



# HPU2 Journal of Sciences: Natural Sciences and Technology

journal homepage: <https://sj.hpu2.edu.vn>



*Article type: Review article*

## The synthesis of TCNQ-based material with derivative of leucine amino

Thang-Nguyen Vo<sup>a</sup>, Ngoc-Ha Doan Thi<sup>a</sup>, Duc-Manh Tran<sup>a,\*</sup>

<sup>a</sup>The University of Da Nang - University of Science and Education, Da Nang, Vietnam

### Abstract

A new material,  $\text{Leu}(\text{CH}_3)_4\text{-TCNQ}$ , has been successfully synthesized from Tetracyanoquinodimethane (TCNQ) and amino acid ester, N,N,N-Trimethyl-L-Leucine Methyl ester ( $\text{Leu}(\text{CH}_3)_4^+$ ). This material was characterized by modern physicochemical methods such as: X-ray diffraction technique (XRD), Raman, Infrared (FT-IR) and UV-Vis spectroscopy and voltammetric technique. This result will offering a new direction for the synthesis of new materials from TCNQ and other amino acids.

**Keywords:** TCNQ, material, structure, synthesis, amino acids

### 1. Introduction

Amino acids are the most essential bio-molecules and play an important role in the synthesis of proteins and other bio-molecules. Over the past few years, there have been a number of studies on methods of determining amino acids such as: lysin, histidin, thiocystein and axit glutamic [1]. Organic anions hitherto composed of pyrrol, TCNE (tetracyano-*p*-benzoquinon), DDQ (2,3-diclo-5,6-dicyano-*p*- benzoquinon) and TNF (2,4,5,7-tetranitro-9-florenon) are typical for combination with amino acids to form substances which are capable of exchanging charges and potential for the synthesis of bio-sensors [2,3]. Doing research on new materials based on the TCNQ (Tetracyaniquinondimethane) and its derivatives with metal cations has been carried out over the past time and applied in the fields of electricity, optics, magnetism.

TCNQ is acceptor of one electron with an affinity of about 2,88 eV [4]. Radical anion  $\text{TCNQ}^{\bullet-}$  can be composed by chemical reduction [5,6], optical reduction [7] or electrochemical reduction [8] from TCNQ. Through the process of reduction, a charge exchange reaction occurs, TCNQ is reduced to form  $\text{TCNQ}^{\bullet-}$  anions (confusing) and  $\text{TCNQ}^{\bullet-}$  anions will rearrange in different directions creating many interesting properties such as: semiconducting, magnetic, catalytic...[4, 9].

Although TCNQ has been researched for a long time, there have just been a few studies about synthesis of material from free radical anion of TCNQ and cations of amino acid derivatives recently.

\* Corresponding author. E-mail: [tdmanh@ued.edn.vn](mailto:tdmanh@ued.edn.vn)

<https://doi.org/10.56764/hpu2.jos.2022.1.1.71-79>

Received date: 25-8-2022 ; Revised date: 26-8-2022 ; Accepted date: 30-8-2022

This is licensed under the CC BY-NC-ND 4.0

In 2004, Jiang et al. reported some results of determining color of cysteine by using a molecular complex of dihydroxymethyl-di-(2-pyroly)methane with TCNQ. Padhiyar et al also reported the formation of charge-conversion complexes of four amino acids with TCNQ shown by IR spectroscopy [3]. Previously published studies mainly described the formation of materials between TCNQ and cyclic amino acids. The combination of TCNQ and cyclic amino acids can occur due to the  $\pi$ - $\pi$  interaction between two rings of adjacent radical anion of TCNQ $^{\bullet-}$ , and hydrogen bonding between donor (amino acid) and acceptor (TCNQ). [12]. Along with the series of studies on materials of TCNQ and amino acids. In this article, we report the material synthesis between TCNQ and unbranched amino acid ester, N,N,N-Trimethyl-L-Leucine methyl ester (Firuge 1). The crystal structure of the material and the physicochemical properties in both solution and solid state of charge transfer materials [Leu(CH<sub>3</sub>)<sub>4</sub>]TCNQ were also researched .

## 1. Materials and methods or Experiments

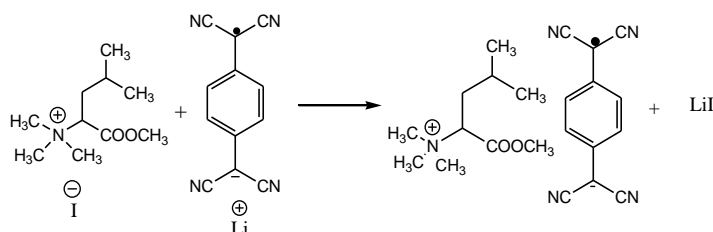
### 2.1. Experiment

#### 2.1.1. Chemicals and instruments

N,N,N-trimethyl-L-Leucine methyl ester iodua, 7,7,8,8-tetracyanoquinondimetan (TCNQ), CH<sub>3</sub>CN, CH<sub>3</sub>COCH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub>, C<sub>5</sub>H<sub>12</sub> are bought from Aldrich (99.99%). TCNQ is recrystallized in CH<sub>3</sub>CN before using, Tetra-n-butylamonihexaflopposphate (Bu<sub>4</sub>NPF<sub>6</sub>) was recrystallized from C<sub>2</sub>H<sub>5</sub>OH three times and dried under vacuum before using. Infrared spectroscopy was measured on Spectrac Diamond ATR. Raman spectroscopy was measured on Raman Renishaw RM2000 spectrometer and UV-Vis spectroscopy was measured on UV Varian Cary 5000- Vis NIR spectrometer, cuvet' length was 1.0 cm. Electrochemical experiments were performed on Bioanalytical Systems (BAS) 100 W device using a three-electrode system: working electrode Au (S = 0,0314 cm<sup>2</sup>), counter electrode Pt, and reference electrode Ag/AgCl. X-ray diffraction data used a Bruker X8 Apex II. The structure was analyzed by using SHELXS-97 software.

#### 2.1.2. Chemical synthesis Leu(CH<sub>3</sub>)<sub>4</sub>TCNQ

1,0 mmol N,N,N-trimetyl-L-Leucin metyl ester iodua was dissolved in 10 mL H<sub>2</sub>O under nitrogen gas condition. A solution of 0,1 mmol of LiTCNQ (synthesized according to [7]) dissolved in 15 mL H<sub>2</sub>O was slowly added to the solution of N,N,N-trimetyl-L-Leucin metyl ester iodua at room temperature (Firuge1).



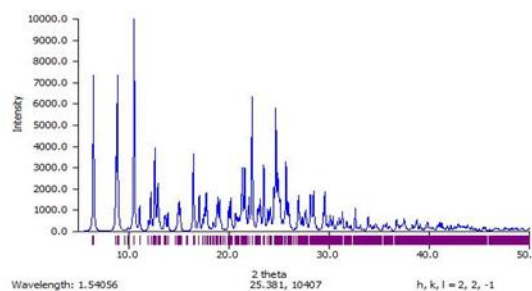
**Firuge 1.** Sythesis of Leucin metyl este with LiTCNQ

A dark brown colored microcrystal was instantly precipitated. After 1 hour, the precipitate was collected by filtration. The precipitate was washed several times with 5 mL diethylene until the yellow colored solution was not remained and dried under vacuum at 40<sup>0</sup>C in 1 day. Dark blue colored monocrystalline of [Leu(CH<sub>3</sub>)<sub>4</sub>]TCNQ was obtained by diffusing n-pentane into the product in aqueous acetone.

### 2.2. Result and discussion

2.2.1. Analyse the crystal structure of [Leu(CH<sub>3</sub>)<sub>4</sub>][TCNQ]

The X-Ray diffraction pattern of Leu(CH<sub>3</sub>)<sub>4</sub>TCNQ is described in Figure 2



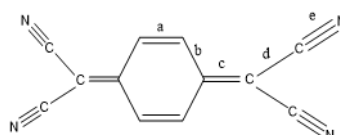
**Figure 2.** The X-Ray diffraction pattern of [Leu(CH<sub>3</sub>)<sub>4</sub>][TCNQ]

The structural analysis of the materials obtained the crystal structure parameters shown in Table 1.

**Table 1.** Data of Crystal Leu(CH<sub>3</sub>)<sub>4</sub>TCNQ

<b>Formula</b>	C <sub>39</sub> H <sub>6</sub> N <sub>8</sub> O <sub>4</sub>
<b>Space group</b>	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<b>Length of unit cell (Å)</b>	<b>a</b> 6.5080(13) <b>b</b> 11.931(2) <b>c</b> 27.908(6)
<b>Angles of unit cell</b>	<b>α</b> 90.00 <b>β</b> 125.12 (4) <b>γ</b> 90.00
<b>Volume of unit cell (Å<sup>3</sup>)</b>	2167.0(7)
<b>Z, z'</b>	<b>Z</b> ; 4 <b>Z'</b> : 0
<b>Coefficient R (%)</b>	13.12

This material crystallizes with crystals which have orthorhombic space groups P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> with unit cell of one [Leu(CH<sub>3</sub>)<sub>4</sub>]<sup>+</sup> cation and one TCNQ<sup>-</sup> anion. Charge displacement ( $\rho^*$ ), calculated from the bond lengths in the TCNQ radical is -1.07 and closes to the -1 charge of the TCNQ<sup>-</sup> radical monoanion (Table 2).



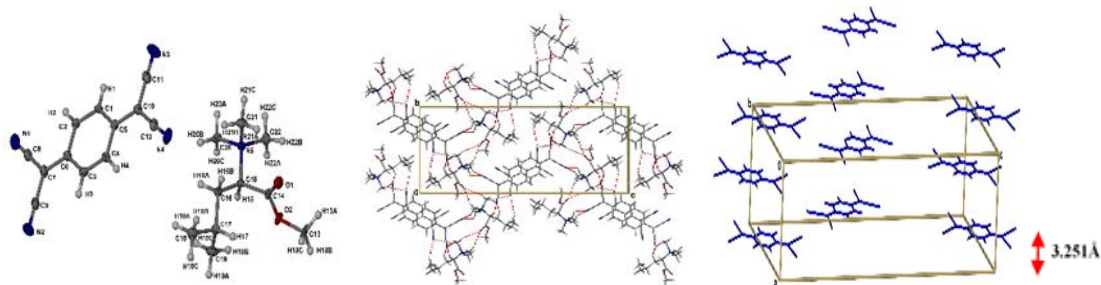
**Table 2.** Main bond lengths of C-C and CN in materials

	a	b	c	d	e	$\rho^*$
TCNQ of material	1,3665	1,4170	1,4150	1,4192	1,1635	-1,07
TCNQ <sup>0</sup> [11]	1,346	1,448	1,374	1,440	1,138	0
TCNQ <sup>-</sup> [11]	1,362	1,424	1,413	1,417	1,149	-1,0

$\rho^*$  is the charge of TCNQ molecule,  $\rho^* = -\frac{r-r^0}{r^1-r^0}$  in which  $r = \frac{c}{b+d}$

Almost every TCNQ<sup>-</sup> radical anion is positioned in the same side of plane and forms  $\pi$  columns stacking along the axis with the distance between two radical anion of 3.251 Å (Figure 3).

$[\text{Leu}(\text{CH}_3)_4]^+$  cations interact with each other through hydrogen bonding of the CH and O group of  $[\text{Leu}(\text{CH}_3)_4]^+$  cations and form a 2D sheet. These  $[\text{Leu}(\text{CH}_3)_4]^+$  cations are linked to the columns of  $\text{TCNQ}^-$  anion by hydrogen bonding between  $-\text{CH}$  group of  $[\text{Leu}(\text{CH}_3)_4]^+$  cation and  $-\text{CN}$  group of  $\text{TCNQ}^-$  anion to form 2D lattice structure.

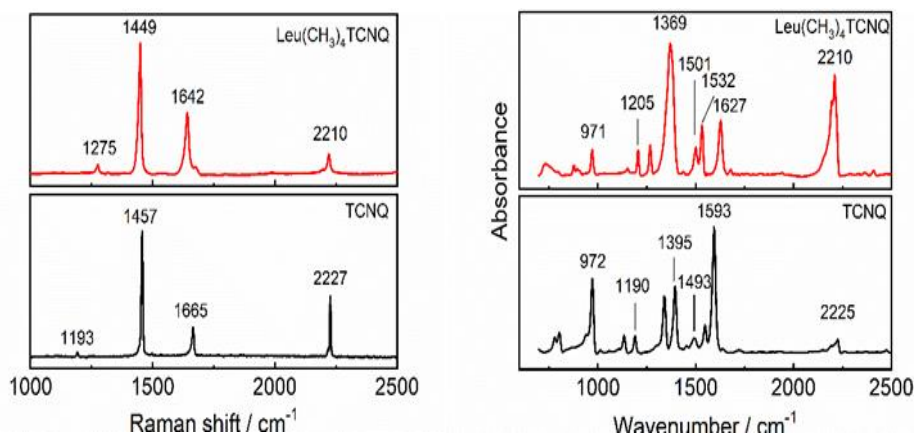


**Figure 3.** Crystal structure of  $[\text{Leu}(\text{CH}_3)_3][\text{TCNQ}]$  material

### 2.2.2. The properties of material

#### 2.2.2.1. Raman spectroscopy

Raman spectroscopy is a useful tool to distinguish between the free  $\text{TCNQ}^0$  and the  $\text{TCNQ}^-$  anion. The product's Raman spectroscopy is shown in Figure 4. The vibrations of  $\text{C}=\text{C}-\text{H}$  bond (out of ring),  $\text{C}=\text{C}$  ring and  $-\text{C}\equiv\text{N}$  respectively characterize  $\text{TCNQ}$  at 1457, 1665 và 2227  $\text{cm}^{-1}$ .



**Figure 4.** Raman and Infrared (FT-IR) spectroscopy of  $[\text{Leu}(\text{CH}_3)_4][\text{TCNQ}]$

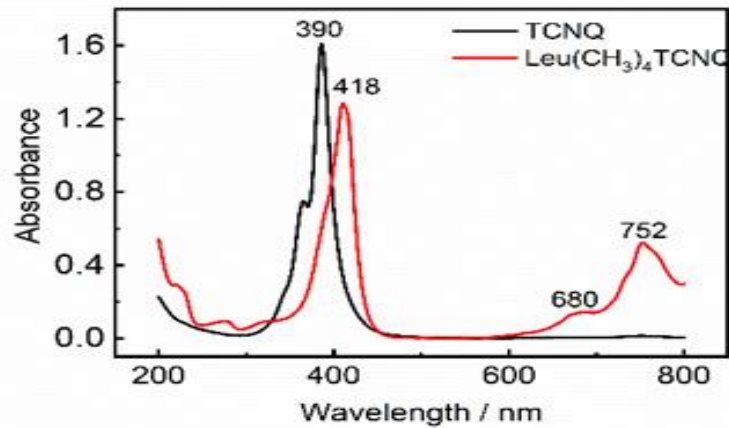
According to the material's Raman spectroscopy, the characteristics of above groups are tending to get lower energy than neutral  $\text{TCNQ}$ . The  $\text{C}\equiv\text{N}$  group shifts from 17  $\text{cm}^{-1}$  to 2210  $\text{cm}^{-1}$ , while  $\text{C}=\text{C}$  group shifts from 08  $\text{cm}^{-1}$  to 1449  $\text{cm}^{-1}$ , and  $\text{C}=\text{C}-\text{H}$  group (out of ring) shifts from 23  $\text{cm}^{-1}$  to 1193  $\text{cm}^{-1}$ . These characteristics demonstrate the presence of  $\text{TCNQ}^-$  anion inside the material [10, 11].

#### 2.2.2.2. Infrared (FT-IR) spectroscopy

The IR at 2210  $\text{cm}^{-1}$  ( $\nu$  ( $\text{C}\equiv\text{N}$ )), 1532  $\text{cm}^{-1}$  ( $\text{C}=\text{C}$  ring), 1369  $\text{cm}^{-1}$  ( $\text{C}=\text{C}$  out of ring) (Figure 4) show the shifting to get lower energy, which indicates the presence of  $\text{TCNQ}^-$  anion [10, 11].

#### 2.2.2.3. UV-Vis spectroscopy of solution on dissolving $[\text{Leu}(\text{CH}_3)_4][\text{TCNQ}]$ into $\text{CH}_3\text{CN}$

The UV-Vis spectroscopy of  $[\text{Leu}(\text{CH}_3)_4][\text{TCNQ}]$  was carried out by dissolving the material under  $\text{CH}_3\text{CN}$  solvent (Figure 5).



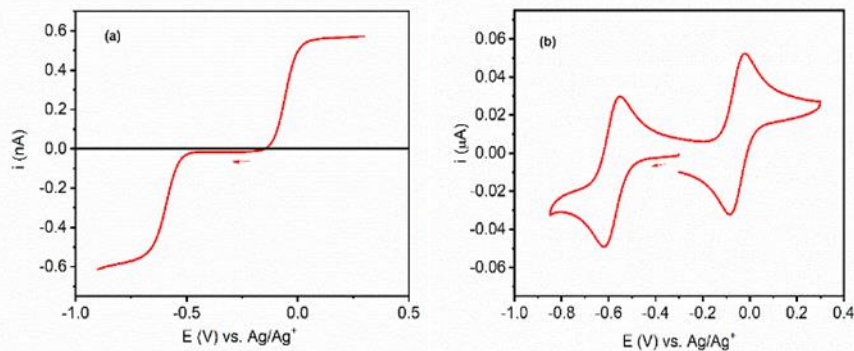
**Figure 5.** UV-Vis spectroscopy of  $[\text{Leu}(\text{CH}_3)_4][\text{TCNQ}]$

For this spectroscopy of TCNQ,  $\lambda_{\text{max}}$  is defined at 390 nm and it has no pic for absorbance at 600-800 nm. All product'  $\lambda_{\text{max}}$  at 418 nm, 686nm và 752 nm (Firuge 6) illustrate the presence of TCNQ<sup>-</sup> inside synthesized material[7].

Electrochemical properties of material

Measure of redox reaction of  $[\text{Leu}(\text{CH}_3)_4][\text{TCNQ}]$  crystal is defined by Current–voltage curve. In principle, the presence of neutral TCNQ<sup>0</sup> in solution leads to the negative curve (reduction) from -100 to 600 mV because one electron of TCNQ leads to form TCNQ<sup>-</sup> for reduction. Conversely, oxidation of TCNQ<sup>-</sup> in solution leads to form TCNQ<sup>0</sup>, which creates positive curve in the same potential range.

Observing the zero line of potentiodynamic scan of  $[\text{Leu}(\text{CH}_3)_4][\text{TCNQ}]$  crystal using fiber microelectrodes C 11  $\mu\text{M}$  indicates that solution just has TCNQ<sup>-</sup> anion, so TCNQ<sup>-</sup> can be oxidated to form TCNQ<sup>0</sup> and produce an oxidation current from -100 to 600 mV. At the same time it is reduced to form TCNQ<sup>2-</sup> and produces reduction current from -100 to -800 mV, the zero line is exactly between two processes (Firuge 6a).



**Figure 6.** (a) Current–voltage curve and (b) Cyclic current –voltage of solution on dissolving  $[\text{Leu}(\text{CH}_3)_4][\text{TCNQ}]$  into  $\text{CH}_3\text{CN}$  (0,1 M  $\text{Bu}_4\text{NPF}_6$ )

Cyclic current – voltage of solution on dissolving  $[\text{Leu}(\text{CH}_3)_4][\text{TCNQ}]$  into  $\text{CH}_3\text{CN}$  is illustrated in Firuge (6b). The potential scanning starts from -0,3V, shown by zeron line, and scans towards negative side until -0,9V before reversing. The Current–voltage curve shows reversible and electrochemical processes, TCNQ<sup>0/-1</sup> ( $E_1 = -0,052$  V) and TCNQ<sup>0/-2</sup> ( $E_2 = -0,585$  V). This curve also point the presence of TCNQ<sup>-</sup> in solution. It is important that there is only reversible process in the potential scanning area, and no other redox process but the redox of TCNQ. These datas show that

only single crystals are present in solution.

### 3. Conclusions

Successfully synthesized material N,N,N-trimethyl-L-leucin methyl ester with TCNQ, the molecular structure of the material is described by the formula  $[\text{Leu}(\text{CH}_3)_4][\text{TCNQ}]$ . This is a two-dimensional material with crystals having an orthorhombic space group  $P2_12_12_1$  with unit cell of one  $[\text{Leu}(\text{CH}_3)_4]^+$  cation and one  $\text{TCNQ}^-$  anion. The physicochemical properties of this product at both solid and solution state confirm the presence of  $\text{TCNQ}^-$  monoanion, completely correspond with the crystal structure. This result, together with the results of research on Prolin-TCNQ, shows that it is possible to produce crystals of different proportions using both cyclic and unbranched amino acids. It is hopeful that the results of research on this material can offer knowledge of biomolecules, which can be used in biosensors.

### References

- [1] Liu, K.; He, L. J.; He, X. M.; Guo, Y.; Shao, S. J.; Jiang, S. X, *Calix[4]pyrrole-TCBQ assembly: a signal magnifier of TCBQ for colorimetric determining amino acids and amines*, Tetrahedron Letters, 48, 24, 2007, 4275 – 4279.
- [2] Singh, V.; Sahai, R (1986), *Interaction of some biomolecules with  $\pi$ - and  $\sigma$  acceptors*, Monatshefte Fur Chemie, 117, 345 – 350.
- [3] Padhiyar, A.; Patel, A. J.; Oza, A. T , *Spectroscopy of charge transfer complexes of four amino acids as organic two-dimensional conductors*. Journal of Physics-Condensed Matter, 19, 48, 2007, 6214.
- [4] D. Jérôme, *Organic Conductors: From Charge Density Wave TTF-TCNQ to Superconducting  $(\text{TMTSF})_2\text{PF}_6$* , Chem. Rev, 104, 11, 2004, 5565 – 559
- [5] D. S. Acker, R. J. Harder, W. R. Hertler, W. Mahler, L. R. Melby, R. E. Benson, W. E. Mochel, *7,7,8,8-Tetracyanoquinodimethane and its electrically conducting anion-radical derivatives*, J. Am. Chem. Soc, 82, 24, 1960, 6408 – 6409
- [6] N. Uyeda, T. Kobayashi, K. Ishizuka, Y. Fujiyoshi , *Crystal structure of  $\text{Ag} \cdot \text{TCNQ}$* , Nature, 285, 1980, 95 – 97.
- [7] C. Zhao, A. M. Bond, *Photoinduced Oxidation of Water to Oxygen in the Ionic Liquid  $\text{BMIMBF}_4$  as the Counter Reaction in the Fabrication of Exceptionally Long Semiconducting Silver-Tetracyanoquinodimethane Nanowires*, J. Am. Chem. Soc. 131, 12, 2009, 4279 – 4287.
- [8] A. Nafady, A. M. Bond, A. Bilyk, A. R. Harris, A. I. Bhatt, A. P O'Mullane, R. De Marco, *Tuning the Electrocrystallization Parameters of Semiconducting  $\text{Co}[\text{TCNQ}]_2$ -based Materials to Yield Either Single Nanowires or Crystalline Thin Films*, J. Am. Chem. Soc. 129, 8, 2007, 2369 – 2382.
- [9] H. Alves, A. S. Molinari, H. X. Xie, A. F. Morpurgo, *Metallic conduction at organic charge-transfer interfaces*, Nat. Mater, 7, 2008, 574.
- [10] Bond, A. M.; Qu, X.; Nafady, A.; Mechler, A.; Zhang, J.; Harris, A. R.; O'Mullane, A. P.; Martin, L. L, *AFM study of morphological changes associated with electrochemical*

- solid–solid transformation of three-dimensional crystals of TCNQ to metal derivatives (metal = Cu, Co, Ni; TCNQ = tetracyanoquinodimethane)*, J. Solid State Electrochem. 12, 6, 2008, 739 – 746.
- [11] A. Hoeskstra, T. Spoelder, A. Vos, *The crystal structure of rubidium-7,7,8,8-tetracyanoquinodimethane, Rb-TCNQ, at -160°C*, Acta Crystallogr. Sect. B, 28, 1972, 14 – 25.
- [12] Xiaohu, Jinzhen Lu, Lisandra Martin, *An amino acid Derived Semiconductor*, Angewandte Chemie, 50(7), 2011, 1589 – 1592.