

## A Study on the Structural, Electrical and Dielectric Properties of Fluorescein Dye as a New Organic Semiconductor Material

A Salem

Solid State Lab, Physics Department, Faculty of Science, South Valley University, Qena, Egypt.

**Abstract:** In this article the structural, electrical, dielectric and optical properties of a new semiconductor material (fluorescein dye) have been investigated. Measurements showed that fluorescein dye activation optical band gap value is less than half that of intrinsic semiconductors. The DC-, AC-conductivities, dielectric permittivity ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) of fluorescein dye have been measured in the temperature range 330-423 K and in the frequency range 50 Hz - 1MHz. Conductivity studies were conducted under the influence of a DC and AC electric fields. The DC electrical conductivity of fluorescein dye exhibited almost a similar behavior to that of organic semiconductors. The mechanism of the AC conductivity of fluorescein dye is controlled by the correlated barrier hopping model, as confirmed by an observed reduction in activation energy. Also, the lattice parameters were calculated from the XRD results.

**Keywords:** New Organic Semiconductor Materials, Structural, Electrical, Dielectric Properties.

### I. Introduction

Fluorescein compounds are widely used as organic dyes for many practical purposes. Recently, they have attracted great attention due to their interesting electronic features. They possess many advantages like light weight, cheap cost, ease of preparation and designation of the devices prepared from them at the micro level as well as their high absorption coefficient and ease of handling. They can be easily functionalized to attain the required quality of electrical and optical properties desirable for various technological applications. The chemical formula of fluorescein is  $C_{20}H_{12}O_5$  with a molecular weight of 332.31 and the chemical structures of fluorescein is shown in Figure 1 [1].

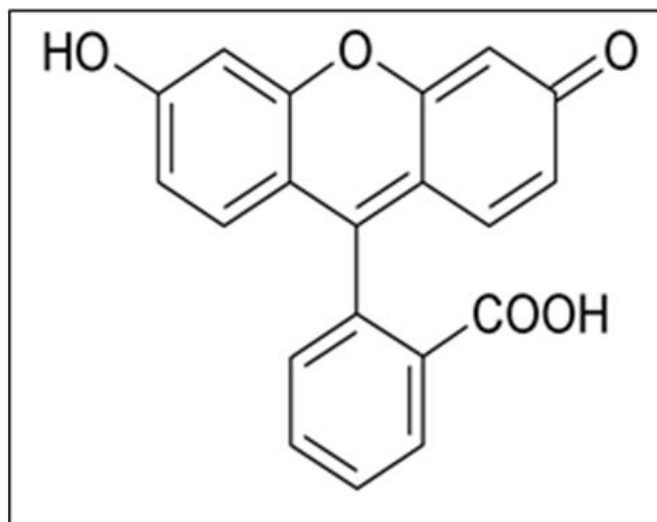


Figure. 1 The chemical structure of fluorescein dye. [1].

Fluorescein dye belongs to the family of Xanthenes. It is prepared by heating resorcinol with phthalic anhydride (2:1) at 200 °C for 10 min. As a result, water insoluble red powder is formed which can be used in the form of a dilute solution of the dye in caustic soda. When exposed to light, it exhibits a chartreuse fluorescence (a strong yellow-green fluorescence). Fluorescein has an absorption maximum at 494 nm and emission maximum of 512 nm (in water).

These substances are used for the manufacturing of photoreceptors as generators for shipments in light photography as well as for the production of photovoltaic cell. Many of them, of particular crystalline phase (which has electrical properties in case of blackouts and similar semiconductor lighting classic) are known and some of which are characteristics of intrinsic semiconductor [1].

The present study focuses on the investigation of the structural, optical and electrical properties (under the influence of a DC and AC electric field) of fluorescein dye and also on the measurement of its dielectric constant as such data is not available in the literature.

## II. Experimental details

Fluorescein dye was purchased from Sigma Aldrich Co., and the powder samples were pressed to a disk using the hydraulic piston (Hydraulic pressure = 9 ton). The diameter of the sample is 1 cm and its thickness equals 1 mm. The samples were characterized using Shimadzu X-ray Diffractometer (XRD - 6000) with  $\text{CuK}_\alpha$  irradiation ( $\lambda = 1.54187 \text{ \AA}$ ). Precise measurements of the DC electrical conductivity were carried out and the DC-measurement circuit consists of holder measurable. The holder was connected to a high-voltage battery (up to 1000 V), voltmeter, ammeter (have high sensitivity to measure the electrical current in the extent of pico-ammeter) and Lemaitre with high sensitivity to measure the electrical current in the extent of pico-ammeter. This circuit is designed to measure high resistance under the influence of DC current. The circuit is placed inside an oven which is connected with a temperature organizer. It is also worth mentioning that the circuit is designed to measure high resistance under the effect of continuous current and the holder placed inside the oven is connected with a digital temperature control for precise regulation of temperatures up to  $150^\circ\text{C}$ . For measuring the electrical conductivity under the influence of the AC field, HP/ Agilent 4284 A Precision LCR Meter was used to measure each of the impedance and the capacitance of the fluorescein dye sample at different temperatures in the frequency range starting from 150 Hz up to 1 MHz. Fluorescein dye sample was kept in a special holder inside the oven and the temperature was gradually raised up to  $150^\circ\text{C}$ .

## III. Results and discussion

### 3.1. Structure measurements (study of crystal structure of fluorescein dye)

Figure 2 shows the crystal structure of fluorescein dye. Miller indices and the crystal parameters of it were calculated. Crysfire and Checkcell programs (CRYSFIRE & CHECKCELL, 2000) [2-3] were used to index all the diffraction lines, calculate the Miller indices (hkl) and the interplanar spacing ( $d_{hkl}$ ) values for each diffraction peak and finally to calculate the lattice parameters for the sample under study, where there is no known card [4-5]. It has been found that the crystal is orthorhombic that it has three axes of unequal length intersecting at an angle of  $90^\circ$  and the lattice parameters of the unit cell are as follows:

$$a = 10.0690 \text{ \AA}, \quad b = 13.2910 \text{ \AA}, \quad c = 21.4670 \text{ \AA}, \quad \alpha = \beta = \gamma = 90^\circ$$

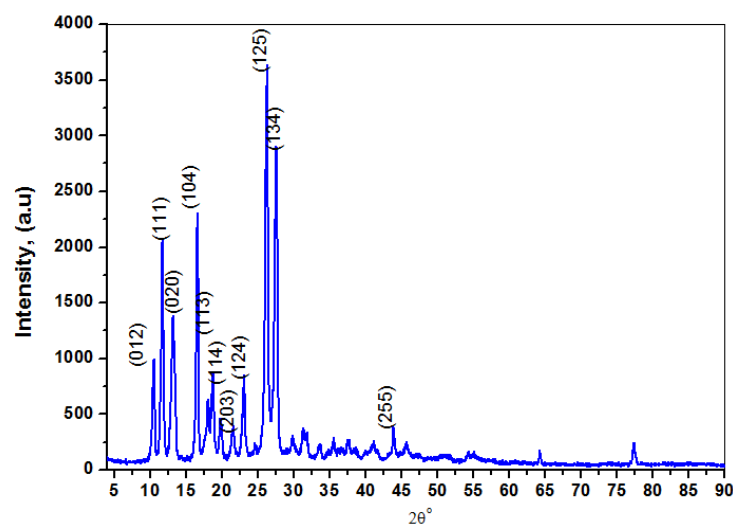


Figure. 2 The powder XRD patterns of fluorescein dye

### 3.2. Electrical measurements

In semiconductors, at low temperatures the valence band is completely filled and the conduction band is completely empty. As the temperature is raised, some electrons from the valence band are able to jump across to the conduction band, leaving behind a gap in the valence band, thus contributing to what is known as the intrinsic conductivity [6]. If an external electric field is applied to this material, some of the electrons can gain a small amount of energy and jump to a higher state in the previously unoccupied section of the conduction band and thus gaining the so-called fast drift velocity [7]. In this process there are two types of charge carriers, electrons in conduction band and holes in the valence band and the intensity of the output current is equal to the total current density yield for both electrons and holes [8]:

$$\bar{J} = \bar{J}_N + \bar{J}_P = (Ne\mu_N + Pe\mu_P) \bar{E} \quad (1)$$

Where:  $J_N$ ,  $J_P$ : current density of electrons and holes.  $P$ ,  $N$ : the number of electrons and holes for the unit volume.  $e$ : electron charge.  $\mu_N$ ,  $\mu_P$ : is the mobility of each of the electron and the holes, respectively.  $E$ : the applied field.

From equation (1) we can find that the electrical conductivity of the semiconductor equals to the conductivity resulting from the negative charge carriers (electrons) and from the positive charge carriers (holes) and therefore the conductivity equation can be written as follows [8]:

$$\sigma = Ne\mu_N + Pe\mu_P \quad (2)$$

In the above equation, we can see that the electrical conductivity depends on two factors: the density of charge carriers and the mobility of these carriers inside the material under the influence of an electric field. The mobility of charge carriers is determined by the interactive(interaction of) electrons and the lattice waves or phonon and is dependent on temperature, where it is found that the mobility in general depends on  $T^{-3/2}$ . the semiconductor has a high negative coefficient of thermal resistance.

The change in conductivity can be described with the temperature equation:

$$\sigma = \sigma_0 \exp\left(\frac{-\Delta E_a}{k_B T}\right), \quad (3)$$

Where:

$\sigma_0$ : a very steady (limit) conductivity at high temperatures.

$E_a$ : activation energy for electrical conductivity.

$K_B$ : Boltzmann's constant.

$T$ : absolute temperature.

$K_B = 1.38 \times 10^{-23} \text{ J / K}$

At high temperatures conductivity is generated because of a thermionic emission process possess enough energy to cross the potential barrier.

The electrical conductivity is calculated under the influence of DC field from the following equation:

$$\sigma_{dc} = \frac{t}{R_{dc} A}, \quad (4)$$

Where:

$R$ : is the resistance of the sample measured by the DC-measurement circuit (ohms).

$t$ : Material thickness (m)

$A$ : The sample area ( $m^2$ ).

In terms of electrical properties, solids are divided into dielectrics, semiconductors, and conductors. The AC conductivity measurement of the material results in important information about the nature of the conduction mechanism of the material using electrical conductivity as a function of the frequency of the AC electric field. Measurements of transmission of carriers in insulating materials are of great significance in recent times because they provide information about the electronic structure of these materials. Many studies have been conducted on the electrical properties and several models for the mechanical electrical conductivity were developed. Experiments showed that there are two types of charge carriers: electrons or ions and there are different mechanisms through which charge carriers can be transmitted in the area under the influence of applied field. Also, insulating materials enters in a lot of electrical systems and are used in a lot of areas, either at the level of micro-electronics or in areas of high pressure [9].

The insulating materials differ from conduction and semiconducting materials where the conduction band is almost empty of free electrons and it is also possible that contain free electrons. In the insulators the valence band is full once again, but in these substances there is an energy gap between this and the empty conduction band which is very large. It would take a great deal of energy to make an electron jump the gap causing the insulator to break down. In spite of the limited movement of the electrons and the non-applicability of the current in the material, this restricted movement is of great importance in determining the properties of the insulating material [9]. When a voltage is applied on an insulating material it leads to variable current so this insulating material could represent the electric circuit called impedance. The impedance results from the resistance and capacity tied in parallel represent the nature of the material. Molecules of dielectric material

consists of positive charges and negative charges and often the center of negative charges applicable to the center of positive charges for these molecules, but when an external electric field is applied on these molecules, the positive charges drift toward the field while the negative charges drift in the opposite direction and as a result, the center of positive charge is no longer applicable to the center of negative charge, but separated by a small distance, causing the emergence of electric dipoles. Thus we can say that the molecule has become polarized and gained dipole moment. These particles of insulating material which is distinguished as such molecules are called non-polar molecules but there are particles of other dielectric materials where the center of the negative charge separate permanently from the center of positive charge. These molecules have permanent dipole moment and are called polar molecules but the directions of these moments are random. If these molecules are placed under the influence of external electric field AC, these moments will rotate towards the field [10].

The impedance can be represented by the following equation [10]:

$$Z = R / \sqrt{1 + R^2 W^2 C^2} = R / \sqrt{1 + JWRC} \tag{5}$$

Where:

$$J = \sqrt{-1}$$

Z: is the impedance of the circle (RC) in parallel

When connecting resistance with capacitor in parallel, the total current value can be represented by the following equation

$$I = I_p + JI_q \tag{6}$$

Where:

$I_p$ : is the current flowing in the resistance,  $I_q$ : is the current flowing in the condenser AC: current which arising from the applied alternating voltage (v) across the capacitor (C) before the voltage the angle of the voltage ( $90^\circ$ ) and describes the following equation [10]:

$$I_q = JwcV \tag{7}$$

If we assume that the condenser consists of two plates of area A and separated by a distance d and between the two plates a thick insulator of permittivity  $\epsilon$  then, the value of capacitance of the condenser is given the relationship:

$$C = \epsilon_0 \epsilon_r A / d \tag{8}$$

Where:  $\epsilon_0 / \epsilon = \epsilon_r$ , the relative permittivity and represent the ambient / vacuum permittivity. The relationship between the dielectric constant  $\epsilon'$ , dielectric loss  $\epsilon''$  and impedance Z is presented by the following two equations [11]:

$$\epsilon' = Z_0 / 2\pi f C_0 (Z_R^2 + Z_C^2) \tag{9}$$

$$\epsilon'' = Z_R / 2\pi f C_0 (Z_R^2 + Z_C^2) \tag{10}$$

Where:

$Z_R$ : the real part of impedance and  $Z_C$ : the imaginary part.  $Z_R$  and  $Z_C$  can be written as follows

$$Z_R = Z \cos\phi \tag{11}$$

$$Z_C = Z \sin\phi \tag{12}$$

The electrical conductivity under the influence of the AC current in dielectric is a measure of the heat generated as a result of rotation of dipoles in their places and depends on the value of the frequency, as shown by the following equation [11]:

$$\sigma = w\epsilon_0 \epsilon'' \tag{13}$$

### 3.3. Electrical conductivity under the influence of DC electric field.

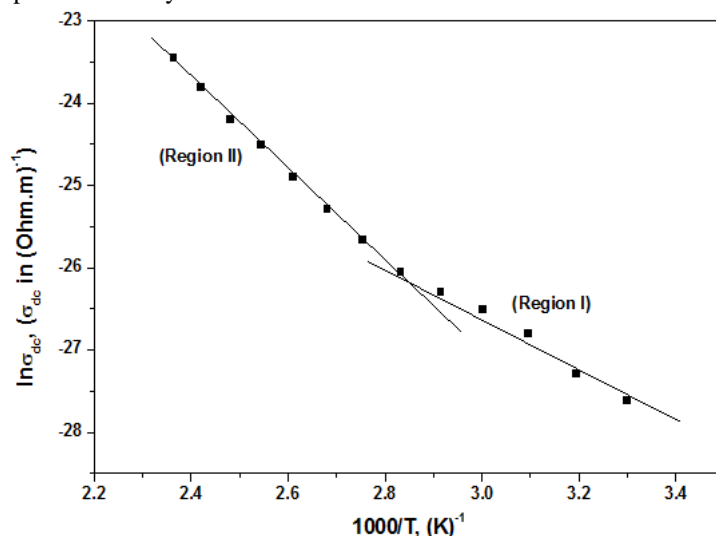
The dc conductivity and resistance are related according to:

$$\sigma = \frac{1}{RA}$$

$\sigma$	=	conductivity	units: $S \cdot cm^{-1}$ or $\Omega^{-1} \cdot cm^{-1}$
$l$	=	thickness	units: cm
$R$	=	resistance	units: $\Omega$
$A$	=	area	units: $cm^2$

Figure 3 Shows a Semi-logarithmic plot of the temperature dependence of the DC electrical conductivity of fluorescein dye. The solid lines represent the best linear fits to the data. It is evident that the electrical conductivity increases with increasing temperature, indicating that fluorescein dye behaves like conventional

semiconductors and represents a new semiconductor material. Two electrical connections through the temperature range studied have been observed, which explains the presence of two mechanisms of electrical conductivity of the sample under study.



**Figure. 3** A Semi-logarithmic plot of the temperature dependence of the DC electrical conductivity of fluorescein. The solid lines represent the best linear fits to the data.

The variation for  $\sigma_{dc}$  of fluorescein at different temperatures.

DC electrical conductivity increases with increasing temperature due to the high mobility of free charges (namely polarons and free ions) at higher temperature indicating that it is fitted to Arrhenius exponential law equation as depicted in Figure 6, which presents the study of electrical conductivity change under the influence of DC power with temperatures by the equation [11-12]

$$\sigma = \sigma_{01} e^{(-\Delta E_1 / KT)} + \sigma_{02} e^{(-\Delta E_2 / KT)} \quad (14)$$

where T is the absolute temperature;  $\sigma_{01}$  and  $\sigma_{02}$  are the highest temperature limits of conductivity, for region I and II, respectively,  $-\Delta E_1$  and  $-\Delta E_2$  are the DC conduction activation energy in joule of the first and second regions, respectively. KT is associated with temperature variation in the measurement where K is Boltzmann constant. The linear regression of the Arrhenius plot  $\ln \sigma_{dc}$  versus  $1000/T$  gives the slope of  $-\Delta E_1$  and  $-\Delta E_2$  values, indicating that there are two conduction mechanisms in the temperature range studied. The conduction activation energy of the conductivity influenced by temperature is the minimum energy required to overcome potential barrier. For both the samples it was observed that there are two straight lines with differing slopes. This means that there are two regions of differing activation energies, one for higher temperature region and the other for lower temperature region. This result also indicates that there are two conduction mechanisms. The activation energies and pre-exponential factors were determined using the least-squares fit of the experimental data to a straight line via origin software. The values  $\Delta E_1$  and  $\sigma_{01}$  for region (I) were found to be 0.294 eV, and  $7.8 \times 10^{-8} (\Omega \text{ m})^{-1}$ , respectively and the values  $\Delta E_2$  and  $\sigma_{02}$  for region (II) were determined to be 0.461 eV, and  $3.23 \times 10^{-5} (\Omega \text{ m})^{-1}$ , respectively. Temperature-dependent measurements of  $\sigma$  reveal that the electrical conduction mechanism is thermally activated process and DC conductivity increases exponentially with increasing temperature over the studied range of temperatures [13]. Electrical conductivity and dielectric relaxation behavior of fluorescein sodium salt (FSS) [14]. The electrical conductivity of all investigated samples was increased with increasing temperature indicating that their electrical conduction mechanism is similar to that of semiconductors.

### 3.4. The study of electrical conductivity under the influence of the AC current.

Electrical conductivity has been calculated under the influence of the AC current ( $\sigma_{tot.ac}(\omega)$ ) through measuring the value of the impedance (Z) at different frequencies and different temperatures. It can be written as follows:

$$\sigma_{tot.ac} = \frac{t}{Z A}, \quad (15)$$

Where:

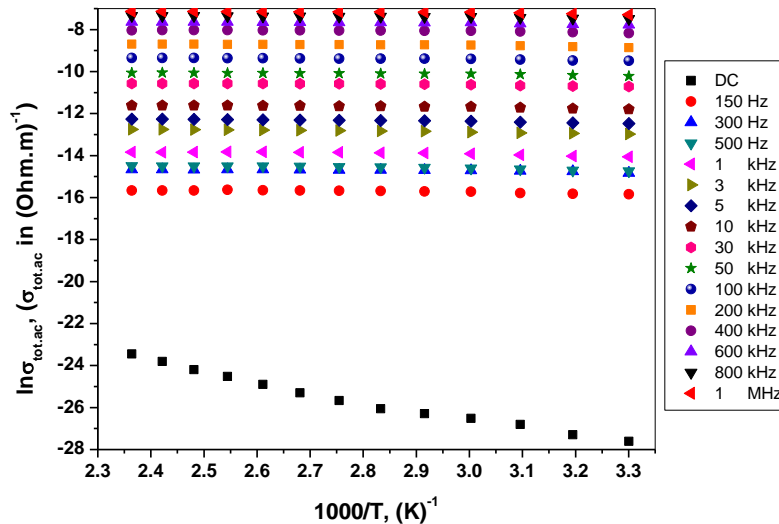
Z: is the measured impedance of the sample through the measuring circuit (ohms).

t: material thickness (m)

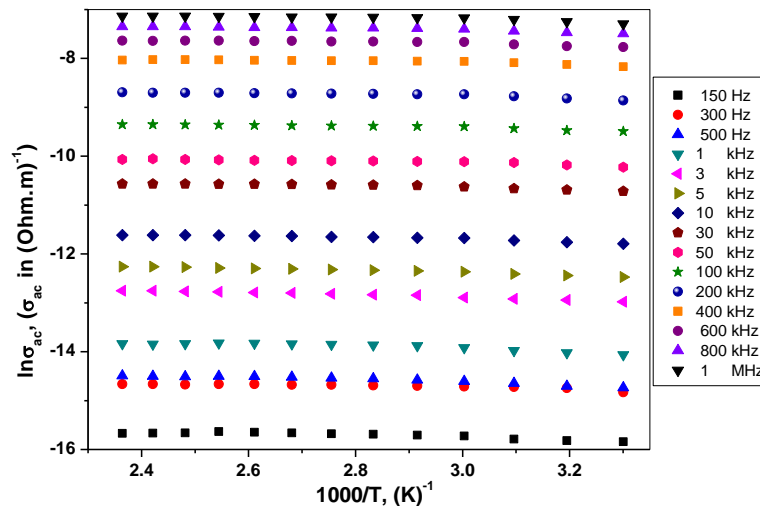
A: area of the sample (m<sup>2</sup>). The measured conductance, G (ω) from 150 Hz up to 1 MHz was used to calculate ac conductivity; σ<sub>AC</sub> (ω) is shown in Figure (4) and using the following expression [15-16]:

$$\sigma_{tot.ac}(\omega) = \sigma_{ac}(\omega) + \sigma_{dc}(\omega \rightarrow 0) , \tag{16}$$

where ω is the temporal frequency. The first part is a frequency and temperature-dependent term which is related to the dielectric relaxation of bound charge carriers (dipoles) as determined from orientational polarization. This accounts for the free charges resident in the bulk and is often taken to be independent of frequency [16-19]. At high temperatures, compositions with high conductivity show Arrhenius behavior and the variation with frequency is small.



**Figure. 4** Temperature dependence of the calculated total electrical conductivities σ<sub>Total.AC</sub>(ω) plotted in Arrhenius coordinates at different frequencies for fluorescein dye.



**Figure. 5.** Double logarithmic plots of temperature dependence of the AC conductivity σ<sub>AC</sub>(ω) for fluorescein dye at various frequencies.

At low temperatures, AC conductivity shows only a weak temperature dependence and a little bit higher and with the increase in temperature dependence on temperature becomes clear and also with increasing frequency. It has been observed that under the influence of the AC field electrical conductivity increase, means improving the conductivity with the existing values of the AC field.

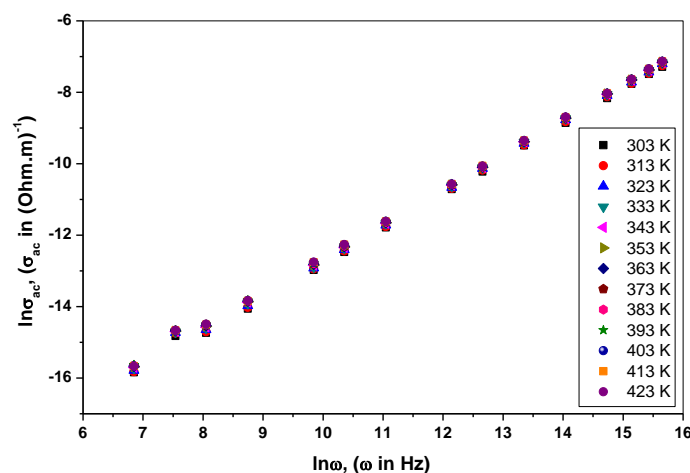
Figure 4 shows the frequency dependence of AC conductivity σ<sub>AC</sub>(ω) for the fluorescein dye at the different temperatures. A common feature to all amorphous semiconductors is that AC electrical conductivity σ<sub>AC</sub>(ω)

increases with increasing frequency according to the equation. The AC conductivity of the sample is expressed with the help of following equation [15-19]:

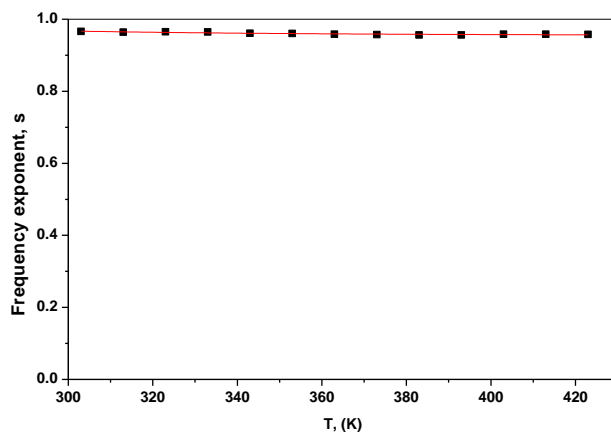
$$\sigma_{AC}(\omega) = \sigma_{tot}(\omega) - \sigma_{DC} = A(\omega)^s, \tag{17}$$

where  $\omega$ : the angular frequency ( $\omega = 2 \pi \nu$ ),  $\sigma_{tot}(\omega)$ : the measured total electrical conductivity,  $\sigma_{DC}$ : the DC electrical conductivity,  $s$ : the frequency exponent ( $s < 1$ ) and  $A$ : a constant dependent on temperature. The frequency exponent ( $s$ ) is characteristic of many of the objects interactions: electrons charges and impurities found in the body.

Figure 5 shows double logarithmic plots of temperature dependence of the AC conductivity  $\sigma_{AC}(\omega)$  for fluorescein dye at various frequencies. The value ranges from zero up to one and the frequency exponent ( $s$ ) is related to charge carriers or to intrinsic-dipoles arising from impurities or defects in the material [15-17, 20]. The frequency exponent ( $s$ ) is very important factor in the electrical measurements under the influence of the AC field which can clarify the type of conductivity mechanism of the sample under study. The  $s$  values were calculated from the slope of straight lines in Figure 6 according to the relationship  $\ln \sigma_{ac}(\omega) = f(\omega)$ . Figure 7 shows the temperature dependence of the frequency exponent  $s$  for fluorescein dye and it is clear from this figure that  $s$  decreases with temperature which suggests that the frequency dependence of  $\sigma_{ac}(\omega)$  for present material can also be explained by the correlated barrier hopping (CBH) model [15].



**Figure. 6** Frequency dependence of the AC conductivity ( $\sigma_{ac}$ ) for fluorescein dye at various temperatures.



**Figure. 7** Temperature dependence of the frequency exponent  $s$  for fluorescein dye.

#### IV. Conclusions

A new organic dye which can be used in the field of organic semiconductors and their applications in various electronic devices and Photovoltaic has been proposed. Optical measurements, the DC-, AC-conductivities, dielectric permittivity ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) of fluorescein dye have been measured for the first time. An X-ray diffraction instrument has been used to determine the structural and crystalline size of

fluorescein dye.

### References

- [1]. U B RACKMANN (*Lambda Physic* 2000), 3<sup>rd</sup> edition.
- [2]. R Shirley The Lattice Press, *Guildford Surrey GU2 7NL*, England, (2000).
- [3]. A A M Farag and I S Yahia *Synthetic Metals* **161** 32–39 (2011).
- [4]. I S Yahia M S Abd El-sadek, F Yakuphanoglu *Dyes and Pigments* **93** 1434-1440 ( 2012).
- [5]. J Laugier, B Bochu ENSP/*Laboratoire des Matériaux et du Génie Physique Saint-Martind'Hères*, France, vol.**46**, pp.38042, (2000).
- [6]. J S Blakemore, A E de Barr, and J B Gunn *Rep. Prog. Phys.* **16 160**. doi:10.1088/0034-4885/16/1/305 (1953).
- [7]. SOLID STATE PHYSICS PART II Optical Properties of Solids – MIT.
- [8]. Chapter 2: Semiconductor Fundamentals. Online textbook by B. Van Zeghbroeck.
- [9]. P Gonon , A Sylvester "*Material Science and Engineering*" **83** 158 (2001).
- [10]. H Yang, *HWang* **116** 418 – 421 (2008).
- [11]. M Rama Roa, D Roy and J K D Verma *J. Phys.* **18** 517 (198).
- [12]. Sh A Mansour, I S Yahia, F Yakuphanoglu *Dyes and Pigments* **87** 144 (2010).
- [13]. Mansour Sh A, Yahia I S, Yakuphanoglu F. *Dyes Pigments*; **87**: 144.AND Mansour Sh A, Yahia IS, Sakr GB (2010).
- [14]. *Solid State Commun*; 150:1386e91 (2010).
- [15]. S R Elliott *Adv. Phys.* **36** 135 (1987).
- [16]. N F Mott, E A Davis *Clarendon Press Oxford* (1971).
- [17]. A K Jonscher, *Nature* **267** 673 (1977).
- [18]. M A Afifi, A E Bekheet, E Abd El Wahabb, H E Atyia *Vacuum* **61** 9–17 (2001).
- [19]. N F Mott, E A Davis, *Clarendon Press, Oxford*, (1971).
- [20]. Yakuphanoglu F, Erol I *Physica B* 352 352 (2004).