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A General Strategy to Enhance the Performance of Dye-sensitized Solar Cells by Incorporating Light-harvesting Dye with Hydrophobic Polydiacetylene Electrolyte-blocking Layer

Mekonnen Abebayehu Desta,[a,b,c] Chia-Wei Liao[a] and Shih-Sheng Sun *[a]

Abstract: A unique strategy for effectively suppressing charge recombination and enhancing light harvesting in dye-sensitized solar cells (DSSCs) is demonstrated by designing a new dipolar organic dye functionalized with a diacetylene unit, which is capable of undergoing photoinduced cross-linking reaction to generate a hydrophobic polydiacetylene layer. The polydiacetylene layer serves as not only an electrolyte-blocking layer to effectively block the approaching of the oxidized redox mediator and supress the dark current but also light-harvesting role by efficient energy transfer to the dipolar dyes. A 15% efficiency improvement is achieved from monomer dye (J_{SC} = 13.5 mA/cm^2, V_{oc} = 0.728 V, FF = 0.73, η = 7.17%) to cross-linked dye (J_{SC} = 14.9, V_{oc} = 0.750, FF = 0.74, η = 8.27%) under AM1.5 condition.

Introduction

In the past two and half decades, dye-sensitized solar cells (DSSCs) have received unprecedented attention both in industry and academic research due to their cost effective manufacturing processes and high photon-to-electron conversion efficiencies.[1] A prototype DSSC consists of three components that play key roles toward high power conversion ability; a photosensitizer adsorbed on a nanocrystalline TiO_2 film as the photoanode, a counter electrode and redox electrolytes. Among them, the sensitizers certainly play an important role as they are in charge of light harvesting. Currently, the cell efficiencies (AM 1.5) of single dye-based DSSCs have achieved 11% and higher.[2-4] To further improve the performance of DSSCs in satisfying energy demand, remarkable research efforts focusing on realizing the complex TiO_2/dye/electrolyte interfacial processes of DSSCs have been devoted by designing novel sensitizers, electrolytes combination and other new materials.[5] The power conversion efficiency up to 14% has been achieved with collaborative sensitization.[6]

One of the critical factors for an efficient DSSC is to slow down the charge recombination process between the electrons in the conduction band of TiO_2 with the oxidized redox mediator to suppress the dark current under working condition.[7] Thus, searching for a better way to block charge recombination is essential to the performance of DSSC and is urgently demanding. Several strategies for minimizing such efficiency loss in DSSCs have been reported including the coating of inorganic barrier layers,[8] saccharides,[9] dendrimers,[10] cocktail with co-adsorbents, co-sensitization, and structurally engineered sensitizers; most commonly by introducing of long alkyl chains.[11]

Recently, a polystyryl-based organic sensitizer devised to reduce the charge recombination has been reported.[12] However such modification is effective when the dye is cocktailed with the co-adsorbent CDCA. Structural tuning on the hydrophobic side chains of such system to limit the use of co-adsorbent and optimization for satisfactory efficiency could be quite challenging

In this work, therefore, we report a unique structural modification by introducing the polydiacetylene (PDA) unit, which in principle could be applied to any sensitizer to achieve high cell efficiency without changing the current working condition. The multiple applications of PDA system from the development of organic films to immobilization of molecules[13] inspired us to design a novel dipolar organic dye functionalized with diacetylene unit in the peripheral position of the donor moiety, where it can potentially undergo photopolymerization under UV irradiation to form PDA blocking layer. The resulting cross-linked hydrophobic layer in the exterior dye ensemble would form a shield that effectively blocks the approaching of the oxidized redox mediator and reduces the dark current. Moreover the conjugated network of PDA provides an additional light-harvesting function that can enhance the photocurrent generation by efficient energy transfer to the dipolar dyes.

Results and Discussion

Synthesis

The synthetic routes for preparing the monomer, **MA164**, and the model compound (**12**) are depicted in Scheme 1. The synthesis began with commercially available 4-iodotoluene (**1**). 1-(bromomethyl)-4-iodobenzene (**2**)[14] and (4-(4-iodophenyl)but-1-yn-1-yl)trimethylsilane (**3**)[15] were synthesized with a slight modification of the reference procedures. Compound **9** was synthesized through a series of palladium(II) catalyzed Buchwalde−Hartwig amination, Suzuki-Miyaura borylation, Suzuki-Miyaura coupling reaction with 5,8-dibromo-2,3-diphenylquinoxaline, and desilylatation and in-situ bromination, and Cadiot-Chodkiewicz coupling with 4-methylpent-1-yne.

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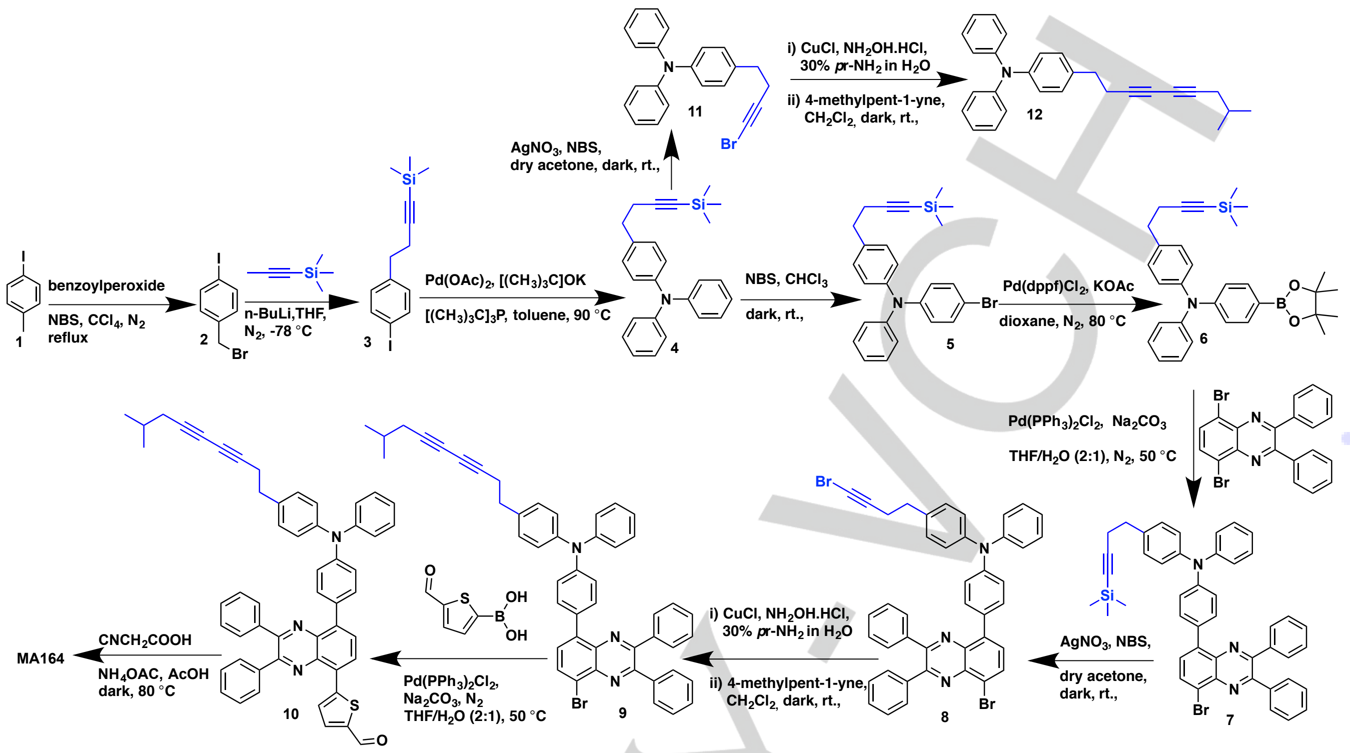

Scheme 1. Synthesis of diacetylene-based organic dye (**MA164**) and the model compound **12**

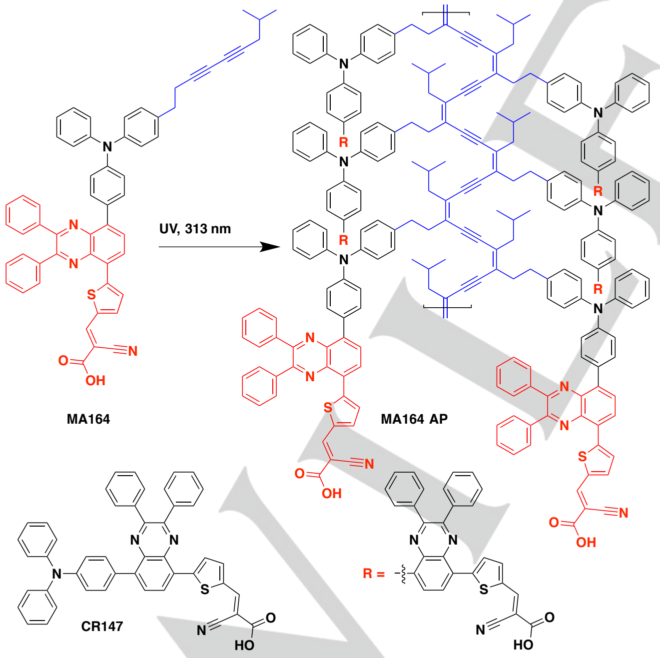

Figure 1. Molecular structures of the diacetylene monomer **MA164**, portion of cross-linked assemblies **MA164 AP**, and the reference dye **CR147**

Subsequently, Suzuki-Miyaura coupling reaction of compound **9** with (5-formylthiophen-2-yl)boronic acid followed by a Knoevenagel condensation with cyanoacetic acid in the presence of ammonium acetate yielded the target sensitizer **MA164**. All the intermediates and final compounds were fully characterized by using ^{1}H and ^{13}C NMR spectroscopy as well as high-resolution mass spectrometry (HRMS). The data were all consistent with the proposed molecular structures.

Optical and electrochemical properties

Figure 1 illustrates the molecular structures and portion of the cross-linked assemblies of the sensitizers. It is known that the diacetylene derivatives undergo photo-polymerization in solution through UV irradiation to produce a conjugated PDA network with only minimal structural rearrangements.[16] The resulting conjugated PDA networks often absorb light in the visible spectral region.[17] Figure 2 shows the UV-vis absorption spectra of **MA164** recorded in DMF and the cross-linked sensitizer, **MA164 AP**, after 1 hour UV irradiation of **MA164**. The corresponding data are summarized in Table 1. Two distinct bands from 400 to 600 nm were observed for both dyes. The band located at shorter wavelength is attributed to the π–π* transition and the other at longer wavelength is attributed to the internal charge transfer transition. Notable molar extinction coefficient enhancement of the absorption between 375 to 500 nm was observed upon formation of the cross-linked D-A-π-A structure owing to the extended π conjugation in PDA moiety. A similar absorption enhancement in the visible region was observed for a model compound (**12**) with diacetylene functionalized TPA-donor after photopolymerization (Figure S1).

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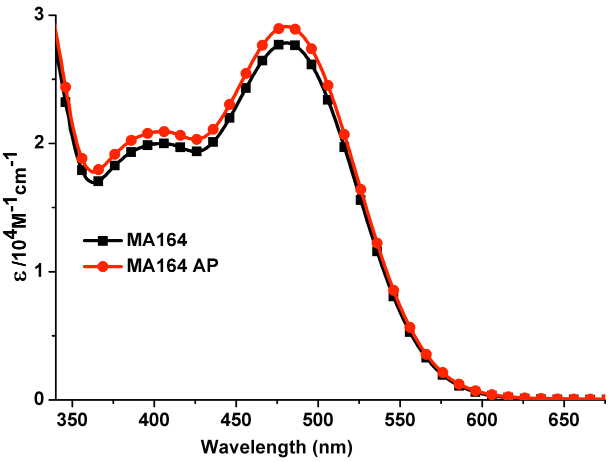

Figure 2. Absorption spectra of the diacetylene monomer **MA164** and the cross-linked **MA164** after photopolymerization (**MA164 AP**).

Table 1. Optical and electrochemical data of **MA164** and **MA164 AP**

Dye	λ_{abs} nm (10^4 $M^{-1}cm^{-1}$)[a]	E (S^+/S) V[a]	$E_{0\text{-}0}$ V[b]	E (S^+/S^*) V[c]	E_{gap} V[d]
MA164	406 (2.00), 481 (2.78)	1.09	2.22	-1.13	0.63
MA164 AP	405 (2.10), 481 (2.91)		-	-	-

[a] Data were measured in DMF solution. [b] $E_{0\text{-}0}$ value was estimated from the intersection of the normalized absorption and emission spectra. [c] E (S^+/S^*) was calculated from E (S^+/S) – $E_{0\text{-}0}$. [d] Energy gap between the excited-state oxidation potential and TiO_2 conduction band edge.

To further confirm the formation of cross-linked dye assemblies upon photoirradiation and the effect on the electrode surface, the diacetylene monomers adsorbed on the TiO_2 surface were subjected to UV-irradiation at room temperature. After one-hour UV-irradiation, the cross-linked dye assemblies were desorbed from TiO_2 and the molecular weight distribution was determined by gel permeation chromatography (GPC). The GPC analysis revealed that the cross-linked dye assemblies contain predominant hexamers with a narrow polydispersity index (M_w/M_n) of 1.02. The hydrophobicity of the monomer dyes and the cross-linked dye assemblies coated on a 12 µm TiO_2 film were evaluated by the water contact angle measurements. The static contact angle values averaged out of 10 measurements were found to be 127° and 134° for monomer dyes and the cross-linked dye assemblies, respectively, which confirms the enhancement of hydrophobicity of TiO_2 film upon photoinduced cross-linking of the monomer dyes.

Table 1 summarizes the photophysical and electrochemical data of all dyes investigated in this work. It is clear that both driving forces for charge injection from photoexcited dyes to the conduction band of TiO_2 as well as the dye regeneration from redox mediators to oxidized dyes are thermodynamic feasible.[18]

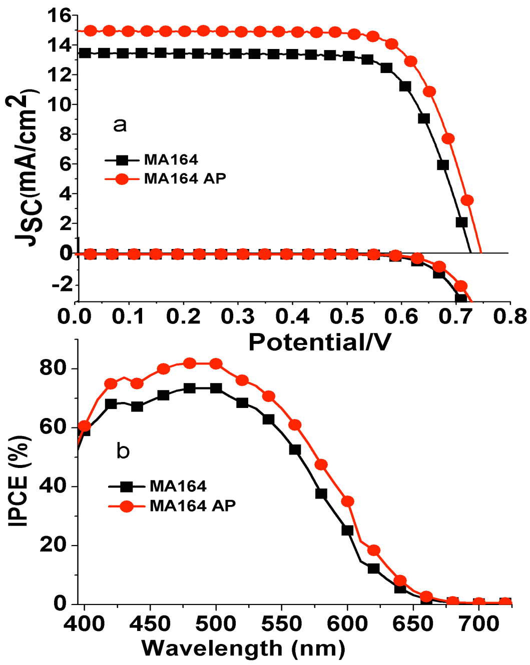

Figure 3. a) Photocurrent-voltage curves with DSSCs based on the diacetylene monomer **MA164** and the cross-linked **MA164 AP** obtained from the same cell, under illumination and in the dark. b) The IPCE (%) plots.

Table 2. DSSC performance parameters of dyes[a]

Dye	J_{SC}[mAcm^{-2}]	V_{OC}[V]	FF	η (%)
MA164	13.5	0.728	0.73	7.17
MA164 AP	14.9	0.750	0.74	8.27
CR147	13.6	0.711	0.73	7.05
N719	14.9	0.797	0.72	8.41

[a] Cells composed of 12 µm thick transparent TiO_2 layer with a scattering layer 4 µm in thickness. Working area of 0.20 cm^2. Electrolyte: SOLARONIX, Iodolyte HI-30. Dye bath: 0.3 mM dye in dichloromethane.

Photovoltaic performance

The DSSCs with diacetylene monomer **MA164** and cross-linked **MA164 AP** as the sensitizers were fabricated and subjected to the performance measurements. The devices with **N719** and **CR147** dyes[19] were also prepared as references for comparison. The photovoltaic performance parameters of all the devices tested under standard conditions (AM 1.5 G, 100 mW/cm^2) are collected in Table 2.

Figure 3a shows the photocurrent-voltage (J-V) plots under illumination and in the dark. The **MA164** sensitized cell gave a J_{SC} of 13.5 mAcm^{-2}, a V_{OC} of 0.729 V, and a fill factor (FF) of 0.73, which correspond to an overall conversion efficiency (η) of 7.17%. Remarkably, the cell sensitized with cross-linked **MA164 AP** generated from post UV treatment of **MA164** adsorbed on TiO_2 gave a J_{SC} of 14.9 mAcm^{-2}, a V_{OC} of 0.75 V, and a FF of

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0.74, which correspond to an efficiency of 8.27%. Under the same conditions, the **CR147** sensitized cell gave a J_{SC} of 13.6 mAcm^{-2}, a V_{OC} of 0.711 V, and a FF of 0.73, which correspond to η = 7.05%. The most striking feature is that the DSSCs based on the cross-linked dye exhibited higher V_{OC} and J_{SC} values than both the diacetylene monomer **MA164** and the reference dye **CR147**. A significant improvement in the incident monochromatic photon-to-current conversion efficiency (IPCE) was observed in the cell photosensitized by the cross-linked **MA164 AP** in the entire visible region (Figure 3b). The effective energy transfer from the PDA network to dipolar dyes, which accounts for the photocurrent enhancement, was confirmed by the fluorescence titration experiment as shown in Figure S3.

Generally, an increase in V_{OC} can be achieved by an upward shift of the conduction band edge of TiO_2 or suppression of charge recombination between the injected electrons in TiO_2 and the oxidized redox species.[20] Charge extraction experiments were employed to measure the charge and electron density at the TiO_2 electrode as a function of voltage. The results are depicted in Figure 4a. The higher charge accumulation in the cell sensitized by cross-linked **MA164 AP** indicates a 60 mV downward shift of the TiO_2 conduction band edge with respect to the cell sensitized by **MA164**. The result of downward shift is indeed in contrast to the increase in the V_{oc} of cell sensitized by cross-linked **MA164 AP**.

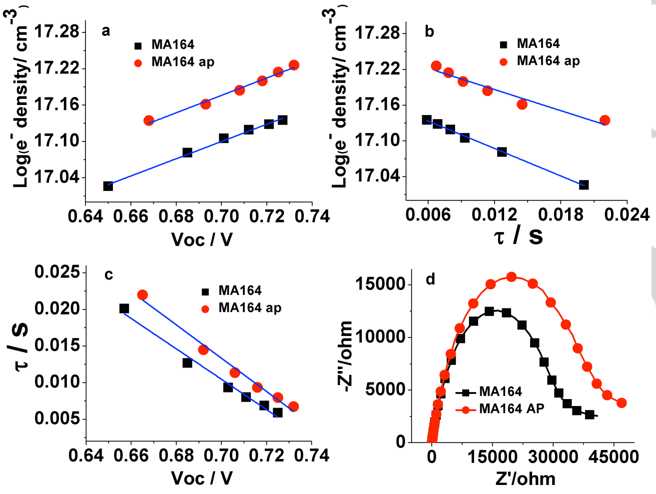

Figure 4. a) V_{OC} as a function of the charge density of DSSCs based on charge extraction technique. b) V_{OC} as a function of Electron lifetime c) Electron lifetime against the electron density of DSSCs based on IMVS studies. (D) ESI (Nyquist plots) of DSSCs measured in the dark under 0.45 V bias.

In order to rationalize the enhancement of the photovoltage of cross-linked **MA164 AP** sensitized DSSC, the electron recombination losses from the TiO_2 to the electrolyte was examined by ploting the charge density at open circuit potential as a function of electron lifetime (Figure 4b). At a fixed charge density (Q), the electron lifetime for the cross-linked **MA164 AP** is 10-fold higher than the diacetylene monomer **MA164**, clearly indicative of more effective suppression of the dark current in the cross-linked **MA164 AP** sensitized cell as a result of efficient shielding effect of cross-linked hydrophobic PDA layer from the approaching of oxidized redox mediators.

Additional evidence for the slower charge recombination kinetics is provided by the plots of the electron lifetimes as a function of V_{OC} measured by the intensity modulated photovoltage spectroscopy as shown in Figure 4c. At fixed V_{OC}, the electron lifetime of the cell sensitized by cross-linked **MA164 AP** is longer than that of the monomer **MA164** indicative of suppressed charge recombination in **MA164 AP**-based cell, which is consistent with the observed V_{OC}. The cross-linked chain could also capable of suppressing the dye aggregation and generate poly-anchoring supramolecular assemblies on the TiO_2 surface, which is beneficial for long-term stability.

Further support for the effective suppression of the dark current is illustrated in Figure 4d by electrochemical impedance spectra (EIS) (diacetylene-based **MA164** vs. polydiacetylene-based **MA164 AP**) generated from the same cell. The Nyquist plots under dark condition displayed larger electron recombination resistance (R_{rec}) in the cell sensitized with cross-linked **MA164 AP** than that with diacetylene monomer **MA164**. The results suggest that the electron recombination rate is relatively slower for the polymer dyes compared to the monomer Thus, the cross-linked hydrophobic shell effectively inhibits back electron transfer from TiO_2 to I_3^- ions and results in a higher V_{OC}. The characteristic frequency peaks (inverse of the recombination lifetime in the TiO_2 film) in the Bode phase shown in Figure S4 shifted to a lower frequency for **MA164 AP** based device.

Figure 5 shows the long-term stability test for DSSCs based on **MA164** and **CR147** under continuous light soaking (100 mW/cm^2) at 70 °C. The PCE in **MA164** maintained above 96% of the initial value after 600 h light soaking at a harsh condition while **CR147** started decreasing after 500 h, demonstrating the merit of crosslinking on the long-term stability of the devices under long-term photoirradiation.

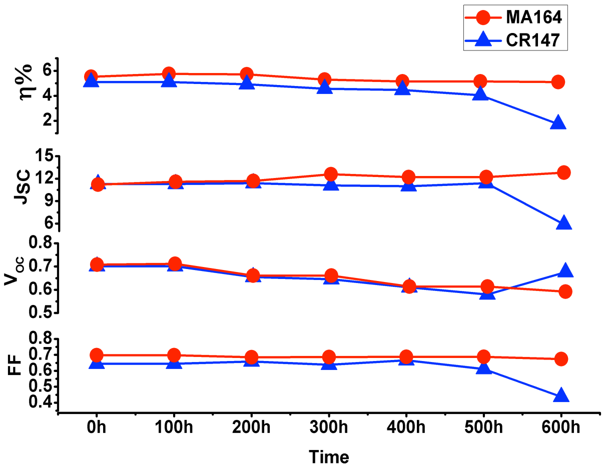

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Figure 5. Long-term stability test for DSSCs based on **MA164** and **CR147** and electrolyte (SOLARONIX, Iodolyte Z-150) under light soaking (100 mW/cm^2) at 70 °C.

Conclusions

A new organic dye with photoinduced cross-linking shell as the hydrophobic electrolyte-blocking layer has been designed and successfully synthesized. The resulting polydiacetylene network is demonstrated to be an effective strategy for blocking the oxidized redox mediator approaching the TiO_2 surface and thus can be applied in any sensitizers for DSSCs to achieve higher V_{OC} as well as J_{SC} by minimizing the charge recombination and providing additional light harvesting. Up to 15% efficiency enhancement for cross-linked **MA164 AP** sensitized cell is achieved. In addition, the cross-linked diacetylene network is believed to provide enhanced stability due to the multiple anchoring groups in each dye assemblies. The current work provides a proof-of-concept structural design of efficient organic sensitizers and could in principle be applied to many other sensitizers.

Experimental Section

General remarks: All chemical reagents were purchased from commercial sources and used without further purification unless specified. All solvents used were carefully dried and freshly distilled according to standard laboratory practices. All manipulations were carried out under inert nitrogen atmosphere. All reactions were monitored using pre-coated TLC plates and purified by column chromatography. Column chromatography was performed on silica (60-120 mesh). Absorption and fluorescence spectra were obtained with a Varian Cary 300 UV-vis spectrophotometer and a Jobin-Yvon FL3-21 Horiba fluorolog fluorimeter, respectively. ^{1}H and ^{13}C NMR spectra were recorded on a Brüker AVANCE III 400 MHz, Ultra Shield 400 MHz instruments. The HRMS were conducted on an Applied Biosystems 4800 Proteomics Analyzer equipped with an Nd/YAG laser (335 nm) operating at a repetition rate of 200 Hz. Cyclic voltammetry (CV) were carried out on CHI Model 621B Electrochemical Analyzer with a three-electrode configuration consisting of a platinum working electrode, a platinum wire auxiliary electrode, and a non-aqueous $Ag/AgNO_3$ reference electrode. The experiments were performed in degassed DMF containing 0.1 M tetrabutylammonium hexafluorophosphate and 1.0 mM of the analyte. The potentials were quoted against the ferrocene/ferrocenium (Fc/Fc^+) redox couple as the internal standard and converted to NHE by addition of 0.63 V. Contact angles were measured by the sessile drop method using a GBX Digidrop contact angle meter equipped with a CCD camera. The reported experimental values are averages of at least five measurements performed on different parts of each TiO_2 coated sample. The static contact angle values are the average of 10 measurements and the drop size as small as (1 μL); hence the gravitational force is neglected. Photocurrent-voltage characteristics of the DSSCs were recorded with LSQE-IV Class AAA solar simulator (SAN-EL ELECTRIC Co., Ltd.) at a light intensity of 100 mW/cm^2 calibrated by an Oriel reference solar cell (Oriel 91150, Newport®). Electrochemical impedance spectra (EIS) were recorded for DSSCs in dark at −0.45 V bias potential at room temperature. Intensity-modulated photovoltage spectroscopy (IMVS) was carried out on the electrochemical workstation (Zahner, Zennium) with a frequency response analyzer under an intensity modulated (10 to 300 W m^{-2}) white light emitting diode. The frequency range was set from 1 kHz to 100 mHz.

Device Fabrication and Photopolymerization

Fluorine-doped tin oxide (FTO) glass plates were pre-cleaned sequentially by sonicating in acetone bath, detergent, DI-water and isopropanol at room temperature, each for 15 min. The FTO sheets were subsequently pretreated with 40 mM Aquarius $TiCl_4$ solution at 70 °C for 60 min then washed with DI-water and ethanol. Afterwards, the coated FTO substrate was heated at 480 °C for 40 min on which the 12 μm transparent nanocrystalline TiO_2 layer in direct contact with the FTO substrate was deposited using a doctor-blade technique. Then, the TiO_2 films were heated at 480 °C for 40 min. The processes was repeated to introduce 4 μm thickness of light scattering TiO_2 particle. The thickness of TiO_2 films was measured by veeco dektak 150 surface profilometer. The annealed TiO_2 electrodes were immersed in DCM containing 0.3 mM photosensitizer (**MA164**, **CR147** and **N719**) for 24 h at room temperature. The active area of all DSSCs is 0.20 cm^2. Pt counter electrodes were prepared by spreading a droplet of 5 mM H_2PtCl_6 in ethanol on top of a FTO substrate, wiped with smooth paper to make it uniform and was heated at 500 °C for 60 min for deposition of platinum. The two electrodes were sealed with 30 mm thick thermoplastic Surlyn (Solaronix) and the redox electrolyte (Iodolyte HI-30 purchased from SOLARONIX) was injected through a hole drilled in the counter electrode. The two holes on the counter electrode were sealed once again with 30 mm thick Surlyn and microscope slide. After recording all the performance measurements based on the monomeric **MA164**, the assembled cell were subjected into a photochemical reactor PR-2000 to generate its corresponding cross-linked **MA164 AP**. All the performance measurements of **MA164** and **MA164 AP** were generated from the same cells.

Long-term stability data of a DSSC based on **MA164** and **CR147** and electrolyte (SOLARONIX, Iodolyte Z-150) under the irradiance of AM 1.5 G full sun visible light soaking at 70 °C. Atlas Suntest CPS+ Xenon Test Instrument use air-cooled xenon lamps to simulate UV and visible solar radiation. The cells were covered with a black mask with an aperture size of 0.25 cm^2 and UV light filter glass. Prior to measurements the sensitized cells were cooled to room temperature.

Synthesis

1-(bromomethyl)-4-iodobenzene (2). *N*-bromosuccinimide (3.6 g, 20.22 mmol) and dibenzyol peroxide (0.14 g, 0.4 mmol) was added to a solution of 4-iodotoluene (**1**) (4.06 g, 18.6 mmol) dissolved in 40 mL of anhydrous carbon tetrachloride and refluxed overnight. Afterwards the reaction mixture was filtered and the solvent removed under reduced pressure to give a residual solid, which was purified by column chromatography using hexane/DCM as eluent affording the target product as an off-white solid (4.7 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm, 7.68 (d, 2H, *J* = 8.4 Hz), 7.13 (d, 2H, *J* = 8.4 Hz), 4.42 (s, 2H).

(4-(4-iodophenyl)but-1-yn-1-yl)trimethylsilane (3). A two-necked round bottom flask charged with trimethyl(prop-1-yn-1-yl)silane (2.94 mL, 19.8 mmol) in THF (30 mL) was cooled to -78 °C and kept under nitrogen atmosphere. Then *n*-BuLi (13.6 mL, 21.8 mmol) was added drop-wise and the resulting solution was slowly allowed to warm to -20 °C in 1 h. A solution of compound **2** (5 g, 15.2 mmol) in THF (20 mL) was then added slowly via syringe and the reaction mixture was allowed to stir at room temperature for 12 h. The reaction was quenched with water (100 mL), extracted with DCM (3 × 50 mL), and dried over anhydrous $MgSO_4$. The filtrate was concentrated and flashed with silica gel chromatography

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(hexane/DCM) to afford a light yellow oil (4.1 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm, 7.62 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 8.1 Hz, 2H), 2.77 (t, *J* = 7.4 Hz, 2H), 2.48 (t, *J* = 7.4 Hz, 2H), 0.1 (s, 9H) . ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm, 140.1, 137.2, 130.6, 106.0, 91.5, 85.7, 34.4, 21.9, 0.04.

***N,N*-diphenyl-4-(4-(trimethylsilyl)but-3-yn-1-yl)aniline (4).** Compound **3** (4.0 g, 12.18 mmol), diphenylamine (1.72 g, 10.15 mmol), palladium acetate (0.109 g, 0.49 mmol), toluene (40 mL), tri-*tert*-butylphosphine (0.124 g, 0.61 mmol) and sodium *tert*-butoxide (3.5 g, 36 mmol) were placed in a two-necked round bottom flask under N_2 atmosphere and the mixture was heated at 90°C for 16 h. The reaction solution was cooled to room temperature and poured into water (150 mL). The mixture was extracted with CH_2Cl_2. Solvent was removed under reduced pressure. The resulting light yellowish oil was purified by column chromatography (silica gel, hexane/DCM) to give compound 4 as a dark green, viscos oil (3.75 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm, 7.23 (t, *J* = 7.8 Hz, 4H), 7.11-7.06 (m, 6H), 7.03-6.98 (m, 4H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.50 (t, *J* = 7.6 Hz, 2H), 0.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm, 147.9, 146.1, 135.2, 129.4, 129.1, 124.4, 123.8, 122.4, 106.7, 85.4, 34.4, 22.2, 0.1. HRMS (FAB) m/z: $[M+H]^+$ calcd for $C_{25}H_{27}NSi$, 369.1907; found, 369.1898.

4-bromo-*N*-phenyl-N-(4-(4-(trimethylsilyl)but-3-yn-1-yl)phenyl)aniline (5). *N*-bromosuccinimide (1.52 g, 8.6 mmol) was added at once in dark to a solution of compound **4** (3 g, 8.11 mmol) dissolved in 30 mL chloroform and stirred at room temperature for 12 h. The mixture was poured into water (100 mL) and extracted with DCM (3 × 50 mL). The combined organic layers were washed with water and dried over anhydrous sodium sulfate. Solvent was removed under reduced pressure. The resulting viscos oil was purified by column chromatography (silica gel, hexane/DCM) to give compound 5 (3.02 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm, 7.31-7.24 (m, 4H), 7.22-7.05 (m, 7H), 7.01-6.91 (m, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.50 (t, *J* = 7.6 Hz, 2H), 0.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 147.4, 147.1, 145.5, 135.8, 132.1, 129.5, 129.3, 124.8, 124.6, 124.2, 123.0, 114.4, 106.6, 85.5, 34.4, 22.2, 0.1. HRMS (FAB) m/z: $[M+H]^+$ calcd for $C_{25}H_{26}BrNSi$, 447.1012; found, 447.1014.

***N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N-(4-(4-(trimethylsilyl)but-3-yn-1-yl)phenyl)aniline (6).** Compound **5** (3 g, 6.69 mmol), bis(pinacolato)diborane (2.0 g, 8 mmol), (dppf)$PdCl_2$ (0.25 g, 0.34 mmol), and KOAc (1.97 g, 20.0 mmol) were kept in a two necked-round bottom flask under N_2 atmosphere and dissolved in 30 mL degassed dioxane. The reaction mixture was stirred at 80 °C for 24 h. Afterwards the solution was cooled to room temperature, poured into 100 mL water and extracted with DCM (3x 50 mL). The organic phase was collected, dried over magnesium sulfate and evaporated the solvent. The residue was subjected to silica gel column chromatography to obtain the desired product as light green solid (2.22 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm, 7.66 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 7.10 (t, *J* = 11 Hz, 4H), 7.04-6.99 (m, 5H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.50 (t, *J* = 7.6 Hz, 2H), 1.33 (s, 12H), 0.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm, 150.7, 147.5, 145.6, 135.8, 129.5, 129.3, 125.1, 124.8, 123.2, 121.5, 106.7, 85.4, 83.5, 34.5, 24.9, 22.2, 0.10. HRMS (FAB) m/z: $[M+H]^+$ calcd for $C_{31}H_{38}BNO_2Si$, 495.2759; found, 495.2752.

4-(8-bromo-2,3-diphenylquinoxalin-5-yl)-*N*-phenyl-*N*-(4-(4-(trimethylsilyl)but-3-yn-1-yl)phenyl)aniline (7). A degassed solution of THF (20 mL) and H_2O (10 mL) was added to a flask containing the compound **6** (1.5 g, 3 mmol), 5,8-dibromo-2,3-diphenylquinoxaline (1.33 g, 3 mmol), Na_2CO_3 (1.6 g, 15 mmol), and $Pd(PPh_3)_2Cl_2$ (0.105 g, 0.15 mmol). The resulting mixture was stirred for 6 h at 50°C under a N_2 atmosphere. The mixture was extracted with DCM, dried over $MgSO_4$, and purified by column chromatography with hexane/DCM as the eluent to yield the desired compound 7 as a yellow solid (1.51 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm, 8.10 (d, *J* = 7.6 Hz, 1H), 7.72-7.68 (m, 5H), 7.57 (t, *J* = 8 Hz, 2H), 7.40-7.14 (m, 16H), 7.05 (t, *J* = 7.6 Hz, 1H), 2.83 (t, *J* = 7.4 Hz, 2H), 2.51 (t, *J* = 7.6 Hz, 2H), 0.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm, 152.7, 152.4, 147.8, 147.7, 145.8, 139.7, 139.3, 138.7, 138.6, 138.5, 135.7, 133.0, 131.6, 130.9, 130.2, 130.1, 129.5, 129.3, 129.1, 128.3, 128.2, 125.0, 124.7, 123.0, 122.4, 122.2, 106.7, 85.4, 34.5, 29.7, 22.2, 0.10. HRMS (FAB) m/z: $[M+H]^+$ calcd for $C_{45}H_{38}BrN_3Si$, 730.2080; found, 730.2067.

4-(8-bromo-2,3-diphenylquinoxalin-5-yl)-*N*-(4-(4-bromobut-3-yn-1-yl)phenyl)-*N*-phenylaniline (8). A solution of dry acetone (20 mL) containing compound **7** (0.90 g, 1.24 mmol), *N*-bromosuccinimide (0.178 g, 1 mmol), and silver nitrate (63 mg, 0.37 mmol) was stirred at room temperature for 4 h. The solvent was removed in vacuo and the resulting product was dissolved in DCM and passed through a short silica gel column to afford compound **8** as an orange red solid (0.82 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm, 8.10 (d, *J* = 7.6 Hz, 1H), 7.72-7.67 (m, 5H), 7.58-7.56 (m, 2H), 7.57 (t, *J* = 9.2 Hz, 2H), 7.40-7.12 (m, 16H), 7.04 (t, *J* = 7.2 Hz, 1H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.52 (t, *J* = 7.6 Hz, 1H). HRMS (FAB) m/z: $[M+H]^+$ calcd for $C_{42}H_{29}Br_2N_3$, 733.0785; found, 733.0776.

4-(8-bromo-2,3-diphenylquinoxalin-5-yl)-*N*-(4-(8-methylnona-3,5-diyn-1-yl)phenyl)-*N*-phenylaniline (9). CuCl (10.6 mg, 0.11 mmol) was added to a 30% *n*-$BuNH_2$ (5 mL) aqueous solution at room temperature that resulted in the formation of a blue solution immediately. A few crystals of hydroxylamine hydrochloride were added to discharge the blue color. The resulting colorless solution indicated the formation of Cu(I) salt. Subsequently, 4-methylpent-1-yne (264 mg, 3.21 mmol) was added to the solution at room temperature to form a yellow acetylide suspension that was immediately cooled down with an ice-water bath. The solution of compound **8** (0.787 g, 1.07 mmol) in DCM was added at once and the ice bath was removed. After 6 h of stirring at room temperature, the reaction was finished according to TLC. The product was diluted with water and repeatedly extracted with DCM, dried over $MgSO_4$, concentrated with reduced pressure and the crude product was further purified by flash column chromatography on silica gel to afford the title product as an orange red solid (0.64 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm, 8.10 (d, *J* = 8.0 Hz, 1H), 7.71-7.67 (m, 5H), 7.56 (t, *J* = 8.4 Hz, 2H), 7.39-7.12 (m, 16H), 7.05 (t, *J* = 7.6 Hz, 1H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.57 (t, *J* = 7.6 Hz, 2H), 2.16 (d, *J* = 6.4 Hz, 2H), 1.87-1.84 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm, 152.7, 152.4, 147.8, 147.7, 145.9, 139.7, 139.3, 138.7, 138.6, 135.3, 133.0, 131.6, 130.9, 130.2, 130.1, 129.5, 129.3, 129.1, 128.3, 128.2, 125.0, 124.7, 123.0, 122.4, 122.3, 76.5, 68.0, 66.1, 66.0, 34.2, 28.4, 28.0, 25.6, 22.0, 21.5. HRMS (FAB) m/z: $[M+H]^+$ calcd for $C_{48}H_{38}BrN_3$, 736.2322; found, 736.2350.

5-(8-(4-((4-(8-methylnona-3,5-diyn-1-yl)phenyl)(phenyl)amino)phenyl)-2,3-diphenylquinoxalin-5-yl)thiophene-2-carbaldehyde (10). A degassed solution of THF (10 mL) and H_2O (5 mL) was added into a round bottom flask containing compound **9** (0.60 g, 0.814 mmol), 5-formyl-2-thiopheneboronic acids (0.156 g, 1 mmol), Na_2CO_3 (0.53 g, 5 mmol), and $Pd(PPh_3)_2Cl_2$ (0.035 g, 0.05 mmol). The resulting mixture was stirred for 12 h at 50°C under N_2 atmosphere. The mixture was extracted with DCM, dried over anhydrous $MgSO_4$, and purified by column chromatography (gradients of hexane/DCM as the eluent) to yield the desired product as a red solid (0.444 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm, 9.99 (s, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.78-7.73 (m, 5H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.43-7.14 (m, 15H), 7.07 (t, *J* = 7.2 Hz, 1H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.57 (t, *J* = 7.6 Hz, 2H), 2.16 (d, *J* = 6.8 Hz, 2H), 1.87-1.80 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm, 183.3, 151.8, 148.7, 147.9, 147.6,

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145.9, 144.9, 140.6, 138.8, 138.6, 138.4, 137.5, 135.6, 135.4, 131.7, 131.0, 130.3, 130.1, 129.7, 129.3, 129.0, 128.4, 128.2, 126.9, 125.3, 125.1, 124.8, 124.7, 123.2, 123.0, 122.2, 121.9, 110.3, 76.5, 66.1, 66.0, 34.2, 29.7, 28.4, 28.0, 22.0. HRMS (FAB) m/z: $[M+H]^+$ calcd for $C_{53}H_{41}N_3OS$, 768.3043; found, 768.3050.

Synthesis of the diacetylene monomere, MA164. Compound **10** (0.23 g, 0.30 mmol), cyanoacetic acid (0.128 g, 1.5 mmol) and ammonium acetate (0.023 g, 0.30 mmol) was introduced into an aluminum foil covered two necked round bottom flask containing a mixture of glacial acetic acid/THF (5:2, 7 mL) under N_2 atmosphere and heated at 80 °C for 24 h. After cooling, the resulting precipitate was filtered, washed several times with water and a mixture of hexane and DCM. The residue was dried under high vacuum to yield the product as a dark red powder (0.21 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm, 8.4 (s, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.79-7.75 (m, 5H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.44-7.42 (m, 3H), 7.35-7.05 (m, 14H), 2.84 (t, *J* = 7.4 Hz, 2H), 2.57 (t, *J* = 7.4 Hz, 2H), 2.16 (d, *J* = 6.4 Hz, 2H), 1.87-1.80 (m, 1H), 0.99 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm, 167.3, 152.3, 152.1, 150.2, 148.1, 148.0, 147.6, 145.8, 140.9, 138.7, 138.5, 138.1, 138.0, 137.2, 131.7, 130.8, 130.5, 130.1, 129.3, 129.0, 128.9, 128.7, 128.2, 128.0, 126.9, 125.3, 125.1, 124.9, 124.7, 123.2, 122.0, 121.8, 115.8, 96.2, 66.2, 66.0, 34.2, 29.7, 28.4, 28.0, 22.0, 21.5. HRMS (FAB) m/z: $[M+H]^+$ calcd for $C_{56}H_{42}N_4O_2S$, 835.3101; found, 835.3139.

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

[2] S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, B. F. E. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin and M. Grätzel, *Nat. Chem.,* **2014**, 6, 242.

[3] Z. Yao, H. Wu, Y. Li, J. Wang, J. Zhang, M. Zhang, Y. Guo and P. Wang, *Energy Environ. Sci.,* **2015**, 8, 3192.

[4] C. Y. Chen, M. Wang, J. Y. Li, N. Pootrakulchote, L. Alibabaei, C. H. Ngocle, J. D. Decoppet, J. H. Tsai, C. Grätzel, C. G. Wu, S. M. Zakeeruddin and M. Grätzel, *ACS Nano,* **2009**, 3, 3103.

[5] a) A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem. Rev.,* **2010** , 110, 6595; b) C.-P. Lee, Ryan Y.-Y. Lin, L.-Y. Lin, C.-T. Li, T.-C. Chu, S.-S. Sun, J.-T. Lin and K.-C. Ho, *RSC Adv.,* **2015**, 5, 23810.

[6] K. Kakiage, Y. Aoyama, T. Yano, K. Oya, J. Fujisawa and M. Hanaya, *Chem. Commun.,* **2015**, 51, 15894.

[7] a) B. C. O'Regan, S. Scully, A. C. Mayer, E. Palomares and J. Durrant, *J. Phys. Chem. B,* **2005**, 109, 4616; b) Z. Zhang, S. M. Zakeeruddin, B. C. O'Regan, R. Humphry-Baker and M. Grätzel, *J. Phys. Chem. B,* **2005**, 109, 21818.

[8] a) E. Palomares, J. N. Clifford, S. A. Haque, T. Lutz and J. R. Durrant, *Chem. Commun.,* **2002**, 1464; b) E. Palomares, J. N. Clifford, S. A. Haque, T. Lutz and J. R. Durrant, *J. Am. Chem. Soc.,* **2003**, 125, 475.

[9] a) S. Handa, S. A. Haque and J. R. Durrant, *Adv. Funct. Mater.,* **2007**, 17, 2878; b) H. Choi, S. Kang, J. Ko, G. Gao, H. Kang, M.-S. Kang, Md. K. Nazeeruddin and M. Grätzel, *Angew. Chem. Int. Ed.,* **2009**, 48, 5938.

[10] a) N. Satoh, T. Nakashima and K. Yamamoto, *J. Am. Chem. Soc.,* **2005**, 127, 13030; b) T. Nakashima, N. Satoh, K. Albrecht and K. Yamamoto, *Chem. Mater.,* **2008**, 20, 2538.

[11] a) N. Koumura, Z.-S. Wang, S. Mori, M. Miyashita, E. Suzuki and K. Hara, *J. Am. Chem. Soc.,* **2006**, 128, 14256; b) S. Ito, H. Miura, S. Uchida, M. Takata, K. Sumioka, P. Liska, P. Comte, P. Pechy and M Grätzel, *Chem. Commun.,* **2008**, 41, 5194; c) Z.-S. Wang, N. Koumura, Y. Cui, M. Takahashi, H. Sekiguchi, A. Mori, T. Kubo, A. Furube and K. Hara, *Chem. Mater.,* **2008**, 20, 3993; d) K.-F. Chen, Y.-C. Hsu, Q. Wu, M. C.-P. Yeh, S-S. Sun, *Org. Lett.,* **2009**, 11, 377; e) K.-F. Chen, C.-W. Chang, J.-L. Lin, Y.-C. Hsu, Q. Wu, M. C.-P. Yeh, C.-P. Hsu, S-S. Sun, *Chem. Eur. J.,* **2010**, 16, 12873; f) Z. Ning, Y. Fu and H. Tian, *Energy Environ. Sci.,* **2010**, 3, 1170; g) J. Xu, H. Wu, X. Jia and D. Zou, *Chem. Commun.,* **2012**, 48, 7793; h) C. Lan, H. Wu, T. Pan, C. Chang, W. Chao, C. Chen, C. Wang, C. Lin and E. W. Diau, *Energy Environ. Sci.,* **2012**, 5, 6460; i) S. Qu, C. Qin, A. Islam, Y. Wu, W. Zhu, J. Hua, H. Tian and L. Han, *Chem. Commun.,* **2012**, 48, 6972; j) R. Agosta, R. Grisorio, L. De Marco, G Romanazzi, G. P. Suranna, G. Gigli and M. Manca, *Chem. Commun.,* **2014**, 50, 9451; k) X. Sun, Y.-Q. Wang, X. Li, H. Ågren, W.-H. Zhu, H. Tian and Y.-S. Xie, *Chem. Commun.,* **2014**, 50, 15609.

[12] J.-Y. Su, C.-H. Tsai, S.-A. Wang, T.-W. Huang, C.-C. Wu and K.-T. Wong, *RSC Adv.,* **2012**, 2, 3722.

[13] a) T. Kim, R. M. Crooks, M. Tsen and L. Sun, *J. Am. Chem. Soc.,* **1995**, 117, 3963; b) H. Menzel, M. D. Mowery, M. Cai and C. E. Evans, *Adv. Mater.,* **1999**, 11, 131; c) D. H. Charych, J. O. Nagy, W. Spevak and M. D. Bednarski, *Science,* **1993** , 261, 585; d) J. Tsibouklis, *Adv. Mater.* **1995**, 7, 407; e) N. Fujita, Y. Sakamoto, M. Shirakawa, M. Ojima, A. Fujii, M. Ozaki and S. Shinkai, *J. Am. Chem. Soc.,* **2007**, 129, 4134.

[14] M. I. Mangione and R. A. Spanevello, *Macromolecules,* **2013**, 46, 4754.

[15] J. A. Bergman, K. Hahne, J. Song, C. A. Hrycyna, and R. A. Gibbs, *ACS Med. Chem. Lett.,* **2012**, 3, 15.

[16] a) B. Tieke, G. Wegner, D. Naegele and H. Ringsdorf, *Angew. Chem., Int. Ed.,* **1976**, 15, 764; b) B. Tieke, H.-J. Graf, G. Wegner, B. Naegele, H. Ringsdorf, A. Banerjie, D. Day and J. B. Lando, *Colloid Polym. Sci.,* **1977**, 255, 521.

[17] a) D. J. Ahn and J.-M. Kim, *Acc. Chem. Res.,* **2008**, 41, 805; b) C. Zhu, L. Liu, Q. Yang, F. Lv and S. Wang, *Chem. Rev.,* **2012**, 112, 4687; c) B. Yoon, S. Lee and J.-M. Kim, *Chem. Soc. Rev.,* **2009**, 38, 1958; d) X. Sun, T. Chen, S. Huang, L. Li and H. Peng, *Chem. Soc. Rev.,* **2010**, 39, 4244.

[18] A. Hagfeldt and M. Grätzel, *Chem. Rev.,* **1995**, 95, 49.

[19] a) S.-R. Li, C.-P. Lee, H.-T. Kuo, K.-C. Ho and S.-S. Sun, *Chem. Eur. J.,* **2012**, 18, 12085; b) S.-R. Li, C.-P. Lee, P.-F. Yang, C.-W. Liao, M. M. Lee, W.-L. Su, C.-T. Li, H.-W. Lin, K.-C. Ho and S.-S. Sun, *Chem. Eur. J.,* **2014**, 20, 10052; c) S.-R. Li, C.-P. Lee, C.-W. Liao, W.-L. Su, C.-T. Li, K.-C. Ho and S.-S. Sun, *Tetrahedron,* **2014**, 70, 6276; d) C.-T. Li, C.-P. Lee, C.-T. Lee, S.-R. Li, S.-S. Sun, K.-C. Ho, *ChemSusChem,* **2015**, 8, 1244.

[20] M. Xu, M. Zhang, M. Pastore, R. Li, F. D. Angelis and P. Wang, *Chem. Sci.,* **2012**, 3, 976.

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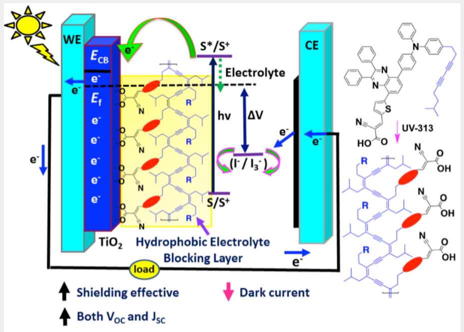

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Page No. – Page No.

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