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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

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Content

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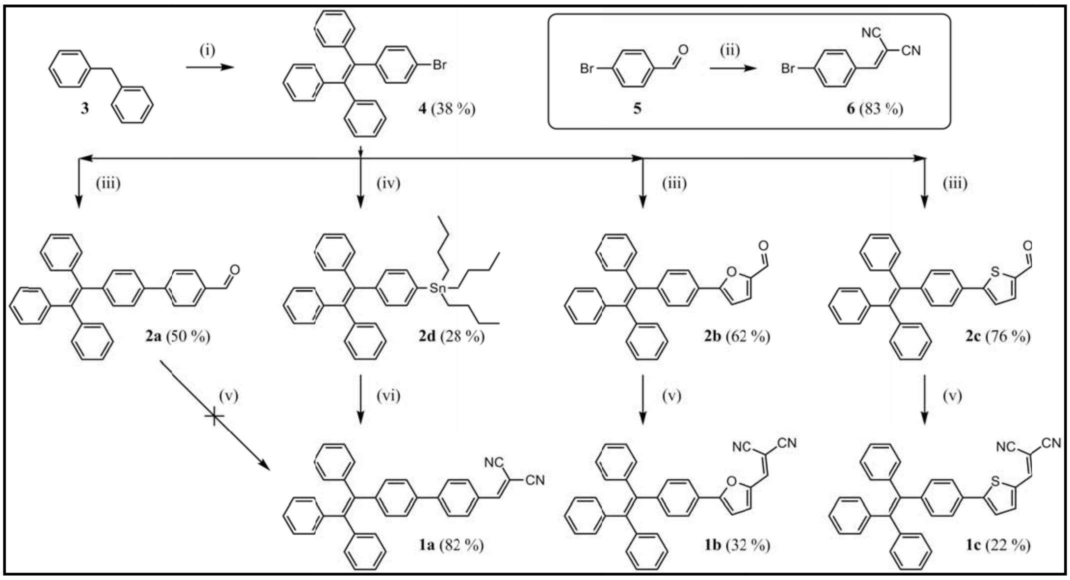
1. Synthesis and characterization

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(dppf)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-boromobenzophenone (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.

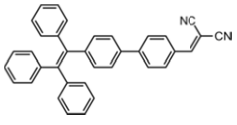
Reaction (iii): A mixture of 4 (1.0 g, 2.4 mmol), 4-formylphenylboronic acid (729 mg, 4.9 mmol, for **1a**) / 5-formylfuran-2-boronic acid (680 mg, 4.9 mmol, for **1b**) / 5-formylthiophene-2-boronic acid (758 mg, 4.9 mmol, for **1c**), Pd(dppf)Cl_2 (89 mg, 5.0 mol%) and K_2CO_3 (1.7 g, 12.2 mmol) were 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 $MgSO_4$. 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 Et_3N (or piperidine). The reaction mixture was stirred under 30 °C for 16h. The resulting mixture was dried over anhydrous $MgSO_4$. 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**).

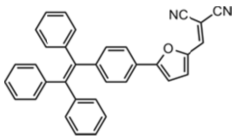
Reaction (vi): A mixture of **2d** (360 mg, 0.6 mmol), **6** (135 mg, 0.6 mmol) and $Pd(PPh_3)_4$ (33 mg, 5 mol%) in 25mL of toluene was stirred and refluxed for 16 h. The resulting solution was evaporated and the residue was purified by silica gel chromatography using hexane and DCM (1 : 1) as eluent to afford **1a**.

Compound characterizations:



1a

*2-((4'-(1,2,2-triphenylvinyl)biphenyl-4-yl)methylene)malononitrile (**1a**).* Yellow solid (yield 82 %). $R_f = 0.38$ (Hex : DCM = 1 : 2). ^{1}H-NMR (300 MHz, $CDCl_3$, 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). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 159.4, 147.1, 145.1, 143.7, 143.7, 143.6, 142.2, 140.3, 136.6, 133.3, 132.4, 132.1, 131.6, 131.6, 131.6, 131.5, 129.9, 128.1, 128.1, 128.0, 127.9, 127.0, 126.9, 126.9, 126.7, 114.3, 113.2, 81.9. MALDI-MS: m/z calcd for $C_{36}H_{24}N_2^+$ 484.1939, found 484.2264.

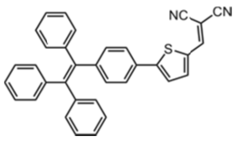


1b

*2-((5-(4-(1,2,2-triphenylvinyl)phenyl)furan-2-yl)methylene)malononitrile (**1b**).*

Orange solid (yield 32 %). $R_f = 0.56$ (Hex : DCM = 1 : 4). ^{1}H-NMR (300 MHz, $CDCl_3$, 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). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 161.7, 147.4, 146.9, 143.5, 143.3, 142.6, 140.2, 132.5, 131.6, 131.5, 128.2, 128.1, 127.9, 127.1, 127.0, 127.0, 126.1, 125.3, 114.8, 113.8, 109.8, 75.1. MALDI-MS: m/z calcd for $C_{34}H_{22}N_2O^-$ 474.1732, found 474.1664.

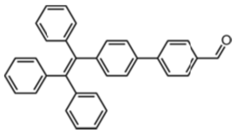
*2-((5-(4-(1,2,2-triphenylvinyl)phenyl)thiophen-2-yl)methylene)malononitrile (**1c**).*



1c

Orange solid (yield 22 %). R_f = 0.52 (Hex : DCM = 1 : 3). ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 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, $CDCl_3$, δ): 156.7, 150.8, 146.5, 143.5, 143.5, 143.4, 142.6, 140.4, 140.0, 134.2, 132.6, 131.6, 131.6, 131.5, 130.2, 128.2, 128.2, 128.0, 127.2, 127.1, 127.0, 126.1, 124.7, 114.5, 113.7, 76.5. MALDI-MS: m/z calcd for $C_{34}H_{22}N_2S^+$ 490.1504, found 490.1055.

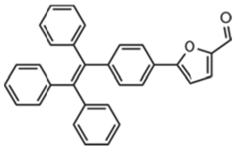
*4'-(1,2,2-triphenylvinyl)biphenyl-4-carbaldehyde (**2a**).*



2a

Yellow solid (yield 50 %). R_f = 0.60 (Hex : DCM = 1 : 2). ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 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, $CDCl_3$, δ): 192.1, 146.9, 144.5, 143.8, 143.8, 141.9, 140.4, 137.5, 135.3, 132.3, 131.7, 131.6, 131.6, 130.5, 128.1, 128.1, 128.0, 127.6, 127.0, 126.9, 126.9, 126.8. MALDI-MS: m/z calcd for $C_{33}H_{24}O^+$ 436.1827, found 436.1654.

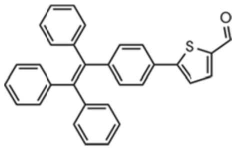
*5-(4-(1,2,2-triphenylvinyl)phenyl)furan-2-carbaldehyde (**2b**).*



2b

Yellow solid (yield 62 %). R_f = 0.31 (Hex : DCM = 1 : 2). ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 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, $CDCl_3$, δ): 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, 124.9, 107.9. MALDI-MS: m/z calcd for $C_{31}H_{22}O_2^+$ 426.1620, found 426.1465.

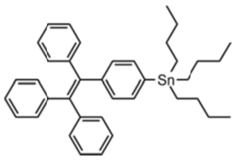
*5-(4-(1,2,2-triphenylvinyl)phenyl)thiophene-2-carbaldehyde (**2c**).*



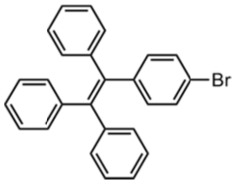
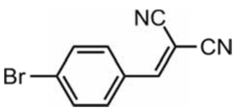
2c

Yellow solid (yield 76 %). R_f = 0.40 (Hex : DCM = 1 : 2). ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 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, $CDCl_3$, δ): 183.0, 154.4, 145.5, 143.7, 143.6, 143.5, 142.3, 142.2, 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 calcd for $C_{31}H_{22}OS^+$ 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, $CDCl_3$, δ): 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-NMR (75 MHz, CDCl$_3$, δ): 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, 127.8, 126.6, 126.5, 29.3, 27.6, 14.0, 9.8. MALDI-MS: m/z calcd for $C_{38}H_{44}Sn^-$ 620.2621, found 620.0860.
 **4**	*(2-(4-bromophenyl)ethene-1,1,2-triyl)tribenzene (**4**).* White solid (yield 37 %). R$_f$ = 0.56 (Hex : DCM = 2 : 1). ^{1}H-NMR (300 MHz, CDCl$_3$, δ): 7.31 (d, 2H, J = 8.5 Hz), 7.22-7.11 (m, 15H), 7.01 (d, 2H, J = 8.6 Hz). ^{13}C-NMR (75 MHz, CDCl$_3$, δ): 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. MALDI-MS: m/z calcd for $C_{26}H_{19}Br^+$ 410.0670, found 410.0552.
 **6**	*2-(4-bromobenzylidene)malononitrile (**6**).* White solid (yield 83 %). R$_f$ = 0.23 (Hex : DCM = 1 : 1). ^{1}H-NMR (300 MHz, CDCl$_3$, δ): 7.77 (d, 2H, J = 8.6 Hz), 7.72 (s, 1H), 7.68 (d, 2H, J = 8.7 Hz). ^{13}C-NMR (75 MHz, CDCl$_3$, δ): 158.7, 133.3, 132.1, 130.2, 129.9, 133.7, 112.6, 83.7. MALDI-MS: m/z calcd for $C_{10}H_5BrN_2^-$ 231.9636, found 231.9223.

2. Absorption and emission spectra of Y083 in LDS film

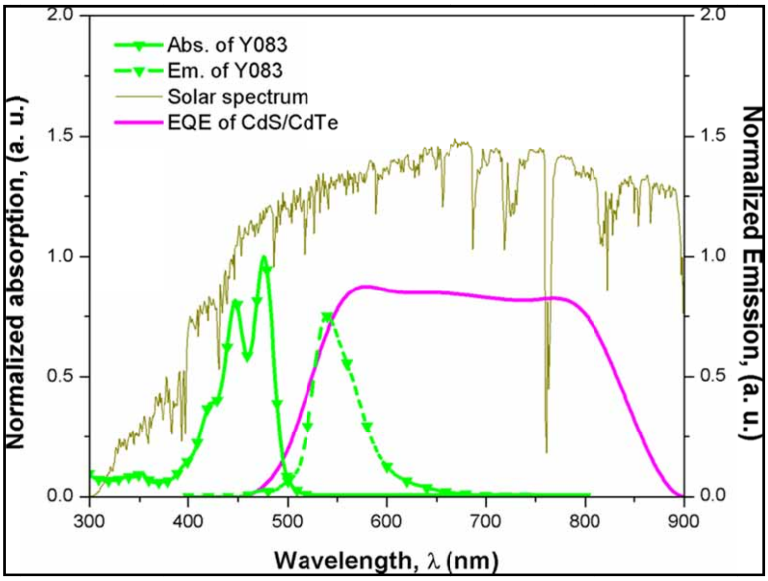


Figure S1. Normalized absorption (solid lines) and emission (dash lines) spectra of Y083 (λ_{ex} = 472 nm, green, ▼) associated with AM1.5G solar spectrum (dark yellow) and spectral response of CdTe solar cell (magenta).

3. Transition dipole moment change

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

$$\left(v_{abs}^{ICT} - v_{flu}^{ICT}\right) \cong \left(v_{abs}^{vac} - v_{flu}^{vac}\right) + \frac{2\left(\mu_e - \mu_g\right)^2}{hca_0^3}\Delta f$$

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

Where v 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; μ_e and μ_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 Δf value was tuned by different mixtures of 1,4-dioxane and acetonitrile. It is calculated by:

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

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

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

Fluorophore[a]	slope, cm^{-1}	r^2	$u_e - u_g$, D
1a	11545 ± 1156	0.9251	24.2 ± 1.2
1b	9186 ± 1123	0.8799	21.6 ± 1.3
1c	10537 ± 1306	0.8769	23.2 ± 1.4

[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 (S_0) and excited (S_1) states on donor (TPE) group. The difference indicates ICT rate (%).

	Absorption			Emission		
	S_0	S_1*	ICT rate	S_1	S_0*	ICT rate
1a	94 %	11 %	83 %	12 %	96 %	84 %
1b	82 %	17 %	65 %	19 %	92 %	73 %
1c	86 %	16 %	70 %	21 %	91 %	70 %

* Non-equilibrium state.

5. Fluorescence lifetime measurements

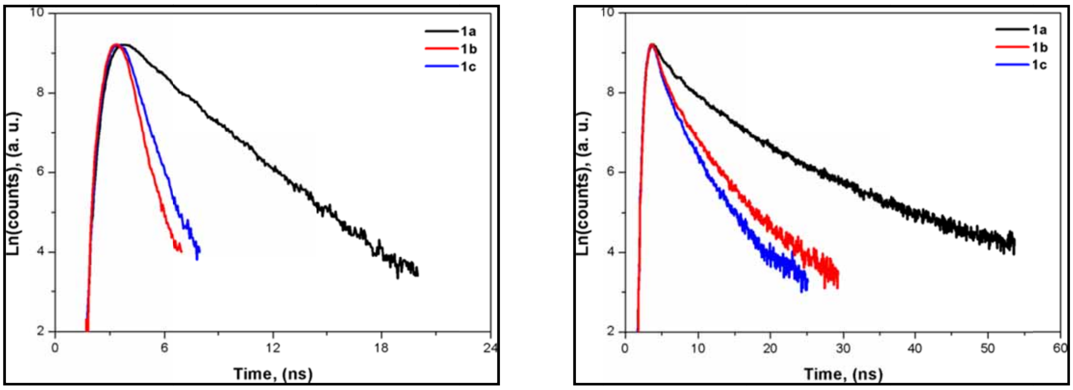


Figure S2. Fluorescent lifetimes of fluorophores **1a-c** in acetonitrile ($f_w = 0$) (left) and mixture ($f_w = 95$ %) (right). The fluorophore concentration is 15μM.

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 α is the represent the amplitudes of the components at $t = 0$ and τ_f is the average fluorescence lifetime.

The fitting results are:

	single-exponential	two-exponential		
Compd	τ_f (ns)	τ_1 (ns)	τ_2 (ns)	τ_f (ns)
1a	1.92	2.19	9.43	5.70
1b	1.05	1.75	5.98	2.35
1c	1.01	1.38	4.32	1.72

6. Image of aggregated nanoparticles

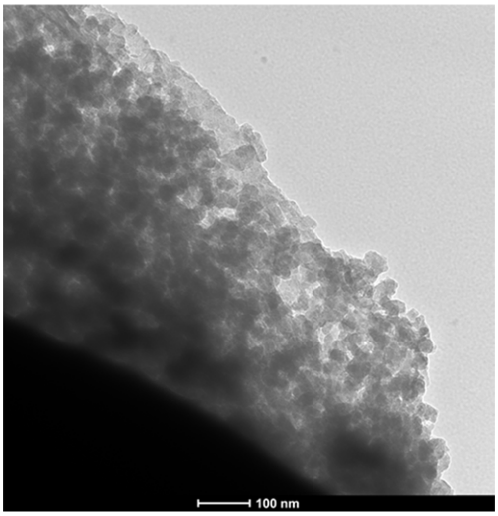


Figure S3. TEM image of aggregated nanoparticles of fluorophore **1a** prepared from its acetonitrile solution with 95 % of water fraction. Due to the hydrophobic nature of fluorophore **1a**, the aggregated nanoparticles in TEM adhesive onto the polymer edge of the sample substrate.

7. Thermal stability measurements

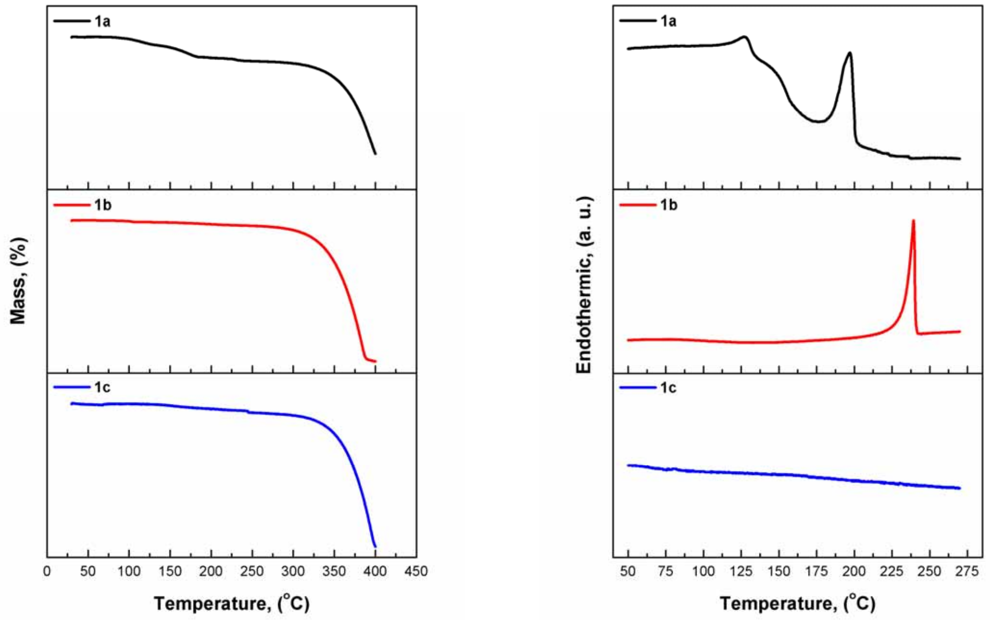


Figure S4. Results of TGA and DSC measurements. Decomposition temperature: **1a**, 132 °C, **1b**, 291 °C and **1c**, 245 °C. Melting point: **1a**, n/a (decomposed first), **1b**, 239 °C and **1c**, n/a.

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 (J_{sc}):

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

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 cm^2.

Both the short circuit current (I_{sc}) with and without the LDS film were measured. Assuming A is proportional to I_{sc}, the change of I_{sc} is equal to the change of J_{sc}:

$$\frac{I_{sc,with\ film} - I_{sc,without\ film}}{I_{sc,without\ film}} = \frac{J_{sc,with\ film} - J_{sc,without\ film}}{J_{sc,without\ film}} \left(= \frac{J}{J_0}\right)$$

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 cm^2. The EQE of a CdTe solar cell with LDS film was calculated by the following equation:

$$\frac{I_{sc,with\ film}(\lambda)}{I_{sc,ref}(\lambda)} = \frac{EQE_{with\ film}(\lambda)}{EQE_{ref}(\lambda)}$$

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