



## Electronic functionality of Gd-bisphthalocyanine: Charge carrier concentration, charge mobility, and influence of local magnetic field

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### ABSTRACT

Gadolinium bisphthalocyanine (GdPc<sub>2</sub>) has been placed among the highest ranked molecular materials considered namely for modern optoelectronic applications including organic solar cells. To improve understanding of the correlation between GdPc<sub>2</sub> magnetic properties and its electronic functionality, we experimentally and theoretically studied charge carrier concentration, charge mobility, and influence of local magnetic field on charge carrier transport. For better clearance, all the main studied properties of GdPc<sub>2</sub> bisphthalocyanine were compared with Zn phthalocyanine (ZnPc) as a reference material. Conductivity and charge carrier mobility were measured in materials incorporated in FET active channels. UV Vis spectroscopy, Electron Paramagnetic Resonance Spectroscopy, and IR spectroscopy were also applied. The narrow band gap together with small ionization potential of GdPc<sub>2</sub> lead to high free charge carrier concentration. Among parameters affecting charge carrier mobility, molecular arrangement and intermolecular and intramolecular charge carrier pathways were highlighted. The possibility that the interaction of the mobile charge carriers with the local magnetic field of GdPc<sub>2</sub> molecules reduces charge carrier mobility is also discussed.

### 1. Introduction

Organic electronics is a fast growing area of research activities of many scientific groups. The use of small organic molecules can provide cheap and easy to process devices (roll-to-roll processing) with a large commercial potential. A characteristic feature of molecular materials is the almost infinite possibility to modify their physical properties because of their large susceptibility to change the molecular structure [1–15]. The low-voltage operation of organic thin film is of considerable interest for a variety of inexpensive applications [9,16–20].

One of the most important and complicated phenomena in the case of materials for molecular electronics is the charge carrier transport, which differs from that of inorganic semiconductors. It limits the electrical conductivity of organic semiconductors, their functionality in electronic devices, and represents a very complex process affected by many parameters, particularly by charge carrier delocalization within the single molecule and supramolecular structure. Each step forward in this area is extremely important for practical applications of materials for organic electronics in general, particularly for field-effect transistors

and light-emitting diodes, where improving the charge carrier mobility is a very desirable issue [8,9].

Phthalocyanines are typical materials with electrical conductivity still subjected to comprehensive research [1–7,13,14,21–23]. Particularly, the molecular setup in bisphthalocyanines offers additional possibilities relative to typical mono-phthalocyanine compounds. Lanthanide bisphthalocyanines, LnPc<sub>2</sub> (Pc = C<sub>32</sub>H<sub>16</sub>N<sub>8</sub> is the phthalocyanine ligand), manifested a specific chemistry toward diverse electron acceptor and/or donor species and displayed unusual photochemical activity. Therefore, LnPc<sub>2</sub> derivatives have been placed among the highest ranked molecular materials considered important for hi-tech applications [5,11,13,16–19,21–25]. Particularly the optical and electronic properties of LuPc<sub>2</sub> are well described [7,26–32]. The GdPc<sub>2</sub> complex belongs to a new class of paramagnets with a large magnetocaloric effect due to the gadolinium atom located in a coordination site of conjugated phthalocyanine macrocycles. Contrary to the closed shell structure of Lu<sup>3+</sup> in LuPc<sub>2</sub>, the Gd<sup>3+</sup> ion in the GdPc<sub>2</sub> molecule represents an open shell system, and the electronic properties of this Pc complex are likely to be different [12,13,28,33,34].

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In this work, by using theoretical and experimental methods, we determined and explained which parameters influence the charge transfer in magnetic gadolinium bisphthalocyanine (GdPc<sub>2</sub>) in comparison with the reference material – zinc phthalocyanine (ZnPc). To obtain the charge carrier mobility, we used measurements of the output characteristics of an organic field effect transistor (OFET) in which GdPc<sub>2</sub> was used for an active channel. Although the electric conductivity of GdPc<sub>2</sub> was relatively high, and hence the output characteristics of OFET were far from ideal, by careful analysis the mobility could be determined and compared with ZnPc as a reference material. The conductivity derived from FET measurements was confirmed by the van der Pauw method. UV–vis spectroscopy and IR spectroscopy were performed as well. As charge carrier mobility is affected by the local magnetic field, Electron Paramagnetic Resonance Spectroscopy (EPR) was applied to properly describe GdPc<sub>2</sub> magnetic properties. In order to explain and demonstrate the fundamental difference between ZnPc and GdPc<sub>2</sub> charge transfer properties, both materials were modeled by hybrid Hartree-Fock theory/density functional theory (DFT) methods [33–39].

## 2. Materials and methods

### 2.1. Preparation and characterization of GdPc<sub>2</sub> and ZnPc thin films

Zinc phthalocyanine (ZnPc) powder was obtained from Sigma Aldrich. Gadolinium bisphthalocyanine (GdPc<sub>2</sub>) was synthesized according to the procedure described in the literature [24]; both materials were used as received. Thin films were deposited by vacuum sublimation on FET substrates composed of n-doped Si with a SiO<sub>2</sub> layer of thickness  $d = 230$  or  $300$  nm, equipped with an Au interdigital system of electrodes, providing channel width  $W = 10$  mm or  $18$  mm and different channel lengths  $L$  from  $20$  to  $50$  μm. The substrates were only cleaned by a standard procedure, without any further treatment. An evaporator used for thin film deposition was equipped with a low temperature quartz effusion cell (NTEZ) from Dr. Eberl MBE-Komponenten GmbH. The effusion temperature was set to  $450$  °C, the deposition pressure was  $2 \times 10^{-4}$  Pa.

Output characteristics were measured in an electrical circuit with a common grounded drain, using electrometer Keithley K6517A in the gate branch and source-meter Keithley K2400 in the source-drain branch. Measurements were performed at  $22$  °C, first in air, then in a glovebox in N<sub>2</sub> atmosphere (60 ppm O<sub>2</sub>, 2 ppm moisture) after storing the samples in the glovebox for 24 h prior to the measurements.

The output and transfer characteristics were measured in the range of the source-drain voltage  $U_{SD}$  from  $+40$  to  $-40$  V and the gate voltage  $U_{GD}$  from  $+40$  to  $-40$  V,  $0.4$  s per each experimental point. For GdPc<sub>2</sub>, the interval of gate voltage was expanded to  $\pm 100$  V. Prior to the measurement of each output characteristic, the gate voltage was allowed to settle for  $10$  s. In the case of GdPc<sub>2</sub>, the background current was subtracted from the source-drain current-voltage characteristics (see Results section for the details) in order to obtain the real field-effect characteristics of very conductive samples. Besides directly measured transfer characteristics, additional transfer characteristics for the mobility evaluation were derived from the output characteristics. The mobility was calculated from the transfer characteristics in the saturated region according to the Eq. (1)

$$\mu_{\text{sat}} = \frac{2L}{WC_i} \left( \frac{\partial \sqrt{|I_{SD,\text{sat}}|}}{\partial U_{GD}} \right)^2, \quad (1)$$

where  $C_i$  is the capacitance of the dielectric layer per unit area.

Conductivity  $\sigma$  was calculated from the source-drain current  $I_{SD}$  at the source-drain voltage  $U_{SD} = -40$  V at the gate voltage  $U_{GD} = 0$  V using the formula

$$\sigma = \frac{L}{TW} \left( \frac{I_{SD}}{U_{SD}} \right), \quad (2)$$

where  $T$  is the sample thickness,  $W$  is the width and  $L$  is the length of the active channel of the transistor. The gate current was measured in the same conditions and found to be always at least two orders of magnitude lower than the source-drain current  $I_{SD}$ . The approach of neglecting the gate current was also crosschecked by disconnecting the gate circuit; no difference in the measurement using zero gate voltage was observed.

Conductivity of the GdPc<sub>2</sub> films was also measured by the van der Pauw method. Before the measurement, the films deposited on glass were provided with Al/Au (40 nm/50 nm) contacts evaporated in the corners of  $10$  mm  $\times$   $10$  mm square samples. Linearity and symmetry of the contacts was found satisfactory (deviations  $< \sim 2\%$ ). The four-point conductivity measurement was carried out at room temperature, ( $296 \pm 1$ ) K, using a Keithley 6221 current source, two Keithley 6514 electrometers and a Keithley 2182A nanovoltmeter. The latter instrument operated as a read-out voltmeter measuring the differential signal of the electrometers. Guarded triax cable configuration and PTFE insulating elements were employed to suppress possible leakages.

Continuous wave (CW) EPR measurements were performed in a Bruker X-/Q-band E580 FT/CW ELEXSYS spectrometer at X,Q-bands with the microwave frequencies  $9.3$ – $9.5$  and  $33$ – $35$  GHz, respectively, at the temperature range from  $10$  to  $296$  K.

Both the external and the local magnetic field influence the electrical conductivity of a sample [40,41]. The external magnetic field was applied to GdPc<sub>2</sub> exclusively in the EPR experiment, whereas other experimental techniques were run in their common regimes, i.e., without the external magnetic field, so the influence of the external magnetic field on the GdPc<sub>2</sub> sample conductivity was not studied experimentally at all. The magnetic properties of the GdPc<sub>2</sub> were considered as a mechanism helping to understand the electronic properties of the investigated material.

UV–vis spectra were measured in dimethylformamide (DMF) solution in the range of  $\lambda = 190$ – $1100$  nm using a Jasco-670 UV–vis-NIR spectrophotometer and Spectra Manager v.2 software, in standard  $10$  mm quartz cuvettes.

The chemical structure of phthalocyanines was analyzed by Fourier transform infrared spectroscopy (FTIR) by using a Thermo Nicolet 6700 FTIR Spectrometer with a Thermo Continuum FTIR microscope. The spectra were scanned in the range of  $1800$ – $650$  cm<sup>-1</sup> with resolution  $8$  cm<sup>-1</sup> and number of sample scans  $128$ .

### 2.2. Quantum chemical modeling

In order to investigate the charge transfer in ZnPc and GdPc<sub>2</sub>, we used quantum chemical modeling with the aid of the Gaussian 09 software package [42]. The initial geometry of ZnPc dimers and GdPc<sub>2</sub> molecule was obtained from the Cambridge Structural Database (CSD-PTHCZN and CSD-161055) [32,43,44]. The molecular geometries of the investigated systems were optimized by means of the hybrid Hartree-Fock (HF)/density functional theory (DFT) method PBE0 introduced by Adamo [9,45,46] with and without the inclusion of empirical Grimme's dispersion correction D3 [47]. Hybrid HF/DFT methods were successfully used for the calculations of the conformations, population analyses, excitation energies, and many other properties of different  $\pi$ -conjugated systems, including ion-radicals [48–51]. In addition to conformations of isolated molecules, geometries of their dimers were also calculated. Grimme's dispersion correction D3 makes it possible to determine accurate mutual positions of adjacent phthalocyanine moieties in the GdPc<sub>2</sub> molecule, since it significantly improves performance of the DFT-based methods for medium-range dispersion interactions, see e.g. [39]. Geometry optimization was done using the polarized Pople-type 6-31G(d) basis set [52] on N, C, and H atoms and Stuttgart/Dresden relativistic effective core pseudopotentials

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