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Effect of solvent and encapsulation in β -cyclodextrin on the photophysical properties of 4-[5-(thiophen-2-yl)furan-2-yl]benzamidine

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ABSTRACT

Photophysical characteristics of the ground and excited states of the bichalcophene derivative 4-[5-(thiophen-2-yl)furan-2-yl]benzamidine (TFB) were investigated in different solvents and in β -cyclodextrin (β -CD). The photophysical properties of TFB were correlated with the two commonly used solvent polarity parameters viz., E_T^N and reaction field factor Δf . In addition, the photophysical properties of TFB were also found to be well correlated with Kamlet–Taft relationship. Multiple linear regression analysis of solvent dependent photophysical parameters indicated that both non-specific dipolar interaction and specific hydrogen bonding interactions play important roles in determining the photophysical properties of TFB. It has been found that the non-specific dipolar interaction is the dominating parameter. Fluorescence decay curves are well fitted to double exponential decay function, with shorter component having the higher relative integrated intensity. Molecular encapsulation of TFB by β -CD in aqueous solution has been studied by steady state and time resolved fluorescence techniques. Steady state measurements show that the fluorescence quantum yield is enhanced strongly upon the addition of β -CD and increases from 0.03 ± 0.01 in aqueous solution to 0.11 ± 0.02 at 7.5 mM concentration of β -CD. Steady state fluorescence measurements show 1:1 inclusion of TFB in the β -cyclodextrin cavity with an association constant of $2.3 \pm 0.2 \times 10^3 \text{ M}^{-1}$, while data derived from time resolved measurements gave very close value for the association constant of $2.6 \pm 0.3 \times 10^3 \text{ M}^{-1}$. Time resolved measurements and global analysis of the results indicated that the excited state lifetime is strongly affected by the presence of β -CD. The changes observed for the chemical shifts of TFB and β -CD ^1H NMR spectra and corresponding ^1H NMR spectra of their mixture confirmed the formation of the inclusion complex and showed that TFB is partially encapsulated in β -CD cavity.

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1. Introduction

Cyclodextrins (CD's) (also referred to as cycloamyloses or Schardingerdextrins) are shaped like a truncated cone polysaccharides made up of six to eight $\text{D-(+)}\text{-glucopyranose}$ monomers connected at the 1 and 4 carbon atoms. The cavities of CD's are relatively hydrophobic and have an internal diameter of 4.7–8.3 Å [1]. This difference in the cavity size allows binding specificity to be tailored based on substrate size and geometry. It is known that cyclodextrins (CDs) have the property of forming inclusion

complexes with guest molecules with suitable characteristics of polarity and dimension [2]. This ability has been widely used in studies of food and pharmaceutical industries [3].

Dsouza et al. [4] in their comprehensive review article showed that fluorescent dyes are good molecular probes not only to determine microenvironmental parameters, such as the polarity of media, but also to follow their relocation and distribution dynamics in microheterogeneous systems such as membranes, micelles, and cellular media as well as interfaces, polymers, and discrete supramolecular systems. The inclusion of the dye into molecular containers (generally hydrophobic nanocavities) is accompanied by a large change in the microenvironmental parameters, which has been abundantly used in supramolecular chemistry to determine, on one hand, the association thermodynamics and kinetics and, on the other hand, the binding of

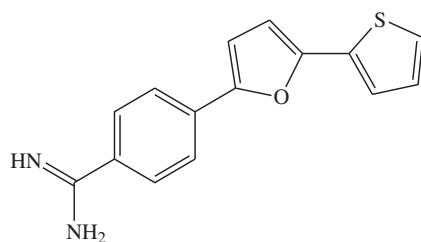
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competitors by indicator displacement methodologies [4]. For a long time cyclodextrin and their derivatives have received considerable attention as carriers able to improve solubility, stability and bioavailability of drugs [5,6].

The optical properties of compounds containing 2,2'-bithiophene, 2,2'-bifuran, and 2,2'-furanthiophene cores make them an ideal candidate in many fields such as nonlinear optical devices [7], sensors [8], solar cells [9], and other advanced materials [10] in addition to their importance in the field of antibacterial [11], antiprotozoal [12] and anticancer [13] studies.

Recently [14], TFB has shown good anticancer activity with weak solubility in water. However, TFB solubility in water is strongly enhanced in the presence of β -cyclodextrin. In this study, the changes in the photophysical properties of TFB with different solvents and inclusion in β -CD are to be examined by absorption, steady state, time resolved emission and ^1H NMR techniques. The changes observed in the absorption and emission maxima in different solvents and in β -cyclodextrin allowed for detailed spectroscopic investigations of the effect of solvents and inclusion on the excited state properties of TFB. ^1H NMR spectroscopy was used to confirm the mode of TFB inclusion in β -CD cavity.



4-[5-(thiophen-2-yl)furan-2-yl]benzamidinium (TFB)

2. Experimental

4-[5-(Thiophen-2-yl) furan-2-yl]benzamidinium hydrochloride salt (TFB) was synthesized as in literature [14] and recrystallized three times from ethanol/water. β -Cyclodextrin and organic solvents were of highest purity grade from Aldrich and were used as received. Deionized water was used. Absorption spectra were recorded on an Agilent diode array 8453 spectrophotometer. Steady state fluorescence measurements were obtained using Jasco FP-6200 spectrofluorophotometer. Excited state lifetimes were measured with EasyLife from OBB using 340 nm LED as an excitation light source. ^1H NMR spectra were recorded in D_2O on a Varian Mercury VX-300 spectrometer. ^1H NMR data analysis was carried out using MestReC 4.9.9 software. Chemical shifts have been expressed in parts per million (ppm) relative to HDO signal as

a reference at 4.80 ppm. For ^1H NMR measurements, the concentrations of TFB and β -CD were about 1 mM and 7 mM, respectively. The 2D-NOESY (Nuclear Overhauser effect spectroscopy) NMR experiments were recorded on a Bruker Avance III 400 MHz—recording the proton at 400 MHz with proton pulse sequence zg30 and 128 scans. All measurements were carried out at 25 °C.

The fluorescence quantum yield (Φ_f) were estimated using the following relationship:

$$\Phi_f = \frac{F_f}{F_s} \times \frac{(1 - 10^{-A_s})}{(1 - 10^{-A_f})} \times \frac{n_f^2}{n_s^2} \times \Phi_s \quad (1)$$

where the subscripts f and s refer to the sample and the standard, respectively. Φ is the fluorescence quantum yield, F is the integrated emission area across the band, A is the absorbance at the excitation wavelength and n_f and n_s are the indices of refraction of the solvent containing the sample and standard, respectively. The fluorescence quantum yields in different solvents were measured relative to diphenylanthracene in cyclohexane ($\Phi_s = 0.90$) or quinine sulfate in 1N H_2SO_4 ($\Phi_s = 0.55$) [15]. Absorbance of the sample and reference were the same the excitation wavelength which was taken as $\lambda_{\text{abs}}^{\text{max}}$ of TFB in each solvent.

3. Results and discussion

3.1. Effect of solvents on the photophysical properties of TFB

3.1.1. Absorption and emission spectra

Photophysical properties of TFB in different solvents are compiled in Table 1. TFB has maximum absorption at about 362 nm in most solvents with slight red shift in protic solvents. Unlike the relatively solvent independent absorption spectra, the fluorescence emission spectra show a large solvent effect (see Fig. 1 and Table 1) collected at $\lambda_{\text{abs}}^{\text{max}}$ of TFB in each solvent. The observed broad unresolved vibronic structure and relatively large Stokes shift of fluorescence emission bands in different solvents are typical fluorescence from the relaxed intramolecular charge transfer (ICT) states [16–20].

Fluorescence emission spectra were also recorded with a range of excitation wavelengths that cover the absorption band (320–380 nm). When the fluorescence emission spectra were recorded with short excitation wavelengths, the fluorescence emission spectra exhibit dual fluorescence in aprotic solvents which originated from the locally excited (LE) state and intramolecular charge transfer (ICT) state. However, with the increase of the excitation wavelength, the short wavelength emission band gradually decreases until only one emission band is observed with excitation wavelength $\geq \lambda_{\text{abs}}^{\text{max}}$ (Fig. 2). In protic solvents, only

Table 1

Absorption, emission spectral characteristics and excited state lifetimes of TFB in different solvents (Errors unless otherwise stated are $\leq 10\%$).

	Solvent	$\nu_{\text{abs}}/\text{cm}^{-1}$	$\nu_{\text{em}}/\text{cm}^{-1}$	$\Delta\nu/\text{cm}^{-1}$	Φ_f	a_1	τ_1/ns	a_2	τ_2/ns	$\langle\tau\rangle/\text{ns}$	χ^2
1	Water	27624.3	19193.9	8430.5	0.03 \pm 0.01	0.99	0.2 \pm 0.02	0.01	3.7 \pm 0.2	0.77	1.11
2	Methanol	27397.3	20000.0	7397.3	0.30 \pm 0.03	0.95	2.2 \pm 0.1	0.04	6.0 \pm 0.8	2.62	0.93
3	Ethanol	27173.9	20202.0	6971.9	0.44 \pm 0.05	0.88	2.4 \pm 0.1	0.12	6.2 \pm 0.5	3.38	1.04
4	2-Propanol	26954.2	20449.9	6504.3	0.50 \pm 0.05	0.91	2.4 \pm 0.1	0.09	6.5 \pm 0.7	3.28	1.18
5	1-Butanol	27027.0	20408.2	6618.9	0.48 \pm 0.05	0.91	2.0 \pm 0.1	0.09	6.3 \pm 0.5	3.02	1.09
6	Ethylacetate	27777.8	21505.4	6272.4	0.54 \pm 0.05	0.49	1.6 \pm 0.2	0.51	2.6 \pm 0.2	2.25	1.1
7	Ecetonitrile	27624.3	19762.8	7861.5	0.26 \pm 0.03	0.85	1.1 \pm 0.1	0.15	3.4 \pm 0.2	1.89	0.92
8	DMSO	27100.3	19802.0	7298.3	0.34 \pm 0.03	0.66	2.0 \pm 0.1	0.34	3.8 \pm 0.3	2.87	1.04
9	1,4-Dioxane	27548.2	21929.8	5618.4	0.55 \pm 0.05	0.89	1.5 \pm 0.1	0.11	3.1 \pm 0.4	1.83	1.08
10	CH_2Cl_2 (MC)	27100.3	20533.9	6566.4	0.48 \pm 0.05	0.59	1.5 \pm 0.1	0.41	3.8 \pm 0.5	2.97	1.17
11	Cyclohexane	27700.8	24509.8	3191.0	0.48 \pm 0.05	0.96	0.8 \pm 0.1	0.04	5.1 \pm 0.5	1.54	1.02
12	CHCl_3	26738.0	20790.0	5947.9	0.47 \pm 0.05	0.74	1.9 \pm 0.1	0.26	3.7 \pm 0.4	2.63	1.18

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