

# Phthalocyanine-based fluorescent chemosensor for the sensing of Zn (II) in dimethyl sulfoxide-acetonitrile

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Received: 5 January 2011 / Accepted: 29 June 2011 / Published online: 23 July 2011  
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**Abstract** A tetra-substituted phthalocyanine based on 4-[2-(4-nitrophenoxy)ethoxy]phthalonitrile carrying nitrophenyl group for the sensing of  $Zn^{2+}$  has been prepared and characterized by elemental analysis, FT-IR,  $^1H$  and  $^{13}C$  NMR, and MS spectral data. The sensing of  $Zn^{2+}$  is based on the fluorescence quenching of Pc. Both absorbance and fluorescence spectra of ZnPc exhibit distinct changes in visible region in response to treatment with  $Zn^{2+}$  ion in dimethyl sulfoxide. The fluorescence spectrum of the ligand showed quenching in the intensity of the signal at 688 nm for  $Zn^{2+}$ . The complex composition of ZnPc was found 1:1 by means of spectrophotometric and spectrofluorimetric titration data. The spectrofluorimetric method showed good sensitivity for  $Zn^{2+}$  with linear range and detection limit of  $4.0 \times 10^{-6}$ – $4.4 \times 10^{-5}$  and  $2.4 \times 10^{-7}$  M, respectively.

**Keywords** Phthalocyanine · Fluorescence spectroscopy · Complex composition ·  $Zn^{2+}$  ion · Chemosensor

## Introduction

Metal-free phthalocyanines ( $H_2Pc$ ), have become the focus of intense research interest due to their interesting properties for diverse applications [1]. These macrocyclic ligands have a chromophoric nature due to their structure

containing extended  $\pi$ -electron delocalisation. Most synthetic organic pigments in the blue to green color range are Pc derivatives. They also show some properties such as low solubility, high thermal stability and electrochromism, which allow them to be utilized in technological applications [2–5], such as optical data storage, nonlinear optics, gas sensor, laser technology, catalysis and photodynamic therapy [6, 7].

It is well known that phthalocyanines and complexes strongly absorb light in the red portion of the visible spectrum, thus characteristically these dyes are blue or greenish [8, 9]. Phthalocyanines have two absorption bands, a strong Q band in the red region (600–700 nm) and a medium strength Soret band in UV region (350 nm). Due to the attractive property of high fluorescence efficiency in red wavelength region, phthalocyanines are potentially useful as wavelength transfer devices absorbing the short wavelength and emitting longer red wavelengths.

Phthalocyanines are suitable materials for the development of chemical sensors, such as electronic conductance sensors, mass-sensitive sensors, surface acoustic-wave (SAW) sensors, and optical sensors. Gas sensitivity of some metal phthalocyanines is known well [10, 11]. Recently, functional phthalocyanines have been of particular interest because of their capability of binding multiple metal ions and hence providing metal sensing in solution [12–14].

Recently, our efforts have been focused on the preparation, characterization and electrochemical measurements of peripherally substituted phthalocyanines having some electron donor or acceptor groups [15]. In this study, we report a new type of tetra substituted metal-free phthalocyanine and the photophysical changes upon complexation of the ligand with  $Zn^{2+}$ . Our aim is to disclose the effect of nitrophenyl groups located peripherally on the phthalocyanine frame on the fluorescence properties of the metal-free phthalocyanine

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during complexation. The complex composition and complex stability constant were determined by using spectrophotometric and spectrofluorimetric titration in DMSO-acetonitrile (1/1).

## Experimental

### Chemicals

DMSO from Merck (spectrometric grade) was the solvent for absorption and fluorescence measurements. Zinc perchlorate purchased from Acros was of the highest quality available and vacuum dried over blue silica gel before use.

### Apparatus

IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer using KBr pellets.  $^1\text{H}$  and  $^{13}\text{C}$  measurements were performed on a Varian 200 A spectrometer, using DMSO- $d_6$  with TMS as the internal reference. Elemental analysis was performed on Costech 4010 CHNS instrument. Mass spectra were measured with a Micromass Quatro LC-MS/MS spectrometer. UV-Vis spectra were recorded on a Thermo Evolution 60 model spectrophotometer with the use of standard 1-cm quartz cell. Fluorescence study was performed on a Photon Technologies International Quanta Master Spectrofluorimeter.

### Measurements

Stock solution of the ligand was prepared in DMSO and the ligand solutions used for all spectrometric and spectrofluorimetric titrations were prepared from these solutions by dilution. Any changes in titration experiments were recorded upon addition of perchlorate of the respective metals to its DMSO solution, while the ligand concentration was kept constant ( $4 \times 10^{-5}$  M). The solution of the metal perchlorates was prepared in acetonitrile. The concentration of metal perchlorates was between  $4 \times 10^{-5}$  and  $9.6 \times 10^{-5}$  M. Fluorescence emission spectra were recorded in the range 678–800 nm.

The stoichiometry of the complex and the complex stability constant were determined according to molar-ratio method [16] and Valeur's method [17], respectively.

### Synthesis

#### Synthesis of (3)

The precursor 2-(4-nitrophenoxy)ethanol (1) was purchased from Merck. 2-(4-nitrophenoxy)ethanol (2 g, 10.93 mmol) and 4-nitrophthalonitrile (2) (1.89 g, 10.93 mmol) were

dissolved in 20 mL DMF under argon atmosphere in a Schlenk system connected to a vacuum line at room temperature. Dry  $\text{K}_2\text{CO}_3$  (5.36 g, 38.88 mmol) was added to this yellow solution in equal portions for 2 h. The brown solution was refluxed under argon atmosphere at 50 °C for 72 h. The reaction mixture was poured on ice (200 g) and this mixture was stirred at room temperature for 24 h. At the end of this period, the reaction mixture was filtered and rinsed with diethyl ether and then with water. The resultant yellow-green solid was dried in vacuo with  $\text{P}_2\text{O}_5$ . The yellow solid was obtained by crystallization via ethyl alcohol. Yield (% 52), M.p: 129–132 °C.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.23 (d, 2H, Ar-H), 8.09 (d, 1H, Ar-H), 7.85 (s, 1H, Ar-H), 7.54 (d, 1H, Ar-H), 7.21 (d, 2H, Ar-H), 4.53 (m, 4H,  $\text{CH}_2\text{-O}$ ) ppm.  $^{13}\text{C}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 163.35, 161.74, 142.24, 135.56, 126.22, 126.16, 119.94, 119.77, 117.74, 115.78, 115.40, 114.80, 108.15, 67.43, 66.77 ppm. IR (KBr):  $\nu/\text{cm}^{-1}$  = 3084 (CH aromatic), 2972–2923 ( $\text{CH}_2$  aliphatic), 2232 ( $\text{C}\equiv\text{N}$ ), 1595, 1564, 1509, 1493, 1343, 1298, 1266, 1255, 1178, 1110, 968, 927, 841, 522  $\text{cm}^{-1}$ . MS (FAB $^+$ ): ( $m/z$ ) = 309 [ $\text{M}$ ] $^+$ .  $\text{C}_{16}\text{H}_{11}\text{N}_3\text{O}_4$  (390): calcd. C 62.14, H 3.58, N 13.58; found C 60.04, H 3.12, N 12.88.

#### Synthesis of ligand (4)

The phthalonitrile derivative (3) (250 mg, 0.81 mmol), dry *n*-pentyl alcohol (2.0 mL) and three to four drops of DBU was added in a standard Schlenk tube. The reaction mixture was degassed and heated at reflux (160 °C) for 18 h. Then, diethyl ether (2–3 mL) was added into the reaction mixture, which cooled at room temperature. The precipitated green solid was filtered off and dried. The reaction product was purified by column chromatography on silica gel [chloroform/methanol/pyridine (100:10:1)]. The combined solvents were evaporated and dark green product was obtained and then dried in vacuo. Yield: 117 mg (47%). M.p. > 300 °C.  $^1\text{H}$  NMR (200 MHz, DMSO- $d_6$ ):  $\delta$  = 7.64 (m, 8H, Ar-H), 7.43 (m, 8H, Ar-H), 7.21 (m, 12H, Ar-H), 4.16 (m, 16H,  $\text{CH}_2\text{O}$ ) ppm. IR (KBr):  $\nu/\text{cm}^{-1}$  = 3292 (N-H), 3060 (CH aromatic), 2923–2851 ( $\text{CH}_2$  aliphatic), 1610 ( $\text{C}=\text{N}$ ), 1593–1508–1341 ( $\text{NO}_2$ ), 790–751 (C-N)  $\text{cm}^{-1}$ . UV/Vis (Pyridine):  $\lambda_{\text{maks}}(\log \epsilon)$  nm = 317 (5.02), 608 (4.47), 641 (4.55), 668 (4.85), 707 (4.92). MS (FAB $^+$ ): ( $m/z$ ) = 1238 [ $\text{M}$ ] $^+$ .  $\text{C}_{64}\text{H}_{46}\text{N}_{12}\text{O}_{16}$  (1238): calcd. C 62.04, H 3.74, N 13.56; found C 61.01, H 2.98, N 12.83.

## Results and discussion

### Characterization of compounds 3 and 4

Starting from 2-(4-nitrophenoxy)ethanol (1) and 4-nitrophthalonitrile (2), the general synthetic route for the synthesis of

new phthalonitrile (**3**) is given in Scheme 1. The new phthalonitrile **3** was obtained with a yield of 52%. The IR spectra of the phthalonitrile compound (**3**) clearly indicate the presence of C≡N group by the intense stretching bands at  $2232\text{ cm}^{-1}$ . Disappearance of the sharp O–H stretching vibration belonging to compound (**1**) confirmed formation of the new phthalonitrile (**3**). The  $^1\text{H}$  NMR spectra of phthalonitrile compound **3** was recorded in  $\text{CDCl}_3$ . In the  $^1\text{H}$  NMR spectrum of compound (**3**), OH group of 2-(4-nitrophenoxy)ethanol (**1**) disappeared as expected. In the  $^1\text{H}$  NMR spectrum of phthalonitrile (**3**), the aromatic protons appear at 8.23 (d, 2H, Ar–H), 8.09 (d, 1H, Ar–H), 7.85 (s, 1H, Ar–H), 7.54 (d, 1H, Ar–H), 7.21 (d, 2H, Ar–H) ppm. The  $^{13}\text{C}$  NMR spectrum of compound (**3**) indicates the presence of nitrile carbon atom at  $\delta = 115.78, 115.40$  ppm. In the mass spectra of phthalonitrile compound (**3**), the molecular ion peak was observed at  $m/z$  309  $[\text{M}]^+$ . The elemental analysis confirmed the presence of the desired compound (**3**).

Cyclotetramerization of the phthalonitrile derivative **3** to the metal-free phthalocyanine (**4**) was accomplished in *n*-pentanol in the presence of a few drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong base at  $160\text{ }^\circ\text{C}$  in sealed tube and the yield was 47%. Cyclotetramerization of the dinitrile (**3**) to the metal-free phthalocyanine (**4**) was confirmed by the disappearance of the sharp C≡N vibration at  $2232\text{ cm}^{-1}$ . IR band characteristic of the metal-free

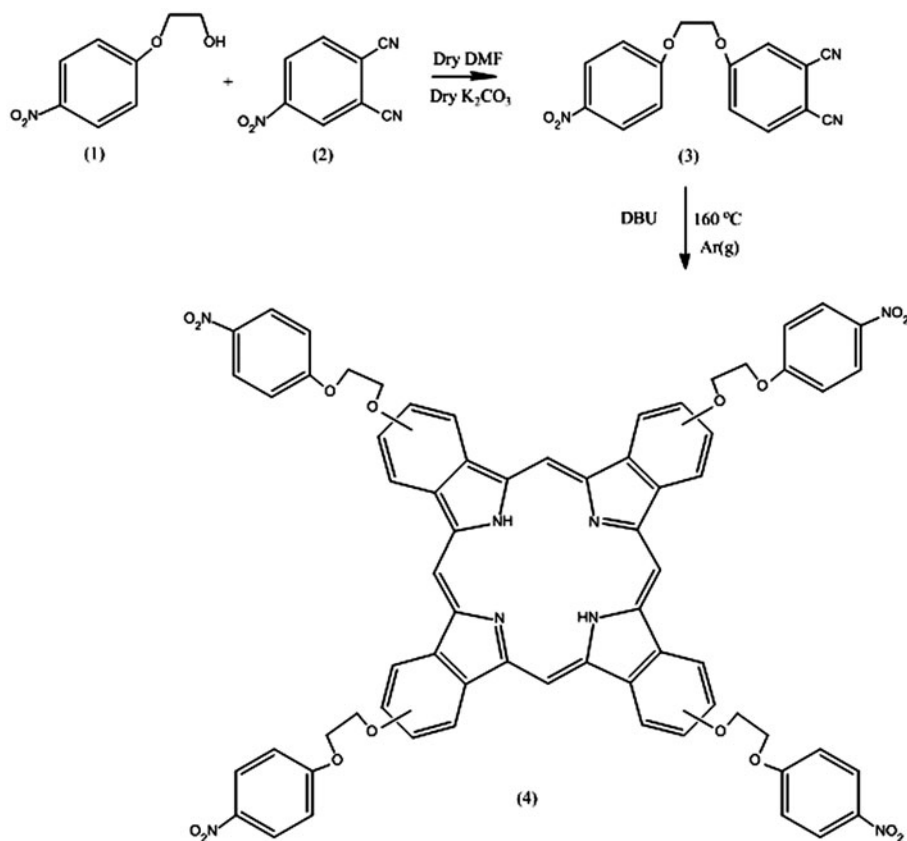
phthalocyanine ring is an N–H stretching at  $3292\text{ cm}^{-1}$ . The IR spectra of metal-free (**4**) and phthalonitrile (**3**) are very similar, except for these  $\nu(\text{NH})$  vibrations of the inner phthalocyanine core in the metal-free molecule (**4**). In the  $^1\text{H}$  NMR spectrum of (**4**), the typical shielding of inner core protons couldn't be observed due to the probable strong aggregation of the molecules [18]. The aromatic protons appear at 7.64 (m, 8H, Ar–H), 7.43 (m, 8H, Ar–H), 7.21 (m, 12H, Ar–H) ppm. In the mass spectra of metal-free phthalocyanine (**4**), the molecular ion peak was observed at  $m/z$  1238  $[\text{M}]^+$ . The elemental analysis confirmed the presence of the desired metal-free phthalocyanine (**4**).

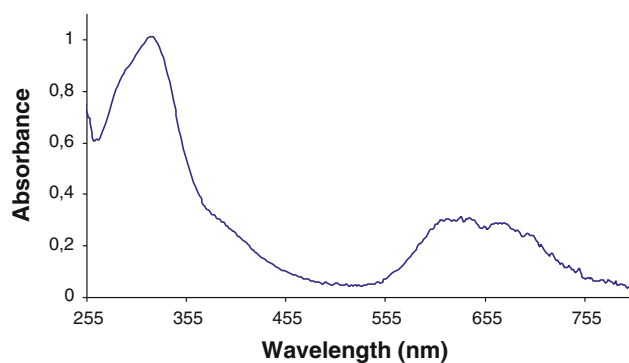
#### Absorption spectra

Figure 1 shows the absorption and emission spectra of the ligand (**4**). The absorption spectra of the ligand (**4**) in DMSO-acetonitrile (1/1) display two absorption bands, a Q band in the red region (655 nm) and a Soret band in UV region (340 nm), which is characteristic to phthalocyanines [19]. Molar absorption coefficients are  $2.5 \times 10^4$  and  $7.5 \times 10^3\text{ cm}^{-1}\text{ M}^{-1}$  for these wavelengths, respectively.

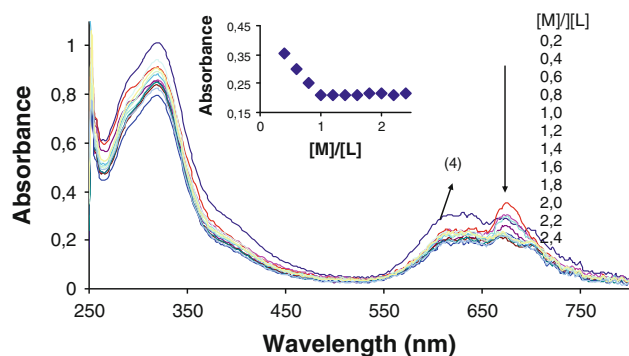
The change in the absorption spectra of the ligand (**4**) with increasing concentrations of  $\text{Zn}^{+2}$  in the range  $8 \times 10^{-6}$  and  $1 \times 10^{-4}$  is shown in Fig. 2. The decrease in absorbance at 676 nm provided the determination of the

**Scheme 1** Synthetic pathway to the new phthalocyanine used in this study

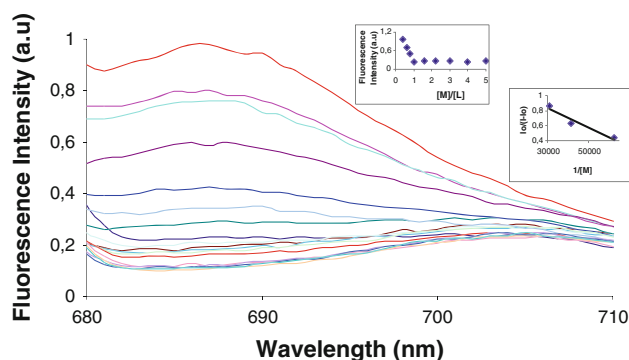




**Fig. 1** The absorption spectra of the ligand (**4**) in DMSO-acetonitrile (1/1). Ligand concentration is  $4.0 \times 10^{-5}$  M

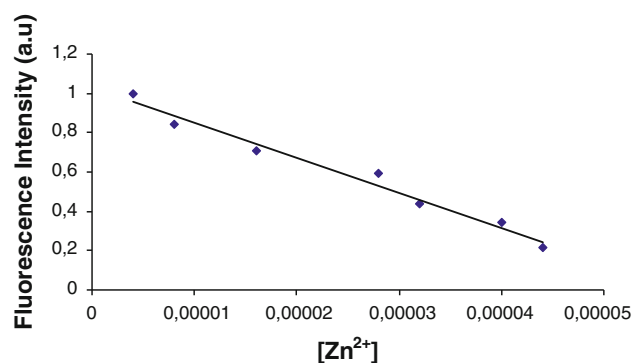


**Fig. 2** Absorption spectra of (**4**) complexed with  $Zn^{2+}$ . The spectral changes during the addition of 0–2.4 equivalents of  $Zn(ClO_4)_2$ . Ligand concentration:  $4 \times 10^{-5}$  M



**Fig. 3** The variation of the fluorescence ( $\lambda_{exc} = 674$  nm) of the ligand (**4**) with increasing amounts of  $Zn^{2+}$  ions.  $[L]: 4 \times 10^{-5}$  M

complex composition of  $Zn^{2+}$ -ligand (**4**). As seen from Fig. 2 (inset), the inflection point was 1.0 ( $[M]/[L]$ ), suggesting that the ligand (**4**) formed a stable 1:1 complex with  $Zn^{2+}$ . A regular change in the absorption spectra of the ligand (**4**) wasn't found with increasing concentrations of  $Ni^{2+}$ ,  $Co^{2+}$  and  $Cd^{2+}$  cations, implying that the phthalocyanine molecule prefers to complex with  $Zn^{2+}$  ion in comparison to these ions.



**Fig. 4** Fluorescence intensity of the ligand (**4**) versus  $Zn^{2+}$  concentration for the spectrofluorimetric titration. Wavelength: 681 nm, ligand concentration =  $4 \times 10^{-5}$  M

#### Fluorescence spectra

The complex formation was monitored by the effect of gradual addition of zinc perchlorate to the solution of the ligand (**4**). The change in the fluorescence spectra of  $4.0 \times 10^{-5}$  M of ligand (**4**) with increasing concentrations of  $Zn^{2+}$  in the range  $8 \times 10^{-6}$  and  $4 \times 10^{-4}$  M is shown in Fig. 3. The successive decrease of the emission intensity with addition of  $Zn^{2+}$  was observed for the fluorimetric titration. Molar ratio plot, which was used to determine the complex composition for  $Zn^{2+}$ , clearly shows the formation of a 1:1 (M:L) complex for the ligand (**4**) with  $Zn^{2+}$ , as shown in Fig. 3 (inset above). The values of  $I$  at 688 nm was plotted against the ratio of  $[M]/[L]$ .  $I$  is the fluorescence intensity of the solution involving  $Zn^{2+}$  cation. In order to determine the complex stability constant, the ratio of  $I_0/(I-I_0)$  was plotted versus  $1/[M]$ , as in Fig. 3 (inset below), which gave a good straight line. The stability constant was calculated from the ratio of intercept/slope [16]. The value of  $\log K$  was 5.11 for the  $Zn^{2+}$ -ligand (**4**) complex. The proper data for the stability constant could be obtained from the change of absorbance at 688 nm.

Figure 4 shows the regular fluorescence enhancement depending on increasing  $Zn^{2+}$  concentrations with the ligand (**4**). A linear response of the fluorescence intensity at 681 nm as a function of  $Zn^{2+}$  concentration was observed from  $4.0 \times 10^{-6}$  to  $4.4 \times 10^{-5}$  M with linearly dependent coefficient  $R^2 = 0.9700$  (Fig. 4). The detection limit calculated as three times the standard deviation of the blank signal was found to be  $2.4 \times 10^{-7}$  M. A regular change wasn't found in the fluorescence spectra of the ligand (**4**) with increasing concentrations of  $Ni^{2+}$ ,  $Co^{2+}$  and  $Cd^{2+}$  cations as in the case of absorption spectra. Our results showed that the phthalocyanine molecule does not prefer interacting with these metal ions. However,  $Zn^{2+}$  is a preferable ion in complexation with the phthalocyanine (**4**), implying that the ligand (**4**) shows selective complexation to  $Zn^{2+}$  rather than  $Ni^{2+}$ ,  $Co^{2+}$  and  $Cd^{2+}$  ions. The

reported study may highlight the versatile sensing of  $Zn^{2+}$  ion.

**Acknowledgment** This study was supported by the Research Fund of Karadeniz Technical University.

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