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Study the fluorescent and conductivity properties of a 4-hydroxy-3-nitro-1,8-naphthalic anhydride

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Abstract. The compound of (4-hydroxy-3-nitro-1,8 -naphthalic anhydride) and the dopant material (4-hydroxy-m-benzene-disulfonic acid) were synthesized. The UV- Vis absorption and fluorescence spectra of the compound were recorded. The bathochromic shifts in absorption due to the changes in the solvent polarity was observed, in DMSO solvent, the compound shows different peaks, three bands in the UV region and one band in the visible region, one absorption peak at 402 nm, which might be attributed to the (ICT) band. The emission spectra of this compound were sensitive to the solvent polarity. They moved to lower energies with increasing the polarity of the solvent. The influence of the solvent polarity on the fluorescence maximum was more pronounced compared with the absorption maximum, showing *ca.* 3 nm red shift on moving from butanol to DMSO. The effect of the dopant material on the conductivities (ionic and specific) of the compound was studied, the ionic conductivity was increased as the weight of the dopant material increases, and the ionic conductivity (G) was measured in water as a solvent. the (G) of the compound was 2.4×10^{-6} Siemens at 0.01 gm of the dopant material, and was 2.62×10^{-4} Siemens after the dopant material was added (0.1 gm).

1. Introduction

There are many photophysical properties for the 1,8-naphthalimide compounds for example, the stability of these compounds (i.e. optical, thermal and chemical stabilities) in addition to high quantum yield and the medical applications for example, anticancer operators, these compounds are used in the fields of high-tech , such as liquid crystal displays, and transformation of solar energy [1]. The internal charge transfer (ICT) obtains when an amine or hydroxyl is attached in the 4-position of 1,8-naphthalimide, which gives the efficient fluorophore. The 4-substituted derivatives show excellent properties such as, large Stokes Shift and cell permeable. The compound of 4-hydroxy-1,8-naphthalimide fluorophore is used as a fluorescent for the cellular imaging of nitroxyl. The ratiometric probes can be designed by the esterification of the hydroxyl analogues, which give the hypsochromic shift (is a change of spectral band position in the absorption, or emission spectrum of a compound to a shorter wavelength of the fluorescence maximum [2]).

The 1,8-naphthalimides compounds are used for many applications for example optoelectronic and organic electronics, therefore it is important to prepare new derivatives compounds which are essential to use in the photo-physics, pH/metal/anion sensing and chemical photostability. The other applications of naphthalimide derivatives in the organic electronic area, the photovoltaic cells which require the compounds show good charge separation capability, in addition to these derivatives can be



used as energy donor or acceptor in many energy transfer systems. The extending of the π - conjugation results to the shift to longer wavelengths [3]. There are many potential applications of the derivatives of the naphthalimide which are related to organic production of electric current which is defined as a photovoltaics. The using for the example the compound 4-bromo- naphthalic anhydride which is used as a starting material, and the push-pull chromophores are obtained by the substituents. Naphthalimide-setup systems are utilized as fluorescent signs in the imaging applications and molecular biology [4].

The 1,8- naphthalimide derivatives have been used as fluorescent dyes, and metal sensors due to the good fluorescence properties, such as excellent emission and quantum yields and high absorption coefficients, large Stokes Shifts, and good stability. The naphthalimide derivatives contain an O,N,S- substituted group, or heterocycle with five-member in the C-4 position contain an electron donating group, which it is important to extend the materials, including different groups, such as (electron-donating), for example hydroxyl or ester group to explore the fluorescence property [5]. The mechanism of intramolecular charge transfer is obtained by the 1,8-naphthalimide compound which contains the groups of an electron donor, an acceptor and its derivatives for example, 4,5-diamino-1,8-naphthalimide and 3,4-diamino-1,8-naphthalimide [6]. The 1,8-naphthalimide derivatives have been used in the DNA intercalates and cellular imaging agents therefore they appeared the good antitumor activities, the 4-Bromo-1,8-naphthalimide exhibited a good inhibitor in the blood products [7].

The compound of 6-Dimethylamino-2,3-naphthalimide (6-DMN) is displayed intramolecular charge transfer fluorophore which appears positive solvatofluorochromism, the fluorescence of the compounds 5- and 6-amino-2,3-naphthalimides is affected by the solvent which the colour changed covering the visible region [8]. The compound of 1,8-Naphthalimide appears high photostability which the fluorescence wavelength in the visible region. Therefore, the naphthalimide- markers fluorescent has many excellent properties for example solubility is low in water, and low changes in the environment for example temperature and oxygen concentration [9].

The 1,8- naphthalimide derivatives show good emission, therefore they are used as colorants in the industry of polymer, emission probes for biological applications, and in the organic light-emitting diodes. The 1,8-naphthalimide possesses a good fluorescent properties, depend on the groups which are strong electron-donating, for example alkoxy and alkyl amine at the C-4 position [10]. The naphthalimide compounds are used as colourful dyes and absorbing dyes, and in the artificial light harvesting arrays, in addition to in the fluorescent chemical probes for the sensing in the biological applications [11].

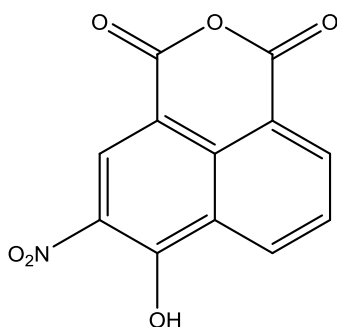


Figure 1. The structure of the compound

In the current work, we report the synthesis of 4-hydroxy-3-nitro,1,8-naphthalic anhydride, figure 1 explains the structure of the prepared compound, the dye was synthesized by a direct method. The UV- visible absorption and fluorescence properties and ionic conductance were elaborated. Application in conductance by using dopant material (4-hydroxy-m-benzene-disulfonic acid) was investigated.

2. Material and methods:

2.1. Synthesis:

1. The synthesis of 4-hydroxy-3-nitro-1,8-naphthalic anhydride: 4-bromo-3-nitro-1,8-naphthalic anhydride (32.2 gm, 0.1 mole) was stirred in 200 ml of aqueous sodium hydroxide (20%) for eight hours at 80-85°C. The solution (dark red) was cooled, poured into ice-cold (500 ml) of 10% hydrochloric acid, stirred and filtered to give the sallow yellow deposit [12].
2. Synthesis of 4-hydroxy-m-benzene-disulfonic acid: In a dry 500 ml flask, phenol 31 gm (0.33 M) and concentrated sulphuric acid 116 gm were mixed. A boiling water bath was used to heat the mixture, in three hours by using the mechanical stirrer. The mixture was cooled to room temperature or below in ice water, and a solution of (95 gm of NaOH in 235 ml water) was added slowly, the solid product was separated [13].

3. Results and discussion:

3.1. The photophysical properties (UV-Visible absorption)

The UV-Visible absorption of the compound 4-hydroxy-3-nitro-1,8-naphthalic anhydride in different solvents, for example dimethyl sulfoxide DMSO, ethanol, and butanol was listed to study its spectral features in many solvents of various polarity figures 2, 3 and 4. The wavelengths identical to the spectral peaks are shown in table (1).

Table(1). Absorption and emission data for the 4-hydroxy-3-nitro-1,8-naphthalic anhydride compound in different solvents.

Solvents	Absorption maxima (nm)	Fluorescence maxima (nm)
ethanol	244	362
butanol	220	356
DMSO	284, 292, 308, 402	359, 302
DMF	-	356

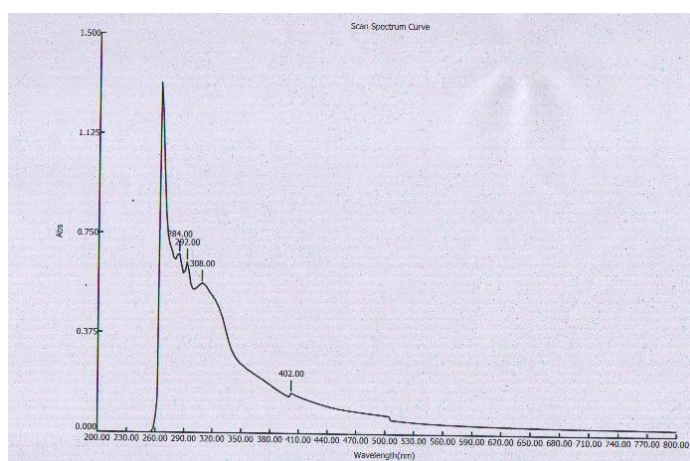


Figure 2. The UV-Visible in DMSO solvent for the 4-hydroxy-3-nitro-1,8-naphthalic anhydride compound

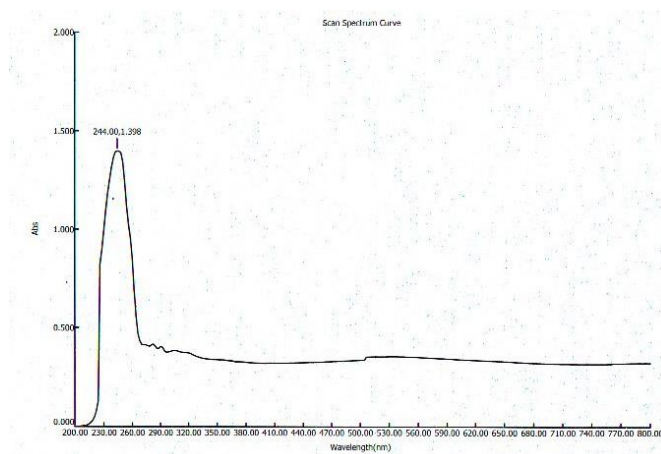


Figure 3. The UV- Visible in ethanol solvent for the 4-hydroxy-3-nitro-1,8-naphthalic anhydride compound

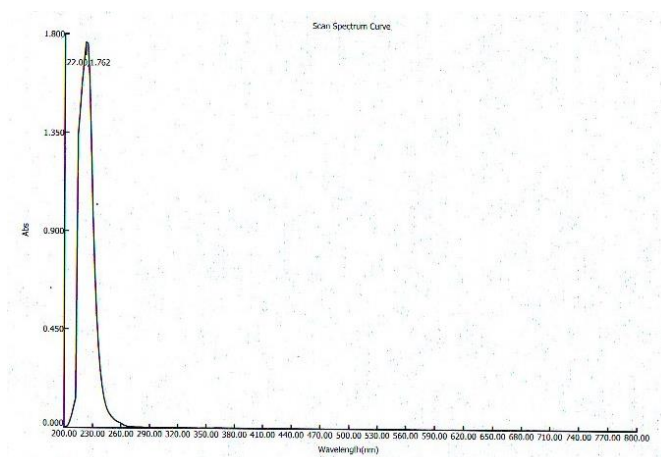


Figure 4. The UV- Visible in butanol solvent for the 4-hydroxy-3-nitro-1,8-naphthalic anhydride compound

As shown in the absorption spectra, the compound has a normal high-energy broad band at 244 nm in some solvents, such as ethanol. In butanol solvent the absorption maxima is 220 nm compared with the other solvents such as ethanol and DMSO (244, 284) nm respectively. Therefore, the bathochromic shifts in absorption due to the changes in the polarity of the solvent was shown, such as in ethanol the compound had a λ_{max} value at 244 nm, and a red shift in absorption for the solvent that was more polar, DMSO at 284 nm. The impact of the substituents groups at C-4 was studied, it can be seen that the ability of the methoxy ethoxy groups as a stronger electron-donating than methoxy [10]. In DMSO solvent, the compound shows different peaks, three bands in the UV region and one band in the visible region, one absorption peak at 402 nm, which might be attributed to the (ICT) band [11]. The peak of this absorption band shows at about 244 nm in ethanol solvent, which red shifted for about 24 nm in proportional to that of this compound in butanol solvent. In DMSO solvent, the compound shows the absorption peak at 402 nm, which can be attributed to the ICT, and another band in the UV region 284 nm, which might be attributed to the absorption of naphthalic ring transition. The replacement of ethanol with DMSO leads to a 40 nm red-shift on the band in the UV-region, depends on the solvent polarity, while the replacement of ethanol with butanol, leads to a 24 nm blue shift.

The red shift on the maximum in the absorption spectrum band of this compound in polar solvents compared with less polar-solvent is due to the stabilization of the polar ICT excited states which leads

to reduce the energy gap between the states i.e. ground and excited, and leads to the red-shift on the maximum absorption band [11].

It could be easily followed from the data that there is a significant downward shift in the wavelength of the absorption with decrease in the polarity of the solvents, for example ($\lambda_{\max, \text{DMSO}} = 284$ nm, $\lambda_{\max, \text{ethanol}} = 244$ nm, $\lambda_{\max, \text{butanol}} = 220$ nm). The absorption maximum of the compound in DMSO solvent is 64 nm bathochromic shifted than that of this compound in butanol. The position of the electron-donating group, such as amino group leads to increase the intramolecular hydrogen bond strength [14].

The fluorescence spectra:

The fluorescence spectra of the compound 4-hydroxy-3-nitro,1,8-naphthalic anhydride are displayed in figures 5,6,7 and 8. It can be showed from the figures that the emission spectra of this compound were sensitive to the polarity of the solvent. They moved to lower energies with increasing the solvent polarity (table 1). The influence of the solvent polarity on the fluorescence maximum was more pronounced compared with the absorption maximum, showing *ca.* 3 nm red shift on moving from butanol to DMSO, the compound of 4-amino-1,8-naphthalimides have ICT character in the excited states of these compounds [15]. The fluorescence maxima is equal to 356 nm in butanol compared to other solvents such as DMSO and DMF (359, 356 nm) respectively. The fluorescence maximum shifts to red in polar solvent, such as in DMSO ($\lambda_{\max} = 359$ nm) while in less polar solvent, such as DMF ($\lambda_{\max} = 356$ nm). The three peaks (301, 350, 600) nm in butanol solvent so it is expected that it might make CT complex with the electron donating in polar solvent.

This can be qualified to the polar solvents solvation to the polar ICT excited states, therefore the energy of the excited states is decreased, and then caused the significant red-shift of the fluorescence maximum peak [11]. Therefore, the polarity of the solvent is caused the red shift at the luminescence wavelength. In general, the emission intensity is shifted to a longer wavelength as the solvent polarity is increased [16]. The red-shifted might be result from the capabilities of the electron-withdrawing and electron-donating groups of the substituents of the benzene. The hydroxyl group is exerted a steric effect, and influenced in the fluorescence maximum and resulted in a bathochromic shift, such as in 1-butanol and DMF ($\lambda_{\max} = 356$ nm).

The presence of electron-deficient substituent or less electron-rich is caused a ICT-induced blue shift in the fluorescence peak [17]. The solvent polarity triggered a significant bathochromic shift 3 nm of the emission wavelength of this compound with increasing solvent polarity from DMF to DMSO, and 6 nm from butanol to ethanol, in DMSO it is expected that it might make CT complex with the electron donating. The fluorescence maximum is correlated with solvent polarity, which is result in the stabilization in the less polar solvent, such as ethanol $\lambda_{\max} = 362$ nm, the π - π^* is responsible for its fluorescence which is the lowest singlet excited state [18].

FT-IR spectroscopy:

The FT-IR was used for the characterization of the compound (4-hydroxy-3-nitro,1,8-naphthalic anhydride), figure 9, the FT-IR data showed stretching band at 1554 cm^{-1} for C=C, and the band at 3070 cm^{-1} for the stretching (C-H) (19), the bands at $1438, 1388 \text{ cm}^{-1}$ are due to the NO_2 stretching (asymmetry and symmetry) (20). The bands at $1604, 1635 \text{ cm}^{-1}$ are due to the C=O (carbonyl stretching) [19], the aromatic C-H bending at about 1033 cm^{-1} [20]. The C-N band at 1195 cm^{-1} , the OH band at 3421 cm^{-1} and the band C-OH cm^{-1} at 1033 cm^{-1} [21].

The ionic conductivity:

The ionic conductivity (G) was measured in water as a solvent, and the cell constant is equal to 9.5 cm^{-1} . The effect of the dopant material (4-hydroxy-m-benzene disulfonic acid) on the conductivities for this compound is shown in figure 10.

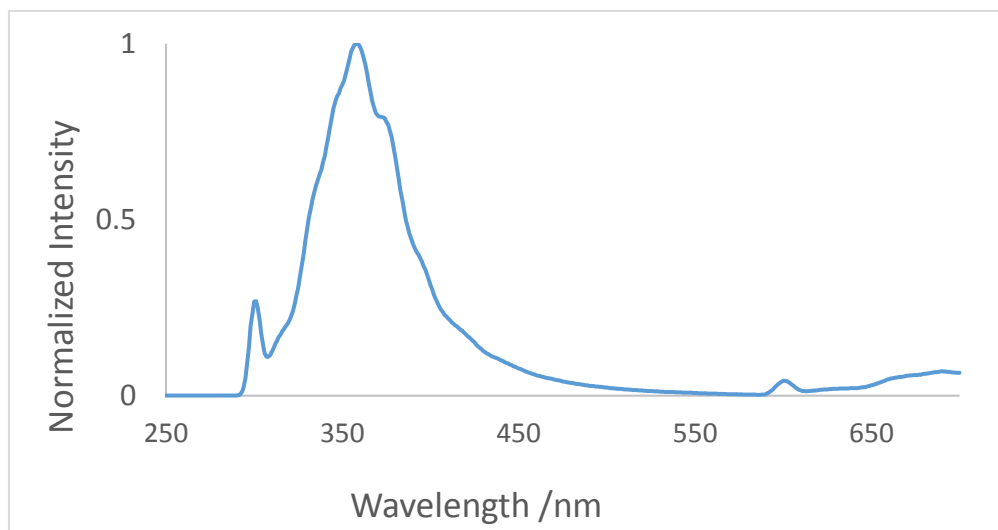


Figure 5. The fluorescence spectrum of the compound in DMSO for the 4-hydroxy-3-nitro-1,8-naphthalic anhydride compound

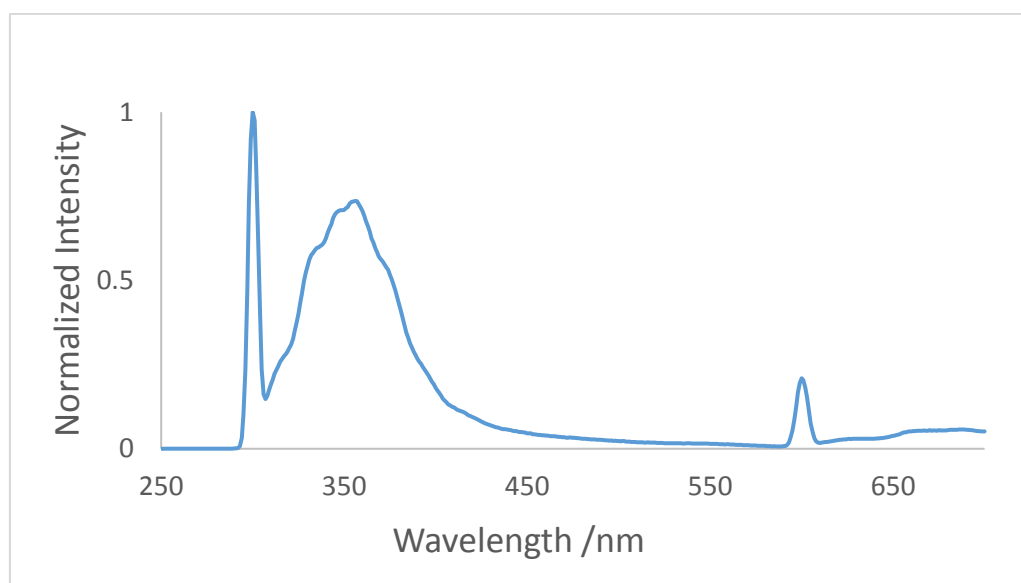


Figure 6. The fluorescence spectrum of the compound in DMF for the 4-hydroxy-3-nitro-1,8-naphthalic anhydride compound

It is apparent that the conductivity increases as the increasing of the dopant material weights, the (G) of the compound was 2.4×10^{-6} Siemens at 0.01 gm of the dopant material, and was 2.62×10^{-4} Siemens after the dopant material was added (0.1 gm), therefore the ionic conductivity depends on the concentration of this material, figure 11 shows the relationship between the specific conductivity and the weights of the dopant material, it can be showed the same behaviour which was seen in the ionic conductivity, (table 2).

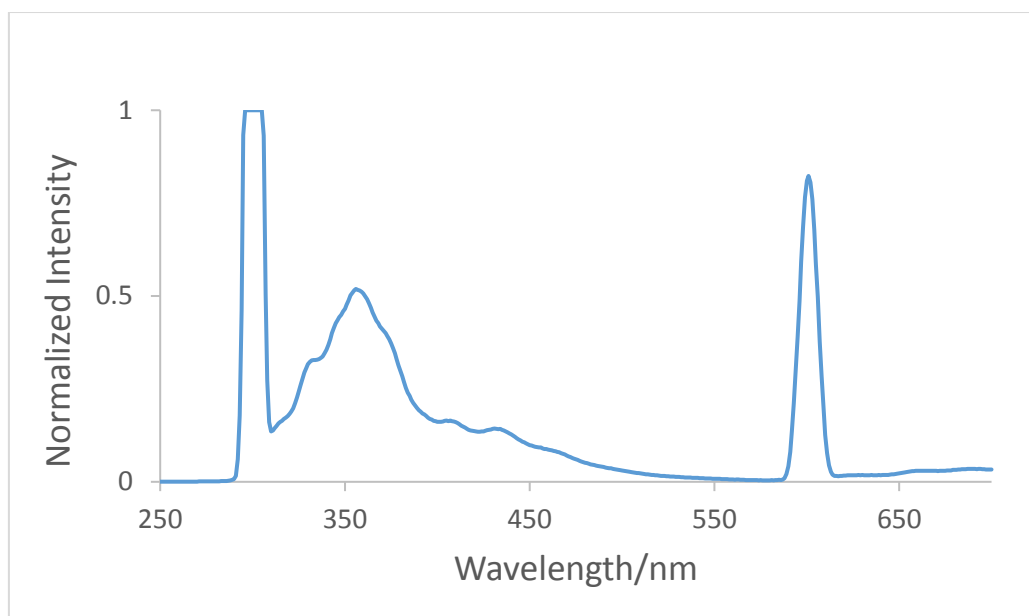


Figure 7. The fluorescence spectrum of the compound in butanol for the 4-hydroxy-3-nitro-1,8-naphthalic anhydride compound

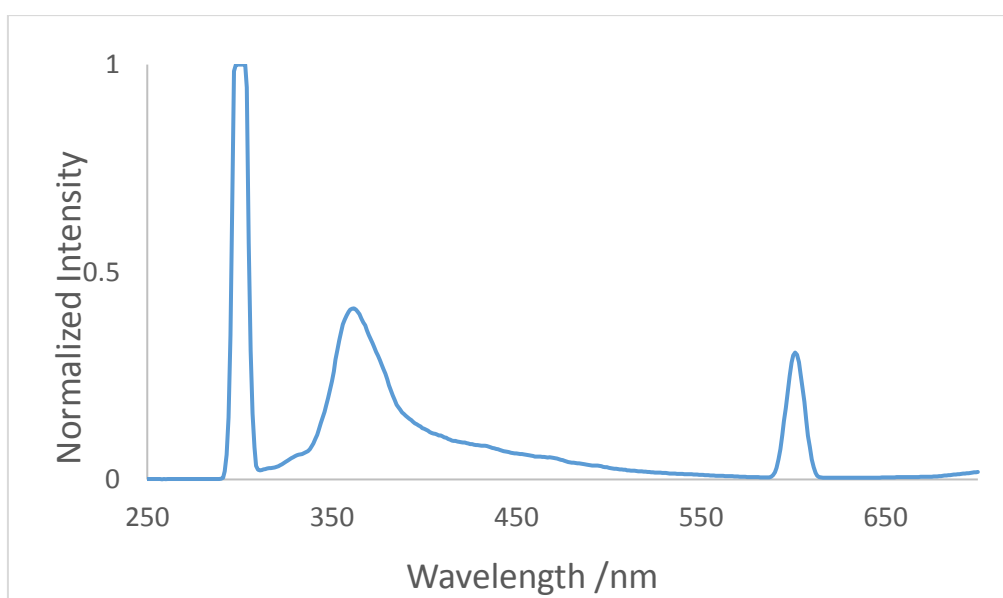


Figure 8. The fluorescence spectrum of the compound in ethanol for the 4-hydroxy-3-nitro-1,8-naphthalic anhydride compound

4. Conclusions

In this paper, the compound of (4-hydroxy-3-nitro-1,8 -naphthalic anhydride) and the dopant material (4-hydroxy-m-benzene-disulfonic acid) were prepared. The UV- Vis absorption and fluorescence spectra of the compound were recorded. The emission spectra of this compound were sensitive to the polarity of the solvent. They moved to lower energies with increasing the solvent polarity. The

influence of the solvent polarity on the fluorescence maximum was more pronounced compared with the absorption maximum, showing *ca.* 3 nm red shift on moving from butanol to dimethyl sulfoxide DMSO.

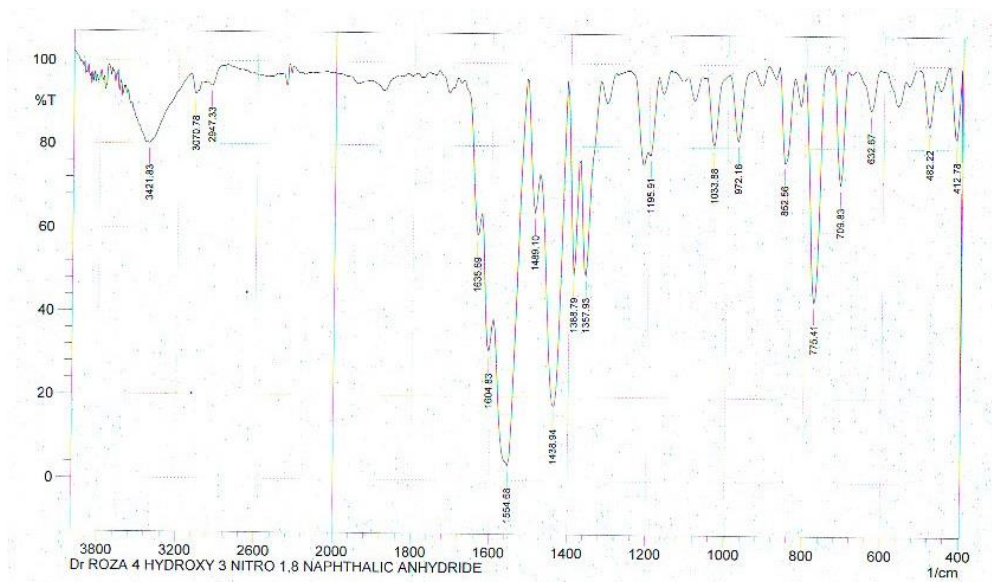


Figure 9. The FT-IR spectrum for the 4-hydroxy-3-nitro-1,8-naphthalic anhydride compound

Table (2). The values of conductivity and specific conductivity for the 4-hydroxy-3-nitro-1,8-naphthalic anhydride compound after doped with the dopant material

Weight /gm	conductivity / ohm^{-1}	Specific conductivity / $\text{ohm}^{-1}.\text{cm}^{-1}$
0.01	2.40E-05	1.39E-04
0.02	5.10E-05	2.96E-04
0.03	8.70E-05	5.05E-04
0.04	1.17E-04	6.79E-04
0.05	1.32E-04	7.66E-04
0.06	1.27E-04	7.37E-04
0.07	1.82E-04	1.06E-03
0.08	2.02E-04	1.17E-03
0.09	1.87E-04	1.08E-03

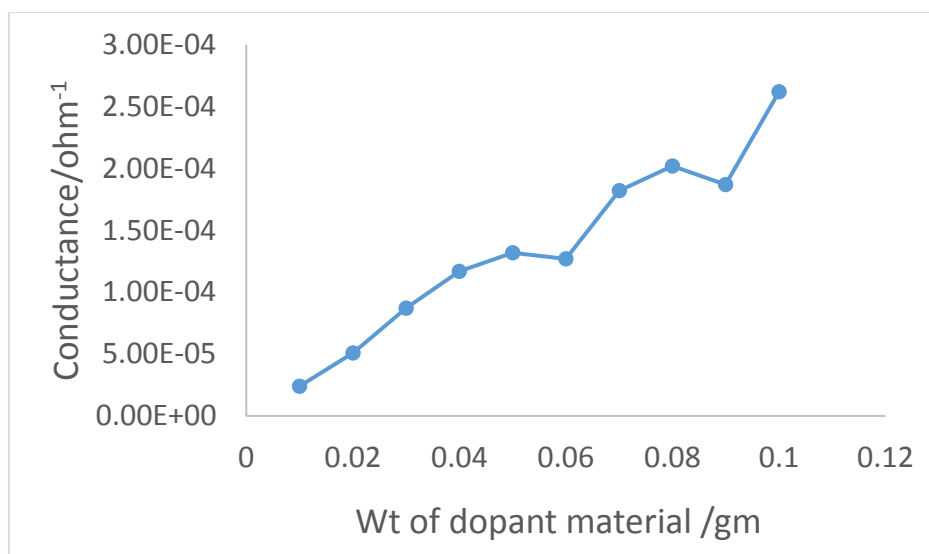


Figure 10. The ionic conductivity curve for the compound

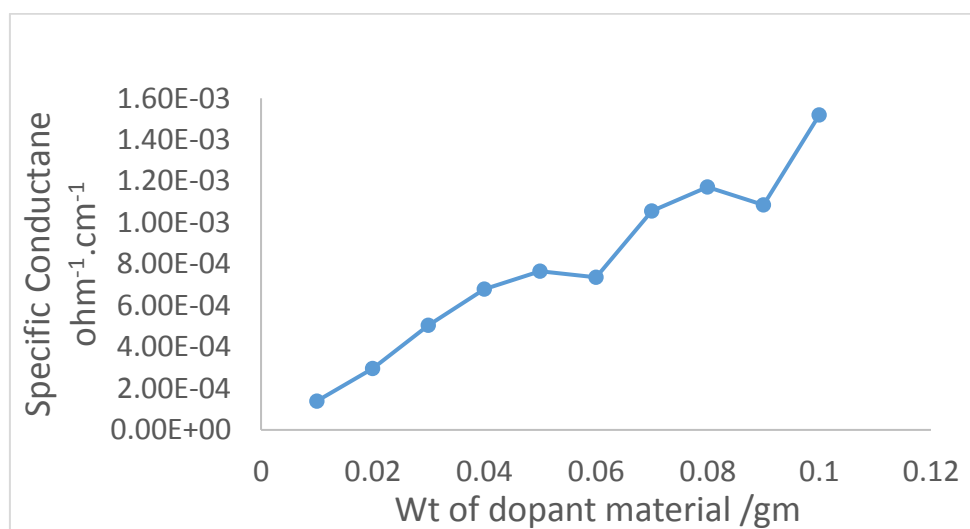


Figure 11. The specific conductivity curve for the compound

The effect of the dopant material on the conductivities (ionic and specific) of the compound was studied, the ionic conductivity was increased as the weight of the dopant material increases.

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