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Remarkable Solvent-Dependent Excited-State Chirality: A Molecular Modulator of Circularly Polarized Luminescence

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Abstract: The photochemical control of ground- and excited-state chirality of (*M*)-*cis*-(**1**) and (*P*)-*trans*-(**2**)-2-nitro-7-(dimethylamino)-9-(2′,3′-dihydro-1′*H*-naphtho[2,1-*b*]-thiopyran-1′-ylidene)-9*H*-thioxanthene is described. It is shown that while ground state chirality can be controlled photochemically by irradiation with light of different wavelengths, the excited state chirality can be tuned either photochemically in a similar way or by appropriate choice of solvent. In benzene solution, circularly polarized luminescence of the two isomers with opposite ground-state helicity, (*M*)-*cis*-**1** and (*P*)-*trans*-**2**, revealed corresponding excited states of opposite helicity. On the contrary, in *n*-hexane solution, circularly polarized luminescence was identical for the two forms indicating identical excited state chirality. Circularly polarized luminescence (CPL), steady-state and time-dependent fluorescence, and time-resolved microwave conductivity (TRMC) measurements in both *n*-hexane and benzene are reported, which provide an explanation for the remarkable solvent dependence of excited-state chirality.

Introduction

Photochemical isomerization is an essential feature in important light-induced conversions in Nature, most evident in the process of vision.[1] The basic chemical principle is also used in synthetic systems, which are designed to achieve changes in response to light and applied, for example, as information storage materials and devices.[2] Photoisomerization has been exploited to control magnetic[3] or electronical properties,[4] binding and transport,[5] catalytic activity,[6] molecular motion,[7] molecular architecture,[8] and organization.[9] In particular the cis−trans isomerization of alkenes,[10] and especially stilbene[11] and tetraphenylethylene,[12] is the subject of intensive studies. Our interest in photochemical isomerization processes involves the cis−trans isomerization of sterically overcrowded alkenes, molecules which have been essential in the construction of chiroptical molecular switches[13] and unidirectional molecular rotary motors.[14] Due to the intrinsic chirality and photochemical bistability of these sterically overcrowded alkenes, the modulation of (*P*)- and (*M*)-helicity is achieved in a fully reversible manner, employing light of different wavelengths. The distinct advantage of these systems, compared to several other photochromic materials, is that nondestructive read-out is possible using chiroptical methods.

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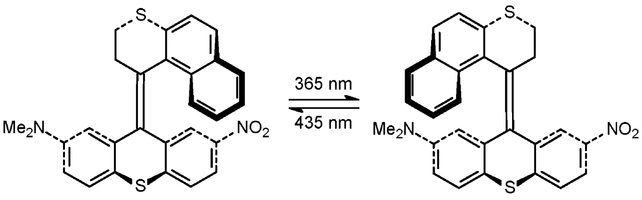
Scheme 1. A Chiroptical Molecular Switch Based on the Photoisomerization of Optically Active, Sterically Overcrowded Alkenes (*M*)-*cis*-**1** and (*P*)-*trans*-**2**



(*M*)-*cis*-**1** (*P*)-*trans*-**2**

It has been shown that for the sterically overcrowded alkenes *cis*-(**1**) and *trans*-2-nitro-7-(dimethylamino)-9-(2′,3′-dihydro-1′*H*-naphtho[2,1-*b*]-thiopyran-1′-ylidene)-9*H*-thioxanthene (**2**) switching between the cis and the trans form is very efficient and shows excellent reversibility (Scheme 1).[15] A stereoselective photochemical interconversion of the two diastereoisomers (*M*)-*cis*-**1** and (*P*)-*trans*-**2**, which can be considered pseudoenantiomers,[16] can be accomplished by irradiation with light of two different wavelengths. The photostationary states are governed by the ratio of the extinction coefficients (ϵ) of the two forms at a particular wavelength together with the ratio of the quantum yield (Φ) for interconversion of the two forms, following eq 1. The cis−trans isomerization is accompanied by reversal of helicity, from negative (*M*) helicity in case of *cis*-**1** to positive (*P*) helicity in case of *trans*-**2** and vice versa. In *n*-hexane solution, irradiation at 435 nm results in a photostationary state with an excess of 80% in favor of the cis isomer ((*M*)-*cis*-**1**:(*P*)-*trans*-**2** = 90:10) whereas 365 nm irradiation results in a photostationary state with an excess of 40% in favor of the trans isomer ((*M*)-*cis*-**1**:(*P*)-*trans*-**2** = 30:70), respectively. Circular dichroism (CD) measurements confirm the opposite ground-state helicity of (*M*)-*cis*-**1** and (*P*)-*trans*-**2** (vide infra).

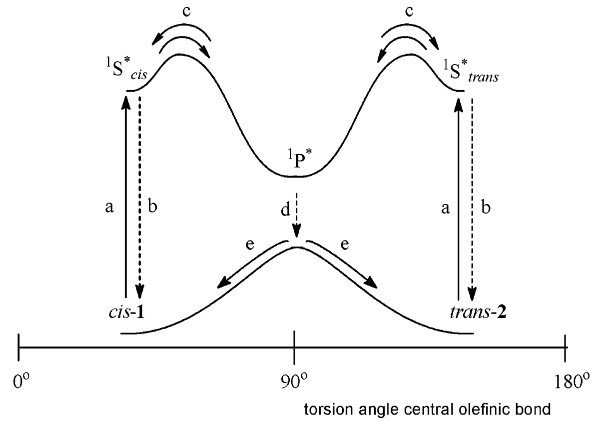


Figure 1. Simple singlet model for the photoisomerization of the molecular switch system consisting of *cis*-**1** and *trans*-**2** (see test for details).

$$[(M)\text{-}cis\text{-}\mathbf{1}]/[(P)\text{-}trans\text{-}\mathbf{2}] = (\epsilon_{(P)-trans-\mathbf{2}}\Phi_{(P)-trans-\mathbf{2}\rightarrow(M)-cis-\mathbf{1}})/(\epsilon_{(M)-cis-\mathbf{1}}\Phi_{(M)-cis-\mathbf{1}\rightarrow(P)-trans-\mathbf{2}}) \quad (1)$$

Figure 1 shows a simplified model of the main processes and states expected to be involved in photoisomerization of this chiroptical molecular switch. This model is based on the potential energy diagram determined for ethylene first reported by Mulliken.[17] Although the overall picture is expected to be considerably more complex than as presented in Figure 1, due to, for example, the steric hindrance around the central olefinic bond and the presence of both donor and acceptor groups and sulfur heteroatoms, this simplified scheme only serves as a working model for our current investigation. Photoisomerization is expected to occur in the first singlet excited state where the bond order of the olefinic C−C bond is substantially reduced. Starting from either the *cis*-**1** or the *trans*-**2** ground state, photoexcitation (a) is expected to results in the corresponding first singlet excited states $^1S^*_{cis}$ and $^1S^*_{trans}$, respectively. From these states either (luminescent or nonluminescent) decay to the ground state (b) or interconversion between the cis and the trans olefins (c) can take place. This interconversion implies a rotation around the excited central olefinic bond, and there is considerable evidence that this process involves a perpendicular or phantom excited state ($^1P^*$).[18] From this minimum energy state also decay to a perpendicular ground-state geometry (d) can take place. In the ground-state the system will release its energy by rotation of the central olefinic bond (e) to form again either *cis*-**1** or *trans*-**2** in their ground-state configuration. The model presented in Figure 1 is an oversimplified picture for complicated stilbene-type alkenes as **1** and **2**, as the influence of charge transfer and involvement of triplet excited states, for example, are neglected.[19]

To elucidate the excited-state processes involved in photoisomerization of the chiroptical molecular switch system

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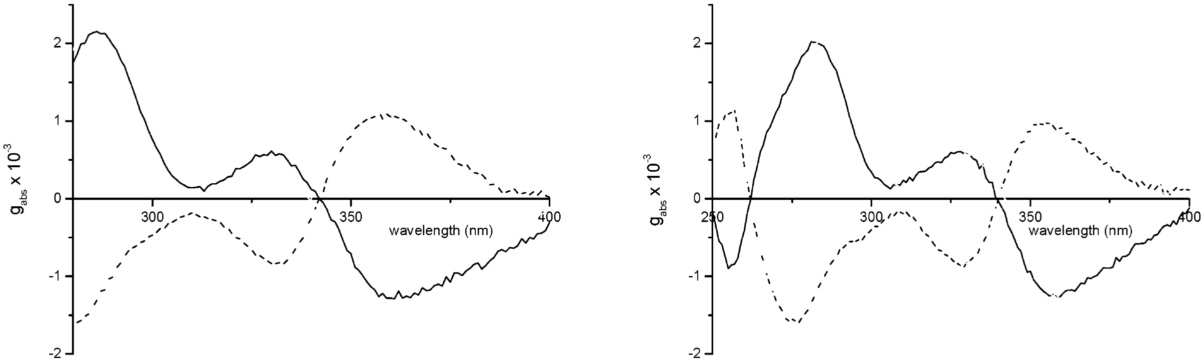

Figure 2. *g*-values of absorption of (*M*)-*cis*-**1** (solid) and (*P*)-*trans*-**2** (dashed) in both benzene (left) and *n*-hexane (right) solution.

consisting of (*M*)-*cis*-**1** and (*P*)-*trans*-**2** and in particular to get information on the chiral nature of the excited states, circularly polarized luminescence (CPL) studies were performed. CPL spectroscopy offers an attractive tool to probe the excited-state chirality.[20] These chiral sterically overcrowded alkenes are particularly suitable substrates to study excited-state processes in alkene isomerization because photoisomerization is associated with a change in helical chirality. Chiroptical techniques like CPL spectroscopy can give additional information compared to common spectroscopic techniques, and the use of chirality, as far as we know, provides a new approach to probe olefin isomerization processes. The distinct advantage of the use of chiroptical techniques to probe isomerization processes is that changes in the chiral nature of any olefin can directly be monitored with large sensitivity. It was envisioned that with these chiral alkenes additional information on the exact photophysical processes involved in switching and changes in the excited-state geometry upon photoisomerization in general can be obtained. We present here a remarkable dependency of excited-state chirality on the medium resulting in a modulation of circularly polarized luminescence. Steady-state and time-dependent fluorescence and time-resolved microwave conductivity (TRMC) studies have been performed to support the interpretation of our results.

Results and Discussion

Circularly Polarized Luminescence. Compound (*M*)-*cis*-**1** and (*P*)-*trans*-**2** were obtained in enantiomerically pure form as previously reported.[15] Circular dichroism (CD) measurements of the two diastereoisomeric forms of the switch system, (*M*)-*cis*-**1** and (*P*)-*trans*-**2**, both in benzene and *n*-hexane solution, show near mirror image behavior indicating opposite ground-state chirality and their pseudoenantiomeric relation.[16] This is further reflected in the dissymmetry factor *g* of absorption (g_{abs}), which is defined according to eq 2 (where $\Delta\epsilon = \epsilon_L - \epsilon_R$, the difference in absorption between left- and right-handed circularly polarized light, and ϵ the extinction coefficient[21]) and depicted for (*M*)-*cis*-**1** and (*P*)-*trans*-**2** in Figure 2.

$$g_{abs} = \Delta\epsilon/\epsilon \tag{2}$$

CPL measurements were performed in two solvents to probe the excited-state chirality of (*M*)-*cis*-**1** and (*P*)-*trans*-**2**. Where CD spectroscopy reflects the geometry of the compounds in their ground state, CPL is a complementary technique that probes the chirality of the luminescent excited states. The chirality in the excited state of these molecules was monitored by CPL in both benzene and *n*-hexane solution and quantified by a *g*-value of luminescence (g_{lum}). This *g*-value is defined analogous to g_{abs} according to eq 3 (where $\Delta I = I_L - I_R$, the difference in luminescence of left- and right-handed circularly polarized light, and *I* the total emission intensity[20]).

$$g_{lum} = \Delta I/I \tag{3}$$

In benzene, CPL measurements for (*M*)-*cis*-**1** and (*P*)-*trans*-**2** (λ_{em} = 590 nm; λ_{ex} = 360 nm) indicate that the difference in chirality in the ground state is retained in the excited state, as is shown by the opposite *g*-values of fluorescence for (*M*)-*cis*-**1** and (*P*)-*trans*-**2** of $+5.6(\pm0.8) \times 10^{-4}$ and $-7.8(\pm0.7) \times l0^{-4}$, respectively. Remarkably, these anisotropy factors associated with the excited states are opposite in sign compared to those based on the ground-state chirality as the 360 nm absorptions have *g*-values (g_{abs}) for (*M*)-*cis*-**1** and (*P*)-*trans*-**2** of -1.28×10^{-3} and $+1.06 \times 10^{-3}$, respectively. As can be seen from Figure 2, however, the g_{abs} values are strongly wavelength dependent and the fact that at 360 nm g_{abs} is opposite in sign compared to g_{lum} for both pseudoenantiomers is apparently purely coincidental. It should be noted that over the entire wavelength range (except for very small regions near the abscissas of the *x*-axis) the g_{abs}-values are opposite for both pseudoenantiomers in both *n*-hexane and benzene.

In *n*-hexane, analogous to benzene solution, g_{abs} (300 nm) is opposite for (*M*)-*cis*-**1** and (*P*)-*trans*-**2** ($+2.68 \times 10^{-4}$ and -3.60×10^{-4}, respectively). Surprisingly, both forms display negative circularly polarized fluorescence with the same *g*-value of $-4.2(\pm0.8) \times 10^{-4}$ (λ_{em} = 520 nm; λ_{ex} = 300 nm). For the enantiomeric pair (*P*)-*cis*-**1** and (*M*)-*trans*-**2** in *n*-hexane, positive CPL is observed. All other measurements on this pair of isomers are consistent with the reported results. For both isomers this g_{lum}-value remains unchanged upon variation of the excitation wavelength (λ_{ex} = 300−435 nm) indicating luminescence from the same excited state over this wavelength region. Due to the fact that after prolonged irradiation a photostationary state resulting from the cis−trans equilibrium is reached, the numerical values of g_{lum} do not pertain to pure (*M*)-*cis*-**1** and (*P*)-*trans*-**2**. However, the sign of the circular polarization of the luminescence of both (*M*)-*cis*-**1** and (*P*)-*trans*-**2** in *n*-hexane is

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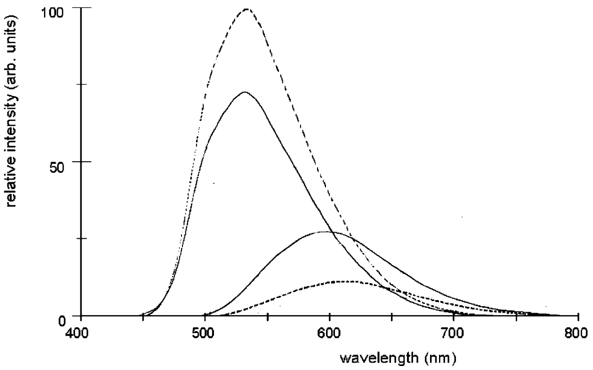

Figure 3. Steady-state fluorescence of *cis*-**1** (solid lines) and *trans*-**2** (dashed lines) in both benzene (maxima at 575 and 620 nm, respectively) and *n*-hexane (maxima at 528 and 531 nm, respectively).

negative as is evident from measurements using fresh samples and measurements after varying irradiation times. This implies that, in contrast to benzene solution, starting from both the (*M*)-*cis*-**1** or the (*P*)-*trans*-**2** ground state (with opposite g_{abs}) upon photoexcitation excited states are reached which show the same chirality in CPL. To elucidate this remarkable effect, steady-state fluorescence, time-resolved fluorescence, and flash photolysis time-resolved microwave conductivity (TRMC) experiments were performed.

Steady-State Fluorescence. At low intensity of the excitation light ($\lambda_{ex} = 300$ nm) the steady-state fluorescence spectra of *cis*-**1** and *trans*-**2** in benzene have their maxima (λ_F) at 575 and 620 nm, respectively (Figure 3). The fluorescence intensity (I_F) for *cis*-**1** is higher than for *trans*-**2** (I_F(*cis*-**1**)/I_F(*trans*-**2**) = 2.8). Both compounds show broad structureless bands of similar shape. In *n*-hexane, the emission spectra of both *cis*-**1** and *trans*-**2** are strongly blue-shifted to 528 and 531 nm. This solvatochromism indicates substantial charge-transfer (CT) character of the luminescent state, as expected for a donor−acceptor substituted aromatic compound. In *n*-hexane the intensity of the *trans*-**2** fluorescence is higher than that of *cis*-**1**. The fluorescence quantum yields in this solvent were determined to be $\Phi_{cis-\mathbf{1}} = 0.026$ (at 531 nm) and $\Phi_{trans-\mathbf{2}} = 0.043$ (at 528 nm).[22,23] Careful analysis of the spectral curves shows that a slight hypsochromic broadening of the spectrum of *cis*-**1**, rather than a shift of the complete band, is responsible for the slight blue-shift of the maximum from 531 nm for *trans*-**2** to 528 nm for *cis*-**1**.

The solvatochromism of both *cis*-**1** and *trans*-**2** caused by the CT character of the luminescent state is further illustrated in Figure 4. For both *cis*-**1** and *trans*-**2**, luminescence shows a general decrease of fluorescence intensity (I_F) and a red-shift of fluorescence wavelength (λ_F) with solvent polarity (indicated by Reichardt's E_T^{30} values[24]) in a range of solvents with E_T^{30} values ranging from 31.0 (*n*-hexane), 32.4 (tetrachloromethane), and 34.3 (benzene) to 36.0 (dioxane). In solvents of higher polarity (chloroform, ethanol, and dichloromethane were tested) no fluorescence is observed. The solvatochromic effect is larger for *trans*-**2**, and as a result, in benzene (and in solvents of higher polarity) the fluorescence of *cis*-**1** is more intense than that of *trans*-**2**, in contrast to the fluorescence intensities in *n*-hexane solution.

Time-Resolved Fluorescence. The fluorescence decay of *cis*-**1** and *trans*-**2** upon excitation at 337 nm in benzene is found to be monoexponential at all monitored wavelengths (λ_{em} = 575, 620, and 665 nm) with lifetimes of 2.3 and 0.9 ns for *cis*-**1** and *trans*-**2**, respectively (Figure 5). These luminescent excited states were assigned the first singlet states for both *cis*-**1** ($^1S^*_{cis-\mathbf{1}}$) and *trans*-**2** ($^1S^*_{trans-\mathbf{2}}$).

For *cis*-**1** in *n*-hexane (λ_{ex} = 300 nm), a short-living fluorescence ($\tau < 300$ ps) in the region of 495 nm is apparent at very short times (Figure 6). Immediately after the flash however the spectrum relaxes to a form with λ_{max} = 531 nm and a lifetime of $\tau = 2.2$ ns. The fluorescence spectrum for *trans*-**2** in *n*-hexane shows a monoexponential decay with λ_{max} = 531 nm and a lifetime of $\tau = 2.2$ ns. The wavelength and lifetime of this luminescent state found for *trans*-**2** are identical to those of the second state observed for *cis*-**1**. In the case of *cis*-**1**, however, the intensity of the 531 nm emission is only approximately 15% of the value found for the fluorescence of a solution of *trans*-**2**. Again, as in the CPL measurements, all data are in agreement with expectation, except for the photochemistry observed for *cis*-**1** in *n*-hexane.

Time-Resolved Microwave Conductivity (TRMC). TRMC measurements on *cis*-**1** and *trans*-**2** were performed to get additional information on the luminescent and nonluminescent states upon excitation and involved in the photoisomerization processes of **1** and **2**. TRMC allows monitoring of both luminescent and nonluminescent states and provides information on the dipole moments of these different states. The decay pathways and excited-state lifetimes determined by TRMC in both benzene and *n*-hexane are consistent with the time-resolved fluorescence measurements. In benzene (Figure 7), the luminescent excited states ($^1S^*$) observed for *cis*-**1** and *trans*-**2** have large dipole moments of 21.0 and 30.8 D, respectively, and lifetimes of 2.3 and 0.9 ns, in full accordance with the lifetimes obtained from the time-resolved fluorescence measurements. From the determined dipole moments, which are of the same order of magnitude as excited-state dipole moments determined for asymmetrically substituted stilbene compounds,[25] it can again be concluded that there is a large charge separation in both luminescent excited states.

We attribute the smaller dipole moment for the cis isomer to the fact that the donor group in the CT excited state of these compounds (i.e. both *cis*-**1** and *trans*-**2**) is the thionaphthalene moiety instead of the dimethylanilino moiety. In the ground state, and presumably also in the luminescent excited state, this thionaphthalene moiety is in closer proximity to the nitrophenyl acceptor in *cis*-**1** as compared to *trans*-**2**.

From TRMC measurements, two additional (nonluminescent) excited states are apparent for both *cis*-**1** and *trans*-**2**. Although for a full understanding of these states additional measurements are required, we denote the two excited states X* and Y*. The first of these nonluminescent states (X*) has a dipole moment of 7.0 D and a lifetime of $\tau = 25$ ns for *cis*-**1** and a dipole

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[22] Quantum yields were determined using quinine bisulfate in 1 N H_2SO_4 as a reference (according to: Eaton, D. F. *Pure Appl. Chem.* **1988**, *60*, 1107−1114); slight deviations caused by isomerization cannot be excluded.

[23] Huck, N. P. M.; Feringa, B. L. *J. Chem. Soc., Chem. Commun.* **1995**, 1095−1096.

[24] Reichardt, C. *Angew. Chem.* **1965**, *77*, 30−40.

[25] Excited-state dipole moments of 21.9−25.8 and 19.3 D are for example reported for 4,4′-(dimethylamino)nitrostilbene (DMANS) and 4,4′-methoxynitrostilbene (MONS), respectively: McLellan, A. L. *Tables of Experimental Dipole Moments*; Rahara Enterprises: El Cerrito, CA, 1974; Vol. 2.

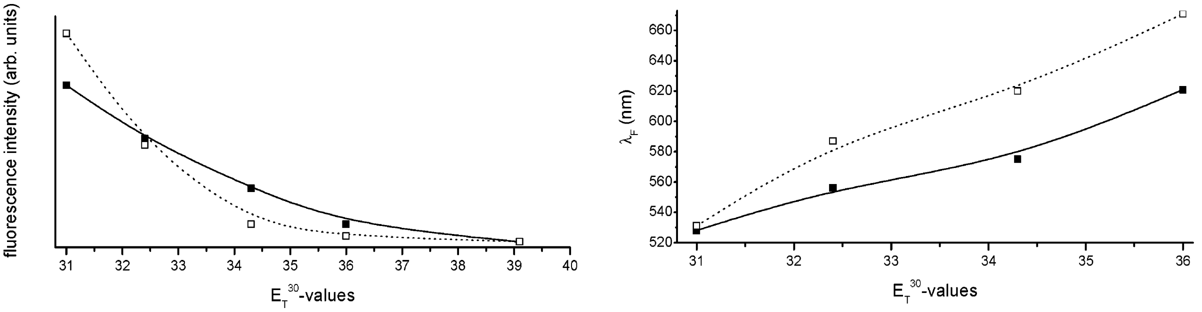

Figure 4. Fluorescence intensity (left) and wavelength (λ_F, right) as a function of the Reichardt solvent polarity parameter E_T^{30} for (*M*)-*cis*-**1** (closed squares; solid lines) and (*P*)-*trans*-**2** (open squares; dashed lines).

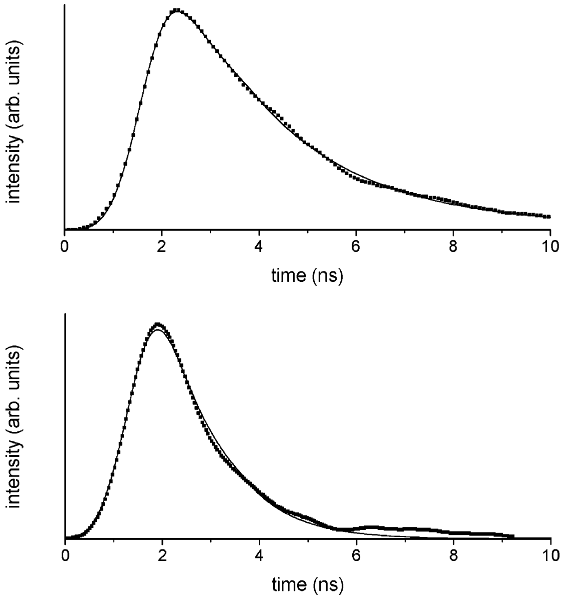

Figure 5. Fluorescence decay curves (■) and fits (—) for *cis*-**1** ($\lambda_{ex} = 337$ nm; $\lambda_{em} = 575$ nm; top) and *trans*-**2** ($\lambda_{ex} = 337$ nm; $\lambda_{em} = 620$ nm; bottom) in benzene.

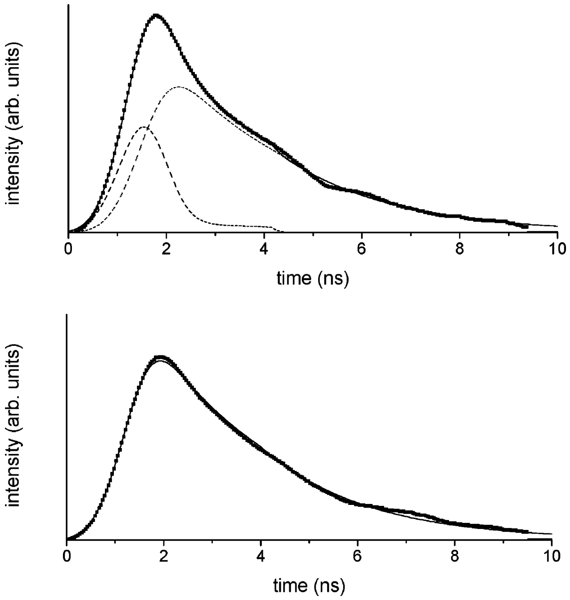

Figure 6. Fluorescence decay curves (■) and fits (—) for *cis*-**1** ($\lambda_{ex} = 337$ nm; $\lambda_{em} = 530$ nm; top) and *trans*-**2** ($\lambda_{ex} = 337$ nm; $\lambda_{em} = 530$ nm; bottom) in *n*-hexane. (For *cis*-**1**, the fluorescence decay is fitted by two monoexponential decays separately shown as dashed lines.)

moment of 6.5 D and a lifetime of $\tau = 25$ ns for *trans*-**2**. These states are proposed to be some kind of intramolecular exciplex, where charge transfer between the thionaphthalene upper half and the nitroarene moiety in the lower half of the molecule has occurred. The decrease in dipole moments, relative to that of the first excited states, is attributed to the decrease in distance between the DA couple in this proposed intramolecular exciplex state. Possibly this excited-state X* corresponds to the perpendicular or phantom state (Figure 1: ^{1}P*), which at least for ethylene is known to be zwitterionic in nature and displays nonradiative decay.[18] The second nonluminescent state (Y^*) has a smaller dipole (4.6 and 5.1 D for *cis*-**1** and *trans*-**2**, respectively) and a lifetime more than several milliseconds for both **1** and **2**. This state is probably a Coulomb-contracted ground state caused by the zwitterionic character of the charge-transfer excited states and might correspond to a ground state with perpendicular geometry formed after decay of the perpendicular excited state that slowly relaxes back to either the *cis*-**1** or *trans*-**2** ground state.

In *n*-hexane (Figure 8), exactly the same excited states were determined for **1** and **2**: a first singlet excited state with a dipole moment of 19.2 D and a lifetime of $\tau = 2.2$ ns and two longer living excited-state X* and Y* with dipole moments of 6.5 and 4.5 D and lifetimes of $\tau = 30$ ns and 1 s, respectively. The two latter states are the same as those found in benzene solution, and their properties are only slightly different in the less polar *n*-hexane. The short-living luminescent state ($\tau < 300$ ps) found in time-resolved fluorescence measurements cannot be observed in TRMC due to the lower resolution of this technique.[26]

To gain more information on the exact processes that takes place upon excitation, single-shot experiments were performed. A large TRMC transient was found for *trans*-**2**, which tended to decrease somewhat after repeated flash-photolysis of the solution to approximately 70% of the initial height. The initial TRMC signal for *cis*-**1** in *n*-hexane was small and corresponded to approximately 15−20% of the initial signal height found for the trans-isomer. On repeated flash photolysis, the signal increased substantially and eventually approached that found on repeated irradiation of the *trans*-**2** solution. Continued flash-photolysis eventually resulted in a steady-state mixture of the two isomers with a trans−cis ratio of approximately 70:30, which is equal to the equilibrium ratio of the isomers found in previous measurements on the basis of the optical absorption changes on irradiation at short wavelengths.[15] Apparently, during

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(26) For time-dependent fluorescence and TRMC experimental procedures and instrumentation: (a) de Haas, M. P.; Warman, J. M. *Chem. Phys.* **1982**, *73*, 35−53. (b) Schuddeboom, W. Ph.D. Thesis, Delft University of Technology, Delft, The Netherlands, 1994; ISBN 90-73861-21-7. (c) Piet, J. J. Ph.D. Thesis, Delft University of Technology, Delft, The Netherlands, 2001; ISBN 90-407-2252-8.

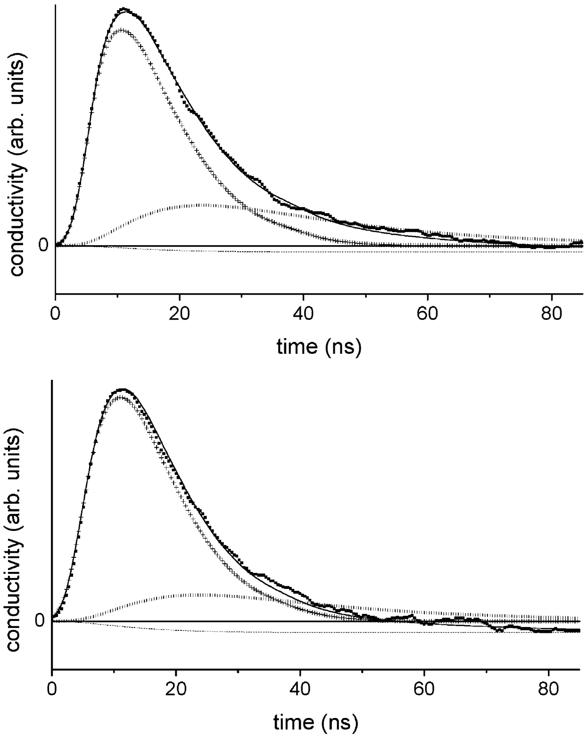


Figure 7. TRMC decays for *cis*-1 (top) and *trans*-2 (bottom) in benzene: ■ = measured data; fit (—) = ^{1}S* (+) + X*(|) + Y* (---).

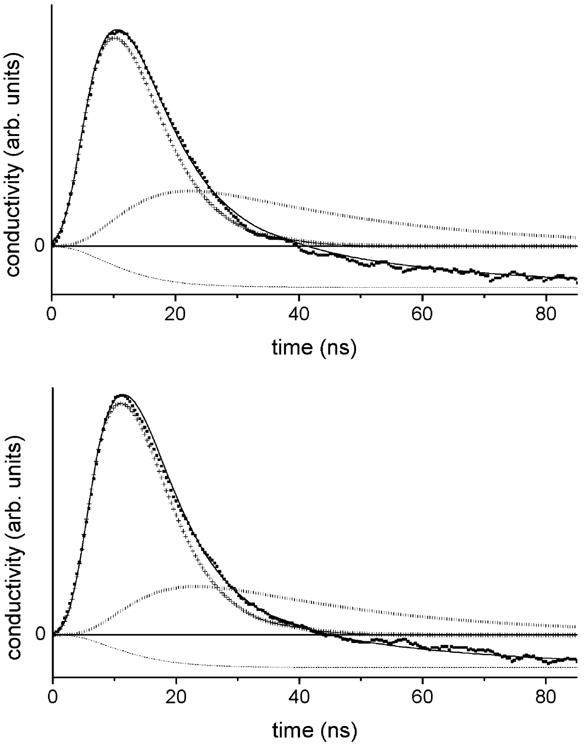
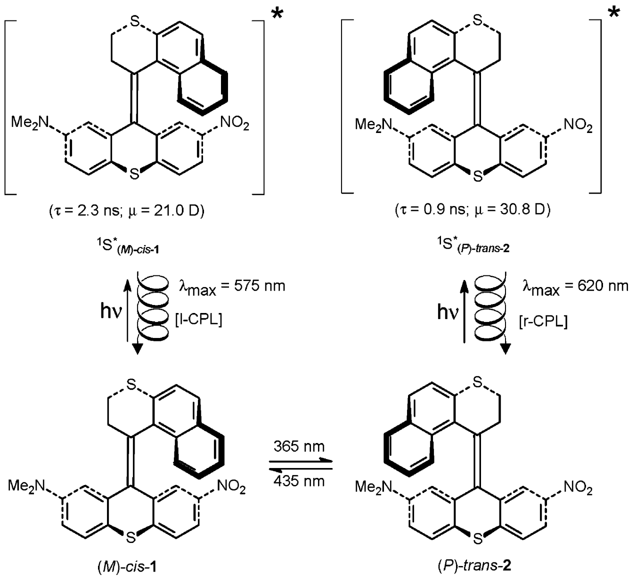


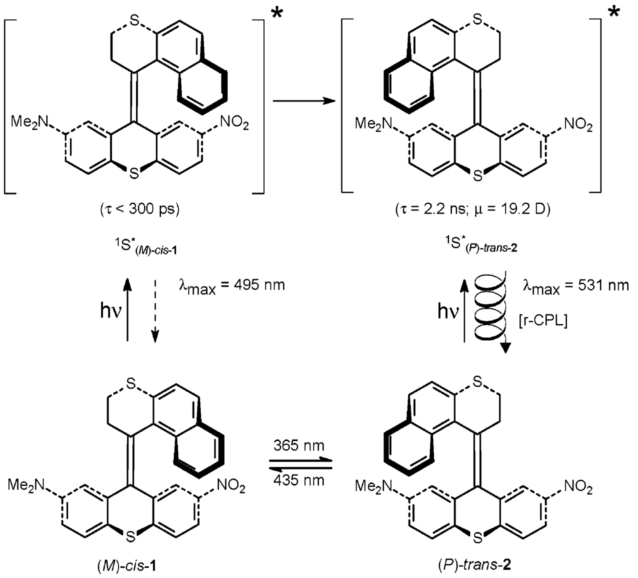
Figure 8. TRMC decays for *cis*-**1** and *trans*-**2** in *n*-hexane: ■ = measured data; fit (—) = ^{1}S* (+) + X* (|) + Y* (---).

the measurement some cis−trans isomerization takes place. From single-shot experiments a dipole moment of 23 D was determined for the first excited state in the case of *trans*-**2** in *n*-hexane solution.

Scheme 2. Luminescence Mechanism, Observed Sign of CPL, and Dipole Moments and Lifetimes of the Excited States for (*M*)-*cis*-**1** and (*P*)-*trans*-**2** in Benzene



Scheme 3. Luminescence Mechanism, Observed Sign of CPL, and Dipole Moments and Lifetimes of the Excited States for (*M*)-*cis*-**1** and (*P*)-*trans*-**2** in *n*-Hexane



Discussion

The combined data led to a model for the isomerization and luminescent excited-state processes for **1** and **2** in benzene (Scheme 2) and *n*-hexane (Scheme 3). In benzene solution, photoexcitation of (*M*)-*cis*-**1** and (*P*)-*trans*-**2** results in the corresponding luminescent first singlet excited states, $^1S^*_{(M)-cis-\mathbf{1}}$ and $^1S^*_{(P)-trans-\mathbf{2}}$. The chirality of the system in the ground state is retained in the excited state, and the opposite chirality of the $^1S^*_{(M)-cis-\mathbf{1}}$ and the $^1S^*_{(P)-trans-\mathbf{2}}$ excited states is reflected in the emission of *l*-CPL and *r*-CPL, respectively. Both time-resolved fluorescence and time-resolved microwave conductivity measurement indicate different decay lifetimes for the two forms, and TRMC also indicated different dipole moments.

In *n*-hexane, for both pseudoenantiomers, (*M*)-*cis*-**1** and (*P*)-*trans*-**2**, the same circular polarization of luminescence is observed. For (*P*)-*trans*-**2** this polarization is similar to that in benzene solution and the luminescent excited state can be assigned $^1S^*_{(P)-trans-\mathbf{2}}$. In the case of (*M*)-*cis*-**1** a biexponential decay is observed in *n*-hexane solution and the circular polarization of luminescence is opposite compared to that in benzene solution. We tentatively explain these observations in the following way (Scheme 3): The first weak short-living 495 nm emission ($\tau < 300$ ps) is the "regular" fluorescence from an excited singlet state with (*M*)-*cis* like geometry $^1S^*_{(M)-cis-\mathbf{1}}$, comparable to benzene solution. This short-living state is not observed in TRMC due to lower resolution and has only a small contribution to the circularly polarized luminescence measured. The main fluorescence at 531 nm is due to a more stable $^1S^*$ excited state with (*P*)-*trans* geometry $^1S^*_{(P)-trans-\mathbf{2}}$, which is formed from the initial (*M*)-*cis*-**1** in the excited state via internal conversion. Since the contribution of the 495 nm fluorescence to the total luminescence is weak, the CPL of (*M*)-*cis*-**1** is expected to be equal to that of (*P*)-*trans*-**2** while it also explains the small differences in the steady-state emission band shapes. Both time-resolved fluorescence and TRMC measurements are in accordance with this explanation. An identical first luminescent excited state was found for *cis*-**1** and *trans*-**2**. This is a mutual singlet excited state of (*P*)-*trans* like geometry formed either by direct excitation in case of (*P*)-*trans*-**2** or interconversion in the excited state in the case of (*M*)-*cis*-**1**. The absence of internal conversion in benzene is due to the dipolar character of the $^1S^*_{(M)-cis-\mathbf{1}}$ state. Although the $^1S^*_{(M)-cis-\mathbf{1}}$ is less polar than the $^1S^*_{(P)-trans-\mathbf{2}}$ excited state, $^1S^*_{(M)-cis-\mathbf{1}}$ in benzene is stabilized by 0.35 eV compared to $^1S^*_{(M)-cis-\mathbf{1}}$ in *n*-hexane. This results in a much larger barrier for rotation about the central double bond and consequently greatly reduced internal conversion from $^1S^*_{(M)-cis-\mathbf{1}}$ to $^1S_{(P)-trans-\mathbf{2}}$. Consequently, the two isomers display their own unique fluorescence characteristics in benzene solution.

An alternative explanation involves the formation of one single isomer of a perpendicular ($^1P^*$) or phantom excited state from both (*M*)-*cis*-**1** and (*P*)-*trans*-**2** (see Figure 1). In this case, however, excitation of one single enantiomer would result in a 50−50 mixture of (*M*)-*cis*-**1** and (*P*)-*trans*-**2**, which is seen neither in time-dependent fluorescence or in TRMC. Also this alternative explanation does not account for the absence of this state in benzene solution and the fact that the circular polarization of luminescence reflects the (*P*)-*trans* geometry. Although the vibrationally relaxed excited states can have a common perpendicular geometry during photoisomerization, a feature often considered in photochemical cis−trans isomerization processes of alkenes,[18] it has been demonstrated that this perpendicular state is not involved in the unique luminescence of (*M*)-*cis*-**1** and (*P*)-*trans*-**2**. As in TRMC measurements, the formation of two additional nonluminescent excited states was observed; the formation of a perpendicular or phantom state upon excitation and a ground state of perpendicular geometry formed as a result of radiationless decay of this perpendicular excited-state cannot be excluded.

Conclusion

We demonstrated the unique excited-state properties of chiroptical molecular switches based on sterically overcrowded alkenes and showed that circularly polarized luminescence offers an excellent tool to probe excited-state processes in chiral olefins. Time-resolved fluorescence and time-resolved microwave conductivity were used to support the model proposed for the excited-state processes leading to the observed circular polarization of luminescence. It was shown that the photoswitchable system of (*M*)-*cis*-**1** and (*P*)-*trans*-**2** can act as a molecular modulator of circularly polarized light in benzene. In this solvent fluorescence takes place from two pseudoenantiomeric excited states which show opposite circular polarization of luminescence. The excited-state chirality reflects the ground-state chirality and can be controlled by appropriate choice of irradiation wavelength. Furthermore, the predominant luminescent excited state of (*M*)-*cis*-**1** can be controlled by appropriate choice of solvent. While in both *n*-hexane and benzene the ground-state chirality is opposite for (*M*)-*cis*-**1** and (*P*)-*trans*-**2**, in *n*-hexane the excited-state chirality and thus the circular polarization of emitted light is equal, irrespective of which of the two pseudoenantiomers is used. It has been shown that this phenomenon is due to emission from a mutual excited state with a (*P*)-*trans*-like geometry ($^1S^*_{(P)-trans-\mathbf{2}}$). In benzene, however, the emission of (*M*)-*cis*-**1** and (*P*)-*trans*-**2** takes place from two different pseudoenantiomeric excited states of opposite chirality ($^1S^*_{(M)-cis-\mathbf{1}}$ and $^1S^*_{(P)-trans-\mathbf{2}}$, respectively). A single enantiomer of *cis*-**1** can therefore be tuned to emit either left- or right-handed CPL depending on the use of *n*-hexane or benzene as the solvent.

Experimental Methods

CPL measurements were performed on an Optitron NR-1B-Xe lamp in combination with a Spex Minimate monochromator, and a Halle Glan calcite prism was used as the light source. A Monvue Hinds International photoelastic modulator and an EMF 9789 QB photomultiplier were used to monitor the data. The complete setup is described elsewhere.[27] Steady-state fluorescence measurements were performed on a SIM-AMINCO SPF 500 C spectrofluorometer.

Fluorescence decay times were measured by flash photolysis of diluted solutions using a 0.8 ns, 337 nm pulse from a PRA LN1000 nitrogen laser. After passage through a Jobin-Yvon monochromator, the emitted light was detected using a Photek PMT-113-UHF channel-plate photomultiplier with a rise time of 150 ps.

For time-resolved microwave conductivity measurements the sample was excited using a Lumonics HyperEX 400 excimer laser (XeCl: 308 nm), and a Gunn Oscillator MC 16/34B was used as the microwave source. Oxygen was removed from the solutions by bubbling with CO_2, which is also a good scavenger for mobile electrons that might be formed in low-yield multiphoton ionization events. The power output of the laser was monitored routinely using a Scientec 365 power meter, and the fraction of photons entering the TRMC cell was determined using a solution of 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene (DMANS) in benzene as an internal actinometer. All transients were measured at the resonance frequency of the cavity. A full description of the microwave circuitry and data handling has been given elsewhere.[26]

All reported measurements were performed on samples with a concentration of ca. 4×10^{-5} mol dm^{-3}. All solvents used were UVASOL grade (Merck) and degassed by ultrasonic irradiation or with Ar (unless stated otherwise). For synthesis, resolution, and characterization, see ref 15.

Supporting Information Available: UV−vis and circular dichroism (CD) spectra of (*M*)-*cis*-**1** and (*P*)-*trans*-**2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA036874D

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(27) Rexwinkel, R. B.; Schakel, P.; Meskers, S. C. J.; Dekkers, H. P. J. M. *Appl. Spectrosc.* **1993**, *47*, 731−740.