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Magnetism in (Semi)Conducting Macrocycles of pi-conjugated Polymers

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14. ABSTRACT <p>The objectives of this project involve the investigation of potential magnetic properties of macrocycles of pi-conjugated polymers. This research was initially motivated by the observation of extremely strong Faraday rotation, a nonlinear magneto-optic effect, in films of pristine highly regioregular poly(3-alkylthiophene)s as well as by the subsequently observed ferromagnetic hysteretic behavior at low temperature (T < 20K) in these polymers. Concomitantly nanoscopic doughnut structures (~12 nm) in spincoated thin films of these polymers were observed by AFM. Interestingly the magnetic properties and doughnut structures are strongly linked to the regioregularity of the poly(3-alkylthiophene)s. All these experimental observations led to the working hypothesis that the magnetic properties in the regioregular poly(3-alkylthiophene)s are linked to these nanoscopic doughnut (supramolecular) structures. In this project the new hypothesis that macrocycles of (semi)conducting polythiophenes would sustain fluctuating or persistent currents resulting in large magnetic moments and, consequently important magnetic properties in stable organic systems was investigated. Extensive DFT simulations (at different levels) of macrocycles of nm-dimensions were done with the aim to guide an extensive program of synthesis. In collaboration with researchers at Yonsei University analysis of electronic structures of macrocycles was investigated for their optical properties. The findings of these investigations suggested that such macrocycles, especially when oxidized, are organic quantum rings in analog to quantum dots and thus leads to a new field to explore.</p>					
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Magnetism in (Semi)Conducting Macrocycles of π -conjugated Polymers

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Magnetism in (Semi)Conducting Macrocycles of π -conjugated Polymers

Abstract and Summary of Project-Objectives.

The objectives of the proposal “Magnetism in (Semi)Conducting Macrocycles of π -conjugated Polymers are the investigation of potential magnetic properties of macrocycles of π -conjugated polymers. This research was initially motivated by the observation of extremely strong Faraday rotation, a nonlinear magneto-optic effect, in films of pristine highly regioregular poly(3-alkylthiophene)s as well as by the subsequently observed ferromagnetic hysteretic behavior at low temperature ($T < 20\text{k}$) in these polymers. Concomitantly nanoscopic doughnut structures ($\text{\O} \sim 12\text{ nm}$) in spin-coated thin films of these polymers were observed by AFM. Interestingly the magnetic properties and doughnut structures are strongly linked to the regioregularity of the poly(3-alkylthiophene)s. [1]

All these experimental observations led us to the working hypothesis that the magnetic properties in the regioregular poly(3-alkylthiophene)s are linked to these nanoscopic doughnut (supramolecular) structures. In this project we expanded this working hypothesis to the new hypothesis that macrocycles [2] of (semi)conducting polythiophenes would sustain fluctuating or persistent currents resulting in large magnetic moments and, consequently important magnetic properties in stable organic systems. We made extensive DFT simulations (at different levels) of macrocycles [5] of nm-dimensions, also with the aim to guide an extensive program of synthesis. In collaboration with Dongho Kim, Yonsei University, Korea we analyzed the electronic structure of macrocycles investigated for their optical properties in his group. During our investigations it occurred to us that such macrocycles, especially when oxidised, are in fact **organic quantum rings** [3] –the ring analog of quantum dots – leading us to a new field worthwhile to explore.

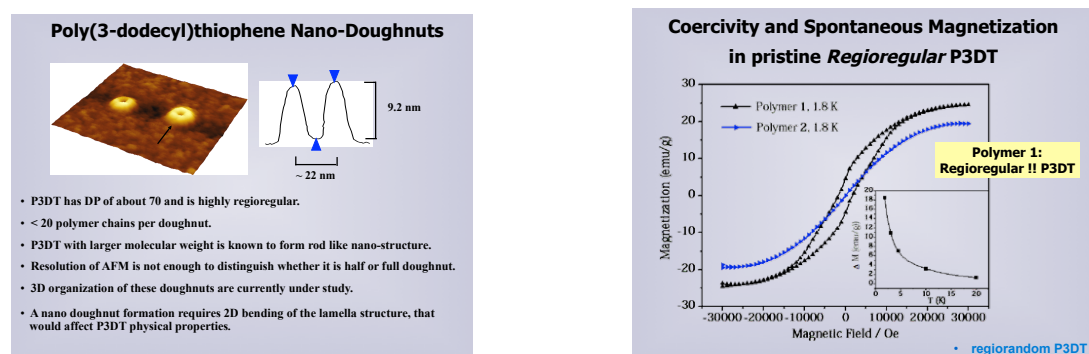


Figure 1. Doughnut structure in thin films of poly(3-dodecylthiophene) and ferromagnetic transition at 1.8K in pristine regioregular poly(3-dodecylthiophene).

New directions

As seen from the abstract the key issue for this project is the role of nanosized rings or macrocycles mainly based upon 3-alkylthiophene units. A completely new direction in our research is the realization that such (semi)conducting rings of nanometer dimensions ($\varnothing \sim 1 - 2$ nm) are **quantum rings**, a “playground” for quantum-physical phenomena whereby persistent currents [4] may offer a completely new approach to organic magnetism in organic media with good environmental stability. The project strongly focused preliminary on the synthesis of such cyclic structures. In view of the utmost complexity of the synthesis we did extensive computational work, by Density Functional Theory (DFT, B3LYP with different basis sets) on these macrocycles mainly to guide the synthesis and develop new synthetic approaches. Concomitantly a theoretical approach was initiated also relying on DFT results for different macrocyclic structures. These investigations may be instrumental in the development of new organic materials with magnetic properties for nanotechnology applications. It did not escape our attention that these macrocycles may show many properties comparable to quantum dots, up to now a strict inorganic semiconductor field.

This work is carried out in close collaboration with the research group of Dongho Kim, Yonsei University, S. Korea, who investigate physico-chemical properties of macrocycles.

Theoretical approach and computational results.

Quantum rings

Over the past decades research on materials at nanosize dimensions has an important focus in material sciences. These investigations have been mainly on inorganic materials whereby nanodots have been an important research theme. More recently quantum rings became of interest as witnessed from the strong increase in publications and books. However organic materials are strikingly absent from most research efforts although organic semiconductors, small molecules, linear π -conjugated polymers are increasingly used in important applications, e.g. solar cells and smart windows.

We realized that macrocycles of (semi)conducting polymers, e.g. polythiophenes, with dimensions of 1 to 2 nanometer are to be considered as **organic quantum rings** and the investigation of these ring structures are opening a new research field.

An important property of such quantum rings, a characteristic property, is the presence of persistent currents. Such persistent currents present a perpetual flow of electrons through a resistive material and do not require an external power source. The possibility of persistent currents in non-superconducting materials was predicted by quantum mechanical treatments, even going back to the 30's. These persistent currents are the result of quantum mechanical fluctuations influencing itinerant electrons inside materials with length scales equivalent to electronic phase coherence length – hence the nanotechnological aspects and the recent emergence of the interest in these (quantum physical) phenomena. Persistent currents can exist in rings of resistive materials, with

ring circumference shorter than the phase coherence of the electron and at sufficiently low temperature where inelastic scattering from phonons and other electrons are minimal. This is obviously a counterintuitive idea since a current in a resistor always dissipates energy and, even more fundamental, a current in only one sense should be forbidden by time-reversal symmetry (clockwise and counterclockwise current have strictly the same probability). This stringent time-reversal symmetry requirement could be removed by placing the ring in a magnetic field, imposing a favored direction, as seen in the Aharonov-Bohm effect.

In quantum rings of diffusive (electronic) systems persistent currents of 1 – 0.01 nA could generate as much as 100 μ_B to 1 μ_B (μ_B Bohr magneton) of magnetic moment per ring with, according to theory, the theoretical maximum at (with E_F the Fermi energy and r is the radius):

$$\frac{1.54 \cdot 10^{-11}}{r \text{ (in m)}} \sqrt{E_F \text{ (in MeV)}} \quad \text{Ampère}$$

From this it is clear that quantum rings of organic materials, e.g. macrocycles of (semi)conducting polymers could be the basis of environmentally stable organic magnetic material.

The primary focus in this project was on the synthesis of macrocycles of thiophene taking into account some stringent conditions for the possibility of persistent currents. First the circumference length of the ring should be smaller than the phase coherence length of the electron. This requirement is usually met by the macrocycles of 10 – 20 monomers of thiophene with a circumference of 7 – 17 nm. Another requirement is the absence of defects in the ring which would result in electron localization. Obviously for a persistent current to be *persistent* no inelastic scattering of the electrons destroying the coherence would be allowed requiring the organic rings to be “defect-free”. However, elastic scattering, remembering the phase shift, would not have a deleterious effect. Since we argue that such persistent currents could be generated even in absence of a magnetic field and resulting from fluctuations in the electron density along the ring we have the problem that a current in only one sense is forbidden by time-reversal symmetry (clockwise and counterclockwise current have strictly the same probability). This problem may be resolved by incorporating chirality in the ring which is breaking the symmetry.

All these stringent conditions for the macrocycles envisioned require a very detailed synthesis program. We therefore developed an extensive program of simulations (DFT calculations) of macrocycles to define those which could be valuable candidates and taking into account synthetic feasibility. Especially the manner of closing the ring is of the utmost importance, synthesis-wise and avoiding a break in the continuity of the macrocycle.

As a first criterion we tested the continuity of the electron orbitals over the ring since this clearly indicates any defect or inability of a continuous motion of the electron along the ring.

DFT calculations of macrocycles.

Candidates for the new promising macrocycles can be screened relatively fast and inexpensively by calculating the respective electronic properties. Property changes by, often minor, changes in structure are analyzed properly. In addition to the calculation of the electronic structure of the macrocycles by DFT these calculations supplements and guides the synthetic approach. In this respect **a powerful desktop – MAC PRO 8 core 3.0 GHz/16GB and 1 TB SSD - required for this project is a most essential and highly valuable “instrument” and enabled DFT at different levels calculations in a reasonable time frame.**

Most DFT calculations, using the GAMESS program, are done at the Effective Core Potential (ECP) valence basis set which neglects explicitly the core electrons. Although analogous to semi-empirical methods this ECP approach gives good results at a fraction of the cost of a calculation involving all electrons. This approach has been chosen since our interest is obviously in the orbital structure of the outer shells. As ECP potentials we have used SBKJIC. All structures of the macrocycles analyzed have been drawn by the AVOGADRO program and optimized by the MMFF94 force field using conjugate gradients before starting a DFT calculation. MACMOLPLT program is used to visualize the orbitals. Some of the results obtained have been checked by higher levels of DFT (B3LYP, 6-311++G(2d,p), 6-31+G(2d,p) or G-31+G(d,p)).

We will give here the different macrocycles we simulated as well as the energies of the orbitals around the top edge (HOMO, LUMO, LUMO+1, HOMO-1...). We give the structure of the macrocycle calculated as well as indicating a short name * to specifying the macrocycle, e.g. RRMethylDecaRing means a macrocycle built from regular 3-Methylthiophene in a 10-ring:

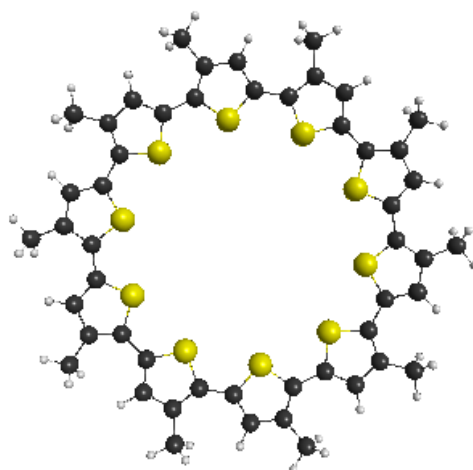


Fig. 2 Regular DecaMethyl Thiophene Ring (geometrically optimized structure DFT, B3LYP, ECP) In general for all macrocycles: Yellow= Sulfur, Black = Carbon, White = Hydrogen.

* The official IUPAC name for this Macrocycle: **1³,2⁴,3⁴,4⁴,5⁴,6⁴,7⁴,8⁴,9⁴,10³-decamethyl-1,2,3,4,5,6,7,8,9,10(2,5)-decathiophenacyclodecaphane** is prohibitive to use.

RRDecaMethylthiophene macrocycle

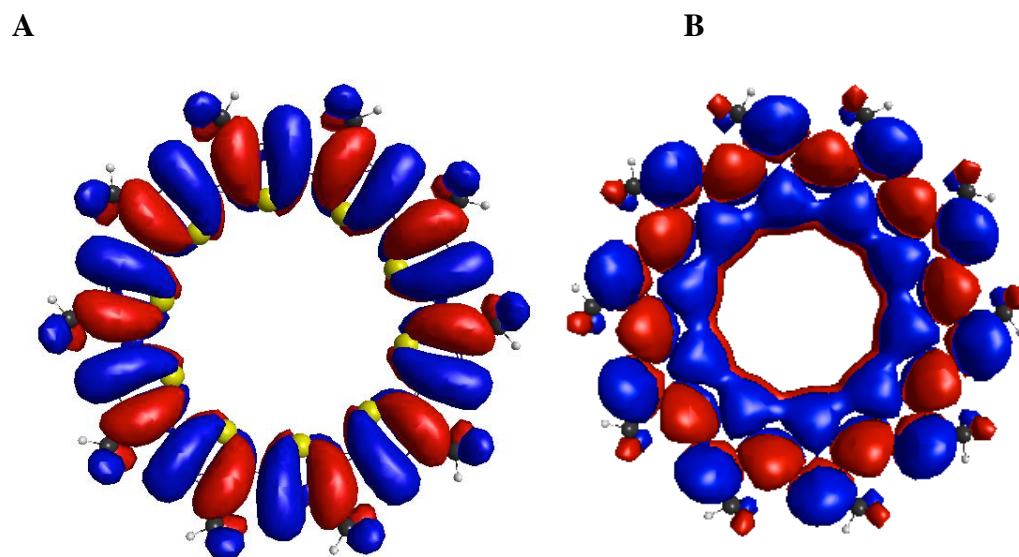


Fig. 3 A HOMO (-4.44 eV) en B LUMO (-2.07 eV) molecular orbitals of RRDecaMethylThiophene macrocycle – ring-size (opposing S-S distance) $\varnothing = 1.06$ nm

For the RRdecaMethylThiophene macrocycle we see nice continuous and highly symmetric HOMO and LUMO orbitals as would be expected from the symmetrical structure obtained after geometrical optimization. The energy gap or bandgap for this macrocycle, $\Delta E = 2.37$ eV in accordance with the fact that we have an undoped pristine “polymer” where the energy gap is too large for a significant excitation of charge carriers by thermal excitation.

In subsequent simulations we investigated the role of a regular defect, of a chiral side-group and of the effects from oxidation, mono- and dication, of the DecaMethyl Thiophene macrocycle.

The macrocycle DecaMethylThiophene should be actually seen as the “ideal” macrocycle but the synthetic possibilities have no easy access to such a perfect ring. We therefore calculated macrocycles with different closures to assess the possible breaking of the conjugation over the ring by the closure group.

rrDecaMethylThiophene Macrocycle

In this ring we considered the potential effect of a regular defect (as indicated) given in the structure:

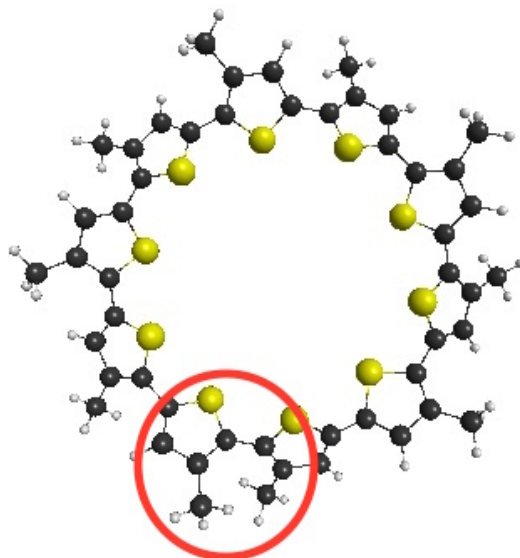
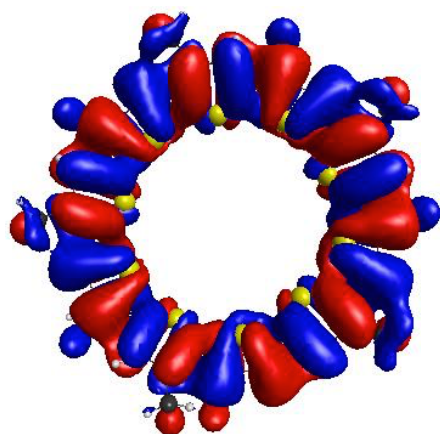


Fig 4. Structure of the rrMethylDecaThiophene ring indicating the structural defect.

The HOMO en LUMO are presented in Fig. 5.

A



B

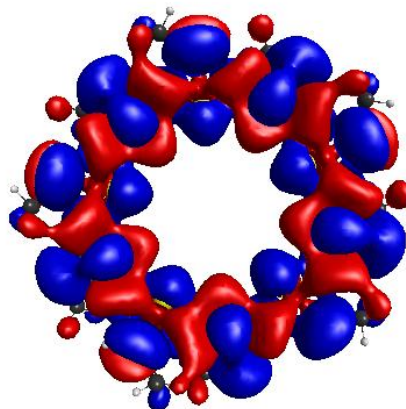


Fig. 5 **A.** HOMO (- 4.93 eV) and **B.** LUMO (- 1.58 eV) molecular orbitals of rrDecaMethylThiophene macrocycle – ring-size (opposing S-S distance) $\varnothing = 1.06$ nm

Here also the electron conjugation is continuous over the ring. However, we see a marked difference in the orbital energies, presumably indicating the strain in the ring as a consequence of the regular defect. The energy gap is 3.35 eV, far too large for any conductance over the ring.

Chiral RRnonamethyl(2-methylbutyl)DecaThiophene Macrocycles

We investigated macrocycle RRDecaMethylThiophene rings where one methyl group was replaced by a chiral alkyl group to assess the possibility of chiral induction in the ring resulting in a directional sense to the macrocycle ring.

The macrocycle structure calculated is:

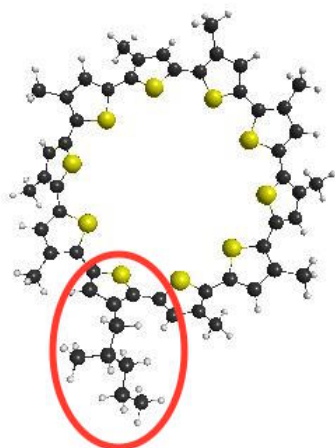


Fig. 6 Structure of the chiral nonamethyl-(2-methylbutyl) DecaThiophene Macrocycle.

The HOMO en LUMO are presented in Fig. 7.

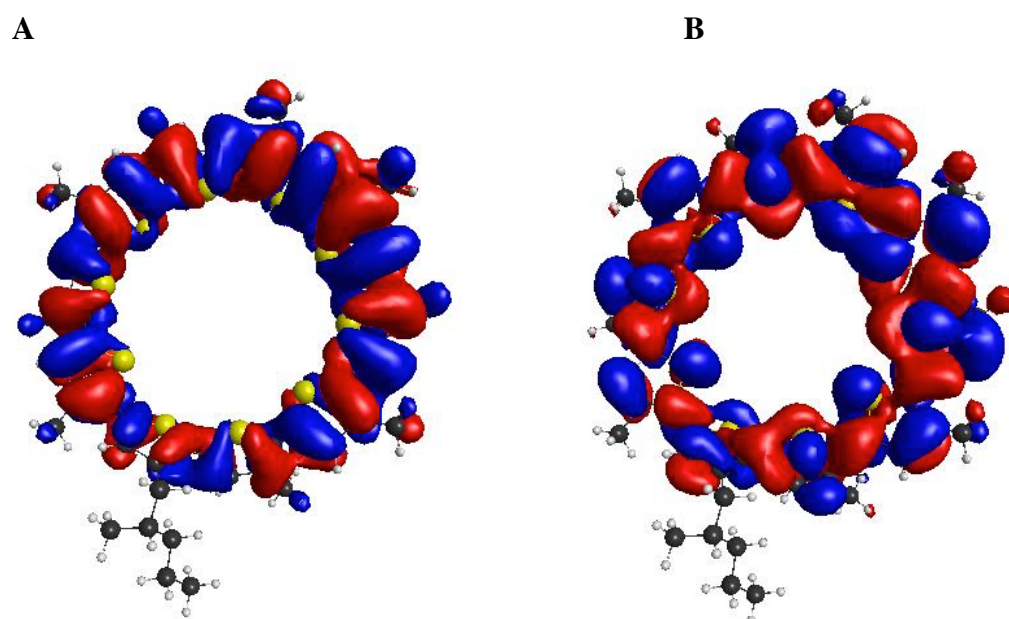


Fig 7 A. HOMO (- 4.95 eV) and **B.** LUMO (- 1.55 eV) molecular orbitals of chiral RRnonamethyl-(2-methylbutyl) DecaThiophene Macrocycle.

In fig. 7 we see a slight deformation of the frontier orbitals around the chiral group. This may be due to the chirality but we can not exclude an effect of a strain in the ring due to the bulkier alkyl group present - this argument may be corroborated by the fact that the energies for HOMO and LUMO are equal to those found for the rrDecaMethylThiophene macrocycle.

Since the molecular geometry is chiral the wavefunction is also chiral and since the calculation is done for a single enantiomer there is no possibility of racemization. However it may be that the chirality is not necessarily visible from analyzing the frontier orbitals. In particular, the chirality is associated with the pending group so that the related molecular orbitals should better exhibit chirality. On the other hand, for the ring, the chirality is like a perturbation and its amplitude is expected to be rather small. Still, we do not have at this moment a more quantitative approach to measure the chirality in the ring; so far, just the topology of the molecular orbitals can be used. Moreover, there is also a missing point concerning the relationship between the wavefunction chirality and the chirality of the individual molecular orbitals. To elucidate this somewhat in more detail we calculated a macrocycle consisting of ten thiophene groups with a chiral 2-methylbutyl group in the 3-position with DFT B3LYP at the 6-311++G(2d,p) level. The ring structure is given in Fig. 8 and the frontier orbitals in Figure 9.

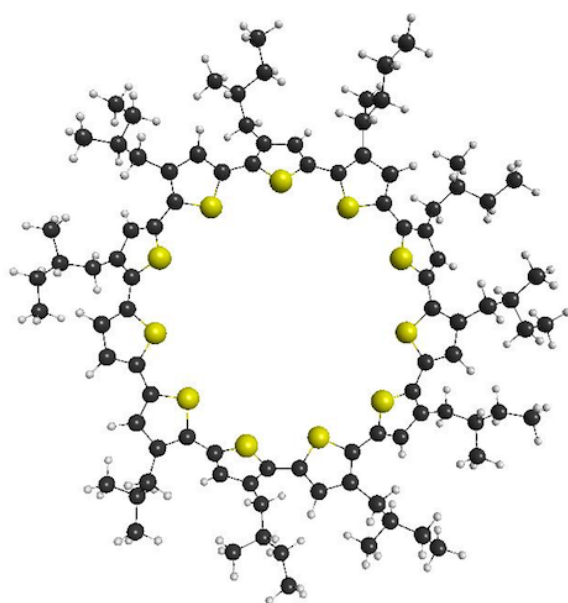


Fig. 8 Structure of all-chiral RR(2-methylbutyl)DecaThiophene macrocycle

The HOMO en LUMO of all-chiral RR(2-methylbutyl)DecaThiophene macrocycle are presented in Fig. 9

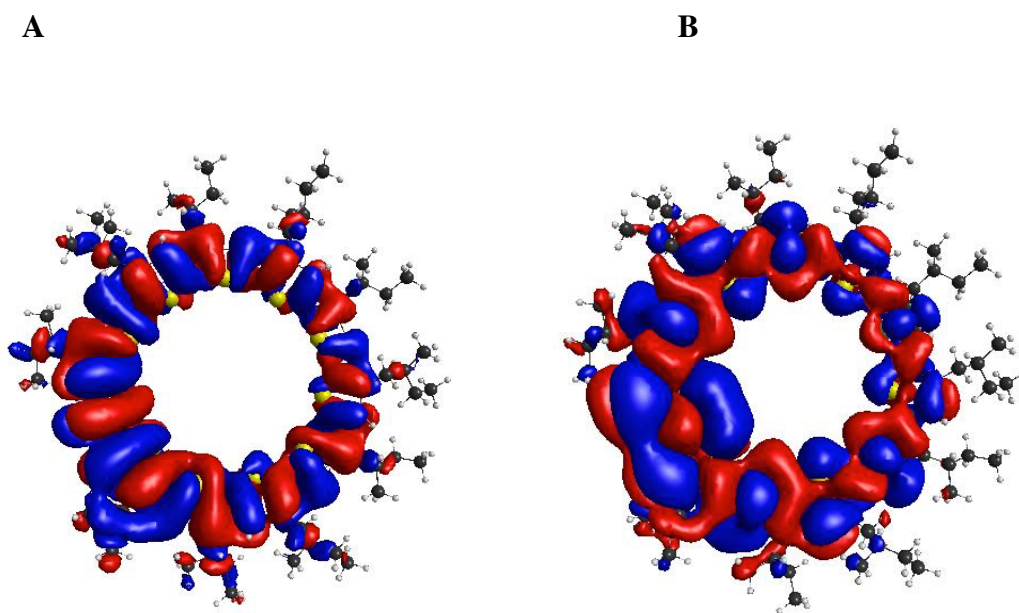
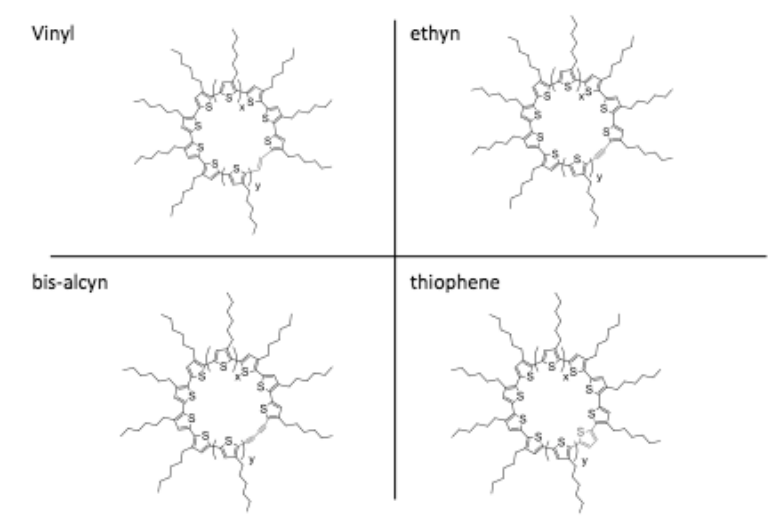


Fig. 9 A. HOMO (- 5.07 eV) and B. LUMO (- 1.47 eV) molecular orbitals of chiral RR (2-methylbutyl) DecaThiophene Macrocycle.

Again we see here a deformation of the frontier orbitals and the same discussion applies as for the RRnonamethyl-(2-methylbutyl) DecaThiophene Macrocycle.

In view of the great difficulties in the synthesis of pure thiophene rings – the ring closure often presents problems – we set up a calculation program for different closing group with the aim to see if the closing group is not breaking the electronic conjugation in the ring. The different closing groups proposed are summarized as:



RRVinylmethyl decaThiophene Macrocycle

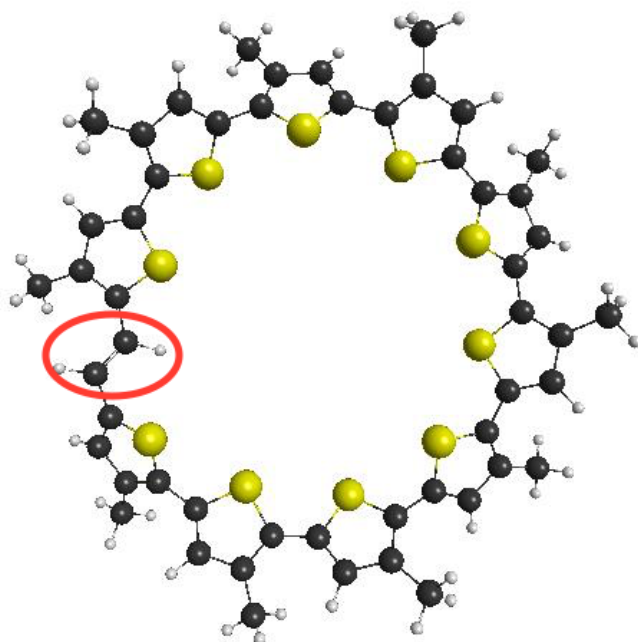


Fig. 10 Structure of the RRVinylMethyl Decathiophene macrocycle

The HOMO en LUMO of RRVinylMethyl Decathiophene macrocycle are presented in Fig. 11.

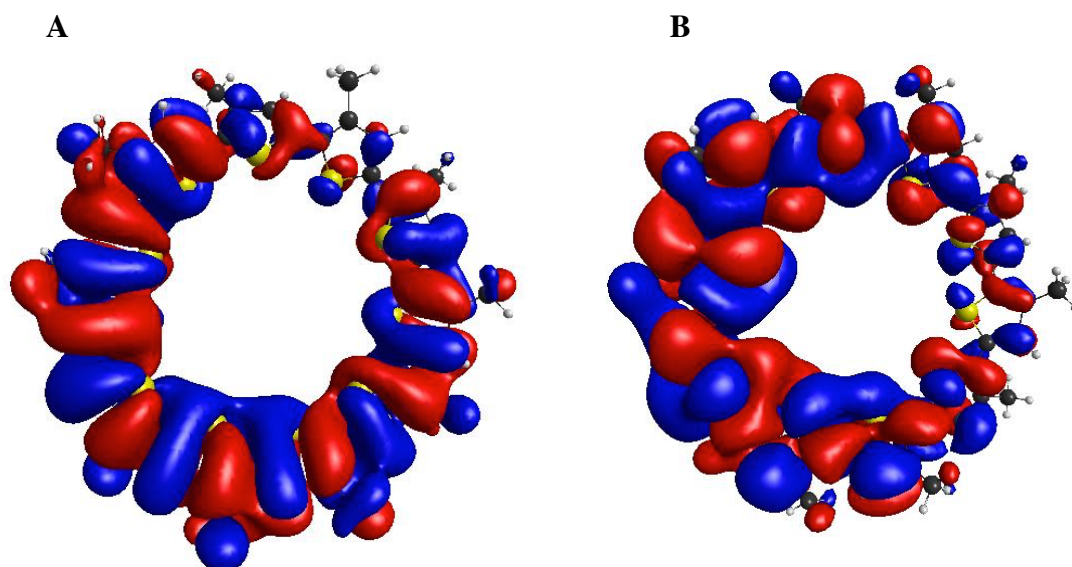


Fig. 11 HOMO (- 4.93 eV) and B. LUMO (- 1.69 eV) molecular orbitals of RRVinylMethyl Decathiophene macrocycle.

The frontier orbitals are not continuous over the ring; presumably the double bond of the vinyl closure group is drawing electron density away from the ring.

BisAlkynmethyl decaThiophene Macrocycle

In view of the synthetic difficulties with the monoalkyne closure this macrocycle was not studied. Here we address the closure by a bisalkyne group, easier to implement synthetically.

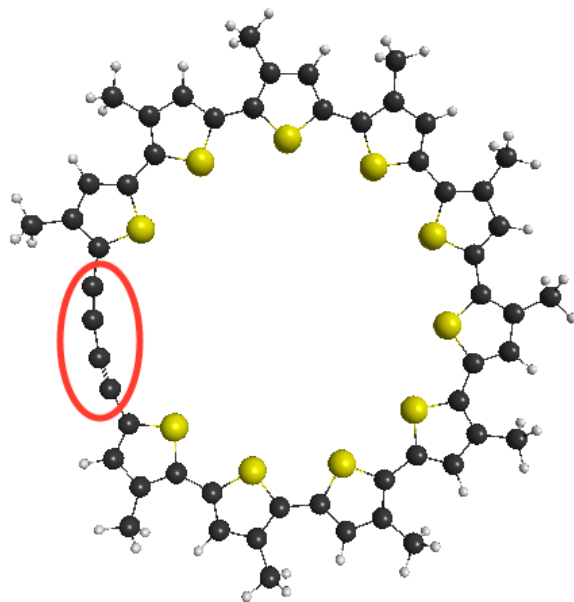


Fig. 12 structure of the RRBisAlkynmethyl DecaThiophene macrocycle.

The HOMO and LUMO of RRBisAlkynmethyl DecaThiophene macrocycle are presented in Fig. 13.

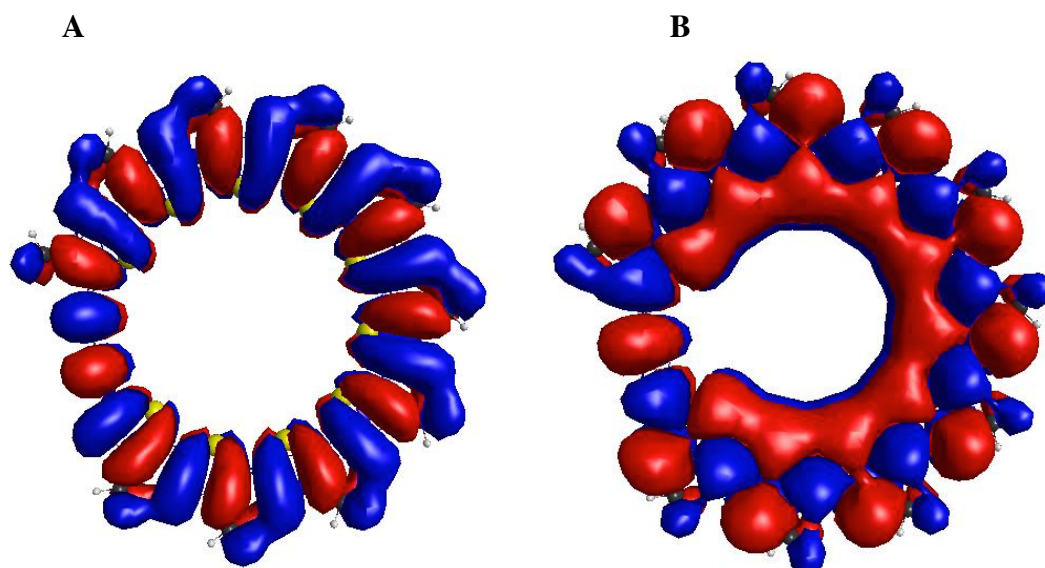


Fig. 13 HOMO (- 4.53 eV) and **B.** LUMO (- 1.67 eV) molecular orbitals of RRBisAlkynmethyl DecaThiophene macrocycle.

We see already a reasonable continuity in the HOMO orbital. Here the electron density is, as expected, somewhat drawn into the thiophene part of the macrocycle.

RRMethylThiophenyl DecaThiophene Macrocycle

A last structure, synthetically “easily” derived from the bisalkyne macrocycle is the RRMethylThiophenyl DecaThiophene Macrocycle which already closely resembles the perfect decathiophene ring.

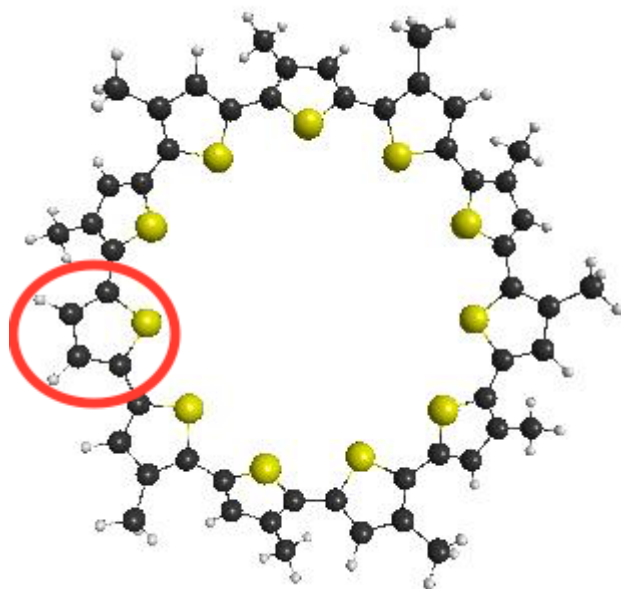
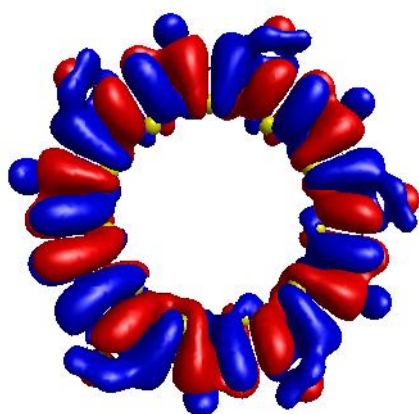


Fig. 14 structure of the RRMethylThiophenyl DecaThiophene Macrocycle

A



B

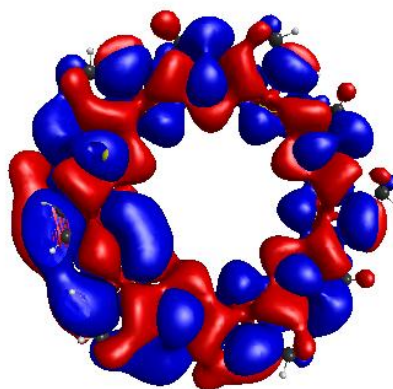


Fig. 15 HOMO (- 5.01 eV) and **B.** LUMO (- 1.82 eV) molecular orbitals of RRBisAlkynmethyl DecaThiophene macrocycle.

Not unexpectedly this macrocycle shows to be almost identical to the perfect 10-ring altho the symmetry of the LUMO is somewhat disturbed, not easy understood at this point.

In view of the interesting result we calculated also a macrocycle with a thiopenyl closing group and a methyl exchanged by a chiral 2-methylbutyl group to see if there could be a better coupling of the chiral group to the electronic conjugation we have also investigated this macrocycle the structure of which is presented in Fig. 10.

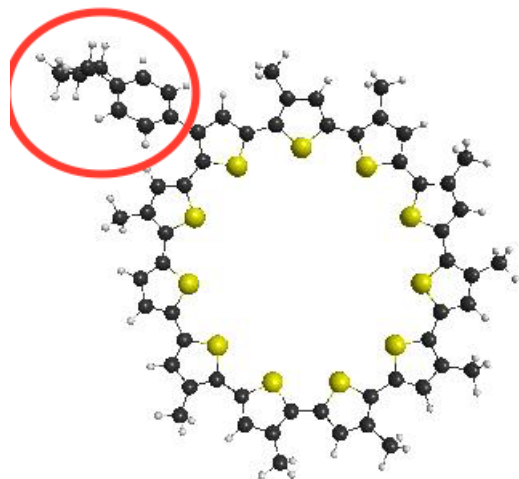


Fig. 16 Structure of Chiral RRNonaMethyl(4-(2-methylbutyl)benzyl) DecaThiophene macrocycle

The HOMO en LUMO of this RRNonaMethyl(4-(2-methylbutyl)benzyl) DecaThiophene macrocycle are presented in Fig. 17

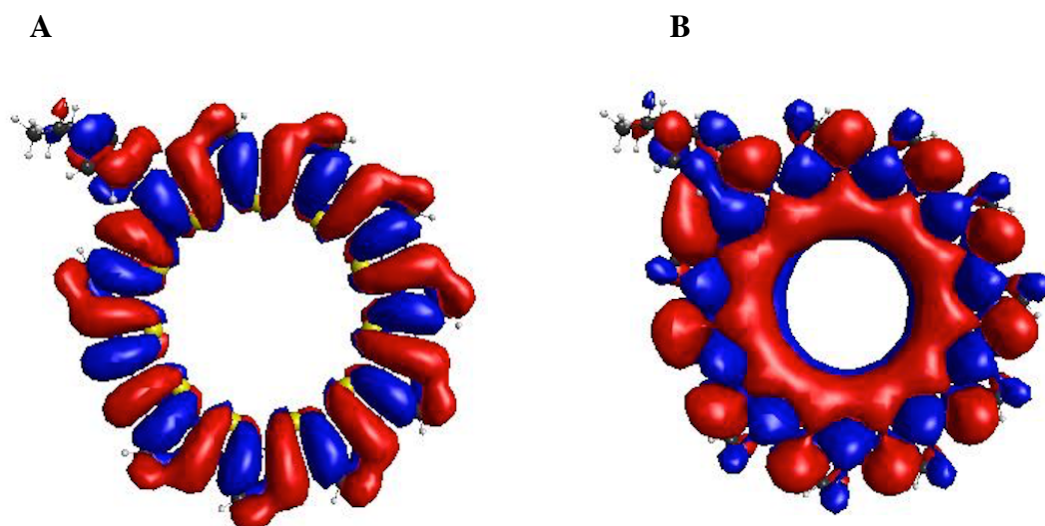


Fig. 17 A. HOMO (4.69 eV) and B. LUMO (- 2.29 eV) molecular orbitals of chiral RRNonaMethyl(4-(2-methylbutyl)benzyl) DecaThiophene macrocycle.

Surprisingly but very pleasingly we clearly see in the HOMO orbital the appearance of a handedness – a first indication that a chirality can be induced in the macrocycle by a single chiral side group. The gap energy is also markedly decreased, $\Delta E = 2.40$ eV, the same as for the perfect ring. Although this gap energy is still rather high the accordance with the RRDecaMethylThiophene macrocycle energy gap proves that the chiral side group does not influence the front orbital energies.

Larger Rings (> 10 thiophenes).

The synthesis of the macrocycles usually starts from carefully prepared regular oligothiophenes. However, these oligothiophenes are not monodisperse and we have to take into account a certain dispersity in the macrocycles, e.g. the presence of larger rings. We therefore calculated large macrocycles with 16 monomers in the ring. These calculations immediately pointed to an important problem, the conformational flexibility and nonplanarity of the rings.

This can be seen from the geometrically optimized (DFT) structure of RRMethylHexaDecaThiophene Ring:

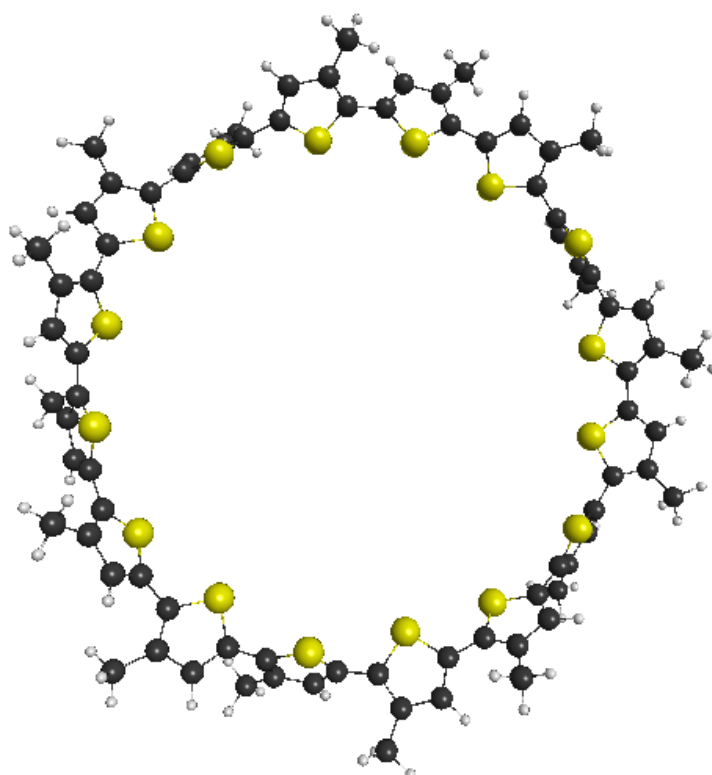


Fig. 18 Geometrically optimized structure of the *HexaDecaRing* - ring-size (opposing S-S distance) $\varnothing = 1.80$ nm

The HOMO, LUMO and HOMO-1 and LUMO+1 are presented in Figure 19.

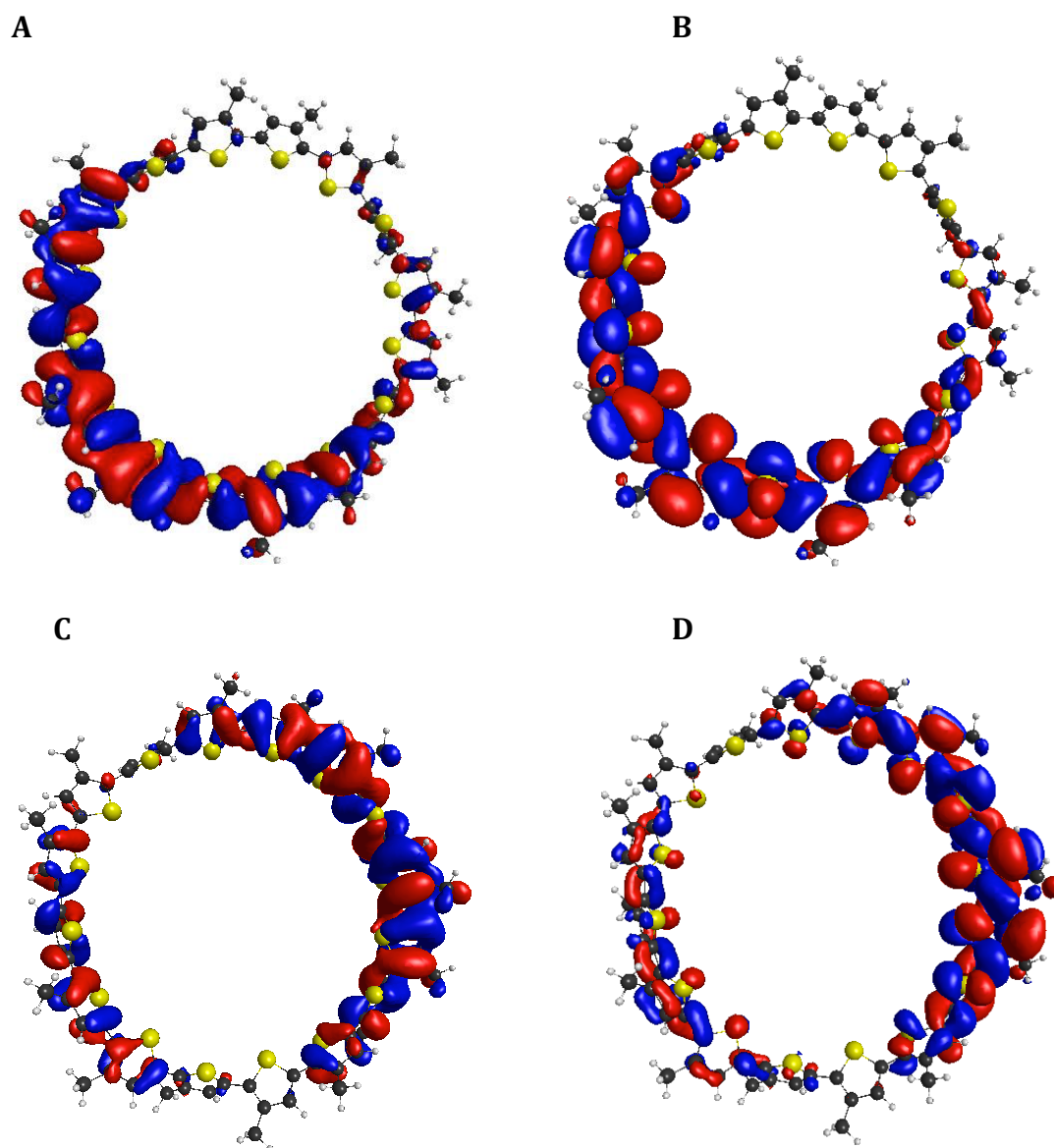


Fig. 19 A HOMO (- 5.14 eV), B. LUMO (- 1.25 eV) C HOMO-1 (-5.20 eV) and D LUMO+1 (-1.20 eV) molecular orbitals of RRMethylHexaDecaThiophene Macrocycle.

The result of the calculations for this Hexadeca ring indicates clearly the importance of the conformational lability of the ring. It seems as if the thiophene groups which are rotated out of the plane of the ring blocks the conjugation, almost making of the ring two independent halves (molecules). We see for example that the ΔE (LUMO - HOMO) = 3.89 eV and the ΔE (LUMO+1 - HOMO-1) = 4.00 eV.

This result points to a fundamental problem for organic macrocycles as quantum rings since the electronic conjugation is easily broken by the conformational lability of the ring. Therefore, we have to develop methods and techniques should to planarize the rings.

In the previous calculations we see that the macrocycles, pristine oligothiophene rings, are essentially insulators and currents in the rings could therefore not be present – although fluctuations in the electron density along the ring may show some “current” effects.

In the following we will discuss some approaches how to address the aforementioned problems.

Oxidised macrocycles.

As is well known oligothiophenes show a strong increase in conductivity by several orders of magnitude upon doping (oxidation) and become semiconductors (even metallic behaviour), even at very low levels of doping smaller than 1%. We therefore investigated the cations, mono- and dications, of the polythiophene macrocycles (the anions were not considered in view of the experimentally near impossibility to reduce polythiophenes).

Monocation of RRMethyl DecaThiophene macrocycle

As a first calculation we addressed the simple RRMethylDecaRing to see how the energies of the frontier orbitals were affected by the doping and to assess the change in energy gap. The HOMO and LUMO orbitals of the monocation – singly occupied – are given in Fig.20.

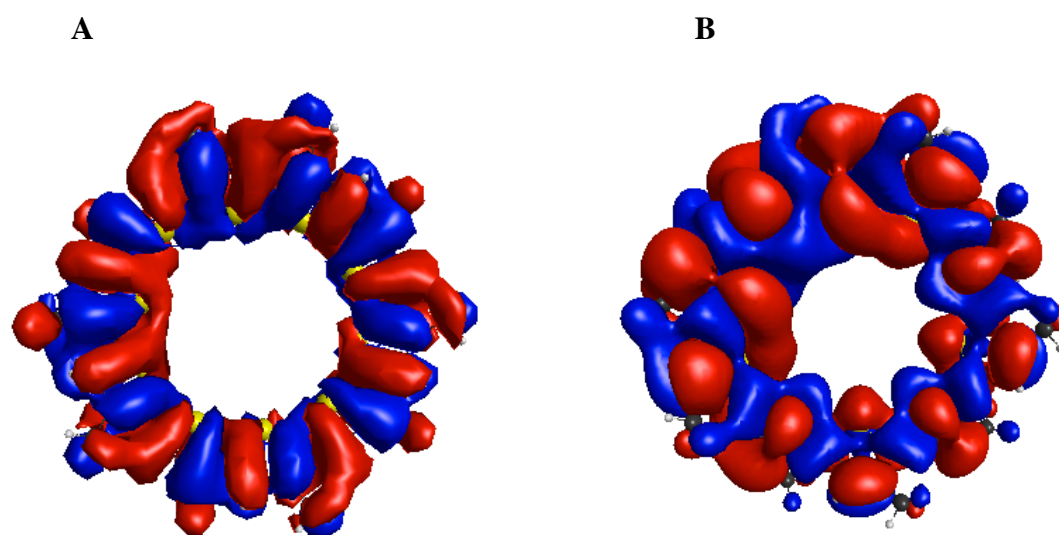


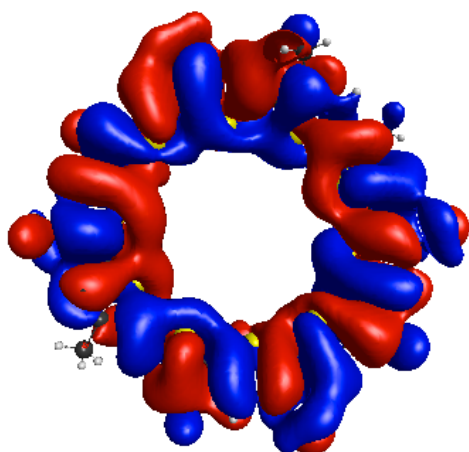
Fig. 20 A HOMO (- 6.88 eV), B. LUMO (- 3.92 eV) molecular orbitals of RRMethylDecaThiophene Monocation Macrocycle.

We see from this calculation a good continuous HOMO orbital. The energy separation $\Delta E = 2.96$ eV is higher than in the neutral macrocycle, a result difficult to understand which is also the case of the clear distortion in the LUMO orbital.

Dication of RRMethyl DecaThiophene macrocycle.

The HOMO and LUMO orbitals are given in Fig. 21 for the dication of RRMethyl DecaThiophene macrocycle.

A



B

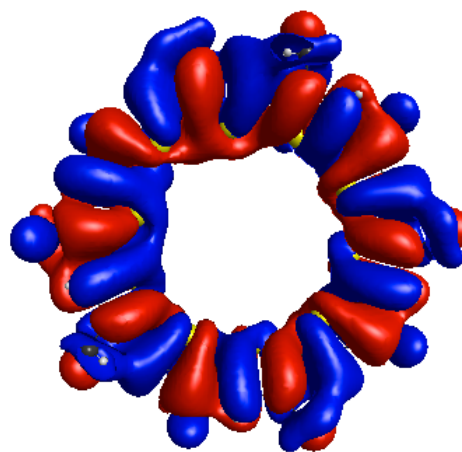


Fig. 21 A HOMO (- 9.47 eV), B. LUMO (- 8.87 eV) molecular orbitals of RRMethylDecaThiophene Dication Macrocycle

We see here continuous frontier orbital over the ring with a $\Delta E = 2.96$ eV with a small energy gap $\Delta E = 0.60$ eV which is consistent with a semiconductor behaviour.

Monocation of RRMethyl HexaDecaThiophene macrocycle.

The mono- and dications of the HexaDeca ring were calculated to assess the influence of the oxidation of this larger ring upon the energy levels and, especially, upon the planarity. It was hypothesized that, due to the strongly increased conductivity, the ring current would force the ring to go to a more planar conformation.

See Fig. 18 for the structure of the ring. Since the monocation is an open shell system (unpaired electron) we have to take this into account in the DFT calculations (done at the level of ECP with SBKJC basis set).

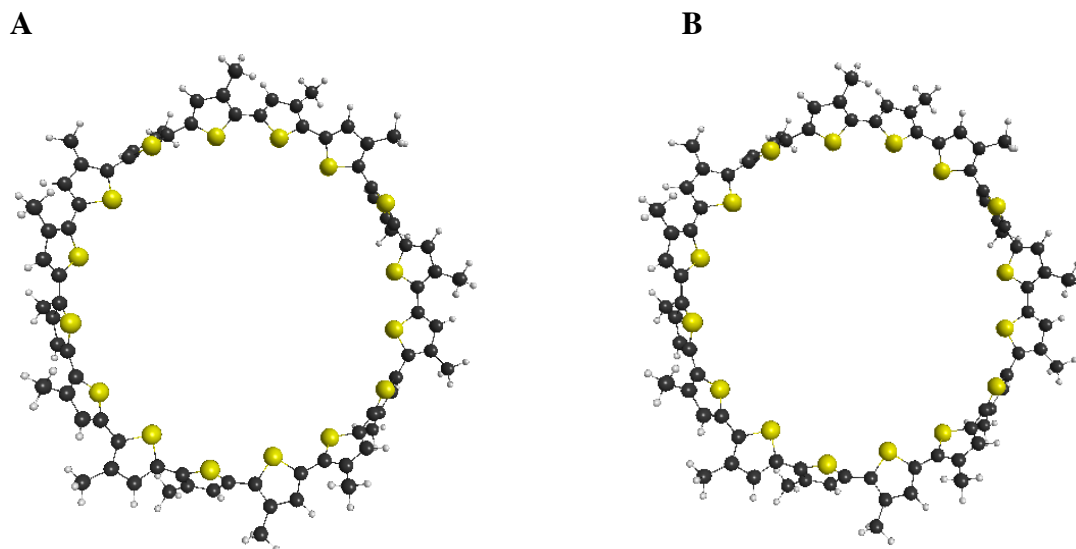


Fig. 22 Optimized structures of **A** Neutral RRMethyl HexaDecaThiophene and **B** the RRHexaMethyl DecaThiophene Monocation

Remark in Fig. 22 the similarity in structure **A** and **B**, both optimized in a different DFT calculation.

In Fig. 23 we present the HOMO and LUMO of the monocation - these orbitals are single occupied – as well as the HOMO-1 and LUMO+1

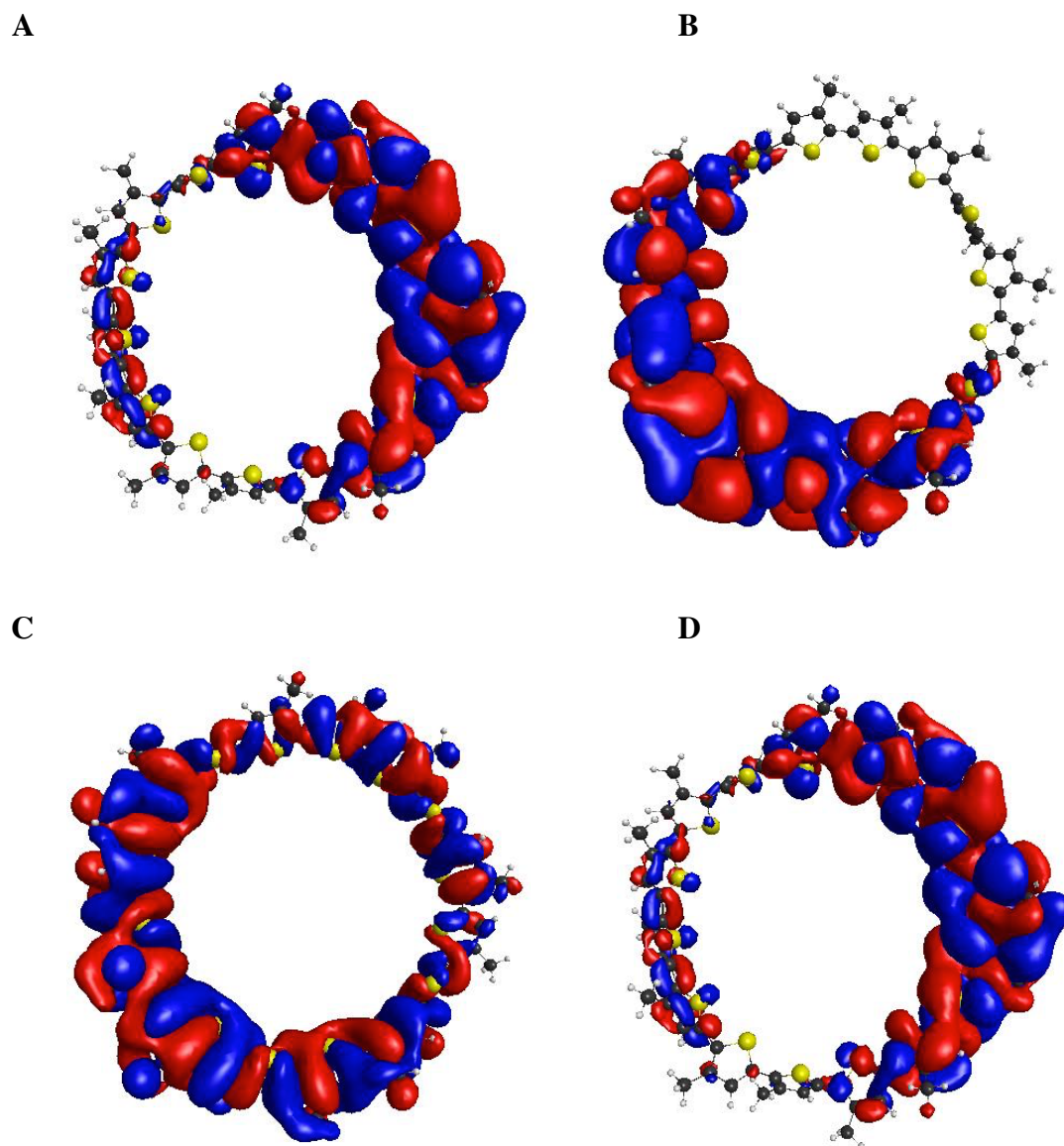


Fig. 23 A HOMO (- 6.64 eV), B. LUMO (- 2.99 eV) C HOMO-1 (-6.67 eV) and D LUMO+1 (-2.86 eV) molecular orbitals of RRMethylHexaDecaThiophene Monocation Macrocycle.

No great effects are seen as from the neutral macrocycle, except that the HOMO (single occupied) and the HOMO-1 (fully occupied) have now some more continuous distribution in the electron density.

Dication of RRMethyl HexaDecaThiophene macrocycle.

The structure of the ring, and compared to the neutral ring, is presented in Fig. 24.

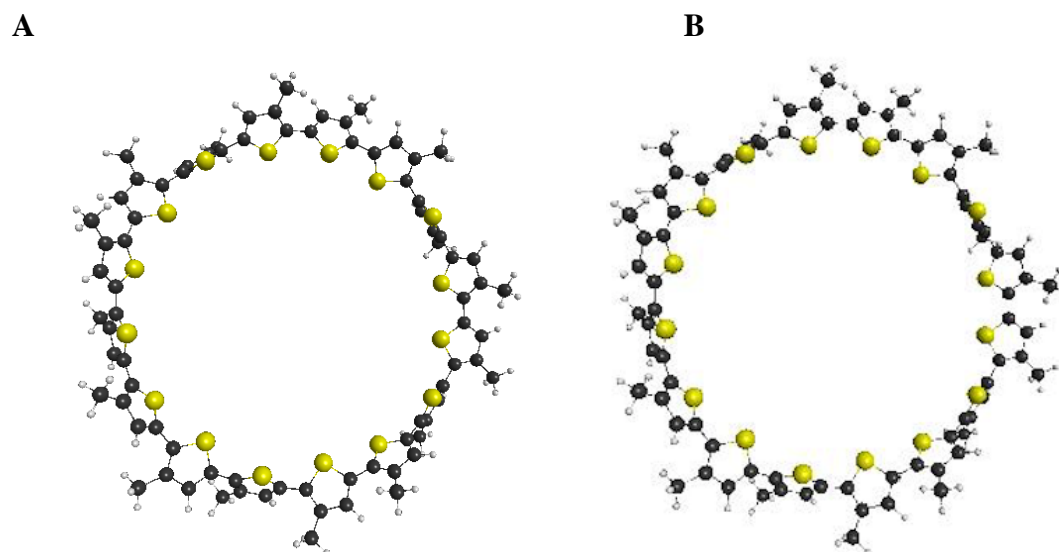


Fig. 24 Optimized structures of RRMethyl HexaDecaThiophene **A**, respectively RRMethyl HexaDecaThiophene Dication, **B**

Again, we see a strong similarity between the structures of the neutral macrocycle and the dication, hinting at the fact that the oxidation has no marked influence on the conformation of the ring.

In Fig. 25 we present the HOMO, LUMO, HOMO-1 and LUMO+1 of the dication. Of course all these orbitals are fully occupied.

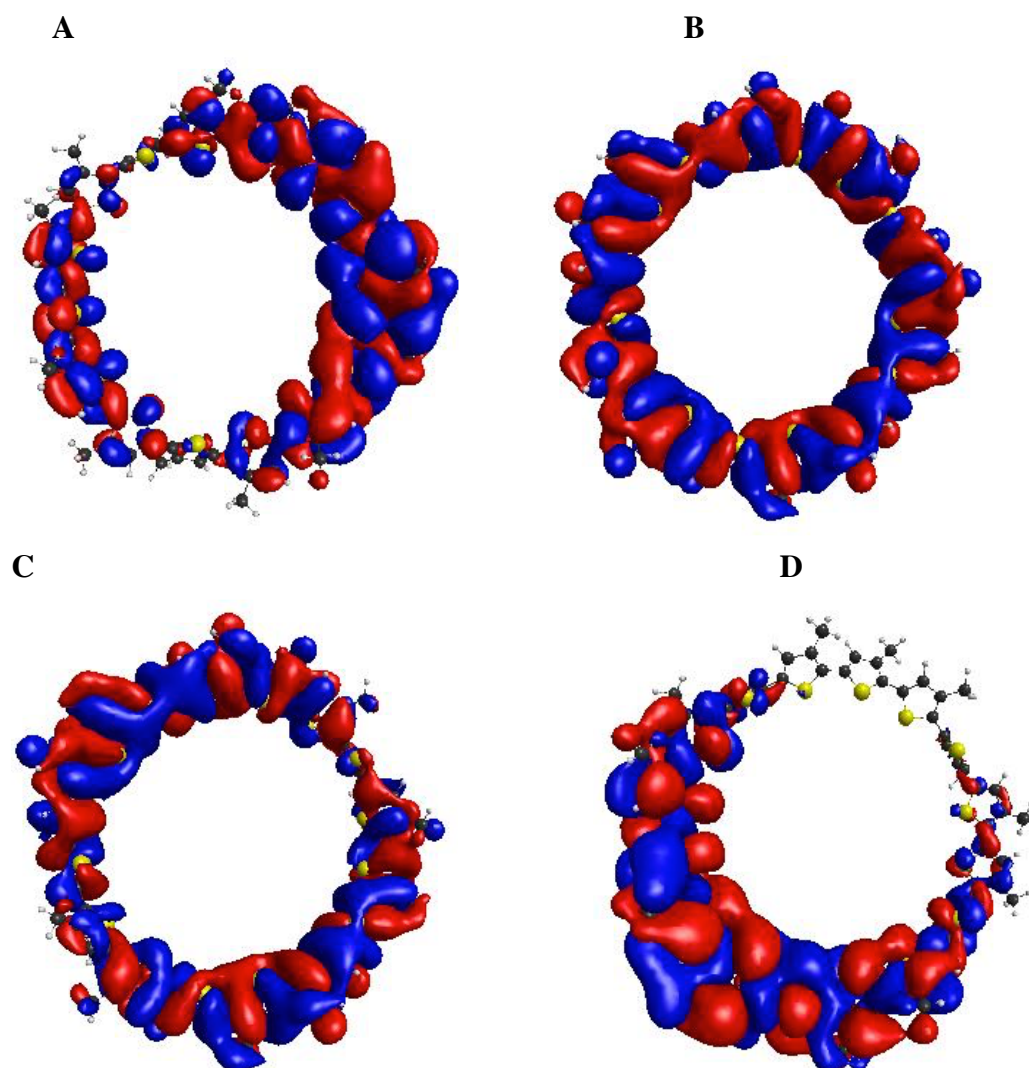


Fig. 25 A HOMO (- 8.33 eV), B. LUMO (- 8.11 eV) C HOMO-1 (-8.38 eV) and D LUMO+1 (-4.57 eV) molecular orbitals of RRMethylHexaDecaThiophene Dication Macrocycle.

Here we see the appearance of the expected continuity in the orbitals and, very important a small energy gap between HOMO, LUMO and HOMO-1, being ΔE (HOMO – LUMO) = 0.22 eV and ΔE (HOMO-1 – HOMO) = 0.05 eV and ΔE (HOMO-1 – LUMO) = 0.27 eV. This clearly identifies the dication of this macrocycle as having semiconductor properties and therefore a valuable candidate for ring currents.

The further planarization of the ring, and avoiding defects due to conformational lability, will be the next problem to solve. Here we propose the adsorption of the dication on a gold surface – which would also allow to do optical measurements.

A very recent *experiment* (December 02/12) proves the importance of oxidation of these macocycles: UV-Vis spectra of neutral cyclic and oxidized cyclic P3HT (DP18, Mn=3000 g/mol) show a large difference between neutral and oxidized with a clear decrease of the optical gap, from 2.3 to 1.6 eV.

Conjugated Macrocycles in the Dongho Kim collaboration.

In collaboration with Dongho Kim, Yonsei University, Korea we calculated the conjugated macrocycles rings for which Dongho Kim is investigating the spectral properties.

The rings studied by Dongho Kim have butyl groups as the side chains in 2 and 3 position of the thiophene moiety but for more economy in the calculations we used methyl groups, avoiding the complexities due to the conformation of the butyl groups.

The structure of a decaring with 10 thiophene groups (Dongho name C10) is:

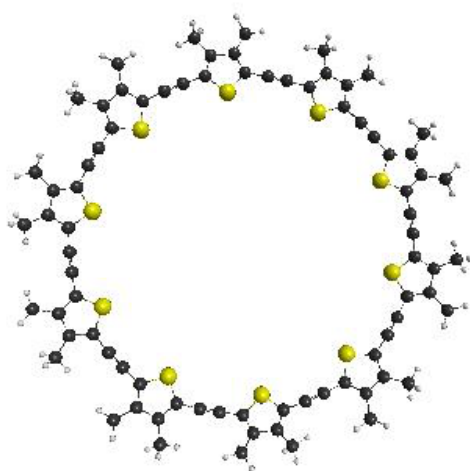


Fig. 26 Structure of RRMethyl Deca(Thiophene-alkynyl) macrocycle for short, MethylC10

The HOMO and LUMO of RRMethylC10 Macrocycle are presented in Fig. 27

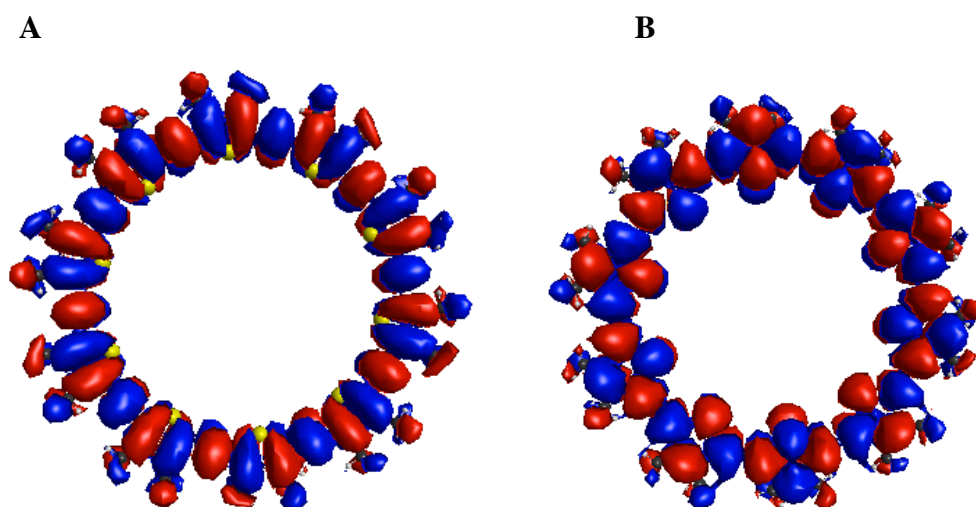


Fig. 27 A HOMO (- 4.68 eV), B. LUMO (- 1.99 eV) molecular orbitals of RRMethylC10 Macrocycle.

We see that this macrocycle-type is very promising having very homogeneous and continuous molecular frontier orbitals and already a relatively small energy gap (bandgap) of $\Delta E = 2.69$ eV.

At the request of our synthesis group we calculated also the MethylC10 Macrocycle where an alkyne-bridge was changed into a Bisalkyne group since this would allow an easier way of closing the rings. The HOMO and LUMO orbitals are presented in Fig. 28.

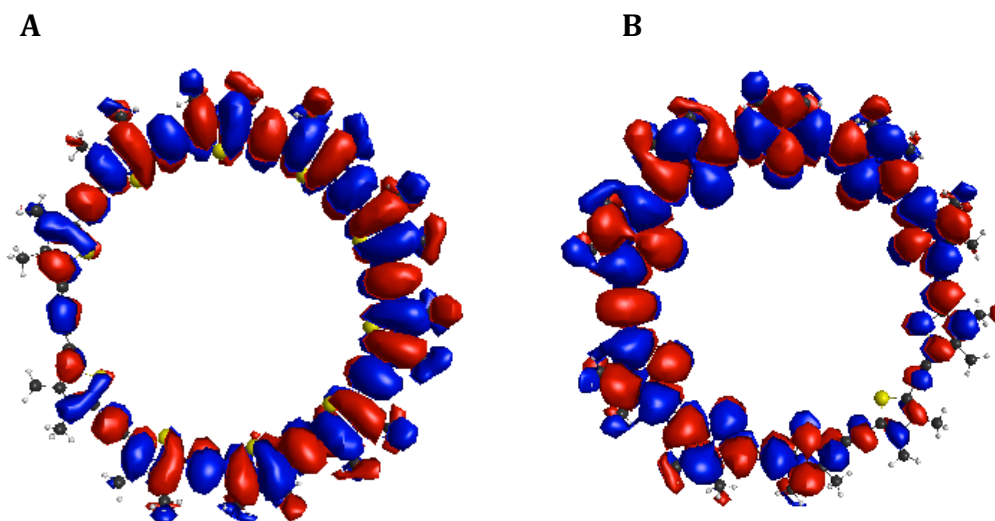


Fig. 28 **A** HOMO (4.76 eV) and **B** LUMO (1.96 eV) for the MethylC10- bisalkyne bridge Macrocycle

We see here that the continuity in the HOMO orbital is relatively well preserved and that the bandgap is still relatively small, $\Delta E = 2.80$ eV

In view of the pleasingly low energy gap and the excellent structure of the frontier orbitals we calculated the effects of oxidation, or doping of this rings yielding the monocation and the dication.

The results are given in Figs. 29 and Fig. 30.

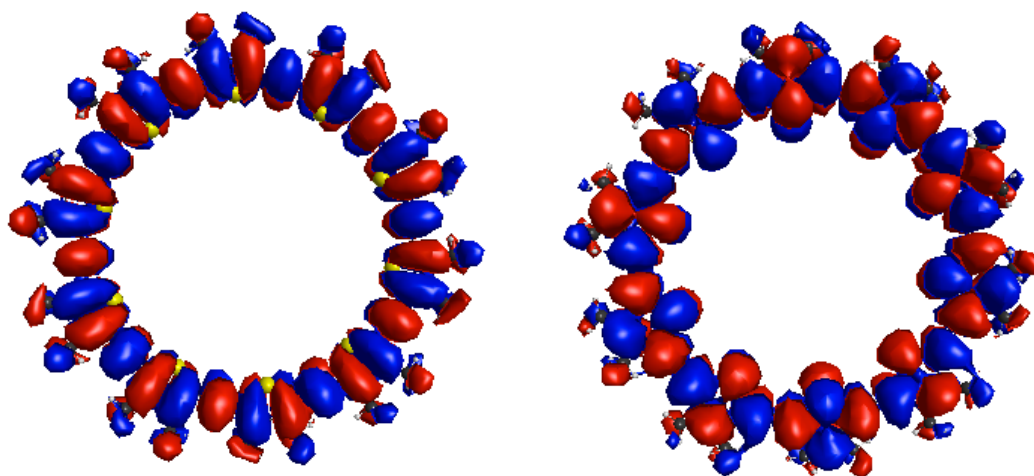


Fig. 29 **A** HOMO (6.12 eV) and **B** LUMO (3.70 eV) – single occupation - for the MethylC10 Monocation Macrocycle.

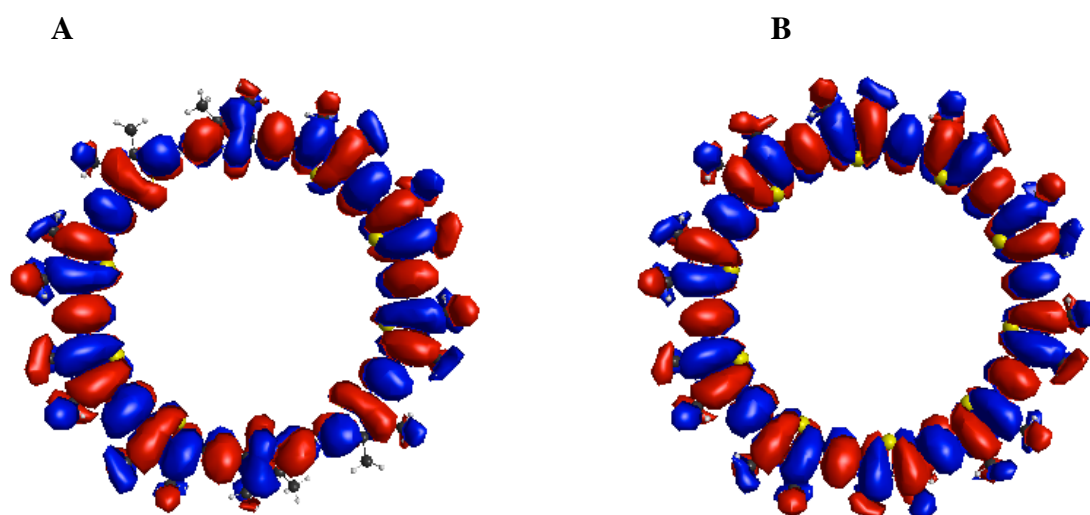


Fig 30 **A** HOMO (8.00 eV) and **B** LUMO (7.56 eV) for the MethylC10 Dication Macrocycle.

From these results we see that the frontier orbitals are very homogeneous and continuous over the rings. The energy gap for the monocation is also decreased vs. the neutral macrocycle, e.g. $\Delta E = 2.42$ eV vs. $\Delta E = 2.69$ eV. Most impressive, and a very important result, is the result for the dication where the energy gap is almost disappearing, $\Delta E = 0.44$ eV making this ring potentially a preferred candidate for further investigations of organic quantum rings. **This is perceived as a most important result of the collaboration between our groups.**

In view of the positive results obtained with the MethylC10 ring we calculated also the MethylC12 ring, this is the ring with 12 thiophene groups – compare Fig. 26, also investigated by Dongho Kim - to assess potential problems with conformational lability.

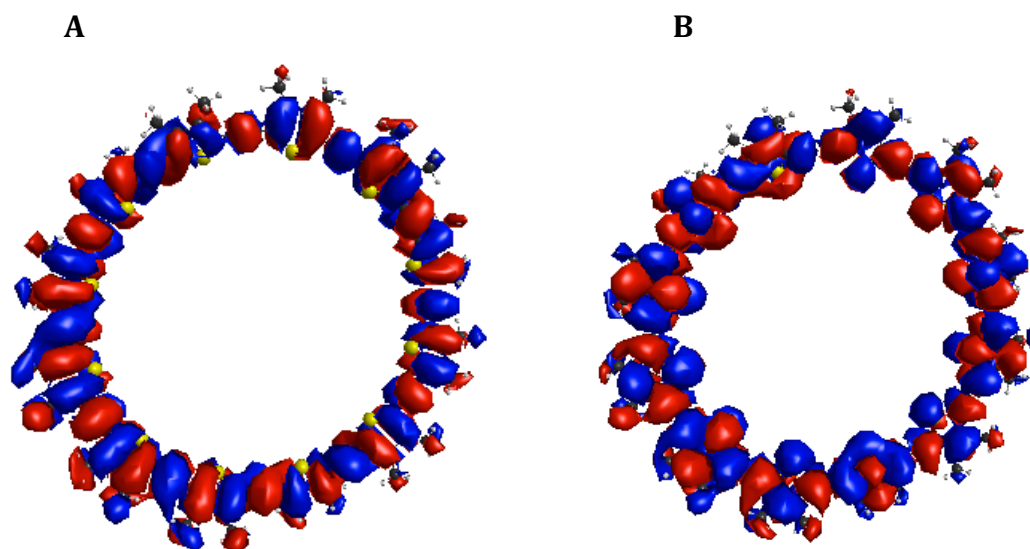


Fig. 31 A HOMO (4.84 eV) and B LUMO (1.89 eV) for the MethylC12 Macrocycle.

We see that even the C12 ring, apart from some skewness in the orbitals, presents a nice continuity in the orbitals with an energy gap equal to the energy gap in the MethylC10 ($\Delta E = 2.69$ eV).

Finally, in view of our interest in introducing chirality into conjugated macrocycles we investigated a ring whereby one methyl group in the MethylC10 was substituted by a chiral 2-methylButyl group. The results for the HOMO and LUMO in such a ring are shown in Fig. 33.

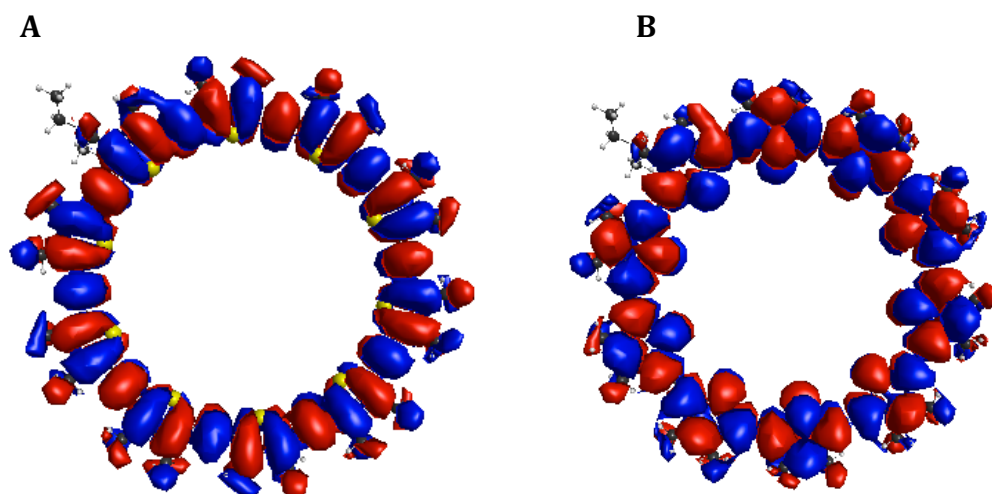


Fig. 32 A HOMO (4.68 eV) and B LUMO (1.99 eV) for chiral MethylC10 Macrocycle.

Judged from these results we see no influence of the chiral side group and the orbital energies are not changed from the MethylC10.

From this result we have to conclude that other methods of "molecular engineering" will be needed to induce a chirality in the ring.

Our interest in chirality in the ring is spurred by the fact that electrons moving in a chiral environment will induce a magnetic field which couples to the electron spin so that we may have a strong spin-orbit coupling. Such a "spiral" motion of the electrons in the ring will therefore result in a magnetic moment, possibly stabilizing a persistent current. It is important to realize that the introduction of chirality is "relatively" easy in organic systems, an important advantage for organic quantum rings.

Synthesis of Thiophene macrocycles

Introduction.

The final purpose of this research is to probe the magnetic properties of fully π -conjugated macrocyclic structures and particularly, the existence of persistent current after an external magnetic field was applied, or even in the absence of any external field.

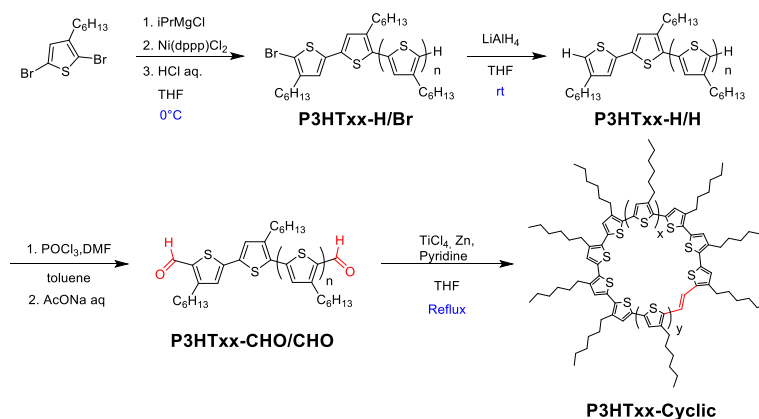
In a chemical point of view of the preparation of macrocyclic structures, the chosen strategy was the ring closure technique of a linear functionalized poly(3-alkylthiophene). Poly(3-alkylthiophene)s were chosen, since they allow cyclization (in contrast to *e.g.* poly(phenylenes and poly(phenylene ethynylene)), and can be prepared using a controlled polymerization with perfect end group fidelity, which is a requisite for cyclization. The actual cyclization is an oxidative coupling between a thiophene, bearing a H-atom in the 5-position and a phenylene bearing a H-atom in the 4-position. In order to realize the actual polymerization, the polymerization was performed using the Kumada catalyst transfer condensative polymerization, initiated by an *o*-tolyl initiator, and terminated with acid. In this way, the desired polymer could be made. ¹H NMR spectroscopy was used to determine the degree of polymerization and confirm the nature of the end-groups. GPC reveals the molecular weight and the dispersity, preferably as narrow as possible.

Synthesis of ethylene bridged macrocycle

Our main initial strategy for the preparation of macrocyclic structures was the ring closure technique of a linear functionalized poly(3-hexylthiophene), P3HT. Different chain lengths of P3HT have been synthesized, functionalized at both chain ends with aldehyde moieties and finally cyclized following the McMurry reaction in a pseudo high dilution process (scheme 1).

The Kumada Catalyst Transfer Polymerisation (KCTP) is used to obtain controlled molar mass polymer with low polydispersity, below 1.3, estimated from SEC characterization. The NMR spectra of the P3HT_x-H/H gave an estimation of the chain length or the number of repetitive thiophene units, which were for the four samples 18, 25, 33 and 42. The formyl moieties at both chain ends are introduced according the reaction of Vilsmeier, with POCl₃ and DMF. The ring closure is done via McMurry conditions with Zn powder, TiCl₂ (obtained in situ) and pyridine in pseudo high dilution. The success of each chain end functionalization has been confirmed by MALDI-TOF analysis.

The confirmation of the high-yielded intramolecular coupling came from the decrease of the hydrodynamic radius measured by SEC and correlated to the conservation of the mass distribution by MALDI-TOF and by the very low content of residual linear precursor estimated by NMR. This allow a direct comparison of the properties of macrocyclic and linear P3HT and a comparison of short and long system.



Scheme 1: Synthetic pathway of ethylene bridged macrocyclic structures

Different aggregation behavior between linear and cyclic and between short and long systems have been pointed out by DSC and UV-Vis absorption spectroscopy. The thermal transitions (temperature and enthalpy) are lower for cyclic than for linear structures.

The UV-Vis absorption spectra of the shortest (P3HT₁₈) and longest (P3HT₄₂) system are presented below. Spectra of linear and cyclic has been recorded in CHCl₃, which is a good solvent for these polymers, and in a mixture of CHCl₃ and MeOH (V_{CHCl₃}:V_{MeOH}=20:80), which induce an aggregation of the polymer chains. The maximum absorption is bathochromically shifted.

For linear systems, the increase of the molar mass induces a more pronounced shift to higher wavelengths (from 469 nm to 526 nm). A shoulder around 600 nm appears, indicating a small aggregation for small system P3HT₁₈ and for longer system P3HT₄₂, vibronic bands appears at 550 and 620 nm. In the latter case, the chains are highly aggregated and a fibrillar organisation become predominant.

For shorter cyclic systems, the ring strain induce, in solution, a twist between adjacent thiophene rings leading to lower wavelength absorption compare to linear. On the contrary, at solid state, those macrocycles present an “infinite” conjugation, and consequently, absorption at higher wavelengths.

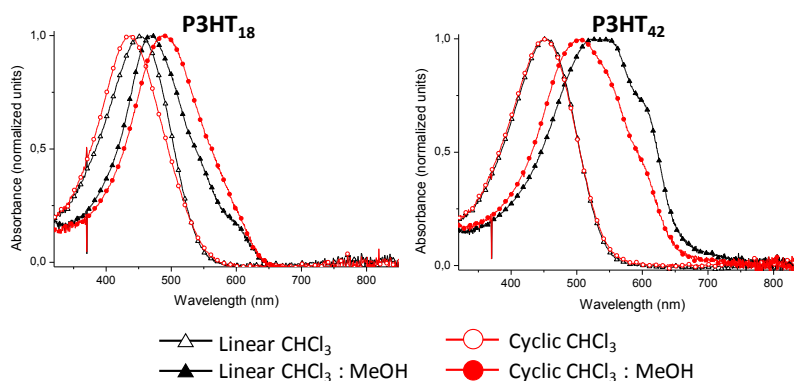


Fig. 1S UV-Vis spectra in solution of linear (black triangle) and cyclic (red circle) in CHCl₃ (dashed line) and CHCl₃:MeOH (20:80) (solid line) for the P3HT of DP = 18 and DP = 42.

For larger cyclic systems, the maximum absorption is lower than the linear equivalent by 19 nm. This can be attributed to shorter effective conjugation length due to the bent conformation of the cyclic structure and also probably to the steric hindrance of the regiodeflect. Moreover, the intensities of the vibronic band at 550 and 620 nm are clearly lower for P3HT₄₂ which indicate a lower π - π interaction upon aggregation, coherent with the less organized giant cyclic structure.

When chains are aggregated, a higher disorder is observed compare to linear counterparts and we estimate that long cyclic structures present similar aggregation behavior than long linear ones mainly due to the folding of those chains.

To assess the possibility of magnetic properties of the macrocycles we did initially some SQUID measurements analogous to the SQUID measurements done on the poly(3-dodecylthiophene) where we observed a clear ferromagnetic hysteresis at cryogenic temperatures. The polymer chosen was the P3HT₃₃. The sample has been prepared as schematized in Figure 2S. The crude powder has been sandwiched between two pieces of cotton in the plastic tube classically used for this kind of experiment.

The temperature of the sample has been cooled down to 5K and magnetic field is applied. By increasing the intensity of this field, the magnetic response of the sample is recorded. As illustrated on the curve below, the remanent magnetization is very low.

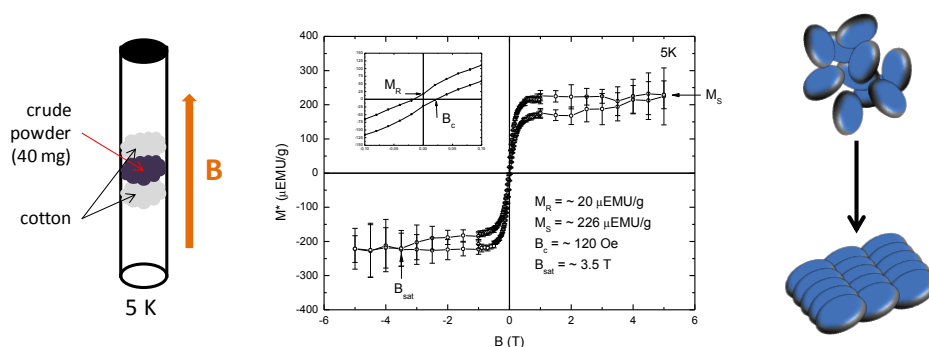


Fig. 2S Sample preparation, remanent magnetization in fonction of applied magnetic field, and schematic supramolecular organization

Two factors can be at the origin of this disappointing result. First, the electrons may not be delocalized on the whole macrocycle. That means, firstly, that the frontier orbitals (HOMO and LUMO) are not fully localized on the macrocycle. Secondly, another effect may be important e.g. the supramolecular organization of the macrocycles in the sample may not be efficient for this kind of application. Indeed, if all the macrocycles are not parallel together, the induce magnetization could not influence the overall sample. That could mean that most of the macrocycle is not affected by the magnetic field and so the remanent magnetization (or persistent current) is very low.

This result spurred to probe the first hypothesis about the continuous localization of the electrons on the macrocycle by DFT calculations of the frontier molecular orbitals (HOMO and LUMO) for decathiophene macrocycles closed with *different bonds*, ethylene, bis-acetylene or thiophene. The calculations showed clearly – see the

computational results - that the chemical structure of the bridge has an important influence on the complete delocalization of the electron on the entire macrocycle.

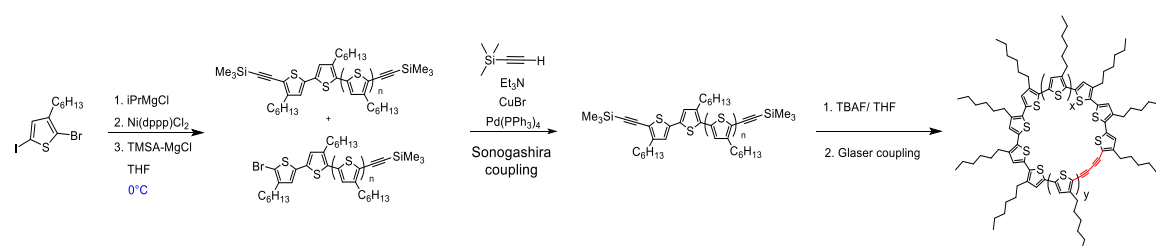
Also, in view of the perceived role of regioregularity (the ferromagnetic transition in poly(3-dodecylthiophene) is only observed in regioregular (RR) polymers) we paid particular attention to this factor, starting all synthesis of macrocycles from fully regioregular linear precursors. From a practical viewpoint we need also good solubility of the macrocycles which is obtained by the introduction of longer alkyl side chains like butyl or hexyl, though this may induce some problems with conformational lability. Simulation by DFT of these effects is currently underway. Moreover, the synthetic pathway used result in a regiodeflect in the ring which could create a deleterious defect by some twist between adjacent thiophene rings and decreasing the conjugation efficiency, as shown in the DFT calculations. Particularly, the ring closure reaction will suffer from a head-to-head coupling, even if both thiophene ring are separated by an ethylene, bis-ethynyl or thiophene groups.

Synthesis of Bis-ethynyl bridged macrocycle

The Glaser coupling reaction between two ethynyl moieties has already been used to cyclize short oligomers and long linear chains, the latter was not fully conjugated.

A Glaser coupling reaction between two acetylenic moieties directly connected to the thiophene backbone could reach the desired properties. But an important problem was the introduction of ethynyl groups at both chain end of the polythiophene. We have pointed out that a protected triple bond is imperative to avoid natural oxidative coupling of two aromatic alkynes during the purification and the storage of the samples.

For now, it appears that a combination of end chain functionalization by a quenching agent (trimethylsilylacetylene magnesium chloride) and post polymerization functionalization by a Sonogashira coupling reaction is required (scheme 2).



Scheme 2: Synthetic pathway of bis-ethynyl bridged macrocycle

The sample obtained after the chain end functionalization by quenching the polymerization with trimethylsilylacetylene magnesium chloride (TMSA-MgCl) has been analyzed by the MALDI-TOF technique. The spectrum is presented figure 4S. Two populations are clearly identified as the difunctionalized P3HT- TMSA/TMSA and the mono-functionalized P3HT-Br/TMSA. Different attempts, varying the number of equivalents of quenching agent, the concentration of this quenching solution, the speed of addition and the reaction time after the quenching lead to the same result, a mixture of

mono- and di-functionalized. Since the remaining chain end is a bromine atom, a Sonogashira coupling reaction has been realized with trimethylsilylacetylene and the catalytic system Pd(PPh₃)₄, Et₃N, CuBr. The MALDI-TOF of the polymer after purification is presented on figure 4S. The major population is the desired bis-ethynyl P3HT. It still has to be taken into account that the side reaction leads to the formation of mono-functionalized chains. It will induce a dimerization and those longer chains could be difficult to separate from the cyclized one.

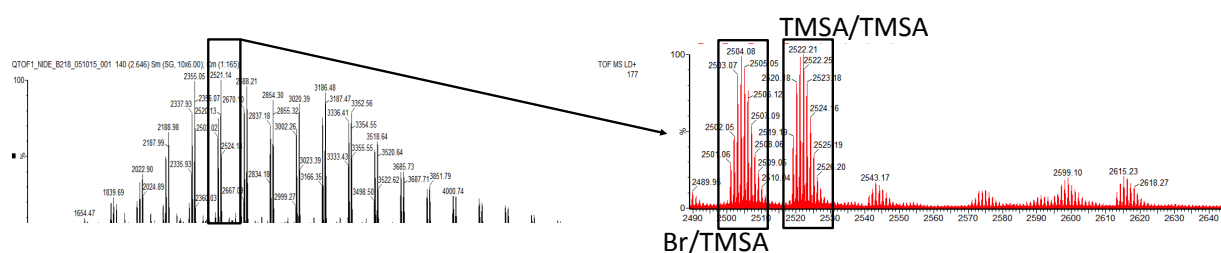


Fig. 3S MALDI-TOF spectra of polymer batch obtained after the chain end functionalization by quenching agent.

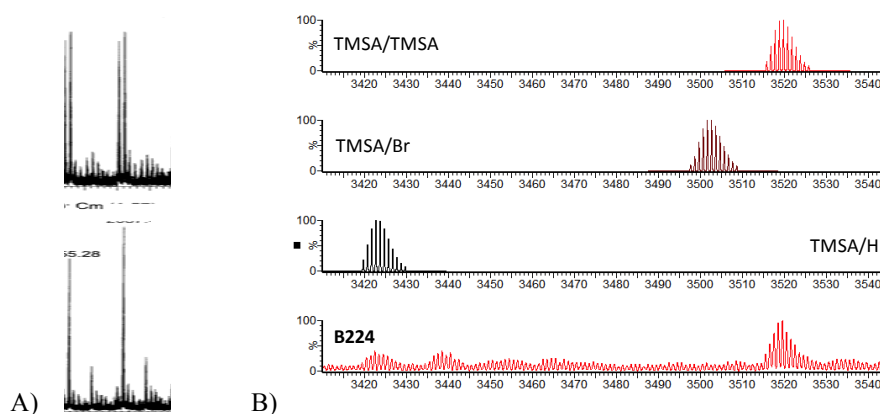
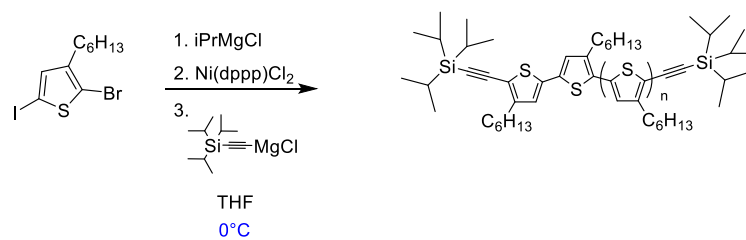


Fig. 4S **A** MALDI-TOF spectra of polymer batch before and after the Sonogashira post-polymerization chain end functionalization and **B** isotopic model of the different population present in the final batch.

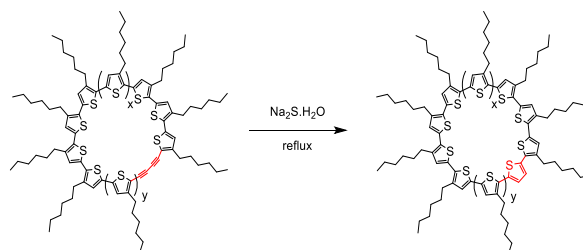
According to different publications, it seems that the Nickel catalyst forms a complex with the ethynyl moiety. To avoid this interaction, we used a quenching agent with a more sterically hindered protective group, like a triisopropylsilylacetylene (scheme 3). This reaction has been realized, and MALDI-TOF analysis is in progress.



Scheme 3: Synthetic pathway of bis-ethynyl P3HT with TiPS protective groups.

Synthesis of fully Thiophenic macrocycle

The bis-ethynyl bridge macrocycles can be converted into a thiophene bridged macrocycles by reaction with sulfur (Scheme 4). But unfortunately, this reaction reported in the literature has never been complete, and the mixture of the two population cannot be separated. This reaction is at the moment optimized on a linear system, which has a lower synthetic cost.



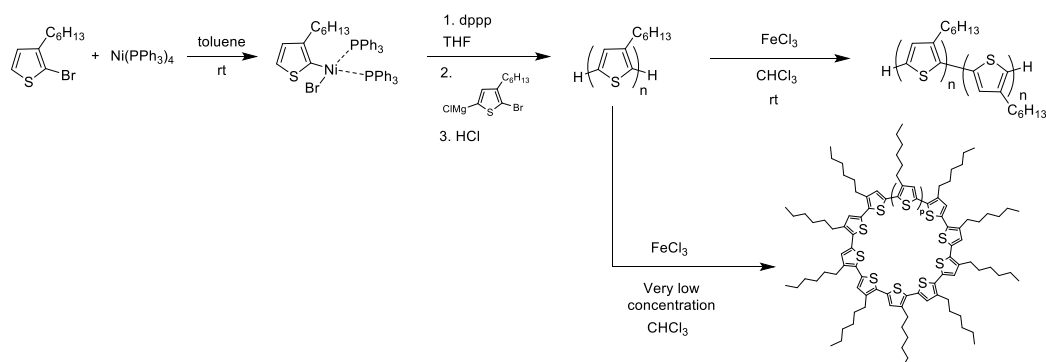
Scheme 4: Synthetic pathway of thiophene bridged macrocycle

The synthetic strategy presented below will lead to fully regioregular macrocycle with only thiophene rings. The polythiophene was obtained by KCTP initiated with the 3-hexylthiophene Nickel catalyst. The grow of the chain will occur in one direction through a Head to Tail coupling (HT). The intramolecular chain ends coupling will be an HT dyad.

The catalyst is prepared by reacting $\text{Ni}(\text{PPh}_3)_4$ with 2-bromo-3-hexylthiophene in toluene during 18h. The desired product is isolated by precipitation in hexane. Before the polymerization, a ligand exchange operation is done by addition of 1.8 equivalents of diphenylphosphinopropane (dppp) to the catalyst during 15 minutes. The thiophene ring is activated by GRIMM reaction between the 2-bromo-5-iodo-3-hexylthiophene and isopropylmagnesium chloride, and added to the solution of catalyst in THF at 0°C. The polymerization reaction is quenched by addition of 5M HCl aqueous solution after 2 hours. This should lead to exclusively Hydrogen terminated chains. The GPC analysis gives M_n and M_p values in polystyrene equivalents of 7.3 and 9.1 kDa, respectively. It is well known that the molar mass value obtained by GPC overestimate the real mass by a factor of 1.4, meaning an average molar mass of this polymer around 5.2 kDa, which corroborate the Maldi results.

In first attempts, the reaction of rr-P3HT was performed at a concentration which favor the intermolecular coupling to estimate the efficiency of the reaction, and optimized the conditions. Iron Chloride (FeCl_3) has been used in the first synthesis of poly(alkylthiophene) but suffer for a lack of regiocontrol. Nevertheless, this oxidative

agent can oxidize both chain ends of linear P3HT, leading to radicals, which can associate together.



Scheme 5: Synthetic pathway of fully thiophenic bridged macrocycle by oxidative coupling (with FeCl_3)

Different temperatures, concentration and catalyst loading have been tested and each sample has been analyzed by SEC (colored curves on figure 6) and compare to the elugram of the starting polymer (black curves on figure 6). With 20 equivalent of catalyst, The polymers tend to dimerize but large amount of starting materials did not react. By increasing the catalyst loading to 10 equivalents, the starting polymer is faster consumed in 1 hour. After 20 hours and then 70 hours, it seems that the coupling bonds break, since the increase of the signal of the starting polymer.

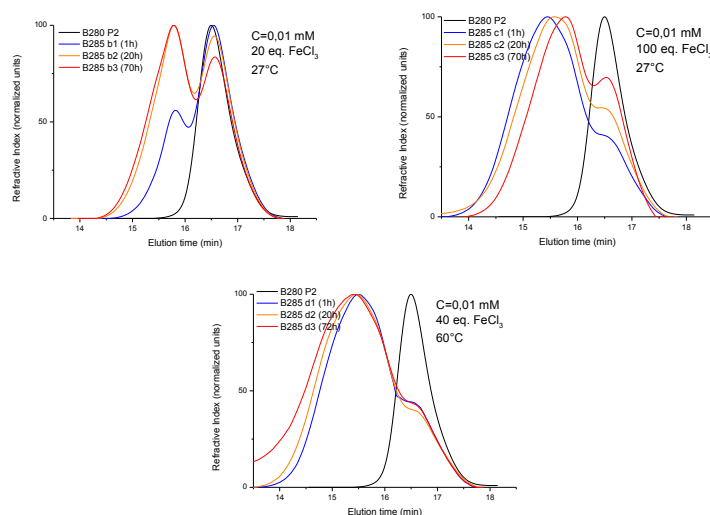
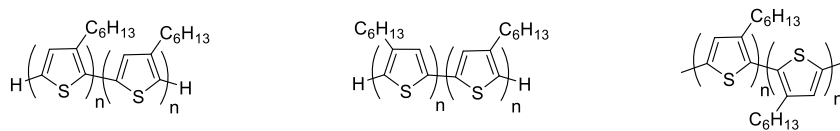


Fig. 5S SEC elugram after different time of reactions of linear P3HT (black) with FeCl_3 . The conditions are depicted on each graph.

Scheme 6 represents the different coupling which can occur during the reaction at elevated concentration. It will form 3 different dyads according to the position of the alkyl side chains of adjacent thiophene rings, the Head-to-Tail, the Tail-to-Tail and the Head-to-Head. The HH dyads suffer from a twist between the aromatic ring due to the high steric hindrance of the hexyl side chains.



Scheme 6 chemical structure of the different coupling of rr-P3HT (HT, TT, HH)

To validate this hypothesis, a polymer terminated at each side with the Head of thiophene ring and a similar molar mass has been reacted at low concentration with iron chloride. The intermolecular and intramolecular coupling can occur only through a head to head dyad. The SEC elugrams are presented on figure 6S. After 24 hours, it seems that decoupling reactions takes place during the course of the experiment.

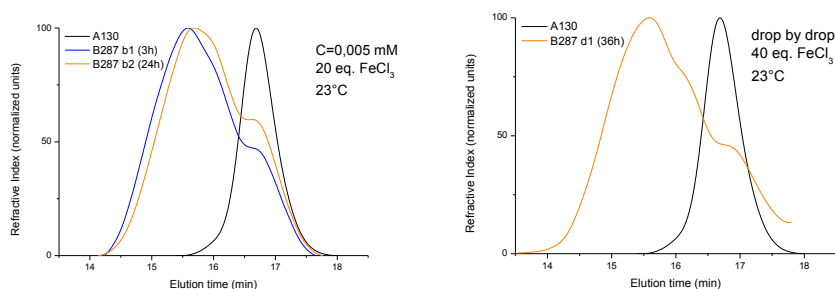
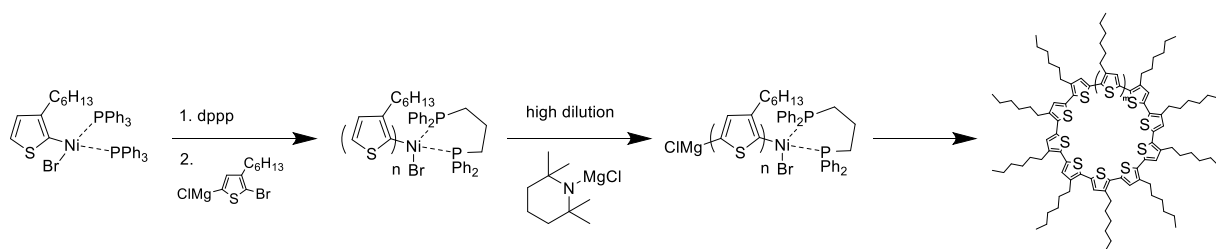


Fig. 6S SEC elugram after different time of reactions of linear P3HT (black) with FeCl_3 . The conditions are depicted on each graph.

The polymer sample has been reacted in pseudo high dilution conditions (slow addition into a large solution of the catalyst) which should favor the intramolecular coupling. The SEC elugram indicate that high molar mass chains are present in the sample and that no formation of cyclic structure happened, characterized by higher elution time in SEC analysis. This is an indication that the intramolecular coupling through a head to head dyad is not effective since the ring strain and the sterically hinder.

One pot synthesis

Finally, to economize our strategic efforts a one pot strategy has been designed, still to be optimized. It consists of the polymerization of 2-bromo-5-chloromagnesio-3-hexylthiophene from an externally initiated catalyst on 3-hexylthiophene. Since this polymerization reaction is living, the catalyst remains active at the chain end. The media will be then slowly added to a large solution of sterically hindered Grignard reagent (TMP-MgCl) to activate the α chain end of the polymer. The catalyst at the ω chain end should be intramolecularly coupled with the freshly activated alpha position, leading to a fully thiophenic macrocycle without isolation of the linear precursor



Scheme 7: Synthetic strategy of fully regioregular macrocyclic polythiophene in one pot.

Two attempts have been made, first in concentrated solution (figure 7S left) to favor intermolecular coupling and validate the effectiveness of this reaction and then in pseudo high dilution (figure 7 right).

The polymerization of 3-hexylthiophene is realized in a classical condition, and some aliquot has been taken and add to different volume of THF solution containing the TPClMg. An aliquot has been taken and the polymerization quenched in acid. Finally, the Grignard agent has been directly add to the polymerization flask. The SEC elugram of the latter (red on figure 8 left) clearly presents a signal at lower retention time, indicating that the linear chains (in black) efficiently couple to each other. Unfortunately, the diluted polymers, which have been taken out the reaction flask and add to another flask, did not present any coupling. The same SEC elugram is obtained as the starting polymer. This could mean that the catalyst did not remain at the chain end.

In the next approach, the polymer has been cannulated directly to a large volume of THF containing the Grignard reagent. The SEC elugram of the sample obtained 10 hours after the end of the addition is presented in red on figure 7S right. A slight increase in the molar mass distribution indicates the realization of intermolecular coupling. The intramolecular coupling which should lead to a cyclic structure did not occur.

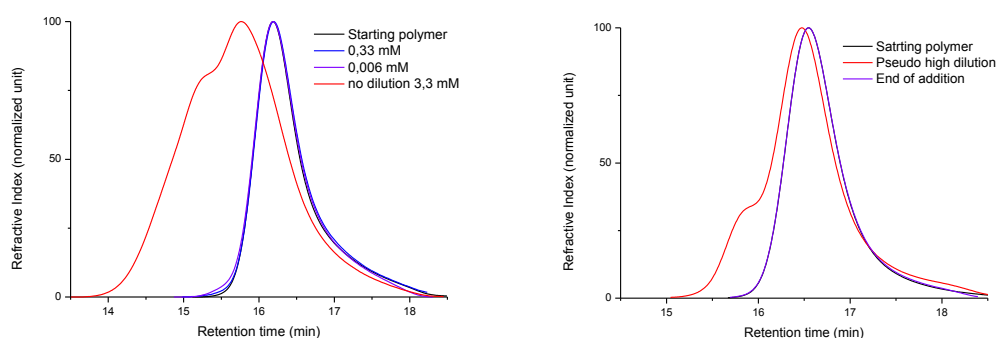


Fig. 7S SEC elugrams at different concentration of the one-pot linear chain coupling (starting polymer in black).

This type of reaction need to be optimized by reducing the polymerization time to avoid the degradation of the catalyst and by slowing down the speed of addition.

We also have identified that our catalyst, synthesized in the laboratory, is probably not pure enough. The estimated molar mass by NMR analysis is higher than the theoretical one and the one estimated by MALDI. This means that the polymerization is also

initiated by Ni(PPh₃)₄ and lead to linear chain with the same chain end, i.e. the head of thiophene ring, with alkyl side chain hindering the activation by the Grignard reagent (TMPMgCl). A better purification of the catalyst need to be performed prior the polymerisation reaction. For that, the catalyst will be introduced on 2-bromo-3-butylthiophene in order to be probed by MALDI-TOF characterization”.

Synthesis of many polythiophenes used for this research were reported previously in the final report on the project “Magnetism in pristine π -conjugated polymers” (EOARD grant FA8655-11-1-3016: FINAL REPORT 2011 -2014).

CONCLUSION and REALISATION of OBJECTIVES.

In this one-year project we obtained a wealth of results, computational as well as experimental. The collaboration with the group of Dongho Kim, Yonsei University, Korea, was instrumental in the choice of macrocycles to be studied. The computational investigations on these macrocycles are complemented by detailed optical studies in the group of Dongho Kim. It should be clearly stated here that **the availability of a powerful desktop computer (MAC PRO with 8 cores) was instrumental for this project** since the DFT calculations (GAMESS program) were indispensable as a feedback to the, often very complex, synthesis of macrocycles – this computer allows, even advanced calculations to be done in 6 – 12 h, instead of days (up to 8 days) with the previously used smaller desktops. Also, calculations for larger systems, often imposed by synthetic requirements, became a possibility. **The intense research effort of several excellent teams, at several universities, has set the stage of a worldwide interest in these macrocycles and their quantum ring behavior**, as witnessed by many invitations of the PIs and collaborators to international meetings. **The most important result of this project is the opening of a new new and promising research field of organic quantum rings**, the quantum chemical analogue to quantum dots, and leading the way of developing new organic magnetic materials, environmentally stable – the main objective of this project. An important portfolio of macrocycles has been developed, accelerating the experimental approaches. The availability of these well-characterized stable macrocycles of thiophenes will allow a follow on project oriented towards more detailed experimental investigations of the magnetic properties of these quantum ring materials by SQUID and optical measurements.

Other topics to explore, some ongoing already and a sequel to this project, are the development of a quantum chemical models of organic quantum rings, whereby advanced DFT methods such as CDFT (Current) and BDFT (Magnetic field) will be used and which allow the description of magnetic properties. Theoretical and experimental investigations of the relation between chirality and magnetism, the development of chiral stacks from macrocycles as advanced materials for the generation of spin polarized currents, the potential of “split” organic macrocycles as metamaterials...are all topics which are introduced by this project.

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Publications, and collaborations

Conference presentations

A. Persoons, “*New applications of Faraday rotation in organics for magnetic sensors*” Conference on “Electro-optic and magneto-optic properties of conjugated molecules and polymers” Korea-Belgium bilateral symposium, Leuven, Belgium 22-24 February 2016.

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A. Persoons, “*Applications of Faraday rotation in π -conjugated polymers for magnetic sensors*” 4th International Workshop on Novel Magnetic and Multifunctional Materials Paris, France 4 – 8 July 2016.

A. Persoons, G. Koeckelberghs, P. Gangopadhyay, N. Peyghambarian, N. Delbosc, “*From Nonlinear Optics to Brain Science*” 5th International workshop on Advanced Nano- and Biomaterials and their Device Applications, jointly with French-Romanian Topical Meeting on Nano and biomaterials, Constanta, Romania 20 – 25 September 2016.

A. Persoons G. Koeckelberghs, P. Gangopadhyay, N. Peyghambarian N. Delbosc, “*Nonlinear Magneto-optics in (Semi)Conducting π -conjugated Polymers and macrocycles*” 14th ICFPAM Conference, Daejeon, Korea, October 31 - November 4, 2016

Thierry Verbiest, “*Faraday rotation in organic conjugated molecules*” 14th ICFPAM Conference, Daejeon, Korea, October 31 - November 4, 2016

Manuscripts

A manuscript on the synthesis of macrocycles is submitted to *Macromolecules*:

N. Delbosc, S. Moins, J. De Winter, P. Dubois, A. Persoons, O. Coulembier, “*Macrocyclic P3HT obtained by intramolecular McMurry coupling of linear bis aldehyde polymer: a direct comparison with linear homologue*”

Manuscript attached to this report.

Collaborations

This project was carried out in close collaboration with Prof. Dongho Kim, Yonsei University, Daejeon, Korea who is investigating optical and physico-chemical properties of macrocycles.

The main collaboration on synthesis, especially Prof. G. Koeckelberghs is with the group of Prof. P. Dubois, Laboratory of Polymeric and Composite Materials, Center of Innovation and Research in Materials and Polymers (CIRMAP), University of Mons, B-7000 Mons, Belgium.

An important collaboration is with the group of Prof. B. Champagne, Université de Namur ASBL, Département de Chimie, B-5000 Namur, Belgium. Prof. B. Champagne is a co-developer of the GAMESS program and an invaluable help for the development of the DFT programs described in the project.

A longstanding collaboration with the group of Prof. N. Peyghambarian, University of Arizona, Tucson, AZ, USA, is still very active and centered on potential applications of the new macrocyclic materials for the development of ultrasensitive magnetic sensors for MCG and MEG.

Longstanding collaborations are with the Technical University of Eindhoven, Prof. B. Meijer (physico-chemistry and synthesis of thiophene polymers) and B. Koopmans (SQUID measurements).