Influence of Solvent and Bridge Structure in Alkylthio-Substituted Triphenylamine Dyes on the Photovoltaic Properties of Dye-Sensitized Solar Cells

Chun Sakong,^[a] Se Hun Kim,^[a] Sim Bum Yuk,^[a] Jin Woong Namgoong,^[a] Se Woong Park,^[b] Min Jae Ko,^[b] Dong Hoe Kim,^[a] Kug Sun Hong,^[a] and Jae Pil Kim^{*[a]}

Abstract: Three new triphenylamine dyes that contain alkylthio-substituted thiophenes with a low bandgap as a π -conjugated bridge unit were designed and synthesized for organic dye-sensitized solar cells (DSSCs). The effects of the structural differences in terms of the position, number, and shape of the alkylthio substituents in the thiophene bridge on the photophysical properties of the dye and the photovoltaic performance of the DSSC were investigated. The introduction of an alkylthio substituent at the 3-position of thiophene led to a decrease in the degree of red-

shift and the value of the molar extinction coefficient of the charge-transfer band, and the substituent with a bridged structure led to a larger redshift than that of the open-chain structure. The introduction of bulky and hydrophobic side chains decreased the short-circuit photocurrent (J_{sc}), which was caused by the reduced amount of dye adsorbed on TiO₂. This resulted in a decrease in

Keywords: adsorption • dyes/ pigments • solvent effects • thiophene • triphenylamine the overall conversion efficiency (η) , even though it could improve the open-circuit voltage (V_{oc}) due to the retardation of charge recombination. Furthermore, the change in solvents for TiO₂ sensitization had a critical effect on the performance of the resulting DSSCs due to the different amounts of dye adsorbed. Based on the optimized dye bath and molecular structure, the ethylene dithio-substituted dye (**ATT3**) showed a prominent solar-to-electricity conversion efficiency of 5.20%.

Introduction

Dye-sensitized solar cells (DSSCs) have attracted considerable attention in the field of renewable energy because of their easy processing and low production cost.^[1] The most typical sensitizers used in DSSCs are the ruthenium(II) polypyridyl complex series, and these sensitizers show a high solar-to-electric conversion efficiency above 10% under the conditions of AM 1.5-simulated irradiation (100 mW cm⁻²).^[2] Although ruthenium-complex dyes exhibit high efficiency and superior stability,^[3] they have the disadvantages of high production cost and difficulties in synthesis and purification. On the other hand, metal-free organic dyes have shown

- [a] C. Sakong, S. H. Kim, S. B. Yuk, J. W. Namgoong, D. H. Kim, Prof. K. S. Hong, Prof. J. P. Kim Department of Materials Science and Engineering Seoul National University 30-402, Daehak-dong, Kwanak-gu Seoul 151-744 (Korea) Fax: (+82)2-885-1748 E-mail: jaepil@snu.ac.kr
 [b] S. W. Park, Dr. M. J. Ko
- Solar Cell Research Center Materials Science and Technology Division Korea Institute of Science and Technology (KIST) Seoul 136-791 (Korea)
- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201200814.

a relatively lower efficiency than ruthenium-complex dyes. Recently, many groups have studied the synthesis of metalfree organic dyes due to their advantages of low cost, ease of structural modifications, ease of synthesis, and high molar extinction coefficients. These groups have published results on triphenylamine, indoline, coumarin, cyanine, perylene, and phenothiazine.^[4] Among them, indoline.^[5] and triphenylamine-based^[6] organic dyes showed conversion efficiencies of approximately 10%, which are close to those of ruthenium-complex dyes.

Some of the main drawbacks of organic dyes are that the absorption wavelength is in the blue region and the narrow absorption band shape. Therefore, the optimal organic dyes for efficient DSSCs should have a broad and redshifted absorption spectrum. Most organic dyes have a molecular structure with donor (D)-to-acceptor (A) moieties connected by a π -conjugated bridge unit such as a methine chain, thiophene, and furan to obtain a broad and redshifted absorption spectrum. Recently, the most successful approaches have been the introduction of thiophene and furan as a π conjugated bridge unit into the organic dye framework, which not only increased the molar extinction coefficient but also broadened and redshifted the absorption spectrum of the organic dye.^[7] As a result, the investigated organic dves showed noticeably improved solar-to-electric conversion efficiencies.

Chem. Asian J. 2012, 00, 0-0

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



1

In recent years, Liu and coworkers have reported a series of organic dyes with 3,4-ethylenedioxythiophene (EDOT) as a π -conjugated bridge unit^[8] that have been widely used as a monomer for conductive polymers, poly(ethylene-3,4-dioxythiophene) (PEDOT). They have exceptional hole-injection properties, and high conductivity and physical/chemical stability.^[9] EDOT has a lower oxidation potential and bandgap properties than thiophene due to the strong electron-donating effect of two alkoxy groups at the 3- and 4-positions of the thiophene ring.^[10] Through the introduction of EDOT with high electron density and low bandgap properties as a π -conjugated bridge unit, the dye showed a significant redshift in the absorption band and a high



Scheme 1. Synthetic routes for the synthesis of the dyes: a) 3-methylbutylthiol or 1,2-dithiolethane, *p*-toluenesulfonic acid, toluene, 80–90 °C; b) NBS, 40 °C, CH₂Cl₂; c) 1.6 m BuLi, DMF, THF, $-78 \text{ }^{\circ}\text{C} \rightarrow \text{RT}$; d) NBS, DMF, RT; e) [Pd(PPh₃)₄], 2 m K₂CO₃ aqueous solution, THF, 75 °C; and f) cyanoacetic acid, piperidine, acetonitrile, heated to reflux.

solar-to-electric conversion efficiency of up to 7.33%, which is slightly inferior to ruthenium dyes, N719.

In this study, to broaden and redshift the absorption spectra of the dyes, alkylthio-substituted thiophenes with a low bandgap were introduced as a π -conjugated bridge unit to connect the triphenylamine donor and cyanoacrylic acid anchoring group in the dye molecules. In the thiophene series, alkylthio substituents are stronger donors than alkoxy ones. Therefore, 3,4-ethylenedithiathiophene (EDTT), in which two oxygen atoms of EDOT are replaced by sulfur, shows an oxidation potential 0.13 V lower than that of EDOT (EDTT: 1.22 V versus EDOT: 1.35 V).^[11] Moreover, to examine the effect of the structural difference on the photophysical properties and conversion efficiency, dyes with open-chain, bridged, symmetric, and asymmetric bridge-unit structures were designed and their photophysical, electrochemical, and photovoltaic properties were analyzed.

Results and Discussion

Synthesis

The synthetic routes and structures of the triphenylamine dyes with alkylthio-substituted thiophene bridges are shown in Schemes 1 and 2, respectively. Alkylthio-substituted thiophene derivatives as the important intermediates in this study have been synthesized by means of several common reactions and the detailed synthetic procedures are described in the Supporting Information.

Intermediates **1**, **4**, and **7** were obtained by the substitution of the methoxy group starting from 3-methoxythiophene and 3,4-dimethoxythiophene in reasonable yields.^[12]





ATT3: bridged, asymmetric structure

Scheme 2. Molecular structures of the triphenylamine dyes with alkylthio-substituted thiophene bridges.

These nucleophilic substitutions take place upon reaction with approximately 5 equivalents of the appropriate thiol in the presence of *p*-toluenesulfonic acid at 80 °C. On the other hand, in the case of a cyclic compound, a higher temperature and larger excess amount of 1,2-dithiolethane (10 equiv) is essential for obtaining the intermediate **7** in 29 % yield. Bromination and formylation reactions of compounds **1**, **4**, and **7** were performed with *N*-bromosuccinimide (NBS) at ambient temperature and *n*BuLi in *N*,*N*-dimethylformamide (DMF) at -78 °C, respectively. Suzuki coupling was carried out with 4-(diphenylamino)phenyl boronic acid and intermediates **3**, **6**, and **9** to directly yield the aldehydes **10–12**, which are necessary in the final reactions. Finally, intermediates **10–12** with an aldehyde group were condensed with cyanoacetic acid by using the Knoevenagel

. 2

www.chemasianj.org

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

reaction in the presence of piperidine and converted to **ATT1–ATT3**.

Photophysical Properties of the Dyes in Solution and TiO₂ Film

The absorption spectra of a $5 \times 10^{-5} \, \text{M}$ solution of the three dyes in dichloromethane are shown in Figure 1a, and the corresponding data are listed in Table 1. All the dyes exhibited two major prominent absorption bands, which appear at below 350 nm and at 450-550 nm, respectively. The former is due to a localized π - π * transition, and the latter is attributed to the intramolecular charge-transfer transition (ICT) from the triphenylamine donor part to the cyanoacrylic acid acceptor group.^[13] This assignment is supported by the solvatochromic behavior of the dyes. As shown in Figure 1c, the π - π * transition bands at 302 nm are nearly solvent-polarity independent, whereas the ICT bands at 490 nm exhibit negative solvatochromism (i.e., a blueshift of λ_{max} in more polar solvents). A comparative examination of the absorption spectra between ATT2 (or ATT3) and ATT1 indicates that the absorption bands have significant contributions from the substituent at the C(3) position of the 2,3,4-substituted thiophene. ATT2 and ATT3 showed a blueshift and relatively weaker redshift in the ICT band, respectively. They also had smaller extinction coefficients in the ICT band relative to ATT1 with only a C(4)-donating substituent, even though they had two donating substituents at the C(3) and C(4) of the thiophene bridge. This might be due to the decreased overlap of delocalized π electrons between the triphenylamine donor and alkylthio-substituted thiophene bridge, which results from the effect of the C(3) substituent on the coplanarity of the dye. As shown in Figure 2, the coplanarity of ATT2 and ATT3 between the triphenylamine donor and thiophene bridge decreased significantly, and the dihedral angles between the benzene of the donor group and thiophene bridge were 39.2 and 40.9°, respectively. On the other hand, ATT1 has a flatter molecular geometry, and the dihedral angle between the benzene of the donor group and the thiophene bridge was 18.1°. Therefore, it can be stated that ATT2 and ATT3 had a more twisted molecular geometry than ATT1 because of the steric hindrance caused by the substituent at the C(3) position, and the overlap of the delocalized π electron would be decreased significantly. In the case of ATT3, although the dihedral angle between the benzene of the donor group and the thiophene bridge is close to that of ATT2, its absorption band was redshifted considerably relative to that of ATT2. This might be due to the enhancement of π -electron delocalization by the bridged structure of EDTT.^[14]

The absorption spectra of the dyes adsorbed on TiO_2 are shown in Figure 1b and the corresponding data are listed in Table 1. All the dyes showed a blueshift in absorption compared to those in solution, and there was a larger shift in **ATT1** (56 nm) and **ATT3** (54 nm) than in **ATT2** (38 nm). Such blueshifts in the absorption spectra by adsorption onto TiO₂ have also been observed in other organic dyes. Either



Figure 1. Absorption spectra of the dyes in a) CH_2Cl_2 , b) adsorbed onto TiO_2 (**a** ATT1, **•** ATT2, **A** ATT3), and c) absorption spectra of ATT1 in different solvents (**a** toluene, **•** THF, **A** EtOH, **v** DMF).

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

b. KGaA, Weinheim www.chemasianj.org 3 These are not the final page numbers! 77

Table 1.	Photophysical	and el	lectrochemical	properties	of th	e synthesized	dyes
----------	---------------	--------	----------------	------------	-------	---------------	------

	$\lambda_{\rm max} [{\rm nm}] (\epsilon \times 10^{-4} {\rm m}^{-1} {\rm cm}^{-1})^{[{\rm a}]}$	$\lambda_{\rm max}$ (TiO ₂) [nm]	$E_{ox} \left[eV \right]^{[b]}$	$E_{0-0} [eV]^{[c]}$	$E_{\rm ox} - E_{0-0} [{\rm eV}]$
ATT1	302 (2.08) 400 (3.68)	434	1.19	2.21	-1.02
ATT2	490 (3.08) 322 (2.70) 478 (2.21)	440	1.21	2.22	-1.01
ATT3	478 (2.31) 280 (1.79) 492 (2.30)	438	1.15	2.18	-1.03

[a] Absorption and emission spectra were measured for solutions in CH₂Cl₂. [b] The oxidation potentials (E_{ox}) of the dyes were obtained by cyclic voltammetry in CH₂Cl₂ with 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) with a scan rate of 100 mV s⁻¹ and converted to NHE. [c] The zeroth-zeroth transition E_{0-0} values were estimated from the intersection of the normalized absorption and emission spectra.

a polar interaction with TiO₂ and/or deprotonation of carboxylic acid or H-aggregation of the dyes has been suggested to account for such a blueshift.^[15]

Electrochemical Properties of the Dyes

When the LUMO level of a dye is more negative than the conduction band of TiO_2 , the electrons of the dye excited by light are injected into TiO_2 effectively. In addition, oxidized dyes can be easily regenerated by the electrolyte when the HOMO level of a dye is more positive than the redox potential of the electrolyte.

The oxidation potential (E_{ox}) that corresponds to the HOMO level of the dye was measured in dichloromethane by using cyclic voltammetry (CV). The CV curves of the dyes are shown in Figure 3 and the corresponding data are collected in Table 1. The HOMO levels of the three dyes were positive enough relative to the redox potential of the electrolyte, 0.4 V (versus the normal hydrogen electrode (NHE)), thereby indicating that the oxidized dyes could be regenerated effectively by the electrolyte. From these values, the different shapes (open-chain and bridged structure) of the substituents in the thiophene bridge affected the HOMO levels, and the ring-closed structure of the substituents made the HOMO levels of the dyes more negative. For example, ATT3 showed a more negative HOMO, 1.15 V (versus NHE), than those of ATT1 and ATT2, 1.19 and 1.21 V (versus NHE), respectively.

The LUMO levels of these dyes were calculated by $E_{\rm ox}-E_{0-0}$, in which E_{0-0} is the zeroth-zeroth energy of the dyes estimated from the intersection between the normalized absorption and emission spectra, and the corresponding data are listed in Table 1. The LUMO levels of the three dyes were more negative than the conduction band of TiO₂, -0.5 V (versus NHE), thus indicating that the excited electrons of the dyes could be injected effectively into the conduction band of TiO₂.

Dye Adsorption in Various Solvents and the Performances of DSSCs

According to the literature, dyes in various solvents exhibit diverse interactions with the solvents, which could alter the physical and chemical interactions between the dyes and the TiO₂ surface.^[15] Therefore, optimization of the solvent system for TiO₂ sensitization is very important for obtaining good conversion efficiency (η) in DSSCs. To optimize the solvent systems for the dyes synthesized, TiO₂ films were sensitized with the dyes in various solvents (EtOH, mixed solvent (MeOH/CHCl₃ 1:1), and CHCl₃). Figure 4 shows the dependence of the photocurrent

density-voltage (J-V) curves of the DSSCs in three different solvents, and corresponding photovoltaic performance data are collected in Table 2. The DSSCs fabricated in the three different solvents showed large variations in their perform-

Table 2. Photovoltaic performances of the DSSCs based on the synthesized dyes sensitized in different solvents. $^{[a]}$

	Solvent	$J_{\rm sc}[{ m mAcm^{-2}}]$	$V_{\rm oc} [{ m mV}]$	FF	η[%]
ATT1	EtOH	10.40	664.9	72.69	5.03
	$MeOH + CHCl_3$	10.06	646.6	75.67	4.92
	CHCl ₃	5.62	655.8	76.27	2.81
ATT2	EtOH	8.10	680.9	76.90	4.24
	$MeOH + CHCl_3$	7.53	664.3	76.21	3.81
	CHCl ₃	2.49	613.2	72.89	1.11
ATT3	EtOH	10.47	650.9	76.25	5.20
	$MeOH + CHCl_3$	9.85	619.0	75.41	4.60
	CHCl ₃	7.70	617.2	74.52	3.54
N719	EtOH	14.11	822.6	67.62	7.85

[a] The concentration was maintained at 5×10^{-4} M in different solvents, with 0.5 M 1-methyl-3-propylimidazolium iodide (PMII), 0.2 M LiI, 0.05 M I₂, and 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile/valeronitrile (85:15) solution. Performance of the DSSC was measured with a 0.45 cm² working area.

ances. When EtOH was used to sensitize TiO₂, the DSSCs based on **ATT1–ATT3** showed the highest η values of 5.03, 4.24, and 5.20%, respectively. The DSSCs fabricated in a mixed solvent had a slightly lower performance than those in EtOH. On the other hand, the DSSCs fabricated in CHCl₃ gave the lowest η values. In particular, among the photovoltaic performance parameters, short-circuit photocurrent density (J_{sc}) values of the DSSCs fabricated in CHCl₃ decreased dramatically relative to those in the other solvents.

The absorption spectra of the three dyes on TiO_2 films sensitized in different solvents were measured to determine the reason for such variations in their performances. The results are shown in Figure 5. Also, the amounts of anchored dyes on TiO_2 films were estimated by the methods explained in the Experimental Section, and the corresponding data are collected in Table 3. The amounts of dyes adsorbed onto TiO_2 films were higher in EtOH and mixed solvent than in CHCl₃. This result shows that the strength of the J_{sc} of the DSSCs fabricated in various solvents has a direct rela-

www.chemasianj.org

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim







Figure 2. a) Optimized molecular geometry and b) Frontier molecular orbitals of the HOMO (left) and LUMO (right) of the synthesized dyes calculated with DFT at the B3LYP/6-31+G(d,p) level.

tionship with the amounts of dyes adsorbed. This is because the increased amounts of dyes adsorbed onto TiO_2 films leads to a broader incident monochromatic photon-to-current conversion efficiency (IPCE) spectrum and higher IPCE value of the resulting DSSC.^[16]



Figure 3. Cyclic voltammograms (CV) curves of the three dyes in CH_2Cl_2 (**\blacksquare ATT1**, **\blacksquare ATT2**).

Potential / V vs Ag/AgCl

Photovoltaic Properties of DSSCs Based on the Synthesized Dyes

Three DSSCs were fabricated by using the synthesized dyes according to the methods described in the Experimental Section. The photovoltaic performances of these DSSCs fabricated in EtOH under standard AM 1.5 G irradiation conditions are listed in Table 2, and the respective J-V curves are shown in Figure 6. The incident monochromatic photonto-current conversion efficiencies of the DSSCs fabricated in EtOH are shown in Figure 7. The range of the IPCE spectrum based on ATT1 was up to 660 nm, and a high IPCE value (>70%) was observed from 410 to 550 nm with the maximum value of 78.57 % at 470 nm. The range of the IPCE spectrum based on ATT3 was up to 680 nm, and a high IPCE value (>70%) was observed from 410 to 550 nm, with the maximum value of 77.12% at 470 nm. These two DSSCs have high and broad IPCE spectra. On the other hand, the range of the IPCE spectrum based on ATT2 (up to 640 nm) was narrower than those of the former two dyes. Moreover, it also exhibited a lower IPCE value (the maximum IPCE value of 71.94% at 470 nm). The rather narrow and low IPCE value for ATT2 is responsible for the lower J_{sc} and inferior η . It is well known that a larger amount of dye adsorbed on TiO2 leads to a broader IPCE spectrum and higher IPCE value of the DSSC, which contribute to the higher η . Therefore, the results might be due to the smaller amount of ATT2 adsorbed onto TiO₂ caused by its bulky and twisted molecular structure.

The performance of the DSSCs improved in the order of ATT2 < ATT1 < ATT3. It is important to note that the amounts of dye adsorbed vary according to the structure of the thiophene bridge $(7.20 \times 10^{-8} \text{ (ATT1)}, 7.00 \times 10^{-8} \text{ (ATT2)}, 1.34 \times 10^{-7} \text{ mol cm}^{-2} \text{ (ATT3)})$, hence the influence of the amount of dye adsorbed on the cell performance was considered important in our discussion (Table 3).

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

5



Figure 4. J-V curves of the DSSCs based on a) **ATT1**, b) **ATT2**, and c) **ATT3** in different solvents (\blacksquare EtOH, \bullet MeOH+CHCl₃, \blacktriangle CHCl₃).

As shown in Scheme 3, it seems that the different amount of dye adsorbed is due to the different coverage area per

Figure 5. Absorption spectra of a) **ATT1**, b) **ATT2**, and c) **ATT3** adsorbed onto TiO_2 in different solvents (\blacksquare EtOH, \blacklozenge MeOH+CHCl₃, \blacktriangle CHCl₃).

molecule on the TiO_2 surface according to the molecular size of the dye. **ATT3** showed the highest amount of adsorp-

www.chemasianj.org

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Tabl	e 3.	The amount	of	anchored	dyes	on	TiO_2	films	in	various	sol	vent	ts
------	------	------------	----	----------	------	----	---------	-------	----	---------	-----	------	----

	EtOH [mol cm ⁻²]	$MeOH+CHCl_3 [mol cm^{-2}]$	$CHCl_3 [mol cm^{-2}]$
ATT1	7.20×10^{-8}	3.36×10^{-8}	6.50×10^{-10}
ATT2	7.00×10^{-8}	2.64×10^{-8}	2.70×10^{-10}
ATT3	1.34×10^{-7}	1.28×10^{-7}	1.53×10^{-9}
ATT3	1.34×10^{-7}	2.64×10^{-8} 1.28×10^{-7}	$2.70 \times 10^{-1.53} \times 10^{-1.53}$



Scheme 3. Schematic diagram of the TiO_2 surface sensitized with **ATT2** and **ATT3**.



Figure 6. Photocurrent density-voltage (J–V) curves for the DSSCs based on the synthesized dyes under AM 1.5 G simulated solar light (100 mW cm⁻²) (**a** ATT1, **b** ATT2, **b** ATT3, **v** N719).

tion on TiO₂ although it had the most twisted molecular structure. This might be due to the smaller molecular size of **ATT3** caused by the bridged structure of the substituent. A larger amount of dye adsorbed onto TiO₂ leads to a higher J_{sc} and superior η of the DSSC. On the other hand, **ATT1** and **ATT2** had a larger molecular size than **ATT3** because of the bulky open-chain structure of the 3-methylbutylthio substituent and thus they had a smaller amount of dye adsorbed on TiO₂, thereby leading to a lower J_{sc} . Although **ATT1** had a smaller amount of dye adsorbed, its J_{sc} was sim-



Figure 7. Incident photon-to-current conversion efficiencies spectra for the DSSCs based on the synthesized dyes (\blacksquare ATT1, \bullet ATT2, \blacktriangle ATT3, \blacktriangledown N719).

ilar to that of **ATT3** due to the higher molar extinction coefficient.

The open-circuit voltage (V_{oc}) increased in the order of ATT3 < ATT1 < ATT2. It is considered that the bulky and hydrophobic 3-methylbutylthio substituents of ATT1 and ATT2 suppressed the diffusion of the electrolyte to the TiO₂ surface, thereby resulting in a retardation of charge recombination.^[17] To elucidate the correlation of $V_{\rm oc}$ with the dyes, electrochemical impedance was measured in the dark. The Nyquist plots of the DSSCs based on the three dyes under a forward bias of -0.65 V with a frequency range of 0.1 Hz to 100 kHz are shown in Figure 8a. The Bode phase plots are also shown in Figure 8b. Three semicircles were observed in the Nyquist plots. The smaller semicircle at high frequency is assigned to the redox charge-transfer response at the Pt/electrolyte interface.^[18] The large one at the intermediate frequency represents the electron-transfer impedance at the TiO₂/dye/electrolyte interface, and the last one at low frequency shows the Nernst diffusion response of the electrolyte. The charge recombination resistance at the TiO₂ surface, $R_{\rm rec}$, can be estimated from the radius of the middle semicircle in the Nyquist plots. The charge recombination resistance is related to the charge recombination rate, such that a smaller $R_{\rm rec}$ means a large charge recombination rate. The $R_{\rm rec}$ values increased in the order of ATT3 < ATT1 < ATT2. The result appears to be consistent with the increase of $V_{\rm oc}$ in the DSSCs based on ATT1 and ATT2 that bear a 3-methylbutylthio side chain. The increased $R_{\rm rec}$ values imply the retardation of charge recombination between the injected electron and electron acceptor (I_3^-) in the electrolyte, with a consequent increase in the V_{oc} . Correspondingly, the frequency of the characteristic peak in the Bode plots increased in the order of ATT3 < ATT1 < ATT2, thereby suggesting that the DSSCs based on ATT1 and ATT2 that bear a 3-methylbutylthio side chain have longer electron

I.

7



Figure 8. Electrochemical impedance spectra of DSSCs based on the three dyes measured in the dark under -0.65 V bias: a) Nyquist plots, b) Bode phase plots (**•** ATT1, **•** ATT2, **•** ATT3).

lifetimes due to the slower recapture of the conductionband electron by I_3^- . This result corresponded to the sequence of the V_{oc} in the photovoltaic performances of DSSCs based on the three dyes.

Conclusion

A new series of novel triphenylamine dyes with different alkylthio-substituted thiophene moieties as a π -conjugated bridge were designed and synthesized for applications in DSSCs. The photophysical properties of these dyes and the photovoltaic performances of the DSSCs markedly depended on the molecular structure of the dyes in terms of the position, number, and shape of the alkylthio substituents in the thiophene bridge. The introduction of an additional bulky alkylthio substituent with an open-chain structure at the 3position of the thiophene led to a decrease in η , despite the enhancement of V_{oc} . This was attributed to the lower J_{sc} caused by the blueshift of the absorption spectrum and decrease in the amount of dye adsorbed on TiO₂. On the other hand, the introduction of a substituent with a bridged structure at the same position led to an improvement in $J_{\rm sc}$ due to the relatively redshifted absorption spectrum and the larger amount of dye adsorbed, which resulted in the increase in η . In addition, the DSSCs fabricated in different solvents showed large variations in their performances due to the amount of dye adsorbed. Therefore, designing the molecular structure to have a larger amount of dye adsorbed and optimizing the solvent system for TiO₂ sensitization is needed to obtain highly efficient DSSCs.

Experimental Section

General Information

3-Methoxythiophene, 3,4-di(methoxy)thiophene, 3-methylbutylthiol, 1,2dithiolethane, and p-toluenesulfonic acid purchased from Sigma-Aldrich; and 4-(diphenylamino)phenyl boronic acid from TCI were used without further purification. All chemicals used in this study were of synthesis grade. ¹H and ¹³C NMR spectra were recorded with a Bruker Avance 500 at 500 MHz using CDCl_3 and $[D_6]\text{DMSO}$ as the solvent and TMS as the internal standard. Mass spectra were measured with a JEOL JMS-600W Agilent 6890 Series, and FTIR spectra were measured with a Thermo Scientific Nicolet 6700. UV-visible absorption spectra were measured with an HP 8452A spectrophotometer and emission spectra were recorded with a QuantaMaster UV/Vis spectrofluorometer. Cyclic voltammetry was performed with a three-electrode electrochemical cell on a Potentostat/Gavanostat PAR Model 273A. Glassy-carbon, platinum wire, and Ag/Ag+ were employed as the working, counter, and reference electrodes, respectively. Tetrabutylammonium tetrafluoroborate (TBATFB) was used as the supporting electrolyte and ferrocene was added as an internal reference for calibration.

Synthesis of 2-Cyano-3-{5-[4-(diphenylamino)phenyl]-3-(3methylthio)thiophene-2-yl}acrylic acid (ATT1)

A mixture of the intermediate 10 (0.6 g, 1.3 mmol), cyanoacetic acid (0.28 g, 3.25 mmol), and piperidine (0.51 mL, 5.2 mmol) was dissolved in acetonitrile (60 mL) and heated at reflux for 6 h at 92 °C under nitrogen. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using dichloromethane/methanol (8:1, v/v). The product was dissolved in dichloromethane (120 mL) and then 0.1 M HCl aqueous solution was added to this solution. The solution was vigorously stirred for 2 h and the organic layer was dried over anhydrous MgSO₄. The solvent was removed by rotary evaporation and subsequently dried in a vacuum oven to afford ATT1 (0.46 g, 67%) as a dark red solid. ¹H NMR (CDCl₃, 500 MHz): $\delta = 8.69$ (s, 1 H), 7.54 (d, J =8.7 Hz, 2H), 7.31 (t, J=7.9 Hz, 4H), 7.13 (m, 7H), 7.05 (d, J=8.7 Hz, 2H), 3.02 (m, 2H), 1.74 (m, 1H), 1.57 (m, 2H), 0.93 ppm (m, 6H); ¹³C NMR ([D₆]DMSO, 500 MHz): $\delta = 163.38$, 151.30, 148.54, 148.70, 145.71, 141.51, 129.24, 127.04, 126.94, 124.62, 123.99, 123.79, 120.81, 116.07, 95.84, 37.23, 31.74, 26.23, 21.51 ppm; HRMS (FAB+): m/z calcd for C₃₁H₂₈N₂O₂S₂: 524.1637; found: 524.1635; elemental analysis calcd (%) for $C_{31}H_{28}N_2O_2S_2$: C 70.96, H 5.38, N 5.34; found: C 70.59, H 5.17, N 5.06.

Synthesis of 2-Cyano-3-{5-[4-(diphenylamino)phenyl]-3,4-bis(3methylthio)thiophene-2-yl]acrylic acid (**ATT2**)

This compound was synthesized by using the method established for **ATT1**. The crude product was purified by column chromatography on silica gel using dichloromethane/methanol (8:1, v/v) to afford **ATT2** (0.34 g, 55%) as a red solid; ¹H NMR (CDCl₃, 500 MHz): δ =9.02 (s, 1H), 7.68 (d, *J*=8.5 Hz, 2H), 7.32 (t, *J*=7.7 Hz, 4H), 7.16 (d, *J*=8.2 Hz,

www.chemasianj.org

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

4H), 7.12–7.07 (m, 4H), 3.02 (m, 2H), 2.73 (m, 2H), 1.72 (m, 1H), 1.53 (m, 1H), 1.46 (m, 2H), 1.28 (m, 2H), 0.91 (m, 6H), 0.79 ppm (m, 6H); ¹³C NMR ([D₆]DMSO, 500 MHz): δ =162.87, 151.32, 148.21, 147.64, 145.86, 143.48, 133.99, 131.84, 129.72, 129.23, 124.47, 123.67, 120.66, 115.57, 99.51, 37.38, 36.95, 34.38, 32.65, 26.03, 25.84, 21.48, 21.39 ppm; HRMS (FAB⁺): *m*/*z* calcd for C₃₆H₃₈N₂O₂S₃: 626.2112; found: 626.2108; elemental analysis calcd (%) for C₃₁H₂₈N₂O₂S₂: C 68.97, H 6.11, N 4.47; found: C 68.66, H 5.93, N 4.23.

Synthesis of 2-Cyano-3-{5-[4-(diphenylamino)phenyl]-3,4-(ethylenedithio)thiophene-2-yl/acrylic acid (**ATT3**)

This compound was synthesized by using the method established for **ATT1**. The crude product was purified by column chromatography on silica gel using dichloromethane/methanol (5:1, v/v) to afford **ATT3** (0.19 g, 52%) as a dark red solid. ¹H NMR (CDCl₃, 500 MHz): δ =8.50 (s, 1H), 7.49 (m, 2H), 7.32 (t, *J*=7.5 Hz, 4H), 7.16 (d, *J*=8.0 Hz, 4H), 7.12 (m, 2H), 7.07 (t, *J*=7.5 Hz, 2H), 3.38 (m, 2H), 3.24 ppm (m, 2H); ¹³C NMR (CDCl₃, 500 MHz): δ =168.26, 155.03, 151.23, 149.47, 147.20, 146.91, 134.67, 133.20, 130.30, 129.51, 125.37, 124.05, 121.52, 115.55, 97.08, 35.78, 34.02 ppm; HRMS (FAB⁺): *m/z* calcd for C₂₈H₂₀N₂O₂S₃: 512.0715; found: 512.0711; elemental analysis calcd (%) for C₃₁H₂₈N₂O₂S₂: C 65.60, H 3.93, N 5.46; found: C 65.31, H 3.78, N 5.28.

Fabrication of Dye-Sensitized Solar Cells

Fluorine-tin oxide (FTO) glass plates (Pilkington, TEC-8, 8 Ω/square, 2.3 mm thick) were cleaned with ethanol by ultrasonication for 10 min, and then treated in a UV-O3 system for 20 min. The FTO layer was first covered with 7.5 % Ti^{IV} bis(ethyl acetoacetato)diisopropoxide solution by using a spin-coating method. For the transparent nanocrystalline layer, TiO₂ paste (230(M2331)-2T) was coated on the FTO glass plates by doctor blade printing, and then sintering was carried out at 500 °C for 30 min. TiO₂ paste (CCIC-1T) for the scattering layer was prepared using the same method. The resulting layer was composed of a $9\,\mu\text{m}\text{-thick}$ transparent layer and 4 µm-thick scattering layer. The active area of the TiO_2 films was about 0.45 cm². The TiO₂ electrodes were immersed into the different solutions (0.5 mm in EtOH, MeOH/CHCl_3, and CHCl_3) and kept at room temperature for 24 h. Counter electrodes were prepared by dropping a 0.7 mM H₂[PtCl₆] solution on FTO glass and heating it at 400 °C for 20 min. The dye-adsorbed TiO₂ electrode and the counter electrode were sealed using 25 µm-thick Surlyn film (Dupont 1702). An electrolyte solution was introduced through a drilled hole on the counter electrode, in which the electrolyte solution consisted of 0.5 M 1-methyl-3propylimidazolium iodide (PMII), $0.2\,\text{m}$ LiI, $0.05\,\text{m}$ $I_2,$ and $0.5\,\text{m}$ 4-tert-butylpyridine (TBP) in acetonitrile/valeronitrile (85:15).

Photovoltaic Measurements

Photovoltaic measurements were performed with a Keithly model 2400 source measuring unit. A 1000 W Xe lamp (Spectra-physics) served as a light source and its light intensity was adjusted using a national renewable energy laboratory (NREL)-calibrated silicon solar cell equipped with a KG-5 filter to approximate AM 1.5 G of sunlight intensity. IPCE was measured as a function of wavelength from 300–800 nm using a specially designed IPCE system for dye-sensitized solar cells (PV Measurements, Inc.). A 75 W Xe lamp was used as the light source for generation of a monochromatic beam. Calibrations were performed using a silicon photodiode, which was calibrated using NIST-calibrated photodiode G425 as a standard, and IPCE values were collected at a low chopping speed of 10 Hz.

Measurements of the Amount of Dye Adsorbed and Absorption Spectra on TiO_2

The preparation method of TiO₂ films was the same as the procedure above. The 9 µm-thick (area: 20×10 mm) TiO₂ film without the scattering layer was immersed into the different solutions (0.5 mm in EtOH, MeOH/CHCl₃, and CHCl₃) and kept at room temperature for 24 h. The dye-adsorbed TiO₂ films were washed with the solvent and subsequently dried. Absorption spectra of dye-adsorbed TiO₂ films were measured with an HP 8452A spectrophotometer. The amount of dye adsorbed was estimated by measuring the absorption spectrum of the resulting solution after desorption of the dye in a basic solution (0.1 M NaOH aqueous/ethanol (1:1) mixed solvent).

Computational Study

All calculations were carried out with the Gaussian 09 software program.^[19] The molecular geometry and the electron distributions of the synthesized dyes for the HOMO and LUMO state were calculated with DFT at the B3LYP/6-31 + G(d) level.

Acknowledgements

This work was supported by a grant from the Korean Evaluation Institute of Industrial Technology funded by the Korean government (MKE).

- [1] a) B. O'Regan, M. Grätzel, *Nature* 1991, 353, 737–740; b) M. Grätzel, *Nature* 2001, 414, 338–344.
- [2] a) Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide, L. Han, Jpn. J. Appl. Phys. 2006, 45, L638–L640; b) M. K. Nazeeruddin, F. D. Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, B. Takeru, M. Grätzel, J. Am. Chem. Soc. 2005, 127, 16835–16847; c) Z.-S. Wang, T. Yamaguchi, H. Sugihara, H. Arakawa, Langmuir 2005, 21, 4272–4276.
- [3] P. Wang, S. M. Zakeeruddin, J. E. Moser, M. K. Nazeeruddin, T. Sekiguchi, M. Grätzel, *Nat. Mater.* 2003, 2, 402–407.
- [4] A. Mishra, M. K. Fischer, P. Bäuerle, Angew. Chem. 2009, 121, 2510–2536; Angew. Chem. Int. Ed. 2009, 48, 2474–2499.
- [5] S. Ito, H. Miura, S. Uchida, M. Takata, K. Sumioka, P. Liska, P. Comte, P. Péchy, M. Grätzel, *Chem. Commun.* 2008, 5194–5196.
- [6] G. Zhang, H. Bala, Y. Cheng, D. Shi, X. Lv, Q. Yu, P. Wang, Chem. Commun. 2009, 2198–2200.
- [7] a) H. Choi, C. Baik, S. O. Kang, J. Ko, M. S. Kang, M. K. Nazeeruddin, M. Grätzel, Angew. Chem. 2008, 120, 333-336; Angew. Chem. Int. Ed. 2008, 47, 327-330; b) K. Hara, M. Kurashige, Y. Dan-Oh, C. Kasada, A. Shinpo, S. Suga, K. Sayama, H. Arakawa, New J. Chem. 2003, 27, 783-785; c) S.-L. Li, K.-J. Jiang, K.-F. Shao, L.-M. Yang, Chem. Commun. 2006, 2792-2794; d) D. P. Hagberg, T. Edvinsson, T. Marinado, G. Boschloo, A. Hagfeldt, L. Sun, Chem. Commun. 2006, 2245-2247; e) R. Chen, X. Yang, H. Tian, X. Wang, A. Hagfeldt, L. Sun, Chem. Mater. 2007, 19, 4007-4015; f) J. T. Lin, P.-C. Chen, Y.-S. Yen, Y.-C. Hsu, H.-H. Chou, M.-C. Yeh, Org. Lett. 2009, 11, 97-100.
- [8] a) W.-H. Liu, I.-C. Wu, C.-H. Laia, C.-H. Lai, P.-T. Chou, Y.-T. Li, C.-L. Chen, Y.-Y. Hsu, Y. Chi, *Chem. Commun.* **2008**, 5152–5154; b) K.-J. Jiang, K. Manseki, Y.-h. Yu, N. Masaki, J.-B. Xia, L.-M. Yang, Y.-I. Song, S. Yanagida, *New J. Chem.* **2009**, *33*, 1973–1977.
- [9] S. Kirchmeyer, K. J. Reuter, J. Mater. Chem. 2005, 15, 2077–2088.
- [10] a) N. Sakmeche, J. J. Aaron, M. Fall, S. Aeiyach, M. Jouni, J. C. Lacroix, P. C. Lacaze, *Chem. Commun.* 1996, 2723–2724; b) B. Sankaran, J. R. Reynolds, *Macromolecules* 1997, *30*, 2582–2588; c) F. Jonas, L. Schrader, *Synth. Met.* 1991, *41*, 831–836; d) H. Huang, P. G. Pickup, *Chem. Mater.* 1998, *10*, 2212–2216; e) Y. Fu, H. Cheng, R. L. Elsenbaumer, *Chem. Mater.* 1997, *9*, 1720–1724.
- [11] a) J. Roncali, *Chem. Rev.* 1992, 92, 711–738; b) C. Wang, J. L. Schindler, C. R. Kannewurf, M. G. Kanatzidis, *Chem. Mater.* 1995, 7, 58–68; c) P. Blanchard, A. Cappon, E. Levillain, Y. Nicolas, P. Frère, J. Roncali, *Org. Lett.* 2002, 4, 607–609.
- [12] F. Goldoni, B. W. Langeveld-Voss, E. W. Meijer, Synth. Commun. 1998, 28, 2237–2244.
- [13] a) S. Roquet, A. Cravino, P. Leriche, O. Alévêque, P. Frère, J. Roncali, J. Am. Chem. Soc. 2006, 128, 3459–3466; b) K. R. Justin Thomas, Y.-C. Hsu, J. T. Lin, K.-M. Lee, K.-C. Ho, C.-H. Lai, Y.-M. Cheng, P.-T. Chou, Chem. Mater. 2008, 20, 1830–1840.
- [14] J.-M. Raimundo, P. Blanchard, N. Gallego-Planas, N. Mercier, I. Ledoux-Rak, R. Hierle, J. Roncali, J. Org. Chem. 2002, 67, 205–218.

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.chemasianj.org

These are not the final page numbers! **77**

9

- [15] a) R. Chen, G. Zhao, X. Yang, X. Jiang, J. Liu, H. Tian, Y. Gao, X. Liu, K. Han, M. Sun, L. Sun, J. Mol. Struct. 2008, 876, 1–8; b) H. Tian, X. Yang, R. Chen, R. Zhang, A. Hagfeldt, L. Sun, J. Phys. Chem. C 2008, 112, 11023–11033.
- [16] E. L. Tae, S. H. Lee, J. K. Lee, S. S. Yoo, E. J. Kang, K. B. Yoon, J. Phys. Chem. B 2005, 109, 22513–22522.
- [17] a) J.-H. Yum, D. P. Hagberg, S.-J. Moon, K. M. Karlsson, T. Marinado, L. Sun, A. Hagfeldt, M. K. Nazeeruddin, M. Grätzel, *Angew. Chem.* **2009**, *121*, 1604–1608; *Angew. Chem. Int. Ed.* **2009**, *48*, 1576– 1580; b) Z.-S. Wang, N. Koumura, Y. Cui, M. Takahashi, H. Sekiguchi, A. Mori, T. Kubo, A. Furube, K. Hara, *Chem. Mater.* **2008**, *20*, 3993–4003.
- [18] a) J. van de Lagemaat, N.-G. Park, A. J. Frank, J. Phys. Chem. B 2000, 104, 2044–2052; b) R. Kern, R. Sastrawan, L. Ferber, R. Stangl, J. Luther, *Electrochim. Acta* 2002, 47, 4213–4225; c) Q. Wang, J.-E. Moser, M. Grätzel, J. Phys. Chem. B 2005, 109, 14945–14953; d) D. Kuang, S. Ito, B. Wenger, C. Klein, J. E. Moser, R. Humphry-Baker, S. M. Zakeeruddin, M. Grätzel, J. Am. Chem. Soc. 2006, 128, 4146–4154.
- [19] Gaussian 09, Revision A.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Received: September 28, 2011 Revised: January 3, 2012 Published online:

10

www.chemasianj.org

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Chem. Asian J. **0000**, *00*, 0–0

Structure and solvent effects: Three novel triphenylamine dyes with different alkylthio-substituted thiophene bridges were synthesized for dye-sensitized solar cells (DSSCs). The photovoltaic performances of the DSSCs showed a marked dependence on the bridge structure and solvent system due to the different amounts of dye adsorbed (see scheme).



Solar Cells

Chun Sakong, Se Hun Kim, Sim Bum Yuk, Jin Woong Namgoong, Se Woong Park, Min Jae Ko, Dong Hoe Kim, Kug Sun Hong, Jae Pil Kim*_____

Influence of Solvent and Bridge Structure in Alkylthio-Substituted Triphenylamine Dyes on the Photovoltaic Properties of Dye-Sensitized Solar Cells

11