unit can adopt two conformations that allow both double bonds to assume the proposed orientation. If interconversion between these two conformations is rapid, the spectra (and thus the calculated orientation) would reflect the average of both. Furthermore, jumping between the two could also reduce the effective order parameters to values such as those found for our system. Our results may, therefore, reflect the existence of two interconverting, relatively ordered states. We plan to use specific motional models to investigate this hypothesis and thus gain a better understanding of the average structure and ordering of lipids containing more than one double bond.

The analysis presented in this paper is unique in that no assumptions were required to define the ordering of the system. Direct observation of the deuteron-deuteron dipolar coupling provided the additional parameter necessary to define completely both the ordering tensor and the average orientation of the methylene segment. Although deuterium homonuclear dipolar couplings have been measured in other cases,[3,9,10] this is the first direct observation in spectra recorded from a deuteriated acyl chain in a phospholipid bilayer. The spectra and subsequent analysis illustrate the salutary effect of proton decoupling and demonstrate that more detailed information regarding the ordering of lipid systems can be obtained if an approach similar to ours is used.

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Ordered DNA-Polypeptide Complexes of Extreme Chirality: Effects of Polypeptide Handedness on DNA Long-Range Asymmetry

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Under appropriate conditions of ionic strength and in the presence of various polymers or dehydrating agents, DNA molecules undergo a remarkable cooperative compaction process.[1] The resulting structures, which attracted much interest due to their potential relevance to compact states of DNA invariably found in vivo, are characterized by nonconservative circular dichroism spectra whose magnitudes are significantly larger than those of dispersed DNA molecules.[2] Both the shape and the size of the CD signals indicate that the condensation process is accompanied by the formation of ordered tertiary structures in which well-defined, long-range couplings between chromophores are induced. Of particular interest are the phenomena observed when the DNA is condensed by dehydrating agents at high ionic strength conditions.[3] In 35% (v/v) ethanol and 0.8 M NaCl the DNA molecules undergo a cooperative transition into compact species that exhibit a nonconservative CD spectrum with a large positive signal centered around 265 nm. The magnitude of the signal is diminished as the salt concentrations are increased; a sign reversal and large negative bands are finally obtained (Figure 1a).[3] It occurred to us that reactions between the ordered structures thus obtained and species of a given, long-range, secondary conformation should be strongly affected by the asymmetry of the DNA molecules. This assumption is borne out: the interaction between condensed forms of nucleic acids and polypeptides result in hitherto unknown types of complexes of extremely large asymmetry which is determined by the DNA long-range order and the handedness of the polypeptide.

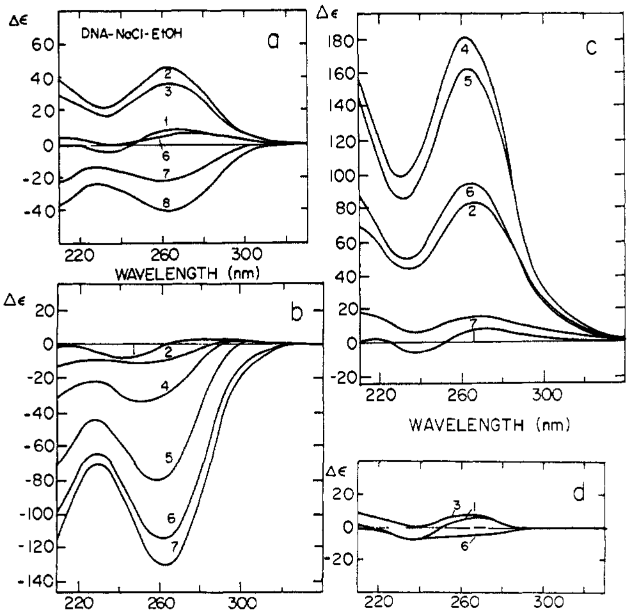

Figure 1. Circular dichroism spectra of condensed DNA molecules in H_2O-ETOH (35% v/v) solution containing the following NaCl concentrations (in M): (1) 0; (2) 0.8; (3) 1.0; (4) 1.2; (5) 1.4; (6) 1.6; (7) 1.8; (8) 2.0. a, DNA; b, DNA + poly-L-lysine; c, DNA + poly-D-lysine; d, DNA + poly-DL-lysine (DNA concentration, $5 \cdot 10^{-5}$ M in bp, polypeptide concentration $5 \cdot 10^{-5}$ M in amino acid residues).

When DNA condensation is induced in the presence of poly-L-lysine, the CD absorptions are substantially altered; instead of the large positive band obtained at 0.8 M NaCl, a negative signal is observed. Increasing NaCl concentrations are accompanied by a gradual increase of the absolute magnitude of the CD bands. Significantly, *negative ellipticities are observed at all salt concentrations* (Figure 1b), in clear contrast with the system in which the polypeptide is absent. The CD signals which characterize the DNA-poly-D-lysine complexes are, on the other hand, *invariably positive* with maximal intensity exhibited at 1.4 M NaCl (Figure 1c). It should be noted that the highest intensity of the CD bands in both cases where polypeptides are present is about four times larger than the maximal signal magnitude revealed by the compact species devoid of polylysines. In contrast, inclusion of a random polymer composed of L- and D-lysines in a 1/1 ratio in the condensation mixtures results in very small CD bands (Figure 1d), indicating complete disruption of any long-range order.[4]

In order to obtain the phenomena illustrated in Figure 1, strict length requirements have to be met by both nucleic acids and polypeptides: CD anomalies are detected only when the DNA

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(4) The described CD spectra are basically different from those reported for species obtained by a high to low salt dialysis of DNA-polylysine mixtures in the absence of dehydrating agents. In these cases, the condensation process is *induced by the polypeptides*, probably by excluded volume effects similar to those revealed by other polymers that affect condensation. In these cases, identical CD spectra for both poly-L- and poly-D-lysines are observed. See: (a) Shapiro, J. T.; Leng, M.; Felsenfeld, G. *Biochemistry* **1969**, *8*, 3219-3232. (b) Carroll, D. *Biochemistry* **1972**, *11*, 421-426.

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duplex is longer than 600 base pairs. Likewise, interaction between condensed DNA and polylysines shorter than 60 residues results in CD spectra that are identical with those obtained in the absence of the polymers; 70 amino acids are required to produce the above described phenomena at their full scale. Electron microscopy studies conducted on the DNA condensates may point toward a plausible interpretation for the length requirements revealed by the DNA duplex. When observed under electron microscope, certain shapes of the condensed forms, namely toroids, spools, and rod-shaped structures, reoccurred quite independently of the condensing agents. The rod-shaped forms obtained either upon EtOH-induced condensation,[5a] or upon DNA interaction with basic polypeptides,[5b,c] were found to be approximately 2000 Å long and of variable width. It has been suggested that the DNA molecule is packed in parallel arrays 2000 Å in length with folding back and forth at the end of the rod.[5a] A duplex of 600 bp is approximately 2000 Å long and assumedly cannot be condensed by dehydrating agents, whereas a longer segment may fold on itself, leading to tight-packing and efficient interhelical chromophore couplings. The CD spectra revealed by the DNA–NaCl–EtOH system (Figure 1a) may be interpreted as resulting from this strong coupling combined with a salt concentration dependent twist in between the contiguous DNA segments. The notion of a minimal duplex length required for the compaction processes is further buttressed by endonuclease digestion experiments carried out on DNA condensates.[1d] These experiments indicated that only fragments larger than 600 bp can be induced to collapse by polymers such as poly(ethylene oxide) into condensed phases.

The CD spectra shown in Figure 1 (parts b, c, and d) are obtained whether the polypeptide is present during the DNA condensation or added after the compaction process has been induced by the dehydrating agent. This observation indicates that the complexes responsible for the altered optical phenomena result from the interaction between polylysines and DNA molecules already condensed into ordered, compact species. Since short polypeptides—or monomeric lysines—fail to alter the CD spectra of the DNA condensates, and as polylysines exhibit a disordered, random coil conformation in neutral aqueous or H_2O–EtOH solutions,[6] it is conceivable that upon such interaction, the polypeptides adopt a long-range ordered structural motif. We suggest that the handedness related to this putative ordered motif and defined by the uniform chirality of the amino acids in the poly-L- or poly-D-lysines stabilizes specifically one sense of the interhelical twist of the above described DNA tertiary structures over the other. Interaction between condensed DNA and poly-DL-lysine, a copolymer that cannot adopt a long-range handedness, results in a complete distortion of the ordered DNA molecules.[7]

In addition to the modification of the DNA tertiary structures, the polylysines seem to induce the formation of large aggregates whose asymmetric quaternary conformation is, again, determined by the polypeptide handedness. This is based on the observation that upon increasing the solid angle of CD detection[8] the magnitudes of the CD spectra exhibited by DNA–polylysine species are reduced to about half their initial intensity, whereas those revealed by compact DNA devoid of polypeptides are not affected (data not shown). These findings indicate that besides differential absorption which characterize nucleic acids compact forms, DNA–polypeptides complexes exhibit differential scattering, typical of aggregates of long-range asymmetry.[2,9] Thus, if long enough—and hence the rather sharp size requirements—the polypeptides can attach a number of compact DNA molecules in an asymmetric form, resulting in ordered, chiral aggregates.

We are currently studying the structures of nucleic acids compact forms, their interactions with proteins and drugs, and the effects of various condensing agents in the hope of acquiring a deeper insight into DNA species as organized in biological systems.

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(7) It should be noted that whereas the sign and magnitude of the CD bands are substantially modified upon formation of the compact DNA–polylysine complexes, their position remains unaltered. This observation and the fact that polylysines, at all possible conformations, absorb at wavelengths shorter than 225 nm indicate that in all cases the observed optical phenomena are dominated by specific couplings between the DNA chromophores. Thus, the polypeptides affect the CD spectra by modifying the DNA structures and not by inducing new modes of DNA–protein chromophore couplings.

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Long-Lived Light-Induced Charge Separation in a Zeolite L-Based Molecular Triad

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Several examples of donor–sensitizer–acceptor (D–S–A) molecular triads now exist.[1-3] In these molecules, D^+–S–A^- states which persist for several microseconds in fluid solution can be created by using visible light excitation. The corresponding lifetimes of charge separation in the synthetically more accessible D–S or S–A diads[4-6] are generally much shorter. Learning to control the rates of charge separation and recombination in these multicomponent systems is important both in modeling the electron-transfer reactions of natural photosynthesis and in designing efficient processes for light-to-chemical energy conversion.

Zeolites are microporous, crystalline aluminosilicates which have been used as templates for organizing photochemically active molecular diads and triads.[7] We report here the photochemistry of a sensitizer–acceptor–secondary acceptor complex which organizes spontaneously at the surface of a zeolite L particle. The sensitizer–acceptor portion consists of a covalently linked tris(bipyridine)ruthenium(II)–*N*,*N*′-dialkyl-2,2′-bipyridinium (RuL_3^{2+}–nDQ^{2+}) complex **1**. The secondary acceptor is a benzylviologen (BV^{2+}) ion contained within the zeolite framework.

Intramolecular electron-transfer quenching of the RuL_3^{2+} MLCT state by the nDQ^{2+} moiety in **1a–c** occurs within 5 ns in acetonitrile/water solutions,[5] so no luminescence from the MLCT state is observed. When **1a** and **1b** are ion-exchanged onto the

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