

Dynamic Control and Amplification of Molecular Chirality by Circular Polarized Light

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The enantiomers of a racemic photoresponsive material represent two distinct states that can be modulated with irradiation at a single wavelength by changing the handedness of the light. Dynamic control over molecular chirality was obtained by the interconversion of enantiomers of helically shaped molecules with either left or right circular polarized light (CPL). Photoresolution of the bistable compound as a dopant in a nematic liquid crystalline phase by CPL irradiation led to a chiral mesoscopic phase. The chiral information inherent to CPL is therefore transmitted to the bistable molecule, followed by amplification and macroscopic expression of the chirality.

The development of organic materials for reversible optical data storage and photochemical switches requires components whose structures and physical properties can be modulated by light (1–3). Photochromic compounds exist in two distinct, interconvertible forms but often suffer from poor fatigue resistance and destructive read-out (3). Nondestructive read-out has been achieved by monitoring changes in the optical activity of chiral optical switches (4). This requires bistable, nonracemic molecules with sufficiently different optical spectra so that the individual diastereoisomers can be addressed (5). Switching between the enantiomers in a racemic photoresponsive material would constitute a novel approach to a molecular memory element in a binary logic system. Because of the identical optical spectra of enantiomers, distinct states cannot be reached with irradiation unless the unique interaction of enantiomers with CPL can be exploited (6, 7).

We show that photoresolution of helical alkene **1** (Fig. 1A) as well as photomodulation of the helicity is possible with CPL, and that the very small bias for one enantiomer upon CPL irradiation can be macroscopically expressed. Distinct from photochemical molecular switches reported so far, switching between the enantiomers of a racemic compound and modulation of the chiroptical properties and three-dimensional structure have been achieved exclusively by modulation of the chirality of the light. The photochemical modulation of mesophases and physical properties of liquid crystalline (LC) materials is a further challenge for information technology (8). We show that amplification of the chirality from molecule to mesophase and switching

between chiral and achiral mesophases are also affected by CPL irradiation of racemic **1**, added as a dopant to a nematic LC phase.

Of many sterically overcrowded chiral alkenes that we synthesized, compound **1** (Fig. 1A) meets the requirements for a successful switch: (i) The enantiomers are stable at ambient temperatures (free enthalpy of racemization, $\Delta G_{\text{rac}} = 25.9 \pm 0.2$ kcal mol⁻¹) and fatigue resistant. (ii) A stereospecific photochemical isomerization process takes place that reverses the helicity of the molecules. (iii) Large circular dichroism (CD) absorptions and optical rotations, essential for detection, are observed.

Racemic **1**, 12-(9'-H-thioxanthene-9'-ylidene)-12H-benzo[a]xanthene, was resolved by chiral high-pressure liquid chromatography (HPLC) on a (+)-poly(triphenylmethylmethacrylate) column. The CD spectrum of M-**1** shows a negative Cotton effect at 314 nm (difference in extinction coefficient, $\Delta\epsilon = -51.3$ cm² mol⁻¹) in *n*-hexane:isopropanol (9:1) (Fig. 2A). The anisotropy factor (*g*) is decisive for the selectivity of a CPL switch. The maximum enantiomeric excess that can be achieved upon irradiation with CPL is $g/2$, and for practical purposes the chiral alkene must exhibit sufficiently large *g* values at wavelengths above 300 nm. The experimental *g* values for alkene **1** at selected wavelengths are as follows: $g \times 10^3 = 2.8$ ($\lambda = 236$ nm; $\Delta\epsilon$ at maximum = 128.6 cm² mol⁻¹), -6.4 (314 nm, -51.3 cm² mol⁻¹), and 0.4 (356 nm, 5.0 cm² mol⁻¹) (units for $\Delta\epsilon$ are omitted hereafter).

Irradiation of P-**1** at 300 nm resulted in rapid photoisomerization into M-**1** without notable degradation. The quantum yield for the photochemical racemization was $\Phi = 0.40$ (pure *n*-hexane). Next, we examined photoisomerization of racemic **1** under the influence of *l*-CPL and *r*-CPL. CD spectroscopy was used as a detection technique to establish optical enrichment, that is, de-

racemization, upon irradiation with CPL. Irradiation of the racemate MP-**1** (9×10^{-5} mol liter⁻¹, *n*-hexane) with *l*-CPL at 313 nm resulted in a negative CD absorption at 313 nm and spectral features comparable with the CD spectrum of M-**1** ($g = 4.2 \times 10^{-6}$) (Fig. 2A). Because weak CD effects were expected, we sampled both at 313 nm, where $\Delta\epsilon$ reaches a maximum, and at 400 nm, where no CD absorption is found. Through use of this method, the effects of CPL irradiation on the difference in $\Delta\epsilon$ at $\lambda = 313$ nm and at $\lambda = 400$ nm ($\Delta\epsilon_{313} - \Delta\epsilon_{400}$) could be determined accurately. Upon successive irradiations with *l*- and *r*-CPL at 313 nm, a modulation of CD absorptions was observed (Fig. 2B). This modulation was entirely reproducible in independent experiments, and no deterioration of the modulated CD signal was seen during eight switching cycles.

For a solution of MP-**1** in *n*-hexane of 9×10^{-5} mol liter⁻¹ ($\Delta\epsilon_{313} = 0.7$), the magnitude of the modulation of $\Delta\epsilon$ was 1×10^{-5} when an irradiation time of 30 min was used. These results indicate that switching occurs between photostationary states with excess P and M helices, with an enantiomeric excess (EE) of 0.07 and -0.07% , respectively. The EE values are smaller than anticipated, but taking into account that the light is 90% circular polarized at best and that the bandwidth is 10 nm at most, EEs of no greater than 0.1 to 0.2% can be expected.

A potential data storage system based on racemic **1** can be envisioned (Fig. 1B). Irradiation of a racemate (MP) with *r*-CPL or *l*-CPL for the writing process generates P-enriched or M-enriched regions, respectively. Detection (read-out) is achieved through use of linearly polarized light (LPL) by measuring CD, or optical rotation in transmis-

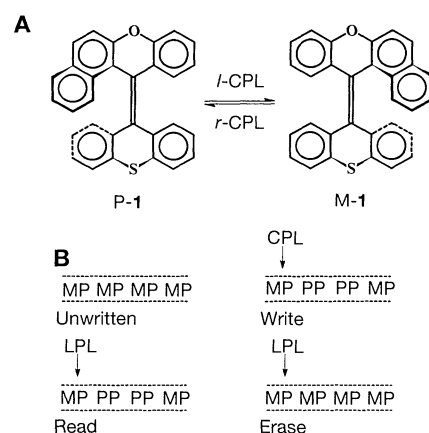


Fig. 1. (A) Photochemical interconversion of P (right-handed) and M (left-handed) helices of **1** upon irradiation with *l*- or *r*-CPL light. (B) Proposed optical data storage system based on the chiral optical switch **1**. Writing is with CPL, and reading and erasing are with LPL.

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sion, or reflection outside the absorption band. Written information can be erased by LPL (or unpolarized light) at the original wavelength, regenerating MP-1. An erasable direct read after write (EDRAW) process might be executed by changing the chirality of the light at a particular wavelength. In principle, this system constitutes a three-position switch of racemic, P-enriched, and M-enriched **1**, with the distinct advantage that all the processes can be performed at a single wavelength.

Once the switching process with CPL irradiation had been firmly established, we studied the photoisomerization in LC materials using racemic **1** as a dopant (**10**, **11**). A stable nematic phase was obtained from 20 weight % MP-1 and 4'-(pentyloxy)-4-biphenylcarbonitrile **2**. Differential scanning calorimetry showed a solid-nematic transition ($T_{s \rightarrow N}$) at 48.2°C [enthalpy change, ΔH , = 71 J/g; for pure **2** the transition occurs at 52.4°C (ΔH = 96 J/g)]. Irradiation of a thin film of racemic **2**, doped with MP-1 at 313 nm for 90 min with *l*-CPL, analogous to the experiments in solution, resulted in a cholesteric phase (Fig. 3A), showing that the photostationary state $P-1 \rightleftharpoons M-1$ with an optical enrichment in M-1 is also reached in the LC phase. The formation of the cholesteric phase was accompanied by a change in phase transition ($T_{s \rightarrow N}$ at 48.7°C, ΔH = 66 to 69 J/g). Control experiments showed that a similar effect on the phase transition occurred with doping of **2** with 20 weight % of racemic **1**, 1.5% enriched in either P-1 or M-1 ($T_{s \rightarrow N}$ at 48.7°C, ΔH = 69 J/g).

In a separate experiment on a thin film of **2** doped with racemic **1** in which *r*-CPL was used instead of *l*-CPL, photoderacemization was again observed. Irradiation of the film of the cholesteric phase reached

after CPL irradiation, containing excess M-1, with unpolarized light at 313 nm resulted in a nematic phase. This is a consequence of the formation of a 50:50 ratio of opposite helices of **1**; that is, photoracemization occurred. A large pitch (p = 580 μm based on helical twisting power 0.1) is seen in the cholesteric phase as a result of low resolution of **1** by CPL irradiation. We performed control experiments to establish independently the optical enrichment of dopant **1** as the origin of the induced cholesteric phase. An LC phase was prepared from

2 and 20 weight % racemic **1** enriched with 1.5% M-1. A cholesteric texture (Fig. 3B) was obtained similar to that observed after CPL irradiation (Fig. 3A).

Because of the high amount of dopant, some phase separation (demixing) was observed after CPL irradiation (Fig. 3A). This phenomenon, reminiscent of conglomerate or racemate formation in the solid state (12), was observed in several experiments and points to differences in the stability of chiral and racemic phases at low enantiomeric excesses of the dopant. The photochemical switching processes of the LC phases are completely controlled by the changes in chirality of the light at a single (313 nm) wavelength: (i) switching between LPL and CPL results in a nematic to cholesteric modulation, and (ii) switching between *l*-CPL and *r*-CPL modulates the chirality of the cholesteric phase (left-handed and right-handed cholesteric phases, respectively). Great care was taken in all experiments to exclude chiral contamination or any other sources besides CPL irradiation of the induced chirality resulting in a cholesteric phase. It should be emphasized that rather large amounts of racemic dopant are required, compared with optically active dopants (10), to observe the cholesteric phase; on the basis of an EE of 0.07% in solution, 0.14% enrichment can be achieved when the LC phase is doped with 20 weight % of MP-1. An increase of the helical twisting power and anisotropy factor of the dopant, by structural modifications of the chromophore in **1**, may decrease the required dopant concentration.

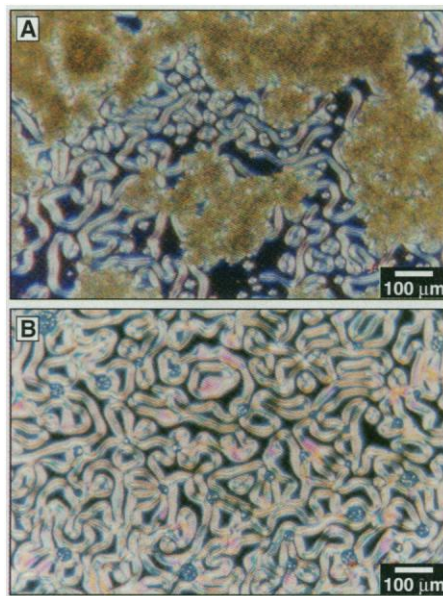
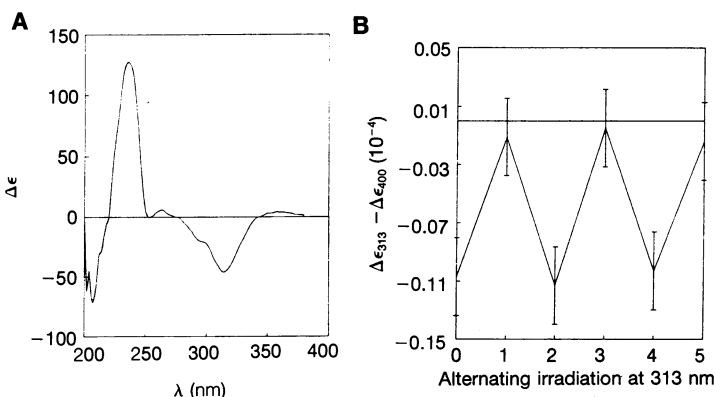


Fig. 3. (A) Cholesteric texture observed for 4'-(pentyloxy)-4-biphenylcarbonitrile (**2**) doped with 20 weight % racemic **1** after irradiation with 313-nm *r*-CPL light. Phase separation can be seen. (B) Cholesteric structure obtained for **2** doped with 20 weight % racemic **1** enriched with 1.5 weight % M-1. A similar cholesteric structure as in (A) can be observed. Bar indicates 100 μm .

Fig. 2. (A) CD spectrum of M-1 taken in hexane:isopropanol (9:1). (B) The difference in CD absorption at 313 and 400 nm ($\Delta\epsilon_{313} - \Delta\epsilon_{400}$) for a solution of **1** (9×10^{-5} mol liter $^{-1}$) in *n*-hexane upon alternating irradiation with *l*- and *r*-CPL. Irradiation was carried out with a 200-W high-pressure mercury lamp equipped with a water filter, a 10-nm bandwidth mercury line filter (313 or 340 nm), a polarization filter, and a $\lambda/4$ plate (340 nm). The desired wavelength was selected by an interference filter. LPL was generated with a polarization filter, and CPL was generated from this LPL with a 340-nm $\lambda/4$ plate. Irradiations of degassed alkene solutions were performed in 2-cm quartz CD cells.



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 - We thank R. M. Kellogg, H. A. van Doren, and J. van Esch for useful comments.

31 May 1996; accepted 18 July 1996

Identification of the "Active Sites" of a Surface-Catalyzed Reaction

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The dissociation of nitric oxide on a ruthenium(0001) surface was studied by scanning tunneling microscopy. The distribution of nitrogen atoms after the dissociation allowed the identification of the "active sites" for this reaction, which are formed by the low-coordinated, top metal atoms of atomic steps. It is proposed that their activity is caused by local changes in the electronic structure. The structure of the steps determines whether they remain active or become deactivated by oxygen atoms. The results demonstrate the complex manner in which the structure of a catalytic surface determines the reactivity of the catalyst and confirm the active sites concept.

The notion of "active sites" (1) is fundamental to heterogeneous catalysis. It reflects experimental evidence (2, 3) that many catalytic surfaces are not uniformly active but exhibit activity only at sites distinguished by a special arrangement of the surface atoms or by a special chemical composition. However, the exact nature of the active sites and hence the mechanism by which they act are still largely a matter of speculation. Taylor first formulated the idea in 1925 (1) that defect sites, formed by low-coordinated surface atoms with unsaturated valencies, are essential. The importance of defects is, in fact, indicated by the frequent variation of activity with particle size, which led to the classification of "structure-sensitive reactions" (2, 3). According to the Adlineationstheorie of Schwab and Pietsch (4), one-dimensional defects play a role. These might be identified with atomic steps, which were shown to accelerate chemical reactions on single-crystal surfaces (5). However, on the basis of considerations about electronic structure (6), it was suggested that the highly coordinated atoms at the bottom of the steps were the sites of enhanced activity, in contrast to the original idea. The validity of these concepts cannot be decided by the

ordinary, laterally integrating methods, because the effects of defects as a whole are measured. It is therefore crucial to directly identify the atomic sites responsible for the active-site effect.

Here we present direct evidence by means of scanning tunneling microscopy (STM) for the active sites for the dissociative chemisorption of NO, a decisive step in the catalytic reduction of nitric oxides for which Ru is the most selective catalyst (7). A clean Ru(0001) sample was prepared under ultrahigh-vacuum conditions and exposed to NO at 300 K or slightly higher temperatures. It is known (8, 9) that under these conditions NO dissociates completely. The distribution of the chemisorbed N and O atoms thus formed on the surface was then investigated by STM at 300 K.

In the STM topograph of the Ru(0001) surface (Fig. 1A), taken 0.5 hour after exposure to 0.3 L of NO, a large number of small dark dots is discernible on both sides of a monoatomic step. The individual, disordered spots closer to the step represent N atoms, the small clusters at larger distances from the step are islands of O atoms, and the dark dashes are individual O atoms in equilibrium with the islands. This interpretation is based on experiments with pure N or O layers, in which it was found that O atoms partially cluster in islands with a (2 × 2) structure, whereas the N atoms are randomly distributed (10). In addition, the

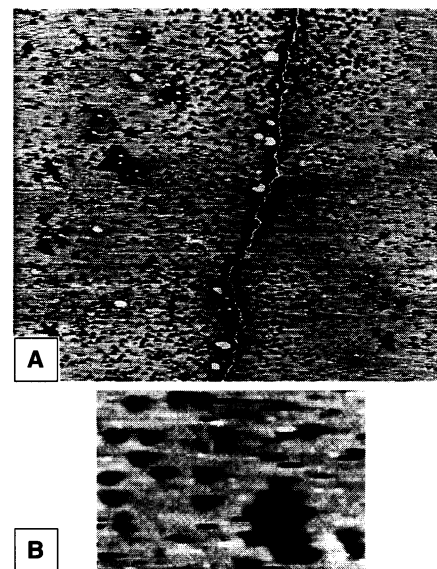


Fig. 1. STM images of a Ru(0001) surface after the dissociative adsorption of 0.3 L (1 L = 1 langmuir = 1.3×10^{-6} mbar-s) of NO at 315 K. The gray shading was done for the two terraces individually with brightness scaled according to height. Tunneling voltage (V_{sample}) = -0.6 V; tunneling current (I_{tunnel}) = 1 nA; T = 300 K. **(A)** Image (380 Å by 330 Å) showing two terraces (upper one to the left, lower one to the right) separated by a monoatomic step (black stripe). **(B)** Close-up (60 Å by 40 Å) of the area marked in (A), showing an O island and individual N atoms. Individual O atoms are imaged as dashes (see arrow) parallel to the scan lines because most of them jump between subsequent scan lines.

N and O atoms are imaged slightly differently by the STM, with the O atoms appearing black and the N atoms gray in the gray-scale representation of Fig. 1B (11). Individual N and O atoms can also be discriminated on the basis of their mobilities, the hopping rate of O atoms being comparable to the scanning frequency (this lets them appear as dashes in the images) whereas the N atoms hop only on the time scale of the full frames (12).

The distribution of the product atoms and their different mobilities suggest a mechanism according to which the NO molecules, which are extremely mobile and not detected by the STM at 300 K, have dissociated at the step into N and O atoms, whereafter the latter have rapidly diffused away from the step onto the terraces. The N atoms have moved away from the step more slowly, so that, when the image was recorded, a diffusion profile, with its origin at the step, could still be recognized. The N atoms thus serve as markers for the reaction sites (13). Therefore, the atomic steps, which exist with a finite density even on well-prepared, single-crystal surfaces, must be the active sites for the dissociation of NO

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