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Poly(amine/imine) Dendrimers Bearing Planar Chiral Terminal Groups - Synthesis and Chiroptical Properties

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Abstract: New functional dendrimers bearing up to 16 planar-chiral units on their surface were synthesized from achiral polyamine dendrimers and planar chiral 5-formyl-4-hydroxy[2.2]paracyclophane. The CD spectra of the new dendrimers were compared with the circular dichroism of the paracyclophane aldehyde and discussed in the light of their properties to complex metal cations for the design of new homogenous catalysts. The absolute configuration of 5-formyl-4-hydroxy[2.2]paracyclophane (FHPC) was deduced by comparison of experimental and theoretical CD spectra. The excited electronic states are discussed on the basis of multireference configuration interaction (MRD-CI) calculations. The synthesis and X-ray diffraction structural studies of the first chiral salen analogue with two planar chiral salicylidene type units are reported.

INTRODUCTION

Since polyamine cascade molecules were first prepared in our laboratory in 1978[1] a new renaissance is in the offing and the functionalisation of these dendritic compounds has attracted increasing attention[2]. The recent publications of Meijer,[3] Mülhaupt,[4] and ourselves[5] are based on improvements concerning the reduction method of nitrile dendrons. With these new methods amine dendrimers are now available in large amounts. Meijer et al. recently reported the synthesis of dendrimers thereof with chiral terminal units[6]. When only the chiral surface unit contains one stereogenic carbon atom the dendrimers turned out to exhibit low or vanishing optical activity with increasing generation number in contrast to dendrimers with rigid chiral units.
We now meet the challenge of synthesizing chiral dendrimers with stable planar-chiral building blocks to avoid racemisation. In addition, the chiral information should be useful for further reactions, e. g. in the field of homogenous catalysis. There is great scope for the development of new materials that combine the advantages and/or minimize disadvantages associated with individual homogeneous and heterogeneous catalysts[7]. Dendrimer construction might offer a better means of controlling the disposition of pendant metal-containing catalytic sites in soluble, polymer-based catalysts[8]. Catalytic dendrimers with nanoscale dimensions may be recycled by using filtration methods to easily remove the catalyst from the reaction mixture. No effort has been reported to date towards developing versatile asymmetric catalyst systems based on dendrimers with planar chiral terminal units.

RESULTS AND DISCUSSION

The chiral unit of our choice was the recently described 5-formyl-4-hydroxy[2.2]paracyclophane (FHPCP) (**1**).[9] In analogy to salcomines it should react with various dendritic polyamines to achieve multisalen dendrimers able to form multinuclear metal complexes with metal salts, e.g. cobalt(II)-chloride.[10] Cobalt-salen derivatives are well known for their ability to reversibly binding oxygen. They have been reported to be efficient catalysts for oxo-transfer reactions, e.g. for the epoxidation of unfunctionalized olefins.[11] Extremely high enantioselectivity has been achieved with asymmetric Mn-salen complexes; there is a rich activity in this area of research.

FHPCP (**1**) was synthesized by following the preparative pathway first reported by Belokon et al.[9b] and modified by Hopf et al.[9a] The enantiomeric resolution of the racemic aldehyde could be performed by the method of Belokon et al.[9b] via diasteriomeric Cu-Schiff's base-complexes with 60%ee. Separation by HPLC[12] yielded the enantiomerically pure aldehyde. The crystal and molecular structure could be determined as well (Fig. 1).

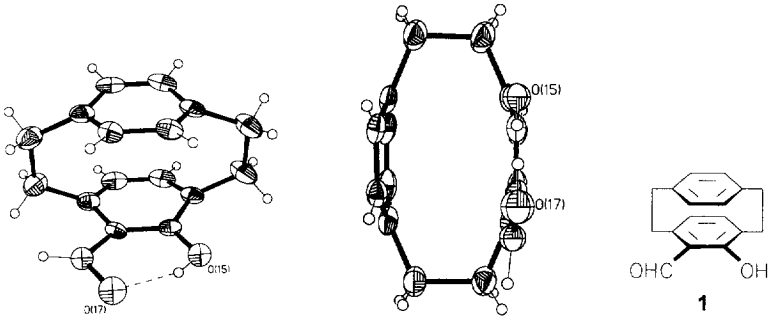
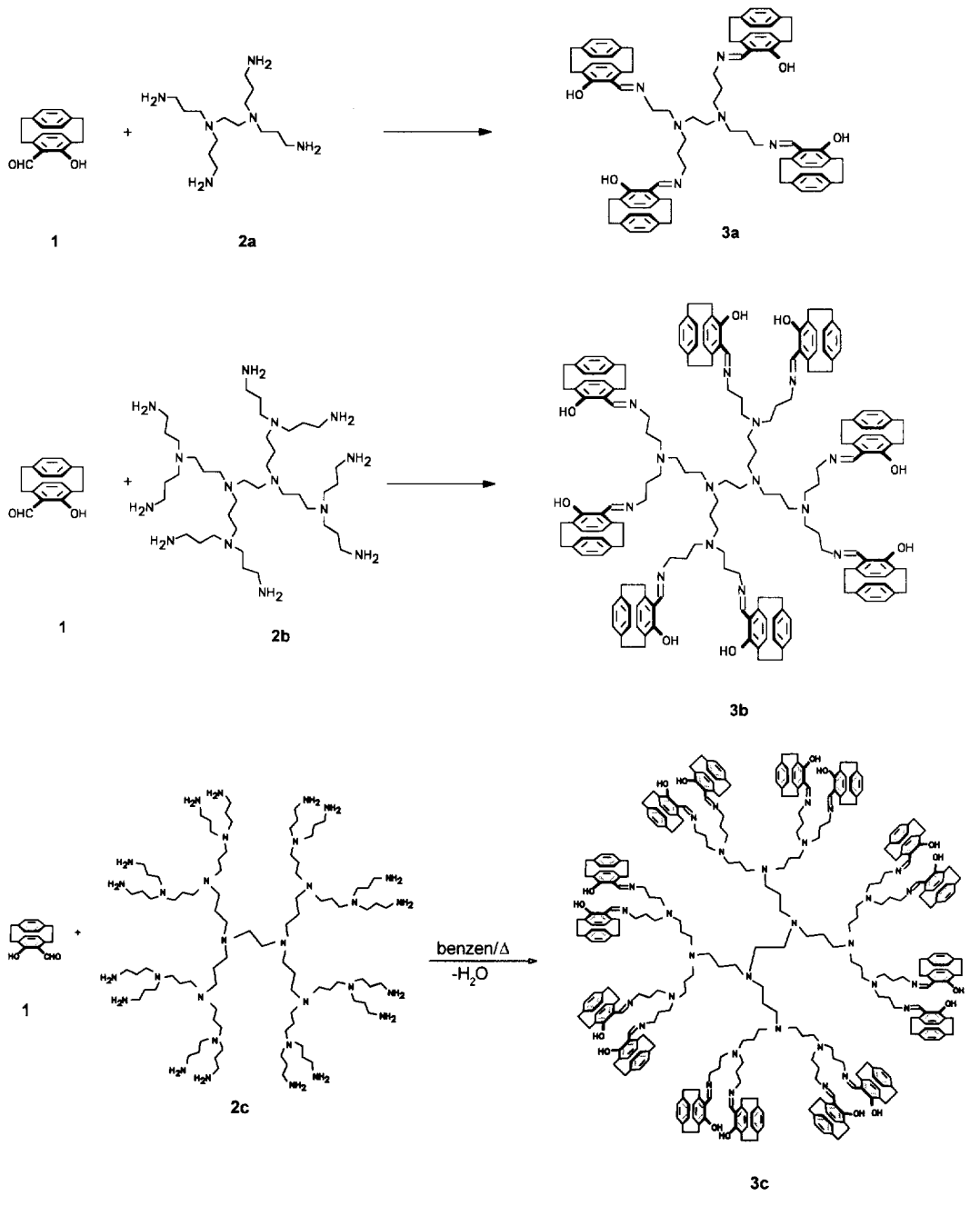


Figure 1. Crystal structure[13] of (±) 5-formyl-4-hydroxy[2.2]paracyclophane **1** (FHPCP)

The aldehyde and the hydroxy functions are disorderd in the crystal. The probability that they have opposite positions is about 61:39. Condensation of the enantiomerically enriched and of the pure aldehyde **1** with dendritic polyamines (1st to 3rd tier, bearing four **2a**, eight **2b** or sixteen **2c** NH_2-Groups) at room temperature in dichloromethane/sodium sulfate or refluxing in a flask equipped with a Dean-Stark trap using benzene as the solvent affords the tetra-, octa- and hexadodeca-imines **3a-c** (see scheme 1). The salen analogous product **4** was obtained in the same manner. After the reaction is completed the yield and the amount of unreacted aldehyde in relation to the dendritic imines can easily be determined by integration over the signal of the imine and the aldehyde proton via ^1H NMR spectroscopy. If necessary, the crude product was purified by several washing procedures with hot methanol. The dendritic imines were obtained as orange-yellow solids.



Scheme 1. Reaction of 1st to 3rd generation amine dendrimer **2a-c** (4, 8 and 16 NH_2-groups) with FHPCP.

Single cyrstals of the chiral comparison compound **4** were obtained from a hexane/*iso*-propanol solution by slow evaporation.(Fig. 2)

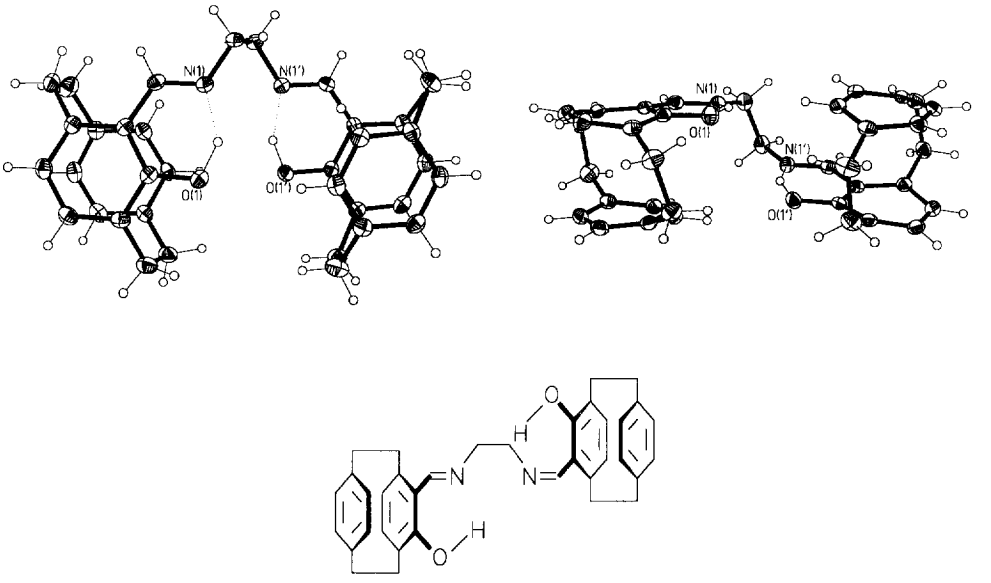


Figure 2. Crystal structure[14] of the chiral salen analogoue **4**.

As shown in Fig. 2 the N and O atoms in the molecule are almost in plane. The maximum torsion angle is about 6.4 degree. The intramolecular hydrogen bond has the following parameters: O(1)-N(1) 2.523 (2.513) Å, O(1)-H(1) 1.09 (1.05) Å, N(1)-H(1) 1.59 (1.54) Å, O(1)-H(1)..N(1) 140° (147°).

As hitherto the CD spectrum of the aldehyde **1** has not been published a more detailed discussion seems to be appropriate at this point. Very recently the absolute configuration of **1** has been determined by an X-ray diffractional structural study of the Schiff's base derived from (R)-α-phenylethylamine and $(+)_D$-(R)-FHPCP by Belokon et al.[9c] We carried out theoretical NDDO/multireference singles + double excitations CI(MRD-CI) calculations[15] which allow a certain assignment and interpretation of the transitions involved in a particular CD band. Satisfying accordance of the theory with the experiment for the CD spectra has been obtained by this new combination of methods for metacyclophanes reported previously.[16]

The experimental CD spectra of **1, 3a-c** and **4** in the range 200-450 nm (see Figure 3, 4.) show six distinct bands A-F (in the case of the Schiff's bases Band E is absent; band C is splitted and the shoulder of band C of **1** is resolved). The comparison of the experimental and the theoretically simulated spectra shows an overall good agreement (see Fig. 3 and Tab. 1) demonstrating the reliability of the theoretical approach. However, one should keep in mind that the calculation refers to gas phase and that only a vertical spectrum is considered, i.e. vibrational effects which may have a large influence especially for low intensity CD transitions are neglected. The first broad band (A) with a maximum at 390 nm is assigned as a localized $\pi\pi^*$ transition to a L_b type excited state in the substituted ring.

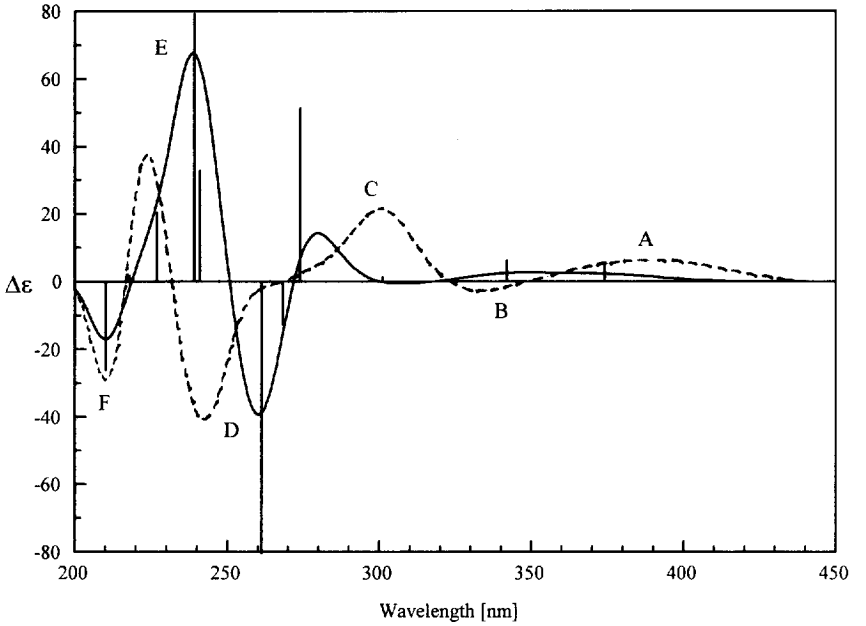


Figure 3. Comparison of the simulated (——) and the experimental CD-Spectra (----) of (R)-**1**. Calculated CD-transitions are shown as vertical lines in the diagramm. Simulation of the circular dichrogramm is achieved by superposition of Gaussian curves for each CD transition with a constant mean half width of 0.3eV (right).

The large red shift of 120 nm found for this transition compared to benzene itself is caused by the CHO/OH substitution pattern and by the boat-type deformation of the aromatic rings. In agreement with previous observations the weak negative band B is attributed to the $n\pi^*$ excited state. This is the only band for which the MRD-CI treatment predicts the wrong CD sign. This band band has been used for the application of the modified octant rule.[17] The correct assignment and interpretation of this transition is essential as well for the determination of the configuration from optical data as for the understanding of metal complexation. The negative Cotton effect (CE) of the $n\pi^*$ transition of numerous monosubstituted derivatives of the $(-)_D$-4-carboxy[2.2]paracyclophane was correlated with the absolute configuration (R) by Schlögl et al.[18] The correlation was later confirmed unambigously by X-ray diffraction structural studies. ^{1}H NMR experiments of **1-3** and the X-ray diffraction structural study of **1** prove that the aldehyde function (and also the imino groups in **3, 4**) is (are) oriented *s-cis*. This is in significant difference to the derivatives of the $(-)_D$-(R)-4-carboxy-[2.2]paracyclophane, which are *s-trans*. Simultaneously by the transition from 4-carboxy-[2.2]paracyclophane to FHPCP the absolute configuration changes due to the higher priority of the carbon atom 5. The double inversion is the reason for the assignment $(+)_D$-(R)-FHPCP.

The positve band C in the spectrum of **1** is composed of two transitions which is seen experimentally as a shoulder around 280 nm. Next follow three intense bands with alternating CD sign (D-F). Although these bands are obtained from several transitions they are correctly reproduced by the calculation. The bands C-F

involve coupled $\pi\pi^*$ transitions of both rings with various contributions of substituent π-orbitals for the higher lying states.

Table 1. NDDO/MRD-CI[a] results for the eleven lowest vertical excited singlet states of (1). Experimental[b] band maxima (in nm) and signs of the CD transitions are compared with theoretical rotatory strengths (in 10^{-40} cgs units). States where no assignment is given are characterrized as coupled $\pi\pi^*$ states of both rings.

state (S0-Sn)	band	λ (exp)	CD-sign	λ (calc)	R	oscillator strengths	assignment
S1	A	390	+	374	+5.3	0.05	Lb (subst.ring)
S2	B	335	-	342	+5.5	0.002	$n\pi^*$
S3				301	+0.8	0.0001	
S4	C	300	+	274	+50.7	0.017	
S5				268	-12.2	0.071	
S6	D	240	-	261	-80.7	0.103	
S7				241	+32.1	0.085	
S8	E	225	+	239	+78.8	0.044	
S9				227	+19.6	0.002	
S10				218	+0.9	0.019	
S11	F	210	-	210	-25.5	0.090	

[a]All theoretical transition energies have been red-shifted by 0.6 eV to obtain an overall good agreement of simulated and experimental spectra. The shift of the theoretical transition energies results from the neglect of most of the valence electrons and parts of the virtual space in the MRD-CI treatment.

[b]In dichloromethane at room temperature.

The success of exciton-chirality models for the explanation of paracylophane CD spectra can be attributed to the fact that the π-systems are strongly isolated from each other and σ-π mixing is in spite of the ring deformation small (the transtion densities to the higher lying states show negligible mixing with the sigma orbitals).

As to the discussion of the CD spectra of the planar chiral salen **4** and the dendrimers **3a-c**, the transitions and the signs of the CE of **4** and **3a-c** are very similar. The dendrimers **3a-c** have nearly constant optical activity with increasing generation in accordance with Meijer's investigation about dendrimers with rigid chiral units. After addition of anhydrous cobalt(II) chloride to solutions of the dendrimers in dichloromethane the circular dichrogramm shows significant differences in the low energy region to that recorded without metal cations. These observations are in accordance with the assumption that the low lying energies wich are localized in the substituted paracyclophane ring are in interaction with the low energy orbitals of the metal ion. Preliminary investigations show similar effects with many other transition metal cations, e.g. manganese(II), copper(II).

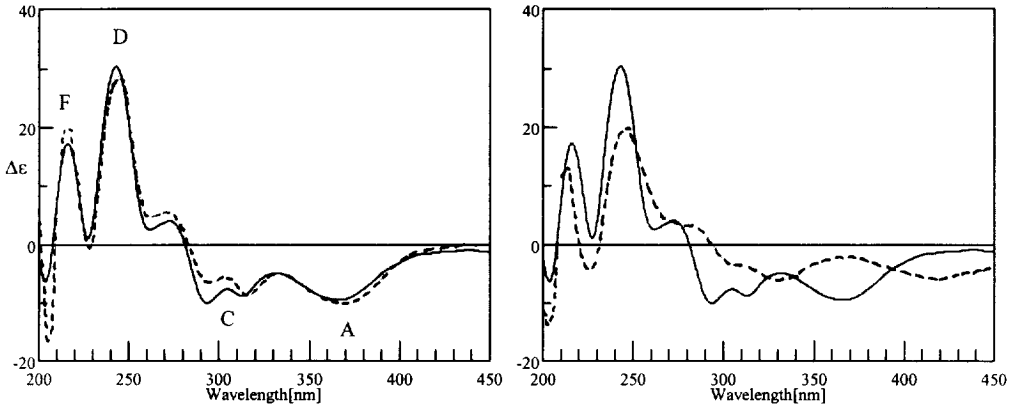


Figure 4. Comparison of the experimental CD-spectra of (S,S)-**4** (----) and **3c** (——) dissolved in dichloromethane (left). Comparison of the experimental CD-spectra of dendritic imine **3c** solved in dichloromethane in the absence of metal cations (——) and after addition of anhydrous cobalt(II)-chloride (----) (right).

CONCLUSION

In conclusion the circular dichrograms clearly indicate that chiral dendrimers based on derivatives of [2.2]paracyclophanes can be employed for complexation of a couple of metal cations. As shown for the [2.2]paracyclophane-aldehyde derivative **1** above circular dichroism assisted by theoretical calculations is useful for the determination of absolute configurations. The reported dendrimers are precisely built nanoscopic molecules with physical characteristics such as size, solubility and dispersity of complexation sites. A number of applications of metal-containing dendrimers, such as asymmetric homogenous catalysts (chiral dendrimers) and oxygen-storing materials (non-chiral dendrimers) are foreseen. Moreover we hope that dendrimers with a dense surface of catalytic sites have the ability to split water as has recently been shown for non-dendritic manganese-salen complexes.[19] In the attempt to understand how the oxygen evolving center of the photosystem II of green plants works, model complexes are of great help. In these studies polynuclear mangangese complexes derived from the pesented poly-salen dendrimers may meet the requirements of such model compounds.

EXPERIMENTAL SECTION

General procedure for the preparation of Schiff's bases **3a,b,c, 4**

3b: 7.5 mg (0.03 mmol) $(+)_D$-(R)-5-formyl-4-hydroxy-[2.2]paracyclophane (**1**) was dissolved in 25 ml benzene. 2.7 mg (0.004 mmol) of the octaamine (**2b**) dissolved in 10 ml benzene were added at 60°C. Then the mixture was refluxed 8 h in a flask equipped with a Dean-Stark trap for. The remaining yellow-orange solution was evaporated under reduced pressure. The oily residue was washed three times with hot methanol and dried in vacuum. The purity of the resulting Schiff-bases has been proven by ^{1}H NMR-spectroscopy to be almost 95%. Yield 7.0 mg (69%), orange-yellow solid, fp 42°, $[\alpha]_D^{25°}$= +478 (c = 0.2 in CH_2Cl_2); ^{1}H NMR (400 Hz, $CDCl_3$, 25°C) : δ = 1.5-1.6 (m, 16H, CH_2), 1.7-1.8 (m, 16H, CH_2), 2.42-2.57

(m, 36H, CH_2), 2.59-2.80 (m, 16H, CH_2), 2.88-2.97 (m, 8H, CH_2), 2.99-3.14 (m, 16H, CH_2), 3.24-3.32 (m, 8H, CH_2), 3.33-3.42 (m, 8H, CH_2), 3.46-3.57 (m, 16H, CH_2), 6.06 (d, ^3J(H,H) = 7.6 Hz, 8H, CH), 6.12 (dd, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.7 Hz, 8H, CH), 6.34 (dd, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.7 Hz, 8H, CH), 6.39 (d, ^3J(H,H) = 7.6 Hz, 8H, CH), 6.50 (dd, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.7 Hz, 8H, CH), 6.77 6.(dd, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.7 Hz, 8H, CH), 8.06 (s, 8H, CHN), 14.2 (br.s, OH); ^{13}C NMR (100 Hz, $CDCl_3$, 25° C) : δ = 24.7 (C_s), 28.9 (C_s), 29.9 (C_s), 32.2 (C_s), 33.9 (C_s), 35.3 (C_s), 51.7 (C_s), 52.2 (C_s), 56.9 (C_s), 119.1 (C_q), 123.7 (C_t), 126.6 (C_t), 128.1, 130.5 (C_t), 132.0 (C_t), 133.4 (C_t), 137.4 (C_t), 137.5 (C_q), 140.1 (C_q), 142.0 (C_q), 162.2 (CH=N), 163.0 (C_q); MS (positive-FAB, NBA) *m/z* = 2620.7 (M^+ [$C_{174}H_{204}N_{14}O_8$]+H, 20%), $C_{174}H_{204}N_{14}O_8$ (2619.6); CHN-analysis (ber.:) H: 7.85%, C: 79.87%, N: 7.49%, O 4.89%.

3a:

^{1}H NMR (400 Hz, $CDCl_3$, 25°C) : δ = 1.81 (t, ^3J(H,H) = 6.2 Hz, 8H, CH_2), 2.45- 2.76 (m, 24H, CH_2), 2.93 (td, 4H, CH_2), 3.0-3.1 (m, 8H, CH_2), 3.25-3.40 (m, 8H,CH_2), 3.45-3.60 (m, 8H, CH_2), 6.07 (dd, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1 Hz, 4H, CH), 6.13 (d, ^3J(H,H) = 7.9 Hz, 4H, CH), 6.34 (dd, ^3J(H,H) = 7.9 Hz, ^4J(H,H) = 1.7 Hz, 4H, CH), 6.40 (d, ^3J(H,H) = 7.6 Hz, 4H, CH), 6.50 (d, ^3J(H,H) = 7.9 Hz, 4H, CH), 6.78 6.(dd, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 1.7 Hz, 4H, CH), 8.06 (s, 4H, CHN), 14.2 (br.s, OH); ^{13}C NMR (100 Hz, $CDCl_3$, 25°C) : δ = 24.7 (C_s), 28.9 (C_s), 29.9 (C_s), 32.2 (C_s), 33.9 (C_s), 35.3 (C_s), 51.7 (C_s), 52.2 (C_s), 56.9 (C_s), 119.1 (C_q), 123.7 (C_t), 126.6 (C_t), 128.1, 130.5 (C_t), 132.0 (C_t), 133.4 (C_t), 137.4 (C_t), 137.5 (C_q), 140.1 (C_q), 142.0 (C_q), 162.2 (CH=N), 163.0 (C_q); MS (positive-FAB, *m*-NBA) *m/z* = 1225.8 (M^+ [$C_{82}H_{92}N_6O_4$]+H, 100%), $C_{82}H_{92}N_6O_4$ (1224.72). CHN-analysis (ber.:) H: 7.57%, C: 80.36%, N: 6.86%, O 5.22%.

3c:

^{1}H NMR (400 Hz, $CDCl_3$, 25°C) : δ = 1.5-1.85 (br.s, 64H, CH_2), 2.3-2.7 (m, 124H, CH_2), 2.85-2.95 (m, 16H, CH_2), 3.0-3.15 (m, 32H, CH_2), 3.2-3.4 (m, 32H, CH_2), 3.45-3.6 (m, 32H, CH_2); 6.06 (d, ^3J(H,H) = 7.6 Hz, 16H, CH), 6.12 (d, ^3J(H,H) = 7.6 Hz, 16H, CH), 6.34 (d ^3J(H,H) = 7.6 Hz, 16H, CH), 6.39 (d, ^3J(H,H) = 7.6 Hz, 16H, CH), 6.50 (d, ^3J(H,H) = 7.6 Hz, 16H, CH), 6.77 .(d, ^3J(H,H) = 7.6 Hz, 16H, CH), 8.06 (s, 16H, CHN), 14.2 (br.s, OH); ^{13}C NMR (100 Hz, $CDCl_3$, 25°C) : δ = 29.4 (C_s), 28.5 (C_s), 29.9 (C_s), 32.2 (C_s), 33.9 (C_s), 35.3 (C_s), 51.4 (C_s), 56.6 (C_s), 119.1 (C_q), 123.7 (C_t), 126.6 (C_t), 128.1, 130.5 (C_t), 132.0 (C_t), 133.4 (C_t), 137.4 (C_t), 137.5 (C_q), 140.1 (C_q), 142.0 (C_q), 162.5 (CH=N), 163.0 (C_q); MALDI-TOF(Matrix: DHB) *m/z* = 5422.1 (M^+ [$C_{358}H_{428}N_{30}O_{16}$] + CH_2), $C_{358}H_{428}N_{30}O_{16}$ (5407.53); CHN-analysis $C_{358}H_{428}N_{30}O_{16}$. 4 $HCCl_3$ ber. (gef.)%: H: 7.40 (7.71), C: 73.88 (73.77), N: 7.14 (7.06).

Enantiomeric separation by HPLC. Column: Cellulose-tris(3,5-dimethylphenylcarbamate) (CDMPC), 500 x 4.6 mm. Eluent: *n*-hexane/*iso*propanol 9:1, 0.3 mL min^{-1}. Pressure: 3 bar. Temperature 25°C. Detection: UV, λ = 254 nm; t_r [(+)$_D$-**1**] = 26 min; t_r [(-)$_D$-**1**] = 35 min; k' [(-)$_D$-**1**] = 4.54; k' [(+)$_D$-**1**] = 5.92; α = 1.30; R = 1.89. $[\alpha]_{578}^{20}[(R)-1]$ = +588 (c=0.02, CH_2Cl_2) Polarimeter Perkin-Elmer 241. CD-Measurement: JASCO-Spectropolarimeter J 720, 0.001 g/ml solution in dichloromethane, 0.02mm cell

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REFERENCES AND NOTES

[1] E. Buhleier, W. Wehner, F. Vögtle, *Synthesis*, **1978**, 137-139.

[2] a) J. Issberner, R. Moors, F. Vögtle, *Angew. Chem.* **1994**, *106*, 2507-2514; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2413-2420; b) H. B. Mekelburger, W. Jaworek, F. Vögtle, *ibid.* **1992**, *104*, 1609 - 1614 bzw. **1992**, *31*, 1571 - 1576; c) D. A. Tomalia, H. D. Durst, *Top. Curr. Chem.* **1993**, *165*, 193-313.

[3] E. M. M. de Brabander-van den Berg, E. W. Meijer, *ibid.* **1993**, *105*, 1370 - 1372 bzw. **1993**, *31*, 1308 - 1311.

[4] C. Wörner, R. Mülhaupt, *Angew. Chem.* **1993**, *105*, 1367 - 1370; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1306 - 1308;

[5] R. Moors, F. Vögtle, *Chem. Ber.* **1993**, *126*, 2133-2135.

[6] J. F. G. A. Jansen, H. W. I. Peerlings, E. M. M. de Brabander-van den Berg, E. W. Meijer, *Angew. Chem.* **1995**, *107*, 1321 - 1324; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1206 - 1209;

[7] J. W. J. Knapen, A. W. van der Made, J. C. de Wilde, P. W. N. M. van Leeuwem, P. Wijkens, D. M. Grove, G. van Koten, *Nature*, **1994**, *Vol. 372*, 659-663.

[8] a) B. B. De, B. B. Lohray, S. Sivaram, P. K. Dhal, *Tetrah. Asymmetry*, **1995**, *6(9)*, 2105-2108 and references therein; b) R. S. Drago, J. Gaul, A. Zombeck, D. K. Straub, *J. Am. Chem. Soc.* **1980**, *102*, 1033-1038; c) R. S. Drago, J. P. Cannady, K. A. Leslie, *J. Am. Chem. Soc.* **1980**, *102*, 6041-6019; d) G. Henrici-Olivé, S. Olivé, *Angew. Chem.* **1974**, *86*, 1-56.

[9] a) H. Hopf, D. G. Barrett, *Liebigs Ann.* **1995**, 449-451; b) V. Rozenberg, V. Kharitonov, D. Antonov, E. Sergeeva, A. Aleshkin, N. Ikonnikov, S. Orlova, Y. Belokon, *Angew. Chem.* **1994**, *106*, 106-108; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 91; D. Y. Antonov, Y. N. Belokon, N. S. Ikonnikov, S. A. Orlova, A. P. Pisarevsky, N. I. Raevski, V. I. Rozenberg, E. V. Sergeeva, Y. T. Struchkov, V. I. Tararov, E. V. Vorotsov, *J. Chem. Soc., Perkin Trans. I*,. **1995**, 1873-1879.

[10] R. Moors, F. Vögtle, *Adv. in Dendritic Macromolecules*, **1995**, *2*, 41-73.

[11] a) S. Chang, J. M. Galvin, E. N. Jacobsen, *J. Am. Chem. Soc.* **1994**, *116*, 6937-6938; b) H. Sasaki, R. Irie, T. Katsuki, *Synlett*, 1994, 356-358; c) P. A. Ganeshpure, S. Satish, *Tetrahedron Lett.* **1988**, *29*, 6629-6632..

[12] Column: Cellulose-tris(3,5-dimethylphenylcarbamate) (CDMPC), 500 x 4.6 mm. Eluent: *n*-hexane/*iso*propanol 95:5.

[13] X-ray Structure of **1**: Crystal data: $C_{17}H_{16}O_2$, MW 252.3 g mol-1, yellow plates, dimensions 0.43 x 0.40 x 0.10 mm, $d_{calc.}$ = 1.33 g cm-1, monoclinic, space group $P2_1/c$ (No. 14), a = 9.308(2), b = 7.792(1), c = 17.395(3) Å, β = 90.26(1)°, V = 1261.6(4) Å^3, Z = 4, F(000) = 536. A total of 3843 reflections were recorded on a Enraf Nonius CAD4 diffractometer (graphite monochromator, λ=(Cu-Kα) = 1.54178 Å), μ(Cu-Kα) = 0.68 mm^{-1}) at T = 293 K. Of these, 1878 independent reflections were used for the structure solution (SHELXTL-Plus[20]) and refinement (170 parameters and 6 restraints, SHELXL-93[21]). Non-hydrogen atoms were refined anisotropically (full-matrix least-squares refinement on F^2); H atoms were refined using a riding model, wR2 = 0.3410 (R for I>2σ(I) = 0.107). Largest difference peak 0.27 and -0.30 eÅ^{-3}. An extinction correction was applied. The aldehyde and the hydroxyl functions are disorderd (61:39).

[14] X-ray Structure of **4**: Crystal data: $C_{36}H_{36}N_2O_2$, MW 528.7 g mol-1, orange plates, dimensions 0.50 x 0.35 x 0.10 mm, $d_{calc.}$ = 1.27 g cm-1, orthorhombic, space group $P2_12_12_1$ (Nr. 19), a = 7.519(2), b = 13.801(4), c = 26.753(5) Å, V = 2776(1) Å^3, Z = 4, F(000) = 1128. A total of 5419 reflections were recorded on an Enraf-Nonius CAD4 diffractometer (graphite monochromator, λ=(Cu-Kα) = 1.54178 Å), μ(Cu-Kα) = 0.61 mm^{-1})1 at T = 293 K. Of these, 4717 independent reflections were used for the structure solution (SHELXTL-Plus[20]) and refinement (368 parameters, SHELXL-93[21]). Non-hydrogen atoms were refined anisotropically (full-matrix least-squares refinements on F^2); H atoms were refined using a riding model, HCO were applied free, wR2 = 0.149 (R for I>2σ(I) = 0.052). Largest difference peak 0.20 and -0.15 eÅ^{-3}. The absolute configuration could not be determined due to the absence of atoms normally used for anomalous X-ray diffraction. An absorption correction on the basis of Ψ-scans ($T_{max/min}$= 1.000/0.411) and an extinction correction were applied.

[15] All semiempirical NDDO-MO calculations were performed with a modified version of the MOPAC 6.0 program system (J. J. P. Stewart, *QCPE Bull.*, **1985**, *5*, 133). The molecular geometries used for the calculation of the CD spectra were completely optimized with the semiempirical AM1 Hamiltonian (Dewar et al). All structural parameters including the hydrogen bond in (1) are in good agreement with experimental X-ray data (RO-O = 2,78Å, O··H-O = 138°). Subsequent multi-reference singles+double configuration interaction calculations (MRD-CI) were performed in the standard manner of Buenker and Peyerimhoff (*Theoret. Chim. Acta* **1974**, *35*, 33; **1975**, *39*, 217) using the MOs and one- and two-electron integrals from a semiempirical NDDO calculation. The atomic parameters in the NDDO Hamiltonian have been reoptimized for a description of excited states of organic molecules (the parameter set is based on an orginal PM3 set). As one-particle basis functions in the CI treatment ground state SCF MOs have been employed. To reduce the computational effort in the MRD-CI treatment only the highest lying occupied and the lowest lying virtual MOs have been included (20 electrons were distributed in 32 MOs). With 57 reference configurations for the lowest twelve states a MRD-CI space of 2x10^6 configurations was generated from which 23797 state functions were selected and treated variationally in the CI expansion. Oscillator and rotatory strengths were then calculated with this CI wavefunction using the deorthogonalized NDDO-AO basis as described in ref 17.

[16] S. Grimme, S. D. Peyerimhoff, S. Bartram, F. Vögtle, A. Breest, J. Hormes, *J. Chem. Phys. Lett.* **1993**, *213*,32; S. Grimme, I. Pischel, F. Vögtle, M. Nieger, *J. Amer. Chem. Soc.* **1995**, *117*, 157-162; S. Grimme, R. Lemmerz, F. Vögtle, *Chem. Ber.* **1994**, *127*, 2081-2088.

[17] G. Snatzke, *Tetrahedron*, **1965**, *21*, 413-450.

[18] H. Falk, P. Reich-Rohrwig, K. Schlögl, *Tetrahedron* **1970**, *26*, 511-527.

[19] M. Watkinson, A. Whiting, C. A. McAuliffe, *J. Chem. Soc. Chem. Commun.* **1994**, 2141-2143.

[20] G. M. Sheldrick, *SHELXTL-Plus*, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, **1989**.

[21] G. M. Sheldrick, *SHELXL-93*, Universität Göttingen, **1993**.

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