

PHOTOVOLTAIC EFFECT IN ASYMMETRICAL
DONOR-ACCEPTOR ORGANIC SUPERLATTICES

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We predict a novel photovoltaic mechanism in donor-acceptor superlattices. We consider an asymmetrical organic superlattice such as...*D-A-N-D-A-N-D-A-N*..., where *D*, *A* and *N* indicate layers of materials which are, respectively, donor, acceptor and neither donor nor acceptor, all neutral in the ground state. In such a structure, the lowest lying electronic excitations are charge-transfer excitons (CTEs) at the *D-A* interfaces with electrons displaced from the donor to the acceptor side. We show that the excitation of CTEs under illumination is accompanied by the appearance of a macroscopic voltage drop along the growth direction. The resulting average electric field can separate and drive the photogenerated free carriers (partly coming from the ionization of the CTEs themselves) producing a photovoltaic current.

A large effort has recently been devoted to the experimental study of organic crystalline layered structures [1]. The possibility of growing organic multilayers analogous to the inorganic quantum wells and superlattices opens up a new field of research, very promising from the technological as well as the scientific viewpoint. Aspects of the optical properties of such systems have been theoretically discussed; for example, in coupled organic-inorganic quantum wells, a novel type of electronic excitations, which are due to the hybridization of Frenkel and Wannier exciton states and give rise to enhanced optical nonlinearities, have been predicted [2]. Other structures in which new and unusual properties are expected are donor-acceptor (*D-A*) interfaces and superlattices. The charge-transfer excitons (CTEs) at a *D-A* interface are accompanied by large static electric dipole moments (all oriented in the same direction, i.e., perpendicular to the interface). As a consequence, they experience a strong dipole-dipole repulsion which can lead to an insulator to metal transition [3] and to striking optical nonlinearities [4]. It is the purpose of this paper to discuss the peculiar electro-optical properties of donor-acceptor (*D-A*) interfaces and to point out the possibility of a novel photovoltaic effect in asymmetrical *D-A* superlattices.

Earlier, single *D-A* interfaces were prepared in Langmuir-Blodgett films [5], but the new organic superlattices [6] have a periodic stack of *D-A* interfaces: using the molecule C_{60} as acceptor (*A*) and molecules perylene, coronene and others which are good donor of electrons (*D*), a structure of the type ...*AAA|DDD|AAA|DDD*... has been grown, where the vertical dashes indicate the donor-acceptor interfaces. The technological progress in molecular organic beam deposition is very fast and there is little doubt that many more systems will be synthesized in the near future. With this in mind, we have devised an asymmetrical structure in which the CTEs at the *D-A* interfaces not only act as an efficient source of photogenerated free carriers [7], but also provide a macroscopic potential drop

that can drive a photovoltaic current. We consider a superlattice of the type ...DDD|AAA|NNN|DDD|AAA|NNN..., where N stands for a material which is neither a good donor nor a good acceptor, and all molecules in the ground state are neutral. In such a noncentrosymmetrical structure, when CTEs are generated by the pumping light, all the interface CTE dipoles point in the same direction and the potential differences due to the dipole layers at each $D-A$ interface add up to a macroscopic voltage across the superlattice. The corresponding electric field will drive the free electrons and holes produced by the absorption of light providing a photovoltaic current.

To estimate the potential profile determined by the interface CTEs, we consider first a single $D-A$ interface with a two-dimensional (2D) density of CTEs n of order 10^{12} cm^{-2} , each one having an electric dipole moment μ of about 20 Debye. Such large dipole moments are not unusual for CTEs and the 2D density above, taking a superlattice period of a few tens of monolayers, would correspond to a bulk concentration of excited molecules of order 10^{-4} , which is not problematic in relation to the photochemical stability of the organic materials. In a first approximation, this CTE configuration corresponds to a uniform static dipole moment per unit area μn perpendicular to the $D-A$ interface. As the CTEs repel each other [3, 4] through the dipole-dipole interaction $\Delta H = \mu^2/\rho^3$ (ρ being the exciton-exciton distance) and as their mobility is not negligible, they tend indeed to be uniformly spaced along the interface; for instance, a similar system of dipoles moving classically along a plane and oriented perpendicular to it have been shown [8] to order in a 2D-lattice at low temperatures and to form a homogeneous liquid at high temperatures. In this approximation of a uniform dipole layer, the resulting electrostatic potential [9,10] has the form of a sharp step of height $\Delta V = 4\pi \mu n \simeq 0.1 \text{ V}$ at the interface; probably, it is impossible to create a density of CTEs much larger than that considered above because the insulator to metal transition [3] leading to the ionization of the CTEs sets a limit on n .

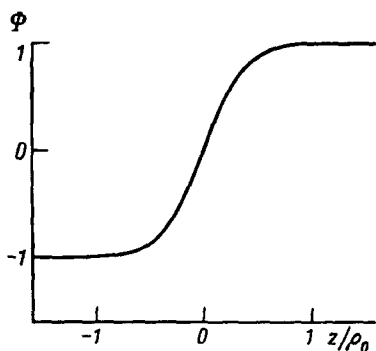


Fig.1. Potential profile across a $D-A$ interface in the presence of a CTE density $n \simeq 1/\rho_0^2$

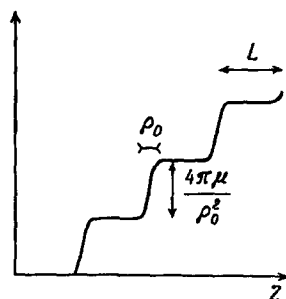


Fig.2. Electrostatic potential along a $D-A-N$ superlattice in the presence of 2D CTEs at the $D-A$ interfaces (see text for details)

However, for a typical intermolecular spacing a of about 5 \AA and the exciton densities considered here, the average distance ρ_0 between two excitons along

the interface plane ($n \simeq 1/\rho_0^2$) is much larger than the interface thickness; as a consequence, the potential does not exhibit an abrupt jump and the electric field corresponding to ΔV is not restricted to the interface, but extends on either side over a layer of width comparable to ρ_0 , as shown in Fig.1. Taking for the sake of simplicity the CTEs located at the sites of a square lattice, this figure shows $\phi(z) = V(z)/(2\pi\mu n)$ where $V(z)$ is the electrostatic potential along a direction perpendicular to the D - A interface and passing through the center of a square unit cell. Even in the case of a homogeneous disordered 2D-distribution of CTEs, the average electric field profile is not expected to be much different than for a 2D-square lattice of equal density. When considering an asymmetrical superlattice in which all the interface voltage drops add up, the qualitative shape of the total electrostatic potential profile will be determined by the ratio between the distance between successive D - A interfaces, i.e., the superlattice period L and ρ_0 : if L is larger than ρ_0 (i.e., at a high density n) the potential will resemble a staircase as shown in Fig.2, otherwise (i.e., at a low density n) it will have a rather uniform slope. In either case, the average electric field in the direction of growth will be given by $E_o = \Delta V/L$ and can be comparable to the electric field in the depletion layer of a typical semiconductor p - n junction (for the values of μ and n estimated above and $L \simeq 300 \text{ \AA}$, for instance, E_o is about $3 \cdot 10^4 \text{ V/cm}$). Of course, the uniformity along the superlattice planes will never be perfect in a real structure and, in general, a rather complicated spatial pattern of electric field force lines (and therefore current filaments) can be expected.

Under steady illumination, a condition of dynamical equilibrium will be reached with a constant 2D-density of interface CTEs. Free carriers will also be present, either photogenerated directly or, for instance, as a result of the thermal ionization of the CTEs [7] at room temperature. The electric field above will effectively separate the electrons and holes and drive a current along the superlattice crossing the D - A interfaces from the donor to the acceptor side. We are neglecting the effects of the periodic changes of the band edges due to the superlattice compositional changes (such discontinuities could be minimized by a proper choice of materials) with respect to the additive effect of the potential variations at the D - A interfaces. Of course, these effects would be important to estimate the electron and hole mobilities along the growth axis. In the structures here considered, electrons could be effectively injected into the valence band on the acceptor side through a contact with a large work function metal and extracted from the conduction band on the donor side through a contact with a small work function metal (as done in the reverse direction in LED devices); such a current would deliver power to the external circuit load at the expense of the light absorbed. In the absence of sufficient experimental information on structures of the kind we propose, we are unable to comment on the expected efficiency of photovoltaic conversion; we have only pointed out an interesting new physical mechanism to provide the internal electric field necessary to separate and drive the photogenerated carriers.

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