



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

Richard Murdey^{a,*}, Keiichi Katoh^b, Masahiro Yamashita^{b,c,d}, Naoki Sato^a

^a Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

^b Department of Chemistry, Graduate School of Science, Tohoku University Aramaki-Aza-Aoba, Aoba-ku, Sendai 980-8578, Japan

^c WPI Research Center, Advanced Institute for Materials Research, Tohoku University, Aramaki-Aza-Aoba, Aoba-ku, Sendai 980-8578, Japan

^d School of Materials and Engineering, Nankai University, 300350, Tianjin, China

ARTICLE INFO

Keywords:

Electrical conduction
Molecular electronics
Phthalocyanine
Thin films
Organic radicals
Organic semiconductors

ABSTRACT

The temperature and field dependence of the electrical conductance of neutral radical bis(phthalocyaninato)terbium(III) (TbPc₂) 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 TbPc₂ 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,

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

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[•]) and bisphthalocyanine (MPc₂) 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

* Corresponding author.

E-mail address: rmurdey@e.kuicr.kyoto-u.ac.jp (R. Murdey).

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,

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

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 TbPc₂ film enhances the relative significance of the pre-exponential linear term and, second, the electrical stability of the annealed TbPc₂ 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)₃·4H₂O (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 CHCl₃. The green extracts were combined, concentrated, and purified using column chromatography (C-200 silica gel, Wako). The eluent was 98:2 CH₂Cl₂/MeOH. The green fraction, which was also the first fraction, was collected while being careful not to contaminate with the anionic [TbPc₂]^{−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” CH₂Cl₂ were obtained by using a different solvent. The green precipitate (8 mg) was dissolved in 20 mL of CHCl₃ and filtered. *n*-hexane was layered on the top of green filtrate. After two weeks, deep green needle-like crystals of

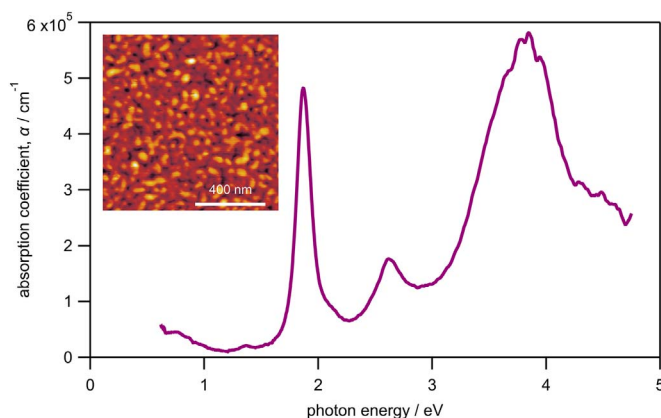


Fig. 1. The optical absorbance spectrum of a TbPc₂ thin film deposited under the same conditions as the sample used for the electrical measurements, and the film topology.

TbPc₂ were obtained. ESI-MS (*m/z*): 1183.224 (100) [M⁺].

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. TbPc₂ 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 TbPc₂ 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,

$$\sigma = \frac{dI}{dV} \frac{l}{wt} = \frac{dJ}{dE}. \quad (3)$$

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, $\ln \sigma$ vs. $1/T$,

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

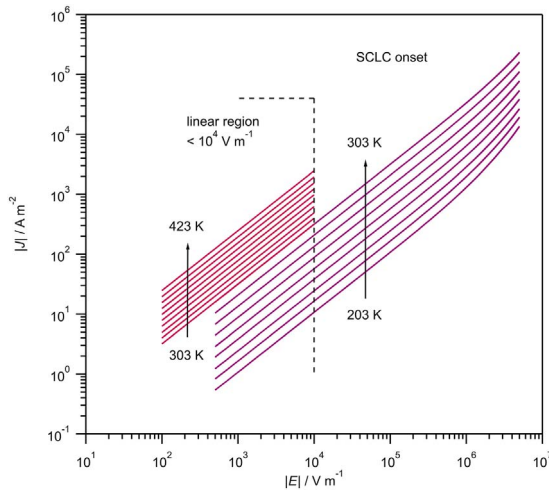


Fig. 2. Current density vs. applied field. Each dataset is an average of two separate runs, one obtained during a heating ramp and the other during a cooling ramp. The conductivity was determined from the data in the linear region below 10^4 V m^{-1} applied field.

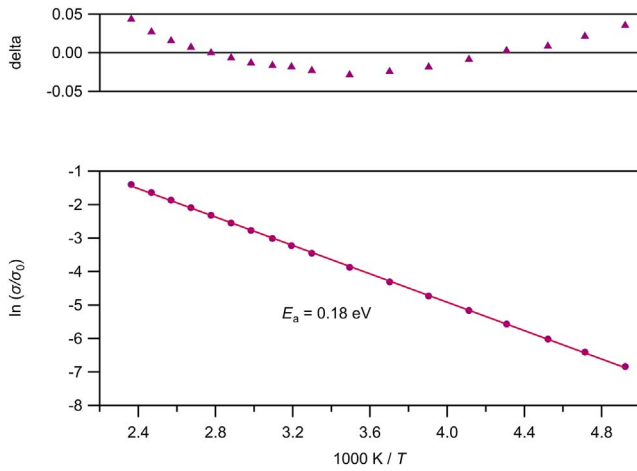


Fig. 3. Arrhenius plot for the sample conductivity calculated from the low-field, linear sections of the current voltage curves. The activation energy is determined to be 0.18 eV, though the difference between the experimental data and the linear fit displays a small degree of upwards curvature.

As shown in Fig. 3, the slope yields $E_a = 0.18 \text{ eV}$. Closer inspection, however, reveals that the experimental data points deviate from the linear fit with a small degree of upwards curvature. The activation energy according to Eq. (4) will therefore depend on the temperature range of the conductance measurements used to calculate the linear regression.

Next, to examine the influence of the curvature, we calculated the activation energy using only the conductivity at each consecutive pair of temperatures,

$$E_a(T_m) = -k \frac{\Delta \ln \sigma}{\Delta(1/T)} = -k \frac{\ln \sigma_2 - \ln \sigma_1}{1/T_2 - 1/T_1}. \quad (5)$$

An ‘average inverse temperature’, T_m , defines the midpoint of two consecutive data points in the Arrhenius plot and serves as the reference temperature for each calculated value of the activation energy,

$$T_m = \frac{2T_1 T_2}{T_1 + T_2}. \quad (6)$$

As shown in Fig. 4, the activation energy calculated for each temperature interval increases linearly with temperature with a slope equal within experimental error to the Boltzmann constant. Using least mean

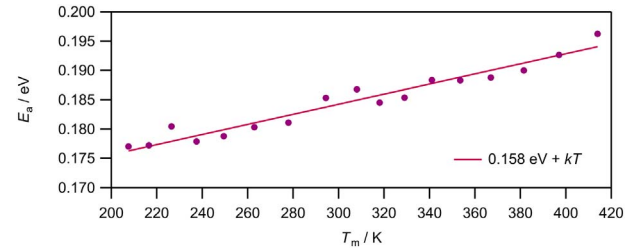


Fig. 4. The activation energy calculated for each successive temperature interval. The variation with temperature is linear, with a slope equal to kT . The zero-temperature intercept determined by least squares analysis is 0.158 eV.

squares fitting the temperature-variable apparent activation energy, is,

$$E'_a = 0.158 \text{ eV} + kT. \quad (7)$$

This apparent variation of activation energy with temperature is an artifact introduced by the incorrect assumption in Eq. (1) that the conductivity pre-exponential factor σ_0 is temperature invariant, brought forward into the Arrhenius fit as Eq. (4). It can be shown that a temperature dependence T^n in the pre-exponential factor introduces an additional term kT^n to the effective activation energy derived from the slope of the Arrhenius plot. Starting from,

$$\sigma = \sigma_0 T^n e^{-\frac{E_a}{kT}}, \quad (8)$$

and taking the logarithm of both sides,

$$\ln \sigma = \ln \sigma_0 + n \ln T + \frac{-E_a}{kT}. \quad (9)$$

Substituting $\ln(T)$ as $-\ln(1/T)$ and calculating the differential ($d \ln \sigma / d(1/T)$),

$$\frac{d \ln \sigma}{d(1/T)} = \frac{-E_a}{k} - nT, \quad (10)$$

and after multiplying through by k and rearranging,

$$-k \frac{d \ln \sigma}{d(1/T)} = E_a + nkT. \quad (11)$$

For $n = 1$, i.e. Eq. (2), the Arrhenius expression becomes,

$$-k \frac{d \ln \sigma}{d(1/T)} = E_a + kT. \quad (12)$$

A similar derivation verifies that an activation energy with a temperature dependent form ($E_a + kT$) would result in an Arrhenius plot with a slope of E_a . If the activation energy had a kT dependence on temperature, in other words, this would go undetected in the Arrhenius plot. The experimental result of Eq. (7) therefore uniquely designates a conductivity equation with a linear temperature dependence in the pre-exponential factor and confirms Eq. (2) as the correct conductance equation for this system.

The value of the pre-exponential factor σ_0 as defined by Eq. (2) is constant with temperature within experimental error. As shown in Fig. 5, the value is $0.0448 \text{ S m}^{-1} \text{ K}^{-1}$. The temperature independent

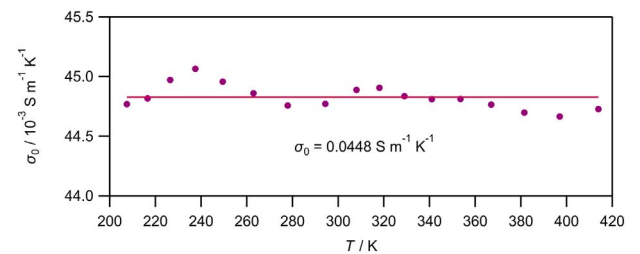


Fig. 5. The pre-factor coefficient for the revised model expression for the conductivity, $\sigma = \sigma_0 T \exp(-E_a/kT)$, with $E_a = 0.158 \text{ eV}$.

activation energy is 0.158 eV, obtained directly from the fit in Fig. 4.

The energy gap of LuPc₂ thin films was previously estimated at 0.4 ± 0.1 eV using photoemission and inverse photoemission spectroscopy [18] and 0.48 eV from redox potentials [8]. The transport energy estimated as $2E_a$ from the present determination of the activation energy is 0.316 eV, in good agreement with these experiments and lending credible support to the previous designation of the material as an intrinsic semiconductor. It is not possible, however, to rule out alternative processes. Possibilities include de-trapping from shallow trap states 0.158 eV from the mobility edge, or, as Brinkmann [12] suggested, thermally activated hopping transport – either between molecular stacks or at grain boundaries.

In this context, we offer some comment regarding the observed temperature dependence of the pre-exponential factor.

Theoretical treatments of hopping transport based on Marcus theory [19,20] and the various Miller-Abrahams hopping/polaron models [21–25] return aggregate values for the mobility expressed as function of charge density, disorder, electric field, and temperature. The temperature dependence of the mobility is complex and includes both exponential and non-exponential terms. We note also that intrinsic thermal charge generation is not considered in the models, the charge density being either held constant or swept as a free variable. It is not too surprising then that the Marcus/Miller-Abrahams theoretical framework does not help explain the present experimental results.

The key point of difference is that the TbPc₂ system remains comparatively static over the range of observed temperatures and applied fields. The thermal activation energy is a constant value of 0.158 eV, and conductance is Ohmic. It therefore seems reasonable to try and explain the results in terms of energy levels. We propose the linear temperature dependence of the conductance equation is the consequence of thermal excitation either from fixed energy states having a distribution in energy greater than kT or equivalently over energy barriers with a similar distribution in energy. As shown in Eq. (13), simple integration over the range of accessible states results in the observed temperature dependence. For a constant density of states, N_t , populated up to a well-defined energy, E_t , the excitation rate to a mobility edge at zero energy is,

$$\frac{dn}{dt} = N_t \int_{E_t}^{\infty} A e^{-\frac{E}{kT}} dE = N_t A k T e^{-\frac{E_t}{kT}}. \quad (13)$$

Even if the DOS is an exponential, as it is generally assumed [26], as long as the characteristic energy of the exponential decay characterizing the DOS is greater than kT the result of Eq. (13) is generally valid. It can be applied to a distribution of trap states or intrinsic charge carrier generation, and even inter-grain/inter-stack energy barriers. In the latter case, the energy barriers distribute over a range of energies, rather than the initial states. If the distribution of relevant energies is sufficiently wide we can therefore expect a linear dependence of the pre-exponential factor for any of these conductance mechanisms on the condition that the rate of the recombination/back process is not also temperature dependent.

4. Conclusions

Radical organic semiconductor terbium bisphthalocyaninato (TbPc₂) thin films have exceptional electrically stability which enabled precise measurements of the current-voltage relationships as a function of temperature. At applied fields below 10^{-4} V m⁻¹ the conductivity is Ohmic, with a value of 0.032 S m⁻¹ at 303 K. The activation energy is 0.158 eV. The pre-exponential factor has a linear dependence with temperature, which results in an overestimation of the activation

energy determined from an Arrhenius plot by approximately kT if not treated explicitly in the analysis.

Acknowledgements

This work was financially supported by a Grant-in-Aid for Scientific Research (20225003) and Grant-in-Aid for Young Scientists (24750119) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), and Scientific Research (15K05467) from CREST, JST (JPMJCR12L3), Japan.

References

- [1] H. Meier, *Organic Semiconductors*, Verlag Chemie, Weinheim, 1974.
- [2] A. Sussman, Electrical properties of copper phthalocyanine thin films as influenced by the ambient, *J. Appl. Phys.* 38 (1967) 2748.
- [3] C. Hamann, On the electric and thermoelectric properties of copper phthalocyanine single crystals, *Phys. Status Solidi B* 20 (1967) 481.
- [4] J. Simon, J.-J. André, *Molecular Semiconductors*, Springer-Verlag, Berlin, 1984.
- [5] S.E. Harrison, K.H. Ludewig, Conductivity and crystal phase change in phthalocyanines, *J. Chem. Phys.* 45 (1966) 343–348.
- [6] G.H. Heilmeyer, S.E. Harrison, Charge transport in copper phthalocyanine single crystals, *Phys. Rev.* 132 (1963) 2010–2016.
- [7] R. Madru, G. Guillaud, M. Al Sadoun, M. Maitrot, J.P. Schunck, Mobility experiments on lutetium bisphthalocyanine thin films, *Chem. Phys. Lett.* 168 (1990) 41–44.
- [8] M. Bouvet, J. Simon, Electrical properties of rare earth bisphthalocyanine and bisnaphthalocyanine complexes, *Chem. Phys. Lett.* 172 (1990) 299–302.
- [9] J.-J. André, K. Holczer, P. Petit, M.-T. Riou, C. Clarisse, R. Even, M. Fourmigue, J. Simon, Electrical and magnetic properties of thin films and single crystals of bis(phthalocyaninato)lutetium, *Chem. Phys. Lett.* 115 (1985) 463–466.
- [10] M. Maitrot, G. Guillaud, B. Boudjema, J.-J. André, H. Strzelecka, J. Simon, R. Even, Lutetium bisphthalocyanine: the first molecular semiconductor. Conduction properties of thin films of p- and n-doped materials, *Chem. Phys. Lett.* 133 (1987) 59–62.
- [11] Z. Belarbi, C. Sirlin, J. Simon, J.-J. André, Electrical and magnetic properties of liquid crystalline molecular materials - lithium and lutetium phthalocyanine derivatives, *J. Phys. Chem.* 93 (1989) 8105–8110.
- [12] M. Brinkmann, C. Chaumont, J.J. André, Dark conductivity in the α and β polymorphs of lithium phthalocyanine, *Thin Solid Films* 324 (1998) 68–77.
- [13] P. Bassoul, M. Bouvet, J. Simon, Relationship between the structure and the electrical properties of lutetium bisphthalocyanine thin films, *Synth. Met.* 61 (1993) 133–137.
- [14] A. De Cian, M. Moussavi, J. Fischer, R. Weiss, Synthesis, structure, and spectroscopic and magnetic properties of lutetium(III) phthalocyanine derivatives: LuPc₂.CH₂Cl₂ and [LuPc(OAc)(H₂O)₂].H₂O.2CH₃OH, *Inorg. Chem.* 24 (1985) 3162–3167.
- [15] K. Yoshino, S.B. Lee, T. Sonoda, H. Kawagishi, R. Hidayat, K. Nakayama, M. Ozaki, K. Ban, K. Nishizawa, K. Ohta, H. Shirai, Optical properties of substituted phthalocyanine rare-earth metal complexes, *J. Appl. Phys.* 88 (2000) 7137–7143.
- [16] A. Rose, Space-charge-limited currents in solids, *Phys. Rev.* 97 (1955) 1538–1544.
- [17] M.A. Lampert, Simplified theory of space-charge-limited currents in an insulator with traps, *Phys. Rev.* 103 (1956) 1648–1656.
- [18] R. Murdey, M. Bouvet, M. Sumimoto, S. Sakaki, N. Sato, Direct observation of the energy gap in lutetium bisphthalocyanine thin films, *Synth. Met.* 159 (2009) 1677–1681.
- [19] R.A. Marcus, Electron transfer reactions in chemistry. Theory and experiment, *Rev. Mod. Phys.* 65 (1993) 599–610.
- [20] J.A. Freire, G. Voss, Master equation approach to charge injection and transport in organic insulators, *J. Chem. Phys.* 122 (2005) 124705.
- [21] P.M. Borsenberger, L. Pautmeier, H. Bässler, Charge transport in disordered molecular solids, *J. Chem. Phys.* 94 (1991) 5447–5454.
- [22] H. Bässler, Charge transport in disordered organic photoconductors a Monte Carlo simulation study, *Phys. Status Solidi B* 175 (1993) 15–56.
- [23] I.I. Fishchuk, A. Kadashchuk, H. Bässler, S. Nešpůrek, Nondispersive polaron transport in disordered organic solids, *Phys. Rev. B* 67 (2003) 224303.
- [24] I. Fishchuk, V. Arkhipov, A. Kadashchuk, P. Heremans, H. Bässler, Analytic model of hopping mobility at large charge carrier concentrations in disordered organic semiconductors: polarons versus bare charge carriers, *Phys. Rev. B* 76 (2007) 045210.
- [25] N. Lu, L. Li, W. Banerjee, P. Sun, N. Gao, M. Liu, Charge carrier hopping transport based on Marcus theory and variable-range hopping theory in organic semiconductors, *J. Appl. Phys.* 118 (2015) 045701.
- [26] P. Stallinga, *Electrical Characterization of Organic Electronic Materials and Devices*, Wiley, UK, 2009.