Figure S1. A more detailed analysis of drift time profiles of the trimeric TRI^{+6} signal from Fig. 4(b). Isotopic envelopes of all signals detected for WT Aβ1-40 (upper panel), and two mutants G25P (middle panel) and K28A (lower panel) indicating unequivocally the presence of monomeric, dimeric and trimeric signals resolved in the domain of the drift time. Figure shows the presence of the compact variant of trimeric species in K28A (denoted 3*).

Figure S2. The effect of proline substitution of hydrophobic residues, studied in two mutants: 3xPro ($L_{17}P$, $V_{18}P$, $F_{19}P$) and 5xPro, in which $I_{32}P$, $I_{34}P$ mutations were added to 3xPro mutations, on relative population of compact and extended form of Aβ oligomeric species. The coexistence of both compact and extended species in the control changes in the 3xPro mutant to the domination of the compact form and in 5xPro to the lack of extended form in DIM^{5+} (a), TRI^{6+} (b), TET^{7+} (c) and PEN^{8+} (d) signals. Also a gradual decrease of the compact form drift time is observed when the number of proline residues increases, for DIM^{5+}, from 7.6 ms to 7.28 ms and 7.06 ms, for TRI^{6+} from 8.6 ms to 8.27 ms and 8.05 ms, respectively, and to similar extent for TET^{7+} and PEN^{8+}. Upon proline mutation the extended form becomes less frequent and compact form is characterized the smaller collisional cross section than in WT Aβ oligomers.

Figure S3. Molecular modeling of Aβ1–40 oligomer with 5xPro substitution.

Figure S4. Two fragments of IMS-MS spectrum of Aβ1-40 collected at negative ionisation mode, along with isotopic envelopes, as indicated and drift time profiles (lower insets). (a) the signal for dimeric species (DIM^{5-}) is shown indicating the split in the domain of the drift time into two structural variants of the dimer, of the same isotopic envelope. (b) group of signals corresponding to monomers (MON^{2-}), dimers (DIM^{4-}) accompanied by trimers (TRI^{6-}).