Synthesis of Substituted 4-Styrylcoumarins via Wittig Reaction: An Approach to Photophysical and DFT Studies

Umesh B. Hunagund[a] , Arpita A. Shanabhag[a], Nagashree U Hebbar[a] , Lokesh A. Shastri[a]*,Ganesh N. Alawandi[b]

Department Of Chemistry, Karnatak University, Dharwad-580 003, India
Department Of Chemistry, S.D.M. College, Honavar, Karnataka, India.

Abstract
*A novel coumarin derivative of4-(4-aminostyryl)-7-methyl-2H-chromen-2-one (**5**)was synthesized by the reaction of 4-(bromomethyl)-7-methyl-2H-chromen-2-one and p-nitro benzaldehyde using toluene at 120C⁰ via standard Wittig reaction condition. The molecules were characterized by spectral analysis and the photophysicalproperties for organic electronic applications were examined, such as thermal stability, strong and broad optical absorption and emission studies. Optical properties are explicated by UV-Vis absorption and fluorescence spectroscopy andoptical band gaps of the molecules **4** and **5** are found to be 3.35eV-3.65eV as estimated from their onset absorption edge. The 4-(4-aminostyryl)-2H-chrome-2-one a coumarin showed high thermal stability up to 239-367 °C. Density functional theory computations were performed to understand intermolecular charge transfer property.*

Keywords: *4-(4-Aminostyryl)-7-methyl-2H-chromen-2-one, UV-Vis absorption, Thermogravimetry, Photo physical studies,Density functional theory (DFT).*

I. Introduction

Coumarin derivatives have delighted much more significant interest due to their widespread pharmaceutical activities [1-5] and exhibitfluorescence in visible region in electronic spectrum, which is significantly influenced by the medium [6].For this reason,they are one of the most important fluorescent molecules and have been studied extensively for the applications of fluorescent receptors[7]. Moreover they exhibit favourablephoto physical properties such as excellent light stability, large Stokes shifts, nontoxicity and high fluorescence quantum yields[8-10]. Certainly, the coumarin derivativeswere used as emissive dopants in organic light-emitting diodes (OLEDs) applications and potential fluorescence materials[11,12]. Optical appeal of these compoundshave been broadly investigated such as nonlinear optical chromophores, laser dyes, fluorescent probes, fluorescent whiteners, optical recording solar energy collectors and polymer science [13-17].Strong fluorescence of coumarin is due to the charge transfer fromthe styryl to the lactone carbonyl group [18]. The absorption and fluorescence properties of coumarins are considerably altered by proper substitutions on the coumarinnucleus[19,20].As reportedincreasing the conjugated system in coumarin analogue which enhanced the absorption and emission wavelengths[21,22].Coumarin especially amino substituted coumarin derivatives are strong fluorescent.While, many of coumarin based fluorescent probes have been reported with strong fluorescence,high stability and excellent biocompatibility[23].

In view of the more importance of amino substitutedcoumarinheterocycles in organic electroluminescent devices, photovoltaic cells and organic dye sensitizer,here we conceptualized the amino derivativeof coumarinto develop a new lead possessing resourceful and selective candidate for organic electronic and fluorescent dyes applications.The above mentioned findings, the present work coverthe synthesis and characterization of nitro and amino substituted styralcoumarinderivative, aiming atobtaining new materials with higher fluorescent properties. The photophysical, thermal stabilities and Density functional theory (DFT) studies of novel amino substituted derivative of coumarin suggest,this materialis viablecandidate for fluorescent dyes and organic electronic applications.

II. Materials and Method

The chemicals were gained commercially and used without any additional purification. The melting points were taken by the open capillary technique and are uncorrected. IR spectra were measured by aVERTEX 70 FT-IR (Bruker Optics)**.** Mass spectra on a Shimadzu TOFMSES+5.31e5. All ^{1}H and ^{13}C-NMR spectra were recorded on the *JEOL-Delta* Ver.5 400 MHz spectrometer at 25 °C with TMS as internal standards. Chemical

shifts are reported in ppm (δ). Density functional theory (DFT) were carried out with a Becke-3-parameter-Lee-Yang-Parr (B3LYP) functional levels for the 6-311+ +G(d,p) as basis sets. Fluorescence measurements and UV–vis spectra were performed on a Hitachi F-7000, and a U-4100 UV–vis-NIR spectrometer (Hitachi) respectively. Thermo gravimetric analysis (TGA) was carried under a nitrogen atmosphere at a heating rate of 10°C min^{-1} with a SDTQ600V26.9Build20 TA instruments. Differential scanning calorimetry experiments were carried out using DSCQ20V24.11Build124 instrument.

General procedure for the synthesis of 4-(4-aminostyryl)-7-methyl-2H-chromen-2-one

A solution of 4-(bromomethyl)-7-methyl-chromen-2-one(**1**, 1.0mmol) and triphenyl phosphine(1.0mmol) in the presence of K_2CO_3 was stirred at room temperature(RT) in DMF for about4 hours and the coumarin triphenyl phosphonium salt a ylide (**2**)was formed which was isolated by washing with ethanol. The ylide(**2**, 1.0mmol) was mixed with *p*-nitrobenzaldeyde(**3**, 0.3mmol) andrefluxed in toluene(10ml) at 90 ^{0}C for about 8-9 hours.The reaction was monitored by TLC,after completion ,the reaction mixture was cooled to room temperature and ice cold water(10ml) was added, the precipitate was collected by filtration and dried to obtain the compound(**4**).Further, the nitro group from **4** was reduced using iron powder in saturated NH_4Cl(8ml) and ethanol(20ml) by refluxing at 80^{0}C for about 3hours.The desired product4-(4-aminostyryl)-7-methyl-2H-Chromen-2-one(**5**) was obtained in good yield.

4-(4-Nitrostyryl)-7-methyl-2H-chromen-2-one (4)

Light yllow solid (0.46 g, 88%). M.P. 142-144°C; IR(v) cm^{-1}:1720; ^{1}H NMR (CDCl$_3$, 400 MHz, δppm) δ: 2.43 (s, 3H), 6.15(s,1H), 6.97 (d, 1H, J = 12.4 Hz), 7.14-7.20 (m, 2H), 7.24-7.29 (m, 2H), 7.50-7.57 (m, 2H), 8.08-8.14 (m, 1H), 8.28(d, 1H, J = 8.4 Hz);^{13}C NMR: δ: 160.23, 159.65, 153.57, 150.92, 149.24, 143.15, 142.30, 141.87, 135.52, 131.97, 129.93, 126.98, 125.47, 116.91, 115.26, 113.30, 109.29, 21.05. LC-MS: 308 [M+1]

4-(4-Aminostyryl)-7-methyl-2H-chromen-2-one (5)

Orange solid (0.49 g, 87%).M.P. 156-158°C; IR(v) cm^{-1}: 1687, 3351-3340; ^{1}H NMR (CDCl$_3$, 400 MHz, δppm) δ: 2.49(s, 3H, CH$_3$), 5.60 (br,s, 2H, NH$_2$), 6.23 (m, 2H), 6.39-6.81 (m, 4H), 6.94-7.23(m, 2H), 7.54-8.22 (m, 3H);^{13}C NMR: δ: 160.54, 152.91, 150.76, 142.95, 139.10, 136.30, 129.56, 128.65, 125.77, 124.86, 123.34, 122.35, 117.18, 116.50, 115.63. 113.60, 112.81. 21.01. LC-MS: 279 [M+1)

III.   Results and Discussion

Synthesis and characterization

Based on our expertise, in designing coumarin containing molecules /scaffolds as photo chromic materials, for the various optoelectronic applications, we have extended our research interests to synthesize the stable styrel system at C$_4$ position of coumarin , which have the extended conjugation from styrenyl to lactone carbonyl. As shown in the scheme**1** a simple, convenient and efficient synthetic method was followed for the synthesis of target compounds 4 and 5. Coumarin methyl bromide**1** is treated with triphenyl phosphineat RT in DMF solution in the presence of base $K_2CO_3$to obtain the required intermediate precursor coumarin ylide(**2**). Further,the coumarin ylide(**2**) was used in standard Wittig reaction with p-nitro benzaldehyde(**3**) in toluene at 90^{0}Cresulted compound **4** in good yield. The isolated styrel analogous(**4**)has both end electron withdrawing (acceptor-acceptor) functional groups in order to introduce the extended conjugation or donor-acceptor (D-A), nitro group was reduced to amine from **4** to compound **5** by using ammonium chloride and iron in ethanol. Both the compounds **4** and **5** were confirmed from their analytical data. The IR spectrum of compound **4** showed lactone stretching frequency of carbonyl at 1720cm^{-1} while in compound **5** the carbonyl frequency is decreased and a new absorption band for amino group are observed at 1687, 3351-3340cm^{-1} respectively.
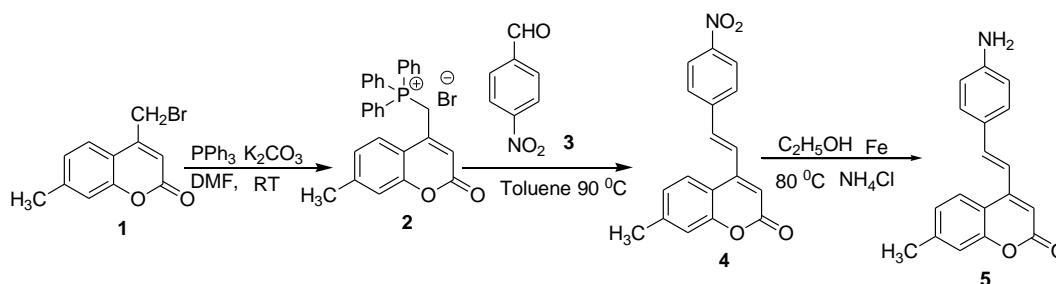
Scheme 1- Synthetic pathway for the synthesis of target compounds **4**and **5**

Photophysical studies
Absorbancestudy

The optical properties of the synthesized compounds 4 and 5 have been investigated in five different solvents of various polarities, to observe its behavior. The UV-Vis absorption spectra of compounds 4 and 5 are depicted in figure 1 and 2 and their photo physical data are summarized in table-1.From figure 2the normalized absorption of compound**5** in the range 295nm to 320nm. In all the solvents the shape of spectrum remains almost same with small shift in wave length maxima. In DMF the peak stands at 320nm and decreasing permittivity value. For polar protic solvents like ethyl alcohol and aproticsolvent acetone the absorption peak is at 295nm and 300nm respectively.

From figure 1 compound **4** has shown normalized absorption range maximum at 240nm to 275 nm, it indicate that blue shift as compared with compound **5**.The blue shift due to electron withdrawing functional groups leads to synergy of conjugation effect. Theabsorptiononset(ʎonset)are obtainedat339nm – 370nm.The optical band gaps were calculated by extrapolating the absorption edges. The optical band gaps have found to be 3.35 to 3.65ev. The results of absorption onset (ʎ$_{onset}$)as well as optical band gap of the synthesized compounds are tabulated in table 1.

Table 1: The photophysical data of the synthesized compounds

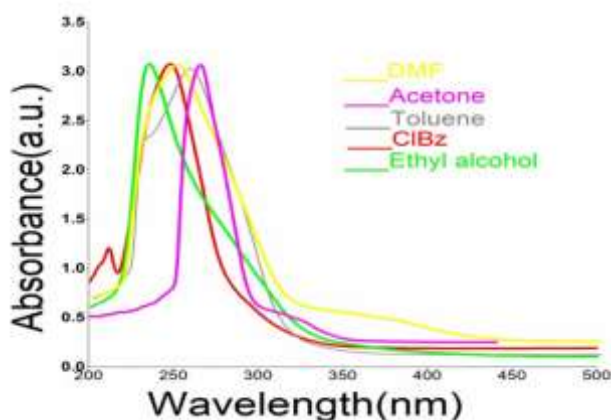| Solvents	ʎ$_{max}$absorption (nm)		ʎ$_{onset}$ absorption (nm)	E$_{g\ [ev]}^{b}$
	Compound 4	Compound 5	Compound 5	
Ethanol	240	295	340	3.64
Acetone	275	300	350	3.54
Chlorobenzene	250	305	350	3.54
Toluene	270	310	339	3.65
DMF	260	320	370	3.35

Figure 1 The normalized absorption spectra of compound **4** in different solvents
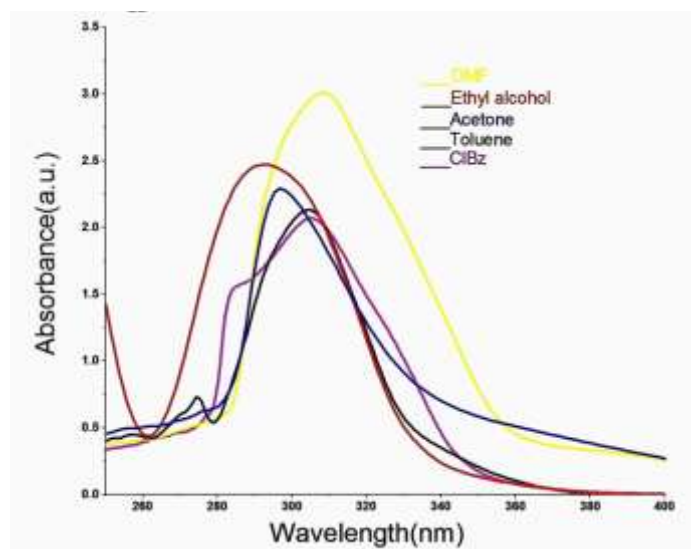

Figure 2 The normalized absorption spectra of **5** in different solvents

Fluorescence Study

The luminescence spectra of synthesized compound **5** was carried out in different solvents such as DMF, ethyl alcohol, acetone and chlorobenzeneat 10^{-5}M concentration(Figure 3).Compared with emission in solution of compound 5 it showed that in chlorobenzene the emission spectrum found to be slight blue shift while in DMF showed higher intensity. Moreover, the Solvatochromism properties of compound 5 showed obviously expected result, that is inter molecular charge transfer(ICT) chromophores with an electron donor andan electron accepter moleculesare often possess useful solvatochromic properties. In our case compound **5** have electron donor amino group and electron acceptor lactone carbonyl group with proper electron delocalization from amino to carbonyl. The fluorescence spectral measurements of the synthesized compound 5 with metal ions were performed in dilute solution of DMF at room temperature, in order to examine the selectivity.The variety of metal ions such as $Co^{2+}, Cr^{2+}, Fe^{2+}, Cu^{2+}, Hg^{2+}, Mn^{2+}, Ni^{2+}, Sn^{2+}$ and $Zn^{2+}$are used.The fluorescence intensity of the compound **5**from figure 4 we noticed that all the metal ions have been able to induce much significant change in the fluorescence intensity of compound at concentration $1x10^{-5}$.From study quenching of quenching of fluorescence was observed for the most of the metal ions
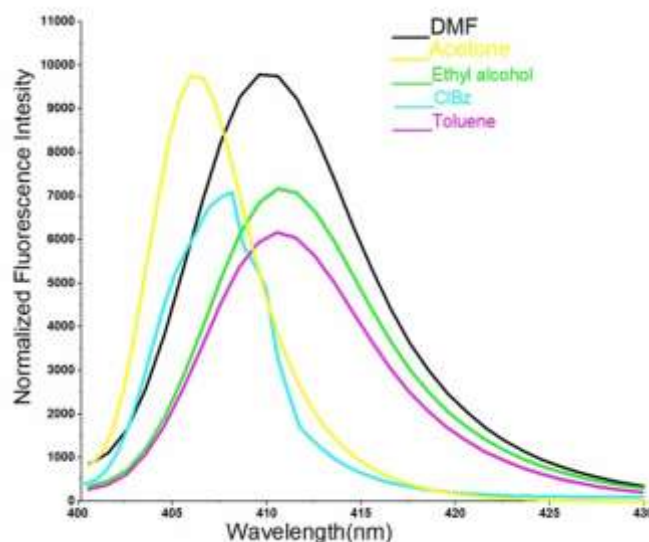

Figure 3 Normalized Fluorescence Spectrum of 5in $1x10^{-5}$M Concentration

The emission intensity of the compound 5 is gradually increased at 402nm by decreasing the metal ions concentration(Figure 4&5). Figure 4 represents metal ion concentration at 10^{-4}M with chromophore in DMF solvent. It indicates that most of the metal ions are quenched the fluorescent intensity of the compound 5, where in Fe^{2+} is quenched more significantly, at 10^{-4}M concentration and increasing the emission intensity of the compound 5 is observed at lower concentration (10^{-6}M,Figure 5),it may due to less concentration of metal ions not attending the equilibrium.
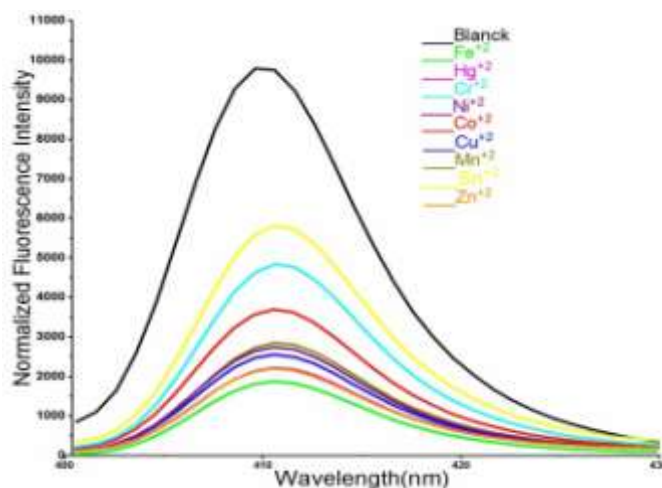

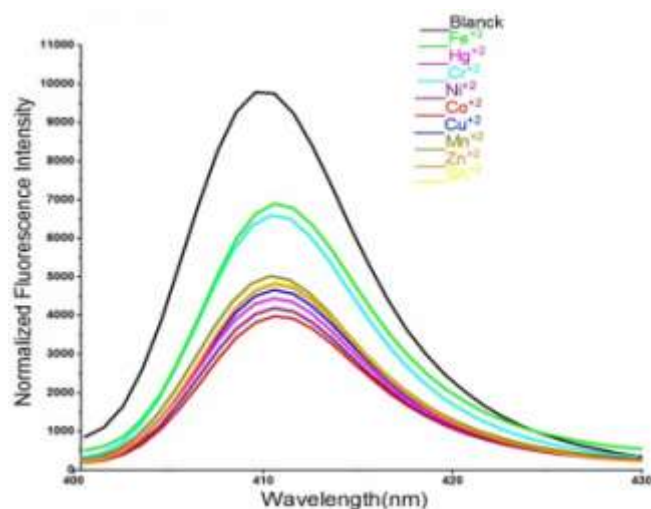**Figure 4**NormalizedFluorescence Spectrum of5 with different metal ion

Figure5 NormalizedFluorescence Spectrumof 5 in 1×10^{-6}M

Computational Modeling of the molecule

Computational calculations were carried out using density functional theory (DFT) with the B3LYP theory 6-311G++(d p) as basis sets. Computing the electronic structure gives information about themolecule, molecular orbitals, electrostatic potential curve, charge on each atom, etc .Theresults are discussed below.
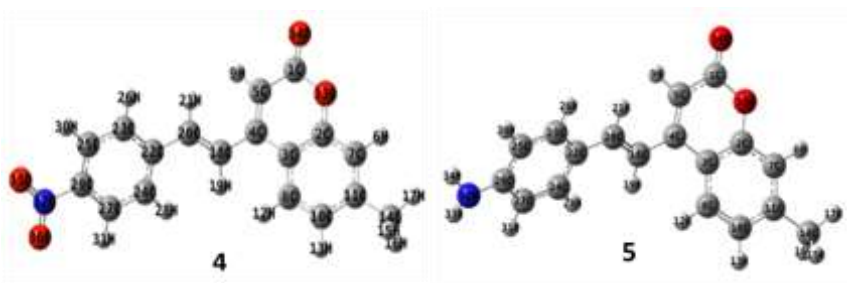

Figure 6 Geometry of optimizedstructures **4** and**5**

The figure 6 shows optimized ground state geometry of the molecules **4** and **5** respectively. The frequency calculation along with the optimization for the two molecules have been carried out using 6-311G++(d,p) initial step under DFT/B3LYP model. All calculations were carried out in gas phase, and the dipole moment values obtained 5.117 and 8.145 Debye respectively.Along with structure and geometry, the electronic molecular orbitals with energy and shape were estimated using Gaussian Program. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital(LUMO) are one of the important finding to characterize electronic stateof molecule. Figure 7 revel that HOMO-LUMO states of compounds 4 and 5 respectively. The values of HOMO-LUMO are given in eV. and corresponding bond gapes are calculated theoretically, the energy gap for 4 and 5 are 3.4ev and 3.5ev respectively.
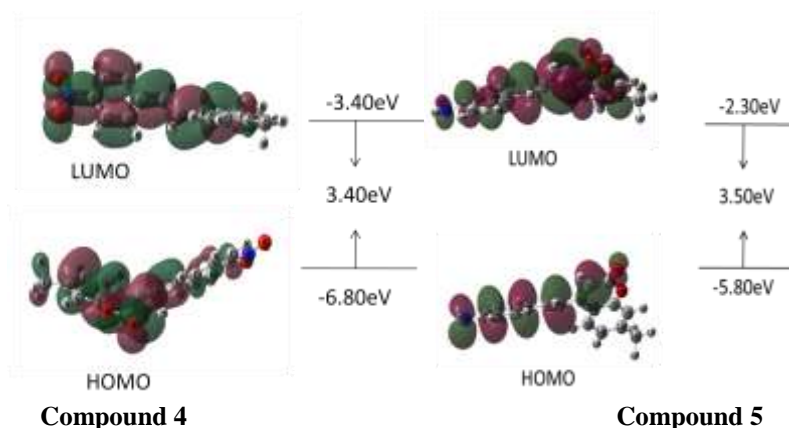

Compound 4   **Compound 5**
Figure 7 HOMO-LUMO gaps and visualization of molecular orbitals of 4 and 5

Molecular Electrostatic Potential (MEP) Map

To predict the reactivity and electrons density around the molecule, by obtaining a molecular electrostatic potential surface. The MEP maps for these molecules are presented in figure 8. In general the red region shows electron rich region and blue region resembles the electron deficient region. The green region usually shows that neutrally charged space. In the molecules, the space around oxygen atom with a double bond in coumarin part is the electron rich region. The NH_2 group shows there is an electron deficient around it which is the reason for large dipole moment for compound **5**. The lower dipole moment value for 4 can be reasoned by MEP diagram of it, where the electron deficiency and richness is distributed throughout the molecule.
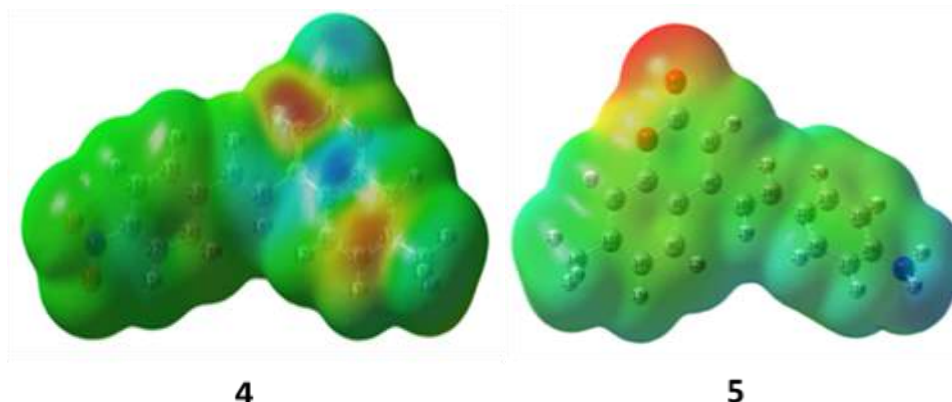

4   **5**

Figure8. The molecular Electrostatic potential Map for**4** and **5**Molecule

Thermal Properties

The thermal properties and morphological stabilities of synthesized compound is determined by using thermal gravimetric(TGA) and differential calorimetry(DSC)
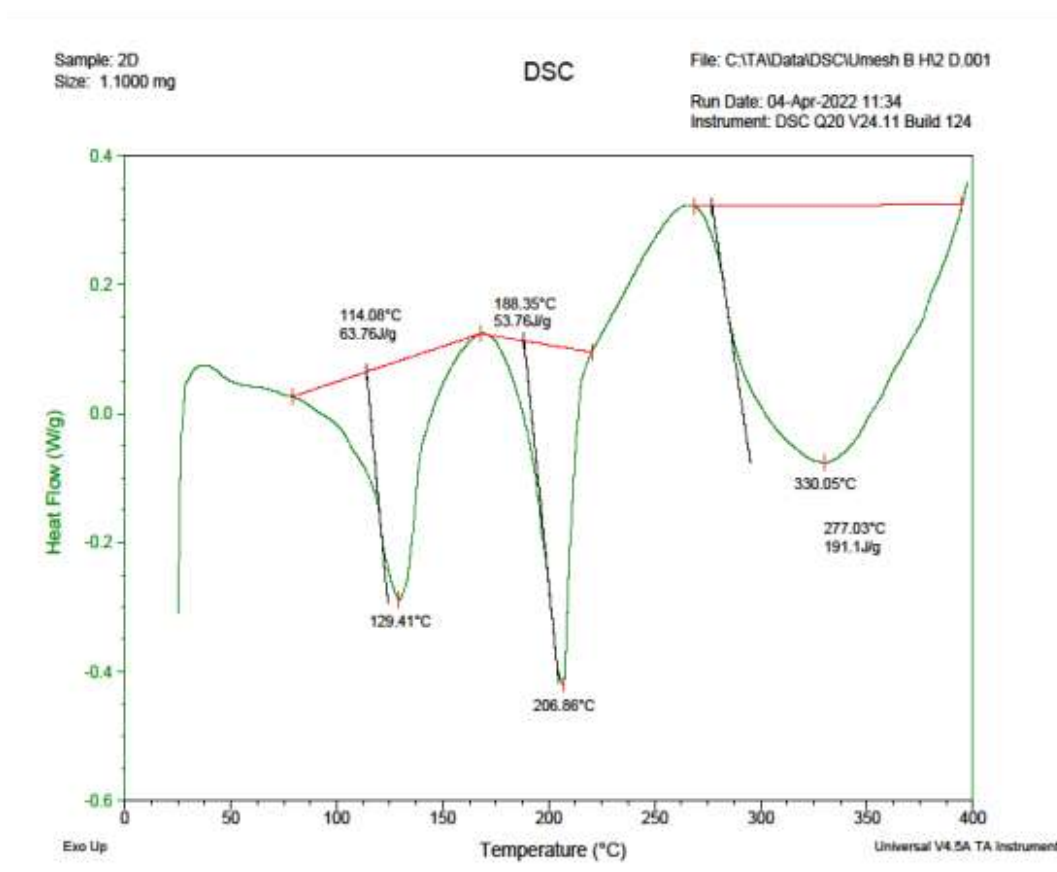

Figure 9. DSC of compound **5**

DSC was carried out in the temperature range 25-400°C with heating rate of 10°C min⁻¹ under nitrogen atmosphere. An endothermic base line shift in the DSC curves of compound represent their melting point(T_m). Which is centered at 188.35°C. It is noticed that high melting point of a compound 5 revel that their good thermal stability(Figure 9).
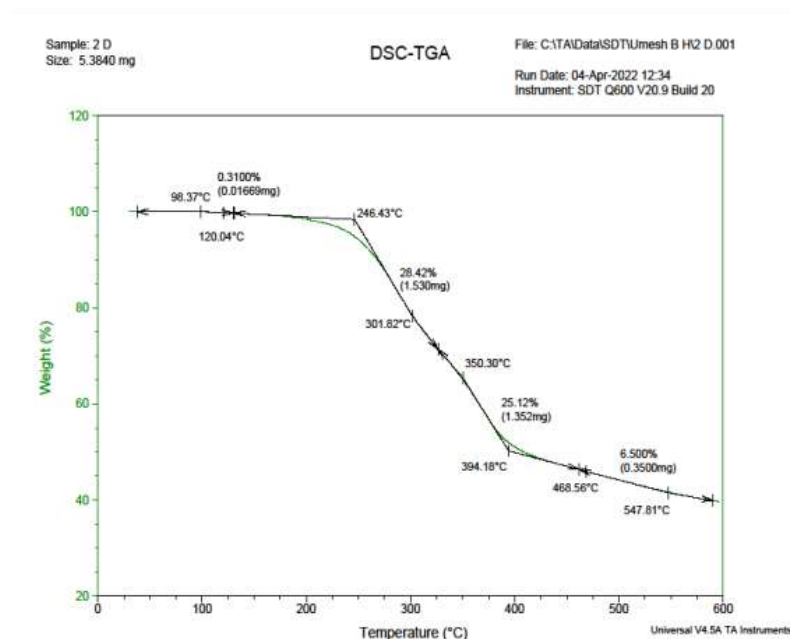

Figure 10.TGA of compound **5**

From TGA results,3% weight loss temperature(T5d) of compound under nitrogen atmosphere is about 246.43°C.It shows that compound 5(Figure 10) is thermally stable. The synthesized compound showed zero weight loss from 0 to 120°C,which indicates that there is no water or organic solvent residues on the surface of the compound.

IV. Conclusions

In conclusion, we have reported here two coumarin based styrene materials bearing nitro and amino substituted candidates. The synthesized compounds were analyzed their optical, solvatochromism, thermal properties and their theoretical investigation was made. The optical properties are found to be good for optoelectronics application which showed band gaps 3.35ev for compound **5** and the compound **5** is stable upto 240 °C. The fluorescent measurement of compound **5** with metal ions showed quenching of fluorescentintensity.Photo physical studies designate that, the synthesized material is viable competitor and recreate an important part in organic electronic applications.

Conflict of Interest: None

References
[1]   J. Klenkar, M.Molnar, J. Chem. Pharm. Res. 7 (2015) 1223-1238.
[2]   P. K.Jain, H. Joshi, J Appl Pharm Sci. 02 (2012) 236-240.
[3]   C. Kontogiorgis, D. Hadjipavlou-Litina, J. Enzyme Inhib. Med. Chem. 18 (2003) 63-69.
[4]   S. Muratovic, K. Duric, E. V. A. Osmanovic, D. Softic, D. Zavrsnik, Asian J Pharm Clin Res. 6 (2013)132-134.
[5]   D. Hadjipavlou-Litina, C. Kontogiorgis, E. Pontiki, M. Dakanali, A. Akoumianaki, H. E. Katerinopoulos, J. Enzyme Inhib. Med. Chem. 22 (2007) 287–292.
[6]   J. Donovalova, M. Cigan, H. Stankovicova, J. Gaspar, M. Danko, A. Gaplovsky, P. Hrdlovic, Molecules. 17 (2012) 3259-3276.
[7]   Y. Shiraishi, N. Hayashi, M. Nakahata, S. Sakaic, T. Hiraia, Rsc Adv. 7 (2017) 32304-32309.
[8]   B. D. Wagner, Molecules. 14 (2009) 210-237.
[9]   C. J. Hua, K. Zhang, M. Xin, T. Ying, J. R.Gao,J. H. Jia, Y. J. Li,**Rsc Adv. 6**(2016) 49221-49227.
[10]   Y. K. Al-Majedy, A. A. Al-Amiery, A. H. Kadhum, A. B. Mohamad, Molecules 20(2015)366-383.
[11]   M. T. Lee, C. K. Yen, W. P. Yang, H. H. Chen, C. H. Liao, C. H. Tsai, C. H. Chen, Org. Lett. 6(2004) 8.