



Non-peripherally tetrasubstituted phthalocyanines: Synthesis, characterization and, photophysical investigation



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ABSTRACT

The synthesis, characterization and photophysical properties of novel, non-peripherally tetrasubstituted metal-free and metallophthalocyanines (MPcs) (Zn, In) bearing morpholinoethoxy groups have been reported. The new compounds were characterized by using elemental analysis, ¹H NMR, UV–Vis and FT-IR spectroscopy and mass spectrometry. The aggregative properties of the novel compounds were investigated in different concentrations. General trends for fluorescence quantum yields and lifetimes of metal-free and metallophthalocyanines were also described in tetrahydrofuran (THF). The fluorescence of these compounds is effectively quenched by 1,4-benzoquinone (BQ) in THF.

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1. Introduction

Since the accidental discovery of phthalocyanines (Pcs), much effort has been done to modulate the properties of their derivatives to achieve ideal molecules for a variety of applications, such as catalysis [1,2], chemical sensing [3–5], liquid crystals [6,7], semiconductors [8], dye sensitized solar cells [9,10] and non-linear optics [11,12]. In recent years there has been growing interest in the applications of phthalocyanines (Pcs) and related compounds in medicine [13,14]. Owing to the strong absorption in the red visible region and high efficiency in producing reactive oxygen species, this class of compounds have been found to be highly promising as second-generation photosensitizers [15–17].

Nitrogen-containing heterocyclic compounds are an important class of chemical compounds with a remarkable potential for industrial, pharmaceutical, and agrochemical applications [18]. Whether they are natural or synthetic one, owing to their interesting biological properties they are very often involved as key components in biological processes [19]. Moreover nitrogen containing heterocycles such as piperazine and morpholine derivatives have been extensively investigated by organic chemist due to their

close association with various types of biological activities and clinical applications in the therapy of functional diseases [20]. Morpholine derivatives show a variety of biological activities including anti-inflammatory, analgesic, HIV-protease inhibitors, anticancer, antidepressant, antiplatelet, selective inhibitor of protein kinase C, neuroprotective, antitumor, antituberculosis, anti-malarial, antiparasitic, hypocholesterolemic and hypolipidemic activities and they have been frequently synthesized to be used as drugs in pharmaceutical industry [21–25].

Development of novel and efficient methods for synthesis of phthalocyanines containing nitrogen heterocyclic groups is an active area of research in industry and academia. Recently, it was reported that Pcs carrying piperidineethanol groups on the peripheral or non-peripheral positions revealed good solubilities in polar organic solvents and increased photocytotoxicity [26]. In addition, piperazine substituted phthalocyanines exhibited anti-fungal photodynamic activity as a result of better amphiphilicity [27]. An insertion of a morpholine moiety into the structure of phthalocyanines, has been shown as an important factor modulating their physicochemical properties, thus facilitating their potential applications in medicine [28–30]. Moreover, novel silikon Pcs which have been modified axially with morpholine derivatives and their quaternary salts indicated antifungal photodynamic activity and good solubility [31,32].

In our previous work, the synthesis, characterization,

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electrochemical and physicochemical properties of novel symmetric and unsymmetric phthalocyanines carrying morpholine moieties were described [33,34]. In this paper, we describe the synthesis and characterization of non-peripherally tetra substituted metal-free and metolophthalocyanines (Zn, In) carrying morpholinoethoxy moieties. Further, the wavelength of the absorption of the Q band and the aggregation properties of the compounds (2–4) were investigated. We also report the photo-physical (fluorescence quantum yields and lifetimes) and quenching properties of these compounds.

2. Experimental

2.1. Materials and equipment

All reported ^1H -NMR spectra were recorded on a Agilent VNMRS 500 MHz spectrometer. Chemical shifts were reported (δ) relative to Me_4Si as internal standard. 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. IR spectra were recorded on a Perkin-Elmer One FT-IR spectrophotometer and electronic spectra were recorded using Scinco LabProPlus UV/Vis spectrophotometer with 1 cm path length quartz cuvettes in the spectral range of 300–800 nm. Fluorescence spectra were recorded on a Perkin-Elmer LS55 fluorescence spectrophotometer. Aluminium oxide 90 active neutral was used in the separation and purification of compounds by column chromatography. The homogeneity of the products was tested in each step by Thin Layer Chromatography (TLC). 4-(2-Hydroxyethyl)morpholine (2-Morpholinoethanol) and 3-nitrophthalonitrile were purchased from Aldrich. All the reagents and solvents were of reagent grade quality and were obtained from commercial suppliers.

2.2. X-ray crystallographic data of 4-(2-morpholinoethoxy) phthalonitrile (1)

The single crystal of **1** with dimensions $0.01 \times 0.03 \times 0.3$ mm was grown by slow evaporation of the chloroform solution. Crystal was mounted on a microamount and attached to a goniometer head on a Bruker D8 VENTURE diffractometer equipped with PHOTON100 detector using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) and scanned with 0.5° Φ -rotation frames at room temperature. Crystal parameters and refinement results of **1** are summarized in Table 1. The structure has been solved by intrinsic method SHELXS-1997 [35] and refined SHELXL-2014/7 [36]. ORTEP drawings with the atom numbering scheme and the packing motif of **1** are given in Fig. 1. Molecular drawings are generated using OLEX2. Ver. 1.2-dev [37]. Thermal ellipsoids are plotted at the 50% probability level. Selected bond lengths, bond and torsion angles of **1** are given in Table 2. The crystal and instrumental parameters used in data collection are summarized in the supporting information. CCDC 1471012 contains the supplementary crystallographic data for this paper. Further details on crystal data, data collection, and refinements can be found on the supporting information.

2.3. Synthesis

2.3.1. 3-(2-Morpholinoethoxy)phthalonitrile (1)

3-Nitrophthalonitrile (1 g, 5.78 mmol) was dissolved in 40 mL of dry DMSO and 2-morpholinoethanol (1.07 mL, 8.67 mmol) was added. After stirring for 15 min, 3.2 g of finely ground anhydrous K_2CO_3 (23.10 mmol) was added in small portions for 2 h with efficient stirring. The reaction mixture was stirred under nitrogen at room temperature for 72 h. Then, the mixture was poured into

Table 1

Crystal data and structure refinement parameters for 3-(2-morpholinoethoxy) phthalonitrile (**1**).

	Phthalonitrile 1
Empirical formula	$\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}_2$
Formula weight	257.29
T(K)	304(2)
λ (Å)	0.71073
Crystal system	Triclinic
Space group	P – 1
Unit cell dimensions: (Å, °)	
a	22.8906(18)
b	7.8385(6)
c	7.7759(6)
V (Å 3)	1395.03(19)
α	90.005(4)
β	89.074(4)
γ	89.945(4)
Z	4
Absorption coefficient (mm^{-1})	0.084
Dcalc (g/cm^3)	1.225
F(000)	544
Crystal size (mm)	$0.01 \times 0.03 \times 0.3$
θ range for data collection (°)	2.67 to 24.99
Index ranges	$-27 \leq h \leq 27$ $-9 \leq k \leq 9$ $-9 \leq l \leq 9$
Reflections collected	45369
Independent reflections	4907
Coverage of independent reflections (%)	100
Data/parameters	4907/344
Max. and min. transmission	0.999/0.975
Final R indices [$I \geq 2\sigma(I)$]	$R1 = 0.1324$ $wR2 = 0.3807$
R indices (all data)	$R1 = 0.1969$ $wR2 = 0.4122$
Goodness-of-fit on F^2	1.175
Largest difference in peak and hole ($e \text{ \AA}^{-3}$)	0.362/–0.340

250 mL of ice-water mixture and, the precipitate was filtered off, washed with water until the filtrate was neutral, and dried in vacuo. Finally, a white product was obtained by column chromatography on alumina using 1:1 ethylacetate:hexane as eluent Yield: 0.86 g, (58%), m.p.: 119°C ; anal. calcd. for $\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}_2$: C, 65.35; H, 5.88; N, 16.33%; found: C, 65.10; H, 5.70; N, 16.40%; IR $\nu_{\text{max}}/\text{cm}^{-1}$: 3084 (Ar-H), 2939–2804 (Aliph-CH), 2228 (C \equiv N), 1583, 1469, 1294, 1255, 1113 cm^{-1} ; ^1H NMR (CDCl_3): δ , ppm: 7.67–7.63 (t, 1H, Ar-H), 7.38–7.36 (d, 1H, Ar-H), 7.25–7.18 (d, 1H, Ar-H), 4.29–4.27 (t, 2H, O–CH $_2$), 3.73–3.71 (t, 4H, O–CH $_2$), 2.91–2.88 (t, 2H, N–CH $_2$), 2.64–2.62 (t, 4H, N–CH $_2$).

2.3.2. 1,8(11), 15(18),22(25)-Tetrakis-(2- morpholinoethoxy) phthalocyanine (2)

A solution of **1** (0.3 g, 1.16 mmol) and a catalytic amount of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in 1-pentanol (1 mL) was stirred and heated at 145°C for 24 h under nitrogen. After 24 h the reaction mixture was cooled to room temperature and then diluted with diethyl ether until the crude product precipitated. The precipitate was centrifuged and then dried in vacuo. Finally, the green compound was chromatographed on alumina using THF: CH $_3\text{OH}$ (5:1) as eluent. Yield: 0.08 g, (25%). M.p. $> 200^\circ\text{C}$; anal. calcd. for $\text{C}_{56}\text{H}_{62}\text{N}_{12}\text{O}_8$: C, 65.23; H, 6.06; N, 16.30%; found: C, 65.10; H, 6.00; N, 16.22%; IR $\nu_{\text{max}}/\text{cm}^{-1}$: 3283 (N–H), 3068 (Ar-H), 2949–2857 (Aliph-CH), 1590, 1491, 1447, 1331, 1265, 1143, 1112 cm^{-1} ; ^1H NMR (CDCl_3): δ , ppm: 7.74–7.65 (m, 12H, Ar-H), 4.85–4.71 (t, 8H, O–CH $_2$), 3.84–3.77 (t, 16H, O–CH $_2$), 3.48–3.42 (t, 8H, N–CH $_2$), 3.03–2.97 (t, 16H, N–CH $_2$), –0.96 (br s, 2H, NH); UV–vis (THF): λ_{max} , nm (log ϵ): 321 (4.99), 691 (4.92), 722(4.93); MS (MALDI-TOF): m/z 1031.03 [M] $^+$.

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