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Study of photoemission and electronic properties of dye-sensitized solar cells

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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.

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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

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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*-butylphenoxy)-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].

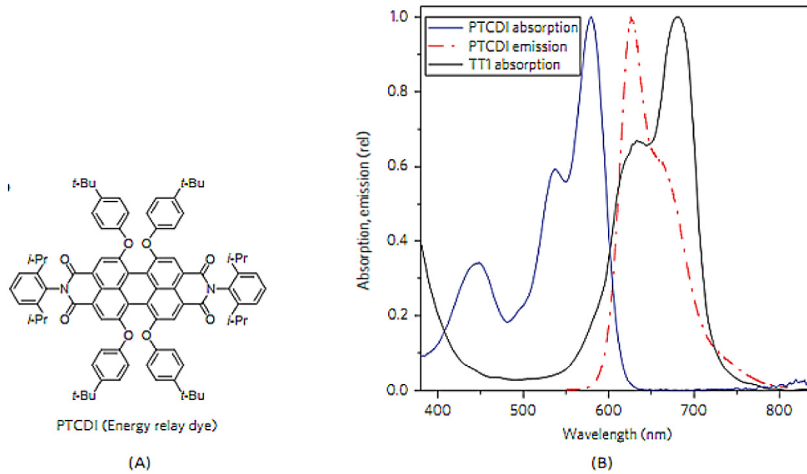


Fig. 1. A-Chemical structures of sensitized PTCDI dye and B-The absorption and emission of PTCDI [10].

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]:

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

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

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

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{D}_M^D is the potential energy.

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

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

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

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

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

$$h\vartheta = \mathfrak{D}_M^D + \mathfrak{T}_M^D \quad (5)$$

where $\vartheta = \frac{c}{\lambda}$ is frequency, c is speed of light and λ 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].

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

The average coupling of energy levels as [16].

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

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

$$\wp_{M-D}(\mathfrak{T}_S^D, |\mathfrak{M}_T|^2, T) \approx \frac{2\pi}{\hbar} \frac{NV^{Sem}}{\beta_{ET}} (\mathfrak{N}\mathfrak{T}_M^D)^{-\frac{1}{2}} \langle \left| \overline{\mathfrak{M}_D^D(0)} \right|^2 \rangle e^{-\frac{\pi (\mathfrak{D}_M^D + \mathfrak{T}_M^D)^2}{\mathfrak{N}\mathfrak{T}_M^D}} \left[\pi k_B T - \frac{(\pi k_B T)^2}{16\pi \mathfrak{T}_M^D} \right] \quad (8)$$

The transfer energies for DCSC system is [18].

$$\mathfrak{T}_M^D(eV) = \frac{e^2}{8\pi\epsilon_0} \left[\frac{1}{R_{Dye}} \mathfrak{f}(n_S, \epsilon_S) - \frac{1}{2d_{Dye-Sem}} \mathfrak{f}(n_S, n_{Sem}, \epsilon_S, \epsilon_{Sem}) \right] \quad (9)$$

where e is charge of electron, ϵ_0 is the permittivity of space, $\mathfrak{f}(n_S, \epsilon_S) = \left(\frac{1}{n_S^2} - \frac{1}{\epsilon_S} \right)$ and $\mathfrak{f}(n_S, n_{Sem}, \epsilon_S, \epsilon_{Sem}) = \left(\frac{n_{Sem}^2 - n_S^2}{n_{Sem}^2 + n_S^2} \frac{1}{n_S^2} - \frac{\epsilon_{Sem}^2 - \epsilon_S^2}{\epsilon_{Sem}^2 + \epsilon_S^2} \frac{1}{\epsilon_{Sem}^2} \right)$ are the polarity of solvent and dye-semiconductor system respectively, n_S and ϵ_S are the refractive index and dielectric constant of the solvent, n_{Sem} and ϵ_{Sem} are the refractive index and dielectric constant of the semiconductor, R_{Dye} is the dye radius, and $d_{Dye-Sem}$ is the distance between semiconductor and dye. The dye molecule radii could be estimation by [19].

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

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

3. Experimental details

The N, N' -di(2, 6-diisopropylphenyl)-1, 6, 7, 12-tetra(4-tert-butylphenoxy)-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.

The absorption spectra of PTCDI measure in three different solvents: dimethylsulfoxide, N, N-dimethylformamide and chloroform. The three absorbance spectra in solutions have recorded using UV spectrophotometer at room temperature. The top absorption spectra were observed 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. On the other hand, The experimental absorption energy agreement with an experiment of Mircea Oltean et.al for fluorescence spectra of excitation energy that is recorded for PTCDI dye with DMSO, DMF and Chloroform solvents used Jasco LP-6500 spectrofluorimeter, that is shown in Fig. 2 [21].

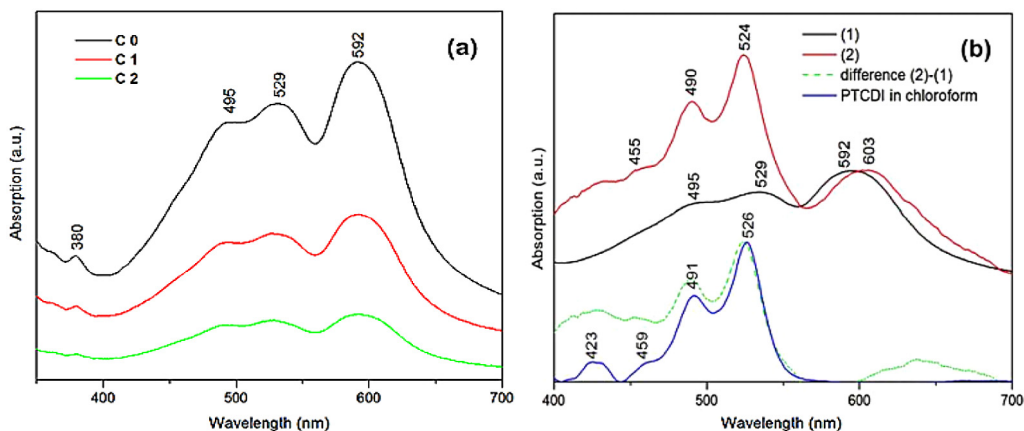


Fig. 2. UV spectrum of PTCDI in DMSO (a), DMF and chloroform (b) [21]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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 $R_{\text{PTCDI}} = 4.450 \text{ \AA}$. 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 ₂ H ₆ O1S ₁	1.101	1.476	46.6
N,N-dimethylformamide	73	C ₃ H ₇ N1O1	0.945	1.427	36.7
Chloroform	119	C ₁ H ₁ Cl ₃	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

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

Properties	TiO ₂ [24]	ZnO [24]
Molecular weight g/mol	79.866	81.38
Crystal structure	Tetragonal rutile	Wurtzite
Mass Density (g/cm ³)	4.23	5.66
Refractive index	2.609	2.0033
Dielectric constant	10.2	8.5
Density of state N _s (cm ⁻³)	1.163 × 10 ¹⁹	22.2 × 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 × 10 ⁻²⁹	5.498 × 10 ⁻²⁹
Electron affinity	4.2 eV	4.3 eV

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

Solvent	Empirical formula	Refractive index [23]	Dielectric constant [23]	Transition energy for PTCDI/TiO ₂	Transition energy for PTCDI/ZnO
Dimethylsulfoxide	C ₂ H ₆ O1S ₁	1.476	46.6	0.5148	0.6484
N,N-dimethylformamide	C ₃ H ₇ N1O1	1.427	36.7	0.5324	0.6775
Chloroform	C ₁ H ₁ Cl ₃	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 \mathcal{D}_M^D (eV)							
	Dimethylsulfoxide		Wave length (nm)	N,N-dimethylformamide		Wave length (nm)	Chloroform	
	PTCDI/TiO ₂	PTCDI/ZnO		PTCDI/TiO ₂	PTCDI/ZnO		PTCDI/TiO ₂	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 $\beta_{ET} = 1 \times 10^8 \text{ cm}^{-1}$ [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 higher concentration of PTCDI with chloroform than dimethylsulfoxide and dimethylformamide solvents that are observed in experimental in [21]. The rate of electron transfer reported in a Tables 5 and 6 show the same

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

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

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

\mathcal{D}_M^D [25]	Electronic rate \wp_{M-D} ($\text{cm}^4 \text{ s}^{-1}$) at PTCDI/ZnO								
	Dimethylsulfoxide			N,N-dimethylformamide			Chloroform		
	$ \overline{\mathfrak{M}}_{M/D}(0) ^2$			$ \overline{\mathfrak{M}}_{M/D}(0) ^2$			$ \overline{\mathfrak{M}}_{M/D}(0) ^2$		
	0.038 [26]	0.022	0.012	0.038	0.022	0.012	0.038	0.022	0.012
-0.4	1.123×10^{-2}	3.773×10^{-3}	1.122×10^{-3}	9.153×10^{-3}	3.068×10^{-3}	9.128×10^{-4}	3.759×10^{-2}	1.260×10^{-2}	3.748×10^{-3}
-0.2	1.312×10^{-3}	4.398×10^{-4}	1.308×10^{-4}	9.854×10^{-4}	3.303×10^{-4}	9.827×10^{-5}	1.586×10^{-2}	5.317×10^{-3}	1.582×10^{-3}
0	4.453×10^{-5}	1.492×10^{-5}	4.441×10^{-6}	3.257×10^{-5}	1.091×10^{-5}	3.248×10^{-6}	8.267×10^{-4}	2.771×10^{-4}	8.245×10^{-5}
0.2	4.401×10^{-7}	1.475×10^{-7}	4.389×10^{-8}	3.305×10^{-7}	1.108×10^{-7}	3.296×10^{-8}	5.321×10^{-6}	1.783×10^{-6}	5.307×10^{-7}
0.4	1.266×10^{-9}	4.246×10^{-10}	1.263×10^{-10}	1.030×10^{-9}	3.452×10^{-10}	1.027×10^{-10}	4.230×10^{-9}	1.417×10^{-9}	4.218×10^{-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} – $10^{-16} \text{ cm}^4 \text{ s}^{-1}$. 10^{-7} 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 the electronic energy state of ZnO and molecular level of PTCDI at the interfaces compare a less 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.

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