

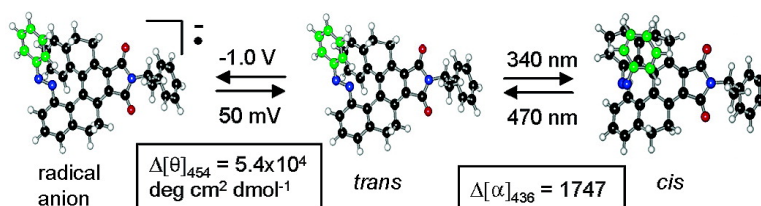
Communication

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Dual Modulation of a Molecular Switch with Exceptional Chiroptical Properties

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Interconversion of the two bistable chiral forms can result from responses of the chiral molecules to external stimuli such as heat, light, pressure, pH, chemicals, magnetic and electric fields.^{1–5} Photomodulation is the most common method^{4,5} and utilizes photoisomerization reactions of a variety of chromophores including diarylethenes, spiropyrans, fulgides, rotaxanes, and azobenzenes.^{6–13} Nearly all the known photomodulation results from a change in the magnitude of optical activity caused by a high-barrier reversal of the helix sense in one-handed chiral chromophores or polymers, which in turn is triggered by isomerization of the ethylene or azobenzene groups.^{10–16} Electrochemically modulated chiroptical switches, although less known, can operate in principle based on detection of the chiroptical properties of the two redox forms of the molecule.¹⁷ Such a switch was demonstrated with optically active copper complexes^{17a} and bispyrene compounds,^{17b} as a result of changes in the molecular symmetry and electronic state (i.e., neutral to radical anion) between the two redox forms, respectively.

We show in this work that a new chiroptical molecular switch that operates in a dual mode, both photochemically and electrochemically, based on changes in the electronic state rather than in the configuration of the chiral molecule can be realized. Here, such a chiral molecule (i.e., **4**) is designed to have three desired features. (i) The molecule should possess high optical activity, and to ensure high sensitivity in signal reading, its optical activity varies significantly with a minimum change in its electronic state. Thus, it should preferably have a helical structure such as that of helicenes, as the optical activity of helicenes depends strongly on the π -electron conjugation within the helical loop,^{21–24} from $[\alpha]_{589} = 3640$ for P-[6]helicene up to $[\alpha]_{589} = 9620$ for P-[13]helicene.^{21,22} (ii) It should contain a trigger that is both photoresponsive and redox-active and is linked in conjugation to the chiral chromophore. (iii) Photomodulation or electrochemical modulation should result in only small structural changes but large electronic variations, or changes in dipole moment and π -conjugation, within the molecule.

Some resolved helically twisted *o*-terphenyl compounds analogous to unresolved **1** were found to have optical rotations that are comparable to that of higher helicenes.^{25,26} Small variations in dihedral angles or changes in the degree of conjugation within these molecules resulted in significant changes in their optical activity, e.g., $[\alpha]_{436} = -349$ for compound **2** (larger twist or less conjugation) and -7100 for **3** (Figure 1). A new chiroptical switch shown in this work is based on the helical *o*-terphenyl **4** having the photoresponsive azobenzene and electrochemically active imide groups.^{18,27,28} Since both triggers are directly attached to the conjugated terphenyl unit, the small *cis*–*trans* structural change of the azobenzene moiety and the formation of a radical anion on the imide group upon electrochemical reduction should alter the overall electronic state of this chromophore, which in turn is expected to lead to a large change in chiroptical responses at various wavelengths.

(S)(–)- α -Methylbenzylamine was used for imidization of racemic anhydride **3** in boiling *N,N*-dimethylformamide to form the redox-active imide and to resolve the diastereomers. Reduction

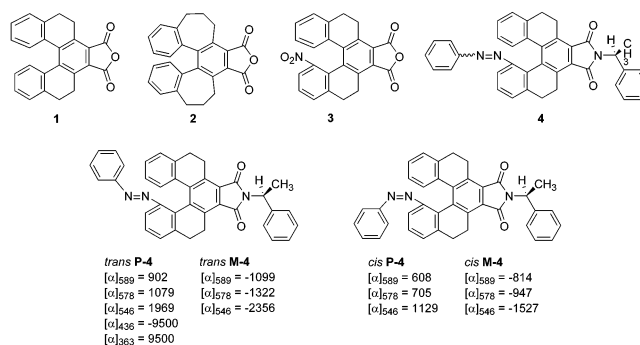


Figure 1. Helically twisted *o*-terphenyl derivatives.

of the nitro group with hydrogen (40 psi over PtO₂ catalyst) and subsequent reaction with nitrosobenzene in chloroform at room temperature afforded **4** containing the *trans*-diastereomers as a major product. The two diastereomers were separated by chromatography using a (S,S)-Whelk-01 column with hexane/2-propanol as an eluent or by repeated recrystallization from acetone/methanol/water into *trans*-**P-4** (mp = 201 °C, see Supporting Information) and *trans*-**M-4** (mp = 225 °C). The X-ray structure of **M-4** reveals that the *trans*-azobenzene moiety is located on the track of the helical loop (see Supporting Information). Optically pure *cis*-isomers were obtained by irradiation (340 nm) of *trans*-isomers **4**, followed by chromatographic separation. *trans*-**P-4** and *trans*-**M-4** show exceptionally optical activity (e.g., $[\alpha]_{436} = -9500$), giving rise to the larger read-out difference ($\Delta[\alpha]$), such as 840 at 546 nm between *trans*-**P-4** and *cis*-**P-4** and 829 at 546 nm between *trans*-**M-4** and *cis*-**M-4**. Such a large difference in optical activity is presumably due to that fact that the azobenzene moiety for the *cis*-isomer is located outside the helical loop or the *cis*-isomer is less conjugated within the chiral moiety. The intense peak in the CD spectrum of **P-4** was seen at 240 nm with a molar ellipticity of 311,000 deg·cm²·dmol⁻¹. For the **P** isomer, positive CD peaks were also visible at 279 and 390 nm, and negative peaks appeared at 332 and 454 nm, which correlate well to the measured specific optical rotation values. For the **M** isomer, an identical CD spectrum with opposite sign was obtained (Figure 2).

In addition to displaying exceptionally high optical activity, these chiral molecules show no significant **P**–**M** racemization during measurements at room temperature. Kinetic studies on thermal racemization of the **P** isomers were carried out at 49.8 ± 0.1 °C, and the results indicated that the half-life of **P-4** was 3600 min. *cis*-**P-4** was also quite resistant to structural relaxation (i.e., *cis*–*trans* azobenzene isomerization), with a half-life of 12 days at ambient temperature in the dark. While the lifetime of *cis*-azobenzene is 4.7 days under similar conditions,²⁹ it has been shown that substituted azobenzenes can have lifetimes ranging from seconds to days.^{9,13,29,30} In our case, the azo group is locked within the “pocket” of the helical loop, thus restricting its mobility toward isomerization via the most likely inversion process.³⁰

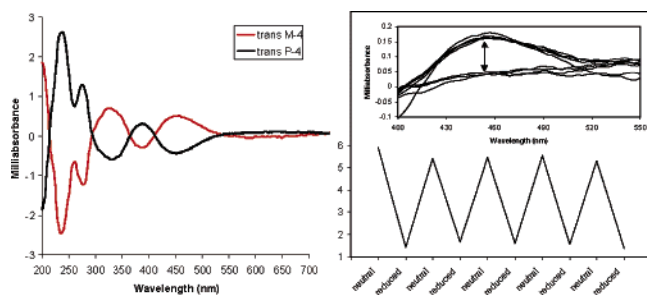


Figure 2. (Left) CD spectra of **M-4** and **P-4** in acetonitrile (10^{-5} M). (Right) Electrochemically induced variation in the ellipticity of **M-4** monitored at 454 nm. (Inset) CD spectra obtained during the electrochemical modulation study.

Photomodulation studies were first carried out using **P-4** in solution and monitored by UV/vis spectroscopy, HPLC analysis, and optical rotation measurements. The *trans*-isomer shows two strong absorption bands with λ_{\max} values of 280 and 340 nm. The *cis*-isomer has two main peaks at 280 and 370 nm and a very weak broad band near 450 nm (see Supporting Information). Upon irradiation with 340-nm light for 10 s, one photostationary state (state 1) switched to another (state 2) containing 54% *trans*- and 46% *cis*-isomers as determined by HPLC. Subsequent irradiation with visible light (470 nm) brought it back to state 1 containing 67% *trans*- and 33% *cis*-isomers (see Supporting Information). The switch between the two states can be repeated continuously, as indicated by the similarity of the first and final UV spectra of the irradiated solutions. As expected, the *cis*–*trans* isomerization of the azobenzene moiety induced large changes in optical activity. Upon irradiation of **P-4** with 340-nm light, the $[\alpha]_{589}$ value decreased to 700 from 902 and $[\alpha]_{546}$ to 1300 from 1969. Upon irradiation with 470-nm light, the values were recovered ($[\alpha]_{589} = 800$, $[\alpha]_{546} = 1500$). The chiroptical changes are wavelength dependent, as the changes in specific optical rotations were found to be 134, 215, 403, and 1747 at the wavelengths of 589, 578, 546, and 436 nm, respectively. Thus, the higher chiroptical activity at a certain wavelength will lead to higher magnitude of the changes in optical signals or better read-out ability in the binary format.

Photomodulation studies were also conducted in the solid state, using a thin film (0.03 mm) of polycarbonate containing 2 wt % of **P-4**, obtained by casting a 10% chloroform solution on a glass plate. A switching behavior similar to that in solution was observed (see Supporting Information). The absorption at 340 nm decreased, which was accompanied by a decrease in optical rotation ($\Delta\alpha = 0.01$ at 436 nm). Subsequent irradiation with visible light restored the absorption peak at 340 nm and its high readable value ($\alpha = 0.06$). Photomodulation could be repeated many times without a significant decrease in signal intensity.

The chiroptical properties of **4** could also be modulated electrochemically, due to the change in the overall electric moment of the chiral molecule upon reduction of the imide functionality. For the electrochemical modulation study, a potential was chosen that would result in reduction of the imide functional group only. The ability and reversibility of chiroptical switch were readily monitored in situ using CD by alternating the applied potential of the system between 50 mV (neutral) and -1000 mV (reduced). The large differences in the molar ellipticity ($\Delta[\theta]$) were found to be 54,000 and 285,000 $\text{deg}\cdot\text{cm}^2\cdot\text{dmol}^{-1}$ at 454 and 240 nm, respectively, upon reduction of the imide group (Figure 2). Repeated redox cycles resulted in virtually the same optical activity for each of the bistable states, indicating good reversibility of this chiroptical switch.

In conclusion, we have demonstrated a photo- or electrochemically modulated molecular system that changes its electronic state rather than its helical configuration, allowing for further development of molecular switches, molecular devices, sensors, and other optoelectronic devices.^{4,5}

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Supporting Information Available: X-ray crystal structure of *trans*-**M-4**, DSC of **P-4** and **M-4**, HPLC and UV–vis of **P-4** in solution and in polymer film during photomodulation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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