Fast and inexpensive synthesis of pentacene with high yield using 6,13-pentacenequinone as precursor

María L. Mota [a, b, *], Bibiana Rodriguez [b], Amanda Carrillo [b], Roberto C. Ambrosio [c], Priscy A. Luque [d], Marcela Mireles [e], Israel Vivaldo [c], Manuel A. Quevedo [f]

[a] CONACYT, Universidad Autónoma de Ciudad Juárez, C.P 32310, Ciudad Juárez, Chihuahua, Mexico
[b] Instituto de Ingeniería y Tecnología, Universidad Autónoma de Ciudad Juárez, Ave. Del Charro 610, C.P 32310, Ciudad Juárez, Chihuahua, Mexico
[c] Faculty of Electronics, Benemérita Universidad Autónoma de Puebla, C.P 72000, Puebla, Mexico
[d] Universidad Autónoma de Baja California FIAD, C.P 22860, Ensenada, B. C, Mexico
[e] Rochester Institute of Technology, 1 Lomb Memorial Dr. Rochester, NY 14623, USA
[f] Universidad de Sonora. Hermosillo, Sonora, C.P. 83000, Mexico

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ABSTRACT

Pentacene is an important semiconductor in the field of organic electronics. In this work is presented an alternative synthesis procedure to obtain pentacene from 6,13-pentacenequinone as a precursor. Synthesis of pentacene was performed in two reactions, Diels-Adler cycloaddition of 6,13-pentacenequinone followed by 6,13-pentacenequinone reduction to pentacene, employing $LiAlH_4$ as reducing agent. The products were characterized by Fourier Transform Infrared Spectroscopy (FTIR), 1H-Nuclear Magnetic Resonance Spectroscopy (1H-NMR), X-Ray Diffraction (XRD), Thermogravimetric Analysis (TGA) and Ultraviolet—Visible Spectroscopy (UV-VIS). In this work, 6,13-pentacenequinone was synthetized with a high yield (55%) using an alternative method. The optimization process resulted in an overall reduction of reaction time while exhibiting high yield. The method presented here provides an affordable pentacene synthesis route with high purity, which can be further applied for research and development of organic electronic applications.

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1. Introduction

Pentacene is a well-known p-type semiconductor in the organic electronics field. Its high field effect mobility —around 2.2 cm^2 V^{-1} s^{-1} [1] and stability make it a remarkable material in the development of organic transistors. The first successful synthesis of pentacene was reported in 1929 by Clar and collaborators. Although, yield was not reported, pentacene was obtained via dehydrogenation of 6,14-dihydropentacene using phenantraquinone [2]. Since the implementation of organic semiconductors in large area electronics, specifically in light switching speed transistors, pentacene became an alternative to amorphous silicon due to its similar performance to inorganic semiconductors [3]. Moreover, the use of organic semiconductors greatly reduces the processing temperatures, hence enabling the use of polymeric substrates which are applied in flexible electronic devices. In order to further advance the development of such devices, active organic materials such as pentacene must be researched through simple and low cost routes. Cava and collaborators have reported that one of the precursors of pentacene is 6,13-pentacenequinone, as a byproduct in the synthesis of quinone compounds. The synthesis was conducted using TBOX as a reactive intermediate that cyclizes spontaneously with 1,4-benzoquinone in the presence of sodium iodide; 6,13-pentacenequinone was obtained with low yield (7%) [4]. Bruckner and Tomasz synthetized pentacene by continuous aldol condensations with two equivalents of o-phtalaldehyde and one equivalent of 1,4-ciclohexanodione. A mixture of Al in cyclohexanol or Al/HgCl$_2$ mixture in cyclohexanol/carbon tetrachloride. This synthesis required a long reaction time (48 h) involving toxic reactants (HgCl$_2$) [5]. (see Scheme 1)

Another example is the synthesis of pentacene with 92% yield reported from 5,14–dihydropentacene in the presence of Pd/C to produce hydrogenation [6]. Very high yield was obtained at the

* Corresponding author.
E-mail addresses: mdllmotago@conacyt.mx (M.L. Mota), al131353@alumnos.uacj.mx (B. Rodriguez), amanda.carrillo@uacj.mx (A. Carrillo), roberto.ambrosio@correo.buap.mx (R.C. Ambrosio), pluque@uabc.edu.mx (P.A. Luque), mmrbme@rit.edu (M. Mireles), israelvivac@gmail.com (I. Vivaldo), mquevedo@utdallas.edu (M.A. Quevedo).
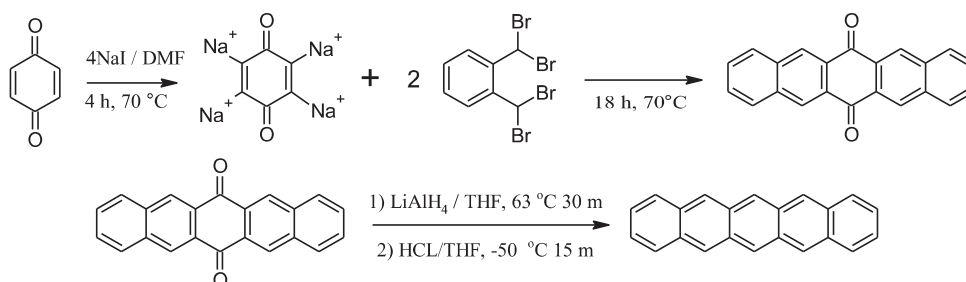
Scheme 1. Synthesis of pentacene. (a) Synthesis of 6,13-pentacenequinone, (b) 6,13- pentacenequinone reduction to pentacene.

expense of long reaction time (3 days) and use of a toxic catalyst. Vets and collaborators reported a synthesis route with 6,13-pentacenquinone using LiAlH$_4$ for the reduction of the carbonyl group to produce 6,13-pentacenediol followed by acid dehydrations to produce pentacene with a 54% yield. The procedure was done for each carbonyl group, first with LiAlH$_4$ to reduce the carbonyl groups to alcohol and then with HCl to expel water from the molecule [7]. The syntheses described in this introduction, involve the presence of a metallic catalyst (HgCl$_2$, PD/C), long reaction time, inaccessible and expensive reactants or equipment. In this manuscript, we report the results on the synthesis of 6,13-pentacenequinone and pentacene. As reported by Clar and collaborators, 6,13-pentacenequinone was prepared from a Diels-Addler adduct; however, a higher yield (55%) was achieved through he optimization of reaction conditions and purification protocol of the final product. Pentacene was prepared by performing the reduction of both 6,13-pentacenequinone carbonyl groups in only one step, avoiding the isolation of a highly unstable intermediate (6,13-pentacendiol). The final product was obtained with a 51% yield. The advances presented in this work allow the simple and low cost production of pentacene enabling research laboratories to advance the organic and flexible electronics field.

2. Results and discussions

2.1. Chemical characterization

The attenuated total reflection of Fourier Transform Infrared (FTIR-ATR) spectrums of 6,13-pentacenequinone and pentacene are shown in Fig. 1. For the 6,13-pentacenequinone the principal
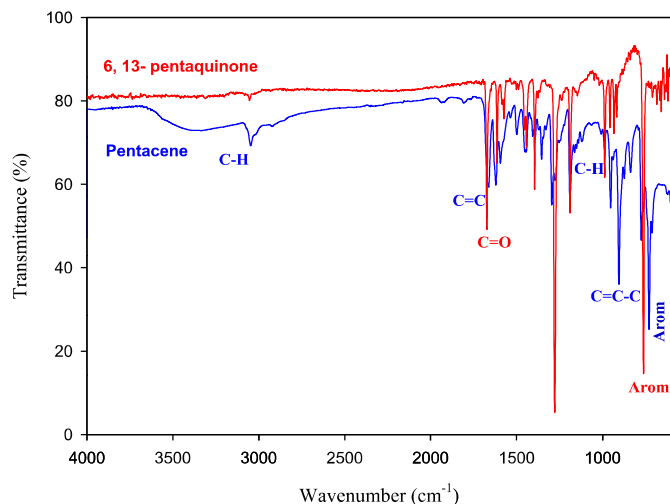
identification of conjugation with two carbonyl (C=O) groups in the same ring results in delocalization of the π electrons of both unsaturated groups. Conjugation of phenyl groups may cause a reduction in frequency of C=O band in the 1672 cm^{-1} region, with extended conjugation. Steric effects of C=O groups reduces the coplanarity of the conjugated system.

The common region for carbonyl absorption band shows the two signature peaks; overtone of C=O stretch at 3350 cm^{-1} and C=O stretch peak at 1672 cm^{-1}. Other absorption peaks in the 6,13-pentacenequinone spectrum are present and associated to a stretch of C—H aromatic bond at 3054 cm^{-1}, the C=C stretch corresponding to the ring consist of peaks at 1612 cm^{-1}, 1443 cm^{-1} and 1396 cm^{-1}. The absorption of bending vibrations in the aromatic ketones (C—C=O—C) absorb at a higher frequency at 1277 cm^{-1} than 1230-1100 cm^{-1} region as the literature remark and an aromatic ring stretch of C=C—C at 758 cm^{-1} [8,9]. For pentacene ^{1}H NMR spectroscopy was utilized to verify the structure and purity of the synthesized pentacene (see supplementary material). Furthermore, FTIR was also employed and the results can be seen also in Fig. 1. Pentacene spectrum exhibited bands assigned to vibration of C=C conjugated bond around 1632 cm^{-1}, a strong vibration stretch of aromatic C—H bond at 841 cm^{-1}, and strong signals corresponding to the aromatic conjugated C=C—C bond from 671 cm^{-1} to 601 cm^{-1}, according to IR peaks identifications previously reported [10]. A peak for O—H stretching was observed at 3425 cm^{-1} due to the presence of moisture in the pentacene sample.

2.2. Thermal stability

The TGA thermograms corresponding to 6,13-pentacenequinone and pentacene are depicted in Fig. 2. Thermogravimetric analysis revealed that the 6,13-pentacenequinone compound is thermally stable up to 330 °C, the latter is due to its intermolecular π- π stacking arrangement.

Yuan and collaborators reported a commercially available 6,13-pentacenequinone compound to be thermally stable up to 360 °C [11]. Furthermore, the TGA results for the 6,13-pentacenequinone compound synthesized in this work showed a singular deflection, indicating a simple process of decomposition which suggests a high purity obtained. The TGA thermogram obtained for pentacene indicates a dynamic process of degradation showing two important deflections. As shown, the pentacene sample starts to decompose around 150 °C with 7 wt% loss associated to CO removal. However, the pentacene shows to be stable up to 305 °C, before thermal decomposition occurs as a vaporization process [12].

2.3. Structural characterization

The structural analysis of 6,13 pentacenequinone and pentacene was performed using XRD (Fig. 3).
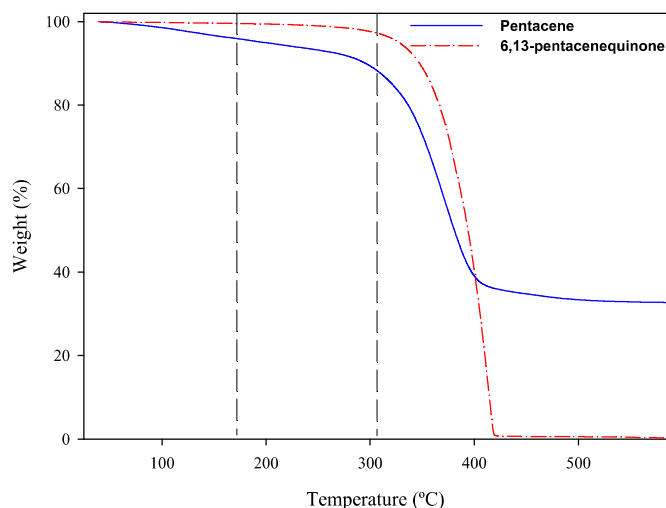
For 6,13-pentacenequinone (Fig. 3a) the diffraction peaks

Fig. 1. FTIR Spectrum of 6,13-pentacenequinone and pentacene.

Fig. 2. TGA thermogram for 6,13-pentacenequinone and pentacene.

located at 11.7, 14.6, 23.6, and 27.7° match to the (002) (012), (112), and (104) diffraction planes reported in the JCPDS database (JCPDS no. 47-2123) and [8,13—15]. The XRD pattern of pentacene is shown in Fig. 3b. The diffractogram shows five distinct Bragg diffraction peaks located at 2θ = 5.9, 12.1, 18.9, 23.7, 27.9° that correspond to the (001), (020), (003), (004) and (005) diffraction planes respectively [16,17].

2.4. Optical characterization

The UV—Vis absorbance spectrum for 6,13-pentacenequinone is shown in Fig. 4a. The 6,13-pentacenequinone was measured in chloroform. The absorbance peaks observed at 388 and 404 nm correspond to the $\pi-\pi^*$ and $n-\pi^*$ transitions, with a band gap of 2.9—2.96 eV respectively. The peak centered at 388 nm is attributed to an aromatic ring according to reference [11], and the peak centered at 404 nm is attributed to the carbonyl groups. The positions of these two peaks have been observed in these range before [18,19], however the intensity of n-p* is at least one order of magnitude lower than p-p*, the difference observed here with respect to other reports [17,18] may be due to higher purity of the 6-13 pentacenequinone obtained in this work, as demonstrated by RMN. The low band gap value reported here can be a result of the

modified synthesis route which avoids diol reduction.

In this work is reported the optical behavior of pentacene in two different solvents with different polarity. In this way is possible to observe changes in the maximum absorption according to solvation process [19]. The main absorption peak found is related to diketone at 404 nm (marked in Fig. 4a) which disappeared in the synthesis process to obtain pentacene, and another characteristics peaks are emerged at 535 and 579 nm and 531 and 575 nm, it is due when the pentacene is dispersed in 1-2-dichlorobenzene or chloroform respectively, due to the extended pentacene's π-conjugation ($\pi-\pi^*$ transitions) (Fig. 4b). Furthermore, a strong absorption bands at 326—346 nm and 313—400 nm ranges are present as vibronic progressions in the same analysis dispersions. In pentacene UV—Vis absorption spectrum a higher absorption assigned to the π-π* is observed when chloroform is used as a solvent than 1-2 dichloro-benzene, thus is possible inferred that pentacene in chloroform provide a better expression in optical studies by UV—Vis related to its behavior reported by others [19]. Similar studies were reported showing red-shifted or hyperchromic effect in the optical study with the use of different common solvents [20].

3. Experimental

3.1. Materials

Anhydrous solvents were purchased from Sigma-Aldrich and used without further purification: Tetrahydrofuran and *N,N*-dime-thylformamide. A $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-o-xylene, *p*-benzoquinone (Sigma-Aldrich) (Aldrich), sodium iodide (Sigma-Aldrich), *N,N*-dimethylformamdide (Sigma-Aldrich), lithium aluminum hydride (Aldrich), hydrochloric acid (37%, J.T. Baker), chloroform (Sigma-Aldrich), sodium sulfite (Aldrich) were recently purchased for this work.

3.2. Synthesis procedure

The synthesis of 6,13-pentacenequinone (PQ) started by substitution of hydrogen atoms for charged sodium ions in the *p*-benzoquinone molecule. Subsequently, $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-o-xylene was added in a molar ratio of 2:1 with respect to *p*-benzo-quinone. An intermediate compound between Na$^+$ and iodide atoms instantly forms as well as double bonds between TBOX and PQ. Purification and drying of the resulting PQ, was followed by solubilization and heating of the compound. The reducing agent
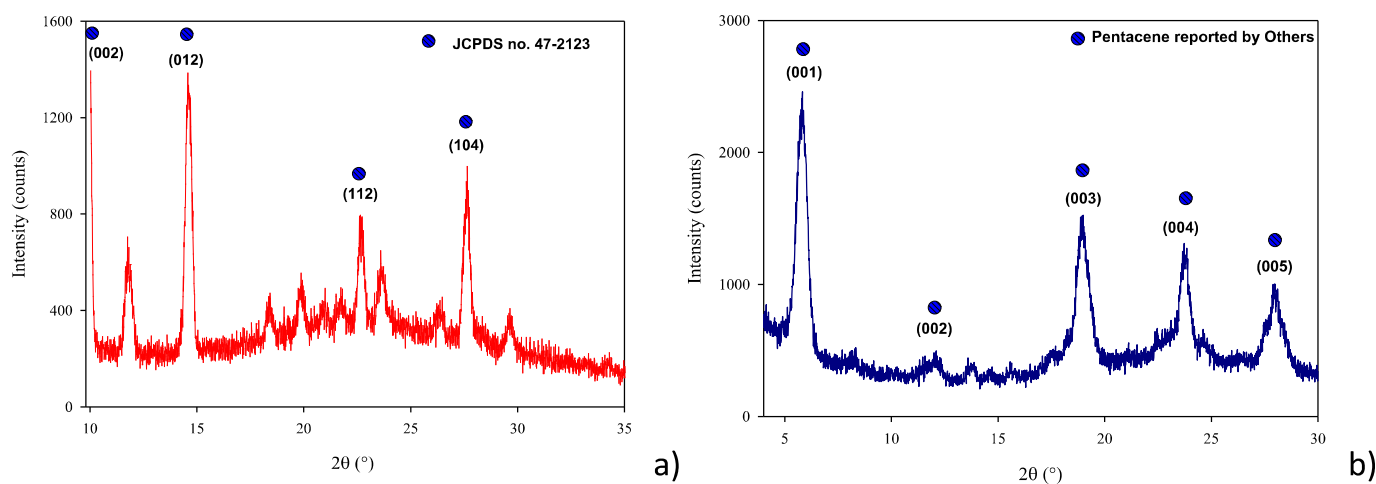

Fig. 3. X-ray diffraction pattern obtained for a) 6,13-pentacenequinone and b) pentacene.
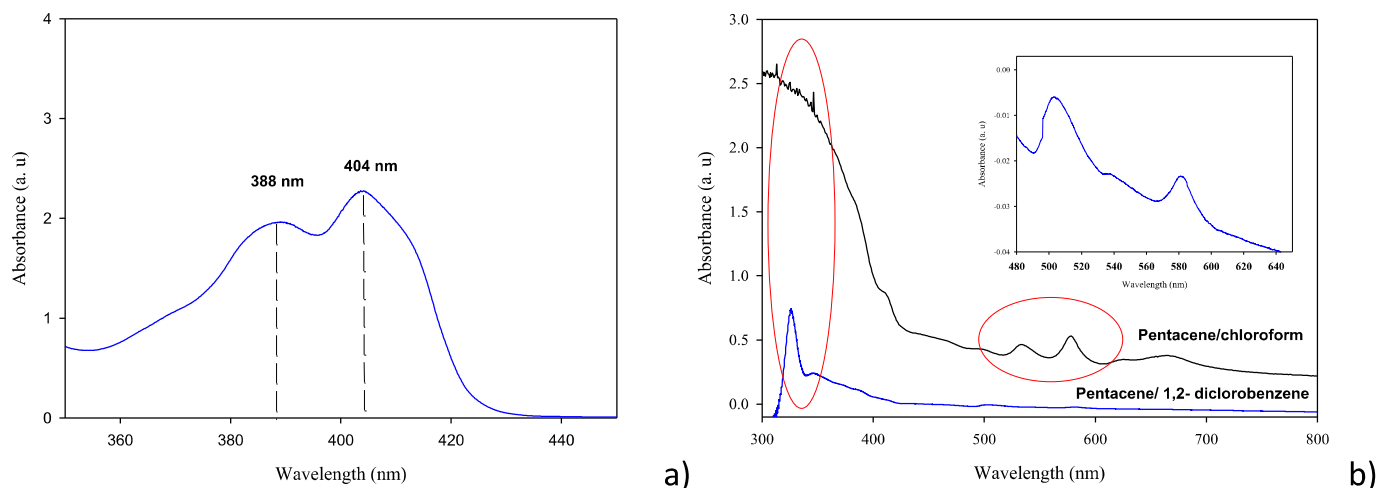
Fig. 4. UV–Vis absorption spectrum for a) 6,13-pentacenequinone and b) pentacene.

LiAlH$_4$ was chosen for this reaction due to its ability to reduce quinoid compounds. Previous methodologies tried prior to this reaction were attempted at room temperature and with slow addition of LiAlH$_4$ but pentacene was not successfully synthesized in measurable weight. Finally, concentrated HCl is added to this mixture to expel hydroxyl functional groups from the molecules as water.

3.3. 6,13-Pentacenequinone

A 500 ml three-necked round-bottom flask (previously cleaned) equipped with stirring bar and argon atmosphere was used to dissolve 0.52 g (4.81 mmol) of p-benzoquinone in 150 ml anhydrous DMF. The reaction mixture was stirred at 200 rpm until a homogeneous solution was achieved. After setting heating bath to 70 °C in a hotplate, 2.88 g of NaI (19.24 mmol) was added to the reaction flask and the mixture was stirred for 2 h. Next, 4.057 g (9.62 mmol) of TBOX were added and the reaction was continued for 18 h. The reaction mixture was cooled to room temperature and 50 ml of ice cold water were added to the reaction. The content was slowly transferred to a Coors Buchner funnel equipped with a Whatman filter paper #1 and rinsed with 0.5 M sodium sulfite and DMF. A bright yellow solid is obtained and dried in an oven at 40 kPa and 25 °C for 24 h. The obtained yield was 28%, 1H-RMN (300 MHz, TDF δ = ppm): 8.99 (s, 2H), 8.14 (m, 4H), 7.75 (m, 4H), 7.28 (s, 4H).

3.4. Pentacene

6,13-pentacenequinone obtained as described in the previous section was reduced to pentacene (PC), this process will be described next. A 500 mL three-necked round-bottom flask equipped with stirring and argon atmosphere (previously cleaned) was used to prepare a suspension of 0.3 g (0.9729 mmol) 6,13-pentacenequinone and anhydrous THF. A heating bath was utilized at 60 °C, under reflux conditions. LiAlH$_4$ (13.1752 mol) was added to the dropping funnel. THF was then transferred with a double tipped needle to the dropping funnel to suspend the reducing agent. The reducing agent was added in a constant streak to the PQ/THF suspension and stirred for 30 min. The system was isolated from light and changed to a cooling dry ice/acetone bath. Cold concentrated HCl (15 ml) (37%) was quickly added to crude reaction mixture via dropping funnel and stirred for 15 min. Finally, the crude reaction solution was poured in a Buchner funnel with a

Whatman filtering paper #6, and the solid product was washed with cold acetone and cold water. A deep blue powder was obtained from this synthesis. Powder was dried under vacuum (-40 kPa) for 48 h. Yield was 51%, 1H-RMN (500 MHz, TDF) δ (ppm) 8.98 (m, 4H), 8.14 (m, 4H), 7.75 (m, 4H), 7.35 (s, 2H).

3.5. Chemical, thermal, structural and optical analyses

The chemical structure of 6,13-pentacenequinone and pentacene were verified by ^{1}H NMR using a 500 MHz Jeol spectrometer (JNM-ECO300) and CDCl$_3$ as solvent. Infrared spectroscopic measurements were carried out using a FTIR Nicolet Is10 infrared spectrometer with a diamond ATR attachment. The thermal stability of compounds was determined in vacuum dried samples and using a thermal analyzer from Dupont Instruments (TGA 951) connected to a nitrogen vector gas with heating rate of 10 °C/min from 30 to 800 °C. The crystalline structure of 6,13-pentacenequinone and pentacene were analyzed in a Rigaku Ultima III X-ray diffractometer with CuKα (λ) = 1.54 Å, operated at 40 kV and 44 mA. The 2θ scan rate was 0.5°/min. The optical properties were studied using a UV/VIS JENWAY 6850 UV/visible spectrophotometer.

4. Conclusions

We have synthesized 6,13 pentacenequinone and pentacene in two reactions a high final yield (55% and 51% respectively). The synthesis route reported in this work simplifies the number of steps by obtaining both 6,13-pentacenequinone and pentacene through a single reduction reaction.

The chemical characterization performed by FTIR and H[1] MNR showed the main peaks corresponding to 6,13-pentacenequinone and pentacene, the purity of the obtained compounds was also confirmed. The XRD pattern allowed determining the phase for 6,13-pentacenequinone and pentacene products and their stability which is in agreement with the literature. The Uv–Vis showed the maximum absorption centered at the expected value for each product. The use of 1-2- chloroform as solvent to disperse pentacene improved the obtained UV–Vis spectra when compared to the use of dichlorobenzene. Both solvents and in different solution-dispersion UV–Vis analysis showed the extended π-conjugation like π–π* transitions mechanism. In summary, the results obtained in this work contribute to the advancement of active organic electronic materials and their application. Additionally, the

advantageous synthesis offered in this work represents a valuable alternative route for the production active organic electronic materials with high yield and high purity at a low cost.

Acknowledgments

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.molstruc.2017.10.070.

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