Journal of Medicinal and Chemical Sciences 6 (2023) 62-70

Journal of Medicinal and Chemical Sciences

Journal homepage: http://www.jmchemsci.com/

Original Article

A Core-extended Pyromellitic Diimide as A p-Channel Semiconductor

Ahmed Khudhair Kadhim*, Muna Ismael Khalaf

Baghdad University, College of Science, Department of Chemistry, Baghdad, Iraq

ARTICLE INFO

Article history

Receive: 2022-04-30
Received in revised: 2022-06-13
Accepted: 2022-07-19
Manuscript ID: JMCS-2204-1492
Checked for Plagiarism: **Yes**
Language Editor:
Dr. Behrouz Jamalvandi
Editor who approved publication:
Professor Dr. Ali Delpisheh

DOI:10.26655/JMCHEMSCI.2023.1.8

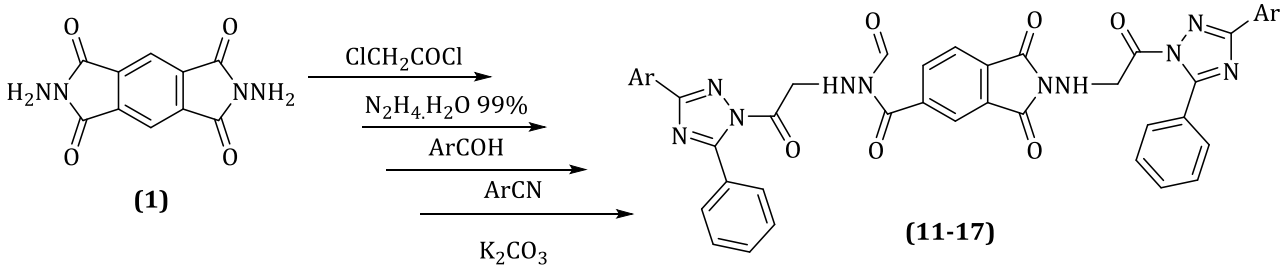
KEYWORDS

Pyromellitic
Diimide
1,2,4- Triazole
Energy gap
Semiconductor
p-Type

ABSTRACT

New π-conjugated system compounds were synthesized by pyromellitic diimide core coupled with side chain containing 1,2,4-triazole rings. The new compounds were characterized by some physical properties, FT-IR and ^{1}H-NMR and the compounds showed a high melting point with some above 300 °C depending on high intramolecular attractive and the Vander Waals attraction between various substituent groups. The optical properties of the prepared compounds were investigated by UV–vis measurement and optical energy gap were estimated by about 2.85-4 e.v. Electro physical properties showed the compounds to behave as p-type semiconductor with acceptable mobility.

GRAPHICAL ABSTRACT



* Corresponding author: Ahmed Khudhair Kadhim
✉ E-mail: Email: ahmedkhudair751@gmail.com

Introduction

Pyromellitic diimide (PMDI), as considered as the smallest of aromatic diimides, has received significantly less interest than the analogue naphthalene and perylene diimides in spite of present favorable attitude in electronic settings [1-3]. To meet the requirements for the forward implementation in the intense environment, the mechanical properties of polyimides and diimides need to be highly afflicted [4] while maintaining the good thermal properties and chemical resistance, which is also a duty and importance of research at all times [5-7].

1,2,4- triazole five-membered heterocyclic is one of the most common heterocycles. Triazoles have been shown to have confirmed eligible characteristics, like reduction conditions, high acid-base hydrolysis stability and metabolic degradation-resistance [8,9]. They include electrical, mechanical, magnetic, optical and corrosion properties far better than their individual components, because of their electro-active and conductive nature [10-13].

Materials and Methods

Chemicals and instruments

- Infrared spectra were recorded using Fourier Transform infrared SHIMADZU (8300) (FTIR) infrared spectrometer, Japan, KBr disc in the (4000-600) cm^{-1}. Spectral range was performed by Baghdad university /college of science/ chemistry department
- ^{1}H-NMR and ^{13}C-NMR spectra were recorded in Iran using recorded on EGELENT, Ultra shield 500MHz using tetramethyl silane as internal standard and (DMSO-d_6 or dis. Water) as a solvent.
- Uv-vis scan was scanned by UV spectrophotometer SHIMADZU (UV-1800)
- All chemicals were used sullied from BDH, Alpha and Merk.

*Synthesis of N,N′- bis (2-amino acetyl chloride) pyromellitic diimide (**2**,**14**,**15**)*

N,N′-bis amino pyromellitic diimide (5 mmol, 1.23 g) was added to chloro acetyl chloride (1-2 mL) and refluxed on steam bath for 2-3 h; after cooling, yellow precipitate was formed, dried and recrystallized by benzene (Scheme 1).

*Synthesis of N,N′-bis (2-amino acid hydrazide) pyromellitic diimide (**3**,**16**)*

A mixture of the *N,N′*-bis (2-amino acetyl chloride) pyromellitic diimide (**2**) and hydrazine hydrate (0.015 mol, 0.75 mL) in ethanol (50 mL) was refluxed for 10 h. The reaction mixture was allowed to cool and the separated product was filtered and dried. Crystallization of the crude product was conducted with benzene (Scheme 1).

*Synthesis of shiff base: N, N′-bis[2-amino acet hydrazine benzylidene]-pyromellitic diimide (**4-10**)*

2 drops of glacial acetic acid (0.1 mL) was added to different derivatives of aldehydes (2 mmol) and refluxed for 15-20 min, then *N,N′*-bis (2-amino aceto hydrazide) pyromellitic diimide compound (**3**) (0.4 g, 1 mmol) was added and refluxed for 3-6 h, controlled by TLC; the product was dried and washed with ether, recrystallized from di ethyl ether and petroleum ether (Scheme 1).

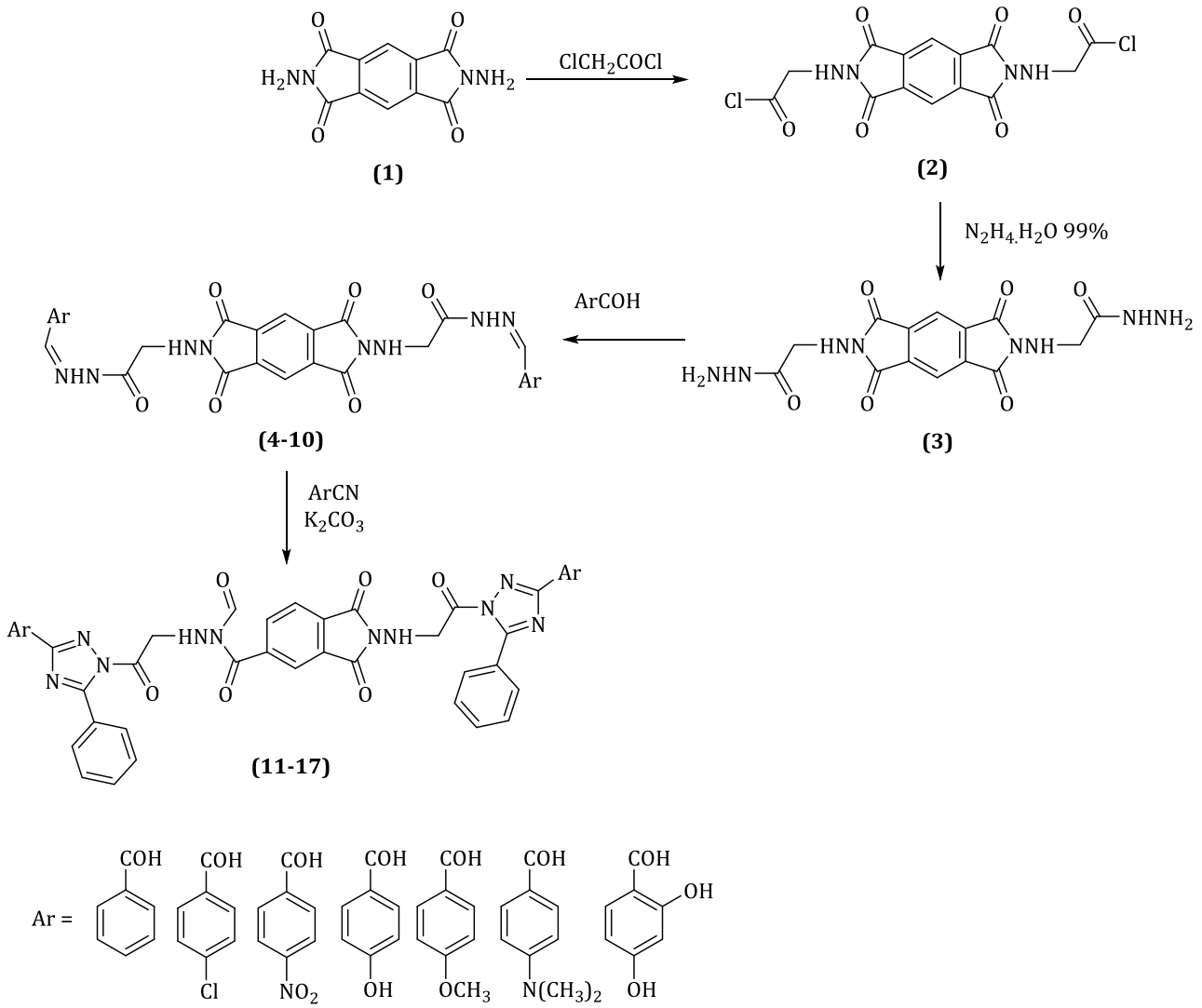
*Synthesis of N,N′- bis 1,2,4-triazole pyromellitic diimide (**11-17**)*

Benzonitrile (0.2 mL, 2 mmol) was added to Shiff basses compounds (11-19) dissolved in (butanol or ethanol) in presence of K_2CO_3 and refluxed for 24 h. The product was dried and recrystallized from petroleum ether (Scheme 1).

Results and discussion

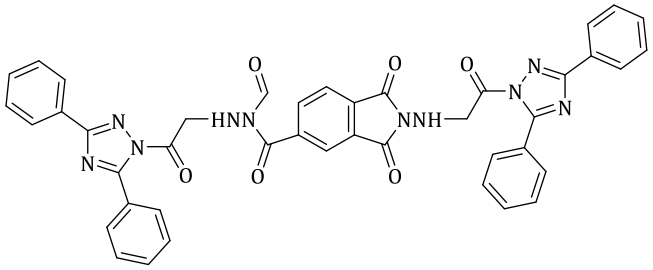
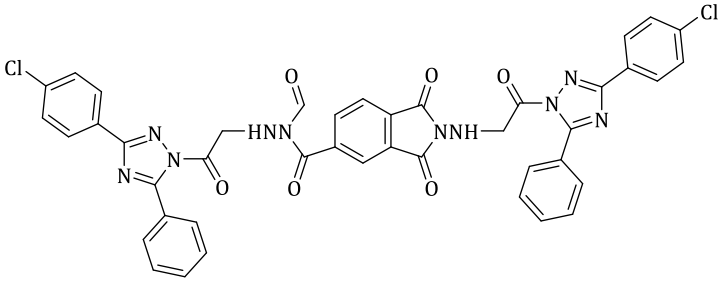
In this study, new 1,2,4- triazole heterocyclic compounds based on pyromellitic diimide core were prepared in 4 steps from *N,N′*- bis amino pyromellitic diimide, initially reacting with chloro acetyl chloride and getting heated on a steam bath then reacting with hydrazine hydrate 99%. Then, at step 3 it reacted with different aromatic aldehyde by Schiff base reaction. Step four included synthesizing a factional group 1,2,4-triazole by reacting with benzo nitrile in presence of potassium carbonate.

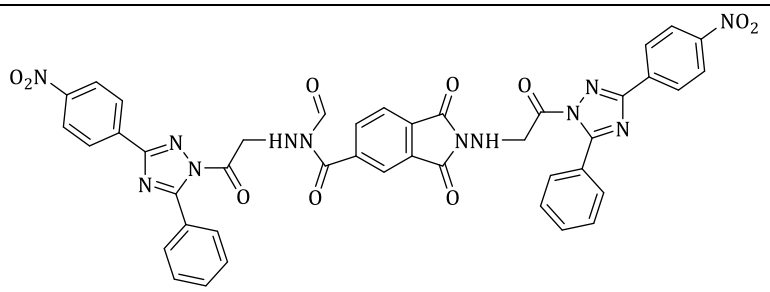
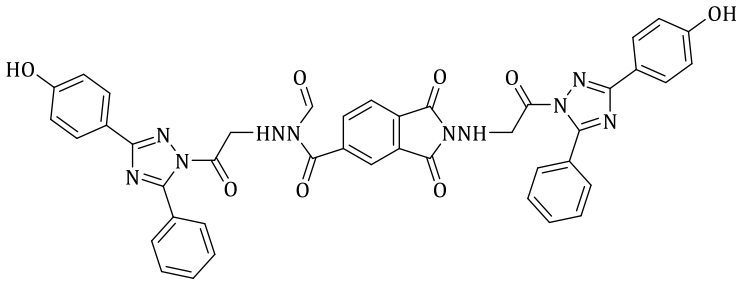
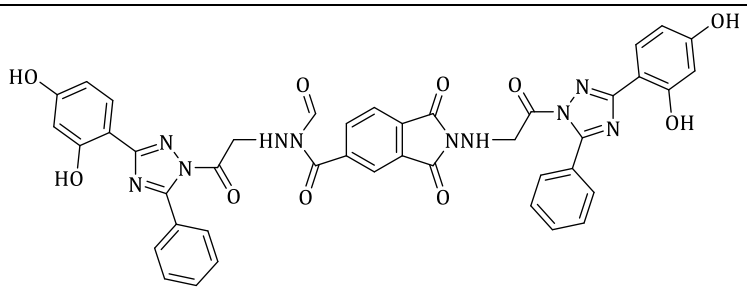
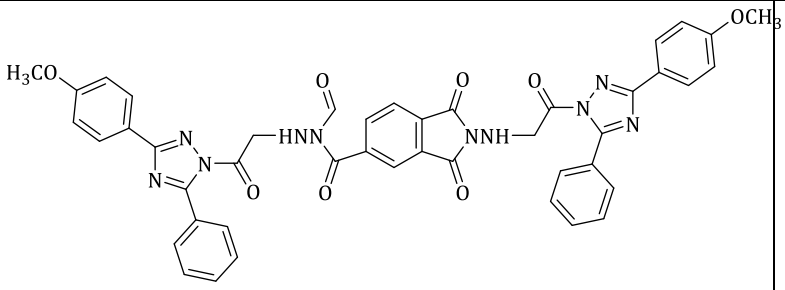
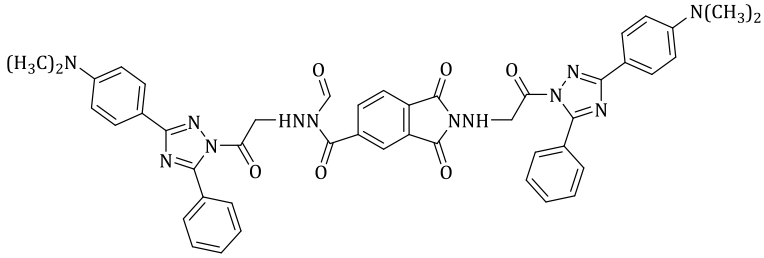
The physical properties of prepared compounds are listed in Table 1.



Scheme 1: The chemical steps for the synthesis of compounds (**1-17**)

Table 1: Some of the physical properties for prepared compound (**11-17**)

Compound No.	Compound structure	m.p (°C)	Color	Yiel d%
11		>300	Rid-brown	78
12		>300	Yellow	76

13		>300	Yellow	76
14		>300	Yellow	80
15		278-280	Yellow	76
16		>300	Yellow	80
17		290-292	Yellow	80

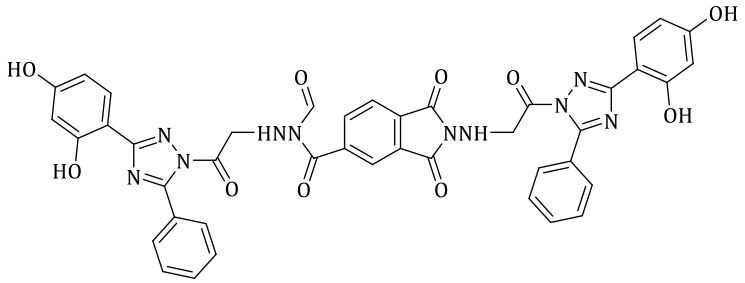
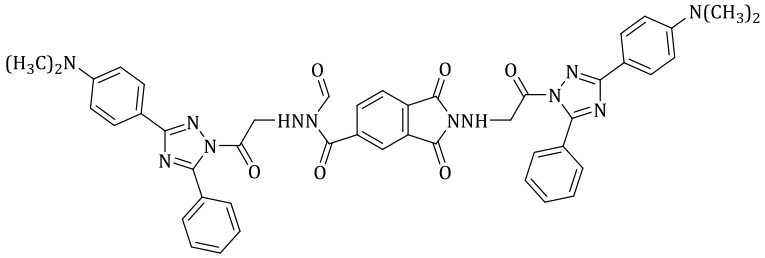
The FT-IR spectrum (Table 2) for compounds (**11-17**) showed a stretching new band in range of 1446-1521 cm^{-1} due to N-N triazole and N-H amide appearance at the range of 3159-3286 cm^{-1}. A hard-stretching band at rang 1618-1677 cm^{-1} refers to carbonyl imide and weak band at range 1699-1766 cm^{-1} (**17**) due to carbonyl amide. Other specific bands are listed in Table 2.

Table 2: characteristic IR absorbtion data compounds (**11-17**)

Compound NO.	ν (NH)	ν(C-H) aromatic	ν(C-H) aliphatic	ν(C=C) aromatic	ν(C=O) Imide amide	ν $(N-N)_{triazole\ ring}$	ν(C-N)
11	3240	3068	2937,2806	1595,1552	1710 1629	1446	1350
12	3276	3026	2875,2870	1558,1544	1699 1618	1508	1373
13	3251	3050	2925,2902	1487,1402	1743 1652	1562	1369
14	3286	3033	2910,2840	1550,1461	1714 1677	1517	1379
15	3191	3041	2979	1425-1575	1728 1658	1521	1363
16	3159	3060	2977,2927	1577,1508,1492	1776 1652	1512	1336
17	3201	3043	2891,2937	1512,1573	1740 1658	1450	1326

Compounds (**15**) and (**17**) were characterized by ^{1}H-NMR. Compound (**15**) in the ^{1}H-NMR spectrum of (Table 3) showed signals at δ 6.26 ppm for (s, 4H, OH), at δ 8.27 ppm for (s, 2H, NH) and δ (7.14-10.15) ppm for (m, 18H, Ar-H) where compound (**17**) showed signals at δ2.55 ppm for (s, 6H, CH_3), at δ (6.26-10.73) ppm for (m, 20H, Ar-H), at δ 8.77 ppm for (s, 2H, NH).

Table 3: ^{1}H-NMR data for compound (**15,17**)

Compound NO.	Structure	Spectral data (δppm)
15		6.26(s, 4H, OH) 8.27(s, 2H, NH) 7.14-10.15(m, 18H, Ar-H)
17		2.55 (s, 6H, CH_3) 6.26-10.73 (m, 20H, Ar-H) 8.77 (s, 2H, NH)

Application

Optical properties

The UV scan for compounds showed λ_{max} for compound **15** at 434,411, respectively, and λ_{max} at 327,252 nm, respectively for compound **16**.

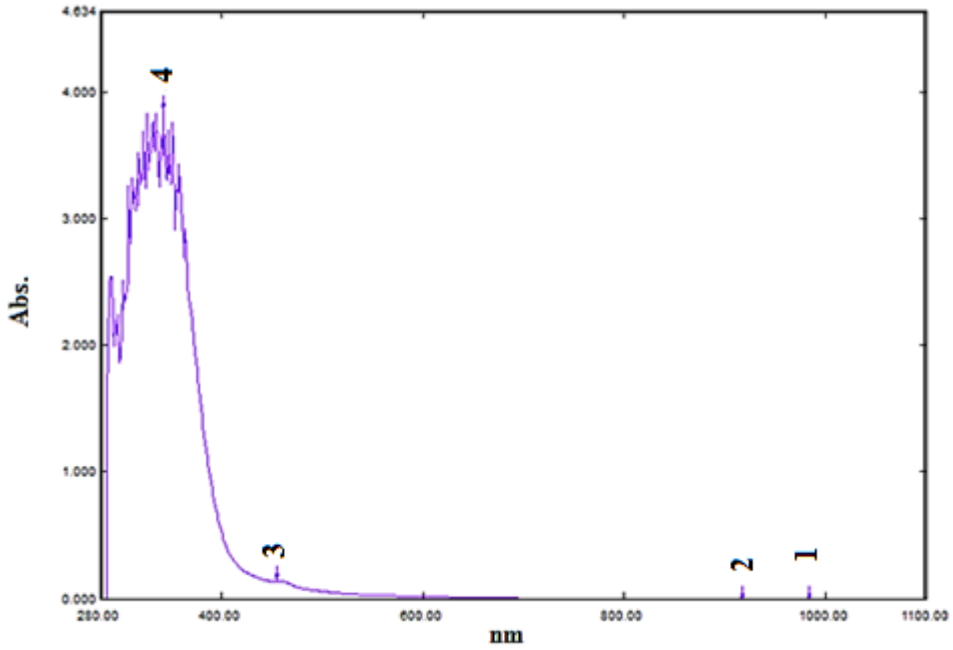


Figure 1: UV-VIS for compound 15

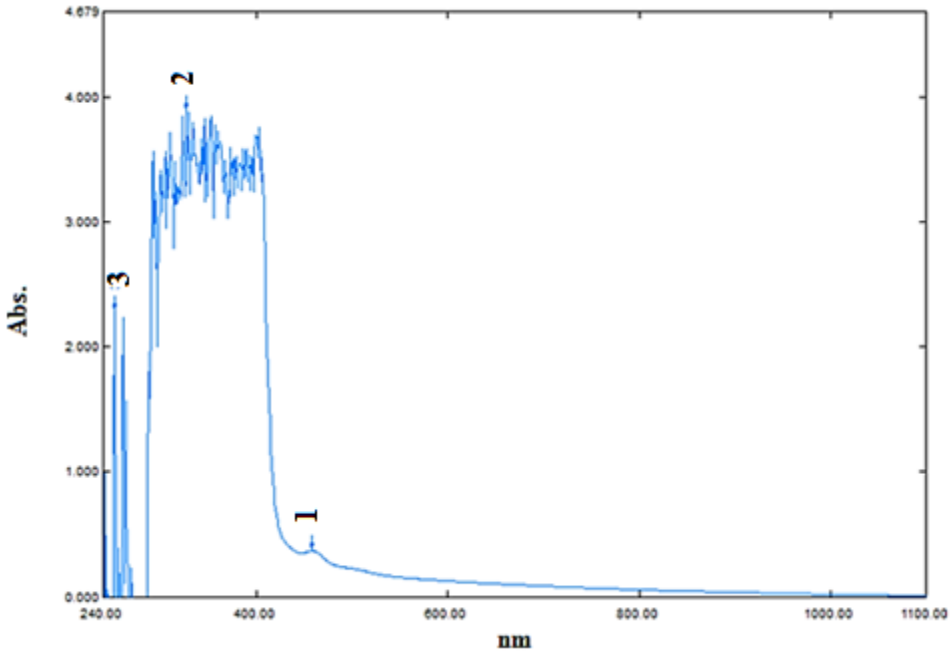


Figure 2: UV-VIS for compound 17

The estimated direct energy gaps [18] are listed in Table 4.

The electro physical characteristics were calculated by Hall Effect [19] for compound **15** showed p-type behavior and other electro physical characteristics are listed in Table 5.

Table 4: estimated direct energy gaps (**18**)

Comp.	λ_{max}	Eg e.v
15	434	2.85
	411	3.017
17	327	3.79
	252	4.92

Table 5: p-type behavior and other electro physical characteristics

parameter	Value	
Conductivity	3×10^{-7}	$1/\Omega$ cm
Mobility	0.39	Cm^2/Vs
Resistivity	3.28×10^{6}	Ω Cm

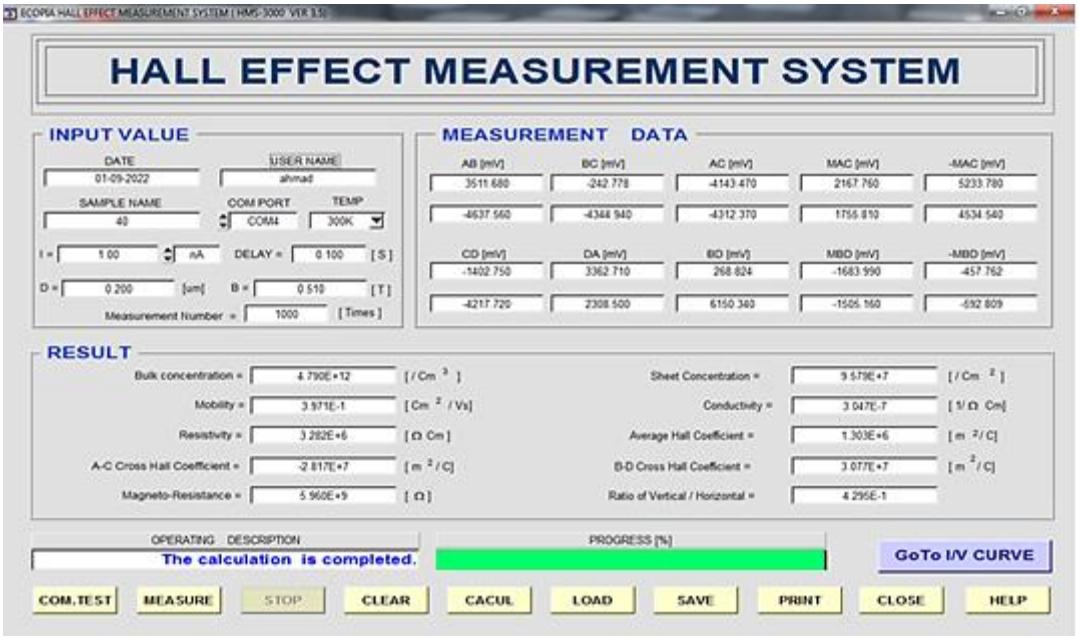


Figure 3: Hall effect parameter

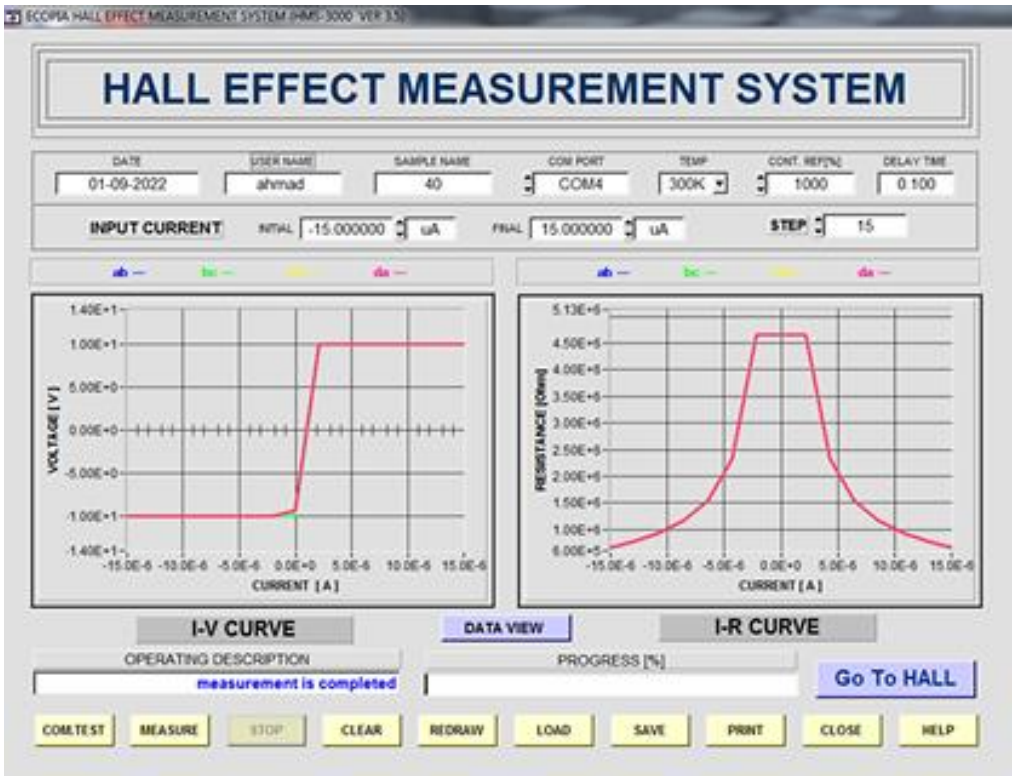


Figure 4: I-V & I-R curves for compound (**15**)

Conclusion

New 1,2,4- triazole heterocyclic compounds based on pyromellitic diimide core were synthesized. This compounds were characterized by FT-IR and ^{1}H-NMR. The optical properties of the prepared compounds were investigated by UV–vis

measurement and optical energy gap were estimated by about 2.85-4 e.v. The electric physical experiment of the compounds can be used in solar cell as p-type semiconductor.

Funding

This research did not receive any specific grant from fundig agencies in the public, commercial, or not-for-profit sectors.

Authors' contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

Conflict of Interest

There are no conflicts of interest in this study.

ORCID:

Ahmed Khudhair Kadhim

https://www.orcid.org/0000-0002-9387-4051

References

[1]. Greenlee A.J., Ofosu C.K., Xiao Q., Modan M.M., Janzen D.E., Cao D.D., Pyridinium-functionalized pyromellitic diimides with stabilized radical anion states, *ACS omega,* 2018, **3**:240 [Crossref], [Google Scholar], [Publisher]

[2]. Al Kobaisi M., Bhosale S.V., Latham K., Raynor A.M., Bhosale S.V., Functional naphthalene diimides: synthesis, properties, and applications, *Chemical reviews*, 2016, **116**:11685 [Crossref], [Google Scholar], [Publisher]

[3]. Kim D.J., Hermann K.R., Prokofjevs A., Otley M.T., Pezzato C., Owczarek M., Stoddart J.F., Redox-active macrocycles for organic rechargeable batteries, *Journal of the American Chemical Society*, 2017, **139**:6635 [Crossref], [Google Scholar], [Publisher]

[4]. Abid Hubeatir K., Kamil F., Al-Amiery A.A., Kadhum A.A.H., Mohamad A.B., Polymer solar cells with enhanced power conversion efficiency using nanomaterials and laser techniques, *Materials technology*, 2017, **32**:279 [Crossref], [Google Scholar], [Publisher]

[5]. Kanosue K., Augulis R., Peckus D., Karpicz R., Tamulevičius T., Tamulevičius S., Gulbinas V., Ando S., Polyimide and Imide Compound Exhibiting Bright Red Fluorescence with Very Large Stokes Shifts via Excited-State Intramolecular Proton Transfer II. Ultrafast Proton Transfer Dynamics in the Excited State, *Macromolecules*, 2016, **49**:1848 [Crossref], [Google Scholar], [Publisher]

[6]. Liang N., Fujiwara E., Nara M., Ishige R., Ando S., Colorless Copolyimide Films Exhibiting Large Stokes-Shifted Photoluminescence Applicable for Spectral Conversion, *ACS Applied Polymer Materials*, 2021, **3**:3911. [Crossref], [Google Scholar], [Publisher]

[7]. Hameury S., Kunz S., Sommer M., Expanding the Scope of Electron-Deficient C–H Building Blocks: Direct Arylation of Pyromellitic Acid Diimide, *ACS Omega*, 2017, **2**:2483 [Crossref], [Google Scholar], [Publisher]

[8]. Al-Tamimi E.O., Abd Al-Hassan H.M.A., Synthesis & Characterization Of Poly [N-acryl-N-sulfonic acid-N\yL-2-substituted-4-oxo-thiazolidine] Maleic and Succinic DiImide, *Iraqi Journal of Science*, 2014, **55**:912 [Google Scholar], [Publisher]

[9]. ŞERBAN G., 1, 2, 4-Triazoles as Intermediates for the Synthesis of Hybrid Molecules, *FARMACIA Учредителu: Uniunea Societatilor de Stiinte Medicale din Rumania*, 2016, **64**:549 [Google Scholar], [Publisher]

[10]. Sadiq A.S., Al-Tamimi E.O., Synthesis and Characterization of New Polymers Bearing Tetrazole and Triazole Moieties with Studying their Corrosion Protection of Stainless Steel Surface in Hydrochloric Acid, *Iraqi Journal of Science*, 2020, **61**:2467 [Crossref], [Google Scholar], [Publisher]

[11]. Komissarova E.A., Zhulanov V.E., Mokrushin I.G., Vasyanin A.N., Shklyaeva E.V., Abashev G.G., Synthesis and study of N, N′-disubstituted derivatives of pyromellitic diimide, *Russian Chemical Bulletin*, 2020, **69**:1944 [Crossref], [Google Scholar], [Publisher]

[12]. Kuila S., Garain S., Banappanavar G., Garain B.C., Kabra D., Pati S.K., George S.J., Ambient Room Temperature Phosphorescence and Thermally Activated Delayed Fluorescence from a Core-Substituted Pyromellitic Diimide Derivative, *The Journal of Physical Chemistry B*, 2021, **125**:4520 [Crossref], [Google Scholar], [Publisher]

[13]. Redzicka A., Czyżnikowska Ż., Wiatrak B., Gębczak K., Kochel A., Design and synthesis of N-substituted 3, 4-pyrroledicarboximides as potential anti-inflammatory agents, *International journal of molecular sciences*, 2021, **22**:1410 [Crossref], [Google Scholar], [Publisher]

[14]. Kadhima A.K., Khalafa M.I., Kadhimb M., Synthesis, characterization, band gap and optical properties of new pyromellittic diimide core dervatives, *Eurasian Chemical Communications*, 2021, **3**:872 [Crossref], [Google Scholar], [Publisher]

[15]. Kadhim A.K.K., Khalaf M.I.. New Low Bandgap Compounds Comprised of Pyromellitic Diimide and Imine Units, *Chemical Methodologies*, 2022, **6**:418 [Crossref], [Google Scholar], [Publisher]

[16]. Mohamed F.K., Synthesis, reactions and antimicrobial activity on some novel phthalazinones derivatives, *Der Chemica Sinica*, 2010, **1**:20 [Crossref], [Google Scholar], [Publisher]

[17]. Saeed A.M., AlNeyadi S.S., Abdou I.M., Anticancer activity of novel Schiff bases and azo dyes derived from 3-amino-4-hydroxy-2*H*-pyrano [3, 2-c] quinoline-2, 5 (6*H*)-dione. *Heterocyclic Communications*, 2020, **26**:192 [Crossref], [Google Scholar], [Publisher]

[18]. Geng Y., Tang A., Tajima K., Zeng Q., Zhou E., Conjugated materials containing dithieno [3, 2-b: 2′, 3′-d] pyrrole and its derivatives for organic and hybrid solar cell applications, *Journal of Materials Chemistry A*, 2019, **7**:64 [Crossref], [Google Scholar], [Publisher]

[19]. Kong F., Lin M., Qiu T., The effect of imide substituents on the optical properties of perylene diimide derivatives, *Luminescence*, 2018, **33**:1209 [Crossref], [Google Scholar], [Publisher]

HOW TO CITE THIS ARTICLE
Ahmed Khudhair Kadhim, Muna Ismael Khalaf. A Core-Extended Pyromellitic Diimide as a P-Channel Semiconductor. *J. Med. Chem. Sci*., 2023, 6(1) 62-70
https://doi.org/10.26655/JMCHEMSCI.2023.1.8
URL: http://www.jmchemsci.com/article_153753.html