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Influence of Functional Groups on the Photophysical Properties of 1-(4-Methylsulfonyl Phenyl)-3-(4-n, n Dimethyl (amino Phenyl)-2-Propen-1-One Chalcone as Laser Dye

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Authors' contribution

This work was carried out in collaboration among all authors. Authors MFA, AAE, KHI and AOE conceived of the presented idea. Authors MFA, AAE, KHI and AOE developed the theory and performed the computations and verified the analytical methods. All authors discussed the results and contributed to the final manuscript.

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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 were investigated. These include absorption, fluorescence, stokes shift, and amplified spontaneous emission (ASE). The

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absorption spectra of MSPPP showed a wavelength band in the range 404 - 427 nm, whereas the fluorescence spectra exhibited a band at 473 - 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 to 548 nm.

Keywords: Dimethylamino chalcone; amplified spontaneous emission; functional groups; optical properties; synthesis.

1. INTRODUCTION

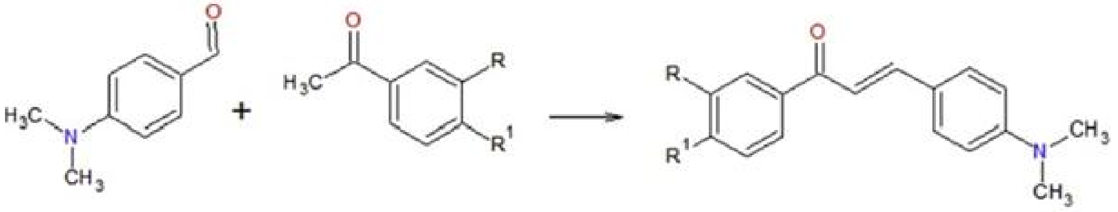
In the past few decades, studies on photophysical properties of organic fluorescent compounds have been a subject of intensive investigation due to their increasing application in electronic and optoelectronic devices, biomedical imaging, and fluorescence sensors [1–5]. Chalcone derivatives are extensively 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 (Scheme1). 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 Sheme1.

2. EXPERIMENTAL

2.1 Synthesis

A green synthesis of chalcones was performed using a condensation reaction of 4- dimethylamino benzaldahyde (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 UVvis spectroscopy. δH: (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. δC: 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±100); λ_{max} (methanol 421 nm).



C1, R = H, R^1 = H, C2, R = H, R^1 = Me

Scheme1. Chemical reaction of chalcones preparation

C2 confirmed by H1 NMR and UV – Vis spectroscopy, (400 MHz, from 0 to 11 ppm) ^{1}H 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).

2.2 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 to 800 nm. The fluorescence spectrawere measured by a Perkin-Elmer LS55 spectrofluorometer, with a wavelength range of 200 to 900 nm, at room temperature. For the ASE experiments, the solutions were placed in a quartz cuvette with dimensions (1×1×4 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 – 10 Hz. A cylindrical quartz lens (f = 5 cm) was used to focus the pump beam on the cuvette [15].

3. RESULT AND DISCUSSION

3.1 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 π 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 0.015mM 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 Fig. 1. 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 Fig. 2.

The fluorescence spectra of C1 and C2 compounds in acetone at a concentration of 0.015mM were recorded. C1 compound showed a band at 519 nm. By adding donor groups C2 compounds the fluorescence spectra is blue shifted to 511 and 516 nm as shown in Fig. 3. The effect of methoxy group is clearly higher than that of the methyl group, as the methoxy group enriches the π system via conjugation. The Fluorescence spectra of the chalcones in different solvents illustrated in Fig. 4.

3.2 Stokes Shift

C1 and C2 compounds were dissolved in various organic solvents that have different dielectric constants (Table 1). The concentration was kept at 0.015mM 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

$$v_a - v_f \approx \left(\frac{(\varepsilon-1)}{(2\varepsilon+1)} - \frac{(n^2-1)}{(2n^2+1)}\right)\frac{(\mu_e-\mu_g)^2}{a^3\,hc} \qquad (1.a)$$

$$D_f = \left(\frac{(\varepsilon-1)}{(2\varepsilon+1)} - \frac{(n^2-1)}{(2n^2+1)}\right) \qquad (1.b)$$

Fig. 5 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.

3.3 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/cm^2, 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

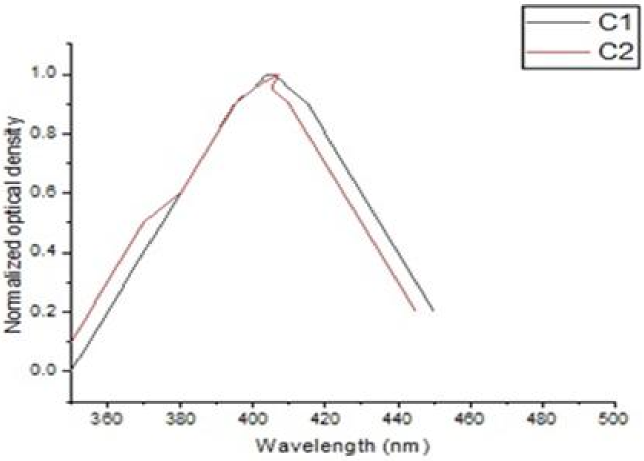


Fig. 1. Absorption spectra of the chalcones in acetone

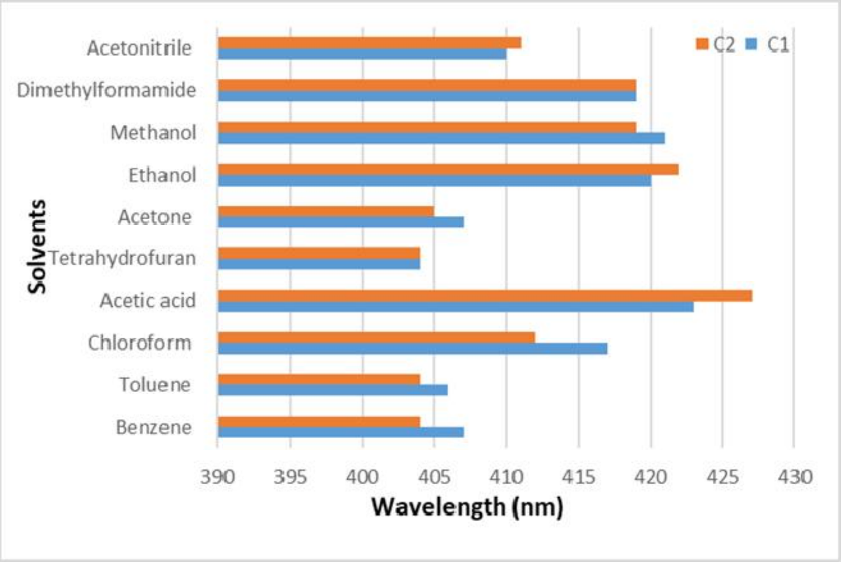


Fig. 2. Absorption spectra of the chalcones in acetone

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

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

of donor groups in C2 compound consists in a blue shift (518 and 523 nm, respectively) as shown in Fig. 6.

The influence of the FG in the other solvents showed similar behavior as in acetone illustrated in Fig. 7. At concentrations higher than 1 mM., under identical operating conditions, the ASE spectra did not change. The ASE of C1 and C2compounds 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.

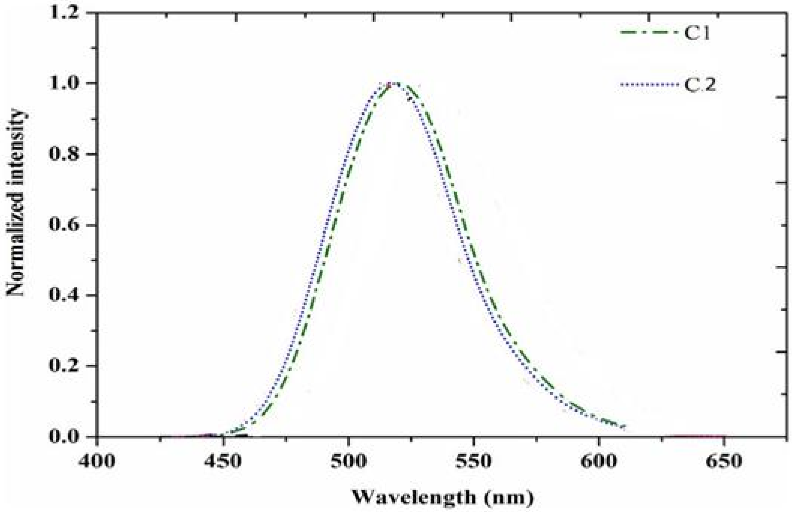


Fig. 3. Fluorescence spectra of the chalcones in acetone

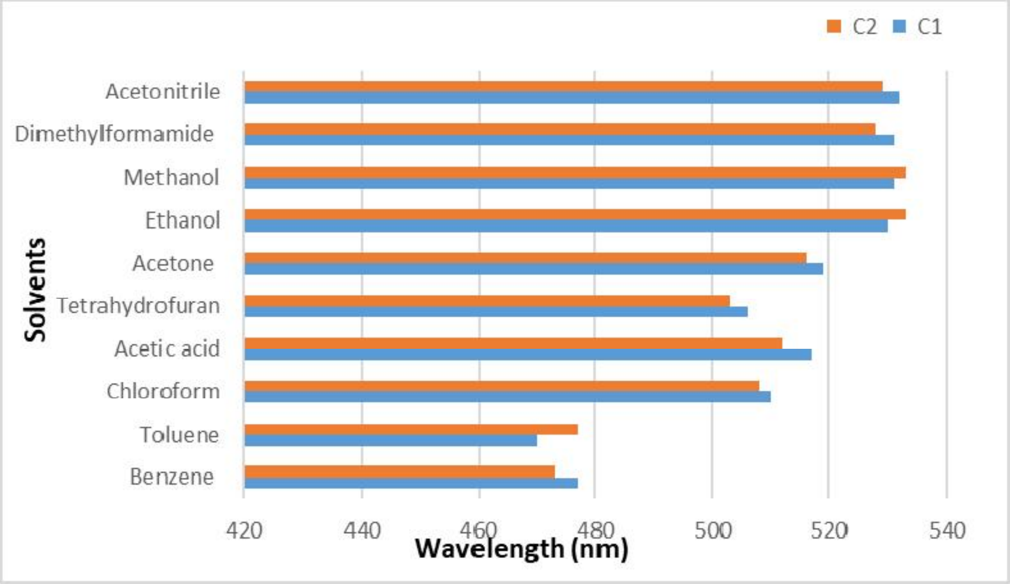


Fig. 4. Fluorescence spectra of the chalcones in different solvents

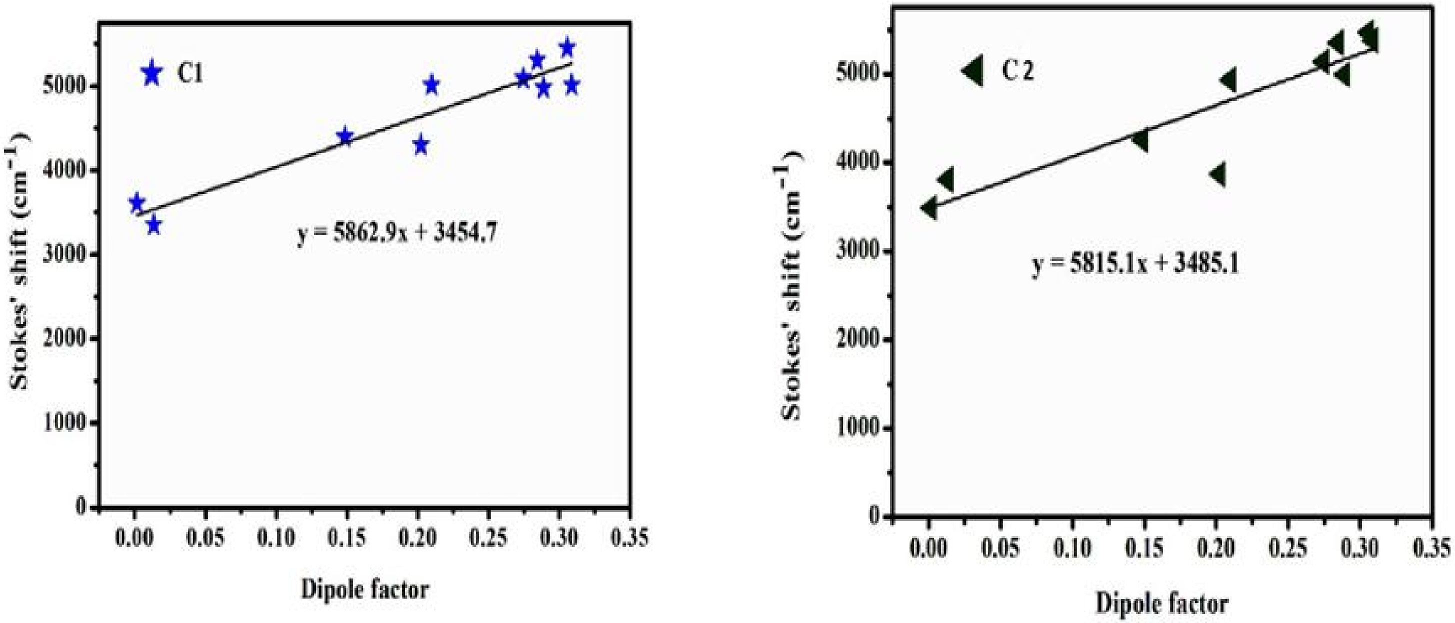


Fig. 5. Variation in the stokes' shift of the chalcones in solution with a dipole factor for different solvents

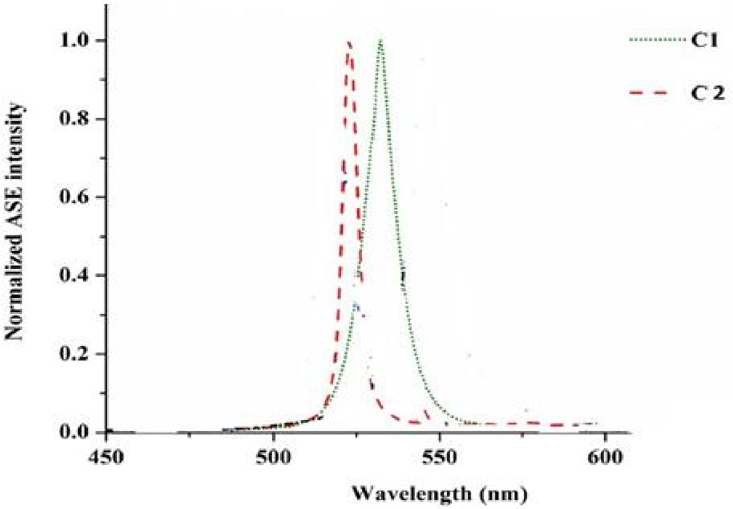


Fig. 6. ASE spectra of the chalcones in acetone

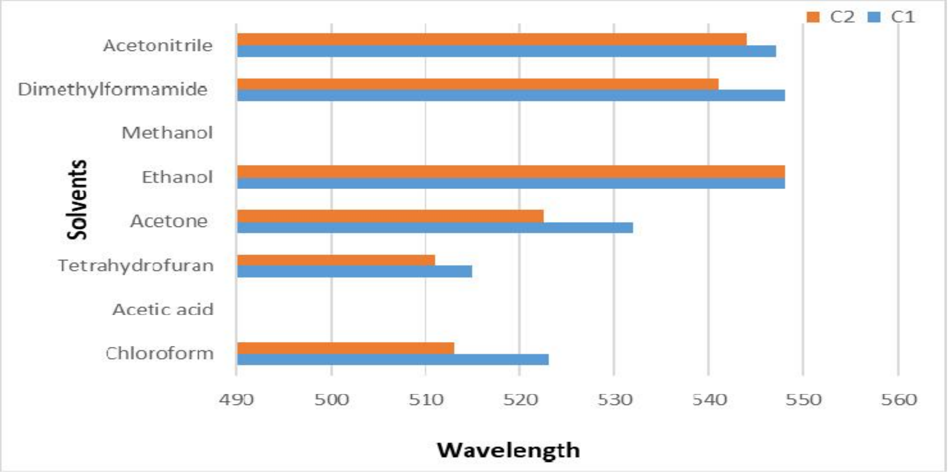


Fig. 7. ASE spectra of the chalcones in different solvents

4. CONCLUSION

The absorption spectra of MSPPP showed a wavelength band in the range 404 - 427 nm, whereas the fluorescence spectra exhibited a band at 473 - 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 to 548 nm. 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.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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