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Synthesis, spectral behaviour and photophysics of donor–acceptor kind of chalcones: Excited state intramolecular charge transfer and fluorescence quenching studies



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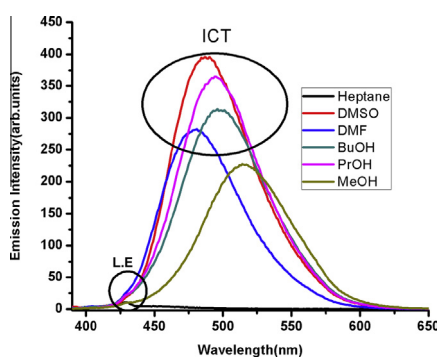
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HIGHLIGHTS

- Chalcones with electron donor acceptor group has been studied.
- The absorption and emission spectrum were sensitive to solvent polarity.
- Fluorescence quantum yield highly depend on polarity of solvents.
- Both chalcones show fluorescence quenching by silver nanoparticles.

GRAPHICAL ABSTRACT



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ABSTRACT

The spectral and photophysical properties of two chalcones containing electron donating and accepting groups with intramolecular charge transfer characteristics were synthesized and characterized by ¹H NMR, ¹³C NMR and X-ray crystallography. Both compounds show very strong solvent polarity dependent changes in their photophysical characteristics, namely, remarkable red shift in the emission spectra with increasing solvent polarity, large change in Stokes shift, significant reduction in the fluorescence quantum yield; indicating that the fluorescence states of these compounds are of intramolecular charge transfer (ICT) character. The solvent effect on the photophysical parameters such as singlet absorption, molar absorptivity, oscillator strength, dipole moment, fluorescence spectra, and fluorescence quantum yield of both compounds have been investigated comprehensively. For both dyes, Lippert–Mataga and Reichardt's correlations were used to estimate the difference between the excited and ground state dipole moments ($\Delta\mu$). The interactions of dyes with colloidal silver nanoparticles (Ag NPs) were also studied in ethanol using steady state fluorescence quenching measurements. The fluorescence quenching data reveal that dynamic quenching and energy transfer play a major role in the fluorescence quenching of dyes by Ag NPs.

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Introduction

Organic molecules featuring intramolecular charge transfer (ICT) has gained a substantial research interest owing to its potential application in making photoelectronic and nonlinear optical devices [1,2], chemical sensing [3], understanding photochemical and photobiological processes [4,5]. Pi-conjugated organic fluorophores containing donor acceptor groups that are separated by an ethenyl or keto-vinyl bridge, exhibiting the phenomenon of dual fluorescence are of special interest because the material properties can be tuned and tailored by structural modification for their potential applications in molecular electronics, dye sensitised solar cells [6,7] and other all optical devices [8,9]. The highly polar excited states and large charge separation exhibited by these molecules are sensitive to changes in its micro environment such as pH, viscosity, polarity, heat and light that can be exploited in various fields.

Chalcones symbolize a class of organic compounds in which two aromatic planar rings are connected through a three carbon α , β -unsaturated carbonyl system, with significant biological activities have been observed over the past two decades including anti-ulcer, anti-cancer, anti-mitotic, anti-inflammatory, anti-malarial, anti-fungal, and anti-oxidant activities [10–13]. Apart from these very important medicinal applications, chalcones have interesting optical and spectral properties depending on the substituent attached to the aromatic rings that find applications in metal sensing, optoelectronic and nonlinear optical devices [14,2]. The asymmetrically substituted electron-donating and electron-accepting substituents in these molecules are connected through a pi-conjugated system of alternate single and double bonds and exhibit different degrees of charge transfer in the ground and excited states. The photophysical properties of these conjugate intramolecular charge transfer compounds strongly depend on the nature of the substituent, solvent polarity and temperature.

Metallic nanoparticles possess unique spectroscopic, electronic and chemical properties due to their small size and high surface to volume ratios that are different from those of the individual atoms as well as their bulk counterparts. The optical properties of noble metal nano particles have received considerable attention because the surface plasmon absorption band of noble metal nanoparticles appears in the visible region of the spectrum to provide important contribution towards sensing and bio-medical applications. Interaction of metallic nanoparticles (NPs) with fluorophores has become an active area of research for the last two decades with applications ranging from material science to biomedical science [15–17]. The fluorescence of a dye molecule is quenched or enhanced in the close proximity of the metallic nanoparticles and these phenomena can be used to probe the micro environment of the fluorophore. The emission behaviour of a dye molecule can be altered by using metallic nanoparticles and quenching or enhancement of photoluminescence of a dye by silver nanoparticles (AgNPs) depend upon the distance between the dye molecule and NPs [18–20]. The quenching processes are of three types: static, dynamic and by electron/energy transfer. In static quenching, the decrease in emission intensity is caused by the adsorption of dye molecule on the surface of the metallic NPs, forming a non fluorescent complex between the fluorophore and quencher where as in dynamic quenching, the reduction of emission intensity is due to the direct interaction or collision of excited fluorophore with a quencher during their excited state life time. The third type of quenching process takes place by non-radiative energy/electron transfer between the dye molecule and NPs [21,22]. The quenching of fluorescence dominates over enhancement at shorter distances and it is attributed to the efficient non-radiative energy transfer between the dye molecule and the metallic NP [23].

The present work aims at setting up a scheme which can efficiently predict the excited state intramolecular charge transfer process applying steady state spectroscopy, quantum yield calculation with variation of polarity of the solvents. For this purpose, we have synthesized and characterized two chalcone derivatives, namely, 3-(1-Benzyl-1H-3-indol-3-yl)-1-naphthalen-2-yl-propenone and 3-(1-Benzyl-1H-3-indol-3-yl)-1-thiophene-3-yl-propenone; and studied the effect of solvents in detail. Lippert–Mataga and Reichardt's correlations were applied to calculate the difference between the excited and ground state dipole moments ($\Delta\mu$). To explore the effect of metallic nanoparticles with the synthesized fluorophores, we also investigate fluorescence quenching by colloidal silver nanoparticles in ethanol using steady state emission measurements.

Experimental

Materials and methods

All solvents and chemicals used in this work were of spectroscopic grade obtained from Sigma–Aldrich and used without further purification. Synthetic procedure and characterization of silver nanoparticles are given in the supporting information and TEM image of Ag NPs with absorption spectrum shown as an inset in Fig. S1. Indole-3-carbaldehyde, 3-acetylthiophene and 2-acetonaphthone were purchased from Sigma–Aldrich.

Spectral measurements

All solvents and chemicals used in this work were of spectroscopic grade obtained from Sigma Aldrich and used without further purification. Melting points were determined on a Gallenkamp melting point apparatus and the infrared (IR) spectra were recorded on Shimadzu FT-IR 8400S infrared spectrophotometer using the KBr pellet technique. The NMR (^1H and ^{13}C) spectra were recorded on a Bruker DPX-600 at 600 MHz and 150 MHz, respectively, using tetramethylsilane as the internal standard. The chemical shift values are recorded on δ scale and coupling constants (J) in Hertz; Splitting patterns were designated as follows: *s*: singlet; *d*: doublet; *m*: multiplet. UV–Vis electronic absorption spectra was recorded on a Shimadzu UV-160A spectrophotometer, and the steady-state fluorescence spectra were measured using Shimadzu RF 5300 spectrofluorophotometer using a rectangular quartz cell of dimensions 0.2 cm \times 1 cm. The emission was monitored at right angle. The fluorescence quantum yield (ϕ_f) was measured using an optically diluted solution of quinine sulfate as reference according to Eq. (1):

$$\phi_u = \phi_s \times \frac{I_u}{I_s} \times \frac{A_s}{A_u} \times \frac{n_u^2}{n_s^2} \quad (1)$$

where ϕ_u , ϕ_s are the fluorescence quantum yields of the unknown and standard, respectively, I is the integrated emission intensity; A is the absorbance at excitation wavelength, and n is the refractive index of the solvent. The subscript u and s refers to unknown and standard, respectively.

Procedure for the synthesis of 1-Benzyl-1H-3-indolecarbaldehyde (2)

To a solution of indole-3-carbaldehyde (1.5 g, 0.010 mol) in ethanol (50 mL), KOH pellets were added (0.69 g, 0.012 mol) and the mixture were stirred at room temperature until total solubilisation. The ethanol was completely removed in vacuum and acetone (50 mL) was added followed by benzyl bromide (0.010 mol, 1.2 mL). A precipitate was formed instantly on addition of benzyl bromide

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