

SPECTROSCOPIC, PHOTOPHYSICAL INVESTIGATION AND MICELLIZATION FOR CRITICAL MICELLE CONCENTRATION OF 3-(3,4-DIMETHOXYPHENYL)-1-(2,5-DIMETHYLFURAN-3-YL)PROP-2-EN-1-ONE DYE****S. A. Khan^{1*}, A. M. Asiri^{1,2}**

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3-(3,4-Dimethoxyphenyl)-1-(2,5-dimethylfuran-3-yl)prop-2-en-1-one (DDFP) was prepared by the reaction of 3-acetyl-2,5-dimethylfuran and 3,4-dimethoxybenzaldehyde. Data obtained from FT-IR, ¹H-NMR, ¹³C-NMR, EI-MS, and elemental analysis were consistent with the chemical structure of the newly prepared DDFP. Electronic absorption and emission spectrum of DDFP have been measured in different solvents; DDFP dye exhibits red shift in emission spectrum as solvent polarity increases, indicating a large change in dipole moment of DDFP molecule upon excitation due to intramolecular charge transfer in excited DDFP. Excited state intermolecular hydrogen bonding affects the energy of emission spectrum and fluorescence quantum yield of DDFP molecule. DDFP dye undergoes solubilization in different micelles and may be used as a probe or quencher to determine the critical micelle concentration (CMC) of CTAB and SDS. The photoreactivity and net photochemical quantum yield (ϕ) of DDFP are determined in solvents CHCl₃, CH₂Cl₂, CCl₄, and DMSO. The dye is relatively photostable in DMSO and displays photodecomposition in chloromethane solvents.

Keywords: chalcone, Stokes shift, oscillator strength, dipole moment, photoreactivity, fluorescence quantum yield.

СПЕКТРАЛЬНЫЕ, ФОТОФИЗИЧЕСКИЕ ИССЛЕДОВАНИЯ И МИЦЕЛЛООБРАЗОВАНИЕ В КРАСИТЕЛЕ 3-(3,4-ДИМЕТОКСИФЕНИЛ)-1-(2,5-ДИМЕТИЛФУРАН-3-ИЛ)ПРОП-2-ЕН-1-ОН КРИТИЧЕСКОЙ МИЦЕЛЛЯРНОЙ КОНЦЕНТРАЦИИ**S. A. Khan^{1*}, A. M. Asiri^{1,2}**

УДК 535.37:547.97

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(Поступила 26 октября 2016)

3-(3,4-Диметоксифенил)-1-(2,5-диметилфуран-3-ил)проп-2-ен-1-он (ДДФП) получен в результате реакции 3-ацетил-2,5-диметилфурана и 3,4-диметоксибензальдегида. Данные ИК-фурье-спектроскопии, ¹H ЯМР, ¹³C ЯМР, электроионизационной масс-спектрометрии и элементного анализа согласуются с химической структурой синтезированного ДДФП. Электронные спектры поглощения и излучения ДДФП измерены в различных растворителях. Для красителя ДДФП характерно красное смещение в спектре излучения при увеличении полярности растворителя, что указывает на значительное изменение дипольного момента молекулы ДДФП при возбуждении за счет внутримолекулярного переноса заряда в возбужденном ДДФП. Возбужденное состояние межмолекулярных водородных связей влияет на энергетический спектр излучения и квантовый выход флуоресценции моле-

** Full text is published in JAS V. 84, No. 4 (<http://springer.com/10812>) and in electronic version of ZhPS V. 84, No. 4 (http://www.elibrary.ru/title_about.asp?id=7318; sales@elibrary.ru).

кулы ДДФП. Краситель ДДФП в различных мицеллах подвергается солюбилизации и может быть использован в качестве зонда или тушителя для определения критической концентрации мицелл цетилтриметиламмония бромида и додецилсульфата натрия. Фотореактивность и результирующий фотохимический квантовый выход ДДФП определены в растворителях CHCl_3 , CH_2Cl_2 , CCl_4 и диметилсульфоксиде. Краситель относительно фотостабилен в диметилсульфоксиде и распадается под действием света в хлорметановых растворителях.

Ключевые слова: халконы, стоксов сдвиг, сила осциллятора, дипольный момент, фотореактивность, квантовый выход флуоресценции.

Introduction. Chalcones are one of the most important classes of natural occurring organic molecules and possess versatile applications in medicinal chemistry [1, 2]. They are used as antibacterial [3], anticancer [4], anti-HIV [5], anti-inflammatory [6] drugs. Chalcones are also known as α,β -unsaturated ketone. Due to presence of the α,β -unsaturated ketone framework, chalcone gives photochemical products by hydrogen abstraction [7]. Due to the long π bond conjugation systems, chalcone is also known as chromophores [8]. Donor and acceptor groups such as $\text{N}(\text{CH}_3)$, OCH_3 (donor), CN and NO_2 (acceptor) containing chalcones have reasonable stability and good solubility and are extensively investigated for electronic and photonic applications such as charge-transfer agents, solar energy collectors, and nonlinear optical materials [9–11]. They are useful as optical brighteners, laser dyes, electroluminescent materials, two photon absorption (TPA) materials, as well as fluorescent labels and probes in biology and medicine [12–14]. It is well known that the property of fluorescence in the chalcone system is significantly altered by appropriate substituents of donor and acceptor groups [15]. Appropriately substituted chromophores find application as fluorescent dyes for synthetic fibers and as daylight fluorescent pigments, which impart vivid brilliance to paints and printing inks [16]. Various heterocyclic organic compounds such as pyrazoline, pyrazole, pyrimidine, pyridine, thiazole, and oxazole are synthesized from chalcones. They are also used in the field of inorganic chemistry. Chalcones are used ligands for the coordination of various metals such as $\text{Cu}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Co}(\text{II})$, and $\text{Zn}(\text{II})$. Photophysical parameters such as solvatochromic, piezochromic, oscillator strength, dipole moment, fluorescent quantum yield, and photostability are also important for determining the behavior of compounds [17]. In this paper we report the synthesis of chalcone (DDFP), and its physicochemical properties such as electronic absorption, oscillator strength, dipole moment, fluorescence quantum yield, photochemical quantum yield, and the critical micelle concentration (CMC) of the surfactant are also determined.

Experimental. The appropriate 3-acetyl-2,5-dimethylfuran and 3,4-dimethoxybenzaldehyde was purchased from Acros Organic. Other reagents and solvents (A.R.) were obtained commercially and used without further purification, except dimethylformamide (DMF), ethanol, and methanol.

Melting points were recorded on a Thomas Hoover capillary melting apparatus without correction. FT-IR spectra were recorded on a Nicolet Magna 520 FT-IR spectrometer. ^1H and ^{13}C NMR experiments were performed in CDCl_3 on a Bruker DPX 600 MHz spectrometer using tetramethylsilane (TMS) as internal standard at room temperature. 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 a Shimadzu RF 5301 PC spectrofluorophotometer with a rectangular quartz cell. Emission spectra were monitored at right angles. All fluorescence spectra were blank subtracted before proceeding to data analyses.

A solution of 3-acetyl-2,5-dimethylfuran (0.96 g, 0.0069 mol) and 3,4-dimethoxybenzaldehyde (2 g, 0.0069 mol) in an ethanolic solution of NaOH (1 g in 5 mL of ethanol) was stirred for 4 h at room temperature. The solution was poured onto ice-cold water of pH ~ 2 (pH adjusted by HCl). The separated solid was filtered off, washed several times with a saturated solution of NaHCO_3 and left to dry. The residue was recrystallized from methanol/chloroform

Yellow solid: m.p 140°C ; EI-MS m/z (rel. int. %): 288(75) $[\text{M}+1]^+$; IR (KBr) ν_{max} , cm^{-1} : 3122 (C–H), 2961 (C–H), 1654 (C=O), 1587 (C=C); ^1H NMR (600MHz CDCl_3) δ : 7.60 (d, C=CH, $J = 15.6$ Hz), 7.20 (d, CH, $J = 1.2$ Hz), 7.19 (d, CH, $J = 1.8$ Hz), 7.11 (s, CH), 6.89 (d, CO=CH, $J = 15.6$ Hz), 6.34 (s, CH), 2.61 (s, $-\text{OCH}_3$), 2.53 (s, $-\text{OCH}_3$), 2.29 (s, $-\text{CH}_3$), 2.25 (s, $-\text{CH}_3$); ^{13}C NMR (CDCl_3) δ , ppm: 186.01, 157.69, 151.12, 149.95, 149.12, 142.91, 127.87, 122.89, 122.15, 111.02, 109.91, 105.69, 55.98, 55.92, 14.45, 13.29. Anal. calc. for $\text{C}_{17}\text{H}_{18}\text{O}_4$ (%): C 71.31, H 6.39. Found (%): C 71.27, H 6.35.

Results and discussion. *Characterization of DDFP.* The purified dye was characterized by EI-MS m/z (rel. int.%), FT-IR, ^1H NMR, ^{13}C NMR, and elemental analysis. The FT-IR spectra show that the characteristic band at 1668 cm^{-1} of the $\nu(\text{C}=\text{O})$ peak for Act-furane is shifted to a lower frequency of 1654 cm^{-1} for

DDFP. This is due to the conjugation of the π -electrons on the benzene moiety with those on the ethylene moiety in the enone linkage. In the ^1H -NMR spectra, assignments of the signals were based on chemical shift and intensity pattern. The ^1H -NMR spectra of DDFP show two doublets at 7.60 ppm ($J = 15.6$) for the $\text{CH}=\text{C}$ and 6.89 ppm ($J = 15.6$ Hz) for the $\text{CO}=\text{CH}$, indicating that the ethylene moiety in the enone linkage is in the *trans*-conformation, confirming the formation of DDFP. The ^{13}C NMR (CDCl_3) spectrum of DDFP was recorded in CDCl_3 , and the spectral signals are in good agreement with the probable structure. The carbonyl carbon of DDFP usually appears at 186.01 in its ^{13}C NMR spectrum. The α, β -carbon atom with respect to the carbonyl group give rise to characteristic signals at $\delta = 127.87$ and 142.91 , respectively, which can also be readily identified by their characteristic appearance. Details of the ^{13}C -NMR spectra of DDFP are given in the experimental section. Finally, characteristic peaks were observed in the mass spectra of DDFP by the molecular ion peak. The mass spectrum of DDFP shows a molecular ion peak (M^+) m/z 288.

Spectral behavior of DDFP in different media. The steady-state absorption and fluorescence parameters of 1×10^{-5} mol/dm³ DDFP recorded in various nonpolar, polar aprotic, and polar protic solvents are summarized in Table 1. The absorption and emission spectra of DDFP are shown in Fig 1. As seen in Fig. 1a, the polarity of the solvent has little effect on absorption maxima, indicating the weak polar character of DDFP in the ground state. The emission spectrum of DDFP exhibits two emission bands. The emission peak around 380 nm corresponds to the locally excited (LE) state, and the other band situated around 384–465 nm is the emission from the intramolecular charge transfer (ICT) state. The emission spectra, however, are broad and red shifted (Fig. 1b) as the solvent polarity increases. The red-shift from 384 nm in *n*-heptane to 465 nm in DDFP indicates that photoinduced intramolecular charge transfer (ICT) occurs in the singlet excited state [18], and therefore the polarity of DDFP increases on excitation. The red shift of the fluorescence peak in alcoholic solvents is assigned to solute–solvent hydrogen bonding interaction in the singlet excited state, which causes an extra red shift in the observed spectra [19] (Table 1).

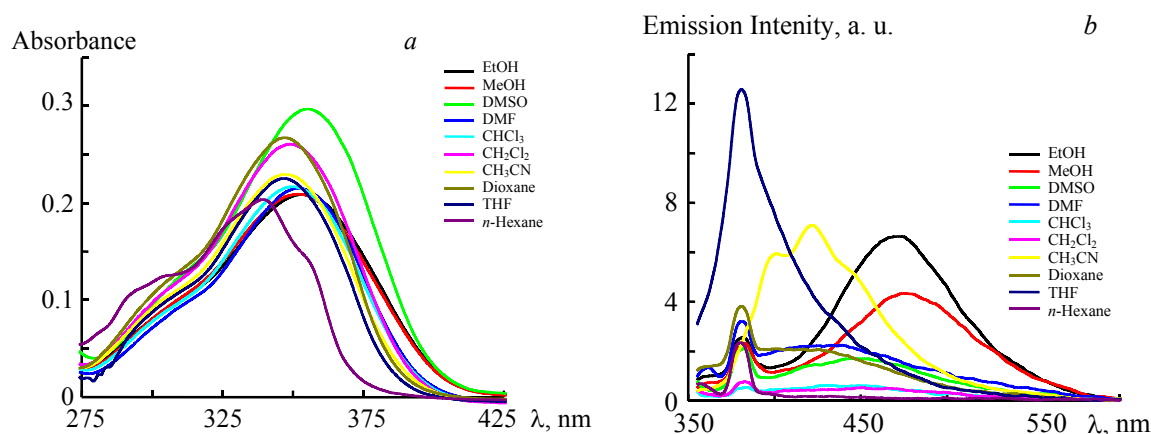
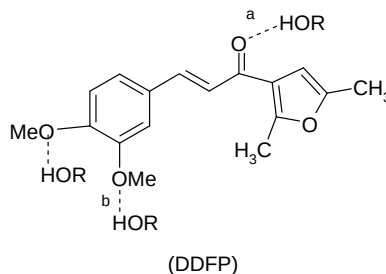


Fig. 1. a) Electronic absorption spectra of 1×10^{-5} mol/dm³ of DDFP in different solvents; b) emission spectra of 1×10^{-5} mol/dm³ of DDFP in different solvents ($\lambda_{\text{ex}} = 345$ nm).

TABLE 1. Spectral Data of DDFP in Different Solvents

Solvent	Δf	E_T^N	$E_T(30)$, kcal/mol	λ_{abs} , nm	λ_{em} , nm	E , $\text{M}^{-1} \cdot \text{cm}^{-1}$	f	μ_{12} , D	$\Delta\nu$, cm^{-1}	Φ_f
EtOH	0.305	0.654	51.9	358	483	20580	0.59	6.68	7229	0.44
MeOH	0.299	0.762	55.4	357	485	20530	0.60	6.73	7393	0.29
DMSO	0.266	0.441	54.1	363	465	29130	0.45	5.88	6043	0.080
DMF	0.263	0.404	43.8	358	446	20620	0.45	5.84	5511	0.16
CHCl_3	0.217	0.259	39.1	355	445	21190	0.48	6.00	5752	0.041
CH_2Cl_2	0.255	0.320	40.7	353	447	24200	0.57	6.53	5957	0.029
Acetonitrile	0.304	0.472	45.6	351	429	22830	0.47	5.91	5180	0.43
Dioxan	0.274	0.164	36	350	425	26490	0.53	6.26	5042	0.11
THF	0.148	0.210	37.4	346	387	22270	0.31	4.76	3486	—
<i>n</i> -Hexane	0.0014	0.012	31.1	341	384	20250	0.26	4.33	3284	—

A simplified description of hydrogen bonding of DDFP is shown in Scheme 1. Type (a) hydrogen bonding is strengthened in the excited state, since the charge density at the carbonyl oxygen is enhanced in the ICT excited state. On the other hand, type (b) hydrogen bonding is weakened on photoexcitation, because the charge densities at the OCH₃ decrease in the excited state.



The energy of absorption (E_a) and emission (E_f) spectra of DDFP in different solvents correlated with the empirical Dimroth polarity parameter $E_T(30)$ [20] of the solvent (Fig. 2a). A linear correlation between the energy of absorption and emission of solvents with various polarity was obtained, implying potential application of these parameters to probe the microenvironment of DDFP:

$$E_a = 75.17 - 0.1032E_T(30), \quad (1)$$

$$E_f = 68.28 - 0.257E_T(30). \quad (2)$$

Analysis of solvatochromic behavior allows estimating the difference in the dipole moment between the excited and ground states ($\Delta\mu_e - \Delta\mu_g$). This was achieved by applying the simplified Lippert–Mataga equation [21]:

$$\Delta\nu_{st} = 2(\mu_e - \mu_g)^2 \Delta f / hca^3 + \text{const}, \quad (3)$$

$$\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1), \quad (4)$$

where $\Delta\nu_{st}$ is the Stokes shift, which increases with increase in the solvent polarity, pointing to stronger stabilization of the singlet excited state in a polar solvent, h is Planck's constant, c is the speed of light, and a is the Onsager cavity radius, and ϵ and n are the dielectric constant and refractive index of the solvent. The constant represents higher order terms, which are usually neglected. The Onsager cavity radius was taken as 5.7 Å [22]. Figure 2b shows the plot of Stokes shift versus the orientation polarizability (Δf). The changes of dipole moment ($\Delta\mu$) upon excitation was calculated from the slope of the plot and the cavity radius is $\Delta\mu = 9.16$ D. This change in dipole moment is caused by redistribution of atomic charges in the excited state as a result of charge transfer from the electron rich $-\text{OCH}_3$ group to the electron acceptor keto-furanyl fragment.

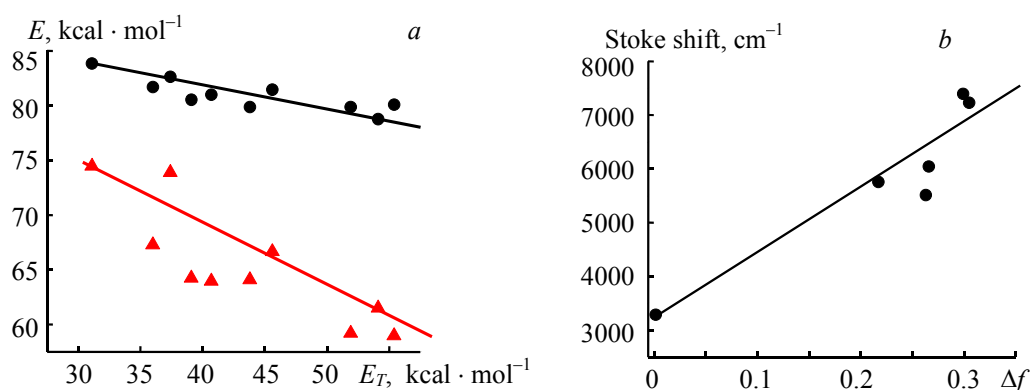


Fig. 2. a) Plot of energy of absorption (E_a) and emission (E_f) versus $E_T(30)$ of different solvents; b) plot of Δf versus Stokes shift ($\Delta\nu$).

The oscillator strength (f) and transition dipole moment (μ_{12}) of electronic transition for DDFP from ground to excited singlet state ($S_0 \rightarrow S_1$) was calculated in different solvents using the equation [23]:

$$f = 4.32 \times 10^{-9} \int \epsilon(\nu) d\nu, \quad (5)$$

$$(\mu_{12})^2 = f / 4.72 \times 10^{-7} E_{\max}, \quad (6)$$

where ϵ is the numerical value for molar decadic extinction coefficient measured in $\text{dm}^3/\text{mol} \cdot \text{cm}$, ν is the

value of wavenumber measured in cm^{-1} , and E_{max} is the energy maximum of absorption band in cm^{-1} . The values of f and (μ_{12}) are listed in Table 1 and indicate that the $S_0 \rightarrow S_1$ is a strongly allowed transition.

Fluorescence quantum yield. The fluorescence quantum yield (ϕ_f) of DDFP was measured using the optically diluted solution to avoid the reabsorption effect (absorbance at excitation wavelength ≤ 0.1), relative to the method with a solution of quinine sulfate in $0.5 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ ($\phi = 0.55$). Using the same excitation wavelength, the unknown quantum yield is calculated using the equation:

$$\phi = \phi_r I_x A_r x n^2 / I_r x A_x n_r^2, \quad (7)$$

where ϕ is the quantum yield, I is the integrated emission intensity, A is the absorbance at excitation wavelength, and n is the refractive index of the solvent. The subscript r refers to the reference fluorophore of known quantum yield. The photochemical quantum yield (ϕ_c) was calculated using the method described in detail previously [23], and light intensity was measured by using ferrioxalate actinometry [24]. The fluorescence quantum yield (ϕ_f) of DDFP depends strongly on the solvent properties (Table 1). The ϕ_f value increases with increasing solvent polarity expressed as $E_T(30)$ [25].

Effect of surfactant on emission spectrum of DDFP. A positively charged CTAB and negatively charged SDS surfactants were selected for evaluating the emission behavior of the DDFP dye. The two specified surfactants were chosen because the ionic charges possessed by DDFP dye can be influenced by the positively charged CTAB and negatively charged SDS. Thus, the charge attraction accounts for the DDFP emission behavior. The fluorescence emission spectra of DDFP in the absence and presence of CTAB and SDS were measured. The fluorescence intensities of DDFP increase with increase in concentration of CTAB from 2×10^{-4} up to $1.6 \times 10^{-3} \text{ mol/dm}^3$, as shown in Fig. 3a. Such enhancement in the fluorescence intensity of $1 \times 10^{-5} \text{ mol/dm}^3$ DDFP at fixed concentrations with increase in CTAB concentration may likely be ascribed to the association mechanism of DDFP with CTAB. The fluorescence intensity of DDFP is quenched with increase in SDS concentration (2×10^{-3} up to $1.6 \times 10^{-2} \text{ mol/dm}^3$). Moreover, more significant reductions were noticed in the fluorescence intensities of DDFP with SDS. The quenching of DDFP upon increasing SDS concentration can likely be ascribed to the association of DDFP with SDS. Figure 3b shows the influence of SDS on the relative emission intensity of $1 \times 10^{-5} \text{ mol/dm}^3$ DDFP. It can be observed that there was a subsequent decrease in the relative emission intensity of DDFP with increase in SDS concentration, demonstrating that there was an interaction between DDFP and SDS. It seems that the dye molecules located in the hydrocarbon core of CTAB aggregates, while in SDS the dye is located at the micelle–water interface, showing the quenching role of water. As shown in Fig 3a, b, the emission intensity of DDFP increases with increase in concentration of the surfactant; an abrupt change in fluorescence intensity is observed at a surfactant concentration of 8.7×10^{-4} and $6.5 \times 10^{-3} \text{ mol/dm}^3$ which is very close to the critical micelle concentration of CTAB and SDS. Thus DDFP can be employed as a probe to determine the CMC of a surfactants. It is well known that aromatic molecules were generally solubilized in the palisade layer of the micelle [26, 27]. Thus, the enhancement of emission intensity is attributed to the passage of dye molecule from the aqueous bulk solution to the palisade layer of the micelle. The decrease in polarity of the microenvironment around the dye molecule results in the reduction of the non-radiative transfer rate from the ICT state to the low-lying singlet or triplet state due to the increase in the energy gap between them, which leads to an increase in emission intensity.

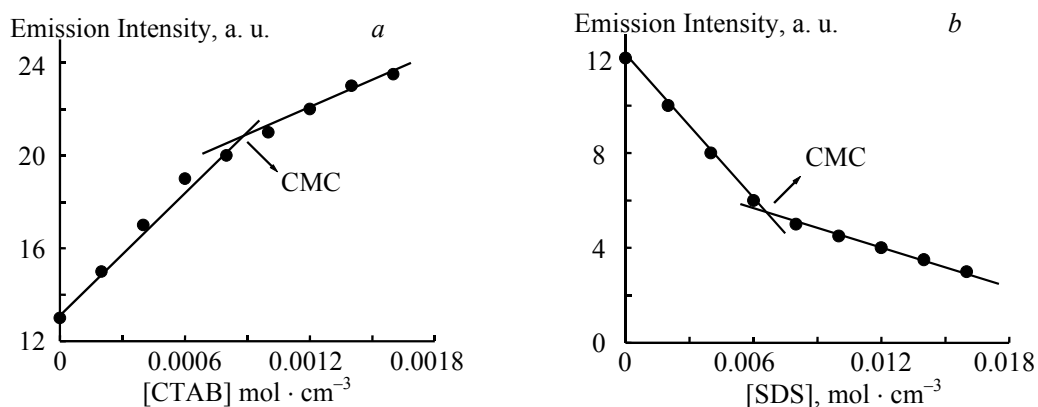
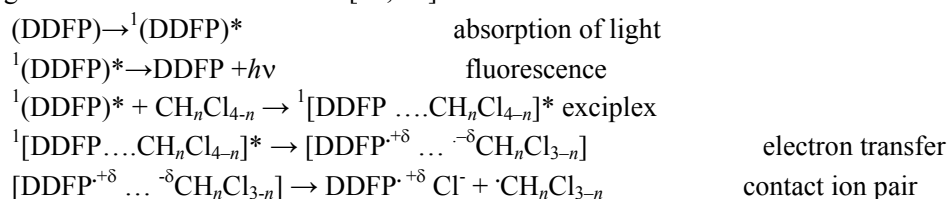


Fig. 3. a) Plot of I_f versus the concentration of CTAB; b) plot of I_f versus the concentration of SDS.

Photoreactivity of DDFP in different solvents. The photoreactivity of DDFP has been studied in different solvents, namely DMSO, CH_2Cl_2 , CHCl_3 , and CCl_4 . DDFP with $1 \times 10^{-5} \text{ mol/dm}^3$ concentration was irradiated at 345 nm. The absorbance of DDFP decreased with increasing irradiation time until a photostationary state was reached. As shown in Fig. 4, no new absorption appeared, indicating the absence of a photoproduct. The net photochemical quantum yields (ϕ_c) are listed in Table 2 and indicate that the DDFP dye is more photostable in DMSO than in CHCl_3 , CH_2Cl_2 , and CCl_4 . It seems that the photodecomposition of DDFP in chloromethane solvents takes place by electron transfer from the excited dye molecule to the solvent according to a well-known mechanism [28, 29]



It was supposed that the electron transfer from the excited singlet DDFP to $\text{CH}_n\text{Cl}_{4-n}$ within the transient excited charge transfer complex (exciplex) is the main primary photochemical process. It leads to the appearance of the DDFP radical cation, a chloride ion and a chloromethyl radical in the solvent cage. The formation of a contact ion pair usually occurs by electron transfer from the excited donor to the electron acceptor depending on the electron affinity (E_A) of the acceptor.

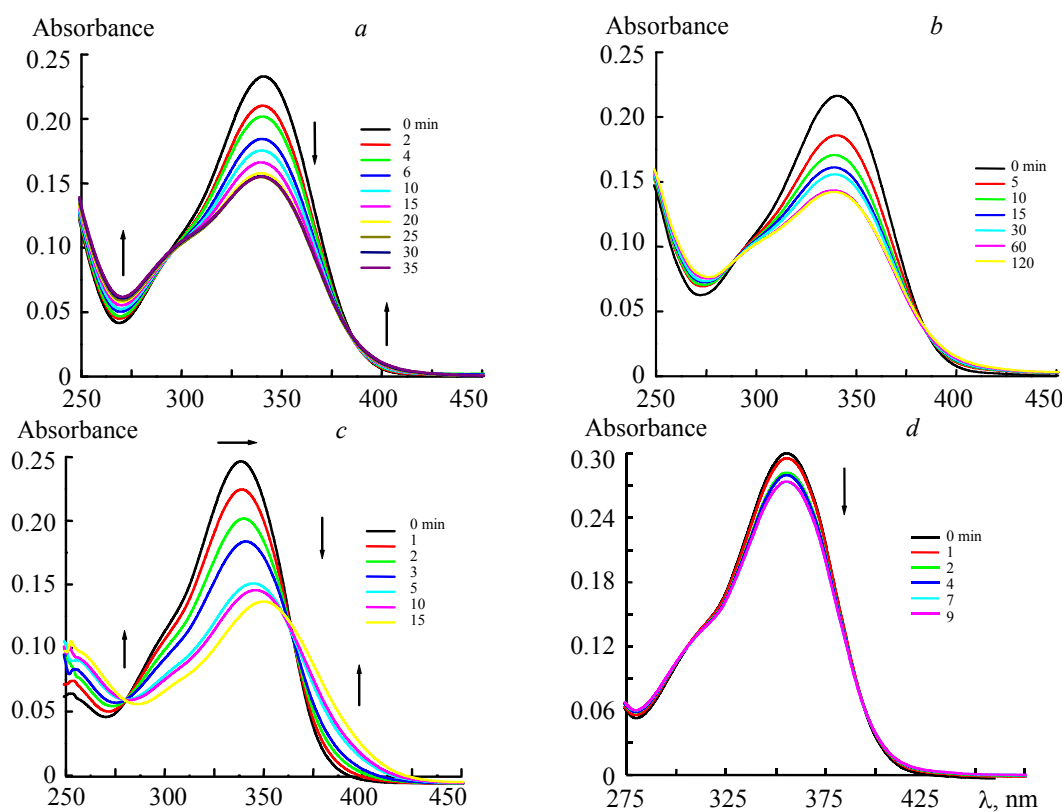


Fig. 4. Effect of irradiation ($\lambda_{\text{ex}} = 345 \text{ nm}$) on the electronic absorption spectrum of $1 \times 10^{-5} \text{ mol/dm}^3$ in CH_2Cl_2 (a), CHCl_3 (b), CCl_4 (c), and DMSO (d).

TABLE 2. Data of Photodecomposition of $1 \times 10^{-5} \text{ mol/dm}^3$ DDFP in Different Solvent

Solvent	ϕ_c
CHCl_3	0.0023
CH_2Cl_2	0.0020
CCl_4	0.0049
DMSO	0.00006

Conclusion. A new chalcone dye (DDFP) was successfully synthesized via the reaction of 3-acetyl-2,5-dimethylfuran with 3,4-dimethoxybenzaldehyde. Spectroscopic and elemental analysis of DDFP were in agreement with the chemical structure of DDFP. In addition, the spectral properties, physicochemical parameters, photostability and polarity behavior of the newly synthesized chalcone dye in organic media were investigated. A fluorescence enhancement of DDFP with CTAB was noticed, while a fluorescence quenching of DDFP with SDS was observed under the same experimental and instrumental conditions. Moreover, there was an abrupt change in fluorescence intensity at the CMC. DDFP dye displays photodecomposition in chloromethane solvents via electron transfer from excited DDFP to solvent leading to the formation of contact ion pair.

Acknowledgment. The authors are thankful to the Chemistry Department at King Abdulaziz University for providing research facilities.

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