The synthesis, photophysical and dielectric properties of ball-type dinuclear zinc phthalocyanine

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Dedicated to Professor Tebello Nyokong on the occasion of her 60\textsuperscript{th} birthday

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ABSTRACT: The synthesis of ball-type dinuclear Zn(II) phthalocyanine containing four 4,4′-(9H-fluorene-9,9-diyl)diphenol substituents at the non-peripheral position is presented. The structure of the synthesized compound was characterized using elemental analyzes, and UV-vis, FT-IR, \textsuperscript{1}H NMR and mass spectroscopies. The $\Phi_T$ value was 0.16 and $\Phi_R$ value was 0.72. The complex showed reasonably long triplet lifetimes with $\tau_\text{T}$ 7210 $\mu$s in DMSO. The frequency and temperature dependence of the dielectric properties of ZnPc were also investigated in the frequency range of 40–10$^5$ Hz and in the temperature range of 300–440 °K. It has been observed that both dielectric constant $\varepsilon'$ and dielectric loss $\varepsilon''$ decrease with the rise in frequency as they increase with the rise in temperature. The decrease in $\varepsilon'$ with increasing frequency is attributed to the fact that as the frequency increases, the polarizability contribution from orientation sources decreases and finally disappears.

KEYWORDS: Zn ball-type phthalocyanine, photodynamic therapy, non-peripheral phthalocyanine, triplet quantum yield, dielectric properties.

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 ($^1O_2$), forming excited singlet state oxygen ($^1O_2$. High triplet state quantum yields and long triplet lifetimes are required for efficient photosensitization. Synthesis, 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 [17–24]. 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

\textsuperscript{0}SPP full member in good standing

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two Pc units affects the degree of interactions between the rings.

The electrical conductivity and relaxation process in phthalocyanine compounds play an important role and these are often the deciding factors about the suitability of the material for particular device applications. Therefore, the extraction of true intrinsic nature of electrical conduction and dielectric mechanism is essential for a material.

In this paper, we describe the synthesis and photophysical properties of new symmetrically substituted ball-type ZnPc complex containing substituents at the non-peripheral position ($\alpha$). The dielectric behavior of the compound was also investigated as a function of frequency and temperature in the ITO/ZnPc/Au structure. This is the first time that the dielectric behavior of a ball type phthalocyanine is presented in the ITO/ZnPc/Au configuration.

**EXPERIMENTAL**

**Materials**

Anhydrous zinc(II) acetate was 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.

**Equipments**

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 using a m/z range of 400–3000. The voltages 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, using 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 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 program OriginPro 7.1.

**Synthesis**

3-Nitrophthalonitrile 1 was synthesized according to literature [25]. 4,4'-(9H-fluorene-9,9-diyl)di phenol 2 was obtained from commercial suppliers. The synthesis of compounds 3 has been reported in literature [22]. All solvents were dried and purified as described by Perrin and Armarego [26]. Complex 4 was prepared using solid phase in presence a metal salt (zinc(II) acetate) and the phthalonitrile derivative 3 (Scheme 1).
Quantum yields of internal conversion (ΦIC) were obtained from Equation 4, which assumes that only three processes (fluorescence, intersystem crossing and internal conversion), jointly deactivate the excited singlet state of complex 4.

\[
\Phi_{IC} = 1 - (\Phi_F + \Phi_T) 
\]

### Dielectric measurements

In order to prepare thin film of the ZnPc organic compound, firstly indium tin oxide (ITO) coated glass substrate was washed successively with ethanol/acetonitrile mixture and de-ionized water, and then dried in a vacuum. The compound was dissolved in DMF at concentrations of \(5 \times 10^{-3}\) M. Twenty microlitres of this solution was added with a glass pipette onto the ITO substrate held onto spinner (Speciality Coatings Systems Inc., Model P6700 Series). The substrate was spun at 2000 rpm for 80 s and then the film was dried at 100 °C for 2 h to evaporate the solvent. The substrate temperature was kept constant at 300 °K during deposition of the Pc compounds. After spinning process, circular dots of 1 mm in diameter and 1500 Å thick Au contacts were deposited onto the Pc surface of the ITO substrate through a metal shadow mask in high vacuum system in the pressure of \(1.5 \times 10^{-5}\) mbar.

The device was connected to Keithley 3330 LCZ meter for impedance measurement equipped with a suitable coaxial cable. Impedance measurements were performed between 300 °K and 450 °K and in the frequency range, \(40-10^5\) Hz. All measurements were performed under vacuum (\(\leq 10^5\) mbar) and in the dark. Impedance data were recorded using an IEEE-488 data acquisition system incorporated into a personnel computer.

### RESULTS AND DISCUSSION

#### Synthesis and characterization

The ball-type binuclear Zn(II)Pc complex 4 was prepared as a mixture of isomers by the reaction of compound 3 with Zn(CH\(_3\)O)\(_2\)). Complex 4 was prepared using solid phase method in the presence of Zn(CH\(_3\)O)\(_2\) at 320 °C from the phthalonitrile derivative 3. Column chromatography on silica gel using CHCl\(_3\) as mobile phase was used twice to purify the complex. The structure and purity of the ZnPc derivative was confirmed by UV-vis, \(^1\)H NMR, IR and mass spectral data and elemental analyses.

A diagnostic feature of the formation of 4 from the phthalodinitrile derivatives 3, is the disappearance of the sharp CN vibration of the latter at 2228 cm\(^{-1}\). The \(^1\)H NMR spectra of 4, recorded in DMSO, shows the aromatic protons between 8.02–6.99 ppm, integrating for a total of 88 for protons. Elemental analysis results are also consistent with the theoretical values of proposed structures of 4. The purified phthalocyanines were further characterized by mass spectra. The expected mass values
corresponded with the found values for complex using dithranol as the matrix. The results were repeated twice to give the observed molecular peaks. Protonated molecular ion peak ZnPc is found at 2542.51 amu.

The UV-vis spectrum of 4 in CHCl₃ shown in Fig. 1. The phthalocyanines show typical electronic spectra with two absorption regions, one in the UV region at about 300–400 nm (B-band) and the other in the visible region at 600–700 nm (Q-band). The characteristic Q-band transition of metallophthalocyanines with D₄h symmetry is observed as a single band of high intensity in the visible region. Complex 4 show Q-band absorption at 696 nm both in CHCl₃ and DMSO and B-bands absorptions at 309 and 322 nm in CHCl₃. The Q-band for 4 is red shifted as is typical of non-peripheral substitution. It is well-known that α substitution result in red shifting of the spectra in MPcs this is due to the electron density enhancement caused by the substitution at α position [20, 22]. However, complex 4 in CHCl₃ has an extra band near 742 nm, which could be associated with loss of symmetry often observed in chlorinated solvents. This band was not observed in DMSO. The observation of the extra band in chloroform is due to protonation since this solvent may contain small amounts of acid as observed before [24].

Aggregation behavior of Pc is depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes and it is dependent on concentration, nature of solvent and substituents, metal ions and temperature [32]. Aggregation in MPcs is typified by broadened or split Q-band, with the high energy band being due to the aggregate and the low energy band due to the monomer. A well defined band between 610 nm and 675 nm in ball-type phthalocyanines is due to exciton coupling between the two Pc rings [17–24]. The spectra of complexes 4 in DMSO shows bands in this region, which may be attributed to intermolecular interactions between the rings in agreement with literature.

Fluorescence spectra and quantum yields

The absorption, fluorescence excitation and emission spectra of complex 4 in DMSO are shown in Fig. 2. The absorption and excitation spectra show the same Q-band maxima. The proximity of the wavelength of each component of the Q-band absorption to the Q-band maxima of the excitation spectra for the complex suggests that the nuclear configurations of the ground and excited states are similar and not affected by excitation. The emission spectra are mirror images of the excitation spectra. Stoke’s shifts were 9 nm, typical of ZnPc complexes [21, 23, 24].

The fluorescence quantum yield (Φₓ) values are typical of MPc complexes for the ZnPc derivative. The Φₓ values was 0.16 in DMSO for 4. Face-to-face interaction of the two monomers in dimers is expected to decrease the energy gap between the singlet state and the triplet state and enhance the formation of triplet state (i.e. intersystem crossing increases) decreasing fluorescence [21, 23, 24]. However, in this work the Φₓ values are similar to those of monomeric phthalocyanines, showing the interaction between the two rings in minimal.

Triplet quantum yields and lifetimes

Figure 3 shows a representative triplet decay curve for the complex. Triplet quantum yields represent the
fraction of absorbing molecules that undergo intersystem crossing to the metastable triplet excited state. The triplet quantum yields ($\Phi_T$) value for 4 is 0.72. High $\Phi_T$ values and correspondingly low $\Phi_F$ values are observed for ZnPc derivative, due to a more efficient intersystem crossing (ISC), for the complex. Complex 4 have low $\Phi_F$ values (= 0.11). The complex showed reasonably long triplet lifetime of $t_T = 7210 \mu$s.

Dielectric behaviors

Dielectric properties represent the response of the material to the disturbance caused by the externally applied electric field. The components of the complex dielectric function, $\varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega)$, were calculated from the measured impedance spectra using the expression [33],

$$
\varepsilon^* = \frac{Y^*}{j\omega C_0} = \varepsilon' - j\varepsilon'' = \frac{C - jG}{\omega C_0},
$$

where $Y^*$ is the measured admittance, $C_0$ is the capacitance of the empty measuring cell, $C$ and $G$ are the measured capacitance and conductance of the Pc and $\omega$ is the angular frequency of the applied signal. The real part, $\varepsilon'(\omega)$, of the complex dielectric function is usually called the dielectric constant and the complex part, $\varepsilon''(\omega)$, the dielectric loss or dielectric loss factor.

The total polarizability of a material medium is mainly due to the contribution of deformational polarization (electronic and ionic) and relaxation polarization (orientational and interfacial). The various polarizabilities may be segregated from each other because each contribution has its own characteristic features which distinguishes it from the others. At low frequencies, all four sources of polarization are important, whereas at optical frequencies, i.e. above optical phonon frequencies, only the electronic polarization comes into play. Dispersion curves of the real part of the dielectric function for ITO/ZnPc/Au structure at selected temperatures is shown in Fig. 4. As could be noticed from Fig. 4, at low frequencies, $\varepsilon'$ is strongly frequency dependent, while at higher frequencies a weak dependence is observed. A rapid decrease in $\varepsilon'$ is clear in the low frequencies for all temperatures. It is also clear that the values of $\varepsilon'$ approach a constant value with further increase in frequency. The high values of $\varepsilon'$ at lower frequencies can be attributed to the presence of different types of polarizations (viz. electronic, dipolar, orientational, ionic, etc.) [34, 35]. A reasonable explanation for the observed decrease in $\varepsilon'$ with frequency can be given as follows: When the frequency of the applied signal is increased, the dipoles will no longer be able to rotate sufficiently rapidly. So, their oscillations begin to lag behind those of the field. As the frequency is further increased, the dipole will be completely unable to follow the field and the polarizability contribution from orientation sources decreases and finally disappears because of the frequency and temperature dependence of orientation polarization, so $\varepsilon'$ decreases at a higher frequency approaching a constant value due to the interfacial polarization [36].

Figure 5 shows the variation of $\varepsilon'$ with temperature at some fixed frequencies. As can be seen from Fig. 5 $\varepsilon'$ increases with the increase in temperature and it exhibits strong temperature dependence at higher temperature and lower frequencies. This type of temperature dependence of $\varepsilon'$ reveals that ZnPc behaves like polar dielectric in which the orientation of dipoles is frozen at low temperatures and facilitated with rising temperature and thereby the dielectric constant is increased.

The dielectric loss, $\varepsilon''(\omega)$, was also determined as function of frequency and temperature. Figure 6 shows the dependence of the imaginary part of dielectric function, $\varepsilon''$, on the frequency. It is clear from the
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The electrical response of disordered solids are characterized in the frequency domain by permittivity loss as:

\[ \varepsilon'' = A \omega^n \]  

where A is a temperature dependent constant. The values of the power n were obtained from the slope of the ln (\(\varepsilon''\)) vs. ln (\(\omega\)) plots. The variation of the exponent n with temperature is shown in the inset of Fig. 6. The values of n decrease linearly with temperature. This behavior is known as the non-Debye type behavior [37].

CONCLUSION

The synthesis, photophysical and dielectric properties of the ball-type Zn(II)Pc complex 4 is presented. ZnPc derivatives 4 show long \(\tau_T\) of 7210 \(\mu\)s and a large triplet state quantum yield of \(\Phi_T = 0.72\). High triplet state quantum yields and long triplet life are required for efficient photosensitization. From the dielectric measurements it was found that the dielectric constant, \(\varepsilon'\), and dielectric loss, \(\varepsilon''\), decrease with the increase in frequency and increase with the increase in temperature. The observed temperature dependence of \(\varepsilon'\) revealed that the thin film ZnPc sample exists in the form of molecular dipoles.

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M. Canlıca et al.


