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Peripherally tetra-benzimidazole units-substituted zinc(II) phthalocyanines: Synthesis, characterization and investigation of photophysical and photochemical properties

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ABSTRACT

The context of this study is based on the synthesis of 4-(4-(1H-benzo[d]imidazole-2yl)phenoxy group substituted phthalocyanine (**4**) and 4-(4-(1-allyl-1H-benzo[d]imidazole-2yl)phenoxy group substituted phthalocyanine (**5**). These phthalocyanine derivatives (**4, 5**) are reported for the first time with four functional groups containing benzimidazole derivatives that are linked through oxygen bridges to the macrocyclic core. All novel compounds synthesized in this study were fully characterized by general spectroscopic techniques such as FT-IR, UV–vis, ^{1}H NMR, ^{13}C NMR, elemental analysis and mass spectroscopy. The compound 4-(4-(1-allyl-1H-benzo[d]imidazole-2yl)phenoxy)phthalonitrile (**3**) was obtained as single crystal and exact structure of these compounds have also been determined using X-ray diffraction technique at 296 K. Weak intra and intermolecular C—H···N interactions and a C—H···π interaction link molecules into a three-dimensional network. Then, spectral, photophysical (fluorescence quantum yields) and photochemical (singlet oxygen generation and photodegradation under light irradiation) properties of the new complexes were investigated in DMSO solutions. These new phthalocyanines (**4** and **5**) showed good singlet-oxygen generation ($\Phi_\Delta = 0.65$ for **4** and $\Phi_\Delta = 0.68$ for **5**) in DMSO.

1. Introduction

The synthesis of phthalocyanine macrocycle has great attention in recent years. A comprehensive review of this class of compounds continues with increasing interest because of their exclusive properties [1].

Phthalocyanines (Pc) have been used as dyes and pigments for many years and have been recently studied extensively as applicable materials in catalysis [2], non-linear optics [3], chemical sensors [4], nanotechnology [5] and photodynamic cancer therapy (PDT) [6] due to their chemical, photochemical, thermal stability, coordination properties and improved spectroscopic characteristics.

These applications require smart modification of the phthalocyanine macrocycle to obtain molecules with the targeted properties. For example, in order to obtain photosensitizers in photodynamic therapy (PDT) of cancer, molecules containing diamagnetic ions such as Zn(II) are important because of their ability to generate high singlet oxygen ($^{1}O_2$) which is toxic for tumor cells [7]. Furthermore, the PDT properties of the phthalocyanines are strongly influenced by the substituents introduced on the periphery of the Pcs.

Benzimidazole derivatives are a very important class as nitrogen containing aromatic heterocyclic compounds. They have interesting photophysical properties and a wide range of applications in medicinal chemistry [8–10]. They have attracted particular interest because of their anticancer activities [11,12]. The benzimidazole derivatives are a key species for organic fluorescent chromophores. Fluorescence characteristic of these compounds can be changed with substitution of different groups from NH position of benzimidazole skeleton [13]. Benzimidazoles have also been commonly used in molecular recognition of all cations, anions, and neutral molecules [14].

In combination with the functional groups is a challenging topic at the center of molecular engineering. In view of the photosensitizer importance of both benzimidazoles and phthalocyanines, the construction of multicomponent systems including these functional structures might be considered as complementary systems with excellent molecular architecture resulting in potential photosensitizer.

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Thus, we report the zinc-Pcs carrying benzimidazole groups through oxygen bridges as new functionalized materials. We describe the synthesis, characterization and spectroscopic behavior of the synthesized starting phthalonitrile compounds and their Pc derivatives. The photophysical and photochemical studies on new benzimidazole group substituted phthalonitriles and their Pc complexes are presented, comparatively, as well.

2. Experimental

2.1. Chemicals and instruments

The following chemicals were obtained from Sigma-Aldrich; o-phenylenediamine, 4-hydroxybenzaldehyde, allyl bromide, acetonitrile, hexane, ethylacetate, dimethylformamide (DMF), chloroform ($CHCl_3$), n-pentanol, methanol (MeOH), ethanol (EtOH), diethylether, 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), $CoCl_2{\cdot}6H_2O$, K_2CO_3, anhydrous $ZnCl_2$. All other reagents and solvents were reagent grade quality and obtained from commercial suppliers. All solvents were stored over molecular sieves (4 Å) after they dried and purified as described by Perrin and Armarego [15]. Oxygen free inert atmosphere was supplied by argon through dual-bank vacuum-gas manifold system. Thin-Layer chromatography (TLC) was performed using silica gel 60-HF254 as an adsorbent. Column chromatography was performed with silica gel (Merck grade 60) and the size exclusion chromatography with Biobeads gel (SX-1). Melting points (m.p.) were determined using a Barnstad-Electrotermel 9200 apparatus and are uncorrected. Electronic spectra were recorded on a Shimadzu UV-2600 Pc-spectrophotometer with quartz cell of 1 cm. Infrared spectra were recorded on a Perkin Elmer Spectrum two FT-IR spectrophotometer equipped with Perkin Elmer UATR-TWO diamond ATR and corrected by applying the atr-correction function of Perkin Elmer Spectrum software. ^1H and ^{13}C NMR spectra were recorded a Varian Mercury Plus 300 MHz spectrometer. For Maldi-TOF spectra, the experiments were carried out using a Bruker microTOF (Germany) in Gebze Institute of Technology. The elemental compositions of the samples were analyzed by an element analyzer (Flash 2000, Thermo Scientific). Absorption spectra in the UV–visible region were obtained with a Shimadzu 2001 UV spectrophotometer. Fluorescence spectra were measured using a Varian Eclipse spectrofluorometer using 1 cm path length cuvettes at room temperature. Photo-irradiations were done using a General Electric quartz line lamp (300 W). A 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet, visible, and infrared radiations respectively. An interference filter (Intor, 700 nm with a bandwidth of 40 nm) was additionally placed in the light path before the sample. Light intensities were measured with a POWER MAX 5100 (Mol electron detector incorporated) power meter.

2.2. Synthesis

2.2.1. 4-(4-(1H-benzo[d]imidazole-2yl)phenoxy)phthalonitrile (2) and 4-(4-(1- allyl-1H-benzo[d]imidazole-2yl)phenoxy)phthalonitrile (3)

The preparation of **1** was carried out by reaction of o-phenylenediamine and 4-hydroxybenzaldehyde according to the published literature [16]. The preparation of **3** has been performed in two steps. 4-nitrophthalonitrile was reacted at first with **1** to give the 4-(4-(1H-benzo[d]imidazole-2yl)phenoxy)phthalonitrile (**2**) within 96% yield. In the second step, 4-(4-(1-allyl-1H-benzo[d]imidazole-2yl)phenoxy) phthalonitrile (**3**) was obtained by the reaction of **2** and allyl bromide by applying the our literature procedure resulting in 95% yield [17]. The obtained spectroscopic data are accordance with the literatures.

2.2.2. Tetrakis [4-(4-(1H-benzo[d]imidazole-2yl)phenoxy)phthalocyaninato zinc(II) (4)

4-(4-(1H-benzo[d]imidazole-2yl)phenoxy)phthalonitrile (**2**) (0.1 g, 0.297 mmol), anhydrous $ZnCl_2$ (0.01 g, 0.074 mmol) and n-pentanol (2 mL) were placed in a standard Schlenk tube in the presence of DBU (0.01 mL, 0.06 mmol). The reaction mixture was purged by argon at room temperature and held at reflux temperature for 12 h. After cooling to the room temperature, the reaction mixture was precipitated by adding water/methanol (1/1). The precipitate was collected by centrifugation, washed several times with ethanol and water to dissolve any unwanted organic impurity and any unreacted metal salt and dried. Further purification of the phthalocyanine was performed by size exclusion chromatography on Biobeads gel (SX-1). The crude product was put onto the column and eluted with $CHCl_3$, and the collected phases were concentrated on a rotary evaporator and re-precipitated with methanol. The desired pure ZnPc (**4**) was obtained as a green solid. Yield: 82% (0,85 g). m.p. > 250 °C. FT-IR (UATR-TWO™) ν max/cm^{-1}: 3398 (NH), 3194-2543 (C–H (Ar) and intermolecular H bonding), 1644 (C=N), 1604 (C=C), 1471-1394 (C-C), 1231 (Asym., Ar-O-Ar), 1169 (C-N), 1089 (Sym., Ar-O-Ar), 743. ^1H NMR (DMSO) δ (ppm): 13.00 (s, br, 1H), 8.91 (d, 2H), 8.52 (d, 1H), 8.47-8.14 (m, 1H), 8.37–8.30 (m, 1H), 7.86–7.77 (m, 1H), 7.65 (d, 1H), 7.60–7.54 (m, 2H), 7.02 (d, 2H). UV–vis (DMSO-1 × 10^{-5} M): λmax (nm) (log ε) 680 (4,96), 612 (4,27), 348 (4,62), 310 (4,82) MS (MALDI-TOF): *m/z* 1410.799 $[M]^+$. Anal. Calc. for $C_{84}H_{48}N_{16}O_4Zn$ (%): C, 71.51; H, 3.43; N, 15.89; O, 4.54; Zn, 4.63; Found (%): C, 71.13; H, 3.52; N, 15.63.

2.2.3. Tetrakis [4-(4-(1-allyl-1H-benzo[d]imidazole-2yl)phenoxy)phthalocyaninato zinc(II) (5)

In a standard schlenk tube, a mixture of 4-(4-(1-allyl-1H-benzo[d] imidazole-2yl)phenoxy)phthalonitrile (**3**) (0.1 g, 0.266 mmol), anhydrous $ZnCl_2$ (0.009 g, 0.067 mmoL), and DBU (0.01 mL, 0.05 mmol) were mixed in n-pentanol (2 mL). The reaction mixture was purged by argon at room temperature and held at reflux temperature for 12 h. After cooling to the room temperature, the reaction mixture was precipitated by adding water/methanol (1/1). The precipitate was collected by centrifugation, washed several times with ethanol and water to dissolve any unwanted organic impurity and any unreacted metal salt and dried. Further purification of the phthalocyanine was performed by size exclusion chromatography on Biobeads gel (SX-1). The crude product was put onto the column and eluted with $CHCl_3$, and the collected phases were concentrated on a rotary evaporator and re-precipitated with methanol. The desired pure ZnPc (**5**) was obtained as a green solid. Yield: 84% (0,87 g). m.p. > 250 °C. FT-IR (UATR-TWO™) ν max/cm^{-1}: 3062 (Ar., C-H), 2986-2862 (Aliph., C-H), 1655 (C=N), 1603–1528 (C=C), 1471–1391 (C-C), 1231 (Asym., Ar-O-Ar), 1168 (C-N), 1089 (Sym., Ar-O-Ar), 744. ^1H NMR (DMSO) δ (ppm): 8.81 (d, 2H), 8.42 (s, 1H), 8.08–8.01 (m, 1H), 7.97–7.90 (m, 1H), 7.84 (d, 1H), 7.77–7.63 (m, 2H), 7.49 (d, 1H), 7.25 (s, 2H), 6.15–5.99 (m, 1H), 5.19 (d, 1H), 4.99 (s, 1H), 4.91 (s, 2H). UV–vis (DMSO-1 × 10^{-5} M): λmax (nm) (log ε) 678 (5,24), 612 (4,53), 352 (4,84), 292 (4,94). MS (MALDI-TOF): *m/z* 1572.631 $[M+1]^+$. Anal. Calc. for $C_{96}H_{64}N_{16}O_4Zn$ (%): C, 73.39; H, 4.11; N, 14.27; O, 4.07; Zn, 4.16; Found (%): C, 73.08; H, 4.22; N, 14.08.

2.3. X-ray crystal structure determination

Intensity data were recorded on a STOE IPDS II diffractometer. We also used ORTEP III [18] and WinGX software [19] programs to construct figures and to prepare manuscript for publishing. This program used for solving for the molecular structure were the direct methods procedure in SHELXS-97 and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F2 using SHELXL-97 [20]. The systematic absences and intensity symmetries indicated the triclinic *P*-1 space group. The general-purpose crystallographic tool PLATON [21] was used for the structure analysis. A summary of the key crystallographic information is given in Table 1.

Crystallographic data were deposited in CSD under CCDC registration number 1549235. These data can be obtained free of charge from