

CYCLODEXTRINS IN ROTAXA-CONJUGATED POLYMERS SYNTHESIS

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The present manuscript reports an overview of the design and conceptual approaches to the synthesis of rotaxa-conjugated polymers (R-CP), such as aromatic polyazomethines, alternating or random polyfluorene copolymers encapsulated inside native CD cavities. Their synthesis correlated with an overview of the photophysical properties, surface morphology and electrochemical behaviours, which are advantageous for the generation of active layers in organic electronic devices, are considered in this review.

Keywords: supramolecular chemistry, cyclodextrins, rotaxanes, fluorescence, energy band gap

INTRODUCTION

Over the last decades, conjugated polymers (CP) have received particular interest and tremendous effort has been devoted to tune their photophysical and transport properties through molecular design.¹⁻³ Despite the enormous interest in this domain, their strong tendency for aggregate formation limits considerably the application of these materials as semiconductors in optoelectronic devices. Although modern organic synthesis tools have made it possible to achieve significant progress in new CP synthesis with improved photophysical and electronic properties, over the last two decades attention has been focused on the field of supramolecular chemistry, which offers great opportunities for new concepts, new materials with unique properties and novel practical applications.⁴ The incorporation of non-covalent interactions in the construction of rotaxinated supramolecular architectures provides an efficient strategy to achieve an “insulation” of individual molecular wires and subsequently generates smart polymeric functional materials.⁵⁻⁹ The construction of R-CP is one of the most fruitful concepts in supramolecular chemistry, they consisting of linear π -conjugated axis molecule encapsulated into macrocyclic cavities through non-covalent interactions.

The first step in the preparation of rotaxinated structures consists in threading macrocyclic compounds (hosts) onto linear chains (guests) when inclusion complexes or pseudorotaxanes are obtained. To avoid dethreading, in the second step, a blocking

reaction of both ends of the guest molecule with bulky groups (also known as stoppers) is required. Depending on the location of the host molecules on the conjugated backbones, these supramolecular compounds can be divided into main-chain or side-chain rotaxinated architectures.¹⁰ The threading of macrocyclic molecules onto the conjugated chains does not disrupt the π -conjugation and can additionally improve the solubility, the thermal stability, and provide better film forming ability combined with a high transparency and lower quenching effect.¹¹ In addition, the presence of macrocycles suppresses intermolecular interactions and effectively inhibits inter-strand interactions by increasing separation distances between the conjugated backbones.

A wide variety of macrocyclic compounds have been utilized as building blocks in supramolecular systems in combination with CP.¹²⁻¹⁶ Native cyclodextrins (CDs) are by far the most intensively investigated macrocyclic molecules in the synthesis of R-CP. Due to their availability and solubility in water and polar organic solvents, CDs have been extensively investigated in combination with a variety of organic or inorganic guest molecules to form inclusion complexes.^{8,10} According to the capability of CD host molecules, various π -conjugated small molecules or polymers have been proved to form supramolecular architectures by simply threading their backbones through the host cavities without formation of any covalent

bonds between them. As a result of the encapsulation by the CDs, a large number of R-CP have been reported and have been shown to be a remarkable class of supramolecular compounds to investigate the influence of intermolecular interactions on the photophysical characteristics of CP. Aromatic polyazomethines, alternating or random polyfluorene copolymers, which are complexed with CDs, will be covered here. Meanwhile, the photophysical properties will be compared to those of non-rotaxinated homologues.

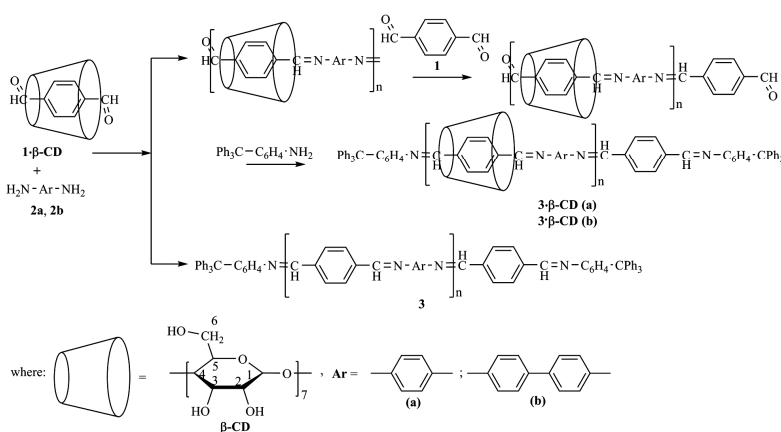
AROMATIC ROTAXA- POLYAZOMETHINES

Aromatic polyazomethines (PAs) have gained widespread interest due to their electronic and non-linear optical properties.¹⁷ The main properties of these compounds, which require improvement prior to application, are the rigidity of the chain structure, high melting temperatures and low solubility in common organic solvents. An improvement of PAs solubility has been attempted through careful selection of the starting reagents, but the results obtained are far from being optimal, as undesirable intermolecular interactions affect their electronic properties. Even if the synthetic availabilities provided improvements of the solubility in most of the cases, the final results are questionable because of the undesirable intermolecular interactions, which affect the charge mobility and electroluminescence efficiency.^{18,19} Among the synthetic strategies, the synthesis of rotaxinated compounds offers a new way to obtain PAs with improved solubility, as well as photophysical

characteristics. There are two available routes to obtain rotaxa-PAs. The first route involves the alternating polycondensation reaction of aromatic diamine with dialdehyde as monomers encapsulated inside CD cavities, followed by blocking the macromolecular end chains with bulky groups. The second way of constructing CD-rotaxinated PAs consists in blocking the guest ends with monofunctional bulky moieties to form a [2]-rotaxane, followed by its C-C coupling reaction.

First route of rotaxa-PAs synthesis

CDs have been successfully employed for the synthesis of rotaxa-PAs, and the first reported supramolecular compound involved the condensation reaction of terephthalaldehyde (1) encapsulated into β -CD cavities (1- β -CD) with 1,4-phenylenediamine or 4,4'-diamino-biphenyl (2a, 2b), followed by blocking the end of the macromolecular chains with p-aminophenyltriphenylmethane,^{20,21} which yielded 3- β -CD (a) and 3- β -CD (b) rotaxa-PAs (Scheme 1). Due to the presence of β -CD macrocyclic molecules, rotaxa-PAs have a higher solubility in DMF, DMSO or NMP. On the contrary, the solubility of the reference 3 in the above-mentioned solvents (after sonication with heating) was very low. Unfortunately, doping of these supramolecular structures with iodine (I₂) showed a smaller enhancement of the electrical conductivity (σ). Probably, the doping process is limited only to non-encapsulated domains.



Scheme 1: Synthesis of 3- β -CD rotaxa-PAs and its reference 3 counterpart

By using fullerene as a bulky stopper at the end of polycondensation of (1) with (2a) in the presence of β -CD, another research group also yielded rotaxa-PAs.²² The observation that the rotaxa-PAs are soluble in water is intriguing, if one takes into account the lower solubility of β -CD in water and the lack of water solubility of conjugated PAs chains. Liu *et al.* also prepared PAs pseudorotaxanes through the reaction of the inclusion complexes of (1) and *o*-tolidine, both monomers encapsulated into β -CD cavities.²³ It is worth mentioning that these rotaxa-PAs displayed different physical and photophysical characteristics compared with the reference counterparts.

On the basis of these investigations, it is perceivable that the most important characteristics of rotaxa-PAs with respect to their reference counterparts are their enhanced solubility in organic solvents, improved fluorescence efficiency and morphological characteristics. It is well known that almost all the investigated PAs are not soluble in common organic solvents, whereas the formation of rotaxinated structures improves their solubility.

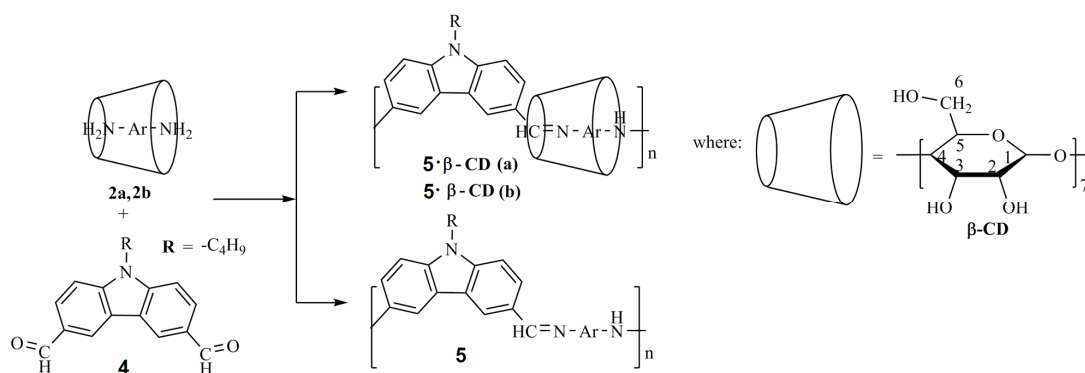
Second route of rotaxa-PAs synthesis

The second route consists in blocking the guest ends with monofunctional bulky moieties to form a [2]-rotaxane, followed by an oxidative condensation reaction. In the first reported example, the oxidative coupling of (2a) or (2b) encapsulated into β -CD with *N-n*-butyl-3,6-

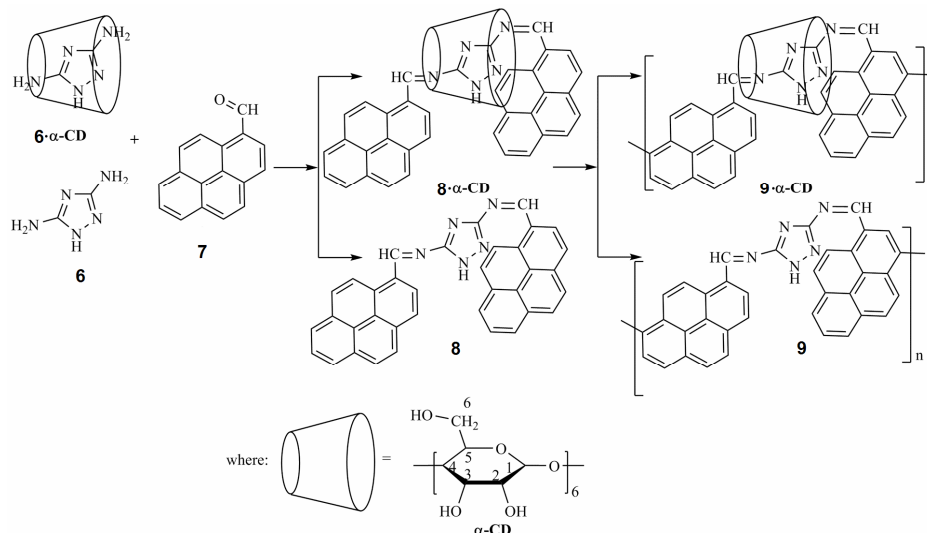
diformyl carbazole (4) as bulky group, led to rotaxa-PAs synthesis (Scheme 2).^{24,25}

In another more recent example, 3,5-diamino-1,2,4-triazole (6) as an inclusion complex with α -CD (6· α -CD) and 1-pyrenecarboxaldehyde (7) were selected to build 8· α -CD as [2]-rotaxane monomer.^{26,27} The enthalpy value of 6· α -CD formation ($\Delta H = -6.04 \text{ kJ}\cdot\text{mol}^{-1}$) suggests that hydrophobic interactions should be responsible for the threading process. Semiempirical calculations confirmed a particular arrangement of (6) inside α -CD and the ability of molecule 7 to partially penetrate the macrocycle cavity.²⁸ The oxidative C-C coupling of 8· α -CD, as well as its non-rotaxinated counterpart 8, in *N,N*-dimethylacetamide (DMAc) or DMF/toluene 1/1 v/v as solvents by using RuCl_3 as catalyst at room temperature afforded then 9· α -CD rotaxa-PAs and the reference 9 counterpart, respectively (Scheme 3).^{26,27}

A value of $11600 \text{ g}\cdot\text{mol}^{-1}$ was established for the number-average molecular weight (M_n) of 9· α -CD by size exclusion chromatography (SEC). The peak of free α -CD was not present in the chromatogram of 9· α -CD, and this point clearly evidenced that the rotaxa-sample is not a physical mixture between components and that 9· α -CD rotaxa-polymer is stable under SEC analysis conditions (no dethreading of α -CD occurs). In addition, 9· α -CD presented good solubility in polar solvents, which was reflected in better film forming ability on glass substrates (a solid fine dispersion was obtained from the reference 9).



Scheme 2: Synthesis of 5- β -CD rotaxa-PAs architectures and counterpart



Scheme 3: Synthesis of azomethine monomers and their corresponding rotaxinated oligomers or polymers

The effect of α -CD macrocyclic encapsulation on oligomeric states have also been investigated. It was found that 9 oligomer and 9- α -CD oligorotaxa-compound are conveniently accessible in high yields (58-70%) in DMF, thus complementing the synthesis in DMAc. The optical properties of 9 and 9- α -CD polymers are studied by UV-vis and fluorescence (PL) spectroscopy. From the absolute PL intensity at 414 nm, it has been found that there is a striking *ca.* 200 times fluorescence enhancement for 9- α -CD compared to the starting monomer 8- α -CD (when normalized to the same OD and excited at 363 nm). Increased PL properties were attributed as a consequence of the extended conjugation of the macromolecular chain.²⁶ Surprisingly, in the PL emission spectrum of the reference 9 in the DMF solution, there is no emission maximum with respect to the 9- α -CD sample, which can be attributed to its lower solubility. From a morphological point of view, the surface of the reference 9 showed a globular formation with an agglomeration tendency, while the encapsulated 9- α -CD rotaxinated compound exhibited a smoother surface, comprised by smaller grains uniformly distributed on the surface of the solid film.²⁶ The doping of these compounds results in a smaller enhancement of the σ value, which presents a trade-off with their better solubility, processability and surface morphological characteristics. As results from these investigations, perhaps the most important characteristics of rotaxa-PAs, compared to their non-rotaxane counterparts, are their enhanced

solubility in polar organic solvents, PL and their surface morphology characteristics.

ROTAXA-POLYFLUORENES

Polyfluorenes (PF) have been intensively studied as emitting materials owing to their pure blue emission.^{29,30} Major drawbacks for their use in practical application are their high ionization potential associated with low PL efficiency, their rather large band gap and facile photochemical degradation.³¹ Among the different strategies that have been employed with a view to reducing these undesirable effects, an important approach is the encapsulation of PF backbones into macrocyclic cavities to produce rotaxa-PF homo- or copolymers.^{5,32,33}

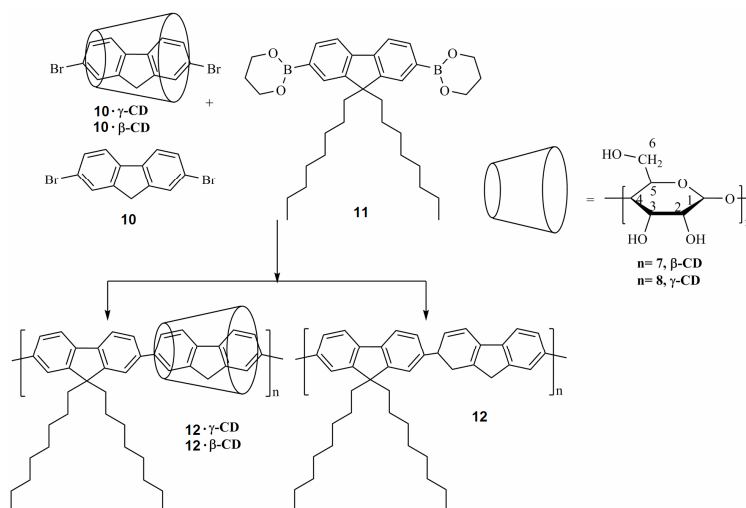
Alternating rotaxa-polyfluorenes

The alternating rotaxa-PF architectures have been synthesized through the Suzuki cross-coupling reaction of 2,7-dibromofluorene (10) encapsulated into γ - or β -CD cavities (10- γ -CD, 10- β -CD) and 2,7-dibromo-9,9-dioctylfluorene (11) as bulky stopper units (Scheme 4).³⁴⁻³⁶

The encapsulation of monomer 10 into macrocycle cavities has been used to protect position 9 of the fluorene moiety against oxidative degradation. The presence of γ - or β -CD in 12- γ -CD and 12- β -CD rotaxinated copolymers induces an improvement in solubility in polar solvents and high transition temperature. PL emission of 12- γ -CD and 12- β -CD exhibited typical well resolved blue emission bands arising from the fluorene

chromophore units. The rotaxinated 12· γ -CD copolymer displayed a longer lifetime (τ_F), induced by a partial protection of the rotaxinated copolymer molecules from the solvent. The surface morphology of the rotaxa-PF 12· γ -CD films shows globular formations over the same scanning scale area with a distinctive texture. By studying the temperature dependence of the electrical resistance, the results indicated that the

electrical properties are similar to those observed in inorganic semiconductors. It was experimentally established that samples with a stable structure could be obtained by subjecting them, after preparation, to a heat treatment consisting of several successive heating/cooling cycles within a certain temperature range, ΔT , characteristic of each polymer.



Scheme 4: Synthesis of rotaxa-PF 12· γ -CD and 12· β -CD and its reference 12 counterpart

After the heat treatment, the temperature dependence of the σ became reversible. The resistance curve was characterized by two distinct parts: a part with a larger slope (within the higher temperature range) and a part with a smaller slope (within the lower temperature range). These results are similar to extrinsic and intrinsic temperature ranges observed in inorganic semiconductors. The values of the σ for 12· γ -CD and 12 films are $6.4 \cdot 10^{-7}$ and $8.2 \cdot 10^{-8}$ S·cm $^{-1}$, respectively, indicating semiconducting properties.³⁴ The higher σ value of 12· γ -CD is presumably due to its molecular structure, which affords extended conjugation of the electrons in the copolymer chain and reduces aggregation by partial encapsulation of single polymer chains.

Random polyfluorenes with electron-donating and rotaxa-electron-accepting moieties

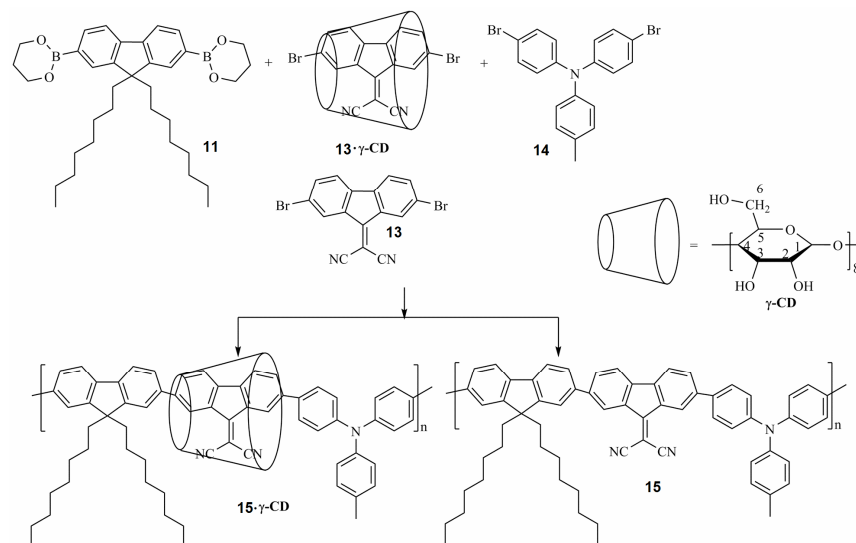
The random incorporation of donor-acceptor (D-A) units into PF backbones offers the opportunity to tune the relative position of the frontier energy-levels with lower band gaps, and as results such architectures may be advantageous

for photovoltaic (PV) applications.³⁷⁻³⁹ Therefore, the development of copolymers with low band gap has become an essential research topic in the development of new materials for electro-optical applications. The synergetic combination of organic synthesis and supramolecular chemistry is being exploited for the development of new smart materials, which will find a vast number of applications. As a result, the encapsulation of 2,7-dibromo-9,9-(dicyanomethylene) fluorene (13) (as acceptor units) into γ -CD cavities and then Suzuki cross-coupled with 4,4'-dibromo-4''-methyl-triphenylamine (14) (as electron-donor unit) and 11 (as bulky groups) in a 1/1 v/v toluene/DMF mixture and 5:4:1 molar ratio allowed the synthesis of 15· γ -CD random rotaxa-PF (Scheme 5).⁴⁰

The encapsulation of (13) has been employed with a view to diminish its quenching effect against the solvent, impurities or oxygen molecules.⁴¹ Due to the enhanced rigidity of the macromolecular chains, differential scanning calorimetry (DSC) data indicated higher glass transition temperature (T_g) of rotaxinated 15· γ -

CD, compared with its reference 15. The influence of the rotaxination on the optical properties was also investigated by UV-Vis and PL measurements in THF solutions or in solid state. The results for the absorption in solid state for 15- γ -CD revealed a strong absorption at about 380, 385 and 383 nm, which can be assigned to the π - π^* transition derived from the conjugated fluorene backbones.⁴⁰ The fluorescence efficiency (Φ_{PL}) of rotaxinated 15- γ -CD copolymer is about three times greater than that of its reference, thus proving lower quenching of cyan groups by the solvent or impurities.⁴¹ It should be noted that 15- γ -CD presented almost identical normalized absorbance in solution and film state, suggesting similar ground-state electronic structures. Electrochemical properties investigated by cyclic voltammetry (CV) indicated that 15- γ -CD and its reference 15 exhibited typical semi-conducting properties, i.e., with an insulating behavior in a wide range of potential from -2.0 to 1.0 V, respectively. The usually high stabilities of the *p*-doping processes, compared to the *n*-doping processes of 15- γ -CD, strongly suggest that the γ -

CD molecules do not hamper the redox behavior of the π -conjugated systems.⁴⁰ The slightly lower energy band gap (ΔE_g)s of the rotaxinated 15- γ -CD than those of the reference 15 counterpart can be attributed to its improved charge injection between films and the electrode surfaces. The HOMO/LUMO energy levels of the reference 15 and its corresponding 15- γ -CD rotaxa-compound, in combination with the electronic potentials of the anodic indium tin oxide (ITO) glass substrate (-4.75 eV) and cathodic aluminum (-2.2 eV), prove that the required energy level is fulfilled for fabrication of organic light-emitting diodes (OLEDs). The relative position of the frontier energy levels of such architectures may also be advantageous to PV applications. Furthermore, these results suggest that 15- γ -CD could be useful for the fabrication of diffuse hetero-junctions between interpenetrating networks of *n*- and *p*-type semiconductors.⁴² Overall, the HOMO/LUMO energy levels of studied rotaxa-PF proved that these complex structures, as well as their reference, are electrochemically accessible as electron-transporting materials.



Scheme 5: Synthesis of rotaxinated 15- γ -CD PF and its reference 15 counterpart

CONCLUSION

These rotaxinated architectures showed interesting photophysical characteristics, which makes them suitable for optoelectronic applications. The presence of native CDs results in improved solubility in polar organic solvents, which allows R-CP processing by spin-coating. The broad range of properties as outlined here can

be tuned by straightforward structural modifications designed to make them suitable alternate replacements for the non-rotaxinated counterparts, especially if one takes into account their good fluorescence efficiency, surface morphology, high oxidative and chemical stability, and quenching strength. Despite the interest in synthetic approaches, interdisciplinary

collaborations serve to continue extensive research with regard to potential applications. There is no doubt that R-CP as suitable materials for optoelectronic applications will remain as one of the hot research areas in the future.

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