Siliconized Triarylamines As Redox Mediator in Dye-Sensitized Solar Cells

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Ⓢ *Supporting Information*

ABSTRACT: A new class of triarylamine compound functionalized with bulky triisopropylsilyl ether (−OTIPS) groups is used as a hole transport material in dye-sensitized solar cells (DSSCs). Using both optical and photoelectrochemical techniques, we compared the performance of this compound with that of a parent compound containing methyl ethers as well as the conventional I_3^-/I^- redox couple. DSSCs fabricated with the triisopropylsilyl ether-substituted triarylamine exhibited high open circuit potentials ($V_{oc} > 0.9$ V on average) and efficiencies of up to 1.9%. However, cells fabricated with triarylamine containing methyl ethers performed very poorly, pointing to the importance of −OTIPS in the overall performance of this material.

KEYWORDS: *dye-sensitized solar cells, hole transport materials, triarylamines, triisopropylsilyl ether functionalization, photovoltage*
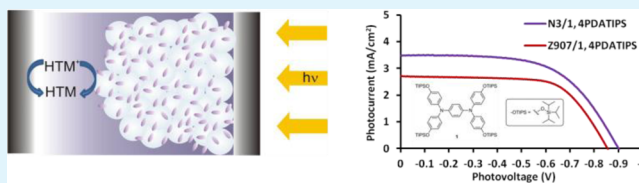
INTRODUCTION

It has been recently suggested that major improvements in the performance of dye sensitized solar cells may be achieved by (1) developing redox couples that produce larger open-circuit voltage (V_{oc}) and (2) by using solid hole conductors instead of the prototypical liquid I_3^-/I^- redox electrolyte.[1] As a result, there has been considerable activity directed toward the development of novel redox couples and hole conducting materials.[2−9]

One category of material studied as a replacement for the I_3^-/I^- redox couple are wholly organic hole transport materials (HTMs) such as triarylamines.[10] Triarylamines are a well-known class of HMTs and have been used in many organic electronic devices such as organic light emitting diodes (OLEDs), photovoltaics, organic field effect transistors (OFETs), and xerographic photoreceptors (OPRs).[11] Triarylamines are generally easy to synthesize, are open to chemical variability, and have good redox stability. Their chemical variability allows for a wide range of electronic and physical properties to be achieved.[12] Several triarylamine derivatives have been shown to work as redox couples in DSSCs. The first reported example used N,N′-di-m-tolyl-N,N′-diphenylbenzidine (TPD) as a redox mediator in solution.[6] For highly doped solutions of TBD (10% doping), the cells performed poorly reportedly because of the occurrence of rapid charge recombination between the redox mediator and ruthenium dye upon photoexcitation. Significantly better performance was achieved by passivating the anode.[13] The liquid triarylamine, tris(4-methoxyethoxyphenyl)amine was used as a neat redox couple in a DSSC achieving an efficiency of 2.4% under AM1.5 illumination.[14] The solid triaylamine, denoted spiro-MeOTAD, displayed the highest performance to date for an organic hole transport material with power conversion efficiencies (PCE) of

up to 7%.[6,9,15] More recently, PCEs of 2.94% were achieved using nanoporous TiO_2 sensitized with Z907 and a novel high solubility and low-T_g triarylamine where the core of spiro-OMeTAD[6] was replaced by a N-hexyl-2,7-carbazole.[16]

In this letter, we wish to report that a novel siliconized triarylamine containing silyl ethers can function as a redox mediator in a DSSC. We also compare its performance to that of the methyl ether containing analog and show that although the silyl ether groups are isoelectronic to methyl ethers, their presence is critical to DSSC performance.

EXPERIMENTAL SECTION

In this work, N,N′-diphenyl-1, 4-phenylenediamine, 4-tetra-triisopropylsilyl ether (triarylamine **1**, 0.26M) or N,N′-diphenyl-1, 4-phenylenediamine, 4-methyl ether (triarylamine **2**, 0.26 M) is dissolved in tertiary-butyl pyridine (1.6M), bis (trifluoromethane) sulfonamide lithium salt (2.8×10^{-2} M) in dicholoromethane and used as electrolytes in nanoporous TiO_2 N3 or Z907 sensitized solar cells. The detailed cell fabrications can be found in the Supporting Information (section A2). The PEC experiments were carried out under AM1.5 illumination and IPCE experiments were obtained by adding a PTI101/102 monochromator at the source. The results for cells prepared with TiO_2 films of ca. 2 μm in thickness sensitized with N3 and Z907 dyes and triarylamine **1** as electrolyte are presented in Table 1 (data for cells prepared with I_3^-/I^- electrolyte are also shown for comparison).

RESULTS AND DISCUSSION

We have previously reported the synthesis and characterization of siliconized triaryalmine **1**.[17] In the present work, DSSCs

Table 1. DSSC Composition, Current−Voltage Characteristics under Illumination, and Performances for Our Best Cells Based on Their Efficiencies

cell composition dye/ electrolyte	V_{oc} ± 1 (mV)	J_{sc} ± 0.04 (mA/cm²)	ff ± 0.1 (%)	efficiency ± 0.1 (%)	avg TiO₂ thickness ± 0.05 (μm)	[dye] on TiO₂[a] (× 10^{-8} mol/cm²)
N3/1, 4PDATIPS	−899	3.46	59.7	1.9	1.47	6.1 ± 0.4
Z907/1, 4PDATIPS	−857	2.72	66.2	1.5	1.91	7.5 ± 0.3
N3/I_3^-,I^-	−786	5.95	61.3	2.9	1.65	6.8 ± 0.2
Z907/I_3^-,I^-	−778	8.33	41.6	2.7	1.42	5.8 ± 0.2

[a]Average values are obtained from the surface concentration of three sensitized TiO₂ samples.

were fabricated with triarylamine **1** using two standard ruthenium based dyes N3 and Z907 on nanoporous TiO₂. Dye Z907 was chosen because of its long alkyl chain attached to one of the dipyridine groups, which makes it more hydrophobic compared with N3. We could therefore study the difference in hydrophobicity and its effects on the performance of the DSSCs. In addition, the presence of an alkyl chains can suppress recombination between sensitizer and redox couple by altering the rate of charge separation kinetics.[18]

DSSC exhibited high values for open circuit photovoltage (V_{oc}) of 910 ± 74 mV on average with the best DSSC having a V_{oc} of 899 mV and an efficiency of 1.9% (see Table 1). Figure 1
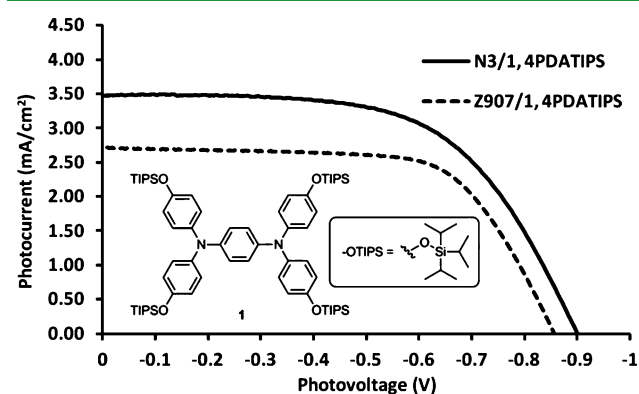
Figure 1. Photoelectrochemical J−V curves for our best cells prepared with N3 (solid line) and Z907 (dashed line) sensitized TiO₂ film and a solution of triarylamine **1** as HTM. Insert: structure of triarylamine **1** (see also Table 1).

shows current−voltage (J−V) curves with corresponding data for the best cells (Table 1); additional data such as J−V curves for all DSSCs together with averages for all cells characterized are given in the Supporting Information accompanying this article. For some champion DSSCs with the same configuration, V_{oc} values of more than 1 V were achieved (see Figure S1 in the Supporting Information). This value compares to a V_{oc} of ∼780 mV for the analogous DSSCs fabricated with the I_3^-/I^- electrolyte. Because V_{oc} is partially determined by the

potential difference between the Fermi level of TiO₂ and redox potential of the electrolyte, the V_{oc} increase can be mostly attributed to a higher redox potential of triarylamine **1** (E_{redox} = 0.621 V vs NHE[17]) compared with that of I_3^-/I^- (E_{redox} = 0.480 V vs NHE[19,20]).[21]

Overall, there is little effect of the nature of the ruthenium sensitizer (N3 and Z907) on the cell's efficiencies when triarylamine **1** is used. On average, efficiencies of ca. 1.23% are obtained (see Table 2). When the performance of several cells is considered, the average data indicates that the J_{sc} value for Z907/triarylamine **1** is higher than that of N3/triarylamine **1** (Table 2). This can be explained by noting the slightly thicker TiO₂ film used in Z907 cell, which consequently had more adsorbed dye on the surface and hence higher photocurrent density (J_{sc}) (average TiO₂ film thicknesses are given in Table 1). The significantly higher V_{oc} value in N3 DSSCs (ca. −900 mV) is balanced out by the higher J_{sc} of Z907 DSSCs that results in similar overall efficiency on average. The PEC results confirm that triarylamine **1** can successfully regenerate both N3 and Z907 sensitizers, indicating that triarylamine **1** functions as a successful redox couple with both dyes. However, the somewhat larger standard deviations reported in Table 2 for cells using triarylamines **1** as HTM can be associated with pore filling issues as discussed elsewhere.[22−27]

To better understand the parameters that affect the cell performance when triarylamine **1** is used, we compared the UV−vis spectra of N3 and Z907 dyes with their respective IPCE spectra (Figure 2a). It is evident that absorption by the dye takes place over a wide range of visible wavelengths (UV−vis absorption spectra of the dyes (N3 and Z907) and triarylamine **1** are shown for reference in Figure 2b); however, when triarylamine **1** is used, electron injection does not occur over the same absorption range. The range of photon absorption and electron injection is significantly narrower compared to the case where I_3^-/I^- is employed (data not shown). The low IPCE values obtained at higher wavelength for the cells with triarylamine **1** can be linked to inefficient electron injection or charge collection.[28] Note that triarylamine **1** has very low absorption at wavelengths >400 nm and hence cannot be the reason for the IPCE values reported here (see Figure 2b). As shown in Figure 2c, light harvesting efficiency

Table 2. Average Performance Values for Cells Prepared with Triarylamine 1 (corresponding J−V plots are shown in Supporting Information, Figure S1)[a]

cell composition dye/electrolyte	avg V_{oc} (mV)	avg J_{sc} (mA/cm²)	avg ff (%)	avg efficiency (%)	avg IPCE[b] (%)
N3/1, 4PDATIPS	−910 ± 74	1.9 ± 0.8	61 ± 3	1.0 ± 0.3	21 ± 1
Z907/1, 4PDATIPS	−789 ± 55	2.8 ± 0.2	55 ± 14	1.4 ± 0.1	18 ± 1
N3/I_3^-, I^-	−773 ± 9	5.4 ± 0.4	62.1 ± 0.5	2.6 ± 0.2	20 ± 1
Z907/I_3^-, I^-	−729 ± 33	6.0 ± 1.6	56 ± 10	2.3 ± 0.3	19 ± 2

[a]Average dye surface concentrations and TiO₂ film thicknesses are listed in Table 1. [b]Average values are obtained from at least three IPCE values obtained for different cells.
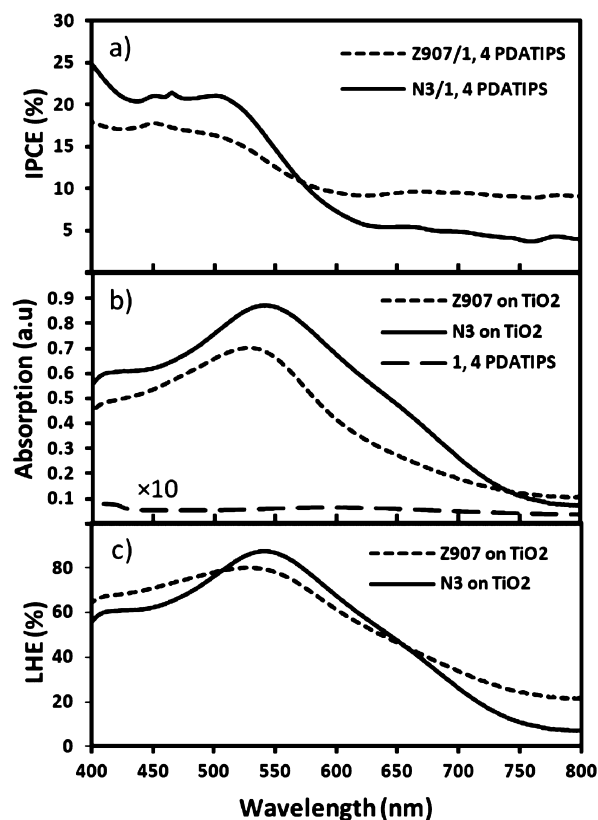
Figure 2. Comparison of (a) IPCE of solar cells fabricated with N3 and Z907 sensitized TiO$_2$ films using triarylamine **1** as HTM; (b) UV−vis spectra of N3 and Z907 dye-sensitized TiO$_2$ and solution of triarylamine **1**; and (c) LHE for the cells characterized in a.

(LHE) of the films is high, implying that photon absorption is not the hindering factor. These losses were evaluated using open-circuit photovoltage decay (OCVD) and are given in the Supporting Information. The lifetime (τ_n) versus V_{oc} were calculated from these measurements for N3 and Z907-sensitized solar cells (Figure 3 and Figure S6 in the Supporting Information, respectively) and suggest much faster recombination from conduction band of TiO$_2$ back to the redox mediator
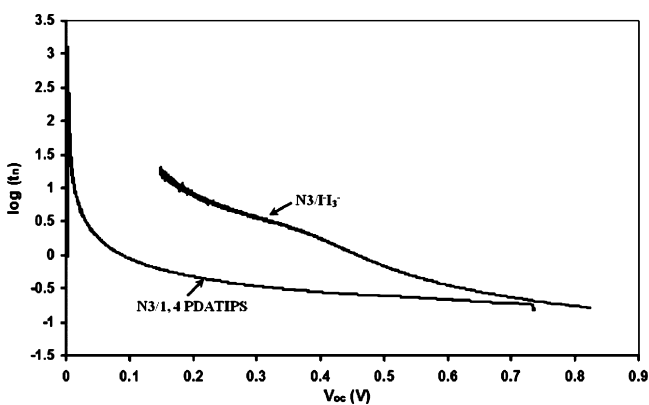
Figure 3. Lifetime (τ_n) versus V_{oc} plots derived from corresponding open circuit voltage potential decays for N3-sensitized TiO$_2$ in contact with compound **1** and I$_3^-$/I$^-$ as redox mediators (see Figure S5a in the Supporting Information for OCVD data). Similar data were also obtained when Z907 was used as the sensitizer (see Figures S5b and S6 in the Supporting Information).

when triarylamine **1** is used versus I$_3^-$/I$^-$ regardless of the sensitizer used.[29,30]

When comparing compound **1** with other HTM molecules[6,16,14] (see Table 3) it is clear that the size of the molecules

Table 3. Summary of Current−Voltage Characteristics under Illumination for THM 1 and Previously Reported HTMs under Similar Conditions[14,16]

cell composition dye/electrolyte	E_{redox} (V vs NHE)	J_{sc} (mA/cm^2)	$[V_{oc}]$ (V)	η (%)
Z907/Spiro-OMeTAD[16]	0.565	5.9	0.78	2.9
Z907/AS37[16]	0.446	5.1	0.69	2.0
Z907/AS44[16]	0.434	5.1	0.71	2.3
Z907/**1** (N3/**1**)	0.621[17]	2.7 (3.5)	0.86 (0.90)	1.5 (1.9)
TMEPA[14]	0.57	4.6	0.77	2.4

and of their substituents is an important factor. Spiro-OMeTAD, AS37, AS44, and TMEPA are listed in order of decreasing size in Table 3. A smaller HTM, such as TMEPA, can more easily approach the TiO$_2$ surface, resulting in an increased electron−hole recombination at the titania interface. This will consequently lower V_{oc} and J_{sc}. A similar behavior is observed for HTM **1** where J_{sc} of cells prepared with this HTM were found to be much lower than the values reported for the other HTMs. However, despite the reduction of J_{sc}, caused by increased recombination, cells made with HTM **1** still show higher V_{oc} values than all other HTMs due to its large E_{redox} (ca. 50 mV below the E_{redox} of other HTMs reported in Table 3).

Although TMEPA has a smaller size than HTM **1**, its overall performance outperforms HTM **1** most likely due to the fact that K51, a dye with bulky substituents, was employed in this study.[14] In this case, the dye structure is more efficient than N3 at blocking recombination. Similar behavior was observed on average when Z907 was used instead of N3 with HTM **1** (Table 2).

It was initially assumed that the electronically inert TIPS groups would slow down electron transfer and limit performance due to the large percentage of molecular mass (and molecular volume) they occupy on each molecule. To investigate how these bulky groups impact the performance of the redox mediator, the analogous triarylamine (triarylamine **1**) with methoxy ether groups (in place of the silyl ether groups) was fabricated into a DSSC (Scheme S.1). Surprisingly, when triarylamine **2** was used no significant photoconversion was observed (see Figure S2 in the Supporting Information), this is in spite of the near identical redox potentials of triarylamines **1** and **2**.[17] Comparison of the dark currents of the cells prepared with triarylamines **1** and **2** reveals no distinguishable differences (see Figure S2 in the Supporting Information).

DFT calculations were performed on triarylamines **1** and **2**. The calculations reveal that the two molecules, consistent with their near identical oxidation potentials,[17,31] have almost identical HOMO and LUMO energies (see Table S1 in the Supporting Information) and that there is an absence of charge density at the terminal groups whether they be triisopropylsilyl or methyl ether groups (see Figure S3 in the Supporting Information). Although good orbital overlap can play an important role in the dye regeneration, given each triarylamines orbital shape and distribution, it is not obvious how triarylamine **1** would differ compared to triarylamine **2** in this respect. One then needs to turn to physical arguments rather

than energetic ones. It could be argued that the presence of OTIPS may afford appropriate spacing between the sensitized surface and the HTM to give rise to good regeneration while slowing down recombination. We come to this conclusion after ruling out hydrophobicity and the possibility that the OTIPS groups become hydrolyzed in situ, forming another triarylamine to become chemically bound to the TiO_2 surface. For example, we show hydrophobicity of the OTIPS had little effect because performances are roughly the same with N3 and Z907. Z907 is known to be more hydrophobic (it is C9 substituted) compared to N3 (Tables 1 and 2). Although unlikely, the hydrolysis of OTIPS was investigated as a possible modification of triarylamine **1** during processing by purposefully hydrolyzing triarylamine **1** with aqueous hydrochloric acid (see the Supporting Information, section B). Hydrolysis had a negative effect on the cell performance (see Figure S4 in the Supporting Information). In further studies, the effect of the structure of OTIPS groups will be investigated to better understand the role of OTIPS groups on charge transport kinetics.

■ CONCLUSION

In summary, we have shown a silyl-ether functionalized triarylamine (triarylamine **1**) functions as a redox couple for DSSCs. Cells using triarylamine **1** as a redox mediator show very high V_{oc} values (ca. 910 mV on average) and promising overall efficiencies of up to 1.9% using N3 as a sensitizer (a value of 2.9% was obtained using I_3^-/I^- for the same TiO_2 thickness). Uniquely, when the analogous triarylamine without silyl-ether functionality was used (triarylamine **2**), no photo conversion was observed. We suggest that the presence of bulky, electronically inert groups is critical to the performance of the triarylamine redox mediator in this example. Further investigations will focus on the effect of other bulky silyl-ether groups and variations in the triarylamine molecular structure to determine if this effect is universal.

■ ASSOCIATED CONTENT

⑤ Supporting Information
Experimental details, additional scheme, table and figures: J−V curves for all cells studied including measurements with triarylamine **2**, dark current curves, DFT calculations, effect of hydrolysis of triarylamines on cell performance, lifetime of injected electron determination (PDF). This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Peter, L. M. *J. Phys. Chem. Lett.* **2011**, *2*, 1861−1867.

(2) Hamann, T. W.; J.W. Ondersma, J. W. *Energy Environ. Sci.* **2011**, *4*, 370−381.

(3) Leea, H.; Baea, S.; Jo, Y.; Kimb, K.; Junc, Y.; Han, C. *Electrochim. Acta* **2010**, *55*, 7159−7165.

(4) Camerona, P. J.; Peter, L. M.; Zakeeruddin, S. M.; Grätzel, M. *Coord. Chem. Rev.* **2004**, *248*, 1447−1453.

(5) Bonhote, P.; Dias, A.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. *Inorg. Chem.* **1996**, *35*, 1168−1178.

(6) Bach, U.; Lupo, D.; Comte, P.; Moser, J. E.; Weissortel, F.; Salbeck, J.; Spreitzer, H.; Gratzel, M. *Nature* **1998**, *395*, 583−585.

(7) J. Burschka, J.; Brault, V.; Ahmad, S.; Breau, L.; Nazeeruddin, M. K.; Marsan, B.; Zakeeruddin, S. M.; Gratzel, M. *Energy Environ. Sci.* **2012**, *5*, 6089−6097.

(8) Jovanovski, V.; González Pedro, V.; Giménez, S.; Azaceta, E.; Cabañero, G.; Grande, H.; Tena-Zaera, R.; Mora-Seró, I.; Bisquert, J. *J. Am. Chem. Soc.* **2011**, *133*, 20156−20159.

(9) Tiana, H.; Sun, L. *J. Mater. Chem.* **2011**, *21*, 10592−10601 and references therein..

(10) (a) Shirota, Y. *J. Mater. Chem.* **2000**, *10*, 1−25. (b) Shirota, Y. *J. Mater. Chem.* **2005**, *15*, 75−93. (c) Ning, Z. J.; Chen, Z.; Zhang, Q.; Yan, Y. L.; Qian, S. X.; Tian, H.; Cao, Y. *Adv. Funct. Mater.* **2007**, *17*, 3799−3807.

(11) (a) Shirota, Y.; Kageyama, H. *Chem. Rev.* **2007**, *107*, 953−1010. and references therein (b) Xu, D.; Adachi, C. *Appl. Phys. Lett.* **2009**, *95*, 53304. (c) Hendrickx, E.; Guenther, B. D.; Zhang, Y.; Wang, J. F.; Staub, K.; Zhang, Q.; Marder, S. R.; Kippelen, B. L.; Peyghambarian, N. *Chem. Phys.* **1999**, *245*, 407−415. (d) Ribierre, J.; Aoyama, T.; Kobayashi, T.; Sassa, T.; Muto, T.; Wada, T. *J. Appl. Phys.* **2007**, *102*, 33106. (e) Ribierre, J. C.; Aoyama, T.; Muto, T.; Imase, Y.; Wada, T. *Org. Electron.* **2008**, *9*, 396−400.

(12) Bender, T. P.; Graham, J. F.; Duff, J. M. *Chem. Mater.* **2001**, *13*, 4105−4111.

(13) Gregg, B. A.; Pichot, F.; Ferrere, S.; Fields, C. L. *J. Phys Chem. B* **2001**, *105*, 1422−1429.

(14) Snaith, H. J.; Zakeeruddin, S. M.; Wang, Q.; Peechy, P.; Gratzel, M. *Nano Lett.* **2006**, *6*, 2000−2003.

(15) Burschka, J.; Dualeh, A.; Kessler, F.; Baranoff, E.; Cevey-Ha, N.; Yi, C.; Nazeeruddin, M. K.; Gratzel, M. *J. Am. Chem. Soc.* **2011**, *133*, 18042−18045.

(16) Leijtens, T.; Ding, I.-K.; Giovenzana, T.; Bloking, J. T.; McGehee, M. D.; Sellinger, A. *ACS Nano* **2012**, *6*, 1455−1462.

(17) Kamino, B. A.; Castrucci, J.; Bender, T. P. *Silicon* **2011**, *3*, 125−137.

(18) Schmidt-Mende, L.; Kroeze, J. E.; Durrant, J. R.; Nazeeruddin, M. K.; Gratzel, M. *Nano Lett.* **2005**, *5*, 1315−1320.

(19) Kay, A.; Humphry-Baker, R.; Gratzel, M. *J. Phys. Chem.* **1994**, *98*, 952−959.

(20) Cahen, D.; Hodes, G.; Gratzel, M.; Guillemoles, J. F.; Riess, I. *J. Phys. Chem. B* **2000**, *104*, 2053−2059.

(21) Oskam, G.; Bergeron, B. V.; Meyer, G. J.; Searson, P. C. *J. Phys. Chem. B* **2001**, *105*, 6867−6873.

(22) Schmidt-Mende, L.; Kroeze, J. E.; Durrant, J. R.; Nazeeruddin, M. K.; Gratzel, M. *Nano Lett.* **2005**, *5*, 1315−1320.

(23) Ding, B. I.; Tetreault, N.; Brillet, J.; Hardin, B. E.; Smith, E. H.; Rosenthal, S. J.; Sauvage, S.; Gratzel, M.; McGehee, M. D. *Adv. Funct. Mater.* **2009**, *19*, 2431−2436.

(24) Schmidt-Mende, L.; Gratzel, M. *Thin Solid Films* **2006**, *500*, 296−301.

(25) Snaith, H. J.; Schmidt-Mende, L. *Adv. Mater.* **2007**, *19*, 3187−3200.

(26) Kroeze, J. E.; Hirata, N.; Schmidt-Mende, L.; Orizu, C.; Ogier, S. D.; Carr, K.; Gratzel, M.; Durrant, J. R. *Adv. Funct. Mater.* **2006**, *16*, 1832−1838.

(27) Barbe, C. J.; Arendse, F.; Comte, P.; Jirousek, M.; Lenzmann, F.; Shklover, V.; Gratzel, M. *J. Am. Ceram. Soc.* **1997**, *80*, 3157−3171.

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

(29) Bisquert, J.; Zaban, A.; Greenshtein, M.; Mora-Sero, I. *J. Am. Chem. Soc.* **2004**, *126*, 13550−13559.

(30) Zaban, A.; Greenshtein, M.; Bisquert, J. *Chem. Phys. Chem.* **2003**, *4*, 859−864.

(31) Lambert, C.; Noll, G. *J. Am. Chem. Soc.* **1999**, *121*, 8434−8442.