

Spectroscopic characterization of alanyl, homoalanyl, and norvalyl peptide nucleic acid oligomers

H-(AlaG-AlaG-AlaC-AlaG-AlaC-AlaC)-Lys-NH₂ **8**

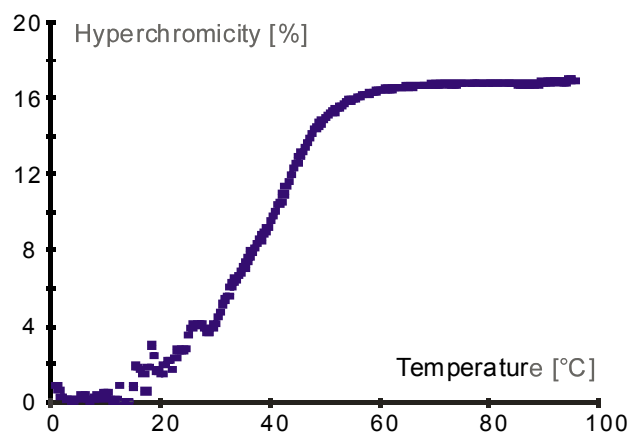


Fig. 1 Oligomer **8**: $T_m = 40^\circ\text{C}$ (12 μM ; 16 %H)

H-(AlaG-AlaG-AlaC-AlaG-AlaC-AlaC)-Lys-NH₂ **8** +
H-(AlaG-AlaG-AlaC-AlaG-AlaC-AlaC)-Lys-NH₂ ent-**8**

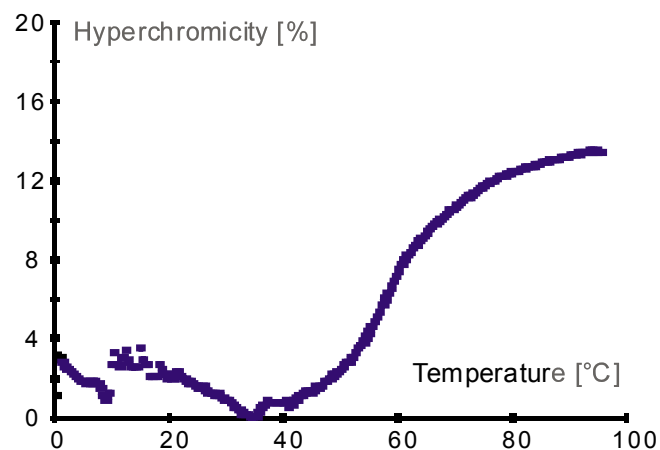


Fig. 2 Oligomers **8** + ent-**8**: $T_m = 58^\circ\text{C}$ (6 μM each; 13 %H)

H-(AlaG-HalG-AlaC-HalG-AlaC-HalC)-Lys-NH₂ ent-**9**

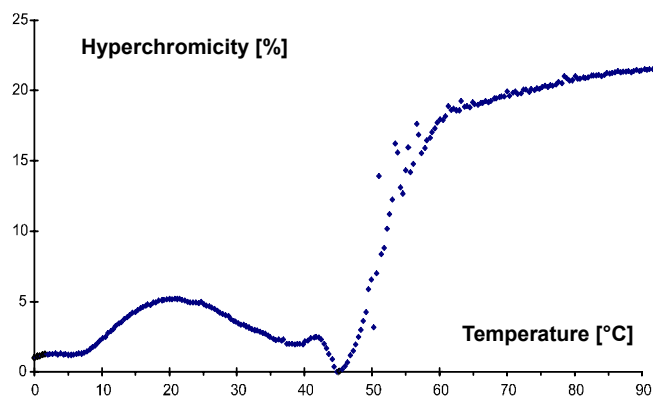


Fig. 3 Oligomer ent-**9**: $T_m = 52^\circ\text{C}$ (12 μM ; 22 %H)

H-(AlaG-HalG-AlaC-HalG-AlaC-HalC)-Lys-NH₂ **9** +
H-(AlaG-HalG-AlaC-HalG-AlaC-HalC)-Lys-NH₂ ent-**9**

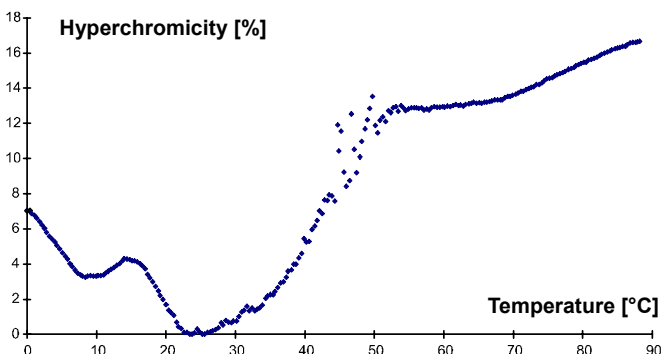


Fig. 4 Oligomers **9** + ent-**9**: $T_m = 42^\circ\text{C}$ (3 μM each; 14 %H)

H-(AlaG-HalG-AlaC-HalG-AlaC-HalC)-Lys-NH₂ ent-9

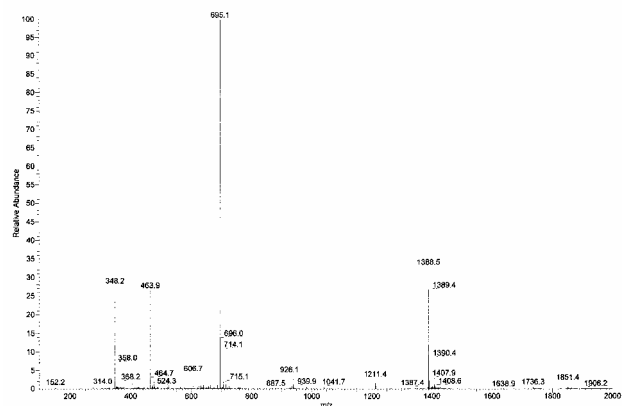


Fig. 5 Oligomer **ent-9**: ESI-MS m/z : 1388.4 $[M + H]^+$

H-(AlaG-HalG-AlaC-HalG-AlaC-HalC)-Lys-NH₂ ent-9

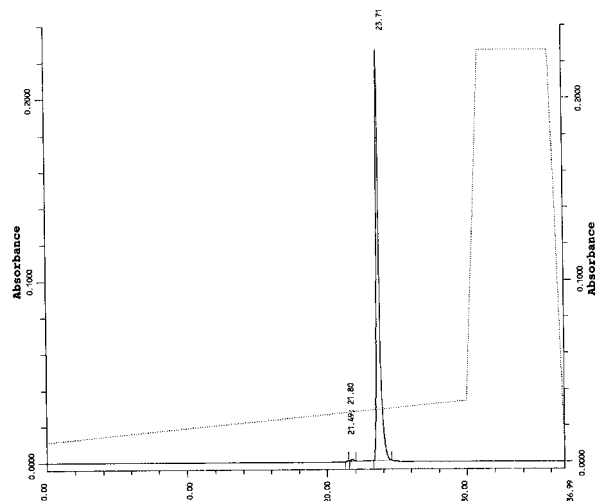


Fig. 6 Oligomer **ent-9**: HPLC (gradient: 5 – 15% B' in 30 min):
 $t_R = 23.7$ min

H-(HalG-HalG-HalC-HalG-HalC-HalC)-Lys-NH₂ 10

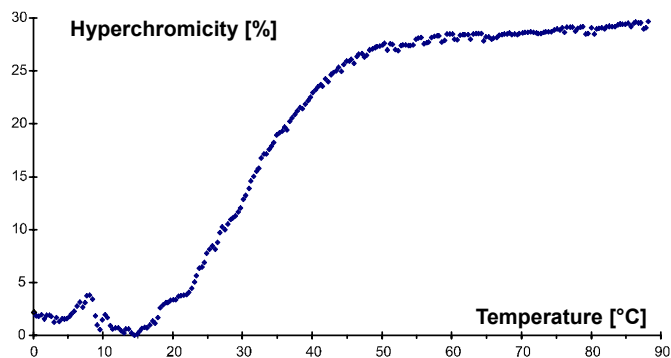


Fig. 7 Oligomer **10**: $T_m = 33$ °C (12 μ M; 28 %H)

**H-(HalG-HalG-HalC-HalG-HalC-HalC)-Lys-NH₂ 10 +
H-(AlaG-HalG-HalC-HalG-HalC-HalC)-Lys-NH₂ ent-10**

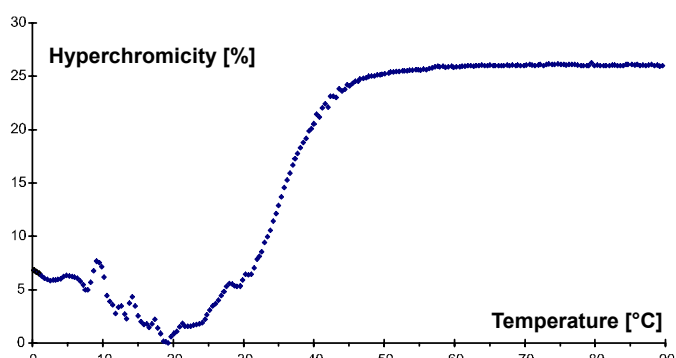


Fig. 8 Oligomers **10** + **ent-10**: $T_m = 37$ °C (6 μ M each; 25 %H)

H-(HalG-HalG-HalC-HalG-HalC-HalC)-Lys-NH₂ 10

H-(HalG-HalG-HalC-HalG-HalC-HalC)-Lys-NH₂ 10

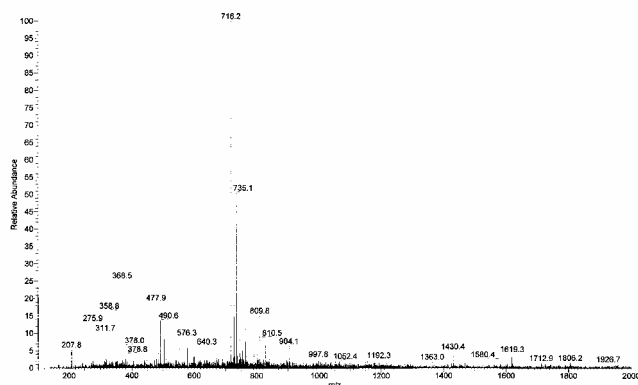


Fig. 9 Oligomer 10: ESI-MS m/z : 716.2 $[M + 2H]^+$

H-(AlaG-NvaG-AlaC-NvaG-AlaC-NvaC)-Lys-NH₂ 11

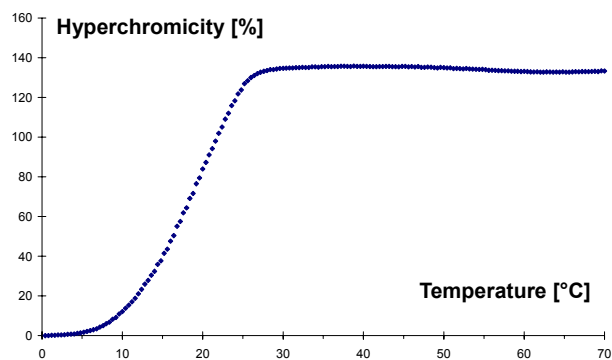


Fig. 11 Oligomer 11: $T_m = 18^\circ\text{C}$ (12 μM ; 135 %H)

H-(AlaG-NvaG-AlaC-NvaG-AlaC-NvaC)-Lys-NH₂ 11

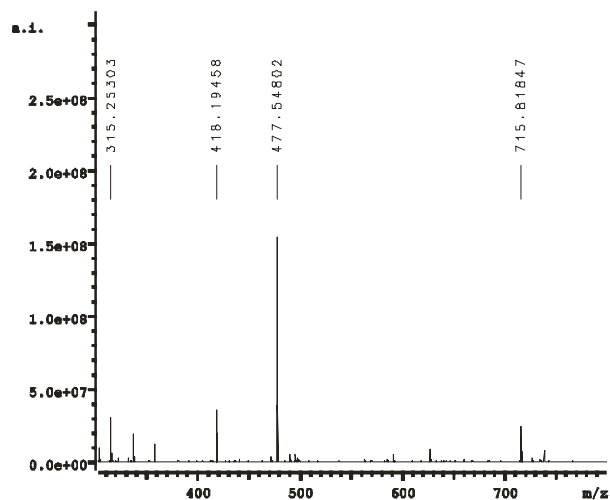


Fig. 13 Oligomer 11: ESI-HRMS calcd for $\text{C}_{57}\text{H}_{75}\text{N}_{33}\text{O}_{13}$ $[M + 2H]^{2+}$ 715.8184, found 715.8185

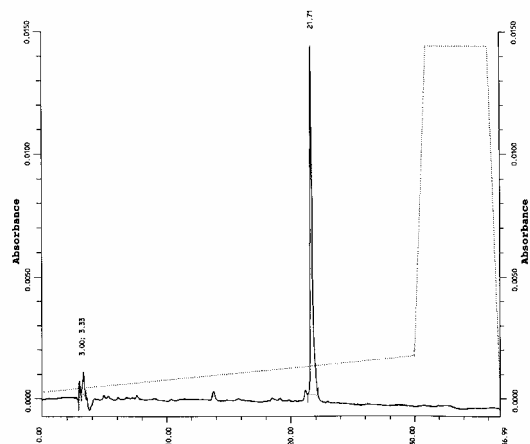


Fig. 10 Oligomer 10: HPLC (gradient: 5 – 15% B' in 30 min):
 $t_R = 21.7$ min

H-(AlaG-NvaG-AlaC-NvaG-AlaC-NvaC)-Lys-NH₂ 11+
H-(AlaG-NvaG-AlaC-NvaG-AlaC-NvaC)-Lys-NH₂ ent-11

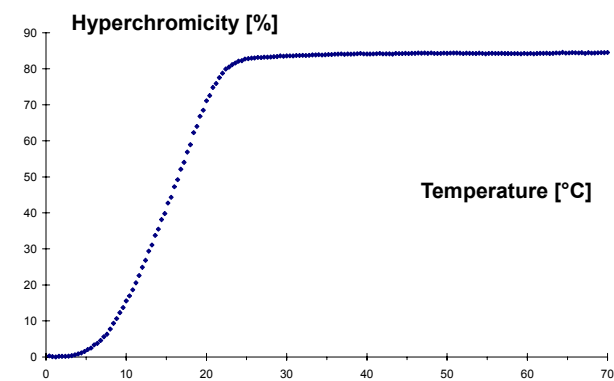
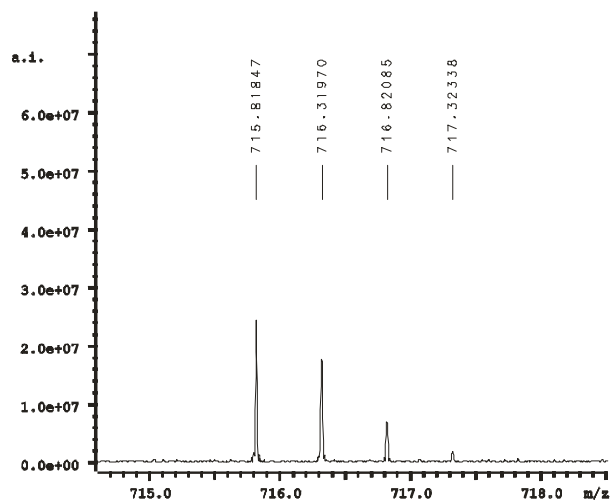


Fig. 12 Oligomers 11 + ent-11: $T_m = 16^\circ\text{C}$ (6 μM each; 85 %H)



H-(AlaG-NvaG-AlaC-NvaG-AlaC-NvaC)-Lys-NH₂ ent-11

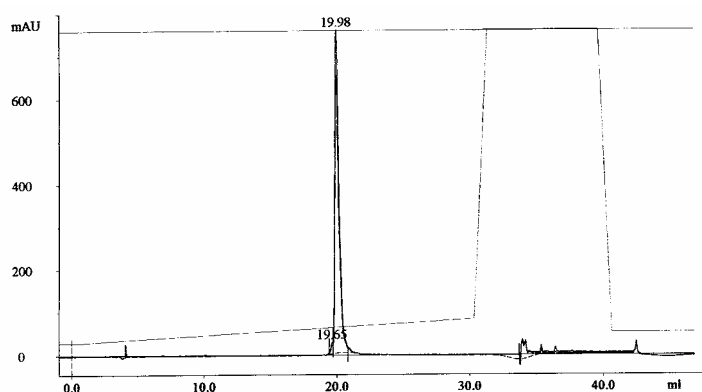


Fig. 14 Oligomer **ent-11**: HPLC (gradient: 7 – 14% B' in 30 min): $t_R = 20.0$ min

H-(NvaG-NvaG-NvaC-NvaG-NvaC-NvaC)-Lys-NH₂ 12

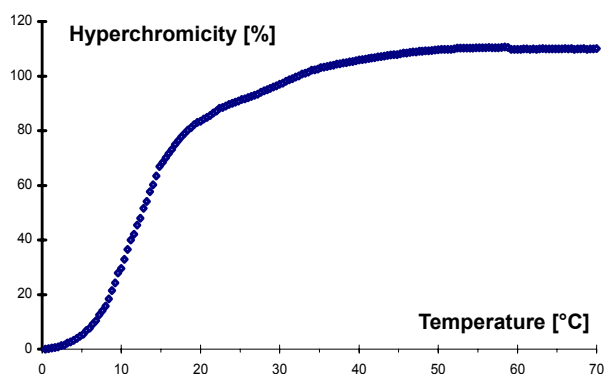


Fig. 15 Oligomer **12**: $T_m = 13$ °C (12 μ M; 90 %H)

**H-(NvaG-NvaG-NvaC-NvaG-NvaC-NvaC)-Lys-NH₂ 12 +
H-(NvaG-NvaG-NvaC-NvaG-NvaC-NvaC)-Lys-NH₂ ent-12**

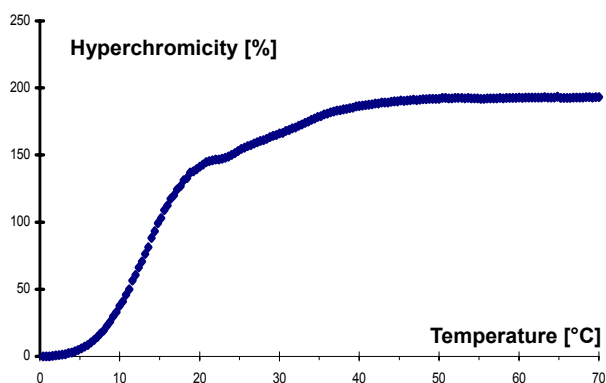


Fig. 16 Oligomers **12** + **ent-12**: $T_m = 15$ °C (6 μ M each; 160 %H)

H-(NvaG-NvaG-NvaC-NvaG-NvaC-NvaC)-Lys-NH₂ 12

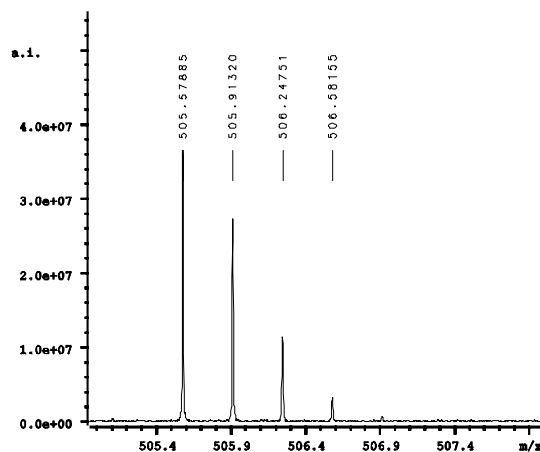
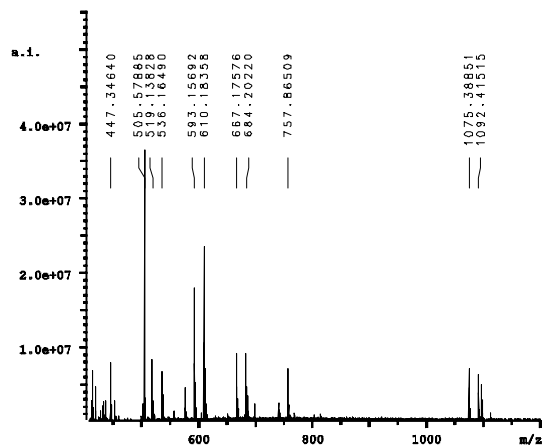


Fig. 17 Oligomer **12**: ESI-HRMS calcd for C₆₃H₈₇N₃₃O₁₃ [M + 3H]³⁺ 505.5793, found 505.5789

H-(NvaG-NvaG-NvaC-NvaG-NvaC-NvaC)-Lys-NH₂ 12

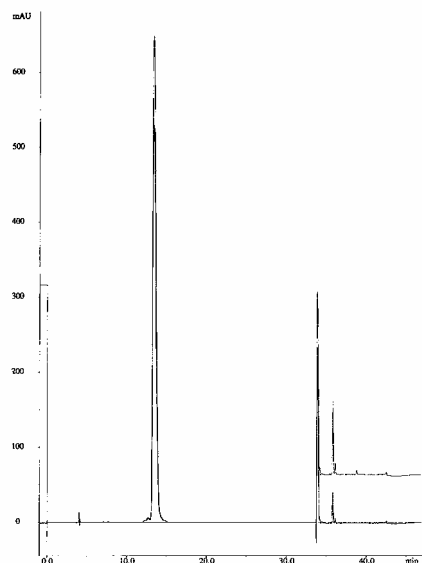


Fig. 18 Oligomer **12**: HPLC (gradient: 10 – 12% B' in 30 min): $t_R = 13.4$ min

H-(AlaA-AlaA-AlaT-AlaA-AlaT-AlaT)-Lys-NH₂ ent-13

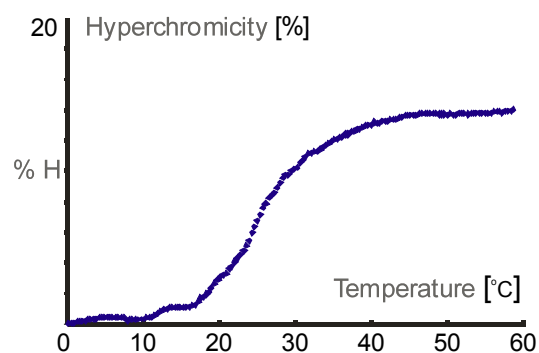


Fig. 19 Oligomer **ent-13**: $T_m = 25$ °C (6 μ M; 14 %H)

**H-(AlaA-AlaA-AlaT-AlaA-AlaT-AlaT)-Lys-NH₂ 13 +
H-(AlaA-AlaA-AlaT-AlaA-AlaT-AlaT)-Lys-NH₂ ent-13**

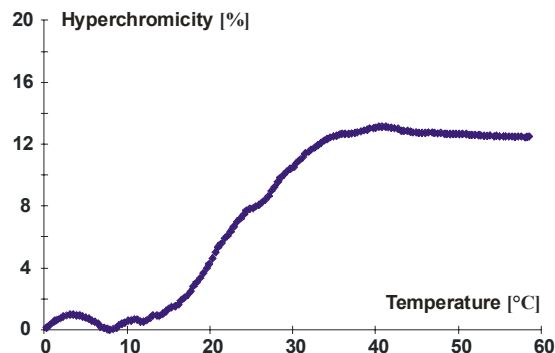


Fig. 20 Oligomers **13** + **ent-13**: $T_m = 25$ °C (6 μ M each; 14 %H)

H-(HalA-HalA-AlaT-HalA-AlaT-AlaT)-Lys-NH₂ 14

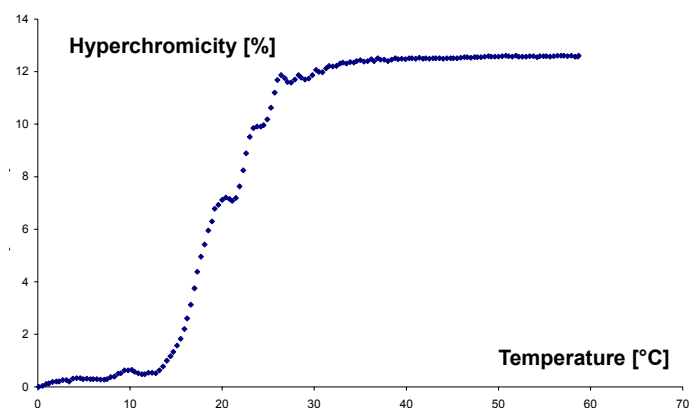


Fig. 21 Oligomer **14**: $T_m = 22$ °C (6 μ M; 12 %H)

H-(HalA-AlaT-HalA-AlaT-HalA-AlaT)-Lys-NH₂ 15

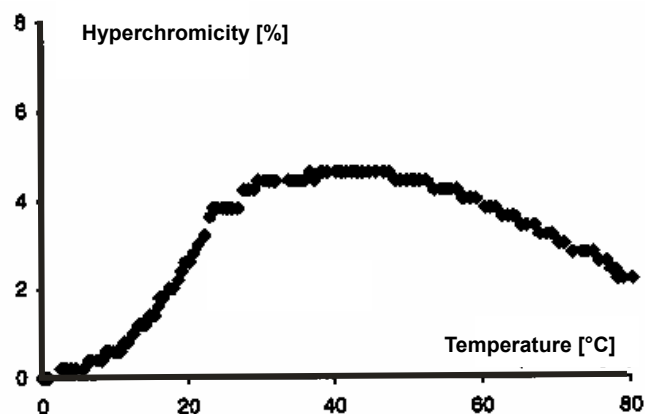


Fig. 22 Oligomer **15**: $T_m = 19$ °C (6 μ M; 5 %H)

H-(NvaA-NvaA-NvaT-NvaA-NvaT-NvaT)-Lys-NH₂ 16

**H-(NvaA-NvaA-NvaT-NvaA-NvaT-NvaT)-Lys-NH₂ 16 +
H-(NvaA-NvaA-NvaT-NvaA-NvaT-NvaT)-Lys-NH₂ ent-16**

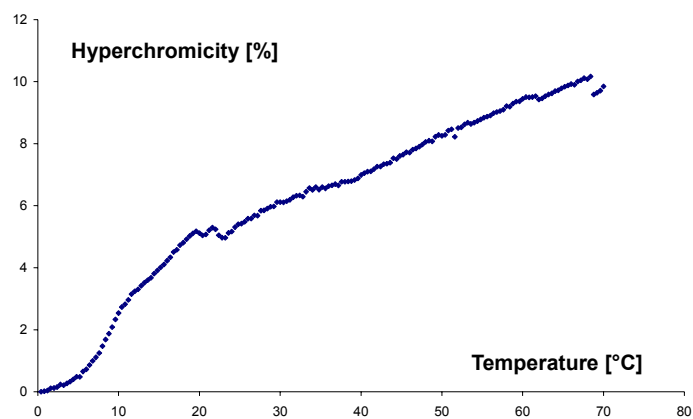


Fig. 23 Oligomer **16**: $T_m = 11\text{ }^{\circ}\text{C}$ (12 μM ; 6 %H)

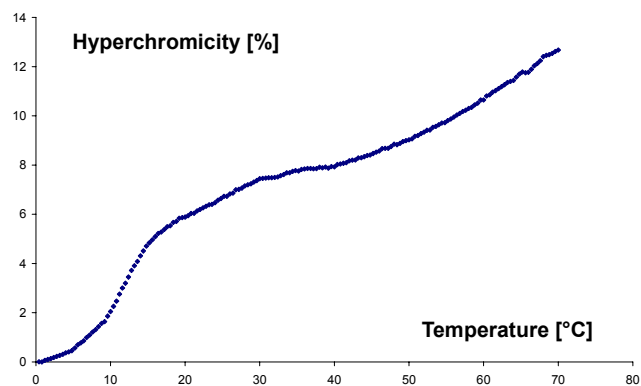


Fig. 24 Oligomers **16** + **ent-16**: $T_m = 13\text{ }^{\circ}\text{C}$ (6 μM each; 8 %H)

H-(NvaA-NvaA-NvaT-NvaA-NvaT-NvaT)-Lys-NH₂ 16

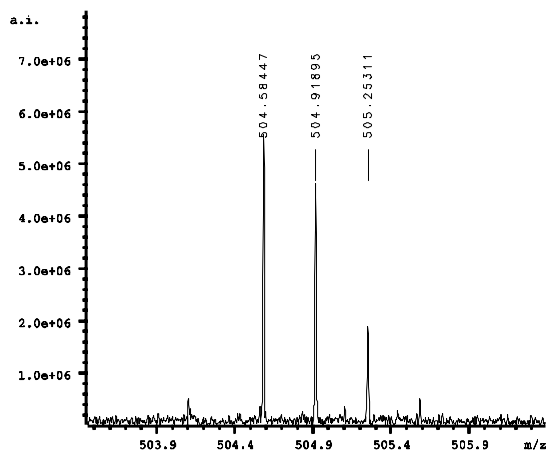
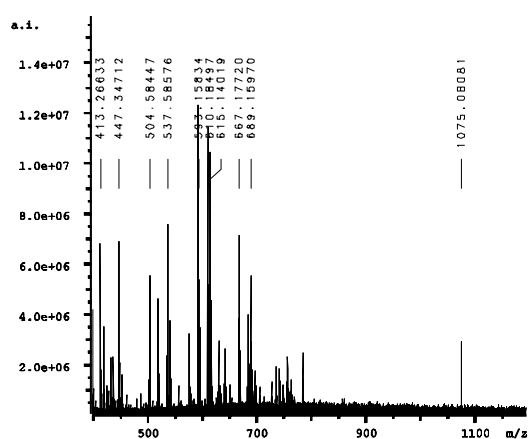


Fig. 25 Oligomer **16**: ESI-HRMS calcd for $\text{C}_{66}\text{H}_{90}\text{N}_{30}\text{O}_{13} [\text{M} + 3\text{H}]^{3+}$ 504.5841, found 504.5845