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Mechanism of Charge Transport along Zinc Porphyrin-Based Molecular Wires

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Abstract: In this study charge transport along zinc porphyrin-based molecular wires is simulated, considering both bandlike and hopping mechanisms. It is shown that bandlike transport simulations yield significantly overestimated hole mobility values. On the basis of kinetic and thermodynamic considerations, it is inferred that charge transport along zinc porphyrin-based molecular wires occurs by small polaron hopping. Hole mobility values on the order of 0.1 cm^2 V^{-1} s^{-1} are found from small polaron hopping simulations, which agree well with previously reported experimental results. It is suggested that the experimentally observed increase of the charge carrier mobility on formation of supramolecular ladderlike structures is determined by two factors. One of these is an increase of charge transfer integrals between monomer units due to molecular wire planarization. A more important factor is the reduction of the amount of energetic disorder along the molecular wire and in its environment. General guidelines for determining the mechanism of charge transport along molecular wires are discussed.

1. Introduction

In its ongoing quest for miniaturization, the electronics industry is rapidly approaching circuit sizes that are of molecular dimensions. This trend stimulates the development of both new integrated circuit architectures and new materials for electronic applications.[1−4] It is of fundamental interest to study charge transport on the scale of the smallest imaginable functional devices—that is, on the scale of single molecules. The most basic element of an electronic circuit is a conducting wire. Several classes of materials, including single-wall and multiwall carbon nanotubes,[5−7] graphitized carbon nanowires on diamond substrates,[8−10] and organic π-conjugated oligomers,[4,11] have been considered as interconnects for molecular-scale electronics. Among these materials π-conjugated organic wires stand out because of their great diversity, which allows tuning them chemically to a wide range of desired specifications,[12−15] as well as the possibility of chemical functionalization to promote self-assembly into supramolecular structures[16,17] and potentially low processing costs.[11]

In the past decade it has become possible to measure the conductance of single organic molecules between metal electrodes, e.g., in a break junction,[18] or between mercury drops.[19] These methods provide insight into the transport of charges through the molecule; however, the results of such measurements are to a large extent determined by effects related to contacts between the electrodes and the molecule. In many cases, the conductance can be considered to occur via a bridge-mediated superexchange mechanism in which the charge tunnels from one electrode to the other, without becoming localized on the molecular bridge.[20,21] Hence, these measurements do not provide information about the mobility of charges that are localized on the molecule. However, the mobility of charges on isolated molecules can be measured in pulse-radiolysis time-

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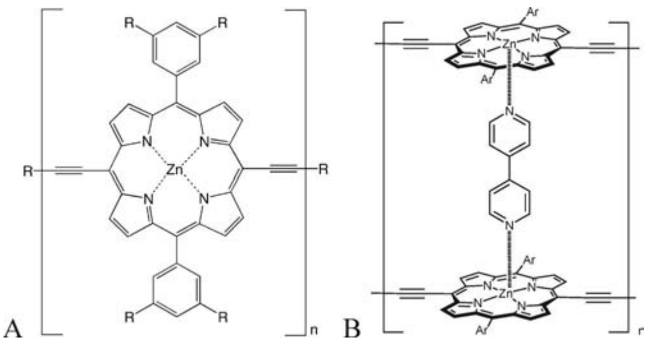

Figure 1. Zinc porphyrin-based molecular wires: (A) molecular structure; (B) ladderlike supramolecular arrangement formed upon addition of 4,4′-bipyridyl (R = $Si(C_6H_{13})_3$, Ar = m-$C_6H_3[Si(C_6H_{13})_3]_2$).

resolved microwave conductivity (PR-TRMC) experiments.[22,23] In this case, irradiation with high-energy electrons is used to generate charges on oligomer or polymer chains in solution, and thus, there is no need for charge injection from contacts. The mobility of charges moving along molecular wires is also determined without the use of electrodes by measuring the absorption of microwaves. Thus, the method is fully contactless, and information on the *intrinsic* charge transport properties of the molecular wires is obtained.

PR-TRMC measurements have been performed for a variety of conjugated polymers, and it has been found that the mobility of charges along isolated conjugated polymer chains depends strongly on the chemical composition and conformation of the backbone. Intrachain hole mobility values as high as 600 $cm^2\ V^{-1}\ s^{-1}$ have been reported for some conjugated polymers (ladder-type poly(p-phenylenes)[24]). For others (e.g., poly(3-hexylthiopene)[25] and recently zinc porphyrin-based molecular wires[26]) the hole mobility was found to be below 0.1 $cm^2\ V^{-1}\ s^{-1}$.

In this paper we focus on a theoretical description of charge transport along zinc porphyrin-based molecular wires,[26] consisting of zinc porphyrins linked at the *meso*-position by butadiyne units (Figure 1A). The possibility of efficient charge transport through such porphyrin-based molecules has been demonstrated in donor bridge−acceptor[27] and molecule between electrodes[28] experiments. The hole mobility value for these molecular wires determined by PR-TRMC is 0.084 $cm^2\ V^{-1}\ s^{-1}$. Interestingly, addition of 4,4′-bipyridyl to the benzene solution of the molecular wires leads to the formation of ladderlike supramolecular structures[26,29] (Figure 1B). This results in an increase of the hole mobility by an order of magnitude.

Charge transfer in molecular wires can occur by several different mechanisms.[30,31] The charge transport mechanism is determined by different factors, and there is no simple criterion to decide a priori what the mechanism is for a specific polymer. One of the important factors determining the charge transport mechanism can be structural disorder in the polymer chain and in its surroundings. A theoretical model that describes charge transport in molecular wires should take such disorder explicitly into account.

In this paper we describe simulations based on bandlike and small polaron hopping models, as well as theoretical considerations, which allow determination of the charge transfer mechanism that is operative in zinc porphyrin-based molecular wires studied in ref 26. Disorder is included in the description for both of these models. An explanation for the increase of the hole mobility in supramolecular ladderlike structures (Figure 1B) is discussed. These considerations can also be used as guidelines in predicting the charge transport mechanism in general and thus the conducting properties of other π-conjugated polymers, which could aid chemists in the design of new efficient molecular wires with desired properties.

2. Calculation of Charge Transport Parameters

The theoretical description of charge transport requires accurate values of electronic couplings for charge transfer (also referred to as charge transfer integrals or hopping matrix elements) and site energies (energy of a charge when it is localized on a particular monomer unit) as a function of the geometric conformation of the molecular wire. In further discussion it is assumed that the equilibrium site energy is the same for all identical monomer units and independent of their surroundings. It is also assumed that the charge transfer integral between any two neighboring monomer units only depends on the dihedral angle between their planes.

The charge carrier is described within the tight-binding approximation, taking into account interactions between nearest neighbor sites only. In this case the Hamiltonian for the charge carrier can be written in the form

$$\mathbf{H} = \sum_i \varepsilon_i a_i^+ a_i + \sum_{i,j=i\pm1} J_{ij} a_i^+ a_j \tag{1}$$

where a_i^+ and a_i are the creation and annihilation operators of a charge on the ith monomer unit, $\varepsilon_i = \langle\varphi_i|\mathbf{H}|\varphi_i\rangle$ is the site energy of the charge, and $J_{ij} = \langle\varphi_i|\mathbf{H}|\varphi_j\rangle$ is the charge transfer integral involving the orbitals on monomer units i and j, as specified below.

The wave function Ψ of a hole on the molecular wire can, to a good approximation, be written as a linear superposition of the highest occupied molecular (fragment) orbitals φ_i (HOMOs) on the different monomer units:

$$\Psi(t) = \sum_i c_i(t)\varphi_i \tag{2}$$

The HOMO, φ_i, of an individual monomer unit was calculated using density functional theory (DFT) methods, implemented in the ADF program[32] with a basis set consisting of atomic orbitals. The site

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energies and charge transfer integrals in eq 1 were then obtained by utilizing a unique feature of the ADF program, namely, the possibility to exploit fragment orbitals, φ_i, as a basis set in calculations on systems consisting of two or more monomer units. The ADF program solves the Kohn−Sham equation $\mathbf{h}_{KS}\mathbf{C} = \mathbf{SCE}$. The eigenvector matrix $\mathbf{C}$, the overlap matrix $\mathbf{S}$, $S_{ij} = \langle\varphi_i|\varphi_j\rangle$, and the (diagonal) eigenvalues matrix $\mathbf{E}$ of the total system composed of two (or more) monomer units are provided in the standard output. The matrix elements of the Kohn−Sham Hamiltonian, $\langle\varphi_i|\mathbf{h}_{KS}|\varphi_j\rangle$, can readily be obtained by using the relation[33] $\mathbf{h}_{KS} = \mathbf{SCEC}^{-1}$. The site energies ε_i are the diagonal elements of the Kohn−Sham Hamiltonian.

The method allows direct calculations of the charge transfer integrals, including their signs, without invoking the assumption of zero spatial overlap. However, when the spatial overlap $\mathbf{S}$ is not taken into account in the charge transport calculations based on the Hamiltonian in eq 1, the generalized charge transfer integral[33,34]

$$J_{ij}' = J_{ij} - \frac{1}{2}S_{ij}(\varepsilon_i + \varepsilon_j) \tag{3}$$

rather than the exact J_{ij} value has been shown to provide a good approximation for the charge transfer integral. If both site energies in eq 3 are equal ($\varepsilon_i = \varepsilon_j = \varepsilon$), then eq 3 reduces to $J_{ij}' = J_{ij} - S_{ij}\varepsilon$.

Site energies and charge transfer integrals for zinc porphyrin-based molecular wires were calculated by considering a system of two monomer units, analogous to the polymer shown in Figure 1A. The dimer geometry was first optimized with the program Gaussian[35] using DFT with the BLYP density functional (Becke gradient correction to the exchange part,[36] Lee−Yang−Parr correlation correction[37−39]) and the 6-31G(d,p) basis set.[40,41] The optimized geometry was used for further single-point electronic structure calculations with the ADF program.[32] Fragment (single-monomer) orbitals were calculated using a double-ζ basis set of atomic orbitals and the asymptotically correct statistical average of orbital potentials (SAOP) exchange-correlation functional.[42] Dimer orbitals were then calculated, using fragment orbitals as the basis set for different dihedral angles θ between the planes of the two porphyrin rings (Figure 1A). The angular dependence of the calculated values of the generalized charge transfer integral was found to follow a cosine:

$$J_{ij}'(\theta_{ij}) = J'(0)\cos\theta_{ij} \tag{4}$$

where $J'(0) = 0.27$ eV. It can be shown (see, e.g., ref 33) that if the site energies $\varepsilon_i = \varepsilon_j = \varepsilon$, and coupling takes place exclusively between the HOMOs of the two monomer units, then $J_{ij}' \approx {}^1/_2\Delta E$, where ΔE is the energy splitting between the HOMO and HOMO − 1 levels. Indeed, the charge transfer integral calculated in such a way is described well by eq 4 with $J'(0) = 0.3$ eV.

Equation 4 shows that the generalized charge transfer integral J_{ij}' between two monomer units is a function of the dihedral angle θ_{ij} between the planes of the monomer units, making charge transport along the molecular wire strongly dependent on its conformation. Finding the distribution of charge transfer integrals in the molecular wire is equivalent to finding the distribution of dihedral angles θ_{ij} between adjacent monomer units. The latter is determined by the torsion potential (Figure 2), which was calculated by optimizing the molecular geometry while keeping the dihedral angle θ_{ij} fixed. This optimization was performed using the program Gaussian,[35] employing DFT with the BLYP density functional and the 6-31G(d,p) basis set. The results of this calculation match very well with the results of a similar calculation reported in ref 43 and show good agreement with AM1 semiempirical calculations on a similar porphyrin dimer[44] and experimental values reported for diphenylethyne- and diphenylbutadiyne-linked porphyrins.[45]

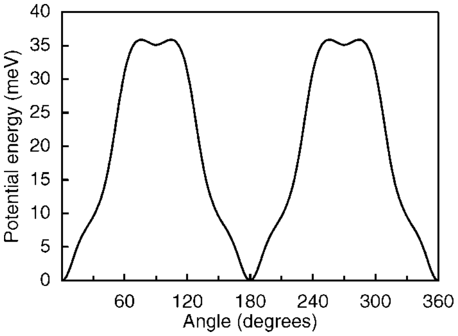

Figure 2. Calculated potential barrier for relative rotation of two adjacent monomer units as a function of the dihedral angle θ between them.

The very low barrier for rotation ($V_{\mathrm{tor}}^{\max} \approx 35$ meV) implies that there is a broad distribution of dihedral angles θ_{ij} in the molecular wire at room temperature. This conclusion is supported by the ground-state absorption spectra of the porphyrin dimer.[43] The dihedral angles θ_{ij} are at any given moment in time distributed according to the Boltzmann distribution

$$P(\theta_{ij}) = \frac{\exp\left[-\dfrac{V_{\mathrm{tor}}(\theta_{ij})}{k_{\mathrm{B}}T}\right]}{\displaystyle\int_0^{2\pi}\exp\left[-\dfrac{V_{\mathrm{tor}}(\theta_{ij})}{k_{\mathrm{B}}T}\right]\mathrm{d}\theta_{ij}} \tag{5}$$

where $V_{\mathrm{tor}}(\theta_{ij})$ is the torsion potential between adjacent monomer units, k_{B} is the Boltzmann constant, and T is the temperature (taken to be 293 K).

3. Bandlike Transport Simulation

3.1. Hole Mobility Calculation Algorithm. A calculation of the hole mobility in zinc porphyrin-based molecular wires, based on a combination of the tight-binding description of the charge carrier (hole) on the molecular wire and a classical description of the dynamic structural disorder in the system,[31] is considered. This model has previously been successfully employed to describe charge transport in DNA,[46−48] discotic liquid crystalline materials,[33] and some (e.g., phenylenevinylene) molecular wires.[49,50]

It is assumed that the site energies ε_i are constant and equal for all monomer units. The initial dihedral angles θ_{ij} between adjacent monomer units are sampled from the Boltzmann distribution, eq 5, and the corresponding generalized charge transfer integrals J_{ij}' are given by eq 4.

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The wave function Ψ of the hole on the molecular wire, given by eq 2, is propagated according to the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi(t)}{\partial t} = \mathbf{H}(t)\, \Psi(t) \tag{6}$$

with the initial condition $\Psi(0) = \varphi_n(0)$, equivalent to $c_i(0) = \delta_{in}$ (see eq 2), where δ_{in} is the Kronecker δ. The mobility can be obtained by taking a wave function initially localized on one monomer unit n, as discussed in ref 31. Note that this does not imply that the hole on the molecular wire is localized. The wave function was propagated in the simulations with a time step of one atomic unit (2.4189×10^{-17} s).

The Hamiltonian $\mathbf{H}$ in eq 6 is time-dependent, because the generalized charge transfer integrals J_{ij}' vary with conformational changes (relative rotation of the monomer units) in the molecular wire. The change of dihedral angles θ_{ij} in time is determined by a combination of rotational drift and rotational diffusion. During a small time step Δt the change of the angles is given by[51]

$$\Delta\theta_{ij} = -\frac{D_{\rm rot}}{k_{\rm B}T}\frac{{\rm d}V_{\rm tor}(\theta_{ij})}{{\rm d}\theta_{ij}}\Delta t + \Delta\theta_{ij}^{\rm diff} \tag{7}$$

The first term in eq 7 is the rotational drift due to the torsion potential. The second term accounts for the random diffusive rotation, such that $\langle(\Delta\theta_{ij}^{\rm diff})^2\rangle = 2D_{\rm rot}\Delta t$, with $D_{\rm rot} = (2\tau_{\rm rot})^{-1}$ and $\tau_{\rm rot}$ being the diffusion rotation time of a monomer unit (defined as a time required for a root-mean-square rotation of the monomer unit by 1 rad). The dihedral angles θ_{ij} were propagated in the simulations with the same time step as that for the wave function of the hole, i.e., one atomic unit. The dihedral angles θ_{ij} were assumed to evolve independently of the presence of charge on monomer units i and j, as its effect is proportional to the amount of charge present on both sites i and j, which is negligible in the limit of completely delocalized charges (and zero for one of the sites in the limit of localized charges).

The diffusion rotation time $\tau_{\rm rot}$ for the zinc porphyrin-based monomer in benzene was estimated using the procedure described in refs 52 and 53, with molecular volumes calculated on the basis of the volume increments of individual groups taken from refs 54 and 55. It was found that $\tau_{\rm rot}$ values on the order of several hundred picoseconds to several nanoseconds should be expected. The value of the diffusion rotation time $\tau_{\rm rot}$ used implicitly describes the effect of the solvent on the molecular dynamics.

Solving eq 6 gives a set of time-dependent site coefficients $c_i(t)$ in the hole wave function expansion, eq 2. The mean squared displacement of the charge as a function of time can be expressed in terms of these coefficients as

$$\langle \Delta x^2(t)\rangle = \sum_{i,n} f(n)|c_i(t,n)|^2(i-n)^2a^2 \tag{8}$$

where $f(n)$ describes the initial distribution of the charge, a is the length of a repeat unit (1.4 nm for zinc porphyrin-based molecular wires), $(i - n)a$ is the distance between the orbitals at sites i and n, and $c_i(t,n)$ is the coefficient of the orbital at site i at time t for the case of the hole wave function being initially localized at site n.

According to the work of Kubo, the frequency-dependent (one-dimensional) mobility of charge carriers is given by[56−58]

$$\mu_{\rm ac}^{\rm 1D} = -\frac{e\omega^2}{2k_{\rm B}T}\int_0^\infty \langle \Delta x^2(t)\rangle \cos(\omega t)\,{\rm d}t \tag{9}$$

where e is the elementary charge, ω is the (radial) frequency of the probing electric field. An implicit convergence factor $\exp(-ot)$ $(\lim_{o\to 0})$ is understood in the integral.[57,58] For normal Gaussian diffusion the mean squared displacement of charge carriers moving along an infinitely long molecular wire increases linearly with time:

$$\langle \Delta x^2(t)\rangle = 2Dt \tag{10}$$

where D is the diffusion constant. In this special case, the mobility is frequency independent, and eq 9 reduces to the Einstein relation

$$\mu_{\rm dc}^{\rm 1D} = \frac{e}{k_{\rm B}T}D \tag{11}$$

In the presence of structural disorder, eqs 10 and 11 are not valid. In that case the charge carrier mobility μ can be obtained from the mean squared displacement $\langle \Delta x^2(t)\rangle$ calculated on the basis of the numerical simulation and given by eq 8, using eq 9.

Simulations of charge transport were performed on both finite (10−200 monomer units long) and "infinite" (1000 monomer units long) chains. In the case of finite chains, the hole motion is limited by the chain ends, and thus, the initial position of the charge on the molecular wire may influence its mean squared displacement. In this case the initial probabilities of finding the charge on any of the monomer units were assumed to be equal. For "infinitely long" molecular wires the charge was initially localized in the middle of the molecular wire and did not reach the chain ends within the time scale of the simulation. In both cases the squared displacement of the hole was averaged over a few hundred realizations, which was sufficient for convergence.

3.2. Bandlike Transport Simulation Results and Discussion. The calculated dc hole mobility $\mu_{\rm dc}$ on an infinitely long zinc porphyrin-based molecular wire is shown in Figure 3 as a function of the monomer unit rotation time $\tau_{\rm rot}$. For physically reasonable rotation times $\tau_{\rm rot}$ of the order of several hundred picoseconds to several nanoseconds the mobility does not vary much (3−12 cm^2 V^{-1} s^{-1}). Such dc mobility values, calculated

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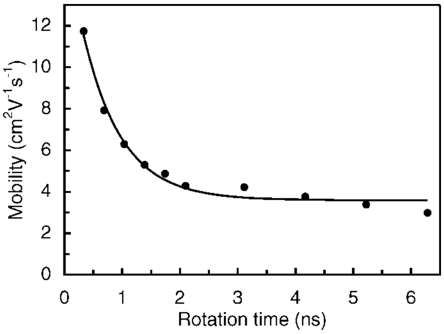

Figure 3. Hole mobility along zinc porphyrin wires calculated with the bandlike model of charge transport as a function of the time τ_{rot} of the relative rotation of adjacent monomer units.

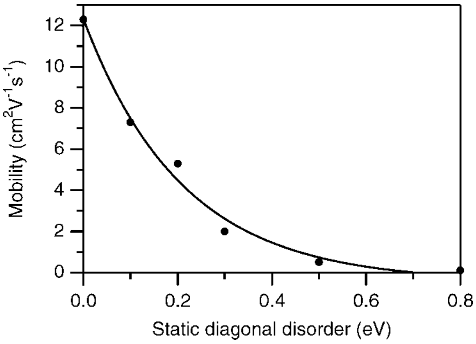

Figure 4. Hole mobility along zinc porphyrin wires calculated with the bandlike model of charge transport as a function of the amplitude of static diagonal disorder (at $\tau_{\text{rot}} = 2$ ns).

for an infinite chain, are more than an order of magnitude higher than the values found in PR-TRMC experiments ($\mu < 0.1$ cm^2 V^{-1} s^{-1}).[26]

The relatively low experimental mobility could, in principle, have several explanations within the band-like model. The following three issues that affect the charge carrier mobility have been considered.

First, the disorder in the site energies ε_i has so far been neglected, and only disorder in the charge transfer integrals J_{ij}' due to the torsional motion of the monomer units was taken into account. However, other vibrational modes also contribute to the charge transfer integrals and to the site energies. To obtain insight into the effect of the latter on the charge carrier mobility, fluctuations in the site energies and additional fluctuations in the charge transfer integrals were introduced into the simulation as uncorrelated stochastic processes.[59] The amplitudes of the fluctuations were sampled from a uniform distribution centered at zero: $\delta\varepsilon_i(t) \in [-A,A]$ and $\delta J_{i,i\pm1}(t) \in [-B,B]$. The time correlation of the fluctuations was assumed to decay exponentially: $\langle\delta\varepsilon_i(t)\ \delta\varepsilon_i(0)\rangle = A^2 \exp(-t/\tau_\varepsilon)$ and $\langle\delta J_{i,i\pm1}(t)\ \delta J_{i,i\pm1}(0)\rangle = B^2 \exp(-t/\tau_J)$. Fluctuation amplitudes A and B were varied within the intervals 0−1 and 0−0.2 eV, respectively, and characteristic time scales of the fluctuations τ_ε and τ_J within the interval from 10 fs to ∞.

Second, scaling of the site energies with the amount of charge on each site (coefficient c_i in the wave function in eq 2) was introduced to account for possible molecular geometry relaxation due to the presence of the charge.[30,60]

Third, the chain length distribution of molecular wires in the sample (assumed to be the Flory distribution,[61] typical for products of polymerization reactions in which termination by combination is negligible) was taken into account.

The second and third refinements only led to small decreases in the charge carrier mobility; however, neither of them (as well as their combination) reduced the calculated mobility value below 1 cm^2 V^{-1} s^{-1}. Introduction of additional disorder in the charge transfer integrals (within the above-specified energy and time scale range) had a small effect on the charge carrier mobility for smaller disorder amplitudes and an effect similar to that produced by changing the rotation time τ_{rot} (see Figure 3) for larger disorder values. This is not surprising, since the upper limit of the amplitude of disorder $\delta J_{i,i\pm1}$ in the charge transfer integrals was taken to be close to the amplitude of the charge transfer integrals themselves. Considering higher values of $\delta J_{i,i\pm1}$ was deemed unphysical, as torsional degrees of freedom have a dominant effect on the charge transfer integral values.[62,63] Moreover, off-diagonal (charge transfer integral) disorder in conjugated polymers generally does not exceed 0.1 eV.[62] Thus, none of the above considerations can explain the relatively low mobility values observed in the experiments.[26]

Introducing static disorder in the site energy, $\delta\varepsilon_i$, with amplitude A significantly exceeding the maximum charge transfer integral value, $J'(0) = 0.27$ eV, was found to have the largest effect on the charge carrier mobility. In Figure 4 the mobility calculated within the framework of the bandlike model is shown as a function of the amplitude of the static diagonal (site energy) disorder. To obtain mobilities on the order of the experimental values,[26] static disorder with an amplitude of about 0.8 eV had to be introduced. This is significantly larger than diagonal disorder values reported in the literature (typically within the range 0.05−0.15 eV; see, e.g., refs 62 and 64 and references therein). Additionally, such a high degree of disorder in the site energies, $\delta\varepsilon_i \gg J'(0)$, would make charge transport slower than the decoherence (dephasing) time (on the order of 100 fs) and hence lead to a loss of coherence of charge transfer.[50] A model for incoherent transport would thus have to be used to calculate the mobility in this regime.

Of course, it must be taken into account that PR-TRMC measurements[26] were performed on relatively short oligomer chains (10−50 monomer units) at a high probing frequency (34 GHz). Therefore, chain end effects could have a limiting effect on the measured mobility. Indeed, when simulations of charge transport are performed on 10 unit long chains, a mobility value of about 0.1 cm^2 V^{-1} s^{-1} is obtained. However, for longer (37−50 units long) chains, the calculated mobilities at 34 GHz already approach the dc mobility values (Figure 3). Thus, the calculated mobility demonstrates strong chain length dependence, while no such effect is observed in the experiments.[26]

This discrepancy between experimental and calculated mobility dependence on the chain length could, in principle, be due to conjugation breaks (single bonds in place of double or triple bonds), distributed uniformly along oligomer chains. A charge

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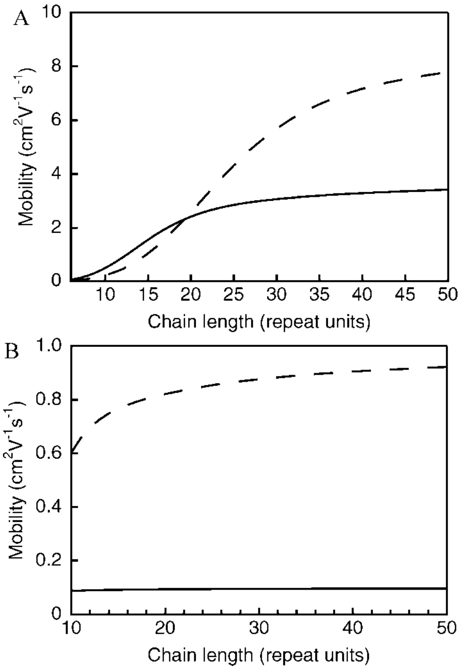

Figure 5. Hole mobility along zinc porphyrin-based oligomers calculated on the basis of eq 12 at $f = 34$ GHz ($\omega = 2\pi f$) as a function of the oligomer chain length for different values of the diffusion coefficient: (A) $D = 0.1$ cm^2 s^{-1} (solid line), $D = 0.25$ cm^2 s^{-1} (dashed line); (B) $D = 2.5 \times 10^{-3}$ cm^2 s^{-1} (solid line), $D = 2.5 \times 10^{-2}$ cm^2 s^{-1} (dashed line).

on a molecular wire segment, limited by conjugation breaks, would not be able to pass to the next segment. Thus, the conjugation breaks would effectively reduce the chain length. To determine whether the hole mobility on zinc porphyrin-based molecular wires[26] is inherently low (even for infinitely long molecular wires without defects) or limited by conjugation breaks separating short segments of the molecular wire, additional considerations are needed.

A theoretical analysis of the microwave mobility dependence on the molecular wire length can be found in ref 65. It is shown that the (complex) frequency-dependent mobility of charge carriers moving along an oligomer chain with reflecting chain ends is given by

$$\mu_{\mathrm{ac}}^{\mathrm{1D}}(\omega) = \frac{8eD}{k_{\mathrm{B}}T}\sum_{j=0}^{\infty}\frac{\zeta_j^{-2}}{1 + D\zeta_j^{2}/(i\omega n^2 a^2)} \qquad (12)$$

where e is the elementary charge, D is the one-dimensional diffusion coefficient of a charge along the chain, n is the number of repeat units in an oligomer chain, a is the length of a repeat unit, $\zeta_j = 2\pi(j + 0.5)$, and $i = \sqrt{-1}$. For an infinitely long polymer chain eq 12 reduces to eq 11.

The mobility at $f = 34$ GHz, calculated as a function of the oligomer chain length using eq 12, is shown in Figure 5A for $D = 0.1$ cm^2 s^{-1}. This diffusion coefficient value corresponds to a mobility value of approximately 4 cm^2 V^{-1} s^{-1} (see eq 11), which is similar to mobilities found from bandlike transport simulations. It can be seen that, for chains shorter than approximately 10 monomer units, mobility values close to the experimentally observed mobility[26] of 0.084 cm^2 V^{-1} s^{-1} can be obtained. However, for such short effective chain lengths formation of ladderlike supramolecular structures (Figure 1B) would not lead to an increase in the charge carrier mobility, in contrast to the experiments.[26] The planarization will, of course, lead to an increase in the diffusion coefficient (and, consequently, an increase in the dc mobility of holes on infinitely long chains). However, for a chain of 10 monomer units the 34 GHz mobility calculated using eq 12 will go down. This is evident from comparing the chain length dependence of the mobility for $D = 0.1$ cm^2 s^{-1} and $D = 0.25$ cm^2 s^{-1} (Figure 5A). Thus, the relatively low hole mobility $\mu \approx 0.1$ cm^2 V^{-1} s^{-1} along single-strand zinc porphyrin molecular wires[26] cannot be caused by the limited chain length or conjugation breaks. If this were the case, the experimentally observed microwave mobility increase upon formation of ladderlike supramolecular structures (Figure 1B) would not be possible.

A much better agreement with experimental results is obtained when lower values for the diffusion coefficient are considered. In this case the variation in theoretical mobility values for both the isolated molecular wires and the ladderlike structures is small when the chain length is varied between 10 and 50 monomer units; see Figure 5B.

It can thus be concluded that the hole mobility is, indeed, chain length independent and on the order of 0.1 cm^2 V^{-1} s^{-1} even for infinitely long single-strand zinc porphyrin molecular wires without defects. As the mobilities calculated using the bandlike model are more than an order of magnitude higher than this value (for all reasonable parameter values), it may be inferred that the charge transport mechanism in zinc porphyrin-based molecular wires is not bandlike. In the next section small polaron hopping[31,60] is considered as a possible mechanism of charge transport.

4. Hopping Transport Simulations

In this section arguments in favor of the hopping mechanism of charge transport in zinc porphyrin-based molecular wires are presented. The algorithm and results of hopping transport simulations are discussed.

4.1. Conditions for Charge Carrier Localization. To determine whether small polaron hopping is a feasible mechanism of charge transport in zinc porphyrin-based molecular wires, it is important to know the extent to which a mobile charge on the molecular wire distorts the nuclear geometry to form a polaron. A parameter characterizing the above is the internal reorganization energy λ, defined as[31]

$$\lambda = [E^q(g^0) - E^q(g^q)] + [E^0(g^q) - E^0(g^0)] \qquad (13)$$

where $E^q(g^0)$ is taken to be the internal energy of a monomer unit with an excess charge $q = \pm 1$ (in elementary charge units), while the nuclear geometry g^0 corresponds to that for the neutral monomer unit in equilibrium, etc. Other terms in eq 13 are defined analogously. Note that the external reorganization energy is ignored, since the experiments in ref 26 were carried out on molecular wires in a nonpolar solvent, for which the static and high-frequency dielectric constants are virtually the same.

Internal reorganization energies can be calculated using Hartree–Fock, DFT, or Møller–Plesset perturbation theory.[66] The calculated reorganization energy value often depends

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significantly on the theoretical method used.[67,68] The reorganization energy for a zinc porphyrin-based dimer calculated with the program Gaussian[35] using DFT (BLYP density functional, 6-31G(d,p) basis set) was found to be 0.36 eV. The value calculated using Hartree–Fock theory with the same basis set was found to be somewhat higher (0.50 eV). Small polarons (localized on a single monomer unit) can be expected to form when the reorganization energy λ significantly exceeds the effective charge transfer integral J_{ij}'.[31] In the case of zinc porphyrin-based molecular wires the reorganization energy calculated with DFT (0.36 eV) is only slightly larger than the maximum value of the charge transfer integral ($J_{ij}'(0) = 0.27$ eV). Therefore, complete localization of a charge on a single monomer unit is not likely to occur. This conclusion is consistent with the experimentally observed decrease in the first oxidation potential,[27] as well as with changes in the radical cation absorption spectrum,[43] on going from a zinc porphyrin monomer to a dimer to a tetramer.

A necessary condition for small polaron formation is that charge localization is thermodynamically favorable. This condition can be quantified by introducing the relative stability η, defined as

$$\eta = E^{+1,0}(g^{+1}, g^{0}) - E^{+0.5,+0.5}(g^{+0.5}, g^{+0.5}) \tag{14}$$

where $E^{+1,0}(g^{+1},g^{0})$ is the energy of a dimer with the excess charge completely localized on one of the monomer units and $E^{+0.5,+0.5}(g^{+0.5},g^{+0.5})$ is the energy of a dimer with the excess charge equally distributed between two monomer units. The total excess charge is in both cases +1, and the geometry is in both cases optimized for the corresponding charge distribution.

It follows from eq 14 that if the relative stability $\eta < 0$, then it is thermodynamically favorable for the excess charge to localize on a single monomer unit. If $\eta > 0$, then it is thermodynamically favorable for the excess charge to delocalize over two or more monomer units.

The relative stability η was calculated with the program Gaussian,[35] using Hartree–Fock theory and the 6-31G(d,p) basis set. The value of η, given by eq 14, was found to be between -0.3 and -0.5 eV depending on the dihedral angle θ between the planes of the monomer units. Since $|\eta|$ significantly exceeds the thermal energy, charge localization is thermodynamically favorable, and consequently, polaron hopping is likely to occur. It is important to note that charge transport occurring by the polaron hopping mechanism does not necessarily imply that the charge is localized. In fact, it only means that there is decoherence between quantum states on different localization sites. The wave function of the charge can still be delocalized over more than a single monomer unit.[31]

One should also note that the relative stability η is a thermodynamic parameter. However, the kinetic condition for polaron formation must also be fulfilled. The average hopping frequency $\Gamma_{\mathrm{h}} \approx 10^{11}$ s^{-1} that would correspond to experimental mobility values is much smaller than the frequency of most vibrational modes of the zinc porphyrin rings. Therefore, sufficient time for polaron formation is allowed, making hopping transport indeed plausible.

4.2. Charge Transport Simulation Based on Marcus Theory. In the presence of a charge-induced lattice deformation the hopping rate of a charge carrier can (in the classical limit $k_{\mathrm{B}}T \gg \hbar\omega$) be described by the Marcus, or small polaron, theory.[69−73] In this theory the rate of transfer is given by

$$\Gamma_{\mathrm{h}} = \frac{2\pi}{\hbar}|J_{ij}'|^2\sqrt{\frac{1}{4\pi\lambda k_{\mathrm{B}}T}}\exp\left[-\frac{(E_j - E_i + \lambda)^2}{4\lambda k_{\mathrm{B}}T}\right] \tag{15}$$

where J_{ij}' is the generalized charge transfer integral between sites i and j, λ is the reorganization energy, and E_i and E_j are equilibrium energies of sites i and j, with the hole localized on the respective site.

In the charge transport simulation based on the Marcus rate equation the initial dihedral angles θ_{ij} between the planes of adjacent monomer units were sampled from the Boltzmann distribution, eq 5, in the same way as in the bandlike transport simulations discussed in section 3.1. The charge transfer integrals J_{ij}' were then calculated using eq 4. The disorder in site energies E_i and E_j was assumed to be Gaussian, $f(E) = f_0 \exp(-E^2/2\sigma_E^2)$, with f_0 being the normalization factor and the standard deviation σ_E of the distribution taken as a parameter representing the degree of disorder, which was varied from 0 to 0.1 eV. The reorganization energy λ was also considered a parameter and varied from the value of 0.36 eV, calculated using DFT, to 0.8 eV. These values were introduced into eq 15 to calculate the hopping rate Γ_{h} between sites i and j. The hopping distance was assumed to be the same as in the bandlike transport simulation (1.4 nm, corresponding to the equilibrium distance between the centers of two monomer units in zinc porphyrin-based molecular wires).

The average lifetime of the hole at any given site i on an infinite chain can be calculated as $\tau_{\mathrm{h}} = (\Gamma_{i\to i+1} + \Gamma_{i\to i-1})^{-1}$, where $\Gamma_{i\to i+1}$ and $\Gamma_{i\to i-1}$ are hopping rates from site i to sites $i + 1$ and $i - 1$, respectively. The probability density that no hop occurs after time t was assumed to decay exponentially, $p(t) = \tau_{\mathrm{h}}^{-1} \exp(-t/\tau_{\mathrm{h}})$. After each hopping event the charge localized on site i was displaced to either site $i + 1$ or site $i - 1$, with probabilities proportional to the corresponding hopping rates. The dihedral angles between monomer units of the molecular wire were propagated in time using eq 7 in the same way, as was done in the bandlike transport simulations, with a time step of 1 ps or after each hop, whichever was less. The mean squared displacement $\langle \Delta x^2(t) \rangle$ of the hole as a function of time was obtained by averaging over several hundred realizations of the initial conditions, which was found sufficient for convergence. The (dc) hole mobility was then calculated from the mean squared displacement using eqs 10 and 11.

4.3. Hopping Transport Simulation Results and Discussion. The calculated hole mobility μ on an infinitely long zinc porphyrin-based molecular wire is shown in Figure 6 as a function of the reorganization energy λ for several values of the site energy disorder parameter σ_E. It can be seen that for the value of the reorganization energy estimated from DFT calculations, $\lambda = 0.36$ eV, and no energy disorder the mobility $\mu \approx 12.4$ cm^2 V^{-1} s^{-1} is 2 orders of magnitude higher than the experimental values ($\mu \approx 0.1$ cm^2 V^{-1} s^{-1}).[26] However, one can see from Figure 6 that the hole mobility μ is extremely

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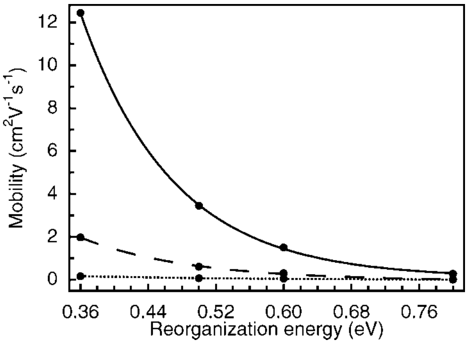

Figure 6. Hole mobility along zinc porphyrin wires calculated with the small polaron hopping model as a function of the reorganization energy λ for different values of disorder σ_E: 0 (solid line), 0.05 eV (dashed line), 0.1 eV (dotted line).

sensitive to changes in λ and σ_E (decreases exponentially with both parameters). For example, if λ increases from 0.36 to 0.72 eV (due to uncertainties in the calculated internal reorganization energy or the contribution of the solvent) and $\sigma_E = 0$, the mobility decreases to approximately 0.5 cm^2 V^{-1} s^{-1}, i.e., by more then 1 order of magnitude. If $\lambda = 0.36$ eV, and energy disorder with $\sigma_E = 0.1$ eV is introduced, the mobility decreases by about 2 orders of magnitude to 0.16 cm^2 V^{-1} s^{-1}.

It can be seen from Figure 6 that varying parameters λ and σ_E within a reasonable range can produce mobility μ values which agree very well with the experimental results.[26] This, in combination with considerations discussed in the previous sections, shows that the charge transport mechanism in zinc porphyrin-based molecular wires is well described by small polaron hopping theory.

A note should be made about the physical meaning of the energy disorder in the hopping transport simulation. Since all monomer units in a zinc porphyrin-based molecular wire are identical, the equilibrium energy difference $E_j - E_i$ in eq 15 could be expected to be zero. However, on the time scale of the charge transfer processes, sites i and j have different environments (organization of solvent molecules and other monomer units around them), and thus, $E_j - E_i \neq 0$.

Finally, consider the reasons for increased charge carrier mobility in ladderlike supramolecular structures composed of zinc porphyrin-based molecular wires (see Figure 1B). One of the possible causes of this effect, as suggested in ref 26, is the increase of charge transfer integrals J_{ij}' due to planarization of the molecular wire. However, for $\lambda = 0.36$ eV and $\sigma_E = 0$ complete planarization of the molecular wire causes the charge carrier mobility to increase by approximately a factor of 4. This is smaller than the increase in the mobility by an order of magnitude observed in the experiments.[26] Moreover, when energy disorder with $\sigma_E = 0.1$ eV is introduced, the charge mobility increases by only about 10% due to complete planarization of the molecular wire. This means that, even though the increase of the charge transfer integrals J_{ij}' due to molecular wire planarization does enhance the hole mobility, it is not the dominant factor. On the other hand, Figure 6 demonstrates that relatively small changes in λ or σ_E lead to large changes in the mobility. Such changes may be a result of the change in the environment of the zinc porphyrin-based wires upon formation of supramolecular structures. Both λ and σ_E can be lowered by a reduction in the number of degrees of freedom, which would cause the mobility to increase.

This argument also allows further discrimination against the possibility of bandlike transport, as in this case a disorder-controlled increase in the charge carrier mobility would require a decrease in the disorder from 0.8 to approximately 0.3 eV. This is a very large change, much higher than can be expected to occur due to solvent reorganization.

5. Summary and Conclusions

Charge transport along zinc porphyrin-based molecular wires is simulated, using the bandlike and the hopping models.

The mobility calculated with a bandlike model is more than an order of magnitude higher than the experimental value[26] ($\mu \approx 0.1$ cm^2 V^{-1} s^{-1}). It is shown that this discrepancy cannot be explained by chain end effects or conjugation breaks in the molecular wire.

On the basis of thermodynamic and kinetic considerations, it is concluded that small polaron hopping theory should adequately describe the experimental mobility values. Within the framework of small polaron hopping theory, the experimentally observed increase in the charge carrier mobility to approximately 1 cm^2 V^{-1} s^{-1} upon formation of ladderlike supramolecular structures is only in part due to larger charge transfer integral values for planarized molecular wires. It is inferred that the increase is mainly due to the smaller amount of disorder in the site energies. The latter is caused by additional constraints placed on the system when ladderlike supramolecular structures are formed, which reduces the total number of degrees of freedom.

Thus, both the (relatively) low hole mobility value in zinc porphyrin-based molecular wires and the higher mobility value in ladderlike structures formed by these wires, experimentally observed in ref 26, can be explained if the charge transport mechanism along these molecular wires is assumed to be small polaron hopping.

To further confirm that the charge transfer mechanism is indeed small polaron hopping, it would be interesting to see whether the transport is really thermally activated, as suggested by eq 15. This could be done in a temperature-dependent conductivity measurement; however, such measurements are difficult to perform in solution, particularly over a relatively wide temperature range.

The results show that polaron hopping transport along a molecular wire is extremely sensitive to disorder (both within the wire and in its environment). Molecular wires for which the bandlike transport mechanism is realized are much less sensitive to disorder. The origin of this difference lies in the fact that in the bandlike mechanism the charge does not have to become fully localized on high-energy sites. It can pass such sites by tunneling, without acquiring the full amount of energy necessary to become localized on a high-energy site. In the hopping model the charge behaves classically and thus has to fully transfer to the high-energy site.

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Supporting Information Available: Complete ref 35, coordinates of structures on which electronic structure calculations were performed, and absolute energies of these structures (hartrees). This material is available free of charge via the Internet at http://pubs.acs.org.

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