Donor–Acceptor Substituted Polyenes: Orientation in Mono- and Multilayers**

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Large molecules containing different chemical units whose interactions within the molecule result in new macroscopically observable effects, have become increasingly important.[11] The organization of molecules of this type in ordered structures leads to functional molecular materials.[12] Their use in molecular electronics[13] requires that the units exhibit specific electronic properties.[14]

Recently, we reported on the intramolecular energy transfer through terminally substituted conjugated polyenes.[15] An intramolecular electron transfer within donor–acceptor substituted polyenes can be achieved by introducing suitable terminal groups.[6]

In the present communication we describe phenyl- or anthryl-polyenyl-pyridinium salts 4, their ability to form ordered monolayers on the water surface, the transfer of these monolayers onto solid supports by the Langmuir-Blodgett technique[7] and the characterization of the resulting films by UV/vis spectroscopy and angle-dependent second harmonic generation (SHG).[8]

In compounds 4, anthracene was chosen as the electron donor moiety for its selective excitability when linked to polyenes[16] and for its donor potential with respect to photoinduced electron transfer.[9] Pyridinium acceptors were used not only for their high reduction potential but also because of their ionic nature rendering molecules 4 amphiphilic and thus self-organizable into monolayers. The polyenyl-pyridinium salts 4 were obtained via Wittig and Horner reactions (Scheme 1).[10]

The UV/vis absorption spectra of 3e and 4e (Fig. 1) display absorption maxima at 256 nm corresponding to the excitation of the 1B, state (S, → S, transition) of anthracene.[50, 12] The long-wavelength absorption is attributed to the pyridinyl-polyene excitation (polyene S, → S, band).

The bathochromic shift of about 100 nm in the polyenyl-pyridinium compounds 4 compared to polyenyl-pyridines 3 is due to the enhanced charge-transfer character which results from the greater electron affinity of the pyridinium

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**Scheme 1.** 1: From 2,7-dimethyl- or 2,7-dicyclohexylpentadecanedioic acid [10b, 22] a) (4,4-Dimethoxy-1-methyl-2-butyryl)triphenylphosphonium chloride [23]/1/CH,OH/CH,Cl,; CH,OH/NaOCH, = 1 h; 1 h stirring; chromatography on SiO,CH,Cl,; recrystallization from toluene/CH,OH. b) 1 or 2/4-diphenylphosphinyl)benzyl}-pyridine [24]/18-crown-6/THF/Nal/2 h/room temperature; chromatography on Al,OCI/CH,Cl,; recrystallization from CH,Cl,/CH,OH. c) Trimethyloxonium-tetrafluoroborate/CH,Cl,; solution of 3 in CH,Cl,; 2 h/room temp.; recrystallization from acetone/methyl ether. 4g: Analogous to 17-(9-anthryl)-2,6,11,15-tetramethylheptadecacontene [22]. All compounds gave correct elementary analyses (4g: correct molecular ion composition in mass spectrometry). The all-cis stereochemistry of polyenones was confirmed by HPLC, 'H-NMR, and UV/vis spectroscopy.

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![Fig. 1. UV/vis absorption spectra of compounds 4c and 3e in dichloromethane (20 °C, 4c: ε = 1.05 × 10^4 M, 3e: ε = 6.63 × 10^4 M).](image-url)
Compounds 4 show bathochromic shifts of 40–50 nm in chlorinated hydrocarbons (solvatochromism).

The spreading of anthryl polyene amphiphiles 4 from CH_2Cl_2 solutions on a water surface revealed a considerable chain-length dependence of the monolayer formation due to the balance between the water solubility of the compounds with shorter chains and the tendency for aggregation of the compounds with longer chains. Even with the addition of polyelectrolytes (like polyacrylic acid) to the subphase 4a and 4b did not give monolayers at air–water interfaces. The reduced water solubility of 4c and 4d allowed the formation of monolayers from these compounds (Fig. 2).

Fig. 2. Pressure–area diagrams of 4c and 4d (Langmuir-measuring system, subphase water, 20°C, rate of compression 13.3 Å²/molecule/min).

Ethyl substituents along the polyene chain as in 4d markedly influence the pressure–area isotherms. They give rise to less rigid monolayers as seen from a less steep slope in the solid phase coexistence region, a more distinct collapse at diminished collapse pressure, and the easier transfer of the monolayers onto solid supports compared to 4c. It is very interesting that there is a coexistence region of fluid and ordered phases for monolayers of both 4c and 4d. However, the formation of domains in this region is accompanied by a noticeable water solubility as seen either at a reduced speed of compression or higher temperature of the aqueous subphase. The former resulted in a diminished surface pressure in the coexistence region while the latter additionally gave a smaller collapse area.

Although compounds 4e and 4f are of the same length as 4c, d (but bear the phenyl instead of the anthryl moiety) they do not form stable monolayers. Even if sodium polystyrene sulfonate is added to the subphase in varying amounts (0.5–12.5 mg/l) 4f did not give reproducible pressure–area isotherms.

The phase coexistence region is even more pronounced with 4g which is almost insoluble in water (Fig. 3). Despite of identical procedure each spreading gives a different isotherm in the pressure-range below 20 mN/m because of patches of aggregated 4g.

in the phase coexistence region, where patches of aggregated 4g are directly observable. A comparison of the data reveals that the area occupied by anthryl-polyenyl-compounds 4 is mainly governed by the anthryl group and by coulomb repulsion of the pyridinium ion (Table 1).

Monolayers of 4c and 4d were transferable onto solid supports by the Langmuir–Blodgett technique. Using pure water as subphase, only two monolayers of 4c were transferable onto hydrophobic glass or quartz glass slides using Y-type deposition with a transfer ratio equal to 1.0. Upon further dipping, previously transferred LB film floated off. The less rigid monolayers of 4d were transferred more easily than 4c and up to 30 monolayers were built up on hydrophobic substrates (glass, quartz glass). The transfer ratio was equal to 1.0 for the first double layer. For the second and the following dipping cycles it was approximately 0.6 for the downstroke and 1.0 for the upstroke.

In the UV/vis spectra of LB films of 4d the longest-wavelength band is broadened and slightly hypsochromically shifted compared to solutions in non-chlorinated solvents. A

![Fig. 3. Pressure–area diagrams of 4g on pure water (Langmuir-measuring system, 20°C, 13 Å²/molecule·min). Despite of identical procedure each spreading gives a different isotherm in the pressure-range below 20 mN/m because of patches of aggregated 4g.](image)

![Table 1: Pressure–area data of 4c, d, and g and literature data of similar compounds 5, 6 (Langmuir-measuring system, subphase water, 20°C, 13.3 Å²/molecule·min).](image)
much larger hypsochromic shift of about 35 nm is found when aggregation is induced by addition of methanol/water to a solution of 4c in ethanol, a typical method of studying the effect of aggregation on the spectra of carotenoids.\cite{1,4}

Because of the alignment of the transition dipole moment of the polyene $S_0 \rightarrow S_2$ band parallel to the polyene axis, information on the orientation of the polyene molecules within the LB layers could be obtained even from linear UV/vis spectra recorded with perpendicular incidence of light.\cite{15} Thus, the absorptions of LB films of 4c, d are in agreement with an isotropic distribution of molecular tilt angles.

Further information on the orientation of chromophores within non-centrosymmetric films could be obtained from angle-dependent second-harmonic generation (SHG).\cite{16} Large conjugated donor-acceptor substituted systems have large second-order polarizabilities \cite{1} and hence give effective second harmonic generation as demonstrated by calculation \cite{18} and experiment \cite{17}.

Though the preparation of each of the LB films of 4c was carried out using an identical method and all films had the same linear UV/vis absorption, the results obtained for SHG for each monolayer differed markedly in susceptibilities $\chi$ \cite{21} and in the calculated tilt angles (Fig. 4). Obviously, the preparation of LB films from these stiff monolayers was not completely controllable.

Aggregation within polyene monolayers at the air-water interface can be determined by reflection spectroscopy using light polarized vertical (s) or parallel (p) to the incidence plane.\cite{19,20} If p-polarized light is applied, the longest-wavelength band in the reflection spectra of monolayers of 4c on pure water is shifted hypsochromically with respect to the band which dominates the reflection spectra obtained under p-polarization (Fig. 5). This has to be attributed to the formation of H-aggregates of polyenes 4c which are not observed using p-polarized light. The degree of aggregation of polyenes within these pure monolayers was not controllable, as inferred from the varying intensities of the respective bands in Fig. 5.

**Experimental**

Mono- and multilayers: The compounds were spread from dichloromethane solutions ($c=7 \times 10^{-4}$ to $1.4 \times 10^{-4}$ mol/l) on a pure (distilled and Millipore purified) water subphase and the pressure-area diagrams were recorded using a Lauda Langmuir film balance. The LB layers were prepared with a Lauda Langmuir film balance at a transfer pressure of $20 \text{ mN/m}$. Glass and quartz glass slides were purified with alkaline hydrogen peroxide solution and then hydrophobized with dichlorodimethylsilane in chloroform solution.

Nonlinear optics: Angle-dependent SHG was measured with apparatus described previously\cite{22}, by excitation with a Nd:YAG laser (p-p-polarization). As standard, a quartz crystal with a quartz crystal with $d_1 = 1.2 \times 10^{-4}$ esu was used. For all calculations (formalism see [21]; estimated refractive index and film thickness: $\alpha(1064 \text{ nm}) = 1.5, 532 \text{ nm} = 1.8; \nu = 1.5 \text{ nm}$) a nonlinear polarization parallel to the polyene axis was assumed.

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Superconductor Thin Films: In Situ X-Ray Study on the Reaction of Hydrogen with Epitaxial YBa$_2$Cu$_3$O$_y$ Layers**

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Thin-layer systems represent a particular class of materials of increasing importance in various fields of application (optical components, superconducting junctions, photovoltaic cells, quantum wells etc.). They are characterized by a strong correlation between form and function and their specific physical properties are influenced by the morphology and dimensional restrictions in the nanometer range. Interesting properties—differing from those of the bulk material—should also be expected in terms of chemical reactivity, particularly for epitaxially grown films and superlattices. We recently started systematic investigations on chemical reactions of thin-layer materials and report here on an in situ X-ray study of the reaction of molecular hydrogen with superconducting epitaxial YBa$_2$Cu$_3$O$_y$ films which led to the detection of an unusual type of reaction mechanism.

High-temperature superconductors of the oxocuprate type are p-type metals (holes on oxygen and/or transitional metal) and their critical temperatures $T_c$ have been shown to be strongly correlated with the hole concentration which can be varied by (i) isomorphic substitution of cationic lattice constituents and (ii) by variation of the oxygen stoichiometry, via thermal processes.[1]

The correlation between hole concentration and critical temperature is generally characterized by a maximum $T_c$ value at a specific hole concentration. A third interesting model for the control of $T_c$ via hole concentration change can be based on the reaction with hydrogen, since the insertion of $H$ should be equivalent to the extinction of a corresponding amount of holes. The reversible formation of hydrogen bromides from metal oxides MoO$_3$ via electrochemical electron/proton transfer (Eq. 1) or by direct hydrogen intercalation and the consequent modification of physical properties of the pristine solids are well known.[2]

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xH^0 + xe^0 + MO_x \rightarrow H_xMO_y
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Hydrogen intercalation in polycrystalline YBa$_2$Cu$_3$O$_y$ has been reported by several groups,[3] changes in lattice parameters were found to be close to the error limit, however, and $T_c$ onset temperatures were not affected after reaction with hydrogen, although a strong broadening of the transition and a decrease in volume susceptibility was noted. Therefore, the results on bulk material remain inconclusive. In order to profit from the single-crystal-like highly ordered state and the minor diffusion length perpendicular to the layer plane we decided to perform an investigation of hydrogen intercalation in epitaxially grown YBa$_2$Cu$_3$O$_y$ thin films.

Thin films of c-axis oriented YBa$_2$Cu$_3$O$_y$ on (100) SrTiO$_3$ single-crystal substrates (thickness 4000 Å) were prepared by the laser ablation technique.[4] The isothermal and isobaric reaction of the thin films with hydrogen and the simultaneous recording of X-ray data was performed in situ on a single-crystal substrate (thickness 400 Å) by the laser ablation technique.[4] The isothermal and isobaric reaction of the thin films with hydrogen and the simultaneous recording of X-ray data was performed in situ on a c-axis oriented YBa$_2$Cu$_3$O$_y$ on (100) SrTiO$_3$ single-crystal substrates (thickness 4000 Å) were prepared by the laser ablation technique.[4]