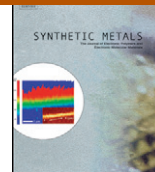




ELSEVIER

Contents lists available at SciVerse ScienceDirect

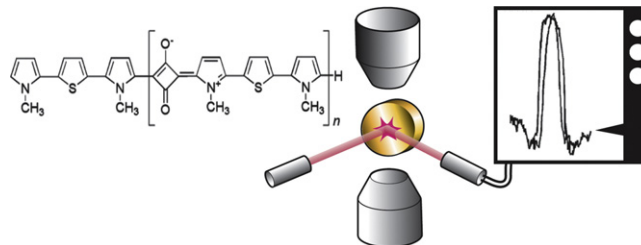
Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Graphical Abstract

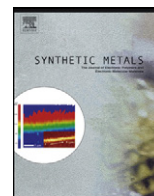
Novel magneto-optic behaviour from a polysquaraine

Daniel E. Lynch*, David M. Newman, M. Lesley Wears, Raphael J. Matelon



Contents lists available at [SciVerse ScienceDirect](http://www.elsevier.com/locate/locate/synmet)

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Novel magneto-optic behaviour from a polysquaraine

Daniel E. Lynch^{a,*}, David M. Newman^{a,1}, M. Lesley Wears^{a,1}, Raphael J. Matelon^{a,1}^a Faculty of Health and Life Sciences, Coventry University, Coventry CV1 5FB, UK

ARTICLE INFO

Article history:

Received 31 October 2012

Received in revised form 25 February 2013

Accepted 10 March 2013

Available online xxx

Keywords:

Squaraine

Polysquaraine

Magneto-optic effect

Magnetism

Electrical conductivity

X-ray diffraction

ABSTRACT

We report that poly((2,5-bis(1-methylpyrrol-2-yl)thiophene)squaraine) can be synthesized as a dark green insoluble powder which when subjected to shear force and pressed as a disk exhibits a gold-green near optical quality surface with semi-metallic behaviour. Reflectivity measurements at a wavelength of 819 nm reveal a high (72°) pseudo-Brewster angle and non-zero p-reflectivity whilst electrical measurements using a four-point probe return a conductivity of $1 \times 10^{-5} \text{ } \Omega^{-1} \text{ cm}^{-1}$. Unexpectedly the disks also exhibit magneto-optic (MO) activity which it appears must arise from a weak magnetic component intrinsic to the samples. In both the longitudinal and transverse Kerr configurations large fractional changes in reflectivity ($\Delta I/I \approx 2.5 \times 10^{-2}$) are observed across a wide range of angles of incidence for wavelengths between 400 nm and 1064 nm on application and reversal of a magnetic field. Anomalously for these configurations all the MO effects observed are quadratic in the applied field and no first-order effects linear in applied field are observed for any state of incident polarisation. Examined using conventional magnetometry disk samples return saturation magnetization values of $4.13 \times 10^{-3} \text{ emu g}^{-1}$ on a vibrating sample magnetometer and smaller samples similarly processed and prepared for examination by Squid magnetometer confirmatory values of $4.9 \times 10^{-3} \text{ emu g}^{-1}$. Magnetization curves from both instruments have a similar form saturating at about 1.14 kOe and are also in close correspondence with curves derived by plotting the magneto-optic signal as a function of field after allowance for the quadratic nature of the observed MO response. Similarly both the magnetic and magneto-optic behaviour of all samples is isotropic in plane.

Taken together all experimental observations on this fully organic polymer appear, surprisingly, to be commensurate with the development at room temperature of some form of magnetic state throughout very limited regions of the material. A very tentative model able to reconcile the magnetic and MO observations on the supposition that the magnetic state may be of a reduced dimensional nature is presented. We are very aware that the appearance of an intrinsic room temperature magnetism in the material studied is highly unlikely and that this interpretation of the results presented is strongly dependent on using MO evidence to support chemical analysis, which included multi-elements scans on an ICP and ESR, in precluding contamination.

© 2013 Published by Elsevier B.V.

1. Introduction

Pyrrolic squaraines [1–55] hold a unique place in the overall field of squaraine chemistry. They were the first squaraines reported [1–3], they are one of the few squaraines that can be produced in alcohol without the azeotropic removal of water [1,3–8,10,13–15,18,21,23,41], they can easily form both dimeric squaraine dyes [1–4,6–8,10–12,14–17,21,22,24,25,29–31,34–36,39,42,44–46,51–55] and polysquaraines [5,9–13,16–20,23,

[26–28,32,33,37,38,40–43,47–50,54] (depending on the availability of the α -H's), they can simultaneously form a mixture of both 1,2- and 1,3-squarate analogues [10,13,40,48,50], and they can form a 1,2,3-squarate variant [2,5,51,53]. Yet given their versatility they have remained, until relatively recently, one of the least studied squaraine variants, especially with respect to X-ray crystal structure studies (the only known structure being in Ref. [39]). Pyrrolic polysquaraines have been studied for a variety of reasons including electrical conduction [9,12,16,18–20,48,50] and electro-optic properties [5,10,40,42,43], as well as applications that utilize both their particulate shape [23,32,41,56] and colour [33]. Within the known set of pyrrolic polysquaraines, there are essentially two subsets; one where there is only one pyrrole in the repeat unit (polymerizing through the two α -sites on the same pyrrole molecule) [5,9–13,16,17,23,26,32,33,37,43,47–49] and one where there are two linked pyrrole molecules [18–20,27,28,38,42,50,54]. All of these latter cases, except the first, involve bispyrroles

* Corresponding author. Current address: Exilica Limited, The Technocentre, Puma Way, Coventry CV1 2TT, UK. Tel.: +44 24 7688 8505.

E-mail addresses: d.lynch@exilica.co.uk (D.E. Lynch), D.M.Newman@ex.ac.uk (D.M. Newman).

¹ Current address: School of Engineering, Physical Science & Mathematics, University of Exeter, Exeter EX4 4QF, UK. Tel.: +44 1392 723728; fax: +44 1392 217965.

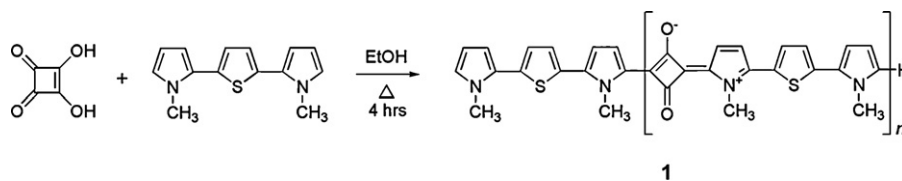


Fig. 1. Schematic showing the synthetic route used in this study.

linked by divinylarenes, thus maintaining a π -conjugated system with the intention of creating a low band gap in the resultant polysquaraine. However, in an attempt to deviate from that particular chemical model and utilising known bispyrroles of a previous study on the structure and properties of a series of conjugated terarenes containing two outer 1-methylpyrroles [57], a series of polysquaraines were prepared in order to investigate their electrical conduction properties. It was intended that this study would compliment a similar study on the electrical properties of poly(oligo(1-methylpyrrol-2-yl)squaraine)s [18], but it was found that one analogue, the polysquaraine of 2,5-bis(1-methylpyrrol-2-yl)thiophene, displayed an optical quality surface when pressed as a disk for four-point probe electrical conduction experiments. In addition to the electrical measurements a series of studies were also undertaken investigating the optical reflectivity of disk surfaces and with the majority of automated optical instrumentation in our laboratories designed for and directed towards magneto-optic measurements these were fortuitously included as a matter of routine. Here we report clear and repeatable evidence of extensive magneto-optic activity in prepared disks of poly((2,5-bis(1-methylpyrrol-2-yl)thiophene)squaraine) (**1**) (Fig. 1).

2. Materials and methods

2.1. Synthesis

1-Methylpyrrole (Aldrich) was distilled before use under reduced pressure and stored over semiconductor grade KOH pellets (Aldrich). THF (Sigma-Aldrich) was obtained sealed under nitrogen. ZnCl_2 (Sigma-Aldrich) was dried and stored over P_4O_{10} (Sigma-Aldrich) in a desiccator. *t*-Butyllithium (1.6M), 2,5-dibromothiophene, bis(diphenylphosphinopropane)nickel(II) chloride, squaric acid, absolute ethanol and ethyl acetate were obtained from Lancaster and were used without further purification. 2,5-Bis(1-methylpyrrol-2-yl)thiophene was prepared and identified according to the Kumada procedure [57].

2.1.1. Poly(thiophene-*alt*-(2,5-bis(1-methylpyrrol-2-yl)ene)cyclobutene-1,3-diolate) (**1**)

Squaric acid (100 mg, 0.88 mmol) and 2,5-bis(1-methylpyrrol-2-yl)thiophene (212 mg, 0.88 mmol) were refluxed for 16 h in absolute ethanol (30 mL). Upon cooling, a dark green powder was collected *in vacuo*, washed with cold ethanol and air dried. The low molecular weight compounds were removed from the polymer mass via soxhlet extraction using ethyl acetate. Yield: 180 mg (58%). ν_{max} : 1608 (C=O).

2.2. Instrumentation

Infrared spectra were recorded as KBr discs using a Nicolet 205 FT-IR spectrometer. Thermogravimetric analysis was performed on a Setram TGA/DTA 92-12 with a gas flow rate of 50 mm min^{-1} . All electrical conductivity measurements were performed using the four-point probe method under atmospheric conditions at

room temperature. Powder X-ray diffraction (XRD) patterns were measured on a Philips PW1700 system diffractometer (Cu $K\alpha$ X-radiation). Scanning electron micrographs were taken on a Joel JSM 35CF scanning microscope using a gold overlay. Transmission electron microscope images were obtained using a Philips CM200 TEM, operated at 200 kV in the STEM mode. Multi-element analysis was undertaken using a Perkin-Elmer 5300DV ICP. Electron spin resonance spectra were collected on a Bruker ER200D X-band ESR (EPR) spectrometer for samples in the uncrushed powder state. The experimental conditions for magneto-optic experiments are described in Ref. [58]. The vibrating sample magnetometer used in this study was constructed based on Foner's design [59]. Superconducting Quantum Interference Device or Squid magnetometer experiments were undertaken at the Dresden High Magnetic Field Laboratory, Germany. All fixtures that supported any of the materials for magnetic measurements of either kind were either made of glass or PTFE polymer. All fixtures were examined independently of sample for any magnetic interference signals.

2.3. Supplementary data

The infrared spectrum, thermal gravimetric data and electron spin resonance spectra (of material produced in ethanol and butanol) of **1**, and an illustration of the crystal structure, X-ray powder diffraction pattern and electron spin resonance spectrum of poly((2,5-bis(1-methylpyrrol-2-yl)furan)squaraine), as well as the chemical diagrams of the bispyrroles listed in footnote 1, have been deposited as supplementary material.

3. Results and discussion

3.1. Synthesis and structure

The original, and simplest, synthesis of pyrrolic polysquaraines involves refluxing an equimolar mixture of squaric acid and the pyrrole/linked bispyrrole in alcohol with the product precipitating from the reaction mixture. More recent syntheses have included 50:50 solvent mixtures of 1-butanol and either benzene or toluene, and both with and without the azeotropic removal of water (i.e. using a Dean and Stark apparatus). However, in the preparation of a series of polysquaraines based on conjugated terarenes containing two outer 1-methylpyrroles,² consistency with the previously published series of poly(oligo(1-methylpyrrol-2-yl)squaraine)s [18], meant employment of the original synthesis³ illustrated in Fig. 1, with purification of the insoluble powder proceeding via solvent extraction of the low molecular weight materials.

² Involving 2,5-bis(1-methylpyrrol-2-yl)furan, 2,5-bis(1-methylpyrrol-2-yl)thiophene, 2,6-bis(1-methylpyrrol-2-yl)pyridine, 1,4-bis(1-methylpyrrol-2-yl)phenyl, 4,4'-bis(1-methylpyrrol-2-yl)biphenyl, 9,10-bis(1-methylpyrrol-2-yl)anthracene, ethyl-3,6-bis(1-methylpyrrol-2-yl)carbazole and 4,4'-bis(1-methylpyrrol-2-yl)dibenzenevinyl.

³ Compound **1** was separately prepared in methanol, ethanol and butan-1-ol and although the products from the latter two were structurally identical (by XRD analysis), it was the product from ethanol that produced disks with greater optical reflectance and stronger MO effects.

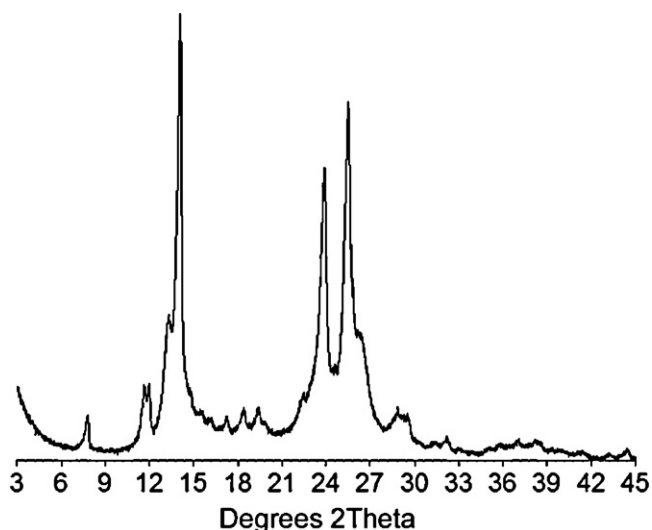


Fig. 2. X-ray powder diffraction pattern for **1**.

Compound **1** was collected as a dark green insoluble powder. Infrared analysis (IR) of **1** gives a strong single C–O peak at 1608 cm^{-1} and little indication of the presence of any peaks around 1750 cm^{-1} , suggesting that the majority of the polysquaraine consists of the preferred 1,3-squarate form (that illustrated in Fig. 1). The infrared spectrum of **1** also displays a characteristic of low band-gap polymers with a decreasing baseline from 1800 cm^{-1} to higher wavenumbers. Thermogravimetric analysis was performed under dry air and shows that thermal degradation occurs over $300\text{ }^{\circ}\text{C}$; common for short-alkyl squaraine compounds.

General structural analysis of **1** was undertaken using powder X-ray diffraction techniques with the resultant pattern shown in Fig. 2. Being fully conjugated polymers, polysquaraines are primarily expected to be flat with the possibility of donor-acceptor stacked polymer ribbons dominating the structure. It was previously reported in the study of poly(oligo(1-methylpyrrol-2-yl)squaraine)s [18] that although mostly amorphous, the majority of the polymers studied exhibited a small degree of order with diffraction peaks indicating interplanar distances of 3.4 \AA and above. In fact the only polymer with a peak at $d=3.4\text{ \AA}$ was also the only one that exhibited electrical conduction properties and it was surmised that the two were linked. The powder diffraction pattern of **1** indicates a higher degree of crystallinity than those previously studied and that the polymer chains in **1** have at least one-dimensional stacking order with strong diffraction peaks at $d=3.50, 3.73, 6.27$ and 7.72 \AA , and a shoulder peak at $d=3.36\text{ \AA}$. However, transmission electron microscope (TEM) diffraction patterns of single sub-particulate lathes (Fig. 3(a) and (b)) indicate that there are actually two packing phases, both containing a similar one-dimensional pattern, but one also displaying order

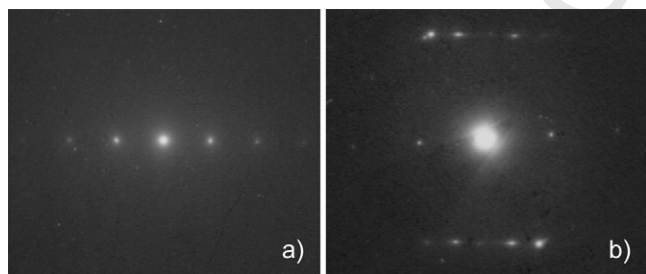


Fig. 3. TEM diffraction images from isolated sub-particulate lathes indicating separate (a) one-dimensional and (b) two-dimensional structures.

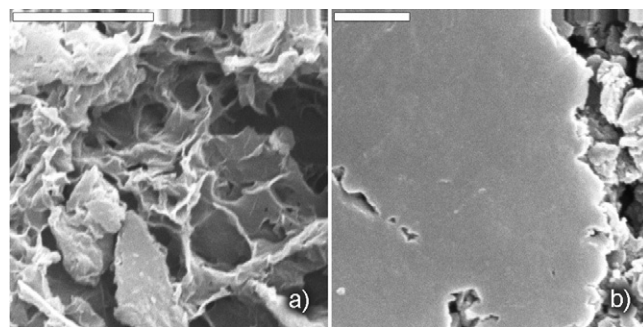


Fig. 4. SEM images of a particulate grain of **1** indicating the amorphous network of (a) sub-particulate lathes (scale bar = $5\text{ }\mu\text{m}$) and (b) the effect of applying a shear force to the lathes (scale bar = $2\text{ }\mu\text{m}$).

in a second dimension. Both small molecule dimeric squaraines and polysquaraines are known to form ordered stacks in their solid-state structures [20] with different polymorphs in dimeric squaraines arising from differing interplanar distances [60].

Fig. 4(a) is a scanning electron microscope (SEM) image of a grain of the powder of **1** and shows that the particles comprise a network of amorphously arranged lathes. When subjected to shear forces, such as in the preparation of a pressed disk for electrical conduction measurements, the lathes collapse and align to create a relatively flat surface (Fig. 4(b)).

Further evidence that **1** is a flat polymer can be gained by inference to the crystal structure of 2,5-bis(1-methylpyrrol-2-yl)furan, which is chemically identical to 2,5-bis(1-methylpyrrol-2-yl)thiophene except for one atom. The single crystal X-ray structure of 2,5-bis(1-methylpyrrol-2-yl)furan was determined, as was the structure of 2,6-bis(1-methylpyrrol-2-yl)pyridine, as part of the broader study into the polysquaraines of these materials and shows that the furan variant is flat with the maximum dihedral angle between the rings being $<3.3^{\circ}$ [61]. A flat linked bispyrrole would invariably mean a flat polysquaraine because the conjugation between squarate linked pyrroles dictates flatness, as observed in the only known crystal structure of a pyrrolic squaraine [39] (and also observed in almost all known crystal structures of squaraine dyes). For comparison, the X-ray powder diffraction pattern of the polysquaraine made from 2,5-bis(1-methylpyrrol-2-yl)furan also reveals strong diffraction peaks at $d=3.49, 3.63, 3.86$ and 6.88 \AA [61].

3.2. Electrical conduction measurements

Four-point probe electrical conduction measurements undertaken on finely ground and pressed solid disk samples ($12\text{ mm dia} \times 1\text{ mm thick}$) of **1** returned conductivity values of $1 \times 10^{-5}\text{ S cm}^{-1}$, which is comparable to the highest values reported for non-doped polysquaraines.

3.3. Magneto-optic measurements

Pressed disk samples of **1**⁴ exhibited unexpected yet significant levels of apparent magneto-optic (MO) behaviour in the two Kerr configurations (transverse and longitudinal) (Fig. 5) for which the magnetic field is applied and reversed along orthogonal directions confined to the plane of the sample surface. Behaviour identical in nature but of a reduced magnitude was also recorded from a

⁴ $12\text{ mm diameter} \times 200\text{ }\mu\text{m}$ ($\pm 10\%$) disks of all materials were prepared using a standard stainless steel KBr die and disk press with disks produced under $10\text{ atm pressure for } 5\text{ min}$. All disks (unless otherwise stated in the text) were made of pure material. Disks of $100\text{ }\mu\text{m}$ or less were found to be too fragile for handling.

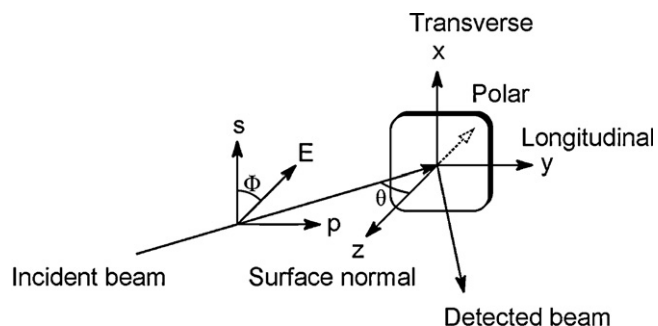


Fig. 5. Illustration demonstrating the optical configuration for the magneto-optic geometries. The magnetic field is applied in the plane of the sample, parallel to the plane incidence (longitudinal effect) or perpendicular to the plane of incidence (transverse effect). E is the amplitude of the electric field and p and s refer to the state of incident light polarization.

disk sample (of **1**) diluted by crushing with dried potassium bromide (KBr), as a sample for infrared analysis would normally be prepared. Measurements for both samples were readily obtained in both these configurations across a wide range of angles of incidence for wavelengths between 400 nm and 1064 nm. However, no MO activity was detectable in the polar Kerr configuration in which the field is applied and reversed normal to the sample surface and the measurements in the transverse and longitudinal configuration were anomalous in several respects. First, in contrast with previous reports [62–64] of very weak MO effects in organic and metal-organic compounds the magnitude of the effects observed are very large; the values recorded for the fractional change in reflected intensity $\Delta I/I_0 \approx 2.5 \times 10^{-2}$ for example being more typical of those expected from the continuous surface of bulk ferromagnetic metals. This is illustrated in Fig. 6 where $\Delta I/I_0$ as a function of angle of

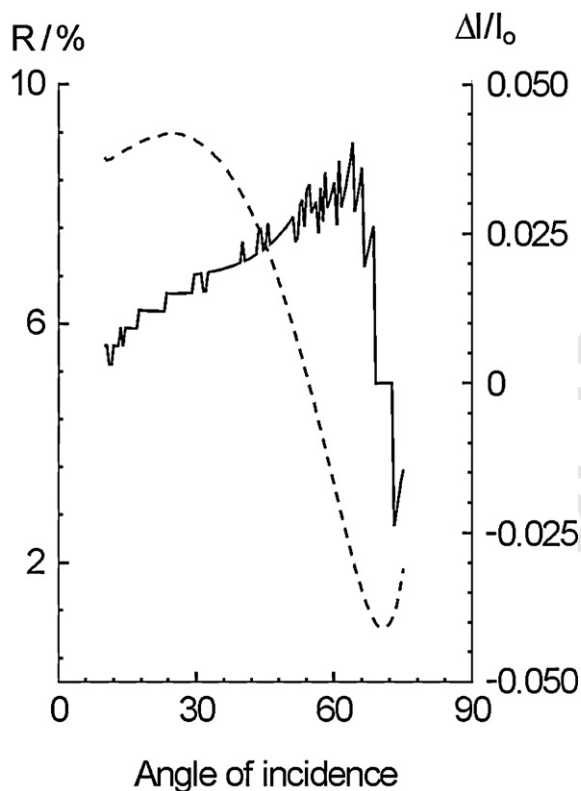


Fig. 6. Disk reflectivity (---) and fractional change in reflection (—) on magnetization reversal in the transverse Kerr configuration for a wavelength of 819 nm at 25° angle of incidence.

incidence is plotted for p-polarised radiation at a wavelength of 819 nm and shown together with the conventional reflectivity revealing a high (72°) pseudo-Brewster angle and non-zero p-reflectivity. Second, the effects observed in both the transverse and longitudinal configurations appear to arise only from second-order phenomena even in nature and thus quadratic in the applied field. Such effects are usually extremely small and only observable in these configurations when first order effects vanish such as for example at normal incidence. Irrespective of the polarisation state of the incident radiation, samples of **1** exhibited no first-order magneto-optic effects, i.e. effects linear in the applied field, in any configuration studied. The final anomalous feature of the magneto-optic behaviour of these samples is that they saturate so that when plotted as a function of applied field yield curves of the form shown in Fig. 7(a). Curves of this form are typical of those obtained from ferromagnetic materials by measurement techniques which are insensitive to the direction of magnetization (M). Magneto-resistance⁵ [65] is perhaps the best-known phenomenon displaying in this manner but as pointed out above second-order magneto-optic effects can also display behaviour of this form from ferromagnetic surfaces under certain very specific experimental conditions [58] for which first-order magneto-optic effects linear in M are identically zero. It is reemphasised that this is not the case with the present samples for which no first-order MO effects were detectable in any realizable experimental configuration.

The saturation of the apparent MO activity observed from sample(s) **1** in applied fields a little over 1 kOe implies one of two possible mechanisms is responsible for its manifestation. The samples may be becoming birefringent as a result of a magnetic field induced structural or molecular reorientation as happens in the Cotton-Mouton effect which also returns signals quadratic in applied field or they have an intrinsic or extrinsic (contaminant) ferromagnetic component. The possibility of structural modification was excluded when X-ray diffraction measurements conducted with and without a static applied magnetic field revealed no detectable differences between the two patterns to the limits of instrument sensitivity. This mechanism was further precluded by the absence of any detectable anisotropy in the magnitude of both the transverse and longitudinal effects as the samples were rotated about the surface normal. Extrinsic contamination by ferromagnetic elements may also be deemed extremely unlikely as it would result in first-order MO effects and not the second-order effects recorded. Nevertheless a further careful check for metallic impurities was undertaken. A portion (100 mg) of a disk sample was decomposed in a 50:50 mixture of 100 vol. hydrogen peroxide (5 mL) and conc. sulphuric acid (5 mL), diluting in water (to 100 mL), then running the solution on a multi-element scan through an ICP. The only metal ions found present were sodium (8.75 mg/g) and potassium (55.625 mg/g). There are several possible sodium sources throughout the synthesis procedure⁶ and the presence of potassium is most likely introduced from the surface of the mortar and pestle used to finely grind all the powders including KBr disks for infrared analysis.

3.4. Verification of magnetic behaviour

Verification of magnetic behaviour was immediately sought by conventional magnetometry. In its precipitated form (as per Fig. 4(a)) the polymer exhibited no magnetic behaviour detectable

⁵ Although organic magneto-resistance is an area of recent interest (refer [82]), no such experiments were undertaken on **1**.

⁶ The two starting materials were also analysed by multi-element scans on the ICP and sodium was the only metal element in appreciable amounts that was detected.

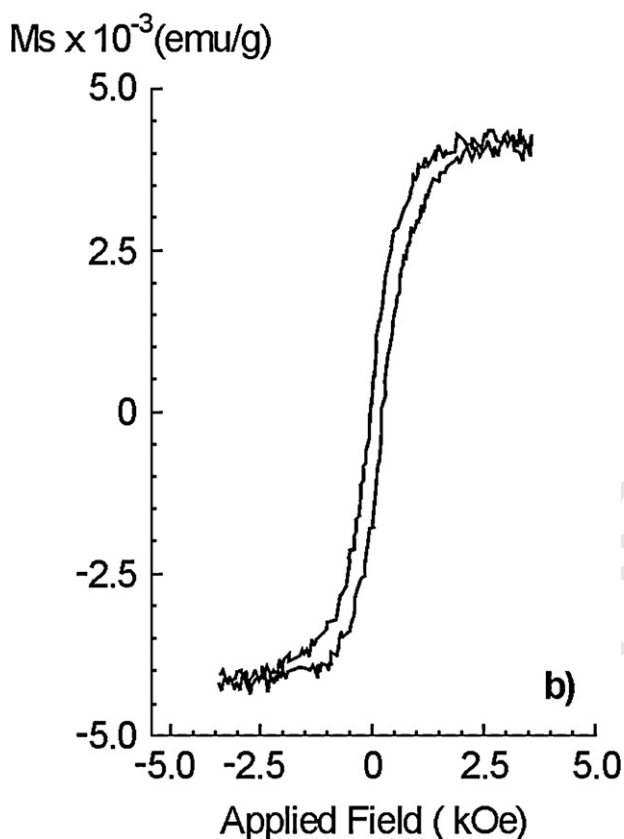
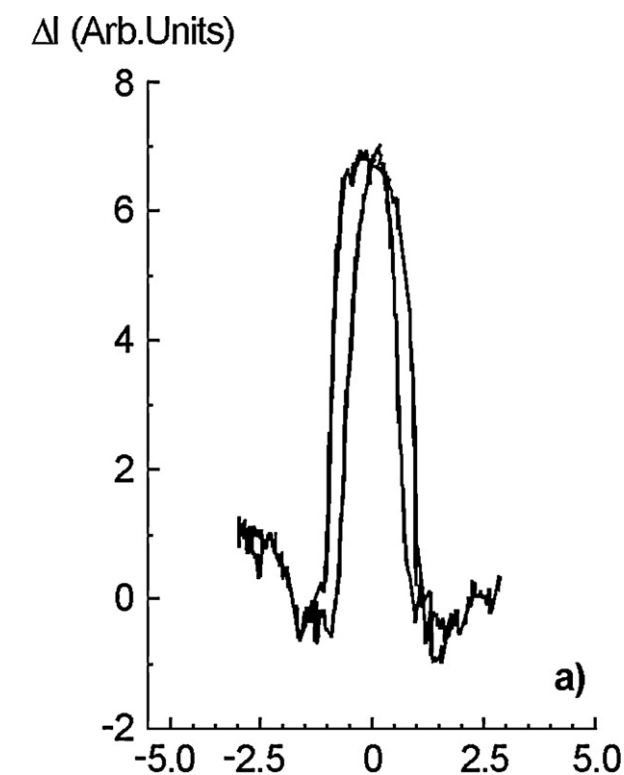


Fig. 7. Magnetization curves obtained (a) by change in reflected intensity in the transverse Kerr configuration and (b) by VSM.

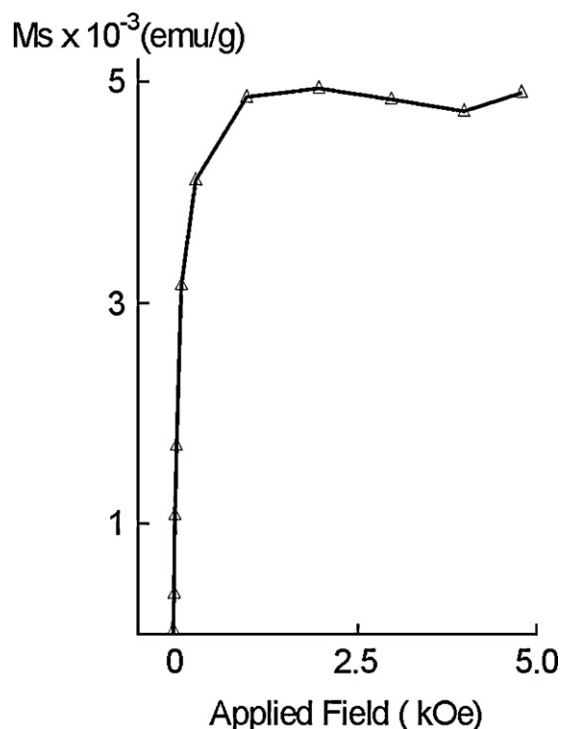


Fig. 8. Magnetization curve obtained by the Squid magnetometer.

by either vibrating sample magnetometry (VSM) or electron spin resonance (ESR) techniques. The disk samples however returned saturation magnetization (M_s) values of $4.13 \times 10^{-3} \text{ emu g}^{-1}$ on the VSM whilst smaller samples similarly processed and prepared for examination by Squid magnetometry provided confirmatory values of $4.9 \times 10^{-3} \text{ emu g}^{-1}$. The differences are readily attributable to variations in processing. Magnetization (M) curves shown for both instruments in Figs. 7(b) and 8 have a similar form, saturating at about 1.14 kOe. A small ($H_c \approx 0.135 \text{ kOe}$) but significant degree of coercivity and remanence is evident and the samples are magnetically isotropic in plane. Squid magnetometry (M_s) measurements were recorded from 4 K to 350 K (77 °C), over which the $M_s(T)$ curve is essentially flat. There is no current indication of what the Curie temperature is for disk samples of 1.

3.5. Consideration of magnetic behaviour

In Fig. 7, there is evidently a close correspondence between the magnetic hysteresis loops obtained using the MO signal, recorded in the transverse Kerr configuration, Fig. 7(a), and those taken using the VSM, Fig. 7(b), once allowance is made for the quadratic nature of the MO interaction. Both exhibit the same form, slope and coercivity, demonstrating the validity of using MO effects to draw further inference regarding the apparent magnetism of this material. Specifically, the nature of the magneto-optic effects observed may be employed to argue powerfully against the presence of contamination by ferromagnetic metals. As pointed out by Miller [66] in his cautionary review of polymer ferromagnets, when a material has a low saturation magnetization it is essential to ensure that it is intrinsic rather than extrinsic in nature. Many previous observations of organic ferromagnetism are most likely attributable to contamination by trace amounts of ferromagnetic metals, although no previous experiments of this nature included the study of MO effects. In the present samples the rigorous purity control essential in claims of this nature is supplemented by the required and observed complete absence of any magneto-optic effects linear in magnetization that must, in at least one of the configurations and

wavelengths studied, accompany the presence of any contamination by ferromagnetic metals or compounds at the level necessary to give rise to the conventionally detected moment. If the possibility of contamination is allowed then, knowing the detected moment, there are three forms in which it may be considered to exist. In terms of increasing likelihood these are (i) as an anomalous thin surface layer, (ii) as a dispersion of very fine particles uniformly and homogeneously distributed throughout the volume of the samples and (iii) as a very few large particles randomly distributed throughout the sample volume with low likelihood that any particle is close enough to the surface to be accessible to the optical beam. Whilst all may demonstrate the magnetic loops recorded with the VSM and Squid it is difficult to conceive of how any, either singularly or collectively, can give rise to the combination of magnetic and MO effects observed. Possibilities (i) and (ii) must show linear MO effects, thus Fig. 7(a) would be identical to Fig. 7(b). Moreover, to homogeneously disperse the contamination throughout the sample, as considered in (ii), would require particles structured at a scale too small to sustain ferromagnetism, when the hysteresis loops are clearly indicating ferromagnetic rather than superparamagnetic behaviour. Possibilities (i) and (ii) would also have shown some metal content in both the ICP analysis and ESR spectra. Consideration of the most probable form (iii) in which contamination might exist, given the way the disks are prepared, requires some mechanism whereby a few buried magnetic particles can induce large quadratic MO effects throughout the material that express uniformly across the surface of the polymer. Perhaps however, the most compelling evidence for the absence of contamination is provided by consideration of the uniqueness of this particular polysquaraine **1** in comparison with the analogous polysquaraine derivative of 2,5-bis(1-methylpyrrol-2-yl)furan [61] which, when prepared and processed in exactly the same manner, into an optically reflective disk, exhibits near identical behaviour to **1**, including an intrinsic electrical conductivity of $2 \times 10^{-5} \text{ S cm}^{-1}$, but crucially, no evidence of magnetic behaviour or MO activity.⁷ The consensus of evidence available therefore tends to favour the interpretation that the magnetization and associated anomalous magneto-optic effects detected arise in some way from the polymer and are at a fundamental level a consequence of a unique molecular and physical structure appropriately developed on processing. It should finally be noted that the grade of stainless steel that is used to manufacture the disk press does not demonstrate MO activity and all chemistry samples were handled using plastic spatulas and tweezers.

3.6. Organic ferromagnets

The possibility of synthesising organic ferromagnets has been the subject of continuing [67–77] interest since the proposal was first mooted in the late 1970s [67]. However, of the many and varied routes proposed for the realisation of such materials, that conceived by Fukutome et al. [78] and subsequently the subject of a detailed theoretical study by Tanaka et al. [79] is perhaps most relevant when attempting to understand the present observations. This introduced the concept of polaronic polymers, wherein spin supplier blocks (SSBs) and spacer units (SUs) are alternatively positioned along continuous polymer chains such that when the SUs are optimally dimensioned, ferromagnetic coupling may arise between the spins on the SSBs. Considering the polysquaraine under discussion, on this basis the three five-membered heterocyclic rings may together be taken to constitute a single SSB possessing unit spin multiplicity. These types of organic ring

systems, being flat and fully conjugated, can stabilise the resonant π -electrons and allow them to pass along the chain, which makes these polyheterocycles electrically conductive [57]. In the case of **1**, the squarate groups are electron traps (electron accepting) with the \neg ve charge delocalized across the squarate oxygens. Spin mobility between the (electron donating) pyrrole ring SSBs is therefore constrained, or totally precluded, and correct separation may then allow the possibility of exchange coupling between spins. Furthermore, at the molecular scale the crystal structure of the analogous precursor to 2,5-bis(1-methylpyrrol-2-yl)furan is known to be flat [61] so, as previously stated, it is reasonable to assume that the precursor pyrrole of **1** is also flat and that, because of the resonant nature of the molecular chain, this property carries through to the backbone of **1** itself. Being flat the chains have the ability to stack, a property enhanced by the interlayer attraction existing between the SSBs and the squarate spacer groups as a result of the overlapping of the electron donating and electron accepting charge distributions, which can result in the flat polymer system stacking in parallel planes promoting 1D and possibly 2D order. Evidence for the development of such order in the present polysquaraine is provided by X-ray and electron diffraction measurements. Furthermore, in their study of the magnetic properties of substituted polythiophenes, Vandeleene et al. [76,77] “hypothesize that the magnitude of the magnetization is governed by the fraction of planar polymer chains, while the coercivity seems to depend on the molecular structure and, related to this, the efficiency of π -interactions between different polymer chains.” A review of the magneto-optical properties of spun-coated films of regioregular poly(3-alkyl)thiophenes has also been published [80].

3.7. Magnetic behaviour of **1**

For **1**, evidence of magnetic behaviour only emerges on repeatedly crushing and grinding the as precipitated powder before pressing into disks. The forces imposed during the preparation of the material in disk form are therefore supposed to first separate the lathes and then compress and orientate the lathes such that the molecular structure within them is pseudo-ordered parallel to the disk surface resulting in a flat reflective surface. Processing in this manner is also presumed to bring the molecular structure in close correspondence with that of the model considered by Tanaka (with the triheterocyclic SSBs of **1** substituting for the terthiophene SSBs used in Tanaka’s model) thereby optimising the opportunity for magnetic interactions along, and possibly across, the flat stacked polymer chains. However, given the relative crudity of the processing, and in light of the physical structure discussed above, it seems unlikely that long range spin coupling occurs in three dimensions throughout the material but is rather of reduced dimensionality and constrained to very small regions so that only a small fraction of the material composing any of the samples studied exhibits magnetic behaviour. This fraction is estimated as 0.024% by taking the mass of the polymer formula unit as 270.31 and assuming a spin multiplicity of one. Furthermore, averaged over the whole of a sample the effective magnetization is $\approx 2.31 \times 10^{-4} \mu_B$ per formula unit, which is broadly comparable to that reported by Zaidi et al. [73] for an organic magnet derived from polyaniline prior to concentration of its magnetic component by two orders of magnitude using magnetic separation.

3.8. Mechanism for magnetic behaviour

Having established that the MO activity recorded is not associated with any structural reorientation detectable by X-ray analysis, a mechanism is required to explain its presence in the absence of linear MO behaviour if the polymer is magnetic. Magneto-optic effects arise as a consequence of a magnetically imposed anisotropy

⁷ In fact none of the polysquaraines involving the remainder of the linked pyrroles listed in footnote 1, similarly processed as **1**, displayed any magnetic or MO effects.

on the optical permittivity (ϵ) of a material. Phenomenologically, effects observed from a given material are quantified by the Voigt parameter Q , which is proportional to M , and governed by symmetry constraints placed on the form taken by the permittivity tensor on application of an applied field or the development of magnetization. When magnetism fully permeates the three dimensional structure of a medium the permittivity is well described by a skew-symmetric tensor such as shown below for the specific case of the transverse Kerr configuration with the magnetization in the z -direction (Fig. 5). Note that to the second order in Q its off-diagonal and diagonal elements separately describe magneto-optic effects, linear and quadratic in magnetization respectively. Similar forms hold for the longitudinal and polar configurations. In all cases the upper and lower \pm signs in front of the off-diagonal elements are associated with M in the $+x$ or $-x$ directions respectively so that any phenomena arising from the existence of these terms reverse with the magnetization.

$$[\epsilon] = \epsilon_0 \begin{bmatrix} (1 + fQ^2) & 0 & 0 \\ 0 & (1 + fQ^2) & \pm iQ \\ 0 & \mp iQ & 1 \end{bmatrix}$$

In attempting to reconcile the form of the spin coupling conjectured above with the observed MO behaviour it is essential to explain not only the complete absence of MO phenomena linear in M (Q) but also why all effects observed are even in M . Since both diagonal and off-diagonal elements contain Q , albeit in different orders, Q can not become zero or all effects vanish. Clearly effects even in M , such as those observed, can arise from the Q^2 terms in the diagonal elements. These second-order effects are however expected to be small since Q is small and first-order effects arising from the off-diagonal elements should dominate. A mechanism is required that renders the off-diagonal elements insensitive to magnetization reversal so that they manifest as even observable phenomena. Such a mechanism is provided by reducing the dimensionality of the system of magnetic interactions. It can be shown that, if spin-coupling does not permeate the medium but is instead confined to a series of planes (xy in the above example) then although the form of the tensor remains unchanged, the reduced symmetry determines that the \pm signs in front of the off-diagonal elements become identical, irrespective of the direction of magnetization. Under these circumstances the medium will display first-order MO effects even in M as the result of the appearance of the off-diagonal elements on magnetization together with smaller effects associated with the Q^2 term of the diagonal elements. This is what is observed in all measurements made.

The picture that emerges is therefore one in which the observed magnetic behaviour arises only from small regions uniformly dispersed throughout the processed disks in which it is further constrained to 2D sheets perpendicular to the plane of the disk surface. That is, there are small but extended regions in which spins couple along the chains together with some vertical coupling between the close stacked chains. The absence of any observable MO behaviour in the polar configuration attests the strength of the anisotropy energy associated with ordering in this manner. The spin vectors, and hence magnetization, are perpendicular to these planes so that the magnetization is confined to the plane of the disk, but randomly orientated within the plane such that there is no in-plane anisotropy. The strength of the apparent spin coupling at elevated temperatures remains puzzling but clearly the extent of the regions is sufficient for them to maintain ferromagnetic rather than superparamagnetic behaviour at room temperature. This could suggest that the anisotropy energy of the system is a significant factor in stabilising the reduced dimensional magnetism as discussed for the reduced dimensional cobalt system in Ref. [81].

4. Conclusions

We conclude that all experimental observations on this fully organic polymer **1** appear, surprisingly, to be commensurate with the development at room temperature of some form of magnetic state throughout very limited regions of the material. We appreciate that the appearance of an intrinsic magnetic component in the material studied is highly unlikely and that this current interpretation of the results presented is also strongly dependent on using MO evidence to support chemical analysis in precluding contamination. The apparent strength and stability of the exchange coupling is particularly puzzling and requires further detailed study. Chemical analysis has eliminated the possibility of contamination at a level required to produce the moment recorded and we can find no explanation of how contamination might yield the even MO effects observed. We therefore present the results for comment by the community.

Acknowledgements

The authors wish to thank the Faculty of Health and Life Sciences for financial assistance and thank Thor Bostrom (Queensland University of Technology, Australia) for TEM studies, Martin Vickers (Birkbeck College, UK) for support with the SEM studies, David Hunter (The University of Queensland, Australia) is thanked for ESR studies, Axel Handstein (Dresden High Magnetic Field Laboratory, Germany) for blind confirmatory magnetic measurements.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.synthmet.2013.03.010>.

References

- [1] A. Triebs, K. Jacob, *Angewandte Chemie International Edition* 8 (1965) 694.
- [2] A. Triebs, K. Jacob, *Liebigs Annalen der Chemie* 699 (1966) 153–167.
- [3] A. Triebs, K. Jacob, *Liebigs Annalen der Chemie* 712 (1968) 123–137.
- [4] P.M. Kazmaier, G.K. Hamer, R.A. Burt, *Canadian Journal of Chemistry* 68 (1990) 530–536.
- [5] L.P. Yu, M. Chen, L.R. Dalton, X.F. Cao, J.P. Jiang, R.W. Hellworth, *Materials Research Society Symposia Proceedings* 173 (1990) 607–612.
- [6] B. Patrick, M.V. George, P.V. Kamat, S. Das, K.G. Thomas, *Journal of the Chemical Society, Faraday Transactions* 88 (1992) 671–676.
- [7] S. Das, K.G. Thomas, P.V. Kamat, M.V. George, *Proceedings of the Indian Academy of Sciences (Chemical Science)* 105 (1993) 513–525.
- [8] M. Samoc, A. Samoc, B. Luther-Davies, M. Woodruff, *Pure and Applied Optics* 5 (1996) 681–687.
- [9] A. Ajayaghosh, C.R. Chenthamarakshan, S. Das, M.V. George, *Chemistry of Materials* 9 (1997) 644–646.
- [10] D.E. Lynch, U. Geissler, I.R. Peterson, M. Floersheimer, R. Terbrack, L.F. Chi, H. Fuchs, N.J. Calos, B. Wood, C.H.L. Kennard, G.J. Langley, *Journal of the Chemical Society, Perkin Transactions* 2 (1997) 827–832.
- [11] C.R. Chenthamarakshan, A. Ajayaghosh, *Tetrahedron Letters* 39 (1998) 1795–1798.
- [12] C.R. Chenthamarakshan, A. Ajayaghosh, *Chemistry of Materials* 10 (1998) 1657–1663.
- [13] D.E. Lynch, U. Geissler, N.J. Calos, B. Wood, N.N. Kinaev, *Polymer Bulletin* 40 (1998) 373–380.
- [14] D.E. Lynch, I.R. Peterson, M. Floersheimer, D. Essing, L.F. Chi, H. Fuchs, N.J. Calos, B. Wood, C.H.L. Kennard, G.J. Langley, *Journal of the Chemical Society, Perkin Transactions* 2 (1998) 779–784.
- [15] G.J. Ashwell, G. Jefferies, A. Green, K. Skjonnemand, N.D. Rees, G.S. Bahra, C.R. Brown, *Thin Solid Films* 327–329 (1998) 461–464.
- [16] C.R. Chenthamarakshan, J. Eldro, A. Ajayaghosh, *Macromolecules* 32 (1999) 251–257.
- [17] C.R. Chenthamarakshan, J. Eldro, A. Ajayaghosh, *Macromolecules* 32 (1999) 5846–5851.
- [18] D.E. Lynch, U. Geissler, K.A. Byriel, *Synthetic Metals* 124 (2001) 385–391.
- [19] A. Ajayaghosh, J. Eldro, *Organic Letters* 3 (2001) 2595–2598.
- [20] J. Eldro, A. Ajayaghosh, *Chemistry of Materials* 14 (2002) 410–418.
- [21] M. Buschel, A. Ajayaghosh, E. Arunkumar, J. Daub, *Organic Letters* 5 (2003) 2975–2978.

- [22] R. Bonnett, M. Motevalli, J. Siu, Squaraines based on 2-arylpyrroles, *Tetrahedron* 60 (2004) 8913–8918.
- [23] D.E. Lynch, Y. Nawaz, T. Bostrom, *Langmuir* 21 (2005) 6572–6575.
- [24] L. Beverina, A. Abbotto, M. Landenna, M. Cerminara, R. Tubino, F. Meinardi, S. Bradamante, G.A. Pagani, *Organic Letters* 7 (2005) 4257–4260.
- [25] S.J. Chung, S. Zheng, T. Odani, L. Beverina, J. Fu, L.A. Padilha, A. Biesso, J.M. Hales, X. Zhan, K. Schmidt, A. Ye, E. Zojer, S. Barlow, D.J. Hagan, E.W. Van Stryland, Y. Yi, Z. Shuai, G.A. Pagani, J.-L. Bredas, J.W. Perry, S.R. Marder, *Journal of the American Chemical Society* 128 (2006) 14444–14445.
- [26] A.C. Sant'Ana, L.J.A. de Siqueira, P.S. Santos, M.L.A. Temperini, *Journal of Raman Spectroscopy* 37 (2006) 1346–1353.
- [27] E.F. Huo, J.Y. Wu, B.F. Song, Y. Li, Q. Jiang, M.G. Xie, *Chinese Chemical Letters* 18 (2007) 1531–1534.
- [28] J.Y. Wu, E.F. Huo, Z. Wu, Z. Lu, M.G. Xie, Q. Jiang, *e-Polymers* 077 (2007) 1–10.
- [29] S. Sreejith, K. Divya, A. Ajayaghosh, *Angewandte Chemie International Edition* 47 (2008) 7883–7887.
- [30] L. Beverina, M. Crippa, M. Landenna, R. Ruffo, P. Salice, F. Silvestri, S. Versari, A. Villa, L. Ciaffoni, E. Collini, C. Ferrante, S. Bradamante, C.M. Mari, R. Bozio, G.A. Pagani, *Journal of the American Chemical Society* 130 (2008) 1894–1902.
- [31] F. Silvestri, M.D. Irwin, L. Beverina, A. Facchetti, G.A. Pagani, T.J. Marks, *Journal of the American Chemical Society* 130 (2008) 17640–17641.
- [32] D.E. Lynch, Particulate materials, US Patent 2008/0188611.
- [33] S. Hasegawa, M. Tian, Y. Ito, K. Hirokawa, M. Watanabe, M. Furuki, Black color material and toner, US Patent 2009/0240065.
- [34] M. Binda, T. Agostinelli, M. Caironi, D. Natali, M. Sampietro, L. Beverina, R. Ruffo, F. Silvestri, *Organic Electronics* 10 (2009) 1314–1319.
- [35] F. Silvestri, I. Lopez-Duarte, W. Seitz, L. Beverina, M.V. Martinez-Diaz, T.J. Marks, D.M. Guldi, G.A. Pagani, T. Torres, *Chemical Communications* (2009) 4500–4502.
- [36] L. Beverina, R. Ruffo, G. Patriarcar, F.D. Angelis, D. Roberto, S. Righetto, R. Ugo, G.A. Pagani, *Journal of Materials Chemistry* 19 (2009) 8190–8197.
- [37] W. Zhang, Z. Wang, Y.S. Tang, Z.G. Xu, Y. Li, Q. Jiang, *Chinese Chemical Letters* 21 (2010) 245–248.
- [38] H.-C. Lu, W.-T. Whang, B.-M. Cheng, *Chemical Physics Letters* 500 (2010) 267–271.
- [39] D. Bagnis, L. Beverina, H. Huang, F. Silvestri, Y. Yao, H. Yan, G.A. Pagani, T.J. Marks, A. Facchetti, *Journal of the American Chemical Society* 132 (2010) 4074–4075.
- [40] H.C. Lu, W.T. Whang, B.M. Cheng, *Synthetic Metals* 160 (2010) 1002–1007.
- [41] S. Begum, I.P. Jones, C. Jiao, D.E. Lynch, J.A. Preece, *Journal of Materials Science* 45 (2010) 3697–3706.
- [42] Q. Shi, W.-Q. Chen, J. Xiang, X.-M. Duan, X. Zhan, *Macromolecules* 44 (2011) 3759–3765.
- [43] W. Zhang, F. Tao, K. Meng, Z. Wang, L. Xi, Y. Li, Q. Jiang, *Journal of Material Science* 46 (2011) 5363–5370.
- [44] S. Paek, H. Choi, C. Kim, N. Cho, S. So, K. Song, M.K. Nazeeruddin, J. Ko, *Chemical Communications* 47 (2011) 2874–2876.
- [45] L. Beverina, M. Drees, A. Facchetti, M. Salamone, R. Ruffo, G.A. Pagani, *European Journal of Organic Chemistry* (2011) 5555–5563.
- [46] E. Collini, S. Carlotto, C. Ferrante, R. Bozio, A. Polimeno, J. Bloino, V. Barone, E. Ronchi, L. Beverina, G.A. Pagani, *Physical Chemistry Chemical Physics* 13 (2011) 12087–12094.
- [47] C.J. Ko, Y.L. Chang, Y.N. Hsiao, P.L. Chen, S.H. Lin, W.T. Whang, K.Y. Hsu, M.H. Tsai, W.Y. Tsang, *Journal of Modern Optics* 58 (2011) 1215–1219.
- [48] H.C. Lu, W.T. Whang, B.M. Cheng, *Journal of Materials Chemistry* 21 (2011) 2568–2576.
- [49] W. Zhang, F. Tao, K. Meng, L. Xi, Z. Wang, Y. Li, Q. Jiang, *Polymer Bulletin* 68 (2012) 349–360.
- [50] M.C. Ho, C.H. Chao, C.H. Chen, R.J. Wu, W.T. Whang, *Macromolecules* 45 (2012) 3010–3016.
- [51] L. Beverina, R. Ruffo, M.M. Salamone, E. Ronchi, M. Binda, D. Natali, M. Sampietro, *Journal of Materials Chemistry* 22 (2012) 6704–6710.
- [52] H.Y. Ahn, Y. Sheng, X. Wang, K.D. Belfield, *ACS Applied Materials & Interfaces* 4 (2012) 2847–2854.
- [53] S. So, H. Choi, H.M. Ko, C. Kim, S. Paek, N. Cho, K. Song, J.K. Lee, J. Ko, *Solar Energy Materials & Solar Cells* 98 (2012) 224–232.
- [54] E. Huo, D. Yang, Z. Zhang, Z. Lu, H. Sun, X. Xin, Y. Huang, Y. Liu, Q. Jiang, *Journal of Applied Polymer Science* 128 (2013) 1632–1639.
- [55] M. Sassi, M. Crippa, R. Ruffo, R. Turrissi, M. Drees, U.K. Pandey, R. Termine, A. Golemme, A. Facchetti, L. Beverina, *Journal of Materials Chemistry A* 1 (2013) 2631–2638.
- [56] S. Begum, I.P. Jones, D.E. Lynch, J.A. Preece, *Journal of Experimental Nanoscience* 7 (2012) 1–16.
- [57] U. Geissler, M.L. Hallensleben, N. Rhode, *Macromolecular Chemistry and Physics* 197 (1996) 2565–2576.
- [58] R. Carey, D.M. Newman, M.L. Wears, *Physical Review B* 58 (1998) 14175–14178.
- [59] S. Foner, *Review of Scientific Instruments* 30 (1959) 548–557.
- [60] J. Bernstein, E. Goldstein, *Molecular Crystals and Liquid Crystals* 164 (1988) 213–229.
- [61] Unpublished data.
- [62] T. Roth, G.L.J.A. Rikken, *Physical Review Letters* 85 (2000) 4478–4481.
- [63] T. Roth, G.L.J.A. Rikken, *Physical Review Letters* 88 (2002) 063001.
- [64] G.L.J.A. Rikken, C. Strohm, P. Wyder, *Physical Review Letters* 89 (2002) 133005.
- [65] J.Q. Xiao, J.S. Jiang, C.L. Chien, *Physical Review Letters* 68 (1992) 3749–3752.
- [66] J.S. Miller, *Advanced Materials* 4 (1992) 435–438.
- [67] A.A. Ovchinnikov, *Theoretica Chimica Acta* 47 (1978) 297–303.
- [68] Y.V. Korshak, T.V. Medvedeva, A.A. Ovchinnikov, N.V. Spector, *Nature* 326 (1987) 370–372.
- [69] M.M. Matsushita, A. Izuoka, T. Sugawara, T. Kobayashi, N. Wada, N. Takeda, M. Ishikawa, *Journal of the American Chemical Society* 119 (1997) 4369–4379.
- [70] A. Rajca, J. Wongsriratanakul, S. Rajca, R. Cerny, *Angewandte Chemie International Edition* 37 (1998) 1229–1232.
- [71] T.L. Makarova, B. Sundqvist, R. Höhne, P. Esquinazi, Y. Kopelevich, P. Scharff, V.A. Davydov, L.S. Kashevarova, A.V. Rakhmanina, *Nature* 413 (2001) 716–718.
- [72] A. Rajca, J. Wongsriratanakul, S. Rajca, *Science* 294 (2001) 1503–1505.
- [73] N.A. Zaidi, S.R. Giblin, I. Terry, A.P. Monkman, *Polymer* 45 (2004) 5683–5689.
- [74] S.J. Blundell, F.L. Pratt, *Journal of Physics: Condensed Matter* 16 (2004) R771.
- [75] Y. Wang, Y. Huang, Y. Song, X. Zhang, Y. Ma, J. Liang, Y. Chen, *Nano Letters* 9 (2009) 220–224.
- [76] S. Vandeelen, M. Jivanescu, A. Stesmans, J. Cuppens, M.J. Van Bael, H. Yamada, N. Sato, T. Verbiest, G. Koeckelberghs, *Macromolecules* 43 (2010) 2910–2915.
- [77] S. Vandeelen, M. Jivanescu, A. Stesmans, J. Cuppens, M.J. Van Bael, T. Verbiest, G. Koeckelberghs, *Macromolecules* 44 (2011) 4911–4919.
- [78] H. Fukutome, A. Takahashi, N. Matsumoto, *Chemical Physics Letters* 133 (1987) 34–38.
- [79] K. Tanaka, H. Ago, T. Yamabe, *Synthetic Metals* 72 (1995) 225–229.
- [80] P. Gangopadhyay, G. Koeckelberghs, A. Persoons, *Chemistry of Materials* 23 (2011) 516–521.
- [81] P. Gambardella, A. Dallmeyer, K. Malti, M.C. Malagoll, W. Eberhardt, K. Kern, C. Carbone, *Nature* 416 (2002) 301–304.
- [82] M. Wohlgenannt, Organic magnetoresistance and spin diffusion in organic semiconductor thin film devices, *Physica Status Solidi (RRL)* 6 (2012) 229–242.