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# Novel Chiral Macrocycles Containing Two Electronically Interacting Arylene Chromophores

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**Abstract:** Novel chiral macrocycles consisting of two rigid oligoarylene rods and two chiral spiroindane clips have been synthesized by condensation of spiroindane diols and $CF_3$-activated $\alpha$-$\omega$-difluorooligoaryls. Since a broad variety of planar aromatic macrocycles is known, our non-planar, chiral rings represent a new class of macrocyclic compounds. The first two examples, which contain quaterphenylene and diphenylbithiophene rods, are presented in this communication; for one of them a crystal structure is given. The chiroptical properties of the macrocycles can be interpreted as an interplay of the "intra-rod" helicity of individual oligoarylene rods and the "inter-rod" helicity between both chromophores of the macrocycle. The macrocycles can act as chiral dopands of commercially available, and novel, polymeric nematic liquid crystals (emissive polyfluorenes). The "intra-rod" helicity of individual oligoarylene rods is the main feature in determining the resulting helical twisting power (HTP). The cholesteric induction in mesogenic, emissive polyfluorenes is of special interest for a realization of electronic devices that have a circularly polarized electroluminescence. The results are also important for an understanding of larger ensembles of chiral rodlike molecules, especially their $\pi-\pi$ interactions.

**Keywords:** chirality · cholesteric induction · circular dichroism · liquid crystals · macrocycles

## Introduction

Helically arranged, electronically interacting chromophores represent the key principle of novel chiroptical materials, especially light sources that emit circularly polarized light.[1, 2] Such materials consist of chiral ensembles of electronically interacting chromophores; the resulting chiroptical effects can be interpreted on the basis of the so-called exciton coupling model,[3] which describes the electronic interaction of two chromophores in a chiral environment. Such chiral interactions can be experimentally studied on model dimers composed of two chromophores that are fixed at a chiral core unit,[4] for example, a chiral 3,4-diaminodecaline core. However, this type of chiral model compound is characterized by a comparably high degree of remaining conformational freedom. An alternative to overcome the disadvantages of such chiral, noncyclic dimers leads to more rigid, cyclic dimers. They should be composed of two rigid chromophores that are fixed by two chiral clips on both ends of the interacting chromophores.

In this communication we describe the synthesis and optical/chiroptical characterization of two novel semirigid, chiral macrocycles that are composed of two electronically interacting arylene chromophores and two chiral spiroindane clips. The four structural components of the macrocycles are thereby connected through four aryl-O-aryl ether bridges.

## Results and Discussion

The starting point of our investigations was the finding that a low molecular weight oligomeric fraction is formed in addition to the expected polymer fraction in the base-catalyzed polycondensation of the spiroindane bisphenol **1**[5] and the bis-*ortho*-$CF_3$-activated quaterphenylene difluoride **2**[6] to give aromatic oligo- and polyethers (Scheme 1).

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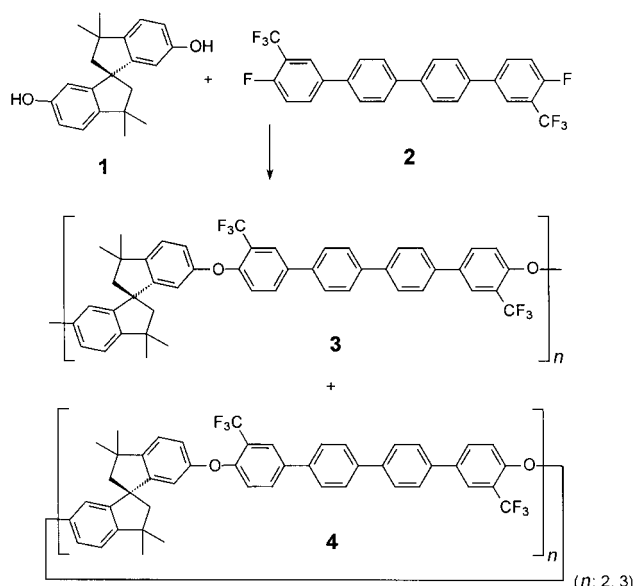
Scheme 1. Synthesis of linear polymers **3** and chiral macrocycles **4**; the *aR*-configuration of the chiral spiroindane moiety is shown.

Gel permeation chromatography (GPC; polystyrene (PS) calibration) of the condensation product gave a polymeric fraction **3** ($M_n$: ca. 10000) and two oligomeric peaks (**4**, $M_n$: 1500 and 2200, respectively), which we have assigned to the formation of cyclic di- and trimers **4a** ($n = 2$) and **4b** ($n = 3$) (the macrocycles are depicted with an *aR*-configuration of the chiral spiroindane clip).
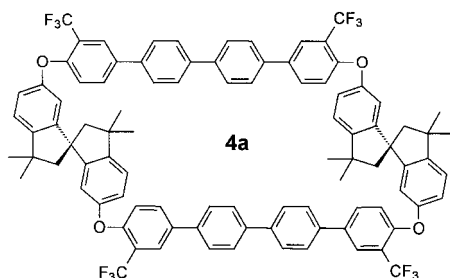


The optimization of the yield of nonpolymeric, cyclic products, and the subsequent separation and purification of cyclic oligomers are the next steps which we have addressed during our investigations. In doing this, we switched to nonstoichiometric ratios of the starting compounds **1** and **2**; a threefold excess of the bis-phenol component **1** was used. In this case, the reaction mixture **3/4** contains exclusively hydroxy-terminated linear oligomers (so-called telechelics) and the fraction of cyclic oligomers. Now an (atmospheric pressure) liquid chromatographic separation of the reaction mixture on silica (petroleum ether (PE)/THF 3:1) is possible because the mixture contains linear and cyclic species of rather different polarity.

After achieving the synthesis and purification of **4** starting from the racemic monomer *rac*-**1**, we then switched to enantiomerically pure **1** for the synthesis of enantiopure macrocycles **4**. Enantiomerically pure **1** can be isolated after the kinetic resolution[7] of the bishexanoic ester of the

bisphenol **1**, which was treated with cholesterol esterase in *tert*-butyl methyl ether.[8]

By performing the condensation with (*aR*)-**1**, we could isolate a raw macrocycle fraction that contains (*aR,aR*)-**4a** and (*aR,aR,aR*)-**4b** (molecular ratio ca. 10:1). Further column chromatography on silica gel with PE/THF (3:1) gave pure (*aR,aR*)-**4a**. The purification of **4b** will be the subject of further studies.

Compound **4a** was characterized by MS spectrometry and UV-visible and circular dichroism (CD) spectroscopy. The MS spectrum displays only the molecular ion peak $[M]^+$ of the cycle at 1493 along with the $[M]^{2+}$ peak at 746.5.

The UV-visible spectrum (Figure 1) of (*aR,aR*)-**4a** displays a long wavelength absorption band centred at 301 nm, which is characteristic of the $\alpha,\omega$-oxysubstituted quaterphenylene
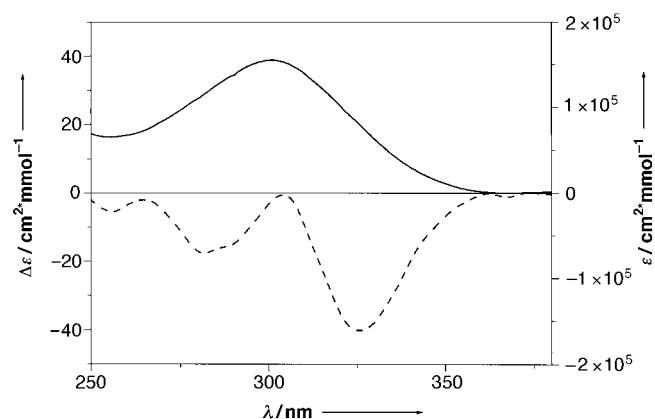


Figure 1. UV-visible (solid) and CD (dashes) spectra of the chiral macrocycle (*aR,aR*)-**4a** (dilute solution, solvent: dioxane).

chromophore. The CD spectrum of (*aR,aR*)-**4a** (Figure 1) exhibits a "pseudo"-bisignated Cotton effect in the region of the delocalized long-axis polarized $\pi-\pi^*$ transition of the quaterphenylene chromophore[9] with two maxima at 325 nm ("negative lobe") and 304 nm ("positive lobe"), and a point of inflexion at about 313 nm. The shape of the CD band and the position of the maxima indicate the occurrence of an electronic coupling (negative exciton coupling[3]) between the two quaterphenylene chromophores. However, this effect is superimposed by a second monosignated, negative Cotton effect in the $\pi-\pi^*$ transition region; this should originate from a chiral (helical) conformation of single quaterphenylene rods in the macrocycle (*aR,aR*)-**4a**. According to Mislow, this negative Cotton effect correlates to a *P* helicity of the quaterphenylene moiety.[11] The amplitude of the overall CD effect is only moderate ($g_{abs}$: $2 \times 10^{-4}$), probably due to a relatively weak mutual distortion angle between the two linear quaterphenylene rods.

This interpretation of the optical and chiroptical properties was supported by a structure optimization of (*aR,aR*)-**4a** based on ab initio molecular orbital (MO) calculations.[12] The structure of the quaterphenylene macrocycle (*aR,aR*)-**4a** can be described as follows: i) One of the two quaterphenylene rods exhibits a well-defined *P* helicity along the oligophenylene chain, while the helicity of the other rod is not fully defined (only 3 phenylenes in *P* helicity). ii) The mutual

distortion of both quaterphenylene rods is only weak, with a calculated distortion angle of approximately 7°. The only weak mutual "inter-rod" torsion of both quaterphenylene rods is reflected by the only moderate bisignated component of the CD spectrum (weak exciton coupling).

A similar overlay of monosignated and bisignated CD bands was detected for the corresponding polymer (all-*aR*)-**3**,[13] which shows a positive monosignated Cotton effect in dilute solution indicating a helical conformation (in this case a *M* helicity) of the single quaterphenylene rods. In poor solvents, solvent/non-solvent mixtures, or in the solid sate, this effect is superimposed by a stronger bisignated Cotton effect (negative couplet, *M* skew) due to an ongoing aggregation of individual polymer chains under formation of chiral (helical) aggregates (exhibiting exciton coupling, Figure 2).
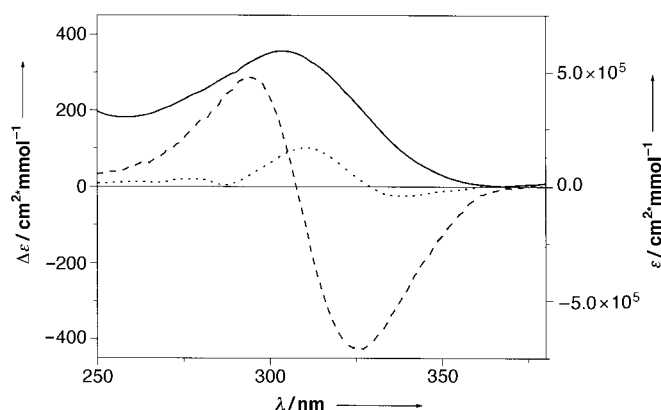


Figure 2. UV-visible (solid) and CD spectra of the chiral polymer (all-*aR*)-**3** (dilute solution in dioxane (dots) and 1-decanol (dashes)).

Inspired by the findings described above we varied the chemical structure of the arylene building blocks of the macrocycles. Doing this, we replaced the rigid quaterphenylene rods by phenylene-thienylene-thienylene-phenylene moieties (5,5′-diphenyl-2,2′-bithiophene), in the hope that a macrocycle with a higher mutual distortion of the two chromophores would result.

The diphenylbithiophene chromophore 1) gives rise to an increased flexibility of the macrocycle **5** as result of the nonlinear (kinked) structure of the central thienylene units,
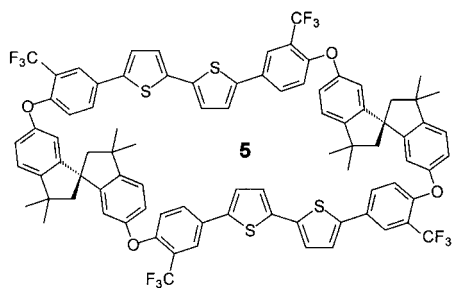


and 2) effects a bathochromic shift of the long-axis-polarized $\pi-\pi^*$ transition[10] of **5** ($\lambda_{max}$: 380 nm, 423 nm (sh); Figure 3). Thereby, the observation of vibronic side bands in the UV-visible spectrum indicates a more flattened structure of the
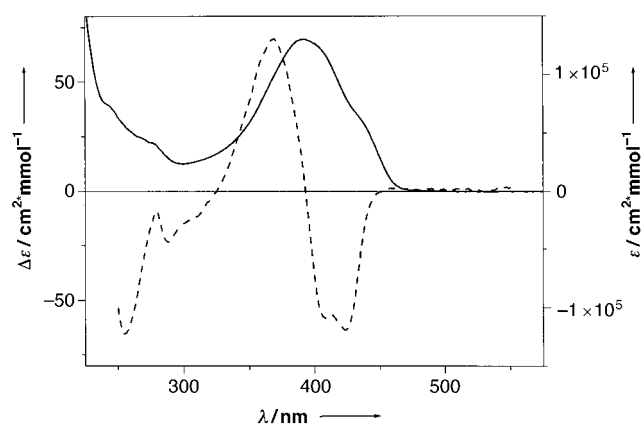


Figure 3. UV-visible (solid) and CD (dashes) spectra of the chiral macrocycle (*aR,aR*)-**5** (dilute solution, solvent: dioxane).

diphenylbithiophene chromophore. The CD spectrum of (*aR,aR*)-**5** (Figure 3) displays a symmetric bisignated negative couplet with a vibronic splitting of both lobes, which are centred at 425, and 370 nm, respectively. The *g* value of **5** was calculated to be about $9 \times 10^{-4}$ (at 391 nm), a value which is in the range of the *g* value of related, noncyclic chiral dimers, for example, the chiral terthiophene dimers that were described by Meijer et al.[4] The shape of the CD spectrum indicates an *M* skew formed by the two diphenylbithiophene rods. The complete absence of an underlying monosignated component in the CD spectrum again indicates a nonhelical, flattened geometry of individual diphenylbithiophene chromophores. The increased *g* value of **5**, if compared with that of the quaterphenylene macrocycle **4a**, can be interpreted as result of the significantly increased mutual distortion of the two chromophores in **5**.

At 80 K (low-temperature UV-visible measurement in 2-methyltetrahydrofurane (2-MeTHF); Figure 4), a slight bathochromic shift and significant sharpening of the absorption spectrum of **5** occur, resulting in the appearance of three
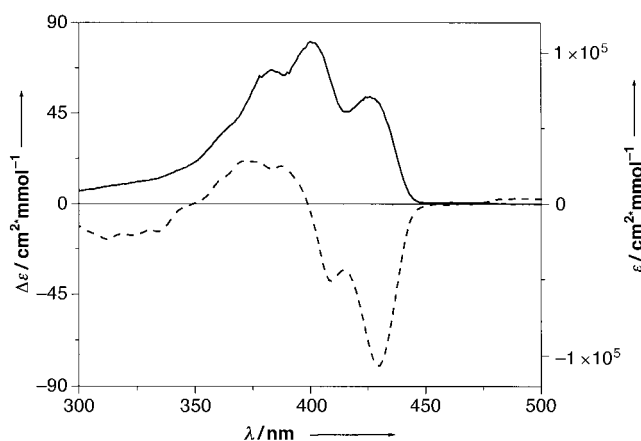


Figure 4. Low-temperature UV-visible (solid) and CD (dashes) spectra of the chiral macrocycle (*aR,aR*)-**5** (80 K, glass, solvent: 2-MeTHF).

well-separated peaks at 425 nm (0-0), 400 nm (0-1), and 383 nm (0-2). The changes in the UV-visible spectrum at lower temperature are reflected in the low-temperature CD spec-

trum of **5**, which also sharpens and exhibits a series of vibronically coupled CD transitions. The observed CD spectrum is a superposition of the Davydov split, individual absorption modes. Hereby, two low-energy, negative CD signals at 414 and 430 nm, and two high-energy, positive CD peaks at 376 and 387 nm occur. The low-temperature CD spectrum of **5** suggests, that the Davydov splitting is in the order of about 120–150 meV, somewhat lower as the frequency of the main vibration mode (ca. 190 meV).

The structure simulation[12] of the diphenylbithiophene macrocycle (*aR,aR*)-**5** reflects this more pronounced skew; the distortion between both diphenylbithiophene chromophores was calculated to be approximately 28°. The two diphenylbithiophene rods are, as expected, significantly flattened.

The X-ray structure analysis of (*aR,aR*)-**5** (Figure 5) displays the expected *M* skew of the two chromophores with a mutual distortion between both rods of about 30°. The
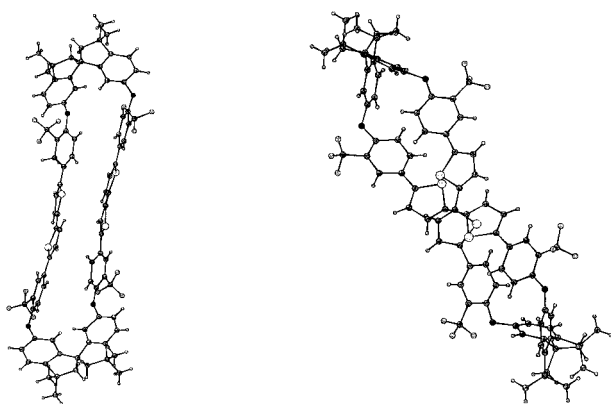


Figure 5. Crystal structure of the chiral macrocycle (*aR,aR*)-**5**.[21]

individual diphenylbithiophene moieties are distinctly flattened and nonhelical (slight *M* twist of the bithiophene units, slight *P* twist of all phenylthienyl units). The minimum distance between both diphenylbithiophene rods is about 3.65 Å.

It has been known for a long time that small amounts of optically active guests added to nematic liquid-crystalline (LC) hosts can induce twisted nematic (cholesteric) LC phases.[14] The characteristics of the resulting cholesteric phase strongly depends on the structure of the chiral dopant.[15] We tested the suitability of (*aR,aR*)-**4a** as chiral dopant (helical-twisting agent) of achiral, nematic LC materials, both low molecular weight and polymeric hosts. In first experiments, we estimated the helical-twisting power (HTP)[16] of (*aR,aR*)-**4a** as dopant of four commercially available, low molecular weight, nematic liquid crystals: MBBA (benzylideneaniline derivative): + 36.8; E7 (cyanobiphenyl derivative): + 37.1; Phase 1052 (phenyl benzoate derivative): + 33.7; ZLI 2359 (cyanobicyclohexyl derivative): + 64.0 μm$^{-1}$. The positive sign of the HTP correlates with the *P* helicity of individual quaterphenylene arms in the macrocycle (*aR,aR*)-**4a**.[17] Surprisingly, **4a** displays nearly similar HTP values in three of the nematic LCs (MBBA, E7, Phase 1052) that we investigated. This is a somewhat unexpected behavior, since the majority of known helical twisting agents (substituted

biaryls, biaryl-based macrocycles) displays strongly different HTP values in different nematic LC hosts.[17] Polymer (all-*aR*)-**3** has an HTP with E7[18] that is drastically increased and has the opposite sign (E7: −290 μm$^{-1}$) in relation to **4a**. The negative HTP correlates with the *M* helicity of the individual quaterphenylene rods of polymer (all-*aR*)-**3** (positive Cotton effect in the CD spectrum, see Figure 2).

Another set of experiments was directed towards an application of **4a** as chiral dopant of nematic LC polymers, especially emissive LC polymers of the polyfluorene type (**PF**, **6**),[19] since we are interested in emitters that have circular polarization of photo- and, especially, electroluminescence.[20]

For this purpose, spin-coated films of achiral, liquid crystalline poly(9,9-dialkylfluorene-2,7-diyl)s **6** (R: *rac*-2-ethylhexyl) doped with 2% of the chiral macrocycle (*aR,aR*)-**4a** have been prepared. The pristine film (after simple spin-coating) displays only a weak Cotton effect (circular dichroism) in the absorption range of the polyfluorene chromophore between 380 and 420 nm. However, after annealing into the thermotropic LC state (180–200 °C) of **6** for two hours, the film exhibits a significantly increased chiroptical anisotropy of the delocalized π–π* absorption band of the conjugated polyfluorene (**PF**) chromophore ($g_{abs}$: ≈0.002 at 390 nm for 2% (*aR,aR*)-**4a** in **6** with R = *rac*-2-ethylhexyl; Figure 6). Compound **4a** itself shows no
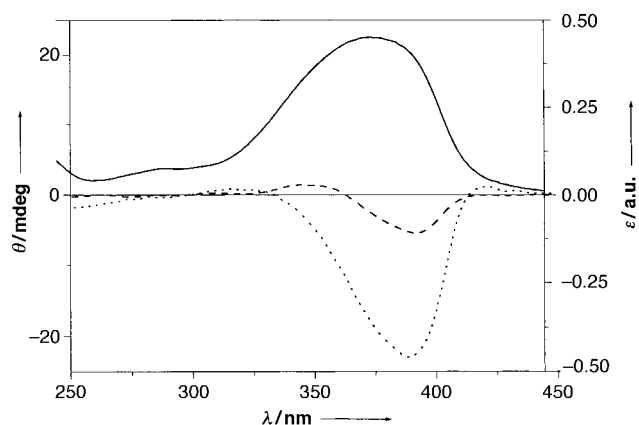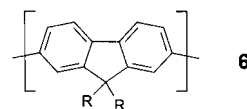


Figure 6. UV-visible (solid) and CD spectra of a blend of 2% of the chiral macrocycle (*aR,aR*)-**4a** in poly[9,9-bis(*rac*-2-ethylhexyl)fluorene] **6**; CD spectra: a) after spin-coating (dashes) and b) after annealing for 2 h to 200 °C (dots).

absorption in this wavelength region (see Figure 1). This findings suggest that **4a** is able to induce a chiral (cholesteric) LC phase in the originally achiral LC polymer **6**. Further experiments are now directed towards a maximization of this effect as well as on the execution of similar tests with the diphenylbithiophene macrocycle **5** and the corresponding polymers (e.g., **3**).

First HTP measurements with the diphenylbithiophene macrocycle (*aR,aR*)-**5** have displayed a reduced helical twisting power (MBBA: +11.0; E7: +22.3 μm$^{-1}$) with respect to the quaterphenylene macrocycle (*aR,aR*)-**4a**. The smaller HTP of **5** could be connected to the essentially flattened

quaterarylene unit of **5**. This finding supports the hypothesis that the "intra-rod" helicity of individual quaterarylene chains is the main feature in determining the cholesteric induction and that the sense of the induced cholesteric phase correlates with the sense of the "intra-rod" helicity.

## Experimental Section

**Measurements**: $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AMX 300 spectrometer, $^{19}$F NMR spectra on a Bruker AMX 500 spectrometer; chemical shifts are reported in case of $^1$H and $^{13}$C NMR in ppm downfield to TMS as an internal, in case of $^{19}$F NMR to fluorobenzene as an external standard ($\delta = -113$). UV/Vis spectra were recorded on a Perkin–Elmer Lamda 9, CD spectra on a Jasco J-715 and Jasco J-700 spectrometer. Mass spectra were measured with a Zab 2 SE FPD mass spectrometer.

**Macrocycle synthesis**: The spiroindane bisphenol **1** (3 mmol), the difluoroarylene compound (1 mmol) and $K_2CO_3$ (2.2 mmol) were placed in a flask equipped with a Dean–Stark trap. Toluene (60 mL) and 1-methyl 2-pyrrolidone (NMP; 30 mL) were added. The mixture was heated under reflux for 5 h to remove all water. Afterwards the mixture was heated up for another 8 h at 200 °C. After cooling to RT the product was poured into methanol/aqueous HCl. The precipitate was filtered, washed several times with hot water, and dried in vacuum. The macrocycles were isolated and purified by liquid chromatography on silica gel with PE/THF (3:1) as eluent.

**Compound 4a**: Compound **1** (924 mg, 3.00 mmol), compound **2** (478 mg, 1.00 mmol), and $K_2CO_3$ (304 mg, 2.2 mmol) gave **4a** (158 mg, 21.0 %). $R_f = 0.95$ (PE/THF 4:1); MS (70 eV, FD): $m/z$ (%): 1493 (100) $[M]^+$, 746.5 (21) $[M]^{2+}$; elemental analysis calcd (%) for $C_{94}H_{72}F_{12}O_4$ (1493.58): C 75.59, H 4.86, F 15.26; found C 75.28, H 4.80; $^{19}$F NMR ([D$_8$]THF): $\delta = -61.33$, $-61.28$

**Compound 5**: Compound **1** (924 mg, 3.00 mmol), 2,2′-bis(4-fluoro-3-trifluoromethylphenyl)bithiophene (495 mg, 1.00 mmol), and $K_2CO_3$ (304 mg, 2.2 mmol) gave **5** (145 mg, 19.0 %). MS (70 eV, FD): $m/z$ (%): 1518 (100) $[M]^+$; elemental analysis calcd (%) for $C_{86}H_{64}F_{12}O_4S_4$ (1517.70): C 68.06, H 4.25, S 8.45, F 15.26; found C 67.89, H 4.17, S 8.68; $^{19}$F NMR (495 MHz, [D$_8$]THF): $\delta = -61.47$, $-61.40$

The $^1$H and $^{13}$C NMR spectra of **4a** and **5** are very complex, their detailed analysis would need additional NMR experiments.

**Polymer synthesis**: The spiroindane bisphenol **1** (924 mg, 3.00 mmol), the quaterphenyl derivative **2** (1430 mg, 3.00 mmol), and pottasium carbonate (912 mg, 6.6 mmol) were dissolved in a mixture of toluene (50 mL) and NMP (25 mL). The following condensation procedure was similar to that used in the synthesis of the macrocycles **4** and **5**. The resulting mixture was precipitated into methanol/HCl (600 mL, 30:1). The crude product was washed several times with hot water, dried under vacuum, re-dissolved in THF, and re-precipetated into methanol. The cyclic compounds **4** as well as low molecular weight oligomers were removed by preparative GPC (500 Å PS gel, column length: 60 cm, solvent: THF, flow rate: 10 mL min$^{-1}$). 780 mg (35 %) of colorless polymer **3** were obtained. $M_n = 7000$ g mol$^{-1}$, $M_w = 11000$ g mol$^{-1}$ (GPC, PS calibration); $^1$H NMR (300 MHz, C$_2$D$_2$Cl$_4$, TMS): $\delta = 7.77$ (s, 1 H), 7.53 – 7.49 (m, 5 H), 7.11 (s, 1 H) 6.83 – 6.81 (m, 2 H), 6.60 (s, 1 H), 2.39 (d, $J = 8$ Hz, 1 H), 2.26 (d, $J = 8$ Hz, 1 H), 1.33 (s, 6 H); $^{13}$C NMR (75 MHz, C$_2$D$_2$Cl$_4$, TMS): $\delta = 156.14$, 155.32, 152.87, 149.22, 139.60, 138.44, 134.63, 131.71, 127.79, 127.49, 125.71, 123.79, 122.10, 120.92, 120.50, 119.65, 118.39, 116.43; $^{19}$F NMR (495 MHz, C$_2$D$_2$Cl$_4$, C6H5F): $\delta = 61.76$; elemental analysis calcd (%) for $(C_{47}H_{36}F_6O_2)_n$ (746.79)$_n$: C 75.59, H 4.86, F 15.26; found C 74.61, H 4.62.

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[21] monoclinic cell: $a = 11.1048$, $b = 18.6284$, $c = 22.9385$ Å, $\beta = 98.007°$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-163545. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).