

SOLAR CELLS

Later rather than sooner

Long-lasting charge separation is key to the performance of solar cells. A new design for larger conjugated dye-sensitizer molecules effectively retards the recombination of the charge-separated state and promises improved energy conversion efficiency.

JACQUES-E. MOSER

is at the Laboratory for Photonics and Interfaces, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland.

e-mail: je.moser@epfl.ch

Functional nanostructured and hybrid materials form an exciting new research field in modern materials science. These systems foretell alluring new applications for energy conversion, information storage and photo-electrochromic displays¹, as well as chemical and biological sensors². In particular, since the invention of dye-sensitized nanocrystalline solar cells, research activities on organic-inorganic photovoltaic devices (which transform light into electric current) have feverishly increased. Now Saif Haque *et al.*, writing in the international edition of *Angewandte Chemie*, report the spectacular performance of supramolecular systems that extend the lifetime of light-induced charge-separated states³. The new supersensitizer molecules attached to a semiconductor surface promise to improve the photovoltaic conversion efficiency and hence the practical viability of hybrid solar cells, photo-electrochromic devices and sensors for ever more demanding applications.

The basic design of the dye-sensitized solar cells comprises an electrode made of a molecular layer adsorbed onto a porous film of nanocrystalline semiconductor particles, typically TiO₂. The molecular layer contains a sensitizer dye, a molecule containing a chromophore that, on light irradiation, absorbs energy and enters a photo-excited state. From this state the chromophore readily injects an electron into the solid semiconductor. The semiconductor's conduction band constitutes a continuum of electron-accepting energy levels. Because the solid has ample space available, the injected electron quickly delocalizes in the semiconductor and forms a charge-separated state with the positive charge (hole) localized on the dye molecule. Long-lasting charge separation is key to all light-induced electron transfer and, in particular, photovoltaic processes. But all good things come to an end and the charge-separated state is no exception. Thermodynamics dictates that recombination of the electron and hole to return to the initial ground state should be the most favoured path. The kinetics of this

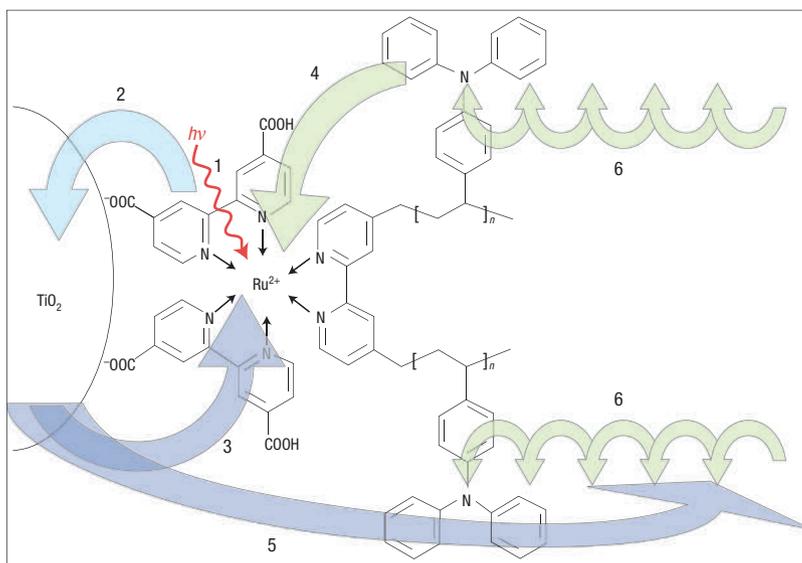


Figure 1 Hybrid supermolecule. This is the structure of the redox triad that gave the most efficient charge separation in the report by Haque and colleagues³. The triad is made of a ruthenium complex (the chromophore) anchored to nanocrystalline TiO₂ (the electron acceptor) and covalently linked to polymeric chains of triphenyl-amine groups (the electron donor). Arrows represent the direction of the electron transfer process. The first step of the electron transfer is the light-induced excitation of the chromophore (process 1). Following this an electron is readily injected from the chromophore excited state into the conduction band of the TiO₂ semiconductor (process 2). The direct recombination of primarily separated charges (process 3) would degrade the absorbed energy into heat. In this supermolecule this is avoided through the fast reduction of the ruthenium by the linked triphenyl-amine electron donor groups (process 4). The secondary recombination process (process 5) between the injected electron and the oxidized amine radical is made increasingly slow because the positive charge can hop from one triphenylamine function to the adjacent one along the chain (process 6) and the hole moves away from the TiO₂ surface. The overall photo-initiated process thus results in unidirectional electron flow from the end of the polymeric chains to the oxide (from right to left) and a very long-lived charge-separated state.

path largely control the external quantum efficiency of the photovoltaic conversion.

The strategy used by Haque and colleagues was to endow the sensitizer dye adsorbed on the surface of TiO₂ particles with multifunctional redox properties so as to realize a multistep charge-transfer cascade. The idea is to attach to the sensitizer molecule a tail that draws the positive charge. Thus the charge

recombination process is retarded by the larger distance between the TiO₂ surface and the positively charged moiety and it is indeed possible to achieve unidirectional electron transfer towards the TiO₂ surface. This molecular design paid off, as it extended the lifetime of the charge-separated state by several orders of magnitude — from microseconds or milliseconds to seconds.

In practice, what Haque and colleagues needed was a third redox participant, an electron donor judiciously placed as far as possible from the electron-accepting TiO₂ surface. So they built sensitizer dye molecules made of two main components: a ruthenium complex acting as the chromophore and a triphenyl-amine acting as the donor group (Fig. 1). The ruthenium complex had carboxylic groups on its sides that anchored it to the TiO₂ surface. The triphenyl-amine groups were covalently attached to the chromophore moiety in three different modes: as monomeric groups (TPA), as conjugated dimeric triphenyl-amine groups (TPD), or as poly(vinyl triphenylamine) chains (poly-TPA), a supermolecule with around 100 repeat units.

Supramolecular systems such as these, containing a chromophore between an acceptor and a donor are called triads. In this specific case they are called heterotriads because the acceptor is a semiconducting inorganic surface. Redox heterotriads on TiO₂ films were first applied by Meyer, Bignozzi and co-workers⁴. Later Bonhôte and colleagues showed that ruthenium complex dyes linked to a triphenyl-amine donor moiety and anchored to the surface through a phosphonate group were suitable for achieving efficient light-induced charge separation⁵. The TPA-functionalized ruthenium complex of Haque *et al.* is derivative of these earlier reports⁶. But the multistep charge-transfer cascade that takes place with TPD and poly-TPA departs from those previous examples, as it is much better at delocalizing the positive charge away from the surface.

Haque and colleagues observed that electron transfer from the donor groups to the ruthenium centre is fast (less than a few nanoseconds) in all three dyes (process 2 in Fig. 1). But the recombination dynamics differ significantly for the three dyes (process 5 in Fig. 1): TPA, TPD and

poly-TPA-based supermolecules showed decay half-times of 350 μ s, 5 ms and 4 s, respectively. The retardation of the charge recombination is clearly correlated with the dimensions of the molecules and the physical separation of dye cation from the TiO₂ surface (TPA being the smallest and poly-TPA being the largest). In TPD and poly-TPA-based molecules, positive charges can apparently hop from one TPA group to the adjacent one and allow for multistep transfer of the oxidized moiety away from the semiconductor surface (process 6 in Fig. 1). Lateral electron transfer (hopping of holes between co-adsorbed molecules) is not considered by the authors. This additional degree of freedom for the delocalization of positive charges might, however, play an important role in preventing adverse effects of back-folding of the supramolecular edifice.

Hopping of positive charges (holes) from a conjugated aromatic amine group to an adjacent one is at the basis of the functioning of a class of organic hole-conducting materials used in particular in organic light-emitting diodes. In this context, dye-sensitized heterojunctions of mesoporous TiO₂ with the amorphous organic hole-transport material *spiro*-OMeTAD seem promising⁷. But in practice this system is marred by poor contact between the dye adsorbed on the inorganic semiconductor and the hole-transport material that has to penetrate the porous TiO₂ nanostructure. The polymeric supermolecular sensitizer proposed by Haque and colleagues looks like an ideal transition between a simple ruthenium complex and the hole-conducting TAD medium. It is hoped that it will be effective at electrically interfacing the chromophore with the organic material and will allow the development of solid-state dye-sensitized solar cells with improved efficiency.

REFERENCES

1. Grätzel, M. & Moser, J.-E. in *Electron Transfer in Chemistry* Vol. 5 (eds Balzani, V. & Gould, I. R.) 589–644 (Wiley-VCH, New York, 2001).
2. Beer, P. D., Gale, P. A. & Chen, G. Z. *Coord. Chem. Rev.* **3**, 185–186 (1999).
3. Haque, S. A. *et al. Angew. Chem. Int. Edn Engl.* **44**, 5740–5744 (2005).
4. Argazzi, R., Bignozzi, C. A., Heimer, T. A., Castellano, F. N. & Meyer, G. J. *J. Am. Chem. Soc.* **117**, 11815–11816 (1995).
5. Bonhôte, P. *et al. J. Am. Chem. Soc.* **121**, 1324–1336 (1999).
6. Hirata, N. *et al. Chem. Eur. J.* **10**, 595–602 (2004).
7. Bach, U. *et al. Nature* **395**, 583–585 (1998).