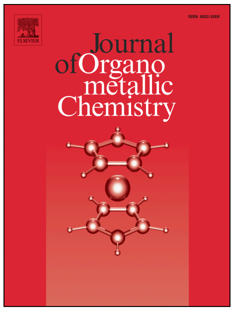

Synthesis, characterization, and solid-state polymerization properties of two diacetylene derivatives containing phenyl ferrocene

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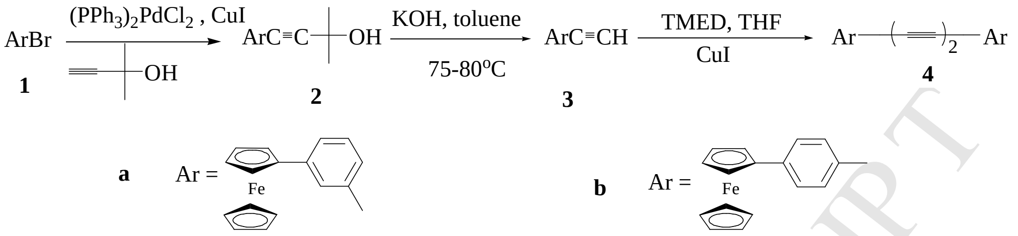
Graphic Abstract



Two diacetylene complexes , 1,4-bis(3- ferrocenylphenyl)- 1,3-butadiyne(**4a**) and 1,4-bis(4-ferrocenylphenyl)-1,3- butadiyne (**4b**), have been prepared. The solid-state polymerization properties of **4a** and **4b** were also investigated.

Synthesis, characterization, and solid-state polymerization properties of two diacetylene derivatives containing phenyl ferrocene

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Synthesis, characterization, and solid-state polymerization properties of two diacetylene derivatives containing phenyl ferrocene

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Abstract

Two diacetylene complexes, 1, 4-bis(3-ferrocenylphenyl)-1,3-butadiyne(**4a**) and 1,4-bis(4-ferrocenylphenyl)-1,3-butadiyne (**4b**), were prepared in this study. 4-(Iodo ethynylene) phenylene) ferrocene (**4b$_1$**) was also obtained. The acetylene complex **4b$_1$** was an important intermediate for the synthesis of **4b**. The molecular structures of **4a** and **4b$_1$** were determined by single-crystal X-ray studies, and the solid-state polymerization properties of the complexes were investigated.

Keywords: Diacetylene complexes； Ferrocene； Cyclic voltammetry； Solid-state polymerization

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[*] † Electronic supplementary information (ESI) available: View along the c axis showing the organization of **4b1** in the crystalline state(Fig. S1) , Powder XRD patterns of **4b** and its partial polymer(Fig. S2) , UV spectra of 4b cast film irradiated by 254 nm (Fig. S3) and heated at 80℃at different time(Fig. S4). CCDC reference numbers 836849 - 836850.

1. Introduction

Polydiacetylenes (PDAs) are uniquely conjugated with highly crystalline features and display important electronic and nonlinear optical properties [1]. PDAs may be applied in molecular electronics, optoelectronic devices, and chemical sensors [2]. Given the rapid progress research in this active field, the design and synthesis of new molecular materials is the subject of current interest. PDAs can be obtained by topological polymerization of butadiyne compounds [3]. In principle, when the molecular alignment satisfies the appropriate alignment (Scheme 1), single crystals of butadiyne compounds can undergo 1,2-addition or 1,4-addition reaction in the solid state to produce PDAs by thermal and photochemical irradiation. However, tailoring molecular spacings and orientations in the resultant crystals is difficult to achieve [4]. Despite the high electron transmission efficiency of PDAs, their thermal and photochemical instability also has severe drawbacks [5]. Results obtained show that all side-chain groups have a significant influence on the thermal stability and solid-state polymerization of the products (PDAs) [6]. Many functional groups have been introduced into butadiyne compounds to design novel architecture [7]. In previous studies, we used substituted carbazolyl [8]and pyridyl groups [9] to prepare PDAs. The design of such DAs is based on the premise that the aromatic side group benefits the backbone conjugation and provides effective conjugation lengths.

Molecular wires comprising mixed-valence metallic fragments have been developed as a new promising class of nonlinear optical materials [10]; these wires have attracted significant research attention because they combine the advantages of both organic molecules and inorganic semiconductors [11]. The ferrocenyl group (Fc) has strong electron donating properties [12]and exhibits reversible one-electron transfer electrochemical behavior [13]. Ferrocene derivatives constitute a family of new functional materials because of their high thermal stability, good solubility and excellent electrochemical property [14]. Since the first report on diferrocenylacetylene [15], the interest in metal-capped linear polycarbon chains as models for materially useful material compounds has dramatically increased [9,16]. Some obsvervations reported the synthesis and polymerization of conjugated ferrocenylacetylenes compounds and the resulting polymers exhibit a remarkable stability against air and thermal treatment [17]. Our research group has recently initiated a program for phenyl ferrocene complexes. The phenyl ferrocene moiety, by virtue of its aromatic interactions with adjacent molecules can increase the probability that the monomer may be stacked appropriately in the crystal for topochemical polymerization. As a continuation of our attempts to the design of ferrocene-based oligoacetylenic complexes materials, the present paper describes the synthesis, characterization, and solid-state polymerization properties of two diferrocenylacetylene complexes.

2. Experimental

2.1. Materials and methods

All chemicals used were of reagent grade and were obtained from commercial sources. Solvents were distilled from appropriate drying agents under nitrogen, and all reactions were run under dry nitrogen. The starting compounds (3-bromophenyl) ferrocene (**1a**) [18]， (4-bromophenyl) ferrocene (**1b**) [18]， 2-methyl-4-(3 (ferrocenyl) phenyl)-3-butdiyn-2-ol (**2a**) [9] , 2-methyl-4-(4-(ferrocenyl) phenyl)-3-butdiyn-2-ol (**2b**) [9] , (3-ethyny phenylene) ferrocene (**3a**) [9] and (4-ethyny phenylene) ferrocene (**3b**) [9] were prepared by reported procedures.

Melting points were measured using a WC-1 microscopic apparatus and are reported were uncorrected. C, H, and N analyses were performed on a FLASH EA1112 analyzer. Infrared spectra were recorded on a Bruker VECTOR22 spectro-photometer in KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer in $CDCl_3$ with TMS as an internal standard. Mass spectral data were acquired on an LC-MSD-Trap-XCT instrument. The X-ray measurements were made on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo-K*a* radiation (λ= 0.71073 Å). Photo-chemical polymerizations were conducted under UV light (peak intensity: 254 nm) and on a cold plate that maintained the sample temperature at approximately 5 °C. The X-ray diffractometry (XRD) experiments were performed on a Rigaku Saturn 724 area-detector diffractometer using graphite-monochromated Mo-K*a* radiation.

2.2. Preparation of DA thin films

Quartz slides were cleaned prior to modification by sonication in deionized water, ethanol, and acetone. The slides were subsequently dried in a stream of nitrogen. Diacetylene monomer **4a** or **4b** was added to a flask containing $CHCl_3$. The solution was stirred for 20 min, and the resulting solution was filtered through a 0.2 μm Teflon filter and spin-coated onto fresh quartz slides. The films were dried in a vacuum at room temperature.

2.3. UV measurements

The UV spectra of the monomers were measured before and after UV irradiation or annealing. Cast films containing the sample on quartz slides were prepared and then irradiated with a UV source (254 nm) for different amounts of time.

2.4. Electrochemical measurements

Electrochemical experiments were performed with a CHI 650A electrochemical analyzer (CH Instruments, USA). A conventional three-electrode electrochemical cell was used with a glassy carbon electrode (GCE) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the auxiliary electrode. The number of electrons transferred for the compounds were estimated by comparing the peak height of the respective ferrocene redox wave with an equal concentration of the ferrocene standard added in the same system. All experiments were carried out at a temperature of 25 °C.

*2.5. Preparation of complexes (**4a**, **4b**)*

*2.5.1. Preparation of 1,4-bis(3 ferrocenylphenyl)-1,3-butadiyne (**4a**)*

A 1.14 g portion of **3a** (4 mmol) was placed in a three-necked flask and dissolved in 20 mL of dry THF with oxygen. *N,N,N,N*-Tetramethyl ethylenediamine (1 mL) was added to the mixture, followed by CuI (1 mmol). The reaction solution was stirred thoroughly at room temperature, and oxygen was bubbled through the solution. The reaction was monitored by TLC (petroleum ether / ethyl acetate, 15:1) and found to be complete after 30 min. The compound was passed through a silica gel column using petroleum ether / ethyl acetate (15:1) as the eluent and **4a** was obtained in pure form as a brown yellow solid. The yield of the product was 30%. m. p. 186-188 °C. ^{1}HNMR ($CDCl_3$, 400 MHz) δ_H 7.64 (1H, s, C_6H_4), 7.47 (1H, d, $J_{\text{H-H}}$ = 6.8 Hz, C_6H_4), 7.35 (1H, d, $J_{\text{H-H}}$ = 6.0 Hz, C_6H_4), 7.24 (1H, m, C_6H_4), 4.66(2H, t, $J_{\text{H-H}}$ = 1.8 Hz, C_5H_4), 4.35(2H, t, $J_{\text{H-H}}$ = 1.6 Hz, C_5H_4), 4.07 (5H, s, C_5H_5). ^{13}CNMR ($CDCl_3$, 100 MHz) δ_C 139.9 (Ph), 129.8 (Ph), 129.0(Ph), 128.5 (Ph), 126.9 (Ph), 121.7 (Ph), 84.0 (Ph-C≡), 81.8 (C_5H_4), 73.6 (C≡C), 69.7 (C_5H_4), 69.3 (C_5H_4), 66.5 (C_5H_4). MS: 571$[M+H]^+$. Analytical calculation for $C_{36}H_{26}Fe_2$ C, 75.58%; H, 4.50%; Found: C, 75.80%; H, 4.75%.

*2.5.2. Preparation of 1,3-bis(3-ferrocenylphenyl)-1,3-butadiyne (**4b**)*

4b was synthesized using the same method used for **4a** synthesis. The starting material in this case was **3b** (1.14 g, 4 mmol). The product obtained was called 4-(iodo ethynylene) phenylene ferrocene (**4b$_1$**). The yield of the product was 35%. ^{1}HNMR ($CDCl_3$, 400 MHz) δ_H 7.36 (2H, d, $J_{H\text{-}H}$ = 2.0 Hz,C_6H_4), 7.23 (2H, d, $J_{H\text{-}H}$ = 8.0 Hz,C_6H_4), 4.61 (2H, t, $J_{H\text{-}H}$ =1.8 Hz, C_5H_4), 4.31 (2H, t, $J_{H\text{-}H}$ = 1.6 Hz,C_5H_4), 4.00 (5H, s, C_5H_5); ^{13}CNMR ($CDCl_3$, 100 MHz) δ_C 140.5 (Ph), 132.2 (Ph), 125.6 (Ph), 120.4 (Ph), 94.3 (Ph-C≡), 83.9 (C≡C), 69.7 (C_5H_4), 69.6 (C_5H_4), 69.3 (C_5H_4), 66.5 (C_5H_4). MS: 414 [M^+]. Analytical calculation for $C_{18}H_{13}FeI$ C, 52.47%; H, 3.18%; Found: C, 52.75%; H, 3.48%.

Repeating the above experiment, another coupling compound designated **4b** was isolated as a brown powder using hexane/chloroform (3/1) as the eluent. The yield of the product was 30%.^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.45 (2H, d, $J_{H\text{-}H}$ = 2.0 C_6H_4), 7.43 (2H, d, $J_{H\text{-}H}$ = 8.0 C_6H_4), 4.67 (2H, d, $J_{H\text{-}H}$ = 2.0 C_5H_4), 4.37 (2H, d, $J_{H\text{-}H}$ = 1.8 C_5H_4), 4.05 (5H, s, C_5H_5); ^{13}CNMR ($CDCl_3$, 100 MHz) δ_C 141.0 (Ph), 132.5 (Ph), 125.8 (Ph), 118.8 (Ph), 82.1 (Ph-C≡), 76.6 (C≡C), 73.6 (C_5H_4), 69.8 (C_5H_4), 69.6 (C_5H_4), 66.6 (C_5H_4). MS: 570 [M^+]. Analytical calculation for $C_{36}H_{26}Fe_2$ C, 75.58%; H, 4.50%; Found: C, 75.85%; H, 4.80%.

3. Results and discussion

*3.1. Synthesis of **4a**, **4b** and **4b$_1$***

4a and **4b** were synthesized according to the route shown in Scheme 2. Sonogashira coupling reaction of 2-methyl-1,3-butadyne-2-ol with **1** produced 2-methyl-4-(3 or 4-(ferrocenyl)phenyl)-3-butdiyn-2-ol (**2**) after conversion of **2** to (3 or 4-ethyny phenylene) ferrocene (**3**) under a strong base. **4a** and **4b** were obtained by

Cadiot-Chodkiewicz coupling reaction [18] of **3a** and **3b** using CuI/TMED as a catalyst. Interestingly, we obtained **4b$_1$** during **4b** synthesis. Wai-Yeung et al. [16] obtained **4b** through simultaneous oxidative coupling of 4-ethynylphenyl ferrocene in the presence of a trace amount of atmospheric O_2 and studied the crystal structure of this compound. Hay used CuI as an oxidizing agent [19] in the larger-scale preparative examples. Thus, we believe that the iodide anion is oxidized into iodine to produce **4b$_1$** [20] , which undergoes a coupling reaction to produce **4b**.

*3.2. Crystal Structures of **4a** and **4b$_1$***

X-ray crystallography images of the molecular structures of **4a** and **4b$_1$** are illustrated in Figs. 1 and 2, respectively. The crystal structure data and important bond parameters, along with selected dihedral angles, are tabulated in Tables 1–3. The structure of **4a** reveals a 1,3-butadiyne linear chain with two ferrocenylphenyl substituents in positions 1 and 4 of the chain. Each ferrocenylphenyl moiety is located on opposite sides of the mean plane and C_5H_4 rings, with a symmetry center at the mid-point of the C(18)-C(18A) bond. The C(17)–C(18) bond is 1.190(9) Å, whereas the C(18) –C(18A) bond [1.3746(35) Å] distance is similar to that observed in 1,4-diferrocenyl-1,3-butadiyne [21] [1.198(4) and 1.373(3) Å] and **4b** [16] [1.184(8) and 1.391(14) Å], respectively.

When viewed along the crystallographic *a* axis, the structure of **4a** resembles stacks(Fig. S1see the supporting information). The presence of a layer-by-layer stacking arrangement is evident. The carbon-to-carbon distance (dCC) recommended for 1,4-propagation during polymerization is 6.0108(44) Å (Fig. 3). This distance is larger than the upper limit of the geometrical criteria for polymerizability (Scheme 1, d < 5 Ǻ). Thus, it is too far way from one another for diacetylenic units to undergo topochemical polymerization.

Each molecule of **4b$_1$** consists of a ferrocene unit and an iodine acetylene group [C(17)–C(18) = 1.180(7) Å] appended to the phenylene group ring in the 1,4-position. However, the structure of **4b$_1$** is different from that of **4a** in that DAs now pile up in stacks (Fig. S2 see the supporting information).

In these cases, the cyclopentadienyl rings of the ferrocenyl group are essentially planar and the tilt angles lie within the narrow range of 0.1°–1.8°. No intermolecular interactions were observed in the crystal lattices of the complexes.

3.3. Electrochemical tests

The electrochemical behavior of **4a**, **4b** and ferrocene at the GCE electrode were investigated using cyclic voltammetry (CV). Initial CV scans from 0.0 to 1.1 V showed only one well-defined and stable redox wave, which corresponds to the Fc^+/Fc redox process. The electrochemical parameters of the complexes are summarized in Table 4. The formal potentials [$E^0 = (E_{pa} + E_{pc})/2$] of **4a** and **4b** (0.514 V, 0.513 V) are very close, which indicates that the ferrocene subunits in both cases are in equivalent environments. The two compounds undergo a single-step two-electron redox reaction. The formal potentials of **4a** (**4b**) also shift to more positive potentials compared with that of ferrocene, which suggests that unsaturation of the ethynyl bridge prevents the removal of electrons in the complexes [22].

3.4. Solid-state polymerization

3.4.1. XRD studies

The XRD patterns of **4a** and the corresponding polymer after UV irradiation (254 nm) and heating (120 °C) is shown in Fig. 4. The sharp XRD peaks of **4a** at a low diffraction angle (2θ = 5°) indicate its crystalline nature. After UV irradiation or heating for 30 min, the monomer crystalline peaks completely disappeared. These data support the large movement of the monomer units from their lattice points to decrease the crystallinity in the course of the solid-state polymerization. Similar spectral and XRD changes during UV irradiation or annealing to those of **4a** were also observed for **4b** (Fig. S3 see the supporting information), suggesting that these monomers polymerize in a similar by manner in the solid state.

3.4.2. UV spectroscopy

UV spectra of the monomers were measured before and after UV irradiation. As shown in Fig. 5, three UV absorption peaks of **4a** appear at 292, 314, and 334 nm; these peaks arise from π-π^* electronic transitions of the relevant organic groups [16]. The absorbance of the peaks decreased and shifted toward longer wavelengths with increasing irradiation time. However, although the absorption tail became broader and extended nearer the infrared region, no obvious absorption peak was observed at long wavelengths. These results suggest that solid-phase polymerization does not proceed via 1,4-addition; instead, polymerization may occur through some irregular pathway to react with C≡C bonds. UV light may be unable to penetrate through the crystals because of the polymers produced on the complex surfaces.

Sample (**4a**) was pelletized and heated at different temperatures (from 80 °C to 120 °C) in an oven before annealing. The color of the samples changed from deep red to nearly black during polymerization when heated above 80 °C (Fig. 6). This finding is inconsistent with the expected color of 1,4-addition polymerization reaction products [23]. The products were taken out of the oven at certain time intervals and their UV spectra were recorded. Bands at 292, 314, and 334 nm, indicating conjugated phenylferrocenyl groups, became weak and the absorption tail extended toward the long-wavelength region, where no absorption peak of polydiacetylene was observed, and broadened. This result proves that polymerization takes place with the extension of π-conjugation, which indicates that solid-state polymerization occurs through a mechanism inconsistent with that of 1,4-addition. Spectral changes similar to those of **4a** were observed during UV irradiation and annealing of **4b**, which indicates that **4b** polymerizes in the same manner (Fig. S 4-5 see the supporting information)

3.4.3. Micrographical study

Fig. 7 shows optical micrographs of **4a** obtained before and after heating for 30 min. The polymer shows a regular round loop. We propose that the polymer aggregates and assembles to form a certain regular shape.

4. Conclusions

We have successfully synthesized two diacetylenes functionalized with phenyl ferrocene moieties. **4b$_1$**, an important intermediate for **4b** synthesis, was also obtained. The phenyl ferrocene side groups of **4a** and **4b** were linked directly to the diacetylene backbone to obtain maximum π-conjugated effects. The two compounds underwent a single-step two-electron redox reaction. The crystal structure of **4a** reveals inhibition of topochemical polymerization. The *meta* and *para* positions of the diacetylenes indicate a polymerization pattern inconsistent with that of 1,4-addition, which demonstrates the importance of steric factors in solid-state polymerization reactions.

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Figure Captions

Scheme1 Solid-state polymerization of diacetylene (d <5Ǻ, D<4Ǻ and $\varphi \approx 45^\circ$).

Scheme 2 Syntheses of compounds **4a** and **4b**.

Fig.1. An ORTEP diagram of **4a** with a probability of 50%.

Fig. 2. An ORTEP diagram of $\mathbf{4b_1}$ with a probability of 50%.

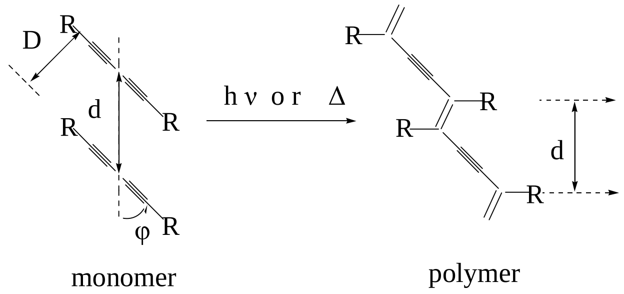
Fig. 3. The carbon-carbon distance (dCC) of **4a** in the crystalline state for 1,4-propagation during polymerization.

Fig. 4. Powder XRD patterns of 4a(a). its partial polymer obtained by UV irradiation 254 nm (b) and by heating at 120°C for 30min (c).

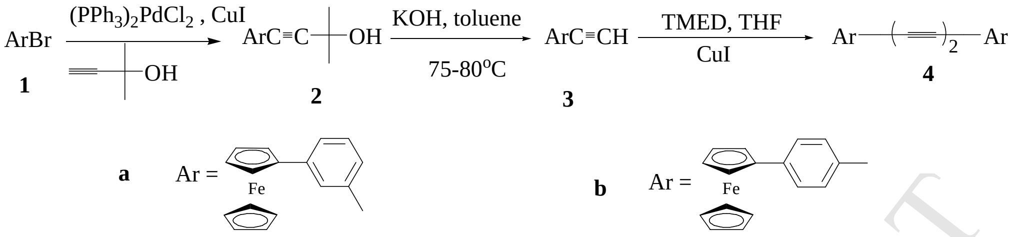
Fig.5. UV spectra of **4a** cast film by irradiated at 254 nm with different time.

Fig.6.UV spectra of **4a** cast film heated at 80℃at different time.

Fig.7.Optical micrograph of **4a** cast film beforeand after heating for 30min.



Scheme1 Solid-state polymerization of diacetylene (d <5Å, D<4Å and $\varphi \approx 45^{\circ}$).



Scheme 2 Syntheses of compounds **4a** and **4b**.

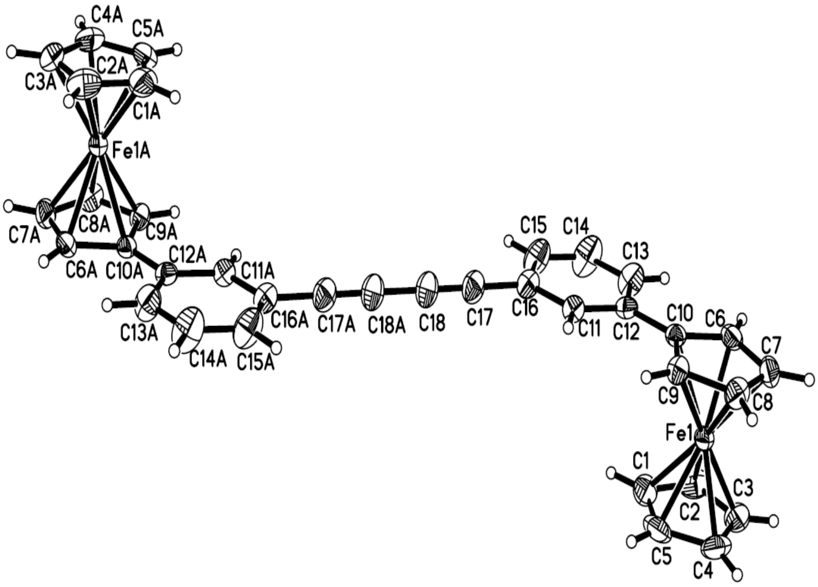


Fig.1. An ORTEP diagram of **4a** with a probability of 50%.

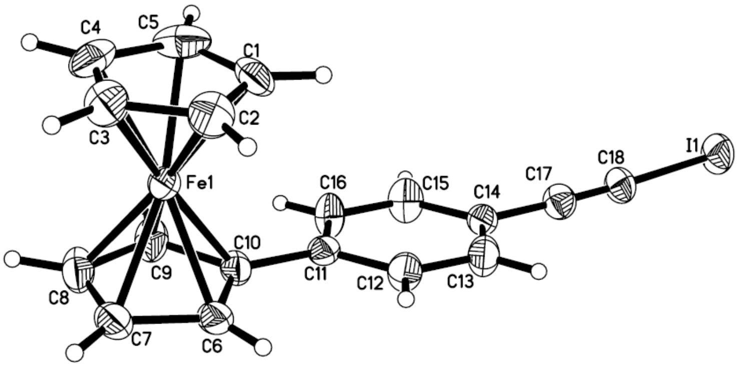


Fig. 2. An ORTEP diagram of $\mathbf{4b_1}$ with a probability of 50%.

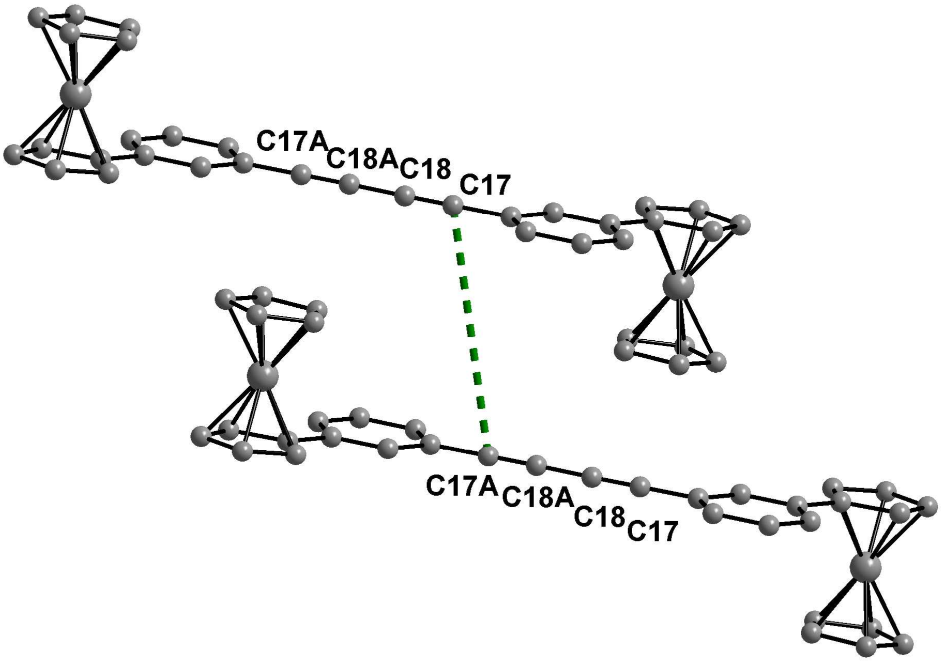


Fig. 3. The carbon-carbon distance (dCC) of **4a** in the crystalline state for 1,4-propagation during polymerization.

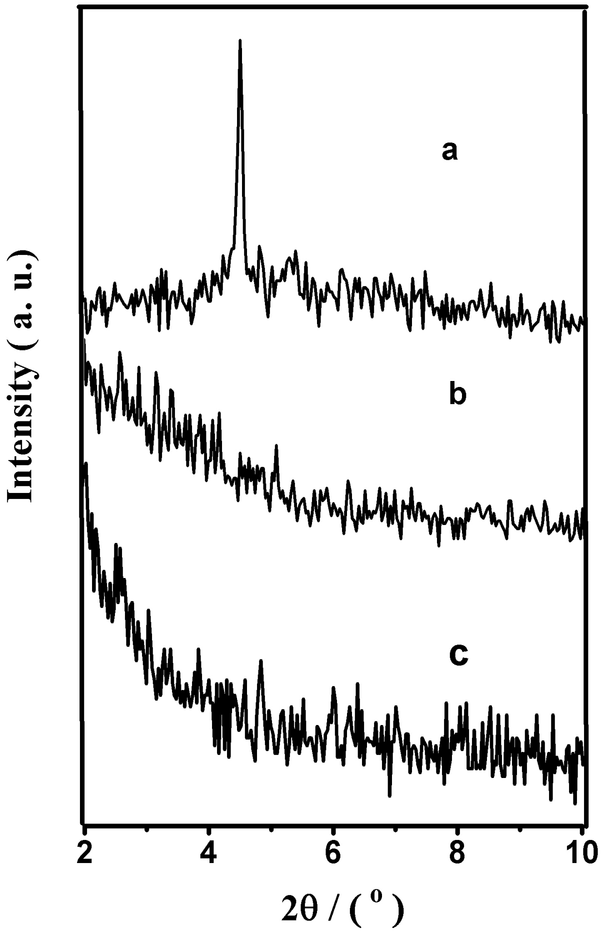


Fig. 4. Powder XRD patterns of **4a**(**a**). its partial polymer obtained by UV irradiation 254 nm (**b**) and by heating at 120°C for 30min (**c**).

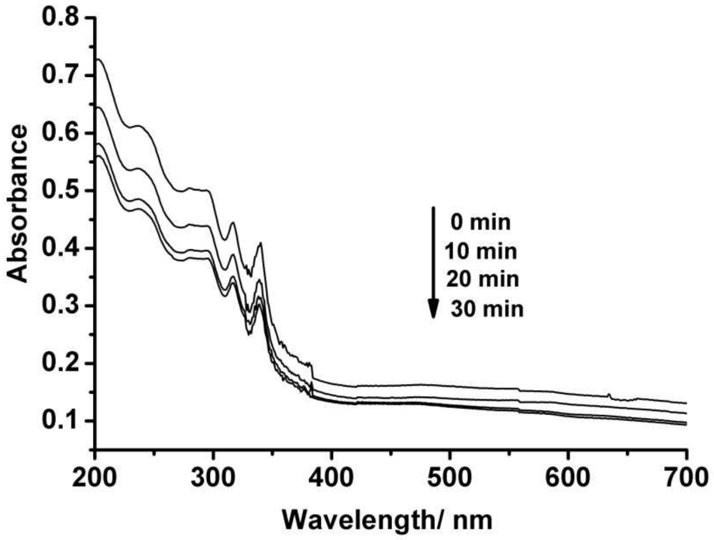


Fig.5. UV spectra of **4a** cast film by irradiated at 254 nm with different time.

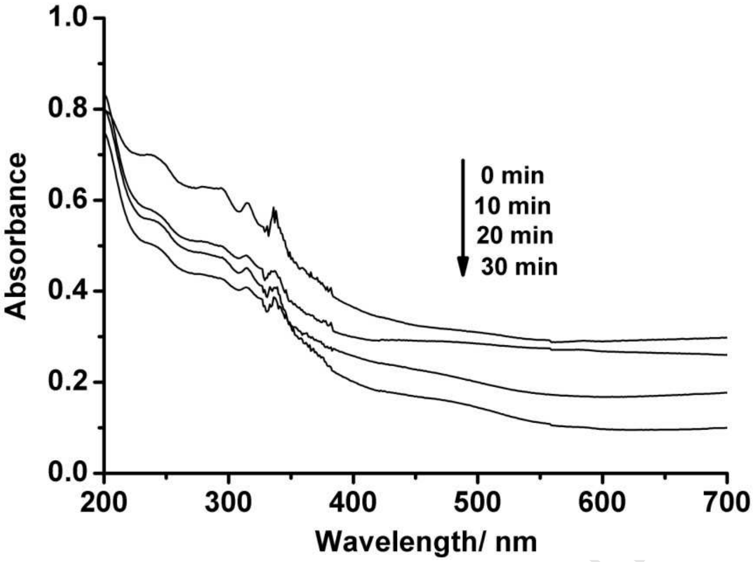


Fig.6. UV spectra of **4a** cast film heated at 80℃at different time.

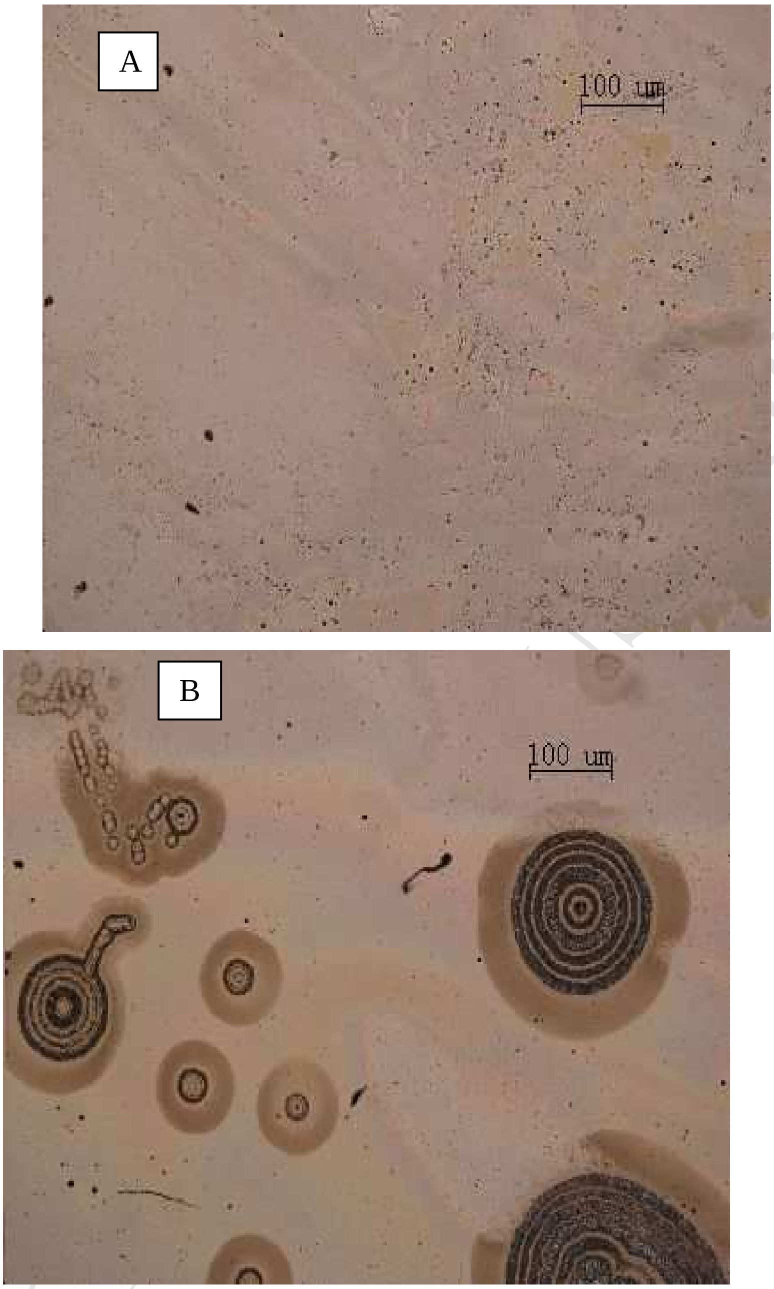


Fig.7. Optical micrograph of **4a** cast film before(A) and after (B) heating for 15min.

Table 1 Summary of Crystal structure data for complexes **4a** and **4b$_1$**

	4a	**4b$_1$**
Formula	$C_{36}H_{26}Fe_2$	C18 H13 FeI
*M*r	570.27	412.03
crystal size (mm)	0.40 x 0.20 x 0.20	0.18 x 0.16 x 0.16
a (Å)	7.9868(6)	15.7092(4)
b (Å)	17.0952(13)	13.4346(4)
c (Å)	20.1909(13)	14.4912(4)
α (°)	90	90
β (°)	90	97.224(2)
γ (°)	90	90
U(Å^3)	2756.8(4)	3034.04(15)
Z	4	8
space group	Pbca	P2(1)/c
D_{calc} (g cm^{-3})	1.374	1.804
M(Mo-K$_a$) (mm^{-1})	1.075	3.015
θ range (°)	2.99-26.37	2.97-26.37
Number of data collected	7919	13923
Number of unique data	2810	6188
Observed reflections [$I > 2\sigma(I)$]	2145	4423
No. of parameters	172	361
R_1, wR_2 [$I > 2\sigma(I)$]	0.0377 0.0793	0.0433 0.0825
R_1, wR_2 (all data)	0.0555 0.0874	0.0703 0.0939
peak/hole (e·Å^{-3})	0.189/ -0.346	0.576 / -0.816

Table 2 Selected bond lengths (Å) and angles(°) for complexes **4a**.

Fe (1)-Cp	1.6345
Fe (1)-C_5H_4	1.6450
C(17)-C(18)	1.190(9)
C(18)-C(18)	1.3746(35)
Dihedral angles (°) between planes	
A and B	1.0
A and C	2.8
B and C	2.2

Planes: A, C(1)- C(2)- C(3)-C(4)-C(5); B, C(6)- C(7)- C(8)-C(9)-C(10); C, C(11)-C(12)- C(13)-C(14)-C(15)-C(6).

Table 3 Selected bond lengths (Å) and angles(°) for complexes **4b$_1$**.

Fe (1)-Cp	1.6359
Fe (1)-C_5H_4	1.6414
C(17)-C(18)	1.180(7)
Dihedral angles (°) between planes	
A and B	0.1
A and C	7.3
B and C	7.3

Planes: A, C(1)- C(2)- C(3)-C(4)-C(5); B, C(6)- C(7)- C(8)-C(9)-C(10); C, C(11)-C(12)- C(13)-C(14)-C(15)-C(6).

Table 4 Electrochemical data[a] for ferrocene and ferrocene derivatives

Compound	E_{pa}/V	E_{pc}/V	ΔE^{b}_{p}/V	$E^{0\,b}$ /V	i_{pc} / i_{pa}
Fc	0.541	0.418	0.123	0.479	1.01
4a	0.577	0.445	0.132	0.514	1.32
4b	0.606	0.419	0.185	0.513	1.20

[a] All potentials are referred to the saturated calomel electrode (SCE) in CH_2Cl_2 + 0.1 mol/L tetra-n-butylammonium hexafluorophosphate (TBHP) solution, v=100 mV/s.

[b] $\Delta E_p = (E_{pa} - E_{pc})$, $E^0 = (E_{pa} + E_{pc})/2$

Highlights

- synthesis and structural characterization of two new compounds, namely, 1,4-bis(3 ferrocenylphenyl)-1,3-butadiyne and 4-(iodo-ethynylene) phenylene ferrocene.
- The acetylene complex (4-(Iodo ethynylene) phenylene) ferrocene) was an important intermediate for the synthesis of 1,4-bis(4-ferrocenylphenyl) -1,3-butadiyne.
- The solid-state polymerization properties of two binuclear complexes were investigated by UV-vis spectroscopy, powder XRD and optical microscopy.

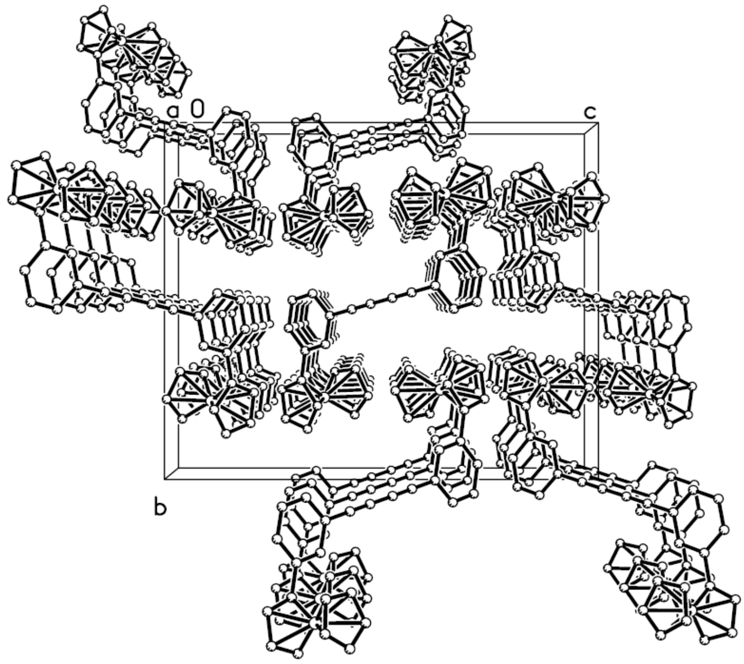


Fig. S1.View along the a axis showing the organization of **4a** in the crystalline state.

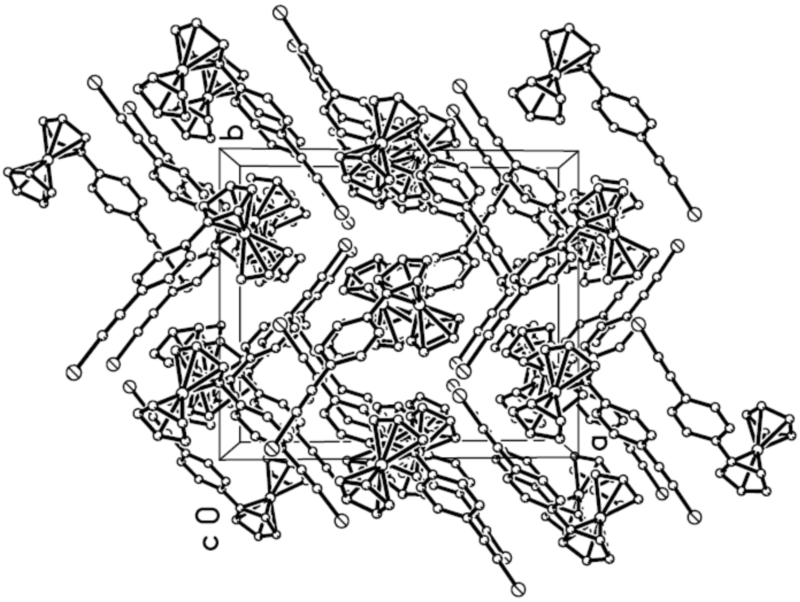


Fig. S2. View along the c axis showing the organization of **$4b_1$** in the crystalline state.

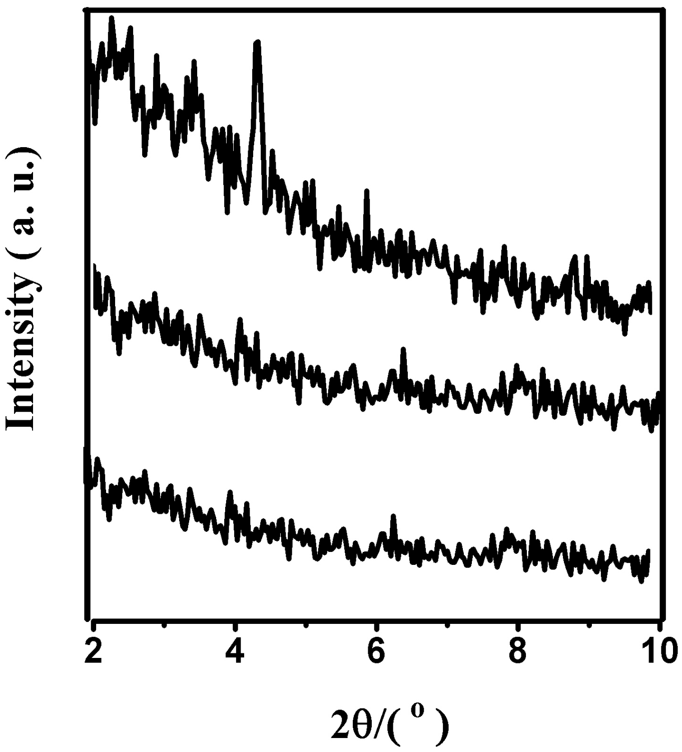


Fig. S3. Powder XRD patterns of **4b** (**a**). its partial polymer obtained by UV irradiating at 254 nm (**b**) and by heating at 120°C for 30min (**c**).

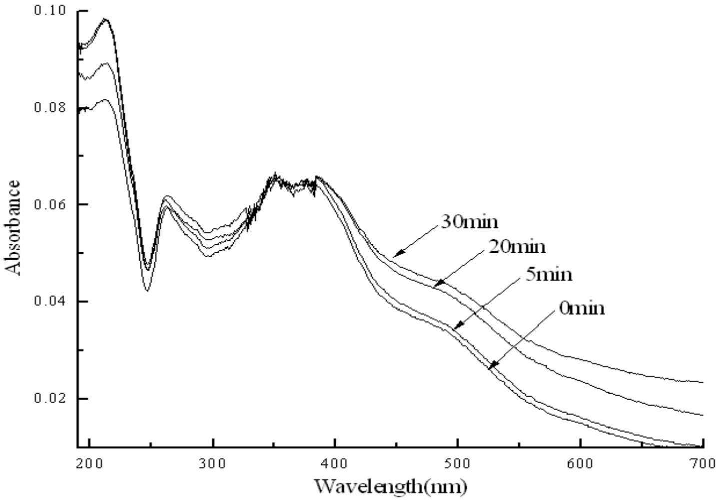


Fig. S4. UV spectra of **4b** cast film irradiated by 254 nm at different time.

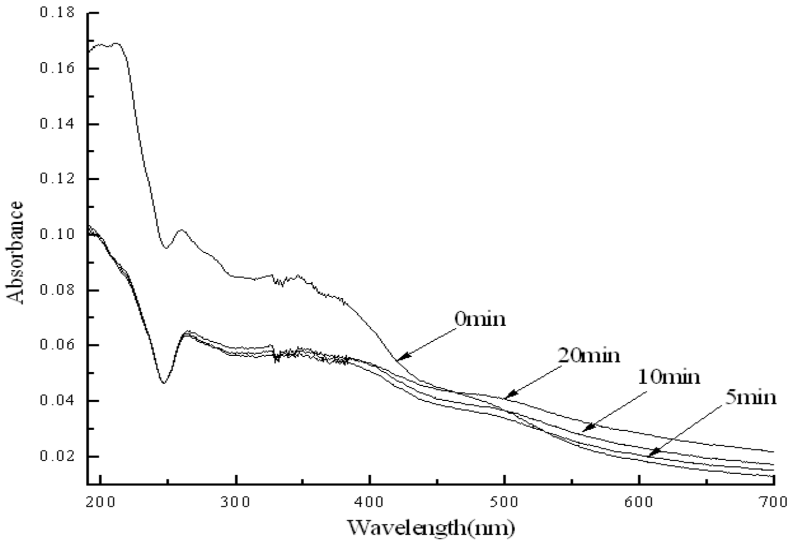


Fig. S5. UV spectra of **4b** cast film heated at 80℃at different time.