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Jun Cheng, Fang Zhang, Ke Li, Jie Li, Xiaoqing Lu, Jingxia Zheng, Kunpeng Guo, Shihe Yang, Qingchen Dong

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# **Graphical Abstract**



The self-assembled *J*-aggregates of a newly synthesized planar dithiafulvene sensitizer optimized the  $TiO_2/dye$  interface, uplifting the power conversion efficiency from 4.68% to 7.48% alongside with a high open-circuit voltage of above 850 mV.

## A planar dithiafulvene based sensitizer forming *J*-aggregates on TiO<sub>2</sub>

## photoanode to enhance the performance of dye-sensitized solar cells

Jun Cheng, <sup>a</sup> Fang Zhang, <sup>a</sup> Ke Li, <sup>c</sup> Jie Li, <sup>a</sup> Xiaoqing Lu, <sup>c</sup> Jingxia Zheng, <sup>a</sup> Kunpeng Guo, <sup>\*a</sup> Shihe Yang, <sup>\*b</sup> Qingchen Dong<sup>a</sup>

a Ministry of Education Key Laboratory of Interface Science and Engineering in Advanced Materials, Research Center of Advanced Materials Science and Technology, Taiyuan University of Technology, Taiyuan 030024, P. R. China

b Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

c College of Science, China University of Petroleum, Qingdao, Shandong 266555, China.

Corresponding Author: <a href="mailto:guokunpeng@tyut.edu.cn">guokunpeng@tyut.edu.cn</a>; <a href="mailto:chsyang@ust.hk">chsyang@ust.hk</a>

### Abstract

A newly planar dithiafulvene sensitizer (**DTF-C4**) trending to form *J*-aggregates on the surface of mesoporous  $TiO_2$  by simply rinsing with a poor solvent acetonitrile was synthesized. We further show that the self-assembled *J*-aggregates optimized the  $TiO_2$ surface utilization, enhanced the light harvesting ability by broadening and red-shifting the absorption, and suppressed the electron recombination, thereby significantly promoting the solar cell efficiency. Compared to the photoanode surface modified with **DTF-C4** and the classical coadsorbent chenodeoxycholic acid (CDCA), the DSC based the **DTF-C4** compact *J*-aggregates exhibited a dramatically improved performance without the loss of adsorbed dyes, uplifting the power conversion efficiency from 4.68% to 7.48% alongside with a high open-circuit voltage of above

850 mV, which is higher than that of the commercial N719-based cell (770 mv).

**KEYWORDS:** dye-sensitized solar cells; planar dithiafulvene; *J*-aggregates; surface engineering; light harvesting; electron recombination

### 1. Introduction

Dye-sensitized solar cells (DSCs) consisting of sensitizers adsorbed on mesoporous semiconducting metal oxide (e.g., TiO<sub>2</sub>) that convert sunlight to electricity have generated considerable research and commercial interest. This interest is brought about by the fact that their low cost and ease of device fabrication [1]. Compared to ruthenium-polypyridyl complex sensitizers, donor- $\pi$ -bridge-acceptor (D- $\pi$ -A)-type metal-free organic sensitizers exhibit cost-effective synthesis and flexibility of molecular structure tailoring to meet practical demand [2, 3]. Recently, an N-annulated indenoperylene (NIP) as electron-donor based metal-free organic dyes has achieved power conversion efficiency ( $\eta$ ) of 12.5%, close to the DSCs record efficiency of 13% based on zinc porphyrin sensitizer [4,5]. In parallel with the development of sensitizers, the dye adsorption motifs on the surface of TiO<sub>2</sub> have also attracted much attention for understanding the photovoltaic behavior and for optimizing the device performance, as the charge separation takes place right at the TiO<sub>2</sub>/dye interface [6-12]. The present work seeks to address the challenge of developing a special dye adsorption motif that can enhance DSC performance.

It is well known that organic dyes are prone to form aggregates when adsorbed onto TiO<sub>2</sub> surface, which is conventionally regarded as an adverse behavior for decreasing

the DSCs performance [13-15]. This is because the vacant sites on the  $TiO_2$  surface between dye aggregates would lead to adverse electron recombination, thus decreasing the open-circuit voltage ( $V_{oc}$ ) [16-18]. In order to tackle this problem, several strategies have been developed that include the coating of inorganic barrier layers, the introduction of co-adsorbents and deposit insulating and transparent SiO<sub>2</sub> onto the vacant sites of TiO<sub>2</sub> surface [19-24]. Among them, utilization co-adsorbents, e.g., chenodeoxycholic acid (CDCA), that is regarded as a simple way to suppress dye aggregation and/or electron recombination by competitive adsorption with dyes [22, 23]. However, in order to further improve the DSCs performance, full coverage of the TiO<sub>2</sub> surface by the dye self-assembled layer is considered to be the most efficient TiO<sub>2</sub>/dye interface configuration of a cell [25, 26]. Full dye coverage can address the issue of keeping the amount of adsorbed dye on TiO<sub>2</sub>, which is expected to maximize the light absorption efficiency, as well as short-circuit current density  $(J_{sc})$  of a DSC. Further, a compact dye block layer will reduce recombination losses by separating the oxidized species in electrolyte and the TiO<sub>2</sub>, leads to improve  $V_{oc}$ . In this context, turning the unfavorable aspects of dye molecule aggregates to positive effects on DSCs performance is a challenge [9, 27].

Crystallization and precipitation from poor solvent result in molecular stacking with well-defined motifs in many organic dyes that exhibit advanced photo-electronic properties have been reported [28, 29]. Inspired by this, we exploit the strong S-S interactions between adjacent dithiafulvenyl unit and poor solubility of dithiafulvene sensitizers in acetonitrile to form dye aggregates on TiO<sub>2</sub> surface for efficient DSCs.

Herein, we introduce a surface modification strategy of  $TiO_2$  photoanodes with a planar geometry dithiafulvene sensitizer (**DTF-C4**, Fig. 1) self-assembled *J*-aggregates to realize an optimized  $TiO_2$  surface utilization by pristine dyes and, as a result, to enhance the light harvesting capability and to retard electron recombination more effectively than with part dye aggregates covering and classical disturb dye aggregates with co-adsorbents CDCA.



Fig. 1 Molecular structure of DTF-C4.

## 2. Experimental section

### 2.1. Materials and reagents

All solvents and reagents, unless otherwise stated, were of purist quality and used as received. 3,4-ethoxylene dioxy thiophene, 4-formylphenylboronic acid, triethyl phosphite, Pd(PPh<sub>3</sub>)<sub>4</sub>, and cyanoacetic acid were purchased from Energy Chemical. FTO conductive glasses (sheet resistance of 15  $\Omega$ /sq, Nippon Sheet Glass) were used. 2.2. *Characterization* 

NMR spectra (<sup>1</sup>H and <sup>13</sup>C) were recorded at room temperature on Bruker AV 400MHz, Data are listed in parts per million (ppm) on the delta scale ( $\delta$ ) and coupling constants were reported in Hz. The splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet) and br (broad). UV-Vis spectra of dye in solution and loading on TiO<sub>2</sub> films were measured with a HITIACH

U-3900 spectrometer at room temperature. Photoluminescent (PL) spectrum was recorded in a Horiba Fluoromax 4 spectrometer in diluted THF solution  $(1 \times 10^{-5} \text{ M})$ . Cyclic voltammetry of dye was carried out on a CHI600E Electrochemical Analyzer at a scan rate 0.1V s<sup>-1</sup>. The oxidation potential of the sensitizer was measured in DMF with TBAPF<sub>6</sub> (0.1 M) as electrolyte and glassy carbon as working electrode, Ag/Ag+ as reference electrode, Pt as counter electrode. The potential of the reference electrode was calibrated with Fc/Fc+ as an internal reference and converted to normal hydrogen electrode (NHE) by addition of 630 mV.

### 2.3. Fabrication and characterization of DSCs

The preparation of DSCs photoanode and electrolyte as follows the previous literature [30]. In cell assembly, for type I based cells, the DTF-C4 was loaded onto the TiO<sub>2</sub> (~ 12µm thick) film by immersion into its THF solutions (0.5 mM dye) with CDCA (10 mM) for 24 h at room temperature. For type II and type III based cells, the **DTF-C4** was loaded onto the TiO<sub>2</sub> films by immersion into their THF solutions (0.5 mM dye) with dye) without any coabsorbants for 24 h at room temperature. Before drying under vacuum, the type I and type III films were rinsed with acetonitrile to remove the unabsorbed dyes multiple times until the solution became clear, and, the type II based films were rinsed with THF. Then, the films were assembled into a solar cell together with a Pt–sputtered FTO counter electrode and acetonitrile / valeronitrile (85:15, volume ratio) electrolyte containing 0.6 M 1, 2–dimethyl–3–propylimi dazolium iodide, 0.03 M I<sub>2</sub>, 0.1 M guanidinium thiocyanate, and 0.5 M 4–tert-butylpyridine. The active area of the photoanode film for the DSC performance test was typically

 $0.25 \text{ cm}^{-2}$ . In the interest of making comparison, N719 DSCs were also fabricated and evaluated under the same conditions.

The photocurrent density-voltage (*J-V*) characteristics curves were measured by the Newport PVIV-3A system. The light source (Oriel solar simulator, 450 W Xe lamp, AM 1.5 global filter) was calibrated to 1 sun (100 mW cm<sup>-2</sup>). Incident Photon to Current Efficiency (IPCE) was measured at varying wavelengths (350-850 nm) with an interval of 5 nm. Intensity modulated photovoltage spectroscopy (IMVS) was measured on the same electrochemical workstation (Zahner, Zennium) with a frequency response analyzer under an intensity modulated (5-70W m<sup>-2</sup>) light emitting diode (525 nm) driven by a Zahner (PP211) source supply. The frequency range was set from 100 KHz to 0.1 Hz.

### 2.4. Synthetic procedures

### 2.4.1. 5,7-dibromo-2,3-dihydrothieno[3,4-b][1,4]dioxine (A4)

A THF (20 mL) solution of 3,4-ethoxylene dioxy thiophene (1.42 g, 10.60 mmol), N-bromosuccinimide (3.74 g, 12.80 mmol) and acetic acid (20 mL) were charged sequentially into a round-bottom flask. The mixture was stirred for 2h at room temperature. After the reaction, pouring the reaction mixture into distilled water and stirring with a glass rod, precipitate was filtered to afford **A4** as a white solid (2.50 g, 8.30 mmol, yield 83%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,ppm):  $\delta$ =4.27 (s, 4H).

### 2.4.2. 4,4'-(2,3-dihydrothieno[3,4-b][1,4]dioxine-5,7-diyl)dibenzaldehyde (**B**4)

4-formylphenylboronic acid (2.40 g, 16.00 mmol) was treated with A5 (2.00 g,

6.70 mmol) in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (0.49 g, 426 μmol), 1 N aqueous solution of K<sub>2</sub>CO<sub>3</sub> (25 mL) and 1,2-dimethoxyethane (100 mL). The mixture was refluxed for 6 h. After cooling down to room temperature, the solvent was removed by rotary evaporation and the residue was purified by silicon gel column chromatography with petroleum ether: aceticether (6: 1, v:v) as eluent to afford **B4** as a yellow powder (1.41 g, yield 60%).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$ =9.98 (s, 2H); 7.93 (d, 4H, *J* = 6.4 Hz, ); 7.88 (d, 4H, *J* = 6.4 Hz); 4.44 (s, 4H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$ =190.86, 139.93, 137.88, 133.76, 129.57, 125.64, 115.70, 64.02. MALDI-TOF: m/z [M]<sup>+</sup> cacld. C<sub>20</sub>H<sub>14</sub>O<sub>4</sub>S, 350.0613; found: 350.0609.

2.4.3. 4-(7-(4-((4,5-bis(hexylthio)-1,3-dithiol-2-ylidene)methyl)phenyl)-2,3dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzaldehyde (**C4**)

**HDT**(1.01 g, 2.76 mmol) and B4 (0.80 g, 2.70 mmol) were dissolved in 25 mL of boiling toluene under a nitrogen atmosphere, then P(OEt)<sub>3</sub> (8 mL) was added. The resulting mixture was refluxed for 3 h. After cooling and addition of dichloromethane, the mixture was washed with brine and dried on magnesium sulfate. Solvents were removed by rotary evaporation and the residue was purified by silicon gel column chromatography with petroleum ether: aceticether (4: 1, v:v) as eluent to afford **C4** as yellow solid (0.81 g, yield 52%).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,ppm):  $\delta$ =9.83 (s, 1H); 7.82 (q, 4H, *J*= 8.4 Hz); 7.69 (d, 2H, *J*= 4.4 Hz); 7.17 (t, 3H, *J*= 7.2 Hz); 6.39 (s, 1H); 4.33 (d, 4H, *J*= 5.2 Hz); 2.76 (t, 4H, *J*= 7.2 Hz); 1.58 (m, 4H, *J*=5.2Hz); 1.35 (m, 4H); 1.23 (m, 8H); 0.82 (q, 6H, *J*=6.8Hz). <sup>13</sup>C-NMR (151 MHz, DMSO, ppm):  $\delta$ =191.91,

141.07, 139.23, 138.12, 134.55, 133.83, 131.27, 130.13, 129.40, 127.08, 126.93, 125.75, 125.35, 123.78, 116.42, 114.25, 112.62, 64.78, 64.49, 35.21, 35.14, 30.73, 29.31, 29.15, 27.43, 27.39, 21.99, 21.98, 13.83, 13.82. MALDI-TOF: m/z [M]<sup>+</sup> cacld. C<sub>35</sub>H<sub>40</sub>O<sub>3</sub>S<sub>5</sub>, 668.1581; found: 668.1578.

# 2.4.4. (E)-3-(4-(7-(4-((4,5-bis(hexylthio)-1,3-dithiol-2-ylidene)methyl)phenyl)-2,3dihydrothieno[3,4-b][1,4]dioxin-5-yl)phenyl)-2-cyanoacrylic acid (**DTF-C4**)

A CH<sub>3</sub>CN (25 mL) solution of compound C4(0.80 g,0.52 mmol), cyanoacetic acid (66 mg,0.78 mmol) and two drops of piperidine were charged sequentially into a three-necked flask and heated to reflux till no starting material C4 was detected by the TLC plate. After cooling to room temperature, solvents were removed by rotary evaporation, and the residue was purified by silica gel column chromatography with CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>OH (6:1, v:v) as eluent to afford the dye **DTF-C4** as a dark-red solid (0.26g, yield 36%). <sup>1</sup>H NMR (400 MHz, DMSO,ppm):  $\delta$ =7.92 (d, 3H, *J*= 8.4 Hz); 7.79 (d, 2H, *J*= 8.4 Hz); 7.72 (d, 2H, *J*= 8.8 Hz); 7.25 (d, 2H, *J*= 8.8 Hz); 6.71 (s, 1H); 4.42 (s, 4H); 2.85 (t, 4H, *J*= 7.2 Hz); 1.55 (m, 4H, *J*=6.8Hz); 1.35 (m, 4H); 1.23 (m, 8H); 0.85 (q, 6H, *J*=7.2Hz). <sup>13</sup>C-NMR (151 MHz, DMSO, ppm):  $\delta$ =166.94, 162.05, 140.82, 139.27, 134.49, 131.17, 130.68, 126.97, 125.74, 125.40, 123.86, 115.86, 114.33, 112.98, 64.76, 64.52, 35.18, 35.13, 30.71, 29.30, 29.13, 27.40, 27.35, 21.96, 13.83. MALDI-TOF: m/z [M]<sup>+</sup> cacld. C<sub>38</sub>H<sub>41</sub>NO<sub>4</sub>S<sub>5</sub>, 735.1639; found: 735.1637.

### 3. Results and discussion

### 3.1 Synthesis of DTF-C4

The synthetic procedure to DTF-C4 is depicted in Scheme 1. 4,5-bis(hexylthio)-1,3-dithiole-2-thione (HDT) was synthesized according to our previous work [30]. Bromination of compound 3,4-ethoxylene dioxy thiophene with NBS produced the brominated intermediates, and then Suzuki cross-coupling of brominated 5,7-dibromo-2,3-dihydrothieno[3,4-b][1,4]dioxine A4 and 4-formylphenylboronic acid produced the aromatic dialdehyde **B4**. Horner-Wittig condensation of HDT and aromatic dialdehyde B4 produced the key intermediate  $\pi$ -extended DTF-bearing aldehyde C4. Finally, Knoevenagel reaction of the resulting aldehyde C4 and cyanoacetic acid in the presence of piperidine afforded the target sensitizer compounds DTF-C4.



### 3.2 Theoretical calculations

The investigated **DTF-C4**, adopting a dithiafulvenyl unit as electron donor and phenyl- 3,4-ethoxylene dioxy thiophene-phenyl as  $\pi$ -bridge and cyanoacetic acid as electron acceptor and anchor group. To gain deep insight into the molecular geometry of **DTF-C4**, time-dependent functional theory (DFT) calculation was carried out at

the B3LYP/6-31+g\*\* level. The optimized molecular geometry of **DTF-C4** is shown in Fig. 2(a). Different from some organic sensitizers, e.g., triphenylamine based sensitizers with a sp<sup>3</sup> hybridization of the nitrogen atom, possess inherent huge sterically hindered configuration leads to large intermolecular distance, thus they reduce dye aggregation and intermolecular interactions on TiO<sub>2</sub> surface. The dihedral angel between the donated dithiafulvenyl unit and the  $\pi$ -bridge of **DTF-C4** is about 18°, implying a good planar geometry of this molecule, which makes the molecule trending to aggregate more closely in solid state compare to other organic sensitizer systems.



**Fig. 2** (a) Optimized molecular geometry of **DTF-C4** based on the B3LYP/6-31G\* level and (b) Electron-density distribution for the HOMO and LUMO of the **DTF-C4**.

DFT calculations further revealed the photoinduced charge separation of **DTF-C4**. As shown in Fig. 2(b), the HOMO electron density of **DTF-C4** is mainly distributed on the dithiafulvenyl donor part and the adjacent aromatic rings, while the LUMO electron density is shifted to the acceptor unit. Therefore, upon excitation, the HOMO-LUMO excitation can efficiently transfer the electron from donor part to the acceptor part anchored on  $TiO_2$ , which is desirable for the required charge separation

in DSCs.



3.3 UV-vis absorption and electrochemical characterization

**Fig. 3** (a) Absorption and PL spectra of **DTF-C4** in THF (10<sup>-5</sup>M). (b) UV-Vis absorption spectra of **DTF-C4** in THF/acetonitrile mixtures with different acetonitrile fraction. (c) Cyclic voltammograms of **DTF-C4** in DMF.

**DTF-C4** is well soluble in THF, however, nearly insoluble in acetonitrile. The UV-Vis absorption spectrum of **DTF-C4** in dilute tetrahydrofuran (THF) is shown in Fig. 3. (a), and the corresponding spectroscopic parameters extracted are summarized in Table 1. At concentration  $10^{-5}$ M, it was found that the absorption maximum ( $\lambda_{max}$ ) of **DTF-C4** in monomeric state peaks at 435 nm (molar extinction coefficient  $\varepsilon = 4.18 \times 104 \text{ M}^{-1} \text{ cm}^{-1}$ ), which can be attributed to the intramolecular charge transfer transition. The absorption band of the monomer extends to ~ 550 nm. However, the absorption begins to show red-shifting when a large amount of poor solvent acetonitrile is added to the THF/acetonitrile mixture, as shown in Fig. 3. (b). Compare with its pure THF solution, red-shifted absorption onsets by ~ 50 nm is observed when acetonitrile fraction reaches 90% indicates that *J*-aggregation may occur.

Cyclic voltammograms (CV) in combination with the excitation transition energy  $(E_{0-0})$  determined by the intersection of absorption and PL spectra were carried out to

determine the molecular orbital energy levels of **DTF-C4**, as shown in Fig. 3 (a) and (b). As indicated in Table 1, the highest occupied molecular orbital (HOMO) energy level of **DTF-C4**, corresponds to the first oxidation potentials ( $E_{ox}$ ), is 1.48V vs NHE, which is sufficiently positive than the iodine/iodide redox potential (0.4V vs NHE), indicating the regeneration of the photooxidized **DTF-C4** by accepting electrons from the surrounding  $\Gamma$  ions would be efficiently. The lowest unoccupied orbital (LUMO) energy level of **DTF-C4** is -1.07V, calculated as  $E_{ox} - E_{0.0}$ , is sufficiently negative relative to the conduction-band edge of TiO<sub>2</sub> (-0.5 V vs NHE), ensuring an efficient thermodynamic driving force for the electron injection.

 Table 1 Absorption and electrochemical properties of DTF-C4.

Sensitizer	$\lambda_{max}$	З	Eox	$E_{0-0}^{abs/em}$	$E_{ox} - E_{0-0}$
	(nm)	$(M^{-1} cm^{-1})$	(V vs NHE)	(eV)	(V vs NHE)
DTF-C4	435	$4.18 \times 10^{4}$	1.48	2.55	-1.07

3.4. DTF-C4 aggregated motifs on TiO<sub>2</sub> photoanodes



Fig. 4 UV-Vis absorption spectra of DTF-C4 on  $4\mu m$  TiO2 films under various conditions.

The profiles of the absorption spectra of TiO<sub>2</sub> films (4 $\mu$ m) with **DTF-C4** loading

and rinsing under various conditions show dramatically broaden and red-shift absorption relative to its solution spectrum, as shown in Fig. 4. Experimentally, all of the  $TiO_2$  films were immersed in solution of **DTF-C4** in good solvent THF with concentration of 0.5 mM, which ensure there are no aggregates in dye bath.



Fig. 5 Schematic illustration of the proposed three models of dye aggregated motifs on the  $TiO_2$  films under various conditions.

Firstly, to test the solvent effect impact on molecular stacking, dye-absorbed  $TiO_2$  films that before drying under vacuum were rinsed with good solvent THF and poor solvent acetonitrile, respectively. It was found the absorption band of dye loading films both rinsed by THF and acetonitrile extending to 650 nm, indicating the *J*-aggregates formation. Note that the absorption intensity in the region between 400 nm to 550 nm of the film rinsed by acetonitrile was a little higher than that of the film rinsed by THF when the two films have same thickness. This result suggests that different dye loading amounts on  $TiO_2$  films under these two conditions, and, the **DTF-C4** aggregated motifs on  $TiO_2$  surface show rinsing solvents solubility dependence. For acetonitrile, revealing a dominant compact *J*-aggregates formation that undergoes re-crystallization due to its poor solubility. For THF, due to its good solubility for **DTF-C4**, some absorbed **DTF-C4** molecules on the outermost surface

of TiO<sub>2</sub> film were rinsed, and, both *J*-aggregates and random dye aggregates formed. To prevent dye aggregation on the TiO<sub>2</sub> films, **DTF-C4** loading with co-absorbents CDCA (10 mM) were also investigated. It was found that whether rinsed with THF or acetonitrile, one observes a decreased intensity and narrowed absorption band for TiO<sub>2</sub> film with co-absorbents CDCA compare to those without co-absorbents ones, suggesting inhomogeneous distribution of the dye or dye aggregates throughout the TiO<sub>2</sub> surface due to the competitive adsorption result in lower amount of **DTF-C4** loading. Based on the current study, from disturbance of dye aggregation to *J*-aggregation formation, three models (A, B and C) of aggregated motifs for **DTF-C4** on TiO<sub>2</sub> films are proposed in Fig. 5.

3.5. Photovoltaic performance



**Fig. 6** (a) Photocurrent-voltage curves of the three types of DSCs and (b) Incident photon to current efficiency (IPCE) spectra of the three types of DSCs.

In order to evaluate the functions of the various dye aggregates on  $TiO_2$  films for DSCs performance, three types of cells based the above mentioned aggregated motifs were investigated by assembling ~  $12\mu m$  TiO<sub>2</sub> films as photoanode and  $\Gamma/I^{3-}$  as

electrolyte. The photocurrent density-voltage curves of the cells were measured under an irradiance of 100 mW cm<sup>-2</sup>, simulated AM 1.5 sunlight. Type I cells based model A were first selected as the aggregation disturbed devices. As shown in Fig. 6 (a) and Table 2, the type I based cells showed average power conversion efficiency  $(\eta)$  of 4.69%, with  $J_{sc}$  of 9.33 mA cm<sup>-2</sup>,  $V_{oc}$  of 716 mv and fill factor (FF) of 0.70. This result seems acceptable according to the UV-Vis spectrum of DTF-C4 in dilute solution. The average  $\eta$ ,  $J_{sc}$ ,  $V_{oc}$  and FF for type II cells base model B were 6.97%, 12.60 mA cm<sup>-2</sup>, 787 mv and 0.70, respectively. While the trend of  $J_{sc}$  is plausible according to Fig. 4., such a  $V_{oc}$  and  $\eta$  improving as the result of the J-aggregates forming is counter to conventional results. From Table 2, we find that the dye absorbed amounts of type II cells are higher than type I cells, indicating the J-aggregation formation based planar geometry of DTF-C4 on TiO<sub>2</sub> films is presumably to increasing DSCs performance with keeping the amounts of dye loading. To further test the J-aggregates domain effect for DSCs, type III cells based model C were explored. As expected, one observes a dramatically increased  $\eta$ ,  $J_{sc}$  and  $V_{oc}$  for type III cells. The average  $\eta$  and  $J_{sc}$  of the J-aggregates domain based type III cells were 7.48% and 13.48 mA cm<sup>-2</sup>, respectively. These values were over 1.5-fold and 1.4-fold higher than those in type I cells. Notably, a very impressive  $V_{oc}$  of 856 mv was obtained based type III cells, which was about 1.2-fold and 1.1-fold higher than that in type I cells and N719 based cells, respectively. The increased dye adsorbed amounts of type III cells also indicate more compact and ordered J-aggregation formation.

The incident photon-to-current conversion efficiency (IPCE) spectra shown in Fig. 6 (b) have confirmed the trend of  $J_{sc}$  variation in the order of type III > type II > type I. For type I, relatively low IPCE value (slightly higher than 60%) was observed. For type III, the IPCE curve is both broad in width extending from 350 nm to 580 nm and high in magnitude with values over 70%. Taken the dye absorbed amounts and red-shifting UV-Vis spectra into together, this difference in IPCE shows that the *J*-aggregates domain of the **DTF-C4** dye formed on TiO<sub>2</sub> films leads to enhanced light absorption capabilities and charge carrier injection, thus raising the *J*sc.

	I	$V_{ m oc}$	EE		Dye absorbed
Cells	$J_{\rm sc}$			η	amounts
	$[\mathrm{mAcm}^{-2}]$	[mv]		[%]	$[mol cm^{-2}]$
Type I	9.33	716	0.70	4.69	$(1.64\pm0.1) \times 10-7$
Type II	12.60	787	0.70	6.97	$(2.37\pm0.1) \times 10-7$
Type III	13.48	856	0.65	7.48	(2.52±0.1) × 10-7
N719	17.16	770	0.63	8.28	

Table 2 Photovoltaic performance of DSCs based on DTF-C4

### 3.6 Intensity-modulated photo-voltage spectroscopy

To understand the  $V_{oc}$  enhancement from type I to type III caused by the *J*-aggregation formation of the **DTF-C4** dye, we measured the injected electron lifetimes in the conduction band of TiO<sub>2</sub> by intensity-modulated photo-voltage spectroscopy (IMVS) as shown in Fig.7. It is well known the variation of electron lifetimes were attributed to different electron recombination times with respect to the redox electrolyte, which would influence  $V_{oc}$  dominantly. Obviously, the electron

lifetimes of the three types of cells showed a correlation between the *J*-aggregates and electron recombination. Especially, type III based cells with *J*-aggregates domain and hold the longest electron lifetime which is almost 10-fold higher than that of type I based cells. This result suggests that compact *J*-aggregates of **DTF-C4** form a thicker dye layer, thus preventing redox electron acceptors from approaching the TiO<sub>2</sub> surface efficiently. Namely, rinsing the absorbed planar geometry of **DTF-C4** on TiO<sub>2</sub> films with poor solvent acetonitrile would produce more *J*-aggregates, thus increase in  $V_{oc}$ .



Fig.7 Variation of electron lifetime for the three types of DSCs with incident light intensity.

### 4. Conclusion

In conclusion, we have developed a surface modification strategy with formation of J-aggregates of planar dithiafulvene sensitizer to improve the energy conversion efficiency of DSCs. The planar geometry of **DTF-C4** dye molecule and poor solvent acetonitrile effect endow **DTF-C4** molecules tend to form compact J-aggregates on the TiO<sub>2</sub> surface, extending the absorption spectra and without losing the amount of absorbed **DTF-C4** dyes, which enhancing the light absorption capability in solid state, thus increasing the photocurrent. Moreover, the compact J-aggregates of dye

molecules on the  $TiO_2$  surface passivating the surface to reduce the electron recombination significantly, resulting in an impressive Voc of 856 mv. This work paves a practical way to optimize dye/TiO<sub>2</sub> interface by *J*-aggregates of more efficient planar geometry dithiafulvene sensitizers for developing high-performance DSCs.

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# Highlights

- A newly planar geometry of dithiafulvene sensitizer **DTF-C4** was synthesized.
- Formation of *J*-aggregates of **DTF-C4** on TiO<sub>2</sub> by rinsing with a poor solvent acetonitrile.
- Increasing the *J*-aggregates of **DTF-C4** on TiO<sub>2</sub> lead to uplift PCE to 7.48% and V<sub>oc</sub> above 850 mv.
- *J*-aggregates of **DTF-C4** enhanced light harvesting ability and retarded electron recombination.

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