

Green Synthesis, Physicochemical and Polarity Studies of Some Novel Biologically Active Donor Acceptor Chromophores

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Chalcones were synthesized by the reaction of acetyl ferrocene and corresponding aldehhyde under microwave irradiation. Results obtained from spectroscopic (FT-IR, ¹H NMR, ¹³C NMR, EI-MS) and elemental analysis of synthesized compounds was in agreement with their chemical structures. UV-visible and fluorescence spectroscopy measurements provided that compound **1** and **2** are good absorbent and fluorescent. Fluorescence polarity study demonstrated that these compounds were sensitive to the polarity of the microenvironment provided by different solvents. In addition, spectroscopic and physicochemical parameters, including electronic absorption, extenction coefficient, Stokes shift, oscillator strength and transition dipole moment, were investigated in order to explore the analytical potential of synthesized compounds. The antibacterial activity of the compound **1** and **2** were first studied *in vitro* by the disk diffusion assay against two Gram-positive and two Gram-negative bacteria. The minimum inhibitory concentration was then determined with the reference of standard drug chloramphenicol.

Keywords: Chalcones, Physicochemical, Antibacterial activity, Chloramphenicol.

INTRODUCTION

Donor acceptor conjugated chromophores are defined the chromophores which have an electron donor group (D) and an electron accepter (A) group that exhibit intramolecular charge transfer through the $\pi^{1.2}$. The compounds which have end-capped with electron donating and accepting group arranged in either symmetrical A- π -A, D- π -D or asymmetrical A- π -D are known as chromophore orientations³. The molecules having the donor acceptor conjugated framework have been largely investigated for optical-electrical applications from photophysical studies such as nonlinear optical properties⁴, photonic materials⁵, devices⁶, optical limiting⁷, electrochemical sensing⁸, light-emitting devices⁹, langmuir film¹⁰ and solar cell materials¹¹.

Chalcones are one of the compounds which have donor acceptor framework. Several reactions were reported for the synthesis of donor acceptor chromophores¹². However, aldol condensation is one of the most important reactions for the formation of donor acceptor chromophores by the nucleophilic addition reaction¹³. Various synthetic methods have been reported so far, such as refluxing in an organic solvent¹⁴, the solvent-free solid-phase reaction¹⁵, ultrasonication¹⁶, photosen-

sitization¹⁷ and microwave radiation¹⁸. Chalcone derivatives also reported earlier as important probes of medium viscosity¹⁹. This property is particularly important in assessing the microenvironments in micelles, microemulsions and vesicles²⁰. Chalcones are known as physiological active substances produced within tissues that appear to control the mitosis of the cell of specific tissues that produce them²¹. Hetero-aryl chalcone derivatives have several applications in many areas. They have been applied in food industry²², fluorescent probes for sensing DNA²³ and photoreactive polymers²⁴. Also, chalcones have been used for numerous optical applications including photo-alignment layer of liquid crystal display²⁵.

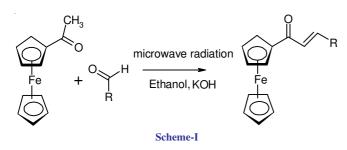
Due to whiled applications of the donor-acceptor chromophores (chalcones). In this paper we are reporting the synthesis of novel chalcones by green synthesis and their Physicochemical studies such as electronic absorption, molar absorptivity, oscillator strength and dipole moment of donor acceptor chromophores were also determined.

EXPERIMENTAL

Acetyl ferrocene and corresponding active aldehyde were purchased from Acros Organic. Other reagents and solvents (A.R.) were obtained commercially and used without further purification, except dimethylformamide, 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 NMR and ¹³C NMR experiments were performed in CDCl₃ on a Brucker DPX 600 MHz spectrometer using tetramethyl silane (TMS) as internal standard at room temperature. UV-visible 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 spectrofluorphotometer with a rectangular quartz cell. Emission spectra were monitored at right angle. All fluorescence spectra were blank subtracted before proceeding in data analyses.

General method for the synthesis of chalcones: To a solution of acetyl ferrocene (0.34 g, 2.5 mmol) and corresponding active aldehyde (2.5 mmol) in dry ethanol (20 mL) taken in a beaker (100 mL), a catalytic quantity of potassium hydroxide (0.05 g, 1.25 mmol) was added and the reaction mixture was heated inside a microwave oven for 48-62 s (at 210 W, *i.e.* about 30 % microwave power)²⁶⁻²⁸. The reactions were monitored through TLC using solvent system ethyl acetate:benzene (2:8), when the reaction was complete the reaction mixture was filtered, washed with ethanol followed by washing with water till the washings were neutral and recrystallized from distilled ethanol and chloroform (Scheme-I and Table-1).



1-Ferrocenyl-3-(9-ethyl-9*H***-carbazol-3-yl)-2-propen-1-one (1):** m.p. 163 °C; EI-MS *m/z* (rel. int. %): 434 (78) [M + 1]⁺.; IR (KBr, v_{max} , cm⁻¹): 2980 (C-H), 1685 (C=O), 1571 (C=C); ¹H NMR (600 MXz CDCl₃) δ : 8.62 (s, CH), 8.38 (s, CH), 8.18 (d, CH, *J* = 7.7 Hz), 8.13 (dd, CH, *J* = 7.8 Hz), 8.05 (d, CH, *J* = 15.6 Hz), 7.81 (d, CH, 8.4 Hz), 7.55-7.28 (m, 4H,

CH), 7.21 (d, CH, J = 15.6 Hz), 4.97 (s, 2H, ferrocene), 4.59 (s, 2H, ferrocene), 4.42 (t, CH₂-CH₃), 4.24 (s, 5H, ferrocene), 1.48 (q, CH₂-CH₃); ¹³C NMR (CDCl₃) δ : 193.12, 191.84, 142.45, 141.22, 140.48, 126.74, 126.16, 126.29, 123.49, 122.86, 121.29, 120.82, 120.67; Anal. (%) calc. for C₂₇H₂₃NOFe: C, 74.85, H, 5.31, N, 3.23. Found: C, 74.79, H, 5.27, N, 3.18.

1-Ferrocenyl-3-(N, N-di-methylphenyl)-2-propen-1one (2): m.p.: 162 °C; EI-MS *m/z* (rel. int. %): 360 (72) [M + 1]⁺.; IR (KBr, v_{max} , cm⁻¹): 3138 (C-H), 2803 (C-H), 1609 (C=O), 1557 (C=C); ¹H NMR (600 MXz CDCl₃) δ : 7.77 (d, CH, *J* = 15 Hz), 7.56 (d, CH, *J* = 7.8 Hz), 6.97 (d, CH, *J* = 15.6 Hz), 6.72 (d, CH, *J* = 7.8 Hz), 4.90 (s, 2H, ferrocene), 4.54 (s, 2H, ferrocene), 4.20 (s, 5H, ferrocene), 3.04 (s, N-CH₃); ¹³C NMR (CDCl₃) δ : 193.13, 151.76, 141.60, 130.05, 122.89, 118.04, 111.92, 81.26, 77.23, 77.02, 76.80, 72.25, 70.01, 69.60, 40.20; Anal. (%) calc. for C₂₁H₂₁NOFe: C, 70.22, H, 5.85, N, 3.90. Found: C, 70.16, H, 5.79, N, 3.85.

in vitro Screening: Disc-diffusion and micro dilution assay: Antibacterial activity was done by the disk diffusion method with minor modifications. S. aureus, S. pyogenes, S. typhimurium and E. coli were sub-cultured in BHI medium and incubated for 18 h at 37 °C, and then the bacterial cells were suspended, according to the McFarland protocol in saline solution to produce a suspension of about 10⁻⁵ CFU mL⁻¹: 10 µL of this suspension was mixed with 10 mL of sterile nutrient agar at 40 °C and poured onto an agar plate in a laminar flow cabinet. Five paper disks (6 mm diameter) were fixed onto nutrient agar plate. 1 mg of each test compound was dissolved in 100 µL DMSO to prepare stock solution from stock solution different concentration 10, 20, 25, 50, and 100 µg/ µL of each test compound were prepared. These compounds of different concentration were poured over disk plate on to it. Chloramphenicol (30 µg/disk) was used as standard drug (positive control). DMSO poured disk was used as negative control. The susceptibility of the bacteria to the test compounds was determined by the formation of an inhibitory zone after 18 h of incubation at 36 °C reports the inhibition zones (mm) of each compound and the controls. The minimum inhibitory concentration (MIC) was evaluated by the macro dilution test using standard inoculums of 10⁻⁵ CFL mL⁻¹. Serial dilutions of the test compounds, previously dissolved in dimethyl sulfoxide were prepared to final concentrations of 512, 256, 128, 64, 32, 16, 8, 4, 2 and 1 µg/mL to each tube was added 100 µL of a 24 h old inoculum. The MIC, defined as the lowest

TABLE-1 PHYSICOCHEMICAL DATA OF THE SYNTHESIZED COMPOUNDS (1 AND 2)							
Compound No.	R′	Molecular formula	Crystallization	Yield (%)	Reaction time (micro wave)		
1		C ₂₇ H ₂₃ NOFe	CHCl ₃	85.7	48 s		
2	N	C ₂₁ H ₂₁ NOFe	CH ₂ Cl ₂	87.8	56 s		

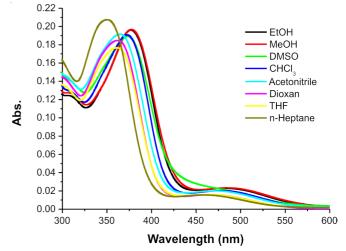
concentration of the test compound, which inhibits the visible growth after 18 h, was determined visually after incubation for 18 h, at 37 °C. Dimethyl sulfoxide and chloramphenicol were using as negative and positive controls.

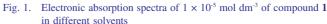
RESULTS AND DISCUSSION

Chalcone derivatives were synthesized by the reaction of acetyl ferrocene and corresponding active aldehyde (Scheme-I and Table-1). The purified product was characterized by the FT-IR, ¹H NMR, ¹³C NMR and EI-MS spectra. The IR spectrum of compounds (1 and 2) shows the characteristic band. The v(C=O) peak of acetyl ferrocene observed at 1668 cm⁻¹ shifts to a lower frequency of 1685-1609 cm⁻¹ of chacones. This is due to the conjugation of the π -electrons on the benzene moiety with those on the ethylene moiety in the enon linkage. ¹H NMR spectra, which prove diagnostic tool for the positional elucidation of the proton. Assignments of the signals are based on chemical shift and intensity pattern. The ¹H NMR spectra of all the compound (1 and 2) measured at room temperature shows two doublets at 7.75-8.06 ppm (J = 15.6) for the CH=C and 6.90-7.21 ppm (J = 15.6 Hz) for the CO=CH indicating that the ethylene moiety in the enon linkage is in the transconformation which conform the formation of mono and bis chalcone.

¹³C NMR (CDCl₃) spectra of chalcones (1 and 2) were recorded in CDCl₃ and spectral signals are in good agreement with the probable structures details of ¹³C NMR spectra of all compounds and those data are given in the experimental section.

Spectral behavior of ferocenyl chalcones in different media: Absorption and emission spectra of 1×10^{-5} mol dm⁻³ compounds (1 and 2) in various non-polar, polar aprotic and protic solvents were studied (Figs. 1 and 2). Calculated physico-chemical parameters obtained from steady state absorption and fluorescence spectra are tabulated in Tables 2 and 3. A close examination of Figs. 1 and 2 displays that the polarity of





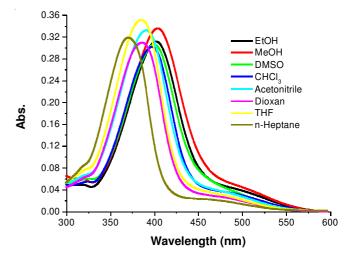


Fig. 2. Electronic absorption spectra of 1×10^{-5} mol dm⁻³ of compound **2** in different solvents

	TABLE-2 SPECTRAL DATA OF COMPOUND NO. 1 IN DIFFERENT SOLVENTS							
Solvent	Δf	E_{T} (30) Kcal mol ⁻¹	$\lambda_{ab} \left(nm \right)$	$\lambda_{em} (nm)$	$\epsilon (M^{-1} cm^{-1})$	f	μ (Debye)	$\Delta \overline{\nu}$ (cm ⁻¹)
Dioxane	0.021	75.63	378	488	18600	0.30	4.95	4133
CHCl ₃	0.188	74.26	385	484	19420	0.41	5.79	5312
THF	0.2096	75.83	377	451	17850	0.34	5.25	4854
CH ₃ CN	0.304	75.43	379	428	19410	0.23	4.33	3020
DMSO	0.263	74.45	384	506	19310	0.48	6.27	6278
EtOH	0.288	73.31	390	544	19910	0.57	6.86	7258
MeOH	0.308	72.93	392	558	19820	0.60	7.06	7589
<i>n</i> -Heptane	0.0004	77.27	370	452	20420	0.40	5.65	4903

TABLE-3 SPECTRAL DATA OF COMPOUND NO. 2 IN DIFFERENT SOLVENTS E_T (30) Kcal mol⁻ Solvent f $\Delta \overline{V}$ (cm⁻¹) Δf λ_{ab} (nm) λ_{em} (nm) $\epsilon (M^{-1} cm^{-1})$ μ (Debye) Dioxane 0.021 72.01 397 504 30690 0.65 7.42 5347 CHCl₃ 0.188 70.24 407 534 30050 0.70 7.78 5843 396 34800 0.80 8.22 THF 0.2096 72.19 514 5797 400 0.94 CH₃CN 0.304 71.47 558 33200 8.92 7078 DMSO 0.263 70.07 408 556 30660 0.80 8.35 6584 EtOH 0.288 69.39 412 557 31200 0.78 8.29 6318 MeOH 0.308 68.89 415 561 33200 0.83 8.54 6271 0.0004 74.84 382 504 31470 0.79 7.99 6336 n-Heptane

solvent has slight effect on absorption maxima, indicating the weak polar character of compounds (1 and 2) in the ground state. However, the emission spectra of these compounds are broad and red shifted as the solvent polarity increases (Figs. 3 and 4). The red-shift in *n*-heptane to MeOH indicates that photoinduced intramolecular charge transfer (ICT) occurring in the singlet excited state²⁹. As a result, the dipole moment of compounds (1 and 2) increases on excitation.

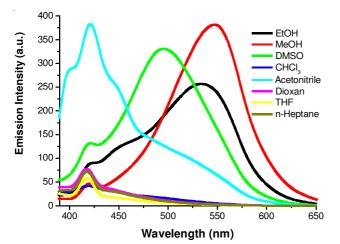


Fig. 3. Emission spectra of 1×10^{-5} mol dm⁻³ of compound 1 in different solvents

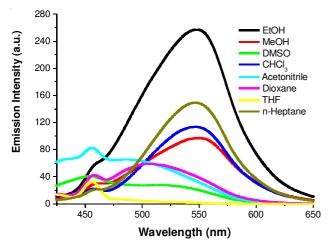


Fig. 4. Emission spectra of 1×10^{-5} mol dm⁻³ of compound 2 in different solvents

Determination of dipole moment: The solvatochromic behavior in compound (1 and 2) allows one to determine the difference in the dipole moment between the excited singlet and the ground state ($\Delta \mu = \mu_e - \mu_g$). This difference can be obtained using the simplified Lippert-Mataga equation as follows^{29,30}:

$$\Delta \overline{v}_{st} = \frac{2(\mu_e - \mu_g)^2}{hca^3} \Delta f + \text{Const.}$$
(1)

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

where $\Delta \overline{\mathbf{v}}_{st}$ is the Stokes-shift³¹, which increases with increasing the solvent polarity pointing to stronger stabilization of the

excited state in polar solvents, *h* denotes Planck's constant, *c* refers to the speed of light in vacuum and *a* is the Onsager cavity radius. Parameters D and n, in eqn. 2, correspond to the dielectric constant and refractive index of the solvent, respectively. The Onsager cavity radius was chosen to be 4.2 Å because this value is comparable to the radius of a typical aromatic fluorophore³². Stokes shifts ($\Delta \overline{v}_{ss}$) of compound (**1** and **2**) in different solvents were calculated, as shown in Tables 2 and 3, using the following the eqn²⁹:

$$\Delta \overline{\mathbf{v}}_{\rm ss} = \overline{\mathbf{v}}_{\rm ex} - \overline{\mathbf{v}}_{\rm em} \tag{3}$$

where \overline{v}_{ex} and \overline{v}_{em} denote the wavenumbers of excitation and emission maxima (cm⁻¹), respectively.

The change in dipole moments ($\Delta\mu$) between the excited singlet and ground state were calculated as 5.86 and 4.19 Debye for compound 1 and 2, respectively, indicating that the excited sate of compoun 1 and 2 is more polor than the ground state.

The effective number of electrons transition from the ground to excited state is usually described by the oscillator strength, which provides the absorption area in the electronic spectrum. The oscillator strength, f, can be calculated using the following equation³³:

$$f = 4.32 \times 10^{-9} \left[\epsilon(\overline{\nu}) \, d\overline{\nu} \right]$$
(4)

where ε is the extinction coefficient (L mol⁻¹ cm⁻¹), and represents the numerical value of wavenumber (cm⁻¹). Oscillator strength values of compounds (1 and 2) in different solvents are reported in Tables 2 and 3. In addition, the transition dipole moment (μ) for compound 1 and 2 from ground to excited state in Debye was estimated in different solvents (Tables 2 and 3) using the following relation³⁴:

$$\mu^2 = \frac{f}{4.72 \times 10^{-7} \times E_{\text{max}}}$$
(5)

where E_{max} is the energy of maximum absorption expressed in cm⁻¹

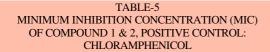
Antimicrobial activity: Disc-diffusion and micro dilution assay: The compounds (1 and 2) were tested for their antibacterial activities by disc-diffusion method using nutrient broth medium [contained (g/L): beef extract 3 g; peptone 5 g; pH 7.0]^{35,36}. The Gram-positive bacteria and Gram-negative bacteria utilized in this study consisted of *S. aureus*, *S. pyogenes*, *S. typhimurium* and *E. coli*. The results showed that the nitrogen containing heterocyclic chalcone increased the antibacterial activity. Carbazole containing of chalcone (1) showed good antibacterial activity on *S. aureus* and *S. pyogenes*. The results are presented in Tables 4 and 5 for disc-diffusion method and MIC method.

Conclusion

Chalcone derivatives were synthesized by the reaction of acetyl ferrocene and corresponding aldehyde under microwave irradiation. In addition, studying spectroscopic and physicochemical properties of chalcone derivatives may show considerable promise towards their potential applications. Compound 1 and 2 have high molar absorption, large stock shift in emission spectra and the dipole moment of singlet excited state in higher

TABLE-4 ANTIBACTERIAL ACTIVITY OF COPMPOUND 1 AND 2, POSITIVE CONTROL CHLORAMPHENICOL (CHLORA.) AND NEGATIVE CONTROL (DMSO) MEASURED BY THE HALO ZONE TEST (Unit, mm)

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Compounds	Corresponding effect on microorganisms				
Compounds	S. aureus	S. pyogenes	S. typhimurium	E. coli	
1	14.2 ± 0.2	12.2 ± 0.2	13.5 ± 0.3	12.8 ± 0.4	
2	10.3 ± 0.2	11.2 ± 0.4	9.8 ± 0.2	10.2 ± 0.4	
Chlora.	17.0 ± 0.5	18.2 ± 0.4	17.2 ± 0.8	20.0 ± 0.2	
DMSO	-	-	-	-	



Bacterial	MIC	(µg mL ⁻¹)	Positive
Strain	1	2	control
S. aureus	128	128	32
S. pyogenes	64	128	32
S. typhimurium	64	128	32
E. coli	128	256	32

than the ground state. The antibacterial activity of these compounds was investigated using culture of bacteria. Results demonstrated that the nitrogen containing compound increased the antibacterial activity.

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