Molecular Magneto-Optics

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ABSTRACT

We report on recent studies of magneto-optic properties and Faraday rotation of polythiophenes and macrocycles of 3-alkylthiophenes. The hypothesis of the existence of persistent currents, analogous to the persistent currents in mesoscopic metal structures, is forwarded as a relevant mechanism basic to the large Faraday rotation in conjugated polymers as well as for the ferromagnetic transition in these polymers at cryogenic temperatures. Macrocycles of alkylthiophenes are presented and discussed as fundamental structures to investigate persistent currents in nanoscopic organic materials.

Keywords: Faraday rotation, ferromagnetism, polymer, regioregular substituted poly(3-alkylthiophene)s, macrocyles, persistent currents

INTRODUCTION: NONLINEAR OPTICS

Since the first measurement of second harmonic generation from a crystal at optical frequencies, the famous Franken experiment[1], nonlinear optics became a field of intense research with wide and often unexpected ramifications. Further investigations of the hyperpolarisabilities of organic molecules and polymers, using electric field induced second harmonic generation (EFISHG)[2] and since the 90s Hyper Rayleigh scattering (HRS)[3], gave rise to new fields of organic photonics, electro-optical devices, biomedical technologies, etc…

Commonly the fundamental equation governing nonlinear optics is the optical polarisation written as a series expansion of the electric field strength in the optical field:

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

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. The $\chi^{(2)}$, $\chi^{(3)}$ are second, third order terms, the nonlinear susceptibilities, actually tensors of the third and fourth order, making nonlinear optics sometimes difficult but very rich in possibilities due to the symmetries involved. These nonlinear susceptibilities are very small, identifying nonlinear optics mainly as a laser field with the high optical field intensities accessible in (focused) laser beams. It is also easy, and 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. This is presented in Fig. 1 where it is clearly seen that the interplay between electric dipole radiation and magnetic dipole radiation in a helical structure, the basis of all chiral structures, is resulting in the rotation of polarization since the magnetic dipole radiation is

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perpendicular to the oscillating magnetic dipole (Maxwell's equation again), recognized as the hallmark of optical activity.

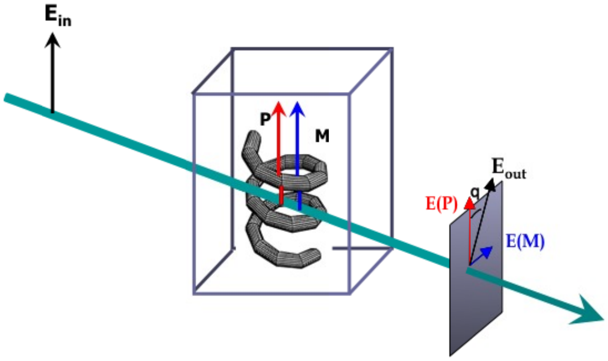


Fig. 1 The interaction of an optical field with a chiral structure, electric dipole and magnetic dipole radiation result in rotation of polarization.

Focusing on the second-order nonlinear polarization at the optical frequency ω, and specifying for second-harmonic generation, we now take into account magnetic interactions (it is not by accident that we were forced to take this into account when studying chiral systems) and write:

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

(and neglecting higher order magnetic effects). We write now χ^{eee}, resp. χ^{eem} for the $\chi^{(2)}$ 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). "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 superscripts mee, being two photons annihilated in the electric dipole interaction and the harmonic photon created in a magnetic dipole interaction.[4] We see here that we have to introduce a new linear term, the magnetisation:

$$\mathrm{M}^{NL}(\omega) = \chi^{mee}\ \mathrm{E}^{2}(\omega) \tag{3}$$

It is now 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 the magnetic fields are described by axial vectors, not changing sign upon inversion. This could have 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.

Experimentally we could prove the failure of the electric-dipole approximation to fully describe second-harmonic generation from a chiral polythiophene film.[5] A chiral material had been chosen for these experiments since it could be expected that magnetic effects would be more prominent in chiral systems – as known from optical activity. In general we could write for the intensity of the second-harmonic signal, as function of the polarization states – p- and s-polarized – of the fundamental optical field:

$$\mathrm{I}(2\omega) = |\, \mathrm{f}\,\mathrm{E}_{\mathrm{p}}^{2}(\omega) + \mathrm{g}\mathrm{E}_{\mathrm{s}}^{2}(\omega) + \mathrm{h}\,\mathrm{E}_{\mathrm{p}}(\omega)\mathrm{E}_{\mathrm{s}}(\omega)\,|^{2} \tag{4}$$

the coefficients f, g and h are linear combinations of the components of the tensors χ^{eee}, χ^{eem} and χ^{mee}. A detailed analysis gave for example:

$$g \sim \chi^{eem}_{xxz} + \chi^{mee}_{zxx} \tag{5}$$

A nonzero value for g, and rather large as experimentally measured, was a convincing indication of the presence of the "magnetic" tensors with components determined by symmetry. The value of the coefficient g measured gave a magnetic contribution to the second-harmonic signal of the same order as the electric contribution, probably due to the partial suppression of the electric contribution as the result of the near centrosymmetry in the film.

[A note of caution: the magnetic contributions as measured in the chiral polythiophene films cannot be directly linked to chirality. Indeed measurements of second-harmonic generation from strongly chiral helicene films[6] gave no indication of any magnetic contribution and the signal was largely defined by chiral tensor components in χ^{eee}]

FARADAY ROTATION EXPERIMENTS

The oldest nonlinear optical effect – long before the laser-area and properly a nonlinear effect since an optical field is coupled to a magnetic field – was discovered by Faraday[7], now known as Faraday rotation, i.e. the rotation of the plane of polarization of linearly polarized light due to magnetic field induced birefringence. Faraday rotation is now commonly used in optical isolators and modulators. The effect is completely described by the rotation angle θ of the plane of polarization and given by the simple equation $\theta = VLB$ with V the Verdet constant, B the component of the magnetic field parallel to the light propagation direction and L the sample length. This Verdet constant, a material constant, is usually obtained from the amount of polarization rotation and is wavelength dependent, decreasing strongly away from resonance. Typically used materials for applications, e.g.Terbium Gallium Garnet (TGG), have a Verdet constant around 10^4 °/Tm at visible wavelengths.

Guided by eq. 1, but now including magnetic interactions and a magnetic field at low frequency we write:

$$P(\omega) = \chi^{(1)} E(\omega) + \chi^{eem} E(\omega)\, B(0) = \chi^{M} E(\omega) \tag{6}$$

If we take properly account of the tensor symmetries and the Faraday rotation experiment with the low frequency field B(0) along the direction of light propagation (z-axis) and the incoming light linearly polarized along the x-axis it is straightforward to derive for the χ^M :

$$\chi^{M} = \begin{pmatrix} \chi_{xx} & \chi^{eem}_{xyz} B \\ \chi^{eem}_{yxz} B & \chi_{yy} \end{pmatrix} \tag{7}$$

and, since we consider an isotropic medium we have $\chi_{xx} = \chi_{yy} = \chi$. Also, and again from symmetry considerations, $\chi^{eem}_{xyz} = -\chi^{eem}_{yxz} = \chi^{m}$ and we write hence for the tensor χ^M :

$$\chi^{\mathrm{M}} = \begin{pmatrix} \chi & \chi^{\mathrm{m}}\mathrm{B} \\ -\chi^{\mathrm{m}}\mathrm{B} & \chi \end{pmatrix} \tag{8}$$

But this is exactly the same tensor as used in the description of optical activity.[8] Faraday rotation is therefore completely analogous to optical rotation from chiral samples, except that Faraday rotation is non-reciprocal due to the fact that the orientation of the magnetic field has opposite direction when the light beam is reversed and the rotation is adding up for Faraday rotation – canceled in the case of optical activity. For Faraday rotation the off-diagonal elements in the tensor are dependent upon the field.

It is now straightforward – using the description of circular polarized light – to deduce the relation between the Verdet constant, the angle of rotation and the nonlinear susceptibility component χ^{m} :

$$\mathrm{V} = \frac{4\pi^2}{\mathrm{n}_0\,\lambda}\, i\, \chi^{\mathrm{m}} \qquad \text{and} \qquad \theta = \left(\frac{4\pi^2}{\mathrm{n}_0\,\lambda}\, i\, \chi^{m} \right) \mathrm{L\,B} \tag{9}$$

As expected we see that the imaginary part of χ^{m} defines the value of the Verdet constant – and in a lossless medium χ^{m} (or χ^{eem}) is imaginary. With these relations the quantumchemical calculation of the Verdet constant, at least for small molecules, becomes feasible.[9]

The χ^{m} values, more properly the imaginary part of $\chi^{\mathrm{eem}}_{\mathrm{xyz}}$ as measured for (chiral) polythiophene films are of the order of 0.4 pm/V. Using these values, and neglecting dispersion, we estimate a Verdet constant for these polymer films of about 2 10^5 °/Tm, to be compared with 0.7 10^4 °/Tm (633 nm) for the inorganic material TGG. It is very rewarding that measurements of the Faraday rotation of polymer films of polythiophenes gave indeed such surprising large values. For example, a film of highly regioregular poly(3-octyloxythiophene) showed a Verdet constant of 2.5 10^6 °/Tm at 800 nm, still 10^6 °/Tm at the technologically important wavelength of 1550 nm. This opens towards important applications, e.g. ultrasensitive magnetometers approaching the sensitivity of SQUID magnetometers, but at room temperature – such sensors are currently in development for magneto-encephalography (MEG) and could make this intricate medical technique routinely available. However, for the application of these materials in devices we still have to further our knowledge and understanding of the Faraday rotation in these conjugated polymers. First we have to elucidate the relation between the high Verdet constant and the regioregularity of the polythiophenes whereas we see that the Verdet constant is strongly dependent upon the regioregularity. Another point of focus is the relation between the Faraday rotation and the structure of the polymer films, usually obtained by spincoating – it is also possible that regioregualrity and film structure are intricately related. As an example of the critical role of the film structure the Faraday rotation in a blue film of poly(dioctylcyclopentadithiophene) was very large with a Verdet constant of V = 2.5 10^5 °/Tm (670 nm) after preparation of the film by spincoating, but fading slowly away over days with a concomitant change to a purple color. This is presumably due the formation of a new supramolecular structure, or crystallization although no melting is seen in DSC, resulting in polymer chain interactions unfavourable for Faraday rotation. This hypothesis is supported by measurements of the Faraday rotation of poly(3-octylthiophene) in solutions (0.25 mg/ml) of mixtures of good and poor solvents. In THF, a good solvent for these polymers, where the polymer chains are not aggregating, a Faraday rotation of 0.35°/T is measured in a sample cell of 1 mm. This would be equivalent to about 10^5 °/Tm for the (solid) pure poly(3-octylthiophene if no chain interactions are assumed. Upon changing the solvent gradually to a mixture of THF and methanol, a poor solvent wherein the polymer chains show aggregation, the Faraday rotation diminish markedly, albeit in a rather, poorly understood, complex way – see Fig. 2.

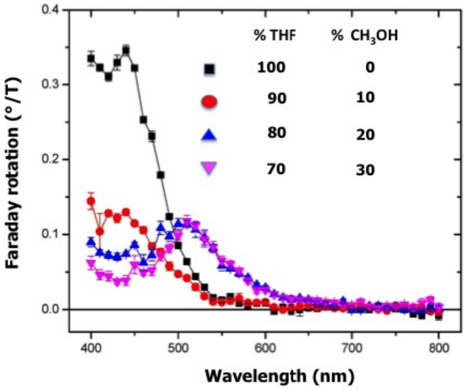


Fig. 2. Faraday rotation in solutions of poly(3-octylthiophene) in different solvent compositions at a concentration of 0.25 mg/ml, sample cell of 1 mm thickness

THE FARADAY ROTATION MECHANISM

Although the very high Faraday rotation in polythiophenes is of great practical interest the effect remains as yet largely unexplained (as well as the very large nonlinear magnetic susceptibilities measured in films of these polymers). Some mechanistic elements such as the importance of the polymer structure – regioregularity is an essential requirement – as well as the supramolecular structure of the polymer films are well documented, and giving an important feedback to synthesis, but the relation to the Faraday rotation is not yet clearly understood.

A most important clue for the a further explanation of these large magnetic effects may be found in the observation by AFM of circular structures, doughnut shapes, in spincoated films of poly(3-dodecylthiophene), as shown in Fig. 3

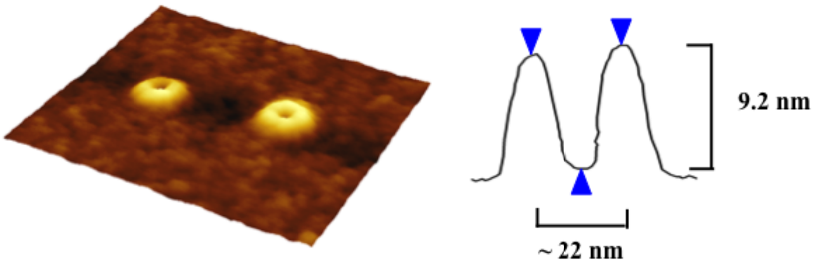


Fig. 3 AFM picture of a film showing the presence of doughnut structures in films of poly(3-dodecylthiophene).

Based upon the observation of such circular structures we advanced the hypothesis of the presence of persistent currents in these doughnuts of (semi)conducting polythiophenes. Such persistent currents would imply the presence of magnetic moments which could be relatively large, depending upon the mobility of the π-electrons in these ring structures and their size. The concept of persistent currents in organic rings may be a concept difficult to accept but somewhat analogous to the notion of persistent currents in mesoscopic metal rings of Cu and Au, theoretically predicted[10] in the 80s and shown experimentally[11] in the 90s.

As a first and crude estimate we take one electron going around at the Fermi velocity in the doughnut ring (diam 22 nm) – the doughnut as a nanomagnet – obtaining a current of 10^{-5} A and hence a magnetic moment of about 500 Bohr magneton.

Such magnetic effects present in circular structures of polythiophenes may be also at the basis of the very stable ferromagnetic transition seen in SQUID measurements in pristine regioregular poly(3-dodecylthiophene) at cryogenic temperatures.[12] Only the regioregular polymer is showing this behavior which may be linked to supermolecular annular

structures present – absent in the regiorandon polymer. [Note: for the SQUID measurements the polymers, as well as the sample holders, were thoroughly analyzed by ICP AES for the presence of ferromagnetic impurities].
In an investigation of the magnetic effects in poly(3-S-3,7-dimethyloctylthiophene) SQUID measurements indicated a number of Bohr magnetons of about $3\ 10^{17}$/g polymer while ESR measurements on the same polymer gave $1.3\ 10^{16}$ spins/g polymer (for a polymer with $\overline{M}_n$ 7 kD, polymers with higher $\overline{M}_n$ showing comparable results).[13] The number of Bohr magnetons being much larger than the spin density numbers obtained from ESR measurements points to the presence of an additional spin system. The magnetic hysteresis effect observed at cryogenic temperatures may therefore be due to orbital magnetism.

MACROCYCLES OF POLYTHIOPHENES

The availability of macrocycles structures of polythiophenes[14] opens new possibilities to investigate the role of annular structures in the Faraday rotation and the ferromagnetic transitions observed in these polymers. Although very difficult to synthesize – cyclisation reactions are always in an unfavorable competition with interchain coupling reactions – the group of Philippe Dubois at the University of Mons, Belgium, has now an extensive program for the synthesis of large macrocycles of 3-alkylthiophenes. A first macrocycle obtained by his group, a polyhexylthiophene macrocycle,[15] was used in the study of Faraday rotation in chloroform solution. Although this macrocycle has the drawback of an imperfect ring closure, resulting in the breaking of the conjugation along the ring, the solution showed a very strong Faraday rotation as shown in Fig. 4. The rotation values around 430 nm allows to estimate a Verdet constant in the order of 10^5 °/Tm for the pure macrocycle material, assuming no effects of unfavorable interactions due to aggregation, an assumption which may be more valid than in the case of linear (regioregular) polymers.

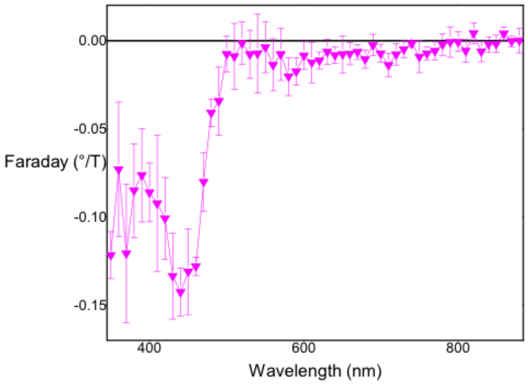
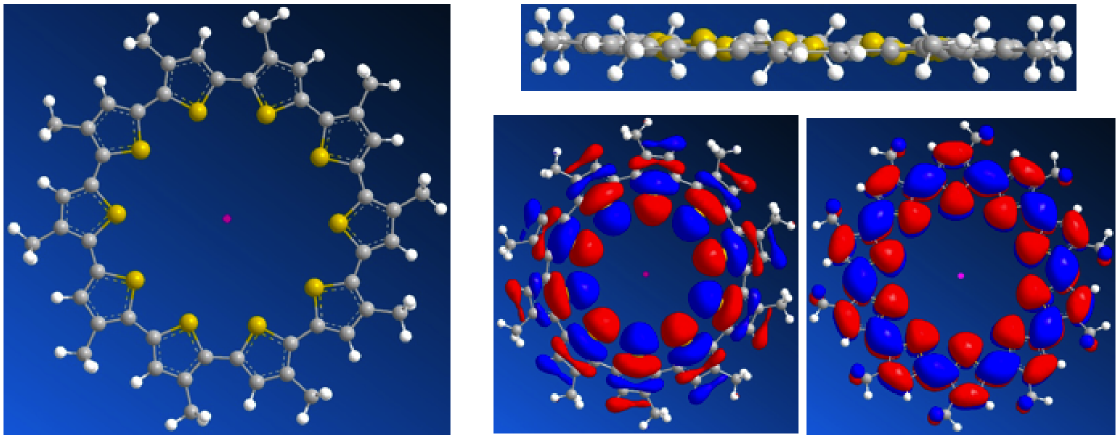


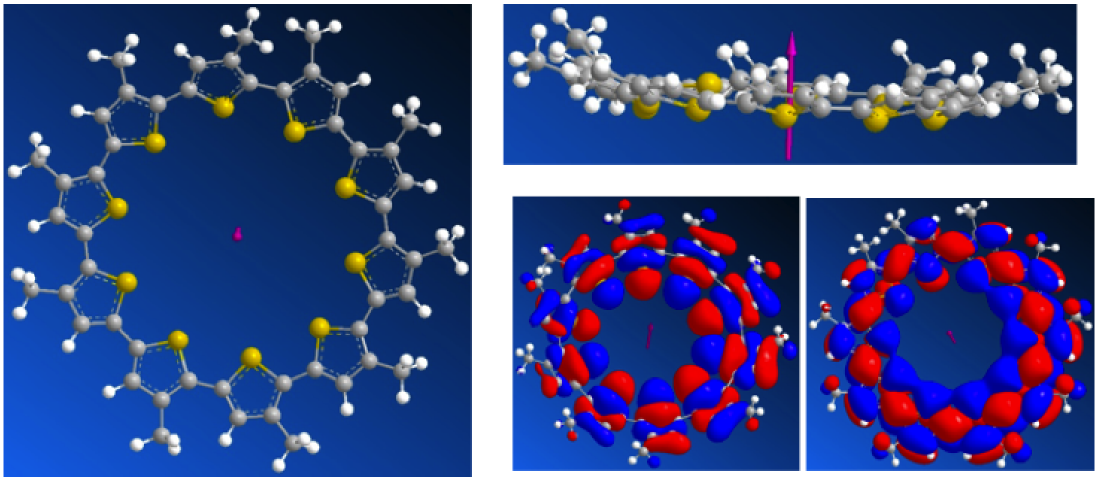
Fig. 4 Faraday rotation measured in a chloroform solution 0.7 mg/ml of the “Coulembier” macrocycle; sample cell thickness 1 mm

Since this first macrocycle investigated has a nonflat structure, as determined from simulations, the synthesis program has been increasingly directed to the synthesis of fully conjugated (regioregular) macrocycles of 3-alkylthiophenes. In view of the complexity of these syntheses a program is initiated of simulation of the macrocycles (GAMESS) to assess the structure and electronic properties of ring structures, currently limited to a size of 10-rings of 3-methylthiophene due to the available computer power – see Figs. 5 and 6.



HOMO **LUMO**

Fig. 5. 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.

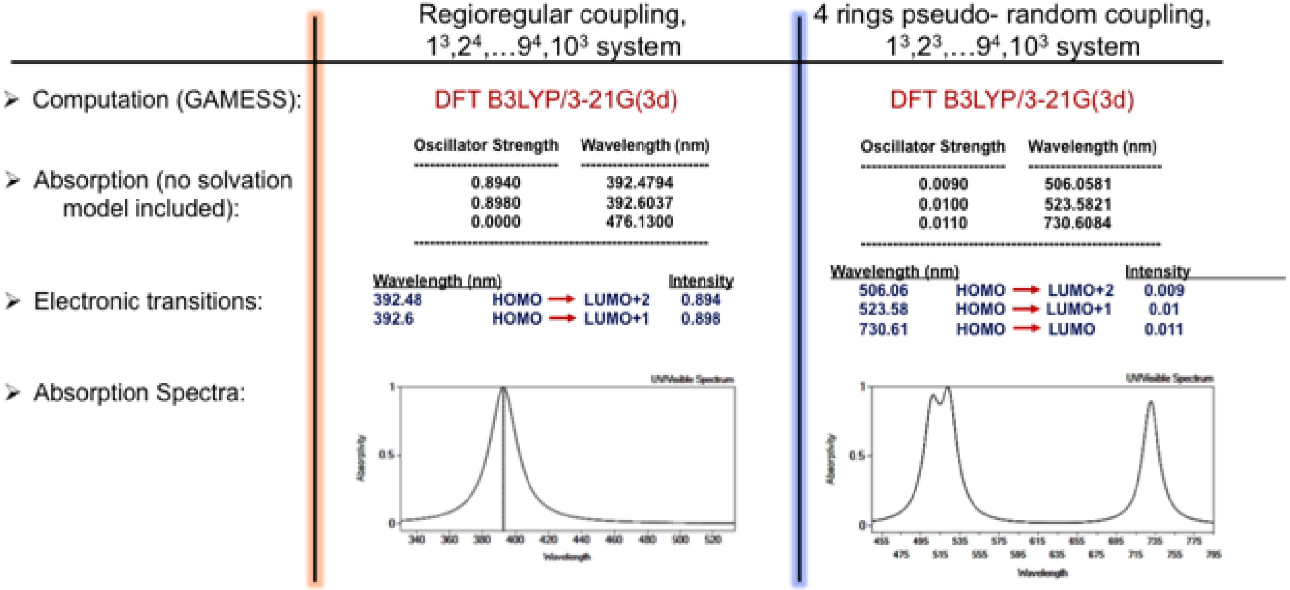


HOMO LUMO

Fig. 6 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.

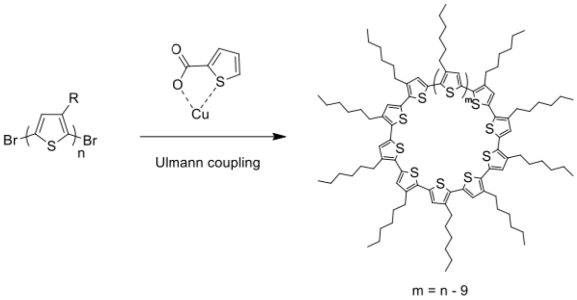
Interestingly the purely regioregular ring is rather flat – the thiophene rings inclined about 6° from the plane of the ring – and has therefore a very small dipole moment of about 0.7 D. A single absorption around 392 nm is calculated, indicating a rather large gap between HOMO and LUMO. In contrast to the results for the a regiodefect ring (4-ring pseudo-random coupling) is not flat, with a dipole moment of about 4.45 D and, interestingly, showing 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 which 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 difficulties with ring closure.

Table I Comparison between regioregular and regiodefect 10-ring macrocycles

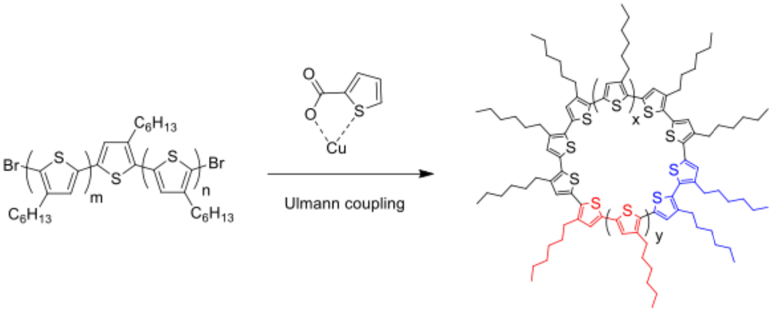


	Regioregular coupling, $1^3,2^4,\ldots 9^4,10^3$ system	4 rings pseudo- random coupling, $1^3,2^3,\ldots 9^4,10^3$ system
➢ Computation (GAMESS):	DFT B3LYP/3-21G(3d)	DFT B3LYP/3-21G(3d)
➢ Absorption (no solvation model included):	Oscillator Strength / Wavelength (nm) 0.8940 / 392.4794 0.8980 / 392.6037 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:		

The strategy for synthesis of fully conjugated rings of 3-alkylthiophenes relies upon Ullmann coupling of a regioregular poly(3-alkylthiophene) brominated (or iodinated) at the ends. This coupling may not yield a fully regioregular ring which is, as mentionned, not a necessity although still fully conjugated:



However we mostly obtain a double-defect macrocycle using this coupling strategy:



A very difficult problem in the synthesis is the strong competition with interchain coupling requiring synthesis at (extremely) high dilution. Moreover the separation of the macrocyles from linear polymers – both having comparable chemical properties – is as yet an unresolved issue.

CONCLUSION

The very large Faraday rotation, as well as the magnetic hysteresis at cryogenic temperatures, observed in regioregular poly(3-alkylthiophene)s are tentatively related to the cyclic structures present in these polymers as seen by AFM. A program is initiated on the investigation of macrocycles of poly(3-alkylthiopene)s, both theoretical (simulations and quantumchemical calculation) and experimental, to assess the possibility of persistent currents in such rings analogous to persistent currents observed in mesoscopic and nanoscopic metal rings.

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REFERENCES

1. P. A. Franken, A. E. Hill, C. W. Peters, and G. Weinreich, "Generation of optical harmonics" Phys. Rev. Lett. **7**, 118-119 (1961)

2. a) B. F. Levine and C. G. Bethea "Second and third order hyperpolarizabilities of organic molecules" J. Chern. Phys., 63, (1975); b) J. R. Heflin, Y. M. Cai, and A E Garito "Dispersion measurements of electric-field- induced second-harmonic generation and third-harmonic generation in conjugated linear chains" J. Opt. Soc. Am. B 8, (1991); c) Kenneth D. Singer, Mark G. Kuzyk, and John E. Sohn "Second-order nonlinear-optical processes in orientationally ordered materials: realtionship between molecular and macroscopic properties" J. Opt. Soc. Am. B 4, (1987).

3. a) Terhune, R. W.; Maker, P. D. and Savage, C. M. "Measurements of nonlinear light scattering" Phys. Rev. Lett. 14, 681 (1965); K. Clays and A. Persoons, "Hyper-Rayleigh-Scattering in solution" Phys. Rev. Lett. 66, 2980 (1991); K. Clays, and A. Persoons, "Hyper-Rayleigh-Scattering in solution" Rev. Sci. Instrum. 63, 3285 (1992); K. Clays, A. Persoons, and L. De Maeyer, L. "Hyper-Rayleigh-Scattering in solution". Adv. Chem. Phys. 85 (III), 455 (1994); E. hendrickx, Koen Clays and A. Persoons, "Hyper-Rayleigh Scattering in Isotropic Solution" Acc. Chem. Res. 31, 675 (1998); T. Verbiest, K. Clays and V. Rodriguez "Second-order nonlinear optical characterization techniques" CRC Press, Boca Raton (2009)

4. a) E. W. Meijer, E. E. Havinga, and G. L. J. A. Rikken, "Second-Harmonic Generation in Centrosymmetric Crystals of Chiral Molecules" Phys. Rev. Lett. 65, 37 (1990); b) J. J. Maki, M. Kauranen, and A. Persoons, "Surface second-harmonic generation from chiral materials" Phys. Rev. B, 51, 1425 (1995); M. Kauranen, J. J. Maki, T. Verbiest, S. Van Elshocht, and A. Persoons, "Quantitative determination of electric and magnetic second-order susceptibility tensors of chiral surfaces" Phys. Rev. B, 55, R1985 (1997), J. J. Maki and A. Persoons, "One-electron second-order optical activity of a helix" J. Chem. Phys., 104, 9340 (1996).

5. S. Van Elshocht, T. Verbiest, M. Kauranen, A. Persoons, B.M.W. Langeveld-Voss, E.W. Meijer, "Direct evidence of the failure of electric-dipole approximation in second harmonic generation from a chiral polymer film" J. Chem. Phys., 107, 8201 (1997).

6. T. Verbiest, S. Van Elshocht, M. Kauranen, L. Hellemans, J. Snauwaert, C. Nuckolls, T.J. Katz, A. Persoons, "Strong enhancement of nonlinear optical properties through supramolecular chirality," Science, 282, 913– (1998).

7. a) Barr, E. S. "Men and Milestones in Optics. V: Michael Faraday," Appl. Opt., **6**, 631-637 (1967). b) M. Mansuripur, "Classical optics and it applications" chap.10, Cambridge University Press, Cambridge, (2002).

8. L. D. Barron, "Molecular Light Scattering and Optical Activity" Cambridge University Press, (1982).

9. E. Botek, B. Champagne, T. Verbiest, P. Gangopadhyay, A. Persoons, "A joint theoretical-experimental investigation of the Faraday effect in benzene, toluene, and p-xylene," Chem. Phys. Chem., **7**, 1654 (2006).

10. M. Büttiker, Y. Imry, R. Landauer, "Josephson behavior in small normal one-dimensional rings" Physics Letters, 96A, 365 (1983); H. Bouchiat and G. Montambaux, "Persistent currents in mesoscopic rings: ensemble averages and half-flux-quantum periodicity" J. Phys. (Paris*)* 50, 2695 (1989); D. Wohlleben, M. Esser, P. Freche, E. Zipper and M. Szopa, "Possibility of Orbital Magnetic Phase Transitions in Mesoscopic Metallic Rings" Phys. Rev. Lett., 24, 3191 (1991); D.Wohlleben, P. Freche, M. Esser, E. Zipper and M. Szopa, "Spontaneous currents in mesoscopic rings" Mod. Phys. Lett*.* B, 6, 1481 (1992).

11. L. P. Levy, G. Dolan, J. Dunsmuir and H. Bouchiat, "Magnetization of Mesoscopic Copper Rings: Evidence for Persistent Currents" Phys. Rev. Lett. 17, 2074 (1990); V. Chandrasekhar, R. A. Webb, M. J. Brady, M. B. Ketchen, W. J. Gallagher, and A. Kleinsasser, "Magnetic Response of a Single, Isolated Gold Loop" Phys. Rev. Lett. 67, 3571 (1991).

12. P. Gangopadhyay, G. Koeckelberghs and A. Persoons, "Ferromagnetism in pristine Polythiophene at low temperature" Proc. SPIE 7935, 79350U ((2011).

13. S. Vandeleene, M. Jivanescu, A. Stesmans, J Cuppens, M. J. Van Bael, T. Verbiest, and G. Koeckelberghs "Influence of the Supramolecular Organization on the Magnetic Properties of Poly(3-alkylthiophene)s in Their Neutral State" Macromolecules 44, 4911 (2011)

14. K. Nakao, M. Nishimura, T. Tamachi, Y. Kuwatani, H. Miyasaka, T. Nishinaga, and M. Iyoda, "Giant Macrocycles Composed of Thiophene, Acetylene, and Ethylene Building Blocks" J. Am. Chem. Soc. 128, 16740 (2006); M. Iyoda, J. Yamakawa, and M. J. Rahman, "Conjugated Macrocycles: Concepts and Applications" Angew. Chem. Int. Ed., 50, 10522 (2011); F. Zhang, G. Götz, H. D. F. Winkler, C. A. Schalley, and P. Bäuerle, "Giant Cyclo[n]thiophenes with Extended π-Conjugation" Angew. Chem. Int. Ed., 48, 6632 (2009); E. Mena-Osteritz, F. Zhang, G. Götz, P. Reineker and P. Bäuerle, "Optical properties of fully conjugatedcyclo[*n*]thiophenes – An experimental and theoretical approach" Beilstein J. Nanotechnol., 2, 720 (2011).

15. O. Coulembier, G. Deshayes, M. Surin, J. De Winter, F. Boon, C. Delcourt, P. Leclere, R. Lazzaroni, P. Gerbaux and Ph. Dubois, "Macrocyclic regioregular poly(3-hexylthiophene): from controlled synthesis to nanotubular assemblies" Polym. Chem., 4, 237 (2013).