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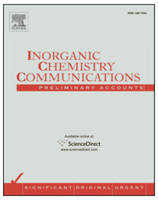

Short communication

Thin films of fluorinated groups substituted metallophthalocyanines as an optical material

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ABSTRACT

In this study, we report the synthesis and characterization of palladium(II)phthalociyanine including fluoro-4′-hexylthio-benzyloxy groups for the first time. The optical properties of a series of pentafluorobenzyloxy and tetrafluoro-4′-hexylthio-benzyloxy metallo-phthalocyanines were studied. Thin films of these compounds were obtained by using spin coating technique. Optical transmittance of thin films was measured using a spectrophotometer in the wavelength range of 200–1000 nm. Optical band gaps of thin films were also calculated. In addition, surface morphologies and thickness of the films were investigated by Scanning Electron Microscopy. Results showed that the transmittance, band gap and morphology of the films are highly dependent on the metals and substituted groups of the phthalocyanines.

The phthalocyanines (Pcs) were found in the early 20th century and their construction was clarified between 1933 and 1940. Pcs obtained in excellent blue and green colours are used in different areas such as printing and paint sector, oxidation of hydrocarbons, fuel cells, semiconductor material, liquid crystal technology, and photodynamic cancer treatment. Researchers continue to investigate the physical and chemical properties of Pcs and their derivatives on their potential applications in different fields [1]. Unsubstituted Pcs with high molecular absorption coefficient in the visible region of ultraviolet have excellent properties such as resistance to heat, chemical and oxidation. However, the lack of solubility in many organic solvents due to intramolecular interactions between macrocycles greatly limits their usage [2]. Pcs have the ability to bind a large number of metal and ametal ions into cavity of the ring. It is also possible to link a wide range of substituent mixtures that change the electronic structure of the Pc to the macrocyclic structure. If these groups are in the hydrophobic or bulky chain structure, the solubility of the phthalocyanines in the organic solvents is increased [3,4]. Presently research studies focus on fluorinated Pcs. The presence of fluorinated groups on the periphery of the Pc ring improves their solubility in organic solvents and brings further functionality [5].

Thin films are widely used in optical coatings, magnetic recording systems, detection systems and semiconductor devices in recent years. The differences in the coating methods and the various treatments during the coating can result in many features not found in the voluminous material, such as in thin films of these materials [6]. One of the most widely used methods for thin films of soluble Pcs is the spin coating process [7–9]. The thickness of the thin films obtained by this method is the same all over the surface and a pure coating is obtained. The ability to prepare thin films with a pure and homogeneous structure at low temperatures saves energy. With spin coating method, it is possible to coat all kinds of materials with appropriate geometric shapes. The microstructure of the coated thin film in is easily controllable [10–12]. It is possible to make a multi-layer coating with spin coating technique and the method is not limited to the geometry of the coated structure.

We have previously reported the synthesis and characterization of a series of zinc(II)Pc containing 2′,3′,4′,5′,6′-pentafluorobenzyloxy (**1**) [13] and zinc(II) (**2**) and cobalt(II) (**3**) Pcs containing 2′,3′,5′,6′-tetrafluoro-4′-hexylthio-benzyloxy [14] groups on the periphery. In this study, we also describe the synthesis and characterization of palladium(II) Pc (**4**) containing 2′,3′,5′,6′-tetrafluoro-4′-hexylthio-benzyloxy groups on the periphery. Thin films of these complexes have been obtained by using spin coating methods. The optical parameters and surface morphology of the thin films have been determined and discussed.

The MPcs (**1**–**3**) included fluorinated groups were prepared according to the reported procedures (Scheme 1) [13,14]. The synthetic route of newly synthesized tetrakis[(2′,3′,5′,6′-tetrafluoro-4′-hexylthio-benzyloxy)phthalocyaninato]palladium(II)(**4**) was given supplementary information. All MPcs (**1**–**4**) were identified through various spectroscopic techniques such as elemental, UV–Vis, FT-IR and MALDI-TOF. The spectral data for the all MPcs (**1**–**4**) were in accordance with the assigned formulations. The solubility of MPcs (**1**–**4**) was remarkably high in $CHCl_3$, CH_2Cl_2, THF, acetone, DMF and DMSO.

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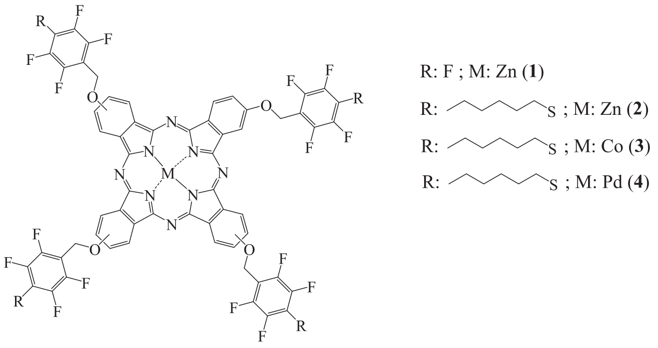

Scheme 1. Structure of MPcs (**1**–**4**).

The electronic absorption spectra are especially important for identifying the structure of all Pcs. Pcs show typical electronic spectra with two strong absorption regions, one of them is in the UV region at about 300–400 nm (B band) and the other one is in the visible part of the spectrum around 600–700 nm (Q band) attributed to the π-π* transitions. The UV–Vis spectra of the synthesized MPcs (**1**–**4**) included fluorinated groups showed characteristic absorption in the Q band region at 678 nm for **1**, 685 nm for **2**, 674 nm for **3** and 666 nm for **4**. When we compare compounds 1 and 2, substitution of the fluorine groups with hexylthio groups in the para position results in red shift in solution. Because, hexylthio groups have electron-donating properties [14,15]. The B band region observed at 351 nm for **1**, 356 nm for **2**, and 326 nm for **3** and 332 nm for **4** (Fig. 1).

The transmittance spectra of the prepared MPc films (Zn(II) (**1**), Zn(II) (**2**), Co(II) (**3**) and Pd(II) (**4**)) are shown in Fig. 2. While Zn(II) (**1**) has a single peak at 698 nm (with a transmittance value of 69%) in the spectrum, Zn(II) (**2**) appears to have two peaks at 630 nm and 687 nm (with a transmittance value of 70%). A blue shift in the Q band peak position of Zn(II) (**2**) compared to Zn(II) (**1**) is observed. Substitution of the electron-withdrawing fluorine with the electron-donating thiol results in an 11 nm blue shift in the Q band at transmittance spectra of thin films. The blue shift state is also valid for Co(II) (**3**) with two peaks at 614 nm and 674 nm (with a transmittance value of 66% and 72%, respectively) and with a single weak peak for Pd(II) (**4**) at 674 nm (with a transmittance value of 82%). The transmittance is over 82% for all films in the 500 nm wavelength region and near infrared region.

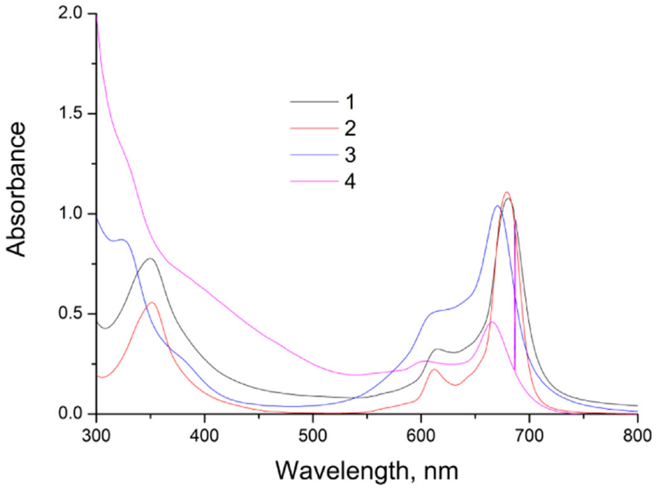

Fig. 1. UV–vis spectra of MPcs (**1**–**4**) in CH_2Cl_2 (01 × 10^{-5} M).

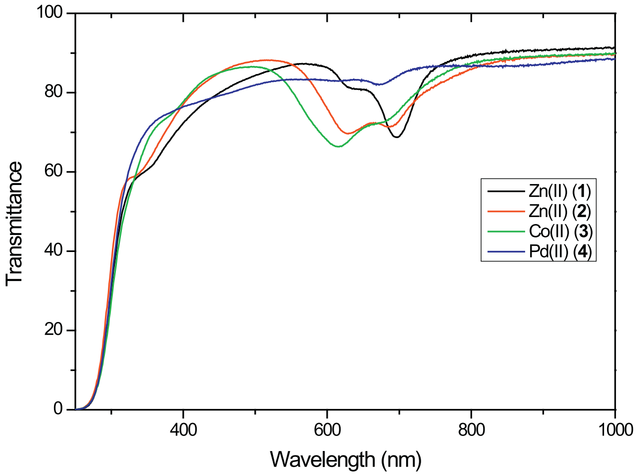

Fig. 2. Transmittance spectra of Zn(II) (**1**), Zn(II) (**2**), Co(II) (**3**) and Pd(II) (**4**) films.

It is seen that different metal ions and different (fluorine or hexylthio) groups both change the value of peak transmittance and its position. This can also be seen from the absorption spectrum taken at the same wavelength range (Fig. 3). When we compare the absorption spectra of thin films for MPc (**1**) and MPcs (**2**–**4**), long chain hexylthio groups have increased the tendency to aggregate in thin films [16]. For this reason, new peaks were observed at around 615–630 nm. However, it has been observed that the metal size increases and the tendency of aggregation decreases. As a result, the peak at 630 nm was disappeared for Pd(II) (**4**). When we compare the optical absorption spectra of the Zn(II) (**1**), Zn(II) (**2**), Co(II) (**3**) and Pd(II) (**4**) in CH_2Cl_2 solution with the corresponding optical absorption of the thin films, we can have observed that Zn(II) (**1**), Zn(II) (**2**), Co(II) (**3**) and Pd(II) (**4**) thin films spectra show a red-shift in the Q absorption region with respect to corresponding CH_2Cl_2 solutions [17].

It is possible to calculate the optical energy band gap of the MPc films according to the following relation (1);

$$\alpha = A\left(h\nu - E_g\right)^m \tag{1}$$

where A is a constant, and m equals to 1/2 for direct allowed transitions. Linear part of the graph of $(\alpha h\nu)^2$ vs. $h\nu$ is extrapolated to photon

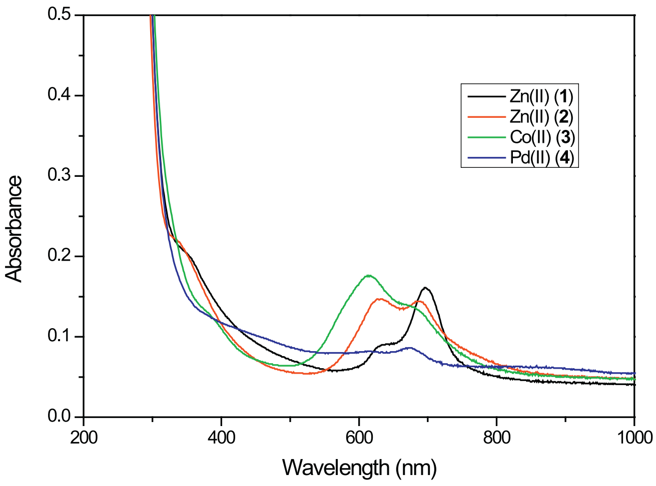

Fig. 3. Absorption spectra of Zn(II) (**1**), Zn(II) (**2**), Co(II) (**3**) and Pd(II) (**4**) films.