Electronic Supplementary Information

Molecular Engineering of indoline based organic sensitizers for highly efficient dye-sensitized solar cells

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Contents:

1. Scheme S1: Synthetic routes of C-CA and F-CA

2. Synthesis of intermediates 1, 1', 3, 3', 4, 4'.

3. Fig. S1: Comparison of absorption spectra of C-CA in CHCl3, on 4μm TiO2 electrode with 0 and 30 mM DCA.

4. Fig. S2: Evaluation of band gap of four dyes while adsorbed on TiO2.

5. Fig. S3: Optimized geometry of C-CA.

6. Table S1: Simulated excitation energies for the lowest transition.

7. Fig. S3-S6: 1H NMR and 13C NMR spectra and HR-MS of C-CA and F-CA
Synthesis of intermediates 1, 1', 3, 3', 4, 4'.

Scheme S1. Synthetic routes of C-CA and F-CA: i) NaH, THF; ii) n-BuLi, DMF, THF; iii) piperidine, CH₃CN.

Intermediates 1 and 1' were synthesized according to the literature method (M. Matsui, A. Ito, M. Kotani, Y, Kubota, K, Funabiki, J. Jin, T, Yoshida, H. Minoura, H. Miura, Dyes Pigments 2009, 80, 233) except using n-pentyl substituted carbazol or fluorene as an additional donor.

Their characterizations were shown as follows:

1: The product was obtained as a yellow solid (2790 mg, 66%). $^1$H NMR (500 MHz, CDCl₃, δ, ppm): 9.66 (s, 1H, -CHO), 8.06, (d, $J = 7.5$ Hz, 1H, carbazole-ArH), 7.98 (s, 1H, indoline-ArH), 7.65 (s, 1H, carbazole-ArH), 7.36-7.50 (m, 5H, indoline-ArH and carbazole-ArH), 7.23 (d, $J = 7.5$ Hz, 1H, carbazole-ArH), 6.55 (d, $J = 8.0$ Hz, 1H, indole-ArH), 4.99 (t, $J = 8.5$ Hz, 1H, N-CH₂), 4.31 (t, $J = 7.0$ Hz, 2H, N-CH₂), 3.90 (t, $J = 8.5$ Hz, 1H, N-CH₂), 2.04-2.14 (m, 1H, cyclopentyl-H), 1.54-1.74 (m, 4H, cyclopentyl-H), 1.48-1.54 (m, 1H, cyclopentyl-H), 1.36-1.41 (m, 4H, CH₃-C₂H₂-C₂H₂), 0.90 (t, $J = 6.0$ Hz, 3H, CH₃).

1': The product was obtained as a yellow liquid (3540 mg, 72%). $^1$H NMR (500 MHz, $d_6$-Acetone, δ, ppm): 9.71 (s, 1H, -CHO), 7.85, (d, $J = 8.0$ Hz, 1H, fluorene-ArH), 7.78 (d, $J = 7.0$ Hz, 1H, fluorene-ArH), 7.65 (s, 1H, indole-ArH), 7.50 (m, 1H, fluorene-ArH), 7.44-7.46 (m, 1H, fluorene-ArH), 7.30-7.36 (m, 2H, indole-ArH and fluorene-ArH), 6.87 (d, $J = 8.5$ Hz, 1H, indole-ArH),
5.18 (t, J = 8.5 Hz, 1H, N-CH₂), 3.92 (t, J = 8.5 Hz, 1H, N-CH₂), 2.11-2.19 (m, 1H, cyclopentyl-CH₂), 1.79-1.89 (m, 3H, cyclopentyl-CH₂), 1.67-1.73 (m, 1H, cyclopentyl-CH₂), 1.47-1.57 (m, 1H, cyclopentyl-CH₂), 1.03-1.14 (m, 8H, 2×CH₂-CH₂-CH₂), 0.78-0.90 (m, 8H, 2×CH₃-CH₂-CH₂), 0.73 (t, J = 7.0 Hz, 3H, CH₃), 0.68 (t, J = 7.0 Hz, 3H, CH₃).

**Synthesis of 3:** 2 (439 mg, 1 mmol) was dispersed in dry THF (15 mL) followed by the addition of NaH (30 mg, 1.25 mmol). The mixture was stirred at ambient temperature under nitrogen atmosphere for 1 h. 1 (359 mg, 1 mmol) was added and the reaction mixture was allowed to stir at ambient temperature for another 48 h. Then the mixture was poured into 0.1 M HCl solution (100 mL) and extracted with DCM (200 mL). The organic phase was dried over Na₂SO₄, then filtered through a plug of silica gel with petroleum ether/ethyl acetate mixture (100:1), and a crude intermediate 3 was obtained as a mixture of isomers, which was used directly in the next step without further purification.

**Synthesis of 3’:** The synthesis procedure is similar with described above. The product was obtained as a yellow solid.

**Synthesis of 4:** 3 was dissolved in THF (15 mL) and the solution was cooled to -78 º C under nitrogen atmosphere. N-Butyl lithium (0.8 mL, 2.2 M hexane solution) was added dropwise over 5 min and the mixture was stirred at -78 ºC for 1 h. Then the mixture was allowed to warm to 0 ºC and stirred for 30 min. The mixture was once again cooled to -78 ºC and DMF (0.1 mL, 1.3 mmol) was added. The reaction was allowed to warm to ambient temperature and stirred for 2 h. The reaction was quenched by the addition of 0.5 M HCl (100 mL) and extracted with DCM. After drying over Na₂SO₄, the combined organic extract was concentrated by rotary evaporation and column chromatography over silica gel with petroleum ether/ethyl acetate mixture (15:1). The trans-type isomerization 6 was obtained as a red solid (180 mg, 34%). ^1H NMR (500 MHz, d₆-Acetone, δ, ppm): 9.87 (s, 1H, -CHO), 8.18 (d, J = 8.0 Hz, 1H, carbazole-ArH), 8.14 (m, 1H, indoline-ArH), 7.85 (d, J = 4.0 Hz, 1H, thiophene-H), 7.64 (d, J = 9.0 Hz, 1H, carbazole-ArH), 7.59 (d, J = 8.5 Hz, 1H,
carbazole-\(\mathrm{ArH}\), 7.47-7.50 (m, 3H, thiophene-\(\mathrm{H}\), indoline-\(\mathrm{ArH}\) and carbazole-\(\mathrm{ArH}\)), 7.20-7.26 (m, 5H, \(\mathrm{CH}=\mathrm{CH}\) and carbazole-\(\mathrm{ArH}\)), 6.66 (d, \(J=8.0\ \text{Hz}\), 1H, indoline-\(\mathrm{ArH}\)), 5.05 (t, \(J=8.5\ \text{Hz}\), 1H, N-CH\(\equiv\)H), 4.46 (t, \(J=7.0\ \text{Hz}\), 2H, N-CH\(\equiv\)H), 3.92 (t, \(J=8.5\ \text{Hz}\), 1H, N-CH-C\(\equiv\)H), 2.10-2.17 (m, 1H, cyclopentyl-\(\mathrm{H}\)), 1.89-1.98 (m, 4H, cyclopentyl-\(\mathrm{H}\)), 1.68-1.80 (m, 3H, N-CH\(\equiv\)H and cyclopentyl-1\(\mathrm{H}\)), 1.38-1.43 (m, 4H, CH\(\equiv\)CH-CH \(\equiv\)CH), 0.90 (t, \(J=7.0\ \text{Hz}\), 3H, CH\(\equiv\)C).

**Synthesis of 4\(^{\prime}\)**: The synthesis procedure is similar with described above. The product was obtained as a red solid (220 mg, 37%). \(^1\)H NMR (500 MHz, \(d_6\)-Acetone, \(\delta\), ppm): 9.87 (s, 1H, -CHO), 7.85 (d, \(J=4.0\ \text{Hz}\), 1H, thiophene-\(\mathrm{H}\)), 7.78 (d, \(J=8.0\ \text{Hz}\), 1H, fluorene-\(\mathrm{ArH}\)), 7.72 (d, \(J=7.5\ \text{Hz}\), 1H, fluorene-\(\mathrm{ArH}\)), 7.50 (s, 1H, indoline-\(\mathrm{ArH}\)), 7.42-7.43 (m, 2H, thiophene-\(\mathrm{H}\) and fluorene-\(\mathrm{ArH}\)), 7.26-7.35 (m, 6H, indoline-\(\mathrm{ArH}\), CH=CH-thiophene, and fluorene-\(\mathrm{ArH}\)), 7.22 (d, \(J=16.0\ \text{Hz}\), 1H, CH=CH-thiophene), 6.95 (d, \(J=7.5\ \text{Hz}\), 1H, indoline-\(\mathrm{ArH}\)), 5.06 (t, \(J=8.5\ \text{Hz}\), 1H, N-CH\(\equiv\)H), 3.89 (t, \(J=8.5\ \text{Hz}\), 1H, N-CH-C\(\equiv\)H), 2.10-2.18 (m, 1H, cyclopentyl-\(\mathrm{H}\)), 1.86-1.93 (m, 3H, cyclopentyl-\(\mathrm{H}\)), 1.60-1.72 (m, 1H, cyclopentyl-\(\mathrm{H}\)), 1.46-1.55 (m, 1H, cyclopentyl-\(\mathrm{H}\)), 1.06-1.11 (m, 8H, 2\times\text{CH}_2-\text{CH}_2), 0.83-0.90 (m, 8H, 2\times\text{CH}_3-\text{CH}_2), 0.73 (t, \(J=7.0\ \text{Hz}\), 3H, CH\(\equiv\)C), 0.68 (t, \(J=7.0\ \text{Hz}\), 3H, CH\(\equiv\)C).
Fig. S1. Comparison of absorption spectra of C-CA in CHCl$_3$, on 4 $\mu$m TiO$_2$ electrode with 0 and 30 mM DCA.
Fig. S2. Estimation of band gaps of C-CA, F-CA, and I-3 adsorbed on 4 μm TiO₂ films.
Fig. S3. Optimized geometry of C-CA (front view and side view) calculated at the hybrid density functional theory (B3LYP) with 6-31G* basis set as implemented in the Gaussian 03 program.
Table S1 Calculated TDDFT excitation energies for the lowest transition (eV, nm), oscillator strengths (f) and experimental absorption maxima

<table>
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<th></th>
<th>E (eV, nm)</th>
<th>f</th>
<th>exp. (eV, nm)</th>
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<tbody>
<tr>
<td>C-CA</td>
<td>2.24 (553)</td>
<td>1.3637</td>
<td>2.37 (523)</td>
</tr>
<tr>
<td>F-CA</td>
<td>2.22 (558)</td>
<td>1.3290</td>
<td>2.46 (504)</td>
</tr>
<tr>
<td>I-3</td>
<td>2.31 (537)</td>
<td>1.2936</td>
<td>2.52 (491)</td>
</tr>
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a) TDDFT excited states calculation was performed at the B3LYP/6-31G* level in vacuum with the optimized ground-state geometry.
Fig. S3. $^1$H NMR and $^{13}$C NMR spectra of C-CA recorded in $d_6$-DMSO.
Fig. S4. HR-MS (FAB+) spectrum of C-CA
Fig. S5. $^1$H NMR and $^{13}$C NMR spectra of F-CA recorded in $d_6$-Acetone.
Fig. S6. HR-MS (FAB+) spectrum of F-CA.