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Novel highly soluble fluoro, chloro, bromo-phenoxy-phenoxy substituted zinc phthalocyanines; synthesis, characterization and photophysicochemical properties

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ABSTRACT

The three new phthalocyanine precursors, 4-[4-(bromo phenoxy)phenoxy]phthalonitrile, 4-[4-(chlorophenoxy)phenoxy]phthalonitrile, 4-[4-(flourophenoxy)phenoxy]phthalonitrile (**1**, **2** and **3**) were synthesized and characterized. The photochemical properties (singlet oxygen quantum yields and photodegradation quantum yields) and photophysical properties (fluorescence quantum yields and fluorescence behavior) of their peripherally tetra substituted zinc phthalocyanines (4)-tetra[bromo phenoxy]phthalocyaninato zinc(II), (4)-tetra[chlorophenoxy]phthalocyaninato zinc(II), (4)-Tetra [flourophenoxy]phthalocyaninato zinc(II) (**4**, **5** and **6**) were reported for the first time. The new compounds (**1**–**6**) were characterized by using spectroscopic methods, FT-IR, ^{1}H NMR spectroscopy, electronic spectroscopy and mass spectra as well as elemental analysis. General trends focus on fluorescence, photodegradation and singlet oxygen quantum yields of these compounds in dimethylsulfoxide (DMSO), dimethylformamide (DMF) and tetrahydrofuran (THF). The nature of the substituent and solvent effects on the photophysical and photochemical parameters of the chloro, fluoro, bromo-phenoxy-phenoxy substituted phthalocyanines (**4**, **5** and **6**) was also reported.

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1. Introduction

Phthalocyanine (Pcs) dyes have been studied extensively over thirty years due to their spectroscopic and photoelectric properties. They can be applied in many branches: in the fields of physics, medicine, chemistry and other sciences. Some phthalocyanines are characterized by significant absorption in the visible region [1,2]. This property has led to great interest in different scientific and technological areas such as photoconducting agents in photocopying devices, chemical sensors, molecular metals, liquid crystals, non-linear optics and catalysis [3–5]. In recent years, the use of Pcs as photosensitizers is important for photodynamic cancer therapy (PDT) [6–11]. Photodynamic therapy involves management of a tumor localizing photosensitizing agent, followed by activation of the agent by light of a specific wavelength. This therapy results in a sequence of photochemical and photobiologic processes that cause irreversible photodamage to tumor tissues [12,13]. During the past decades, a great number of potential photosensitizers for PDT have been studied. In particular, Pcs are considered as the promising photosensitizers for PDT owing to their intense absorption in the phototherapeutic window (600–900 nm), high efficiency to generate reactive oxygen species (ROS), high phototoxicity and low dark toxicity [14–19]. They show long-wavelength absorption with high extinction coefficients ($\varepsilon > 105$ M^{-1} cm^{-1}), red fluorescence emission approaching NIR wavelengths for deeper tissue imaging, and high singlet oxygen quantum yields [20]. In previous studies made by our group synthesis, photophysical and photochemical properties of Pcs carrying different substituents were investigated [21–28]. The zinc phthalocyanines bearing halogen atoms (F, Cl, Br) substituted phenoxy ring groups were used since they are also known as photosensitizers [17,27,28].Thus, the addition of a halogen atom such as fluorine, bromine, chlorine on phthalocyanine skeletons is aimed at enhancing the photosensitizer activity due to halogen atom effect. Other than the recent work reported by Kılıçaslan et al. [29], who studied phenoxy-phenoxy substituted phthalocyanines in the presence of a linker, no other study has been reported on photophysicochemical properties of phenoxy-phenoxy derivatized Zn Phthalocyanines

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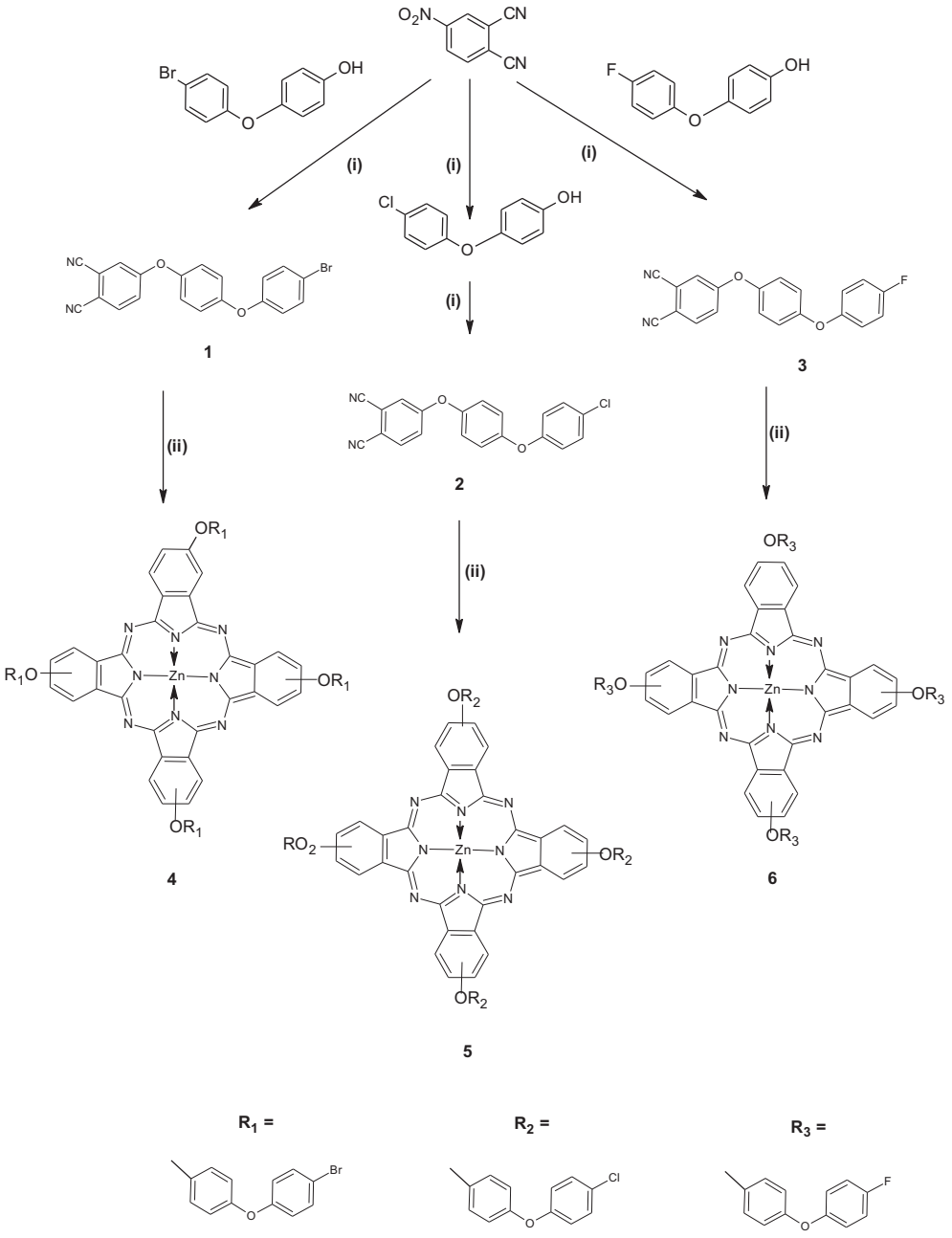
complexes. One of the obtained results about the complexes whose bulky group substituted at the peripheral positions was a decreasing in aggregation [30]. This property is a very important requirement in PDT applications. Aggregation is an unwanted behavior of Pc in solution for their applications. In this study, the photophysical and photochemical properties of the three novel zinc-phthalocyanines peripherally tetra substituted with bulky fluoro, chloro, bromo phenoxy-phenoxy groups (Scheme 1, complexes **4**–**6**), which shows good solubility in common organic solvents such as dimethylsulfoxide, tetrahydrofuran, dimethylformamide, toluene, chloroform and dichloromethane. All complexes (**4**–**6**) did not show aggregation behavior which is worked with. The solvent effects on photophysicochemical properties of Pcs synthesized also discussed in this work.

2. Experimental

2.1. Materials and equipment

Dimethylsulfoxide (DMSO), 1-pentanol, methanol, *n*-hexane, chloroform ($CHCl_3$), methanol (MeOH), tetrahydrofuran (THF), acetone, dichloromethane (DCM), K_2CO_3, ethanol and dimethylformamide (DMF) were purchased from Merck, 1,8-diaza bicyclo[5.4.0]undec-7-ene (DBU), 1,3-diphenylisobenzofuran (DPBF), 4-nitrophthalonitrile, 3-nitrophthalonitrile, 4,5-dichlorophthalonitrile, zinc acetate, zinc phthalocyanine, 4-(4-bromophenoxy)phenol, 4-(4-clourophenoxy)phenol and 4-(4-Flourophenoxy)phenol were purchased from Sigma Aldrich. Column chromatography was performed on silica gel 60 (0.04–0.063 mm).



Scheme 1. Synthetic route of three new phthalonitriles (**1**, **2** and **3**), (i) DMF, K_2CO_3, 24 h; and their zinc phthalocyanines derivatives (**4**, **5** and **6**) (ii) anhydrous $Zn(Ac)_2$, hexanol 15 h, DBU, argon atm.

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