



Properties of Perylene Bisimide Derivatives: DFT Investigation and Structure Determination

BOWEI CHEN^{1,2,3,*}, ZHENG TONG HAO^{1,2} and YEWEI XU³

¹School of Physics and Electronic Engineering, Mianyang Normal University, Mianyang 621000, P.R. China

²Research Center of Computational Physics, Mianyang Normal University, Mianyang 621000, P.R. China

³Research Center of Laser Fusion, China Academy of Engineering Physics, Mianyang 621900, P.R. China

*Corresponding author: Fax: +86 816 2200063; E-mail: cbwelder@sina.com

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Perylene bisimide derivatives are typical semiconductor materials of *n*-type. The HOMO and LUMO energy levels' structures of perylene bisimide derivatives were adjusted successfully by substituted atoms or groups in the bay positions. The electronic structures of perylene bisimide derivatives were successfully investigated by density functions theory (DFT) in this paper. The results indicated that the bromine atoms in the bay positions were replaced by phenoxy and the LUMO energy levels of perylene bisimide derivatives would be increased. Furthermore, the red shift of UV-visible absorption spectra of perylene bisimide derivatives matched the change of the band gap of theoretical investigation *via* DFT. Additionally, the crystal structures of perylene bisimide derivatives were analyzed with X-ray powder diffraction data (XRD) and one type of the perylene bisimide derivatives' crystal system of one type of perylene bisimide derivatives was monoclinic space group P1n1. The R_{WP} and R_F were also in reasonable range, 11.66 and 9.17 %, respectively.

Key Words: Perylene bisimide derivatives, DFT, XRD, Molecular orbital, Refinement.

INTRODUCTION

Perylene bisimide derivatives (PBIs) have attracted widespread attention owing to their outstanding characters, such as strong absorption in the visible region, higher electron affinity and great thermal stability¹⁻⁵. The imide regions of perylene bisimides were modified to improve its weak solubility. Moreover, bay regions were substituted by bromine or phenoxy groups to reform absorption range of light wavelength⁶⁻⁸. Zhang *et al.*⁹ has synthesized some compounds successfully, as follows: N,N'-didodecyl-1,7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide (**1**), N,N'-didodecyl-1,6,7,12-tetrabromoperylene-3,4,9,10-tetracarboxylic acid bisimide (**2**), N,N'-didodecyl-1,7-di(4-*tert*-butylphenoxy)perylene-3,4,9,10-tetracarboxylic acid bisimide (**3**) and N,N'-didodecyl-1,6,7,12-tetra(4-*tert*-butylphenoxy) perylene-3,4,9,10-tetracarboxylic acid diimide (**4**) (Fig. 1).

The ground-state and excited-state of π -conjugated perylene bisimide derivatives were intensively investigated^{8,10-12}. The UV-visible absorption spectra of perylene bisimide derivatives were changed due to the substitution on bay regions or imide regions^{8,13-16}. According to DFT calculation, the variation of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy levels were in good agreement with the transformation in UV-visible absorption

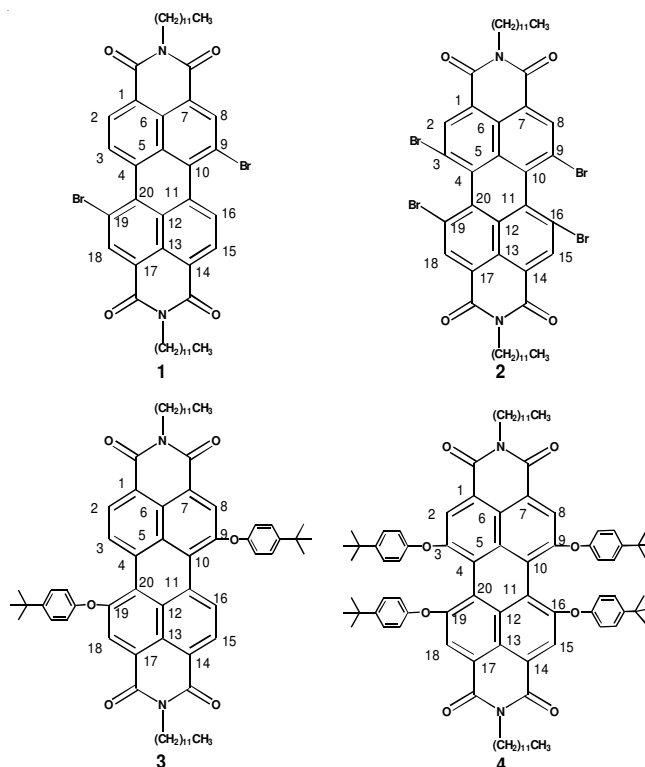


Fig. 1. Carbon-atom numbered structures of perylene bisimide derivatives

spectra. A few papers reported the DFT calculation of perylene bisimide derivatives' molecular orbitals which revealed the molecular geometry and the electronic structures^{10,11,15}. Furthermore, *ab initio* crystal structures of perylene bisimide derivatives were determined through X-ray powder diffraction by using the simulated technique of the refinement which provided space group, unit cell parameters and other parameters¹⁷⁻²⁰. In this paper, perylene bisimide derivatives (compounds **1**, **2**, **3** and **4**) were prepared and the crystal structure of **3** was simulated. Through the application of advanced laboratory X-ray powder diffractometers and the use of *ab initio* and Rietveld techniques, a number of crystal structures of organic compounds were solved.

COMPUTATIONAL METHOD

DFT methodology: Large numbers of π -conjugated molecules intensively investigated in materials science. Some empirical models were illustrated through the key π - π^* bond in the absorption spectrum²¹, while others were explained by the extended Huckel tight-binding model²². Nevertheless, the excitation energies of perylene tetracarboxylic diimides (PTCDIs) were obtained through the TD-HF/TZV(P) level by Zhao *et al.*¹¹, which clearly proved the electronically excited states. The neutral and radical ion states of PTCDIs were optimized by DFT with the B3LYP function and the 6-31++G** basis in the Gaussian03 program, Deigado *et al.*¹⁰. Moreover, the optical properties of perylene bisimide derivatives were successfully calculated and the excitation energies demonstrated a good match with the experimental data. The theoretical absorption spectra of π -conjugated molecules were in perfect accordance with experimental data analyzed by quantum-chemistry method^{8,12,14,16,23}. Firstly, the ground-state energies for perylene bisimide derivatives of **1**, **2**, **3** and **4** were computed with DFT theory in quantum chemical using the BLYP/DND level and the analysis provided insight for the electronic structures. Secondly, the visible light absorption properties of perylene bisimide derivatives were interpreted through the DFT method using the BLYP/DND level. All computations were preformed with the Doml3 program package. The calculations on molecular orbital energies revealed that the additional bay substituents suppressed the aggregation of perylene bisimide derivatives core and gave a red-shifted absorption in the UV-visible absorption spectra^{15,16}.

Structure refinement: Initial X-ray powder diffraction data of compounds were recorded at room temperature by using a XRD diffractometer equipped (X'Pert PRONetherlands PAN alytical Company) with Cu K α 1 radiation ($\lambda = 1.540598$ Å, 40 kV generator voltage and 40 mA tube current). The diffraction pattern was scanned with a step size of 0.02° (2 θ) and counting time 1s/step over an angular range of 3-80° (2 θ) through the use of the Bragg-Brentano geometry. All data were collected by using a step scan 0.02° (2 θ)/step, 2s/step and the range of 2-60° (2 θ). The X-ray powder diffraction patterns of **1**, **2**, **3** and **4** were auto-indexed with the program DICVOL91²⁴⁻²⁷. Peak profiles were modeled with a Pseudo-Voigt function that contained the average crystallite size. Pawley refinement was used to fit the peak profiles and adjust various parameters to minimize the weight profile R-factor^{28,29}. After working on ten cycles of Pawley refinement, the choice of unit cell and

space group was confirmed. Furthermore, crystal structure was solved through Powder Solve algorithm. The algorithm uses Monte Carlo simulated annealing approach to generate considerable trial structures which are automatically compared between the experimental patterns and the simulated powder ones^{30,31}. The creditable structure was resolved and ultimately selected for further Rietveld refinement³². The hydrogen atoms positions and structure of unit cell were refined by the Rietveld method. Finally, all the refinements contributed to the emergence of a satisfactory crystal structure.

RESULTS AND DISCUSSION

Electronic structure: To better understand the effect of bay substituents on the electronic spectra of compounds, molecular orbitals of **1**, **2**, **3** and **4** were calculated by DFT. All the calculations and characters strongly demonstrated that perylene bisimide derivatives were typically *n*-type semiconducting materials owing to its lower LUMO energy level. perylene bisimide derivatives are exhibited a low LUMO energy level, so that it possessed a strong electron affinity and are easy to reduced^{12,33-35}. Furthermore, the HOMO and LUMO levels were easily varied by bay substituents with atoms or groups. The details of HOMO and LUMO orbitals of **1**, **2**, **3** and **4** perylene bisimide derivatives are illustrated in Fig. 2, while Table-1 gives an overview of the calculated HOMO and LUMO levels of these perylene bisimide derivatives. And the HOMO and LUMO energy levels are also removed in carbon bonds owing to the investigation on application of different bay-substituted perylene bisimide derivatives. The HOMO and LUMO are entirely located on carbon bonds on the Perylene core and the details are listed in Table-2. The charge densities for the HOMO and LUMO in **1**, **2**, **3** and **4** (Fig. 2) indicate very little charge accumulation on the hydrogen atoms. This description has revealed the relationship between electro-optical properties and the perylene core. A phenoxy group to enrich an electron and a bromine group to induce the electrons deficiency on the perylene core were employed for compounds of **1**, **2**, **3** and **4**. As a result, the bay regions were substituted by bromine atoms and the electrophilicity of perylene bisimide derivatives was increased. The LUMO level of **2** dropped to -4.25 eV, lower than **1**. Consequently, **2** obtained two more bromine substituents in bay regions than **1**; as a result, its impact on electronic excitation was greater than **1** and its reduction potential was more negative. Similarly, when the bromine atoms were replaced by the phenoxy, the LUMO level of **3** raised to -3.78 eV. Since **4** had two more substituents than **3**, its reduction potential was lower. The LUMO level of **4** was -3.40 and 0.38 eV higher than **3**.

TABLE-1
CALCULATED ENERGY LEVELS OF **1**, **2**, **3** AND **4**

| | LUMO (eV) | HOMO (eV) |
|----------|-----------|-----------|
| 1 | -4.14 | -5.57 |
| 2 | -4.25 | -5.67 |
| 3 | -3.78 | -5.25 |
| 4 | -3.40 | -4.65 |

According to molecular orbital theory, HOMO and LUMO levels are important factors influencing optical properties of the perylene bisimide derivatives. The absorption spectra of

TABLE-2
HOMO AND LUMO OF 1, 2, 3 AND 4

| | HOMO (located on carbon bonds) | LUMO (located on carbon bonds) |
|---|---|---|
| 1 | C3-C4, C7-C8, C9-C10, C11-C16, C17-C18, C19-C20 | C1-C21, C2-C3, C4-C20, C7-C23, C8-C9, C10-C11, C14-C24, C15-C16, C17-C26, C18-C19 |
| 2 | C3-C4, C7, C9-C10, C11-C16, C19-C20 | C1-C21, C2-C3, C4-C20, C7-C23, C8-C9, C10-C11, C14-C24, C15-C16, C17-C26, C18-C19 |
| 3 | C3-C4, C7-C8, C9-C10, C11-C16, C17-C18, C19-C20 | C1-C21, C2-C3, C4-C20, C7-C23, C8-C9, C10-C11, C14-C24, C15-C16, C17-C26, C18-C19 |
| 4 | C3-C4, C7, C9-C10, C11-C16, C19-C20 | C1-C21, C2-C3, C4-C20, C7-C23, C8-C9, C10-C11, C14-C24, C15-C16, C17-C26, C18-C19 |

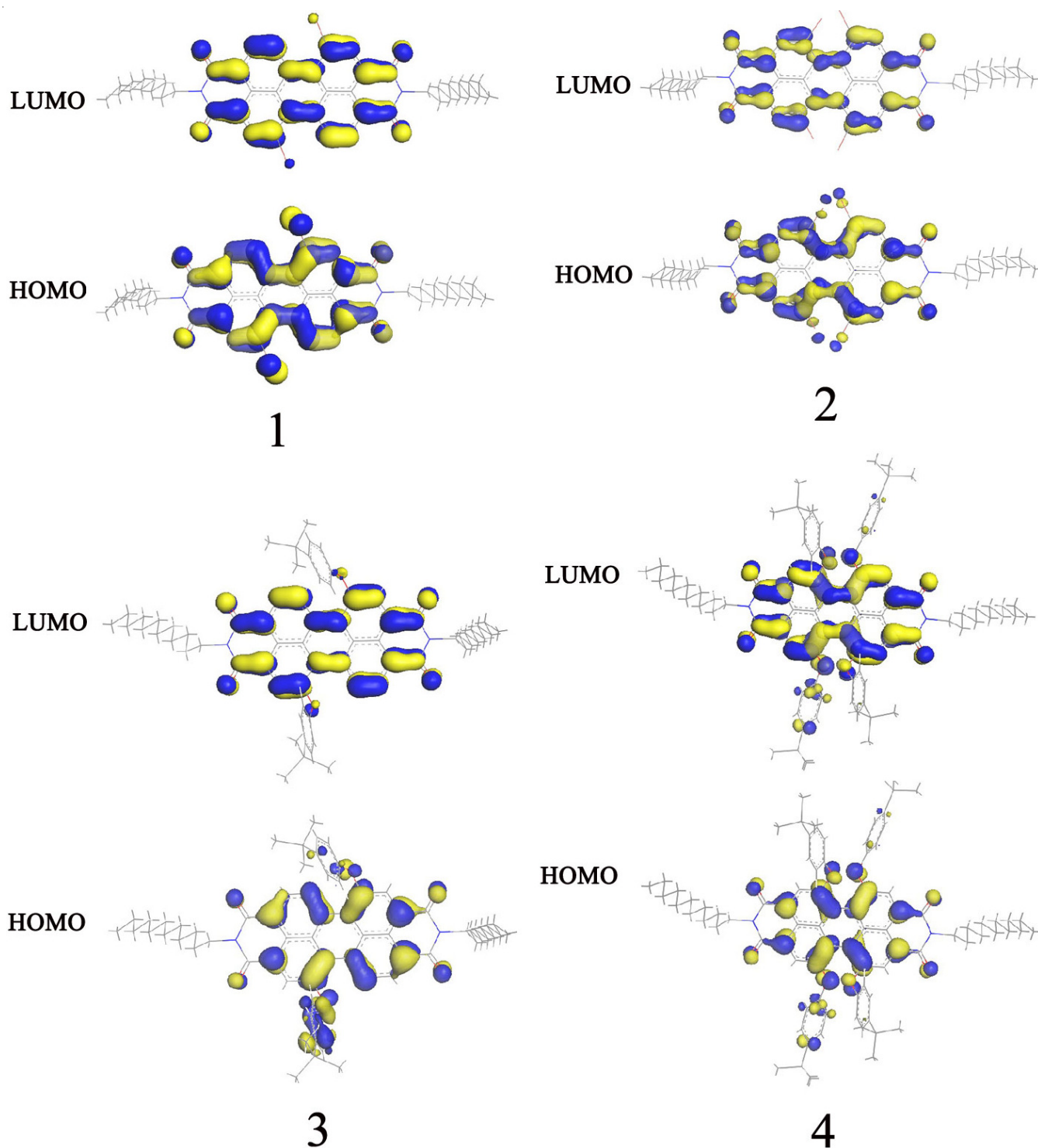


Fig. 2. Illustration of the frontier molecular orbitals for 1, 2, 3 and 4

these perylene bisimide derivatives in CHCl_3 are shown in Fig. 3. Additionally, the examination of UV-visible absorption in Fig. 3 reveals that bay substituents of the perylene bisimide derivatives lead to a significant red shift of absorption maxima and threshold. The orbital partitioning in perylene bisimide derivatives is mostly affected by the strong electron donating or accepting group in the bay positions of perylene bisimide derivatives; nonetheless, the groups in the bay substituents affect the optical properties as well. The absorption maxima of **1**, **2**, **3** and **4** in UV-visible absorption are shown in Table-3 together with the significant trend of red shift. As what is shown in the red shift of the UV-visible absorption spectra, the band gaps of **2**, **3** and **4** perylene bisimide derivatives (Table-3) become smaller than **1** (Fig. 3) Just as expected, it shows red-shifted absorption threshold at 550 nm that are the asymmetrally disubstituted compounds of **2**, **3** and **4** perylene bisimide derivatives with bromine atom or phenoxy group at the bay positions of the perylene core.

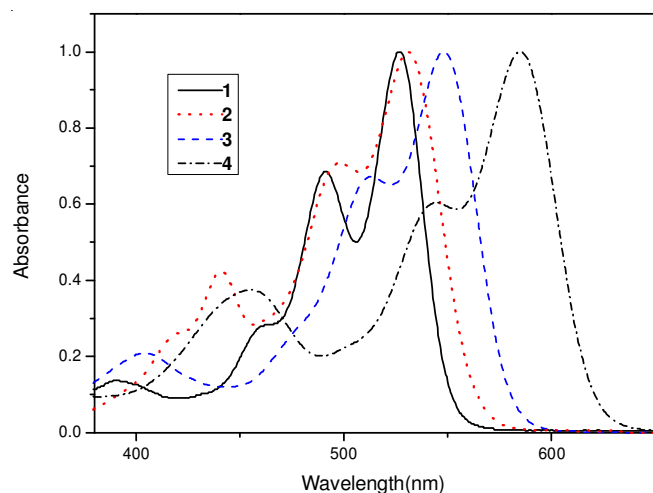


Fig. 3. UV-visible absorption spectra of **1**, **2**, **3** and **4** in CHCl_3

| TABLE-3 TAKE A AS THE FRAME OF REFERENCE | | | | | |
|---|-------------------------------|----------------|---------------------------|----------------|---------------|
| | Maximum absorption peaks (nm) | Red shift (nm) | Absorption threshold (nm) | Red shift (nm) | Band gap (eV) |
| 1 | 526 | 0 | 550 | 0 | 2.25 |
| 2 | 532 | 6 | 566 | 6 | 2.19 |
| 3 | 549 | 17 | 580 | 24 | 2.14 |
| 4 | 585 | 35 | 625 | 60 | 1.98 |

The investigation on absorption characteristics shows that bay substituents with atoms or groups markedly change the optical properties of the perylene bisimide derivatives. By analysis on both of the HOMO and LUMO energy levels, the effects of bay substituents are proved to have potential to derive: The LUMO potential of all compounds demonstrates more reduction (Table-1), which reflects the fact that the LUMO is

located on the Perylene core (Fig. 3). The HOMO potential of all compounds demonstrates more oxidization varying the acceptance in the bay position, compounds of **1**, **2**, **3** and **4** perylene bisimide derivatives have a evident effect on the HOMO potential in Fig. 3. A phenoxy group and a bromine atom substituent in the bay position slightly narrow the band gap. Concerning the absorption characteristics of the perylene bisimide derivatives, compounds of **1**, **2**, **3** and **4** perylene bisimide derivatives successively appear green, yellow, orange and red to the human eye, with absorption maxima 526, 532, 549 and 585 nm in CHCl_3 , respectively (Fig. 3 and Table-3).

Crystal structure determination: Final Rietveld refinement is shown in Fig. 4. The final refinement details and parameters of unit cell dimensions are listed in the Table-4.

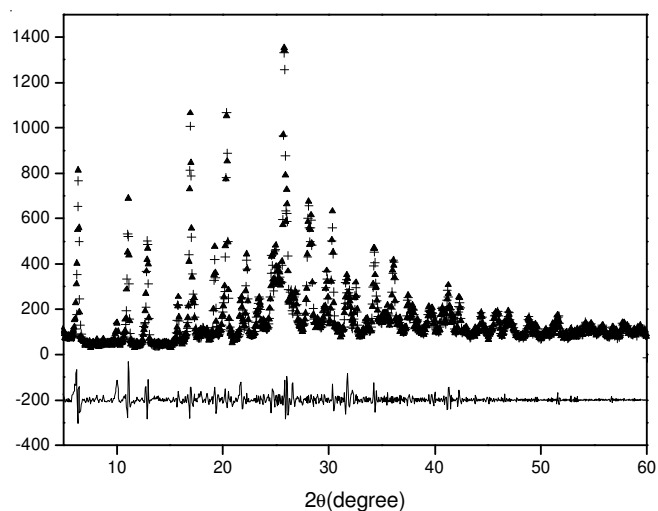


Fig. 4. Experimental (+ marks), calculated (% marks) and difference (lower line) powder X-ray diffraction profiles for the final Rietveld refinement of compound **2**

To explore relationships between the electro-optical properties and structural properties in the solid state, the crystal structure of **2** has been determined. The X-ray powder diffraction of **2** is indexed by the program DICVOL91 giving the unit cell (Table-1). Systematic absences are consistent with the monoclinic space group $P1n1$ and the density considerations suggest that there are two molecules in the unit cell. The structure with the lowest R_{wp} was obtained for the final Rietveld refinement ($R_{wp} = 11.66\%$, $R_p = 9.17\%$). All atoms were refined, including bond lengths, bond angles, global isotropic temperature factors, preferred orientation parameters and atomic coordinates.

Conclusion

Perylene bisimide with a phenoxy group or a bromine atom on the bay position, possesses better qualities for application. To reach a more scientific and reasonable result, DFT was employed to analyze the details. By means of that analysis,

| TABLE-4 CRYSTAL STRUCTURE OF 2 OBTAINED BY XRD REFINEMENT | | | | | | |
|---|--------------------------------|----------------|----------------|--------------------------|--------------|-----------|
| Pattern range 2θ (°) | Step size $\Delta 2\theta$ (°) | Wavelength (Å) | Crystal system | Space group | a (Å) | b (Å) |
| 2-60 | 0.02 | 1.540598 | Monoclinic | $P1n1$ | 17.2285 | 7.95327 |
| c (Å) | α (°) | β (°) | γ (°) | Volume (Å ³) | R_{wp} (%) | R_p (%) |
| 16.5733 | 90.0000 | 110.580 | 110.580 | 2125.99 | 11.66 | 9.17 |

authors discovered that its HOMO and LUMO energy level were altered correspondently with appreciable quantity, which contributed to transferring a satisfactory range in UV-visible absorption spectra. Furthermore, the crystal structure of **b** has been analyzed by X-ray powder diffraction. XRD refinement was applied to the previous data. Successfully, the RWP and R_p were in reasonable range $R_{WP} = 11.66\%$, $R_p = 9.17\%$, respectively and the crystal system of **2** was monoclinic space group $P1n1$.

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