

Green Synthesis, Characterization, Photophysical and Electrochemical Properties of Bis-chalcones

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Donor-acceptor conjugated dienes (bis-chalcones) were synthesized via an ultrasonic radiation, accomplished by the reaction between 3-acetyl-2,5-dimethylthiophene/1 (2,5-dimethyl-furan-3-yl)-ethanone and terephthalaldehyde. Bis-chalcones were investigated with the aim to elucidate the contribution of their interaction with solvent molecules upon intramolecular charge transfer. The chemical structure of bis-chalcones was confirmed by elemental analysis, FT-IR, ¹H NMR, ¹³C NMR and GC-MS spectral analysis. UV-visible and emission spectra indicated the properties of furan and thiophene bis-chalcones had a significant effect on the visible absorption and emission maxima. In addition, a pronounced effect on the absorption maxima and fluorescent maxima were observed upon increasing the solvent polarity.

Keywords: Bis-Chalcone; Absorbance; Fluorescence; Electrochemistry

1. INTRODUCTION

Claisen-Schmidt reaction is the one of the most important reaction for the synthesis of donor-acceptor conjugated dienes, known as chalcones [1]. It is generally synthesized by the reaction of acetophenone and benzaldehyde under acids and bases condition [2]. Some derivatives of the chalcone class compounds have been described in literature as inhibitors of ovarian cancer cell proliferation [3] and pulmonary carcinogenesis [4]. In recent years, chalcones have been used in the field of material

science as non-linear optical (NLO) [5], optical limiting [6], electrochemical sensing [7] and langmuir film [8]. Various chalcone derivatives are notable materials for their second harmonic generation (SHG) [9]. In addition, different synthetic methods have been reported so far, such as, refluxing in an organic solvent [10], the solvent-free solid-phase reaction [11], ultrasonication [12] photosensitization [13] and microwave radiation [14]. A nonlinear optical (NLO) property has been the subject of intense research due to their application in a wide range of technologies such as optical computing and optical communication [15-17].

In the past years, much attention has been paid to organic NLO materials due to their promising application in optoelectronics technology [18, 19], large nonlinear response, extremely fast switching time and convenient optimization routes through molecular engineering compared to the currently studied inorganic materials [20, 21]. To have strong second-order NLO properties, the compound must possess a large first-order molecular hyperpolarizability and must crystallize in a non centrosymmetric structure to have a nonzero. Besides the strong NLO response, the NLO materials must also fulfill some other technological requirements for practical applications such as wide transparency extending down to UV region, fast response, thermal stability, chemical stability, mechanical stability and high laser damage threshold [22].

The precise molecular recognition between chalcones and their guest provides a good opportunity for studying key aspects of supramolecular chemistry, which are also significant in a variety of disciplines including chemistry, biology, physics, medicine and related science and technology [23]. The recent growing interest in the electrochemistry (reduction and oxidation process) of macrocyclic complexes derived from recognition of biological importance of the less common oxidation states of metals [24, 25]. Redox potentials of M(II)/M(I) depends on the relative thermodynamic stabilities of the two oxidation states in a given ligand environment. The structural features include ring size, degree and arrangement of unsaturation and substitution [26-28]. In accordance, this study was devoted to the synthesis, characterization, photophysical and electrochemical properties of bis-chalcones.

2. EXPERIMENTAL

2.1. Chemicals and Reagents

All the chemicals and solvents used in this study were obtained from Merck (Germany) and Aldrich chemical company (USA).

2.2. Instrumentation

Melting points of the synthesized compounds were determined in open-glass capillaries on Stuart- SMP10 melting point apparatus and are uncorrected. FT-IR absorption spectra were recorded on Shimadzu FTIR-8400s using KBr pellets in the range of 4000–400 cm^{-1} . ^1H and ^{13}C NMR spectra were recorded on BRUCKER-AVANCE-III 600 MHz spectrophotometer and TMS (tetramethylsilane)

as an internal standard. The ^1H and ^{13}C NMR chemical shifts were reported as parts per million (ppm) downfield from TMS (Me_4Si). The splitting patterns are designated as follows; s, singlet; d, doublet; m, multiplet. Mass spectra were recorded on GC-MS spectrometer. FT-IR, ^1H NMR, ^{13}C NMR and mass spectra were consistent with the assigned structures. Elemental analysis (C, H, N) were done on a CHN rapid analyzer. All compounds gave C, H and N analysis within 0.03% of the theoretical values. Purity of compounds was checked by thin layer chromatography (TLC) on Merck silica gel 60 F_{254} precoated sheets in chloroform/methanol mixture, and spots were developed using iodine vapours/ultraviolet light as visualizing agent.

Cyclic voltammetry measurements were made using a conventional three electrode cell configuration linked to an *EG* and *G* model 283 Potentiostat. The platinum electrode surface was $7.85 \times 10^{-3} \text{ cm}^2$ as a working electrode, coiled platinum wire as a counter electrode and saturated Ag/AgCl as a reference electrode. The potential was calculated with relative to the Ag/AgCl reference electrode at 25°C and 0.1 mol/L tetraethyl ammonium chloride (*TEACl*) as background electrolyte. Cyclic voltammograms were recorded after background subtraction and *iR* compensation to minimize double-layer charging current and solution resistance. The working electrode was polished on a polisher Ecomet grinder. Cyclic voltammetric data were obtained at scan rate ranging from 0.02 to 5 V/s in non aqueous media at $(25 \pm 2)^\circ\text{C}$. All working solutions were thoroughly degassed with oxygen free nitrogen, and a nitrogen atmosphere was maintained above the solution throughout experimental studies.

2.3. *2E,2'E-3,3'-(1,4-Phenylene)bis(1-(2,5-dimethylfuran-3-yl)prop-2-en-1-one)* (1)

3-acetyl-2,5-dimethylfuran (2.34 mL, 0.028 mol) and terephthalaldehyde (2 g, 0.014 mol) 95% EtOH (20 mL) and NaOH (5 g in 10 ml EtOH ml) were taken into a 100 mL conical flask. The mixture was irradiated by an ultrasonic generator in a water bath at $30\text{--}35^\circ\text{C}$ for 5 min. The solid product so formed was diluted with water and neutralized with 2N HCl (3 mL) then it was filtered washed well cold water purified by the chromatography $\text{CH}_2\text{Cl}_2/n\text{-hexane}$ (1:1).

Yield: 72%; M.p. 182°C ; ^1H NMR (DMSO-*d*6) (δ/ppm): 7.72 (d, 2H, $J = 15.6$ Hz, C=CH), 7.22 (d, 2H, $J = 15.6$ Hz, CO=CH) 7.63 (s, 4H, Ar-H), 6.34 (s, 2H, thiophene-H), 2.62 (s, CH₃), 2.30 (s, CH₃), 2.09 (s, CH₃), 1.93 (s, CH₃); ^{13}C NMR (600 MHz, CDCl_3) δ : 185.65, 158.20, 150.17, 141.60, 136.70, 128.99, 125.00, 122.41, 105.54, 14.53, 13.05; GC-MS *m/z* (rel. int.%): 376 (76) $[\text{M}+1]^+$. FT-IR (KBr) $\nu_{\text{max}} \text{ cm}^{-1}$: 2956 (C-H), 1655 (C=O), 1567 (C=C); Anal. calc. for $\text{C}_{24}\text{H}_{22}\text{O}_4$: C, 76.99, H, 5.92, O, 17.09; Found: C, 76.95, H, 5.88, O, 19.98.

2.4. *(2E,2'E)-3,3'-(1,4-Phenylene)bis[1-(2,5-dimethyl-3-thienyl)prop-2-en-1-one]* (2)

3-acetyl-2,5-dimethylthiophene (0.029 mol), terephthalaldehyde (2g, 0.014 mol) 95% EtOH (20 mL) and NaOH (5g in 10 ml EtOH) were taken into a 100 mL conical flask. The mixture was irradiated by an ultrasonic generator in a water bath at $30\text{--}35^\circ\text{C}$ for 5 min. The solid product so formed

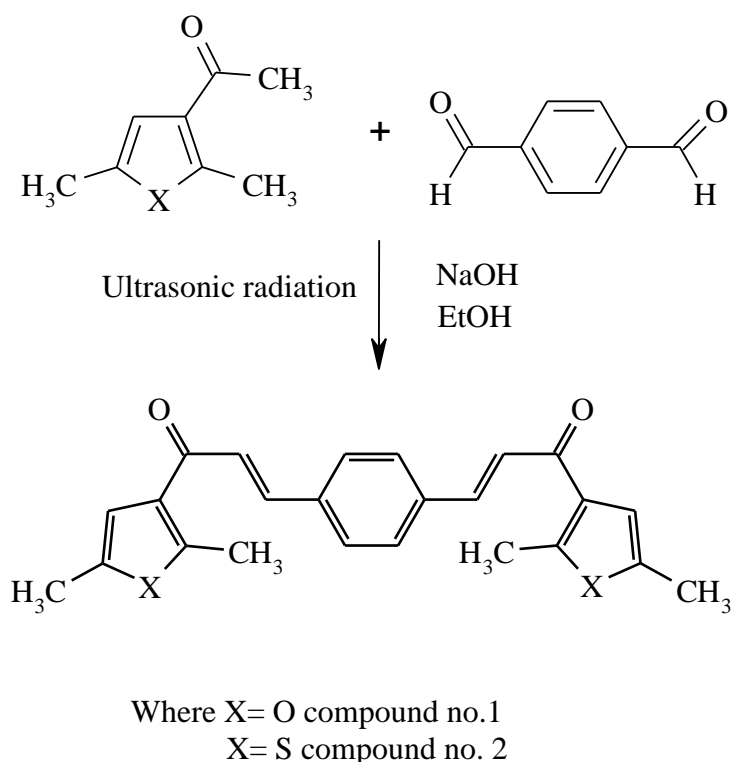
was diluted with water and neutralized with 2N HCl (3 mL) then it was filtered washed well cold water purified by the chromatography $\text{CH}_2\text{Cl}_2/n\text{-hexane}$ (1:1).

Dark yellow solid (Chloroform); Yield: 75%; m.p. 194-195 °C. FT-IR (KBr) ν_{max} cm^{-1} : 3050 (Ar-H), 2914 (C-H), 1648 (C=O), 1585 (C=C); ^1H NMR ($\text{DMSO-}d_6$) (δ/ppm): 7.71 (d, 2H, $J = 15.6$ Hz, C=CH), 7.30 (d, 2H, $J = 15.6$ Hz, CO=CH), 7.64 (s, 4H, Ar-H), 7.09 (s, 2H, thiophene-H), 1.61 (s, CH₃); ^{13}C NMR ($\text{DMSO-}d_6$) (δ/ppm): 186.09, 147.77, 142.36, 136.77, 136.47, 135.46, 130.21, 125.76, 15.98, 15.07; GC- MS m/z (rel. int.%): 407 (40) $[\text{M}+1]^+$, 255 (70), 153 (45); Anal. calc. for $\text{C}_{24}\text{H}_{22}\text{O}_2\text{S}_2$: C, 70.91, H, 5.41, S, 15.57, Found: C, 70.86, H, 5.35, S, 15.52.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization

Bis-chalcone derivative were synthesized via the ultrasonic radiation using aldol condensation method, achieved by the reaction between 3-acetyl-2,5-dimethylthiophene/3-acetyl-2,5-dimethylfuran and terephthalaldehyde (Scheme 1).



Scheme 1. Indicating the synthesis of bis-chalcones

The purification of bis-chalcones was not easily achieved by column chromatography when eluting with CH_2Cl_2 , as compared to the mono chalcone. The crude product of bis-chalcone loaded on the chromatography column was first eluted with $\text{CH}_2\text{Cl}_2/n\text{-hexane}$ (1:1) in order to separate the

possible side products and unreacted compounds, and then eluted with CH_2Cl_2 to collect bis-chalcones. The purified product was characterized by the GC-MS m/z (rel. int.%): FT-IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and elemental analysis. The GC-MS m/z data of bis chalcone 1 and 2 show the mother peak compound 1 (M^+) at $m/z = 376$ with 76% and for compound 2 at $m/z = 407$ with 40%. The $\nu(\text{C=O})$ peak of Act-thiophen observed at 1668 cm^{-1} shifts to a lower frequency of 1648 and 1655 cm^{-1} for bis-chalcones. This is due to the conjugation of the π -electrons on the benzene moiety with those on the ethylene moiety in the enon linkage. The $^1\text{H NMR}$ spectra measured at room temperature show two doublets at 7.72 ppm ($J = 15.6\text{ Hz}$) and 7.22 ppm ($J = 15.6\text{ Hz}$) for compound 1 and at 7.71 ppm ($J = 15.6\text{ Hz}$) and 7.30 ppm ($J = 15.6\text{ Hz}$) for compound 2 indicating that the ethylene moiety in the enon linkage is in the *trans*-conformation which conform the formation of bis-chalcone. $^{13}\text{C NMR}$ spectra of the mono and bis-chalcone were taken in CDCl_3 , and the signal obtained further confirmed the proposed structures. Details of the $^{13}\text{C-NMR}$ spectra of all compounds are given in the experimental section.

3.2. Effect of Solvent on the Absorption Spectrum

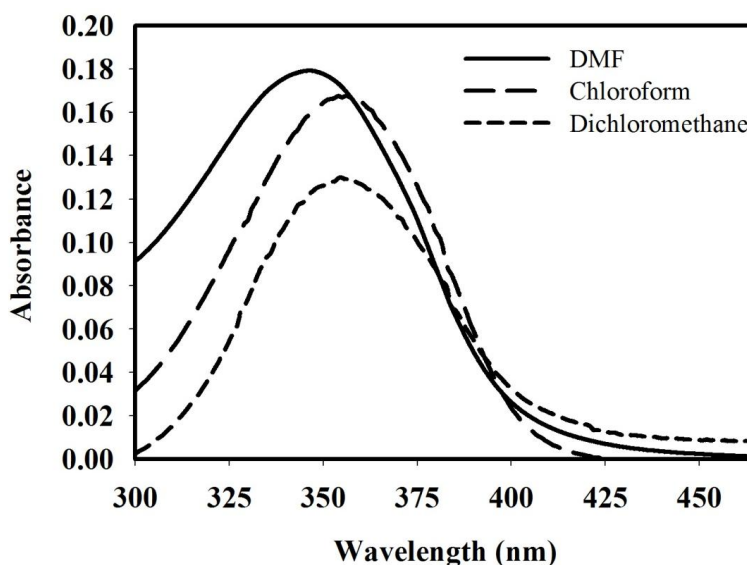


Figure 1a. Electronic absorption spectra of $6.6 \times 10^{-6}\text{ mol dm}^{-3}$ of furan bis-chalcone in different solvents.

Table 1. Spectral data of furan bis-chalcone in different solvents.

Solvent	Δf	$E_T(30)$ Kcal mol $^{-1}$	$\lambda_{ab}(\text{nm})$	$\lambda_{cm}(\text{nm})$	ϵ M $^{-1}\text{cm}^{-1}$	f	μ_{12} Debye	$\Delta\bar{\nu}_{ss}$ (cm^{-1})
CH_2Cl_2	0.255	80.08	357	448	19651	0.44	5.76	5690 (91)
DMF	0.208	81.68	350	398	27212	0.37	5.23	3446 (48)
CHCl_3	0.217	80.30	356	518	25393	0.89	8.19	8784 (162)

The effect of solvent on the absorption spectrum of the two chalcones is summarized in Table 1 and 2 for bis-furan and bis-thiophen chalcones, respectively. In DMF, two absorption bands can be

clearly observed at λ_{\max} of 260 nm and 350 nm. However, the band at 260 is absent while broad bands at 356 and 357 nm in dichloromethane and chloroform, respectively (Fig. 1a and 2a). This is possibly due to different interaction between the solute and solvent.

3.3. Reasons for Broad Band Absorption of Chalcones

In the covalently linked donor-acceptor system, the vibrational frequencies of the donor and acceptor are influenced by the medium and the σ - and π -bonds of the spacer connecting the donor and acceptor. This mixing of the electronic states may influence the rate of donor-acceptor electron transfer.

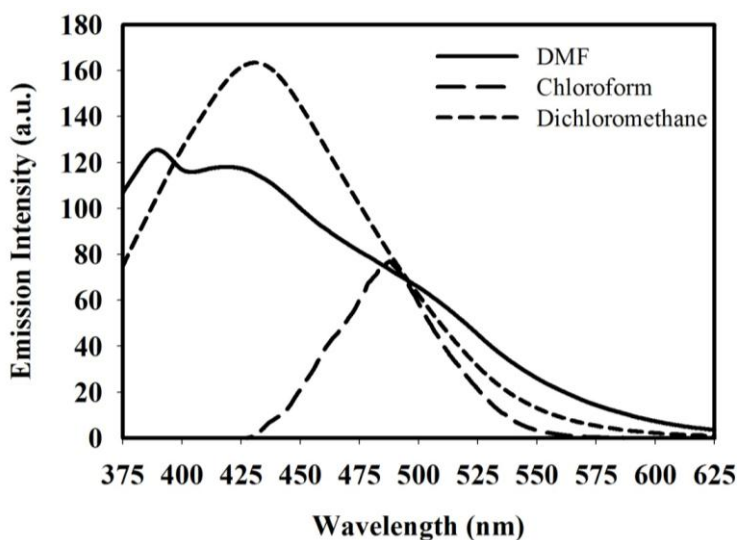


Figure 1b. Emission spectra of $6.6 \times 10^{-6} \text{ mol dm}^{-3}$ of furan bis-chalcone in different solvents.

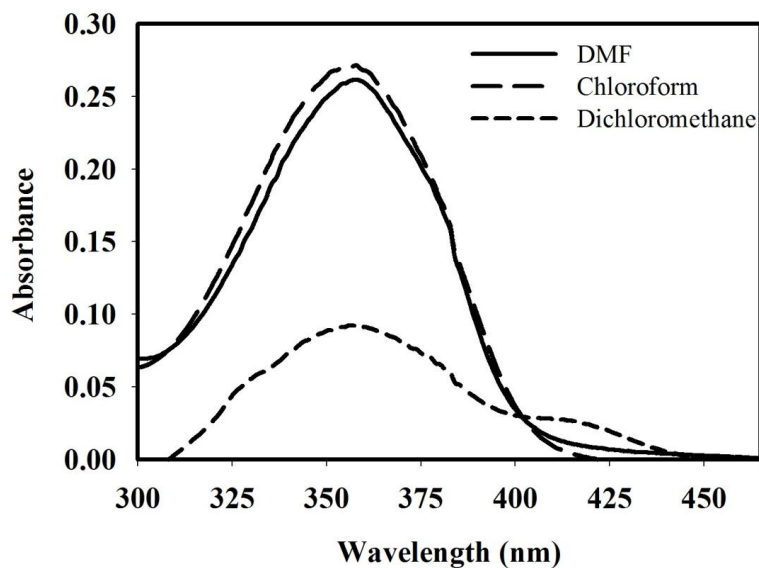


Figure 2a. Electronic absorption spectra of $6.6 \times 10^{-6} \text{ mol dm}^{-3}$ of thiophene bis-chalcone in different solvents.

Thus, several virtual states of the spacer may contribute to the overall electronic configuration of the donor-spacer-acceptor system [29, 30]. In the ground state, the molecule adopts covalent configuration; however, the excited state is more ionic. As a result, the relatively large change in electronic structure results in different nuclear equilibrium geometry for the ground state and the charge transfer excited state. This leads to the broad absorption band of the two compounds.

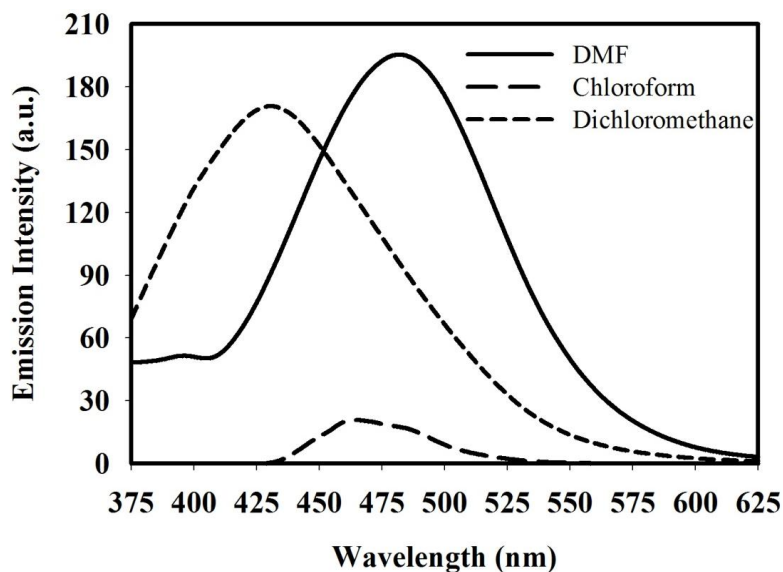


Figure 2b. Emission spectra of 6.6×10^{-6} mol dm⁻³ of thiophene bis-chalcone in different solvents.

UV absorption λ_{max} increases by 10 nm from compound 1 with furan ring to compound 2 with thiophene ring which imparts a strong electron donating capability than furan or may effect J-type aggregation. Thiophene bis-chalcone has higher extinction coefficient ($\epsilon = 39318 \text{ M}^{-1}\text{cm}^{-1}$) than furan bis-chalcone ($\epsilon = 27212 \text{ M}^{-1}\text{cm}^{-1}$), indicating that the absorption capacity of thiophene is enhanced by its electron donating ability. Red shift of the thiophene and high epsilon favor the light harvesting and hence photocurrent generation in dye sensitized solar cells

3.4. Fluorescence Study

The enlargement of the fluorescence spectra of the two compounds reveals a so called dual fluorescence. The dual fluorescence can be attributed to a twisted intramolecular charge transfer state [31]. The fluorescence spectra of the two compounds in dichloromethane, DMF and chloroform are shown in Fig.1b and 2b. The long-wavelength band can be ascribed to the emission from the charge transfer state [32-34]. Changes in the in the fluorescence spectra show that these compounds could be used as tunable fluorophore in molecular electronics, especially in case of furan. These compounds represent a promising new future, which may be further explored to design and develop donor-acceptor fluorophores with efficient switchable emission properties.

3.5. Determination of oscillator strength and transition dipole Moment of Bis-Chalcones

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 expressed using the following equation [35].

$$f = 4.32 \times 10^{-9} \int \epsilon(\bar{\nu}) d\bar{\nu} \quad (1)$$

where ϵ is the extinction coefficient ($\text{Lmol}^{-1}\text{cm}^{-1}$), and $\bar{\nu}$ represents the numerical value of wave number (cm^{-1}). Oscillator strength values of compounds (1 and 2) in three solvents are reported in Table 1 and 2.

Table 2. Spectral data of Thiophene bis-chalcone in different solvents.

Solvent	Δf	E_T (30) Kcal mol ⁻¹	$\lambda_{ab}(\text{nm})$	$\lambda_{em}(\text{nm})$	ϵ M ⁻¹ cm ⁻¹	f	μ_{12} Debye	$\Delta\bar{\nu}_{ss}$ (cm ⁻¹)
CH ₂ Cl ₂	0.255	79.64	359	450	13929	0.31	4.82	5633
DMF	0.208	79.41	360	405	39318	0.48	6.08	3086
CHCl ₃	0.217	79.41	360	460	40590	0.98	8.84	6038

In addition, the transition dipole moment (μ) for compounds (1 & 2) from ground to excited state in Debye was estimated in three solvents (Table 1 and 2) using the following relation [36].

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

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

3.6. Electrochemical Properties of Bis-chalcones

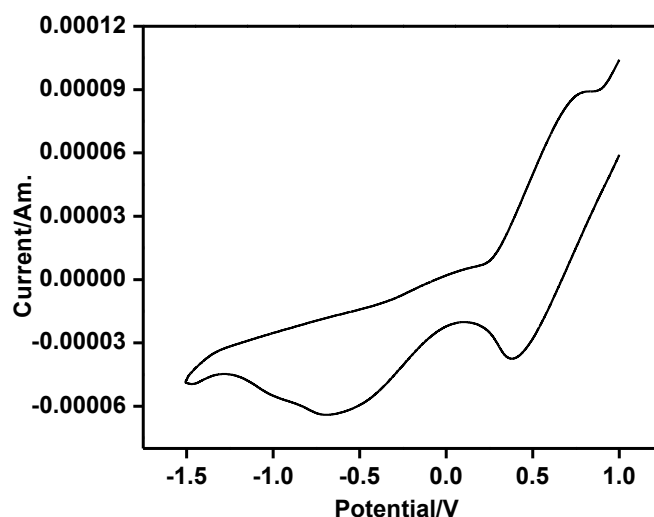


Figure 3. Cyclic voltammograms of furan bis-chalcone (1) in acetonitrile.

In order to determine the highest occupied molecular orbital (HOMO) energy levels, cyclic voltammetric measurements were performed [37].

Figures 3 and 4 show cyclic voltammograms for furan and thiophene bis-chalcones where 1.0 mM of each dye were prepared in acetonitrile. The HOMO energy levels of furan and thiophene bis-chalcones were calculated from the onset oxidation potential of cyclic voltammogram. The HOMO energy level of furan bis-chalcone is determined to be 0.811 V versus saturated calomel electrode (SCE) (-5.66 eV versus vacuum), and that of thiophene bis-chalcone lies at 0.792 V versus SCE (-5.59 eV versus vacuum). Based on the offset absorption spectra and HOMO energy, lowest unoccupied molecular orbital (LUMO) energy levels are determined to be -2.843 eV and -2.760 eV for furan and thiophene bis-chalcones, respectively. Energetic data for furan and thiophene bis-chalcones are listed in Table 3. From cyclic voltammogram, It Seems the electrochemical behavior of Chalcone derivatives follow EC mechanism.

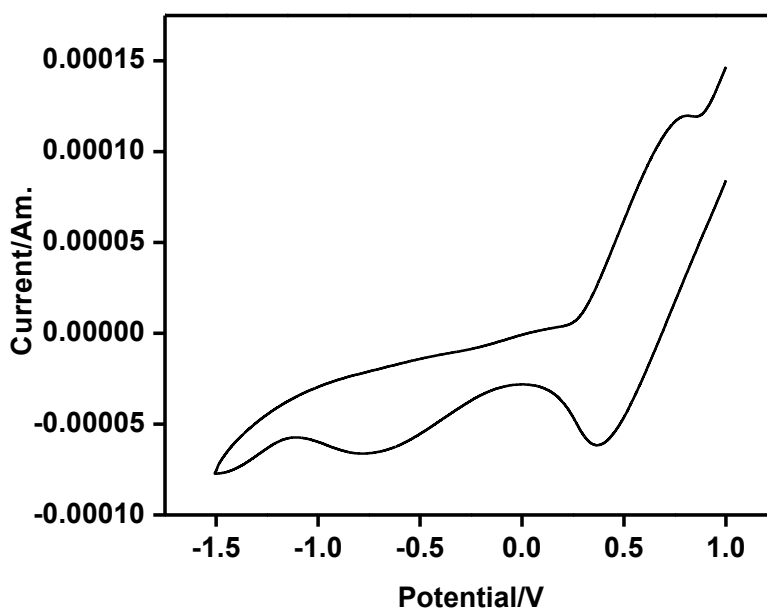


Figure 4. Cyclic voltammograms of thiophene bis-chalcone (2) in acetonitrile.

Table 3. Electrochemical and spectroscopic data of the compounds (1-2)

Compounds	$E_{1/2}$	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE_{spect} (eV)	$\lambda_{cut\ off}$ (nm)	β
1	0.8113	-5.6613	-2.843	2.768	449	1.7530×10^{-24}
2	0.7918	-5.5918	-2.760	2.831	439	9.7352×10^{-28}

4. CONCLUSION

The prepared bis-Chalcones were further investigated by UV/Vis absorption spectroscopy, fluorescence spectroscopy, cyclic voltammetry as well as quantum-chemical calculations. From the performed analysis, one can deduce that optical properties of bis-chalcones can be easily tuned by the appended acceptor. The absorption spectra of bis-chalcones exhibit an intramolecular charge transfer band; which showed a positive solvatochromism in different solvents. The emission spectra of bis-chalcones also supported that there was an intramolecular charge transfer band character. These findings confirmed that there was a significant electron transfer between the donating moiety and accepting fragment through the π -conjugated core. The features of the accepting moieties ultimately proved their behavior as a versatile and an efficient acceptor unit.

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References

1. A. M. Asiri, S. A. Khan, *J. Hetrocyl. Chem.*, 49, (2012) 1434.
2. A. M. Asiri, S. A. Khan, *Molecules*, 16 (2011) 523.
3. A. Sharma, B. Chakravarti, M. P. Gupt, J. A. Siddiqui, R. Konwar, R. P. Tripathi, *Bioog. Med. Chem.*, 18 (2010) 4711.
4. R. Abonia, D. Insuasty, J. Castillo, B. Insuasty, J. Quiroga, M. Noguerras, J. Cobo, *Eur. J. Med. Chem.*, 57 (2012) 29.
5. S. Shetharam, G. Umesh, K. Chandrasekharan, B. K. Sarojini, *Opt. Mater.*, 30 (2008) 1297.
6. S. Shettigar, K. Chandrasekharan, G. Umesh, B. K. Sarojini, *Polymer*, 47 (2006) 3565.
7. A. Delavaux, B. Nicot, J. Maynadie, D. Lavabre, *J. Organometalic. Chem.*, 692 (2007) 874.
8. E. I. Gasull, S. E. Blanco, F. H. Ferretti, *J. Mol. Struct. (Theochem)*, 579 (2002) 121.
9. Y. Goto, A. Hayashi, Y. Kimura, M. Nakayama, *J. Crystal. Growth*, 108 (1991) 688.
10. S. A. El-Daly, A. M. Asiri, S. A. Khan, K. A. Alamry, M. A. Hussein, *Chin. J. Chem.*, 29 (2011) 2557.
11. E. Perozo-Rondon, R. M. Martin-Aranda, B. Casal, C. J. Duran-Valle, W. N. Lau, X. F. Zhang, K. L. Yeung, *Catalysis Today*, 114 (2006) 183.
12. J. Li, W. Yang, S. Wang, S. Li, T. Li, *Ultrasonics Sonochemistry*, 9 (2002) 237.
13. Y. Yesuthangam, S. Pandian, K. Venkatesan, R. Gandhidasan, *J. Photochem. Photobiol B: Biol.*, 102 (2011) 200.
14. S. A. Khan, A. M. Asiri, K. A. Alamry, S. A. El-daly, M. A. M. Zayed, *Russ. J. Bioorg. Chem.*, 39 (2013) 353.
15. J. K. Ranka, R. S. Windeler, A. J. Stentz, *Optics Lett.*, 25 (2000) 796.
16. A. Zakery, S. R. Elliott, *J. Non-Crystalline Solids*, 330 (2003) 1.
17. B. P. Singh, P. N. Prasad, *Polymer*, 29 (1988) 1940.
18. B. Zhao, W. O. Lu, Z. H. Zhou, Y. Wu, *J. Mater. Chem.*, 10 (2000) 1513.
19. S. D. Bella, I. Fragala, I. Ledoux, M. A. D. Garcia, T. J. Marks, *J. Am. Chem. Soc.*, 119 (1997) 9550.
20. J. L. Bredas, C. Adant, P. Tackx, A. Persoons, B. M. Pierce, *Chem. Rev.*, 94 (1994) 243.
21. B. J. Coe, *Acc. Chem. Res.*, 39 (2006) 383.

22. A. M. Asiri, S. A. Khan, *Mater. Lett.*, 65 (2011) 1749.
23. R. A. Sheikh, S. Shreaz, L. A. Khan, A. A. Hashmi, *J. Chem. Pharm. Res.*, 2 (2010) 172.
24. J.A. Streeky, D.G. Pillsburg, D.H. Busch, *Inorg. Chem.*, 19 (1980) 3148.
25. A.A. Isse, A. Gennaro, E. Vianello, *J. Chem. Soc., Dalton Trans.* (1993) 2091.
26. P.D. Beer, N. Berry, M.G.B. Drew, O.D. fox, M.E. Padilla-Tosta, S. Patel, *Chem. Commun.*, (2001)199.
27. R. A. Shiekh, I. A. Rahman, M. A. Malik, S. M. Masudi, N. Luddin, *Int. J. Electrochem. Sci.*, 7 (2012) 12829.
28. R. A. Sheikh, I.A. Rahman, M. A. Malik, N. Luddin, S. M. Masudi, S. A. Al-Thabaiti, *Int. J. Electrochem. Sci.*, 8 (2013) 6972.
29. Mc Connel, H. M., *J. Chem. Phys.* 35 (1961) 508.
30. A. M. Kuznestov, J. Ulstrup, *J. Chem. Phys.* 75 (1981) 2047.
31. W. Rettin, *Top. Curr. Chem.* 169 (1994) 253.
32. A. B. J. Parusel, K. Rechthaler, D. Piorum, A. Danel, P. Tomasik, K. Khatchatryan, *J. Fluoresc.* 8 (1998) 375.
33. K. Rechthaler, K. Rotkiewicz, G. Kohler, A. Danel, P. Tomasik, K. Khatchatryan, *J. Fluoresc.* 7 (1997) 301.
34. C. Bosshard, K. Shutter, P. Pretre, J. Hulliger, M. Florsheimer, P. Kaatz, P. Gunter, *Organic Nonlinear Optical Materials*, Gordon and Breach Publishers, Basel 1995.
35. N. J. Turro, *Molecular photochemistry (frontiers in chemistry)*, 1st ed., W. A. Benjamin, Inc., Reading, MA, (1965) 286.
36. B. J. Coe, J. A. Harris, I. Asselberghs, K. Clays, G. Olbrechts, A. Persoons, J. T. Hupp, R. C. Johnson, S. J. Coles, M. B. Hursthouse, K. Nakatani, *Adv. Funct. Mater.*, 12 (2002) 110.
37. Q. Yu, S. Lu, M. Zhang, P. Wang, *Journal of physical Chemistry C* 113 (2009) 14559-14566.