZnPc) bearing four ethynylcyclohexyloxy terminal moieties was achieved by cyclotetramerization of novel 4-(2-ethynylcyclohexyloxy) phthalonitrile in pentanol in the presence of DBU and zinc acetate without any protective/deprotective chemistry. Subsequently, this new zinc(II) phthalocyanine derivative was reacted with 6-azido-hexanoic acid under "click-chemistry" conditions to give phthalocyanine-hexanoic acid conjugates linked by 1,2,3-triazole units. The new compounds have been characterized by using elemental analyses, UV-vis, FTIR, ^{1}H NMR and mass spectroscopic data. The aggregation properties of the compounds were investigated in different concentrations. General trends are also described for fluorescence quantum yields and lifetimes of novel zinc derivatives in tetrahydrofuran. The fluorescence of the tetrasubstituted zinc(II) phthalocyanine complexes is effectively quenched by 1,4-benzoquinone (BQ) in THF.

KEYWORDS: phthalocyanine, fluorescence, click chemistry, aggregation, quantum yield.

INTRODUCTION

Phthalocyanines (Pcs) are tetrabenzo[5,10,15,20]-tetraazaporphyrins known for their very interesting industrial applications due to their high stability, architectural flexibility, diverse coordination properties, and good spectroscopic characteristics [1]. The properties and effects of phthalocyanines are diverse and cover many important hi-tech applications, including photodynamic therapy, optical data storage, reverse saturable absorbers and solar screens [2]. The functions of phthalocyanine derivatives are usually based on their electron transfer reactions, because of their π-electron conjugated ring system [3]. The Pcs with different functional groups situated at peripheral positions may have increased solubility and enhanced the spectral properties and applications [4–7]. Synthesis of substituted Pc systems with different functional groups follows the classical route of cyclotetramerization of suitably substituted phthalonitriles and in this context most synthetic efforts have focused on the preparation of substituted phthalonitriles with different reactive end groups like hydroxy, amine, azide or alkynyl functional groups on the aromatic system [8–11].

In the last decades, Cu(I)-catalyzed 1,3-dipolar cycloaddition reactions between alkynes and azides, known as "click reactions," have been recognized as a facile synthetic methodology due to their fast, reproducible, quantitative nature and being resistant to side-reactions and performing under quite mild reaction conditions [12–15]. Although 'click' chemistry has been thoroughly explored in recent years and applied considerably in preparation and functionalization of new materials, relatively few examples of Pc functionalization *via* this versatile reaction can be found most likely due to the limited solubility of most Pcs [16–22].

In the present study, we have synthesized tetra cyclohexylalkynyloxy-substituted zinc phthalocyanine without protective/deprotective chemistry *via* cyclotetramerization

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[◊] SPP full member in good standing

*Correspondence to: Ahmet Gül, email: ahmetg@itu.edu.tr, tel: +90 212-285-6827, fax: +90 212-285-6386 of novel 4-(2-ethynylcyclohexyloxy) phthalonitrile in pentanol in the presence of DBU. Additionally, we have applied Cu(I)-catalyzed click reaction to the synthesis of soluble tetratriazole-functionalized zinc phthalocyanine under very mild reaction conditions. We also report spectroscopic characterization, aggregation behavior as well as photophysical (fluorescence quantum yields and lifetimes) and quenching properties of novel ZnPc complexes.

RESULTS AND DISCUSSION

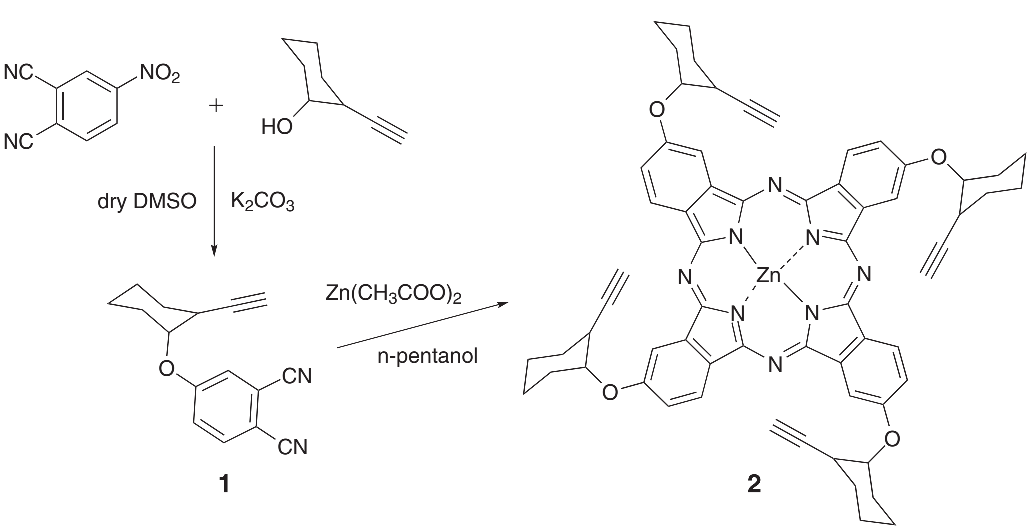
Synthesis and characterization

The new zinc phthalocyanine with terminal cycloalkyne groups was synthesized in two steps. In the first step, the 4-(2-ethynylcyclohexyloxy)phthalonitrile **1** was synthesized by nucleophilic displacement reaction of 4-nitrophthalonitrile with 2-ethynylcyclohexanol at 50 °C under nitrogen atmosphere in dry dimethylsulphoxide in the presence of potassium carbonate as a base. Then, phthalocyanine **2** was prepared by the standard method of cyclotetramerization of 4-(2-ethynylcyclohexyloxy) phthalonitrile in the presence of DBU and anhydrous $Zn(CH_3COO)_2$ in pentanol for 24 h (Scheme 1). Product **2** was purified by column chromatography using silica gel as the stationary phase and hexane/THF (2:1) mixture as the eluent. The zinc phthalocyanine obtained is soluble only in certain organic solvents such as DMF, THF and DMSO.

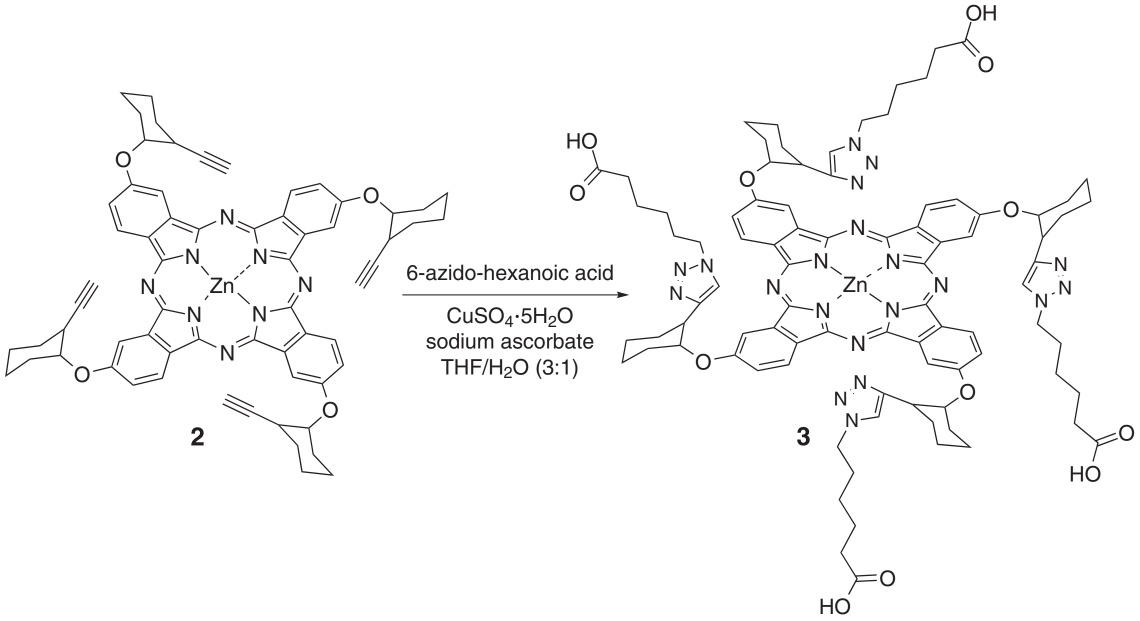
The 1,3-dipolar cycloaddition of compound **2** with 6-azido-hexanoic acid was carried out in THF/H_2O (3:1) at room temperature using $CuSO_4 \cdot 5H_2O$ as a catalyst and sodium ascorbate as the reducing agent (Scheme 2). The crude product was purified by column chromatography with silica gel as the stationary phase and first dichloromethane and then THF/hexane (1:1) as the eluent. After click reaction, compound **3** became much more soluble in a wide variety of solvents including chloroform, DCM, THF, and acetone as compared to the precursor **2**, which was only soluble in THF, DMSO, and DMF.

All the synthesized compounds were fully characterized by NMR, IR, and UV-vis spectral methods and the purity was confirmed by elemental analysis. In the FT-IR spectra of the cycloalkynyl substituted phthalonitrile **1**, the characteristic H–C and –C≡C– stretching vibrations of alkynyl moiety were observed at 3289 cm^{-1} and 2107 cm^{-1}, respectively. Cyclotetramerization of the dinitrile **1** was confirmed by the disappearance of the sharp C≡N vibration at 2230 cm^{-1} after phthalocyanine formation. Besides, the characteristic bands of cycloalkynyl groups maintained their positions. After the click reaction, the characteristic C–H vibration at high wavenumbers disappeared completely and a broad band around 2500–3300 cm^{-1} (COOH) and an intense sharp band at 1730 cm^{-1} (C=O) corresponding to carboxylic acid moiety was revealed. Additionally, increasing intensity of aliphatic C–H vibrations proved the assigned structure of **3** (Fig. 1).

The ^1H NMR spectra of the phthalonitrile derivative **1** and phthalocyanines **2** and **3** are in excellent agreement with the proposed structures. The dominant features in the NMR spectra of (**1–3**) are the aliphatic group resonances. Besides, in the ^1H NMR spectrum of compounds **2** and **3**, as a consequence of the presence of four constitutional isomers and supramolecular association, the signals are very broad and the integration values of the many assignable signals are consistent with the expected values [9]. The molecular ion peak of phthalonitrile derivative **1** was observed at $m/z = 250$ $[M + 1]^+$ by using GC-MS (ESI) technique. The peaks for the molecular ion by using MALDI-TOF technique were found at $m/z = 1066.47$ $[M]^+$ for **2**, and $m/z = 1693.82$ $[M + 1]^+$ for **3**.



Scheme 1. Synthetic route of 4-(2-ethynylcyclohexyloxy) phthalonitrile and related zinc(II) phthalocyanine **2**



Scheme 2. Preparation of compound **3** *via* "click" reaction

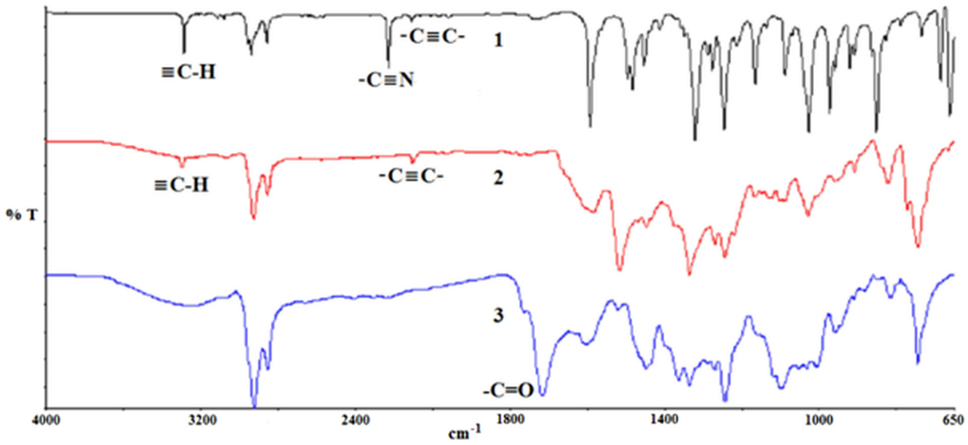


Fig. 1. FTIR spectra of synthesized compounds **1–3**

Ground state electronic absorption and fluorescence spectra

The UV-vis spectra of the studied phthalocyanines **2** and **3** in THF were given in Figs 2 and 3. The π–π* transitions for the Q-band absorptions were observed at 694 nm for **2** and 706 nm for **3** (Table 1). When we compare the Q-band absorption bands of **2** with Q-band absorption bands of **3**, after click reaction, a significant red shift (12 nm) and increased intensity in Q-band wavelengths was observed [23–26]. Aggregation is usually depicted as a coplanar association of phthalocyanine core progressing from monomer to dimer and higher order complexes. It is dependent on the concentration, nature of the solvent, nature of the substituents, complexed metal ions and temperature [27]. As anticipated, the UV-vis absorption spectra of **2** and **3** have no evidence of aggregation as shown by the position and the appearance of the intense Q-bands (Figs 2 and 3). In this study the aggregation behavior of **2** and **3** was studied at different concentrations in THF. As depicted in Figs 2 and 3, the appearance of the Q-band absorption maxima remained unchanged as the concentration increases and its apparent molar extinction coefficient remains almost constant (insert figures in Figs 2 and 3) indicating the existence of a purely monomeric form which obeyed the Beer–Lambert Law in the outlined range of concentration [28]. By evaluating these observations, it can be clearly concluded that the **2** and **3** did not show any aggregation behavior in THF between 2×10^{-5} M and 1.25×10^{-6} M [29].

Table 1. Absorption, excitation and emission spectral data for zinc phthalocyanine complexes (**2** and **3**) in THF

Comp.	Q-band λ_{max}, nm	(log ε)	Excitation λ_{Ex}, nm	Emission λ_{Em}, nm	Stoke shift Δ_{Stokes}, $\times 10^5$ cm^{-1}
2	694	4.73	691	708	7.14
3	706	5.04	707	719	7.69
ZnPc	666[a]	5.19[a]	666[a]	673[a]	14.28[a]

[a] Reference 32.

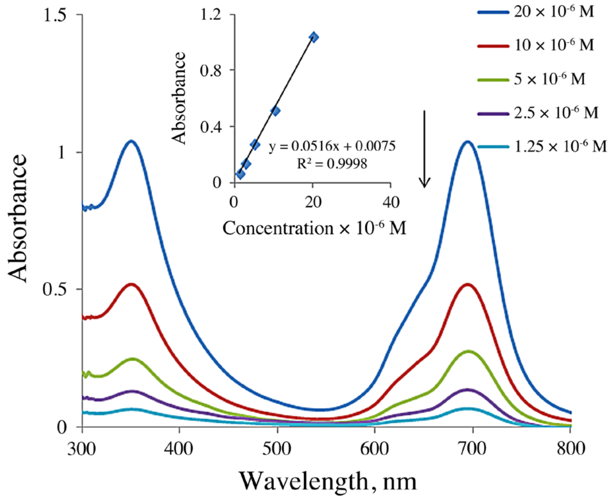


Fig. 2. Aggregation behavior of **2** in THF at different concentrations

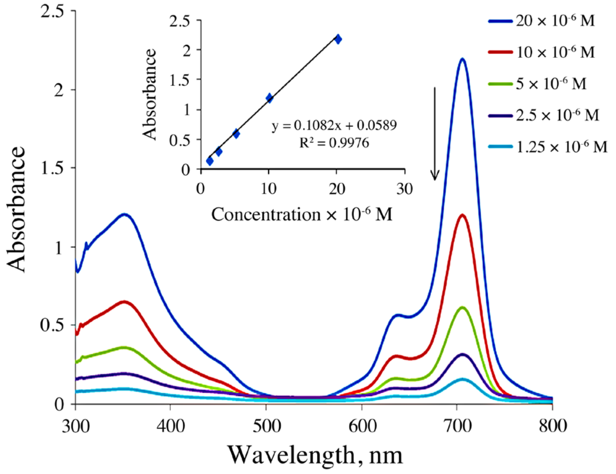


Fig. 3. Aggregation behavior of **3** in THF at different concentrations

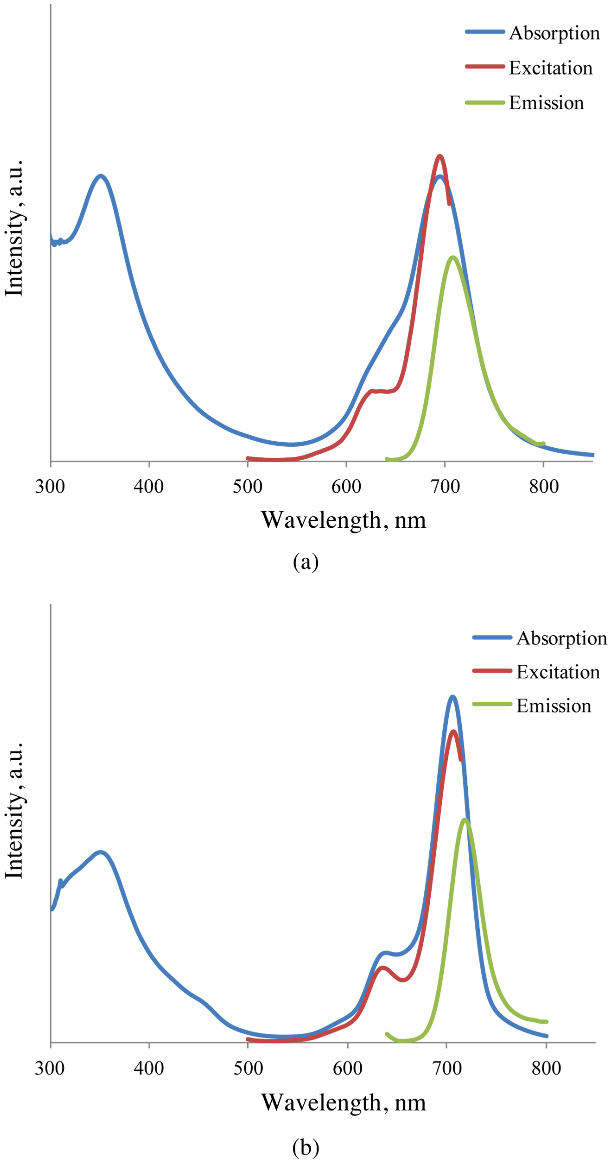
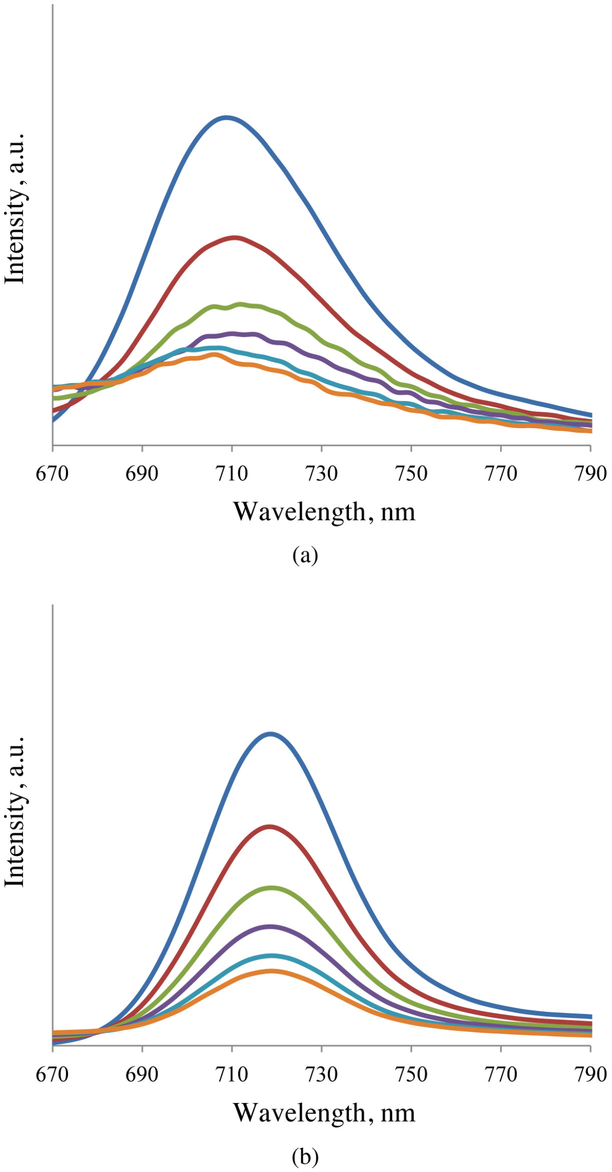


Fig. 4. Absorption, excitation and emission spectra for compound **2** (a) and **3** (b) in THF. Excitation wavelength = 623 nm for **2** and 635 nm for **3** in THF

The fluorescence behavior of zinc phthalocyanine complexes (**2** and **3**) was studied in THF. Figure 4 shows the absorption, fluorescence emission and excitation spectra for complex **2** and **3** in THF. Fluorescence emission peaks were observed at 708 nm for **2** and 719 nm for **3** (Table 1). The observed Stokes shifts were within the region ~10–15 nm observed for zinc Pc complexes and they were typical of phthalocyanine complexes [30]. Both studied zinc Pc complexes (**2** and **3**) showed similar fluorescence behavior in THF. The excitation spectra were similar to absorption spectra and both were mirror images of the fluorescent spectra for both zinc Pc complexes. The proximity of the wavelength of each component of the Q-band absorption to the Q-band maxima of the excitation spectra for both zinc Pc complexes suggested that the nuclear configurations of the ground and excited states are similar and not affected by excitation.

Fluorescence quantum yields and lifetimes

The fluorescence quantum yields (Φ_F) of zinc phthalocyanines (**2**) and (**3**) were studied in THF. Fluorescence quantum yields (Φ_F) were determined by the comparative method (Equation 1). Unsubstituted ZnPc was used as standard in DMF ($\Phi_F = 0.17$) [31] and both the sample and the standard were excited at the same wavelength. The fluorescence quantum yields were calculated as 0.21 for **2** and 0.15 for **3**. Φ_F values of zinc phthalocyanine complexes (**2** and **3**) are lower than unsubstituted ZnPc ($\Phi_F = 0.25$) [32] and typical of phthalocyanine complexes (Table 2) in THF. This implies that the presence of peripheral cycloalkynyloxy and triazole hexanoic acid substituents caused some fluorescence quenching of the parent **2** and **3**. According to these results we can say that after click reaction additionally triazole hexanoic acid substituents in **3** caused more fluorescence quenching of complex **3** compared to **2** as shown in Table 1. In our study, the fluorescence lifetimes (τ_F) were calculated using the Strickler–Berg equation (Equation 2). The τ_F values of the Pc complexes **2** and **3** (3.37 and 0.26 ns, respectively) are lower compared to unsubstituted ZnPc complexes in THF [31], suggesting more quenching by substitution. The natural radiative lifetime (τ_o) and the rate constants for fluorescence (k_F) values are also shown in Table 2. The k_F values of studied zinc phthalocyanine complexes (**2** and **3**) are higher than unsubstituted ZnPc in THF.



(a)

(b)

Fig. 5. Fluorescence emission spectral changes of **2** (a) (4×10^{-6} M) and **3** (b) (4×10^{-6} M) on addition of different concentrations of BQ in THF. [BQ] = 0, 0.008, 0.016, 0.024, 0.032 and 0.040 M

Fluorescence quenching studies by 1,4-benzoquinone (BQ)

The fluorescence quenching of zinc phthalocyanine complexes (**2** and **3**) by benzoquinone (BQ) in THF was found to obey Stern–Volmer kinetics, which is consistent with diffusion-controlled bimolecular reactions. Figure 5 shows fluorescence emission spectral changes of **2** and **3** on addition of different concentrations of BQ in THF. The Stern–Volmer plots for studied complexes (**2** and **3**) gave straight lines, depicting diffusion controlled quenching mechanisms (Fig. 6). The slope of the plots shown at Fig. 6 gave K_{SV} values, listed in Table 2. The bimolecular quenching constant (k_q) values for the BQ quenching of phthalocyanine complexes in THF are also listed in Table 2. The K_{SV} values of the phthalocyanine complexes **2** and **3** are higher than Std-ZnPc in THF.

Table 2. Photophysical and photochemical parameters along with fluorescence quenching data of zinc phthalocyanine complexes (**2** and **3**) in THF

Comp.	Φ_F	τ_F, ns	τ_o, ns	k_F, s^{-1} ($\times 10^8$)[a]	K_{SV}	k_q, s^{-1} ($\times 10^{11}$)
2	0.21	0.7	3.37	2.96	66.5	0.95
3	0.15	0.04	0.26	38.2	72.5	18.13
ZnPc	0.25[b]	2.72[b]	10.9[b]	0.92[b]	48.48[b]	1.78[b]

[a] k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$. [b] Reference 32.

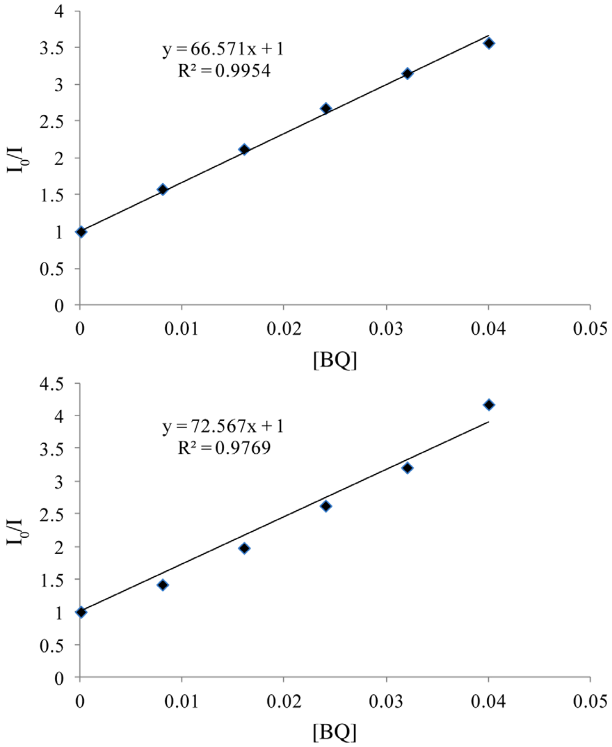


Fig. 6. Stern–Volmer plots for benzoquinone (BQ) quenching of **2** (a) [ZnPc] = 4.00×10^{-6} M and **3** (b) [ZnPc] = 4.00×10^{-6} M in THF. [BQ] = 0, 0.008, 0.016, 0.024, 0.032 and 0.04 M

EXPERIMENTAL

Materials

IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer with ATR capability, electronic spectra were recorded on a Scinco SD 1000 single-beam ultraviolet-visible (UV-vis) spectrophotometer using 1 cm path length cuvettes at room temperature. Fluorescence spectra were recorded on a Perkin-Elmer LS55 fluorescence spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker 250 MHz spectrometer using TMS as internal reference. Melting points were determined on a Büchi Melting Point B-540 apparatus. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Centre. Mass spectra were performed on Bruker Microflex MALDI-TOF/MS and Perkin-Elmer Clarus 500 mass spectrometers. All reagents and solvents were of reagent grade quality obtained from commercial suppliers. The homogeneity of the products was tested in each step by TLC (SiO_2). All reactions were carried out under nitrogen atmosphere in dried solvents. The solvents were stored over molecular sieves. 4-nitrophthalonitrile was synthesized according to published methods [33].

Photophysical parameters

Fluorescence quantum yields and lifetimes. The comparative method was used to determine the fluorescence quantum yields (Φ_F) according to the following equation [34], utilizing unsubstituted ZnPc in DMF as the standard ($\Phi_F = 0.17$) [31]:

$$\varnothing_F = \varnothing_F(\text{Std}) \frac{F A_{\text{Std}} \eta^2}{F_{\text{Std}} A \eta^2_{\text{Std}}} \qquad (1)$$

where F and F_{Std} are the areas under the fluorescence curves of the zinc phthalocyanines and the standard, respectively. A and A_{Std} are the respective absorbances of sample and standard at the excitation wavelengths (which was around 0.04–0.05 in all solvents used), and η and η_{Std} are the refractive indices of solvents used for the sample and standard, respectively.

Radiative or natural lifetimes (τ_o) were estimated using Photochem CAD program which uses the Strickler–Berg equation [35]. Finally, the fluorescence lifetimes (τ_F) were calculated using the following equation:

$$\varnothing_F = \frac{\tau F}{\tau O} \qquad (2)$$

Fluorescence quenching by 1,4-benzoquinone. Fluorescence quenching experiments on zinc phthalocyanines were carried out by the addition of different concentrations of BQ to a fixed concentration of the complex, and the concentrations of BQ in the resulting mixtures were 0.008, 0.024, 0.032, 0.040 and 0.048 M, respectively. The fluorescence spectra of compound **2** and **3** at each BQ concentration were recorded, and the changes in fluorescence intensity related to BQ concentration by the Stern–Volmer (SV) equation [36]:

$$\frac{I_0}{I} = 1 + k_{SV}[BQ] \qquad (3)$$

where I_0 and I are the fluorescence intensities of fluorophore in the absence and presence of quencher, respectively. [BQ] is the concentration of the quencher and K_{SV} is the Sterne–Volmer constant which is the product of the bimolecular quenching constant (k_q) and the τ_F and is expressed in Equation 4:

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

The ratios of I_0/I were calculated and plotted against [BQ] according to Equation 4, and K_{SV} is determined from the slope.

Synthesis

4-(2-ethynylcyclohexyloxy)phthalonitrile (1). 2-ethynylcyclohexanol (0.124 g, 1 mmol) and 4-nitrophthalonitrile (0.173 g, 1 mmol) were added successively with stirring to dry DMSO (6 mL). After they were dissolved, anhydrous K_2CO_3 (0.250 g, 11.56 mmol) was added portion wise for 2 h and the mixture was stirred vigorously at 50 °C for 72 h under nitrogen. Then the solution was poured into ice water (200 mL). The solution was acidified with conc. HCl until precipitation occured (pH = 1–2). The yellow brownish product was collected by centrifugation and rinsed with ethanol. Finally the solid was dissolved in minimum chloroform and then added to n-hexane dropwise. The brownish crystals were filtered and dried. Yield 0.133 g (53.2%); mp 69.4 °C. IR: ν, cm^{-1} 3289 (–C≡C–H), 3079 (Ar–H), 2940–2850 (alkyl CH), 2230 (C≡N), 2107 (C≡C), 1244 (C–O–C). ^{1}H NMR (250 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 7.68 (1H, s, Ar–H), 7.63 (1H, d, *J* = 8.20 Hz, Ar–H), 7.52 (1H, d, *J* = 7.90 Hz, Ar–H), 2.78 (1H, s, –C≡CH), 2.10 (1H, q, –O–CH), 1.89 (1H, q, –C≡C–CH), 1.68–1.56 (4H, m, CH_2), 1.40–1.33 (4H, m, CH_2). MS (GC-MS, scan EI$^+$): *m/z* 250 [M + 1]$^+$. Anal. calcd. for $C_{16}H_{14}N_2O$: C, 76.58; H, 5.64; N, 11.19%. Found C, 76.14; H, 5.62; N, 11.01%.

Tetrakis(2-ethynylcyclohexyloxy)phthalocyaninatozinc(II) (2). A mixture of dinitrile **1** (0.15 g, 0.6 mmol), anhydrous $Zn(CH_3COO)_2$ (0.033 g, 0.24 mmol) and a catalytic amount of DBU in n-pentanol (1.5 mL) was heated at 145 °C with stirring for 24 h. The reaction mixture was cooled to room temperature. The precipitate was filtered off and washed with methanol. After extraction of the crude product with chloroform, the purification was carried out by column chromatography on silica gel using hexane/THF (2:1) as the eluent to afford **2** as a green solid. Yield 0.032 g, 20%. IR: ν, cm^{-1} 3289 (–C≡C–H), 3075 (Ar–H), 2928–2853 (alkyl CH), 2222 (C≡C), 1254 (C–O–C). ^{1}H NMR (250 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 7.61–7.48 (8H, b, Ar–H), 6.96 (4H, s, Ar–H), 3.46 (4H, s, –C≡C–H), 2.25 (4H, b, –O–CH–), 1.59 (4H, b, –C≡C–CH–), 1.41–0.93 (32H, m, CH_2). UV-vis (in THF): λ, nm (log ε) 350 (4.72), 694 (4.73). MALDI-TOF MS: *m/z* 1066.47 [M]$^+$. Anal. calcd. for $C_{64}H_{56}N_8O_4Zn$: C, 72.07; H, 5.25; N, 10.59%. Found C, 72.14; H, 5.32; N, 10.65%.

Preparation of 3 using click chemistry. A mixture of **2** (0.075 g, 0.07 mmol), 6-azido-hexanoic acid (0.055 g, 0.35 mmol), $CuSO_4.5H_2O$ (0.070 g, 0.28 mmol) and sodium ascorbate (0.056 g, 0.28 mmol) were dissolved in 4 mL of THF/H_2O (3:1). The mixture was stirred at room temperature for 24 h under nitrogen. The solvent was removed under reduced pressure, and the residue was taken-up in dichloromethane, washed with water and dried over $MgSO_4$. After the filtration and evaporation of the solvent, the product was washed with methanol to remove unreacted 6-azido-hexanoic acid. Final purification of the product was accomplished by column chromatography with silica gel using first dichloromethane and then THF/hexane (1:1) as eluent. Yield 0.065 g, 55%. IR: ν, cm^{-1} 3400–2650 (broad, carboxylic acid OH), 2924–2853 (alkyl CH), 1716 (C=O), 1243 (C–O–C). ^{1}H NMR (250 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 7.79–7.64 (8H, b, Ar–H), 7.52 (4H, s, Ar–H), 7.39 (4H, s, Ar–H), 5.03 (8H, b, N–CH_2), 4.28(4H, b, –O–CH–), 2.87–2.73 (8H, b, –CH–C=O), 2.25–0.94 (60H, m, –CH_2). UV-vis (in THF): λ, nm (log ε) 351 (4.78), 706 (5.04). MALDI-TOF MS: *m/z* 1693.82 [M + 1]$^+$, 1810.11 [M + 3K]$^+$. Anal. calcd. for $C_{88}H_{100}N_{20}O_{12}Zn$: C, 62.35; H, 5.95; N, 11.52%. Found C, 62.44; H, 5.92; N, 11.47%.

CONCLUSION

We have been planning to prepare sufficiently soluble Pcs with carboxylic acid substituents applicable in biomolecule interaction or dye sensitized solar cells. In the presented work, the synthesis of new terminal alkynyl group-substituted zinc phthalocyanine without protective/deprotective chemistry was described. In addition, we have applied click chemistry to the synthesis of more soluble tetratriazole-functionalized zinc phthalocyanine. The characterization, aggregation behavior, photophysical and photochemical properties of these novel zinc phthalocyanines have been also investigated. It was also observed that solubility of compound **3** is increased after click reaction. The click product **3** is very soluble in a number of organic solvents, such as chloroform, DCM, THF and acetone. The photophysical fluorescence properties of these zinc(II) phthalocyanine complexes (**2** and **3**) were investigated in THF. The phthalocyanines **2** and **3** show lower fluorescence quantum yields and shorter lifetimeswhen compared to unsubstituted zinc phthalocyanine and it was concluded that after click reaction additional triazole hexanoic acid substituents in **3** caused more fluorescence quenching. The fluorescence of **2** and **3** is effectively quenched by 1,4-benzoquinone in THF.

Acknowledgements

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REFERENCES

1. McKeown NB. *Phthalocyanine Materials: Materials, Synthesis, Structure, and Function*, Cambridge University Press: Cambridge, 1998.
2. Gregory P. *J. Porphyrins Phthalocyanines* 2000; **4**: 432–437.
3. Bekaroglu O. *Structure and Bonding, in Functional Phthalocyanine Molecular Materials*, Springer-Verlag: Berlin, Heidelberg, 2010; p 105.
4. Sevim AM, Arıkan S, Koca A and Gül A. *Dyes Pigm.* 2012; **92**: 1114–1121.
5. Sevim AM, Ilgün C and Gül A. *Dyes Pigm.* 2011; **89**: 162–168.
6. Özçeşmeci M, Özçeşmeci İ and Hamuryudan E. *Polyhedron* 2010; **29**: 2710–2715.
7. Arslanoğlu Y, Sevim AM, Hamuryudan E and Gül A. *Dyes Pigm.* 2006; **68**: 129–132.
8. Özçeşmeci İ, Okur Aİ and Gül A. *Dyes Pigm.* 2007; **75**: 761–765.

9. Yılmaz Y, Şener MK, Erden İ and Avcıata U. *Polyhedron* 2009; **28**: 3419–3424.
10. Quinton D, Antunes E, Griveau S, Nyokong T and Bedioui F. *Inorg. Chem. Commun.* 2011; **14**: 330–332.
11. Chen X, Thomas J, Gangopadhyay P, Norwood RO, Peyghambarian N and McGrath DV. *J. Am. Chem. Soc.* 2009; **131**: 13840–13843.
12. Liang L and Astruc D. *Coord. Chem. Rev.* 2011; **255**: 2933–2945.
13. Vogt AP and Sumerlin BS. *Macromolecules* 2006; **39**: 5286–5292.
14. Ornelas J, Aranzaes JR, Cloutet E and Alves D. *Angew. Chem. Int. Ed.* 2007; **46**: 872–877.
15. Joralemon MJ, O'Reilly RK, Hawker CJ and Wooley KL. *J. Am. Chem. Soc.* 2005; **127**: 16892–16899.
16. Novakova V, Zimcik P, Miletin M, Kopecky K and Ivincová J. *Tetrahedron Lett.* 2010; **51**: 1016–1018.
17. Yoshiyama H, Shibata N, Sato T, Nakamura S and Toru T. *Org. Biomol. Chem.* 2008; **6**: 4498–4501.
18. Campidelli S, Ballesteros B, Filoramo A, Diaz DD, de la Torre G, Torres T, Rahman GMA, Ehli C, Kiessling D, Werner F, Sgobba V, Guldi DM, Cioffi C, Prato M and Bourgoin JP. *J. Am. Chem. Soc.* 2008; **130**: 11503–11509.
19. Zorlu Y, Dumoulin F, Bouchu D, Ahsen V and Lafont D. *Tetrahedron Lett.* 2010; **51**: 6615–6618.
20. Juríček M, Kouwer PHJ, Rehák J, Sly J and Rowan AE. *J. Org. Chem.* 2009; **74**: 21–25.
21. Dumoulin F and Ahsen V. *J. Porphyrins Phthalocyanines* 2011; **15**: 481–504.
22. Ermeydan MA, Dumoulin F, Basova TV, Bouchu D, Gürek AG, Ahsen V and Lafont D. *New J. Chem.* 2010; **34**: 1153–1162.
23. Özçeşmeci İ, Güner S, Okur Aİ and Gül A. *J. Porphyrins Phthalocyanines* 2007; **11**: 531–536.
24. Özçeşmeci İ, Güney O, Okur Aİ and Gül A. *J. Porphyrins Phthalocyanines* 2009; **13**: 753–759.
25. Yıldırım Ö, Sevim AM and Gül A. *Color. Technol.* 2012; **128**: 236–243.
26. Westlund R, Glimsdal E, Lindgren M, Vestberg R, Hawker C, Lopes C and Malmström E. *J. Mater. Chem.* 2008; **18**: 166–175.
27. Dominguez DD, Snow AW, Shirk JS and Pong RS. *J. Porphyrins Phthalocyanines* 2001; **5**: 582–592.
28. Evren E, Burat AK, Özçeşmeci İ and Sesalan BŞ. *Dyes Pigm.* 2013; **96**: 475–482.
29. Özçeşmeci M, Ecevit ÖB, Sürgün S and Hamuryudan E. *Dyes Pigm.* 2013; **96**: 52–58.
30. Zorlu Y, Dumoulin F, Durmuş M and Ahsen V. *Tetrahedron* 2010; **66**: 3248–3258.
31. Durmus M and Nyokong T. *Spectrochim. Acta A* 2008; **69**: 1170–1177.
32. Saka ET, Durmus M and Kantekin H. *J. Organomet. Chem.* 2011; **696**: 913–924.
33. Young JG and Onyebuagu W. *J. Org. Chem.* 1990; **55**: 2155–2159.
34. Masilela N and Nyokong T. *Dyes Pigm.* 2011; **91**: 164–169.
35. Du H, Fuh RCA, Li J, Corkan LA and Lindsey JS. *Photochem. Photobiol.* 1998; **68**: 141–148.
36. Rose J. *Advanced Physico-Chemical Experiments*, 1st ed., Sir Isaac Pitman & Sons Ltd.: London, 1964; pp 257.