Figure S1: $^1$H-$^{13}$C HSQC spectra of peptoid/retropeptoid 7 and 8. Peptoid concentration was ~2 mM in dACN, and spectra were acquired at 25°C.
Figure S2: CD spectra of the peptoid/retropeptoid pair 13 and 14. Helical wheel diagrams of these two sequences are shown in Figure S5.

Figure S3: A comparison of the CD spectra of analogous peptoid hexamers 17 and 18. While they have the same percentage of chiral residues and the same C-termini, the inclusion of Nme as an achiral residues, as compared to Npm, reduces overall helicity.
ADDITIONAL TEXT:

The helix-stabilizing effect of an 'aromatic face'. Helices with cis-amide bonds are the predominant Nspe peptoid conformer at a 5-8mer length and have approximately three residues per turn, according to both modeling and 2D-NMR structural studies.\textsuperscript{1,2} The Nrpe helices studied here have the same type of helical structure, with opposite screw sense\textsuperscript{3}. To investigate the importance of side chain interactions for the stabilization of this class of helices, we synthesized a series of peptoid hexamers designed to have varying numbers of “aromatic faces” around the turns of the cis-amide helix. We define an aromatic face as a plane of aromatic rings running down the longitudinal axis of the helix, where the formation of an aromatic face should be possible if aromatic groups are placed every third residue.

We observe that not only is the presence of an aromatic face significant, but that the number of aromatic faces in a given peptoid helix affects peptoid helicity. In general, peptoids and retropeptoids with three aromatic faces display stronger helical spectra than analogous peptoids and retropeptoids having only one aromatic face. In the first sequences we compared, 7 and 23, each with one-half \( \alpha \)-chiral aromatic side chains (diagrammed schematically in Fig. SI5), the CD spectrum of peptoid 7 with three aromatic faces has twice the intensity of 23 with one aromatic face (Fig. SI4). Similar trends were observed in another pair of sequences, 14 and 26, each with two-thirds \( \alpha \)-chiral aromatic residues (diagrammed schematically in Fig. SI5), where the CD spectrum of 14 with three aromatic faces has a significantly greater intensity than 26 with one aromatic face (Fig. SI6A). The same effect is seen when the spectra of 13 and 25 (which are retropeptoid versions of 14 and 26, respectively) are compared (Fig. SI6B). We attribute the increased helicity of Npm-containing peptoid oligomers relative to Nme-containing oligomers to favorable aromatic-carbonyl and aromatic-aromatic interactions, as well as to mutual steric avoidance of these bulky groups. This is consistent with the 2D-NMR and molecular modeling results previously put forth.\textsuperscript{1,2}

Figure S4: Comparison of the CD spectra of analogous peptoid hexamers 7 and 23, for which helical wheel diagrams are shown in Figure S5. The inclusion of Nme as an achiral residue in 23 dramatically destabilizes the peptoid helix as compared to 7 in which the achiral residue is Npm.
Figure S5: Helical wheel diagrams for six peptoid oligomers of interest, whose CD spectra are compared in Figures S4, S6A, and S6B. Previous studies have shown that peptoid helices have cis-amide bonds and three residues per turn.
Figure S6A: Comparison of the CD spectra of hexamers 14 and 26, for which helical wheel diagrams are shown in Figure S5. Dramatic differences in helicity are seen although they both have 50% chiral residues and identical chain-terminating residues. We attribute this difference to the formation of three 'aromatic faces' in 14 as compared to only one for 26.

Figure S6B: Comparison of the CD spectra of hexamers 13 and 15, for which helical wheels are shown in Figure S5. Dramatic differences in helicity are seen although they both have 67% chiral residues and identical chain-terminating residues. We attribute this difference to the formation of three 'aromatic faces' in 13 as compared to only one for 25.