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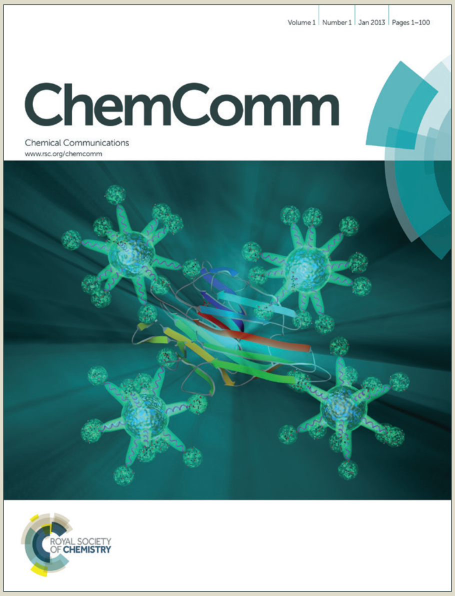

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Cosensitizers for simultaneous filling up both absorption valleys of porphyrins: a novel approach for developing efficient panchromatic dye-sensitized solar cells

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

XS1–XS3 have been synthesized by introducing an auxiliary acceptor to D-π-A dyes for simultaneous filling up both absorption valleys of porphyrin dyes around 550 and 380 nm. Thus, panchromatic DSSCs with the highest efficiency of 10.75% were achieved by cosensitization. This work provides a strategy of designing cosensitizers for porphyrin dyes.

Serious energy crisis and environmental pollution associated with fossil fuels are leading to increasing demand for accessible and renewable energy sources. In this respect, solar energy has been demonstrated to be a promising alternative, and dye-sensitized solar cells (DSSCs) have attracted considerable interests owing to their relatively high power-conversion efficiencies, low production costs, ease of fabrication and modifiable aesthetic features such as vivid colour and high transparency.[1] Thus, continuous efforts have been devoted to the construction of efficient sensitizers with typical donor-π-acceptor (D-π-A) structures.[2] In this respect, porphyrins have demonstrated their potential owing to the strong absorption in a large wavelength range as well as facile structural modification.[3] Most highly efficient porphyrin sensitizers contain bis(*ortho*-alkoxy) wrapped *meso*-phenyl groups for suppressing dye aggregation, which have been well elucidated by Diau, Yeh and coworkers.[4] Recently, Grätzel and coworkers reported wrapped porphyrins incorporating a benzothiadiazole moiety, and thus achieving the highest solar-to-electric power conversion efficiency (PCE) of 13.0% by using a cobalt-based electrolyte.[5] However, an intrinsic drawback for typical porphyrin-based dyes is the extremely weak absorption in the ranges of 500–600 nm and 350–410 nm, which hampers further improvement of the DSSC efficiencies,[4] and thus examples of porphyrin dyes exhibiting DSSC efficiencies higher than 10% are still very rare.[4-6] One of the promising approaches for overcoming this problem is cosensitization, which normally utilizes two sensitizers with complementary absorption spectra for achieving highly efficient light harvesting.[7] However, the reported D-π-A type small-molecule cosensitizers usually display a π-π* transition band around 300 nm and an intramolecular charge transfer (ICT) band between 500 and 600 nm,[8] which may be employed to fill up the absorption valley of porphyrin dyes at 500–600 nm. However, the other valley of most porphyrins at 350–410 nm was completely neglected, despite of the distribution of considerable solar energy in this wavelength range. Hence, it is highly desired to develop cosensitizers to simultaneously fill up both of the porphyrin absorption valleys and thus the DSSC efficiencies may be further improved. Fortunately, it was found that an additional absorption peak between 350~410 nm would appear if an auxiliary acceptor is introduced to a normal D-π-A type non-porphyrin dye.[9] It can be envisioned that this approach may be employed for developing efficient cosensitizers for simultaneous filling up both of the absorption valleys of typical porphyrin dyes.

Based on the aforementioned background, a nonplanar butterfly-shaped phenothiazine (PTZ) moiety[10] and a thiophenyl cyanoacrylic acid moiety were employed as the electron donor and acceptor, respectively. And an electron-deficient diketopyrrolo-pyrrole (DPP) moiety[11] was introduced as the auxiliary acceptor to construct cosensitizers **XS1**–**XS3** (Fig. 1). Hexyloxyl and hexyl groups were introduced to these dyes for suppressing the dye aggregation effect. Compared with **XS1**, an additional ethynylene bridge was introduced into **XS2** to expand the π-conjugation framework and enhance the absorption.[12] In addition, a hexyl group was introduced into the thiophenyl unit of **XS3** to further suppress the dye aggregation effect.[9] As expected, these dyes really exhibit a broad peak around 400 nm in addition to that around 520 nm, which may simultaneously fill up both absorption valleys of typical porphyrin dyes. Hence, **XS1**–**XS3** were applied as cosensitizers for our recently reported efficient porphyrin dyes **XW3** and **XW4**,[13] thus achieving strong panchromatic light harvesting and the highest efficiency of 10.75% for **XS3**+**XW4** cosensitized cells. These results provide an effective approach for developing cosensitizers to simultaneously fill up both of the absorption valleys of porphyrin dyes, especially for highly efficient panchromatic cosensitized DSSCs. Successful application of all the three designed cosensitizers to two porphyrin dyes indicates the general applicability of this approach.

The synthetic details are described in the Supporting Information. The phenothiazine donor was attached to the DPP moiety through a Suzuki coupling reaction. Then, the acceptor was introduced *via* a Sonogashira coupling reaction. The chemical structures were characterized with ^{1}H NMR, ^{13}C NMR and HRMS (Fig. S1–S21).

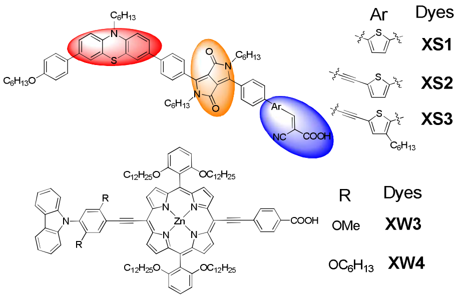

Fig. 1 Molecular structures of cosensitizers **XS1-XS3** and the porphyrin dyes **XW3** and **XW4**.

As expected, the absorption spectra of **XS1–XS3** in THF (Fig. 2, S22, Tables S1 and S2) exhibit two distinct broad absorption peaks in the wavelength ranges of 350–450 nm 450–600 nm, which can well fill up the absorption valleys of the porphyrins. In addition, these dyes show relatively high molar absorption coefficients of 33000~55000 M^{-1} cm^{-1}, with the absorption strength sequence of **XS1** < **XS2≈XS3**, indicating that the ethynylene bridge is really effective for improving the light absorption ability. Upon adsorption onto the nanocrystalline TiO_2 films, the absorption peaks of **XS1–XS3** were significantly broadened (Fig. S23), which is favourable for light harvesting.

In addition to the excellent light-harvesting ability, energy levels are also important parameters for DSSC dyes. Hence, cyclic voltammetry (Fig. S24) was measured for **XS1–XS3** and the corresponding data were summarized in Table S3. The LUMO levels were estimated to be within the range of -1.56~-1.51 V, which are more negative than the conduction band edge (CB) of TiO_2 (-0.5 V vs. NHE), providing the possibility of electron injection. The HOMO levels were observed to be within the range of 0.63~0.66 V (Fig. S25), lying well below the iodide/triiodide redox potential value (0.4 V vs. NHE), indicating that the oxidized dyes could be regenerated by the electrolyte. All these results indicate that the electron injection and dye regeneration processes are thermodynamically favourable for **XS1–XS3**.[14]

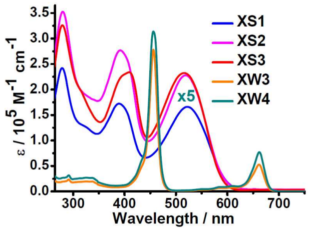

Fig. 2 Absorption spectra of dyes **XS1**, **XS2**, **XS3**, **XW3** and **XW4** in THF.

Density functional theory (DFT) calculations were utilized to analyze the electron-density distributions of the frontier orbitals (Fig. S26). In the ground state, the phenothiazine moiety adopts a nonplanar butterfly-like conformation, which may be favorable for suppressing the dye-aggregation. The HOMO levels are delocalized throughout the phenothiazine donor and the DPP moieties, while the LUMO lies mainly on the cyanoacrylic acid acceptor and the DPP moiety, which would have a favorable effect on the electron redistribution from the donor to the acceptor when the electron is transferred from the HOMO to the LUMO. Hence, DSSCs were fabricated using these dyes as the sensitizers.

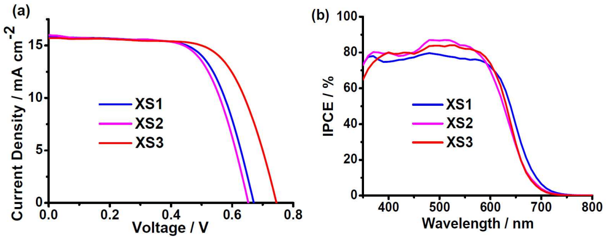

Fig. 3 *J–V* characteristics (a) and IPCE action spectra (b) of DSSCs based on **XS1**, **XS2** and **XS3**.

The current density–voltage (*J–V*) curves (Fig. 3a) of the DSSCs fabricated from the individual dyes of **XS1**, **XS2** and **XS3** were measured under simulated AM 1.5G irradiation (100 mW cm^{-2}), with the photovoltaic parameters summarized in Table 1. **XS1** exhibits a PCE of 7.27%. Upon introduction of an additional ethynylene bridge, the PCE was lowered to 6.95% for **XS2** despite the higher molar absorption coefficient, which may be ascribed to the more severe dye aggregation caused by the extended π framework.[12] An additional hexyl chain was incorporated into **XS3** to improve the cell efficiency by suppressing the dye aggregation. Accordingly, the corresponding PCE value was improved to 8.02%.

Table 1 Photovoltaic parameters of the DSSCs under AM 1.5G illumination (power 100 Mw cm^{-2})

Dye	J_{sc}/mA cm^{-2}	V_{oc}/mV	FF	η/%
XS1	15.84 (±0.3)	672 (±2)	0.68 (±0.02)	7.27 (±0.3)
XS2	16.12 (±0.2)	653 (±3)	0.66 (±0.01)	6.95 (±0.15)
XS3	15.73 (±0.1)	748 (±4)	0.68 (±0.02)	8.02 (±0.2)
XW3[a]	15.60 (±0.2)	694 (±1)	0.68 (±0.02)	7.32 (±0.1)
XW4[a]	16.22 (±0.3)	702 (±2)	0.70 (±0.01)	7.94 (±0.15)
XS1+XW3[b]	19.26 (±0.2)	679 (±5)	0.70 (±0.01)	9.19 (±0.1)
XS2+XW3[b]	19.10 (±0.3)	688 (±2)	0.69 (±0.03)	9.04 (±0.2)
XS3+XW3[b]	19.89 (±0.2)	720 (±2)	0.73 (±0.02)	10.45 (±0.2)
XS1+XW4[b]	19.62 (±0.1)	700 (±4)	0.70 (±0.02)	9.58 (±0.2)
XS2+XW4[b]	19.85 (±0.2)	696 (±1)	0.68 (±0.01)	9.43 (±0.1)
XS3+XW4[b]	19.96 (±0.2)	728 (±3)	0.74 (±0.01)	10.75 (±0.1)
N719	17.65 (±0.3)	806 (±2)	0.68 (±0.02)	9.63 (±0.15)

[a] Reported by reference 13. [b] The cosensitization was performed through an optimized stepwise approach: the TiO_2 electrode was immersed in a 0.2 mM porphyrin solution in a mixture of toluene and ethanol (volume ratio of 1:4) for 10 h and then immersed in a 0.3 mM solution of the cosensitizer in a mixture of chloroform and ethanol (volume ratio of 6:4) for 1 h. Then, the cosensitized films were assembled into DSSC devices. The photovoltaic parameters obtained during optimization of the cosensitized DSSCs are listed in Table S4.

We continued to investigate effects of the dye structures on the cell current characteristics. The incident-photon-to-current conversion efficiency (IPCE) curves are plotted in Fig. 3b as a function of wavelength. All of **XS1–XS3** display a broad plateau, with the IPCE values lying above 70% within 350–600 nm (Fig. 3b). The IPCE values for **XS2** and **XS3** are higher than those of **XS1** in most of the wavelength range, indicating that incorporation of an ethynylene bridge and an alkyl chain can effectively lead to enhanced DSSC cell currents. The broad IPCE plateaus observed for **XS1–XS3** are in sharp contrast to the IPCE valleys around 380 and 500 nm observed for porphyrin dyes **XW3** and **XW4**,[13] indicating that **XS1–XS3** may be perfect cosensitizers for **XW3** and **XW4** by filling up both of the absorption valleys. Hence, more DSSCs were fabricated by employing **XS1**–**XS3** as the cosensitizers for **XW3** and **XW4**. The photovoltaic behaviour and the corresponding parameters are shown in Fig. 4, Fig. S29 and Table 1. The light-harvesting efficiency (LHE) and the absorbed photon-to-electric current generation efficiency (APCE) spectra for these three dyes (Fig. S27 and S28) are indicative of the relatively good performance of the dyes.[15,19*a*]

As expected, the IPCE valleys around 380 and 500 nm for **XW3** and **XW4** were really fully filled up, with the IPCE values lying above 80% roughly within a large wavelength range of 350–680 nm (Fig. 4). And the highest IPCE value reaches *ca.* 91%. In consequence, the cosensitized devices showed enhanced J_{sc} values within the range of 19.10–19.96 mAcm^{-2}, as compared with those of 15.60–16.22 mA cm^{-2} observed for the corresponding individual dye sensitized devices, and these values are also higher than the previously reported cosensitization systems,[13] which may be related to the relatively higher IPCE values in the 350~420 nm wavelength range associated with the absorption bands around 400 nm observed for **XS1**–**XS3**. We also noticed that the J_{sc} values estimated from the IPCE spectra are smaller than those obtained from the *J*–*V* curve (Table 1, Fig. 4 and Fig. S29).[2*d*] For example, integration of the IPCE curve for **XS3+XW4** affords a calculated J_{sc} value of 18.05 mA cm^{-2}, which is slightly lower than the experimental value of 19.96 mA cm^{-2}. These observations may be interpreted in terms of the more efficient charge transport and collection[16] and more pronounced thermal effect for the full sunlight irradiation.[17-18] Actually, similar observations have been reported for a number of porphyrin dyes.[2*d*,7*a*]

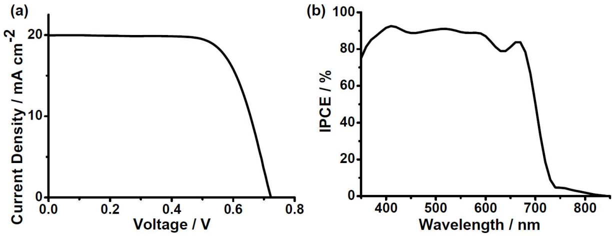

Fig. 4 *J*–*V* characteristics (a) and IPCE action spectra (b) for the cosensitized DSSC based on **XS3/XW4**.

In addition to the large J_{sc} values, high open circuit voltages (V_{oc}) are also prerequisites for developing highly efficient DSSCs. For typical cosensitization systems, the V_{oc} lies intermediate between those of the individual dye sensitized cells.[19] The relatively high V_{oc} of 748 mV for **XS3** sensitized cells resulted in enhanced V_{oc} values of 720 and 728 mV for the cosensitized DSSCs with respect to those of 694 and 702 mV for the corresponding DSSCs sensitized by the individual porphyrins **XW3** and **XW4**, respectively. In consequence, the cosensitization with **XS3** results in enhanced J_{sc}, V_{oc} and efficiencies relative to the individual porphyrin dyes. At last, high efficiencies of 10.45 and 10.75% were achieved for the cosensitization of **XS3** with **XW3** and **XW4**, respectively. In contrast, relatively lower V_{oc} values were observed for the cells sensitized individually by **XS1** or **XS2** as compared with that of **XS3**. Hence, the cosensitization of these two dyes only enhanced the cell efficiencies of **XW3** and **XW4** to a smaller extent.

To further understand the factors affecting V_{oc}, electrochemical impedance spectroscopy (EIS) measurements were performed. The chemical capacitance (C_{μ}), the interfacial charge transfer resistance (R_{CT}) and the electron lifetime (τ) could be acquired by fitting the EIS spectra.[20] As shown in Fig. S30, the C_{μ} values decrease in the sequence of **XS2** > **XS3** > **XS1**, implying a sequential negative shift of the conduction band edge.[5,19*a*,20] At a given voltage bias, the fitted τ values decrease in the order of **XS3** > **XS1** ≈ **XS2**, indicating the same order of decreasing charge recombination rate and increasing electron lifetime, which is in consistence with that of the V_{oc} values. These results imply that the V_{oc} values are predominantly determined by the charge recombination process rather than the position of the TiO_2 conduction band.[21] Similar results were observed for the cosensitized cells (Fig. S31).

In addition to high cell efficiencies, photo-stability is another key parameter for DSSCs.[22] Hence, dyes **XS1**–**XS3** adsorbed on nanocrystalline TiO_2 films were illuminated with simulated solar light without redox mediators for 30 min, and the absorbance was only slightly decreased (Fig. S32), indicative of satisfactory photo-stability of these dyes. The composition of redox electrolytes as well as encapsulation of cell devices also influences the device stability. Figs. S33 and S34 show the photovoltaic performance during a long term accelerated aging under AM 1.5G visible-light soaking for 500 hours, which indicate that the DSSCs are stable under this condition.

Finally, to facilitate feasible applications, we also tried the quasi-solid-state electrolyte instead of the liquid electrolyte, and the cosensitized cells of **XS3+XW3** and **XS3+XW4** demonstrate high power conversion efficiencies of 8.02% and 8.12%, respectively (Fig. S35, Table S5). These efficiencies rank among the best ones observed for quasi-solid-state DSSCs.[23]

In summary, for the purpose of designing cosensitizers which can be used to simultaneously fill up both of the absorption valleys of porphyrin dyes in the ranges of 350–410 nm and 500–600 nm and thus developing efficient cosensitized panchromatic solar cells, an electron-deficient diketopyrrolopyrrole (DPP) moiety was introduced as the auxiliary acceptor to the D-π-A type of small-molecule dyes. Thus, **XS1**, **XS2**, and **XS3** were designed by combining a nonplanar phenothiazine-based electron donor, a DPP moiety and a thiophenyl cyanoacrylic acid-based acceptor. The absorption spectra of **XS1**–**XS3** exhibit two distinct broad absorption peaks in the wavelength ranges of 350–450 nm and 450–600 nm, which can perfectly compensate the absorption valleys of the porphyrin dyes. Thus, the cosensitization of **XS3** with porphyrin dyes **XW3** and **XW4** affords high efficiencies of 10.45% and 10.75%, respectively. These values well exceed that of 9.63% obtained for the Ru(II)-based N719 dye (Table 1) and those obtained for our previously reported cosensitized DSSCs.[13] This work provides an effective strategy for designing cosensitizers for simultaneous filling up both of the absorption valleys of the porphyrin dyes, and thus highly efficient panchromatic DSSCs could be developed. The general applicability of this approach has been demonstrated by the successful application of all the three designed cosensitizers to the two porphyrin dyes.

Acknowledgements

This work was supported by NSFC/China (21472047, 91227201), the Science Fund for Creative Research Groups (21421004), the Oriental Scholarship, NCET-11-0638, and the Fundamental Research Funds for the Central Universities (WK1013002).

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† Electronic Supplementary Information (ESI) available: 1H NMR, 13C NMR and HRMS spectra of intermediates and target products. See DOI: 10.1039/b000000x/

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