Electronic Supplementary Information (ESI) of the manuscript:

Shape persistent macrocycles comprising perfluorinated benzene subunits: synthesis, aggregation behaviour and unexpected μ-rod formation

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1. Concentration and temperature dependent ^{1}H-NMR investigations

Chemical shifts of the *exo*-annular and the *endo*-annular protons of the macrocycle **2**-**4** and **6** at different concentrations and temperatures are listed in **Table 1** to **4**. Chemical shifts for the monomer (δ_{Mono}) and the dimer (δ_{Dim}) or association (δ_{Ass}) as well as the dimerization constants (K_{Dim}) or association constants (K_{Ass}) at different temperatures were obtained by fitting the data to the equation 1 for larger aggregation of cycle **2** and equation 2 for cycle **3**, **4** and **6** according to the dimer-model below applying the Origin® software from Microcal™.

Equation 1: $\delta = \delta_{Mono} + (\delta_{Ass} - \delta_{Mono})\ [1+\{(1-(4\cdot K_{Ass}\cdot C_{tot} + 1)^{1/2}/(2\cdot K_{Ass}\cdot C_{tot})\}]$

Equation 2: $\delta = \delta_{Mono} + (\delta_{Dim} - \delta_{Mono})\ [1+\{(1-(8\cdot K_{Dim}\cdot C_{tot} + 1)^{1/2}/(4\cdot K_{Dim}\cdot C_{tot})\}]$

Table 1. Chemical shifts of *exo*-annular (H_b) and the *endo*-annular (H_a) protons of cycle **2** at different concentrations and temperatures, calculated chemical shifts for monomer, aggregation and association constants.

Temp (°C)	40		30		20		10		0	
Conc.[a]	H_a	H_b	H_a	H_b	H_a	H_b	H_a	H_b	H_a	H_b
4,621	7,717	7,557	7,699	7,54	7,669	7,515	7,631	7,482	7,576	7,435
4,33	7,718	7,558	7,701	7,542	7,673	7,52	7,633	7,484	7,58	7,441
4,124	7,719	7,559	7,702	7,543	7,675	7,521	7,636	7,487	7,583	7,443
3,883	7,72	7,56	7,703	7,545	7,677	7,523	7,638	7,489	7,592	7,45
3,596	7,721	7,561	7,705	7,546	7,681	7,526	7,642	7,493	7,595	7,454
3,351	7,722	7,562	7,708	7,548	7,683	7,528	7,647	7,496	7,604	7,46
3,064	7,723	7,563	7,709	7,55	7,687	7,531	7,653	7,5	7,609	7,463
2,771	7,725	7,564	7,712	7,552	7,689	7,533	7,655	7,502	7,614	7,469
2,578	7,726	7,565	7,714	7,554	7,694	7,536	7,661	7,507	7,621	7,474
2,377	7,727	7,566	7,717	7,556	7,697	7,539	7,666	7,512	7,627	7,477
2,104	7,728	7,567	7,718	7,557	7,7	7,541	7,672	7,518	7,633	7,484
1,792	7,73	7,568	7,719	7,559	7,702	7,544	7,676	7,525	7,64	7,49
1,409	7,732	7,569	7,724	7,564	7,71	7,548	7,689	7,533	7,655	7,503
0,989	7,734	7,571	7,728	7,566	7,716	7,553	7,7	7,541	7,674	7,52
0,503	7,735	7,574	7,731	7,57	7,722	7,562	7,708	7,55	7,695	7,542
δ_{Mono}[b]	7,738 ±0,001	7,576 ±0,001	7,736 ±0,001	7,575 ±0,001	7,731 ±0,001	7,568 ±0,001	7,727 ±0,003	7,566 ±0,003	7,729 ±0,003	7,572 ±0,004
δ_{Ass}[c]	7,293 ±0,28	7,187 ±0,264	7,247 ±0,263	7.187 ±0,129	7,095 ±0,195	7,203 ±0,082	7,277 0,075	7,184 ±0,062	7,211 ±0,037	7,200 ±0,021
K[d]	11,8 ±8,4	11,0 ±8,2	19,6 ±12,8	23,4 ±9,8	25,6 ±9,8	41,4 ±13,2	76,8 ±22,2	82,0 ±24,2	122,2 ±19,2	190,6 ±29,2
K_{Ass}[e]	11,4 ±8,8		21,4 ±14,6		33,4 ±21,2		79,4 ±26,8		156,4 ±63.4	

[a] Total concentration of cycle **2** (in mM). [b] calculated chemical shift for the aromatic proton of monomer. [c] calculated chemical shift (in ppm) for the aromatic proton of the aggregates. [d] calculated aggregation constant (in M^{-1}) for different protons. [e] Average association constant (in M^{-1})

From **Fig. 1** , we get A = -15.46 ± 0.82, B = 5602.4 ± 239.5

Here, A = ΔS/R, B = -ΔH/R (R: 8.314 $Jmol^{-1}K^{-1}$)

Thus, it can be calculated that, ΔS = A×R = -15.46 × 8.314 = -128.5 ± 6.8 $J{\cdot}mol^{-1}{\cdot}K^{-1}$,

ΔH = - B×R = 5602.4 × 8.314/1000 = - 46.6 ± 2.0 KJ · mol^{-1},

and at 20°C , $\Delta G_{293\,k}$ = ΔH - TΔS = - 46.6 – 293* (-128.5)/1000 = -8.9 ± 4.0 KJ · mol^{-1}.

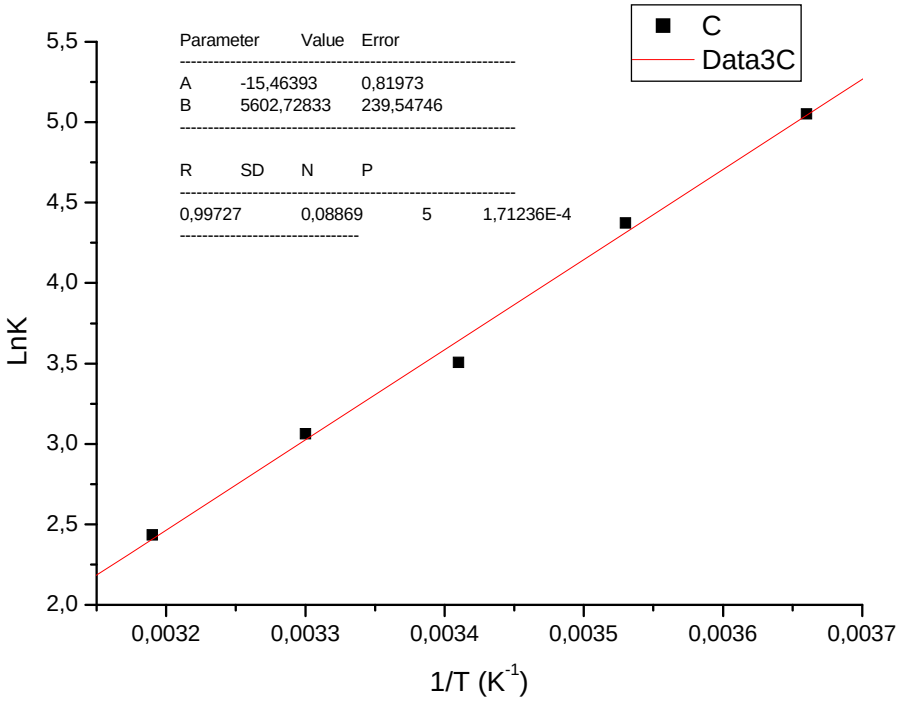

Fig. 1. *Van`t Hoff* plot for self-assembly of cycle **2** in $CDCl_3$

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Table 2. Chemical shifts of *exo*-annular (H_b) and the *endo*-annular (H_a) protons of SPM **3** at different concentrations and temperatures, calculated chemical shifts for monomer and dimer as well as dimerization constants.

Temp (°C)	25		15		5		-5		-15	
Conc.[a]	H_a	H_b	H_a	H_b	H_a	H_b	H_a	H_b	H_a	H_b
1,59	7,545	7,317	7,501	7,248	7,456	7,194	7,402	7,123	7,331	7,052
1,08	7,563	7,326	7,528	7,279	7,484	7,228	7,415	7,151	7,35	7,068
0,83	7,572	7,335	7,545	7,297	7,503	7,255	7,443	7,182	7,369	7,094
0,63	7,579	7,339	7,557	7,313	7,521	7,271	7,463	7,208	7,391	7,128
0,48	7,583	7,346	7,565	7,32	7,534	7,288	7,479	7,226	7,412	7,153
0,35	7,588	7,349	7,574	7,331	7,549	7,306	7,51	7,243	7,45	7,194
0,27	7,591	7,352	7,579	7,336	7,559	7,318	7,527	7,285	7,477	7,228
0,2	7,594	7,355	7,584	7,343	7,567	7,327	7,539	7,3	7,493	7,25
0,15	7,597	7,355	7,589	7,346	7,576	7,331	7,548	7,31	7,512	7,267
δ_{Mono}[b]	7,602 ±0,001	7,361 ±0,001	7,598 ±0,001	7,357 ±0,001	7,759 ±0,001	7,358 ±0,003	7,617 ±0,021	7,394 ±0,026	7,675 ±0,066	7,432 ±0,058
δ_{Dim}[c]	5,984 ±1,28	5,178 ±1,95	6,498 ±0,368	5,859 ±0,538	7,264 ±0,021	6,646 ±0,088	7,185 0,055	6,869 ±0,062	7,167 ±0,099	6,822 ±0,067
K[d]	11,6 ±9,9	9,8 ±9,3	39,3 ±11,2	26,6 ±11	182,0 ±15,2	123 ±25	678 ±304	707 ±311	2174 ±1347	1556 ±834
K_{Dim}[e]	10,7 ±10,8		32,9 ±12,8		152,5 ±54,5		692,5 ±325,5		1865 ±1656	

[a] Total concentration of cycle **3** (in mM). [b] calculated chemical shift for the aromatic proton of monomer. [c] calculated chemical shift (in ppm) for the aromatic proton of dimer. [d] calculated dimerization constant (in M^{-1}) for different protons. [e] Average dimerization constant (in M^{-1})

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From **Fig. 2**, we get A = -31.9 ± 1.9, B = 10260 ± 541.

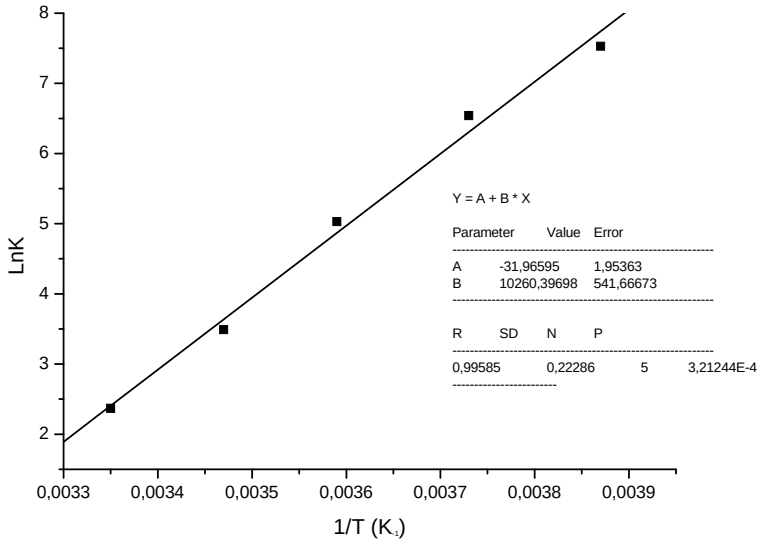

Fig. 2. *Van`t Hoff* plot for self- assembly of cycle **3** in $CDCl_3$

Here, $A = \Delta S/R$, $B = -\Delta H/R$ (R: 8.314 $Jmol^{-1}K^{-1}$)

So, it can be calculated that, $\Delta S = A \times R = -31.9 \times 8.314 = -265.2 \pm 15.7\ J \cdot mol^{-1} \cdot K^{-1}$,

$\Delta H = - B \times R = 10488 \times 8.314/1000 = - 85.3 \pm 4.4\ KJ \cdot mol^{-1}$,

and at 20°C , $\Delta G_{293\ k} = \Delta H - T\Delta S = - 85.3 – 293^* (-265.2)/1000 = -7.6 \pm 4.8\ KJ \cdot mol^{-1}$.

$K_{20} = 22.6\ (M^{-1})$

Table 3. Chemical shifts of *exo*-annular (H_b) and the *endo*-annular (H_a) protons s of SPM **4** at different concentrations and temperatures, calculated chemical shifts for monomer, dimer and association constants.

Temp (°C)	40		30		20		10		0	
Conc.[a]	H_a	H_b	H_a	H_b	H_a	H_b	H_a	H_b	H_a	H_b
27,4	7,397	6,777	7,344	6,686	7,286	6,589	7,223	6,485	7,17	6,397
24,96	7,405	6,785	7,354	6,7	7,292	6,597	7,233	6,498	7,177	6,406
22,84	7,417	6,805	7,362	6,711	7,3	6,609	7,24	6,509	7,185	6,416
20,43	7,435	6,834	7,373	6,728	7,31	6,623	7,247	6,52	7,188	6,422
18,57	7,451	6,858	7,387	6,75	7,322	6,641	7,258	6,535	7,195	6,431
16,7	7,458	6,869	7,399	6,768	7,331	6,655	7,265	6,546	7,203	6,442
14,79	7,469	6,896	7,412	6,789	7,345	6,676	7,278	6,565	7,213	6,457
12,88	7,479	6,903	7,426	6,811	7,358	6,696	7,292	6,586	7,226	6,475
11,15	7,493	6,927	7,444	6,839	7,374	6,721	7,306	6,605	7,239	6,494
9,42	7,52	6,968	7,456	6,857	7,39	6,745	7,321	6,63	7,25	6,513
8,13	7,543	7,008	7,477	6,892	7,405	6,772	7,335	6,648	7,267	6,531
6,724	7,56	7,038	7,497	6,927	7,427	6,804	7,352	6,678	7,279	6,557
5,417	7,581	7,074	7,523	6,968	7,451	6,842	7,378	6,718	7,299	6,587
4,296	7,592	7,098	7,548	7,012	7,479	6,889	7,399	6,752	7,323	6,619
2,044	7,668	7,207	7,618	7,135	7,562	7,001	7,482	6,892	7,4	6,745
δ_{Mono}[b]	7,756 ±0,016	7,352 ±0,024	7,737 ±0,007	7,377 ±0,016	7,745 ±0,008	7,247 ±0,014	7,667 ±0,013	7,293 ±0,029	7,622 ±0,021	7,199 ±0,036
δ_{Dim}[c]	7,09 ±0,035	6,268 ±0,053	7,077 ±0,012	6,300 ±0,025	7,075 ±0,014	6,244 ±0,022	7,04 0,022	6,235 ±0,052	7,026 ±0,037	6,200 ±0,067
K[d]	45,4 ±8,2	44,2 ±7,8	65,7 ±4,8	91,6 ±7,6	127,3 ±7,7	104,9 ±8,0	148,0 ±13,9	243,0 ±25,2	231,2 ±31,1	375,4 ±45,1
K_{Dim}[e]	44,8 ±8,8		78,6 ±20,6		116,1 ±19,2		195,5 ±72,7		303,3 ±117	

[a] Total concentration of cycle **4** (in mM). [b] calculated chemical shift for the aromatic proton of monomer. [c] calculated chemical shift (in ppm) for the aromatic proton of dimer. [d] calculated dimerization constant (in M^{-1}) for different protons. [e] Average dimerization constant (in M^{-1}).

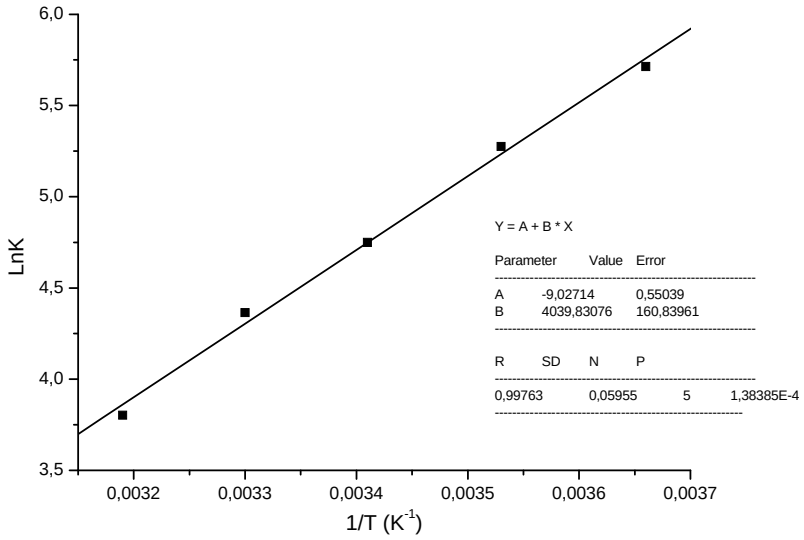

Fig. 3. *Van`t Hoff* plot for self- assembly of cycle **4** in $CDCl_3$.

From Fig. 3, we get A = -9.03 ± 0.55, B = 4039 ± 160

Here, $A = \Delta S/R$, $B = -\Delta H/R$ (R: 8.314 $Jmol^{-1}K^{-1}$)

So, it can be calculated that, $\Delta S = A \times R = -9.03 \times 8.314 = -75.1 \pm 4.6\ J \cdot mol^{-1} \cdot K^{-1}$,

$\Delta H = - B \times R = 4029 \times 8.314/1000 = - 33.6 \pm 1.3\ KJ \cdot mol^{-1}$,

and at 20°C , $\Delta G_{293\ k} = \Delta H - T\Delta S = - 33.6 – 293^* (-75.1)/1000 = -11.6 \pm 2.7\ KJ \cdot mol^{-1}$.

Table 4. Chemical shifts of *exo*-annular (H_b) and the *endo*-annular (H_a) protons of SPM **6** at different concentrations and temperatures, calculated chemical shifts for monomer, dimer and association constants.

Temp (°C)	4 0		30		20		10		0	
Conc.[a]	H_a	H_b	H_a	H_b	H_a	H_b	H_a	H_b	H_a	H_b
2	7,673	7,184	7,627	7,123	7,56	7,03	7,502	6,957	7,423	6,864
1,886	7,676	7,189	7,634	7,131	7,577	7,051	7,507	6,962	7,431	6,882
1,752	7,6802	7,198	7,646	7,148	7,582	7,058	7,514	6,971	7,442	6,889
1,584	7,692	7,221	7,656	7,163	7,596	7,078	7,523	6,983	7,452	6,899
1,397	7,699	7,236	7,669	7,181	7,609	7,095	7,538	7,001	7,467	6,919
1,223	7,708	7,246	7,68	7,198	7,62	7,113	7,551	7,02	7,48	6,929
1,055	7,716	7,257	7,685	7,212	7,638	7,131	7,571	7,043	7,49	6,945
0,909	7,721	7,273	7,701	7,231	7,65	7,152	7,585	7,063	7,512	6,971
0,773	7,726	7,28	7,713	7,252	7,667	7,176	7,606	7,089	7,532	6,995
0,634	7,734	7,29	7,722	7,263	7,686	7,207	7,627	7,122	7,554	7,028
0,351	7,753	7,321	7,745	7,3	7,723	7,257	7,682	7,198	7,62	7,112
0,184	7,76	7,335	7,755	7,323	7,748	7,302	7,728	7,243	7,69	7,205
δ_{Mono}[b]	7,77 ±0,003	7,359 ±0,006	7,778 ±0,005	7,356 ±0,005	7,79 ±0,006	7,359 ±0,008	7,808 ±0,006	7,345 ±0,014	7,839 ±0,013	7,449 ±0,030
δ_{Dim}[c]	6,653 ±0,448	6,178 ±0,482	6,88 ±0,243	6,081 ±0,181	7,09 ±0,062	6,368 ±0,073	7,159 0,017	6,481 ±0,048	7,16 ±0,021	6,576 ±0,046
K[d]	26,6 ±12,9	49,9 ±24,8	58,6 ±23,1	67,2 ±14,6	173,3 ±33,1	179,0 ±28,5	434,0 ±37,2	386,0 ±66,2	983,2 ±117,1	1461,4 ±254,0
K_{Dim}[e]	38,2 ±36.4		62,9 ±27,4		176,2 ±35,9		410,0 ±90,2		1222,3 ±493	

[a] Total concentration of cycle **6** (in mM). [b] calculated chemical shift for the aromatic proton of monomer. [c] calculated chemical shift (in ppm) for the aromatic proton of dimer. [d] calculated dimerization constant (in M^{-1}) for different protons. [e] Average dimerization constant (in M^{-1})

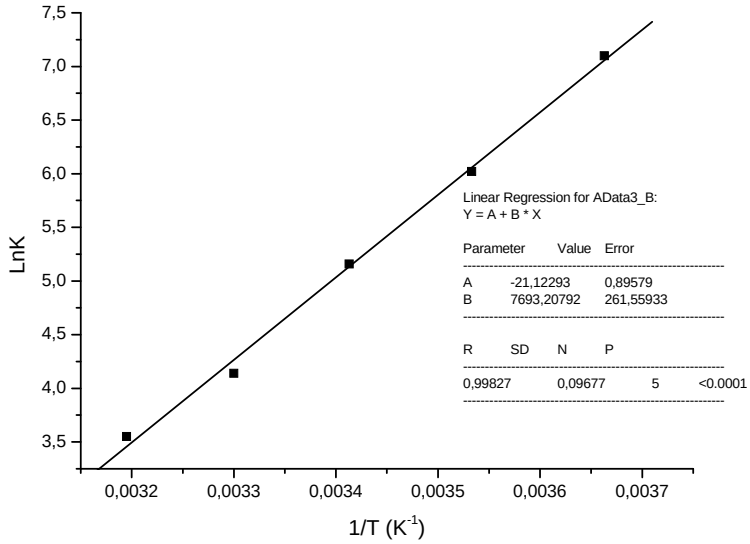

Fig. 4. *Van`t Hoff* plot for self- assembly of cycle **6** in $CDCl_3$.

From Fig. 4, we get A = -20.8 ± 1.0, B = 7611.2 ± 311.9

Here, A = ΔS/R, B = -ΔH/R (R: 8.314 $Jmol^{-1}K^{-1}$)

So, it can be calculated that, ΔS = A×R = -20.8 × 8.314 = -172.9 ± 8.3 $J{\cdot}mol^{-1}{\cdot}K^{-1}$,

ΔH = - B×R = 7611.2 × 8.314/1000 = - 63.3 ± 2.5 $KJ \cdot mol^{-1}$,

and at 20°C , $\Delta G_{293\,k}$ = ΔH - TΔS = - 63.3 – 293* (-172.9)/1000 = -12.6 ± 4.9 $KJ \cdot mol^{-1}$.

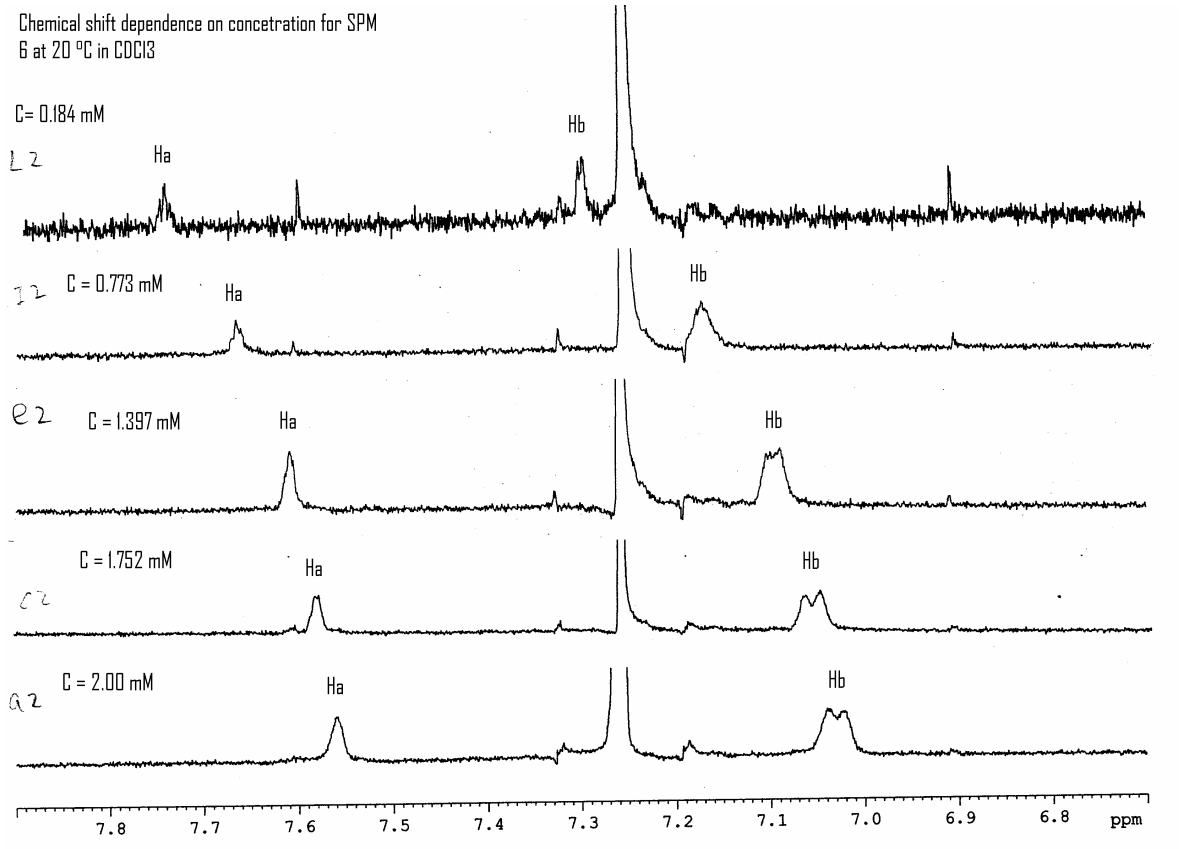

Fig. 5. Aromatic regions of the ^{1}H-NMR spectra of SPM **6** in various concentrations in $CDCl_3$ at 20°C. The series of spectra illustrates the concentration dependent chemical shifts of the *exo*-annular (H_b) and the *endo*-annular (H_a) protons.

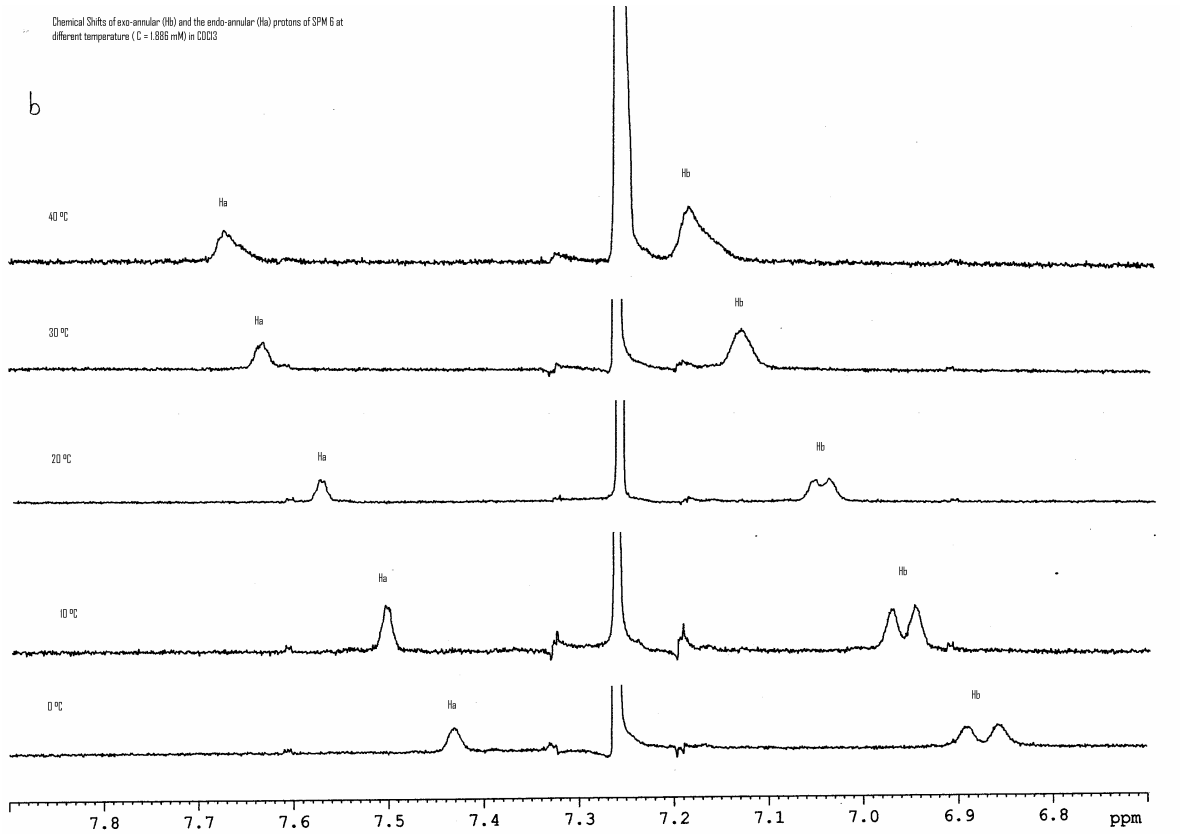

Fig. 6. Aromatic regions of the ^{1}H-NMR spectra of SPM **6** (1.866 mM) in $CDCl_3$ recorded at various temperature. The series of spectra illustrates the temperature dependence of the chemical shifts of the *exo*-annular (H_b) and the *endo*-annular (H_a) protons.

2. Determination of the solubility of cycle 1-6 in chloroform at 20 °C

The solubility of various SPMs was determined by the weight of added CHCl3 required to dissolve a known amount of the SPM under investigation. The procedure was the following: To a 5 mL small bottle with cap was added certain SPM. Subsequently, a small portion of $CHCl_3$ was added and the sample was shacked extensively for some minutes and put it to a 20 °C water bath for several minutes. This process is repeated until the sample was dissolved completely. Then the weight of $CHCl_3$ added was weighted.

For example, 3.8 mg of SPM **3** with a molecular weight of 1225 g mol^{-1} were deposited in the 5 mL flask.

Thus, 0.0038 g / 1225 g mol^{-1} = $3.1 \cdot 10^{-6}$ mol SPM **3** were in the flask.

To dissolve this portion completely 2.33 g $CHCl_3$ were required. With the density of $CHCl_3$ of 0.6773 mL/g this corresponds to 1.58 mL $CHCl_3$.

The concentration of SPM **3** is given as:

0.0031 mmol/1.58 mL = 0.00196 mol/L or 1.96 mmol/L.

Table 5 : Solubility of macrocycle **1-6** in $CHCl_3$ at 20 °C

	SPM **1**	SPM **2**	SPM **3**	SPM **4**	SPM **5**	SPM **6**
Solubility[a] mM(mMol/L)	2,75	5,15	1,96	31,0	25,1	2,64

3. Data of Figure 2

Table 6: Data for the concentration dependentce of the ^{1}H NMR chemical shifts of the *endo*-annular protons (δ_A)of the macrocycles **1-6** in $CDCl_3$ at 10 °C (in Figure 2)

SPM **1**		SPM **2**		SPM **3**		SPM **4**		SPM **5**		SPM **6**	
C[a]	δ_A[b]	C	δ_A	C	δ_A	C	δ_A	C	δ_A	C	δ_A
1,724	7,743	4,621	7,631	1,59	7,476	27,4	7,223	11,062	7,057	2	7,502
1,438	7,744	4,33	7,633	1,08	7,506	24,96	7,233	10,257	7,06	1,886	7,507
1,152	7,744	4,124	7,636	0,83	7,521	22,84	7,24	9,4681	7,064	1,752	7,514
0,815	7,745	3,883	7,638	0,63	7,539	20,43	7,247	8,7936	7,069	1,584	7,523
0,387	7,744	3,596	7,642	0,48	7,548	18,57	7,258	7,8944	7,073	1,397	7,538
0,208	7,745	3,351	7,647	0,35	7,568	16,7	7,265	6,8039	7,083	1,223	7,551
		3,064	7,653	0,27	7,572	14,79	7,278	6,0767	7,087	1,055	7,571
		2,771	7,655	0,2	7,577	12,88	7,292	4,9521	7,101	0,909	7,585
		2,578	7,661	0,15	7,584	11,15	7,306	4,163	7,11	0,773	7,606
		2,377	7,666			9,42	7,321	3,6155	7,121	0,634	7,627
		2,104	7,672			8,13	7,335	2,9563	7,14	0,351	7,682
		1,792	7,676			6,724	7,352	2,3963	7,153	0,184	7,728
		1,409	7,689			5,417	7,378	1,8382	7,181		
		0,989	7,7			4,296	7,399	1,342	7,211		
		0,503	7,708			2,044	7,482	0,9125	7,254		
								0,6232	7,302		

[a]C (concentration of cycles in mM), [b]δ_A (chemical shifts in ppm)

4. Data of Figure 3

Table 7: Data for the v*an´t Hoff* plot for **Figure 3**

SPM **2**		SPM **3**		SPM **4**		SPM **5**		SPM **6**	
1/T[a]	LnK[b]	1/T	LnK	1/T	LnK	1/T	LnK	1/T	LnK
0,00319	2,434	0,00335	2,37	0,00319	3,802	0,00319	5,624	0,00319	3,64
0,0033	3,063	0,00347	3,49	0,0033	4,364	0,0033	6,633	0,0033	4,14
0,00341	3,508	0,00359	5,03	0,00341	4,75	0,00341	7,536	0,00341	5,17
0,00353	4,374	0,00373	6,54	0,00353	5,275	0,00353	8,377	0,00353	6,02
0,00366	5,052	0,00387	7,53	0,00366	5,714	0,00366	9,273	0,00366	7,1

[a]T (K), [b]K (M^{-1}).