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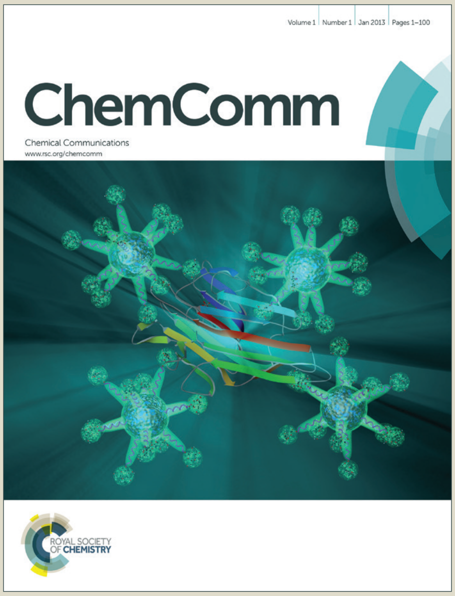

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Highly-efficient dye-sensitized solar cells with collaborative sensitization by silyl-anchor and carboxy-anchor dyes†

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Kenji Kakiage,[a] Yohei Aoyama,[a] Toru Yano,*[a] Keiji Oya,[a] Jun-ichi Fujisawa[b] and Minoru Hanaya*[b]

In the dye-sensitized solar cells co-photosensitized with an alkoxysilyl-anchor dye of ADEKA-1 and a carboxy-anchor organic dye of LEG4, LEG4 was revealed to work collaboratively by enhancing the electron injection from the light-excited dyes to the TiO_2 electrodes, and the cells exhibited a high conversion efficiency over 14% under the one sun illumination.

Dye-sensitized solar cells (DSSCs), which are composed of mesoporous nanocrystalline-TiO_2 thin layers modified by photosensitizing dyes as working electrodes, redox electrolytes and counter electrodes, have been actively investigated as the photovoltaic device in next generation of the alternative to conventional silicon-based inorganic solar cells (Fig. S1, ESI†), because of a potential low cost for the production, shorter energy and CO_2 payback time, low toxicity of constituting elements and relatively high light-to-electric energy conversion efficiencies (η) especially under low-light intensity and scattered light conditions.[1-4] In the DSSCs, η of 11-13% under the simulated sunlight at one sun have been reported up to now by the photosensitization using polypyridyl and porphyrin complexes of metals such as ruthenium or zinc and a few metal-free organic dyes with carboxy-anchor moieties for binding to the surface of the TiO_2.[1-9]

Organosilicon compounds such as silanols and alkoxysilanes have high bonding ability to metal-oxide surfaces by forming firm Si-O-metal bonds. With paying attention to the characteristics of silanols and alkoxysilanes, we have focused on the development of photosensitizing dyes for DSSCs possessing silyl-anchor moieties,[10-12] and recently we succeeded in achieving over 12% conversion efficiency in the cells by using a carbazole/alkyl-functionalized oligothiophene/alkoxysilyl-anchor moiety type compound, **ADEKA-1** (Fig. 1a), as the photosensitizer.[13] Besides the high photovoltaic performance, the TiO_2 photoelectrode sensitized with **ADEKA-1** possesses much higher durability to solvents, e.g. nitrile, water and mixtures of them, and to surface modification using wet processes than those sensitized with carboxy-anchor dyes. The durability of the photoelectrode allows co-adsorption of another sensitizing dye to the electrode for producing a co-sensitization effect, and actually we succeeded in improving the η to 12.8% by means of the co-sensitization of **ADEKA-1** and a silyl-anchor coumarin dye of **SFD-5**.[14]

For further improvement in the efficiency of **ADEKA-1**-sensitized DSSCs, we have expanded the study of co-sensitizers for the cells to widely developed carboxy-anchor dyes, which have been demonstrated to possess high sensitizing property as photosensitizers in DSSCs. In the investigation we found that the **ADEKA-1**-sensitized cells with the co-sensitizer of **LEG4**[15] (Fig. 1b) exhibited considerably higher photovoltaic performance by a collaborative sensitization of the dyes, and succeeded in achieving over 14% conversion efficiency in the cells. The efficiency shows the high potential of DSSCs as practical light-to-electric energy conversion device in the near future.

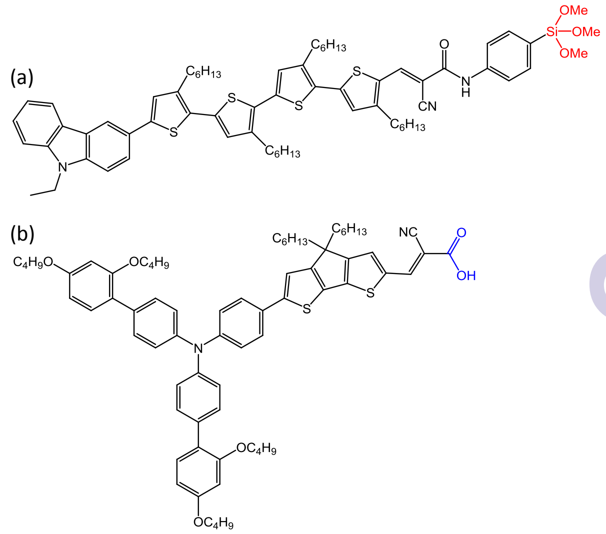

Fig. 1 Molecular structures of photosensitizing dyes: (a) silyl-anchor dye of **ADEKA-1** and (b) carboxy-anchor dye of **LEG4**.

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[a] Environmental & Energy Materials Laboratory, ADEKA CORPORATION, 7-2-35 Higashiogu, Arakawa, Tokyo 116-8554, Japan. E-mail: yanotoru@adeka.co.jp
[b] Division of Molecular Science, Graduate School of Science and Technology, Gunma University, 1-5-1 Tenjin-cho, Kiryu, Gunma 376-8515, Japan.
E-mail: mhanaya@gunma-u.ac.jp

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As the co-sensitizers for the **ADEKA-1**-sensitized DSSCs, we selected the carboxy-anchor organic sensitizing dyes reported to have a high sensitizing property and an absorption band in the shorter wavelength region than **ADEKA-1** of **LEG4**, **D35**, **L0** and **D131** (Figs. S2-S6 and Table S1, ESI†). To check the potential of those dyes as the co-sensitizer to **ADEKA-1**, we fabricated the cells sensitized by **ADEKA-1** and by **ADEKA-1** with the dyes using an electrolyte solution containing I_3^-/I^- redox mediator (Cell-A; the fabrication procedures of the cells were described in ESI†). Among the cells, significant and the largest improvement in the incident monochromatic photon-to-current conversion efficiency (IPCE) was observed in the cell photosensitized by **ADEKA-1** with **LEG4** (Fig. 2a and Fig. S7 in ESI†). The cell exhibited much higher IPCE values close to 90% than those of the cells sensitized only by **ADEKA-1** and only by **LEG4** in all the visible region. The increment of the open-circuit photovoltage (V_{oc}) and the short-circuit photocurrent density (J_{sc}) from those of the cell sensitized by **ADEKA-1** resulted in the improvement of the η by a factor of 1.3 under the simulated sunlight at one sun (AM-1.5G, 100 mW cm^{-2}; Table S2, ESI†).

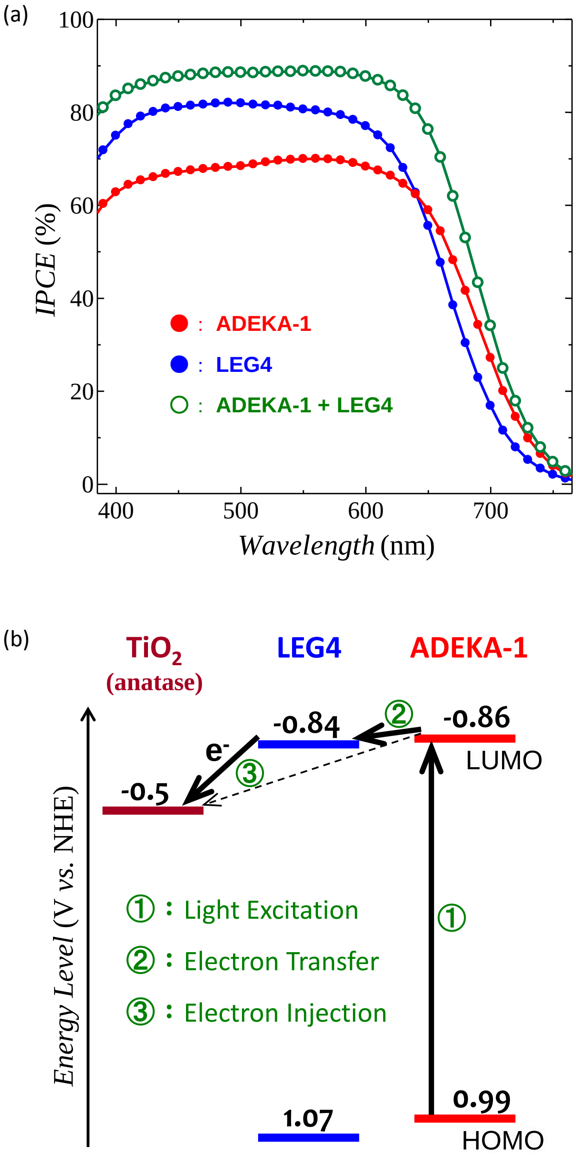

Fig. 2 (a) IPCE spectra of the cells photosensitized by **ADEKA-1**, by **LEG4** and by **ADEKA-1** with **LEG4** (Cell-A) and (b) schematic drawing of the charge separation processes for the TiO_2 electrode sensitized collaboratively by **ADEKA-1** and **LEG4**.

In the cell photosensitized by **ADEKA-1** with **LEG4**, in which the relative amount of the dyes adsorbed on the TiO_2 electrode was estimated to be 1.0 : 0.25 for **ADEKA-1** : **LEG4**, the improvement of IPCE values from those of the **ADEKA-1**-sensitized cell was observed not only in the light-absorption wavelength region of **LEG4** but also in the longer wavelength region where the light absorption by **LEG4** was absent (Fig. S7, ESI†), differently from the other co-sensitized cells. In order to clarify the origin of the peculiar and large improvement in the IPCE by the co-sensitization with **LEG4**, we examined MO calculations of the dyes (Figs. S9, S10 and Tables S3, S4 in ESI†). The light-to-electric energy conversion in DSSCs proceeds via the light excitation of the sensitizing dye and following charge separation produced through the electron injection from the LUMO of the light-excited dye to the conduction band of TiO_2. In **ADEKA-1** the alkoxysilyl-anchor moiety links to the chromophore (carbazole/alkyl-functionalized oligothiophene moiety) *via* the phenyl-amide moiety, and the LUMO has a small electron distribution around the silyl-anchor moiety. On the other hand, the LUMO of **LEG4** has a large electron distribution around the carboxy-anchor moiety and thus **LEG4** is expected to have a higher electron injection efficiency from the LUMO to the TiO_2 conduction band than **ADEKA-1** (Fig. S9, ESI†). When comparing the energy levels of LUMOs of the dyes, only **LEG4** has lower LUMO than that of **ADEKA-1** differently from other dyes of **D35**, **L0** and **D131** (Fig. S6, ESI†), and emission analyses by the use of the Al_2O_3 porous film modified by **ADEKA-1** with **LEG4** showed that the emission from **ADEKA-1** was quenched almost completely by the existence of **LEG4** as the co-adsorbent (Fig. S11, ESI†). From the MO properties and the result of the emission analyses, the large improvement of the photovoltaic performance in the cell photosensitized by **ADEKA-1** with **LEG4** is considered to be brought by the collaborative sensitization of the dyes through an electron injection enhancement effect due to the existence of the **LEG4** molecules near the **ADEKA-1** molecules on the TiO_2 electrode; the electron transfers from the light-excited **ADEKA-1** to the co-adsorbent of **LEG4** and immediate electron injection occurs from the **LEG4** to the conduction band of TiO_2 with much higher efficiency than the direct electron injection from the light-excited **ADEKA-1** (Fig. 2b). Internal quantum efficiency (IQE) measurements revealed a considerably high electron injection efficiency in the cell photosensitized by **ADEKA-1** with **LEG4**, and the maximum IQE was evaluated to be 99±2% (Fig. S12, ESI†). The increment of V_{oc} (Table S2, ESI†), the decrease of the dark-current (Fig. S13, ESI†) and the elongation of the electron lifetime in the TiO_2 conduction band estimated from the transient open-circuit voltage decays (Fig. S14, ESI†) observed in the co-sensitization with **LEG4** indicate that the

Table 1 Photovoltaic parameters of the cells sensitized collaboratively by **ADEKA-1** and **LEG4** (Cell-B) under the illuminations of the simulated sunlight (AM-1.5G)

Entry	Electrolyte : Redox[a]	Counter Electrode	Light Intensity	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)
1	A : I_3^-/I^-	FTO/Pt	100 mW cm^{-2}	19.11	0.783	0.748	11.2
2	F : $[Co(phen)_3]^{3+/2+}$	FTO/Pt	100 mW cm^{-2}	17.77	1.018	0.765	13.8
3[b]	F : $[Co(phen)_3]^{3+/2+}$	FTO/Au/GNP	100 mW cm^{-2}	18.27	1.014	0.771	14.3
4	F : $[Co(phen)_3]^{3+/2+}$	FTO/Au/GNP	50 mW cm^{-2}	9.55	0.994	0.776	14.7

[a] Electrolyte: A) 0.07 M I_2, 0.05 M LiI, 0.05 M NaI, 0.50 M DMPImI, 0.10 M EMImI, 0.05 M TBAI, 0.05 M THAI, 0.40 M TBP, 0.10 M MP, 0.10 M GuSCN in MeCN/VN/THF (8:1:1 in volume); F) 0.20 M $[Co^{2+}(phen)_3](PF_6^-)_2$, 0.05 M $[Co^{3+}(phen)_3](PF_6^-)_3$, 0.07 M $LiClO_4$, 0.02 M $NaClO_4$, 0.03 M TBAPF, 0.01 M TBPPF, 0.01 M HMImPF, 0.30 M TBP, 0.10 M TMSP, 0.10 M MP, 0.05 M CPrBP, 0.10 M CPeBP, 0.05 M COcBP in MeCN. The data for the cells with other electrolytes (B-E) are listed in Table S6 (ESI†). [b] The values are the averages of the results of the four cells prepared separately (Table S5, ESI†).

adsorbed **LEG4** on the TiO_2 electrode works also as the suppressor for preventing the back electron transfer from the TiO_2 electrode to the electrolyte by covering the naked surface of the TiO_2 electrode with its plural alkyl-chain substituents.[15-18] By using the I_3^-/I^- redox electrolyte solution with an experimentally optimized composition, the cell photosensitized collaboratively by **ADEKA-1** and **LEG4** (Cell-B; the fabrication procedures of the cell were described in ESI†) exhibited the η of 11.2% under the AM-1.5G one sun illumination (Entry 1 in Table 1).

The maximum photovoltage (V_{max}) obtained in the DSSC is attributed to the energy gap between the quasi-Fermi level of the TiO_2 [approximately the energy level of the conduction-band edge ($E_{C.B.}$)] and the redox potential of the electrolyte, and the improvement of the efficiency of DSSCs is possible by the increment of the photovoltage with using the electrolyte having more positive (lower) redox potential than the I_3^-/I^- redox.[1-4,7-9,11,13-15] The redox potential of a cobalt(III/II) tris(1,10-phenanthroline) complex ($[Co(phen)_3]^{3+/2+}$) is lower than that of the I_3^-/I^- redox by ca. 0.2 V,[19] and the values of the HOMO levels of **ADEKA-1** and **LEG4** are still more positive than the redox potential of the cobalt(III/II) complex (Fig. S15, ESI†), which provides the thermodynamic driving force for the dye regeneration reaction by the electron transfer from the Co^{2+}-complex electrolyte to the oxidized dye.[13-15] Thus we employed $[Co(phen)_3]^{3+/2+}$ as the redox electrolyte to the co-sensitized cell by **ADEKA-1** and **LEG4** for further improvement of the η of the cells.

In the fabrication of the cells using the cobalt(III/II) complex redox electrolytes (Cell-B), compositions of the electrolyte solutions as to the ratio of Co^{2+}/Co^{3+}, the kind of the counter anion of the cobalt(III/II) complex and the electrolyte additives were optimized experimentally according to the literatures[7,13,14,20,21] with using a platinum-deposited F-doped SnO_2 (FTO)-coated glass plate as the counter electrode. The cell using the electrolyte solution with the optimized composition exhibited the high V_{oc} above 1 V and the η was improved to 13.8% under the AM-1.5G one sun illumination (Entry 2 in Table 1) as was expected from the more positive redox potential of $[Co(phen)_3]^{3+/2+}$. However, the decrease of the J_{sc} was also observed in the cell from that in the cell with the I_3^-/I^- redox electrolyte solution. In order to recover the J_{sc}, we employed graphene nanoplatelets (GNP) as the material for the counter electrode and composed the counter electrode on a FTO-coated glass plate with a structure of FTO/Au/GNP, because the counter electrode has been reported to produce higher J_{sc} and a fill factor (FF) in the photocurrent-voltage property than the usually applied platinum electrodes.[8,22,23] Figure 3 shows an example of the *J-V* curve under the AM-1.5G one sun illumination (100 mW cm^{-2}) and the IPCE spectrum of the cell co-sensitized by **ADEKA-1** and **LEG4**. The photovoltaic parameters assessed as the averaged values from the *J-V* curves of the separately prepared four cells are listed in Table 1 as Entry 3 (Table S5, ESI†). The J_{sc} was improved actually in the cell from 17.8 to 18.3 ± 0.1 mA cm^{-2} by using the FTO/Au/GNP counter electrode and the maximum value in the IPCE spectrum was reached up to 91%, resulting in the η of 14.3% with V_{oc} above 1 V. The better photovoltaic performance in the lower light intensity is a characteristic of DSSCs. That is also in the present cell and the cell exhibited the η close to 15% under the simulated sunlight with 50 mW cm^{-2} intensity (Entry 4 in Table 1 and Figs. S16, S17 in ESI†).

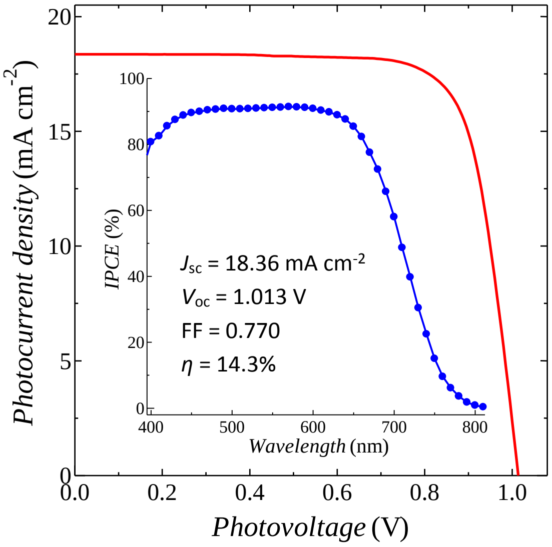

Fig. 3 A typical *J-V* property of the cell photosensitized collaboratively by **ADEKA-1** and **LEG4** with the efficiency over 14% (Entry 3a in Table S5, ESI†) under the illumination of the simulated sunlight (AM-1.5G, 100 mW cm^{-2}). Inset shows the IPCE spectrum of the cell.

In conclusion, a carboxy-anchor organic dye of **LEG4** was revealed to work effectively as the collaborative sensitizer to the silyl-anchor dye of **ADEKA-1** in DSSCs, and we succeeded in obtaining the high IPCE up to 91%, V_{oc} above 1 V and 14.3% conversion efficiency in the cell with the optimized cobalt(III/II) complex redox electrolyte solution and the GNP counter electrode. The result is attributed basically to the strong adsorption property of **ADEKA-1** to the TiO_2 electrode and shows the validity of silyl-anchor dyes as the photosensitizers for DSSCs. The observation over 14% conversion efficiency in the DSSC indicates a high potential of DSSCs as a light-to-electric energy conversion device. The collaborative sensitization by plural organic dyes including silyl-anchor dyes, which would bring a further improvement to DSSCs in their photovoltaic performance, are considered as a promising way to produce practical DSSCs.

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Notes and references

1 M. D. McGehee, *Science*, 2011, **334**, 607.
2 M. Grätzel, *Acc. Chem. Res.*, 2009, **42**, 1788.
3 A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, **110**, 6595.
4 K. Kalyanasundaram, ed., *DYE-SENSITIZED SOLAR CELLS*, EPFL Press, Lausanne, 2010.
5 M. A. Green, K. Emery, Y. Hishikawa, W. Warta and E. D. Dunlop, *Prog. Photovolt: Res. Appl.*, 2015, **23**, 805.
6 M. K. Nazeeruddin, F. D. Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, B. Takeru and M. Grätzel, *J. Am. Chem. Soc.*, 2005, **127**, 16835.
7 A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W.-G. Diau, C.-Y. Yeh, S. M. Zakeeruddin and M. Grätzel, *Science*, 2011, **334**, 629.
8 S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, B. F. E. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin and M. Grätzel, *Nat. Chem.*, 2014, **6**, 242.
9 M. Zhang, Y. Wang, M. Xu, W. Ma, R. Li and P. Wang, *Energy Environ. Sci.*, 2013, **6**, 2944.
10 K. Kakiage, M. Yamamura, E. Fujimura, T. Kyomen, M. Unno and M. Hanaya, *Chem. Lett.*, 2010, **39**, 260.
11 K. Kakiage, T. Tokutome, S. Iwamoto, T. Kyomen and M. Hanaya, *Chem. Commun.*, 2013, **49**, 179.
12 S. K. Matta, K. Kakiage, S. Makuta, A. Veamatahau, Y. Aoyama, T. Yano, M. Hanaya and Y. Tachibana, *J. Phys. Chem. C*, 2014, **118**, 28425.
13 K. Kakiage, Y. Aoyama, T. Yano, T. Otsuka, T. Kyomen, M. Unno and M. Hanaya, *Chem. Commun.*, 2014, **50**, 6379.
14 K. Kakiage, Y. Aoyama, T. Yano, K. Oya, T. Kyomen and M. Hanaya, *Chem. Commun.*, 2015, **51**, 6315.
15 H. Ellis, S. K. Eriksson, S. M. Feldt, E. Gabrielsson, P. W. Lohse, R. Lindblad, L. Sun, H. Rensmo, G. Boschloo and A. Hagfeldt, *J. Phys. Chem. C*, 2013, **117**, 21029.
16 H. Tian and L. Sun, *J. Mater. Chem.*, 2011, **21**, 10592.
17 S. M. Feldt, P. W. Lohse, F. Kessler, M. K. Nazeeruddin, M. Grätzel, G. Boschloo and A. Hagfeldt, *Phys. Chem. Chem. Phys.*, 2013, **15**, 7087.
18 M. Liang and *J. Chen, Chem. Soc. Rev.*, 2013, **42**, 3453.
19 S. M. Feldt, G. Wang, G. Boschloo and A. Hagfeldt, *J. Phys. Chem. C*, 2011, **115**, 21500.
20 P. Salvatori, G. Marotta, A. Cinti, E. Mosconi, M. Panigrahi, Giribabu, M. K. Nazeeruddin and F. D. Angelis, *Inorg. Chim Acta*, 2013, **406**, 106.
21 T. M. Koh, H. Li, K. Nonomura, N. Mathews, A. Hagfeldt, M. Grätzel, S. G. Mhaisalkar and A. C. Grimsdale, *Chem. Commun.*, 2013, **49**, 9101.
22 L. Kavan, J.-H. Yum and M. Grätzel, *Nano Lett.*, 2011, **11**, 5501.
23 J. Yang, P. Ganesan, J. Teuscher, T. Moehl, Y. J. Kim, C. Yi, P. Comte, K. Pei, T. W. Holcombe, M. K. Nazeeruddin, J. Hua, S. M. Zakeeruddin, H. Tian and M. Grätzel, *J. Am. Chem. Soc.*, 2014, **136**, 5722.