# **ECONSTOR** Make Your Publications Visible.

A Service of

ZBW

Leibniz-Informationszentrum Wirtschaft Leibniz Information Centre for Economics

Saadon, Abbas K.; Al-agealy, Hadi J. M

### Article

# Study of photoemission and electronic properties of dyesensitized solar cells

**Energy Reports** 

#### **Provided in Cooperation with:** Elsevier

*Suggested Citation:* Saadon, Abbas K.; Al-agealy, Hadi J. M (2020) : Study of photoemission and electronic properties of dye-sensitized solar cells, Energy Reports, ISSN 2352-4847, Elsevier, Amsterdam, Vol. 6, Iss. 3, pp. 28-35, https://doi.org/10.1016/j.egyr.2019.10.015

This Version is available at: https://hdl.handle.net/10419/243976

#### Standard-Nutzungsbedingungen:

Die Dokumente auf EconStor dürfen zu eigenen wissenschaftlichen Zwecken und zum Privatgebrauch gespeichert und kopiert werden.

Sie dürfen die Dokumente nicht für öffentliche oder kommerzielle Zwecke vervielfältigen, öffentlich ausstellen, öffentlich zugänglich machen, vertreiben oder anderweitig nutzen.

Sofern die Verfasser die Dokumente unter Open-Content-Lizenzen (insbesondere CC-Lizenzen) zur Verfügung gestellt haben sollten, gelten abweichend von diesen Nutzungsbedingungen die in der dort genannten Lizenz gewährten Nutzungsrechte.

#### Terms of use:

Documents in EconStor may be saved and copied for your personal and scholarly purposes.

You are not to copy documents for public or commercial purposes, to exhibit the documents publicly, to make them publicly available on the internet, or to distribute or otherwise use the documents in public.

If the documents have been made available under an Open Content Licence (especially Creative Commons Licences), you may exercise further usage rights as specified in the indicated licence.



ND https://creativecommons.org/licenses/by-nc-nd/4.0/



# WWW.ECONSTOR.EU



Available online at www.sciencedirect.com



Energy Reports 6 (2020) 28-35

www.elsevier.com/locate/egyr

## Tmrees, EURACA, 04 to 06 September 2019, Athens, Greece Study of photoemission and electronic properties of dye-sensitized

### solar cells

Abbas K. Saadon, Hadi J.M Al-agealy\*

Department of Physics, College of Education for pure science Ibn Al-Haitham, University of Baghdad, Iraq

Received 20 September 2019; accepted 18 October 2019 Available online 11 February 2020

#### Abstract

We have investigated the photoemission and electronic properties at the PTCDI molecules interface on TiO2 and ZnO semiconductor by means of charge transition. A simple donor acceptor scenario used to calculate the rate for electron transfer of delocalized electronics in a non-degenerately TiO2 and ZnO electrodes to redox localized acceptors in an electrolytic. The dependent of electronic transition rate on the potential at contact of PTCDI with TiO2 and ZnO semiconductors, it has been discussion using TiO2 and ZnO electrodes in aqueous solutions. The charge transfer rate is determining by the overlapping electronic coupling to the TiO2 and ZnO electrodes, the transition energy, potential and polarity media within the theoretical scenario of the electronic transition, it can be expected the transition rate at electrodes interface with PTCDI dye using computer program.

© 2019 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

Peer-review under responsibility of the scientific committee of the Tmrees, EURACA, 2019.

Keywords: Photoemission; Electronic properties; PTCDI dye

#### 1. Introduction

In recent years, an active researches have been pointed on organic materials with many applications in electronic devices [1]. The organic materials have much more interesting properties such flexibility, self-organization and optoelectronic properties. Charge transfer reactions is a simple reaction process in donor–acceptor system, it occurs in redox reactions at many physical, chemical and biological system [2]. The Study and understand the behavior of electronic at different materials interfaces constitute a main research of technological significance field [3]. Electron transfer field has been advanced in past half century ago according to the Marcus research [4]. Study of charge transfer process make to understand the mechanism of transfer in donor–acceptor system and the dependent of rate on properties of material energy levels [5]. The formation between interface of the organic and inorganic material (semiconductor or metal) are of special interest, because it influences the structure of the molecular layers and morphology of material. Therefore, a detailed investigating of the charge transfer processes taking place at

\* Corresponding author. *E-mail address:* alagealyhadi@yahoo.com (H.J.M. Al-agealy).

https://doi.org/10.1016/j.egyr.2019.10.015

2352-4847/© 2019 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/ licenses/by-nc-nd/4.0/).

Peer-review under responsibility of the scientific committee of the Tmrees, EURACA, 2019.

the two miscible contact and the effect of electronic properties on the structure of organic/inorganic system [6]. PTCDI (N, N'-di(2, 6-diisopropylphenyl)-1, 6, 7, 12-tetra(4-tert-butylphenyoxy)-perylene-3, 4, 9, 10-tetracarboxylic diimide) are highly luminescent chromophores molecules in electrolytic liquid, which has been extensively discussed in the recent years. These molecules are absorbing higher energy photons and an active transfer energy near-infrared sensitizing dye, increasing the absorption bandwidth of the DSC [7]. Several studies focused on the Dye-sensitized solar cells (DSCs) and structural properties of sensitized dye attached to a different semiconductor [8]. Particularly, for DSCs have been composed mainly of abundant, nontoxic materials to the development of higher efficiency cells. Even in the regime DSCs forms have large domains absorbing light ranging from 350 to 700 nm, have efficiency over 11% [9]. Fig. 1, shows the two chemical structures and the absorption and emission of sensitizers PTCDI and TT1 dyes [10].



Fig. 1. A-Chemical structures of sensitized PTCDI dye and B-The absorption and emission of PTCDI [10].

The energy levels of molecular due to the energy level of metal are playing he an important rule for charge transfer through metal–organic system, because the potential barrier highest depending on position of energy levels at metal–molecule interfaces [11]. In this paper, we focused on the study the electronic properties **of** the PTCDI interface on Au due to calculate the rate of the electrons.

#### 2. Basic expressions for electron-transfer rate at interface constants

To unify the electronic rate  $\wp_{ET}$  for transition processes at DCSC, we refer to a theoretical scenario, based on donor acceptor due to Fermi's golden rule, which given [12]:

$$\wp_{ET} = \frac{2\pi}{\hbar} \left| \mathfrak{M}_{\underline{M}} \right|^2 \mathfrak{G}_{M-D} \tag{1}$$

where  $\mathfrak{M}_{\frac{M}{D}}$  is the coupling overlapping energy levels and  $\mathfrak{G}_{M-m}$  is weighted Franck–Condon (density of state). The Franck–Condon density  $\mathfrak{G}_{M-D}$  is [13].

$$\mathcal{G}_{M-D} = (\aleph \mathcal{T}_M^D)^{\frac{-1}{2}} exp - \frac{\pi \left( \mathcal{D}_M^D + \mathcal{T}_M^D \right)^2}{\aleph \mathcal{T}_M^D}$$
(2)

where  $\aleph = 4\pi k_B T$  is correlation factor where  $k_B$  is Boltzmann constant and T is room temperature,  $\mathcal{T}_M^D$  is the transition energy,  $\mathcal{Q}_M^D$  is the potential energy.

Inserting Eq. (2) in Eq. (1) with Fermi density state  $F_{(\epsilon)}$  to results.

$$\wp_{ET} = \frac{2\pi}{\hbar} \int_{-\infty}^{\infty} \left| \mathfrak{M}_{\underline{M}} \right|^2 (\mathfrak{N}\mathcal{T}_{\underline{M}}^D)^{\frac{-1}{2}} exp - \frac{\pi \left( \mathfrak{O}_{\underline{M}}^D + \mathfrak{T}_{\underline{M}}^D \right)^2}{\mathfrak{N}\mathcal{T}_{\underline{M}}^D} F_{(\epsilon)} d\epsilon$$
(3)

Here  $f_{(\epsilon)}$  is the Fermi of electronic density of state at dye sensitized solar cell could be written to [14].

$$F_{(\epsilon)} = \frac{1}{1 + e^{\frac{\epsilon - \epsilon_F}{k_B T}}}$$
(4)

The potentials at PTCDI interfaces with TiO2 and ZnO electrodes in Eq. (3) can be written as.

$$h\vartheta = \mathfrak{O}_M^D + \mathfrak{T}_M^D \tag{5}$$

where  $\vartheta = \frac{c}{\lambda}$  is frequency, c is speed of light and  $\lambda$  is the wave length of absorption energy.

Substituting Eqs. (5) and (4) in Eq. (3) and solving the integral using higher mathematical physics to resulted [15].

$$\wp_{ET} \approx \frac{2\pi}{\hbar} (\aleph \mathcal{T}_M^D)^{\frac{-1}{2}} (\frac{NV^{Sem}}{\sum_0^\infty \rho(E) f_o(E)}) exp - \frac{\pi \left(\mathfrak{O}_M^D + \mathcal{T}_M^D\right)^2}{\aleph \mathcal{T}_M^D} \left|\mathfrak{M}_M^{-1}\right|^2 \left[\pi k_B T - \frac{(\pi k_B T)^2}{16\pi \mathcal{T}_M^D}\right]$$
(6)

The average coupling of energy levels as [16].

$$\langle \left| \overline{\mathfrak{M}_{\frac{M}{D}}(0)} \right|^2 \rangle = \frac{\left| \mathfrak{M}_{\frac{M}{D}} \right|^2}{\sum_0^\infty \rho(E) f_o(E)}$$
(7)

Then the electronic rate relative to attenuation decay  $\beta_{ET}$  is  $\wp_{M-D} = \frac{1}{N\beta_{ET}} \wp_{ET}$  [17]. Then Eq. (6) with Eq. (7) results to

$$\wp_{M-D}(\mathfrak{T}^{D}_{S},|\mathfrak{M}_{T}|^{2},T) \approx \frac{2\pi}{\hbar} \frac{NV^{Sem}}{\beta_{ET}} (\mathfrak{K}\mathfrak{T}^{D}_{M})^{\frac{-1}{2}} \langle \left|\overline{\mathfrak{M}_{\underline{M}}(0)}\right|^{2} \rangle e^{-\frac{\pi(\mathfrak{D}^{D}_{M}+\mathfrak{T}^{D}_{M})^{2}}{\mathfrak{K}\mathfrak{T}^{D}_{M}}} \left[\pi k_{B}T - \frac{(\pi k_{B}T)^{2}}{16\pi\mathfrak{T}^{D}_{M}}\right]$$
(8)

The transfer energies for DCSC system is [18].

$$\mathcal{T}_{M}^{D}(eV) = \frac{e^{2}}{8\pi\epsilon^{\circ}} \left[ \frac{1}{R_{Dye}} \mathbb{f}(n_{S}, \epsilon_{s}) - \frac{1}{2d_{Dye-Sem}} \mathbb{f}(n_{S}, n_{Sem}, \epsilon_{s}, \epsilon_{Sem}) \right]$$
(9)

where e is charge of electron,  $\epsilon_{\circ}$  is the permittivity of space,  $f(n_{S}, \epsilon_{s}) = \left(\frac{1}{n_{S}^{2}} - \frac{1}{\epsilon_{s}}\right)$  and  $f(n_{S}, n_{Sem}, \epsilon_{s}, \epsilon_{Sem}) = \left(\frac{n_{Sem}^{2} - n_{S}^{2}}{n_{Sem}^{2} + n_{S}^{2}} \frac{1}{n_{S}^{2}} - \frac{\epsilon_{Sem}^{2} - \epsilon_{S}^{2}}{\epsilon_{Sem}^{2} + s} \frac{1}{\epsilon_{Sem}^{2}}\right)$  are the polarity of solvent and dye-semiconductor system respectively,  $n_{S}$  and  $\epsilon_{s}$  are the refractive index and dielectric constant of the solvent,  $n_{Sem}$  and  $\epsilon_{Sem}$  are the refractive index and dielectric constant of the solvent,  $n_{Sem}$  and  $\epsilon_{Sem}$  is the distance between semiconductor and dye. The dye molecule radii could be estimation by [19].

$$R_{PTCDI} = \left(\frac{3}{4\pi} \frac{M_{PTCDI}}{N\rho_{PTCDI}}\right)^{\frac{1}{3}}$$
(10)

Here  $M_{\text{PTCDI}}$  is the PTCDI dye molecular weight, N is Avogadro's number, and  $\rho_{\text{PTCDI}}$  is the PTCDI dye mass density.

#### 3. Experimental details

The N, N'-di(2, 6-diisopropylphenyl)-1, 6, 7, 12-tetra(4-tert-butylphenyoxy)-perylene-3, 4, 9, 10-tetracarboxylicdiimide (PTCDI) solution prepared according Ref. [20] with 2.7 g, 18 mmol 4-tert-butylphenol, and 2.9 g, 18 mmol potassium carbonate in 50 ml anhydrous N-methyl pyrrolidinone has been stirred at 135 °C for 15 h. Next it was rapidly poured into 200 ml of HCl and precipitate isolated by vacuum. It was filtration and washing by water and stored at room temperature. The precipitate dissolves in three solvent: Dimethylsulfoxide, N, N-dimethylformamide and chloroform, it extracts with water again. On the other hand the layers of solvents are dried over Na2SO4 and concentration. The product purified with flash column chromatography to yielded red solid about. The product purifies due to recrystallize (1 g dissolved in 100 ml dichloromethane) and placed in a 1000 ml graduated cylinder. A 200 ml methanol has layered be carefully at top of the dichloromethane. The two layers are mix slowly for one week to yield 740 mg of red crystals are isolated by filtration and dried under vacuum. According to the procedure, we obtained dimethylsulfoxide, N, N-dimethylformamide and transparent chloroform solutions.



Fig. 2. UV spectrum of PTCDI in DMSO (a), DMF and chloroform (b) [21]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

#### 4. Results

Under quantum considerable and experiment of measurement of redox potential at semiconductor electrodes for photovoltaics cell, we have been calculation the electronic rate at PTCDI sensitized with TiO2 and ZnO system. Firstly, we focused on calculation the transfer energy that is reconfiguration the system to transfer in organic solvent media using Eq. (9) after estimation the radii of PTCDI molecule using Eq. (10) with molecular weight  $M_{\text{PTCDI}} = 392.316$  [22] and mass density  $\rho_{\text{PTCDI}} = 1.764 \frac{\text{gm}}{\text{cm}^3}$  [22], results is  $R_{\text{PTCDI}} = 4.450$  Å. The critical transition energy for PTCDI/TiO2 and PTCDI/ZnO are calculation using Eq. (9) with inserting all refractive and dielectric constant for solvent and semiconductor from a Tables 1 and 2 respectively. Data results are listed in Table 3

Table 1. Physical properties of solvents [23].

| • • •                 |                  |  |                  |                  |                     |
|-----------------------|------------------|--|------------------|------------------|---------------------|
| Solvent               | Molecular weight | Empirical formula                              | Specific gravity | Refractive index | Dielectric constant |
| Dimethylsulfoxide     | 78               | C <sub>2</sub> H <sub>6</sub> O1S <sub>1</sub> | 1.101            | 1.476            | 46.6                |
| N,N-dimethylformamide | 73               | C <sub>3</sub> H <sub>7</sub> N1O1             | 0.945            | 1.427            | 36.7                |
| Chloroform            | 119              | $C_1H_1C13$                                    | 1.480            | 1.444            | 4.8                 |

The real understanding of the transfer mechanisms that determine the electric properties of the PTCDI/TiO2 and PTCDI/ZnO interface system relative to potential energy levels and electron carrier transport states, its useful goal to reach for known behavior of DSSC device. According to the absorption spectra of PTCDI molecule in dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF) and chloroform solvents we have been estimation the potential due to Eq. (5), its shown the potential as function to absorption energy at wavelengths of 449, 496, 534 and 598 nm for DMF, 386, 513, 572 and 603 nm for DMSO and 438, 466, 501 and 538 nm for Chloroform solutions and transition energy from Table 3, results are shown in Table 4.

The electronic transition rate at PTCDI/TiO2 and PTCDI/ZnO interface systems were evaluation mainly using the energetic state of organic-semiconductor interfaces using the experimental techniques directly and inverse photoemission spectroscopies (PES, IPES) to measurement absorption patterns of PTCDI in DMSO, DMF and chloroform solutions that is shown in Fig. 2 respectively. For substituting the transition energy values from Table 3 in

| 1 1  |                         |                         |
|--|-------------------------|-------------------------|
| Properties                                 | TiO <sub>2</sub> [24]   | ZnO [24]                |
| Molecular weight g/mol                     | 79.866                  | 81.38                   |
| Crystal structure                          | Tetragonal rutile       | Wurtzite                |
| Mass Density (g/cm <sup>3</sup> )          | 4.23                    | 5.66                    |
| Refractive index                           | 2.609                   | 2.0033                  |
| Dielectric constant                        | 10.2                    | 8.5                     |
| Density of state $N_s$ (cm <sup>-3</sup> ) | $1.163 \times 10^{19}$  | $22.2 \times 10^{24}$   |
| Lattice constant (Å)                       | a = 4.5936 c = 2.9587   | a = 0.3249, c = 0.5206  |
| Radius (Å)                                 | 1.956                   | 3.8025                  |
| Unit cell volume $(m^{-3})$                | $6.243 \times 10^{-29}$ | $5.498 \times 10^{-29}$ |
| Electron affinity                          | 4.2 eV                  | 4.3 eV                  |
|  |                         |                         |

Table 2. General properties of InAs and ZnO semiconductor [24].

Table 3. Results of transition energy for PTCDI/TiO2 and PTCDI/ZnO system.

| Solvent               | Empirical<br>formula                           | Refractive<br>index [23] | Dielectric<br>con-<br>stant [23] | Transition energy for PTCDI/TiO <sub>2</sub> | Transition energy for<br>PTCDI/ZnO |
|-----------------------|--|--------------------------|----------------------------------|--|------------------------------------|
| Dimethylsulfoxide     | C <sub>2</sub> H <sub>6</sub> O1S <sub>1</sub> | 1.476                    | 46.6                             | 0.5148                                       | 0.6484                             |
| N,N-dimethylformamide | C3H7N1O1                                       | 1.427                    | 36.7                             | 0.5324                                       | 0.6775                             |
| Chloroform            | $C_1H_1Cl3$                                    | 1.444                    | 4.8                              | 0.2457                                       | 0.3825                             |

Table 4. Data of estimation potential of PTCDI/TiO2 and PTCDI/ZnO system.

| Wave length (nm) | The potential $\mathfrak{D}_M^D$ (eV) |           |  |                        |                  |            |                        |           |  |
|------------------|---------------------------------------|-----------|--|------------------------|------------------|------------|------------------------|-----------|--|
|                  | Dimethylsulfoxide                     |           | Wave length N,N-dimethylformamide (nm) |                        | Wave length (nm) | Chloroform |                        |           |  |
|                  | PTCDI/TiO <sub>2</sub>                | PTCDI/ZnO |  | PTCDI/TiO <sub>2</sub> | PTCDI/ZnO        |            | PTCDI/TiO <sub>2</sub> | PTCDI/ZnO |  |
| 449              | 2.241                                 | 2.107     | 386                                    | 2.672                  | 2.527            | 438        | 2.579                  | 2.442     |  |
| 496              | 1.979                                 | 1.845     | 513                                    | 1.879                  | 1.734            | 466        | 2.409                  | 2.272     |  |
| 534              | 1.802                                 | 1.668     | 572                                    | 1.630                  | 1.485            | 501        | 2.224                  | 2.087     |  |
| 598              | 1.554                                 | 1.420     | 603                                    | 1.519                  | 1.374            | 538        | 2.054                  | 1.917     |  |

Eq. (8) with density of state and unit cell volume for TiO2 and ZnO from Table 2 and using  $\beta_{ET} = 1 \times 10^8$  cm<sup>-1</sup> [17]. Results are shown in Tables 5 and 6 for PTCDI/TiO2 and PTCDI/ZnO systems respectively.

#### 5. Discussion

The present calculations of electron transfer rate depending on support data using experimental results for absorption energy and potential energy that is leading to estimates the transition energy and potential energy with the rate of the electrons based on quantum mechanical models. Due to experimental absorption of PTCDI molecules, it can be noticed the peak of energy is 2.069 eV at wave length 598 nm with DMSO solvent compare to the peak of energy is 2.052 eV at wavelength 603 nm with DMF and peak energy is 2.300 eV at wavelength 538 nm with Chloroform solvents. Although the absorption spectrum for PTCDI molecule systems has been studied In three solvent continuously, it can find a gap in results for chloroform while equivalent approximately for DMSO and DMF solvents, this indicates the results of an electronic rate that similar for two systems with DMSO and DMF solvents and different for results with chloroform. We used TiO2 and ZnO semiconductors as electrodes exactly in our research to understanding the fundamental processes of electron transition. The PTCDI/ZnO was the best system with chloroform solvent for PTCDI to occur a large possibility of charge transition this indicates the results of electron transfer reported in a Tables 5 and 6 show the same

| $\mathfrak{D}^D_M$ [25] | Electronic rate $\wp_{M-D}()$ at PTCDI/TiO2 (cm <sup>4</sup> s <sup>-1</sup> ) |                         |                         |   |                         |                         |   |                         |                         |
|-------------------------|--|-------------------------|-------------------------|---|-------------------------|-------------------------|---|-------------------------|-------------------------|
|                         | Dimethylsul  | foxide                  |                         | N,N-dimet   | hylformamide            |                         | Chloroform  | n                       |                         |
|                         | $\left \overline{\mathfrak{M}_{M/D}(0)}\right ^2$                              |                         |                         | $\left \overline{\mathfrak{M}_{M/D}(0)}\right ^2$ |                         |                         | $\left \overline{\mathfrak{M}_{M/D}(0)}\right ^2$ |                         |                         |
|                         | 0.038 [26]   | 0.022                   | 0.012                   | 0.038   | 0.022                   | 0.012                   | 0.038   | 0.022                   | 0.012                   |
| -0.4                    | $1.506 \times 10^{-7}$   | $5.047 \times 10^{-8}$  | $1.501 \times 10^{-8}$  | $1.376 \times 10^{-7}$                            | $4.613 \times 10^{-8}$  | $1.372 \times 10^{-8}$  | $1.064 \times 10^{-7}$                            | $3.569 \times 10^{-8}$  | $1.061 \times 10^{-8}$  |
| -0.2                    | $2.837 \times 10^{-8}$   | $9.511 \times 10^{-9}$  | $2.829 \times 10^{-9}$  | $2.401 \times 10^{-8}$                            | $8.048 \times 10^{-9}$  | $2.394 \times 10^{-9}$  | $2.577 \times 10^{-7}$                            | $8.639 \times 10^{-8}$  | $2.570 \times 10^{-8}$  |
| 0                       | $1.130 \times 10^{-9}$   | $3.788 \times 10^{-10}$ | $1.127 \times 10^{-10}$ | $9.322 \times 10^{-10}$                           | $3.124 \times 10^{-10}$ | $9.296 \times 10^{-11}$ | $2.404 \times 10^{-8}$                            | $8.060 \times 10^{-9}$  | $2.398 \times 10^{-9}$  |
| 0.2                     | $9.519 \times 10^{-12}$  | $3.190 \times 10^{-12}$ | $9.492 \times 10^{-13}$ | $8.054 \times 10^{-12}$                           | $2.699 \times 10^{-12}$ | $8.032 \times 10^{-13}$ | $8.647 \times 10^{-11}$                           | $2.898 \times 10^{-11}$ | $8.623 \times 10^{-12}$ |
| 0.4                     | $1.694 \times 10^{-14}$  | $5.680 \times 10^{-15}$ | $1.689 \times 10^{-15}$ | $1.506 \times 10^{-14}$                           | $5.191 \times 10^{-15}$ | $1.544 \times 10^{-15}$ | $1.198 \times 10^{-14}$                           | $4.016 \times 10^{-15}$ | $1.195 \times 10^{-15}$ |

 Table 5. Rate of electron transfer at PTCDI/TiO2.

 Table 6. Rate of electron transfer at PTCDI/ZnO.

| $\mathfrak{D}^D_M$ [25] | Electronic rate $\wp_{M-D}()$ at PTCDI/ZnO (cm <sup>4</sup> s <sup>-1</sup> )      |                         |                         |   |                         |                         |  |                        |                         |  |
|-------------------------|--|-------------------------|-------------------------|---|-------------------------|-------------------------|--|------------------------|-------------------------|--|
|                         | $\frac{\text{Dimethylsulfoxide}}{\left \overline{\mathfrak{M}_{M/D}(0)}\right ^2}$ |                         |                         | N,N-dimetl  | nylformamide            |                         | Chloroform   | Chloroform             |                         |  |
|                         |  |                         |                         | $\left \overline{\mathfrak{M}_{M/D}(0)}\right ^2$ |                         |                         | $\left \overline{\mathfrak{M}_{M/D}(0)}\right ^2$      |                        |                         |  |
|                         | 0.038 [26]   | 0.022                   | 0.012                   | 0.038   | 0.022                   | 0.012                   | 0.038  | 0.022                  | 0.012                   |  |
| -0.4                    | $1.123 \times 10^{-2}$   | $3.773 \times 10^{-3}$  | $1.122 \times 10^{-3}$  | $9.153 \times 10^{-3}$                            | $3.068 \times 10^{-3}$  | $9.128 \times 10^{-4}$  | $3.759 \times 10^{-2}$                                 | $1.260 \times 10^{-2}$ | $3.748 \times 10^{-3}$  |  |
| -0.2                    | $1.312 \times 10^{-3}$   | $4.398 \times 10^{-4}$  | $1.308 \times 10^{-4}$  | $9.854 \times 10^{-4}$                            | $3.303 \times 10^{-4}$  | $9.827 \times 10^{-5}$  | $1.586 \times 10^{-2}$                                 | $5.317 \times 10^{-3}$ | $1.582 \times 10^{-3}$  |  |
| 0                       | $4.453 \times 10^{-5}$   | $1.492 \times 10^{-5}$  | $4.441 \times 10^{-6}$  | $3.257 \times 10^{-5}$                            | $1.091 \times 10^{-5}$  | $3.248 \times 10^{-6}$  | $\begin{array}{c} 8.267 \times \\ 10^{-4} \end{array}$ | $2.771 \times 10^{-4}$ | $8.245 \times 10^{-5}$  |  |
| 0.2                     | $4.401 \times 10^{-7}$   | $1.475 \times 10^{-7}$  | $4.389 \times 10^{-8}$  | $3.305 \times 10^{-7}$                            | $1.108 \times 10^{-7}$  | $3.296 \times 10^{-8}$  | $5.321 \times 10^{-6}$                                 | $1.783 \times 10^{-6}$ | $5.307 \times 10^{-7}$  |  |
| 0.4                     | $1.266 \times 10^{-9}$   | $4.246 \times 10^{-10}$ | $1.263 \times 10^{-10}$ | $1.030 \times 10^{-9}$                            | $3.452 \times 10^{-10}$ | $1.027 \times 10^{-10}$ | $4.230 \times 10^{-9}$                                 | $1.417 \times 10^{-9}$ | $4.218 \times 10^{-10}$ |  |

behavior in peak structure to the absorption. This indicate that absorption energy is an active parameters which control of electronic transfer according to photoexcited carriers from TiO2 and ZnO semiconductors into redox PTCDI active molecules acceptors dissolved in solution. Then find a less shifting between the energy peaks in the absorption spectra in PTCDI with DMSO and DMF solvents comparing with a lot with chloroform solvent, the absorption spectrum shifts about 5 nm between DMSO and DMF solvents and 65 nm. In order to noted that effect of transition energy on transition of electrons discussion the different transition rate in Tables 5 to 6, we find the rate is larger for two systems with chloroform solvent compare with two DMSO and DMF solvents because the two systems with chloroform solvent have low transition energy compare with the other solvents, this view in calculated results being collected in Tables 5–6. The kinetic of electronic transfer processes at contact two systems is obviously crucial in either theoretically or experimentally to the coupling coefficient that is for overlapping for electronic state levels. It can show that dielectric constant of the solvent is forces effected on the absorption spectra and transition. As easily show the peak with DMF and DMSO are equalities comparing to the peak with Chloroform solutions. The rate of electron transfer at PTCDI/TiO2 is smaller than rate at PTCDI/ZnO with same solvents, that is because the effect of transition energy and dielectric effect of solvent and semiconductor. The electronic rate for two systems was obviously distributed and different from experimental potential energy. The electronic rate approximately  $10^{-17}-10^{-16}$  cm<sup>4</sup> s<sup>-1</sup>.10<sup>-7</sup> To  $10^{-14}$  for PTCDI/TiO2 and  $10^{-2}$  to  $10^{-9}$  for PTCDI/ZnO. These results are in accord with potential energy data obtained experientially for semiconductor dye contacts. As shown in Tables 5 and 6, the electronic rate of transition for two PTCDI/TiO2 and PTCDI/ZnO systems with DMSO is approximation equivalent to electronic rate with DMF solvent, this lead to equivalent absorption spectrum. Moreover, compared rate of PTCDI/TiO2 system with PTCDI/ ZnO system to DMSO, DMF, Chloroform solution reduced in different intensity of rate between Tables 5 and 6 with respect to transition energy forming to the transfer processes. The difference between the rate in Tables 5 and 6 gives the difference in transition energy in two systems, it is indicated to the different of the difference in the polarity of solvent media for two systems. We can see very similar behavior rate that observed in Tables 5 to 6 due to coupling constant, its confirming that in less decreases shift in electronic rate with decreases coupling coefficient in three solution.

On the other hand, we can notable small shift in the electronic rate of the PTCDI with TiO2 and ZnO semiconductor with Chloroform solvent, Chloroform has different energy band corresponding to the absorption spectrum. The PTCDI/TiO2 has similar behavior rate of PTCDI/ZnO to observed DMSO, DMF, Chloroform solvents. The experiments of potential energy via cyclic voltammetry in a nonaqueous electrolyte of the PTCDI using Au electrodes at different (pH 1, pH 7 and pH 13) with using Ag/AgCl (3 M KCl) reference electrodes [25] to provide suitable data for such an analysis. Moreover, the data for electron rate is consistent with the upper transfer rate from (-0.4 and -0.2) and lowering with (0.2 and 0.4) potential. The coupling overlapping between energy levels of molecule dye and semiconductor has been assumed to be a continuum in Eq. (7). It note that the rate increases with increases the coupling parameters and vice versa and data in Tables 5 and 6 show the same behavior of two systems and appear to agree closely with DMSO and DMF solvents approximately. Theoretical data of transfer rate are explained a nice alignment between TiO2 and molecular of PTCDI this indicates to suggested that PTCDI/TiO2 system is different in alignment level.

#### 6. Conclusions

In summarize, we present the rate of electronic transition depending on theoretical calculation and experimental results using spectroscopic methods for the PTCDI/TiO2 and PTCDI/ZnO interface. The theoretical data of electron transfer rate that is obtained for both systems gives clear information that the interaction at interface between PTCDI molecules and the TiO2 surface is very weak compare with ZnO. The results indicate that PTCDA is provided by an electronic energy states of the ZnO substrate cross organic layer of dye that is leads to more transfer of electrons compare to TiO2.

#### References

- [1] Hardis Morkoc, Advanced semiconductor and organictechniques, Academic Press, London, 2003.
- [2] W. Wibren Du, W.H. Gispen, Electron transfer in donor-bridge-acceptor system and derived materials (Ph. D. thesis), Debye Institute and University of Utrecht, Chapter (1), 2002, pp. PP1–10.
- [3] H.G. Nien, M.W. Chung, B.H. Charles, Portrait of the potential femtosecond studies of electron dynamics at interfaces, Acc Chem Res 33 (2000) 111–118.
- [4] H. Jing, Design, characterization, and electron transfer properties of synthetic metalloproteinase (Ph.D thesis), Graduate College of Bowling Green State University, 2006.
- [5] F. Schmickler, Interfacial electrochemistry, Oxford University Press, Oxford, 1996.
- [6] M. Pope, Ch.E. Swenberg, Electronic processes in organic crystals and polymers, University Press, Oxford, 1999.
- [7] Y.K. Jung, J.B. Allen, Organic donor/acceptor heterojunction photovoltaic devices based on zinc phthalocyanine and a liquid crystalline perylene diimide, Chem Phys Lett 383 (2004) 11–15.
- [8] H.J. Snaith, L. Schmidt-Mende, Advances in liquid-electrolyte and solid-state dye-sensitized solar cells, Adv Mater 19 (2007) 3187–3200.
- M.K. Nazeeruddin, et al., Combined experimental and DFT-tddftcomputational study of photoelectrochemical cell ruthenium sensitizers, J Am Chem Soc 127 (2005) 16835–16847.
- [10] B.E. Hardin, E.T. Hoke, P.B. Armstrong, J.H. Yum, P. Comte, T. Torres, J.M. Fréchet, M.K. Nazeeruddin, M. Grätzel, M.D. McGehee, Increased light harvesting in dye-sensitized solar cells with energy relay dyes, Nat Photonics 3 (7) (2009) 406.
- [11] J.C. Ellenbogen, J. Cerog love, IEEE 88 (2000) 386-426.
- [12] H.J.M. Al-Agealy, R.I.N. AL-Obaidi, Electron transfer at semiconductor/liquid. interfaces, Ibn AL-Haitham J Pure Appl Sci 22 (2) (2009).
- [13] Y.Q. Gao, R.A. Marcus, On the theory of electron transfer reactions at semiconductor/liquid interfaces. II. A free electron model, J Chem Phys 113 (15) (2000) 6351–6360.
- [14] P. Würfel, Physics of solar cells: from basic principles to advanced concepts, John Wiley & Sons, 2009.
- [15] M. Andrea, Marcus theory for electron transfer a short introduction, MPIP J Club-Mainz (2008).
- [16] S.G. Shachi, Electron transfer at metal surfaces (Doctoral Dissertation, Ph. D, theses), California Institute of TechnologyPasadena, California, 2002.

- [17] Y.Q. Gao, Y. Georgievskii, R.A. Marcus, On the theory of electron transfer reactions at semiconductor electrode/liquid interfaces, J Chem Phys 112 (7) (2000) 3358–3369.
- [18] C. Creutz, B.S. Brunschwig, N. Sutin, Interfacial charge-transfer absorption: 3. Application to semiconductor- molecule assemblies, J Phys Chem B 110 (50) (2006) 25181–25190.
- [19] Hadi J.M. Al-Agealy, Theoretical analysis of the kinetics electron transport at solid/solid interface. J Phys Sci Appl 1(6):1-11.
- [20] H.A. Klok, J.R. Herna 'ndez, S. Becker, K. Mullen, Star-shaped fluorescent polypeptides, J Polym Sci Part A: Polym Chem 39 (2001) 1572–1583.
- [21] Mircea Oltean, Adrian Calborean, George Mile, Mihai Vidrighin, Monica Iosin, Loredana Leopold, Dana Maniu, Nicolae Leopold, Vasile Chis, Absorption spectra of PTCDI: A combined UV-vis and TD-DFT study, Mol Biomol Spectrosc 97 (2012) 703–710.
- [22] T. Ogawa, K. Kuwamoto, S. Isoda, T. Kobayashi, N. Karl, 3,4:9, 10-perylenetetracarboxylic dianhydride (PTCDA) by electron crystallography, Acta Crystallogr Sect B: Struct Sci 55 (1) (1999) 123–130.
- [23] Ian M. Smallwood, Handbook of organic solvent properties, Copublished in the Americas by Halsted Pres, 1998.
- [24] Hadi J.M. Al-Aagealy, A.M. Adil, Mohsin A. Hassooni, Theoretical study of probability of electron transfer at nano electron device, J Chem Biol Phys Sci 5 (3) (2015) 3325–3335.
- [25] M. Warczak, M. Gryszel, M. Jakešová, V. Đerek, E.D. Głowacki, Organic semiconductor perylenetetracarboxylic diimide (PTCDI) electrodes for electrocatalytic reduction of oxygen to hydrogen peroxide, Chem Commun 54 (16) (2018) 1960–1963.
- [26] H.J. Al-Aagealy, T.S. AlMaadhede, M.A. Hassooni, A.K. Sadoon, A.M. Ashweik, H.A. Mahdi, R.Q. Ghadhban, Theoretical study of electronic transfer current rate at dye-sensitized solar cells, AIP Conf Proc 1968 (1) (2018) 030055, AIP Publishing.