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.

Acknowledgment. This work has been supported by a "Bat-Sheva de Rothschild" Grant No. 3879/1.

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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 *n*DQ^{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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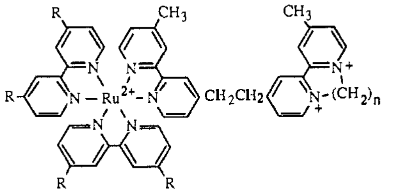


1a, R = H; n = 3
1b, R = CH_3; n = 3
1c, R = CH_3; n = 2

surface of zeolite L powder in roughly monolayer quantities,[8] strong luminescence at 620 nm from the MLCT state is seen with 460-nm excitation of the zeolite/water suspension. These complexes luminesce presumably because the formal potential of the $RuL_3^{2+*/3+}$ moiety is shifted positive several hundred millivolts, relative to its value in aqueous solution, by adsorption onto the zeolite surface;[9] similar shifts are *not* observed for the potentials of $3DQ^{2+/+}$, $2DQ^{2+/+}$, and other viologen couples.[10] Intramolecular electron-transfer quenching is therefore energetically unfavorable for **1a** and **1b** on zeolite L. **1c** is not emissive on zeolite L, indicating that electron-transfer quenching by the more positive $2DQ^{2+}$ moiety ($E^{\circ\prime} \simeq -0.75$ V vs SCE[11]) occurs within 5 ns or less.[12] Transient diffuse reflectance spectra[13] of an aqueous suspension of **1c** on zeolite L show a peak of 390 nm following 10 ns laser excitation at 532 nm. This transient, which is attributed to the Ru^{3+}–$2DQ^+$ intramolecular charge-separated state, decays via single exponential first-order kinetics with a lifetime of 0.44 μs. We note that immobilization on the zeolite has significantly extended the lifetime of this state, which lives <5 ns in fluid solution.[5] The complex may orient on the zeolite surface in such a way that the $2DQ^{2+}$ end enters the open (anionic) structure as shown in Scheme I. The RuL_3^{2+} end is size excluded from the 7.1 Å zeolite "window". This arrangement should inhibit motion about the flexible ethylene bridge in **1c** and would be expected to slow down both forward and back intramolecular electron transfer.

When **1c** is exchanged onto the surface of zeolite L which has been previously ion-exchanged with BV^{2+} ($E^{\circ\prime} \simeq -0.59$ V[10a]), the transient spectrum shown in Figure 1 is obtained. Spectral maxima at 400 and 600 nm and a minimum at 480 nm are due respectively to the formation of a monomeric reduced viologen and bleaching of the $Ru(bpy)_3^{2+}$ chromophore, i.e., formation of the Ru^{3+}–BV^+ charge-separated state. These spectral features appear together on the shortest time scale we can observe following the laser flash (ca. 100 ns), indicating that electron transfer from $2DQ^+$ (which does not absorb significantly at 600 nm[5b]) to BV^{2+} is complete within ≤100 ns. Luminescence studies with the model compound $Ru[(CH_3)_2bpy]_3^{2+}$ exchanged onto BV^{2+}-loaded zeolite L show only modest quenching of the MLCT state by BV^{2+}; hence it is unlikely that direct quenching of the RuL_3 moiety **1c** by BV^{2+} is competitive with rapid intramolecular quenching to form Ru^{3+}–$2DQ^+$, followed by rapid electron transfer from $2DQ^+$ to BV^{2+}. The Ru^{3+}–BV^+ state decays via first-order kinetics with a lifetime of 37 ± 5 μs. The quantum yield for formation of this state was found to be 17 ± 5% from flash photolysis/transient absorbance measurements carried out in aqueous sucrose suspensions, in which the refractive index of the zeolite and suspending medium are matched.

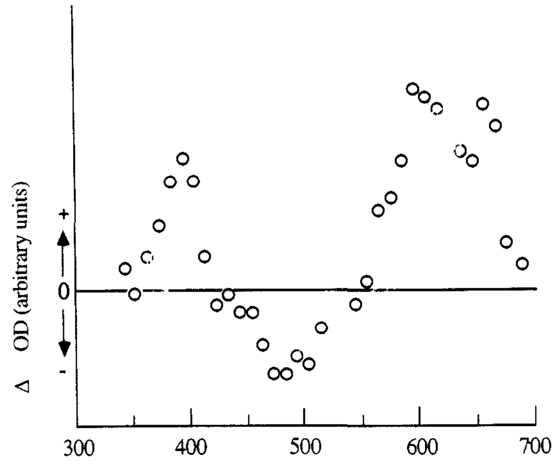
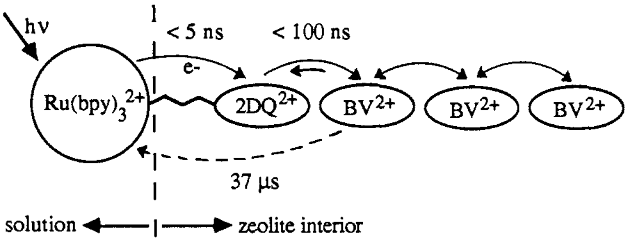
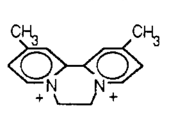


Figure 1. Transient diffuse reflectance spectrum recorded 11 μs after a 532-nm laser flash of 10-ns duration. The sample is a 2.5-mL aqueous suspension of 80 mg of zeolite L powder which contains 3 × 10^{-6} mol/g of **1c** and 1.5 × 10^{-4} mol/g of BV^{2+}.

Scheme I. Possible Spatial Arrangement of **1c** and BV^{2+} at the Zeolite L/Aqueous Solution Interface



The quantum yield for charge separation and lifetime of the charge-separated state are independent of the BV^{2+} loading in the zeolite, within the accuracy of our measurements, for BV^{2+} loadings between 1.0 and 2.0 × 10^{-4} mol BV^{2+}/gram zeolite. For higher BV^{2+} loadings the amount of **1c** adsorbed on the outer surface decreases markedly. A similar quantum yield and lifetime (35 μs) are obtained when zeolite Y is substituted for zeolite L. Both BV^{2+} and the model compound **2** exchange readily into zeolites L and Y.[14] Interestingly, neither cation exchanges into the bulk of mordenite, which has only slightly smaller 12-ring pores than do zeolites L and Y.[15] The smaller methylviologen cation exchanges readily into mordenite, L, and Y.



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Taken together these data argue for a spatial arrangement of **1c** and BV^{2+} like that shown in Scheme I. Close contact of BV^{2+}, which is contained within the zeolite and transiently formed $2DQ^+$, is required for fast and efficient formation of BV^+. The long lifetime of the Ru^{3+}–BV^+ state can also be attributed to good

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[8] **1a–c** were exchanged onto the surface of ca. 1 μm diameter zeolite L particles (Union Carbide, Linde Division) from 2 × 10^{-4} M solutions of the hexafluorophosphate salts in acetonitrile/water. The loading of these complexes on the zeolite surface, determined spectrophotometrically from the filtered solutions, was typically 3–5 × 10^{-6} mol/g zeolite, corresponding to approximately monolayer coverage of the zeolite outer surface. The functionalized zeolite powders were washed with copious amounts of water and air dried at ambient temperature before use.

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[11] Potential estimated from cyclic voltammetry of zeolite Y-modified electrodes ion-exchanged with CH_3bpy–CH_2CH_2–$2DQ^{2+}$. The technique is described in ref 9 and 10.

[12] The very weak luminescence from **1c** on zeolite L, which probably arises from trace $Ru[(CH_3)_2bpy]_3^{2+}$ impurities in the sample, establishes 5 ns as an upper limit for the lifetime of the MLCT state.

[13] The transient diffuse reflectance optics were similar to those described by Willsher, C. J. *J. Photochem.* **1985**, *28*, 229. Flash photolysis experiments were typically carried out with 100 mg of the appropriately ion-exchanged zeolite powder suspended in 2.0 mL distilled water. The suspension was deoxygenated by purging with nitrogen for 5–10 min. Other experimental details of the flash photolysis experiments are given in ref 7c.

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spatial separation of Ru^{3+} and BV^{+} and may be limited by the fact that the potentials of the $2DQ^{2+/+}$ and $BV^{2+/+}$ couples are separated by only 160 mV, so that back electron transfer from BV^{+} to Ru^{3+} via $2DQ^{2+/+}$ is possible. It is likely that isoenergetic electron exchange along the BV^{2+} chain depicted in Scheme I significantly enhances the charge-separated state lifetime; in zeolite Y this electron-hopping rate, measured electrochemically,[10a] is on the order of 10^5 s^{-1}. We note finally that this self-assembling zeolite-based triad resembles the membrane-bound special pair–pheophytin–quinone triad in the reaction center of photosynthetic bacteria;[16] there, a similar spatial arrangement and ordering of redox potentials contribute to two extremely fast forward electron-transfer steps and to a long-lived charge-separated state.[17]

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Organometallic Dioxygen Activation: Formation of (Pentamethylcyclopentadienyl)chromyl Dibromide

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We wish to describe an unusual example of an organometallic process for the activation of dioxygen as oxide. In our search for organometallic oxidants,[1] we had found that the $CpMCl_3^{0/-}$ electrochemical couple increases 750 mV by changing from M = Ti to M = V. This observation prompted an examination of (cyclopentadienyl)chromium halides and oxohalides. Complexes of the type $[CpCrX_2]_2$ (Cp = η^5-C_5H_5) are well known, but their redox properties have not been reported.

Reaction of $[Cp^*Cr(CO)_2]_2$[3] (Cp* = η^5-C_5Me_5) with excess Br_2 in CH_2Cl_2 produces a green microcrystalline solid after filtration and solvent removal.[4] Extraction of the solid with THF yields blue $[Cp^*CrBr_2]_2$ (**1**) isolated in 97% yield.[5] Analogous to the known $[CpCrCl_2]_2$,[6] **1** can be described as *trans*-$[Cp^*CrBr(\mu\text{-}Br)]_2$ with Cr–Br distances of 2.521 (5) Å (av, bridging) and 2.437 (3) Å (terminal).[4]

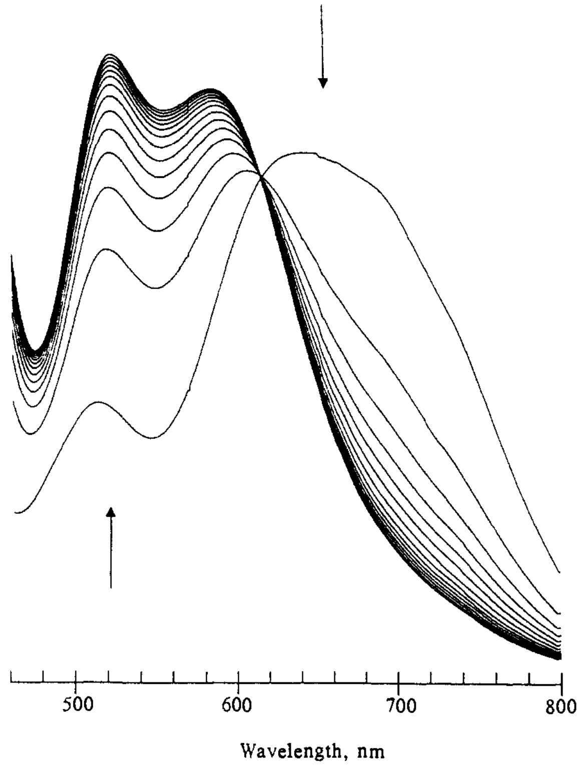

Figure 1. Sequential UV-vis spectra for the oxygenation of $[Cp^*CrBr_2]_2$ (**1**) in CH_2Cl_2 (0.001 M [**1**], 0.34 M [THF], ca. 3 atm P[O_2], Δt = 5 min). The first scan is that *after* addition of O_2, and the arrows indicate positions of initial and final maxima.

The instability of monomeric Cp^*CrBr_x ($x > 2$) from **1** and Br_2 led us to next attempt the synthesis of a mixed oxo–halo chromium complex. The π-donating ability of the oxo group has a decidedly strong influence on the redox properties of organometallic compounds. For example, the recently reported $[Cp^*CrO_2]_2$,[7] despite its label as a high oxidation state complex, is not oxidizing. This species is electrochemically reduced only at quite negative potentials ($E_{1/2}$ = −1360 mV vs Ag/AgCl).

Dilute solutions of **1** (≤2 mM) in CH_2Cl_2 react within minutes with dry O_2 to form red Cp^*CrOBr_2 (**2**), isolated in 97% yield.[8] The rate of this oxidation is slowed by coordinating solvents such as THF or CH_3CN. When this transformation (with added THF) is monitored by optical spectroscopy, we observe a clean isosbestic point at 612 nm (Figure 1). Interestingly, concentrated solutions of **1** (≥100 mM) are not noticeably O_2 sensitive. Furthermore, the μ-oxo compound $[Cp^*CrBr_2]_2O$ is not observed when solutions of **1** and **2** are combined. Compound **1** represents one of the few isolable complexes which cleanly *adds* oxygen to give an oxide.[9,10] Further mechanistic and thermodynamic studies of the relationship

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(4) We have fully characterized the *adduct* $[Cp^*CrBr_2]_2 \cdot Br_2$. This species will be described separately, as will the structure of $[Cp^*CrBr_2]_2$.

(5) Anal. Calcd for $C_{10}H_{15}CrBr_2$: C, 34.61; H, 4.36; Cr, 14.98. Found: C, 34.64; H, 4.39; Cr, 14.92. ^1H NMR ($CDCl_3$/TMS, 293 K) δ −58.

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(8) Anal. Calcd for $C_{10}H_{15}CrOBr_2$: C, 33.09; H, 4.16; Cr, 14.32. Found: C, 33.18; H, 4.08; Cr, 14.23. ^1H NMR ($CDCl_3$, 293 K) δ −12.

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