



Original Research Article

New Low Bandgap Compounds Comprised of Pyromellitic Diimide and Imine Units

Ahmed Khudhair Kadhim* , Muna Ismael Khalaf

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

ARTICLE INFO

Article history

Submitted: 2022-03-28

Revised: 2022-04-03

Accepted: 2022-04-06

Manuscript ID: CHEMM-2203-1463

Checked for Plagiarism: Yes

Language Editor:

Dr. Fatimah Ramezani

Editor who approved publication:

Professor Dr. Ali Ramazani

DOI:10.22034/CHEMM.2022.335391.1463

KEYWORDS

Diimide

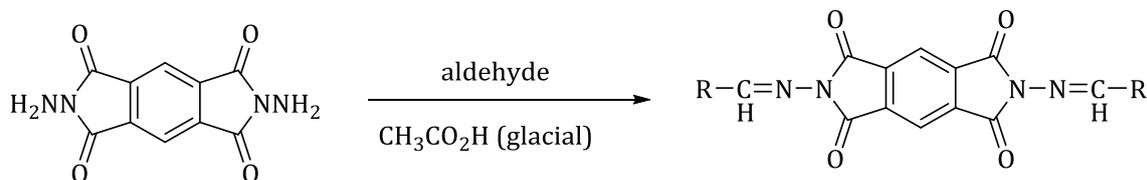
Pyromellitic diimide

Electrochemistry energy gap

ABSTRACT

New bisimide derivatives, low molecular compounds with π - π^* conjugated system consisting of a pyromellitic diimide core and imine linkages were synthesized by Schiff bases reactions, the studied compounds were prepared from *N,N'*-bis amino pyromellitic diimide which was condensed with different derivatives of aldehydes, the materials show a high melting point and some above 300 °C depended intramolecular attractive and the Vander Waals attraction between various substituent groups. The optical properties of the prepared compounds were investigated by UV-vis measurement. The prepared compounds showed the highest intensity with maximum absorbance at 243-908 nm. In all studied molecules, the electrochemically estimated theoretical HOMO level is in the range of -7.515 to -7.320 eV, whereas the LUMO level is close to 7.219 eV and -5.889 eV. The estimated compounds exhibited low electrochemical band gap (<2 eV).

GRAPHICAL ABSTRACT



* Corresponding author: Ahmed Khudhair Kadhim

✉ E-mail: ahmedkhudair751@gmail.com

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Introduction

The development of organic low and high molecular weight conjugated systems for (opto)electronic devices such as field effect transistors (FETs), photovoltaic cells (PCs), or emitting diodes (LEDs) is a challenging topic of current research [1,2]. The main advantage of organic semiconductors is the wide range of ability of their optical [3], charge transport, and optoelectronic properties by chemical synthesis. Intense research efforts have been focused on the development of new charge-transport organic compounds with either hole, that is, electron-donating (D) or electron transporting, that is, electron-accepting (A) properties, or with both properties in one polymer chain as they displayed profound academic values and potential industry applications [4,5]. Between the electron accepting and electron donation structural units allows to shift the position of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of a given compound to those which are the most appropriate for the desired applications [6,7]. Electro active, low band gap materials are suitable for a variety of applications [8-10]. Among a lot of conjugated systems arylene imides-based compounds from small molecules and polymers constitute a promising family of materials whose properties can be explored in (opto) electronic devices mainly because of their excellent thermal properties, good chemical and oxidative resistance [11]. Moreover, they consist of electron-accepting imide and electron donating amine units, forming charge transfer complexes [12]. Naphthalene and perylene derivatives exhibited large electron affinities which facilitate electron accumulation and easy addition of varied substituents to the imide N atoms, which enable tuning of transport properties or even air stability for their devices [13], while the relatively easy synthesis of pyromellitic diimide compared to that of other rylene derivatives making these molecules interesting systems to be explored. On the other hand, the other promising conjugated compounds are which are also known as imines and Schiff bases. Due to presence of imine bonds (N=CH) is isoelectronic to their carbon analogues,

making them suitable alternatives to conventional conjugated materials and can be exploited for various applications [14,15]. It was found that compounds containing imine linkages or six-membered imide rings have prospective applications in organic (opto)electronics and related fields, exemplary as materials for high efficiency solar cells [16], for fabrication of field effect transistors (FETs) [17,18] or light-emitting diodes (OLEDs) [19-21] and are highly desirable for photonic technology [22]. In this paper, we report the synthesis and characterization of new Schiff bases pyromellitic compounds can be considered as a new type of pyromellitic bisimides. Compounds can be considered as a new type of pyromellitic bisimides. These compounds constitute a promising family of materials whose properties can be explored in various types of devices. Taking into account, the literature related to the idea of compounds preparation with both imine and six-membered diimide moieties, the previous works [23,24]. It has been undertaken the investigations of conjugated double bonds structure in the Schiff bases diimides compounds. The investigations of their properties and structure-property relationship might form the basis for a "molecular engineering" approach to (opto) electronic compounds. This involves the determination of their thermal, optical, and redox properties.

Materials and Methods

The materials used in the experiment Pyromellitic dianhydride (BDH), a hydrazine hydrate 99% (ALPHA), glacial acetic (BDH), derivatives of aldehydes, magnetic stirrer, condenser, round bottom flask, and the results were characterized and analyses by the instrument 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. $^1\text{H-NMR}$ spectra were recorded in Jordan using recorded on Burker, Ultra shield 500 MHz using tetramethyl silane as internal standard and $\text{DMSO-}d_6$ as a solvent.

Synthesis of *N,N'*-bis amino pyromellitic diimide (1)
Pyromellitic dianhydride (1 g, 4 mmol) was added slowly to excess of a hydrazine hydrate 99% for 10-20 times in ice bath, stirred for 4 hour and left overnight; a yellow precipitate was formed. Then, dried and recrystallized by ethyl acetate.

Synthesis of *N,N'*-bis(aryl imine)pyromellitic diimide

2 Drops of glacial acetic acid (0.1 mL) was added to different derivatives of aldehydes (4 mmol) and

reflux for 15-20 min. Then 2 mmol of *N,N'*-bis amino pyromellitic diimide (1) (0.492 g) was added and reflux for 3-4 h (controlled by TLC).

Result and Discussion

We have focused our interest on compounds containing six membered imide rings and imine linkages as potential materials for (opto) electronics. In this article, we continue our effort in synthesis of new Schiff base diimides.

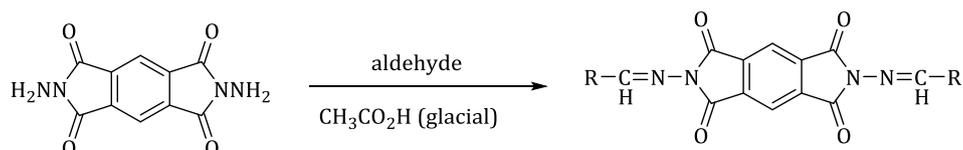


Figure 1: Synthesis of *N,N'*-bis(aryl imine)pyromellitic diimide

The reaction mechanism involved a nucleophilic attack by the amino group on electron –deficient carbon in derivatives of aldehyde following by water moiety removal to create derivatives of Schiff bases.

The chemical structures and some physical properties of the compounds synthesized in this study are presented in Table 1.

Table 1: The chemical structures and some physical properties of the compounds

Compound No.	Compound structure.	Molecular formula	M.wt (g/mol)	m.p (°C)	Color
1		C ₁₀ H ₆ N ₄ O ₄	246	>320	yellow
2		C ₂₄ H ₁₄ N ₄ O ₄	422	>300	Orange
3		C ₂₄ H ₁₄ N ₄ O ₆	454	283-286	yellow
4		C ₂₈ H ₂₄ N ₆ O ₄	508	266-271	Orange
5		C ₂₆ H ₁₈ N ₄ O ₆	482	181-186	Light brown
6		C ₂₄ H ₁₄ N ₄ O ₈	486	>300	yellow
7		C ₂₈ H ₁₈ N ₄ O ₄	474	Dec. 268	brown

Characterization

FT-IR Spectral data for prepared compounds

All prepared compounds were characterized by physical properties (Table 1), FT-IR (Table 2), ¹H-NMR (Table 3).

The FT-IR spectra depicted stretching bands at 3026-3099 cm⁻¹ for CH aromatic, while CH

aliphatic appeared between 2873-2937 cm⁻¹. The carbonyl groups of imide gave strong stretching bands 1658 cm⁻¹. Band in the region of 1461-1564 cm⁻¹ referred to C=C aromatic, while C=N appeared at 1600 cm⁻¹. The detailed infrared spectral data is illustrated Table 2

Table 2: Characteristic IR absorption data compounds (1-7)

Compound NO.	$\nu(\text{C-H})$ aromatic	$\nu(\text{C-H})$ aliphatic	$\nu(\text{C=C})$ aromatic	$\nu(\text{C=N})$	$\nu(\text{C=O})$	$\nu(\text{C=O})$	$\nu(\text{O-H})$	$\nu(\text{C-O-C})$	$\nu(\text{N-H})$
1	3099		1550-1488		1654			3323, 3440 (NH ₂)	
4	3026	2904-2866	1521,1544	1600	1658			-	
5	3033	2840-1927	1461-1564	1600	1658		1249	-	
6	3043	2885-2937	1560-1512	1614	1649	3465-3517	-	-	
7	3028	2754-2873	1562-1515	1600	1658	-	-	-	1407 (C=C)

The ¹H-NMR spectra for compounds 4 revealed singlet signals in the region 3.03 ppm for (CH₃, 12H), and singlet signals in the region (8.49 ppm) for (N=CH, 2H), while aromatic protons showed double singlet signals at (6.62-7.65 ppm).

The ¹H-NMR spectra for compound 4 demonstrated singlet signals in the region (3.82 ppm) for (CH₃, 6H), and singlet signals in the region (8.62 ppm) for (N=CH, 2H), while aromatic protons indicated three singlet signals at (6.86-7.68 ppm)

Table 3: ¹H-NMR spectral data for compounds

Compound No.	Structures	¹ HNMR spectral data (δ ppm)
4		3.03 (s, 12 H, CH ₃), 6.67-6.77 (d, 4H, C-HAr), 7.62-7.65 (d, 4H, Ar-H), 8.49 (s, 2H, N=CH)
5		3.82 (s, 6H, CH ₃ methyl), 6.86-7.42 (d, 4H, Ar-H), 7.45-7.8 (d, 4H, Ar-H), 7.68 (s, 2H, Ar-H), 8.62 (s, 2H, N=CH)

Optical properties

Ultraviolet-visible investigations the UV-vis absorption spectra of prepared compounds in DMSO solution are presented in Figures 1, 2 and 3.

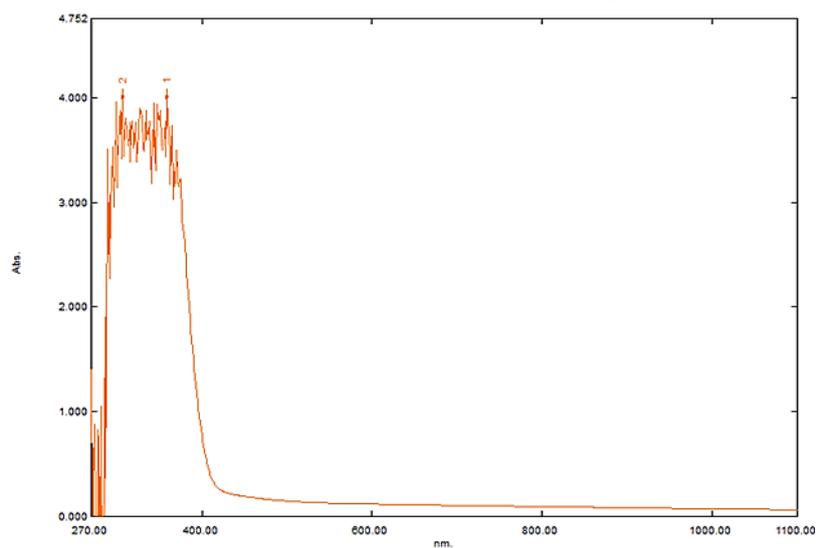


Figure 1: UV-vis absorption for compound 3

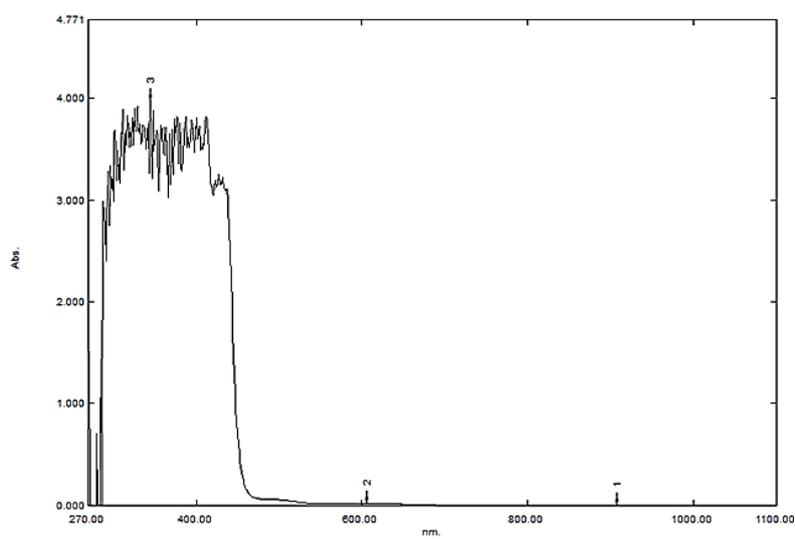


Figure 2: UV-vis absorption for compound 4

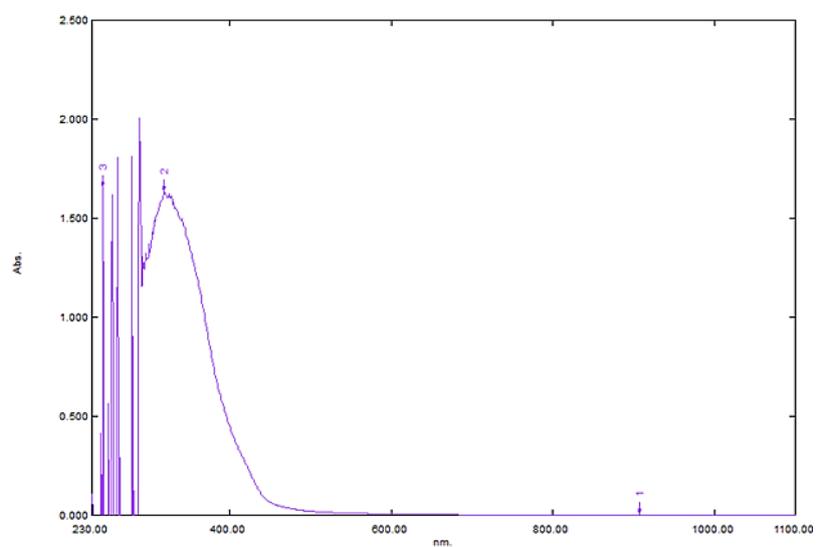


Figure 3: UV-vis absorption for compound 7

The transmission for studied compounds are displayed in Figures 4-6.

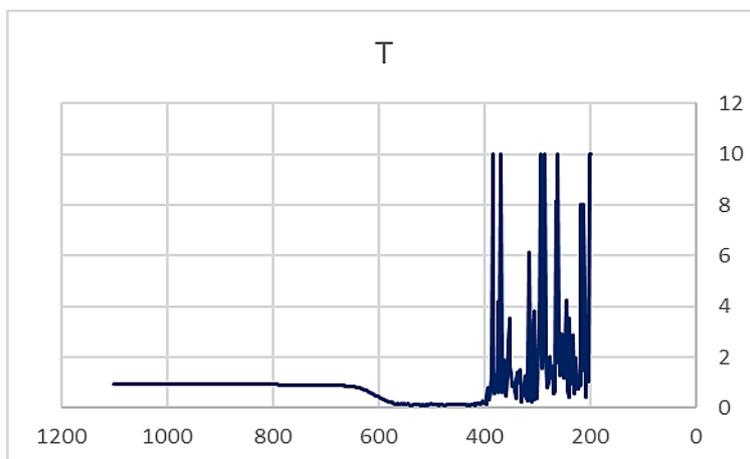


Figure 4: transmission for compound 3

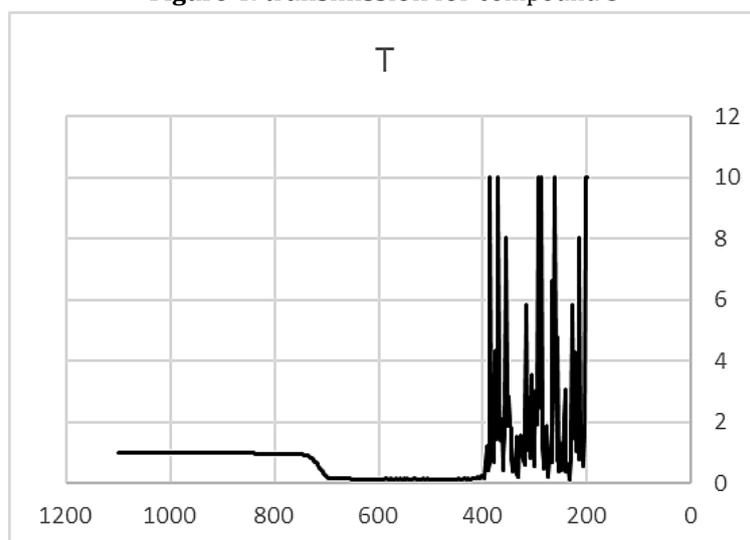


Figure 5: transmission for compound 4

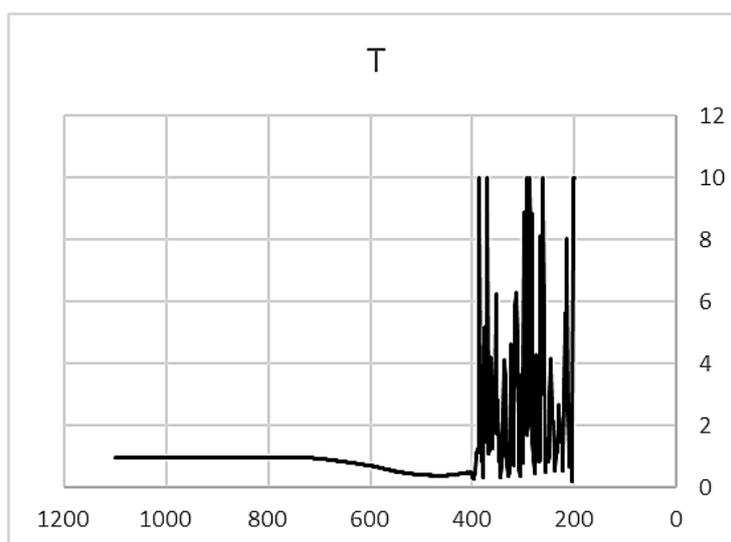


Figure 6: transmission for compound 7

Energy gap

The theoretical energy gap was calculated computational program (Chem. Office, 2010) by

calculation the minimum m^2 to 3D structure in the space and calculate hückel orbital exhibited a low lying LUMO level and a relatively high lying HOMO level (Figures 7-9).

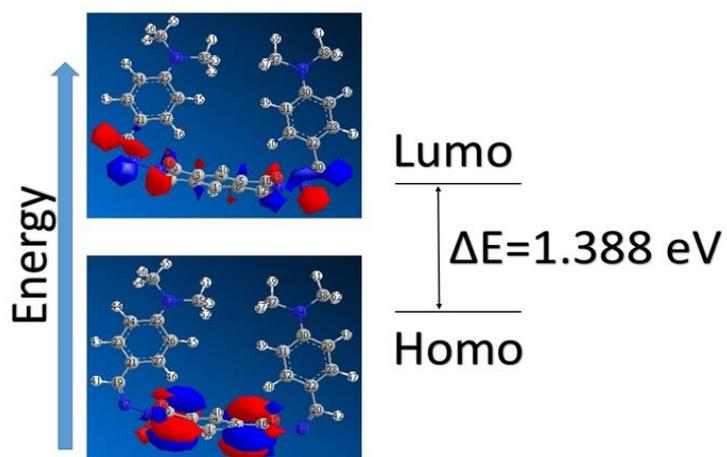


Figure. 7: energy gap for compound 4

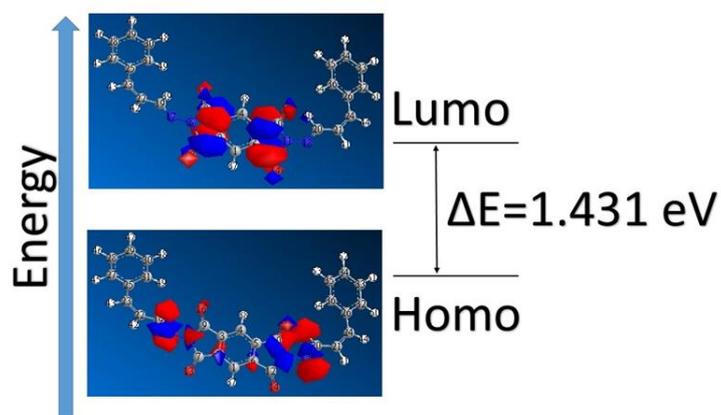


Figure 8: energy gap for compound 3



Figure 9: energy gap for compound 7

The energy gap was calculated by blank equation $E = h \nu = hc/\lambda = 1240/\lambda$
1.

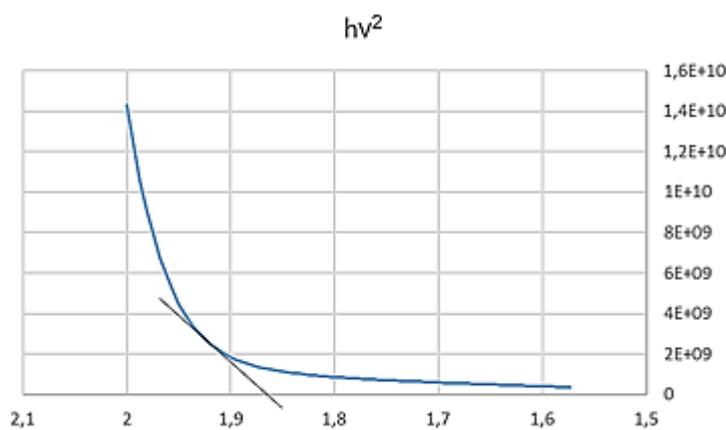
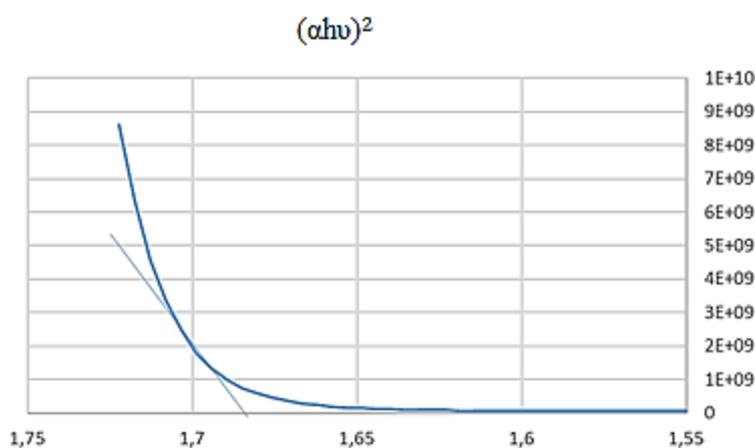
Table 4: energy gap was calculated

Comp.	λ_{\max}	E _g
3	359	3.454
	307	4.039
4	907	1.367
	606	2.046
	345	3.594
7	908	1.365
	319	3.887
	243	5.102

The optical energy band gap values (E_g) at about (< 2 eV) calculated from the onset of UV-vis absorption band. Direct band gap energy can be calculated from Tauc model, from the equation

$$(\alpha h\nu)^2 = A_0 (h\nu - E_g)$$

Where A₀ is a constant, hν is the photon energy and E_g is the optical band gap energy, α is optical absorption coefficient deduced from the absorption data (Figures 10 and 11).

**Figure 10:** Tauc model for compound 3**Figure 11:** Tauc model for compound 4

Conclusion

To sum up, we have synthesized new bisimide derivatives containing imine linkages. These new

pyromellitic diimides derivatives showed resistance against to thermal decomposition up to 300 °C, which renders advantages in various applications. They exhibited a low lying LUMO

level and a relatively high lying HOMO level, yielding, by consequence, a low electrochemical band gap in the range from 0.224 to 1.431 eV. Such low band gap materials can be suitable for a variety of applications. In conclusion, the results could lead to further developments of new family compounds, which could guide the design of optoelectronic devices.

ORCID

Ahmed Khudhair Kadhim

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

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HOW TO CITE THIS ARTICLE

Ahmed Khudhair Kadhim, Muna Ismael Khalaf. New Low Bandgap Compounds Comprised of Pyromellitic Diimide and Imine Units. *Chem. Methodol.*, 2022, 6(5) 418-427

<https://doi.org/10.22034/CHEMM.2022.335391.1463>

URL: http://www.chemmethod.com/article_147876.html