Article

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Enhancements of Trifluoroacetic Acylated Five-membered Heterocyclic Compounds Using as Additives in Dye Sensitized Solar Cells

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In this study, five-membered heterocyclic compounds are trifluoroacetic acylated for the purpose of providing more long pairs to enhance electrolyte in dye sensitized solar cells (DSSCs). Four five-membered heterocyclic compounds will be trifluoroacetic acylated with trifluoroacetic anhydride by Friedel-Crafts acylation: furan, thiophene, pyrrole and N-methylpyrrole. The properties will be measured by cyclic voltage (CV), Fourier transform infrared spectroscopy (FTIR), solar simulator, and electrochemical impedance spectroscopy (EIS). We find out that furan and thiophene which we add in electrolyte as additives can increase short circuit current and photovoltaic efficiency, and furthermore, all the trifluoroacetic acylated heterocyclic compounds perform better photoelectric abilities than non-trifluoroacetic acylated one. The photovoltaic efficiency will be increased from 4.439% to 5.197% when 1wt% trifluoroacetic acylated thiophene is added in electrolyte as additives.

Keywords: Friedel-Crafts acylation; Heterocyclic; Trifluoroacetic anhydride; DSSCs.

INTRODUCTION

The generation of energy is one of the most important and imperative problems nowadays. Solar energy[1] which is radiant light and heat continuously from the Sun using a range of technologies such as solar heating and photovoltaic seems like a feasible solution for this issue. Photovoltaic cell which converts the energy of light directly into electricity by the photovoltaic effect is one of the possible devices that we used recently and widely.[2-6] DSSCs developed by Grätzel and coworkers are high efficiency,[7] low-cost, and flexible alternative for photovoltaic cells. Remarkably high quantum efficiency has been reported with conversion efficiency up to 13%.[8]

Heterocycle is a cyclic compound that has atoms of at least two different elements as members of its ring.[9] Every carbocyclic compound, regardless of structure and functionality, may be converted into a heterocyclic compound by replacing one or more of the ring carbon atoms with a different element in theory. There are one or more than one lone pairs on oxygen, nitrogen, and sulfur. These are the most common heterocyclic elements that we usually used.[10] Heterocycle is often activated towards cation-π binding[11,12] when the lone pair on the heterocyclic element is incorporated into the aromatic system. When the lone pair does not contribute to aromaticity, heterocyclic element will weaken the cation-π binding ability conversely. Most of the heterocyclic elements are poor electron donors when it comes to cation-π binding. Cation-heterocycle interaction is not always a cation-π interaction, in some cases it is more favorable for the cation to be bound directly to a lone pair, like the case in pyridine-Na+ complexes,[13] for example. The interaction between the cation and the carbonyl oxygen is a common example of a Lewis acid and base reaction. The carbonyl oxygen (the Lewis base) donates a pair of electrons to the cation (the Lewis acid). This interaction has the very important effect of increasing the polarity of the carbon-oxygen double bond. The mechanism is shown in Scheme 1.

Friedel-Crafts acylation which is the acylation of aromatic rings using a strong Lewis acid catalyst with an acyl chloride or acid anhydride has been reported since 1877. The reaction conditions are similar to the Friedel-Crafts alkylation.[14] Due to the electron withdrawing effect of the carbonyl group, the ketone product is always less reactive than the original molecule. That's why there is no carbocation rearrangement[15] occurring. There are lots of catalysts suitable for Friedel-Crafts acylation such as aluminum chloride ($AlCl_3$),[16] zinc chloride ($ZnCl_2$),[17] iodide (I_2),[17] ferric chloride ($FeCl_3$),[17] iron (Fe),[17] and antimony pentafluoride (SbF_5).[18] It is inconvenience that most of

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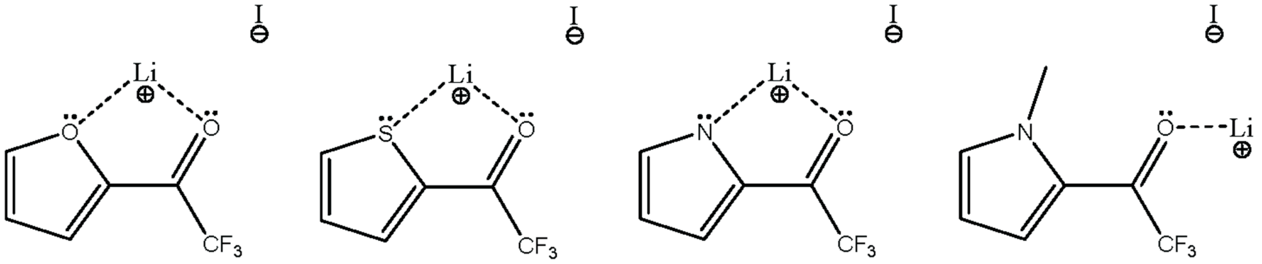
Scheme 1 The iodide anion will be freer to redox in the electrolyte because both the cation-heterocycle interaction and the lone pairs on the carbonyl oxygen are attracted by the lithium cation



these catalysts are anhydrous. Minute amount of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) has been reported as catalyst for Friedel-Crafts acylation of pyrrole and substituted pyrrole,[19] and production yield is excellent. It is also appropriate for furan[20,21] and thiophene,[22,23] and furthermore it is not necessary anhydrous.

In this study, five-membered heterocyclic compounds will be trifluoroacetic acylated in order to combine cation-heterocycle interaction and the lone pairs in carbonyl group these two characteristics. Both of these major properties are attracted by cations. The iodide anion will be freer to redox in the electrolyte because heterocyclic compounds are attracted by the lithium cation. We hope it will be helpful for enhancing iodine/iodide electrolyte and increasing photovoltaic efficiency in DSSCs.

EXPERIMENTAL

Trifluoroacetic acylation of five-membered heterocyclic compounds: Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) had been found as an effective catalyst for Friedel-Crafts acylation of furan, thiophene, pyrrole, and N-methylpyrrole.[19-23] In the process of trifluoroacetic acylation, furan was reacted with the same molar ratio trifluoroacetic anhydrate and minute amount of ferric chloride hexahydrate, which was used as catalyst, at room temperature for hours until trifluoroacetic anhydrate was exhausted. Chloroform was used as solvent. Reaction termination was determinate by thin layer chromatography[24] (TLC). The trifluoroacetic acylation of thiophene was similar to the previous process, but it had to be heated under reflux temperature. Ferric chloride was removed from solution by silica column filtration, and hexane would be used as eluent. Hexane would be separated during rotary evaporatoration. Trifluoroacetic acylated furan (TFAA_Furan): FTIR: 1692 cm^{-1} (C=O); ^{1}HNMR (200 Hz, $CDCl_3$, in ppm) δ 6.67 (q, 1H, $-H_4$), δ 7.46 (m, 1H, $-H_3$), δ 7.79 (q, 1H, $-H_5$) and trifluoroacetic acylated thiophene (TFAA_Thiophene): FTIR: 1690 cm^{-1} (C=O); ^{1}HNMR (200 Hz, $CDCl_3$, in ppm) δ 7.172, δ 7.805 were extracted through simple distillation directly, and pure chloroform would be recycled during distillation.

Trifluoroacetic acylated pyrrole and N-methylpyrrole were prepared by the same steps but reacted in ice bath. Liquid phase extraction would be used in the process of removing ferric chloride, and 1N sodium hydroxide (NaOH) solution was added in adjusting pH value to 10~11.[25] The bottom layer solution of liquid phase extraction was collected and crystallized for purification of trifluoroacetic acylated pyrrole (TFAA_Pyrrole): FTIR: 3340 (N-H), 1660 cm^{-1} (C=O); ^{1}HNMR (200 Hz, $CDCl_3$, in ppm) δ 6.41 (m, 1H, $-H_4$), δ 7.20~7.26 (m, 2H, $-H_3$, $-H_5$), δ 9.60 (br, 1H, -N-H). Trifluoroacetic acylated N-methylpyrrole (TFAA_N-Methylpyrrole): FTIR: 1670 cm^{-1} (C=O); ^{1}HNMR (200 Hz, $CDCl_3$, in ppm) δ 3.97 (s, 3H, $-N-CH_3$), δ 6.24 (q, 1H, $-H_4$), δ 7.02 (m, 1H, $-H_3$), δ 7.02 (m, 1H, $-H_5$) would be received by simple distillation from the bottom layer solution of liquid phase extraction.

Assembly of DSSCs: Fluorine doped tin oxide glasses (FTO) were cleaned with methanol, acetone, and deionized water (DI water) in ultrasonic bath (DELTA DC300H) for each 20 minutes and dried in a vacuum oven. Titanium dioxide[26] (TiO_2) working electrode anode film with a thickness of 16-20 μm was prepared by spin coating on FTO in high temperature annealed at 450 °C for two hours. TiO_2 paste was made from 9 g titanium oxide powder (Degussa P25), 1 g polyethylene glycol (PEG, Mw = 6000), 2 ml Acetylacetone, 0.2 ml Triton-X 100, and 18 ml DI water. The paste was ball milled for 60 minutes and ultrasonic for 24 hours. The TiO_2 anodes was further sensitized by immersing into a 0.5 mM anhydrous ethanol solution of N719 dye (bis(tetrabutylammonium)-cis-bis(thiocyanato)bis(2,2'-bipyridine-4,4'-dicarboxylate)-Ru(II)).[27-29] The cell was fabricated by sandwiching redox electrolyte between dye sensitized TiO_2 working electrode and platinum (Pt) counter electrode[7,30] which was supported on FTO glass. The redox electrolyte was composed of 0.5 M lithium iodide (LiI), 0.05 M iodine (I_2), 0.5 M 4-tert-butylpyridine[31,32] (4-TBP), 5 ml acetonitrile, and 5 ml propylene carbonate (PC). 1 wt% of trifluoroacetic acylated five-membered heterocyclic compounds would be added to electrolyte in the experimental group.

Electrochemical and photovoltaic characterizations: The electrochemical behaviors were recorded on a conventional electrochemical workstation CHI614D. It is including a Pt working electrode, a saturated calomel reference electrode (SCE), and a platinum sheet counter electrode (CE). The cyclic voltammetry (CV) curves were recorded from -1.0 to +0.6 V. Before the measurement, the supporting electrolyte consisting of 0.115 mg heterocyclic compound, 50 mM LiI, 10 mM I_2, and 500 mM $LiClO_4$ in 10 ml acetonitrile was degassed using nitrogen for 10 minutes.[33]

The photovoltaic testing of DSSCs could be measuted using simulated solar light as well as light from a Xenon arc lamp. The incident light intensity was controlled at 1000 W/m^2 (AM1.5).[30] Electrochemical impedance was measured in a frequency range of 10^{-1} Hz to 10^6 Hz and an AC amplitude of 5 mV at room temperature under the same simulated solar light as photovoltaic testing.[34,35]

Other characterizations: Fourier transform infrared spectrometry (FTIR) and Nuclear magnetic resonance (NMR) would be used to identify the functional groups and structures. FTIR spectra were recorded on Perkin-Elmer Spectrum 100 FTIR spectrometer from 4000 cm^{-1} to 650 cm^{-1}. NMR spectra were measured by Varian Mercury-300 NMR spectrometer, and D-solvent would be D-chloroform ($^1H\delta = 7.26$ ppm).

RESULTS AND DISCUSSION

Trifluoroacetic acylation

Five-membered heterocyclic compounds are useful to enhance the short circuit current in DSSCs because of providing extra lone pair electrons.[36-38] Comparing with methyl group on the carbonyl carbon, trifluoromethyl group is more electronegative. It will make the carbonyl carbon more positive and the carbonyl oxygen more negative. In the other words, the bond length between the carbonyl oxygen and the carbonyl carbon will be longer. That is why we choose trifluoroacetic acylated five-membered heterocyclic compounds which are acylated by Friedel-Crafts acylation to offer a carbonyl group and extra lone pair electrons in this experiment. According to Planck's Equation:

$$E = h\nu = hc/\lambda$$

A photon has an energy E, and this energy is proportional to its frequency ν where h is Planck's constant, λ is the wavelength, and c is the speed of light. Oxygen is far more electronegative than carbon, so the oxygen atom pulls electron density away from the carbon. When the carbon is more positive, the bond length between oxygen and carbon will be longer. The energy of the carbonyl will be decreased, and the wavelength will be increased.[39,40] Figure 1 shows that the difference of the wavelengths of the carbonyl group between the acetylthiophene and the TFAA_Thiophene in FTIR. The wavelengths of the carbonyl group between the acetylthiophene and the TFAA_Thiophene are shifted from 1657 cm-1 to 1690 cm-1. As we have expected, trifluoromethyl group pulls electron away from the carbonyl carbon atom causing the oxygen much more negative. Figure 2 shows that the redox peaks of acetylthiophene and TFAA_Thiophene in CV. The details are shown in Table 1. In Figure 2 and Table 1 we can obvi-

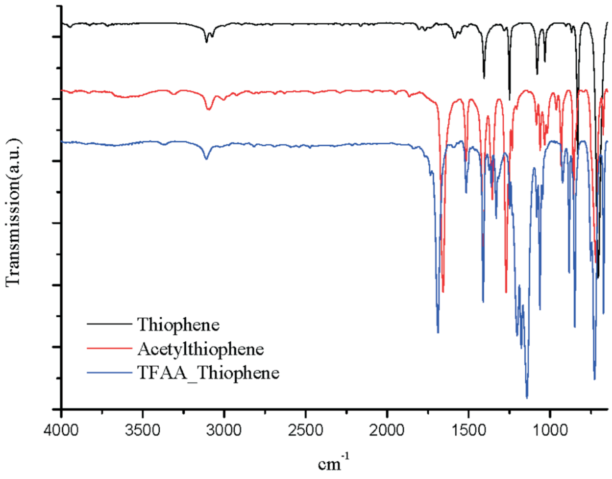


Fig. 1. The difference of the wavelength of the carbonyl group between acetylthiophene and TFAA_Thiophene in FTIR.

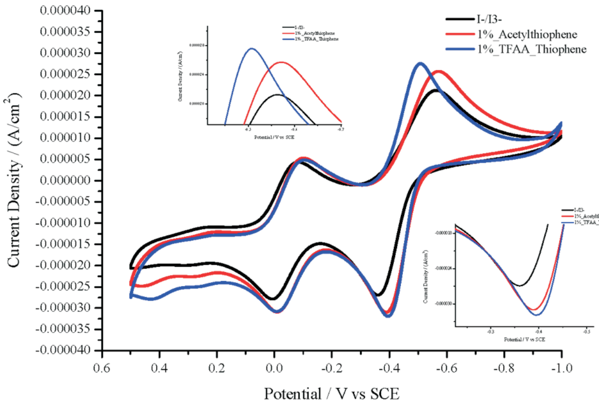


Fig. 2. The difference of redox peaks of acetylthiophene and TFAA_Thiophene in CV.

Table 1. The parameters of each redox peaks of acetylthiophene and TFAA_Thiophene in CV

	E_{Red1} (V)	E_{Ox1} (V)	I_{Red1} (A)	I_{Ox1} (A)
I^-/I_3^-	-0.562	-0.359	1.665E-5	2.651E-5
1%_Acetylthiophene	-0.571	-0.389	2.383E-5	3.162E-5
1%_TFAA_Thiophene	-0.508	-0.395	2.849E-5	3.448E-5

ously find out that the current of reduction peak of I_3^- to I^- and the oxidation peak of I^- to I_3^- in TFAA_Thiophene are bigger than the current in acetylthiophene. Comparing the FTIR and CV, trifluoroacetic acylation is better than acetylation for providing extra lone pair electrons.[1]

Electrochemical behaviors

From the stacking CV curves added thiophene in electrolyte at different scan rates, we can find out an outward extension of all the peaks in Figure 3a. By plotting peak current density corresponding to $I_3^- \leftrightarrow I^-$ *versus* square root of scan rate, linear relationship is observed in Figure 3b. This result indicates that the redox reaction is a diffusion controlled mechanism on Pt counter electrode and also in heterocyclic compound added electrolyte system.[41] According to the book of Bard, A. J., for fast electron transfer process with diffusion limited, the peak current is proportional to the square root of the scan rate.[42] In other words, scan rate will not affect the electrochemical potential but only proportional to current density. It looks like that adding heterocyclic compounds in electrolyte is still a reversible system. Because of the CV curve becoming unstable under higher scan rate, it will be suggested to run with medium scan rate.

Iodine/iodide based electrolytes can be optimized in terms of efficiency and stability. Heterocyclic compounds added in DSSCs are used for helping electrolyte to enhance short circuit current density. Although the concentration is proportional to current in a reversible Nernstian system, but the original iodine/iodide based electrolyte is still supplanted by the heterocyclic additives. The optimal weight percent of heterocyclic compounds that we shall add in electrolyte will be determined by cyclic voltammetry. The CV results of different weight percent thiophene additives added in iodine/iodide based electrolyte from 0.1 wt% to 10 wt% are shown in Figure 4a and 4b. Concentration is not proportional to current density obviously. That is because more heterocyclic compounds that we add in, less iodine/iodide based electrolyte will remain. Although heterocyclic compounds are helpful for catching lithium ions in iodine/iodide based electrolyte, but too much weight percentage[38] that we add in won't enhance current anymore. The optimal concentration of heterocyclic compounds that we add in electrolyte as additives will be 1wt% in this study.

The appropriate scan rate and the optimal concentration of additives are 0.05 V/s and 1 wt% in both electrochemical and photovoltaic testing. Trifluoroacetic acylated five-membered heterocyclic compounds are synthesized by Friedel-Crafts acylation[19-23] in the previous experiments. Figure 5a and 5b show the difference between adding five-membered heterocyclic compounds and trifluoroacetic acylated five-membered heterocyclic compounds in CV. We can clearly observe the electrolytes which we add pyrrole and N-methylpyrrole in as additives are very different with the other five-membered heterocyclic compounds in Figure 5a. The oxidation peaks at $2I_3^- - 2e^- \rightarrow 3I_2$ in pyrrole and N-methylpyrrole are obviously bigger than the others three redox peaks. Electropolymerization[43-46] of pyrrole

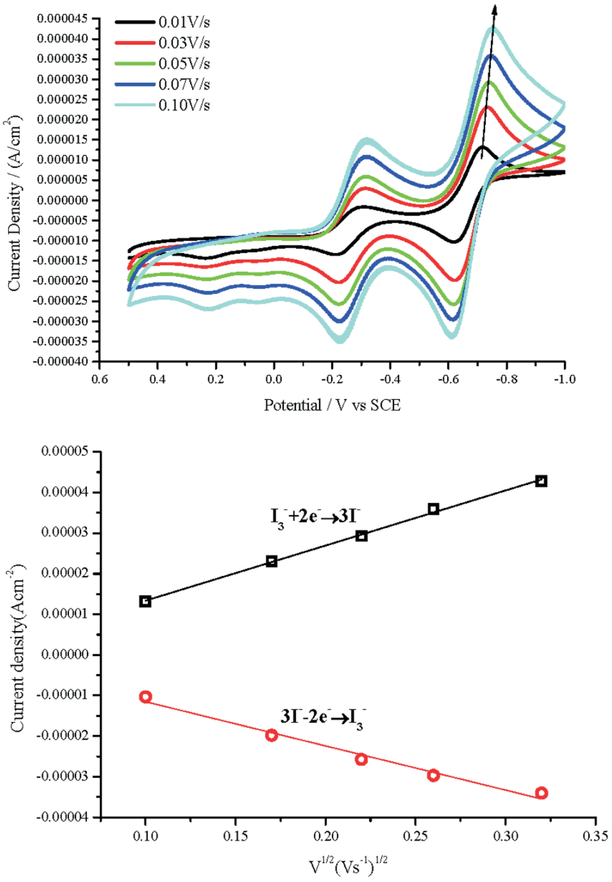


Fig. 3. (a) The stacking CV curves of thiophene added electrolyte at different scan rates. (b) The relationship between peak current density and square root of scan rates.

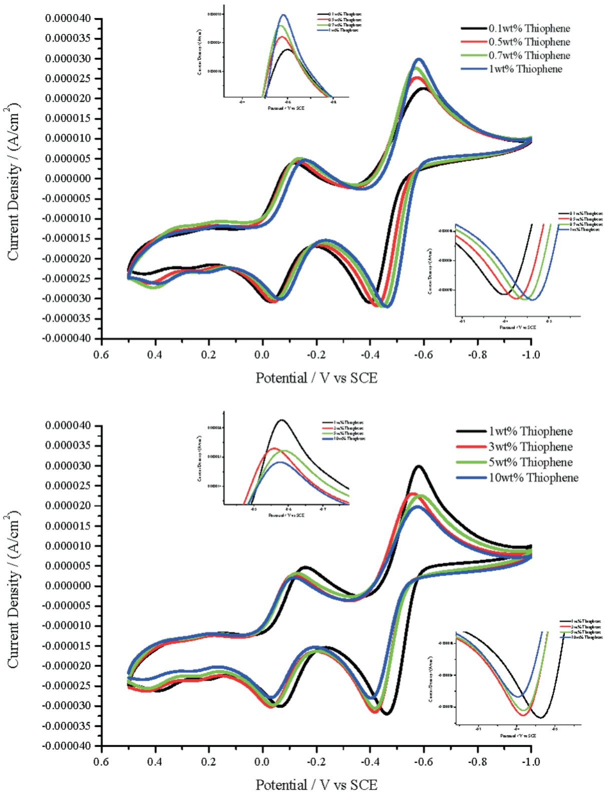


Fig. 4. (a) The different weight percent of thiophene we add in iodine/iodide based electrolyte from 0.1 wt% to 1 wt%. (b) The different weight percent 1 wt% to 10 wt%.

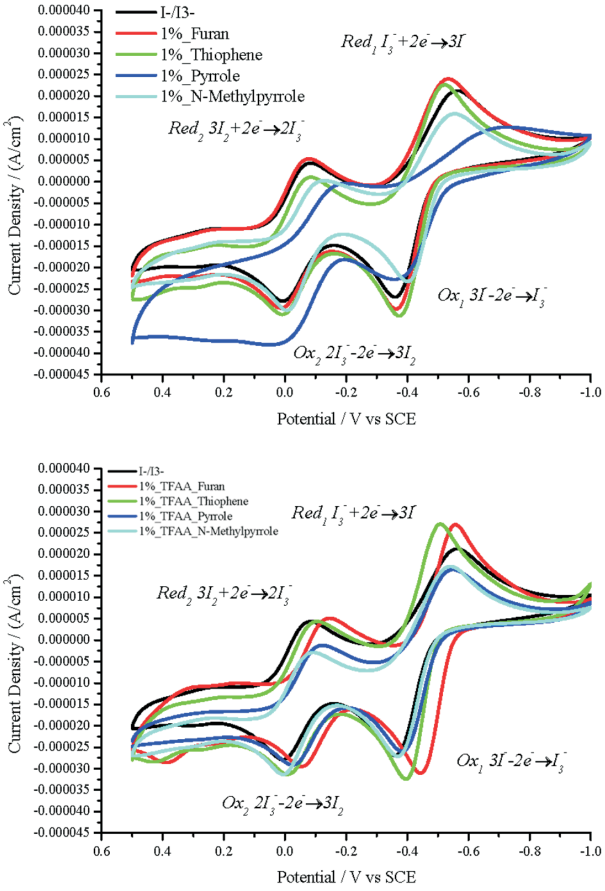


Fig. 5. (a) The difference between adding five-membered heterocyclic compounds in CV. (b) The difference between adding trifluoroacetic acylated five-membered heterocyclic compounds.

and N-methylpyrrole are considered to be synthesized at this working potential. It causes the concentration changed and affects electrons transportation in electrolyte unfortunately. In contrast, electropolymerization[47] won't occur when five-membered heterocyclic compounds trifluoroacetic acylated, and it is helpful for interrupting electropolymerization occurring and enhancing the redox current in CV in Figure 5b. According to atomic orbital,[48] furan (O: $[He]2s^22p^4$) and thiophene (S: $[Ne]3s^23p^4$) have two pairs of lone pair. Pyrrole (N: $[He]2s^22p^3$) has only one pair of lone lair, and N-methylpyrrole has no extra lone pair because of methyl group. So furan and thiophene will be better than pyrrole and N-methylpyrrole for providing extra lone pairs attracted by cation, and TFAA_Furan and TFAA_Thiophene are also better than TFAA_Pyrrole and TFAA_N-Methylpyrrole. Furthermore, sulfur atom is bigger than oxygen atom in periodic table and therefore causes the lone pair in the outermost electron shell of atom more negative. That is the reason why thiophene added electrolyte is better than furan, and TFAA_Thiophene is also better than TFAA_Furan in electrochemical behaviors. These results and theories will be applicable for all the next experiments in this study.

Photovoltaic and EIS performances

Figure 6a and 6b show the photovoltaic characteristics of DSSCs, and the parameters reflecting DSSCs properties are summarized in Table 2. Figure 6a shows the DSSCs added furan and thiophene in as additives get higher efficiency (η) than pyrrole, N-methylpyrrole, and the un-added one in photovoltaic testing. These results may be attributed to the electropolymerizations[44-46] of polypyrrole (PPy) and polymethylpyrrole occurring during photovoltaic testing. Although the DSSC added pyrrole in as additive achieves higher short circuit current[13] at beginning, the polymerization occurring during photovoltaic testing changes electrolyte concentration, and causes the cell unstable.[42] The DSSCs added trifluoroacetic acylated

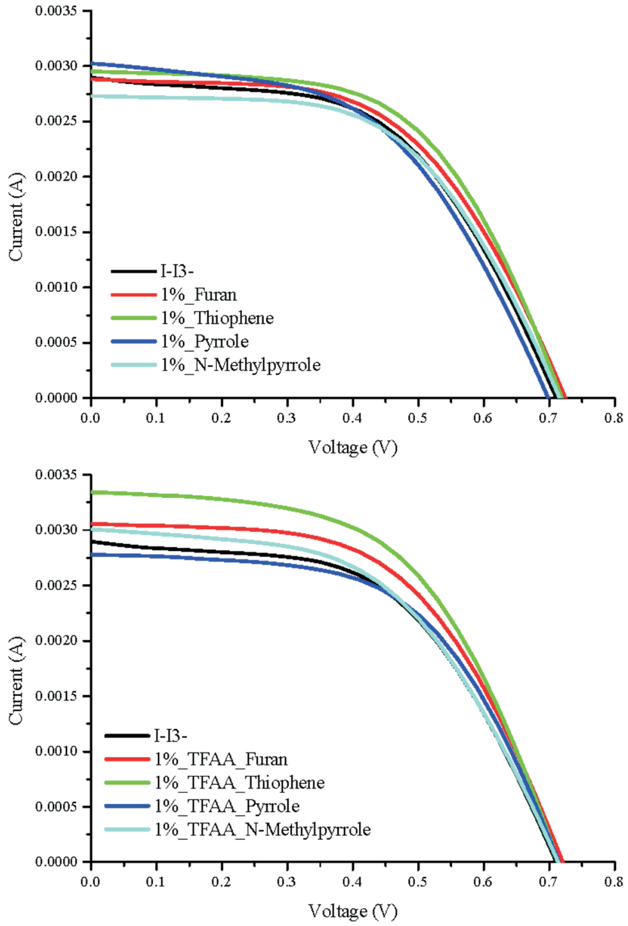


Fig. 6. (a) The I-V curve of DSSCs added heterocyclic compounds. (b) The I-V curve of DSSCs added trifluoroacetic acylated heterocyclic compounds.

Table 2. The parameters of DSSCs added heterocyclic compounds and trifluoroacetic acylated heterocyclic compounds individually in photovoltaic testing

	V_{oc} (V)	J_{sc} (A/cm^2)	*FF*	η (%)
I^-/I_3^-	0.7113	1.159E-02	53.86	4.439
1%_Furna	0.7245	1.154E-02	55.00	4.597
1%_Thiophene	0.7190	1.181E-02	56.88	4.830
1%_Pyrrole	0.6984	1.209E-02	51.27	4.331
1%_N-Methylpyrrole	0.7158	1.092E-02	56.12	4.387
1%_TFAA_Furan	0.7208	1.224E-02	55.01	4.852
1%_TFAA_Thiophene	0.7138	1.338E-02	54.43	5.197
1%_TFAA_Pyrrole	0.7141	1.112E-02	56.33	4.472
1%_TFAA_N-Methylpyrrole	0.7137	1.203E-02	52.18	4.480

five-membered heterocyclic compounds in as additives achieve better efficiency than the five-membered heterocyclic compounds and the un-added one in Figure 6b. For TFAA_Furan and TFAA_Thiophene, trifluoroacetic acylation provides a carbonyl group for an extra lone pair, and it is helpful for increasing short circuit current in DSSCs. For TFAA_Pyrrole and TFAA_N-methylpyrrole, trifluoroacetic acylation stops the electropolymerization[47] occurring, and also provides a carbonyl group for enhancing short circuit current in photovoltaic testing. The optimal additive for $I_3^- \leftrightarrow I^-$ redox reaction in this study is TFAA_Thiophene which achieves the higher J_{sc} in photovoltaic testing. There is a significant enhancement in DSSCs, and the highest efficiency is 5.197% with 1 wt% TFAA_Thiophene in comparison with 4.439% with un-added pure iodine/iodide based electrolyte. The further relationship between additives and resistance will be discussed in electrochemical independence spectra.

Nyquist plots in Figure 7 illustrate the electrochemical impedance characteristics of five-membered heterocyclic compounds and trifluoroacetic acylated five-membered heterocyclic compounds that we added in DSSCs as additives. According to the Randles-type circuit[49,50] that inserts in Figure 7, the intercept on the real axis represents the series resistance (R_s) which is a reflection of total resistance. Then the first semicircle (R_1) from the left is related with counter electrode which is Pt in this study, the second one (R_2) is associated with TiO_2/dye/electrolyte interface where the electrons transfer occurred, and the third one (R_3) is the diffusion rate of I^-/I_3^- inner electrolyte.[50] The detail parameters are summarized in Table 3. It can be easily found out that the most difference at Nyquist plots in electrochemical independence spectra is the second semicircle R_2. For furan, thiophene, TFAA_Furan, and TFAA_Thiophene that we add in I^-/I_3^- electrolyte, the resistances of R_2 are obviously decreased due to that the additives[12,36] are helpful for improving short circuit current in DSSCs. These results can be compared with Table 2. For pyrrole and N-methylpyrrole that we add in I^-/I_3^- electrolyte, the resistances of R_2 are much bigger than the un-added one because of the electropolymerization[44,46] which will affect the concentration and increase the interface resistance between working electrode and electrolyte occurring. It is particular that adding pyrrole in electrolyte will also increase the resistance R_3 which is the diffusion rate of I^-/I_3^- inner electrolyte. It is associated with electropolymerization of polypyrrole[44] which will change the concentration and disturb electrons transfer in electrolyte. For TFAA_Pyrrole and TFAA_N-methylpyrrole that we add in I^-/I_3^- electrolyte, R_2 are clearly smaller than pyrrole and N-methylpyrrole. It is because that trifluoroacetic acylation will interrupt electro-

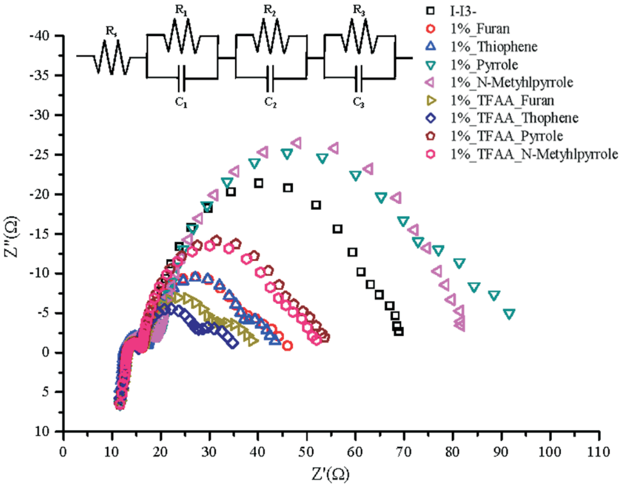


Fig. 7. The electrochemical impedance characteristics of each five-membered heterocyclic compounds and trifluoroacetic acylated five-membered heterocyclic compounds we added in DSSCs.

Table 3. The electrochemical impedance parameters of each five-membered heterocyclic compounds and trifluoroacetic acylated five-membered heterocyclic compounds we added in DSSCs

	R_1 (Ω)	R_2 (Ω)	R_3 (Ω)
I^-/I_3^-	5.511	43.996	7.772
1%_Furan	4.484	23.310	6.626
1%_Thiophene	5.527	19.978	6.318
1%_Pyrrole	7.775	53.400	18.752
1%_N-Methylpyrrole	6.741	53.646	9.597
1%_TFAA_Furan	4.493	15.087	7.511
1%_TFAA_Thiophene	3.805	12.312	6.988
1%_TFAA_Pyrrole	4.604	31.075	6.324
1%_TFAA_N-Methylpyrrole	4.396	28.135	7.835

polymerization[47] occurring, and furthermore increase the short circuit current in DSSCs. According to a series of comprehensive and scientific analyses, it can be concluded that the photovoltaic performances are in agreement with the electrochemical behaviors and EIS results.

CONCLUSIONS

Performances of the dye sensitized solar cells with five-membered heterocyclic compounds and trifluoroacetic acylated five-membered heterocyclic compounds that we add in electrolyte as additives have been explored in this study. The highest photovoltaic efficiency is 5.197% that 1 wt% TFAA_Thiophene is added in I^-/I_3^- electrolyte as additive. Electropolymerization will occur when pyrrole and N-methylpyrrole added in electrolyte as additives, and reduces photovoltaic efficiency by reason of the resistance between the working electrode and the electrolyte increasing. Trifluoroacetic acylation which can provide more long pairs and prevent electropolymerization occurring is helpful for five-membered heterocyclic compounds, furthermore, the current density and the short circuit current will increase significantly in electrochemistry and photovoltage.

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