Conducting Oligomers

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High Electrical Conductance of Single Molecules: A Challenge in the Series of Conjugated Oligomers

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Owing to their electrical, optical and optoelectronic properties, conjugated oligomers and polymers play an important role in materials science. Special attention has been paid to oligomers with terminal donor–acceptor substitution D–πB–A.[1] The electronic coupling between the donor D and the acceptor A through a π-conjugated bridge πB comprises a wide range from the resonance case D–πB–A↔D$^+$–πB–A$^-$ to the existence of an additional zwitterionic state A–πB–D⇄D$^+$–πB–A$^-$. A weak coupling in a triad can originate from large dihedral angles between the π planes of D and A and the π plane of the bridge. When, for example, pentacene is attached in 6-position to the 4-position of a terminal benzene ring of an oligo(1,4-phenylenevinylene) chain, a dihedral angle of 70° can be expected.[2] This decreases the resonance energy by the factor $\cos^2 70° = 0.12$. Another reason for a weak coupling is a large energy gap ΔE between the bridge states and the termini D/A. Well-separated π→π* transitions of the partial structures provide a reliable indication for a weak coupling. However, in many cases overlapping bands have to be deconvoluted for this purpose.

The electronic coupling V_{DA} of the superexchange type[3,4] decays exponentially with the distance R between D and A. In rigid-rod systems, R is a linear function of the number n of repeat units.[5] The attenuation factor is conventionally designated as β [Eq. (1)]. Corresponding exponential laws

$$V_{DA} \propto e^{-0.5\beta R} \quad (1)$$

are used to express the rate k_{ET} of electron (hole) transport in charge-separation or charge-recombination processes [Eq. (2)] and for the electrical conductance σ_M of molecular

$$k_{ET} \propto e^{-\beta R} \quad (2)$$

wires [Eq. (3)]. Semilogarithmic plots of the relationships in

$$\sigma_M \propto e^{-\beta R} \quad (3)$$

Equations (1)–(3) exhibit linear correlations. An alternative or additional mechanism is given by electron-hopping processes. In contrast to the superexchange D–πB–A→D$^+$–πB–A$^-$, in which the bridge just mediates the electron transfer, the hopping process involves charged bridge states: D–πB–A→D$^+$–πB$^-$–A→D$^+$–πB–A$^-$. The exponential distance dependance is not valid for hopping processes, for which an algebraic function [Eq. (4)] is used for the charge transfer rate.[6]

$$k_{ET} \propto m^{-\eta} \quad m = \text{number of hopping steps for the distance } R \quad 1 \le \eta \le 2 \quad (4)$$

The attenuation factors β have a very strong influence on the decrease of V_{DA}, k_{ET}, and σ_M. A metallic wire has $\beta = 0$, such that conductivity (conductance per unity of cross section and unity of length of the wire) can be defined. Molecules have $\beta > 0$. When R is increased, for example from 10 to 100 Å, the conductance σ_M decreases, according to Equation (3), by a factor of about 8.2×10^{-40}, 1.2×10^{-4}, and 4.1×10^{-1}, respectively, for $\beta = 1.0$, 0.1, and 0.01 Å^{-1}. Originally the β value was thought to be specific for a certain bridge. Saturated bridges (σB) have β values around 1 Å^{-1}; for π bridges (πB) typically β values between 0.5 and 0.1 Å^{-1} have been found. However, it turns out that β also depends on the appended donor D and acceptor A.[7] Small β values ($\beta <$ 0.1 Å^{-1}) are important for all applications of molecular wires, but they are very rare.[6–8]

Recently, Anderson et al.[6] found an ultralow attenuation of σ_M for oligo(ethynylene-10,20-porphyrindiylethynylene)s $\mathbf{1}_n$, in which zinc is the central atom, solubilizing 3,5-bis(octyloxy)phenyl groups are in positions 5 and 15, and 4-(acetylsulfanyl)phenyl units are the end groups E (Figure 1). The sulfur serves to promote the contact to gold surfaces.

The synthetic approach to the monodisperse compounds $\mathbf{1}_n$ was based on the related oligomer series $\mathbf{2}_n$. Deprotection (tetrabutylammonium fluoride/CH_2Cl_2, $CaCl_2$) and Sonogashira cross-coupling ([Pd(dba)$_3$] (CuI)/PPh_3/THF, toluene/NEt_3] with thioacetic acid *S*-(4-iodophenyl) ester transformed $\mathbf{2}_n$ to $\mathbf{1}_n$ ($n = 1$–3) in yields between 57 and 80%.[6] The precursor series $\mathbf{2}_n$ was constructed previously by iterated protodesilylations and Glaser–Hay coupling reactions.[8,9]

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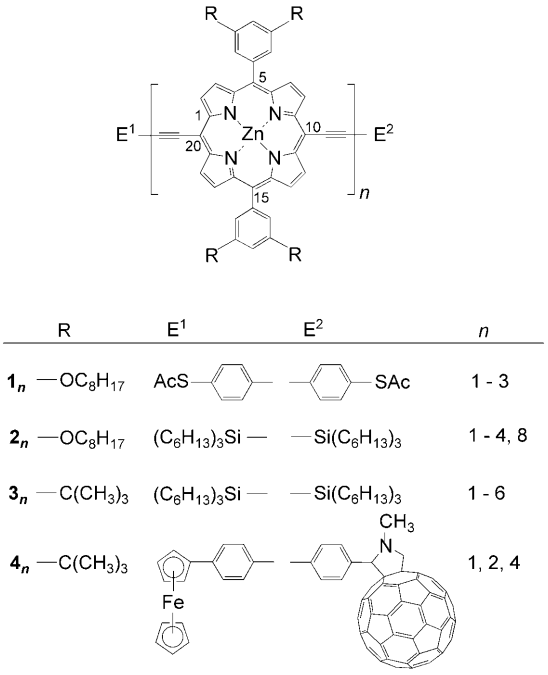

Figure 1. Zinc-complexed oligo(ethynylene-10,20-porphyrindiylethynylene)s $\mathbf{1}_n$–$\mathbf{4}_n$.

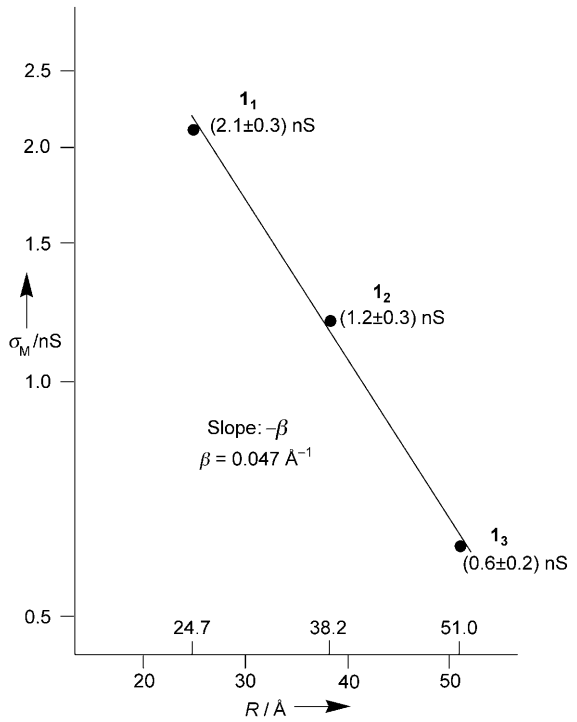

Figure 2. Semilogarithmic plot of the single-molecule conductance σ_M ($I(s)$ method, $V_{bias} = 0.6$ V) versus the calculated distance R between the sulfur atoms of the oligomers $\mathbf{1}_n$ ($n = 1$–3).

The σ_M measurement of $\mathbf{1}_n$ ($n = 1$–3), according to the methods developed by Haiss et al.,[10] used scanning tunneling microscopy (STM).[6] The substrate surface and STM tip were both of gold. Molecules $\mathbf{1}_n$ formed stretched wires in the STM gap. The current–distance dependence $I(s)$ was obtained by pulling the tip. In the alternative $I(t)$ technique, the stochastic formation of molecular bridges in the fixed STM gap was monitored by current jumps over time. The two methods gave almost identical results. Figure 2 shows the conductance σ_M of $\mathbf{1}_n$ ($n = 1$–3) depending on the SS distance R (n), which was calculated by molecular modeling (SPARTAN).

1,4-Bis(4-acetylsulfanylphenyl)-1,3-butadiyne could be included as a standard in the linear correlation of $\ln\sigma_M$ and R. The extremely low value $\beta = 0.04 \pm 0.006$ Å^{-1} could be established for the attenuation factor.[6] The twofold registration of linear semilogarithmic plots $\ln\sigma_M(R)$, does not mean that hopping processes can be completely excluded. Superexchange and hopping mechanisms can take place within one system, when they have similar activation barriers.[11]

The composite repeat unit of zinc 10,20-porphyrindiyl and two ethyndiyl segments provides an ideal wire of conjugated oligomers. The porphyrin ring systems with their extended conjugation can adopt a coplanar arrangement as a matter of principle, since there is no mutual steric hindrance. The oligomer series $\mathbf{1}_n$,[6] $\mathbf{2}_n$,[9] and $\mathbf{3}_n$[12] have long-wavelength absorption maxima (Q-band) at the Vis/NIR border (630–820 nm). They show a monotonous, convergent red-shift to λ_∞ with an increasing number n of repeat units. Interestingly, their total effect of conjugation $(\bar{\nu}_1 - \bar{\nu}_\infty)$[1] is relatively small—a feature that can be attributed to the flat well of the potential energy surface $E_{pot}(\alpha, \theta, \ldots)$ for small deformations of the 180° bond angles α and small angles θ between neighboring porphyrin planes.[13] The effective conjugation length n_{ECL}[1] amounts to 8–9 for $\mathbf{2}_n$ and $\mathbf{3}_n$ and should be similar for $\mathbf{1}_n$.

A comparison of attenuation factors β is difficult when oligomer series are investigated by different methods. Nevertheless, the triads $\mathbf{4}_n$ have to be included in the discussion here. Photoelectron transfer (PET) generates D^+–πB–A^- states from $\mathbf{4}_n$ with ferrocene as D^+ and C_{60} as A^-. The charge recombination (CR) mediated by the excellently conducting bridges was characterized by a rate constant k_{CR}, which was almost the same for $n = 2$ and $n = 4$).[8] This result is independent proof of ultralow β values for oligo(zinc 10,20-diethynylene-porphyrin)s. The high-lying HOMOs of these oligomers favor the formation of positive polarons as charge carriers, but the intramolecular charge recombination in a zwitterion and the charge transmission through a molecule between gold contacts can have different mechanisms.

Extended, conjugated oligomers like the 372 Å long 96-mer of a 2,5-thienylene[14] are desirable for molecular electronics. However, their electrical conductance σ_M should have a very low attenuation ($\beta \approx 0.01$ Å^{-1}). The systems studied by Anderson et al. represent a new, promising entry in this field.

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[1] H. Meier, *Angew. Chem.* **2005**, *117*, 2536–2561; *Angew. Chem. Int. Ed.* **2005**, *44*, 2482–2506.
[2] Force field calculation MM2, unpublished results.
[3] H. M. McConnell, *J. Chem. Phys.* **1961**, *35*, 508–515.

[4] Although originally saturated bridges in α,ω-diphenyloligomethylenes were considered,[3] Equation (1) can also be applied for conjugated systems.
[5] H. Meier in *Carbon-rich Compounds: Molecules to Materials* (Eds.: M. M. Haley, R. R. Tykwinski), Wiley-VCH, Weinheim, **2006**, pp. 476–528.
[6] G. Sedghi, K. Sawada, L. J. Esdaile, M. Hoffmann, H. L. Anderson, D. Bethell, W. Haiss, S. J. Higgins, P. J. Nichols, *J. Am. Chem. Soc.* **2008**, *130*, 8582–8583, and references therein.
[7] M. P. Eng, B. Albinsson, *Angew. Chem.* **2006**, *118*, 5754–5757; *Angew. Chem. Int. Ed.* **2006**, *45*, 5626–5629.
[8] H. U. Winters, E. Dahlstedt, H. E. Blades, C. J. Wilson, M. J. Frampton, H. L. Anderson, B. Albinsson, *J. Am. Chem. Soc.* **2007**, *129*, 4291–4297.
[9] P. N. Taylor, H. L. Anderson, *J. Am. Chem. Soc.* **1999**, *121*, 11538–11545; M. Drobizhev, Y. Stepanenko, A. Rebane, C. J. Wilson, T. E. O. Screen, H. L. Anderson, *J. Am. Chem. Soc.* **2006**, *128*, 12432–12433.
[10] W. Haiss, R. J. Nichols, H. van Zalinge, S. J. Higgins, D. Bethell, D. J. Schiffrin, *Phys. Chem. Chem. Phys.* **2004**, *6*, 4330–4337; W. Haiss, H. van Zalinge, S. J. Higgins, D. Bethell, H. Hobenreich, D. J. Schiffrin, R. J. Nichols, *J. Am. Chem. Soc.* **2003**, *125*, 15294–15295.
[11] C. Lambert, G. Noll, J. Schelter, *Nat. Mater.* **2002**, *1*, 69–73.
[12] P. N. Taylor, J. Hunskonen, G. Rumles, R. T. Aplin, E. Williams, H. L. Anderson, *Chem. Commun.* **1998**, 909–910.
[13] A cyclic hexamer revealed that regular deformations of the linear/coplanar arrangement can even lead to better conjugation than the normal, stochastic deformations of the chain. See M. Hoffmann, J. Kärnbratt, M. H. Chang, L. M. Herz, B. Albinsson, H. L. Anderson, *Angew. Chem.* **2008**, *120*, 5071–5074; *Angew. Chem. Int. Ed.* **2008**, *47*, 4993–4996.
[14] T. Izumi, S. Kobashi, K. Takimiya, Y. Aso, T. Otsubo, *J. Am. Chem. Soc.* **2003**, *125*, 5286–5287. For the electrical conductance of oligo(2,5-thienylene)s (oligothiophenes), see R. Yamada, H. Kumazawa, T. Noutoshi, S. Tanaka, H. Tada, *Nano Lett.* **2008**, *8*, 1237–1240.

