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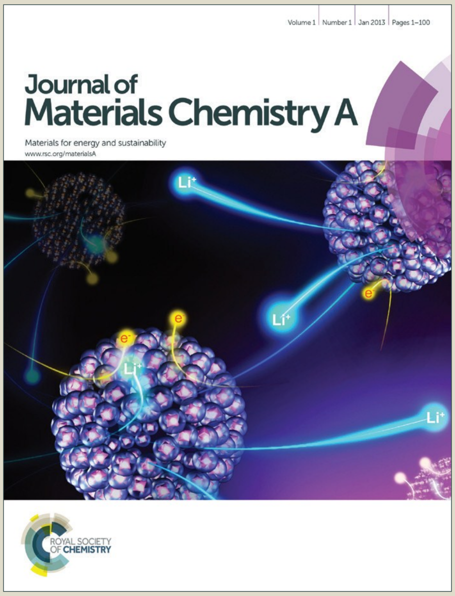

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Effects of the structural optimization on the performance of dye-sensitized solar cells: spirobifluorene as a promising building-block to enhance V_{oc}

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We prepared three new push-pull dyes JA3, JA4 and JA0 through structure optimization, and applied in DSSCs. Obviously, judicious molecular structure optimization of dyes can significantly improve the performance of DSSCs. Spirobifluorene as a building-block was introduced onto the phenothiazine donor groups. Compared to JA1, the steric effect of spirobifluorene building-block can effectively reduce the charge recombination by preventing the I_3^- of the electrolyte penetrating into the TiO_2 surface, thus the V_{oc} of JA3 increased from 701 mV to 800 mV. In order to further improve the light-harvesting ability of the DSSC, we introduced benzothiadiazole unit (BTD) and prepared D-A-π-A dye JA4. Just as expected, the J_{sc} of JA4 increased from 12.32 to 14.43 mA cm^{-2} compared to that of JA3, and the device reached the highest PCE of 7.0%. Moreover, considering extending the π-conjugated system always decreases the V_{oc} of DSSC, we got rid of the porphyrin unit and synthesized dye JA0. Notably, the DSSC based on JA0 reached a very high V_{oc} of 840 mV and a high PCE of 6.69%, to our knowledge, this is the highest V_{oc} for DSSC based on phenothiazine dyes with I^-/I_3^- electrolyte.

Introduction

With the energy crisis and environment pollution becoming more and more serious, the development and utilization of new energy has become one of the immediate tasks for human. Solar energy has great potential for exploitation, the characteristics of rich resources, convenient collection and clean pollution-free completely meets the requirements of sustainable development of human society.[1,2] In 1991, Grätzel and co-workers first reported the dye-sensitized solar cells (DSSC), they obtained 7.1% of power conversion efficiency (PCE) with low cost.[3] Over the next 20 years, DSSC got rapid development with the continuous efforts of many researchers, a large number of excellent dyes and the related materials have been developed.[4-8] Recently, Kakiage prepared the silyl-anchor dye ADEKA-1, which exhibited a high PCE of 14.3% with cobalt-based redox electrolyte. To our knowledge, this is the highest PCE by far for DSSC.[9]

A complete DSSC is made of photoanode, sensitizer, electrolyte and counter electrode.[10-12] The core of DSSC is to use sensitizer to absorb photons and generate electrons, thus, the development of novel and efficient sensitizers is one of the most direct and effective ways to improve the performance of DSSC. D-π-A (donor-π-acceptor) is the most common framework for efficient dyes.[13-15] The framework has outstanding efficient intra-molecular charge transfer (ICT) properties, moreover, it is very easy to be modified.[16-19] Many groups devote to optimizing the dye molecular structure, because this strategy can achieve the following purposes: (i) improve the spectral response of dyes, thereby enhancing the light-harvesting ability of DSSC; (ii) adjust the energy levels of dyes, thereby enhancing the electron injection rate and dye regeneration rate; (iii) suppress dye aggregation and reduce charge recombination, thereby enhancing the J_{sc} (short-circuit current density) and V_{oc} (open-circuit photovoltage) of DSSC; (iv) improve the photostability and adsorption stability of dyes, thereby enhancing the long-term stability and durability of DSSC.[20-22] Through the continuous efforts and exploration of the researchers, many new frameworks such as D-D-π-A, D-π-A-π-A, D-π-$(A)_n$ and D-A-π-A have been explored.[23-26] Particularly D-A-π-A, the additional acceptor can adjust the energy levels of dyes, improve the spectral response, enhance the photovoltaic performances and greatly improve the photostability of dyes, Zhu et al. have discussed about this in detail.[27,28] Thus, the structure optimization of dyes plays a very important role in improving the performance of DSSC. Impressively, the PCE of YD2-*o*-C8 was 12.3% in 2011, later, SM315 was prepared after further optimization in 2014, and the PCE of SM315 reached 13%.[29,30]

Phenothiazine is often used as a donor in DSSC for its efficient π-conjugated system and unique hole-transporting ability.[31-35] In our previous work, we used phenothiazine unit containing a long alkyl to modify the porphyrin dye JA1. The DSSC based on JA1 exhibited a PCE of 5.76%, with the V_{oc} of 701 mV, J_{sc} of 12.10 mA

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cm^{-2}, and FF of 67.8%.[36] Herein, we further modified the molecular structure of JA1 and prepared JA3, JA4 and JA0 (Fig. 1). Spirobifluorene as a building-block was introduced onto the phenothiazine donor groups, we deduced that the steric effect of spirobifluorene can effectively prevent the I_3^- of the electrolyte penetrating into the TiO_2 surface, thereby reducing the charge recombination, thus the V_{oc} of JA3 has increased to 800 mV. In order to improve the light-harvesting ability of the DSSC, benzothiadiazole (BTD) was added in D-A-π-A dye JA4. BTD has been widely used in the design of D-A-π-A dyes.[37] Herein, the additional strong electron-withdrawing unit exhibits significant broadening of Soret and Q-band absorbance features compared to JA3, yielding improved light-harvesting and efficiency. Because the absorption property of JA4 has been a good improvement compared to JA3, so the J_{sc} of JA4 increased from 12.32 to 14.43 mA cm^{-2}. In addition, Incorporation of BTD into JA4 as an electron trap is in favour of electron distribution, and facilitating the electron migration direction to the acceptor. Moreover, considering porphyrin units can cause dye aggregation and π-π stacking, so we got rid of the porphyrin unit and synthesized dye JA0. Notably, the DSSC based on JA0 reached a very high V_{oc} of 840 mV and a high PCE of 6.69%, to our knowledge, this is the highest V_{oc} for DSSC based on phenothiazine dyes with I^-/I_3^- electrolyte. Because the theoretical V_{oc} is about 900 mV with I^-/I_3^- electrolyte, thus, this strategy is very beneficial to improve the performance of DSSC. We mainly investigated the optical properties and photovoltaic performance of the three dyes, and analyzed these differences caused by the different structures.

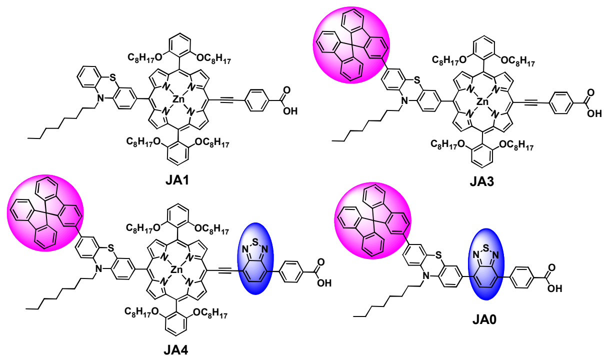

Fig. 1 Chemical structures of **JA1**, **JA3**, **JA4** and **JA0**.

Experimental

Synthesis of dyes

The chemical structures of JA1, JA3, JA4 and JA0 were shown in Fig. 1, and the synthetic route was depicted in Scheme S1. The synthesis details and characterization data were shown in supporting information.

Fabrication of DSSCs

The working electrode (active area is 0.196 cm^2) was prepared by screen printing the TiO_2 paste on Fluorine-doped tin oxide (FTO) glass plates (15 Ω / square). For preparation of the DSSCs, FTO glass plates were cleaned in a detergent solution using an ultrasonic bath for 30 min for two times and then rinsed with water and ethanol. Then, the plates were immersed into 40 mM $TiCl_4$ (aqueous) at 70℃ for 30 min and washed with water and ethanol. The TiO_2 paste consisted of 12 μm thick films (particle size, 20 nm, pore size 32 nm). The TiO_2 films were performed with a programmed procedure: (1) 80℃ for 15 min; (2) 135℃ for 10 min; (3) 325℃ for 30 min; (4) 375℃ for 5 min; (5) 450℃ for 15 min, and (6) 500℃ for 15 min. Then the films were treated again with $TiCl_4$ at 70℃ for 30 min and sintered at 500℃ for 30 min. Then the electrode was immersed into dye solution (0.3 mM of JA0, 0.2 mM of JA3 and JA4, THF/EtOH=1/4) for 18 h at room temperature. The working electrode and the Pt counter electrode were then sealed with a Surlyn film (25 μm) by heating the sandwich-type cell at 110℃. The electrolyte was introduced through pre-drilled holes in the counter electrode and was driven into the cell via vacuum backfilling, and the hole was sealed with a Surlyn film and a thin glass (0.1 mm thickness) cover by heating. The electrolyte was composed of 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 50 mM I_2, 50 mM LiI, 0.5 M tert-butylpyridine and 0.1 M guanidiniumthiocyanate (GuNCS) in acetonitrile.

Characterizations of DSSCs

The photocurrent-voltage (I-V) curves of the DSSCs were measured on a Keithley 2400 source meter under standard global AM 1.5G solar irradiation supplied by a xenon light source (Oriel). The incident photo-to-electron conversion efficiency (IPCE) spectra of the DSSCs were measured by a DC method. The light source was a 300 W xenon lamp (Oriel 6258) coupled with a flux controller to improve the stability of the irradiance. The single wavelength was selected by a monochromator (Cornerstone 260 Oriel74125). Light intensity was measured by a NREL traceable Si detector (Oriel 71030NS) and the short circuit currents of the DSSCs were measured by an optical power meter (Oriel 70310).

Theoretical calculations

Density function theory (DFT) calculations were performed at the DFT-B3LYP/LanL2DZ level with Gaussian 09 suite of programs.

UV-Vis spectra, photoluminescence, electrochemical properties and measurement of the amounts of dye adsorption

The UV-Vis absorption spectra were recorded on a Shimadzu UV-3600 spectrometer. Fluorescence spectra were recorded on a Perkin Elmer LS55 spectrophotometer. The fluorescence lifetimes of the dyes were measured on a FLS920 spectrometer. The cyclic voltammograms of the dyes were recorded by IM6EX Electrochemical Workstation. Electrochemical Impedance Spectroscopy was studied using a Chenhua CHI660D model Electrochemical Workstation (Shanghai).

The amounts of dye adsorption on the TiO_2 films were measured by a Shimadzu UV-3600 spectrometer. The sensitized electrodes were immersed into a 0.1 M NaOH solution in a mixed solvent (H_2O/THF=1/1), which resulted in desorption of each dye.

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Results and discussion

Optical properties

The UV-Vis absorption spectra of JA0, JA3 and JA4 in THF are shown in Fig. 2, and the corresponding data are collected in Table 1. D-π-A dye JA3 exhibited typical porphyrin absorption characteristics at the Soret and Q bands. The absorption below 400 nm can be attributed to electronic transitions from π-π*, and the 400-700 nm range can be attributed to intramolecular charge transfer (ICT). At the Soret bands, dye JA3 showed a high molar extinction coefficient (3.66×10^5 M^{-1} cm^{-1}) at 447 nm. When the benzothiadiazole unit was added in D-A-π-A dye JA4, the spectrum was changed obviously, most evident by the splitting of the Soret band, resulting in a shoulder at 459 nm on the maximum at 435 nm. The whole spectrum became broader compared to JA3, especially at the Q bands, the band at 574 nm had a little change compared to that of JA3, but the lowest-energy Q-band absorption of JA4 was significantly redshifted to 648 nm. For JA0, there was no porphyrin unit in the molecular structure, thus, dye JA0 displayed a narrow absorption. The maximum absorption peak of JA0 lay at 452 nm with the molar extinction coefficient of 8.2×10^3 M^{-1} cm^{-1}. The major emission bands of JA3, JA4 and JA0 lay at 638 nm, 685 nm and 567 nm, respectively, it is consistent with the trend of the absorption spectra of the three dyes (Fig. S1). The absorption spectra of the three dyes sensitized 12 μm thick TiO_2 substrate were further investigated (Fig. S2). All the spectra showed a broader and higher absorption compared to the spectra in THF. After anchored on TiO_2 surface, the ICT bands of dye JA3 and JA4 displayed a slight blue-shift (H-aggregation), which can be ascribed to deprotonation of the carboxylic acid. Obviously, the ICT bands of dye JA0 displayed red-shift (J-aggregation), we thought that the amounts of dye adsorption will increase sharply due to lack of porphyrin units, the result will cause J-aggregation.[38] This speculation can be supported by the absorption spectra of the dyes on TiO_2 films with 10 mM chenodeoxycholic acid (CDCA). We found that the ICT bands of JA3 and JA4 displayed a slight red-shift and the ICT band of JA0 displayed blue-shift. Though dye aggregation may quench the excited state and hamper electron injection, the J-aggregation also can enhance the performance of the DSSC due to the enhanced light-harvesting at longer wavelengths.[39,40]

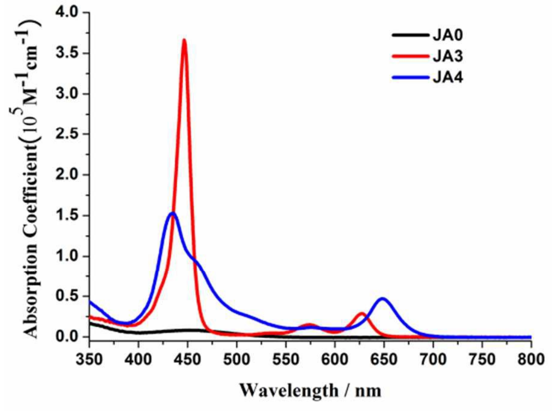

Fig. 2 UV-Vis absorption spectra of **JA0**, **JA3** and **JA4** in THF.

Table 1 Optical and electrochemical properties of dyes

Dye	$^a\lambda_{max}$/nm ($\varepsilon\times10^5$ M^{-1} cm^{-1})	$^b\lambda_{max}$/nm	$^cE_{OX}$/V (NHE)	$^dE_{0\text{-}0}$/eV	$^eE^*_{OX}$/V (NHE)
JA0	452(0.082)	567	0.98	2.41	-1.43
JA3	447(3.66),574(0.15) 627(0.29)	638	1.11	2.07	-0.96
JA4	435(1.52),459(0.92) 576(0.12),648(0.47)	685	1.04	1.90	-0.86

[a] Absorption maximum in THF solution (1×10^{-6} M), [b] emission maximum in THF solution (1×10^{-6} M), [c] the ground state oxidation potentials, [d] $E_{0\text{-}0}$ was estimated from the intercept of the normalized absorption and emission spectra, [e] E^*_{OX} was calculated by the formula: $E^*_{OX} = E_{OX}-E_{0\text{-}0}$.

Electrochemical studies

We measured the cyclic voltammetry curves of the three dyes to evaluate the possibility of electron transfer from the excited dyes to the conduction band of TiO_2. The cyclic voltammetry curves were shown in Fig. S3, and the corresponding data were collected in Table 1. We knew that the ground state oxidation potentials (E_{OX}) of JA0, JA3 and JA4 were 0.98 V, 1.11 V and 1.04 V (versus NHE), respectively. Because the redox potential of the I^-/I_3^- couple is about 0.4 V (versus NHE), and the E_{OX} of the three dyes are all positive than 0.4 V, thus, the three oxidized dye molecules can be regenerated by the reducing species in the iodine electrolyte. As shown in Fig. S4, the zero-zero excitation energy ($E_{0\text{-}0}$) was estimated from the intercept of the normalized absorption and emission spectra. The values of JA0, JA3 and JA4 are 2.41 eV, 2.07 eV and 1.90 eV, respectively. Hence, the corresponding excited oxidation potentials (E^*_{OX}) of JA0, JA3 and JA4 are -1.43 V, -0.96 V and -0.86 V, respectively. The values are all more negative than the CB level of the TiO_2 (-0.5 V versus NHE), which implies an efficient electron injection process from the excited dye into the conduction band of TiO_2. Especially for JA0, such high electron injection driving force suggests that the DSSC based on JA0 will has a good electron injection rate.

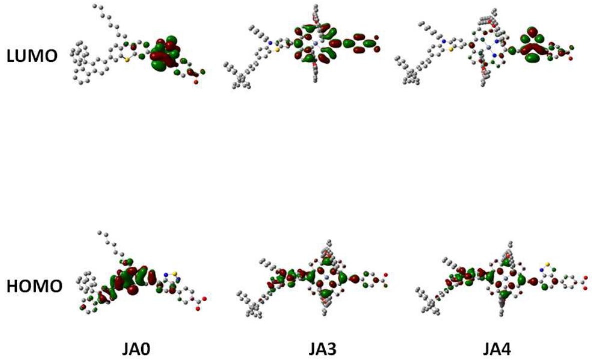

Fig. 3 The HOMO and LUMO frontier molecular orbitals of **JA0**, **JA3** and **JA4** calculated at the DFT-B3LYP/LanL2DZ level with the Gaussian 09 suite of programs.

Theoretical Calculations

Density function theory (DFT) calculations at the DFT-B3LYP/LanL2DZ level with Gaussian 09 suite of programs were utilized to insight into the electron-density distributions of the three

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dyes. As shown in Fig 3, the HOMO levels of porphyrin dyes JA3 and JA4 are delocalized throughout the phenothiazine donors and the porphyrin rings, and the HOMO levels of JA0 are delocalized in the phenothiazine donor. When the benzothiadiazole unit was added in D-A-π-A dyes JA0 and JA4, the electron-density distributions are significantly different from D-π-A dye JA3. For JA3, the LUMO orbitals are mainly delocalized in porphyrin ring and acceptor. For JA0 and JA4, the LUMO orbitals are mainly delocalized in the BTD units and acceptors. The electronic properties of the three dyes indicate that such a well-separated orbital distribution is conducive to the electron transfer from HOMO to LUMO and can induce the photoinduced charge injection from the LUMO to the conduction band of TiO_2.

We performed the time-resolved luminescence in THF and on TiO_2 surface to insight into the electron injection dynamics of the three dyes (Fig. S5).[29,30] The fluorescence lifetimes of JA0, JA3 and JA4 in THF are 6.42 ns, 2.51 ns and 4.83 ns, respectively. When the three dyes anchored on TiO_2 surface, the emission of the three dyes are all strongly quenched. The lifetimes of JA0, JA3 and JA4 on TiO_2 are about 600 ps, 610 ps and 570 ps, respectively. The results suggest that the three dyes all have high electron injection efficiency, as a result of efficient photoinduced charge injection from the LUMO of the dyes to the conduction band of TiO_2.

Photovoltaic performance of DSSCs

The DSSCs based on the three dyes were fabricated under the same conditions. The photocurrent-density-photovoltage (J–V) curves of were shown in Fig. 4, and the photovoltaic parameters were collected in Table 2. In our previous work, the DSSC based on JA1 exhibited a PCE of 5.76%, with the V_{oc} of 701 mV, J_{sc} of 12.10 mA cm^{-2}, and FF of 67.8%. When the spirobifluorene unit was added in phenothiazine donor, the DSSC based on JA3 exhibited a PCE of 6.27%, with the V_{oc} of 800 mV, J_{sc} of 12.33 mA cm^{-2}, and FF of 63.52%. It is clear that the J_{sc} has a little change, in contrast, the V_{oc} increased 99 mV. We deduced that the steric effect of spirobifluorene can effectively prevent the I_3^- of the electrolyte penetrating into the TiO_2 surface, thereby reducing the charge recombination, thus the V_{oc} of JA3 increased 99 mV compared to that of JA1. When BTD unit was added in JA4, the PCE of the device reached the highest value of 7.0%, and the J_{sc} increased from 12.33 to 14.44 mA cm^{-2}. But the V_{oc} decreased 28 mV, the reason was that the conjugation extension may cause dye aggregation and π-π stacking, thereby resulting in a decreased V_{oc}. Interestingly, if we get rid of porphyrin unit, the DSSC based on JA0 still exhibited a high PCE of 6.69%, although there was a decrease in the J_{sc}, but the V_{oc} reached the highest value of 840 mV. To our knowledge, this is the highest V_{oc} for DSSC based on phenothiazine dyes with I^-/I_3^- electrolyte. As we all known, with the same electrode materials and the same electrolyte for DSSCs, the key to improving the V_{oc} is to improve the electron density of the TiO_2 conduction band. We can improve the electron injection rate or reduce the electron recombination to achieve this purpose. Wang et al. designed a series of double D-π-A dyes, this strategy was favorable for reducing intermolecular interaction and retarding charge recombination, thus the V_{oc} was greatly improved.[41-44] Herein, the LUMO of JA0 is sufficiently high for electron injection, in addition, the steric effect of spirobifluorene can effectively retard charge recombination, thus the V_{oc} of JA0 is very high.

Table 2 Photovoltaic parameters of the DSSCs obtained from the J-V curves

Dye	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	η (%)
[a] JA0	12.32	0.840	64.63	6.69
[b] JA1	12.10	0.701	67.80	5.76
[a] JA3	12.33	0.800	63.52	6.27
[a] JA4	14.44	0.772	62.77	7.00

[a] The size of the active area for each cell is 0.196 cm^2, the DSSCs were all measured under standard global AM 1.5G solar irradiation, [b] the DSSC based on JA1 was reported in ref. 36.

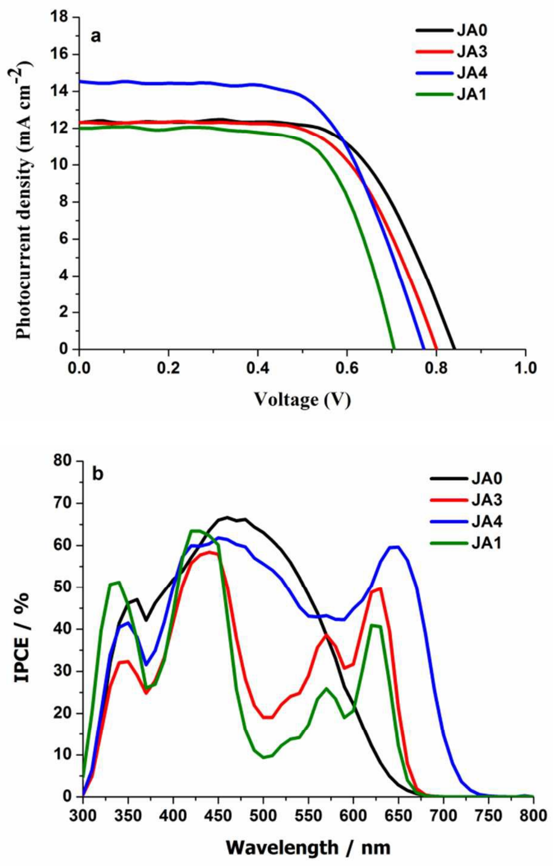

Fig. 4 (a) The J–V curves of DSSCs based on **JA0, JA1, JA3** and **JA4**; (b) The IPCE curves of DSSCs based on **JA0, JA1, JA3** and **JA4**.

As shown in Fig. 4b, the incident photon-to-current conversion efficiency (IPCE) spectra of the devices were also measured. The IPCE curves of JA1 and JA3 all exhibited photocurrent generation up to about 680 nm, but the values of JA3 were higher that of JA1 in the range of 450-680 nm. JA4 displayed impressively high IPCE values in the whole visible range, with photocurrent generation up to about 750 nm, demonstrating the utility of the BTD unit for improvements in visible and infrared light-harvesting properties. Interestingly, we found JA0 had an excellent IPCE spectrum, the DSSC based on JA0 not only exhibited photocurrent generation up to about 680 nm, but also had a higher value in the whole visible range. It is consistent with the J_{sc} of the DSSCs. We measured the

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amounts of dye adsorption of the three dyes anchored on TiO_2 surface. The values of JA0, JA3 and JA4 are 6.95, 1.25 and 1.56×10^{-7} mol cm^{-2}, respectively. This may be another reason for the differences between the J_{sc} of the DSSCs.

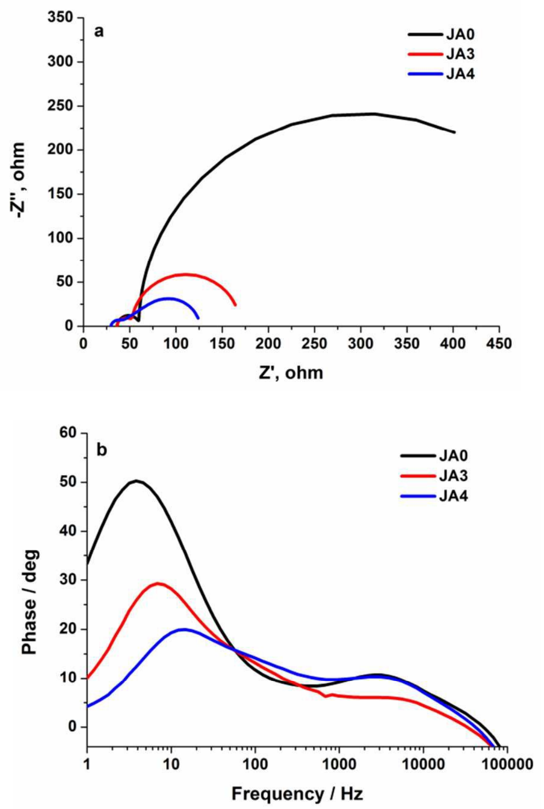

Fig. 5 (a) Nyquist plots of DSSCs based on **JA0**, **JA3** and **JA4**; (b) Bode phase plots of DSSCs based on **JA0**, **JA3** and **JA4**.

Electrochemical impedance spectroscopy analysis

With the same electrode materials and the same electrolyte for DSSCs, the fluctuation of electron density (charge recombination rate in DSSCs) has an important influence on the V_{oc}. At a given photocarrier generation flux, the electron density is mainly determined by the interfacial recombination rate of TiO_2 electrons. We investigated the electrochemical impedance spectroscopy (EIS) under dark to study the charge recombination dynamics of the DSSCs.[45-47] The applied voltage was -0.7 V and scanned from 10^5 to 1 Hz.[48,49] As shown in Fig. 5, the large semicircle represents the charge recombination resistance (R_{rec}) at the TiO_2/dye/electrolyte interface. Obviously, the radius of the large semicircle decreased in the order: JA0 > JA3 > JA4, this suggested that the JA0 based-device had the largest R_{rec}. The results suggested that JA0 can efficiently reduce the charge recombination. In generally, extending the π-conjugated system always decreases the V_{oc} of DSSCs. It is in agreement with the V_{oc} of the DSSCs based on the three dyes. Moreover, the peak frequency (*f*) at lower frequency region from the Bode phase plots of the DSSCs can be obtained (Fig. 5b). The electron lifetime (τ) can be calculated by $\tau=1/(2\pi f)$.[50-52] The *f* of JA0, JA3 and JA4 is 3.8, 7.0 and 13.5 Hz, respectively. The corresponding electron lifetime value of JA0, JA3 and JA4 is 41.9, 22.7 and 11.8 ms, respectively. The longer electron lifetime corresponds to lower dark current. Thus, the DSSC based on JA0 has the highest V_{oc}.

Conclusions

In summary, we prepared three new push–pull dyes JA0, JA3 and JA4, and applied in DSSCs. Compared to JA1, the steric effect of spirobifluorene building-block can effectively reduce the charge recombination, thus the V_{oc} of JA3 increased from 701 mV to 800 mV. The BTD unit added in dye JA4 can further optimize the molecular structure. The additional acceptor of the BTD unit adjacent to donors can improve the distribution of donor electrons and enhance the light-harvesting ability, thus the J_{sc} of JA4 increased from 12.32 to 14.43 mA cm^{-2} and the device reached the highest PCE of 7.0%. Moreover, considering extending the π-conjugated system always decreases the V_{oc} of DSSCs, we get rid of the porphyrin unit and synthesized dye JA0. Notably, the DSSC based on JA0 reached a very high V_{oc} of 840 mV and a high PCE of 6.69%, to our knowledge, this is the highest V_{oc} for DSSC based on phenothiazine dyes with I^-/I_3^- electrolyte. Thus, judicious molecular structure optimization of push-pull dyes can significantly improve the performance of DSSCs.

Acknowledgements

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Table of contents entry

Judicious structure optimization of push-pull dyes can significantly improve the performance of DSSCs. Obviously, the V_{oc}, J_{sc} and PCE of the DSSC based on JA4 were all improved after optimization compared to that of JA1.