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Theoretical study on electronic and absorption characters of *p*-type

D-A- π -A triaryamine sensitizer

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Abstract: The structural and electronic properties of well known 4,4'-(4-(5-(2,2-dicyanovinyl)thiophen-2-yl)phenylazanediyldibenzoic acid (**O2**) and its hypothetical dyes **O3-O7** were investigated by computational techniques. The absorption properties were probed. By replacing the 2-methylidenepropanedinitrile acceptor with 1,3-diethyl-5-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

22 1. Introduction

23 Since the invention of metallo-organic ruthenium sensitizer by Grätzel and
24 co-workers in 1991¹, several researchers focused on molecular engineering of metal
25 free organic sensitizers (MFOS) for dye sensitized solar cell applications due to their
26 high molecular extinction coefficient (ϵ) and low cost device fabrication²⁻⁴. The vast
27 studies on MFOS based on coumarin⁵⁻⁸, merocyanine⁹⁻¹⁰, carbazole¹¹⁻¹²,
28 phenothiazine¹³, hemicyanine¹⁴⁻¹⁵, and cyanine¹⁶⁻¹⁷ have reported photonversion
29 efficiencies (η) lower than 10%. Recent studies exposed that triarylamine and indoline
30 based *n*-type sensitizer of Y123 and WS-51 were shown to exhibit efficiency $\sim 10\%$ ¹⁸.
31 A series of highly efficient *n*-type dyes with auxiliary withdrawing group have been
32 studied for better absorption¹⁹. However, the energy conversion efficiency of 2.5% in
33 *p*-type dye sensitized solar cell (DSSC)²⁰ lags far behind that of *n*-type, which
34 restricts the fabrication of high-efficiency tandem *pn*-DSSCs²¹.

35 Generally, the typical configuration of the Donor- π -linker-Acceptor (D- π -A)
36 sensitizers was widely investigated for their good performance in generating
37 charge-separated state during the intra-molecular electron transfer by light-excitation.
38 Later, "D-A- π -A" has been proposed by inserting in a secondary electron acceptor in
39 the π -spacer in order to decrease band gap and facilitate charge transfer.
40 Benzotriazole, quinoxaline and phthalimide based D-A- π -A featured organic
41 sensitizers have been systematically investigated. It turned out that an additional
42 acceptor unit can efficiently red-shift the absorption of the dyes and adjust the
43 molecular optical band-gap²²⁻²³. For instance, Zhang et al investigated the D-A- π -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 π -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 π -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- π -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,

66 4-(2-thienyl)-2*H*-benzo[d][1,2,3]triazole and
67 2-octylphenyl-4-(2-thienyl)-2*H*-benzo[d][1,2,3]triazole, respectively.

68 2. Theoretical background and computational details

69 Herein, all calculations were accomplished by using Gaussian 09 package. The
70 geometries of all systems have been fully optimized by using B3LYP functional
71 combined with 6-31G(d,p) basis set which has been proved to be suitable for the
72 geometry optimization. Based on optimized ground-state geometries, 20 lowest
73 excited states of all the sensitizers are calculated using time-dependent density
74 functional theory (TD-DFT) ²⁹. Dye characters were tested by three common
75 functionals of B3LYP ³⁰⁻³¹, LC-BLYP ³² and CAM-B3LYP ³³ with 6-31G(d,p) basis
76 set. CAM-B3LYP was finally chosen as an appropriate one. Both the experimental
77 results from references and the calculated results were shown in Table 1. Additionally,
78 Solvent effect was taken into consideration and all calculations were performed in
79 solvent DMF and the polarized continuum model (PCM) is adopted throughout ³⁴⁻³⁵.
80 In *p*-type DSSCs, the energy conversion efficiency (η) is a vital parameter to estimate
81 whether the sensitizer is good or not, while η depends on three main factors: the
82 short-circuit photocurrent density (J_{sc}), the open-circuit photovoltage (V_{oc}) and the fill
83 factor (FF), and their relation is showed as follow:

$$84 \quad \eta = \frac{J_{sc} V_{oc}}{I_s} FF$$

85 Where I_s represents the total solar power incident.

86 J_{sc} can be calculated by ³⁶⁻³⁸

$$J_{sc} = e \int_{\lambda} LHE(\lambda) \phi_{inj} \eta_{reg} \eta_{coll} I_s(\lambda) d\lambda$$

$$= e \int_{\lambda} IPEC(\lambda) \phi_{ph.AM1.5G} d\lambda$$

where $LHE(\lambda)$ represents the light-harvesting efficiency at each specific wavelength. Φ_{inj} , η_{reg} and η_{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 Φ_{inj} . $LHE(\lambda)$ is expressed as³⁹

$$LHE = 1 - 10^{-f}$$

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 ΔG_{inj} and ΔG_{reg} that are expressed as following equations respectively⁴⁰.

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

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

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

104

105 3. Results and discussion

106 3.1 Electronic structures

The electronic distribution of HOMO and LUMO for **O2** and the designed dye **O3-O7** at B3LYP/6-31G(d,p) level were calculated and displayed in Fig. 2. According

109 to the diagram, electrons of HOMO distribute mainly on donors and π -spacers except
110 for **O2**, which is beneficial to the hole injection from the excited dyes to the valence
111 band of NiO. And LUMO of all the dyes predominantly distribute on the π -spacer and
112 acceptor moieties. Theoretically, electrons should be transited from the donors to the
113 acceptors with the π -spacers acting as an important bridge. Based on this mechanism,
114 the designed molecules can probably delivery the electrons from the donors to the
115 acceptors smoothly, thus it could be considered as a good candidate of sensitizers.

116 On the other hand, as a good *p*-type sensitizer, the HOMO energy of the
117 sensitizer should lie below the valence band edge of semiconductor like NiO, while
118 the LUMO energy should be higher than that of the electrolyte. The molecular orbital
119 energy levels calculated from B3LYP and CAM-B3LYP of dyes O2-O7 are shown in
120 Fig.3. As we can see that the HOMO levels of all the dyes are below the valence band
121 of NiO. Compared with O2, the HOMO energy levels of dyes O4-O7 up-shift a little
122 but still under the VB of NiO, which ensures sufficiently hole injection from the
123 excited dyes to the VB of NiO⁴¹. Apparently, the LUMO levels of all the investigated
124 dyes are more positive than the commonly used I₃⁻/I⁻ electrolyte -4.80 eV, indicating
125 that these dyes have sufficient driving force for the regeneration of reduced dyes⁴²⁻⁴³.

126 The hole injection from NiO to the excited dye will decrease when the HOMO
127 energy level of dye is close to VB of NiO. As for dyes **O3-O7** the HOMO of **O3** is
128 same with **O2** while the others' are up-shifted and the LUMOs are down-shifted in
129 comparison with **O2**. Consequently, the driving force for the hole injection and the
130 dye regeneration slightly decrease. However, this decrease does not change the

131 driving force essentially. Furthermore, the energy gaps between LUMO and HOMO
132 decrease, resulting in red-shifted absorptions of **O3-O7**. This overwhelmingly makes
133 up for the influence of slightly decreased driving force.

134

135 3.2 UV-visible absorption spectra

136 An important character of high efficiency sensitize for DSSCs is to have a
137 broader and stronger absorption. To evaluate the reliability of the functionals for the
138 absorption character and the excitation energies of these designed *p*-type dyes, we
139 chose **O2** as a prototype that has experimental data. Some common functionals such
140 as B3LYP, LC-BLYP and CAM-B3LYP have been tested. As can be seen in Table 1,
141 the E_{gap} value from B3LYP is much closer to the experiment than LC-BLYP and
142 CAM-B3LYP, indicating the former is reliable in comparison with the latter. The MO
143 contours from B3LYP and CAM-B3LYP are almost identical. The HOMO energies
144 from CAM-B3LYP are lower than those from B3LYP, but the LUMO energies from
145 CAM-B3LYP are higher than those from B3LYP, resulting in a much larger E_{gap}
146 from CAM-B3LYP. Nevertheless, the orders of E_{gap} values for the titled dyes are the
147 same from B3LYP and CAM-B3LYP. Besides, the calculated results revealed that the
148 most intense transition of **O2** obtained by CAM-B3LYP functional was found at 428
149 nm in *N,N*-dimethylformamide (DMF), which is somewhat comparable to the
150 experimental data of 478 nm in DMF and better than the results of other functionals.
151 Therefore, we chose CAM-B3LYP to calculate the absorption spectra of the designed
152 dyes.

153 To analysis the influence of structures and solvent on the dye properties, we
154 calculated the absorption spectra of **O2-O7** with 6-31G(d,p) basis set and PCM model
155 in DMF solvent. The peak (λ_{max} /nm), oscillator strengths (f), vibration strength of
156 molecular absorptions and the major components of electronic transitions were
157 summarized in Table 2. Compared with **O2**, the absorption spectrum of **O3** is
158 red-shifted by the replacement of acceptor. Based on it, **O4-O7** were constructed by
159 attaching additional acceptors of 4-(2-thienyl)-2,1,3-benzothiadiazole,
160 2-(2-thienyl)-thiazolo[5,4-d]thiazole, 4-(2-thienyl)-2H-benzo[d][1,2,3]triazole and
161 2-octylphenyl-4-(2-thienyl)-2H-benzo[d][1,2,3]triazole, respectively. The absorptions
162 of **O4-O7** are also red-shifted due to their increasing π -conjugations. The maximum
163 absorption wavelengths of dye **O4-O7** increase in the order: **O5** (505 nm) < **O6** (512
164 nm) = **O7** (512 nm) < **O4** (539 nm). **O6** and **O7** have similar maximum absorption
165 wave lengths and similar HOMO and LUMO, although **O7** is derived by replacing
166 one of **O6**'s hydrogen with an alkyl chain. This indicates that the alkyl chain does not
167 change the frontier molecular orbitals of **O6**. By contrast, an additional acceptor
168 4-(2-thienyl)-2,1,3-benzothiadiazole in **O4** increases the conjugation much more.
169 Besides, the maximum absorption bands of all dyes are originated from the electron
170 transfer from the TPA to the acceptors. These transitions are beneficial to the hole
171 injection from the dye to the valance band of NiO.

172

173 The absorption spectra of **O2-O7** were shown in Fig. 4. All the absorptions of
174 dyes **O3-O7** have been improved and have two absorption bands in the range of near

175 ultraviolet 300 nm to 360 nm and visible spectra of 400 nm to 800 nm, while **O2** has a
176 third band around 230 nm. The strong absorption band mainly depends on the electron
177 transfer from HOMO to LUMO that dominantly distributes on the acceptor and
178 π -linker moieties. When the conjugation increases, the absorption band red-shifts
179 greatly and has more overlap with the visible spectra. The other absorption bands
180 mainly consist of the transitions HOMO-1 to the LUMO which is also caused by
181 $\pi \rightarrow \pi^*$ transition. The absorption at 300-400 nm is enhanced a little as the change of
182 acceptor. **O4** has the most noticeable red-shift and broad band, but a decreasing peak
183 value. The maximum absorption band of **O5**, **O6** and **O7** are around 540 nm, but
184 clearly **O5** is stronger and broader with two bands in the range of 300 nm to 350 nm
185 and 400 nm to 700 nm. From this aspect, **O5** is the best one. Therefore, it is an
186 effective way to improve the absorption character by inserting in an additional
187 acceptor of 2-(2-thienyl)-thiazolo[5,4-*d*]thiazole.

188

189 3.3 The performance of dyes in DSSCs

190 Based on the equations mentioned in the theoretical background, more attention
191 should be paid to the values of LHE, ΔG_{inj} and ΔG_{reg} due to their indirect influence on
192 the energy conversion efficiency. From Table 3, it can be seen that all the LHE values
193 of **O2-O7** are in the range of 0.969 to 0.997. The LHE of **O5** is the largest, which is
194 consistent with the results of having the largest f value in its optical properties. The
195 large LHE could be beneficial to the incident photon-to-electron conversion efficiency
196 (IPCE) of the dye. **O5**, **O6** and **O7** are much better than that **O2**, **O3** and **O4**. 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 ΔG_{inj} and ΔG_{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^{35,44}. The values of ΔG_{inj} and ΔG_{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 (λ) and adequate ΔG_{inj} and ΔG_{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- π -A conjugation of **O2**, we constructed the D-A₁- π -A₂ conjugation of **O3-O7**, where A₁ 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]triazole combines with thiophene as a

219 π spacer, and A_2 is
220 1,3-diethyl-5-methylene-2-thioxo-dihydropyrimidine-4,6(1H,5H)-dione unit. The
221 HOMO levels of **O2-O7** are below the VB of NiO and the LUMO levels are higher
222 than the I_3^-/I^- redox level, which is beneficial to the hole injection and dye
223 regeneration. Compared to prototype **O2**, all designed dyes **O3-O7** have the
224 red-shifted absorptions and the larger LHE. The ΔG_{inj} and ΔG_{reg} are all more negative
225 than -0.2 eV, resulting in an sufficient hole injection and dye regeneration. **O5** is
226 expected to be an excellent dye due to its red-shifted adsorption character, higher
227 light-harvest capability as well as better performance of hole injection and dye
228 regeneration than those of prototype **O2**.

229

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234

235 Reference

- 236 1. O'Regan, B.; Grätzel, M., *Nature* **1991**, 353 (6346), 737.
- 237 2. Zhang, G.; Bala, H.; Cheng, Y.; Shi, D.; Lv, X.; Yu, Q.; Wang, P., *Chemical Communications*
238 **2009**, (16), 2198.
- 239 3. Clifford, J. N.; Martinez-Ferrero, E.; Viterisi, A.; Palomares, E., *Chemical Society reviews*
240 **2011**, 40 (3), 1635.

- 241 4. Zhang, X.; Xu, Y.; Giordano, F.; Schreier, M.; Pellet, N.; Hu, Y.; Yi, C.; Robertson, N.; Hua,
242 J.; Zakeeruddin, S. M.; Tian, H.; Grätzel, M., *Journal of the American Chemical Society* **2016**, *138*
243 (34), 10742.
- 244 5. Hara, K.; Sato, T.; Katoh, R.; Furube, A.; Ohga, Y.; Shinpo, A.; Suga, S.; Sayama, K.;
245 Sugihara, H.; Arakawa, H.; *Journal of Physical Chemistry B* **2003**, *107* (2), 597.
- 246 6. Wang, Z. S.; Cui, Y.; Hara, K.; Dan oh, Y.; Kasada, C.; Shinpo, A.; *Advanced Materials* **2007**,
247 *19* (8), 1138.
- 248 7. Wang, Z. S.; Cui, Y.; Dan oh, Y.; Kasada, C.; Shinpo, A.; Hara, K., *Journal of Physical*
249 *Chemistry C* **2007**, *111* (19), 7224.
- 250 8. Tai, C. K.; Chen, Y. J.; Chang, H. W.; Yeh, P. L.; Wang, B. C., *Computational and Theoretical*
251 *Chemistry* **2011**, *971* (1–3), 42.
- 252 9. Sayama, K.; Hara, K.; Mori, N.; Satsuki, M.; Suga, S.; Tsukagoshi, S.; Abe, Y.; Sugihara, H.;
253 Arakawa, H., *Chemical Communications* **2000**, (13), 1173.
- 254 10. Sayama, K.; Tsukagoshi, S.; Hara, K.; Ohga, Y.; Shimpou, A.; Abe, Y.; Suga, S.; Arakawa, H.,
255 *Journal of Physical Chemistry B* **2002**, *106* (6), 1363.
- 256 11. Koumura, N.; Wang, Z. S.; Mori, S.; Miyashita, M.; Suzuki, E.; Hara, K., *Journal of the*
257 *American Chemical Society* **2006**, *128* (44), 14256.
- 258 12. Kim, D.; Lee, J. K.; Kang, S. O.; Ko, J., *Tetrahedron* **2007**, *63* (9), 1913.
- 259 13. Tian, H.; Yang, X.; Chen, R.; Pan, Y.; Li, L.; Hagfeldt, A.; Sun, L., *Chemical*
260 *Communications* **2007**, (36), 3741.
- 261 14. Wang, Z. S.; Li, F. Y.; Huang, C. H., *Journal of Physical Chemistry B* **2001**, *105* (38), 9210.
- 262 15. Wang, Z. S.; Li, F. Y.; Huang, C. H., *Chemical Communications* **2000**, (20), 2063.

- 263 16. Ma, X.; Hua, J.; Wu, W.; Jin, Y.; Meng, F.; Zhan, W.; Tian, H., *Tetrahedron* **2008**, *64* (2), 345.
- 264 17. Zhan, W. h.; Wu, W. j.; Hua, J. l.; Jing, Y. h.; Meng, F. s.; Tian, H., *Tetrahedron Letters* **2007**,
- 265 48 (14), 2461.
- 266 18. Tsao, H. N.; Yi, C.; Moehl, T.; Yum, J. H.; Zakeeruddin, S. M.; Nazeeruddin, M. K.; Grätzel,
- 267 M., *ChemSusChem* **2011**, *4* (5), 591.
- 268 19. Yang, Z.; Liu, Y.; Liu, C.; Lin, C.; Shao, C., *Spectrochimica Acta Part A: Molecular and*
- 269 *Biomolecular Spectroscopy* **2016**, *167*, 127.
- 270 20. Yu, Z.; Perera, I. R.; Daeneke, T.; Makuta, S.; Tachibana, Y.; Jasieniak, J. J.; Mishra, A.;
- 271 Bauerle, P.; Spiccia, L.; Bach, U., *NPG Asia Mater* **2016**, *8*, e305.
- 272 21. Nattestad, A.; Mozer, A. J.; Fischer, M. K. R.; Cheng, Y. B.; Mishra, A.; Bauerle, P.; Bach, U.,
- 273 *Nat Mater* **2010**, *9* (1), 31.
- 274 22. Wu, Y.; Zhu, W., *Chemical Society reviews* **2013**, *42* (5), 2039.
- 275 23. Zhang, F.; Yu, P.; Shen, W.; Li, M.; He, R., *Computational and Theoretical Chemistry* **2016**,
- 276 *1095*, 118.
- 277 24. Zhang, T.; Guan, W.; Yan, L.; Ma, T.; Wang, J.; Su, Z., *Physical Chemistry Chemical Physics*
- 278 **2015**, *17* (7), 5459.
- 279 25. Yen, Y. S.; Chen, W. T.; Hsu, C. Y.; Chou, H. H.; Lin, J. T.; Yeh, M. C. P., *Organic Letters*
- 280 **2011**, *13* (18), 4930.
- 281 26. Ji, Z.; Natu, G.; Huang, Z.; Wu, Y., *Energy & Environmental Science* **2011**, *4* (8), 2818.
- 282 27. Nazim, M.; Ameen, S.; Akhtar, M. S.; Khaja Nazeeruddin, M.; Shin, H. S., *Solar Energy*
- 283 *Materials and Solar Cells* **2017**.
- 284 28. Zhang, Z.; Peng, B.; Liu, B.; Pan, C.; Li, Y.; He, Y.; Zhou, K.; Zou, Y., *Polymer Chemistry*

- 285 **2010**, *1* (9), 1441.
- 286 29. Bauernschmitt, R.; Ahlrichs, R., *Chemical Physics Letters* **1996**, *256* (4-5), 454.
- 287 30. Chengteh, L.; Weitao, Y.; Parr, R. G., *Physical Review B (Condensed Matter)* **1988**, *37* (2),
- 288 785.
- 289 31. Becke, A. D., *Physical Review A (General Physics)* **1988**, *38* (6), 3098.
- 290 32. Iikura, H.; Tsuneda, T.; Yanai, T.; Hirao, K., *Journal of Chemical Physics* **2001**, *115* (8),
- 291 3540.
- 292 33. Yanai, T.; Tew, D. P.; Handy, N. C., *Chemical Physics Letters* **2004**, *393* (1-3), 51.
- 293 34. Wang, Y.; Li, H., *Journal of chemical physics* **2010**, *133* (3), 034108.
- 294 35. Tomasi, J.; Mennucci, B.; Cammi, R., *Chemical reviews* **2005**, *105* (8), 2999.
- 295 36. Odobel, F.; Pellegrin, Y.; Gibson, E. A.; Hagfeldt, A.; Smeigh, A. L.; Hammarström, L.,
- 296 *Coordination Chemistry Reviews* **2012**, *256* (21), 2414.
- 297 37. Wang, J.; Cong, S.; Wen, S.; Yan, L.; Su, Z., *Journal of Physical Chemistry C* **2013**, *117* (5),
- 298 2245.
- 299 38. Wang, J.; Li, H.; Ma, N. N.; Yan, L. K.; Su, Z. M., *Dyes and Pigments* **2013**, *99* (2), 440.
- 300 39. Feng, J.; Jiao, Y.; Ma, W.; Nazeeruddin, M. K.; Grätzel, M.; Meng, S., *Journal of Physical*
- 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.
- 304 41. Zhu, L.; Yang, H.; Zhong, C.; Li, C. M., *Chemistry—An Asian Journal* **2012**, *7* (12), 2791.
- 305 42. Odobel, F.; Pellegrin, Y., *Journal of Physical Chemistry Letters* **2013**, *4* (15), 2551.
- 306 43. Cui, J.; Lu, J.; Xu, X.; Cao, K.; Wang, Z.; Alemu, G.; Yuang, H.; Shen, Y.; Xu, J.; Cheng, Y.,

307 *Journal of Physical Chemistry C* **2014**, *118* (30), 16433.

308 44. Qin, P.; Zhu, H.; Edvinsson, T.; Boschloo, G.; Hagfeldt, A.; Sun, L., *Journal of the American*

309 *Chemical Society* **2008**, *130* (27), 8570

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311 Table 1 Calculated absorption spectra of **O2** in DMF by different methods

Methods	λ_{max} (nm)	$\Delta\lambda= \lambda_{\text{exp}}-\lambda_{\text{cal}} $ (nm)	E_{gap} (eV)
(Expt.)	478	—	2.18
B3LYP	548	70	2.57
LC-BLYP	386	92	6.92
CAM-B3LYP	428	50	4.78

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Table 2 Computed maximum absorption wavelengths (λ_{max} /nm), oscillator strengths (f), transition natures and the electron density difference maps of **O2-O7** corresponding to $S_0 \rightarrow S_1$

No.	E_{gap} (eV)	λ_{max} (nm)	f	Main configurations ^a	$S_0 \rightarrow S_1$ ^b
O2	2.57	428	1.5061	H-1 $\rightarrow$ LUMO (16%), HOMO $\rightarrow$ LUMO (78%)
O3	2.46	572	1.8242	H-1 $\rightarrow$ LUMO (18%), HOMO-1 $\rightarrow$ LUMO (75%)
O4	2.03	539	1.7481	H-1 $\rightarrow$ LUMO (24%), HOMO $\rightarrow$ LUMO (66%)
O5	2.04	505	2.5941	H-1 $\rightarrow$ LUMO (34%), HOMO $\rightarrow$ LUMO (50%)
O6	2.14	512	2.0509	H-1 $\rightarrow$ LUMO (24%), HOMO $\rightarrow$ LUMO (65%)
O7	2.14	512	2.0414	H-1 $\rightarrow$ LUMO (23%), HOMO $\rightarrow$ LUMO (66%)

^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.

321 Table 3 Computed LHE, $E_{0-0}(\text{dye}^*)$, $E_{\text{red}}(\text{dye})$, ΔG_{inj} , ΔG_{reg} of systems **02-07**

System	LHE	$E_{0-0}(\text{dye}^*)$	$E_{\text{red}}(\text{dye})$	ΔG_{inj}	ΔG_{reg}
02	0.969	2.57	-2.92	-0.51	-1.88
03	0.985	2.46	-3.02	-0.50	-1.78
04	0.982	2.03	-3.26	-0.31	-1.54
05	0.997	2.04	-3.31	-0.37	-1.49
06	0.991	2.14	-3.13	-0.29	-1.67
07	0.991	2.14	-3.11	-0.27	-1.69

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327 Figure 1 Molecular structures of **O2-O7**

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Figure 2 The HOMO and LUMO of **O2-O7** by B3LYP

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349 Figure 3 The frontier molecular orbital energy levels for O2-O7 from B3LYP (a) and
 350 CAM-B3LYP (b), together with the experimental NiO conduction valence band edge
 351 E_{VB} and I_3^-/I^- redox level $E(I_3^-/I^-)$

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Figure 4 Absorption spectra of **O2-O7**

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356 Graphical Abstract

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358 Highlights

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360 ➤ Modifying the prototype dye of **O2** with 1,3-diethyl-5-methylene-2-thioxo-
361 dihydropyrimidine-4,6(1H,5H)-dione and an additional acceptor.

362 ➤ The designed dyes have significant red shifts and large absorption in visible light
363 region.

364 ➤ The designed *p*-type dyes have large light-harvesting efficiency and sufficient
365 hole injection efficiency.

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