mA/cm^2. At this time the turnover number of **1** was at least 10^4, assuming complete coverage of the electrode by a monolayer of **1**, a roughness factor of 100, and a radius for **1** of ca. 8 Å.

The achievement of 44% incident photon to current conversion efficiency is unprecedented. Apart from the rough structure of the electrode surface acting as a light trap, this is due to the unique sensitizing properties of **1**. In the pH domain of interest, **1** is an anion and therefore electrostatically attracted to the semiconductor. In addition, carboxylate groups adsorb specifically at the surface of TiO_2[14] resulting in the intimate contact required for efficient sensitization.[15] For $Ru(bpy)_3^{2+}$, the ratio of charge injection to recombination rates is unfavorable. Interstingly, ruthenium bis(2,2'-bipyridyl)(2,2'-bipyridyl-4,4'-dicarboxylate) (**2**), chemically attached to a TiO_2 electrode, gives only ϕ_{inj} = 0.0025.[3e,f,g] The current action spectrum of **2** is structureless, indicating that chemical attachment of **2** to the surface of TiO_2 creates semiconductor (t_{2g})/dye (π^*) surface states acting as recombination centers.[3f] This increases k_b sharply, reducing drastically the efficiency of sensitization. The action spectrum obtained for **1** matches its absorption spectrum indicating that this type of interaction is absent in the case of **1**.

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Registry No. TiO_2, 13463-67-7; $Ru(bpy(COO^-)_2)^{4-}$, 78338-26-8; anatase, 1317-70-0.

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Photoinduced Aggregation Changes in Photochromic Polypeptides

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Several photoresponsive effects have been recently observed in azobenzene-containing photochromic systems.[1-16] Here we report some CD data providing evidence that azobenzene-containing poly(L-glutamic acid) can undergo reversible "aggregation changes" upon exposure to light or dark conditions.

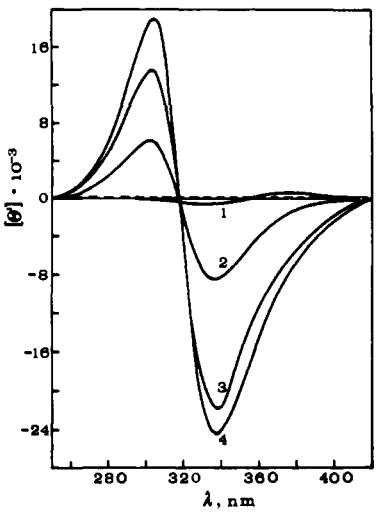

Figure 1. Poly(L-glutamic acid) containing 21 mol % azobenzene units. Time dependence of side-chain CD bands in TMP/H_2O = 50/50. (1) Freshly prepared solution, (2) 1-day old solution; (3) 2-day old solution, (4) 3-day old solution. (—) Dark-adapted, (---) irradiated at any time. Data are expressed in terms of azobenzene molar ellipticity.

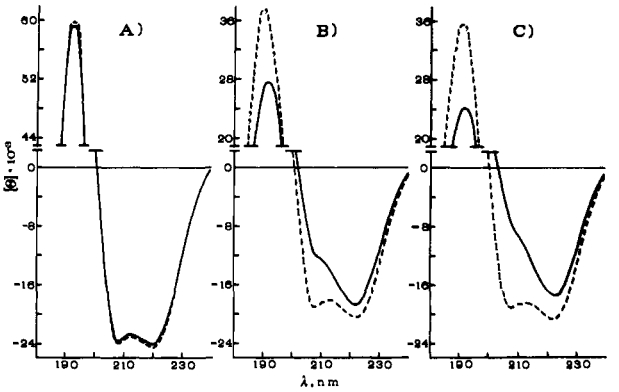

Figure 2. Poly(L-glutamic acid) containing 21 mol % azobenzene units. CD spectra in TMP/H_2O = 50/50, recorded at various aging times. (A) Freshly prepared, (B) 1-day old, (C) 2-day old solution. (—) Dark-adapted, (---) irradiated samples. Molar ellipticity is based on the mean residue weight.

A photochromic polymer containing 21 mol % azo units was obtained by modification of poly(L-glutamic acid) ($\bar{M}_v$ = 200000), as previously described.[16,17] Its photochromic behavior is correlated with the reversible trans ⇌ cis photoisomerization of azobenzene moieties. High trans-to-cis photoconversions can be obtained by irradiating at λ = 370 nm. The opposite cis-to-trans isomerization is obtained by irradiating at λ = 450 nm or by dark adaptation.[16,17]

The CD spectra in trimethyl phosphate (TMP) exhibit the two negative bands at 222 and 208 nm typical of α-helical polypeptides. The dark-adapted samples (all trans azo groups) show also an intense positive CD couplet centered at 350 nm, in correspondence to the $\pi-\pi^*$ transition of the azo chromophore.[16,17]

Remarkable variations of the CD spectra occur when increasing amounts of water are added to the TMP solutions stored in the dark. Side-chain CD bands progressively decrease by increasing water concentration and disappear when its concentration is higher

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than 50%. However, no appreciable variation of the α-helix CD pattern is observed.

This initial rapid step is followed by a further slow variation of CD spectra over a much longer period of time (about 3 days). This last slow step is characterized by the gradual appearance of an intense side-chain CD couplet, whose chirality is opposite with respect to that observed in pure TMP (Figure 1). At the same time the spectra become more and more distorted in the peptide region, with red shifting of the 222-nm band toward 225 nm and progressive flattening of the 208- and 193-nm bands (Figure 2).

CD spectra exhibit the same distortions as α-helical poly(L-glutamic acid) does, when aggregation progresses below pH 4.[18-21] The same features of the spectra are observed when CD measurements are carried out on turbid suspensions of membrane proteins.[22,23] Indeed, this type of spectra has been used as a diagnostic tool to detect aggregates of α-helices,[24] as the main sources of these distortions are due to the absorption flattening effect and to the differential scattering of left and right circularly polarized light, produced by ordered aggregates of chromophores.[21-27]

Therefore, the initial step brought about by the addition of the polar solvent must be related to a change of the conformation of the side chains involved in a regular array on the periphery of the helix backbone.[17] In contrast, the subsequent slow step should be associated with an aggregation process of the helical polypeptide chains.[20-32] Accordingly, light-scattering intensity increases with time and long aging of the solutions.[33]

Irradiation at λ = 370 nm completely cancels the side-chain CD bands. At the same time in the peptide region, CD spectra revert to the initial not distorted ones (Figure 2). As can be observed in the CD spectra recorded on the freshly prepared solutions, the photoisomerization itself of the azo chromophore does not affect the CD spectra in the peptide region. So the light effect cannot be masked by eventual differential contributions of the trans and the cis configuration of azo chromophores. The variation of the spectra upon illumination can be well interpreted as resulting from dissociation of the aggregates induced by light.[34]

By dark adaptation the side-chain CD bands gradually appear again and the spectra revert again to the distorted ones with approximately the same time scale, thus confirming the reversibility of the change. The cycle can be repeated at any time of the aging of the solutions (Figure 2).

Aggregation may be formed between azobenzene moieties in the presence of water, through hydrophobic interactions and ordered stacking of azo groups.[28-32,35,36] These interactions are favored in dark-adapted samples, as *trans*-azobenzene moieties are planar and very hydrophobic. Light induces the disaggregation process, as the cis form is more polar and not planar,[37] thus enhancing the polymer solubility and inhibiting the associative conditions. Therefore, it is likely that the different polarity and the different geometry between the trans and the cis form of the azo moieties provide the driving force for the photoinduced aggregation–disaggregation process.[38]

In naturally occurring photoreceptors, photoexcitation of photochromic molecules is known to induce reversible changes both in the conformation[39,40] and in the aggregation[41,42] of the attached protein matrix. Thus, the described data can be particularly relevant to the phenomenon of photoregulation in biological systems.

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Dielectric Relaxation Studies Demonstrate a Peptide Librational Mode in the Polypentapeptide of Elastin

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The elastic fiber of biological tissues contains the repeating pentameric sequence (L-Val[1]-L-Pro[2]-Gly[3]-L-Val[4]-Gly[5])$_n$ where n is as much as 13 in chick tissue without a single variation.[1,2] This polypentapeptide of elastin has been synthesized with n greater than 100;[3] it has been variously cross-linked and found to be elastomeric.[3-5] Conformational studies[6-10] have led to the description of a class of helical conformations called β-spirals[11]

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