

# A two-dimensional model for molecular based thin-film photovoltaic devices

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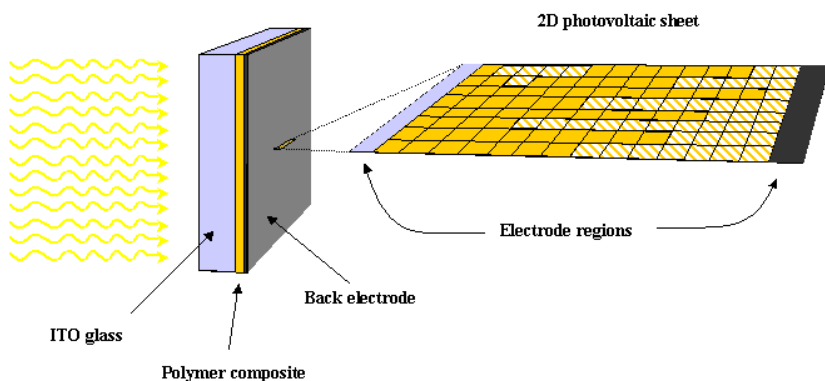
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A theoretical model for molecular based thin-film photovoltaic devices has been formulated in order to rationalize the photovoltaic effect in the context of recent composite polymer based devices. For such disordered systems the notions of band theory are not applicable and thus we sought a model based entirely on hopping mediated charge transport (CT) treated within a *simple* kinetic scheme.

The physical device is approximated as a multitude of non-interacting two-dimensional (2D) photovoltaic sheets, one of which is displayed in Figure 1. Each such sheet maps the discretized 2D representation of the bulk morphology at the intersecting plane of the particular sheet. The individual squares on the grid of the photovoltaic sheet account for regions of either p- (filled squares) or n-type (hatched squares) character. All sheets are interfaced at the first and last row with the boundaries of the electrodes.



**Figure 1: Schematic illustration of a 2D photovoltaic sheet with the discretized representation of the bulk morphology at intersecting plane of the sheet. Filled squares represent donor sites and hatched acceptor sites. The incident radiation is assumed constant as it travels from left to right within the plane of the sheet.**

A priori, no assumption in terms of the resolution of the grid in Figure 1 is made. Therefore, a square in Figure 1 may equally well refer to a part of domain with either p- or n-type characteristics or an individual molecule with either donor (D) or acceptor (A) type properties.

In the present implementation, however, we adopt a resolution of the grid such that each square –

referred to as a site – contains either a donor or an acceptor molecule. Consequently, rates for CT between sites correspond to average molecular CT rates.

Working with molecular resolution allows for inquiring on how super-molecular topological effects influence the photovoltaic current. In particular, one may address questions as to what type molecular arrangements will minimize electron-hole recombination and maximize charge separation and charge migration into the electrode regions.

To provide an illustration of the electron dynamics of the model we refer to Figure 2 which shows a simple photovoltaic 'sheet' consisting of a D-D-A-A chain interfaced with electrodes. Each site is described in terms of a two-level representation with energy levels corresponding to HOMO and LUMO energies of the molecule residing at the particular site. One electron per site is free to move about in the sample provided that sites are always in either of the following states;  $X$ ,  $X^*$ ,  $X^-$  or  $X^+$  with  $X=(D,A)$ . The CT occurs via various nearest-neighbor hopping processes as indicated by solid arrows in Figure 2. Describing CT by hopping (thermal equilibration of the electron at each site between hopping events) is indeed appropriate for composite polymer devices where

the degree of molecular ordering is low and operational temperatures ambient or higher. Being in the hopping regime implies that forward and backwards rates may be Boltzmann related, by which the sample temperature ( $T$ ) is introduced into the model. The increase of free energy of the electrons comes about by the vertical photoinduced transitions (dashed arrows) between HOMO and LUMO levels within a site. The rates for these transitions (stimulated emission/absorption and spontaneous emission) are derived from the Einstein coefficients for a two-level system in equilibrium with radiation from a black body at temperature  $T_{\text{sol}}$ . Although very approximate,  $T_{\text{sol}}$  is then a convenient means of describing the intensity of the radiation impinging on the photovoltaic device, avoiding any explicit reference to the terrestrial intensity profile of the sun. Further, for the intensity we assume no attenuation as the light travels through the polymer region.

To summarize, the model is defined in terms of two types of parameters. The *microscopic* parameters are HOMO and LUMO energies, molecular electron transfer rates and oscillator strengths, all quantities that should either be extracted from experimental data or computed quantum chemically. The *macroscopic* parameters refer to the temperature  $T$  of the device, the radiation intensity as described by  $T_{\text{sol}}$ , the voltage across the cell.

We acknowledge that the model in many aspects is far too simple. In particular the assumption of no interaction between adjacent sheets indeed is a gross approximation.

However, reducing the treatment from three to two dimensions simplifies the analysis tremendously without it loosing the important topological characteristics that - on the other hand - are beyond any one-dimensional model. Also, since we adopt a molecular resolution of

the grid, currently the size of the 2D photovoltaic sheets is not representative of real sized photovoltaic cells.

Hence, the model in its current implementation can be used to analyze effects pertaining to the topology of the D-A network and intermolecular CT rates, but only for a smaller patch representative of the entire 2D sheet. The photovoltaic yield for different types of molecular networks of such patches will be presented and discussed.

Further, by analyzing patches with similar topology but different sizes, the scaling properties of a given D-A network can be estimated. Using such scaling properties we will attempt to estimate the photovoltaic current of real sized devices.

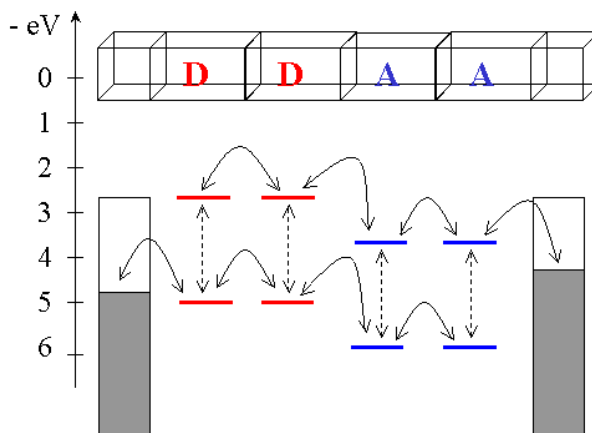


Figure 2: Schematic representation of a very simple one-dimensional M[D-D-A-A]M photovoltaic patch in which all possible CT processes of the current model are shown by arrows. Filled arrows signify hopping processes where forward and backward rates are Boltzmann related and the dashed (vertical) arrows indicate optical transitions. Each site is represented in terms of a two-level model using the HOMO and LUMO energies of the molecules at the particular site.