2-(4-Butoxyphenyl)-N-hydroxyacetamide: An Efficient Preadsorber for Dye-Sensitized Solar Cells

Su Htike Aung,†‡ Yan Hao,† Than Zaw Oo,‡ and Gerrit Boschloo*†‡

†Department of Chemistry—Ångström Laboratory, Uppsala University, P.O. Box 523, 75120 Uppsala, Sweden
‡Department of Physics, Materials Sciences Research Laboratory, University of Mandalay, Mahaungmyay township (100103), Mandalay, Myanmar

ABSTRACT: The effect of chemical modification of mesoporous TiO2 electrodes by 2-(4-butoxyphenyl)-N-hydroxyacetamide (BPHA) before dye adsorption is investigated in dye-sensitized solar cells (DSCs). Two organic dyes, LEG4 and Dyenamo blue, were used in combination with the cobalt (II/III) tris(bipyridine) redox couple. The photovoltaic performance of the DSCs is clearly enhanced by BPHA. Preadsorption of mesoporous TiO2 electrodes with BPHA lowered the amount of adsorbed dye but improved the short-circuit current densities and the power conversion efficiencies by 10–20%, while keeping the open-circuit potential essentially unaffected. Notably, BPHA improved the LEG4 performance, whereas it has been reported for this dye that chenodeoxycholic acid as a coadsorbent lowers solar cell efficiency. Faster dye regeneration was found to be one reason for improved performance, but improved electron injection efficiency may also contribute to the favorable effect of BPHA.

INTRODUCTION

Dye-sensitized solar cells (DSCs) have attracted much scientific attention after the breakthrough report in 1991 by O’Regan and Grätzel, who described the first efficient DSCs with efficiencies exceeding 7% in simulated sunlight. They used a ruthenium complex as the sensitizer, which was attached to a mesoporous TiO2 electrode, and a redox-based electrolyte based on iodide/triiodide used to regenerate the sensitizer. Most of the following work on DSCs worldwide was carried out on similar systems, which eventually reached a record efficiency of 12%. In 2010, Feldt et al. demonstrated a way toward higher efficiencies in DSCs, by switching to organic dyes as sensitizers and to cobalt-based complexes as redox mediators. By using a one-electron redox mediator, much lower overpotential losses compared with iodide/triiodide are obtained, and by implementing organic dyes with suitable peripheral groups, electron recombination to the redox mediator, a serious problem for DSCs with one-electron mediators, is slowed down. This work was followed up by research focusing on novel dyes on the stability of the cobalt electrolyte and on counter electrodes suitable for this redox mediator. After tedious optimization, a record efficiency of 14% has recently been reported for a DSC cosensitized by two organic dyes (LEG4 and ADEKA-1) and using a cobalt phenanthroline-based electrolyte.

To suppress unwanted recombination reactions in DSCs, several electrode treatments and additives to the electrolyte are applied. Coadsorbents are frequently added in the dye bath to improve the performance of the solar cells. Cholic acid derivatives are used to suppress dye aggregation. Long alkyl chain acids such as 1-decylphosphonic acid are used to suppress dark current and to improve solar cell stability. Guanidinoalkyl acids have been found to shift the TiO2 conduction band to a higher energy and to slow down electron recombination to the electrolyte. Han et al. used small donor–acceptor-type coadsorbents, which absorb blue light and prevent aggregation of the ruthenium black dye, and achieved a certified record for DSCs (11.4%). Similarly, Song et al. developed a triarylamidine-based coadsorbent that prevented π–π stacking of organic dye molecules (NKKX2677) and contributed to the light-harvesting effect at short wavelengths.

In this work, the effect of molecular modification of the mesoporous TiO2 electrode by 2-(4-butoxyphenyl)-N-hydroxyacetamide (BPHA, see Figure 1) is investigated in DSCs with a cobalt-complex-based electrolyte. The binding group in BPHA is hydroxamic acid, which has recently been successfully used in sensitizers for DSCs. The best performance was obtained by adsorbing BPHA onto the mesoporous TiO2 electrode before dye-sensitization by the two dyes investigated here, LEG4 and Dyenamo blue (DB). The power conversion efficiency (PCE) of the two different organic dyes with a D–π–A structure, LEG4 and DB, was improved by a full percent unit in both cases. The underlying mechanism is investigated here.
In the dye baths, containing either 0.2 mM LEG4 in ethanol or 0.5 mM DB in a 1:1 acetonitrile/tert-butanol mixture, followed by rinsing with the solvent. Counter electrodes were prepared by electropolymerization of PEDOT onto TEC8 conducting glass. Solar cells were assembled using a 30 μm thick thermoplastic frame (Surlyn) in a hot press (HeptaChroma). The electrolyte solution was introduced through the hole predrilled in the counter electrode using a vacuum backfilling, and a final seal was made using Surlyn and a thin glass plate. The electrolyte was composed of 0.22 M Co(bpy)$_3$(PF$_6$)$_2$, 0.05 M Co(bpy)$_3$(PF$_6$)$_2$, 0.1 M LiClO$_4$, lithium perchlorate, and 0.2 M 4-tert-butylpyridine (TBP) in acetonitrile. Silver paste was applied on the edges of the working and counter electrodes.

**Optical Characterization.** Transparent mesoporous TiO$_2$ films with a thickness of approximately 3 μm were used for UV−vis measurements that were recorded on an Ocean Optics spectrophotometer (HR-2002).

**Solar Cell Characterization.** The photovoltaic performance was measured using a Keithley 2400 source/meter in combination with a Newport Solar simulator (model 911160) under an AM1.5G illumination (1000 W m$^{-2}$) that is calibrated by using a certified reference solar cell (Fraunhofer ISE). A black metal mask with an aperture of 0.5 × 0.5 cm$^2$ was placed on the top of the solar cell and defines the active area. Incident photon-to-current conversion efficiency (IPCE) spectra were recorded using a computer control setup comprising a xenon light source (Spectral Products ASB-XE-175), a monochromator (Spectral Products CM110), and a digital acquisition board (Labjack U6). An in-house-made system consisting of a white LED (Luxeon Star, 1 W), a 16-bit resolution digital acquisition board (National Instruments) in combination with a current amplifier and electromagnetic switches, was used to record voltage and current transients following small light modulations, from which electron lifetimes and transport time were derived.

**Nanosecond Transient Absorption Spectroscopy.** The electron transfer kinetics were measured using a laser flash photolysis spectrometer (Edinburgh instrument LP920) with a Nd:YAG laser/OPO system (Continuum Surelite) tuned to 530 nm. The pulse intensity is attenuated to 0.2 mJ cm$^{-2}$ per pulse by using neutral density filters. Kinetics were recorded at 750 nm for LEG4 and 760 nm for DB.

### EXPERIMENTAL SECTION

**Materials and Experimental Methods.** The organic sensitizers and redox couples were purchased from Dyenamo AB (Sweden) and the other chemicals from Sigma-Aldrich. BPHA was available from a previous study.

**Device Preparation.** Fluorine-doped tin oxide glass substrates (TEC15, Pilkington) were pretreated in a 40 mM TiCl$_4$ solution at 70 °C for 30 min. TiO$_2$ films with an active area of 0.5 × 0.5 cm$^2$ were then screen-printed using TiO$_2$ paste (Dyesol DSL 30NRD-T) with a 120T screen. The thicknesses of the films were measured using a profilometer (Veeco Dektak 3). Two light scattering layers with a thickness of approximately 3 μm for each layer were printed on the top of an approximately 4 μm mesoporous transparent TiO$_2$ layer. After printing each layer, the films were dried at 120 °C for 5 min in an oven. Then, the TiO$_2$ substrates were sintered in an air atmosphere to get the optimized crystallinity in the same oven using a temperature-gradient program, with four steps at 180 °C for 10 min, 320 °C for 10 min, 390 °C for 10 min, and 500 °C for 60 min. The films were kept overnight inside of the oven for cooling. Thereafter, the electrode films were subjected to another TiCl$_4$ treatment, followed by another heating cycle. After cooling to 90 °C, the electrodes were immersed in a 1 mM BPHA solution in ethanol for 1 h, followed by rinsing with ethanol and drying in air. Then, the samples were left overnight in the dye baths, containing either 0.2 mM LEG4 in ethanol or 0.5 mM DB in a 1:1 acetonitrile/tert-butanol mixture, followed by rinsing with the solvent. Counter electrodes were prepared by electropolymerization of PEDOT onto TEC8 conducting glass. Solar cells were assembled using a 30 μm thick thermoplastic frame (Surlyn) in a hot press (HeptaChroma). The electrolyte solution was introduced through the hole predrilled in the counter electrode using a vacuum backfilling, and a final seal was made using Surlyn and a thin glass plate. The electrolyte was composed of 0.22 M Co(bpy)$_3$(PF$_6$)$_2$, 0.05 M Co(bpy)$_3$(PF$_6$)$_2$, 0.1 M LiClO$_4$, lithium perchlorate, and 0.2 M 4-tert-butylpyridine (TBP) in acetonitrile. Silver paste was applied on the edges of the working and counter electrodes.

**RESULTS AND DISCUSSION**

**Effect of BPHA on Dye Coverage on Mesoporous TiO$_2$ and Solar Cell Performance.** Figure 2 shows the UV−vis spectra of the two dyes, LEG4 and DB, adsorbed onto the mesoporous TiO$_2$ films. The DB-sensitized films are clearly darker in color than the LEG4 films. Preadsorption of BPHA onto mesoporous TiO$_2$ has a significant effect on the adsorption of both organic dyes. It leads to a decrease in the absorbance, which is directly related to a decreased amount of the adsorbed dye. For LEG4, the decrease in absorbance was small, only 7%, but for DB, it was rather large, 27%. BPHA molecules will bind to the mesoporous TiO$_2$ surface through the hydroxamate group. In the dye bath, dye molecules will bind to the mesoporous TiO$_2$ through the hydroxyacetamide group. On the basis of the 7% decrease in absorbance, it may be estimated that the binding constant for LEG4 adsorption on TiO$_2$ is roughly 10 times stronger than that of BPHA. The
much stronger effect that BPHA has on the adsorption of DB may point to some aggregation of this dye on the TiO$_2$ surface when BPHA is absent. It can be noted in this respect that structurally similar diketopyrrolopyrrole (DPP)-based sensitizers are usually adsorbed from a dye bath containing a large excess of cholic acid derivatives (in a 50 to 100 times larger concentration) that can reduce dye aggregation on the surface.\textsuperscript{14,15,18}

DSCs were prepared with LEG4 and DB, with and without BPHA pretreatment of the TiO$_2$ electrodes. Cobalt tris(bipyridine) was used as the redox mediator in the electrolyte. This one-electron redox couple is highly suited for DSCs, but it requires a densely packed dye monolayer with electron transfer blocking properties.\textsuperscript{20} Current–voltage ($I–V$) curves of champion devices under 1 sun illumination are shown in Figure 3a. The main solar cell parameters averaged for seven devices are summarized in Table 1. For LEG4, the open-circuit potential remains unchanged by BPHA preadsorption, but a significant increase in short-circuit current density ($J_{SC}$) by approximately 9% is found. Also, for DB, an increased $J_{SC}$ is observed, by 18% on average, but this is accompanied by a slight decrease ($\sim 20$ mV) in the open-circuit potential ($V_{OC}$). Slight improvements in the fill factor (FF) are found for both dye systems. There is a clear increase in the PCEs because of BPHA pretreatment of the TiO$_2$ electrode, by approximately 10 and 20% for LEG4 and DB, respectively. Here, we find that the efficiency of LEG4 is 6.89% for standard sensitization, which increases to 7.57% with BPHA pretreatment. In our previous work on the LEG4 dye, we found the efficiency to be 6.5% for standard sensitization with LEG4 and a decrease to 4.3% with sensitization in the presence of 10 mM chenodeoxycholic acid.\textsuperscript{8}

This suggests that BPHA preadsorption may work in fundamentally different ways than coadsorption and that it can significantly improve solar cell performance for dyes that do not require cholic acid coadsorbents.

IPCE spectra, recorded using low-intensity monochromatic light, are presented in Figure 3b. The IPCE maximum of an LEG4-sensitized solar cell with BPHA is $\sim 90\%$, which is 10% higher than the solar cell without BPHA, whereas that of DB with and without BPHA is 80 and 60%, respectively. The improvements are consistent with the improved $J_{SC}$ found under solar irradiation. Considering that light absorption is lower for the devices with BPHA pretreatment, it is clear that their improved performance must come from more favorable electron transfer kinetics in the solar cell. These will be investigated in the next section.

**Effect of BPHA on Electron Transfer Kinetics in the DSCs.** Several methods were used to investigate electron transfer kinetics in the DSCs. Complete devices were used to measure electron transport times and lifetimes by means of photocurrent and voltage response to small modulations in the light; see Figure 4. The electron lifetimes correspond to the time for a recombination of electron in mesoporous TiO$_2$, to the oxidized component in the electrolyte, Co(bpy)$_3^{3+}$, and to the oxidized dye if dye regeneration is sluggish. For the LEG4 dye, BPHA pretreatment has little or no effect on the electron lifetime. By contrast, a decrease in lifetime is found for DB with BPHA. Suppression of electron recombination by DB is not as good as that by LEG4, and the BPHA treatment, which lowers the DB amount by approximately 20%, further decreases the electron blocking properties of the adsorbed dye layer. This explains the lower $V_{OC}$ values found for DB and BPHA–DB devices. For DB, the BPHA pretreatment lowered the electron lifetime significantly by a factor of $\sim 3$. This is attributed to the less dense packing of DB on the mesoporous TiO$_2$ surface, which results in poorer blocking of the electron recombination from TiO$_2$ to Co(bpy)$_3^{3+}$ in the electrolyte.\textsuperscript{20} Charge extraction measurements for devices with and without BPHA did not display significant differences, suggesting that BPHA does not significantly affect the energy levels (data not shown). The

![Figure 2](https://example.com/figure2.png)

**Figure 2.** UV–vis spectra of LEG4 and DB absorbed onto mesoporous TiO$_2$ showing the effect of preadsorption with BPHA. The TiO$_2$ film thickness was 3 $\mu$m.

![Figure 3](https://example.com/figure3.png)

**Figure 3.** (a) $I–V$ curves of LEG4- and DB-sensitized DSCs with and without BPHA under AM1.5G illumination (1000 W m$^{-2}$) and (b) IPCE spectra of LEG4- and DB-sensitized DSSCs with and without BPHA. Electrolyte: 0.22 M Co(bpy)$_3$(PF$_6$)$_2$, 0.05 M Co(bpy)$_3$(PF$_6$)$_3$, 0.1 M LiClO$_4$, and 0.2 M TBP.
electron transport times in the mesoporous TiO₂ films were not significantly affected by the type of dye or BPHA treatment; see Figure 4b.

Finally, nanosecond transient absorption spectroscopy (TAS) was used to probe the electron transfer kinetics. Specifically, the kinetics for reduction of the oxidized dye that exists in the cell after electron injection are probed. This reduction occurs either by the redox mediator (Co(bpy)₃²⁺) or by electron recombination from the TiO₂. Kinetic traces of the systems in the presence and in the absence of redox electrolyte are shown in Figure 5. Although the data are rather noisy, it can be seen that dye regeneration is slightly improved in films with BPHA pretreatment for both dyes. This is also apparent from the fit parameters shown in Table 2. From the determined decay half times, in the presence of inert electrolyte, where the kinetics reflect electron recombination with the oxidized dye, and in the presence of redox electrolyte, where the kinetics are from both recombination and dye regeneration, the regeneration efficiency \( \phi_{\text{reg}} \) is determined according to eq 1

\[
\phi_{\text{reg}} = \frac{k_{\text{reg}}}{k_{\text{reg}} + k_{\text{rec}}} = 1 - \frac{t_{1/2 \text{redox}}}{t_{1/2 \text{inert}}}
\]

The calculated \( \phi_{\text{reg}} \) values show a significant trend: BPHA pretreatment leads to higher regeneration efficiencies, by approximately 5% for LEG4 to 20% for DB. A faster regeneration with a lower dye load on the mesoporous TiO₂ surface was observed previously by Pazoki et al. The lower coverage of dye molecules could give better access to the Co(II) species in the electrolyte.

One aspect that was not investigated experimentally in this study (due to experimental limitations) is the electron injection from an excited dye to the TiO₂ conduction band. An estimation can be made using eq 2

\[
\text{IPCE} = \text{LHE} \times \phi_{\text{inj}} \times \phi_{\text{reg}} \times \phi_{\text{cc}}
\]

where LHE is the light-harvesting efficiency, \( \phi_{\text{inj}} \) is the electron injection efficiency, and \( \phi_{\text{cc}} \) is the charge collection efficiency, assumed to be 100% under short-circuit conditions. The latter assumption comes from the fact that the Fermi level in the mesoporous TiO₂ electrode under short-circuit conditions is much lower in energy than that under open-circuit conditions. Assuming a 100 meV difference, it is found that the electron transport time is much smaller than the electron lifetime, and the collection efficiency is near unity under short-circuit conditions. LHE (or absorptance) is the fraction of the incoming light that is absorbed by the dye, and is given by LHE = 1 – \( T + R \), where \( T \) and \( R \) are transmittance and reflectance, respectively. \( R \) is approximately 10% in these devices, whereas \( T \) is close to zero at the absorption maxima of the dyes, so that LHE is approximately 0.90. With these assumptions, \( \phi_{\text{inj}} \) is calculated to be unity for all devices. This simple analysis suggests that regeneration losses are mainly responsible for losses in IPCE and thus lowered \( J_{sc} \) in the solar cells. Through BPHA pretreatment, regeneration of the dyes is improved perhaps because of better accessibility of the redox couple to the dye because there is less adsorbed dye on the mesoporous TiO₂ surface. However, because regeneration studies were rather noisy, injection losses cannot be excluded in the DSCs. It seems reasonable to believe that BPHA preadsorption leads to adsorption of a more orderly dye layer, which can lead to better electron injection.

CONCLUSIONS

Molecular modification of the mesoporous TiO₂ before dye adsorption is a suitable way to improve DSC performance. In DSCs using LEG4 and DB organic dyes as sensitizers and cobalt trisbipyridine as the redox mediator, significant improvements in the solar cell efficiency, by 10 to 20%, were obtained through the pretreatment of the TiO₂ electrode with BPHA. This treatment leads to a decreased amount of adsorbed dye but to improved photocurrents and faster dye regeneration. It is

Table 1. Photovoltaic Performance of LEG4- and DB-Sensitized DSCs, with and without BPHA Preadsorption under AM1.5G Illumination (1000 W m⁻²)

| device     | \( V_{OC} \) (V) | \( J_{SC} \) (mA cm⁻²) | FF  | PCE (%) |
|------------|------------------|-------------------------|-----|---------|
| LEG4       | 0.85 ± 0.01      | 11.7 ± 0.2              | 0.67 ± 0.02 | 6.89 ± 0.13 |
| BPHA-LEG4  | 0.85 ± 0.01      | 12.7 ± 0.4              | 0.70 ± 0.01 | 7.57 ± 0.19 |
| DB         | 0.79 ± 0.01      | 9.6 ± 0.6               | 0.69 ± 0.01 | 5.22 ± 0.30 |
| BPHA-DB    | 0.77 ± 0.01      | 11.3 ± 0.7              | 0.71 ± 0.01 | 6.26 ± 0.28 |

*Average performance of 7 devices for each series, with standard deviation indicated.*

Figure 4. (a) Electron lifetimes under open-circuit conditions and (b) electron transport times under short-circuit conditions of LEG4- and DB-sensitized DSCs with and without BPHA.
likely that the injection efficiency is improved too. Notably, BPHA improved the performance of the popular LEG4 dye, whereas it has been reported for this dye that chenodeoxycholic acid as the coadsorbent lowers solar cell efficiency.

## AUTHOR INFORMATION

**Corresponding Author**

*E-mail: gerrit.boschloo@kemi.uu.se (G.B.).

**ORCID**

Gerrit Boschloo: 0000-0002-8249-1469

**Notes**

The authors declare no competing financial interest.

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## REFERENCES

(1) O’Regan, B.; Grätzel, M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films. *Nature* 1991, 353, 737–740.

(2) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. Dye-Sensitized Solar Cells. *Chem. Rev.* 2010, 110, 6595.

(3) Feldt, S. M.; Gibson, E. A.; Gabrielsson, E.; Sun, L.; Boschloo, G.; Hagfeldt, A. Design of Organic Dyes and Cobalt Polypyridine Redox Mediators for High-Efficiency Dye-Sensitized Solar Cells. *J. Am. Chem. Soc.* 2010, 132, 6595.

(4) Dai, P.; Dong, H.; Liang, M.; Cheng, H.; Sun, Z.; Xue, S. Understanding the Role of Electron Donor in Truxene Dye Sensitized Solar Cells with Cobalt Electrolytes. *ACS Sustainable Chem. Eng.* 2017, S, 97–104.

(5) Yella, A.; Lee, H.-W.; Tsao, H. N.; Yi, C.; Chandiran, A. K.; Nazeeruddin, M. K.; Diao, E. W.-G.; Yeh, C.-Y.; Zakeeruddin, S. M.; Grätzel, M. Porphyrin-Sensitized Solar Cells with Cobalt (II/III)-Based Redox Electrolyte Exceed 12 Percent Efficiency. *Science* 2011, 334, 629–634.

(6) Tsao, H. N.; Yi, C.; Moehl, T.; Yum, J.-H.; Zakeeruddin, S. M.; Nazeeruddin, M. K.; Grätzel, M. Cyclopentadiithiophene Bridged Donor–Acceptor Dyes Achieve High Power Conversion Efficiencies in Dye-Sensitized Solar Cells Based on the tris-Cobalt Porphyrine Redox Couple. *ChemSusChem* 2011, 4, 591–594.

(7) Gabrielson, E.; Ellis, H.; Feldt, S.; Tian, H.; Boschloo, G.; Hagfeldt, A.; Sun, L. Convergent/Divergent Synthesis of a Linker-
Varied Series of Dyes for Dye-Sensitized Solar Cells Based on the D35 Donor. *Adv. Energy Mater.* 2013, 3, 1647−1656.

(8) Ellis, H.; Eriksson, S. K.; Feldt, S. M.; Gabrielson, E.; Lohse, P. W.; Lindblad, R.; Sun, L.; Rensmo, H.; Boschloo, G.; Hagfeldt, A. Linker Unit Modification of Triphenylamine-Based Organic Dyes for Efficient Cobalt Mediated Dye-Sensitized Solar Cells. *J. Phys. Chem. C* 2011, 117, 21029−21036.

(9) Bella, F.; Vlachopoulos, N.; Nonomura, K.; Zakeeruddin, S. M.; Grätzel, M.; Gerbaldi, C.; Hagfeldt, A. Direct light-induced polymerization of cobalt-based redox shuttles: an ultrafast way towards stable dye-sensitized solar cells. *Chem. Commun.* 2015, 51, 15894−15897.

(10) Jiang, R.; Anderson, A.; Barnes, P. R. F.; Xiao, L.; Law, C.; O’Regan, B. C. 2000 hours photostability testing of dye sensitised solar cells using a cobalt bipyridine electrolyte. *J. Mater. Chem. A* 2014, 2, 4751−4757.

(11) Ellis, H.; Vlachopoulos, N.; Hägglund, L.; Perruchot, C.; Jouini, M.; Boschloo, G.; Hagfeldt, A. PEDOT counter electrodes for dye-sensitized solar cells prepared by aqueous micellar electrodoposition. *Electrochim. Acta* 2013, 107, 45−51.

(12) Liu, I.-P.; Hou, Y.-C.; Li, C.-W.; Lee, Y.-L. Highly electrocatalytic counter electrodes based on carbon black for cobalt(iii)/(ii)-mediated dye-sensitized solar cells. *J. Mater. Chem. A* 2017, 5, 240−249.

(13) Kakiage, K.; Aoyama, Y.; Yano, T.; Oya, K.; Fujisawa, J.; Hanaya, M. Highly-efficient dye-sensitized solar cells with collaborative sensitization by silyl-anchor and carboxy-anchor dyes. *Chem. Commun.* 2015, 51, 15894−15897.

(14) Holcombe, T. W.; Yum, J.-H.; Yoon, J.; Gao, P.; Marszalek, M.; Cenko, D. D.; Rakstys, K.; Nazeeruddin, M. K.; Graetzel, M. A structural study of DPP-based sensitizers for DSC applications. *Chem. Commun.* 2012, 48, 10724−10726.

(15) Yum, J.-H.; Holcombe, T. W.; Kim, Y.; Rakstys, K.; Moehl, T.; Teuscher, J.; Delcamp, J. H.; Nazeeruddin, M. K.; Grätzel, M. Blue-Coloured Highly Efficient Dye-Sensitized Solar Cells by Implementing the Diketopyrrolopyrrole Chromophore. *Sci. Rep.* 2013, 3, 2446.

(16) Kay, A.; Grätzel, M. Artificial photosynthesis. I. Photo-sensitization of titania solar cells with chlorophyll derivatives and related natural porphyrins. *J. Phys. Chem.* 1993, 97, 6272−6277.

(17) Hara, K.; Dan-oh, Y.; Kasada, C.; Ohga, Y.; Shinpo, A.; Suga, S.; Sayama, K.; Arakawa, H. Effect of Additives on the Photovoltaic Performance of Coumarin-Dye-Sensitized Nanocrystalline TiO2 Solar Cells. *Langmuir* 2004, 20, 4205−4210.

(18) Qu, S.; Wu, W.; Hua, J.; Kong, C.; Long, Y.; Tian, H. New Diketopyrrolopyrrole (DPP) Dyes for Efficient Dye-Sensitized Solar Cells. *J. Phys. Chem. C* 2010, 114, 1343−1349.

(19) Wang, P.; Zakeeruddin, S. M.; Humphry-Baker, R.; Moser, J. E.; Grätzel, M. Molecular-scale interface engineering of TiO2 nanocrystals: Improving the efficiency and stability of dye-sensitized solar cells. *Adv. Mater.* 2003, 15, 2101−2104.

(20) Zhang, Z.; Evans, N.; Zakeeruddin, S. M.; Humphry-Baker, R.; Grätzel, M. Effects of o-Guainidinalkyl Acids as Coadsorbents in Dye-Sensitized Solar Cells. *J. Phys. Chem. C* 2007, 111, 398−403.

(21) Han, L.; Islam, A.; Chen, H.; Malapaka, C.; Chiranjeevi, B.; Zhang, S.; Yang, X.; Yanagida, M. High-efficiency dye-sensitized solar cell with a novel co-adsorbent. *Energy Environ. Sci.* 2012, 6, 6057−6060.

(22) Song, H. M.; Seo, K. D.; Kang, M. S.; Choi, I. T.; Kim, S. K.; Eom, Y. K.; Ryu, J. H.; Ju, M. J.; Kim, H. K. A simple triaryl amine-based dual functioned co-adsorbent for highly efficient dye-sensitized solar cells. *J. Mater. Chem.* 2012, 22, 3786−3794.

(23) McNamara, W. R.; Milot, R. L.; Song, H.-e.; Snoeberger, R. C.; III; Batista, V. S.; Schmuttenmaer, C. A.; Brudvig, G. W.; Crabtree, R. H. Water-stable, hydroxamate anchors for functionalization of TiO2 surfaces with ultrafast interfacial electron transfer. *Energy Environ. Sci.* 2010, 3, 917−923.

(24) Brewster, T. P.; Konezny, S. J.; Sheehan, S. W.; Martini, L. A.; Schmuttenmaer, C. A.; Batista, V. S.; Crabtree, R. H. Hydroxamate Anchors for Improved Photoconversion in Dye-Sensitized Solar Cells. *Inorg. Chem.* 2013, 52, 6752−6764.