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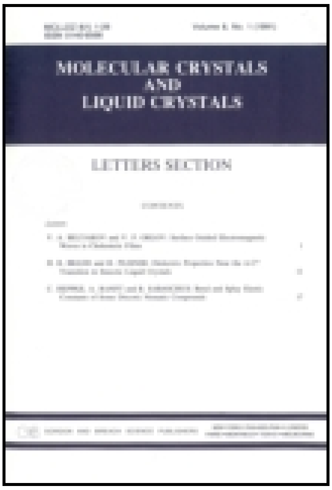

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A Near-IR Organic Sensitizer with Squaraine and Phenothiazine Unit for Dye-Sensitized Solar Cells

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A Near-IR Organic Sensitizer with Squaraine and Phenothiazine Unit for Dye-Sensitized Solar Cells

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*A new unsymmetrical squaraine-based near-IR sensitizer (**SGT-202**), where electron-rich bithiophene conjugated fragment was used to link to the squaraine core and phenothiazine unit as electron-donating group, was synthesized and applied for dye-sensitized solar cells. The **SGT-202** dye exhibits the* λ_{max} *of 667 nm and a strong luminescence maximum wavelength at 765 nm. The photovoltaic performance based on a newly developed squaraine dye shows a short-circuit photocurrent density* (J_{SC}) *of 8.6 mA/cm*^{2}*, an open-circuit voltage* (V_{OC}) *of 435V, and a fill factor* (FF) *of 0.68 corresponding to an overall conversion efficiency* (η) *of 2.6%.*

Keywords panchromatic dye; squaraine; phenothiazine; near-IR dye; dye-sensitized solar cells

1. Introduction

Dye-sensitized solar cells (DSSCs) have undergone continuous improvement since their introduction in 1991 and have now been incorporated into some commercial products. [1] Several polypyridyl ruthenium sensitizers have achieved power conversion efficiencies over 11% [2]. Recently, interest in metal-free organic dyes as an alternative to noble metal complexes has increased due to their many advantages, such as the diversity of molecular structures, high molar extinction coefficients in the far-red/near-IR region, simple synthesis, as well as low cost and negligible environmental issues [3–6]. To further increase solar-to-electric power conversion efficiencies, it would be useful to develop sensitizers with the enhanced light-harvesting ability in the near-infrared (NIR) region. Recently, squaraines with attractive intrinsic far-red absorption and extraordinary high molar absorption coefficient have been developed for DSSCs [7–10]. In general, the squaraine dye for DSSCs can efficiently be used as a co-sensitizer for organic dyes with a complementary absorption profile [10] but also good candidates to be combined with luminescent energy-relay dyes [11]. Recently, use of extended aromatic or heterocycle unit allows us to shift the absorption maxima of the squaraine dye to the longer wavelength region [12]. By introduction of π-bridge groups, such as phenyl, thienyl, and pyrrole groups, between donor and acceptor groups in the squarine dyes, the moiety has been shown to lead to a red shift in the absorption

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maximum and show the longest edge of incident photon-to-current conversion efficiencies (IPCEs) in the NIR region (up to *ca.* 850 nm) [13]. In this paper, we report the design, synthesis and characterization of new unsymmetrical squaraine dyes, coded as **SGT-202** in which thienyl group possessing large conjugation systems were used link to the squaraine core unit and the phenothiazine derivative as a donating group, for the first time. A phenothiazine-based dye contains electron-rich nitrogen and sulfur heteroatoms in a heterocyclic structure with high electron-donating ability, and its nonplanar butterfly conformation can sufficiently inhibit molecular aggregation and the formation of intermolecular excimers [14, 15]. Meanwhile, the 10-substituent on nitrogen can further enhance the charge separation at the oxide solution interface. Furthermore, the two phenyl groups are arranged in a small torsion angle related to nitrogen and sulfur atoms, so that $\pi-$delocalization can be extended over the entire chromophore [16]. A (4-(2-ethylhexyloxy))phenyl group as an electron donor on the opposite side, and an alkyl chain at the N atom of phenothiazine as a block against the electrolyte. The linear planar 4-(2-ethylhexyloxy)phenyl donor group together with the electron-rich phenothiazine moiety provides a satisfied electron migration from donor to acceptor [17].

2. Experimental

2.1 Materials

All reactions were carried out under a nitrogen atmosphere. Solvents were distilled from appropriate reagents. All reagents were purchased from Aldrich. 3,4-Dichlorocyclobut-3-ene-1,2-dione (**6**), 5-carboxy-2,3,3-trimethyl-1-octyl-3H-indolium iodide (**8**) [8], 3,7-dibromo-10-hexyl-10*H*-phenothiazine (**1**), 2-(4-(2-ethylhexyloxy) phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**) [18], bithiophen-5-yl-tributylstannane (**4**) [19] were synthesized by following the same procedures as described previously.

2.2 Measurements

^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature with AVANCE III HD (700 MHz) spectrometers and chemical shifts were reported in ppm units with tetramethylsilane as the internal standard. Mass of the intermediates as well as **SGT-202** was confirmed by MALDI-TOF-mass (Voyager-DETM STR Biospectrometry Workstation) or fast ion bombardment (FAB) mass in positive ion monitoring mode (JMS-700, 6890 Series). FT-IR spectra were taken on a JASCO, 4200 spectrophotometer. UV-visible absorption spectra were obtained in THF on a Shimadzu UV-2401PC spectrophotometer. Cyclic voltammetry was carried out with a Versa STAT3 (AMETEK). A three electrode system was used and consisted of a reference electrode (Ag/AgCl), a a working electrode, and a platinum wire electrode. The redox potential of dye on TiO_2 was measured in CH_3CN with 0.1 M $TBAPF_6$ with a scan rate between 50 mV s^{-1}.

2.3 Synthesis

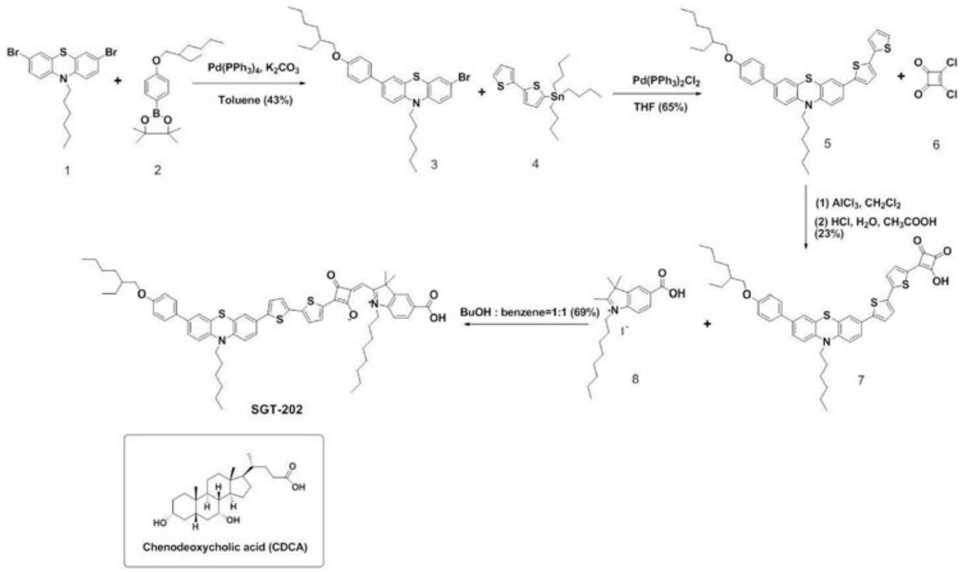
*2.3.1. 5-Carboxy-3,3-dimethyl-1-octyl-3*H*-indolium-2-yl)methylene-2-(5'-(7-(4-(2-ethylhexyloxy)phenyl)-10-hexyl-10*H*-phenothiazin-3-yl)-2,2'-bithiophen-5-yl)-3-oxocyclobut-1-enolate (**SGT-202**).* Compound **7** (0.10 mmol), compound **8** (0.20 mmol) were dissolved in a mixture of *n*-butanol (40ml) and benzene (40ml). The mixture was refluxed with the Dean-Stark apparatus for 20 hours. After the mixture was cooled to the room temperature, the solvent was removed by evaporation under vacuum to obtain the crude product. The crude product was purified by silica gel column chromatography with (DCM:MeOH = 40:1). The physical and spectral data are shown below. Yield 70%, deep green solid. FT-IR (KBr, cm^{-1}): 3425, 2961, 2923, 2853, 1738, 1709, 1606, 1563, 1511, 1425, 1352, 1307, 1241, 1170, 1081. ^1H NMR (700 MHz, DMSO-d_6) δ (TMS, ppm): 8.24 (s, 1H); 8.08 (dd, 2H); 8.07 (d, 1H); 7.80(d, 1H); 7.70 (d, 1H); 7.50-7.53 (dd, 3H); 7.49 (d, 2H); 7.42 (d, 2H); 7.04 (s, 2H); 6.97 (d, 2H); 6.31 (s, 1H); 4.41 (t, 2H); 3.88 (t, 2H), 3.59 (d, 2H); 1.77 (s, 6H); 1.67-1.69 (m, 1H); 1.38-1.44 (m, 4H); 1.22-1.34 (m, 24H); 0.80-0.89 (m, 12H). ^{13}C NMR (700 MHz, DMSO-d_6) δ (TMS, ppm): 189.37, 180.24, 178.31, 177.09, 166.87, 162.34, 160.46, 158.35, 151.49, 144.51, 144.35, 143.20, 142.66, 141.99, 139.22, 134.61, 134.45, 131.10, 130.18, 129.55, 128,89, 128.07, 127.36, 127.15, 126.12, 125.38, 124.93, 124.49, 123.98, 123.64, 123.55, 123.33, 123.22, 116.14, 116.02, 114.90, 113.35, 92.48, 70.01, 67.04, 51.08, 48.53, 46.65, 45.07, 43.29, 34.40, 31.29, 31.13, 30.86, 30.44, 29.95, 29.04, 28.86, 28.74, 28.57, 28.50, 28.46, 27.36, 26.76, 26.70, 26.16, 26.00, 25.84, 25.15, 24.98, 23.94, 23.33, 22.54, 22.1, 22.04, 21.05, 13.97, 13.94, 13.87, 10.93. MALDI-TOF: calculated for $C_{64}H_{72}N_2O_5S_3$, 1045.46 and found 1046.79.

3. Results and Discussion

Scheme 1 describes the synthetic routes to obtain squaraine sensitizer containing squaraine core and phenothiazine moiety, the **SGT-202** dye. Semisquaric acids were synthesized by condensation of 3,4-dichloro-3-cyclobutene-1,2-dione with compound **5**, followed by hydrolysis to obtain semi-squaraine dyes (**7**). For the synthesis of **SGT-202** dye, the resulting the semi-squaraine dyes (**7**) were reacted with indolenine (**8**) under azeotropic conditions afforded squaraine dyes with an iodine substitution (**SGT-202**) [16].

Figure 1 exhibits the absorption and emission spectra of the **SGT-202** measured in THF solution and adsorbed onto a 2.8 μm TiO_2 film. The UV-visible absorption spectrum of the **SGT-202** shows an absorption maximum wavelength (λ_{max}) at 667 nm with a relatively high molar extinction coefficient ($\varepsilon = 75100\ M^{-1}\ cm^{-1}$) arising from π - π^* transition of the conjugate system. It indicates the easy formation of the charge transfer character from the donor part to the acceptor group. When the **SGT-202** was excited within the CT absorption band at room temperature in an air-equilibrated THF solution, a strong luminescence maximum wavelength at 765 nm was observed. It was similar to that of reported squaraine dyes with π-bridge groups, such as phenyl, thienyl, and pyrrole groups, between donor and acceptor groups [13]. In the absorption spectraum of the **SGT**-sensitizer attached to TiO_2 films under the co-adsorbent free condition, The absorption spectrum was broadened and blue shifted absorptions were observed for the dyes indicating the formation of H-aggregates that usually restrict the efficient electron injection into the conduction band of TiO_2 (Fig. 1), which leads to the reduction of photocurrent [20]. Typically, the blue-shift on TiO_2 is a common phenomenon for most organic dyes, which is regarded as the result of a strong interaction between the dye and the semiconductor surface. A similar trend has been demonstrated when dyes were deprotonated in the presence of a base [4].

The electrochemical properties were investigated by cyclic voltammetry (CV) to obtain the HOMO and LUMO levels of the **SGT-202** dye. The cyclic voltammograms were obtained from a three electrode cell in 0.1 M $TBAPF_6$ in CH_3CN at a scan rate of 50 mV s^{-1}, using a dye coated TiO_2 electrode as the working electrode, a Pt wire counter-electrode, and an Ag/AgCl (saturated KCl) reference electrode (+0.197 V vs. NHE) which was calibrated with ferrocene. All of the measured potentials were converted to the NHE scale. The



Scheme 1. Synthetic route to **SGT-202**. a) Compound 1 (1.0 equiv), compound 2 (0.8 equiv), Toluene, K_2CO_3 (10 equiv), $Pd(PPh_3)_4$ (0.05 equiv); b) Compound 3 (1.0 equiv), compound 4 (1.2 equiv), THF, $Pd(PPh_3)_2Cl_2$ (0.08 equiv); c) (1) Compound 5 (1.0 equiv), compound 6 (3.0 equiv), dichloromethane, $AlCl_3$ (1.0 equiv), (2) H_2O : acetic acid = 1 : 1; d) Compound 7 (1.0 equiv), compound 8 (1.0 equiv), benzene : n-butanol = 1 : 1.

band gap was estimated from the absorption edges of the UV-visible spectra and LUMO energy levels were derived from the HOMO energy levels and the band gap. The HOMO value (0.89 V vs. NHE) was more positive than the I^-/I_3^- redox couple (0.4 V vs. NHE) employed as an electrolyte in DSCCs. The optical transition energy, $E_{0\text{-}0}$, of the **SGT-202**

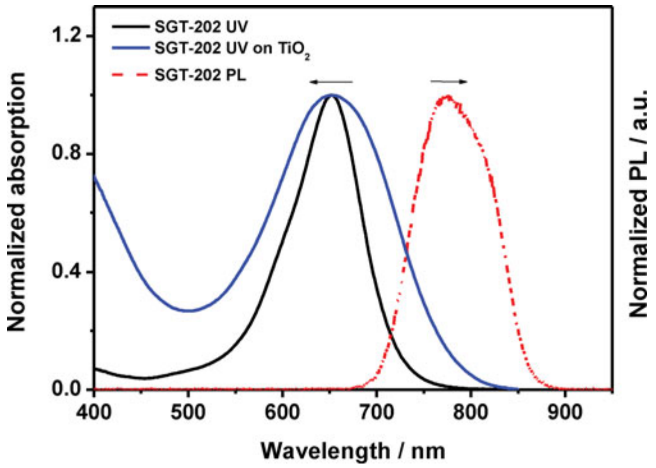


Figure 1. Normalized UV-visible absorption (black-line) and emission spectra (red-line) of the **SGT-202** in THF at room temperature. Absorption spectra of the **SGT-202** adsorbed on the TiO_2 film (blue line).

determined from the intersection of absorption and emission spectra measured in THF is 1.68eV, yielding the potentials of the LUMO for the dye to be -0.79 V. Electron injection from the excited dyes to the conduction band of TiO_2 should be energetically facile because of the more negative LUMO values compared to the conduction band edge energy level of the TiO_2 electrode [21].

To evaluate the cell performances of DSSCs based on a SGT-sensitizer, we have fabricated solar cells using the transparent TiO_2 film and measured the incident monochromatic photon-to-current conversion efficiency (IPCE) of the cells and the photovoltaic performances based on the **SGT-202**, which are displayed in Figure 2.

The screen-printed double layer TiO_2 film consisting of a 12 μm transparent layer and a 4 μm scattering layer was prepared and the TiO_2 electrodes were immersed into the dye solution (0.2 mM) in THF/EtOH (2:1) and 30 mM chenodeoxycholic acid (CDCA) as an additive. The electrodes were dipped into the dye solution at room temperature, and the dye-coated electrodes were rinsed quickly with ethanol and used as such for photovoltaic measurements. To effectively suppress dye aggregation for DSSCs, the coadsorbent of CDCA was used. Both open-circuit voltage (V_{OC}) and short-circuit photocurrent density (J_{SC}) were dramatically enhanced by the coadsorption of CDCA with the dye, due to the efficient retardation of charge recombination arising from the prevention of π–π stacking [22].

Figure 2 shows the photocurrent action spectrum obtained with a sandwich cell. DSSCs based on the series of **SGT-202** not only exhibit the panchromatic response (covers the window of the whole visible light) but also extend the photovoltaic performance to the NIR region. The carboxylic acid-anchored squaraine dye demonstrated a significant low η value. **SGT-202** exhibited the broadest IPCE spectrum; however, the lower intensity (about 30% max.) led to a slightly diminished J_{SC} value. Aggregation is known to become frequently problem for zwitter ionic dyes that are adsorbed onto TiO_2 films [22]. The optimal device with **SGT-202** included additional deaggregating CDCA and exclusive of CDCA. The peak was observed in the lower wavelength region compared to its absorption on TiO_2, indicating that the aggregation of **SGT-**sensitizer characterized in the absorption spectrum makes a contribution to the photovoltaic performance. Under standard global AM 1.5 solar condition, the squaraine-sensitized cell gave a J_{SC} of 8.6 mA/cm^2, V_{OC} of 435V, and a fill factor (FF) of 0.68 corresponding to an overall conversion efficiency corresponding to an

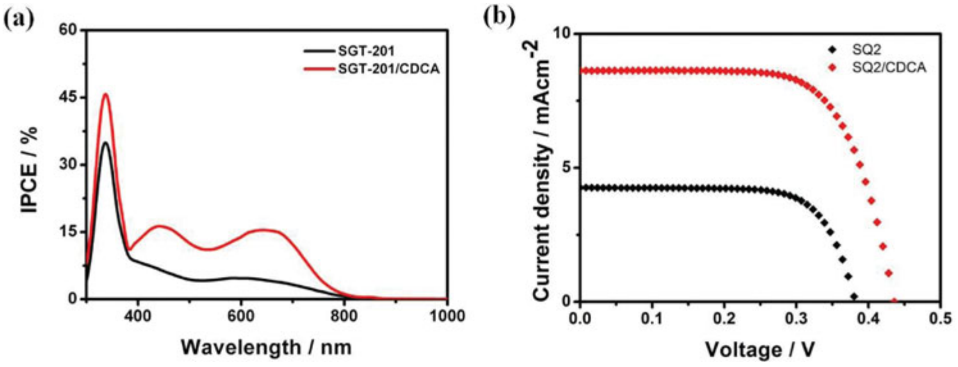


Figure 2. (a) Typical action spectra of incident photon-to-current conversion efficiencies (IPCE) obtained for nanocrystalline TiO_2 solar cells sensitized by **SGT-202** dye. (b) Photocurrent-voltage characteristics of representative TiO_2 electrodes sensitized with **SGT-202** dye.

overall conversion efficiency (η) of 2.6%. Despite panchromatic response of the **SGT-202**, the result showed low J_{SC} value and because of the low LUMO levels. More sensitizers were red-shift by introducing $\pi-$bridge, the lower band gap was that is, the LUMO levels of the sensitizers are low. The low LUMO levels caused insufficient electron flow from excited dye to the TiO_2 surface and consequentially, this indicated that low J_{SC} value [24, 25].

4. Conclusions

We successfully designed and synthesized the new unsymmetrical squaraine near-IR sensitizer (**SGT-202**), in which electron-rich bithiophene conjugated fragment was used to link to the squaraine core and phenothiazine unit as electron-donating group. The **SGT-202** dye exhibits the λ_{max} of 667 nm with relatively high molar extinction coefficient (ε = 75100 M^{-1} cm^{-1}) and a strong luminescence maximum wavelength at 765 nm. The high molar absorption coefficient was favorable for the light-harvesting efficiency of DSSCs. As a result, the solar cell based on the **SGT-202** dye with CDCA showed better photovoltaic performance than solar cells based on SGT-202, with J_{SC} of 8.6 mA/cm^2, V_{OC} of 435V, and a fill factor (FF) of 0.68 corresponding to an overall conversion efficiency corresponding to an overall conversion efficiency η of 2.6%.under standard AM 1.5 irradiation.

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References

[1] O'Regan, B. and Grätzel, M. (1991) *Nature*, *353*, 737.

[2] (a) Nazeereddin, M d. K., De Angelis, F., Fantacci, S., Selloni, A., Viscardi, G., Liska, P., Ito, S., Takeru, B. and Grätzel, M. (2005). *J. Am. Chem. Soc.*, *127*, 16835 (b) Chiba, Y., Islam, A., Watanabe, Y., Komiya, R., Koide, N. and Han, L. (2006). *Jpn. J. Appl. Phys.*, *45*, L638 (c) Gao, F., Wang, Y., Shi, D., Zhang, J., Wang, M., Jing, X., Humphry-Baker, R., Wang, P., Zakeeruddin, S. M. and Grätzel, M. (2008). *J. Am. Chem. Soc.*, *130*, 10720.

[3] Seo, K. D., Song, H. M., De Angelis, F., Nazeeruddin, M d. K., Gräetzel, M., Kim, H. K., *et al.* (2011). *Dye and Pigment.*, *90*, 304.

[4] Seo, K. D., Choi, I. T., Park, Y. G., Kang, H. S., Lee, J. Y. and Kim, H. K. (2012). *Dye and Pigment.*, *94*, 469.

[5] Kang, S. H., Choi, I. T., Kang, M. S., Eom, Y. K., Ju, M. J., Hong, J. Y., Kang, H. S. and Kim, H. K. (2013). *J Mater Chem A.*, *1*, 3977.

[6] Seo, K. D., You, B. S., Choi, I. T., Ju, M. J., You, M., Kang, H. S. and Kim, H. K. (2013). *ChemSuSChem.*, *6*, 2069.

[7] Yum, J. H., Walter, P., Huber, S., Rentsch, D.; Geiger, T., Nue··sch, F., Angelis, F. D., Grätzel, M., Nazeeruddin, M. K. (2007). *J. Am. Chem. Soc.*, *129*, 10320.

[8] Geiger, T., Kuster, S., Yum, J. H., Moon, S. J., Nazeeruddin, M. K., Grätzel, M., Nuësch, F. (2009). *AdV. Funct. Mater.*, *19*, 2720.

[9] Choi, H., Kim, J. J., Song, K., Ko, J., Nazeeruddin, M. K., Grätzel, M. (2010). *J. Mater. Chem.*, *20*, 3280.

[10] Choi, H., Kim, S., Kang, S. O., Ko, J., Kang, M. S., Clifford, J. N., Forneli, A., Palomares, E., Nazeeruddin, M. K., Grätzel, M. (2008). *Angew. Chem., Int. Ed.*, *47*, 8259.

[11] J. H., Hardin, B. E., Moon, S. J., Baranoff, E., Nue··sch, F., McGehee, M. D., Grätzel, M., Nazeeruddin, M. K. (2009). *Angew. Chem., Int. Ed.*, *48*, 9277.

[12] Inoue, T., Pandey, S. S., Fujikawa, N., Yamaguchi, Y. and Hayase, S. (2010). *J Photochem Photobiol A.*, *213*, 23.

[13] (a) Beverina, L. and Salice, P. (2010). *Eur J Org Chem* 1207–25. (b) Paek, S., Choi, H., Kim, C., Cho, N., So, S., Song, K., Nazeeruddin, M d. K. and Ko, J. (2011). *Chem Commun.*, *47*, 2874 (c) Li, J. Y., Chen, C. Y., Lee, C. P., Chen, S. C., Lin, T. H., Tsai, H. H., Ho, K. C. and Wu, C. G. (2010). *Org Lett.*, *12*, 5454.

[14] Tian, H. N., Yang, X. C., Chen, R. K., Pan, Y. Z., Li, L., Hagfeldt, A. and Sun, L. C. (2007). *Chem Commun.*, *43*, 3741.

[15] Wu, W. J., Yang, J. B, Hua, J. L, Tang, J., Zhang, L., Long, Y. T and Tian, H. (1772). *J Mater Chem.*, *201*, 20.

[16] (a) Chang, Y. J., Chou, P. T., Lin, Y. Z., Watanabe, M., Yang, C. J., Chin, T. M. and Chow, T. J. (2012). *J Mater Chem.*, *22*, 21704. (b) Chen, C. J., J. Y. Liao, Chi, Z. G., Xu, B. J., Zhang, X. Q., Kuang, D. B., Zhang, Y., Liu, S. W. and Xu, J. R. (2012). *J Mater Chem.*, *22*, 8994. (c) Xie, Z. B., Midya, A., Loh, K. P., Adams, S., Blackwood, D. J., Wang, J., Zhang, X. J. and Chen, Z. K. (2010). *Prog Photovoltaics.*, *18*, 573.

[17] Hua, Y., Chang, S., Huang, D., Zhou, X., Zhu, X., Zhao, Z., Chen, T., Wong, W. Y. and Wong, W. K. (2013). *Chem Mater.*, *25*, 2146.

[18] Choi, I. T., Dr. Ju, M. J., Song, S. H., Kim, S. G., Cho, D. W., Im, S. and Kim, H. K. (2013). *Chem Eur J.*, *19*, 15545.

[19] Shi, Y. R., Hill, R. B. M., Yum, J. H., Dualeh, A., Barlow, S., Grätzel, M., Marder, S. R and Nazeeruddin, M d. K. (2011). *Angew Chem Int Ed.*, *50*, 6619.

[20] Hara, K., Dan-oh, Y., Kasada, C., Ohga, Y., Shinpo, A., Suga, S., Sayama, K. and Arakawa, H. (2004). *Langmuir.*, *20*, 4205.

[21] Beverina, L., Ruffo, R., Patriarca, G., De Angelis, F., Roberto, D., Righetto, S., Ugo, R. and Pagani, G. A. (2009). *J. Mater. Chem.*, *19*, 8190.

[22] Yum, J. H., Moon, S. J., Humphry-Baker1, R., Walter, P., Geiger, T., Nüesch, F., Grätzel, M and Nazeeruddin, M. d K. (2008). *Nanotechnology.*, *19*, 424005.

[23] Zeng, W., Cao, Y., Bai, Y., Wang, Y., Shi, Y., Zhang, M., Wang, F., Pan, C. and Wang, P. (2010). *Chem Mater.*, *22*, 1915.

[24] Kim, B. G., Chung, K. and Kim, J. (2013). *Chem Eur J.*, *19*, 5220.

[25] Maeda, T., Arikawa, S., Nakao, H., Yagi, S. and Nakazumi, H. (2013). *New J Chem.*, *37*, 701.