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# Tribenzotriquinacenes Based on Regioselective Bis-formylation: Optical Resolution and Absolute Configuration of Inherently Chiral Derivatives and Synthesis of the First Cyclophane-Type Tribenzotriquinacene Dimers

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**Abstract:** Enantiomerically pure tribenzotriquinacenes (TBTQs) bearing two monofunctionalized aromatic nuclei were synthesized for the first time and their optical properties and absolute configuration determined. A remarkably regioselective bis-formylation of the fully bridgehead methylated parent TBTQ hydrocarbon with $MeOCHCl_2/TiCl_4$ afforded a mixture of two $C_s$-symmetrical (achiral) difunctionalized derivatives together with one $C_1$-symmetrical (chiral) isomer. Reduction and subsequent column chromatography furnished the three respective benzylic TBTQ dialcohols. Optical resolution of the racemic 2,6-bis(hydroxymethyl) derivative was achieved via the diastereomeric (*R*)-1,1′-bi-2-naphthol ethers and the absolute configuration of the enantiomers was determined by CD exciton model analysis. The electronic circular dichroism (ECD) spectra and the specific rotation of the enantiomers were found to agree with the results of DFT calculations. Among the $C_s$-symmetrical isomers, the "proximal" 2,11-dialdehyde and the corresponding benzylic dialcohol were identified by 2D NMR spectroscopy and X-ray crystallographic analysis, respectively, and used as the starting point for the synthesis of several novel dithiametacyclophanes. These include the first "dimeric" tribenzotriquinacene-based cyclophanes bearing the bowls of the two TBTQ units attached to each other in a *syn* (concave–concave) or *anti* (convex–concave) configuration. The usefulness of such thiacyclophanes as fluorescent chemosensors for different metal ions is also demonstrated.

**Keywords:** configuration determination · formylation · regioselectivity · synthetic methods · tribenzotriquinacenes

## Introduction

Tribenzotriquinacene (TBTQ, **1a**) and its bridgehead-methylated analogues (**1b** and **1c**)[1–4] represent fully benzoannelated congeners of triquinacene[5] and prototypical members of the centropolyindane family of polycyclic aromatic hydrocarbons.[6,7] Recently, various applications of TBTQ derivatives have been suggested on the basis of the unique, mutually orthogonal orientation of the three indene wings in the TBTQ framework.[4,6] Combined with the large chemical versatility offered by the multiple functionalization of the peripheral positions of their three benzene nuclei, the supramolecular chemistry of TBTQ-based compounds promises to be a rich field of research. Thus, complexes with the $C_{60}$ and $C_{70}$ fullerenes[8,9] and the introduction of three mutually orthogonally oriented chromophoric groups have been reported recently.[10] In fact, both peripheral three-fold functionalization of the TBTQs, such as in the trinitro derivatives **2** and **3**,[11] and six-fold functionalization, such as in

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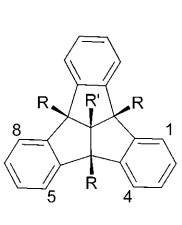
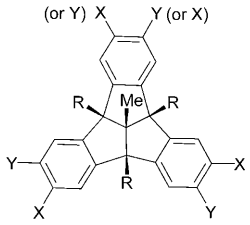
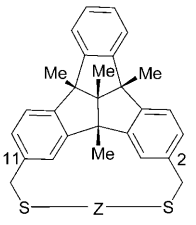
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201001620. It contains experimental procedures, characterization data for all new compounds, $^1H$ and $^{13}C$ NMR spectra, computational data of the five compounds **13**–**15**, *anti*-**11**, and *syn*-**11** obtained at the B3LYP/6–31G*//HF/6–31G* level, HPLC and the computation chemistry method of ECD spectra and OR, and fluorescence chemosensor data of **9a**, **9b**, *anti*-**11**, and *syn*-**11** coordinated to different metal ions.



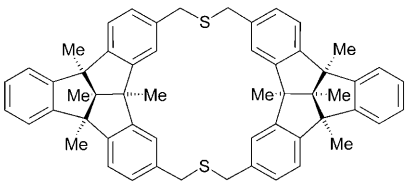

**1a** (R = R' = H)
**1b** (R = H, R' = Me)
**1c** (R = R' = Me)



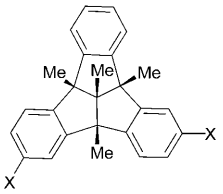

**2** ($C_3$), **3** ($C_1$) (R = H, X = $NO_2$, Y = H)
**4a**, **4b** ($C_{3v}$) (R = Me, X = Y = $NH_2$, S-Alkyl)
**5a**, **5b** ($C_{3v}$) (R = Me, X = Y = $CH_2Cl$, $CH_2SH$)



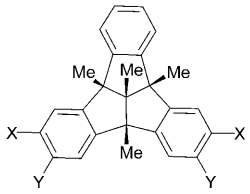

**9a**, **9b** ($C_s$) [Z = $(CH_2)_n$, *n* = 2, 3]
**10** ($C_s$) (Z = $CH_2$-*p*$C_6H_4$-$CH_2$)




*syn*-**11** ($C_s$)




**6** ($C_1$) (X = CHO)




**7** ($C_s$) (X = CHO, Y = H)
**8** ($C_s$) (X = H, Y = CHO)

**4a**[4,12] and **4b**[4,9,12] and in **5a** and **5b**,[13] besides the mere introduction of bridgehead functional groups,[4,14] have already been studied by our groups.[6,15] In particular, the readily accessible $C_{3v}$-symmetrical key intermediate **5a** allowed us to synthesize the first TBTQ-based three-fold metacyclophanes.[13] Related bowl- and basket-shaped TBTQ derivatives may be of great interest for the design of receptors of cations, anions, and also neutral molecules, similar to the growing families of the calixarenes and cyclotriveratrylenes, and other host compounds derived therefrom.[16,17]

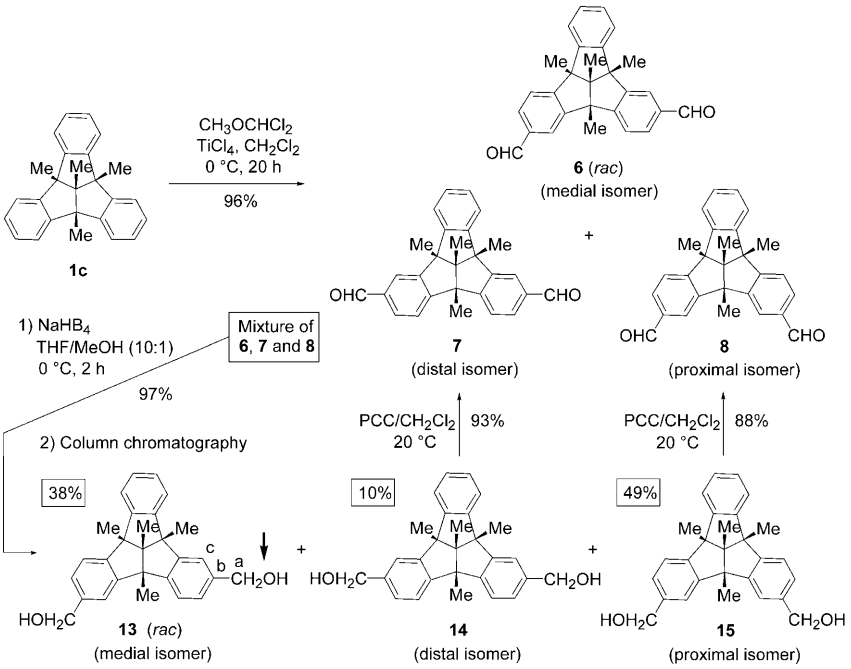
At variance from the three- and six-fold functionalization, the regioselective introduction of functional groups at a single or at only two individual benzene units of the tribenzotriquinacene skeleton has not been reported yet. It had become evident from our previous work that the three π-electron systems react largely independently, which renders partial functionalization difficult. Moreover, introduction of two functional groups suffers from the fact that mixtures of isomers can be expected. Nevertheless, two-fold monofunctionalized TBTQ derivatives would present important building blocks for the construction of novel "dimeric" derivatives bearing two TBTQ bowls in a mutually concave–concave orientation. In this vein, our research now revealed that two-fold formylation represents a viable approach, giving rise to a mixture of the three bis(formyl)tribenzotriquinacenes **6**, **7**, and **8**. As will be demonstrated in the present report, this finding has allowed us to develop two novel extensions of the TBTQ chemistry: 1) The first separation and characterization of the enantiomers of inherently chiral tribenzotriquinacenes, by starting from dialdehyde **6**, and 2) the synthesis of several $C_s$-symmetrical difunctionalized tribenzotriquinacenes, derived from dialdehyde **8**. This latter approach includes the synthesis of several thiacyclophane derivatives, such as compounds **9** and **10**, and the first macrocyclic thiacyclophanes containing two TBTQ units ("tribenzotriquinacenophanes"), for example, the concave–concave *syn*-isomer **11**.

Finally, the X-ray structural analysis of some of these cyclophanes and the correlation between their structures and properties as fluorescent chemosensors for potential application in metal-cation recognition will be addressed. In this way, the extension of tribenzotriquinacene chemistry may contribute new facets to some of the diverse subfields of supramolecular chemistry.[18–20]

## Results and Discussion

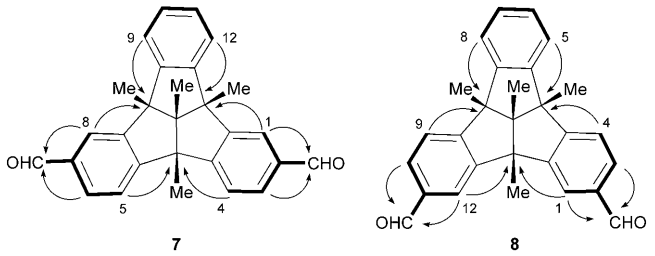
**Introduction of two peripheral functional groups**: The two-fold formylation of the tribenzotriquinacene framework was studied by using the fully bridgehead-methylated derivative **1c** as the starting material.[4] Best results were achieved by treating this hydrocarbon with a mixture of dichloromethyl methyl ether and titanium tetrachloride in dichloromethane.[21] When the molar ratio of $[CH_3OCHCl_2]/[TiCl_4]/[\mathbf{1c}] = 4.2:4.2:1$ was used, a mixture of the three diformyl derivatives **6**–**8** was obtained in 96% yield after flash chromatography (Scheme 1). Singly and triply substituted congeners were not formed in significant amounts, as shown by EI mass spectrometry of the crude product. Whereas, quite surprisingly, only one single spot was observed upon TLC analysis of the mixture, the $^{13}C$ NMR spectrum indicated the presence of a mixture of isomers because at least 23 different resonances appeared in the aromatic region. Assuming, in line with our previous observations on electrophilic substitution of the centropolyindanes,[6,10,11] a random ("statistical") attack of the electrophiles at the six outer positions of the three benzene rings of **1c**, the $C_1$-symmetrical (and thus chiral) isomer **6** and the two $C_s$-symmetrical (achiral) isomers **7** and **8** should be formed in a ratio of 2:1:1. However, when the mixture of the diformyl derivatives was reduced to the corresponding two-fold benzylic alcohols **13**–**15** by the use of sodium borohydride in THF/MeOH (10:1, v/v), TLC analysis showed three well-separated spots. Column chromatography through silica gel furnished the distal 2,7-isomer **14** as the first-eluting component in 10% yield, followed by the medial 2,6-isomer **13** in 38% yield. Again surprisingly, the most polar, proximal 2,11-diol **15** was isolated as the dominant product in 49% yield. The $^{13}C$ NMR spectra of the racemic diol **13** reflected its molecular $C_1$-symmetry (14 of 18 possible arene




Scheme 1. Synthesis of the dialcohols **13**–**15** via the mixture of dialdehydes **6**–**8** and subsequent access to the pure $C_s$-symmetrical dialdehydes **7** and **8**.

resonances), whereas those of the achiral isomers **14** and **15** confirmed their $C_s$ symmetry (nine arene resonances in either case). Separate reoxidation of the diols **14** and **15** with pyridinium chlorochromate (PCC) in $CH_2Cl_2$ regenerated the corresponding dialdehydes **7** and **8** in 93 and 88% yield, respectively, which allowed us to identify these $C_s$-symmetrical isomers by means of 2D NMR spectroscopy ($^1$H,$^1$H COSY and HMBC, see Scheme 2) and thus indirectly assign the constitutions of the distal and proximal diol isomers **14** and **15** as well. The racemic isomer **13** was found to be much more soluble in acetone than the $C_s$-symmetrical isomers **14** and **15**. In fact, single-crystal structural analysis of the latter isomer enabled the confirmation the $^{13}$C NMR spectra-based structural assignment of the four $C_s$-symmetrical compounds **7**, **8**, **14**, and **15** (see below).




Scheme 2. $^1$H,$^1$H-COSY (——) and key HMBC correlations (arrows) detected for dialdehydes **7** and **8**, enabling the distinction of these two $C_s$-symmetrical isomers.

The $^1$H NMR and the $^1$H,$^1$H COSY spectra clearly reflected the three independent arene spin systems of the two $C_s$-symmetrical dialdehydes **7** and **8**. In particular, the different splitting patterns of the six *ortho*-H atoms (4-H/5-H, 1-H/8-H, and 9-H/12-H) allowed us to distinguish the two isomers. HMBC long-range correlations of the three quaternary outer-bridgehead C atoms with the H atoms of the aromatic nuclei were also useful (Scheme 2). The $^1$H NMR spectrum of the distal isomer **7** is characterized by a narrow low-field doublet for the *ortho*-protons 1-H and 8-H ($\delta = 7.90$ ppm, $^4J = 1.2$ Hz) exhibiting a strong cross-peak with the resonances of C-12b and C-8b at $\delta = 63.1$ ppm (2C intensity), respectively, whereas the *ortho*-protons 4-H and 5-H resonate at a relatively high field as a large doublet ($\delta = 7.53$ ppm, $^3J = 8.0$ Hz), which shows a strong cross-peak with the quaternary C-4b at $\delta = 62.7$ ppm (1C only). Likewise, the $^1$H NMR spectrum of the proximal isomer **8** exhibits a narrow low-field doublet for the *ortho*-protons 1-H and 12-H and a large high-field doublet for the *ortho*-protons 4-H and 9-H. The respective correlation with the single bridgehead carbon atom C-12b and with the two bridgehead carbon atoms C-4b and C-8b further corroborates the assignment (see the Supporting Information).

The structural identity of the dialcohol **15** was unambiguously established by its X-ray crystal structure (Figure 1).[22] Single crystals suitable for X-ray diffraction analysis were grown by slow evaporation of the solvent from solutions of **15** in [D$_6$]acetone at 0°C. In this way, the presence of the two hydroxymethyl groups in a proximal orientation at C-2 and C-11 of the TBTQ framework were established as were, indirectly, the structures of the corresponding dialdehyde **8** and of the respective isomers **14** and **7**. The crystal structural analysis of diol **15** also revealed that, in the solid state, the orientation of the two hydroxymethyl groups relative to the TBTQ skeleton is opposite with a torsional angle of 62°. Notably, the three aromatic rings retain their planarity and even the three indane units do not exhibit any significant distortion.[22] One [D$_6$]acetone molecule was found to be coordinated at the rim of the concave side of dialcohol **15** due to the intermolecular hydrogen bonding between a hydroxy group and the oxygen atom of the [D$_6$]acetone molecule as well as due to multiple interactions through C–H···π stacking. Selected hydrogen bonds are depicted in Figure 1b.

In contrast to the $C_s$-symmetrical structures of the dialdehydes **7** and **8** and the corresponding dialcohols **14** and **15**, their respective $C_1$-symmetrical isomers **6** and **13** are inherently chiral. To define the descriptor for the enantiomers of

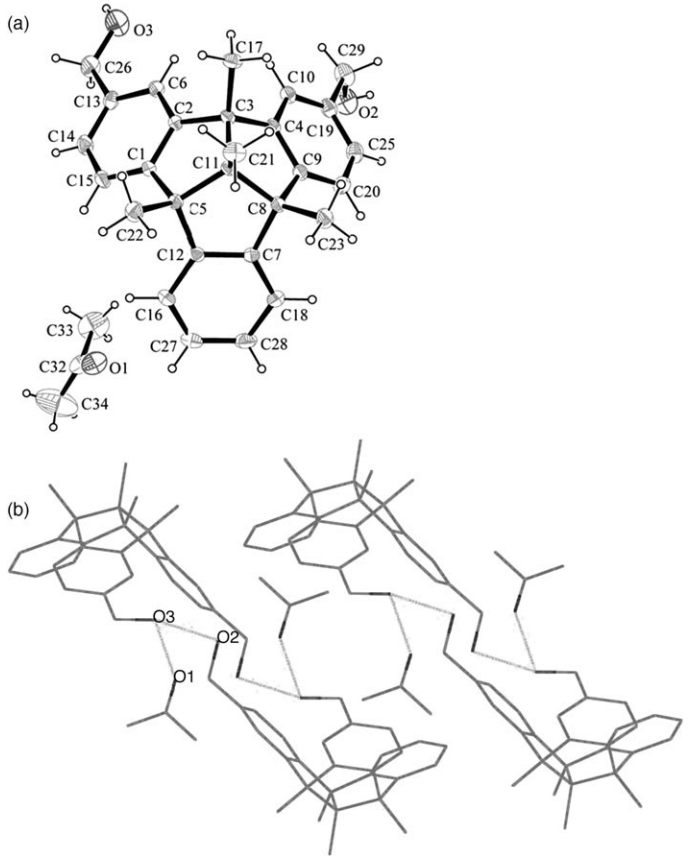
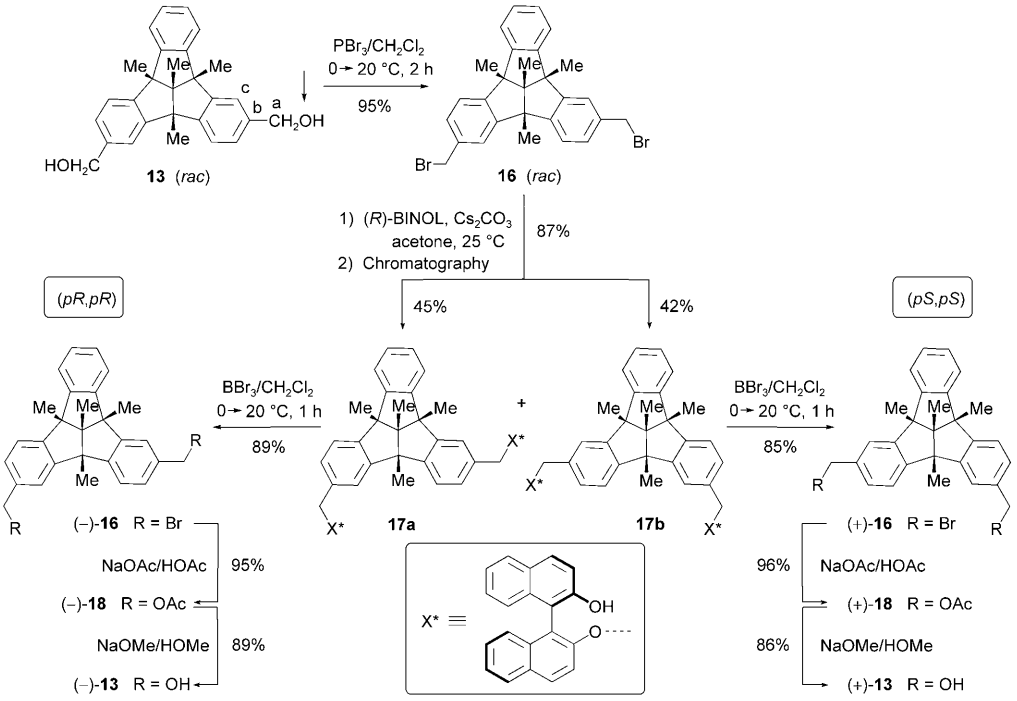



Figure 1. X-ray crystal structure of dialcohol **15** (recrystallized from [$D_6$]acetone). a) Top view and b) selected hydrogen bonds: O(2)–H(2)···O(3), $d=2.903$ Å, $\theta=161°$; O(3)–H(3) ···O(1), $d=2.750$ Å, $\theta=167°$.

**6** and of **13**, one of the oxygen atoms closest to a given plane of chirality (marked with an arrow in Scheme 1 for the case of **13**) was used as a pilot atom. The plane of chirality was considered to be the aromatic ring,[23] and as the adjacent three atoms marked a, b, and c describe a clockwise array in the chiral plane, the absolute configuration of this chiral plane is *pR*. On the basis of this result, the configurations of the dialcohols (−)-**13** and (+)-**13** (Scheme 3) were assigned to be *pR*,*pR* and *pS*,*pS*, respectively. An analogous assignment has been made for the enantiomeric dialdehydes (−)-**6** and (+)-**6**.

As mentioned above, the ratio of the three TBTQ dialdehydes was found to be [**6**]/[**7**]/[**8**]≈4:1:5 and thus far different from the ratio expected for random electrophilic attack in the second step (2:1:1). This finding is in stark contrast to our previous observations for three-fold nitration[6a,10,11] and three-fold acetylation[24] of the TBTQ periphery giving racemates of the $C_3$- and $C_1$-symmetrical derivatives of the type **2** and **3** in the "statistical" ratios of 1:3. As expected, an estimation of the relative thermochemical stabilities of the isomers, carried out by means of the DFT approach (B3LYP/6-31G*//HF/6-31G*) level, revealed that all three structures have very close heats of formation (within $\Delta E \leq 0.2$ kcal mol$^{-1}$, see the Supporting Information). As a consequence, the second step of the substitution has to be the subject of kinetic control. In fact, we found that the total yield of diformylation of **1c** was higher when the reaction was run at 0 °C compared with the yield obtained at room temperature. Therefore, we assume that the second formylation step takes place in a complex aggregate, in which the reagent for the second formylation is coordinated to the pri-




Scheme 3. Optical resolution of the TBTQ diols (−)-**13** and (+)-**13** via the diastereomeric (*R*)-BINOL diethers **17a** and **17b**.

marily formed functional group. In such a complex, a geometrically favorable, intracomplex transfer of the electrophile to one of the proximal positions (e.g., by an aggregate pending at C-2 and acting exclusively on the proximal position C-11, cf. Scheme 2) competes successfully with an intermolecular attack of a second electrophile. From the inspection of models it may be suggested that an aggregation of the type [Ar−CHCl($OCH_3$)···$TiCl_x$···O($CH_3$)($CHCl_2$)], under catalytic action of another $TiCl_4$-derived Lewis acid, may form a suitable template for preferred proximal bis-formylation, eventually generating dialdehyde **8** and thus discriminating the formation of the medial and distal isomers **6** and **7**, as observed. It can even be further speculated that the lower but still relatively large amount of the medial isomer **7** (38%) may reflect the geometrically less favorable but statistically twice-favored intracomplex attack at both C-7 and C-11, whereas intracomplex attack at the single, distal position C-10 is largely suppressed.

**Optical resolution of the 2,6-TBTQ-dialcohol 13**: After thoroughly examining the possibilities to separate the enantiomers by the use of chiral auxiliaries,[25] we decided to convert the racemic diol **13** into the corresponding diastereomeric bis[(*R*)-1,1′-bi-2-naphthol] (BINOL) diethers **17** (Scheme 3). In the first step, *rac*-**13** was refunctionalized to the related bis(bromomethyl) derivative *rac*-**16** by treatment with phosphorous tribromide in dichloromethane in 95% yield. Subsequently, the racemate of **16** was reacted with (*R*)-BINOL (4.0 equiv) in acetone at room temperature in the presence of cesium carbonate (4.2 equiv), affording the expected pair of diastereomers **17a** and **17b**. Separation of the mixture by column chromatography on silica gel gave the pure diastereomers in >99% *de* (*de* = diastereomeric excess) each (by HPLC analysis) and in excellent yields (45 and 42%, respectively). It is obvious that the spatial interaction of the two bulky (*R*)-BINOL groupings pending at the chiral and rigid TBTQ core gives rise to efficient differentiation of the two diastereomers.

Despite many attempts to grow crystals of the diastereomeric diethers **17a** or **17b**, none of them was found to be suitable for X-ray crystal structure determination. Therefore, the separated diastereomers **17a** and **17b** were converted into the optically pure dibromides (−)-**16** and (+)-**16** by treatment with boron tribromide in dichloromethane (89 and 85%, respectively). The specific optical rotation for (−)-**16** and (+)-**16** was found to be $[\alpha]_D^{20} = -40.0$ and +40.0 and their CD spectra (Figure 2) displayed a perfect mirror-image relationship, confirming their enantiomeric nature and purity. An attempt to assign the absolute configuration of (−)-**16** and (+)-**16** by the use of the CD exciton chirality method[26] was undertaken since these compounds possess three easily distinguishable aromatic chromophores allowing a rational application of the method. The $^1B_{1u}$ electronic transition moments of the two trisubstituted benzene rings are polarized along the 1–4 axes of the two α-bromo-*para*-xylene units as shown in Figure 3. The CD spectra of (−)-**16** exhibited positive chirality resulting from the exciton coupling of a nondegenerate system comprising the two chromophores at 230 ($\Delta\varepsilon = -17.1$, $\pi \rightarrow \pi^*$ transition) and 251 nm ($\Delta\varepsilon = +6.8$, $\pi \rightarrow \pi^*$ transition), and the positive chirality of (−)-**16** revealed that the transition dipole transition dipole moments of the two chromophores were oriented in a clockwise manner. The absolute configuration of the dibromide (−)-**16** was thus assigned as *pR*,*pR*. Accordingly, the absolute stereochemistry of (+)-**16** was determined to be *pS*,*pS*, as depicted. Independently, calculation of electronic circular dichroism (ECD) by the use of time-dependent DFT (TD-DFT) and optical rotation at the B3LYP/6-31G* level, a method that has greatly improved the determination of absolute configuration in recent years,[27] was used to confirm the above conclusions. For both enantiomers of **16**, the ECD spectra exhibit an intense band at 230 nm and two weaker

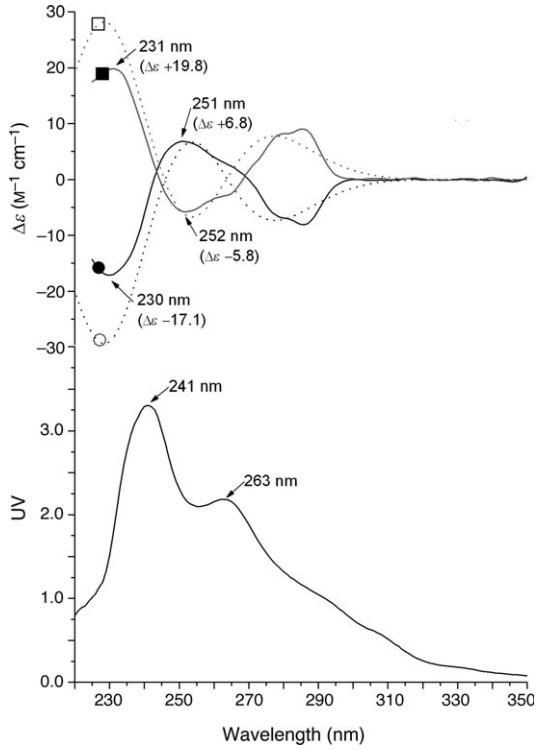



Figure 2. ECD spectra of the dibromides (−)-**16** (exptl: ●; calcd: ○) and (+)-**16** (exptl: ■; calcd: □) (top) and UV spectrum of (−)-**16** (bottom).

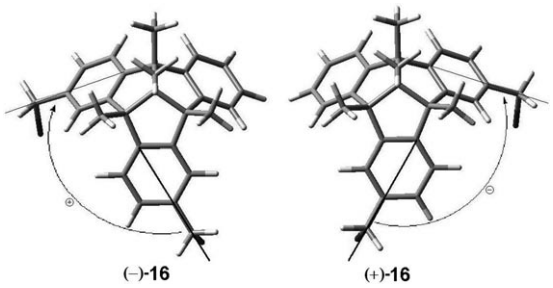



Figure 3. Optimized geometry of the dibromides (−)-**16** and (+)-**16** at the B3LYP/6-31G* level of theory and predicted sign of the first Cotton effect (—— indicate the electric transition dipoles of the chromophores).

bands at higher wavelengths, which qualitatively agree with the theoretical ECD for (−)-**16** and (+)-**16**. The $[\alpha]_D^{20}$ values calculated for the enantiomers were also found to closely match the experimental ones (calcd: −40.8 and +42.3, respectively, see the Supporting Information).

Treatment of each of the dibromides (−)-**16** and (+)-**16** with sodium acetate in glacial acetic acid furnished the corresponding diesters (−)-**18** and (+)-**18** in 95 and 96% yield, respectively (Scheme 2). Subsequent saponification of the latter compounds by using sodium methoxide[13] gave the bis(hydroxymethyl)tribenzotri-quinacenes (−)-**13** and (+)-**13** in 89 and 86% yield, respectively. The specific optical rotation was found to be $[\alpha]_D^{20} = -31.0$ for (−)-**13** and $[\alpha]_D^{20} = +31.0$ for (+)-**13**, and the mirrorlike CD spectra of these enantiomers (Figure 4) again confirmed the optical purity of

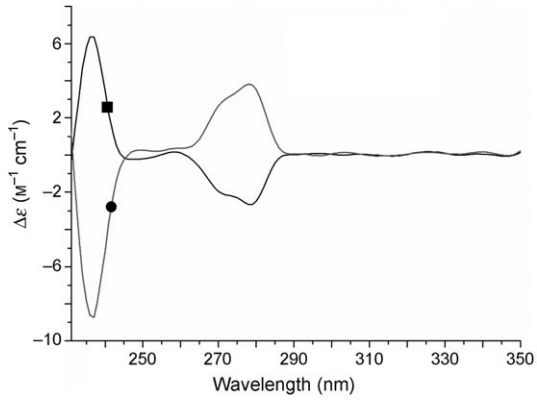
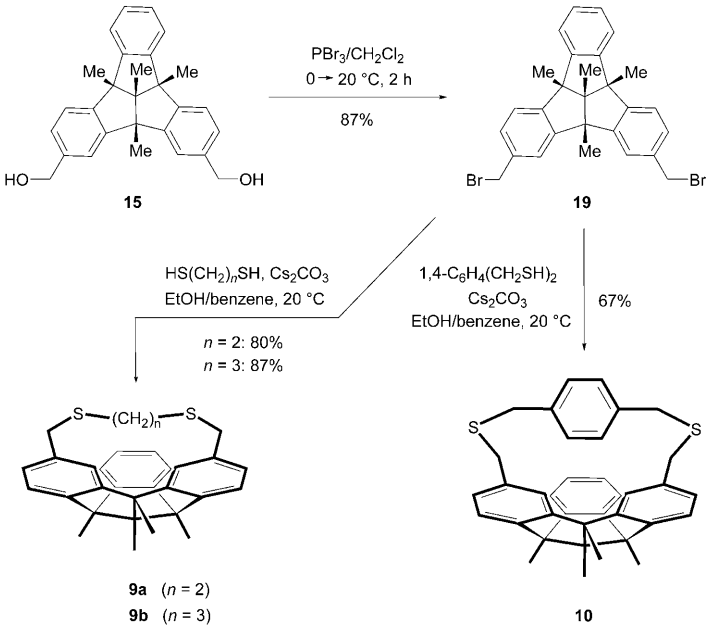



Figure 4. ECD spectra of the TBTQ-dialcohols (−)-**13** (■) and (+)-**13** (●) in $CH_2Cl_2$ recorded at 25°C.

these compounds. The absolute configuration assignment of (−)-**13** and (+)-**13** paralleled to that of (−)-**16** and (+)-**16** since the diols were derived from these latter compounds.

**Synthesis of the TBTQ-based dithiametacyclophanes 9 and 10 and the bis(dithiametacyclophanes) 11 and 12**: Cyclophanes are known for their structural diversification and constitute a still-growing class of organic compounds.[28] Notably, the synthesis of apparently simple cyclophanes can be a challenging goal. Except for some recent examples involving the hexafunctionalized tribenzotriquinacenes **5a** and **5b**,[13] the unique and highly versatile tribenzotriquinacene motif has not yet been used for the construction of novel cyclophanes, although the convex–concave shape of the TBTQ framework promises to be a unique building block for this purpose. Since, in the present work, the proximal diol **15** was found to be accessible in comparatively high yield from the parent hydrocarbon **1c**, and since bridging between the two functionalities at C-3 and C-6 geometrically would parallel the above-mentioned three-fold bridging in the tris-thiametacyclophanes derived from **5a**,[13] the synthesis of a series of metacyclophanes derived from the $C_s$-symmetrical diol **15** was studied in detail.

In analogy to the conversion of dialcohol **13** discussed above, dibromide **19** can be easily obtained by refunctionalization of diol **15** with phosphorous tribromide in dichloromethane in high yield (87%, Scheme 4). Subsequent treat-

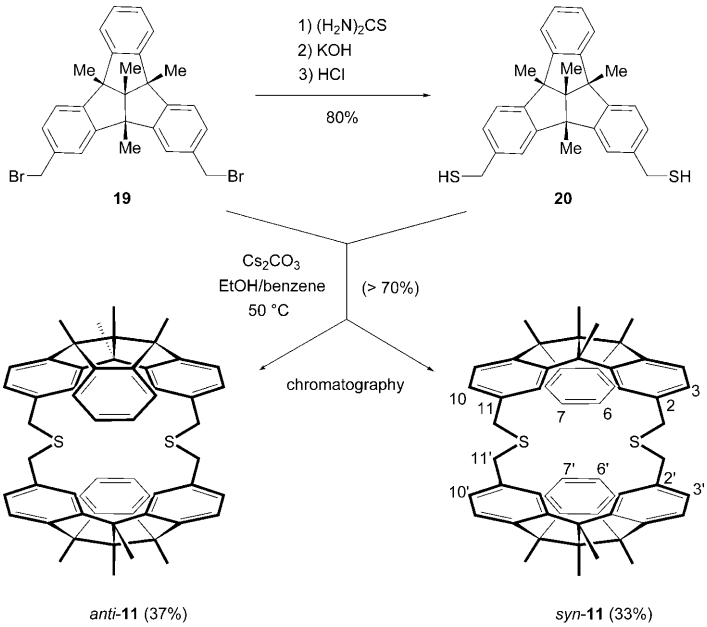



Scheme 4. Synthesis of $C_s$-symmetrical dithiametacyclophanes **9a**, **9b**, and **10**.

ment of **19** with 1,2-ethanedithiol, 1,3-propanedithiol, or α,α′-dimercapto-*para*-xylene in ethanol/benzene (1:1, v/v) solution in the presence of cesium carbonate furnished the corresponding cyclophanes **9a**, **9b**, and **10** in relatively good yields (80, 87, and 67%, respectively) after chromatography. $^1H$ and $^{13}C$ NMR spectra of these compounds confirmed the $C_s$-symmetrical incorporation of 1,2-ethano-, 1,3-propano-, and 1,4-benzenedimethano units, respectively, in each case. Similar to the $C_{3v}$-symmetrical tris(dithiametacyclophanes) derived from **5a** and **5b**,[13] the benzylic methylene protons adjacent to the TBTQ core of the new cyclophanes **9a**, **9b**, and **10** generated the expected pronounced AB spin systems in each case ($^2J = 14.7$ Hz for both **9a** and **9b** and $^2J = 14.1$ Hz for **10**). We assume that the cone conformation formed by the aromatic cavity of the TBTQ skeleton contributes to the distinct chemical shifts of the methylene protons in these thiacyclophanes.[29]

Conversion of the dibromide **19** to the corresponding dithiol **20** was achieved by treatment with thiourea and subsequent decomposition of the intermediary isothiuronium salts (Scheme 5).[13] The bis(mercaptomethyl)tribenzotriquinacene **20** was obtained in 80% yield as a stable compound when stored under argon. Addition of a highly diluted solution containing both **19** and **20** in an 1:1 molar ratio in benzene to a solution of cesium carbonate in ethanol gave rise to the formation of two isomeric cyclophanes, namely, *anti*-**11** and *syn*-**11**, which were obtained in pure form and in relatively good yields (37 and 33%, respectively) by chroma-




Scheme 5. Synthesis of the *syn*- and *anti*-bis(triquinaceno)dithiametacyclophanes **11**. The arbitrary positional numbering in *syn*-**11** is given for clarity (see text).

tography through silica gel. There was no evidence for the formation of higher cyclocondensation products. The $^{1}$H and $^{13}$CNMR spectra of the two conformers were rather similar, but the splitting patterns of the benzylic methylene protons of the two bridges were found to be different. The $^{1}$H spectrum of cyclophane *anti*-**11** reflects an AB spin system centered at $\delta = 3.6$ ppm with $^{2}J = 12.8$ Hz, whereas the spectrum of the *syn*-**11** isomer exhibits an apparent singlet resonance at $\delta = 3.32$ ppm. Although different chemical shifts were observed for the methyl groups and the arene protons, an unambiguous assignment of the stereoisomers by NMR spectroscopy was not possible. Fortunately, the X-ray analysis of *syn*-**11** (see below) revealed the concave–concave orientation of the two TBTQ units which, at the same time, allowed us to assign the convex–concave assembly of the TBTQ units in *anti*-**11**. Theoretical calculations at the B3LYP/6-31G*//HF/6-31G* level of theory suggested that *anti*-**11** is more stable than *syn*-**11** by $\Delta E = -5.0$ kcal mol$^{-1}$ (see the Supporting Information).

**Crystal structures of the cyclophanes 9a, 9b, and *syn*-11**: The solid-state structures of the two alkylene-bridged tribenzotriquinacenes **9a** and **9b** and the bis(tribenzotriquinaceno)dithiacyclophane *syn*-**11** were characterized by single-crystal X-ray crystallography. In each case, suitable colorless crystals were obtained by slow evaporation of the solvent from the solutions of these compounds in dichloromethane at 25 °C. The presence of a 13- or 14-membered ring in the TBTQ-dithiametacyclophanes **9a** and **9b**, respectively, and of a 20-membered ring in the bis-TBTQ-dithiametacyclophane *syn*-**11** was clearly confirmed (Figures 5 and 6). A $C_s$-symmetrical conformation was found in the case of solid-state **9a**, whereas a nonsymmetrical ($C_1$) conformation was observed for solid-state **9b**. In contrast to the parent hydrocarbons **1**, in which the three indane wings are almost perfectly oriented at right angles, the crystal structure analyses of **9a** and **9b** revealed that the two indane wings that are connected by the α,ω-dithiaalkylene bridging units are significantly bent towards each other, giving rise to a dihedral angle of 85.6° in the case of **9a** and even 74.3° in the case of **9b**, probably enforced by the draught of the bridge. The crystal structure of **9a** consists of arrays of pairs of oppositely oriented molecules. Each dimer looks like regular barrels arranged along the crystallographic *b* axis (Figure 5c), in each of which the convex side of one molecule is tilted into the concave side of the other one with an obvious C–H···π interaction. The crystal structure of **9b** was found to be quite different. It revealed considerable intermolecular cavities (Figure 5f), which suggests a potential application of this cyclophane for cation recognition and host-guest chemistry.[30]

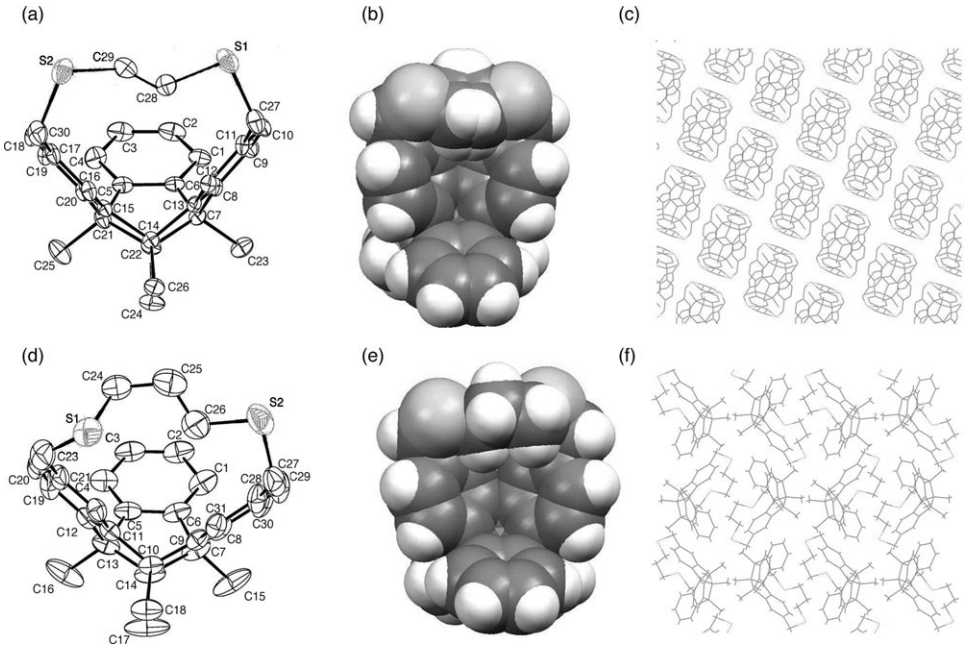



Figure 5. a–c) X-ray crystal and molecular structure of **9a**: a) 30% thermal ellipsoids, b) top view onto a space-filling model, and c) side view onto the molecular packing along the *b* axis. d–f) X-ray crystal and molecular structure of **9b**: d) 30% thermal ellipsoids, e) top view onto a space-filling model, and f) side view onto the molecular packing along the *a* axis.

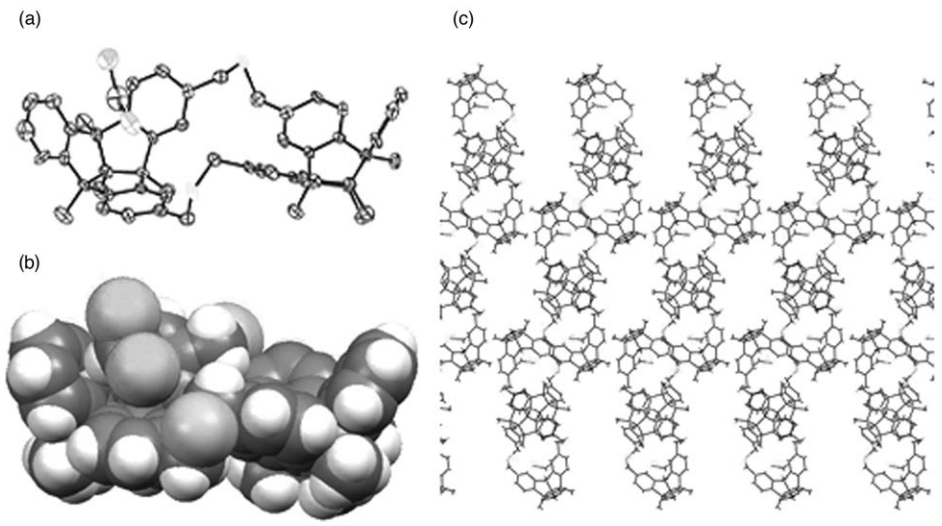



Figure 6. a) X-ray molecular structure of *syn*-**11** (30% thermal ellipsoids), incorporating one molecule of $CH_2Cl_2$ per cyclophane unit, b) space-filling representation, and c) side view onto the molecular packing along the *b* axis.

The bis-TBTQ-dithiametacyclophane *syn*-**11** adopts a $C_1$-symmetrical molecular structure in the solid state (Figure 6a). One solvent molecule (dichloromethane) was found to be incorporated in the more extended cavity formed at the concave side of the TBTQ framework (Figure 6b). Closer inspection of the molecular structure of *syn*-**11** revealed that the mutual attachment of the two TBTQ units does not induce a marked distortion of their intrinsically $C_{3v}$-symmetrical frameworks. The two planes comprising the molecular rims (i.e., the two sets of peripheral atoms C-2, C-3···C-11 and C-2′, C-3′···C-11′ cf. Scheme 5) of the two parent TBTQ units were found to be oriented at a dihedral angle 51.2°. Obviously, the molecular structure of *syn*-**11** is allowed to stretch out its Ar–$CH_2$–S–$CH_2$–Ar units such that they can adopt unstrained conformations and give rise to a shell-like overall molecular shape. This flexibility may be considered in line with the above-mentioned finding that the protons of the four methylene groups give rise to a singlet resonance in the $^1$H NMR spectrum of *syn*-**11** at room temperature. In contrast to the AB partial spectra observed for **9a**, **9b**, and even *anti*-**11**, the crystal structure of *syn*-**11** revealed two types of channels of different sizes along the *b* axis, which may result from a C–H···π interaction. Aromatic π–π stacking arrangements were not found in the crystal structure of the bis-TBTQ-(dithiametacyclophane) *syn*-**11**.

**Complexation with metal ions**: So far, many kinds of sulfur-containing macrocycles have been reported for complexation with metal ions and for their application as fluorescent chemisensors and for metal-ion separation.[31] We have assumed that the novel TBTQ-based dithiametacyclophanes **9**–**11** may be useful for cation recognition and host–guest chemistry; therefore, the first steps into this field of research work have been undertaken. In fact, compounds **9a**, **9b**, *anti*-**11**, and *syn*-**11** were found to respond to the presence of various metal cations by fluorescence, and some selected results for the case of dithiametacyclophane **9b** are illustrated in Figure 7 (see the Supporting Information for more details). As shown in Figure 7a, negligible suppression of the fluorescence (<5%) was observed for an acetone solution containing **9b** and an excess of $Mg^{2+}$ or $Ca^{2+}$ ions (10 equiv) in the presence of $Na^+$, $Cs^+$, $Hg^{2+}$, $Co^{2+}$, $Cd^{2+}$, $Zn^{2+}$, and $Ni^{2+}$, whereas $K^+$ and $Ag^+$ ions (all added as the chlorides in water) were found to attenuate the fluorescence by 22 and 31%, respectively. The effect of $Cu^{2+}$ ions is especially worth noting: Whereas these ions do not affect the fluorescence of **9b** in the absence of $Mg^{2+}$ or $Ca^{2+}$ ions, the emission was almost completely quenched (by 97% at $\lambda = 400$ nm) when an excess of both $Cu^{2+}$ and $Mg^{2+}$ (or $Ca^{2+}$) ions was used. Fluorescence titration of **9b** with $Cu^{2+}$ ions in acetone/water in the presence of an excess (10 equiv) of $Mg^{2+}$ or $Ca^{2+}$ ions resulted in a gradual decrease in the range up to 1.0 equiv of $Cu^{2+}$ addition (Figure 7b and c). The results suggest that $Mg^{2+}$, $Ca^{2+}$, and $Cu^{2+}$ ions coordinate to TBTQ-dithiametacyclophane **9b** in solution by formation of 1:1 complexes [**9b**···$M^{2+}$] and that metal–metal interactions in the case of $Cu^{2+}$ ions gives rise to a strong suppression of the fluorescence. This finding could be interesting in application as an organic molecular probe (OMP).

## Conclusion

Difunctionalized tribenzotriquinacenes bearing a functional group at two of their three aromatic rings have become synthetically accessible for the first time. Based on an efficient two-fold formylation of the parent TBTQ hydrocarbon **1c**, a convenient synthesis of bis(hydroxymethyl)-substituted tribenzotriquinacenes was achieved. One isomer among these, the medial 2,6-di(hydroxymethyl) derivative **13**, represents the first inherently chiral tribenzotriquinacene which has been successfully subjected to optical resolution by means of the diastereomeric (*R*)-BINOL diethers **17a** and **17b**. In this way, the absolute configurations of four difunctionalized tribenzotriquinacenes, namely, the diols (+)-**13** and (−)-**13** and the dibromides (+)-**16** and (−)-**16**, all obtained in enantiopure form, were determined by OR and ECD calculation. All experimental data, including the ECD spectra and optical rotation, were found to be consistent with those calculated by use of the CD exciton model analysis and the ECD and OR theory computation. Based on the proximal 2,11-

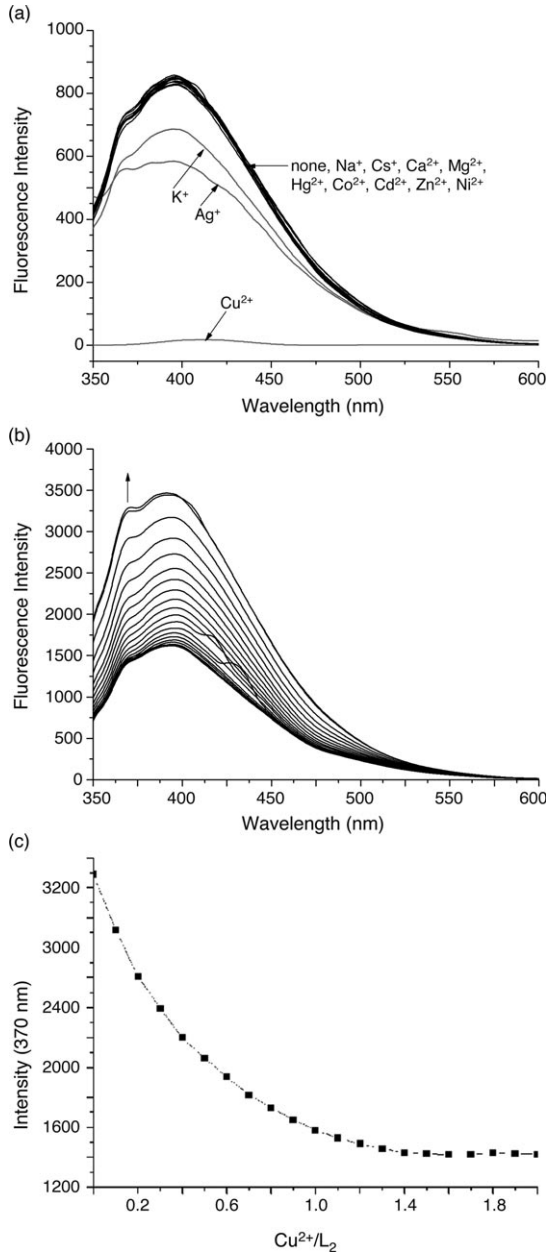



Figure 7. a) Fluorescence spectra solution of solutions of **9b** and of $Mg^{2+}$ or $Ca^{2+}$ ions (in excess) in acetone after addition of metal salts dissolved in water (10 equiv, 5.0 μL). b) Fluorescence titration of **9b** with $Cu^{2+}$ ions in acetone in the presence of $Mg^{2+}$ and $Ca^{2+}$ ions (10 equiv). c) Job plot of fluorescence intensity (370 nm) against $Cu^{2+}$/**9b** suggesting a 1:1 complexation.

di(hydroxymethyl)tribenzotriquinacene **15**, five TBTQ-based dithiametacyclophanes were synthesized, three of which bear a single bridge across the concave surface formed by the indane wings. The other two cyclophanes, namely, the stereoisomers *anti*-**11** and *syn*-**11**, represent the first examples of TBTQ-based cyclophanes containing two tribenzotriquinacene units. The stereochemical assignment has been based on the X-ray crystal structure analysis of the *syn* stereoisomer. Finally, cyclophane **9b**, in particular, bearing the $-(CH_2)_3-$ group within its bridging unit, was used to demonstrate the potential of TBTQ-based cyclophanes for cation recognition. Fluorescence spectrosopy indicated the propensity of **9b** to coordinate metal cations. In summary, it has been shown that inherently chiral and achiral tribenzotriquinacenes, such as the difunctionalized derivatives presented here, may be considered highly versatile building blocks for the construction of novel bowl- and basket-shaped organic networks and for the design of chiral receptors and advanced chiral materials.

## Experimental Section

**General**: All reactions that required anhydrous conditions were carried by standard procedures under an argon atmosphere. Commercially available reagents were used as purchased without further purification. The solvents were dried by distillation over the appropriate drying agents. The petroleum ether (PE) used had a b.p. range of 60–90 °C. Reactions were monitored by TLC on silica gel (GF 254) plates. Column chromatography was generally performed through silica gel (200–300 mesh). IR spectra were obtained with KBr discs on a Bomem MB-100 FTIR spectrometer and are given wavenumbers ($cm^{-1}$). Melting points were determined by use of a Reichert Microscope apparatus and are uncorrected. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker AM 400 MHz or a Mercury Plus-300 spectrometer, as were the DEPT 135 experiments. Chemical shifts ($\delta$) are reported in ppm relative to tetramethylsilane (TMS). Residual solvent signals in the $^1H$ and $^{13}C$ NMR spectra were used as an internal reference ($CDCl_3$: $\delta_H=7.26$, $\delta_C=77.0$ ppm; $[D_6]$acetone: $\delta_H=2.04$, $\delta_C=29.8$ ppm). Coupling constants ($J$) are given in Hz. Accurate mass measurements were obtained on a Bruker Daltonics APEX II 47e FTICR mass spectrometer or on a Fisons VG Autospec double-focusing sector-field instrument. Single-crystal X-ray diffraction measurements were made on a Bruker X8 APEX diffractometer working with graphite monochromated $Mo_{K\alpha}$ radiation. The *de* values were obtained by using a Waters 600 HPLC instrument. CD spectra were recorded with a DSM 1000 spectrometer (Olis). Fluorescent chemisensors were determined on a Perkin–Elmer LS55 and the metal salts used in the complexation experiment are all commercial metal-ion chlorides (Merck, p.a.).

**Bis-formylation of tetramethyltribenzotriquinacene 1c**: $TiCl_4$ (0.28 mL, 2.52 mmol) and $CH_3OCHCl_2$ (0.23 mL, 2.52 mmol) were added dropwise to a stirred solution of **1c** (200 mg, 0.60 mmol) in anhydrous $CH_2Cl_2$ (4 mL) at 0 °C under argon. The mixture was stirred for another 1 h at 0 °C and then for a period of 20 h at room temperature. The mixture was then quenched with ice/water (10 mL). After vigorous stirring for 1 h, the mixture was extracted with dichloromethane (3×15 mL) and the combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. Flash chromatography of the residue over silica gel (PE/EtOAc, 10:1) afforded a mixture of the dialdehydes **6–8** as a pale-yellow solid (225 mg, 96%). M.p. range 128–132 °C; $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta=9.94$–$9.92$ (m, 2H; CHO), 7.92 (d, $J_{H,H}=8.1$ Hz, 2H; Ar-H), 7.72–7.67 (m, 2H; Ar-H), 7.59–7.52 (m, 2H; Ar-H), 7.40–7.37 (m, 2H; Ar-H), 7.24–7.19 (m, 2H; Ar-H), 1.70 (s, 3H; $CH_3$), 1.68 (s, 6H; 2×$CH_3$), 1.37 ppm (s, 3H; $CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta=191.7$ (q, CHO), 156.1 (q), 155.8 (q), 155.1 (q), 150.0 (q), 149.2 (q), 149.0 (q), 148.0 (q), 147.6 (q), 147.4 (q), 136.6 (q), 136.5 (q), 130.7 (t), 130.6 (t), 130.0 (t), 128.3 (t), 128.2 (t), 128.1 (t), 124.3 (t), 123.8 (t), 123.7 (t), 123.6 (t), 123.0 (t), 122.9 (t), 70.22 (q), 70.18 (q), 63.0 (q), 62.6 (q), 62.5 (q), 62.1 (q), 25.8 (p), 25.5 (p), 15.9 ppm (p); IR (KBr): $\tilde{\nu}=2966$, 1692, 1602, 1161, 755, 574 $cm^{-1}$; EI-MS (70 eV): $m/z$ (%): 392 (26) $[M^+]$, 377 (100) $[M-CH_3]^+$; accurate mass (ESI-MS): $m/z$: calcd for $C_{28}H_{28}NO_2$: 410.2113 $[M+NH_4]^+$; found: 410.2119.

**Synthesis of the bis(hydroxymethyl)-substituted tribenzotriquinacenes 13–15**: $NaBH_4$ (33 mg, 0.87 mmol) was added in one portion to a stirred solution of the mixture containing the aldehydes **6–8** (112 mg, 0.29 mmol)

in THF/MeOH (10/1, 5 mL) at 0 °C under argon. The solution was stirred for 2 h at this temperature and then quenched with ice/water. The mixture was concentrated and the residue was dissolved in EtOAc (15 mL) and washed with brine (2×15 mL). The organic layers were dried over sodium sulfate, filtered, and then concentrated under reduced pressure. Flash chromatography of the residue over silica gel (PE/EtOAc 2:1) afforded the three dialcohols **13** (43 mg, 38%), **14** (11 mg, 10%), and **15** (56 mg, 49%).

*Medial isomer*: *2,6-Bis(hydroxymethyl)-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (*rac-***13***)*: Colorless solid; m.p. 240–242 °C; $^1$H NMR (300 MHz, [D$_6$]acetone, 25 °C, TMS): $\delta$ = 7.50–7.41 (m, 6H; Ar-H), 7.15–7.11 (m, 4H; Ar-H), 4.54 (s, 4H; C*H*$_2$OH), 3.08 (s, 2H; OH), 1.65 (s, 9H; CH$_3$), 1.38 ppm (s, 3H; CH$_3$); $^{13}$C NMR (75 MHz, [D$_6$]acetone, 25 °C, TMS): $\delta$ = 150.0 (q), 149.82 (q), 149.76 (q), 149.7 (q), 148.6 (q), 142.6 (q), 127.2 (t), 127.1 (t), 127.0 (t), 123.8 (t), 123.7 (t), 123.5 (t), 123.4 (t), 122.0 (t), 70.7 (q), 64.7 (s, CH$_2$OH), 63.4 (q), 63.2 (q), 63.1 (q), 26.2 (p), 26.09 (p), 26.06 (p), 16.3 ppm (p) (overlapping signals: 2 arene C (q), 2 arene C (t), and 1 C (s)); IR (KBr): $\tilde{\nu}$ = 3390, 2963, 1705, 1421, 1365, 1224, 1027, 830, 752, 577 cm$^{-1}$; EI-MS (70 eV): *m*/*z* (%): 396 (17) [*M*$^+$], 381 (100) [*M*−CH$_3$]$^+$; accurate mass (ESI-MS): *m*/*z*: calcd for $C_{28}H_{32}NO_2$: 414.2425 [*M*+NH$_4$]$^+$; found: 414.2422.

*Diastal isomer: 2,7-Bis(hydroxymethyl)-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (***14***)*: Colorless solid; m.p. 216–218 °C; $^1$H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): $\delta$ = 7.51–7.42 (m, 6H; Ar-H), 7.16–7.13 (m, 4H; Ar-H), 4.54 (s, 4H; C*H*$_2$OH), 3.00 (s, 2H; OH), 1.66 (s, 9H; CH$_3$), 1.40 ppm (s, 3H; CH$_3$); $^{13}$C NMR (100 MHz, [D$_6$]acetone, 25 °C, TMS): $\delta$ = 149.9 (q), 149.7 (q), 148.8 (q), 142.7 (q), 128.2 (t), 127.1 (t), 123.9 (t), 123.5 (t), 122.1 (t), 70.7 (q), 64.7 (s, CH$_2$OH), 63.5 (q), 63.0 (q), 26.3 (p), 26.0 (p), 16.3 ppm (p); IR (KBr): $\tilde{\nu}$ = 3365, 2965, 1482, 1027, 813, 736, 575 cm$^{-1}$; ESI-MS: *m*/*z*: 414.2 [*M*+NH$_4$]$^+$; accurate mass (ESI-MS): *m*/*z*: calcd for $C_{28}H_{32}NO_2$: 414.2425 [*M*+NH$_4$]$^+$; found: 414.2418.

*Proximal isomer: 2,11-Bis(hydroxymethyl)-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (***15***)*: Colorless solid; m.p. 236–238 °C; $^1$H NMR (300 MHz, [D$_6$]acetone, 25 °C, TMS): $\delta$ = 7.50–7.43 (m, 6H; Ar-H), 7.16–7.12 (m, 4H; Ar-H), 4.53 (s, 4H; C*H*$_2$OH), 3.01 (s, 2H; OH), 1.66 (s, 9H; CH$_3$), 1.39 ppm (s, 3H; CH$_3$); $^{13}$C NMR (75 MHz, [D$_6$]acetone, 25 °C, TMS): $\delta$ = 149.9 (q), 149.7 (q), 148.7 (q), 142.7 (q), 128.1 (t), 127.1 (t), 123.8 (t), 123.5 (t), 122.1 (t), 70.7 (q), 64.6 (s, CH$_2$OH), 63.4 (q), 63.2 (q), 26.3 (p), 26.1 (p), 16.3 ppm (p); IR (KBr): $\tilde{\nu}$ = 3277, 2952, 1480, 1449, 1010, 826, 748, 572 cm$^{-1}$; ESI-MS: *m*/*z*: 414.2 [*M*+NH$_4$]$^+$; accurate mass (ESI-MS): *m*/*z*: calcd for $C_{28}H_{32}NO_2$: 414.2425 [*M*+NH$_4$]$^+$; found: 414.2433.

**Synthesis of the bis(bromomethyl)-substituted tribenzotriquinacene *rac*-16**: PBr$_3$ (0.1 mL, 1.12 mmol) was added dropwise to a stirred solution of **13** (100 mg, 0.25 mmol) in anhydrous CH$_2$Cl$_2$ (5 mL) at 0 °C. The mixture was stirred for 2 h at room temperature and then quenched with water (15 mL) and extracted with dichloromethane (3×15 mL). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated. Flash chromatography of the residue over silica gel (petroleum ether/AcOEt 20:1) afforded *rac*-**16** (124 mg, 95%). Colorless solid; m.p. 214–216 °C; $^1$H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): $\delta$ = 7.37–7.30 (m, 6H; Ar-H), 7.19–7.13 (m, 4H; Ar-H), 4.42 (m, 4H; CH$_2$Br), 1.64, 1.63 (each s, 9H; 3×CH$_3$), 1.32 ppm (s, 3H; CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): $\delta$ = 149.4 (q), 149.3 (q), 149.1 (q), 148.9 (q), 148.4 (q), 148.3 (q), 137.2 (q), 137.1 (q), 128.7 (t), 127.8 (t), 127.7 (t), 123.6 (t), 123.5 (t), 123.3 (t), 123.2 (t), 122.9 (t), 122.8 (t), 70.2 (q), 62.6 (q), 62.5 (q), 62.3 (q), 33.9 (s, CH$_2$Br), 25.9 (p), 25.71 (p), 25.68 (p), 16.0 ppm (p) (overlapping signals: 1 arene C (t) and 1 C (s)); IR (KBr): $\tilde{\nu}$ = 2962, 2923, 1731, 1480, 1207, 1034, 750, 575 cm$^{-1}$; EI-MS (70 eV): *m*/*z* (%): 524 (6) [$^{81}$Br$_2$−*M*$^+$], 522 (12) [$^{81}$Br$_1$$^{79}$Br$_1$−*M*$^+$], 520 (6) [$^{79}$Br$_2$−*M*$^+$], 509 (9) [$^{81}$Br$_2$−*M*−CH$_3$]$^+$, 507 (20) [$^{81}$Br$_1$$^{79}$Br$_1$−*M*−CH$_3$]$^+$, 505 (10) [$^{79}$Br$_2$−*M*−CH$_3$]$^+$, 443 (96) {$^{81}$Br$_1$−[*M*−Br]}$^+$, 441 (96) {$^{79}$Br$_1$−[*M*−Br]}$^+$, 381 (97), 174 (100); accurate mass (ESI): *m*/*z*: calcd for $C_{28}H_{30}NBr_2$: 538.0737 [*M*+NH$_4$]$^+$; found: 538.0745.

**Synthesis of diastereomeric (*R*)-BINOL diethers 17a and 17b**: A solution of *rac*-**16** (62 mg, 0.12 mmol), (*R*)-BINOL (79 mg, 2.2 equiv), and $Cs_2CO_3$ (90 mg, 2.3 equiv) in acetone (10 mL) was stirred for 60 h at room temperature. After this time, the mixture was concentrated and the residue was dissolved in water (15 mL) and extracted with dichloromethane (3×15 mL). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated. Flash chromatography of the residue over silica gel (PE/EtOAc 3:1) afforded **17a** (50 mg, 45%) and **17b** (47 mg, 42%), respectively.

*2,6-Bis[(*R*)-1-(2-hydroxynaphthalen-1-yl)naphthyl-2-oxymethyl]-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo-[2,3:4,5]pentaleno[1,6-*ab*]indene (***17a***)*: Colorless solid; m.p. 130–132 °C; $[\alpha]_D^{20}$ = −15.0 (*c* = 0.1 in CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): $\delta$ = 8.01–7.85 (m, 8H; Ar-H), 7.46 (t, *J*(H,H) = 10 Hz, 2H; Ar-H), 7.37–7.11 (m, 16H; Ar-H), 7.04 (t, *J*(H,H) = 7.2 Hz, 1H; Ar-H), 6.93 (t, *J*(H,H) = 7.2 Hz, 1H; Ar-H), 6.84 (d, *J*(H,H) = 7.6 Hz, 1H; Ar-H), 6.76–6.70 (m, 3H; Ar-H), 6.58 (d, *J*(H,H) = 7.6 Hz, 1H; Ar-H), 6.44 (d, *J*(H,H) = 7.6 Hz, 1H; Ar-H), 5.05–4.87 (m, 6H; 2×CH$_2$, 2×OH), 1.52 (s, 3H; CH$_3$), 1.34 (s, 3H; CH$_3$), 1.28 (s, 3H; CH$_3$), 1.20 ppm (s, 3H; CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): $\delta$ = 155.07 (q), 155.03 (q), 151.38 (q), 151.35 (q), 148.9 (q), 148.6 (q), 148.4 (q), 148.3 (q), 148.1 (q), 136.1 (q), 135.9 (q), 134.11 (q), 134.07 (q), 133.91 (q), 133.87 (q), 131.0 (t), 129.82 (t), 129.80 (t), 129.7 (t), 129.2 (t), 129.1 (t), 128.3 (t), 128.1 (t), 127.5 (t), 127.3 (t), 126.4 (t), 125.9 (t), 125.8 (t), 125.0 (t), 124.97 (t), 124.94 (t), 124.3 (t), 123.3 (t), 123.0 (t), 122.7 (t), 122.52 (t), 122.47 (t), 120.93 (t), 120.86 (t), 117.6 (t), 116.44 (t), 116.39 (t), 115.5 (t), 115.4 (q), 115.22 (t), 115.16 (q), 70.96 (s, CH$_2$O), 70.92 (s, CH$_2$O), 69.8 (q), 62.4 (q), 62.3 (q), 62.1 (q), 25.8 (p), 25.4 (p), 25.3 (p), 15.9 ppm (p) (overlapping signals: 7 arene C (q) and 5 arene C (t)); IR (KBr): $\tilde{\nu}$ = 3412, 2964, 2924, 1695, 1595, 1509, 1267, 1211, 814, 750, 575 cm$^{-1}$; ESI-MS: *m*/*z*: 950.4 [*M*+NH$_4$]$^+$; accurate mass (ESI): *m*/*z*: calcd for $C_{68}H_{56}NO_4$: 950.4195 [*M*+NH$_4$]$^+$; found: 950.4217.

*2,6-Bis[(*R*)-1-(2-hydroxynaphthalen-1-yl)naphthyl-2-oxymethyl]-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo-[2,3:4,5]pentaleno[1,6-*ab*]indene (***17b***)*: Colorless solid; m.p. 134–136 °C; $[\alpha]_D^{20}$ = +43.0 (*c* = 0.1 in CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): $\delta$ = 8.00–7.84 (m, 9H; Ar-H), 7.48–7.20 (m, 12H; Ar-H), 7.16–7.01 (m, 7H; Ar-H), 6.91–6.72 (m, 6H; Ar-H), 5.04–4.95 (m, 6H; 2×CH$_2$, 2×OH), 1.52 (s, 3H; CH$_3$), 1.34 (s, 3H; CH$_3$), 1.26 (s, 3H; CH$_3$), 1.19 ppm (s, 3H; CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): $\delta$ = 155.04 (q), 154.98 (q), 151.32 (q), 151.29 (q), 148.9 (q), 148.6 (q), 148.4 (q), 148.3 (q), 148.0 (q), 136.1 (q), 136.0 (q), 134.0 (q), 133.83 (q), 133.78 (q), 130.9 (t), 129.9 (t), 129.62 (t), 129.60 (t), 129.14 (t), 129.10 (t), 128.13 (t), 128.09 (t), 127.5 (t), 127.4 (t), 127.3 (t), 126.5 (t), 125.9 (t), 125.8 (t), 124.93 (t), 124.87 (t), 124.83 (t), 124.33 (t), 124.31 (t), 123.3 (t), 123.1 (t), 122.9 (t), 122.6 (t), 122.5 (t), 120.9 (t), 117.5 (t), 117.4 (t), 116.33 (t), 116.25 (t), 115.5 (q), 115.23 (t), 115.19 (q), 70.82 (s, CH$_2$O), 70.76 (s, CH$_2$O), 69.8 (q), 62.4 (q), 62.3 (q), 62.1 (q), 25.8 (p), 25.43 (p), 25.36 (p), 15.9 ppm (p) (overlapping signals: 8 arene C (q) and 4 arene C (t)); IR (KBr): $\tilde{\nu}$ = 3314, 2965, 2925, 1620, 1593, 1508, 1266, 1213, 1080, 814, 750, 575 cm$^{-1}$; ESI-MS: *m*/*z*: 950.4 [*M*+NH$_4$]$^+$; accurate mass (ESI): *m*/*z*: calcd for $C_{68}H_{56}NO_4$: 950.4195 [*M*+NH$_4$]$^+$; found: 950.4198.

**Synthesis of the optically pure bis(bromomethyl)tribenzotriquinacenes (−)-16 and (+)-16**: A solution of BBr$_3$ (0.1 mL, 0.80 M in CH$_2$Cl$_2$) was added dropwise by a syringe to a stirred solution of **17a** (25 mg, 0.03 mmol) in anhydrous CH$_2$Cl$_2$ (5 mL) under argon at 0 °C. The mixture was stirred for 1 h at room temperature, then quenched with aqueous 10% NaOH (2 mL). The separated organic layer was washed with aqueous 10% NaOH (10 mL) and water, dried over sodium sulfate, filtered, and concentrated under reduced pressure. Flash chromatography of the residue over silica gel (PE/EtOAc 20:1) afforded (−)-**16** (14 mg, 89%). In analogy, ether cleavage of **17b** (22 mg, 0.02 mmol) gave the enantiomer (+)-**16** (9 mg, 85%).

*(−)-2,6-Bis(bromomethyl)-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodi-benzo[2,3:4,5]pentaleno[1,6-*ab*]indene [(−)-***16***]*. Colorless solid; m.p. >370 °C; $[\alpha]_D^{20}$ = −40.0 (*c* = 0.1 in CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): $\delta$ = 7.38–7.33 (m, 6H; Ar-H), 7.24–7.18 (m, 4H; Ar-H), 4.46, 4.45 (each s, 4H; CH$_2$Br), 1.68, 1.67 (each s, 9H; 3×CH$_3$), 1.36 ppm (s, 3H; CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): $\delta$ = 149.5 (q), 149.4 (q), 149.1 (q), 149.0 (q), 148.43 (q), 148.40 (q),

137.2 (q), 137.1 (q), 128.7 (t), 127.81 (t), 127.79 (t), 123.6 (t), 123.5 (t), 123.3 (t), 123.2 (t), 122.88 (t), 122.85 (t), 70.3 (q), 62.63 (q), 62.55 (q), 62.4 (q), 33.8 (s, $CH_2Br$), 25.9 (p), 25.7 (p), 16.0 ppm (p) (overlapping signals: 1 arene C (t), 1 C (s), and 1 C (p)); IR (KBr): $\tilde{\nu}$ = 2923, 2853, 1733, 1462, 1262, 1075, 800, 744 $cm^{-1}$; EI-MS (70 eV): *m/z* (%): 524 (8) [$^{81}Br_2$–$M^+$], 522 (16) [$^{81}Br_1{}^{79}Br_1$–$M^+$], 520 (8) [$^{79}Br_2$–$M^+$], 509 (12) {$^{81}Br_2$–[$M$–$CH_3$]}$^+$, 507 (22) {$^{81}Br^{79}Br$–[$M$–$CH_3$]}$^+$, 505 (11) {$^{79}Br_2$–[$M$–$CH_3$]}$^+$, 443 (98) {$^{81}Br$–[$M$–Br]}$^+$, 441 (98) {$^{79}Br$–[$M$–Br]}$^+$, 381 (96), 174 (100); accurate mass (ESI): *m/z*: calcd for $C_{28}H_{30}NBr_2$: 538.0737 [$M$+$NH_4$]$^+$; found: 538.0744.

*(+)-2,6-Bis(bromomethyl)-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodi-benzo[2,3:4,5]pentaleno[1,6-*ab*]indene [(+)-**16**]*: Colorless solid; m.p. >370 °C; $[\alpha]_D^{20}$ = +40.0 (*c* = 0.1 in $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 7.39–7.33 (m, 6H; Ar-H), 7.24–7.18 (m, 4H; Ar-H), 4.46, 4.45 (each s, 4H; $CH_2Br$), 1.68, 1.67 (each s, 9H; 3 × $CH_3$), 1.38 ppm (s, 3H; $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 149.5 (q), 149.3 (q), 149.1 (q), 149.0 (q), 148.43 (q), 148.40 (q), 137.2 (q), 137.1 (q), 128.7 (t), 127.81 (t), 127.79 (t), 123.6 (t), 123.5 (t), 123.3 (t), 123.2 (t), 122.88 (t), 122.85 (t), 70.3 (q), 62.63 (q), 62.55 (q), 62.4 (q), 33.8 (s, $CH_2Br$), 25.9 (p), 25.7 (p), 16.1 ppm (p) (overlapping signals: 1 arene C (t), 1 C (s), and 1 C (p)); IR (KBr): $\tilde{\nu}$ = 2927, 2855, 1734, 1462, 1253, 1071, 835, 776 $cm^{-1}$; EI-MS (70 eV): *m/z* (%): 524 (7) [$^{81}Br_2$–$M^+$], 522 (14) [$^{81}Br^{79}Br$–$M^+$], 520 (7) [$^{79}Br_2$–$M^+$], 509 (10) {$^{81}Br_2$–[$M$–$CH_3$]}$^+$, 507 (20) {$^{81}Br^{79}Br$–[$M$–$CH_3$]}$^+$, 505 (10) {[$^{79}Br_2$–[$M$–$CH_3$]}$^+$, 443 (97) {$^{81}Br$–[$M$–Br]}$^+$, 441 (97) {$^{79}Br_1$–[$M$–Br]}$^+$, 381 (98), 174 (100); accurate mass (ESI): *m/z*: calcd for $C_{28}H_{30}NBr_2$: 538.0737 [$M$+$NH_4$]$^+$; found: 538.0744.

**Synthesis of the optically pure bis(acetoxymethyl)tribenzotriquinacenes (−)-18 and (+)-18**: Compound (−)-**16** (45 mg, 0.08 mmol) was added in one portion to a stirred solution of sodium acetate (141 mg, 1.52 mmol) in glacial acetic acid (5 mL). The mixture was refluxed for 12 h, then the solvent was removed under reduced pressure. The residue was diluted with water (5 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. Flash chromatography of the residue over silica gel (PE/EtOAc 20:1) afforded (−)-**18** (36 mg, 95 %). The analogous conversion of (+)-**16** (48 mg, 0.09 mmol) gave the enantiomer (+)-**18** (41 mg, 96 %).

*(−)-2,6-Bis(acetoxymethyl)-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodi-benzo[2,3:4,5]pentaleno[1,6-*ab*]indene [(−)-**18**]*: Colorless solid; m.p. 119–120 °C; $[\alpha]_D^{20}$ = −36.0 (*c* = 0.1 in $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 7.38–7.33 (m, 6H; Ar-H), 7.22–7.16 (m, 4H; Ar-H), 5.04, 5.03 (each s, 4H; 2 × $CH_2OAc$), 2.07, 2.06 (each s, 6H; 2 × $COCH_3$), 1.67 (s, 9H; 3 × $CH_3$), 1.36 ppm (s, 3H; $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 170.9 (q, $COCH_3$), 149.3 (q), 149.2 (q), 149.0 (q), 148.9 (q), 148.6 (q), 148.5 (q), 135.32 (q), 135.26 (q), 128.28 (t), 128.25 (t), 127.73 (t), 127.72 (t), 123.29 (t), 123.23 (t), 123.11 (t), 123.05 (t), 122.9 (t), 122.8 (t), 70.1 (q), 66.4 (s, $ArCH_2$), 62.6 (q), 62.5 (q), 62.4 (q), 25.9 (p), 25.77 (p), 25.75 (p), 21.0 (p, $COCH_3$), 16.0 ppm (p) (overlapping signals: 1 carbonyl, 1 C (s), and 1 C (p)); IR (KBr): $\tilde{\nu}$ = 2925, 2858, 1733, 1229, 1075, 826, 751, 577 $cm^{-1}$; ESI-MS: *m/z*: 498.4 [$M$+$NH_4$]$^+$; accurate mass (ESI): *m/z*: calcd for $C_{32}H_{36}NO_4$: 498.2635 [$M$+$NH_4$]$^+$; found: 498.2636.

*(+)-2,6-Bis(acetoxymethyl)-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodi-benzo[2,3:4,5]pentaleno[1,6-*ab*]indene [(+)-**18**]*: Colorless solid; m.p. 118–120 °C; $[\alpha]_D^{20}$ = +36.0 (*c* = 0.1 in $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 7.39–7.33 (m, 6H; Ar-H), 7.22–7.17 (m, 4H; Ar-H), 5.05, 5.04 (each s, 4H; 2 × $CH_2OAc$), 2.07, 2.06 (each s, 6H; 2 × $COCH_3$), 1.68 (s, 9H; 3 × $CH_3$), 1.37 ppm (s, 3H; $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 170.9 (q, $COCH_3$), 149.3 (q), 149.2 (q), 149.0 (q), 148.9 (q), 148.6 (q), 148.5 (q), 135.32 (q), 135.26 (q), 128.28 (t), 128.25 (t), 127.73 (t), 127.72 (t), 123.29 (t), 123.23 (t), 123.11 (t), 123.05 (t), 122.9 (t), 122.8 (t), 70.2 (q), 66.4 (s, $ArCH_2$), 62.6 (q), 62.5 (q), 62.4 (q), 25.9 (p), 25.77 (p), 25.75 (p), 21.0 (p, $COCH_3$), 16.0 ppm (p) (overlapping signals: 1 carbonyl, 1 C (s), and 1 C (p)); IR (KBr): $\tilde{\nu}$ = 2924, 2855, 1737, 1227, 1027, 826, 752, 576 $cm^{-1}$; ESI-MS: *m/z*: 498.4 [$M$+$NH_4$]$^+$; accurate mass (ESI): *m/z*: calcd for $C_{32}H_{36}NO_4$: 498.2635 [$M$+$NH_4$]$^+$; found: 498.2628.

**Synthesis of the optically pure bis(hydroxymethyl)tribenzotriquinacenes (−)-13 and (+)-13**: A small piece of sodium was added to a stirred solution of diester (−)-**18** (30 mg, 0.06 mmol) in anhydrous methanol (5 mL). Stirring was continued for 2 h at ambient temperature, and then the mixture was neutralized by the addition of ion-exchange resin (100 mg, $H^+$ form). The resulting mixture was filtered, washed with methanol, and concentrated under reduced pressure. Flash chromatography of the residue over silica gel (EtOAc/MeOH 5:1) afforded diol (−)-**13** (22 mg, 89 %). In analogy, saponification of diester (+)-**18** (28 mg, 0.05 mmol) gave the dibromide (+)-**13** (17 mg, 86 %).

*(−)-2,6-Bis(hydroxymethyl)-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydro-dibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene [(−)-**13**]*: Colorless solid; m.p. 240–242 °C; $[\alpha]_D^{20}$ = −31.0 (*c* = 0.1 in $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 7.39–7.34 (m, 6H; Ar-H), 7.18–7.14 (m, 4H; Ar-H), 4.61 (s, 2H; $CH_2OH$), 4.60 (s, 2H; $CH_2OH$), 1.66 (d, 9H; $CH_3$), 1.36 ppm (s, 3H; $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 149.3 (q), 149.2 (q), 148.8 (q), 148.6 (q), 148.4 (q), 140.5 (q), 140.4 (q), 127.7 (t), 126.80 (t), 126.77 (t), 123.07 (t), 123.05 (t), 122.9 (t), 122.8 (t), 121.7 (t), 121.6 (t), 70.1 (q), 65.5 (s, $CH_2OH$), 62.7 (q), 62.5 (q), 62.4 (q), 26.0 (p), 25.8 (p), 16.1 ppm (p) (overlapping signals: 1 arene C (q) and 1 arene C (t), 1 C (s), and 1 C (p)); IR (KBr): $\tilde{\nu}$ = 3381, 2922, 1652, 1453, 1373, 1026, 827, 751 $cm^{-1}$; ESI-MS: *m/z*: 414.2 [$M$+$NH_4$]$^+$; accurate mass (ESI-MS): *m/z*: calcd for $C_{28}H_{32}NO_2$: 414.2425 [$M$+$NH_4$]$^+$; found: 414.2425.

*(+)-2,6-Bis(hydroxymethyl)-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydro-dibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene [(+)-**13**]*: Colorless solid; m.p. 241–242 °C; $[\alpha]_D^{20}$ = +31.0 (*c* = 0.1 in $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 7.40–7.34 (m, 6H; Ar-H), 7.18–7.13 (m, 4H; Ar-H), 4.60 (s, 4H; $CH_2OH$), 1.67 (s, 9H; $CH_3$), 1.36 ppm (s, 3H; $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 149.3 (q), 149.2 (q), 148.7 (q), 148.57 (q), 148.55 (q), 148.4 (q), 140.5 (q), 140.4 (q), 127.7 (t), 126.8 (t), 123.1 (t), 122.9 (t), 122.8 (t), 121.64 (t), 121.56 (t), 70.1 (q), 65.4 (s, $CH_2OH$), 62.7 (q), 62.5 (q), 62.4 (q), 26.0 (p), 25.8 (p), 16.0 ppm (p) (overlapping signals: 3 arene C (t), 1 C (s), and 1 C (p)); IR (KBr): $\tilde{\nu}$ = 3370, 2923, 1709, 1453, 1383, 1027, 827, 750 $cm^{-1}$; ESI-MS: *m/z*: 414.2 [$M$+$NH_4$]$^+$; accurate mass (ESI-MS): *m/z*: calcd for $C_{28}H_{32}NO_2$: 414.2425 [$M$+$NH_4$]$^+$; found: 414.2426.

**General procedure for the synthesis of dithiametacyclophanes 9a, 9b, 10, *anti*-11, and *syn*-11**: A solution of both dibromide **15** (0.15 mmol) and the appropriate dithiol (0.15 mmol) in anhydrous benzene (50 mL) was added dropwise within 4 h to a stirred solution of $Cs_2CO_3$ (150 mg, 0.46 mmol) in ethanol (50 mL) under argon. Stirring was continued for another 8 h at ambient temperature and then the solvent was removed under reduced pressure. The residue obtained was diluted with water (10 mL) and extracted with $CH_2Cl_2$ (3 × 15 mL). The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure. Flash chromatography of the residue through silica gel (PE/EtOAc 20:1) afforded the corresponding cyclophanes.

*4b,8b,12b,12d-Tetramethyl-3,6-(methanothioethanothiomethano)-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (**9a**)*: This compound was obtained as a colorless solid (54 mg, 80 %); m.p. 307–309 °C; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 7.43–7.39 (m, 2H; Ar-H), 7.30–7.24 (m, 4H; Ar-H), 7.17 (d, $J_{H,H}$ = 8.1 Hz, 2H; Ar-H), 6.94 (d, $J_{H,H}$ = 8.1 Hz, 2H; Ar-H), 3.74, 3.64 (AB, $J_{H,H}$ = 14.7 Hz, 4H; $ArCH_2S$), 2.29, 2.24 (AB, $J_{H,H}$ = 14.7 Hz, 4H; 2 × $ArCH_2SCH_2$), 1.81 (s, 3H; $CH_3$), 1.63 (s, 6H; $CH_3$), 1.41 ppm (s, 3H; $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 150.1 (q), 148.3 (q), 146.5 (q), 137.8 (q), 127.8 (t), 127.7 (t), 123.9 (t), 122.8 (t), 122.7 (t), 69.5 (q), 63.0 (q), 61.8 (q), 37.4 (s, $ArCH_2S$), 32.1 (s, $SCH_2$), 26.6 (p), 21.9 (p), 15.8 ppm (p); IR (KBr): $\tilde{\nu}$ = 2962, 2920, 1482, 1421, 1031, 738, 704, 578 $cm^{-1}$; accurate mass (ESI-MS): *m/z*: calcd for $C_{30}H_{30}S_2Na$: 477.1681 [$M$+Na]$^+$; found: 477.1681.

*4b,8b,12b,12d-Tetramethyl-3,6-(methanothiopropanothiomethano)-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (**9b**)*: Colorless solid (62 mg, 87 %); m.p. 339–340 °C; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 7.43–7.40 (m, 4H; Ar-H), 7.26–7.21 (m, 4H; Ar-H), 7.01 (d, $J_{H,H}$ = 8.1 Hz, 2H; Ar-H), 3.74, 3.64 (AB, $J_{H,H}$ = 14.7 Hz, 4H; $ArCH_2S$), 2.18–2.10, 1.90–1.81 (each m, 4H; $ArCH_2SCH_2$), 1.74 (s, 3H;

$CH_3$), 1.68 (s, 6H; $CH_3$), 1.50–1.40 (m, 2H; $ArCH_2SCH_2CH_2$), 1.38 ppm (s, 3H; $CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 149.3$ (q), 148.5 (q), 147.2 (q), 136.8 (q), 128.6 (t), 127.7 (t), 123.3 (t), 123.0 (t), 122.8 (t), 70.0 (q), 62.6 (q), 62.1 (q), 36.1 (s, $ArCH_2S$), 29.9 (s, $SCH_2$), 28.3 (s, $CH_2$), 26.4 (p), 23.9 (p), 16.1 ppm (p); IR (KBr): $\tilde{\nu} = 2962$, 2919, 1484, 1450, 819, 751, 576 $cm^{-1}$; EI-MS (70 eV): *m*/*z* (%): 468.2 (25) [$M^+$], 362.2 (100), 205.1 (27); accurate mass (EI): *m*/*z*: calcd for $C_{31}H_{32}S_2$: 468.1938 [$M$]$^+$; found: 468.1952.

*4b,8b,12b,12d-Tetramethyl-3,6-[methanothio(1,4-benzenedimethano)thiomethano]-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (**10**)*: Colorless solid (54 mg, 67%); m.p. 274–276 °C; $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.29$–7.21 (m, 4H; Ar-H), 7.22–7.03 (m, 4H; Ar-H), 6.97 (s, 4H; Ar-H), 6.74 (s, 2H; Ar-H), 3.71 (t, $J_{H,H} = 11.7$ Hz, 4H; $PhCH_2S$), 3.52 (t, $J_{H,H} = 5.7$, 6.3 Hz, 4H; $PhCH_2S$), 1.62 (s, 6H; $CH_3$), 1.53 (s, 3H; $CH_3$), 1.26 ppm (s, 3H; $CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 148.9$ (q), 148.7 (q), 147.9 (q), 137.8 (q), 137.6 (q), 129.1 (t), 127.8 (t), 127.4 (t), 124.2 (t), 122.7 (t), 122.0 (t), 70.0 (q), 62.3 (q), 62.1 (q), 36.6 (s, $ArCH_2S$), 34.8 (s, $SCH_2$), 26.3 (p), 25.5 (p), 16.0 ppm (p); IR (KBr): $\tilde{\nu} = 2962$, 2921, 1483, 1424, 1029, 824, 738, 572 $cm^{-1}$; EI-MS (70 eV): *m*/*z* (%): 530.2 (64) [$M^+$], 515.2 (100); accurate mass (EI): *m*/*z*: calcd for $C_{36}H_{34}S_2$: 530.2089 [$M$]$^+$; found: 530.2095.

anti-*2,2′,11,11′-Bis(methanothiomethano)di{4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene}*anti-***11***: Colorless solid (44 mg, 37%); m.p. 335–337 °C; $^1H$ NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.41$ (d, $J_{H,H} = 3.6$ Hz, 4H; Ar-H), 7.29 (d, $J_{H,H} = 8.0$ Hz, 4H; Ar-H), 7.24–7.23 (m, 4H; Ar-H), 7.19 (s, 4H; Ar-H), 7.12 (d, $J_{H,H} = 7.6$ Hz, 4H; Ar-H), 3.64, 3.56 (AB, $J_{H,H} = 12.8$ Hz, 8H; Ar-H), 1.63 (s, 12H; $CH_3$), 1.59 (s, 6H; $CH_3$), 1.32 ppm (s, 6H; $CH_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 149.2$ (q), 148.9 (q), 147.4 (q), 137.9 (q), 128.5 (t), 127.7 (t), 123.5 (t), 123.0 (t), 122.8 (t), 70.1 (q), 62.5 (q), 62.4 (q), 37.1 (s, $ArCH_2S$), 26.1 (p), 25.4 (p), 16.1 ppm (p); IR (KBr): $\tilde{\nu} =$ 2924, 2854, 1727, 1457, 1265, 1028, 750, 576 $cm^{-1}$; DEI-MS (70 eV): *m*/*z* (%): 788.4 (78) [$M^+$], 773.3 (23), 755.4 (25), 724.4 (100); accurate mass (DEI): *m*/*z*: calcd for $C_{56}H_{52}S_2$: 788.3493 [$M^+$]; found: 788.3516.

syn-*2,2′,11,11′-bis(methanothiomethano)di{4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene}*syn-***11***. Colorless solid (39 mg, 33%); m.p. 360–362 °C; $^1H$ NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.45$ (s, 4H; Ar-H), 7.42–7.38 (m, 8H; Ar-H), 7.23–7.18 (m, 8H; Ar-H), 3.32 (s, 8H; $CH_2$), 1.86 (s, 6H; $CH_3$), 1.69 (s, 12H; $CH_3$), 1.41 ppm (s, 6H; $CH_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 148.6$ (q), 148.0 (q), 147.6 (q), 138.7 (q), 129.2 (t), 127.7 (t), 124.2 (t), 122.9 (t), 122.8 (t), 70.4 (q), 62.5 (q), 62.3 (q), 33.3 (s, $ArCH_2S$), 25.9 (p), 25.5 (p), 16.1 ppm (p); IR (KBr): $\tilde{\nu} = 2920$, 1703, 1482, 1027, 750, 574 $cm^{-1}$; DEI-MS (70 eV): *m*/*z* (%): 788.3 (100) [$M^+$], 773.3 (76), 755.3 (79), 724.4 (96); accurate mass (DEI): *m*/*z*: calcd for $C_{56}H_{52}S_2$: 788.3493 [$M^+$]; found: 788.3504.

**X-ray crystallography**: X-ray diffraction data for single crystals were collected by using a Bruker APEX. The crystal structures were solved by the direct method and refined by full-matrix least-squares by using SHELX97. CCDC-753737 (for **15**), −753738 (for **9a**), −753739 (for **9b**), and −753740 (for *syn*-**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] D. Kuck, *Angew. Chem.* **1984**, *96*, 515–516; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 508–509.
[2] a) D. Kuck, A. Schuster, B. Ohlhorst, V. Sinnwell, A. de Meijere, *Angew. Chem.* **1989**, *101*, 626–628; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 595–597; b) D. Kuck, T. Lindenthal, A. Schuster, *Chem. Ber.* **1992**, *125*, 1449–1460; c) D. Kuck, E. Neumann, A. Schuster, *Chem. Ber.* **1994**, *127*, 151–164.
[3] R. Haag, B. Ohlhorst, M. Noltemeyer, R. Fleischer, D. Stalke, A. Schuster, D. Kuck, A. Meijere, *J. Am. Chem. Soc.* **1995**, *117*, 10474–10485.
[4] D. Kuck, A. Schuster, R. A. Krause, J. Tellenbröker, C. P. Exner, M. Penk, H. Bögge, A. Müller, *Tetrahedron* **2001**, *57*, 3587–3613.
[5] a) R. B. Woodward, T. Fukunaga, R. C. Kelly, *J. Am. Chem. Soc.* **1964**, *86*, 3162–3164; b) L. T. Jacobson, *Acta Chem. Scand.* **1967**, *21*, 2235–2237; c) A. de Meijere, D. Kaufmann, O. Schallner, *Angew. Chem.* **1971**, *83*, 404–405; *Angew. Chem. Int. Ed. Engl.* **1971**, *10*, 417–418; d) P. Deslongchamps, U. O. Cheriyan, Y. Lambert, J. C. Mercier, L. Ruest, R. Russo, P. Soucy, *Can. J. Chem.* **1978**, *56*, 1687–1689; e) A. K. Gupta, G. S. Lannoye, G. Kubiak, J. Schkeryantz, S. Wehrli, J. M. Cook, *J. Am. Chem. Soc.* **1989**, *111*, 2169–2179.
[6] Most recent reviews: a) D. Kuck, *Chem. Rev.* **2006**, *106*, 4885–4925; b) D. Kuck, *Pure Appl. Chem.* **2006**, *78*, 749–775.
[7] Selected previous reviews: a) D. Kuck, *Top. Curr. Chem.* **1998**, *196*, 167–220; b) D. Kuck, *Liebigs Ann.* **1997**, 1043–1057; c) D. Kuck, *Synlett* **1996**, 949–965.
[8] B. Bredenkötter, S. Henne, D. Volkmer, *Chem. Eur. J.* **2007**, *13*, 9931–9938.
[9] P. E. Georghiou, L. N. Dawe, H. A. Tran, J. Strübe, B. Neumann, H. G. Stammler, D. Kuck, *J. Org. Chem.* **2008**, *73*, 9040–9047.
[10] H. Langhals, M. Rauscher, J. Strübe, D. Kuck, *J. Org. Chem.* **2008**, *73*, 1113–1116.
[11] a) J. Tellenbröker, Doctoral thesis, Bielefeld University (Germany), **2000**; b) J. Strübe, B. Neumann, H. G. Stammler, D. Kuck, *Chem. Eur. J.* **2009**, *15*, 2256–2260.
[12] J. Tellenbröker, D. Kuck, *Angew. Chem.* **1999**, *111*, 1000–1004; *Angew. Chem. Int. Ed.* **1999**, *38*, 919–922.
[13] L. Zhou, T. X. Zhang, B. R. Li, X. P. Cao, D. Kuck, *J. Org. Chem.* **2007**, *72*, 6382–6389.
[14] A. Schuster, D. Kuck, *Angew. Chem.* **1991**, *103*, 1717–1720; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1699–1702.
[15] T. X. Zhang, L. Zhou, X. P. Cao, D. Kuck, *J. Org. Chem.* **2007**, *27*, 946–957.
[16] For reviews, see: a) C. D. Gutsche in *Calixarenes Revisited* (Ed.: J. F. Stoddart), RSC, Cambridge, **1998**; b) *Calixarenes 2001*, (Eds.: Z. Asfari, V. Bohmer, J. Harowfield), Kluwer Academic, Dordrecht, **2001**.
[17] a) A. Collet, *Tetrahedron* **1987**, *43*, 5725–5759; b) A. Collet, J. P. Dutasta, B. Lozach, J. Canceill, *Top. Curr. Chem.* **1993**, *165*, 103–129; c) C. Schmuck, W. Wienand, *Synthesis* **2002**, 655–663; d) T. Brotin, J. P. Dutasta, *Chem. Rev.* **2009**, *109*, 88–130.
[18] a) D. J. Cram, *Nature* **1992**, *356*, 29–36; b) L. R. MacGillivray, J. L. Atwood, *Angew. Chem.* **1999**, *111*, 1080–1096; *Angew. Chem. Int. Ed.* **1999**, *38*, 1018–1033; c) A. Jasat, J. C. Sherman, *Chem. Rev.* **1999**, *99*, 931–968.
[19] a) J. Issberner R. Moors, F. Vögtle, *Angew. Chem.* **1994**, *106*, 2507–2514; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2413–2420; b) S. M. Grayson, J. M. Fréchet, *Chem. Rev.* **2001**, *101*, 3819–3868.
[20] a) J. L. Shaw, J. Wolowska, D. Collison, J. Howard, E. J. L. Mclnnes, M. Jonathan, A. J. Blake, C. Wilson, S. Martin, *J. Am. Chem. Soc.* **2006**, *128*, 13827–13829; b) D. E. Janzen, K. N. Patel, D. G. VanDerveer, G. J. Grant, *Chem. Commun.* **2006**, 3540–3546; c) M. Vetrichelvan, Y. H. Lai, K. F. Mok, *Dalton Trans.* **2003**, 295–301.
[21] a) C. Poriel, Y. Ferrand, P. L. Maux, J. Rault-Berthelot, G. Simonneaux, *Synth. Met.* **2008**, *158*, 796–801; b) L. Mattiello, G. Fioravanti, *Synth. Commun.* **2001**, *31*, 2645–2649; c) S. Nishida, Y. Morita,

  

A. Ueda, T. Kobayashi, K. Fukui, K. Ogasawara, K. Sato, T. Takui, K. Nakasuji, *J. Am. Chem. Soc.* **2008**, *130*, 14954–14955.

[22] X-ray crystal data for **15**: $C_{31}H_{34}O_3$; $M=454.58$; triclinic; $a=8.7662(12)$, $b=10.7826(14)$, $c=14.0500(18)$ Å; $\alpha=93.314(2)$, $\beta=101.883(2)$, $\gamma=104.801(2)°$; $V=1247.9(3)$ Å$^3$; space group $P\bar{1}$; $Z=2$; $\rho_{calcd}=1.210$ Mg m$^{-3}$; $T=294(2)$ K; $\lambda(Mo_{K\alpha})=0.71073$ Å; 4596 reflections collected, 3217 independent reflections ($R_{int}=0.0671$), 644 parameters refined on $F^2$, $R_1=0.2082$, $wR_2[F^2]=0.1837$ (all data); GOF on $F^2=1.030$.

[23] a) G. Q. Lin, Y. M. Li, A. S. C. Chan, *Principles and Applications of Asymmetric Synthesis*, Wiley, New York, **2001**; b) A. Dalla Cort, L. Mandolini, C. Pasquini, L. Schiaffino, *New J. Chem.* **2004**, *28*, 1198–1201.

[24] J. Strübe, D. Kuck, unpublished results.

[25] a) H. Y. Peng, C. K. Lam, T. C. W. Mark, Z. W. Cai, W. T. Ma, Y. X. Li, H. N. C. Wong, *J. Am. Chem. Soc.* **2005**, *127*, 9603–9611; b) Y. D. Cao, J. Luo, Q. Y. Zheng, C. F. Chen, M. X. Wang, Z. T. Huang, *J. Org. Chem.* **2004**, *69*, 206–208.

[26] a) N. Haratr, K. Nakanishi, *Circular Dichroism Spectroscopy—Exciton Coupling in Organic Stereochemistry*, University Science Books, New York, **1983**; b) K. Hör, O. Gimple, P. Schreier, H. U. Humpf, *J. Org. Chem.* **1998**, *63*, 322–325; c) S. Superchi, M. I. Donnoli, C. Rosini, *Org. Lett.* **1999**, *1*, 2093–2096; d) J. Zhang, A. E. Holmes, A. Sharma, N. R. Brooks, R. S. Rarig, J. Zubieta, J. W. Canary, *Chirality* **2003**, *15*, 180–189.

[27] a) C. Diedrich, S. Grimme, *J. Phys. Chem. A* **2003**, *107*, 2524–2539; b) P. J. Stephens, F. J. Devlin, *J. Org. Chem.* **2007**, *72*, 4707–4715; c) P. L. Polavarapu, N. Jeirath, S. Walia, *J. Phys. Chem. A* **2009**, *113*, 5423–5431.

[28] a) T. Kawase, H. Kurata, *Chem. Rev.* **2006**, *106*, 5250–5273; b) C. A. Christensen, A. S. Batsanov, M. R. Bryce, *J. Am. Chem. Soc.* **2006**, *128*, 10484–10490; c) *Modern Cyclophane Chemistry* (Eds.: R. Gleiter, H. Hopf), Wiley-VCH, Weinheim, **2004**; d) F. Vögtle, *Cyclophane Chemistry*, Wiley, New York, **1993**; e) F. Diederich, *Cyclophanes*, RSC, Cambridge, **1991**.

[29] J. Seo, S. S. Lee, W. T. Gong, K. Hiratani, *Tetrahedron Lett.* **2008**, *49*, 3770–3774.

[30] a) M. C. Daniel, D. Astruc, *Chem. Rev.* **2004**, *104*, 1983–2031; b) A. Ikeda, S. Shinkai, *Chem. Rev.* **1997**, *97*, 1713–1734.

[31] A. Senthilvelan, I. T. Ho, K. C. Chang, G. H. Lee, Y. H. Liu, W. S. Chung, *Chem. Eur. J.* **2009**, *15*, 6152–6160.

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