



Influence of Functional Groups on the Photophysical Properties of Msppp Chalcone as Laser Dye

M F Attia ^{1*}, Abdelrahman A Elbadawi ², K H Ibaouf ^{2,3} and AO Elzupir ⁴

¹Department of Physics, Shaqra University, Shaqra, Saudi Arabia

²Deptment of Science, Alneelain University, Khartoum, Sudan.

³Department of Physics, Al Imam Mohammad Ibn Saud Islamic University (IMSIU), Riyadh, Saudi Arabia.

⁴Department of Science, Al Imam Mohammad Ibn Saud Islamic University (IMSIU), Riyadh, Saudi Arabia.

*Corresponding Author: Dr. M F Attia, Department of Physics, Shaqra University, Shaqra, Saudi Arabia, E-mail: mohana@emp.su.edu.sa

Received date: February 09, 2021; Accepted date: February 24, 2021; Published date: March 03, 2021

Abstract

In this work, 1-(4-methylsulfonyl phenyl)-3-(4-N, N dimethyl amino phenyl)-2-propen-1-one (MSPPP) chalcone was synthesized and examined as optical materials. The absorption and fluorescence characteristics of MSPPP chalcone were recorded in ten different solvents. The influence of Functional Groups (FG) and solvents on their photophysical properties was investigated. These include absorption, fluorescence, stokes shift, and Amplified Spontaneous Emission (ASE). The absorption spectra of MSPPP showed a wavelength band in the range 404 nm-427 nm, whereas the fluorescence spectra exhibited a band at 473 nm-533 nm. The FGs and solvents had an adorable effect on the optical properties of the synthesized materials. ASE was observed under pump pulse laser excitation, and the wavelengths were attuned from 511 nm-548 nm.

Keywords: Dimethylamino chalcone; Amplified Spontaneous Emission (ASE); Functional groups; Optical properties; Synthesis.

Introduction

In the past few decades, studies on photophysical properties of organic fluorescent compounds have been a subject of intensive investigation due to their increasing application in electronic and optoelectronic devices, biomedical imaging, and fluorescence sensors [1–5]. Chalcone derivatives are extensively used in optoelectronic fields such as photorefractive polymers [6], nonlinear materials [7], chromophore sensors [8], and in the study of photo-alignment layer of liquid crystal displays [9]. The dye lasers based on rhodamine and coumarin derivatives are excellent laser media, but they have some shortcomings, such as a lack of photochemical stability [10]. According to the chemical structure, the compound discussed in this paper has better photochemical and thermal stability [11–13]. Hence, the chalcones should result in good dye lasers. However, the photophysical properties depending on solvent environment and the influence of the FGs have not been fully studied. In earlier study, we showed that 3-(4-(dimethyl amino) phenyl) -2-phenyl-(2E) - propen

-1-one (C1) produced ASE under pulsed Nd: YAG laser excitation at 532 nm [14]. The result revealed that C1 has a large Stokes shift, an excellent photo stability, and high intensity lasing action (Figure1). The major objective of the present study is to report on the photophysical and ASE behaviors, with a particular focus on electrons withdrawing and donating groups. To achieve this goal, we have designed and synthesized a 1-(4-methylsulfonyl phenyl)-3-(4-N, N dimethyl (amino phenyl)-2-propen-1-one chalcone (MSPPP) (C2). We compare their photophysical properties with C1 compound with no functionality in ring A, as shown in Figure 1.

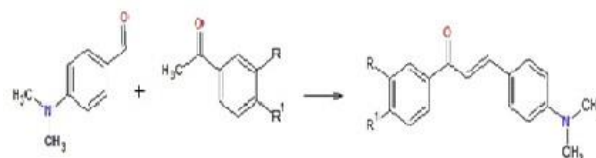


Figure 1: Chemical reaction of chalcones preparation. C1: R=H, R1=H, C2: R=H, R1=Me.

Materials and Methods

Synthesis

A green synthesis of chalcones was performed using a condensation reaction of 4- dimethylamino benzaldehyde (0.01 mol) and acetophenones derivatives (0.01 mol) in a basic solution of sodium hydroxide (1.0 gm) and ethanol (50 ml). The product was recrystallised from ethanol and water, filtered, washed with water, and left to dry.

C1 confirmed by H1-NMR, C13-NMR, mass, and UV *vis* spectroscopy. δ H: (400 MHz, CDCl₃, Me₄Si), 3.05 (6H, s, NMe₂), 6.67 (2H, d, J=8.9 Hz), 7.32 (1H, d, J=15.5 Hz), 7.48 (2H, t, J=7.7 Hz), 7.52 (3H, m, ph), 7.76 (1H, d, J=15.5 Hz), 7.99 (2H, d, J=8.3 Hz) ppm. δ C: 40(N(CH₃)₂); 112(C=C); 117(C=C); 122(Ph); 128.3(Ph); 128.4(Ph); 130.5(Ph); 132(Ph); 139.5(Ph); 146(Ph); 152(Ph); 190(C=O). M/z (%): 251 (M \pm 100); λ _{max} (methanol 421 nm).

C2 confirmed by H1-NMR and UV *vis* spectroscopy, (400 MHz, from 0 ppm to 11 ppm) 1H NMR: δ 2.86 (6H, s), 3.07 (3H, s), 6.47 (1H, d, J=15.6 Hz), 6.84 (2H, ddd, J=8.2, 1.2, 0.4 Hz), 7.47-7.58 (3H, 7.51 (d, J=15.6 Hz), 7.55 (ddd, J=8.2, 1.5, 0.5 Hz)), 7.81 (2H, ddd, J=7.9, 1.9, 0.5 Hz), 8.01 (2H, ddd, J=7.9, 1.5, 0.5 Hz), λ _{max} (methanol 419 nm).

Spectral analysis

A set of solutions was prepared by dissolving synthetic chalcones using different solvents. The absorption spectra were measured using a perkin-elmer lambda 590 spectrophotometer with a wavelength range from 200 nm-800 nm. The fluorescence spectra were measured by a perkin-elmer LS55 spectrofluorometer, with a wavelength range of 200 nm-900 nm, at room temperature. For the ASE experiments, the solutions were placed in a quartz cuvette with dimensions (1 cm \times 1 cm \times 4 cm). The excitation source used was the 3rd harmonic of a nd:yag laser (355 nm) with pulse duration of 6 ns and repetition rate of 1 Hz–10 Hz. A cylindrical quartz lens (f=5 cm) was used to focus the pump beam on the cuvette [15].

Results and Discussion

Steady-state spectra

The most important characteristics of the chalcone based laser dye is an ICT from the highly donated group of N, N dimethyl in ring B to the electron withdrawing carbonyl groups of enone *via* the system. To study the influence of FGs in chalcone based lasers, we synthesised two chalcones. We investigated the change on ring A. In C1 compound there is no functional group, in C2 compounds methoxy and methyl groups are added to ortho or para position as donating groups. The absorption spectra of C1 and C2 compounds in acetone at a concentration of 0.015 mM were recorded. The results showed that C1 compound exhibits a single absorption band at 407 nm. No noticeable effect has been seen when donor groups were added to ring A (C2 compound) as seen in Figure 2. Under the same operational conditions, C1 and C2 compounds were dissolved in various organic solvents having different dielectric constant and the absorption spectra for these chalcones were recorded as seen in Figure 3.

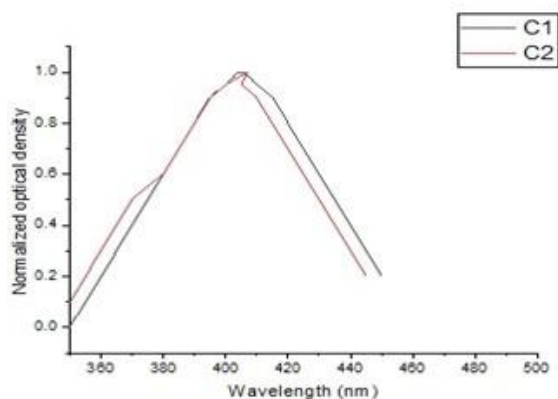


Figure 2: Absorption spectra of the chalcones in acetone.

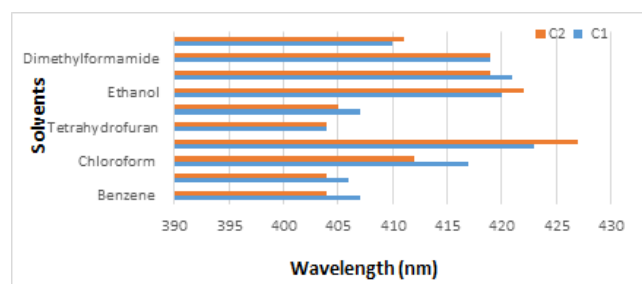


Figure 3: Absorption spectra of the chalcones in acetone.

The fluorescence spectra of C1 and C2 compounds in acetone at a concentration of 0.015 mM were recorded. C1 compound showed a band at 519 nm. By adding donor groups C2 compounds the fluorescence spectra is blue shifted to 511 nm and 516 nm as shown in Figure 4. The effect of methoxy group is clearly higher than that of the methyl group, as the methoxy group enriches the system *via* conjugation. The fluorescence spectra of the chalcones in different solvents illustrated in Figure 5.

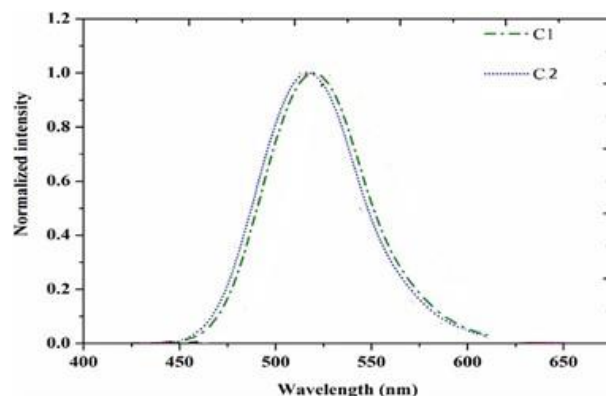


Figure 4: Fluorescence spectra of the chalcones in acetone.

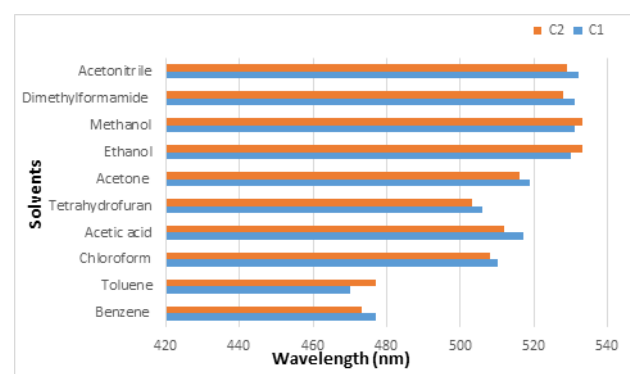


Figure 5: Fluorescence spectra of the chalcones in different solvents.

Stokes shift

C1 and C2 compounds were dissolved in various organic solvents that have different dielectric constants (Table 1). The concentration was kept at 0.015 mM to avoid any reabsorption effect. Calculation of the Stokes shift has been described previously [16], the Stokes shift has a linear variation with the dipole factor, which is written between square brackets in the expression

$$V_a - V_f \approx \left(\frac{(\epsilon - 1)}{(2\epsilon + 1)} - \frac{(n^2 - 1)}{(2n^2 + 1)} \right) \frac{(\mu_e - \mu_g)}{a^3 hc}$$

$$D_f = \left(\frac{(\epsilon - 1)}{(2\epsilon + 1)} - \frac{(n^2 - 1)}{(2n^2 + 1)} \right)$$

Solvents	λ_{max} (nm)		λ_{max} emission (nm)		λ_{max} ASE (nm)	
	C1	C2	C1	C2	C1	C2
Benzene	407	404	477	473	-	-
Toluene	406	404	470	477	-	-

Chloroform	417	412	510	508	523	513
Acetic acid	423	427	517	512	-	-
Tetrahydrofuran	404	404	506	503	515	511
Acetone	407	405	519	516	532	522.5
Ethanol	420	422	530	533	548	548
Methanol	421	419	531	533	-	-
Dimethylformamide	419	419	531	528	548	541
Acetonitrile	410	411	532	529	547	544

Table 1: The spectral and ASE properties of the chalcones in different solvents.

Figure 6 shows plots of the Stokes shift as a function of dipole factor for representative solvents. It was found that these compounds exhibited large Stokes shifts. This indicates that all of these compounds display great variations in the dipole moment in the excited state. The fg did not show a significant change in Stokes' shifts.

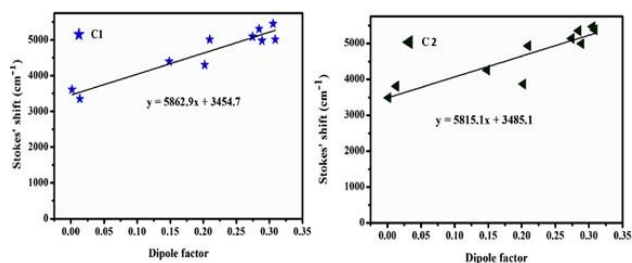


Figure 6: Variation in the Stokes' shift of the chalcones in solution with a dipole factor for different solvents.

Amplified Spontaneous Emission (ASE)

To study the ASE properties of the synthesised compounds under high-intensity pulsed laser excitation, C1 and C2 compounds were dissolved in acetone at a concentration of 1 mM. These solutions were transversely excited with a UV laser ($\lambda_{ex}=355$ nm). At a pump power density of 10 mJ/cm², the ASE spectra were observed. This was the minimum concentration and pump power required for these compounds to produce ASE spectra. The ASE from C1 compound was observed at 532 nm. The effect of donor groups in C2 compound consists in a blue shift (518 nm and 523 nm, respectively) as shown in figure 7.

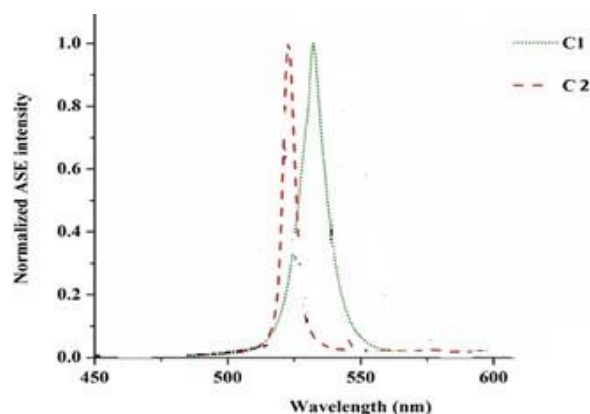


Figure 7: ASE spectra of the chalcones in acetone.

The influence of the FG in the other solvents showed similar behavior as in acetone illustrated. At concentrations higher than 1 mM, under identical operating conditions, the ASE spectra did not change. The ASE of C1 and C2 compounds in benzene, toluene, and acetic acid was not detected even at high pump pulse energies and concentrations. This may be due to the poor solubility of these compounds in toluene and benzene, while in acetic acid it may be due to the protonation of nitrogen of N, N-dimethyl amino groups. In alcoholic solvents, the intensities of the fluorescence and ASE were weak; this may be due to the hydrogen bonds. The use of different solutions led to significant changes in the emission and ASE spectra. The laser spectra were in the range from 511 nm in tetrahydrofuran to 548 nm dimethylformamide.

Conclusion

The effects of FGs and organic solvents on these compounds have been observed in absorption, emission, and ASE spectra. Contrary to expectations, the addition of donor groups determines a blue shift of fluorescence and ASE spectra, while the electrons withdrawing groups led to a shift of the spectra to longer wavelengths. The current results demonstrate that these amino chalcones can be used as new efficient laser materials in the future.

References

1. Elzupir AO, Saeed AE, Barakat IE, Van der westhuizen JH (2013) Ultrasound irradiation promoted synthesis of chalcones, analogues, homologues and related furanyl containing compounds and their antibacterial activity. Int J Curr Pharmaceut Res 5: 23-25.
2. Tainaka K, Tanaka K, Ikeda S, Nishiza KI, Unzai T, et al. (2007) Prodan-conjugated DNA: Synthesis and photochemical properties. J Am Chem Soc 129: 4776.
3. Attia MF (2019) Synthesis, properties of a new (polymer and chalcone). AJOPACS 7: 1-9.
4. Szydłowska I, Kyrychenko A, Nowacki J, Herbich J (2003) Photoinduced intramolecular electron transfer in 4-dimethylaminopyridines. Phys Chem Chem Phys 5: 1032-1038.
5. Kumar Sk, Hager E, Pettit C, Gurulingappa H, Davidson NE et al. (2003) Design, synthesis, and evaluation of novel boronic-

- chalcone derivatives as antitumor agents. *J Med Chem* 46: 2813-2815.
- Sun SJ, Schwarz G, Kricheldorf HR, Chang TC (1999) New polymers of carbonic acid. XXV. Photoreactive cholesteric polycarbonates derived from 2,5-bis(4'-hydroxybenzylidene) cyclopentanone and isosorbide. *J Polym Sci Polym Chem* 37: 1125-1133.
 - Shkir M, Patil PS, Arora M, Alfaify S, Algarni H (2017) An experimental and theoretical study on a novel donor-acceptor bridge type 2,4,5 trimethoxy-4'-chlorochalcone for optoelectronic applications: a dual approach. *Mol Biomol Spectrosc* 173: 445-456.
 - Bowden K, Duah CK, Ranson R J (1991) Reactions in strongly basic media. part 10. base-catalysed isomerisation of z- to e-substituted chalcones. *J Chem Res* 109-112.
 - Sato Y, Morimoto M, Segawa H, Shimidzu T (1995) Twisted intramolecular charge-transfer state of a donor-acceptor molecular system with a beta-diketone bridge: tuning of emission through structural restriction by metal cation coordination. *J Phys Chem* 99: 35-39.
 - Ibaouf KH, Prasad S, Aldwayyan AS, AlSalhi MS, Masilamani V (2012) Amplified spontaneous emission spectra from the superexciplex of coumarin 138. *Spectrochim Acta Mol Biomol Spectrosc* 97: 1145-1151.
 - Mallikarjun KG (2004) Thermal decomposition kinetics of Ni (II) chelates of substituted chalcones. *J Chem* 1: 105-109.
 - Furtado P, Figueiredo P, Neves HD, Pina F (1993) Photochemical and thermal degradation of anthocyanidins. *J Photochem Photobiol Chem* 75: 113-118.
 - Shettigar V, Patil PS, Naveen S, Dharmaprakash SM, Sridhar MA et al. (2006) Crystal growth and characterization of new nonlinear optical chalcone derivative: 1-(4-Methoxyphenyl)-3-(3, 4-dimethoxyphenyl)- 2-propen-1-one. *J Cryst Growth* 295: 44-49.
 - Attia M (2019) Synthesis, properties of a new (polymer and chalcone). *AJOPACS* 7: 1-9.
 - Masilamani V (2007) Laser properties of a conjugate polymer (MEH-PPV) in the liquid-excimeric state. *Laser Phys* 17: 1367-1373.

10.