

Absorption Spectra and Electron Injection Study of the Donor Bridge Acceptor Sensitizers by Long Range Corrected Functional

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ABSTRACT: *Ground state geometries have been computed using Density Functional Theory (DFT) at B3LYP/6-31G(d,p) level of theory. The excitation energies and spectroscopic parameters have been computed using Long range Corrected (LC) hybrid functional by Time Dependent Density Functional Theory (TDDFT) with LC-BLYP level of theory. The Polarizable Continuum Model (PCM) has been used for evaluating bulk solvent effects at all stages. The efficient materials have been predicted and electron injection (ΔG^{inject}), electron coupling constant ($|V_{RP}|$) and Light Harvesting Efficiency (LHE) has been discussed. By elongating the bridge all these three parameters ΔG^{inject} , $|V_{RP}|$ and LHE enhanced which revealed that new designed sensitizers would be efficient.*

KEY WORDS: *Dye-sensitized solar cells, Absorption, Light harvesting efficiency, Electronic coupling constant, Electron injection.*

INTRODUCTION

Dye Sensitized Solar Cells (DSCs) are currently attracting considerable attention because of their high light-to-electricity conversion efficiencies, ease of fabrication, and low production costs [1]. Following their inception in 1985 [2], DSCs are often included in the Organic PhotoVoltaic (OPV) family because of the organic nature of at least part of its constituents. The DSC is the only photovoltaic device that uses molecules to absorb photons and convert them to electric charges without the need of intermolecular transport of electronic excitation. It is also the only solar cell that separates the two functions of light harvesting and charge-carrier transport, whereas conventional and all of the other known OPV devices perform both operations simultaneously. In the DSC,

the recombination of charge carriers occurs across the phase boundary separating the electron from the hole conductor medium. This inherent geometry offers the unique prospective to fashion the interface in a judicious manner to retard the back-electron-transfer reaction. One promising approach to accomplish this goal is the molecular engineering of sensitizers forming a self-assembled compact monolayer alone or in conjunction with a co-adsorbent at the oxide surface. Such an insulating film would impair the flow of dark current across the junction, reducing the back-reaction rate and increasing the overall solar to electric power conversion efficiency of the cell.

However, most of these devices generally consist of expensive sensitizers such as ruthenium (II) polypyridyl

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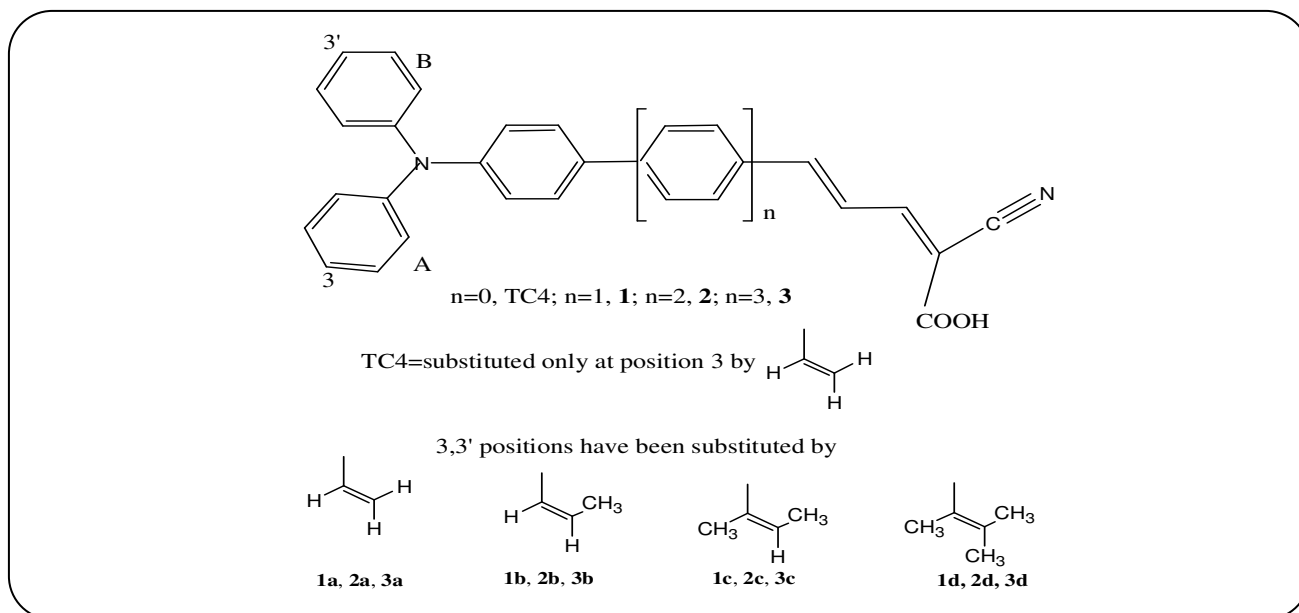


Fig. 1: The structures of 1a-3d investigated in the present study.

complexes (with carboxylated ligands) and electrolytes with volatile solvents [1,3]. Most of the organic sensitizers applied in DSCs have three important parts: 1) the electron donor such as the indoline moiety, 2) the electron acceptor such as the rhodanine ring, and 3) the linker units for the pi conjugation to enhance the molar absorption coefficient [4]. Generally, organic dyes for excellent DSCs are required to possess broad and intense spectral absorption in the visible light region and have suitable excited-state redox potential with the energy of the conduction band edge. The major factors in the low conversion efficiency of DSCs based on organic dyes are the formation of dye aggregation on the semiconductor surface and the recombination of conduction band electrons with triiodide in the electrolyte [5]. The Ru complexes photosensitizers show a solar energy to electricity conversion efficiency of 10% in average. Nevertheless, an increasing interest for purely organic DSCs as substitutes for Ru complexes raised in recent years due to their key advantages, e.g. a high molar extinction coefficient, a simple and relatively inexpensive preparation processes, a more straightforward compliance with environmental rules [6]. Moreover, several solid-state DSCs based on organic dyes appear to have equivalent performances than inorganic complexes, suggesting promising commercial applications [7]. Therefore, metal-free dyes like coumarin [8],

merocyanine [9], indoline [10], xanthenes [11], hemicyanine [12], hydroquinones [13,14] perylene [15], fluorine [16] and triphenylamine (TPA) [17] have been tested in this framework.

To model and design efficient metal-free sensitizers for DSCs, appropriate Donor Bridge Acceptor (DBA) systems are required whose properties can be tuned by applying the passable structural modifications. The DSC based on 2-cyano-5-(4-(phenyl(4-vinylphenyl) amino)phenyl) penta-2,4-dienoic acid (TC4) showed efficiency 4.82% [17a]. Xu et al. attached vinyl unit at position 3 of A-ligand to enhance the electron-donor ability of TPA [17a]. In the present study we designed DBA systems where TPA moiety as donor, cyanoacetic acid as acceptor and benzene rings (extended 1-3 in number) as bridge. In our previous study it was examined that positions 3 (A-ligand) and 3' (B-ligand) are favorable to design better sensitizer [17b]. Thus in the present study not only we have substituted the vinyl at position 3 and 3', we have also modeled new systems by replacing the hydrogens of vinyl with CH_3 to enhance the donor ability of TPA moiety, see Fig. 1 (detail can be found in computational details). The Quantum chemical calculations have been performed to gain insight into electronic properties of the new designed sensitizers. The structure-property relationship has been discussed.

Computational detail

The ground state geometries have been computed using Density Functional Theory (DFT) with Gaussian09 package [18]. The orbital energies have been accurately predicted by reparametrization of the Becke-3 hybrid exchange-correlation functional [19,20] *Preat et al.* optimized the ground state geometries of the TPA based dyes at B3LYP/6-31G(d,p) level of theory. They concluded that this level of theory is adequate for TPA based sensitizers [21,22]. Xu et al. optimized TC4 by means of the B3LYP/6-31G(d,p) level of theory. The B3LYP/6-31G(d,p) level has been used for geometrical and electronic properties of the TC4 [17a]. The geometries of TPA based sensitizers have been optimized by using different Pople basis sets as 6-31G(d,p), 6-31+G(d,p), 6-311G(d,p), 6-31G(2d,2p), 6-311G(2d,2p), and 6-311G(2df,2pd) [22]. It was concluded that the B3LYP bond lengths do not depend upon the basis set and are almost identical to the MP2/6-31G(d,p) values [22]. They validated B3LYP for optimizing the geometry of TPA based sensitizers. Moreover, B3LYP/6-31G(d,p) level which is adequate for TPA based sensitizers has been applied to optimize the ground state geometries and shed light on the electronic properties [21-26]. Thus in the present study, ground state geometries have been computed by using popular three parameter B3LYP functional [23], in which the exchange is a combination of Hartree-Fock exchange, Slater functional, and Becke's Generalized Gradient Approximation (GGA) correction [24], whereas the correlation part combines local and Lee Yang Parr (LYP) functional [25]. We have used 6-31G(d,p) [17b, 26] basis set for the ground-state geometries.

Stein et al. studied the charge-transfer excitations in a series of coumarin-based donor-bridge-acceptor dyes. They explained that excitation energies well reproduced by using a range-separated hybrid functional within the generalized Kohn Sham approach to TDDFT [27]. The absorption and fluorescence properties in a class of oligothiophene push pull biomarkers have been investigated with a Long range Corrected (LC) density functional method [28]. The excited-state properties in a series of coumarin solar cell dyes were investigated with LC-BLYP [29]. The range-separation technique is based on a more physical model of the exchange potential. The B3LYP hybrid functional underestimates vertical

excitation energies, especially for larger dye molecules. As a benchmark study, we have computed the absorption spectra of TC4 at TD-B3LYP/6-31G** level of theory in methanol, the absorption spectra was overestimated, i.e., 526 nm compared to experimental data 425 nm. It has been already reported that the choice of the range separation parameter is strongly system dependent [30-33]. The long range (LC-BLYP) has been applied to investigate the excitation energies for TPA based dyes. In our investigated systems organic sensitizers consisted electron donor and acceptor separated from each other by conjugated units. Thus we have used LC-BLYP range separated functional. The electronic absorption spectra require calculation of the allowed excitations and oscillator strengths. The TDDFT was used to investigate the absorption properties of molecules which have been proved an efficient approach [34-36]. The iodine/iodide couple is used as regenerator in DSCs, implying that the solar cells work in solvent phase. Thus UV/Vis experimental data for TPA-based dyes are reported in solvent. The polarizable continuum model (PCM) [37-40] is used for evaluating bulk solvent effects at all stages. The calculations have been carried out in methanol according to the experimental set up [17a].

Molecular orbitals were visualized by using Gaussview. To enhance the electron donor ability of TPA moiety Xu et al. synthesized the TC4 where vinyl unit has been substituted at position **3** [17]. Recently, we showed that substitution of vinyl at position **3** and **3'** are more favorable toward enhancing the electron injection and reducing the HOMO-LUMO energy gap [17b]. It is well known that CH₃ enhance the electron donor ability [34] and the sensitizers where charge transferred from donor to acceptor moiety are good towards high efficiency [22,23]. Thus to augment the donor ability of TPA unit, we have replaced the hydrogens of vinyl by CH₃. We substituted positions 3,3' by vinyl (**1a**, **2a** and **3a**), in second step, we have replaced one hydrogen by CH₃ (**1b**, **2b** and **3b**), third step we substituted two CH₃ (**1c**, **2c** and **3c**) and finally three CH₃ were substituted in place of three hydrogens (**1d**, **2d** and **3d**) of vinyl at positions **3** and **3'**. Moreover, to check the effect of bridge on the electronic properties we have extended the benzene rings; one benzene ring between TPA moiety and anchoring group (**1**), two benzenes (**2**) and three benzenes as bridge (**3**).

Table 1: The absorption wavelength (λ_a), ΔG^{inject} , oxidation potential, Light Harvesting Efficiency (LHE), $|V_{RP}|$ of investigated dyes at TD-LC-BLYP//B3LYP/6-31G and PCM-B3LYP/6-31G** level of theory.**

| System | λ_a | ΔG^{inject} | ΔG_r^{inject} | E_{OX}^{dye} | E_{OX}^{dye} | E_{OX}^{dye*} | λ_{max}^{ICT} | f | LHE | $ V_{RP} $ |
|--------|-------------|---------------------|-----------------------|----------------|----------------|-----------------|-----------------------|--------|-------|------------|
| 1a | 348 | -2.53 | 1.20 | 5.03 | 1.47 | 3.56 | 2.1805 | 0.9934 | 1.265 | |
| 1b | 349 | -2.63 | 1.25 | 4.92 | 1.37 | 3.55 | 2.1873 | 0.9935 | 1.315 | |
| 1c | 349 | -2.60 | 1.23 | 4.95 | 1.40 | 3.55 | 2.1371 | 0.9927 | 1.300 | |
| 1d | 349 | -2.58 | 1.22 | 4.97 | 1.42 | 3.55 | 2.1271 | 0.9925 | 1.290 | |
| 2a | 341 | -2.71 | 1.28 | 4.93 | 1.29 | 3.64 | 2.3668 | 0.9957 | 1.355 | |
| 2b | 341 | -2.78 | 1.32 | 4.86 | 1.22 | 3.64 | 2.3557 | 0.9956 | 1.390 | |
| 2c | 341 | -2.73 | 1.29 | 4.91 | 1.27 | 3.64 | 2.3269 | 0.9953 | 1.365 | |
| 2d | 341 | -2.75 | 1.30 | 4.88 | 1.25 | 3.63 | 2.3302 | 0.9953 | 1.375 | |
| 3a | 339 | -2.76 | 1.31 | 4.90 | 1.24 | 3.66 | 2.4158 | 0.9962 | 1.380 | |
| 3b | 339 | -2.83 | 1.34 | 4.82 | 1.17 | 3.65 | 2.4146 | 0.9961 | 1.415 | |
| 3c | 339 | -2.79 | 1.32 | 4.86 | 1.21 | 3.65 | 2.3956 | 0.9960 | 1.395 | |
| 3d | 339 | -2.82 | 1.34 | 4.83 | 1.18 | 3.65 | 2.3996 | 0.9960 | 1.410 | |
| TC4 | 373 | -2.11 | 1.00 | 5.22 | 1.89 | 3.33 | 1.7622 | 0.9827 | 1.055 | |

RESULTS AND DISCUSSION

Absorption

The absorption spectra of TC4 has been computed at PCM-TD-LC-BLYP/6-31G** and PCM-TD-B3LYP/6-31G** level of theories. The PCM-TD-B3LYP overestimates the absorption wavelength about 101 nm compared to experimental maximum absorption wavelength. The maximum absorption wavelength at PCM-TD-LC-BLYP/6-31G** is 373nm which better reproduce the experimental evidence. Thus we have computed the absorption spectra of new designed sensitizers at PCM-TD-LC-BLYP/6-31G** level of theory. In addition, the absorption wavelengths of **1a-1d** are 25 nm blue shifted, see Table 1. The maximum absorption wavelength of **2a-2d** is 32 nm while **3a-3d** is 34 nm blue shifted compared to TC4. The excitation energies, absorption wavelengths, oscillator strengths and transition contribution are listed in Table 1 and Fig. S1 (see supporting information). Electronic transitions up to 10 states were studied for all new designed sensitizers.

In **TC4**, the maximum transition for first state is caused by HOMO \rightarrow LUMO with 70% contribution. The second state caused by HOMO \rightarrow LUMO+1 with 62% contribution. The seventh state has 55% contribution from HOMO-8 \rightarrow LUMO. The transition contribution for

third, fourth, fifth, sixth, eighth, ninth and tenth states for all the frontier molecular orbitals is less than 50%.

In **1a**, S0-S1 state remains dominated with maximum absorption and this state is caused by HOMO-1 \rightarrow LUMO with 55% contribution. The second state caused by HOMO \rightarrow LUMO+1 with 77% contribution. The fifth state showed 51% contribution from HOMO-6 \rightarrow LUMO. The third, fourth, sixth, seventh, eighth, ninth and tenth states have less than 50% contribution for transitions. In **1b** the main transitions having more than 50% contributions are as follows: HOMO-1 \rightarrow LUMO for first state (53%), HOMO \rightarrow LUMO+2 for third state (70%), HOMO \rightarrow LUMO+3 for fourth state (60%). In **1c**, S0-S1 transition is caused by HOMO-1 \rightarrow LUMO with 51% contribution. Maximum absorption has been observed in this state. Transition of third state is dominated with 75% contribution from HOMO \rightarrow LUMO+2. Transitions in fourth and ninth states are mainly caused by HOMO \rightarrow LUMO+3, and HOMO-11 \rightarrow LUMO, with the contribution of 66% and 54%, respectively. Other states of this molecule have major contribution less than 50%. In **1d**, S0-S1 state remains dominated with maximum absorption and this state is caused by HOMO-1 \rightarrow LUMO with 50% contribution. The third state caused by HOMO \rightarrow LUMO+2 with 69% contribution. The fourth

state has 64% contribution from HOMO->LUMO+3. The ninth state caused by HOMO-11 ->LUMO with 55% contribution. The second, fifth, sixth, seventh, eighth, and tenth states are derived from frontier orbitals having contribution less than 50%.

In **2a**, S0-S1 state remains dominated with maximum absorption spectrum which is caused by HOMO-1 ->LUMO with 66% contribution. The second state caused by HOMO ->LUMO+1 with 52% contribution. The third state has 76% contribution from HOMO->LUMO+2. The fourth state has 57% contribution from HOMO->LUMO+4. The fifth, sixth, seventh, eighth, ninth and tenth states have less than 50% contribution from which these have been derived. In **2b**, S0-S1 state remains dominated with maximum absorption and this state is caused by HOMO-1 ->LUMO with 65% contribution. The third state caused by HOMO ->LUMO+2 with 78% contribution. The fourth state has 66% contribution from HOMO->LUMO+4. The fifth state caused by HOMO-9 ->LUMO with 54% contribution. In **2c**, S0-S1 state remains dominated with maximum absorption and this state is caused by HOMO-1 ->LUMO with 65% contribution. The third state has 78% contribution from HOMO->LUMO+2. The fourth state caused by HOMO ->LUMO+3 with 67% contribution. The fifth state caused by HOMO-9->LUMO with 54% contribution. The tenth state has 54% contribution from HOMO-13 ->LUMO. In **2d**, S0-S1 state remains dominated with maximum absorption and this state is caused by HOMO-1 ->LUMO with 64% contribution. The third state has 74% contribution from HOMO->LUMO+2. The fourth state caused by HOMO ->LUMO+3 with 67% contribution. The fifth state caused by HOMO-10 ->LUMO with 54% contribution. The tenth state has 54% contribution from HOMO-13 ->LUMO.

The main transition in **3a** is HOMO-1 ->LUMO with the contribution 57%. The HOMO ->LUMO+2, HOMO ->LUMO+4, and HOMO-9 ->LUMO transition are responsible for 3rd, 4th and 6th state with the contribution 77%, 56% and 55%, respectively. In **3b** main transition showed contribution 56% is responsible for HOMO-12 ->LUMO. The major contributors of this system in each state having contribution more than 50% are as follows, HOMO->LUMO+2, HOMO ->LUMO+4, HOMO-10 ->LUMO, having contribution 77%, 68% and 55% for 3rd, 4th, and 6th states. In **3c**, S0-S1 state remains dominated

with maximum absorption and this state is caused by HOMO-1 ->LUMO with 58% contribution. The third state has 76% contribution from HOMO->LUMO+3. The fourth state caused by HOMO ->LUMO+4 with 69% contribution. The sixth state has 55% contribution from HOMO-11 ->LUMO. In **3d**, S0-S1 state remains dominated with maximum absorption and this state is caused by HOMO-1 ->LUMO with 57% contribution. The third state caused by HOMO->LUMO+3 with 75% contribution. The 55% contribution has been observed for sixth state transition from HOMO-12 ->LUMO.

It is noteworthy that in all these new designed molecules S0-S1 state show maximum absorption and this state is mainly derived from HOMO-1 -> LUMO transition. In fact, the maximum absorption wavelength ($\lambda_{\text{max abs}}$) is red shifted and the oscillator strength increases from 1.7622 to reach 2.4158 in new modeled sensitizers compared to TC4.

Electron injection

The description of the electron transfer from a dye to a semiconductor, the rate of the charge transfer process can be derived from the general classical Marcus theory, [34,41-43].

$$k_{\text{inject}} = \left| V_{\text{RP}} \right| \left(\frac{2}{h} (\pi \lambda k_{\text{B}} T) \right)^{1/2} \exp \left[-(\Delta G^{\text{inject}} + \lambda) / 2 \lambda k_{\text{B}} T \right] \quad (1)$$

In eq. (1), k_{inject} is the rate constant (in s^{-1}) of the electron injection from dye to TiO_2 , k_{B} is the Boltzmann thermal energy, h the Planck constant, ΔG^{inject} is the free energy of injection, $-\Delta G^{\text{inject}}$ is the affinity for injection and λ is the reorganization energy of the system, $|V_{\text{RP}}|$ is the coupling constant between the reagent and the product potential curves. Eq (1) revealed that larger $|V_{\text{RP}}|$ leads to higher rate constant which would result better sensitizer. The use of the Generalized Mulliken-Hush formalism (GMH) allows evaluating $|V_{\text{RP}}|$ for a photoinduced charge transfer [41,42]. *Hsu et al.* explained that $|V_{\text{RP}}|$ can be evaluated as [42]

$$|V_{\text{RP}}| = \Delta E_{\text{RP}} / 2 \quad (2)$$

The injection driving force can be formally expressed within Koopmans approximation as

$$\Delta E_{\text{RP}} = \left[E_{\text{LUMO}}^{\text{dye}} + 2E_{\text{HOMO}}^{\text{dye}} \right] - \left[E_{\text{LUMO}}^{\text{dye}} + E_{\text{HOMO}}^{\text{dye}} + E_{\text{CBO}}^{\text{TiO}_2} \right] \quad (3)$$

Where $E_{\text{CBO}}^{\text{TiO}_2}$ is the conduction band edge. It is difficult to accurately determine $E_{\text{CBO}}^{\text{TiO}_2}$, because it is highly sensitive to the conditions (e.g. the pH of the solution) thus we have used $E_{\text{CBO}}^{\text{TiO}_2} = -4.0$ eV [44] which is experimental value corresponding to conditions where the semiconductor is in contact with aqueous redox electrolytes of fixed pH 7.0 [45,46].

More quantitatively for a closed-shell system $E_{\text{LUMO}}^{\text{dye}}$ corresponds to the reduction potential of the dye ($E_{\text{RED}}^{\text{dye}}$), whereas the HOMO energy is related to the potential of first oxidation (i. e., $-E_{\text{HOMO}}^{\text{dye}} = E_{\text{OX}}^{\text{dye}}$). As a result, Eq. (3) becomes,

$$\Delta E_{\text{PR}} = \left[E_{\text{OX}}^{\text{dye}} + E_{\text{OX}}^{\text{TiO}_2} \right] \quad (4)$$

The eq (4) can be rewritten as

$$\Delta E_{\text{PR}} = E_{0-0}^{\text{dye}} - \left[2E_{\text{CB}}^{\text{TiO}_2} + E_{\text{RED}}^{\text{dye}} + E_{\text{CB}}^{\text{TiO}_2} \right] \quad (5)$$

The free energy change (eV) for the electron injection can be expressed as, [45]

$$\Delta G^{\text{inject}} = E_{\text{OX}}^{\text{dye}*} - E_{\text{CB}}^{\text{TiO}_2} \quad (6)$$

Where $E_{\text{OX}}^{\text{dye}*}$ is the oxidation potential of the dye in the excited state, and $E_{\text{CB}}^{\text{TiO}_2}$ is the reduction potential of the semiconductor conduction band. Two models can be used for the evaluation of $E_{\text{OX}}^{\text{dye}*}$ [47]. The first implies that the electron injection occurs from the unrelaxed excited state. For this reaction path, the excited state oxidation potential can be extracted from the redox potential of the ground state, $E_{\text{OX}}^{\text{dye}}$ which has been calculated at the PCM-B3LYP-6-31G** approach and the vertical transition energy corresponding to the photoinduced intramolecular CT (ICT),

$$E_{\text{OX}}^{\text{dye}*} = E_{\text{OX}}^{\text{dye}} - \lambda_{\text{max}}^{\text{ICT}} \quad (7)$$

Where $\lambda_{\text{max}}^{\text{ICT}}$ is the energy of the ICT. Note that this relation is only valid if the entropy change during the light absorption process can be neglected. For the second model, one assumes that electron injection occurs after relaxation. Given this condition, $E_{\text{OX}}^{\text{dye}*}$ is expressed as [48]:

$$E_{\text{OX}}^{\text{dye}*} = E_{\text{OX}}^{\text{dye}} - E_{0-0}^{\text{dye}} \quad (8)$$

Where E_{0-0}^{dye} is the 0-0 transition energy between the ground state and the excited state. To estimate the 0-0 "absorption" line, we need both the S_0 (singlet ground state) and the S_1 (first singlet excited state) equilibrium geometries, Q_{S0} and Q_{S1} , respectively:

$$E_{0-0} = E_{S0}(Q_{S0}) - E_{S1}(Q_{S1}) \quad (9)$$

The absolute difference between the relaxed and unrelaxed ΔG^{inject} is constant and is of the same order of magnitude than the $E_{\text{OX}}^{\text{dye}}$ and $E_{\text{OX}}^{\text{dye}*}$ [45]. Here, ΔG^{inject} and $E_{\text{OX}}^{\text{dye}*}$ have been evaluated using Eqs. (6) and (7).

The Light Harvesting Efficiency (LHE) of the dye has to be as high as possible to maximize the photocurrent response. Here, LHE is expressed as [49].

$$\text{LHE} = 1 - 10^{-A} = 1 - 10^{-f}$$

Where A (f) is the absorption (oscillator strength) of the dye associated to the $\lambda_{\text{max}}^{\text{ICT}}$. The oscillator strength is directly derived from the TDDFT calculations and writes:

$$f = \frac{2}{3} \lambda_{\text{max}}^{\text{ICT}} \left| \bar{\mu}_0 - \text{ICT} \right|^2$$

Where $\bar{\mu}_0 - \text{ICT}$ is the dipolar transition moment associated to the electronic excitation. In order to maximize f , both $\lambda_{\text{max}}^{\text{ICT}}$ and $\bar{\mu}_0 - \text{ICT}$ must be large [50,51].

We have presented the λ_a , ΔG^{inject} , $E_{\text{OX}}^{\text{dye}}$, $E_{\text{OX}}^{\text{dye}*}$, $\lambda_{\text{max}}^{\text{ICT}}$, relative LHE (RLHE), and $\Delta G_r^{\text{inject}}$ in Table 1. The ΔG^{inject} of TC4 is -2.11, by increasing the one benzene ring between TPA and acceptor moieties (**1a**) it boosts up to -2.53. The substitution of mono-methyl (**1b**) improves the electron injection to -2.63. By increasing the two benzene rings between TPA and acceptor moieties (**2a**) enhanced the ΔG^{inject} to -2.71. The substitution of mono-methyl (**2b**) enhances the electron injection to -2.78. Three benzene rings between TPA and acceptor moieties advance the ΔG^{inject} to -2.76 (**3a**) and mono-methyl (**3b**) enhance the electron injection to -2.83. We have also observed that substitution of di- and tri-methyl (**c** and **d** derivatives) diminishes the ΔG^{inject} to some extent compared to mono-methyl (**b** derivatives). On other hand di- and tri-methyl substituted sensitizers have higher

ΔG^{inject} than vinyl substituted ones. The ΔG^{inject} of new designed photosensitizers is superior to TC4. The trend of the $\Delta G_r^{\text{inject}}$ has been observed as $3 > 2 > 1 > \text{TC4}$ ($\mathbf{b} > \mathbf{c} > \mathbf{d} > \mathbf{a}$) except $3\mathbf{d}$ which revealed that new designed photosensitizers would be efficient. In TC4, the electronic coupling constant $|V_{\text{RP}}|$ is 1.055 which improved to 1.265 by increasing the one benzene ring between TPA moiety and acceptor unit ($1\mathbf{a}$). The $|V_{\text{RP}}|$ reaches up to 1.315, 1.300 and 1.290 in the same sensitizer by substitution of mono-, di- and tri-methyl. By increasing the two benzene rings between TPA and acceptor moieties ($2\mathbf{a}$) the $|V_{\text{RP}}|$ boost up to 1.355 which enhanced to 1.390 by substitution of mono-methyl to improve the donor ability. It can be seen from Table 1 that by increasing the three benzene rings between TPA moiety and acceptor unit increase the $|V_{\text{RP}}|$ to 1.380 which further improved to 1.415 by substituting mono-methyl. Generally, the $|V_{\text{RP}}|$ of new designed sensitizers are higher than TC4. The improved ΔG^{inject} , $\Delta G_r^{\text{inject}}$, and $|V_{\text{RP}}|$ than TC4 is due to the reason that (1) methyl substitution at vinyl hydrogen at position 3 and 3' is more electron donor which are favorable to promote the electron injection and electronic coupling constant. (2) Enhanced bridge is encouraging to promote the electron injection and electronic coupling constant.

The light harvesting efficiency of TC4 has been observed 0.9827. By increasing the one benzene ring between TPA moiety and anchoring group as bridge improve the LHE to 0.9934. Two benzene rings between TPA moiety and anchoring group leads improve the LHE to 0.9957. By further elongating the bridge (three benzene rings) enhances the LHE to 0.9962. The donor group has no significant effect to improve the LHE. It can be seen from Fig. 2 that by elongating the bridge efficiency enhanced.

CONCLUSIONS

The PCM-TD-B3LYP provides absorption wavelengths that are 101 nm too large compared to experimental data. The PCM-TD-LC-BLYP/6-31G** level better reproduce the experimental absorption wavelengths. The absorption spectra of new designed sensitizers are 25-34 nm blue shifted. In TC4, the maximum transition for first state is caused by HOMO -> LUMO while for new designed sensitizers it is caused by HOMO-1 -> LUMO. By increasing the benzene rings

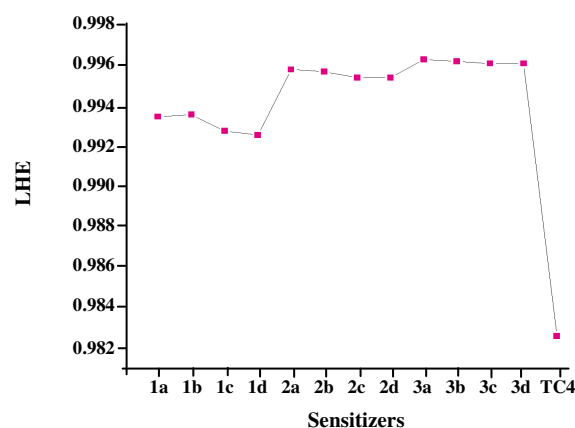


Fig. 2: The light harvesting efficiency of investigated sensitizers (LHE along Y-axis and sensitizers along X-axis).

between TPA and acceptor moieties electron injection boost up. The substitution of di- and tri-methyl (\mathbf{c} and \mathbf{d} derivatives) diminishes the electron injection compared to mono-methyl (\mathbf{b} derivatives). On other hand di- and tri-methyl substituted sensitizers have higher ΔG^{inject} than vinyl substituted ones. The electron injection of new designed photosensitizers is superior to TC4. The electronic coupling constant also improved to by increasing the benzene rings between TPA moiety and acceptor unit. The improved ΔG^{inject} , $\Delta G_r^{\text{inject}}$, and $|V_{\text{RP}}|$ than TC4 is due to the reason that (1) methyl substitution at vinyl hydrogen at position 3 and 3' is more electron donor which are favorable to promote the electron injection and electronic coupling constant. (2) Enhanced bridge is encouraging to promote the electron injection and electronic coupling constant. Light harvesting efficiency improved by elongating. The donor group has no significant effect to improve the LHE.

Acknowledgement

Authors are thankful to King Khalid University support and their facility to carry out the research work.

Received : March 21, 2013 ; Accepted : Jan. 28, 2014

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Appendix

Absorption spectrum of TC4 at PCM-TD-B3LYP/6-31G level of theory and %age contribution**

| No. | Energy (cm-1) | Wavelength (nm) | Osc. Strength | Major contribs | Minor contribs |
|-----|---------------|-----------------|---------------|---|----------------|
| 1 | 19005.77984 | 526.15 | 1.0987 | HOMO->LUMO (99%) | |
| 2 | 27526.27968 | 363.29 | 0.4872 | H-1->LUMO (81%), HOMO->L+1 (16%) | |
| 3 | 29405.56448 | 340.07 | 0.1827 | H-1->LUMO (15%), HOMO->L+1 (79%), HOMO->L+3 (2%) | |
| 4 | 30657.3456 | 326.19 | 0.2124 | H-2->LUMO (78%), H-5->LUMO (3%), H-4->LUMO (7%), HOMO->L+2 (3%), HOMO->L+3 (6%) | |
| 5 | 31377.60368 | 318.69 | 0.0185 | H-4->LUMO (21%), H-2->LUMO (12%), HOMO->L+2 (52%)H-5->LUMO (7%), H-3->LUMO (5%) | |
| 6 | 32089.79616 | 311.62 | 0.0159 | H-3->LUMO (90%), HOMO->L+2 (6%) | |
| 7 | 32745.52944 | 305.38 | 0.0875 | H-5->LUMO (12%), H-4->LUMO (43%), HOMO->L+2 (30%), HOMO->L+3 (8%) | |
| 8 | 33685.17184 | 296.86 | 0.0071 | H-5->LUMO (63%), H-4->LUMO (22%), HOMO->L+3 (4%), HOMO->L+4 (8%) | |
| 9 | 33840.83792 | 295.50 | 0.0863 | HOMO->L+3 (73%), H-6->LUMO (2%), H-5->LUMO (2%), H-4->LUMO (6%), H-2->LUMO (5%), HOMO->L+2 (3%) | |
| 10 | 34876.46096 | 286.72 | 0.0001 | H-7->LUMO (96%) | |

Absorption spectrum of TC4 at PCM-TD-LC-BLYP/6-31G level of theory and %age contribution**

| No. | Energy (cm-1) | Wavelength (nm) | Osc. Strength | Major contribs | Minor contribs |
|-----|---------------|-----------------|---------------|--|----------------|
| 1 | 26830.2184 | 372.71 | 1.7622 | H-1->LUMO (18%), HOMO->LUMO (70%), HOMO->L+3 (3%) | |
| 2 | 37029.97616 | 270.05 | 0.2181 | H-1->LUMO (11%), HOMO->L+1 (62%) H-1->L+1(9%) | |
| 3 | 38827.7984 | 257.54 | 0.003 | HOMO->L+2 (34%), HOMO->L+3 (14%) H-5->LUMO (9%), H-4->LUMO (9%), H-1->LUMO (6%), H-1->L+4 (3%), HOMO->L+4 (4%) | |
| 4 | 39556.12208 | 252.80 | 0.4407 | H-2->LUMO (12%), H-1->LUMO (17%), HOMO->L+2 (15%), HOMO->L+3 (22%) H-6->LUMO (6%), H-2->L+3 (2%), H-1->L+1 (3%), HOMO->LUMO (4%), HOMO->L+1 (7%) | |
| 5 | 41230.54064 | 242.54 | 0.0058 | HOMO->L+4 (30%) H-5->LUMO (9%), H-5->L+1(4%), H-4->L+1 (7%), H-3->L+1 (7%), H-2->L+5 (2%), H-1->L+2 (9%), H-1->L+5 (4%), HOMO->L+2 (6%), HOMO->L+5 (3%) | |
| 6 | 43176.76992 | 231.61 | 0.0085 | H-2->L+2 (10%), HOMO->L+5 (32%) H-6->L+2 (2%), H-6->L+5 (3%), H-5->LUMO (2%), H-5->L+3 (3%), H-4->L+1 (5%), H-3->L+3 (8%), H-3->L+6 (6%), H-2->L+4 (3%), H-2->L+5 (8%), H-1->L+5 (3%), HOMO->L+2 (4%) | |
| 7 | 44415.64608 | 225.14 | 0.0002 | H-8->LUMO (55%), H-8->L+7 (23%) H-8->L+3 (9%), H-8->L+6 (5%) | |
| 8 | 45758.56848 | 218.54 | 0.1898 | HOMO->L+3 (23%), HOMO->L+6 (12%) H-6->LUMO (6%), H-4->LUMO (3%), H-2->LUMO (3%), H-2->L+1 (6%), H-2->L+3 (3%), H-1->LUMO (5%), H-1->L+1 (5%), HOMO->LUMO (9%), HOMO->L+4 (6%) | |
| 9 | 47137.78608 | 212.14 | 0.2381 | H-5->LUMO (18%), H-4->LUMO (14%), HOMO->L+2 (15%) H-4->L+1 (2%), H-2->LUMO (2%), H-1->LUMO (4%), H-1->L+1 (5%), HOMO->LUMO (4%), HOMO->L+1 (3%), HOMO->L+3 (4%), HOMO->L+4 (9%) | |
| 10 | 48161.31072 | 207.63 | 0.0192 | H-2->L+1 (11%), H-1->LUMO (10%), H-1->L+1 (11%), HOMO->L+6 (10%) H-5->LUMO (4%), H-4->LUMO (4%), H-3->L+1 (2%), H-2->LUMO (3%), H-1->L+3 (6%), HOMO->LUMO (4%), HOMO->L+1 (4%), HOMO->L+2 (4%), HOMO->L+3 (7%) | |

Absorption spectrum of 1a at PCM-TD-LC-BLYP/6-31G level of theory and %age contribution**

| No. | Energy (cm-1) | Wavelength (nm) | Osc. Strength | Major contribs | Minor contribs |
|-----|---------------|-----------------|---------------|--|----------------|
| 1 | 28760.31648 | 347.70 | 2.1805 | H-1->LUMO (55%), HOMO->LUMO (27%), H-3->LUMO (4%), HOMO->L+2 (6%) | |
| 2 | 35191.01936 | 284.16 | 0.8866 | HOMO->L+1 (77%) H-2->L+2 (4%), H-2->L+3 (2%), H-2->L+4 (2%), H-1->L+1 (6%), HOMO->L+11 (3%) | |
| 3 | 35428.148 | 282.26 | 0.1577 | H-3->LUMO (10%), H-1->LUMO (15%), HOMO->L+2 (48%) H-2->L+1 (3%), HOMO->LUMO (8%), HOMO->L+8 (4%) | |
| 4 | 38498.72192 | 259.75 | 0.0121 | HOMO->L+3 (46%), HOMO->L+4 (20%) H-5->L+2(3%), H-4->L+1 (3%), H-3->L+6 (3%), H-2->L+7 (6%), H-1->L+6 (2%) | |
| 5 | 40172.33392 | 248.93 | 0.0092 | H-6->LUMO (51%), H-1->L+5 (15%), H-8->L+5 (2%), H-6->L+2 (5%), H-6->L+3 (3%), H-6->L+4 (4%), H-6->L+8 (3%), HOMO->L+5 (7%) | |
| 6 | 41332.1672 | 241.94 | 0.0295 | HOMO->L+6 (35%) H-7->L+2 (7%), H-3->L+3 (4%), H-3->L+6 (2%), H-2->L+7 (4%), H-1->L+3 (3%), HOMO->LUMO (2%), HOMO->L+4 (5%), HOMO->L+5 (3%) | |
| 7 | 41587.84672 | 240.45 | 0.0153 | HOMO->L+7 (43%) H-7->L+1 (8%), H-5->L+1 (4%), H-4->L+1 (3%), H-4->L+2 (3%), H-4->L+4 (2%), H-2->L+3 (8%), H-2->L+4 (3%), H-2->L+6 (4%), H-1->L+7 (5%) | |
| 8 | 42150.8256 | 237.24 | 0.1741 | H-3->LUMO (11%), HOMO->LUMO (20%), HOMO->L+4 (15%), H-8->LUMO (5%), H-2->L+1 (9%), H-1->L+2 (5%), HOMO->L+2 (7%), HOMO->L+3 (4%), HOMO->L+6 (6%) | |
| 9 | 45831.15888 | 218.19 | 0.0233 | H-1->L+2 (21%), HOMO->LUMO (34%) H-8->LUMO (3%), H-2->L+1 (3%), H-1->LUMO (7%), H-1->L+3 (3%), H-1->L+4 (2%), HOMO->L+2 (7%), HOMO->L+8 (2%) | |
| 10 | 46423.98048 | 215.40 | 0.0444 | H-8->LUMO (17%), H-2->L+1 (17%), HOMO->L+8 (13%), H-9->LUMO (6%), H-6->L+5 (2%), H-3->LUMO (5%), H-3->L+2 (6%), H-1->L+3 (4%), H-1->L+4 (5%), HOMO->L+4 (2%) | |

Absorption spectrum of 1b at PCM-TD-LC-BLYP/6-31G level of theory and %age contribution**

| No. | Energy (cm-1) | Wavelength (nm) | Osc. Strength | Major contribs | Minor contribs |
|-----|---------------|-----------------|---------------|---|----------------|
| 1 | 28636.9128 | 349.20 | 2.1873 | H-1->LUMO (53%), HOMO->LUMO (26%), H-3->LUMO (6%), HOMO->L+1 (6%) | |
| 2 | 35312.80992 | 283.18 | 0.3744 | H-1->LUMO (12%), HOMO->L+1 (51%) H-3->LUMO (9%), HOMO->LUMO (7%), HOMO->L+8 (3%) | |
| 3 | 35801.58528 | 279.32 | 0.7395 | HOMO->L+2 (70%) H-3->LUMO (2%), H-2->L+4 (4%), H-1->LUMO (2%), H-1->L+2 (2%), HOMO->LUMO (2%), HOMO->L+11 (2%) | |
| 4 | 38383.38384 | 260.53 | 0.0139 | HOMO->L+3 (60%) H-5->L+1 (4%), H-4->L+2 (4%), H-3->L+6 (2%), H-2->L+7 (4%), HOMO->L+4 (6%) | |
| 5 | 40152.16992 | 249.05 | 0.0094 | H-6->LUMO (47%), H-1->L+5 (14%), H-7->LUMO (5%), H-6->L+1 (5%), H-6->L+4 (5%), H-6->L+8 (2%), H-1->L+3 (2%), HOMO->L+5 (7%) | |
| 6 | 41299.9048 | 242.13 | 0.0472 | HOMO->L+6 (18%), HOMO->L+7 (21%) H-7->LUMO (2%), H-7->L+1 (7%), H-5->L+2 (3%), H-5->L+8 (2%), H-4->L+1 (3%), H-3->L+3 (4%), H-3->L+6 (2%), H-2->L+7 (4%), H-1->L+3 (5%), HOMO->L+4 (3%), HOMO->L+5 (3%) | |
| 7 | 41516.06288 | 240.87 | 0.0187 | HOMO->L+6 (24%), HOMO->L+7 (20%) H-7->L+2(6%), H-5->L+1 (3%), H-5->L+2 (3%), H-4->L+2 (3%), H-4->L+4 (4%), H-2->L+3 (9%), H-2->L+6 (6%), H-1->L+7 (3%) | |
| 8 | 42085.49424 | 237.61 | 0.2029 | H-3->LUMO (11%), HOMO->LUMO (23%), HOMO->L+4 (20%)H-8->LUMO (6%), H-2->L+2 (8%), H-1->L+1 (4%), HOMO->L+1 (6%), HOMO->L+7 (3%) | |
| 9 | 45564.99408 | 219.47 | 0.0335 | H-1->L+1 (20%), HOMO->LUMO (32%) H-8->LUMO (3%), H-2->L+2 (4%), H-1->LUMO (7%), H-1->L+2 (3%), HOMO->L+1 (6%), HOMO->L+4 (3%), HOMO->L+8 (3%) | |
| 10 | 46411.07552 | 215.46 | 0.0487 | H-8->LUMO (15%), H-2->L+2 (12%), HOMO->L+8(12%), H-10->LUMO (2%), H-9->LUMO (7%), H-3->LUMO (4%), H-3->L+1 (7%), H-2->L+1 (6%), H-1->L+4 (8%) | |

Absorption spectrum of 1c at PCM-TD-LC-BLYP/6-31G level of theory and %age contribution**

| No. | Energy (cm-1) | Wavelength (nm) | Osc. Strength | Major contribs | Minor contribs |
|-----|---------------|-----------------|---------------|---|----------------|
| 1 | 28645.78496 | 349.09 | 2.1371 | H-1->LUMO (51%), HOMO->LUMO (28%), H-3->LUMO (5%), HOMO->L+1 (6%) | |
| 2 | 35733.02768 | 279.85 | 0.169 | H-3->LUMO (10%), H-1->LUMO (13%), HOMO->L+1 (44%), H-8->LUMO (4%), HOMO->LUMO (9%), HOMO->L+4 (2%), HOMO->L+5 (2%), HOMO->L+8 (3%) | |
| 3 | 37430.83648 | 267.15 | 0.7817 | HOMO->L+2 (75%), H-2->L+5 (3%), H-1->L+2 (5%) | |
| 4 | 38621.31904 | 258.92 | 0.039 | HOMO->L+3 (66%), H-5->L+1 (4%), H-4->L+2 (3%), H-2->L+7 (3%) | |
| 5 | 40153.78304 | 249.04 | 0.0071 | H-7->LUMO (26%), H-6->LUMO (26%), H-10->L+4 (2%), H-7->L+1 (3%), H-7->L+5 (2%), H-6->L+1 (4%), H-1->L+4 (9%), H-1->L+5 (4%), HOMO->L+4 (6%), HOMO->L+5 (2%) | |
| 6 | 41517.676 | 240.86 | 0.0361 | HOMO->L+6 (28%), HOMO->L+7 (16%), H-8->L+3 (3%), H-7->LUMO (3%), H-7->L+1 (5%), H-6->L+1 (3%), H-4->L+2 (6%), H-3->L+3 (3%), H-2->L+7 (4%), H-1->L+3 (6%) | |
| 7 | 42026.61536 | 237.94 | 0.0174 | HOMO->L+6 (15%), HOMO->L+7 (30%), H-9->L+3 (2%), H-7->L+2 (2%), H-6->L+2 (3%), H-5->L+2 (6%), H-4->L+1 (3%), H-4->L+5 (3%), H-2->L+3 (9%), H-2->L+6 (5%), H-1->L+7 (4%) | |
| 8 | 42841.24096 | 233.42 | 0.1561 | HOMO->LUMO (25%), HOMO->L+5 (16%), H-10->LUMO (3%), H-8->LUMO (9%), H-3->LUMO (8%), H-2->L+2 (6%), H-1->L+1 (4%), HOMO->L+1 (8%), HOMO->L+4 (9%) | |
| 9 | 44123.67136 | 226.63 | 0.0002 | H-11->LUMO (54%), H-11->L+1 (10%), H-11->L+9 (21%), H-11->L+5 (3%), H-11->L+8 (5%) | |
| 10 | 45890.84432 | 217.91 | 0.04 | H-1->L+1 (28%), HOMO->LUMO (28%), H-10->LUMO (6%), H-8->LUMO (5%), H-1->LUMO (8%), HOMO->L+1 (6%) | |

Absorption spectrum of 1d at PCM-TD-LC-BLYP/6-31G level of theory and %age contribution**

| No. | Energy (cm-1) | Wavelength (nm) | Osc. Strength | Major contribs | Minor contribs |
|-----|---------------|-----------------|---------------|--|----------------|
| 1 | 28629.65376 | 349.28 | 2.1271 | H-1->LUMO (50%), HOMO->LUMO (31%), H-3->LUMO (5%), HOMO->L+1 (6%) | |
| 2 | 35970.15632 | 278.01 | 0.1253 | H-1->LUMO (15%), HOMO->LUMO (10%), HOMO->L+1 (42%) H-6->LUMO (6%), H-3->LUMO (7%), HOMO->L+5 (6%) | |
| 3 | 38490.65632 | 259.80 | 0.3169 | HOMO->L+2 (69%) H-1->L+2 (3%), HOMO->L+3 (5%) | |
| 4 | 39047.18272 | 256.10 | 0.4346 | HOMO->L+3 (64%) H-5->L+1 (2%), HOMO->L+2 (8%) | |
| 5 | 40155.39616 | 249.03 | 0.0056 | H-9->LUMO (19%), H-8->LUMO (23%), H-7->LUMO (10%), H-1->L+4 (12%), H-10->L+4 (3%), H-9->L+1 (3%), H-8->L+1 (4%), H-8->L+5 (2%), HOMO->L+4 (8%) | |
| 6 | 41740.28656 | 239.57 | 0.0415 | HOMO->L+6 (44%), H-9->L+1 (2%), H-7->L+1 (5%), H-6->L+3 (5%), H-4->L+2 (7%), H-2->L+7 (3%), H-1->L+2 (2%), H-1->L+3 (4%), HOMO->L+4 (4%) | |
| 7 | 42413.76416 | 235.77 | 0.0116 | HOMO->L+7 (45%), H-8->L+2 (4%), H-7->L+2 (4%), H-6->L+7 (2%), H-5->L+2 (3%), H-5->L+3 (5%), H-4->L+5 (4%), H-2->L+3 (5%), H-2->L+6 (2%), H-1->L+7 (6%) | |
| 8 | 43330.01632 | 230.78 | 0.1548 | H-6->LUMO (12%), HOMO->LUMO (25%), HOMO->L+5 (21%), H-10->LUMO (6%), H-3->LUMO (4%), H-1->L+1 (3%), HOMO->L+1 (9%), HOMO->L+4 (3%) | |
| 9 | 44126.8976 | 226.61 | 0.0002 | H-11->LUMO (55%), H-11->L+1 (11%), H-11->L+9 (19%), H-11->L+5 (5%), H-11->L+8 (6%) | |
| 10 | 46121.52048 | 216.81 | 0.0412 | H-1->L+1 (29%), HOMO->LUMO (25%), H-10->LUMO (9%), H-6->LUMO (5%), H-1->LUMO (9%), H-1->L+5 (2%), HOMO->L+1 (6%) | |

Absorption spectrum of 2a at PCM-TD-LC-BLYP/6-31G level of theory and %age contribution**

| No. | Energy (cm-1) | Wavelength (nm) | Osc. Strength | Major contribs | Minor contribs |
|-----|---------------|-----------------|---------------|---|----------------|
| 1 | 29362.01024 | 340.57 | 2.3668 | H-3->LUMO (14%), H-1->LUMO (66%), HOMO->LUMO (7%), HOMO->L+1 (3%) | |
| 2 | 34858.71664 | 286.87 | 0.5756 | HOMO->L+1 (52%), HOMO->L+3 (11%), H-3->LUMO (6%), H-3->L+1 (2%), H-2->L+2 (3%), H-1->LUMO (3%), HOMO->LUMO (4%) | |
| 3 | 35018.41552 | 285.56 | 0.9159 | HOMO->L+2 (76%), H-2->L+3 (5%), H-1->L+2 (4%), HOMO->L+13 (3%) | |
| 4 | 38471.29888 | 259.93 | 0.0147 | HOMO->L+4 (57%), H-5->L+1 (3%), H-4->L+2 (5%), H-3->L+8 (3%), H-2->L+9 (6%), HOMO->L+3 (9%) | |
| 5 | 40218.30784 | 248.64 | 0.0084 | H-7->LUMO (49%), H-1->L+5 (14%), H-8->LUMO (5%), H-7->L+1 (3%), H-7->L+3 (4%), H-7->L+7 (5%), H-1->L+6 (2%), H-1->L+7 (2%) | |
| 6 | 40786.12608 | 245.18 | 0.0649 | H-3->LUMO (13%), H-1->L+1 (19%), HOMO->L+3 (16%), H-8->LUMO (7%), H-2->L+2 (5%), HOMO->LUMO (7%), HOMO->L+4 (5%) | |
| 7 | 41493.4792 | 241.00 | 0.0119 | HOMO->L+8 (33%), H-9->L+1 (4%), H-5->L+1 (3%), H-4->L+2 (5%), H-3->L+4 (6%), H-2->L+9 (3%), H-1->L+4 (2%), HOMO->L+6 (5%), HOMO->L+9 (2%) | |
| 8 | 41528.16128 | 240.80 | 0.0234 | HOMO->L+9 (41%), H-9->L+2 (8%), H-5->L+2 (5%), H-4->L+1 (2%), H-4->L+3 (5%), H-2->L+4 (9%), H-2->L+8 (4%), H-1->L+9 (3%) | |
| 9 | 42266.97024 | 236.59 | 0.0004 | H-6->LUMO (10%), H-6->L+1 (24%), H-1->L+6 (11%), H-8->L+6 (3%), H-6->L+3 (4%), H-6->L+11 (5%), H-3->L+5 (2%), H-3->L+6 (3%), H-1->L+5 (6%), H-1->L+7 (2%), HOMO->L+5 (3%), HOMO->L+6 (3%), HOMO->L+8 (5%) | |
| 10 | 44726.97824 | 223.57 | 0.0545 | H-2->L+2 (18%), HOMO->L+7 (12%), H-10->LUMO (5%), H-8->LUMO (7%), H-3->L+1 (7%), H-1->LUMO (2%), H-1->L+3 (7%), HOMO->L+1 (2%), HOMO->L+3 (7%), HOMO->L+6 (3%), HOMO->L+11 (2%) | |

Absorption spectrum of 2b at PCM-TD-LC-BLYP/6-31G level of theory and %age contribution**

| No. | Energy (cm-1) | Wavelength (nm) | Osc. Strength | Major contribs | Minor contribs |
|-----|---------------|-----------------|---------------|--|----------------|
| 1 | 29332.97408 | 340.91 | 2.3557 | H-3->LUMO (15%), H-1->LUMO (65%), HOMO->LUMO (7%), HOMO->L+1 (3%) | |
| 2 | 34962.76288 | 286.01 | 0.5439 | HOMO->L+1 (49%), HOMO->L+3 (15%), H-3->LUMO (6%), H-3->L+1 (3%), H-2->L+2 (3%), H-1->LUMO (2%), H-1->L+1 (2%), HOMO->LUMO (5%) | |
| 3 | 35981.44816 | 277.92 | 0.9509 | HOMO->L+2 (78%), H-2->L+3 (5%), H-1->L+2 (4%), HOMO->L+13 (3%) | |
| 4 | 38474.52512 | 259.91 | 0.0241 | HOMO->L+4 (66%), H-5->L+1 (3%), H-4->L+2 (5%), H-3->L+8 (3%), H-2->L+9 (6%) | |
| 5 | 40208.62912 | 248.70 | 0.0088 | H-9->LUMO (54%), H-1->L+5 (14%), H-9->L+1 (4%), H-9->L+3 (6%), H-9->L+7 (5%), H-1->L+6 (3%) | |
| 6 | 40945.0184 | 244.22 | 0.0652 | H-7->LUMO (10%), H-3->LUMO (12%), H-1->L+1 (20%), HOMO->L+3 (18%), H-10->LUMO (3%), H-2->L+2 (4%), HOMO->LUMO (7%), HOMO->L+9 (3%) | |
| 7 | 41444.27904 | 241.28 | 0.025 | HOMO->L+8 (39%), H-10->L+4 (2%), H-8->L+1 (5%), H-8->L+3 (3%), H-5->L+1 (3%), H-5->L+7 (3%), H-4->L+2 (5%), H-3->L+4 (8%), H-3->L+8 (2%), H-2->L+9 (4%), H-1->L+4 (4%), HOMO->L+6 (5%) | |
| 8 | 41590.2664 | 240.44 | 0.0258 | H-2->L+4 (11%), HOMO->L+9 (43%), H-11->L+4 (2%), H-8->L+2 (7%), H-5->L+2 (6%), H-4->L+3 (5%), H-2->L+8 (4%), H-1->L+9 (3%) | |
| 9 | 42248.41936 | 236.69 | 0.0005 | H-6->LUMO (10%), H-6->L+1 (25%), H-1->L+6 (13%), H-7->L+5 (2%), H-7->L+6 (4%), H-6->L+3 (2%), H-6->L+11 (5%), H-3->L+6 (3%), H-1->L+5 (7%), HOMO->L+5 (3%), HOMO->L+6 (4%), HOMO->L+8 (6%) | |
| 10 | 45127.032 | 221.59 | 0.0478 | H-2->L+2 (17%), HOMO->L+7 (15%), H-12->LUMO (3%), H-10->LUMO (6%), H-7->LUMO (7%), H-3->L+1 (7%), H-1->LUMO (2%), H-1->L+3 (8%), HOMO->LUMO (4%), HOMO->L+3 (6%) | |

Absorption spectrum of 2c at PCM-TD-LC-BLYP/6-31G level of theory and %age contribution**

| No. | Energy (cm-1) | Wavelength (nm) | Osc. Strength | Major contribs | Minor contribs |
|-----|---------------|-----------------|---------------|---|--|
| 1 | 29336.20032 | 340.87 | 2.3269 | H-3->LUMO (13%), H-1->LUMO (65%) | HOMO->LUMO (8%), HOMO->L+1 (3%) |
| 2 | 35355.5576 | 282.84 | 0.5381 | HOMO->L+1 (49%), HOMO->L+4 (16%) | H-3->LUMO (6%), H-3->L+1 (3%), H-1->LUMO (3%), H-1->L+1 (3%), HOMO->LUMO (5%) |
| 3 | 37769.59168 | 264.76 | 0.7354 | HOMO->L+2 (78%) | H-2->L+9 (2%), H-1->L+2 (5%), HOMO->L+13 (2%) |
| 4 | 38778.59824 | 257.87 | 0.0472 | HOMO->L+3 (67%) | H-11->L+7 (2%), H-10->L+8 (2%), H-6->L+1 (3%), H-5->L+2 (3%), H-3->L+7 (3%), H-2->L+8 (4%) |
| 5 | 40206.20944 | 248.71 | 0.0095 | H-9->LUMO (54%), H-1->L+5 (12%) | H-9->L+1 (4%), H-9->L+4 (7%), H-9->L+9 (3%), H-1->L+6 (5%) |
| 6 | 41348.2984 | 241.84 | 0.0554 | H-3->LUMO (11%), H-1->L+1 (21%), HOMO->L+4(16%) | H-11->LUMO (8%), H-5->LUMO (3%), H-4->LUMO (7%), HOMO->LUMO (7%) |
| 7 | 41654.7912 | 240.06 | 0.0384 | HOMO->L+7 (35%) | H-11->L+3 (3%), H-8->L+1 (4%), H-8->L+4 (3%), H-7->L+1 (3%), H-6->L+1 (2%), H-5->L+2 (4%), H-3->L+3 (6%), H-2->L+8 (4%), H-1->L+3 (4%), HOMO->L+5 (2%), HOMO->L+6 (6%), HOMO->L+9 (3%) |
| 8 | 42177.44208 | 237.09 | 0.0267 | HOMO->L+8 (44%) | H-10->L+3 (4%), H-8->L+2 (7%), H-6->L+2 (5%), H-5->L+4 (3%), H-5->L+9 (2%), H-2->L+3 (8%), H-2->L+7 (3%), H-1->L+8 (4%) |
| 9 | 42258.90464 | 236.63 | 0.002 | -7->LUMO (10%), H-7->L+1 (25%), H-1->L+6(11%) | H-7->L+9 (2%), H-7->L+11 (4%), H-4->L+6 (3%), H-3->L+6 (2%), H-1->L+5 (7%), HOMO->L+5 (3%), HOMO->L+6 (4%), HOMO->L+7 (9%) |
| 10 | 44092.21552 | 226.79 | 0.0002 | H-13->LUMO (54%), H-13->L+10 (24%) | H-13->L+1 (8%), H-13->L+4 (6%), H-13->L+9 (3%) |

Absorption spectrum of 2d at PCM-TD-LC-BLYP/6-31G level of theory and %age contribution**

| No. | Energy (cm-1) | Wavelength (nm) | Osc. Strength | Major contribs | Minor contribs |
|-----|---------------|-----------------|---------------|--|---|
| 1 | 29315.22976 | 341.11 | 2.3302 | H-3->LUMO (10%), H-1->LUMO (64%) | H-4->LUMO (5%), HOMO->LUMO (8%), HOMO->L+1 (3%) |
| 2 | 35386.20688 | 282.59 | 0.5389 | HOMO->L+1 (48%), HOMO->L+4 (15%) | H-4->LUMO (4%), H-3->LUMO (4%), H-3->L+1 (2%), H-1->LUMO (3%), H-1->L+1 (3%), HOMO->LUMO (5%), HOMO->L+5 (2%) |
| 3 | 38469.68576 | 259.94 | 0.5051 | HOMO->L+2 (74%) | H-1->L+2 (4%) |
| 4 | 38902.00192 | 257.05 | 0.2537 | HOMO->L+3 (67%) | HOMO->L+2 (4%) |
| 5 | 40202.17664 | 248.74 | 0.0096 | H-10->LUMO (54%), H-1->L+5 (11%) | H-10->L+1 (4%), H-10->L+4 (7%), H-10->L+9 (3%), H-1->L+4 (3%), H-1->L+6 (5%) |
| 6 | 41435.40688 | 241.33 | 0.054 | H-11->LUMO (10%), H-4->LUMO (12%), H-1->L+1 (21%), HOMO->L+4 (14%) | H-3->LUMO (6%), HOMO->LUMO (7%), HOMO->L+5 (3%), HOMO->L+9 (3%) |
| 7 | 41702.37824 | 239.79 | 0.0456 | HOMO->L+7 (36%) | H-11->L+3 (3%), H-9->L+8 (2%), H-8->L+1 (3%), H-8->L+4 (3%), H-7->L+1 (4%), H-5->L+2 (3%), H-4->L+3 (2%), H-3->L+3 (3%), H-2->L+8 (3%), H-1->L+3 (3%), HOMO->L+5 (3%), HOMO->L+6 (7%) |
| 8 | 42250.03248 | 236.68 | 0.0033 | H-7->L+1 (24%), H-1->L+6 (11%), HOMO->L+7 (11%) | H-7->LUMO (9%), H-7->L+9 (3%), H-7->L+11 (3%), H-4->L+5 (3%), H-4->L+6 (4%), H-1->L+5 (6%), HOMO->L+5 (3%), HOMO->L+6 (4%) |
| 9 | 42365.37056 | 236.04 | 0.0267 | HOMO->L+8 (45%) | H-9->L+3 (4%), H-9->L+7 (2%), H-8->L+2 (7%), H-6->L+2 (3%), H-5->L+9 (2%), H-4->L+8 (2%), H-2->L+3 (6%), H-2->L+7 (2%), H-1->L+8 (5%) |
| 10 | 44092.21552 | 226.79 | 0.0002 | H-13->LUMO (54%), H-13->L+10 (23%) | H-13->L+1 (8%), H-13->L+4 (6%), H-13->L+9 (3%) |

Absorption spectrum of 3a at PCM-TD-LC-BLYP/6-31G level of theory and %age contribution**

| No. | Energy (cm-1) | Wavelength (nm) | Osc. Strength | Major contribs | Minor contribs |
|-----|---------------|-----------------|---------------|--|---|
| 1 | 29499.12544 | 338.99 | 2.4158 | H-2->LUMO (26%), H-1->LUMO (57%) | H-4->LUMO (4%) |
| 2 | 34617.5552 | 288.87 | 1.1046 | HOMO->L+1 (44%), HOMO->L+3 (24%) | H-3->L+2 (3%), H-2->LUMO (3%), H-2->L+1 (4%), H-1->L+1 (4%), HOMO->L+11 (2%) |
| 3 | 34969.21536 | 285.96 | 0.9105 | HOMO->L+2 (77%) | H-3->L+3 (5%), H-2->L+2 (2%), H-1->L+2 (4%), HOMO->L+15 (3%) |
| 4 | 38437.42336 | 260.16 | 0.029 | HOMO->L+4 (56%) | H-6->L+2 (4%), H-5->L+1 (2%), H-5->L+3 (2%), H-3->L+10 (6%), H-2->L+9 (2%), HOMO->L+3 (4%), HOMO->L+5 (4%) |
| 5 | 39507.72848 | 253.11 | 0.0897 | H-1->L+1 (30%), HOMO->L+3 (13%), H-11->LUMO (3%), H-4->LUMO (8%), H-4->L+1 (2%), H-3->L+2 (2%), H-2->LUMO (8%), H-2->L+1 (2%), H-1->LUMO (2%), H-1->L+3 (3%), HOMO->L+4 (3%), HOMO->L+5 (4%) | |
| 6 | 40246.53744 | 248.46 | 0.0104 | H-9->LUMO (55%) | H-9->L+3 (5%), H-9->L+5 (4%), H-9->L+11 (3%), H-2->L+6 (2%), H-1->L+5 (3%), H-1->L+6 (7%), H-1->L+7 (5%) |
| 7 | 41447.50528 | 241.26 | 0.0084 | HOMO->L+9 (26%), HOMO->L+10 (15%) | H-10->L+1 (2%), H-10->L+2 (3%), H-10->L+3 (2%), H-6->L+2 (2%), H-5->L+1 (2%), H-5->L+2 (2%), H-4->L+4 (2%), H-3->L+4 (3%), H-3->L+10 (3%), H-2->L+4 (4%), HOMO->L+7 (2%) |
| 8 | 41520.09568 | 240.84 | 0.0238 | HOMO->L+9 (12%), HOMO->L+10 (29%) | H-10->L+2 (6%), H-6->L+3 (3%), H-5->L+2 (3%), H-3->L+4 (7%), H-3->L+9 (3%) |
| 9 | 42250.83904 | 236.68 | 0.0024 | H-8->L+1 (12%), H-1->L+6 (12%), H-1->L+7 (10%) | H-11->L+8 (3%), H-8->LUMO (7%), H-8->L+3 (6%), H-8->L+11 (3%), H-7->L+1 (9%), H-4->L+6 (3%), H-2->L+7 (3%), H-1->L+8 (3%), HOMO->L+6 (2%), HOMO->L+7 (3%), HOMO->L+9 (2%) |
| 10 | 42629.11568 | 234.58 | 0.0001 | H-7->L+1 (18%), H-1->L+8 (15%) | H-11->L+7 (3%), H-8->LUMO (4%), H-8->L+1 (9%), H-8->L+3 (3%), H-7->L+5 (3%), H-7->L+14 (4%), H-4->L+8 (2%), H-2->L+7 (5%), H-2->L+8 (5%), H-1->L+7 (2%), HOMO->L+7 (2%), HOMO->L+8 (4%), HOMO->L+9 (3%) |

Absorption spectrum of 3b at PCM-TD-LC-BLYP/6-31G level of theory and %age contribution**

| No. | Energy (cm-1) | Wavelength (nm) | Osc. Strength | Major contribs | Minor contribs |
|-----|---------------|-----------------|---------------|---|----------------|
| 1 | 29474.92864 | 339.27 | 2.4146 | H-2->LUMO (24%), H-1->LUMO (56%), H-4->LUMO (5%), H-3->LUMO (2%) | |
| 2 | 34688.53248 | 288.27 | 1.0675 | HOMO->L+1 (42%), HOMO->L+3 (25%) H-3->L+2 (2%), H-2->LUMO (3%), H-2->L+1 (4%), H-1->L+1 (5%) | |
| 3 | 35945.95952 | 278.19 | 0.9504 | HOMO->L+2 (77%) H-3->L+3 (3%), H-3->L+6 (2%), H-1->L+2 (4%), HOMO->L+15 (3%) | |
| 4 | 38467.26608 | 259.96 | 0.0256 | HOMO->L+4 (68%) H-6->L+1 (2%), H-6->L+3 (3%), H-5->L+2 (4%), H-3->L+10 (5%), H-2->L+9 (2%) | |
| 5 | 39548.05648 | 252.85 | 0.0989 | H-1->L+1 (32%), HOMO->L+3 (14%) H-11->LUMO (4%), H-4->LUMO (9%), H-4->L+1 (3%), H-2->LUMO (7%), H-1->LUMO (3%), H-1->L+3 (3%), HOMO->L+6 (2%) | |
| 6 | 40236.05216 | 248.53 | 0.0105 | H-10->LUMO (55%) H-10->L+3 (6%), H-10->L+6 (3%), H-10->L+11 (3%), H-2->L+5 (3%), H-1->L+5 (8%), H-1->L+7 (5%) | |
| 7 | 41449.1184 | 241.25 | 0.0254 | HOMO->L+9 (39%) H-9->L+1 (4%), H-9->L+3 (4%), H-6->L+1 (3%), H-6->L+11 (2%), H-5->L+2 (4%), H-4->L+4 (3%), H-4->L+9 (2%), H-3->L+10 (4%), H-2->L+4 (7%), H-1->L+4 (3%), HOMO->L+7 (3%), HOMO->L+8 (3%) | |
| 8 | 41553.9712 | 240.65 | 0.0213 | H-3->L+4 (11%), HOMO->L+10 (44%) H-13->L+4 (2%), H-9->L+2 (7%), H-6->L+2 (6%), H-5->L+3 (4%), H-5->L+6 (2%), H-3->L+9 (4%), H-2->L+10 (2%), H-1->L+10 (3%) | |
| 9 | 42224.22256 | 236.83 | 0.0031 | H-8->L+1 (12%), H-7->L+1 (10%) H-14->L+8 (2%), H-11->L+8 (3%), H-8->LUMO (7%), H-8->L+3 (5%), H-8->L+11 (3%), H-4->L+6 (2%), H-2->L+7 (2%), H-1->L+5 (7%), H-1->L+6 (9%), H-1->L+7 (9%), H-1->L+8 (3%), HOMO->L+7 (2%), HOMO->L+9 (2%) | |
| 10 | 42613.79104 | 234.66 | 0.0 | H-8->L+1 (10%), H-7->L+1 (18%), H-1->L+8 (15%) H-11->L+7 (2%), H-8->LUMO (4%), H-8->L+3 (3%), H-7->L+6 (3%), H-7->L+14 (4%), H-4->L+8 (3%), H-2->L+7 (4%), H-2->L+8 (4%), H-1->L+7 (2%), HOMO->L+7 (2%), HOMO->L+8 (4%), HOMO->L+9 (3%) | |

Absorption spectrum of 3c at PCM-TD-LC-BLYP/6-31G level of theory and %age contribution**

| No. | Energy (cm-1) | Wavelength (nm) | Osc. Strength | Major contribs | Minor contribs |
|-----|---------------|-----------------|---------------|---|--|
| 1 | 29478.96144 | 339.22 | 2.3956 | H-2->LUMO (24%), H-1->LUMO (58%) | H-4->LUMO (4%), HOMO->LUMO (2%) |
| 2 | 35056.32384 | 285.25 | 1.0687 | HOMO->L+1 (42%), HOMO->L+2 (23%) | H-2->LUMO (4%), H-2->L+1 (4%), H-1->L+1 (5%) |
| 3 | 37744.58832 | 264.93 | 0.7366 | HOMO->L+3 (76%) | H-2->L+3 (2%), H-1->L+3 (4%), HOMO->L+15 (2%) |
| 4 | 38775.372 | 257.89 | 0.0453 | HOMO->L+4 (69%) | H-12->L+10 (2%), H-6->L+1 (2%), H-6->L+2 (2%), H-5->L+3 (3%), H-3->L+10 (3%), H-2->L+9 (3%) |
| 5 | 39802.92944 | 251.23 | 0.0837 | H-1->L+1 (31%), HOMO->L+2 (13%) | H-9->LUMO (6%), H-4->LUMO (8%), H-4->L+1 (3%), H-2->LUMO (8%), H-1->LUMO (3%), H-1->L+2 (3%), HOMO->L+7 (3%) |
| 6 | 40236.85872 | 248.52 | 0.0108 | H-11->LUMO (55%), H-1->L+5 (11%) | H-11->L+2 (7%), H-11->L+7 (3%), H-2->L+5 (3%), H-1->L+6 (3%), H-1->L+8 (2%) |
| 7 | 41673.34208 | 239.96 | 0.0354 | HOMO->L+9 (38%) | H-10->L+1 (3%), H-10->L+2 (4%), H-9->L+4 (3%), H-6->L+11 (2%), H-5->L+3 (5%), H-3->L+10 (4%), H-2->L+4 (6%), H-1->L+4 (3%), HOMO->L+6 (4%), HOMO->L+8 (2%) |
| 8 | 42141.95344 | 237.29 | 0.0234 | HOMO->L+10 (45%) | H-12->L+4 (4%), H-10->L+3 (7%), H-6->L+3 (6%), H-5->L+2 (2%), H-5->L+7 (2%), H-3->L+4 (9%), H-3->L+9 (3%), H-2->L+10 (3%), H-1->L+10 (4%) |
| 9 | 42231.4816 | 236.79 | 0.0048 | H-8->L+1 (13%), H-1->L+5 (11%), H-1->L+6 (12%) | H-8->LUMO (7%), H-8->L+2 (5%), H-8->L+11 (3%), H-7->L+1 (9%), H-4->L+5 (2%), H-4->L+6 (2%), H-2->L+6 (3%), H-1->L+8 (3%), HOMO->L+6 (3%), HOMO->L+9 (3%) |
| 10 | 42616.21072 | 234.65 | 0.0001 | H-8->L+1 (10%), H-7->L+1 (18%), H-8->LUMO (4%), H-8->L+2 (2%), H-7->L+14 (3%), H-2->L+6 (4%), H-2->L+7 (3%), H-1->L+7 (8%), H-1->L+8 (8%), HOMO->L+6 (2%), HOMO->L+7 (3%), HOMO->L+9 (4%) | |

Absorption spectrum of 3d at PCM-TD-LC-BLYP/6-31G level of theory and %age contribution**

| No. | Energy (cm-1) | Wavelength (nm) | Osc. Strength | Major contribs | Minor contribs |
|-----|---------------|-----------------|---------------|--|--|
| 1 | 29466.05648 | 339.37 | 2.3996 | H-2->LUMO (18%), H-1->LUMO (57%) | H-4->LUMO (6%), H-3->LUMO (4%), HOMO->LUMO (2%) |
| 2 | 35075.68128 | 285.09 | 1.0743 | HOMO->L+1 (42%), HOMO->L+2 (23%) | H-2->LUMO (3%), H-2->L+1 (3%), H-1->L+1 (6%), HOMO->L+8 (3%) |
| 3 | 38397.09536 | 260.43 | 0.6058 | HOMO->L+3 (75%) | H-1->L+3 (4%) |
| 4 | 38847.15584 | 257.41 | 0.1675 | HOMO->L+4 (68%) | H-11->L+10 (2%), H-6->L+2 (2%), H-5->L+3 (2%), HOMO->L+3 (2%) |
| 5 | 39841.64432 | 250.99 | 0.0755 | H-1->L+1 (31%), HOMO->L+2 (13%) | H-13->LUMO (2%), H-8->LUMO (7%), H-4->LUMO (6%), H-4->L+1 (3%), H-2->LUMO (5%), H-1->LUMO (3%), H-1->L+2 (3%), HOMO->L+8 (6%) |
| 6 | 40232.01936 | 248.55 | 0.011 | H-12->LUMO (55%), H-1->L+5 (11%) | H-12->L+2 (8%), H-12->L+8 (4%), H-2->L+5 (2%), H-1->L+6 (4%) |
| 7 | 41707.2176 | 239.76 | 0.0414 | HOMO->L+9 (38%) | H-11->L+10 (3%), H-10->L+1 (3%), H-10->L+2 (3%), H-8->L+4 (4%), H-7->L+1 (2%), H-5->L+3 (6%), H-3->L+10 (2%), H-2->L+4 (5%), H-1->L+4 (2%), HOMO->L+6 (4%), HOMO->L+7 (4%) |
| 8 | 42216.96352 | 236.87 | 0.0053 | H-9->L+1 (13%), H-1->L+5 (11%), H-1->L+6 (12%) | H-9->LUMO (7%), H-9->L+2 (5%), H-9->L+11 (3%), H-8->L+7 (3%), H-7->L+1 (9%), H-4->L+6 (2%), H-1->L+7 (2%), HOMO->L+5 (2%), HOMO->L+6 (3%), HOMO->L+9 (4%) |
| 9 | 42303.26544 | 236.38 | 0.0249 | HOMO->L+10 (45%) | H-11->L+4 (4%), H-11->L+9 (2%), H-10->L+3 (7%), H-6->L+3 (4%), H-6->L+4 (2%), H-5->L+8 (3%), H-3->L+4 (6%), H-3->L+9 (2%), H-1->L+10 (4%) |
| 10 | 42608.14512 | 234.69 | 0.0001 | H-9->L+1 (10%), H-7->L+1 (17%), H-1->L+7 (15%) | H-13->L+6 (2%), H-9->LUMO (4%), H-7->L+8 (3%), H-7->L+14 (3%), H-4->L+7 (3%), H-2->L+6 (3%), H-2->L+7 (3%), HOMO->L+6 (2%), HOMO->L+7 (5%), HOMO->L+9 (4%) |