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- Chem. Eur. J. -

- Full Paper -

## **Stereospecific winding of polycyclic aromatic hydrocarbons into Trinacria propellers**

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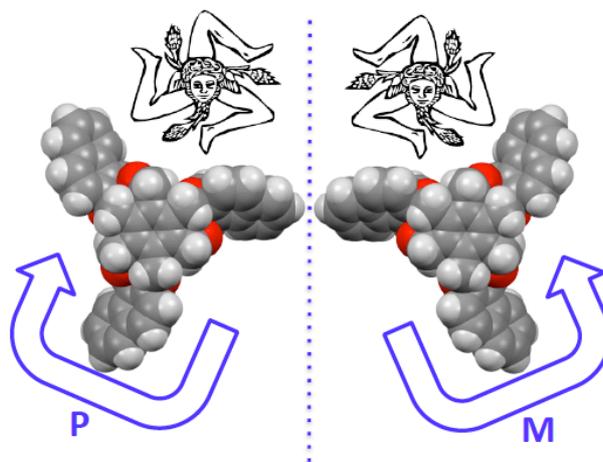
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Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. 1037158 (1), 1037157 (2), 1548318 (5).

**Keywords:** polycyclic aromatic hydrocarbons, molecular propellers, molecular motors, chiral nanocarbons, aromatic embrace.

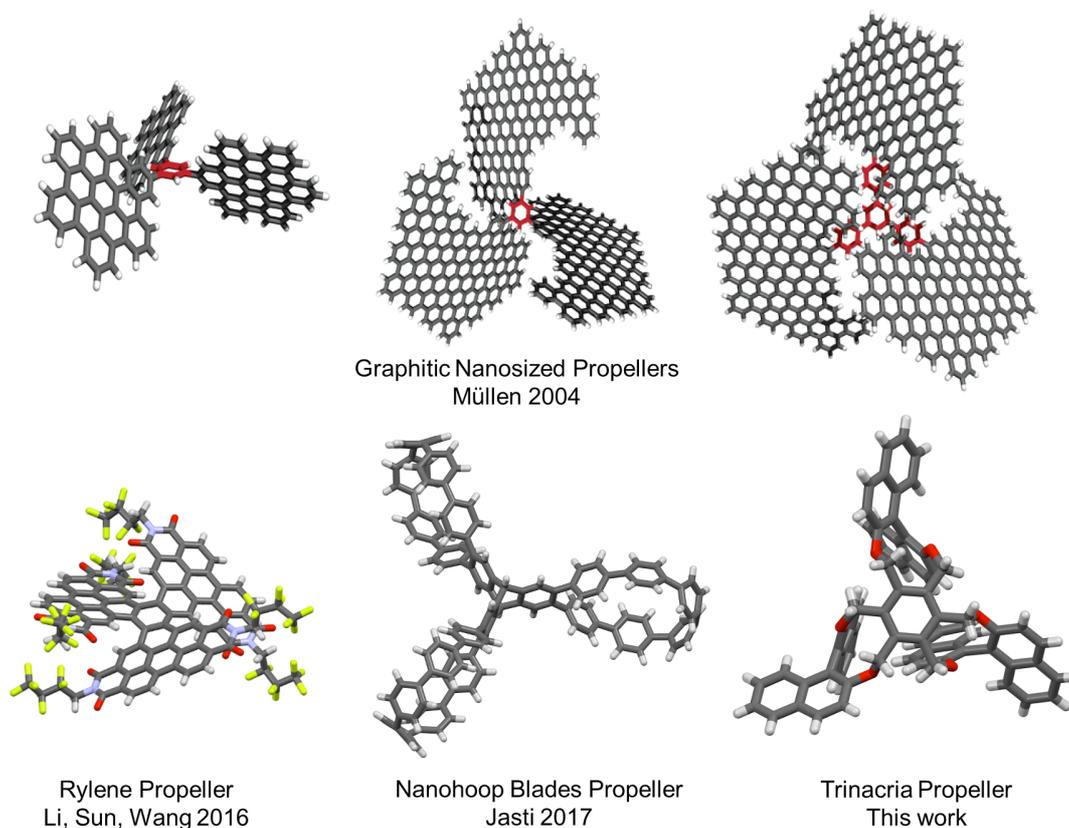
**Abstract:** The stereospecific trimerization of enantiomerically-pure binaphthols with hexakis(bromomethyl)benzene gives access in one step to enantiomerically-pure molecular propellers, in which three binaphthyl rings are held together through dioxecine rings. X-Ray diffraction analysis revealed that three out of the six naphthyl moieties are folded in a (EF)<sub>3</sub>-type arrangement held by three intramolecular C-H $\cdots$  $\pi$  interactions. This slips outward the three remaining naphthyl rings in a blade-like fashion, just like in three-folded propeller components. This peculiar conformation shows striking similarity to the mythological Sicilian symbol of Trinacria, from which the name "trinacria propeller" derives. The propeller conformation is also preserved in chlorinated solutions, as displayed by the presence of a peak at 4.7 ppm typical of an aromatic proton resonance engaged in a C-H $\cdots$  $\pi$  interaction. The denaturation of the propeller-like conformation is obtained at high temperature, corresponding to activation energy for the ring inversion of ca. 18.2 kcal mol<sup>-1</sup>. Notably, halide-functionalized molecular propellers exposing I-atoms at the leading and trailing edges could be prepared stereo- and regiospecifically by choosing the relevant iodo-bearing BINOL derivative.

**Figure for the table of contents**



## Introduction.

Pioneered by the 2016 Nobel Prizes awardees Sauvage, Stoddart and Feringa,<sup>[1]</sup> the organic synthesis of molecular analogues of some fundamental components of machinery (cogwheels, shuttles, pistons, etc) have attracted a great interest, reaching an unprecedented degree of complexity.<sup>[2]</sup> The idea is that such structures could be the molecular components of synthetic nanoscopic devices or materials that could function through external inputs inducing molecular-level motions.<sup>[2j, 21, 3]</sup>



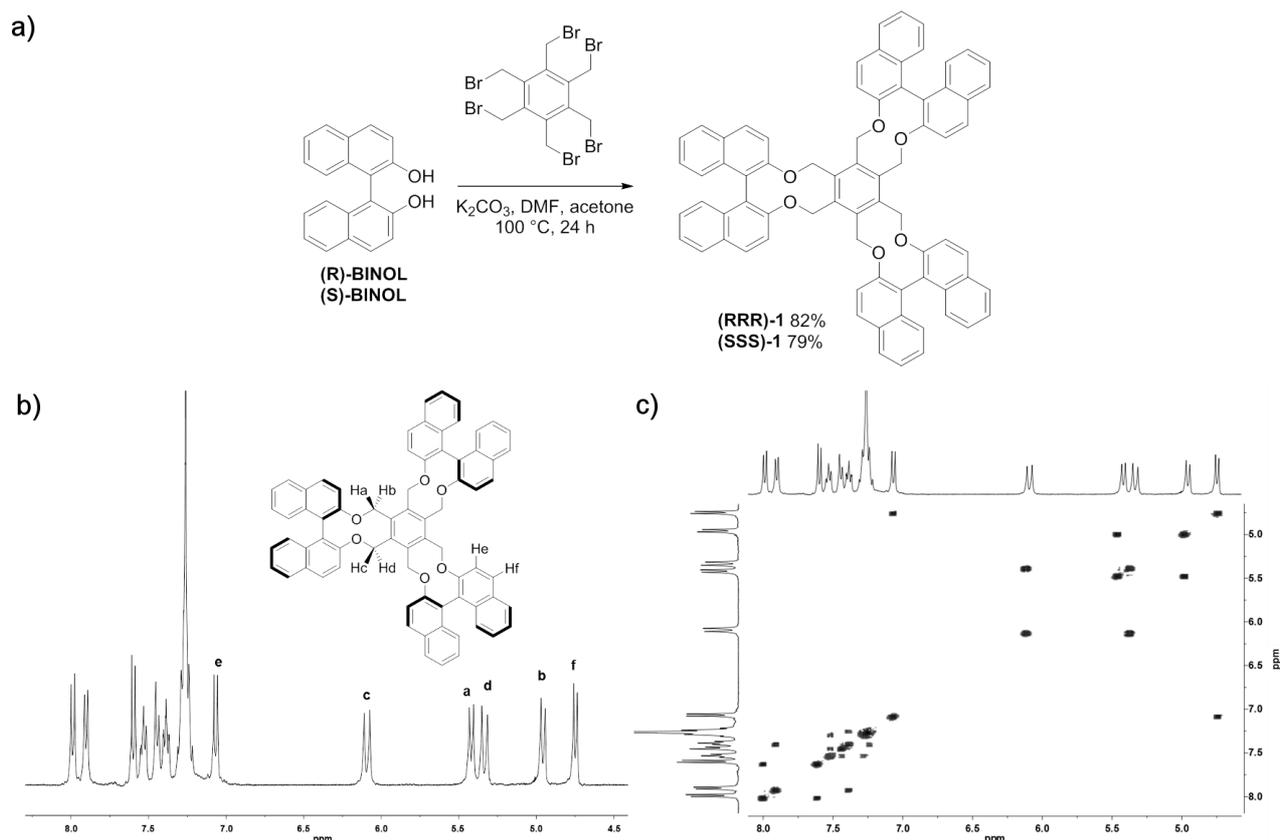
**Figure 1.** Three-bladed molecular propellers synthesized by Müllen and co-workers,<sup>[4]</sup> Meng and co-workers,<sup>[5]</sup> Jasti and co-workers<sup>[6]</sup> and us (this work).

Among the different nanoscopic analogues of macroscopic machines, the family of molecular propellers, in which aromatic moieties are arranged as blades around a central core, certainly represents one of the oldest ideas.<sup>[7]</sup> Building on the first biphenyls-based molecular propellers developed by Christie and Kenner,<sup>[7a]</sup> several reports describing structures of increasing complexity have

appeared subsequently.<sup>[8]</sup> Among these, polyarene 3D nanostructures developed by Müllen and coworkers (Figure 1), in which polycyclic aromatic hydrocarbons were arranged as blades around either a central aromatic scaffold or an atom, represent exemplary structural evolutions.<sup>[4]</sup> Other striking examples (Figure 1) include the three-bladed propellers from Meng and co-workers<sup>[5]</sup> and the recently described NanoHoop-bladed propeller from Jasti and co-workers.<sup>[6]</sup> However, these structures are often obtained as racemic mixtures.<sup>[4-6]</sup> Among the different causes, the restricted numbers of stereospecific and stereoselective oligomerization approaches<sup>[8n]</sup> and low-energy activation barriers of the racemization reactions<sup>[8a, 9]</sup> are the main limitations toward the preparation of enantiomerically pure molecular propellers. Ourselves we serendipitously stumbled in this field while designing novel BINOL-based chiral building blocks for preparing H-bonded supramolecular polymers.<sup>[10]</sup>

## Results and Discussions.

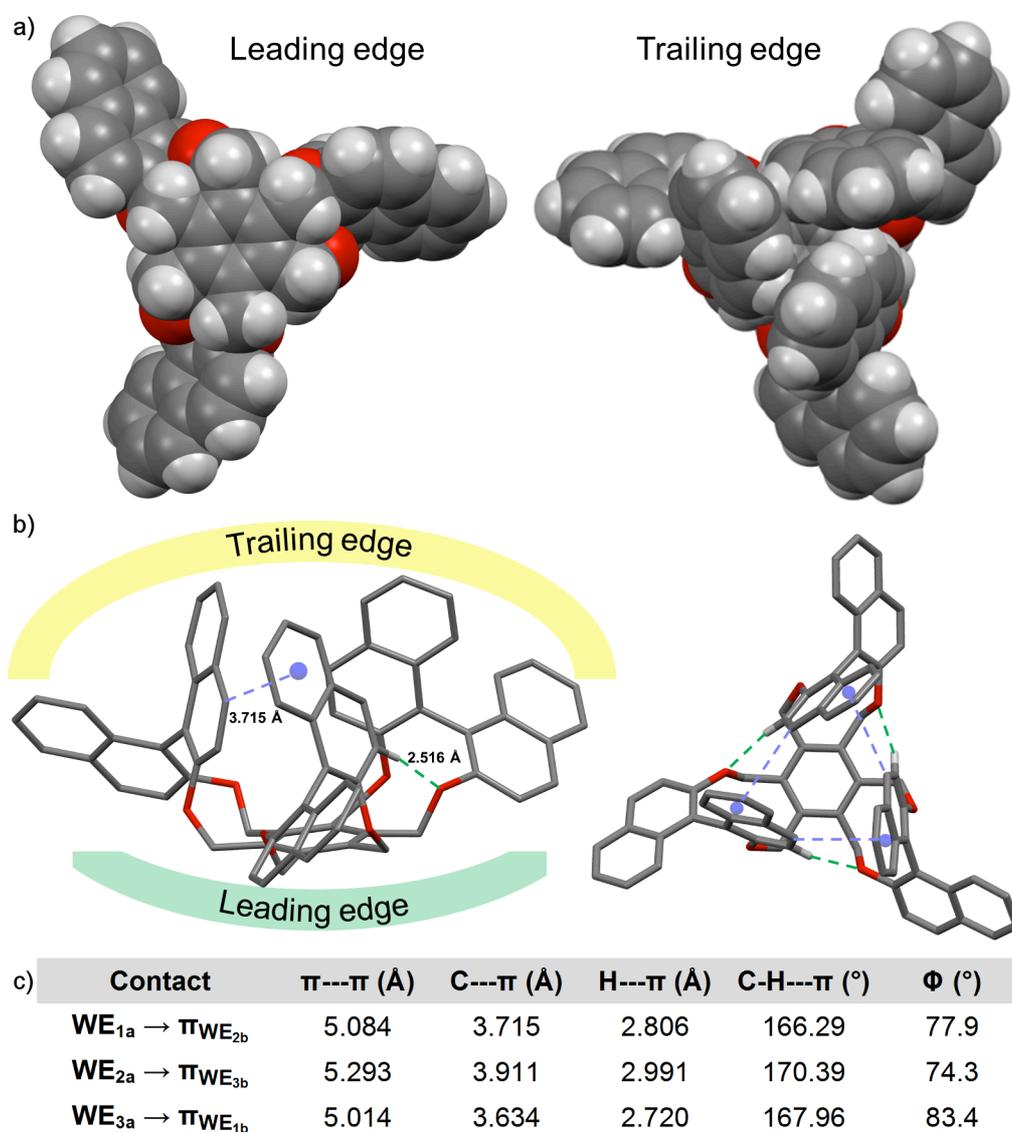
While assessing different aromatic modules to be functionalized with BINOLs, we noticed that the three-folded hexakis(methylenyl)benzene scaffold has never been used to covalently arrange three BINOLs through dioxecine linkages. Led by pure curiosity, we decided to react enantiomerically pure BINOLs with hexakis(bromomethyl)benzene following an adapted version of the protocol previously developed by Meijer and coworkers.<sup>[11]</sup> Specifically, Williamson cycloetherification of enantiomerically pure (R)-BINOL and (S)-BINOL with hexakis(bromomethyl)benzene in the presence of K<sub>2</sub>CO<sub>3</sub> in DMF at 100 °C allowed the simultaneous formation of three dioxecine rings, giving trimeric molecules **(RRR)-1** and **(SSS)-1** in very high yields, respectively (Figure 2a).



**Figure 2.** a) Synthesis of compounds **(RRR)-1** and **(SSS)-1**; b)  $^1\text{H-NMR}$  spectrum of **(RRR)-1** at rt in  $\text{CDCl}_3$ , c) COSY NMR spectrum of **(RRR)-1** showing the presence of a deshielded aromatic proton resonance at 4.7 ppm ( $\delta$  (ppm):  $H(f)$ : 4.75;  $H(b)$ : 4.96;  $H(d)$ : 5.33;  $H(a)$ : 5.42;  $H(c)$ : 6.09;  $H(e)$ : 7.07).

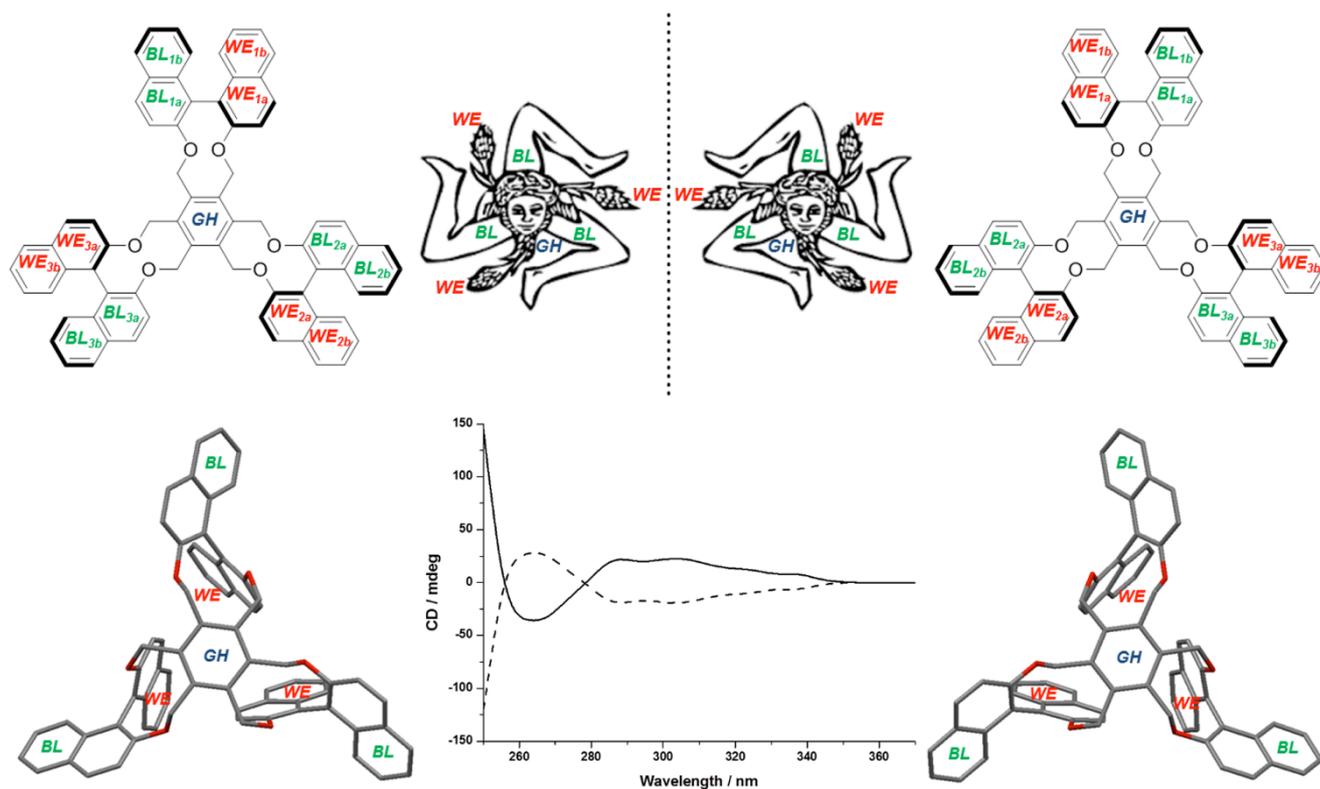
The occurrence of the trimerization reaction was firstly demonstrated by HR-MALDI mass spectrometric analysis, which displayed the presence of the molecular ion at  $m/z$  1047.3132 ( $[\text{M}+\text{K}]^+$ , calc. 1047.3088). To shed light on the conformational properties of the trimeric molecule, single crystals of **(RRR)-1** suitable for X-ray diffraction analysis were grown by vapor diffusion of hexane to a solution of **(RRR)-1** in  $\text{CHCl}_3$ . To our surprise, the X-ray structure of **(RRR)-1** depicted in Figure 3a reveals the propeller-like arrangement of the binaphthyl structures. Driven by three simultaneous intramolecular C-H $\cdots$  $\pi$  interactions established by proton H(f) and the aromatic ring of a neighboring naphthyl group (blue dotted line in Figure 3b, centroid-to-centroid distance of ca. 5 Å and C $\cdots$  $\pi$  = 3.911 – 3.634 Å), three out the six naphthyl moieties are folded in a  $(\text{EF})_3$ -type

arrangement.<sup>[12]</sup> This slips outward the three remaining naphthyl rings in a blade-like fashion.



**Figure 3.** a) Top (leading edge) and bottom (trailing edge) views of the crystalline structure of compound **(RRR)-1** showing the folded conformation in the solid-state; b) side-view showing the edge-to-face C-H $\cdots\pi$  interactions holding the three-fold (EF)<sub>3</sub>-type naphthalene embrace (in blue) and the H-bonding contacts (in green); c) structural parameters of the three-fold naphthalene embrace at the solid state. Space group: *P1*.

This embrace is further enforced by intramolecular H-bonding interactions established by naphthyl proton H(e) and the oxygen atom of a neighboring dioxecine ring (green dotted line in Figure 2b).



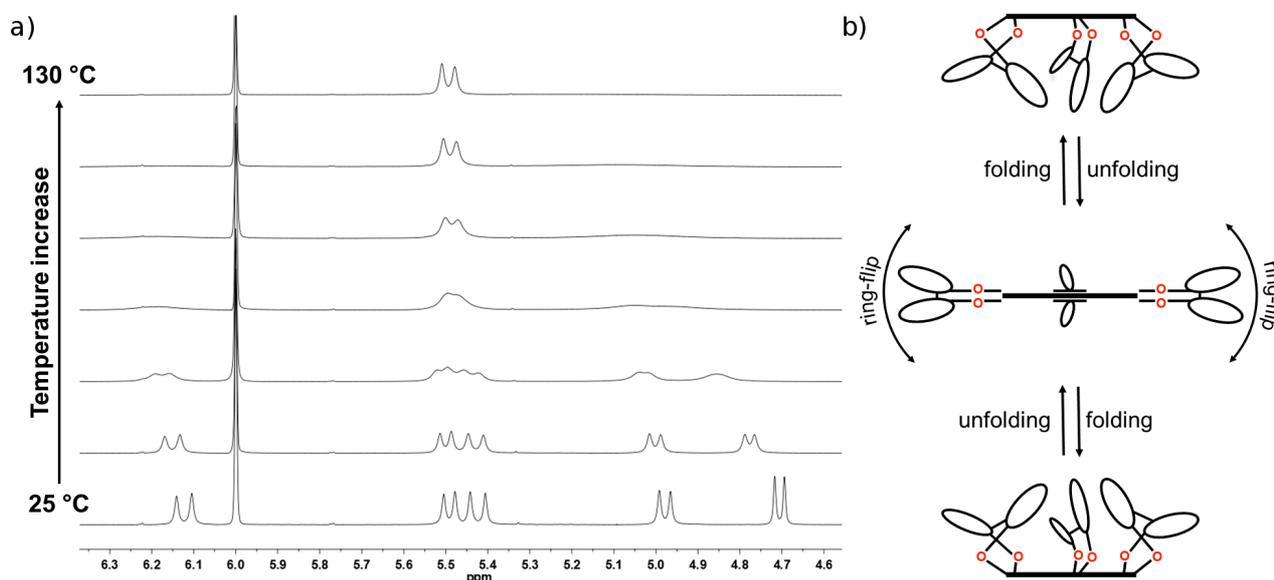
**Figure 4.** Description of the three-folded molecular propeller through the Trinacria symbol along with the ECD of (—) **(RRR)-1** and (---) **(SSS)-1** measured in  $\text{CHCl}_3$  at rt.

Given the peculiar conformational properties of this molecular propeller for which the embrace of three naphthyl units triggers the blade-type slipping of the remaining aromatic bicyclic rings, this structure can be regarded as the Sicilian mythological symbol of Trinacria (Figure 4).<sup>[13]</sup> Belonging to the general group of the triskelion motifs, the modern Trinacria is composed of a central winged Gorgon head from which three bent human legs and three wheat ears develop (Figure 4). Each of Trinacria's elements can be assimilated to molecular element of our molecular propeller, namely the winged Gorgon's head to the central hexakis(methylenyl)benzene core (labeled as GH), the wheat ears and human legs to the three-embraced and three-slipped naphthyl rings (labeled as WE and BL), respectively (Figure 4). As mentioned above, enantiomer **(SSS)-1** was also prepared. As expected, this isomer displays the same conformational properties as those of **(RRR)-1** both in solution and in the solid state only with opposite configuration. Electronic circular dichroism (ECD)

measurements displayed the characteristic Cotton band of binaphthyl moieties in  $\text{CHCl}_3$  (between 260 nm and 360 nm) and the typical band mirroring for enantiomers **(RRR)-1** and **(SSS)-1**. These observations further confirmed our hypothesis for which stable molecular propellers featuring P and M chirality can be prepared stereospecifically starting from (R)- and (S)-BINOLs, respectively.

Building on the solid-state structural evidences, we next turned our gaze toward the study of the conformation of trimer **1** in solution by means of  $^1\text{H-NMR}$  spectroscopy. In Figure 2b, the  $^1\text{H-NMR}$  spectrum (400 MHz,  $\text{CDCl}_3$ , rt) of **(RRR)-1** shows the typical pattern of a three-folded architecture, in which the binaphthyl residues are chemically equivalent. Beside the peaks of the aromatic protons located downfield (between 7.1 and 8.0 ppm), the spectrum shows typical doublets between 4.7 and 6.1 ppm that can be reasonably attributed to the diastereotopic methylene H-atoms of the central hexakis(methylenyl)benzene scaffold. However, the presence of five doublets out of the four resonances expected for protons H(a), H(b), H(c) and H(d) insinuates that one peak should be attributed to an aromatic proton. This conjecture was confirmed by DQF-COSY NMR measurements at rt, which allowed the unambiguous assignment of the resonance centered at 4.7 ppm to aromatic protons H(f) (Figure 2c). The unusual high-field location of aromatic proton resonances can only suggest that the relevant protons statistically rest atop the shielding region of an aromatic ring, likely engaged in C-H $\cdots$  $\pi$  interactions. Such signal pattern is in unambiguous agreement with the postulated three-folded conformation observed in the solid state, in which three naphthyl units out of the six are winded into an embrace through C-H $\cdots$  $\pi$  interactions. To investigate the dynamic properties of the conformation of **(RRR)-1**, variable temperature (VT)  $^1\text{H-NMR}$  investigations in TCE- $d_2$  ( $\text{C}_2\text{D}_2\text{Cl}_4$ ) were performed (Figure 5a). By following the temperature-induced shifts of H(f) and those of the methylene resonances, a thermal conformational motion involving

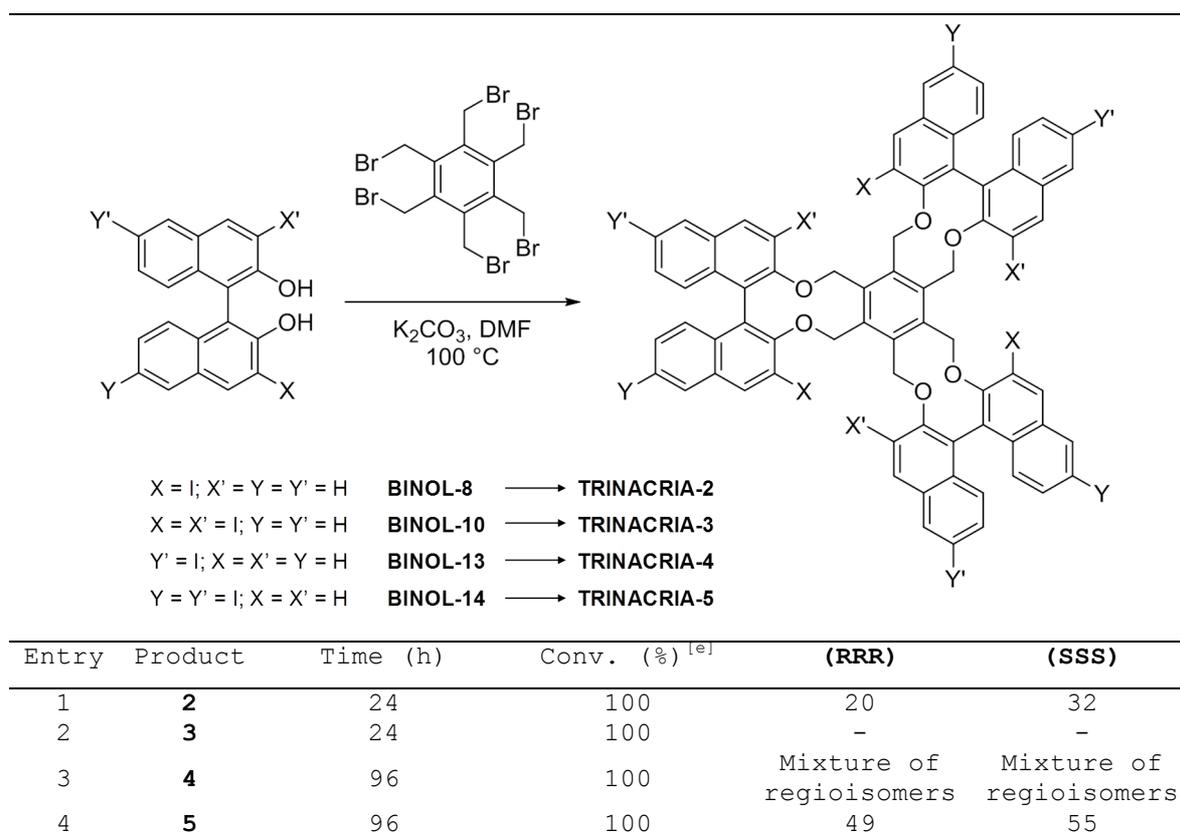
the *i*) unfolding of the embrace followed by the *ii*) ring-flip<sup>[9]</sup> of the dioxecine rings is observed (Figure 5b). The latter conformational motion leads to a BL-to-WE ring inversion of the molecular trinacria. While the first motional phenomenon (*i*) is monitored following the temperature dependence of the downfield shift of the H(f) resonances centered at 4.7 ppm, the ring-flip motion (*ii*) could be detected by tracking the coalescence of the methylene resonances H(a), H(b), H(c), H(d) at high temperature. Given this conformational behavior, the free-energy activation  $\Delta G^\ddagger$  for the motion could be estimated using Eyring's equation (see SI), revealing to be ca. 18.2 kcal mol<sup>-1</sup>.



**Figure 5.** VT <sup>1</sup>H-NMR spectra of **(RRR)-1** at 25, 50, 75, 100, 110, 120 and 130 °C (from bottom to top) in TCE-d<sub>2</sub> showing *T*-induced coalescence of the methylene proton resonances of **(RRR)-1** suggesting the presence of a complex dynamic equilibrium involving unfolded and folded conformers; b) schematic representation of the conformational inversion process of **(RRR)-1**.<sup>[9]</sup>

Interestingly, when the cycloetherification trimerisation reaction is performed with a racemic mixture of BINOLs, a mixture containing a 1:1 ratio of **(SSS)-1** and **(RRR)-1** is exclusively obtained. Any attempts to obtain other diastereoisomers, i.e. **(RSS)-1** or **(RRS)-1** as either enantiopure or racemic mixtures, miserably failed. Taken all together, these observations indirectly confirm the stereospecific character of this dioxecine-controlled trimerisation reaction.

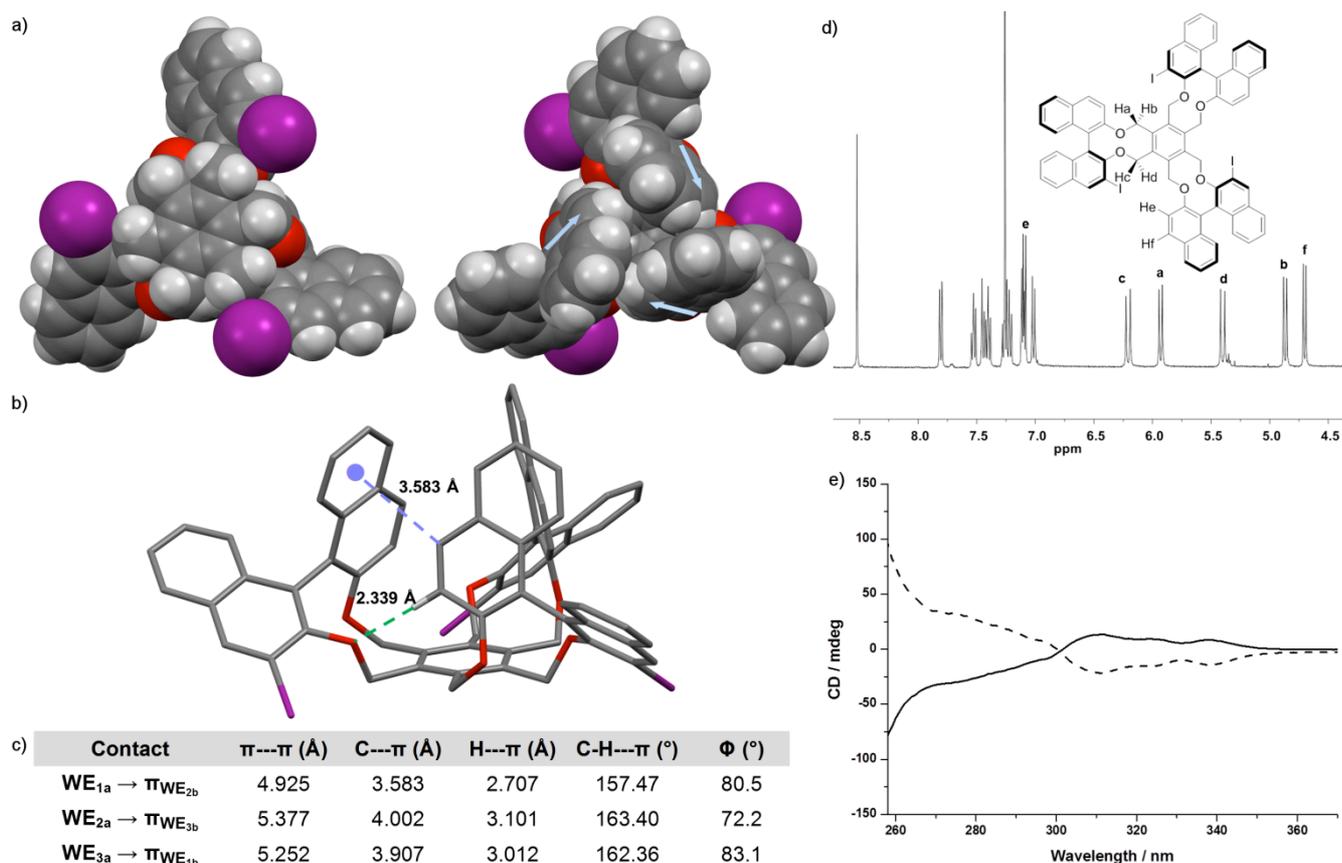
Inspired by these results, we have explored the possibility of stereospecifically preparing enantiomerically-pure trinacria propellers bearing functional groups that, after transformation, could expand the chemical space of these newly-discovered chiral scaffolds. Given the chemical versatility of aromatic halides, we have decided to prepare I-functionalized Trinacria propellers. Starting from iodo-functionalized BINOLs bearing one I-atom in either position 3 or 6 and two iodine atoms in positions 3,3' and 6,6' (for the synthesis of the iodo-BINOLs derivatives please see the SI), trimerisation reactions were performed following the above-described protocol (Scheme 1). It is expected that the BINOLs derivatives bearing the I-atoms at the 3 and 3' positions, will exclusively yield molecular trinacria featuring the I-atoms at the leading edges, whereas those bearing the I-atoms at the 6 and 6' to propellers functionalized at the trailing edges.



**Scheme 1.** Synthesis of functionalized molecular Trinacria.

When reacting hexakis(bromomethyl)benzene with (S)- and (R)-3-

iodo-BINOLs (for the synthesis see SI), trimeric compounds **(SSS)-2** and **(RRR)-2** could be synthesized. To confirm the folded conformation, crystals of **(SSS)-2** suitable for X-ray analysis were grown by slow diffusion of pentane in a  $\text{CH}_2\text{Br}_2$  solution. As observed for molecule **1**, molecule **2** also adopts the folded propeller-like conformation (Figures 6a-b) in which the WE naphthyl rings are held together by  $\text{C}\cdots\pi$  interactions ( $\text{C}\cdots\pi = 3.583 - 4.002 \text{ \AA}$ , Figure 6).



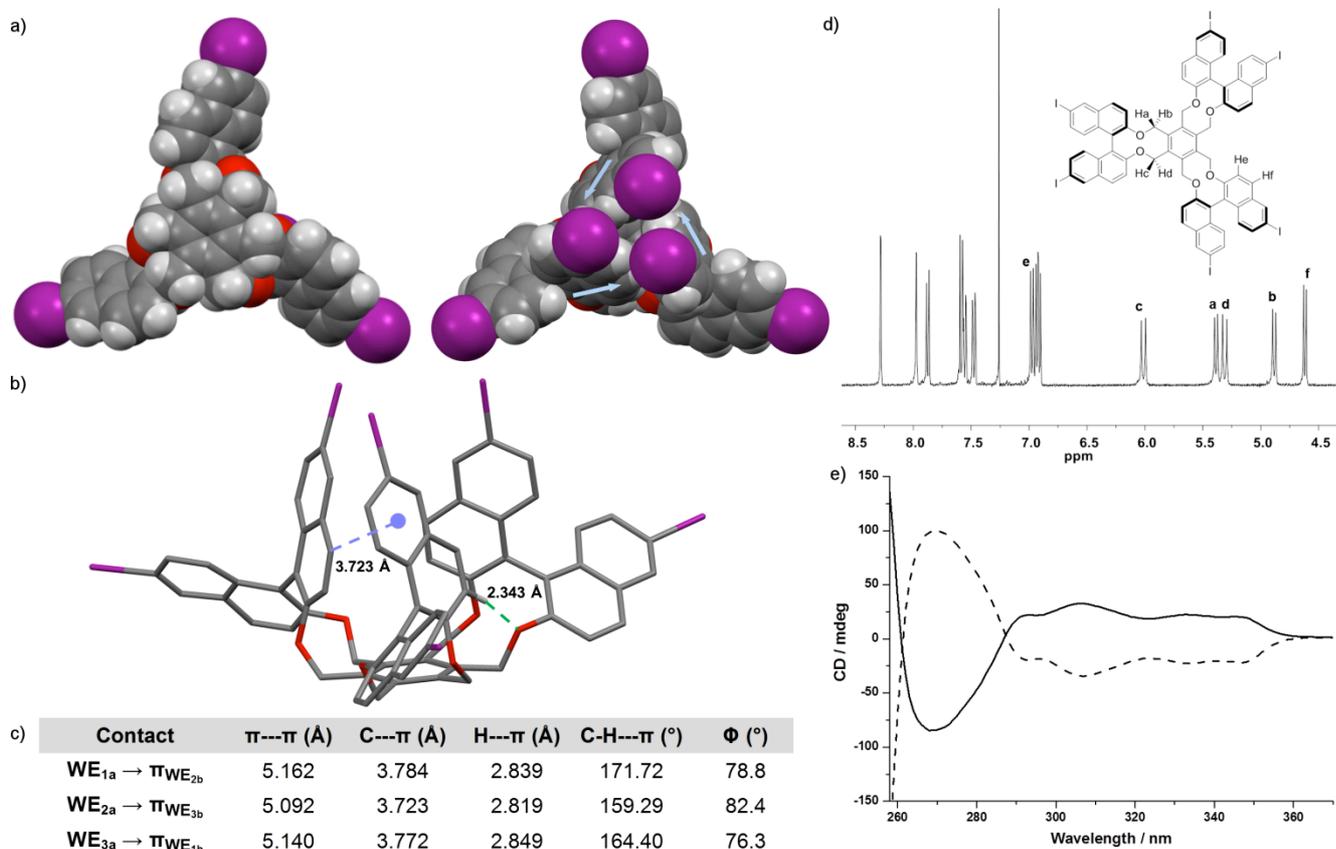
**Figure 6.** a) Top and bottom view of the crystalline structure of **(SSS)-2** showing the folded conformation in the solid-state; b) side view showing the edge-to-face  $\text{C-H}\cdots\pi$  interaction holding the three-fold naphthyl embrace (in blue) along with the H-bonding contact (in green); c) structural parameters of the three-fold naphthalene embrace; d)  $^1\text{H-NMR}$  spectrum of **(SSS)-2** at rt in  $\text{CDCl}_3$  ( $\delta$  (ppm):  $H(f)$ : 4.70;  $H(b)$ : 4.87;  $H(d)$ : 5.40;  $H(a)$ : 5.93;  $H(c)$ : 6.21;  $H(e)$ : 7.09); e) ECD of (—) **(RRR)-2** and (---) **(SSS)-2** measured in  $\text{CHCl}_3$  at rt.

Given the stereospecific character of the reaction, only the isomer in which the three I-atoms are located at the leading edges on the BL rings is obtained (Figures 7a-b). As observed for the

enantiomer couple **(SSS)-1** and **(RRR)-1**, ECD measurements displayed the typical band mirroring for enantiomers **(RRR)-2** and **(SSS)-2**, featuring P and M helical chirality, respectively (Figure 6e). As observed for molecule **1** in solution, also the <sup>1</sup>H-NMR spectra of **(SSS)-2** and **(RRR)-2** in CDCl<sub>3</sub> reveal the presence of a highly shielded aromatic proton signal at ca. 4.7 ppm, fingerprinting the naphthyl embrace (Figure 6d) and thus the presence of the propeller conformation also in solution. However, VT <sup>1</sup>H-NMR investigations in TCE-d<sub>2</sub> revealed that propeller **2** does not show any appreciable changes in the <sup>1</sup>H-NMR spectrum and no coalescence is visible at temperatures as high as 130 °C (Figure S52). Contrary to molecule **1**, propeller **2** does not undergo any *T*-induced conformational changes advocating for a conformationally-locked structure, in which the relevant I-atoms sterically prevent any dioxecine ring-flip motions and unfolding of the naphthyl embrace. Considering that the dioxecine flipping leads to an inversion between the BL and WE rings, this result suggests that the I-atoms can only be located on the BL rings (i.e., I<sub>3</sub>-BL) in accordance with the regiospecificity of the reaction.

When reacting hexakis(bromomethyl)benzene with (S)- and (R)-3,3'-diiodo-BINOLs (see SI for their synthesis), no products could be isolated and only a complicated mixture of products is obtained. This suggests that the presence of the two I-atoms in 3,3' positions sterically prevents the formation of the dioxecine ring. However, when (S)- and (R)-6,6'-diiodo-BINOLs (see SI for their synthesis) are reacted with hexakis(bromomethyl)benzene, products **(SSS)-5** and **(RRR)-5** could be obtained, respectively (Scheme 1). As for molecular trinacrias **1** and **2**, ECD measurements displayed band mirroring for enantiomers **(SSS)-5** and **(RRR)-5**. As shown by the X-ray structure of **(RRR)-5** depicted in Figures 7a-b (chiral crystals obtained by slow diffusion of pentane into a CHCl<sub>3</sub> solution), the molecule also adopts a propeller-like conformation, in which three naphthyl rings are embraced through C-H $\cdots$  $\pi$  interactions (C $\cdots$  $\pi$  = 3.723 - 3.784 Å). Contrary to propeller **2**, molecule **5** exposes six I-

atoms at the trailing edges, one for each BL and WE rings (i.e., I<sub>3</sub>-BL/I<sub>3</sub>-WE Figures 7a-c).



**Figure 7.** a) Leading edge and trailing edge view of the crystalline structure of **(RRR)-5** showing the folded conformation in the solid-state; b) side view showing the edge-to-face C-H $\cdots\pi$  interaction holding the three-fold naphthyl embrace (in blue) along with the H-bonding contact (in green); c) structural parameters of the three-fold naphthalene embrace; d) <sup>1</sup>H-NMR spectrum of **(RRR)-5** at rt in CDCl<sub>3</sub> ( $\delta$  (ppm): H(f): 4.70; H(b): 4.87; H(d): 5.40; H(a): 5.93; H(c): 6.21; H(e): 7.09), e) ECD of (—) **(RRR)-5** and (---) **(SSS)-5** measured in CHCl<sub>3</sub> at rt.

<sup>1</sup>H-NMR spectrum of molecule **5**, also presents a highly shielded aromatic signal at ca. 4.6 ppm, indicating that also in this case the molecule is in its folded conformation in solution (Figure 7d). This suggests that the I-atoms at the trailing edges do not prevent the naphthyl rings to establish edge-to-face interactions. VT <sup>1</sup>H-NMR measurements for molecule **5** show the high-field chemical shift of the aromatic hydrogen involved in the edge-to-face interaction as well as a coalescence of the methylene protons at ca. 5.4 ppm at 120 °C (Figure S52). As observed for **2**, a thermally-induced conformational motion involving the unfolding of

the embrace and the ring-flip of the dioxecine rings is also observed for this I-bearing propeller. This suggests that, contrary to the substituents at the leading edges, those positioned in the trailing edges have a negligible effect on the conformational dynamicity of the propeller. In this case, the estimated activation energy barrier for the conformational motion to take place accounts for ca. 20 kcal mol<sup>-1</sup> (see SI).

Finally, when reacting hexakis(bromomethyl)benzene with (S)- and (R)-6-iodo-BINOLs (see SI for their preparation), an inseparable mixture of different regioisomers was obtained (as also confirmed by X-ray analysis). Contrary to molecule **2** in which the three I-atoms are situated on a unique position at the leading edges of the BL naphthyl rings, a mixture of four functionalized molecular propellers bearing three I-atoms at the trailing edges statistically distributed on the BL and WE rings (i.e., I<sub>3</sub>-BL, I<sub>2</sub>-BL/I-WE, I-BL/I<sub>2</sub>-WE and I<sub>3</sub>-WE) was obtained. As expected, these observations suggest that no effect on the regioselectivity of the propeller folding can be expected when the substituent is distantly located from the dioxecine rings.

## Conclusions

In conclusion, in this paper we have described the first stereospecific synthesis of a new class of molecular propeller, defined as Trinacria propeller. In particular, trimerization of enantiomerically-pure BINOLs with hexakis(bromomethyl)benzene gives access in one step to trimeric nanostructures, in which three binaphthyl rings are held together to a central aryl scaffold through dioxecine rings. Solid-state X-Ray diffraction analysis and <sup>1</sup>H-NMR studies in solutions revealed that three out the six naphthyl moieties are folded in a (EF)<sub>3</sub>-type embrace held by three intramolecular C-H...N interactions. The embrace slips outward the three remaining naphthyl rings in a blade-like fashion, ultimately leading to the observed propeller conformation. Upon increasing the temperature, a denaturation of

the propeller conformation can be obtained in solution as displayed by VT-NMR measurements. Inspired by these results, we further expanded the chemical space of this class of molecules preparing functionalized propeller derivatives in a stereospecific and a regiospecific fashion. In particular, propellers bearing I-atoms at the trailing and leading edges starting from opportunely I-functionalized (R)- and (S)-BINOLs precursors have been also described.

Although of serendipitous discovery, we are confident that the unique stable conformation of the molecular scaffold along with its easy synthesis will attract a considerable attention in the scientific community for preparing chiral three-dimensional nanostructures. Given the perfect propeller-like structure, these molecular scaffolds could be used as fundamental components of unique molecular machinery undergoing unidirectional movements upon application of an external stimulus.

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