Supplementary Material (ESI) for Chemical Communications

The isolation and photochemistry of individual atropisomers of photochromic diarylethenes

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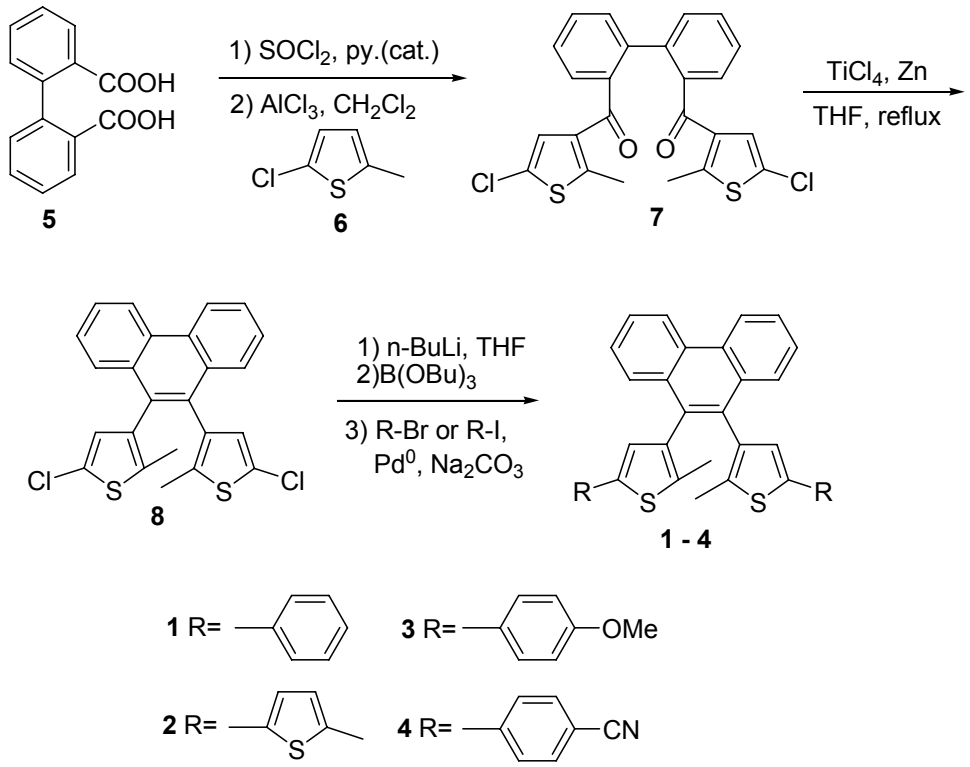
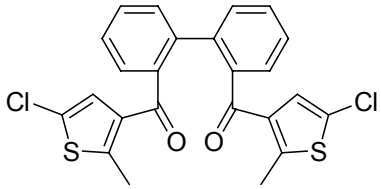
Electronic supplementary information

Reaction Scheme

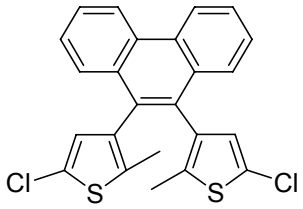
Synthesis of the compounds **1-4** was performed according to the following scheme and procedures



Experimental details

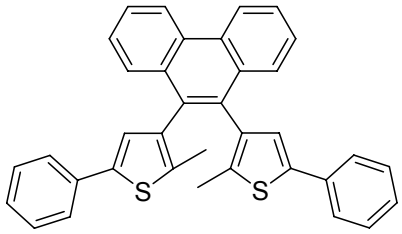


2,2'-Bis-(5-Chloro-2-methylthiophene-3-carbonyl)-biphenyl (7)
Diphenic acid **5** (9.69 g, 40 mmol) was suspended in $SOCl_2$ (58 ml, 95.2 g, 0.8 mol) and heated to reflux for 4 h, while protected from moisture. The unreacted $SOCl_2$ was evaporated and 2-chloro-5-methylthiophene **6**[1] (10.6 g, 80 mmol) in CH_2Cl_2 (100 ml) was added. The mixture was cooled in an ice-bath to 0°C and $AlCl_3$ (13.3 g, 100 mmol) was added in several portions. After 30 min stirring at 0°C the temperature was allowed to rise to r.t. and stirring continued at this temperature for 16 h. Ice-cold water was then slowly added to destroy the $AlCl_3$, the organic layer was separated and the water layer extracted with Et_2O (3x100 ml). The combined organic extracts were then dried over Na_2SO_4 and the solvents evaporated. Purification by chromatography (silica gel, Hexane:Ethylacetate / 9:1) yielded 11.89 g (63%) of product **2.9** as a white solid.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.49 (s, 6H), 6.75 (s, 2H), 7.33 – 7.41 (m, 6H), 7.47 – 7.52 (m, 2H).
^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 16.59 (q), 124.94 (s), 127.92 (d), 129.57 (d), 130.29 (d), 131.76 (d), 132.48 (d), 136.30 (s), 140.29 (s), 141.29 (s), 150.30 (s), 191.92 (s).
MS (EI): 470 [M^+]; HRMS calcd. for $C_{24}H_{16}Cl_2O_2S_2$: 469.9969. Found: 469.9967.



9,10-Bis-(5-chloro-2-methylthien-3-yl)-phenanthrene (8)
$TiCl_4$ (1.65 ml, 2.85 g, 15 mmol) was added dropwise to Zn-dust (1.3 g, 20 mmol) suspended in a dry THF (25 ml) kept under a nitrogen atmosphere. This mixture was heated at reflux for 1 h, cooled to r.t. and the diketone **7** (4.71 g, 10 mmol) was added. The mixture was again heated at reflux for 4 h. After cooling to the r.t. pentane (50 ml) was added, the slurry was filtered through silica gel pad on a fritted funnel which was subsequently washed with Et_2O (50 ml). The solvents from the filtrate were evaporated and the residue purified by column chromatography (silica gel, Hexane:Toluene / 19:1) to give 2.33 g (53%) of product **8** as a white solid. m.p. 157-159 °C
^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.00, 2.04 (2s, 6H), 6.56, 6.57 (2s, 2H), 7.55 – 7.73 (m, 6H), 8.79(d, J = 8.1 Hz, 2H),
^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 14.25 (q), 122.87 (d), 125.43 (d), 125.59 (s), 125.66 (s), 127.11 (d), 127.18 (d), 127.24 (d), 127.99 (d), 128.36 (d), 129.18 (d), 130.37 (s), 130.41 (s), 131.24 (s), 131.38 (s), 132.49 (s), 132.52 (s), 134.82 (s), 134.95 (s), 135.14 (s), 135.48 (s).
MS (EI): 438 [M^+]; HRMS calcd. for $C_{24}H_{16}Cl_2S_2$: 438.0070. Found: 438.0076.
Anal. calcd. for $C_{24}H_{16}Cl_2S_2$: C, 65.6; H, 3.67. Found: C, 65.2; H 3.59.

The general procedure for the Suzuki coupling in the synthesis of the compounds 1-4.
The dichloride **8** (879 mg, 2 mmol) was dissolved in anhydrous THF (15 ml) under a nitrogen atmosphere, and n-BuLi (2.5 ml of 1.6M solution in hexane, 4 mmol) was added slowly at 0°C. Subsequently the reaction mixture was allowed to warm to r.t. and stirred for 1 h. Then B(n-OBu)$_3$ (1.22 ml, 1.04 g, 4.5 mmol) was added, followed by stirring for the next 1 h at r.t. Degassed aq. Na_2CO_3 (5 ml of 2M solution), $Pd(PPh_3)_4$ (46 mg, 0.04 mmol) and the corresponding arylhalide (5 mmol) were added and the mixture was heated at reflux for 3 h. Next water (50 ml) was added and the mixture was extracted with Et_2O (3 x 50 ml). The combined extracts were dried over Na_2SO_4 and the solvents evaporated. Purification by chromatography on silica gel using the hexane-toluene mixtures as an eluent gave pure products as a solids in 50-97% yields.



9,10-Bis-[5-phenyl-2-methylthien-3-yl]-phenanthrene (1)
This compound was synthesized according to the general procedure using iodobenzene (0.56 ml, 1.02 g, 5 mmol) as the

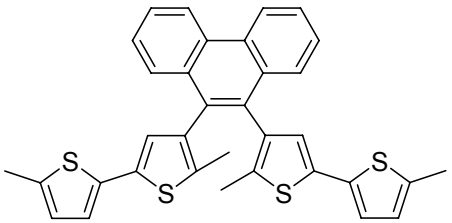
arylhalide component. Purification was done by chromatography (silica gel, Hexane:Toluene / 9:1) to give 715 mg (68%) of the product as a white solid. m.p. 182-183 °C

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.10, 2.17 (2s, 6H), 7.03, 7.04 (2s, 2H), 7.20 – 7.36 (m, 6H), 7.44 – 7.60 (m, 6H), 7.69 – 7.83 (m, 4H), 8.83 (d, *J* = 8.4 Hz, 2H),

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 14.48 (q), 14.56 (q), 122.79 (d), 122.82 (d), 125.45 (s), 125.57 (s), 125.74 (d), 126.84 (d), 127.09 (d), 127.18 (d), 127.43 (d), 127.57 (d), 128.89 (d), 128.95 (d), 130.30 (s), 130.36 (s), 131.55 (s), 131.81 (s), 133.22 (s), 133.29 (s), 134.69 (s), 134.75 (s), 135.82 (s), 136.27 (s) 136.84 (s), 137.25 (s), 139.80 (s).

MS (EI): 522 [M^+]; HRMS calcd. for $C_{36}H_{26}S_2$: 522.1476. Found: 522.1488.

Anal. calcd. for $C_{36}H_{26}S_2$: C, 82.7; H 5.01. Found: C, 82.9; H, 4.96.



9,10-Bis-[5-(5-methylthien-2-yl)-2-methylthien-3-yl]-phenanthrene (2)

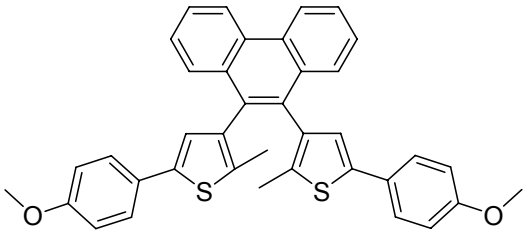
This compound was synthesized according to the general procedure using 2-bromo-5-methylthiophene (0.57 ml, 885 mg, 5 mmol) as the arylhalide component. Purification was done by chromatography (silica gel, Hexane:Toluene / 9:1) to give 698 mg (62%) of the product as a white solid. m.p. 144-146 °C

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.07, 2.13 (2s, 6H), 2.45, 2.46 (2s, 6H), 6.61 – 6.65 (m, 2H), 6.80 – 6.87 (m, 4H), 7.54 – 7.60 (m, 2H), 7.68 – 7.79 (m, 4H), 8.82 (d, *J* = 8.1 Hz, 2H),

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 14.30 (q), 14.35 (q), 15.46 (q), 122.79 (d), 122.88 (d), 123.11 (d), 125.45 (d), 125.82 (d), 125.91 (d), 126.85 (d), 126.93 (d), 127.08 (d), 127.41 (d), 127.52 (d), 130.30 (s), 130.36 (s), 131.51 (s), 131.74 (s), 133.05 (s), 133.17 (s), 133.51 (s), 133.57 (s), 134.76 (s), 135.01 (s), 135.56 (s), 135.62 (s), 136.41 (s), 136.76 (s), 138.58 (s), 138.67 (s).

MS (EI): 562 [M^+]; HRMS calcd. for $C_{34}H_{26}S_4$: 562.0917. Found: 562.0921.

Anal. calcd. for $C_{34}H_{26}S_4$: C, 72.6; H, 4.66. Found: C, 72.9; H, 4.73.



9,10-Bis-[5-(4-methoxyphenyl)-2-methylthien-3-yl]-phenanthrene (3)

This compound was synthesized according to the general procedure using 4-bromoanisole (0.63 ml, 935 mg, 5 mmol) as the arylhalide component. Purification was done by chromatography (silica gel, Hexane:Toluene / 1:1) to give 610 mg (52%) of the product as a white solid. m.p. 164-166 °C

ratio after synthesis RR,SS/Meso 64/36

Racemate

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.17 (s, 6H), 3.83 (s, 6H), 6.90 (d, *J* = 8.4 Hz, 4H) 6.93 (s, 2H), 7.44 (d, *J* = 8.4 Hz, 4H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.70 – 7.78 (m, 4H), 8.84 (d, *J* = 8.1 Hz, 2H),

^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 14.48 (q), 55.48 (q), 114.34 (d), 122.76 (d), 124.62 (d), 126.72 (d), 126.77 (d), 127.05 (d), 127.47 (d), 127.66 (s), 130.33 (s), 131.85 (s), 133.38 (s), 134.69 (s), 137.13 (s), 139.61 (s), 158.95 (s)

MS (EI): 582 [M^+]; HRMS calcd. for $C_{38}H_{30}O_2S_2$: 582.1687. Found: 582.1674.

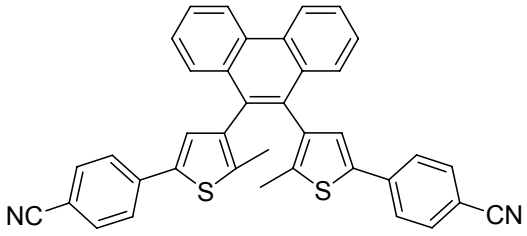
Meso form

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.08 (s, 6H), 3.81 (s, 6H), 6.83 (d, *J* = 8.4 Hz, 4H) 6.91 (s, 2H), 7.38 (d, *J* = 8.4 Hz, 4H), 7.58 (t, *J* = 7.7 Hz, 2H), 7.70 (t, *J* = 7.7 Hz, 2H), 7.82 (d, *J* = 7.7 Hz, 2H), 8.83 (d, *J* = 7.7 Hz, 2H),

^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 14.40 (q), 55.47 (q), 114.28 (d), 122.79 (d), 126.22 (d), 126.76 (d), 127.00 (d), 127.03 (d), 127.60 (d), 127.73 (s), 130.27 (s), 131.60 (s), 133.28 (s), 135.22 (s), 136.71 (s), 139.56 (s), 158.95 (s)

MS (EI): 582 [M^+]; HRMS calcd. for $C_{38}H_{30}O_2S_2$: 582.1687. Found: 582.1673.

Anal. calcd. for $C_{38}H_{30}O_2S_2$: C, 78.3; H, 5.19. Found: C, 78.5; H, 5.30.



9,10-Bis-[5-(4-cyanophenyl)-2-methylthien-3-yl]-phenanthrene (4)

This compound was synthesized according to the general procedure using 4-bromobenzonitrile (900 mg, 5 mmol) as the arylhalide component. Purification was done by chromatography (silica gel, Toluene) to give 1.12 g (97%) of the product as a white solid. m.p. 303-305 °C

Racemate

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.21 (s, 6H), 7.12 (s, 2H), 7.47 – 7.55 (m, 10H), 7.63 – 7.73 (m, 4H), 8.84 (d, J = 8.1 Hz, 2H),

^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 14.62 (q), 110.10 (s), 118.96 (s), 122.94 (d), 125.43 (d), 127.05 (d), 127.16 (d), 127.26 (d), 127.36 (d), 130.40 (s), 131.27 (s), 132.63 (s), 132.73 (d), 137.81 (s), 137.91 (s), 138.42 (s), 138.57 (s)

MS (EI): 572 [M^+]; HRMS calcd. for $C_{38}H_{24}N_2S_2$: 572.1381. Found 572.1383.

Meso form

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.14 (s, 6H), 7.13 (s, 2H), 7.47 – 7.62 (m, 10H), 7.71 – 7.77 (m, 4H), 8.85 (d, J = 8.4 Hz, 2H),

^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 14.63 (q), 110.30 (s), 118.91 (s), 122.99 (d), 125.55 (d), 127.23 (d), 127.31 (d), 128.45 (d), 128.85 (d), 130.42 (s), 131.18 (s), 132.64 (s), 132.80 (d), 137.48 (s), 137.72 (s), 138.71 (s), 139.03 (s)

MS (EI): 572 [M^+]; HRMS calcd. for $C_{38}H_{24}N_2S_2$: 572.1381. Found 572.1379.

Anal. calcd. for $C_{38}H_{24}N_2S_2$: C, 79.7; H, 4.22; N 4.89. Found: C, 79.9; H, 4.26; N, 4.81.

Spectroscopic data

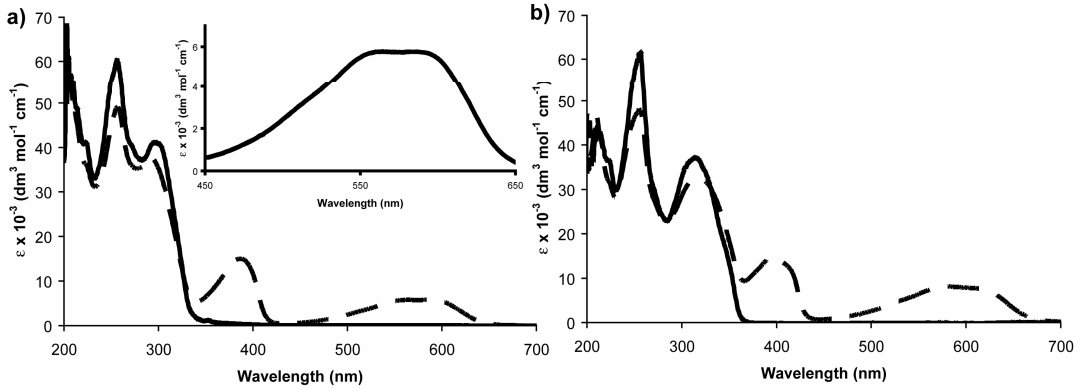


Figure 1 The UV-vis spectra of a) **1** and b) **2** in the open form (—) and in the photostationary state (---). Inset in the panel a) shows detail of the double absorption maximum in the visible region

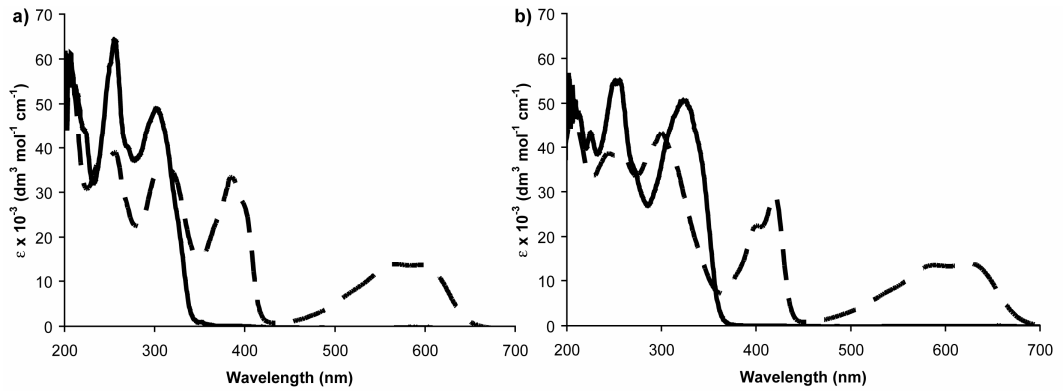


Figure 2 The UV-vis spectra of the anti-parallel (photochemically active) isomers of a) **3** and b) **4** in heptane. The open form (—) and the photostationary state (---).

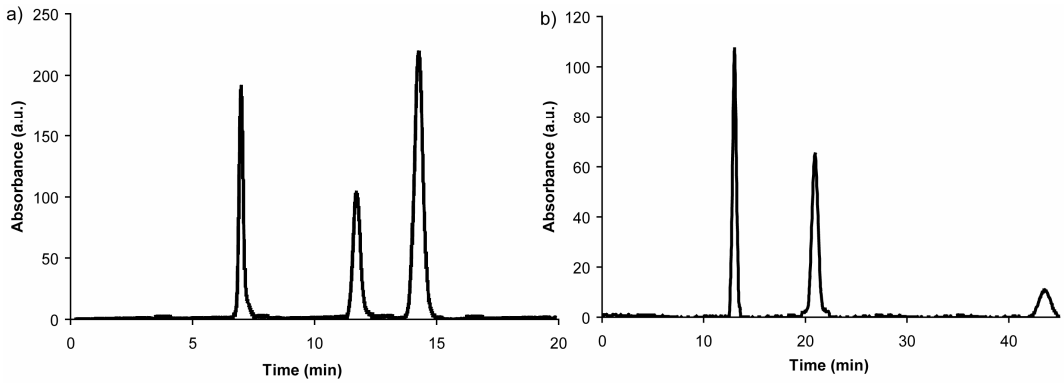


Figure 3 The HPLC traces of a) **3** (eluent heptane/isopropanol : 97/3) and b) **4** (eluent heptane/isopropanol 90/10) on a Chiracel-AD (Daicel) column

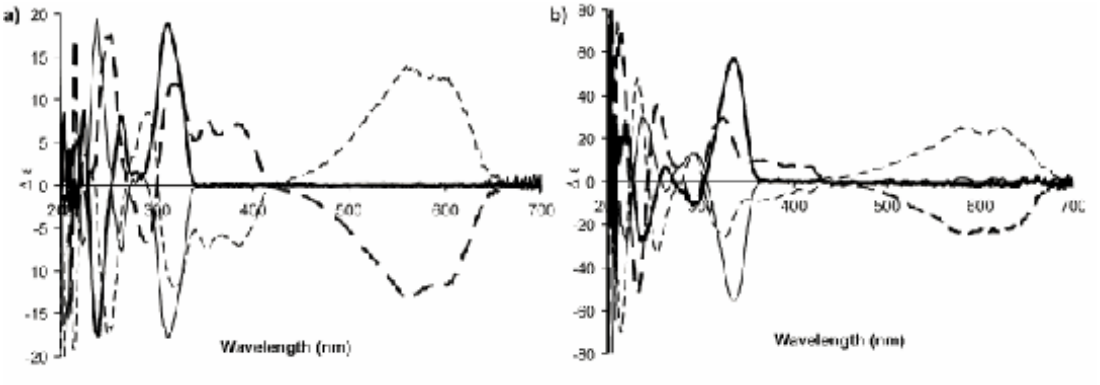
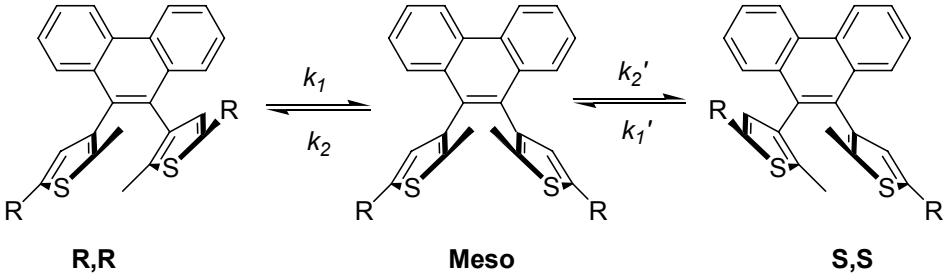


Figure 4 The CD spectra of the anti-parallel (photochemically active) isomers of a) **3** and b) **4** in heptane. The open form (—) and in the photostationary state (**---**). The curves for the isomer with the shortest retention time are thick and the curves for the isomer with second shortest retention time are thin.

Kinetics of the isomerization

Although the kinetics of the racemisation looks quite complicated involving three species and four rate constants, we have found that the change in the circular dichroism can be expressed as a first order kinetic process dependent only on the temperature and the rate constant of the isomerisation of one of the enantiomers to the Meso form.

There are three species in the mixture under an equilibrium conditions, the chiral enantiomeric forms the "R,R" and the "S,S" together with the nonchiral "Meso" form. Their mutual interconversions occur *via* rotation about the single bonds connecting the thiophene ring with the phenanthrene unit and consequently are first order reactions. We can assign each reaction its rate constant, k_1 and k_1' for the reaction producing the Meso form starting from the R,R or the S,S form respectively and k_2 and k_2' for the reverse reactions.



Scheme The racemization pathway

However, in the nonchiral environment the energies of the R,R and the S,S forms are equal which means that also their rate constants for the interconversion with the Meso form will be equal. Thus we can write $k_1 = k_1'$ and $k_2 = k_2'$.

The rate of the change of the concentration of R,R has then two contributions: it is depleted by the reaction leading to the Meso form with the rate $v = k_1[\mathrm{R,R}]$ and replenished by the reverse reaction $v = k_2[\mathrm{Meso}]$. The net rate is then described by the equation 1.

$$\frac{d[\mathrm{R,R}]}{dt} = -k_1[\mathrm{R,R}] + k_2[\mathrm{Meso}] \qquad \mathbf{1}$$

The same holds for the change of the concentration of the S,S isomer (Equation 2).

$$\frac{d[\mathrm{S,S}]}{dt} = -k_1[\mathrm{S,S}] + k_2[\mathrm{Meso}] \qquad \mathbf{2}$$

The rate of the change of the Meso isomer is more complicated since it can be replenished by the isomerisation of the R,R isomer with the rate $v = k_1[\mathrm{R,R}]$ as well as of the S,S isomer with the rate $v = k_1[\mathrm{S,S}]$. The depletion has also two channels which both depend on the concentration of the Meso form $v = k_2[\mathrm{Meso}]$. The rate is then described by the equation 3.

$$\frac{d[\mathrm{Meso}]}{dt} = -2k_2[\mathrm{Meso}] + k_1[\mathrm{R,R}] + k_2[\mathrm{S,S}] \qquad \mathbf{3}$$

Our objective was to be able to determine the reaction rates using circular dichroism measurements. The isolated pure chiral isomer, either the R,R or the S,S, has a characteristic CD spectrum. During the isomerization this signal should be weakened and finally disappear at the point when the equilibrium is reached. The rate of the signal weakening is dependent on the rate of the isomerization of the pure isomer to the Meso form as well as on the reverse reaction and the formation of the opposite enantiomer from the Meso form. This looks like a very complex kinetics but as shown in the following analysis it reduces to the first order process.

The circular dichroism $\Delta\varepsilon$ of a solution depends on the concentrations of the two enantiomers and molar circular dichroism of one of them, since the molar circular dichroism of the other enantiomer is exactly opposite. (Equation.4).

$$\Delta\varepsilon = \Delta\varepsilon_{(R,R)}[R,R] - \Delta\varepsilon_{(R,R)}[S,S] = \Delta\varepsilon_{(R,R)}([R,R] - [S,S]) \quad \mathbf{4}$$

The time dependence of the circular dichroism can be expressed as in equation 5.

$$\frac{d\Delta\varepsilon}{dt} = \Delta\varepsilon_{(R,R)}\left(\frac{d[R,R]}{dt} - \frac{d[S,S]}{dt}\right) \quad \mathbf{5}$$

After substituting the concentration changes of the R,R and the S,S in the equation 5 for the terms from equations 1 and 2, respectively, the equation 6 is obtained.

$$\frac{d\Delta\varepsilon}{dt} = \Delta\varepsilon_{(R,R)}[(-k_1[R,R] + k_2[Meso]) - (-k_1[S,S] + k_2[Meso])] \quad \mathbf{6}$$

This equation can be rewritten in the following form (Equation 7).

$$\frac{d\Delta\varepsilon}{dt} = -k_1\Delta\varepsilon_{(R,R)}([R,R] - [S,S]) \quad \mathbf{7}$$

The right part of the equation 7 after the $-k_1$ is identical with the right part of the equation 4. The substitution finally leads to equation 8 which is actually equation for the first order reaction kinetics in the differential form..

$$\frac{d\Delta\varepsilon}{dt} = -k_1\Delta\varepsilon \quad \mathbf{8}$$

Integration of this equation leads to the equation 9 where the $\Delta\varepsilon_0$ is the circular dichroism at the beginning of the measurement (i.e. at the t = 0).

$$\Delta\varepsilon = \Delta\varepsilon_o e^{(-k_1 t)} \quad \mathbf{9}$$

The linear version of the same equation which gives the rate constant as the slope is 10.

$$\ln\Delta\varepsilon = \ln\Delta\varepsilon_o - k_1 t \quad \mathbf{10}$$

The main advantage of the determination of the rate constant for the isomerization by this method is that it is not necessary to have one pure isomer. Any mixture containing excess of one of the optically active isomers is sufficient without even knowing their ratio. Also the information about the molar circular dichroism of one of the enantiomers is not required since only the circular dichroism ($\Delta\varepsilon_0$) at the beginning of the measurement appears in the equation and even that can be obtained from the intercept.

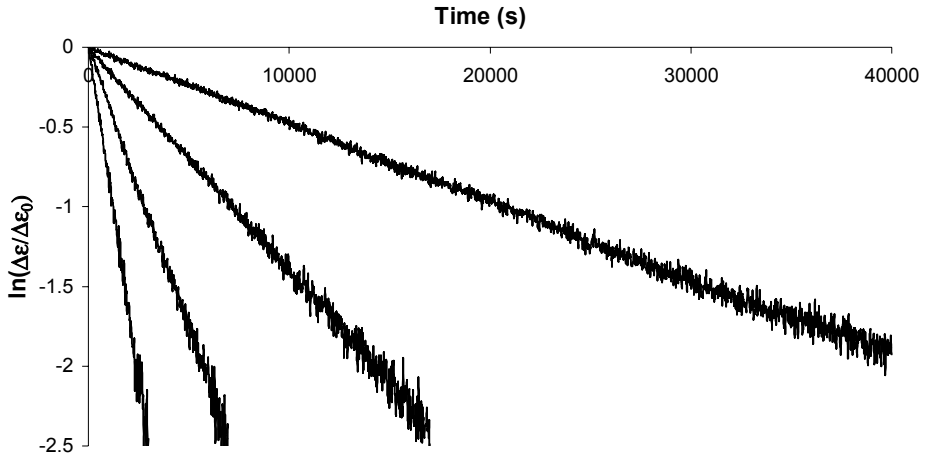


Figure 5 The plot of $\ln(\Delta\varepsilon/\Delta\varepsilon_0)$ *vs.* time for the different temperatures (from left to right 70°C, 80°C, 90°C, 100°C) for the compound **3** . The slope corresponds to the negative value of the rate constant (-k).

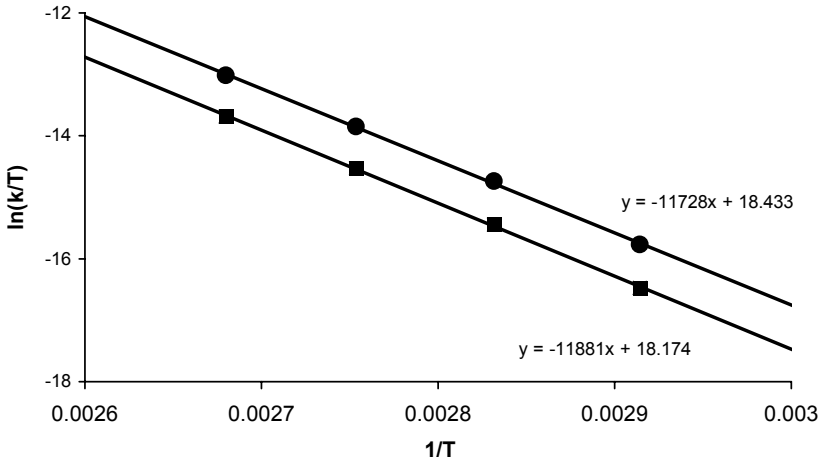


Figure 6 The Eyring plot for the racemization of the compound **3** (full circles) and **4** (full squares)

[1] Lucas, L. N.; van Esch, J.; Kellogg, R. M.; Feringa, B. L. *Chem. Commun.* **1998**, 2313-2314.