

## Synthesis, Photophysical and Antioxidant studies of Ethenyl Indoles

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### Abstract

Light induced fluorescence and photochemical properties in conjugated systems play a vital role in various biological and industrial applications. Here we have presented synthesis, fluorescence and antioxidant properties of ethenyl indoles substituted with various electron withdrawing and electron donating substituents.

### Introduction

Light induced fluorescence and photochemical properties in conjugated molecules play an important role in many biological [1-2] photoreceptors such as Rhodopsin in vision, medicine (antioxidant, anticancer) and in industrial applications like organic electronics (Nonlinear Optics, Solar cell, Organic light emitting diodes). In order to understand the light induced properties of conjugated molecules (particularly, the fluorescence and *trans-cis* or *cis-trans* photoisomerisation, excited state dipole moment), extensive studies have been carried out on diphenylpolyenes as a model compounds [3]. In addition to that conjugated molecule with hydroxyl and amino substituent exhibits medicinal properties such as antioxidant [4].

Generally, when light is absorbed, the donor-acceptor (D-A) conjugated molecule is excited to its locally planar excited state (S<sub>1</sub>, LE, singlet excited state), which further undergoes twisting to yield the phantom excited state (P\*) . From this P\* state the *cis-trans* isomerisation around the carbon - carbon double bond (>C=C<) occurs . On the other side, charge transferred excited state in the molecule causes a remarkable energy gap for P\* state, whether it is singlet or triplet excited state due to which the molecule shows inefficiency towards photoisomerisation [5]. The donor-acceptor substituent can increase or lower the energy barrier and subsequently, the excited state properties of conjugated molecules.

We have recently begun to characterise the structure and photochemical properties of heterocyclic and aryl based ethenyl systems . Here we have presented synthesis, fluorescence and antioxidant properties of ethenyl indoles substituted with various electron withdrawing and electron donating substituents.

### Material and methods :

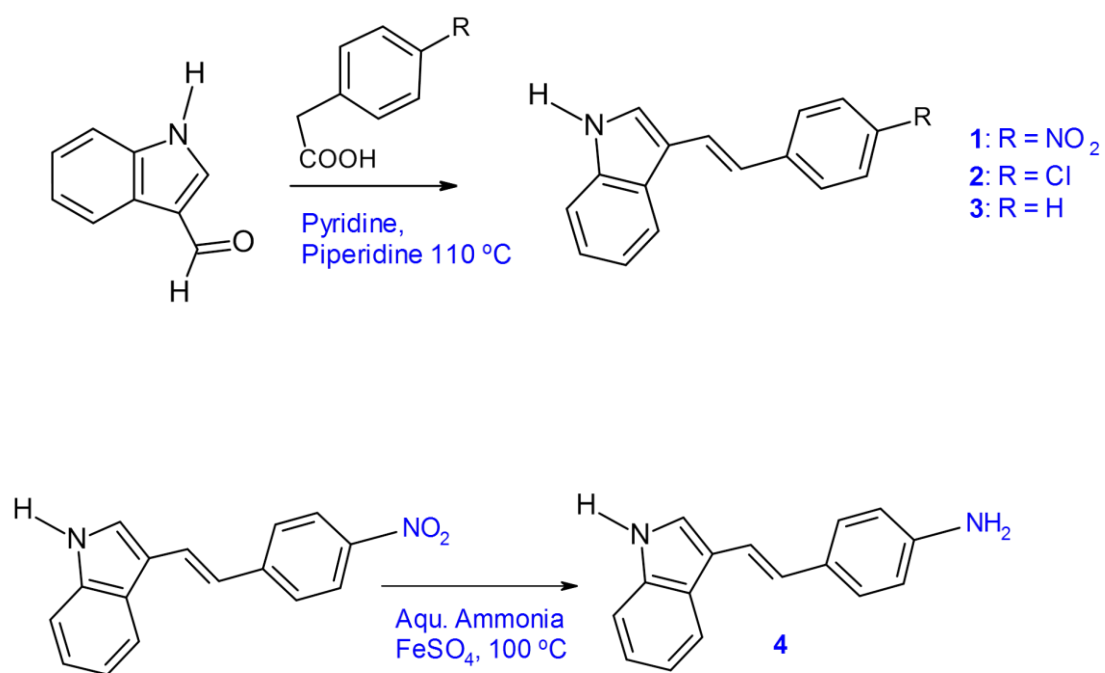
Compounds were synthesized with indole-3 aldehyde and corresponding substituted phenyl acetic acid [e.g. *p*-nitro phenyl acetic acid (for **1**), *p*-chloro phenyl acetic acid (for **2**) and phenyl acetic acid (for **3**)] in pyridine and piperidine mixture as described [6-8]. Compound **4** was synthesized by reduction of **1** as shown in reaction scheme . Synthesized compounds were characterized using UV spectroscopy, Infra Red spectroscopy, <sup>1</sup>H and <sup>13</sup>C NMR and Mass spectroscopy.

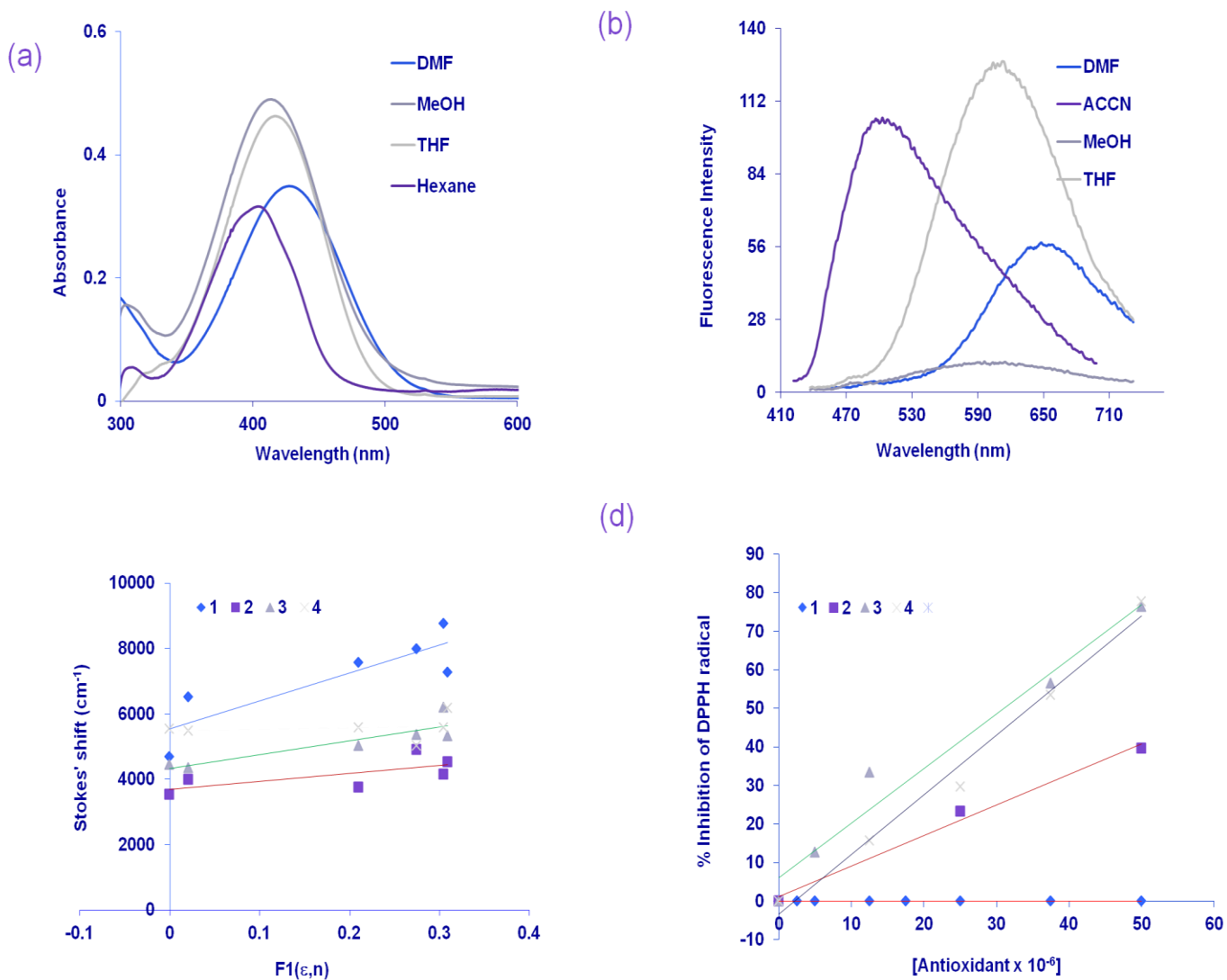
The change in excited state dipole moment of compounds **1-4** is calculated with Lippert-Mataga equation :  $\nu_a - \nu_f = \{ [2(\mu_e - \mu_g)^2 / hca^3] F(\epsilon, \eta) \} + \text{constant}$ ;  $F(\epsilon, \eta) = \{ \{ (\epsilon - 1) / (2\epsilon + 1) \} - \{ (\eta^2 - 1) / (2\eta^2 + 1) \} \}$ , where

- $\nu_a$  is absorption maximum wave number.
- $\nu_f$  is fluorescence maximum wave number.
- $\nu_a - \nu_f$  is the Stokes' shift.
- $\mu_e$  and  $\mu_g$  represents the excited state dipole moment and ground state dipole moment respectively.
- $\mu_e - \mu_g = \Delta\mu$  which shows the change in excited state dipole moments,
- $h$  is the Planck's constant ( $6.62 \times 10^{-34}$  joule sec).
- $c$  represent the velocity of light in vacuum ( $3 \times 10^8$  meter/sec).
- $\epsilon$  is the relative permittivity (*i.e.* dielectric constant) and  $\eta$  is the refractive index of the solvent
- Fluorescence quantum yields ( $\Phi_f$ ) of these compounds were determined using quinine sulfate in 0.1N H<sub>2</sub>SO<sub>4</sub> ( $\Phi_f = 0.51$ ) and rhodamine B in ethanol ( $\Phi_f = 0.69$ ) as a reference standard .
- The calculations were made using equation:  $\Phi = \Phi_{\text{std}} \times (\eta_{\text{std}}^2 / \eta^2) \times (\text{Abs}_{\text{std}} / \text{Abs}) \times (\text{Area} / \text{Area}_{\text{std}})$
- Antioxidant studies were carried out using DPPH assay in methanol.

## Synthesis

Synthesis of ethenyl indoles :





**FIGURE 1.** (a) Absorption and (b) Fluorescence spectra of **1** in solvent of varying polarity, (c) Lippert-mataga Plot and (d) Antioxidant activity of **1-4** in DPPH assay.

**Table 1.** Absorption and Emission wavelength maximum, Fluorescence Quantum Yield, Excited state Dipole moment change for **1-4**.

Compound	Solvent	$\lambda_{\text{abs}}$ (nm)	$\lambda_{\text{f}}$ (nm)	Stokes' shift ( $\text{cm}^{-1}$ )	$\Phi_{\text{f}}$	$\Delta\mu$ (Debye)	$\text{IC}_{50}$ ( $10^{-6}$ M)
1	Hexane	403	497	4693	0.051	15.2	Nil
	THF	416	607	7564	0.059		
	DMF	427	648	7987	0.025		
2	Hexane	338	384	3544	0.026	8.3	63
	THF	338	387	3746	0.020		
	DMF	333	398	4905	0.023		
3	Hexane	328	384	4446	0.001	10.0	-41
	THF	331	397	5023	0.001		
	DMF	332	404	5368	0.001		
4	Hexane	320	389	5544	0.036	6.1	-34
	THF	325	397	5581	0.033		
	DMF	333	400	5030	0.005		

## Conclusion

It is presented that the excited state of ethenyl indole is very sensitive to the solvent polarity and the substituents present on it. It is found that **1** with a strong electron-withdrawing nitro substituent, exhibits charge transfer and highly dipolar excited state in comparison to other ethenyl systems. As shown compound **1** exhibit charge transfer and highly dipolar excited state and does not show antioxidant activity. On the other hand, ethenyl indoles with weak electron donating or withdrawing substituent exhibit efficient antioxidant property. Such molecule has non-polar excited state with highly electron rich center and able to quench the free radical through electron transfer mechanism. The present studies on characterisation of excited state properties of substituted ethenyl indoles provide a new direction in designing and developing novel molecules for biological applications.

## Acknowledgement

Jagdeep Kumar gratefully acknowledges AMRC IIT Mandi and HNB Garhwal Central University for their constant support in carrying out characterization work. The authors are highly thankful to the reviewers for giving their valuable suggestions and comments.

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