

## Supplementary Information

### **Rational Design of Tetraphenylethylene-based Luminescent Down-Shifting Molecules: Photophysical Studies and Photovoltaic Applications on CdTe Solar Cell from Small to Large Unit**

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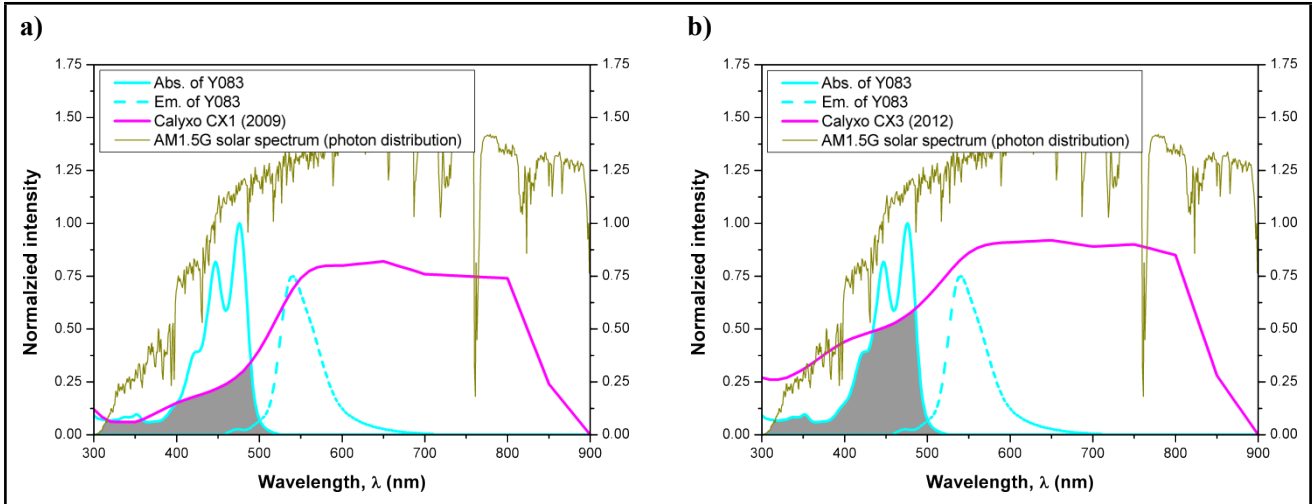
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## 1. Percentage of $J_{sc}$ loss ( $J_{loss}\%$ ) and emission matching factor ( $F_{em}$ ) of Y083

The CdTe solar cells used for the comparison are large PV modules produced by Calyxo. They are Calyxo CX1 (2009) and Calyxo CX3 (2012). Their EQE data are adapted from D. Ross et al., *IEEE Journal of Photovoltaics* **2014** 4(1) 457-464.



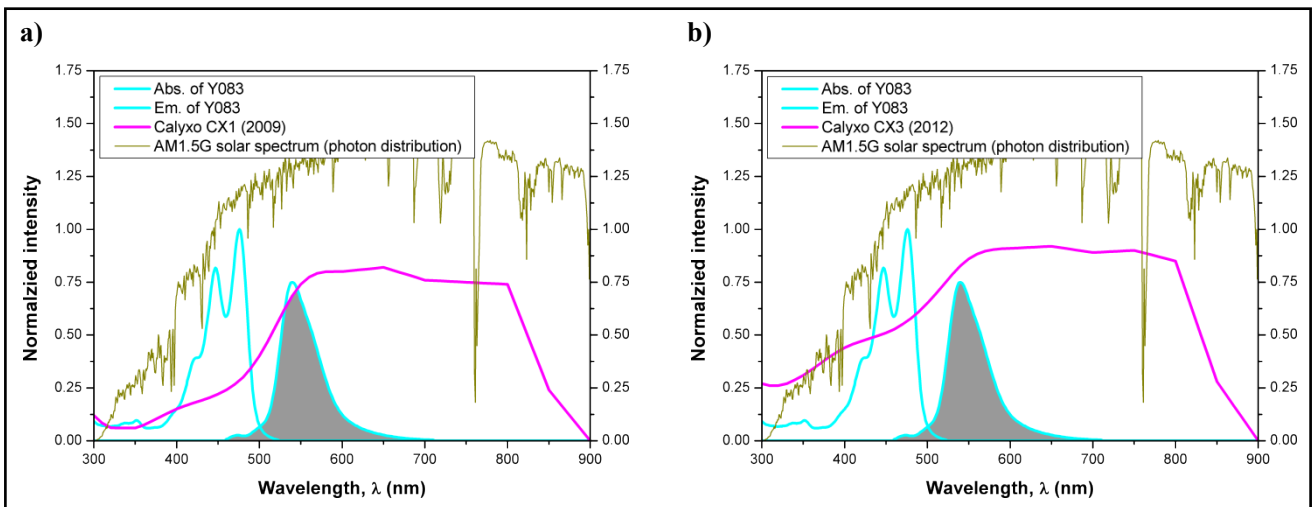
**Figure S1.** Comparison of the parasitic absorption effect (indicated as gray area) of Y083 between **a)** an outdated CdTe solar cell and **b)** a latest one.

The calculation method of the  $J_{sc}$  loss percentage ( $J_{loss}\%$ ) is:

$$J_{loss}\% = \frac{\int_{300\text{ nm}}^{900\text{ nm}} Abs(\lambda)EQE(\lambda)\phi(\lambda)d\lambda}{\int_{300\text{ nm}}^{900\text{ nm}} EQE(\lambda)\phi(\lambda)d\lambda} \times 100\%$$

where  $Abs(\lambda)$  is the normalized absorption spectrum (normalized to 1),  $EQE(\lambda)$  is the external quantum efficiency of the cell and  $\phi(\lambda)$  is the normalized AM1.5G solar spectrum in the form of photon distribution (normalized to 1.5). Higher  $J_{loss}\%$  value means more  $J_{sc}$  loss.

The calculated  $J_{loss}\%$  values for **a)** and **b)** are 3.8 % and 6.6 %, respectively.



**Figure S2.** Comparison of the emission spectral match (indicated as gray area) of Y083 between **a)** an outdated CdTe solar cell and **b)** a latest one.

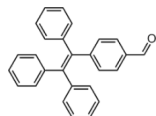
The calculation method of the emission spectral matching factor ( $F_{em}$ ) is:

$$F_{em} = \frac{\int_{300\text{ nm}}^{900\text{ nm}} EQE(\lambda)Em(\lambda)d\lambda}{\int_{300\text{ nm}}^{900\text{ nm}} Em(\lambda)d\lambda}$$

where  $Em(\lambda)$  is the normalized emission spectrum (normalized to 0.75). Higher  $F_{em}$  value means more emission spectral match.

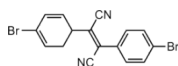
The calculated  $F_{em}$  values for **a)** and **b)** are 0.70 and 0.84, respectively.

## 2. Synthetic procedures and compound characterizations



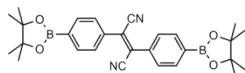
### 4-(1,2,2-triphenylvinyl)benzaldehyde (**2**).

*Reaction (i)*: A mixture of 2-bromo-1,1,2-triphenylethylene (1.0 g, 3.0 mmol), 4-formylphenylboronic acid (895 mg, 6.0 mmol), Pd(dppf)Cl<sub>2</sub> (109 mg, 5 mol%) and K<sub>2</sub>CO<sub>3</sub> (2.1 g, 14.9 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 (2 : 1) as eluent to afford compound **2** (isolated yield 91 %). Light yellow solid. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ): 9.91 (s, 1H), 7.64 (d, 2H, J = 8.0 Hz), 7.23 (d, 2H, J = 8.4 Hz), 7.16-7.03 (m, 15H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, δ): 192.1, 150.8, 143.3, 143.2, 143.1, 140.0, 134.5, 132.2, 131.6, 131.5, 131.5, 129.4, 128.2, 128.0, 127.3, 127.2, 127.1. MALDI-MS: m/z calcd for C<sub>27</sub>H<sub>20</sub>O<sup>+</sup> 360.1514, found 360.1518.



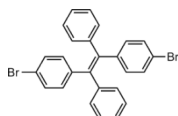
### 2,3-bis(4-bromophenyl)fumaronitrile (**3**).

*Reaction (iii)*: To a solution of 4-bromophenylacetonitrile (10.0 g, 51.0 mmol) and iodine (12.9 g, 51.0 mmol) in 200 mL of diethyl ether was added dropwise a solution of CH<sub>3</sub>ONa (5.5 g, 102.0 mmol) in 50 mL of MeOH at -78 °C under N<sub>2</sub> for over 30 min. The reaction mixture was allowed to warm to room temperature and kept stirring for 4 h. During this time, more and more precipitate was formed in the solution. Then the reaction was quenched with 100 mL of 2N HCl at 0 °C. The precipitate was collected by filtration and washed by water and methanol. The residue was purified by silica gel chromatography using Hex/DCM (1 : 1) as eluent to afford compound **3** (isolated yield 80 %). Pale yellow solid. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ): 7.70 (s, 8H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, δ): 132.9, 130.8, 130.3, 127.0, 124.9, 116.3. MALDI-MS: m/z calcd for C<sub>16</sub>H<sub>8</sub>Br<sub>2</sub>N<sub>2</sub><sup>-</sup> 385.9054, found 385.8833.



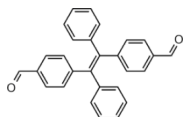
### 2,3-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)fumaronitrile (**4**).

*Reaction (iv)*: A mixture of compound **3** (600 mg, 1.5 mmol), B<sub>2</sub>pin<sub>2</sub> (942 mg, 3.7 mmol), Pd(dppf)Cl<sub>2</sub> (113 mg, 10.0 mol%) and KOAc (759 mg, 7.7 mmol) in 50 mL of 1,4-dioxane was stirred at 100 °C for 16 h. Then the reaction mixture was cooled down and extracted with DCM. The combined organic layer was dried over MgSO<sub>4</sub> anhydrous and filtered. The solvent was removed and the residue was purified by silica gel chromatography using Hex/DCM (1 : 3) as eluent to afford compound **4** (isolated yield 50 %). White solid. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ): 7.96 (d, 4H, J = 8.4 Hz), 7.82 (d, 4H, J = 8.4 Hz), 1.36 (s, 24H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, δ): 135.7, 134.5, 128.0, 126.2, 116.7, 84.5, 25.1. MALDI-MS: m/z calcd for C<sub>28</sub>H<sub>32</sub>B<sub>2</sub>N<sub>2</sub>O<sub>4</sub><sup>-</sup> 482.2548, found 482.2219.



### 1,2-bis(4-bromophenyl)-1,2-diphenylethene (**5**).

*Reaction (vi)*: 21.1 mL of TiCl<sub>4</sub> (1.0 M in toluene) was added to a mixture of 4-bromobenzophenone (5.0 g, 19.1 mmol) and zinc dust (2.5 g, 38.3 mmol) in 50 mL of THF. After reflux for 20 h, the reaction mixture was cooled to room temperature and filtered. The solvent was removed and the residue was purified by silica gel chromatography using hexane as eluent to afford compound **5** (isolated yield 57 %). White solid. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ): 7.31 (s, 4H), 7.14 (d, 10H, J = 16.9 Hz), 6.99 (s, 4H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, δ): 133.3, 131.6, 131.5, 131.3, 128.4, 128.2, 128.1, 127.3, 127.2. MALDI-MS: m/z calcd for C<sub>26</sub>H<sub>18</sub>Br<sub>2</sub><sup>+</sup> 487.9975, found 488.0349.



*4,4'-(1,2-diphenylethene-1,2-diyl)dibenzaldehyde (6)*.

*Reaction (vii)*: 8.2 mL of n-BuLi (1.6 M in hexane) was added to a solution of compound **5** (1.0 g, 2.0 mmol) in 50 mL of THF at -78 °C. After stir at -78 °C for 2 h, 1 mL of DMF anhydrous was added. The reaction mixture was allowed to warm to room temperature and stirred overnight. After 2 mL of water was added, the reaction mixture was extracted by DCM twice, dried over MgSO<sub>4</sub> anhydrous and filtered. The solvent was removed and the residue was purified by silica gel chromatography using Hex/EtOAc (5 : 1) as eluent to afford compound **6** (isolated yield 35 %). Yellow solid. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ): 9.91 (s, 2H), 7.64 (dd, 4H, J = 8.5 Hz), 7.20 (d, 4H, J = 8.1 Hz), 7.16-7.12 (m, 6H), 7.03-6.99 (m, 4H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, δ): 192.0, 192.0, 149.9, 149.9, 142.5, 142.4, 142.0, 141.9, 134.9, 134.8, 132.2, 132.1, 131.5, 131.4, 129.6, 129.5, 128.4, 128.3, 127.7, 127.6. MALDI-MS: m/z calcd for C<sub>28</sub>H<sub>20</sub>O<sub>2</sub><sup>-</sup> 388.1463, found 388.0880.

### 3. Thermal stability measurements

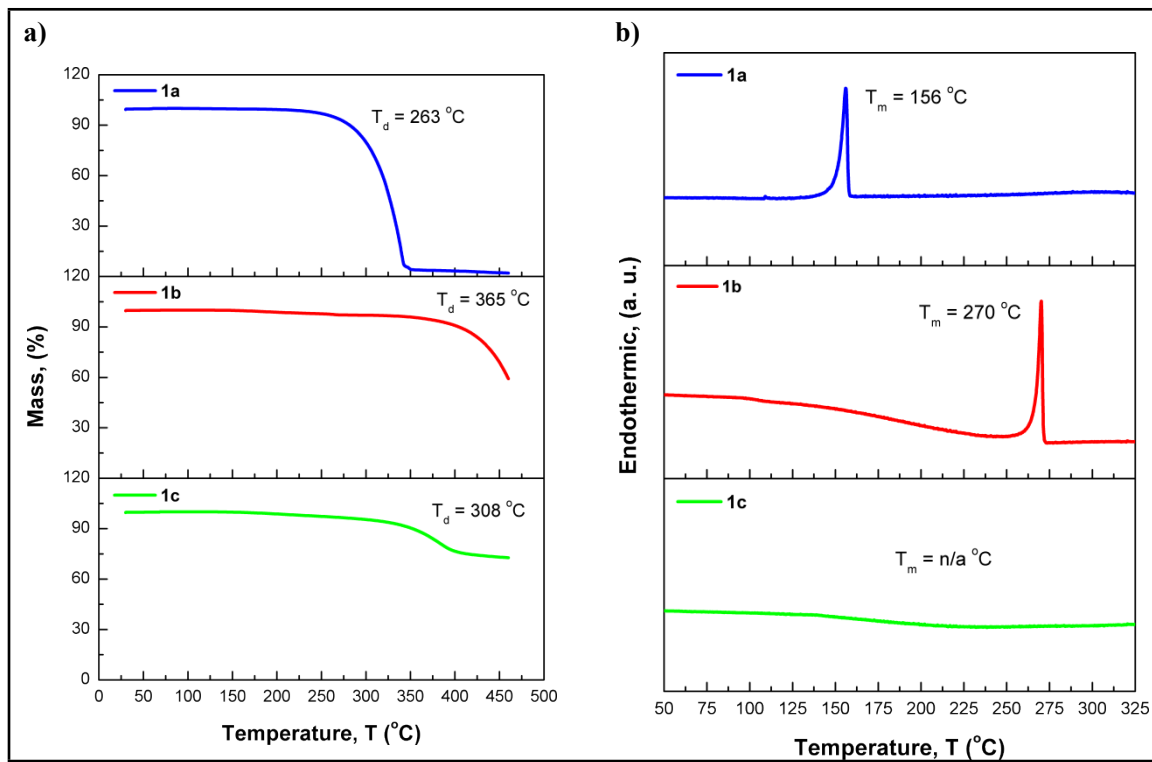


Figure S3. TGA and DSC results of fluorophore 1a-c.

#### 4. Solvatochromism measurements and theoretical calculations

Absorption ( $\lambda_{abs}$ , nm) and emission ( $\lambda_{em}$ , nm) wavelengths were measured in the 1,4-dioxane/acetonitrile mixtures. The Stokes shift ( $\Delta\nu$ ,  $\text{cm}^{-1}$ ) is calculated by the following equation:

$$\Delta\nu^{ICT} = \left( \frac{1}{\lambda_{abs}} - \frac{1}{\lambda_{em}} \right) \times 10^7$$

The solvent orientation polarizability ( $\Delta f$ ) of 1,4-dioxane/acetonitrile mixture is calculated by the following equation:

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

$$\epsilon = \chi_{DXE} \epsilon_{DXE} + \chi_{ACN} \epsilon_{ACN}$$

$$n = \sqrt{\chi_{DXE} n_{DXE}^2 + \chi_{ACN} n_{ACN}^2}$$

Where  $\epsilon$  is the dielectric constant,  $n$  is the refractive index of the solvent, and  $\chi$  is the solvent mole fraction.

The Lippert-Mataga equation is:

$$\Delta\nu^{ICT} = \Delta\nu^{vac} + \frac{2(\mu_e - \mu_g)^2}{hca_0^3} \Delta f$$

Where  $\Delta\nu^{ICT}$  is the Stokes shift ( $\text{cm}^{-1}$ ) in solvent;  $\Delta\nu^{vac}$  is the Stokes shift ( $\text{cm}^{-1}$ ) without any surrounding environment;  $\mu_e$  and  $\mu_g$  are transition dipole moment (D, 1 D =  $10^{-18}$  esu cm) on ground and excited states, respectively;  $h$  is Planck's constant ( $6.63 \times 10^{-27}$   $\text{cm}^2 \cdot \text{g} \cdot \text{s}^{-1}$ );  $c$  is the speed of light ( $3 \times 10^{10}$   $\text{cm} \cdot \text{s}^{-1}$ ),  $a_0$  is cavity radius (nm, 1 nm =  $10^{-7}$  cm) of Onsagar's reaction field around a fluorophore, which is approximate to 40 % of the longest axis for a nonspherical molecule of its ground state geometry; and  $\Delta f$  is solvent orientation polarizability.

By linear fitting the  $\Delta\nu^{ICT}$  vs.  $\Delta f$ , the values of  $\Delta\nu^{vac}$  and  $|\mu_e - \mu_g|$  can be obtained from the intercept and the slope, respectively.

**Table S1.** Linear fitting and calculation results of solvatochromism measurements.

Compd	$r^2$	intercept ( $\text{cm}^{-1}$ )	slope ( $\text{cm}^{-1}$ )	length (nm)	$a_0$ (nm)	$ \mu_e - \mu_g $ (D)	$\Delta(\Delta\nu)/\Delta(\Delta f)$ ( $\text{cm}^{-1}$ )
<b>1a</b>	0.76	$6349 \pm 279$	$8020 \pm 1477$	1.54	0.616	$13.6 \pm 1.3$	9343
<b>1b</b>	0.76	$7186 \pm 277$	$7914 \pm 1468$	2.47	0.988	$27.5 \pm 2.6$	9418
<b>1c</b>	0.78	$6907 \pm 113$	$3570 \pm 663$	1.92	0.768	$12.6 \pm 1.2$	3984

<sup>a</sup> In order to make the  $r^2$  on the same level, all the 10 data were used on fitting **1a** and **1b**, but the first 9 data were used on fitting **1c**.

**Table S2.** Calculated charge distribution (%) of donor (TPE group) on HOMO and LUMO of ground ( $S_0$ ) and excited ( $S_1$ ) states. The difference indicates CT rate (%).

	Absorption			Emission		
	$S_0$	$S_1^*$	CT rate	$S_1$	$S_0^*$	CT rate
<b>1a</b>	94 %	43 %	51 %	46 %	97 %	51 %
<b>1b</b>	95 %	38 %	57 %	42 %	96 %	54 %
<b>1c</b>	87 %	48 %	39 %	61 %	88 %	27 %

\* Non-equilibrium state.



## 5. Fluorescence lifetime analyses

The data in **Figure 3b** was fitted by two-exponential decay equation:

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

The average lifetime  $\langle\tau\rangle$  is given by:

$$\langle\tau\rangle = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2}$$

The data in the figure inserted in **Figure 3b** was fitted by single-exponential decay equation:

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

## 6. Emission spectra in water/acetonitrile mixtures

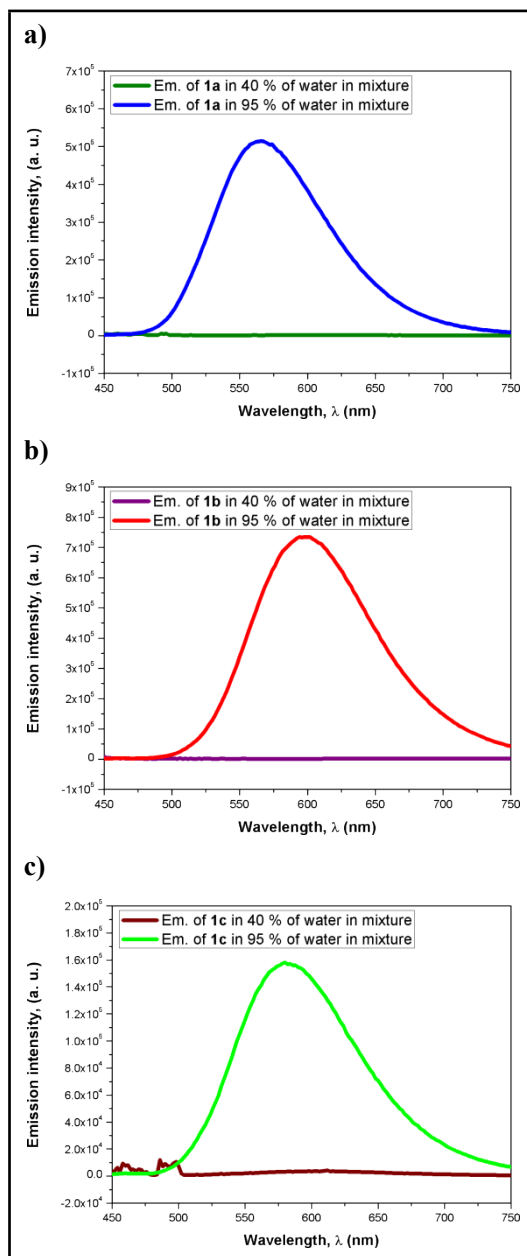
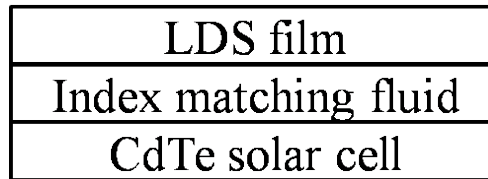


Figure S4. Emission spectra in 40 % and 95 % of water in mixture of a) **1a**, b) **1b** and c) **1c**.

## 7. Schematic structure of the LDS film on CdTe solar cell

For the small CdTe solar cell, we used index matching fluid between the interface of LDS film and CdTe solar cell to minimize photon loss due to the refraction of the air:



For the large CdTe solar panel, we directly doped the LDS film on the front surface of the CdTe solar cell. So there is no need to use any index matching fluid.

