Supplementary Information

Increasing the Power Outputs of a CdTe Solar Cell via Luminescent Down Shifting Molecules with Intramolecular Charge Transfer and Aggregation-Induced Emission Characteristics

Yilin Li\textsuperscript{ab}, Zhipeng Li\textsuperscript{a}, Yang Wang\textsuperscript{b\textsuperscript{\dagger}}, Alvin Compaan\textsuperscript{c}, Tianhui Ren\textsuperscript{a\ast}, Wen-Ji Dong\textsuperscript{b\ast}

\textsuperscript{a} School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China;
\textsuperscript{b} Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99164, USA;
\textsuperscript{c} Department of Physics and Astronomy, The University of Toledo, Toledo, OH 43606, USA.

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\ast Corresponding authors: Wen-Ji Dong, Tel: +01-509-335-5798; e-mail: wdong@vetmed.wsu.edu; Tianhui Ren, Tel: +86-21-54747118; email: thren@sjtu.edu.cn; \dagger undergraduate summer intern from Department of Chemistry, University of California Berkeley.
1. Synthesis and characterization

Unless otherwise noted, all reagents were used as received and without further purification. Chromatographic purification was carried out using 60-200 mesh silica gel for flash columns. NMR spectra were collected on a 300 MHz spectrometer at room temperature. Mass spectra were recorded on a 4800 MALDI TOF/TOF analyzer. All reaction products were characterized by $^1$H-NMR, $^{13}$C-NMR and MALDI-MS. Additional elemental analysis (C, H, N percentage) have been done for the final products to prove the enough purity for the spectroscopic measurements.

Scheme S1. Synthetic route of fluorophores 1a-c. Reaction regents and conditions: (i) n-BuLi, THF, 0 °C, 30 min, 4-bromobenzophenone, rt, 6 h, TsOH·H$_2$O, toluene, reflux, 16 h; (ii) malononitrile, piperidine, EtOH, rt, 16 h; (iii) 4-formylphenylboronic acid (for 1a) / 5-formylfuran-2-boronic acid (for 1b) / 5-formylthiophene-2-boronic acid (for 1c), Pd(dpdpf)Cl$_2$, K$_2$CO$_3$, toluene: MeOH = 1 : 1, 75 °C, 16 h; (iv) n-BuLi, THF, -78 °C, N$_2$, 1 h, tributyltin chloride, rt, 16 h; (v) malononitrile, piperidine (for 1b) / Et$_3$N (for 1c), DCM, 30 °C, 16 h; (vi) Pd(PPh$_3$)$_4$, toluene, reflux, 16 h.

General procedures:

Reaction (i): To a solution of 3 (2.0 g, 11.9 mmol) in 20 mL of anhydrous THF was added a 1.6 M solution of n-BuLi in hexanes (7.4 mL, 11.9 mmol) at 0 °C under an nitrogen atmosphere. The resulting solution was stirred for 30 min at that temperature. To this solution was added 4-bromobenzophenone (3.1 g, 11.9 mmol) and the reaction mixture was allowed to warm to room temperature with stirring during a 6 h period. The reaction was quenched with the addition of water, the organic layer was extracted with DCM twice and the combined organic layers were dried over anhydrous MgSO$_4$. The solvent was evaporated, and the resulting crude alcohol was dissolved in about 80 mL of toluene in a 150 mL flask fitted with a Dean-Stark trap. A catalytic amount of p-toluenesulphonic acid monohydrate (500 mg, 2.6 mmol) was added, and the mixture was refluxed for 16 h and cooled to room temperature. The toluene layer was washed with water and extracted with DCM twice. The combined organic layers were dried over anhydrous MgSO$_4$.
and evaporated to afford the crude 4. The pure product 4 was obtained by purification on silica gel chromatography using hexanes as eluent.

Reaction (ii): To a solution of 5 (6.0 g, 32.4 mmol) and malononitrile (1.8 g, 27.0 mmol) in 20 mL of EtOH was added 3 drops of piperidine. The mixture was stirred at room temperature for 16 h. The resulting precipitate was collected by filtration and washed by EtOH twice to obtain pure 6 directly.

Reaction (iii): A mixture of 4 (1.0 g, 2.4 mmol), 4-formylphenylboronic acid (729 mg, 4.9 mmol, for 1a) / 5-formylfuran-2-boronic acid (680 mg, 4.9 mmol, for 1b) / 5-formylthiophene-2-boronic acid (758 mg, 4.9 mmol, for 1c), Pd(dppf)Cl₂ (89 mg, 5.0 mol%) and K₂CO₃ (1.7 g, 12.2 mmol) were dissolved in 50 mL of MeOH and toluene (1 : 1). The reaction mixture was stirred at 75 °C for 16 h. The resulting reaction mixture was filtered and the solvent was removed. The residue was purified by silica gel chromatography using hexanes and DCM (1 : 1) as eluent to afford 2a, 2b or 2c.

Reaction (iv): 1.6 M n-BuLi in hexanes (5.0 mL, 7.3 mmol) was added to a solution of 4 (1.0 g, 2.4 mmol) in 25 mL of anhydrous THF at -78 °C under nitrogen with stirring for 1 h. The solution was added tributyltin chloride (2.0 mL, 7.3 mmol) and then warmed to room temperature with stirring for 16 h. The resulting mixture was quenched with the addition of water, extracted by DCM and dried over anhydrous MgSO₄. Due to the decomposition of 2d on the silica gel, only a small portion of 2d was isolated using hexanes as eluent.

Reaction (v): To a solution of 2b (or 2c) and malononitrile (2.0 equivalent) in 25 mL of DCM was added 10 drops of Et₃N (or piperidine). The reaction mixture was stirred under 30 °C for 16 h. The resulting mixture was dried over anhydrous MgSO₄. The solvent was evaporated and the residue was purified by silica gel chromatography using hexanes and DCM (1 : 1) as eluent to afford 1b (or 1c).

Reaction (vi): A mixture of 2d (360 mg, 0.6 mmol), 6 (135 mg, 0.6 mmol) and Pd(PPh₃)₄ (33 mg, 5 mol%) in 25 mL of toluene was stirred and refluxed for 16 h. The resulting solution was evaporated and the residue was purified by silica gel chromatography using hexane and DCM (1 : 1) as eluent to afford 1a.

Compound characterizations:

2-(((4'-((1,2,2-triphenylvinyl)biphenyl-4-yl)methylene)malononitrile (1a).
Yellow solid (yield 82%). Rₜ = 0.38 (Hex : DCM = 1 : 2). ¹H-NMR (300 MHz, CDCl₃, δ): 7.96 (d, 2H, J = 8.5 Hz), 7.76 (s, 1H), 7.72 (d, 2H, J = 8.5 Hz), 7.42 (d, 1H, J = 8.4 Hz), 7.18-7.04 (m, 17H). ¹³C-NMR (75 MHz, CDCl₃, δ): 159.4, 147.1, 145.1, 143.7, 143.6, 143.3, 140.3, 136.6, 133.3, 132.4, 132.1, 131.6, 131.6, 131.5, 129.9, 128.1, 128.1, 128.0, 127.9, 127.0, 126.9, 126.9, 126.9, 114.3, 113.2, 81.9. MALDI-MS: m/z calcd for C₃₆H₂₅N₂⁺ 484.1939, found 484.2264.

2-(((5-(4-((1,2,2-triphenylvinyl)furan-2-yl)methylene)malononitrile (1b).
Orange solid (yield 32%). Rₜ = 0.56 (Hex : DCM = 1 : 4). ¹H-NMR (300 MHz, CDCl₃, δ): 7.60 (d, 2H, J = 8.6 Hz), 7.36 (s, 1H), 7.26 (s, 1H), 7.16-7.01 (m, 17H), 6.87 (d, 1H, J = 3.9 Hz). ¹³C-NMR (75 MHz, CDCl₃,
2-((5-(4-(1,2,2-triphenylvinyl)phenyl)thiophen-2-yl)methylene)malononitrile (1c).  
Orange solid (yield 22 %). R$_f$ = 0.52 (Hex : DCM = 1 : 3). $^1$H-NMR (300 MHz, CDCl$_3$, $\delta$): 7.76 (s, 1H), 7.67 (d, 1H, J = 4.1 Hz), 7.44 (d, 2H, J = 8.4 Hz), 7.37 (d, 1H, J = 4.1 Hz), 7.17-7.04 (m, 17H). $^{13}$C-NMR (75 MHz, CDCl$_3$, $\delta$): 156.7, 150.8, 146.5, 143.5, 143.3, 143.4, 142.6, 140.4, 140.0, 134.2, 132.6, 131.6, 131.6, 131.5, 130.2, 128.2, 128.0, 127.2, 127.1, 127.0, 126.1, 124.7, 114.5, 113.7, 76.5. MALDI-MS: m/z calc for C$_{34}$H$_{22}$N$_2$O$^+$ 474.1732, found 474.1664.

4’-((1,2,2-triphenylvinyl)bisphenyl-4-carbaldehyde (2a).  
Yellow solid (yield 50 %). R$_f$ = 0.60 (Hex : DCM = 1 : 2). $^1$H-NMR (300 MHz, CDCl$_3$, $\delta$): 10.04 (s, 1H), 7.93 (d, 2H, J = 8.5 Hz), 7.72 (d, 2H, J = 8.2 Hz), 7.43 (d, 2H, J = 8.6 Hz), 7.19-7.07 (m, 17H). $^{13}$C-NMR (75 MHz, CDCl$_3$, $\delta$): 192.1, 146.9, 144.5, 143.8, 143.8, 141.9, 140.4, 137.5, 135.3, 132.3, 131.7, 131.6, 130.5, 128.1, 128.1, 128.0, 127.6, 127.0, 126.9, 126.8. MALDI-MS: m/z calc for C$_{32}$H$_{20}$O$^+$ 436.1827, found 436.1654.

5-(4-(1,2,2-triphenylvinyl)phenyl)furan-2-carbaldehyde (2b).  
Yellow solid (yield 62 %). R$_f$ = 0.31 (Hex : DCM = 1 : 2). $^1$H-NMR (300 MHz, CDCl$_3$, $\delta$): 9.61 (s, 1H), 7.57 (d, 2H, J = 8.7 Hz), 7.28 (d, 1H, J = 3.7 Hz), 7.15-7.03 (m, 17H), 6.75 (d, 1H, J = 3.7 Hz). $^{13}$C-NMR (75 MHz, CDCl$_3$, $\delta$): 177.3, 159.7, 152.1, 145.8, 143.6, 143.4, 142.3, 140.3, 132.2, 131.6, 131.6, 131.5, 128.1, 128.1, 128.0, 127.1, 127.0, 126.9, 126.8. MALDI-MS: m/z calc for C$_{34}$H$_{22}$O$_2$ 426.1620, found 426.1465.

5-(4-(1,2,2-triphenylvinyl)thiophene-2-carbaldehyde (2c).  
Yellow solid (yield 76 %). R$_f$ = 0.40 (Hex : DCM = 1 : 2). $^1$H-NMR (300 MHz, CDCl$_3$, $\delta$): 9.87 (s, 1H), 7.70 (d, 1H, J = 4.0 Hz), 7.43 (d, 2H, J = 8.6 Hz), 7.34 (d, 1H, J = 4.0 Hz), 7.17-7.03 (m, 17H). $^{13}$C-NMR (75 MHz, CDCl$_3$, $\delta$): 183.0, 154.4, 145.5, 143.7, 143.6, 143.5, 142.3, 140.2, 137.7, 132.4, 131.6, 131.6, 131.5, 131.1, 128.2, 128.1, 127.9, 127.1, 127.0, 126.9, 125.9, 124.1. MALDI-MS: m/z calc for C$_{34}$H$_{22}$O$^+$ 442.1391, found 442.1098.

tributyl(4-(1,2,2-triphenylvinyl)phenyl)stannane (2d).  
Colorless liquid (yield 28 %). R$_f$ = 0.19 (Hex). $^1$H-NMR (300 MHz, CDCl$_3$, $\delta$): 7.21 (d, 2H, J = 8.0 Hz), 7.13-7.04 (m, 15H), 6.99 (d, 2H, J = 8.0 Hz), 1.58-1.47 (m, 6H), 1.36-1.29 (m, 6H), 1.02 (t, 6H), 0.90 (t, 9H).
2d \[ ^{13}C\text{-NMR (75 MHz, CDCl}_3, \delta): 144.1, 144.1, 144.0, 143.4, 141.4, 141.0, 140.2, 135.9, 131.6, 130.9, 129.2, 128.7, 127.8, 126.8, 126.6, 126.5, 29.3, 27.6, 14.0, 9.8. \text{MALDI-MS: } m/z \text{ calcd for } C_{38}H_{44}Sn^+ 620.2621, \text{ found 620.0860.} \]

(2-(4-bromophenyl)ethene-1,1,2-triyl)tribenzene (4).
White solid (yield 37%). \( R_f = 0.56 \) (Hex : DCM = 2 : 1). \( ^1H\text{-NMR (300 MHz, CDCl}_3, \delta): 7.31 \text{ (d, 2H, } J = 8.5 \text{ Hz), 7.22-7.11 \text{ (m, 15H), 7.01 \text{ (d, 2H, } J = 8.6 \text{ Hz).} \] \( ^{13}C\text{-NMR (75 MHz, CDCl}_3, \delta): 143.8, 143.7, 143.6, 143.0, 141.9, 140.0, 133.4, 131.7, 131.6, 131.6, 131.2, 128.2, 128.1, 128.0, 127.1, 127.0, 127.0, 120.8. \text{MALDI-MS: } m/z \text{ calcd for } C_{26}H_{19}Br^+ 410.0670, \text{ found 410.0552.} \)

2-(4-bromobenzylidene)malononitrile (6).
White solid (yield 83%). \( R_f = 0.23 \) (Hex : DCM = 1 : 1). \( ^1H\text{-NMR (300 MHz, CDCl}_3, \delta): 7.77 \text{ (d, 2H, } J = 8.6 \text{ Hz), 7.72 \text{ (s, 1H), 7.68 \text{ (d, 2H, } J = 8.7 \text{ Hz).} \] \( ^{13}C\text{-NMR (75 MHz, CDCl}_3, \delta): 158.7, 133.3, 132.1, 130.2, 129.9, 133.7, 112.6, 83.7. \text{MALDI-MS: } m/z \text{ calcd for } C_{10}H_{5}BrN_2^+ 231.9636, \text{ found 231.9223.} \)
2. Absorption and emission spectra of Y083 in LDS film

![Absorption and emission spectra of Y083 in LDS film](graph.png)

**Figure S1.** Normalized absorption (solid lines) and emission (dash lines) spectra of Y083 ($\lambda_{\text{ex}} = 472$ nm, green, ▼) associated with AM1.5G solar spectrum (dark yellow) and spectral response of CdTe solar cell (magenta).
3. Transition dipole moment change

The dipole moment change was calculated by linear Lippert-Mataga equation:

\[
\left( \nu'_{\text{ICT}} - \nu_{\text{ICT}} \right) \cong \left( \nu_{\text{abs}} - \nu_{\text{flu}} \right) + \frac{2(\mu_e - \mu_g)}{hca_0^3} \Delta f
\]

\[
\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}
\]

Where \( \nu \) is the wavenumber (cm\(^{-1}\)); the superscript ICT and vac mean ICT and gas states, respectively; the subscript abs and flu mean absorption and emission processes, respectively; \( \mu_e \) and \( \mu_g \) are dipole moment (1 D = 10\(^{-18}\) esu cm) of the excited and ground state, respectively; \( h \) is the Planck’s constant (6.63×10\(^{-27}\) erg s); \( c \) is the speed of light (3×10\(^{10}\) cm s\(^{-1}\)) and \( a_0 \) (cm) is the cavity radius of Onsagar’s reaction field. The \( \Delta f \) value was tuned by different mixtures of 1,4-dioxane and acetonitrile. It is calculated by:

\[
\epsilon = \chi_{\text{DXE}}\epsilon_{\text{DXE}} + \chi_{\text{ACN}}\epsilon_{\text{ACN}}
\]

\[
n = \sqrt{\chi_{\text{DXE}}n_{\text{DXE}}^2 + \chi_{\text{ACN}}n_{\text{ACN}}^2}
\]

Table S1. Calculation of transition dipole moment change (\( u_e - u_g \)) of fluorophores 1a-c.

<table>
<thead>
<tr>
<th>Fluorophore</th>
<th>slope, cm(^{-1})</th>
<th>( r^2 )</th>
<th>( u_e - u_g ), D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>11545 ± 1156</td>
<td>0.9251</td>
<td>24.2 ± 1.2</td>
</tr>
<tr>
<td>1b</td>
<td>9186 ± 1123</td>
<td>0.8799</td>
<td>21.6 ± 1.3</td>
</tr>
<tr>
<td>1c</td>
<td>10537 ± 1306</td>
<td>0.8769</td>
<td>23.2 ± 1.4</td>
</tr>
</tbody>
</table>

\( a \) average value of the longest axis for fluorophores 1a-c is 2 nm.
4. Theoretical computations

**Table S2.** Calculated charge contribution (%) on molecular orbitals of ground (S₀) and excited (S₁) states on donor (TPE) group. The difference indicates ICT rate (%).

<table>
<thead>
<tr>
<th></th>
<th>Absorption</th>
<th></th>
<th>Emission</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S₀</td>
<td>S₁*</td>
<td>ICT rate</td>
<td>S₁</td>
</tr>
<tr>
<td>1a</td>
<td>94 %</td>
<td>11 %</td>
<td>83 %</td>
<td>12 %</td>
</tr>
<tr>
<td>1b</td>
<td>82 %</td>
<td>17 %</td>
<td>65 %</td>
<td>19 %</td>
</tr>
<tr>
<td>1c</td>
<td>86 %</td>
<td>16 %</td>
<td>70 %</td>
<td>21 %</td>
</tr>
</tbody>
</table>

* Non-equilibrium state.
5. Fluorescence lifetime measurements

**Figure S2.** Fluorescent lifetimes of fluorophores 1a-c in acetonitrile ($f_w = 0$) (left) and mixture ($f_w = 95\%$) (right). The fluorophore concentration is 15μM.

Data in Figure S2 left was fitted by single-exponential decay equation:

$$I = \alpha e^{-\frac{t}{\tau_f}}$$

Data in Figure S2 right was fitted by two-exponential decay equation:

$$I = \alpha_1 e^{-\frac{t}{\tau_1}} + \alpha_2 e^{-\frac{t}{\tau_2}}$$

$$\tau_f = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2}$$

Where $\alpha$ is the represent the amplitudes of the components at $t = 0$ and $\tau_f$ is the average fluorescence lifetime.

The fitting results are:

<table>
<thead>
<tr>
<th>Compd</th>
<th>$\tau_f$ (ns)</th>
<th>$\tau_1$ (ns)</th>
<th>$\tau_2$ (ns)</th>
<th>$\tau_f$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>1.92</td>
<td>2.19</td>
<td>9.43</td>
<td>5.70</td>
</tr>
<tr>
<td>1b</td>
<td>1.05</td>
<td>1.75</td>
<td>5.98</td>
<td>2.35</td>
</tr>
<tr>
<td>1c</td>
<td>1.01</td>
<td>1.38</td>
<td>4.32</td>
<td>1.72</td>
</tr>
</tbody>
</table>
6. Image of aggregated nanoparticles

![TEM image of aggregated nanoparticles](image_url)

**Figure S3.** TEM image of aggregated nanoparticles of fluorophore 1a prepared from its acetonitrile solution with 95% of water fraction. Due to the hydrophobic nature of fluorophore 1a, the aggregated nanoparticles in TEM adhesive onto the polymer edge of the sample substrate.
7. Thermal stability measurements

Figure S4. Results of TGA and DSC measurements. Decomposition temperature: 1a, 132 °C, 1b, 291 °C and 1c, 245 °C. Melting point: 1a, n/a (decomposed first), 1b, 239 °C and 1c, n/a.
8. LDS measurements

The measurements of LDS effect on the CdTe solar cell is based on the definition of cell EQE and the output short circuit current density (Jsc):

\[
J_{sc} = e \int_{\lambda_{min}}^{\lambda_{max}} \text{EQE}(\lambda) \phi_{ss}(\lambda) \, d\lambda = \frac{dI_{sc}}{dA}
\]

Where \( \phi_{ss}(\lambda) \) is the output light profile of the solar simulator and A is the active area of the CdTe solar cell, which is 0.5 cm².

Both the short circuit current (Is) with and without the LDS film were measured. Assuming A is proportional to Isc, the change of Isc is equal to the change of Jsc:

\[
\frac{I_{sc, with \, film} - I_{sc, without \, film}}{I_{sc, without \, film}} = \frac{J_{sc, with \, film} - J_{sc, without \, film}}{J_{sc, without \, film}} = \frac{J}{J_0}
\]

A CdTe solar cell was used as reference in the LDS film EQE measurement. This solar cell was fabricated with a thin CdS layer (about 70 nm) and it shows short-wavelength response (300 – 500 nm). It is active area is 0.5 cm². The EQE of a CdTe solar cell with LDS film was calculated by the following equation:

\[
\frac{I_{sc, with \, film}(\lambda)}{I_{sc, ref}(\lambda)} = \frac{\text{EQE with film}(\lambda)}{\text{EQE ref}(\lambda)}
\]

The output Isc at each individual wavelength was directly measured by a multimeter. The individual wavelength light was selected by connecting a monochromator to the solar simulator.