Accepted Manuscript

Effects of meta or para connected organic dyes for dye-sensitized solar cell

Yunfei Jiao, Le Mao, Shuaishuai Liu, Tianwen Tan, Donglin Wang, Dapeng Cao, Baoxiu Mi, Zhiqiang Gao, Wei Huang

PII: S0143-7208(18)30292-4

DOI: 10.1016/j.dyepig.2018.05.037

Reference: DYPI 6766

To appear in: Dyes and Pigments

Received Date: 6 February 2018

Revised Date: 17 May 2018

Accepted Date: 17 May 2018

Please cite this article as: Jiao Y, Mao L, Liu S, Tan T, Wang D, Cao D, Mi B, Gao Z, Huang W, Effects of meta or para connected organic dyes for dye-sensitized solar cell, *Dyes and Pigments* (2018), doi: 10.1016/j.dyepig.2018.05.037.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Graphical Abstract



Effects of Meta or Para Connected Organic Dyes for Dye-sensitized Solar Cell

Yunfei Jiao^{a, 1}, Le Mao^{b, 1}, Shuaishuai Liu^a, Tianwen Tan^b, Donglin Wang^a, Dapeng
Cao^b, Baoxiu Mi^{a,*}, Zhiqiang Gao^{b,**}, Wei Huang^{a, b, c, ***}

5

^a Key Laboratory for Organic Electronics & Informat ion Displays (KLOEID),
Jiangsu Key Laboratory for Biosensors (KLB), Institute of Advanced Materials
(IAM), Nanjing University of Posts & Telecommunications (NUPT), 9 Wenyuan
Road, Nanjing 210023, China
^b Jiangsu Engineering Center for Plate Displays & Solid State Lighting, Jiangsu

11 National Synergetic Innovation Center for Advanced Materials (SICAM), School of

Material Science and Engineering, Nanjing University of Posts &
Telecommunications (NUPT), 9 Wenyuan Road, Nanjing 210023, China

^c Shaanxi Institute of Flexible Electronics (SIFE), Northwestern Polytechnical

15 University (NPU), 127 West Youyi Road, Xi'an 710072, China

16

¹ These authors contributed equally to this work.

- 18 ^{*} E-mail: <u>iambxmi@njupt.edu.cn</u>
- 19 ^{**} E-mail: <u>iamzqgao@njupt.edu.cn</u>
- 20 ^{***} E-mail: <u>wei-huang@njtech.edu.cn</u>
- 21 Declarations of interest: none

22 Abstract

Two novel phenothiazine-based organic dyes have been designed and synthesized as 23 24 sensitizers for dye-sensitized solar cell (DSSC). In these dyes, we have employed carbazole as donor, phenothiazine as π -bridge, and rhodanine acetic acid as acceptor. 25 For comparison, a benzene group has been introduced as the π -linker between 26 carbazole donor and phenothiazine π -bridge with meta or para connection mode. 27 Using the dye with the para-connected method, the DSSC devices exhibited higher 28 power conversion efficiency of 5.57% than those based on dye with meta-connection 29 mode (4.56%). The improved performance mainly came from better short-circuit 30 photocurrent current. Photophysical, electrochemical, theoretical calculations and 31 electrochemical impedance spectroscopy have been further investigated to disclose 32 33 corresponding device mechanisms. 34 35 36 37 38 39 40 41 42 **Keywords:** Dye-sensitized solar cell; Metal-free organic dyes; D- π -A; Phenothiazine; Rhodanine acetic acid. 43

44 **1. Introduction**

Confronted with the enormous challenges of energy scarcity and environmental safety, scientists and engineers are eager to develop new energy resources. Given the great advantages of cleanliness, abundance and easy availability, solar energy has been widely recognized as the most promising candidate to solve the problems. In order to harvest solar energy, solar cells, which can firsthand generate electricity from sun light, have long been proposed and proved as vital devices, and among which the dye-sensitized solar cell (DSSC) is one major category.

After the first demonstration in 1991 by Michael Grätzel et al. [1], DSSC has made tremendous progresses. There are some recent milestones including the highest power conversion efficiency (*PCE*, 14.3%) of DSSC based on two co-sensitized dyes under simulated AM 1.5G irradiation (100 mW/cm²) [2], which is suitable for the outdoor large module photovoltaic power generation; and the *PCE* of 28.9% from device with two dyes under indoor illumination of 1000 lux [3], which is promising for small module photovoltaic devices under ambient lighting.

Typically, the conventional structure for DSSC consists of TiO_2 photoanode, dye sensitizer, redox coupled electrolyte system and counter electrode [4]. Within the aforesaid components, the dye sensitizer, which serves as the dominant light harvesting element, plays an essential role in determining the *PCE* of a DSSC device. There are two major classes of dyes, i.e., metal complex dyes and metal-free organic dyes. Although the former, taking Ru-complexes dye as an example, has a high performance when applied in DSSC, they are restricted from low natural abundance,

complicated purification process and expensiveness [5]. Alternatively, metal-free organic dyes have recently been intensively studied, owing to their easy design, facile synthetic method, high molar extinction coefficient (ε) and low toxicity/cost. Using metal-free organic dyes as a sensitizer, high *PCE*s of 11 to 13% have been reported [6-9], demonstrating their great potential for real applications.

To design pure organic dyes for DSSC, numerous aspects need to be considered, 71 such as material bandgap, electronic structure, light absorption and the dye stacking 72 mode on the photoanode [10]. A common strategy for such molecular engineering is 73 to design molecules with donor- π -acceptor (D- π -A) type structures. It has been well 74 documented that due to the efficient intramolecular charge transfer (ICT) which 75 originates from the electron pull-push effect between the D and the A moieties, $D-\pi$ -A 76 77 type of molecules generally exhibit rather high ε in the ICT bands [11-14], beneficial to the harvesting of solar energy. 78

In a wide range of D- π -A dyes for DSSC applications, carbazole (as D), 79 phenothiazine (PTZ, as D or π) moieties have been employed as building block 80 individually or combinationally [15, 16]. Among them, carbazole is famous for its 81 82 good hole-transport and electron donating abilities as well as its high thermal stability, which is intensively used as building block in functional materials for OLED [17, 18], 83 OPV [19] and DSSC [20] applications. One of the highest PCEs from a DSSC device 84 with a carbazole-containing dye is 12.5% [21]. Compared to carbazole, PTZ possesses 85 two-folder more lone-electron pairs originating from both nitrogen and sulfur atoms, 86 hence PTZ is also a hole transport group due to the good electron-donating ability. 87

Furthermore, different from the planar molecular conformation, such as carbazole, the 88 fused non-planar heterocyclic rings of PTZ exhibit butterfly conformation, which can 89 90 sufficiently inhibit dye aggregation, beneficial to DSSC device performance [22-24]. On the other hand, within a PTZ scaffold, since the two phenyl groups on both sides 91 of the central heterocyclic ring are located in a small torsion angle, successive 92 π -delocalization is possible, which is preferential to carrier transport [8, 25, 26]. When 93 PTZ was grafted in a dye for DSSC application, good PCEs of 10.4% [27] and 9.98% 94 [28] have been reported. 95 In terms of electron accepting and photoanode anchoring functionalities in a 96 D- π -A dye, rhodanine acetic acid moiety has gain much attention [25, 29], though it is 97 not as widely used as cyanoacrylic acid. It has been reported that rhodanine acetic 98 acid based organic dyes exhibited high PCE up to 9.5% [30, 31]. A rhodanine acetic 99

acid based organic dyes exhibited high *PCE* up to 9.5% [30, 31]. A rhodanine acetic
acid dye with PTZ donor gave *PCE* up to 4.8% [32]. Another reported pure organic
dye with rhodanine acetic acid as electron acceptor and the N-alkyl substituted PTZ as
electron donor exhibited a *PCE* of 2.26% when assembled in a DSSC device [33].
Although carbazole, PTZ and rhodanine acetic acid all involved dye has been
designed and applied to DSSC devices with *PCE* of 4.38% [29], besides the not
satisfied *PCE*, dyes with the combination of these three moieties are less reported.
Further research toward this aspect is needed.

107 In this paper, two metal-free organic dyes, named **mCPPR** and **pCPPR**, have 108 been synthesized, and the chemical structures are shown in Fig. 1. Both dyes comprise 109 PTZ unit as π -bridge, carbazole as donor, rhodanine acetic acid as acceptor and alkyl

110 chains as dye aggregation and charge recombination suppression unit. In addition, we have introduced a benzene group between the carbazole donor and PTZ π -bridge to 111 investigate the effects of molecular linking mode. The DSSC devices with pCPPR 112 dye exhibited high PCE of 5.57% with a short-circuit photocurrent density (J_{SC}) of 113 15.12 mA/cm², an open-circuit photovoltage (V_{OC}) of 0.71 V and a fill factor (*FF*) of 114 0.52 under simulated AM 1.5G irradiation (100 mW/cm²). pCPPR based devices 115 have a higher J_{SC} value than **mCPPR** devices, which comes from broader/stronger 116 absorption, efficiently charge transfer/electron injection, higher dye loading and lower 117 recombination rate, thereby enhance DSSC PCE. 118



119



Fig. 1. Chemical structures of mCPPR and pCPPR.

121 **2. Experimental section**

122 2.1 Materials

All solvents were purified using standard techniques. Commercially available reagents were used without further purification. All NMR solvents were used as received.

126 2.2 Methods and instrumentations

Experimental details for ¹H-and ¹³C-NMR, gas chromatography-mass 127 spectrometer (GC-MS), matrix-assisted laser desorption/ionization time-of-flight 128 mass spectrometry (MALDI-TOF), ultraviolet-visible spectra (UV-vis), cyclic 129 voltammetry analysis (CV) and steady-state photoluminescence spectroscopy (PL) 130 can be found in our previous paper [18]. High resolution mass spectrometer (HRMS) 131 data were obtained using a Thermofisher ltg-orbitrap XL. Time-resolved 132 photoluminescence (TRPL) were performed with an Edinburgh Instruments FLS920 133 spectrometer. IR data were recorded with PerkinElmer Spectrum Two Fourier 134 transform infrared spectrometer (FT-IR). The geometry optimization and frontier 135 molecular orbitals were performed using density functional theory (DFT) with the 136 Gaussian 09 program under Becke's 3-parameters employing the Lee-Yang-Perdew 137 function (B3LYP) with the 6-31G (d) basis set. 138

139 *2.3 Synthesis*

140

The synthesis route of **mCPPR** and **pCPPR** is shown in Scheme 1.



Scheme 1. Synthetic route of mCPPR and pCPPR.

143 2.3.1 10-hexyl-10H-phenothiazine (1)

A mixture of phenothiazine (200 mg, 1 mmol), bromohexane (216.7 mg, 1.3 144 mmol), KOH (168.3 mg, 3 mmol), tetrabutylammonium bromide (TBAB, 96.6 mg, 145 0.3 mmol) in dimethyl sulfoxide (DMSO, 1.5 mL) was stirred at room temperature 146 under a nitrogen atmosphere for 10 h. When the reaction was completed, water 147 aqueous solution was added to quench the reaction. The crude product was extracted 148 with dichloromethane (DCM) and saltwater for three times and dried over anhydrous 149 Na₂SO₄. The solvent was removed with rotary evaporators, and the crude product was 150 purified by column chromatography using petroleum ether (PE)/DCM (15:1) as the 151 eluent to give compound 1 as colorless liquid in a yield of 88% (250 mg). ¹H NMR 152 (CDCl₃, 400 Hz, ppm): δ 7.21-7.13 (m, 4H), 6.97-6.85 (m, 4H), 3.86 (t, J = 7.1 Hz, 153 2H), 1.87-1.77 (m, 2H), 1.51-1.40 (m, 2H), 1.37-1.28 (m, 4H), 0.95-0.86 (m, 3H). 154 GC-MS: Anal. Calcd. for C₁₈H₂₁NS: 283.43, Found: 283.14. 155

156 2.3.2 10-hexyl-10H-phenothiazine-3-carbaldehyde (2)

POCl₃ (0.269 mL, 2 mmol) was added into dry N,N-Dimethylformamide 157 dimethyl acetal (DMF, 0.538 mL, 7 mmol) in an ice water bath, and then the reaction 158 mixture stirred at room temperature for 1 h. Compound 1 (283 mg, 1 mmol) in DMF 159 (0.6 mL) was added slowly. Then the mixture was stirred and heated at 80 °C to reflux 160 under a nitrogen atmosphere for 10 h. When the reaction was completed, water was 161 added to quench the reaction. The crude product was extracted with DCM and 162 saltwater for three times and dried over anhydrous Na₂SO₄. The solvent was removed 163 with rotary evaporators, and the crude product was purified by column 164 chromatography using PE/DCM (1:2) as the eluent to give compound 2 as yellow 165 solid in a yield of 81% (253 mg). ¹H NMR (CDCl₃, 400 Hz, ppm): δ 9.79 (s, 1H), 166 7.64 (dd, J = 8.4, 2.0 Hz, 1H), 7.58 (d, J = 1.9 Hz, 1H), 7.19-7.08 (m, 2H), 7.00-6.93 167

168	(m, 1H), 6.91-6.85 (m, 2H), 3.91-3.85 (m, 2H), 1.81 (m, $J = 15.0, 7.5 Hz, 2H$),
169	1.49-1.39 (m, 2H), 1.34-1.27 (m, 4H), 0.91-0.84 (m, 3H). GC-MS: Anal. Calcd. for
170	C ₁₉ H ₂₁ NOS: 311.44, Found: 311.13.
171	2.3.3 7-bromo-10-hexyl-10H-phenothiazine-3-carbaldehyde (3)
172	Compound 2 (311 mg, 1 mmol) was added into CHCl ₃ (1 mL), and then the

reaction mixture stirred in an ice water bath for 6 h. N-Bromosuccinimide (NBS, 177 173 174 mg, 1.2 mmol) was added in batches into mixture in the first two hours. When the reaction was completed, water was added to quench the reaction. The crude product 175 176 was extracted with DCM and saltwater for three times and dried over anhydrous Na₂SO₄. The solvent was removed with rotary evaporators, and the crude product was 177 purified by column chromatography using PE/DCM (1:1) as the eluent to give 178 179 compound **3** as yellow liquid in a yield of 58% (230 mg). ¹H NMR (CDCl₃, 400 Hz, ppm): δ 9.79 (s, 1H), 7.65 (dd, J = 8.4, 1.9 Hz, 1H), 7.58 (t, J = 2.8 Hz, 1H), 7.27-7.21 180 (m, 3H), 6.90 (d, J = 8.5 Hz, 1H), 6.72 (d, J = 8.6 Hz, 1H), 3.85 (t, 2H), 1.78 (m, J = (m, 3H)181 14.8, 7.4 Hz, 2H), 1.41 (m, J = 15.1, 6.9 Hz, 2H), 1.32-1.27 (m, 4H), 0.91-0.83 (t, 3H). 182 MALDI-TOF (m/z): Anal. Calcd. for C₁₉H₂₀BrNOS: 389.04, 391.04, Found: 389.15, 183 391.17. 184

185 2.3.4 7-(3-(9H-carbazol-9-yl)phenyl)-10-hexyl-10H-phenothiazine-3-carbaldehyde
 186 (4a)

А mixture of compound 3 (389 mg, 1 mmol), 187 3-(9H-Carbazol-9-yl)phenylboronic acid (574 mg, 2 mmol), K₂CO₃ (345 mg, 2.5 188 mmol), Pd[P(C₆H₅)₃]₄ (100 mg, 0.1mmol) and TBAB (96.6 mg, 0.3 mmol) in DCM 189 190 (15 mL) was stirred and heated to reflux under a nitrogen atmosphere for 18 h. When the reaction was completed, water was added to quench the reaction. The crude 191 product was extracted with DCM and saltwater for three times and dried over 192

193	anhydrous Na ₂ SO ₄ . The solvent was removed with rotary evaporators, and the crude
194	product was purified by column chromatography using PE/DCM (2:1) as the eluent to
195	give compound 4a as yellow solid in a yield of 82% (455 mg). ¹ H NMR (CDCl ₃ , 400
196	Hz, ppm): δ 9.80 (s, 1H), 8.17 (d, J = 7.7 Hz, 2H), 7.73 (d, J = 1.6 Hz, 1H), 7.68-7.61
197	(m, 3H), 7.59 (d, J = 1.9 Hz, 1H), 7.53 (dt, J = 7.2, 1.9 Hz, 1H), 7.48-7.38 (m, 6H),
198	7.34-7.28 (m, 2H), 6.92 (dd, J = 10.7, 8.5 Hz, 2H), 3.94-3.87 (m, 2H), 1.88-1.79 (m,
199	2H), 1.45 (dd, J = 15.1, 7.1 Hz, 2H), 1.32 (dt, J = 7.1, 3.4 Hz, 4H), 0.88 (d, J = 7.1 Hz,
200	3H). MALDI-TOF (m/z): Anal. Calcd. for C ₃₇ H ₃₂ N ₂ OS: 552.74, Found: 552.11.
201	2.3.5 7-(4-(9H-carbazol-9-yl)phenyl)-10-hexyl-10H-phenothiazine-3-carbaldehyde
202	(4b)

А mixture of compound 3 (389 mg, 1 mmol), 203 4-(9H-Carbazol-9-yl)phenylboronic acid (574 mg, 2 mmol), K₂CO₃ (345 mg, 2.5 204 mmol), $Pd[P(C_6H_5)_3]_4$ (100 mg, 0.1 mmol) and TBAB (96.6 mg, 0.3 mmol) in DCM 205 (15 mL) was stirred and heated to reflux under a nitrogen atmosphere for 18 h. When 206 207 the reaction was completed, water was added to quench the reaction. The crude product was extracted with DCM and saltwater for three times and dried over 208 anhydrous Na₂SO₄. The solvent was removed with rotary evaporators, and the crude 209 product was purified by column chromatography using PE/DCM (2:1) as the eluent to 210 give compound **4b** as yellow solid in a yield of 80% (443 mg). ¹H NMR (DMSO, 400 211 Hz, ppm): δ 9.77 (s, 1H), 8.23 (d, J = 7.0 Hz, 1H), 7.97-7.88 (m, 1H), 7.77-7.55 (m, 212 3H), 7.42 (s, 2H), 7.34-7.13 (m, 2H), 4.01-3.96 (m, 1H), 1.77-1.65 (m, 1H), 1.40 (d, J 213 = 3.3 Hz, 1H), 1.25 (s, 2H), 0.89-0.75 (m, 2H). MALDI-TOF (m/z): Anal. Calcd. for 214 215 C₃₇H₃₂N₂OS: 552.74, Found: 552.11.

216 2.3.6 3-(9H-Carbazol-9-y1)Phenyl-7-(N-hexyl-10H-phenothiazine-rhodanine-3-acetic
 217 acid (mCPPR)

218 A mixture of compound 4a (553 mg, 1 mmol), rhodanine-N-acetic acid (570 mg, 3 mmol) and NH₄Ac (77 mg, 1 mmol) in CH₃COOH (10 mL) was stirred and heated 219 to reflux under a nitrogen atmosphere for 24 h. When the reaction was completed, 220 water was added to quench the reaction. The crude product was extracted with DCM 221 and saltwater for three times and dried over anhydrous Na₂SO₄. The solvent was 222 removed with rotary evaporators, and the crude product was purified by column 223 chromatography using methanol (MeOH)/DCM (1:20) as the eluent to give mCPPR 224 as crimson solid in a yield of 95% (691 mg). ¹H NMR (DMSO, 400 Hz, ppm): δ 8.24 225 (d, J = 7.7 Hz, 2H), 7.85 (s, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.75-7.67 (m, 2H), 7.57 (dd, 226 J = 14.8, 7.6 Hz, 3H), 7.41 (dt, J = 22.6, 10.3 Hz, 6H), 7.28 (ddd, J = 8.0, 5.3, 2.8 Hz, 227 2H), 7.11 (dd, J = 12.3, 8.8 Hz, 2H), 4.66 (s, 2H), 3.91 (s, 2H), 1.67 (d, J = 6.6 Hz, 228 2H), 1.29-1.17 (m, 6H), 0.79 (d, J = 5.1 Hz, 3H). ¹³C NMR (DMSO, 101 Hz, ppm): δ 229 193.14, 167.72, 166.84, 147.16, 143.10, 141.14, 140.60, 138.01, 134.69, 133.31, 230 131.26, 129.95, 127.53, 126.81, 125.82, 124.63, 123.90, 123.30, 120.97, 120.53, 231 119.26, 117.04, 116.56, 110.20, 47.44, 45.82, 31.26, 26.51, 26.19, 22.53, 14.28. FT-IR 232 (KBr) v cm⁻¹: 3437, 3052, 2954, 2924, 2853, 1711, 1595, 1574, 1470, 1454, 1403, 233 1363, 1333, 1275, 1249, 1229, 1196, 1113, 1026, 960, 904, 874, 812, 792, 750, 724, 234 703, 657, 570. HRMS (ESI, m/z): [M+H]⁺ Anal. Calcd. for C₄₂H₃₅N₃O₃S₃: 726.1919, 235 Found: 726.1914. 236

237 2.3.7 4-(9H-Carbazol-9-y1)Phenyl-7-(N-hexyl-10H-phenothiazine-rhodanine-3-acetic
 238 acid (pCPPR)

A mixture of compound **4b** (553 mg, 1 mmol), rhodanine-N-acetic acid (570 mg, 3 mmol) and NH₄Ac (77 mg, 1 mmol) in CH₃COOH (10 mL) was stirred and heated to reflux under a nitrogen atmosphere for 24 h. When the reaction was completed, water was added to quench the reaction. The crude product was extracted with DCM

and saltwater for three times and dried over anhydrous Na2SO4. The solvent was 243 removed with rotary evaporators, and the crude product was purified by column 244 chromatography using MeOH/DCM (1:20) as the eluent to give pCPPR as crimson 245 solid in a yield of 94% (684 mg). ¹H NMR (DMSO, 400 Hz, ppm): δ 8.25 (d, J = 7.8 246 Hz, 2H), 7.87 (s, 1H), 7.80 (d, J = 7.5 Hz, 1H), 7.72 (s, 2H), 7.59 (dd, J = 19.1, 11.0 247 Hz, 3H), 7.42 (d, J = 17.4 Hz, 5H), 7.28 (s, 2H), 7.23-7.00 (m, 2H), 6.84 (s, 1H), 4.58 248 (s, 2H), 3.93 (s, 2H), 1.69 (s, 2H), 1.24 (s, 6H), 0.81 (s, 3H). ¹³C NMR (DMSO, 101 249 Hz, ppm): δ 193.16, 167.61, 166.92, 147.15, 143.16, 141.18, 140.62, 138.02, 134.71, 250 131.25, 129.96, 127.61, 126.83, 126.30, 124.66, 123.94, 123.32, 120.97, 120.53, 251 117.09, 116.59, 110.21, 47.45, 31.26, 29.45, 26.44, 25.74, 22.53, 14.28. FT-IR (KBr) v 252 cm⁻¹: 3745, 3436, 2594, 2924, 2853, 1711, 1596, 1574, 1488, 1472, 1453, 1405, 1365, 253 1334, 1277, 1251, 1229, 1197, 1114, 1058, 909, 793, 750, 724, 704, 666, 571, 514. 254 HRMS (ESI, m/z): $[M+H]^+$ Anal. Calcd. for $C_{42}H_{35}N_3O_3S_3$: 726.1919, Found: 255 726.1909. 256

257 2.4 DSSC fabrication and photovoltaic measurements

DSSC fabrication details, current-voltage measurement (*J-V*), incident photon-to-current efficiencies (*IPCEs*) and electrochemical impedance spectroscopy (EIS) can be found in our previous paper [34-36]. EIS was measured under both dark and illumination conditions.

For the open-circuit voltage decay (OCVD) measurements, the cell was first illuminated for 20 s to a steady voltage by using the solar simulator, then the illumination was turned off for 200 s and the OCVD curve was recorded by Bio analytical Systems CHI660E.

266 **3. Result and discussions**

267 3.1. Photophysical properties

268 The UV-Vis absorption spectra of **mCPPR** and **pCPPR** in DCM solution as well as those adsorbed on TiO_2 films are shown in Fig. 2 (a) and (b). The corresponding 269 spectroscopic parameters are compiled in Table 1. As shown in Fig. 2 (a), in solution 270 both dyes exhibit broad absorption with two distinct bands. The higher energy ones 271 locating at 240-400 nm are assigned to the aromatic $\pi - \pi^*$ electron transitions of the 272 dve molecule. The lower energy bands are peaked at 486 nm for **mCPPR** and 493 nm 273 for **pCPPR**, with ε of 12100 and 18900 mol⁻¹ dm³ cm⁻¹, respectively. These low 274 energy bands are attributed to the ICT between the carbazole donor and rhodanine 275 276 acetic acid acceptor [29]. As can be seen, in **pCPPR** with carbazole donor grafting to the para position C(4) of benzene, the ICT peak is slightly red-shifted and the 277 corresponding ε has significantly improved, compared to mCPPR linking at meta 278 position C(3), indicating that the relevant linear type of **pCPPR** gives an optimized 279 framework for better conjugation and light harvesting. 280

When **mCPPR** and **pCPPR** have been adsorbed on TiO_2 films, the ICT bands show broadening and red-shifting, indicating a J-aggregation of the both dyes after adsorption on the TiO_2 films [8, 9, 37]. It can be forecasted that the broadening and red-shifting in ICT absorption will be beneficial to *PCE* improvement, due to the improved light harvesting ability.

Ċ



287

286

Fig. 2. UV-Vis absorption spectra of mCPPR and pCPPR (a) dissolved in DCM and (b) adsorbed



on a 6 μm TiO_2 film.

290 Table 1

Dye	$\lambda_{\max}(nm)$	$\boldsymbol{\varepsilon} (\mathrm{mol}^{-1} \mathrm{dm}^{3} \mathrm{cm}^{-1})$	$E_{\rm ox}^{a}({\rm eV})$	E_{g}^{b} (eV)	$E_{\rm red}^{\rm c}({\rm eV})$
mCPPR	486	12100	-5.25	2.13	-3.12
pCPPR	493	18900	-5.13	2.08	-3.05

291 Photophysical and electrochemical properties of **mCPPR** and **pCPPR**.

^a Measured in DCM with 0.1 M TBAPF₆ as electrolyte and calibrated with ferrocene/ferrocenium

293 (Fc/Fc⁺) as an internal reference of 0.46 eV. Finally, calculated by $-(E_{ox}+4.8-E_{(Fc/Fc+)ox})$.

^b Estimated from the onset wavelength of absorption spectra in DCM solution.

295 ^c Calculated by $E_{ox} + E_g$.

296 *3.2. Electrochemical studies*

To evaluate the energy level matching-characteristics of mCPPR and pCPPR in 297 a traditional DSSC device with TiO_2 photoanode and I/I_3 electrolyte, e.g., the ability 298 of electron injection from the lowest unoccupied molecular orbitals (LUMO) of a dye 299 to TiO₂ conducting band (CB) and the regeneration of the dye from its oxide state via 300 the electrolyte, CV analysis was performed. The curves are shown in Fig. 3 and the 301 corresponding data are collected in Table 1. The first oxidation potentials (E_{ox}) , which 302 303 is correlated to the highest occupied molecular orbitals (HOMO), occur at 0.90 V and 304 0.78 V (vs. Ag/AgCl) for mCPPR and pCPPR, respectively. Accordingly, the HOMO levels of mCPPR and pCPPR are calculated to be -5.25 and -5.13 eV, respectively. 305 Both of them are more negative than the $I^{/}I_{3}^{-}$ (-4.8 eV vs. vacuum), suggesting 306 sufficient dye regeneration driving force from the oxidized dye along with the 307 electrolyte. Based on the HOMO values and the band gaps (E_g) calculated from onset 308 wavelength of the UV-visible absorption spectra, the LUMO levels of mCPPR and 309 **pCPPR** could be calculated as -3.12 and -3.05 eV, respectively, using $E_{ox} + E_g$ [9, 10, 310 38]. According to these calculation, the schematic energy level diagrams of the 311 mCPPR and pCPPR based DSSC devices can be drawn as Fig. 4. The LUMOs of the 312

313 two dyes are more positive than the CB of TiO₂ (-4.0 eV vs. vacuum), providing efficient electron injection from the excited dye molecules to the CB of TiO₂. It is 314 found that compared to mCPPR with meta-linked carbazole through the benzene 315 group, the para grafting of carbazole moiety in **pCPPR** resulted in higher HOMO and 316 LUMO levels, as well as narrower bandgap. This is understandable, since 317 para-linkage can enlarge effective conjugation and render electron more delocalized, 318 leading to narrow bandgap and raised HOMO level. Since para-linkage conjugation 319 can increase electron-donating ability [39] and reduce electron affinity, hence the 320 321 LUMO level is lifted.







Fig. 4. Schematic energy levels (*vs.* vacuum) of TiO₂, electrolyte, mCPPR and pCPPR. *3.3. Photoluminescence studies*

In order to understand the electron dynamics between the dye and the TiO_2 photoanode, the steady-state and time-resolved photoluminescence spectroscopies based on dye-adsorbed TiO_2 films were investigated. Blank experiments were carried out on mesoporous Al_2O_3 film, since almost no charge dissociation occurs when dyes are adsorbed on it due to the unmatched electron levels.

As illustrated in Fig. 5 (a), the PL intensity for both dyes with charge extracting layers (TiO₂ films) are much weaker than those with Al_2O_3 films. The strong exciton quenching verifies the high-efficiency of injecting electron from the excited dye into the TiO₂ photoanode. PLs of **pCPPR** exhibit a higher intensity difference between TiO₂ and Al_2O_3 films than those of **mCPPR**, implying that the DSSC device based on **pCPPR** dye can inject electrons into TiO₂ film more efficiently after exciton generation, which may give rise to high device performance [40, 41].

The TRPL decay curves and the relative fitting curves of TiO_2 and Al_2O_3 films with the dyes are shown in Fig. 5 (b). Decay times (τ) and corresponding amplitudes (*A*) are summarized in Table 2. The measured TRPL signals were fitted by two exponentials as follows:

$$I_{\rm PL} = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$$

where A_i denotes the proportion of each exponential that meets the relationship of A_1 + $A_2 = 1$, and τ_1/τ_2 represents the time constant of each exponential component.

For dye-coated Al₂O₃ films, the PL decay reflects the lifetime of dye itself. The 345 longer PL decay time for pCPPR/Al₂O₃ (2.24 ns) than that for mCPPR/Al₂O₃ (2.05 346 ns) implies higher excited state stability, which may result from the optimized 347 molecular structure of **pCPPR** with para-grafting. Compared to the corresponding 348 Al₂O₃ films, the PL lifetime of the dye-coated TiO₂ films decreased significantly, both 349 for mCPPR and pCPPR, because of the efficient electrons injection from the excited 350 state of molecules into the CB of TiO₂. The PL decay is found to be slightly faster for 351 pCPPR (0.22 ns) than for mCPPR (0.26 ns), though it might be attributed to 352 experimental errors and can't definitely conclude that the electron injection efficiency 353 from **pCPPR** is more efficient. However, by comparing with the control films based 354 on Al_2O_3 , the injection efficiency can be calculated [42]. As can be seen, **pCPPR** 355 shows relatively higher electron injection efficiency (90.20%) than mCPPR (87.37%), 356 which is consistent with the steady state PL measurement (see Fig. 5 (a)). 357



359

Fig. 5. (a) Steady-state photoluminescence spectra and (b) time-resolved photoluminescence
decay curves (dash lines represent for fitting) of mCPPR and pCPPR on TiO₂ and Al₂O₃ films.

362 Table 2

Dye	Film	$A_{1}(\%)$	τ_1 (ns)	$A_{2}(\%)$	τ_2 (ns)	$ au_{av}^{a}$ (ns)	$\eta_{\rm inj}$ ^b (%)
mCDDD	TiO ₂	88.94	0.14	11.06	1.21	0.26	87 37
IIICI I K	Al_2O_3	86.13	1.43	13.87	5.87	2.05	01.37
nCDDD	TiO ₂	88.43	0.12	11.57	0.98	0.22	00.20
рсггк	Al_2O_3	85.25	1.74	14.75	5.13	2.24	90.20

363 The fitting decay time (τ) and corresponding amplitude (A) of **mCPPR** and **pCPPR** from TRPL.

364 ^a The values of τ_{av} were determined with $\tau_{av} = A_1 \tau_1 + A_2 \tau_2$.

- 365 ^bCalculated by $\eta_{inj} = 1 \frac{\tau_{dye/TiO_2}}{\tau_{dye/Al_2O_3}}$.
- 366 *3.4. Theoretical calculations*

To investigate frontier molecular orbital distributions and ICT pathway, DFT 367 calculations were performed by the Gaussian 09 package at the B3LYP/6-31G(d) 368 level [43-45]. Fig. 6 shows the front/top view optimized structure and the 369 HOMO/LUMO distribution of the dyes. It can be inferred from the optimized 370 structure that the geometry of PTZ core is non-planar, showing a butterfly shape with 371 a ~155° angle between two phenyl groups. This framework can reduce $\pi - \pi^*$ stacking 372 hence suppress dye-aggregation [24]. The HOMO of both dyes locates over PTZ core 373 and extends to the nearby benzene group. It is worth noting that when the 374 peri-carbazole is connected in a para-mode in pCPPR, part of HOMO electron 375 extends to the carbazole moiety, contrasting to the almost zero-distribution of HOMO 376 electron in the carbazole part of mCPPR with meta connection. To investigate this 377 difference, we have tabulated the torsion angles from the Gaussian calculations, as 378 shown in Table 3. The optimal dihedral angles of carbazole/benzene groups (56° vs. 379 54°) and benzene/PTZ groups (36° vs. 36°) are similar for mCPPR and pCPPR. 380 381 However, large difference is observed in terms of the dihedral angle of carbazole/benzene, i.e., 18° for **pCPPR** and 48° for **mCPPR**. Smaller dihedral angle 382 means smaller steric hindrance, which can extend the electron delocalization. As a 383

384 result, better conjugation and more efficient ICT for pCPPR were achieved, which is consistent with the narrower optical bandgap and more efficient ICT absorption as 385 disclosed previously. The LUMO of mCPPR and pCPPR are mainly distributed on 386 rhodanine acetic acid acceptor and partly on the neighboring PTZ π -linker. The 387 electronic distribution for both dyes shows a sufficient overlap of frontier molecular 388 orbitals on PTZ unit, guaranteeing a facile charge transfer from donor to acceptor 389 upon irradiation and hence ensuring efficient ICT process. Additionally, considering 390 hardly any HOMO electron distributes on the alkyl chain-substituted, it can efficiently 391 392 prevent electron recombination [46].





Fig. 6. Optimized ground state geometry and the frontier molecular orbital distributions of mCPPR and pCPPR.

394 Table 3

Groups	Carbazole/Benzene ^a	Benzene/PTZ ^a	Carbazole/PTZ ^b
Schematic	$() + N_{*}^{*} + () + () + () + () + () + () + () + ($	() = () = () = () = () = () = () = () =	S N C ₆ H ₁₃
mCPPR	56°	36°	48°
pCPPR	54°	36°	18°

395 T	forsion and	le of	carbazole/	benzene/PTZ	of m(CPPR a	ind pC	PPR.
-------	-------------	-------	------------	-------------	-------	--------	---------------	------

^a The dihedral angle is indicated by the four stars.

^b Dihedral angle between carbazole unit and closer-phenyl in PTZ core.

398 *3.5. Photovoltaic performances of DSSC*

The J-V curves of DSSC sensitized by mCPPR and pCPPR are plotted in Fig. 7 399 (a) and the parameters are listed in Table 4. The DSSC based on mCPPR exhibits a 400 PCE of 4.56% with a J_{SC} of 12.53 mA/cm², a V_{OC} of 0.69 V and a FF of 0.53. 401 402 Compared to **mCPPR**, device with **pCPPR** shows significantly improved $J_{SC}(15.12)$ mA/cm²), generating an overall PCE of 5.57%. The relatively higher J_{SC} from 403 pCPPR device is mainly ascribed to the follow reasons: 1) broader and stronger 404 absorption (see Fig. 2 and Table 1), 2) efficient charge injection (see Fig. 4), 3) higher 405 dye loading amount (see Table 4). The lower part of Fig. 7 (a) presents the dark 406 currents of the devices, which reflect the dark reactions related to the charge 407 recombination between the electrons in the TiO₂ photoanode and the hole on the redox 408 couple [47, 48]. Under the same bias voltage, the dark current for pCPPR DSSC is 409 smaller than **mCPPR**, indicating weaker recombination, thus leading to the slightly 410 increased V_{OC} in **pCPPR** device. 411

Fig. 7 (b) shows the *IPCEs* for the DSSC devices. As shown, both dyes show good ability to convert light to photocurrent in the region of 400-750 nm. The *IPCE* values from **pCPPR** device reaches the highest value of 56.9% at 495 nm, while 50.2%

415 at 495 nm for **mCPPR** device. The relatively higher *IPCE* for **pCPPR** leads to larger 416 photocurrents, which is well consistent with the higher J_{SC} value resulting from the 417 *J-V* curves.





422 Table 4

419

420

421

423 Photovoltaic parameters of DSSC sensitized by mCPPR and pCPPR.

Dye	$J_{\rm SC}$ (mA/cm ²)	$V_{\rm OC}(\rm V)$	FF	<i>PCE</i> (%)	Dye loading (mol/cm ²)
mCPPR	12.53	0.69	0.53	4.56	2.92×10 ⁻⁷
pCPPR	15.12	0.71	0.52	5.57	4.04×10 ⁻⁷

To better understand charge recombination kinetics, an OCVD measurement, which monitors the procedure of V_{OC} transient from illumination condition to the dark equilibrium, was implemented. Fig. 8 (a) presents OCVD curves of **mCPPR** and **pCPPR** devices. The lifetimes of the photogenerated electrons in the device, τ_n , can be evaluated according to equation [10]:

429
$$au_{\rm n} = -\frac{K_{\rm B}T}{\rm e} \left(\frac{dV_{\rm OC}}{dt}\right)^{-1}$$

430 where K_B is the Boltzmann constant and *T* is the temperature.

431	The calculated τ_n values are plotted in Fig. 8 (b). At the potential values of
432	illuminated quasi equilibrium state, the τ_n of DSSC devices based on mCPPR and
433	pCPPR are ~40 ms and ~100 ms, respectively. It can be seen that under the same
434	potential the DSSC based on pCPPR has longer electron lifetime, which is ascribed
435	to the slower electron recombination rate and accounts for the relative higher PCE.





438 Fig. 8. (a) OCVD for DSSC devices based on mCPPR and pCPPR and (b) electron lifetime
439 derived from OCVD measurement.

440 3.6. Electrochemical impedance spectroscopy analysis

437

The EIS measurement was performed under a bias of V_{OC} from 10^{-1} Hz to 10^{5} Hz 441 both under the dark and the illumination conditions to get elucidation on the interface 442 charge-transfer and recombination processes in our DSSC devices. The results are 443 shown in Fig. 9 and the corresponding data are summarized in Table 5. The EIS 444 values are fitted through ZSimpWin software and the equivalent circuit is shown in 445 the inset of Fig. 9 (a). In Nyquist plot (Fig. 9 (a)), the X-intercept value is 446 corresponding to the lumped series resistance (R_s) for external circuit outside of the 447 cell. The semicircle at high-frequency region is attributed to charge transfer resistance 448 at the electrolyte/Pt electrode interface (R_{Pt}). The large semicircle in low-frequency is 449 attributed to the electron diffusion in the TiO₂ film and electron back reaction with 450 oxidized redox species at the TiO₂/electrolyte interface (R_{ct}) [49], which has most 451

452 significant effect on DSSC performance.

Under dark condition, the R_{ct} mainly reflects the charge recombination resistance at the interface between TiO₂/dye/electrolyte [8, 42, 49-52]. The R_{ct} values for **mCPPR** and **pCPPR** are estimated to be 19.27 and 25.24 Ω , respectively. The larger R_{ct} value for **pCPPR** devices corresponds to the decrease of charge recombination, in agreement with its better device performance. The electron lifetime (τ_e) for DSSC can be calculated from the Bode plots (Fig. 9 (b)) by using the following equation [53-55]:

459
$$au_{\rm e} = \frac{1}{2\pi f_{\rm r}}$$

460 where f_p is the peak frequency at low frequency region.

It turned out that the electron lifetime (10.85 ms) for pCPPR device is longer
than mCPPR device (8.96 ms), reflecting longer electron diffusion distance hence
better photovoltaic result [8, 42].

Contrast to dark condition, the Nyquist plots under illumination show 464 dramatically reduced arcs at low frequency region and negligible variation in high 465 frequencies, resulting in smaller R_{ct} and comparable R_{Pt}/R_s values. Upon illumination, 466 large density of photocarriers is produced, greatly improving device conductivity. 467 Therefore, under illumination the signal of R_{ct} should be dominated by carrier 468 transport and the reduced diameters in the Nyquist plots are ascribed to the improved 469 conductivity [9, 56]. Compared to mCPPR DSSC, the R_{ct} of pCPPR (16.57 vs. 15.21 470 Ω) is smaller, indicating lower charge transport resistance and better carrier transport 471 in **pCPPR** device. 472

473 As calculated from the Bode figures under illumination, both devices show 474 shorter τ_e than those under dark (see Table 5). It can be ascribed to the different I_3^- 475 concentration. Under illumination, I_3^- aggregates at the TiO₂/dye/electrolyte interface 476 after dyes regeneration, whereas in the dark, I_3^- disperses within the electrolyte. The

477 higher local I_3^- concentration under light is expected to increase charge recombination 478 with injected electron and hence shorten their lifetime [53].

It should be noticed that the electron lifetimes (~10 ms) based on EIS measurement are much shorter than those based on OCVD data (about 40 to 100 ms). This discrepancy is mainly caused by the difference in experimental conditions. While the former is taken under external electric field, there is only a built-in electric field without applied bias in the latter case.





486 **Fig. 9.** (a) Nyquist plots and (b) Bode plots for DSSC devices based on **mCPPR** and **pCPPR**.

487 Table 5

485

488 EIS fitting parameters for DSSC sensitized by mCPPR and pCPPR.

Condition	Dye	$R_{\rm s}(\Omega)$	$R_{\rm Pt}(\Omega)$	$R_{\rm ct}(\Omega)$	$f_{\rm p}({\rm Hz})$	$\tau_{\rm e}({\rm ms})$
dork	mCPPR	10.80	6.36	19.27	17.78	8.96
uark	pCPPR	10.32	6.70	25.24	14.68	10.85
illumination	mCPPR	10.56	4.90	16.57	21.54	7.39
mummation	pCPPR	9.97	6.05	15.21	17.78	8.96

489 **4. Conclusions**

In conclusion, two novel metal-free organic dyes **mCPPR** and **pCPPR** have been synthesized and utilized in DSSC. In terms of molecular design, phenothiazine and rhodanine acetic acid have been employed as π -bridge and acceptor, respectively; while the carbazole donor part is connected with the PTZ π -bridge through benzene ring as such that **mCPPR** has a meta-connection at C(3) position, and **pCPPR** has a para-connection at C(4) position. The DSSC device based on **pCPPR** reaches

significantly higher *PCE* of 5.57%, with dominating contribution from higher J_{SC} . After systematic research, we have finally explained the mechanism. For the first, good molecular configuration results in higher dye loading. Second, effective ICT process provides broader and stronger absorption spectra. Third, favorable energy level permits efficient charge injection. And the fourth small charge recombination resistance benefits long electron lifetime. The last, low charge transport resistance creates good charge transport pathway.

503 Acknowledgments

This work was financially supported by the National Natural Science Foundation 504 of China (Nos. 61474064, 61504063); Natural Science Foundation of Jiangsu 505 Province (BK20150836); Nanjing University of Posts and Telecommunications (Nos. 506 Research Program of 507 NY214177); National Basic China 973 Program (2015CB932200); the Ministry of Education of China (IRT1148); the Priority 508 Academic Program Development of Jiangsu Higher Education Institutions 509 (PAPD:YX03001, YX03002); Natural Science Foundation of Universities from 510 Jiangsu Province (15KJB430023); Jiangsu National Synergetic Innovation Center for 511 Advanced Materials (SICAM); and the Synergistic Innovation Center for Organic 512 Electronics and Information Displays. 513

514 **References**

515 [1] B. O'regan, M. Grätzel, A Low-Cost, High-Efficiency Solar Cell Based on
516 Dye-Sensitized Colliodal TiO2 Films, Nature, 1991, 353, 737-740.

517 [2] K. Kakiage, Y. Aoyama, T. Yano, K. Oya, J. Fujisawa, M. Hanaya, 518 Highly-efficient dye-sensitized solar cells with collaborative sensitization by 519 silyl-anchor and carboxy-anchor dyes, Chemical Communications, 2015, 51, 520 15894-15897.

- 521 [3] M. Freitag, J. Teuscher, Y. Saygili, X. Zhang, F. Giordano, P. Liska, et al.,
- 522 Dye-sensitized solar cells for efficient power generation under ambient lighting,
- 523 Nature Photonics, 2017, 11, 372-378.
- 524 [4] H. Anders, B. Gerrit, S. Licheng, K. Lars, P. Henrik, Dye-sensitized solar cells,
- 525 Chemical Reviews, 2010, 110, 6595-663.
- 526 [5] C.Y. Chen, M.K. Wang, J.Y. Li, N. Pootrakulchote, L. Alibabaei, C. Ngocle, et al.,
- 527 Highly efficient light-harvesting ruthenium sensitizer for thin-film dye-sensitized
- solar cells, ACS Nano, 2009, 3, 3103-3109.
- [6] Z.Y. Yao, H. Wu, Y. Li, J.T. Wang, J. Zhang, M. Zhang, et al.,
 Dithienopicenocarbazole as the kernel module of low-energy-gap organic dyes for
 efficient conversion of sunlight to electricity, Energy & Environmental Science, 2015,
 8, 3192-3197.
- 533 [7] Z.Y. Yao, M. Zhang, H. Wu, L. Yang, R.Z. Li, P. Wang, Donor/acceptor 534 indenoperylene dye for highly efficient organic dye-sensitized solar cells, Journal of 535 the American Chemical Society, 2015, 137, 3799-3802.
- [8] C.T. Li, F.L. Wu, C.J. Liang, K.C. Ho, J.T. Lin, Effective suppression of interfacial
 charge recombination by a 12-crown-4 substituent on a double-anchored organic
 sensitizer and rotating disk electrochemical evidence, Journal of Materials Chemistry
 A, 2017, 5, 7586-7594.
- [9] B. Nagarajan, S. Kushwaha, R. Elumalai, S. Mandal, K. Ramanujam, D.
 Raghavachari, Novel ethynyl-pyrene substituted phenothiazine based metal free
 organic dyes in DSSC with 12% conversion efficiency, Journal of Materials
 Chemistry A, 2017, 5, 10289-10300.
- [10] N.J. Zhou, K. Prabakaran, B. Lee, S. H. Chang, B. Harutyunyan, P.J. Guo, et al.,
- 545 Metal-free tetrathienoacene sensitizers for high-performance dye-sensitized solar cells,

Journal of the American Chemical Society, 2015, 137, 4414-4423.

- 547 [11] S. Haid, M. Marszalek, A. Mishra, M. Wielopolski, J. Teuscher, J.E. Moser, et al.,
- 548 Significant improvement of dye-sensitized solar cell performance by small structural
- 549 modification in π -conjugated donor-acceptor dyes, Advanced Functional Materials,
- 550 2012, 22, 1291-1302.
- 551 [12] E. Gabrielsson, H. Ellis, S. Feldt, H.N. Tian, G. Boschloo, A. Hagfeldt, et al.,
- 552 Convergent/divergent synthesis of a linker-varied series of dyes for dye-sensitized
- solar cells based on the D35 donor, Advanced Energy Materials, 2013, 3, 1647-1656.
- 554 [13] Y.Z. Wu, W.H. Zhu, Organic sensitizers from D- π -A to D-A- π -A: effect of the
- internal electron-withdrawing units on molecular absorption, energy levels and
 photovoltaic performances, Chemical Society Reviews, 2013, 42, 2039-2058.
- 557 [14] J.B. Yang, P. Ganesan, J. Teuscher, T. Moehl, Y. J. Kim, C.Y. Yi, et al., Influence
- of the donor size in D- π -A organic dyes for dye-sensitized solar cells, Journal of the
- 559 American Chemical Society, 2014, 136, 5722-5730.
- 560 [15] S.G. Chen, H.L. Jia, X.H. Ju, H.G. Zheng, The impact of adjusting auxiliary
- 561 donors on the performance of dye-sensitized solar cells based on phenothiazine
- 562 D-D- π -A sensitizers, Dyes and Pigments, 2017, 146, 127-135.
- 563 [16] S.B. Wang, H.R. Wang, J.C. Guo, H.B. Tang, J.Z. Zhao, Influence of the terminal
- electron donor in D-D- π -A phenothiazine dyes for dye-sensitized solar cells, Dyes and Pigments, 2014, 109, 96-104.
- [17] J.H. Jou, S. Kumar, A. Agrawal, T.H. Li, S. Sahoo, Approaches for fabricating
 high efficiency organic light emitting diodes, Journal of Materials Chemistry C, 2015,
 3, 2974-3002.
- 569 [18] S.J. Liu, X.L. Zhang, C.J. Ou, S.L. Wang, X.L. Yang, X.H. Zhou, et al.,
- 570 Structure-property study on two new D-A type materials comprising pyridazine

- moiety and the OLED application as host, ACS Applied Materials & Interfaces, 2017,
- **572** *9*, 26242-26251.
- [19] Z.G. Li, X.Y. Zhao, X. Li, Z.Q. Gao, B.X. Mi, W. Huang, Organic thin-film solar
 cells: Devices and materials, Science China Chemistry, 2012, 55, 553-578.
- 575 [20] G. Sathiyan, E. K. T. Sivakumar, R. Ganesamoorthy, R. Thangamuthu, P.
- 576 Sakthivel, Review of carbazole based conjugated molecules for highly efficient
- organic solar cell application, Tetrahedron Letters, 2016, 57, 243-252.
- 578 [21] K. Kakiage, Y. Aoyama, T. Yano, T. Otsuka, T. Kyomen, M. Unno, et al., An
- achievement of over 12 percent efficiency in an organic dye-sensitized solar cell,
- 580 Chemical Communications, 2014, 50, 6379-6381.
- 581 [22] W.J. Wu, J.B. Yang, J.L. Hua, J. Tang, L. Zhang, Y.T. Long, et al., Efficient and
- stable dye-sensitized solar cells based on phenothiazine sensitizers with thiophene
 units, Journal of Materials Chemistry, 2010, 20, 1772-1779.
- [23] D.R. Cao, J.N. Peng, Y.P. Hong, X.M. Fang, L.Y. Wang, H. Meier, Enhanced
 performance of the dye-sensitized solar cells with phenothiazine-based dyes
 containing double D-A branches, Organic Letters, 2011, 13, 1610-1613.
- [24] Y. Hua, S. Chang, D.D. Huang, X. Zhou, X.J. Zhu, J.Z. Zhao, et al., Significant
 improvement of dye-sensitized solar cell performance using simple
- phenothiazine-based dyes, Chemistry of Materials, 2013, 25, 2146-2153.
- [25] Z.S. Huang, H. Meier, D.R. Cao, Phenothiazine-based dyes for efficient
 dye-sensitized solar cells, Journal of Materials Chemistry C, 2016, 4, 2404-2426.
- 592 [26] C. Maglione, A. Carella, C. Carbonara, R. Centore, S. Fusco, A. Velardo, et al.,
- 593 Novel pyran based dyes for application in dye sensitized solar cells, Dyes and
- 594 Pigments, 2016, 133, 395-405.
- 595 [27] Z.J. She, Y.Y. Cheng, L.Q. Zhang, X.Y. Li, D. Wu, Q. Guo, et al., Novel

- ruthenium sensitizers with a phenothiazine conjugated bipyridyl ligand for
 high-efficiency dye-sensitized solar cells, ACS Applied Materials & Interfaces, 2015,
 7, 27831-27837.
- 599 [28] R.Y.Y. Lin, F.L. Wu, C.T. Li, P.Y. Chen, K.C. Ho, J.T. Lin, High-performance
- aqueous/organic dye-sensitized solar cells based on sensitizers containing triethylene
- oxide methyl ether, ChemSusChem, 2015, 8, 2503-2513.
- [29] K. Stalindurai, A. Karuppasamy, J.D. Peng, K.C. Ho, A. Tamilselvan, C.
 Ramalingan, Fused heterocycles possessing novel metal-free organic dyes for
- dye-sensitized solar cells, Tetrahedron, 2017, 73, 278-289.
- [30] S. Ito, S. M. Zakeeruddin, R. Humphry-Baker, P. Liska, R. Charvet, P. Comte, et
- al., High-efficiency organic-Dye-sensitized solar cells controlled by
 nanocrystalline-TiO₂ electrode thickness, Advanced Materials, 2006, 18, 1202-1205.
- 608 [31] S. Ito, H. Miura, S. Uchida, M. Takata, K. Sumioka, P. Liska, et al.,
- High-conversion-efficiency organic dye-sensitized solar cells with a novel indoline
 dye, Chemical Communications, 2008, 5194-5196.
- [32] H.N. Tian, X.C. Yang, R.K. Chen, Y.Z. Pan, L. Li, A. Hagfeldt, et al.,
 Phenothiazine derivatives for efficient organic dye-sensitized solar cells, Chemical
- 613 Communications, 2007, 3741-3743.
- 614 [33] M. Mao, X.L. Zhang, X.Q. Fang, G.H. Wu, Y. Ding, X.L. Liu, et al.,
- 615 2,6-Conjugated Bodipy sensitizers for high-performance dye-sensitized solar cells,
 616 Organic Electronics, 2014, 15, 2079-2090.
- [34] T.J. Zhu, D.H. Mu, H.L. Qin, J. Song, B.X. Mi, X.Y. Zhao, et al., Benefits of
 dispersion solvents with more OH groups in electrospray preparation of TiO₂
 photoelectrode for the improvement of DSSC performance, Organic Electronics, 2014,
 15, 969-976.

- [35] J. Liu, X. Fu, D.P. Cao, L. Mao, J. Wang, D.H. Mu, et al., Stacked graphene-TiO₂
- 622 photoanode via electrospray deposition for highly efficient dye-sensitized solar cells,
- 623 Organic Electronics, 2015, 23, 158-163.
- [36] C. Wang, X.Y. Zhang, D.P. Cao, H.M. Yin, X.Y. Li, P.S. Cheng, et al., In situ
- preparation of hierarchically structured dual-layer TiO_2 films by E-spray method for
- 626 efficient dye-sensitized solar cells, Organic Electronics, 2017, 49, 135-141.
- [37] K. S. V. Gupt, T. Suresh, S. P. Singh, A. Islam, L.Y. Han, M. Chandrasekharam,
- 628 Carbazole based A- π -D- π -A dyes with double electron acceptor for dye-sensitized
- solar cell, Organic Electronics, 2014, 15, 266-275.
- [38] L.Y. Dong, R. Chen, Q. Weng, Z.W. An, X.B. Chen, P. Chen, The effect of furan
- linkers on the properties of cyclic thiourea functionalized triphenylamine dyesensitizers, Dyes and Pigments, 2017, 139, 772-778.
- [39] C. Liu, L. Mao, H.X. Jia, Z.J. Liao, H.J. Wang, B.X. Mi, et al., Influences of
 fluorination on homoleptic iridium complexes with CN=N type ligand to material
 properties, ligand orientation and OLED performances, Science China Chemistry,
 2015, 58, 640-649.
- [40] P. Qin, P. Sanghyun, M. I. Dar, K. Rakstys, H. Elbatal, S. A. Al-Muhtaseb, et al.,
- Weakly conjugated hybrid zinc porphyrin sensitizers for solid-state dye-sensitized
 solar cells, Advanced Functional Materials, 2016, 26, 5550-5559.
- [41] Z.Q. Wan, C.Y. Jia, Y. Wang, X.J. Yao, A strategy to boost the efficiency of
 rhodanine electron acceptor for organic dye: from nonconjugation to conjugation,
 ACS Applied Materials & Interfaces, 2017, 9, 25225-25231.
- 643 [42] Y. K. Eom, I. T. Choi, S. H. Kang, J. Lee, J. Kim, M. J. Ju, et al., 644 Thieno[3,2-b][1]benzothiophene derivative as a new π-Bridge unit in D-π-A structural 645 organic sensitizers with over 10.47% efficiency for dye-sensitized solar cells,

- 646 Advanced Energy Materials, 2015, 5, 1500300.
- 647 [43] C. Lee, W.T. Yang, R.G. Parr, Development of the Colle-Salvetti
- 648 correlation-energy formula into a functional of the electron density, Physical Review
- 649 B, 1988, 37, 785-789.
- [44] B. Miehlich, A. Savin, H. Stoll, H. Preuss, Results obtained with the correlation
- energy density functionals of becke and Lee, Yang and Parr, Chemical Physics Letters,
- **652** 1989, 157, 200-206.

663

- [45] A.D. Becke, A new mixing of Hartree-Fock and local density-functional theories,
- 654 The Journal of Chemical Physics, 1993, 98, 1372-1377.
- [46] C. Chen, X.C. Yang, M. Cheng, F.G. Zhang, J.H. Zhao, L.C. Sun, Efficient
- 656 panchromatic organic sensitizers with dihydrothiazole derivative as π -bridge for
- dye-sensitized solar cells, ACS Applied Materials & Interfaces, 2013, 5, 10960-10965.
- 658 [47] Y.Y. Li, W.H. Guo, H.S. Hao, L.J. Wang, Q. Su, S.S. Jin, et al., Enhancing
- 659 photoelectrical performance of dye-sensitized solar cell by doping 660 $SrTiO_3:Sm^{3+}@SiO_2$ core-shell nanoparticles in the photoanode, Electrochimica Acta, 661 2015, 173, 656-664.
- 662 [48] D.X. Zhao, L.Y. Bian, Y.X. Luo, M.D. Zhang, H. Cao, M.D. Chen,

Three-dimensional D- π -A organic sensitizer with coplanar triphenylamine moiety for

- dye-sensitized solar cells, Dyes and Pigments, 2017, 140, 278-285.
- [49] S. Sarker, A.J.S. Ahammad, H.W. Seo, D.M. Kim, Electrochemical impedance
 spectra of dye-Sensitized solar cells: fundamentals and spreadsheet calculation,
 International Journal of Photoenergy, 2014, 2014, 1-17.
- [50] F.F. Santiago, J. Bisquert, E. Palomares, L. Otero, D. Kuang, S. M. Zakeeruddin,
- 669 et al., Correlation between photovoltaic performance and impedance spectroscopy of
- 670 dye-sensitized solar cells based on ionic liquids, Journal of Physical Chemistry C,

- 671 2007, 111, 6550-6560.
- [51] H. Dong, Z.X. Wu, F. Lu, Y.C. Gao, A. El-Shafei, B. Jiao, et al., Optics-electrics

highways: Plasmonic silver nanowires@TiO₂ core-shell nanocomposites for enhanced
dye-sensitized solar cells performance, Nano Energy, 2014, 10, 181-191.

- [52] B.X. Zhao, J.S. Wang, H.Y. Li, Y. Xu, H.J. Yu, X.J. Jia, et al., Solar-to-electric
- 676 performance enhancement by titanium oxide nanoparticles coated with porous yttrium
- oxide for dye-sensitized solar cells, ACS Sustainable Chemistry & Engineering, 2015,

678 *3*, 1518-1525.

- [53] Q. Wang, J.E. Moser, M. Grätzel, Electrochemical impedance spectroscopic
 analysis of dye-sensitized solar cells, Journal of Physical Chemistry B, 2005, 109,
 14945-14953.
- [54] M. Adachi, M. Sakamoto, J.T. Jiu, Y. Ogata, S. Isoda, Determination of
 parameters of electron transport in dye-sensitized solar cells using electrochemical
 impedance spectroscopy, Journal of Physical Chemistry B, 2006, 110, 13872-13880.
- [55] Z.S. Huang, T. Hua, J. Tian, L.Y. Wang, H. Meier, D. Cao,
 Dithienopyrrolobenzotriazole-based organic dyes with high molar extinction
 coefficient for efficient dye-sensitized solar cells, Dyes and Pigments, 2016, 125,
 229-240.
- [56] J.L. Xu, K. Li, W.Y. Shi, R.J. Li, T.Y. Peng, Rice-like brookite titania as an
 efficient scattering layer for nanosized anatase titania film-based dye-sensitized solar
 cells, Journal of Power Sources, 2014, 260, 233-242.
- 692

694 Supporting Information

695 Effects of Meta or Para Connected Organic Dyes for

696 **Dye-sensitized Solar Cell**

697 Yunfei Jiao^{a, 1}, Le Mao^{b, 1}, Shuaishuai Liu^a, Tianwen Tan^b, Donglin Wang^a, Dapeng

698 Cao^b, Baoxiu Mi^{a,*}, Zhiqiang Gao^{b,**}, Wei Huang^{a, b, c, ***}

699

700

- ^a Key Laboratory for Organic Electronics & Information Displays (KLOEID), Jiangsu
- 702 Key Laboratory for Biosensors (KLB), Institute of Advanced Materials (IAM),
- Nanjing University of Posts & Telecommunications (NUPT), 9 Wenyuan Road,
- 704 Nanjing 210023, China
- ^b Jiangsu Engineering Center for Plate Displays & Solid State Lighting, Jiangsu
- National Synergetic Innovation Center for Advanced Materials (SICAM), School of
- 707 Material Science and Engineering, Nanjing University of Posts &
- Telecommunications (NUPT), 9 Wenyuan Road, Nanjing 210023, China
- ^c Shaanxi Institute of Flexible Electronics (SIFE), Northwestern Polytechnical
- 710 University (NPU), 127 West Youyi Road, Xi'an 710072, China
- 711
- 712
- ¹ These authors contributed equally to this work.
- 714 ^{*} E-mail: <u>iambxmi@njupt.edu.cn</u>
- 715 ** E-mail: <u>iamzqgao@njupt.edu.cn</u>
- 716 ^{****} E-mail: <u>wei-huang@njtech.edu.cn</u>
- 717



¹H NMR spectrum of compound **mCPPR** (DMSO, 400 MHz)



 13 C NMR spectrum of compound **mCPPR** (DMSO, 101 MHz)



¹H NMR spectrum of compound **pCPPR** (DMSO, 400 MHz)



¹³C NMR spectrum of compound **pCPPR** (DMSO, 101 MHz)

Highlights

1. Two novel phenothiazine-based organic dyes have been designed and synthesized as sensitizers for dye-sensitized solar cell.

2. The different effects of meta or para connected mode organic dyes for DSSC devices have been systematic researched.

3. The dye-sensitized solar cell based on dye with para connection mode achieves a high power conversion efficiency of 5.57%.

CER CER