Novel Quinoxaline-Based Organic Sensitizers for Dye-Sensitized Solar Cells

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ABSTRACT
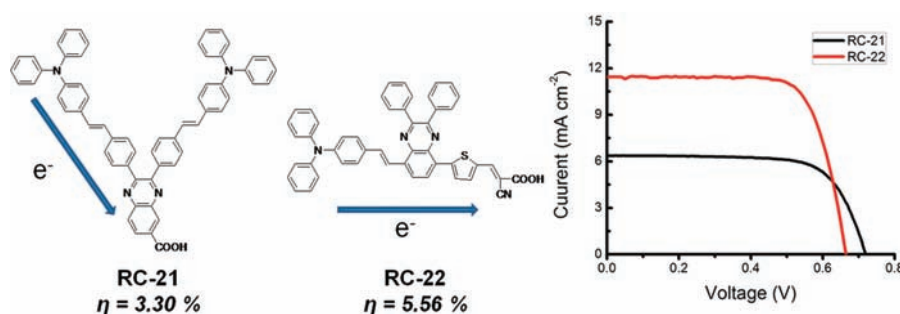
Novel quinoxaline-based organic sensitizers using vertical (RC-21) and horizontal (RC-22) conjugation between an electron-donating triphenylamine unit and electron-accepting quinoxaline unit have been synthesized and used for dye-sensitized solar cells (DSSCs), leading to the relatively high power conversion efficiencies of 3.30 and 5.56% for RC-21 and RC-22, respectively. This result indicates that the quinoxaline electron-accepting unit is quite a promising candidate in organic sensitizers.

Since the sensational report by Grätzel and O'Regan in 1991,[1] dye-sensitized solar cells (DSSCs) have attracted great attention in both academic and industrial communities due to high achievable efficencies at low cost by possible molecular engineering of key elements.[2] With great efforts devoted by many investigators, the power conversion efficiency (η) of DSSCs can now be attainable to about 11% for ruthenium metal-based sensitizers under air mass (AM) 1.5 illumination.[3] Apart from precious metal-based sensitizers, the metal-free organic dyes, generally having a donor-π-acceptor (D-π-A) configuration, have become promising candidates due to their high molar extinction coefficients, low costs, and convenient spectral modifications.[4] In the D-π-A structure, an efficient electron transfer from donor to acceptor can occur upon photoexcitation of the sensitizer, and then the negative

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(1) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.
(2) (a) Grätzel, M. *Acc. Chem. Res.* **2009**, *42*, 1788. (b) Hägfelt, A.; Boschloo, L.; Sun, L.; Kloo, L.; Patterson, H. *Chem. Rev.* **2010**, *110*, 6596.

(3) (a) Chiba, Y.; Islam, A.; Watanabe, Y.; Komiya, R.; Koide, N.; Han, L. *Jpn. J. Appl. Phys.* **2006**, *45*, 24. (b) Gao, F.; Wang, Y.; Shi, D.; Zhang, J.; Wang, M.; Jing, X.; Humphry-Baker, R.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2008**, *130*, 10720.
(4) (a) Mishra, A.; Fischer, M. K. R.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2009**, *28*, 2474. (b) Ooyama, Y.; Harima, Y. *Eur. J. Org. Chem.* **2009**, 2903.

charges accumulated on the acceptor can be injected into the conduction band of a metal oxide semiconductor.

Various functional groups and their derivatives have been tested as an effective part of the D-π-A structure in organic sensitizers. Among them, triphenylamine, thiophene derivatives, and cyanoacetic acid have been widely used as an efficient unit of donor-π conjugation-acceptor, respectively. The excellent electron-donating propertiy and aggreagation-resistant nonplanar molecular configuration of triphenylamine made it an important donor in many sensitizers.[5] Thiophene derivatives have also been widely used as a building block for sensitizers because of their well-known high polarizabilty as well as their tunable spectroscopic and electrochemical properties. In many cases, cyanoacetic acid has been adopted as an acceptor due to its strong electron-withdrawing and anchoring capability onto a TiO_2 surface.
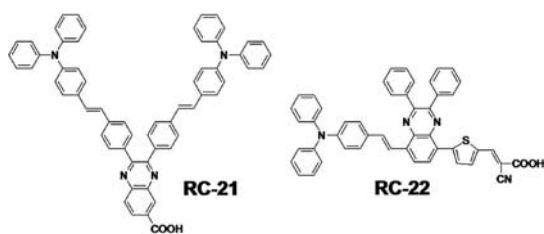

Figure 1. Chemical structures of quinoxaline-based dyes.

Recently, quinoxaline-based conjugated polymers and small molecules have been actively investigated for organic photovoltaic cells (OPVs).[6] It is well-known that quinoxalines are strong electron-accepting materials due to their high electron affinity originated from the two symmetric unsaturated nitrogen atoms. Interestingly, Li and co-workers have demonstrated that the formation of two-dimensional D−A structures around a quinoxaline core in both *vertical* and *horizontal* directions and their applications in OPVs.[7] Thus, the quinoxaline unit can be an attractive component in organic sensitizers due to its diverse structural modifications with the intrinsic strong electron-withdrawing properties. Although there are a few reports on the applications of quinoxaline units for metal-based DSSCs,[8] the utilizaton of quinoxaline units in organic sensitizers has not been reported to our best

knowledge. Herein, we report the design, syntheses, and photovoltaic properties of novel quinoxaline-based sensitizers, **RC-21** and **RC-22** (Figure 1).

As can be seen in Figure 1, triphenylamine, an electron donor, and quinoxaline, an electron acceptor, were coupled together to produce **RC-21** and **RC-22**. When the triphenylamine donor is linked to the para-position of 2,3-diphenyl rings on quinoxaline units, i.e. vertical to quinoxaline, it is denoted as **RC-21**. When the triphenylamine is directly conneted to the 5-position of the quinoxaline unit, i.e. horizontal to quinoxaline, it is denoted as **RC-22**. In **RC-22**, the quinoxaline unit is used as an additional electron acceptor in front of cyanoacrylic acid, which leads to a D-A-π-A configuration.[9] The different configurations between **RC-21** and **RC-22** are expected to significantly affect the final electronic and photovoltaic properties (*vide infra*).

(5) Ning, Z.; Tian, H. *Chem. Commun.* **2009**, 5483.

(6) (a) Wang, E.; Hou, L.; Wang, S.; Hellestram, S.; Zhang, F.; Inganas, O.; Andersson, M. R. *Adv. Mater.* **2010**, *22*, 5240. (b) Mastalerz, M.; Fischer, V.; Ma, Q.; Janssen, R. A. J.; Bäuerle, P. *Org. Lett.* **2009**, *11*, 4500. (c) Kitamura, C.; Tanaka, S.; Yamashita, S. *Chem. Mater.* **1996**, *8*, 570. (d) Zhang, J.; Cai, W.; Huang, F.; Wang, E.; Zhong, C.; Liu, S.; Wang, M.; Duan, C.; Yang, T.; Cao, Y. *Macromolecuels* **2011**, *44*, 894.
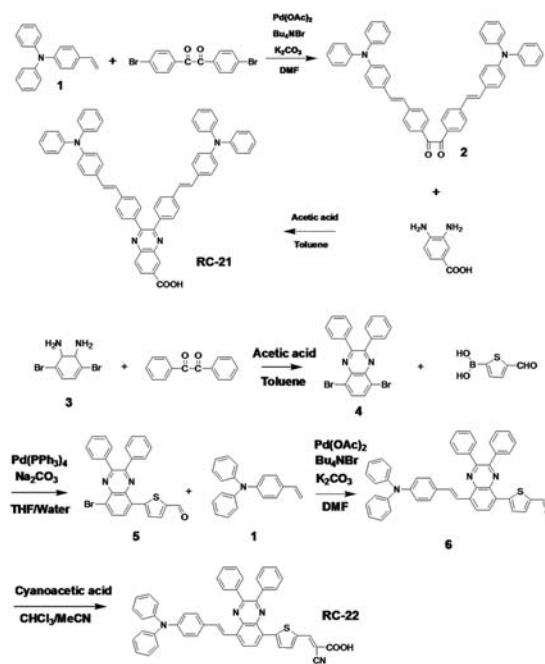
(7) Hou, L.; Tan, Z.; Wang, X.; Zhou, Y.; Han, M.; Li, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 4038.

(8) (a) Gholamkhass, B.; Koike, K.; Neighishi, N.; Hori, H.; Takeuchi, K. *Inorg. Chem.* **2001**, *40*, 756. (b) Eu, S.; Hayashi, S.; Umeyama, T.; Matano, Y.; Araki, Y.; Imahori, H. *J. Phys. Chem. C* **2008**, *112*, 4396. (c) Kira, A; Matsubara, Y.; Iijima, H.; Umeyama, T.; Matano, Y.; Ito, S.; Niemi, M.; Tkachenki, N. V.; Lemmetyinen, H.; Imahori, H. *J. Phys. Chem. C* **2010**, *114*, 11293.

Scheme 1. Synthesis of **RC-21** and **RC-22**

The dyes were synthesized in a moderate yield by the synthetic procedures illustrated in Scheme 1. For the preparation of **RC-21**, **1** and 4,4′-dibromobenzil were coupled by a Heck reaction[10] to produce a ditriphenylamine-containing intermediate, **2**. Then **2** was reacted with diaminobenzoic acid by an acid-catalyzed dehydration reaction to get the final dye with a quinoxaline moiety, **RC-21**. As for **RC-22**, dibromo-quinoxaline, **4**, was first prepared by a similar acid-catalyzed dehydration reaction between **3** and dibromobenzil. Both bromides horizontal to quinoxaline were coupled with thiophene-carbaldehyde

(9) Zhu, W.; Wu, Y.; Wang, S.; Li, W.; Li, X.; Chen, J.; Wang, Z.; Tian, H. *Adv. Funct. Mater.* **2011**, *21*, 756.

(10) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009.

and triphenylamine *via* the consecutive Suzuki coupling[11] and Heck reaction.[10] Finally, a Knoevenagel condensation reaction using cyanoacetic acid in the presence of piperidine was conducted to produce **RC-22**.
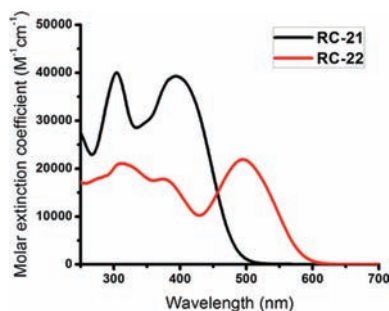

Figure 2. Absorption spectra of dyes in solution.

The absorption spectra of **RC-21** and **RC-22** in chloroform and THF, respectively, are shown in Figure 2. **RC-21** shows a high molar extinction coefficient (ε) of $\sim$40 000 M^{-1} cm^{-1} with two clear peaks located at around 300 and 400 nm, which might be attributed to two triphenylamine-based light absorbing antennae and the efficient $\pi-\pi^*$ transition of conjugated structures.[12] In contrast, **RC-22** reveals a broader and more red-shifted absorption spectrum due to a longer effective conjugation length and efficient formation of an intramolecular charge transfer (ICT) state. In **RC-21**, the benzene rings, attached to the 2,3-position of quinoxaline, were twisted $\sim$36° (Figure S9a in Supporting Information (SI)), which can largely disturb conjugation. On the other hand, the benzene ring, attached to the 5-position of quinoxaline in **RC-22**, was less twisted, $\sim$6° (Figure S9b in SI). These different geometries greatly influence on the electron densities of the highest occupied molecular orbital (HOMO) of dyes (Figure 4). Furthermore **RC-22** shows a lower ε due to one antenna triphenylamine compared to the two antennae of **RC-21**.[13] This kind of modulation in the absorption range by configurational change between the donor and acceptor unit is unique among most dyes reported so far. The approach appears to be promising for the design and development of molecular dyes showing different spectral responses across the visible to near-IR ranges.

To investigate the molecular energy levels, the electrochemical properties of dyes were measured using differential pulse voltammetry (DPV) in DMF solution (Table 1). The Ag wire was used as a quasi-reference electrode with ferrocene as an internal standard. The oxidation potentials (E_{ox}) of **RC-21** and **RC-22**, corresponding to HOMO, were found to locate at 1.03 and 1.01 V, respectively, vs a normal hydrogen electrode (NHE). Both were more positive than the redox couple (I^-/I_3^-, $\sim$0.4 V), ensuring that there is a sufficient driving force for the dye regeneration to efficiently compete with the recapture of the injected electrons by the dye cation. The zero−zero transition energy (E_{0-0}) values, which are related to the band gap energy (E_g), were determined from the intercept of normalized absorption and emission spectra (Figure S10 in SI). The excited-state oxidation potentials of these sensitizers were also more negative than the TiO_2 conduction band ($\sim$−0.5 V vs NHE) for efficient electron injection. Therefore, these new quinoxaline-based dyes are considered to have proper electronic energy levels as a promising sensitizer in DSSCs.

Table 1. Electrochemical Properties of Dyes

dye	$E_{(S+/S)}$[a] (V) vs NHE	$E_{(0-0)}$[b] (eV)	$E_{(S+/S*)}$[c] (V) vs NHE
RC-21	1.03	2.57	−1.54
RC-22	1.01	2.18	−1.17

[a] The ground-state oxidation potential of the dyes was measured with DPV. Potentials measured vs Fc^+/Fc were converted to those vs the normal hydrogen electrode (NHE) by addition of +0.63 V. [b] 0−0 transition energy, $E(0-0)$, estimated from the intercept of the normalized absorption and emission spectra in each solvent used. [c] Estimated LUMO energies, E(LUMO) vs NHE, were obtained from the ground-state oxidation potential (a) by adding the 0−0 transition energy, $E(0-0)$ (b).

The photocurrent density−voltage curves ($J-V$) and the incident photon to current conversion efficiency (IPCE) spectra of DSSCs based on **RC-21** and **RC-22** were shown in Figure 3 with the numerical results summarized in Table 2. During the measurements, a metal mask around the active area was used to avoid the inflated photocurrents from stray light.[14] The cell with **RC-21** showed a short circuit current density (J_{SC}) of 6.40 mA/cm², an open circiut voltage (V_{oc}) of 0.72 V, and a fill factor (*ff*) of 0.71, leading to an overall power conversion efficiency (η) of 3.30%. Considering its relatively narrow range of absorption, the performance observed here from **RC-21** can be ranked at around the top position among dyes showing a similar absorption characteristic.[15] On the other hand, the **RC-22** based cell gave a J_{SC} of 11.40 mA/cm², V_o of 0.66 V, and *ff* of 0.74, which yielded a higher η of 5.56%, although its structure has not been optimized for effective light absorption and charge separation. As for the IPCE values, the **RC-21**-sensitized cell showed over 70% in relatively narrow absorption wavelength ranges from 380 to 480 nm, with a maximum of 75% at 460 nm and an onset at about 550 nm (Figure 3b). The more broadly absorbing **RC-22** based cell gave about 60% IPCE values from 400 to

(11) Suzuki, A. *J. Organimet. Chem.* **1999**, *576*, 147.

(12) Chen, H; Huang, H.; Huang, X.; Clifford, J. N.; Forneli, A.; Palomares, E.; Zheng, X.; Zheng, L.; Wang, X.; Shen, P.; Zhao, B.; Tan, S. *J. Phys. Chem. C* **2010**, *114*, 3280.

(13) Gadisa, A.; Mammo, W.; Andersson, L. M.; Admasse, S.; Zhang, F.; Andersson, M. R.; Inganäs, O. *Adv. Funct. Mater.* **2007**, *17*, 3836.

(14) Ito, S.; Nazeeruddin, Md. K.; Liska, P.; Comte, P.; Charvet, R.; Pechy, P.; Jirousek, M.; Kay, A.; Zakeeruddin, S. M.; Grätzel, M. *Prog. Photovolt. Res. Appl.* **2006**, *14*, 589.

(15) (a) Baek, N. S.; Yum, J.-H.; Zhang, X.; Kim, H. K; Nazeeruddin, M. K.; Gratzel, M. *Energy Environ. Sci.* **2009**, *2*, 1082. (b) Lee, K.; Park, S. W.; Ko, M. J.; Kim, K.; Park, N.-G. *Nat. Mater.* **2009**, *8*, 665.

600 nm with the maximum value of 65% at 540 nm and photocurrent signal up to about 700 nm. Although the light harvesting efficiency (LHE: $1-10^{-\text{Absorbance}}$) of the **RC-22** dye-sensitized TiO$_2$ film was higher than that of the **RC-21** dye-sensitized one, the IPCE values around the maximum were higher in the latter than the former. This observation indicates that the internal IPCE (or absorbance-to-photocurrent conversion efficiency, APCE) is higher in the latter than the former, maybe due to a lower chance of recombination from the bulkier structure of **RC-21** compared to **RC-22**. More detailed studies on the relation between the dye structure and IPCE (or APCE) are currently underway.
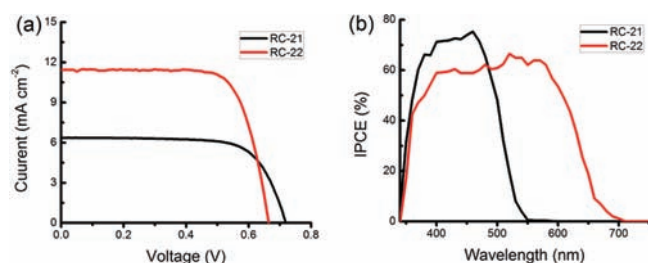

Figure 3. (a) $J-V$ characteristics of DSSCs and (b) IPCE spectra of DSSCs based on **RC-21** and **RC-22**.

The open circuit voltage for the **RC-21**-sensitized cell was measured to be 60 mV higher than that for its **RC-22** counterpart, maybe due to a longer electron lifetime imparted by a bulkier donor structure of the former than the latter.[16] The photocurrent from the **RC-22** sensitizer was almost double when compared to **RC-21**, which was dictated by a broader photoresponse of the former than the latter as can be seen clearly in IPCE spectra (Figure 3b).

Further insight into the molecular electron distributions and energy levels of dyes were obtained from density functional theory (DFT) calculations at the B3LP/6-31G** level in the Gaussian 09 program.[17] Figure 4 shows the electron distribution of the HOMO and LUMO of dyes with calculated energy levels. In both dyes, the HOMO shows the highest electron density near the electron-donating triphenylamine moieties, while it is located near electron-withdrawing quinoxaline and cyanoacrylic acid units in LUMO. Thus the efficient photoexcited eletcron trans-

(16) Miyashita, M.; Sunahara, K.; Nishikawa, T.; Uemura, Y.; Koumura, N.; Hara, K.; Mori, A.; Abe, T.; Suzuki, E.; Mori, S. *J. Am. Chem. Soc.* **2008**, *130*, 17874.
(17) Kusama, H.; Sugihara, H.; Sayama, K. *J. Phys. Chem. C.* 2011, *115*, 9267 and references cited therein.
(18) Hagberg, D. P.; Edvinsson, T.; Marinado, T.; Boschloo, G.; Hägfelt, A.; Sun, L. *Chem. Commun.* **2006**, 2245.

Table 2. Photovoltaic Performance Parameters of Dyes

dye	J_{sc} (mA/cm^2)	V_{oc} (V)	fill factor (ff)	η (%)
RC-21	6.4	0.72	0.71	3.30
RC-22	11.4	0.66	0.74	5.56

fer from the LUMO of dyes to the conduction band of TiO$_2$ is expected through the close position of LUMO to the anchoring group in the excited state.[18]

In summary, we developed novel quinoxaline-containing organic dyes with different configurations in connecting the donor with the acceptor units. The resultant **RC-21** and **RC-22** metal-free dye sensitizers showed different spectral responses and have been demonstrated to be an effective acceptor in metal-free organic dyes in DSSCs. However, there is still much room left for further enhancement of spectral responses, for example by simultaneously connecting the donors to the quinoxaline acceptor in a vertical and horizontal direction. We believe that the
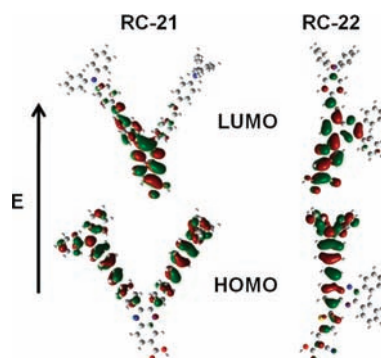

Figure 4. Frontier molecular orbitals of dyes calculated at the B3LYP/6-31G** level.

synthetic strategy developed in this study would open up a new avenue in designing dyes with more versatile optoeletronic properties and controllable molecular structures.

Supporting Information Available. Syntheses, characterization of **RC-21** and **RC-22**, experimetal procedures, and Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.