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# 1 Photoluminescence modulation in the graphene oxide 2 dispersed 4-n-octyl-4'-cyanobiphenyl molecular system

3 A. Shah,<sup>a</sup> M. S. Sannaikar,<sup>b</sup> S. R. Inamdar,<sup>b</sup> B. Duponchel,<sup>c</sup> R. Douali<sup>a</sup> and  
4 D. P. Singh,<sup>\*a</sup>

5 <sup>a</sup>Univ. Littoral Côte d'Opale, UR 4476, UDSMM, Unité de Dynamique et Structure des  
6 Matériaux Moléculaires, F-62228 Calais, France.

7 <sup>b</sup>Laser Spectroscopy Programme, Department of Physics, Karnatak University,  
8 Dharwad-580003, India.

9 <sup>c</sup>Univ. Littoral Côte d'Opale, UR 4476, UDSMM, Unité de Dynamique et Structure des  
10 Matériaux Moléculaires, F-59140 Dunkerque, France.

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## 11 Abstract

12 Herein, we investigate the mechanism of photoluminescence modulation (PLM)  
13 in the 4-n-octyl-4'-cyanobiphenyl liquid crystal (LC) in the presence of various  
14 doping concentrations (0.02 to 0.4 wt%) of 2D-GO (two-dimensional graphene  
15 oxide) nanoflakes. The role of intermolecular interactions on PLM and the sub-  
16 sequent effect on the decay lifetime is also examined via time-resolved PL mea-  
17 surements. The presence of intermolecular interactions is additionally confirmed  
18 by means of differential scanning calorimetry and polarized optical microscopy.  
19 The successive addition of GO nanoflakes sharpens the absorption band of pure  
20 8CB LC; consequently, it is blue shifted. The PL properties of the 8CB LC  
21 enhance due to the addition of GO nanoflakes which might be attributed to  
22 electron-phonon interaction between 8CB molecules and GO nanoflakes. The  
23 PL enhancement has been further supported by the time-resolved PL decay  
24 time measurement. The longest and shortest fluorescence lifetimes have been  
25 recorded for the 0.1 and 0.4 wt % GO/8CB composites, respectively. The in-  
26 vestigated composites have shown their potential applications for fluorescent  
27 optical devices; however, the quantum efficiency needs to be further improved.

28 *Keywords:* Liquid crystal material; Graphene oxide; Photoluminescence;  
29 UV-visible absorbance; fluorescence decay lifetime.

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## 30 1. Introduction

31 After the first demonstration of polarised organic light-emitting diodes (OLEDs)  
32 in 1995, luminescent liquid crystalline (LLC) materials have attracted immense  
33 interests for organic optoelectronic applications, in particular the linearly po-  
34 larised emission, as it combines the easy alignment of molecules and their lumi-  
35 nescence properties [1, 2]. Calamitic LC materials are comparatively insignif-

36 icant for OLED application in comparison to the discotic LC materials which  
37 shows visible light emission [3, 4]. In contrast, calamitic LC exhibits the ul-  
38 traviolet absorption and emission that could also be transformed via doping a  
39 nanostructured materials [5, 6, 7, 8, 9, 10, 11, 12, 13]. Such transformation in  
40 PL property of a host matrix remarkably depends on several factors like shape,  
41 size, concentration, excitation wavelength, etc. of the guest dopant. Moreover,  
42 the absorption and emission properties of the dopant is one of the factors that  
43 determines the overall PL properties of the composites. For example, the be-  
44 havior of metallic [13], semiconducting [7] and insulating nanoparticles [9, 11]  
45 in the liquid crystalline matrices is found to be completely state of affairs for  
46 enhancing or quenching the PL properties. Some reports show the enhancement  
47 in PL emission of the LC materials due to the dispersion of different nanopar-  
48 ticles [9, 13]; meanwhile, on the other hand, the presence of quantum materials  
49 has quenched photoluminescence of LCs [14, 15, 16]. Moreover, the incorpora-  
50 tion of specific nanoparticles has also produced an induced photoluminescence  
51 in a non-luminescent LC material [17]. Despite using several kinds of nanopar-  
52 ticles and quantum dots, fewer investigations have been carried out with the  
53 two-dimensional (2D) nanosheets or flakes like graphene oxide (GO) or reduced  
54 graphene oxide (rGO) [18, 19].

55 Graphene shows superior electronic and mechanical properties as compared  
56 to its mother element graphite and it represents a single layer of graphite, in  
57 which  $sp^2$  bonded carbon atoms are hexagonally arranged. GO is derived from  
58 graphite by chemical oxidation and subsequent exfoliation and it is readily dis-  
59 persible in aqueous medium. The physical properties of GO depend on the  
60 degree of oxidation. The dispersion of graphene, GO and rGO has revealed  
61 some superior properties in the LCs [20, 21, 22, 23, 24]. The most of investi-  
62 gated regimes with the dispersion of graphene, GO and rGO include the study  
63 of electro-optical, electronic and thermal properties, but it has not been done  
64 so well for the photoluminescence. Therefore, this field has plenty of opportu-  
65 nities for further investigations to realize better composites for next-generation  
66 fluorescent displays and photonic devices.

67 In our previous article [23], we have investigated the graphene oxide (GO)  
68 dispersed 4-n-octyl-4'-cyanobiphenyl (8CB) hybrid system to disclose the long-  
69 range molecular interactions between GO and 8CB molecules. In this report, it  
70 has been seen that the orientation of 8CB molecules successively changes from  
71 planar to homeotropic depending on the dispersion concentration of GO. This  
72 study was focused on the molecular interaction and electronic properties of the  
73 hybrid system, but the investigation of photophysical properties for the hybrid  
74 system along with the pristine 8CB material has not been performed so far;  
75 therefore, in the present article, we have quantitatively studied the photolumi-  
76 nescence modulation in the 4-n-octyl-4'-cyanobiphenyl (8CB) liquid crystalline  
77 material dispersed with various concentrations of 2D-graphene oxide nanoflakes.  
78 The photoluminescence modulation (PLM) depends upon the intermolecular  
79 interactions between the 8CB molecules and the 2D-GO nanoflakes. The reduc-  
80 tion in full width at half maxima (FWHM) of the absorption band and slight  
81 shifting in the PL band supports the existence of intermolecular interactions.

82 The underlined mechanism has been further supported by the time-resolved  
83 PL measurements. The investigated composites indicate their applications for  
84 optical energy storage which is discussed within the scope of this paper.

## 85 **2. Experimental details**

### 86 *2.1. Host material: 4-n-octyl-4'-cyanobiphenyl (8CB) liquid crystal material*

87 Figure 1(a) represents the molecular structure of the 4-n-octyl-4'-cyanobiphenyl  
88 (8CB) liquid crystalline material. It exhibits smectic A and nematic mesophases  
89 including the transitions between crystalline and smectic A phases. The phase  
90 sequence of the 8CB LC material is as follows-

91 Smectic A 33.63 (0.32) Nematic 40.72 (3.68) Isotropic [in heating cycle]  
92 Isotropic 40.57 (4.44) Nematic 33.33 (0.50) Smectic A [in cooling cycle]

93 Transition temperatures are represented in  $^{\circ}\text{C}$  and corresponding transition  
94 enthalpies, shown in the brackets, are mentioned in  $\text{J g}^{-1}$ . The FTIR and NMR  
95 data for the 8CB LC material is given as supplementary information.

### 96 *2.2. Dopant material: Graphene oxide nanoflakes*

97 2D-GO nanoflakes were synthesized from commercially available graphite  
98 following the Hummers method as previously described in our previous articles  
99 [18, 19, 23]. We have utilized the same 2D-GO nanoflakes in this study which  
100 is already reported in our previous articles [19, 23]. To prepare GO suspension  
101 in DMF, 0.65 mg of 2D-GO nanoflakes were dissolved in 160 microliter of DMF  
102 and sonicated for 2.5 hours. This suspension was deposited on a Si wafer by  
103 drop casting technique and dried for 4 hours at  $50^{\circ}\text{C}$ . The SEM image of 2D-  
104 GO nanoflakes is presented in figure 1(b). The width size distribution of 2D-GO  
105 nanoflakes was in the range of 10–40 nm, whereas the lateral size distribution was  
106 found to be  $\approx 50\text{ nm}-25\ \mu\text{m}$ . As the characterization data of 2D-GO nanoflakes  
107 have already been published; therefore, we are not providing all characterization  
108 data here and only referring to the size and SEM image of nanoflakes.

### 109 *2.3. Preparation of the 8CB/GO composites*

110  $0.1\text{ mg ml}^{-1}$  suspension of 2D-GO was first prepared in the toluene. The sus-  
111 pension was homogenized by ultrasonication for several hours. After obtaining  
112 a homogenous suspension, it was added to the 8CB LC maintaining the wt/wt%  
113 from 0.02 to 0.4. The higher dispersion concentrations of GO were deferred as  
114 they started showing a high tendency of agglomeration beyond the 0.4 wt%.

### 115 *2.4. Differential scanning calorimetry (DSC)*

116 Usually, the dispersion of an external guest dopant causes the shifting of the  
117 mesophase transition temperatures of a LC material; therefore, it is essential  
118 to study the phase transitions of the 8CB/GO composites. For this purpose,  
119 phase thermograms were obtained using the TA Instruments Q1000 differential  
120 scanning calorimeter with a  $2\text{ K min}^{-1}$  heating/cooling rate. Later on, the DSC  
121 thermograms were normalized according to the weight of the samples taken for  
122 the DSC study.

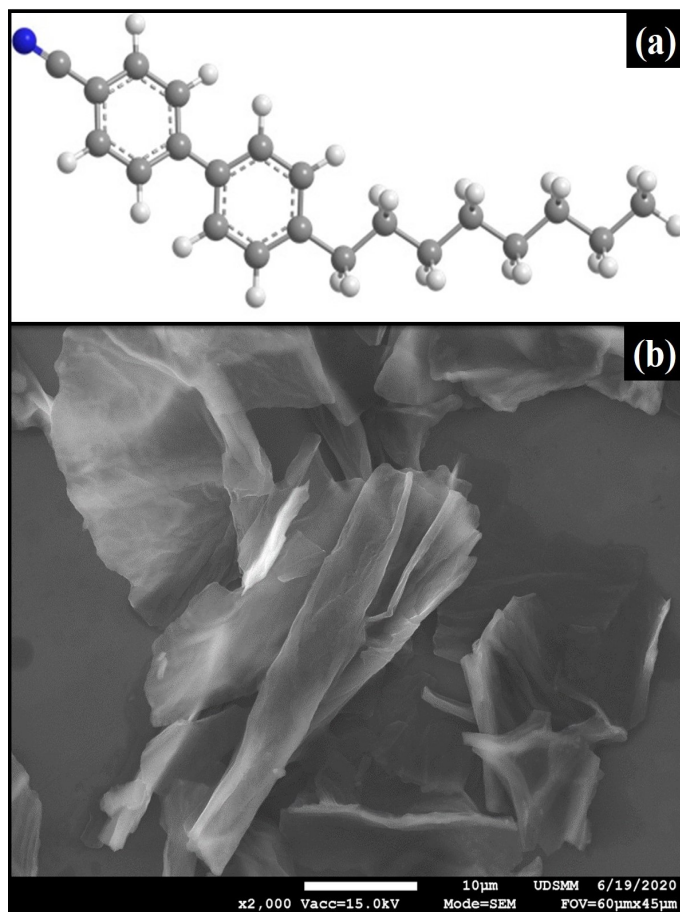


Figure 1: (a) Molecular structure of the 4-n-octyl-4'-cyanobiphenyl (8CB) liquid crystalline material and (b) scanning electron microscopic (SEM) image of 2D-graphene oxide (2D-GO) nanoflakes.

123 *2.5. Polarized optical microscopy (POM)*

124 Polarized optical microscopy is a fundamental tool to ensure the homoge-  
125 nous distribution of dopants in a LC matrix; therefore, polarized optical mi-  
126 croscopic (POM) observations were performed on the ZEISS AXIO equipped  
127 with Infinity2 image capturing software. During the POM measurements, the  
128 temperature of materials was controlled with a Linkam TMS 94 hotstage. The  
129 pure 8CB and its GO nanoflakes composites were filled in 50 µm thick unaligned  
130 commercial sample cells (purchased from AWAT, Poland) to perform polarized  
131 optical microscopy.

132 *2.6. UV-visible absorption spectroscopy*

133 UV-visible absorption measurements were performed using a NIR-UV-VIS  
134 Spectrophotometer (Jasco, V670). UV-visible spectra were recorded in the so-  
135 lution state (concentration = 1 mg ml<sup>-1</sup>), using toluene as solvent [11, 12].  
136 Absorption measurements were carried out in the range from 200 to 750 nm by  
137 keeping the both entrance and exit slit width equal to 5nm. The baseline and  
138 background corrections were done before performing the absorption measure-  
139 ments for the pristine 8CB LC and mixtures.

140 *2.7. Photoluminescence (PL) studies*

141 The photoluminescence spectra of pure 8CB and its 2D-GO composites were  
142 recorded with the help of a Fluoromax-4 Spectrofluorometer (JY, Horiba). All  
143 the samples were excited by a monochromatic light of wavelength 300 nm since  
144 the 8CB and 8CB/GO composites have a strong absorption band at this wave-  
145 length as rendered from UV-visible absorption measurements.

146 *2.8. Time-resolved PL Measurements (TRPL)*

147 In steady-state spectral measurement, the detector adds up all the photons  
148 emitted by the sample molecules, starting with the instance of excitation and  
149 ending with a time when the last excited molecule is decayed to the ground  
150 state. Time-resolved measurements, using time correlated single photon count-  
151 ing (TCSPC) technique, were performed; since they contain more information  
152 than is available from the steady-state data. Owing to spectral overlap of ab-  
153 sorption and emission, it is usually not possible to resolve the emission from  
154 the multiple residues from the steady-state data. Further, one can distinguish  
155 between static and dynamic quenching using lifetime measurements. Moreover,  
156 probe concentration can change during the measurement due to photobleaching  
157 leading to difficulty in making quantitative use of the local intensities. In con-  
158 trast, fluorescence lifetimes are typically independent of the probe concentration  
159 and are not influenced by the fluctuations in the lamp intensity. We have used  
160 a pulsed LED as an excitation source (296 nm) to measure the decay times of  
161 these composites at their maximum PL peak using a time-domain based ISS  
162 ChronosBH TCSPC Spectrometer. All the optical measurements were carried  
163 out at room temperature.

164 **3. Results and discussion**

165 *3.1. Differential scanning calorimetric (DSC) study*

166 The effect of GO dispersion on the mesophase transition temperatures of  
167 the 8CB LC material has been studied. Figure 2 shows the normalized differen-  
168 tial scanning calorimetric (DSC) curves of the 8CB and its composites having  
169 different concentrations of 2D-GO nanoflakes. As stated in the experimental  
170 section, the 8 CB LC exhibits smectic A (SmA) and nematic (N) mesophases.  
171 The SmA-N and N-Iso phase transitions took place at 33.63 and 40.72 °C, re-  
172 spectively during the heating process. It is observed in all composites that

173 the addition of different concentrations of GO in the 8CB causes a lowering in  
174 the N-Iso phase transition temperature. As the nematic-to-isotropic (N-I) is a  
175 weakly first-order transition; therefore, it might be due to lowering of the orien-  
176 tational order of the pure 8CB material after the dispersion of GO into different  
177 concentrations. In addition to this, it is also observed that the SmA-N phase  
178 transition has been weakened. It is probably due to lowering in the positional  
179 order of the SmA phase originated because of the change in layer arrangement.  
180 Usually, 2D-GO nanoflakes align with orientational directions along their long  
181 axes and the 8CB molecules tend to align along with the flakes; however, the  
182 global orientation does not relay in a single direction resulting in the reduction  
183 in the order parameter.

### 184 *3.2. Polarized optical microscopic study*

185 Polarized optical micrographs (POMs) of the 8CB and its GO nanoflakes  
186 composites are presented in figure 3. In general, the molecules of the pure 8CB  
187 LC material preferentially orient along with the director ( $\vec{n}$ ). The pristine 8CB  
188 LC material renders the typical fan-shaped texture of in smectic A phase (figure  
189 3a, at 25 °C) and traditional schlieren texture in the nematic phase (figure 3b,  
190 at 35 °C). The temperature for recording the POMs of 8CB/GO composites  
191 in a desired phase was chosen from their corresponding phase schemes. It is  
192 observed that the presence of 2D-GO flakes significantly changes the molecular  
193 orientation of the 8CB; as a result, the exemplary optical textures of the SmA  
194 and N phases have not been observed for the composites because of the GO  
195 flakes migrate closer to ITO substrate/LC interface due to viscous drift [23].  
196 As the dispersion concentration of GO is successively increased, the molecular  
197 orientation of the 8CB changes accordingly, and a homeotropic orientation has  
198 been achieved for the dispersion 0.4 wt% of GO. At this particular concentration  
199 of GO, global homeotropic orientation is visible (figure 3k,l); however, some  
200 illuminated regions are also observed which is might be due to the scattering  
201 of incident light through the edges of GO flakes. The observed homeotropic  
202 orientation is because of the interaction between the polar C≡N functional group  
203 of the 8CB molecules with the GO surface via an electron-phonon interaction.  
204 This postulate is recently reported by us [23]. For the intermediate dispersion  
205 concentration of 2D-GO nanoflakes, the orientation of 8CB molecules represents  
206 a merged state of the planar and homeotropic orientations.

### 207 *3.3. UV-visible absorption study*

208 The absorption spectrum of any material is the result of its electronic, vi-  
209 brational, and rotational transitions. The absorption peak corresponds to the  
210 electronic transition line, and the rest of the spectrum is formed by a series  
211 of lines that correspond to rotational and vibrational transitions. Therefore,  
212 the absorption spectrum provides in-depth information about the structure  
213 and transitions. The UV-visible absorption spectra of the pure 8CB LC and  
214 8CB/2D-GO nanoflakes composites containing different GO concentrations (i.e.  
215 0.02, 0.1, 0.2, 0.3 and 0.4 wt%) were recorded. These spectra were taken in the

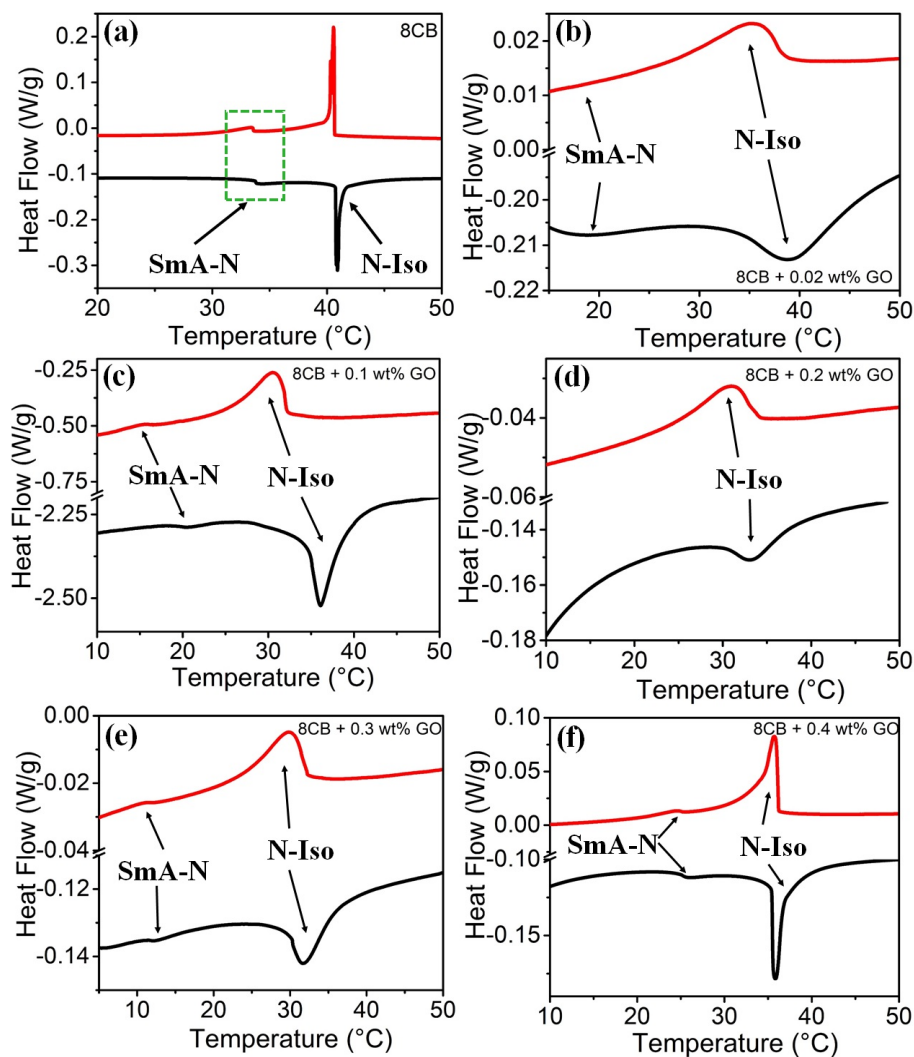


Figure 2: Normalized differential scanning calorimetric (DSC) curves of (a) 8CB, (b) 8CB + 0.02, (c) 8CB + 0.1, (d) 8CB + 0.2, (e) 8CB + 0.3 and (d) 8CB + 0.4 wt% dispersion of 2D-GO nanoflakes with a heating/cooling rate of  $2 \text{ K min}^{-1}$ .

216 solution having toluene as solvent and 1mg/ml solution concentration. Figure 4  
 217 shows the normalized absorption spectra of the pure 8CB LC and 8CB/2D-GO  
 218 nanoflakes composites.

219 It is noticed that the 8CB LC shows a strong absorption band nearly at  
 220 300 nm which is attributed to  $\pi$ - $\pi^*$  transitions in  ${}^1A_{1g} - {}^1B_{1u}$ . The  ${}^1A_{1g} - {}^1B_{1u}$   
 221 is a spin allowed, symmetry-forbidden, but vibronically allowed transition [25].  
 222 Additionally, we have previously reported that the 2D-GO flakes exhibit two ab-



223 sorption peaks at 230 and 300 nm, (supplementary figure S1), attributed to  $\pi-\pi^*$   
 224 transitions of C=C bonds and to  $n-\pi^*$  transitions of C=O bonds, respectively  
 225 [19, 26]. In 8CB/2D-GO composites, the successive addition of increasing weight  
 226 concentration of GO results a trivial narrowing in the absorption bandwidth.  
 227 Inset of figure 4 depicts the full-width half maxima (FWHM) for the pure 8CB  
 228 and 8CB/2D-GO nanoflakes composites. The FWHM varies nonlinearly with  
 229 the increasing concentration of GO nanoflakes in the solution. Besides, the nar-  
 230 rowing in the FWHM of the absorption band also caused a feeble blue shifting.  
 231 Steady-state spectral parameters are represented in Table 1. The sharpening in  
 232 the UV-visible absorption spectra of the 8CB/GO composites can be explained  
 233 by the modified Beer-Lambert law [27], which is as follows-

$$I = I_o(-c)^n \exp(\epsilon l) \quad (1)$$

234 where,  $I_o$  and  $I$  are the intensities of the incident and transmitted radiations,  
 235 respectively.  $c$  and  $l$  are the solution concentration and optical path length,  
 236 respectively, and  $\epsilon$  is the absorption coefficient.  $n$  is the power exponent.

237 In our study, the sharpness of the absorption band (slightly blue shifting)  
 238 might be associated with the dipole-dipole interactions between the 8CB LC  
 239 molecules and GO nanoflakes. If the dipole-dipole interaction is strong, the  
 240 energy required for an absorption will also be large, i.e., the position of the  
 241 absorption band will be located at lower wavelengths [28, 29].

#### 242 3.4. Photoluminescence (PL) study

243 The room temperature PL spectra of the pure 8CB LC and its composites  
 244 with GO nanoflakes are presented in figure 5. The pure 8CB LC exhibits a  
 245 strong PL emission peak at 336 nm, whereas 2D-GO nanoflakes emit a violet  
 246 band of 362 nm, (see supplementary figure S2), attributed to the  $n-\pi^*$  transition  
 247 of the isolated  $sp^2$  domains within the carbon-oxygen  $sp^3$  matrix [19, 26]. In  
 248 this study, we have not contemplated about the contribution of the disorder-  
 249 induced long-wavelength PL band (visible at  $\approx 700$  nm) of the GO nanoflakes  
 250 as the 8CB/GO composites only show a single PL emission nearly at 340 nm.  
 251 Interestingly, PL intensity of the 8CB/GO composites increases as compared to  
 252 the pure 8CB LC. This modulation in the PL emission might be related to the  
 253 combined effect of the change in optical density of 8CB LC after the addition  
 254 of different concentrations of GO nanoflakes and electron-phonon interaction  
 255 between the 8CB molecules and GO surface. In addition to this, the change in  
 256 molecular orientation could also be a factor that leads to PL modulation in the  
 257 composites. The optical density of a material is related to the PL emission in  
 258 the following manner.

259 At a particular excitation wavelength, the PL emission intensity can be  
 260 explained as follows [29]-

$$I_{PL(\lambda)} = 2.3I_o\epsilon(\lambda)cl\phi_{PL} \quad (2)$$

261 where,  $\phi_{PL}$  is the photoluminescence quantum yield and other abbreviations  
 262 are the same as explained in equation 1.

263 It is clear by the aforementioned equation that the PL intensity is propor-  
 264 tional to the optical density i.e.  $\epsilon c l$ . With the addition of GO nanoflakes in the  
 265 8CB LC, optical density changes nonlinearly due to the interfacial properties of  
 266 GO surface and 8CB molecules that govern the changes in the PL emission.

267 Besides, a nonlinearity in the PL emission as a function of GO concentration  
 268 for the 8CB/GO composites has also been observed. For the composites, maxi-  
 269 mum and minimum PL intensities have been observed for the 0.4 and 0.3 wt% of  
 270 GO, respectively. In addition to the change in the PL intensity, the broadening  
 271 of the PL band has also changed. The change in the broadening of the PL band  
 272 is probably due to the contribution of the PL of GO nanoflakes. We have also  
 273 analyzed this nonlinear change in the photophysical property by plotting the  
 274 Stokes shift versus GO concentration in the 8CB LC which is shown in figure 6.  
 275 A maximum Stokes shift (difference between the emission and absorption peak  
 276 wavelengths) of about 48 nm is detected for 0.1 % wt GO. A comparison of the  
 277 steady-state spectral properties of the 8CB LC and its composites with various  
 278 GO nanoflakes concentrations are listed in Table 1.

279 The fluorescence quantum yield of a sample is determined using a relative  
 280 optical method. The absorption factor should be estimated accurately for solu-  
 281 tions with a low absorbance, typically  $A \cong 0.1$ , to avoid internal filter effects and  
 282 errors arising from uneven distribution of the excited species in the detected vol-  
 283 ume. The fluorescence quantum yields ( $\varphi_s$ ) were obtained by comparison with  
 284 a standard dye using Equation-

$$\varphi_s = \varphi_r \left( \frac{I_s A_r n_s^2}{I_r A_s n_r^2} \right) \quad (3)$$

285 where,  $I_s$  and  $I_r$  are the integrated fluorescence emissions of the samples  
 286 (binary mixtures) and the standard dye (Coumarin 440, QY = 0.98) in ethanol,  
 287 respectively [30].  $A_s$  and  $A_r$ , respectively, are the absorbances at the excitation  
 288 wavelength of the samples and the reference, while  $\varphi_s$  and  $\varphi_r$ , respectively,  
 289 are the quantum yields of the sample and the reference,  $n$  being the refractive  
 290 index. The values of  $I_s$  and  $I_r$  are determined from the photoluminescence  
 291 spectra corrected for the instrumental response, by integrating the emission  
 292 intensity over the desired spectral range.

293 The results substantiate that the monotonical increase of quantum yield for  
 294 0.02, 0.2 and 0.4wt% of GO is in accordance with the results of photolumi-  
 295 nescence modulation of 8CB upon addition of GO. Further, quantum efficiency  
 296 for 0.1 and 0.2 wt% of GO are more as compared to that of pure 8CB. Hence,  
 297 GO has modulated and enhanced the photoluminescence properties of the 8CB  
 298 system.

### 299 3.5. Time Resolved Photoluminescence Measurements (TRPL)

300 The fluorescence decay profiles of the pure 8CB LC and 8CB/GO composites  
 301 are presented in figure 7. The decay curves were fitted by a bi-exponential decay  
 302 function and results are listed in Table 2. The average decay lifetime, ( $\langle \tau \rangle$ ), was  
 303 calculated from the following equation [27]-

$$\langle \tau \rangle = \frac{\tau_1 A_1 + \tau_2 A_2}{A_1 + A_2} \quad (4)$$

304 where,  $\tau_1$  and  $\tau_2$  represents the shorter and longer lifetime components with  
 305 their normalized amplitude components  $A_1$  and  $A_2$ , respectively. The fast decay  
 306 process with a lifetime around 1 ns, ( $\tau_1$ ), can be attributed to the non-radiative  
 307 re-combination, while the slow decay process ( $\tau_2$ ) originates from the radiative  
 308 decay.

309 The pure 8CB LC has a fluorescence decay lifetime of 1.32 ns; however, after  
 310 the dispersion of GO into various proportions, the decay lifetime also changes.  
 311 The gradually increasing dispersion concentration of GO in the 8CB LC from  
 312 0.0 to 0.1 wt % leads to an enhancement of the decay lifetime from 1.32 ns to  
 313 1.81 ns. Further addition of GO into the 8CB LC, reduces the decay lifetimes.  
 314 The longest fluorescence lifetime is detected for the 8CB+0.1 wt % GO com-  
 315 posite; whereas, the shortest decay lifetime is noticed for the 0.4 wt % GO/8CB  
 316 composite. The variation of average decay lifetime of the 8CB LC and its com-  
 317 posites with different concentrations of 2D-GO nanoflakes is presented in figure  
 318 8. The increased decay lifetimes indicate that the PL properties of the 8CB LC  
 319 have been enhanced after the dispersion of GO concentration up to 0.1 wt%. In  
 320 this situation, PL decays are dominated by the radiative process. Beyond this  
 321 critical concentration, average decay lifetime decreases which suggests that the  
 322 non-radiative decay processes are taking place in the composites and might be  
 323 resulting in the quenching of PL intensity. This study indicates that the small  
 324 dispersion concentration of 2D-GO nanoflakes are superior in PL properties;  
 325 thus, such composites could be used for fluorescent displays and optical devices.

#### 326 4. Conclusions

327 In conclusion, various concentrations of 2D-GO nanoflakes were dispersed  
 328 in a commercially available 4-n-octyl-4'-cyanobiphenyl (8CB) liquid crystalline  
 329 (LC) material and characterized via differential scanning calorimetry (DSC),  
 330 polarized optical microscopy, UV-visible, photoluminescence and time-resolved  
 331 PL techniques. DSC thermograms reveal that the dispersion of GO nanoflakes  
 332 lowers the weakly first-order nematic-isotropic (N-Iso) phase transition temper-  
 333 ature. This lowering of the N-Iso phase transition temperature might be due  
 334 to weaker orientational order parameter in the composites. The change in the  
 335 smectic A to nematic (SmA-N) phase transition is associated with the reduction  
 336 of positional ordering in the composites. 8CB LC exhibits a strong absorption  
 337 band at 300 nm attributing to the  $\pi$ - $\pi^*$  transitions, whereas GO nanoflakes  
 338 show two absorption peaks at 230 and 300 nm attributed to  $\pi$ - $\pi^*$  transitions of  
 339 C=C bonds and to n- $\pi^*$  transitions of C=O bonds, respectively. The dispersion  
 340 of GO nanoflakes causes the sharpening of the absorption band which has been  
 341 explained by the modified Beer-Lambert law. The presence of GO nanoflakes  
 342 has enhanced the PL emission of 8CB LC which is probably associated with the  
 343 combined effects of electron-phonon interaction and change in optical density.

344 The enhancement in PL properties has been further supported by the time-  
345 resolved PL measurements. The longest fluorescence lifetime has been detected  
346 for the 8CB+0.1 wt % GO composite; whereas, the shortest decay lifetime is no-  
347 ticed for the 0.4 wt % GO/8CB composite and their recorded values were found  
348 to be 1.81 and 1.06 ns, respectively. All the optical properties including the  
349 quantum efficiency were found to be nonlinear as a function of GO concentra-  
350 tion. The nonlinearity in the optical properties might be due to the interfacial  
351 properties of 8CB molecules and GO surface. The enhanced PL properties for  
352 small dispersion concentration of GO nanoflakes would be interesting for the  
353 fluorescent displays and optical devices.

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### 359 **Conflict of interest**

360 The article is original and has been written by the stated authors who are  
361 aware of its content and approve its submission. This article has neither been  
362 published previously nor under consideration for the publication elsewhere. We  
363 also declare "No conflict of interest exists".

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## Tables

Sample	$\lambda_{abs}$ (nm)	$FWHM_{abs}$ (nm)	$\lambda_{em}$ (nm)	Stokes shift ( $\Delta\lambda$ , nm)	PL Intensity (arb. units)	QY
8CB	300	34.00	336	36	11838	0.0976
2D-GO nanoflakes	300	-	362	62	11335	-
8CB + 0.02 wt% GO	299	29.85	341	42	30698	0.5448
8CB + 0.1 wt% GO	297	30.10	345	48	26764	0.3951
8CB + 0.2 wt% GO	297	25.74	337	40	43419	0.6362
8CB + 0.3 wt% GO	297	30.09	337	40	19265	0.3924
8CB + 0.4 wt% GO	297	25.73	335	38	112279	0.8180
C440 (C120)			430			0.9800*

Table 1: Steady-state spectral properties of the 8CB LC and its composites having different concentrations of 2D-GO nanoflakes. QY is abbreviated for quantum yield. \*Quantum yield of reference dye.

Sample	$\tau_1$ (ns)	$\tau_2$ (ns)	$A_1$ (%)	$A_2$ (%)	$\tau$ (ns)	$\chi^2$
8CB	0.21	1.35	2.47	97.53	1.32	1.2209
2D-GO nanoflakes	1.29	1.15	96.81	3.19	1.28	1.2
8CB + 0.02 wt% GO	1.20	3.35	87.35	12.65	1.47	1.2506
8CB + 0.1 wt% GO	1.28	3.55	76.63	23.37	1.81	1.2173
8CB + 0.2 wt% GO	1.03	2.68	86.95	13.05	1.24	1.3294
8CB + 0.3 wt% GO	0.95	1.40	59.73	40.27	1.12	1.0605
8CB + 0.4 wt% GO	0.20	1.10	4.3	95.7	1.06	1.0722

Table 2: Fluorescence decay parameters of 8CB and 8CB+GO mixtures fitted by bi-exponential fit.

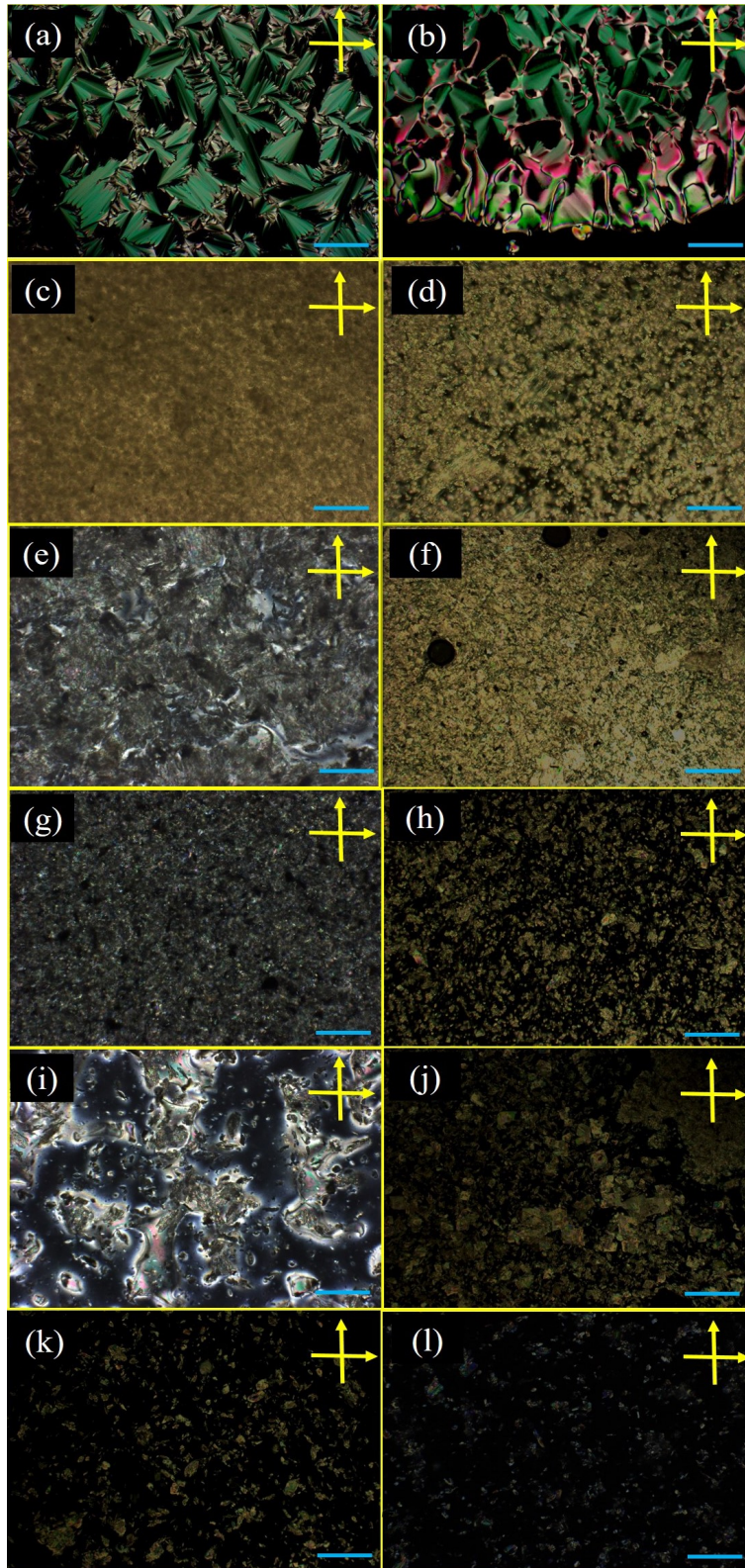


Figure 3: Polarized optical micrographs (POMs) of the (a),(b) 8CB, (c),(d) 8CB + 0.02, (e),(f) 8CB + 0.1, (g),(h) 8CB + 0.2, (i),(j) 8CB + 0.3 and (k),(l) 8CB + 0.4 wt% dispersion of 2D-GO nanoflakes in the smectic A and nematic phases, respectively. The crossed arrows represent the crossed polarizer-analyzer condition at which POMs have been taken. The scale bar is  $100 \mu\text{m}$  in all POMs.

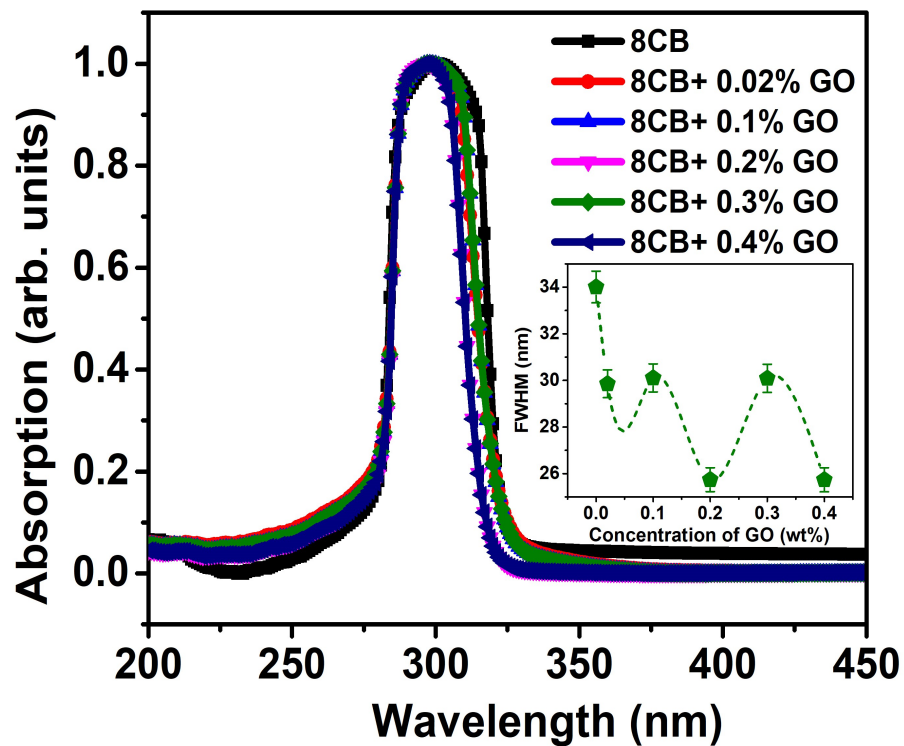


Figure 4: Absorption spectra of the 8CB and its composites with 2D-GO nanoflakes. Inset shows the variation of full width at half maxima (FWHM) of absorption band with the variation of dispersion concentration of GO. The concentration of solution was equivalent to 1mg/ml.

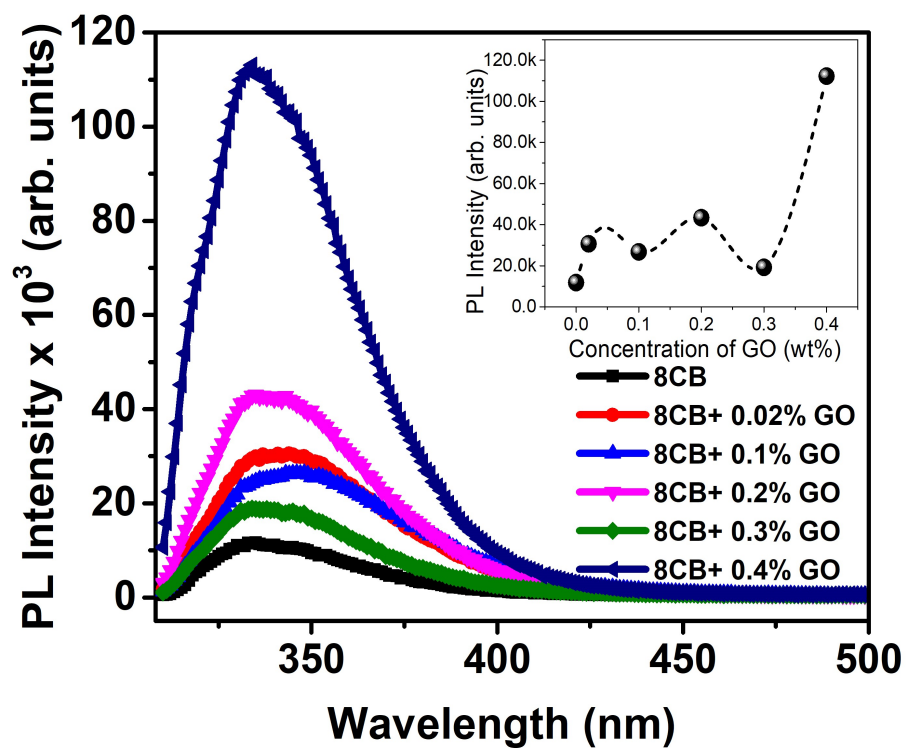


Figure 5: Photoluminescence (PL) spectra of the 8CB and its composites having different 2D-GO nanoflakes as a function of wavelength. Inset represents the variation of PL intensity with the change in the dispersion concentration of GO. The concentration of solution was equivalent to 1mg/ml.

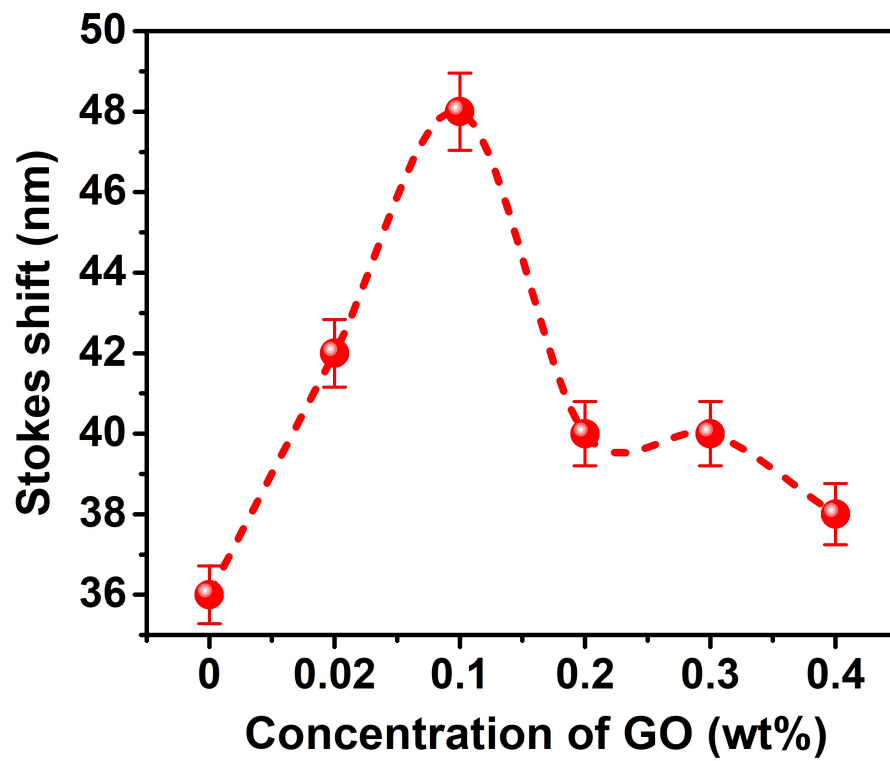


Figure 6: Stokes shift of the pure 8CB LC and its composites having different concentrations of 2D-GO nanoflakes.

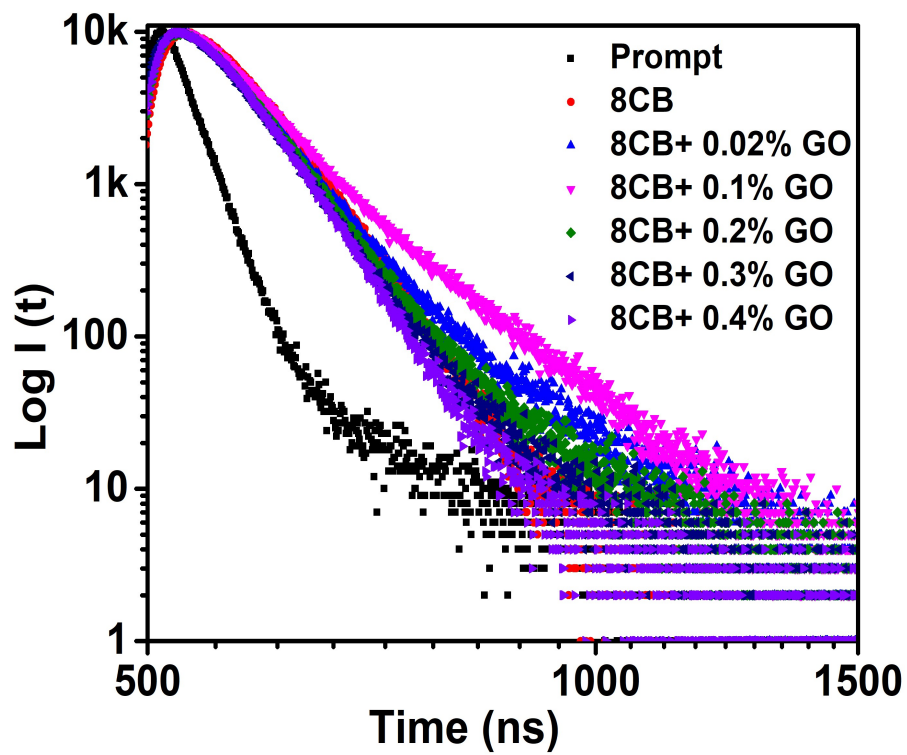


Figure 7: Time-resolved decay profile of the 8CB LC and it's composites having different concentrations of 2D-GO nanoflakes. The 8CB-GO pairs were excited by 296 nm wavelength.

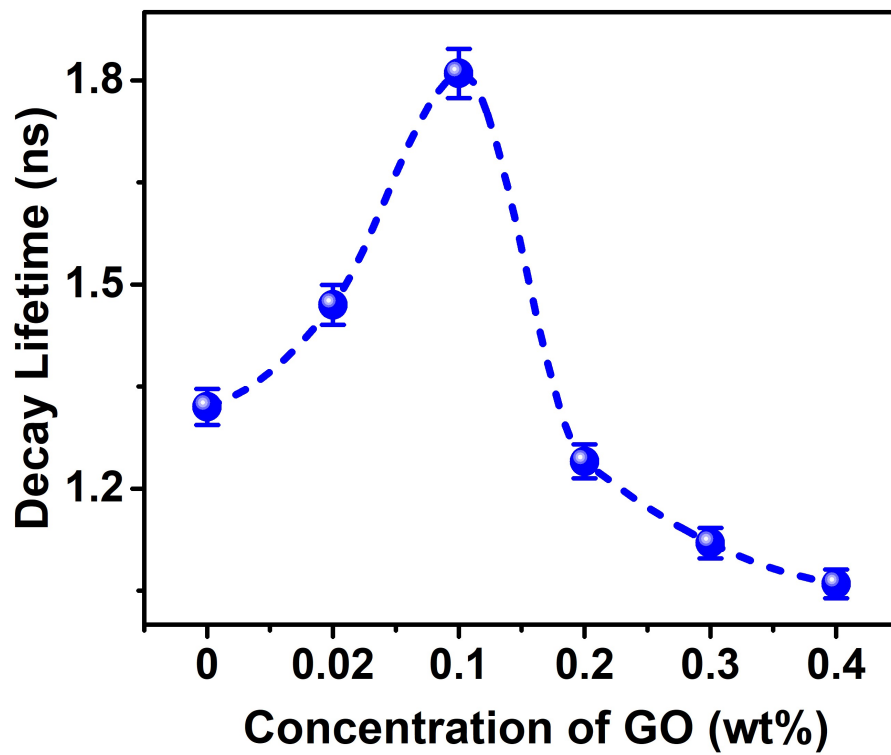


Figure 8: Variation of average decay lifetime with the change in 2D-GO nanoflakes concentrations in the 8CB LC.

