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# Title: High Performance Organic Dyes with Electron-Deficient Quinoxalinoid Heterocycles for Dye-Sensitized Solar Cells under One Sun and Indoor Light

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((Optional Dedication))

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A series of Y shaped D-A- $\pi$ -A sensitizers incorporating quinoxaline or quinoxalinoid moieties (**MM-1~MM-6**) were prepared and applied onto dye-sensitized solar cells (DSSCs). By the introduction of quinoxalinoid functionalities, the absorption extinction coefficient can be enhanced. The molecular structures were modified by introducing an extra acceptor group between the donor and the  $\pi$ -bridge, and also by incorporating electron donating substituents at various positions. Dyes **MM-5** and **MM-6** were found to perform remarkably good lightharvesting efficiency under both sunlight and indoor light. The DSSCs made with mixtures of **MM-3** and **MM-6** displayed efficiency 7.92% under one sun (AM 1.5G). While operated under indoor light, the efficiency was boosted to 27.76, 28.74, and 30.45% under 600 & 1000 & 2500 lux illuminations, respectively. The high performance of **MM-3** and **MM-6** mixtures can be ascribed partly to a better dye-coverage on the TiO<sub>2</sub> surface.

#### **1. Introduction**

Despite intermittent problems, solar energy is the most abundant renewable energy source and generally recognized to be a promising alternative energy source. Solar energy can be harvested and converted into electricity for practical applications by various technologies such as silicon-based solar cells (SSCs), dye-sensitized solar cells (DSSCs), organic photovoltaic (OPVs) and perovskite solar cells (PSCs). In the past two decades, dye-sensitized solar cells (DSSCs) have received considerable attention due to their facile fabrication process, lightweight, cost-effective device module, and suitability for indoor applications, compared with silicon-based photovoltaic cells.<sup>1-4</sup> Current researches have demonstrated even a new trend of an integration system by using a single device to harvest the energy and to store it simultaneously. These integrated solar cells combine the technologies of the new-generation solar cells (SSCs, DSSCs, OPVs, and PSCs) and the storage devices (lithium-ion batteries (LIBs) and supercapacitors (SCs)) together.<sup>5-6</sup>

One of the most crucial components in the development of DSSC is the design of highperformance organic sensitizers. O'Regan and Grätzel have reported the deposition of ruthenium-based sensitizers N3, N719, and black dye onto nanoporous TiO<sub>2</sub>, and achieved an optimal power conversion efficiency over 11%.<sup>7-10</sup> Another report using porphyrin and indenoperylene dyes has achieved a maximal efficiency up to 12%. However, the production of these dyes were hampered by their low yields, complicated synthetic procedures, and difficulty of purification.<sup>11-12</sup> Yano and Hanaya used an alkoxysilyl anchored dye (**ADEKA-1**) as a co-sensitizer along with the metal-free organic dye **LEG-4** to achieve a high performance of 14.3 %.<sup>13</sup> Current reports had also showed the efficiency of DSSCs can be optimized by using a cobalt electrolyte and a Pt-free counter electrode.<sup>14-15</sup>

An enormous amount of metal-free organic dyes has been investigated and developed for DSSCs. Organic dyes have the advantages of environmental friendliness, lower cost, higher structural flexibility, and easier preparation, etc. Most of them are molecules of linear shape that consists of an electron donor (D) and an electron acceptor (A) that are separated by a  $\pi$ -

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bridge to form a dipolar D- $\pi$ -A system.

Manipulating the morphology of sensitizer on nanocrystalline TiO<sub>2</sub> surface is expected to enhance electron injection and therefore suppresses the rate of charge recombination. Increasing the loading amount on TiO<sub>2</sub> surface may lead to a more compact dye layer, which can prevent the electrode from direct contact with the electrolyte, and therefore improves the photocurrent ( $J_{sc}$ ). A good compact layer is usually formed with controlled intermolecular aggregation. In generally, there are two ways to control intermolecular aggregation: the first is by co-absorbing sterically rigid molecules, such as deoxycholic acid derivatives (DCA or CDCA) that can help the sensitizer align parallel to each other and stand vertical to the surface of TiO<sub>2</sub>. The second way is by introducing sterically hindered alkyl chains to the sensitizer molecules to enhance their coverage on TiO<sub>2</sub> surface. A commonly used strategy of structural design is to synthesize X- or Y-shaped rigid molecules attached with long alkyl substituents.<sup>16-19</sup>

Recently, Zhu designed a new type organic sensitizer in "D-A- $\pi$ -A" system by inserting an extra A group between the D group and the  $\pi$ -bridge.<sup>20-22</sup> These molecules displayed better photovoltaic performance by broadening the absorption spectra, therefore extending the lightabsorption range. A variety of auxiliary A groups have been reported previously, such as benzothiadiazole,<sup>23-27</sup> benzotriazole,<sup>28-30</sup> diketopyrrolopyrrole,<sup>31-34</sup> fluoro-substitented,<sup>35-36</sup> isoindgo,<sup>37-38</sup> quinoxaline,<sup>39-43</sup> thioazole,<sup>44-48</sup> and triazine<sup>49</sup> to tailor the absorption energy levels. In our earlier report, we have shown that by the introduction of quinoxaline and quinoxalinoid functionalities, the absorption extinction coefficient may be doubled.<sup>50-51</sup> In this work, we continue these designs by incorporating quinoxalinoid groups in six Y-shaped D-A- $\pi$ -A systems (**MM-1~MM-6**), and apply them onto DSSCs (Figure 1). The synthetic procedures are shown in Scheme 1, whilst all compounds were confirmed by spectroscopic analysis.

The effect of inserting quinoxaline or quinoxalinoid into the dye structure is apparent. The

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dye with a phenothiazine moiety at the 5-position of quinoxaline (**MM-5**) displayed higher photocurrent and PCE values under AM1.5 solar condition (100 mW·cm<sup>-2</sup>) than those without (**MM-3** and **MM-4**). This observation is consistent with our previous reports, due to more effective formation of an intramolecular charge transfer state.<sup>52-53</sup> Although the bulky moiety of 9,9-dihexyl-N,N-diphenyl-9H-fluoren-2-amine can increase the absorption intensity through  $\pi$ - $\pi$ \* transitions, it also reduces the dye-loading amount on TiO<sub>2</sub> surface. The sensitizer structure was further modified by replacing the bulky moiety by a smaller phenyl ring, and the resulted **MM-6** displayed a high conversion efficiency of 6.96% with shortcircuit current ( $J_{sc}$ ) 15.5 mA·cm<sup>-2</sup>, open-circuit voltage ( $V_{oc}$ ) 701 mV and fill factor (*ff*) 0.64 under DCA treatment at AM1.5 solar condition.

The effect of panchromatic co-sensitizationIn is also evaluated, which may enhance the performance of DSSCs by improving film morphology and dye-coverage.<sup>22, 54-59</sup> We found that upon co-sensitization of **MM-3** and **MM-6** the intensity of light absorption increased due to an improvement of dye-coverage on TiO<sub>2</sub> surface (Table S3). The best performance of the device with co-sensitization of **MM-3** and **MM-6** displayed a short-circuit current ( $J_{sc}$ ) 17.7 mA·cm<sup>-2</sup>, an open-circuit voltage ( $V_{oc}$ ) 717 mV, a fill factor (*ff*) 0.63, corresponding to an overall conversion efficiency 7.92% under AM1.5 solar condition.

In addition to sunlight, indoor light is also essential to our daily life. Indoor light is used to brighten our offices, factories, hospitals, stores, laboratories, libraries, production halls, first aid rooms, and showrooms, etc., where most people spend more than half of their lifetimes. The intensity of indoor light, mostly generated by luminescent devices such as fluorescent and LED lamps, rages typically in 300–1500 lux. It would be beneficial if indoor light can be harvested to provide the electric power of certain indoor applications. In this regard, DSSC is recognized to be a more efficient device than silicon cells, because it performs better in longer long wavelength region.

It is encouraging that through optimizing the spectral match with light sources (TL84,

D65 and CWF), many effective organic sensitizers have been developed. Grätzel and Hagfeldt's group has demonstrated that by using **XY1** and **D35** dyes with a copper-based electrolyte the PCE can be promoted to a remarkable level of 28.9% under 1000 lux of fluorescent light.<sup>60</sup> Wei and Yeh's group reported that an acetylene-based anthracene sensitizer **TY6** yielded 28.56% PCE under 6000 lux T5 fluorescent light.<sup>61</sup> Recently, Lin and Wei used pyrazine-incorporated panchromatic sensitizer **MD7** that reached PCE values of 18.85% and 27.17%, respectively, under 300 lux and 6000 lux of T5 fluorescent light.<sup>62</sup> By mixing our dyes **MM-3** and **MM-6**, we achieved PCE values of 27.76%, 28.74% and 30.45% under 600 lux, 1000 lux and 2500 lux, respectively, under TL84 fluorescent light.

<< Figure 1 >>

#### 2. Results and discussion

#### 2.1 Synthesis of Sensitizers

The synthesis of compounds **MM1~MM-6** started from 2,7-dibromo-9,9-dihexyl-9H-fluorene (1) (Scheme 1). The bromo group of 1 was first modified by condensing it with an arylamine via a Buchwald-Hartwig reaction to produce compound 2. The central acetylene moiety was constructed by coupling two units of 2 with acetylenedicarboxylic acid simultaneously through a Sonogashira reaction to yield compounds 3 in 60% yield.<sup>50</sup> Compound 3 was then subjected to an oxidation with KMnO<sub>4</sub> to afford the  $\alpha$ -diketone 4 in 90%. The reaction of diketone 4 with various quinoxalinoid *ortho*-diamines produced the respective products of 5, 7 and 12.<sup>51</sup> The length of  $\pi$ -bridge can be elongated by inserting an extra thiophene or phenylene unit through Stille coupling reaction to produce the aldehydes 6, 8, 15 and 17 in 60%–76%. Finally, all the aldehydes were subjected to Knoevenagel condensation reactions to yield the target compounds. More details of the synthesis were described in ESI<sup>†</sup>.

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<< Scheme 1 >>

#### 2.2 Absorption spectra

The ultraviolet-visible absorption spectra of all dyes, measured in  $3.0 \times 10^{-5}$  M CH<sub>2</sub>Cl<sub>2</sub> solutions, were shown in Figure 2. The MM-series dyes exhibited two broad, high-intensity absorption peaks in the range of 359–484 nm. The short wavelength absorptions (265–383 nm; 3.78-8.87x10<sup>4</sup> M<sup>-1</sup>cm<sup>-1</sup>) are attributed to localized  $\pi - \pi^*$  transitions, whereas the long wavelength ones (435–484 nm; 3.57-8.62x10<sup>4</sup> M<sup>-1</sup>cm<sup>-1</sup>) are assigned to the characteristic intramolecular charge transfer (ICT) transitions between the donor group and acceptor cyanoacrylic acid moiety. Compared with phenylene  $\pi$ -spacers MM-1 and MM-3, an extension of  $\pi$ -conjugation by the insertion of a thiophene  $\pi$ -linkage in **MM-2** and **MM-4** redshifts the absorption spectra by approximately 18-22 nm. The ICT bands of MM-5 and MM-6 are quite similar to each other, however, in the  $\pi$ - $\pi$ \* transition region the absorption intensity of MM-5 displays a higher intensity due to the presence of two substituents 9,9dihexyl-N,N-diphenyl-9H-fluoren-2-amine at the 2,3-positions of quinoxaline. Comparing with the absorption spectra in solutions, the spectra of dyes in solid films on TiO<sub>2</sub> exhibit similar yet broader ICT bands due to a stronger interaction between the dyes and TiO<sub>2</sub> surface. The ICT bands of MM-1 and MM-2 exhibit slight red-shift as a result of intermolecular Jaggregation. The blue-shifted ICT bands of MM-4 and MM-6 may be ascribed either to Haggregation or to the deprotonation of cyanoacrylic acid moiety.<sup>63-64</sup> By measuring the offset of absorption band, the zero-zero energy of all dyes can be estimated to be in the ranges of 2.07-2.54 eV.

<< Figure 2 >>

#### 2.3 Cyclic voltammetry

To examine the electro-stability and the HOMO and LUMO energies of dyes MM-1~MM-6, cyclic voltammetry experiments were performed. All the MM-series dyes displayed nearly reversible waves (Figure S26). Repeated scans (15 cycles) were performed on dyes MM-3 and MM-6, while no apparent difference was observed on the redox waves (Figure S27). This result indicated that our dyes are electrochemically stable under an ambient condition.<sup>65-</sup> <sup>67</sup> The donor and acceptor moieties at the 5,8-position of quinoxaline (**MM-5** and **MM-6**) strongly influence their oxidation potentials. The HOMO energy levels of MM-5 and MM-6 are 0.19-0.22 eV higher than those of MM-1~MM-4. It leads to narrower HOMO-LUMO energy gaps in a range of 0.14-0.47 eV (Figure 3). The introduction of fluorene side arms to quinoxalinoid of MM-1~MM-4 shows virtually no effect to the HOMO levels, nevertheless the HOMO-LUMO gaps of MM-1 and MM-2 are slightly smaller. This result is consistent with the red-shift of ICT bands in the absorption spectra, and can be verifies by the difference of dipole moments according to theoretical computations (Table S1 and Figure S24). The narrower HOMO–LUMO energy gaps of MM-2 and MM-4, compared with those of MM-1 and MM-3, are apparently induced by the presence of a thiophene unit. The LUMO levels of the dyes were determined by measuring the  $E_{ox}$  and the zero-zero band gaps at the offset of the absorption spectra (Figure 2a and Table 1). The estimated HOMO and LUMO levels are illustrated in Figure 3. The variation of energy levels was analysed by using theoretical computations as discussed in the following.

#### << Figure 3 >>

#### 2.4 Theoretical computations

The optimized structures of all compounds were obtained by time-dependent density functional theory (TD-DFT) calculations using B3LYP/6-31G(d) basis set in Gaussian 16W. Compounds containing phenylene groups, i.e. **MM-1** and **MM-2**, displayed a similar degree of co-planarity comparing with others that possessing thiophene groups (Figure S24). The

electron density distributions in the frontier orbitals of all dyes are illustrated in Figure 4 and Figure S25. The electron density in the HOMOs is mainly localized around the arylamine donor moieties, while that of the LUMOs around the cyanoacrylic acid acceptor moieties. The calculated HOMO/LUMO levels were -4.89/-2.71 eV for **MM-1**, -4.89/-2.79 eV for **MM-2**, -4.88/-2.62 eV for **MM-3**, -4.92/-2.70 eV for **MM-4**, -4.83/-2.73 eV for **MM-5**, and -4.83/-2.82 eV for **MM-6**. These results are consistent with the observed  $\lambda_{\text{max}}$  values in the absorption spectra, i.e., 569 nm, 590 nm, 549 nm, 558 nm, 590 nm, and 617 nm for **MM-1**,  $-\mathbf{MM-6}$ , respectively.

Upon photoexcitation an electron is promoted from the HOMO to the LUMO and therefore it induces a considerable amount of electron density redistribution. The donor-acceptor chromophore across the 5,8-position of quinoxaline in **MM-5** and **MM-6** shows a larger degree of electron density shift upon photoexcitation than those along the 2,3-position of quinoxaline in **MM-1~MM-4**. Such a charge redistribution can be clearly verified by the calculated dipole moments, i.e. **MM-6** (9.4549 D) > **MM-5** (9.4514 D) > **MM-2** (7.6565 D) > **MM-1** (7.5003 D)> **MM-4** (6.5937 D)> **MM-3** (5.7328 D). Therefore, the ICT bands in the dyes **MM-5** and **MM-6** exhibit a bathochromic shift comparing with that the dyes **MM-1 -MM-4**. The physical and theoretical parameters and the ICT transition dipole moments of the **MM**-series dyes are summarized in Table S1.

#### << Figure 4 >>

#### 2.5 Photovoltaic performance of DSSCs

The DSSC devices were fabricated by using the designed dyes as photosensitizers, which were absorbed on the TiO<sub>2</sub> surface according to standard procedure. The electrolyte used in the devices contained a  $I^{-}/I_{3}^{-}$  solution (including LiI (0.5 M) and I<sub>2</sub> (0.05 M)). Deoxycholic acid (DCA) was used in the experiments of co-absorption, and **N719** was served as the

reference dye. The incident photocurrent conversion efficiency (IPCEs) and photocurrent– voltage (*J–V*) curve of all dyes were measured either under AM 1.5 solar light (100 mW·cm<sup>-2</sup>) or under indoor light using a D65 (6500 K, average north USA sky daylight), a TL84 (4100 K, European shop fluorescent), or a CWF (4150 K, cool white fluorescent, shop lighting) lamp. The short-circuit current ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), fill factor (FF), and solar-toelectrical photocurrent density ( $\eta$ ) are summarised in Table 1.

The *J*–*V* curve and IPCE of all devices are plotted in Figure 5. Compared with **MM-1** and **MM-2**, an apparent improvement of 76–80 mV in  $V_{oc}$  was observed for dyes **MM-3**, **MM-4**, and **MM-5** that contain more long-chain alkyl substituents. Sensitizer **MM-6** also exhibited a higher  $V_{oc}$  value of 663 mV without DCA co-absorbent, due to a better morphology and higher loading amount (Table S3). Higher morphology quality leads to a better coverage of TiO<sub>2</sub> surface, and reduces the degree of contact between Li<sup>+</sup> or I<sub>3</sub><sup>-</sup> ions and the TiO<sub>2</sub> surface. A better surface blocking increases the energy gap between the Fermi levels of TiO<sub>2</sub> and electrolyte, therefore enhances the value of  $V_{oc}$ .<sup>68-70</sup> The dye morphology on the TiO<sub>2</sub> surface plays a key factor for reducing the charge recombination in DSSCs.<sup>71-73</sup>

<< Figure 5 >> << Figure 6 >> << Table 1 >>

In order to optimize the dye alignment on the TiO<sub>2</sub> surface, the addition co-absorbent DCA was used to prevent the dye molecules from lying down onto the TiO<sub>2</sub> surface. An imporved dye alignment can reduce the rate of charge recombination. Upon adding DCA (10 mM) as a co-absorbent, the  $V_{oc}$  of DSSCs can increase in 1.66%–5.89% (Table 1). In the case of **MM-6** the  $J_{sc}$  decreased slightly by the addition of DCA due to the reduction of loading amount, yet the  $V_{oc}$  was enhanced significantly to 5.89%. This result indicated that the smaller

size of **MM-6** enabled better vertical alignment on the TiO<sub>2</sub> surface (Table S3). Both FF and  $V_{oc}$  were improved and the power conversion efficiency increased by 3.88%. The device performance of **MM-6** displayed a short-circuit current ( $J_{sc}$ ) 15.5 mA·cm<sup>-2</sup>, an open-circuit voltage ( $V_{oc}$ ) 701 mV, a fill factor (*ff*) 0.64, corresponding to an overall conversion efficiency 6.96% with DCA treatment under AM1.5 solar condition. However, the power conversion efficiencies of **MM-1~MM-5** reduced slightly in 0.01~0.26% due to the bulky substituents leading to lower loading amount in the presence of DCA co-absorbent.

We further investigated the effect of co-deposite of **MM-3** and **MM-6** together in different ratios in order to search for better spectral coverage and higher photocurrent. Dye **MM-3** was deposited on TiO<sub>2</sub> first, followed by **MM-6**. The most appropriate deposition times for **MM-3** and **MM-6** were 4 hr and 8 hr, respectively. The device exhibited even higher  $J_{sc}$  and  $V_{oc}$  values than the co-deposition of **MM-6** and DCA, i.e., a  $J_{sc}$  value of 17.7 mA·cm<sup>-2</sup> with broad IPCE (Figure 5 (c)-(d)) and a high  $V_{oc}$  of 717 mV.

Electrochemical impedance spectroscopy (EIS) was examined to further analyze the photovoltaic properties of the DSSCs devices. Nyquist and Bode plots were drawn based on a forward bias under dark condition (Figure 6). In the Nyquist plots the major semicircles that observed for each sensitizer are associated with charge recombination resistance ( $R_{rec}$ ) at the TiO<sub>2</sub>/electrolyte/dye interface. A larger semicircle relates to  $R_{rec}$  at low frequency, indicating a lower tendency of charge recombination and thus a smaller dark current.<sup>75</sup> The radii of the semicircles increase in the order of **MM-1** (132  $\Omega$ ) < **MM-2** (144  $\Omega$ ) < **MM-3** (180  $\Omega$ )  $\approx$  **MM-4** (186  $\Omega$ ) < **MM-5** (196  $\Omega$ )  $\approx$  **MM-6** (194  $\Omega$ ) < **MM-6+DCA** (244  $\Omega$ ) < **MM-6+MM-3** (255  $\Omega$ ) < N719 (270  $\Omega$ ). This trend is consistent with the  $V_{oc}$  of the dyes, i.e., **MM-1** (583 mV) < **MM-2** (585 mV) < **MM-3** (661 mV)  $\approx$  **MM-4** (661 mV) < **MM-5** (663 mV)  $\approx$  **MM-6** (662 mV) < **MM-6+DCA** (701 mV) < **MM-6+MM-3** (717 mV) < N719 (736 mV). The high performance of co-deposition of **MM-3** and **MM-6** is confirmed by a larger arc of the major semicircle (255  $\Omega$ ) in Nyquist plot and a longer electron lifetime (46.2 ms). The optimal

device power conversion efficiency of 7.92% under one sun AM1.5 condition is higher than that using standard N719 (7.75%) dye under the same condition.

The electron diffusion lifetime ( $\tau_e$ ) of the device was related to the value of  $1/2\pi f$ . A shift to lower frequency (f) in a Bode plot corresponds to a longer electron lifetime. The electron lifetime of the dyes increases in the order of **MM-1** (17.0 ms) < **MM-2** (18.7 ms) < **MM-3** (35.3 ms)  $\approx$  **MM-4** (36.8 ms) < **MM-5** (38.1 ms)  $\approx$  **MM-6** (38.8 ms) < **MM-6+DCA** (40.8 ms) < **MM-6+MM-3** (46.2 ms), where a higher  $\tau_e$  indicates a lower charge recombination rate (Fig. 6b & 6d). The larger charge recombination resistance and the longer electron diffusion lifetime may be attributed to compact packing of the dyes.

The presence of 5 or 6 long alkyl/alkoxy chains in the structure of dyes **MM-3**, **MM-4**, and **MM-5** improves the morphology and coverage on TiO<sub>2</sub> surface, thus results in higher values of  $R_{\text{rec}}$  and  $\tau_e$  than those of **MM-1** and **MM-2**. Sensitizer **MM-6** is an exception, i.e., it also exhibits higher values of  $R_{\text{rec}}$  and  $\tau_e$  even without the long-chain substituents. The high degree of regular shape of **MM-6** induces a more compact molecular packing, therefore blocks the Li<sup>+</sup> or I<sub>3</sub><sup>-</sup> ions in electrolyte effectively from a direct contact with the electrode and reduces the dark current.

<< Figure 7 >> << Table 2 >> << Figure 8 >>

#### 2.6 DSSCs performance under indoor light condition

We have demonstrated that the solar cells made with the **MM**-series dyes showed promising conversion efficiency under 1 sun illumination. We continued to explore the possibility of using these dyes under indoor light illuminations in the intensity range of 600-2500 lux using three kinds of lamps (D65, 6500 K; TL84, 4100 K; CWF, 4150 K). These MM-dyes display a high degree of spectral overlap with the indoor light emission wavelength (Fig. S28).

The indoor-light cell efficiency and parameters at 600, 1000 and 2500 lux are summarized in Table 2. The current density-voltage (J-V) curve of the DSSCs under 2500 lux TL84 fluorescent light is shown in Figure 7. The devices made with sensitizers MM-1~MM-4 showed cell efficiencies less than 13% even under a stronger illumination of 2500 lux (TL84), due to the narrow absorption band widths that is similar to the situation under one sun. The two sensitizers **MM-5** and **MM-6**, which possesses the donor and acceptor at 5,8-positions of quinoxaline, displayed efficiencies higher than 18% under 1000 lux (TL84). Sensitizer MM-6 showed the highest performance among all, i.e., 24.37% under 600 lux, 27.58% under 1000 lux, and 27.82% under 2500 lux. These efficiencies are comparable to those of the N719based cells under similar conditions, i.e., 17.21% (600 lux), 20.10% (1000 lux) and 24.63% (2500 lux), respectively. The performance of **MM-6** is only slightly lower than the recordhigh **TY6** (28.56% at 6000 lux) reported by Wei and Yeh.<sup>61</sup> The performance of **MM-6** in this work with DCA co-absorbent showed improved performance of 25.42% (600 lux), 27.40% (1000 lux) and 28.95% (2500 lux). Moreover, the co-sensitization of MM-3 and MM-6 exhibited remarkable performance of 27.76% (600 lux), 28.84% (1000 lux) and 30.45% (2500 lux). Such performance is highly competitive with the co-sensitization system of XY-1 and D35 using Cu(II/I)(tmby) as the redox mediator (25.5% at 200 lux; 28.9% at 1000 lux), which has been developed by Grätzel and Hagfeldt.<sup>60</sup>

We compared the efficiency of DSSCs made with the following three different compositions under illumination of indoor light sources D65, CWF, and TL84: (1) **MM-6** only; (2) **MM-6** co-absorbed with DCA; and (3) **MM-6** co-absorbed with **MM-3**. The results are shown in Figure 8 and Table S4. The efficiency of D65 at 1000 lux is similar to that of one sun, because the spectrum of D65 is a mimic of sunlight shining through a window. Compared with the CWF condition, a better result is observed under TL84 illumination (Figure 8). The co-sensitization of **MM-3** and **MM-6** performed the best after fine-tune the mole ratios to achieve an optimal morphology on TiO<sub>2</sub> surface. The best performance PCE was found to be

12

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higher than 30% (30.45 % at 2500 lux) under a TL84 fluorescent indoor light source.

A stability test on the devices were performed at 25 °C under TL84 indoor light and AM1.5 in an ambient condition. The device co-sensitized with **MM-3** and **MM-6** retained 81.42% (600lux), 80.80% (1000lux), and 82.53% (2500lux) efficiency, respectively, after 168 h. The plots of decay curves of PCEs are shown in **Figure S29**, and the list of parameters is provided in **Table S5**.<sup>76</sup> And stability test on device co-sensitized with **MM-3** and **MM-6** retained 95% after 1hr under AM1.5 continuous illumination in **Figure S30**, this result indicated our devices possesses good stability under an ambient condition.

#### 3. Conclusion

We demonstrated the successful application of a series D-A- $\pi$ -A sensitizers incorporating quinoxaline or quinoxalinoid moieties (MM-1~MM-6) in high-performance DSSC under one sun and indoor light illumination (D65, CWF and TL84) conditions. Six Y-shaped metal-free organic dyes (MM-1~MM-6) were synthesized through stepwise modifications on the quinoxalinoid moieties. Dyes with donor substituents at 5,8-positions of quinoxaline (MM-5 and MM-6) displayed higher photocurrent and PCE than those at 2,3-positions (MM-3 and MM-4). The dye MM-6 displayed a remarkable performance for DSSC upon co-deposition with DCA, even without the two large fluorene chromophores. It showed short-circuit current  $(J_{sc})$  15.5 mA·cm<sup>-2</sup>, open-circuit voltage  $(V_{oc})$  701 mV, and fill factor (ff) 0.64, corresponding to an overall conversion efficiency of 6.96% under AM1.5 solar condition. We also found that a co-deposition of MM-3 and MM-6 together can improve the dye-coverage on TiO<sub>2</sub> surface. The best performance of the device co-deposited with MM-3 and MM-6 displayed shortcircuit current ( $J_{sc}$ ) 17.7 mA·cm<sup>-2</sup>, open-circuit voltage ( $V_{oc}$ ) 717 mV, and fill factor (ff) 0.63, corresponding to an overall conversion efficiency of 7.92% under AM1.5 solar condition. The most impressive result was obtained when MM-3 and MM-6 were used on indoor applications. The devices co-sensitized with MM-3 and MM-6 achieved the highest

13

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performance of PCE exceeding 30% (30.45 % at 2500 lux) under a TL84 fluorescent lamp.

#### 4. Experimental Section

Characterization and reagents: All reactions and manipulations were performed under a nitrogen atmosphere, and solvents were freshly distilled according to standard procedures. The <sup>1</sup>H and <sup>13</sup>C NMR were recorded on a Bruker AVIII HD 400. The <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were reported on  $\delta$  scale downfield from Me<sub>4</sub>Si. The coupling constants (J) were given in hertz. Absorption spectra were recorded on a SHIMADZU UV-1800 spectrophotometer. Redox potentials were measured using cyclic voltammetry on a CHI 620 analyser. All measurements were performed in  $CH_2Cl_2$  solution containing 0.1 M tetrabutylammonium hexaflourophosphate as supporting electrolyte under ambient conditions after purging the solution with N<sub>2</sub> for 10 min. The conventional three-electrode configuration was employed that consists of a glassy carbon working electrode, a platinum counter electrode, and an Ag/Ag<sup>+</sup> reference electrode calibrated with ferrocene/ ferrocenium (Fc/Fc<sup>+</sup>) as an internal reference. Mass spectra were recorded on a JEOL JMS-700 double-focusing mass spectrometer. Analytical thin layer chromatography (TLC) was performed on Silica gel 60 F 254 Merck. Column chromatography was performed using the silica gel from Merck (Kieselgel Si 60; 40-63 µm). Solvent THF was distilled with sodium benzophenone ketyl. Toluene and methylene chloride were distilled with CaH<sub>2</sub>. All other solvents and reagents were reagent grade, purchased from Acros, Alfa, Merck, Lancaster, TCI, Sigma-Aldrich, and Showa, separately, and used without further purification.

*Fabrication and Characterization of DSSCs*: The FTO conducting glass (2.2 mm thick, fluorine doped tin oxide over-layer, transmission >90% in the visible, sheet resistance 7  $\Omega$ /square), titania-oxide pastes of Ti-Nanoxide T/SP (adsorption layer) and Ti-Nanoxide

R/SP (scattering layer) were purchased from Solaronix. A thin film of TiO<sub>2</sub> (adsorption layer~12 $\mu$ m; scattering layer: ~6 $\mu$ m) was coated on a 0.28 cm<sup>2</sup> FTO glass substrate. It was immersed in a methylene chloride solution containing  $3 \times 10^{-4}$  M dye sensitizers for 12 h, then rinsed with anhydrous acetonitrile and dried. The other piece of FTO with sputtering 100 nm thick Pt was used as a counter electrode. The active area was controlled at a dimension of 0.28 cm<sup>2</sup> by adhering 60  $\mu$ m thick polyester tape on the Pt electrode. The photocathode was placed on top of the counter electrode and was tightly clipped together to form a cell. Electrolyte was then injected into the seam between two electrodes. An acetonitrile solution containing LiI (0.5 M), I<sub>2</sub> (0.05 M) and 4-tert-butylpyridine (TBP) (0.5 M) was used as the electrolyte. Devices made with commercial dye N719 under the same condition (3  $\times$  10<sup>-4</sup> M, Solaronix S.A., Switzerland) were used as references. The cell parameters were obtained under incident light that had an intensity of 100 mW·cm<sup>-2</sup> measured using a thermopile probe (Oriel 71964), which was generated by a 300 W solar simulator (Oriel Sol3A Class AAA Solar Simulator 9043A, Newport), and passed through an AM 1.5 filter (Oriel 74110). The light intensity was further calibrated using an Oriel reference solar cell (Oriel 91150) and adjusted to 1.0 sun. The monochromatic quantum efficiency was recorded using a monochromator (Oriel 74100) under a short circuit condition. Electrochemical impedance spectra of DSSCs were recorded by an Impedance/CIMPS/IVMS analyzer (Zahner Ennium).

*Fabrication of dye-loading TiO*<sub>2</sub> *on FTO glass*: The dye-loading TiO<sub>2</sub> on FTO glass (7  $\Omega$ /sq) was used as working electrode, which has 3 x 1 cm dimension (8  $\mu$ m thick). The film TiO<sub>2</sub> (Ti-Nanoxide T/SP, SOLARONIX) was adhered on FTO glass by screen-printing. It was pre-dried 1 h at 100 °C, followed by heating at 500 °C. It was then immersed in a solution of the dye (3 x 10<sup>-4</sup> M in anhydrous CH<sub>2</sub>Cl<sub>2</sub>) for 12 h, then rinsed with anhydrous CH<sub>2</sub>Cl<sub>2</sub> and dried.

*Device performance under indoor light*: The system of stabilized indoor light sources (model CMS-PV101, designed by Industrial Technology Research Institute, Taiwan) consisted of D65 (6500 K, Average North USA sky daylight), TL84 (4100 K, European shop fluorescent), CWF (4150 K, cool white fluorescent, shop lighting), U30 (3000 K, shop lighting) and A (2856 K, typical home lighting) lamps, which meet the standards of SEMI PV80-0218 and CIE. All light sources are intensity adjustable in a range of 0 to 2500 lux, with non-uniformity less than 2 % (within the area of 20 cm  $\times$  20 cm) and temporal instability less than 2 %. A calibrated spectroradiometer (ISM-Lux, Isuzu Optics, Japan) was embed at underlying system. The acquired illuminance value was attained by altering LED lamp lifting platform to a moderate position and incessantly confirmed by spectroradiometer until it reached firmly stable condition. After then, the DSSC device as put at the upper site of the spectroradiometer and the *J-V* curves were measured via a computer-controlled digital source meter (Keithley 2401, USA) under various dim light illumination, followed the requirements of SEMI PV57-1214.

*Quantum Chemistry Computations*: Geometry optimization of the dyes were accomplished by Gaussian G16W program (B3LYP/6-31G\* hybrid functional). For excited states, the time-dependent density functional theory (TDDFT) and the B3LYP functional were used. The frontier orbital plots of the highest occupied and lowest unoccupied molecular orbitals (hereafter abbreviated as HOMO and LUMO, respectively) were drawn using GaussView 06.

#### **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. Organic sensitizers of MM-series.

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**Scheme 1.** Synthesis condition of organic dye sensitizer: (i) Pd<sub>2</sub>(dba)<sub>3</sub>, dppf, sodium *tert*butoxide, diphenylamine, toluene, 110 °C; (ii) Acetylenedicarboxylic acid, dppb, DBU, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, DMSO (iii) KMnO<sub>4</sub>, NaHCO<sub>3</sub>, Aliquat 336, CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O; (iv) CH<sub>3</sub>COOH, 110 °C; (v) (4-(1,3-dioxolan-2-yl)phenyl)tributylstannane/(5-(1,3-dioxolan-2-yl)thiophen-2yl)tributylstannane, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, DMF, 100 °C; then THF/HCl, rt.; (vi) CNCH<sub>2</sub>COOH, piperidine, chloroform, reflux.; (vii) HBr, Br<sub>2</sub>, 60 °C; (viii) NaBH<sub>4</sub>, ethanol, rt.; (ix) (10-(4-(hexyloxy)phenyl)-10H-phenothiazin-3-yl)boronic acid, Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, THF/toluene.



**Figure 2.** (a) Absorption spectra of dyes **MM-1~MM-6** in THF  $(3.0 \times 10^{-4} \text{M})$ ; (b) Absorption spectra of dyes **MM-1~MM-6** on TiO<sub>2</sub> thin film.



Figure 3. HOMO-LUMO energy levels of MM-series organic sensitizers.



Figure 4. The frontier HOMO and LUMO orbitals of MM-series organic sensitizers estimated by time-dependent DFT/B3LYP (6-31G\* basis set).

Table 1	Photochemical	and electrochemical	parameters of	f the dyes.
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Sensitizer	$\lambda_{max}^{a}(nm)/$	$\lambda_{max}$	E <sub>ox</sub> <sup>b)</sup>	E <sub>0-0</sub>	E <sub>red</sub> <sup>c)</sup>	J <sub>sc</sub> (mA·cm <sup>-2</sup> )	$V_{oc}(mV)$	FF(%)	$PCE^{d}(\%)$
	$(\epsilon (M^{-1}cm^{-1}))$	$(TiO_2)$	(V)	(eV)	(V)	wo/w DCA	wo/w	wo/w DCA	wo/w DCA
							DCA		
MM-1 <sup>e)</sup>	435	440	0.74	2.31	-1.57	7.75(±0.2)/	583(±4)/	61.3(±0.2)/	2.77(±0.10)/
	$(4.63 \times 10^4)$					6.84(±0.1)	613(±5)	66.0(±0.3)	2.76(±0.08)
MM-2 <sup>e)</sup>	457(4.20	466	0.74	2.21	-1.47	8.05(±0.3)/	585(±3)/	66.1(±0.1)/	3.11(±0.13)/
	x10 <sup>4</sup> )					7.51(±0.1)	603(±2)	63.5(±0.3)	2.85(±0.08)
MM-3 e)	427(8.06	425	0.71	2.54	-1.83	7.93(±0.2)/	661(±2)/	67.4(±0.2)/	3.53(±0.11)/
	x10 <sup>4</sup> )					7.35(±0.2)	680(±2)	68.1(±0.3)	3.40(±0.12)
MM-4 e)	445(8.62	436	0.73	2.43	-1.70	9.08(±0.1)/	661(±5)/	64.6(±0.2)/	3.88(±0.08)/
	x10 <sup>4</sup> )					8.51(±0.2)	672(±3)	66.2(±0.1)	3.79(±0.10)
MM-5 e)	470(3.65	470	0.54	2.10	-1.56	14.0(±0.2)/	663(±2)/	63.1(±0.1)/	5.86(±0.11)/
	x10 <sup>4</sup> )					12.7(±0.3)	681(±2)	65.2(±0.1)	5.64(±0.16)
MM-6 e)	484(3.57	474	0.52	2.07	-1.55	17.1(±0.3)/	662(±3)/	59.2(±0.2)/	6.70(±0.17)/
	x10 <sup>4</sup> )					15.5(±0.2)	701(±2)	64.1(±0.3)	6.96(±0.14)
MM-3+MM-6						16.5(±0.3)/	685(±2)/	64.5(±0.4)/	7.29(±0.20)/
						—			
(2nr+10nr) MM_3+MM_6						177(+0.2)/	717(15)/	(28(102))	7.02(+0.22)/
f)						17.7(±0.2)/	/1/(±3)/	02.8(±0.2)/	7.92(±0.22)/
(4hr+8hr)									
MM-3+MM-6						15.2(±0.3)/	703(±4)/	65.2(±0.3)/	6.95(±0.27)/
f)						_			
(6hr+6hr)			1 100)	0 (0 ()	1 509)	17.5( 0.0)	7264 114	60.1/ 0.1)/	7 75( 0 10)
N/19			1.10 <sup>g</sup>	$2.60^{g}$	-1.50 <sup>g</sup>	1/.5(±0.2)/	/36(±4)/	60.1(±0.1)/	/./5(±0.13)/

<sup>a)</sup>Absorption and Emission are in CH<sub>2</sub>Cl<sub>2</sub>; <sup>b)</sup>Oxidation potential in THF (10<sup>-3</sup> M) containing 0.1 M (n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NPF<sub>6</sub> with a scan rate 50 mV·s<sup>-1</sup> (*vs.* NHE); <sup>c)</sup> $E_{red}$  calculated by  $E_{ox} - E_{0-0}$ ; <sup>d)</sup> Performance of DSSCs measured in a 0.28 cm<sup>2</sup> working area on a FTO (8Ω/square) substrate. Electrolyte: LiI (0.5 M), I<sub>2</sub> (0.05 M), and TBP (0.5 M) in MeCN; <sup>e)</sup>The TiO<sub>2</sub> electrode was dipped in methene chloride of sensitizer with 3 x 10<sup>-4</sup> M for 12hr; <sup>f)</sup>The TiO<sub>2</sub> electrode was dipped in methene chloride of **MM-3** (3 x 10<sup>-4</sup> M), rinsed with ACN, then dipped in methene chloride of MM-6 (3 x 10<sup>-4</sup> M); <sup>g)</sup>see reference 74.



**Figure 5.** (a) *J-V* plots and (b) IPCE of DSSCs devices of **MM-1~6** without DCA coabsorbent. (c) *J-V* plots and (d) IPCE of DSSCs devices of **MM-6** by adding DCA coabsorbent and cosensitization system with **MM-3**. The plots were measured under the light intensity of 1.0 sun.

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**Figure 6.** Impedance spectra of **MM**-series dyes in CH<sub>2</sub>Cl<sub>2</sub> (**a-b**) Nyquist plots (**c-d**) Bode phase plots at -0.73 V bias in the dark. The electron diffusion lifetime  $\tau_e = 1/2\pi f$ .



**Figure 7.** *J-V* plots and of **MM-5**, **MM-6**, **MM6** with DCA and co-sensitization of **MM-3** and **MM-6** under TL84 illuminance (2500 lux).

Table 2. Photovo	Itaic paramete	ers of the MM-	series dyes	measured us	ing TL84 ii	ndoor light.
Sensitizer	Irradiance	Illuminance (lux)	$I_{(\mu\Lambda,cm^{-2})}$	$V_{\rm m}V$	FE(0/2)	<b>DCE</b> $(0/a)^{(a)}$

Sensitizer	Irradiance	Illuminance (lux)	$J_{\rm sc}$ ( $\mu A \cdot cm^{-2}$ )	$V_{\rm oc}(\rm mV)$	FF(%)	PCE (%) <sup>a)</sup>
	(mW/cm <sup>2</sup> )					
<b>MM-1</b>	0.110	600	21.7(±1.3)	405(±4.5)	55.84(±0.72)	4.43(±0.41)
	0.185	1000	40.3(±3.5)	415(±4.3)	83.33(±2.27)	7.50(±0.97)
	0.462	2500	120(±7.2)	462(±3.7)	64.08(±0.78)	7.72(±0.59)
<b>MM-2</b>	0.110	600	30.5(±2.1)	419(±3.5)	58.21(±0.27)	6.71(±0.61)
	0.185	1000	48.1(±4.5)	459(±4.8)	71.55(±1.53)	8.52(±1.08)
	0.462	2500	133(±6.9)	481(±3.5)	65.25(±0.88)	9.03(±0.67)
<b>MM-3</b>	0.110	600	31.7(±1.9)	427(±2.1)	60.16(±0.31)	7.35(±0.57)
	0.185	1000	65.8(±2.5)	436(±3.9)	62.28(±0.55)	9.64(±0.56)
	0.462	2500	131(±5.5)	492(±3.1)	70.70(±1.12)	9.86(±0.64)
<b>MM-4</b>	0.110	600	44.2(±1.7)	417(±5.1)	61.17(±0.37)	10.16(±0.67)
	0.185	1000	78.6(±1.5)	444(±3.9)	58.72(±0.19)	11.07(±0.35)
	0.462	2500	170(±6.1)	496(±4.6)	66.51(±0.46)	12.14 (±0.63)
<b>MM-5</b>	0.110	600	52.0(±2.2)	480(±4.5)	55.15(±0.33)	12.38(±0.86)
	0.185	1000	95.1(±3.5)	550(±2.8)	67.27(±0.89)	18.99(±1.09)
	0.462	2500	248(±8.7)	570(±3.7)	65.02(±1.13)	19.89(±1.19)
<b>MM-6</b>	0.110	600	75.6(±3.5)	555(±4.5)	64.53(±0.57)	24.37(±1.82)
	0.185	1000	128(±3.7)	570(±4.8)	70.72(±1.22)	27.58(±1.85)
	0.462	2500	309(±7.9)	597(±3.3)	69.68(±0.85)	27.82(±1.22)
MM-6+DCA(10mM) <sup>b)</sup>	0.110	600	75.4(±2.2)	562(±4.3)	66.64(±0.55)	25.42(±1.42)
	0.185	1000	129(±4.1)	620(±3.2)	63.44(±0.24)	27.40(±1.15)
	0.462	2500	303(±4.3)	625(±2.7)	70.54(±0.88)	28.95(±0.86)
MM-6+MM-3	0.110	600	84.5(±2.8)	537(±3.1)	67.84(±0.18)	27.76(±1.39)
(8hr+4hr) <sup>c)</sup>	0.185	1000	137(±3.8)	598(±2.5)	64.96(±0.25)	28.74(±1.06)
	0.462	2500	312(±4.7)	621(±3.6)	72.59(±1.02)	30.45(±1.06)
N719	0.110	600	61.5(±2.8)	493(±2.5)	62.91(±0.27)	17.21(±1.08)
	0.185	1000	107(±3.2)	530(±4.8)	65.62(±1.55)	20.10(±1.39)
	0.462	2500	273(±4.5)	611(±3.5)	68.22(±1.53)	24.60(±1.11)

<sup>a)</sup> $V_{oc}$ : open-circuit voltage;  $J_{sc}$ : short-circuit current; FF: fill factor; PCE: power-conversion efficiency. The data are based on three measurements. Experiments were conducted by using TiO<sub>2</sub> photoelectrodes, with approximately 12 mm thickness and 0.28 cm<sup>2</sup> working area on FTO (8 $\Omega$ /square) substrate; <sup>b)</sup>The TiO<sub>2</sub> soaked with dyes and DCA (10 mM); <sup>c)</sup>The TiO<sub>2</sub> was dipped in methene chloride of **MM-3** (3 x 10<sup>-4</sup> M) for 4hr, rinsed with ACN, then dipped in methene chloride of **MM-6** (3 x 10<sup>-4</sup> M) for 8 hr.



Figure 8. Photovoltaic parameters of MM-6, MM-6 with DCA and co-sensitization of MM-3 and MM-6 under D65, CWF and TL84 illuminance (600~2500 lux).

#### The table of contents entry should be 50–60 words long, and the first phrase should be bold.

Through co-sensitization of D-A- $\pi$ -A dyes **MM-3** and **MM-6**, the DSSCs exhibited a PEC of 7.92% under one sun (AM 1.5G) illumination, and 27.76%, 28.74% and 30.45%, respectively, under 600 lux, 1000 lux and 2500 lux indoor light using a TL84 fluorescent lamp.

#### Keyword

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**Title:** High Performance Organic Dyes with Electron-Deficient Quinoxalinoid Heterocycles for Dye-Sensitized Solar Cells under One Sun and Indoor Light

