Photovoltaic Devices

International Edition: DOI: 10.1002/anie.201502951
German Edition: DOI: 10.1002/ange.201502951

Tropolone as a High-Performance Robust Anchoring Group for Dye-Sensitized Solar Cells**

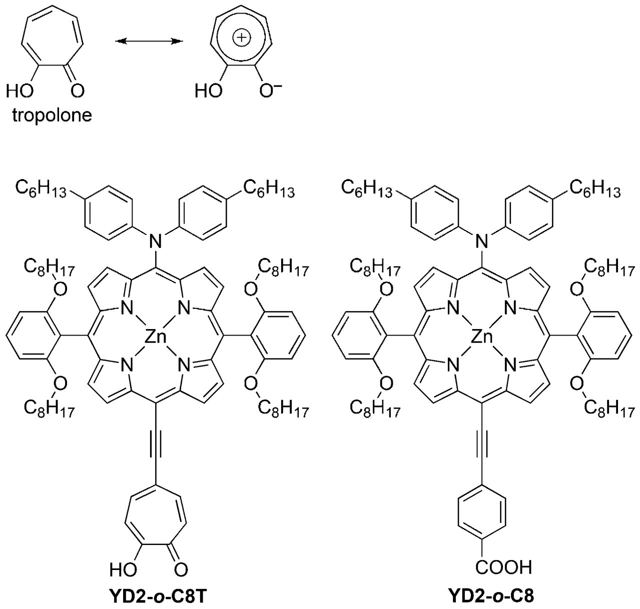
*Tomohiro Higashino, Yamato Fujimori, Kenichi Sugiura, Yukihiro Tsuji, Seigo Ito, and Hiroshi Imahori**

Abstract: *A tropolone group has been employed for the first time as an anchoring group for dye-sensitized solar cells (DSSCs). The DSSC based on a porphyrin,* ***YD2-o-C8T,*** *with a tropolone moiety exhibited a power-conversion efficiency of 7.7%, which is only slightly lower than that observed for a reference porphyrin,* ***YD2-o-C8****, with a conventional carboxylic group. More importantly,* ***YD2-o-C8T*** *was found to be superior to* ***YD2-o-C8*** *with respect to DSSC durability and binding ability to* TiO_2*. These results unambiguously demonstrate that tropolone is a highly promising dye-anchoring group for DSSCs in terms of device durability as well as photovoltaic performance.*

In recent years, increasing energy consumption and concern about environmental issues have led to a strong demand for the utilization of sunlight as an alternative, clean, and infinite energy source. Photovoltaic devices for the direct conversion of solar energy into electricity are viewed as promising technologies. Since pioneering studies reported by O'Regan and Grätzel in 1991,[1] dye-sensitized solar cells (DSSCs) have attracted a great deal of attention as an alternative to silicon-based solar cells owing to their low-cost production and high power-conversion efficiency (η). Various organometallic/organic dyes have been explored for their application to DSSCs.[2–5] For example, porphyrins are regarded as promising candidates because of their intense absorption in the visible and near-infrared (NIR) regions and versatile molecular design.[4] Indeed, push–pull-type porphyrin sensitizers have displayed excellent light-harvesting ability and demonstrated high η values of more than 10% in DSSCs.[5]

Until now, carboxylic acids, such as benzoic acid and cyanoacrylic acid groups, have been the most widely used groups in DSSCs for the anchoring of dyes to a TiO_2 surface. However, carboxylic acids are prone to dissociate from the TiO_2 surface during device operation. In terms of the durability of DSSCs for practical application, such detachment of the adsorbed dye from the TiO_2 is undesirable.[6] For this reason, the identification of novel anchoring groups with a greater ability to bind to the TiO_2 surface than that of conventional carboxylic acids is pivotal to the development of improved DSSCs of this type. He and co-workers found that 8-hydroxyquinoline (HOQ) is an attractive candidate for replacement of the benzoic acid group.[7] Although the η value of a DSSC based on a HOQ-modified porphyrin was moderate, the dye displayed higher stability on TiO_2 than that of its analogue with benzoic acid as the anchoring group.

Tropolones are well-known compounds that can be synthesized readily and form stable complexes with various metal ions.[8] A resonance structure, the aromatic tropylium ion, contributes to the electronic structure of tropolones (Scheme 1). In this respect, tropolones can act as an electron-withdrawing motif in π systems. Reports based on the use of tropolones as the key motif of functional molecules are still limited, whereas metal complexes of tropolones have been employed as building blocks for supramolecular coordination complexes[9] and stable liquid crystals.[10] For example, Shio-



Scheme 1. Resonance structure of tropolone and molecular structures of the porphyrins used in this study.

---

[*] Dr. T. Higashino, Y. Fujimori, K. Sugiura, Y. Tsuji,
Prof. Dr. H. Imahori
Department of Molecular Engineering
Graduate School of Engineering, Kyoto University
Nishikyo-ku, Kyoto, 615-8510 (Japan)
E-mail: imahori@scl.kyoto-u.ac.jp
Prof. Dr. S. Ito
Graduate School of Engineering, University of Hyogo
2167 Shosha, Himeji, Hyogo, 671-2280 (Japan)
Prof. Dr. H. Imahori
Institute for Integrated Cell-Material Sciences (WPI-iCeMS)
Kyoto University
Nishikyo-ku, Kyoto, 615-8510 (Japan)

[**] This research was supported by the Advanced Low Carbon Technology Research and Development Program (ALCA) of JST and a Grant-in-Aid (No.25220801 to H.I.) from MEXT (Japan).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201502951.

noya and co-workers used tropolone as a bidentate ligand to construct the stable high-order structure of multinuclear complexes.[9a] They revealed that tropolone–titanium(IV) complexes were more stable than HOQ–Ti^{IV} complexes. Thus, we envisioned that the tropolone moiety would be suitable for the robust anchoring of dyes to TiO_2. Herein, we report the use of tropolone as a dye-anchoring group for DSSCs. The representative porphyrin sensitizer **YD2-*o*-C8** was chosen as a reference,[5b] and the benzoic acid group was replaced with a tropolone moiety to yield **YD2-*o*-C8T** (Scheme 1).

The synthetic route to **YD2-*o*-C8T** is illustrated in Scheme 2. The reference porphyrin **YD2-*o*-C8** and porphyrin precursor **1** were synthesized by previously reported methods.[5b] Deprotection of **1** with tetrabutylammonium fluoride (TBAF) and subsequent Sonogashira coupling with 5-iodo-2-methoxytropone[11] provided tropolone ether **2** in 90 % yield. The reaction of **2** with potassium hydroxide furnished **YD2-*o*-C8T** in satisfactory yield (42 %). **YD2-*o*-C8T** was purified by repeated reprecipitation from CH_2Cl_2/acetonitrile owing to its lack of suitability for column chromatography as a result of severe adsorption of the tropolone moiety to silica gel (see Figures S1–S3 in the Supporting Information for details of the synthesis and characterization).

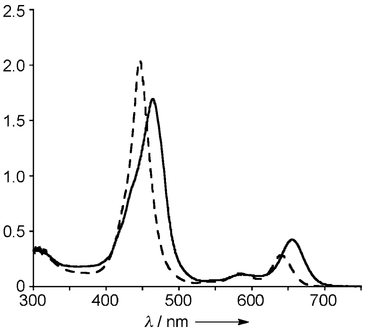
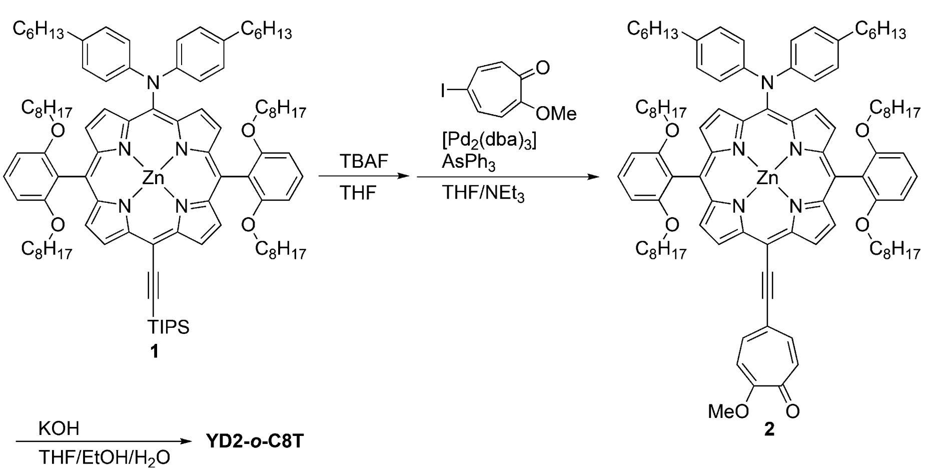


Figure 1. UV/Vis absorption spectra of **YD2-*o*-C8T** (solid line) and **YD2-*o*-C8** (dashed line) in THF.



Scheme 2. Synthesis of **YD2-*o*-C8T**. dba = dibenzylideneacetone, TIPS = triisopropylsilyl.

The Soret and Q bands in the UV/Vis absorption spectrum of **YD2-*o*-C8T** are shifted toward longer wavelengths than those of **YD2-*o*-C8** (Figure 1), thus demonstrating the higher light-harvesting ability of **YD2-*o*-C8T** as compared to that of **YD2-*o*-C8** in the visible region as a result of the enhanced push–pull character. Steady-state fluorescence spectra were also measured in THF (see Figure S4). From the intersection of the normalized absorption and fluorescence spectra, the zero–zero excitation energy (E_{0-0}) was calculated to be 1.86 eV for **YD2-*o*-C8T** and 1.89 eV for **YD2-*o*-C8**.

The electrochemical properties of the porphyrin dyes were studied by differential pulse voltammetry (DPV) in THF versus NHE with tetrabutylammonium hexafluorophosphate as the electrolyte (Table 1; see also Figure S5). The first oxidation potential (E_{ox}) of **YD2-*o*-C8T** (0.79 V) is almost the same as that of **YD2-*o*-C8** (0.81 V), whereas the first reduction potential (E_{red}) of **YD2-*o*-C8T** (−1.14 V) is shifted in the positive direction by 0.12 V with respect to that of **YD2-*o*-C8** (−1.26 V). This result supports the higher electron-withdrawing ability of tropolone as compared to that of benzoic acid. The electrochemical HOMO–LUMO gap of **YD2-*o*-C8T** (1.93 V) is smaller than that of **YD2-*o*-C8** (2.07 V), in agreement with the trend in the optical HOMO–LUMO gaps (Table 1). From the spectroscopic and electrochemical measurements, we calculated the driving forces for electron injection (ΔG_{inj}) from the porphyrin excited singlet state into the conduction band (CB) of TiO_2 (−0.5 V vs. NHE)[5c] and for reduction of the porphyrin radical cation (ΔG_{reg}) by the I^-/I_3^- redox couple (+ 0.4 V vs. NHE).[5c] Since these driving forces are more negative than −0.3 eV, the electron injection and dye-regeneration processes are exergonic, and the driving forces are sufficient for efficient electron transfer.

Table 1: Electrochemical properties of **YD2-*o*-C8T** and **YD2-*o*-C8**.

Dye	E_{ox}[a] [V]	E_{red}[a] [V]	E_{0-0}[b] [eV]	E^*_{ox}[c] [V]	ΔG_{inj}[d] [eV]	ΔG_{reg}[e] [eV]
YD2-*o*-C8T	0.79	−1.14	1.86	−1.07	−0.57	−0.39
YD2-*o*-C8	0.81	−1.26	1.89	−1.08	−0.58	−0.41

[a] First oxidation and reduction potentials (versus the normal hydrogen electrode, NHE). [b] The E_{0-0} value was determined from the intersection of the normalized absorption and emission spectra. [c] The E^*_{ox} value was determined by adding the E_{0-0} value to the E_{ox} value (vs. NHE). [d] Driving force for electron injection from the porphyrin excited singlet state into the CB of TiO_2 (−0.5 V vs. NHE). [e] Driving force for dye regeneration by the I^-/I_3^- redox shuttle (+ 0.4 V vs. NHE).

To obtain insight into the ground-state geometry and electronic structures of the frontier orbitals of the porphyrins, we performed DFT calculations on the model porphyrins at the B3LYP/6-31G(d) level (see Figure S6).[12] Both porphyrins displayed similar electron densities in the HOMO and LUMO as well as the ground-state geometry. The calculated HOMO–LUMO gaps of **YD2-*o*-C8T** and **YD2-*o*-C8** were determined to be 2.23 and 2.32 eV, respectively, which parallel the optical and electrochemical HOMO–LUMO gaps. The electron-density distribution on the oxygen atoms of the tropolone moiety in the LUMO of **YD2-*o*-C8T** is 2.8 %, which is even higher than that of the carboxyphenyl moiety in the LUMO of **YD2-*o*-C8** (2.3 %). Thus, the tropolone moiety ensures efficient electron injection and robust binding to TiO_2.

We examined the adsorption properties of the tropolone moiety on TiO_2 (see Figure S7). A TiO_2 film was immersed in a 4:1 mixture of ethanol and toluene with the porphyrin (0.2 mM) to give a porphyrin-stained TiO_2 film. The porphyrin surface coverage (Γ) on the TiO_2 film was determined by measuring the absorbance of the porphyrin after it had been dissolved from the porphyrin-stained TiO_2 film into an alkaline 1:1 mixture of THF and H_2O. During immersion, the two porphyrins showed almost identical adsorption profiles as a function of immersion time, and a constant Γ value on TiO_2 was reached in 3 h. The saturation Γ values of 8.3×10^{-11} mol cm^{-2} for **YD2-*o*-C8T** and 8.5×10^{-11} mol cm^{-2} for **YD2-*o*-C8** are virtually the same. Taking into account the comparable saturation Γ values together with the dye sizes, we concluded that both porphyrins form well-packed monolayers on TiO_2.

The FTIR spectrum of **YD2-*o*-C8T** for the solid sample showed characteristic peaks at 1585 cm^{-1} arising from ν(C=O) and around 1250 cm^{-1} arising from ν(O−H) and ν(C−O) (see Figure S8).[13] After adsorption on TiO_2, the spectrum showed broadening of the peaks, as observed for tropolone–metal bidentate complexes.[8] To gain further information on the binding mode, we conducted X-ray photoelectron spectroscopy (XPS) measurements for TiO_2 stained with **YD2-*o*-C8T** as well as reference compounds (see Figures S9–S11). The O1s photoelectron spectrum exhibited three oxygen peaks. The peak observed at 529.9 eV originates from oxygen atoms of the TiO_2 surface. The remaining peaks at 532.8 and 531.5 eV are ascribed to four oxygen atoms of the octyloxy moiety and two oxygen atoms of the tropolone moiety attached to the TiO_2 surface, respectively. From these XPS measurements, combined with the FTIR spectra, we assigned the binding mode of **YD2-*o*-C8T** on TiO_2 as symmetrical bidentate coordination.

We then measured the photovoltaic properties of the porphyrin DSSCs under standard AM 1.5 conditions by using an electrolyte solution containing an I^-/I_3^- redox shuttle. To optimize the cell performance, we first examined the effect of immersion time (see Figure S12). DSSCs based on **YD2-*o*-C8T** and **YD2-*o*-C8** displayed optimized η values of 5.3 and 7.9 % in immersion times of 3 and 4 h, respectively. By fixing the respective immersion time, we also sensitized each porphyrin at various concentrations of chenodeoxycholic acid (CDCA), a coadsorbent for the suppression of dye aggregation (see Figure S13). However, the η values decreased upon the addition of CDCA, thus suggesting that the four octyloxy groups around the porphyrin core sufficiently inhibit dye aggregation. The DSSCs were further kept under dark conditions to improve the cell performance. All DSSCs attained the highest η values after aging for several days (see Figure S14).[5c,14] The photocurrent–voltage characteristics of the DSSCs based on **YD2-*o*-C8T** and **YD2-*o*-C8** under the optimized conditions are depicted in Figure 2. The IPCE spectrum of the DSSC based on **YD2-*o*-C8T** exhibited photocurrent generation up to 800 nm, thus reflecting its higher light-harvesting ability than that of **YD2-*o*-C8**. Detailed photovoltaic parameters are listed in Table 2. The maximal DSSC performance of **YD2-*o*-C8T** ($\eta = 7.7$ %) is slightly lower than that of **YD2-*o*-C8** ($\eta = 8.8$ %). Notably, **YD2-*o*-C8T** showed the highest η value among porphyrin DSSCs with anchoring groups other than a carboxylic acid.[7,15]

We applied electrical impedance spectroscopy (EIS) to rationalize the difference in the open-circuit voltage (V_{OC}) of

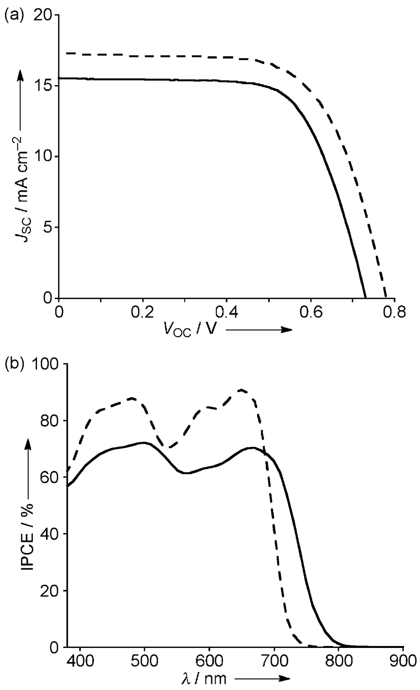


Figure 2. a) Photocurrent–voltage characteristics and b) photocurrent action spectra of the DSSCs based on **YD2-*o*-C8T** (solid line) and **YD2-*o*-C8** (dashed line). IPCE = incident-photon-to-current efficiency.

Table 2: Photovoltaic performance of DSSCs based on **YD2-*o*-C8T** and **YD2-*o*-C8**.[a]

Dye	J_{SC} [mA cm^{-2}]	V_{OC} [V]	Fill factor	η [%]
YD2-*o*-C8T	15.6 (15.6 ± 0.1)	0.73 (0.71 ± 0.02)	0.68 (0.69 ± 0.01)	7.7 (7.6 ± 0.1)
YD2-*o*-C8	17.3 (17.4 ± 0.1)	0.78 (0.77 ± 0.01)	0.65 (0.65 ± 0.02)	8.8 (8.7 ± 0.1)

[a] Values given are the photovoltaic parameters for which the highest η value was observed. The average value from five independent experiments is shown in parenthesis in each case.

the DSSCs based on the two porphyrin dyes. EIS Nyquist plots were obtained under standard AM 1.5 illumination and open-circuit conditions (see Figure S15). The electron-transfer process at the TiO_2–dye–electrolyte interface is represented by R_p. A small R_p value implies a small charge-recombination resistance between TiO_2 and the electrolyte. The R_p value of the DSSC based on **YD2-*o*-C8T** (22.0 Ω) was smaller than that of the DSSC based on **YD2-*o*-C8** (28.7 Ω), which is consistent with the slightly lower V_{OC} value found for **YD2-*o*-C8T**.

Finally, we investigated the long-term durability of DSSCs based on **YD2-*o*-C8T** and **YD2-*o*-C8**. The porphyrin-stained TiO_2 films were immersed in a 1:1 mixture of THF and H_2O with acetic acid (28 mM) or NaOH (1 mM). The amount of the dye on TiO_2 was then determined as a function of immersion time from the absorbance of the TiO_2 film (Figure 3a). Although **YD2-*o*-C8** completely dissociated from the TiO_2 surface within 1 h under both acidic and basic conditions, more than 95% of **YD2-*o*-C8T** was retained in 8 h. This result unambiguously corroborates the superior robustness of tropolone as an anchoring group as compared to benzoic acid. Furthermore, the long-term durability of the DSSCs based on **YD2-*o*-C8T** and **YD2-*o*-C8** were assessed under continuous white-light illumination (100 mW cm^{-2} at 25 °C; Figure 3b). The **YD2-*o*-C8T** and **YD2-*o*-C8** cells showed a 13 and 33% decrease in efficiency in 500 h, which strongly indicates the advantage of the tropolone anchoring group in terms of the long-term durability of DSSCs. To the best of our knowledge, no quantitative comparison of the long-term durability of DSSCs has been made previously in terms of the use of different anchoring groups.

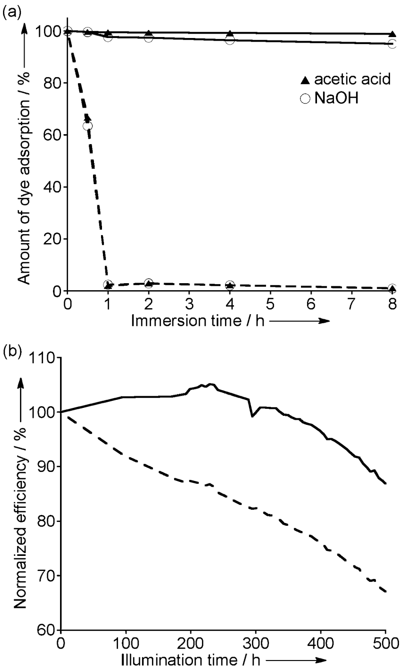


Figure 3. a) Plots of the amount of porphyrin on the TiO_2 surface as a function of immersion time for **YD2-*o*-C8T** (solid lines) and **YD2-*o*-C8** (dashed line) and b) plots of the normalized η value (average of two independent experiments) as a function of illumination time for DSSCs based on **YD2-*o*-C8T** (solid line) and **YD2-*o*-C8** (dashed line).

In summary, we have employed tropolone for the first time as an anchoring group for DSSCs. A DSSC based on **YD2-*o*-C8T** with a tropolone group exhibited a power-conversion efficiency of 7.7%, which is comparable to that of a DSSC based on **YD2-*o*-C8** with benzoic acid as the anchoring group. More importantly, **YD2-*o*-C8T** was found to be superior to **YD2-*o*-C8** in terms of both DSSC durability and binding ability to TiO_2. We believe that the tropolone could be used with any kind of dye for DSSCs to ensure high device durability as well as excellent photovoltaic performance.

Keywords: anchoring groups · light harvesting · porphyrinoids · sensitizers · solar cells

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 9052–9056
Angew. Chem. **2015**, *127*, 9180–9184

[1] B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737–740.

[2] a) M. K. Nazeeruddin, F. De Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, T. Bessho, M. Grätzel, *J. Am. Chem. Soc.* **2005**, *127*, 16835–16847; b) F. Gao, Y. Wang, D. Shi, J. Zhang, M. Wang, X. Jing, R. Humphry-Baker, P. Wang, S. M. Zakeeruddin, M. Grätzel, *J. Am. Chem. Soc.* **2008**, *130*, 10720–10728; c) C. Chen, M. Wang, J. Li, N. Pootrakulchote, L. Alibabaei, C.-h. Ngoc-le, J. Decoppet, J. Tsai, C. Grätzel, C. Wu, S. M. Zakeeruddin, M. Grätzel, *ACS Nano* **2009**, *3*, 3103–3109; d) L. Han, A. Islam, H. Chen, C. Malapaka, B. Chiranjeevi, S. Zhang, X. Yang, M. Yanagida, *Energy Environ. Sci.* **2012**, *5*, 6057–6060.

[3] a) Y. Ooyama, Y. Harima, *Eur. J. Org. Chem.* **2009**, 2903–2934; b) A. Mishra, M. K. R. Fischer, P. Bäuerle, *Angew. Chem. Int. Ed.* **2009**, *48*, 2474–2499; *Angew. Chem.* **2009**, *121*, 2510–2536; c) W. Zeng, Y. Cao, Y. Bai, Y. Wang, Y. Shi, M. Zhang, F. Wang, C. Pan, P. Wang, *Chem. Mater.* **2010**, *22*, 1915–1925; d) M. Zhang, Y. Wang, M. Xu, W. Ma, R. Li, P. Wang, *Energy Environ. Sci.* **2013**, *6*, 2944–2949; e) K. Kakiage, Y. Aoyama, T. Yano, T. Otsuka, T. Kyomen, M. Unno, M. Hanaya, *Chem. Commun.* **2014**, *50*, 6379–6381.

[4] a) H. Imahori, T. Umeyama, S. Ito, *Acc. Chem. Res.* **2009**, *42*, 1809–1818; b) M. V. Martínez-Díaz, G. de La Torre, T. Torres, *Chem. Commun.* **2010**, *46*, 7090–7108; c) L.-L. Li, E. W.-G. Diau, *Chem. Soc. Rev.* **2013**, *42*, 291–304; d) M. Urbani, M. Grätzel, M. K. Nazeeruddin, T. Torres, *Chem. Rev.* **2014**, *114*, 12330–12396; e) K. Ladomenou, T. N. Kitsopoulos, G. D. Sharma, A. G. Coutsolelos, *RSC Adv.* **2014**, *4*, 21379–21404; f) T. Higashino, H. Imahori, *Dalton Trans.* **2015**, *44*, 448–463.

[5] a) T. Bessho, S. M. Zakeeruddin, C.-Y. Yeh, E. W.-G. Diau, M. Grätzel, *Angew. Chem. Int. Ed.* **2010**, *49*, 6646–6649; *Angew. Chem.* **2010**, *122*, 6796–6799; b) 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, M. Grätzel, *Science* **2011**, *334*, 629–634; c) K. Kurotobi, Y. Toude, K. Kawamoto, Y. Fujimori, S. Ito, P. Chabera, V. Sundström, H. Imahori, *Chem. Eur. J.* **2013**, *19*, 17075–17081; d) A. Yella, C.-L. Mai, S. M. Zakeeruddin, S.-N. Chang, C.-H. Hsieh, C.-Y. Yeh, M. Grätzel, *Angew. Chem. Int. Ed.* **2014**, *53*, 2973–2977; *Angew. Chem.* **2014**, *126*, 3017–3021; e) S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, B. F. E. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin, M. Grätzel, *Nat. Chem.* **2014**, *6*, 242–247; f) J. Luo, M. Xu, R. Li, K.-W. Huang, C. Jiang, Q. Qi, W. Zeng, J. Zhang, C. Chi, P. Wang, J. Wu, *J. Am. Chem. Soc.* **2014**, *136*, 265–272.

[6] M. I. Asghar, K. Miettunen, J. Halme, P. Vahermaa, M. Toivola, K. Aitola, P. Lund, *Energy Environ. Sci.* **2010**, *3*, 418–426.
[7] a) H. He, A. Gurung, L. Si, *Chem. Commun.* **2012**, *48*, 5910–5912; b) L. Si, H. He, K. Zhu, *New J. Chem.* **2014**, *38*, 1565–1572.
[8] a) T. Asao, Y. Kikuchi, *Chem. Lett.* **1972**, 413–416; b) M. C. Barret, M. F. Mahon, K. C. Molloy, J. W. Steed, P. Wright, *Inorg. Chem.* **2001**, *40*, 4384–4388; c) K. Nomiya, K. Onodera, K. Tsukagoshi, K. Shimada, A. Yoshizawa, T. A. Itoyanagi, A. Sugie, S. Tsuruta, R. Sato, N. C. Kasuga, *Inorg. Chim. Acta* **2009**, *362*, 43–55.
[9] a) Y. Sakata, S. Hiraoka, M. Shionoya, *Chem. Eur. J.* **2010**, *16*, 3318–3325; b) H. Otani, C. Sumi, H. Shimizu, M. Hasegawa, M. Iyoda, *Chem. Lett.* **2014**, *43*, 1710–1712.
[10] a) J. R. Chipperfield, S. Clark, J. Elliott, E. Sinn, *Chem. Commun.* **1998**, 195–196; b) J. M. Elliott, J. R. Chipperfield, S. Clark, S. J. Teat, E. Sinn, *Inorg. Chem.* **2002**, *41*, 293–299; c) A. Mori, R. Mori, M. Takemoto, S. Yamamoto, D. Kuribayashi, K. Uno, K. Kubo, S. Ujiie, *J. Mater. Chem.* **2005**, *15*, 3005–3014.
[11] J. Potenziano, R. Spitale, M. E. Janik, *Synth. Commun.* **2005**, *35*, 2005–2016.
[12] M. J. Frisch et al., Gaussian 09, revision D.01, Gaussian, Inc., Wallingford, CT, **2013**.
[13] a) H. P. Koch, *J. Chem. Soc.* **1951**, 512–515; b) Y. Ikegami, *Bull. Chem. Soc. Jpn.* **1961**, *34*, 94–98.
[14] a) K. Wagner, M. J. Griffith, M. James, A. J. Mozer, P. Wagner, G. Triani, D. L. Officer, G. G. Wallace, *J. Phys. Chem. C* **2011**, *115*, 317–326; b) M. J. Griffith, K. Sunahara, A. Furube, A. J. Mozer, D. L. Officer, P. Wagner, G. G. Wallace, S. Mori, *J. Phys. Chem. C* **2013**, *117*, 11885–11898.
[15] a) B. J. Brennan, M. J. Llansola Portolés, P. A. Liddell, T. A. Moore, A. L. Moore, D. Gust, *Phys. Chem. Chem. Phys.* **2013**, *15*, 16605–16614; b) D. Daphnomili, G. D. Sharma, S. Biswas, K. R. Justin Thomas, A. G. Coutsolelos, *J. Photochem. Photobiol. A* **2013**, *253*, 88–96; c) F. Gou, X. Jiang, R. Fang, H. Jing, Z. Zhu, *ACS Appl. Mater. Interfaces* **2014**, *6*, 6697–6703.

Received: March 31, 2015