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1. Introduction

Dye-sensitized solar cells (DSSCs) are promising nextgeneration alternatives to conventional silicon-based photovoltaic devices because of their great advantages light weight, low cost and easy processing.¹⁻⁴ Since O'Regan and Grätzel reported a high-efficiency (7.10%) DSSC based on Ru-complex dye and nanocrystalline TiO₂ mesoporous film in 1991,¹ a lot of interest has been generated on this topic.⁵⁻⁸ Dye as the most crucial element in DSSCs has attracted considerable attention, and most research focuses on synthesis of new dyes,^{9,10} low-cost natural dyes, and co-sensitizing using multicolor dyes.¹¹⁻¹³ The co-sensitization strategy is proved to be an effective approach to enhance device performance by combination of two or more dyes that have larger molar extinction coefficients or dyes that have

Enhance the performance of dye-sensitized solar cells by co-sensitization of 2,6-bis(iminoalkyl)pyridine and N719⁺

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Three organic dyes 2,6-bis(iminoalkyl)pyridines $[2,6-(2,6-R_2C_6H_2N=CMe)_2]C_5H_3N$ (R = methyl, ethyl, isopropyl) (named DM, DE and DP, respectively) were synthesized and assembled onto nanocrystalline TiO₂ film to prepare 2,6-bis(iminoalkyl)pyridine/N719 co-sensitized photoelectrodes for dye-sensitized solar cell (DSSCs) applications, and their photoelectrochemical performances were studied. In each of the three composite electrodes, the aggregation of N719 was alleviated and its spectra response was enhanced by the 2,6-bis(iminoalkyl)pyridines in region of 400 to 750 nm, and the total resistance of DSSCs was decreased after co-sensitizing with 2,6-bis(iminoalkyl)pyridine, all of which facilitate to improve efficiency of DSSCs. The optimized cell which was co-sensitized with DM gave a short circuit current density of 16.57 mA cm⁻², an open circuit voltage of 0.72 V and a fill factor of 0.59 corresponding to an overall conversion efficiency of 7.00% under standard global AM1.5 solar irradiation conditions, which is 28.91% higher than that for DSSCs only sensitized by N719 (5.43%). The incident photo-to-current conversion efficiency, electrochemical impedance spectroscopy, surface photovoltage spectroscopy and UV-visible adsorption spectra were used to analyze their photoelectrochemical performances, and X-ray single-crystal structural analysis was used to analyze the structures of 2,6-bis(iminoalkyl)pyridines.

complement absorption bands sensitized on semiconductor film together, extending the light harvesting ability so as to increase photocurrents of the devices. Ehret et al. studied the nanocrystalline TiO₂ solar cell sensitized by various dicarboxylated cyanines and found that the use of mixed cyanine dyes could improve photoelectric conversion efficiency.14 Zhang and coworkers examined the mechanism of the co-sensitization with squarylium and N3 dyes by time-resolved spectroscopy.15 Grätzel and coworkers combined bisthiophene dye (JK2) with squarylium cyanine dye (SQ1) as co-sensitizers and obtained an overall conversion efficiency of 7.43%.¹⁶ Wang et al. reported that the enhanced performance of chlorophyll-sensitized solar cells have been obtained by co-sensitization of a-type Chl with b-, or c-type Chl.17 Phthalocyanine dye (TT1) co-sensitized with various organic dyes (JK2 or D2) exhibited an enhanced device performance.18,19 Co-sensitization of TiO_2 films with a black dye and organic dyes (D131 or Y1) significantly enhanced photocurrent and the device performance attained $\eta = 11.0-11.4\%$.^{20,21} In 2011, the highest value reported for the power conversion efficiency of DSSCs has reached 12.3% through co-sensitization method,²² which is a new milestone in this research field, stimulating investigation of the development of new sensitizer to promote device performance by co-sensitization. Presently, metal-free organic dyes

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have attracted much attention and were widely used for co-sensitization of DSSCs. $^{23-27}$

In our previous work, metal-organic complexes were used to co-sensitize DSSCs and the performances were enhanced, 13,28,29 while in this paper, three metal-free organic dyes 2,6-bis(iminoalkyl)pyridines $[2,6-(2,6-R_2C_6H_2N=CMe)_2]C_5H_3N$ (R methyl, ethyl, isopropyl) (named DM, DE and DP, respectively), whose chemical structure are shown in Fig. 1, were selected as co-sensitizers to study the photoelectrochemical performances of dye-sensitized solar cells. Since DM, DE and DP are isostructural, but substitute groups on the 2- and 6-positions of phenyl groups are different, the relationships between molecule structure and photoelectrochemical performance have also been investigated. Through co-sensitization of these organic dyes with N719 sensitizer, respectively, we have achieved a higher efficiency than that for single N719 sensitized solar cells. 2,6-bis(iminoalkyl)pyridines play an important role in matching optimization with dyes in complexes for increasing photoelectrical conversion efficiencies.

2. Experimental section

2.1. Synthesis of DM, DE and DP

The 2,6-diacetylpridine was prepared according to a published procedure.³⁰ DM, DE and DP were synthesized according to modified published procedures in a good yield by condensation of 2,6-diacetylpyridine with the corresponding aniline in refluxing absolute methanol in the presence of a catalytic amount of formic acid (Scheme 1).^{31,32}

2.2. Fabrication of DSSCs

Dye-sensitized solar cells were fabricated using the following procedure. The TiO₂ paste was cast onto the FTO substrate (90% transmittance in the visible, 15 Ω per square, purchased from NSG, Japan) by the screen-printing method, followed by drying at 100 °C for 5 min and this process was repeated six times, then followed by sintering at 500 °C for 15 min in air to obtain a transparent TiO₂ photoelectrode with the thickness of *ca.* 10 µm. The mesoporous TiO₂ photoelectrode was immersed in 0.3 mM [*cis*-bis(isothio-cyanato)bis(2,2-bipyridyl-4,4-dicarboxylato)-ruthenium(π)bistetrabutylammonium] (known as N719, Solaronix Company, Switzerland) solution in absolute ethanol solution for 14 h and washed with ethanol to remove the unabsorbed N719



Fig. 1 Molecular structures of DM, DE and DP.

and dried with blower to complete the loading of N719. The co-sensitized electrodes were prepared by further immersing the electrode in saturated (*ca.* 0.3 mM) 2,6-bis(iminoalkyl)-pyridine in absolute ethanol solution for 2 h to complete the co-sensitizer loading and then dried with blower again. The electrolyte used in this work was 0.5 M LiI + 0.05 M I₂ + 0.1 M *tert*-butyl pyridine in a 1 : 1 (volume ratio) of acetonitrile-propylene carbonate. The platinum counter electrode was prepared by depositing H_2PtCl_6 paste onto the FTO glass substrates and then sintered at 450 °C for 30 min. The cells were assembled by sandwiching the electrolyte between the dye sensitized photoanode and the counter electrode and assembly was held together using mini-binder clips.

2.3. Characterization

All characterizations were carried out under ambient pressure and temperature. Photocurrent-photovoltage (I-V) curves were recorded by Keithley model 2400 digital source meter using a mask with an aperture area of 0.16 cm⁻². The irradiance of AM1.5 global sunlight from a filtered 500 W xenon lamp light source was set at 100 mW cm⁻² and was calibrated by a standard silicon solar cell (no. NIMMS1123, calibrated by National Institute of Metrology, P. R. China). Based on I-V curve, the fill factor (FF) is defined as: FF = $(J_{\text{max}} \times V_{\text{max}})/(J_{\text{sc}} \times V_{\text{oc}})$ where J_{max} and V_{max} are the photocurrent density and photovoltage for maximum power output; J_{sc} and V_{oc} are the short-circuit photocurrent density and open-circuit photovoltage, respectively, the overall energy conversion efficiency η is defined as: η = (FF $\times J_{\rm sc} \times V_{\rm oc})/P_{\rm in}$ where $P_{\rm in}$ is the power of the incident light, J_{sc} and V_{oc} are also the short-circuit photocurrent density and open-circuit photovoltage, respectively, and FF is the fill factor. EIS were recorded by CHI660D Electrochemical Analyzer (Chenhua, China), and the measurements were taken over a frequency range of 0.1-100 kHz under standard global AM1.5 solar irradiation, or in the dark by applying a forward bias equivalent to Voc. IPCE was measured on an EQE/IPCE spectral response system (Newport). The SPS instrument was assembled by Jilin University. Monochromatic light was obtained by passing light from a 500 W xenon lamp through a double-prism monochromator (SBP300, China), and the signals were collected by a lock-in amplifier (SR830, Stanford). UV-visible absorption spectra of DM, DE and DP in ethanol solution were recorded on a Germany Jena model SPECORD S600 UV-visible spectrophotometer and the spectra of co-sensitized TiO₂ films were recorded on a Japan Shimadzu model UV-2250 spectrophotometer. The single-crystal X-ray diffraction data for DM, DE and DP were collected on a Rigaku R-AXIS RAPID IP diffractometer equipped with graphite-monochromated Mo KR radiation ($\lambda = 0.71073$ Å), operating at 293 \pm 2 K. The structures were solved by direct methods and refined by full-matrix leastsquares based on F^2 using the SHELXTL 5.1 software package (G M. Sheldrick, SHELXTL NT Crystal Structure Analysis Package [CP], version 5.10; Bruker AXS, Analytical X-ray System: Madison, WI, 1999). The hydrogen atoms residing on the carbon atoms were located geometrically. All non-hydrogen atoms were refined anisotropically.



DM: $R = -CH_3$; DE: $R = -CH_2CH_3$; DP: $R = -CH(CH_3)_2$

3. Results and discussion

3.1. Structure of 2,6-bis(iminoalkyl)pyridines

The main difference of DM, DE and DP is the substitute groups on the 2- and 6-positions of phenyl groups, which are methyl, ethyl and isopropyl, respectively, as shown in Fig. 1.

The X-ray structural analysis of the single-crystals reveals that DM, DE and DP are isostructural. The dyes DM, DE and DP possess the structures with an approximate C_s symmetry about a plane bisecting the central pyridine ring. As shown in Fig. 2, the pyridyl ring of DP as an example is coplanar with the two imino functional groups. The two imino C==N bonds have typical double-bond characteristics, with bond lengths of 1.266(3) and 1.272(3) Å, which are similar to that in DM and DE.^{33,34} The two 2,6-diisopropyl-substituted phenyl rings are approximately perpendicular to the ethylidenepyridine ring, with the dihedral angles being 87.059(79) and 72.949(88)°. The dihedral angles are decreased with the increased size of substituted alkyls. Although the complex includes three N atoms, there are no obvious hydrogen-bond or π - π interactions in the crystal structure.

3.2. Molecular orbitals and band structure calculations of DM, DE and DP

Energy-level matching is crucial in selecting sensitizer. In order to further understand the energy band structure in DM, DE and DP, we performed *ab initio* calculations for the molecular orbitals based on the time-dependent density functional theory (TD-DFT) with 6-31G basis set. The geometric parameters obtained from X-ray diffraction analyses were fully optimized in



Fig. 2 The asymmetric unit of DP.

conjunction with the solvent model. The electronic distributions of the frontier molecular orbitals of the DM, DE and DP in ethanol are shown in Fig. 3. The highest occupied molecular orbital (HOMO) of DM, DE and DP contributes to the two 2,6-dialkyl-substituted phenyl rings (donor) and the lowest unoccupied molecular orbital (LUMO) contributes to the pyridyl rings (acceptor). The two imino functional groups with conjugated C=N bridge work as a π conjugated bridge, so DM, DE and DP are donor- π -conjugated-acceptor (D- π -A) type metal free organic dyes. The HOMO and LUMO energy level of DM, estimated from DFT calculations are -5.61 and -2.93 eV, respectively, and for DE and DP they are -5.64 and -2.89 eV, -5.63 and -2.85 eV, respectively.

To ensure effective electron injection from the LUMO of the sensitizer into the conduction band of semiconductor (TiO_2) , the LUMO level of the dye must be higher than the conduction band edge of TiO_2 .³⁵ It is observed that E_{LUMO} for DM, DE and DP is more positive than the conduction band of TiO_2 (-4.40 eV).³⁶ This provides a substantial driving force for electron



Fig. 3 The electronic distribution of the frontier molecular orbitals of DM, DE and DP computed in the ethanol using TDFT/MPWIK/6-31G.

Scheme 1 Synthesis process of 2,6-bis(iminoalkyl)pyridines

injection. The potential of the reduced DM, DE and DP ($E_{\rm HOMO}$) is more negative than the redox potential of I^-/I_3^- (-4.85 eV)³⁷ and far below that of the conduction band of TiO₂. This gives sufficient driving force for dye regeneration (Scheme 2). It shows that the energy levels of DM, DE and DP are appropriate for the DSSCs system containing TiO₂.

3.3. UV-visible absorption spectra of 2,6-bis(iminoalkyl)pyridine in ethanol and co-sensitized TiO₂ photoelectrodes

The absorption spectra of DM, DE and DP in ethanol and co-sensitized with N719 on TiO₂ films is shown in Fig. 4(a) and (b), respectively. It can be seen from Fig. 4(a) that DM, DE and DP all display a large absorption peak at about 279 nm and a small absorption peak at about 335 nm, respectively. When DM, DE and DP is mixed with N719, respectively, the absorption spectra show that the absorption of N719 is enhanced only in the region of 250-450 nm. The enhanced band seems too narrow and too close to the UV region that it does not work when they are used to co-sensitize TiO₂ photoelectrodes with N719. But when DM, DE and DP was used to co-sensitize with N719 on TiO₂ films, respectively, it gives a surprising result that the absorption of N719 was remarkably enhanced in the UV-visible region as shown in Fig. 4(b). Fig. 4(b) shows the absorption spectra of DM, DE and DP on N719/TiO₂ films, respectively. The experimental results indicate that aggregation of N719 occurred on TiO₂ nanocrystal surface. Aggregations of dye was reported as early as in 1936,³⁸ and from then on it is accepted that the dyes have a strong tendency to aggregate at the solid/liquid interface due to strong attractive forces between molecules.39 Usually, dye aggregates have three forms: blue-shifted H-aggregates (parallel orientation), red-shifted J-aggregates (tilted orientation), and both red- and blue-shifted herring-bone aggregates.⁴⁰⁻⁴⁴ As shown in Fig. 4(b), the two maximum absorption peaks shifted from 383 to 367 nm and 525 to 559 nm, respectively, compared with in ethanol solution; after with 2,6-bis(iminoalkyl)pyridine, co-sensitization the two maximum absorption peaks shifted back to 375 and 547 nm, respectively. This result indicates that herring-bone aggregates



Scheme 2 Schematic energy diagram of HOMO and LUMO for dyes compared to the energy levels calculated for TiO₂.

occurred for N719 adsorbed on TiO_2 , but co-sensitization with DM, DE and DP prevents the aggregation of N719 and adjusts the arrangement of N719 molecules toward a more uniform orientation which is beneficial for charge transfer. Moreover, the adsorption was increased in the region of 350–750 nm, which could render better light-harvesting in this region and further enhance the performance of co-sensitized DSSCs.

3.4. Surface photovoltage spectrum analysis of 2,6-bis(iminoalkyl)pyridine co-sensitized photoelectrodes

The surface photovoltage spectrum (SPS) method is commonly applied to TiO₂ for DSSCs, which is a well-established contactless technique for surface state distribution.45,46 Fig. 5 is the SPS of photoanodes sensitized with single N719 sensitizer and cosensitized with 2,6-bis(iminoalkyl)pyridine. The curves in Fig. 5 indicate that co-sensitizing could enhance the photovoltage signal between 300 and 750 nm. The photovoltage signals increase with the order of DM/N719 > DE/N719 > DP/N719 > N719, which indicates that the separate efficiency of electrons and holes correlate strongly with DM, DE, DP. The results of UV-visible absorption spectra and SPS demonstrate that the composite TiO₂ is beneficial to enhance the spectra response after co-sensitization in DSSC photoelectrodes. The improvement of composite photoelectrode co-sensitized by DM is more evident than that by DE and DP. It is known that the electron-donating ability of the alkyl group is in the order of 2,6dimethylphenyl > 2,6-diethylphenyl > 2,6-diisopropylphenyl and the steric hindrance on the 2,6-dialkyl-substituted phenyl ring is in the order of 2,6-dimethylphenyl < 2,6-diethylphenyl < 2,6diisopropylphenyl. Stronger electron-donating ability and lower steric hindrance of the alkyl group on the 2,6-dialkylsubstituted phenyl ring is more suitable for enhancing the spectra response.

3.5. Photoelectrochemical performance of dye-sensitized solar cell

The 2,6-bis(iminoalkyl)pyridine co-sensitized and single dye sensitized photoanodes were assembled with counter electrodes and electrolyte to prepare organic dye/N719 co-sensitized DSSCs devices or single dye sensitized DSSCs. Fig. 6 presents the performances of the co-sensitized DSSCs in terms of J_{sc} and V_{oc} , and the results of all DSSCs are listed in Table 1. Fig. 6 and Table 1 indicate that the performances of cells co-sensitized with 2,6-bis(iminoalkyl)pyridine and N719 are improved in the order of DM/N719 > DE/N719 > DP/N719 > N719. As shown in Table 1, take the DM/N719/TiO₂ composite photoelectrode as an example, the co-sensitized solar cell based on a DM/N719/TiO2 electrode yields a remarkably high photocurrent density (J_{sc}) of 16.57 mA cm⁻² under standard global AM1.5 solar irradiation conditions without an expense of lower open circuit voltage (V_{oc}) but a little increased from 0.71 V to 0.72 V. The cell shows a better photo-electricity conversion efficiency of 7.00%, which is higher than that for DSSCs using single N719 (5.43%) and DM (0.69%). In this way the cell efficiency was improved by more than 28.91% compared with that for single N719. This

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g. 4 UV-visible absorption spectra of dyes in ethanol solution and on TiO₂ photoelectrodes (a) in ethanol solution and (b) on TiO₂ photoelectrodes.



Fig. 5 SPS of co-sensitized photoelectrodes and N719 sensitized photoelectrode.



Fig. 6 *J–V* curves for DSSCs based on co-sensitized photoelectrodes and N719 sensitized photoelectrode.

 Table 1
 J-V performance of DSSCs based on different photoelectrodes

Photoelectrode	$J_{\rm sc} ({ m mA}~{ m cm}^{-2})$	$V_{\rm oc}$ (V)	FF	η (%)	
N719/TiO ₂	12.68	0.71	0.60	5.43	
DM/TiO ₂	3.65	0.51	0.37	0.69	
DE/TiO ₂	2.46	0.55	0.49	0.66	
DP/TiO ₂	2.44	0.45	0.45	0.49	
DM/N719/TiO ₂	16.57	0.72	0.59	7.00	
DE/N719/TiO ₂	15.83	0.72	0.61	6.99	
DP/N719/TiO ₂	15.64	0.71	0.62	6.91	

result suggests that co-sensitization of TiO_2 photoelectrode with the 2,6-bis(iminoalkyl)pyridine and N719 is an effective way to improve the efficiency of DSSCs.

Meanwhile, the effect of DM, DE and DP soaking time on the performances of co-sensitized DSSCs was also investigated. As shown in Fig. 7, η and photocurrent density increased within 2 hours soaking time of DM, DE and DP, and do not change too much after soaking more than 2 hours; voltage for DM co-sensitized DSSCs increases slightly with the increase of soaking time and for DE co-sensitized DSSCs it firstly decreases and then increases, while for DP co-sensitized DSSCs it is reversed, but all the voltage value for DM, DE and DP co-sensitized DSSCs are around 0.7 V; fill factor for DM, DE and DP co-sensitized DSSCs keep stable with the increase of soaking time. The photovoltaic parameters shown in Fig. 7 indicate that all the parameters could reach the maximum value when soaking time of DM, DE and DP is 2 hours, and prolonging soaking time does not enhance the performances of DSSCs too much. Therefore, 2 hours soaking time for DM, DE and DP is appropriate for the DSSCs co-sensitized with N719 whose soaking time is 14 h. This is also the reason why 2 hours is fixed as DM, DE and DP soaking time in all our experiments.

IPCE is defined as the number of electrons generated by light in the external circuit divided by the number of incident photons. The IPCE spectra of different devices are plotted as a function of excitation wavelength and are presented in Fig. 8. It is found that DM, DE and DP co-sensitized with N719, respectively, could enhance the spectral response in the whole visible region and consequently enhance the photocurrent performance. Herein, co-sensitization of the nanostructured TiO₂ electrodes could markedly increase the photocurrent density as reported in Table 1. As can be seen from the spectra in Fig. 7, the spectrum obviously exhibits an upward shift in the wavelength range from 400 to 750 nm. It shows that co-sensitization of 2,6-bis(iminoalkyl)pyridine with N719 has higher lightharvesting. Compared with the results of UV-visible absorption spectra and SPS, it is clear that the improvement of IPCE performance is attributed to the enhanced spectral response, better charge transfer and higher light-harvesting.

3.6. Electrochemical impedance spectroscopy (EIS)

EIS is a useful technique for the analysis of electronic and ionic transport processes in an electrochemical device. It is a steady state method to measure current response based on the application of an AC voltage at different frequencies.^{47–49} The EIS



Fig. 7 Effect of DM, DE and DP soaking time on the performances of co-sensitized DSSCs (a) efficiency, (b) open circuit voltage, (c) short circuit current and (d) fill factor.



Fig. 8 IPCE spectra of DSSCs based on single N719 sensitized and co-sensitized photoelectrodes.

investigation of the DSSC device provides valuable information for the understanding of photovoltaic parameters (J_{sc} , V_{oc} , FF, and η). Herein, we utilize EIS to analyze charge carrier dynamics in the interfacial regions of solid–liquid layers and the effect of 2,6-bis(iminoalkyl)pyridine in composite photoelectrodes on the performance of DSSCs. Impedance spectra of DSSC devices with different 2,6-bis(iminoalkyl)pyridine/ N719 co-sensitized photoanode were measured under standard global AM1.5 solar irradiation or in the dark by applying a forward bias equivalent to open circuit potential. As indicated in Fig. 9, a typical EIS spectrum exhibits three semicircles in the Nyquist plot or three characteristic frequency peaks in a Bode phase angle presentation. In the order of increasing frequency the features are attributed to the Nernst diffusion in the electrolyte (not clearly visible), electron transfer at the TiO_2 /electrolyte interface, and redox charge transfer at the counter electrode, respectively.

Under light illumination, the second semicircle radius in the Nyquist plot decreased after co-sensitizing with 2,6-bis(iminoalkyl)pyridine, and the values are in the order of DM/N719 < DE/N719 < DP/N719 < N719, which indicates a decrease of the electron transfer impedance and an increase of charge transfer rate at this interface (Fig. 9(a)); while in the dark, this semicircle radius in the Nyquist plot increased after co-sensitizing with 2,6-bis(iminoalkyl)pyridine, and the values are in the order of DM/N719 > DE/N719 > DP/N719 > N719, which indicates an increase of electron recombination impedance and a reduction of the interfacial charge recombination rate (Fig. 9(c)).

It was reported that under V_{oc} conditions, the electrons injected into the oxide semiconductor should be recombined at the oxide/dye/electrolyte interface because there is no current passing through the external circuit.50 Thus the lifetime of electrons in the oxide film (τ_r) can be estimated according to the equation: $\tau_r = 1/(2\pi f_{max})$, where f_{max} is the maximum frequency of the mid-frequency peak.⁵¹ As shown in Fig. 8(b), the $f_{\rm max}$ value shifts to lower frequency after co-sensitizing with 2,6-bis(iminoalkyl)pyridine, which for N719 sensitized DSSC is 21.5 Hz, bigger than the value for co-sensitized DSSCs (17.4, 21.2 and 21.2 Hz for DM/N719, DE/N719 and DP/N719, respectively). Therefore, the electron lifetimes for DM/N719, DE/N719 and DP/N719 are calculated to be 9.2, 7.5, 7.5 ms, respectively, longer than 7.4 ms for single N719. The same trend also can be seen in the dark bode phase plot (Fig. 9(d)). The longer electron lifetime and higher value of recombination resistance for co-sensitized DSSCs indicates more effective suppression of the



Fig. 9 Impedance spectra of DSSC devices based on different photoelectrodes measured under standard AM1.5 G solar irradiation (a and b) or in the dark (c and d). Nyquist plots: (a) and (c); Bode phase plots: (b) and (d).

back reaction between photoelectrons in the conduction band of TiO₂ and the electrolyte.⁵² It is possibly due to the better coverage of the 2,6-bis(iminoalkyl)pyridine/N719/TiO₂ photoelectrode, which inhibits the surface recombination of electrons at the electrode/electrolyte interface, this is confirmed by Fig. 8(c). Lower steric hindrance make it easy to adhere on the surface of TiO₂ films and lead to better coverage, as the steric hindrance is in the order of DM < DE < DP, the coverage of DM is better than DE and DP. On the other hand, as discussed above, co-sensitizing with 2,6-bis(iminoalkyl)pyridine could prevent the aggregation of N719 and adjust arrangement of the N719 molecules towards a more uniform orientation which is beneficial for charge transfer and further prolongs electron lifetime. On all accounts, the longer electron lifetime and better suppression of back electron recombination enable co-sensitized DSSCs to achieve a higher solar cell efficiency.

In order to further understand the complex charge transfer process in DSSCs, a physical model has been proposed,^{53,54} and the equivalent circuit represented in Fig. 10, $R_s[C_1(R_1O)](R_2Q_2)$, is used to model this system, representing interfaces in



Fig. 10 Equivalent circuit used to represent interfaces in DSSCs consisting of FTO glass substrate/TiO₂/dye/l₃⁻/l⁻||Pt/FTO glass substrate.

composite solar cells. The symbols *R* and *C* describe a resistance and a capacitance, respectively, R_s is series resistance, R_1 and R_2 are the charge transfer resistance, *O*, which depends on the parameters $Y_{o,1}$ and *B*, accounts for a finite-length Warburg diffusion (Z_w) and *Q* is the symbol for constant phase element, CPE (its parameters are $Y_{o,2}$ and *n*).

Table 2 lists parameters obtained by fitting the impedance spectra of composite solar cells measured under standard AM1.5 G solar irradiation using the equivalent circuit in Fig. 10. As shown in Table 2, the series resistance R_s does not obviously change; the resistance R_1 which is estimated from the high frequency range semicircle in Nyquist plots decrease with the introduction of 2,6-bis(iminoalkyl)pyridine, and the resistance R_2 which is estimated from the second semicircle of Nyquist plots also decrease with the introduction of 2,6-bis(iminoalkyl)pyridine, and the total resistance of every co-sensitized DSSCs with 2,6-bis(iminoalkyl)pyridine decrease compared with single N719 sensitized DSSCs, these are all consistent with the results list in Fig. 9. The total resistance decrease is beneficial for electron transfer and further improving the performance of DSSCs. This suggests that the high performances in DSSCs sensitized with 2,6-bis(iminoalkyl)pyridine/N719 are also due to decreases of internal cell resistance.

3.7. Relationship between structures and photoelectrochemical properties

Photoelectrochemical performances indicate that DM, DE and DP which are isostructural could prevent the aggregation of

DSSC samples	$R_{\rm s}\left(\Omega ight) \qquad C_1\left(10^{-4} ight)$		F) $R_1(\Omega)$	0			<i>Q</i> ₂	
		$C_1 \left(10^{-4} \text{ F} \right)$		$Y_{\rm o,1} (10^{-1} \rm S)$	$B\left(\mathbf{S}^{1/2} ight)$	$R_2(\Omega)$	$Y_{ m o,2} \left(10^{-5} \ { m S}^{1/2}\right)$	n
N719/TiO ₂	25.66	6.24	15.56	1.38	0.50	14.03	9.03	0.77
DM/N719/TiO ₂	25.62	7.38	12.42	1.34	0.51	11.45	8.92	0.75
DE/N719/TiO ₂	25.46	6.47	12.81	1.23	0.51	11.65	7.50	0.76
DP/N719/TiO ₂	26.02	7.15	11.84	1.32	0.54	12.93	10.30	0.75

Table 2 Parameters obtained by fitting the impedance spectra of solar cells measured under standard AM1.5 G solar irradiation using the equivalent circuit

N719 and adjust the arrangement of the N719 molecules toward a more uniform orientation, enhance spectra response in the whole visible region, and further improve the photoelectrochemical performances. However, the substituent groups on the 2- and 6-positions of phenyl groups are different, they are isopropyl, methyl and ethyl, respectively, these make a little difference in their performances. It is very interesting that the electron-donating ability of the alkyl group (2,6-dimethylphenyl > 2,6-diethylphenyl > 2,6-diisopropylphenyl) is in line with the overall energy conversion efficiency of co-sensitized DSSCs. Meanwhile, lower steric hindrance on the 2,6-dialkyl-substituted phenyl ring (2,6-dimethylphenyl < 2,6-diethylphenyl < 2,6-diisopropylphenyl) leads to a higher efficiency of co-sensitized DSSCs. It is well known that higher electron-donating ability contributes better electron transfer and smaller steric hindrance making it easier to adsorb on TiO₂ film and inhibit the surface recombination of electrons at the electrode/electrolyte interface more efficiently. Both of them are responsible to enhance the performance of co-sensitized DSSCs. Meanwhile, the different substitutes on the 2- and 6-positions of phenyl groups make the calculated energy levels for DM, DE and DP a little different, as shown in Fig. 3 and Scheme 2, the E_{LUMO} of DM was closer to conduction band of TiO₂ than that for DE and DP, which could mean that it is easier to inject electrons into the conduction band of TiO₂ during the transfer process. Furthermore, the gap between electrolyte and the E_{HOMO} of DM is smaller than that of DP and DE, leading to easier transfer of electrons from electrolyte to DM. These also make the energy conversion efficiency of co-sensitized DSSCs in the order of DM/N719 > DE/N719 > DP/N719.

From the synthetic chemists' point of view, the geometric and electronic structure of the sensitizer also plays an important role. When all these factors are taken into account, it should be possible to design a more sophisticated and appropriate dye structures that satisfy the need of DSSCs technology.

4. Conclusions

In conclusion, we have designed a co-sensitized system with 2,6bis(iminoalkyl)pyridine and N719; the co-sensitized devices exhibit enhanced performance and significant improvement of J_{sc} in the order of DM/N719 > DE/N719 > DP/N719 > N719. The DM/N719 co-sensitized device yields the best overall efficiency of 7.00%, which is 28.91% greater than that of the device containing only N719 (5.43%). $J_{\rm sc}$ is enhanced because the aggregation of N719 is alleviated and its spectral response is enhanced in the region of 400–750 nm by 2,6-bis(iminoalkyl)-pyridines, and the total resistance of DSSCs is decreased after co-sensitizing with 2,6-bis(iminoalkyl)pyridines which are good for charge transfer. It is worth noting that the newly developed co-sensitized electrode is prepared only by a simple sequential adsorption process, which is inexpensive and easily handled, and thereby deserves to be explored for the application in DSSCs.

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