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Novel Organic Dyes Based on Bulky Tri(triphenylamine)-Substituted Styrene for Dye-Sensitized Solar Cells[†]

Zhang, Zhiyun[a](张志云) Han, Jinlong[a](韩金龙) Li, Xin[b](李昕)
Cai, Shengyun[a](蔡升云) Su, Jianhua*,[a](苏建华)

[a] *Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, China*
[b] *Department of Theoretical Chemistry and Biology, School of Biotechnology, KTH Royal Institute of Technology, SE-10691 Stockholm, Sweden*

Three novel donor-π-acceptor (D-π-A) metal-free organic dyes (**TB**, **TS** and **TF**) based on tri(triphenylamine)-substituted styrene as donor with various conjugated linkers (benzene, thiophene and furan) were synthesized, characterized and used for the application of dye-sensitized solar cells (DSSCs). Under the same condition, The photo-to-electrical conversion efficiency of the DSSCs sensitized with **TB**, **TS** and **TF** reach 1.84%, 4.10% and 4.52%, respectively, which are lower than that sensitized with **R1** (5.02%) with one triphenylamine unit. The results suggest that these bulky donor-based sensitizers are unfavorable to DSSCs.

Keywords dye-sensitized solar cells, triphenylamine, styrene, π-linker, bulky donor

Introduction

Dye-sensitized solar cells (DSSCs) offer a bright future for their capability to convert solar light to electricity with low production costs and environment pollution compared with conventional semiconductor photovoltaic devices.[1] Thanks to continuous studies in DSSCs in the last two decades, the current certified best conversion efficiency of 11.4% was achieved with a Ru complex dye,[2] but the wide application of Ru complexes is difficult due to the limited resources and elaborated purification. In the same time, organic metal-free dyes have also been developed for DSSCs and offered competitive alternatives because of their pretty excellent properties,[3] such as high molar extinction coefficient, facile molecular design and synthesis, low cost and no resource concern on the rare metal. Recently, a number of metal-free organic dyes such as merocyanine,[4] hemicyanine,[5] cyanine,[6] coumarin,[7] perylene,[8] indoline,[9] oligothiophene,[10] phenothiazine,[11] and triphenylamine dyes[12] have been reported, which make the organic dyes fruitful in the application of DSSCs.

Dye aggregation often observed with organic dyes (particularly near-infrared dyes)[13] is detrimental to DSSC performance, because the close π-π aggregation can lead to self-quenching and reduction of electron injection into TiO_2.[14] Much effort has been made to solve the dye aggregation problem, such as coadsorption of deoxycholic acid[15] and introduction of long alkyl chains[16] or twisted non-planar units[17] onto the dye molecules. Triphenylamine has been widely used in opto- and electroactive materials for its good electron donating and transporting capability, as well as its special propeller molecular configuration.[12a] Several groups have successfully developed dendritic or starburst triphenylamine derivatives for suppressing dye aggregation in DSSCs.[18] Very recently, a two donor (D)-π-acceptor (A)-type branched organic dye based on triphenylamine as donor and 1-phenylstylyl as π-spacer has been reported by Han's group.[19] Comparison to the analogue planar dye, the twisted dye shows excellent potential as a new aggregation-free organic dye for DSSCs.

In our design, a further improvement was expected to be accomplished by introducing three triphenylamine to the double bond of styrene to form a bulky twisted π electron donor. We fixed the donor as the huge multi-triphenylamine unit and acceptor as the 2-cyanoacetic acid unit, and changed the π bridge from phenyl to thiophene and furan moiety so as to synthesize the final dyes of **TB**, **TS** and **TF** (Scheme 1). The sensitizer **R1**

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* E-mail: bbsjh@ecust.edu.cn; Tel.: 0086-021-64252288; Fax: 0086-021-64252288
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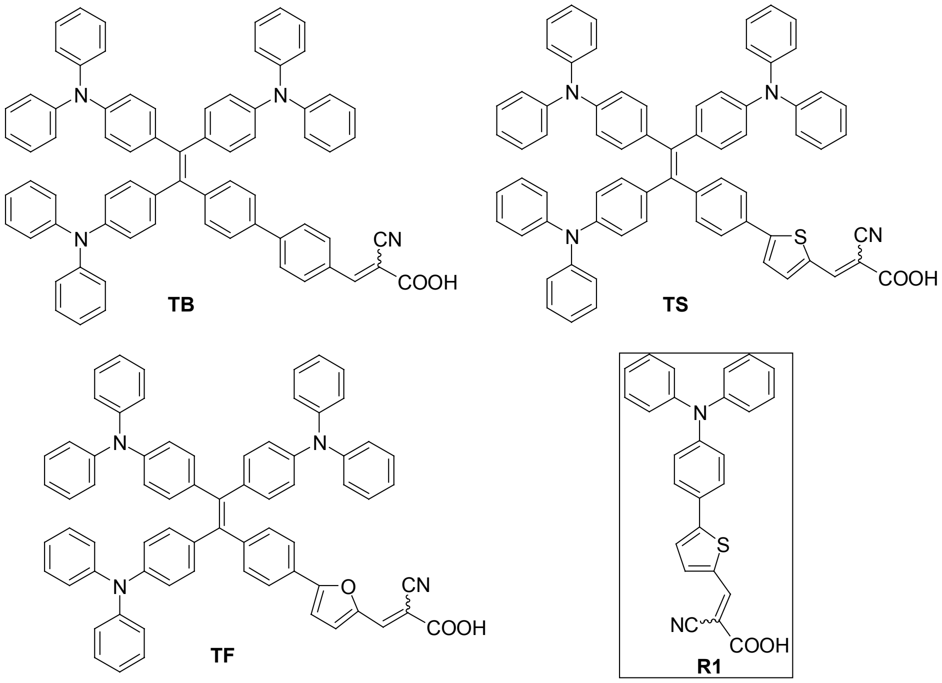
with one triphenylamine was selected as a reference to investigate whether this bulky donor is favor to DSSCs.

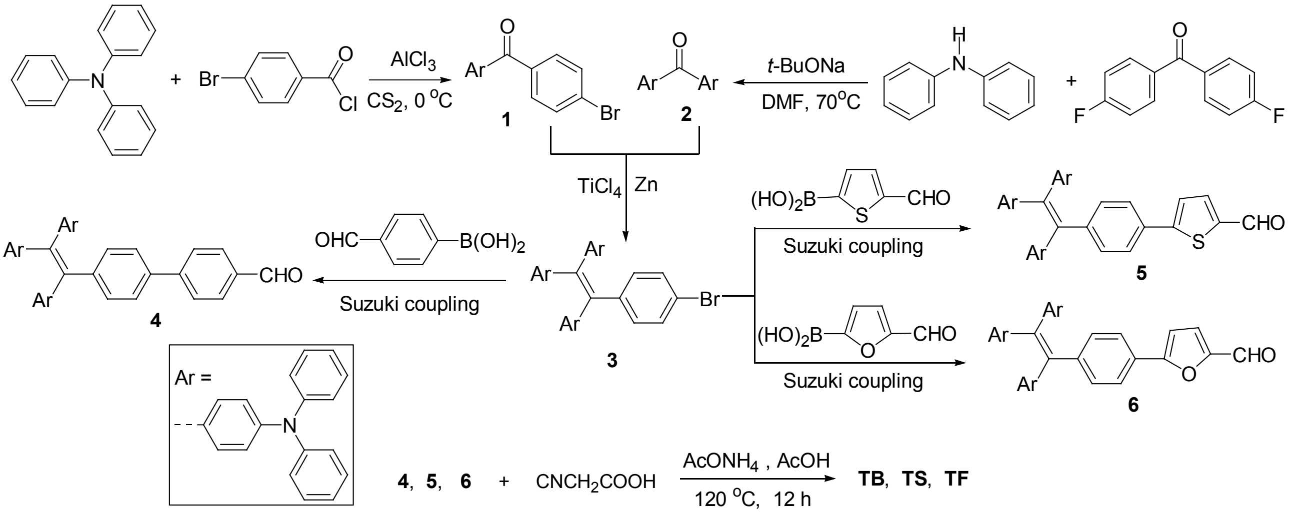
Results and Discussion

The synthetic route to the three dyes (**TB**, **TS** and **TF**) is depicted in Scheme 2. The Frieldel-Crafts reaction of triphenylamine with 4-bromobenzoyl chloride afforded **1**. In parallel the reaction of fluoride substitution can easily synthesize compound **2** which can be purified by recrystallization from acetonitrile. In the next step compounds **1** and **2** were combined in the $TiCl_4$/Zn situation. Compound **2** should be over dosed in order to minimize side products and fortunately the compound **3** can be separated by column chromatography. The bromo-intermediate **3** was reacted with (4-formylphenyl)boronic acid, (5-formylthiophen-2-yl)boronic acid or (5-formylfuran-2-yl)boronic acid by Suzuki coupling reaction to give the corresponding aldehyes. Finally the target dyes (**TB**, **TS** and **TF**) were synthesized via the Knoevenagel condensation reaction of aldehydes with cyanoacetic acid in the presence of acetic acid and ammonium acetate. All the key intermediates and three new multi-triphenylamine sensitizers were confirmed by ^{1}H NMR, ^{13}C NMR, and HRMS. The reference dye **R1** was synthesized by using a literature procedure.[12c]

Scheme 1 Molecular structures of the organic dyes and the reference dye **R1**



Scheme 2 Synthesis of the organic dyes



The photophysical and electrochemical properties of these sensitizers were preliminary studied (Table 1). In dichloromethane (DCM) solution, all target dyes exhibit three major bands at 300—500 nm (Figure 1a). In the visible region, the absorption bands corresponding to the intramolecular charge transfer (ICT) from the triphenylamine donor part to the cyanoacetic acid (CA) acceptor part were observed to display a shoulder peak round 440 nm (1.09×10^4 mol^{-1}•L•cm^{-1}), 460 nm (1.05×10^4 mol^{-1}•L•cm^{-1}) and 460 nm (1.53×10^4 mol^{-1}•L•cm^{-1}) for **TB**, **TS** and **TF**, respectively, and intense absorption bands corresponding to π-π^* transitions were observed below 400 nm. Compared with **TS** and **TF**, **TB** exhibits about a 20 nm blue-shift in absorption, suggesting that the thiophene or furan unit is more effective in increasing conjugation than the phenyl. This may be caused by the decrease of coplanarity between the electron donor and the electron acceptor due to the introduction of the benzene unit. Compared with the target dyes, **R1** showed an obvious absorption peak at 470 nm with higher molar extinction coefficient (2.20×10^4 mol^{-1}•L•cm^{-1}) meaning that the worse light-harvesting abilities in the visible region of the bulky donor-based dyes than that of **R1** could be expected.

Table 1 Optical and electrochemical properties of all dyes

Dye	$\lambda_{max}{}^{UVa}$/nm ($\varepsilon\times10^{-4}$ mol^{-1}•L•cm^{-1})	HOMO^c/ V	$E_{0\text{-}0}{}^d$/ eV	LUMO^e/ V
TB	311 (5.32), 343 (4.89) 440^b (1.09)	0.63	2.46	−1.83
TS	309 (3.72), 380 (2.86) 460^b (1.05)	0.59	2.23	−1.64
TF	310 (5.19), 381 (3.61) 460^b (1.53)	0.58	2.32	−1.74
R1	303 (1.71), 470 (2.20)	1.16^f	2.38^f	-1.22^f

[a] As measured in CH_2Cl_2 solution. [b] Shoulder peak. [c] HOMO of the dyes (vs. NHE) were measured on TiO_2 film. [d] $E_{0\text{-}0}$ of the dyes was estimated from the absorption thresholds from absorption spectra of dyes adsorbed on the TiO_2 film. [e] LUMO is estimated by subtracting $E_{0\text{-}0}$ to HOMO. [f] Ref. [12c].

The absorption spectra of all dyes on TiO_2 film after 12 h adsorption in DCM dyes solution bath were shown on Figure 1b. The absorption spectra of these dyes exhibit a slightly red-shifted and broad absorption compared to that in solution. In the visible region, the shoulder peaks of the target dyes which could be found in solution are immerged in broad absorption bands on TiO_2. The red shifts of the absorption spectra on TiO_2 of the three dyes could be ascribed to the aggregation or electronic coupling of the dyes on the TiO_2 surface. In addition, the amount of the target dyes adsorbed on TiO_2 films estimated by desorbing the dye with NaOH solution[12d] (Table 2) was less than half of that of **R1**.

Cyclic voltammetry (CV) was employed to evaluate the possibility of electron transfer from the excited dye to the conduction band (CB) of TiO_2. CV were carried in acetonitrile solution using Pt as the counter electrode, TiO_2 films stained with sensitizer as working electrode, a saturated calomel electrode (SEC) as reference electrode and 0.1 mol/L tetrabutylammonium hexafluorophosphate as the supporting electrolyte. All the dyes exhibit reversible redox waves at a moderately high oxidation potential which were shown in Figure 2. The excitation transition energies ($E_{0\text{–}0}$) of **TB**, **TS**, and **TF** were estimated from their absorption thresholds of dye-sensitized TiO_2 films to be 2.46, 2.23 and 2.32 eV, respectively. HOMO levels of these dyes on TiO_2 films corresponding to their first redox potential were checked to be 0.62, 0.59 and 0.58V vs. NHE, respec-

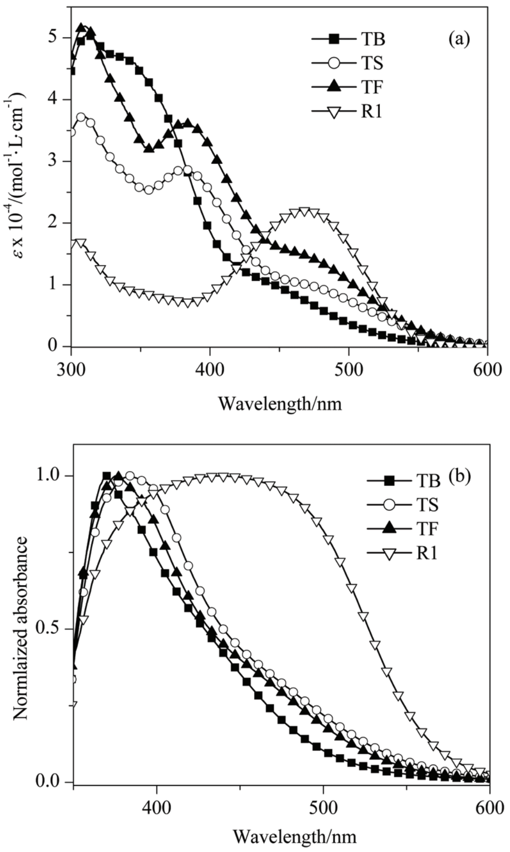


Figure 1 Normalized absorption spectra of dyes **TB**, **TS**, **TF** and **R1** in DCM solution (a) and on TiO_2 film (b).

Table 2 Photovoltaic parameters of the DSSCs based on **TB**, **TS**, **TF** and **R1**^{a}

Dye	$A_{dye}{}^b$/(μmol•cm^{-2})	J_{sc}/(mA•cm^{-2})	V_{oc}/V	*ff*	η/%
TB	0.109	5.49	0.65	0.52	1.84
TS	0.106	8.53	0.71	0.68	4.10
TF	0.102	8.87	0.75	0.66	4.52
R1	0.246	10.34	0.66	0.68	5.02

[a] Illumination: 100 mW•cm^{-2} simulated AM 1.5G solar light; electrolyte containing: 0.1 mol/L LiI+0.05 mol/L I_2+0.6 mol/L PMII+0.5 mol/L TBP in the mixed solvent of acetonitrile and 3-methoxypropionitrile (7∶3, *V*/*V*). [b] A_{dye}: amount of dye adsorbed on TiO_2.

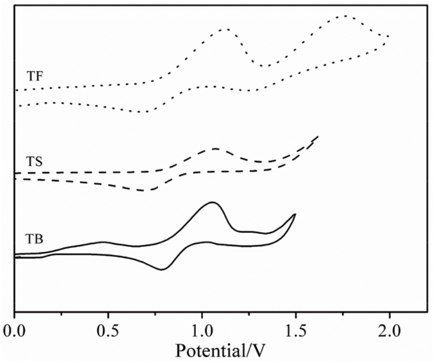


Figure 2 Cyclic voltammetry plots of the dyes.

tively. These redox potentials were more positive than the iodine/iodide redox potential value (0.4 V), which indicated sufficient driving force for dye regeneration. It also indicated that altering the link bridge in the dye molecular, changing from phenyl moiety to thiophene and furan moieties, could modify the redox potential value in an efficient way. The LUMO levels of these dyes calculated from $E_{\mathrm{HOMO}}-E_{0\text{-}0}$, are -1.83, -1.64 and -1.74 V vs. NHE, respectively. These LUMO levels are much more negative than the TiO_2 CB (-0.5 V vs. NHE), providing thermodynamic feasibility for electron injection.

To gain insight into the geometrical and electronic structures of the three triphenylamine-based sensitizers, density functional theory (DFT) calculations were performed at B3LYP/6-31G* level of theory using the Gaussian 09 program package.[20] As illustrated in Figure 3, in the optimized structures, the π-conjugation of these dyes with three propeller triphenylamine units was largely twisted, and therefore, it is expected that the intermolecular π-π interactions may be suppressed. The electron clouds of the HOMO orbitals are mainly delocalized over the mutil-triphenylamine entities, while the LUMO orbitals are localized over the π-spacer and cyanoacrylic acid groups. Spatial distributions of frontier molecular orbitals suggest that these mutil-triphenylamine-based dyes exhibit fine electron separation between the HOMO and LUMO. The effective ICT process indicates that the electron injection from the excited dyes to TiO_2 CB is theoretically permitted.

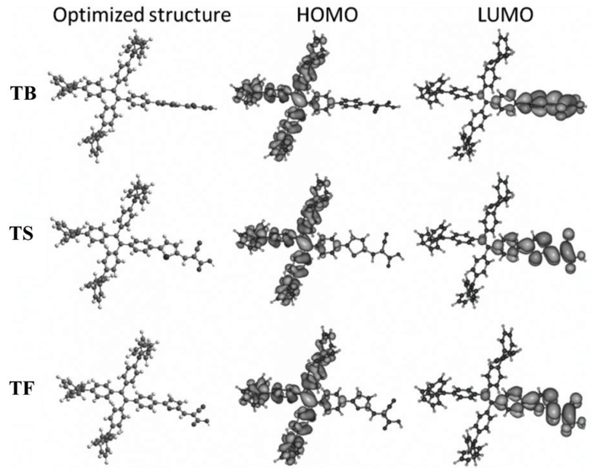


Figure 3 Frontier molecular orbital contours of the dyes.

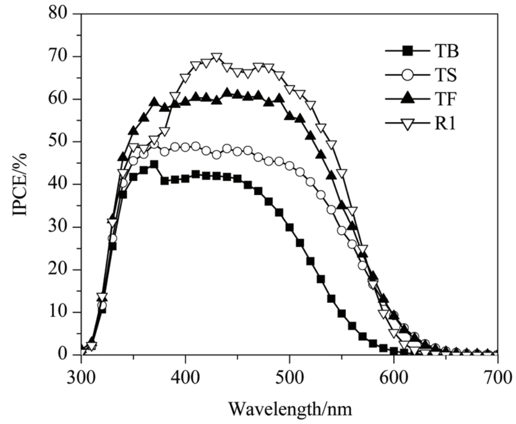


Figure 4 IPCE spectra for DSSCs based on **TB**, **TS**, **TF** and **R1**.

The DSSCs were prepared with dye-coated TiO_2 film as working electrode, platinized FTO glass as the counter electrode and 0.6 mol/L PMII, 0.05 mol/L I_2, 0.10 mol/L LiI and 0.5 mol/L 4-*tert*-butylpyridine in acetonitrile and methoxypropionitrile (volume ratio, 7 : 3) mixture solution as the redox electrolyte. Figure 4 shows the spectra of incident photo-to-current conversion efficiency (IPCE) for DSSCs with **TB**, **TS**, **TF** and **R1** obtained with a sandwich-type two electrode cells. **TB** reached its maximum IPCE at 370 nm (44%) and in the range of 350—450 nm the IPCE was above 40%. **TS** reached its maximum IPCE at 375 nm (49%) and in the range of 350—490 nm the IPCE was above 45%. **TF** reached its maximum IPCE at 440 nm (61%) and in the range of 350—520 nm the IPCE was above 50%. The rather high IPCE value for **TF** than that of **TB** and **TS** indicates that furan moiety is a good link bridge in DSSC. Due to stronger light-harvesting abilities and larger adsorption amount, **R1** exhibited higher IPCE value than that of the target dyes and reached its maximum IPCE at 431 nm (70%) and in the range of 387—514 nm the IPCE was above 60%. Compared to the absorption spectra on TiO_2 film, the IPCE spectra were broadened significantly. This may be caused by the lateral interaction in the adsorbed layer of the sensitizer and the exact mechanism needs furtherer studies.[11a]

Figure 5 shows the current-voltages characteristics of DSSCs fabricated with these dyes (**TB**, **TS**, **TF** and **R1**) as sensitizers under standard global AM 1.5 solar light condition. The detailed parameters of short-circuit current density (J_{sc}), open-circuit voltages (V_{oc}), fill factor (*ff*), and photovoltaic conversion efficiency (η) are summarized in Table 2. Compared with the statistic listed in Table 2, we could find that the η of the cells sensitized with TB, TS and TF were 1.81%, 4.10%, and 4.52%, respectively, which were lower than that sensi-

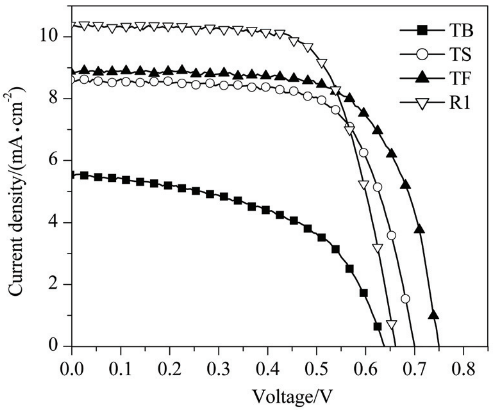


Figure 5 Current-potential (*I-V*) curves for the DSSCs based on **TB**, **TS**, **TF** and **R1** under AM 1.5 irradiation (100 Mw•cm^{-2}).

tized with **R1** (5.02%), indicating that the introduction of bulky tri(triphenylamine)-substituted styrene is unfavorable to improve the conversion efficiencies of the DSSCs. The J_{sc} values for the devices based on **TB**, **TS** and **TF** were also decreased compared with that based on **R1**, because J_{sc} is related to the molar extinction coefficient of the dye molecule, in which a higher molar extinction coefficient has good light-harvesting ability and yields a higher short circuit. In the multi-triphenylamine dyes system, the furan moiety in **TF** showed a pretty good property which gave a J_{sc} of 8.89 mA•cm^{-2}, V_{oc} of 763 mV, and a *ff* of 0.66, corresponding to an overall conversion efficiency of 4.52%. From the adsorption amounts and the short-circuit photocurrents in Table 2, the contribution of one mole of dye molecules to the short-circuit photocurrent could be calculated: one mole of **TF** produced 8.69×10^7 mA short-circuit photocurrent, while the short-circuit photocurrents generated by one mole of **R1** are 4.20×10^7 mA. Although the photovoltaic conversion efficiency of **TF** is lower than that of **R1** due to the lower molar absorption coefficient, adsorption amount and short-circuit current density of **TF**, the single molecule's efficiency of **TF** is higher than that of **R1**. This may be caused by dye aggregation happened to **R1**.

Electrochemical impedance spectroscopy (EIS) analysis was performed to further explore the effect of changing the link bridge in the three dyes on the V_{oc} in sensitized DSSCs. The Nyquist plots of the DSSCs based on the three dyes under a forward bias of -0.70 V with a frequency range of 0.1 Hz to 100 kHz are shown in Figure 6a. The Bode phase plots are shown in Figure 6b. To observe these semicircles in the Nyquist plot: the smaller semicircles and larger semicircles are attributed to the charge-transfer at the counter electrode and the electron transport at the TiO_2/dye/electrolyte interface, respectively. The radius of the larger semicircle increases in the order **TF**>**R1**>**TS**>**TB**, indicating the electron recombination resistance increases from **TB**, **TS**, **R1** to **TF** and is reflected in the improvements seen in the V_{oc}. This result is in agreement with the observed shift in the V_{oc} value under standard global AM 1.5 illumination.

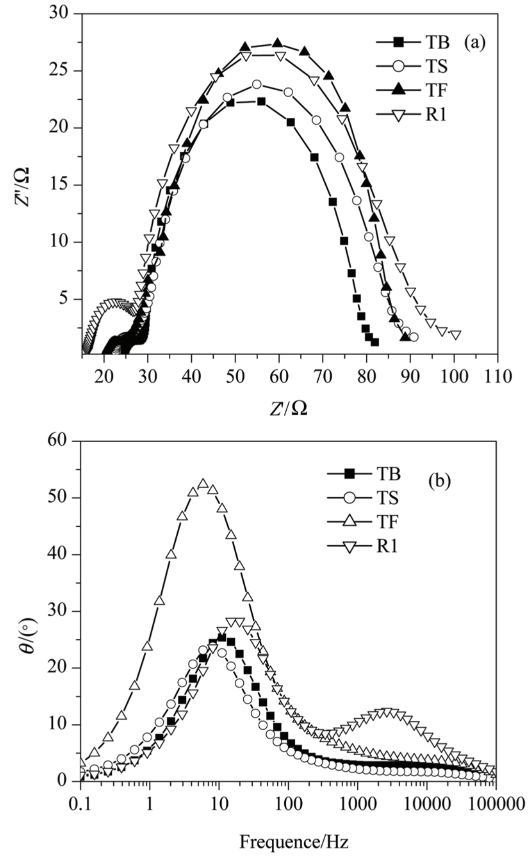


Figure 6 Nyquist plots of impedance spectra (a) and Bode phase plots of the impedance spectra (b) of DSSCs based on **TB**, **TS**, **TF** and **R1**.

Conclusions

In summary, we have synthesized three metal-free organic dyes containing tri(triphenylamine)-substituted styrene as donor for the use of DSSCs. The analyses of photovoltaic experiments showed that the change in link-bridge would influence the property of the dyes in a huge degree. Among these dyes, DSSCs based on **TF** exhibited the best electricity conversion efficiency of 4.52% (J_{sc}=8.89 mA•cm^{-2}, V_{oc}=0.76 V, *ff*=0.66) under AM 1.5 irradiation (100 mW•cm^{-2}). The performances of devices based on the three dyes with the bulky donor were worse than the reference dye **R1** (η =5.02%) with one triphenylamine due to lower light-harvesting abilities and adsorption amount. Further structural modification of these dyes is anticipated to improve the light absorption in the red and near-IR ranges for higher DSSCs performance.

Experimental

Materials and measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bücker AM 400 spectrometer. Mass spectra were measured with an HP5989 mass spectrometer. The UV-vis spectra were recorded with a Varian Cary 500 spectrophotometer. Cyclic voltammograms were performed with a Versastat II electrochemical workstation. Detailed device fabrications and the photoelectrochemical measurements are written in support information. Fluorine-doped SnO_2 conducting glass (FTO glass, transmission＞90% in the visible, sheet resistance 15 Ω/square) was obtained from Geao Science and Educational Co. Ltd. of China. Tetra-*n*-butylammonium hexafluorophosphate (TBAPF6), 4-*tert*-butylpyridine (4-TBP), and lithium iodide were bought from Fluka and iodine, 99.999%, was purchased from Alfa Aesar. All other solvents and chemicals used were produced by Sinopharm Chemical Reagent Co., Ltd., China (reagent grade) and used as received. Solvents were distilled from appropriate reagents.

Synthesis and characterizations

The detailed synthetic procedures and characterizations of the three dyes were described in the supporting information.

Device fabrication

The DSSCs sensitized by the four dyes were fabricated according to the previous literature.[21] A screen-printed double layer of TiO_2 particles was used as photoelectrode. A 10 μm thick film of 13 nm sized TiO_2 particles (Ti-Nanoxide T/SP) was first printed on the FTO conducting glass and further coated with a 4 μm thick second layer of 400 nm light-scattering anatase particles (Ti-Nanoxide 300). Sintering was carried out at 450 ℃ for 30 min. Before immersion in the dye solution, these films were immersed into a 40 mmol/L aqueous $TiCl_4$ solution at 70 ℃ for 30 min and washed with water and ethanol. Then the films were heated again at 450 ℃ for 30 min followed by cooling to 80 ℃ and dipping into a 3×10^{-4} mol/L solution of dye in acetonitrile for 12 h at room temperature. To prepare the counter electrode, the Pt catalyst was deposited on the cleaned FTO glass by coating with a drop of H_2PtCl_6 solution (0.02 mol/L in 2-propanol solution) with the heat treatment at 400 ℃ for 15 min. A hole (0.8 mm diameter) was drilled on the counter electrode using a drill-press. The perforated sheet was cleaned with ultrasound in an ethanol bath for 10 min. For the assembly of DSSCs, the dye-covered TiO_2 electrode and Pt-counter electrode were assembled into a sandwich type cell and sealed with a hot-melt gasket of 25 μm thickness made of the ionomer Surlyn 1702 (DuPont). The size of theTiO_2 electrodes used was 0.25 cm^2 (*i.e.*, 5 mm×5 mm). A drop of the electrolyte was put on the hole in the back of the counter electrode. It was introduced into the cell via vacuum backfilling. The hole in the counter electrode was sealed with a film of Surlyn 1702 and a cover glass (0.1 mm thickness) using a hot iron bar.

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