JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. **11** No 2, 02028(3pp) (2019)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том **11** № 2, 02028(3cc) (2019)

Excitonic Properties of Perylene Diimide Based Dyes

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(Received 17 January 2019; revised manuscript received 03 April 2019; published online 15 April 2019)

The paper is devoted to the comprehensive study of the electronic properties of eight molecules in the framework of the density functional theory (DFT) implemented in the ABINIT code. The *first stage* of calculations is based on the semi-local variant of the DFT approach, which involves the use of a generalized gradient functional for exchange-correlation energy (GGA). Optimization of the structure of molecules is performed within the framework of DFT-GGA theory. At the *second stage*, the electronic structure of the molecules in the ground state was calculated. The *third stage* was to determine the role of the static electron-hole interaction in the formation of the electron energy spectrum. The Green's function necessary for its realization was based on the eigenvalues and wave functions found at the previous stage within the DFT-GGA formalism. The Green's function method allows to obtain the energy of quasiparticle excitations including the static electron-hole interaction, which is not taken into account in the DFT-GGA approach. Quasiparticle energies are obtained in the first order perturbation of the Green's function, that is, in the GW approximation. The *fourth step* of our study was to clarify the role of the dynamic interaction of an electron and a hole in the formation of optical constants taking into account exciton effects. It was implemented using the Bethe-Salpeter equation (BSE), whose parameters were based on the solutions obtained in the previous stages. It was found that the smallest value of E_g found in the GGA approximation belongs to the PR 178 molecule, and in the GW approximation it is acquired by the PB 32 molecule. The BSE formalism leads to the smallest value of E_g for the PR 178 molecule. The largest value of E_g in the GGA approach belongs to the PR 179 molecule, in the GW formalism – to the molecule PR 190, and in the BSE theory – to the PB 31 molecule. It was found that in the GGA approach the band gap E_g lies in the energy range of $0.52 \le E_g \le 1.47$ eV, in the GW approximation, $6.08 \le E_g \le 7.92$ eV, and in the BSE formalism, $0.08 \le E_g \le 1.35$ eV.

Keywords: Perylene, Diimide, Dyes, Quasiparticle, GW, BSE.

DOI: 10.21272/jnep.11(2).02028 PACS numbers: 31.15.A, 42.70.Jk

1. INTRODUCTION

Non-fullerene acceptor materials are to solve and overcome the fullerene disadvantages such as processability, stability and good solubility in halogen-free solvents [1-3]. Small molecule materials are attractive due to their well-defined molecular structure, stability and purity. Perylene diimide (PDI) materials are already used as pigments and dyes. They show excellent thermal, chemical, photochemical stability [4, 5]. Intensive investigations of different PDI derivatives for photovoltaic purposes are supposed to improve excitation properties, such as exciton binding energy and diffusion length, the donor-acceptor coverage for higher bulk heterojunction efficiency [6-10]. As the result, we can observe rising power conversion efficiency over 9 % [10].

This work is supposed to perform ab initio study of several well-known PDI-dyes in order to show the variation of electronic properties on different substitution in peri-position. The list of molecules include red, black and violet pigments (color index, C.I.): Pigment Red 149 (PR 149, C.I. 71137), Pigment Red 178 (PR 178, C.I. 71155), Pigment Red 179 (PR 179, C.I. 71130), Pigment Red 189 (PR 189, C.I. 71135), Pigment Red 190 (PR 190, C.I. 71140), Pigment Violet 29 (PV 29, C.I. 71129), Pigment Black 31 (PB 31, C.I. 71132), and Pigment Black 32 (PB 32, C.I. 71133).

2. METHODS

The ground state (GS) single-particle energies and eigenfunctions are obtained within the generalized gradient approximation (GGA) [11] using the norm-conserving pseudopotentials [12, 13]. Then the Green's function (GF) is built on the base of GS data. The GF allows us to evaluate the quasi-particle energies. Here we have employed the self-consistent GW (scGW) approach based on the first order perturbation of the GF. The frequency dependence of the screened interaction has been obtained using contour deformation method. For molecular materials we used spherical expressions of the Coulomb term in reciprocal space [14]. The excitonic effects have been derived from the Bethe-Salpeter equation (BSE). The macroscopic dielectric function (DF) was calculated by means of direct diagonalization of the exciton Hamiltonian. All the calculations have been performed using ABINIT package [15].

3. RESULTS AND DISCUSSION

The optimal plane-wave cut-off energies (E_{cut}) have been derived from our convergence study. The values of E_{cut} which ensure the convergence of the calculation are as follows: 816 eV for ground-state runs, 68 eV for the RPA dielectric matrix (scGW), 82 eV for the BSE formalism, and 1090 eV for the exchange part of the self-energy operator, respectively.

The electron energy gaps E_g obtained within three different approaches and HOMO energies (E_{HOMO}) are listed in Table 1. The smallest E_g^{GGA} is obtained to be 0.52 eV for a molecule of PR 178. PR 179 has the widest GGA gap (1.47 eV). The obtained E_g^{GW} values are much higher and vary from 6.08 eV for PB 31 to 7.92 eV for PR 190 (Table 1).

BSE calculations show quite different results comparing to the previous step. Here E_g^{BSE} are smaller than E_g^{GGA}. Considering obtained DOS and DF distributions we can note that all materials have states in the infrared range (0-1.6 eV). And all materials have non-zero DF in this interval, except PR 189 and PB 32, where absorption is recorded for energies higher than 2 eV.

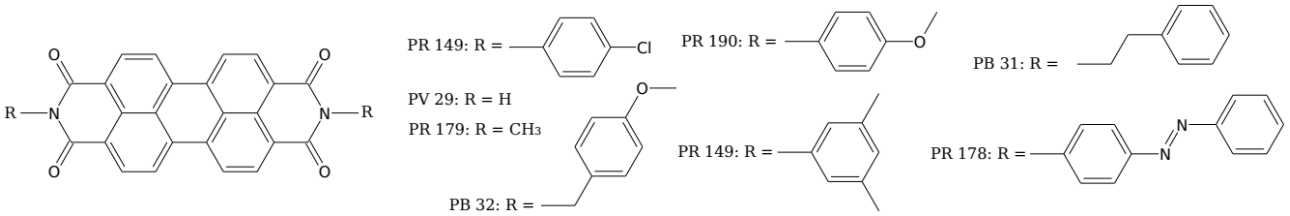

Fig. 1 – Chemical structure of PDI dyes

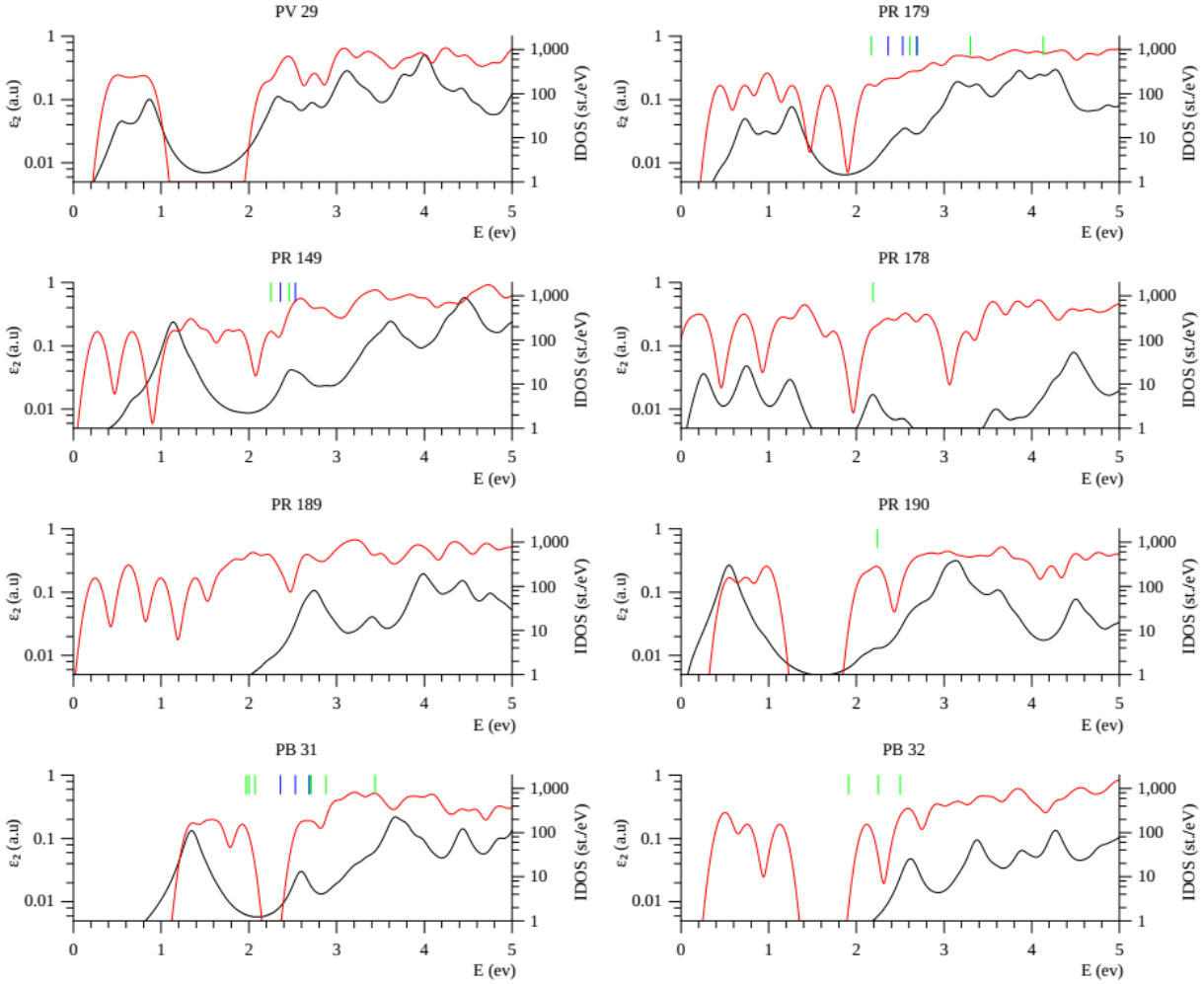

Fig. 2 – Imaginary part of the BSE dielectric function ε_2 (black) and density of states (DOS) (red). Green dash lines present available experimental absorption data for solid-state materials [16-20]. Blue dash lines correspond to spectra for solutions [19, 20]

Table 1 – The parameters of electronic structure: the band gap E_g and the highest occupied orbital energy E_{HOMO}

Molecule	E_g^{GGA}, eV	E_g^{GW}, eV	E_g^{BSE}, eV	E_{HOMO}, eV
PV 29	1.45	6.23	0.45	– 5.61
PR179	1.47	6.58	0.45	– 6.99
PR 149	1.30	7.20	0.27	– 7.42
PR 178	0.52	7.61	0.08	– 7.98
PR 189	1.22	7.19	0.25	– 7.76
PR 190	0.82	7.92	0.55	– 8.22
PB 31	1.44	6.74	1.35	– 7.16
PB 32	1.02	6.08	0.47	– 5.53

The most of calculated DF peaks agree well with both experimental absorption data, measured for the solid-state, and as well as for solutions, except a number of molecules (PR 179, PR 190, PB 31, PB 32, around 2 eV), where the DOS maxima agree with the experimental peaks instead of DF (Fig. 2).

4. CONCLUSIONS

We have performed the four-stage ab initio analysis of eight PDI derivatives. All calculations were performed using the ABINIT program. We initially optimized the structure of all molecules. Then we have obtained the electron energy spectrum of eight molecules within the framework of the DFT-GGA theory. We found that obtained band gaps E_g lie in the range from 0.52 to 1.47 eV. The next step was to clarify the effect of quasiparticle effects on the formation of the parameters of the electronic energy spectrum. It turned out that quasiparticle excitations result in large corrections to electron energies. For example, for PV 29 molecule, the values of band gaps E_g, obtained here in the GGA and GW approaches, are equal to 1.47 and 6.23 eV, respectively. We also found that in all the molecules examined here, the exciton effects are very significant. For the same molecule, PV 29, the band gap taking into account exciton effects is 0.45 eV. That is, the exciton binding energy E_b equals 5.78 eV. As can be seen from the results obtained here, the band gaps satisfy the condition $E_g^{BSE} < E_g^{GGA} < E_g^{GW}$. However, earlier we found that in semiconductor and dielectric crystals this inequality looks like [21, 22]: $E_g^{GGA} < E_g^{BSE} < E_g^{GW}$.

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Екситонні властивості барвників на основі перилен-диімідів

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Ця праця присвячена комплексному вивченню електронних властивостей восьми молекул в рамках теорії функціонала повної електронної густини (DFT), імплементованої у програмі ABINIT. *Перший етап* розрахунків грунтується на напівлокальному варіанті підходу DFT, який передбачає застосування узагальненого градієнтного функціонала для обмінно-кореляційної енергії (GGA). Оптимізація структури молекул виконана в рамках теорії DFT-GGA. *На другому етапі* була розрахована електронна структура молекул в основному стані. *Третій етап* полягав у визначенні ролі статичної взаємодії електрона й дірки у формуванні параметрів електронного енергетичного спектру. Необхідна для його реалізації функція Гріна будувалась на власних енергіях і хвильових функціях, знайдених на попередньому етапі у формалізмі DFT-GGA. Метод функції Гріна дозволяє отримати енергії квазічастинкових збуджень з урахуванням електронно-діркової взаємодії, яка не враховується у підході DFT-GGA. Квазічастинкові енергії отримуються у першому порядку збурення функції Гріна, тобто у наближенні GW. *Четвертий крок* нашого дослідження полягав у виясненні ролі динамічної взаємодії електрона й дірки у формуванні оптичних констант з урахуванням екситонних ефектів. Він був реалізований за допомогою рівняння Бете-Солпітера (BSE), параметри якого будувались на основі розв'язків, отриманих на попередніх етапах. Встановлено, що найменше значення E_g, знайдене в наближенні GGA, має молекула PR 178, а в наближенні GW його набуває молекула PB 32. Формалізм BSE приводить до найменшого значення E_g для молекули PR 178. Найбільше значення E_g у підході GGA має молекула PR 179, у формалізмі GW – молекула PR 190, у теорії BSE – молекула PB 31. Виявлено, що знайдені у підході GGA $0.52 \le E_g \le 1.47$ еВ, у наближенні GW $6.08 \le E_g \le 7.92$ еВ, у формалізмі BSE $0.08 \le E_g \le 1.35$ еВ.

Ключові слова: Перилен, Диімід, Барвники, Квазічастинки, GW, BSE.