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Journal Name

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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A supramolecular assembling of metal-free organic dye with zinc porphyrin chromophore for dye-sensitized solar cells

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Two porphyrin chromophores P1 and P2 were prepared and have been used as antenna units to coordinate with metalfree organic dye JH1 containing pyridine groups, this supramolecular self-assembly strategy can not only effectively improve the light-harvesting ability of the devices, but also effectively reduce electron recombination by preventing the I_3 ⁻ of the electrolyte penetrating into the TiO₂ surface. The DSSC based on organic dye JH1 showed a PCE of 2.46%, with the V_{oc} of 615 mV, J_{sc} of 6.54 mA cm⁻², and FF of 61.18%. After supramolecular self-assembly, the J_{sc} and V_{oc} of the device were both greatly improved. Especially for the device based on JH1+P2, the PCE reached 4.39%, which increased about 78% compared with the PCE of the device based on JH1, this is mainly due to the J_{sc} increase of 2.85 mA cm⁻² and the V_{oc} increase of 93 mV. Compared to co-sensitization, supramolecular self-assembly does not require tedious optimization steps, thus, this may be a promising and convenient way to improve the overall performance of DSSCs.

Introduction

It is well known that the world is facing an energy crisis, the search for new energy is imminent for mankind. Dye-sensitized solar cells (DSSCs) as a promising optoelectronic technology have aroused the interest of many researchers, owing to their low manufacturing costs and simple fabrication techniques.^{1,2} Since Grätzel and coworkers first reported DSSCs in 1991,³ the power conversion efficiency (PCE) has made a series of key breakthroughs. The initial PCE was only 7.1%, in 2015, Toru Yano and co-workers prepared the alxoxysilyl-anchor dye ADEKA-1, the PCE of the DSSC based on ADEKA-1 and co-photosensitizer LEG4 reached up to 14.3%.⁴

As a wide band gap semiconductor with innocuity, stabilization and cheapness, TiO_2 is one of the best materials for preparing the anodes of DSSCs, however, the absorption of light from the ultraviolet region is a major defect. The sensitizers play a very important role in improving spectral response range and initiating electron transfer, the developing of efficient sensitizers is seen as one of the most direct and effective ways to improve the PCE of DSSCs.⁵⁻⁸ Up to now, many excellent dyes have been developed, the most important of these are ruthenium complexes, porphyrin dyes and metal-free organic dyes.⁹⁻¹² Ruthenium complexes were studied earlier, N3 and N719 are both excellent high efficiency dyes, a great deal of work has focused on the improvement of the kind of dyes, however, the expensive metal ruthenium limits the development of

such dyes.¹³ Porphyrin dyes hve excellent optical properties, which show broad absorption at the Soret band (400-450 nm) and moderate absorption at the Q-bands (550-600 nm), have become one of the hottest studied sensitizers for DSSCs.^{14,15} The DSSC based on porphyrin dye SM315 showed a very high PCE of 13.0% by Grätzel in 2014.¹⁶ The organic dyes have developed very rapidly in recent years, the cheap and easy to design features attract more and more attention. Some excellent dyes, such as SGT-137, C281, IQ21, YA422 have been successfully prepared.¹⁷⁻²¹ However, most excellent dyes require complex synthetic steps, the yield is not high. As we know, excellent light harvesting capability is an important prerequisite for efficient dyes. For single layer dyes, in order to achieve this goal, the researchers have to design lengthy synthetic routes. Supramolecular self-assembly may be one of the more convenient ways to increase the light harvesting capability.²²⁻²⁷ The porphyrins, phthalocyanines and ruthenium complexes are often used as building blocks for assembling supramolecular systems. Compared with the cosensitization method, 28,29 supramolecular self-assembly can eliminate lengthy optimization steps and no need have to be tedious to find the suitable adsorption conditions. The conditions for cosensitization need to be carefully explored, many factors influence the final result, such as types of cosensitizers, cosensitization mode, cosensitization solvent, cosensitization time, in addition, competitive adsorption often occurs between the main dye and cosensitizer. In contrast, supramolecular self-assembly is very easy to operate, which can be accomplished by metal coordination, H- bond and so on. Moreover, this method does not reduce dye loading, what's even more surprising is that the antenna unit of the supramolecular systems can not only improve the spectral response, but also reduce charge recombination by their steric effect. Up to now, there are not many reports related to this,

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Electronic Supplementary Information (ESI) available: synthesis details and characterization data; Details for all physical characterizations. See DOI: 10.1039/x0xx00000x

DOI: 10.1039/C7DT03373G Journal Name

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Han and co-workers increased the PCE of the DSSC based on ZnPA by about 47% by using this method. 30

In this work, in order to study the influence of supramolecular systems on the performance of DSSCs, we prepared a basic $D-\pi$ -A metal-free organic dye JH1. In the donor of JH1, two pyridine groups were introduced, which can enhance the electron donating ability, more importantly, the two pyridine groups can coordinate with many metal complexes chromophores. Herein, we used two porphyrin intermediates P1 and P2 of YD2-o-C8 as antenna units to coordinate with triphenylamine dye JH1 containing pyridine groups (Fig. 1).¹⁴ The DSSC based on JH1 showed a PCE of 2.46%, with the V_{oc} of 615 mV, J_{sc} of 6.54 mA cm⁻², and FF of 61.18%. After supramolecular self-assembly, the overall performance of the device has been greatly improved. Especially for the DSSC based on JH1+P2, the device showed a PCE of 4.39%, with the V_{oc} of 708 mV and J_{sc} of 9.39 mA cm⁻². The supramolecular systems effectively improve the light harvesting capability of the device, so the J_{sc} increases from 6.54 to 9.39 mA cm⁻². In addition, both P1 and P2 act as antenna units, they can effectively prevent the I_3 of the electrolyte penetrating into the TiO₂ surface, thereby reducing the charge recombination and improving the V_{oc} . The supramolecular self-assembly strategy is very beneficial to improve the overall performance of the DSSCs, we studied the optical properties and photovoltaic performance of the DSSCs based on the supramolecular systems.



Fig. 1 Schematic diagram of supramolecular self-assembly of JH1 with P1 or P2.

Results and discussion

Synthesis

The chemical structures of JH1, P1, P2 and the synthetic route were shown in Scheme S1. The synthesis details and characterization data were shown in supporting information.

Optical properties

The absorption spectra of JH1. P1 and P2 in THF are shown in Fig. 2a. The D- π -A type dye JH1 shows an unsatisfactory spectral response, the highest molar extinction coefficient at 399 nm is 1.40×10^4 M⁻¹ cm⁻¹. The two znic porphyrin chromophores P1 and P2 exhibit typical porphyrin absorption characteristics. The absorption below 400 nm may be attributed to electronic transitions from π - π *, and the 400-650 nm range may be attributed to intramolecular charge transfer (ICT). P1 shows a high molar extinction coefficient (2.00×10⁵ M⁻¹ cm⁻¹) at 426 nm in Soret band, and shows the molar extinction coefficient of 0.05×10^5 M⁻¹ cm⁻¹ at 596 nm in Q band. Compared with P1, the absorption spectra of P2 show a pronounced red shift. At 431 nm in Soret band, P2 shows a high molar extinction coefficient of 2.04×10⁵ M⁻¹ cm⁻¹, and the lowestenergy Q-band absorption of P2 was redshifted to 608 nm. After anchored on TiO₂ substrate, the absorption spectra became broader (Fig. 2b). The ICT bands of JH1 showed a significant red shift, the spectral response exceeds 600 nm, this may be attributed to J-aggregation.^{31,32} After supramolecular self-assembly, the absorption spectra of JH1+P1 and JH1+P2 have changed dramatically compared to JH1. Since P1 and P2 have no anchoring groups, the two chromophores can not be adsorbed on TiO₂. We tried to immerse TiO₂ into P1 and P2 solution for 24 h (Fig. S1), as a result, the absorption spectra showed no change (Fig. S2).



Fig. 2 (a) UV-Vis absorption spectra of JH1, P1 and P2 in THF, (b) UV-Vis absorption spectra of JH1, JH1+P1 and JH1+P2 anchored on TiO_2 surface.

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If we immersed the TiO₂ which have been sensitized with JH1 into P1 and P2 solution for 24 h, obviously, great changes have taken place in the surface of TiO₂ (Fig. S3). As shown in Fig. 2b, compared with JH1, the absorption spectra of JH1+P1 and JH1+P2 became broader and higher, their spectral response are both over 650 nm, such superior light harvesting capability is very beneficial to improve the short-circuit current of the device. But in Soret band, we found that the absorption intensity of JH1+P1 is lower than that of JH1+P2, in view of this, we further measured the dye loading under the same conditions. After supramolecular self-assembly, the dye loading for P1 is about 5.36×10^8 mol cm⁻², and the dye loading for P2 is about 7.65×10^{-8} mol cm⁻², the larger dye loading for P2 can compensate the absorption ability, this may be the main reason for the difference in Soret band.

Electrochemical studies

The cyclic voltammetry curves of JH1, JH1+P1 and JH2+P2 anchored on TiO₂ was measured to study the proprety of electron transfer form excited dyes to the conduction band of TiO₂.³³ As shown in Fig. S4, we used phtoanode as working electrode, Pt as counter electrode, Ag/Ag^{+} as reference electrode. From the Fig. 3, we can see that the ground state oxidation potentials (Eox) of JH1, JH1+P1 and JH1+P2 were 1.19 V, 1.12 V and 1.15 V (versus NHE), respectively. Obviously, they are all positive than the redox potential of the I^{\prime}/I_{3}^{-} couple (0.4 V), this shows that the oxidized dyes can be effectively recycled.^{34,35} The zero-zero excitation energy (E₀₋₀) was estimated from their absorption spectra, the values of JH1, JH1+P1 and JH1+P2 are 2.54 eV, 1.98 eV and 1.91 eV, respectively. Therefore, the excited oxidation potentials (E^*_{OX}) of JH1, JH1+P1 and JH1+P2 are -1.35 V, -0.92 V and -0.80 V, respectively. They are all negative than the conduction band of TiO₂ (-0.5 V versus NHE), this illustrates that the electron from the excited dyes of JH1, JH1+P1 and JH1+P2 all can efficiently inject into the conduction band of TiO₂.³⁶



Fig. 3 Schematic energy diagram of JH1, JH1+P1 and JH1+P2.

Photovoltaic performance of DSSCs

In order to investigate the photovoltaic property of the supramolecular systems, we fabricated the DSSCs based on JH1, JH1+P1 and JH1+P2 under the same conditions. The photovoltaic parameters are collected in Table 1, and the photocurrent-density-photovoltage (J–V) curves of are shown in Fig. 4a. Histogram of PCE

Table 1 Photovoltaic parameters of the DSSCs obtained from the J-V c	urves
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DOI: 10.1039/C7DT03373G

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Dye	$J_{\rm sc}$ (mA cm ⁻²)	V _{oc} (V)	FF (%)	η (%)	
JH1	6.54	0.615	61.18	2.46	
JH1+P1	8.16	0.664	67.91	3.68	
JH1+P2	9.39	0.708	65.99	4.39	

The size of the active area for each cell is 0.25 cm^2 , the DSSCs were all measured under standard global AM 1.5G solar irradiation.



Fig. 4 (a) The J–V curves of DSSCs based on JH1, JH1+P1 and JH1+P2; (b) The IPCE curves of DSSCs based on JH1, JH1+P1 and JH1+P2.

of DSSCs is shown in Fig. S5, the PCE of DSSC based on JH1 is 2.46%, with the V_{oc} of 615 mV, J_{sc} of 6.54 mA cm⁻², and FF of 61.18%. In order to improve the overall performance of the DSSCs, we designed to use the pyridine groups of JH1 to coordinate with porphyrin chromophores P1 and P2, just as expected, the J_{sc} and V_{oc} of this type of supramolecular DSSCs are both successfully improved. Compared to JH1, the Jsc of DSSC based on JH1+P1 was increased from 6.54 to 8.16 mA cm⁻², this should be attributed to improvements in the light harvesting capability. Surprisingly, the V_{oc} has also been greatly improved, the value was increased from 615 to 664 mV, we inferred that the main reason was that antenna units can effectively prevent the I₃ of the electrolyte penetrating into the TiO₂ surface, thereby reducing the charge recombination.³⁷⁻³⁹ When P2 as antenna unit, the PCE of the device reached the highest value of 4.39%, which increased about 78% compared with the PCE of the device based on JH1. Because P2 has better optical properties, the corresponding J_{sc} reached 9.39 mA cm⁻². The

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supramolecular systems of JH1+P2 may be more conducive to reducing electron recombination, as we known that we can improve the V_{oc} by increasing the electron injection rate or reducing electron recombination, so the V_{oc} increased from 615 to 708 mV.

For further analysis the differences of $J_{sc'}$ we measured the incident photon-to-current conversion efficiency (IPCE) spectra of the devices (Fig. 4b). Light harvesting capability affects the J_{sc}, from Table 1 we can see that the J_{sc} of the DSSCs follow the order: JH1<JH1+P1<JH1+P2, this trend is consistent with the IPCE spectra of the devices. As shown in Fig. 4b, the IPCE curves of JH1 exhibited narrower response range, the photocurrent generation up to about 550 nm. In the visible region, the highest value of JH1 is only 49.7% at 405 nm. The introduction of P1 as antenna units on the donors segment improve the spectral response range of the device, obviously, consequently the Jsc is improved. The IPCE spectrum of JH1+P1 is more broader than that of JH1, although the values of JH1+P1 is slightly lower than that of JH1 in the shortwave region, this may be due to a slight decrease of dye loading for JH1 during the supramolecular self-assembly process. However, the IPCE spectrum of JH1+P1 is much higher than that of JH1 after 425 nm, this should be attributed to the contribution of P1 in light harvesting performance. The photocurrent of JH1+P1 generation up to about 650 nm, in the long-wave region, the value is about 16.3% at 596 nm. The device based on JH1+P2 exhibits broader and higher IPCE curve from 400 to 650 nm range, especially in the longwave region, the value is about 29.5% at 615 nm, this is consistent with the J_{sc} of the DSSCs.

Electrochemical impedance spectroscopy measurements

The electrochemical impedance spectroscopy (EIS) under dark was often measured to study the electron recombination dynamics of the DSSCs, under the same conditions (with the same electrode materials and electrolyte), electron recombination rate has an important influence on the open-circuit voltage $(V_{oc})^{40-43}$ In order to analyze the difference between open-circuit voltages of the DSSCs, we measured the EIS under the applied voltage of -0.7 V and scanned from 10⁵ to 1 Hz. The equivalent circuit was presented in Fig. 5c, R_h in the high frequency range corresponds to the sheet resistance of FTO and the contact resistance between the FTO and TiO₂, R₁ and R₂ in the high and middle frequency regions are assigned to charge transfer resistance at Pt/electrolyte and TiO₂/dye/electrolyte interface, respectively. Nyquist plots of DSSCs are shown in Fig. 5a, we can see two semicircles, the small semicircle corresponds to the transport resistance at the Pt/electrolyte and the large semicircle corresponds to the charge transfer resistance at the TiO₂/dye/electrolyte interface. It is clear that radius of the large semicircle of JH1+P1 is larger than that of JH1, the obvious enhancement of R₂ for JH1+P1 indicates that the supramolecular systems is effective in TiO₂/dye/electrolyte interface modification, and this implies that the supramolecular systems effectively reduces the electron recombination rate, this also explains why V_{oc} of JH1+P1 increased by 49 mV. In addition, the R₂ of JH1+P2 is larger than that of JH1+P1, this shows that the P2 unit is more conducive to suppressing electron recombination, it is in agreement with the V_{oc} of the DSSCs. In generally, the longer electron lifetime represents the lower dark current, this is beneficial to improve the open-circuit voltage of the devices. We further

analyzed the electron lifetimes of the devices by bode phase plots (Fig. 5b). We can get the peak frequency (*f*) at lower frequency region from the bode phase plots and the electron lifetime (τ) can be calculated by τ =1/(2 π f).^{44,45} The bode phase plots show that the *f* of JH1, JH1+P1 and JH1+P2 is 16.5, 12.1 and 5.0 Hz, respectively. Thus, the corresponding electron lifetime value of JH1, JH1+P1 and JH1+P2 is 9.7, 13.2 and 31.8 ms, respectively. This also explains why the DSSCA based on JH1+P2 has the highest V_{oc}.



Fig. 5 (a) Nyquist plots of DSSCs based on JH1, JH1+P1 and JH1+P2; (b) Bode phase plots of DSSCs based on JH1, JH1+P1 and JH1+P2; (c) The equivalent circuit (R_h , R_1 , and R_2 are the series resistance, charge transfer resistance at Pt/electrolyte, and at TiO₂/dye/electrolyte interface, respectively; CPE1 and CPE2 are the constant phase element for the TiO₂/dye/electrolyte and Pt/electrolyte interface, respectively).

Conclusions

In summary, we have prepared a metal-free organic dye JH1 containing pyridine groups and two porphyrin chromophores P1

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and P2. These porphyrin chromophores were successfully as antenna units to coordinate with organic dye JH1, this supramolecular system has superior performance in improving spectral response and reducing charge recombination. The PCE of DSSC based on JH1 is only 2.46%, interestingly, the PCE of DSSCs based on JH1+P1 and JH1+P2 reached 3.68% and 4.39%, respectively. After supramolecular self-assembly, the lightharvesting ability was improved, especially for JH1+P2, the J_{sc} increased from 6.54 to 9.39 mA cm⁻². In addition, the supramolecular system can effectively prevent the I_3 of the electrolyte penetrating into the TiO₂ surface, thereby reducing the charge recombination and improving the V_{oc} , the V_{oc} of DSSC based on JH1+P2 increased 93 mV compared with that of DSSC based on JH1. More importantly, the DSSCs based on supramolecular selfassembly no need lengthy optimization steps compared with cosensitization, this may be a promising and convenient way to improve performance of DSSCs.

Acknowledgements

This work was supported by grants from the National Natural Science Foundation of China (21701060) and Natural Science Foundation of the Higher Education Institutions of Jiangsu Province (17KJB150015)

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The supramolecular system has superior performance in improving spectral response and reducing charge recombination, this may be a promising and convenient way to improve the performance of DSSCs.

