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Synthesis, spectroscopic characterization and photophysics of a novel environmentally sensitive dye 3-naphthyl-1-phenyl-5-(4-carboxyphenyl)-2-pyrazoline



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ABSTRACT

Synthesis and photophysical properties of a novel pyrazoline – containing fluorophore, 3-naphthyl-1-phenyl-5-(4-carboxyphenyl)-2-pyrazoline (NPCP) **A**, and its proline derivative (NPCP-P) **B** are presented in this work. The highlight of this fluorescent dye is that, it can be prepared from available starting material *via* two synthetic steps, easily converted to the corresponding amide derivative by *in situ* nucleophilic acyl substitution of the corresponding acid chloride, and its purification by simple chromatographic techniques. The structures of the new compounds were verified using various spectroscopic tools. Furthermore, photophysical properties of the new fluorophores were studied and interesting solvatochromic behaviour was observed. Due to the presence of proton acceptor linked to the fluorophore, NPCP displays pH-sensitive absorption and fluorescence emission. The interaction of NPCP and NPCP-P with various micelles has been studied by steady state fluorescence. All results reflect the importance of the medium effect on the analytical application of NPCP as a potential fluorescent label for derivatization of analytes having amine ($-NH_2$) group. Theoretical calculations were performed for both compounds using time dependent density functional theory (TD-DFT) at B3LYP/6-31G(d, p) level. The calculations indicate that the excited state dipole moments are larger than those of the ground state in line with the experimental findings.

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1. Introduction

The design and development of chemical probes for biological labeling and imaging have been the subject of fascination to scientists which led to the introduction of a profound number of novel molecules that exhibited interesting interaction properties with various biological, chemical and medical systems. Reagents are required with sufficient flexibility in their synthetic strategies, increased quantum yields for fluorescence, longer emission wavelengths, larger Stokes shifts and with good photostability.

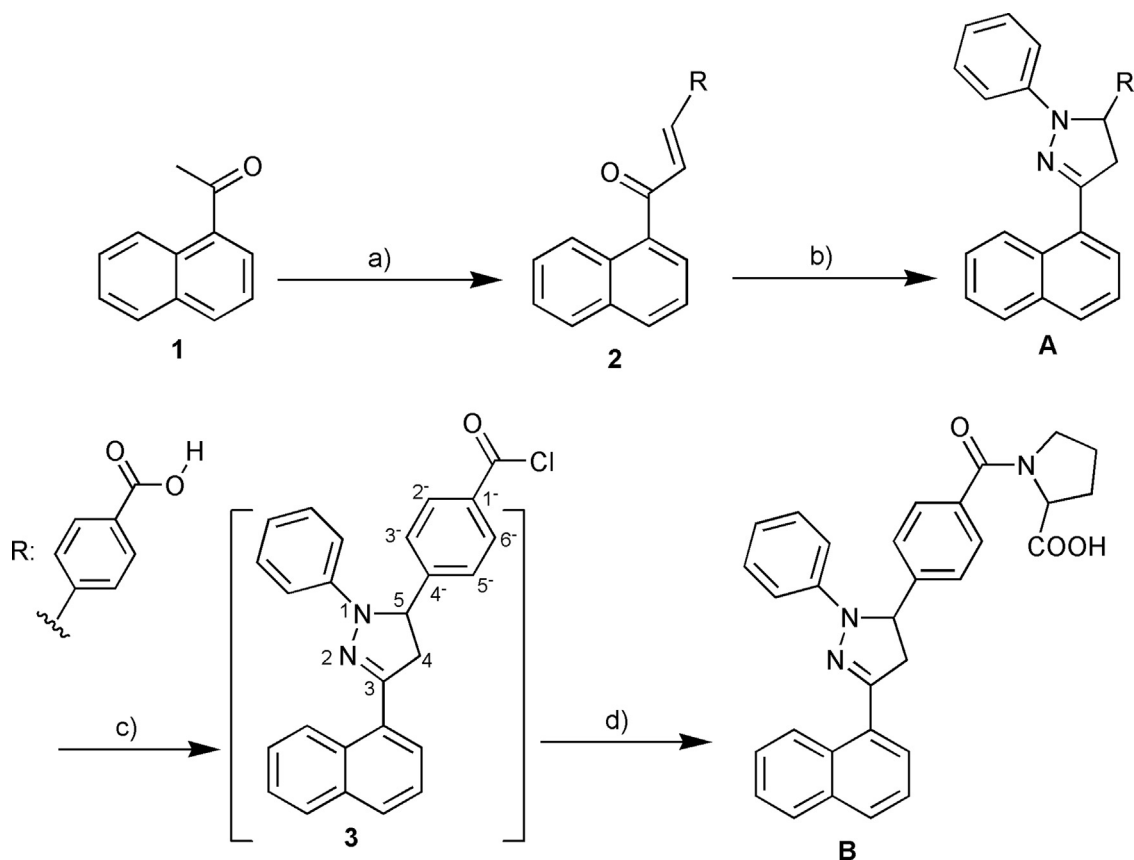
Pyrazoline is a five-membered heterocyclic compound having two adjacent nitrogen atoms within the ring. In addition to its role as a key precursor for the synthesis of novel organic compounds with medicinal properties, pyrazoline ring compounds show stronger fluorescence because of the double bond hindering which occurred due to cyclization [1–4]. Among various possible fluorescent probes, pyrazoline-based fluorophores stand out due to their simple structure and favorable photophysical properties such

as large extinction coefficient and quantum yields. Their attractive properties, including cation or pH-sensitive probes, are known, and the solubility of pyrazoline fluorophores as probes is also explored. Changes in their structure have offered a high degree of diversity that has proven useful for the development of novel probes [1,3,5–8].

On the other hand, interest in naphthalene based fluorophores has grown over the past few years because of their advantageous photophysical properties. Fused heterocyclic systems incorporating the naphthalene moiety and pyrazole ring has been previously synthesized for the purpose of obtaining compounds of biological importance [9]. The synthesis of a new derivative of pyrazoline, 1-phenyl-3-biphenyl-5-(N-ethylcarbazole-3-yl)-2-pyrazoline (PBEP) that show promising applications in the study of DNA has also been reported [7]. Moreover, pyrazoline compounds with biological and medicinal applications have been recently receiving much interest [9–17]. Fluorescence spectra of a series of 1, 3, 5-triaryl-2-pyrazolines indicated that substituents in the 3-phenyl ring resulted in the shifting of fluorescence emission wavelength [18]. Zhenglin and Shinkang have reported that an intramolecular conjugated charge transfer process exists in pyrazoline moiety in the excited state [19]. N-phenyl substituted 2-pyrazoline and its derivative show interesting photophysical properties due to the

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Scheme 1. Reaction conditions (a) 4-formyl benzoic acid, KOH, EtOH, reflux, and 2 h, (b) phenyl hydrazine, EtOH, reflux, 3 h, and dilute sulfuric acid, (c) thionyl chloride, benzene, reflux, 1 h (d) proline, acetonitrile, borate buffer, and reflux.

presence of electron donors and acceptors at N (1) and C (3) positions, respectively [20]. Barberá et al. performed a study on the structure-property relationships in a series of 3-(4-n-decyloxyphenyl)-1-(p-X-phenyl)-2-pyrazoline and they found that if the phenyl ring is substituted or non-substituted, the pyrazoline compounds are fluorescent [8].

In this paper, in view of the photophysical properties of pyrazoline – based dyes and our interest in synthesizing analogous compounds involving fascinating diverse heterocycles, we designed and synthesized a novel pyrazoline-based fluorophore (NPCP) containing phenyl substituted pyrazoline ring (electron-donor) as a channel in between naphthalene moiety (electron-acceptor) and electron withdrawing carboxylic group as side chains and its proline derivative (NPCP-P) (Scheme 1). In combination of pyrazoline moiety with the naphthalene ring, we anticipate the formation of a novel probe for the selective and sensitive trace analysis of analytes having amine ($-\text{NH}_2$) groups using various separation techniques.

2. Experimental

2.1. General

All the reagents and solvents used in this study were obtained from Sigma-Aldrich Chemical Company and used without further purification.

Melting points were determined using Gallen-Kamp melting point apparatus. The purity of the synthesized compounds was checked by TLC and analyses were carried out on 0.25 mm thick pre coated silica plates (Merk Fertigplatten kieselgel 60F₂₅₄). Column chromatography was performed using Merk silica gel 60

(40–63 μm). IR spectra were determined on a Perkin-Elmer FTIR-881 spectrometer (Perkin-Elmer, USA) using KBr pellets. Proton Magnetic Resonance (^1H NMR) spectra were recorded using a 400 MHz Bruker spectrometer (Bruker Corp.,UK) and in particular, the proton chemical shifts were assigned on the basis of (^1H – ^1H) COSY (Correlated Spectroscopy). Carbon Magnetic Resonance (^{13}C NMR) spectra were recorded at a 100.4 MHz Bruker spectrometer (Bruker Corp.,UK) and the multiplicities of ^{13}C NMR resonances were determined by DEPT (90,135) experiments. Chemical shifts (δ_c) are quoted in parts per million (ppm) to the nearest 0.1 and 0.01 and are referenced to the solvent peak (CDCl_3). High resolution mass spectra were obtained using Waters LCT Premier XE Mass Spectrometer instrument (determined at the University of Sheffield, UK).

A Shimadzu (model multispec-1501) UV–vis spectrophotometer (Shimadzu, Japan) and a Perkin-Elmer (model LS 55) Luminescence spectrometer (Perkin-Elmer, USA) were used to collect absorption and fluorescence spectra, respectively. All measurements were performed repeatedly, and reproducible results were obtained. Relative fluorescence quantum yield (ϕ_f) were determined using quinine sulfate as the reference standard ($\phi_f=0.55$ in 0.1 M H_2SO_4) [19]. Lifetime measurements were performed using a Time-Master Fluorescence lifetime spectrometer obtained from Photon Technology International. Excitation was at 380 nm using light emitting diodes. For NPCP and its derivative fluorescence, a cut-off filter (400 nm, Photon Technology International) was used. The system response time as measured from the scattered light was estimated to be approximately 1.5 ns. The observed decays were fitted to multi-exponential functions convoluted with the instrument response function (IRF). The fit was judged by the value of the reduced chi-squared (χ^2) values which were close to unity (0.98–1.2).

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