

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/253563775>

# Electrical and luminescence properties of a poly(amidoamine) dendrimer containing naphthalimide

Article in *Physics of the Solid State* · December 2004

DOI: 10.1134/1.1841398

CITATIONS

8

READS

46

5 authors, including:



Alexander Kukhta

Belarusian State University

125 PUBLICATIONS 525 CITATIONS

SEE PROFILE



Artyom Pochtenny

Belarusian State Technological University

14 PUBLICATIONS 35 CITATIONS

SEE PROFILE



Ivo Grabchev

Sofia University "St. Kliment Ohridski"

194 PUBLICATIONS 3,572 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:



New dendrimers with biomedical application [View project](#)



Synthesis of novel fluorescent polymers with sensor and microbiological activity [View project](#)

## POLYMERS AND LIQUID CRYSTALS

# Electrical and Luminescence Properties of a Poly(amidoamine) Dendrimer Containing Naphthalimide

A. V. Kukhto\*, É. É. Kolesnik\*, A. N. Lappo\*\*, A. E. Pochtenny\*\*, and I. K. Grabchev\*\*\*

\* Institute of Molecular and Atomic Physics, National Academy of Sciences of Belarus,  
pr. F. Skoriny 70, Minsk, 220072 Belarus  
e-mail: kukhta@imaph.bas-net.by

\*\* Belarussian State Technological University, Minsk, 220050 Belarus  
e-mail: root@bstu.unibel.by

\*\*\* Institute of Polymers, Bulgarian Academy of Sciences, Sofia, 1113 Bulgaria  
e-mail: grabchev@polymer.bas.bg

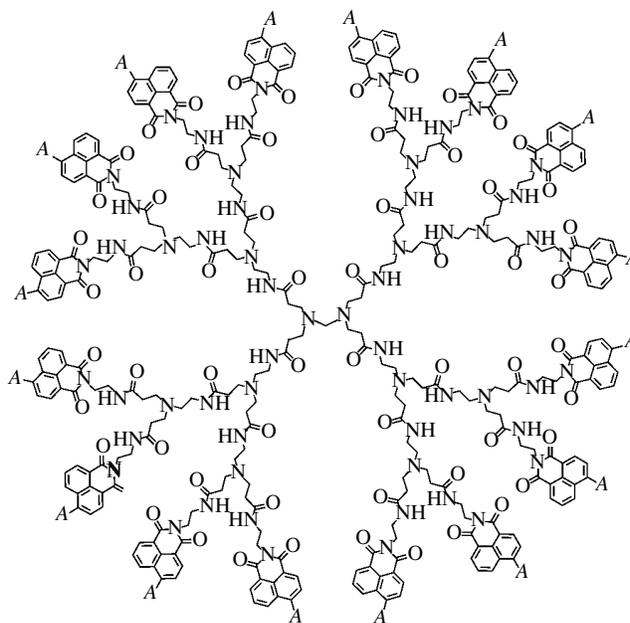
Received February 3, 2004; in final form, April 20, 2004

**Abstract**—The electrical and luminescence properties of a poly(amidoamine) (PAMAM) dendrimer containing naphthalimide are investigated. The influence of adsorbed oxygen on the electrical conductivity of thermally evaporated organic films is analyzed using cyclic thermal desorption. The results obtained are interpreted within a model of two-level hopping electron transfer according to which one of the two systems of energy levels corresponds to intrinsic states of electrons in PAMAM molecules and the other system is associated with the states of electrons in adsorbed oxygen molecules. The use of the cyclic thermal desorption method in combination with the proposed model makes it possible to estimate the localization length of electrons numerically and to determine the states involved in hopping electron transfer. It is demonstrated that the studied compound in the solid state possesses a high luminescence power over a wide spectral range. © 2004 MAIK “Nauka/Interperiodica”.

## 1. INTRODUCTION

In recent years, organic compounds of different classes have been extensively used in electronic devices [1]. Particular interest has been expressed by researchers in dendrimers, because these materials are very promising for use in electroluminescent structures [2], sensors [3], and light-harvesting antennas [3]. Dendrimer molecules consist of a core, conjugated dendrons, and surface groups. Consequently, compounds based on dendrimers can exhibit a great variety of functional and electronic properties [3]. In particular, dendrimer compounds are characterized by a high solubility and weak intermolecular interactions and can be used for manufacturing high-quality films. Moreover, molecules of these compounds possess a high quantum yield of fluorescence. In this work, we investigated the electrical, spectral, and luminescence properties of a poly(amidoamine) (PAMAM) dendrimer containing 1,8-naphthalimide groups in the peripheral part. The procedure of synthesizing this compound was described earlier in [4, 5]. The molecular structure is depicted in Fig. 1. The core of the PAMAM molecule exhibits strong electron-donating properties due to the presence of nitrogen atoms with a lone electron pair, whereas the peripheral part of this molecule is characterized by electron-seeking properties. Grabchev *et al.*

[4] observed photoinduced electron transfer in these molecules, which can have a profound effect on electrical conductivity.



**Fig. 1.** Molecular structure of the studied compound. Designation: A = NH(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>.

## 2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

For our experiments, 50-nm-thick films of the PAMAM compound were prepared on a VUP-5 apparatus through thermal evaporation under vacuum with subsequent deposition of the evaporation products onto substrates.

The electrical measurements were performed using glass substrates whose surfaces were covered with a transparent layer prepared from a mixture of indium and tin oxides. Moreover, a multilayer structure consisting of sequentially deposited layers of the studied material and an upper silver electrode 20 nm thick was grown on the glass substrate. The layers were deposited in one vacuum cycle. The deposition rate did not exceed 1 nm/s.

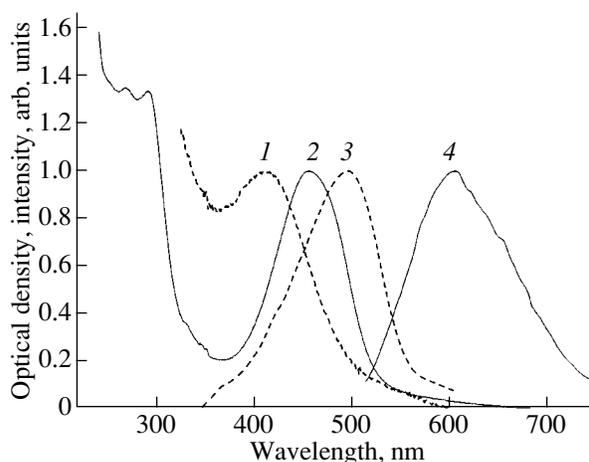
The optical absorption spectra were measured on a Cary 500 Scan UV–VIS–NIR spectrophotometer (Varian Ltd.). The fluorescence spectra were recorded on an SFL-1211A spectrofluorimeter (Solar TII). The temperature dependences of the electrical conductivity of the PAMAM compound were measured on a V7É-42 electrometer (Belvar, Minsk) in air and under vacuum with a residual pressure of  $10^{-2}$  Pa. The electrical measurements were carried out using cyclic thermal desorption [6]. In essence, this method is as follows. The electrical conductivity of many organic compounds depends on the concentration of adsorbed oxygen molecules. This concentration decreases upon heating of an organic sample. Upon heating of the sample under vacuum to a specified temperature, the concentration of molecular oxygen in the sample decreases to a particular value. By cooling the sample under vacuum from this temperature, we can measure the temperature dependence of the electrical conductivity at a constant oxygen concentration in the sample. Sequential heating of the sample to increasingly higher temperatures and measurement of the temperature dependences of the electrical conductivity during cooling from these temperatures make it possible to obtain a set of temperature dependences of the conductivity for different concentrations of adsorbed oxygen molecules in the same sample. The temperature dependence of the electrical conductivity  $G$  for PAMAM films can be described by the relationship

$$G = G_0 \exp\left(-\frac{E_a}{kT}\right), \quad (1)$$

where  $E_a$  is the activation energy for electrical conduction.

## 3. RESULTS AND DISCUSSION

The absorption and fluorescence spectra of PAMAM films and ethanol solutions of the PAMAM compound are shown in Fig. 2. As for the majority of  $\pi$ -conjugated organic compounds, the absorption and fluorescence spectra of the films and solutions under

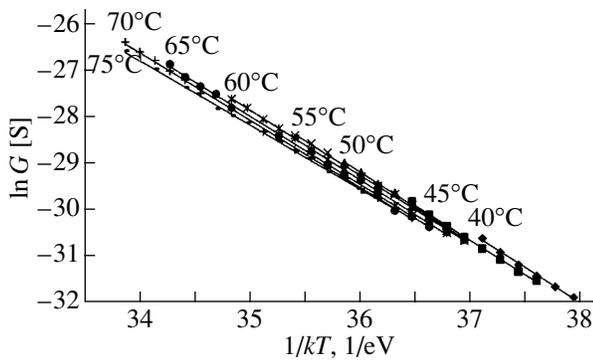


**Fig. 2.** (1, 2) Absorption and (3, 4) fluorescence spectra: (1, 3) ethanol solutions of the PAMAM compound ( $10^{-6}$  mol/l) and (2, 4) PAMAM films.

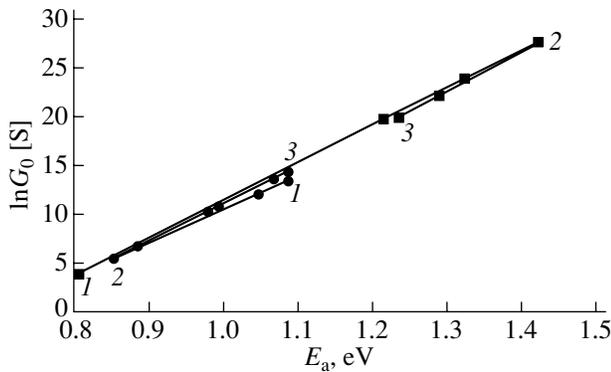
investigation do not radically differ from each other. This indicates that their individual properties are retained in the solid state. The naphthalimide fragments exhibiting luminescence properties in the blue–green spectral region are emitting chromophores [7]. In naphthalimide derivatives, the lower excited state is a charge-transfer state. For the studied compound, the specific interactions in the solid phase are more pronounced than those in the liquid phase. This can be judged from the fact that the fluorescence spectrum of the film is broader and is shifted toward the long-wavelength range as compared to the spectrum of the solution. It should also be noted that, in the solid state, the PAMAM compound retains a high luminescence power and exhibits a fluorescence spectrum over a wide range of wavelengths.

Taking into account the mirror symmetry rule and using the absorption and fluorescence spectra of the studied compound, we found that the lowest unoccupied molecular orbital is located at an energy of 2.4 eV. The barrier to electron injection, which is determined as the difference between the work function and the energy of the lowest unoccupied molecular orbital, amounts to 2.1 eV for both electrodes. Note that the barrier to electron injection can change by 0.5 eV or more due to the inhomogeneities formed in the film upon deposition [8].

The temperature dependences of the electrical conductivity of the PAMAM films measured using the cyclic thermal desorption method in air are depicted in Fig. 3. The set of temperature dependences of the electrical conductivity measured with a gradual increase in the temperature of the PAMAM films from 40 to 75°C was used to determine the preexponential factor  $G_0$  and the activation energy for electrical conduction  $E_a$  in relationship (1) for different concentrations of adsorbed oxygen molecules.



**Fig. 3.** Experimental temperature dependences of the electrical conductivity of the PAMAM films in air.



**Fig. 4.** Correlation between the activation energy and the preexponential factor in the expression describing the temperature dependence of the electrical conductivity of the multilayer structure based on PAMAM according to the results of measurements under high vacuum (circles) and in air (squares).

The results obtained can be interpreted in terms of the relationship between the preexponential factor  $G_0$  and the activation energy  $E_a$ . This relationship accounts for the compensation effect (the Meyer–Neldel rule). The Meyer–Neldel rule asserts that the logarithm of the preexponential factor  $G_0$  in relationship (1) describing the electrical conductivity  $G$  as a function of temperature  $T$  increases linearly with an increase in the activation energy:

$$\ln G_0 = A + BE_a, \quad (2)$$

where  $A$  and  $B$  are constants.

Figure 4 shows a correlation between the activation energy and the preexponential factor in the expression describing the temperature dependence of the electrical conductivity of the multilayer PAMAM structure according to the results of measurements under high vacuum and in air.

The dependence  $\ln G_0(E_a)$  constructed from the results of the measurements of the PAMAM film under

high vacuum is characterized by two portions, namely, portion 1–2 and portion 2–3 (see Fig. 4). In portion 1–2, the preexponential factor increases with an increase in the activation energy. In portion 2–3, the preexponential factor decreases with a decrease in the activation energy. Point 1 is obtained at a minimum temperature of 40°C. Points 2 and 3 correspond to temperatures of 65 and 75°C, respectively. It should be noted that, at a temperature of 75°C, the concentration of adsorbed oxygen molecules reaches a maximum and no evaporation of the sample is observed. The dependence  $\ln G_0(E_a)$  constructed according to the results of measuring the PAMAM film in air is also characterized by two portions (Fig. 4). In portion 1–2, the preexponential factor decreases with a decrease in the activation energy. In portion 2–3, the preexponential factor increases with an increase in the activation energy. In this case, too, point 1 is obtained at a minimum temperature of 40°C. Points 2 and 3 correspond to temperatures of 50 and 75°C, respectively. At 75°C, no evaporation of the sample is observed.

The experimental data obtained in this work made it possible to evaluate the localization length of electrons. According to the results of the measurements performed in air and under high vacuum, the localization lengths of electrons were estimated at 0.61 and 1.13 Å, respectively. The localization length of electrons characterizes the height of the potential barrier between the localized states. The smaller the localization length, the higher the potential barriers separating the localized states and, correspondingly, the deeper the electron energy levels providing charge carrier transfer. For comparison, the localization length of electrons is equal to 8.9 Å for copper phthalocyanine and 1.2 Å for perylene pigment.

In order to interpret the results obtained, we used a model of two-level hopping electron transfer [9], according to which one of the two systems of energy levels corresponds to intrinsic states of electrons in PAMAM molecules and the other system is associated with the states of electrons in adsorbed oxygen molecules. These two systems of energy levels differ in the localization length of electrons. The localization length of electrons in the intrinsic states is designated by  $a_1$ , and the localization length of electrons in the impurity states is denoted by  $a_2$  ( $a_2 > a_1$ ).

The electrical conductivities  $G_1$  and  $G_2$  for the aforementioned two systems of electron energy levels can be written in the form

$$\begin{aligned} G_1 &= (G_{03})_1 \exp\left(-\frac{\alpha}{a_1 n_1^{1/3}} - \frac{E_{a1}}{kT}\right), \\ G_2 &= (G_{03})_2 \exp\left(-\frac{\alpha}{a_2 n_2^{1/3}} - \frac{E_{a2}}{kT}\right), \end{aligned} \quad (3)$$

where  $(G_{03})_1$  and  $(G_{03})_2$  are constants dependent on the localization length of electrons in the intrinsic and

impurity states, respectively;  $\alpha = 1.73$  is the three-dimensional percolation constant;  $n_1$  and  $n_2$  are the concentrations of centers of electron localization in the intrinsic and impurity states, respectively; and  $E_{a1}$  and  $E_{a2}$  are the activation energies for intrinsic and impurity conduction, respectively. The activation energies  $E_{a1}$  and  $E_{a2}$  can be determined from the relationships

$$E_{a1} = \frac{1.61 e^2 n_1^{1/3}}{4\pi\epsilon_0\epsilon}, \quad E_{a2} = \frac{1.61 e^2 n_2^{1/3}}{4\pi\epsilon_0\epsilon}, \quad (4)$$

where  $\epsilon_0$  is the permittivity of free space and  $\epsilon$  is the relative permittivity.

The concentrations of centers of electron localization in the intrinsic and impurity states are related by the expression

$$n_1 + n_2 = n = \text{const}, \quad (5)$$

because the impurity energy levels are formed through splitting off from the band providing electron transfer in a material free from impurities. Therefore, the electrical conductivity in the material containing impurities can be represented by the formula

$$G = G_1 + G_2. \quad (6)$$

In this case, the temperature dependence of the electrical conductivity is adequately described by relationship (1) and the experimentally observed activation energy in this relationship can be calculated from the expression

$$E_a = -\frac{\partial(\ln G)}{\partial(1/kT)}. \quad (7)$$

By using this expression with due regard for relationships (3)–(6), we obtain the formula

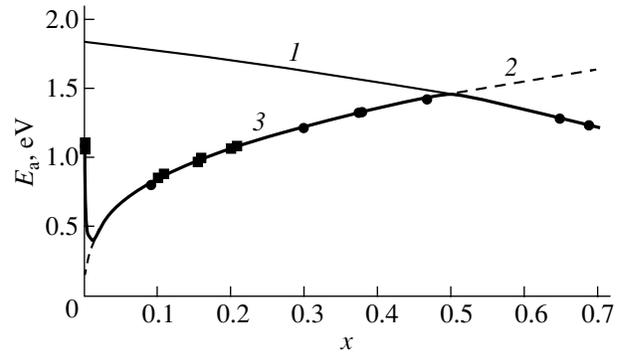
$$E_a = \frac{E_{a1}G_1 + E_{a2}G_2}{G_1 + G_2}. \quad (8)$$

Consequently, the preexponential factor in the expression describing the temperature dependence of the electrical conductivity can be calculated from the relationship

$$G_0 = G \exp\left(\frac{E_a}{kT}\right). \quad (9)$$

When interpreting the experimental results in the framework of the proposed model of two-level hopping electron transfer, it can be assumed that the presence of several portions in the dependences  $\ln G_0(E_a)$  obtained from the measurements in air and under high vacuum (Fig. 4) corresponds to two mechanisms of electrical conduction, namely, conduction through the intrinsic states of electrons in PAMAM molecules and conduction through the impurity states of electrons in adsorbed oxygen molecules.

The experimental dependences of the activation energy on the relative impurity concentration  $x = n_2/n_1$



**Fig. 5.** Dependences of the activation energy on the relative concentration of adsorbed oxygen according to the results of measurements in air (circles) and under high vacuum (squares). Curves represent the results of calculations from relationships (7) and (8) for (1) intrinsic conduction, (2) impurity conduction through the electron states of adsorbed oxygen, and (3) conduction through a combined system of the intrinsic and impurity states.

and the corresponding dependences calculated in the framework of the proposed model [9] are compared in Fig. 5. Analysis of these dependences revealed the following features: (i) charge transfer predominantly occurs through a combined system of intrinsic and impurity states at small relative concentrations  $x < 0.02$ , (ii) a crossover to electrical conduction through the impurity states is observed at larger values of  $x$ , and (iii) charge transfer proceeds through the intrinsic states at  $x > 0.5$ . For the PAMAM film, there are points lying in all three concentration ranges. The calculations were performed for the parameters  $n_1 + n_2 = 9 \times 10^{27} \text{ m}^{-3}$ ,  $a_1 = 0.09 \text{ nm}$ ,  $a_2 = 0.1 \text{ nm}$ , and  $\epsilon = 1$ . Permittivity was chosen equal to unity because the mean distance between the centers of electron localization in organic dyes is relatively small. This circumstance makes it impossible to use the macroscopic parameters of field screening.

Thus, the excellent agreement between the calculated and experimental dependences of the activation energy on the relative concentration of adsorbed oxygen allows us to draw the conclusion that electrical conduction in PAMAM films is associated with the hopping transfer of electrons. Depending on the concentration of adsorbed oxygen, this transfer can proceed either through the intrinsic states of electrons in PAMAM molecules or through the states of electrons in adsorbed oxygen molecules.

## ACKNOWLEDGMENTS

This work was supported in part by the Belarussian Ministry of Education (project no. GB23-119) and the Belarussian Foundation for Basic Research (project no. F03MS-048).

## REFERENCES

1. A. V. Kukhto, Zh. Prikl. Spektrosk. **70**, 151 (2003).
2. T. D. Anthopoulos, J. P. J. Markham, E. B. Namdas, I. D. W. Samuel, S.-C. Lo, and P. L. Burn, Appl. Phys. Lett. **82**, 4824 (2003).
3. K. Inoue, Prog. Polym. Sci. **25**, 453 (2000).
4. I. Grabchev, X. Qian, V. Bojinov, Y. Xiao, and W. Zhang, Polymer **43**, 5731 (2002).
5. I. Grabchev, V. Bojinov, and J.-M. Chovelon, Polymer **44**, 4421 (2003).
6. A. E. Pochtenny, D. I. Sagaridak, G. G. Fedoruk, and A. V. Misevich, Fiz. Tverd. Tela (St. Petersburg) **38**, 2592 (1996) [Phys. Solid State **38**, 1422 (1996)].
7. V. V. Gruzinskiĭ, A. V. Kukhto, É. É. Kolesnik, G. Kh. Shakkakh, and R. A. Minakova, Zh. Prikl. Spektrosk. **64**, 603 (1997).
8. A. V. Kukhta, E. E. Kolesnik, N. A. Shipitsa, and A. L. Zharin, in *Abstracts of the 4th International Conference on Electroluminescence of Molecular Materials and Related Phenomena* (Cheju, Korea, 2003), p. 68.
9. A. E. Pochtenny and A. V. Misevich, Pis'ma Zh. Tekh. Fiz. **29** (1), 56 (2003) [Tech. Phys. Lett. **29**, 26 (2003)].

*Translated by O. Borovik-Romanova*