Original Research Article

Synthesis, Properties of a New (Polymer and Chalcone)

Abstract

This study included two objectives, firstly will examine Synthesis of Polymer {poly 2- [1- phenyl -3-(4- methyl phenyl)-4, 5-dihydropyrazole-5-yl-(4-phenoxy carbonyl)] styrene} PMDPCS and structure characterized by FT-IR, ^{1}H-NMR spectra, Uv/Vis and XRD and secondly study was to investigate 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.

1 Introduction

Chalcones represents an important family of natural as well as synthetic organic compound. 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 effect. 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 own 90 % inhibitory activity versus *Mycobacterium 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 prepared 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 mix was heated with stirring at 85^0 C for 2 hr. The polymers were collected by deposition in ice water and

56 washed several times and dried by diethyl
57 ether at room temperature.

58 **2.2 Part two**

59 **2.2.1 Synthesis of DAPPP**

60 By condensation reaction between 4 –dimethylamino
61 benzaldehyde (0.15 mol) in the presence of NaOH
62 (0.5 g), in (70 mL) ethanol and acetophenone (0.15
63 mol), the DAPPP was fabricated. The container was
64 preserved 12 hours at room temperature and then the
65 yield was recrystallized from ethanol and washed
66 with distilled water and left to yield 95 %. Chalcone
67 characterized by H^1 – NMR, C13 – NMR, mass and
68 UV – vis spectroscopy.

69 **2.2.2 Material Characterization**

70 In different organic solvents, the DAPPP was
71 resolved. Figure 1 showing the molecular structure of
72 DAPPP. The fluorescence spectra and absorption of
73 DAPPP in acetone were studied under a widely
74 domain of concentrations. The spectra of these
75 solutions were measured by a tiny quartz cuvette with
76 an optical path length of 1 cm. A Perkin Elmer
77 lambda 590 spectrophotometer over the range from
78 200 to 800 nm was used to taken the absorption
79 spectra. A Perkin Elmer LS55 luminescence
80 spectrofluorimeter was used to study spectra of
81 fluorescence in the range from 200 to 900 nm, at
82 room temperature. Fourier transform infrared spectra
83 of PMDPCS were obtained using a Nicolet 6700 FT-
84 IR spectrometer at room temperature in the 4000 -
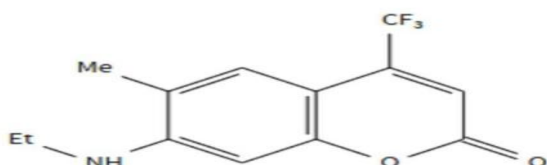85 400 cm^{-1} wavenumber range, with a 4 cm^{-1}
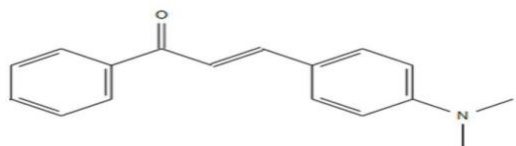
86 resolution.

88 **Fig. 1** Molecular structure of DAPPP

90 The excitation wavelength was 400 nm. The UV laser
91 (λ = 355 nm) was focused by a quartz plan-
92 cylindrical lens with a focal length of 5 cm. the
93 amplified spontaneous emission (ASE) of the DAPPP
94 in solution was compared to that of coumarin 503
95 (see Fig. 2) in ethanol. The structure of the
96 synthesized compounds was certain by IR, Mass and
97 elemental analysis.

99 **Fig. 2** Molecular structure of laser dyes coumarin 503

101 **Results and Discussion**

102 **Part One**

103 PMDPCS was characterized by FT.IR and UV/Vis
104 spectroscopy. Table 1 shows the FT-IR spectral data
105 of PMDPCS. The FT-IR spectrum of PMDPCS (Fig.
106 3) showed the following bands at [2950, 2920] for
107 symmetric and asymmetric stretching vibration of (-
108 CH) aliphatic, (1070) cm^{-1} due to υ (C-O), at (1755)
109 cm^{-1} for υ (C=O). Table 2 shows UV \Vis spectrum
110 of prepared polymer PMDPCS, the patterns of the
111 samples were recorded by a diffractometer (D8
112 Advance Bruker) using Cu-Kα radiation, λ = 0.15406
113 nm, accelerating voltage is 40kV, scanning angle is
114 200 – 750 at room temperature. Figure 4 shows the
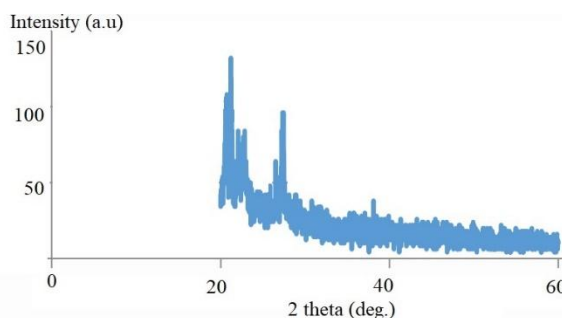115 XRD of PMDPCS.
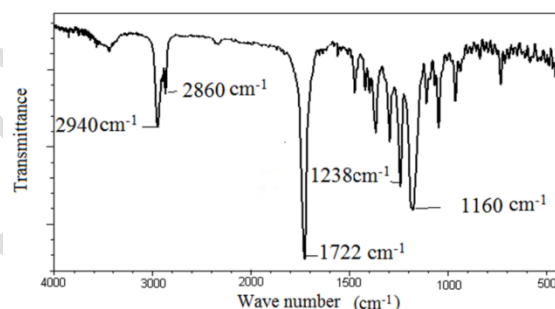
117 **Fig. 3** FT-IR spectrum of PMDPCS

120 **Fig. 4** XRD of PMDPCS

122 **Part two**

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

127 emission spectra as the solvent polarity raised. Table
128 4 shows the influence of the solvents on the
129 absorption and fluorescence spectra. By the above
130 procedure, there is a significant change were
131 observed in absorption and fluorescence spectra. As
132 can be seen from the Fig. 4, the Stokes shift changed
133 as a function of the dipole factor of the solvent, as
134 defined by Lippert and Mataga et al. [23-24]. It can
135 be seen observed that DAPPP in the solution turn
136 strongly polar in the excited state than in the ground
137 state. In most recent studies, the Stokes shift has a
138 linear variation with the dipole factor, which is
139 written by expression;

140 $$v_a - v_f \approx \left(\frac{(\varepsilon-1)}{(2\varepsilon+1)} - \frac{(n^2-1)}{(2n^2+1)} \right) \frac{(\mu_e-\mu_g)^2}{a^3 hc} \quad (1)$$

141 $$D_f = \frac{(\varepsilon-1)}{(2\varepsilon+1)} - \frac{(n^2-1)}{(2n^2+1)} \quad (2)$$

142

143 Where D_f is dipole factor, v_a and v_f are the absorption
144 and fluorescence peaks in wave numbers
145 respectively, ε is the dielectric constant and n is the
146 solvents refractive index. μ_e is the dipole moment of
147 the solute in the excited state. μ_g is representing the
148 dipole moment of the solute the ground states,
149 respectively, and a is the radius of the solvent cage
150 around the solute. The results obtained from the
151 Stokes shift as a function of dipole factor for
152 illustrative solvents are shown in Figure 5. It can be
153 seen that under same identical condition the DAPPP
154 is more polar than coumarin 503. Overall, these
155 results indicate that all these dyes exhibit large
156 changes in the dipole moment in the excited state, but
157 for DAPPP, the change is much greater than for
158 coumarin 503.
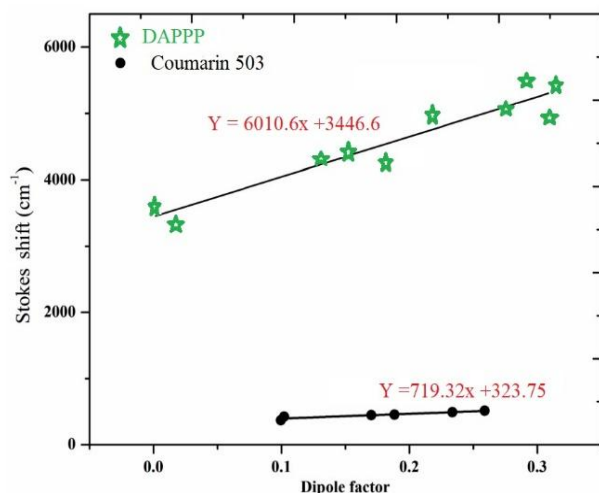
161 **Fig. 5** Variation in the Stokes shift of DAPPP and
162 coumarin 503.

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

168 $$\phi_f(s) = \phi_f(R) \frac{A_R n_s^2 \int I_S(\bar{v}) dv}{A_S n_R^2 \int I_R(\bar{v}) dv} \quad (3)$$

169 where the indices S and R refer to the sample and
170 reference, respectively, and the integral over I
171 represent the area under the fluorescence spectrum. A
172 is the optical density, and n is the refractive index of
173 the solvents. Tables 2 and 3 presents the results
174 obtained from the analysis of the quantum yields of
175 fluorescence (Φ_F) for DAPPP and coumarin 503.
176 From the data, it can be seen that under identical
177 conditions the Φ_F of DAPPP is higher than that of
178 coumarin 503. Under high power excitation, present
179 work study the ASE characteristics of DAPPP, in
180 acetone at a concentration of 2 mM DAPPP was
181 dissolved. Figure 6 provides the ASE spectrum (532
182 nm) with a narrow spectral bandwidth 6 nm (FWHM)
183 at a pump power of 9 mJ. As shown, at 2 mM
184 concentration the ASE peak is coinciding with the
185 maximum of the fluorescence emission spectrum. At

159
160
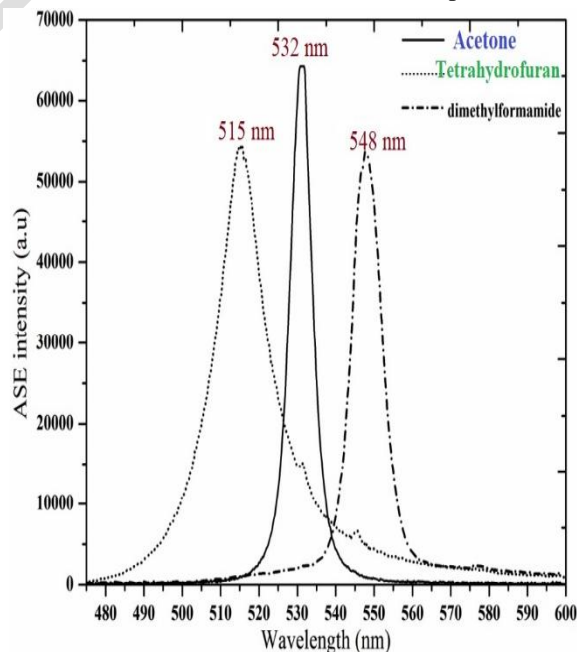
186 6 mM, there was no significant red shift observed.

187

188 **Fig. 6.** ASE spectra of DAPPP in acetone, tetrahy-
189 drofuran, and DMF.

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

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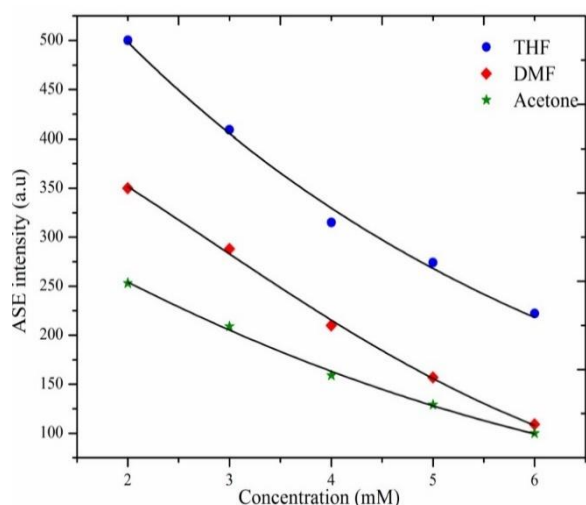
206 mJ. it was found that, when the concentration
207 increased, the intensity of the ASE decreased for each
208 solution, shown in Fig. 7.

209

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

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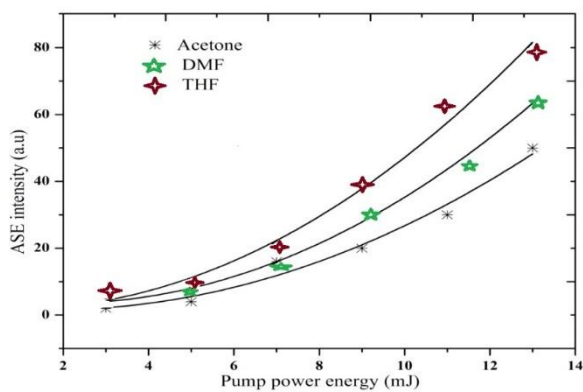
220 DAPPP in acetone increased slowly, while in THF
221 the intensity increased quickly.

222

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

225 To compare the difference between the
226 photochemical stabilization of the DAPPP in DMF at
227 concentration of 2 mM to that of coumarin 503 in
228 ethanol, UV laser of Nd: YAG was pump for this
229 solutions with pulse energy 9 mJ and 10 Hz. The
230 ASE intensity of DAPPP remained constant after
231 30K pulse, while the coumarin 503 drooped 45 % of
232 the initial intensity after 3 K pulses, and disappeared
233 completely at 7 K pulses as shown in Fig. 9.

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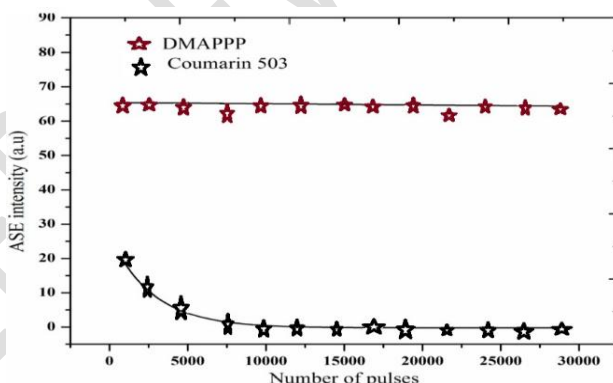
235 **Fig. 9** The photochemical stability of DAPPP in
236 DMF and coumarin 503 in ethanol.

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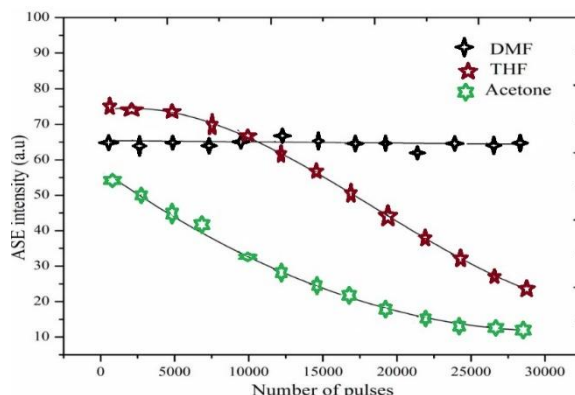
as seen in Fig. 10.

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];

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

where L is the length of excitation and γ is the optical gain.

The results show 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 A.O. Elzupir *et al.*

[26].

Fig. 11 Optical gains vs. pump pulse energy for DAPPP in DMF and coumarin 503 in ethanol
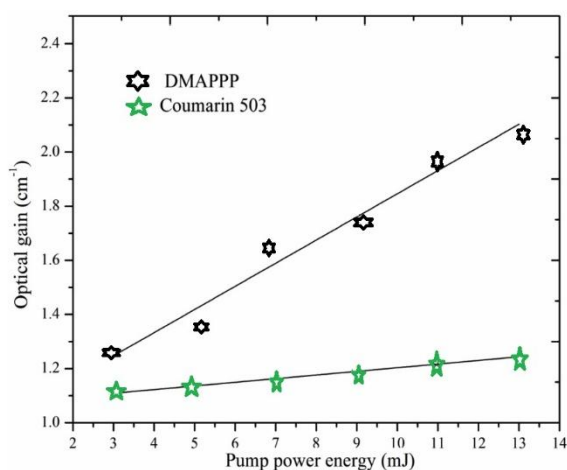
Table 1 FT-IR spectra data of compound

Compound	$\upsilon\,(C-H)$ aliphatic cm^{-1}	$\upsilon\,(C-H)$ aromatic cm^{-1}	$\upsilon\,(C=C)$ cm^{-1}	$\upsilon\,(C-N)$ cm^{-1}	$\upsilon\,(C=O)$ cm^{-1}	Other band $\upsilon\,(C-O)$ cm^{-1}
PMDPCS	2950 2920	3060	1595	1224	1755	1070

Table 2 Data of the impact of the solvents on the absorption and fluorescence spectra

Solvent	ε	λ_{max}			ϕ_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

ε is the dielectric constant, spectral and ASE properties: λ_{max} (nm) for absorption (A), F is the fluorescence and ASE; ϕ_F; ASE efficiency η (%) of DAPPP.

Table 3 Coumarin 503 in different solvent.

Solvent	ε	λ_{max}			ϕ_F	η
		A	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

ε is the dielectric constant, spectral and ASE properties: λ_{max} (nm) for absorption (A), F is the fluorescence and ASE; ϕ_F; ASE efficiency η (%) 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. This study has succeeded to building heterocyclic compounds as monomers to be polymerized.

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