Supramolecular Control of Charge Transport in Molecular Wires

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In the context of the ever-decreasing dimensions of integrated circuits it is of fundamental interest to study charge transport through wires on the smallest imaginable scale; that is wires of molecular dimensions.[1] Organic π-conjugated polymers are attractive candidates as wires in molecular-scale electronics since their properties can be tuned to diverse specifications. Moreover, organic polymers can be modified noncovalently leading to self-organizing electronics.[2] An example of a molecular wire that exhibits such properties is the conjugated porphyrin polymer **1** shown in Scheme 1, consisting of zinc-porphyrins linked at the *meso*-position by butadiyne units.[3] It was shown recently by photoinduced electron transfer measurements that such porphyrin wires can transfer charge efficiently over long distances.[4] EPR measurements on related ethyne-linked porphyrin oligomers indicate that they can mediate essentially barrierless hole transport over distances of up to 75 Å.[5] In solution, the conjugation length of these polymers is limited by the low barrier for rotation of one porphyrin with respect to its neighbors.[6]

The conformation of these polymers can be altered by adding bidentate ligands such as 4,4′-bipyridyl (Bipy), which leads to the formation of double-strand ladderlike assemblies, (Scheme 1).[7,8] In these ladder structures the conjugation length is increased, amplifying the two-photon absorption[7] and nonlinear refraction.[9]

Here we report measurements of the mobility of positive charges (radical-cation centers or holes) along isolated single-strand porphyrin polymers and double-strand porphyrin ladders in solution. We show that the more planar conformation of the ladder structures leads to a 10-fold increase in the charge carrier mobility along molecular wires.

The measurements were performed by a combination of pulse-radiolysis to generate charges, and time-resolved microwave conductivity to measure the conductivity resulting from those charges.[10−12] The porphyrin polymers were dissolved in oxygen-saturated benzene (0.25 mM porphyrin repeat unit concentration) and irradiated with a short pulse (10 ns) of 3 MeV electrons from a Van de Graaff accelerator. This irradiation produces a close to uniform concentration of benzene radical cations (Bz$^+$) and excess electrons. The change in conductivity of the solution upon irradiation was measured using the time-resolved microwave conductivity technique at a microwave frequency of 34 GHz, by measuring the absorption of microwave power by the mobile charges in the solution.

The excess electrons that are formed in benzene on pulse radiolysis are highly mobile[13] (0.13 cm^2/(V s)) and react with the dissolved oxygen within a few nanoseconds. The Bz$^+$ ions are not affected by O$_2$ but can diffuse to the polymer chains where they undergo charge transfer to the polymer, since it has a lower

Scheme 1. Formation of Porphyrin Polymer Ladders
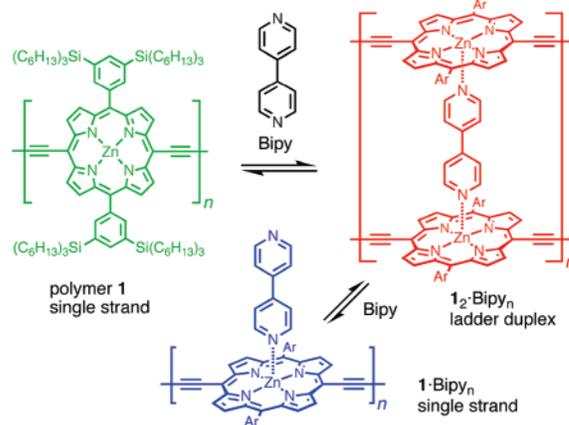
ionization potential, creating positive charges or "holes" on the polymer backbone. An example of a conductivity transient obtained for a dilute solution of isolated chains of **1** is shown in Figure 1a. During the irradiation pulse highly mobile electrons are generated, causing a considerable conductivity during the first 10 ns of the transient. This contribution rapidly decays because of the reaction of the electron with O$_2$. The conductivity of the solution increases for up to ∼1 μs, owing to the diffusion-limited charge-transfer reaction of Bz$^+$ with **1** (eq 1). The increase of the conductivity provides direct evidence that the mobility of holes along the porphyrin wires is higher than that of holes in benzene.

$$Bz^+ + P \rightarrow Bz + P^+ \qquad (1)$$
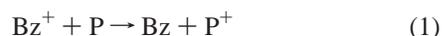
The conductivity subsequently decays on a time scale of hundreds of microseconds. The time scale of this decay becomes faster with increasing dose in the irradiation pulse and is attributed to second-order charge recombination according to

$$P^+ + O_2^- \rightarrow P + O_2 \qquad (2)$$

The conductivity $\Delta\sigma$ at any given time after the pulse is related to the mobility of each charge (with index i) μ_i and their concentration $N_i(t)$ by

$$\Delta\sigma(t) = e \sum_i N_i(t)\,\mu_i \qquad (3)$$

with e the elementary charge. This means that the mobility of the charged species can be obtained if their concentration is known. By numerically solving the differential rate equations for the concentrations of Bz$^+$, O$_2^-$, and P$^+$ quantitative fits to the experimental data could be made, and the value for the mobility of
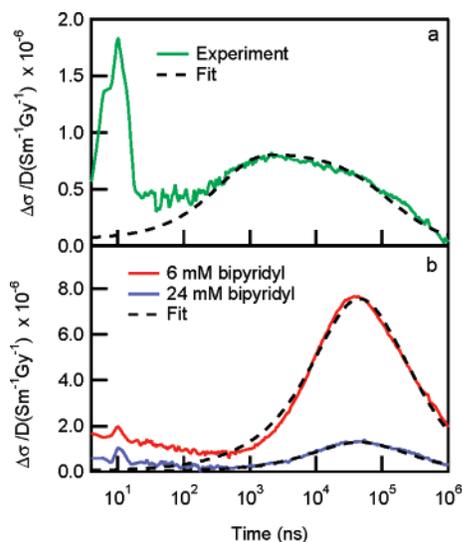
Figure 1. Change in microwave conductivity on irradiation of O_2-saturated solutions of **1** in benzene without (a) and with (b) 4,4′-bipyridyl. The transients are normalized to the irradiation dose, D in gray (1 Gy = 1 J/kg of energy absorbed).

positive charges (which determines the amplitude of the conductivity transients) on the porphyrin chains was obtained.[12] The results of the fits are shown as dashed lines in Figure 1.

From the fit an isotropic mobility of 0.028 cm²/(V s) was derived, for single-strands of polymer **1**. If it is assumed that the porphyrins adopt a straight rodlike conformation then the one-dimensional mobility along the chains is three times this value; 0.084 cm²/(V s). The data shown in Figure 1 were obtained for a porphyrin polymer with a molecular weight corresponding to a number-average degree of polymerization of about 50 monomer units. Additional experiments on porphyrin polymers with average chain lengths of 10 and 37 monomer units yielded similar conductivity transients and mobility values. This is rather interesting since it was found recently that the mobility (at 34 GHz) measured by the same method for MeLPPP[14] and PPV[15] derivatives strongly depends on the chain length. From these experiments it was concluded that the measured mobility is limited by the chain ends and that the actual (DC or low frequency) mobility is considerably higher than the measured value at 34 GHz. Values of 600 cm²/(V s) and 60 cm²/(V s) were estimated for these MeLPPP and PPV polymers.[14,15] In the present case, the mobility does not depend on chain length, which leads to the conclusion that the DC mobility of the charge along the porphyrin chains is equal to the values measured at 34 GHz, that is, 0.084 cm²/(V s).

Addition of Bipy to the solution of polymer **1** leads to the formation of ladder structures as shown in Scheme 1. In Figure 1b the result of a radiation induced conductivity measurement on an oxygen-saturated solution of the porphyrin polymer (0.25 mM in monomer units) containing a 6 mM concentration of Bipy is shown. Under these conditions the polymer exists as the double-strand complex **1**₂·Bipy$_n$. Comparison with the transient in Figure 1a shows that the addition of Bipy leads to an increase in conductivity by roughly an order of magnitude. The isotropic microwave mobility obtained from fits to the transient for the solution containing the porphyrin ladders was 0.31 cm²/(V s), corresponding to a one-dimensional mobility of 0.93 cm²/(V s). This mobility is more than an order of magnitude larger than discussed above for isolated porphyrin wires, showing directly that planarization of the chains strongly accelerates charge transport. The mobility value of 0.93 cm²/(V s) is higher than typical dc mobilities for interchain transport in thin films of conjugated polymers. However, the mobility is lower

than for intrachain transport along defect-free conjugated polymer chains.[14,15] Studies are underway to find the ultimate mobility that can be achieved along porphyrin chains with improved planarity.

Interestingly, the formation of P⁺ is considerably slower in Figure 1b than in absence of Bipy (Figure 1a). We attribute this to a stepwise charge transfer, in which the charges first transfer to Bipy and subsequently to the porphyrin chain. The slower kinetics are explained by either a much lower diffusion coefficient of the Bipy⁺ radical cation, due to formation of cation-π complexes, or non-diffusion-limited kinetics for the reaction in eq 1.

Increasing the concentration of Bipy above 6 mM leads to a decrease in the amplitude of the conductivity transients as shown in Figure 1b, owing to dissociation of ladders to **1**·Bipy$_n$ single strands (Scheme 1).[9] For the solution with a 24 mM concentration of Bipy a mobility value close to that of the uncomplexed single-strand polymer **1** was obtained, and the amplitude of the conductivity transient becomes similar to that in Figures 1a.

In conclusion, we have shown that the mobility of positive charges along porphyrin-based molecular wires can be increased by an order of magnitude by formation of the double-strand 4,4′-bipyridyl ladder complex. This illustrates the scope for using noncovalent supramolecular self-assembly to enhance the conductivity of molecular wires, by increased planarity and conjugation. We plan to extend this study to other multistrand conjugated polymer arrays.

Supporting Information Available: Details of synthesis, polymer characterization, and UV−vis titrations. This material is available free of charge via the Internet at http://pubs.acs.org.

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