Theoretical Modeling on Luminescent Down-Shifting Process: A Discussion on Luminescent Molecule Design

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***Abstract* — A model was developed to describe the luminescent down-shifting (LDS) process in photovoltaic application. The model links the J_{sc} enhancement ($J_{LDS}\%$) of the solar cell to the photophysical properties including absorption (λ_{abs}) and emission (λ_{em}) wavelengths, Stokes shift ($\Delta\lambda$) and spectral cutting point (λ_{SCP}), as well as fluorescence quantum yield (Φ_f), of the luminescent molecules. It suggests that Φ_f is a more crucial parameter than λ_{abs} and λ_{em}. It also suggests that λ_{SCP} is a better parameter than $\Delta\lambda$ on describing $J_{LDS}\%$. The model is tested with luminescent molecules and the results are consistent with the experimental results.**

***Index Terms* — absorption, emission, fluorescence quantum yield, luminescent down-shifting, model.**

I. INTRODUCTION

The approach of luminescent down-shifting (LDS) has been widely used to enhance the short circuit current density (J_{sc}) of solar cells (e.g. c-Si, CdTe and CIGS) with poor short-wavelength responses [1-3]. Generally, a LDS layer is placed on the front surface of a solar cell, which can modify the incident photon distribution before light reaches the solar cell,. The wavelength down-shifting effect of the LDS layer is achieved by the absorption and emission processes of the embedded luminescent molecules, which convert photons in short-wavelength (< 500 mm) into photons in long-wavelength (> 500 nm) [4]. Although LDS application in enhancing solar cell performance have been thoroughly studied from small cell level to large module unit, few luminescent molecules are available for the LDS application [5,6]. Moreover, for the CdTe solar cell, because its poor short-wavelength response has been gradually improved in recent years through the fabrication improvement at the cell structure level, traditional luminescent molecule - BASF Lumogen F dye Y083, no longer exhibits excellent performance on J_{sc} enhancement. The reason is that the fabrication improvement has made the parasitic absorption effect of Y083, i.e. the spectral overlap between the absorption spectrum of Y083 and the spectral response of CdTe solar cell, a major drawback [5]. Thereby, a lot of cell-favorable photons are absorbed by Y083 for LDS process rather than efficiently used by the cell. Therefore, there is a need to develop novel luminescent molecules that have less parasitic absorption effect and better performance in J_{sc} enhancement than that of Y083.

Novel luminescent molecule design requires fully understanding the LDS process. In 2007, Richards and his co-workers performed a ray-tracing program to simulate the LDS effect on J_{sc} enhancement of a CdTe solar cell and analyzed various luminescent molecules [7]. However, there was not much information from the simulation that can help novel luminescent molecule design. Recently, Danos and his co-workers presented a simple theoretical formula describing the LDS process of Y083 in CdTe solar cell application [8], but the model description was incomplete because the parasitic absorption effect was not included. In this paper, we present a new theoretical model describing the LDS process and the model satisfactorily links the J_{sc} enhancement of the solar cell to the photophysical properties of the luminescent molecules. We specially focus on enhancing the J_{sc} of the CdTe solar cell in this study because CdTe solar cell exhibits the weakest short-wavelength response in all types of solar cells. We also primarily focus on the organic luminescent molecules because the organic luminescent molecules are the most promising materials for LDS application and their photophysical properties can be fine-tuned by their chemical structures. Finally, we tested our model with two organic luminescent molecules, and the experimental results were consistent with the theoretical results. Detailed analysis on our theoretical model provided useful information for designing novel luminescent molecules.

II. THEORETICAL BACKGROUND

A. Materials and Methods

MATLAB was used to write calculation programs based on our theoretical model. The detailed calculation methods are described in each of sections A-C. Procedures previously developed in our lab were used to design and synthesize the luminescent molecules and prepare the LDS films in our model testing [9]. CdTe solar cell was provided by the University of Toledo [10]. The method of measuring J_{sc} was described in section E.

B. LDS Model

For a front surface LDS layer, the enhancement in J_{sc} of a solar cell due to LDS effect (J_{LDS}) is defined as:

$$J_{LDS} = J_{cell+LDS} - J_{cell} \qquad (1)$$

where $J_{cell+LDS}$ and J_{cell} are the cell J_{sc} with and without the LDS layer.

The luminescent molecules in LDS layer not only generate useful current (J_{gain}) by converting cell-unfavorable high energy photons into cell-favorable low energy photons, but also cause current loss (J_{loss}) due to the parasitic absorption effect, i.e. the luminescent molecules absorb some of the cell-favorable low energy photons when the absorption spectrum overlaps with the spectral response of the solar cell. Therefore, equation (1) can be expressed as a consequence of J_{gain} and J_{loss}:

$$J_{LDS} = J_{gain} - J_{loss} \qquad (2)$$

The first term in equation (2) – J_{gain} is related to the LDS process, which is a function of photophysical properties (absorption and emission spectra, and fluorescence quantum yield) of the luminescent molecules. J_{gain} can be expressed by three factors and one constant:

$$J_{gain} = F_{abs} \cdot F_{em} \cdot F_{pc} \cdot J_{ideal} \qquad (3).$$

In equation (3), F_{abs} is the absorption spectral matching factor. It corresponds to the percentage of solar photons absorbed by the luminescent molecules, which is determined by the absorption spectrum of the molecule. F_{em} is the emission spectral matching factor. It corresponds to the percentage of photons (emitted by the luminescent molecules) used by the solar cell, which is determined by the emission spectrum of the molecule. F_{pc} is the photon conversion and collection factor, which is determined by the fluorescence quantum yield (Φ_f) of the luminescent molecules and optical photon efficiency (η_{opt}) of the LDS layer. Φ_f is the intrinsic property of the luminescent molecules while η_{opt} accounts for optical losses such as surface and/or side losses of the LDS film. J_{ideal} is the theoretical maximum J_{sc}, assuming all solar photons converted into useful current, which is a constant of 68.77 $mA \cdot cm^{-2}$ calculated for full wavelength using AM1.5G solar spectrum. The detailed expressions of terms, F_{abs}, F_{em} and F_{pc} in equation (3) are:

$$F_{abs} = \frac{\int [1 - T(\lambda)] \cdot \phi(\lambda) d\lambda}{\int \phi(\lambda) d\lambda} \qquad (4)$$

$$F_{em} = \frac{\int EQE(\lambda) \cdot Em(\lambda) d\lambda}{\int Em(\lambda) d\lambda} \qquad (5)$$

$$F_{pc} = \eta_{opt} \cdot \Phi_f \qquad (6)$$

where $T(\lambda)$ and $Em(\lambda)$ are transmission spectrum and emission spectrum of the luminescent molecules, respectively; $\phi(\lambda)$ is the incident solar photon distribution (AM1.5G); and $EQE(\lambda)$ is the spectral response (represented by EQE) of the solar cell. In this paper, we use the EQE of a CdTe module (Calyxo CX3, 2012) for model calculation.

The second term – J_{loss} in equation (2) is parasitic absorption effect and can be expressed by $T(\lambda)$, $EQE(\lambda)$ and $\phi(\lambda)$:

$$J_{loss} = q \cdot \int [1 - T(\lambda)] \cdot EQE(\lambda) \cdot \phi(\lambda) d\lambda \qquad (7)$$

where q is elementary charge (1.6×10^{-19} C) that is used for calculating J_{sc} from the number of photons absorbed by the solar cell.

To quantify the LDS effect on different solar cells with various luminescent molecules as LDS layers, the percentage of the increase in J_{sc} ($J_{LDS}\%$) based on the original J_{sc} of the solar cell (J_{cell}) will be used in this paper:

$$J_{LDS}\% = J_{LDS}/J_{cell} = J_{gain}\% - J_{loss}\% \qquad (8)$$

C. Photophysical Properties of Luminescent Molecules

Photophysical properties of organic luminescent molecules are considered intrinsically depending on the chemical structures [11]. However, for most of the organic luminescent molecules, the absorption ($Abs(\lambda)$) and emission ($Em(\lambda)$) spectra cannot be described by simple mathematical functions due to complicated electron transitions happen in the molecules. To address this critical issue, we assumed that all the organic luminescent molecules exhibit normal distributed (Gaussian-type) absorption and emission spectra with a 100 nm peak width at half height ($W_{2/h}$). Thus, the absorption and emission spectra are the functions of the maximum absorption wavelength (λ_{abs}) and the maximum emission wavelength (λ_{em}), respectively. The absorption and emission spectra of a luminescent molecule can be expressed as:

$$Abs(\lambda, \lambda_{abs}) = e^{-\frac{(\lambda - \lambda_{abs})^2}{2\sigma^2}} \qquad (9)$$

$$Em(\lambda, \lambda_{em}) = e^{-\frac{(\lambda - \lambda_{em})^2}{2\sigma^2}} \qquad (10)$$

where $\sigma = 50/\sqrt{2\ln 2} = 42.47$.

Based on Beer-Lambert law, the relationship between the transmission spectrum ($T(\lambda)$) and absorption spectrum ($Abs(\lambda)$) of a LDS layer containing luminescent molecules can be expressed by:

$$T(\lambda, \lambda_{abs}, OD) = 1 - 10^{-[Abs(\lambda, \lambda_{abs})] * OD} \qquad (11).$$

Therefore, $T(\lambda)$ is determined by λ_{abs} and the optical density (OD) of the LDS layer.

Linking equations (9)-(11) to equations (4)-(7), we conclude that $J_{LDS}\%$ is primarily determined by the variables that are related to photophysical properties (λ_{abs}, λ_{em} and Φ_f) of luminescent molecules and optical properties (OD and η_{opt}) of LDS layer. However, the optical properties of the LDS layer are not intrinsically related to the chemical structures of the luminescent molecules. So in our model, we set OD to 2.00 (99 % of light absorption at λ_{abs}) and η_{opt} to 0.873 (12.7 % of the photon surface loss for a host material with refractive index of 1.49), respectively [12]. Therefore, the final function can be presented as:

$$J_{LDS}\% = f(\lambda_{abs}, \lambda_{em}, \Phi_f) \qquad (12).$$

It should be pointed out that all the parameters in equation (12) are solid state properties of the luminescent molecules.

III. RESULTS AND DISCUSSION

A. Effect of Absorption and Emission Wavelength

The first two parameters are maximum absorption (λ_{abs}) and emission (λ_{em}) wavelengths, which determine the absorption and emission spectra of a luminescent molecule (equations (9) and (10)). Thus, F_{abs} and F_{em} can be calculated from equation (4) and (5), respectively, as well as J_{loss} from equation (7). Fig. 1 shows the effect of λ_{abs} and λ_{em} on $J_{LDS}\%$ in 3D and 2D graphs. $J_{LDS}\%$ is calculated by setting Φ_f to 1.00 but varying λ_{abs} from 300 to 600 nm and λ_{em} from 400 to 900 nm according to equation (12).

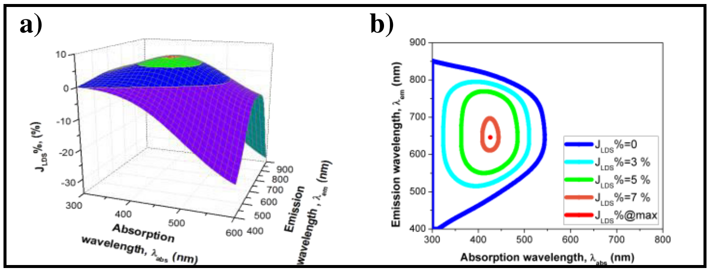

Fig. 1. a) 3D and b) 2D graphs of $J_{LDS}\%$ value depending on λ_{abs} and λ_{em}. The color circles indicate different $J_{LDS}\%$ ranges (listed in TABLE I).

In Fig. 1a, it is noted that when λ_{abs} is fixed, $J_{LDS}\%$ increases and then decreases with increasing λ_{em}. The increase phase indicates the increase in F_{em}, which means more spectral overlap between emission spectrum of the luminescent molecule and spectral response of the solar cell, while the decrease phase is vice versa. The same results are also found when λ_{em} is fixed. The increase in $J_{LDS}\%$ is caused by increase in F_{abs} so that more short-wavelength photons are absorbed and converted. However, further increasing λ_{abs} will cause the increase in $J_{loss}\%$ that results in decrease in $J_{LDS}\%$. The maximum $J_{LDS}\%$ is found 7.22 % when λ_{abs} = 426 nm and λ_{em} = 646 nm.

In Fig. 1b, each color circle indicates $J_{LDS}\%$ range as shown in TABLE I. For example, if λ_{abs} and λ_{em} are between the cyan and green circles, $J_{LDS}\%$ should be 3 – 5 %. Furthermore, each color circle can also provide information on the range of λ_{abs} and λ_{em} that are required to achieve the specific $J_{LDS}\%$. For example, to achieve a $J_{LDS}\%$ over 5 %, λ_{abs} should be in the range 363 – 485 nm while λ_{em} should be 550 – 769 nm (TABLE I). With increasing $J_{LDS}\%$, the color circle shrinks towards to the central maximum point, suggesting a more specific and narrower range of λ_{abs} and λ_{em} is required to achieve a higher $J_{LDS}\%$.

TABLE I
REQUIRED λ_{abs} AND λ_{em} RANGES TO ACHIEVE SPECIFIC $J_{LDS}\%$ RANGES.

$J_{LDS}\%$	color	λ_{abs} (nm)	λ_{em} (nm)
> 0	blue	300 – 544	400 – 851
> 3 %	cyan	324 – 510	515 – 795
> 5 %	green	363 – 485	550 – 769
> 7 %	orange	409 – 444	611 – 697
7.22 %^{a}	red	426	646

^{a} overall maximum.

B. Effect of Stokes shift and Spectral Cutting Point

Stokes shift ($\Delta\lambda = \lambda_{em} - \lambda_{abs}$) is another important photophysical parameter of a luminescent molecule. It is well known that Stokes shift refers to the energy loss during the emission process, which is more dependent on the chemical structure of a luminescent molecule than λ_{abs} and λ_{em}. For organic luminescent molecules, a rigid chemical structure is usually associated with a small $\Delta\lambda$, e.g. perylene-based luminescent molecules (typical $\Delta\lambda$ < 50 nm), while a flexible chemical structure is associated with a large $\Delta\lambda$, e.g. triphenylamine-based luminescent molecules (typical $\Delta\lambda$ > 50 nm) [13,14]. Moreover, $\Delta\lambda$ is also related to the electronic state of a luminescent molecules [15]. A luminescent molecule exhibits different $\Delta\lambda$ in different environment. Solvatochromism spectroscopy and Lippert-Mataga theory suggest such changes in $\Delta\lambda$ is highly related to the transition dipole moment of ground and excited states of a luminescent molecule [16]. Therefore, $\Delta\lambda$ of a luminescent molecule can be fine-tuned by constructing a charge donor-acceptor type structure and manipulating the strength of donor and acceptor moieties. Besides $\Delta\lambda$, in LDS application of a luminescent molecule in LDS application, another important parameter is the spectral cutting point ($\lambda_{SCP} = (\lambda_{abs} + \lambda_{em})/2$). A luminescent molecule will absorb more photons below λ_{SCP} and emit more photons over λ_{SCP}. Fig. 2 shows the 2D graphs, providing the relationship between $\Delta\lambda$ (or λ_{SCP}) and $J_{LDS}\%$. $\Delta\lambda$ and λ_{SCP} are calculated from each λ_{abs} and λ_{em} in Fig. 1a.

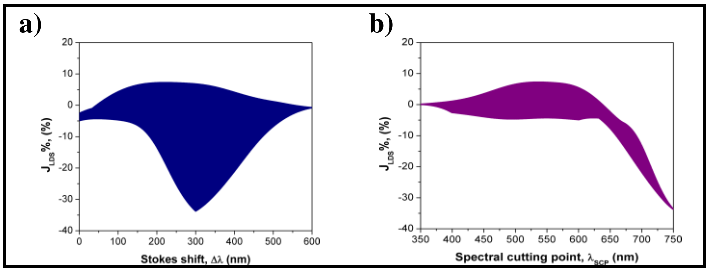

Fig. 2. 2D graphs of relationship between $J_{LDS}\%$ and a) $\Delta\lambda$ (navy area) (or b) λ_{SCP} (purple area)).

It is noted in Fig. 2a that increasing $\Delta\lambda$ does not always lead to positive changes in $J_{LDS}\%$. Actually, it can lead to both positive and negative $J_{LDS}\%$, depending on the corresponding λ_{abs} and λ_{em}. At the maximum $J_{LDS}\%$ (7.22 %), $\Delta\lambda$ is found equal to 181 nm, which is quite a large value for common organic luminescent molecules. In terms of λ_{SCP} in Fig. 2b, λ_{SCP} is a better parameter than $\Delta\lambda$ to describe the relationship between $J_{LDS}\%$ and spectral wavelengths, because $J_{LDS}\%$ does not show much variation with changes of λ_{SCP}. λ_{SCP} is found to be 536 nm for the maximum $J_{LDS}\%$ (7.22 %).

In TABLE II, both minimum $\Delta\lambda$ ($\Delta\lambda_{min}$) and λ_{SCP} ($\lambda_{SCP,min}$) required to achieve a certain $J_{LDS}\%$ are calculated. It is noted that higher $J_{LDS}\%$ requires larger $\Delta\lambda$ and higher λ_{SCP}, suggesting luminescent molecules with more flexible chemical structure can be better candidates for LDS application, because such flexible structure will lead blue-shifted λ_{abs} and red-shifted λ_{em} [14]. For example, 114 nm of $\Delta\lambda_{min}$ and 473 nm of $\lambda_{SCP,min}$ are required to achieve over 5 % changes in $J_{LDS}\%$. Many organic luminescent molecules are known to have such properties.

TABLE II
MINIMUM $\Delta\lambda$ ($\Delta\lambda_{min}$) AND λ_{scp} ($\lambda_{scp,min}$) FOR VARIOUS $J_{LDS}\%$ VALUES.

$J_{LDS}\%$	$\Delta\lambda_{min}$ (nm)	$\lambda_{SCP,min}$ (nm)
0	45	350
3 %	81	443
5 %	114	473
7 %	181	516
7.22 %[a]	220	536

[a] overall maximum.

C. Effect of Fluorescence Quantum Yield

Besides λ_{abs} and λ_{em}, fluorescence quantum yield (Φ_f) is another important parameter in equation (12). It is directly related to photon conversion efficiency of a luminescent molecule. It is known that Φ_f is related to the radiative decay rate constant (k_r) and non-radiative decay rate constant (k_{nr}), described by the following equation:

$$\Phi_f = \frac{k_r}{k_r + k_{nr}} \qquad (13)$$

The parameters k_r and k_{nr} are related to the chemical structures of luminescent molecules. For perylene-based luminescent molecules with rigid chemical structures, $k_r > k_{nr}$. Therefore, perylene-based luminescent molecules usually exhibit high quantum yields. But for triphenylamine-based luminescent molecules with flexible chemical structures, $k_{nr} > k_r$. Therefore, triphenylamine-based luminescent molecules usually exhibit low quantum yields [13,14].

Fig. 3a shows the effects of Φ_f on $J_{LDS}\%$. $J_{LDS}\%$ is calculated by fixing λ_{abs} and λ_{em} (so that the $\Delta\lambda_{min}$ indicated in TABLE II is reached) in each entry (indicated by color from blue to red) in TABLE III and varying Φ_f from 0 to 1.00. Fig. 3b shows the relationship between Φ_f and $\Delta\lambda_{min}$ associated with different $J_{LDS}\%$. In the calculation, $J_{LDS}\%$ of 0, 3 %, 5 % and 7 % (indicated by color from blue to red in Fig. 3b) was firstly calculated with λ_{abs} (300 – 600 nm), λ_{em} (400 – 900 nm) and Φ_f (0 – 1.00). Then the corresponding λ_{abs} and λ_{em} required to achieve the different $J_{LDS}\%$ were identified to calculate $\Delta\lambda$, which was then used to plot Fig. 3b.

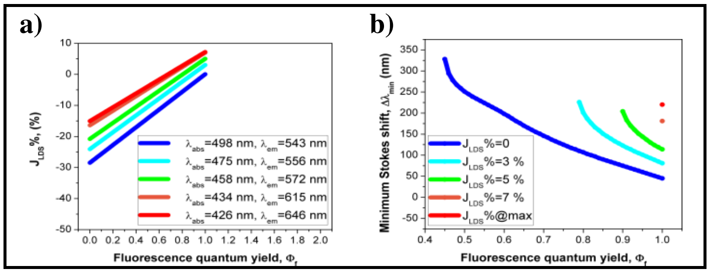

Fig. 3. a) Effect of Φ_f on $J_{LDS}\%$ and b) relationship between Φ_f and $\Delta\lambda_{min}$ associated with different $J_{LDS}\%$.

It is noted in Fig. 3a that unlike λ_{abs} and λ_{em} (or $\Delta\lambda_{min}$), Φ_f exhibits a linear effect on $J_{LDS}\%$, which means the higher Φ_f will definitely results in a higher $J_{LDS}\%$. In other words, in equation (12), Φ_f is more important than other parameters (λ_{abs} and λ_{em}) due to its linear effect on $J_{LDS}\%$. For each given λ_{abs} and λ_{em}, the minimum Φ_f ($\Phi_{f,min}$) for a positive $J_{LDS}\%$ ($J_{LDS}\% > 0$) and the maximum $J_{LDS}\%$ ($J_{LDS}\%$@max) with $\Phi_f = 1.00$ are listed in TABLE III. For example, if $\lambda_{abs} = 458$ nm and $\lambda_{em} = 572$ nm with $\Delta\lambda = 114$ nm, 0.81 of $\Phi_{f,min}$ is required to achieve $J_{LDS}\% > 0$, and 5.04 % of $J_{LDS}\%$@max can be achieved when $\Phi_f = 1.00$. In TABLE III, it is also noted that for $J_{LDS}\% > 0$, increasing $\Delta\lambda$ leads to decrease in Φ_f. Fig. 3b provides a detailed results for the relationship between Φ_f and $\Delta\lambda_{min}$. It is noted that for each $J_{LDS}\%$, $\Delta\lambda_{min}$ always decreases along with increase in Φ_f. In Fig. 3b, for example, to achieve $J_{LDS}\% > 5$ % with $\Phi_f = 0.81$, $\Delta\lambda_{min}$ should be 204 nm (or $\Delta\lambda > 204$ nm), but with $\Phi_f = 1.00$, $\Delta\lambda_{min}$ needs to be 114 nm (or $\Delta\lambda > 114$ nm). In summary, for the organic luminescent molecule design, to achieve a positive $J_{LDS}\%$ ($J_{LDS}\% > 0$, blue curve in Fig. 3b), either high Φ_f (0.45 – 1.00) or large $\Delta\lambda$ (45 – 328 nm) is required.

TABLE III
$\Phi_{f,min}$ REQUIRED TO ACHIEVE $J_{LDS}\% > 0$ AND $J_{LDS}\%$@max THAT CAN BE ACHIEVED WHEN $\Phi_f = 1.00$ FOR EACH GIVEN λ_{abs} AND λ_{em}.

λ_{abs}, λ_{em} (nm)	$\Delta\lambda$ (nm)	color	$\Phi_{f,min}$	$J_{LDS}\%$@max
498, 543	45	blue	1.00	0.06 %
475, 556	81	cyan	0.89	3.04 %
458, 572	114	green	0.81	5.04 %
434, 615	181	orange	0.71	7.01 %
426, 646	220	red	0.68	7.22 %[a]

[a] overall maximum.

D. Organic Luminescent Molecule Design Strategy

As discussed above, our model calculations suggest that to achieve a positive $J_{LDS}\%$ ($J_{LDS}\% > 0$) of CdTe solar cell using LDS layer, λ_{abs} and λ_{em} of luminescent molecules need to be 300 – 544 nm and 400 – 851 nm, respectively (TABLE I), and the corresponding minimum $\Delta\lambda$ ($\Delta\lambda_{min}$) and λ_{SCP} ($\lambda_{SCP,min}$) need to be 45 nm and 350 nm, respectively (TABLE II). Since $\Delta\lambda$ decreases when Φ_f increase (Fig. 3b), to achieve positive $J_{LDS}\%$ ($J_{LDS}\% > 0$), luminescent molecule need to have either high Φ_f (0.45 – 1.00) or large $\Delta\lambda$ (45 – 328 nm).

It well known Φ_f and $\Delta\lambda$ for most organic luminescent molecules are compensative parameters, e.g. increasing the value of one will cause decrease in the other. On the other hand, Φ_f exhibits linear effect on $J_{LDS}\%$ (Fig. 3a) while $\Delta\lambda$ does not (Fig. 2a). Therefore, achieving high Φ_f should be priority consideration in the organic luminescent molecule design.

Most commercial available organic luminescent molecules show high Φ_f but small $\Delta\lambda$, e.g. Y083 ($\Phi_f = 0.92$, $\Delta\lambda = 64$ nm). The small $\Delta\lambda$ will lead to high values of $J_{loss}\%$ due to the parasitic absorption (equation (7)). To address this issue, we recently developed some novel luminescent molecules with both high Φ_f and large $\Delta\lambda$, e.g. LmA (as is presented in next section, Φ_f = 0.99, $\Delta\lambda$ = 140 nm). Those luminescent molecules have very specific chemical structures that minimize the common compensative relationship between Φ_f and $\Delta\lambda$.

E. Test the LDS model with Organic Luminescent Molecules

To test the LDS model, two organic luminescent molecules were used. They are traditional Y083 and a novel compound named LmA. Their solid states were achieved by doping the luminescent molecules in poly(methyl methacrylate) (PMMA) films. Their absorption and emission spectra were measured by UV-Vis spectrometer and fluorescence photon counter. Solid state quantum yields were measured by an integrating sphere. The absorption and emission spectra, chemical structures of each compound, associated with AM1.5G solar photon distribution and spectral response (EQE) of the CdTe solar cell are depicted in Fig. 4. The photophysical parameters (λ_{abs}, λ_{em}, $\Delta\lambda$ and Φ_f) of each compound are listed in TABLE IV.

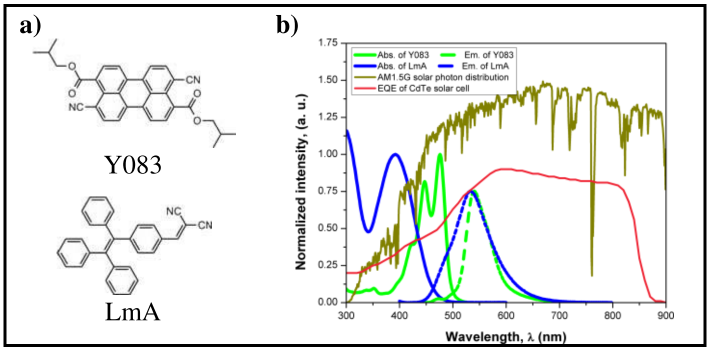

Fig. 4. The absorption and emission spectra, chemical structures of each compound, associated with AM1.5G solar photon distribution and spectral response (EQE) of the CdTe solar cell

These two luminescent molecules have two different types of chemical structures. Y083 has a perylene core with cyano and carboxylate groups. It has a rigid chemical structure, and thus it exhibits perylene-like absorption and emission spectra with high Φ_f (0.92) but a small $\Delta\lambda$ (64 nm). LmA is a tetraphenylethylene (TPE)-based luminescent molecule modified by a methylene malononitrile group. The overall structure of the molecule is a charge donor-acceptor (D-A) type. It is known that TPE-based compounds exhibit aggregation-induced emission (AIE) characteristic, showing high Φ_f in solid state [17,18], while the D-A type luminescent molecules exhibit intramolecular charge transfer (ICT) characteristic, showing large $\Delta\lambda$ [19,20]. Thus, LmA possesses both AIE and ICT properties with high Φ_f (0.99) and large $\Delta\lambda$ (140 nm).

To evaluate J_{sc} enhancement of Y083 and LmA, each one was doped into PMMA to form LDS film with a thickness of 85 μm. The weight concentration of the luminescent molecule in LDS films was 1.0 %. All edges of the CdTe solar cell with LDS film on its surface were wrapped by aluminum foil to minimize the photon side loss. Index matching fluid was applied on the interface between the cell surface and the film. In the experiment, J_{sc} were measured by EQE method. EQE of the cell with each LDS film was first measured. Then the EQE data was integrated with the AM1.5G solar photon distribution to obtain the short circuit current density of the cell with LDS film ($J_{cell+LDS}$). Experimental $J_{LDS}\%$ was finally calculated by equation (1) and (8). In the theoretical part, the absorption and emission spectra of each luminescent molecule were fitted by the normal distribution function in equation (9) and (10), respectively. The λ_{abs} and λ_{em} were then obtained from the best fitting results. Theoretical $J_{LDS}\%$ was finally calculated by equation (12) using Φ_f from the experimental results. Theoretical parameters F_{abs}, F_{em}, F_{pc}, $J_{gain}\%$ and $J_{loss}\%$ were calculated by equation (3)-(7), respectively. The experimental and theoretical results are summarized in TABLE IV.

TABLE IV
PHOTOPHYSICAL PROPERTIES, AND EXPERIMENTAL AND THEORETICAL, INCLUDING PARAMETERS RESULTS FOR Y083 AND LmA.

Experimental:					
Compd	λ_{abs} (nm)	λ_{em} (nm)	$\Delta\lambda$ (nm)	Φ_f	$J_{LDS}\%$
Y083	476	540	64	0.92	3.77 %
LmA	392	532	140	0.99	4.05 %
Theoretical:					
Compd	λ_{abs} (nm)	λ_{em} (nm)	$\Delta\lambda$ (nm)	Φ_f	$J_{LDS}\%$
Y083	455	550	95	0.92	2.97 %
LmA	375	537	162	0.99	4.50 %
Parameters:					
Compd	F_{abs}	F_{em}	F_{pc}	$J_{gain}\%$	$J_{loss}\%$
Y083	0.24	0.78	0.80	22.45	19.48
LmA	0.12	0.75	0.86	11.33	6.83

In TABLE IV, $J_{LDS}\%$ is 3.77 % and 4.05 % for Y083 and LmA in experiment, respectively. Theoretical calculation also gave the same results, showing that LmA exhibits superior J_{sc} enhancement to that of Y083. The differences on $J_{LDS}\%$ between experimental and theoretical results are mainly due to variations in absorption and emission spectral fittings, e.g. the absorption spectrum of Y083 was not well-fitted by a normal distributed curve. In Fig. 4b, although these two luminescent molecules exhibit similar emission spectra, the absorption spectra of LmA is more blue-shifted, thus leads to less parasitic absorption effect than that of Y083. Observing the parameters listed in TABLE IV, it is interesting to note that although Y083 has higher F_{abs} with similar F_{em} and F_{pc} as LmA, which lead to higher $J_{gain}\%$, its overall $J_{LDS}\%$ is less than that of LmA. This is because of its high $J_{loss}\%$ caused by its severe parasitic absorption effect. In other words, F_{abs} of LmA is only half of Y083, leading 50 % decrease in $J_{gain}\%$, but the low F_{abs} also leads 65 % decrease in $J_{loss}\%$ that is more than the negative effects on $J_{gain}\%$. Therefore, LmA exhibits overall higher $J_{LDS}\%$ larger than that of Y083, suggesting minimizing parasitic absorption effect is a more practical strategy of developing novel luminescent molecules for LDS application in CdTe photovoltaic cell.

IV. CONCLUSIONS

In conclusion, we have developed a new theoretical model to describe LDS processes that associated with photovoltaic cell applications. The model satisfactorily links the Jsc enhancement of the solar cell to the photophysical properties of luminescent molecules and is supported by our experimental results. It is suggested that the J_{sc} enhancement ($J_{LDS}\%$) is the result of $J_{gain}\%$ and $J_{loss}\%$, where $J_{gain}\%$ can be further expressed by the factors F_{abs}, F_{em} and F_{pc}, related to maximum absorption (λ_{abs}) and emission (λ_{em}) wavelengths and fluorescence quantum yields (Φ_f) of luminescent molecules. In addition, we also analyzed effects of Stokes shift ($\Delta\lambda$) and spectral cutting point (λ_{SCP}) on $J_{LDS}\%$. The model suggests that Φ_f is more crucial than λ_{abs} and λ_{em}, which should be the first consideration when designing luminescent molecules. It also suggests that λ_{SCP} is better parameter than $\Delta\lambda$ on describing $J_{LDS}\%$. For LDS application of a given solar cell, the absorption and emission ranges, minimum Stokes shifts ($\Delta\lambda_{min}$) and fluorescence quantum yields ($\Phi_{f,min}$) of the potential luminescent molecules can be calculated by our model. These information can provide valuable insight for novel luminescent molecule design. Our study suggests that less parasitic absorption and high fluorescent quantum yield should be the priority consideration in developing novel luminescent molecules for LDS application.

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