## FULL PAPER

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# Synthesis of tetracyanoethylene-substituted ferrocene and its device properties

<sup>1</sup>Department of Chemistry, Faculty of Sciences, Van Yüzüncü Yil University, Van, Turkey

<sup>2</sup>Cal Vocational High School, Pamukkale University, Denizli, Turkey

<sup>3</sup>Department of Chemical Engineering, Faculty of Engineering, Yeditepe University, Istanbul, Turkey

<sup>4</sup>Department of Chemical Engineering, Faculty of Engineering and Architecture, Selçuk University, Konya, Turkey

<sup>5</sup>Department of Chemical Engineering, Faculty of Engineering, Van Yüzüncü Yil University, Van, Turkey

#### Correspondence

Arif Kivrak, Department of Chemistry, Faculty of Sciences, Van Yüzüncü Yil University, 65080 Van, Turkey. Email: akivrak@yyu.edu.tr

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## **1** | INTRODUCTION

In the last few decades, microwave-assisted organic synthesis has gained great importance for various novel organic reactions including radical reactions, oxidation rearrangement, condensation reactions, coupling reactions, cyclization reactions and nucleophilic substitution reactions.<sup>[1]</sup> Microwave-assisted methods are advantageous compared to traditional ones because microwaveassisted methods require shorter reaction time, and mostly give higher yield and regioselectivity.<sup>[2]</sup> Moreover,

Small organic molecules are promising candidates for cheaper, flexible and good-performance sources for organic solar cells (OSCs) due to their easy fabrication, low cost and slightly cheaper processing. However, the lower power conversion efficiency of OSCs is the main problem for their applications. Ferrocene structures could be the best candidates for the active layers of OSCs due to their unique properties such as thermal and chemical stability. The electrochemical, electro-optical and solar cell performances of 2,5-dicyano-3-ferrocenyl-4-ferrocenylethynylhexa-2,4-dienedinitrile (DiCN-Fc) structures were investigated. First, the electrochemical and electro-optical properties were examined for finding the highest occupied and lowest unoccupied molecular orbital values and bandgap of DiCN-Fc. The best photovoltaic performance was obtained with 7 wt% of DiCN-Fc loading, with a power conversion efficiency of about 4.27%. In the light of our investigations, ferrocenyl-substituted small organic molecules could contribute to the development of organic photovoltaic devices.

#### KEYWORDS

ferrocene, organic photovoltaics, organic solar cells, tetracyanoethylene

environmentally friendly microwave reactions<sup>[3]</sup> have been applied for the preparation of biologically active compounds and materials for optoelectronic applications.<sup>[4]</sup> Recently, small organic molecules containing active donor–acceptor groups<sup>[5]</sup> have been mostly used in organic transistors,<sup>[6]</sup> organic photovoltaics (OPVs),<sup>[7]</sup> biosensors,<sup>[8]</sup> dye-sensitized solar cells,<sup>[9]</sup> sensors<sup>[10]</sup> and electrochromic devices.<sup>[11]</sup> Hence, the designs of new efficient small organic molecule-based materials appear to be more attractive for photovoltaic applications. Researchers have concentrated on the design of 2 of 8 WILEY Organometallic Chemistry

efficient small-molecule materials for OPVs.<sup>[12]</sup> Organic molecules have low molecular weight with strong internal charge transfer properties and broad absorption bands. Various kinds of organic compounds have been designed and synthesized including those with strong donor and acceptor groups in their structures. The most popular and efficient OPVs could be those involving donor–acceptor (D–A) type organic structures, because they have high charge mobility, more flexibility and more electrochemical stability.<sup>[13]</sup>

It was reported that if electron-rich alkynes (1) are allowed to react with tetracyanoethylene (TCNE; 2), firstly tetracyanocyclobutene (3) intermediates are formed, which subsequently undergo ring-opening reaction for the formation of 1,1,4,4-tetracyanobutadienes (4) (Figure 1).<sup>[14]</sup> This kind of reaction was named as [2 + 2]cycloaddition-retroelectrocyclization (Ca-Re) with a high atom economy.<sup>[15]</sup> It was also called a click reaction, because only product 4 was obtained after formation of cyclobutene intermediates. In addition, when TCNE was allowed to undergo cycloaddition reactions with electron-rich aromatic compounds, quinodimethane derivatives were obtained.

Ferrocenyl-substituted organic compounds have great potential in materials studies<sup>[16]</sup> due to their properties. When ferrocene is combined with organic molecules, their innate properties are improved or new properties are created.<sup>[17-19]</sup> Ferrocene is used for optoelectronic devices because of its redox properties, with lower oxidation potential. Ferrocene and its derivatives are also known as donors. so ferrocene in an important candidate for cycloaddition reactions. Mochida and Yamazaki prepared ferrocenyl-1,1,4,4-tetracyano-1,3-butadienes as formal [2 + 2] cycloaddition products by the reaction of ethynylferrocene with TCNE (Figure 2).<sup>[20]</sup> Various ferrocene-substituted organic compounds were obtained with a variety of  $\pi$ -electron systems (Figure 2).<sup>[21]</sup> Moreover, Misra et al. investigated the optical properties of new ferrocenyl-substituted hetero-aromatics including benzothiadiazoles,<sup>[22]</sup> thiazoles<sup>[23]</sup> and triphenylamines.<sup>[24]</sup> Although intramolecular charge transfer properties and nonlinear optical properties were investigated, many ferrocene-based organic compounds as organic solar cell (OSC) materials have not been explored yet.

In the work presented here, a new and efficient method for the synthesis of 2,5-dicyano-3-ferrocenyl-4-ferrocenylethynylhexa-2,4-dienedinitrile (DiCN-Fc; **5**)

was developed with microwave-assisted Ca-Re reactions. The highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy levels were investigated using electro-optical and electrochemical properties of DiCN-Fc and computational methods. Finally, the performance of D–A type DiCN-Fc in OSCs was investigated.

#### 2 | EXPERIMENTAL

A new D-A type DiCN-Fc was synthesized for application in OSCs. All compounds including intermediates were investigated using HR-MS and <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained using an Agilent NMR (400 MHz) spectrometer. Chemical shifts were measured in parts per million (ppm) downfield from an internal tetramethylsilane reference. Thick-walled glass columns and 'flash grade' silica (Merck 230-400 mesh) were used for flash chromatography, and commercially prepared 0.25 mm silica gel plates were applied for TLC. A Thermo Scientific Multiskan Go UV-VIS spectrophotometer was used to obtain absorption spectra. A CHI Model cyclic voltammetry (CV) instrument was used for the determination of electrochemical properties. Mass analysis was performed using a Thermo O Exactive LC-MS/MS. All glassware was washed and dried in an oven prior to use. (2-Formyl-1-(**9**)<sup>[19]</sup> chlorovinvl)ferrocene and ethynylferrocene  $(10)^{[18]}$  were prepared according to procedures given in the literature (Figure 3).

## 2.1 | Synthesis of Compounds

## 2.1.1 | Diferrocenethynyl (11)

To a solution of ethynylferrocene (250 mg, 0.74 mmol) in tetrahydrofuran (THF; 20 ml) were successively added PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (53 mg, 0.075 mmol), CuI (8 mg, 0.037 mmol) and diisopropylamine (5 ml) at room temperature under argon. The mixture was stirred at 65 °C for 8 h. Then, the mixture was extracted with chloroform (3 × 20 ml), dried over anhydrous MgSO<sub>4</sub> and filtered. The solvent was removed under vacuum, and the crude mixture was purified by column chromatography over silica gel with chloroform to afford **11** as a red solid in 51% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 4.51 (s, 4H), 4.25 (m, 14H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm):



**FIGURE 1** Reaction mechanism of Ca-Re reactions between alkynes (1) and TCNE (2)





FIGURE 3 Synthesis of diferrocenethynyl

89.5, 79.3, 72.3, 71.1, 70.4, 63.84. LC–MS/MS: calcd 418.01019  $[M + H]^+$ ; found 418.01022  $[M + H]^+$ . The spectral data were in agreement with those reported previously for this compound.<sup>[20]</sup>

## 2.1.2 | DiCN-Fc (5)

To a solution of diferrocenethynyl (100 mg, 0.27 mmol) in dichloroethane (20 ml) was added TCNE (173 mg, 1.35 mmol) under argon in a 30 ml microwave vial. The mixture was stirred at 130 °C for 3 h under microwave irradiation (Figure 4). After completion of the reaction, crude product was extracted with dichloromethane  $(3 \times 20 \text{ ml})$ , dried over anhydrous MgSO<sub>4</sub> and filtered. The solvent was removed under vacuum. Following this, the crude mixture was purified by column chromatography over silica gel with chloroform to afford 5 as blue solid in 89% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 5.37 (m, 1H), 5.05 (m, 1H), 5.0 (m, 1H), 4.92 (m, 1H), 4.77 (m, 1H), 4.71 (m, 1H), 4.68 (m, 2H), 4.41 (s, 5H), 4.38 (s, 5H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ, ppm): 168.9, 147.5, 128.8, 124.36, 113.9, 112.9, 112.2, 111.5, 88.6, 85.4, 76.6, 76.2, 75.7, 74.3, 73.7, 73.6, 73.5, 73.48, 73.4, 72.9, 72.8, 71.5, 70.5. IR (cm<sup>-1</sup>): 3089, 2961, 2928, 2227, 2166, 1723, 1631, 1457, 1444, 1327, 1283, 1068, 763, 752, 694. LC-MS/MS: calcd 547.03031 [M + H]<sup>+</sup>; found 547.03027  $[M + H]^+$ . The spectral data were in agreement with those reported previously for this compound.<sup>[20]</sup>

#### 2.2 | Electrochemical Measurements

A CHI 660E potentiostat was used for electrochemical measurements in dichloromethane using CV. Tetrabutylammonium hexafluorophosphate (NBu<sub>4</sub>PF<sub>6</sub>; 1 M) was used a supporting electrolyte. A platinum disc (0.2 cm<sup>2</sup>) was applied as working electrode, and a platinum wire was chosen as counter electrode. Saturated Ag/AgCl was used as reference electrode, and Fc/Fc<sup>+</sup> couple was used for calibration. The HOMO energy levels were calculated from oxidation potential ( $E_{ox}$ ) values, and the LUMO energy levels were obtained from reduction potential ( $E_{red}$ ) using CV.<sup>[25]</sup>

#### 2.3 | UV-Visible Spectral Measurements

DiCN-Fc was dissolved at  $10^{-5}$  M in a variety of organic solvents for determining the bandgap using a UV-visible spectrophotometer. After obtaining the UV absorption spectrum, the optical bandgap  $E_{opt}$  was predicted using Planck's equation. The optical bandgap was calculated in terms of electron volts (eV).



**FIGURE 4** Synthesis of 2,5-dicyano-3ferrocenyl-4-ferrocenylethynylhexa-2,4dienedinitrile (**5**) 4 of 8 WILEY Organometallic Chemistry

## 2.4 | Computational Methodology

The geometry of DiCN-Fc was optimized with B3LYP/6-31G(d) using Gaussian 09 to calculate its HOMO–LUMO energy levels.<sup>[26]</sup>

#### 2.5 | Device Measurements

## 2.5.1 | Fabrication of solar cell

A mixture of HCl and H<sub>2</sub>SO<sub>4</sub> in conventional wet-etching process was used for the patterning of indium tin oxide (ITO)-coated glasses. Then, the ITO-coated glass was washed with various solvents (acetone, water and isopropanol) in an ultrasonic bath for 15 min. The ITO substrates were then treated with oxygen plasma for 5 min for the formation of activated surface. Poly(3,4ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS from Clevious) was applied on the ITO glasses using spin-casting (Laurel) with 40 nm at 2000 rpm. Then the PEDOT:PSS-coated glasses were dried at 120 °C for 30 min. For the preparation of active layer, poly(3-hexylthiophene) (P3HT) and phenyl-C61butyric acid methyl ester (PCBM) blends undoped and doped with various amounts of ferrocenyl structure were spin-cast at 1000 rpm for 1 min. The substrates were dried at 130 °C for 30 min. In the last step, an aluminium (Al) cathode (100 nm) was deposited by thermal evaporation (Leybold) through a shadow mask giving an active area of 0.12 cm<sup>2</sup>. OSC based on DiCN-Fc was fabricated in a glove box (MBRAUN) under inert atmosphere. Different ratios of DiCN-Fc (1, 3, 5 and 7%) were doped for active lavers. Cells were tested under AM 1.5 solar simulator

radiation (ATLAS; Keithley 2400 source meter). The fabrication process for the solar cell is shown in Figure 5.

#### **3** | **RESULTS AND DISCUSSION**

#### 3.1 | Synthesis

Diferrocenethynyl was synthesized from ethynylferrocene (10) which was obtained from commercially available acetylferrocene (8). Firstly, 8 was reacted with Vilsmeier-Haack reagent,<sup>[27]</sup> obtained in situ from the reaction between dimethylformamide and POCl<sub>3</sub>, to afford (2-formyl-1-chlorovinyl)ferrocene 9. Then, compound 9 was treated with NaOH in refluxing dioxane, 10 being formed as the only product (70%; Figure 3). Then, 10 was allowed to undergo a self-coupling reaction in the presence of Pd/Cu catalyst under microwave irradiation, the desired product 11 being formed in 51% yield (Figure 3). After isolation of compound 11, we focused on the synthesis of tetracyanosubstituted ferrocene structures. In the light of our previous knowledge, strong acceptors may lead to novel optoelectronic properties.<sup>[28]</sup> Therefore, Ca-Re reactions were used for the synthesis of ferrocene structures. When diethynylferrocene and TCNE were stirred in a microwave reactor at 130 °C for 3 h, only 5 was formed in 89% yield (Figure 4).

## 3.2 | Electro-Optical Properties

The UV-visible absorption spectrum of 5 in  $10^{-5}$  M chloroform solution is displayed in Figure 6.



FIGURE 5 Schematic of solar cell fabrication process



FIGURE 6 Absorption spectra of DiCN-Fc (5) in various solvents

Compound 5 has a characteristic pattern of multiple intense charge transfer absorption bands between 300 and 600 nm. Various kinds of solvents were used to absorption spectra including chloroform, obtain EtOAc, dichloromethane, 1,2-dichloroethane, THF, dioxane and MeOH. Surprisingly, MeOH was not a good solvent for UV absorption. When comparing the solvents, all of them gave similar peaks and similar shifts on the UV absorption spectra. Therefore, chloroform was chosen as the best solvent for the detection of onset point. Compound 5 gives red-shifted absorption due to strong electron-withdrawing groups. In addition, the intramolecular charge transfer interaction  $(\pi - \pi^*$  transition) of **5** gives an absorption at 350 nm.<sup>[29]</sup> Compound **5** has the strongest absorption peak at 625 nm. Onset point of 5 was calculated as 780 nm. The bandgap of 5 was found to be 1.60 eV using Planck's equation.

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## 3.3 | Electrochemical Properties

CV measurements were employed for the determination of HOMO and LUMO energy levels and the bandgap energy of **5** (Figure 7). HOMO and LUMO levels can be obtained from cathodic and anodic currents, respectively.<sup>[25,30]</sup> The redox properties of **5** were measured using CV in dichloromethane with NBu<sub>4</sub>PF<sub>6</sub> (0.1 M) supporting electrolyte at 100 mV s<sup>-1</sup> scan rate. The reduction–oxidation potentials were observed after one cycle. A three-electrode system was used consisting of a platinum electrode as working electrode, Ag/AgCl as reference electrode and Pt wire as counter electrode.  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  (eV) were found using the following equations:<sup>[31]</sup>

$$E_{\text{HOMO}} = -e(E_{\text{ox-vs-NHE}} + 4.75)$$
  
 $E_{\text{LUMO}} = -e(E_{\text{red-vs-NHE}} + 4.75)$   
 $E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.197$ 

Compound **5** displayed a reduction peak at 0.6 V and an oxidation peak at 1.9 V versus Ag/AgCl (Figure 7). The values for  $E_{LUMO}$  and  $E_{HOMO}$  calculated from CV data are  $E_{LUMO} = -5.55$  eV and  $E_{HOMO} = -6.85$  eV. The bandgap energy determined from CV is 1.3 eV, which is in good agreement with that obtained from the optical absorption spectrum (1.6 eV) (Table 1).

## 3.4 | Computational Results

The geometry optimizations were conducted using the DFT/B3LYP/6-31G(d) method in the gas phase. The optimized structures of DiCN-Fc and **11** have different geometries due to electron-withdrawing groups. The HOMO, LUMO and bandgap levels are shown in Figure 8. As clearly seen in Figure 8, HOMO and LUMO transfer of the electrons is from the ferrocene ring to the electron-withdrawing cyano groups. The electron density for DiCN-Fc is higher than that for **11**, and the bandgap is expectedly lower than that of **11**. When computational results were compared with experimental results, the lowest bandgap was obtained as 1.3 eV from CV measurements (Table 1).

#### 3.5 | Device Measurement Results

In the present study, a donor (ferrocene)–acceptor (cyano groups) type of new organic molecule was selected and used for the investigation of solar cell properties (Figure 9). Recently, Patil *et al.*<sup>[32,33]</sup> reported that strong electron-withdrawing groups such as cyano and nitro groups have very critical roles for OSCs and nonlinear optics, because they shift the electronic absorption to the near-infrared region, and they also stabilize the



FIGURE 7 Electrochemical characterization of DiCN-Fc (5) in dichloromethane/NBu<sub>4</sub>FP<sub>6</sub> with a scan speed of 100 mV s<sup>-1</sup>

TABLE 1	Electro-optical	and electrochemical	properties of Di	CN-Fc
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Compound	$\lambda_{\max}$ (nm)	$\lambda_{\text{onset}}$ (nm)	$E_{\rm ox}$ (V)	$E_{\rm red}$ (V)	$E_{\rm g}~({\rm eV})$	HOMO (eV)	LUMO (eV)
DiCN-Fc	625	780	1.9	0.6	1.3 <sup>1a</sup> (1.6) <sup>b</sup> (2.88) <sup>c</sup>	$-6.85^{a} (-6.08)^{c}$	$-5.55^{a} (-3.20)^{c}$

<sup>a</sup>Calculated from external reference NHE.

<sup>b</sup>Calculated from UV absorption.

<sup>c</sup>Calculated from Gaussion 09.



FIGURE 8 HOMO and LUMO orbitals of structures of 11 and DiCN-Fc

LUMO level. Moreover, those authors synthesized new polymers obtained from tetracyanobutadiene derivatives of diketopyrrolopyrroles with higher power conversion efficiency in solar cell devices.<sup>[32]</sup> Rout *et al.*<sup>[34]</sup> prepared

two unsymmetric small molecules with D–A–D– $\pi$ –D configuration including phenothiazine, triphenylamine and strong electron-acceptor groups, and the photovoltaic performance of the molecules was reported as 7.35 and



FIGURE 9 *I–V* characteristics for 5

TABLE 2 Solar cell performance of DiCN-Fc (5)

	$I_{ m sc}$	$V_{ m oc}$	FF	Efficiency (%)
1%	6.90	650	0.409	3.06
5%	8.15	650	0.444	3.92
7%	6.61	650	0.596	4.27
10%	5.90	550	0.387	2.10
Standard	6.55	650	0.578	4.10

4.81% for OSCs. In the light of recent studies, our designed molecule DiCN-Fc (**5**) was applied for cell fabrication. Firstly, **5** was used as a dopant for P3HT:PCBM blends. Doping ratios of 1, 3, 5, 7 and 10% were applied for investigating the solar cell performance of **5**. We observed a significant change for short circuit current ( $I_{sc}$ ) and fill factor (FF) of our fabricated cell compared with standard. The best performance of **5** was obtained at a doping level of 7%, and the efficiency was calculated as 4.27% (Figure 9). All the obtained results for our material are summarized in Table 2. It was found that ferrocene and tetracyano groups in our molecule improved the solar cell performance, so these kinds of organics could be a new generation of small organic molecules for increasing the performance of OSCs.

#### 4 | CONCLUSIONS

In the present study, DiCN-Fc (5) was synthesized using a microwave irradiation methodology. Microwave-assisted reaction gave higher yield and required shorter time for the formation of DiCN-Fc. Electrochemical and electrooptical properties were obtained using CV and UV-visible spectroscopy, respectively. Moreover, computational methods were used for the determination of HOMO, LUMO and bandgap energies of DiCN-Fc. After fabrication of DiCN-Fc, an OSC containing it at a doping level of 7% gave the best performance of 4.27%. In conclusion, ferrocene with strong electron-withdrawing groups significantly influences the performance of OSCs.

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#### ORCID

Arif Kivrak D http://orcid.org/0000-0003-4770-2686

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