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Exploring Novel Spintronic Responses from Advanced Functional Organic Materials

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Exploring Novel Spintronic Responses from Advanced Functional Organic Materials

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ABSTRACT

Magneto-optical properties of different organic molecules, mesogenics and conjugated polymers, mainly poly(3-alkylthiophene)s, have been investigated by Faraday rotation (FR) measurements and Verdet constants determined.
New materials have been developed based upon macrocycles of conducting polythiophenes. In view of the complexity of such materials all structures have been simulated by quantumchemical methods, also as guidance to synthesis. We initiated experiments on “super”macrocycles which are 2D polymers reminiscent of graphene. Semi-empirical calculations indicate the important structure of such new polymeric structures.
SQUID and FR measurements on a macrocycle of polythiophene, with a vinyl closure of the ring, indicated the crucial role of conjugation in the ring. The negative results obtain for this material, i.e. very low magnetic moments from SQUID and low FR at cryogenic temperature, could be explained by DFT calculations showing a break in conjugation by the vinyl closure.
To assess hyperpolarisability tensor components, electric as well as magnetic, of the materials investigated we developed a new instrument that allows measuring spatial dependence of linear and nonlinear light scattering (HRS). These data is very important since the Verdet constant (FR) is related to the nonlinear magnetic susceptibility.

INTRODUCTION

Spintronics is an analogue of electronics but relying upon the spin of the electron and not the charge. Spintronics is exploiting the ability of conduction electrons to carry spin-polarized current. At this moment research in spintronics focuses on metals and inorganic semiconductors as basic materials to develop new techniques for information processing. The two states of electron spin, up and down, or standing for 1 and 0, are naturally adapted to digital information processing.

An essential prerequisite for spintronics is 1) the formation of spin-polarized currents and 2) the preservation of the spin orientation, or the spin transport. Spin-polarized currents are usually obtained by injection from ferromagnetic electrodes into the spin-conduction material. The preservation of spin orientation has also some intricate problems due to spin-spin interaction (spin – nuclear charge) and hyperfine interaction (spin – nuclear spin), both effects perturbing the spin orientation. Since these perturbing effects are both stronger for heavy atoms (proportional to Z^4) organic materials, with the lighter atoms, could become materials of choice for spintronic applications since the (very) weak spin-orbit interaction results in large spin-relaxation times. This makes organic semiconductors very valuable candidates for organic spintronics although electron mobility in these materials is rather low and has concomitantly complex transport mechanisms. It is also fair to say that injection of spin-polarized carriers from a ferromagnetic electrode into an organic layer is still a vexing problem where many open questions remain. The generation of spin-polarized currents in chiral (semi-)conducting polymers will be a valuable pathway to implement organic spintronics.

Emerging from our research is therefore the importance of magnetic properties of organic molecules. Intrinsically magnetic properties of organic materials are essential basic data for organic spintronics.

I. Magnetic properties of organics - Motivation

Based upon the long standing experience of our group in nonlinear magneto-optics of organic media we focused in our part of the project on studies of the Faraday rotation of an array of organic molecules and conjugated polymers
.
Taking into account magnetic interactions we have to write for nonlinear polarizations: Commonly the fundamental equation governing nonlinear optics is the optical polarization written as a series expansion of the electric field strength in the optical field:

$$\mathbf{P}(\omega) = \chi^{(1)}\mathbf{E}(\omega) + \chi^{(2)}\mathbf{E}^{(2)}(\omega) + \chi^{(3)}\mathbf{E}^{(3)}(\omega) + \ldots$$

here the linear term in E(ω) describes most, if not all, of linear optics, as the constitutive equation in Maxwell's equations, while the higher terms describe the nonlinear response. $\chi^{(2)}$ $\chi^{(3)}$ are second, third order terms, the nonlinear susceptibilities, tensors of the third and fourth order. It is important to see that uneven nonlinear susceptibilities are present in all matter while the second-order (or even-order) susceptibility tensor $\chi^{(2)}$ is strictly absent in a centrosymmetric system, molecule or crystal, *within the electric dipole approximation*. This approximation is in fact the neglect of magnetic effects, usually validated in most cases by the fact that magnetic forces are extremely small compared to electric forces. However in some, and very important phenomena, the neglect of magnetic effects is not allowed. For example, to understand optical activity in molecules or crystals it is absolutely necessary to take into account magnetic interactions, *linking chirality with magnetic effects*.

In this research we focused exclusively on the second-order nonlinear polarization at the optical frequency ω and we take into account magnetic interactions:

$$\mathbf{P}^{\mathrm{NL}}(\omega) = \chi^{\mathrm{eee}}\mathbf{E}^{(2)}(\omega) + \chi^{\mathrm{eem}}\mathbf{E}(\omega)\mathbf{B}(\omega)$$

We write χ^{eee}, resp. χ^{eem} for the usual $\chi^{(2)}$ susceptibilities as a useful bookkeeping method. The two last superscripts indicate the process in which two photons from the fundamental beam are annihilated in a second harmonic generation process while the first superscript indicates the process in which the second-harmonic photon is formed (e meaning electric dipole interaction and m magnetic dipole interaction). For the case of second harmonic generation "eem" will thus indicate the annihilation of one photon in the electric dipole interaction, one in the magnetic dipole, and a new photon at double frequency generated in the *electric dipole* interaction. It is intuitively clear that we may ask also about the meaning of the superscript mee, being two photons annihilated in the electric dipole interaction and the harmonic photon created in a *magnetic dipole* interaction. We have to introduce a new nonlinear term, the magnetisation:

$$\mathbf{M}^{\mathrm{NL}}(\omega) = \chi^{\mathrm{mee}}\,\mathbf{E}^{2}(\omega)$$

It is also very important to realize that the tensor χ^{eee} has a different spatial symmetry compared to the tensors χ^{eem} and χ^{mee}. Indeed, the "magnetic" tensors are present in all matter whatever the symmetry – easily understood if it is noted that magnetic fields are described by axial vectors, not changing sign upon inversion. This has important practical applications: a material with e.g. a large χ^{eem} could efficiently be used for second harmonic processes without the stringent requirement of noncentrosymmetry – a requirement which has been a stumbling block in the development of organic nonlinear devices.

It is now instructive to consider a Taylor series expansion of the polarization as a function of electric and magnetic field, P = P(E,B):

$$\mathbf{P(E,B) = P(0,0)} + \left(\frac{\partial \mathbf{P}}{\partial \mathbf{E}}\right)\mathbf{E} + \frac{1}{2}\left(\frac{\partial^2 \mathbf{P}}{\partial^2 \mathbf{E}}\right)\mathbf{E}^2 + \left(\frac{\partial \mathbf{P}}{\partial \mathbf{B}}\right)\mathbf{B} + \left(\frac{\partial^2 \mathbf{P}}{\partial \mathbf{E}\, \partial \mathbf{B}}\right)\mathbf{E\ B}$$

We can write $\left(\frac{\partial^2 \mathbf{P}}{\partial \mathbf{E}\, \partial \mathbf{B}}\right)\mathbf{E\ B}$ also as $\frac{\partial}{\partial \mathbf{B}}\left(\frac{\partial \mathbf{P}}{\partial \mathbf{E}}\right)\mathbf{E\ B} = \left(\frac{\partial\, \varepsilon}{\partial \mathbf{B}}\right)\mathbf{E\ B}$

where ε is the dielectric constant. From the general equation for P we see therefore that:

$$\left(\frac{\partial\, \varepsilon}{\partial\, \mathbf{B}}\right) = \chi^{\mathbf{eem}}$$

Experimentally the dependence of the dielectric constant upon magnetic field is very difficult to measure. However, χ^{eem} is easy accessible from Faraday rotation measurements. Faraday rotation, the rotation of the plane of polarization of light due to magnetically induced circular birefringence, is described by $\theta = \mathbf{V}\, B\, L$, where θ is the rotation angle, B is the component of the magnetic field parallel to the propagation of the light, L the sample length and **V** the Verdet constant, a phenomenological constant which measures the strength of the Faraday rotation.
This Verdet constant can be related to χ^{eem} by an equation derived from the nonlinear polarization $\mathbf{P}^{\mathbf{NL}}$:

$$\mathbf{V} = \frac{\mathbf{4\pi^2}}{\mathbf{n}\ \lambda}\, \mathbf{i}\, \chi^{\mathbf{eem}}$$

where n is the index of refraction of the medium, λ the wavelength; i is the imaginary unit, present since χ^{eem} is a complex quantity out of phase with χ^{eee}.

This equation is the core equation for all our studies of magnetic and magneto-optical properties of organic systems and is a guideline for this report. It should be noted that this equation is fully confirmed experimentally from second harmonic generation of thin films of polythiophenes whereby χ^{eem} Is obtained in full accordance with the independently measured Verdet constant.

[See: A. Persoons, “*Nonlinear optics, chirality, magneto-optics: a serendipitous road [invited]*” Optical Materials Express, **1**, 5-16 (2011)]

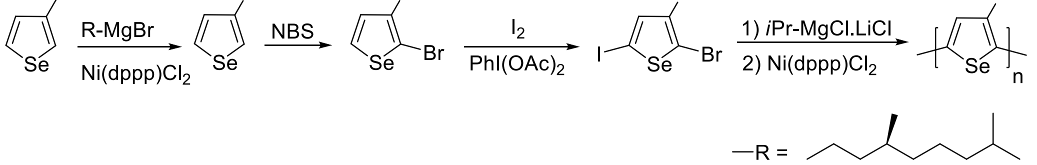
II. Structure-Property relations.

Few structure-property relations for magneto-optical properties of organics are as yet available and, still puzzling, no full explanation for the often very large Faraday rotation of some organics is as yet available. Furthering the hypothesis that spin-orbit coupling may be of importance we investigated the Faraday rotation of polyselenophene to see if a “heavy-atom effect” (Se is about 3 times heavier than S) may result in a more pronounced spin-orbit coupling and hence more pronounced magnetic properties.

A. Polyselenophene

The synthesis of a chiral, regioregular poly(3-alkylselenophene) (P3AS) was targeted. We prefer chiral polymers for the reduction in symmetry often simplifying analysis of NLO experiments.

The synthesis started from selenophene, which was converted to 3-iodothiophene using well-known procedure. Subsequently a Kumada coupling introduced the chiral substituent that was prepared from commercial citronellol in two steps. Bromination using *N*-bromosuccinimide (NBS), followed by iodination with I_2 and iodobenzene diacetate furnished the precursor monomer. It was chosen to use the monobromo-monoiodo compound and not the dibromo analogue, which was already successfully used for the synthesis of P3AS, to obtain a polymerization with maximal features of a living polymerization. The polymer itself was prepared by a selective GRIM using *i*PrMgCl.LiCl at 0°C, followed by the addition of Ni(dppp)Cl_2 (dppp = 1,3-bisdiphenylphospinopropane). After work-up and purification, regioregular P3AS was obtained. ^{1}H NMR analysis confirmed the very high degree of regioregularity – apart from the inevitable presence of one TT-coupling, no defects were found. GPC revealed a Mn = 9,9 kg/mol and a very low polydispersity of 1.1, indicative for a living polymerization.



Synthesis of the poly(3-alkylselenophene).

The Faraday rotation of spincoated films from this polyselenophene showed a surprisingly low value of the Verdet constant. There is clearly no heavy-atom effect present. Indeed analoguous spincoated films of polythiophene show a vey large Faraday rotation At this moment the study of polyselenophenes has been discontinued, but the material is available and will be studied again after some quantum-chemical calculations and simulations.

B. Polythiophenes

Extensive studies, over many years, have consistently shown that Faraday rotation in polythiophene-films (and analogues) is often irreproducible. Recently it became clear that this is might be due to aggregation effects. Indeed, the Faraday rotation properties of polythiophenes in thin films or solid state depend in general on factors such as annealing history, surface treatment of the substrate, spincoating or drop casting solvent,… and while solid samples are desirable for applications, from a fundamental point of view it makes more sense to determine Faraday rotation of molecularly dissolved polythiophene in solution.

To separate molecular effects in Faraday rotation from the (deleterious?) effects of aggregation phenomena we investigated Faraday rotation in poly(3-hexylthiophene) in solution of a good solvent (THF). In order to be able to perform measurements over a very broad wavelength range, an experimental set-up was constructed consisting of a very stable laser pumped xenon lamp, a photo-elastic modulator and a superconducting tabletop magnet.

In the figure we show a measurement of Faraday rotation of a THF solution of poly(3-hexylthiophene) at a concentration of 0.3 mg/ml for two different path lengths (1 mm and 2 mm).

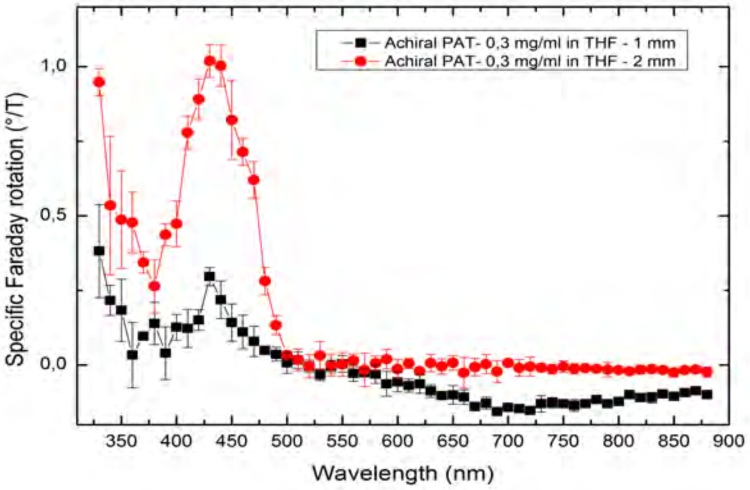


Fig. 1 Faraday rotation of poly(3-hexylthiophene) in THF solution.

It can be clearly seen that Faraday rotation is strongly wavelength dependent and that there is a very strong Faraday rotation (up to 1°/T) in the region below 500 nm, which is due to the presence of a strong resonance. If we assume that the density of pure (solid) polythiophene is on the order of

1000mg/ml, then we can estimate the Verdet constant of solid polythiophene as follows: if a 2 mm path length and 0.3 mg/ml yields a rotation of 1°/T, then 1000mg/ml would yield a rotation of 3333 °/T. Using this value and $\theta = VBL$, we obtain a Verdet constant $V = 1.67\text{x}10^{6}$ °/Tm, an order of magnitude higher than what is usually observed for polyalkylthiophenes in the solid state. Off course, in the solid state polythiophene is present in an aggregated form which does not correspond to the structure in solution. Nevertheless, this seems to indicate that up to now we have not been able to fully exploit the potential of polyalkylthiophenes in terms of Faraday rotation.

Therefore, it is interesting to see what happens when we induce aggregation by adding nonsolvent (typically methanol). This is shown in Fig. 2. It is clear that Faraday rotation strongly decreases upon adding nonsolvent and is present in its aggregated state. Typically Faraday rotation decreases by a factor 3 to 4 which would give a Verdet constant on the order of $5\text{x}10^{5}$ °/Tm, close to what is usually observed in solid samples.

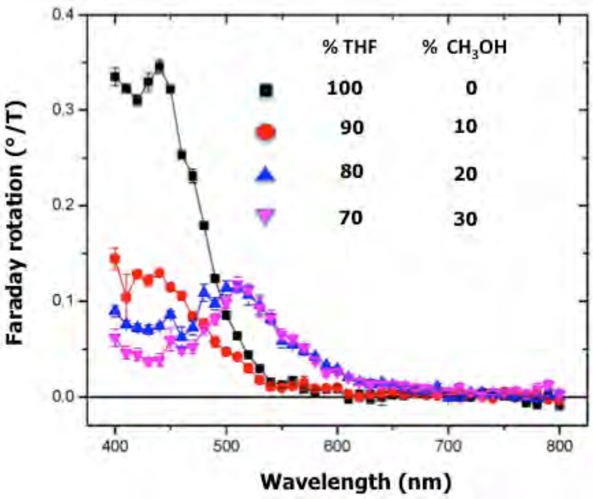


Fig. 2. Faraday rotation in solutions of poly(3-octylthiophene) in different solvent compositions (concentration 0.25 mg/ml, sample cell 1 mm)

Finally, we would like to note that Faraday rotation in solution strongly depends on how well the polythiophene is dissolved – which may partly explain the weak Faraday rotation observed in the measurement of polyselenophene solutions. Temperature and solvent seem to be very important parameters. For example, we have indications that if a polythiophene is not well dissolved the Faraday rotation can completely disappear. This seems to agree with the fact that aggregation is an important factor for Faraday rotation. We are currently investigating into more detail how these factors exactly influence the Verdet constant.

Results published in: P. Gangopadhyay, G. Koeckelberghs and A. Persoons, "*Molecular Magneto-optics*" Proc. SPIE 9181, 91810L (2014)

In order to tackle the influence of supramolecular organization, a series of regioregular P3ATs with an increasing degree of bulkiness of the alkyl side chain has been successfully synthesized with Ni(dppp)Cl_2 as a catalyst. UV-Vis spectroscopy was used to study the supramolecular aggregation of the polymer both in poor solvent and in film. More in particular, deconvolution of the spectra allowed to “quantify” the π-interactions and planarization of the polymer chains. It was shown that as the bulkiness of the polymers’ side chain increases, the π-interactions and planarization diminishes. In poor solvent, the polymer with the most bulky substituent does not aggregate, while in film, this polymer does stack, showing a band originating from π-interactions, but the aggregate formation takes 30-45 minutes to occur. This delayed aggregation was confirmed by DSC measurements; XRD measurements confirmed that powders of all polymers are semi-crystalline. ESR measurements, performed on powder samples at 300 K, revealed a steady increase in linewidth and change in shape of the singly observed signal as the polymers’ substituent becomes more bulky, which denotes an increase in disorder. Thus, the ESR data reflect the same trend as previously found from the optical data.

Results published in: H. Peeters et al., “*Influence of the Bulkiness of the substituent on the aggregation and Magnetic Properties of Poly(3-alkylthiophene)s*” J. Polymer Science Part A-polymer chemistry, **52**, 76-86 (2014)

Extensive efforts to synthesize poly(3-alkylthiophenes) highly regioregular in the polymer chain but randomized in the alkyl-groups, e.g. a random sequence of hexyl, dodecyl, methyl… which would prevent aggregation in the solid state were initiated. The aim is to obtain polythiophenes (films of) polythiophenes as amorphous as possible. A major difficulty, not yet solved, is to obtain a regioregular polymer that is 100% amorphous. Copolymers hexyl-dodecyl, ethylhexyl-dodecyl and hexyl-ethoxyhexyl have been synthesized and extensively characterized. However all these polymers were crystalline, at different composition and temperature. The synthesis of a copolymer with alkyl-cyclohexyl is currently underway.

To better assess the physico-chemical properties of polythiophenes a thorough study of the hydrodynamics and conformations of regioregular poly(3-hexylthiophene) was carried out. Hydrodynamic properties and conformational characteristics of poly(3-hexylthiophene) (P3HT) were studied in chloroform solutions. The values of specific partial volume and intrinsic viscosity [η] of the polymer were determined. The values of translational diffusion coefficients D were determined by dynamic light scattering while isothermal translational diffusion obtained from the sedimentation data. Good agreement between the values of D obtained by different methods was obtained. Diffusion coefficients for individual macromolecules were determined. The obtained values of D, [η] and flotation coefficients (s_0) were used to calculate characteristic values of molecular masses according to the Svedberg formula. The Mark-Kuhn-Houwink equations for [η], D and s were obtained. The exponents in the equations for translational diffusion coefficient and intrinsic viscosity are higher than 0.5. The value of the Tsvetkov-Klenin constant was calculated; it significantly exceeds the value of this constant indicating a Gaussian coil conformation. Hydrodynamic properties of molecules were analyzed within the framework of the worm-like spherocylinder and the straight spherocylinder. The length of a monomer unit projection onto the extended macromolecule was determined (λ = 0.37 nm); this value correlates well with the corresponding value for poly(3-alkylthiophenes). Conformational parameters of the polymer were calculated (equilibrium rigidity AD = 6.7 nm, $A[\eta]$ = 6 nm, and hydrodynamic diameter of a molecule d = 0.9 nm). This work was carried out in close collaboration with A Yakimansky, Russian Academy of Sciences, St Petersburg, Russia.

This work is submitted for publication to Macromolecules: A. Yakimansky et al., "*Poly(3-hexylthiophene): hydrodynamic properties and conformation in dilute solutions"*

C. Mesogenic organics

For practical applications of Faraday rotation of organics linear absorption is often detrimental especially when thick samples are required. This motivated our continuous search for molecules with (very) high Verdet constants and concomitant low linear absorption. In search of these properties, we studied Faraday rotation in mesogenic organic molecules, an unexplored class of molecules for these magnetic effects. A Verdet constant of almost 2.5 10^5 deg/Tm at 520 nm was found for the mesogenic material TTB ((1,3,5-tris[(4-nitrophenyl)ethynyl]-2,4,6-tris(n-decyloxy)-benzene). This Verdet constant is *three orders* of magnitude larger than the largest known for organic molecules in a region *without* spectral features. This extremely large Faraday rotation is attributed to a resonant enhancement by a triplet excitation not appearing in the linear absorption spectrum and to near-resonant enhancement by low-energy singlet excitations. Furthermore we are able to switch the Faraday rotation by changing the liquid crystal phase of the compound. These results demonstrate a new class of Faraday rotating materials with great potential to replace current materials and improve existing applications. The inherent flexibility in the synthesis of this class of molecules opens a new field of research in Faraday rotation.
This work is carried out in collaboration with the group of Guenther Hennrich, University of Madrid, Spain.

Some of our results on Faraday rotation in a film of TTB are presented in Fig. 3. The large value of the Verdet constant around 520 nm is associated with a triplet excited state not visible in the absorption spectrum. In this figure we also indicate the changes in Faraday rotation with the changes in phase of the liquid crystalline material. Faraday rotation is almost completely absent in the isotropic phase.

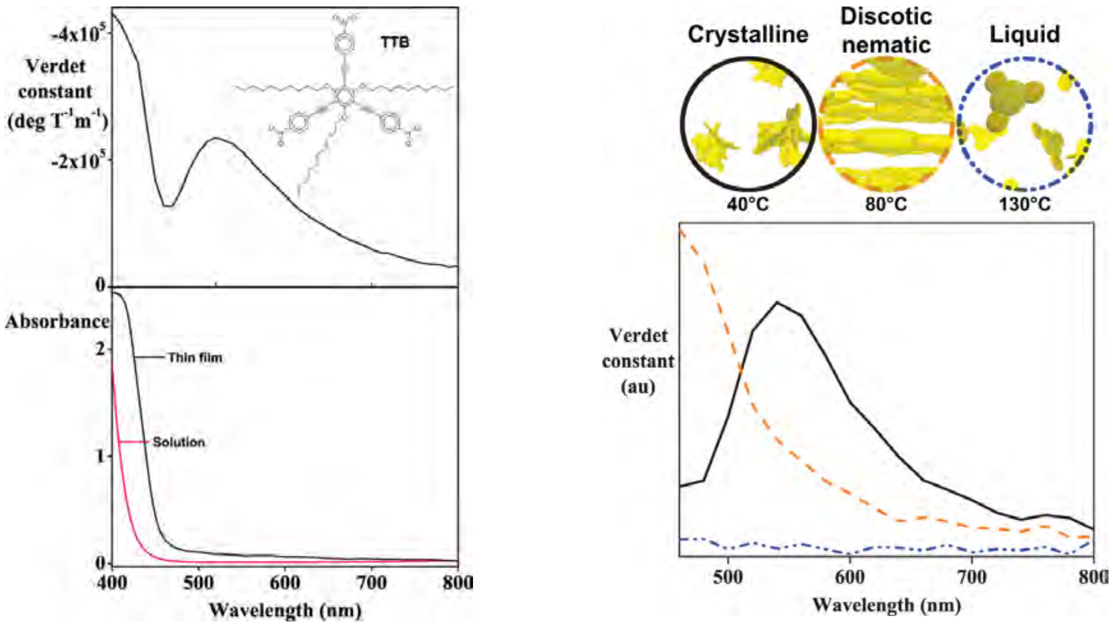


Fig. 3 Faraday rotation spectrum and UV-Vis spectrum of a 1.8 µm film of TTB.

This work was published by the Leuven group (S. Vandendriessche et al. “*Giant Faraday Rotation in Mesogenic Organic Molecules*” Chem. Mater. **25**, 1139–1143 (2013).

D. Small molecules

We set up, together with Benoit Champagne, Université de Namur, Belgium, a long standing program to investigate small molecules whereby the Verdet constant can be obtained from quantumchemical calculations. [See: E.Botek et al., “*Theoretical evaluation of the Faraday effect in organic compounds*” Computing Letters (CoLe), 3, 193-200 (2007)].

In this project we investigated the Faraday rotation from phenylacetylene derivatives. The Faraday rotation is measured in a standard set-up whereby the compounds are melted and drawn into 3 micron LC cells through capillary action. For phenylacetylene no meaningful Faraday rotation could be measured while there is a relatively large Faraday rotation for the higher homologues diphenylacetylene and 1,4 bis(phenylethynyl)benzene although no increase upon going to the higher homologue. For diphenylacetylene a reasonably large Verdet constant of 188000 deg/Tm was obtained at 420 nm. However, these preliminary results have to be carefully checked because we observed a thickness effect, e.g. the Verdet constant for diphenylacetylene at 420 nm was reduced to 79000 deg/Tm in a cell of 5 micron thickness. This could be due to surface effects or different contributions of the cell windows.

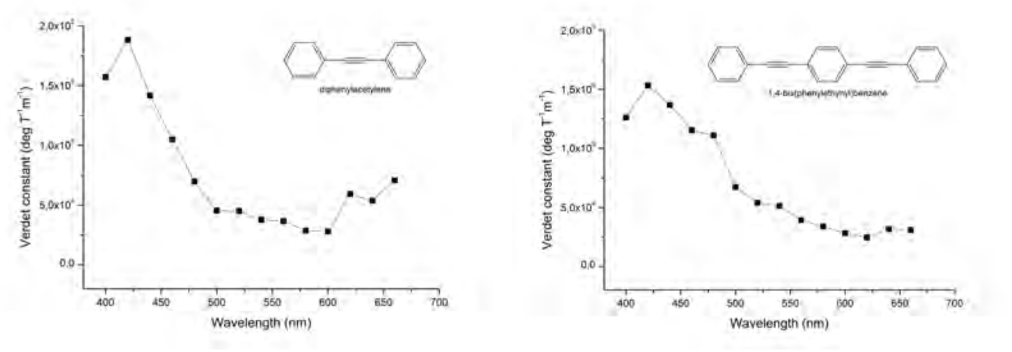
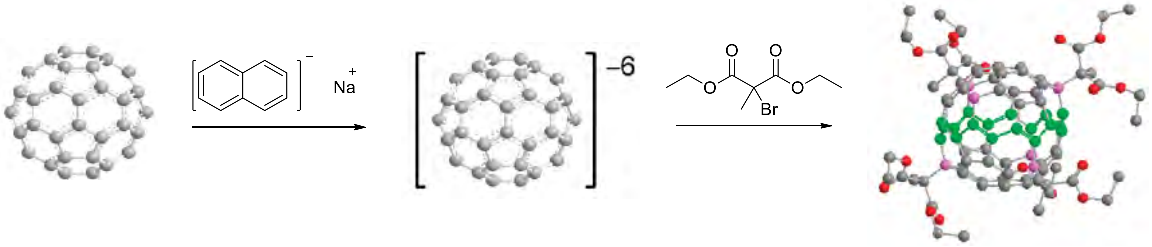


Fig. 4 Verdet constants as function of wavelength (400 – 625 nm) for diphenylacetylene and1,4 bis(phenylethynyl)benzene

Recently we started also the synthesis of D_{3d}-2-methylmalonato[60]fullerene. This molecule, actually a stable form of [18] annulene, is actually obtained by “killing” the electronic conjugation in the northern and southern hemisphere of C60. Theoretical calculations on the hyperpolarisability and Verdet constant of this [18] annulene, a prototype of a ring-structure with a potential for magnetic properties, are initiated.



The synthesis was done according to the procedure described by Popov et al. (A. Popov et al., J. Phys. Chem. Lett., 2011, **2**, 2296-2299). In the article by Popov, the product is purified by PTLC (THF/Toluene 1/9). However, we did not manage to purify the product in this manner. The remaining naphthalene was removed in vacuo. There is however still a small amount of naphthalene remaining. NMR analysis was carried out on the synthesized sample. Since the compound obtained is very poorly soluble in $CDCl_3$. NMR’s are taken in CS_2 with a small amount of deuterated solvent to lock the magnetic field. ^{1}H-NMR was taken in CS_2 with a small amount of $CDCl_3$. The compound does not give an intense NMR-signal, so the spectrum is dominated by pentane and water. The small peaks could tentatively be attributed to the compound. However, the presence of unreacted C_{60}-fullerene cannot be excluded, since it gives no signal.

^{13}C-NMR is taken in CS_2 with a small amount of benzene-d6. The spectrum only shows small peaks at 128.3 ppm and 126.2 ppm apart from the benzene-triplet at 128 ppm. These peaks do not originate from C_{60}-fullerene.

III. Multi-angle Hyper-Rayleigh Scattering.

Faraday rotation can be theoretically linked to second-order magneto-optical susceptibilities that are also responsible for magnetic-dipole allowed second-harmonic generation. In solid samples (e.g. thin films), it is very straightforward to measure these susceptibilities using second-harmonic generation and relate these to Faraday data. However, in solution it remains a challenge to determine these susceptibilities since many tensor components may be present, electric dipole (χ^{eee}), and magnetic dipole (χ^{eem} and χ^{eme}) nonlinear susceptibilities, each with their intricate symmetry dependence. We are currently studying all these relations from a theoretical point of view to see how we can extract all the relevant components. At this time theoretical developments to link all the tensor components to the observed hyper-Rayleigh-Scattering are still in progress but it turns out to be an intricate major and new problem in statistical physics and will require an intense study of the relations between the molecular properties and the macroscopically observed scattering. Especially the relations as a function of the polarization states of incoming fundamental and of the hyperscattered light at different angles is a major theoretical problem. Moreover it should be noted that, although all χ^{eee} components are absent from isotropic solutions, this is not the case for the molecular hyperpolarisabilities since hyperscattering (HRS) is caused by orientational fluctuations. We have therefore to take into account not only the components of the β^{eee}-tensor but also components of the β^{eem}- and β^{mee}-tensors – with the additional complication that these tensors have different symmetries. A potential approach is to isolate scattering from the β^{mee}-tensor components since this is *magnetic* dipole scattering with a scattering pattern markedly different from electric dipole scattering (β^{eee} and β^{eem}). This may be a guideline for the experimental approach envisioned. These studies would address the measurement of β^{mee} and β^{eem}, molecular parameters as yet never investigated.

We developed a very involved but simple, yet elegant method based on angle dependent hyper-Rayleigh scattering to determine these components of the nonlinear second order susceptibilities. In our new approach the excitation light is strongly focused and excites a very small volume of solution inside a cuvette. To a good approximation such a small volume may be considered as a point source. The scattered light at the double frequency is then collimated by a collector lens with a high numerical aperture, and focused by a second lens (see figure 1). In the focal point of the system all angular resolution is lost, but before (or after) this point the projection of the light (e.g. on a screen) transforms the angular distribution into a spatial distribution. Indeed, it is obvious that scattering in the forward direction will project axially with the optical system (coordinate (0,0)), while higher angles will be projected at higher coordinates.

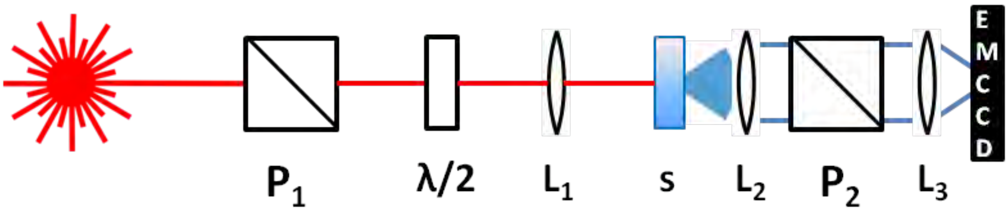


Fig. 5. Schematic depiction of the new experimental HRS set-up.

The general concept of the new technique is explained in figure 5. The polarization of the fundamental laser light (red) is controlled by a combination of a polarizer (P_1) and a motorized halfwaveplate (λ/2). The laser light is then focused inside a cuvette containing the sample. The generated HRS pattern is then imaged onto an electron multiplied CCD camera with near single-photon sensitivity by a combination of lenses. A second polarizer (P_2) on a motorized rotation stage can be mounted in the detection system to select s or p-polarized components of the HRS generated. Appropriate long pass and short pass filters to filter out SHG from the optical set-up and laser light are used.

Although we originally planned to use an array of 16 fibers to detect the spatially resolved angular scattering pattern, we preferred a more efficient and simpler detection using an EMCCD camera (Andor, Ixon 897). This allows for a much higher sensitivity and resolution, almost continuously at an angular cone of 70°. To avoid chromatic aberrations and unwanted internal reflections (lens flare) parabolic mirrors are used to focus and collimate the light (with the focal volumes of the focusing and collecting lens matched to avoid aberrations). These have the additional advantage that higher NA's can be achieved. *In this way a range of 70° and more can be collected by one mirror and with very high spatial resolution.* Two collecting mirrors are placed at 90 and 180° to achieve all possible angular information. Appropriate filters are used to filter out the excitation light. All angles are detected at once by a highly sensitive detector (approaching 1 photon sensitivity) that makes this a new instrument unique for the study of linear and nonlinear light scattering. Moreover the simultaneous detection allows also the study dynamic processes. Further work is still in progress, especially to investigate the best approach to disentangle electric dipole and magnetic dipole scattering, linear as well as nonlinear, which may be possible in view of the high spatial resolution.

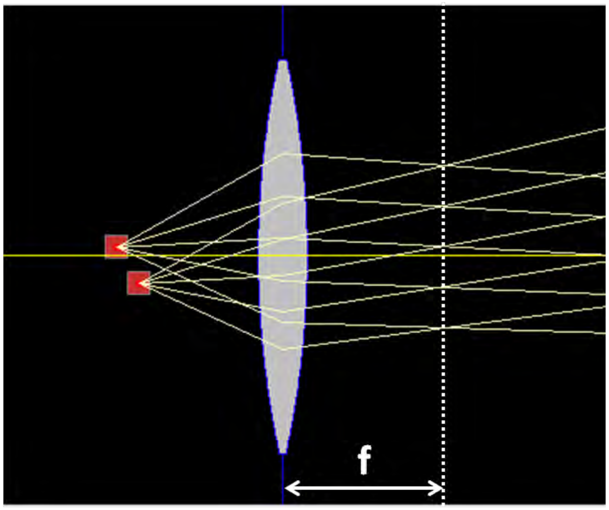


Fig. 6. In the back focal plane or Fourier of a lens, the incident angle of scattered light transforms into position, regardless of the position of the scatterer. Scattering particles are depicted as point sources (squares), in the back focal plane (dashed line) a scattering pattern is formed.

A well-known problem arises when the system under investigation is (multi-photon) fluorescent at the second-harmonic wavelength, i.e. the fluorescence contribution cannot be filtered out. We use an imaging spectrometer (Bruker 500IS, magnification=1) to separate fluorescence from hyper-Rayleigh scattering. In the focal point of this system the spectrometer produces a line, spatially resolving different wavelengths on the detector. However, in the orthogonal direction the spectrometer simply collimates and focuses the light. This again allows measuring the angular distribution in one direction and the spectral distribution in the other. This way the fluorescence contribution can be accounted for at all times.
A rather difficult experimental problem is also the low to very low intensity of the hyperscattered light spread over a wide spatial region.

This new instrument is a very complex optical instrument – developed with the aid of astronomers – but essentially simple to operate.

IV Macrocycles of thiophenes.

From previous studies of Faraday rotation of polythiophene films we obtained some evidence that circular or toroïdal structures may be of relevance to explain the extremely strong Faraday. This has led us to the hypothesis of *persistent currents* in organic systems with the concomitant presence of magnetic moments, in analogy of the persistent currents observed in mesoscopic metal rings. Essential to pursue and test this hypothesis the availability of macrocyclic structures of polythiophenes (or analogous conjugated polymers) is a first requirement, together with SQUID measurements on these structures (neat or in solution).

The synthesis of such macrocycles has been started together with the group of Philippe Dubois and coworkers at the University of Mons, Belgium (Olivier Coulembier, et.al. "*Macrocyclic regioregular poly(3-hexylthiophene): from controlled synthesis to nanotubular assemblies*" Polym. Chem., 2013, 4, 237). First measurements on these macrocycles indicate also a large Faraday rotation, comparable to the values observed in polythiophenes. The first measurements of Faraday rotation on a "Coulembier"macrocycle (Macrocyclic regioregular poly(3-hexylthiophene)) in solution (chloroform), at a concentration of 0.7 mg/ml, are shown in the figure 7.

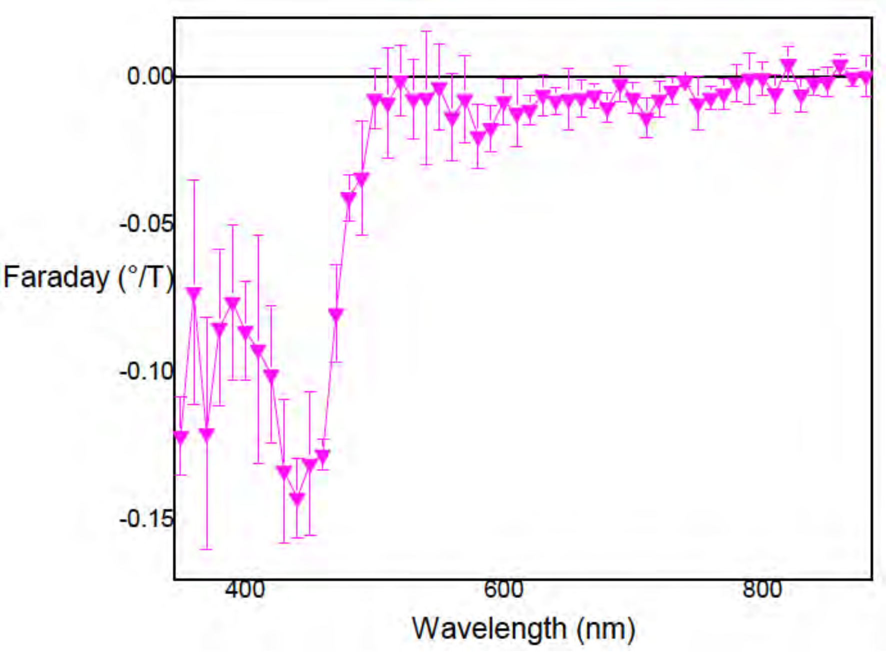


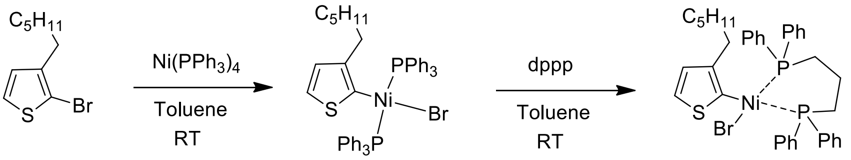
Fig. 7 Faraday rotation spectrum of a solution of the "Coulembier" macrocycle in chloroform solution at room temperature.

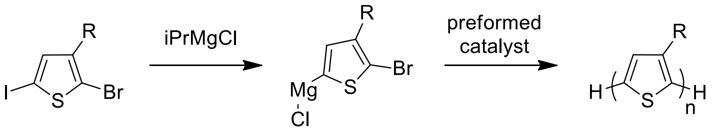
A extensive program on synthesis of fully conjugated macrocycles was initiated together with the group of Philippe Dubois, University of Mons. From our experience with the role of regioregularity in magnetism of polythiophenes our attention was strongly focused on regioregularity aspects in the macrocycle – although complicating often synthesis.

A regioregular macrocycle (RR-MC) was first obtained by the use of preformed catalyst on alkylthiophene. The alkyl chain is oriented in favor of the head to tail coupling reaction during the first step of polymerisation.

A. Synthesis of preformed catalyst and polymers.

1. Ligand exchange:



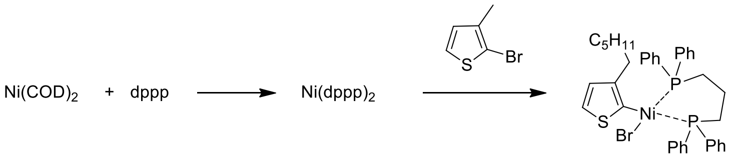


Theoretical DP is 40, i.e. a molar mass of 6650 g/mol and the average degree of polymerisation is 37 (1H NMR), i.e. a mass of 6100 g/mol also confirmed by MALDI TOF spectroscopy. This polymer has been used to optimize the end chain functionalization with halogen.

However, the product is not stable after few days even in glove box. A second polymer prepared with the same catalyst gave an unexpected large distribution and a molecular weight around 12000 g/mol.

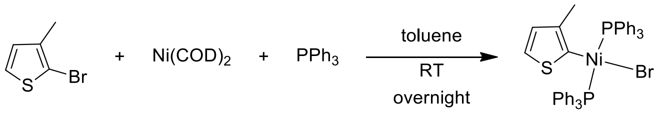
To circumvent these problems encountered a new synthetic pathway has been tried.

2. Ligand exchange from Ni(dppp)$_2$ to preformed catalyst on thiophene



The Ni(dppp)$_2$ is synthesized in laboratory according to literature procedure and purity was confirmed by 31P NMR spectroscopy. The synthesis on 3-hexylthiophene or 3-methylthiophene catalyst from Ni(dppp)$_2$ is not reported in literature. This reaction did not give the desired compound according to the powder appearance (grey instead of yellow-orange) and 31P NMR.

3. The ligand exchange operation, from bis-triphenylphosphine (which gives an air stable catalyst) to bidentate 1,3-diphenylphosphinopropane *will be executed just before the addition of activated monomer.*



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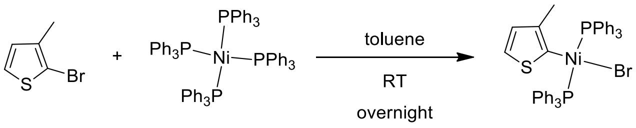

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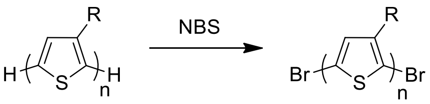
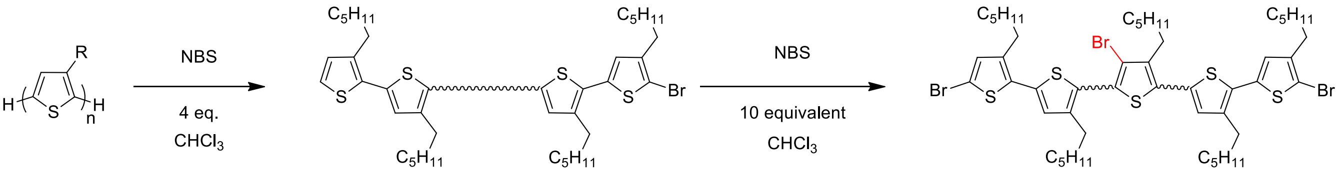
^{31}P as well as ^{1}H NMR indicated a good formation of the catalyst with triphenylphosphine with the signal between 19 and 21 ppm. (However, a second signal in ^{31}P NMR at 17 ppm is present not corresponding to free PPh_3).

Polymerization with this catalyst has been performed according to the usual procedure: catalyst, dppp (1.05 equivalent) is dispersed in THF before the addition of the activated monomer and the solution cooled to 0°C for 30 minutes. *Two* polymers are obtained with a bimodal distribution of molecular weight indicating an instability of the catalyst.

B. End chain halogenation of polythiophene



This reaction is not as simple as it seems. It is relatively easy to bromine the last thiophene (with alkyl chain in alpha position). The thiophenes at the chain end are easily brominated with the use of large equivalent of NBS but it lead to *overbromination* in the 4-position of some thiophene in the chain according to our interpretation of 1H NMR spectroscopy. This deleterious side reaction should be avoided.



C. Reaction of cyclisation.

The first cyclisation reaction was performed on a sample and analyzed by MALDI, which gave a largely major population of P3HT with 2 Br. It could safely be supposed that those two bromines were positioned at the chain ends. The reaction was performed with a copper catalyst coordinated to 2-thienylcarboxylic acid, which allow reaction at milder conditions with a larger variety of solvent. The temperature is fixed at 45°C to favor the cyclic conformation of polymer chain.

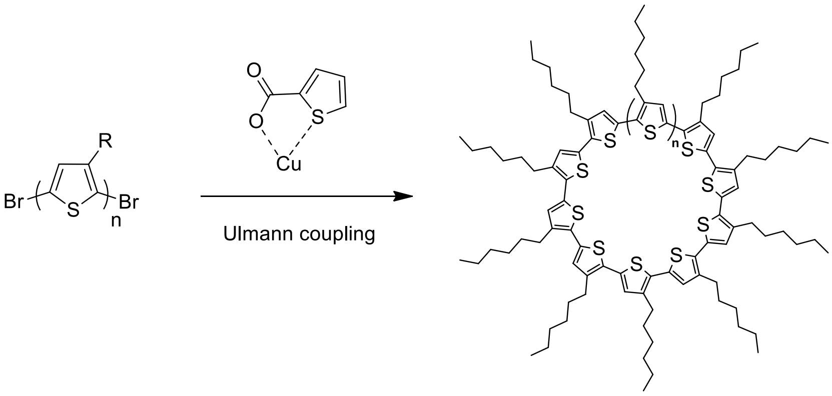


Fig. 8 Reaction of cyclisation according to Ullman mechanism with modified catalyst CuTc.

The GPC elugram after the cyclisation reaction exhibit a shift toward higher retention time meaning a decrease in hydrodynamic volume of product after the cyclisation. This difference was too high to be attributed to the loss of bromine. In DSC, an endothermic transition occur at lower temperature at 100°C (classical P3HT present a melting point around 200°C). In UV-Vis spectroscopy the difference between the maximum absorption is 2.5 nm, maybe not significant.

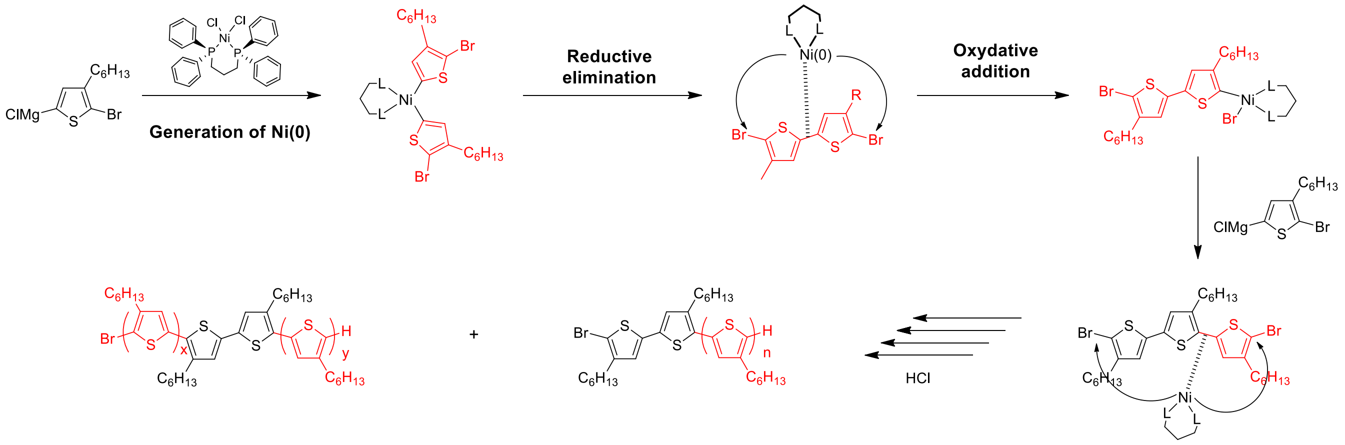
In NMR the presence of typical signal of H termination on the first thiophene (doublet at 7.15 ppm) allowed to conclude that cyclisation cannot be complete and linear polymer is also present in the sample necessitating difficult separation procedures.

The number of bromine in the chain is supposedly due to the fact that the Ullman coupling reaction is not favorised at this position due to steric hindrance of the alkyl chain. Once cyclisation reaction is performed the residual bromine should be removed with $LiAlH_4$ in THF.

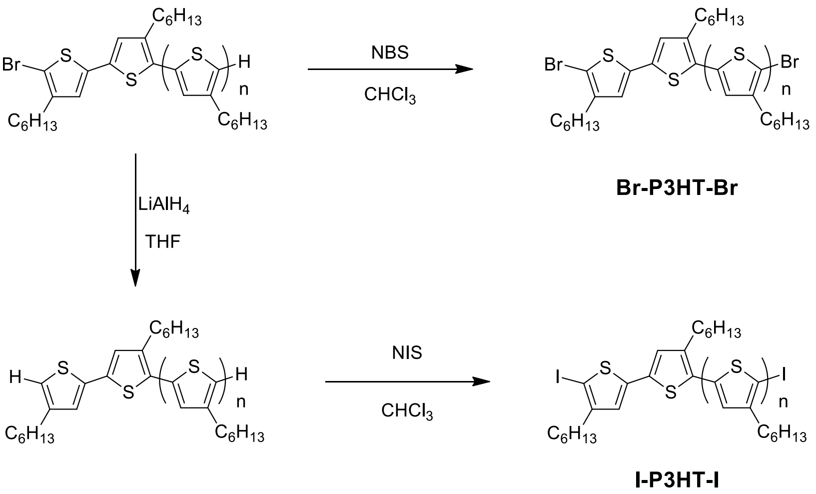
D. A double defect macrocycle

A double defect macrocyle was obtained from a single defect polythiophene according to the first step of polymerization by $Ni(dppp)Cl_2$ catalyst.

1. Synthesis of polymers and end chain halogenation of polythiophene



According to literature, the tail-to-tail defect is not only located at the chain end but anywhere in the chain. This strategy was employed since the bromination is easier when an alkyl chain is present in the alpha position. The main drawback is the reaction of cyclisation which should occur through a head to head coupling and therefore through the steric hindrance of the alkyl chain.



Synthetic pathway of chain end halogenated single regiodefect polythiophene

The optimization of those reactions are still under progress.

2. Reaction of cyclisation

The cyclisation reaction was carried out in THF with a Cu complex of thiophene carboxylate acid at 45°C at high dilution and with slow addition of polymer solution (18 hours, 100 mg in 100 mL added to 500 mL of THF containing 13 mg of catalyst (4 equivalents)).

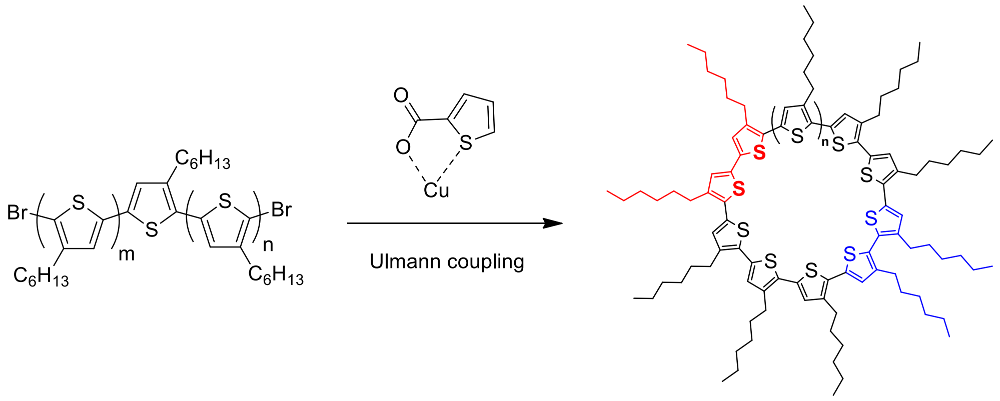


Fig. 9 Reaction of cyclisation according to Ullman mechanism with modified catalyst CuTc – Regiodefects are color-coded.

Very recently a new promising way of closing macrocycles was developed relying upon the McMurry coupling reaction - whereby two aldehydes moieties form a ethylene bridge - apparently a the most effective way to obtain macrocycles. Moreover this synthesis is independent of the quantity of catalyst which is beneficial toward the very high dilution solution needed to avoid intermolecular reactions.

The efficiency of this strategy to cyclisation of polymer chains is confirmed by several measurements:

- GPC elugram shows a shift of peak mass to smaller molecular weight.
- Maldi confirm that almost no bis-aldehydepolythiophene is present and that the population of polymer contains C2H2 as terminal moiety, equivalent to an ethylene bridge.
- UV-Vis of linear and cyclic in chloroform are the same. But, in a 50:50 volume solution of CHCl3:MeOH which force agregation of the polymer chain, a slightly different behavior is observed.

An important benefice of the McMurry coupling is that the double bond created by the ring closure can be reduce into -CH2-CH2- leading to a non-conjugated cycle, with the exact same composition that the conjugated one. This allows the comparison of conjugated to non-conjugated systems with the same chain mass distribution, the same amount of impurity (H/H termination, CHO/CHO termination, H/CHO termination).

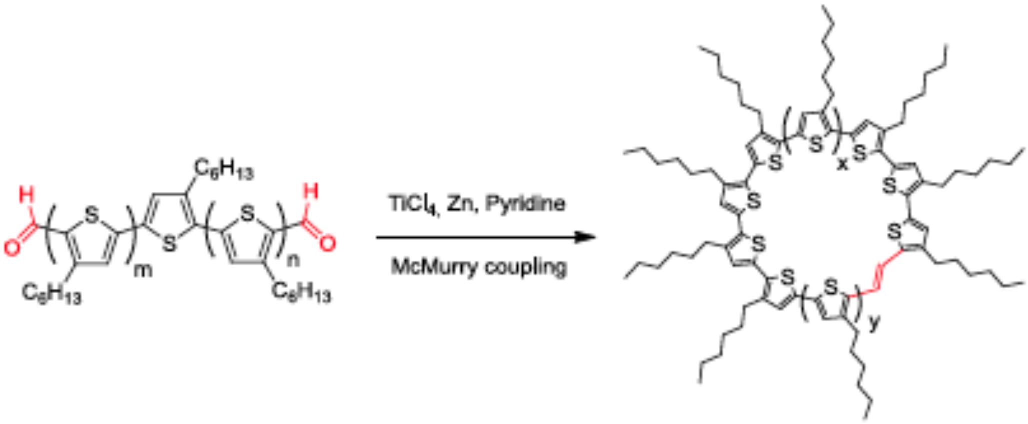


Fig. 10 Ring closure by the McMurry coupling reaction

It should be stressed here that these materials are completely new as functional materials, functional for magneto-optic and magnetic properties of organic materials.

V. Simulations and modelisation of macrocycles

An extensive program, often in collaboration with Dr. Palash Gangopadhyay, University of Arizona and with Prof. Małgorzata Makowska-Janusik, Akademia Jana Dlugosza, Poland, was started to simulate the π-electron distribution in the different macrocycles synthesized. This could give us valuable information on the possibility of persistent currents in these structures and at the same time important feedback for the synthesis program.

The simulations are currently mostly restricted to 10-rings of *methyl*thiophenes due to the available computer power.

In Figure 11 the simulation of a pure regioregular 10-ring of methylthiophene is presented. It is seen that this macrocycle is almost flat. A dipole moment of .7 D would indicate that the thiophene groups are inclined for about 6°.
A single absorption around 392 nm is calculated, indicating a rather large gap between HOMO and LUMO.
Figure 12 gives a simulation of a 10-ring with a regiodefect (two methyl-groups close). Here we see that the flatness is gone with the concomitant increase in dipole moment to 4.45 D. Interestingly, this “defect-ring” shows an absorption at 730 nm apart from a shift and splitting of the primary absorption towards 515 nm, and with much weaker absorption coefficients. The absorption at 730 nm may indicate a defect level in this regiodefect ring that may be important for the conductance in the ring. The results obtained in the simulation of the regiodefect ring give an important feedback for the synthesis since it is convincingly shown that a defect ring, as compared to the fully

regioregular ring, may have some advantages to obtain ring currents. This would substantially relieve the intricate synthetic difficulties with ring closure. Data are given in Table 1.

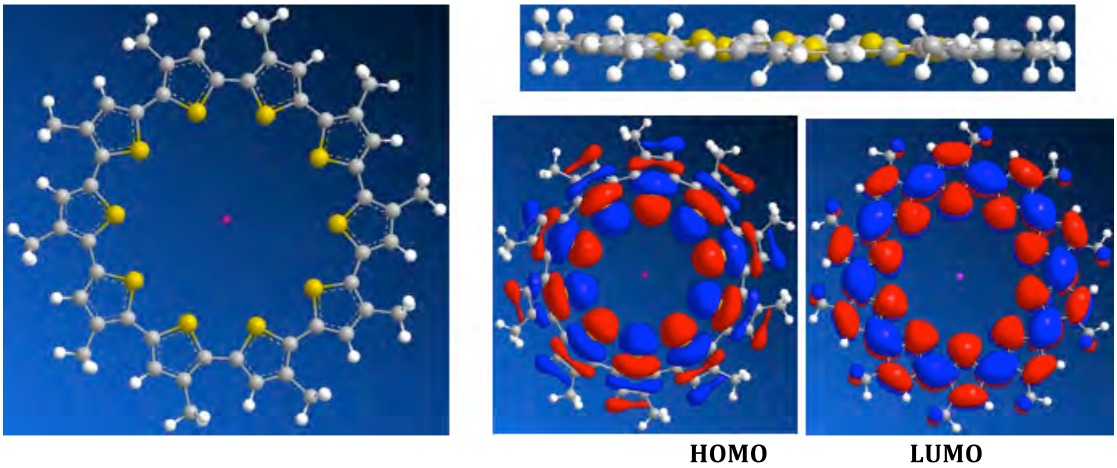


Fig. 11. The regioregular ring ($1^3,2^4,3^4,4^4,5^4,6^4,7^4,8^4,9^4,10^3$-decamethyl-1,2,3,4,5,6,7,8,9,10(2,5)- decathiophenacyclodecaphane).
DFT –B3LYP- CEP 31G* optimized, top right is side view. The violet dot, is the dipole vector projecting upward from the center of the ring, computed moment dipole ~0.7 D.

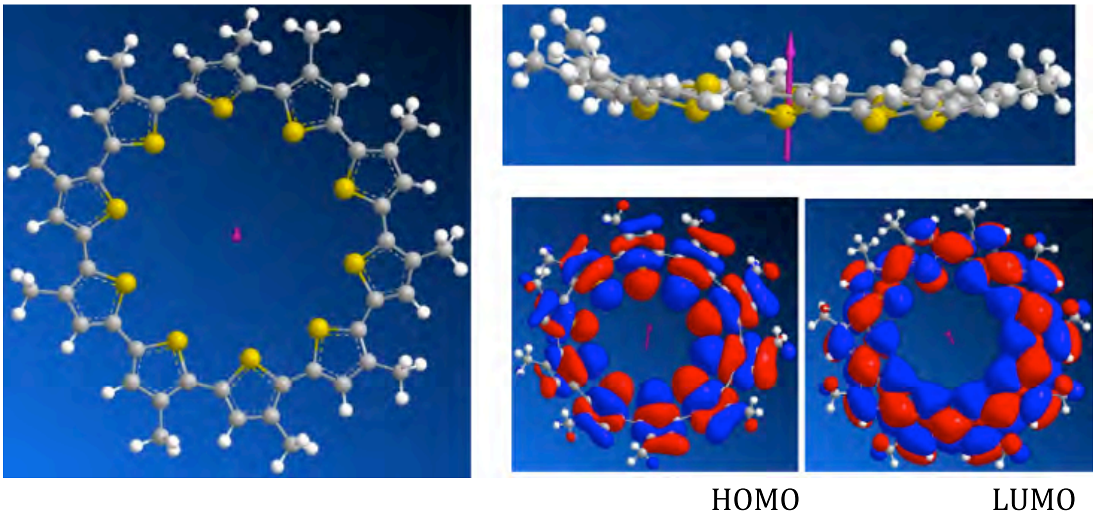
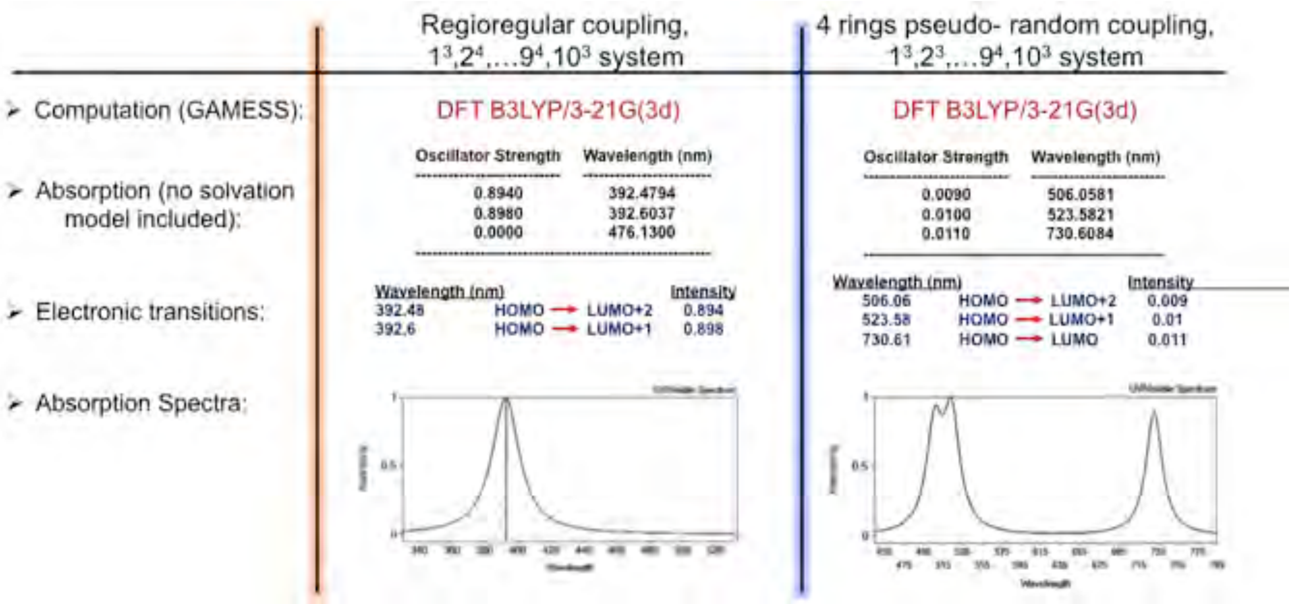


Fig. 12 The regiodefect ring ($1^3,2^3,3^3,4^3,5^3,6^3,7^3,8^4,9^4,10^3$-decamethyl-1,2,3,4,5,6,7,8,9,10(2,5)- decathiophenacyclodecaphane.
DFT –B3LYP- CEP 3G* optimized, top right is side view. The violet arrow, is the dipole vector projecting upward from the center of the ring, computed dipole moment ~ 4.45 D.

Table I Comparison between regioregular and regiodefect 10-ring macrocycles



	Regioregular coupling, $1^3,2^4,\ldots 9^4,10^3$ system	4 rings pseudo- random coupling, $1^3,2^3,\ldots 9^4,10^3$ system
➢ Computation (GAMESS):	DFT B3LYP/3-21G(3d)	DFT B3LYP/3-21G(3d)
➢ Absorption (no solvation model included):	Oscillator Strength Wavelength (nm) 0.8940 392.4794 0.8980 392.6037 0.0000 476.1300	Oscillator Strength Wavelength (nm) 0.0090 506.0581 0.0100 523.5821 0.0110 730.6084
➢ Electronic transitions:	Wavelength (nm) Intensity 392.48 HOMO → LUMO+2 0.894 392.6 HOMO → LUMO+1 0.898	Wavelength (nm) Intensity 506.06 HOMO → LUMO+2 0.009 523.58 HOMO → LUMO+1 0.01 730.61 HOMO → LUMO 0.011
➢ Absorption Spectra:		

Progress with simulations of larger rings is currently achieved and a 20-thiophene ring has been optimized showing rather well the planarity of such rings.

Results published in: P. Gangopadhyay, G. Koeckelberghs and A. Persoons, "*Molecular Magneto-optics*" Proc. SPIE 9181, 91810L (2014)

Most excitedly a simulation of a 10 thiophene ring with chiral pending groups has been accomplished (from the monomer (S)-3-(sec-butyl)-4-methylthiophene). The sense of direction in the π-electron distribution is clearly seen. This may be very important for imposing a sense of direction of fluctuating (or persistent?) currents in such ring structures. It is clear that this may be of prime importance for organic spintronics.

Fig. 13 π-electron distribution in a 10-ring of *chiral*
(S)-3-(sec-butyl)-4-methylthiophene

An important simulation is the simulation of the “McMurry-ring” as shown in figure 10, i.e. the ring closed by an ethylene bridge to preserve the required conjugation.

We have used PM3/MOPAC and CEP 31-G* to optimize geometry of $1^3,2^4,3^4,4^4,5^4,6^4,7^4,8^4,9^4,10^4$-decahexyl-1,2,3,4,5,6,7,8,9,10(2,5)-decathiophenacyclododecaphan-11-ene (The “McMurry” macrocycle, M2 in the figure) and compared with the pure regioregular ring $1^3,2^4,3^4,4^4,5^4,6^4,7^4,8^4,9^4,10^3$-decahexyl-1,2,3,4,5,6,7,8,9,10(2,5)-decathiophenacyclodecaphane (M1).

The key difference between M1 and M2 is the way the rings are closed at the end; whereas M1 is a regioregular polymer with all side chains in the same direction, M2 ring is closed with a vinyl group with a possible regiorandom sidechain at the side. Note also that the sidegroups here are hexyl- groups.

Figure 14 shows the structures of geometry optimized M1 and M2, and their HOMO, LUMO states and a comparison of the HOMO - LUMO energy differences, their computed dipole moments and (hyper)polarizabilities.

The computational results shown in Figure 14 indicate the existence of a stronger dipole in M1 that is perpendicular to the plane of the macrocycle, whereas the dipole in M2 is mostly homogeneous and confined within the plane. With increasing number of thiophene rings (Figure 15), the dipole moment increases drastically in M1, a trend that is much higher than that in M2.

The most surprising result from these calculations, and unfortunate for the potential for persistent currents, is the *complete breakdown* of the electron conjugation with a vinyl closure, against our expectations. Although unfortunate, this is an important feedback for future synthetic work.

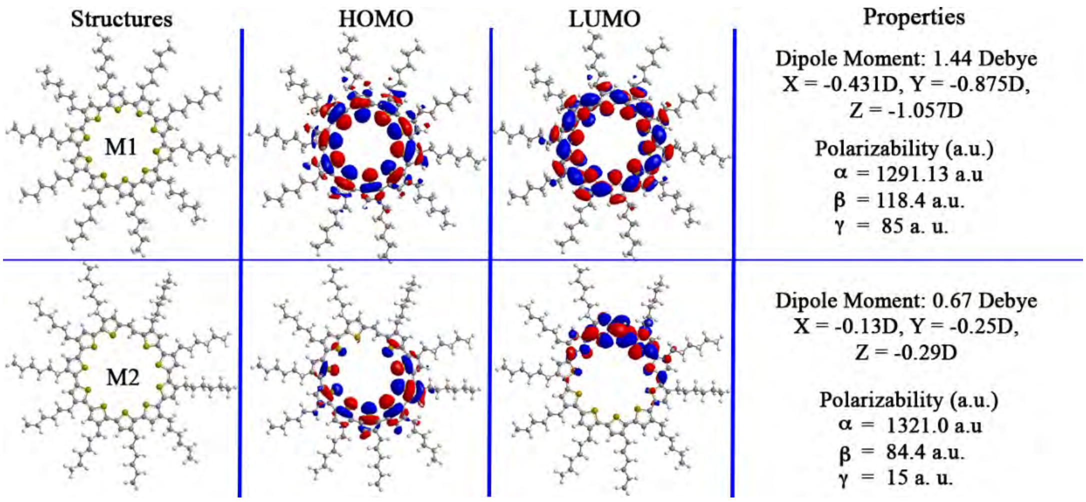


Figure 14 Computed Structures, HOMO- LUMO, dipole moment and Polarizabilities of M1 and M2*.*

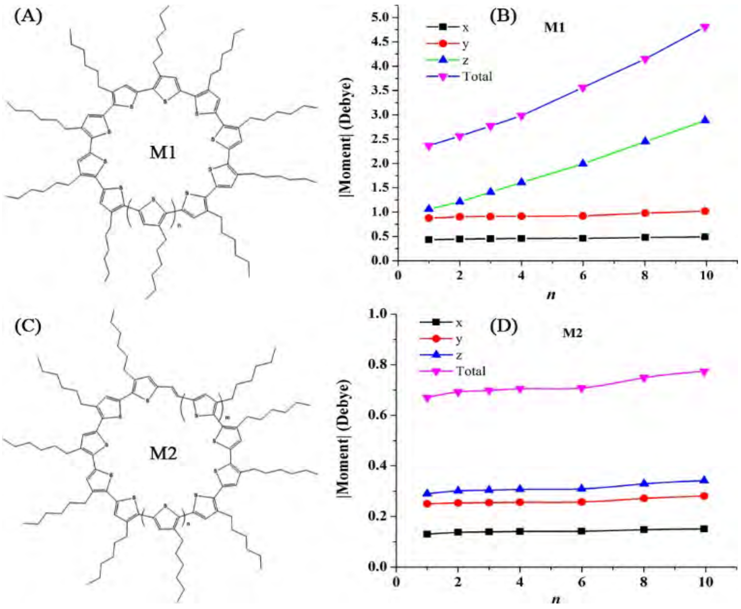


Fig. 15 Change in computed dipole moment with the change in number of thiophene rings in the macrocycle that are regioregularly (M1, A and B), and vinyl-bridge (M2, C and D, y = 1) connected.

Although not a fully conjugated ring we have used this “McMurry ring” for SQUID measurements. The results are presented in Fig. 16.

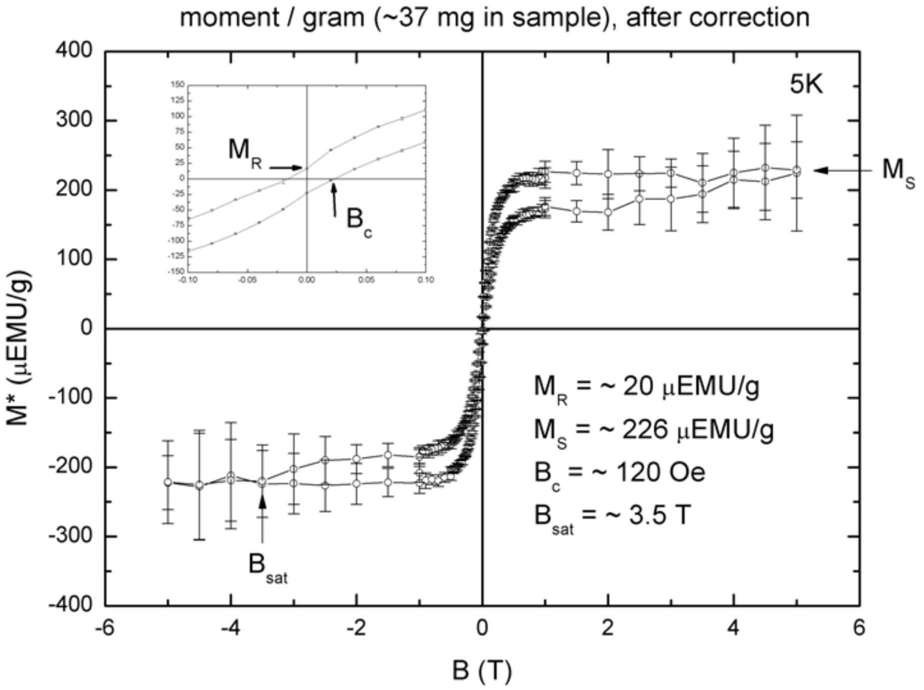


Fig. 16 SQUID measurements on 1^{3},2^{4},3^{4},4^{4},5^{4},6^{4},7^{4},8^{4},9^{4},10^{4}-decahexyl-1,2,3,4,5,6,7,8,9,10(2,5)-decathiophenacyclododecaphan-11-ene at 5K
(the McMurry-ring).

These SQUID measurements were done with the straw/cotton method, i.e. the sample stuck between two cotton wool buds in a plastic straw placed in the SQUID and cooled down to 5K in zero field.

From the results we see that the remnant moment (M_R) is very tiny while the saturation moment M_S is also small compared as to the measurements in literature. In view of the computational results, where it is seen that the electron conjugation in the ring is completely broken this result is not totally unexpected.

Faraday measurements on the same molecule over a wide temperature range yielded also a small Verdet constant. The measurements were done on a 34 nm (AFM) thick film on fused silica (0.5 mm thick) at 470 nm wavelength and the Verdet constant of the film changed from ~1200 at 4K to 740 deg/Tm at room temperature. This again is an indication there is no “ferromagnetic behavour” to be expected from this macrocycle.

SQUID measurements have been carried out in the group of Bert Koopmans, Technical University Eindhoven, Netherlands.

A new development: “thiographene”

During our investigations (simulations) of the magneto-optical properties of polythiophenes we hit the possibility of synthesizing a thiophene-like network that has some reminiscence of graphene. After extensive discussions with the group of Philippe Dubois the synthesis of this molecular structure is possible, although the preparation of the monomer (described in literature) requires synthetic facilities not yet available to us.

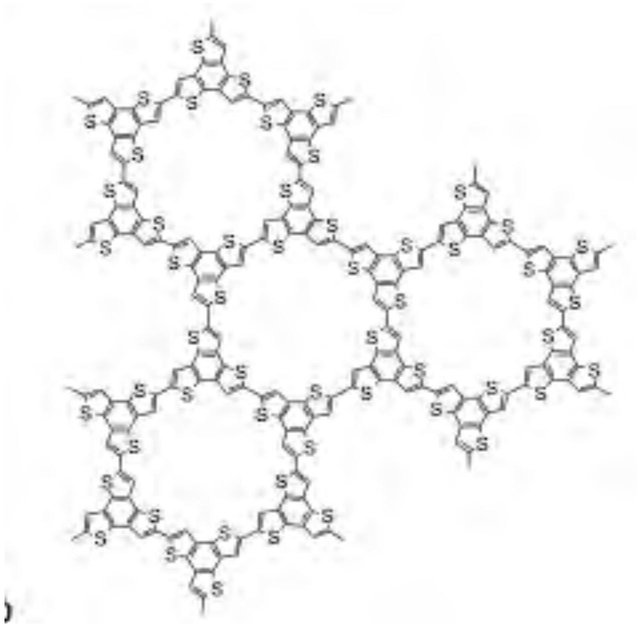


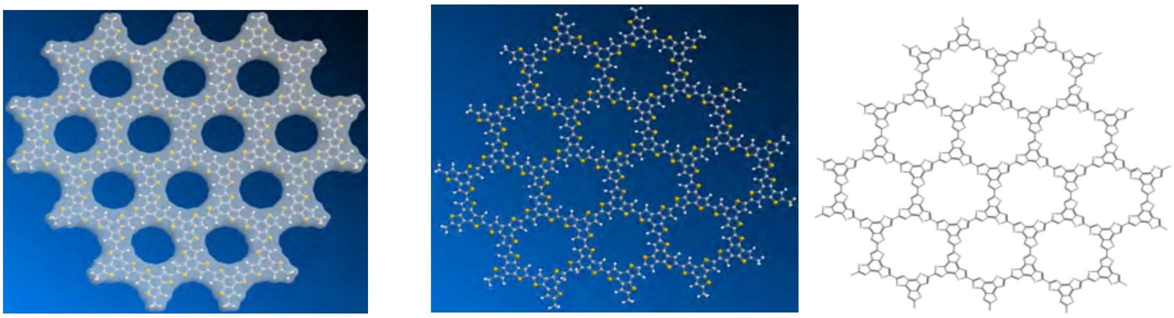
Fig. 17 Structure of 2D graphene-like material – “thiographene”

Using developed synthetic procedures, mainly based upon our recent work on polythiophene chemistry we will synthesize these more involved structures such as the 2D graphene-like structure – see Fig. 17. To date such two dimensional organic materials represent an important branch of modern materials chemistry and offer some unique characteristics such as light weight, flexibility, high conductivity and, according to our recent results on polythiophene, probably strong magneto-optic properties.

The first step of monomer unit synthesis consists on the iodination of the commercially available 1,3,5-trichlorobenzene under refluxing sulfuric acid followed by a Sonogashira coupling reaction between trimethylsilylacetylene and the iodine moiety is performed by a classical method. Finally, the cyclisation on sulfur atom is realized by heating the previous compound with sodium sulfide.

The challenging aspect of this 2D graphene-like material preparation remains unquestionably the polymerization of the benzotrithiophene functional monomer 2,5,8-tribromobenzo[1,2-b:3,4-b’:5,6-b”]trihiophene. Different methods however exist to reach the goal of obtaining such materials: *i*) a polymerization in solution from the brominated derivatives via a Ullman or Yamamoto coupling reaction; *ii*) a template-assisted polymerization and *iii*) a chemical vapor deposition followed by an oxydative coupling reaction.

First semi-empirical simulations of the 12-nanocycle oligomer (simulations restricted by the available computer power) are shown in Fig. 18



Semi-empirical AM1 MOPAC optimized structure: Electron density around the nanocycles

Semi-empirical AM1 MOPAC optimized structure

A oligomer with 12 nanocycles

Side view of the geometry optimized (minimum global HF energy) polymer with 12 nanocycles: shows 2D nature of the sheet.

Fig. 18 2D Conjugated Polymer sheet: Structural simulations

CONCLUSION

This project allowed us to stay at the forefront of the research on magneto-optics of organic media, as witnessed by the invitations and keynote speaker of PI and collaborators on many international high-level meetings.

Highlights are the further development of magneto-optics and magneto-optic materials, the development of a new light-scattering instrument, and the development of entirely new materials, macrocycles of conducting polythiophenes, which have great potential for magneto-optics and organic spintronics.

The ongoing development of *chiral* polythiophene macrocycles will yield the possibility to produce chiral conducting layers of these compounds, an essential step towards the realization of spin-polarized currents – by spin-selection of the electrons moving in a chiral environment - which are at the core of spintronics.