Efficient Dye-Sensitized Solar Cells with Potential-Tunable Organic Sulfide Mediators and Graphene-Modified Carbon Counter Electrodes

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A new class of organic sulfide mediators with programmable redox properties is designed via density functional theory calculations and synthesized for efficient dye-sensitized solar cells (DSCs). Photophysical and electrochemical properties of these mediators derived from systematical functionalization of the framework with electron donating and withdrawing groups (MeO, Me, H, Cl, CF_3 , and NO_2) are investigated. With this new class of organic mediators, the redox potential can be fine-tuned over a 170 mV range, overlapping the conventional I⁻/I₃-couple. Due to the suitable interplay of physical properties and electrochemical characteristics of the mediator involving electrondonating MeO group, the DSCs based on this mediator behave excellently in various kinetic processes such as dye regeneration, electron recombination, and mass transport. Thus, the MeO derivative of the mediator is identified as having the best performance of this series of redox shuttles. As inferred from electrochemical impedance spectroscopy and cyclic voltammetry measurements, the addition of graphene into the normal carbon counter electrode material dramatically improves the apparent catalytic activity of the counter electrode towards the MeO derivative of mediator, resulting in N719 based DSCs showing a promising conversion efficiency of 6.53% under 100 mW·cm⁻² simulated sunlight illumination.

1. Introduction

Dye-sensitized solar cells (DSCs) have received great attention as the potential next-generation solar electricity sources due to their low cost, easy fabrication, and promising efficiency.^[1] A typical DSC is a sandwich structure device composing of dye-sensitized working electrode (WE), catalyst-coated counter electrode (CE) and a redox-active electrolyte to connect the

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electrodes. Among these components, the function of the electrolyte is to transfer electrons from the counter electrode to the oxidized dyes. Until now, the most common electrolyte in high-performance DSCs uses the I⁻/I₃⁻redox couple.^[2] Based on this redox couple, the highest certified photoelectric conversion efficiency about 11.5% was achieved under AM 1.5 illumination of 100 mW·cm⁻².^[3] However, the I^-/I_3^- redox couple also embraces many critical flaws such as corrosive nature, substantial vapor pressure, visible light absorption and low redox potential, which limit both the practicality and the efficiency of DSCs.^[4] Seeking alternative redox shuttles seems to be a solution to these problems, which is a current research topic of high priority and mainly converges on the one-electron iodine-free redox systems or the multi-electron redox species.

One electron iodine-free redox systems, such as ferrocene/ferr-ocenium,^[5] cobalt complexes,^[6] copper complexes,^[7] nickel complexes,^[8] organic radicals,^[9] co-mediators,^[10] have been widely investi-

gated for DSCs. Most recently, through optimizing the working electrode as well as the photosensitizer, consecutive remarkable efficiency enhancement of DSCs was achieved based on some of the one-electron redox mediators.^[5d,6h-k] However, compared to the I^{-}/I_{3}^{-} redox couple, these one electron iodine-free redox systems exhibit higher recombination rates with photoinjected electrons, which seems to be a general problem for this redox systems.^[2b] Moreover, some of these redox shuttles with cationic charge and large size usually present slow mass transport within the porous semiconductor.[6e,f,h] On the contrary, multi-electron iodine-free redox species, including halogenides,^[11] pseudohalogenides,^[12] and inorganic sulfide redox shuttle,^[13] require to transfer more than one electron for their redox reaction, accordingly resulting in slower recombination kinetics compared with the one-electron ones. In addition, the anionic nature of the most multi-electron redox shuttles could prevent them from electrostatically binding to the titania surface, thus, the mass transport limitation of these redox shuttles also can be negligible in organic solvent. However, problems still exist that limit the feasibility of these redox shuttles replacing the conventional I⁻/I₃⁻ couple, such as the corrosivity



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of halogenides and the inefficient dve regeneration of pseudohalogen redox shuttles. Moreover, due to their almost fixed redox potential, the select and use of photosensitizers become much more important. Recently, more and more interest arises in the organic sulfide species as a promising multi-electron candidate to replace traditional I⁻/I₃⁻ system.^[14] In common with the I^-/I_3^- couple, the reason that the organic sulfide redox shuttles works so well appears to be their intrinsic characteristics of very slow electron recombination, rapid dye regeneration and fast mass transport.^[15] In addition, there are some inherent advantages with these organic mediators that the I^-/I_3^- lacks, such as their nonvolatile, noncorrosive, and colorless properties. But what distinguishes the organic sulfide redox shuttles from I⁻/I₃⁻ mediator is that they could offer diverse derivatization options, which makes their optimization and further elaboration possible.^[14d,16]

To speed up the further development of organic sulfide redox shuttles, on one hand, great effort should be still devoted to exploiting and identifying new promising analogues. On the other hand, intense attempts must be also spent in gaining insight into the relationship between the structure of such mediators and the performance of DSCs. Herein, we report the successful application of a new series of organic sulfide redox shuttles to DSCs based on the dye N719. As shown in Scheme 1, these mediators are composed of the 1-aryltetrazole-5-thiolates (AT-s) and their oxidized dimeric bis(1-aryltetrazol-5-yl) disulfides (BATs). A major attraction of their structures is that the π -system of the tetrazole plane is partly conjugated with the phenyl ring, thus the redox potential as well as physical property could be finely tuned through attaching versatile functional groups to the phenyl unit of the AT⁻/BAT backbone,^[17] which offers us an opportunity for directly probing how the electrochemical and physical properties of such mediators affect DSC kinetics and performance in this paper.

Previous studies have indicated that the main reason that the organic sulfide redox shuttle is still outperformed by the traditional I^-/I_3^- mediator can be attributed to the considerably higher charge-transfer resistance (R_{ct}) at the standard Pt



Scheme 1. Synthetic routes and structures of the organic redox shuttle components. I) NaN₃, H₂O, reflux, 5h; II) 30% aq. H₂O₂, EtOH, 60 °C, 2 h; III) Na₂CO₃, EtOH, 45 °C, 12 h.

CE, which result in the low fill factor (FF) and the low overall efficiency of the device.^[14] Such a serious problem is also encountered by the series of AT⁻/BAT redox shuttles reported here. Fortunately, here we have successfully prepared a cheap and easy-fabricated carbon CE containing graphene, which is identified as a promising CE with high apparent electrocatalytic activity towards this new class of organic mediators.

2. Results and Discussion

2.1. DFT Calculations and Synthesis

Tuning the redox potentials (E_{redox}) of the mediators, in order that DSC kinetics are thermodynamically feasible, is thus of primary importance in designing and developing novel organic sulfide redox couples. DFT calculations are capable of predicting an important characteristic of redox couples–that is, the electron affinity (EA) and the ionization potential (IP), which are directly correlated to the one-electron reduction (E_{red}) and oxidation (E_{ox}) energy, and therefore could provide insight into the E_{redox} of redox couples.^[18] In designing new redox couples for DSCs, these simulated data will be particularly valuable, because of the prospect of identifying promising synthetic targets and thereby requiring significantly less experimental effort.

Using DFT calculations, as shown in Scheme 1, we examined several derivatives of the AT⁻/BAT mediator, with the objective of identifying introducing electron-donating and -withdrawing groups (MeO, Me, H, Cl, CF₃ and NO₂) to the AT⁻/BAT backbone at the *para* position of phenyl unit enabling systematically tuning their E_{redox} . The DFT-calculated EA and IP correlated well with the Hammett constants σ —that is, the electron-donating or -withdrawing ability—of these corresponding aryl substituents. In other words, the mediator modified by the substituent with a more positive σ value possesses a more positive EA and IP, implying a more positive E_{redox} (Table S1 in the Supporting Information). Therefore, six AT ⁻/BAT derivatives 3/4 (Scheme 1) were designed to fulfill our expectation of systematically tuning the E_{redox} of the organic sulfide mediators.

The synthetic routes of the organic redox couples are depicted in Scheme 1 and started commercially from available aryl-isothiocyanate **1a-f**, which were transformed into the corresponding 1-aryltetrazol-5-thiols **2a-f** by cycloaddition reaction with sodium azide in refluxing ethanol.^[19] All the oxidized species, BATs **4a-f**, were prepared by the oxidation of the corresponding mercaptans **2a-f** with hydrogen peroxide, and thiolate forms, AT⁻s **3a-f**, were obtained by the deprotonation of mercaptans with sodium bicarbonate. Structures of the above-mentioned redox couples **3/4** were proved by the combination of ¹H NMR spectroscopy, electrospray ionization mass spectroscopy and elemental analyses. More detailed synthesis and characterization are presented in the Supporting Information.

2.2. Spectral Properties

The electrolytes $E_a \cdot E_f$ were prepared from the series of AT^{-/} BAT redox couples 3a/4a, 3b/4b, 3c/4c, 3d/4d, 3e/4e and





Figure 1. Simulated adsorption spectra of organic redox couple (E_a-E_f) and I^-/I_3^- electrolytes in a 12-µm-thick mesoporous photoelectrode (with the porosity around 0.3), which was calculated from the practical adsorption spectra for 25-µm-thick layers of the different electrolytes with a correction coefficient of 0.15.

3f/**4f**, respectively. All of these electrolytes consisted of 0.4 M of the reduced species, 0.05 M of the oxidized species, 0.4 M 18-crown-6, 0.05 M LiClO₄ and 0.5 M 4-*tert*-butylpyridine in acetonitrile. 18-crown-6 was used to significantly increase the solubility of thiolates **3d-f** in acetonitrile. For the purposes of comparison, a standard I⁻/I₃⁻based electrolyte was also prepared with 0.45 M NaI, 0.45 M 18-crown-6, 0.05 M I₂, 0.05 M LiClO₄ and 0.5 M 4-*tert*-butylpyridine in acetonitrile.

The simulated absorption spectra of the organic redox couple (\mathbf{E}_{a} - \mathbf{E}_{f}) and I^{-}/I_{3}^{-} electrolytes in a 12-µm-thick mesoporous photoelectrode are displayed in **Figure 1**. All of the electrolytes \mathbf{E}_{a} - \mathbf{E}_{f} exhibited similar UV-vis absorption spectra, which red-shifted from \mathbf{E}_{a} to \mathbf{E}_{f} with an increase in the electron-with-drawing ability from CH₃O to NO₂ substituents. It is clear that light absorption by the electrolytes \mathbf{E}_{a} - \mathbf{E}_{e} was negligible for $\lambda >$ 380 nm, whereas the **3f**/**4f** based electrolyte \mathbf{E}_{f} absorbed slightly for $\lambda <$ 520 nm. However, compared to the strong absorption of I^{-}/I_{3}^{-} based electrolyte up to 500 nm, considerably less visible light was absorbed by \mathbf{E}_{f} at similar concentration, which in theory should improve the amount of light harvest by the photosensitizer and render better photovoltage and photocurrent in devices.^[14a-c]

2.3. Electrochemical Studies

The $E_{\rm redox}$, as one of the most important parameters of mediator, is not only a decisive factor of the theoretical maximum of open-circuit voltage ($V_{\rm oc}$), but also a main determinant of the dye regeneration and charge recombination in DSCs. To determine the standard $E_{\rm redox}$, E^0 , of the organic mediators **3/4**, cyclic voltammetry measurements were performed with a glassy carbon electrode.

Besides determining the standard redox potential, the voltammogram could as well as allow qualitative assessment of the kinetic (thermodynamic) reversibility of the redox couples. As shown by the cyclic voltammograms of different organic redox couples (Figure S1 and Table S2 in the Supporting Information), The most striking observation was the separations of the anodic



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Figure 2. The standard redox potential (E^0) of different organic redox couples versus Hammett substituent constant σ .

and the cathodic peak potentials, which range from 838 mV for (AT⁻/BAT)–Cl (3d/4d) to 1305 mV for (AT⁻/BAT)–NO₂ (3f/4f). Obviously, the large peak separations imply the redox couples are kinetically irreversible on the glass carbon electrode. As a result, it is not trivial to determine the standard potential from the cyclic voltammograms.^[14d] Under these conditions, the E^0 could be calculated with the Nernst equation from the $E_{\rm redox}$ of an actual electrolyte solution, which measured by potentiometry using a glassy carbon electrode. The potential versus the normal hydrogen electrode (NHE) was calibrated to the ferrocene/ferrocenium (Fc/Fc⁺) couple by introducing a correction of 630 mV.^[20]

Plotting E^0 versus their corresponding Hammett constants σ reveals that there is a good correlation between E^0 and the electron-donating or -withdrawing nature of the aryl substituents (Figure 2), which is in agreement with the predicted trend of the DFT calculation as discussed above. Thereinto, the highest $E_{1/2}$ value of+0.49 V versus NHE has been reached for the 4-nitrophenyl derivative 3f/4f, and the lowest value of +0.32 V for 4-methoxyphenyl derivative 3a/4a. Thus, these results confirm that, via the introduction of different electrondonating and -withdrawing substituents, the $E_{\rm redox}$ of this new class of organic mediators could be fine-tuned over a 170 mV range, overlapping that of the I^{-}/I_{3}^{-} redox couple (+0.35 V vs NHE) (Table S2 in the Supporting Information). To the best of our knowledge, this study is the first example of systematically electronic tuning of multi-electron redox shuttle.^[8b] More importantly, the different redox pair potentials can help us scrutinize the relationship between structures of the redox shuttles and the performance of DSCs, which will be discussed in detail below.

2.4. Initial Screening of Redox Shuttles

To evaluate the influence of AT⁻/BAT redox couples **3**/**4** on DSC performance, both the standard Pt and the normal carbon material with carbon black/graphite mixture (CGM) were adopted as the CEs of DSCs. Due to the varying solubility of the disulfides **4a-f** in acetonitrile, the concentration of the oxidized components in all the electrolytes E_a - E_f was kept low, which resulted in devices with less than optimal performance, but allowed

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Figure 3. *J*–V curves of different electrolytes \mathbf{E}_a - \mathbf{E}_f based DSCs with the CGM CE. The E_{redox} in the inset table is the value vs NHE.

for comparisons in cell performance as a function of mediator structure.

Because of a much lower reduction resistance of the disulfides 4 on CGM CE ($\approx 10 \ \Omega \cdot cm^2$) than on Pt CE ($\approx 800 \ \Omega \cdot cm^2$) (Supporting Information Figure S2), replacement of Pt by CGM produced a considerable increase both in short-circuit current densities (J_{sc}) and *FF* for the DSCs based on the AT⁻/BAT mediators, and therefore a remarkable improvement of the overall energy conversion efficiency (η) from 0.15% – 0.66% to 2.74% – 5.25%, respectively (Supporting Information Figure S3 and Table S3). This implies that CGM is a more suitable catalytic material than Pt for BATs 4 reduction. Thus, unless otherwise stated, all the analytical measurements below were obtained from DSCs with the CGM CE.

As shown in **Figure 3**, there are some noticeable trends in the performances of devices correlating well with electron-donating and -withdrawing nature of the aryl substituents, where use of the mediator functionalized by the substituent with a more negtive Hammett constant σ could produce a higher $J_{\rm sc}$ and FF. As a result, the best efficiency of 5.25% under AM 1.5 illumination of 100 mW · cm⁻² was obtained with **E**_a. Principally, the polar electron-withdrawing groups might have a greater physical or chemical interaction with the dye, resulting in a higher local couple concentration near the TiO₂ photoanode and slower diffusion through the mesoporous TiO₂ network.^[8b] This can partly account for the noticeable trends of $J_{\rm sc}$ and FF as performed here.

2.5. Photoaction Spectra

Photoaction spectra (incident photon to current conversion efficiency, IPCE) is used to estimate J_{sc} and defined as the number of photogenerated charge carriers contributing to the photocurrent per incident photon. Figure 4 presents the IPCEs of DSCs based on the different redox AT⁻/BAT shuttles 3/4 with the CGM CE, and the maximum IPCEs for their DSCs decrease in the trend of 3e/4e (82%) $\geq 3a/4a \approx 3b/4b \approx 3d/4d$ (80%) $\geq 3c/4c$ (78%) >> 3f/4f (60%). These variations in their IPCEs could be ascribed to different rate of dye regeneration, different efficiency of charge collection from the TiO₂ matrix to the external circuit, or some combination of these two processes.^[6f,21]



Figure 4. IPCEs of different electrolytes $\mathbf{E}_{a}\text{-}\mathbf{E}_{f}$ based DSCs with the CGM CE.

The rate of dye regeneration is strongly dependent on the driving force for regeneration, which will be proportional to the energy gaps between the HOMO levels of dyes and the $E_{\rm redox}$ of electrolytes.^[6f,7a,12a,14d] However, as verified by the experiment of IPCE dependence on the reductant concentration (Figure S4 in the Supporting Information), the driving forces for dye N719 regeneration (ca. 0.63–0.8 V) possessed by **3/4** (the HOMO of N719 is 1.12 V vs NHE^[5d]) are high enough and there is not regeneration limited for them, despite their varying $E_{\rm redox}$, which consequently leaves the charge collection efficiency as the main determinant.

The charge collection efficiency is determined by competition between the electron lifetime, τ_n , and the electron transit time, τ_d . A good charge collection efficiency requires a high τ_n and a low τ_d .^[21,22] We therefore performed τ_n and τ_d measurements to study the effects of the structural properties of the mediators on the charge collection efficiency. Since the typical intensity modulated photocurrent spectroscopy (IMPS) results indicated that similar mean τ_d were observed for all the shuttles **3/4** (Figure S5 in the Supporting Information), the values of τ_n measured under illuminated conditions already enable a rather good comparison of the charge collection efficiency.

The injected electron can recombine either with the oxidized species of the redox shuttle or with the photogenerated dye⁺ cation, and both of these two different types of electron recombination losses could be included in the lifetime measured by intensity modulated photovoltage spectroscopy (IMVS) which is an illuminated measurement. However, in cases of 3/4, as confirmed above, the dye⁺ of N719 is regenerated efficiently, so that no significant reaction could be observed between the injected electron and dye+, and thus, the electron lifetimes determined by IMVS should only reflect the electron recombination with oxidized form of the mediator.^[23] To validate this assumption, besides the IMVS measurements, we also performed the applied open-circuit voltage decay (OCVD) technique, which is a dark measurement of the solar cell, and consequently just refers to the electron recombination at the TiO₂/ electrolyte interface.^[24] As displayed in Figure 5, for each of the AT⁻/BAT-based DSCs, the τ_n values obtained by IMVS coincide with those obtained by analysis of the applied OCVD curves (Figure S6 in the Supporting Information),^[24a,25] suggesting the little contribution of the electron recombination with the dye+

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Figure 5. Comparison of the values of τ_n derived from IMVS and that determined by the applied OCVD as a function of extracted charge density (Q_{oc}) for DSCs based on different electrolytes \mathbf{E}_a - \mathbf{E}_{f} .

to the τ_n measured under illuminated conditions and accordingly little to the charge collection efficiency. In other words, the variation of charge collection efficiency as well as the difference in the charge loss time determined by IMVS here should be dominated by reaction of injected electrons with the redox shuttles, but not by the recombination with the dye⁺, which in turn is another indirect indication that dye regeneration is efficient for all these sulfide mediators **3**/4.

Returning to the IMVS results presented in Figure 5, the lifetimes for DSCs based on $E_a\text{-}E_f$ at a given extracted charge density decreased in the order of $E_e \geq E_a \approx E_b \approx E_d \geq E_c >> E_f$. It is clearly that the trend in the electron lifetimes is consistent with their trend in IPCEs. Taken together, all these observations strongly support that it is the electron recombination with the mediator, not regeneration of the dye, that is the significant factor in determining the difference in charge collection efficiency and accordingly in IPCEs for AT⁻/BAT-based DSCs.

2.6. Open-Circuit Voltage

The V_{0c} is determined by the difference between the electron quasi-Fermi level $(E_{\rm F,n})$ in the TiO₂ film under illumination and the *E*_{redox} of redox couple in electrolyte in the dark.^[26] Assuming that the $E_{F,n}$ of electrode is independent of the redox shuttle, the $V_{\rm oc}$ should mirror the increase in $E_{\rm redox}$. As a consequence, one attractive advantage of using this series of redox couples 3/4 in DSCs is that the V_{oc} is expected to be deliberately controlled by carefully tuning their electrochemical potentials through choice of the aryl substituents. However, as shown in the inset table of Figure 3, the trend in $V_{\rm oc}$ is incompletely consistent with this model (i.e., $V_{\rm oc}$ increases with more positive $E_{\rm redox}$). In cases of 3c-e/4c-e functionalized by electron-withdrawing substituents, the $V_{\rm oc}$ increased as their $E_{\rm redox}$ become more positive, indicating Marcus normal-region behavior. On the contrary, concerning 3a-c/4a-c with electron-donating substituents, the V_{oc} increased in the reverse order. The similar phenomenon was also found for a series of Ni^{III}/NiI^V bis(dicarbollide) complexes, as reported by Hupp and co-workers.^[8b]



Figure 6. Extracted charge density as a function of $E_{F,n}$ of the TiO₂ in DSCs based on different electrolytes E_a - E_f .

In fact, the dependence of V_{oc} on the redox energy should be influenced by a number of factors. Besides E_{redox} , the other two most obvious candidates are shifts in the conduction band edge (E_C) of the TiO₂ and differences in the rates of recombination at the TiO₂/electrolyte interface,^[27] both of which are directly influenced by physical and electrochemical characteristics of the redox shuttle.^[11a,28]

Here charge extraction experiments were performed to study the effect of redox shuttle 3/4 on the shifts of $E_{\rm C}$ in TiO₂. As shown in **Figure 6**, $E_{\rm C}$ of the TiO₂ shifted with the redox potential, and its movement direction was directly related to the electron-donating or -withdrawing nature of the substituents. Taking 3c/4c as a reference, the electron-donating substituents MeO and Me induced more negative shifts of $E_{\rm C}$ of TiO₂ as large as about -70 mV for 3a/4a and -40 mV for 3b/4b based DSCs, respectively. By contrast, the electron- withdrawing substituents Cl, CF₃ and NO₂ caused more positive shifts within a relative small range of about +10 mV for 3d/4d and 40 mV for both 3e/4e and 3f/4f, respectively. Then, provided that the shift of E_C is solely responsible for the variation of V_{oc}, regardless of possessing more positive or negative potentials than 3c/4c, all the other AT⁻/BAT mediators will yield predicted V_{oc} enhancements by about 10-50 mV for 3a-b/4a-b and 3d-e/4d-e, and 90 mV for 3f/4f based DSCs, respectively. Actually, compared to that for 3c/4c based DSCs, the net increases in V_{oc} are 35–65 mV for 3a-b/4a-b and 3d-e/4d-e, in addition, the Voc for 3f/4f suffered from an unexpected drop by about 30 mV. Considering that the electron lifetimes for the 3/4-based DSCs decrease in the order of $3e/4e \ge 3a/4a \approx 3b/4b \approx 3d/4d \ge 3c/4c >> 3f/4f$, as shown in Figure 5, therefore, we speculate that the ~2-fold increase in lifetime observed for 3a-b/4a-b and 3d-e/4d-e compared to 3c/4c could account for their additional 10-25 mV of $V_{\rm oc}$ enhancements, on the other hand, the additional drop of $V_{\rm oc}$ by about -120 mV for 3f/4f based DSCs could be attributed to a ≈20-fold decreased lifetime relative to 3c/4c based DSCs.

The above results clearly show that, besides the $E_{\rm redox}$, the change of $V_{\rm oc}$ for the DSCs involving **3/4** is ascribed to the combined effects of the shift in $E_{\rm C}$ of TiO₂ and different recombination rate at the TiO₂/electrolyte interface. Concomitantly, the

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Figure 7. a) Impedance spectra of electrolyte E_A based symmetric cells using CGM and GGCM CEs with 0 V bias voltage. The equivalent circuit model is shown in the inset. R_s : series resistance; R_{ct} : charge transfer resistance of one electrode; N_{bulk} : Nernst diffusion impedance between the electrodes; CPE: constant phase element of one electrode; N_{pore} : Nernst diffusion impedance within electrode pores; b) Cyclic voltammograms of the GGCM and CGM electrodes in **3a/4a** based electrolyte with a scan rate of 50 mV·s⁻¹.

experimental evidences explain the cause that attaching the electron-donating substituent on the parent AT⁻/BAT mediator at the *para* position of phenyl unit can also induce a $V_{\rm oc}$ enhancement as well as attaching the electron-withdrawing substituent do.

2.7. Optimized Photovoltaic Performance

It is evident that all the six AT⁻/BAT redox shuttles **3/4** show promise as potential efficient mediators for DSCs. The **3a/4a** with MeO group is identified as the best working one. To fabricate DSCs with more optimal performances - that is, higher FF and η - the concentration ratio between the reduced and oxidized species in electrolyte **E**_a was first optimized (Supporting Information Figure S7), and a final electrolyte **E**_A containing a relative high concentration (0.08 M) of **4a** while maintaining the same concentrations of the other components as involved in electrolyte **E**_a was employed for the following DSC fabrication. However, mainly attributed to the low FF of the **3a/4a** based DSCs, this new mediator is still outperformed by the traditional I^-/I_3^- shuttle.

In principle, FF can be limited in at least two ways: (1) by inefficient kinetics of the electrochemical reaction for the redox couple at CE, or (2) by slow mass transport of the redox couple in the electrolyte. Since the photocurrent transients studies (Supporting Information Figure S8) show that the low fill factor is not caused by the diffusion of BAT 4a in the electrolyte, the unsatisfactory apparent electrocatalytic activity of the CGM CE for 4a might be considered as the dominant factor. Therefore, further optimization of 3a/4a based DSC performance should focus on the identification of a better CE material to obtain efficient charge transfer. Nowadays, carbon electrodes and carbon derivative CEs are extensively employed in industrial applications of DSCs, due to their promising activity and reduced cost.^[29] Among these materials, graphene seems to be an attractive material for this purpose because it has large number of active sites (edge defects and oxidic groups) which might provide excellent apparent electroactivity towards the redox couples.^[29a-c] In this section, we developed a novel graphenebased carbon composite CE, named GGCM, to replace the normal CGM in catalyzing the redox couple **3a**/**4a**. Accordingly, the DSC based on GGCM CE showed an unexpected η of 6.53% with a $J_{\rm SC}$ value of 14.2 mA·cm⁻², a $V_{\rm oc}$ value of 697 mV, and a FF of 0.66 under 100 mW·cm⁻² simulated sunlight illumination, where the FF and η increased by 16% and 19%, respectively, in comparison to the CGM CE (Supporting Information Figure S9).

To better understand the reason for the improvement of DSC performance with GGCM CE, EIS of the symmetrical dummy cell constructed by two identical CGM or GGCM electrodes was employed. Recently, Roy-Mahew et al.^[29a] proposed a upgraded model for porous carbon electrodes seen in Figure 7a. They attributed the high-frequency semicircle (first semicircle) to a second Nernst diffusion impedance resulting from diffusion through the electrode pores (N_{pore}) . The middle semicircle (second semicircle) represented the charge transfer resistance and the capacitance of the CE/electrolyte interface (R_{ct}, CPE). As in the traditional approach, the low-frequency semicircle was determined by bulk Nernst diffusion (N_{bulk}), while the ohmic serial resistance could be determined from the onset of the first semicircle. In our case, as shown in Figure 7a, the diffusion in pores could obviously be observed and there were also three semicircles in the EIS Nyquist curves of the dummy cells, which is in agreement with the upgraded model proposed by Roy-Mahew. Based on this approach, similar ohmic series resistances could be obtained for the CGM and GGCM electrodes. In addition, we also found that R_{ct} was 0.93 Ω ·cm² for the GGCM electrode, whereas the R_{ct} for the CGM electrode had a value of 6.74 Ω ·cm². The lower transfer resistance of GGCM electrode implies that CE based on this novel graphene composite material exhibits an excellent apparent catalytic activity for 3a/4a. However, based on the EIS results alone, it is hard to determine whether the greater apparent catalytic activity of GGCM is due to an intrinsically higher catalytic activity for the material or to more accessible surface area.^[29a,30] This is of particular importance when comparing different electrode materials, as modifying the normal carbon electrode by graphene component





may change the electrode porosity and, thus, result in different apparent catalytic activities.

To distinguish between the specific catalytic activity and the surface area effects of GGCM CE on the 3a/4a redox reaction, CV was carried out using CGM and GGCM as work electrodes. As shown in Figure 7b, the most striking observation was the separation of the anodic and the cathodic peak potentials $(\Delta E_{\rm P})$, which was 360 mV for GGCM and 450 mV for CGM, respectively. The standard electrochemical rate constant of a redox reaction is negatively correlated with $\Delta E_{\rm P}$. Thus, the GGCM is more intrinsically catalytic toward the 3a/4a redox reaction. At the same time, their corresponding peak currents (and also the capacitive background currents), J_{p} , which strongly rely on the electrode morphology, also exhibit considerable differences.^[29a,30] J_p of the **3a/4a** redox reaction is much higher for the carbon electrode modified by graphene than that for the unmodified one, indicating a higher accessible surface area for GGCM electrode. We then conclude that the observed enhancement in the apparent catalytic activity of the GGCM electrode is caused not only directly through an increase of the intrinsic catalytic activity of the graphene but also indirectly through a change in electrode morphology, thus constitute the main reason for the higher FF observed in the DSCs based on GGCM CEs.

3. Conclusions

Through introducing electron-donating and -withdrawing groups to the AT⁻/BAT backbone at the *para* position of phenyl unit, a promising new class of organic sulfide redox shuttles with programmable redox properties could be readily synthesized. Our purposes for the mediator design were summarized by two major points: 1) to continue exploiting and identifying new promising organic sulfide redox couples, and 2) to probe the effects of physical and chemical characteristics of organic sulfide redox shuttles on DSCs kinetics and performance.

The potentials of these organic mediators can be fine-tuned by introduction of different electron-donating and -withdrawing substituents over a 170 mV range. All of them are much more compatible with normal carbon CE than Pt CE. Although the redox potentials of the mediators with electron-donating substituents are less positive than those with electron-withdrawting substituents, the former can also offer an opportunity to increase the V_{OC} of DSCs as well as the latter do. Due to the suitable interplay of physical properties and redox characteristics of the (AT⁻/BAT)-MeO **3a/4a**, it is identified as the best performing one of this series of organic sulfide mediators.

Furthermore, we successfully prepared a novel graphenemodified CE with dramatically high apparent electrocatalytic activity towards this new class of organic mediators, resulting in a promising conversion efficiency of 6.53% with a FF of 0.66 for DSSC based on **3a/4a** under 100 mW·cm⁻² simulated sunlight illumination.

Most importantly, we have demonstrated that one attractive advantage of using the AT⁻/BAT organic mediators in DSCs was that their physical and chemical properties could be easily tuned through attaching versatile functional groups to phenyl unit of the AT⁻/BAT backbone, offering an avenue to create diverse organic sulfide redox shuttles. Meanwhile, the studies reported here have emphasized that, for design and application of the redox shuttles, besides their redox potentials, the dipole moment, steric bulk, conjugation, polarity, solubility and their effect on the E_c level of semiconductor also should be considered. As we continue to modify, study, and improve these organic sulfide mediators, it should now be possible to identify structures that maximize DSC kinetics and performances, making the realization of truly inexpensive, stable, and efficient DSCs grow nearer.

4. Experimental Section

Materials: The solvents and salts used in this study (puriss. grade) were purchased from Fluka. N719 were synthesized according to reported procedures.^[31] Graphene nanoplatelets were prepared as reported earlier.^[32]

Cell Fabrication: After coating with a dense TiO₂ layer on F-doped tin oxide (FTO) glass (TEC15, Nippon), a 12-µm-thick layer of 18-nm TiO2 nanocrystalline particles (PST-18NR, Japan) and a 4-µm-thick scattering layer of 400-nm TiO₂ particles (PST-400C, Japan) were printed, and then sintered at 450 °C for 30 min and sensitized with N719, which used as the photoanode. The platinized CE was prepared by thermal decomposition of hexachloroplatinic acid onto FTO glass. The carbon black/graphite mixture CE was obtained by screen printing technique with a mixture of graphite, carbon black and 20-nm ZrO₂ (mass ratio 5:1.5:1) onto FTO glass.^[33] The graphene modified graphite/carbon black mixture CE was obtained by screen printing technique with a mixture of a graphene modified graphite, carbon black and 20-nm ZrO₂ (mass ratio 67:20:13) onto FTO glass. The graphene modified graphite powder was prepared with 75 wt% graphite and 25 wt% graphene dispersed in ethanol and sintered at 380 °C for 20 min. The DSCs were fabricated by sealing the Photoanodes and CEs together in a sandwich configuration with a 45-µm-thick hot-melt polymer (Surlyn, Solaronix). The interelectrode space was filled with an electrolyte by vacuum back-filling. The active area was 0.25 cm²

Characterizations and Measurements: The cyclic voltammetry measurements were conducted in a three-electrode system in an argonpurged electrolyte solution on ZAHNER ENNIUM Electrochemical Workstations. Pt wire served as the CE, and Ag⁺/Ag served as the reference electrode. The electrolyte contained 20 mM the reduced species, 10 mM the oxidized species, 20 mM 18-crown-6 and 0.1 M TBAP in acetonitrile. The potential of the reference electrode was adjusted by recording the cyclic voltammogram for 0.01 M ferrocene in acetonitrile containing 0.1 M TBAP. The photocurrent density-voltage characteristics were measured with a Keithley 2400 source/meter under the illumination of air mass 1.5 (AM1.5), 100 mW·cm⁻² by an Oriel 91192 solar simulator (Newport, USA). The illuminated active area was obtained with a black mask containing a circular hole of 0.159 cm². The incident photon conversion efficiency was measured with a QE/IPCE Measurement Kit system (Newport, USA). Electrochemical impedance spectroscopy of the symmetric cell was carried on ZAHNER ENNIUM Electrochemical Workstations in the frequency range 0.1 to 10⁵ Hz with 10 mV AC amplitude. Intensity modulated photocurrent spectroscopy and intensity modulated photovoltage spectroscopy were carried out with a high-intensity green LEDs (530 nm) driven by a ZAHNER Xpot frequency response analyzer. The LED provided both the dc and ac components of the illumination. The ac light intensities were modulated (±8%) by modulating the voltage applied to the LED with sinus waves in the frequency range from 0.2 Hz to 10 kHz for IMPS and from 0.02 to 200 Hz for IMVS. A charge extraction setup identical as in Duffy et al.^[34] was used to determine the charge stored in the films. The open-circuit voltage decay was recorded by an Ecochemie potentiostat equipped with a short interval sampling module. Typically the measurement interval was 5 ms. For the decay measurement, the cell was performed with a

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negative voltage until the voltage reached steady state, then removing the applied voltage, and monitoring the decay in the cell voltage as electrons in the anode were intercepted by the redox shuttle.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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