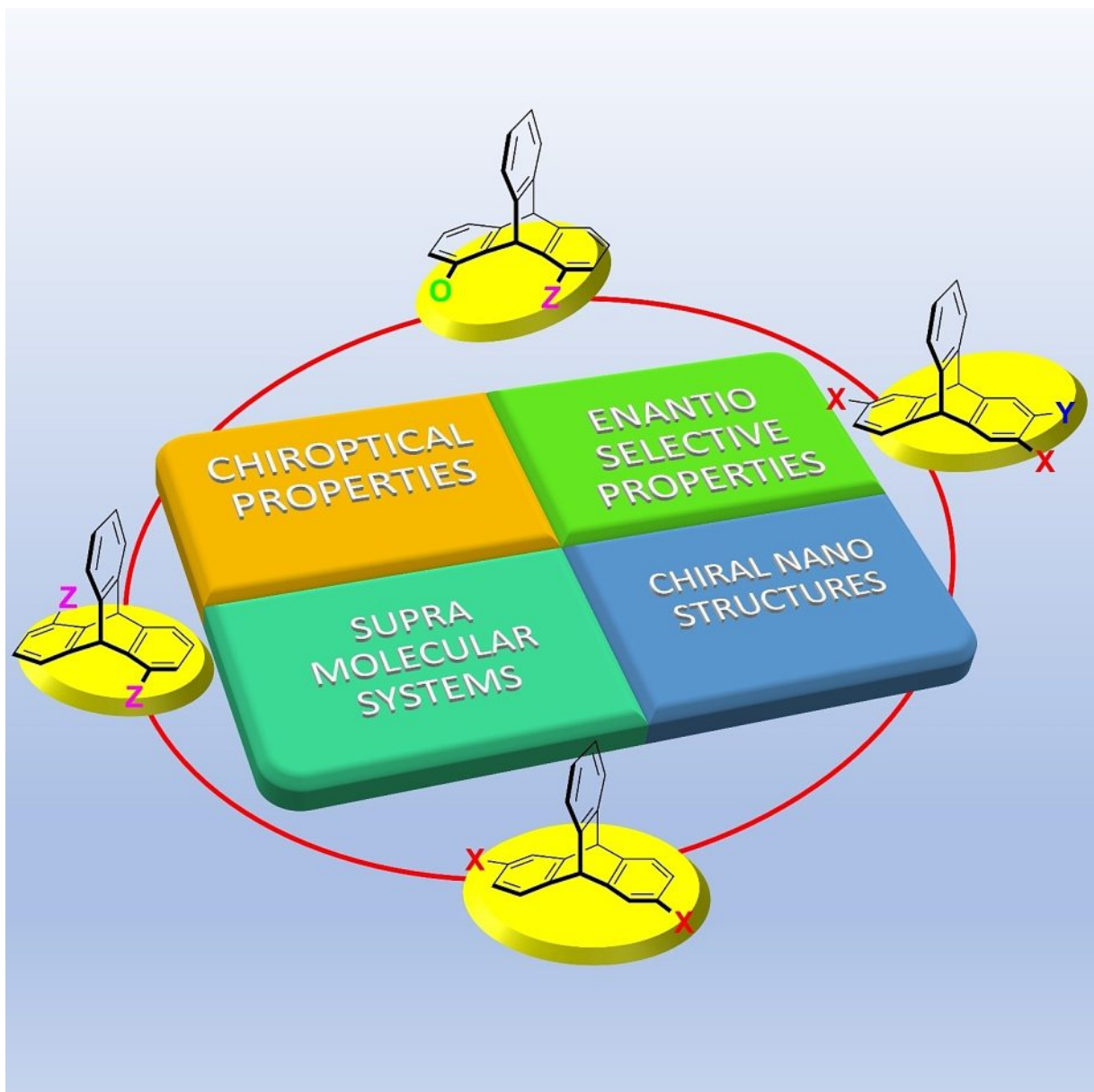




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# Chiral Triptycenes in Supramolecular and Materials Chemistry

Giovanni Preda, Andrea Nitti, and Dario Pasini<sup>\*[a]</sup>*Dedicated to Prof. J. M. Lehn on the occasion of his 80th birthday*

Triptycenes are an intriguing class of organic molecules with several unusual characteristics, such as a propeller-like shape, saddle-like cavities around a symmetrical scaffold, a rigid  $\pi$ -framework. They have been extensively studied and proposed as key synthons for a variety of applications in supramolecular chemistry and materials science. When decorated with an appropriate substitution pattern, triptycenes can be chiral, and,

similarly to other popular chiral  $\pi$ -extended synthons, can express chirality robustly, efficiently, and with relevance to chiroptical spectroscopies. This minireview highlights and encompasses recent advances in the synthesis of chiral triptycenes and in their introduction as molecular scaffolds for the assembly of functional supramolecular materials.

## 1. Introduction

Triptycene is a hydrocarbon molecule, possessing a  $D_{3h}$  molecular symmetry, with a rigid, propeller-like framework. Its name was proposed from its discoverers, Harvard chemists P. D. Bartlett and co-workers,<sup>[1]</sup> and it derives from the book “the triptych of antiquity”, in which a similar geometrical feature was reported. Triptycene belongs to the triptycene family, a class of structurally-related compounds in which aryl rings are fused into a bicyclo[2.2.2]octane framework, and point out forming  $120^\circ$  dihedral angles between each other.

Their unique three-dimensional rigid structure and the ample possibilities for the installment of reactive positions are attractive points for this class of molecules, in order to either modify/tune the  $\pi$ -scaffold, and to introduce reactive handles for further manipulation and integration into nanostructures. Triptycene chemistry focused initially on synthetic aspects, and, since the beginning of the 1980s, potential applications have been gradually approached. In recent years, triptycene derivatives have been applied in the areas of molecular machines, supramolecular chemistry, materials science.<sup>[2]</sup> Their chemistry focuses on functionalization strategies for the introduction of substituents on the aromatic moieties, or the extension of the  $\pi$ -surfaces. The bridgehead protons of these derivatives are inert compared to many reactions that normally occur in the benzylic position.<sup>[3]</sup> However, recently, modifications to the bridgehead positions allowed for the synthesis of intriguing  $\pi$ -extended structures through cyclization.<sup>[4]</sup>

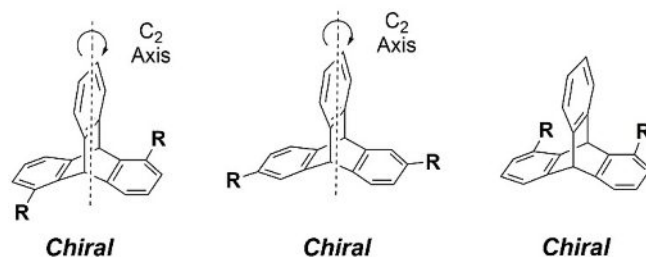
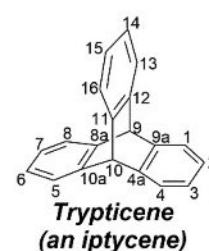
Unmodified triptycene is an achiral molecule. There are several possible ways to introduce chirality into the framework of triptycenes. The straightforward way is perhaps to functionalize their skeleton with substituents bearing elements of chirality: they could in turn be ad hoc designed chiral synthons, or chiral fragments derived from the naturally occurring chiral pool (amino acids, sugars, etc.).<sup>[5]</sup> Chirality can also result from an hindered rotation due to steric hindrance in bridgehead-

substituted triptycene (atropisomerism) as reported in previous examples.<sup>[2]</sup>

The other possibility (the one on which this minireview focuses) to introduce chirality is when at least two substituents are placed onto the triptycene's aromatic rings in a suitable substitution pattern, and Figure 1 illustrates some of the possibilities. Both 1,5-(left) and 2,6-(center) disubstituted triptycenes, and 1,8-(right) asymmetrically substituted triptycenes, exist as nonsuperimposable images. Chirality can be exemplified by the insurgence of two chiral centers (the bridgehead carbon atoms possessing four nonequivalent substituents).


In the left and center case in Figure 1, chirality is embedded into the whole, rigid  $\pi$ -framework, but the presence of some degree of molecular symmetry (a  $C_2$  axis) is actually showing similarities, in terms of shapes, potential properties and optical and chiroptical outcomes, with other, popular chiral synthons in nano-, supramolecular and materials chemistry (atropisomeric binaphthyls).<sup>[6]</sup> Compared to other  $C_2$ -symmetrical chiral synthons, such as 1,1'-binaphthyl, trans-1,2-disubstituted cycloalkanes and 1,1,2,2-tetrasubstituted ethane-based scaffolds, triptycenes exhibit outstanding features that are attractive for the development of new functional molecular design, including a robust chiral backbone and extremely limited conformational structure.


Fundamental studies of the synthesis and characterization of optically active triptycenes began in the 1960s, and over the



**Figure 1.** Some of the substitution patterns affording chiral triptycene derivatives.

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 An invited contribution to a Special Collection dedicated to Functional Supramolecular Systems

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past few years, their practical applications as chiral materials have attracted increasing attention. However, a literature survey dealing specifically with chiral triptycenes is to our knowledge lacking. The present contribution is divided into three main subchapters. The first one illustrates early approaches to the synthesis of enantiopure triptycenes, their characterization and use in catalysis. The subsequent two subchapters take into account more specific applications of chiral triptycenes in the realms of supramolecular and materials chemistry.

## 2. Resolution of Chiral Triptycenes Through Classical Methods and Enantioselective Syntheses

One of the first examples of the synthesis and optical resolution of chiral triptycenes was reported Nakagawa *et al.*<sup>[7]</sup> Compound 1, obtained from anthraquinone-1-carboxylic acid through a cycloaddition reaction with *p*-benzoquinone, could be resolved into the two enantiomers by the formation of co-crystals using a suitable compound from the chiral pool, the naturally-occurring alkaloid brucine, which contains a tertiary amine and could therefore form diastereomeric salts of the enantiomeric mixture of 1 (Figure 2).

The authors obtained crystals with constant optical activity after several recrystallizations of the salt in ethanol. Many optically active triptycenes<sup>[8]</sup> have been synthesized from (+)-1; it was also possible to obtain single crystals suitable for X-ray crystallography of the key compound (+)-2 (obtained from (+)-1 by Curtius rearrangement). The determination of the absolute configuration of (+)-2, which turned out to be (1*R*,6*S*), allowed the assignment of the absolute configuration of (+)-1, and other related derivatives. Nakagawa's group also reported the synthesis and the optical resolution by recrystallization as diastereoisomeric salts of other asymmetric chiral triptycenes,<sup>[9]</sup>

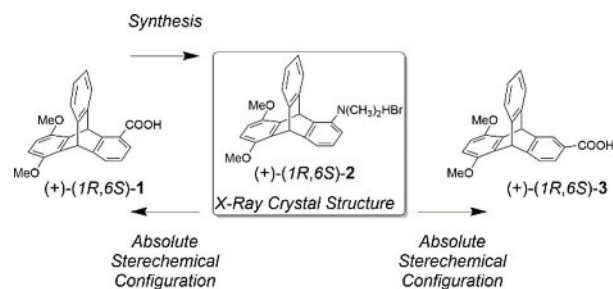


Figure 2. The first enantiomerically pure triptycene derivatives.

such as 3. The determination of the stereochemical configuration of these derivatives in most cases was achieved by chemical correlation with 1 or 2. In 1973, the same group reported the synthesis of compound 4 in which the key step is represented by the cycloaddition reaction between dichloroethylene and 1,5-dimethoxycarbonylanthracene (Figure 3).<sup>[10]</sup> The optical resolution of (–)-4 was obtained by recrystallization with the naturally-occurring alkaloid strychnine, which contains a tertiary amine. Several derivatives have been obtained from (–)-4. Among them, it was possible to obtain single crystals of the 1,5-diammonium salt (–)-5, from which it was possible to determine the absolute configuration, thus establishing by chemical correlation the stereochemistry of (–)-4 to be (9*S*,10*S*).

From this chiral triptycene-precursor, Harada *et al.* synthesized different chiral triptycenes (7–9 in Figure 3) possessing  $C_2$  molecular symmetry,<sup>[11]</sup> through reactions which cannot invert the absolute configuration of the triptycene-precursor (–)-4. Compound (–)-6, instead, was obtained from the corresponding dialdehyde, which in turn was elaborated from (+)-4.

The same authors demonstrated that chiral triptycenes could be successfully used as elaborated model compounds for the validation of the applicability of the CD exciton chirality method for the non-empirical unambiguous determination of



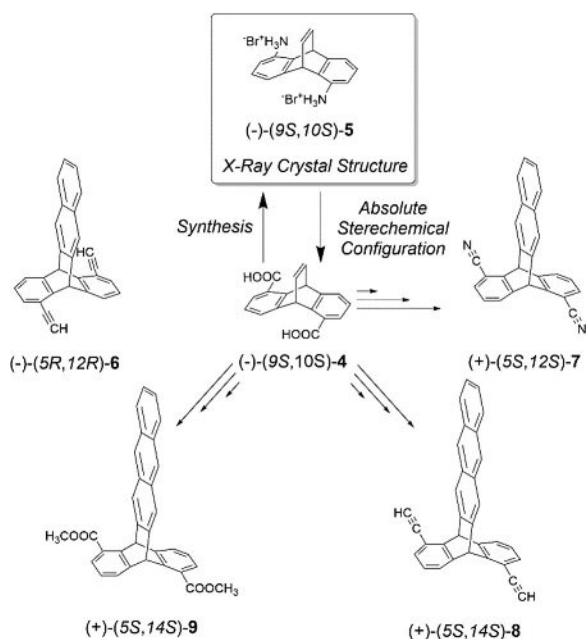
Giovanni Preda obtained his MSc (Laurea, cum Laude) in chemistry from the University of Pavia in October 2019 under the supervision of Prof. Mauro Freccero. In November 2019 he joined the laboratory of Prof. Dario Pasini at the same University to pursue his Ph.D. His research focuses on chiral  $\pi$ -conjugated organic materials.



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Dario Pasini obtained his Ph.D. degree in Chemistry in 1997 from the University of Birmingham, U.K. (advisor: Fraser Stoddart, Nobel Prize in Chemistry 2016). After postdoctoral research at the University of California, Berkeley, U.S.A., in the group of Prof. Jean M. J. Fréchet (1997–1999), he joined the faculty of the Department of Chemistry at the University of Pavia in 2000, where he is now an Associate Professor (with National Qualification to Full Professor, Organic Chemistry, since Nov. 2014), and he develops new scientific approaches in the fields of organic, supramolecular, and polymeric materials. He is a Fellow of the Royal Society of Chemistry. He spent periods of research as visiting Professor with S. Matile (Geneva, CH), L. Shimizu (South Carolina, USA) and T. Swager (MIT, USA). He has been awarded a Gutenberg Chair from the University of Strasbourg (2020).

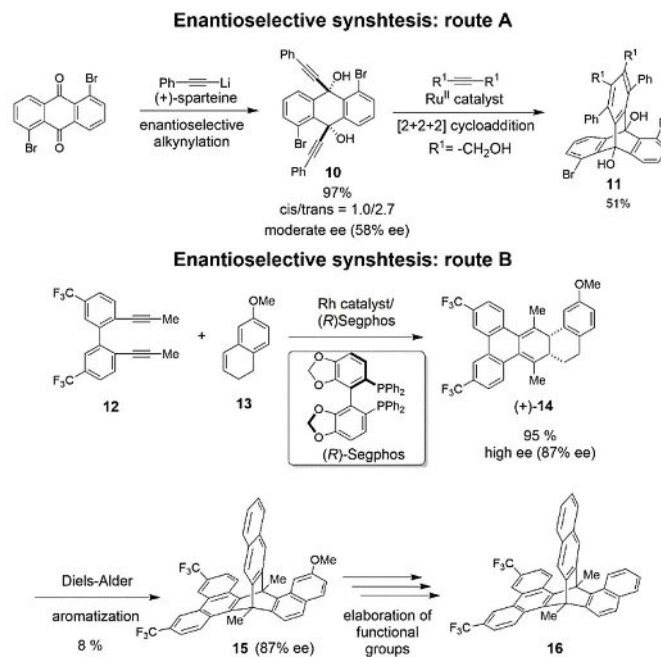


**Figure 3.** Synthesis, determination of the absolute configuration of 4 by chemical correlation, and derivatization to form iptycenes 6, 7, 8 and 9.

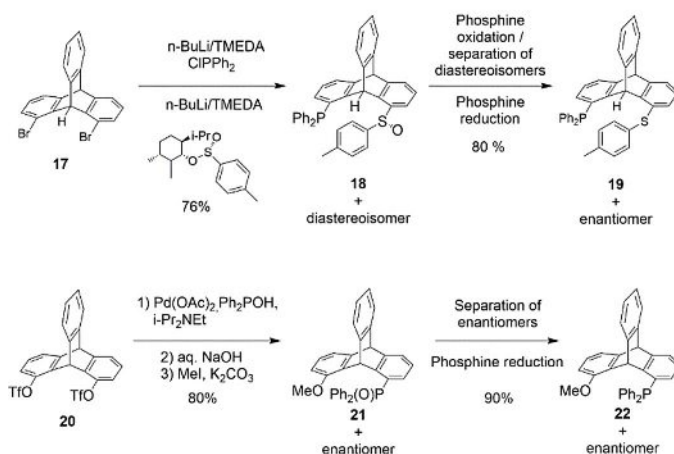
the absolute configuration of organic compounds. The CD exciton chirality method,<sup>[12]</sup> a very powerful method for the determining the absolute configuration of organic compounds, was found to be very suitable for chiral triptycenes because of the three-dimensional fixed-arrangement of the non-conjugated chromophores. They reported the first cases of unequivocal chiroptical determination of the absolute configuration of chiral triptycenes 6–9. The CD studies were associated with quantitative theoretical prediction of the CD spectra (calculated by quantum mechanical method) on the basis of the CD exciton chirality method. The calculated spectra were found to be in excellent agreement with those observed experimentally, establishing the absolute configuration unequivocally.<sup>[13]</sup> More recently, optically active triptycene-compounds have been obtained using chiral HPLC columns, and some examples will be discussed in the following chapters.

To date, only two cases of enantioselective synthesis are reported. In 2015, Shibata *et al.* reported the first enantioselective synthesis of an optically active triptycene.<sup>[14]</sup> It involved enantioselective sparteine-catalyzed alkylation of 1,5-dibromoanthracene-9,10-dione followed by alkyne trimerization to afford triptycene 11 (Figure 4). Although this route represents the first attempt to develop strategies for the enantioselective synthesis of optically active triptycenes, the *ee* of the enantioselective alkylation crucial step to give the *cis*- isomer 10 (as minor product) was only moderate (58%).

Another synthesis based on a [2+2+2] cycloaddition has been proposed by Tanaka and co-workers.<sup>[15]</sup> The crucial step of this synthesis involves a rhodium(I)-catalyzed enantioselective [2+2+2] cycloaddition between the biphenyl-linked diyne 12 and 1,2-dihydronaphthalene 13 to give the chiral polycyclic cyclohexadiene 14. Using a Rh catalyst and (*R*)-Segphos as chiral



#### Sequential syntheses of chiral triptycene-ligands



**Figure 4.** (A) and (B): enantioselective syntheses of optically-active triptycenes. Bottom: sequential syntheses of optically-active triptycene-based ligands for catalysis.

ligand it was possible to obtain 14 in quantitative yield and 87% *ee*. The diastereoselective Diels-Alder reaction between 14 and 1,4-naphthoquinone followed by reduction and aromatization with DDQ proceeded in mild conditions to give the chiral triptycene 15 without racemization. The opposite enantiomer of 14 can be prepared using opposite chiral ligand (*S*)-Segphos following the same synthetic sequence. The authors verified that the use of electron-deficient diyne and electron-rich alkene are necessary to limit undesired stress relieving carbocation rearrangements, which leads to complex product mixture during the DDQ aromatization step. A more elaborated triptycene derivative 16 can be synthesized from the two

enantiomers by demethylation, triflation and Pd(0)-catalyzed C–O cleavage. A single crystal of a precursor of (+)-**14** allowed the assignment of the absolute configuration of (+)-**14** and its derivatives.

Chiral triptycene can be achieved by their functionalization at the 1,8-positions (see also Figure 1) with two different groups. Despite this type of chiral triptycenes is relatively rare due to the synthetic difficulties to obtain them, some representative examples have been investigated in the field of ligand chemistry. In general, the synthetic approach requires as the key step the placement of the phosphine functional group at a later stage of the synthetic sequence. Gelman *et al.* synthesized the chiral robust monophosphine ligand **19** (Figure 4, bottom) and its complexation with PdCl<sub>2</sub> was demonstrated by X-ray crystallography.<sup>[16]</sup> The authors synthesized target molecule **19** starting 1,8-dibromotriptycene with two lithiation/electrophile exchanges in sequence, with chlorodiphenylphosphine an enantiopure *p*-toluenesulfinate. Fukushima *et al.* reported the synthesis of the triptycene-based monophosphine ligand **22** and its use in Pd-catalyzed Suzuki-Miyaura cross-coupling and asymmetric hydrosilylation.<sup>[17]</sup>

### 3. Chiral Triptycenes in Supramolecular Chemistry

Chiral triptycenes have been used recently in the field of interlocked molecules; in this case, the triptycene scaffold is inserted into a complex structure incorporating binaphthyl units as the source of chirality.<sup>[18]</sup> The new chiral[4]pseudorotaxane **24**. 3PF<sub>6</sub> was obtained by mixing a solution of chiral triptycene based tris(crown ether) **23** with three equivalents of ammonium salt “threads” in DCM. Ring-closing metathesis using a second generation Grubbs catalyst under high dilution conditions (1 mM) followed by hydrogenation afforded the chiral[4]catenane **25**. 3PF<sub>6</sub> (Figure 5) in 79% yield.

The spectroscopic properties of the chiral[4]pseudocatene were found to be in accordance with a D<sub>3v</sub> type of molecular symmetry. Deprotonation in DMF or DMSO with DBU and *N*-acylation reaction allowed the installment of three stopper units and the formation of the neutral chiral[4]pseudocatene **26**, whose NMR data were also consistent with the presence of a D<sub>3v</sub> type of molecular symmetry.

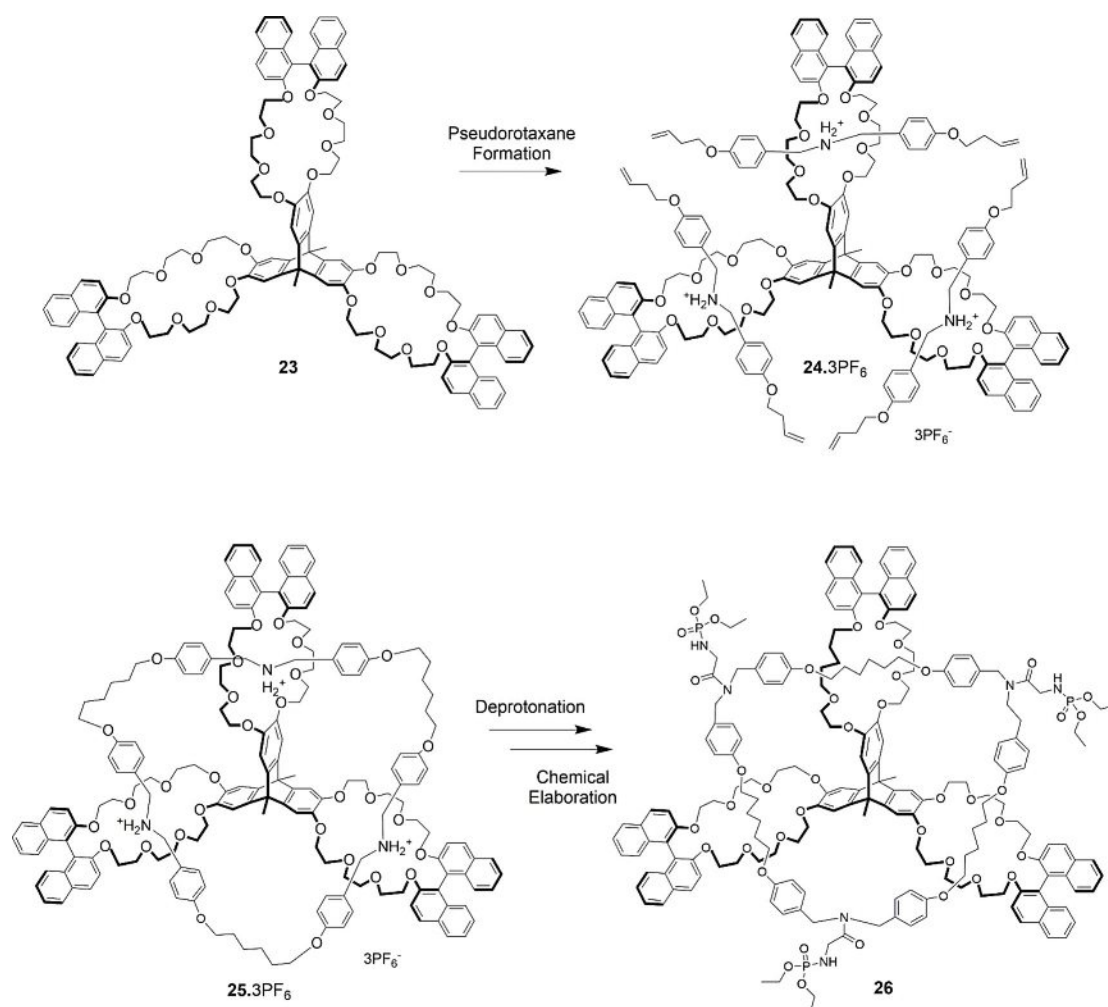


Figure 5. Triptycene-based chiral interlocked molecular structures.

Chen and co-worker synthesized chiral macrocycles containing three triptycene, named 2,6-helix[6]arene, with the general structure shown in Figure 6, in which the chirality is generated by introduction of chiral 2,6-dimethoxyl-3-hydroxymethyltriptycene as a racemic mixture.<sup>[19]</sup> The cyclization, achieved with 15% yield, was performed by treatment of the racemic mixture with a catalytic amount of *p*-toluenesulfonic acid, and generates homochiral macrocycles. Demethylation reaction with  $\text{BBr}_3$  led to the target macrocycle *rac*-27, which was resolved into the two enantiopure forms *P*-27 and *M*-27 through the introduction of a chiral auxiliaries strategy using *D* (+)-camphorsulfonyl chloride. The absolute configurations were confirmed by X-ray diffraction analysis and CD spectroscopy. The macrocycle 28 comprises three chiral triptycene fragments in a symmetrical nut-like structure in which the three methylene groups are positioned as vertices of a hexagonal prism, while the hydroxyl groups point above and below the molecular plane.

The same group optimized the synthetic methodology and extended the library of macrocycles through post functionalization reactions.<sup>[20]</sup> Starting from enantiomerically pure (+)- and (–)-2,6-dimethoxyl-3-hydroxymethyltriptycene, obtained by chiral HPLC resolution, enantiopure *P*-28 and *M*-28 were respec-

tively obtained in very good yields (51% and 53% respectively) by Fe-catalyzed oxidative cyclization. *P*- and *M*-28 were used to extend the library of 2,6-helix[6]arenes through bromination followed by complete demethylation and Suzuki-Miyaura cross-coupling protocols with electron-rich and electron-poor aryl boronic acids, to afford enantiopure homochiral macrocycles 30–33. Given their chiral robustness and large cavity, these macrocycles hold promise for wide potential applications in chiral recognition, stimuli-responsive host-guest complexation and molecular machines. Macrocycle 27 was found to exhibit highly enantioselective recognition toward chiral compounds containing a trimethylamino group.<sup>[19]</sup> *P*-27 resulted to have high affinity toward (*R*)-G1 ( $K_a=1802\text{ M}^{-1}$ ) and low affinity toward (*S*)-G1 ( $K_a=367\text{ M}^{-1}$ ) indicating a pronounced chiral discrimination. Macrocycle *P/M*-28 formed stable complexes with tropylium cation G2.<sup>[21]</sup> The 1:1 complex presented a strong charge-transfer interaction accompanied by a color change of solution from colorless to brown. The authors discovered that following the addition of a reductant, such as  $\text{NaBH}_4$ , the color change from brown to colorless, so that a redox-stimuli responsive behavior of the supramolecular complex could be claimed.

Similar host-guest interactions were observed between the achiral cation chromophore G3 and the macrocycle 29.<sup>[22]</sup> The host-guest complex exhibited enhanced fluorescence centered at 618 nm with mirror-image CD and CPL spectra in aqueous solution, revealing chirality transfer from the macrocycle to the host G3. *P*- and *M*-28 were also used for building mechanically interlocked molecules (MIMs) through a photo-induced proton-transfer (PIPT) strategy.<sup>[23]</sup>

Other, more complex chiral macrocycles such 34 have recently been reported. Huan Cong *et al.* recently reported a complex synthesis in which a formal triptycene fragment is inserted into the oval-shaped framework composed by two oligoparaphenylene nano hoops.<sup>[24]</sup> The crystal structure showed a propeller-like geometry with twisted rings on both sides, and oval-shaped cavities measuring 1.4 nm by 1.0 nm. The racemic mixture could be resolved by chiral HPLC and the chiroptical properties were studied by CD and CPL spectroscopy. The CPL behavior is particularly interesting on both enantiomers, showing a  $g_{lum}$  value of  $+3.24 \times 10^{-3}$  and  $-3.49 \times 10^{-3}$  values.<sup>[24]</sup>

#### 4. Chiral Triptycenes in Materials Science

Ikai *et al.* explored the application of triptycene-synthons for the implementation of new stationary triptycene-based phases for chiral HPLC (Figure 7).<sup>[25]</sup>

The key intermediate triptycene *rac*-35 was resolved in the two enantiomers by chiral HPLC. The alkyne was deprotected with TBAF and the two enantiomers (*R,R*)-36 and (*S,S*)-36 immobilized on silica by Cu(I) catalyzed 1,3-dipolar azide-alkyne cycloaddition. From thermogravimetric analyses it was possible to estimate a content of the triptycene-derivative in silica of 7% wt., from which derives a number of chiral selectors per unit of weight of the modified silica gel of  $6 \times 10^{19}\text{ g}^{-1}$ . The modified silica gel was packed in stainless-steel columns, and the chiral

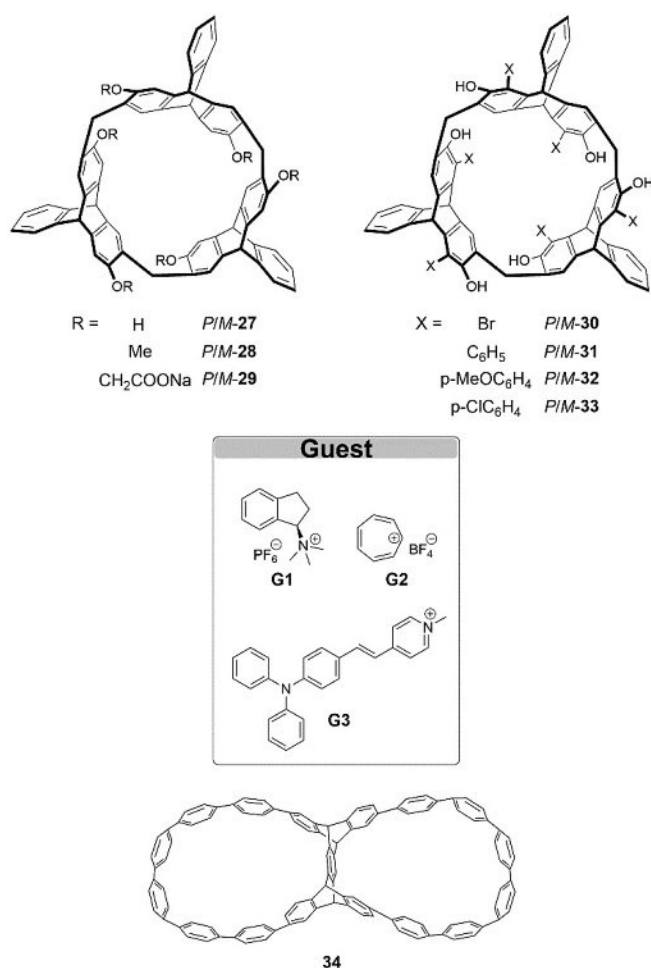


Figure 6. Optically-active triptycene-based macrocycles.

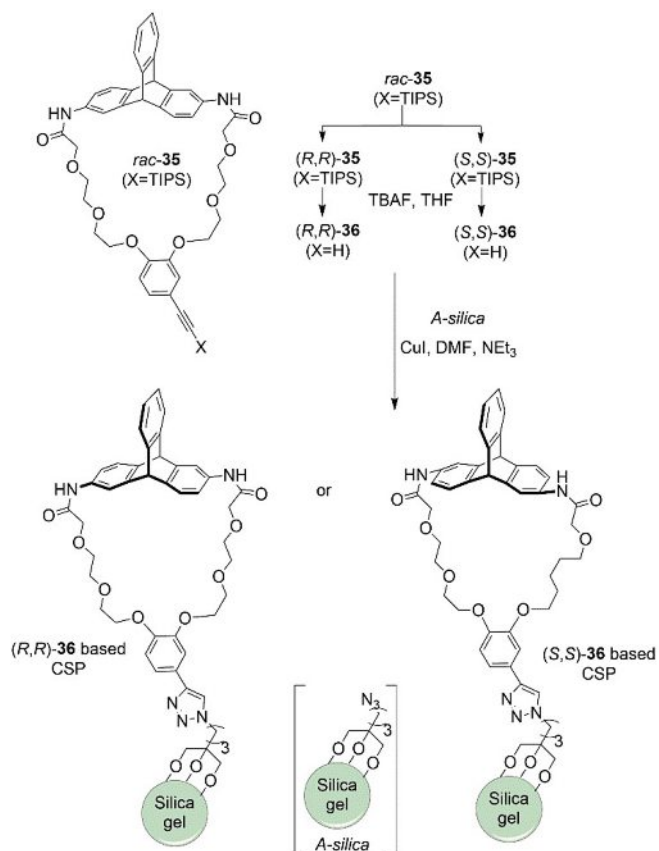


Figure 7. Chiral triptycenes as synthons for new chiral stationary phases.

stationary phase (CSP) showed good chiral recognition abilities toward axially chiral biaryl compounds.

Key to the Ikai procedures is the ability to doubly nitrate triptycene regioselectively,<sup>[25]</sup> which provides access to the amines that can be resolved through classical methods, and it is therefore among the more scalable and useful methods for achieving enantiopure triptycenes put forward.

Circularly Polarized Luminescence (CPL) is attracting growing interest due to the potential impacts in storage devices, security tags, biological probes and 3D displays. The fusion of triptycenes with hexa-*peri*-hexabenzocoronene (HBC) units has been reported, leading to a series of unique derivatives with a ladder-type structure used as fluorescent agents for in vivo fluorescence imaging.<sup>[26]</sup> These ladder-type triptycene structures maintain the molecular symmetry of triptycenes and they are achiral. The substitution of two benzene rings with two HBC moieties proposed by Ikai *et al.* led to HBC-embedded chiral triptycene **37** having a  $C_2$  molecular symmetry, which could be resolved by chiral HPLC or by crystallization in a DCM/hexane solution (Figure 8).<sup>[27]</sup> Enantiomers pairs of **32** showed mirror images CD and CPL spectra with a  $g_{abs}$  value of  $0.9 \times 10^{-3}$ , matching those reported for conjugated chiral organic materials.<sup>[28]</sup>

Ikai *et al.* designed new CPL-active material based on triptycene chiral-synthons (with  $C_2$  symmetry). The precursor was synthesized and resolved by chiral HPLC, then the pyrene-

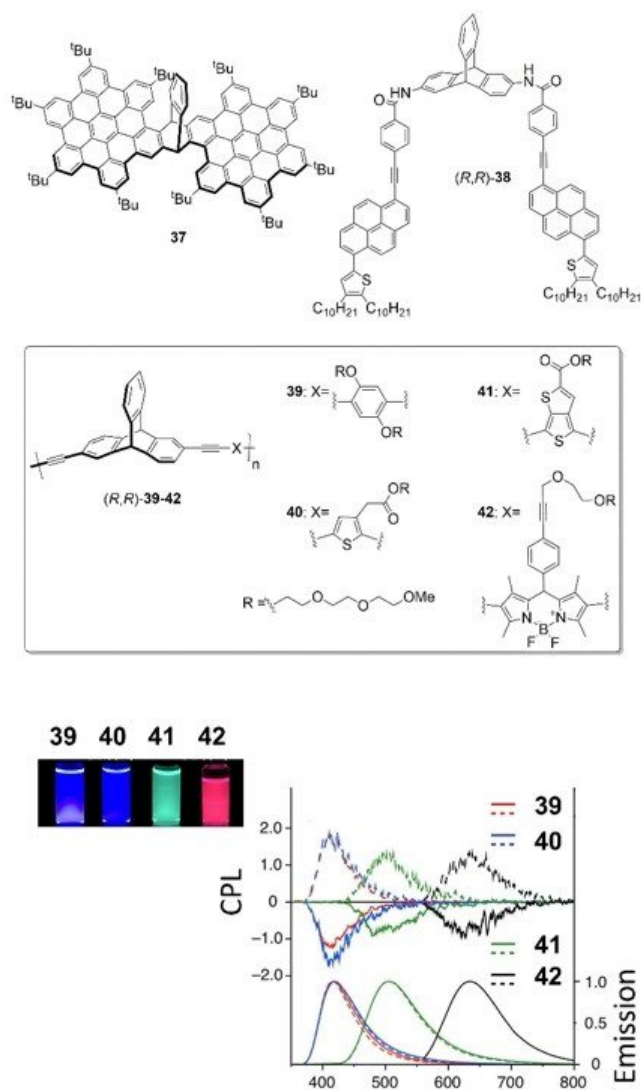


Figure 8. Chiral luminescent triptycene synthons and polymers. Partially reproduced with permission (ref. 30). Copyright: American Chemical Society, 2018.

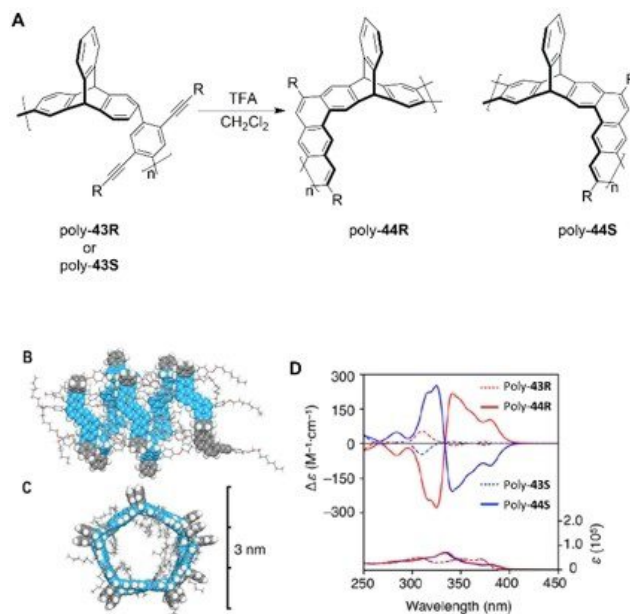
units were attached to form the two enantiomers of **38** (Figure 8).<sup>[29]</sup> The fluorescence emission and the chiroptical properties for (*R,R*)-**38** were found to be solvent dependent. Recording fluorescence spectra in THF/hexane solvent mixtures with increasing hexane volumes (from 100/0 to 1/99 THF/hexane % v/v) resulted in a red-shift of the emission maxima from 470 to 520 nm caused by excimer emission due to intermolecular interactions between pyrene-units. Variations were found between the CD spectra of (*R,R*)-**38** and (*S,S*)-**38** shifting from THF (weak CD signal in the pyrene-chromophore region) to THF/hexane (CD signal increased five times), while a hypsochromic effect in the absorption spectrum was observed as the amount of hexane increased. The chiroptical properties could be attributed to chiral hydrogen bonded aggregates with a preferred handed twist of stacked pyrene units. Dynamic light scattering (DLS) measurements estimated an average aggregate size larger than 200 nm in THF/hexane 1/99 v/v %. Aggregates



showed CPL signal in THF/hexane 1/99 v/v reaching dissymmetry factors as high as  $1.5 \times 10^{-3}$ .

CPL emission occurring only in the aggregate state can represent a limitation, preventing from possible practical applications, due to the need for precise control of temperature, solvent and concentration. It is therefore important to develop new molecular strategies to obtain materials able to exhibit CPL activities independently of external environmental factors.<sup>[30,31]</sup> A series of triptycene-based optically active polymers ((*R,R*)- or (*S,S*)-**39–42**) were obtained via copolymerization of enantiopure 2,6-diethynyltriptycene with a range of diiodoaryls.<sup>[32]</sup> The polymers were obtained from an optically-active, resolved diethynyl precursor, which was copolymerized with several diiodoaryl compounds by Sonogashira-Hagihara coupling in moderate yields with molecular masses greater than  $0.9 \times 10^4 \text{ g mol}^{-1}$ . The polymers showed fluorescence emission ranging from blue to red (with quantum fluorescence yields ranging from 17 to 61%) based on the achiral chromophore incorporated in the polymers (Figure 8). By comparison of the CD spectra of the polymers and of the starting monomer and model compounds, the authors rationalized that the appearance of a specific secondary structure (e.g. helical conformation) in the polymer backbone had to be excluded. The CPL properties of polymers have also been investigated. The  $g_{lum}$  value is almost constant and independent of the incorporated chromophore ( $10^{-3}$  approximately). This indicates that the fluorescence color could be modified by simply changing the achiral chromophore without compromising the CPL response.

Ikai *et al.* employed triptycene-based repetitive units for the synthesis of left and right handed helical ladder polymers.<sup>[33]</sup> For obtaining ladder polymers the reactions used must be highly selective, regioselective and quantitative to prevent the formation of defects that may compromise the structure of the polymer. Their synthesis fulfils these criteria. Poly-**43R** was synthesized via Suzuki-Miyaura coupling copolymerization of (*R,R*)-2,6-diiodotriptycene with a pinacol boronate containing two *p*-alkoxyphenylethynyl pendants. The random coil structure of poly-**43R** was converted into a one-handed helical structure by treatment with TFA: an electrophilic substitution reaction takes place leading to intramolecular cyclization with the formation of poly-**44R**. It is worth nothing that this reaction proceeds in a highly regioselective manner (the position –3 and –7, rather than positions –1 and –5, of the triptycene are the reactive ones towards aromatic electrophilic substitution) and quantitative, producing poly-**44R** with a rigid ladder structure in which chiral triptycene units are alternated with dibenzo[*a,h*]-anthracene-based units. The degree of polymerization of the polymer was estimated to be *ca.* 12. With regard to photoluminescence (PL) properties poly-**44R** exhibited a red shift of the emission maximum of 38 nm compared to poly-**43R**. Significant changes can be observed in the chiroptical properties: poly-**44R** exhibits a more intense signal (independent of temperature in the range of –10 to 55 °C) than poly-**43R**, with the formation of a split type CD band in the region between 250 and 400 nm (Figure 9). An average torsion angle between the repetitive triptycene-units of *ca.* 108°, have been estimated by computational studies, corroborating the thesis that the



**Figure 9.** (A) From triptycene-based enantiopure polymers to helical ladder polymers. (B) side view and (C) top view of molecular structure model proposed for poly-**44**. (D) CD absorption spectra for poly-**43** and poly-**44**. Partially reproduced with permission (ref. 33). Copyright: American Chemical Society, 2019.

dibenzo[*a,h*]anthracene planes are perfectly arranged in a clockwise twisting manner thus producing a right-handed helical ladder geometry. Chiral triptycene is therefore a key structural motif whose inherently three-dimensional geometry promotes the formation of a helical cavity potentially capable of  $\pi$ - $\pi$  interactions with guest substances molecules, polymers and carbon nanotube, and allows access to new polymeric materials.

## 5. Conclusions

Early research on chiral triptycenes mostly dealt with their preparation, with different synthetic routes being considered for achieving them as enantiopure compounds. Several substitution patterns have been explored on the aromatic frameworks in order to make them chiral, all of them with specific advantages and disadvantages. The focus has been gradually shifted from synthetic methodologies to their use for supramolecular and materials applications. Chiral triptycenes have been successfully incorporated into solid-state assemblies, concave hosts, molecular machines, helical polymers.

The field of chiral triptycene-containing supramolecular systems is “opening up” as researchers exploit their unique properties, to develop new chiral materials and supramolecules. One potential area of growth is in the field of chiral nanostructures, especially when their realization is combined with exquisite and peculiar optical properties, such as CPL. The future of chiral triptycenes in supramolecular and materials

chemistry looks bright with many exciting developments and applications to come.

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## Conflict of Interest

The authors declare no conflict of interest.

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