Light Harvesters

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Catching the Rainbow: Light Harvesting in Dye-Sensitized Solar Cells

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Low-cost systems for the exploitation of renewable energy have never been more urgently required: there is a growing consensus that burning fossil fuels is leading to dangerous accumulation of CO_2 in the atmosphere,[1] and fossil fuel resources are in long-term decline. In particular, solar energy is the only source with the proven capacity to meet the increasing world energy needs,[2] and dye-sensitized solar cells have emerged as a low-cost alternative to established silicon solar cells.[3] Photovoltaic systems in which attached dyes sensitize wide-bandgap metal oxides to visible light have been long studied; however the breakthrough work in 1991 by O'Regan and Grätzel[4] showed that use of a nanocrystalline TiO_2 film gives sufficient surface area for efficient light harvesting using charge-transfer sensitizer dyes. Following this development, the same group rapidly developed devices with a solar-to-electric power-conversion efficiency of over 10% by optimizing ruthenium polypyridyl dyes, the stereotypical example being $[Ru\{4,4'-(CO_2H)bipy\}_2(NCS)_2]$ (N3)[5] along with the doubly-deprotonated analogue, N719. The excellent performance of N3 is demonstrated by the incident-photon-to-current efficiency (IPCE) which is maintained at around 70–80% between 400 and 600 nm.[6] Taking into account losses from absorption and scattering by the transparent conducting oxide, this means that almost every photon absorbed by the dye in this region leads to an electron in the external circuit.

Given this remarkable performance, we may however ask why the best efficiency remains well below the theoretical maximum (around 32% for a single-junction solar cell) and also why there has not been significant improvement since 1993, despite extensive work in the development of new dyes. Indeed a superficial look at the field may give the impression that dye optimization has not moved on, however, this impression would be very misleading. For example, research has led to a greater understanding of the key dye characteristics such as charge separation[7] and to new efficient dye types that do not depend on ruthenium, including organic or porphyrin dyes that have reached efficiencies of around 8–9%[8,9] and 7%,[10] respectively. Furthermore, dye design has allowed significant improvement of commercial systems; dyes with higher molar extinction coefficients allow thinner devices to be prepared. This minimizes charge-recombination during transport to the electrode, enabling good efficiencies with nonvolatile electrolyte systems essential for long-term stability. In addition, appended alkyl chains have been used to give greater stability to light soaking and heat by protecting the dye against hydrolysis from the surface.[9,11]

Despite these achievements, an important point to address is the persistent limit to the highest efficiency that is obtained, and a key drawback of existing dyes is the limited light harvesting by the best examples at long wavelengths. The solar spectrum at the earth's surface (Figure 1) extends into the near-IR, and the best dyes such as N3 typically enable high-efficiency energy conversion up to only about 600 nm. Panchromatic absorption with a single dye would require multiple absorption bands than span the solar spectrum. The difficulty lies in extending the dye absorption range while simultaneously avoiding a negative impact on other parameters, such as ground- and excited-state redox potential, intensity of absorption, or stability. For example, the ruthenium-based "black dye"[12,6] maintains an IPCE above 70% out to around 700 nm, but possesses a lower molar extinction coefficient than N3, and overall efficiency is comparable but not significantly better.

As perfecting all the requirements in a single dye has proven so challenging, what other approaches could be taken? The recent work of Nazeeruddin, Torres, and co-workers[14] uses a cosensitization approach; that is, using a combination of dyes to absorb at different parts of the solar spectrum. Although this may sound intuitively sensible, and has indeed been tried before, it is difficult to achieve the real benefits that may be imagined. Several previous studies have shown[15] that the result is often only an efficiency somewhere between that of the individual dyes, and thus poorer than the best of these. This makes sense if we consider that the dyes are presumably competing for space on the metal oxide surface to form the active monolayer and use of multiple dyes gives a lower coverage of each.

One novel approach to bypassing this problem was taken by Durrant and co-workers, who used a cosensitization strategy to add a second dye to a TiO_2 layer that was already fully sensitized with one dye.[16] This method involved

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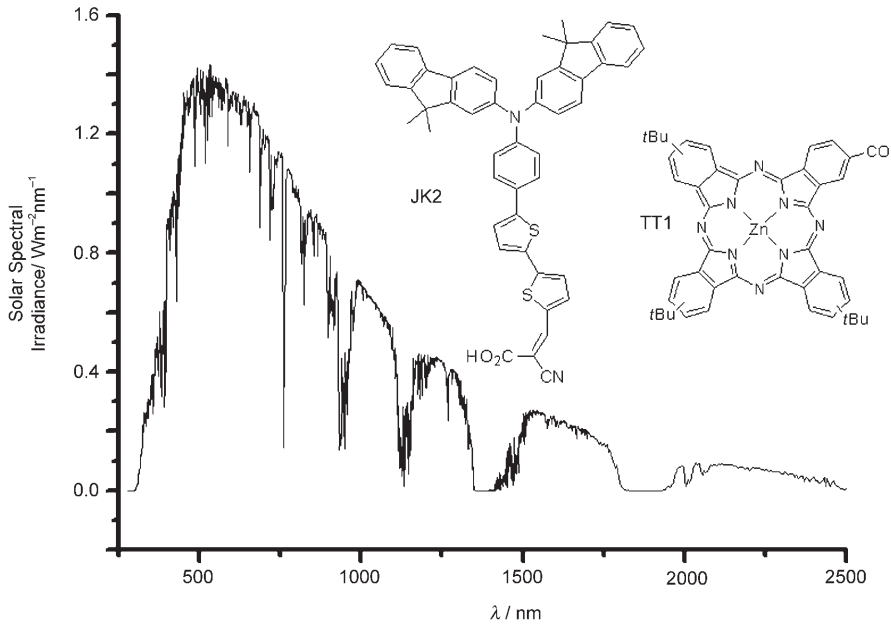

Figure 1. Direct normal solar spectrum at air mass 1.5,[13] and molecular structures of JK2 ($\lambda_{max}=452$ nm) and TT1 ($\lambda_{max}=680$ nm).

generation of a secondary Al_2O_3 layer onto TiO_2 which was already sensitized with one dye. A different dye with longer wavelength absorption was then subsequently bound to the Al_2O_3. The result was a redox cascade that moved the oxidized center from the first to the second dye, namely further from the TiO_2, and therefore extending the charge-separated lifetime. The approach demonstrated an interesting concept, although the strategy was not used to make highly efficient devices.

The group of Wang and Zhang used a combination of three organic dyes, with absorption maxima at 380, 535, and 642 nm, to achieve a higher efficiency than any of the individual dyes alone.[17] These dyes were chosen to give broad coverage across the solar spectrum and also as a strategy to counter the narrow absorption bands typically observed for organic dyes in comparison with ruthenium complexes. Remarkably, an overall efficiency of 6.5 % was observed, which was higher than that obtained for any of the three dyes individually. This was attributed to synergistic effects, whereby dye aggregation, which can lead to reduced performance, was disfavored. It was also suggested that the multiple dyes give a more compact coverage on the TiO_2 which may lessen charge-recombination losses between electrons in the TiO_2 and holes in the redox electrolyte. This study represented the first example where cosensitization led to improvement in properties, and a high IPCE was maintained out to around 700 nm.

Further developments in cosensitization are however impeded by the lack of good long-wavelength dyes that are able to contribute significantly to the efficiency. Phthalocyanines are obvious candidates for long-wavelength absorption through their intense Q band; however their potential has remained hard to capture until recently. Building on recent results,[18] Nazeeruddin, Torres, and co-workers have now used a novel zinc phthalocyanine (TT1; Figure 1) to avoid known drawbacks: bulky groups to prevent aggregation, and the design of directionality into the charge transfer, which enables favorable charge injection and recombination kinetics. This approach has provided[14] the first phthalocyanine dye to give a cell with an efficiency of up to 3.52 %. Importantly however, Nazeeruddin and co-workers have gone on to exploit the opportunity this opens up for panchromatic cosensitization. Combining TT1, having a peak absorption at 680 nm, with an organic dye (JK2; Figure 1) with a peak absorption at 452 nm gave an overall cell efficiency of 7.74 %, which is higher than either of the two dyes alone, and with the IPCE of about 75 % at wavelengths of up to 700 nm. This work has shown the possibilities opened up through development of novel long wavelength dyes capable of displaying good efficiencies.

Why did the approaches taken in reference [14] and earlier in reference [17] lead to enhanced efficiencies when previous cosensitization work had not? It is useful to consider another key aspect of the dye characteristics, the molar extinction coefficient. For solid-state and pseudo-solid-state cells, dyes with a high molar extinction coefficient have recently grown in importance, as they allow thinner devices to be made that minimize transport losses and also allow better pore filling of organic hole-transport materials.[11,19] Such dyes however may also provide the key to cosensitization. With higher-absorbing dyes, less of any one dye should be needed to achieve sufficient optical density with a given thickness of TiO_2 and may allow sufficient space on the TiO_2 surface to attach other dyes with a complementary absorption spectrum. It is notable that in both the work of Wang, Zhang, and co-workers[17] and in that of Nazeeruddin and co-workers,[14] where higher efficiencies have been obtained by cosensitization, organic or phthalocyanine dyes with high molar extinction coefficients were used. With the insight gained, this may yet be the strategy that takes efficiencies beyond the high of 10–11 %.

Note: Four *meso* nitrogen atoms added to TT1 in Figure 1 since publication in *Angewandte Chemie* Early View. The Editor.

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