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Synthesis of Aminothiophene Substituted Squarylium Dyes and Study of their Electrical Conductivity Properties

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Abstract

Squarylium dyes are organic dyes of intense flouresence properties typically in the red to near- infrared region obtained from squaric acid. Squarylium dyes were synthesized from aminothiophene which are low molecular weight compound with good electron donating properties. The molecular weight of the dyes ranges from 276- 434 g/mol with melting point of spanning from 314–336 0C. The FT-IR of band of the squarylium dyes showed sharp absorption bands of 3224.1-3649.1 cm-1 corresponding to the N-H stretch functional group present in the molecule, the C=O group was seen between 1640.0-1796.6 cm-1 and the N=C=S (isothiocyanate) functional group ranged from 2105.9-2206.6 cm -1. The electrical conductivity measurements were obtained by employing a standard process using a programmable LCR meter at a frequency range of 200-100000Hz and the result calculated using the formular σ=L/RA.The electrical conductivity of synthesized dyes were observed to be within the range of 10-5-10-8 S m-1 The electrical conductivity of the dyes and aminothiophene substituted squarylium dyes lies within the range of electrical conductivity for semiconductor which is between 10-12-102 S m-1.

Keywords: squarylium dyes • aminothiophene • FT-IR • electrical conductivity

Introduction

The quest for technological innovations is never-ending, which ensures the design of a plethora of advanced materials with new or improved properties for optimum device performance [1].

Squaraine dyes were first reported by Triebs et al. in 1965 [2], who reported the formation of an insoluble product when pyrrole was reacted with 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid). Squaraines are 1,3-disubstituted squaric acid derivatives with a general structure (Figure 1).

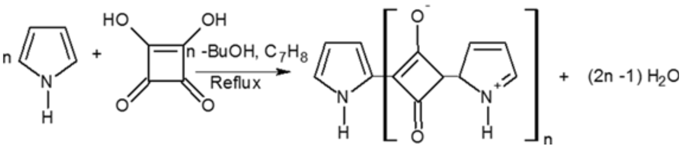

Figure 1. synthesis of squarylium dyes.

Squaraine dyes exhibit a sharp and intense absorption band with high molar extinction coefficients (σ105 L mol-1 cm-1) [3,4]. By varying donor moieties and increasing the π-conjugated systems, the absorption wavelength can cover the long wavelength The colours of these dyes originate by absorbing the light in the visible region of the spectrum due to the delocalization of n- and π- electrons throughout their structures [5,6]. The difference between semiconducting and good conducting materials is that the resistance of the good conductors declines rapidly as the temperature drops off, whereas the resistance of semiconductors increases notably as the temperature falls down to the absolute zero [7]. The structure of the semiconductors tolerates electrical current to pass through and they possess electrical resistivity ranging from 10-2 to 109 Ω- cm at room temperature visible to near-IR region from 550 to 850 nm [8-11].

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Experimental Details

Synthesis of aminothiophene

The starting materials for the synthesis involves the condensation of acetophenone (3.6 ml, 0.03 mol) and malononitrile (3.96 g, 0.06 mol) in toulene using a heterocatalytic system. The reaction mixture was refluxed in the presence of catalytic amount of acetic acid and ammonium acetate to produce arylidenemalononitrile as an intermediate, followed by the cyclisation with sulphur (3 g), using diethylamine as catalysts at 65 ºC for 2- 3 hours to give the desired products.

The thick sticky dark product obtained was cooled overnight, filtered, washed with ethanol, ethanol and water 1:1 and dried. It was purified and recrystallized from a mixture of 1:1 ethanol and acetic acid. This procedure was repeated to obtain other aminothiophene derivatives (Figure 2).

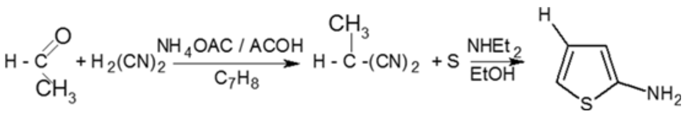

Figure 2. synthesis of aminothiophene.

Synthesis of aminothiophene squarylium dyes

Squaric acid (0.290 g, 2.5 mmole) and the aminothiophenes (5 mmole) were refluxed in a mixture of n-butanol (40 ml) and toluene (20 ml) for 4 hrs and the water formed was removed by azeotropic distillation. The mixture was cooled in a refrigerator overnight and the precipitated dye was filtered off, washed with ethanol and recrystallized from 1-butanol (Figure 3).

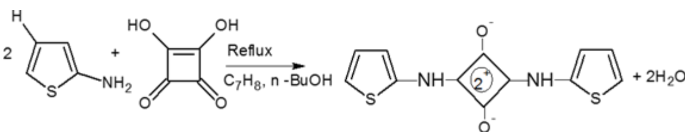

Figure 3. synthesis of aminothiophene squarylium dyes.

Electrical conductivity measurements

The electrical conductivity measurements were obtained by employing a standard process of Bekkali, et al., [12]. A known amount of sample was pressed into pellets using a carver laboratory press. These pellets were then utilized for the measurement of the conductivity of the materials. The sample was placed between two copper discs with radius of 1.9cm. One copper disc was connected to a power source and the other to an ammeter for measuring the current. A graph of current against voltage was plotted. The resistance can therefore be calculated from the inverse of the slope. The thickness and diameter of the sample pallet were measured using a micrometer screw gauge. The pellet thickness of about 1.17 mm and the sample cell diameter of about 1.9 cm were held constant for the electrical resistance measurement at a frequency range of 20-100,000 Hz using a programmable LCR metre and the result obtained was used to calculate the electrical conductivity of samples using the equation below:

$\rho = l/RA$.

Where;

ρ is the electrical resistivity

l is the thickness of the dye pellet (1= 1.17mm) R is the electrical resistance of the dye pellet

A is the cross-sectional area of the dyes. But A = πr2 where r is the radius of sample pellet, which can be calculated from the diameter.

$\sigma = l/\rho$

σ is the electrical conductivity

Results and Discussion

Physical properties of synthesized dyes

Table 1 shows the physical properties of the different aminosquarylium dyes obtained. Each of these dyes showed a unique property of melting point, yield and colour. The dyes obtained gave a high melting point which corresponds to literature that squarylium dyes possess high melting points [13] (Table 1).

Table 1. Infrared spectra of synthesized dyes.

Dye	N – H		OH	C-H		N=C=S	C=O	C-O	C=C
	Str	Ben	Str	Ben	Str	Str	Str	Str	Ben Str
2a	3511.2	-	-	1402.1	3004.2	-	1707.1	1222.6	902.0
2b	3649.1	-	-	1461.1	2952.1	2087.3	1740.7	1215.1	969.1
2c	3328.5	-	-			2113.4	1640.0	1274.7	909.5
2d	3224.1			1461.1	2922.2	2105.9	1654.9	1251.1	972.9
2e	3350.9			1457.4	2928.0	2146.9	1658.7	1274.7	969.1
2f	3339.7				2926.0	2206.6	1647.5	1349.3	857.3
2g	3019.1			1420.1			1710.8	1218.8	745.5
2h	3168.2			1394.0	2963.2	2109.7	1796.6	1259.8	924.4

Infrared spectra of Aminothiophene Squarylium dyes

The IR spectrum (IR vmax cm-1 Table 2) showed absorption at 3019.1 up to 3511.2 due to the N- H stretch while that at 3004.2 represents the aromatic C-H stretch, a signal at 1394.0-1461.1 was also seen which corresponds to the C-H bending vibration. The carbonyl group (C=O) stretch gave a signal at 1640.0-1796.6 and C-O stretch vibration was noticed at 1215.1-1349.3. The signal at 857.3-972.9 corresponds to the C=C bending vibration (Table 2).

Table 2. Uv-vis spectra of synthesized dyes.

Dye	λmax DMF (nm)	λmax Chloroform (nm)	λmax Ethanol (nm)	Molar extinction coefficient ($Lmol^{-1}cm^{-1}$ x 10^5)
2a	421	640	500	2.86
2b	420	636	515	3.37
2c	434	620	498	2.60
2d	458	710	522	3.83
2e	510	670	540	3.18
2f	460	630	516	2.81
2g	518	635	538	3.71
2h	526	705	545	3.04

Uv-vis spectra of aminothiophene squarylium dyes

The visible absorption of dyes 2a-2h were measured in chloroform with the parent dye 6a giving an absorption of 640 nm as can be seen from Table 3.

Dye 2b and 2c gave a hypsochromic shift of -4 nm and -20nm respectively this is attributed to the chloro groups present which are electron withdrawing and create a negative inductive effect (-I effect) in the entire molecule. Dye 2c gave an increased blue shift of -20 nm owing to the presence of two chloro groups unlike dye 6b which contain only one chloro group hence dye 2c has a greater–I effect than dye 2b.

Dyes 2d, 2e and 2h contains electron donating groups; methoxyl, methyl and amino groups respectively. These electron donating groups are capable of forming hydrogen bonds with the dye molecules hence activating the ortho and positions and thus creating a +I effect which results in a bathochromic shift of +70 nm, +34 nm and +65 nm respectively. Similarly dyes 2f and 2g are blue shifted due to the presence of nitro and bromo groups which are electron withdrawing creating a negative inductive effect in the dye structure hence the hypsochromic shift when compared to the parent molecule (dye 2a) (Table 3).

Table 3. Electrical conductivity measurements.

Dye	Electrical Resistivity (Ωcm)	Electrical conductivity ($\Omega^{-1}cm^{-1}$)
2a	1.73×10^{-3}	5.78×10^{2}
2c	6.89×10^{4}	1.45×10^{-5}
2e	7.52×10^{6}	1.33×10^{-6}
2g	5.71×10^{6}	1.75×10^{-7}

Electrical conductivity properties

The electrical resistivity and the electrical conductivity proparties conductivities values of 4 selected aminothiophene squarylium dyes. As earlier stated for the dyes to be considered as semi- conductors, they have to possess electrical resistivity of 10-2 to 109 Ω-cm [7-9]. Resistivity values of 1.73 × 10-3 was obtained for dye 2a which is the parent dye molecule, while resistivity values of 6.89 x 106, 7.52 x 106 and 5.71 x 106 were obtained for dyes 2c, 2e and 2g respectively, these dyes are chloro, methyl and bromo-substituted squarylium dyes. It can therefore be said that halogen substituted groups are good semi-conducting materials, while the high resistivity value seen in the dye 2e can be attributed to the presence of increased conjugation in the dye molecule and therefore can be used as a conducting material.

Conclusion

Squarylium dyes from aminothiophene were synthesized successfully with spectra analysis carried out. Electrical conductivity measurements were also carried out on the dyes. These dyes were found to absorb up to the infrared region of the spectrum, with sharp melting points. The electrical conductivity measurement carried gave resistivity values of 1.73 × 10-3 to 7.52 × 106 which are well within the range to be used as conductors hence, these dyes can be harnessed for the production of dye synthesized solar cells (DSSC).

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