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# The syntheses and photophysical properties of 4,4′-isopropylidendioxydiphenyl substituted ball-type dinuclear Mg(II) and Zn(II) phthalocyanines

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ABSTRACT

The syntheses of ball-type dinuclear Zn(II) and Mg(II) phthalocyanines containing four 4,4′-isopropylidendioxydiphenyl substituents at the peripheral and non-peripheral positions are presented. The structures of the synthesized compounds were characterized using elemental analyses, and UV–Vis, FT-IR, $^1$H NMR and mass spectroscopies. The $\Phi_F$ values were 0.14, 0.11, 0.22, 0.15 and $\Phi_T$ values were 0.84, 0.88, 0.62, 0.74, for **6**–**9**, respectively. The largest triplet yields were observed for the non-peripherally substituted complexes **6** and **7**, showing that non-peripheral substitution favors increased population of the triplet state. All complexes showed reasonably long triplet lifetimes with $\tau_T$ 510, 310, 910 and 350 μs in DMSO, respectively.

## 1. Introduction

Metallophthalocyanines (MPcs) have been studied as materials for many applications including in electronics [1], non-linear optics [2], liquid crystals [3], gas sensors [4], photosensitizers [5,6], electrocatalysis [7], semiconductors [8] and photovoltaic cells [9]. There is considerable interest in MPc complexes containing non-transition metals for use as photosensitizers in the relatively new method of cancer treatment called photodynamic therapy (PDT) [5,6,10–14]. The mode of operation in PDT is based on visible light excitation of a tumor-localized photosensitizer. After excitation, energy is transferred from the photosensitizer (in its triplet excited state) to ground state oxygen ($^3O_2$), forming excited singlet state oxygen ($^1O_2$). High triplet state quantum yields and long triplet lifetimes are required for efficient photosensitization. Syntheses, electrochemical and spectroelectrochemical behavior of ball-type Pc derivatives have been extensively studied since the complexes were published in the literature for the first time in 2002 [15,16]. Ball-type phthalocyanine derivatives show spectroscopic and electrochemical properties which differ significantly from the parent monomer [17–19]. However, the studies on non-peripherally substituted ball-type MPc derivatives are still limited and the photophysical behavior of ball-type molecules in general have also not received much attention. Our interest in ball-type complexes is due to the possibilities of intramolecular interactions between the Pc rings and/or metal centers of these compounds. The electronic properties of ball-type Pcs can change dramatically depending on the bridging compounds or the central metal. The distance between the two Pc units affect the degree of interactions between the rings. In this paper, we describe the syntheses and photophysical properties of new symmetrically substituted ball-type MgPc and ZnPc complexes containing substituents at the non-peripheral (α) and peripheral (β) positions, Scheme 1.

## 2. Experimental

### 2.1. Materials

Anhydrous magnesium(II) chloride and zinc(II) acetate were purchased from Sigma-Aldrich. All solvents for example dimethylsulfoxide (DMSO) and chloroform were from Saarchem. Silica gel for column chromatography was purchased from MERCK. All other reagents were obtained from suppliers and used as received.

### 2.2. Equipment

UV–Vis absorption spectra were obtained using the Varian Cary 500 UV–Vis/NIR spectrometer. Fluorescence excitation and emission spectra were recorded with Varian Eclipse spectrophotometer. FT-IR data were recorded using the Perkin-Elmer spectrum 2000 FTIR spectrometer. $^1$H NMR spectra were obtained using a Bruker EMX 400 MHz spectrometer. Elemental analyses were done on a Vario-Elementar Microcube EL III. Mass spectral data were collected with a Bruker AutoFLEX III Smartbeam MALDITOF/TOF Mass spectrometer. The instrument was operated in positive ion mode

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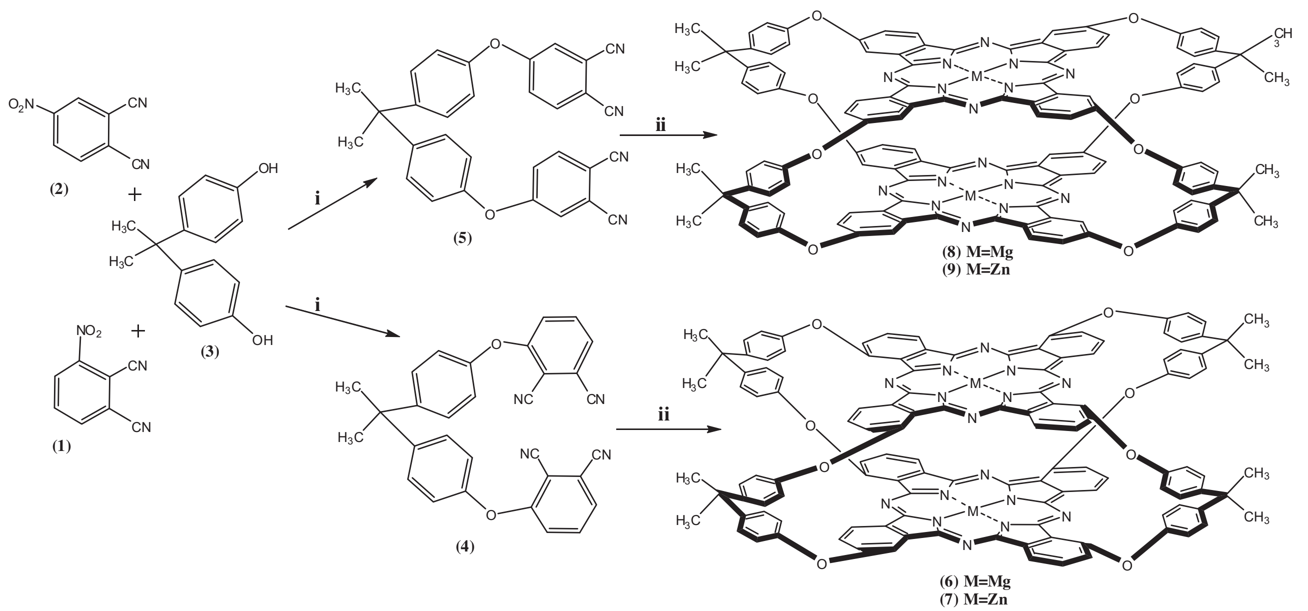

**Scheme 1.** Non-peripherally and peripherally substituted ball-type metallophthalocyanines. i: DMSO, rt, 5 days. ii: $MgCl_2$, 450 °C, 15 min for **6**,**8** and $Zn(CH_3COO)_2$, 300 °C, 12 min for **7**,**9**.

using an $m/z$ range of 400–3000. The voltage of the ion sources were set at 19 and 16.7 kV for ion sources 1 and 2, respectively, while the lens was set at 8.50 kV. The reflector 1 and 2 voltages were set at 21 and 9.7 kV, respectively. The spectra were acquired using dithranol as the MALDI matrix and a 354 nm nitrogen laser. Triplet absorption and decay kinetics were recorded on a laser flash photolysis system, the excitation pulses were produced by a Quanta-Ray Nd: YAG laser providing 400 mJ, 9 ns pulses of laser light at 10 Hz, pumping a Lambda-Physic FL 3002, dye (Pyridin 1 in methanol). The analyzing beam source was from a Thermo Oriel xenon arc lamp, and a photomultiplier tube was used as a detector. Signals were recorded with a two-channel 300 MHz digital real-time oscilloscope (Tektronix TDS 3032C); kinetic curves were averaged over 256 laser pulses. The triplet lifetimes were determined by exponential fitting of the kinetic curves using the OriginPro 7.1.

### 2.3. Syntheses

3-Nitrophthalonitrile **1** and 4-nitrophthalonitrile **2** were synthesized according to literature [20]. 4,4′-Isopropylidendioxydiphenyl **3** was obtained from commercial suppliers. The syntheses of compounds **5** and **9** has been reported in literature [21]. All solvents were dried and purified as described by Perrin and Armarego [22]. Commercial $CHCl_3$ was dried with $P_2O_5$ then distilled. The distilled $CHCl_3$ was stored on activated molecular sieves. Purification of commercial DMSO was achieved by drying overnight with chromatographic grade alumina. It are then refluxed for 4 h over CaO, dried over $CaH_2$, and then fractionally distilled at low pressure. It was then stored over molecular sieves. Both solvents purified freshly before use. Target precursor **4** was prepared by a nucleophilic aromatic substitution reaction between compound **1** and 4,4′-isopropylidendioxydiphenyl **3** in DMSO, Scheme 1.

#### 2.3.1. *3,3′-[4,4′-(Propane-2,2-diyl) bis(4,1-phenylene)]bis(oxy) diphthalonitrile (**4**)*

Compound **3** (2.0 g, 8.67 mmol) was dissolved in dry DMSO (15 mL) and compound **1** (3 g, 17.34 mmol) was added under inert atmosphere. To this reaction mixture finely ground anhydrous potassium carbonate (2.4 g, 17.3 mmol) was added. After 4 h of stirring at room temperature, further potassium carbonate (0.58 g, 4.3 mmol) was added and this same amount was added again after 24 h of stirring. After a total of 5 days of stirring, the reaction mixture was poured into water (200 mL) resulting in the formation of a white precipitate. The crude product was centrifuged and was further purified by chromatography over a silica gel column using a $CHCl_3$ as eluent. This process was repeated once. Finally, the pure product was dried using $P_2O_5$ for one week. Yield: 2.9 g. IR(KBr) ($\mu_{max}$/cm$^{-1}$): 3078 (Ar–CH), 2228 (C≡N), 1573 (C═C), 1256 (C–O–C). $^1$H NMR (DMSO-$d_6$): $\delta$, ppm 7.83 (2H, d, $J$ = 7.6 Hz, Ar–H), 7.37 (2H, d, $J$ = 8.8 Hz, Ar–H), 7.29 (6H, d, $J$ = 7.2 Hz, Ar–H), 7.18 (4H, d, $J$ = 8.4 Hz, Ar–H), 1.69 (6H, s, –$CH_3$). *Anal.* Calc. for $C_{31}H_{20}N_4O_2$: C, 77.49; H, 4.20; N, 11.66%. Found: C, 77.37; H, 3.68; N, 12.03%.

General procedure for **6**–**8**: A mixture of complex **4** or **5** (0.10 g, 0.21 mmol) and magnesium(II) chloride (0.3 g, 0.31 mmol) for **6** and **8** or zinc(II) acetate (0.104 g, 0.313 mmol) for **7** (using **4**) was ground in a quartz crucible and heated in sealed glass tube for 15 min under argon atmosphere at 450 °C for MgPcs **6** and **8** and for 12 min under argon atmosphere at 300 °C for ZnPc **7**, respectively. After cooling to room temperature, the green reaction products were washed with hot methanol and hot water. The products were separated by column chromatography on silica gel using chloroform and a gradient of chloroform-methanol up to 50%. And then, the products were washed with methanol, ethanol, acetonitrile and acetone for 24 h, consecutively in the Soxhlet apparatus. Finally, the green products were obtained by column chromatography on silica gel using chloroform as eluting solvent. All of the compounds are soluble in common solvents such as $CHCl_3$, dichloromethane, dimethylformamide, and DMSO, and had Mp >350 °C.

#### 2.3.2. *1′,11′,15′,25′-[Tetrakis(4,4′-isopropylidenedioxydiphenyl)]bis-phthalocyaninato dimagnesium(II) (**6**)*

Dark green color. Yield: 0.010 g (10%). UV–Vis ($CHCl_3$) $\lambda_{max}$/nm (log $\varepsilon$/dm$^{-3}$ mol$^{-1}$ cm$^{-1}$): 742 (3.72), 700 (4.70), 671 (4.01), 632 (3.97), 320 (4.52). IR[(KBr) $\mu_{max}$/cm$^{-1}$]: 3085 (Ar–CH), 1577 (C═C), 1256 (C–O–C). $^1$H NMR (DMSO-$d_6$): $\delta$, ppm 7.85–7.02 (56H, m, Ar–H), 1.72 (24H, m. –$CH_3$). *Anal.* Calc. For $C_{124}H_{80}N_{16}O_8Mg_2$: C,