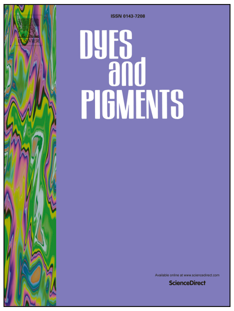

Synthesis and characterization of new green and orange region emitting anthracene based oxazol-5-one dyes

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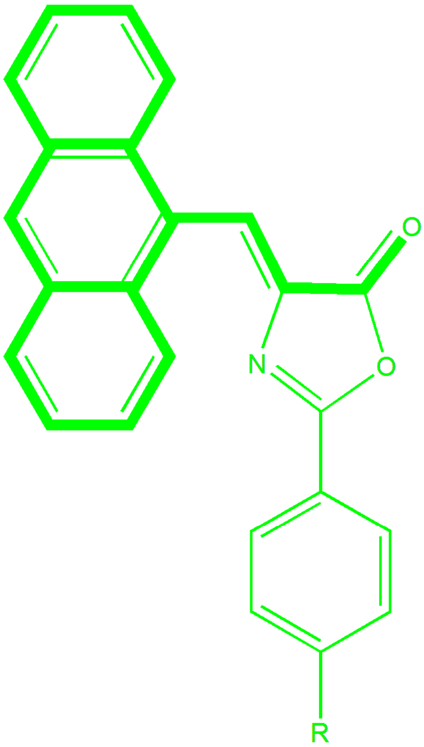
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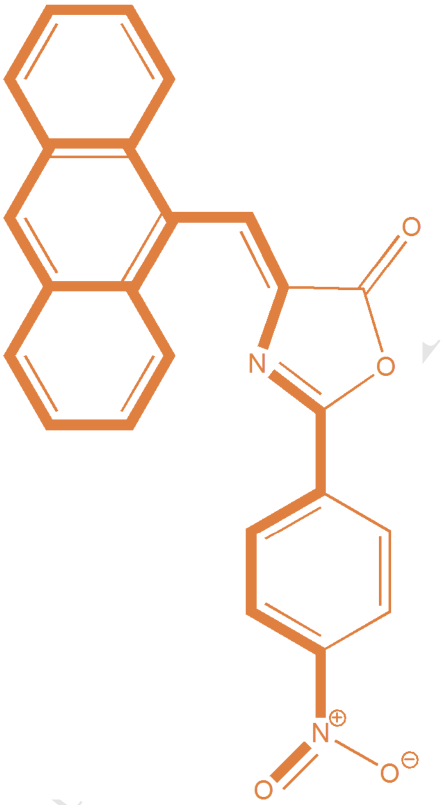
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Synthesis and characterization of new green and orange region emitting anthracene based oxazol-5-one dyes

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ABSTRACT

New anthracene oxazol-5-one dyes featuring an extended π-conjugated electron system have been successfully prepared by Erlenmeyer synthesis, structurally characterized and their spectroscopic properties were investigated by UV-vis absorption spectroscopy and fluorescence spectroscopy. The oxazol-5-ones were attached to the 9-position of the anthracene to obtain the desired structures. The dyes are having extended conjugation throughout their structure with oxazol-5-one ring as the chromophore. The spectral properties of the oxazol-5-one ring were monitored with respect to the substituents at the phenyl ring. All of the dyes synthesized show good solubility in common organic solvents. Also in order to establish whether there was any solvent affects the absorption and emission spectra of the compounds were measured in the solvents of acetonitrile, tetrahydrofuran and chloroform which have different polarity. Moreover, their absorption and emission properties were investigated in plasticized PVC film matrix. In comparison to the solution phase, the dyes displayed enhanced fluorescence emission quantum yield values when embedded in poly(vinyl chloride) polymer film. The anthracene based oxazol-5-ones were found to emit in the green portion of the spectrum for **2a** and **2b**, and in the orange portion of the spectrum for **2c**. By attachment of nitro substituent at the para position of the phenyl ring bound to oxazol-5-one core, the fluorescence maxima could be effectively modulated from the green region of the spectra to the orange region. 4-(9-anthralydene)-2-(4-nitrophenyl)oxazol-5-one (**2c**) exhibits large Stokes shift up to 146 nm presumably due to intramolecular charge transfer.

Keywords: Anthracene, Oxazol-5-one, Fluorescent, Erlenmeyer reaction, PVC

1. Introduction

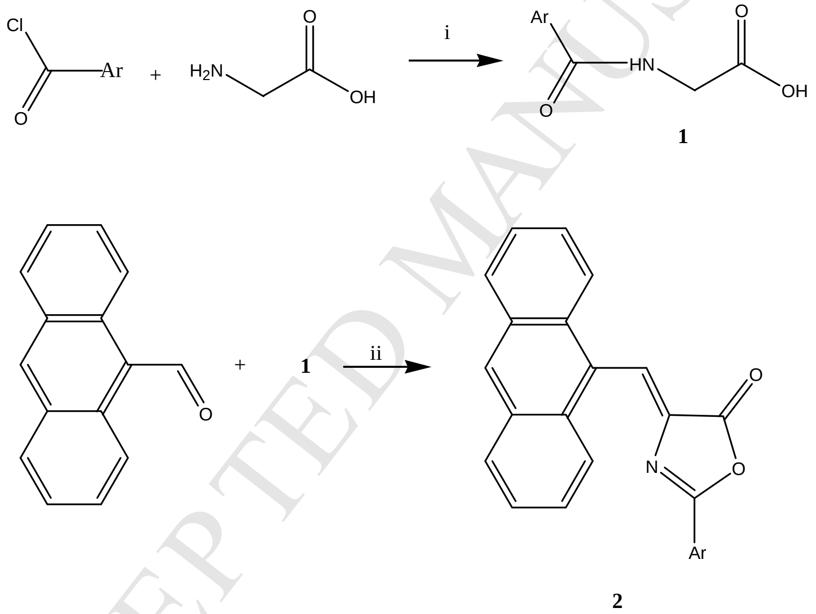
Organic compounds, which have been designed based on different heterocycles, have been extensively studied for their application in many fields of chemistry, biochemistry, biology and industry [1-19]. Most of the molecules are derived from five- and six-membered rings containing one or more nitrogen and/or oxygen heteroatom. For the synthesis of organic compounds for variety of applications, oxazol-5-one is a valuable chemical intermediate [1-22]. Unsaturated oxazol-5-one bearing heterocyclic derivatives can be prepared by reacting of aromatic aldehydes with hippuric acid in dry acetic anhydride which is the most convenient methods [1-6,8,9,11,13-16,18,20-22].

Due to the dependence of the photochemical and photophysical properties of the oxazol-5-ones on their structures, they found broad application areas such as medicine, biosensors, probes, fluorophores, chromophores, non-linear optical materials, photonics, electronics, photoswitches, organic light-emitting diodes and electrophotographic photoreceptors [1-9,15-18]. Their large optical properties in solid state as well as in solutions originate from extensive delocalized π-electron distribution [4,6,13,15].

Anthracenes are a well-known polycyclic aromatic hydrocarbon compounds which find variety of applications in diverse areas such as optoelectronics, high energy physics, bioimaging, sensing and medicine [23-42]. Owing to the extended π-electron system and excellent optical properties such as well-resolved absorption and emission bands, high fluorescence quantum yield values, nanosecond lifetime, high stability and superior electrochemical properties, anthracene derivatives find applications in organic optoelectronic devices including thin film transistors, solar cells, organic semiconductors, supramolecular materials, lasers, photovoltaic devices, molecular transistors, molecular switches, fluorophores, fluoroionophores, luminescentsensors, polymers and light emitting diodes [23-42]. Although different emission colours have been obtained for anthracene-based small molecules, most of the literature reports describe molecules with emission in blue region [23,24,26,28,31-33,39,40]. Anthracene derivatives are particularly valued for easy modification, deep-blue emission and high photostability, which makes them attractive for manufacture of blue emitters [23-26,28,31-33,39,40].

Despite the advantages mentioned above, owing to their unsuitable photophysical properties, unsubstituted anthracene and its derivatives are hard to be directly used for special applications such as bio-imaging due to a short emission wavelength, poor solubility and lack of functional groups [23-25,32]. Moreover, representative anthracene units can undergo intermolecular interaction like excimer or exciplex formation resulting in the decrease of their electroluminescent performances, therefore adequate molecular design is necessary for advanced anthracene derivatives [31,33]. For decades, great efforts have been devoted to develop new fluorescent derivatives with good solubility, long absorption and emission wavelength and large Stokes shift values [23-25,30,31]. Among the fluorophores, anthracene has been widely applied in the field of fluorescent molecules because it is easy to modify the structure [23,27,30-32,35,36]. It has been reported in the literature that structural modifications especially at 9 and 10-positions of the anthracene molecule can greatly improve anthracenes emission properties, thus many anthracene based structures have been synthesized in this manner [23-25,31,32,34-37,39-41].

Inspired by the unique properties of anthracene mentioned above and our promising results obtained with our previously synthesized oxazol-5-ones [20-22,43,44] and literature reveal, herein, we designed and synthesized anthracene oxazol-5-one dyes of 4-(9-anthralydene)-2-phenyloxazol-5-one (**2a**), 4-(9-anthralydene)-2-(4-tolyl)oxazol-5-one (**2b**) 4-(9-anthralydene)-2-(4-nitrophenyl)oxazol-5-one (**2c**) by introducing the oxazol-5-one moiety to the 9- position of the anthracene molecule. The effect of substitution was monitored by the change of substituents located at the phenyl ring. The UV-vis absorption and emission properties of these fluorophores were also investigated in the solvents of acetonitrile (ACN), chloroform ($CHCl_3$), tetrahydrofuran (THF) and in immobilized poly(vinyl chloride) (PVC) phase.



Scheme 1. The synthesis of **2** dyes (Ar: **2a**: phenyl; **2b**: p-tolyl; **2c**: p-nitrophenyl) (i: dil. NaOH sol.; ii: $(CH_3CO)_2O$, CH_3COONa).

2. Experimental

2.1. Materials and Instrumentation

All the solvents (spectroscopic grade and for synthesis), starting materials for synthesis and the PVC membrane components were purchased either from Merck, Fluka or Sigma Aldrich. The polyester support (Mylar type) was provided by Du Pont. The reaction completion was followed by TLC (thin layer chromatography) using silica gel plates (SiO2, Merck 60 F254) and UV light at 254 nm and 325 nm for visualization.

The compounds were characterized by FT-IR (spectra were recorded as KBr pellets by using a Perkin Elmer Spectrophotometer), NMR (Varian Mercury AS 400 NMR spectrometer at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) and by measuring the melting points in sealed tubes using an electrothermal digital melting points apparatus (Southend, UK) and are uncorrected. Elemental analysis (CHN) of the dyes was carried out in a FLASH 2000 analyzer (Thermo Scientific, Billerica, MA, USA). The samples (2 −3 mg) were catalytically combusted at 1200 °C. The steady-state absorption and emission spectra were recorded at room temperature using a Shimadzu 164 UV-1601 spectrophotometer and a Varian-Cary Eclipse Fluorescence spectrofluorimeter, respectively.

2.2. Synthesis

2.2.1. Synthesis of **1** *derivatives*

The hippuric acid derivatives (**1**), precursors of oxazol-5-ones were synthesized by the literature method [45,46].

2.2.2. Synthesis of **2** *derivatives*

Aldehyde (1 eq.), hippuric acid (1 eq.), sodium acetate (1 eq.) and acetic anhydride (3 eq.) were placed in a flask and stirred at room temperature for 10 minutes and then under 100-120˚C during 2 hours. The mixture changed colour upon fusion of all the reagents. After cooling down to room temperature, some ethanol was added and the product precipitated. The solid obtained was filtered and washed first with cold ethanol and then with hot water. If further purification was needed some of the compounds were recrystallized in a suitable solvent. Details of the amounts used for the synthesis and the characterization of the oxazol-5-one derivatives by melting point determination, FT-IR, ^{1}H NMR and ^{13}C NMR are given in the following sub-sections.

*4-(9-anthralydene)-2-phenyloxazol-5-one (**2a**)*

1.0 g (0.0048 mol) 9-antraldehyde, 0.86 g (0.0048 mol) hippuric acid, 0.66 g (0.0048 mol) sodium acetate. Orange solid; yield 14 %; mp: 242˚C. FT-IR (KBr): υ (cm^{-1}) 3048 (=C−H), 1796 (-O-$\underline{\text{C=O}}$), 1658 (-C=N-), 1322 (-C-N), 1185 ($\underline{\text{O-C}}$=O). ^{1}H NMR (CDCl$_3$, 400 MHz, δ (ppm)): 8.55 (s, 1H), 8.33 (s, 1 H, Anthracene-CH=), 8.12-8.10 (m, 2H), 8.05-8.03 (m, 2H,), 7.98-7.96 (m, 2H), 7.54-7.48 (m, 5H), 7.42-7.38 (2, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ (ppm)): 166.6, 164.1, 131.3, 130.3, 130.2, 130.1, 128.9, 128.8, 128.5, 126.5, 125.9, 125.5, 125.4. Anal. Calcd. for $C_{24}H_{15}NO_2$: C 82.50, H 4.33, N 4.01, O 9.16; found: C 82.43, H 4.41, N 3.95, O 9.21.

*4-(9-anthralydene)-2-(4-tolyl)oxazol-5-one (**2b**)*

1.0 g (0.0048 mol) 9-antraldehyde, 0.93 g (0.0048 mol) p-tolylglycine, 0.66 g (0.0048 mol) sodium acetate. Orange solid; yield 11 %; mp: 251˚C. FT-IR (KBr): υ (cm^{-1}) 3043 (=C−H), 1794 (-O-C=O), 1657 (-C=N-), 1326 (-C-N), 1171 (O-C=O). ^{1}H NMR ($CDCl_3$, 400 MHz, δ (ppm)): 8.54 (s, 1H), 8.28 (s, 1H, Anthracene-CH=), 8.12-8.10 (m, 2H), 8.05-8.03 (m, 2H), 7.87-7.85 (m, 2H), 7.51-7.49 (m, 4H); 7.21-7.19 (d, 2H), 2.38 (s, 3H, -CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, δ (ppm)): 166.8, 164.3, 144.6, 137.1, 133.5, 131.3, 130.1, 130.0, 128.9, 128.5, 127.7, 126.5, 126.0, 125.5, 122.8, 122.6, 22.5. Anal. Calcd. for $C_{25}H_{17}NO_2$: C 82.63, H 4.72, N 3.85, O 8.80; found: C 82.55, H 4.79, N 3.92, O 8.74.

*4-(9-anthralydene)-2-(4-nitrophenyl)oxazol-5-one (**2c**)*

1.0 g (0.0048 mol) 9-antraldehyde, 1.1 g (0.0048 mol) p-nitrobenzoylglycine, 0.66 g (0.0048 mol) sodium acetate. Dark red solid; yield 9 %; mp: 294˚C. FT-IR (KBr): υ (cm^{-1}) 3052 (=C−H), 1800 (-O-$\underline{C=O}$), 1649 (-C=N-), 1521 - 1350 (−NO_2), 1316 (-C-N), 1160 ($\underline{O-C}$=O). ^{1}H NMR ($CDCl_3$, 400 MHz, δ (ppm)): 8.60 (s, 1H), 8.57 (s, 1H, Anthracene-CH=), 8.26-8.24 (d, 2H), 8.15-8.05 (m, 6H), 7.54-7.51 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ (ppm)): 166.9, 164.4, 144.8, 131.6, 130.3, 130.2, 129.8, 129.6, 129.1, 128.7, 126.8, 126.7, 126.2, 125.7, 122.8. Anal. Calcd. for $C_{24}H_{15}NO_2$: C 73.09, H 3.58, N 7.10, O 16.23; found: C 72.99, H 3.57, N 7.24, O 16.20.

2.3.Fluorescence quantum yield studies

The fluorescence quantum yield values of the dyes were determined by using Fluorescein in 0.1 M NaOH (Φ_{std} = 0.95) as reference and were calculated by using the following equation (1) [47]:

$$\Phi_F = \Phi_{std} \text{ x } (F\ A_{std}\eta^2) / (F_{std}A\ \eta_{std}^2) \tag{1}$$

Where: F and F_{std} are the areas under the fluorescence emission curves of the samples and the standard, respectively. A and A_{std} are the respective absorbance values of the samples and standard at the excitation wavelength, respectively, and η and η_{std} the refractive indexes of the medium used for the samples and standard, respectively.

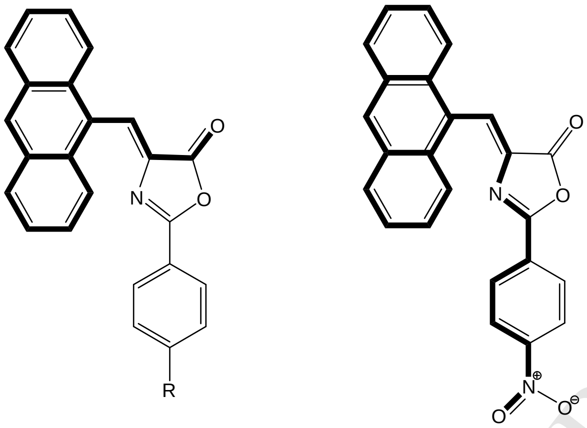
2.4. Polymer film preparation

The polymer films were prepared from a mixture of 120 mg of PVC (high molecular weight), 240 mg of plasticizer (bis-(2-ethylhexyl)phthalate (DOP) or bis-(2-ethylhexyl)adipate) (DOA)), equimolar lipophilic anionic additive potassium tetrakis-(4-chlorophenyl)borate (PTCPB) to the dyes and 1.5 mL of tetrahydrofuran (dry). The concentration of the derivatives were between 10^{-3} - 10^{-4} M (about 20 mmol dye kg^{-1} polymer). The prepared mixtures contained 33 % PVC and 66 % plasticizer by weight. The resulting cocktails were spread onto a 125 µm polyester support (Mylar type) having a width of 120 mm by knife coating. Polyester provides a mechanical support for thin films of PVC which are impossible to be handled without it. The polymer support is optically fully transparent and exhibits good adhesion to PVC. In order to avoid the damage from the ambient air of laboratory and keep the photostability of the membranes, the obtained PVC films were stored in a THF containing desiccator and in the dark. The resulting dye doped PVC films were placed diagonally into the measuring cuvette in order to achieve better reproducibility of the measurements.

3. Results and discussion

3.1. Synthesis and structure

Scheme 1 depicts the synthetic routes and molecular structures of compounds **2(a-c)** (Fig.1**)**. Firstly, we synthesized the key precursors, hippuric acid derivatives (**1**), by the literature methods [45,46]. Then using Erlenmeyer reaction **2** dyes were easily prepared by condensation reaction of 9-anthraldehyde with the prepared precursors, hippuric acid for **2a**, p-tolylglycine for **2b** and p-nitrophenylglycine for **2c** in the presence of sodium acetate and acetic anhydride. The synthons for these dyes, all hippuric acid precursors are colourless crystalline compounds. However, after the condensation of the molecules acquires orange colour for 2a and **2b**, and dark red for **2c.** This is probably because during the condensation, the bond formation between the molecular pairs is brought about when filled π-orbitals of donor overlap with the depleted orbitals of the acceptor as indicated in the literature [4]. The two new molecular orbitals are formed, the lower energy molecular orbitals for the compounds is occupied in the ground state. The transition from this molecular orbital to the new upper molecular orbital is responsible for the new lower energy absorption band observed in Figure 2.



2a (R-H) and **2b** ($R-CH_3$) **2c**

Fig. 1. The structure and conjugation pathway for **2** dyes.

The frequencies of the stretching vibrations of the C=N group was represent at 1658, 1657 and 1649 cm^{-1} for **2a**, **2b** and **2c**, respectively, in line with the literature [2,13,15,16,18]. The strong electron withdrawing nitro group for **2c** decreases the vibration band of C=N group to 1649 cm^{-1}, which also indicates the charge transfer in this dye is from electron donating 9-anthralydene moiety to the electron withdrawing nitro group (Figure 1) and is in agreement with the absorption and emission maxima. The characteristic absorption band of the carbonyl group was found at 1796, 1794 and 1800 cm^{-1} for **2a**, **2b** and **2c**, respectively. Due to the conjugation pathway from 9-anthryl group to carbonyl group for **2a** and **2b** dyes, the stretching vibration frequency is lower than that of the one for **2c**, which is also in agreement with the absorption and emission properties.

3.2. Absorption and emission properties in solution phase

The synthesized anthryl-oxazol-5-one dyes UV/Vis and emission spectra were measured in diverse solvents with different polarity, acetonitrile (polarity 0.460), chloroform (polarity 0.259) and tetrahydrofuran (polarity 0.207), to establish whether there was any solvent effect [9]. The compounds show absorption maxima between 433-495 nm and emission maxima between 515-620 nm (Figure 2, Figure 3 and Table 1), which are different from the anthracenes characteristic structural absorption approximately between 300-390 nm and emission between 360-460 nm [23], indicating formation of a new chromophore systems for **2** dyes as shown in Figure 1. Obviously seen in Figure 2 and Table 1, all the synthesized molecules absorption properties exhibit similar sensitiveness towards solvent polarity, i.e blue-shifts in more polar solvent of acetonitrile. The emission maxima of **2c** presents somewhat different sensitivity towards polarity as it is can be seen form Figure 3 and Table 1. In comparison to **2a** and **2b**, which exhibits red-shift in emission maxima in more polar solvent of acetonitrile, the **2c** dye characterizes a red-shift of the fluorescence band in less polar solvents. Similar evidence has been reported in the literature for branched oxazol-5-one dyes studied by Jedrzewska and co-workers [1]. The emission wavelength of the dyes of **2a** and **2b** is red-shifted only slightly in acetonitrile than that in the solvents with mediate polarity and the emission of **2c** is blue-shifted in polar solvent of acetonitrile. This might be because the photo-induced charge transfer is not significant, in other words the dipole moment of the excited state is not much larger than the ground state. It would arise also from lowered difference of equilibrium geometries between ground and excited states.

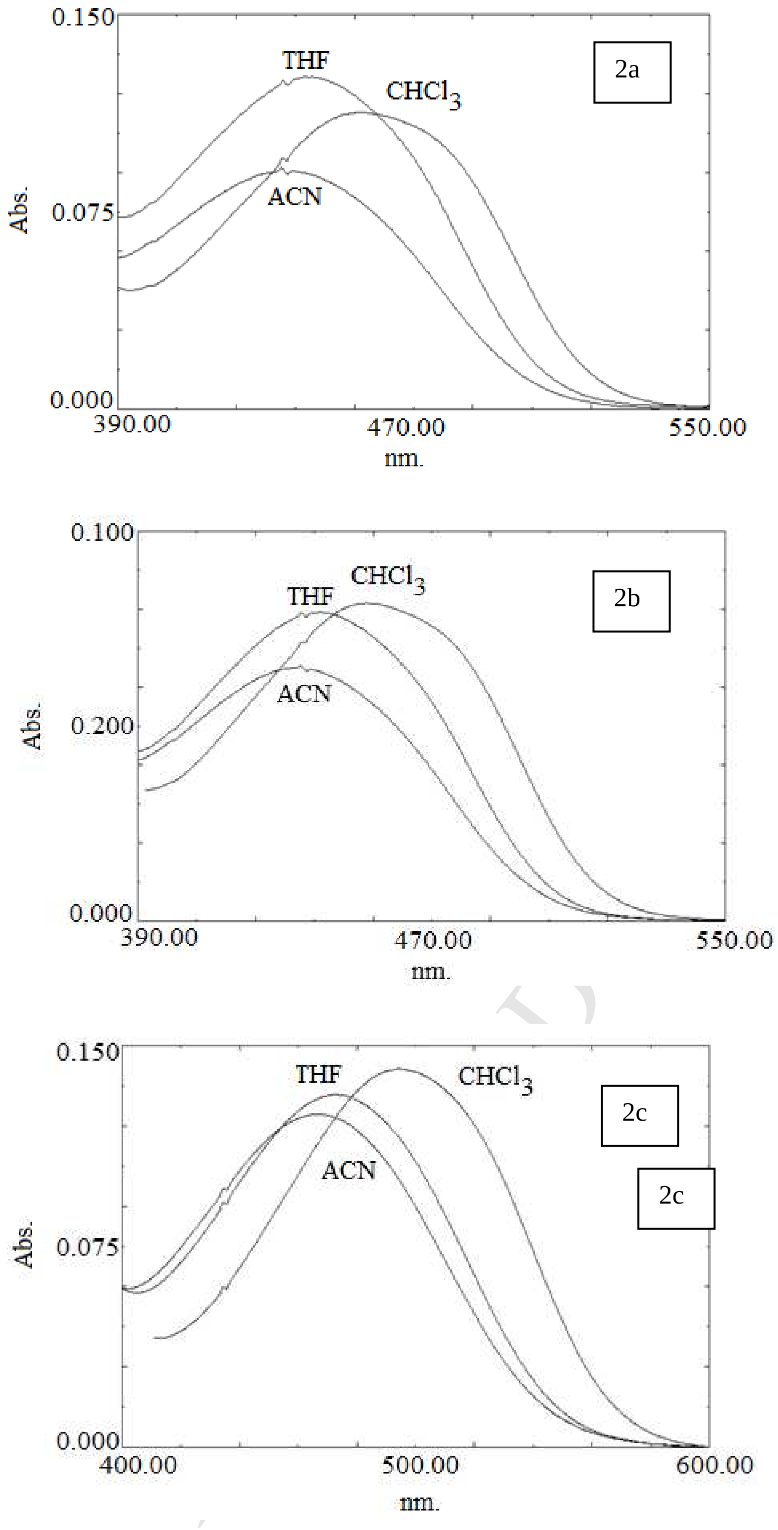


Fig. 2. The UV-vis absorption spectra of **2** in acetonitrile (ACN), chloroform ($CHCl_3$) and tetrahydrofuran (THF).

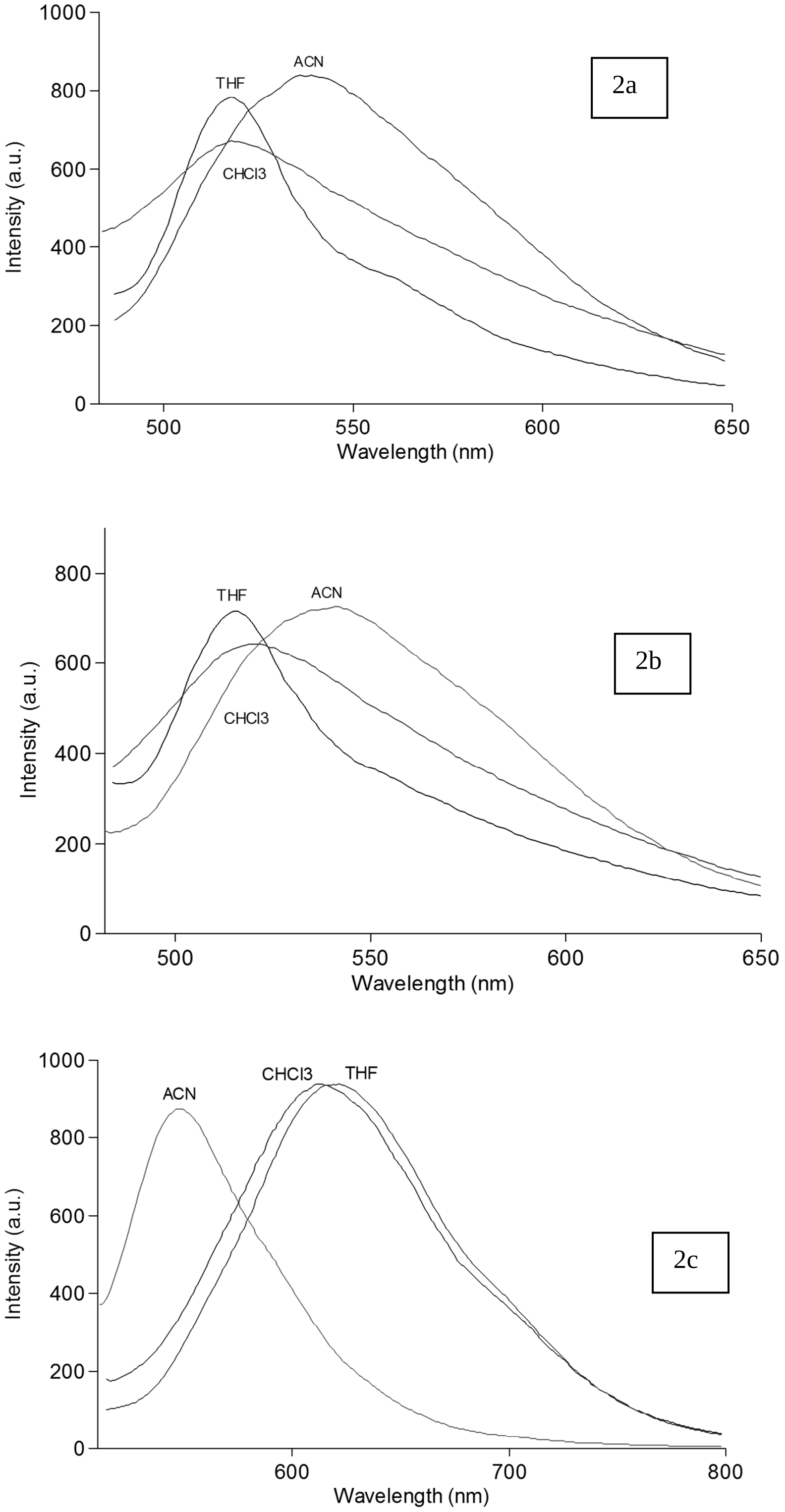


Fig. 3. The fluorescence spectra of **2** in acetonitrile (ACN), chloroform ($CHCl_3$) and tetrahydrofuran (THF).

Table 1

Absorption and fluorescence emission maxima (**λ**, nm), Stokes shifts (Δ**λ**, nm), molar extinction coefficients (ε, 10^3 L.mol^{-1}.cm^{-1}) and fluorescence quantum yields (Φ_F) for compounds **2a–c** in solutions of acetonitrile (ACN), chloroform ($CHCl_3$), tetrahydrofuran (THF) and PVC polymer film.

Compound	Solvent	Plasticiser	λ_{abs}^{max}	λ_{emis}^{max}	Δλ	ε	Φ_F
2a	ACN		436	540	104	13.8	0.0003
	$CHCl_3$		456	518	62	17.0	0.0006
	THF		442	517	75	16.2	0.0008
	PVC	DOP	452	524	72	452.2	0.0469
		DOA	447	524	77	452.2	0.0337
2b	ACN		433	540	107	11.8	0.0006
	$CHCl_3$		453	521	68	14.8	0.0007
	THF		440	515	75	14.4	0.0014
	PVC	DOP	450	525	75	447.1	0.0712
		DOA	445	524	79	447.1	0.0503
2c	ACN		467	547	80	8.2	0.0007
	$CHCl_3$		495	614	119	9.3	0.0012
	THF		474	620	146	8.6	0.0050
	PVC	DOP	486	603	117	437.8	0.0315
		DOA	483	604	121	437.8	0.0348

The synthesized compounds have linear π-conjugated framework end-capped by electron-donating methyl (**2b**) and electron-accepting nitro group (**2c**) (Figure 1). The anthracene moiety was chosen as electron donor group. In order to compare the effect of the electron accepting and electron donating groups on the absorption and emission properties of the synthesized fluorophores, we attached p-tolyl as electron donor (D) group (**2b**), p-nitrophenyl group as electron acceptor (A) group (**2c**) and as a reference phenyl group (**2a**) to the 4th position of the oxazol-5-one ring. The dye **2b** is substituted in a D-π-D arrangement, while **2c** is substituted in a D-π-A arrangement. Compound **2a** was prepared for comparison.

We anticipate that depending on donor/acceptor strength of the substituents, the oxazol-5-one heterocycle can act as an electron acceptor by accommodating an excess charge on the carbonyl group or on the nitro group (Figure 1). **2a** and **2b** dyes possess charge-transfer between the electron-donating 9-antralidene moiety and the electron-withdrawing carbonyl group of the oxazol-5-one ring (Figure 1). The pair of electrons in 9-anthralydene moiety exerts positive mesomeric effect. Thus positive charge is acquired by 9-anthrylidene group and the negative charge by the oxygen of carbonyl group for **2a** and **2b**, and of nitro group for **2c**. For **2c** dye the charge-transfer pathway is extended and different from the one for **2a** and **2b** due to strong electron accepting nitro group, thus it is again from 9-antralydene electron donating group, but this time to strong electron accepting nitro group (Figure 1). This increase of the dimensionality of donor-π-acceptor **2c** dye causes a red-shift of both absorption and emission maxima of **2c** in comparison to **2a** and **2b** dyes (Table 1, Figure 2, Figure 3). The absorption maxima are shifted up to 495 nm and emission maxima are shifted up to 620 nm for **2c**. The little shift in emission in ACN when comparing **2a** and **2b** with **2c** can be attributed to the difference in their attitude toward solvent polarity which is in the opposite direction. For **2a** and **2b** red-shift is observed in the polar solvent of ACN, while for 2c blue-shift is observed in the same solvent. Opposite to THF and $CHCl_3$ where there is a large red-shift in emission of 2c in comparison to 2a and 2b, the slight red shift in ACN is due to the fact that **2c** derivative's dipole dipole interaction with polar nitro group is predominant, thus its electron withdrawing ability and hence conjugation degree decreases. As a result while there is a red-shift of approximately 100 nm in emission maxima of **2c** in THF and $CHCl_3$ in comparison to **2a** and **2b**, there is only 20 nm red-shift in ACN.

It is a desired property to have a dipolar structure bearing electron donating substituent linked to the oxazol-5-one skeleton (electron acceptor) by a π-conjugated bridge [1]. Such structure is conductive in intramolecular charge transfer. 4-(9-anthralydene)-2-(4-nitrophenyl)oxazol-5-one (**2c**) exhibits large Stokes shift up to 146 nm presumably due to intramolecular charge transfer (Table 1).

From Table 1, it can be clearly seen that the fluorescence quantum yield values of the dyes changes regularly in solution media. In the polar solvent of ACN, the fluorescence intensities of **2** derivatives are quenched. The decrease in fluorescence quantum yield upon increasing solvent polarity could be related to some interactions between the excited solute molecules and solvent molecules, which change the excited-state configuration and thus the fluorescence intensity [1]. The highest quantum yield values for solution phase for all the dyes studied were obtained in THF. The rank for the quantum yield values is as 2c > 2b > 2a in solution phase.

3.3. Absorption and fluorescence emission properties in PVC film matrix

Absorption and fluorescence emission data of all three oxazol-5-one molecules in PVC are summarized in Table 1. The absorption maxima of **2** derivatives were in the rage of 524-603 nm (Fig 4). The PVC films which were plasticized with DOP, were slightly red-shifted in the range of 3-5 nm with respect to DOA plasticized polymer films. Compared to the absorption maxima in ACN and THF red-shift and in $CHCl_3$ blue-shift were observed in PVC matrix for all the molecules (Table 1, Fig. 4). The emission maxima in PVC film were observed between 524-604 nm. The emission maxima of **2a** and **2b** were red-shifted in PVC in comparison to ACN and THF, but blue-shifted in comparison to ACN. However **2c** emission maxima were blue-shifted in ACN in comparison to PVC, but red-shifted in comparison to $CHCl_3$ and THF. However there were no significant differences between plasticizers used in PVC. Similar to the results obtained in solution phase also in PVC film both absorption and emission maxima of **2c** are red-shifted in comparison to **2a** and **2b**, which can also be attributed to the longer conjugation pathway of 2**c** as shown in Fig. 1. Fluorescence quantum yield values of the dyes in polymer film matrix has enhanced about 30- to 50 fold, with respect to the quantum yield values observed in solution phase (Table 1). Induced steric effect in immobilized PVC matrix, with respect to solvated derivatives in solution phase, may support the increase in fluorescence emission. Moreover the molar absorption coefficients are about 30- to 50 times higher in polymer matrix in comparison to solution phase. The data obtained reveals that the dye molecules absorb and fluorescence better in immobilized PVC film.

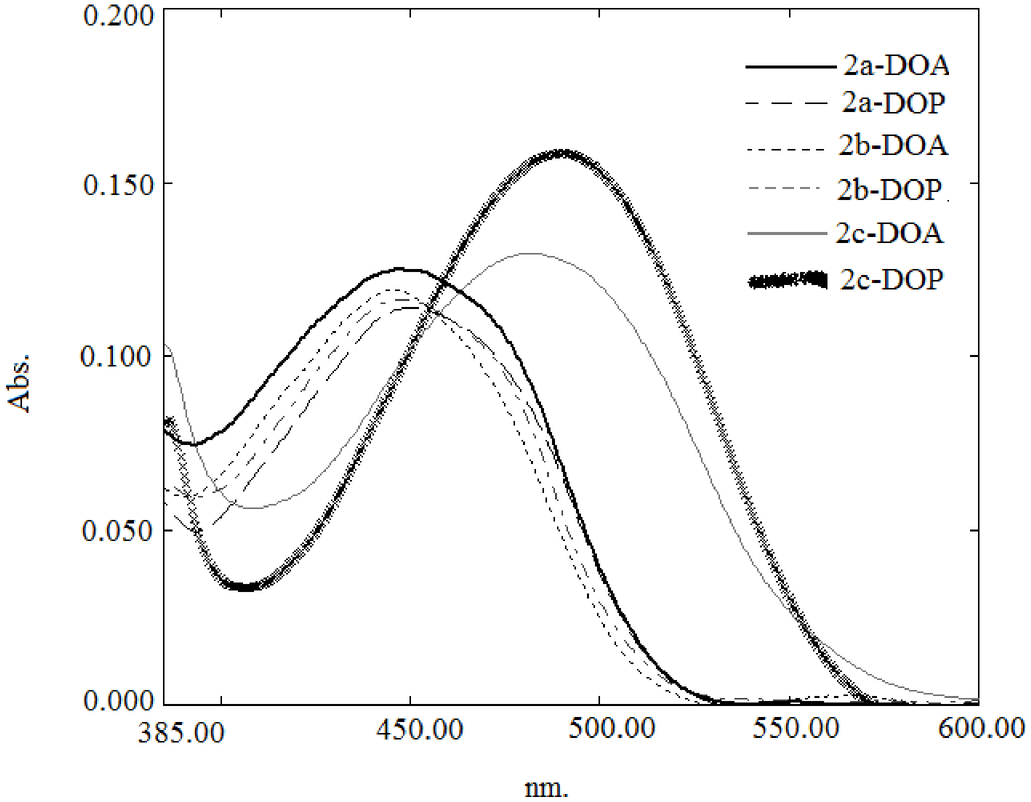


Fig. 4. The absorption spectra of **2** in plasticized PVC film.

At the end, it should be highlighted that the synthesized oxazol-5-one molecules present absorption in the visible region (Fig. 2, Fig. 5), which depending on application is a relevant feature in an efficient photoswitch; because in this case, low-energy light could be used; this is a required condition especially in biological media in which more energetic light could damage the system [9]. Moreover, most of the anthracene incorporating molecules in the literature are defined as blue emitters [23-26,28,31-33,39,40]. We propose novel anthracene based fluorophores which have emission in the different regions of the spectra, i.e 2a and 2b have emission in blue range of the spectrum and 2c in the orange region.

4. Conclusion

In the present study, we have synthesized new substituted oxazol-5-ones incorporating 9-anthracene moiety and characterized structurally by FT-IR, ^{1}H-NMR and ^{13}C-NMR techniques. The frequencies of the stretching vibrations of the C=N and C=O group were found to be significantly influenced by substituent effects. In order to demonstrate and understand the substituent effect on spectral properties, we also investigated their absorption and emission properties in the solvents of acetonitrile, tetrahydrofuran and chloroform and solid matrix of PVC. The oxazol-5-one molecules exhibited much higher fluorescence emission in immobilized polymer film matrices with respect to solution phase. The newly synthesized oxazol-5-one dyes have absorption in the visible region, which is a desired property for biological applications and are fluorescent molecules with emission in the green portion of the spectra for **2a** and **2b**, and in the orange portion of the spectra for **2c**. Also absorption and emission properties were in agreement with the structural features indicating that the charge transfer direction for **2a** and **2b** is from 9-antralidene moiety to carbonyl group, while for **2c** it changes to nitro group. These results show the control of spectral properties by the electron donating/withdrawing effect of the substituent. The asymmetric polarization induced by the presence of electron donor and electron acceptor groups in these π-electron conjugated molecules entails an extensive delocalization of the π-electron distribution, which is expected to favour their nonlinear interaction with light.

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Highlights

- The anthracene based oxazol-5-ones were found to emit in the green and orange portion of the spectrum.

- The derivatives exhibits large Stokes shift up to 146 nm presumably due to intramolecular charge transfer.

- The newly synthesized oxazol-5-one derivatives have absorption in the visible region.