Organic LETTERS

Letter

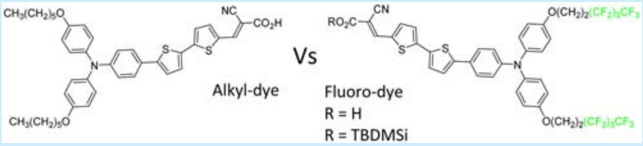
pubs.acs.org/OrgLett

Chemically Altering the Solubility and Durability of Dyes for Sensitized Solar Cells

Subashani Maniam,[†] Andrew B. Holmes,[†,‡] Gary A. Leeke,[§] Ante Bilic,[‖] and Gavin E. Collis*[,†]

[†]CSIRO Manufacturing Flagship, Advanced Fibers and Industrial Chemicals, Clayton South 3169, Victoria Australia
[‡]School of Chemistry, Bio21 Institute, University of Melbourne, Melbourne 3010, Victoria Australia
[§]School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, U.K.
[‖]CSIRO Manufacturing Flagship, Virtual Nanoscience, Parkville 3052, Victoria Australia

Supporting Information



ABSTRACT: By designing dyes with fluoroalkyl groups, the optical and electronic properties of the alkyl analogue were maintained while dramatically altering the solubility. Dyes, F-TABTA (**8**) and its masked derivative F-TABTSi (**9**), that enable them to be deposited under conventional organic solvent and $scCO_2$ conditions, respectively, were developed. In liquid DSSC devices, the fluoroalkyl dye (F-TABTA, **8**) performs slightly better than its alkyl analogue (D21L6, **10**), and interestingly, it was found that the former device showed better stability over time. Deploying the silyl-masked precursor F-TABTSi (**9**), this dye was deposited onto TiO_2 photoanodes from $scCO_2$ in very short contact times (2.5 h), and ECEs of 7.70% were obtained that exceed the performance of the alkyl dye when deposited by conventional methods.

The use of computational modeling to direct synthetic chemistry has resulted in "designed" semiconductor materials with specific chemical, optical, and electronic properties for use in organic electronics.[1−5] The emergence of new dyes for DSSC applications has made significant progress over the past decade because of the development and use of key design rules.[6,7] Chemists have used aromatic and heteroaromatic semiconducting building blocks to access dyes with desirable optoelectronic features, used functional groups that have electron-withdrawing or -donating properties to fine tune the HOMO and LUMO energy levels of the dye to align with the energy levels of the photoanode and electrolyte, and used the positioning of substituents around the dye structure (i.e., linear and branched alkyl groups, polyether groups etc.) to assist the charge-transfer processes at the metal oxide/dye/electrolyte interfaces.[6,8−13] However, less activity has focused around understanding the impact that physical properties (e.g., dye solubility, dye adsorption/deadsorption, molecular assembly, etc.) may have on device performance and stability.[12,14−19]

We have been interested in the use of fluoroalkyl groups to modify the solubility and the electronic interaction between the dye soaking solvent and electrolyte/dye interface, respectively. Unlike the alkyl and polyether groups that are commonly used in DSSC dye design, fluorous materials,[20] which offer very unique electronic, chemical, and physical properties, have found very little application. As proof-of-concept, we showed that replacement of the alkyl substituents with fluoroalkyl groups enabled access to perylene diimide dyes that could be deposited from supercritical carbon dioxide ($scCO_2$) as the solvent.[19] Encouragingly, Fungo, Pozzi, and co-workers recently have shown that donor/acceptor dyes containing bulky fluoroalkoxy substituents have improved power conversion efficiencies when compared to analogous nonfluorous dyes.[21]

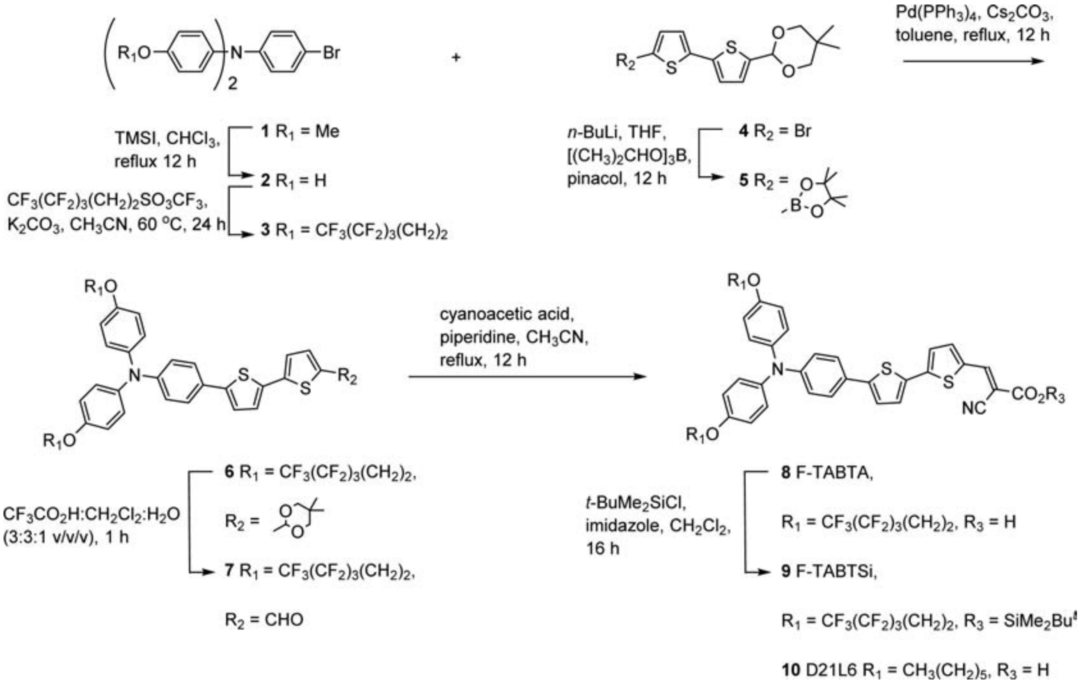
Here, we demonstrate how, by using fluoroalkyl groups, the solubility of an oligothiophene dye can be easily modified to have dual function, whereby it can be deposited under conventional dye soaking solvent protocols or from $scCO_2$. Comparison of the computational modeling and experimental data indicate that the fluoroalkyl-dye, F-TABTA (**8**), and the alkyl-analogue, D21L6 (**10**), show little difference in their electronic and optical properties but dramatically differ in solubility. The DSSC performance of dyes D21L6 (**10**) and F-TABTA (**8**) deposited by conventional solvent methods show that the fluorinated dye produces marginally better energy conversion efficiencies (ECEs). Masking the carboxylic acid group of the fluorinated dye F-TABTA (**8**) as the labile silyl ester F-TABTSi (**9**) delivers a $scCO_2$-compatible dye precursor. DSSC devices fabricated using these precursors under a $scCO_2$ deposition process (14 MPa, 50 °C), which requires only a few hours, achieved ECEs as high as 7.70%. Most noticeable is the enhanced shelf life stability of the fluoroalkyl dye in a device when an organic redox electrolyte is used.

We chose to study three target compounds, F-TABTA (**8**), F-TABTSi (**9**), and D21L6 (**10**)[22] (Scheme 1). Initial DFT modeling of F-TABTA (**8**) indicates the incorporation of the fluorohexyl groups does not significantly alter the HOMO and LUMO levels compared to D21L6 (**10**) and therefore was a suitable target to study (see the Supporting Information, Table S1). A convergent synthetic strategy was developed to access F-

Received: July 5, 2015
Published: August 4, 2015

DOI: 10.1021/acs.orglett.5b01921
Org. Lett. 2015, 17, 4022−4025

Scheme 1. Synthesis of F-TABTA (**8**) and F-TABSi (**9**) Dyes and Structure of D21L6 (**10**)



TABTA (**8**) and F-TABTSi (**9**) (see Scheme 1 and the Supporting Information for full details). *N,N*-Bis(4′-methoxyphenyl)-4-bromoaniline (**1**) was demethylated to afford the bisphenolic compound **2**, which was subsequently alkylated with fluorohexyl methanesulfonate ester/K_2CO_3 to afford the fluorinated ether **3**. The boronate ester **5** was prepared by metal−halogen exchange with the bromo-substituted bithiophene **4** and trapping with trisisopropylborate, followed by transesterification with pinacol. The bithiophene pinacolatoboron **5** was coupled under Suzuki conditions[23] with the brominated triarylamine **3** to afford the product **6** in good yield. Following the biphasic conditions developed previously,[24] the dimethyl-1,3-dioxane acetal protecting group was removed to liberate the aldehyde **7**. Knoevenagel condensation of the aldehyde **7** with cyanoacetic acid and piperidine gave F-TABTA (**8**) in 60% yield. This material was further purified by reversed-phase HPLC and determined to be a mixture of *E*/*Z* isomers that could not be unambiguously assigned but consisted of major and minor isomers in 1:0.05 ratio. Attempts to isomerize the geometric isomers to one favorable form using light,[24] heat, or catalytic iodine in CH_2Cl_2[25] were surprisingly unsuccessful. The transformation of F-TABTA (**8**) into a *tert*-butyldimethylsilyl-masked group was undertaken using a known literature protocol. F-TABTSi (**9**) was found to be easy to prepare, isolate, and use in $scCO_2$ studies, once again consisting of a mixture of *E*/*Z* isomers.

A comparison of the physical properties of the alkyl dye D21L6 (**10**) and fluorinated dyes **8** and **9** in conventional organic solvents and $scCO_2$ was performed. Qualitative solubility studies of these dyes were undertaken in common organic solvents and showed dramatic differences imparted by the fluoroalkyl groups. In acetonitrile, a common dye soaking and electrolyte solvent, D21L6 (**10**) was found to be moderately soluble, while F-TABTA (**8**) was sparingly soluble with the majority of the dye suspended on the surface of the liquid (Figure 1a). In hexane, a solvent commonly used to emulate the solubility of materials in $scCO_2$, the fluoroalkyl groups on F-TABTA (**8**) dye did not appreciably improve the solubility (Figure 1b); presumably, the properties of the dye are heavily dictated by the presence of the polar carboxylic acid functionality. However, the combination of the fluoroalkyl group and silyl-masked carboxylic acid resulted in a dramatic difference whereby dye precursor, F-TABTSi (**9**), was completely dissolved in hexane (Figure 1b). This dramatic variation in solubility between alkylated and fluoroalkyl-substituted systems is consistent with the general behavior of fluorinated compounds.[20] Previously, we have found quantitative solubility measurements of the dye in CO_2 using the Static Precise Mass Measuring method[19] to be extremely useful for getting an indication of how the dye will behave in the $scCO_2$ deposition process (see the Supporting Information for details). The masked fluoroalkyl dye F-TABTSi (**9**) was measured to have a high solubility value of 156 mg/kg (14 MPa and 50 °C) reflecting its solubility in hexane. However, solubility values for D21L6 (**10**) and F-TABTA (**8**) could not be determined as both showed no recordable values; this was attributed to the presence of the polar carboxylic acid group.

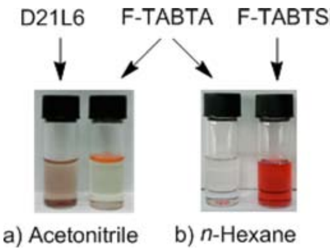


Figure 1. Qualitative indication of solubility of (a) D21L6 (**10**) and F-TABTA (**8**) in acetonitrile and (b) F-TABTA)**8** and F-TABTSi (**9**) in *n*-hexane.

The electronic properties of D21L6 (**10**) and F-TABTA (**8**) were compared by spectroscopic and electrochemical methods. Owing to the limited solubility of the fluorinated dye in acetonitrile, we found a mixture of ethanol/chloroform (1:1 v/

v) to be more suitable for spectroscopic studies and as the dye-soaking solvent system (see later). As expected, the UV−vis absorption spectra for D21L6 (**10**) and F-TABTA (**8**) are very similar. The introduction of the fluoroalkyl group results in a small blue shift of the band from 460 nm (D21L6 (**10**)) to 452 nm (F-TABTA (**8**)) (see the Supporting Information, Figure S1). We attribute this single absorption band to the intramolecular charge transfer from the donor moiety to the acceptor functionality found in both dyes. Furthermore, the molar absorption coefficients of the fluoroalkyl dye F-TABTA (**8**) (ε = 36925 M^{-1} cm^{-1}) increases slightly over D21L6 (**10**) (ε = 35225 M^{-1} cm^{-1}). Encouragingly, the UV−vis spectra of the D21L6 (**10**) and F-TABTA (**8**) adsorbed onto the transparent TiO_2 films (see the Supporting Information, Figure S2), gave very similar UV/vis spectra intensity and absorption maxima to those observed in solution.

Cyclic voltammetry (CV) of D21L6 (**10**) and F-TABTA (**8**) was performed in DMF (0.1 M tetrabutylammonium hexafluorophosphate) with a scan rate of 100 mV/s and internally calibrated with ferrocene/ferrocenium (Fc/Fc^+) (see the Supporting Information, Table S2). The HOMO of D21L6 (**10**) and F-TABTA (**8**) are −5.06 and −5.10 eV, while the LUMO are −3.46 and −3.48 eV, respectively. The experimental data show less deviation from the computational calculations, which suggests that the presence of ethylene spacers on the fluorohexyl groups minimizes the electronic interaction with the conjugated dye core.

D21L6 (**10**) and F-TABTA (**8**) were initially evaluated by the conventional solvent soaking process and tested in liquid electrolyte DSSCs (Table 1). We employed a commercially available TiO_2 photoanode fabricated with tetrapropylammonium iodide (0.5 M), iodine (0.05 M), LiI (0.1 M), and 4-*tert*-butylpyridine (0.5 M) in acetonitrile as the electrolyte. We identified that a mixture of ethanol and chloroform (1:1 v/v), over a period of 15 h, was a suitable solvent system for both D21L6 (**10**) and F-TABTA (**8**). The current−voltage (*J*−*V*) characteristics constructed from this photoanode−electrolyte system are summarized in Table 1. D21L6 (**10**) gave an overall ECE of 4.31%, while F-TABTA (**8**) showed a slight improvement over D21L6 (**10**) with an ECE of 4.40%, and the fill factors (FF) for both devices were comparable.

Table 1. Cell Performance of D21L6 (10) and F-TABTA (8) Sensitizers Deposited from Conventional Organic Solvent, Ethanol/Chloroform (1:1 v/v)

dye	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	ECE (%)
D21L6	11.47	660	0.57	4.31 ± 0.01
F-TABTA	12.28	643	0.55	4.40 ± 0.01

With these fabricated devices, we examined the changes in ECEs over time (shelf life) by storing them in the dark at room temperature. Interestingly, devices fabricated using F-TABTA (**8**) showed better long-term durability than those made with D21L6 (**10**) using this electrolyte (Figure 2). Although it has been previously reported that D21L6 (**10**) is extremely photostable over 1000 h at 1 sun[22] with an ionic liquid electrolyte, we suggest that the higher stability observed with F-TABTA (**8**) under these electrolyte solvent conditions can be attributed to the fluoroalkyl groups, which make the dye less soluble in the acetonitrile electrolyte as shown previously in Figure 1a, and thus unlikely to desorb from the TiO_2 surface. Another plausible reason for the increased durability is that fluorinated self-assembled monolayers are well-known to be hydrophobic,[26] and recent device/dye degradation studies[27] have shown that residual water in organic solvent based DSSCs can lead to hydrolysis of the cyanoacrylic acid dye from the TiO_2/dye interface.

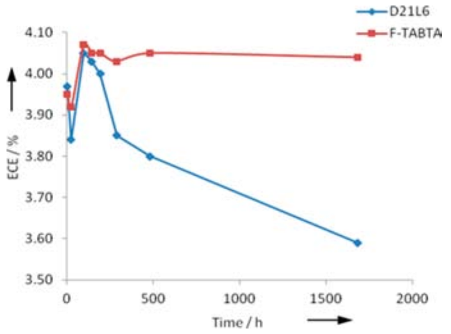


Figure 2. Stability of D21L6 (**10**) and F-TABTA (**8**) in acetonitrile-based electrolyte measure at AM 1.5, 100 mW cm^{-2} at defined time intervals and without the use of an UV filter.

With these promising results, we directed our initial efforts toward $scCO_2$ dye deposition on commercial TiO_2 photoanodes. DSSCs fabricated using the $scCO_2$ method with either D21L6 (**10**) and F-TABTA (**8**) were extremely poor, as expected, because of their extremely low solubility. However, the silyl-masked fluorohexyl dye F-TABTSi (**9**) produced very good photovoltaic responses with an ECE of 4.39 ± 0.01%, V_{oc} = 682 mV, J_{sc} = 10.96 mA/cm^2, and a FF = 0.58. Not only do these results compare well with data for the dyes deposited from conventional organic solvents (Table 1), but the $scCO_2$ method required a 80% shorter dye deposition time (3 h, 14 MPa and 50 °C) compared with the conventional solvent method (15 h). Under the cell configuration employed here, the incident photon-to-current conversion efficiency (IPCE) from the dye precursor F-TABTSi (**9**) using the $scCO_2$ method and of F-TABTA (**8**) from the conventional method are similar over 400−700 nm with a high plateau value above 60% (see the Supporting Information, Figure S3).

Having established that the silyl masked fluorohexyl dye F-TABTSi (**9**) is compatible with $scCO_2$ conditions we explored how photoanode thickness might impact DSSC performance. A multilayer photoanode with 20 and 400 nm particle layers (7 + 5 μm thickness) with $TiCl_4$ treatment was used. In our hands using the conventional solvent soaking method, D21L6 (**10**) and F-TABTA (**8**) were deposited over 15 h and produced ECEs of 7.02 and 7.12%, respectively (see the Supporting Information, Table S3). Using our $scCO_2$ protocols,[19] F-TABTSi (**9**) gave a significantly improved ECE of 7.70%. The improvement in performance is mainly attributed to a higher V_{oc} and FF (Figure 3). This improvement in ECE using the $scCO_2$ method may be associated with the ease by which the dye coated fluid can penetrate the mesoporous TiO_2 achieving better dye coverage.[19]

In summary, the use of fluoroalkyl substituents to decorate dyes for DSSCs offers access to materials with different solubility properties. We are able to use the unique physical features of F-TABTA (**8**) to deposit the dye onto TiO_2 photoanodes using conventional organic solvents (ethanol/chloroform) or $scCO_2$. The fluorinated dye performs slightly better than the alkyl derivative D21L6 when using the conventional dye solvent process. Even higher efficiencies (7.70%) and shorter contact times can be achieved with the

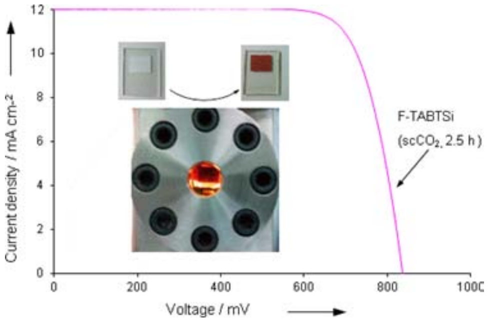


Figure 3. I/V curve of F-TABTSi (**9**) deposition in $scCO_2$ (14 MPa, 50 °C) using a multilayer photoanode architecture. The inserted images show an uncoated and dye-coated TiO_2 photoanode and $scCO_2$ reactor with a view of the photoanode through the sapphire window.

$scCO_2$ process when compared with the alkyl analogue and conventional organic dye soaking. A highly significant benefit of the fluoroalkyl group is the enhanced dye durability in the DSSC device. The use of fluoroalkyl groups may be beneficial in the design of dyes in conventional and next generation redox mediator DSSCs.[28,29]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01921.

> Computational calculations, experimental procedures, NMR data, CO_2 solubilities data, electrochemical data, and DSSC device fabrication methods (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: gavin.collis@csiro.au.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was funded by the CSIRO Future Manufacturing Flagship (Post-doctoral Fellowship for S.M.), CSIRO Fellow-Office of Chief Executive (OCE) Science Team (G.E.C., A.B., and A.B.H.). We thank Mr. Muhammad Kashif and Dr. Udo Bach (Department of Materials Engineering, Monash University) for use of the screen-printing equipment and helpful discussions.

■ REFERENCES

(1) Takimiya, K.; Osaka, I.; Nakano, M. *Chem. Mater.* **2014**, *26*, 587−593.

(2) Hachmann, J.; Olivares-Amaya, R.; Jinich, A.; Appleton, A. L.; Blood-Forsythe, M. A.; Seress, L. R.; Román-Salgado, C.; Trepte, K.; Atahan-Evrenk, S.; Er, S.; Shrestha, S.; Mondal, R.; Sokolov, A.; Bao, Z.; Aspuru-Guzik, A. *Energy Environ. Sci.* **2014**, *7*, 698−704.

(3) Shu, Y.; Mikosch, A.; Winzenberg, K. N.; Kemppinen, P.; Easton, C. D.; Bilic, A.; Forsyth, C. M.; Dunn, C. J.; Singh, T. B.; Collis, G. E. *J. Mater. Chem. C* **2014**, *2*, 3895−3899.

(4) Winzenberg, K. N.; Kemppinen, P.; Scholes, F. H.; Collis, G. E.; Shu, Y.; Singh, T. B.; Bilic, A.; Forsyth, C. M.; Watkins, S. E. *Chem. Commun.* **2013**, *49*, 6307−6309.

(5) Shu, Y.; Collis, G. E.; Dunn, C. J.; Kemppinen, P.; Winzenberg, K. N.; Williamson, R. M.; Bilic, A.; Singh, T. B.; Bown, M.; McNeill, C. R.; Thomsen, L. *J. Mater. Chem. C* **2013**, *1*, 6299−6307.

(6) Mishra, A.; Fischer, M. K. R.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2009**, *48*, 2474−2499.

(7) Kim, B.-G.; Chung, K.; Kim, J. *Chem. - Eur. J.* **2013**, *19*, 5220−5230.

(8) Snaith, H. J. *Adv. Funct. Mater.* **2010**, *20*, 13−19.

(9) Bazzan, G.; Deneault, J. R.; Kang, T.-S.; Taylor, B. E.; Durstock, M. F. *Adv. Funct. Mater.* **2011**, *21*, 3268−3274.

(10) Listorti, A.; O'Regan, B.; Durrant, J. R. *Chem. Mater.* **2011**, *23*, 3381−3399.

(11) Grätzel, M. *Acc. Chem. Res.* **2009**, *42*, 1788−1798.

(12) Zhang, L.; Cole, J. M. *ACS Appl. Mater. Interfaces* **2015**, *7*, 3427−3455.

(13) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. *Chem. Rev.* **2010**, *110*, 6595−6663.

(14) O'Regan, B.; Xiaoe, L.; Ghaddar, T. *Energy Environ. Sci.* **2012**, *5*, 7203−7215.

(15) Wen, P.; Xue, M.; Ishikawa, Y.; Itoh, H.; Feng, Q. *ACS Appl. Mater. Interfaces* **2012**, *4*, 1928−1934.

(16) Chen, X.; Jia, C.; Wan, Z.; Feng, J.; Yao, X. *Org. Electron.* **2014**, *15*, 2240−2249.

(17) Stevens, L. A.; Goetz, K. P.; Fonari, A.; Shu, Y.; Williamson, R. M.; Brédas, J.-L.; Coropceanu, V.; Jurchescu, O. D.; Collis, G. E. *Chem. Mater.* **2015**, *27*, 112−118.

(18) Uam, H.-S.; Jung, Y.-S.; Jun, Y.; Kim, K.-J. *J. Photochem. Photobiol., A* **2010**, *212*, 122−128.

(19) Maniam, S.; Holmes, A. B.; Krstina, J.; Leeke, G. A.; Collis, G. E. *Green Chem.* **2011**, *13*, 3329.

(20) Gladysz, J. A.; Curran, D. P.; Horváth, I. Y. *Handbook of Fluorous Chemistry*; Wiley-VCH: Weinheim, 2004.

(21) Marzari, G.; Durantini, J.; Minudri, D.; Gervaldo, M.; Otero, L.; Fungo, F.; Pozzi, G.; Cavazzini, M.; Orlandi, S.; Quici, S. *J. Phys. Chem. C* **2012**, *116*, 21190−21200.

(22) Yum, J.-H.; Hagberg, D. P.; Moon, S.-J.; Karlsson, K. M.; Marinado, T.; Sun, L.; Hagfeldt, A.; Nazeeruddin, M. K.; Grätzel, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 1576−1580.

(23) Moon, S.-J.; Yum, J.-H.; Humphry-Baker, R.; Karlsson, K. M.; Hagberg, D. P.; Marinado, T.; Hagfeldt, A.; Sun, L.; Grätzel, M.; Nazeeruddin, M. K. *J. Phys. Chem. C* **2009**, *113*, 16816−16820.

(24) Collis, G. E.; Burrell, A. K.; Scott, S. M.; Officer, D. L. *J. Org. Chem.* **2003**, *68*, 8974−8983.

(25) Collis, G. E.; Burrell, A. K.; Blandford, E. J.; Officer, D. L. *Tetrahedron* **2007**, *63*, 11141−11152.

(26) Wang, H.; Xue, Y.; Ding, J.; Feng, L.; Wang, X.; Lin, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 11433−11436.

(27) Chen, C.; Yang, X.; Cheng, M.; Zhang, F.; Sun, L. *ChemSusChem* **2013**, *6*, 1270−1275.

(28) Sauvage, F.; Chhor, S.; Marchioro, A.; Moser, J.-E.; Grätzel, M. *J. Am. Chem. Soc.* **2011**, *133*, 13103−13109.

(29) Wu, J.; Lan, Z.; Lin, J.; Huang, M.; Huang, Y.; Fan, L.; Luo, G. *Chem. Rev.* **2015**, *115*, 2136−2173.