

Doping Molecular Semiconductors: n-Type Doping of a Liquid Crystal Perylene Diimide

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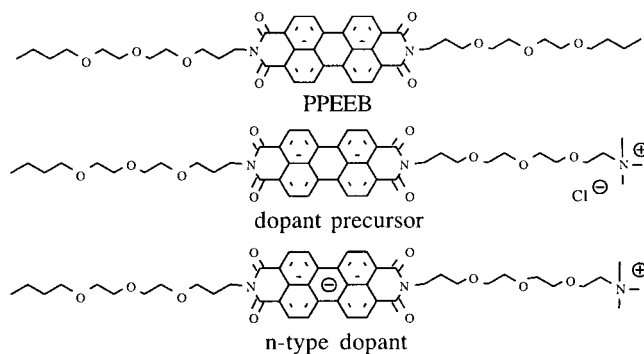
Received June 13, 2001

Revised Manuscript Received July 12, 2001

We describe here a method for doping molecular semiconductors in which the dopant forms an integral part of the semiconductor lattice and does not contain any mobile ionic species. Molecular semiconductors (MSCs) are finding increasing interest, partly because of their recent use in light-emitting diodes, electronic circuit elements, and solar cells.^{1–3} A few MSCs, such as naphthalene diimides⁴ and phthalocyanines,⁵ have been doped to metallic levels, while most are studied without any intentionally added dopants.^{1,2,6,7} But the vast and potentially useful semiconducting range, between the intrinsic material and the molecular metal, remains virtually unexplored. Although doping is infeasible in molecular electronic devices⁸ and undesirable in field effect transistors,^{2,9} it can be vitally important to other applications such as organic solar cells.¹⁰

Individual MSCs are often described as being either p-type or n-type, but this description is more ambiguous than when applied to inorganic semiconductors. For example, dopants in MSCs are generally adventitious and unidentified, their type and concentration being inferred from electrical measurements.^{1,6,11} There are relatively few examples where an MSC containing a known concentration of a known dopant has been prepared and studied, although there are some examples of surface-doping by exposing the film to an oxidant.^{12,13} In most cases where the dopant was known, for example oxygen in phthalocyanines^{1,6–8} or bromine in pentacene,¹⁰ the dopants were volatile and mobile species that were not bound to the semiconductor lattice. Therefore, the equilibrium concentration of dopants in these MSCs depends on the concentration of doping species in the ambient, and the ability of dopants to move through the film results in spatially and temporally unstable electrical junctions. Both fundamental studies and the long-term stability of devices are limited by this approach. As is generally the case with inorganic semiconductors,¹⁴ the stability of an organic p–n junction depends on the *immobility* of the dopant ions (and, in general, on the absence of any mobile ions), a condition that has only rarely,¹⁵ if ever, been met in doped MSCs. We report here the first example of a dopant designed to

Scheme 1



fit in the MSC lattice as well as one whose counterion is covalently bound. This is a necessary first step toward making a true molecular p–n junction. Using this compound, liquid crystal perylene diimide films have been controllably doped n-type over a wide concentration range. The preparation of the dopant and preliminary studies of the conductivity of doped films are described.

To dope organic semiconductors in a manner analogous to the doping of inorganic semiconductors, the following four conditions should be satisfied: (1) the dopant is fixed in the semiconductor lattice, (2) there are no mobile ions in the film, (3) the dopant is not chemically so distinct from the host that it will tend to phase separate from it, and (4) the dopant does not form a deep electrical trap, that is its oxidation and reduction potentials must be similar to those of the host. Our approach to realizing these four conditions is to synthesize a zwitterionic dopant that is a reduced (for n-type) or oxidized (for p-type) derivative of the host molecule. The dopant has a covalently bound counter charge attached to the periphery of the molecule, not in conjugation with the chromophore where it would alter the electronic structure and disturb the crystal packing. As a first example, we have synthesized the n-type dopant shown in Scheme 1 to dope the liquid crystal perylene diimide, PPEEB.^{16,17}

The synthesis of PPEEB was reported previously.¹⁸ The synthesis of the dopant precursor (Scheme 1) is described in the Supporting Information. To produce the zwitterionic, mobile-ion-free dopant, the dopant precursor was dispersed as a powder in dry tetrahydrofuran (THF) at room temperature in an inert atmosphere glovebox. Sodium was added to reduce the perylene diimide, and the suspension was stirred for several hours. The progress of the reaction was monitored by the color of the solution/suspension: the precursor is reddish brown, the desired monoanion of the perylene diimide (the dopant) is blue, and the dianion is purple. Both the dopant precursor and the dianion are practically insoluble in THF (solubility < 0.2 μM); thus these species, as well as the NaCl generated during the reduction and any unreacted sodium, are removed by filtration through a 0.2 μm filter. The zwitterionic dopant is soluble in THF up to about 230 μM ($\epsilon = 36\,000\text{ M}^{-1}\text{ cm}^{-1}$ at 956 nm) and is air-sensitive in solution (but not as a pure, solid film).

A series of n-doped PPEEB films was prepared by adding aliquots of dopant solution to solutions of PPEEB in THF and then spin-coating films onto platinum interdigitated electrodes. Current–voltage, J – V , curves were measured from 0 to $\pm 10^4$ V/cm in the glovebox at room temperature (PPEEB is in the crystalline solid phase below 66 °C). The J – V curves had a slight inverse S-shape, being flatter around 0 V with a somewhat steeper

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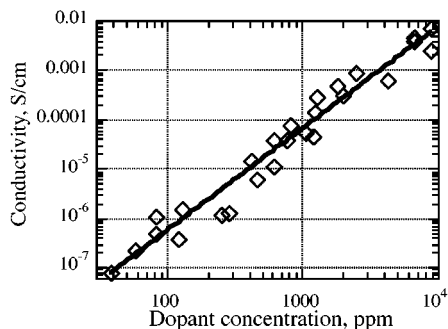


Figure 1. Conductivity, σ , of PPEEB films as a function of dopant concentration. The equation for the best-fit power law curve through the data is $\sigma = 4.1 \times 10^{-11} \times [\text{dopant concentration}]^{2.1}$. 1 ppm = $9.6 \times 10^{14} \text{ cm}^{-3}$.

slope at higher potential. This is characteristic of a material where electron transport is limited by thermal emission over energy barriers, either at each crystal lattice site (hopping conductivity) or at crystal defects or grain boundaries.¹ The shape of the J - V curves, and their consistency over the whole range of dopant concentration, showed that there was no significant electrical junction formed at the PPEEB/electrode interface. Thus, the measured conductivity is controlled by electron transport through the bulk perylene diimide film, not by the contacts. The conductivity was measured from the slope of the J - V curve at $\pm 10^4$ V/cm. As spin-coated the films are in a quasi-amorphous red phase; after several hours they spontaneously transform into a more highly crystalline black phase.^{15,17} This transformation is unaffected by addition of the dopant. The conductivity increases by a factor of 3–10 during this red-to-black phase transition. The conductivities reported here were measured in the black phase. Up to the highest doping densities yet attempted, ~ 1 mol %, we observe no evidence for phase separation of the dopant: the conductivity increases smoothly with increasing doping density, and there is no change in conductivity with time (after the red-to-black phase transition).

The conductivity, σ , shows an unusual dependence on the dopant concentration (Figure 1), increasing over 5 orders of magnitude for an increase in dopant concentration of ~ 2.5 orders of magnitude. Similar behavior, over a small concentration range, was observed recently in vanadyl phthalocyanine films doped with a coevaporated oxidant.¹⁴ As in the case of conducting polymers,^{1,19} Coulombic effects probably play a major role in the doping process. Because of the low dielectric constant of organic materials, and the relatively weak delocalization (small Bohr radius) of charge carriers, most of the added carriers will remain electrostatically confined in the potential well surrounding the counter charge. Therefore, the number of free carriers produced

per added dopant is much less than one. With increasing dopant density, the potential wells around the dopants will begin to overlap, decreasing the effective well depth and increasing the fraction of free carriers. Thus, the conductivity should increase faster than linearly with dopant concentration. But the unexpectedly systematic increase in σ with the square of the dopant concentration suggests that a specific pairing mechanism may be responsible; whether this involves pairing of dopants to produce one charge carrier or pairing of charge carriers is not yet known.

The intercept of the fitted line in Figure 1, $\sigma = 4 \times 10^{-11}$ S/cm for zero added dopant concentration, is near the value measured for pure PPEEB films, $\sigma \approx 10^{-12}$ S/cm,¹⁶ suggesting that the observed trend in σ continues to lower concentrations than we measured. Doping of just 1% leads to an increase in σ of ~ 10 orders of magnitude. The activation energy for the conductivity is a weak function of dopant concentration, decreasing from 340 meV at 83 ppm dopant to 260 meV at 7600 ppm. The activation energy includes contributions from both the concentration of free electrons and their mobility.

Our doping process is somewhat similar to the “self-doping” process in some metallically doped conducting polymers. For example, poly(thiophene) derivatives have been reported with pendant alkylsulfonate groups.²⁰ Upon oxidation to the conducting state, the cation of the sulfonate can be expelled resulting in a conducting zwitterionic polymer containing (in principle) no unbound counterions. Poly(ethylenedioxy thiophene)/poly(styrene sulfonate),²¹ PEDOT-PSS, is another example of a metallically conducting polymer that, in principle, does not require mobile ions and therefore could form stable junctions with n-type organic materials. It should be possible to synthesize mobile-ion-free polymers with covalently bound counterions that are doped to semiconducting, rather than metallic, levels. However, to achieve uniform doping would require the synthesis of a new polymer for each concentration of dopant.

This method of doping MSCs also should be applicable to p-type doping, and such experiments are in progress. Because of the necessity for covalently bound counterions on the dopants, this approach is not compatible with vacuum evaporation of MSC films and thus requires solution processable compounds. Solution processing is, however, a preferred method of making films for energy-sensitive applications such as solar cells.

Acknowledgment. We are grateful to the U.S. Department of Energy, Office of Science, Division of Basic Energy Sciences, Chemical Sciences Division for supporting this research.

Supporting Information Available: Synthesis and characterization of the dopant precursor and the dopant, and J - V curves of doped films (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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