



Synthesis, photophysical and theoretical studies of substituted ethyl 4-(3-(naphthalen-1-yl)-1-phenyl-4,5-dihydro-1H-pyrazol-5-yl)benzoate



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ABSTRACT

A series of five new fluorescent dyes of naphthalene based 2-pyrazoline derivatives with different electron donating/withdrawing substituents at *para* position of N1 phenyl group were synthesized and their structures were elucidated by spectroscopic methods and elemental analysis. The absorption and fluorescence properties of the new fluorescent dyes were studied using steady state and time-resolved techniques. Comparison of the spectroscopic properties of the five derivatives with different electron donating and withdrawing groups in dichloromethane revealed little influence of substituents on absorption spectra. However, the fluorescence spectra of these molecules have been greatly affected. Time-resolved measurements were performed and two lifetimes were obtained. The mean lifetimes for the pyrazolines containing donor groups were found to be higher than those with withdrawing groups. For all compounds, the ground state geometry was optimized in gaseous phase and in dichloromethane using density functional theory (DFT) at B3LYP/6–31G(d) level of theory to obtain frontier molecular orbitals, energy gap and dipole moments. The optimized excited state geometries using TD-DFT at the same level of theory was used to predict absorption and emission energies. HOMO and LUMO energies were also calculated using cyclic voltammetry and were found to have good agreement with those obtained by theoretical calculations. The reorganizational energies calculated theoretically suggest that these compounds can act as good electron and hole transport materials.

1. Introduction

Synthesis of π -conjugated dyes is continuing to receive special attention. The π -conjugated systems constitute the fundamental scaffolds used to develop a wide range of organic materials suitable for a myriad of applications from medicine to nanotechnology. For instance, fluorescent dyes play a pivotal role as probes in biomedical analysis, imaging, and in sensing environmentally important species [1–5]. Lately, we noticed more emphasis is placed on sensors fundamentally based on mechanisms such as intramolecular charge transfer (ICT) and photo-induced charge transfer (PET), among others [6–9]. On the other hand, modern technology driven by the development of display devices focused attention on substances that suit applications such as organic light emitting diodes (OLEDs), dye-sensitized solar cells (DSSCs) and organic photovoltaics [10–12]. The main feature of these organic systems are associated with their versatility, especially the ease by which they can be modified to tune their optical properties.

Among fluorescent molecules, pyrazoline (PZ) a heterocyclic ring system, has received intense interest recently because of the relative ease of synthesis and the intriguing photophysical properties [1,13–19].

Structures containing pyrazoline rings have found many applications in multidisciplinary areas such as in cancer therapy, organic light emitting diodes, whitening and brightening of fibers, and in the construction of nanotubes and nanomaterials [20–24]. To design and synthesize new fluorescent probes certain photophysical requirements are customarily explored, such as large Stokes shifts, high quantum yield, and longer emission and excitation wavelengths.

Tuning of photophysical properties of the pyrazoline molecule is indeed affordable by the virtue of its conjugate charge transfer ability due to the presence of lone pairs of electrons on the nitrogen atoms and the bridging $-C=N$ bond. Hence, attaching substituents to the pyrazoline ring with groups of different electron donating/electron accepting properties lead to fascinating photophysical effects [13–18]. Furthermore, incorporation of substituents, especially conjugated, aromatic chromophores allows modulation of the intramolecular charge transfer (ICT) for optoelectronic applications [25,26]. Electron donating and attracting groups attached on both sides of the PZ ring result in changes of wavelengths of absorption and emission by affecting the HOMO and LUMO energies. Many PZ systems have been designed to tailor the ICT properties for specific application. Pyrazolines containing phenyl

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substituents bearing two methyl groups or two chloro-atoms were reported to significantly influence the charge distributions on the PZ that in turn alters the electronic and emission spectra, but with little effect on the geometry [1,19]. Fahrni et al. have shown that triphenyl-2-pyrazolines with different electron donating/withdrawing substituents in the 1 and 3 positions of the PZ exhibited different photophysical signatures [27]. Photophysical and charge transport properties of PZs were also found to be affected by the type and number of electron donating groups [24]. Phenyl substituents carrying electron withdrawing groups when attached to C1 of the PZ ring facilitates the charge transfer of $\pi \rightarrow \pi^*$ transition and as a result the absorption bands shift to lower wavelength [28].

Insertion of fused rings into the skeleton of PZ compounds is another useful structural scenario used to decipher the effects on the electronic and optical properties of pyrazoline compounds [15,29].

Absorption spectra of compounds containing a pyrazoline moiety exhibit strong absorption bands mainly attributed to the allowed $\pi \rightarrow \pi^*$ transition of the conjugated backbone localized on the PZ ring system. Therefore, presence of electron withdrawing/donating groups on the conjugated system remarkably affect the charge transfer especially on the phenyl substituents at positions 1 and 3 of the PZ ring. Delocalization of the lone pair of electrons of N1 toward the 3-substituent of the ring has significant effect on the charge transfer character of the emission state.

Many studies have been conducted for the effect of substituents on C-3 and C-5 phenyl groups on the conjugated system. However, to-date no comparative studies of the effect of various electron donating/withdrawing groups on the N1 phenyl for naphthyl substituted PZs have been reported. Therefore, this work represents a preliminary study on the effect of these substituents on the photophysics of naphthyl-phenyl pyrazolines. Furthermore, this work is expected to extend the applications of these compounds to new. Recently, we focused our attention on naphthyl-phenyl-pyrazoline fluorophores suitable as labels for applications in biomedical and pharmaceutical analysis [3,30,31]. The extension of the conjugated systems has produced compounds with high quantum yield and large Stokes shifts which are amongst the requirements to achieve lower detection limits in chemical analysis. Our goal is to extend the use of these compounds or their derivatives to construct fluorescent pyrazoline molecules suitable for use as precursor motifs for manufacturing organic nanostructures and for further applications in cell imaging and as OLED compounds. To achieve this objective, we report here the synthesis and characterization of new pyrazoline dyes containing different electron withdrawing and electron-donating substituents on the phenyl moiety attached to N1 of the pyrazoline. Herein, we demonstrate the effect of these substituents on the electronic properties using electrochemical, absorption and emission techniques. Furthermore, TD-DFT calculations are used to study and predict the effect of these substituents on the electronic properties and to gain further insight into the suitability of these compounds as hole/electron transfer materials.

2. Experimental

2.1. General

All reagents were purchased from commercial suppliers and were used without further purification. Moreover, for all spectroscopic studies were performed in HPLC or spectroscopic grade solvents. Ultrapure water was collected in the lab with the aid of Milli-Q water purification system (Millipore, Billerica, MA, USA). Progress of the reaction was monitored by TLC aluminum plates from Merck (Germany) coated with silica gel 60 F254. Purification of synthesized compounds was performed using column chromatography on silica gel from Sigma-Aldrich (Germany) technical grade, pore size 60 Å, 70–230 mesh (63–200 μ), and preparative (PTLC) glass plates from EMD (Merck, Germany), silica gel 60 F254 (1 mm thickness) Using dichloromethane: methanol (9:1)

as mobile phase.

Melting points had been recorded in open capillary on Stuart Scientific apparatus (UK). IR spectra were measured on Agilent technologies Cary 630 FT-IR spectrometer. All ^1H NMR and ^{13}C NMR spectra were carried out in Bruker Avance III HD 700 MHz spectrometer (Germany) equipped with 5 mm TCI H/C/N cryoprobe with CDCl_3 or $\text{DMSO-}d_6$. The proton decoupled ^{13}C NMR experiments were run using composite pulse decoupling scheme operating at 176.08 MHz. ESI-mass spectra for all the dyes dissolved in acetonitrile were recorded in positive and negative modes on Agilent, 6460 Triple quad LC/MS, 1200 Infinity series (Germany) equipped with electrospray ionization (ESI) interface and operated by MassHunter software. The ESI-gas temperature was 300 °C, the gas flow was 0.5 L min⁻¹ with the nebulizer pressure 50 psi, the sheath gas flow was 12 mL min⁻¹, and the capillary voltage was 4000 V. Elemental analyses were performed on EuroVector3000, CHN Elemental Analyzer (Italy). High-resolution mass spectra were run at the University of Sheffield, UK, using Agilent (UK), 6200 series TOF version Q-TOF B. 05. 01 in the positive mode. Absorption measurements were obtained at room temperature using double beam Shimadzu (model multispec-1501, Japan) UV-Vis spectrophotometer with two matched quartz 10 mm cells. Steady state fluorescence spectra were performed on Perkin-Elmer (model LS 55, UK) Luminescence spectrometer using 10 mm quartz cell. The fluorescence quantum yield (ϕ) was obtained by diluting the dyes in dichloromethane with respect to quinine sulfate in 0.1 M H_2SO_4 ($\phi = 0.55$) as a standard using the following equation:

$$\phi_u = \phi_s \frac{A_u n_u^2 I_0^s \lambda_{ex}}{A_s n_s^2 I_0^u \lambda_{ex}} \quad (1)$$

where the subscripts *u* and *s* refer to the dye and standard, respectively, *A* is the integrated area under the corrected emission spectrum, *n* is the refractive index of the solution and $I_0^s \lambda_{ex}/I_0^u \lambda_{ex}$ is the relative intensity of the exciting light [32,33]. Fluorescence lifetime measurements were determined from time resolved fluorescence decay by the method of time-correlated single-photon counting (TCSPC) using a nanosecond laser diode at 340 nm as a light source and a spectrophotometer (Edinburgh, FS5, UK). The experiments were performed at room temperature and the instrument response factor (IRF) was obtained using LUDOX solution. The decay curves were depicted using Fluoracle software, for all lifetime measurements the fluorescence decay curves were analyzed by biexponential fitting program. The fluorescence lifetimes were obtained from the decay curves by fitting the experimental data to the following equation:

$$I(t) = \sum_i^n A_i e^{-t/\tau_i} \quad (2)$$

where $I(t)$ is the intensity of the fluorescence at time *t*, A_i is the pre-exponential factor of the fraction of the fluorescence intensity, τ_i is the fluorescence lifetime of the emitting species and *n* is the total number of emitting species. The values of χ^2 for all fittings was less than 1.200. Average lifetimes were calculated using the following formula, which is used to calculate the intensity weighted lifetime [34]:

$$\tau_i = \frac{\sum_i A_i \tau_i^2}{\sum_i A_i \tau_i} \quad (3)$$

where $A_i \tau_i$ reflects the contribution of the *i*-th component to the steady state fluorescence intensity.

Cyclic voltammetry (CV) was carried out using voltametric analyzer (BAS-50W) work station in three-electrode cell consisting of Glassy carbon working electrode (GCE), platinum coil and Ag/AgCl/KCl(sat.) as the counter and reference electrodes, respectively (all from Bioanalytical System, West Lafayette, IN, USA). Each compound was prepared by dissolving 0.05 g of the dye in 25 mL of 0.1 M tetrabutylammonium hexafluoro phosphate (Bu_4NPF_6) in acetonitrile as supporting electrolyte. The half-wave potentials were referenced to ferrocene/ferrocenium ion as internal standard and the measurements

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