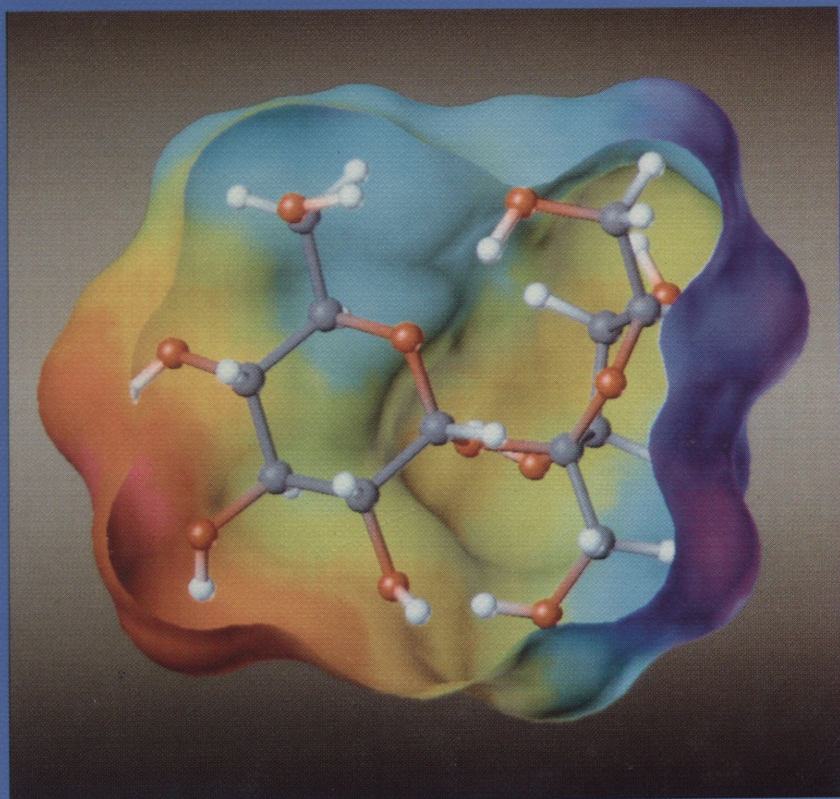# Carbohydrates as Organic Raw Materials

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From Carbohydrates to Pigments : An Exercise in Molecular Material Science and Material Transformation[1-3]

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Summary. The utilization of saccharides as basic materials for the synthesis of high-grade chemicals, optional in electronic and opto-electronic applications, is outlined. A general scheme for the overall procedure is given. The conversion of 5-hydroxymethyl-2-furaldehyde (HMF) – a key chemical of industrial sugar chemistry – into molecular components with electron-transfer and light-sensitive properties is presented. The syntheses of electrochemichromic and photochromic molecular components are described and their application in chemical and physical switching devices is given. Results are presented concerning the chemistry of HMF-based poly(arylene vinylenes) and carbohydrate-modified conducting polymers.

1. Introduction

The quest for renewable resources as substitutes for the fossil raw materials coal, crude oil or natural gas has its ups and downs depending on economic and political actualities.[4] Nevertheless, there is need and interest to outline strategies providing the chemical conversion of renewable resources into compounds and materials which might be of significance for trendsetting technologies. In the following account possibilities are examined to utilize sucrose, glucose, and fructose as the source for molecular materials suitable for electronic and opto-electronic devices.[5,6] Compounds that meet these requirements are pigments with either one of the following properties: (1) electron transfer acitivity, (2) electrochemichromism, (3) photochromism, (4) luminescence, (5) non-linear optical response, and (6) magnetic properties.

Correspondingly, a general description is given on the conversion of "natural" resources into "molecular" materials as exemplified by the use of *sucrose* and

sucrose-derived saccharides for the preparation of molecular materials of electronic and opto-electronic interest. In addition, the elucidation of the properties of those molecular components by physicochemical methods is described.[7]

2. Sucrose : Depot-compound of Solar Energy – Source-compound for Chemical Use

To evaluate the use of sucrose as basic source-material, some general data are given in Table 1 highlighting the energetics of solar irradiation and the availability of sucrose as a renewable energy resource which is industrially exploited by high-standard technology.[8]

Table 1. Sucrose as a biochemically renewable deposit of solar energy on earth

approximate total radiation energy of sun; in W	$3.8\ 10^{26}$	Ref.[a]
solar radiation energy received by earth; in W	$1.7\ 10^{17}$	Ref.[b]
production rate of biomass on earth (total land regions); to/sec	3 170	Ref.[c]
approximate total amount of carbohydrates produced by photosynthesis	(90 % of biomass)	
estimate of total amount of sucrose industrially produced		
worldwide (1989/90); to/sec	3.4	Ref.[d]
total amount of sucrose used for industrial purpose worldwide; to/sec	~0.025	Ref.[4]

a) Enzyklopädie Naturwissenschaft und Technik (K.-H. Schriever, F. Schuh, Eds.), Zweiburgen Verlag, Weinheim, 1981.

b) A. Goetzberger, V. Wittwer, Sonnenenergie – Physikalische Grundlagen und thermische Anwendungen, Teubner, Stuttgart, 1986.
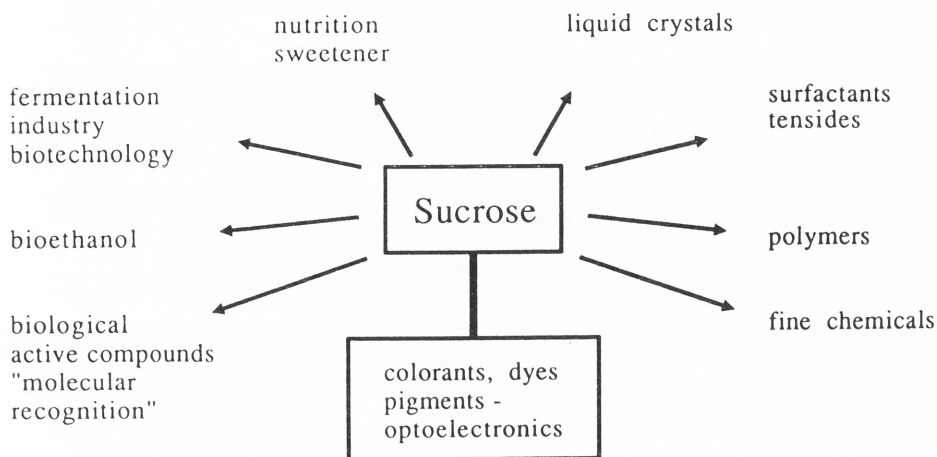
c) W. H. Bloss: Solar, Wind, Waves, Biomass, Heat pumps, Hydraulic energy. Renewable Energy Resources, World Energy Conference, Survey of Energy Resources (F. Bender, K. E. Koch, U. Ranke, W. Süss, Eds.), Munich, London, 1980.

d) Wirtschaftsübersicht: *Zuckerind.* **115** (1990) 215.

Solar energy is an inexhaustible source of energy as is demonstrated by the total amount of irradiation energy generated by nuclear fusion on sun ($> 10^{26}$ W) and the solar irradiation energy received by earth ($> 10^{17}$ W). The biomass produced by photosynthesis, which largely consists of carbohydrates, exceeds 3 000 to/sec. Sucrose industrially produced amounts to more than 3 to/sec worldwide. So far only a minor share is used industrially.

The utilization of sucrose in food and non-food industry is outlined in the following scheme.[5,9] Most of the sucrose is consumed in the food section, other

major fields of application are biotechnology and fermentation processes. Possible applications of sucrose as tensides,[10], surfactants, or liquid crystals[11] are under investigation at different places. Fine chemicals prepared from sucrose are of interest as chiral synthetic units.[12]

nutrition
sweetener

liquid crystals

fermentation
industry
biotechnology

surfactants
tensides

Sucrose

bioethanol

polymers

biological
active compounds
"molecular
recognition"

fine chemicals

colorants, dyes
pigments -
optoelectronics

Sucrose as raw material for food and non-food utilization

As of now, little emphasis was given to saccharides as source-chemicals of functionalized non-carbohydrate polymers or functionalized dyes and pigments with applications in electronics and opto-electronics. In dyes and colourants it is the electronic structure of the chromophors that makes them electron-transfer active as well as suitable for energy transfer interaction. Both of those properties are essential prerequisites for electronic and opto-electronic materials.[13,14]

In the future, new organic opto-electronic materials are expected to gain increasing market shares and pay-offs in technologies for the storage, transformation, and processing of information and energy.[15] Because of its molecular structure and of the high standard of industrial processing, sucrose must be a rich starting material for those chemical components. The same applies to glucose, fructose, cellulose, and starch.

A general strategy for the chemical conversion of carbohydrates into pigments may be outlined as follows:

poly-, oligo-, or monosaccharides $\rightarrow$ $\rightarrow$ π-heterocycles $\rightarrow$ $\rightarrow$
molecular units (molecular materials) for electronic and opto-
electronic applications $\rightarrow$ $\rightarrow$ materials

In the first step, agriculturally harvested materials like poly-, oligo-, or monosaccharides are processed and converted into π-heterocycles which afterwards are transformed into molecular units with dye-behaved functionalization in order to absorb visible light or near infrared irradiation. In the next assembling step, the molecular units attain cooperative behaviour (molecular materials). A final finishing process makes materials ready for practical use.[16] In other words, the conversion of natural materials into those for technical use entails a multistep procedure, of which in this account only the synthesis and characterization of molecular units with electronic and opto-electronic characteristics will be discussed.

3. Five and Six-membered π-Heterocycles from Saccharides

It is well established that a manifold of five and six-membered π-heterocycles can be prepared from sucrose, heptulose, glucose, and fructose, some of which are shown in the following scheme:
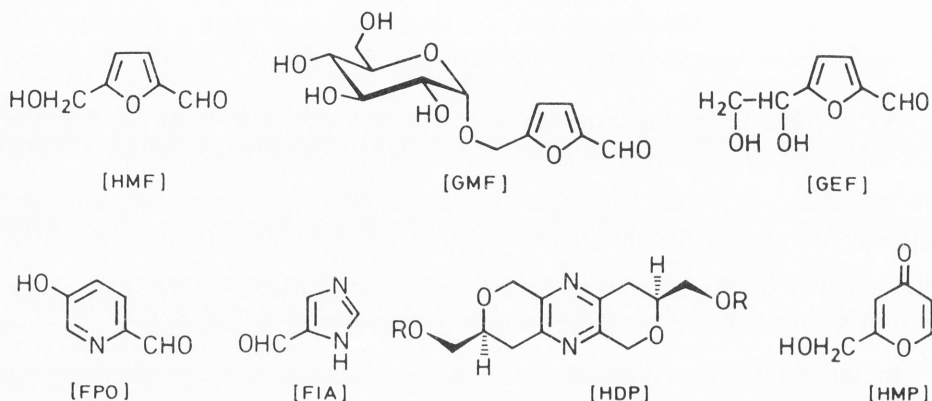

π-Heterocycles with potential use as precursor compounds for electronic and opto-electronic applications

All of these compounds constitute molecular components which, by proper functionalization, can be converted into pigments. The furan and imidazole derivatives 5-hydroxymethyl-furaldehyde (HMF),[17,18] 5-(α-D-glucosyloxymethyl)-furaldehyde (GMF),[19] 5-(dihydroxyethyl)-2-furaldehyde (GEF),[20] and 4-formylimidazole (FIA)[21] are obtained in good yields from glucose (→HMF, FIA), isomaltulose (→GMF), or from sedoheptulose (→GEF). 6-Formyl-3-pyridinol (FPO) is available from (HMF) by electrochemical or chemical conversion.[22]

1,4-Diazines as, for example, palythazin (HDP), again are molecular units with good prospects for reversible electron-transfer behaviour.[23,24] The same applies to the yet unknown 2-hydroxymethyl-4H-pyran-4-one (HMP) which is expected to be convertible into the interesting class of pyrylium salts.[25]

4. 5-Hydroxymethyl-2-furaldehyde (HMF) : Basic Compound for High-grade Chemicals – Molecular Materials for Electronic and Opto-electronic Devices

5-Hydroxymethyl-2-furaldehyde (HMF) turns out to be a versatile π-heterocyclic compound for the conversion into electron-transfer-active (chapter 5) or light-sensitive (chapter 6) molecular components as will be shown by HMF-derived compounds in the ensuing scheme:[26]
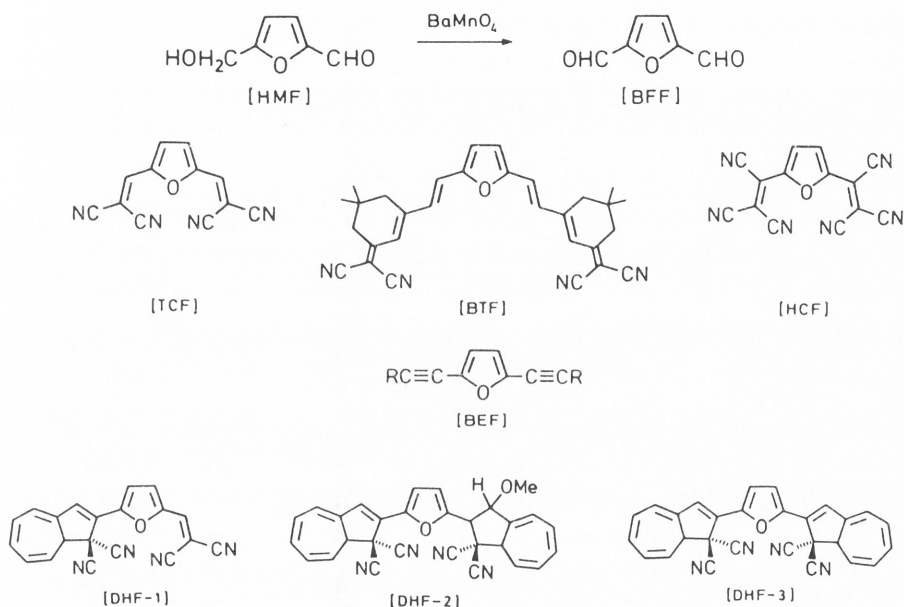
Molecular units derived from 5-hydroxymethyl-2-furaldehyde (HMF)

All of them are prepared from furan-2,5-dicarboxaldehyde (BFF)[27,28] which is synthesized from HMF by oxidation.[29] Tetracyano compound TCF,[30] a key-substance, results by condensation with malononitrile in the presence of base. In the

solid state TCF has a nearly planar structure with an approximate C_{2v}-symmetry and *s-trans* stereochemistry around C-1–C-10[31] (cf. Fig. 1).
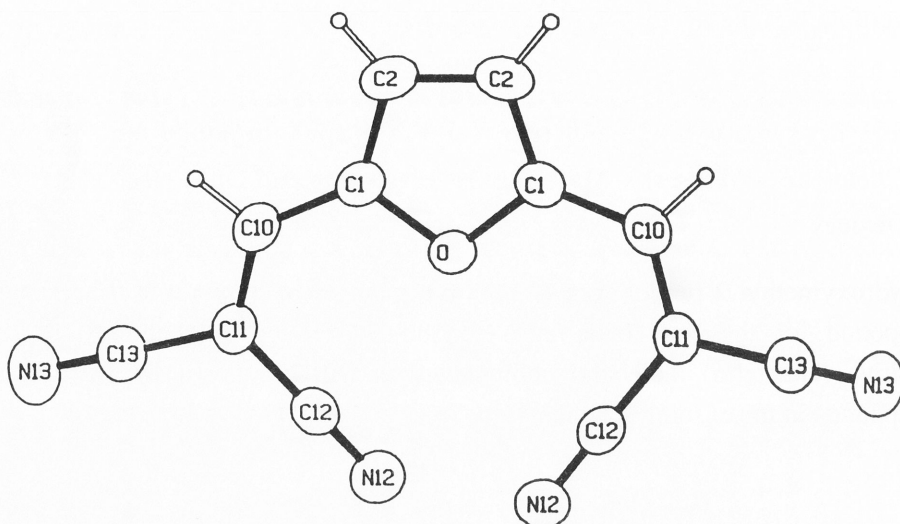

Fig. 1. Crystal structure of TCF. Significant bond lengths: C(1)-C(2) 1.372 Å; C(2)-C(2) 1.401 Å; C(1)-C(10) 1.423 Å; C(10)-C(11) 1.353 Å; C(11)-C(12) 1.429 Å; C(12)-N(12) 1.148 Å

The hexaene furan BTF is formed from the dialdehyde BFF in a two-step sequence: base catalyzed condensation of BFF with isophorone in the first step and subsequent reaction with malononitrile. It turned out, by electrochemical investigations, that TCF and BTF exhibit quite contrasting electron-transfer properties (chapter 5). The hexacyano derivative HCF was synthesized from the tetracyano derivative TCF by twofold addition of cyanide anion (potassium cyanide)[32] and subsequent oxidation of the dianion.[33] The bisacetylene BEF, accessible from BFF in a multistep sequence, is anticipated to be convertible into polyacetylenes and poly(phenylenes), which are of interest as conducting and electrochemichromic polymers.[34,35] Dihydroazulenes DHF-1, DHF-2, and DHF-3 again were synthesized from the tetracyanovinyl derivative TCF in a multistep sequence[34] and differ significantly in their photochromic behaviour as will be shown in chapter 6.[36]

5. Electron-transfer Compounds → Electrochemichromism

The difference of furanoid and benzenoid chemistry, the former representing renewable-resources-chemistry, the latter a typical building block originating from fossil materials, is strikingly substantiated by the electron-transfer behaviour of 2,5-bis(dicyanovinyl)-furan (TCF) and 1,4-bis(dicyanovinyl)-benzene (TCB), which is obtained from terephthal-dialdehyde. Both, cyclic voltammetry[37] and spectroelectrochemistry,[38] disclose significant differences on electrochemical reduction. The results are given in Fig. 2. Unlike the benzenoid TCB, the furan derivative TCF exhibits clear reversible formation of the radical anion (TCF)$^{\bullet-}$ and the dianion (TCF)$^{2-}$. The curvature of the cyclic voltammogram of TCB[39] is best explained by an EC-type mechanism, representing a two-step-reaction consisting of a one-electron reduction to the radical anion (TCB)$^{\bullet-}$ in the first step and a subsequent chemical step leading to dimerization under C-C-bond formation.[40]
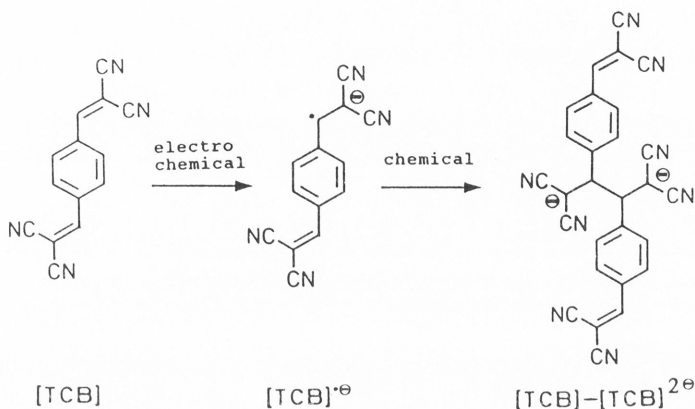
Electron-transfer chemistry (EC-behaviour) of 1,4-bis(dicyanovinyl)-benzene (TCB)
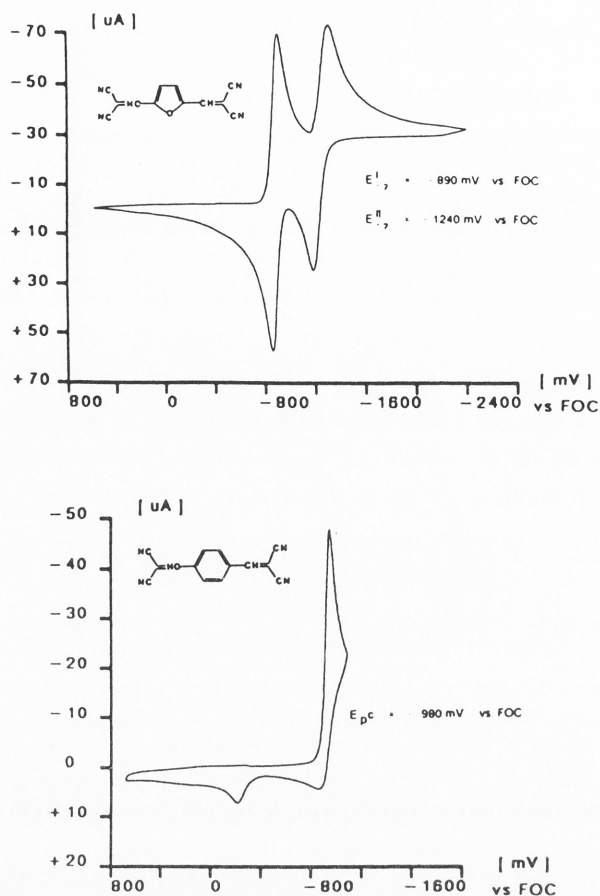
Fig. 2. Cyclic voltammograms of TCF (above) depicting the reversible formation of radical anion and dianion, and of TCB (below) showing the formation of the radical anion and subsequent fast C-C-dimerization[27]

The reversibility of the reduction sequence

$$[TCF] \rightleftharpoons [TCF]^{\bullet-} \rightleftharpoons [TCF]^{2-}$$

is analytically proven by UV/VIS-spectroelectrochemistry (Fig. 3) and by the reversible change of colour (electrochemichromism). In solution, the neutral compound TCF appears to be yellow and turns blue on reduction to the radical anion. Further reduction to the dianion leads to an orange solution (Table 2).
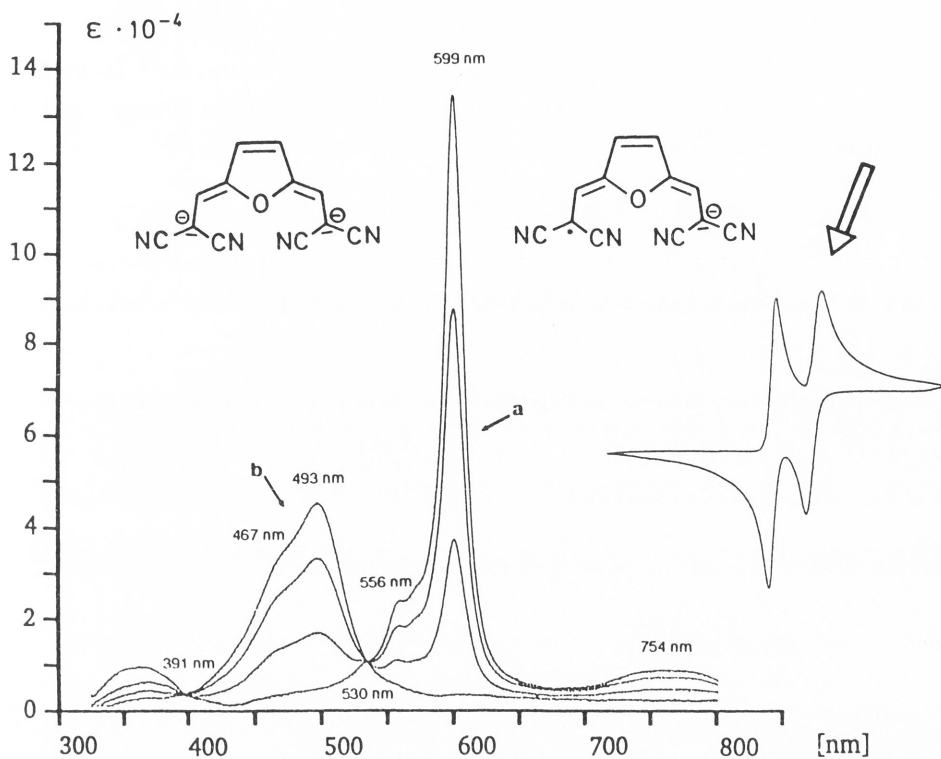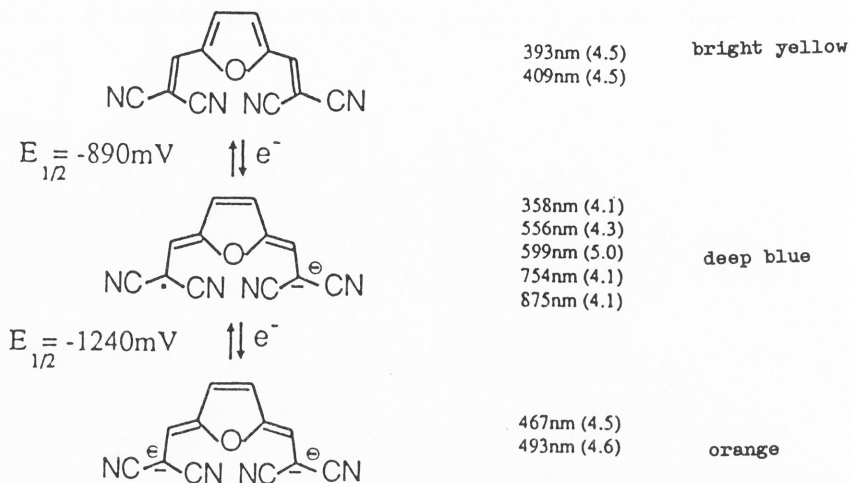
Fig. 3. Electrochemichromism of radical anion / dianion conversion of [TCF]•⁻ and [TCF]²⁻ as shown by UV/VIS-spectroelectrochemistry (Taken from ref.[27]). Insert: Cyclic voltammogram with an arrow indicating the potential of generating the electronic spectra.

Table 2. Electrochemical potential [vs. ferrocene (FOC)] and absorption spectra on reduction of the electron-transfer compounds TCF, HCF, BTF, and TCNQ

Compound	neutral compound λ_{max}(nm)	radical anion		dianion	
		$E_{1/2}$(mV)	λ_{max}(nm)	$E_{1/2}$(mV)	λ_{max}(nm)
TCF	393(4.5)	-890	599(5.0)	-1240	493(4.6)
HCF	423(4.5)	-205	663(5.1)	-570	603(4.5)
BTF	514(4.3)	-1190	mixed potential	-1010	617(4.5)
TCNQ	392(4.8)	-190	842(4.7)	-740	330(4.8)

The molecular description of this electrochemichromic phenomenon is given in the following scheme. Electrochromism (electrochemichromism)[41] is gaining application in optical displays, light valves, electrooptical switching, and as photoconductives.[42]

	393nm (4.5) 409nm (4.5)	bright yellow

$E_{1/2} = -890\text{mV}$ $\updownarrow e^-$

	358nm (4.1) 556nm (4.3) 599nm (5.0) 754nm (4.1) 875nm (4.1)	deep blue

$E_{1/2} = -1240\text{mV}$ $\updownarrow e^-$

	467nm (4.5) 493nm (4.6)	orange

Electron-transfer behaviour, contrasting to [TCF], is exhibited by the polyene BTF (Table 2).[43] The reduction gives a single wave, analyzed as a two-electron reduction, leading in one step to the dianion [BTF]$^{2-}$ with no indication of the paramagnetic radical anion [BTF]$^{\bullet-}$ as an intermediate. Therefore, on the basis of these results, the tetracyano compound TCF is found to be a one-electron mediator, whereas the hexaenic derivative BTF appears to be a two-electron transfer reagent.[44] Applications of the different behaviour in the realm of electron-transfer catalysis[45] are under investigation.

The bis(triscyanovinyl) derivative HCF was synthesized in order to explore access of carbohydrate-derived heterocycles into the chemistry of stable radical ion salts. It is well established that in the solid state radical ions may show electrical conductivity.[46] Due to the six cyano substituents, HCF is reduced at less negative potential compared to the tetracyano compound TCF (Table 2). Furthermore, in comparison with the reduction potential of tetracyanoquinodimethane (TCNQ) it turns out that the radical anions of HCF and TCNQ have rather the same reduction potential. Tetracyanoquinodimethane (TCNQ) is one of the prototypes of "organic metals" with conducting or semiconducting properties.[47] The findings that [HCF]$^{\bullet-}$ and [HCF]$^{2-}$ as well as [TCNQ]$^{\bullet-}$ and [TCNQ]$^{2-}$ are reversibly formed by

electrochemical reduction of the neutral compounds is again verified by UV/VIS/NIR-spectroelectrochemistry as exemplified by the one-electron reduction to the radical anions in Fig. 4 and Fig. 5.
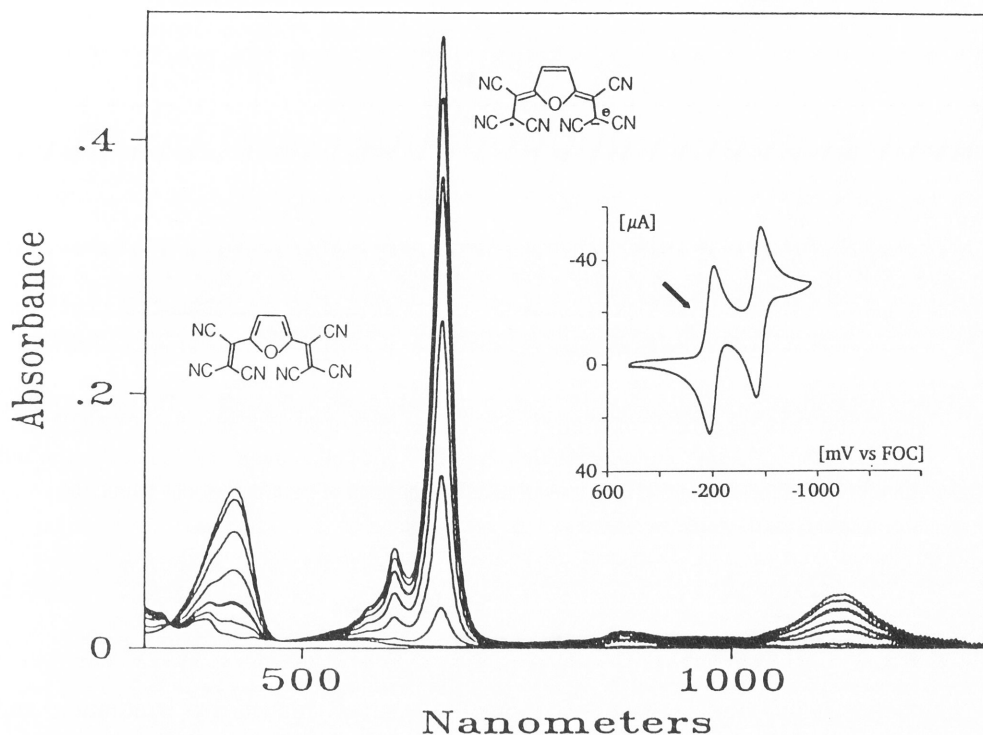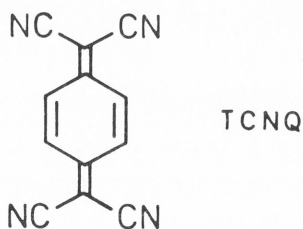

Fig. 4. UV/VIS-spectroelectrochemistry of the formation of the radical anion [HCF]$^{\bullet-}$ from HCF by electrochemical reduction. Insert: Cyclic voltammogram of radical anion and dianion formation of HCF, the arrow indicating the scan of potential under which the absorption spectra were monitored
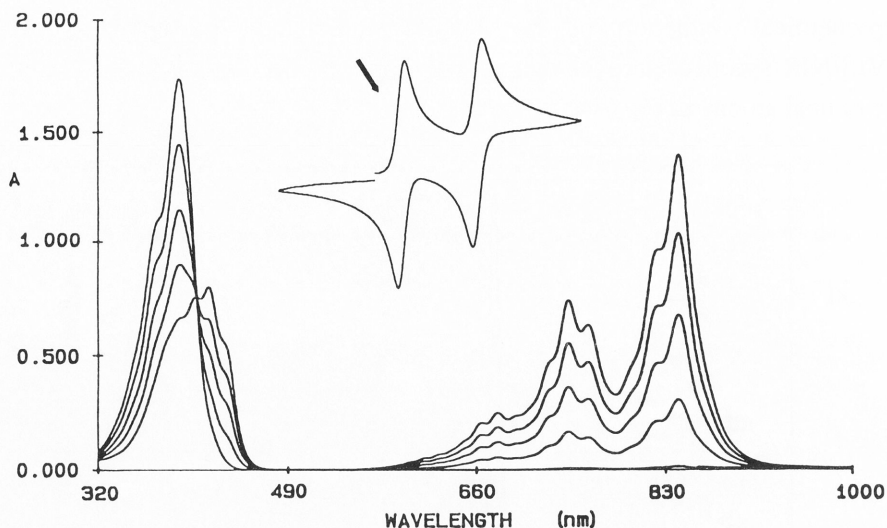
Fig. 5. UV/VIS-spectroelectrochemistry of the formation of the radical anion [TCNQ]$^{\bullet-}$ from TCNQ by electrochemical reduction. Insert: Cyclic voltammogram of radical anion and dianion formation of TCNQ, the arrow indicating the scan of potential under which the absorption spectra were monitored

6. Light-sensitive Compounds – Photochromism

The phenomenon which describes change of colour caused by irradiation and thermal or photochemical bleaching is termed photochromism.[48] Photochromic materials offer interesting applications including the storage and processing of information and the conversion of irradiation energy into heat.[49] Photochromism is abundant in nature, as for example in the processes of vision or photomorphogenesis.[50] Photochromes are expected to be capable of the storage of information as high as the theoretical storage density of 6.5×10^{12} bits/cm^3 at $\lambda_{max} = 532$ nm in a 3D memory.[51]

In his doctoral dissertation, Knöchel[52] made the observation, that a solution of dihydroazulene (DHA), when exposed to sun light, turns deeply red and reverts to yellow in the dark. It turned out that a photorearrangement of dihydroazulene (DHA) to vinylheptafulvene (VHF) occurs, i.e. an electrocyclic 10π-electron arrangement:[53]

DHA   cisoid- VHF   transoid- VHF
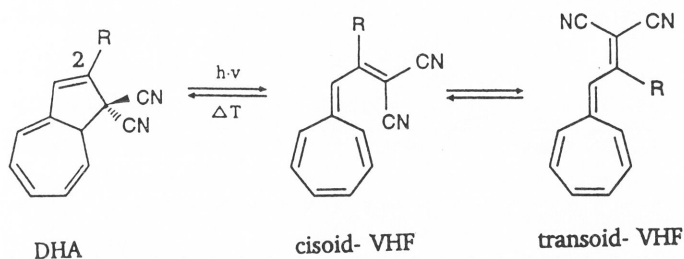
By increasing temperature fading of the colour is achieved by the thermal electrocyclization VHF → DHA. The process is reversible and, since on irradiation a long-wave length absorption appears, the process is termed a "normal" or "positive" photochromism.

A furan substituent at C-2 in DHA has a significant effect on the kinetics of the photochemical and thermal reactions as shown by the photochromes DHF-1, DHF-2, and DHF-3. To observe colouration on irradiation, DHF-1 has to be cooled down to -50 °C. This is explained by a fast thermal back-reaction leading to immediate bleaching at room-temperature. The same is true for DHF-3. In contrast, DHF-2 rearranges at room-temperature photochemically to the red-coloured VHF-2 and, thus, exhibits room-temperature photochromism.

Table 3. Long-wavelength absorption maxima of the photochromic system DHF / VHF

compounds	solvent / temp.	λ_{max}(nm)		$\Delta\lambda_{max}$(nm)
		DHF	VHF	
DHF-1 / VHF-1	EtOH / 200 K	440	548	108
DHF-2 / VHF-2	MeCN / r.t.	369	494	125
DHF-3 / VHF-3	EtOH / 200 K	454	500	46

dark-form
absorption band 440 nm
yellow

DHF-1

light-form
absorption band 548 nm
magenta
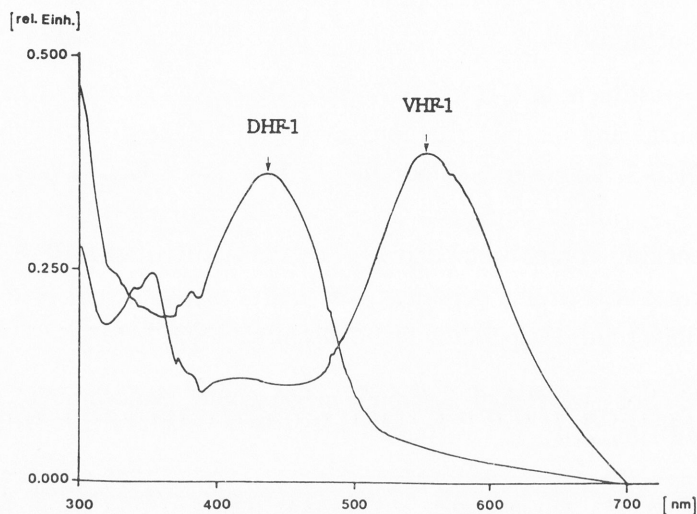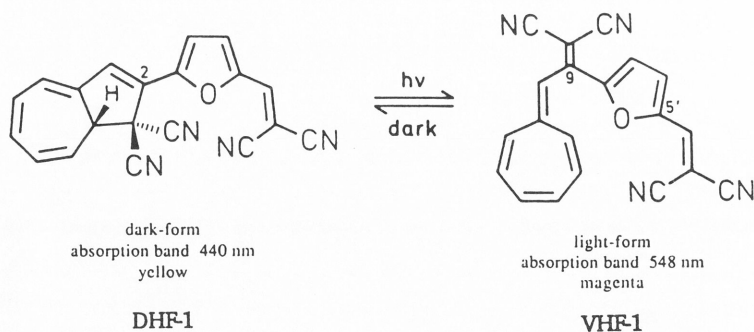
VHF-1

Fig. 6. Photochromism at -50 °C in ethanol, as exemplified by the HMF-derived system DHF-1 ⇌ VHF-1. Light induced process DHF-1 → VHF-1, thermal backreaction VHF-1 → DHF-1 (taken from ref.[27])

7. Light-sensitive Electron-transfer Compounds – Chemical and Physical Switching

The furan derivatized photochromic molecular components led us into an exiting field of new chemistry and physics dealing with functionalized pigments for the chemical and physical switching.[27,54] The underlying concept is to synthesize multifunctional dye compounds contained in light-sensitive and electron-transfer active subunits and to subject those molecular components to physico-chemical investigation by combination-techniques.[55] The HMF-derived photochromic compound DHF-1, composed of the light-sensitive dihydroazulene substructure and

the electron-transfer active dicyanovinylfuryl group, were selected for testing. Since, on conversion of DHF into the deeply coloured vinylheptafulvene VHF, the electron acceptor strength of the dicyanovinylfuran is increased, the electrochemical reduction of the light-adapted vinylheptafulvene form must occur at lower negative reduction potential. This presumption could be proven by cyclic voltammetry of a structurally related compound.[54] A new technique (photomodulation amperometry, cf. Fig. 7), the instrumentation comprising of an electrochemical cell equipped with optically transparent electrodes as working electrodes, a platinum counter electrode, and a reference electrode, was employed. Subjecting a solution of the electron-transfer active photochromic compound to a light-pulse gives, under appropriate instrumental conditions, the current / time (i/t)-diagram as shown on the right in Fig. 7.
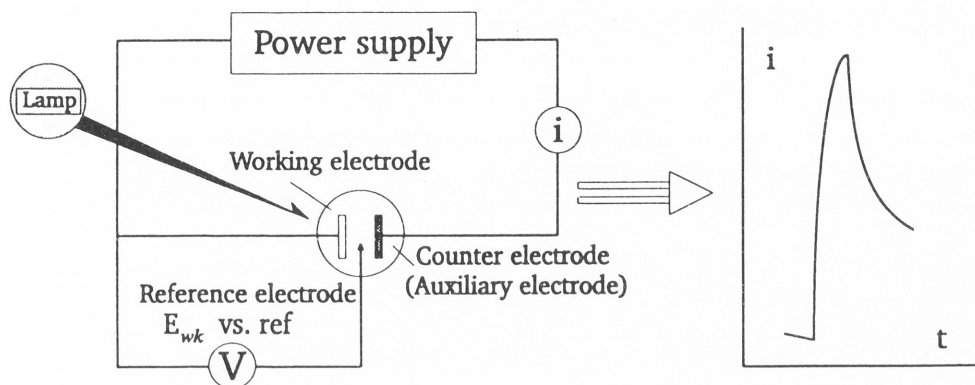

Fig. 7. Schematic representation of the instrumental set-up for photomodulation amperometry

Fig. 8 gives a schematic representation of the molecular processes involved in the described photomodulation-amperometry technique. It is important to note that the electrode potential has to be adjusted so that under "dark"-conditions no response is given. In the first step dihydroazulene DHF-1 is photochemically rearranged into vinylheptafulvene VHF-1, generating a stronger electron-acceptor and leading to an onset of the electric current as long as electroactive species are formed. In the dark the current flow gradually decreases. A sequence of photomodulation obtained by DHF-1 is given in Fig. 9.
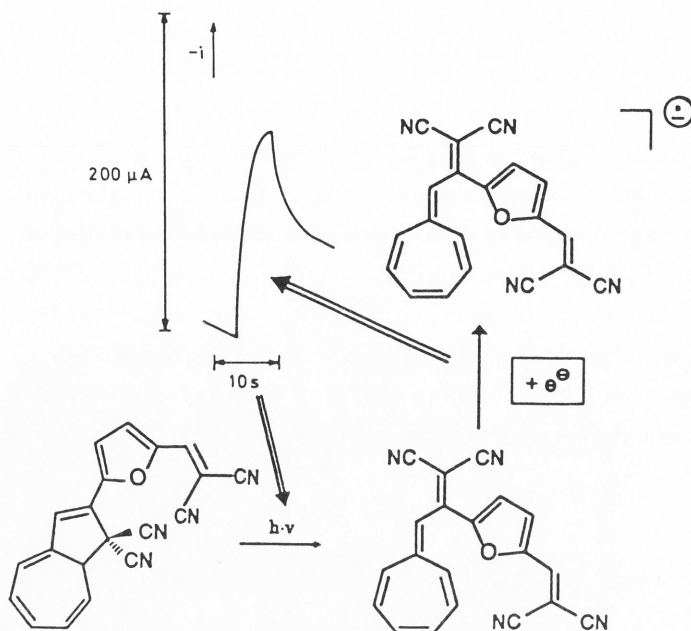
Fig. 8. Light-triggered electron-transfer, monitored by photomodulation amperometry. Instrumental set-up as displayed in Fig. 7.
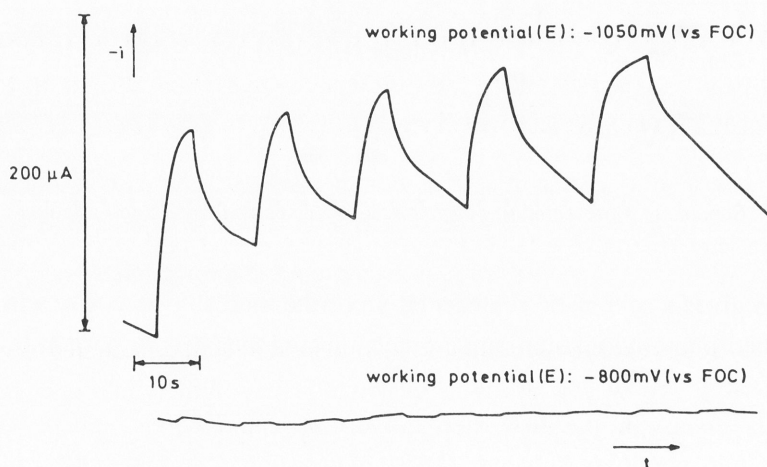

Fig. 9. Photostimulated electron-transfer activation of DHF-1 $\rightleftharpoons$ VHF-1 monitored by photomodulation amperometry (figure taken from ref.[27])

These observations can be explained in a qualitative way by simple molecular-orbital considerations as described in Fig. 10: the occupied energy level, representing the cathodic electrode potential, is maintained constant under this

approximation, whereas the energy of the lowest unoccupied orbital (LUMO), which is assigned to the π-system of the pigment, depends on the structure as indicated in Fig. 10. By light-induced rearrangement, DHF-1 → VHF-1, the energy of the LUMO decreases and the transfer of electrons becomes favourable thermodynamically.
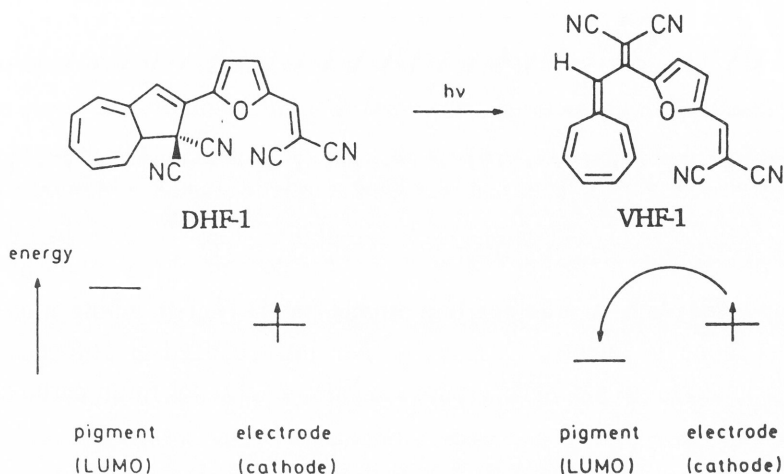

Fig. 10. Schematic description of the electronic changes by photostimulated electron-transfer

This process of switching, at least on a molecular level, allows to transcribe light-puls-information into electrical signals.

8. Conjugated Polyenes from Furan-2,5-dicarbaldehyde – Poly(Arylene Vinylenes)

Poly(arylene vinylenes), being composed of alternating and conjugated arylene and vinylene groups, are of interest with respect to macromolecular semiconductors, photoconductors, and basis material for conducting polymers.[56]

Conjugated polyenes of a structurally related type were obtained by condensation of *p*-xylylene dicyanide (XDC) with 2,5-furan-dicarbaldehyde (BFF) under basic conditions (sodium ethoxide in ethanol).
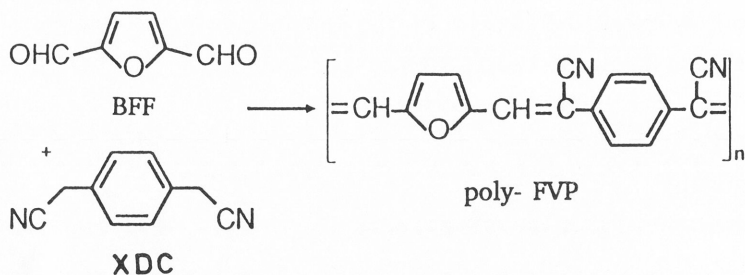
The resulting, high-melting (mp > 300 °C) and insoluble material, separated from low-molecular weight compounds by extraction with toluene, awaits scrutinized structural characterization. Characteristic bands obtained from the FT-IR-spectrum (Fig. 11) give some information on the structure of the polymer. A high-intensity band at 2208 cm^{-1} is typically for the stretching mode of a nitrile group conjugated with a carbon-carbon double bond. The stretching mode for the C=C-double bond is found at 1597 cm^{-1}. The intense band at 1667 cm^{-1}, which must be assigned to an aldehyde group, indicates a terminal furan carboxaldehyde substructure.[57]
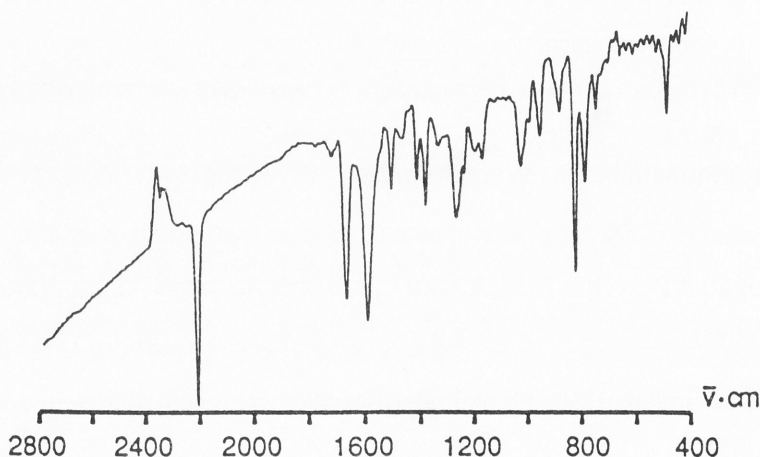

Fig. 11. FT-IR-spectrum of the oligomer or polymer formed by condensation of XDC and BFF

Investigation of the chemical and physical properties of poly(FVP) are in progress.

9. Carbohydrate-modified Conducting Polymers – Functionalised Polyazulenes

In this final section recent results will be presented on carbohydrate-modified conducting polymers. This topic unites several fields of interest:

(i) the chemistry of conducting polymers,

(ii) the relevance and importance of carbohydrates in intermolecular interaction and recognition, and

(iii) the use of carbohydrates as auxiliaries to increase solubility in water.

Conducting organic polymers have potential technical prospects in the following fields: rechargeable batteries, chemical sensors, conducting films, electronic and memory devices,[58] or chemically modified electrodes.[59]

In previous studies we found that C-2 substituted azulenes are versatile monomers for the generation of chemically modified polyazulenes by electropolymerization:[60]

monomer	polymer	electrochemical oxidation
		(anion doping)
GMA	poly- GMA	conducting poly- GMA
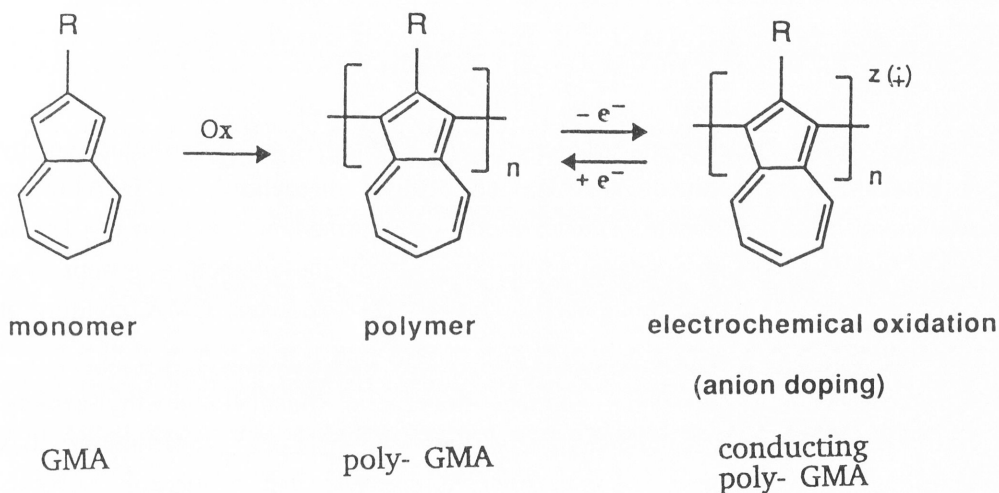
Azulenes are assumed to electropolymerize under bond formation at C-1 and C-3 whereas radical cations are formed in the first step which subsequently dimerize or react with a neutral azulene. From azulene chemistry it is well established that oxidative dimerization occurs regiospecifically at C-1 or C-3. Therefore, substituents at C-2 do not interfere with polymerization. Charging of the polymeric film can be obtained by oxidative or reductive doping furnishing cations or anions, respectively. Doping, in general, leads to an increase in conductivity.

An efficient synthetic route for the monomeric species was developed recently.[61] An extension of this reaction sequence to carbohydrate chemistry gives the azulene-carbohydrate-conjugate GMA with glycosidically linked glucose:[62]

[ABG]
R=Acetyl

HMA

R=H [GMA]
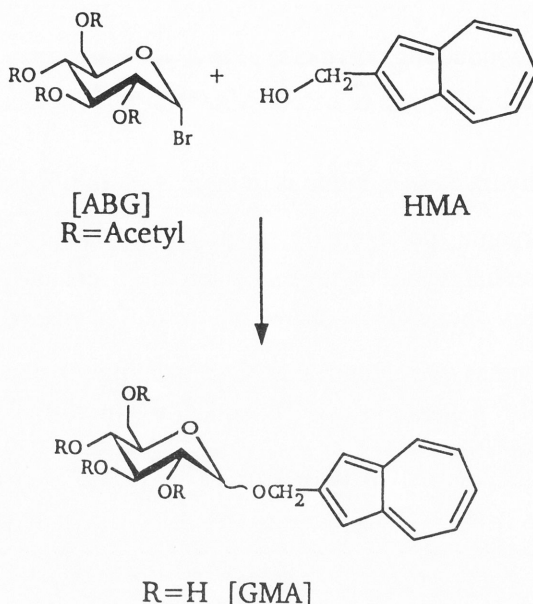
The glucosidation was carried out under Koenigs-Knorr conditions, i.e. by reaction of acetobromoglucose (ABG) with 2-hydroxymethylazulene (HMA) in the presence of silver carbonate. The anomers were formed in a ratio $\alpha:\beta = 1:9$ as shown by ^{1}H-NMR spectroscopy. The removal of the protecting groups was achieved with 10 % methanolic KOH. Unlike other azulenes, GMA, melting at 189 °C, is soluble in water.

The electropolymerization of the monomeric glucosyloxymethyl-azulene (GMA) is shown in Fig. 12, analytically monitored by cyclic voltammetry. It is interesting to note that GMA can be electropolymerized in organic solvents (acetonitrile) and in water as well. The irreversible electrooxidation is demonstrated by the initiation curves in Fig. 12 which clearly show different peak currents for the oxidative and the reductive steps. The overall curvature of the diagram in Fig. 9 clearly indicates the formation of an electrically conducting film with conductive activity at about 600 mV (vs. Ag/AgCl):
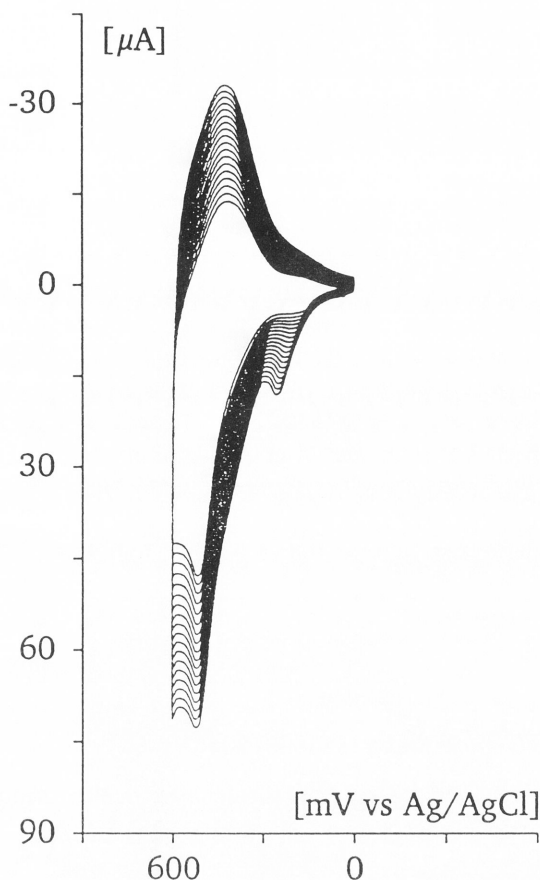
Fig. 12. Electropolymerization of GMA under formation of poly(GMA) and electrochemical activation under formation of an electrically conducting polymer. The polymerization was undertaken in water / 0.1 mol $NaClO_4$ on a Pt-electrode

Investigations on the structure of poly(GMA) and on the physical and chemical properties of carbohydrate modified polymers are in progress.

10. Summary and Conclusions

In the introduction, the chemical conversion of carbohydrates into high-grade chemicals (molecular units) with option and opportunities in the chemistry of information- and energy-transfer, is outlined. Emphasis is given to conceptional strategies. π-Heterocycles play the role of key-intermediates. First encouraging results are given, demonstrating preparation and characterization of electrochemichromic, photochromic, and electrically conducting molecular

components. Further intensive cooperative inquiries at university and industry have to be undertaken in the future. Especially in regard of transforming molecular units into molecular materials. Chirality as an outstanding property of carbohydrates was given only modest consideration at this stage of the study, but will receive stronger accentuation in future work.

References

1. J. Daub: Molekulare Bausteine aus niedermolekularen Kohlenhydraten. *Nachr. Chem. Tech. Lab.* **36** (1988) 896-899.

2. J. Daub: Abstract. *Zuckerind.* **115** (1990) 204.

3. F. W. Lichtenthaler: Niedermolekulare Kohlenhydrate als Rohstoffe für die Chemische Industrie. *Nachr. Chem. Techn. Lab.* **38** (1990) 866.

4. For Reviews on Renewable Resources, see:

    a) H. Baumann, M. Bühler, H. Fochem, F. Hirsinger, H. Zoebelein, J. Falbe: Natürliche Fette und Öle – nachwachsende Rohstoffe für die chemische Industrie. *Angew. Chem.* **100** (1988) 41-62; *Angew. Chem., Int. Ed. Engl.* **27** (1988) 41-62.

    b) D. Osteroth: Von der Kohle zur Biomasse – Chemierohstoffe und Energieträger im Wandel der Zeit. Springer Verlag, Berlin, 1989.

    c) Der Bundesminister für Forschung und Technologie: Nachwachsende Rohstoffe. *Bundesministerium für Forschung und Technologie*, Bonn, 1986.

    d) B. A. Tokay: Biomass Chemicals. *Ullmann's Encyclopedia of Industrial Chemistry* (W. Grehartz, Ed.), 5th Ed., Vol. A4, p. 99 ff., VCH Verlagsgesellschaft, Weinheim, 1985.

5. For Reviews on the Utilization of Saccharides, see:

    a) H. Schiweck, K. Rapp, M. Vogel: Utilization of Sucrose as an Industrial Bulk Chemical – State of the Art and Future Implications. *Chem. Ind (London)* **1988**, 228-234.

b) J. L. Hickson (Ed.): Sucrochemistry. *ACS Symposium Series* **41**, Am. Chem. Soc., Washington D.C., 1977.

6. M. G. Clark: Materials for Optical Storage. *Chem. Ind. (London)* **1985**, 258-263.

7. a) J. Daub, K. M. Rapp, J. Salbeck, H. Schiweck, P. Seitz, R. Wild: Organic Materials Based on Fructose Chemistry: Photochromics and ET-reagents Using 5-Hydroxymethyl furfuraldehyde as Starting Compound. 4th European Carbohydrate Symposium, Darmstadt, 1987, Abstract D-18.

    b) J. Daub, T. Knöchel, K. M. Rapp, J. Salbeck, R. Wild: Materials Science Opportunities in Renewable Resources Chemistry: Molecular Materials Based on Carbohydrate Chemistry. 14th International Cabohydrate Symposium, Stockholm, 1988, Abstract p. 401.

    c) J. Daub, J. Salbeck, K. M. Rapp, H. Schiweck: Furans from Fructose: HMF Derivatives with Special Electrochemical and Electrochromic Properties. 15th International Carbohydrate Symposium, Yokohama, 1990, Abstract D-028.

8. G. G. Birch, K. J. Parker (Eds.): Sugar: Science and Technology. Applied Science Publ., London, 1979.

9. a) A. Gaset, M. Delmas: Products Derived from Sugars. *Comm. Eur. Communities* **1986**, 46; *Chem. Abstr.* **106** (1986) 10603.

    b) R. Khan: Chemistry and New Uses of Sucrose: How Important?. *Pure Appl. Chem.* **56** (1984) 833.

    c) C. E. James, L. Hough, R. Khan: Sucrose and Its Derivatives. *Progr. Chem. Org. Nat. Prod.* **55** (1989) 117-184.

10. T. Böcker, J. Thiem: Synthese und Eigenschaften von Kohlenhydrat-Tensiden. *Tenside* **26** (1989) 318.

11. G. A. Jeffrey: Carbohydrate Liquid Crystals. *Acc. Chem. Res.* **19** (1986) 168-173.

12. N. R. Williams (Ed.): Carbohydrate Chemistry – A Specialist Periodical Report. The Royal Society of Chemistry, London, annually.

13. a) H. Zollinger: Colour Chemistry. VCH Verlagsgesellschaft, Weinheim, 1987.

    b) J. Rochlitz: Farbstoffe für die Energie-Umwandlung. *Chimia* **34** (1980) 131-144.

14. a) F. L. Carter, (Ed.): Molecular Electronic Devices. Marcel Dekker, Inc., New York, 1982.

    b) R. W. Munn: Molecular Electronics. *Chem. Britain* **1984**, 518.

    c) A. Aviram: Molecules for Memory, Logic, and Amplification. *J. Am. Chem. Soc.* **110** (1988) 5687-5692.

15. H. Steppan, G. Buhr, H. Vollmann: Resisttechnik – ein Beitrag der Chemie zur Elektronik. *Angew. Chem.* **94** (1982) 471-485; *Angew. Chem., Int. Ed. Engl.* **21** (1982) 455.

16. For a Similar Approach, see: J. Simon, J.-J. André, A. Skoulios: Molecular Materials. I. Generalities. *Nouv. J. Chim.* **10** (1986) 295.

17. T. El Hajj, A. Masroua, J.-C. Martin, G. Descotes: Synthèse de l'Hydroxyméthyl-5 Furane Carboxaldehyde-2 et de ses Dérivés par Traitement Acide de Sucres sur Résines Échangeuses d'Ions. *Bull. Soc. Chim. Fr.* **1987**, 855-860.

18. O. Theander, D. A. Nelson: Aqueous, High-temperature Transformation of Carbohydrates Relative to Utilization of Biomass. *Adv. Carbohydr. Chem. Biochem.* **46** (1988) 273.

19. F. W. Lichtenthaler: Large-scale Adaptable Routes from Monosaccharides to Versatile Six-Carbon Building Blocks. *Zuckerind.* **115** (1990) 198 and 790-798. See also: *These Proceedings*, p. ... ff.

20. C. Fayet, J. Gelas: Access to a Chirally Substituted Furan. Synthesis of 5-(D-*glycero*-1,2-Dihydroxyethyl)-2-furaldehyde from a Natural Heptulose. *Heterocycles* **20** (1983) 1563-1566.

21. J. R. Totter, W. J. Darby: 4-Hydroxymethyl-imidazole Hydrochloride. *Organ. Synth. Coll.* Vol. III, **1955**, 460-464.

22. a) N. Elming, N. Clauson-Kaas: Transformation of 2-(Hydroxymethyl)-5-(aminomethyl)furan into 6-Methyl-3-pyridinol. *Acta Chem. Scand.* **10** (1956) 1603-16.. .

    b) U. Schöberl: Unpublished work, University of Regensburg, 1989.

23. P. Jarglis, F. W. Lichtenthaler: Eine stereospezifische Synthese von *(S,S)*-Palythazin aus D-Glucose. *Angew. Chem.* **94** (1982) 140-141; *Angew. Chem., Int. Ed. Engl.* **21** (1982) 141-142.

24. W. Kaim: Die vielseitige Chemie der 1,4-Diazine – organische, anorganische und biochemische Aspekte. *Angew. Chem.* **95** (1983) 201-221; *Angew. Chem., Int. Ed. Engl.* **22** (1983) 171.

25. E. Fischer, F. W. Lichtenthaler: Ergiebige Synthese von Zucker-3,2-enolonen aus 2-Hydroxyglykalen und ihre Umwandlung in γ-Pyrone. *Angew. Chem.* **86** (1974) 590-592; *Angew. Chem., Int. Ed. Engl.* **13** (1974) 548-549.

26. J. Daub, K. M. Rapp, P. Seitz, R. Wild (Süddeutsche Zucker AG): Dicyanvinylsubstituierte Furanderivate, Verfahren zu ihrer Herstellung und deren Verwendung. D.B.P. 3 718 917 (1988); *Chem. Abstr.* **110** (1989) P 212593k.

27.   J. Daub, J. Salbeck, T. Knöchel, C. Fischer, H. Kunkely, K. M. Rapp: Lichtsensitive und elektronentransferaktive molekulare Bausteine: Synthese und Eigenschaften eines photochemisch schaltbaren, dicyanvinylsubstituierten Furans. *Angew. Chem.* **101** (1989) 1541-1542; *Angew. Chem., Int. Ed. Engl.* **28** (1989) 1494-1495.

28.   C. Dominguez, A. G. Csaky, J. Magano, J. Plumet: Reactions of 2,5-Furandicarbaldehyde with Stabilized Phosphonium Ylides. Applications to the Synthesis of 5-Vinyl-2-furaldehyde and 2,5-Divinylfuran Derivatives. *Synthesis* **1989**, 172-175.

29.   H. Firouzabadi, E. Ghaderi: Barium Manganate. An Efficient Oxidizing Reagent for Oxidation of Primary and Secondary Alcohols to Carbonyl Compounds. *Tetrahedron Lett.* **1978**, 839-842.

30.   K. Yu. Novitskii, V. P. Volkov, Yu. K. Yurev: Furan-2,5-Dialdehyde and its Reactions with Malonic Acid Derivatives. *J. Gen. Chem. USSR (Engl. Transl.)* **31** (1961) 494-497.

31.   U. Schöberl: Organische Materialien aus niedermolekularen Kohlenhydraten – Wege zur Herstellung lichtsensitiver Verbindungen. *Diploma Thesis*, University of Regensburg, 1989; Structure Determination by Dr. Klement, University of Regensburg and Prof. G. Maas, University of Kaiserslautern.

32.   B. B. Corson, R. W. Stoughton: Reactions of Alpha, Beta-Unsaturated Dinitriles. *J. Amer. Chem. Chem. Soc.* **50** (1928) 2825-2837.

33.   a) U. Schöberl: *Doctoral Dissertation*, University of Regensburg, in preparation.

      b) On the synthesis of functionally related benzenoid compound, see: P. M. Allemand, P. Delhaes, Z. G. Soos, M. Nowak, K. Hinkelmann, F. Wudl: *Synth. Meth.* **27** (1988) B-243.

34.   U. Schöberl: Organische Materialien aus niedermolekularen Kohlenhydraten – Wege zur Herstellung lichtsensitiver Verbindungen. *Diploma Thesis*, University of Regensburg, 1989.

35.   a) C. K. Chiang, A. J. Heeger, and A. G. MacDiarmid: Synthesis, Structure, and Electrical Properties of Doped Polyacetylene. *Ber. Bunsenges. Phys. Chem.* **83** (1979) 407-417.

      b) M. Mastragostino, A. M. Marinangeli, A. Corradini, S. Giacobbe: Conducting Polymers as Electrochromic Materials. *Synth. Meth.* **28** (1989) C501.

36.   U. Schöberl, J. Daub: Manuscript in preparation.

37. Cyclic Voltammetry: In an electrochemical cell containing working electrode, counter electrode and reference electrode, the potential of a stationary electrode in an unstirred solution of the electroactive compound and an inert electrolyte is varied linearly with time by a defined sweep rate. After reaching a certain potential, the potential scan is reversed. The resulting current/potential (i/e)-diagram is monitored. J. Heinze: Cyclovoltammetrie – die "Spektroskopie" des Elektrochemikers. *Angew. Chem.* **96** (1984) 823-840; *Angew. Chem., Int. Ed. Engl.* **23** (1984) 831.

38. Spectroelectrochemistry combines electrochemical and spectroscopic techniques. For measurements an electrochemical cell containing preferentially optically transparent electrodes (OTes) is applied. Electronic spectra depending on the electrochemical potential are obtained:

   a) T. Kuwana, W. R. Heineman: Study of Electrogenerated Reactants Using Optically Transparent Electrodes. *Acc. Chem. Res.* **9** (1976) 241-248.

   b) J. Salbeck, I. Aurbach, J. Daub: CD-Spektroelektrochemie – Eine neue Methode zur Charakterisierung chiraler Elektronentransferreagenzien und chiraler Zwischenstufen – Vorstellung einer spektroelektrochemischen Zelle. *Dechema-Monographien* **112** (1988) 177.

39. a) R. O. Loutfy, C. K. Hsiao, B. S. Ong, B. Keoshkerian: Electrochemical Evaluation of Electron Acceptor Materials. *Can. J. Chem.* **62** (1984) 1877.

   b) M. Sertel, A. Yildiz, H. Baumgärtel: Mechanism of the Electroreduction of 1,1-Dicyanoethylene Derivatives. *Electrochimica Acta* **31** (1986) 1625.

40. On EC-type Mechanisms, see: J. Salbeck, J. Daub: Methoxy-substituierte Acenazulene: Chemische und elektrochemische Reduktion in aprotischem Lösungsmittel – Charakterisierung von Radikalanionen, s-verknüpften Dianionen und cyclisch konjugierten Dianionen. *Chem. Ber.* **122** (1989) 1681-1690, and literature cited there.

41. Short definition of these two terms: Electrochromism denotes the change of a compound's colour if subjected to an electrical field. Electrochemichromism means the change of colour on reductive or oxidative electron transfer.

42. F. G. K. Baucke, J. A. Duffy: Darkening Glass by Electricity. *Chem. Britain* **21** (1985) 643-646.

43. J. Salbeck, U. Schöberl, K. M. Rapp, J. Daub, manuscript submitted.

44. More detailed information on one-electron and two-electron transfer is contained in:

   a) L. Eberson: Electron Transfer Reactions in Organic Chemistry. *Reactivity and Structure Concepts in Organic Chemistry* **25** (1987) 1;

   b) J. K. Kochi: Elektronen- und Ladungsübertragung: Zur Vereinheitlichung der Mechanismen organischer und metallorganischer Reaktionen. *Angew. Chem.* **100** (1988) 1331-1372; *Angew. Chem., Int. Ed. Engl.* **27** (1988) 1227-1268.

c) D. Astruc, M. Lacoste, L. Toupet: How to Design a Fast Two-electron Transfer: Structural Rearrangement in the Second Electron Transfer provides Stabilization. *J. Chem. Soc., Chem. Commun.* **1990**, 558;

d) K. Hinkelmann, J. Heinze: Analysis of "Two-electron" Transfer Processes by Cyclic Voltammetry. *Ber. Bunsenges. Phys. Chem.* **91** (1987) 243-249.

45. H. Lund: Catalysis by Electron Transfer Reagents in Organic Electrochemistry. *J. Mol. Cat.* **38** (1986) 203.

46. For reviews on organic metals, see:

J. H. Perlstein: "Organische Metalle" – Die intermolekulare Wanderung der Aromatizität. *Angew. Chem.* **89** (1977) 534-549; *Angew. Chem., Int. Ed. Engl.* **16** (1977) 519-... .

A. J. Epstein, J. S. Miller: Eindimensionale Leiter. *Spektrum der Wissenschaft* **1979**, 63.

47. For a pertinent review on salts of tetracyanoquinodimethane, see: J. B. Torrance: The Difference between Metallic and Insulating Salts of Tetracyanoquinodimethane (TCNQ): How to Design an Organic Metal. *Acc. Chem. Res.* **12** (1979) 79-86.

48. a) Y. Hirshberg, E. Fischer: Low-temperature Photochromism and its Relation to Thermochromism. *J. Chem. Soc.* **1953**, 629-636.

b) Y. Hirshberg: Reversible Formation and Eradication of Colours by irradiation at Low Temperatures. A Photochemical Memory Model. *J. Am. Chem. Soc.* **78** (1956) 2304-2312.

49. a) R. Dessauer, J. P. Paris: Photochromism. *Adv. Photochem.* **1** (1963) 275.

b) H. Dürr: Perspektiven auf dem Gebiet der Photochromie: 1,5-Electrocyclisierung von heteroanalogen Pentadienyl-Anionen als Basis eines neuartigen Systems. *Angew. Chem.* **101** (1989) 427-445; *Angew. Chem., Int. Ed. Engl.* **28** (1989) 413.

50. K. Schaffner, S. E. Braslavsky, A. R. Holzwarth: Photophysics and Photochemistry of Phytochrome. *Adv. Photochem.* **15** (1990) 229.

51. D. A. Parthenopoulos, P. M. Rentzepis: Three-Dimensional Optical Storage Memory. *Science* **245** 843-845.

52. T. Knöchel: Hydroazulene – Synthese, Funktionalisierung, Photochromie. *Doctoral Dissertation*, University of Regensburg, 1990.

53. J. Daub, S. Gierisch, U. Klement, T. Knöchel, G. Maas, U. Seitz: Lichtinduzierte reversible Reaktionen: Synthese und Eigenschaften photochromer 1,1-Dicyan-1,8a-dihydroazulene und thermochromer 8-(2,2-Dicyanvinyl)heptafulvene. *Chem. Ber.* **119** (1986) 2631-2646.

54.   J. Daub, C. Fischer, J. Salbeck, K. Ulrich: Molecular Materials for Chemical and Physical Switching IV: Photomodulation of Electric Current by Light-Sensitive Electron-Transfer-Compounds – Aryl/Dihydroazulene-Conjugates. *Adv. Mater.* **2** (1990) 366.

55.   C. Fischer, *Doctoral Dissertation*, University of Regensburg, in preparation.

56.   H.-H. Hörhold, M. Helbig, D. Raabe, J. Opfermann, U. Scherf, R. Stockmann, D. Weiß: Poly(phenylenvinylen); Entwicklung eines elektroaktiven Polymermaterials vom unschmelzbaren Pulver zum transparenten Film. *Z. Chem.* **27** (1987) 126.

57.   For the related poly(p-phenylene vinylene), see: H.-H. Hörhold, D. Gräf, J. Opfermann: Poly(arylenecyanoethylenes)-Structural Effects and Optical and Electrophysical Properties. *Plaste und Kautschuk* **17** (1970) 84.

58.   a) R. S. Potember, R. C. Hoffman, H. S. Hu, J. E. Cocciaro, C. A. Viands, R. A. Murphy, T. O. Poehler: Conducting Organics and polymers for Electronic and optical Devices. *Polymers* **28** (1987) 574.

      b) D. C. Bott: Structural Basis for Semiconducting and Metallic Polymers. Conducting Polymers (T. A. Skotheim, Ed.), M. Dekker, New York, 1986, p. 1191.

      c) G. P. Evans: The Electrochemistry of Conducting Polymers. Advances in Electrochemical Science and Engineering (H. Gerischer, C. W. Tobias, Eds.), VCH Verlagsgesellschaft, Weinheim, 1990, p. 1.

59.   J. Schreurs, E. Barendrecht: Surface-modified electrodes (SME). *Recl. Trav. Chim. Pays-Bas* **103** (1984) 205-219; A. Merz: Polymer-modifizierte Elektroden. *Nachr. Chem. Tech. Lab.* **30** (1982) 16-23.

60.   a) A. Mirlach, J. Salbeck, J. Daub: Cyclovoltammetrie und elektrochemische Polymerisation substituierter Azulene. *Dechema-Monographien* **117** (1989) 367.

      b) P. A. Bross, A. Mirlach, J. Salbeck, J. Daub: Azulenkonjugate mit photochromen Teilstrukturen: Vom Monomer zum Polymer – Eine elektrochemische und spektroelektrochemische Untersuchung. *Dechema-Monographien* **121** (1990) 375.

      c) A. F. Diaz, J. Bargon: Electrochemical Synthesis of Conducting Polymers. *Handbook of Conducting Polymers* (T. A. Skotheim, Ed.), M. Dekker, New York, 1986, p. 81.

      d) J. Daub, M. Feuerer, A. Mirlach, J. Salbeck: Functionalized Conducting Polymers with Polyazulene Backbone. *Synthetic Meth.*, submitted.

61.   P. A. Bross: Präparative Nutzung der [8+2]-Cycloaddition – Synthese und Eigenschaften mono- und disubstituierter Azulene. *Diploma Thesis*, University of Regensburg, 1990.

62.   P. A. Bross, U. Schöberl, J. Daub, submitted for publication.

Carbohydrates as Organic Raw Materials

Edited by
Frieder W. Lichtenthaler

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- selective oxidation without protecting groups
- generation of furans
- preparation of polyvinylsugars
- conversion into enantiomerically pure six-carbon building blocks of high synthetic versatility
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