# **Original Research Article**

# Synthesis, Properties of a New (Polymer and Chalcone)

# Abstract

This paper included two objectives: (i) Synthesis of Polymer {poly 2- [1- phenyl -3-(4-methyl phenyl)-4, 5dihydropyrazole-5-yl-(4-phenoxy carbonyl)] styrene } PMDPCS and structure characterized by FT-IR, <sup>1</sup>H-NMR spectra and Uv/Vis and XRD. (ii) Synthesis of chalcone {3-(4-(dimethylamino) phenyl)-2-phenyl-(2E) propen-1-one} (DAPPP) for absorption and fluorescence spectra under different solvents and concentrations. Also, under various concentrations, organic solvents and pump pulse energies of Nd: YAG laser, the amplified spontaneous emission (ASE) was studied. Additionally, under the same identical conditions, the amplified spontaneous emission spectra of DAPPP in solution were compared with a conventional laser dye of coumarin 503. Finally, the gain and the fluorescence quantum yield of DAPPP were determined.

#### Keywords

Chalcone. Solvent effect. Fluorescence. Polymer. Nd: YAG laser.

# 1 Introduction

Chalcones represents an important family of natural as well as synthetic organic compounds. It was firstly secluded from Chinese liquorice [1]. Chalcone and its derivatives are a significant set of natural production and have been recorded to possess different biological and pharmacological activity. These chalcones had stimulated wide research interest owing to their unique structural feature, which has a carbonyl functional group in conjunction with carbon-carbon double bond. This structural arrangement gives rise to numerous chemical, physical, photophysical and biological properties [2-8]. In 2002, Yah et al [9] prepared several series of chalcone derivatives, which are having 90 % activity versus **Mycobacterium** inhibitory tuberculosis. First report on chalcones and related compounds as an optical material came before few decades by Kitaoka et al [10]. In 2003, Fabian et al [11] prepared 10 compounds and examined for leishmanicidal and trypanocidal activity, between that 5 compounds appeared distinguished and strong inhibitory effect on the growth of Trypanosome cruzi and only 2 compounds showed strong inhibitory acripanosoma cruzi and only two compounds showed potent inhibitory activity on the growth of L. braziliensis by in vitro. Recent reports related chalcones are most applied for different optical

applications through second harmonic generation materials in nonlinear optics and fluorescent probes for sensing of metal ions [12-21] However, the photophysical characteristics of these chalcones such as solvent environment, temperature effect and quantum yield of fluorescence were not fully studied. In the present investigation, the researcher attempted to synthesis a few chalcone derivatives, which are biologically important. Also photophysical properties and amplified spontaneous emission (ASE) as well as the photochemical stability of 3-(4-(dimethylamino) phenyl)-2-phenyl-(2E)-propen-1-one (DAPPP), in different solvents and concentrations are described. ASE results were compared with conventional laser dye coumarin 503.

# 2 Materials and Method

#### 2.1 Part one

## 2.1.1 Synthesis of Polymer PMDPCS

By free radical polymerization the polymer was prepared, the poly 2- [1- phenyl -3-(4- methyl phenyl)-4, 5-dihydropyrazole-5-yl- (4-phenoxy carbonyl)] styrene PMDPCS (0.15 gm) in presence of benzoyl peroxide  $C_{14}H_{10}O_4$  (0.002 g) in (15 mL) tetrahydrofuran, the mixture was heated with stirring at 85<sup>o</sup> C for 2 hr. The polymers were collected by deposition in ice water

and washed several times and dried by diethyl ether at room temperature. **2.2 Part two** 

#### 2.2.1 Synthesis of DAPPP

By condensation reaction between 4 –dimethylamino benzaldehyde (0.15 mol) in the presence of NaOH (0.5 g), in (70 mL) ethanol and acetophenone (0.15 mol), the DAPPP was fabricated. The container was preserved 12 hours at room temperature and then the yield was recrystallized from ethanol and washed with distilled water and left to yield 95 %. Chalcone characterized by  $H^1$  – NMR, C13 – NMR, mass and UV – vis spectroscopy.

# 2.2.2 Material Characterization

In different organic solvents, the DAPPP was resolved. Figure 1 showing the molecular structure of DAPPP. The fluorescence spectra and absorption of DAPPP in acetone were studied under a widely domain of concentrations. The spectra of these solutions were measured by a tiny quartz cuvette with an optical path length of 1 cm. A Perkin Elmer lambda 590 spectrophotometer over the range from 200 to 800 nm was used to taken the absorption spectra. A Perkin Elmer LS55 luminescence spectrofluorimeter was used to study spectra of fluorescence in the range from 200 to 900 nm, at room temperature. Fourier transform infrared spectra of PMDPCS were obtained using a Nicolet 6700 FT-IR spectrometer at room temperature in the 4000  $400 \text{ cm}^{-1}$ wavenumber range, with a 4 cm<sup>-1</sup> resolution.



Fig. 1 Molecular structure of DAPPP

The excitation wavelength was 400 nm. The UV laser  $(\lambda = 355 \text{ nm})$  was focused by a quartz plancylindrical lens with a focal length of 5 cm. the amplified spontaneous emission (ASE) of the DAPPP in solution was compared to that of coumarin 503 (see Fig. 2) in ethanol. The structure of the synthesized compounds was certain by IR, Mass and elemental analysis.



Fig. 2 Molecular structure of laser dyes coumarin 503

# **Results and Discussion**

## Part One

PMDPCS was characterized by FT.IR and UV/Vis spectroscopy. Table 1 shows the FT-IR spectral data of PMDPCS. The FT-IR spectrum of PMDPCS (Fig. 3) showed the following bands at [2950, 2920] for symmetric and asymmetric stretching vibration of (-CH) aliphatic, (1070) cm<sup>-1</sup> due to  $\upsilon$  (C-O), at (1755) cm<sup>-1</sup> for  $\upsilon$  (C=O). Table 2 shows UV \Vis spectrum of prepared polymer PMDPCS, the patterns of the samples were recorded by a diffractometer (D8 Advance Bruker) using Cu-K $\alpha$  radiation,  $\lambda = 0.15406$  nm, accelerating voltage is 40kV, scanning angle is 200 – 750 at room temperature. Figure 4 shows the XRD of PMDPCS.









# Part two

In different organic solvents with various dielectric constant, DAPPP was dissolved, and the concentration of these solutions was fixed at 6.5 mM. The big red shift is shown in both absorption and

emission spectra as the solvent polarity raised. By the above procedure, there is a significant change were observed in absorption and fluorescence spectra. As can be seen from the Fig. 4, the Stokes shift changed as a function of the dipole factor of the solvent, as defined by Lippert and Mataga et al. [23-24]. It can be seen observed that DAPPP in the solution turn strongly polar in the excited state than in the ground state. In most recent studies, the Stokes shift has a linear variation with the dipole factor, which is written by expression;

$$\mathcal{V}_{a} - \mathcal{V}_{f} \approx \left(\frac{(\varepsilon - 1)}{(2\varepsilon + 1)} - \frac{(n^{2} - 1)}{(2n^{2} + 1)}\right) \frac{(\mu_{e} - \mu_{g})^{2}}{a^{3}hc} \quad (1)$$

$$D_{f} = \frac{(\varepsilon - 1)}{(2\varepsilon + 1)} - \frac{(n^{2} - 1)}{(2n^{2} + 1)} \quad (2)$$

Where  $D_f$  is dipole factor,  $v_a$  and  $v_f$  are the absorption and fluorescence peaks in wave numbers respectively,  $\varepsilon$  is the dielectric constant and n is the solvents refractive index.  $\mu_e$  is the dipole moment of the solute in the excited state.  $\mu_g$  is representing the dipole moment of the solute the ground states, respectively, and a is the radius of the solvent cage around the solute. The results obtained from the Stokes shift as a function of dipole factor for illustrative solvents are shown in Figure 5. It can be seen that under same identical condition the DAPPP is more polar than coumarin 503. Overall, these results indicate that all these dyes exhibit large changes in the dipole moment in the excited state, but for DAPPP, the change is much greater than for coumarin 503.



Fig. 5 Variation in the Stokes shift of DAPPP and coumarin 503.

By diluted solutions, the fluorescence quantum yields  $(\Phi_F)$  of DAPPP and coumarin 503 was measured at fixed concentration for each solution 0.65 mM. The equation below illustrates how to measure the quantum yield [23];

$$\phi_f(s) = \phi_f(\mathbf{R}) \frac{A_R n_s^2 \int I_S(\overline{\nu}) d\nu}{A_S n_R^2 \int I_R(\overline{\nu}) d\nu}$$
(3)

where the indices S and R refer to the sample and reference, respectively, and the integral over I represent the area under the fluorescence spectrum. A is the optical density, and n is the refractive index of the solvents. Tables 1 and 2 presents the results obtained from the analysis of the quantum yields of fluorescence ( $\Phi_F$ ) for DAPPP and coumarin 503. From the data, it can be seen that under identical conditions the  $\Phi_{\rm F}$  of DAPPP is higher than that of coumarin 503. To study the ASE characteristics of DAPPP under high power excitation, DAPPP was dissolved in acetone at a concentration of 2 mM. Figure 6 provides the ASE spectrum (532 nm) with a narrow spectral bandwidth 6 nm (FWHM) at a pump power of 9 mJ. As shown, at 2 mM concentration the ASE peak is coinciding with the maximum of the fluorescence emission spectrum. At 6 mM, there was no significant red shift observed.



**Fig. 6.** ASE spectra of DAPPP in acetone, tetrahydrofuran, and DMF.

By genetic energy meter (genetc -E), the ASE efficiency of DAPPP in acetone was measured when the input energy was 9 mJ. The energy of ASE was found to be 3 mJ. Table 1 provides that the ASE efficiency depends on the solvent. At a pump energy of 9 mJ, concentration of 2 mM and under identical conditions; the ASE spectra of DAPPP in different solvents having different polarities shown in Table 1. Fig. 6 shows the emission wavelength increasingly red shifted, when the dielectric constant increased.

Table 3 provides the results obtained and compared with coumarin 503 as standard material. The variation in the ASE intensities of DMAPPP as a function of the concentration (2 to 6 mM) for acetone, dimethylformamide (DMF), and tetrahydrofuran (THF), and the pump power was 9 mJ. it was found that, when the concentration increased, the intensity of the ASE decreased for each solution, shown in Fig. 7.



**Fig. 7** ASE intensities of DAPPP in DMF, acetone, and THF.

Under identical condition, Fig. 8 shows the comparison of the ASE intensity of DMAPPP dissolved in different solvents DMF, acetone and THF and these solvents have been chosen because they give high ASE intensities. At fixed concentration 2 mM for each solution, and the pump power was taken from 3 to 15 mJ, it was found that as the pump power was increased, the intensity of DAPPP in acetone increased slowly, while in THF the intensity increased quickly.



**Fig. 8** ASE intensities of DAPPP in DMF, acetone, and tetrahydrofuran (THF).

To compare the difference between the photochemical stabilization of the DAPPP in DMF at concentration of 2 mM to that of coumarin 503 in ethanol, UV laser of Nd: YAG was pump for this solutions with pulse energy 9 mJ and 10 Hz. The ASE intensity of DAPPP remained constant after 30K pulse, while the coumarin 503 drooped 45 % of the initial intensity after 3 K pulses, and disappeared completely at 7 K pulses as shown in Fig. 9.



**Fig. 9** The photochemical stability of DAPPP in DMF and coumarin 503 in ethanol.

By the above procedure, in different solvents and under the same operating conditions, the photochemical stability of DAPPP was studied and after 30 K pulses, the ASE intensity of THF and acetone was dropped to 35% and 22%, respectively as seen in Fig. 10.



**Fig. 10** The photochemical stability of DAPPP in three different solvents.

In DMF at concentration of 2 mM, the optical gain of DAPPP was measured, whereas, Coumarin 503 in ethanol was prepared. Additionally, the pump pulse energy was varied from 3 mJ to 15 mJ and the ASE intensity was measured for two lengths of excitation  $L_1 = 0.5$  cm and  $L_2 = 0.3$  cm [25];

$$\frac{I_1}{I_2} = \frac{e^{\gamma L_1 - 1}}{e^{\gamma L_2 - 1}} \tag{4}$$

where *L* is the length of excitation and  $\gamma$  is the optical gain.

The results are shown that the optical gain of DAPPP in DMF is higher than the coumarin 503 in ethanol at a concentration of 0.6 mM as shown in Fig. 11. The results of second objective of this study are largely consistent with the findings of Elzupir *et al.* [26].



DAPPP in DMF and coumarin 503 in ethanol

Table 1 Data of the impact of the solvents on the absorption and fluorescence spectra

Solvent	ε	$\lambda_{max}$			$\Phi_F$	η
		A	F	ASE		
Methanol	32.5	420	530		0.02	
Ethanol	24.2	419	529	547	0.35	3.8
Acetone	20.5	406	517	533	0.85	30
Toluene	2.6	405	472		0.22	
Benzene	2.23	406	475		0.26	
tetrahydrofuran	7.55	402	504	512	0.98	45

 $\varepsilon$  is the dielectric constant, spectral and ASE properties:  $\lambda_{max}$  (nm) for absorption (A), F is the fluorescence and ASE;  $\varphi_F$ ; ASE efficiency  $\eta$  (%) of DAPPP.

Table 2 Coumarin 503 in different solvent.

Solvent	Е	$\lambda_{max}$			$\Phi_F$	η
		А	F	ASE		
Methanol	32.7	394	490	500	0.42	9.6
Ethanol	24.5	393	492	502	0.37	16
Acetone	20.5	389	489	496	0.53	14
Toluene	2.6	378	455	465	0.21	7
Benzene	2.23	377	449	459	0.26	9
tetrahydrofuran	7.55	384	476	485	0.40	11

 $\varepsilon$  is the dielectric constant, spectral and ASE properties:  $\lambda_{max}$  (nm) for absorption (A), F is the fluorescence and ASE;  $\phi_F$ ; ASE efficiency  $\eta$  (%) of coumarin 503 in different solvent.

# Conclusion

In the present work, under the influence of concentrations, solvent environments, and laser power excitation levels, the spectral and ASE behaviors of DAPPP and coumarin 503 were studied. Also, Quantum yield, the Stokes shift and ASE were studied. One of the more significant findings to emerge from this study is that the DAPPP showed large the Stokes shift, and showed also a strong brightness, and green ASE. Also, this study has succeeded to building heterocyclic compounds as monomers to be polymerized. The spectral data (FT-IR and <sup>1</sup>HNMR) of synthesis monomers were in full agreement with the proposed structure.

# References

[1] Yerra, K. R., S. Fang and Y. M. Tzeng, 2004.
"Differential effects of synthesized 2'-oxygenated chalcone derivatives: modulation of human cell cycle phase distribution", Bioorganic & Medicinal Chemistry, Volume 12, Issue 10, 15 May 2004, Pages 2679-2686.

https://doi.org/10.1016/j.bmc.2004.03.014

[2] Amit R.JagtapVijay S.SatamRajkumar N.RajuleVinod R.Kanetkar."Synthesis of high fluorescent coumarinyl chalcones derived from 8acetyl-1,4-diethyl-1,2,3,4-tetrahydro-7H-pyrano[2,3g]quinoxalin-7-one and their spectral characteristics", Dyes and Pigments, Volume 91, Issue 1, October 2011, Pages 20-25. https://doi.org/10.1016/j.dyepig.2011.01.011Get

[3]Y.F. Sun, Y.P. Cui.,"The synthesis, characterization and properties of coumarin-based chromophores containing a chalcone moiety", Dyes and Pigments, Volume 78, Issue 1, 2008, Pages 65-76. https://doi.org/10.1016/j.dyepig.2007.10.014

[4] Y. Kitaoka, T. Sasaki, S. Nakai, A. Yokotani, Y. Goto, M. Nakayama. "Laser properties of new organic nonlinear optical crystals chalcone derivatives", *Appl. Phys.* Lett. **56**, 2074 (1990); https://doi.org/10.1063/1.102976

[5] J. Indira, P.P. Karat, B.K. Sarojini, J. Cryst. " Growth, characterization and nonlinear optical property of chalcone derivative", Journal of Crystal Growth Volume 242, Issues 1–2, July 2002, Page 209 – 214. <u>https://doi.org/10.1016/S0022-0248(02)01306-</u>4

[6] S.J. Sun, G. Schwarz, R.H. Kricheldorf, T.C. Chang," New polymers of carbonic acid. XXV. Photoreactive cholesteric polycarbonates derived from

2,5- bis(4'- hydroxybenzylidene)cyclopentanone and isosorbide", Volume37, Issue8, 15 April 1999, Pages 1125-1133.

https://doi.org/10.1002/(SICI)10990518(19990415)3 7:8<1125::AID-POLA9>3.0.CO;2-J

[7] K. Krohn, K. Steingröver, M Srinivasa Rao, "Isolation and synthesis of chalcones with different degrees of saturation", Phytochemistry, Volume 61, Issue 8, December 2002, Pages 931-936. https://doi.org/10.1016/S0031-9422(02)00475-2

[8] Y. Sato, M. Morimoto, H. Segawa, T. Shimidzu, "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.1995, 99, 135-39, https://doi.org/10.1021/j100001a007

[9] Yuh-Meei Lin, Yasheen Zhou, Michael T. Flavin, Li-Ming Zhou, Weiguo Nie, Fa-Ching Chen. "Chalcones and flavonoids as anti-tuberculosis agents", Bioorg Med Chem. 2002 Aug;10(8):2795-802. <u>https://doi.org/10.1016/S0968-0896(02)00094-9</u>

[10] Yasuo Kitaoka, Takatomo Sasaki, Sadao Nakai, Atsushi Yokotani, Yoshitaka Goto, and Masaharu Nakayama, "Laser properties of new organic nonlinear optical crystals chalcone derivatives", Appl. Phys. Lett.56,2074(1990).). https://doi.org/10.1063/1.102976

[11] Fabiane Lunardi, Michel Guzela, Andrea T. Rodrigues, Rogério Corrêa, Iriane Eger-Mangrich, Mário Steindel, Edmundo C. Grisard, Jamil Assreuy, João B. Calixto, Adair R. S. Santos. "Trypanocidal and Leishmanicidal Properties of Substitution-Containing Chalcones", Antimicrob Agents Chemother. 2003 Apr;47(4):1449-51.10.1128/AAC.47.4.1449-1451.2003

[12] Andrey O. Doroshenko Alexey V. Grigorovich Eugene A. PosokhovVasyl G. Pivovarenko Alexander P. Demchenko, "Bis-Azacrown Derivative of Di-Benzilidene-Cyclopentanone as Alkali Earth Ion Chelating Probe: Spectroscopic Properties, Proton Accepting Ability and Complex Formation with Mg2+ and Ba2+ Ions", Molecular Engineering, September 1998, Volume 8, Issue 3, pp 199–215. https://doi.org/10.1023/A:1008393201193

[13] Knut Rurack, Julia L. Bricks, Günter Reck, Reiner Radeglia, Ute Resch-Genger, "Chalcone-Analogue Dyes Emitting in the Near-Infrared (NIR): Influence of Donor–Acceptor Substitution and Cation Complexation on Their Spectroscopic Properties and X-ray Structure", J. Phys. Chem. A2000104143087-3109. https://doi.org/10.1021/jp994269k

[14] Nathalie Marcotte, Suzanne Fery-Forgues,
Dominique Lavabre, Sylvie Marguet, Vasyl G.
Pivovarenko, "Spectroscopic Study of a Symmetrical Bis-crown Fluoroionophore of the
Diphenylpentadienone Series", *J. Phys. Chem.*A1999103173163-3170,
https://doi.org/10.1021/jp9846328

[15] P.K. Das, R. Pramanik, D. Banerjee, S. Bagchi, "Studies of solvation of ketocyanine dyes in homogeneous and heterogeneous media by UV/Vis spectroscopic method", *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, Volume 56, Issue 14, 1 December 2000, Pages 2763-2773, https://doi.org/10.1016/S1386-1425(00)00321-8

[16] Z. Xu, G. Bai, C. Dong, "Spectral and photophysical properties of intramolecular charge transfer fluorescence probe: 4'-Dimethylamino-2,5dihydroxychalcone", *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, Volume 62, Issues 4–5, December 2005, Pages 987-990, https://doi.org/10.1016/j.saa.2005.04.019

[17] P. Wang, S. Wu, "Spectroscopy and photophysics of bridged enone derivatives: effect of molecular structure and solvent", *Journal of Photochemistry and Photobiology A: Chemistry*, Volume 86, Issues 1–3, 15 February 1995, Pages 109-113, <u>https://doi.org/10.1016/1010-6030(94)03921-G</u>

[18] N. DiCesare, J.R. Lakowicz, "New Sensitive and Selective Fluorescent Probes for Fluoride Using Boronic Acids", *Analytical Biochemistry*, Volume 301, Issue 1, 1 February 2002, Pages 111-116, https://doi.org/10.1006/abio.2001.5476 [19] Y. Wang, "Photophysics of polarized enones. Intramolecular charge-transfer interaction and solvent effects", *J. Phys. Chem*.1985, 89, 18, 3799-3805, <u>https://doi.org/10.1021/j100264a007</u>

[20] Y.B. Jiang, X.J. Wang, L. Lin, "Fluorescent Probing of the Restriction by Aqueous Micelles of the Formation of the Photoinduced Biradical State P\* of 4-(Dimethylamino)chalcone", *J. Phys. Chem.* 1994, 98, 47, 12367-12372, https://doi.org/10.1021/j100098a035

[21] S.A. El-Daly, M. Gaber, S.S. Al-Shihry, Y.S. El Sayed, "Photophysical properties, excitation energy transfer and laser activity of 3-(4'dimethylaminophenyl)-1-(2-pyridinyl) prop-2-en-1one (DMAPP): A new potential laser dye", *Journal of Photochemistry and Photobiology A: Chemistry*, Volume 195, Issue 1, 5 March 2008, Pages 89-98, https://doi.org/10.1016/j.jphotochem.2007.09.010

[22] Vogel and B. S. Furniss, "Vogel's Textbook of Practical Organic Chemistry", Singapore, ELBS Publications 1996, pp:1032

[23] Ernst Lippert, "Dipolmoment und Elektronenstruktur von angeregten Molekülen", *A Journal of Physical Sciences*, volume 10, issue 7, 2014, <u>https://doi.org/10.1515/zna-1955-0707</u>

[24] Mataga Noboru, Kaifu Yozo, Koizumi Masao, "Solvent Effects upon Fluorescence Spectra and the Dipolemoments of Excited Molecules", *Bulletin of the Chemical Society of Japan*, 1956, Vol.29, No.4. <u>https://doi.org/10.1246/bcsj.29.465</u>

[25] K.H. Ibnaouf, S. Prasad, M.S. AlSalhi, A. Hamdan, M.B. Zaman, L. El Mir, "Influence of the solvent environments on the spectral features of CdSe quantum dots with and without ZnS shell", *Journal of Luminescence*, Volume 149, May 2014, Pages 369-373, https://doi.org/10.1016/j.jlumin.2014.01.054

[26] A.O. Elzupir, K.H. Ibnaouf, H. Idriss, M.A.
Ibrahem, S. Prasad, M.A. Alrajhi, M.S. AlSalhi, A.S.
Alaamer, "Synthesis and Characterization of an Efficient New Liquid Laser Dye Material — Chalcone", ACTA PHYSICA POLONICA A, Vol. 133 (2018),

http://przyrbwn.icm.edu.pl/APP/PDF/133/app133z1p 22.pdf

•