Journal of Organometallic Chemistry 896 (2019) 16–23

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

New ethylferrocenyl based pyranylidene bridge dyads: Synthesis, characterization and investigation of electrochemical and optical properties

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A R T I C L E I N F O

Article history:
Received 22 January 2019
Received in revised form
17 April 2019
Accepted 29 May 2019
Available online 30 May 2019

Keywords:
Conjugated system
Ethylferrocene
4*H*-pyran
Dyad
Push-pull system

A B S T R A C T

In this research, we designed and synthesized six new pyranylidene backbone end-capped with donor and acceptor groups. Ethylferrocene was presented as new donor to evaluate the effect of alkyl chain substituted in ferrocene unit on linear optical and electrochemical properties of push-pull systems and compare it with their unsubstituted ferrocene analogues. Proposed structures were confirmed *via* FT-IR, ^{1}H NMR, ^{13}C NMR, elemental analyses and mass spectra. Optical band gaps were determined in the range of 1.85–2.24 using UV–vis spectroscopy for synthesized chromophores. Electrochemical studies were performed by cyclic voltammetry and show the reversible redox behavior with $\Delta E_p = E_{pa} - E_{pc} \leq 0.08\ V$, and diffusion limited for the redox process.

1. Introduction

Organic compounds with conjugated structure display different properties like unusual luminescent and semi conductivity [1], therefore they have fundamental importance in advanced chemistry science application such as solar cells, organic light-emitting diodes (OLEDs), sensors, nonlinear optical (NLO) devices, solid state lasers and photovoltaic cells, electrode materials for energy storage and thin film transistors [2–4].

Conjugated compounds with both electron-withdrawing and electron-donating group are one of the best alternative for inorganic materials in optical devices. These type of compounds often called push-pull systems. These systems present a good performance when a suitable π-bridge connect the donor and acceptor units [5].

As exemplified in the literature, using pyranylidene derivatives as π spacer allows the extension of novel structures with proper attribute in electro-optical field [6,7]. On the other hand, donor and acceptor groups have important role in the intramolecular charge transfer (ICT) process. Ferrocene with well-defined chemical structure is the subject of many studies over the last few decades. Recently we synthesized some of the ferrocene based conjugated compounds. According to our obtained results, it's clear that ferrocene could perform well enough or rather better than many other donor groups in these type systems [8–11].

Easy functionalization of ferrocene caused the synthesis of a lot of ferrocenyl derivatives for application in different aspects such as anti-cancer drugs, catalysts, electrochemistry, super capacitors, and etc [12–14]. Alkyl chains are classified as donating groups, hence it seems alkylferrocenyls are strong electron donates in compared with ferrocenyl group.

In respect to our previous studies on ferrocene as an ideal electron-donating moiety [15,16], here we used ethylferrocene in synthesis of conjugated ferrocene based compounds with pyranylidene bridge and compared properties of new derivatives with previously obtained results.

2. Material and methods

2.1. Materials and instrumentation

Solvents and reagents were purchased from Merck, Fluka and Aldrich and were used without any kind of purification. The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker FT-400 MHz and 100 MHz spectrometer at 300 K and with CDCl$_3$ as solvent

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https://doi.org/10.1016/j.jorganchem.2019.05.028

respectively. The FT-IR spectra are reported as wavenumbers $\tilde{\nu}$ (cm^{-1}) with band intensities indicated as s (strong), m (medium), w (weak). The mass spectra operated at 70 eV, the most important peaks are reported in *m/z* units with M$^+$ as the molecular ion and with the corresponding intensities in %. Elemental analyses were carried out with an Elementor Vario EL. III instrument. Iron analysis was performed by Analytikjene (novaa 400) atomic absorption spectrophotometer. The electronic absorption spectra were obtained using SPECORD 250 analytik jena UV/Vis spectrophotometer.

Cyclic voltammetry measurements were performed on 1 mM solutions of ferrocene derivative in acetonitrile in the presence of 0.100 M $LiClO_4$ as supporting electrolytes using potentiostat/galvanostat Autolab (PGASTAT 30) equipped with a standard three-electrode cell. A 2-mm-diameter GC was used as the working electrode. A silver/silver chloride (Ag/AgCl) electrode and a platinum electrode were used as the reference and the counter electrodes, respectively. All potentials in this study are reported with respect to the Ag/AgCl.

2.2. Preparation of ethylferrocenecarboxaldehyde (1)

A 250 ml two-necked round bottomed flask was equipped with an ice bath, an argon inlet adapter, magnetic stirrer, and a dropping funnel. Ethylferrocene (12.84 g, 60 mmol) (synthesized according the procedure reported previously [17] dissolved in $CHCl_3$ (85 ml), DMF (9.27 ml, 120 mmol) was added and the mixture was stirred for 10 min in an ice bath. In continues $POCl_3$ (11.20 ml, 120 mmol) was added dropwise to the mixture *via* dropping funnel in the period of 40 min. After the completion of addition, the reaction mixture was stirred for 20 h in 55–60 °C. The reaction mixture poured into the ice-water, aqueous solution neutralized with Sodium carbonate and extracted with Dichloromethane. The organic layer was dried over Na_2SO_4, solvent was removed and Ethylferrocenecarboxaldehyde was purified by column chromatography using EtOAc/hexane 1:9 as eluent. 10.89 g (45 mmol) orange oil obtained in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ [ppm] = 10.2 (br, 1H, C**H**O), 4.25–4.76 (m, 8H, Fc), 2.23–2.42 (m, 2H, C**H**$_2$-Fc), 1.19 (t, 3H, C**H**$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ [ppm] = 192.7, 190.6 (**C**=O), 94.1, 91.0 (**C**$_1$ of Cp), 81.6, 81.3 (**C**$_3$ and **C**$_{1'}$), 66.9–72.9 (8C, Cp), 20.0, 25.4 (Fc-**C**H$_2$), 13.6 (CH$_2$–**C**H$_3$). FT-IR (KBr, cm^{-1}): 3099 (C–H, Aromatic), 2923 (C–H, Aliphatic), 1675 (C=O), 1460-1333 (C=C), 511 (Fe-Cp). MS (70 eV): *m/z* (%): 242 (100) [*M*$^+$]. Elemental analysis: (%) calcd for $C_{13}H_{14}FeO$: C 64.46, H 5.78, Fe 23.14; Found: C 64.23, H 5.74, Fe 23.11.

2.3. Preparation of 4H-pyran derivatives (2)

2-(2, 6-Dimethyl-4*H*-pyran-4-ylidene) malononitrile and 4-(1, 3-indandione)-2,6-dimethyl-4*H*-pyran were synthesized according to literature [18].

2.4. General procedure for synthesis of bis condensed compounds based on ethylferrocene core

A 50 ml round bottomed flask was equipped an argon inlet adapter and magnetic stirrer. A solution of ethylferrocenecarboxaldehyde (**1**) (5.6 mmol), 4*H*-pyran derivatives (**2**) (2.8 mmol) and piperidine (2 drops) dissolved in dry acetonitrile (20 mL) and was refluxed for 24 h under argon atmosphere. After completing the reaction (monitored by TLC) the reaction mixture was cooled to room temperature and concentrated in vacuum. The residue extracted with dichloromethane and water. The organic layer was dried over Na_2SO_4 and then concentrated and the resulting oil was purified by column chromatography on silica gel with ethyl acetate-hexane.

2.4.1. 2,6-bis(ethylferrocenylvinyl)-4H-pyran-4-one (3a)

From 0.34 g (2.8 mmol) 2, 6-dimethyl-4*H*-pyran-4-one and 1.35 g (5.6 mmol) ethylferrocenecarboxaldehyde, 1.28 g (2.2 mmol) crimson oil was purified by column chromatography on silica gel with ethyl acetate-hexane (1:1) as eluant in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ [ppm] = 7.22 (d, 2H, ^3J = 13.5 Hz), 6.32 (d, 2H, ^3J = 13.5 Hz), 6.15 (s, 2H), 4.37–4.50 (m, 7H, Cp), 4.06–4.14 (m, 9H, Cp), 2.17–2.41 (m, 4H, 2C**H**$_2$-Fc), 1.15–1.25 (m, 6H, 2C**H**$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ [ppm] = 179.51 (Pyran-C-4), 160.61 (Pyran-C-2, 6), 135.63, 135.15 (H**C**=CH), 115.62, 115.36 (H**C**=CH), 110.76 (Pyran-C-3, 5), 93.04, 91.29 (Cp), 79.01, 78.00 (Cp), 66.18–70.09 (Cp), 20.55, 21.20, 28.79 (Cp-**C**H$_2$), 13.43 (**C**H$_3$). FT-IR (KBr, cm^{-1}): 3113 (C–H, Aromatic), 2925, 2853 (C–H, Aliphatic), 1641 (C=O), 1463–1527 (C=C), 1123 (C–O), 517 (Fe-Cp). MS (70 eV): *m/z* (%): 572 (100) [*M*$^+$]. Elemental analysis: (%) calcd for $C_{33}H_{32}Fe_2O_2$: C 69.23, H 5.59, Fe 19.58; Found: C 69.02, H 5.56, Fe 19.55.

2.4.2. 2-[2,6-bis(ethylferrocenylvinyl)-4H-pyran-4-ylidene] malononitrile (3b)

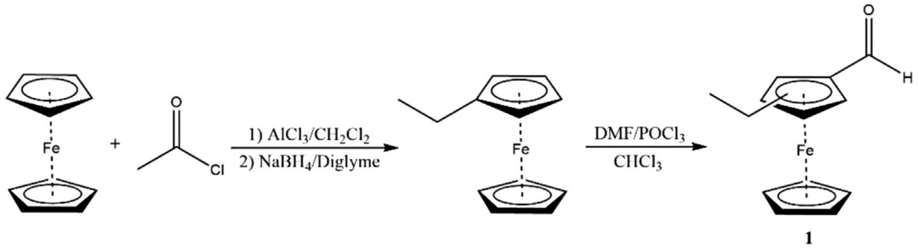
From 0.48 g (2.8 mmol) 2-(2,6-dimethyl-4*H*-pyran-4-ylidene) malononitrile and 1.35 g (5.6 mmol) ethylferrocenecarboxaldehyde, 1.50 g (2.4 mmol) dark red oil was purified by column chromatography on silica gel with ethyl acetate-hexane (3:7) as eluant in 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ [ppm] = 7.33 (d, 2H, ^3J = 14.9 Hz), 6.70 (s, 2H), 6.33 (d, 2H, ^3J = 14.9 Hz), 4.49–4.52 (m, 7H, Cp), 4.11–4.44 (m, 9H, Cp), 2.26–2.44 (m, 4H, 2C**H**$_2$-Fc), 1.15–1.24 (m, 6H, 2C**H**$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ [ppm] = 177.94 (Pyran-C-4), 157.42, 157.39 (Pyran-C-2, 6), 138.62, 138.08 (H**C**=CH), 114.94 (H**C**=CH), 114.08 (**C**≡N), 103.70, 103.63 (Pyran-C-3, 5), 92.56, 91.87 (Cp), 78.50 (Cp),70.93 (NC–**C**–CN), 66.60–70.93 (Cp), 20.56, 21.24, 28.41 (Cp-**C**H$_2$), 13.49 (**C**H$_3$). FT-IR (KBr, cm^{-1}): 3114 (C–H, Aromatic), 2925, 2853 (C–H, Aliphatic), 2201 (C≡N), 1414–1533 (C=C), 1121 (C–O), 515 (Fe-Cp). MS (70 eV): *m/z* (%): 620 (100) [*M*$^+$]. Elemental analysis: (%) calcd for $C_{36}H_{32}Fe_2N_2O$: C 69.67, H 5.16, Fe 18.06, N 4.51; Found: C 69.54, H 5.14, Fe 18.03, N 4.46.

2.4.3. 2-[2,6-bis(ethylferrocenylvinyl)-4H-pyran-4-ylidene]-1, 3-indandione (3c)

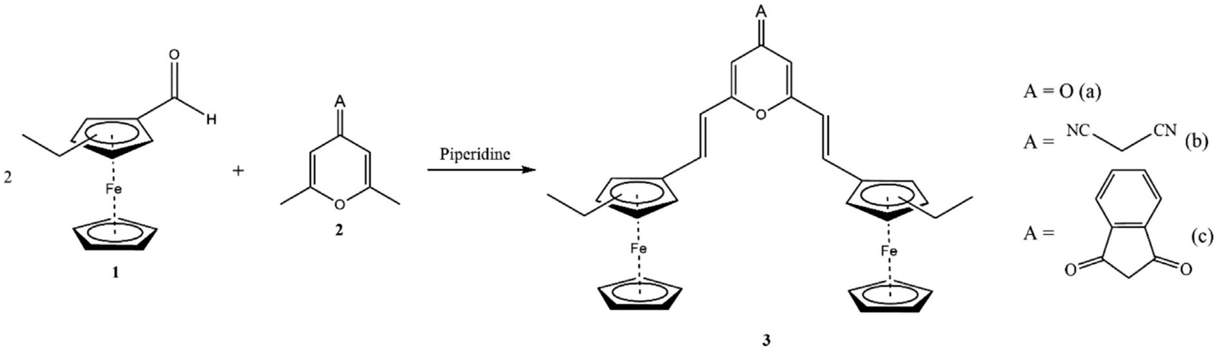
From 0.70 g (2.8 mmol) 2-(2,6-dimethyl-4*H*-pyran-4-ylidene)-1,3-indandione and 1.35 g (5.6 mmol) ethylferrocenecarboxaldehyde, 1.66 g (2.3 mmol) forest green oil was purified by column chromatography on silica gel with ethyl acetate-hexane (3:7) as eluant in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ [ppm] = 8.46 (s, 2H), 7.59–7.75 (m, 4H), 7.29 (d, 2H, ^3J = 15.4 Hz), 6.50 (d, 2H, ^3J = 15.4 Hz), 4.53–4.61 (m, 7H, Cp), 4.20–4.24 (m, 9H, Cp), 2.04–2.35 (m, 4H, 2C**H**$_2$-Fc), 1.04–1.38 (m, 6H, 2C**H**$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ [ppm] = 191.97 (**C**=O), 159.45, 159.20 (Pyran-C-2, 6), 147.61 (Pyran-C-4), 131.85–139.83 (1,3-Indanone), 115.70–119.99 (H**C**=**C**H), 106.08, 105.93 (Pyran-C-3, 5), 94.10, 93.98 (Cp), 78.58 (Cp), 66.75–71.11 (Cp), 20.57, 21.32, 28.55 (Cp-**C**H$_2$), 13.50, 13.41 (**C**H$_3$). FT-IR (KBr, cm^{-1}): 3207, 3115 (C–H, Aromatic), 2924, 2853 (C–H, Aliphatic), 1692, 1645 (C=O), 1465–1520 (C=C), 1123 (C–O), 513 (Fe-Cp). MS (70 eV): *m/z* (%): 700 (100) [*M*$^+$]. Elemental analysis: (%) calcd for $C_{42}H_{36}Fe_2O_3$: C 72.00, H 5.14, Fe 16.00; Found: C 71.84, H 5.12, Fe 15.92.

2.5. General procedure for synthesis of mono condensed compounds based on ethylferrocene core

Mono condensed compounds were synthesized according to the previous method with (1:1) stoichiometric ratio of 4*H*-pyran derivatives and ethylferrocenecarboxaldehyde.



Scheme 1. Synthesis of ethylferrocenecarboxaldehyde.



Scheme 2. Synthesis of bis condensed compounds based on ethylferrocene core.

2.5.1. *2-(ethylferrocenylvinyl)-6-methyl-4H-pyran-4-one (4a)*

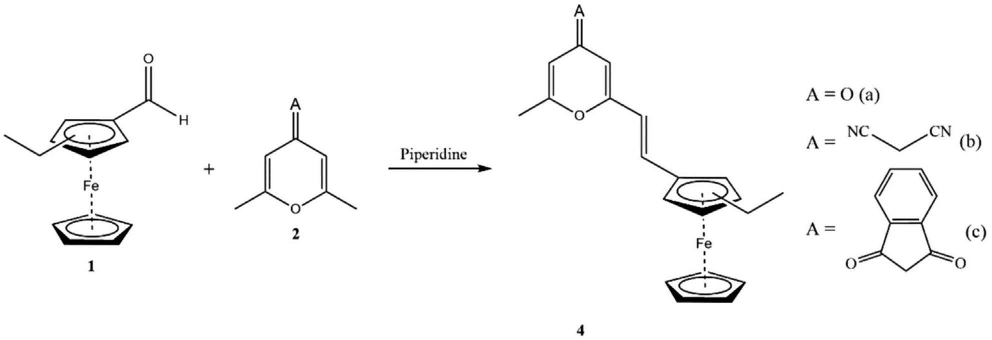
From 0.34 g (2.8 mmol) 2, 6-dimethyl-4*H*-pyran-4-one and 0.67 g (2.8 mmol) ethylferrocenecarboxaldehyde, 0.60 g (1.7 mmol) red oil was purified by column chromatography on silica gel with ethyl acetate-hexane (1:1) as eluant in 62% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 300 K): δ [ppm] = 7.17 (d, 1H, ^3J = 13 Hz, =C**H**), 6.23 (d, 1H, ^3J = 13 Hz, =C**H**), 6.06 and 6.08 (s, 2H, Pyran), 4.06–4.44 (m, 8H, Fc), 2.23–2.39 (m, 5H, Cp-C**H**$_2$ and Pyran-C**H**$_3$), 1.10–1.24 (m, 3H, CH$_2$C**H**$_3$). ^{13}C NMR (100 MHz, CDCl$_3$, 300 K): δ [ppm] = 179.88 (Pyran-C-4), 163.70, 161.41 (Pyran-C-2, 6), 135.72, 135.26 (=**C**H), 115.19, 114.94 (=**C**H), 110.15 (Pyran-C-3, 5), 93.00, 91.28 (Cp), 78.88 (Cp), 66.16–70.11 (Cp), 28.95, 21.19, 20.56 (Cp-**C**H$_2$), 18.85 (Pyran-**C**H$_3$), 13.48, 13.41 (CH$_2$**C**H$_3$). FT-IR (KBr, cm^{-1}): 3113 (C–H, Aromatic), 2925, 2854 (C–H, Aliphatic), 1650 (C=O), 1464–1527 (C=C), 1119 (C–O), 517 (Fe-Cp). MS (70 eV): *m/z* (%): 348 (100) [M^+]. Elemental analysis: (%) calcd for $C_{20}H_{20}FeO_2$: C 68.96, H 5.74, Fe 16.09; Found: C, 68.78, H 5.68, Fe 16.07.

2.5.2. *2-(2-Ethylferrocenylvinyl-6-methyl-4H-pyran-4-ylidene) malononitrile (4b)*

From 0.48 g (2.8 mmol) 2-(2,6-dimethyl-4*H*-pyran-4-ylidene) malononitrile and 0.67 g (2.8 mmol) ethylferrocenecarboxaldehyde, 0.74 g (1.8 mmol) dark red oil was purified by column chromatography on silica gel with ethyl acetate-hexane (2:3) as eluant in 67% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 300 K): δ [ppm] = 7.26–7.29 (dd, 1H, ^3J = 15.3 Hz, =C**H**), 6.54 and 6.59 (s, 2H, pyran), 6.23–6.27 (dd, 2H, ^3J = 15.3 Hz, =C**H**), 4.08–4.46 (m, 8H, Fc), 2.22–2.38 (m, 5H, Cp-C**H**$_2$ and Pyran-C**H**$_3$), 1.10–1.21 (m, 3H, CH$_2$C**H**$_3$). ^{13}C NMR (100 MHz, CDCl$_3$, 300 K): δ [ppm] = 178.57 (Pyran-C-4), 157.55, 157.50 (Pyran-C-2, 6), 138.64, 138.08 (=**C**H), 114.98 (=**C**H), 113.86 (**C**≡N), 103.81, 103.75 (Pyran-C-3, 5) 94.58 (Cp), 77.46 (Cp), 70.91 (NC–**C**–CN), 66.54–70.71 (Cp), 21.76, 22.34, 28.56 (Cp-**C**H$_2$), 18.49 (Pyran-**C**H$_3$), 13.47, 13.41 (CH$_2$–**C**H$_3$). FT-IR (KBr, cm^{-1}): 3113 (C–H, Aromatic), 2924, 2857 (C–H, Aliphatic), 2206 (C≡N), 1462–1548 (C=C), 1121 (C–O), 517 (Fe-Cp). MS (70 eV): *m/z* (%): 396 (100) [M^+]. Elemental analysis: (%) calcd for $C_{23}H_{20}FeN_2O$: C 69.69, H 5.05, Fe 14.14, N 7.07; Found: C 69.55, H 5.02, Fe 14.10, N 7.05.

2.5.3. *2-(2-Ethylferrocenylvinyl-6-methyl-4H-pyran-4-ylidene)-1, 3-indandione (4c)*

From 0.70 g (2.8 mmol) 2-(2,6-dimethyl-4*H*-pyran-4-ylidene)-1,3-indandione and 0.67 g (2.8 mmol) ethylferrocenecarboxaldehyde, 0.88 g (1.8 mmol) dark green oil was purified by column chromatography on silica gel with ethyl acetate-hexane (4:6) as eluant in 66% yield. ^{1}H NMR (400 MHz, CDCl$_3$,



Scheme 3. Synthesis of mono condensed compounds based on ethylferrocene core.

300 K): δ [ppm] = 8.31 and 8.42 (s, 2H, Pyran), 7.59–7.75 (m, 4H, Indanone), 7.26 (d, 1H, $^3J = 22$ Hz, =C**H**), 6.37 (d, 1H, $^3J = 22$ Hz, =C**H**), 4.32–4.75 (m, 8H, Fc), 2.43 (s, 3H, Pyran-C**H**$_3$), 2.12–2.27 (m, 2H, Cp-C**H**$_2$), 1.12–1.25 (m, 3H, CH$_2$C**H**$_3$). ^{13}C NMR (100 MHz, CDCl$_3$, 300 K): δ [ppm] = 192.07 (**C**=O), 159.69, 159.23 (Pyran-C-2, 6), 147.63 (Pyran-C-4), 140.14–132.59 (Indanone), 121.02–115.93 (H**C**=**C**H), 106.09, 105.93 (Pyran-C-3, 5), 91.93(Cp), 78.76 (Cp), 66.27–71.77 (Cp), 28.56, 21.74, 20.56 (Cp-**C**H$_2$), 18.55 (Pyran-**C**H$_3$) 13.43 (CH$_2$**C**H$_3$). FT-IR (KBr, cm^{-1}): 3211, 3116 (C–H, Aromatic), 2925, 2854 (C–H, Aliphatic), 1692, 1646 (C=O), 1465–1524 (C=C), 1125 (C–O), 517 (Fe-Cp). MS (70 eV): *m/z* (%): 476 (100) [M^+]. Elemental analysis: (%) calcd for $C_{29}H_{24}FeO_3$: C 73.10, H 5.04, Fe 11.76; Found: C 72.98, H 5.03, Fe 11.7.

3. Result and discussion

In recent years, conjugated polymers and organic molecules had been raised as serious rivals for inorganic compounds which were used in electro-optical related areas. Although it can be said that, at this time, superiority belongs to polymeric compounds; but light-weight organic molecules with improved charge transfer properties are widely adopted. We know that the push-pull effect of conjugated D-π-A type compounds with terminal donor (D)-acceptor (A) substitution depends on the strength of the donor and acceptor groups and length of π-linker. In order to implement this requirement in this research, we focused on donor group, hence ethylferrocenecarboxaldehyde (EtFc-aldehyde) was synthesized and used as donor material for the analogous donor-acceptor substituted pyranylidene systems.

Ethylferrocene was prepared *via* Friedel-Crafts acylation of ferrocene and reduction of corresponding acetyl group to ethyl group [17]. Then EtFc-aldehyde was synthesized according to Graham method (Scheme 1) [19]. It's mentioned in literature that two substituted ferrocenes can be contained various isomers, in this case 1, 1′ and 1, 3 isomers were observed in ^{1}H NMR spectra. TLC spotting of EtFc-aldehyde show a very close R$_f$ for two isomers, so that the preparative separation of them in large scale was impossible. Hereupon, isomeric mixture was used to synthesize target compounds. Isomers separation performed by thin layer chromatography was used only for identification of two isomers. Significant sign for distinction of isomers is the chemical shift of aliphatic protons in the vicinity of cyclopentadienyl ring, which affected by placement of aldehyde group on same or polar ring; placement of two substitutions on the distinct rings of ferrocene was manifested by lower chemical shift for this protons (^{1}H NMR spectra are given in SI).

Synthesis of target compounds were involved the knoevenagel condensation of pyran derivatives [2, 6-dimethyl-4*H*-pyran-4-one, 2-(2, 6-dimethyl-4*H*-pyran-4-ylidene)malononitrile and 2-(2, 6-dimethyl-4*H*-pyran-4-ylidene)-1, 3-indandione] with EtFc-aldehyde under base (piperidine) catalyzed condition in acetonitrile at the reflux temperature (Schemes 2 and 3).

The yield of this reaction was remarkably good and using stoichiometric ratio of starting materials for control of mono or bis-substituted product formation has been successful. Based on ^{1}H NMR spectra, in addition to peak integrals that clearly show the difference between mono and bis-substituted products, the presence of single peak in 2.40 ppm correspond to protons of methyl in 6-position of pyran ring is a confirmation for the predicted structures (Fig. 1).

Two peaks with different chemical shifts for 3 and 5-position proton of pyran ring in asymmetrical mono-substituted derivatives and one peak for these two protons in symmetrical bis-substituted derivatives prove this point. The elemental analyses, FT-IR, ^{1}H NMR, ^{13}C NMR and mass spectra, all fully support the proposed structures.

The UV–vis spectra of all synthesized compounds were recorded in acetonitrile at a concentration of 12–50 μM in the 250–700 nm (Fig. 2).

Obtained results are given in Table 1. Two energy band in the

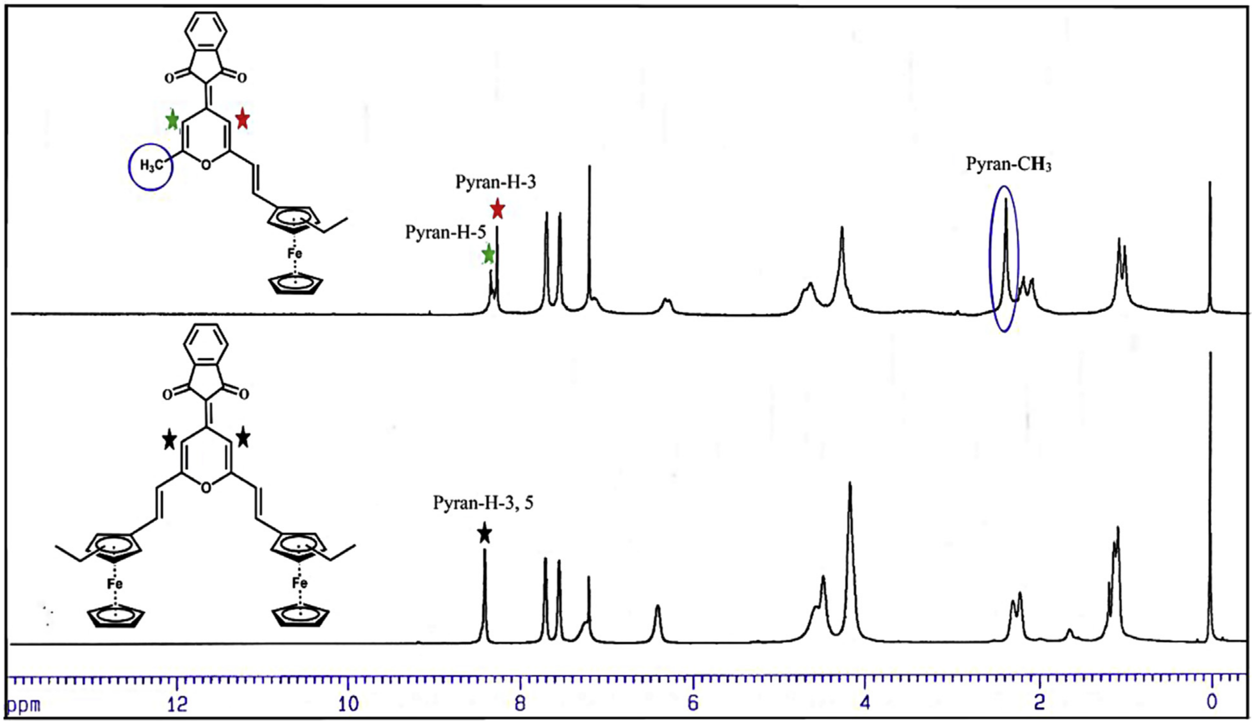


Fig. 1. ^{1}H NMR spectra of 3c and 4c.

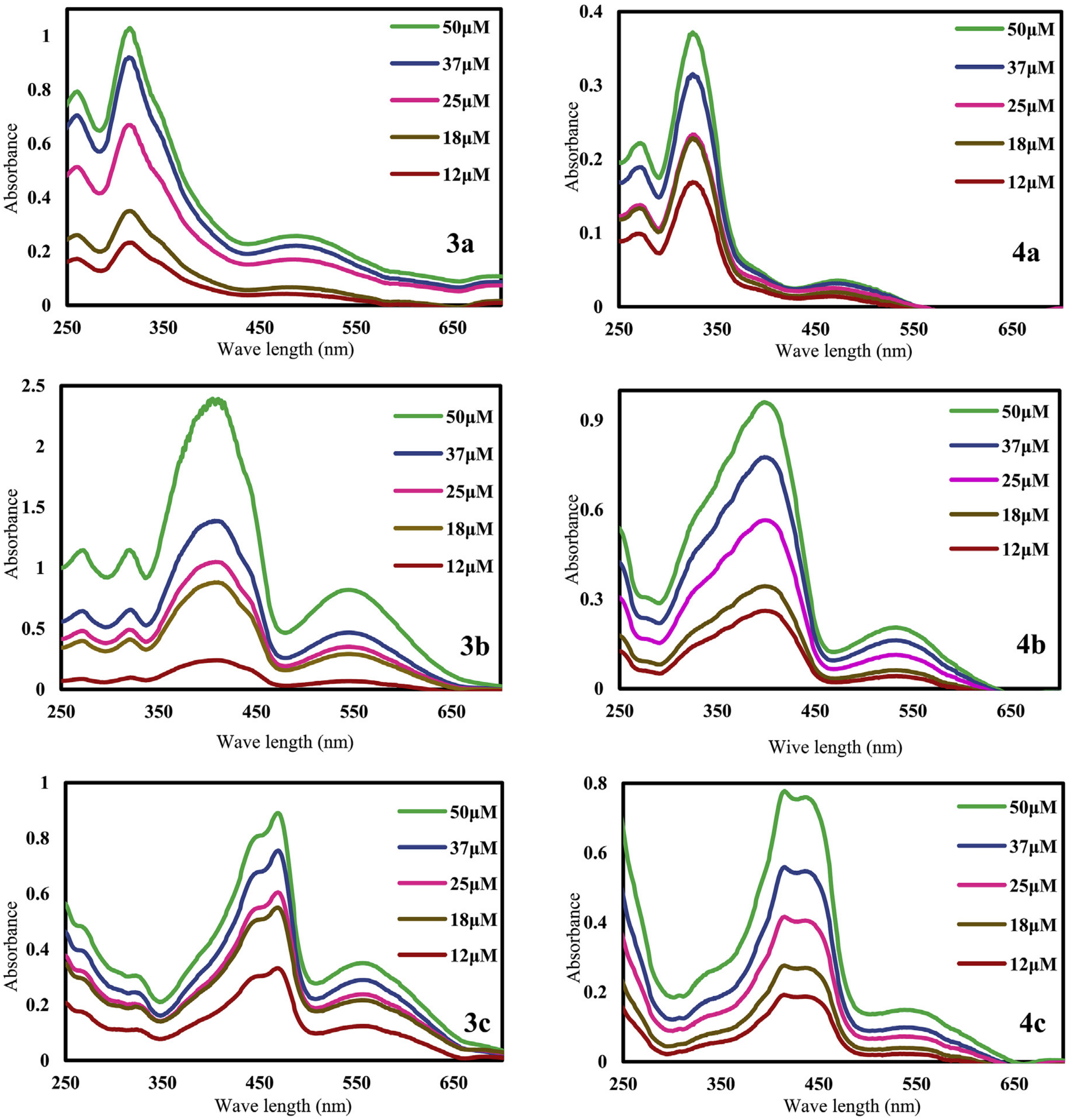


Fig. 2. UV–vis spectra of ferrocenyl based chromophores in acetonitrile solution.

range of 315–468 and 473–556 were observed. The lower wavelength bands can probably be assigned to π-π* transitions which represent ICT between donor and acceptor parts. The higher wavelength with low absorbance was associated to metal to ligand (MLCT) transitions. The introduce of ethyl fragment on the ferrocene unit enhances the ICT, which can be seen with bathochromic shift (red shift) in electronic spectra. Comparison between effect of ferrocene and ethylferrocene as donor groups on push-pull systems were summarized in Table 2. The interpretation of Table 2 corresponds to the strength of ethylferrocene toward ferrocene respect to increasing in chemical shift of H-5 and H-3 pyran which are affected by donors and acceptors in the terminal positions. In the

Table 1
Absorption spectral data of novel ferrocene-based chromophores in acetonitrile.

Entry	Compound	$_{\mathrm{Max}}$ (π-π*)λ	ε (π-π*)	$_{\mathrm{Max}}$ (MLCT)λ	ε (MLCT)	$_{\mathrm{onset}}$λ	Eg (eV)
1	3a	315	20588	490	5138	635	1.95
2	3b	409	47848	544	16396	650	1.90
3	3c	468	17796	556	7008	668	1.85
4	4a	325	7436	488	714	553	2.24
5	4b	410	19226	540	4100	622	1.99
6	4c	467	15548	556	2974	635	1.95

Table 2
Comparison between effect of ferrocene and ethylferrocene as donor groups in push-pull systems.

Acceptor		Chemical shift in ppm Donor is:			λ_{max} in acetonitrile Donor is:		
			Fc	EtFc		Fc	EtFc
Mono	Carbonyl	H-3	6.08	6.08	π-π*	310	325
		H-5	6.06	6.06	MLCT	483	488
	Malononitrile	H-3	6.56	6.59	π-π*	408	410
		H-5	6.52	6.54	MLCT	535	540
	1,3-Indandione	H-3	8.37	8.42	π-π*	461	467
		H-5	8.25	8.31	MLCT	540	556
Bis	Carbonyl	H-3	6.15	6.15	π-π*	309	315
		H-5			MLCT	485	490
	Malononitrile	H-3	6.59	6.70	π-π*	407	409
		H-5			MLCT	534	544
	1,3-Indandione	H-3	8.40	8.46	π-π*	464	468
		H-5			MLCT	542	556

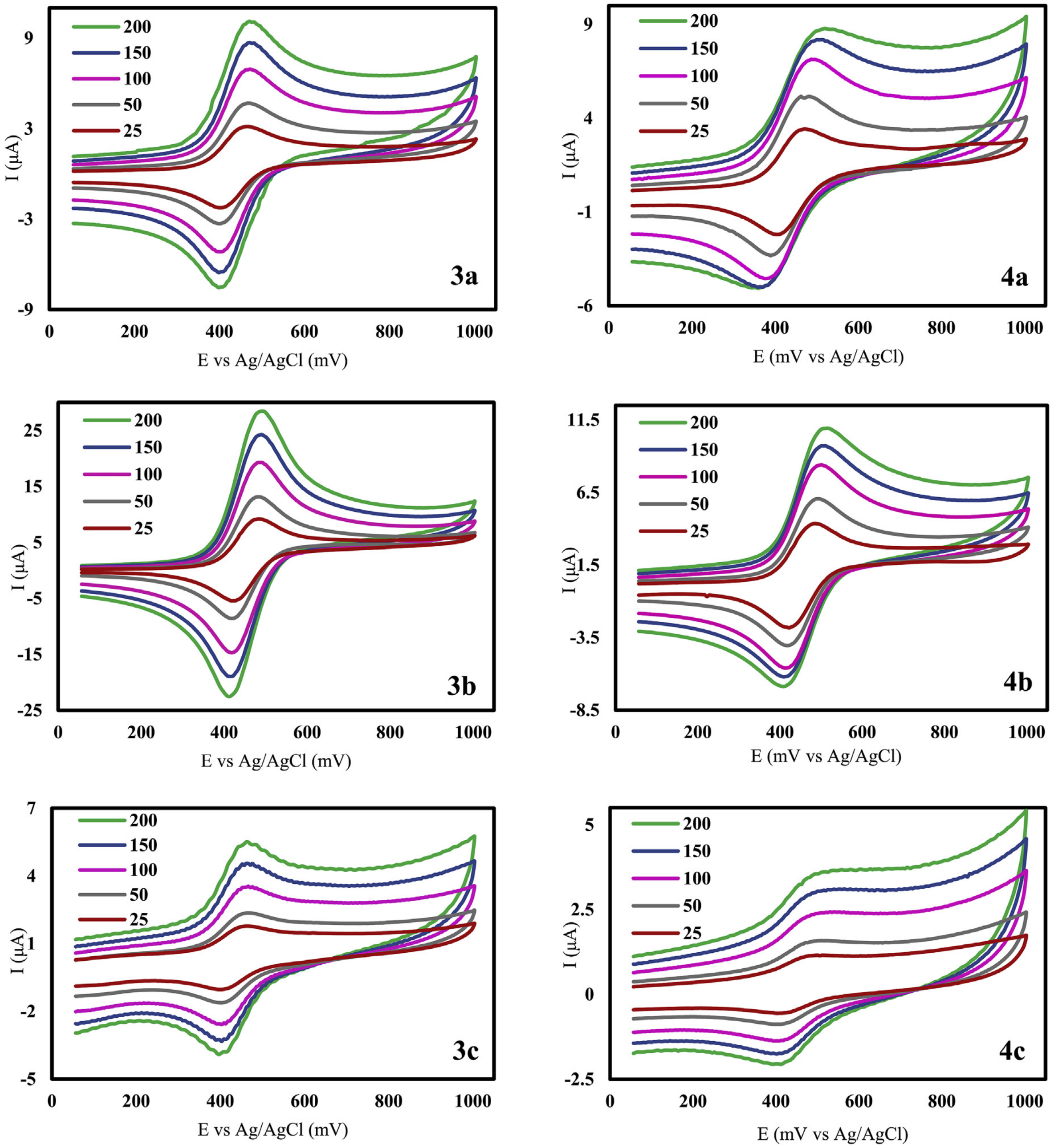


Fig. 3. CV curves of ferrocenyl based chromophores in different scan rates (scan rates given in mV s-1).

Table 3
Cyclic voltammetry data for 1.0 mM solutions of the ferrocenyl based chromophores.

Entry	Compound	ΔE	E_{OX} (V) (experimental CV)	HOMO (eV) (experimental CV)	LUMO (eV) (experimental CV)
1	3a	0.0684	0.363	−4.89	−2.94
2	3b	0.0635	0.382	−4.91	−3.01
3	3c	0.0635	0.359	−4.88	−3.03
4	4a	0.0683	0.357	−4.88	−2.64
5	4b	0.0635	0.390	−4.92	−2.93
6	4c	0.0976	0.370	−4.90	−2.95

other hand, the bathochromic shift in UV spectra was resulted from ability of donor group. Experimental band gap for synthesized compounds were estimated using wavelength at the absorption edge [8]. It's noteworthy that all of them were located in the range of 1–4 eV which are acceptable values for the organic compounds in electro-optical applications. In symmetrical V-shaped bis condensed derivatives, Eg is lower than asymmetrical mono condensed one. In addition, increasing in electron withdrawing ability of acceptor groups is caused the decreasing in Eg values.

Cyclic voltammetric behavior of new dyads was also recorded in anhydrous acetonitrile solution using 0.1 M lithium perchlorate as supporting electrolyte. Fig. 3 shows the CV diagrams in different

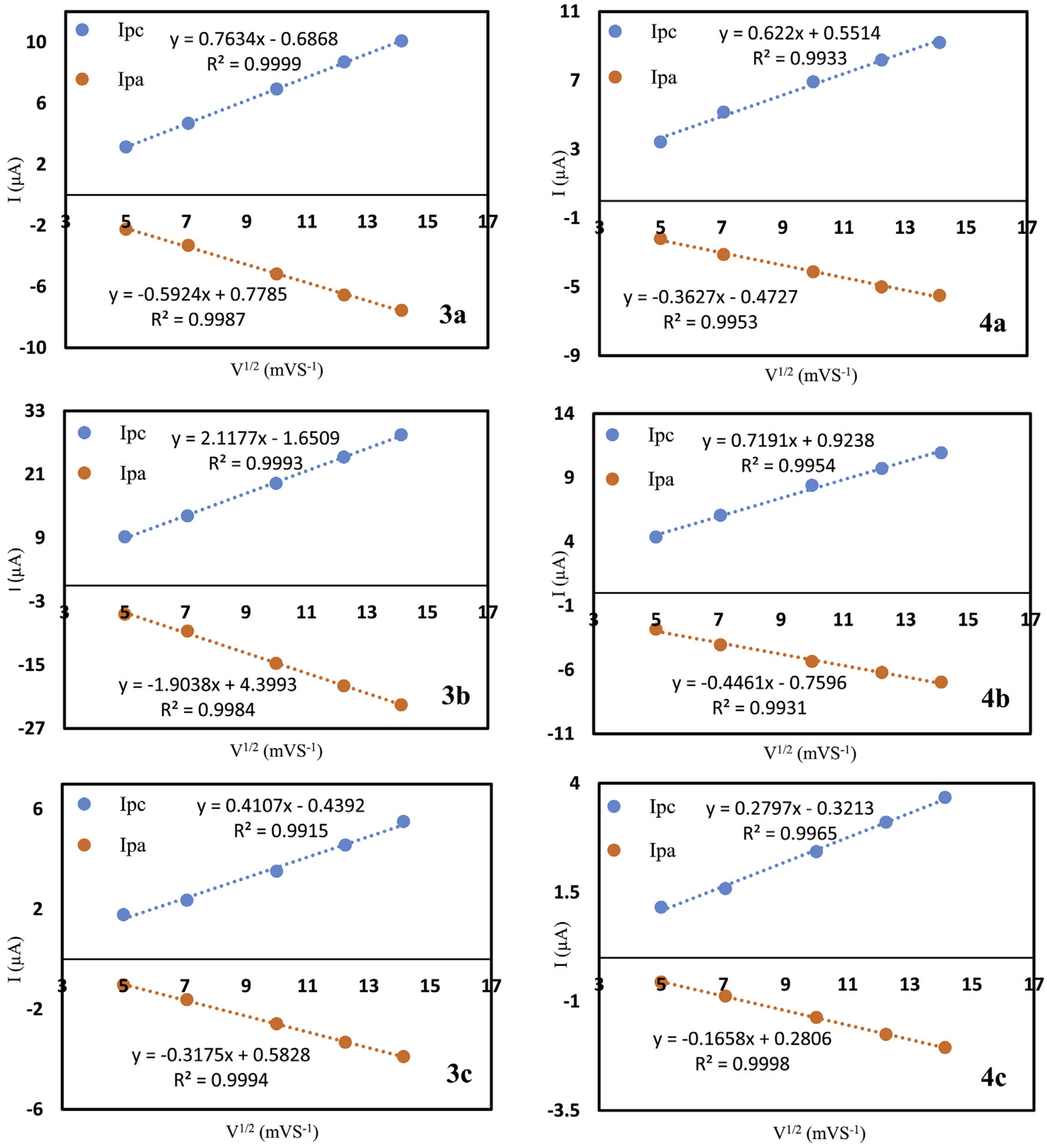


Fig. 4. Linear relationship between the A) cathodic peak current, B) anodic peak current and the square root of scan rates.

scan rates (25-200 mVs^{-1}). CV analysis show a reversible redox behavior with $\Delta E_p = E_{pa} - E_{pc} \leq 0.08\ V$ (Table 3). HOMO/LUMO energies estimate from the oxidation potentials of CV diagrams according to reference 8. Similarly of Eg values of HOMO and LUMO energy levels for bis condensed compounds are lower than mono condensed compounds and their values decrease with increasing in the electron withdrawing ability of acceptor unit in order of carbonyl < Malononitrile <1,3-Indandione.

As can be seen in Fig. 4, the plots of the anodic and cathodic currents versus the square root of scan rates ($v^{1/2}$) show a linear relationship that means the anodic and cathodic peak currents increased with increasing the scan rate. This behavior suggests diffusion limited for the redox process.

4. Conclusion

In this work we described the design, synthesis and the electrochemical behavior as well as the linear optical properties of six push-pull derivatives bearing ethylferrocene electron donating fragment and pyranylidene part as π-linker. The properties of synthesized compounds were compared with their analogues including ferrocene as donor group. All results indicated an acceptable charge transfer through this D-π-A system. Diffusion-limited redox processes observed with plotting anodic and cathodic currents versus the square root of scan rates.

Acknowledgments

We gratefully acknowledge the financial support for post-doctorate grant [grant numbers SAD-27-15/960701] by the Research Council of University of Tabriz.

References

[1] P. Reddy, Y. Lin, H. Chang, Synthesis of novel benzothiazole compounds with an extended conjugated system, Arkivoc 16 (2007) 113–122.
[2] M. Zajac, P. Hrobárik, P. Magdolen, P. Foltínová, P. Zahradník, Donor–π-acceptor benzothiazole-derived dyes with an extended heteroaryl-containing conjugated system: synthesis, DFT study and antimicrobial activity, Tetrahedron 64 (2008) 10605–10618.
[3] A. Heeger, Semiconducting polymers: the third generation, J. Chem. Soc. Rev. 39 (2010) 2354–2371.
[4] S.W. Thomas, G.D. Joly, T.M. Swager, Chemical sensors based on amplifying fluorescent conjugated polymers, Chem. Rev. 107 (2007) 1339–1386.
[5] N.J. Jeon, H.G. Lee, Y.C. Kim, J. Seo, J.H. Noh, J. Lee, S.I. Seok, O-Methoxy substituents in spiro-OMeTAD for efficient inorganic–organic hybrid perovskite solar cells, J. Am. Chem. Soc. 136 (2014) 7837–7840.
[6] P. Strohriegl, J.V. Grazulevicius, Charge-transporting molecular glasses, Adv. Mater. 14 (2002) 1439–1452.
[7] R. Andreu, E. Galán, J. Garín, V. Herrero, E. Lacarra, J. Orduna, R. Alicante, B. Villacampa, Linear and v-shaped nonlinear optical chromophores with multiple 4 H-pyran-4-ylidene moieties, J. Org. Chem. 75 (2010) 1684–1692.
[8] R. Teimuri-Mofrad, K. Rahimpour, R. Ghadari, Synthesis, characterization, and electronic properties of novel Fc-DCM conjugated system; experimental and computational studies, J. Organomet. Chem. 811 (2016) 14–19.
[9] R. Teimuri-Mofrad, K. Rahimpour, R. Ghadari, Design, synthesis and characterization of ferrocene based V-shaped chromophores with modified nonlinear effect, J. Organomet. Chem. 846 (2017) 397–406.
[10] R. Teimuri-Mofrad, K. Rahimpour, R. Ghadari, S. Ahmadi-Kandjani, Ferrocene based nonlinear optical chromophores: synthesis, characterization and study of optical properties, J. Mol. Liq. 244 (2017) 322–329.
[11] R. Teimuri-Mofrad, K. Rahimpour, Experimental and computational studies of novel ferrocene–pyranylidene dyads: synthesis, characterization and electrochemical and linear optical properties, Appl. Organomet. Chem. (2018) e4533.
[12] E.A. Hillard, A. Vessieres, G. Jaouen, Ferrocene functionalized endocrine modulators as anticancer agents, Med. Organomet. Chem. 32 (2010) 81–117.
[13] E.W. Neuse, J.R. Woodhouse, G. Montaudo, C. Puglisi, An iron–organic polymeric smoke suppressant for poly (vinyl chloride), Appl. Organomet. Chem. 2 (1988) 53–57.
[14] M. Saleem, H. Yu, L. Wang, H. Khalid, M. Akram, N.M. Abbasi, J. Huang, Review on synthesis of ferrocene-based redox polymers and derivatives and their application in glucose sensing, Anal. Chim. Acta 876 (2015) 9–25.
[15] K. Rahimpour, R. Teimuri-Mofrad, A. Vaez, Isophorone-based organometallic chromophores: synthesis, characterization and investigation of electro-optical properties, Appl. Organomet. Chem. 32 (2018), e4031.
[16] R. Teimuri-Mofrad, K. Rahimpour, A. Poursadegh, Investigation of 5, 6-dimethoxy-1-indanone derivatives in optical applications: synthesis, characterization and study of linear and nonlinear optical properties, Mater. Chem. Phys. 200 (2017) 384–394.
[17] R. Teimuri-Mofrad, K.D. Safa, K. Rahimpour, Synthesis, characterization and electrochemical properties of novel trinuclear ferrocenyl based organosilane compounds, J. Organomet. Chem. 758 (2014) 36–44.
[18] D.U. Kim, S.H. Paik, S.H. Kim, Y.H. Tak, Y.S. Han, S.D. Kim, K.B. Kim, H.J. Ju, T.J. Kim, Electro-optical characteristics of indandione-pyran derivatives as red emission dopants in electroluminescent device, Mater. Sci. Eng. 24 (2004) 147–153.
[19] P.J. Graham, R.V. Lindsey, G.W. Parshall, M.L. Peterson, G.M. Whitman, Some acyl ferrocenes and their reactions, J. Am. Chem. Soc. 79 (1957) 3416–3420.