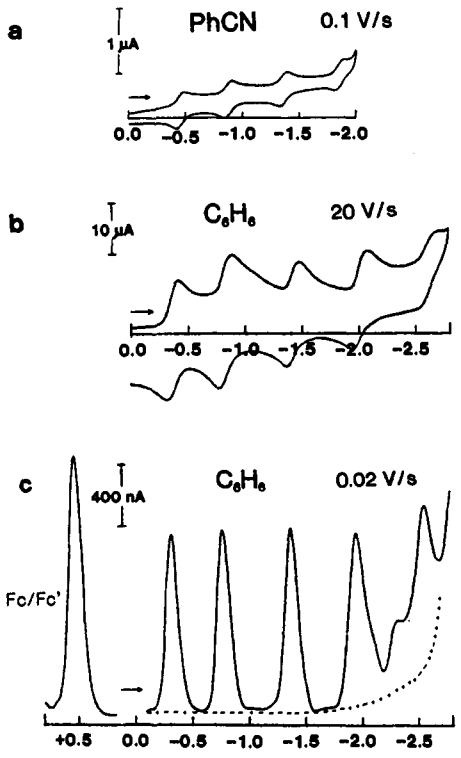

Figure 2. Reduction of C_{60} by (a) cyclic voltammetry in PhCN, 0.1 M $[(n\text{-Bu})_4N](PF_6)$ at 22 °C, and (b) cyclic voltammetry and (c) differential pulse voltammetry (80-mV pulse, 50-ms pulse width, 300-ms period) of C_{60} in C_6H_6 containing $[(n\text{-}C_6H_{13})_4N](ClO_4)$ (0.55 g in 1 cm^3) at 45 °C. The dotted line shows the background current in the absence of C_{60}.

Theory suggests that the LUMO of C_{60} can accept six electrons to form diamagnetic C_{60}^{6-};[6-8] however, observation of more than four electroreductions of C_{60} or C_{70} has been hindered by the lack of a solvent in which they are soluble and which has a reduction potential window that extends beyond −2.0 V vs SCE.[4,9,10] To circumvent this problem, this study utilizes benzene, which has one of the widest known reduction windows.[11] Figure 2 shows cyclic and differential pulse voltammograms of C_{60} in benzene containing $[(n\text{-}C_6H_{13})_4N](ClO_4)$ at 45 °C.[12] Under these conditions, five reductions occur at $E_{1/2}$ = −0.36, −0.83, −1.42, −2.01, and −2.60 V vs SCE (−0.83, −1.29, −1.89, −2.48, and −3.07 V vs Fc/Fc^+). A small peak between the fourth and fifth reductions in the differential pulse voltammograms (Figure 2c) and a similar peak in the cyclic voltammograms at sweep rates below 10 V/s appear to arise from a side reaction of C_{60}^{4-} in benzene. This side reaction is not observed by high scan rate CV, where all five reductions are reversible (Figure 2b).

Differential pulse voltammograms indicate that electrogenerated C_{70}^{3-} and C_{70}^{4-} ions are less stable in benzene than their C_{60} counterparts. Thus, several new peaks appear after the fourth reduction, none of which can be unambiguously assigned to C_{70}^{5-}.

C_{60}^{3-}, C_{60}^{4-}, C_{70}^{3-}, and C_{70}^{4-} can be observed electrochemically in methylene chloride at high scan rates, but are unstable by bulk electrolysis in that solvent.[4a] It is possible, however, to generate C_{60}^{3-} and C_{60}^{4-} by bulk electrolysis using 0.1 M $[(n\text{-Bu})_4N](PF_6)$ in benzonitrile.[4b] Similarly, C_{70}^{3-} and C_{70}^{4-} can be observed by CV at slow scan rates in benzonitrile and are also likely to be stable after bulk electrolysis.

In conclusion, this work presents the first reported observation for an electrochemical oxidation of C_{60} and C_{70} in solution. The overall four-electron oxidation is accompanied by one or more chemical reactions that consume the fulleronium ions. No conclusion can be reached as to whether the initial cation is multiply or singly charged. This report also presents the first reversible generation of C_{60}^{5-} in benzene. The third and fourth reductions of C_{60} give unstable species in CH_2Cl_2,[4] but in benzonitrile the highly reduced fulleride ions appear quite stable. Advantage is being taken of this stability for the electrosynthesis, isolation, and study of new fulleride-containing materials.

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(12) $[(n\text{-}C_6H_{13})_4N](ClO_4)$ (0.55 g) was dissolved in 1 cm^3 of benzene freshly distilled from sodium. The elevated temperature solubilizes and dissociates the supporting electrolyte.

Photochemical Activation of Racemic Mixtures in Biological Matrices

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Optical activation of racemic mixtures by preferential photoconversion of one antipode is a long-known process.[1] This process is to be expected when one antipode is preferentially excited by light of a selected circular polarity or when it is excited (deexcited) by means of energy-transfer processes from (to) a chiral sensitizer (quencher) under irradiation with achiral light. In the case of circularly polarized light (CPL), the enantiomeric excess (ee) obtained depends on Kuhn's dissymmetry factor, g,

$$g(\lambda) = 2(\epsilon_l - \epsilon_r)/(\epsilon_l + \epsilon_r) = \Delta\epsilon(\lambda)/\epsilon(\lambda)$$

and on the extent of substrate photodestruction. For reasonably large ees, almost complete photodestruction of the substrate is required, because g, in general, is small (0.01–0.001) at optical frequencies.[1a,c] The main scope of CPL photolysis probably rests on the determination of g, and hence of enantiomeric $\Delta\epsilon$, from both the measured circular dichroism signal induced on residual substrate and the extent of the photodestruction. This technique has been used in selected instances.[1a,2] With chiral photosensitization processes, optical activation is generally low, and spectroscopic quantities, such as $\Delta\epsilon$, cannot be deduced.[1a]

Herein it is reported that (*S*)-(−)-1,1′-bi-2-naphthol, (−)-**1**, is photoconverted with a large preference over (+)-**1**, so that *with moderate photodestruction*, high ees are obtained in residual **1**. This fact is related to the differences in the absorption spectra of the antipodes when they are complexed with the transport

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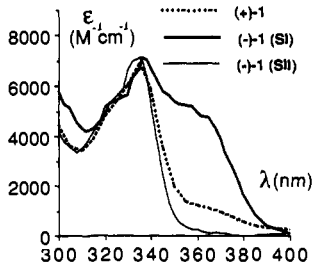

Figure 1.

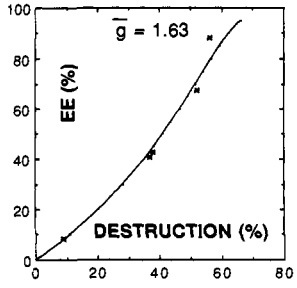

Figure 2.

protein bovine serum albumin (BSA). The optical enrichment is controlled by the difference in light absorption at the irradiation wavelength, and the extent of **1** phototransformation, analogous to the CPL photolysis.

Thus, when crystalline (−)-**1** is dissolved in an aqueous solution of BSA, it reversibly binds in two sites of BSA with binding constants higher than 10^8 M.[3] The properties of (−)-**1** in these binding sites strongly differ, as absorption, circular dichroism, and fluorescence spectra manifest. In particular, (−)-**1** in the higher affinity site, SI, shows a new absorption band in the 355–420-nm spectral region. Here it does not absorb when bonded to the second site, SII, nor when dissolved in CH_3CN, CH_3OH, and C_6H_{14}. When (+)-**1** is dissolved in aqueous BSA, the absorption in the 355–420-nm region is far less intense than that of (−)-**1** in SI[3] (Figure 1).

Finally, when (±)-**1** is dissolved in aqueous BSA, a (±)-**1**/BSA complex is formed.[4] The absorption spectrum of this complex is exactly the arithmetic average of the (+)-**1** and (−)-**1**/BSA complexes having half the concentration in the same BSA solution. When the number of (±)-**1** molecules on each BSA is, on the average, ≤1, practically every (−)-**1** is in SI, as happens when ≤0.5 (−)-**1** molecule is bound to BSA in the (−)-**1**/BSA complex. Thus, at 365 nm, the light absorption of (−)-**1** is $\epsilon^-(SI)/\epsilon^+ = 4850/970 = 5.0$ times greater than the (+)-**1**/BSA absorption. Hence, irradiation of the (±)-**1** complex with 365-nm light would preferentially both excite and, conceivably, photoconvert (−)-**1** so as to cause enrichment in the (+)-**1** antipode.

The ees obtained in a series of five irradiations on the (±)-**1**/BSA complex, 0.000 121/0.000 173 M, respectively, versus the photoconversion degree are reported in Figure 2.[5] The curve shows the ee expected (vide infra).

Here, contrary to classical CPL photolyses, high ees are reached with tolerable photoconversions (e.g., 89% ee with 57% destruction of **1**). The experimental data can be fitted according to the simple kinetic scheme

$$\frac{dc_{+1}}{dt} = -K\phi^+ I^+ = -KI\phi^+ \frac{\epsilon^+ c_{+1}}{\epsilon^- c_{-1} + \epsilon^+ c_{+1} + R} \qquad (1)$$

where ϕ^+ is the quantum yield of phototransformation, c_{+1} the concentration, I^+ the intensity of light absorbed, ϵ^+ the extinction coefficient, at the irradiation wavelength, of (+)-**1** bound to BSA. K and R depend on the volume of the solution and on the presence of other light-absorbing molecules, respectively. Integration of the differential equation obtained by dividing eq 1 by the corresponding equation for (−)-**1** and simple mathematics leads to

$$\bar{g} = \frac{\Delta\bar{\epsilon}}{\bar{\epsilon}} = \left| \frac{\ln [(1 + ee)/(1 - ee)]}{\ln (1 - x) + \frac{1}{2} \ln [1 - (ee)^2]} \right|$$

similar to a valid expression for CPL irradiation.[2]

In this expression, $\bar{\epsilon} = 0.5(\phi^+\epsilon^+ + \phi^-\epsilon^-)$, $\Delta\bar{\epsilon} = \phi^-\epsilon^- - \phi^+\epsilon^+$, and ee is the enantiomeric excess obtained when the fraction x of **1** has been transformed. In the reported experiments, the factor $\bar{g}$ has the value 1.63 ± 0.04, i.e., *3 orders of magnitude* higher than Kuhn's dissymmetry factor for **1**. With the above $\bar{g}$ value and with measured ϵ^+ and ϵ^-, at 365 nm, we calculate the ratio $\phi^+/\phi^- = 0.50$. Thus, BSA–substrate interactions also differently change the excited-state reactivity of the antipodes, doubling that of (−)-**1** with respect to that of (+)-**1**.

An experiment sheds light on the origin of the above-described astonishing capability of the protein to discriminate. In fact, when (−)-**1** is dissolved in aqueous CH_3CN, at pH > 9, we measure UV and CD spectra similar to that of (−)-**1** in SI, i.e., with an intense band in the 355–420-nm range. Accordingly, it is reasonable to deduce that the acidic naphtholic moieties of (−)-**1** in the SI site are in a basic environment not accessible to the (+)-**1** antipode and manifest spectral features typical of anionic forms.

If the above simple interpretation is correct, we expect novel applications, also without intervention of light, of chiral recognition by biological macromolecules, particularly by serum albumins, when acidic or basic substrates, for which strong binding sites are known to be active, are involved.

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Registry No. (+)-1,1′-bi-2-naphthol, 18531-94-7; (−)-1,1′-bi-2-naphthol, 18531-99-2.

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(4) Extraction from the (±)-**1**/BSA solution with diethyl ether gives (±)-**1**.
(5) In each experiment, 5 mL of (±)-**1**/BSA solution, at 10 °C under N_2, was irradiated with the 365-nm emission of a filtered, medium-pressure Hg lamp. Diethyl ether extraction from the irradiated mixtures and HPLC (RP18 column, CH_3CN/H_2O, 70/30 v/v) purification gave (+)-**1** of the reported ee. The optical purity (OP)/ee of samples was measured both with CD/UV, in comparison with samples (OP > 99%) from Aldrich, and with chiral HPLC analysis (TC-DNBPG column), with coincident results. Recovered BSA, after dialysis, was indistinguishable from original BSA as indicated by UV spectra, CD spectra, and new complexation experiments with **1**.

Single-Stranded DNA as a Target for Triple-Helix Formation

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Two strategies have been developed to selectively control gene expression by way of oligonucleotides targeted to nucleic acids. In the "antisense" strategy the oligonucleotide binds to a complementary sequence on messenger RNAs thereby inhibiting translation. In the "antigene" strategy the oligonucleotide recognizes a sequence of double-stranded DNA and forms a triple helix which is expected to block transcription and/or replication (for review, see ref 1). Here we demonstrate that an oligonucleotide can form a stable *triple helix* on a *single-stranded DNA* sequence by forming both Watson–Crick and Hoogsteen hydrogen bonds with the target sequence. In addition, covalent attachment of an intercalating agent to the 5′-end of the oligonucleotide

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