



Synthesis and photophysical properties of a non-symmetrically substituted phthalocyanine-pyrene conjugate

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Abstract: An unsymmetrical zinc phthalocyanine (ZnPc) (**5**) bearing one pyrene (Py) and six *tert*-butylphenoxy units was synthesized in 3 steps. The unsymmetrical zinc phthalocyanine carrying the protecting group was synthesized in the first step. In the second stage, the protecting group was removed and in the final stage pyrene structure was introduced with the Sonagashira coupling reaction. The new compound was characterized by using spectroscopic techniques. The photophysical measurements of the conjugated structure were performed to determine the effect of the pyrene group on the fluorescence of Pc. It was determined that the absorption of the pyrene structure around 350 nm was overlapping with the B-band of phthalocyanine after conjugation. Fluorescence quantum yield (Φ_F) and lifetime (τ_F) were calculated. The fluorescence quenching examinations were performed by adding the different concentration of 1,4-benzoquinone (BQ) in *N,N*-dimethylformamide (DMF) and the Stern-Volmer constant (K_{sv}) and quenching constant (k_q) values of unsymmetrical zinc phthalocyanine (**5**) were determined.

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

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INTRODUCTION

Phthalocyanines (Pcs) have 18 π -electron system and they are disc-like aromatic macrocycles. Due to the π -electron delocalization over the molecule, they have unique photophysical, photochemical, redox, and coordination properties, and high chemical and thermal stability (1). The properties of Pcs depend on both the electronic properties of the central metal cations and the nature of substituents. It is advantageous to substitute the functional groups at the peripheral or non-peripheral positions of the Pcs, since they provide solubility and it also tunes the color of the material. Substitution of functional groups also changes the electron density of the phthalocyanines and allows the use in various fields such as solar cells, sensors, liquid crystals, and nonlinear optics (2-6).

Although Pcs display good chemical and photochemical properties, their fluorescence properties are poor (7). Large central metals reduce the fluorescence by enhancement of the

intersystem crossing to the triple state, hence restricting the applications of phthalocyanines in imaging (8). The fluorescence properties of the aromatic structure may alter by the interaction of a Pc core with a fluorescent probe like pyrene group. The chemical or physical binding of the fluorescent probe to the Pc causes a shift in the spectrum or a change in intensity (9).

It is well known that pyrene (Py) has a high quantum yield of fluorescence and a relatively long lifetime of singlet excited state (10). Pyrene is one of the most popular fluorescent chromophores used for photochemical applications. Pyrene derivatives with high quantum yields and lifetime, and are also valuable molecular probes for fluorescence spectroscopy (0.65 and 410 ns, respectively, in ethanol at 293 K) (11). In addition, pyrene and its derivatives have often been used as anchor groups to facilitate electron transfer into the acceptor domains (12).

Phthalocyanine-pyrene (Pc-Py) conjugates appear to be promising candidates for solar cells, sensors, nonlinear optical and photovoltaic applications because of their photophysical and photochemical properties (13-16). According to the literature, the presence of pyrene groups in the structure of phthalocyanine improves the π - π interaction between the Pc-Py and single-wall carbon nanotubes (SWCNT). Non-covalent functionalization of single-wall carbon nanotubes (SWNTs) with Pc-Py molecules were accomplished by Torres *et al.* to form stable hybrids (17). Durmus and coworkers synthesized hybrids of SWNT with phthalocyanines bearing one pyrene unit and studied their sensory response to ammonia vapor (18). They reported that the pyrene units and its derivatives display a strong affinity towards sp^2 -nanocarbon networks (19, 20). In another study, tri- and tetra-pyrene substituted indium phthalocyanines (InPcs) with strong triplet absorption and high triplet yields were investigated for the third- and second-order nonlinearities by Nykong *et al.* (15).

From the point of view, the aim of this study is to synthesize pyrenyl substituted unsymmetrical zinc phthalocyanine for the preparation of light-harvesting antennae. Although there are symmetrically or unsymmetrically substituted phthalocyanine-pyrene conjugated structures in the literature (21-24), unsymmetrically substituted zinc phthalocyanine in which the pyrenyl group was bound to the phthalocyanine ring, was synthesized for the first time. The photophysical properties of this new compound was investigated by fluorescence measurements.

EXPERIMENTAL SECTION

Materials and methods

All reported ^1H -NMR spectra were recorded on an Agilent VNMRS 500 MHz spectrometer. Fluorescence and UV-Vis spectra were obtained using Perkin-Elmer LS55 fluorescence and Scinco LabProPlus UV/Vis spectrophotometers. FTIR spectra of the compounds were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer. Mass spectra were measured on a Bruker Microflex LT MALDI-TOF MS spectrometer. The isotopic patterns for all assigned signals are in agreement with the calculated natural abundance. 4,5-Bis-(4-tert-butylphenoxy)phthalonitrile (**1**), 4-(3-hydroxy-3-methyl-1-butynyl)phthalonitrile (**2**), 2,3,9,10,16,17-hexakis(tert-butylphenoxy)-23-(3-hydroxy-3-methyl-1-butynyl)phthalocyaninato zinc(II) (**3**) and 2,3,9,10,16,17-hexakis(tert-butylphenoxy)-23-(ethynyl)phthalocyaninato zinc(II) (**4**) were prepared according to reported procedures (25-27).

Preparation

Synthesis of 2,3,9,10,16,17-Hexakis(tert-butylphenoxy)-23-(pyrenyl)phthalocyaninato

zinc(II) (5): 100 mg of compound **4** (0.07 mmol) was dissolved in 10 mL of dry tetrahydrofuran (THF)/trimethylamine (1:1) mixture and then 40 mg of 1-bromopyrene (0.13 mmol), 3 mg of bis(triphenylphosphine)palladium(II) chloride (0.004 mmol), and a catalytic amount of copper(I) iodide (1 mmol, 0.1 mg) were added to this solution. The reaction mixture was heated to 60 °C for 24 h under nitrogen (N_2) atmosphere. Once the ethynyl derivative is consumed, monitored by TLC, the mixture was filtered over celite and the solvent was removed under vacuum. The green product was purified by column chromatography on silica gel using first hexane/dioxane (3:1) and then dichloromethane (DCM)/methanol (MeOH) (50:1) as eluents. Solubility: Soluble in THF, CH_2Cl_2 , DMF, and DMSO. Yield: 0.026 g, (24 %). FT-IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3039 (Ar-C-H), 2957-2869 (Aliph. -C-H), 2206 ($\text{C}\equiv\text{C}$), 1506 (Ar-C=C), 1173 (Ar-O-Ar), 1087 (Ar-O-Ar). UV-Vis λ_{max} (nm) THF: 269, 356, 683; DMF: 267, 365, 684. ^1H -NMR (500 MHz, CDCl_3): δ , ppm 7.65-7.33 (42 H, m, Ar-H) 1.30 (54 H, s, CH_3). Anal. Calc. for $\text{C}_{110}\text{H}_{96}\text{N}_8\text{O}_6\text{Zn}$ (1689.68 g/mol) %: C, 78.11; H, 5.72; N, 6.63 Found: C, 78.12; H, 5.69; N, 6.56. MS (MALDI-TOF): m/z 1689.66 $[\text{M}]^+$.

Photophysical parameters

Fluorescence quantum yields and lifetimes:

The comparative method was used to determine the fluorescence quantum yields (Φ_F) according to the Eq. (1) below (28, 29), utilizing non-substituted ZnPc in DMF as the standard ($\Phi_F = 0.17$) (28, 29):

$$\Phi_F = \Phi_F(\text{Std}) \frac{F_{\text{AStd}} \eta^2}{F_{\text{Std}} A \eta_{\text{Std}}^2} \quad (\text{Eq. 1})$$

where F and F_{Std} are the areas under the fluorescence emission curves of the phthalocyanine (**5**) and the standard, respectively. A_{Std} and A are the respective absorbances at the excitation of standard and **5**, η_{Std} and η are the refractive index of solvent ($\eta_{\text{DMF}} = 1.496$) used for the standard and sample.

The fluorescence lifetime (τ_F), which is the average time of the molecule at the excited state before fluorescing, was found using the PhotochemCAD program and the Strickler-Berg equation. The fluorescence quantum yield (Φ_F) and the fluorescence lifetime (τ_F) value are directly proportional. The natural radiative lifetime (τ_0) was calculated with Eq. (2) (28, 29):

$$\Phi_F = \tau_F / \tau_0 \quad (\text{Eq. 2})$$

Fluorescence quenching by 1,4-benzoquinone:

Fluorescence quenching experiments were carried out in DMF with the addition of BQ solutions ranging from 0 to 0.040 M into the ZnPc solution. With the addition of BQ, an energy

transfer takes place between the excited ZnPc (fluorophore) and the BQ (quencher). The fluorescence spectra of ZnPc were recorded each time after the addition of different concentration of BQ. Changes in fluorescence intensity due to BQ concentration were consistent with the kinetic mechanism of the Stern-Volmer (SV) equation (Eq 3) (30):

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

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 Stern-Volmer constant. K_{SV} is the product of the bimolecular quenching constant (k_q) and the τ_F , and is shown in Eq. (4) (31):

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

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

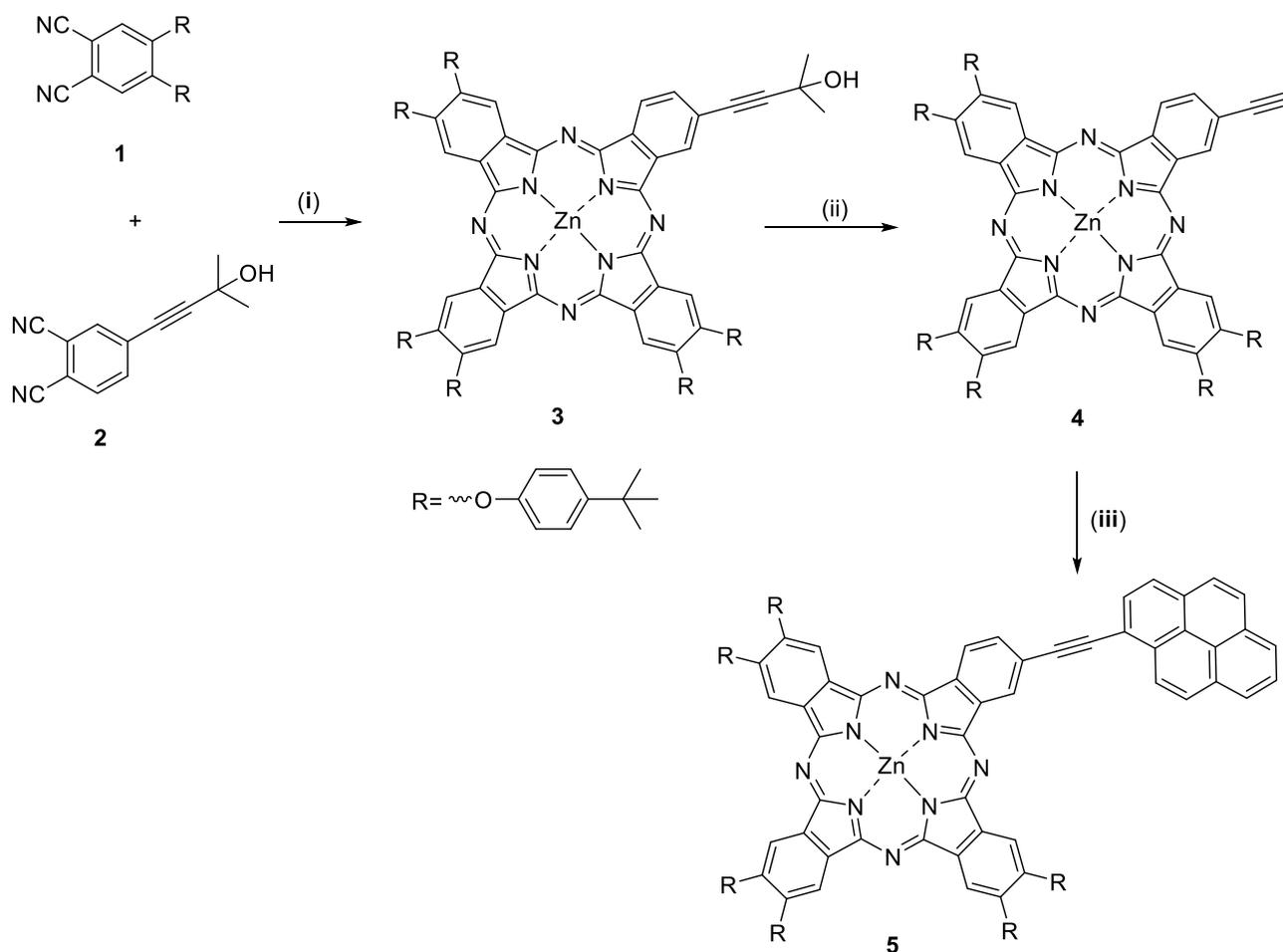
RESULTS AND DISCUSSION

Synthesis and spectroscopic characterization

There are three methods for the preparation of unsymmetrically substituted Pcs. These include a statistical condensation of two different phthalonitriles (32-34), a polymeric support method (35, 36) and a ring-expansion of sub-phthalocyanine (SubPc) (37, 38). Sub-Pcs undergo ring expansion when reacted with diaminoisoindoline or its analogues, resulting in the A_3B type phthalocyanines. Although ring expansion reaction is highly selective and the A_3B phthalocyanine is the major product, this only applies to limited phthalonitriles. It is because the ring expansion reaction is dependent on the experimental conditions and the electronic properties of the reactants (39-42). Despite the variety of commercially available polymeric supports, phthalonitriles having a functional

group that can bind to the polymer and then be separated under acidic or alkaline conditions is limited. Therefore, the synthesis of A_3B type phthalocyanines by the polymeric support route is restricted (43, 44). Since the starting materials used in this study do not have a functional group that can bind to the polymer, the statistical condensation method is preferred. If the reactivities of the two phthalonitrile involved in the condensation are similar, the symmetrical A_4 type Pc (33%), the asymmetrical A_3B type Pc (44%) and the remaining Pcs (23%) can be obtained using a 3 : 1 (A:B) ratio. In this method, the use of phthalonitriles with different solubility properties will facilitate purification of the targeted asymmetric phthalocyanine.

Phthalonitrile **1** and phthalonitrile **2** were used as starting materials. Compound **1** was synthesized from the reaction of 4-tert-butylphenol with 4,5-dichlorophthalonitrile in dimethyl sulfoxide (DMSO). The reaction was completed at 90 °C for 4 hours and potassium carbonate (K_2CO_3) was used as the base (25). Nitrile **2** was prepared by the reaction of 2-methylbut-3-yn-2-ol with 4-iodophthalonitrile under typical Sonogashira reaction conditions (26, 45). The mixed condensation of phthalonitrile precursors **1** and **2** with zinc chloride ($ZnCl_2$) in 2-dimethylaminoethanol (DMAE) at 145 °C afforded the corresponding zinc phthalocyanine (**3**) (Scheme 1). The desired phthalocyanine (**3**) was purified by column chromatography. The dioxane:hexane (1:3) mixture was used as the eluent on silica gel and the compound was obtained in moderate yield (14%) (27). The protecting group was then removed by treatment with sodium hydroxide in toluene to give the ethynyl derivative (**4**) (27). The resulting crude product was purified by column chromatography on silica gel by using dioxane:hexane (1:5) as eluent. Phthalocyanine **4** was obtained as green solid in a 69% yield. The Sonogashira coupling reaction between compound **4** and 1-bromopyrene in THF/trimethylamine with bis(triphenylphosphine)palladium(II)chloride and copper(I)iodide as catalyst at 60 °C under N_2 atmosphere led to the formation of **5** in 24% yield.



Scheme 1. Synthetic route to unsymmetrical ZnPc (**5**) (i) ZnCl_2 , DMAE, 24 h, reflux. (ii) NaOH, toluene, reflux, 6h. (iii) 1-Bromopyrene, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI, THF, Triethylamine, 60 °C, 24h.

The spectroscopic characterization of the newly synthesized compound (**5**) included ^1H NMR, IR, mass and UV-Vis. In the FT-IR spectrum of compound **5**, aromatic CH, aliphatic CH, $\text{C}\equiv\text{C}$ and $\text{C}-\text{O}-\text{C}$ vibrations were observed at 3039, 2957–2869, 2206 and 1266–1212 cm^{-1} , respectively. In the ^1H NMR spectrum of **5**, the aromatic protons were observed between 7.65–7.33 ppm as multiplet in CDCl_3 . The aliphatic CH_3 protons were resonated at 1.30 ppm as singlet. In the mass spectrum of compound **5**, the presence of the characteristic molecular ion peak at $m/z = 1689.66$ $[\text{M}]^+$ confirmed the proposed structure.

In the UV spectra of compounds ZnPc (**4**) and ZnPc-Py (**5**) in DMF, the B bands and Q bands

were detected at 354 (**4**), 356 (**5**) and 678 (**4**), 683 (**5**) nm, respectively (**Figure 1**). Two absorption peaks were observed at 267 and 346 nm in the spectrum of pyrene in DMF (**Figure 1**). The Q band of ZnPc (**5**) slightly red shifted (5 nm) after coordination with Py. The reason for this shift is the extended π conjugation of phthalocyanine structure (**23**). After the conjugation, the B band of ZnPc-Py (**5**) was almost as intense as its Q band because of the pyrene absorption in the B band region (21, 22). As seen in the literature, the Soret band of phthalocyanine (**5**) overlaps with the absorption of pyrene unit at around 346 nm (21-23).

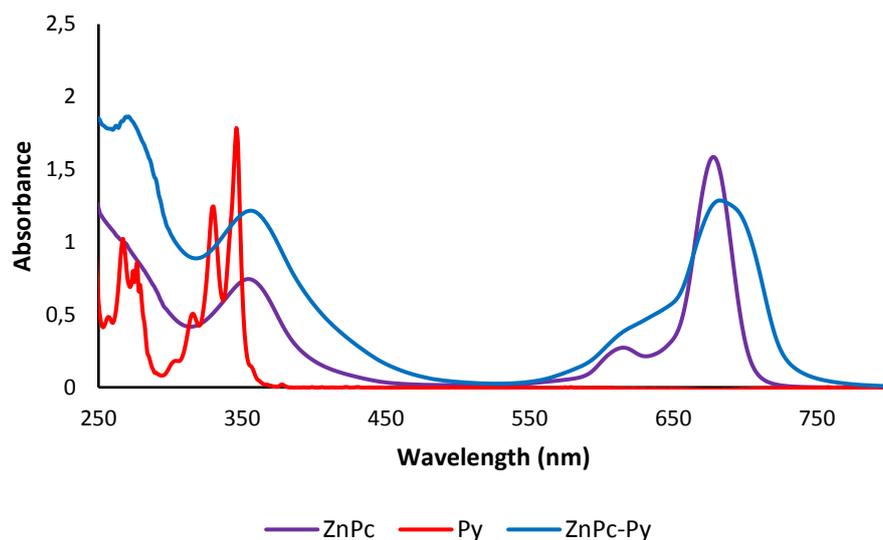


Figure 1. UV/Vis spectra of ZnPc (**4**), ZnPc-Py (**5**) and pyrene (Py) in DMF (6×10^{-5} M)

The fluorescence measurements and fluorescence quenching studies of **5** were performed in DMF upon excitation at 615 nm. The fluorescence emission, excitation, and absorption spectra of **5** were shown in Figure 2. Fluorescence emission peak of **5** was detected at 705 nm and Stokes' shifts was evaluated as 27 nm. The observed Stokes' shift was within the region ~ 20 -30 nm as

typical for Pc complexes (46). The excitation spectrum was similar to absorption spectrum and both were mirror images of the fluorescent spectra for **5** in DMF. This shows that the nuclear configurations of the ground and excited states are similar and not affected by excitation (28, 29).

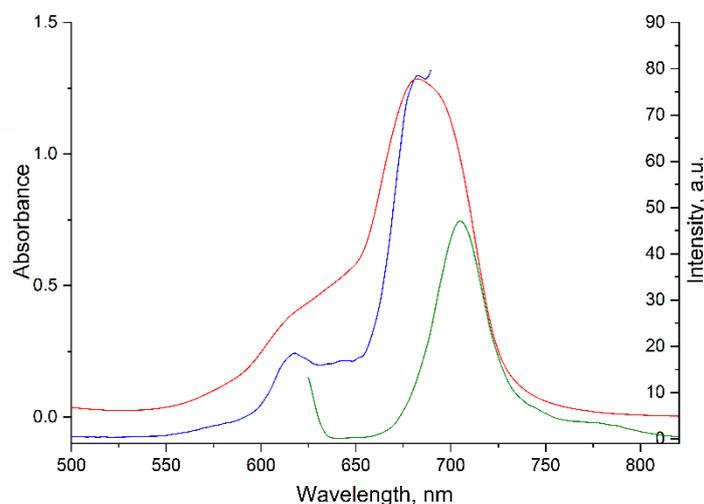


Figure 2. Absorption (red), excitation (blue) and emission (green) spectra of **5** in DMF (4×10^{-6} M)

The fluorescence quantum yield (Φ_F) of compound **5** was calculated as 0.173 which is very close to the Φ_F value of the ZnPc used as reference. According to the literature, the insertion of a diamagnetic central metal is known to increase the fluorescence quantum yield (Φ_F) (47). For standard ZnPc the Φ_F value is known to be 0.17 in DMF (28, 29).

According to the literature, Özçeşmeci and coworkers synthesized phthalocyanines bearing four pyrene units and studied their photophysical properties (21). In another study performed by Sürgün et al., pyrenyl substituted phthalocyanine synthesis and photophysical measurements were

performed (22). In these studies where the pyrene groups were not conjugated to the phthalocyanine ring, the fluorescence quantum yields measured for ZnPc's were close to the value of the standard ZnPc. ZnPc-Py conjugate structure was accomplished by Ogobodu and coworkers (23). They reported that the fluorescence quantum yield of the pyrene substituted unsymmetrical ZnPc was close to the reference yield. In this study, we extend the conjugation of the Pc by adding a pyrenyl group and the fluorescence quantum yield of **5**, was found to be very close to the value in the literature.

The natural radiative lifetime (τ_0) value was calculated as 13.07 ns and the fluorescence lifetime (k_F) value was 2.26 ns. For the unsubstituted ZnPc, the τ_0 and k_F values are 6.05

ns and 1.03 ns, respectively. It was observed that the natural radiative lifetime and the fluorescence lifetime values for **5** were higher than non-substituted ZnPc in DMF.

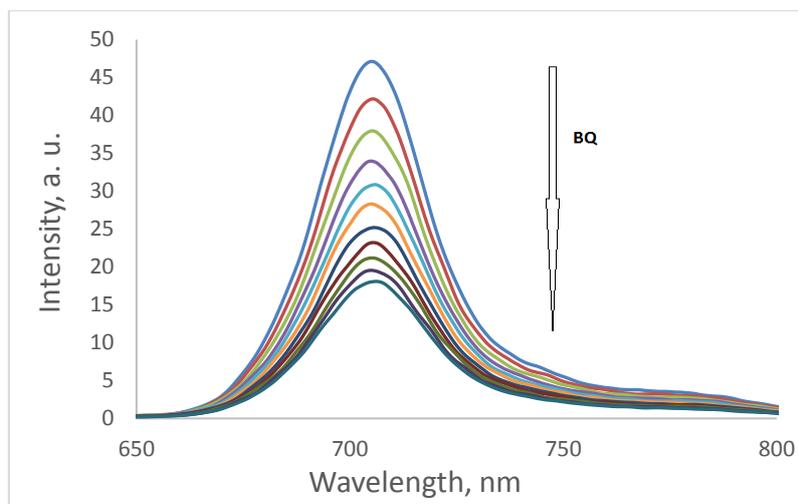


Figure 3. Fluorescent emission spectral changes of **5** (4×10^{-6} M) in DMF in which different concentrations of hydroquinone in DMF were added as quencher. [BQ] = 0.000, 0.008, 0.016, 0.024, 0.032, 0.040 M

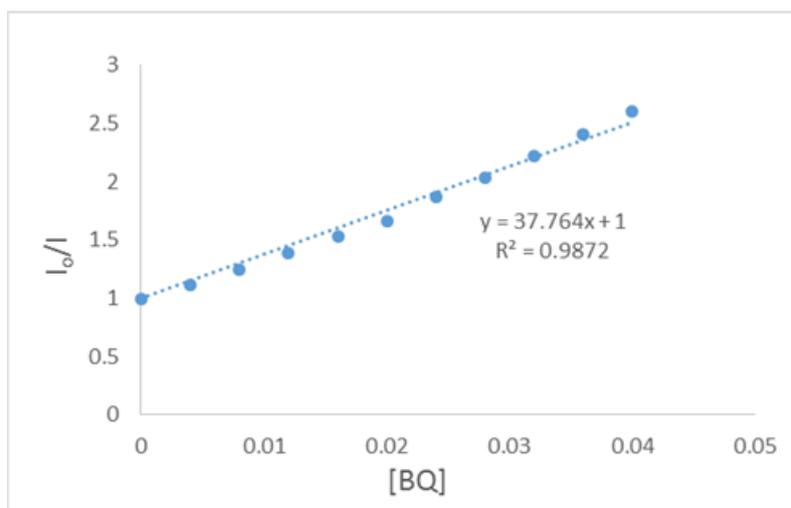


Figure 4. Stern-Volmer plot of **5** for BQ ([BQ] = 0.000, 0.008, 0.016, 0.024, 0.032, 0.040 M)

The fluorescence quenching of the compound **5** by benzoquinone (BQ) in DMF was found to obey Stern-Volmer kinetics, which is consistent with diffusion-controlled bimolecular reactions. The emission spectrum of **5** with the addition of varying concentrations of BQ is shown in **Figure 3**. As the concentration of BQ increases, the intensity of **5** decreases in parallel to the increasing concentration of BQ. The slope of the graph studied for equation 3 is linear, indicating that the diffusion controlled quenching mechanisms. The K_{SV} value from the slope of the graph was found to be 37.76 M^{-1} (**Figure 4**) (28, 29). k_q is the bimolecular quenching constant of **5** in DMF for BQ quenching and the value for **5** is $1.67 \times 10^{10} \text{ s}^{-1}$. The K_{SV} and k_q values of compound **5** are smaller than unsubstituted ZnPc ($K_{SV} = 57.60 \text{ M}^{-1}$, $k_q = 5.59 \times 10^{10} \text{ s}^{-1}$).

CONCLUSION

In the present work, pyrene and *tert*-butylphenoxy substituted unsymmetrical zinc phthalocyanine was synthesized and characterized by various spectroscopic methods and confirmed the proposed structure. The overlap of the Soret band of Py caused an increase in the intensity of B band of compound **5** after conjugation. The slight red shifting of Q band of Pc was also determined after Pc-Py conjugation. The photophysical properties of Pc-Py (**5**) conjugate was investigated and compared with an unsubstituted ZnPc. The fluorescence quantum yield of compound **5** is close to unsubstituted ZnPc, while its lifetime is higher than that of

unsubstituted ZnPc. In addition, the fluorescence quantum yield of compound **5** was compared with the fluorescence quantum yield of other tetrasubstituted ZnPc substituted with pyrene groups in the literature (21-23). The fluorescence quantum yield of **5** is in agreement with the literature values. Furthermore, the fluorescence quenching studies were performed by benzoquinone typically. The Stern-Volmer kinetics were also investigated in DMF. In comparison with unsubstituted zinc phthalocyanine, compound **5** showed lower K_{SV} and k_q values.

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