Theoretical study on electronic and absorption characters of p-type D-A-n-A triaryamine sensitizer

<table>
<thead>
<tr>
<th>Journal:</th>
<th>Canadian Journal of Chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manuscript ID</td>
<td>cjc-2017-0358.R1</td>
</tr>
<tr>
<td>Manuscript Type:</td>
<td>Article</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>23-Nov-2017</td>
</tr>
<tr>
<td>Complete List of Authors:</td>
<td>Yan, Wen; Nanjing University of Science and Technology Sun, Zhi-Dan; Nanjing University of Science and Technology Ju, Xue-Hai; Nanjing University of Science and Technology, Department of Chemistry</td>
</tr>
<tr>
<td>Is the invited manuscript for consideration in a Special Issue?:</td>
<td>N/A</td>
</tr>
<tr>
<td>Keyword:</td>
<td>Dye sensitized solar cells (DSSCs), p-Type sensitizers, Density functional theory, Absorption spectrum</td>
</tr>
</tbody>
</table>

https://mc06.manuscriptcentral.com/cjc-pubs
Theoretical study on electronic and absorption characters of $p$-type

D-A-$\pi$-A triaryamine sensitizer

Wen Yan, Zhi-Dan Sun, Xue-Hai Ju*

Key Laboratory of Soft Chemistry and Functional Materials of MOE, School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. China.

* Corresponding author. E-mail: xhju@njust.edu.cn
Abstract: The structural and electronic properties of well known 4,4'-(4-(2,2-dicyanovinyl)thiophen-2-yl)phenylazanediyl)dibenzoic acid (O2) and its hypothetical dyes O3-O7 were investigated by computational techniques. The absorption properties were probed. By replacing the 2-methylene-2-thioxo-dihydropyrimidine-4,6(1H,5H)-dione, the molecular orbital energy levels were well tuned. The modified dyes meet the basic requirements of both \(-\Delta G_{\text{inj}}\) and \(-\Delta G_{\text{reg}}\) being over 0.2 eV for an efficient hole injection and dye regeneration, respectively. All the designed p-type dyes O3-O7 have smaller energy gap and significant red shift in absorption spectra than that of the reference O2. Finally, our results suggested that O3-O7 have larger light-harvesting efficiencies (LHE) in the visible spectral regions of 400 nm to 700 nm than O2. Among all the dyes, O5 is expected to have an excellent performance as a p-type sensitized dye in solar cells due to its great LHE and sufficient hole injection efficiency.

Keywords: Dye sensitized solar cells (DSSCs); p-Type sensitizers; Density functional theory; Absorption spectrum
1. Introduction

Since the invention of metallo-organic ruthenium sensitizer by Grätzel and co-workers in 1991 \(^1\), several researchers focused on molecular engineering of metal free organic sensitizers (MFOS) for dye sensitized solar cell applications due to their high molecular extinction coefficient (\(\varepsilon\)) and low cost device fabrication \(^2-4\). The vast studies on MFOS based on coumarin \(^5-8\), merocyanine \(^9-10\), carbazole \(^11-12\), phenothiazine \(^13\), hemicyanine \(^14-15\), and cyanine \(^16-17\) have reported photonversion efficiencies (\(\eta\)) lower than 10%. Recent studies exposed that triarylamine and indoline based \(n\)-type sensitizer of Y123 and WS-51 were shown to exhibit efficiency ~10% \(^18\). A series of highly efficient \(n\)-type dyes with auxiliary withdrawing group have been studied for better absorption \(^19\). However, the energy conversion efficiency of 2.5% in \(p\)-type dye sensitized solar cell (DSSC) \(^20\) lags far behind that of \(n\)-type, which restricts the fabrication of high-efficiency tandem \(pn\)-DSSCs \(^21\).

Generally, the typical configuration of the Donor-\(\pi\)-linker-Acceptor (D-\(\pi\)-A) sensitizers was widely investigated for their good performance in generating charge-separated state during the intra-molecular electron transfer by light-excitation. Later, "D-A-\(\pi\)-A" has been proposed by inserting in a secondary electron acceptor in the \(\pi\)-spacer in order to decrease band gap and facilitate charge transfer. Benzotriazole, quinoxaline and phthalimide based D–A–\(\pi\)–A featured organic sensitizers have been systematically investigated. It turned out that an additional acceptor unit can efficiently red-shift the absorption of the dyes and adjust the molecular optical band-gap \(^22-23\). For instance, Zhang et al investigated the D-A-\(\pi\)-A
dyes for high performance $p$-type DSSCs and found that the thiophene inserted as the additional acceptor can improve the efficiency of the dye $^{24}$. The dyes with two anchors have been designed by Lin to improve hole injection which has induced the power conversion efficiencies in the range of 0.06% - 0.11$^{25}$. Wu and co-workers $^{26}$ studied the influence on different $\pi$–linkers for dyes and found that thienyl group shows better Incident Photon-to-Current Efficiency (IPCE) than phenyl. Recently, a few researchers have elongated the $\pi$-spacer with electron-withdrawing units of 2H-benzo[d][1,2,3]triazole, thiazolo[5,4-d]-thiazole and benzo[c][1,2,5]thiadiazole to further enhance the device performance $^{26-27}$. Benzo[c][1,2,5]thiadiazole is efficiently used as additional acceptors and 2H-benzo[d][1,2,3]triazole, thiazolo[5,4-d]-thiazole moieties are extensively applied in $n$-type dye sensitizers because of their low-band-gap character, appropriate electronic levels $^{27-28}$.

Based on the above discussion, we proposed a series of new combinations of D–A–$\pi$–A structural units (Fig. 1). O2 is a known reference dye and O3-O7 are the designed structures. O2 contains a TPA and thiophene units with a 2-methylenemalononitrile acceptor unit. Instead of 2-methylenemalononitrile, 1,3-diethyl-5-methylene-2-thioxo-dihydropyrimidine-4,6(1H,5H)-dione acceptor unit was attached to dye O3-O7 for its better performance in UV-vis absorption $^{26}$. O3 were designed by replacing 2-methylidenepropanedinitrile with 1,3-diethyl-5-methylene-2-thioxo-dihydropyrimidine-4,6(1H,5H)-dione only. O4, O5, O6 and O7 have inserted another acceptors of 4-(2-thienyl)-2,1,3-benzothiadiazole,2-(2-thienyl)-thiazolo[5,4-d]thiazole,
2. Theoretical background and computational details

Herein, all calculations were accomplished by using Gaussian 09 package. The geometries of all systems have been fully optimized by using B3LYP functional combined with 6-31G(d,p) basis set which has been proved to be suitable for the geometry optimization. Based on optimized ground-state geometries, 20 lowest excited states of all the sensitizers are calculated using time-dependent density functional theory (TD-DFT). Dye characters were tested by three common functionals of B3LYP, LC-BLYP and CAM-B3LYP with 6-31G(d,p) basis set. CAM-B3LYP was finally chosen as an appropriate one. Both the experimental results from references and the calculated results were shown in Table 1. Additionally, Solvent effect was taken into consideration and all calculations were performed in solvent DMF and the polarized continuum model (PCM) is adopted throughout.

In p-type DSSCs, the energy conversion efficiency ($\eta$) is a vital parameter to estimate whether the sensitizer is good or not, while $\eta$ depends on three main factors: the short-circuit photocurrent density ($J_{sc}$), the open-circuit photovoltage ($V_{oc}$) and the fill factor (FF), and their relation is showed as follow:

$$\eta = \frac{J_{sc} V_{oc}}{I_s} FF$$

Where $I_s$ represents the total solar power incident.

$J_{sc}$ can be calculated by $^{36-38}$
\[ J_{sc} = e \int_{\lambda} LHE(\lambda) \phi_{inj} \eta_{reg} \eta_{coll} I_s(\lambda) d\lambda \]

where LHE(\lambda) represents the light-harvesting efficiency at each specific wavelength. \( \phi_{inj}, \eta_{reg} \) and \( \eta_{coll} \) represent the electron injection efficiency, the regeneration efficiency of the oxidized dye and the charge collection efficiency, respectively. It is obvious that IPEC(\lambda) is directly determined by LHE(\lambda) and \( \phi_{inj} \). LHE(\lambda) is expressed as

\[ LHE = 1 - 10^{-f} \]

Where \( f \) is oscillator strength which is directly associated to the electronic excitation.

The free energies (in eV) of the highest holes injecting efficiency (HJE) and dye regeneration efficiency (DRE) are \( \Delta G_{inj} \) and \( \Delta G_{reg} \) that are expressed as following equations respectively.

\[ \Delta G_{inj} = E_{VB} - (E_{0-0} (\text{dye}^*) + E_{\text{red}} (\text{dye})) \]

\[ \Delta G_{reg} = E(I_3^-/I^-) - E_{\text{red}} (\text{dye}) \]

Where \( E_{VB} \) is the valence band potential of the semiconductor, \( E_{0-0} (\text{dye}^*) \) is the vertical transition energy of sensitizer, \( E_{\text{red}} (\text{dye}) \) is the reduction potential of sensitizer. \( E(I_3^-/I^-) \) is the reduction potential of the redox mediator.

3. Results and discussion

3.1 Electronic structures

The electronic distribution of HOMO and LUMO for \( \text{O2} \) and the designed dye \( \text{O3-O7} \) at B3LYP/6-31G(d,p) level were calculated and displayed in Fig. 2. According
to the diagram, electrons of HOMO distribute mainly on donors and π-spacers except for O2, which is beneficial to the hole injection from the excited dyes to the valence band of NiO. And LUMO of all the dyes predominantly distribute on the π-spacer and acceptor moieties. Theoretically, electrons should be transited from the donors to the acceptors with the π-spacers acting as an important bridge. Based on this mechanism, the designed molecules can probably delivery the electrons from the donors to the acceptors smoothly, thus it could be considered as a good candidate of sensitizers.

On the other hand, as a good p-type sensitizer, the HOMO energy of the sensitizer should lie below the valence band edge of semiconductor like NiO, while the LUMO energy should be higher than that of the electrolyte. The molecular orbital energy levels calculated from B3LYP and CAM-B3LYP of dyes O2-O7 are shown in Fig. 3. As we can see that the HOMO levels of all the dyes are below the valence band of NiO. Compared with O2, the HOMO energy levels of dyes O4-O7 up-shift a little but still under the VB of NiO, which ensures sufficiently hole injection from the excited dyes to the VB of NiO. Apparently, the LUMO levels of all the investigated dyes are more positive than the commonly used I$_3^−$/I$^−$ electrolyte −4.80 eV, indicating that these dyes have sufficient driving force for the regeneration of reduced dyes.

The hole injection from NiO to the excited dye will decrease when the HOMO energy level of dye is close to VB of NiO. As for dyes O3-O7 the HOMO of O3 is same with O2 while the others' are up-shifted and the LUMOs are down-shifted in comparison with O2. Consequently, the driving force for the hole injection and the dye regeneration slightly decrease. However, this decrease does not change the
driving force essentially. Furthermore, the energy gaps between LUMO and HOMO
decrease, resulting in red-shifted absorptions of **O3-O7**. This overwhelmingly makes
up for the influence of slightly decreased driving force.

3.2 UV-visible absorption spectra

An important character of high efficiency sensitize for DSSCs is to have a
broader and stronger absorption. To evaluate the reliability of the functionals for the
absorption character and the excitation energies of these designed \( p \)-type dyes, we
chose **O2** as a prototype that has experimental data. Some common functionals such
as B3LYP, LC-BLYP and CAM-B3LYP have been tested. As can be seen in Table 1,
the \( E_{\text{gap}} \) value from B3LYP is much closer to the experiment than LC-BLYP and
CAM-B3LYP, indicating the former is reliable in comparison with the latter. The MO
contours from B3LYP and CAM-B3LYP are almost identical. The HOMO energies
from CAM-B3LYP are lower than those from B3LYP, but the LUMO energies from
CAM-B3LYP are higher than those from B3LYP, resulting in a much larger \( E_{\text{gap}} \)
from CAM-B3LYP. Nevertheless, the orders of \( E_{\text{gap}} \) values for the titled dyes are the
same from B3LYP and CAM-B3LYP. Besides, the calculated results revealed that the
most intense transition of **O2** obtained by CAM-B3LYP functional was found at 428
nm in \( N,N \)-dimethylformamide (DMF), which is somewhat comparable to the
experimental data of 478 nm in DMF and better than the results of other functionals.
Therefore, we chose CAM-B3LYP to calculate the absorption spectra of the designed
dyes.
To analysis the influence of structures and solvent on the dye properties, we calculated the absorption spectra of **O2-O7** with 6-31G(d,p) basis set and PCM model in DMF solvent. The peak ($\lambda_{\text{max}}$/nm), oscillator strengths ($f$), vibration strength of molecular absorptions and the major components of electronic transitions were summarized in Table 2. Compared with **O2**, the absorption spectrum of **O3** is red-shifted by the replacement of acceptor. Based on it, **O4-O7** were constructed by attaching additional acceptors of 4-(2-thienyl)-2,1,3-benzothiadiazole, 2-(2-thienyl)-thiazolo[5,4-d]thiazole, 4-(2-thienyl)-2H-benzo[d][1,2,3]triazole and 2-octylphenyl-4-(2-thienyl)-2H-benzo[d][1,2,3]triazole, respectively. The absorptions of **O4-O7** are also red-shifted due to their increasing $\pi$-conjugations. The maximum absorption wavelengths of dye **O4-O7** increase in the order: **O5** (505 nm) < **O6** (512 nm) = **O7** (512 nm) < **O4** (539 nm). **O6** and **O7** have similar maximum absorption wave lengths and similar HOMO and LUMO, although **O7** is derived by replacing one of **O6**’s hydrogen with an alkyl chain. This indicates that the alkyl chain does not change the frontier molecular orbitals of **O6**. By contrast, an additional acceptor 4-(2-thienyl)-2,1,3-benzothiadiazole in **O4** increases the conjugation much more. Besides, the maximum absorption bands of all dyes are originated from the electron transfer from the TPA to the acceptors. These transitions are beneficial to the hole injection from the dye to the valance band of NiO.

The absorption spectra of **O2-O7** were shown in Fig. 4. All the absorptions of dyes **O3-O7** have been improved and have two absorption bands in the range of near
ultraviolet 300 nm to 360 nm and visible spectra of 400 nm to 800 nm, while \( \text{O}_2 \) has a third band around 230 nm. The strong absorption band mainly depends on the electron transfer from HOMO to LUMO that dominantly distributes on the acceptor and \( \pi \)-linker moieties. When the conjugation increases, the absorption band red-shifts greatly and has more overlap with the visible spectra. The other absorption bands mainly consist of the transitions HOMO–1 to the LUMO which is also caused by \( \pi \rightarrow \pi^* \) transition. The absorption at 300-400 nm is enhanced a little as the change of acceptor. \( \text{O}_4 \) has the most noticeable red-shift and broad band, but a decreasing peak value. The maximum absorption band of \( \text{O}_5, \text{O}_6 \) and \( \text{O}_7 \) are around 540 nm, but clearly \( \text{O}_5 \) is stronger and broader with two bands in the range of 300 nm to 350 nm and 400 nm to 700 nm. From this aspect, \( \text{O}_5 \) is the best one. Therefore, it is an effective way to improve the absorption character by inserting in an additional acceptor of 2-(2-thienyl)-thiazolo[5,4-\( d \)]thiazole.

3.3 The performance of dyes in DSSCs

Based on the equations mentioned in the theoretical background, more attention should be paid to the values of LHE, \( \Delta G_{\text{inj}} \) and \( \Delta G_{\text{reg}} \) due to their indirect influence on the energy conversion efficiency. From Table 3, it can be seen that all the LHE values of \( \text{O}_2-\text{O}_7 \) are in the range of 0.969 to 0.997. The LHE of \( \text{O}_5 \) is the largest, which is consistent with the results of having the largest \( f \) value in its optical properties. The large LHE could be beneficial to the incident photon-to-electron conversion efficiency (IPCE) of the dye. \( \text{O}_5, \text{O}_6 \) and \( \text{O}_7 \) are much better than that \( \text{O}_2, \text{O}_3 \) and \( \text{O}_4 \). It is
feasible to know that not all the dyes modified with additional acceptors can achieve high LHE and 4-(2-thienyl)-2,1,3-benzothiadiazole may not be a good electron-trap inserting in the π-spacer. In addition, the redox potentials of all the dyes are also calculated and analyzed. As can be seen in Table 3, both $\Delta G_{\text{inj}}$ and $\Delta G_{\text{reg}}$ are negative which is good for the hole injection and dye regeneration. Earlier researchers have confirmed that the hole injected from the excited dye to the semiconductor and dye regeneration can be smoothly processed with enough driving forces when the values of both $-\Delta G_{\text{inj}}$ and $-\Delta G_{\text{reg}}$ are over 0.2 eV \textsuperscript{35,44}. The values of $\Delta G_{\text{inj}}$ and $\Delta G_{\text{reg}}$ for the designed dyes are larger than this reference value, indicating that all the dyes have sufficient driving force for the hole injection. Thus, in view of the highest LHE ($\lambda$) and adequate $\Delta G_{\text{inj}}$ and $\Delta G_{\text{reg}}$, O5 is the best candidate for the $p$-type DSSCs.

4. Conclusion

Prototype and its modified $p$-type sensitizers with different additional acceptors were investigated by DFT method. The results showed that the maximum absorption wavelength of O2 calculated at the CAM-B3LYP/6-31G(d,p) level are comparable to the experimental data and this guarantees that the method is reliable to prescribe the designed dyes. By modifying the D-$\pi$-A conjugation of O2, we constructed the D-A$_1$-$\pi$-A$_2$ conjugation of O3-O7, where A$_1$ are 4-(2-thienyl)-2,1,3-benzothiadiazole, 2-(2-thienyl)-thiazolo[5,4-$d$]thiazole, 4-(2-thienyl)-2$H$-benzo[d][1,2,3]triazole and 2-octylphenyl-4-(2-thienyl)-2$H$-benzo[d][1,2,3]triazolecouples with thiophene as a
π spacer, and \( A_2 \) is 1,3-diethyl-5-methylene-2-thioxo-dihydropyrimidine-4,6(1H,5H)-dione unit. The HOMO levels of \( O_2-O_7 \) are below the VB of NiO and the LUMO levels are higher than the \( I_3^-/I^- \) redox level, which is beneficial to the hole injection and dye regeneration. Compared to prototype \( O_2 \), all designed dyes \( O_3-O_7 \) have the red-shifted absorptions and the larger LHE. The \( \Delta G_{\text{inj}} \) and \( \Delta G_{\text{reg}} \) are all more negative than \(-0.2 \) eV, resulting in an sufficient hole injection and dye regeneration. \( O_5 \) is expected to be an excellent dye due to its red-shifted adsorption character, higher light-harvest capability as well as better performance of hole injection and dye regeneration than those of prototype \( O_2 \).

Acknowledgements

Yan W thanks the Innovation Project for Postgraduates in Universities of Jiangsu Province and the Innovation Funding from the Graduate School of NJUST (No. SJLX16_0140) for supporting this work.

Reference


285 2010, 1 (9), 1441.
288 785.
291 3540.
294 35. Tomasi, J.; Mennucci, B.; Cammi, R., Chemical reviews 2005, 105 (8), 2999.
296 Coordination Chemistry Reviews 2012, 256 (21), 2414.
298 2245.
301 Chemistry C 2013, 117 (8), 3772.
302 40. Odobel, F.; Le Pleux, L.; Pellegrin, Y.; Blart, E., Accounts of chemical research 2010, 43 (8),
303 1063.
306 43. Cui, J.; Lu, J.; Xu, X.; Cao, K.; Wang, Z.; Alemu, G.; Yang, H.; Shen, Y.; Xu, J.; Cheng, Y.,

Table 1  Calculated absorption spectra of O$_2$ in DMF by different methods

| Methods | $\lambda_{\text{max}}$ (nm) | $\Delta\lambda=|\lambda_{\text{exp}}-\lambda_{\text{cal}}|$ (nm) | $E_{\text{gap}}$ (eV) |
|---------|-----------------------------|-------------------------------------------------|-----------------|
| (Expt.) | 478                         | —                                              | 2.18            |
| B3LYP   | 548                         | 70                                             | 2.57            |
| LC-BLYP | 386                         | 92                                             | 6.92            |
| CAM-B3LYP | 428                       | 50                                             | 4.78            |
Table 2  Computed maximum absorption wavelengths ($\lambda_{\text{max}}$/nm), oscillator strengths ($f$), transition natures and the electron density difference maps of O2-O7 corresponding to $S_0 \rightarrow S_1$

<table>
<thead>
<tr>
<th>No.</th>
<th>$E_{\text{gap}}$ (eV)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$f$</th>
<th>Main configurations$^a$</th>
<th>$S_0 \rightarrow S_1^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2</td>
<td>2.57</td>
<td>428</td>
<td>1.5061</td>
<td>H-1 $\rightarrow$ LUMO (16%), HOMO $\rightarrow$ LUMO (78%)</td>
<td><img src="image1" alt="Image" /></td>
</tr>
<tr>
<td>O3</td>
<td>2.46</td>
<td>572</td>
<td>1.8242</td>
<td>H-1 $\rightarrow$ LUMO (18%), HOMO-1 $\rightarrow$ LUMO (75%)</td>
<td><img src="image2" alt="Image" /></td>
</tr>
<tr>
<td>O4</td>
<td>2.03</td>
<td>539</td>
<td>1.7481</td>
<td>H-1 $\rightarrow$ LUMO (24%), HOMO $\rightarrow$ LUMO (66%)</td>
<td><img src="image3" alt="Image" /></td>
</tr>
<tr>
<td>O5</td>
<td>2.04</td>
<td>505</td>
<td>2.5941</td>
<td>H-1 $\rightarrow$ LUMO (34%), HOMO $\rightarrow$ LUMO (50%)</td>
<td><img src="image4" alt="Image" /></td>
</tr>
<tr>
<td>O6</td>
<td>2.14</td>
<td>512</td>
<td>2.0509</td>
<td>H-1 $\rightarrow$ LUMO (24%), HOMO $\rightarrow$ LUMO (65%)</td>
<td><img src="image5" alt="Image" /></td>
</tr>
<tr>
<td>O7</td>
<td>2.14</td>
<td>512</td>
<td>2.0414</td>
<td>H-1 $\rightarrow$ LUMO (23%), HOMO $\rightarrow$ LUMO (66%)</td>
<td><img src="image6" alt="Image" /></td>
</tr>
</tbody>
</table>

$^a$ H-1 means HOMO-1, and data in parentheses are main configuration contributions.

$^b$ $S_0 \rightarrow S_1$ means an electronic excitation to the first singlet state. The purple and the green colors represent a decrease and increase of charge densities, respectively.
### Table 3  
Computed LHE, $E_{0-0} (\text{dye}^*)$, $E_{\text{red}}$ (dye), $\Delta G_{\text{inj}}$, $\Delta G_{\text{reg}}$ of systems O2-O7

<table>
<thead>
<tr>
<th>System</th>
<th>LHE</th>
<th>$E_{0-0} (\text{dye}^*)$</th>
<th>$E_{\text{red}}$ (dye)</th>
<th>$\Delta G_{\text{inj}}$</th>
<th>$\Delta G_{\text{reg}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2</td>
<td>0.969</td>
<td>2.57</td>
<td>-2.92</td>
<td>-0.51</td>
<td>-1.88</td>
</tr>
<tr>
<td>O3</td>
<td>0.985</td>
<td>2.46</td>
<td>-3.02</td>
<td>-0.50</td>
<td>-1.78</td>
</tr>
<tr>
<td>O4</td>
<td>0.982</td>
<td>2.03</td>
<td>-3.26</td>
<td>-0.31</td>
<td>-1.54</td>
</tr>
<tr>
<td>O5</td>
<td>0.997</td>
<td>2.04</td>
<td>-3.31</td>
<td>-0.37</td>
<td>-1.49</td>
</tr>
<tr>
<td>O6</td>
<td>0.991</td>
<td>2.14</td>
<td>-3.13</td>
<td>-0.29</td>
<td>-1.67</td>
</tr>
<tr>
<td>O7</td>
<td>0.991</td>
<td>2.14</td>
<td>-3.11</td>
<td>-0.27</td>
<td>-1.69</td>
</tr>
</tbody>
</table>
Figure 1  Molecular structures of O2-O7
Figure 2  The HOMO and LUMO of O2-O7 by B3LYP
Figure 3 The frontier molecular orbital energy levels for O2-O7 from B3LYP (a) and CAM-B3LYP (b), together with the experimental NiO conduction valence band edge $E_{VB}$ and $I_3/I_2$ redox level $E(I_3/I_2)$
Figure 4  Absorption spectra of O2-O7
Graphical Abstract
Highlights

- Modifying the prototype dye of O2 with 1,3-diethyl-5-methylene-2-thioxo-
dihydropyrimidine-4,6(1H,5H)-dione and an additional acceptor.
- The designed dyes have significant red shifts and large absorption in visible light
  region.
- The designed $p$-type dyes have large light-harvesting efficiency and sufficient
  hole injection efficiency.