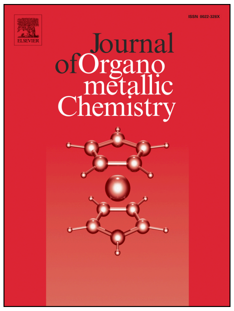
Accepted Manuscript



Synthesis, characterization, and electronic properties of novel Fc- DCM conjugated system; experimental and computational studies

Reza Teimuri-Mofrad, Keshvar Rahimpour, Rahim Ghadari

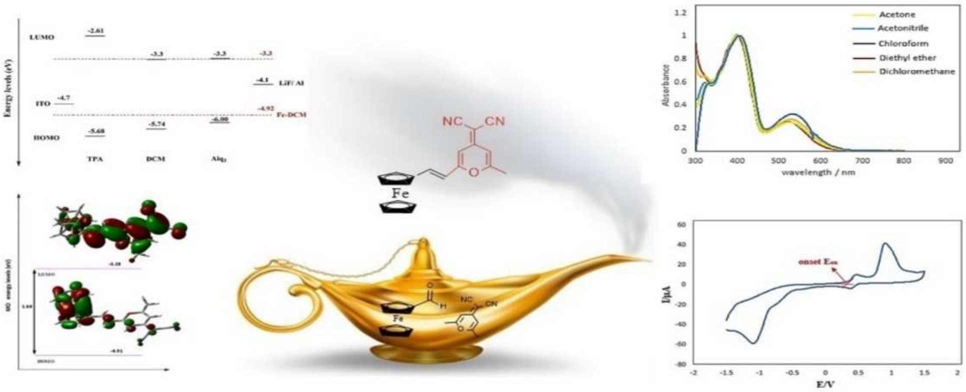
PII: S0022-328X(16)30083-3
DOI: 10.1016/j.jorganchem.2016.03.007
Reference: JOM 19432

To appear in: *Journal of Organometallic Chemistry*

Received Date: 7 January 2016
Revised Date: 24 February 2016
Accepted Date: 8 March 2016

Please cite this article as: R. Teimuri-Mofrad, K. Rahimpour, R. Ghadari, Synthesis, characterization, and electronic properties of novel Fc- DCM conjugated system; experimental and computational studies, *Journal of Organometallic Chemistry* (2016), doi: 10.1016/j.jorganchem.2016.03.007.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Synthesis, characterization, and electronic properties of novel Fc- DCM conjugated system; experimental and computational studies

Reza Teimuri-Mofrad *, Keshvar Rahimpour, Rahim Ghadari

Department of Organic and Biochemistry, Faculty of Chemistry, University of Tabriz, 51664 Tabriz, Iran

Corresponding author Tel.: +98 41 33393105; Fax: +98 411 3340191

E-mail address: teymouri@tabrizu.ac.ir (R. Teimuri-Mofrad)

Abstract

Novel Fc-DCM conjugated compound, 2-(2-ferrocenylvinyl-6-methyl-4H-pyran-4-ylidine) malononitrile, in the form of donor–spacer–acceptor dyad has been synthesized by Knoevenagel condensation. ^{1}H and ^{13}C NMR, FT-IR, CHN analysis and along with atomic absorption spectroscopy supported the predicted structure of the product. The electrochemical behaviour of synthesized compound and the electronic absorption spectra were studied in a variety of solvents. Extensive calculations with various combinations of functionals were carried out to compute energy gap (Eg) of ferrocene derivative. The combined functional and basis set approach PBE/6-31+G(d,p) was found to be well-behaved in the calculation of energy gap. B3LYP/6-31G(d) method was applied to do TD-DFT calculations due to its good agreement with experimental data for prediction of UV-Vis spectra.

Keywords: Ferrocene, Knoevenagel condensation, Cyclic Voltammetry

1-Introduction

Donor–Spacer–Acceptor (DSA) dyads in the forms of both discrete molecules [1] and polymers [2] attract a great deal of scientific and commercial interest. The intramolecular charge transfer (ICT) process in these compounds continues to be a topic of extensive experimental [3] and theoretical [4] studies. Low molecular mass organic compounds with internal charge transport properties are widely adopted in such cases because of their potential applications in optical, electronic and magnetic materials [5], thin film transistors [6], sensors [7], organic light emitting diodes (OLEDs) [8], dye sensitized solar cells (DSSCs) [9], solid state lasers and photovoltaic cells [10]. In the last decade, (OLEDs) have attracted considerable attention due to their useful application in full colour displays. Many scientific research have been focused on the developments in sets of the primary colour emitters of red, green and blue (RGB) [11].

One of the most notable red luminescent materials contains 2,6-dimethyl-4*H*-pyran-4-ylidene fragment as the backbone of molecule. In general, the pyran-4-ylidene has the structure of electron donor-acceptor with a narrow band gap. In DSA type dyads, the structure of π-conjugated spacer plays an important role in charge transfer process. Compounds with extended conjugated π-electron systems are very common for the fabrication of several optical devices.

Pyran and its substituted derivatives are easy to modify and a large number of them are commercially available [12].

Among many kinds of donor groups ferrocene and its derivatives have been extensively studied to be used in molecular wire and nonlinear optical materials. ferrocene and its derivatives have found many applications in materials science including catalysts [13], medicines [14], sensors [15], aerospace materials [16], and electro active materials [17] which could be well corresponded to the favourable electronic properties of the compounds mentioned above.

A suitable combination of the structural features of two small organic or organometallic molecules may result in the creation of new molecules, which could improve the properties which make the new compound to be more efficacious and economical.

In this work, in continuance of our previous studies on various synthesis of ferrocene containing materials, 2-(2-ferrocenylvinyl-6-methyl-4*H*-pyran-4-ylidene) malononitrile has been designed and synthesized through Knoevenagel condensation of ferrocenecarboxaldehyde and 2-(2, 6-dimethyl-4*H*-pyran-4-ylidine) malononitrile. Furthermore, its electrochemical and photochemical properties are studied in different solutions. To analyse the observed spectra, time dependent density functional theoretical (TD-DFT) computation was performed at B3LYP/6-31G(d) level of theory by the Gaussian 09 program. Various methods and basis sets were used for single-point calculation to predict the energy gap. Finally PBE/6-31+G(d, p) method gave the most accurate data for energy gap; therefore, band gap energies were calculated *via* this method for ferrocene compound in different solvents.

2-Results and discussion

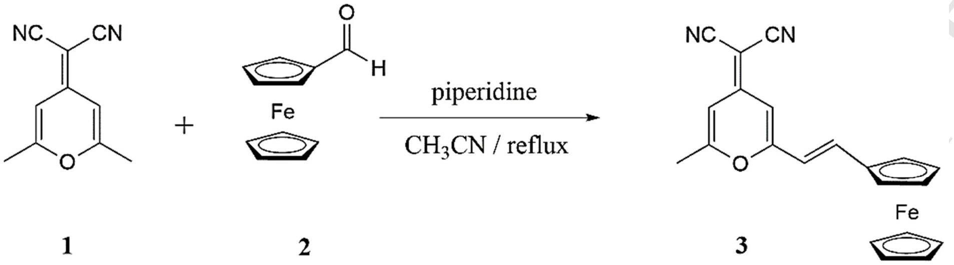
Due to interesting electronic properties of ferrocene and its derivatives, it was decided to use this popular molecule for the synthesis of novel Fc-DCM conjugated compound. Generally, Knoevenagel condensation is considered as a convenient route for the preparation of these types of compounds with extended π-electron conjugation. Since the derivatives of 4-substituted 4*H*-pyran-4-one could be easily obtained by condensation of 2, 6-dimethyl-4*H*-pyran-4-one with active methylene groups, the 2-(2,6-dimethyl-4*H*-pyran-4-ylidene) malononitrile was chosen as the starting material for Knoevenagel condensation with ferrocenecarboxaldehyde.

Ferrocene was put in to reaction with N-methylformanilide and phosphoryl chloride to synthesize ferrocenecarboxaldehyde through Vilsmeier reaction which was done according to the modified procedure described by Graham and co-workers in 71% [18].

The final product, 2-(2-ferrocenylvinyl-6-methyl-4H-pyran-4-ylidine) malononitrile (Scheme 1), in the form of donor–spacer–acceptor dyad was obtained in a considerably good yield by Knoevenagel condensation of 2-(2,6-dimethyl-4*H*-pyran-4-ylidene) malononitrile with ferrocenecarboxaldehyde. The elemental analyses, mass spectra, FT-IR, ^{1}H NMR and ^{13}C NMR spectra all well confirmed the predicted molecular structure. In ^{1}H NMR spectra, the aldehyde

ACCEPTED MANUSCRIPT

peaks disappeared at around 10 ppm, while in 6.29 and 7.31 ppm the doublet peaks with ${}^3J$ = 15.8 Hz were appeared obviously which could be related to -HC=CH- protons. In infrared spectra, the absorptions at 2206 cm^{-1} and 1303 cm^{-1} were assigned to the stretching of cyanide and the vibration of C-O bond of pyran moiety, respectively.



Scheme 1. Synthesis of Fc-DCM by Knoevenagel condensation

The UV-Vis absorption spectra of ferrocene dyads were measured in different solvents with different polarities (5×10^{-5} M) (Fig 1).

[Fig 1]

In the spectrum of Fc-DCM compound, there are two characteristic transitions (λ_{max}) whose position vary in different solvents. The values of lower wavelengths vary between 345 and 402 nm and it has been assigned to π-π* transition; another one is located at a longer wavelengths and the maximum absorption values differ from 520 to 529 nm; this absorption is due to metal-to-ligand charge transfer (MLCT) and finally no absorption observed for d-d transition unless it is covered by the broad MLCT band (Table 1). The two bands are influenced by the polarity of the solvent (Fig 2).

[Fig 2]

[Table 1]

Both transitions showed an unusual small negative solvatochromism with the increasing of solvent polarity which could be assumed to be due to the contribution of the resonance hybrid to the excited state. In addition, these different shifts are not attributed to the solvent polarity alone, but also the interaction of the solute/solvent is effective as well. The experimental band gap energies were calculated (Table 2) according to Eq. (1) [19]:

$$Eg = 1240/\lambda \qquad (1)$$

The wavelength at the absorption edge, λ, was determined as the intercept on the wavelength axis for a tangential line drawn on the absorption spectra (Fig 3).

[Fig 3]

[Table 2]

ACCEPTED MANUSCRIPT

The electrochemical property of Ferrocene derivative was measured by cyclic voltammetry (CV) using a 0.1 M solution of tetrabutylammonium perchlorate (TBAP) in anhydrous dichloromethane, chloroform and diethylether, in acetone and acetonitrile lithium perchlorate were used as supporting electrolyte. Representative CVs of Fc-DCM are presented in Fig 4. The CV data gives valuable information about the oxidation and reduction potentials of materials. In all solvents, a single redox process, showed a reversible voltammetric behaviour for the ferrocenyl group in these compounds with $\Delta Ep = E_{pa} - E_{pc} \leq 0.08$ V at 0.50 V. s^{-1} scan rates. The oxidation corresponds to electron extraction from the HOMO level and can be correlated to the ionization potential, whereas the reduction potential is associated with electron affinity and Indicates that the LUMO level. These processes could be scaled using CV method by measuring the redox potentials. The HOMO energy levels were calculated using equation **2**, where E_{ox} and $E_{ferrocene}$ are the onset oxidation potentials for the dyad sample and the ferrocene against Ag/AgCl reference electrode, while the value – 4.8 eV is the HOMO energy level of ferrocene against vacuum.

[Fig 4]

The LUMO energy levels were calculated with the HOMO levels attained *via* by CV measurements and the optical band gap (E_g) obtained by UV-Vis measurements, equation **3 [**20].

$$E_{\mathrm{HOMO}} = - [E_{\mathrm{ox}} + 4.8 - E_{\mathrm{ferrocene}}] \qquad (2)$$

$$E_{\mathrm{LUMO}} = E_{\mathrm{HOMO}} + E_{\mathrm{g}} \qquad (3)$$

The onset potentials of oxidation are determined from intersection of the tangents between the baseline and the signal current. The onset potentials of ferrocene oxidation vs. Ag/AgCl are reported as following: 0.49, 0.52, 0.53, 0.42 and 0.27, in diethyl ether, CH_2Cl_2, $CHCl_3$, acetone, acetonitrile respectively.

In continue, computational approaches were used to further analyse the observed optical and electrochemical properties. The energies of the frontier orbitals, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), were calculated with various methods and basis sets using Gaussian 09 program in gas phase (Fig 5). The results are summarized in Table 3. From the results presented in Table 3, it is clear that the PBE/6-31+G(d, p) method gives more accurate data for energy gap calculations and therefore it was chosen for further calculation on band gap energies of Fc-DCM compound in different solvents with increasing polarity. The results are in good agreement with experimental data that obtained from UV-Vis and CV spectra (Table 4). Different levels of theories have been used to simulate the observed UV-Vis spectra. After all, it has been found that the B3LYP/6-31G(d) method is the most suitable one to predict the observed λ_{max}. The results of these studies have been summarized in Table 2.

ACCEPTED MANUSCRIPT

[Fig 5]

[Table 3]

[Table 4]

Good consistency between experimental and calculated data indicates that these functionals are reliable in predicting the electronic properties of ferrocene derivatives.

Fig 6 shows the energy levels diagram of the materials, which is usually utilized to fabricate the electroluminescent devices. 4-(Dicyanomethylene)-2-methyl-6-[(dimethylamino)styryl]-4*H*-pyran (DCM) is a well- known red dopant that was used as a reference and the data for DCM, tris(4-(2-phenylethynyl)phenyl)amine (TPA), tris(8- quinolinolato)aluminum (Alq_3), indium tin oxide (ITO) and LiF/Al were cited from the literature [21]. HOMO and LUMO energy levels of Fc- DCM which were calculated at PBE/6-31+G(d, p) method in gas phase, revealed to fall between those of TPA and therefore, energy can easily be transferred from TPA to Fc- DCM. The LUMO of Alq_3 is equal to that of Fc- DCM and HOMO of Alq_3 is lower than HOMO of DCM. Energy level matching between dopant and host materials indicates that our synthetic dyad has the potential to be used in the fabrication of electroluminescent devices as dopants.

[Fig 6]

3-Conclusion

In summary, the design and synthesis of novel Fc-DCM conjugated compound, 2-(2-ferrocenylvinyl-6-methyl-4*H*-pyran-4-ylidene) malononitrile, by Knoevenagel condensation of ferrocenecarboxaldehyde and 2-(2, 6-dimethyl-4*H*-pyran-4-ylidine) malononitrile, has been done successfully in the present research. ^{1}H and ^{13}C NMR, FT-IR, CHN analysis, and atomic absorption spectroscopy supported the predicted structure of the product. The electrochemical behaviour of Fc-DCM compound and the electronic absorption spectra was studied in variety of solvents. Extensive single-point calculations with various combinations of functionals are carried out to compute energy gap (Eg) of the ferrocene derivative. The PBE/6-31+G(d,p) level of theory was found to be well-behaved in the calculation of energy gap. B3LYP/6-31G(d) method was applied to accomplish the TD-DFT calculations due to its good agreement with experimental data for prediction of UV-Vis spectra.

4-Experimental

4.1. Materials and Instrumentation

Solvents and reagents were purchased from Merck, Fluka, Aldrich and Yantai Suny Chem. International Co., Ltd. Commercial compounds were used without any kind of purification.

ACCEPTED MANUSCRIPT

The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker FT-400 MHz spectrometer at 300 K and with $CDCl_3$ as solvent. The FT-IR spectra were recorded on a Bruker-Tensor 270 spectrometer. 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 analytikjena UV/Vis spectrophotometer.

Cyclic voltammetry measurements were performed on 1 mM solutions of ferrocene derivative in different organic solvents (dichloromethane, chloroform, diethyl ether, acetone and acetonitrile) in the presence of 0.100 M $Bu_4N(ClO_4)$ and $LiClO_4$ 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.

4.2. Theoretical Methods

All calculations were carried out through the Gaussian 09 (Rev. D.01) [22] program package by using density functional theory (DFT) and time-dependent DFT (TD-DFT). The frontier orbital energies were predicted with various methods. The functionals used in single-point calculations were B3LYP [23], BLYP [24], HF [25], MP2 [26], M06-2X [27], and PBE [28]. The basis set used were defined as 6-31G(d), 6-31G(d,p), 6-31+G(d,p), 6-31++G(d,p), 6-31G(d), 6-311+G(d,p), and 6-311++G(d,p) [29]. Structure of novel compound was optimized in the gas-phase. For geometry optimizations, the B3LYP level of theory with the $6\text{-}311^{++}G(d,p)$ basis set was employed and no symmetry constraints were imposed. Frequency calculation was done on the optimized structure to ensure the minima nature of the optimized structure by the absence of the imaginary frequency. TD-DFT calculations were performed on the optimized structure to obtain the λ_{max} values. The TDDFT calculations were carried out in gas-phase and in the presence of different solvents using polarizable continuum model (PCM) for the solvents.

4.3. Synthesis of Fc-DCM

Both ferrocenecarboxaldehyde [18] and 2-(2, 6-methyl-4*H*-pyran-4-ylidene) malononitrile [30] were prepared according to the reference method. A solution of 2-(2, 6-methyl-4*H*-pyran-4-ylidine) malononitrile (**1**) (0.14 g, 1.40 mmol), ferrocenecarboxaldehyde (**2**) (0.20 g, 1.40 mmol) and piperidine (1 mL) in dry acetonitrile (10 mL) was refluxed for 24 hours under argon atmosphere. A red fluorescent colour was observed all along the reaction. The reaction was controlled with TLC method by monitoring the compound **1** in the solution of reaction. After the completion of the reaction, the solution was cooled to room temperature and the product was purified using liquid column chromatography over silica gel and hexane: EtOAc (8:2) as eluent. 0.24 g dark red solid was obtained (63% yield), FT-IR (KBr, cm^{-1}): 3115 (Cp-H), 2205 (C≡N), 1690, 1509 (C=C), 1048(Cp); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.31 (d, ^{3}J = 15.80 Hz, 1H, =C**H**), 6.52 and 6.56 (s, 2H, pyran), 6.29 (d, ^{3}J = 15.80 Hz, 1H, =C**H**), 4.53 (t, 2H, C_5H_4), 4.50 (t, 2H,

ACCEPTED MANUSCRIPT

C_5H_4), 4.19 (s, 5H, C_5H_5), 2.39 (s, 3H, C**H**$_3$); ^{13}C NMR (CDCl3, 100 MHz) δ: 160.74, 158.45, 155.51, 138.64, 138.17, 105.21, 104.15, 78.32, 70.39, 69.21, 68.75, 67.30, 18.91; Anal. Found: C, 68.42; H, 4.32; Fe, 15.13; N, 7.56 .Calc. for: $C_{21}H_{16}FeN_2O$: C, 68.50; H, 4.38; Fe, 15.17; N, 7.61%.

Acknowledgment

We gratefully acknowledge the financial support for this work by the Research Council of University of Tabriz.

References

[1] (a) B. Balaganesan, S. W. Wen, C. H. Chen, Tetrahedron Letters, 44 (2003) 145-147;
  (b) L. Cosimbescu, L. Wang, M. L. Helm , E. Polikarpov, J. S. Swensen, A. B. Padmaperuma, International Journal of Organic Chemistry, 2 (2012), 101-110;
  (c) R. W. Sinkeldam, N. J. Greco, Y. Tor, Chem. Rev., 110 (2010), 2579-2619;
  (d) Y. B. Wu, H. M. Guo, T. D. James, J. Z. Zhao, J. Org. Chem., 76 (2011), 5685-5695.
[2] (a) J. H. Kim, H. Lee, Chem. Mater., 14 (2002), 2270-2275;
  (b) B.Y. Hsieh, Y. Chen, Macromolecules, 40 (2007), 8913-8923;
  (c) G. W. Kim, M. J. Cho, Y. Yu, Z. H. Kim, J. Jin, D. Y. Kim, D. H. Choi, Chem. Mater., 19 (2007), 42-50;
  (d) Z. Guo, W. Zhu, H. Tian, Chem. Commun., 48 (2012), 6073-6084.
[3] (a) P. J. Kim, O. P. Kwon, M. Jazbinsek, H. Yun, P. Günter, Dyes and Pigments, 86 (2010), 149-154;
  (b) C. Jianzhong, H. J. Suh, S. H. Kim, Dyes and Pigments, 68 (2006), 75-77;
  (c) S. Wang, S. H. Kim, Current Applied Physics, 9 (2009), 783-788.
[4] (a) P. Zhao, H. Tang, Q. Zhang, Y. Pi, M. Xu, R. Sun, W. Zhu, Dyes and Pigments, 82 (2009), 316-321;
  (b) Y. Li, J. Yao, C. Liu, C. Yang, Journal of Molecular Structure: THEOCHEM, 867 (2008), 59-63;
  (c) Y. L. Li, L. Han, Y. Mei, J. Z. H. Zhang, Chemical Physics Letters, 482 (2009), 217-222;
  (d) F. Ding, S. Chen, H. Wang, Materials, 3 (2010), 2668-2683;
  (e) J. Schäfer, M. Scheurer, B. Speiser, W. Kuz´nik, I.V. Kityk, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 95 (2012), 193-198.
[5] (a) R. L. Carroll, C. B. Gorman, Angew. Chem., Int. Ed. 41 (2002), 4378-4400;
  (b) A. Nitzan, M. A. Ratner, Science, 300 (2003), 1384-1389;
  (c) A. Elangovan, K. M. Kao, S. W. Yang, Y. L. Chen, T. I. Ho, O. Y. Su, J. Org. Chem. 70 (2005), 4460-4469;
  (d) J. A. Marsden, J. J. Miller, L. D. Shirtcliff, M. M. Haley, J. Am. Chem. Soc., 127 (2005), 2464-2476.
[6] A. Heeger, J. Chem. Soc. Rev., 39 (2010), 2354-2371.
[7] W. Samuel, III. Thomas D. J. Guy, M. S. Timothy, Chem. Rev. 107 (2007), 1339-1386.
[8] (a) A. Vembris , E. Zarins, J. Jubels, V. Kokars, I. Muzikante, A. Miasojedovas, S. Jursenas, Optical Materials, 34 (2012), 1501-1506;
  (b) C.J. Huang, , C.C. Kang , T.C. Lee, W.R. Chen, T.H. Meen, Journal of Luminescence, 129 (2009), 1292-1297;
  (c) H. Fukagawa , K. Watanabe, S. Tokito, Organic Electronics, 10 (2009), 798-802.

ACCEPTED MANUSCRIPT

[9] (a) A. Mishra, M. K. R. Fischer, P. Bäuerle, Angew. Chem., Int. Ed. 48 (2009), 2474-2499; (b) J. N. Clifford, M. Planells, E. Palomares, J. Mater. Chem., 22 (2012), 24195-24201.

[10] (a) C. J. Brabec, N. S. Sariciftci, J. C. Hummelen, AdV. Funct. Mater, 11 (2001), 15-26; (b) S. A. Jenekhe, S. Yi, Appl. Phys. Lett., 77 (2000), 2635-2637.

[11] K. H. Lee, S. M. Kim, J. Y. Kim, Y. K. Kim, S. S. Yoon, Bull. Korean Chem. Soc. 31 (2010), 2889-2892.

[12] (a) M. Ghandi, Y. Bayat, R. Teimuri-mofrad, OPPI BRIEFS, 34 (2002), 489-497; (b) B. J. Jung, J. I. Lee, H. Y. Chu, L. M. Do, J. Lee, H. K. Shim, J. Mater. Chem., 15 (2005), 2470-2475.

[13] (a) E.W. Neuse, Adv. Macromol. Chem., 1 (1968), 1; (b) E.W. Neuse, J. R. Woodhouse, G. Montaudo, C. Puglisi, Appl. Organomet. Chem. 2 (1988), 53-57; (c) C. Ornelas, New J. Chem., 35 (2011), 1973-1985.

[14] (a) E.A. Hillard, A. Vessie`res, G. Jaouen, Top. Organomet. Chem, 32 (2010), 81-117; (b) L.V. Snegur, V.N. Babin, A.A. Simenel, Y.S. Nekrasov, L.A. Ostrovskaya, N.S. Sergeeva, Russ. Chem. Bull. Int. Ed, 59 (2010), 2167-2178.

[15] (a) R. Sun, L. Wang, H. Yu, Z. Abdin, Y. Chen, J. Huang, R. Tong, Organometallics, 33 (18) (2014), 4560–4573; (b) M. Saleem, H. Yu, , L. Wang, , Z. Abdin, H. Khalid, M. Akram, N. M. Abbasi, J. Huang, Analytica Chimica Acta, 876 (2015), 9-25.

[16] (a) D. Saravanakumar, N. Sengottuvelan, V. Narayanan, M. Kandaswamy, T. L. VargheseJ. Journal of Applied Polymer Science, 119 (2011), 2517-2524; (b) K. Subramanian, Journal of Polymer Science: Part A: Polymer Chemistry, 37(1999), 4090-4099.

[17] (a) V. Wei, R. Vajtai, Y.Y. Choi, P.M. Ajayan, H. Zhu, C. Xu, D. Wu, Nano Lett., 2 (2002), 1105-1107; (b) A.K. Diallo, C. Ornelas, L. Salmon, J.R. Aranzaes, D. Astruc, Angew. Chem. Int. Ed, 46 (2007), 8644-8648.

[18] P. J. Graham, R. V. Lindsey, G. W. Parshall, M. L. Peterson, G. M. Whitman, J. Am. Chem.Soc., 79 (1957), 3416-3420.

[19] D.S. Bhatkhande, V.G. Pangarkar, A.A. Beenackers, J. Chem. Technol. Biotechnol, 77 (2001), 102-116.

[20] H. Liu, R. Bo, H. Liu, N. Li, Q. Xu, H. Li, J. Lu, L. Wang, J. Mater. Chem. C, 2 (2014), 5709-5716.

[21] Y. S. Yao, J. Xiao, X. S. Wang, Z. B. Deng, B. W. Zhang, Adv. Funct. Mater, 16 (2006), 709-718.

[22] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C.

ACCEPTED MANUSCRIPT

Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
[23] A.D. Becke, J. Chem. Phys, 98 (1993), 5648-5652.
[24] A. D. Becke, Phys. Rev. A, 38 (1988), 3098-3100.
[25] C. C. J. Roothaan, Rev. Mod. Phys., 23 (1951), 69-89.
[26] M. Head-Gordon, J. A. Pople, and M. J. Frisch, Chem. Phys. Lett., 153 (1988), 503-506.
[27] Y. Zhao and D. G. Truhlar, Theor. Chem. Acc., 120 (2008), 215-241.
[28] J.P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 77 (1996), 3865-3868.
[29] (a) R. Ditchfield, W. J. Hehre, J. A. Pople, J. Chem. Phys., 54 (1971), 724-728;
(b) W. J. Hehre, R. Ditchfield, J. A. Pople, J. Chem. Phys., 56 (1972), 2257-2261;
(c) P. C. Hariharan, J. A. Pople, Theor. Chem. Acc., 28 (1973), 213-22;
(d) P. C. Hariharan, J. A. Pople, Mol. Phys., 27 (1974), 209-214;
(e) M. S. Gordon, Chem. Phys. Lett., 76 (1980), 163-168;
(f) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, D. J. DeFrees, J. A. Pople, and M. S. Gordon, J. Chem. Phys., 77 (1982), 3654-3665;
(g) A.D. McLean, G.S. Chandler, J. Chem. Phys., 72 (1980), 5639-5648.
[30] 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, Mater. Sci. Eng: C, 24 (2004), 147-153.

ACCEPTED MANUSCRIPT

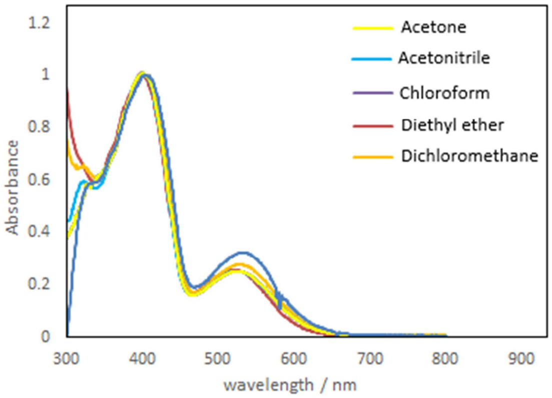


Fig 1. Normalized UV-Vis absorption of Fc-DCM in different solvents

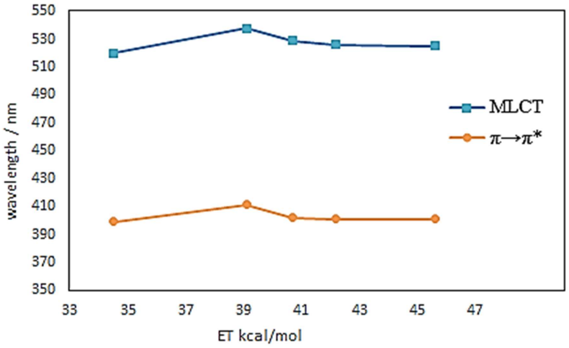


Fig 2. MLCT and π→π* transition in different solvents

ACCEPTED MANUSCRIPT

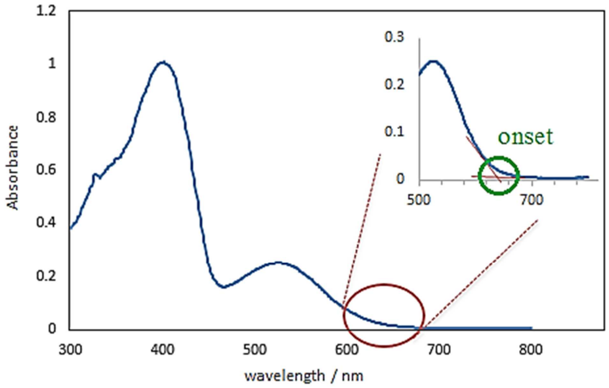


Fig 3. The band gap calculation using UV-Vis spectra.

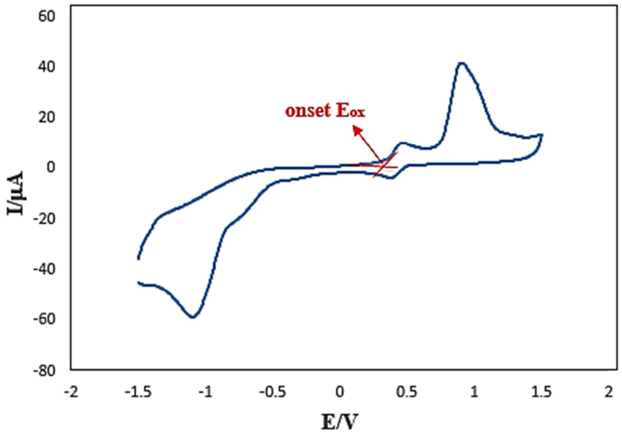


Fig 4. Representative CVs of Fc-DCM (1×10^{-3} M) in CH_3CN/0.100 M $LiClO_4$ at 50 mV s^{-1} vs. Ag/AgCl.

ACCEPTED MANUSCRIPT

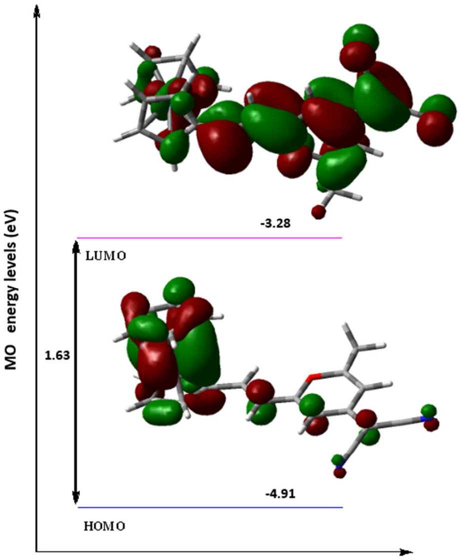


Fig 5. the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for Fc-DCM

ACCEPTED MANUSCRIPT

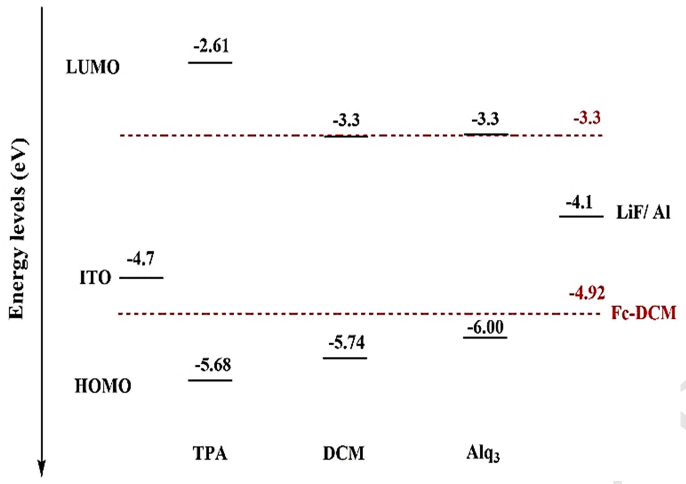


Fig 6. Schematic energy- level diagram of red OLED

ACCEPTED MANUSCRIPT

Table 1. Absorption spectral data of Fc-DCM in various solvents.

	λ_{max}	
Solvent	**π→π***	**MLCT**
Diethyl ether (34.5)[a]	399	520
Dichloromethane (40.7)	402	529
Chloroform (39.1)	411	538
Acetone (42.2)	401	526
Acetonitrile (45.6)	401	525

[a] The solvent parameters E_T in kcal.mol^{-1}

Table 2. HOMO and LUMO energy levels obtained from DFT calculations and experiment, where solvent is specified.

	Diethyl ether	Dichloromethane	Chloroform	Acetone	Acetonitrile
HOMO (DFT)	-4.71	-4.66	-4.70	-4.64	-4.63
HOMO (experiment CV)	-4.89	-4.88	-4.87	-4.88	-4.88
LUMO (DFT)	-3.22	-3.21	-3.22	-3.20	-3.19
LUMO (experiment CV)	-2.89	-2.91	-2.90	-2.89	-2.89
Eg (TDDFT)	1.49	1.45	1.48	1.44	1.44
Eg (experiment UV–Vis)	2.00	1.97	1.98	1.96	1.97

ACCEPTED MANUSCRIPT

Table 3. Energies of the Frontier Molecular Orbitals HOMO and LUMO in gas phase.

		B3LYP	BLYP	HF	MP2	M06-2X	PBE
6-31G*	HOMO (eV)	-5.66	-4.31	-8.12	-8.12	-7.12	-4.53
	LUMO (eV)	-2.37	-2.65	0.92	0.92	-1.63	-2.89
	HOMO - LUMO	**3.29**	**1.66**	**9.04**	**9.04**	**5.49**	**1.64**
6-31G**	HOMO (eV)	-5.66	-5.66	-8.11	-8.11	-7.11	-4.53
	LUMO (eV)	-2.37	-2.37	0.92	0.92	-1.63	-2.90
	HOMO - LUMO	**3.29**	**3.29**	**9.03**	**9.03**	**5.48**	**1.63**
6-31+G**	HOMO (eV)	-5.66	-4.67	-8.27	-8.27	-7.34	-4.83
	LUMO (eV)	-2.37	-3.01	0.43	4.27	-1.89	-3.19
	HOMO - LUMO	**3.29**	**1.66**	**8.7**	**12.54**	**5.45**	**1.69**
6-31++G**	HOMO (eV)	-5.96	-4.67	-8.27	-8.27	-7.34	-4.87
	LUMO (eV)	-2.68	-3.01	0.34	0.34	-1.90	-3.24
	HOMO - LUMO	**3.28**	**1.66**	**8.61**	**8.61**	**5.44**	**1.63**
6-311G*	HOMO (eV)	-5.92	-4.60	-8.25	-8.25	-7.33	-4.78
	LUMO (eV)	-2.61	-2.93	0.76	0.76	-1.85	-3.12
	HOMO - LUMO	**3.31**	**1.67**	**9.01**	**9.01**	**5.48**	**1.66**
6-311+G**	HOMO (eV)	-6.02	-4.72	-8.30	-8.30	-7.41	-4.88
	LUMO (eV)	-2.73	-3.07	0.42	0.42	-1.95	-3.24
	HOMO - LUMO	**3.29**	**1.65**	**8.72**	**8.72**	**5.46**	**1.64**
6-311++G**	HOMO (eV)	-6.02	-4.72	-8.30	-8.30	-7.40	-4.88
	LUMO (eV)	-2.73	-3.07	0.33	0.33	-1.95	-3.24
	HOMO - LUMO	**3.29**	**1.65**	**8.33**	**8.63**	**5.45**	**1.64**

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Table 4. Calculated lowest-energy absorption maxima for Fc-DCM. The theoretical oscillator strength (f) and the experimental extinction coefficient (ε)

	Theory		**Experiment**	
	λ max (nm)	**f**	**λ max (nm)**	**Ε**
Diethyl ether	389	0.8653	399	28640
Dichloromethane	346	1.0594	402	43068
Chloroform	391	0.8861	411	29476
Acetone	391	0.8331	401	29868
Acetonitrile	391	0.8228	401	28164

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Highlights

- 2-(2-Ferrocenylvinyl-6-methyl-4H-pyran-4-ylidine) malononitrile, in the form of donor–spacer–acceptor dyad were synthesized.
- The electrochemical behaviour of synthesized compound and the electronic absorption spectra were studied in a variety of solvents.
- Extensive calculations with various combinations of functionals were carried out to compute energy gap of novel dyad.
- The combined functional and basis set approach PBE/6-31+G(d,p) was found to be well-behaved in the calculation of energy gap.
- B3LYP/6-31G(d) method was applied to do TD-DFT calculations due to its good agreement with experimental data for prediction of UV-Vis spectra.

ACCEPTED MANUSCRIPT