

## Supporting Information

### Energy-Level and Molecular Engineering of Organic D- $\pi$ -A Sensitizers in Dye-Sensitized Solar Cells

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## 1. Materials

All solvents and reagents, unless otherwise stated, were of puriss quality and used as received. Lithium diisopropylamide, 4-bromoaniline, and tetra-*n*-butylammonium hexafluorophosphate were purchased from Aldrich. Guanidinium thiocyanate, 2-cyanoacetic acid, ethyl mercaptoacetate, and 3 $\alpha$ ,7 $\alpha$ -dihydroxy-5 $\beta$ -cholic acid (cheno) were purchased from Fluka. 1-Ethyl-3-methylimidazolium tetracyanoborate and 400-nm-sized TiO<sub>2</sub> anatase particles were received as gifts from Merck and Catalysts & Chemical Ind. Co., respectively. The synthesis of 1,3-dimethylimidazolium iodide and 1-ethyl-3-methylimidazolium iodide were described in our previous paper.<sup>S1</sup> Thieno[3,2-*b*]thiophene,<sup>S2</sup> (thieno[3,2-*b*]thiophen-2-yl)boronic acid,<sup>S3</sup> 1-iodo-4-methoxybenzene,<sup>S4</sup> 1-(hexyloxy)-4-iodobenzene,<sup>S5</sup> 1,4-dimethoxybenzene,<sup>S6</sup> and 1,4-dimethoxy-2-nitrobenzene<sup>S7</sup> were synthesized according to the corresponding literature methods.

## 2. Dye Syntheses

**Synthesis of 2,5-Dimethoxyaniline (1c).** 1,4-Dimethoxy-2-nitrobenzene (15 g) and hydrochloric acid (95 mL) were added to THF (375 mL). Under violent stirring tin powder (48.5 g) was slowly added to the above solution, followed by THF (250 mL). The mixture was stirred at room temperature for 20 min and then poured into a mixture of H<sub>2</sub>O (500 mL) and dichloromethane (1000 mL). After adjusting the solution to be basic through the addition of potassium hydroxide, the solid was filtered off and the separated organic phase was dried over anhydrous sodium sulfate. The removal of

organic solvent gives a white powder. Yield: 92%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  3.73 (s, 3H), 3.80 (s, 3H), 6.25 (q, 1H), 6.34 (d, 2H), 6.69 (d, 2H).

**General Synthesis of Triphenylamines (3a, 3b, 2c and 3d).** A stirring mixture of aryl iodides (12.5 mmol), aryl amine (5 mmol), and 1,10-phenanthroline (1 mmol) in toluene (10 mL) was heated to 100 °C under Ar, while potassium hydroxide (40 mmol) and cuprous chloride (1 mmol) were added. The mixture was refluxed for 12 h, and then poured into water and extracted three times with dichloromethane. The organic layer was washed with a sodium carbonate aqueous solution and  $\text{H}_2\text{O}$ , and subsequently dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was purified on a silica gel column.

***N,N*-Bis(4-diphenyl)-4-bromoaniline (3a).** Hexane was used as eluent and a white powder was obtained at a 65% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  6.94 (d, 2H), 7.02 (t, 4H), 7.06 (d, 2H), 7.25 (t, 4H), 7.32 (d, 2H).

***N,N*-Bis(4-methoxyphenyl)-4-bromoaniline (3b).** Toluene/hexane (2:1, v/v) was used as eluent and a white powder was obtained at a 71% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.79 (s, 6H), 6.77 (d, 2H), 6.80 (d, 4H), 7.02 (d, 4H), 7.22 (d, 2H).

**2,5-Dimethoxy-*N,N*-bis(4-methoxyphenyl)aniline (2c).** Dichloromethane/hexane (5:1, v/v) was used as eluent and a white powder was obtained at a 60% yield.  $^1\text{H NMR}$  ( $\text{DMSO-}d_6$ , 400 MHz):  $\delta$  3.52 (s, 3H), 3.63 (s, 3H), 3.70 (s, 6H), 6.52 (d, 1H), 6.71-6.81 (m, 9H), 6.98 (d, 1H).

***N,N*-Bis(4-hexyloxyphenyl)-4-bromoaniline (3d).** Ethyl acetate/petroleum ether (1:3, v/v) was used as eluent and a white powder was obtained at a 59% yield.  $^1\text{H NMR}$

(DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  0.88 (t, 6H), 1.28-1.32 (m, 8H), 1.39-1.42 (m, 4H), 1.67-1.71 (m, 4H), 3.92 (t, 4H), 6.66 (d, 2H), 6.90 (d, 4H), 7.01 (d, 4H), 7.29 (d, 2H).

**2,5-Dimethoxy-*N,N*-bis(4-methoxyphenyl)-4-bromoaniline (3c).** **2c** (5.28 g) and *N*-bromosuccinimide (2.575 g) were added to carbon tetrachloride (80 mL) solvent and the reaction was performed at room temperature for 4 h under Ar. After that the mixture was poured into water and extracted three times with dichloromethane. The organic layer was washed with H<sub>2</sub>O, and subsequently dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was purified on a silica gel column with dichloromethane/hexane (1:1, *v/v*) as eluent to obtain a white powder (5.78 g). Yield: 90%. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  3.54 (s, 3H), 3.64 (s, 6H), 3.69 (s, 3H), 6.75 (s, 1H), 6.77-6.82 (m, 8H), 7.28 (s, 1H).

**General Synthesis of 4.** Triphenylamines **3** (1 mmol), (thieno[3,2-*b*]thiophen-2-yl)boronic acid (1.5 mmol), and tetrakis(triphenylphosphine)palladium (0.2 mmol) were dissolved in the mixture of THF (30 mL) and 2 N potassium carbonate aqueous solution (3.5 mL) and the reaction was performed at 70 °C for 12 h under Ar. After that the mixture was poured into water and extracted three times with dichloromethane. The organic layer was washed with a sodium carbonate aqueous solution and H<sub>2</sub>O, and subsequently dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residues were purified on a silica gel column.

**5-[*N,N*-Bis(4-diphenylamino)phenyl]thieno[3,2-*b*]thiophene (4a).**

Dichloromethane/hexane (1:10, *v/v*) was used as eluent and a yellow powder was

obtained at a 63% yield.  $^1\text{H NMR}$  ( $\text{DMSO-}d_6$ , 400 MHz):  $\delta$  7.00 (d, 2H), 7.06 (d, 2H), 7.08 (t, 4H), 7.33 (t, 4H), 7.43 (d, 1H), 7.59 (d, 2H), 7.64 (d, 1H), 7.75 (s, 1H).

**5-[*N,N*-Bis(4-methoxyphenylamino)phenyl]thieno[3,2-*b*]thiophene (4b).**

Dichloromethane/hexane (1:1, *v/v*) was used as eluent and a yellow powder was obtained at a 81% yield.  $^1\text{H NMR}$  ( $\text{DMSO-}d_6$ , 400 MHz):  $\delta$  3.75 (s, 6H), 6.79 (d, 2H), 6.93 (d, 4H), 7.06 (d, 4H), 7.40 (d, 1H), 7.48 (d, 2H), 7.60 (d, 1H), 7.66 (s, 1H).

**5-[*N,N*-Bis(4-methoxyphenylamino)-2,5-dimethoxyphenyl]thieno[3,2-*b*]thiophene (4c).** Toluene was used as eluent and a yellow powder was obtained at a 83% yield.  $^1\text{H NMR}$  ( $\text{DMSO-}d_6$ , 400 MHz):  $\delta$  3.61 (s, 3H), 3.71 (d, 9H), 6.75 (s, 1H), 6.79-6.85 (m, 8H), 7.41 (t, 2H), 7.63 (d, 1H), 7.96 (s, 1H).

**5-[*N,N*-Bis(4-hexyloxyphenylamino)phenyl]thieno[3,2-*b*]thiophene (4d).**

Dichloromethane/hexane (1:1, *v/v*) was used as eluent and a yellow powder was obtained at a 60% yield.  $^1\text{H NMR}$  ( $\text{DMSO-}d_6$ , 400 MHz):  $\delta$  0.89 (t, 6H), 1.31-1.32 (m, 8H), 1.39-1.43 (m, 4H), 1.68-1.72 (m, 4H), 3.93 (t, 4H), 6.78 (d, 2H), 6.91 (d, 4H), 7.03 (d, 4H), 7.40 (d, 1H), 7.48 (d, 2H), 7.59 (d, 1H), 7.66 (s, 1H).

**General Synthesis of Carbaldehyde (5).** **4** (1 mmol) and DMF (10 mmol) were dissolved in 1,2-dichloroethane (50 mL). After cooling the solution to 0 °C, phosphorus oxychloride (1.2 mmol) was added dropwise. The reaction was kept at 90 °C for 6 h under Ar. After cooling to room temperature, 20 mL H<sub>2</sub>O was added into the reaction mixture, followed by neutralizing with sodium acetate. The mixture was extracted with dichloromethane, and the organic phase was dried over anhydrous sodium sulfate. After removing the solvent, the residues were purified on a silica gel column.

**5-[*N,N*-Bis(4-diphenylamino)phenyl]thieno[3,2-*b*]thiophen-2-carbaldehyde**

**(5a).** Dichloromethane/hexane (1:1, *v/v*) was used as eluent and a yellow powder was obtained at a 76% yield. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ 6.99 (d, 2H), 7.11 (d, 2H), 7.12 (t, 4H), 7.36 (t, 4H), 7.65 (d, 2H), 7.88 (s, 1H), 8.37 (s, 1H), 9.96 (s, 1H).

**5-[*N,N*-Bis(4-methoxyphenylamino)phenyl]thieno[3,2-*b*]thiophen-2-carbaldehyde (5b).** Ethyl acetate/petroleum ether(1:3, *v/v*) was used as eluent and an orange powder was obtained at a 60% yield. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ 3.76 (s, 6H), 6.78 (d, 2H), 6.95 (d, 4H), 7.10 (d, 4H), 7.56 (d, 2H), 7.80 (s, 1H), 8.35 (s, 1H), 9.94 (s, 1H).

**5-[(*N,N*-Bis(4-methoxyphenyl)amino)-2,5-dimethoxyphenyl]thieno[3,2-*b*]thiophene-2-carbaldehyde (5c).** Ethyl acetate/petroleum ether(1:3, *v/v*) was used as eluent and an orange powder was obtained at a 69% yield. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ 3.61 (s, 3H), 3.71 (d, 6H), 3.74 (s, 3H), 6.75 (s, 1H), 6.84 (m, 8H), 7.49 (t, 1H), 8.13 (s, 1H), 8.37 (s, 1H), 9.96 (s, 1H).

**5-[*N,N*-Bis(4-hexyloxyphenylamino)phenyl]thieno[3,2-*b*]thiophen-2-carbaldehyde (5d).** Chloroform was used as eluent and an orange powder was obtained at a 80% yield. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ 0.89 (t,6H), 1.31-1.33 (m, 8H), 1.42 (m, 4H), 1.69-1.72 (m, 4H), 3.95 (t, 4H), 6.77 (d, 2H), 6.93 (d, 4H), 7.07 (d, 4H), 7.55 (d, 2H), 7.80 (s, 1H), 8.35 (s, 1H) 9.94 (s, 1H).

**General Synthesis of Acrylic Acids (6).** **5** (1 mmol), cyanoacetic acid (1.5 mmol), and piperidine (6.7 mmol) were added to 20 mL chloroform and the mixture was refluxed for 6 h. After that 20 mL water was added to the reaction mixture. The solution

was acidified with 20% aqueous HCl and extracted with chloroform. The organic phase was dried over anhydrous sodium sulfate. The solvent was evaporated on a rotaevaporator under vacuum and the residues were purified on a column chromatography with chloroform as eluent to give the crude products. The crude products were dissolved in chloroform, and washed with a HCl aqueous solution. The remove of solvents under reduced pressure gives the final dyes.

**3-{5-[*N,N*-Bis(4-diphenylamino)phenyl]thieno[3,2-*b*]thiophen-2-yl}-2-cyano-acrylic Acid (6a, C207).** Yield: 72%. IR: 1716  $\text{cm}^{-1}$  (COOH), 2214  $\text{cm}^{-1}$  (CN).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz):  $\delta$  6.99 (d, 2H), 7.10 (d, 2H), 7.13 (t, 4H), 7.36 (t, 4H), 7.65 (d, 2H), 7.92 (s, 1H), 8.29 (s, 1H), 8.54 (s, 1H), 13.65 (s 1H). ESI-MS  $m/z$  calcd. for ( $\text{C}_{28}\text{H}_{18}\text{N}_2\text{O}_2\text{S}_2$ ): 478.1. Found: 477.4.

**3-{5-[*N,N*-Bis(4-methoxyphenylamino)phenyl]thieno[3,2-*b*]thiophen-2-yl}-2-cyano-acrylic Acid (6b, C202).** Yield: 66%. IR: 1716  $\text{cm}^{-1}$  (COOH), 2220  $\text{cm}^{-1}$  (CN).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz):  $\delta$  3.76 (s, 6H), 6.78 (d, 2H), 6.96 (d, 4H), 7.10 (d, 4H), 7.56 (d, 2H), 7.84 (s, 1H), 8.27 (s, 1H), 8.53 (s, 1H), 13.62 (s, 1H). ESI-MS  $m/z$  calcd. for ( $\text{C}_{30}\text{H}_{22}\text{N}_2\text{O}_4\text{S}_2$ ): 538.1. Found: 537.1.

**3-{5-[(*N,N*-Bis(4-methoxyphenyl)amino)-2,5-dimethoxyphenyl]thieno[3,2-*b*]thiophene-2-yl}-2-cyano-acrylic Acid (6c, C208).** Yield: 70%. IR: 1718  $\text{cm}^{-1}$  (COOH), 2215  $\text{cm}^{-1}$  (CN).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz):  $\delta$  3.61 (s, 3H), 3.72 (d, 6H), 3.73 (s, 3H), 6.75 (s, 1H), 6.84 (m, 8H), 7.45 (t, 1H), 7.98 (s, 1H), 8.06 (s, 1H), 8.15 (s, 1H), 13.66 (s, 1H). ESI-MS  $m/z$  calcd. for ( $\text{C}_{32}\text{H}_{26}\text{N}_2\text{O}_6\text{S}_2$ ): 598.1. Found: 597.0.

**3-{5-[*N,N*-Bis(4-hexyloxyphenylamino)phenyl]thieno[3,2-*b*]thiophen-2-yl}-2-cyano-acrylic Acid (6d, C206).** Yield: 70%. IR: 1715 cm<sup>-1</sup> (COOH), 2214 cm<sup>-1</sup> (CN). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ 0.89 (t, 6H), 1.31-1.32 (m, 8H), 1.42 (m, 4H), 1.67-1.72 (m, 4H), 3.95 (t, 4H), 6.77 (d, 2H), 6.93 (d, 4H), 7.07 (d, 4H), 7.55 (d, 2H), 7.84 (s, 1H), 8.27 (s, 1H), 8.53 (s, 1H), 13.64 (s, 1H). ESI-MS *m/z* calcd. for (C<sub>40</sub>H<sub>42</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>): 678.3. Found: 677.1.

### 3. Calculation

All calculations on the reported sensitizers in this article were performed in Gaussian 03 program package. Their geometrical structures were optimized without any symmetrical constraints, employing density functional theory (DFT) method combined with Becke's three parameters hybrid functional and Lee—Yang—Parr's gradient corrected correlation functional. In particular, 6-31G\* basis set<sup>S8</sup> was applied for all atoms. With the same functional and basis incorporated in time density functional theory (TDDFT) method, we further calculated the lowest 30 singlet-singlet vertical electronic transition features based on the optimized model of the sensitizers. Employing the TDDFT results in the SWizard program (<http://www.sg-chem.net/swizard/>), we calculated the absorption profile as a sum of the Gaussian band using the following equation.<sup>S9</sup>

$$\varepsilon(\omega) = 2.174 \times 10^9 \sum_I \frac{f_I}{\Delta_{1/2,I}} \exp\left(-2.773 \frac{(\omega - \omega_I)^2}{\Delta_{1/2,I}^2}\right) \quad (1)$$

Where  $\varepsilon$  is the molar extinction coefficient given in units of  $M^{-1} \text{ cm}^{-1}$ , the energy  $\omega$  of all allowed transitions included in equation 1 is expressed in  $\text{cm}^{-1}$ ,  $f_i$  denotes the oscillator strength, and the half-bandwidths  $\Delta_{1/2}$  is assumed to be  $3000 \text{ cm}^{-1}$ .

#### 4. UV-vis, Emission, FTIR, and Voltammetric Measurements

Electronic absorption spectra were performed on a UNICO WFZ UV-2802PC/PCS spectrometer. Emission spectra were recorded with a PerkinElmer LS55 luminescence spectrometer. The emitted light was detected with a Hamamatsu R928 red-sensitive photomultiplier operated in a single-photon counting mode. The FTIR spectra were measured using a BRUKER Vertex 70 FTIR spectrometer. A computer controlled CHI660C electrochemical workstation was used for square-wave voltammetric measurements in combination with a mini three-electrode electrochemical cell equipped with a  $5 \mu\text{m}$  radius Pt ultramicroelectrode as working electrode. A Pt wire and a silver wire were used as counter and quasi-reference electrodes, respectively. The redox potential values vs. the ferrocene internal reference were converted to those vs. NHE (normal hydrogen electrode).

#### References

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**Figure S1.** Detailed photovoltaic parameters of a cell with the C202 sensitizer and a solvent-free ionic liquid electrolyte measured under the irradiance of AM 1.5G sunlight during successive one sun light-soaking at 60 °C. The solvent-free electrolyte composition is DMII/EMII/EMITCB/I<sub>2</sub>/NBB/GNCS (molar ratio: 12/12/16/1.67/3.33/0.67).

