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

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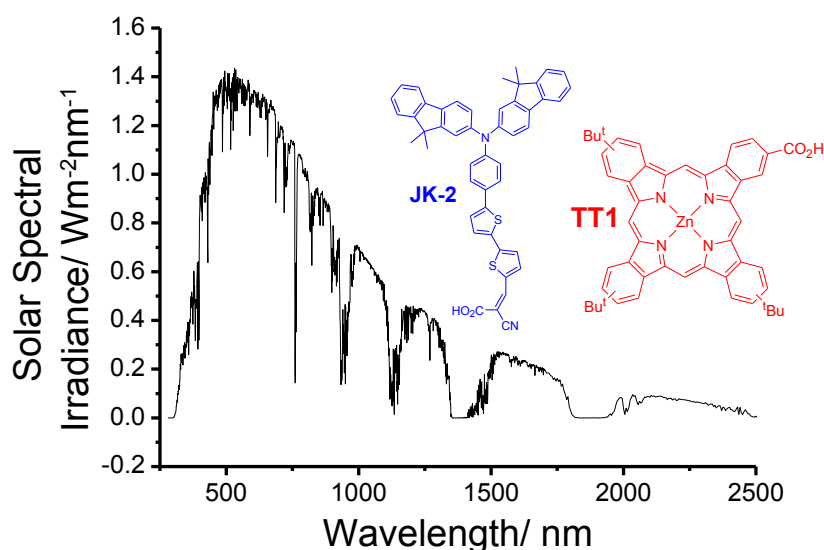
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Graphical abstract:



Synopsis:

Dye-sensitized solar cells have been established as a low-cost photovoltaic system, however development of dyes that harvest solar radiation over a broad spectral range has proven difficult. Co-sensitisation using more than one dye is now emerging as a successful concept to extend the spectral coverage and potentially lead to higher energy-conversion efficiencies.

Main text

Low-cost systems for the exploitation of renewable energy have never been more urgently required due to the growing consensus that burning fossil fuels is leading to dangerous accumulation of CO₂ in the atmosphere,^[1] as well as the inevitable eventual decline in fossil fuel resources. In particular, solar energy is the only source with the proven capacity to meet the increasing world energy needs^[2] and dye-sensitised solar cells have emerged as a low-cost alternative to established silicon solar cells.^[3] Photovoltaic systems based on the sensitisation of wide-bandgap metal oxides to visible light using attached dyes have been long studied, however the breakthrough work in 1991 by O'Regan and Grätzel^[4] showed that use of a nanocrystalline TiO₂ 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 optimising ruthenium-polypyridyl dyes, with the stereotypical example [Ru{4,4'-(CO₂H)-bipy}₂(NCS)₂](N3)^[5] (and the doubly-deprotonated analogue, N719). The excellent performance of N3 is demonstrated by the incident photon to current efficiency (IPCE) which is maintained around 70 – 80% between 400 and 600 nm.^[6] Taking into account losses due to 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 however, we may ask why the best efficiency remains well below the theoretical maximum (around 32% for a single-junction solar cell) and also why it has not significantly improved since 1993 despite extensive work in the development of new dyes. Indeed a superficial look at the field may give the impression that dye optimisation has not moved on, however this would be very misleading. Research has led for example to a greater understanding of the key dye characteristics such as charge-separation^[7] and to new efficient dye types that don't depend on Ru, 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 progress towards improvement of commercial systems whereby dyes with higher molar extinction coefficients allow thinner devices to be prepared. This minimises charge-recombination during transport to the electrode, enabling good efficiencies with non-volatile electrolyte systems essential for long-term stability. Also, in combination with this, appended alkyl chains have been used to give greater stability to heat and light soaking through protection of the dye against hydrolysis from the surface.^[9,11]

Notwithstanding these achievements, the ongoing limit to the record efficiency is still an important point to address and a key drawback of existing dyes is the limited light harvesting at long wavelength of the current best examples. The solar spectrum at the earth's surface (Fig. 1) extends into the near-IR and the best dyes such as N3 typically enable high-efficiency energy conversion only as far as around 600 nm. Panchromatic absorption with a single dye would require multiple absorption bands than span the solar spectrum. Attempts to extend the dye absorption demonstrate the difficulties of achieving this 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 Ru-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.

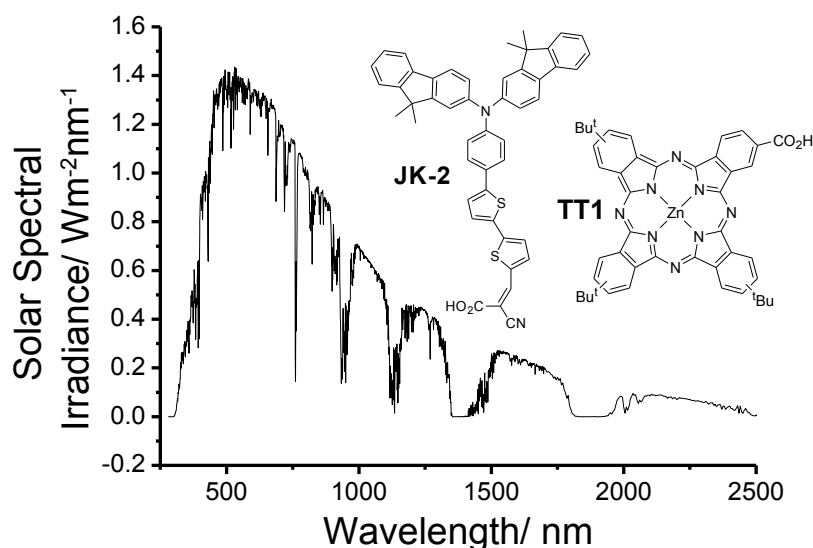


Figure 1. AM 1.5 direct normal solar spectrum^[13] showing molecular structures for JK-2 ($\lambda_{\text{max}} = 452$ nm) and TT1 ($\lambda_{\text{max}} = 680$ nm).

Since 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 co-sensitisation approach, i.e. 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 just an efficiency somewhere between that of the individual dyes and hence 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 co-sensitisation strategy to add a second dye to a TiO₂ layer already fully sensitised with one dye.^[16] This involved generation of a secondary Al₂O₃ layer onto TiO₂ already sensitised with one dye. A different dye with longer wavelength absorption was then subsequently bound to the Al₂O₃. It was shown that this led to a redox cascade that moved the oxidised centre from the first to the second dye, further from the TiO₂ and

extending the charge-separated lifetime. This 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 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 Ru complexes. Remarkably, an overall efficiency of 6.5 % was observed which was higher than that obtained for any of the three dyes alone. This was attributed to synergistic effects whereby dye aggregation, which can lead to reduced performance, was disfavoured. It was also suggested that the multiple dyes give a more compact coverage on the TiO₂ which may lessen charge-recombination losses between electrons in the TiO₂ and holes in the redox electrolyte. This study represented the first example where co-sensitisation led to improvement in properties and a high IPCE was maintained out to around 700 nm.

Further developments in co-sensitisation however are impeded by the lack of good candidate long-wavelength dyes able to contribute significantly to the efficiency. Phthalocyanines are obvious candidates for long-wavelength absorption through their intense Q band however their potential has until recently remained hard to capture. Building on recent results,^[18] Nazeeruddin and Tomas have now used a novel Zn-phthalocyanine (**TT1**) (Fig. 1) to avoid known drawbacks: bulky groups to prevent aggregation and the design of directionality into the charge-transfer which enables favourable charge-injection and recombination kinetics. This has provided^[14] the first phthalocyanine dye to yield a cell of efficiency as high as 3.52%. Importantly however, the authors have gone on to exploit the opportunity this opens up for panchromatic co-sensitisation. Combining **TT1** (peak absorption at 680 nm with an organic dye (**JK2**) (Fig. 1), with a peak absorption at 452 nm gave an overall cell efficiency of 7.74 %, higher than either of the two dyes alone and with the IPCE around 75% as far as 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 ref^[14] and earlier in ref^[17] lead to enhanced efficiencies when previous co-sensitisation work had not? It is useful to consider another key aspect of the dye characteristics, the molar extinction coefficient. High molar extinction coefficient dyes have grown in importance recently in the context of solid-state and pseudo-solid-state cells as they allow thinner devices that minimise transport losses and also allow better pore filling of organic hole-transport materials.^[11, 19] Such dyes however may also provide the key to co-sensitisation. With higher-absorbing dyes, less of any one dye should be needed to achieve sufficient optical density with a given thickness of TiO₂ and this may allow sufficient space on the TiO₂ surface to attach other dyes with a complementary absorption spectrum. It is very notable that the studies so far where higher efficiencies have been obtained by co-sensitisation both involve high molar extinction coefficient organic or phthalocyanine dyes. With the insight gained, this may yet be the strategy that takes efficiencies beyond the high of 10 – 11%.

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