

Bacheloronderzoek Scheikunde (CHBBBOND)

Academisch jaar: 2008-2009

Door: Tom van Leeuwen s 1651676

Titels:

“Controlling Surface Properties using a
Polymerizable Dithienylethene”

En

“Controlling Liquid-Crystalline Phase using
Optically Active Dithienylethene as Dopant”

Onder leiding van en gecorrigeerd door:

Dr. W.R. Browne

Controlling Surface Properties using a Polymerizable Dithienylethene

Tom van Leeuwen s1651676 under supervision of Dr. W.R. Browne

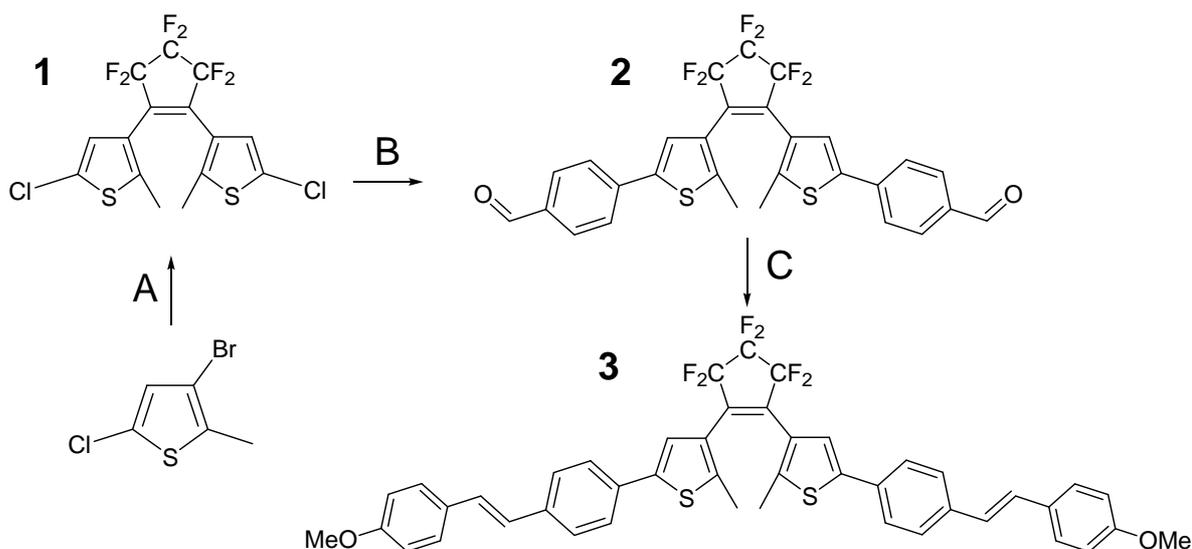
Abstract

The synthesis and analysis of a modified polymerizable dithienylethene based on the previous design (Feringa, B.L et al. *Langmuir* **2008**, 24, 6334) is reported. The photochemical and electrochemical properties of the monomer in solution have been compared to the previous design. The fluorescent properties were found to be different, while the behaviour observed by UV/vis and Raman spectroscopy was as expected for a dithienylethene. The compound polymerized on glassy carbon and ITO forming thin films which were characterized by cyclic voltammetry. The polymer was able to ring close upon irradiation with visible light which was shown by UV/vis spectroscopy.

Introduction

Dithienylethene compounds have been successfully used to control different media reversibly by external stimuli such as light, electric potential or presence of Lewis acids¹. For example the properties of gels², ferroelectrics³ and liquid crystals⁴ have been altered reversibly by the means of light. Also surface properties can be controlled externally by for example light, or electric potential. Such surfaces are called “smart surfaces” and offer promising prospects for applications. One way of making a controllable surface is polymerising dithienylethene compounds on different materials.⁵ Previously a smart surface was made this way by attaching electropolymerizable methoxystyrene groups to a dithienylethene compound.⁶ This design was able to immobilize on conducting surfaces with retention of functions of the photochromic unit but the polymers obtained were of limited thickness regardless of the concentration of

monomer. This was believed to be because of a lack of conductivity of the polymer backbone at potentials required for electropolymerisation and the inability of the dithienylethene core to transfer electrons from electrode to solution at those potentials. By using a hexafluorocyclopentene-based instead of the hexahydro dithienylethene the redox potentials of its oxidation come closer to the potential of electropolymerization. Therefore the dithienylethene component would still be able to transfer electrons and thus prevent insulation of the electrode. The new design will also have different properties such as hydrophobicity and will give the ability of electrochemical ring-opening instead of ring-closing. In this article the synthesis of an electropolymerizable dithienylethene has been given and discussed. The photoisomerisation of the compound in solution has been investigated by UV/vis, Raman and fluorescence spectroscopy. Cyclic



Scheme 1: (A): *n*BuLi at -78°C , C_5F_8 , 38 %, (B): *n*BuLi, $\text{B}(\text{O}i\text{Bu})_3$, *p*-Br(C_6H_4)CHO, $\text{Pd}(\text{PPh}_3)_4$, Na_2CO_3 , 69 %, (C): NaH, *p*-CH₃OC₆H₄CH₂P(O)(OC₂H₅)₂, 50 %.

voltammetry was used to study the redox properties of the compound. The absorbance of the polymerized dithienylene ethene in open and closed form has been studied and based on the results of this study suggestions have been made for future research.

Experimental

General Remark. The syntheses and the storage of **1**, **2** and **3** and the doping of liquid crystals were carried out with exclusion of light

Materials. Chemicals were purchased from Acros, Aldrich, Fluka or Merck. Solvents used for extractions and chromatography were of technical grade. Solvents used in reactions were distilled freshly from their appropriate drying agents before use. Silicagel 60 (230-400 mesh) was used for flash chromatography.

Physical Methods. ^1H NMR spectra were recorded on a Varian VXR-400 (400 MHz) or a Varian Gemini-200 (200 MHz). ^{13}C NMR spectra were recorded

on a Varian Gemini-200 (50 MHz). ^{19}F NMR spectra were recorded on a Varian Gemini-200 (188 MHz). 2D NMR experiments were executed on a Varian Gemini-200. Chemical shifts are denoted in δ values (ppm) referenced to the residual chloroform or dichloromethane peaks. The splitting patterns are designated as follows: s (singlet), d (doublet). Coupling constants, *J*, are denoted in hertz. UV/Vis spectra were recorded using a JASCO 570 UV-VIS-NIR spectrometer or a JASCO 670 UV-VIS-NIR. Fluorescence spectra were recorded with a JASCO F7200 fluorimeter. Raman spectra were recorded at an excitation wavelength λ_{exc} of 785 nm on quartz slides or in quartz cuvettes on a PerkinElmer Raman Station 400F Raman spectrometer. FT-IR spectra were recorded using a PerkinElmer spectrum 400 FT-IR/FT-FIR spectrometer. Electrochemical experiments were performed with a 760C Electrochemical Workstation (CH Instruments). The analyte was dissolved in a solution of 0.1 M tetra-

butylammoniumhexafluorophosphate (TBAPF₆) in anhydrous dichloromethane. A Teflon shrouded glassy carbon electrode and indium tin oxide (ITO) coated glass were employed as a working electrode. A Pt wire was used as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode.

Synthesis of 3,3'-(perfluorocyclopent-1-ene-1,2-diyl)bis(5-chloro-2-methylthiophene) (1). In a flame dried flask under nitrogen atmosphere a stirred solution of 3-bromo-5-chloro-2-methylthiophene (4.0 gram, 19 mmol) in anhydrous diethyl ether (200 mL) was cooled to -78 °C. *n*BuLi (11.8 mL, 1.6 M in hexane, 19 mmol) was added slowly by syringe and stirred for 30 minutes at -78 °C giving a milk white solution. Octafluorocyclopentene (1.8 gram, 8.5 mmol) was added slowly by syringe after which the reaction mixture turned greenish yellow. The mixture was stirred for an additional 4 hours at -78 °C after which it was warmed to room temperature overnight to give a dark solution. Diethyl ether was added (50 mL) and the organic phase was washed with water (100 mL). The aqueous phase was extracted three times with diethyl ether (3 x 50 mL) and the combined organic phases were dried over sodium sulfate and concentrated *in vacuo*. (1) was isolated by column chromatography over silica (heptane, R_f = 0.62, pink) and purified by recrystallization from hexane yielding (1) (1.4 gram, 38 %) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ = 1.95 (s, 6H), 6.95 (s, 2H). ¹⁹F NMR (400 MHz, CDCl₃): δ = 1.95 (s, 6H), 6.95 (s, 2H). **Synthesis of 4,4'-(4,4'-(perfluorocyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-4,2-diyl))dibenzaldehyde (2).** In a flame dried flask under a nitrogen atmosphere

(1) (1.2 gram, 2.65 mmol) was dissolved in anhydrous diethylether (60 mL). *n*BuLi (4.1 mL, 1.6 M in hexane, 6.6 mmol) was slowly added by syringe at room temperature and stirred for 30 minutes. To the dark orange reaction mixture tributylborate (1.83 mL, 6.6 mmol) was slowly added and the mixture was stirred for 40 minutes at room temperature. Under a nitrogen atmosphere a separate flame dried flask containing *p*-bromobenzaldehyde (0.99 gram, 5.3 mmol), tetrakis (triphenylphosphine) palladium (0) (0.33 gram, 0.31 mmol), THF (20 mL), Na₂CO₃ (aq) (14 mL, 2 M) and ethylene glycol (1 mL) was heated to 50 °C. To this flask the reaction mixture containing the boronic ester was added slowly by syringe. The resulting mixture was refluxed over night at 55 °C, subsequently diluted with diethyl ether (50 mL) and washed with brine (50 mL). The brine solution was extracted with diethyl ether (50 mL) and the combined organic phases were dried over sodium sulphate and reduced *in vacuo*. Purification by chromatography over silica (pentane ethyl acetate 5:1, R_f = 0.28, blue) yielded (2) (1.1 gram, 69 %) as a greenish brown solid. ¹H NMR (200 MHz, CDCl₃): δ = 10.01 (s, 2H), 7.90 (d, *J* = 8.2, 4H), 7.70 (d, *J* = 8.2, 4H), 7.43 (s, 2H), 2.01 (s, 6H). ¹³C NMR (50 MHz, CDCl₃): δ = 14.9, 124.5, 126.0, 126.4, 130.8, 135.7, 139.0, 141.0, 143.5, 191.5, MS (APCI): 599.05 (M+Na) **(E)-3,3'-(perfluorocyclopent-1-ene-1,2-diyl)bis(5-(4-(4-methoxystyryl)phenyl)-2-methylthiophene).** In a flame dried flask under a nitrogen atmosphere sodium hydride (0.45 gram, 50% in oil, 9.4 mmol) was suspended in THF (60 mL). Diethyl 4-methoxybenzylphosphonate (1.35 mL, 7.8 mmol) was added by syringe. The

stirred mixture was heated at 55° C for one hour. A solution of **2** (0.61 gram, 1.1 mmol) in THF (20 mL) was added slowly by syringe. The reaction mixture was heated at reflux over night. The mixture was cooled to room temperature quenched with water (1 mL) and washed with water (80 mL). The aqueous layer was extracted with dichloromethane (3x30 mL). The combined organic layers were dried over sodium sulphate and concentrated *in vacuo*. Purification by column chromatography over silica (dichloromethane, $R_f = 1$, green) yielded **3** as a green solid (0,43 g , 50%). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.57 (d, $J = 8.5$ Hz, 4H), 7.53 (d, $J = 8.6$ Hz, 4H), 7.50 (d, $J = 8.7$ Hz, 4H), 7.34 (s, 2H) 7.14 (d, $J = 16.4$ Hz, 2H), 7.01 (d, $J = 16.3$ Hz, 2H), 6.93 (d, $J = 8.7$ Hz, 4H), 3.84 (s, 6H), 2.0 (s, 6H) ^{13}C NMR (50 MHz, CD_2Cl_2): $\delta = 14, 55, 114, 126, 127, 128, 129, 130, 132, 142, 160$, MS: 785.197 (M+H).

Results and Discussion

Synthesis of 1. **1** is obtained in a low yield (36 %). The reason for this is probably not the reaction itself, but the purification of the compound. After column chromatography over silica with heptane as eluents the product was still contaminated with non-fluorinated compounds as was concluded from ^1H NMR and ^{19}F NMR. A recrystallization step was required to remove these impurities. Although hexane proved to be a good solvent for recrystallization for the first crop, for the second crop it was unable to separate product from

impurities.

Synthesis of 2. The generated boronic ester was not isolated from the reaction mixture before the Suzuki coupling reaction was carried out because of the risk of hydrolysis of the boronic ester during isolation. Instead the whole reaction mixture was transferred to a separate flask for the Suzuki coupling.

Synthesis of 3. The sodium hydride needed in the Horner-Wadsworth-Emmons reaction was added as a dispersion in mineral oil. The oil need not to be discarded before the reaction, since it is easily removed and does not interfere with the reaction. Sodium hydride was used in a large excess, because it loses activity over time. This posed no problems, as sodium hydride is not nucleophilic and therefore did not react with the aldehyde.

Geometrical isomerism. **3** was obtained by a double Horner-Wadsworth-Emmons reaction from **2** predominantly as the trans-trans isomer as showed by the ^1H NMR and infrared spectra of **3**: The ^1H NMR spectrum of **3** only showed two doublets belonging to the two vinyl protons. The roofing effect the both doublets exhibit and the fact that the doublets have the same coupling constant prove that to two are coupled. The value of the coupling constant (16.4 Hz) shows that the two coupled vinyl protons have a trans geometry, since coupling constants for protons in cis formation range from 0 Hz to 12 Hz. Coupling constants for protons in trans conformation are larger: 12 Hz to 18 Hz.⁷

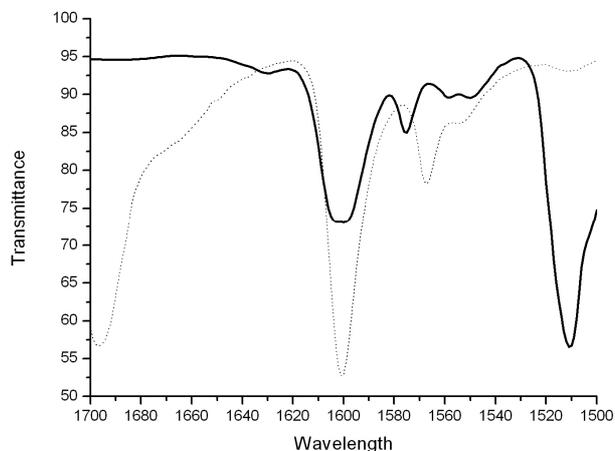


Figure 1: Infrared spectrum (1700 cm^{-1} to 1500 cm^{-1}) of **3o** (black line) and **2o** (grey line)

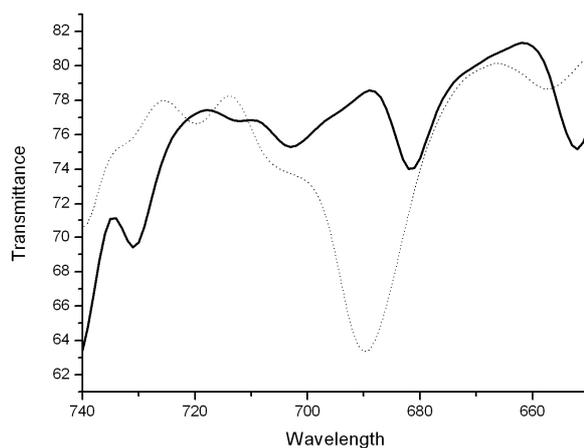


Figure 2: Infrared spectrum (740 cm^{-1} to 650 cm^{-1}) of **3o** (black line) and **2o** (grey line).

To verify this result other techniques must be used to exclude any cis-alkenes such as infrared spectroscopy and Raman spectroscopy. The two strong characteristic bands of the cis alkene due to skeletal vibrations ($500 - 460$) and ($630 - 570$) have not been recorded. The

deformation of the carbon hydrogen bond of a cis alkene vibrates strongly in a range of 730 cm^{-1} to 650 cm^{-1} . The IR spectrum of **3** compared with **2** showed no additional signal in that region. The vibrations in the spectra of **2** and **3** belong to the o.o.p bending of the aryl

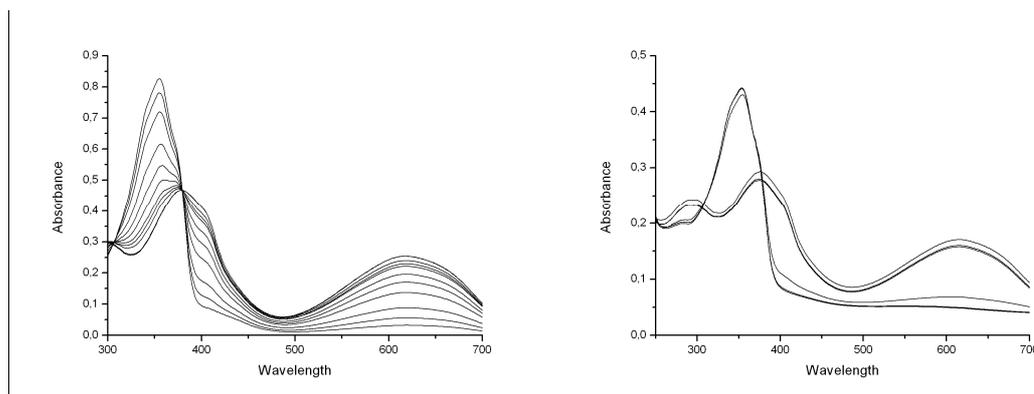


Figure 3: UV/vis absorption spectra of **3** in acetonitrile. Left: conversion of **3o** to **3c**. Right: three cycles of photoisomerization of **3o** to **3c** and vice versa

carbon hydrogen bonds and are shifted up to 7 cm^{-1} relative to each other.

The double bond stretch of conjugated alkenes has a frequency around 1625 cm^{-1} . Due to the pseudo centre of symmetry of the trans double bond stretch, the vibration is very weak or missing. The signal at 1630 cm^{-1} could be attributed to the double stretch of the cyclopentene unit. The possibility that the peak belongs to the cis double bond stretch is unlikely, since the signal of the cis double bond is absent in the region of $650\text{ cm}^{-1} - 730\text{ cm}^{-1}$.⁸

So from the ^1H NMR and IR spectra can be concluded that the reaction yielded almost none to none Z-alkene. However, the absence of the strong characteristic signals of cis alkene skeletal vibrations should be confirmed to exclude any formation of the cis isomer. Raman spectroscopy could also be used to verify this, however **3** is fluorescent and therefore it was hard to observe the alkene vibrations. So no conclusions could be drawn from the Raman spectrum.

UV/vis spectroscopy. Figure 3 shows the change in absorption spectra of **3o** photoisomerizing into **3c** upon irradiation of 365 nm light. When **3** is ring closed, the absorbance in the region

from 400 nm to 700 nm increases with a maximum at 610 nm. The absorbance decreases in the region from 300 nm to 400 nm and the maximum of the open form at 350 nm shifts toward 370 nm. The isosbestic points at 310 nm and 380 nm remain preserved when **3** converts from the open to the photostationary state indicating that no cis/trans isomerization or other photochemical reactions other than cyclisation occur. The previous design also showed the same behaviour but the maximum did not shift towards another wavelength.

In figure 3 UV/vis spectra of **3o** and **3c** are shown. Three cycles of ring opening and closing were performed using 365 nm light for ring closing and $>500\text{ nm}$ light for regeneration of the open form. The isosbestic points are maintained over three cycles and the spectra have not changed after three cycles, which indicates no degradation or photobleaching have occurred. In figure 3 the shift of the maximum is clearly shown.

Raman spectroscopy. The Raman spectra of **3o** and **3c** dissolved in dichloromethane are shown in figure 4. When **3** is ring closed, the vibration at 1490 cm^{-1} greatly increases relative to for example aromatic ring breathing at

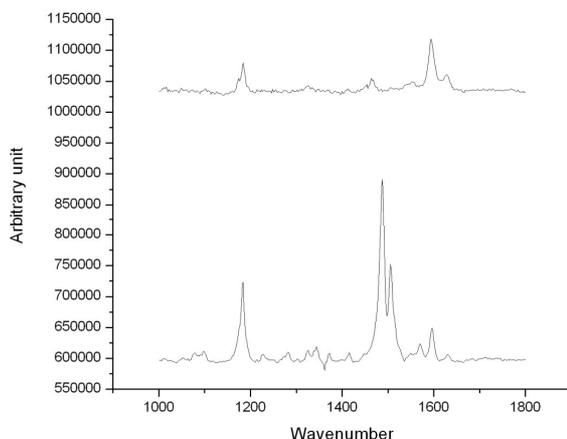


Figure 4: Raman spectra (1000 cm^{-1} to 1800 cm^{-1}) of **3o** (above) and **3c** (below) in dichloromethane. **3c** is offset along the y-axis.

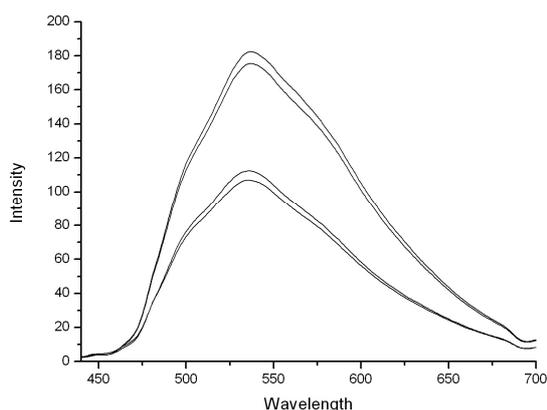


Figure 5: Fluorescence spectra of **3o** (solid) and **3c** (dashed) in acetonitrile with $\lambda_{exc} = 410\text{ nm}$

1600 cm^{-1} . This increase in signal around 1500 cm^{-1} has been observed for previous dithienylethene derivatives and is assigned to the extended conjugated polyenic system based on DFT calculations. The vibrations at 1190 cm^{-1} and 1510 cm^{-1} also increase relative to the aromatic ring breathing at 1600 cm^{-1} upon photoisomerization. These bands are assigned to the *cis*-bis(*trans*-butadiene) unit of the closed form.⁹

Fluorescence spectroscopy. Figure 5 shows the fluorescence spectra of **3o** (solid line) and **3c** (dashed line) in acetonitrile with $\lambda_{exc} = 410\text{ nm}$. Two cycles of ring opening and closure were performed using 365 nm light for ring closing and $>500\text{ nm}$ light for regeneration of the open form. Upon ring closure, **3** becomes less fluorescent but its emittance profile does not change.

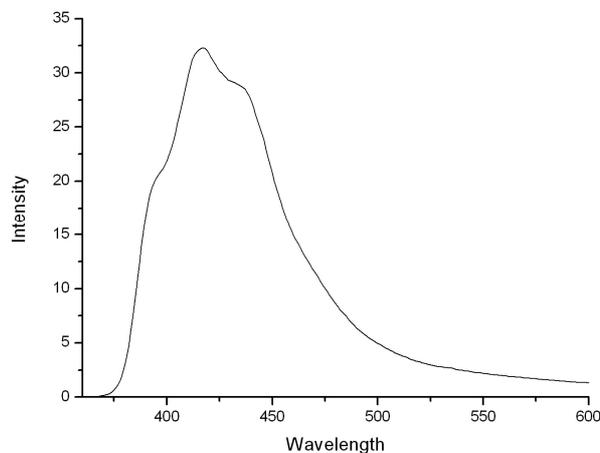


Figure 6: Fluorescence spectrum of **3o** in ethanol with $\lambda_{exc} = 352.5$ nm

However the fluorescence of the closed state seems to be relatively high compared to the open state considering the fact that the closed form of the previous design was nonfluorescent. The same fluorescence characteristics have been observed by Raman spectroscopy. Both **3o** and **3c** was found to be fluorescent by Raman spectroscopy. The quantum yield of **3o** was determined relative to 9,10-diphenylanthracene in ethanol ($\Phi_r = 1$) at $\lambda_{exc} = 352.5$ nm via equation 1

$$\Phi = \Phi_r \times \frac{\text{Integral } A_R n^2}{\text{Integral}_R A n_R^2} \quad \text{eq 1}$$

where Φ is the quantum yield, Φ_r the quantum yield of 9,10-diphenylanthracene, A the absorbance, the integral the area under the fluorescence emittance and n the refractive index of the sample. In figure 6 the fluorescence spectrum of **3o** in ethanol is shown. The quantum yield of fluorescence was found to be 0.3%, more than ten times less than the previous design (4%). The fluorescence behaviour could be interpreted in

different ways: If the assumption is made that the closed form is nonfluorescent the photostationary state consists of more than half of the open state. This is only seen for dithienylethene compounds whose parallel open state is favoured above the anti-parallel.^{10,11} Another explanation is that **3c** is fluorescent, which is unusual for dithienylethene compounds. Another possibility is that **3** is contaminated with a fluorescent by-product. The fact that the emittance profile remains unchanged after photoisomerization and the absence of this product on the H-NMR spectrum, so the quantum yield of this compound must be really high, makes this possibility unlikely. The same fluorescence characteristics have been observed at different conditions: at different excitation wavelengths ($\lambda_{exc} = 325.5$ nm, 352.5 nm, 410 nm and 785 nm by Raman) in different solvents (ethanol, acetonitrile and dichloromethane) with the same photoisomerization techniques used for the UV/vis experiments.

Spontaneous or photoinduced polymerization. **3** was found to polymerize photoinduced or

spontaneously *i.e.* without oxidation or heating. After UV irradiation of a solution of **3** in dichloromethane (concentration approximately 10 mg/mL), insoluble material was formed over time. This is believed to be polymerized **3** which is insoluble in dichloromethane due to the π - π interactions between the polymers.¹² These polymers could be characterized by IR spectroscopy to verify whether the double bond has been polymerized or not. Raman spectroscopy could be used to check if the dithienylethene switch is still active.

3 that has been stored for several weeks showed a fluorescence emittance in the region from 500 nm to 600 nm (See figure S1-S2) whereas freshly prepared **3** did not show emittance in this region. Apparently the emittance of the dithienylethene core red-shifts when embedded in a polymer. A red shift suggests that the conjugation increases which is achieved by polymerization via the phenyl ring and not via the double bond. This polymer was isolated by column chromatography. The ¹H NMR spectrum showed a signal at 7.7 ppm, although the concentration was too low to be properly examined by ¹H NMR. The signal at 7.7 ppm could be assigned to aromatic protons which apparently changes chemical shift upon polymerization.

Oxidative electropolymerization.

The redox properties of **3o** and **3c** were investigated by cyclic voltammetry. In figure 7a a cyclic voltammogram be-

tween 0.0 and 1.6 V (vs SCE, 5 cycles, 0.5 V s⁻¹) of **3o** is shown. The responses at 0.58 (reduction) 0.61 V (oxidation) and 0.94 V (oxidation) increase steadily. The oxidation wave at 1.2 V decreases.

When the scan rate was increased to 5 V s⁻¹ (0.0 V – 1.6 V) an additional signal was observed at 0.9 V. (See figure 7b). This signal appears to be two reduction waves. Also the signal at 0.94 seems to be two oxidation waves in figure although this has not been observed at different conditions (See figure 7a).

Figure 7c shows a cyclic voltammogram between 0.0 and 1.6 V (vs SCE, 20 cycles, 0.5 V s⁻¹) of **3c**. As the number of cycles increases, the reduction wave at 0.75 V decreases while the reduction wave at 0.58 V increases. The signals at 0.61 V and 0.94 V increase while the signal at 1.2 V decreases.

Repetitive cycles between 0 V and 1.6 V resulted in deposition on the electrode. Various cyclic voltammograms have been recorded at different scan speeds of poly-**3**-modified glassy carbon in a monomer free solution (See figure 8 and 9). The current at 0.58 V was found to be linearly dependent on the scan rate, which proves that the electrochemical processes is not diffusion controlled. Therefore the conclusion can be drawn that the dithienylethene is bound to the electrode as film.

The onset potential at which electropolymerization occurs was found to be 1.3 V (versus 1.35 V for the previous system). The physical process corresponding to the reduction wave at

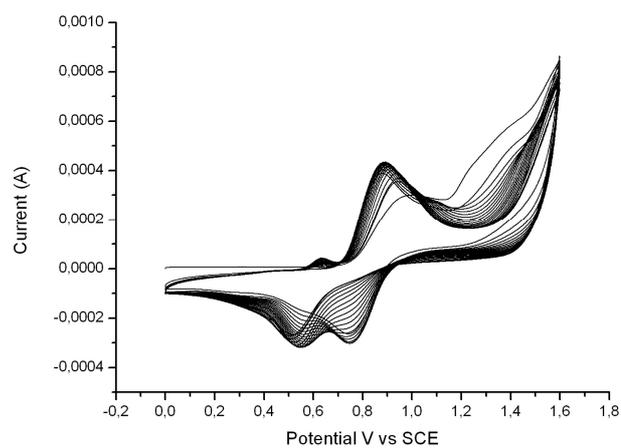
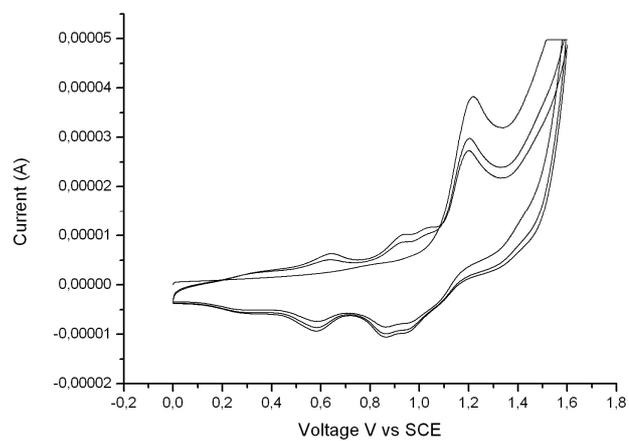
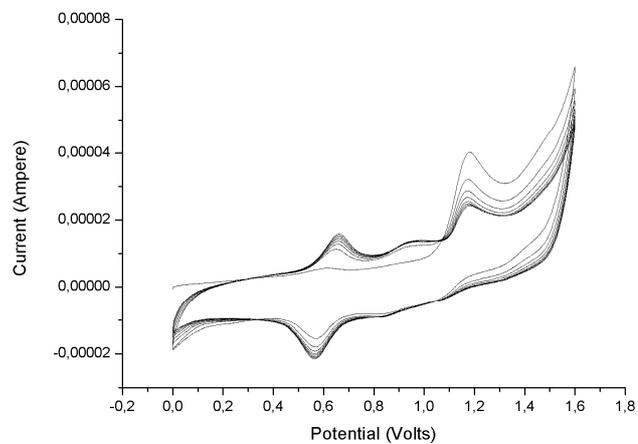


Figure 7: a (above): CV of **3o** between 0.0 and 1.6 V at 0.5 V s^{-1} . b (middle): CV of **3o** between 0.0 and 1.6 V at 5 V s^{-1} . c (below): CV of **3c** between 0,0 and 1.6 V at 0.5 V s^{-1}

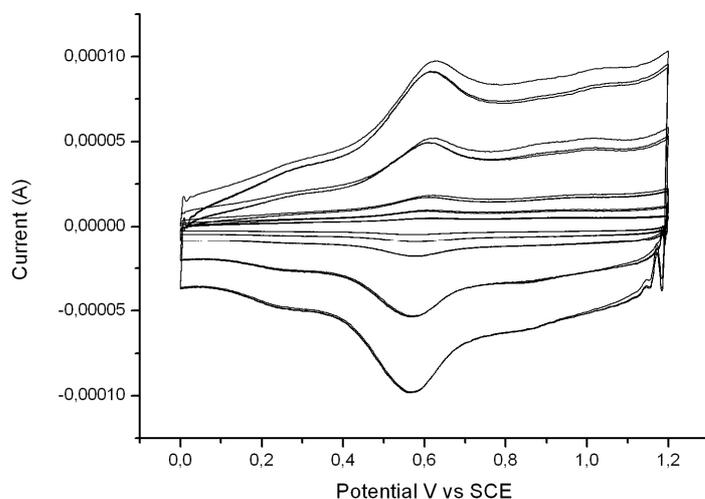


Figure 8: CV of poly-**3** on glassy carbon at 0.5 V s^{-1} , 1 V s^{-1} , 2 V s^{-1} , 5 V s^{-1} and 10 V s^{-1}

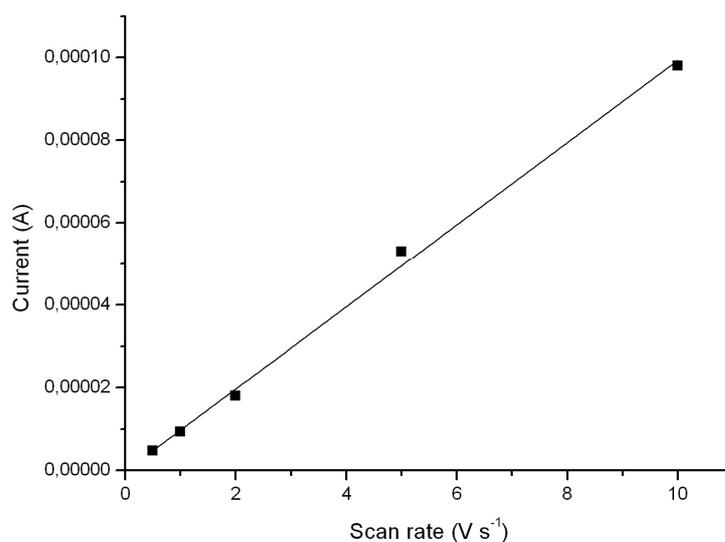


Figure 9: linear dependence of current on scan rate between 0.5 and 10 V s^{-1}

0.9 V is interesting since a poly-**3**-modified glassy carbon electrode is not always reduced at 0.9 V (figure 7a and 7b), but not yet understood. The electrochemical process depicted in figure could be oxidative ring opening. If this is the case, the decreasing signal 0.75 V represents the depletion of **3c**.

The increasing reduction wave at 0.58 V corresponds to reduction of **3o**.

The electrochemical properties of **3** are different than that of the previous design. The nature of the oxidation and reduction steps belonging to the signals is not yet known.

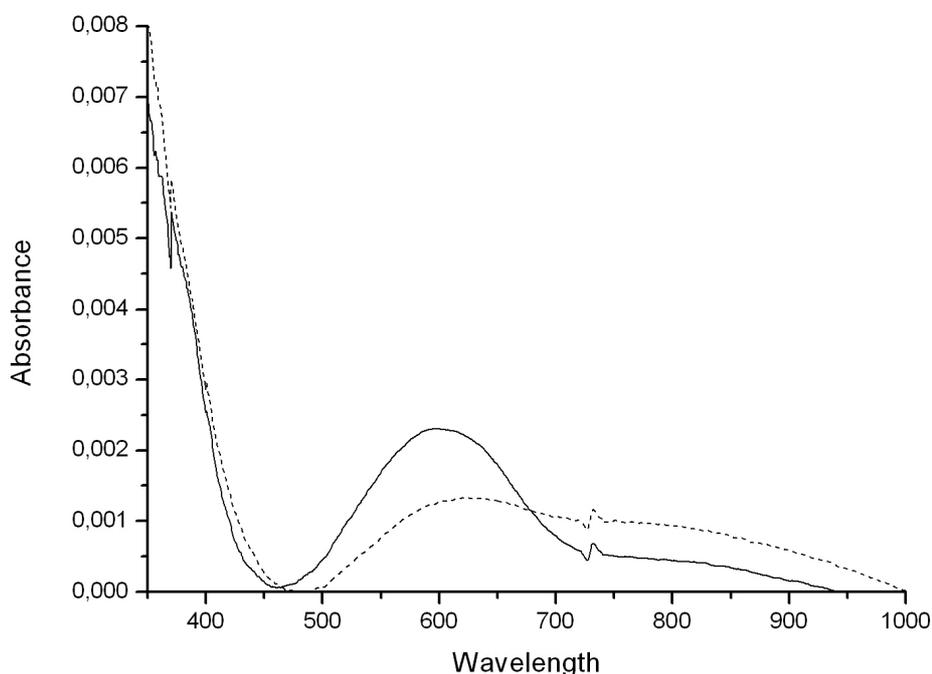


Figure 10: UV/vis spectra of poly-**3o** (solid) and poly-**3c** (dashed)

Poly-**3** on ITO glass slides was studied by UV/vis spectroscopy (figure 10). The polymer showed absorption around 600 nm due to poly-**3o**. After irradiation with >500 nm light for one hour, the absorption at 600 nm decreased due to the conversion of poly-**3o** to poly-**3c**. The isosbestic point at 380 nm seems to be preserved. Ring opening, electrochemically or by UV light, was attempted but did not result in a change in the UV/vis spectrum indicating no photoisomerization took place.

Conclusions

A polymerisable dithienylethene **3** was successfully synthesised in three steps starting from 3-bromo-5-chloro-2-methylthiophene. **3** was obtained (almost) exclusively as trans-trans isomer as shown by ^1H NMR and

infrared spectroscopy. The photoisomerization in solution was studied with UV/vis, Raman and fluorescence spectroscopy. UV/vis spectra showed a conversion of **3o** to **3c** with clear isosbestic points, characteristic of dithienylethene compounds. After three cycles of ring opening and closure, the absorption spectra of the open and closed form were preserved indicating no cis-trans isomerization or photobleaching has occurred. Raman spectroscopy showed a large increase of signal at 1490 cm^{-1} assigned to the extended conjugated polyenic system, as expected for dithienylethene derivatives. The fluorescence emittance of the photostationary state was more than half than that of the open form, which is unusual for dithienylethene switches. The cause of this property is not known,

so further study on this topic should be done. Also **3o** was found to be less fluorescent than the previous design ($\Phi = 0.3\%$ versus $\Phi = 4\%$). The monomer **3** was not stable and polymerized spontaneously or photoinduced. The redox properties of **3o** and **3c** were studied by cyclic voltammetry. **3** polymerized on glassy carbon and ITO coated glass slides as thin films, as shown by the linear dependence of the current on the scan rate. The electrochemical properties of **3** are different than that of the previous design. The nature of the oxidation and reduction steps belonging to the oxidation and reduction waves is not yet known therefore further research is required. The UV/vis spectra of poly-**3** on ITO showed an absorbance around 600 nm corresponding to poly-**3o**. Conversion of poly-**3o** to poly-**3c** was achieved by irradiation with visible light, although photoisomerization of poly-**3c** to poly-**3o** was not accomplished either photochemically or by UV light. In future studies the focus should be on gaining further understanding of the electrochemical and fluorescence properties of the system.

References

- 1 Irie, M. *Chem. Rev.*, **2000**, *100*, 1685-1716
- 2 Masako Akazawa, Kingo Uchida, Jaap J. D. de Jong, Jetsuda Areephong, Marc Stuart, Giuseppe Caroli, Wesley R. Browne and Ben L. Feringa, *Org. Biomol. Chem.*, **2008**, *6*, 1544 - 1547
- 3 Kenneth E. Maly, Michael D. Wand, and Robert P. Lemieux, *J. Am. Chem. Soc.*, **2002**, *124*, 7898-7899
- 4 Denekamp, C.; Feringa, B. *Adv. Mater.* **1998**, *10*, 1080.
- 5 J. Areephong, **2009**, Dithienylethene Optical switches: Multicomponent Molecular Systems, Phd thesis, University of Groningen.
- 6 Philana Wesenhagen, Jetsuda Areephong, Tatiana Fernandez Landaluce, Nicolas Heurreux, Nathalie Katsonis, Johan Hjelm, Petra Rudolf, Wesley R. Browne, and Ben L. Feringa. *Langmuir*, **2008**, *24*, 6334
- 7 "Spectroscopic Methods in Organic Chemistry," Dudley H. Williams and Ian Fleming, 4th ed. revised, McGraw-Hill Book Company (UK) Limited, 1989. Table 3.27
- 8 "Infrared and Raman Characteristic Group Frequencies: Tables and Charts," George Socrates 3rd ed.
- 9 Jaap J. D. de Jong, Wesley R. Browne, Martin Walko, Linda N. Lucas, Lindsay J. Barrett, John J. McGarvey, Jan H. van Esch and Ben L. Feringa, *Org. Biomol. Chem.*, **2006**, *4*, 2387-2392
- 10 Irie, M., *J. Am. Chem. Soc.*, **1992**, *114*, 8715
- 11 Irie, M., *J. Am. Chem. Soc.*, **1994**, *116*, 9864
- 12 E.E. Havinga, L.W. Van Horssen, *Makromol. Chem., Makromol. Symp.*, **1989**, *24*, 67-76

Acknowledgment

Jetsuda Areephong and Thom Pijper are gratefully acknowledged for their help.

Supporting Information

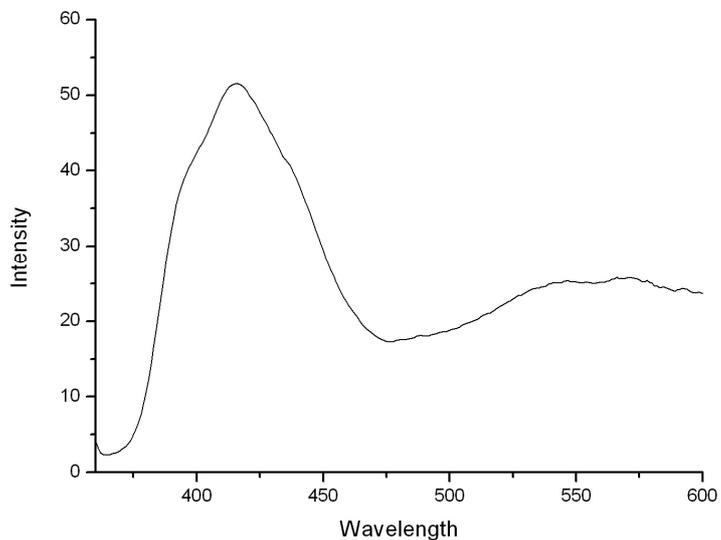


Figure S1: Fluorescence emission spectrum of **3o** probably contaminated with polymerized **3o** ($\lambda_{exc} = 352.5$ nm)

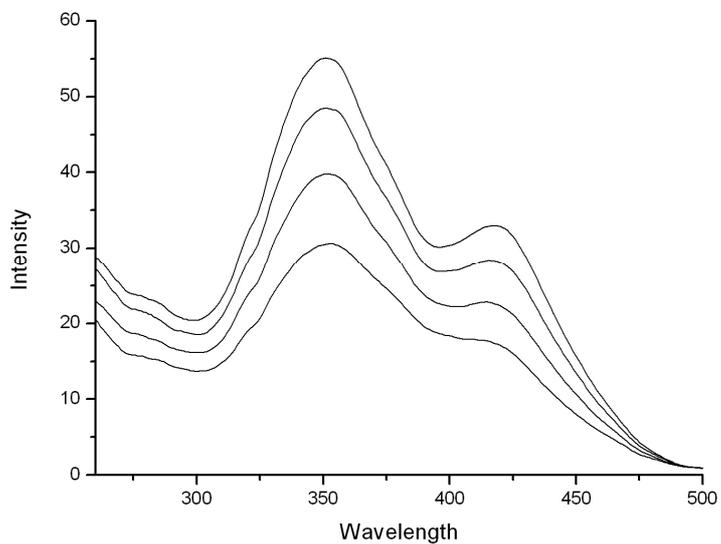


Figure S2: Fluorescence excitation spectra of **3o** to **3c** probably contaminated with polymerized **3** ($\lambda_{em} = 540$ nm)

The excitation spectrum of **3o** have different profiles at different emission ($\lambda_{em} = 540$ nm versus $\lambda_{em} = 435$ nm) indicating that the concentration polymerized **3** is substantial.

Controlling Liquid-Crystalline Phase using Optically Active Dithienylethene as Dopant

Tom van Leeuwen s1651676 under supervision of Dr. W.R. Browne

Abstract

A modified liquid crystal dopant based on the previous design (Feringa, B.L. *Advanced Materials* **1998**, 10, 1081) has been synthesized. It has been found that the dopant induces a cholesteric phase in both E7 and 5CB which undergoes a reversible rotational reorganization upon photoisomerization of the dopant. Three conclusions can be drawn from the determination of the helical twisting power via the Grandjean-Cano method and calculations on the periodicity of the surface modulation: The dopant has a larger helical twisting power than the previous one, the open form has a larger helical twisting power than the closed isomer and the helical twisting power of the dopant is the same in E7 as in 5CB.

Introduction

Dithienylethene compounds have been successfully used to control different media reversibly by the means of light.¹ For example dithienylethene gelators have been discovered which were able to switch between the gel and solution state reversibly upon photoisomerization.² Another example is the doping of a ferroelectric liquid crystal with a dithienylethene. The spontaneous electric polarization of the ferroelectric can be controlled reversibly with light as external stimulus.³ Also nematic liquid crystals have been doped with chiral dithienylethene dopants. The phase of these liquid crystals can be switched between the nematic and cholesteric

phase reversibly upon photoisomerization.⁴⁻⁷ In order to change the properties of the previous system⁴, a new dopant has been designed in a trial and error way. In this article the synthesis of a chiral dithienylethene derivative has been given and discussed. Furthermore two liquid crystals have been doped with the synthesized compound and studied when photoisomerised occurred. The helical twisting power of the open and closed form in both liquid crystals is determined via two methods. Lastly several suggestions have been made for further research.

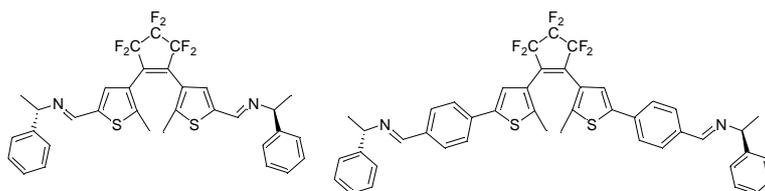
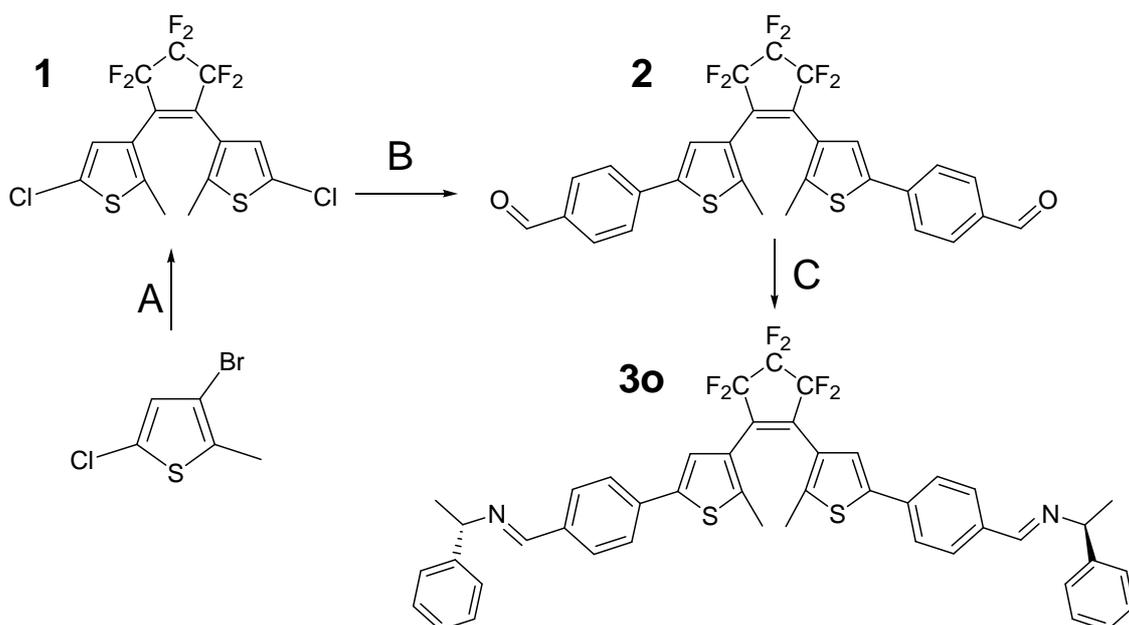


Figure 1: Previous design of the dopant (left) and new design (right)



Scheme 1: (A): *n*BuLi at -78°C , C_5F_8 , 36 %, (B): *n*BuLi, $\text{B}(\text{O}i\text{Bu})_3$, *p*-Br(C_6H_4)CHO, $\text{Pd}(\text{PPh}_3)_4$, Na_2CO_3 , 55 %, (C): (*L*)-(C_6H_5)C(CH_3)NH₂ 50 %.

Experimental

General Remark. The syntheses and the storage of **1**, **2** and **3** and the doping of liquid crystals were carried out with exclusion of light

Materials. Chemicals were purchased from Acros, Aldrich, Fluka or Merck. Solvents used for extractions and chromatography were of technical grade. Solvents used in reactions were distilled freshly from their appropriate drying agents before use. Silicagel 60 (230-400 mesh) was used for flash chromatography.

Physical Methods. ^1H NMR spectra were recorded on a Varian VXR-400 (400 MHz) or a Varian Gemini-200 (200 MHz). ^{13}C NMR spectra were recorded on a Varian Gemini-200 (50 MHz). ^{19}F NMR spectra were recorded on a Varian Gemini-200 (188 MHz). 2D NMR experiments were executed on a Varian Gemini-200. Chemical shifts are denoted in δ values (ppm) referenced to the residual CHCl_3 peaks. The splitting

patterns are designated as follows: s (singlet), d (doublet), q (quartet). Coupling constants, *J*, are denoted in Hertz. Doped liquid crystals were studied on a linearly rubbed polyimide slide in contact with air by an Olympus BX 60 polarized light microscope at room temperature. The helical pitch of the cholesteric phase was determined by the Grandjean-Cano technique¹¹ using a plan-convex converging lens (radius = 25119 μm) and via the period of the surface modulation.

Synthesis of 3,3'-(perfluorocyclopent-1-ene-1,2-diyl)bis(5-chloro-2-methylthiophene) (1). In a flame dried flask under nitrogen atmosphere a stirred solution of 3-bromo-5-chloro-2-methylthiophene (10,0 gram, 47.6 mmol) in anhydrous diethylether (400 mL) was cooled to -78°C . *n*BuLi (29.7 mL, 1.6 M in hexane, 47.6 mmol) was added slowly by syringe and stirred for 30 minutes at -78°C giving a milk white

solution. Octafluorocyclopentene (4.5 gram, 21 mmol) was added slowly by syringe after which the reaction mixture turned greenish yellow. The mixture was stirred for an additional 4 hours at -78°C after which it was warmed to room temperature overnight to give a dark solution. Diethyl ether was added (100 mL) and the organic phase was washed with water (200 mL). The aqueous phase was extracted three times with diethyl ether (3 x 100 mL) and the combined organic phases were dried over sodium sulfate and concentrated *in vacuo*. **(1)** was isolated by column chromatography over silica (heptane, $R_f = 0.62$, pink) and purified by recrystallisation from hexane yielding **(1)** (3.30 gram, 36 %) as a white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 1.95$ (s, 6H), 6.95 (s, 2H). $^{19}\text{F NMR}$ (188 MHz, CDCl_3): $\delta = 1.95$ (s, 6H), 6.95 (s, 2H).

Synthesis of 4,4'-(4,4'-(perfluorocyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-4,2-diyl))dibenzaldehyde (2). In a flame dried flask under a nitrogen atmosphere **1** (3.3 gram, 7.56 mmol) was dissolved in anhydrous diethyl ether (150 mL). *n*BuLi (11.7 mL, 1.6 M in hexane, 18.7 mmol) was slowly added by syringe at room temperature and stirred for 30 minutes. To the dark orange reaction mixture tributylborate (5.22 mL, 18.8 mmol) was slowly added and the mixture was stirred for 40 minutes at room temperature. Under a nitrogen atmosphere a separate flame dried flask containing *p*-bromobenzaldehyde (2.82 gram, 15.2 mmol), tetrakis(triphenylphosphine) palladium (0) (0.33 gram, 0.31 mmol), THF (60 mL), Na_2CO_3 (aq) (40 mL, 2 M) and ethylene glycol (3 mL) was heated to 50°C . To this flask the reaction mixture containing the boronic ester was added slowly by

syringe. The resulting mixture was refluxed over night at 55°C , subsequently diluted with diethyl ether (150 mL) and washed with brine (100 mL). The brine solution was extracted with diethyl ether (100 mL) and the combined organic phases were dried over sodium sulphate and reduced *in vacuo*. Purification by chromatography over silica (pentane ethyl acetate 5:1, $R_f = 0.28$, blue) yielded **2** (2.4 gram, 55 %) as a greenish brown solid. $^1\text{H NMR}$ (200 MHz, CDCl_3): $\delta = 10.01$ (s, 2H), 7.90 (d, $J = 8.2$, 4H), 7.70 (d, $J = 8.2$, 4H), 7.43 (s, 2H), 2.01 (s, 6H). $^{13}\text{C NMR}$ (50 MHz, CDCl_3): $\delta = 14.9$, 124.5, 126.0, 126.4, 130.8, 135.7, 139.0, 141.0, 143.5, 191.5, MS (APCI): 599.05 (M+Na)

Synthesis of (N,N'E,N,N'E)-N,N'-(4,4'-(4,4'-(perfluorocyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-4,2-diyl))bis(4,1-phenylene))bis(methan-1-yl-1-ylidene)bis(1-phenylethanamine) (3). In a flame dried flask under a nitrogen atmosphere **2** (0.20 gram, 0.35 mmol) was dissolved and magnesium sulphate (0.4 gram 3.5 mmol) suspended in anhydrous dichloromethane (100 mL) *L*(-)- α -methylbenzylamine (0.12 gram, 1.0 mmol) was added and the reaction mixture was stirred over night at room temperature. Magnesium sulphate was removed by filtration and the filtrate was concentrated *in vacuo*. The obtained brown solid was recrystallized from ethanol and subsequently washed with cold methanol yielding **3** (140 mg 50 %). $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 8.36$ (s, 2H), 7.79 (d, $J = 8.2$, 4H), 7.56 (d, $J = 8.2$, 4H), 7.43 (d, $J = 7.2$, 4H), 7.35 (m, 6H), 4.56 (q, $J = 8$, 2H), 1.99 (s, 6H), 1.61 (d, $J = 4$, 6H). $^{13}\text{C NMR}$ (50 MHz, CDCl_3): $\delta = 14.9$, 25.0, 125.8, 126.9, 127.1, 128.7, 129.3, 135.9

Doping. Doping of the liquid crystals was done according to the following

procedure: a weighed amount of **3** was dissolved in 1 mL of anhydrous dichloromethane. The mixture was added to the liquid crystal and the solvent was allowed to evaporate over night. The obtained liquid crystal was then heated above the isotropic temperature to increase homogenation. The sample was allowed to cool to room temperature before examination. A sample of **3** (2 milligram) in E7 (95.6 milligram) and **3** (2 milligram) in 5CB (69 milligram) was made according this procedure.

Results and Discussion

Synthesis of 1. **1** is obtained in a low yield (36 %). The reason for this is probably not the reaction itself, but the purification of the compound. After column chromatography over silica with heptane as eluents the product was still contaminated with non-fluorinated compounds as was concluded from ^1H NMR and ^{19}F NMR. A recrystallization step was required to remove these impurities. Although hexane proved to be a good solvent for recrystallization for the first crop, for the second crop it was unable to separate product from impurities. A different solvent or a two solvent system should be used for the recrystallization in order to enhance the yield.

Synthesis of 2. The generated boronic ester was not isolated from the reaction mixture before the Suzuki coupling reaction was carried out because of the risk of hydrolysis of the boronic ester during isolation. Instead the whole reaction mixture was transferred to a separate flask for the Suzuki coupling. This poses no problems as long as the tetrakis (triphenylphosphine) palladium

(0) is active enough, which means that the catalyst must be completely dissolved by using enough ethylene glycol and a sufficient high temperature must be employed.

Synthesis of 3. Imine syntheses are usually carried out with a dehydrating agent present in the reaction mixture to prevent hydrolysis of the imine. For the synthesis of **3** magnesium sulphate was used as dehydrating agent but molecular sieves would have been a good alternative as a dehydrating agent.⁸ Also imine syntheses are normally acid catalysed⁹ and the synthesis of **3** was also carried out with a drop of trifluoroacetic acid present in the reaction mixture, but the non-catalyzed reaction gives the same outcome as the catalyzed one so the procedure for the synthesis of **3** given in the experimental is preferred above the acid catalyzed reaction. Column chromatography is often used for purification of dithienylethene derivatives¹⁰ but the imine was hydrolyzed during chromatography over both silica and basic alumina, so recrystallization had to be used instead as purification method.

Microscope study.

Doped E7 with **3o** (2.1 wt-%) showed a stable cholesteric liquid crystalline phase. (See figure 2.) Upon UV irradiation a rotational reorganization was observed due to the photoisomerization of **3o** to **3c**. The number of rotations is dependent on the thickness of the film. (See figure 3) The periodicity of the surface modulation changed which indicates a change in the helical twisting power. Thus the color and the helical twisting power of the dopant changed when irradiated with UV light.

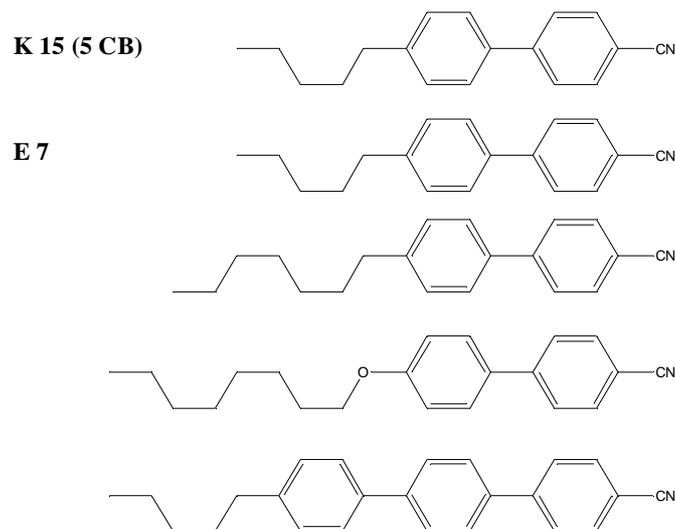


Figure 1: Liquid crystals 5CB and E7. E7 is a blend of 4 molecules. The E7 used in the experiments had an average molecular weight of 274 g/mol

Upon irradiation with visible light the photoisomerization of **3c** to **3o** caused another rotational reorganization changing the color and the helical twisting power back to the original state. The switching is thus reversible but only one cycle was performed so it is unknown how the system reacts to several cycles. Also doped 5 CB with **3o**

(2.9 wt-%) had a stable cholesteric liquid crystalline phase which reorganized in a rotational way when irradiated with UV light. This process was found to be reversible when the system was radiated with visible light. Also in this case only one cycle was tested. Doped 5 CB reacted in the same way as doped E7 upon photoisomerization. The dopant

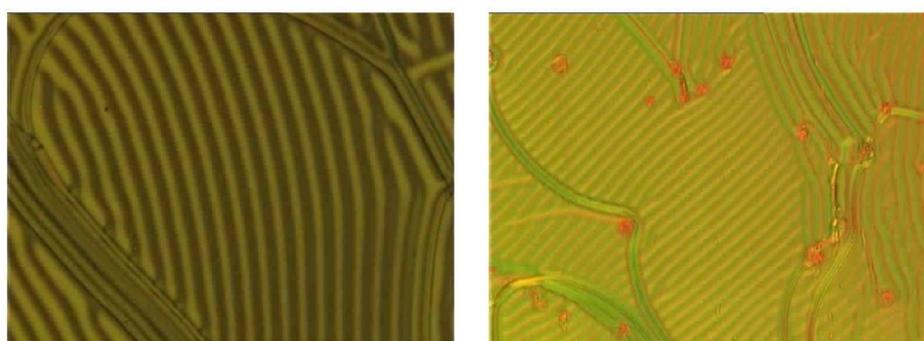


Figure 2: Micrograph of the fingerprint texture of the cholesteric phase. The parallel stripes are an indication of a constant droplet thickness. Arched stripes appear when the thickness varies. The oily streaks form the boundaries of different regions and are defects in the liquid crystalline phase. The periodicity (Λ) of the stripes in the texture is related to the pitch of the helices. (Magnification 20x) Left: **3c** in E7. Right: **3o** in E7.

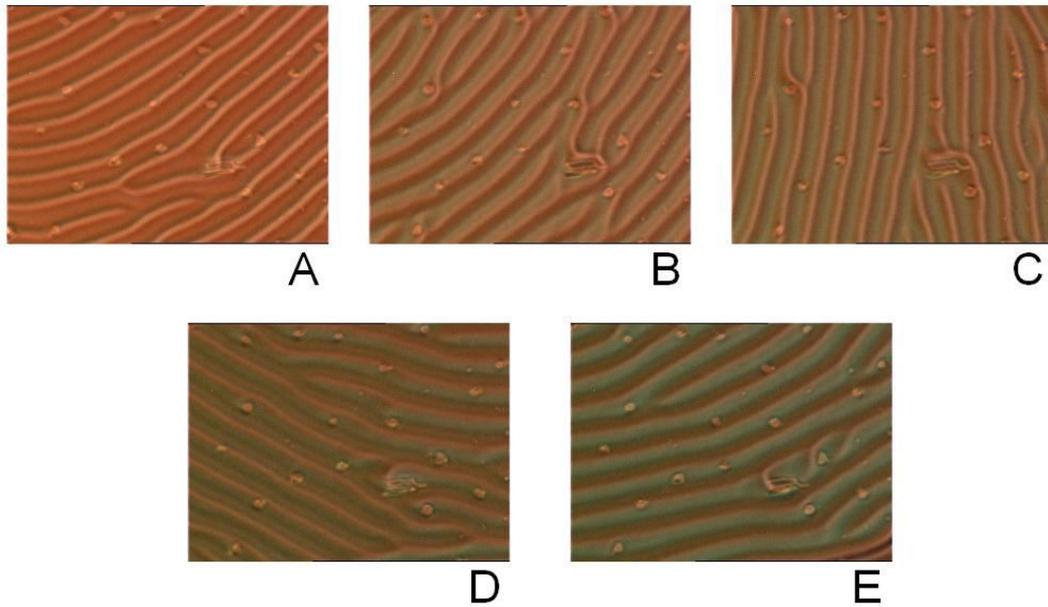


Figure 3: The cholesteric liquid crystal film rotates upon UV irradiation. The sample turns from colorless to blue. (A: initial situation, B: after 1:13 minutes of UV radiation, C: after 1:35 minutes of UV radiation, D: after 2:50 minutes of UV radiation, E: after 4:30 minutes of UV radiation, magnification 40x)

changed helical twisting power and color in both media when irradiated. All micrographs show little spots in the cholesteric texture. These belong to the polyimide surface.

Grandjean-Cano. The helical twisting power was determined by the Grandjean-Cano method.¹¹ (See table 1) When a cholesteric liquid crystalline sample is placed between a flat surface and a plane convex lens and viewed through this lens a serie of concentric lines can be seen which are related to the pitch via equation 1

$$p = \frac{\Delta r^2}{R_{lens}} \quad \text{eq 1}$$

where p stands for the pitch, Δr^2 for the difference of the squared radii of the

consecutive circles and R for the radius of lens. From the pitch the helical twisting power was calculated via equation 2.

$$\beta = \frac{1}{ee c p} \quad \text{eq 2}$$

The pitch was also calculated from the periodicity of the stripes of the cholesteric texture. For E7 on rubbed polyimide the following relationship has been found.¹²

$$\Lambda = 2.16 p \quad \text{eq 3}$$

where Λ stands for the periodicity of the stripes. The periodicity is determined using figure 2 and S1. Via equation 2 the pitches were transformed to the helical twisting powers. (See table 1).

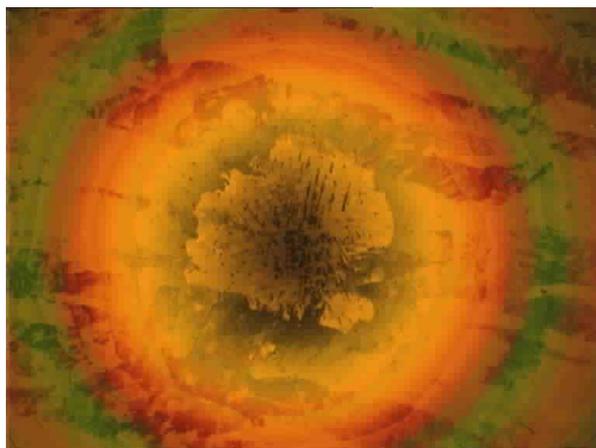


Figure 4: E7 doped with **3o** viewed through a plane convex lens. The pitch can be determined from the radii of the consecutive circles. The micrographs of the other samples are given in the supplementary information. (Magnification 4x)

	β (μm^{-1})	β (μm^{-1})
E7 with 3o	48	36
E7 with 3c	34	21
5CB with 3o	46	40
5CB wtch 3c	30	26

Table 1: The values of the helical twisting power determined by the Grandjean-Cano method (left) and via equation 3 (right). The values determined via the two methods differ, but the Grandjean-Cano method is the more widely accepted one.

Although equation 3 was found for an E7 system, the same equation was used for the 5CB samples for the reason that 5CB and E7 are similar. **3o** has a larger helical twisting power than the previous design (46 to 40 μm^{-1} versus 11 μm^{-1} in 5CB). The reason for this is yet unclear. The closed form has a smaller helical twisting power than the open form, which was also observed for the previous design. The previous system

was capable of switching between the cholesteric and nematic phase. This was not observed for this system because the helical twisting power of the closed form was still high enough to induce a cholesteric phase at 2.1 wt-%. At a certain lower concentration **3o** would still be capable of inducing a cholesteric phase but **3c** would not, so this system would also be able to switch between the cholesteric and nematic phase, but only at low concentrations of dopant.

Future plans. It would be interesting to see how the system reacts upon photoisomerization at different temperatures, so in the future the research on this system should be extended to this topic. The influence of the chiral groups on the helical twisting power could also be studied by replacing the phenylethylamine groups by naphthylethylamine groups.

Conclusions

A liquid crystal dopant **3** was successfully synthesized in three steps starting from 3-bromo-5-chloro-2-

methylthiophene. This dopant induced a cholesteric phase in E7 (2.1 wt-%) and in 5CB (2.9 wt-%) and was photoisomerized upon UV irradiation causing a rotational reorganization of the cholesteric texture. The photoisomerization was found to be reversible when irradiated with visible light. The helical twisting power of **3** was determined by the Grandjean-Cano method and by calculations on the periodicity of the surface modulation. **30** has a larger helical twisting power than **3c**. The dopant has approximately the same helical twisting power in E7 as in 5CB. The fact that **3** has a larger helical twisting power than the previous design is interesting but not yet fully understood. Future research on this system should focus on the question how the temperatures changes the behavior of the liquid crystal and changes in the design such as: the replacement of the phenylethylamine groups by naphthylethylamine groups and the incorporation of solubility enhancing groups.

References

- (1) Irie, M. *Chem. Rev.*, **2000**, *100*, 1685-1716
 (2) Masako Akazawa, Kingo Uchida, Jaap J. D. de Jong, Jetsuda Areephong, Marc Stuart, Giuseppe Caroli, Wesley R. Browne and Ben L. Feringa, *Org. Biomol. Chem.*, **2008**, *6*, 1544 - 1547
 (3) Kenneth E. Maly, Michael D. Wand, and Robert P. Lemieux, *J. Am. Chem. Soc.*, **2002**, *124*, 7898-7899
 (4) Denekamp, C.; Feringa, B. *Adv. Mater.* **1998**, *10*, 1080.
 (5) Uchida, K.; Kawai, Y.; Shimizu, Y.; Vill, V.; Irie, M. *Chem. Lett.* **2000**, 654.

(6) Yamagushi, T.; Inagawa, T.; Nakazumi, H.; Irie, S.; Irie, M. *Chem. Mater.* **2000**, *12*, 869.

(7) Yamaguchi, T.; Inagawa, T.; Nakazumi, H.; Irie, S.; Irie, M. *J. Mater. Chem.* **2001**, *11*, 2453.

(8) A.I. Vogel, *Vogel's Textbook of Practical Organic chemistry*, Longman Publishing Group 1989

(9) J. Clayden, S. Warren, N Greeves, *Organic chemistry*, Oxford University Press 2000

(10) J. Areephong, **2009**, Dithienylethene Optical switches: Multicomponent Molecular Systems, Phd thesis, University of Groningen.

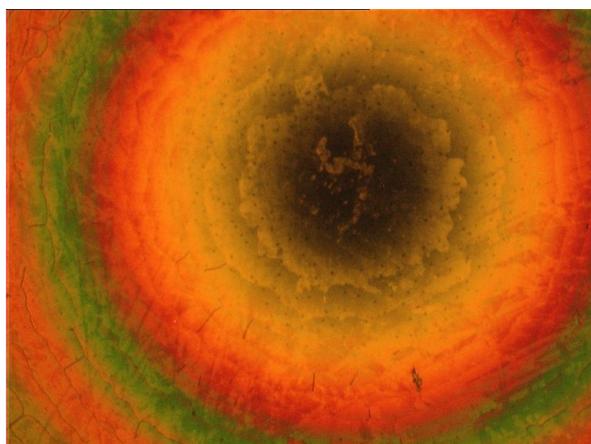
(11) (a) R. Cano, *Bull. Soc. Fr. Mineral.* **1968**, *91*, 20. (b) F. C. R. Granjean, *Hebd. Seances Acad. Sci.* **1921**, *172*, 71.

(12) Alessandro Bosco, Mahthild G. M. Jongejan, Rienk Eelkema, Nathalie Katsonis, Emmanuelle Lacaze, Alberta Ferrarini, and Ben L. Feringa, *J. Am. Chem. Soc.*, **2008**, *130*, 14615-14624

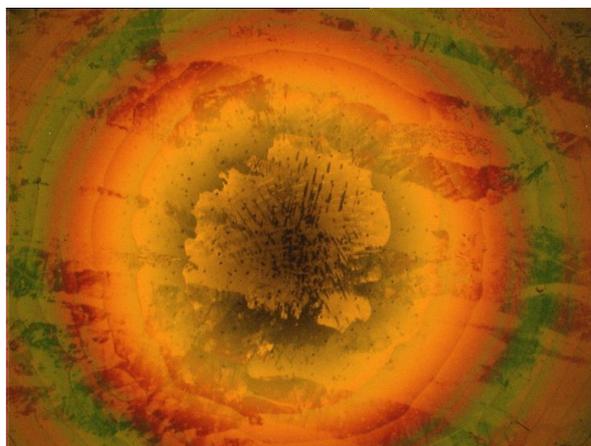
Acknowledgment

Nathalie Katsonis is gratefully acknowledged for her help with microscopy.

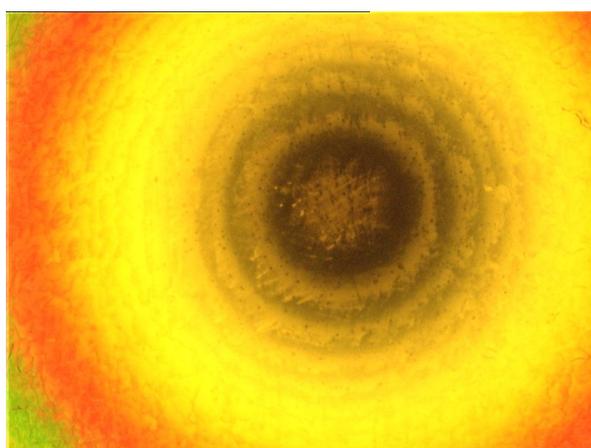
Supporting Information



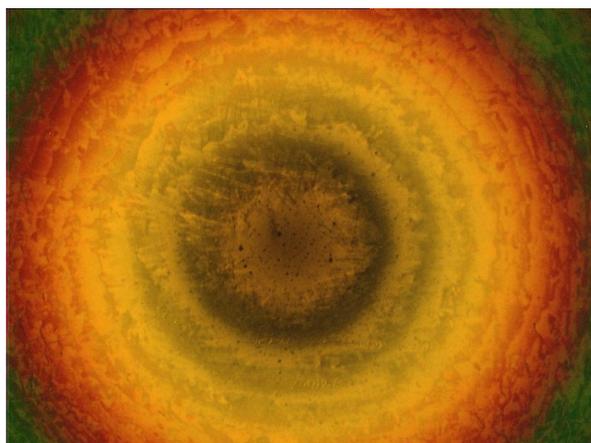
*Figure S1: Grandjean-Cano image of **3o** in E7 (4x)*



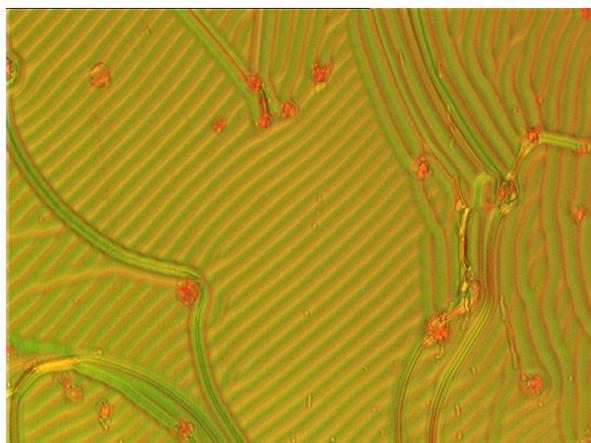
*Figure S2: Grandjean-Cano image of **3c** in E7 (4x)*



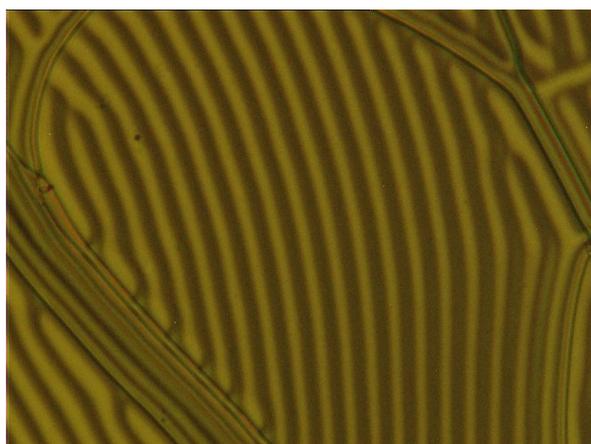
*Figure S3: Grandjean-Cano image of **3o** in 5CB (4x)*



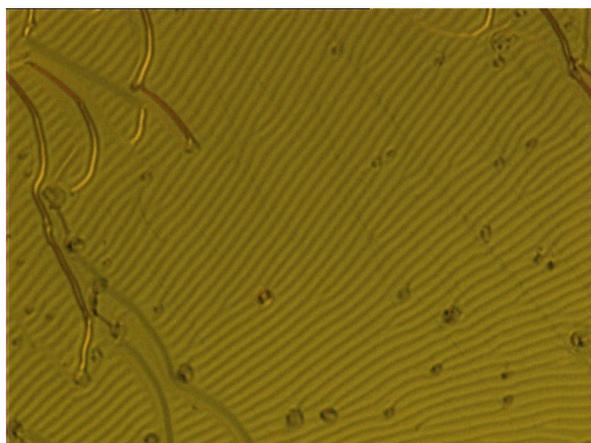
*Figure S4: Grandjean-Cano image of **3c** in 5CB (4x)*



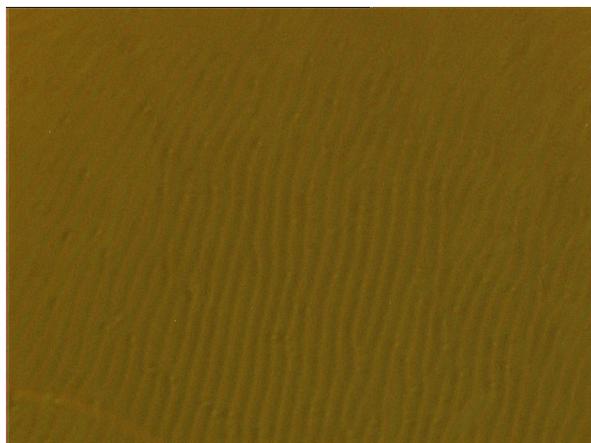
*Figure S5: Micrograph of **3o** in E7 (20x)*



*Figure S6: Micrograph of **3c** in E7 (20x)*



*Figure S7: Micrograph of **3o** in 5CB (10x)*



*Figure S8: Micrograph of **3c** in 5CB (10x)*