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Thermally activated electrical conductivity of thin films of bis(phthalocyaninato)terbium(III) double decker complex

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ABSTRACT

The temperature and field dependence of the electrical conductance of neutral radical bis(phthalocyaninato) terbium(III) ($TbPc_2$) thin films was measured *in situ* under ultrahigh vacuum. The films behave electrically as narrow gap intrinsic semiconductors, having high conductivity and weakly thermally activated conductance. Taking advantage of the exceptionally high electrical stability of the material and the fast-settling response in the low-field region, precise measurements of the temperature dependence could resolve a linear temperature dependence in the pre-exponential factor of the conduction equation. The activation energy of conductance of the annealed $TbPc_2$ film was determined to be 0.158 eV after adjusting the fitting procedure to take into account the temperature dependent pre-exponential. This new conductance equation, which differs only slightly from the usual Arrhenius expression, arises as the natural consequence of thermal excitation of carriers from a continuous density of deep trap states, or a similar activated process where either the states or the barrier heights distribute over a finite width.

1. Introduction

Experimentally, semiconducting organic materials measured under Ohmic conditions (bulk-limited charge transport, homogenous charge density) exhibit a thermally activated dark conductivity, σ, defined as,

$$\sigma = ne\mu = \sigma_0 e^{-\frac{E_a}{kT}}, \tag{1}$$

where k is the Boltzmann constant, T is the temperature, E_a is the activation energy and σ_0 is a constant pre-exponential factor [1]. The expression for conductivity includes the density of charge carriers, n, and charge carrier mobility, μ. e is the unit of electrical charge. The pre-exponential factor may be constant with activation energy [2], but often includes an exponential of the activation energy to describe a compensation effect [3]. As the exponential term typically dominates the temperature dependence the pre-exponential factor is normally taken as invariant over the measured temperature range.

The measured activation energy will be the sum of all thermally activated conduction processes in the measurement system [1,4]. In an ideal case, if charge carrier excitation from trap states or donor/acceptor levels can be neglected and the mobility term μ has no significant temperature dependence, the activation energy will be one half the transport energy, E_g, required for the intrinsic generation of hole-electron pairs. While the activation energy approaches the expected intrinsic value in very pure samples, in most wide gap organic semiconductor samples the activation energy reflects the excitation energy of charge trapped in extrinsic gap states back to the relevant conducting states [2,5,6]. Whether the activation energy results from intrinsic or extrinsic charge generation, together with the energies of the relevant states, is an interesting aspect of organic semiconductors to investigate in detail, but unfortunately it is difficult to obtain accurate measurement of the Ohmic conductivity of pure wide gap materials due to the low density of thermal charge carrier densities. At applied fields needed to record a measureable current, the sample is often already operating in the space charge limited current (SCLC) regime. Injected space charge trapped in deep gap states tends to induce long time scale hysteresis in the current voltage measurements. While performing the measurements at elevated temperature will reduce the influence of SCLC effects, the stability of the organic material eventually becomes a concern.

As a class, solid-state neutral radical phthalocyanine ($MPc^{\cdot-}$) and bisphthalocyanine (MPc_2) materials are fundamentally different from closed shell phthalocyanine complexes. They are characterized by high conductivity [7,8] on the order of 1 $S\,m^{-1}$, fast settling times [7], and

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Ohmic current-voltage curves at moderately high applied fields [9–12]. The activation energies of conductance are typically small, in the range of 0.1 eV to 0.3 eV [8,12], and, in contrast to most open shell molecular semiconductors where conduction proceeds by thermal de-trapping, the activation energy falls after annealing the material in vacuum or inert atmosphere. These facts together with EPR data have led most previous authors to classify radical phthalocyanines as intrinsic semiconductors [7,10]. Brinkman, however, notes the activation energy cannot be assigned *a priori* to the transport energy since shallow trap levels arising from structural disorder may still influence the dark conduction [12]. Electrical currents in these materials will be free from the influence of extrinsic deep trap states, however. Such high conductivity in amorphous organic materials implies a high density of mobile charge carriers, which leads to the observed Ohmic conduction over a wide range of applied fields, and - since the charge transport is free from the influence of deep traps - a fast settling, hysteresis-free response. Crucially these compounds also retain the chemical and thermal stability of the closed shell phthalocyanine ligands [8–10,12,13]. We therefore suggest that a potentially useful facet of these materials, which has until now received little attention, is as a platform for the precise study of the conductance equation for organic semiconductors.

In the present work the electrical conductivity of thin films of the terbium bisphthalocyanine complex, a representative material exhibiting all the properties of the radical phthalocyanine and bisphthalocyaninato complexes described above, is reported as a function of temperature. It is shown that the conductance equation for the thin film takes the form not of Eq. (1), but instead,

$$\sigma = \sigma_0 T e^{-\frac{E_a}{kT}}. \tag{2}$$

The pre-exponential now includes a linear dependence on the temperature, and the constant σ_0 has the units of conductivity/temperature. It has not been possible to resolve the temperature dependence of the pre-exponential in thermally activated conductance until now – even if present, the experimental uncertainties and the large exponential term combine to bury any additional temperature dependence from detection. The linear temperature factor could be resolved in the present work due to the combination of two factors. First, the small activation energy of the $TbPc_2$ film enhances the relative significance of the pre-exponential linear term and, second, the electrical stability of the annealed $TbPc_2$ film in ultrahigh vacuum supports an exceptionally high experimental measurement accuracy.

2. Materials and methods

All reagents were purchased from Wako or Aldrich and used without further purification. The compounds were prepared following a reported procedure with a slight modification [14]. A mixture of 1,2-dicyanobenzene (62.7 mmol), $Tb(OAc)_3{\cdot}4H_2O$ (3.92 mmol) and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) (33.5 mmol) in 200 mL of 1-hexanol was refluxed for 1.5 d. The solution was allowed to cool to room temperature and then filtered. The precipitate was washed with acetic anhydride, cold acetone, and *n*-pentane. Then, the precipitate was dried in air. The crude purple product was extracted with ten 200 mL portions of $CHCl_3$. The green extracts were combined, concentrated, and purified using column chromatography (C-200 silica gel, Wako). The eluent was 98:2 CH_2Cl_2/MeOH. The green fraction, which was also the first fraction, was collected while being careful not to contaminate with the anionic $[TbPc_2]^{-1}$ complex, which was the second fraction (blue-green). The green fraction was concentrated, and *n*-hexane was added until the compound precipitated. The green precipitate was filtered and dried *in vacuo*. In general, the yield was 2%–5%. Deep green crystals of the products “without” CH_2Cl_2 were obtained by using a different solvent. The green precipitate (8 mg) was dissolved in 20 mL of $CHCl_3$ and filtered. *n*-hexane was layered on the top of green filtrate. After two weeks, deep green needle-like crystals of $TbPc_2$ were obtained. ESI-MS (*m/z*): 1183.224 (100) $[M^+]$.

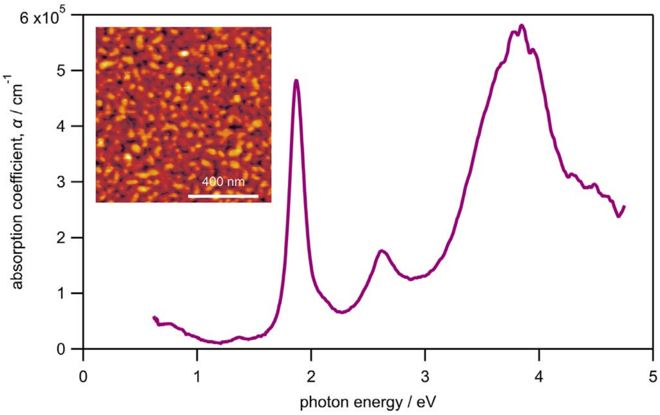

Fig. 1. The optical absorbance spectrum of a $TbPc_2$ thin film deposited under the same conditions as the sample used for the electrical measurements, and the film topology.

Thin films were grown by thermal evaporation under ultrahigh vacuum (UHV) conditions onto a single crystal sapphire substrate which had been air annealed 5 h at 1273 K before two 35 nm thick titanium electrodes separated by 0.1 mm were deposited on the surface. After introduction to the UHV measurement chamber the device was degassed 573 K 1 h before cooling to 398 K prior to film growth. $TbPc_2$ was deposited through a 4 mm square mask to a thickness of 5 nm to give a conducting volume of $l = 0.1$ mm $w = 4$ mm $t = 5$ nm. The sample was annealed briefly up to 543 K to stabilize the film structure before the final set of electrical measurements presented in this work were taken. The absorbance spectrum and surface topology of a typical $TbPc_2$ thin film are shown in Fig. 1. Characteristic low-energy peaks in the absorbance spectrum arise from transitions involving the singly-occupied molecular state [15], confirming that the open shell electronic structure of the molecules remains intact in the measured films. The temperature dependence data was recorded with a Keithley 6487 picoammeter-sourcemeter at a measurement step interval of 2 s. I—V curves at all temperatures were scanned over both increasing and decreasing voltages to confirm the absence of hysteresis or lag. Consistency over multiple repetition of the I—V measurements and temperature ramps confirmed the electrical stability of the sample. The electric fields applied during the measurement experiment (5×10^6 V m^{-1} up to 303 K, 10^4 V m^{-1} up to 423 K) had no lasting influence on the sample conductance which varied less than 2% over the full 48 h measurement period.

3. Results and discussion

The I—V curves are symmetrical with applied voltage and linear at low field before the onset of space charge limited current [16,17]. Conductance in this linear region is interpreted as being Ohmic, *i.e.* arising from bulk limited, homogeneous transport. Fig. 2 shows the compiled dataset obtained between 203 K and 423 K. The conductivity, σ, is determined from the slope of the linear section of data below 10^4 V m^{-1} applied field as,

$$\sigma = \frac{dI}{dV}\frac{l}{wt} = \frac{dJ}{dE}. \tag{3}$$

w, t, and l are the dimensions of the film volume situated between the electrodes, J is the current density while E is the electric field, V/l. The conductivity of the sample at 303 K is 0.032 S m^{-1}.

Starting with a thermally activated conductance equation having the form of Eq. (1), the activation energy is the slope of the Arrhenius plot, ln σ *vs.* $1/T$,

$$E_a = -k\,\frac{d\ \ln\,\sigma}{d(1/T)}. \tag{4}$$