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Electrically insulated molecular wires

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This paper is an up-to-date mini-review based on literature data and own results regarding synthesis and properties of conducting (pseudo)rotaxane supramolecular structures. Conjugated polymers, such as polyarylene, polyheteroarylene, polyaniline, polyarylenevinylene or polyaryleneimine, were used as axle, while the macrocyclic components were cyclodextrins, cucurbiturils, cyclophanes or crown ethers. Properties of the supramolecular structure such as solubility, thermal or chemical stability, conductivity, etc. can be drastically modified by the inclusion of hydrophobic conjugated polymers inside the macrocycle, without any chemical modification. For instance, the photophysical properties (i.e. quantum yield of fluorescence and electroluminescence) of the supramolecular structures were enhanced when compared with uninsulated conjugated polymers. The doping process is also affected, because the access of a dopant to the conjugated chain is limited only to the uncovered domains of the conjugated chain.

Keywords: supramolecular structures; conducting polymers; macrocyclic compounds; pseudorotaxane and rotaxane architecture; electrically insulated molecular nanowires

1. Introduction

Conjugated polymers and their doped forms have recently attracted tremendous interest due to their potential applications in micro- and nanoelectronics and optoelectronics (*1*). Their important role in macromolecular chemistry and material science was recognised by awarding the 2000 Nobel Prize in Chemistry 'for the discovery and development of conductive polymers' to Professors Alan Heeger and Alan MacDiarmid from the USA and Hideki Shirakawa from Japan (*2*). Moreover, their applications in organic light-emitting diodes (OLED) (*3*) and organic field-effect transistors (*4*) had been reported. Recently, work investigating their use as active elements in solar energy conversion as in photovoltaic cells has been very encouraging and many efforts have been directed in this field (*5*). Unfortunately, due to their intrinsic structure, conjugated polymers are insoluble and non-mouldable materials, with poor mechanical and environmental properties and thermal instability. Therefore, their technological applications are limited by processing difficulties and in most cases they cannot be transformed into usable forms after synthesis, meaning the desired form for devices has to be obtained directly during the polymerisation process. Electrochemical polymerisation is the best method from this point of view but is limited only to a few monomers and some applications. Various studies have been undertaken to obtain soluble conjugated polymers, and overcome these drawbacks by changing the structure of monomers or by the introduction of a bent, crankshaft-shaped or lateral substituent in the main chain of the polymer [(*1*) and references therein]. Alternatively, the structural irregularities in the main chain of the polymers can be controlled by copolymerisation. All these variations need new monomers, new polymerisation methods and techniques or sophisticated and expensive catalytic systems. Moreover, the increase in solubility by modifying the main-chain structure is accompanied in most cases by an alteration of electronic conjugation with resulting effects on electronic and optoelectronic properties.

An alternative strategy for improving conducting polymer processability is to build supramolecular structures by wrapping the polymer into several macrocyclic molecules. This usually involves non-covalent interactions between the linear polymer chain and the cyclic component to form a mechanically interlocked molecule such as pseudopolyrotaxane or polyrotaxane (*6–13*). The role of macrocycles is both to insulate the conjugated backbone and to control intermolecular interactions, while the electronic structure of the conjugated core is fully preserved. The macrocycles have freedom to translate or rotate along or around the polymer backbone without affecting the effective conjugation length.

A conducting polymer with (pseudo)rotaxane architecture can be envisioned as an electrically molecular nanowire. It is based on a one-dimensional conjugated macromolecular chain as a good transporter of the charge carriers, electrons and holes, insulated by many macrocycles threaded on it (Figure 1).

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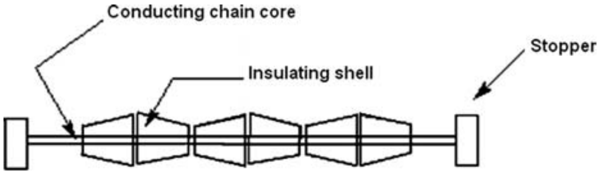


Figure 1. Structure of insulated organic molecular wires.

To prevent dethreading of the macrocycles, the ends of the linear molecular wire are blocked with bulky groups (stoppers), and the pseudorotaxane is transformed into a rotaxane structure. The conducting macromolecular (pseudo)rotaxanes have been synthesised by three routes (*6*):

(1) monomer polymerisation in the presence of a macrocyclic compound,
(2) threading of a preformed linear polymer chain through many macrocycles and
(3) polymerisation of a (pseudo)rotaxane monomer.

Depending on the location of the rotaxane/pseudo (rotaxane) unit, polymeric rotaxanes can be divided into two classes: main-chain or side-chain polyrotaxanes.

Most of the studies reported so far regarding conducting polymers have been focused on the main-chain polyrotaxanes using cyclodextrins (CDs) or cucurbiturils as hosts.

2. Conjugated polymers

It is known that conducting polymers are insoluble in most organic solvents but their rotaxane structures are soluble in polar solvents (DMF, DMAc, THF, etc.) and even in water. The following conjugated polymers were encapsulated in macrocycles: polyheterocycles (polythiophenes and polypyrroles), polyarylenes, polyarylenevinylenes, polyaryleneimines and polyanilines (Figure 2). Heterocyclic polymers, polypyrrole and polythiophene, were synthesised starting from thiophene or pyrrole, either by chemical or electrochemical oxidative polymerisation. In some instances, functional derivatives were successfully polymerised via metal-catalysed polycondensations (*14*, *15*). Polyarylenes (*16*), polyarylenevinylenes (*17*) and polyaryleneimines (*18*) are obtained mostly by polycondensation methods. Polyaniline is another well-known conjugated polymer, which can be synthesised as a powder or a thin film with colours depending strongly on the experimental conditions and doping state (*19*). Polyaniline is of particular interest since it is the only conjugated polymer of the one mentioned above that is usually synthesised in aqueous solution. The good solubility of aniline in 1M HCl aqueous solution makes its oxidative polymerisation possible in this solvent. In contrast, the water solubility of other monomers (pyrrole, thiophene and their derivatives) is very low, but it can be increased by encapsulation in water-soluble macrocyclic compounds such as CDs and crown ethers.

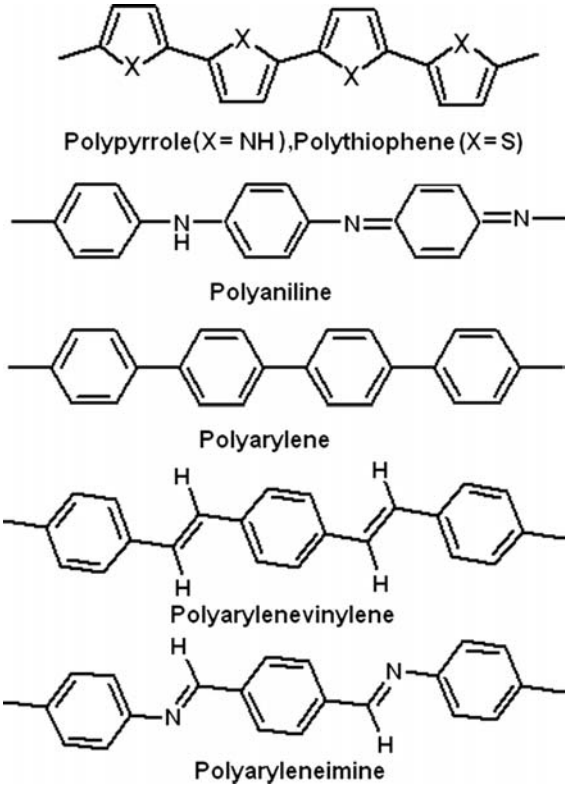


Figure 2. Chemical structure of some conducting polymers used as axles.

3. Macrocyclics as insulating materials

A variety of macrocyclic compounds were tried as shell materials for electrical insulation of conducting polymers. So far, most of the synthesised electrically insulated molecular wires have been based on CDs and cucurbiturils as protecting shell. The chemical structures and average dimensions of CDs and cucurbiturils are presented in Figure 3 and Table 1.

CDs are carbohydrate-based cyclic compounds consisting of six, seven or eight α-(1,4)-linked D-glucopyranose units. They have a torus-shaped structure characterised by hydrophobic cavities and are soluble in water and some protic polar solvents. The CDs can form highly stable inclusion complexes by hydrophobic interactions with a variety of organic guests. This is possible because of their accessibility and good water solubility.

Cucurbit[*n*]urils, abbreviated as CB[*n*], are a family of macrocyclic cavitands that contain *n* units derived from glycoluril linked by 2*n* methylene groups derived from formaldehyde, and are obtained by acid-catalysed condensation of glycoluril and formaldehyde. The molecule is like an open-ended pumpkin with a hydrophobic cavity accessible through two polar and identical carbonyl-fringed

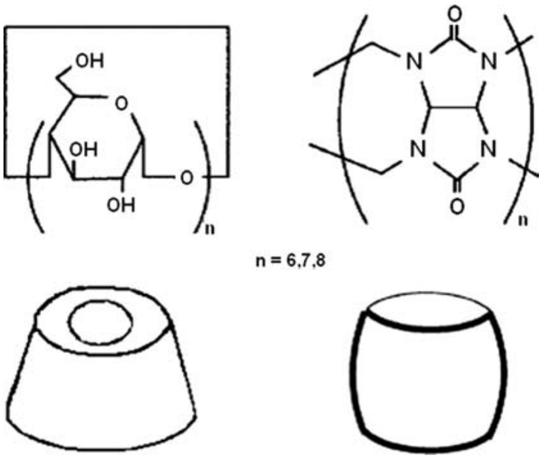


Figure 3. Chemical and geometrical structure of CDs and cucurbiturils.

portals. Similar to CDs, CBs have rigid structures and hydrophobic cavities and are useful building blocks of supramolecular structures. Rotaxane, pseudorotaxane and catenane supramolecular assemblies containing CB[6] and its higher homologues [$n = 7,8$] as hosts and non-conjugated polymers have been synthesised and studied recently (*23–29*). However, unlike CDs, the CB[*n*] compounds are rarely used in molecular wire synthesis, mainly due to lower solubility in common organic solvents. Their solubility in strongly acidic aqueous solutions limits their use because the synthesis of the conjugated polymers is more difficult in these solvents. However, two conjugated polymers (polyaniline and polyphenylenevinylene) have been used to obtain pseudopolyrotaxane structures with CB[6] or CB[7] as macrocycles. Both polymers can be synthesised in aqueous solution either by oxidative polymerisation of aniline (*19*) or alkaline modification of polyelectrolyte precursors (*17*).

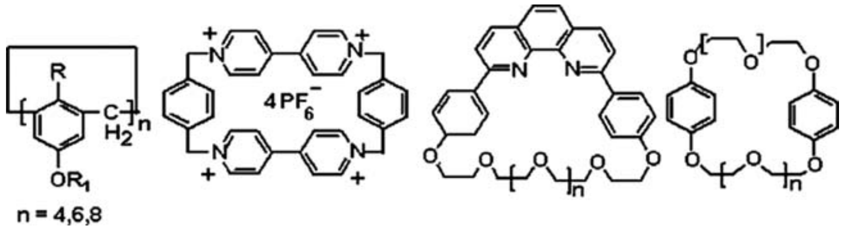
The first members of the two macrocyclic classes, α-CD and CB[5], have small internal diameters, and the inclusion of aniline, thiophene or pyrrole monomers is difficult to induce due to geometric constrictions.

Other macrocyclics used in the synthesis of supramolecular assemblies are presented in Scheme 1.

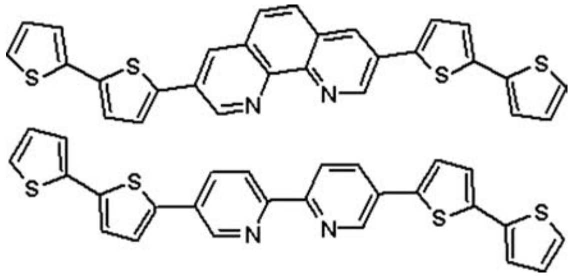
Calix[*n*]arenes, the most accessible type of cyclophanes, are sparingly soluble in some organic solvents and insoluble in aqueous solutions (*30*). The water-soluble calixarenes are obtained by the introduction of anionic (sulphonate) groups on the upper or lower rim or cationic (ammonium) groups on the upper rim (*31*). Calix[*n*]arenes possess architecture similar to CDs but have many conformational isomers because of rotational modes of the phenolic unit. Thus, calix[6]arenes can adopt eight possible conformational forms: cone, partial cone, 1,2-alternate, 1,3-alternate, 1,4-alternate, 1,2,3-alternate, 1,2,4-alternate and 1,3,5-alternate (*32*). This large conformational freedom of calix[*n*]arenes is a disadvantage in rotaxane synthesis compared with CDs and CBs that have a rigid conformation accessible for guest complexation. The inner cavity of calix[6]arene has an opening between 2 and 2.9 Å, while calix[8]arene in its most expanded conformation (cone) has an opening of 4.5 Å or more in diameter. Therefore, only calix[8]arenes

Table 1. Average dimensions of CD[*n*]s and CB[*n*]s.

Macrocycles				Reference
Cyclo[*n*]dextrins	$n = 6$ (α-CD)	$n = 7$ (β-CD)	$n = 8$ (γ-CD)	(*20*, *21*)
Upper portal (nm)	0.47	0.60	0.75	
Lower portal (nm)	0.53	0.65	0.83	
Height of the molecule (nm)	0.79	0.79	0.79	
Cucurbit[*n*]uril	$n = 6$, CB[6]	$n = 7$, CB[7]	$n = 8$, CB[8]	(*22*)
Diameters				
Portal diameter (nm)	0.39	0.54	0.69	
Cavity diameter (nm)	0.58	0.73	0.81	
Outer diameter (nm)	1.44	1.60	1.75	
Cavity volume (Å)^3	164	279	470	
Height of the molecule (nm)	0.91	0.91	0.91	



Scheme 1. Chemical structures of cyclophane-type macrocycles used as the host in rotaxane synthesis.



Scheme 2. Bithiophene–phenanthroline and bithiophene–bipyridine monomers.

possess a large enough annulus to allow an organic guest molecule to pass through openings. There are a few reports in the literature on the use of calix[6]arene for synthesis of a rotaxane (*33*), but a conducting polymer hosted by calixarenes has never been reported. Electron-poor macrocycles such as bipyridinium-based tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene), possess the ability to host electron-rich guest in order to form pseudorotaxane and catenanes (*7–9*, *34*). Recently, the encapsulation of thiophene, bithiophene and terthiophene into an electron-poor macrocycles has been reported, although, in this example, studies on polyrotaxane formation are not described (*35*).

Other cyclophane or crown ether compounds possessing two *p*-phenylene groups or a phenanthroline ring linked by ($-CH_2-CH_2-O-$) can be used as receptors for metal-template synthesis of catenanes and rotaxanes (*6–9*, *34*). For instance, bithiophene–bipyridine and bithiophene–phenanthroline monomers (Scheme 2) have been prepared and used for template synthesis of rotaxane monomers with phenanthroline macrocyclic compounds (*36–39*). In the presence of Cu^+ and Zn^{2+} salts, bithiophene monomer and phenanthroline macrocycle form a pseudorotaxane in a high yield. Then, the pseudorotaxane is electropolymerised to form polymetallorotaxane structures or metal-free polyrotaxanes after demetallation (Scheme 3) (*36*).

Marsella and Swager (*40*) have reported, in a short communication, the inclusion of the electron-deficient poly(pyridinium vinylene) into electron-rich macrocyclic crown ether. Efficient synthesis of rotaxane supramolecular structures is dependent on intermolecular attractive forces between a linear polymer and a cyclic component. These forces are entirely physical in nature: hydrophobic–hydrophilic interactions, hydrogen bonding, dipole–dipole interactions (more important in CDs and CB[*n*] hosts), π–π stacking, π electron donor–acceptor and transition-metal complexation (more important for hosts presented in Scheme 1).

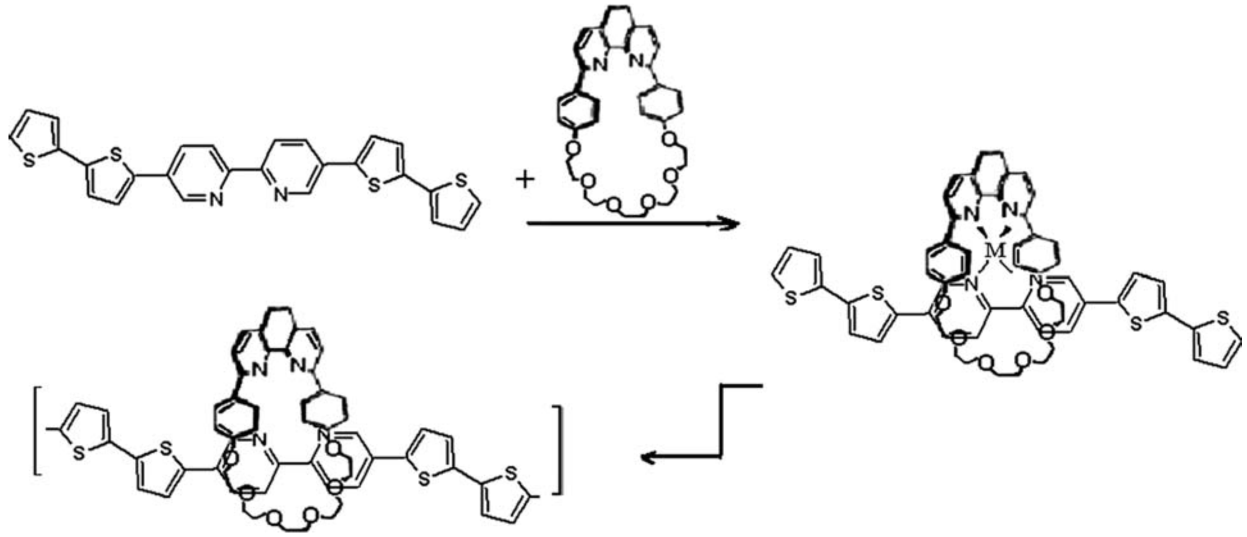
4. Conducting poly(pseudo)rotaxanes

4.1 Polypyrroles and polythiophenes

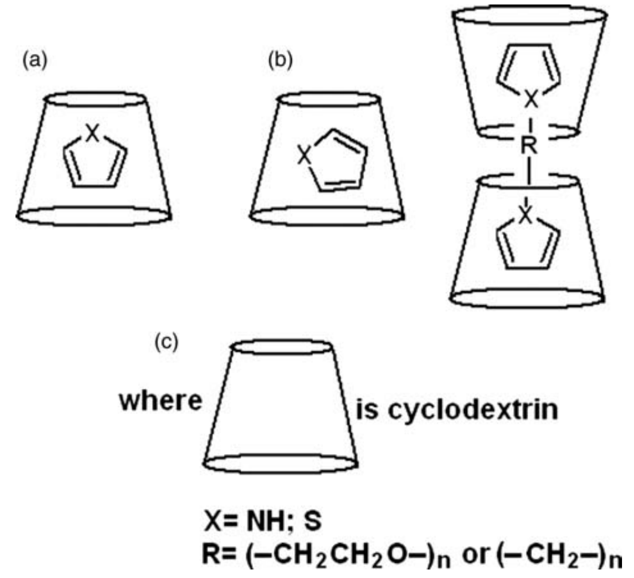
Pyrrole and thiophene are poorly soluble in water but their solubility can be strongly increased by encapsulation inside CDs or hydroxypropyl CDs. When pyrrole or thiophene was added to a saturated aqueous solution of CD at room temperature and with slight heating, the solution became turbid and a crystalline inclusion complex was formed. Guest molecules can be included inside CDs in two extreme conformations, with polymerisable positions 2,5 (a) perpendicular to or (b) parallel to the torus axle (Scheme 4).

In the first case, the heteroaromatic ring has the polymerisable positions sterically blocked by macrocycle walls and polymerisation is impossible, while for the second case, these positions are more accessible.

However, even in the favourable case (b), the monomer is not long enough and the active sites are positioned inside



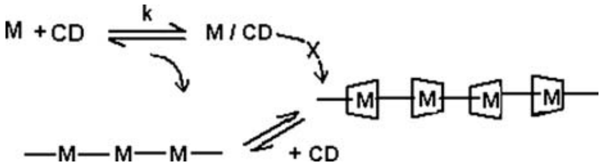
Scheme 3. Synthesis of polyrotaxanes by the metal-template method (*36*).



Scheme 4. Possible structures of the inclusion adducts of pyrrole, thiophene and dipyrrolyl monomers with CDs.

the host. The access of the oxidant in the initiation step or of the monomer molecules in the growing chain step to the aromatic ring is difficult. Therefore, an induction period is observed in all oxidative polymerisation of heterocyclics or aniline inclusion products. In fact, this property of CDs has often been used to protect sensitive drugs, by encapsulation or by time releasing of the drugs.

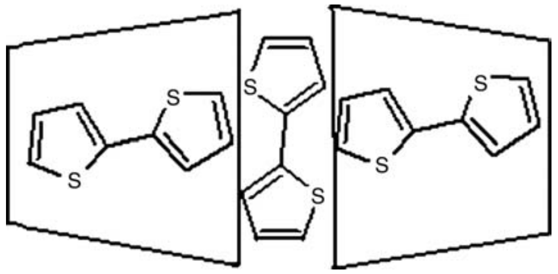
In the rotaxane synthesis, the guest has to preserve its polymerisation ability and to fit inside the host. Additionally, the guest molecules need to be long enough to contain polymerisable sites outside the macrocycle to facilitate the polymerisation. Lacaze et al. (*41*) reported, in 1997, the host–guest complexation of dipyrrolyl monomers with β-CD in aqueous solution. The monomer was modified with aromatic rings linked at *N*,*N*′ atoms by long and flexible (aliphatic or ethyleneoxide) spacers. Every pyrrole ring was separately encapsulated inside CD molecules while the spacer remained free (Scheme 4c). The composition of the inclusion adduct was 1:2. Because the encatenation positions are situated inside the inner macrocycle cavity, they have hindered access to an oxidant or for electrophilic attack to a neutral molecule. The propagation step is more probable as a result of dissociation of the inclusion adduct. The adduct is in dynamic equilibrium with the host and the guest, and addition to the growing polymer chain is performed outside the macrocyclic cavity with the participation of free monomers. Thus, the chemical and electrochemical polymerisation takes place only with monomers in the decomplexed state and, finally, polypyrroles without β-CD are obtained (Scheme 5).



Scheme 5. Proposed mechanism of the oxidative polymerisation of pyrrole monomers in the presence of CDs.

Other heterocycles such as pyrrole and 3,4-ethylenedioxythiophene with α-, β- or γ-CD or randomly dimethylated α-, β- or γ-CD form crystalline adducts in a 1:1 molar ratio, with a herringbone-fashioned cage-type crystal structure (*42*). The chemical oxidative polymerisation of these adducts in water, using $K_2S_2O_8$ or $FeCl_3$ as oxidants, has led to the formation of insoluble polymers. During the polymerisation reaction, because the adduct is decomplexed, CDs remain in solution and insoluble conjugated polymers are obtained (*41*). However, there are few reports on the synthesis of conducting polymers with pseudorotaxane structures using a 2,2′-bithiophene or 5,5-dibromo-2,2′-bithiophene. These monomers were included inside CD only in the parallel configuration and are long enough to have encatenation positions outside the macrocycle. Thus, Lacaze et al. (*43*) have studied the electrochemical polymerisation in aqueous solution of 2.2′-bithiophene hosted inside hydroxypropyl-β-CD. The complex was soluble in water, and soluble polythiophene with low molecular weight was synthesised. Also, Harada et al. (*44*) have obtained a low molecular weight polythiophene (5000 Da) within β-CD or modified β-CD by chemical oxidative polymerisation in the presence of $FeCl_3$ as the oxidant in aqueous solution. X-ray studies of the crystalline adduct 2,2′-bithiophene/β-CD consistently showed a 3:2 complex, regardless of the molar ratio between the guest and the host. Two bithiophene molecules were included inside the β-CD cavity, with a third molecule located horizontally between the two β-CDs on the secondary hydroxyl side (Scheme 6).

The third molecule was easily removed by washing with an organic solvent giving the 1:1 composition between 2,2′-bithiophene and β-CD (*43*). Conducting pseudorotaxanes were also obtained by including polythiophene or poly(3-methyl)thiophene in the cavity of β-CD (*45*). The synthesis of polythiophenes by



Scheme 6. The structure of 2,2′-bithiophene/β-CD (3:2) inclusion adduct.

Scheme 7. Preparation of oligothiophene/β-CD rotaxanes with anthryl groups as the end stopper (*46*).

polycondensation using bromine-functionalised bithiophenes allowed blocking of the ends with bulky groups to prevent the unthreading of macrocycles. The metal-catalysed polycondensation (Yamamoto reaction) of the 5,5′-dibromobithiophene/β-CD inclusion adduct followed by the blocking of the bromine ends with 9-bromoanthracene led to a polythiophene with rotaxane structure soluble in water and DMSO (Scheme 7) (*46*). Usually, polythiophenes with a polymerisation degree greater than 6 are insoluble in any organic solvents but, in this case, the molecular weight of the water-soluble polythiophene determined by the MALDI-TOF method corresponds to a degree of polymerisation of 24.

Small-angle neutron scattering measurements show that the polymer chains have lengths between 4 and 20 nm, while the maximum coverage with β-CDs is 60%. This suggests that rest of the macrocycles were dethreaded during the polymerisation step.

Another interesting example was the electrochemical synthesis of insulated nano-sized wires and nanodots of polypyrrole or polyaniline using thiolated β-CD-modified gold electrodes (*47*, *48*). First, the whole surface of the electrode was covered with β-CD molecules anchored by covalent linkages and contained seed molecules of pyrrole or aniline in the inner cavity. Polymerisation started from within the cavities where single nanofibres grow up and are subsequently aligned, leading to films with well-oriented morphologies. Sulphonated CDs used in the synthesis of polypyrrole play a double role as the host and the dopant of the conjugated chain (*49*). In this case, the presence of sulphonated CDs in the final polymer was evidenced by spectroscopic methods, although the formation of the pseudorotaxane structure was not clearly demonstrated.

4.2 Polyanilines

Only β-CD, CB[6] and CB[7] were used as hosts in the synthesis of polyaniline with pseudorotaxane structure.

Polyaniline/β-CD pseudorotaxanes were synthesised in two ways.

(1) Chemical oxidative polymerisation of aniline/β-CD (*50*) or *N*-phenyl-1,4-phenylenediamine/β-CD (*51*) inclusion adducts, in aqueous solution using ammonium persulphate as the oxidant.

Aniline monomer has a small molecular volume with a cross-sectional diameter of about 0.4 nm. Therefore, it fits closer in the α-CD cavity and results in an 1:1 adduct, while in β- or γ-CD, two aniline molecules can be included but the resulted adduct is less stable due to higher differences between partner dimensions. Chemical oxidative polymerisation of the aniline/β-CD adduct was carried out in aqueous solution in acidic (1 M HCl) or neutral medium (pH = 7). Polyaniline with pseudorotaxane structure was obtained only at pH = 7, while in acidic conditions free PANi emeraldine salt was synthesised (*50*). The inner surface of the CD's cavity is almost neutral and CDs bind preferentially neutral guest molecules. In acidic conditions, aniline monomer exists predominantly as the anilinium cation carrying a highly hydrophilic $-NH_3^{(+)}$ group and the aniline/β-CD inclusion complex dissociates to free partners.

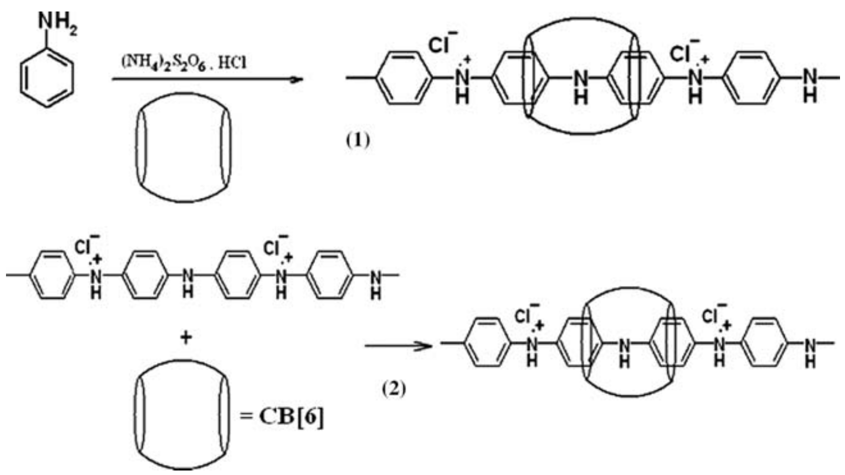
(2) Inclusion of the polyaniline–emeraldine base inside β-CD rings. The process was carried out by mixing the two solutions of polymer and β-CD in two miscible solvents (*50–53*). A blue precipitate was formed, which suggests the formation of the inclusion complex between the two components. Typically, the inclusion of a long linear polymer chain into one or many cyclic molecules is an entropically unfavourable process. However, the hydrophobic interactions, hydrogen–hydrogen and donor–acceptor interactions have promoted the threading of β-CD onto polyaniline when working at lower temperatures (less than 275 K) (*51*, *53*).

Unlike CDs that preferentially host neutral guest molecules, CBs[*n*] can form very stable host–guest complexes with positively charged molecules, such as anilinium cations or polyaniline–emeraldine salt. Therefore, CB[*n*] can form more stable complexes with anilinium cations than β-CD. This property, together with CB solubility in acidic aqueous solution, could explain why the first insulating molecular wire containing cucurbit[6]uril has used polyaniline as its conducting core (*54*). We have synthesised pseudopolyrotaxane polyaniline/CB[6] by two methods (Scheme 8):

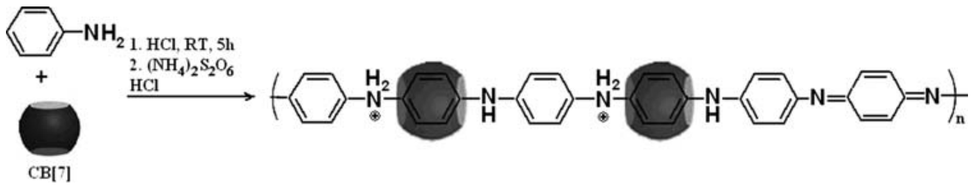
(1) by chemical oxidative polymerisation of aniline in the presence of CB[6] in acidic aqueous solution using ammonium persulphate as the oxidant and
(2) by threading the preformed polyaniline chain through the inner cavity of CB[6]. The second method is entropically unfavourable but is enthalpically driven by non-covalent interactions.

The number of macrocycles threaded onto the polymer chain could not be estimated by elemental analysis or IR and NMR spectroscopy (*54*).

A polymeric pseudorotaxane based on cucurbit[7]uril and polyaniline has been reported by Liu et al. (*55*).



Scheme 8. Synthesis of pseudorotaxane polyaniline/CB[6] by (1) chemical polymerisation of aniline/CB[6] inclusion adduct and (2) encapsulation of polyaniline emeraldine salt in CB[6].



Scheme 9. Synthesis of pseudorotaxane polyaniline by polycondensation of aniline in the presence of CB[7] (*55*).

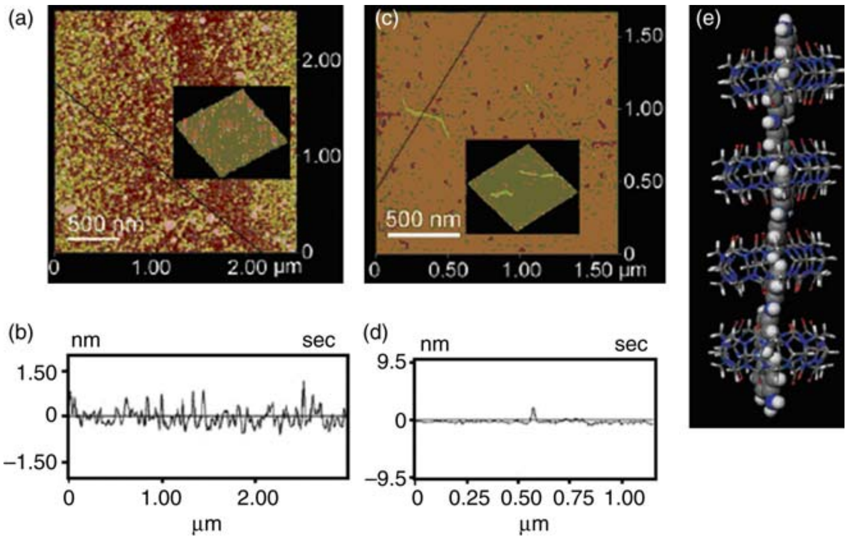


Figure 4. AFM images of (a) polyaniline; (b) section analysis of the black line in (a); (c) polyaniline/CB[7]; (d) section analysis of the black image in (c) and (e) possible structure of polyaniline/CB[7]. Reproduced with permission from Liu, Y.; Shi, J.; Chen, Y.; Ke, C.F. A Polymeric Pseudorotaxane Constructed from Cucurbituril and Aniline, and Stabilization of Its Radical Cation. *Angew. Chem. Int. Ed. 2008*, *47*, 1–5. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

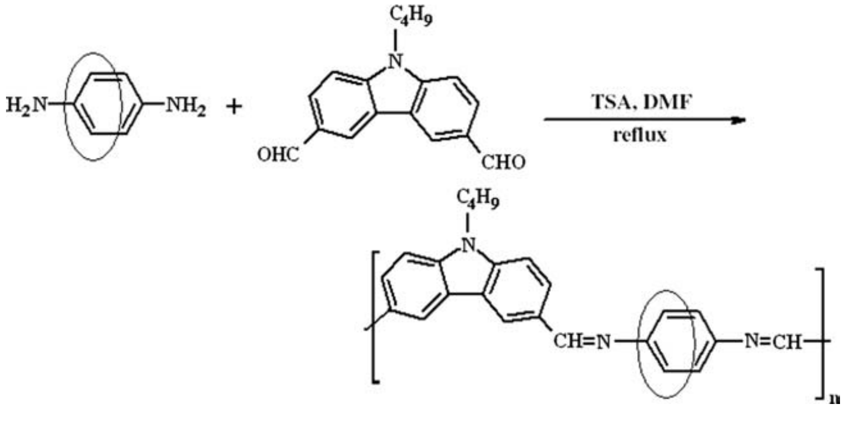
Using NMR spectroscopy, the authors calculated that every repeating unit contains three aniline units and one CB[7] macrocycle, as shown in Scheme 9 (*55*).

The threading of many macrocycles onto a single conjugated conducting polymer is accompanied by a coil–rod transition and electronic conjugation can spread over the whole macromolecule. The AFM images evidenced the existence of many small particles for uncomplexed polyaniline (Figure 4a) and straight fibres for polyaniline/CB[7].

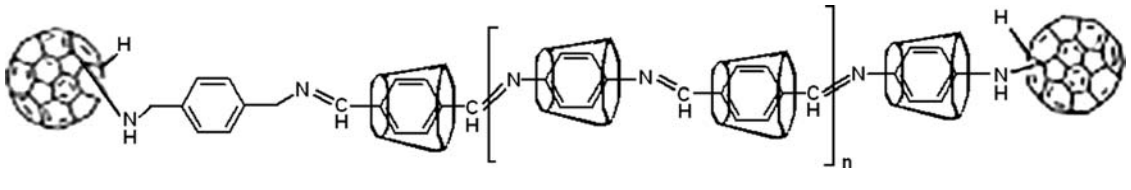
Both samples were synthesised in the same conditions. The widths (*c.* 1.5 nm) of PANi/CB[7] fibres are consistent with the outer diameter of CB[7]. A possible schematic structure of PANi/CB[7] is presented in Figure 4e (*55*). Therefore, the interchain interactions could be avoided by keeping the chains at a distance determined by the thickness of macrocycles, and the electronic properties could be studied for a single conjugated chain. For the first time, Shimomura et al. (*56*) have determined conductivity of a single insulated molecular wire positioned between two electrodes. The wire is based on a polyaniline macromolecule inserted into a CD nanotube followed by doping of PANi with iodine. The value of conductivity ($4 \times 10^{-2}\,\mathrm{S\,cm^{-1}}$) was smaller than that of the PANi/I_2 film and explained by the low doping level. The doping process is slow for the encapsulated polymer and needs a larger quantity of dopant molecules or the process is limited only to uncovered domains because the dopant molecules do not have free access to the conjugated chain to reduce or oxidise it (*52*, *56*).

4.3 Polyaryleneimines

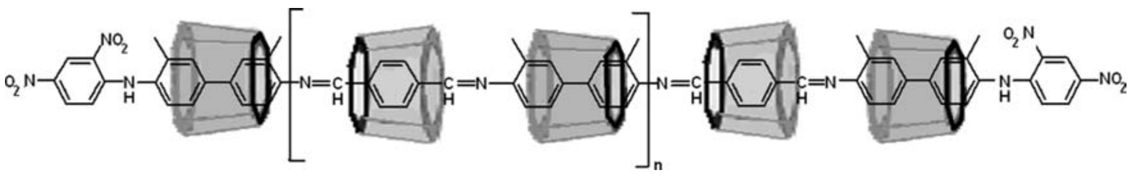
The first aryleneimine polymer (also known as polyazomethines or polyimines) with rotaxane architecture has been synthesised by Simionescu et al. (*57*) by polycondensation in solution of terephthaldehyde with the inclusion adduct α- or β-CD/1,6-diaminohexane. In this case, the chain ends have been blocked with a bulky aromatic amine, i.e. *p*-aniline triphenylmethane, to prevent the macrocycle slipping. Fully conjugated rotaxane polyazomethines have been obtained by polycondensation of *N*-alkyl 3,6-diformyl carbazole with aromatic diamines (1,4-diaminobenzene, 4,4′-diaminobiphenyl) included in α- or β-CD, using *p*-toluene sulphonic acid as a catalyst in *N*,*N*′-dimethylformamide and 4-aniline triphenylmethane as a stopper (*58*–*62*) (Scheme 10). If the alkyl group on the carbazole moiety is butyl or a higher



Scheme 10. Synthesis of poly(azomethine-rotax-α- and β-cyclodextrin).



Scheme 11. Structure of rotaxane polyazomethine/β-CD with [60]fullerene as the end-capping agent (*63*).



Scheme 12. Chemical structure of pseudorotaxane polyazomethine/β-CD end-capped with 2,4-dinitrobenzene groups (*64*).

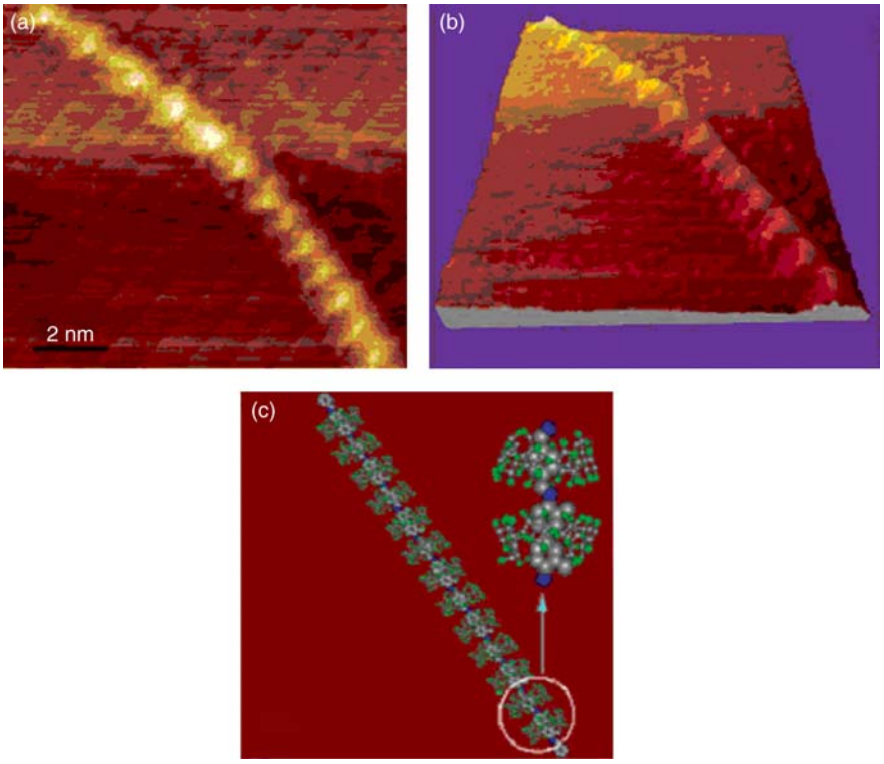


Figure 5. STM images of the pseudorotaxane obtained from the condensation of β-CD/*o*-toluidine with β-CD /*p*-phthaldehyde; (a) on a highly ordered pyrolytic graphite; (b) 3D mode of STM image and (c) the molecular modelling structure of polypseudorotaxane. Reproduced with permission from Liu, Y.; Zhao, Y.L.; Zhang, H.Y.; Li, X.Y.; Liang, P.; Zhang, X.Z.; Xu, J.J. Supramolecular Pseudorotaxane with Conjugated Polyazomethine prepared Directly from Two Inclusion Complexes of β-Cyclodextrin with Tolidine and Phthaldehyde. *Macromolecules* **2004**, *37*, 6362–6369. Copyright 2004 American Chemical Society.

homologue, the use of stoppers at the chain ends for the prevention of macrocycles slippage is not necessary because the movement of the macrocycle along the polymer chain is limited only to the monomer unit. As compared with uninsulated polymers, incorporation of CDs into the imine chain gave a hygroscopic and soluble polymer.

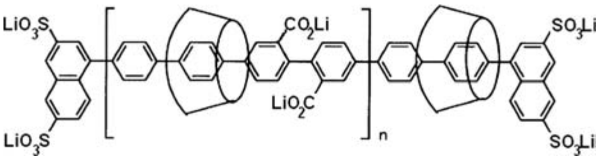
Other authors have used 60-fullerene as an end-capping agent in the polycondensation of terephthaldehyde with 1,4-diaminobenzene in the presence of β-CD (Scheme 11) (*63*). The macrocycles are able to move along the polymer chain without dethreading from the supramolecular arrangement due to bulky end-capping groups.

If the end-capping group agent is not a bulky molecule, for example 2,4-dinitrofluorobenzene, a supramolecular polypseudorotaxane structure was obtained by polycondensation of two complexes, β-CD/*o*-toluidine and β-CD/terephthaldehyde (Scheme 12) (*64*).

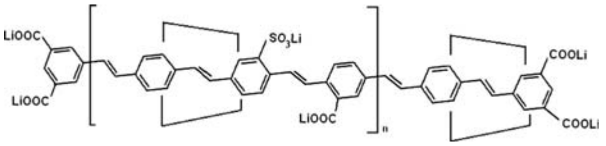
The high-resolution scanning tunnelling microscopy (STM) is a very useful technique to prove the supramolecular structure. The supramolecular aggregates are nanometre-sized molecular wires of ~1.5 nm in diameter (equal to the outer diameter of β-CD) (Figure 5) (*64*). All rotaxane polyimines are more hygroscopic and soluble in polar solvents in comparison with the polymers without rotaxane structure (*58–64*).

4.4 Polyarylenes and polyarylenevinylenes

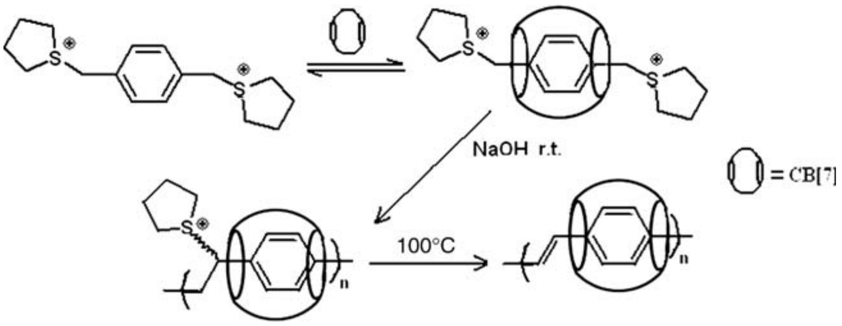
The idea to use polyrotaxane structures to obtain insulated molecular wires came from the Anderson group who have



Scheme 13. Chemical structure of β-CD-rotax-poly-*p*-phenylene (*66*).



Scheme 14. Chemical structure of α- and β-CD-rotax-poly-*p*-phenylenevinylene (*68*).



Scheme 15. Synthesis of polyphenylenevinylene-rotax-CB[7] by the Wessling route. Reproduced with permission from Corma, A.; Garcia, H.; Montes-Novajas, P. A Pseudopolyrotaxane Consisting in PPV threaded in Multiple Cucurbiturils. *Tetrahed. Lett*. **2007**, *48*, 4613–4617. Copyright 2007 Elsevier Ltd.

employed polyarylenes and polyarylenevinylenes (PPV) as conducting axes (*65*). The polyarylene rotaxane oligomers have been synthesised by the Suzuki cross-coupling reaction in aqueous media, e.g. 4,4′-biphenyl *bis*-boronic acid was coupled with 4,4′-diiodobiphenyl 2,2′-dicarboxylic acid in the presence of high excess of α- or β-CD. A bulky water-soluble 1-iodonaphthalene 3,6-disulphonate has been added as a stopper to obtain the rotaxane structure (Scheme 13) (*66*). The rotaxane polyarylenes have an average polymerisation degree, DP = 8, and are soluble in water. This is a useful property as, for instance, polyarylenes with five *p*-phenylene units have very low solubility in any solvent, only 5 mg/l in toluene (*67*).

This method was further extended for synthesis of poly(*p*-phenylenevinylene) rotaxanes using the palladium-catalysed Heck coupling of benzene 1,4-*bis* vinylboronic acid with 4,4′-diiodostilbene derivatives, in the presence of iodoisophthalate or 1-iodonaphthalene 3,6-disulphonate as stoppers and α- and β-CD as hosts (Scheme 14) (*68*). The average polymerisation degree was ~10, while the average number of CD per monomer unit was ~0.7.

It was observed that encapsulation always increased the fluorescence efficiency and fluorescence yield because the non-radiative and quenching processes were reduced by protective CD macrocycles (*69*).

Other attempts to obtain PPV/CB[7] rotaxanes have used the Wessling approach, with *p*-xylylene sulphonium derivatives as intermediates (*70*). The formation of a stable inclusion complex between *bis*-sulphonium salt and CB[7] was observed by mass spectroscopy, NMR and UV spectroscopy. It was shown that the phenylene ring is centred in the CB[7] cavity. The carbonyl portals on CB[7] interacted with the positively charged sulphur atoms via strong ion–dipole interactions. The precursor was very stable and Wessling polymerisation failed (*70*). However, recently, the successful synthesis of *rotax*-polyphenylenevinylene encapsulated in CB[7]s has been reported (Scheme 15) (*71*).

The ylide precursor of PPV could be encapsulated inside CB[6], CB[7] and CB[8] but not inside CB[5], due to spatial restrictions. However, only the ylide/CB[7] complex has been transformed to a pseudorotaxane structure. In other cases, only the PPVs without rotaxane structure were obtained, thought to be due to low stability of the complexes. From chemical analysis based on the N content, it was assumed that a CB[7] macrocycle was threaded at every six phenylenevinylene units. Unfortunately, there are no studies that involve the optical and electronic properties of these materials, especially their use in OLED devices.

5. Properties and applications

Properties of (pseudo)rotaxanes are dependent on the nature of the two components: the macrocycle and the conjugated polymer. Encapsulation of the conjugated polymer chain by macrocycles has a positive impact on the overall polymer properties. Supramolecular assemblies are more hydrophilic and more chemically, thermally and environmentally stable, properties induced mainly by the macrocyclic component. The solubility of pseudopolyrotaxanes and polyrotaxanes is dependent on both the conjugated polymer and the macrocycle nature and content. The threading of hydrophilic CD macrocycles onto a hydrophobic polymer chain makes the supramolecular assembly soluble in water or organic polar solvents (DMF, DMAc, THF, DMSO), while the conjugated polymer is insoluble in these solvents. The conformation of the polymer chain could also be modified by encapsulation. Polyaniline–emeraldine base has a coil conformation but, by its inclusion in CD, the conformation was changed to a rod-like one with extended π-conjugation (*53*). The insulating shells have a protective action against different destructive factors (oxygen, UV radiations, thermal degradation, chemical reactants) and confer greater resistance to fluorescence quenching by impurities. The macrocycles have isolated and separated the single polymer chain preventing intermolecular interactions between conjugated chains and the aggregation tendency, avoiding formation of excimers, with visible effects in photo- and electroluminescence properties. Also in polyrotaxane structures, photo- and electroluminescence efficiency is increased compared with free polymers and blue-shifted emission is observed. The conductivity measurements carried out on a single insulated molecular wire could help to differentiate the contribution of intra- and intermolecular charge transfer. However, these studies are in an incipient stage. There is only a short communication dedicated to conductivity investigation of a single conducting polymer chain isolated in a CD nanotube (*56*).

6. Conclusions

The building of conducting polyrotaxane structures has emerged from the necessity to improve solubility and processability of conjugated polymers. Despite the progress in recent years in supramolecular chemistry, much remains to be done in this specific domain.

In general, the synthesis of insulated molecular wires is performed by two methods:

- polymerisation of inclusion compounds formed between a monomer (as the guest) and a macrocyclic component (as the host) and
- threading of the macrocycles onto the preformed conducting polymer.

In both cases, the compatibility between the monomer/polymer and macrocycles is crucial in the formation of these structures, as well as the physical interactions between the two partners. Moreover, the guest has to fit perfectly in the inner cavity of the macrocyclic compounds and to form stable complexes. If the dimensions of molecular partners are not correlated, they cannot form inclusion adducts (linear partner cannot be threaded inside the inner cavity of macrocyclic compound), or the inclusion adducts are not stable causing macrocycle dethreading. Another requirement is the accessibility of encatenation positions of the monomer included in the cyclic compound to initiator or monomer in the polymerisation or polycondensation steps. Otherwise, polymerisation or polycondensation takes place with free (uncomplexed) monomers. Solvents used in inclusion or polymerisation steps also have to be chemically inert for both partners. Control of the degree of insulation of the molecular wire is very difficult, because during the polymerisation or purification steps, some macrocycles are unthreaded. Fluorescence quantum yield, electroluminescence efficiency and chemical stability, parameters important for LED applications, are enhanced for encapsulated molecular wires.

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