



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-anthralydeno)-2-(4-nitrophenyl)oxazol-5-one (**2c**) exhibits large Stokes shift up to 146 nm presumably due to intramolecular charge transfer.

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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,

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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 (CHCl₃), tetrahydrofuran (THF) and in immobilized poly(vinyl chloride) (PVC) phase.

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 ¹H NMR and 100 MHz for ¹³C 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 min and then under 100–120 °C during 2 h. 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, ¹H NMR and ¹³C NMR are given in the following sub-sections.

2.2.2.1. 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): ν (cm⁻¹) 3048 (=C–H), 1796 (–O–C=O), 1658 (–C=N–), 1322 (–C–N), 1185 (O–C=O). ¹H NMR (CDCl₃, 400 MHz, δ (ppm)): 8.55 (s, 1H), 8.33 (s, 1H, 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). ¹³C NMR (CDCl₃, 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 C₂₄H₁₅NO₂: 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.

2.2.2.2. 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): ν (cm⁻¹) 3043 (=C–H), 1794 (–O–C=O), 1657 (–C=N–), 1326 (–C–N), 1171 (O–C=O). ¹H NMR (CDCl₃, 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, –CH₃). ¹³C NMR (CDCl₃, 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 C₂₅H₁₇NO₂: 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.

2.2.2.3. 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): ν (cm⁻¹) 3052 (=C–H), 1800 (–O–C=O), 1649 (–C=N–), 1521–1350 (–NO₂), 1316 (–C–N), 1160 (O–C=O). ¹H NMR (CDCl₃, 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). ¹³C NMR (CDCl₃, 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 C₂₄H₁₅NO₂: 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 ($\Phi_{\text{std}} = 0.95$) as reference and were calculated by using the following equation (1) [47]:

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