Supplementary Information

Structural Characterization of a Peptoid with Lysine-like Side Chains and Biological Activity using NMR and Computational Methods

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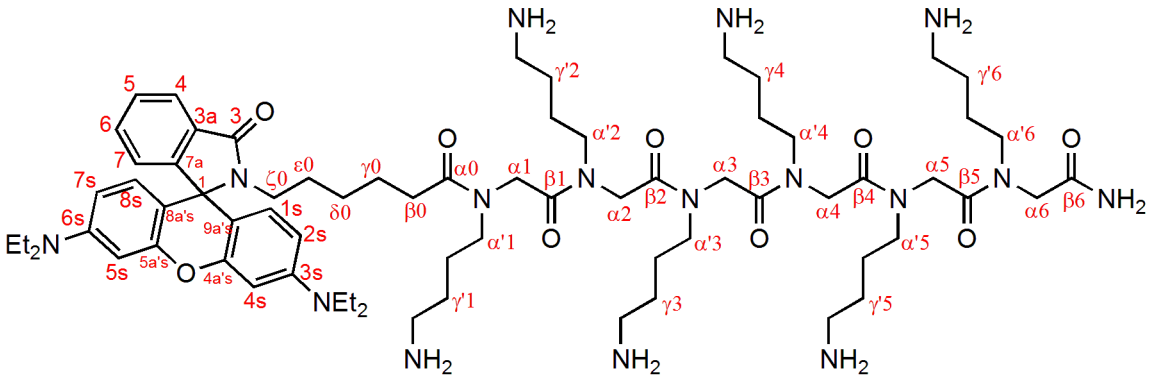

Figure S1: Structure of Rhodamine B-labeled oligo-N-substituted glycine [RhoBSpiro Ahx] $[BUT]_{6A}NH_2$

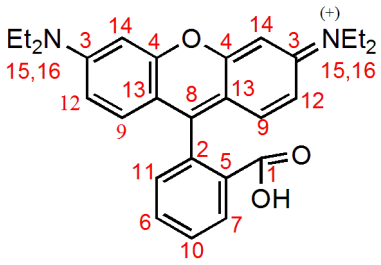

Figure S2: Structure of Rhodamine B. Atom labels were taken from the Spectral Database for Organic Compounds, SDBS No.: 15673 (http:// riodb01.ibase.aist.go.jp/sdbs/)

Table S1: Distances derived from NOESY spectra

Atom1	Atom 2	Distance [Å]
Hα[1,2] Gly [1-6]	Hα[1,2] Gly [1-6]	4.0±1
Hα[1,2] Gly [1-6]	Hα´[1,2] Lys [1-6]	2.5±1
Hα[1,2] Gly [1-6]	Hβ´[1,2] Lys [1-6]	4.5±1

Table S2: Calculated and experimental ^{13}C chemical shifts for the lowest energy structure.

Atom	***cis*-amide conformation**		***trans*-amide conformation**	
	Calculated chemical shift (ppm)	Experimental chemical shift (ppm)	Calculated chemical shift (ppm)	Experimental chemical shift (ppm)
Cα0	173.7	173.0	173.2	173.0
Cβ0	38.4	40.4	39.5	40.4
Cγ0	27.6	25.4	27.4	25.4
Cδ0	31.2	27.6	30.2	27.6
Cε0	29.0	27.1	29.3	27.1
Cζ0	42.2	41.1	41.5	41.1
Cβ_GLY_1	172.7	173.0	172.4	171.8
Cβ_GLY_2	171.3	170.9	172.0	171.8
Cβ_GLY_3	173.1	173.0	172.9	173.0
Cβ_GLY_4	172.2	171.8	171.4	170.9
Cβ_GLY_5	172.2	171.8	173.3	173.0
Cβ_GLY_6	not calculated[1]	not assigned	not calculated[1]	not assigned
Cα_GLY_1	49.1	47.5	48.8	49.2
Cα_GLY_2	49.4	48.9	48.7	47.5
Cα_GLY_3	48.8	47.7	48.9	48.6
Cα_GLY_4	49.1	48.6	49.1	48.9
Cα_GLY_5	49.5	49.2	48.6	47.7
Cα_GLY_6	49.5	49.2	49.3	49.2
Cβ'_LYS_6	29.4	24.3	28.8	23.6
Cγ_LYS_6	29.4	23.6	29.5	24.3
Cδ'_LYS_6	39.1	39.9	38.9	39.2
Cα'_LYS_6	41.9	47.7	42.2	48.1
Cβ'_LYS_5	28.9	23.6	29.2	24.3
Cγ_LYS_5	29.9	24.3	29.8	23.6
Cδ'_LYS_5	39.3	39.9	38.7	39.2
Cα'_LYS_5	41.6	47.7	41.9	47.9
Cβ'_LYS_4	28.8	24.3	29.2	24.3
Cγ_LYS_4	30.1	23.6	29.7	24.3
Cδ'_LYS_4	39.2	39.9	39.3	39.9
Cα'_LYS_4	42.0	47.9	41.7	47.7
Cβ'_LYS_3	29.7	23.6	29.9	24.3
Cγ_LYS_3	29.8	24.3	29.3	23.6
Cδ'_LYS_3	38.1	39.2	38.8	39.9
Cα'_LYS_3	41.5	47.2	41.9	47.7
Cβ'_LYS_2	28.7	23.6	30.3	23.6
Cγ_LYS_2	29.9	24.3	28.8	24.3
Cδ'_LYS_2	38.9	39.2	38.8	39.9
Cα'_LYS_2	42.1	48.1	41.2	47.2
Cβ'_LYS_1	29.9	23.6	29.3	23.6
Cγ_LYS_1	28.7	24.3	29.6	23.6
Cδ'_LYS_1	38.7	39.2	38.1	39.2
Cα'_LYS_1	42.3	48.1	42.4	48.1
C3_Rho	155.5	154.4	155.7	154.4
C5_Rho	125.4	125.1	109.1	111.2

C4_Rho	130.3	130.8	129.7	130.8
C3a_Rho	120.7	123.9	130.3	130.3
C7a_Rho	135.9	134.5	119.8	123.9
C7_Rho	123.0	123.9	136.8	134.5
C6_Rho	130.1	130.3	122.9	125.1
C3s_Rho	134.6	134.5	124.7	123.9
C2s_Rho	127.1	130.8	132.5	132.1
C1s_Rho	124.8	123.9	124.4	130.3
C9as_Rho	125.3	123.9	125.8	125.1
C4as_Rho	130.8	130.3	126.7	125.1
C4s_Rho	112.0	114.7	130.7	130.3
C8as_Rho	126.5	125.1	109.5	114.7
C5as_Rho	131.4	130.8	125.7	123.9
C8s_Rho	125.6	125.1	131.1	130.8
C7s_Rho	127.8	130.3	124.5	123.9
C6s_Rho	132.4	132.1	124.5	130.8
C5s_Rho	110.3	111.2	134.8	134.5
C1	excluded[2]	66.7	excluded[2]	66.7

[1]The values are not calculated because a proper parametrization for the C(sp^2)-N(sp^3) bond type was missing.
[2]Excluded because of steric strain.

The spread of the calculated chemical shifts for the backbone atoms between single structures is < 1 ppm (0.6 ppm for CA_Gly_2). As expected, the spread for the side chains is larger, but < 2 ppm (1.4 for C'_Lys).
The observed large difference between calculated and measured CS values of the CAs_Lys stems from the BPT parametrization and cannot attributed to problems within the side chain conformation. A discussion of these effects is outside the scope of this paper.

Table S3: Calculated and experimental ^{13}C chemical shifts of Rhodamin B in D_2O.

Atom[1]	Calculated chemical shift (ppm)	Experimental chemical shift (ppm)
C3_A	157.0	157.0
C4_A	155.0	155.1
C9_A	120.1	130.5
C12_A	116.6	113.6
C13_A	113.9	112.4
C14_A	97.1	95.7
C3_B	156.8	157.0
C4_B	154.8	155.1
C9_B	123.6	130.5
C13_B	113.8	112.4
C14_B	96.6	95.7
C12_B	117.1	113.6
C1	168.8	168.6
C2	156.2	157.0
C6	131.8	132.4
C7	129.0	130.7
C10	130.4	130.1
C11	129.6	129.8
C8	not assigned	
C5	not assigned	
C15	not calculated	
C16	not calculated	

[1]Atoms 3,4, 9,12, 13,14,which occur in both aromatic ring systems cannot be distinguished in the NMR spectra, but yield different CS values in the calculations. Thus they are named A and B, respectively.

Table S4: Summary of the structure investigation

	cis-peptoid	trans-peptoid
Number of calculated models	500	500
Number of selected models	10	10
Number of 13C CS values per model	60	60
RMS calculated CS to experiment	3.36 ppm	3.55 ppm
Quality CS for the 10 best structures[1]	0.55	0.5
Number of assigned NOE distances per model	80	68
RMS of calculated distances to experiment	0.52 Å	0.54 Å
Quality NOE distances for the 10 best structures[1]	3.7	3.28

[1]The quality is calculated according to $Q = n/\chi^2$ with: $\chi^2 = \sum_i^n \left(\frac{Exp_i - Calc_i}{Error_i} \right)^2$