

Investigation of Spectroscopic Behaviors of Newly Synthesized (2E)-3-(3,4-Dimethoxyphenyl)-1-(2,5-dimethylthiophen-3-yl)prop-2-en-1-one (DDTP) Dye

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Abstract This study introduced spectroscopic properties, physicochemical parameters, and polarity and photostability behaviors of a newly prepared chalcone dye. The chalcone dye, (2E)-3-(3,4-Dimethoxyphenyl)-1-(2,5-dimethylthiophen-3-yl)prop-2-en-1-one (DDTP), was synthesized by the reaction of 3,4-dimethoxybenzaldehyde with 3-acetyl-2,5-dimethylthiophene. Results of FT-IR, ¹H-NMR, ¹³C-NMR and elemental analysis were in conformity with chemical structure of newly prepared DDTP. Data of thermal gravimetric analysis revealed that DDTP has good thermal stability. Increases in fluorescence intensities of DDTP with cetyltrimethyl ammonium bromide (CTAB) were observed. In comparison of fluorescence intensities for DDTP with CTAB, reductions in fluorescence intensities for DDTP with sodium dodecyl sulphate (SDS) were observed under the same experimental and instrumental conditions. Moreover, Benesi-Hildebrand method was applied to determine stoichiometric ratios and association constants of DDTP with CTAB and SDS. The stoichiometric ratio and association constant obtained from Stern-Volmer plot strongly supported those obtained from Benesi-Hildebrand plot of DDTP with SDS. Physicochemical parameters, such as, singlet absorption, molar absorptivity, oscillator strength, dipole moment and fluorescence quantum yield of

DDTP were also estimated. Fluorescence steady-state measurements ultimately displayed that DDTP has a high photostability against photobleaching. Fluorescence polarity study revealed that DDTP was sensitive to the polarity of the microenvironment provided by different solvents.

Keywords DDTP · Stoichiometric ratios · Physicochemical parameters · Fluorescence · Photostability

Introduction

Chalcones are well known donor acceptor chromophores [1]. They are widely used in synthetic fibers [2], fluorescent probes [3], and in some elaborated chemosensors [4]. In addition, chalcones were used in several fields, such as, recognition of inorganic chemistry [5], hole-transport material [6], in the electro photography [7], electroluminescence [8], charge-transfer agents [9], solar energy collectors [10] and nonlinear optical material due to their excellent emitting property [11]. They have high hole transport tendency allowing them to exhibit both intense photoluminescence and fluorescence in solid and liquid states, respectively [12]. Higher hole mobilities in chalcones doped in polymers have also been reported [13]. Chalcones are precursors to the flavonoids and natural products, which play a significant role in the disease and parasite resistance of plants.

Indeed, there is an increasing interest in the use of chalcone derivatives for pharmaceutical purposes, including antibiotic, antitumor and antimalarial agents [14–16]. Beyond these very important applications in biological chemistry, they are also used as intermediate for the synthesis of various open chain and heterocyclic compounds, such as, epoxide, ring opening of epoxidized pyrazoline, pyrazol, pyrimidine thiozole, oxazole [17–19]. Physicochemical studies are one of most important

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studies of compounds. On the bases of these studies, different physicochemical parameters of the compound of interest, for example, high fluorescence quantum yield, high molar absorptivity, large Stokes shift as well as high photostability, can be identified [20, 21]. In accordance, the main focus of the present study was to evaluate spectral properties, stoichiometric ratios, physicochemical parameters, photostability and polarity behaviors of newly prepared chalcone dye in organized media.

Experimental

Chemicals and Reagents

3-acetyl-2,5-dimethylthiophene, 3,4-dimethoxybenzaldehyde and fluorescein were purchased from Sigma-Aldrich (Milwaukee, WI, USA). All solvents, including 1,4-dioxane, chloroform (CH₂Cl₂), dichloromethane (CH₂Cl₂), n-butanol (n-ButOH), isopropanol (iso-PrOH), ethanol (EtOH), methanol (MeOH), acetonitrile (CH₃CN), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF), were of analytical grade. They were also preliminarily checked for the absence of absorbing or fluorescent impurities within the scanned spectral ranges.

Sample Preparation

Stock solutions of DDTP, CTAB and SDS in different spectroscopic grade solvents were prepared and stored in the dark. For the DDTP with CTAB (or SDS) association study, 1×10^{-5} M DDTP standard solutions were prepared from DDTP stock solution and adding appropriate amounts of CTAB (or SDS) stock solutions. In that manner, the concentrations of CTAB (or SDS) were 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, and 1.6×10^{-3} M. In addition, solutions of CTAB (or SDS) were also prepared under the same experimental conditions of DDTP with CTAB (or SDS) solutions. All solutions were allowed to equilibrate in the dark. For the fluorescence quantum yield, polarity study and photostability studies, individual 1×10^{-5} M DDTP standard solutions were prepared in different solvents. In addition, a 1×10^{-6} M fluorescein was prepared in 0.1 M NaOH and selected as reference for determining the fluorescence quantum yield of DDTP in different solvents.

Apparatus

Melting points were performed on a Thomas Hoover capillary melting apparatus without correction. FT-IR measurements were acquired on KBr disks on a Nicolet Magna 520 FT-IR spectrometer. ¹H-NMR and ¹³C-NMR spectroscopic experiments were recorded in CDCl₃ on a Bruker DPX 600 and 125 MHz spectrometers, respectively, using tetramethyl silane (TMS) as an internal standard at room temperature. Microanalyses were

achieved by use of a Perkin Elmer 240B analyzer. UV–vis electronic absorption spectra were acquired on a Shimadzu UV-1650 PC spectrophotometer. Absorption spectra were collected using a 1 cm quartz cell. Steady state fluorescence spectra were measured using Shimadzu RF 5301 PC spectrofluorometer with a rectangular quartz cell. Emission spectra were monitored at right angle and excited at 410 nm for both DDTP and fluorescein with slit widths set for entrance and exit bandwidths of 3 and 3 nm on both excitation and emission monochromators, respectively. All fluorescence spectra were blank subtracted before proceeding in data analyses.

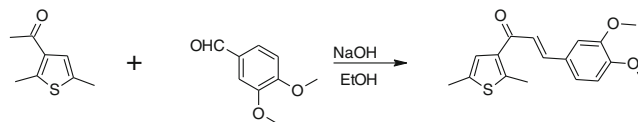
Synthesis Procedures of DDTP

DDTP was prepared and purified based on previously reported procedures by our group [18], and its purity was confirmed by elemental analysis, ¹H-NMR and ¹³C-NMR spectroscopy. The DDTP dye was synthesized by the reaction of 3-acetyl-2,5-dimethylthiophene with 3,4-dimethoxybenzaldehyde (Scheme 1). A solution of 3-acetyl-2,5-dimethylthiophene (0.029 mol) and 3,4-dimethoxybenzaldehyde (0.029 mol) in an ethanolic solution of NaOH (3 g in 10 mL of ethanol) was stirred for 8 h at room temperature. The solution was poured into ice cold water of pH~2 (pH adjusted by HCl). The solid was separated and dissolved in CH₂Cl₂, washed with saturated solution of NaHCO₃ and evaporated to dryness. The residue was recrystallized in chloroform and methanol. Light-yellow solid: m.p 114–115 °C; GC-MS *m/z* (rel. int. %): 304 (72) [M+1]⁺; FT-IR (KBr) ν_{\max} cm⁻¹: 2909 (C-H), 1647 (C=O), 1583 (C=C); ¹H NMR (600 MHz, DMSO-*d*₆) (δ /ppm): 7.66 (d, C=CH, *J*=15.6 Hz), 7.27 (s, CH_{aromatic}), 7.20 (d, CH_{aromatic}, *J*=8.4 Hz), 7.14 (d, CO=CH, *J*=15.6 Hz), 6.89 (d, CH_{aromatic}, *J*=8.4 Hz), 6.89 (s, CH), 3.97 (OCH₃), 3.89 (OCH₃), 2.69 (s, CH₃), 2.44 (s, CH₃); ¹³CNMR (CDCl₃) δ : 185.00, 151.12, 149.09, 146.79, 143.76, 136.78, 135.12, 127.88, 125.91, 122.90, 110.97, 109.82, 77.28, 55.96, 55.91, 15.82, 15.06; Anal. calc. for C₁₇H₁₈O₃S: C, 67.52, H, 6.00, S, 10.60. Found: C, 67.48, H, 5.98, S, 10.56.

Results and Discussion

Characterization of DDTP

DDTP was characterized by the GC-MS *m/z* (rel. int.%), FT-IR, ¹H-NMR, ¹³C-NMR and elemental analysis. FT-IR spectra of DDTP display that a characteristic band at 1,668 cm⁻¹ of the



Scheme 1 Synthetic route of the DDTP

$\nu(\text{C}=\text{O})$ peak for Act-thiophen is shifted to a lower frequency of $1,647\text{ cm}^{-1}$ for DDTP. This is due to the conjugation of π -electrons on the benzene moiety with those on the ethylene moiety in the enon linkage. In $^1\text{H-NMR}$ spectra, assignments of the signals were based on chemical shift and intensity pattern. $^1\text{H-NMR}$ spectra of DDTP show two doublets at 7.66 ppm ($J=15.6$) for the $\text{CH}=\text{C}$ and 7.14 ppm ($J=15.6\text{ Hz}$) for the $\text{CO}=\text{CH}$, indicating that the ethylene moiety in the enon linkage is in the *trans*-conformation and conforming the formation of DDTP. In addition, spectral signals of $^{13}\text{C-NMR}$ spectra were in good agreement with the probable structure details of DDTP, appeared at δ 185.00 for ($\text{C}=\text{O}$), 146.79 for ($\text{C}-\beta$) and 122.90 for ($\text{C}-\alpha$).

Spectral Behavior of DDTP in Organized Media

A positively charged CTAB and negatively charged SDS surfactants were selected for evaluating the emission behavior of the DDTP dye. The two specified surfactants were chosen because ionic charges possessed by DDTP dye can be influenced by the positively charged CTAB and negatively charged SDS. Thus, the charge attraction accounts for the DDTP emission behavior. Fluorescence emission spectra of DDTP in the absence and presence of CTAB and SDS were measured, as illustrated in Fig. 1a. Figure 1a shows a pronounced increase in fluorescence intensities of DDTP when increasing the concentration of CTAB from 2×10^{-4} up to $1.6 \times 10^{-3}\text{ M}$. Such enhancement in the fluorescence intensity of $1 \times 10^{-5}\text{ M}$ DDTP at fixed concentrations with an increase in the CTAB concentration may likely be ascribed to the association mechanism of DDTP with CTAB. In addition, a spectral shape change and stepwise red shift in spectral position of DDTP fluorescence can be observed while the CTAB concentration increases. This phenomenon in emission spectrum of DDTP indicated that a relaxed intramolecular charge transfer state was reached, strongly confirming that there was an interaction between DDTP and CTAB. The influence of CTAB on the relative emission intensity of $1 \times 10^{-5}\text{ M}$ DDTP is illustrated in Fig. 2a. As shown in Fig. 2a, the relative emission intensity of $1 \times 10^{-5}\text{ M}$ DDTP shows a strong increase initially and levels up at higher concentrations of CTAB. This leveling effect can be attributed to the interaction between DDTP and CTAB. For comparison to emission spectra of DDTP with CTAB, fluorescence emission of DDTP in the absence and presence of SDS were examined under the same experimental and instrumental conditions. As displayed in Fig. 1b, the fluorescence intensity of DDTP is quenched with an increase of the SDS concentration. Moreover, more significant reductions were noticed in fluorescence intensities of DDTP with SDS. The quenching of DDTP upon increasing SDS concentration can likely be ascribed to the association of DDTP with SDS. Figure 2b represents the influence of SDS on the relative emission intensity of $1 \times 10^{-5}\text{ M}$ DDTP. It can be observed that there was a

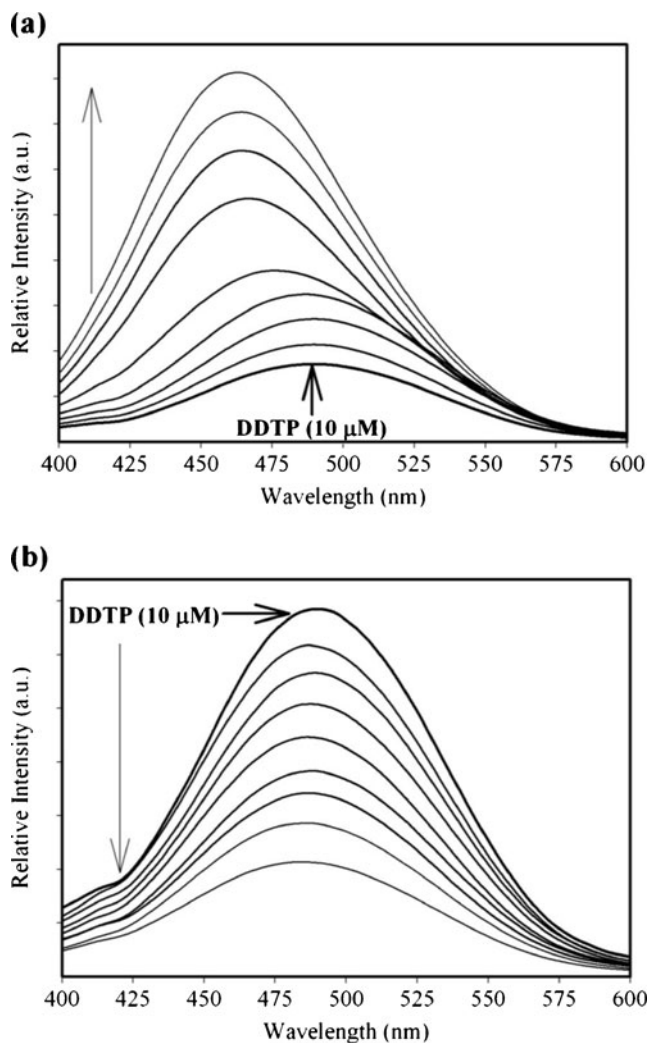


Fig. 1 Emission spectrum of $1 \times 10^{-5}\text{ M}$ DDTP in different concentration of (a) CTAB and (b) SDS. The concentrations of CTAB (or SDS) at increasing emission intensity are 0.0, 2×10^{-4} , 4×10^{-4} , 6×10^{-4} , 8×10^{-4} , 1×10^{-3} , 1.2×10^{-3} , 1.4×10^{-3} and $1.6 \times 10^{-3}\text{ M}$. ($\lambda_{\text{ex}}=410\text{ nm}$)

subsequent decrease in the relative emission intensity of DDTP with an increase in the SDS concentration, strongly providing that there was an interaction between DDTP and SDS. It seems that the dye molecules located in the hydrocarbon core of CTAB aggregates, while in SDS, the dye located at micelle–water interface, with quenching role of water.

Determination of Stoichiometric Ratios and Association Constants

An alteration in fluorescence intensities of DDTP in the presence of CTAB (or SDS) was noted due to inner-filter effect. Indeed, inner-filter effect phenomena can easily interfere with fluorescence intensities at both excitation and fluorescence wavelength peaks of DDTP. This occurs particularly at higher concentrations of CTAB (or SDS) because they usually absorb at both fluorescence excitation and emission regions of DDTP.

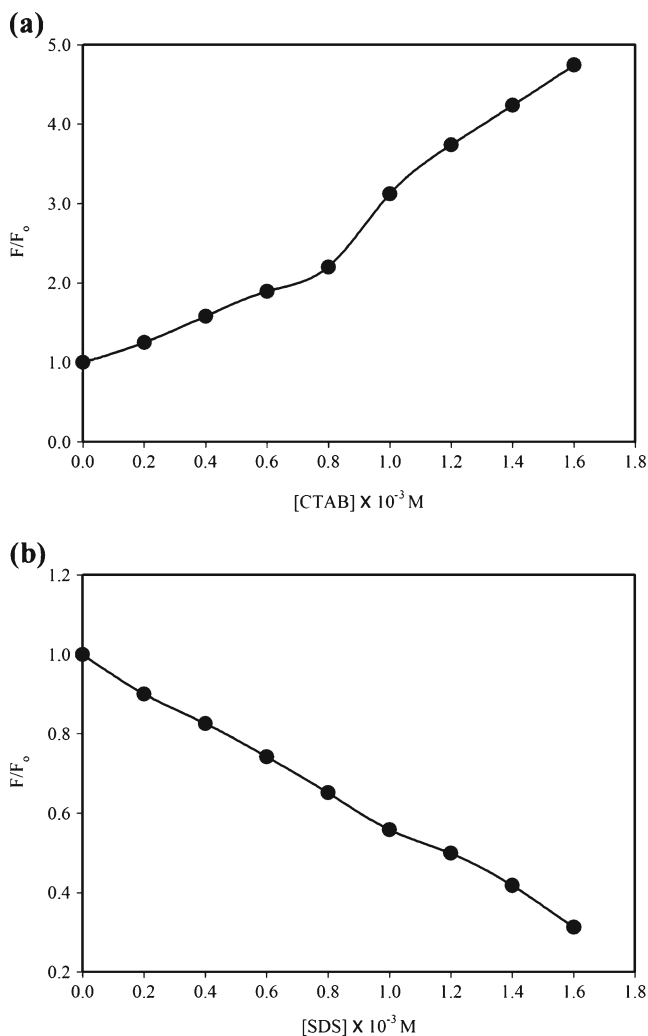


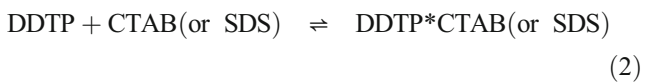
Fig. 2 Influence of (a) CTAB and (b) SDS on the relative emission intensity of 10 μM DDTP

Therefore, corrections of the observed fluorescence intensities for primary and secondary inner-filtering effects were carried out using the following equation [22]

$$F_{corr.} = F_{obs.} \cdot 10^{\frac{(A_{ex}L_{ex} + A_{em}L_{em})}{2}} \tag{1}$$

where $F_{corr.}$ refers to the corrected fluorescence intensity, A and L denote the absorption and cell pathlength, respectively, for both the excitation (ex) and emission (em) wavelengths, and $F_{obs.}$ represents the observed fluorescence intensity.

After correcting for primary and secondary inner-filtering effects, stoichiometric ratios and association constants of DDTP associated with CTAB (or SDS) were estimated using the Benesi-Hildebrand method [23]. The Benesi-Hildebrand plot gives detailed insight into the stoichiometry. If we assume that the equilibrium for DDTP associated by CTAB (or SDS) is as follows:



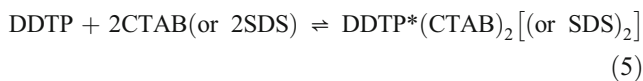
The association constant (K_{oc}) of DDTP with CTAB (or SDS) for the stoichiometric ratio of 1:1 can be described by the following relation:

$$K_{oc} = \frac{[DDTP * CTAB (or\ SDS)]}{[DDTP][CTAB (or\ SDS)]} \tag{3}$$

where $[DDTP]$, $[CTAB (or\ SDS)]$, and $[DDTP*CTAB (or\ SDS)]$ refer to the equilibrium concentrations of DDTP, CTAB (or SDS), and DDTP associated with CTAB (or SDS). The initial concentration of the host molecule CTAB (or SDS) should generally be much larger than that of the guest molecule (DDTP). Based on that, the initial concentration of CTAB (or SDS) is much greater than that of DDTP with CTAB (or SDS), $[CTAB (or\ SDS)]_o \gg [DDTP*CTAB (or\ SDS)]$. The relationship between the fluorescence intensity of DDTP and CTAB (or SDS) concentration can be given by the following equation:

$$\frac{1}{F - F_o} = \frac{1}{(F_{\infty} - F_o)K_{oc}[CTAB (or\ SDS)]_o} + \frac{1}{(F_{\infty} - F_o)} \tag{4}$$

where F denotes the fluorescence intensity of DDTP in the presence of CTAB (or SDS), F_o is the fluorescence intensity of DDTP in the absence of CTAB (or SDS), F_{∞} represents the fluorescence intensity of DDTP associated with CTAB (or SDS), and $[CTAB (or\ SDS)]_o$ is the initial concentration of CTAB (or SDS). The association constant of DDTP associated by CTAB (or SDS) can be determined by a plot of $1/(F - F_o)$ versus $1/[CTAB (or\ SDS)]_o$. If a linear relationship is obtained, this indicates the stoichiometry of the association is 1:1. Similarly, if one assumes that the stoichiometric ratio of DDTP associated with CTAB (or SDS) is 1:2, as displayed below,



The association constant is given by:

$$K_{oc} = \frac{[DDTP * (CTAB)_2(or\ (SDS)_2)]}{[DDTP][CTAB]^2(or\ [SDS]^2)} \tag{6}$$

The relationship between the fluorescence intensity and CTAB (or SDS) concentration, under the assumptions $[CTAB (or\ SDS)]_o \gg [DDTP*(CTAB)_2 (or\ (SDS)_2)] \gg [DDTP*CTAB (or\ SDS)]$, can be expressed as follows:

$$\frac{1}{F - F_o} = \frac{1}{(F_{\infty} - F_o)K_{oc}[CTAB]_o^2 (or\ [SDS]_o^2)} + \frac{1}{(F_{\infty} - F_o)} \tag{7}$$

The association constant of DDTP with CTAB (or SDS) can be estimated by plotting $1/(F - F_o)$ versus $1/[CTAB]_o^2 (or\ [SDS]_o^2)$.

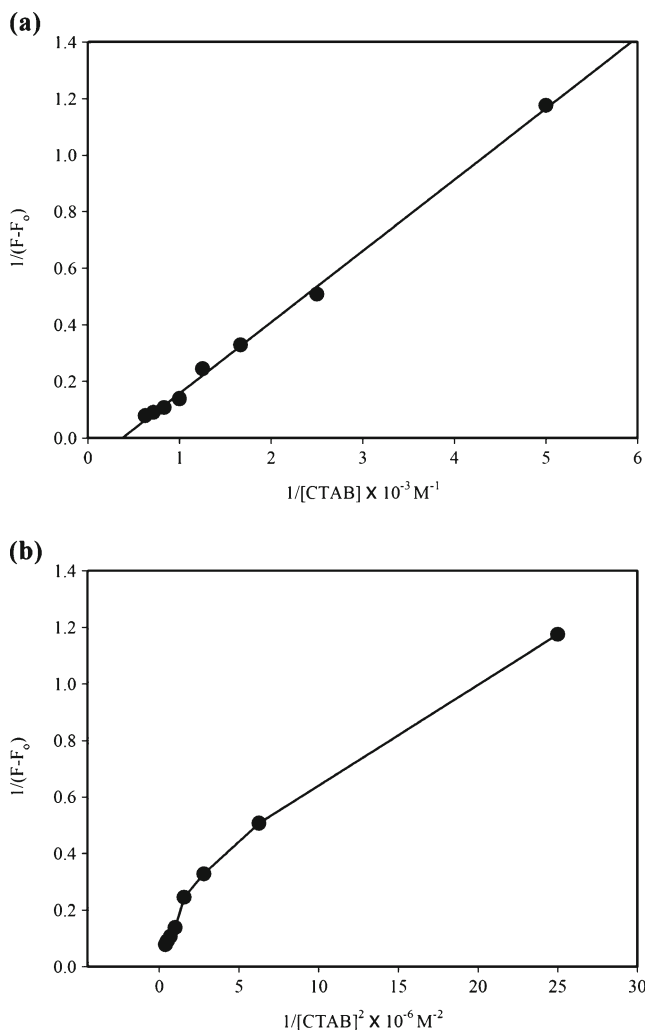


Fig. 3 Double-reciprocal Benesi-Hildebrand plots of (a) 1:1 and (b) 1:2 stoichiometries for DDTP with CTAB

Based on that, the stoichiometric ratio is 1:2 if a linear plot is obtained.

Based on Benesi-Hildebrand method, more reasonable linear relationship was obtained with a stoichiometric ratio of 1:1 in comparison to that of 1:2 (Fig. 3a and b). Figure 3b displayed that a convex and upward curvature is obtained from the stoichiometric ratio of 1:2 in comparison to that of 1:1 (Fig. 3a), strongly indicating that the stoichiometric ratio of DDTP with CTAB is 1:1. The association constant (0.373 Lmol⁻¹) and correlation coefficient ($R^2=0.998$) values of 1:1 stoichiometric ratio between DDTP with CTAB are recorded in Table 1. Also, the stoichiometric ratio was investigated for the association between DDTP and SDS using the Benesi-Hildebrand method. As presented in Fig. 4a and b, more reasonable linear line was obtained for 1:1 as compared to 1:2 stoichiometric ratio. It can be observed that there is downward curvature for stoichiometric ratio of 1:2 (Fig. 4b) as compared to that of 1:1 (Fig. 4a), strongly providing that the stoichiometric ratio of DDTP with SDS is 1:1. The association constant (0.420 Lmol⁻¹) and

Table 1 Stoichiometric ratio, correlation coefficient (R^2), association constant (K_{oc}) and Stern-Volmer constant (K_{sv}) obtained from Benesi-Hildebrand and Stern-Volmer plots for DDTP associated by CTAB (or SDS)

Association	R^2	K_{oc} (Lmol ⁻¹)	K_{sv} (Lmol ⁻¹)
DDTP with CTAB	0.998	0.373	–
DDTP with SDS	0.995	0.420	–
DDTP with SDS	0.987	–	0.439

correlation coefficient ($R^2=0.995$) values of 1:1 stoichiometric ratio between DDTP with SDS are illustrated in Table 1.

In addition to Benesi-Hildebrand plot, the Stern-Volmer plot, typically used for a stoichiometric ratio of 1:1 between the fluorophore and quencher, was also applied. The Stern-Volmer plot provides the relationship between the concentration of quencher present in a sample [Q] and the ratio of the fluorophore in the absence (F_0) and presence (F) of quencher as follows [22].

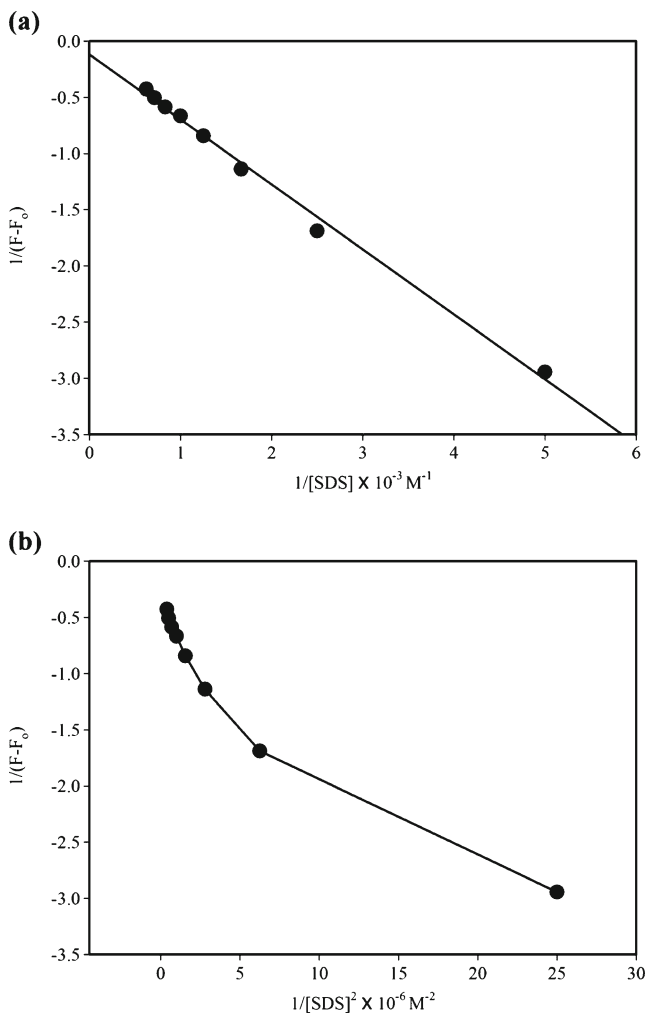


Fig. 4 Double-reciprocal Benesi-Hildebrand plots of (a) 1:1 and (b) 1:2 stoichiometries for DDTP with SDS

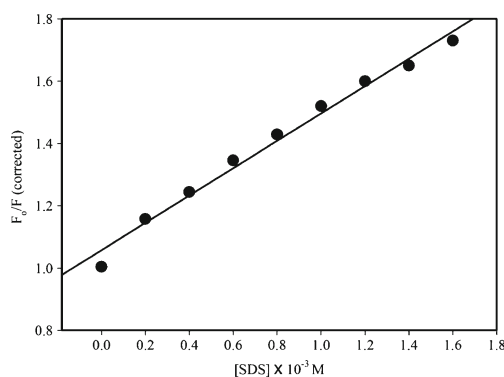


Fig. 5 Stern-Volmer plot of 10 μM DDTP fluorescence quenching in different concentrations range of SDS

$$\frac{F_o}{F} = 1 + K_{sv}[Q] \quad (8)$$

where K_{sv} denotes the Stern-Volmer constant. Interpretation of the K_{sv} is dependent upon whether a static (probe is bound to the quencher) or dynamic (probe collision with the quencher) process dominates.

Stern-Volmer plot was also in good conformity with Benesi-Hildebrand plot of the stoichiometric ratio and association constant between DDTP with SDS (Fig. 5). A close examination of Fig. 5 reveals that a linear relationship with correlation coefficient of $R^2=0.987$ was obtained from the Stern-Volmer plot after correcting measured fluorescence intensities for inner-filtering effects (Table 1). In addition, the resulted Stern-Volmer constant (0.439 Lmol^{-1}) was consistent with that previously obtained from the Benesi-Hildebrand method of 1:1 stoichiometric ratio.

Determination of Fluorescence Quantum Yield of DDTP

The fluorescence quantum yield (ϕ_F) of DDTP was determined in different solvents using an optically diluted solution to avoid

reabsorption effect (absorbance at excitation wavelength ≤ 0.1) [22]. Fluorescein ($\phi_F=0.95$ in 0.1 M NaOH) was chosen as a standard sample because fluorescein absorbs near the excitation wavelength ($\lambda_{\text{max(ex)}}=410 \text{ nm}$) of DDTP [24]. Thus, it can be assumed that the same number of photons are absorbed by fluorescein and DDTP. The fluorescence quantum yield of DDTP can be related to that of the standard by the following relationship [25].

$$\phi_{F(x)} = \left(\frac{A_s}{A_x}\right) \left(\frac{F_x}{F_s}\right) \left(\frac{n_x}{n_s}\right)^2 \phi_{F(s)} \quad (9)$$

where A refers to the absorbance at the excitation wavelength, F denotes the area under the corrected emission curve and n corresponds to the refractive index of solvents. Subscripts s and x refer to the standard and unknown, respectively. Based on the above relation, fluorescence quantum yields of DDTP in different solvents were estimated, as illustrated in Table 2.

Determination of Oscillator Strength and Transition Dipole Moment for DDTP

Stokes shifts ($\Delta\bar{\nu}_{ss}$) of DDTP were also calculated in different solvents, Table 2, using the following equation [26].

$$\Delta\bar{\nu}_{ss} = \bar{\nu}_{ex} - \bar{\nu}_{em} \quad (10)$$

where $\bar{\nu}_{ex}$ and $\bar{\nu}_{em}$ denote the wavenumbers of excitation and emission maxima in cm^{-1} , respectively. The Onsager polarity function, $f(D, n)$, was also calculated in different solvents (Table 2) using the following relation:

$$f(D, n) = \frac{D-1}{2D+1} - \frac{n^2-1}{2n^2+1} \quad (11)$$

where D and n represent the static dielectric constant and refractive index of the solvent, respectively. The oscillator strength

Table 2 Spectroscopic and physicochemical properties of DDTP in different solvents

Solvent	$f(D, n)$	E_T , kcal mol $^{-1}$	$\lambda_{\text{max abs}}$ (nm)	$\lambda_{\text{max em}}$ (nm)	$\Delta\bar{\nu}_{ss}$ (cm $^{-1}$)	ε (Lmol $^{-1}$ cm $^{-1}$)	f	μ (Debye)	Φ_F
THF	0.208	81.45	354	454	6222	28780	0.71	7.32	0.012
1,4-Dioxane	0.028	80.99	355	455	6190	21550	0.53	6.33	0.029
DMF	0.275	79.19	362	461	5932	40120	0.95	8.54	0.002
DMSO	0.263	79.86	359	461	6163	33830	0.83	7.95	0.001
CH $_2$ Cl $_2$	0.218	80.31	356	478	6992	20410	0.57	6.55	0.011
CHCl $_3$	0.1482	82.87	357	467	6597	18350	0.48	6.05	0.002
n-ButOH	0.264	80.53	360	448	5456	25840	0.56	6.53	0.001
iso-PrOH	0.28	83.11	359	447	5483	21170	0.46	5.91	0.008
EtOH	0.29	84.33	358	465	6427	20530	0.527	6.32	0.018
MeOH	0.309	80.53	357	478	7090	26300	0.74	7.48	0.032
E. Glycol	0.276	78.54	363	503	7667	8190	0.25	4.39	0.015
ACN	0.273	80.31	356	475	7037	19000	0.53	6.34	0.107

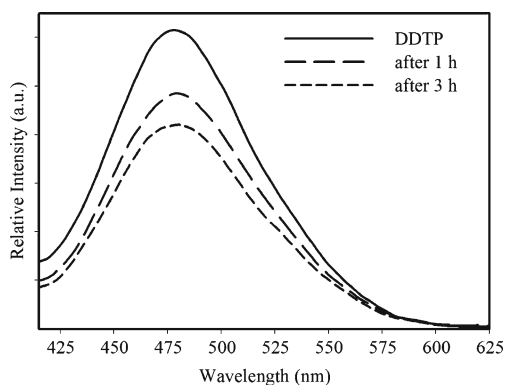


Fig. 6 Effect of photobleaching on the emission spectra of DDTP in EtOH

describes the effective number of electrons transition from the ground to excited state and provides the absorption area in the electronic spectrum. The oscillator strength, f , can be calculated as follows [27].

$$f = 4.32 \times 10^{-9} \int \varepsilon(\bar{\nu}) d\bar{\nu} \quad (12)$$

where ε denotes the extinction coefficient ($\text{Lmol}^{-1}\text{cm}^{-1}$), and $\bar{\nu}$ is the numerical value of wavenumber (cm^{-1}). Oscillator strength values of DDTP in different solvents are tabulated in Table 2. In addition, the transition dipole moment (μ) from ground to excited state in Debye was estimated for DDTP in different solvents (Table 2) using the following equation [28].

$$\mu^2 = \frac{f}{4.72 \times 10^{-7} \times E_{\text{max}}} \quad (13)$$

where E_{max} is the energy of maximum absorption band in cm^{-1}

Photostability Study of DDTP

The behavior of DDTP in terms of its susceptibility to photobleaching was also evaluated (Fig. 6). For photostability study, the DDTP dye was exposed to the greatest amount of radiation for 3 h on air-saturated samples in order to induce the photobleaching. Figure 6 clearly displays the behavior of the DDTP dye in terms of its photostability against photobleaching over 3 h time span. In general, it can be noted that there is minimal loss in fluorescence intensities of DDTP with an increase in the exposure time. The decrease in fluorescence intensities (% photobleaching) of DDTP was calculated based on the difference between the area under the fluorescence peak of DDTP before and after irradiation. As illustrated in Fig. 6, a 20.41 % fraction, as a function of fluorescence intensity, of DDTP was photobleached after 1 h. The photobleached fraction of DDTP was also raised up to 30.30 % by the end of exposure time (3 h). Results of photostability study indicated that the DDTP dye was relatively photostable. Generally, information is so limited concerning the photostability relation to the structure that the conclusion remains open.

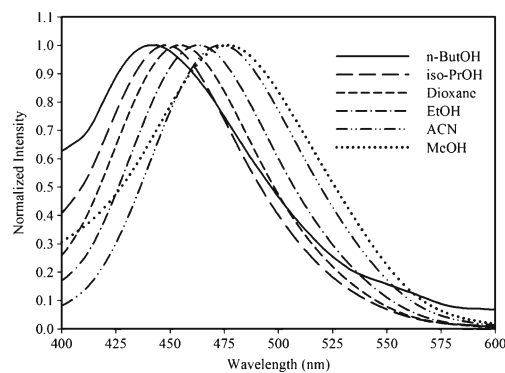


Fig. 7 Normalized emission spectra of 10 μM DDTP in different solvents, excited at 410 nm

Fluorescence Polarity Study of DDTP

The steady state absorption and emission parameters of 1×10^{-5} M DDTP were reported in various polar aprotic and polar protic solvents, as displayed in Table 2. As shown in fluorescence spectra of DDTP (Fig. 7), it can be clearly observed that the polarity of solvent has a strong influence on emission spectra due to the strong polar character of DDTP in the excited state. In general, fluorescence spectra are broad and red shifted as the solvent polarity increases from ButOH to MeOH.

The red (bathochromic) shift from 442 nm in ButOH to 475 nm in MeOH can be attributed to a photoinduced intramolecular charge transfer (ICT) from methoxy groups to keto-group taking place in the singlet excited state and resulting in the observed increase in polarity of DDTP upon excitation. The red shift of the DDTP emission peak in alcoholic solvents was also ascribed to solute–solvent hydrogen bonding interaction in the singlet excited state, resulting in an extra red shift in the observed spectra.

The empirical Dimroth–Reichardt solvent polarity parameter, E_T (30), was also determined using to the following relation [29, 30]:

$$E_T(\text{kcal mol}^{-1}) = \frac{28591}{\lambda_{\text{max}}} \quad (14)$$

where λ_{max} refers to the peak wavelength (nm) in the red region of the intramolecular charge transfer absorption of DDTP dye.

Conclusion

In the current study, a new chalcone dye (DDTP) was successfully synthesized via the reaction of 3,4-dimethoxybenzaldehyde with 3-acetyl-2,5-dimethylthiophene. Spectroscopic and elemental analyses of DDTP were in agreement with the chemical structure of DDTP. In addition, spectral properties, stoichiometric ratios, physicochemical parameters, photostability and polarity behaviors of newly synthesized chalcone dye in organized media were investigated. A fluorescence enhancement of DDTP with CTAB was noticed, while a fluorescence quenching of DDTP

with SDS was observed under the same experimental and instrumental conditions. Stoichiometric ratios and association constants of DDTP with CTAB and SDS were also reported using Benesi-Hildebrand method. Results of Stern-Volmer plot further confirmed the stoichiometric ratio and association constant of DDTP with SDS. Physicochemical parameters, including singlet absorption, molar absorptivity, oscillator strength, transition dipole moment and fluorescence quantum yield of DDTP, were also estimated. The DDTP dye was found to have high extinction coefficient and large Stokes shift. The fluorescence quantum yield of DDTP was dependent on the polarity of solvent. Results of photostability study displayed that DDTP was photostable in terms of its susceptibility to photobleaching. Data of fluorescence polarity study revealed that DDTP was sensitive to the polarity of the microenvironment provided by different solvents. Finally, the preparation and spectroscopic investigation of the DDTP dye may play a significant role toward exploring its potential applications.

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