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Dye-Sensitized Solar Cells

Using Orbital Symmetry to Minimize Charge Recombination in Dye-Sensitized Solar Cells**

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An ideal dye for dye-sensitized solar cells (DSSC) should inject an electron as fast as possible into the semiconductor nanoparticle it is connected to, and in its oxidized form it should be neutralized as slowly as possible by the electrons in the conduction band of the semiconductor.[1] This latter charge-recombination process is always very strongly favored thermodynamically and the only way to limit the charge recombination is to hamper its kinetics. A number of research groups are designing and preparing dyes that, when oxidized, should recombine as slowly as possible with the electrons in the semiconductor, while maintaining a good charge-injection efficiency.[2] The strategy commonly used is to prepare molecules that, when adsorbed on the semiconductor, have their HOMO density localized as far as possible from the semiconductor and the LUMO density localized as close as possible to it. The resulting dyes have a clear donor–acceptor structure so that, in their excited state, there is a partial charge-transfer character with negative charge closer to the semiconductor and, in the oxidized state, the HOMO (positive charge) is spatially separated from the semiconductor. The poor overlap between the HOMO of the dye and the conduction band orbitals of the semiconductors should slow down the recombination, which depends, among other things, on the square of the electronic coupling between the HOMO of the dye and orbitals of the semiconductor. This strategy led to the realization of DSSC with up to 10% efficiency.[3] Herein we show that there is an alternative way of designing organic dyes that have strong coupling with the electrode when they are excited and very weak coupling when they are oxidized, and this is based on few elementary ideas from orbital symmetry and through bond electron tunneling in donor–bridge–acceptor (D-B-A) systems.

In the traditional D-B-A systems studied since the late 1970s, a donor fragment is chemically connected to an acceptor fragment through a chemical bridge. The donor fragment can be excited by radiation and, in its excited state, it can donate an electron to the acceptor.[4] It was realized long ago that a suitable design of the D-B-A system may make the charge separation reaction ($D^{*}\text{-B-A}\rightarrow D^{+}\text{-B-A}^{-}$) symmetry allowed while the charge recombination reaction ($D^{+}\text{-B-A}^{-}\rightarrow \text{D-B-A}$) can be symmetry-forbidden. Such a design, which has been extensively investigated,[5] promotes long-lived charge-separation states and relies on initial and final states of different symmetry (that is, transforming according to different representations, in the language of group theory). Using an orbital picture, if the charge recombination can be seen as a transfer from the LUMO of A to the HOMO of D, these two orbitals must have different symmetry to make the transition symmetry-forbidden and therefore very slow. We can naively try to extend the same idea to the field of DSSC assuming that the role played by the acceptor fragment in isolated molecules is played by the semiconductor in DSSC. This is not an accurate analogy as the acceptor states in DSSC are a continuum of semiconductor states, a fraction of which will always have the right symmetry to be coupled with the HOMO of the donor (that is, the dye in this case). However, if a bridge moiety (the anchoring group or anchor plus linker group) connects the dye and the semiconductor, the dye-semiconductor coupling is mediated by the bridge, that is, it is proportional to the product of the coupling between dye and bridge and between bridge and semiconductor. As we have seen, there is no symmetry rule for the latter, but we can hope to design a bridge that, for symmetry reasons, is not coupled to the HOMO of the dye. We plan, in other words, to design a donor–bridge–semiconductor system that isolates the HOMO of the dye from the semiconducting states and we will use orbital symmetry to do so.

To exemplify our reasoning (a more formal analysis is given in the Supporting Information), Figure 1 shows three simple aromatic molecules that have been modified to generate efficient dyes for DSSC (pyrene,[6] azulene,[7] and fluorene[8]), which are chosen because they have a symmetry plane (illustrated) perpendicular to the conjugation plane and crossing at least one carbon atom of the backbone that can be connected to a bridge (this carbon atom is also indicated). As the molecular orbitals (MOs) of this molecule are either symmetric or antisymmetric with respect to this plane, some of the MOs (the antisymmetric MOs) will have a nodal plane in correspondence with these carbon atoms. The HOMO of pyrene, azulene, and fluorene happens to be antisymetric with respect to the indicated symmetry plane; that is, the orbital density on the carbon atom crossed by the symmetry plane is zero. A bridge that connects the dye with the semiconductor via that carbon atom has the minimum possible coupling with the HOMO of the molecule. The same three dyes have a symmetric LUMO with respect to the same plane;[9] that is, a bridge between them and the semiconductor connected to the same carbon will couple strongly to the LUMO and very weakly to the HOMO. Before quantifying this effect it should be noted that the selected dyes are chosen for their simplicity and not their efficiency as dyes (they adsorb light at too-high

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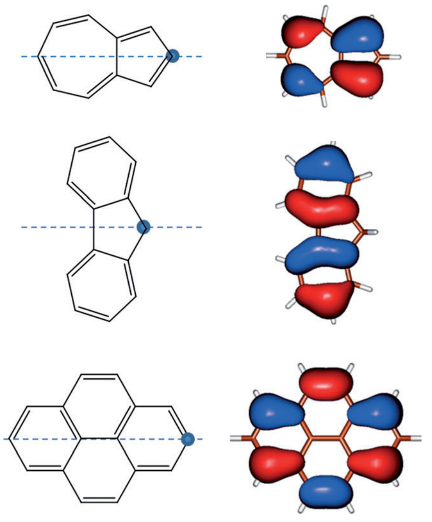

Figure 1. The azulene, fluorene, and pyrene molecules with an illustration of their symmetry plane, which crosses a carbon atom that can be connected to a bridge. The HOMO of these molecules is antisymmetric with respect to this plane.

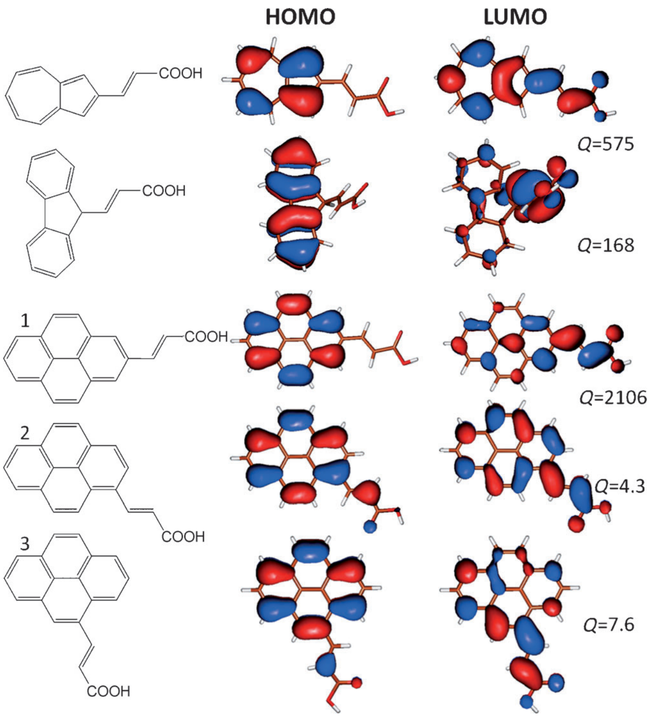

Figure 2. Chemical diagrams and HOMO and LUMO plots of three molecules substituted with a bridge in the symmetry position that isolates the HOMO from the bridge (top three rows). Lower two structures: Alternative, non-symmetric substitutions of pyrene that do not isolate the HOMO from the bridge. The parameter Q is discussed in the text.

energy). The rest of the discussion relies on the assumption that these dyes can be chemically modified to improve their light absorption while retaining the same orbital symmetry characteristics (the likelihood of this is discussed below).

It is not possible to completely prevent the coupling between the bridge and some orbital of the dye because of through-space coupling. To minimize this coupling we therefore consider a thin bridge with chemical structure $-CH{=}CH{-}COOH$, which is very common in DSSCs[10] (the carboxylic acid is the most common anchoring group used in DSSCs; in the Supporting Information, reasons why the saturated bridge may be unsuitable are discussed). It was repeatedly shown that a good coupling between the dye and the semiconductor is determined by the orbital weight of the dye on the atoms of the carboxylic group.[11] Connecting this bridge to the dye through the special symmetry point identified above should: 1) mix the original LUMO density with the bridge orbital and generate good orbital density on the carboxylic group; and 2) leave the HOMO almost unchanged with negligible orbital density on the carboxylic group. Figure 2 shows that this is exactly what happens. The orbital symmetry of the aromatic part of the molecules remains the same as in the unsubstituted molecules,[9] therefore creating a large LUMO weight and a negligible HOMO weight on the carboxylic bridge. To be more quantitative, we can define a quality factor Q as the ratio between the orbital density of the LUMO on the carboxylic acid divided by the same quantity computed for the HOMO (the latter orbital density is the quantity that determines the recombination rate).[12] When Q is close to 1, HOMO and LUMO are equally coupled to the electrodes, while with $Q \gg 1$ the LUMO has a much stronger coupling with the electrode than the HOMO. Q represents the propensity of insulating the HOMO from the semiconductor (compared to insulation/coupling of the LUMO), which is intrinsic in a dye. This quantity is 575, 168, and 2106 for azulene, fluorene, and pyrene, respectively, indicating a very strong localization of the LUMO on the carboxylic bridge group in comparison with the HOMO.

To further illustrate the point we repeated the calculation for pyrene with the same bridge substituted in the two asymmetric positions (**2** and **3** in Figure 2). The effect of HOMO isolation completely disappears and the quantity Q drops to 4 and 8 when the asymmetric substitution is considered. In the Supporting Information, we discuss a similar effect observed in the presence of heteroatoms.

We consider the case of pyrene to provide an even more quantitative analysis. By using a recently proposed computational method[11b] to estimate the charge recombination rate in DSSCs, we can compare the charge recombination rate of pyrene substituted in positions **1**, **2**, and **3**. This calculation relies on the explicit calculation of the coupling between the dye and the semiconductor (TiO_2) and goes well beyond the simple analysis presented so far. As we have discussed previously,[11b] the actual estimate of the rate is affected by a number of assumptions but the relative recombination rate is rather robust for rigid molecules with sp^2 bridges. Using the parameters given in the method section (see also the Supporting Information), we find that the recombination rate for the asymmetric ("wrong") substitution is about 1400 and about 360 times faster than the rate computed when the best symmetric position of the bridge is used (Figure 3). Thus, by using symmetry, the charge recombination rate can be reduced by 2 to 3 orders of magnitude. It is essential for the validity of this analysis that the dye should stand perpendic-

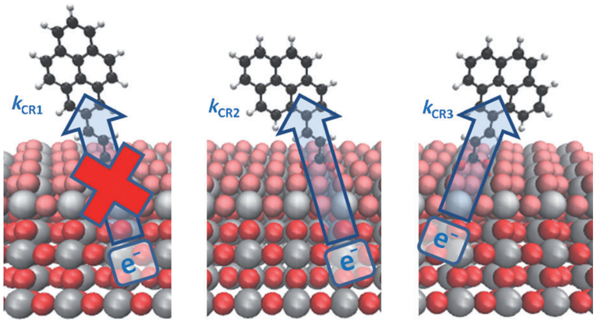

Figure 3. Representation of the adsorption of three substituted pyrenes on anatase(101). The computed charge recombination rate is more than two orders of magnitude lower for the symmetric pyrene **1**, for which the charge recombination is virtually forbidden ($k_{CR1} = 0.43\ s^{-1}$, $k_{CR2} = 625\ s^{-1}$, $k_{CR3} = 156\ s^{-1}$).

ularly to the surface so that through-bond tunneling is much more probable than through space tunneling (more flexible saturated bridges do not allow this type of conformation control).

Symmetry considerations are generally very robust[13] and the concept proposed here is worth considering for the actual design of new dyes. Once the symmetry considerations are satisfied, that is, there is an atom of the dye that can be connected to the bridge and lies on a symmetry plane perpendicular to the plane of the molecule, the likelihood that the relevant orbitals have the right symmetry is very high. Very roughly, we could think that the HOMO and LUMO of these molecules would be antisymmetric and symmetric, respectively, with respect to this plane about one fourth of the time but, as the symmetry of these two orbitals is often different from each other (that is, one symmetric and the other antisymmetric), the actual probability is closer to one half. For this reason it is not essential for the proposed model that the molecules provided in this work are not the ideal dyes because in all three cases they can be substituted symmetrically to modify the energetics of the HOMO and LUMO, and it is extremely likely that some (if not all) of them will retain the desirable MO symmetry. Another advantage of this strategy is that it does not require complicated theory to support the design of new dyes, and additional refinement of the electronic structure models (for example, dispersion or image charge interaction) are not expected to alter the relative advantage of using these symmetrically substituted dyes. The only crucial assumption is that the dye stands perpendicularly to the surface so that through bond tunneling is much more probable than through space tunneling.

In conclusion, we propose that suitably designed symmetric dyes can be used in dye-sensitized solar cells to reduce the charge recombination rate by two to three orders of magnitude.

Computational Methods

The details for the computation of the charge recombination rate are identical to those presented in Ref. [11b], where the methodology has been validated against a number of dyes for which the experimental charge recombination rate is known. Additional data are presented in the Supporting Information. The non-adiabatic rate for charge recombination is expressed in terms of the electronic coupling between the dye and semiconductor orbitals, the local density of states on the semiconductor, the quasi Fermi level in the semiconductor (TiO_2) under illumination, and the reorganization energy of the dye (in acetonitrile). These quantities, computable from standard quantum chemical methods, are complemented by the experimental value of the conduction band edge energy of the semiconductor to yield the absolute charge recombination rate. The calculation involving the TiO_2 surface and its coupling with the dye were performed with the DFT code with localized basis set SIESTA[14] (PBE functional and DZP basis set). Calculations of the dye in solution and isolated (for the MO plots in Figure 1 and Figure 2) are performed at the B3LYP/6-31G* level with the Gaussian 03 code.[15]

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