Solar Cells

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Molecular Engineering Combined with Cosensitization Leads to Record Photovoltaic Efficiency for Non-ruthenium Solar Cells

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Increasing energy requirements and environmental pollution caused by the burning of fossil fuels have necessitated research into clean and renewable energy sources to maintain the activities of modern life.[1] Several types of solar cell have been developed to exploit incident sunlight. Of these, dye-sensitized solar cells (DSSCs) show great promise because of their low cost, simplicity of fabrication, and relatively high photovoltaic efficiencies.[2] Since the first report on DSSCs by Grätzel and co-workers in 1991,[3] polypyridyl ruthenium dyes have been developed as the most successful class of sensitizers, achieving high energy conversion efficiencies owing to their wide-ranging absorption spectra, appropriate energy levels, and long-lived photoexcited states. More recently, organic sensitizers with donor–π–acceptor (D–π–A) structures have been extensively investigated because of their high molar extinction coefficients, tunable spectral properties, easy synthetic variability, and low cost.[4]

Over the last decade, porphyrin sensitizers have been widely employed in DSSCs because of their easily tunable structures and strong, broad absorption bands. A large DSSC efficiency of 13.0 % was achieved by Grätzel et al. by using a Co^{3+}/Co^{2+} electrolyte.[5] However, despite the excellent metrics, use of the cobalt electrolyte often requires additional structural features such as bulky electron donors, which complicates the synthesis, and cell fabrication is more challenging than for those based on the traditional I^-/I_3^- electrolyte. Hence, the development of efficient DSSCs using the traditional I^-/I_3^- electrolyte remains desirable.

Porphyrins exhibit weak absorption in the near-IR region and around 500 nm, which is an obstacle for their use in further improving DSSC photovoltaic efficiency. To address this problem, extension of the π-conjugated framework of the porphyrin dyes might be an effective means to enhance absorption in the near-IR region, while utilization of a cosensitizer may compensate for the weak absorption around 500 nm.[6] These two approaches are both effective for improving light absorption and photocurrent (J_{sc}). However, extending the π-conjugation structures may result in undesirable dye aggregation and decreased photovoltage (V_{oc}), while cosensitization usually leads to decreased or nearly unaffected V_{oc}. To achieve high photovoltaic efficiencies, it is critical to simultaneously improve both the J_{sc} and V_{oc} parameters, preferably by using a molecular-design approach.

With this in mind, Xie, Zhu, and co-workers have systematically developed a design strategy involving rational porphyrin dye structure optimization and cosensitization to obtain efficient DSSCs using the traditional I^-/I_3^- electrolyte.[7–10] Based on a porphyrin derivative containing facially encumbering alkoxy groups to suppress dye aggregation,[7] Xie et al. initially developed the porphyrin dye **XW1** (Figure 1) by employing a carbazole group as an electron donor and a 4-ethynyl benzoic acid moiety as the electron acceptor.[8] An ethynylene bridge was then also introduced (in **XW2**) between the donor and the porphyrin core to extend the absorption to a longer wavelength. Additional aggregation-suppressing alkoxy chains were then introduced to the phenylene group at the donor side of the molecule in **XW3** and **XW4**. Of these compounds, the optimized dye **XW4** exhibits the highest J_{sc} of 16.22 mA cm^{-2}, with an associated efficiency of 7.94 %. Subsequently, the non-porphyrin dye **C1** (Figure 1), which exhibits strong absorption around 500 nm, was used as a cosensitizer (Figure 2). This resulted in a significant enhancement of the J_{sc} to 20.15 mA cm^{-2} and a slightly enhanced V_{oc}, giving a high photovoltaic efficiency of 10.45 %.

Based on this and their further work on porphyrin dye structure optimization and cosensitization,[9] Xie, Zhu, and co-workers recently reported the preparation of three new porphyrin dyes; **XW9**, **XW10**, and **XW11** (Figure 1); with a stronger electron-donating phenothiazine moiety as the donor.[10] In **XW9**, the phenothiazine is directly attached to the *meso* position, which leads to a photovoltaic efficiency of 8.2 % in DSSC. The introduction of an ethynylene bridge between the phenothiazine and the porphyrin framework in **XW10** enhances light absorption in the near-IR region, and thus an improved efficiency of 8.6 % was achieved. A benzothiadiazole (BTD) group was inserted into **XW11** as an additional electron acceptor to strongly red-shift the onset wavelength to 830 nm, giving a high J_{sc} of 18.83 mA cm^{-2}, although efficiency decreased to 7.8 % owing to a decreased

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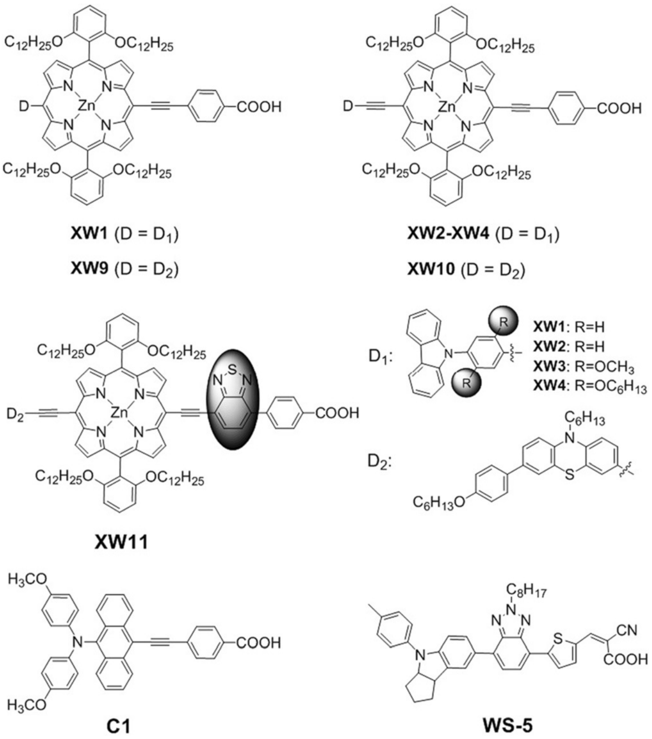

Figure 1. Molecular structures of **XW1**–**XW4**, **XW9**–**XW11**, and the cosensitizers (**C1** and **WS-5**).

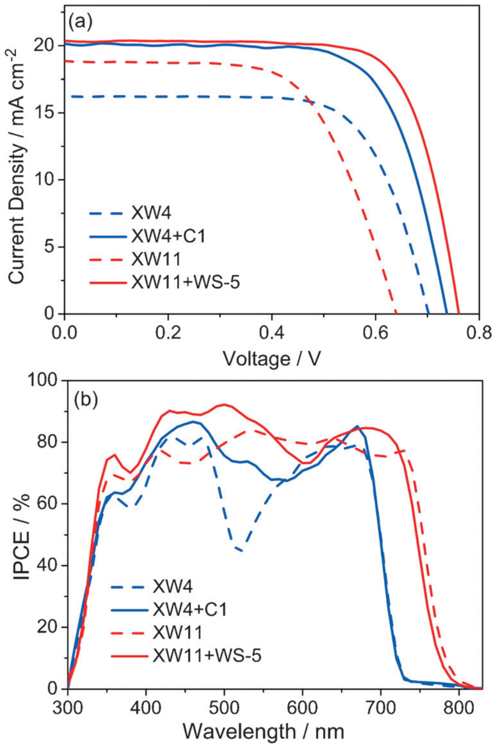

Figure 2. Photocurrent–voltage (*J*–*V*) characteristics (a) and IPCE action spectra (b) for DSSCs based on **XW4** and **XW11**, and for those cosensitized with **C1** and **WS-5** using the I_2/I_3^- electrolyte.

V_{oc} of 645 mV caused by dye aggregation. Based on the high J_{sc} and low V_{oc} of **XW11**, they applied chenodeoxycholic acid (CDCA) as a coadsorbent to suppress dye aggregation, and observed an increase in the V_{oc} to 727 mV, with an associated moderate improvement in the efficiency to 9.3%.

Considering that CDCA does not absorb sunlight, which means that J_{sc} is attenuated owing to competitive adsorption between CDCA and **XW11**, they continued to employ a cosensitization approach to dramatically enhance the photovoltaic efficiency by synergistically improving V_{oc} and J_{sc}. They thus used **C1** to cosensitize with **XW9**–**XW11**. As expected, the IPCE valleys of **XW9**–**XW11** around 500 nm were well filled, thus resulting in enhanced J_{sc} values (17.01–19.52 mA cm^{-2}). Critically, V_{oc} values obtained for **XW9**–**XW11** were simultaneously enhanced from 645–728 mV to 746–764 mV. A high efficiency of 10.6% was thus achieved for the cosensitized **C1** + **XW11** cell through the synergistic enhancement of J_{sc} and V_{oc}.

Based on the successful application of the cosensitizer **C1**, they envisioned that photovoltaic efficiency might be further improved by using a cosensitizer that individually exhibits a higher V_{oc} and a higher efficiency. For this purpose, they employed **WS-5**[2c] (Figure 1), and V_{oc} values were further improved to 760–770 mV. Moreover, the J_{sc} values were also further enhanced to 17.70–20.33 mA cm^{-2} (Figure 2). Finally, cosensitization using **XW11** and **WS-5** afforded a record efficiency of 11.5% for non-ruthenium DSSCs with the I_2/I_3^- electrolyte.

In summary, by considering the structural and photovoltaic characteristics of porphyrin dyes, Xie, Zhu, and coworkers developed a combined strategy involving molecular engineering and cosensitization for improving photovoltaic efficiency through targeted and synergistic optimization of V_{oc} and J_{sc}, thereby achieving a record efficiency of 11.5% for non-ruthenium DSSCs based on the traditional I^-/I_3^- electrolyte. These results represent an excellent example of what can be achieved through the careful design and tuning of porphyrin molecular structure for targeted optoelectronic behavior, which is especially relevant for photovoltaic cell optimization towards a more sustainable society.

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[1] a) A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, *Chem. Rev.* **2010**, *110*, 6595–6663; b) H. Y. Hsu, C. Y. Wang, A. Fathi, J. W. Shiu, C. C. Chung, P. S. Shen, T. F. Guo, P. Chen, Y. P. Lee, E. W. G. Diau, *Angew. Chem. Int. Ed.* **2014**, *53*, 9339–9342; *Angew. Chem.* **2014**, *126*, 9493–9496.

[2] a) H. Imahori, T. Umeyama, S. Ito, *Acc. Chem. Res.* **2009**, *42*, 1809–1818; b) H. P. Wu, Z. W. Ou, T. Y. Pan, C. M. Lan, W. K. Huang, H. W. Lee, N. M. Reddy, C. T. Chen, W. S. Chao, C. Y. Yeh, E. W. G. Diau, *Energy Environ. Sci.* **2012**, *5*, 9843–9848; c) Y. Z. Wu, W.-H. Zhu, *Chem. Soc. Rev.* **2013**, *42*, 2039–2058.

[3] B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737–740.

[4] a) Z. Y. Yao, H. Wu, Y. Li, J. T. Wang, J. Zhang, M. Zhang, Y. C. Guo, P. Wang, *Energy Environ. Sci.* **2015**, *8*, 3192–3197; b) Y. Xie, W. Wu, H. Zhu, J. Liu, W. Zhang, H. Tian, W. H. Zhu, *Chem. Sci.* **2016**,*7*, 544–549; c) S. Ahmad, E. Guillén, L. Kavan, M. Grätzel, M. K. Nazeeruddin, *Energy Environ. Sci.* **2013**, *6*, 3439–3466.

[5] S. Mathew, A. Yella, P. Gao, R. H. Baker, B. F. E. Curchod, N. A. Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin, M. Grätzel, *Nat. Chem.* **2014**, *6*, 242–247.
[6] H. P. Wu, Z. W. Ou, T. Y. Pan, C. M. Lan, W. K. Huang, H. W. Lee, N. M. Reddy, C. T. Chen, W. S. Chao, C. Y. Yeh, E. W. G. Diau, *Energy Environ. Sci.* **2012**, *5*, 9843–9848.
[7] a) C. Y. Lee, J. T. Hupp, *Langmuir* **2010**, *26*, 3760–3765; b) Y. C. Chang, C. L. Wang, T. Y. Pan, S. H. Hong, C. M. Lan, H. H. Kuo, C. F. Lo, H. Y. Hsu, C. Y. Lin, E. W. Diau, *Chem. Commun.* **2011**, *47*, 8910–8912; c) A. Yella, H. W. Lee, H. N. Tsao, C. Y. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W. G. Diau, C. Y. Yeh, S. M. Zakeeruddin, M. Grätzel, *Science* **2011**, *334*, 629–634.
[8] Y. Q. Wang, B. Chen, W. J. Wu, X. Li, W. H. Zhu, H. Tian, Y. S. Xie, *Angew. Chem. Int. Ed.* **2014**, *53*, 10779–10783; *Angew. Chem.* **2014**, *126*, 10955–10959.
[9] a) X. Sun, Y. Q. Wang, X. Li, H. Ågren, W. H. Zhu, H. Tian, Y. S. Xie, *Chem. Commun.* **2014**, *50*, 15609–15612; b) T. T. Wei, X. Sun, X. Li, H. Ågren, Y. S. Xie, *ACS Appl. Mater. Interfaces* **2015**, *7*, 21956–21965.
[10] Y. Xie, Y. Tang, W. Wu, Y. Wang, J. Liu, X. Li, H. Tian, W. H. Zhu, *J. Am. Chem. Soc.* **2015**, *137*, 14055–14058.

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