

## Electronic supplementary information (ESI) for

# “New organic dyes containing *E*- or *Z*-trifluoromethyl acrylic acid as the electron acceptors for dye-sensitized solar cell application: an investigation of the effect of molecular configuration on the power conversion efficiency of the cells”

By Jia Hong,<sup>a</sup> Hua Lai,<sup>a</sup> Yanmei Liu,<sup>a</sup> Chao Yuan,<sup>a</sup> Yuxue Li,<sup>b\*</sup> Ping Liu<sup>c\*</sup> and Qiang Fang<sup>a\*</sup>

<sup>a</sup>Key Laboratory of Organofluorine Chemistry and Laboratory for Polymer Materials, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai, 200032, PR China.  
E-mail: qiangfang@mail.sioc.ac.cn; Fax: (+86) 21-54925337

<sup>b</sup>State Key Laboratory of Organometallic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai, 200032, PR China.

<sup>c</sup>College of Materials and Engineering, South China University of Technology, Guangzhou, 510640, PR China.

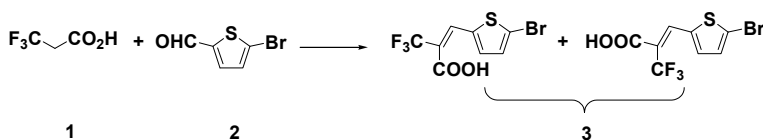
## 1. Materials and Instruments

All chemicals and reagents were used as received from Aldrich without further purification. Anhydrous THF was distilled from sodium under argon before use. Solvents in microwave irradiation were degassed by argon bubbling for 25 min. 10-Butyl-10H-phenothiazin-3-ylboronic acid was synthesized according to a reported procedure.<sup>1</sup>

<sup>1</sup>H and <sup>13</sup>C NMR spectroscopy were recorded on Varian mercury 300 or Bruker DRX spectrometer using CDCl<sub>3</sub> or *d*<sub>6</sub>-DMSO as solvent and tetramethylsilane (TMS) as internal standard. High-resolution mass spectra (HR MS) were obtained using Bruker APEX III FTMS. UV-Vis absorption and Fluorescence spectra were obtained with a Hitachi U-2910 and a Hitachi F-4500 spectrophotometer, respectively. Cyclic voltammetry were performed with Autolab PGSTAT30. Measurements were taken in a CH<sub>2</sub>Cl<sub>2</sub> solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as supporting electrolyte at a scan rate of 50mV s<sup>-1</sup> under nitrogen, using glassy carbon, AgCl/Ag and platinum wire, respectively, as working, reference and counter electrodes. A standard ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple was used to calibrate the oxidation peak.

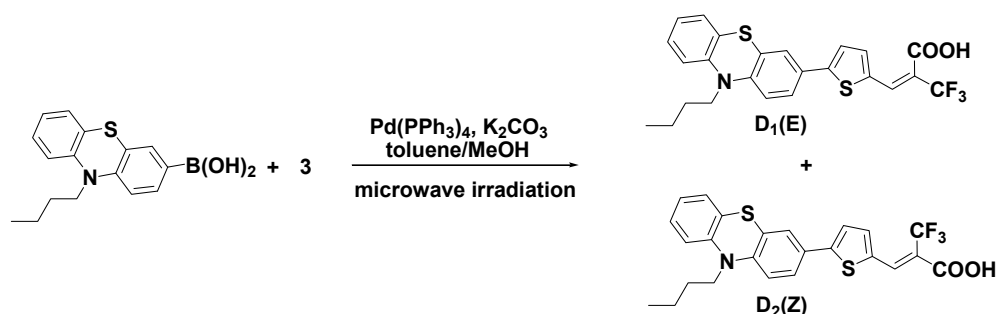
## 2. Synthesis of Organic Dyes

### 2.1 (*Z/E*)-3-(5-bromothiophen-2-yl)-2-(trifluoromethyl)acrylic acid (**3**)<sup>2</sup>



To a stirring solution of 5-bromothiophene-2-carbaldehyde (1.8 mL, 15 mmol), 3, 3, 3-trifluoropropanoic acid (0.88 mL, 0.4 mmol) and anhydrous THF (50 mL) was added  $\text{TiCl}_4$  (1.0 mol/L in  $\text{CH}_2\text{Cl}_2$ , 15 mL, 15 mmol) at room temperature under argon. The mixture was vigorously stirred for 0.5 h, followed by adding  $\text{Et}_3\text{N}$  (5.6 mL, 40 mmol). After being stirred for an additional 40 h, the reaction mixture was quenched by adding water, extracted with  $\text{CHCl}_3$  and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel with  $\text{CHCl}_3/\text{MeOH}$  (90/10) to give the crude product (2.45 g, 82%, Z/E mixture).

## 2.2 Synthesis of $\mathbf{D}_1(\mathbf{E})$ and $\mathbf{D}_2(\mathbf{Z})$



A mixture of 10-butyl-10H-phenothiazin-3-ylboronic acid (600 mg, 2 mmol), **3** (301 mg, 1 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (58 mg, 0.05 mmol), and  $\text{K}_2\text{CO}_3$  (552 mg, 4 mmol) was added in a mixture solution of degassed 10 mL toluene and 5 mL methanol. The mixture was heated by microwave irradiation at 80 °C for 10 min. The reaction was quenched by addition of cold water, extracted with  $\text{CHCl}_3$  and washed with brine. The combined organic extract was dried over anhydrous  $\text{MgSO}_4$  and filtered. After removal of the solvent by rotary evaporation, the obtained residue was purified by column chromatography on silica gel with a mixture of  $\text{CHCl}_3$  and MeOH (90:10, v/v) as the eluent to give  $\mathbf{D}_1(\mathbf{E})$  (30 mg),  $\mathbf{D}_2(\mathbf{Z})$  (100 mg) and a mixture of  $\mathbf{D}_1(\mathbf{E})$  and  $\mathbf{D}_2(\mathbf{Z})$  (120 mg). Characterization:  $\mathbf{D}_1(\mathbf{E})$ ,  $^{19}\text{F}$  NMR (282 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  -65.32;  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  13.73 (s, 1H), 7.87 (s, 1H), 7.80 (d,  $J$  = 3.9 Hz, 1H), 7.55-7.49 (m, 3H), 7.24-7.14 (m, 2H), 7.08-6.93 (m, 3H), 3.90 (t,  $J$  = 6.6 Hz, 2H), 1.70-1.64 (m, 2H), 1.44-1.35 (m, 2H), 0.88 (t,  $J$  = 7.5 Hz, 2H); MS (MALDI-TOF,  $m/z$ ): 475.2 ( $\text{M}^+$ ); HRMS (MALDI): calculated for  $\text{C}_{24}\text{H}_{20}\text{NO}_2\text{F}_3\text{S}_2^+$  475.0879, found 475.0882.  $\mathbf{D}_2(\mathbf{Z})$ ,  $^{19}\text{F}$  NMR (282MHz,  $\text{DMSO}-d_6$ ):  $\delta$  -57.26;  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  13.51 (s, 1H), 8.19 (s, 1H), 7.78 (d,  $J$  = 4.2 Hz, 1H), 7.59-7.53 (m, 3H), 7.24-7.14 (m, 2H), 7.06-6.93 (m, 3H), 3.90 (t,  $J$  = 6.6 Hz, 2H), 1.69-1.60 (m, 2H), 1.42-1.28 (m, 2H), 0.85 (t,  $J$  = 7.5 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  164.91, 152.21, 146.01, 144.40, 141.95, 139.29, 132.18, 128.25,

127.66, 127.23, 125.96, 124.94, 124.57, 124.16, 123.32, 123.20, 121.82, 116.50, 114.92, 114.59, 46.76, 28.62, 19.70, 13.82; MS (MALDI-TOF,  $m/z$ ): 475.2 ( $M^+$ ); HRMS (MALDI): calculated for  $C_{24}H_{20}NO_2F_3S_2^+$  475.0879, found 475.08821.

### 3. $^{19}F$ NMR spectra of the dyes

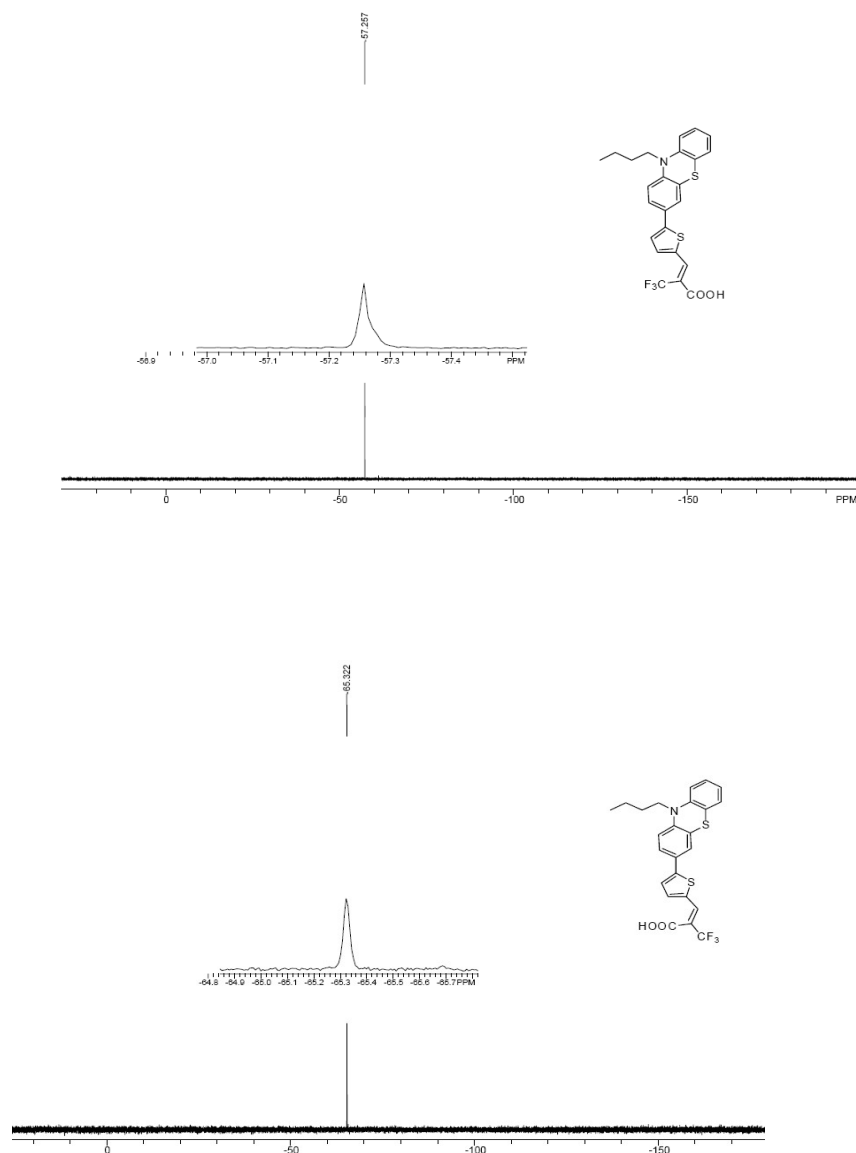


Fig. S1  $^{19}F$  NMR spectra of the dyes. Up: Z-isomer, down: E-isomer.

### 3. Optical properties

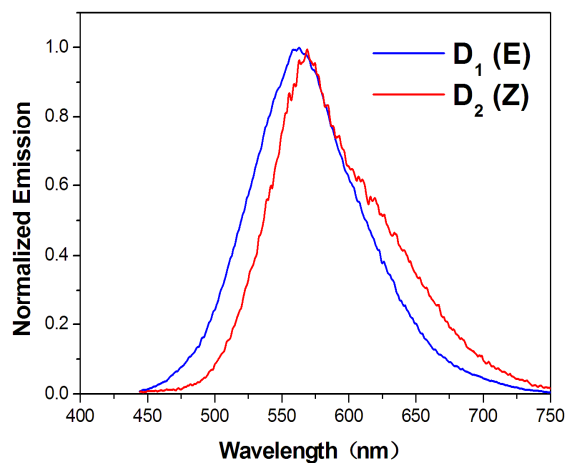


Fig.S2 Photoluminescent spectra of the dyes in CH<sub>2</sub>Cl<sub>2</sub>.

### 4. Electrochemical properties

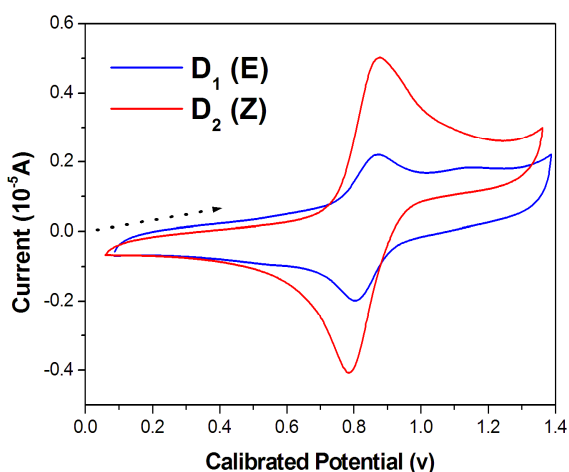


Fig.S3 Cyclic voltammetry curves of the dyes in CH<sub>2</sub>Cl<sub>2</sub>.

### 5. Fabrication and Photovoltaic Performance of DSSCs

The nanocrystalline TiO<sub>2</sub> (13 nm) electrodes (12 μm) and Pt-coated counter electrodes were provided by HeptaChroma Solar Tech Co., China. The TiO<sub>2</sub> electrodes were immersed in CH<sub>3</sub>CN solution containing the dyes with a concentration of 1.0×10<sup>-4</sup> M for 24 h at ambient temperature, and then washed with ethanol and dried under argon atmosphere. The dye-coated film was thus obtained, which was then sealed with a Pt-coated counter electrode using a hot melt adhesive (25 mm, Surlyn, DuPont). The electrolyte, composed of 1.0 M

1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.03 M I<sub>2</sub>, 0.05 M LiI, 0.1 M guanidinium thiocyanate (GuSCN) and 0.5 M 4-tert-butylpyridine (4-TBP) in a mixture solvent of acetonitrile and valeronitrile (85/15 v/v) was injected through a hole in the counter electrode by capillary force. The active area of the TiO<sub>2</sub> film was *ca.* 0.2375 cm<sup>2</sup>.

The photocurrent-voltage characteristics of the DSSCs were measured using a Keithley 2420 sourcemeter under illumination of AM 1.5G solar light from 450W Oriel Class AAA solar simulator (Model 92250A-450). The output power was calibrated by a monocrystalline silicon reference cell (Model 91150a). Incident photo-to-current conversion efficiency (IPCE) of the DSSCs was measured by a direct current (DC) method, using a light source from a 300 W Xenon Lamp (Oriel 6258), a monochromator (Oriel 74125), a Si detector (Oriel 71030NS) and an optical power meter (Oriel 70310).

## References

1. S. H. Kim, H. Kim, C. Sakong, J. Namgoong, S. Park, M. Ko, C. Lee, W. Lee, J. Kim, *Org. Lett.*, **2011**, 5784.
2. Y. Liu, H. Lai, B. Rong, T. Zhou, J. Hong, C. Yuan, S. Zhao, X. Zhao, B. Jiang and Q. Fang, *Adv. Synth. Catal.*, **2011**, 353, 3161.