Synthesis, Characterization, Physicochemical and Electrochemical Studies of Novel Donor Acceptor Chromophores

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Three donor acceptor chromophores were synthesized by Knoevenagel condensation. Structures of the chromophoes were conformed by the elemental analysis and EI-MS, FT-IR, ^{1}H-NMR, ^{13}C-NMR spectroscopy. Absorbance and fluorescence spectra of the chromophores were studied in different solvent provide that all the chromophores are good absorbent and emission. All chromophores give same behavior red shift in absorbance and emission spectra as polarity of the solvents increase. Photophysical properties including, oscillator strength, extinction coefficient, transition dipole moment and stokes shift were investigated in order to investigate the physicochemical behaviors of synthesized chromophores. The HOMO energy levels of compound 1, 2 and 3 respectively were calculated front the onset oxidation potential of cyclic voltammogram in acetonitrile.

1. INTRODUCTION

Donor acceptor chromophores have drawn much attention in the recent decades due to their attractive potential in photonic device [1]. In the last two decades great attempt has been made in the field of synthetic chemistry in order to design the organic molecules used in material sciences [2] such as optical and photonic imaging [3], electrochemical sensing [4], langmuir films and photoinitiated polymerization with high non linear optical properties by enhancing the molecular polarizabilities of the constitute NLO energetic units [5-7]. The compound containing with donor - acceptor framework employable as monomeric active unit is based on the well known donor acceptor system constituted by a л –conjugated system with strong electron donor/withdrawing groups [8]. Use of substituents such as

NO$_2$ and NR$_2$ group can remarkably increase the push pull effect [9]. Photophysical properties such as, dipole moment, oscillator strength, solvatochromic, piezochromic, florescent quantum yield and photostability of the chromophore depends on the efficiency of the intramolecular charge transfer from these two terminal groups (D-π- A), therefore on the nature and the length between the two terminal with π-bond conjugation are also the most significant role to formative the behavior of compounds [10,11]. Many reactions have been reported for the formation of donor-acceptor (D-π- A chromophores. However, Knoevenagel condensation is one of the most imperative reactions for the formation of donor-acceptor chromophores by the reaction of carbonyl compounds with active methylene carbon in the presence of some Lewis acids or Lewis base followed by a nucleophilic addition and dehydration reaction [12]. Different synthetic methods were reported for Knoevenagel reaction, such as normal/refluxing in the solvent [13], ultrasonication, microwave radiation [14], solid-phase reaction and photosensitization [15]. Due to numerous application of donor-acceptor chromophores and continues work on the photophysical studies, in this paper we are reporting the synthesis of novel donor acceptor chromophores and their photophysical, electrochemical investigation.[13].

2. EXPERIMENTAL

2.1. Chemicals and reagents

All the solvents (A.R.) used in this work were of spectroscopic grade, appropriate aldehyde and 6-methoxy-1,2,3,4-tetrahydro-naphthalin-1-one were purchased from Acros Organic.

2.2. Apparatus

UV-Vis electronic absorption spectra were recorded using a 1 cm quartz cell on a Shimadzu UV-1650 PC spectrophotometer. Steady state emission spectra were record using Shimadzu RF 5301 PC spectrofluorphotometer using a rectangular quartz cell of dimension 0.2 cm 3 cm. ^{1}H-NMR and ^{13}C-NMR spectra were recorded in CDCl$_3$ on a Brucker DPX 600 at 600MHz and 150 MHz spectrometer using tetramethyl silane (TMS) as internal standard. IR spectra were recorded on Shimadzu FT-IR 8400S. Thomas Hoover capillary melting apparatus were used to determine the melting points of the chromophores.

2.3. General method for the synthesis of donor acceptor chromophores (1-3)

A mixture of the 6-methoxy-1,2,3,4-tetrahydro-naphthalin-1-one (2 g, 0.011 mol) and appropriate aldehyde (0.011 mol), in ethanol (99.9%) (25 mL) in the prescience of KOH with staring at room temperature for 6-8h. Stirring was continued until all starting material had been consumed. (TLC) solvent system chloroform : methane (2:8). After the completion of the reaction, the reaction

mixture was pored in an ice cooled water and the precipitate thus obtained was filtered washed with distilled water and recrystallized by chloroform and few drop of distilled ethanol.

2.3.1.(2E)-2-[(1-benzyl-1H-indol-3-yl)methyllidene]-6-methoxy-1,2,3,4-tetrahydronaphthalene-1-one (1)

Yellow colure solid (Chloroform); Yield: 77.3%; M.p. 98 °C; EI-MS *m/z* (rel. int. %): 395 (72) $[M+1]^{+}$; IR (KBr) v_{max} cm^{-1}: 2939 (C-H), 1692 (C=O), 1560 (C=C), 1132 (C-N); ^{1}H NMR (600MXz CDCl$_3$) δ: 8.18 (s, 1H, CH), 8.02-6.70 (m, 13H, CH Aromatic), 3.80 (s, 3H, OCH$_3$), 2.96-2.91 (m, 2H, CH$_2$), 2.37 (s, 2H, CH$_2$), 2.17-2.09 (m, 2H, CH$_2$); ^{13}CNMR (CDCl$_3$) δ: 191.83, 186.95, 163.95, 163.42, 145.56 (C- β), 140.40, 139.95, 137.93, 133.10, 130.70, 128.54, 127.40, 126.89, 123, 122.89 120.84, 119.35, 113.22, 112.25, 109.17, 108.72, 55.47, 37.97, 30.19, 29.35, 27.51, 23.40, 13.58, 13.85;; Anal. calc.for C$_{27}$H$_{23}$NO$_2$: C, 82.42, H, 5.89, N, 3.56. Found: C, 82.39, H, 5.83, N, 3.51.

2.3.2.(2E)-6-methoxy-2-[(1-methyl-1H-pyrrol-2-yl)methylidene]-1,2,3,4-tetrahydronaphthalene-1-one (2)

Yellow colure solid (Chloroform); Yield: 76.3%; M.p. 148 °C; EI-MS *m/z* (rel. int. %): 269 (72) $[M+1]^{+}$; IR (KBr) v_{max} cm^{-1}: 2948 (C-H), 1656 (C=O),1584 (C=C), 1132 (C-N); ^{1}H NMR (600MXz CDCl$_3$) δ: 8.14 (s, 1H, CH), 8.02 (d, 1H, CH$_{Ar}$, J= 8.4 Hz), 8.09 (d, 1H, CH$_{Ar}$, J= 9.0 Hz),7.81 (s, 1H, CH$_{Ar}$), 6.81 (d, 1H, CH$_{Ar}$, J=7.8 Hz), 6.72 (dd, 1H, CH$_{Ar}$, J= 6.8 Hz), 6.58 (d, 1H, CH$_{Ar}$, J= 7.8 Hz), 3.69 (s, 3H, OCH$_3$), 2.96-2.91 (m, 2H, CH$_2$), 2.62-2.59 (m, 2H, CH$_2$); ^{13}CNMR (CDCl$_3$) δ: 197.25 (C=O), 186.12, 163.55, 146.97, 145.38 (C- β), 130.48, 125.97, 116.27, 113.76, 109.02, 55.44, 38.93, 36.42, 31.38, 28.63, 27.26; Anal. calc.for C$_{17}$H$_{17}$NO$_2$: C, 76.38, H, 6.41, N, 5.24. Found: C, 76.32, H, 6.38, N, 5.21.

2.3.3.(2E)-2-[(9-ethyl-9H-carbazol-3-yl)methyllidene]-6-methoxy-1,2,3,4-tetrahydronaphthalene-1-one(3)

Yellow colure solid (Chloroform); Yield: 72.5%; M.p. 126 °C; EI-MS *m/z* (rel. int. %): 383 (78) $[M+1]^{+}$; IR (KBr) v_{max} cm^{-1}: 2951 (C-H), 1682 (C=O), 1578 (C=C), 1123 (C-N); ^{1}H NMR (600MXz CDCl$_3$) δ: 8.21 (s, 1H, CH), 8.16-6.70 (m, 10H, CHAromatic) 4.42-4.39 (q, CH$_2$-CH$_3$), 3.85 (s, 3H, OCH$_3$), 2.96-2.91 (m, 2H, CH$_2$), 2.62-2.60 (m, 2H, CH$_2$), 1.49-1.45 (t, N-CH$_2$-CH$_3$); ^{13}CNMR (CDCl$_3$) δ: 195.25 (C=O), 186.95, 163.42, 145.55(C- β), 140.40, 139.95, 137.73, 133.10, 130.37, 128.37, 126.84 (C-Aromatic), 123.06, 120.56, 119.38, 113.20, 109.17, 108.72, 55.47, 38.93, 37.97, 30.19, 29.35, 27.51, 23.40, 13.88, 13.85; Anal. calc.for C$_{26}$H$_{23}$NO$_2$: C, 81.86, H, 6.08, N, 3.67; Found: C, 81.82, H, 6.02 N, 3.63.

2.4. Cyclic voltammetry measurements

All prepared solutions were thoroughly degassed with oxygen free nitrogen, and a nitrogen atmosphere was maintained above the solution throughout experimental studies.

Three electrode cell configuration linked to an *EG* and *G* model 283 Potentiostat were used to measure the cyclic voltammetry of the chrompohores. The surface of platinum electrode was 7.85×10^{-3} cm^2 as a working electrode, Counter electrode as a coiled platinum wire and refrence electrode as a saturated Ag/AgCl. The potential was calculated with relative to the Ag/AgCl reference electrode at 25^oC and 0.1 mol/L tetraethyl ammonium chloride (*TEACl*) as background electrolyte. The functioning electrode was polished on a polisher Ecomet grinder. Cyclic voltammetric information was obtained at scan rate ranging from 0.02 to 5 V/s in non aqueous media at (25 ± 2) ^{o}C. Cyclic voltammograms were recorded after background calculation and iR recompense to reduce double-layer charging current and solution resistance.

3. RESULT AND DISCUSSION

3.1. Chemistry

The synthesis of donor acceptor chromophores (1-3) are straight forward and the compounds were isolated in good yield (Scheme 1). The chromophores were synthesized by the reaction of 6-methoxy-1,2,3,4-tetrahydro-naphthalin-1-one and appropriate aldehyde in the presence of KOH [16]. The newly synthesized chromophores are stable in the in the solution as well as solid state. The structure of all the chrompohores were conformed by the spectral data EI-MS, FT-IR, ^{1}H-NMR, ^{13}C-NMR and purity of the chromophores further conformed by the elemental analysis. The select characteristic IR band positions give important signal for the structure of the chromophores. The chromophores showed intense bands at 1560-1584 cm^{-1} due to *v* (C=C) stretch, which is prove the formation of donor accepter chromophores. Further proof for the formation of chromophores was obtained from the ^{1}H-NMR spectra, which provide indicative tools for the positional clarification of the protons. Assignments of the signals are based on the intensity patterns and chemical shifts. The aromatic protons of chromophores 1 -3 are shown as *s,d, dd, m* in the range ppm for the compounds. A Singlet due to =C-H proton in the chromophores 1-3 were observed at δ 8.14-8.21 respectively. The appearance of singlet, doublet, and multiplets at δ 6.58-8.16 was due to aromatic protons in chromophores 1-3. The appearance of two multiplets at δ 2.96-2.91 and δ 2.62-2.09 was due to the benzylic protons (C5-*H* and C6-*H* respectively) in chromophores 1-3. ^{13}C NMR (CDCl$_3$) spectra of chromophores were recorded in CDCl$_3$ and spectral signals are in good agreement with the possible structures. The carbonyl carbon of the chromophores usually appears at δ 191.83-197.25 for compounds in ^{13}C NMR spectrum. The β- carbon atoms with respect to the carbonyl group give rise to characteristic signals in between δ 145.56-145.38. Finally the structures of the chromophores were conformed by molecular ion peak from the mass spectra. The mass spectrum of chromophores 1 -3 shows a molecular ion peak (M$^+$) m/z 395, 269 and 383. All the chromophores give analogous fragmentation pattern.
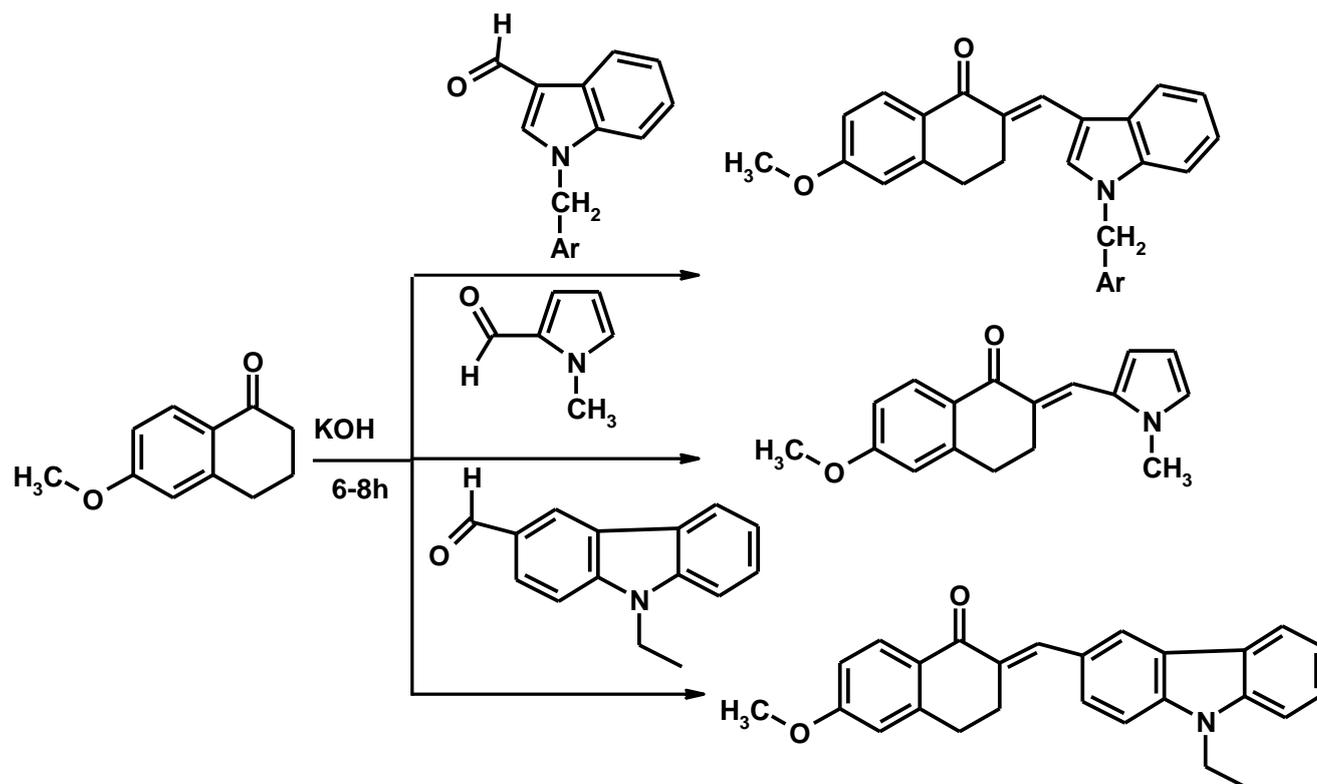
Scheme 1. Schematic diagram showing the synthesis of compounds (1-3).

3.2. Spectral behavior of donor acceptor chromophores in different media (1-3)

Table 1. Physicochemical data of chromophore no. 1

Solvent	Δf	E_T^N	E_T (30) Kcal mol^{-1}	λ_{ab}(nm)	λ_{em}(nm)	ε M^{-1}cm^{-1}	f	μ_{12} Debye	$\Delta\bar{\nu}$ (cm^{-1})
DMSO	0.266	1.52	80.08	357	433	20400	0.40	30.16	4995
EtOH	0.305	1.53	80.53	355	425	37690	0.58	43.62	4640
CHCl$_3$	0.217	1.57	81.68	350	416	25520	0.46	34.25	4533
Acetonitrile	0.274	1.62	83.35	343	421	18900	0.40	29.64	5402
Dioxan	0.148	1.63	83.59	342	416	21200	0.44	31.95	5201
n-Hexane	0.0014	1.67	84.83	337	402	25400	0.48	34.27	4798

Table 2. Physicochemical data of chromophore no. 2

Solvent	Δf	E_T^N	E_T (30) Kcal mol^{-1}	λ_{ab}(nm)	λ_{em}(nm)	ε M^{-1}cm^{-1}	f	μ_{12} Debye	$\Delta\bar{\nu}$ (cm^{-1})
DMSO	0.266	1.30	72.93	392	437	19190	0.20	16.74	2627

EtOH	0.305	1.28	72.19	396	424	25060	0.16	14.09	1668
CHCl$_3$	0.217	1.32	73.49	389	424	19400	0.16	13.57	2122
Acetonitrile	0.274	1.38	75.43	379	425	20350	0.23	18.46	2856
Dioxan	0.148	1.38	75.63	378	423	20080	0.22	18.09	2815
n-Hexane	0.0014	1.47	78.33	365	421	21770	0.31	24.51	3645

Table 3. Physicochemical data of chromophore no. 3

Solvent	Δf	E_T^N	E_T (30) Kcal mol^{-1}	λ_{ab}(nm)	λ_{em}(nm)	ε M^{-1}cm^{-1}	f	μ_{12} Debye	$\Delta\bar{\nu}$ (cm^{-1})
DMSO	0.266	1.35	74.45	384	485	26100	0.56	7.15	5423
EtOH	0.305	1.33	73.87	387	462	23500	0.39	5.99	4194
CHCl$_3$	0.217	1.35	74.65	383	454	27500	0.44	6.33	4083
Acetonitrile	0.274	1.41	76.44	374	489	25300	0.63	7.49	6288
Dioxan	0.148	1.47	78.54	364	446	28000	0.56	7.05	5051
n-Hexane	0.0014	1.55	81.22	352	411	32400	0.52	6.60	4079
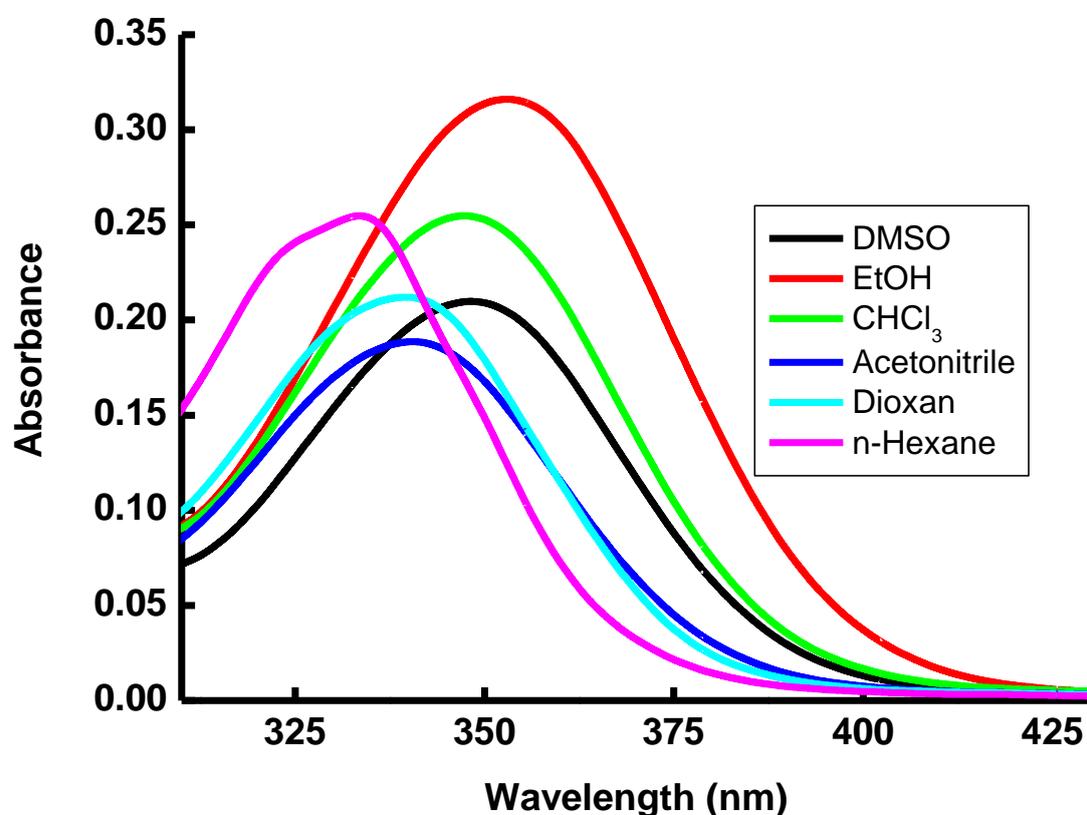
Figure 1a. Electronic absorption spectra of 1×10^{-5} mol dm^{-3} of chromophore **1** in various solvent
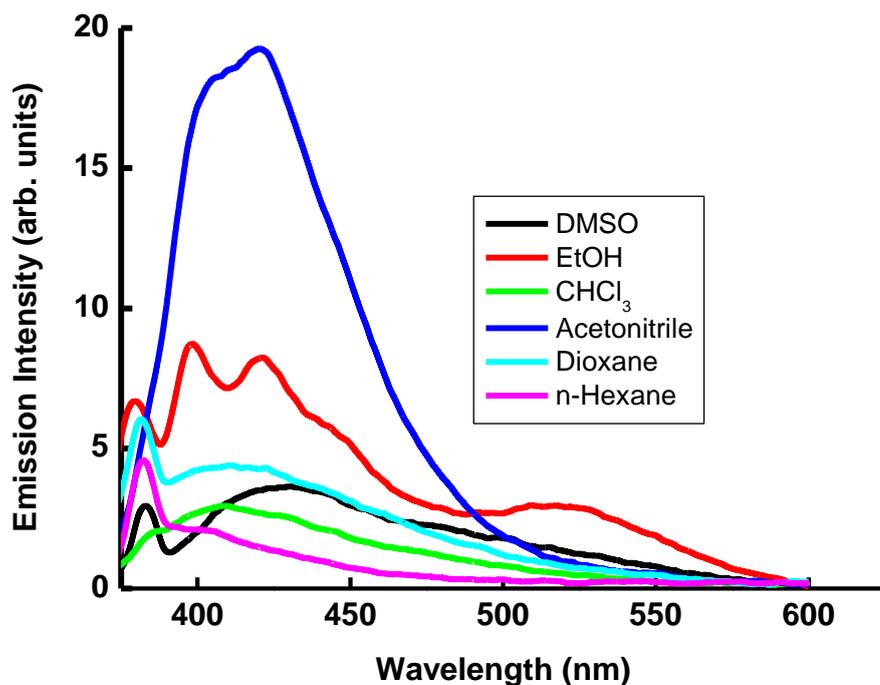
Figure 1b. Emission spectra of 1×10^{-5} mol dm^{-3} of chromophore **2** in various solvent
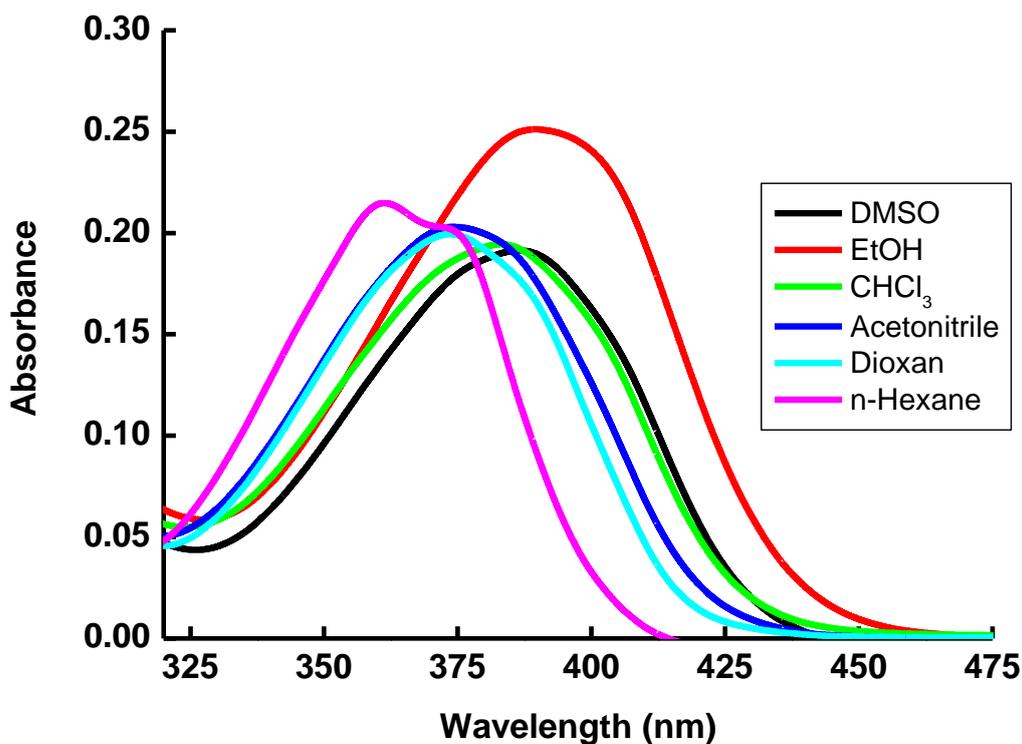
Figure 2a. Electronic absorption spectra of 1×10^{-5} mol dm^{-3} of chromophore **3** in various solvent
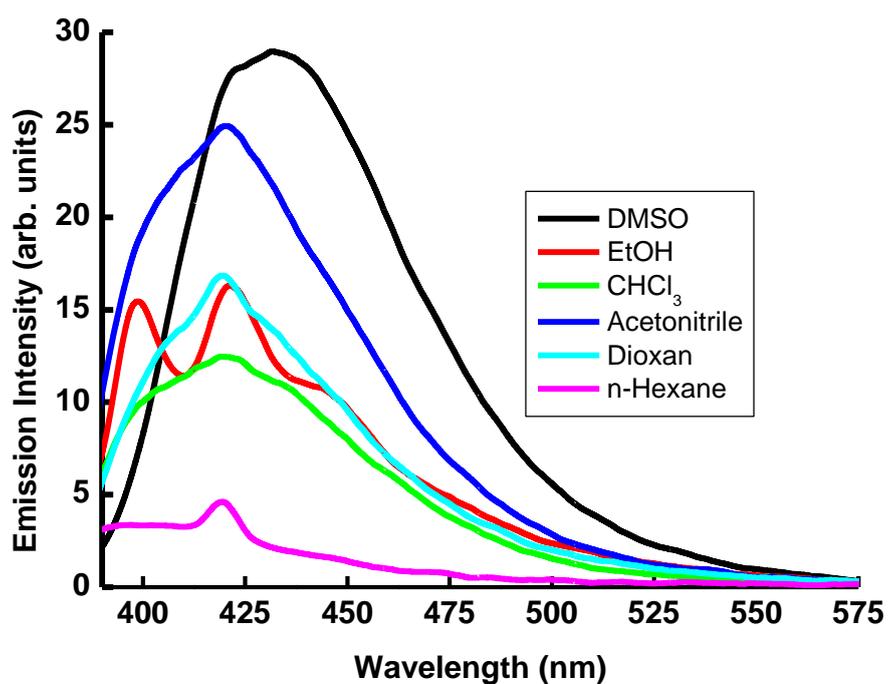
Figure 2b. Emission spectra of 1×10^{-5} mol dm^{-3} of chromophore **2** in various solvent
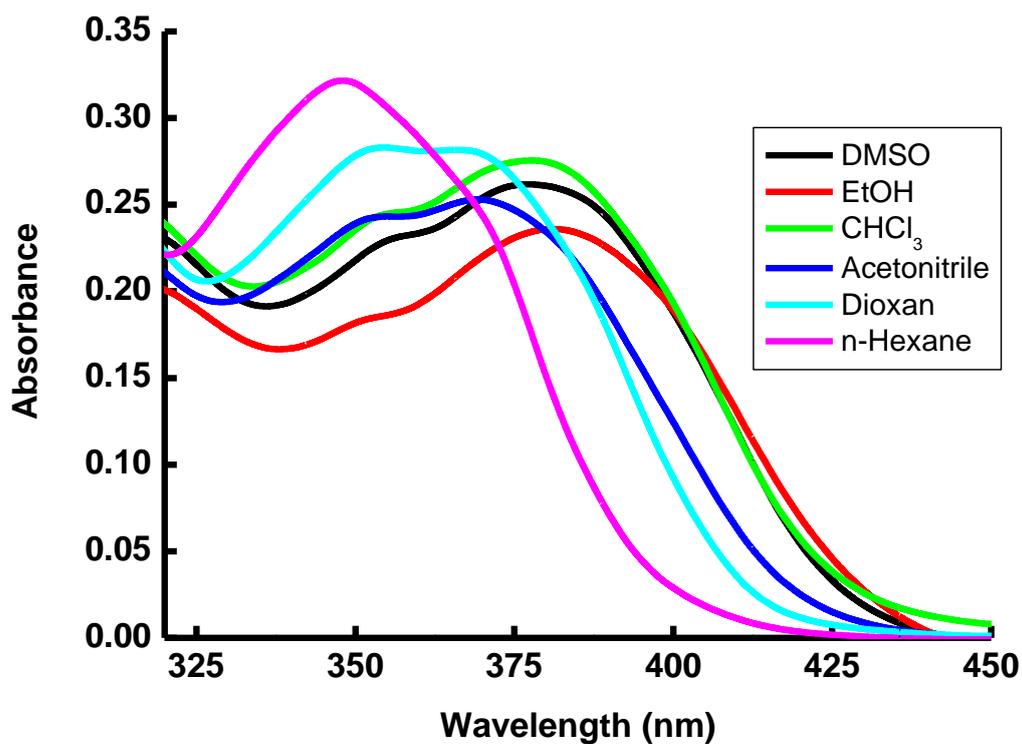
Figure 3a. Electronic absorption spectra of 1×10^{-5} mol dm^{-3} of chromophore **3** in various solvent
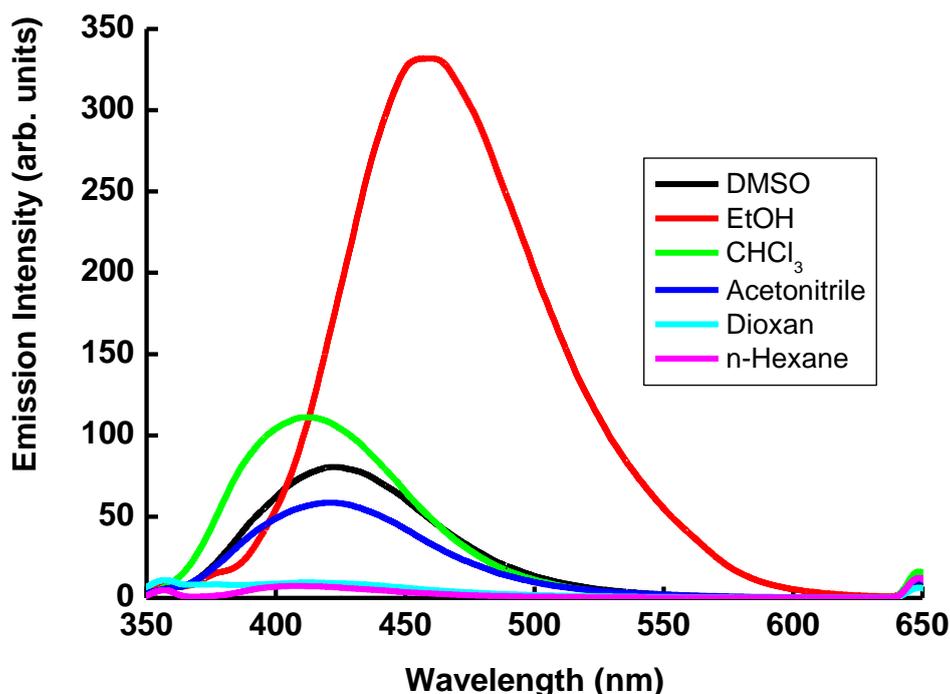
Figure 3b. Emission spectra of 1×10^{-5} mol dm^{-3} of chromophore **3** in various solvent

Absorption and fluorescence spectra of 1×10^{-5} mol dm^{-3} chromophores (1-3) in various protic, polar aprotic and non-polar solvents were deliberate (Fig 1a to Fig 3b). Designed physicochemical properties obtained from steady state absorption and emission spectra are presented in Table 1-3. Absorption spectra of chromophores show Fig.1a-Fig.3a, a red shift of 20 nm for chromophore 1, 23 nm for chromophore 2 and 32 nm for chromophore 3   on changing the solvent polarity from n-hexane to DMSO suggesting some polar character in the ground state. The red shift is probable in chromophores having   donor–acceptor groups in a single chromophore and is due to intramolecular charge transfer (ICT) [17].

3.3. Determination of oscillator strength and transition dipole moment

The solvatochromic performance of choromophores (1-3) allows to establish the difference in the dipole moment between the excited singlet and the ground state ($\Delta\mu = \mu_e - \mu_g$). This variation can be obtained using the simplified Lippert- Mataga equation as follows [17, 18]:

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

$$\Delta f = \quad \frac{D-1}{2D+1} - \frac{n^2-1}{2n^2+1} \tag{2}$$

where $\Delta\bar{v}_{st}$ is known as Stokes–shift which decreasing with decreasing the solvent polarity indicating to week stabilization of the excited state in non polar solvents [19]. Δf is the orientation polarizability of the solvent, μ_e and μ_g are the dipole moments in the excited and ground state,

respectively which measures both electron mobility and dipole moment of the solvent molecule. c is the speed of light in vacuum, a is the Onsager cavity radius and h is Planck's constant, n and ε are the refractive index and dielectric constant of the solvent for equation 2 respectively. The Onsager cavity radius was chosen to be 4.2 Å because this value is comparable to the radius of a typical aromatic fluorophore [20].

$\Delta\bar{v}_{ss}$ is the Stokes shifts of the chromophores (1-3) in different solvents were deliberate, as shown in Table 1-3, using the following the equation [17]:

$$\Delta\bar{v}_{ss} = \bar{v}_{ab} - \bar{v}_{em} \tag{3}$$

where $\Delta\bar{v}_{ss}$ is the difference between λ_{max} of the $\bar{v}_{ab}$ and $\bar{v}_{em}$ indicate the wavenumbers of absorption and emission maxima (cm^{-1}) respectively.

The change in dipole moments ($\Delta\mu$) between the excited singlet and ground state were calculated from the slop of plot of Stokes shifts ($\Delta\bar{v}_{ss}$) and orientation polarizability of the solvent (Δf) as 1.54, -5.95 and 1.28 debye for chromophore 1, 2 and 3 respectively, positive value for chromophore 1 & 3 indicating that the excited sate is more polor than the ground state and negative value for chromophore 2 indicating that the ground sate is more polor than the excited state.

The change in transition dipole moments ($\Delta\mu_{12}$) between the excited singlet and ground state of chromophore 1-3 in various solvents were calculated as in Table 1-3, using the equation 4 [21].

$$\mu_{12}^2 = \frac{f}{4.72 \times 10^{-7} \times E_{max}} \tag{4}$$

where E_{max} is the maximum energy of absorption in cm^{-1} and f is the oscillator strength.

The oscillator strength (f), can be calculated using the following equation:

$$f = 4.32 \times 10^{-9} \int \varepsilon(\bar{v}) \, d\bar{v} \tag{5}$$

where $\bar{v}$ represents the numerical value of wavenumber (cm^{-1}) and ε is the extinction coefficient $(Lmol^{-1}cm^{-1})$. Oscillator strength values of chromophores (1-3) in various solvents were calculated from the equation no. 5 and reported in Table 1-3, [22].

3.4. Fluorescence polarity study of chromophores (1-3)

The emission spectrum of chromophores correlates with increasing polarity of the solvent (Fig. 1b- Fig. 3b). It is apparent that the emission maxima undergo a red shift of 31 nm for chromophore 1, 16 nm for chromophore 2 and 74 nm for chromophores 3 on increasing the polarity from n-Hexane to DMSO, suggesting the emission state is more polar than the ground state [17].

E_T (30) and E_T^N is the empirical Dimroth polarity parameter of chromophores (1-3) was also premeditated according to the following equation [23].

$$E_T^N = \frac{E_T(solvent) - 30.7}{32.4} \tag{6}$$

$$E_T(solvent) = \frac{28591}{\lambda_{max}} \tag{7}$$

where λ_{max} corresponds to the peak wavelength (nm) in the red region of the intramolecular charge transfer absorption of the bitain dye. All the choromophores have bathochromic when solvent polarity increase from n-hexane to DMSO indicates that the polarity of chromophores and photoinduced intramolecular charge transfer (ICT) occurs in the singlet excited state, therefore increasing the excitation.

3.5. Electrochemical properties of chromophores 1-3
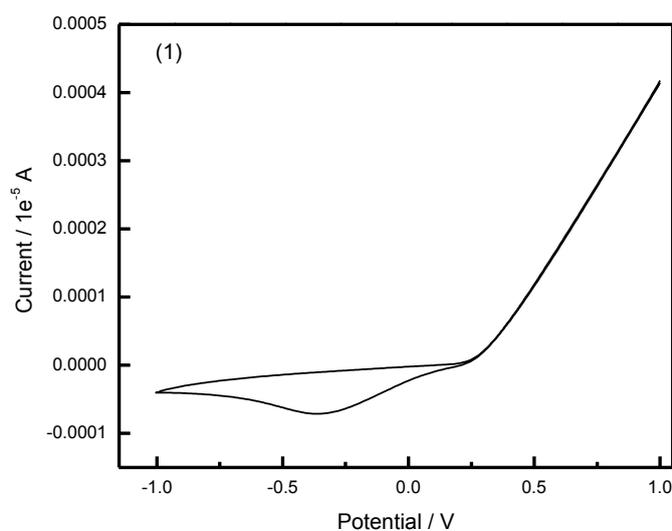
Figure 4. Cyclic voltammogram of chromophore 1 in acetonitrile at scan rate of 2V/s
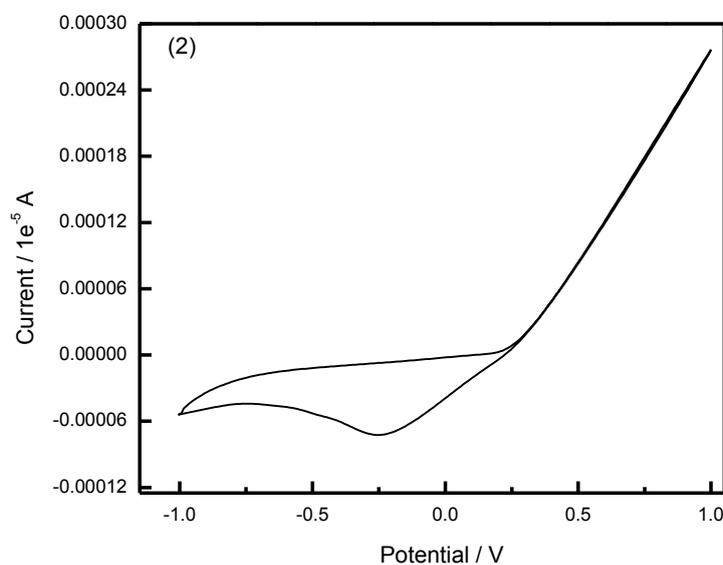
Figure 5. Cyclic voltammogram of chromophore 2 in acetonitrile at scan rate of 2V/s
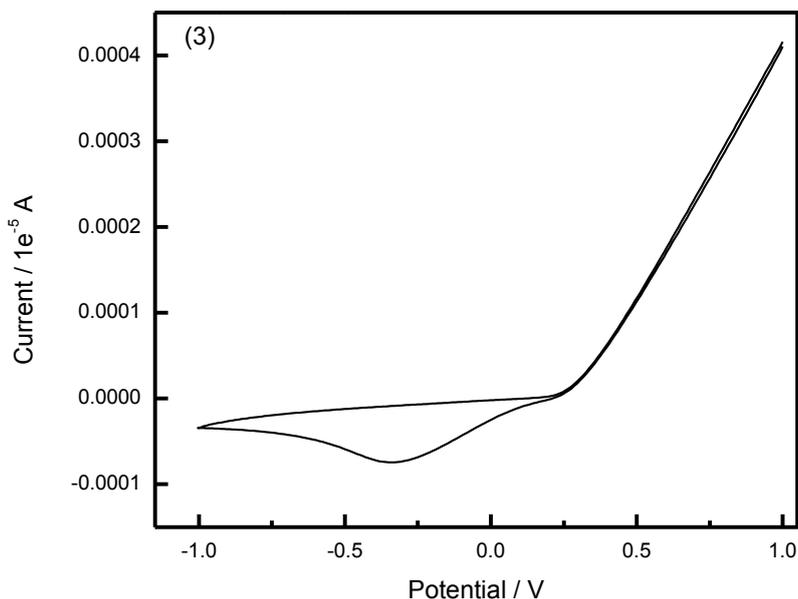
Figure 6. Cyclic voltammogram of chromophore 3 in acetonitrile at scan rate of 2V/s
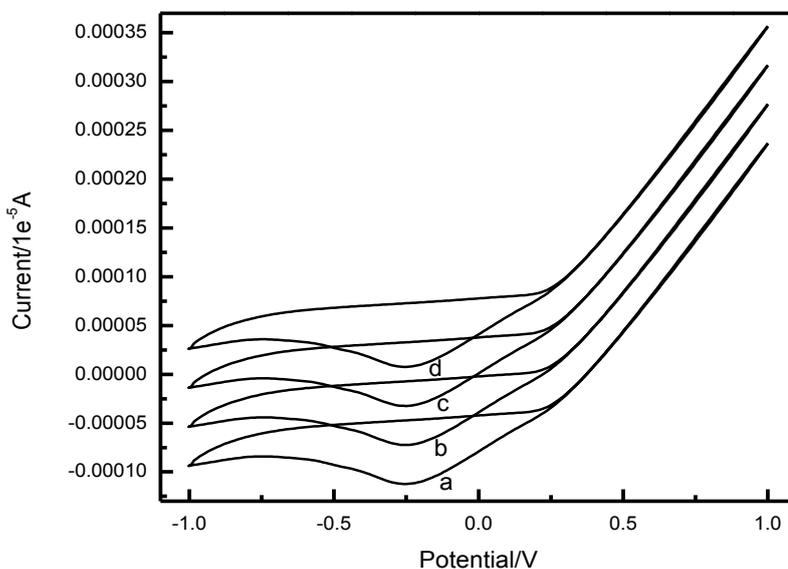
Figure 7. Cyclic voltammogram of chromophore 2 in acetonitrile at (a) scan rate of 5V/s, (b) scan rate of 2 V/s, (c) scan rate of 1 V/s, (d) scan rate of 0.5 V/s.

In order to determine the highest occupied molecular orbital (HOMO) energy levels, cyclic voltammetric measurements were performed [24-26].

Figures 4, 5 and 6 show cyclic voltammograms for chromophores 1, 2 and 3 respectively where 1.0 mM of each chromophore was prepared in acetonitrile. The HOMO energy levels of chromophore 1, 2 and 3 respectively were calculated front the onset oxidation potential of cyclic voltammogram. The HOMO energy level of chromophore 1 is determined to be 0.991 V versus saturated calomel electrode

(SCE) (-5.76 eV versus vacuum), for chromophore 2 lies at 0.982 V versus SCE (-5.63 eV versus vacuum) and for chromophore 3 lies at 0.962 V versus SCE (-5.57 eV versus vacuum). Based on the offset absorption spectra and HOMO energy, lowest unoccupied molecular orbital (LUMO) energy levels are determined to be -2.853 eV, -2.780 eV and -2.750 eV for ch 1, 2 and 3, respectively.

A comparative study of cyclic voltammograms for chromophore 2 in acetonitrile at different scan rates is shown in fig. 7. Energetic data for chromophores 1, 2 and 3, respectively are listed in Table 4.

Table 4. Electrochemical properties of the chromophores 1-3.

Compounds	$E_{1/2}$	E_{HUMO} (eV)	E_{LUMO} (eV)	ΔE_{spect} (eV)
1	0.991	-5.7613	-2.862	2.78
2	0.982	-5.6312	-2.793	2.81
3	0.962	-5.5713	-2.734	2.85

From cyclic voltammogram, It Seems the electrochemical behavior of chromophores 1, 2 and 3 follow EC mechanism.

4. CONCLUSION

Three donor-acceptor chromophores were synthesized by the reaction appropriate aldehyde and 6-methoxy-1,2,3,4-tetrahydro-naphthalin-1-one by Knoevenagel condensation. Photophysical properties including, oscillator strength, extenction coefficient, transition dipole moment and stokes shift were investigated in order to investigate the physicochemical behaviors of synthesized chromophores on the basis of the polarity of solvent. The absorption spectra of chromophores exhibit an intramolecular charge transfer band; which showed a positive solavotochromism in different solvents. The emission spectra of the chromophores also reveal the intramolecular charge transfer band character. These findings confirm that there is a significant electron transfer between the donating moiety and the accepting fragment through the π conjugated. The HOMO energy levels of chromophores 1, 2 and 3 respectively were calculated front the onset oxidation potential of cyclic voltammogram.

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