The control of electron-transfer processes is a major challenge in the design of molecular devices. Novel conjugated oligomers and polymers are presented in which photo- and redoxactive building blocks are linked by different spacers. It is also possible by chemical transformations to extend or interrupt \( \pi \)-conjugation and to switch from localized to delocalized electronic states. By a proper choice of the spacer units the title systems are tailored for electron transfer.

**ABSTRACT**

An attempt is made herein to approach aspects of molecular electronics from the point of view of synthesis and to achieve the function of a device on a molecular basis. We report on the synthesis of oligomers and polymers, which are tailored for inter- and intramolecular electron transfer. Toward that end electro- and photoactive building blocks such as benzene and polycyclic analogues such as naphthalene or anthracene are linked in a sterically and electronically variable fashion. The following modes of linking are considered: (see Scheme 1):

- saturated spacers \( L \) create conjugatively independent subunits \( A \) with localized electronic states while unsaturated spacers \( L \) bring about extended \( \pi \)-systems with far-reaching effective conjugation (case \( a \)); binaryles and polyarylenes with a direct interring bond (case \( b \)) constitute a particularly interesting borderline case: although in a formal sense allowing for extended \( \pi \)-conjugation they can give rise to localized states as a result of steric inhibition of resonance;

- among conjugated systems double-stranded structures (case \( c \)) offer significant advantages over their linear analogues (cases \( a \) and \( b \)). In addition to being configurationally and conformationally defined they are expected to possess low band gaps. This feature is important for high electron-transfer activity, long-wavelength optical absorption, electrical conductivity and non-linear optical properties;

- in oligomers with saturated spacers the conformation and length of the bridging group \( L \) is varied in order to systematically change the distance and spatial
The orientation of the electronically independent building blocks A;
- the polymers with extended π-conjugation are also subjected to thermally or photochemically induced skeletal rearrangements. The π-conjugation is thereby switched on or switched off and macroscopically detectable physical properties systematically changed on a molecular basis.

a.)

\[ \text{A} \quad \text{L} \quad \text{A} \quad \text{L} \quad \text{A} \quad \text{L} \quad \text{A} \quad \text{L} \quad \text{A} \]

b.)

\[ \text{A} \quad \text{A} \quad \text{A} \]

c.)

\[ \text{A} \quad \text{A} \quad \text{A} \]

Scheme 1: Schematic description of the title systems;
A: chromophoric or electrophoric subunit;
L: spacer

The formation of localized states upon photochemical excitation of conjugated polymers has been intensively discussed. In a similar fashion the injection of electrons into a conjugated polymer raises the question of an effective conjugation length. If the subunits A of a polyelectrophoric system are electronically independent, a charging process creates a new situation: this is depicted in Scheme 2 for a biselectrophor which can also constitute a subunit of the corresponding polymers: the excess charge can localize on one A or delocalize over both units; in the former ( bistable) situation a self-exchange process should be possible in which an electron is transferred to the neighboring subunit A. This hopping process can be looked at as a current passing through the spacer L.
rests upon "reductive polymerization", a technique which we have recently described in detail. Scheme 3 depicts the polycondensation of bifunctional nucleophiles and bifunctional electrophiles. A subsequent dehydrogenation gives photo- and electroactive anthracene units as part of the main chain. Chain formation in 5 is highly regioselective; by the choice of the electrophile (e.g. 1, n-dihaloalkane $\text{Br(CH}_2\text{)}_m\text{Br}$; one can also incorporate helix-type oxaethylene or rigid aromatic units) the distance and relative orientation of the anthrylene units can be varied systematically.\textsuperscript{10, 11, 12}

\textbf{Scheme 3: The principle of reductive polymerisation}

The same synthetic technique which implies carbanion formation via initial electron transfer and subsequent quenching of the intermediate carbanions with electrophiles affords systems with orthogonal or coplanar arrangements of the active subunits. Dimer 6 and polymer 7, which are obtained from 8 and 9, respectively, are typical examples.\textsuperscript{13, 14} The importance of molecules with orthogonal subunits has recently been pointed out by Aviram.\textsuperscript{15, 16}

The direct coupling of aryl subunits is achieved by two methods: (i) the nucleophilic attack of aryllithium species upon quinones and subsequent reductive elimination,\textsuperscript{17} and (ii) the palladium catalyzed condensation of arylboronic and arylhalide components.\textsuperscript{18, 19} Typical examples are the anthrylene and naphthylene chains 10 and 11. The latter oligo- and polyarylenes carry n-alkyl or t-butyl groups and are therefore sufficiently soluble in organic solvents.
Compound 2 can be subjected to Diels-Alder cycloadditions with various dienophiles. The reaction occurs at the anthracene and not at the butadiene spacer. By this process it is possible to interrupt the π-conjugation along the chain and to obtain the optical and electrical properties of the -now shorter π-system. In a similar fashion compounds such as dianthrylalkanes 12, which constitute subunits of the polymer 5, can be subjected to intra- and intermolecular [4+4]cycloaddition upon photolytic treatment. This is particularly important since the chromophores have film forming properties. Irradiation of the immobilized material induces photopolymerization which can be used for information storage and for the construction of wave-guides. The photopolymerization can be reversed upon thermal treatment.

An "extension" of anthracene creates the double-stranded polyacene structure 13 which is predicted from molecular orbital calculations to possess a vanishing
Considering the subunit A-L-A (1) as part of an electrical circuit, a control of this process by the above structural parameters should allow one to tailor conjugated oligomers and polymers for use in "molecular devices".

![Diagram of subunit reaction](image)

**Scheme 2: Charging of a biselectrophor**

**SYNTHESIS AND SKELETAL REARRANGEMENTS**

Since anthracene is known as an attractive chromophor and electrophor we have incorporated it as a building block into oligomeric and polymeric main chains according to Scheme 1. Polymer 2 is prepared by a repetitive Heck reaction between 9,10-(butadienyl)-anthracene (3) and 9,10-dibromoanthracene (4) under palladium catalysis.\(^5\), \(^6\) The synthesis of 5
band gap. Polymer 13 and higher oligoacenes are yet elusive which is mainly due to the instability of the products. We have now designed a route\textsuperscript{22} which implies the following steps: (i) the double stranded framework is constructed via a repetitive Diels-Adler cycloaddition (solubility is brought about by alkyl substituents); (ii) the final dehydrogenation to the fully conjugated ladder structure is achieved by a thermally induced retro-cycloaddition without applying any other reagents; (iii) this process is performed for films of the precursor materials so that the product can be stabilized in the immobilized phase. A typical model system is the nonacene precursor 14 which contains two dihydrobarrelene moieties and exists as a mixture of the syn- and anti-isomer. Thermolytic treatment of the films is accompanied by a drastic color change and can be used as a write-in process. Repetition of the ribbon forming cycloaddition allows one to extend molecules such as 14 to well-defined, rigid nano-structures.

\begin{equation}
\text{13}
\end{equation}

\begin{equation}
\text{14}
\end{equation}

**CONTROLLING ELECTRON-TRANSFER PROCESSES**

Injecting an electron into biselectrophoric systems such as 6, 12 and into dimeric model compounds of 7, 10 or 11 produces radical anions which can be characterized by ESR and ENDOR as well as absorption spectroscopy. The crucial question is whether the electron will tend to localize within one redox-active subunit or undergo a rapid transfer process (see above). The magnitude and the multiplicity of the ESR hyperfine coupling constants provide reliable criteria for describing this alternative. It is important thereby to refer to the ESR and UV spectroscopic data of the monomeric building block as model system.

The occurrence of localization or effective delocalization can be controlled by those structural factors which are relevant for the reorganization energy associated with the electron transfer. It appears that the rate of the electron hopping depends upon the (i) nature of the electrophoric subunit $A$; (ii) the length, conformation and position of the spacer $L$; and
(iii) the ion-pair structure.

Some detailed results from the study of the above title systems are as follows:

- localization can be enforced if the injection of an electron into a redox group brings about a significant structural (e.g. conformational) change. A typical example of such a group is cyclooctatetraene;\(^3\), \(^{23}\)

- there is a certain spacer length in systems \(^5\) and \(^7\) beyond which an electron transfer can be excluded;\(^{10}, \(^{14}\)

- for one and the same spacer length the conformation of the spacer can bring about rapid hopping; a major step is the introduction of a helix-type instead of an all-anti chain;\(^{10}\)

- the position at which the spacer \(L\) is attached to the units \(A\) determines the degree of mixing of product and educt wave functions. It is thus possible to bring about localization or rapid hopping, even for systems with the same components \(A\) and \(L\);\(^{24}\)

- the motion of charge is accompanied by a migration of counterions and thus by a reorganization of the ion-pair structure. Immobilization of the latter slows down an electron transfer and creates localized states;\(^{10}, \(^{14}, \(^{24}\)

- depending on the interring torsional angle and upon the wave function describing the aryl subunit, doped oligo- and polyarylenes such as \(^{10}\) and \(^{11}\) can give rise to either localized or delocalized states.\(^{17}, \(^{25}\)

Photophysical investigations of some of the present title systems have pointed out the formation of excimers and the occurrence of TICT fluorescence.\(^{26}, \(^{27}\)

These features sensitively depend upon the chromophoric subunit \(A\), upon the linkage \(L\) and upon medium effects. Thus, \(^{9,9'}\)-bianthryl suffers from a symmetry reduction under charge transfer which is evidenced by strong solvatochromic effects while \(^{1,2}\)-di(1-anthryl)ethane only shows excimer formation without solvatochromism. This situation is thus closely related to the one described above for the electron transfer in the charged derivatives of the title systems.\(^{31}\)

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