

## Chirality-Assisted Synthesis

# A Triptycene-Based Enantiopure Bis(Diazadibenzanthracene) by a Chirality-Assisted Synthesis Approach

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**Abstract:** By applying a chirality-assisted synthesis (CAS) approach enantiopure diaminodibromotriptycenes were converted to rigid chiral helical diazadibenzanthracenes, which show besides pronounced Cotton effects in circular dichroism spectra higher photoluminescence quantum yields as

comparable carbacyclic analogues. For the enantiopure building blocks, a protocol was developed allowing the large scale synthesis without the necessity of separation via HPLC.

## Introduction

The construction of complex but structurally defined molecules by stepwise irreversible reactions is tedious and often leads to low yields of the targeted compounds.<sup>[1]</sup> More sophisticated strategies have successfully been developed to overcome this problem, such as the template syntheses,<sup>[2]</sup> prearranging molecular entities or functional groups in space to make the event of reaction more probable. Another successful approach is the application of dynamic covalent chemistry (DCC),<sup>[3]</sup> where reversible reaction types are exploited in a way that the system can find its thermodynamic minimum, which often represents the objected molecular structures. Here, a template is not necessarily needed and due to the self-assembling manner, often high to quantitative yields are achieved starting from readily available and structurally simple molecular building blocks.<sup>[1d,4]</sup> The chirality assisted synthesis (CAS) can be understood as the next step in the evolution of synthetic methods toward structurally complex molecules.<sup>[5]</sup> Conceptually, chiral information of precursors allows to irreversibly connect the multitude of functional groups of adjacent units precisely and stereospecific, allowing only one product. The CAS concept was introduced in 2015 by Li, Schneebeli and co-workers demonstrating the synthesis of a molecular tweezer in a high overall yield (12%) by this approach.<sup>[5a]</sup> Since this ground-

breaking work, a handful of compounds synthesized by CAS has been reported such as molecular capsules,<sup>[6]</sup> discrete organic cage compounds<sup>[7]</sup> or helical ladder type polymers with one-handed geometry.<sup>[8]</sup> Crucial to the CAS approach is the accessibility of building blocks that possess both molecular rigidity as well as inherent chirality.<sup>[9]</sup> Besides tribenzotriquinacenes,<sup>[6,7,10]</sup> triptycenes or related structures have proven their potential in this respect.<sup>[5a]</sup>

Although initial studies of the synthesis and characterization of optically active triptycenes have been reported already in the 1960s,<sup>[11]</sup> there are still only a few more reports on this topic to date.<sup>[11,12]</sup> In 2019, Swager and co-workers used a chiral 2,6-diido triptycene as key compound to synthesize carbocyclic ladder polymers.<sup>[12f]</sup> The 2,6-disubstituted triptycene was accessed via a resolution step using chiral high-performance liquid chromatography (HPLC) of the racemic material. The limitation of this method is the scalability, because the separation by multiple runs on the chiral HPLC is tedious and impracticable for larger scales. Nevertheless, the synthesis of optically active ladder-type molecules and polymers through intramolecular cyclization of derivatives of these chiral triptycenes has been achieved, in which homoconjugated dibenzo[a,h]anthracene units are helically arranged along the main propagation direction, demonstrating the advantage of the chirality-assisted synthesis (CAS) for precise molecular shape control.<sup>[5]</sup>

Due to the obvious necessity of scalable syntheses of chiral triptycenes, we herein report the straightforward synthesis of optically pure triptycene derivatives in a practical scale by chiral resolution of diastereomeric triptycenes by column chromatography and the subsequent transformation of the obtained chiral building blocks to enantiopure ladder type molecules with extended π-backbone through a Suzuki–Miyaura cross-coupling/imine condensation sequence. The resulting bis(diazadibenzanthracenes) represent nitrogen doped analogues to Swagers dibenzo[a,h]anthracene oligomers.<sup>[12f]</sup>

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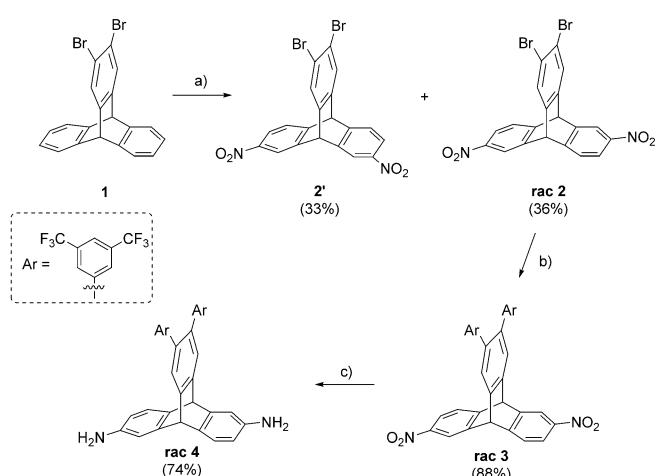
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## Results and Discussion

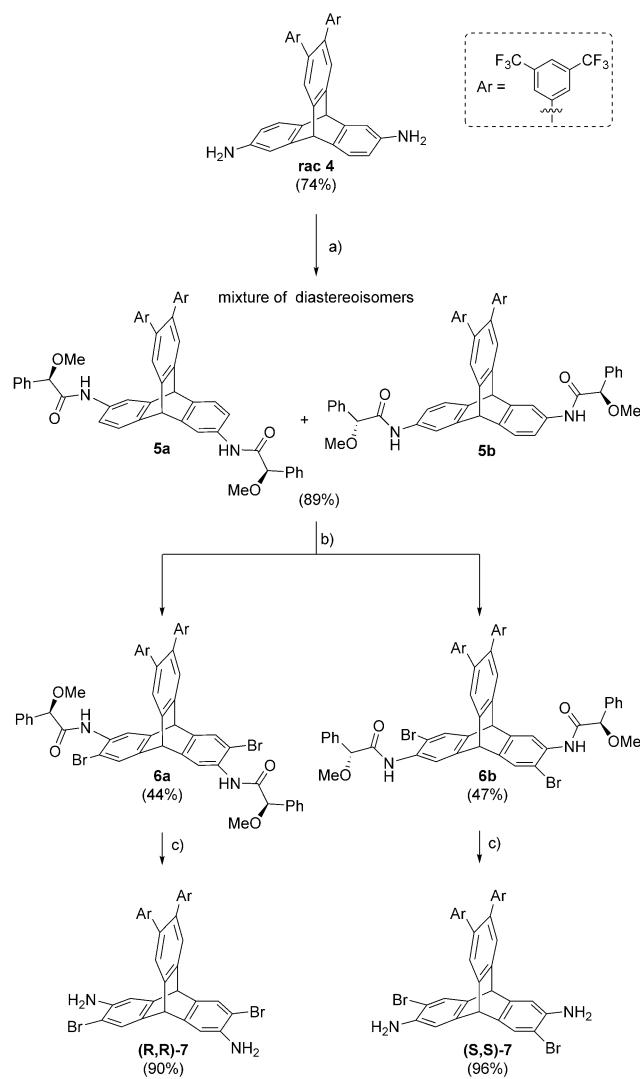
The synthesis started with a two-fold nitration of 2,3-dibromo triptycene **1**,<sup>[13]</sup> giving 36% of the racemic 2,6-dinitrated triptycene **rac-2** along with 33% of the achiral 2,7-dinitrated isomer **2'** (Scheme 1). The next step was a twofold Suzuki–Miyaura cross-coupling reaction of **rac-2** with 3,5-bis(trifluoromethyl)phenyl boronic acid to give **rac-3** in 88% yield. Subsequent reduction of the nitro groups with  $\text{SnCl}_2$  led to diamine **rac-4** in 74%. The attempted separation of enantiomers at this stage by the formation of diastereomeric salts with chiral acids, such as dibenzoyl-D-tartaric acid<sup>[14]</sup> failed and none of the diastereomers were isolated with notable diastereomeric excess.

To separate the enantiomeric mixture of **rac-4** it was twofold coupled with the chiral auxiliary (*R*)-methoxy phenylacetic acid using HATU as coupling reagent,<sup>[15]</sup> forming a diastereomeric mixture of **5a** and **5b** in 89% yield (Scheme 2). Although **5a** and **5b** are separable by preparative column chromatography ( $\text{SiO}_2$ , light petroleum ether/ethyl acetate/ $\text{CHCl}_3$ =10:1:1), the  $R_f$  values of **5a** and **5b** are too close ( $\Delta R_f < 0.05$ ) to allow a practical large scale approach, hence the yields of pure separated isomers were rather low (19% each) along with a 1:1 mixed fraction, that was isolated in 48% yield. To our delight, we found that after bromination of the diastereomeric mixture of **5a/b**, the corresponding diastereomers **6a** and **6b** are much easier separated by column chromatography (light petroleum ether/ethyl acetate=5:1,  $\Delta R_f = 0.1$ ) giving pure **6a** and **6b** in yields of 44% and 47%, respectively. It is worth mentioning that this reaction can be scaled up to give 1.45 g of **6a** and 1.27 g of **6b** (see Supporting Information).

The diastereoisomers **6a** and **6b** can be easily distinguished by  $^1\text{H}$  NMR spectroscopy (Figure 1). The protons  $\text{H}^{\text{a}}$ ,  $\text{H}^{\text{b}}$  and  $\text{H}^{\text{d}}$  of **6a** are slightly downfield shifted by  $\Delta\delta = 0.03\text{--}0.07$  ppm in comparison to **6b**. The relative high-field shift of  $\Delta\delta = 0.09$  ppm of the protons  $\text{H}^{\text{e}}$  is more pronounced (**6a**: 7.49 ppm; **6b**: 7.40 ppm) although the distance of these posi-



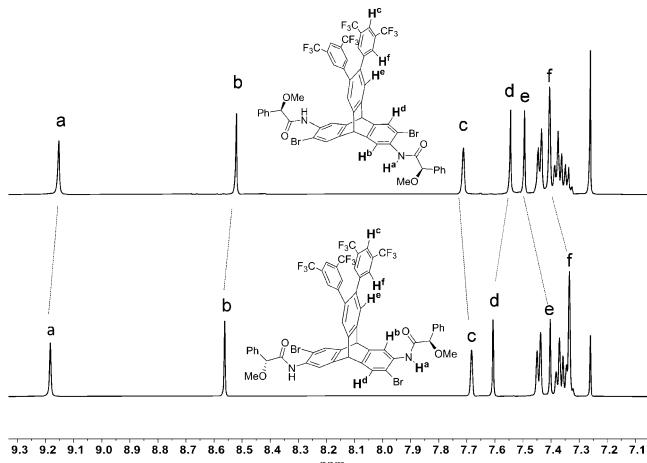
**Scheme 1.** Synthesis of **rac-4**. a)  $\text{HNO}_3$  (fuming),  $\text{AcOH}$ ,  $0^\circ\text{C}$ , 4 h; b) 3,5-bis(trifluoromethyl)phenyl boronic acid (3 equiv),  $\text{Pd}_2(\text{dba})_3$  (8 mol %),  $\text{HP}(\text{tBu})_3\text{BF}_4$  (20 mol %), 1 M  $\text{K}_2\text{CO}_3$ , THF,  $80^\circ\text{C}$ , overnight; c)  $\text{SnCl}_2 \cdot \text{H}_2\text{O}$  (10 equiv), THF/EtOH, rt, overnight.



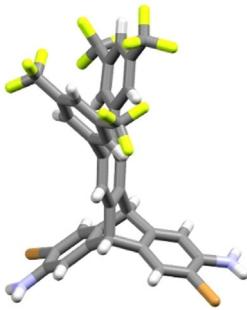
**Scheme 2.** Synthesis of **(R,R)-7** and **(S,S)-7**: a) (*R*)-2-methoxy-2-phenylacetic acid (2.8 equiv), DIPEA (2.8 equiv), HATU (2-(7-Aza-1*H*-benzotriazole-1-yl)-1,1,3,3-tetramethyl-uronium), HOEt (1-hydroxy-7-azabenzotriazole) (2.8 equiv), HOEt-H<sub>2</sub>O (2.8 equiv), DCM, rt, 1 d, 89% total yield for **5a** and **5b**. b)  $\text{Br}_2$  (2.5 equiv),  $\text{AcOH}$ , 2 h, rt, c)  $\text{NaOH}$  (2 M in MeOH), 1,4-dioxane,  $80^\circ\text{C}$ , overnight.

tions to the stereocenter of the chiral auxiliary is the largest (for a detailed discussion of the signal assignment see Supporting Information Figures S71–78). Since, the diastereomers were isolated in a pure fashion as indicated by  $^1\text{H}$  NMR spectroscopy, the diastereomeric excess can be concluded to be  $> 99\%$ . Cleavage of the auxiliaries was achieved by basic hydrolysis with  $\text{NaOH}$  giving the enantiopure **(+)-7** ( $[\alpha]_{365} + 28.5^\circ$  (c 1.0,  $\text{CHCl}_3$ )) and **(-)-7** ( $[\alpha]_{365} - 30.0^\circ$  (c 1.0,  $\text{CHCl}_3$ )) in yields of 90% and 96% (Scheme 2) and ee values of 98% for **(+)-7** and  $> 99\%$  **(-)-7** determined by chiral HPLC analysis with a Chiralpak AD-H column (see Supporting Information).

To determine the absolute configuration of the enantiopure amines, crystals suitable for X-ray diffraction of **(-)-7** were obtained by vapor diffusion of hexane into a solution of **(-)-7** in  $\text{DCM}$  at room temperature (Figure 2). The absolute configuration of the triptycene bridgeheads was determined to be **(S,S)**



**Figure 1.**  $^1\text{H}$  NMR spectra (600 MHz,  $\text{CDCl}_3$ ) of **6a** (top) and **6b** (bottom). Depicted are only the aromatic regions; for full spectra see Supporting Information.



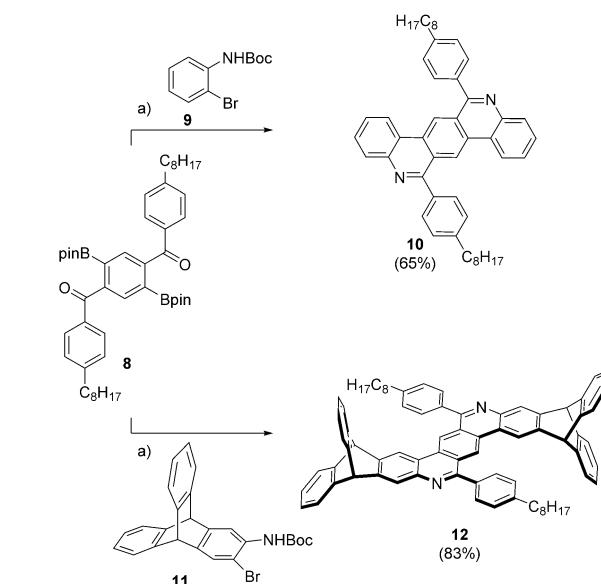
**Figure 2.** Single-crystal X-ray structure of  $(S,S)$ -7 as stick model. Colors: carbon grey; nitrogen blue; bromine orange; fluorine: green; hydrogen white.

spectroscopy in  $\text{CHCl}_3$  exhibit an intense split-type CD band with a maximum  $\theta$  value of  $-54.1 \text{ m}^{-1}\text{cm}^{-1}$  ( $(S,S)$ -7) and  $53.1 \text{ m}^{-1}\text{cm}^{-1}$  ( $(R,R)$ -7) at 270 nm and opposite Cotton effects (Figure S4, Supporting Information).

With the enantiopure dibromodiamino triptycenes  $(S,S)$ - and  $(R,R)$ -7 in hand, these can be used as molecular building blocks for the chirality assisted synthesis of larger rigid chiral heteroacenes with 5,12-diazadibenz[a,h]anthracene units,<sup>[18]</sup> by a cross-coupling approach followed by an imine condensation step.<sup>[19]</sup>

Before using these synthetically valuable triptycene precursors (+) or (-)-7, the reaction was first tested for a model compound by a Pd-catalyzed cross-coupling reaction of the diketo bis(boronic ester) **8** and bromoamide **9**, followed by the in situ removal of the Boc-group under acidic condition and subsequent imine condensation<sup>[20]</sup> in one pot (Scheme 3). The Boc-protected amine was used to avoid the formation of competing by-products by Buchwald-Hartwig aminations.<sup>[21]</sup> Notably, the purification of **10** by column chromatography was difficult because of its very low solubility in common organic solvent

by the single crystal X-ray structure analysis based on the heavy atom effect induced by the bromine substituents (Flack parameter  $0.18 \pm 0.04$ ).<sup>[16]</sup> Since  $(S,S)$ -7 was derived from **6b** which was obtained from **5b** (see Supporting Information and Scheme 2), the absolute configuration of the triptycene bridgeheads of **5b** and **6b** can be concluded to be assigned as  $(S,S)$  as well. Similarly, the absolute configuration of the triptycene bridgeheads of **5a**, **6a** and  $(+)$ -7 is determined as  $(R,R)$ . Investigations of the two enantiomers  $(S,S)$ -7 and  $(R,R)$ -7 by circular dichroism (CD)

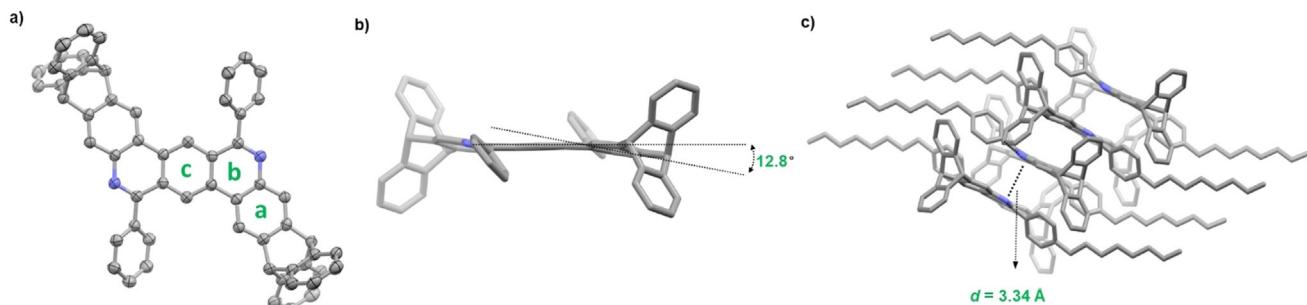


**Scheme 3.** Synthesis of 5,12-diazadibenz[a,h]anthracenes **10** and **12**.

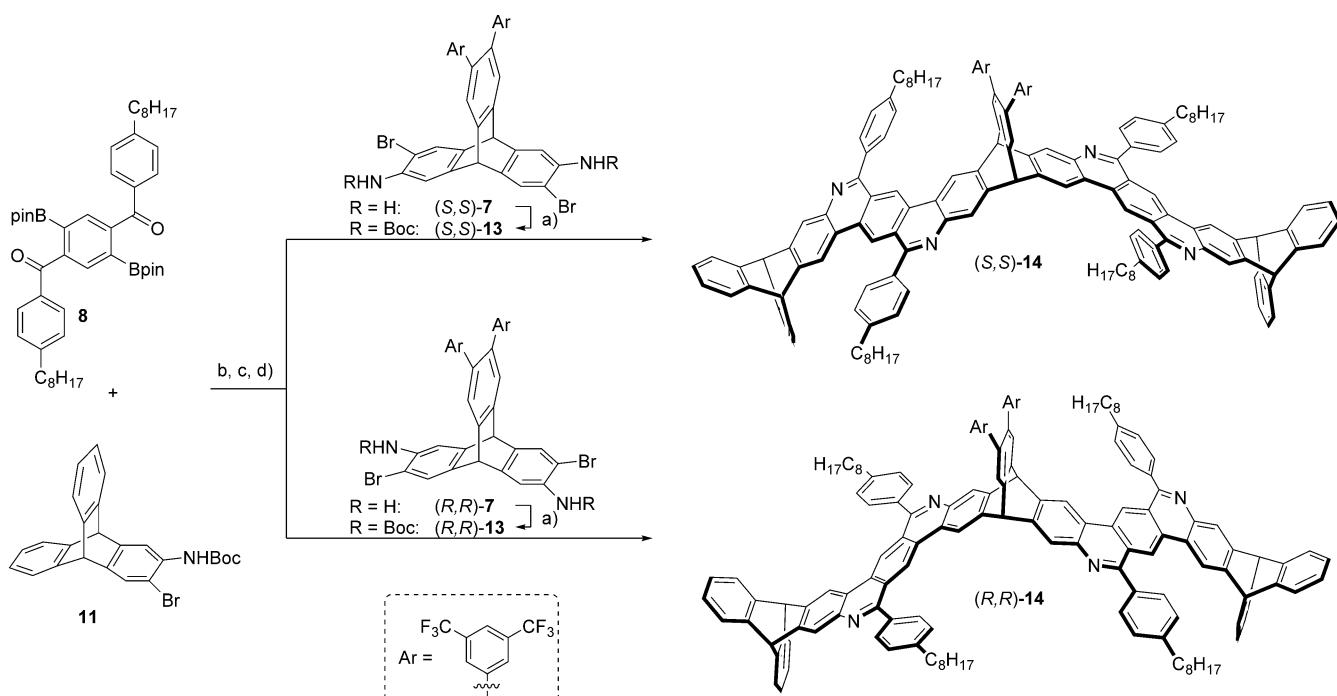
a)  $\text{Pd}(\text{PPh}_3)_4$  (8 mol%), DME, 2 M  $\text{Na}_2\text{CO}_3$ , 90 °C overnight, then  $\text{H}_2\text{SO}_4$ , 15 min.

(DCM,  $\text{CHCl}_3$  DMSO, oDCB, TCE, or EtOAc), although long alkyl chains are present to induce solubility. By washing with MeOH, the impurities could be removed and **10** was isolated in 65% yield.

Previously we have introduced the concept to increase solubility of larger fused aromatic  $\pi$ -systems by end-capping those with two triptycylene units.<sup>[22]</sup> For this purpose, diketone **8** was reacted with functionalized triptycene **11** (see Supporting Information) under the same reaction conditions as used for model compound **10** and triptycene based diazadibenzanthracene **12** was obtained in 83% yield (Scheme 3). In contrast to **10**, **12** showed excellent solubilities in common organic solvents. In  $\text{CHCl}_3$  for instance 120 mg  $\text{mL}^{-1}$  of **12** were dissolved whereas for **10** only 1.1 mg  $\text{mL}^{-1}$  were brought into solution. As reported before, the triptycenyI end groups not only increase the solubility of fused aromatics significantly, but at the same time a high crystallization tendency is remained.<sup>[22]</sup> Consequently, single crystals of **12** suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of pentane into a solution of **12** in DCM (Figure 3). The compound crystallizes in the monoclinic space group  $C_{2/c}$  with four molecules in the asymmetric unit (Figure 3). The molecular  $\pi$ -backbone is slightly twisted, and the angle between the two planes of ring **a** and ring **c** is 12.8° (Figure 3a and b). Close  $\pi$ - $\pi$  interactions were observed between two adjacent molecular  $\pi$ -backbones with a shortest distance of  $d=3.34 \text{ \AA}$  and the molecules pack in a column type arrangement with only weak dispersion interactions between these columns (Figure 3c).<sup>[23]</sup> Finally, the enantiopure amines  $(S,S)$ -7 and  $(R,R)$ -7 were converted to the Boc-protected amides  $(S,S)$ -13 and  $(R,R)$ -13 in 61% and 55% yield,<sup>[24]</sup> before reacting these with diketone **8** and triptycene **11** in a 2:2:1 ratio. Here, the same conditions (Pd-catalyzed cross-coupling and subsequent imine condensation) have been applied to obtain  $(S,S)$ -14 or  $(R,R)$ -14 in 20% and 22%



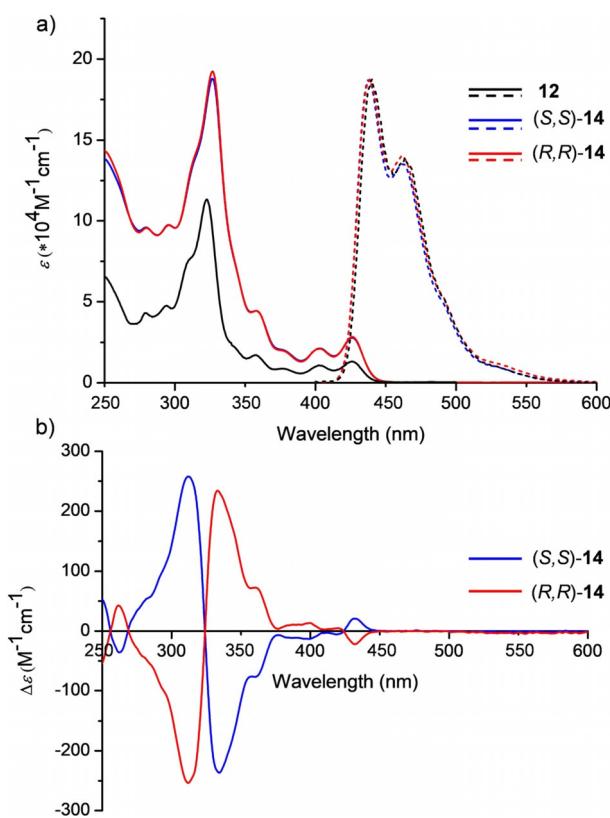
**Figure 3.** Single-crystal X-ray structure of **12**. a) Single molecule in elemental colors (carbon: grey and nitrogen: blue). ORTEP plots with thermal ellipsoids set at 50% probability. b) Slightly twisted  $\pi$ -backbones. In a) and b) the alkyl chains are omitted for clarity. c)  $\pi$ – $\pi$  stacking motifs. In all presentations, hydrogens are omitted for clarity.



**Scheme 4.** Synthesis of **(S,S)-14** and **(R,R)-14**. a)  $\text{NaH}$ ,  $\text{Boc}_2\text{O}$ , THF, reflux, 24 h, 61% for **(S,S)-13** and 55% for **(R,R)-13**. b) **(S,S)-13** or **(R,R)-13** (1 equiv.), **9** (2 equiv),  $\text{Pd}(\text{PPh}_3)_4$  (10 mol %),  $\text{DME}$ ,  $2 \text{ M Na}_2\text{CO}_3$ ,  $90^\circ\text{C}$  overnight. c)  $\text{TFA}$ ,  $\text{DCM}$ , reflux, 7 h. d)  $\text{NaHCO}_3$ ,  $\text{Et}_3\text{N}$ ,  $\text{THF}$ , rt, 12 h, 20% for **(S,S)-14** and 22% for **(R,R)-14** in three steps.

yield after purification by column chromatography, followed by recycling GPC (Gel Permeation Chromatography; Scheme 4). Both compounds were fully characterized. For instance by MALDI mass spectrometry characteristic peaks at  $m/z = 2188.853$  and  $2188.755$  have been detected for **(R,R)-14** and **(S,S)-14** respectively, matching the expected  $m/z$  for  $[\text{M}+\text{H}]^+$  ( $m/z = 2187.990$ ; calcd for  $\text{C}_{148}\text{H}_{127}\text{N}_4\text{F}_{12}^+$ ). In the corresponding  $^1\text{H}$  NMR spectra the most characteristic peaks are the singlets at  $\delta = 6.01$ ,  $5.65$  and  $5.64$  ppm, which can be assigned to the triptycene bridgehead protons of **(S,S)-14** as well as **(R,R)-14**. Since enantiopure starting materials were used, the large and rigid chiral compounds **(S,S)-14** or **(R,R)-14** were enantiopure too, as confirmed by chiral HPLC analysis and CD spectrometry (Figure S3 and discussion below).

Diazadibenz[a,h]anthracene **12** as well as the chiral bis(diazadibenz[a,h]anthracenes) **(R,R)-14** and **(S,S)-14** have been investigated by absorption and emission spectroscopy (Figure 4a, Table 1). All three compounds possess comparably sharp absorption bands and show a highest intensity absorption maximum at  $\lambda = 327 \text{ nm}$ . The most redshifted absorption maximum is found at  $\lambda = 426 \text{ nm}$  and for all these compounds an optical bandgap of  $E_{\text{g,opt}} = 2.8 \text{ eV}$  was estimated from  $\lambda_{\text{onset}} = 446 \text{ nm}$ . In comparison, Swager reported the synthesis and characterization of all carbon analogues to **(R,R)-14** and **(S,S)-14**, which show much broader peaks in the region of  $250$ – $400 \text{ nm}$  and no absorption peaks above  $\lambda = 425 \text{ nm}$ .<sup>[12]</sup> The broadness of the peaks in this case could be derived from aggregation effects, since they did not introduce triptycene



**Figure 4.** a) UV/Vis absorption (continuous line) and normalized emission spectra (dashed line, ex 327 nm) of (S,S)-14 ( $c=5.0\text{ }\mu\text{M}$ ), (R,R)-14 ( $c=3.7\text{ }\mu\text{M}$ ) and 12 ( $c=5.2\text{ }\mu\text{M}$ ) in  $\text{CHCl}_3$  at room temperature. b) CD spectra of enantiopure (S,S)-14 and (R,R)-14.

units as endcaps, to hinder the aggregation by  $\pi$ -stacking interactions.<sup>[22]</sup> Furthermore, the electron-withdrawing pyridinic nitrogens of (R,R)-14 and (S,S)-14 stabilize the frontier molecular orbitals of aza aromatics by 0.6 eV as observed in DFT-calculations (see Supporting Information, Figure S147) and lower the bandgap in comparison to their parent hydrocarbons, explaining the bathochromic shift of  $\Delta\lambda=25\text{ nm}$  for the longest wavelength absorption.<sup>[25]</sup>

12, (R,R)-14 and (S,S)-14 emit at comparable wavelengths of  $\lambda_{\text{em}}=438\text{--}440\text{ nm}$  with corresponding Stokes shifts of  $\Delta\nu=643\text{--}747\text{ cm}^{-1}$ . The almost similar absorption and emission behavior of monomer 12 in comparison to the triptycene bridged dimers (R,R)-14 and (S,S)-14 suggest the absence of electronic coupling between the formally non-conjugated diazadibenzo[a,h]-anthracene chromophores by homo-conjugation.<sup>[11c, 26]</sup>

The fluorescence quantum yields are with  $\Phi=26\%$  (12) to 30% ((S,S)-14) and 32% ((R,R)-14) (see Table 1) by a factor of four higher as for the comparable all carbon analogue ( $\Phi=7\%$ ).<sup>[12f]</sup> The chiroptical analysis of (R,R)-14 and (S,S)-14 by CD-spectroscopy reveals mirror image type spectra with opposite Cotton effects (Figure 4b). The maximum  $|g_{\text{abs}}|$  values are with  $-2.57\times 10^{-3}$  (at 347 nm for (S,S)-14) and  $+2.08\times 10^{-3}$  (at 307 nm for (S,S)-14) in positive as well as negative direction in a comparable range as for the all carbon analogue ( $+2.86\times 10^{-3}$  at 336 nm;  $-3.39\times 10^{-3}$  at 301 nm) proving, that nitrogen doping can be implemented by the presented method to fine tune the optical properties without suppressing the chiroptical effects in comparison to the parent all carbon analogue.<sup>[12f]</sup>

The electronic properties of 12, (S,S)-14 and (R,R)-14 were further studied by cyclic voltammetry (CV) in DCM (Table 1, see Supporting Information Figure S11–S13). According to the commonly used equations<sup>[27]</sup>  $IP_{\text{CV}}=-(E_{\text{onset}}^{\text{ox}}+4.8)\text{ eV}$  and  $EA_{\text{CV}}=-(E_{\text{onset}}^{\text{red}}+4.8)\text{ eV}$ , the ionization potentials ( $IP$ ) can be roughly estimated from the irreversible oxidations to be approx.  $IP_{\text{CV}}=-5.6\text{ eV}$  for all three compounds. The electron affinities (EA) were estimated to be between  $IP_{\text{CV}}=-2.6\text{ eV}$  and  $IP_{\text{CV}}=-2.9\text{ eV}$  (see Table 1) derived from irreversible reduction peaks. The observed trends are correlating to DFT-calculations on a B3LYP-6-311++G\*\* level of theory (see Supporting Information Figure S147). The corresponding electrochemical bandgaps  $E_{\text{gap,CV}}=2.8\text{--}3.0\text{ eV}$  determined by CV fit with the optical bandgaps (Table 1).

## Conclusion

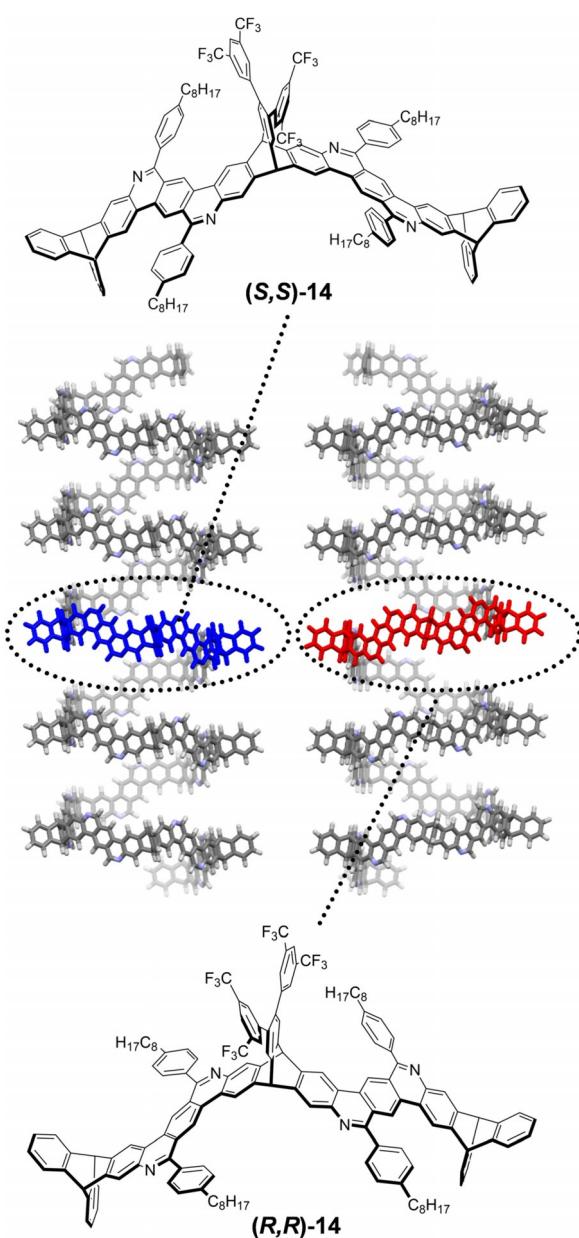
In summary, a facile and straightforward synthesis method was developed to provide triptycene-based enantiopure diamines in gram scale circumventing the use of preparative HPLC or chiral HPLC, which is still the most popular method for the synthesis of chiral triptycene building blocks till date. The enantiopure building blocks have been used in the synthesis of extended chiral ladder-type bis(diazadibenzo[a,h]anthracenes) (R,R)-14 and (S,S)-14 and their photophysical properties have been studied and compared to corresponding model compounds as well as analogue structures with pure hydrocarbon backbones. It is worth mentioning that the introduction of iso-steric nitrogens led to a small redshift in adsorption, but more important to a significant increase of photoluminescence quantum yields by a factor of four ( $\Phi=30\%$  and 32%) in comparison to the pure hydrocarbon analogues. (R,R)-14 and (S,S)-14 represent cut outs of triptycene based helical polymers as

**Table 1.** Summary of the photophysical and electrochemical characterization of 12, (S,S)-14 and (R,R)-14.

Compound	$\lambda_{\text{abs}}$ [nm] <sup>[a,b]</sup>	$E_g^{\text{opt}}$ [eV] <sup>[a,c]</sup>	$\lambda_{\text{em}}$ ( $\lambda_{\text{ex}}$ ) [nm] <sup>[a,d]</sup>	$\Delta\nu$ [cm <sup>-1</sup> ] <sup>[e]</sup>	$\Phi$ [%] <sup>[f]</sup>	$\tau$ [ns] <sup>[g]</sup>	$IP^{\text{CV}}$ [eV] <sup>[h]</sup>	$EA^{\text{CV}}$ [eV] <sup>[h]</sup>	$E_{\text{gap,CV}}$ [eV]
12	426	2.8	440 (396)	747	$25.6\pm 0.1$	$2.37\pm 0.01$	-5.63	-2.88	2.75
(S,S)-14	426	2.8	439 (327)	643	$29.9\pm 0.1$	$2.21\pm 0.01$	-5.60	-2.65	2.95
(R,R)-14	426	2.8	438 (327)	695	$32.2\pm 0.1$	$2.21\pm 0.01$	-5.56	-2.58	2.98

[a] Measured in  $\text{CHCl}_3$  at room temperature. [b] Absorption maximum at the longest wavelength. [c] Estimated from absorption onset. [d] Emission maximum. [e] Stokes shift. [f] Fluorescence quantum yield. [g] Fluorescence lifetime. [h] Measured in 0.1 M  $n\text{Bu}_4\text{NClO}_4$  in DCM at room temperature. The scan speed was 100 mVs<sup>-1</sup>, and ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) was used as internal reference.  $IP_{\text{CV}}=-(E_{\text{onset}}^{\text{ox}}+4.8\text{ eV})$ .  $EA_{\text{CV}}=-(E_{\text{onset}}^{\text{red}}+4.8\text{ eV})$ .

depicted in Figure 5 and the investigation to achieve higher oligomers and polymers of this kind by chirality-assisted synthesis is ongoing in our laboratory.



**Figure 5.** Illustration of (S,S)-14 in blue and (R,R)-14 in red as cut-outs of triptycene based helical polymers depicted as MM2 models.

## Experimental Section

**Crystallographic data:** Deposition numbers 2005892 and 2005893 ((S,S)-7 and 12) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** chiral resolution • chirality • chirality-assisted synthesis • N-heteropolycycles • triptycene

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