Molecular Switching: A Fully Reversible, Optically Active Photochemical Switch Based on a Tetraethynylethene-1,1′-Binaphthalene Hybrid System

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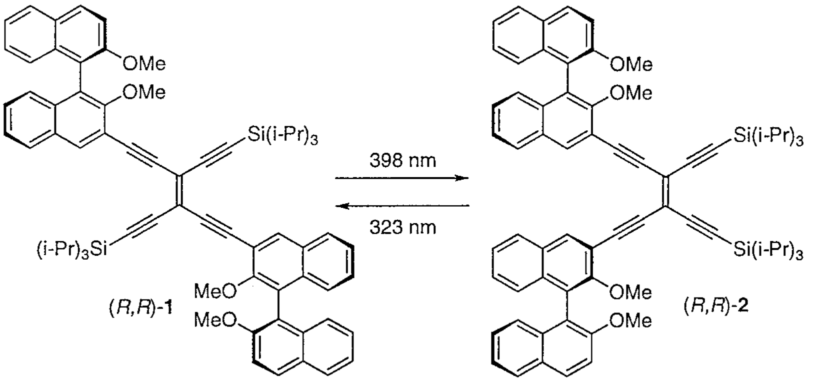
Dedicated to Prof. *Albert Eschenmoser* on the occasion of his 75th birthday

The synthesis, characterization, and physical properties of a novel, fully reversible, light-driven molecular switch, (*R*,*R*)-**1**/(*R*,*R*)-**2**, based on a tetraethynylethene-1,1′-binaphthalene hybrid system are presented. *trans*-Configured (*R*,*R*)-**1** was synthesized in 57% yield by *Stille* cross-coupling between stannylated tetraethynylethene **3** and 3-iodo-1,1′-binaphthalene derivative (*R*)-**4** (*cf. Scheme 2*). The *cis*-isomer (*R*,*R*)-**2** was prepared from (*R*,*R*)-**1** by photoisomerization. X-Ray crystal-structure analyses were obtained for both *cis*- and *trans*-forms of the photoswitch (*Figs. 1* and *2*). In the crystalline state, molecules of the *cis*-isomer (*R*,*R*)-**2** exhibit intramolecular edge-to-face ($C-H\cdots\pi$) interactions between naphthalene rings of the two 1,1-binaphthalene moieties (*Fig. 3*). The switching properties were investigated by electronic absorption spectroscopy (*Table* and *Fig. 4*): irradiation at $\lambda = 398$ nm converts *trans*-isomer (*R*,*R*)-**1** into *cis*-isomer (*R*,*R*)-**2**, whereas switching occurs in the opposite direction upon irradiation at $\lambda = 323$ nm. No thermal interconversion between the two isomers was observed in CH_2Cl_2 at room temperature over a period of 2–3 months, and the system possesses good resistance against photofatigue (*Fig. 5*). Investigations of the circular dichroism of (*R*,*R*)-**1** and (*R*,*R*)-**2** in CH_2Cl_2 solution showed that the chiral binaphthalene moieties induce a weak *Cotton* effect in the achiral tetraethynylethene core (*Fig. 6*). System (*R*,*R*)-**1**/(*R*,*R*)-**2** represents one of the rare switches allowing two-way photochemical interconversions, not perturbed by thermal-isomerization pathways.

1. Introduction. – Molecular switches are systems that possess two or more reversibly interconvertible states [1]. Appropriate switching conditions include photonic, electronic, ionic, or chemical stimuli. In this rapidly expanding field, photoresponsive systems [2] are of particular interest, since the use of light as an external stimulus for the interconversion of two states allows for fast and clean processes. Although many molecular photoswitches have been synthesized and studied, most of these systems undergo a thermal back reaction, and only a few thermally bistable, fully light-driven molecular switches have been reported [3–6]. Probably the most successful class of such photoswitches to date are the diarylethenes, developed by *Irie* and co-workers [3], that have found diverse application in the laboratories of *Lehn* [4]. *Feringa* and co-workers prepared a series of chiroptical molecular photoswitches that can be driven with circularly polarized light or, by appropriate substitution, with nonpolarized light [5]. Also, some fulgides have been reported that react after irradiation with UV light to give dihydrobenzo[*b*]furans, which are thermally stable up to 160° [6]. The back reaction is achieved with visible light. The most practical method to detect the state of these switches is to measure the electronic-absorption spectra, but this often represents a destructive readout procedure and is not suited for applications such as optical storage devices. An elegant alternative is to dope liquid-crystalline phases with the photoswitches to modulate their physical properties with light [5b,d][7]. The detection of any of these properties is an appropriate non-destructive readout process if no light in the absorption region of the photoswitch is used.

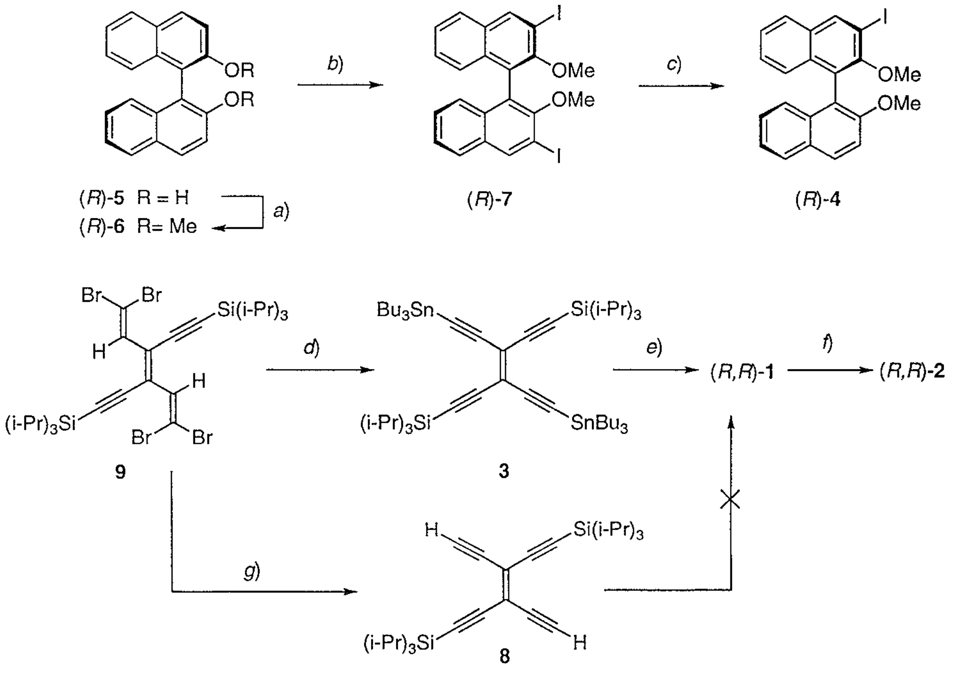
We have recently reported a pH- and light-controllable three-way molecular chromophoric switch based on a tetraethynylethene (TEE; 3,4-diethynylhex-3-ene-1,5-diyne) core [8]. This was the first example where the reversible *cis/trans* photoisomerization of a TEE derivative was used to build a photoswitch. The rapid *cis/trans* photoisomerization of arylated TEEs is a general process with quantum yields up to $\Phi = 0.43$ [9]. Because of the lack of steric hindrance, TEEs – in contrast to stilbenes [10] – are thermally stable in both the *cis*- and *trans*-forms. To establish the role of TEEs as a novel class of fully light-driven molecular photoswitches, we prepared compound (*R*,*R*)-**1**, that reversibly isomerizes to (*R*,*R*)-**2** upon irradiation (*Scheme 1*). It is a hybrid system consisting of a reversibly photoswitchable TEE core linked to two enantiomerically pure (*R*)-configured 1,1′-binaphthalene moieties. 1,1′-Binaphthalene derivatives possess high helical-twisting powers (β), *i.e.*, they are very effective in inducing a cholesteric phase when used to dope a nematic liquid-crystalline phase [7b][11]. The system (*R*,*R*)-**1**/(*R*,*R*)-**2** was designed to display different β values in the two states, thus providing a potential basis for reversible information-storage devices.

Scheme 1. *The Couple (*R,R*)-***1***/(*R,R*)-***2*** Representing a Novel Fully Light-Driven Molecular Switch*



2. Results and Discussion. – 2.1. *Synthesis.* The optically active TEE-1,1′-binaphthalene derivative (*R*,*R*)-**1** was prepared by *Stille* cross-coupling between TEE **3** and enantiomerically pure, monoiodinated 1,1′-binaphthalene (*R*)-**4** (*Scheme 2*). The latter was prepared according to the literature protocol for the synthesis of the corresponding (*S*)-enantiomer [12]. (±)-1,1′-Binaphthalene-2,2′-diol was optically resolved by recrystallization with *N*-benzylcinchonidinium chloride [13] (for a new method for the optical resolution of 1,1′-binaphthalene-2,2′-diol, see [14]), and the (*R*)-enantiomer (*R*)-**5** was methylated (K_2CO_3, MeI, DMF) to give (*R*)-**6**. As monoiodination of (R)-**6** to (R)-**4** proceeds only in poor yields [12a], and it was advantageous to first prepare the 3,3′-diodo derivative (R)-**7** (90% yield) by *ortho*-lithiation (BuLi/TMEDA (= *N,N,N′,N′*-tetramethylethylenediamine)) followed by addition of I_2. Subsequent treatment of (R)-**7** with 1 equiv. of BuLi in THF at − 78° afforded the monolithiated species *via* I/Li exchange, and quenching with aqueous NH_4Cl solution gave (R)-**4** in 65% yield.

Scheme 2. *Synthesis of the Photoswitch* (R,R)-**1**/(R,R)-**2**



a) MeI, K_2CO_3, DMF, 80°, 16 h; 83%. *b*) BuLi, TMEDA, Et_2O, 20°, 5 h, then I_2, Et_2O, − 78° → 20°; 90%. *c*) 1.0 Equiv. BuLi, THF, − 78°, then sat. aq. NH_4Cl soln.; 65%. *d*) LDA, THF, − 78°, then Bu_3SnCl, THF, − 78° → 0°. *e*) (R)-**4**, $[Pd_2(dba)_3] \cdot CHCl_3$, P(2-furyl)$_3$, CuI, THF, Δ; 30 min; 57% (from **9**). *f*) $h\nu$ (366 nm), CH_2Cl_2, 3 h, then recrystallization (2 ×) from CH_2Cl_2/MeOH; 43% ((R,R)-**2**), 36% ((R,R)-**1**), and 18% (4:1 mixture of (R,R)-**1** and (R,R)-**2**). *g*) LDA, THF, − 78°, then sat. aq. NH_4Cl soln.; 100%.

All attempts to prepare (R,R)-**1** by *Sonogashira* cross-coupling between (R)-**4** and TEE derivative **8** [15] failed. Under these conditions ($[PdCl_2(PPh_3)_2]$ or $[PdCl_2(dppf)]$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) as the catalyst in the presence of CuI in (i-Pr)$_2$NH and THF), only polymerization of **8** or other undesired product-formation channels were observed. Slow addition of a solution of **8** over several hours to a solution of (R)-**4** and the catalyst, to keep the concentration of **8** as low as possible [16], did not afford any better results.

The desired cross-coupling reaction did, however, take place under *Stille* conditions [17] with bis-stannylated TEE **3**. This compound was prepared by treatment of tetrabromide **9** [15] with LDA (lithium diisopropylamide) in THF at − 78° and transmetallation of the resulting blue bis(lithium acetylide) with Bu_3SnCl. Successful transmetallation was confirmed by the decoloration of the solution. The stannylated TEE is very sensitive to moisture and must be used immediately without isolation. Cross-coupling between **3** and (*R*)-**4** in the presence of $[Pd_2(dba)_3] \cdot CHCl_3$ (dba = dibenzylideneacetone = 1,5-diphenylpenta-1,4-dien-3-one), CuI, and P(2-furyl)$_3$ in THF under reflux provided (*R*,*R*)-**1** in 57% yield. In the absence of CuI, almost no reaction was observed. When $AsPh_3$ was used instead of P(2-furyl)$_3$, the reaction did not reach completion: a cross-coupling run with $[Pd_2(dba)_3] \cdot CHCl_3$ as catalyst and $AsPh_3$ as ligand in THF at reflux provided only 14% of (*R*,*R*)-**1**, in addition to 28% of an unstable TEE bearing only one coupled 1,1′-binaphthalene moiety. For a successful coupling reaction, Bu_3Sn groups are required. All experiments carried out with bis(trimethyltin)-substituted TEE (which was prepared in the same way as **3**) afforded only decomposition products, probably due to the poor stability of this stannylated compound.

Irradiation of a solution of (*R*,*R*)-**1** in CH_2Cl_2 with UV light of 366 nm afforded a mixture of *trans*-configured starting material and *cis*-isomer (*R*,*R*)-**2**. The two isomers could be separated by crystallization of (*R*,*R*)-**1** from CH_2Cl_2/MeCN. After two successive crystallizations, the mother liquor contained only pure (*R*,*R*)-**2**.

2.2. *X-Ray Crystal-Structure Analyses.* Both (*R*,*R*)-**1** and (*R*,*R*)-**2** furnished suitable single crystals by slow evaporation of solutions of the individual isomer in CH_2Cl_2/MeCN. The *trans*-isomer (*R*,*R*)-**1** crystallizes in the space group *P*2(1) with 2 molecules in the unit cell (*Fig. 1*). The TEE core and the two directly attached naphthalene moieties are nearly coplanar (*Fig. 1,b*) as had been previously observed for numerous arylated TEE derivatives [18].

The conformation of the 1,1′-binaphthalene groups is best described by the dihedral angle θ along their 'chirality axes' passing through C(12)–C(14) and C(37)–C(38), respectively. In crystalline (*R*,*R*)-**1**, both 1,1′-binaphthalene moieties adopt a *cisoid*-conformation with $\theta = 81.0°$ for C(11)–C(12)–C(14)–C(23) and $\theta = 80.4°$ for C(36)–C(37)–C(39)–C(48).

The X-ray measurement of (*R*,*R*)-**2** had to be performed at low temperature (193 K) to preserve the solvent in the crystal. Compound (*R*,*R*)-**2** crystallizes in the space group *P*2(1) (*Fig. 2*). One of the binaphthalene groups is in a *cisoid*-conformation with $\theta = 77.6°$ (C(7)–C(8)–C(16)–C(17)), while the other possesses a *transoid*-conformation with $\theta = 97.5°$ (C(45)–C(46)–C(54)–C(55)). In contrast to (*R*,*R*)-**1**, the TEE core and the adjacent naphthalene groups are not coplanar (*Fig. 2,b*). Rather, the planes of the naphthalenes are twisted by *ca.* 40° and 44°, respectively, with respect to the plane of the central C core. This geometry presumably arises from a favorable intramolecular edge-to-face ($C{-}H \cdots \pi$) interaction between the two naphthalene rings remote from the TEE core (*Fig. 3*). The shortest distance between C-atoms of the two involved aromatic rings, *i.e.*, C(26) $\cdots$ C(64) is 3.59 Å, while the C(27) $\cdots$ C(63) distance amounts to 4.13 Å. By their specific orientation, the two 1,1′-binaphthalene moieties shape a cavity filled by the MeO group at C(11). The molecules in the crystal packing of (*R*,*R*)-**2** are ordered in flat layers. The TEE moieties are stacked with a distance of 8.02 Å between layers. The cavity between two TEEs is filled by a solvent molecule of CH_2Cl_2, which can adopt different orientations. The easy loss of these solvent molecules is probably responsible for the poor stability of the ordered structure in the crystals of (*R*,*R*)-**2**.

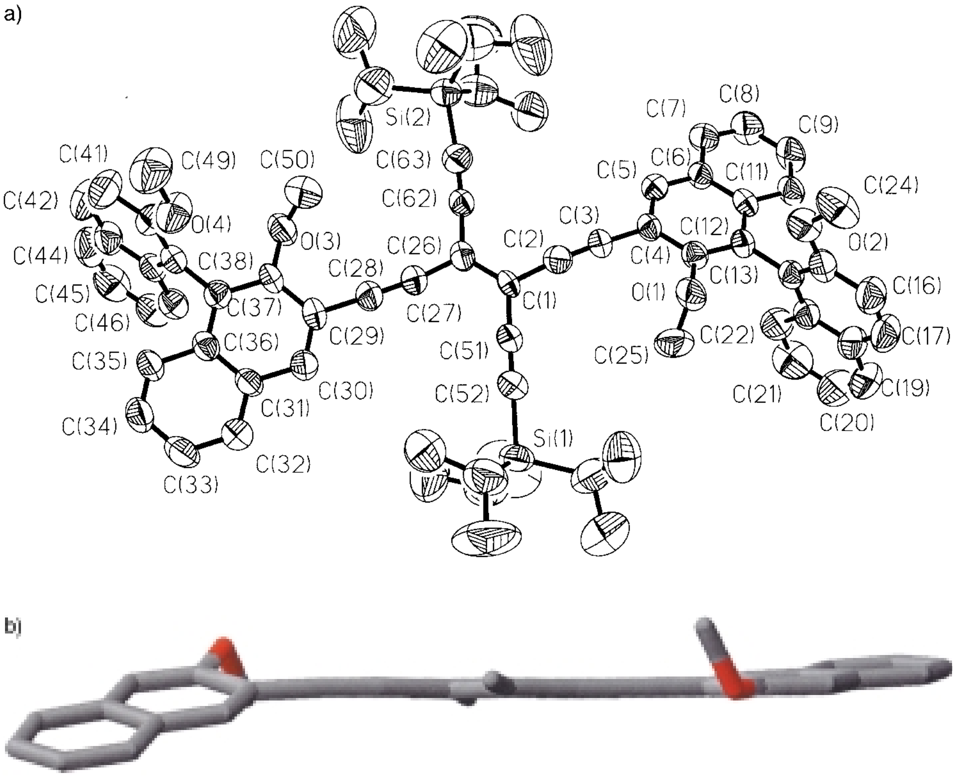


Fig. 1. a) *ORTEP Plot of (*R,R*)*-**1**. Arbitrary numbering. Atomic-displacement parameters obtained at 293 K are drawn at the 50% probability level. b) *Side view of the most expanded π-conjugated chromophore, including the TEE core with the two attached naphthalene groups.*

2.3. *UV/VIS Studies.* The reversible *cis/trans* photoisomerization of (*R*,*R*)-**1**/(*R*,*R*)-**2** was studied by UV/VIS spectroscopy in CH_2Cl_2. *trans*-Isomer (*R*,*R*)-**1** possesses a characteristic absorption maximum at $\lambda_{max} = 398$ nm (ε(*trans*) $= 40000\ l\ mol^{-1}\ cm^{-1}$) (*Fig. 4*). After irradiation with monochromatic light of this wavelength, this band loses intensity, and a new one, characteristic of (*R*,*R*)-**2**, arises at $\lambda_{max} = 323$ nm (ε(*cis*) $= 44000\ l\ mol^{-1}\ cm^{-1}$). The isomerization reaction can be reversed by irradiating the sample with monochromatic light of 323 nm. A series of isosbestic points indicates clean interconversion between *cis*- and *trans*-isomers, not perturbed by any side reactions. For these reasons, the system (*R*,*R*)-**1**/(*R*,*R*)-**2** represents a novel molecular photoswitch. Isomerization is fast, and, in both directions, photostationary states were reached after *ca.* 1 min. The physical data of this molecular photoswitch are listed in the *Table*.

The resistance of this system against photofatigue was tested performing several switching cycles starting with a degassed solution of (*R*,*R*)-**2** and irradiating in 1 min intervals with monochromatic light of $\lambda = 323$ nm or $\lambda = 398$ nm. The resulting graphical representation of the absorption at $\lambda = 323$ nm is presented in *Fig. 5* and does not show any decrease in intensity as a result of photofatigue, even after 10

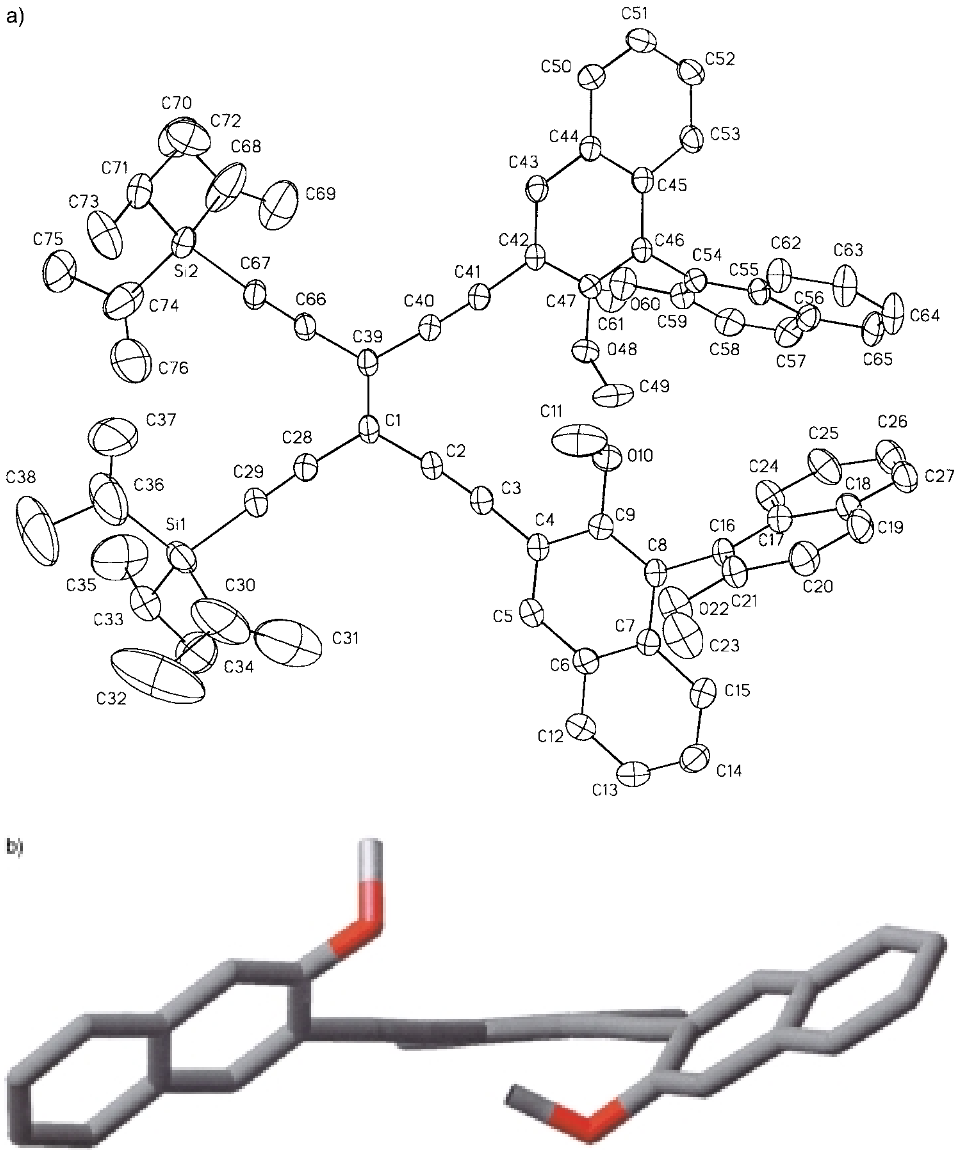


Fig. 2. a) *ORTEP Plot of (*R,R*)*-**2**. Arbitrary numbering. Atomic-displacement parameters obtained at 193 K are drawn at the 30% probability level. b) *Side view of the most expanded π-conjugated chromophore, including the TEE core with the two attached naphthalene groups.*

switching cycles. The thermal stability was tested with a well-sealed sample that was stored in the dark for a couple of months. After this period, no changes in the absorption spectra arising from a (*R*,*R*)-**2** → (*R*,*R*)-**1** isomerization could be observed.

2.4. *Circular-Dichroism Spectra.* The circular-dichroism (CD) spectra of (*R*,*R*)-**1** and (*R*,*R*)-**2** were recorded in CH_2Cl_2 solutions at 25° and are displayed in *Fig. 6*. Three

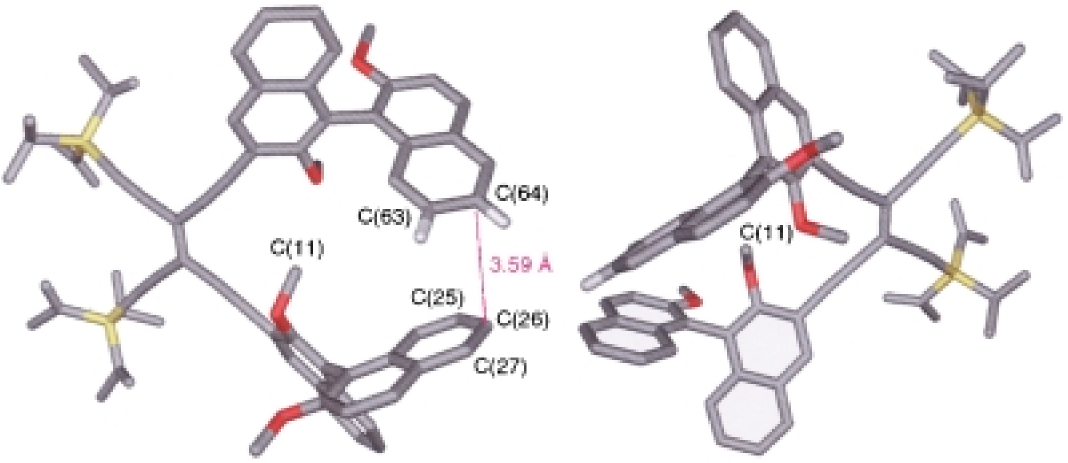


Fig. 3. *Intramolecular edge-to-face interaction between the two binaphthalene units in the crystals of* **2**. The cavity formed by the two groups is filled by the MeO group of C(11).

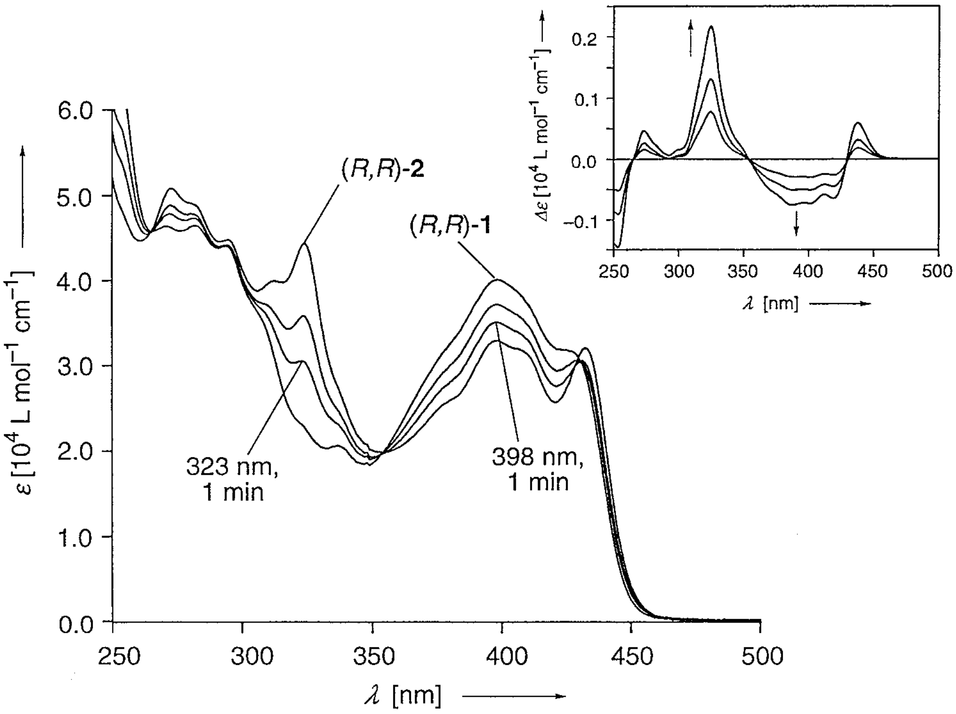


Fig. 4. *Electronic-absorption spectra of (*R,R*)-***1** *($c = 2.69 \cdot 10^{-5}$ M) and (*R,R*)-***2** *($c = 2.75 \cdot 10^{-5}$ M) in CH_2Cl_2 at 25° and of the mixtures at the photostationary states obtained by irradiating for 1 min at 398 and 323 nm, respectively.* In the top right corner, the transient spectral changes upon irradiation at 398 nm, starting from a solution of pure (*R*,*R*)-**1** and leading to increasing concentration of (*R*,*R*)-**2**, are represented.

Table. *Physical Data for the* cis/trans-*Isomerization between (*R,R*)*-**2** *and (*R,R*)*-**1** *in CH_2Cl_2 at 25°*

λ[a]) [nm]	*cis*[b]) [%]	*trans*[b]) [%]	K_{eq}[c])	ε(*cis*)[d]) [l mol^{-1} cm^{-1}]	ε(*trans*)[d]) [l mol^{-1} cm^{-1}]
398	65	35	1.9	33000	40000
323	38	62	1.6	44000	23000

[a]) Irradiation wavelength. [b]) Percentage of *cis*- and *trans*-isomers, respectively, in the photostationary state. [c]) Photoequilibrium constant, *i.e.*, the ratio [product isomer]/[starting isomer] at the photostationary state. [d]) Molar extinction coefficients of the isomers at the irradiation wavelength.

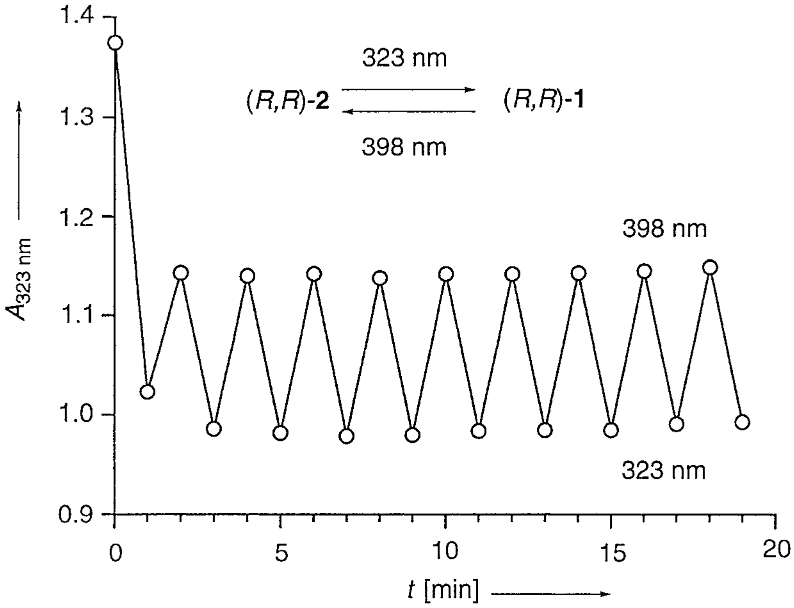


Fig. 5. *Changes in the absorption of a degassed solution of (*R,R*)*-**2**/*(*R,R*)*-**1** ($c_{tot} \approx 2.75 \cdot 10^{-5}$ M in CH_2Cl_2) *recorded at λ = 323 nm and 25°, starting from pure (*R,R*)*-**2**. The sample was irradiated for 1 min intervals at 323 nm ((*R*,*R*)-**2** → (*R*,*R*)-**1**) and 398 nm ((*R*,*R*)-**1** → (*R*,*R*)-**2**), respectively.

regions can be distinguished in these spectra. The first ranges from 260 to 300 nm and shows a strong *Cotton* effect. The two (*R*)-configured 1,1′-binaphthalene groups, with their highly twisted structure, completely dominate the CD spectra in this region. The chiral binaphthalene groups induce a *Cotton* effect in the TEE moiety through asymmetric interaction of the electron densities of the two chromophores. This results in weak CD signals (*ca.* 20 times less intense than those assigned to the binaphthalenes) between 375 and 450 nm. In a mid-region, ranging from 300 to 350 nm, the CD spectra of the two isomers vary the most, with a large difference of $\Delta\Delta\varepsilon = 24$ l mol^{-1} cm^{-1} at 323 nm. This feature should, in principle, allow further enhancement of the concentration of (*R*,*R*)-**1** at the photostationary state of the reaction (*R*,*R*)-**2** → (*R*,*R*)-**1**. In fact, the use of monochromatic negatively circularly polarized light of $\lambda = 323$ nm, instead of nonpolarized light, should allow for a more selective excitation of (*R*,*R*)-**2**, thus leading to a chiroptical switch. This is the subject of further investigations with the system described, as well as with next generations of compounds.

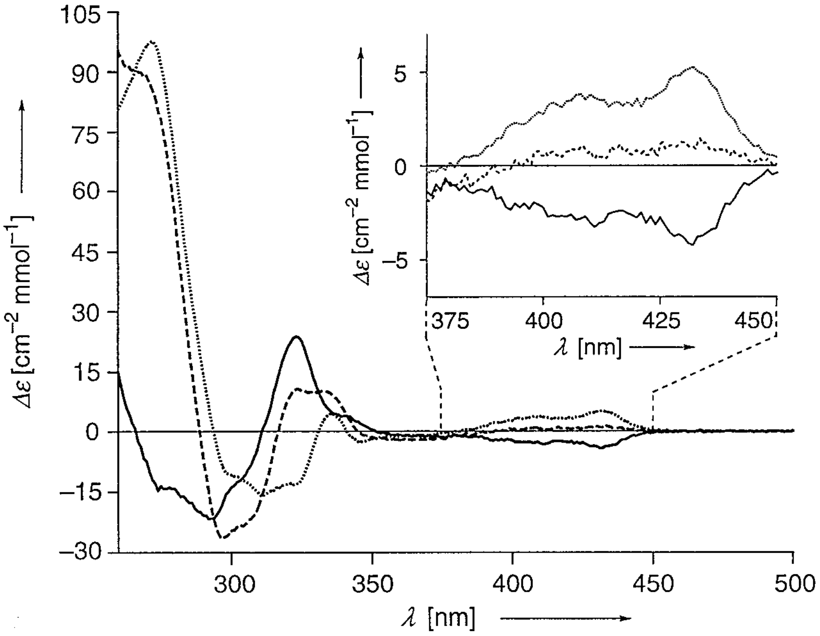


Fig. 6. *CD Spectra of* (R,R)-**1** (----, $c = 2.69 \cdot 10^{-5}$ M) *and* (R,R)-**2** (·····, $c = 2.75 \cdot 10^{-5}$ M) in CH_2Cl_2 at 25°. The solid line (—) shows the difference between the spectra of (*R*,*R*)-**1** and (*R*,*R*)-**2**.

3. Conclusions. – This paper describes the synthesis and the properties of a novel, fully reversible molecular photoswitch based on a hybrid system consisting of a TEE core with two attached (*R*)-configured 1,1′-binaphthalene moieties. It was shown that such a system is best synthesized in a *Stille* cross-coupling reaction between a stannylated TEE and two iodinated 1,1′-binaphthalenes. The ground-state structures of the two *cis/trans*-isomeric states of this photoswitch have been unambiguously proven by X-ray crystal-structure analyses. These investigations also showed that the cavity-type arrangement of the two 1,1′-binaphthalene moieties in the *cis*-isomer (*R*,*R*)-**2** originates from $C{-}H \cdots \pi$ interactions between the two binaphthalene groups remote from the TEE core.

The two isomeric states can be interconverted in CH_2Cl_2 solutions with light of $\lambda = 323$ or $\lambda = 398$ nm. No thermal back reaction was observed over months at room temperature, and the photofatigue resistance proved to be good. Thus, (*R*,*R*)-**1**/(*R*,*R*)-**2** represents a novel, fully light-driven molecular switch, unperturbed by thermal isomerization channels. This work demonstrates that arylated TEEs are appropriate to build such systems, which could become the next generation of information storage and retrieval devices – at a molecular level – in the coming decade. Studies are currently underway to incorporate this molecular switch into macroscopic devices based on liquid-crystalline phases.

We thank the *ETH Research Council* for generous support of this work.

Experimental Part

General. All reactions were carried out under N_2. Solvents and reagents were reagent-grade and commercially available, and used without further purification unless otherwise stated. THF and Et_2O were freshly distilled from sodium benzophenone ketyl. BuLi Solns. in hexane were titrated with 2,4-dimethoxybenzyl alcohol in THF [19]. Evaporation *in vacuo* was conducted at H_2O-aspirator pressure. Degassing of solvents was accomplished by three freeze-thaw-pump cycles. Column chromatography (CC): SiO_2-*60* (230–400 mesh, 0.040–0.063 mm) from *Fluka*. TLC: glass-backed *Polygram* SiO_2-*60 UV₂₅₄* from *Macherey-Nagel*, visualization by UV light (254 or 366 nm) or with a 'mostain' soln. (400 ml of 10% aq. H_2SO_4, 20 g of $(NH_4)_6Mo_7O_{24} \cdot 6\,H_2O$, 0.6 g of $Ce(SO_4)_2$). Prep. gel-permeation chromatography (GPC): *Bio-Beads SX-1* from *Bio-Rad*, eluent CH_2Cl_2 unless otherwise stated. M.p.: *Büchi 510* or *Büchi B-540*, uncorrected. $[\alpha]_D^{r.t.}$: *Perkin Elmer 241* polarimeter with a 1-dm cell at the Na-D line ($\lambda = 589$ nm) at r.t. The concentration *c* is given in g/100 ml. $CHCl_3$ was used as solvent unless otherwise stated. UV/VIS Spectra: *Varian-CARY-5* spectrometer; λ [nm] (ε [l mol^{-1} cm^{-1}]). CD Spectra: *Jasco J-710* spectropolarimeter; λ [nm] ($\Delta\varepsilon$ [l mol^{-1} cm^{-1}]). IR Spectra (cm^{-1}): *Perkin-Elmer 1600-FT IR*. NMR Spectra: *Bruker AMX 500* or *AMX 400*, and *Varian Gemini 300* or *200* at 296 or 300 K, with solvent peak as reference. MS (*m/z* (%)): EI-MS: *VG TRIBRID* spectrometer at 70 eV; FAB-MS: *VG ZAB2-SEQ* spectrometer with 3-nitrobenzyl alcohol (NOBA) as matrix. Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie, ETH-Zürich.

*X-Ray Crystal Structure of (*R,R*)-***1**. Crystal data at 293 K for $C_{72}H_{76}O_4Si_2$ (M_r 1061.5): monoclinic, space group $P2(1)$ (No. 4), $D_c = 1.128$ g cm^{-3}, $Z = 2$, $a = 8.922(10)$, $b = 25.94(4)$, $c = 13.56(2)$ Å, $\beta = 95.20(9)°$, $V = 3125(7)$ Å^3. *Picker-Stoe* diffractometer, CuK_α radiation, $\lambda = 1.54178$ Å. The structure was solved by direct methods (SHELXTL PLUS) and refined with 720 parameters by full-matrix least-squares analysis based on F^2 using experimental weights; all heavy atoms were refined anisotropically, H-atoms were fixed isotropically with positions calculated from stereochemical considerations. Final $R(F) = 0.059$ for 2950 observed reflections with $I > 2\sigma(I)$ and w$R(F^2) = 0.1577$ for all 3299 data. *Cambridge Crystallographic Data Centre* deposition No. CCDC-142095.

*X-Ray Crystal Structure of (*R,R*)-***2**. Crystal data at 193 K for ($C_{72}H_{76}O_4Si_2 \cdot \sim 0.6\ CH_2Cl_2$) ($M_r$ 1146.4): monoclinic, space group $P2(1)$ (No. 4), $D_c = 1.18$ g cm^{-3}, $Z = 2$, $a = 8.018(2)$, $b = 21.576(2)$, $c = 19.055(2)$ Å, $\beta = 101.70(1)°$, $V = 3228.0(9)$ Å^3. Nonius *CAD4* diffractometer, CuK_α radiation, $\lambda = 1.54178$ Å. Yellowish, single crystals were obtained by slow evaporation of a CH_2Cl_2/MeCN soln. The structure was solved by direct methods (SIR92) [20] and refined by full-matrix least-squares analysis (SHELXL-97) [21], with an isotropic extinction correction and an exponentially modified weight factor $r = 2.5$ Å^2 [22]. The solvent CH_2Cl_2 is disordered over at least two orientations, and its geometry is distorted. All heavy atoms were refined anisotropically (H-atoms of the ordered skeleton isotropically, whereby H-positions are based on stereochemical considerations). Final $R(F) = 0.057$, w$R(F^2) = 0.125$ for 740 parameters, 1 restraint, and 4562 reflections with $I > 2\sigma(I)$ and $2.4 < \theta < 64.9°$ (corresponding *R* values based on all 5652 reflections are 0.077 and 0.128, resp.). *Cambridge Crystallographic Data Centre* deposition No. CCDC-140996.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre*. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44(1223)336 033; e-mail: deposit@ccdc.cam.ac.uk).

*(*R*)-2,2′-Dimethoxy-1,1′-binaphthalene* ((*R*)-**6**). To a stirred mixture of (*R*)-**5** (3.00 g, 10.5 mmol) and K_2CO_3 (3.18 g, 23.0 mmol) in anh. DMF (60 ml) at 80° under N_2, MeI (3.27 g, 23.0 mmol) in DMF (35 ml) was slowly added, and the mixture was stirred for 16 h at 80°. After cooling to 20°, H_2O (360 ml) was added, and the aq. phase was extracted with CH_2Cl_2 (3 × 100 ml). The combined org. layers were washed with 0.5M KOH (120 ml), H_2O (120 ml), and sat. aq. NaCl soln. (120 ml), dried ($MgSO_4$), and evaporated. Recrystallization from hexane/toluene 1:1 afforded (*R*)-**6** (2.75 g, 83%). Cream-colored solid. M.p. 222.9–227.0° ([23]: 200–204°; [24]: 198–202°). $[\alpha]_D^{r.t.} = +54.9$ ($c = 1.0$, $CHCl_3$). IR (KBr): 3044*w*, 2933*w*, 2836*w*, 1618*m*, 1590*m*, 1506*m*, 1461*m*, 1354*m*, 1264*s*, 1250*s*, 1091*m*, 1064*m*, 811*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.78 (*s*, 6 H); 7.13–7.36 (*m*, 6 H); 7.47 (*d*, $J = 9.1$, 2 H); 7.87 (*d*, $J = 7.5$, 2 H); 7.99 (*d*, $J = 9.1$, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 56.86; 114.21; 119.56; 123.48; 125.22; 126.26; 127.89; 129.19; 129.36; 133.98; 154.92. EI-MS: 314.2 (100, M^+), 268.2 (86), 255.2 (15), 239.2 (36), 226.1 (21), 141.1 (22), 119.6 (30). Anal. calc. for $C_{22}H_{18}O_2$ (314.38): C 84.05, H 5.77, O 10.18; found: C 83.92, H 5.80, O 10.26.

*(*R*)-3,3′-Diiodo-2,2′-dimethoxy-1,1′-binaphthalene* ((*R*)-**7**). To (*R*)-**6** (2.70 g, 8.59 mmol) and TMEDA (4.77 ml, 31.8 mmol) in dry Et_2O (150 ml) under N_2 at 20°, 1.6M BuLi (19.9 ml, 31.8 mmol) in hexane was added, and the mixture was stirred for 6 h at 20°. After cooling to −78°, I_2 (8.72 g, 34.3 mmol) in Et_2O (45 ml) was

added, and the mixture was warmed to 20°. 1M KOH (300 ml) was added, and the mixture was extracted with Et_2O (300 ml). The org. phase was washed with H_2O (300 ml) and sat. aq. NaCl soln. (300 ml). The aq. phases were extracted once more with Et_2O (300 ml), and the combined org. phases were evaporated. CC (SiO_2-*60* (120 g); hexane/AcOEt 1 : 1) afforded pure (*R*)-**7** (4.32 g, 90%). Cream-colored solid. M.p. 189–193°. $[\alpha]_{\mathrm{D}}^{\mathrm{r.t.}} = -30.0$ ($c = 1.0$, $CHCl_3$). IR (KBr): 2933*m*, 1700*w*, 1556*m*, 1489*m*, 1452*s*, 1384*s*, 1346*s*, 1230*s*, 1144*m*, 1040*s*, 967*s*, 889*s*, 800*s*, 753*s*, 515*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.43 (*s*, 6 H); 7.08 (*d*, $J = 8.3$, 2 H); 7.24–7.31 (*m*, 2 H); 7.39–7.45 (*m*, 2 H); 7.80 (*d*, $J = 8.3$, 2 H); 8.55 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 61.00; 92.38; 125.37; 125.66; 125.76; 126.97; 127.09; 132.17; 133.85; 139.92; 154.52. EI-MS: 566.0 (100, M^+). HR-EI-MS: 565.9232 (M^+, $C_{22}H_{16}O_2I_2$; calc. 565.9243).

(R)-3-Iodo-2,2′-dimethoxy-1,1′-binaphthalene ((*R*)-**4**). A soln. of (*R*)-**7** (4.32 g, 7.63 mmol) in THF (220 ml) was cooled to −78° under N_2, and 1.6M BuLi (4.77 ml, 7.63 mmol) in hexane was slowly added. After stirring for 1 h, sat. aq. NH_4Cl soln. (40 ml) was added, and the mixture was allowed to warm to 20°. Et_2O (300 ml) was added, and the org. layer was washed with H_2O (4 × 150 ml) and sat. aq. NaCl soln. (50 ml). Drying ($MgSO_4$) and evaporation, followed by recrystallization (AcOEt/hexane 1 : 1), afforded (*R*)-**4** (1.46 g, 43%). CC (SiO_2-*60* (180 g); hexane/AcOEt 20 : 1) of the mother liquor gave additional (*R*)-**4** (741 mg, 22%). Colorless needles. M.p. 197°. $[\alpha]_{\mathrm{D}}^{\mathrm{r.t.}} = +41.5$ ($c = 0.5$, $CHCl_3$). IR (KBr): 2931*m*, 2823*w*, 1619*m*, 1593*m*, 1508*m*, 1464*m*, 1390*m*, 1352*m*, 1262*s*, 1248*s*, 1146*m*, 1089*s*, 1054*m*, 1018*s*, 896*m*, 812*s*, 752*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.41 (*s*, 3 H); 3.81 (*s*, 3 H); 7.07–7.13 (*m*, 2 H); 7.20–7.43 (*m*, 4 H); 7.46 (*d*, $J = 8.9$, 1 H); 7.77–7.81 (*m*, 1 H); 7.86–7.90 (*m*, 1 H); 8.03 (*d*, $J = 8.9$, 1 H); 8.50 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 56.47; 60.76; 92.59; 113.32; 118.58; 123.69; 124.98; 125.39; 125.71; 126.65; 126.82; 127.92; 128.93; 130.09; 132.36; 133.75; 134.02; 139.05; 154.36; 154.78. EI-MS: 440.1 (100, M^+), 394.0 (19), 239.1 (14). Anal. calc. for $C_{22}H_{17}O_2I$ (440.28): C 60.02, H 3.89, O 7.27; found: C 60.18, H 4.14, O 7.31.

(E)-1,6-Bis[(R)-2,2′-dimethoxy-1,1′-binaphthalen-3-yl]-3,4-bis[(triïsopropylsilyl)ethynyl]hex-3-ene-1,5-diyne ((*R*,*R*)-**1**). A LDA soln. was prepared at 0° under N_2 by addition of 1.6M BuLi (2.31 ml, 6.39 mmol) in hexane to $(i\text{-}Pr)_2NH$ (0.52 ml, 6.39 mmol) in THF (20 ml). After degassing, the soln. was transferred to **9** [15] (429 mg, 0.57 mmol) in THF (50 ml) at −78°. The resulting deep-blue soln. was stirred for 5 min before the addition of Bu_3SnCl (1.00 ml, 6.39 mmol). The temp. was slowly raised to 0°, which caused the color to disappear. A soln. of (*R*)-**4** (500 mg, 1.14 mmol), $[Pd_2(dba)_3] \cdot CHCl_3$ (59 mg, 0.057 mmol), and $P(2\text{-furyl})_3$ (53 mg, 0.23 mmol) in THF (20 ml), and a suspension of CuI (100 mg, 0.52 mmol) in THF (10 ml) were prepared, degassed, and added. The mixture was stirred in the dark for 30 min under reflux before pouring it into hexane. The org. layer was washed with H_2O (4 × 100 ml) and sat. aq. NaCl soln. (100 ml), and the solvent was evaporated. CC (SiO_2-*60* (50 g); hexane/CH_2Cl_2 2 : 1) followed by recrystallization from AcOEt and GPC (*Bio-Beads SX-1*; CH_2Cl_2) afforded (*R*,*R*)-**1** (348 mg, 57%). Bright-yellow crystals. M.p. 261°. $[\alpha]_{\mathrm{D}}^{\mathrm{r.t.}} = +117.9$ ($c = 1.0$, $CHCl_3$). UV/VIS (CH_2Cl_2): 270 (44600), 282 (44700), 294 (42300), 337 (19300), 375 (sh, 29000), 398 (38500), 425 (sh, 30300). CD (CH_2Cl_2): 270 (+89), 297 (−26), 323 (+11), 332 (+10), 408 (+1.0), 430 (+1.2). IR (KBr): 2939*s*, 2867*s*, 2189*w*, 1617*m*, 1589*m*, 1506*m*, 1458*s*, 1406*m*, 1356*m*, 1264*s*, 1144*m*, 1082*m*, 1011*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.12 (*s*, 42 H); 3.69 (*s*, 6 H); 3.81 (*s*, 6 H); 7.07–7.13 (*m*, 4 H); 7.21–7.43 (*m*, 8 H); 7.47 (*d*, $J = 8.7$, 2 H); 7.79 (*d*, $J = 8.3$, 2 H); 7.88 (*d*, $J = 8.3$, 2 H); 8.01 (*d*, $J = 9.1$, 2 H); 8.16 (*s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 11.36; 18.71; 56.57; 61.09; 91.66; 95.97; 102.20; 103.31; 113.58; 116.73; 117.66; 118.72; 123.60; 125.18; 125.39; 125.73; 126.59; 127.27; 127.81; 127.89; 129.03; 129.74; 130.13; 134.0; 134.36; 134.42; 154.86; 155.64. FAB-MS: 1061.4 (100, M^+). Anal. calc. for $C_{72}H_{76}O_4Si_2$ (1061.54): C 81.46, H 7.22; found: C 81.26, H 7.38.

(Z)-1,6-Bis[(R)-2,2′-dimethoxy-1,1′-binaphthalen-3-yl]-3,4-bis[(triïsopropylsilyl)ethynyl]hex-3-ene-1,5-diyne ((*R*,*R*)-**2**). A stirred soln. of (*R*,*R*)-**1** (108 mg, 0.10 mmol) in CH_2Cl_2 (40 ml) was irradiated at 366 nm for 3 h. The solvent was removed, and the residue was recrystallized twice from CH_2Cl_2/MeCN at −20° to afford pure (*R*,*R*)-**1** (39 mg, 36%) and a 4 : 1 mixture of (*R*,*R*)-**1**/(*R*,*R*)-**2** (19 mg, 18%). Compound (*R*,*R*)-**2** (47 mg, 43%; 95% purity according to ^{1}H-NMR) was isolated from the mother liquor of the second recrystallization by evaporation of the solvent. Yellow crystals. M.p. 203°. $[\alpha]_{\mathrm{D}}^{\mathrm{r.t.}} = +134$ ($c = 0.1$, $CHCl_3$). UV/VIS (CH_2Cl_2): 273 (49600), 282 (sh, 47700), 295 (43600), 311 (38700), 324 (43200), 375 (sh, 23600), 398 (31700), 407 (sh, 30700), 432 (30900). CD (CH_2Cl_2): 272 (+98), 311 (−16), 335 (+4.5), 408 (+3.8), 432 (+5.3). IR (KBr): 2940*s*, 2863*s*, 2178*w*, 2122*w*, 1621*m*, 1594*m*, 1510*m*, 1459*s*, 1408*m*, 1357*m*, 1267*s*, 1147*m*, 1074*m*, 1018*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.12 (*s*, 42 H); 3.67 (*s*, 6 H); 3.75 (*s*, 6 H); 7.37 (*m*, 14 H); 7.45 (*d*, $J = 9.0$, 2 H); 7.90 (*d*, $J = 8.1$, 2 H); 8.01 (*d*, $J = 9.0$, 2 H); 8.28 (*s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 11.32; 18.72; 56.42; 60.96; 92.19; 96.30; 102.33; 103.46; 113.45; 116.70; 116.99; 118.77; 123.64; 125.07; 125.23; 125.37; 125.51; 126.65; 127.24; 127.88; 128.09; 129.03; 129.67; 130.28; 134.03; 134.29; 135.28; 154.79; 155.59. FAB-MS: 2122.9 (8, M_2^+), 1061.3 (100, M^+). Anal. calc. for $C_{72}H_{76}O_4Si_2$ (1061.54): C 81.46, H 7.22; found: C 81.12, H 7.35.

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Received April 19, 2000