Peer-reviewed version available at *Coatings* **2019**, *9*, 669; doi:10.3390/coatings9100669

Thin films of tolane aggregates for Faraday rotation: materials and measurement

Maarten Eerdekens,[†] IsmaelLópez-Duarte,[‡] Gunther Hennrich,[*‡] Thierry Verbiest[*†]

[†]Department of Chemistry, University of Leuven, Celestijnenlaan 200D, 3001 Leuven, Belgium.
[‡]Department of Organic Chemistry, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain.

Abstract: We present organic, diamagnetic materials based on structurally simple (hetero-)tolane derivatives. They form crystalline thin-film aggregates that are suitable for Faraday rotation (FR) spectroscopy. The resulting new materials are characterized appropriately by common spectroscopic (NMR, UV-Vis), microscopy (POM), and XRD techniques. The spectroscopic studies give extremely high FR activities thus makes these materials promising candidates for future practical applications. Other than a proper explanation, we insist in the complexity of designing efficient FR materials starting off from single molecules.

Keywords: Faraday rotation – Thin films – Magneto-optics – Organic material – Tolane derivatives

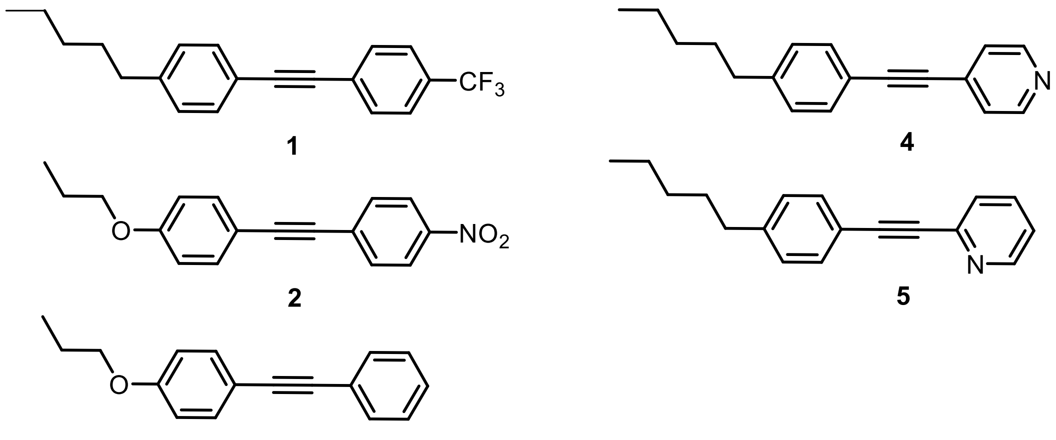
1. Introduction

Faraday rotation (FR) is a magneto-optic (MO) effect that has been discovered more than a century ago.[1] It is the rotation of the plane of polarization in the presence of a longitudinal magnetic field and the rotation angle θ can be described by $\theta = VBL$ with θ the angle of polarization rotation, V the Verdet constant, B the magnetic field parallel to the propagation of light, and L the path length. Applications of FR are of practical relevance for magnetic field sensors, wave guiding, fiber-optics, etc.[2] Traditionally the field of magneto-optics is dominated by inorganic materials or radical species.[3] Only recently diamagnetic organic materials have emerged as novel FR supplies.[4]

Although the exact origin of Faraday rotation in organic molecules is currently unknown, different research groups dedicate their efforts in designing new organic materials for FR applications. Current experiments reported in literature clearly suggest that molecular conjugation and π-stacking are crucial factors to obtain very strong FR. Furthermore, for organic diamagnetic materials it became evident that the macroscopic order of the bulk material is crucial for its optical and MO activity.[4] It is this duality of molecular vs. macroscopic material, i.e. intra- vs. intermolecular processes that complicates a rational correlation of the observed magnetic effects with the nature of molecular units and supramolecular aggregates**.** We have shown recently how the structural simplification of the molecular units (from trigonal to linear) has led to an increase in the FR activity of the respective thin film materials.[5] Nonetheless one has to keep in mind the macroscopic structure of the respective aggregates. A decisive requirement is the capacity to form quality thin films from molecular units or aggregates, either crystalline[6] or liquid crystalline.[7] It was shown that long range electron movement along columnar supramolecular aggregates lead to a dramatically increased Faraday response.[8]

2. Materials and methods

In the present work we present tolane structures that form crystalline thin films and assess their MO activity by FR spectroscopy.



1 **4** **2** **5** **3**

Figure 1. Tolanes (**1** – **3**) and *N*-Hetero-tolane derivatives **4** and **5**.

The diphenyltolanes **1 - 3** present a conventional donor-π-acceptor system. Compounds **2** and **3** have been studied previously for their second-order NLO properties.[9]

Tolane **1** has been synthesized following the literature procedure and is obtained in a 72 % yield.[10] Characterization: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.56 (m, 4H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 2.60 (t, *J* = 7.5 Hz, 2H), 1.61 (q, *J* = 7.5 Hz, 2H), 1.31 (m, 4H), 0.91 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C144.5, 131.9, 131.9, 130.5, 129.6,

Peer-reviewed version available at *Coatings* **2019**, *9*, 669; doi:10.3390/coatings9100669

128.7, 127.6, 125.4, 119.9, 92.3, 87.6, 36.1, 31.6, 31.0, 22.7, 14.1. EI$^+$-MS m/z 316 (M+); Anal. calcd. for: $C_{20}H_{19}F_3$: % C, 75.93; % H, 6.05; found: % C, 75.88; %H, 5.97.

Differential Scanning Calorimetry (DSC) analysis reveals the existence of two main crystalline polymorphs melting at 69.7 and 71.3 ºC, respectively. These transitions stabilize after two heating-cooling cycles (Figure 2).

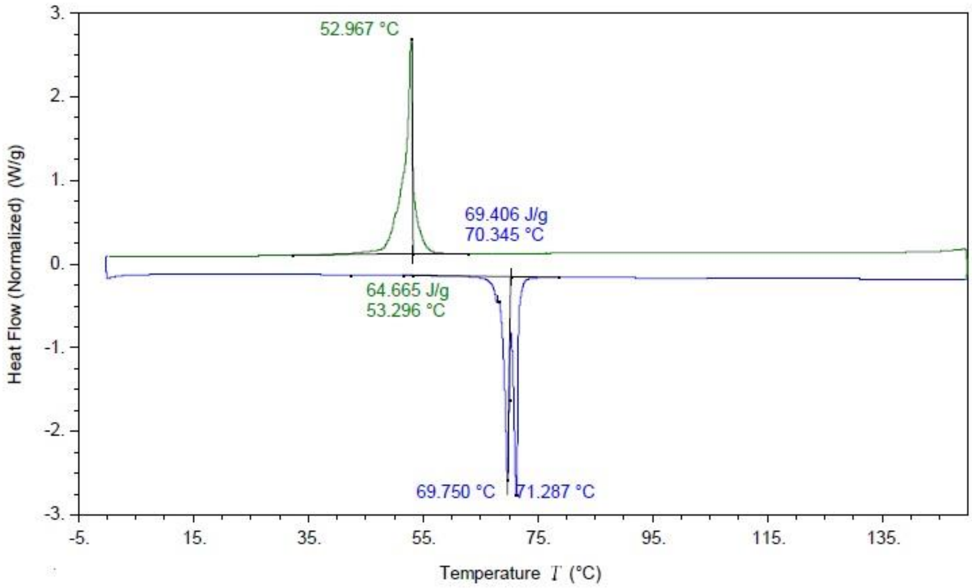


Figure 2. DSC of **1**, second heating (green) and cooling (blue) cycle.

The *N*-pyridyl-tolanes **4** and **5** are solid (**4**) or liquid (**5**) at room temperature, respectively. However, upon protonation (with hydrochloric or terephthalic acid) both form crystalline solids. In addition, solid halogen bond complexes are obtained from **4** and **5** with suitable halogen bond donors. The terephthalate complex of protonated **4** is liquid crystalline over a wide temperature range.[11] Hence, the material can be processed and measured conveniently in a conventional liquid crystal (LC) cell.

UV-Vis Spectra are measured in chloroform at a concentration of1.5×10^{-4}mol/l using a Perkin-Elmer Lambda 900 spectrophotometer. To measure the Faraday rotation as well as polarized optical microscopy (POM),[12] the materials are placed in LC cells with a 3 μm gap. To fill the cells with the organic materials, a heating plate heats the cells to a temperature 5 – 10°C higher than the melting temperature of the desired molecules´. A small amount of material is deposited next to the gap, it subsequently melts, and enters the cell through capillary action. After the LC cell has been filled and cooled, a homemade heating and cooling device reheated the filled LC cells 5°C above the melting temperature of the organic material, and cooled the samples to r.t. by 0.1 °C/min. An Olympus microscope is used for obtaining POM images. Faraday rotation spectra are collected using a photoelastic modulation magneto optical setup described by Vandendriessche et al. from 350 to 700 nm, every 2 nm.[4] The optical rotation was measured at varying magnetic field from 0 - 0.5 T. A blank is also measured to nullify the effects of the glass. Using linear regression, the magnetic rotation is calculated from the slope. The Verdet constant (°/Tm) is then calculated by dividing the magnetic rotation by the thickness of the sample inside the LC cell, i.e. 3 μm. Smoothing of the curves is done using Savitsky-Golay method in Origin. We confirmed that the simple is in plane is otropic by measuring at different amutal angles of the samples at 400 nm (SI).

3. **Results** and **discussion**

Compounds **1** - **4** are crystalline solids at room temperature. The powder X-ray diffractograms are measured on a Malvern PANalytical Empyrean system, with a Cu k-α source with a wavelength of 1.5406 Å, measuring with a Pixcel3D detector. The measurements are done at room temperature. The XRD (and POM) measurements confirm the crystal nature of the samples.

The absorbance spectra of **1** and **2** show a maximum absorbance around 350 nm with a corresponding high FR of several hundred thousands °/Tm. This is not surprising since the FR response is-enhanced near resonances. However, what is surprising is that even far away from resonance strong Faraday rotation is observed. For example, for compound **1** the Verdet constant in the wavelength region 525 – 700 nm nanometers is still on the order of 50 000 – 70 000 °/Tm, while compound **2** exhibits Verdet constants over 150 000 °/Tm around 500 nm. Similar behavior has been observed for other crystalline acetylenes.[5] Both molecules have an electron acceptor group (-NO_2 and -CF_3) within a conjugated π-system. They show very similar FR spectra with several peaks and valleys in the visible part of the spectrum (Figure 3A). Tolane **2** exhibits a higher Faraday response over most part of the spectrum (Figure 3B).

Peer-reviewed version available at *Coatings* **2019**, *9*, 669; doi:10.3390/coatings9100669

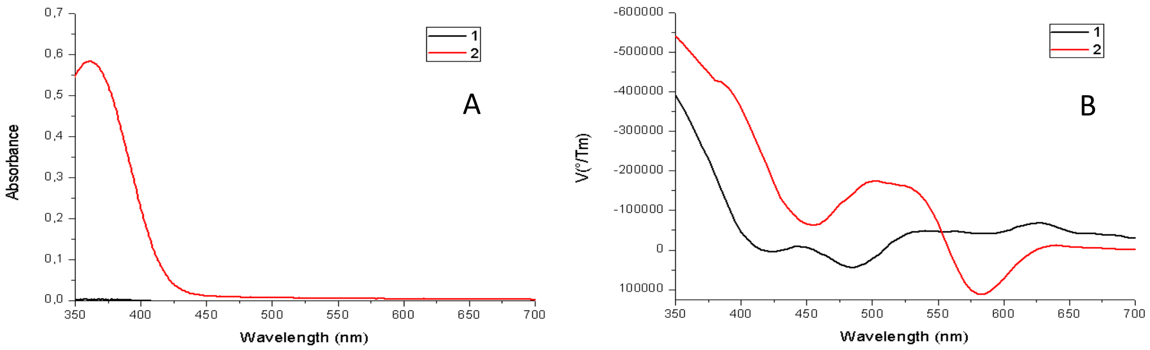


Figure 3.UV-Vis (A) and Faraday rotation spectrum (B) of **1** and **2**.

Our results for compounds **4** and **5**, nicely illustrate the importance of their macroscopic structure. Compound **5** is an isotropic liquid at r.t. temperature, while compound **4** is solid at room temperature. Therefore and in agreement with earlier findings, **4** exhibits a Faraday response that is orders of magnitude higher over the entire °/Tm, even outside regions of absorption.For **5** we measure a featureless and low intensity Faraday spectrum that gradually decreases towards the IR region. Note also that the Faraday spectrum of **4** resembles that of **1** and **2** with a maximum Verdet constant near resonance and a very feature rich shape in the visible part of the spectrum. This seems to indicate that molecular structure does have an impact on the shape of the Faraday spectrum. Moreover the supramolecular organization (either in a crystalline or liquid form) is a necessary requirement to observe strong FR activity.

Of all the samples, the strong increase in FR towards the UV part of the spectrum is due to the presence of the absorbtion band as well the wavelength dependency of the Verdet constant ($V \sim \lambda^{-2}$). We do not know the origin of the peaks and valleys, but recent work on Faraday rotation in other organic molecules suggests crediting them to the presence of spin-forbidden or hidden singlet and/or triplet states. [4] The non-substituted diphenylacetylene **3** exhibits too much birefringence and scattering to perform reliable measurements. Its UV-Vis absorption spectrum can be found in the supporting information.

Peer-reviewed version available at *Coatings* **2019**, *9*, 669; doi:10.3390/coatings9100669

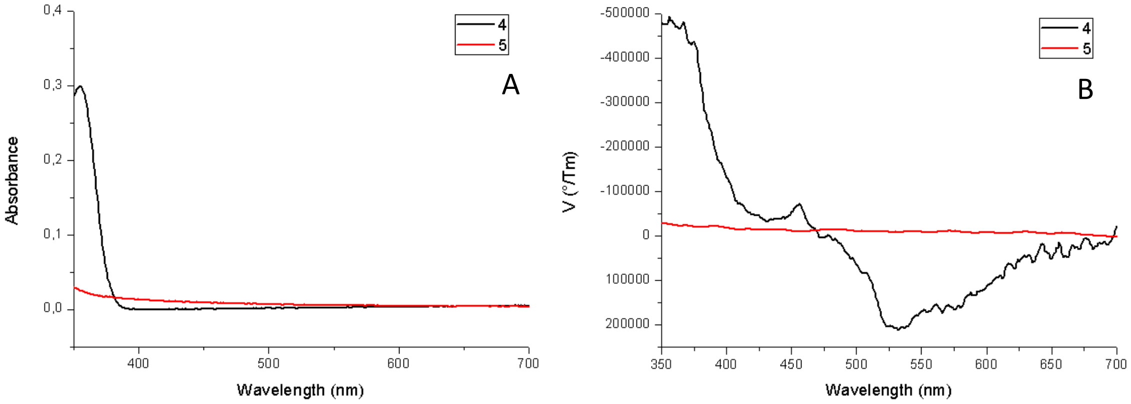


Figure 4. UV-Vis (A) and Faraday rotation spectrum (B) of **4** and **5**;

POM images can be found in the supporting information.

4. Conclusions

We have investigated the FR response of different phenylacethylene derivatives. It is clear that macroscopic organization within the bulk material is a key factor in obtaining a high Faraday response. The molecular structure dictates the macroscopic organization of the building units which, in consequence, determines the FR response of the resulting bulk material. The detailed shape of the Faraday spectrum is a result of this (i.e. the molecular structure), but is in itself not sufficient to create a high Faraday response. Once again, we have to emphasize the aforementioned duality (single molecule vs. macroscopic bulk) that interferes in the design of efficient FR materials.

The tolanes that were crystalline at room temperature showed very high Verdet constants – much higher than typically observed for diamagnetic materials - in regions of the spectrum where there is no optical absorption, making them potentially useful for applications.

Author contributions.

All authors have given approval to the final version of the manuscript and contributed equally. The authors declare no conflict of interest.

Funding.

The financial support by the Spanish government (MINECO, project CTQQ2016-7557-R) is gratefully acknowledged. We also are grateful for the financial support form the KULeuven (C1 project).

Acknowledgements.

The authors would like to thank Prof. B. Goderis for using his POM equipment and Prof. M. Rouffaers and L. Clinckemalie forthe X-ray data analysis.

References

[1] M. Faraday. *Experimental Researches in Electrici*ty; R. Taylor & W. Francis: London, 1839, Vol. III.

[2] (a) D. Jalas, A. Petrov, M. Eich, W. Freude, S. Fan, Z. Yu, R. Baerts, M. Popvic, A. Melloni, J. D. Joannopoulos, M. Vanwolleghem, C. R. Doerr and H. Renner. Whatis – and what is not – an optical isolator. *NaturePhot*. **2013**, *7*, 579 – 582. (b) M. A. Schmidt, L. Wondraczek, H. W. Lee, N. Granzow, N. Da, F. St. J. Russel. Complex Faraday Rotation in Microstructured Magneto-optical Fiber Waveguides. *Adv. Mater*. **2011**, *23*, 2681 – 2688. (c) B. Amirsolaimani, P. Gangopadhyay, A. P. Persoons, S. A. Showghi, L. J. LaComb, R. A. Norwood, N. Peyghambarian. High sensitivity magnetometer using nano-composite polymers with large magneto-optic response. *Opt. Lett*. **2018**, *43*, 4615 – 4618.

[3] (a) Y.-C. Hsiao, T. Wu, M. Li, B. Hu. Magneto-Optical Studies on Spin-Dependent Charge Recombination and Dissociation in Perovskite Solar Cells. *Adv. Mater*. **2015**, *27*, 2899 – 2906. (b) C.-K. Lim, M. J. Cho, A. Singh, Q. Li, W. J. Kim, H. S. Jee, K. L. Fillman, S. H. Carpenter, M. J. Neidig, A. Baev, M. T. Swihart, P. N. Prasad. Manipulating Magneto-Optic Properties of a Chiral Polymer by Doping with Stable Organic Biradicals. *Nano Lett*. **2016**, *16*, 5451 − 5455. (c) J. Ma, J. Hu, C. Li, C.-W. Nan. Recent progress in multiferroicmagnetoelectric composites. *Adv. Mater*. **2011**, *23*, 1062 – 1087. (d) P. Wang, S. Lin, Z. Lin, M. D. Peeks, T. Van Voorhis, T. M. Swager. A Semiconducting Conjugated Radical Polymer: Ambipolar Redox Activity and Faraday Effect. *J. Am. Chem. Soc*.**2018**, *140*, 10881 − 10889.

[4] (a) P. Gangopadhyay, S. Foerier, G. Koeckelberghs, M. Vangheluwe, A. Persoons, T. Verbiest, Efficient Faraday rotation in conjugated polymers. *Proc. SPIE* **2006**, *6331*, 63310Z. (b) G. Koeckelberghs, M. Vangheluwe, K. Vandooreselaere, E. Robijns, A. Persoons, T. Verbiest. Regioregularity in poly(3-alkoxythiophene)s: Effects on the Faraday rotation and polymerization mechanism. *Macromol. Rapid Commun.***2006**, *27*, 1920 – 1925. (c) S. Vandendriessche, S. Van Cleuvenbergen, P. Willot, G. Hennrich, M. Srebo, V. K. Valev, G. Koeckelberghs, K. Clays, J. Autschbach, T. Verbiest. Giant Faraday rotation in mesogenic organic molecules. *Chem. Mater*. **2013**, 25, 1139 - 1145. (d) P. Wang, I. Jeon, Z. Lin, M. D. Peeks, S. Savagatrup, S. E. Kooi, T. Van Voorhis, T. M. Swager. Insights into Magneto-

Peer-reviewed version available at *Coatings* **2019**, *9*, 669; doi:10.3390/coatings9100669

Optics of Helical Conjugated Polymers. *J. Am. Chem. Soc*. **2018**, *140*, 6501–6508. (e) P. Gangopadhyay, G. Koeckelberghs, A.Persoons. Magneto-optic Properties of Regioregular Polyalkylthiophenes. *Chem. Mater*.**2011**, *23*, 516 – 521. (f) J. R. Thompson, J. S. Ovens,V. E. Williams, D. B. Leznoff. Supramolecular Assembly of Bis(benzimidazole)pyridine: An Extended Anisotropic Ligand For Highly Birefringent Materials. *Chem. Eur. J*. **2013**, *19*, 16572 – 16578.

[5] R. Vleugels, L. deVega, W. Brullot, T. Verbiest, B. Gómez-Lor, E. Gutierrez-Puebla, G. Hennrich. Magneto-optical activity in organic thin film materials. *Smart Mater. Struc*.**2016**, *25*, 12LT01 – 08.

[6] G. R. Desiraju, (Ed.), *Perspectives in Supramolecular Chemistry: The Crystal as Supramolecular Entity*. John Wiley&Sons, New York, **2007**.

[7] L. Wang, Q. Li. Stimuli-Directing Self-Organized 3D Liquid-Crystalline Nanostructures: From Materials Design to Photonic Applications. *Adv. Funct. Mater*. **2016**, *36*, 10 – 28.

[8] R. Vleugels, J. Steverlynck, W. Brullot, G. Koeckelberghs. Faraday rotation in discotic liquid crystals by long range electron movement. *J. Phys. Chem. C* **2019**, *123*, 9382 – 9387.

[9] G. Hennrich, M. T. Murillo, P. Prados, H. Al-Saraierh, A. El-Dali, D. W. Thompson, J. Collins, P. E. Georghiou, A. Teshome, I. Asselberghs, K. Clays. Alkynyl Expanded Donor–Acceptor Calixarenes: Geometry and Second-Order Nonlinear Optical Properties. *Chem. Eur. J*. **2007**, *13*, 7753 – 7761.

[10] K. Sonogashira, *J. Organomet. Chem.* **2002**, *653*, 45 – 49.

[11] L. Flores, I. López-Duarte. Gutierrez-Puebla, G. Hennrich. *Manuscript in preparation.*

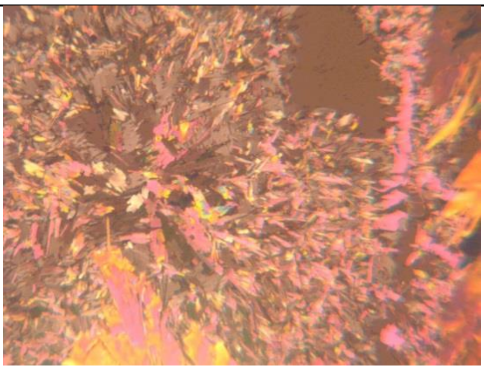
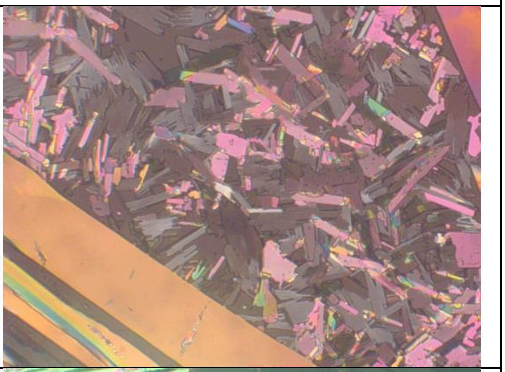
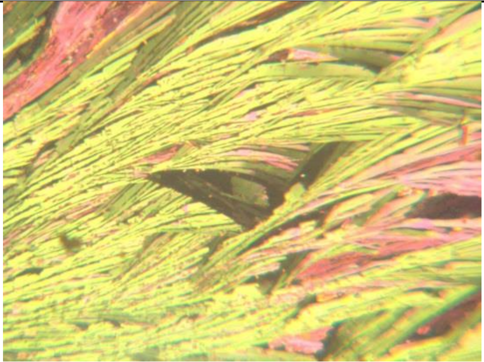
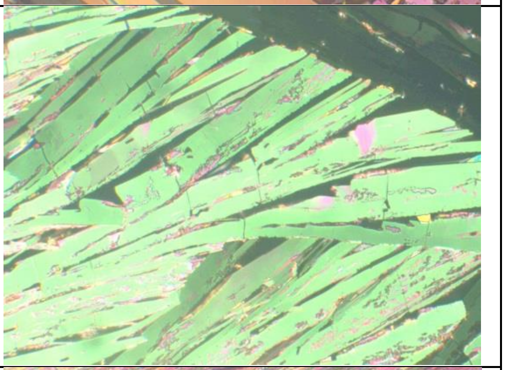
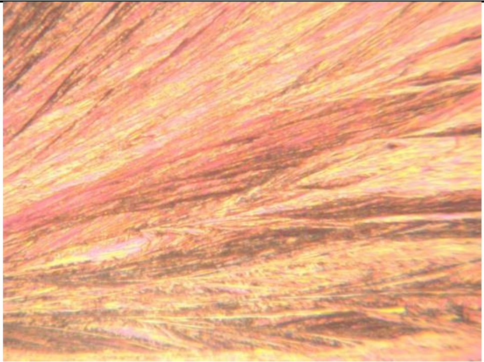
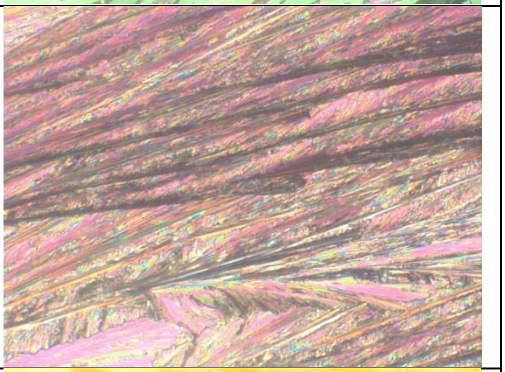
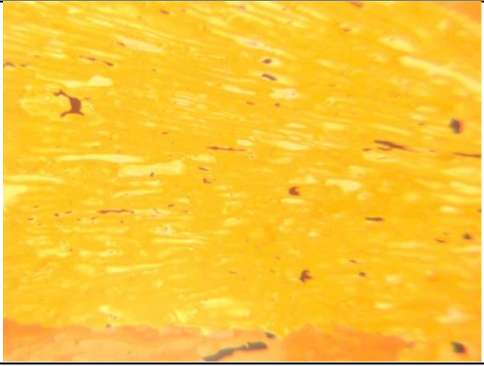
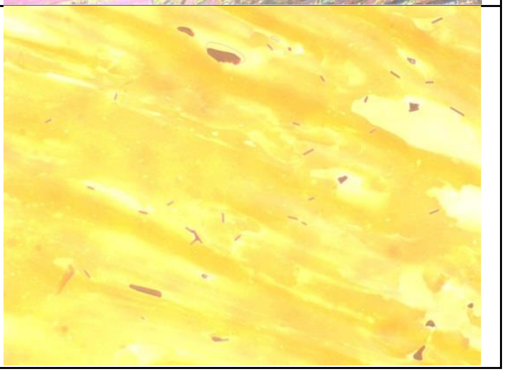
[12] B. Outram, *Liquid Crystals, chap. 3.6: Polarising optical microscopy*. IOP Publishing, Bristol, **2018**.

Peer-reviewed version available at *Coatings* **2019**, *9*, 669; doi:10.3390/coatings9100669

Supplementairy information

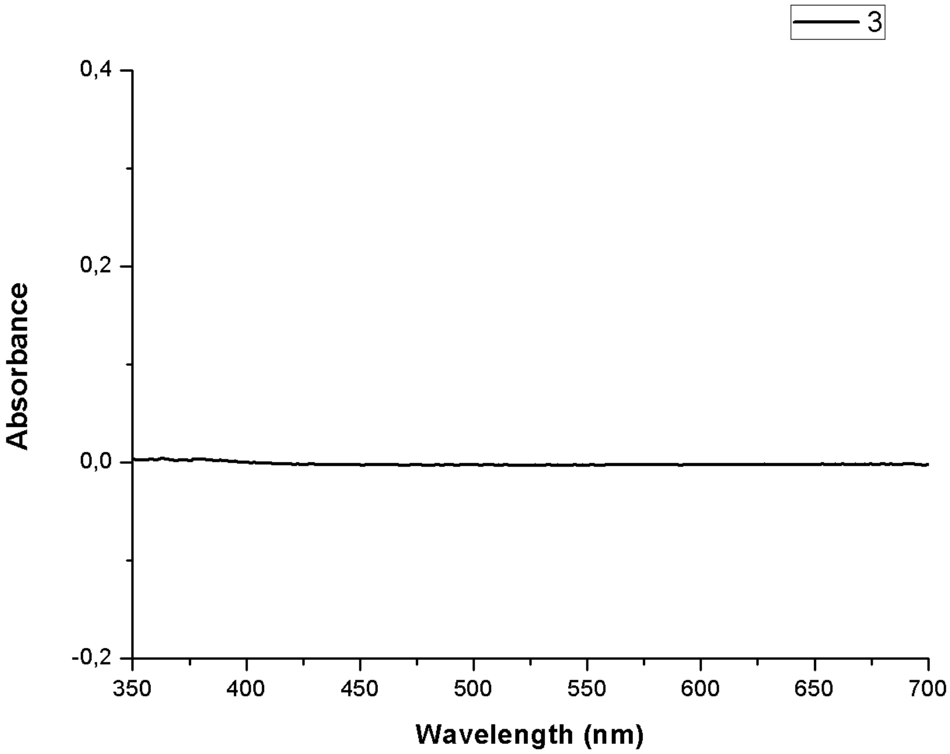
1. Polarised optical microscopy

Polarised optical microscopy images of the materials in the LC cells.

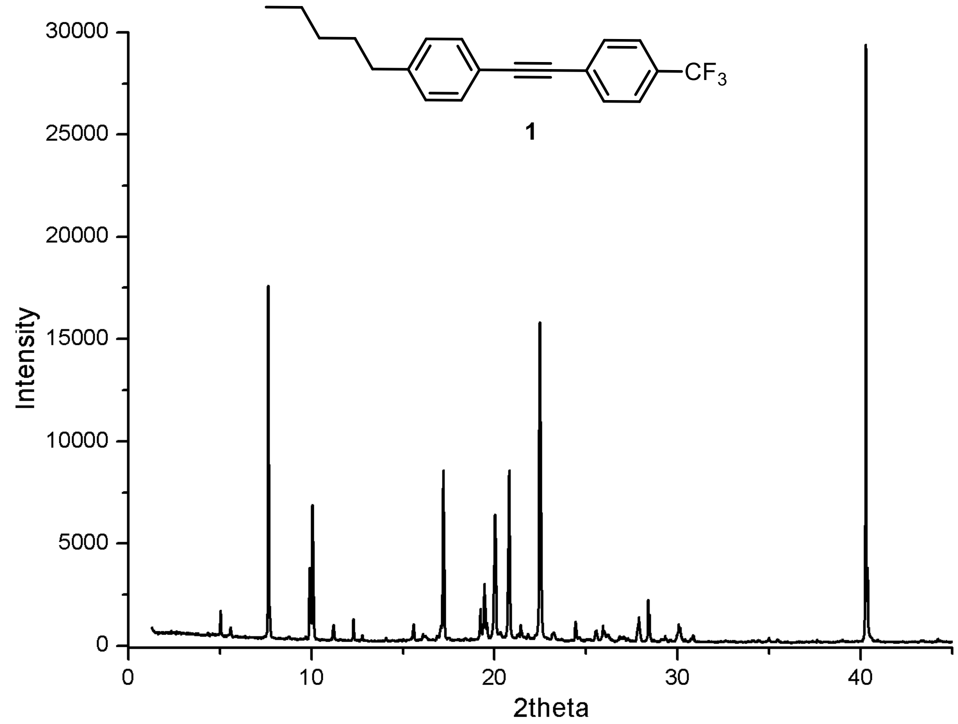
Material	5x zoom	20x zoom
1		
2		
3		
4		

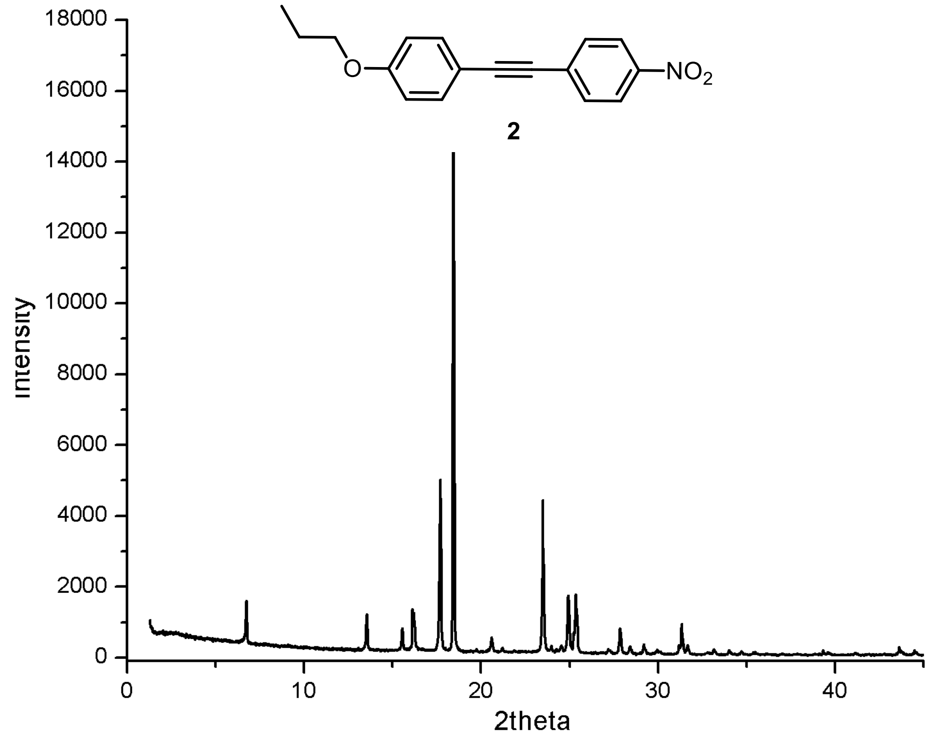
5		

2. UV-Vis absorbance spectrum of the unsubstituteddiphenylacetylene (3)

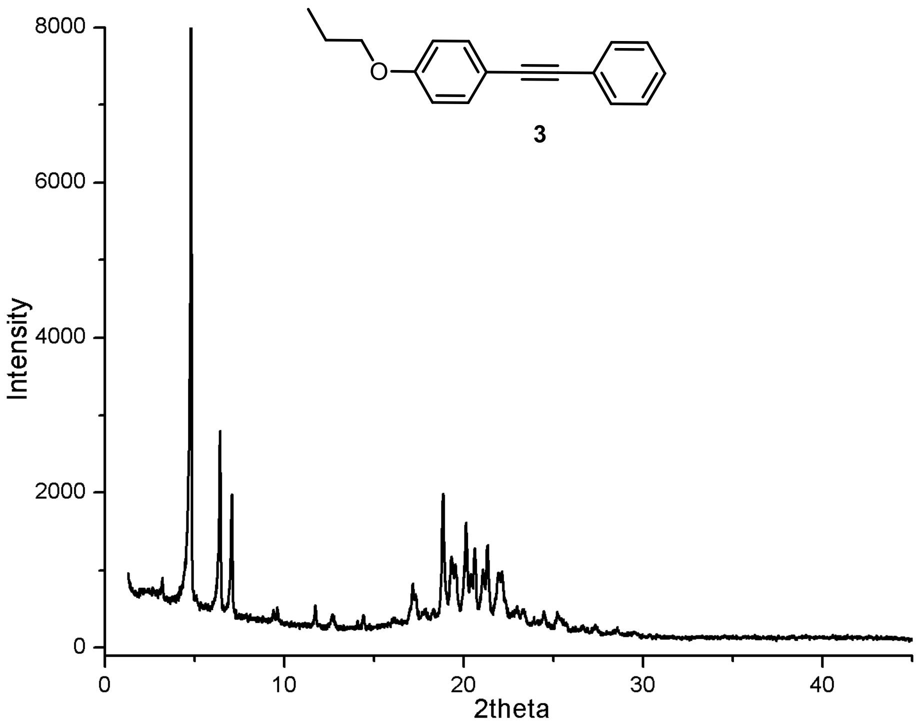


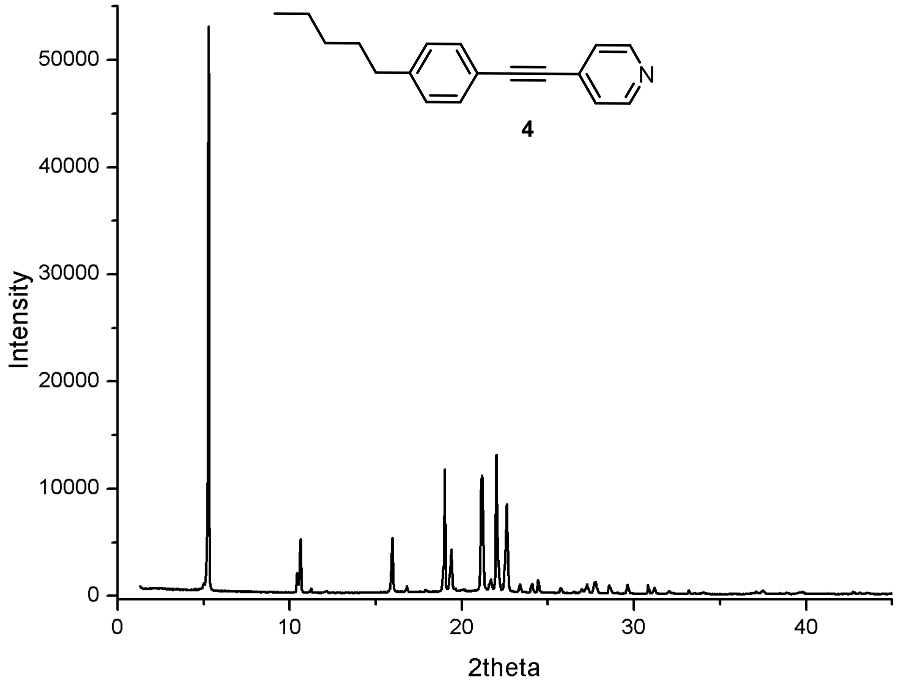
3. X–ray diffractograms





Peer-reviewed version available at *Coatings* **2019**, *9*, 669; doi:10.3390/coatings9100669





Peer-reviewed version available at Coatings 2019, 9, 669; doi:10.3390/coatings9100669

4. Verdet constant measurements at 400nm

Verdet constant of samples 1,2,4 and 5 turned asmuthal 0°, 30°, 60° and 90°. The verdet constant was measured at 400 nm. No dependence of Verdet constant on rotation of asmuthal angle was observed.