Chinese Chemical Letters xxx (2016) xxx-xxx



Contents lists available at ScienceDirect

Chinese Chemical Letters



journal homepage: www.elsevier.com/locate/cclet

2 Original article

3

4

5

6 7

Novel organic dye sensitizers containing fluorenyl and biphenyl moieties for solar cells

Q1 Yan Xie^{a,b}, Liang Han^a, Cheng-Sheng Ge^b, Yan-Hong Cui^a, Jian-Rong Gao^{a,*}

^a College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310032, China
 ^b College of Chemistry and Materials Engineering, Quzhou University, Quzhou 324000, China

ARTICLE INFO

Article history: Received 3 May 2016 Received in revised form 3 June 2016 Accepted 13 June 2016 Available online xxx

Keywords: Dye-sensitized solar cells Triarylamine Fluorenyl Biphenyl Furan bridge Photovoltaic performance

ABSTRACT

Three novel triarylamine dyes (AFL1–AFL3) containing fluorenyl and the biphenyl moieties have been designed and synthesized for application in dye-sensitized solar cells. The light-harvesting capabilities and photovoltaic performance of these dyes were investigated systematically through comparison of different π -bridges. The dye with a furan linker exhibited a higher open-circuit voltage (V_{OC}) and monochromatic incident photon-to-current conversion efficiency (IPCE) compared to thiophene and benzene linker. Thus, AFL3 containing a furan linker exhibited the maximum overall conversion efficiency of 5.81% (V_{OC} = 760 mV, J_{SC} = 11.36 mA cm⁻² and ff = 0.68) under standard global AM 1.5 G solar condition.

© 2016 Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences. Published by Elsevier B.V. All rights reserved.

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted much attention due to their low material cost, flexibility, easy manufacturing process, and high efficiency [1–3]. To date, DSSCs based on Ru complexes have an overall solar energy conversion efficiency (η) approaching 12%. On the other hand, organic dye sensitizers provide the advantages of high molar extinction efficiencies, customized molecular designs, cost effectiveness, and environmental friendliness, which have been extensively investigated. [2– 5] Recently, novel organic dyes based on coumarin [6], carbazole [7], indoline [8], phenothiazine [9], and phenoxazine [10] have been investigated as sensitizers for DSSCs, and solar cells based on triphenylamine have been reported [11] with an energy conversion efficiency exceeding 10%.

The general strategy in the design of highly efficient metal-free dye sensitizers is to design novel structures of D- π -A molecules, especially in electron donor (D) and π -conjugated bridges. The structures of the chromophore donor, bridge linker, and acceptor can be modified independently to tune the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [5,11]. In D- π -A systems, the use longer π -conjugation dye molecules is generally intended

E-mail address: gjrarticle@163.com (J.-R. Gao).

31 to achieve a larger absorption maximum and extend the absorption region. However, long conjugation dye molecules are 32 unstable under irradiation with high-energy photons and prone to 33 unfavorable π - π aggregation [12]. To avoid the aggregation of 34 dyes, organic dyes with D-D- π -A structures, in which two D 35 moieties are connected with a π -bridge, have recently been 36 reported [4,13]. These studies suggested that organic dves with D-37 D- π -A structures might achieve better performances than those 38 with the simple D- π -A structures. 39

Electron donors containing triarylamine moieties have been 40 widely investigated because of their prominent electron-donat-41 ing ability and hole-transport properties; these donors also 42 prevent the direct charge recombination between TiO_2 and I_3^- by 43 covering TiO₂ surfaces with a bulky aryl group [4,11]. We [14] 44 and other researchers [4,15–17] reported novel organic dyes 45 containing a triarylamine unit. Fluorene-based organic dyes are 46 highly stable under UV irradiation and heating conditions; these 47 dyes can also suppress dye aggregation and disrupt molecular 48 stacking because of their nonplanarity [18-20]. In addition to the 49 arylamine moiety (D), an electron-rich biphenyl unit acts as a 50 secondary electron donor; as a result, a D-D- π -A molecular 51 configuration is formed. The π -conjugated bridge connecting the 52 donor and the acceptor in the dye sensitizer influences not only 53 the region of light absorbed by DSSCs but also the degree of 54 electron injection from the excited state of the dye to the TiO₂ 55 surface. Therefore, varying the π -bridges has been demonstrated 56 as an effective strategy to obtain high short-circuit photocurrent 57

http://dx.doi.org/10.1016/j.cclet.2016.06.042

1001-8417/© 2016 Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences. Published by Elsevier B.V. All rights reserved.

^{*} Corresponding author.

2

ARTICLE IN PRESS

Y. Xie et al./Chinese Chemical Letters xxx (2016) xxx-xxx



Scheme 1. Synthesis of AFL1, AFL2, and AFL3.

density (J_{SC}) and open-circuit voltage (V_{OC}) [5,18,21–23]. This 58 study synthesized a series of three novel organic dye sensitizers 59 60 (AFL1-AFL3) consisting of fluorenyl, the biphenyl moieties of triarylamine, and the different π -conjugated linkers of benzene, 61 thiophene, and furan to improve the power conversion efficiency 62 and to investigate the influence of the π -bridge. This study also 63 examined the photophysical and electrochemical properties and 64 65 photovoltaic performance of DSSCs. The synthetic procedures are shown in Scheme 1. 66

67 2. Experimental

68 2.1. Materials and instruments

¹H and ¹³C NMR spectra were recorded by using a spectrometer
at 400 and 125 MHz, respectively. Mass spectra were obtained
using a Waters Xevo Q-Tof mass spectrometer. Absorption spectra
were determined by using a Shimadzu UV spectrophotometer
(model UV2550). Fluorescence spectra were obtained using a
Shimadzu RF-5301PC spectrofluorometer.

Reactions were performed under nitrogen atmosphere. The
solvents and chemicals used in this study were of analytical grade
and used without further purification.

78 2.2. Fabrication of DSSCs

FTO glass slides were cleaned with a detergent solution in an
ultrasonic bath for 15 min and then rinsed with water and
ethanol. Two different titanium dioxide pastes were deposited by

screen-printing to fabricate photoelectrodes; as a result, 0.16 cm² 82 TiO₂ electrodes with light-scattering anatase particles were 83 formed. The total thickness of the TiO₂ film was 18 µm. The 84 TiO₂ electrodes were gradually heated in an air flow at 325 °C for 85 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 86 15 min. Afterward, the electrodes were cooled to 80 °C, immersed 87 in the dye solution in a mixture of THF and CHCl₃ 88 (THF:CHCl₃ = 1:10), and kept at room temperature for 24 h to 89 assure complete dye uptake. The electrodes were then rinsed with 90 THF to remove excess dye. Counter electrodes were prepared by 91 screen-printing a 50 nm Pt layer on the cleaned FTO plates. Open 92 cells were fabricated in air by clamping different photoelectrodes 93 with platinized counter electrodes. The active area of DSSCs was 94 0.16 cm². The electrolyte OPV-AN-I used in this study was 95 contained 0.07 mmol/L I⁻ (Yingkou Opvtech New Energy Co., Ltd.). 96

2.3. Photovoltaic characterization

The photovoltaic performance of DSSCs was evaluated at AM 98 1.5 G illumination (100 mW/cm²; Peccell-L15, Peccell, Japan) by 99 using a Keithley digital source meter (Keithley 2601, USA). The 100 incident light intensity was 100 mW/cm² calibrated with a 101 standard Si solar cell (BS-520, Japan). The action spectra of the 102 monochromatic incident photon-to-current conversion efficiency 103 (IPCE) of the solar cells were obtained by using a commercial setup 104 (PEC-S20 IPCE Measurement System, Peccell, Japan). Electrochem-105 ical impedance spectroscopy (EIS) experiments were conducted 106 using a computer-controlled potentiostat (Zenium Zahner, 107 Germany). The measured frequency ranged from 100 to 1 MHz, 108

97

Y. Xie et al. / Chinese Chemical Letters xxx (2016) xxx-xxx

109 and the AC amplitude was set to 10 mV. The bias of the EIS 110 measurements was set to V_{OC} of the corresponding dye sensitizer. 111 Cyclic voltammetry was recorded with a computer-controlled electrochemical analyzer (IviumStat, Holland) at a constant scan 112 113 rate of 100 mV s⁻¹. Measurements were performed with a three-114 electrode cell in 0.1 M Bu₄NClO₄-N,N-dimethylformamide solu-115 tion, Pt wire as a counter electrode, and an Ag/AgCl reference 116 electrode: the measurements were then calibrated with ferrocene.

117 2.4. Detailed experimental procedures and characterization data

Synthesis of compound 2-amino-N-[(1,1'-biphenyl)-4-yl]-N-(4-118 bromophenyl)-9,9-dimethylfluorene 1: A mixture of 1,4-dibro-119 120 mobenzene (0.2 g, 0.8 mmol), 2-(4-biphenylyl)amino-9,9-121 dimethylfluorene (0.36 g, 1 mmol), Pd(OAc)₂ (0.046 g, 0.2 mmol), 122 $P(t-Bu)_3$ (0.04 g, 0.2 mmol), and Cs_2CO_3 (1.63 g, 5 mmol) in dry 123 toluene (15 mL) was stirred and heated at 110 °C overnight. After 124 the mixture was cooled to room temperature, saturated ammoni-125 um chloride solution was added to the reaction solution. The 126 solution was extracted with dichloromethane, dried with MgSO₄, 127 and subjected to column chromatography (silica gel, dichloro-128 methane/hexanes = 3:1). A yellow solid was obtained with the 129 following properties: yield, 57% (0.24 g); mp 160.1–161.5 °C; ¹H NMR [400 MHz, (CD₃)₂CO]: δ 7.64 (d, J = 8 Hz, 1H), 7.60–7.57 (m, 130 131 3H), 7.50-7.48 (m, 2H), 7.43-7.40 (m, 2H), 7.38-7.26 (m, 5H), 7.25 132 (s, 1H), 7.20 (s, 1H), 7.17 (s, 1H), 7.15 (s, 1H), 7.06-7.02 (m, 3H), 133 1.42 (s, 6H). HRMS: *m*/*z* calcd. for C₃₃ H₂₆ Br N: 516.1321 [M-H]⁻; 134 Found: 516.1337.

135 Synthesis of compound 2a: A mixture of 1 (0.52 g, 0.1 mmol), 4-136 formylphenylboronic acid (0.18 g, 0.12 mmol), $Pd(PPh_3)_4$ (0.14 g, 137 0.012 mmol), K₂CO₃ (0.14 g, 1 mmol), and degassed water (2 mol/ 138 L) in dry THF (15 mL) was refluxed overnight. After the mixture 139 was cooled to room temperature, the solution was extracted with 140 dichloromethane, dried with MgSO₄, and subjected to column 141 chromatography (silica gel, PE:EA = 5:1). A light yellow solid was 142 obtained. Yield: 68% (0.37 g). mp 95.9- 97.7 °C. ¹H NMR [400 MHz, 143 $(CD_3)_2CO$]: δ 10.0 (s, 1H), 7.92 (d, 2H, J = 8 Hz), 7.75 (d, 2H, J = 8 Hz), 144 7.64–7.52 (m, 7 H), 7.40 (q, 2H, J = 4 Hz and 12 Hz), 7.32–7.23 (m, 145 10H), 7.13–7.11 (m, 1H), 1.44 (s, 6H); HRMS: *m/z* calcd. for C₄₀ H₃₁ 146 NO: 542.2478 [M-H] -; Found: 542.2488.

Synthesis of compound 2b: A mixture of 1 (0.52 g, 0.1 mmol), 5-147 148 formylthiophene-2-boronic acid (0.19 g, 0.12 mmol), Pd(PPh₃)₄ (0.14 g, 0.012 mmol), K₂CO₃ (0.14 g, 1 mmol), and degassed water 149 150 (2 mol/L) in dry THF (15 mL) was refluxed overnight. After the 151 mixture was cooled to room temperature, the solution was 152 extracted with dichloromethane, dried with MgSO₄, and subjected 153 to column chromatography (silica gel, PE:EA = 15:1). A yellow solid 154 was obtained. Yield: 49% (0.27 g). mp 102.8- 104.1 °C. ¹H NMR 155 $[400 \text{ MHz}, (\text{CD}_3)_2\text{CO}]: \delta 9.85 (s, 1\text{H}), 7.71 (d, 1\text{H}, J = 4 \text{ Hz}), 7.67-7.53$ 156 (m, 7H), 7.43 (q, 3H, J = 4 Hz and 12 Hz), 7.34-7.22 (m, 8H), 7.17 (d, 157 2H, J = 8 Hz), 7.12 (d, 1H, J = 8 Hz), 1.45 (s, 6H); HRMS: *m*/*z* calcd. 158 for C₃₈ H₂₉ NOS: 548.2043 [M-H]⁻; Found: 548.2019.

159 Synthesis of compound 2c: A mixture of 1 (0.52 g, 0.1 mmol), 160 2-formylfuran-5-boronic acid (0.16 g, 0.12 mmol), Pd(PPh₃)₄ 161 (0.14 g, 0.012 mmol), K₂CO₃ (0.14 g, 1 mmol), and degassed water 162 (2 mol/L) in dry THF (15 mL) was refluxed overnight. After the 163 mixture was cooled to room temperature, the solution was 164 extracted with dichloromethane, dried with MgSO₄, and sub-165 jected to column chromatography (silica gel, PE:EA = 3:1). A 166 yellow solid was obtained. Yield: 47% (0.25 g). mp 101.6-102.5 °C. ¹H NMR [400 MHz, (CD₃)₂CO]: δ 9.59 (s, 1H), 7.69 (d, 4H, J = 8 Hz), 167 168 7.66 (d, 1H, J = 8 Hz), 7.61 (d, 2H, J = 8 Hz), 7.53 (d, 2H, J = 8 Hz), 169 7.42 (q, 2H, J = 8 Hz and 16 Hz), 7.34-7.22 (m, 7H), 7.19 (s, 1H), 170 7.16(s, 1H), 7.11(d, 1H, J = 8 Hz), 6.72(d, 1H, J = 4 Hz), 1.43(s, 6H);171 HRMS: *m*/*z* calcd. for C₃₈ H₂₉NO₂: 532.2271 [M-H] ⁻; Found: 172 532.2278.

Synthesis of compound AFL1: 2a (0.54 g, 0.1 mmol) was mixed 173 with cyanoacetic acid (0.02 g, 0.23 mmol) in dry acetonitrile 174 (15 mL) and piperidine (0.1 mL). The solution was refluxed 175 176 overnight. The solvent was removed in vacuo. The pure product AFL1 was obtained through column chromatography (silica gel, 177 CH₂Cl₂:CH₃OH:HAc = 300:10:1). The following properties were 178 observed: yield, 45% (0.27 g). mp 206.8-208.6 °C. ¹H NMR 179 [400 MHz, $(CD_3)_2CO$]: δ 7.96 (s, 1H), 7.94 (d, 2H, J = 4 Hz), 7.82-180 7.72 (m, 5H), 7.68-7.65 (m, 4H), 7.53 (d, 1H, J = 4 Hz), 7.45 (t, 2H, 181 *I* = 8 Hz), 3.37-7.26 (m, 5H), 7.16 (q, 4H, *J* = 8 Hz and 16 Hz), 7.10-182 7.07 (m, 1H), 1.40(s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ 24.96, 183 26.97, 46.72, 95.00, 107.47, 112.46, 114.61, 119.53, 119.53, 119.91, 184 121.58, 122.23, 122.91, 122.92, 122.98, 123.30, 123.31, 124.27, 185 124.30, 126.43, 126.44, 127.35, 127.95, 127.95, 127.99, 128.06, 186 129.16, 129.16, 130.29, 131.90, 134.81, 134.87, 138.32, 139.64, 187 141.77, 144.97, 145.03, 146.29, 146.61, 150.91, 153.49, 155.26, 188 165.70; HRMS: m/z calcd. for C₄₃H₃₁N₂O₂: 607.2453 [M-H] ⁻; 189 190 Found: 607.2477.

Synthesis of compound AFL2: 2b (0.55 g, 0.1 mmol) was mixed 191 with cyanoacetic acid (0.02 g, 0.23 mmol) in dry acetonitrile 192 (15 mL) and piperidine (0.1 mL). The solution was refluxed 193 overnight. The solvent was removed in vacuo and the residue. 194 195 The pure product AFL2 was obtained through column chromatography (silica gel, CH₂Cl₂:CH₃OH:HAc = 300:10:1). Yield: 37% 196 (0.23 g). mp 207.9- 208.6 °C. ¹H NMR (125 MHz, CDCl₃): δ 7.65 197 (d, 1H, J = 8 Hz), 7.62(d, 1H, J = 8 Hz), 7.60-7.57 (m, 3H), 7.52 (d, 2H, 198 J = 8 Hz), 7.44-7.38 (m, 4H), 7.33-7.28 (m, 2H), 7.26 (m, 6H), 7.21 (s, 199 1H), 7.16 (s, 1 H), 7.13 (s, 1H), 7.11 (q, 1H, J = 4 Hz and 8 Hz), 1.43 (s, 200 6H); ¹³C NMR (100MHz, CDCl₃): δ 24.90, 26.93, 46.84, 94.99, 201 108.85, 119.51, 119.57, 119.60, 119.89, 119.91, 119.96, 121.53, 202 121.57, 122.87, 122.90, 122.94, 122.96, 124.53, 124.66, 126.40, 203 126.40, 126.83, 127.16, 127.19, 127.21, 127.94, 127.96, 129.15, 204 129.15, 134.98, 135.56, 138.26, 139.26, 146.01, 146.31, 147.92, 205 148.54, 154.42, 153.49, 155.26, 164.20; HRMS: m/z calcd. for 206 C₄₁H₂₉N₂O₂S: 607.2453 [M-H]⁻; Found: 607.2477. 207

Synthesis of compound AFL3: A mixture of **2c** (0.55 g, 0.1 mmol) 208 and cyanoacetic acid (0.02 g, 0.23 mmol) in dry acetonitrile 209 (15 mL) and piperidine (0.1 mL) was prepared. The solution was 210 refluxed overnight. The solvent was removed in vacuo and the 211 residue. Then, the pure product AFL3 was obtained through 212 column chromatography (silica gel, CH₂Cl₂:CH₃OH:A-213 cOH = 400:20:1). Yield: 48% (0.28 g). mp 238.6- 240.1°C. ¹H 214 NMR (400 MHz, CDCl₃): δ 7.66-7.64 (m, 2H), 7.63 (s, 2H), 7.60 215 (s, 2H), 7.58 (s, 1H), 7.52 (s, 1H), 7.50 (s, 1H), 7.44-7.38 (m, 4H), 216 7.33-7.26 (m, 3H), 7.22 (s, 1H), 7.20 (s, 1H), 7.18 (s, 1 H), 7.16 (s, 217 1H), 7.10 (d, 1H, J = 8 Hz), 7.02 (s, 1H), 6.76 (d, 1H, J = 4 Hz), 1.42 (s, 218 6H); 13 C NMR (125 MHz, CDCl₃): δ 22.99, 26.84, 46.57, 107.70, 219 107.90, 119.40, 119.47, 119.58, 119.85, 119.89, 121.44, 121.47, 220 121.48, 122.66, 122.82, 124.42, 124.42, 125.79, 125.81, 125.82, 221 126.34, 126.34, 127.06, 127.22, 127.23, 127.85, 127.87, 129.04, 222 129.04, 134.97, 135.07, 138.21, 139.56, 145.91, 146.20, 147.83, 223 148.36, 154.42, 155.20, 156.11, 162.47; HRMS: m/z calcd. for 224 C₄₁H₂₉N₂O₃: 597.2184 [M-H]⁻; Found: 597.2209. 225

3. Results and discussion

3.1. Synthesis

Three novel triarylamine dye sensitizers consisting of cyanoa-228 cetic acid as an electron acceptor and fluorenyl and biphenyl 229 moieties in the donor with various conjugated linkers were 230 prepared. The synthetic routes are shown in Scheme 1. In a typical 231 Ullmann reaction, 1 was obtained from 2-(4-biphenylyl) amino-232 9,9-dimethylflu-orene and 1,4-dibromobenzene with a good yield. 233 Then, the following Suzuki coupling reaction between 1 and 234 arylboronic acids yielded the corresponding aldehydes 2a-2c. The 235

3

226

227

Y. Xie et al. / Chinese Chemical Letters xxx (2016) xxx-xxx



Fig. 1. UV-vis spectra of triarylamine dyes. (a) The UV-vis absorption spectra of AFL1-AFL3 recorded in CHCl₃-CH₃OH at room temperature. (b) The absorption spectra of AFL1-AFL3 adsorbed on thin transparent films.

three dye sensitizers were produced from 2a to 2c after
Knoevenagel condensation reaction occurred with cyanoacetic
acid in the presence of piperidine. The compounds and three new
organic sensitizers (AFL1–AFL3) were confirmed through NMR and
MS.

241 3.2. Photophysical properties

242 The UV-vis absorption spectra of AFL1-AFL3 recorded in CHCl₃-CH₃OH at room temperature are displayed in Fig. 1a, and 243 the corresponding data are summarized in Table 1. The absorption 244 spectra of the triarylamine dye sensitizers display two distinct 245 246 absorption peaks. The band located at the shorter wavelength was 247 attributed to the π - π ^{*} electron transition of the chromophore. The 248 absorption band at 300-391 nm can be ascribed to localized 249 aromatic $\pi - \pi^*$ transitions. The longest absorption peak at 250 approximately 391–600 nm could be attributed to the intramo-251 lecular charge transfer (ICT) from the triarylamine donor to the 252 cyanoacetic acid acceptor mixed with delocalized $\pi - \pi^*$ transition.

253 The maximum absorption peaks of the dye sensitizers are 254 observed in the following order: AFL3 > AFL2 > AFL1. AFL3 255 displays the broadest absorption band and evident red-shifted 256 absorption spectra compared with the other dye sensitizers. This 257 finding could occur possibly because the introduction of thiophene 258 (or benzene) and triphenylamine may twist the molecule; thus, 259 dihedral angles were formed between the donor and the thiophene 260 (or benzene) moiety, and the conjugation of the whole molecule 261 was decreased. Among these dye sensitizers, AFL3 exhibits the 262 highest molar extinction coefficient; this finding could be obtained 263 because the resonance energy of furan (16 kcal mol⁻¹) is smaller than that of thiophene (29 kcal mol⁻¹) and benzene 264 $(36 \text{ kcal mol}^{-1})$. As a result, the molecule undergoes effective 265 266 conjugation and decreases the energy of ICT [18,22,25,26].

The absorption spectra of AFL1-AFL3 adsorbed on thin 267 268 transparent films are shown in Fig. 1b. The maximum absorption 269 peaks of AFL1–AFL3 on the TiO₂ films are located at 398, 423, and 270 393 nm that correspondingly blue shifted at 10, 7, and 43 nm from 271 the solution spectra, respectively. The blue shift of the absorption 272 spectra of AFL1-AFL3 on TiO₂ could be ascribed to the deprotona-273 tion of carboxylic acid once these sensitizers adsorbed on the TiO₂ 274 surface and H-aggregates formed.

Compared with AFL1 and AFL2, AFL3 exhibits a longer blueshift.
This may be caused by the increase of coplanarity between the
triarylamine moiety and the electron acceptor due to the
introduction of the furan unit. Similar phenomena have been

observed for several other organic dyes [26–28]. Similar to the findings in the absorption in the solution, the results revealed that AFL3 yielded the highest absorbance. AFL2 showed lower absorbance than AFL1 does when bound to the TiO₂ film, probably because of AFL2 aggregation, which may reduce the light absorptivity. AFL2 exhibited a broader absorption band on TiO₂.

279

280

281

282

283

284

Cyclic voltammograms (CV) were performed to evaluate the 285 thermodynamically allowed electron transfer processes from the 286 excited dve molecule to the conduction band of TiO₂, and the 287 related data were shown in Table 2. As we can see, the lowest 288 unoccupied molecular orbital (LUMO) levels of these dyes are in 289 the range of -2.69 to -2.65 eV, which are higher than the TiO₂ 290 conduction band (CB) energy level (-4.0 eV), implying that 291 electron injection from the excited dye into the conduction band 292 of TiO2 is energetically permitted. In addition, the highest occupied 293 molecular orbital (HOMO) level of dyes, ranging from -5.41 to 294 -5.32 eV, which are lower than the energy level of the redox 295 couple I^{-}/I_{3}^{-} (-4.9 eV), indicating that the oxidized dyes formed 296

Table 1

Optical properties of triarylamine dyes.

Comp.	$\lambda_{max}^{a}(nm)$	$\varepsilon (\mathrm{Lmol^{-1}cm^{-1}})$	$\lambda_{max}^{b}(nm)$	$\lambda_{em}^{c}(nm)$
AFL1	344, 408	9944, 5685	398	357
AFL2	349, 430	16236, 10786	423	358
AFL3	360, 436	37135, 24966	393	346

^a Maximum absorption wavelength λ_{max} and molar extinction coefficient at λ_{max} of the dye sensitizer measured in CH₃OH-CHCl₃ co-solvent (v:v=1:10).

 $^b\,$ Maximum absorption wavelength λ_{max} of the dye sensitizer on sensitized TiO_2 electrodes.

 $^{\rm c}$ Maximum emission wavelength measured in $\rm CH_3OH-CHCl_3$ co-solvent (v:v = 1:10).

Table 2

Electrochemical properties of triarylamine dyes.

Comp.	Experimental ^a	Calculated ^d				
AFL1 AFL2 AFL3	E _{HOMO} ^а (eV) -5.32 -5.41 -5.37	E_{0-0}^{b} (eV) 2.65 2.40 2.61	E _{LUMO} ^c (eV) -2.69 -2.66 -2.65	Е _{НОМО} (eV) -5.06 -5.14 -5.11	E ₀₋₀ (eV) 2.47 2.43 2.54	E _{LUMO} (eV) -2.59 -2.71 -2.57

^a The oxidation potential Eox in DMF was determined from cyclic voltammograms and used to describe the ground-state energy HOMO.

^b E_{0-0} was calculated from E_{0-0} =1240/ λ_{int} and λ_{int} was the intersection of the normalized absorption and emission spectra.

^c E_{LUMO} was calculated from $E_{\text{ox}} - E_{0-0}$.

^d Calculated at the B3LYP/6-31 G(d) level in vacuum.

Y. Xie et al./Chinese Chemical Letters xxx (2016) xxx-xxx



Fig. 2. Optimized geometries (side view) of triarylamine dyes at the B3LYP/6-31G(d) level.

AFL3



after electron injection into the conduction band of TiO₂ could

298 thermodynamically accept electrons from I[–] ions.

299 3.3. Computational studies

297

300 The geometry of the dye sensitizer was optimized by the B3LYP 301 hybrid density functional method in conjunction with the dpolarized 6-31G (d) basis set implemented in the Gaussian 302 303 03 program [29] to obtain insights into the relationship between 304 structural and photophysical properties. The wave function was 305 then analyzed by Multiwfn [30]. The fully optimized geometrical 306 structures of the three dye sensitizers are shown in Fig. 2. In the ground state, the geometry of the dye sensitizer is not planar. Fig. 2 307 308 displays the dihedral angles between the neighboring units in the 309 conjugated spacer. For AFL1-AFL3, the ground-state structures of 310 the dyes between two benzene units in the donor are characterized 311 by twist angles of 36.2, 36.4, and 36.4. The twist angle in the donor 312 corresponds to a less planar configuration. The dihedral angles 313 between a donor and a bridge (benzene, thiophene, or furan) are 31.5, 15.6, and 1.6, respectively. Inserting a furan unit instead of a 314 315 thiophene (or benzene) moiety close to the acceptor can twist the 316 whole molecule to a less extent, because the steric hindrance of a 317 small oxygen atom is less pronounced [31,32]. Thus, the 318 conjugation of AFL3 is increased to some extent.

319 The HOMO energy level shown in Fig. 3 is located at -5.14 320 to -5.06 eV, which is lower than the potential of the redox couple 321 I^{-}/I_{3}^{-} (- 4.9 eV). The LUMO energy level is concentrated on -2.71 322 to -2.57 eV and higher than the TiO₂ CB energy level (-4.0 eV). 323 This means that these dyes can favorably inject the electrons into 324 the CB edge of TiO₂, and the oxidized dyes can be reduced by the 325 electrolyte successfully. The HOMOs of AFL2 and AFL3 are farther 326 from the TiO₂ CB when compared to that of AFL1, which will reduce 327 charge recombination between the oxidized sensitizer and the

Fig. 4. Electronic distributions in the frontier molecular orbitals of the triarylamine dyes.

injected electrons in TiO_2 conduction band. Further, the LUMO 328 level of AFL3 is higher than that of AFL1 and AFL2, indicating that 329 AFL3 dye has more efficient electron injection, in accordance with 330 the geometrical and experimental result. 331

The electronic distribution in the frontier molecular orbitals 332 HOMO and LUMO is shown in Fig. 4. The HOMO of the dye 333 sensitizer is delocalized over the whole molecules. Conversely, the 344 LUMO of the dye sensitizer is mainly found on the π -bridge and the 335 acceptor; the latter favors an efficient electron transfer from the 336 excited state of the dye sensitizer to the TiO₂ conduction band 337 edge. 338

3.4. Electrochemical properties

Electrochemical impedance spectroscopy (EIS) analysis was 340 performed to investigate the electron recombination in the DSSCs 341 sensitized by the triarylamine dye sensitizer. The Nyquist plots and 342 Bode plots of the DSSCs in forward bias with a frequency range of 343 0.1-100 kHz are shown in Fig. 5a. The Bode phase plots are also 344 shown in Fig. 5b. The reaction resistance of DSSCs was analyzed 345 with ZSimpWin by using an equivalent circuit (Fig. 5c) containing a 346 constant phase element (CPE) and resistance (R). In the equivalent 347 circuit, $R_{\rm S}$ corresponds to the overall series resistance; $R_{\rm ct}$ and $R_{\rm ce}$ 348

339

6

ARTICLE IN PRESS

Y. Xie et al./Chinese Chemical Letters xxx (2016) xxx-xxx



Fig. 5. Electrochemical impedance spectra of DSSCs based on triarylamine dyes. (a) The Nyquist plots and Bode plots of the DSSCs in forward bias. (b) The Bode phase plots. (c) The reaction resistance of DSSCs.

349represent charge transfer resistances at the photoanode/electro-350lyte interface and the counter electrode (CE), respectively. R_s and351 R_{ct} are listed in Table 2. The DSSCs show similar series resistances352of approximately 8.8–9.6 Ω because of the same surface area,353electrolyte, and electrode in the materials.

354 Two semicircles were observed in the Nyquist plots. The small 355 semicircle at a high frequency (1-100 kHz) is assigned to the redox 356 charge transfer response at the Pt/electrolyte interface. The large semicircle at the intermediate frequency (1 Hz $-\sim$ 1 kHz) repre-357 sents the charge transfer resistances (R_{ct}) at the photoanode/ 358 359 electrolyte interface; a large R_{ct} corresponds to a more difficult 360 electron recombination from the conduction band to the electro-361 lyte [14]. In Fig. 5a and Table 2, the semicircle of AFL3 at 362 intermediate frequency is the largest among the semicircles of the 363 three triarylamine dye sensitizers. This finding indicated that AFL3 364 exhibited the longest charge recombination lifetime and the 365 highest V_{OC} with furan as a bridge. Although AFL2 with a thiophene 366 bridge yielded the least charge recombination, this sensitizer obtained only a moderate V_{OC} because of its lower electron 367 368 injection efficiency. Therefore, we conjecture that electron 369 injection efficiency rather than charge recombination play the 370 primary role in V_{OC} among these dyes [33].

371In the Bode phase plots, the peak position of the middle372frequency is related to the lifetime of electrons; for example, a shift373to a low frequency corresponds to a long electron lifetime. The374Bode phase plots shown in Fig. 5b support the differences in the375electron lifetime of TiO2 films derived using the three dyes. These376plots further support the order of V_{OC} of DSSCs based on these dye377sensitizers.

378 3.5. Photovoltaic performance of DSSCs

379 The IPCE action spectra of DSSCs based on triarylamine dye 380 sensitizers were obtained in an AM 1.5 G irradiation of 100 mW/ 381 cm² (Fig. 6). AFL3-sensitized DSSCs display a higher IPCE than AFL1 382 does because of the introduction of furan to the π -conjugation 383 system. AFL3-sensitized DSSC exhibits an IPCE exceeding 60% from 384 380 to 539 nm and a maximum of 70% at 460 nm; its photocurrent 385 signal reaches approximately 700 nm possibly because of its 386 highest absorbance and broad absorption spectrum compared to 387 the other tested dyes. The IPCE values of AFL3 are the highest in a 388 wide range of spectra; this finding indicated that this dye likely 389 generates a large photocurrent. With the highest IPCE and almost 390 the broadest spectra of the IPCE values, AFL3-sensitized TiO₂



Fig. 6. IPCE curves of the DSSCs based on triarylamine dyes.

electrode possibly exhibits a higher conversion yield than the other dye sensitizers do. However, AFL2 possesses a broader spectral range than AFL1 and AFL3, which confirms that the electron-rich thiophene is beneficial to the broadening of the spectrum [34].

391

392

393

394

395

396

397

The photocurrent density–photovoltage (*J*–V) curves of the DSSCs based on triarylamine dye sensitizers are shown in Fig. 7. Key parameters, including short-circuit current density



Fig. 7. Current-potential curves (J-V) of the DSSCs based on triarylamine dyes.

Y. Xie et al./Chinese Chemical Letters xxx (2016) xxx-xxx

Table 3

Parameters obtained by fitting the impedance spectra of DSSCs based on triarylamine dyes with the equivalent circuit.

Comp.	$R_{ m S}(\Omega{ m cm}^{-2})$	$R_{\rm ce}~(\Omega{ m cm}^{-2})$	$R_{ m CT}$ ($\Omega{ m cm}^{-2}$)
AFL1	8.825	4.92	18.82
AFL2	8.377	5.03	7.697
AFL3	9.599	5.35	84.5

Table 4

Parameters of the DSSCs based on triarylamine dyes.

Comp.	$V_{\rm OC}~({\rm mV})$	$J_{\rm SC}$ (mA cm ⁻²)	ff	η (%)
AFL1	640	4.96	0.72	2.28
AFL2	680	9.99	0.71	4.83
AFL3	750	11.36	0.68	5.81

398 (J_{SC}) , open-circuit voltage (V_{OC}) , fill factor (ff), and overall power 399 conversion efficiency (η), are summarized in Table 3. J_{SC} is related 400 to the molar extinction coefficient of the dye molecule, with a 401 higher molar extinction coefficient showing good light-harvesting 402 ability and yielding a higher short-circuit current. As mentioned, 403 the short-circuit current density of the dyes assume the following 404 order: AFL3 > AFL2 > AFL1. Less charge recombination and more 405 efficient electron injection lead to higher Voc. Accordingly, AFL3 has 406 superior $V_{\rm oc}$ to AFL1. AFL3 shows the highest $V_{\rm oc}$ among three 407 Q2 triarylamine dye (Table 4). Because of its highest J_{SC} and V_{OC}, AFL3 408 exhibits the most efficient photoelectricity conversion efficiency 409 and maximum η of 5.81% (V_{0C} = 760 mV, I_{SC} = 11.36 mA/cm², and

410 ff = 0.68) under the simulated AM 1.5 G irradiation (100 mW/cm²).

411 **4. Conclusion**

412 We synthesized three novel triarylamine dye sensitizers contain-413 ing fluorenyl and biphenyl moieties in a triarylamine donor unit, a conjugate bridge with benzene, thiophene, and furan, and a 414 415 cyanoacrylic acid acceptor. We applied the synthesized dye sensitizer 416 to DSSCs. The spectral, photovoltaic, and electrochemical properties 417 of the synthesized dye sensitizers were systematically investigated 418 and compared on the basis of the differences in π -bridges. Compared 419 with the benzene bridge, the thiophene and furan bridges improved 420 the spectral properties of the sensitizers. The light absorptivity of the 421 sensitizers was improved. AFL2 and AFL3 possessed a long absorption 422 maximum and a broad light-harvesting region.

423 The introduction of thiophene and furan linkers increased the 424 short circuit photocurrent (I_{SC}) and reached high efficiency. Among 425 the three triarylamine dye sensitizers, the cell-based on the furan 426 (AFL3) linkers exhibited the highest photoelectricity conversion 427 efficiency of 5.81% (V_{OC} = 760 mV, J_{SC} = 11.36 mA/cm², and 428 ff = 0.68). The results reveal that these organic triarylamine dyes 429 are promising in the development of DSSCs and the optimization of 430 their chemical structure and the device is in progress to further 431 improve their energy conversion efficiency. In order to broaden the 432 absorption spectrum and decrease the LUMO energy of the dyes, D-433 D-A- π -A system can be designed.

434 Uncited reference

435 **Q3** [24].

436 Acknowledgments

The authors gratefully acknowledge for funding: NationalNatural Science Foundation of China (No. 21176223); National

Natural Science Foundation of China (No. 21406202) and Natural 439 Science Foundation of Zhejiang province (No. LY15B020009). 440

References

- A. Mishra, M.K.R. Fischer, P. Bäuerle, Metal-free organic dyes for dye-sensitized solar cells: from structure: property relationships to design rules, Anew. Chem. Int. Ed. Engl. 48 (2009) 2474–2499.
- [2] R.K. Kanaparthi, J. Kandhadi, L. Giribabu, Metal-free organic dyes for dye-sensitized solar cells: recent advances, Tetrahedron 68 (2012) 8383–8393.
- [3] S. Mathew, A. Yella, P. Gao, et al., Dye-sensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers, Nat. Chem. 6 (2014) 242–247.
- [4] Z. Ning, H. Tian, Triarylamine: a promising core unit for efficient photovoltaic materials, Chem. Commun. (2009) 5483–5495.
- 5] S.B. Wang, J.C. Guo, L. He, et al., Influence of thiophene and benzene unit in triphenylamine dyes on the performance of dye-sensitized solar cells, Synth. Met. 168 (2013) 1–8.
- [6] L. Alibabaei, J.H. Kim, M. Wang, et al., Molecular design of metal-free D-π-A substituted sensitizers for dye-sensitized solar cells, Energy Environ. Sci. 3 (2010) 1757–1764.
- [7] K. Hara, Z.S. Wang, Y. Cui, A. Furube, N. Koumura, Long-term stability of organicdye-sensitized solar cells based on an alkyl-functionalized carbazole dye, Energy Environ. Sci. 2 (2009) 1109–1114.
- [8] T. Horiuchi, H. Miura, K. Sumioka, S. Uchida, High efficiency of dye-sensitized solar cells based on metal-free indoline dyes, J. Am. Chem. Soc. 126 (2004) 12218–12219.
- [9] W.J. Wu, J.B. Yang, J.L. Hua, et al., Efficient and stable dye-sensitized solar cells based on phenothiazine sensitizers with thiophene units, J. Mater. Chem. 20 (2010) 1772–1779.
- [10] H.N. Tian, X.C. Yang, R.K. Chen, A. Hagfeldt, L.C. Sun, A metal-free "black dye" for panchromatic dye-sensitized solar cells, Energy Environ. Sci. 2 (2009) 674–677.
- [11] Y. Numata, I. Ashraful, Y. Shirai, L.Y. Han, Preparation of donor-acceptor type organic dyes bearing various electron-withdrawing groups for dye-sensitized solar cell application, Chem. Commun. 47 (2011) 6159–6161.
- [12] Y.Z. Wu, M. Marszalek, S.M. Zakeeruddin, et al., High-conversion-efficiency organic dye-sensitized solar cells: molecular engineering on D–A– π -A featured organic indoline dyes, Energy Environ. Sci. 5 (2012) 8261–8272.
- [13] S. Namuangruk, R. Fukuda, M. Ehara, et al., D-D-π-A-type organic dyes for dyesensitized solar cells with a potential for direct electron injection and a high extinction coefficient: synthesis, characterization, and theoretical investigation, J. Phys. Chem. C 116 (2012) 25653–25663.
- [14] C.J. Zhong, J.R. Gao, Y.H. Cui, T. Li, L. Han, Coumarin-bearing triarylamine sensitizers with high molar extinction coefficient for dye-sensitized solar cells, J. Power Sources 273 (2015) 831–838.
- [15] W.X. Gao, M. Liang, Y.L. Tan, et al., New triarylamine sensitizers for high efficiency dye-sensitized solar cells: recombination kinetics of cobalt(III) complexes at titania/dye interface, J. Power Sources 283 (2015) 260–269.
- [16] X.Z. Wang, J. Yang, H. Yu, et al., A benzothiazole-cyclopentadithiophene bridged D-A-π-A sensitizer with enhanced light absorption for high efficiency dyesensitized solar cells, Chem. Commun. 50 (2014) 3965–3968.
- [17] W.D. Zeng, Y.M. Cao, Y. Bai, et al., Efficient dye-sensitized solar cells with an organic photosensitizer featuring orderly conjugated ethylenedioxythiophene and dithienosilole blocks, Chem. Mater. 22 (2010) 1915–1925.
- [18] K.S.V. Gupta, S.P. Singh, A. Islam, L. Han, M. Chandrasekharam, Simple fluorene based triarylamine metal-free organic sensitizers, Electrochimi. Acta 174 (2015) 581–587.
- [19] K.R.J. Thomas, N. Kapoor, C.P. Lee, K.C. Ho, Organic dyes containing pyrenylaminebased cascade donor systems with different aromatic π linkers for dye-sensitized solar cells: optical, electrochemical, and device characteristics, Chem. Asian J. 7 (2012) 738–750.
- [20] F. Wu, J.L. Liu, L.T.L. Lee, et al., Dye-sensitized solar cells based on functionalized truxene structure, Chin. Chem. Lett. 26 (2015) 955–962.
- [21] S.Y. Qu, B. Wang, F.L. Guo, et al., New diketo-pyrrolo-pyrrole (DPP) sensitizer containing a furan moiety for efficient and stable dye-sensitized solar cells, Dyes Pigm. 92 (2012) 1384–1393.
- [22] J.X. He, F.L. Guo, X. Li, et al., New bithiazole-based sensitizers for efficient and stable dye-sensitized solar cells, Chem. Eur. J. 18 (2012) 7903–7915.
- [23] P. Shen, X.P. Liu, S.H. Jiang, et al., Effects of aromatic π-conjugated bridges on optical and photovoltaic properties of N,N-diphenylhydrazone-based metal-free organic dyes, Org. Electron. 12 (2011) 1992–2002.
- [24] J.B. Yang, F.L. Guo, J.L. Hua, et al., Efficient and stable organic DSSC sensitizers bearing quinacridone and furan moieties as a planar π -spacer, J. Mater. Chem. 22 (2012) 24356–24365.
- [25] J.X. He, J.L. Hua, G.X. Hu, et al., Organic dyes incorporating a thiophene or furan moiety for efficient dye-sensitized solar cells, Dyes Pigm. 104 (2014) 75–82.
- [26] M. Liang, W. Xu, F.S. Cai, et al., New triphenylamine-based organic dyes for efficient dye-sensitized solar cells, J. Phys. Chem. C 111 (2007) 4465–4472.
- [27] K.R.J. Thomas, Y.C. Hsu, J.T. Lin, et al., 2,3-disubstituted thiophene-based organic dyes for solar cells, Chem. Mater. 20 (2008) 1830–1840.
- [28] Z.S. Wang, K. Hara, Y. Dan-oh, et al., Photophysical and (photo) electrochemical properties of a coumarin dye, J. Phys. Chem. B 109 (2005) 3907–3914.
- [29] R.G. Parr, W.T. Yang, Density-functional theory electronic structure of molecules, Annu. Rev. Phys. Chem. 46 (1995) 701–728.

Please cite this article in press as: Y. Xie, et al., Novel organic dye sensitizers containing fluorenyl and biphenyl moieties for solar cells, Chin. Chem. Lett. (2016), http://dx.doi.org/10.1016/j.cclet.2016.06.042

,

441

442

443

444

445

446

447

448

449

450

451

452

453

454

455

456

457

458

459

460

8

ARTICLE IN PRESS

Y. Xie et al./Chinese Chemical Letters xxx (2016) xxx-xxx

- 522 523 524 525 526 527 528 529
- [30] Z.M. Wu, C.Y. Rong, T. Lu, P.W. Ayers, S.B. Liu, Density functional reactivity theory study of S_N2 reactions from the information-theoretic perspective, Phys. Chem. Chem. Phys. 17 (2015) 27052–27061.
- [31] S. Chaurasia, Y.C. Chen, H.H. Chou, Y.S. Wen, J.T. Lin, Coplanar indenofluorene-based organic dyes for dye-sensitized solar cells, Tetrahedron 68 (2012) 7755–7762.
- [32] S.Y. Cai, X.H. Hu, J.L. Han, et al., Efficient organic dyes containing dibenzo heterocycles as conjugated linker part for dye-sensitized solar cells, Tetrahedron 69 (2013) 1970–1977.
- [33] L. Han, X.Y. Zu, Y.H. Cui, et al., Novel D-A-π-A carbazole dyes containing benzothiadiazole chromophores for dye-sensitized solar cells, Org. Electron. 15 (2014) 1536–1544.
- [34] K. Hara, M. Kurashige, Y. Dan-oh, et al., Design of new coumarin dyes having thiophene moieties for highly efficient organic-dye-sensitized solar cells, New J. Chem. 27 (2003) 783–785.