

FULL PAPER

Synthesis, characterization, band gap and optical properties of new pyromellitic diimide core derivatives

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This study is an overview of recent advances in development of high performance diimide derivatives and their optical properties. It covered pyromellitic diimide that conjugated a 1,2,3-triazole heterocyclic molecules containing π -conjugated molecules, which gave the molecule optoelectronic properties. The new N-amino diimide compound [1] was prepared from hydrazine and pyromellitic dianhydride which could react with chloroacetyl chloride controlled by heat to give N,N'- bis (2-amino acetyl chloride) pyromellitic diimide [2] then react with sodium azide to give N,N'- bis (2-amino acetyl azide) pyromellitic diimide [3] that could conjugate with α - β unsaturated aldehyde derivatives when heated at 110°C for 24 hrs to give 1,2,3-triazole heterocyclic. The prepared compounds were characterized by FT-IR spectrum and ¹H-NMR and physical properties. The UV-vis spectrum showed the maximum wavelength for the prepared compounds >200 nm where the calculated direct band gap energy from tauc model for expected transition state was about ≥ 4.7 eV. The studied energy gap for prepared compounds approved the energy gap that decreased by about 0.1 eV when their molecule had π -electron, which conjugated with π electrons in 1,2,3-triazole heterocyclic ring.

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KEYWORDS

Pyromellitic; diimide; triazole; optical; energy gap.

Introduction

In recent years a lot of Planar aromatic molecules have been designed and synthesized that have received considerable attention as organic semiconductors and optoelectronic materials, due to their high fluorescence in solution, and high thermal and chemical stability [1,2,3,4].

Up to now, rylene diimides are probably the most studied, modified, synthesized as π -conjugated system with aromatic core [5,6,7]. But the relatively easy synthesis of pyromellitic diimide compared with that of other rylene derivatives has made these molecules interesting systems to be explored [8]. The pyromellitic diimide is one of a planar

aromatic compound with π -conjugated system that could be conjugated into larger multicomponent assemblies through intercalation [9-13] and give derivatives that are used widely for molecular recognition [14], molecular sensors [15], molecular machines, chemical catalysis and drug delivery [16,17,18,19]. Pyromellitic diimide derivatives decorated with fluorinated side chains have been used as active layers in n-type organic thin-film transistors, which show field-effect mobilities up to 0.079 cm² V⁻¹ s⁻¹ and Ion/Ioff ratios of 10⁶ [20,21], suggesting that the moiety has high performance to other analogues due to the close π - π conjugated electron between the benzene molecules and diimide cores [22]. The pyromellitic diimide

also has been one order of magnitude lower than that of the naphthalene diimide analogue [23], due to the smaller size of the aromatic (benzene) core. The side chain of N,N'-substituents has strongly influenced the electrical characteristics, showing the importance of carrying out the current study on pyromellitic derivatives properties.

Experiment

Synthesis of N, N'- bis amino pyromellitic diimide [1]

Pyromellitic dianhydride (1gm, 4 mmol) was added slowly to excess of a hydrazine hydrate 99% 10-20 times in ice bath, stirred for 4 hour and left overnight; a yellow precipitate was formed, dried and recrystallized by ethyl acetate.

Synthesis of N,N'- bis (2-amino acetyl chloride) pyromellitic diimide (2)[24,25]

N,N'- bis amino pyromellitic diimide (1.23 gm, 5mmol) was added to chloro acetyl chloride (1-2 mL) and refluxed on steam bath for 2-3

hrs.; after cooling yellow precipitate was formed, dried and recrystallized by ether.

Synthesis of N,N'- bis (2-amino acetyl azide) pyromellitic diimide (3)[26]

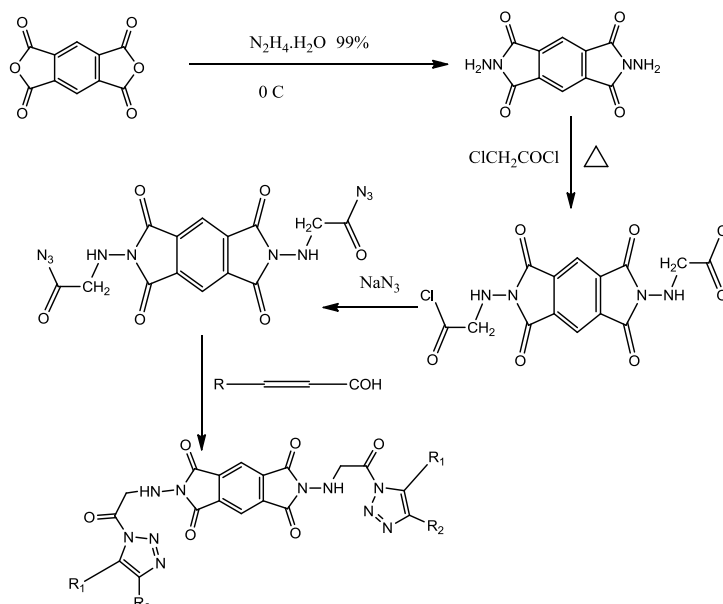
Sodium azide (0.1625 gm, 2.50 mmol) was added to N,N'- bis (2-amino acetyl chloride) pyromellitic diimide (0.5 gm, 1.25mmol.) in 250 mL of dimethyl formamide and refluxed for 6 hrs, then cooled to home temperature and precipitate was formed, dried and recrystallized.

Synthesis of N,N'- bis 1,2,3-triazole pyromellitic diimide [4-7]

N,N'- bis (2-amino acetyl azide) pyromellitic diimide (0.1 gm, 2.4 mmol) was added to α - β unsaturated aldehyde derivatives (4.8 mmol) in DMF, refluxed at 110 °C for 24 hrs., washed with ether; a brown precipitate was formed, dried and recrystallized.

Results and discussion

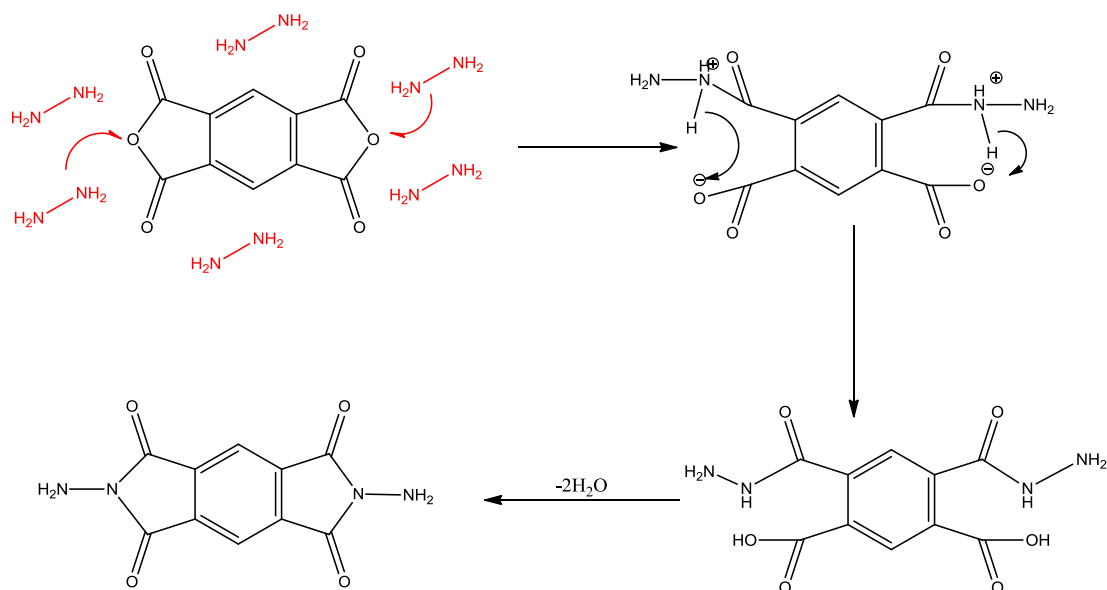
Scheme 1 shows the prepared compounds:



SCHEME 1

In the first reaction, we used excess of hydrazine to avoid condensation and

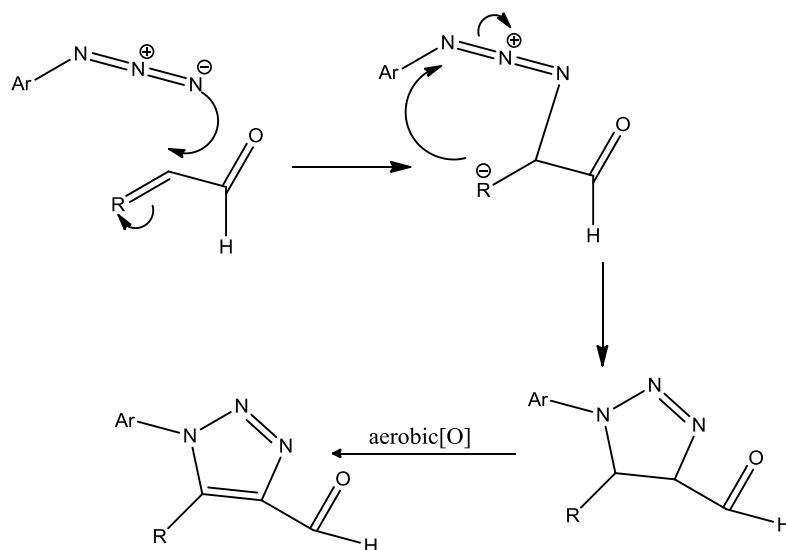
polymerization; the mechanism is shown in Scheme 2.



SCHEME 2

Scheme 3 shows the triazole ring formed by 1,3- dipolar cycloaddition in side of 1,3- dipolar cycloaddition, and the azide with

carbonyl; the double bond in α - β unsaturated aldehyde can be formed; and trizoline can be oxidized by aerobic oxygen to triazole [27].



SCHEME 3

All prepared compounds were characterized by physical properties (Table 1), FT-IR (Table 2), $^1\text{H-NMR}$ (Table 3).

The FT-IR spectra showed stretching bands at 3031-3099 cm^{-1} for CH aromatic, while CH aliphatic appeared between 2896-2925 cm^{-1} . The carbonyl groups of imide gave strong

stretching bands (1631-1654 cm^{-1}). The band in the region of 1400-1566 cm^{-1} was referred to as C=C aromatic while N=N appeared at 1325 cm^{-1} . The N-H appeared at 3186-3286 cm^{-1} . The detailed infrared spectral data is illustrated in Table 2 [28-30].

TABLE 1 Physical properties for prepared comps

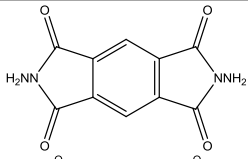
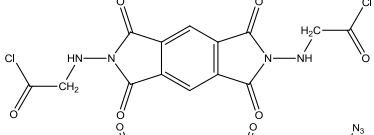
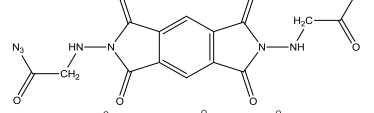
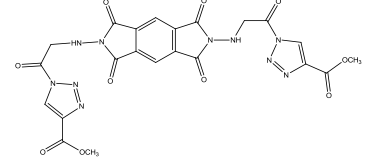
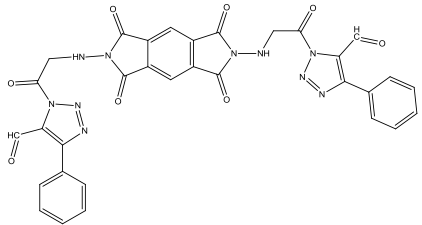
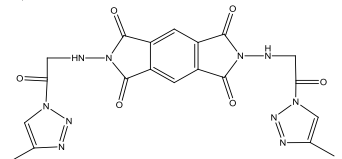
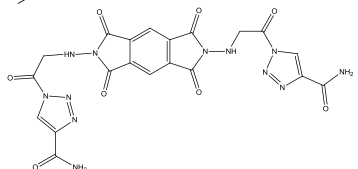
Comp. No.	Compound structure.	Molecular formula	M.wt (g/mol)	m.p (°C)	Color
1		C ₁₀ H ₆ N ₄ O ₄	246	>320	YELLOW
2		C ₁₄ H ₈ N ₄ O ₆ Cl ₂	400	>320	YELLOW
3		C ₁₄ H ₈ N ₁₀ O ₆	412	>320	BROWN
4		C ₂₂ H ₂₀ N ₁₀ O ₁₀	584	258-262	BROWN
5		C ₃₂ H ₂₄ N ₁₀ O ₈	704	>320	BROWN
6		C ₂₀ H ₁₆ N ₁₀ O ₆	492	>320	BROWN
7		C ₂₀ H ₁₈ N ₁₂ O ₈	∞∞∞	272-275	BROWN

TABLE 2 FT-IR Spectral data for prepared comps

COMP.	ν (N-H)	ν (C-H) _{AR.}	ν (C-H) alif.	ν (C=O)	ν (C=C) _{Ar.}	OTHERS
1	-	3099		1654	1488,1550,1446	3323,3440 (NH ₂) 146 ν (CH ₂)
2	3201	3068	2925	1697	1467,1542,1566	187 ν (COCl) 1155(C-N)
3	3286	3051		1633	1494,1554	2208, 2358(N ₃)
4	3197	3033	2920,2850	1631-1733	1400,1492	1325(N=N),1492(CH ₂)
5	3252	3053	2896,2999	1631,1733	1494,1537	1323(N=N),1469(CH ₂), (2763,2792)(C-H)ald.
6	3191	3045	2898,2910	1633,1654	1492,1467	1325(N=N),1467(CH ₂)
7	3186	3031	2898,2918	1635,1652	1490	1323(N=N), 1469(CH ₂)

The $^1\text{H-NMR}$ spectra showed singlet signals in the region 2.54 – 4.18 ppm for (CH_2 , 4H), and singlet signals in the region 0.87 –

2.04 ppm) for N-H, 2H, while Aromatic protons showed SINGLE signals at 7.55–7.95 ppm and multipalte in compound [5].

TABLE 3 $^1\text{H-NMR}$ spectral data for compounds

Comp.	Spectral data (δppm)
1	4.7 (s,2H,NH ₂), 7.55(s,2H,H-Ar)
2	1.29(s,2H,NH), 4.18 (s,4H,CH ₂) 8.78(s,2H,H-Ar)
3	0.87(s,2H,NH), 2.93(CH ₂ , 7.75(s,2H,H-Ar)
4	1.23(s,2H,NH), 2.77(s,4H,CH ₂), 3.59(s,6H,CH ₃), 8.5 (S,2H,CH), 8.7 (s,2H,CH-Ar)
5	2.04(S,2H, NH), 2.54 (s,4H, CH ₂),7.06 (s,2H,CH),7.95 (m,H-Ar), 8.95 (s,COH)

UV-VIS

The optical properties of the prepared compounds [4-7] were analyzed by UV-Vis absorption spectroscopy. Absorption spectra showed similar characteristics and the

maximum (λ_{max}) appeared at uv range of 200-300 nm. The absorption band being responsible for π - π^* transition in the amine group is covered by absorption of the pyromellitic units (Figures 1-5).

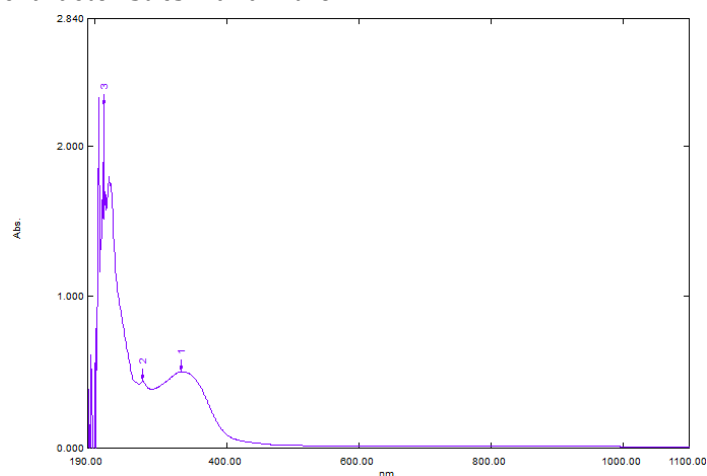


FIGURE 1 UV-vis spectra for compound (4)

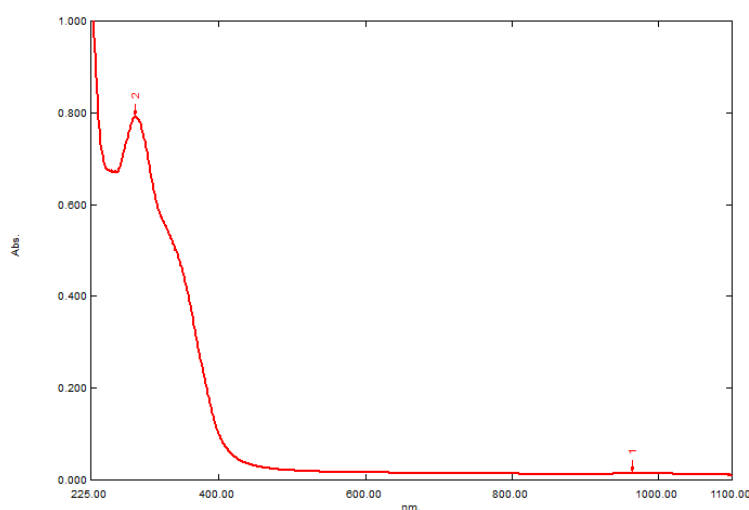
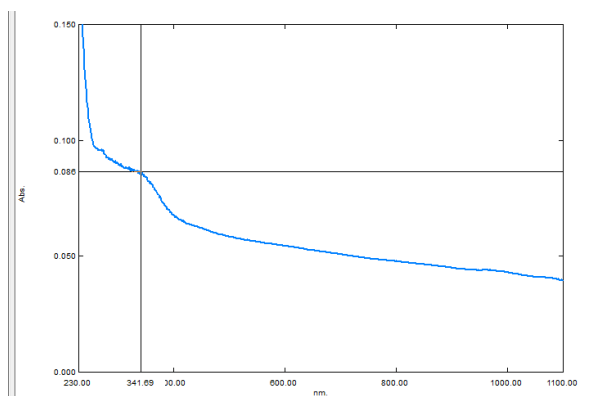
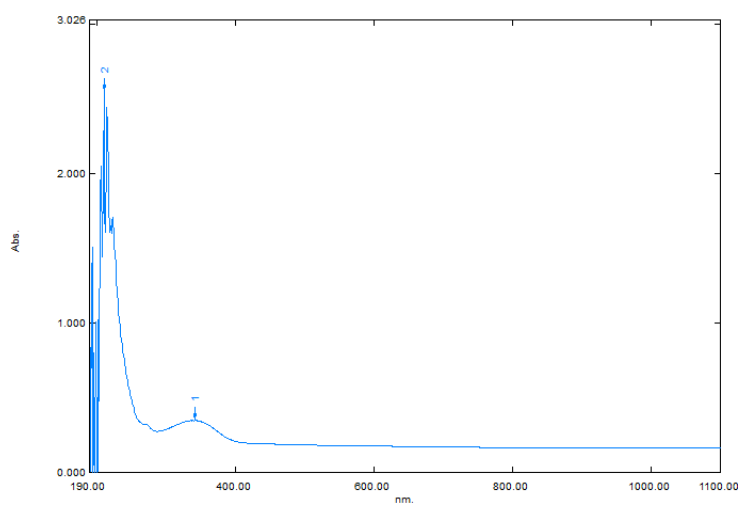
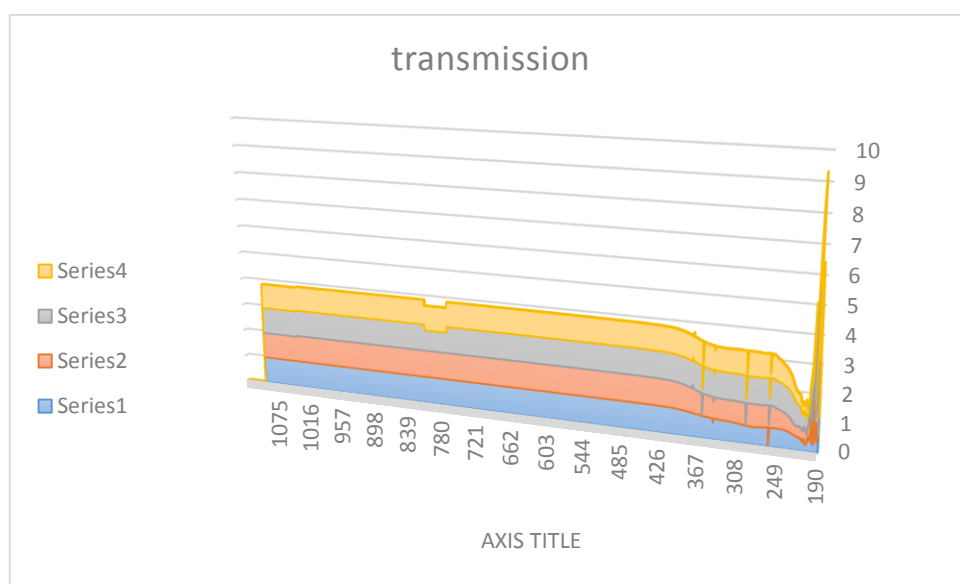


FIGURE 2 UV-vis spectra for compound (5)

**FIGURE 3** UV-vis spectra for compound (6)**FIGURE 4** UV-vis spectra for compound (7)**FIGURE 5** The transmission of the studied compounds

Energy gap

The optical energy band gap values (E_g) at about (≥ 4.7 eV) was calculated from the onset of UV-vis absorption band. Direct band gap energy can be calculated from tauc model, from the following Equation:

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

Where A_0 is a constant, $h\nu$ is the photon energy, E_g is the optical band gap energy, and α is optical absorption coefficient deduced from the absorption data.

TABLE 4 Energy gap for comps. (4-7)

Comp.	Energy gap (ev)
4	4.72
5	4.7
6	4.91
7	4.82

The energy band gap in transition state (> 4 ev.), showed in Figures 6-8, are calculated from tauc models.

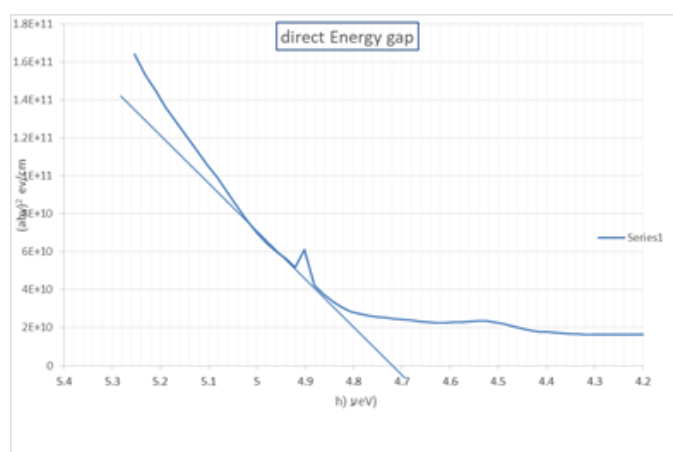


FIGURE 6 Direct energy gap for comp.4

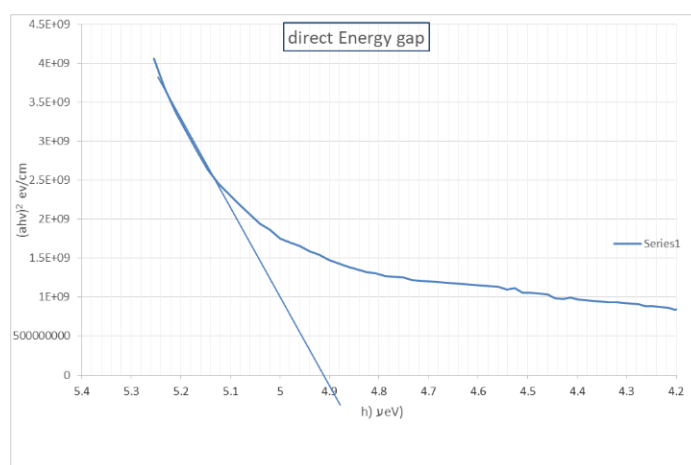


FIGURE 7 Direct energy gap for comp.6

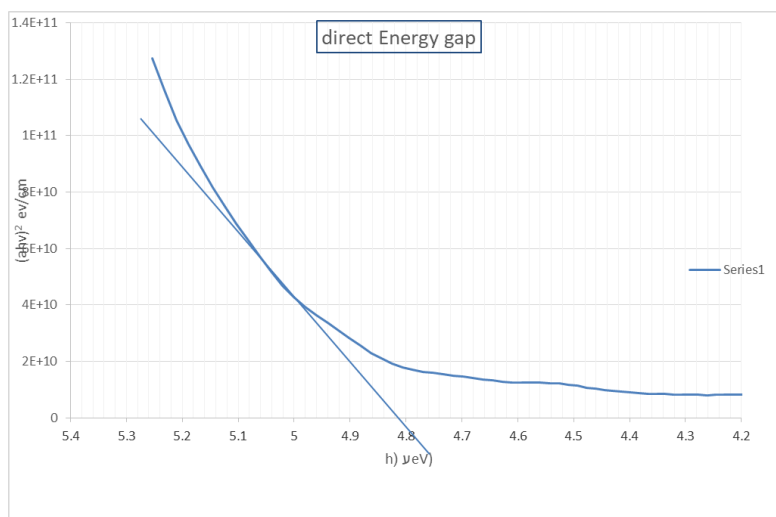


FIGURE 8 Direct energy gap for comp.7

Conclusion

An electrical property of a wide energy gap ($E_g \geq 3.3$ eV) is critical for semiconductors to realize full transparency with excellent photostability in the visible range [31]. The four compounds [4-7] show a good expected optical energy gap that can be used as n-type materials in solar cell although showing a good optical sensitive for UV wave length (near visible wave length in compound [4] and [7] that can be used as detector or chemical sensors for these wave length.

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