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1,2,3-Triazolium-Based Peptoid Oligomers

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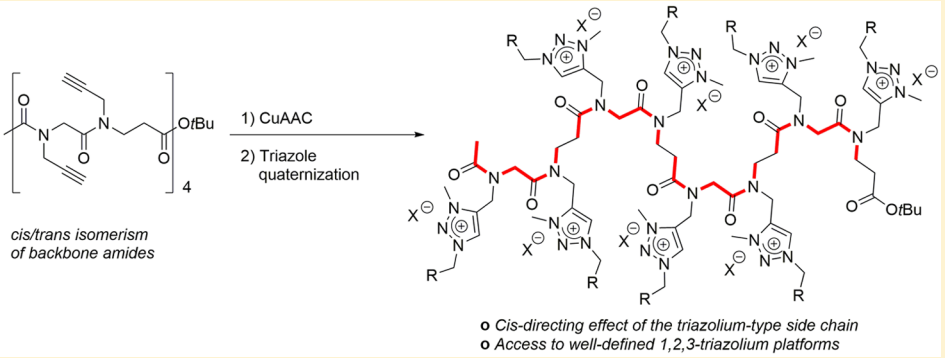
Supporting Information



ABSTRACT: The cis-directing effect of the 1,2,3-triazolium-type side chain was studied on dimeric peptoid models with various patterns: *αα*, *αβ*, *βα* and *ββ*. Low influences of the sequence and of the solvent were observed, the cis conformation of the amide carrying the triazolium ranging from 83 to 94% in proportion. The synthesis of peptoid homooligomers with four or eight pendant 1,2,3-triazolium side chains is described. *α*-, *β*- and *α*,*β*-peptoids carrying propargyl groups were subjected to CuAAC reaction using alkyl azides, and the resulting triazoles were quaternized providing well-defined multitriazolium platforms. The influence of the counteranion (PF_6^-, BF_4^- or I^-) on the conformation was also studied.

INTRODUCTION

Intrinsic properties of 1,2,3-triazolium salts make them interesting entities in organocatalysis, ionic liquids development and supramolecular chemistry.[1] Their study has rapidly grown over the past years with the achievement of the Copper-Catalyzed Azide−Alkyne Cycloaddition (CuAAC)[2] enabling an easy access to a large diversity of 1,2,3-triazolium salts upon alkylation of the formed 1,2,3-triazoles. The ability of 1,2,3-triazolium rings to act as hydrogen bond donor for anion recognition was first demonstrated by Pandey and coll.,[3] then applied in catalysis,[4] for selective anion binding and sensing,[5] for anion-templated formation of rotaxane systems[6] and for the design of interlocked molecular machines.[7] 1,2,3-Triazolium salts can also be regarded as ionic liquids when constituted of at least one flexible substituent and a bulky hydrophobic anion (NTf_2^-, BF_4^-, PF_6^-).[8] 1,2,3-Triazolium-based polyionic liquids (PILs) have been introduced by Drockenmuller and coll. by a click chemistry polyaddition strategy.[9] Their thermodynamical properties and high tenability make these PILs a promising class of polyelectrolytes for materials science.[10] Nanostructuration of *N*-alkyl triazolium side-chain polymethacrylates has also been explored.[11] The synthesis of polypeptoids carrying 1,2,3-triazolium pendant groups has been recently reported by Schlaad and coll.[12] In the field of peptoids, our group also showed that the intrinsic properties of the 1,2,3-triazolium ring (i.e., hydrogen-bond donor and *π*-interactions abilities) strongly influence the conformation of peptoid monomeric models.[13] Peptoids are *N*-substituted glycines oligoamides (Figure 1a) which can fold, among others, into stable helical structures although they are deprived of internal hydrogen bonding capabilities.[14] Peptoid folding is driven by side chains which control the *cis*/*trans* isomerism of backbone *N*,*N*-disubstituted amides.[15] The all-*trans* PolyProline type-II (PPII) helical structure is adopted by *N*-aryl peptoids.[16] Indeed the aryl side chain exhibits a complete trans-directing effect due to destabilizing electronic repulsion in the *cis* amide conformation. On the contrary, a PolyProline type-I (PPI) helix can be built using side chains which stabilize the *cis*-amide conformation. The *cis*-amide control can arise from steric interactions and/or $n \rightarrow \pi^*_{Ar}$ donation from the oxygen of a carbonyl (O_{i-1}) to the antibonding orbital of an aromatic side chain on residue *i*.[17] The best *cis*-directing side chains reported to date are based on steric effect, the 1-naphthylethyl (*1npe*)[18] and the *tert*-butyl (*t*Bu),[19] or based on $n \rightarrow \pi^*_{Ar}$ interaction, the 4-methylpyridinium (*4mpy*)[17b] and the triazolium-type side chain.[13] The *cis*-directing

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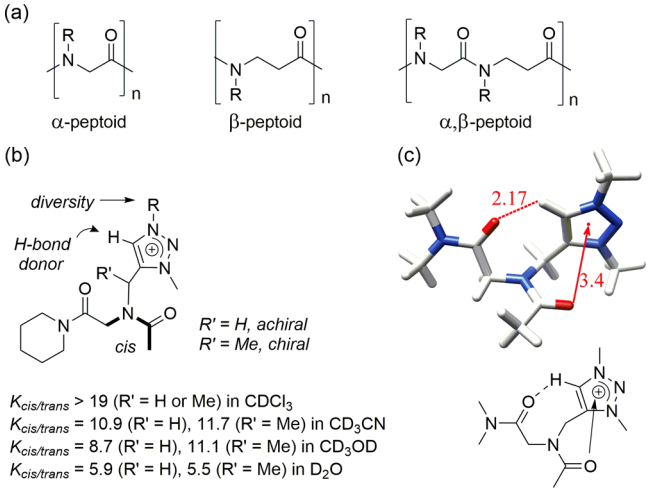


Figure 1. (a) Chemical structures of *α*-, *β*- and *α,β*-peptoids, (b) Peptoid monomer model with the triazolium-type peptoid side chain and $K_{cis/trans}$ values for the btm^+ (R = benzyl and R′ = H) and bte^+ (R = benzyl and R′ = Me) side chains. (c) Lowest-energy conformation calculated at the B3LYP/6-31G+* level.[13]

effect of the later was studied in monomeric peptoid model carrying 1-(benzyltriazolium)methyl (btm^+) or 1-(benzyltriazolium)ethyl (bte^+) side chains (Figure 1b). The electron deficient triazolium ring enables a strong $n \rightarrow \pi^*_{Ar}$ donation to occur and consequently favor the *cis* conformation in different solvents. Additionally, a nonclassical CH···O hydrogen-bonding[20] between the triazolium CH and the C═O carbonyl amide of the same residue was observed in $CDCl_3$ (Figure 1c) and can act cooperatively with the $n \rightarrow \pi^*_{Ar}$ delocalization to promote the *cis*-amide conformation.[13]

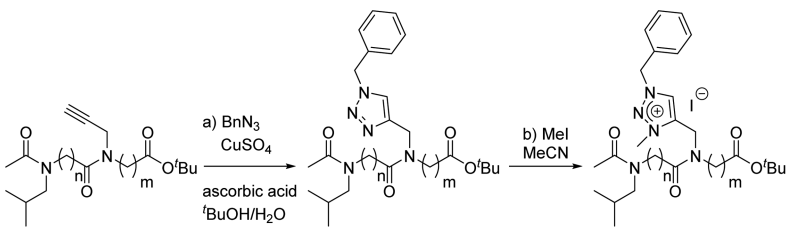
In addition to its exceptional *cis*-promoting effect, the triazolium side chain allows for the introduction of a wide variety of substituents (R in Figure 1b), this chemical diversity being crucial for their applications as peptidomimetic foldamers or materials. Due to its *cis*-directing effect and its accessible chemical diversity, the introduction of triazolium side chains is of great interest for stabilizing the structure of oligoamides for diverse applications. The triazolium side chain can be incorporated in a discrete manner within peptoid or mixed peptoid/peptide sequences to fix one selected amide in the *cis* conformation. Furthermore, homooligomers carrying triazolium side chains could be built to access all *cis*-amide oligomers featuring a PPI helical structure. The aim of the present work was to study the influence of the triazolium side chain on the conformational behavior of *α*-, *β*- and *α,β*-peptoid oligomers and to demonstrate triazolium homooligomers accessibility.

RESULTS AND DISCUSSION

The influence of the triazolium group was first studied on dimeric models carrying one triazolium side chain and one aliphatic side chain, the isobutyl group. Four *N*-acetylated dimeric peptoids with the *αα*, *ββ*, *αβ* or *βα* patterns (Figure 1a, Scheme 1) were synthesized in solution by the submonomer method combining acylation and substitution steps.[21] The use of volatile primary amines during the substitution enabled rapid preparation of the dimers *αα*-**1**, *αβ*-**2**, *βα*-**3**, and *ββ*-**4** in good to excellent overall yields ranging from 61 to 97% .[22] The alkyne side chain of compound **1**−**4** was further transformed into triazolium by the Cu-catalyzed azide−alkyne cycloaddition followed by subsequent methylation. The Huisgen reaction was performed by reacting **1**−**4** with benzyl azide in the presence of $CuSO_4$ and ascorbic acid in a *tert*-butanol/water mixture,[23] to furnish the dimers *αα*-**5**, *αβ*-**6**, *βα*-**7**, and *ββ*-**8** in good yield. The total conversion of the triazole rings into triazoliums was achieved using methyl iodide. The triazolium peptoids *αα*-**9**, *αβ*-**10**, *βα*-**11**, and *ββ*-**12** were thus obtained with an average 70% yield after column chromatography purifications.

Depending on the *cis* or *trans* peptoid amide conformation, for each dimeric peptoid, up to four conformers (*cc*, *ct*, *tt* and *tc*) can coexist in solution and be observed by NMR. The energy barrier between the *cis* and *trans* amide conformations in peptoid is high enough to prevent any fast exchange between *cis* and *trans* conformations at room temperature.[15,17] The proportion of each rotamer can thus be determined by simple integration of characteristic signals in ^{1}H NMR experiment. ^{1}H NMR spectra of all peptoid models **1**−**12** were recorded in CD_3CN, $CDCl_3$, CD_3OD, acetone-d_6 and D_2O. For the dimers carrying an alkyne side chain (**1**−**4**) or a triazole side chain (**5**−**8**), the four rotamers *tt*, *cc*, *ct* and *tc* were present in similar proportions in all of the solvents studied with the exception of chloroform where two conformers were predominant. For instance, four rotamers of the *αα*-**5** were observed in proportions 28:27:23:22 in CD_3OD and 47:31:13:8 in $CDCl_3$. Two dimensional ^{1}H−^{1}H and ^{1}H−^{13}C NMR experiments did not allow us to attribute the amide conformation to each of the rotamers. By contrast, the rotamer distribution for the dimers **9**−**12** shifted in favor of one major species. The proportion of conformers in each NMR solvent was determined by relative proton integration of a number of characteristic signals (Table 1 and see Supporting Information). For each dimer studied, the rotameric distribution was very similar in protic (CD_3OD, D_2O) or aprotic (CD_3CN) solvents indicating that the *cis*/*trans* isomerism is not much influenced by the environment, as previously observed for triazolium monomeric models.[13] In the

Scheme 1. Synthesis of Dimeric Model *α*-, *β*- and *α,β*-Peptoids



n, m = 1: αα-**1**, 61 %
n = 1, m = 2: αβ-**2**, 87 %
n = 2, m = 1: βα-**3**, 80 %
n, m = 2: ββ-**4**, 97 %

n, m = 1: αα-**5**, 85 %
n = 1, m = 2: αβ-**6**, 77 %
n = 2, m = 1: βα-**7**, 83 %
n, m = 2: ββ-**8**, 59 %

n, m = 1: αα-**9**, 69 %
n = 1, m = 2: αβ-**10**, 74 %
n = 2, m = 1: βα-**11**, 76 %
n, m = 2: ββ-**12**, 75 %

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Table 1. Relative Proportion of Rotamers in Different Solvents for the Dimeric Models 9−12[a]

Cpd	CD_3CN	$CDCl_3$	CD_3OD	D_2O
***αα*-9**	57:28:11:4	82:12:6:0	61:26:11:2	62:24:11:3
***αβ*-10**	66:24:10:0	85:8:7:0	70:19:9:2	69:18:10:3
***βα*-11**	57:27:11:5	73:19:7:0	57:26:12:5	56:27:12:4
***ββ*-12**	60:28:8:4	76:18:5:1	60:27:10:4	60:28:10:3

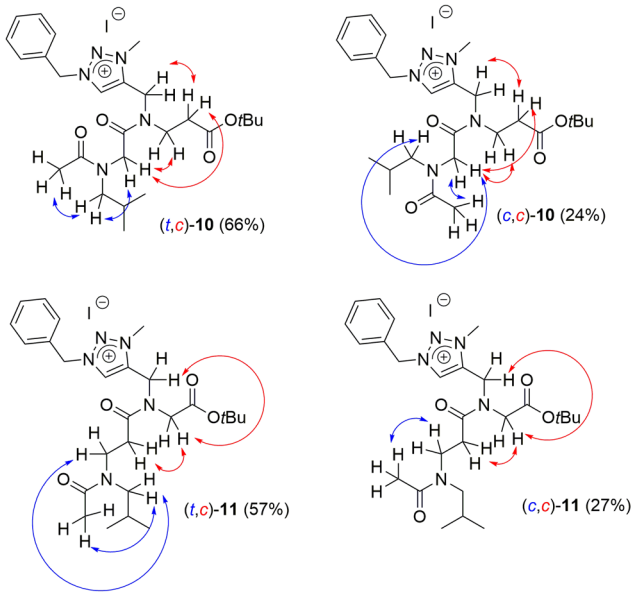
[a]Determined by integrating and averaging several (typically 2−3) ^{1}H NMR signals of peptoid at 15 mM at 298 K.[25]

field of foldamers, one major challenge is to build folded architecture stable in biological media. On this point, the structuration mode of peptoid oligomers possesses a great advantage over folding based on intramolecular hydrogen bonding which can be disrupted in protic solvents.[24] We show here that the control of the *cis*/*trans* isomerism by the triazolium group can efficiently operate in protic or aprotic media.

A particular behavior was however observed in $CDCl_3$. One predominant conformer is detected at 73 to 85% in proportion depending of the *αα*, *ββ*, *αβ* or *βα* patterns. The best results were obtained for the *α*,*α*-peptoid **9** and *α*,*β*-peptoid **10** which exist in 82% and 85%, respectively, in the same rotameric form. This special trend in $CDCl_3$ may be attributed to an intramolecular hydrogen-bonding between the triazolium CH and the backbone carbonyl of the same residue, as supported by NMR and molecular modeling on a monomeric model (Figure 1c).[13] The downfield shift of the triazolium protons in $CDCl_3$ (δ_H 9.25−9.80 ppm versus 8.30−8.80 ppm in CD_3CN, CD_3OD or D_2O) for all the dimers suggests their involvement in hydrogen bonding according to relevant literature data[26] (see the Supporting Information, Figures S1 and S2). The amide conformation of each rotamer in equilibrium could be determined by 2D NOESY experiments whenever possible when ^{1}H NMR dispersion allowed it. A careful analysis of *α*,*α*-peptoid **9** and *β*,*β*-peptoid **12** by COSY ^{1}H/^{1}H, HSQC ^{1}H/^{13}C and HMBC ^{1}H/^{13}C experiments showed overlapping signals preventing conformational analysis. By contrast, in the case of the *α*,*β*- and *β*,*α*-models **10** and **11**, each signal for the methylene protons of the backbone were well separated in CD_3CN or $CDCl_3$ thus allowing for the determination of the amide conformation (Scheme 2, Figure 2 and see the Supporting Information).

Three rotameric forms of dimer **10** were present in solution in acetonitrile in proportion 66:24:10 (Table 1). A combination of 2D NMR experiments (COSY, HSQC and HMBC) enabled us to assign the resonances of each of the rotamers, termed A, B and C from the major one to the minor one. For the most populated conformation A, the NOESY experiments showed a correlation between the protons of the acetamide (quoted 7A in Figure 2) and the side chain NC*α* protons 18A, but no correlation between the acetamide protons 7A and the backbone methylene protons 5A. These observations are indicative of a *trans* conformation of the acetamide (amide I in Figure 2). The correlation between the two backbone methylene protons 5A and 3A and the absence of correlation between the protons 5A and the methylene of the triazolium side chain (10A) revealed a *cis* conformation of the amide II. For the second rotamer named B, the correlation 7B/5B together with the absence of correlation between the protons 7B and 18B, showed a *cis* conformation of amide I. The correlation 5B/3B and the absence of correlation 5B/10B also clearly indicated a *cis* conformation of the amide II as in rotamer A. The NOE

Scheme 2. Structures of the Major Rotamers of Peptoid Dimers 10 and 11 in CD_3CN[a,b]



[a]NOESY experiments performed in CD_3CN at 10 mM; observed characteristic NOE correlations are shown with blue and red double arrows. [b]Relative proportion of each rotamer in brackets.

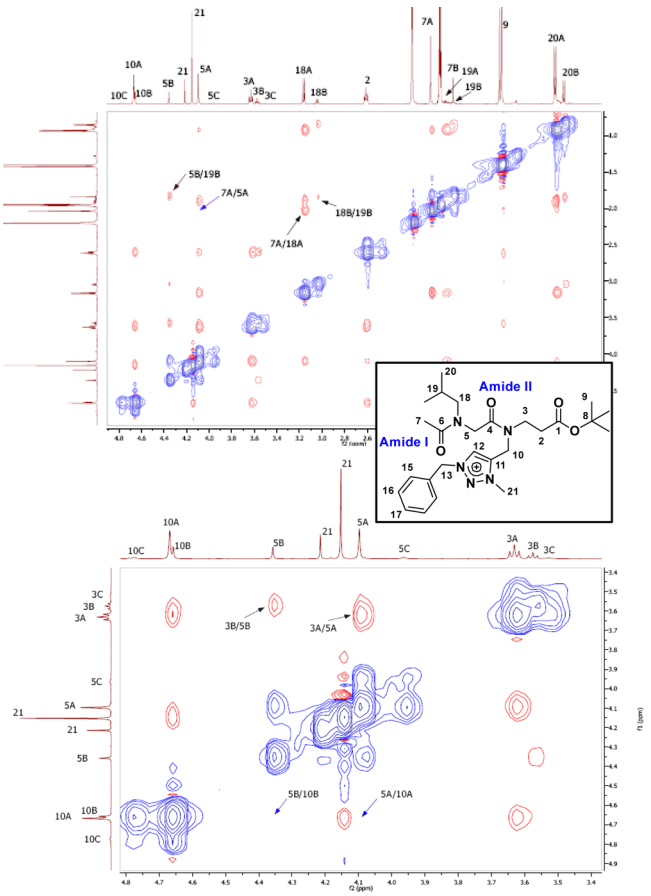


Figure 2. NOESY spectrum of peptoid **10** (10 mM) in CD_3CN at 298 K (A, B, C codes were assigned to the three rotamers in proportions 66/24/10).

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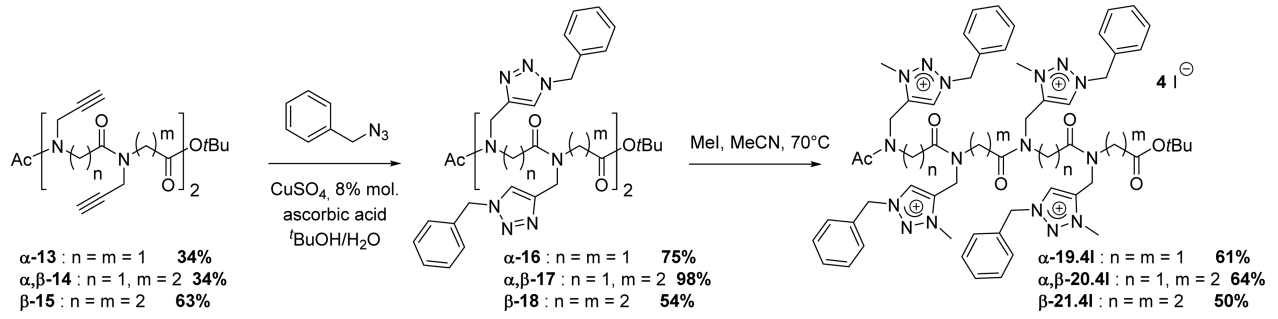
Scheme 3. Synthesis of Tetrameric Peptoids Carrying *btm*$^+$ Side Chains



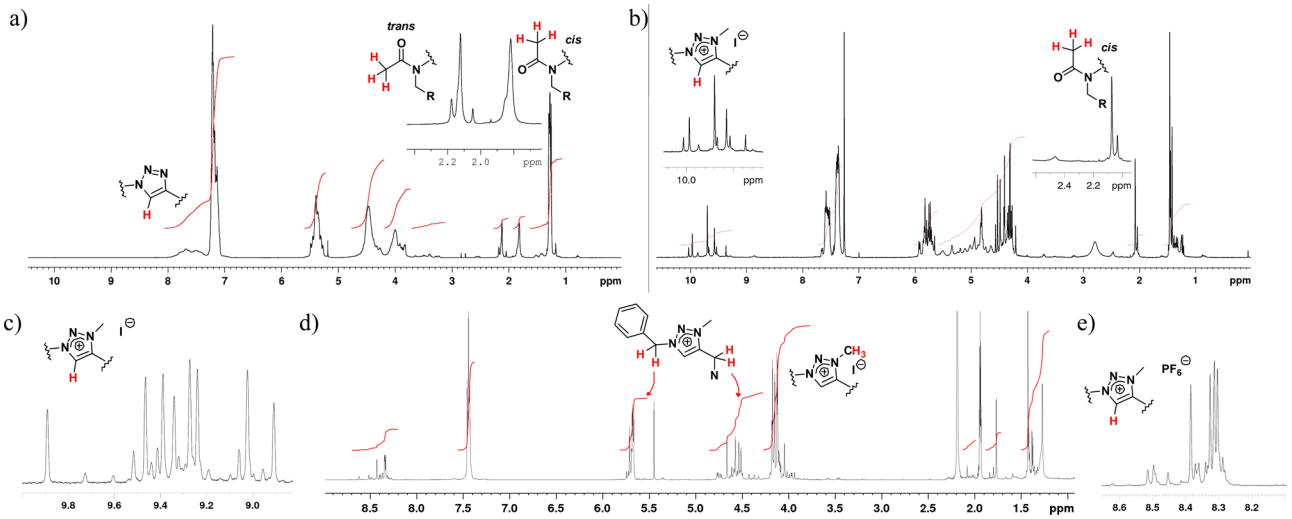


Figure 3. ^{1}H NMR spectra for (a) triazolyl α-peptoid **16** in $CDCl_3$ (15 mM), (b) triazolium α-peptoid **19.4I** as iodide salt in $CDCl_3$ (15 mM), (c) triazolium α-peptoid **19.4I** in CD_3CN (15 mM) (triazolium proton region), (d) triazolium α-peptoid **19.4PF$_6$** in CD_3CN (5 mM), and (e) triazolium α-peptoid **19.4PF$_6$** in CD_3CN (15 mM) (triazolium proton region).

correlations unequivocally enabled to attribute a *trans*−*cis* conformation for the major rotamer (relative proportion 66%) and a *cis*−*cis* conformation for the second one (relative proportion 24%) (Scheme 2). Therefore, the amide carrying the triazolium side chain was at 90% in *cis* in CD_3CN, i.e., a $K_{cis/trans}$ of 9 similar to the value obtained for the α-monomeric model ($^{btm+}K_{cis/trans}$ = 10.9)[13] even though the more flexible β-residue was involved. By analysis of NOESY experiments of peptoid **11**, the same amide geometries were assigned, *trans*−*cis* for the predominant rotamer (relative proportion 57%) and *cis*−*cis* for the second most represented rotamer (relative proportion 27%), the amide carrying the triazolium side chain being in this case at 84% in *cis* in CD_3CN. The isobutyl side chain like other aliphatic side chains (Et, Pr, Bu) is known to favor the *trans* conformation ($K_{cis/trans}$ ∼ 0.5 in CD_3CN or CD_3OD),[27] this tendency was also observed for the dimers $\alpha\beta$-**10** and $\beta\alpha$-**11**. Indeed, the proportion of the *trans*−*cis* conformer was 2-fold higher than those of the *cis*−*cis* conformer in CD_3CN, CD_3OD and D_2O. In $CDCl_3$, the proportion of *trans*−*cis* conformer further increases, especially for peptoids $\alpha\alpha$-**9** and $\alpha\beta$-**10** (82% and 85% respectively). This ability of $CDCl_3$ to greatly favor the *trans* conformation of amide carrying a nonbulky aliphatic side chain was previously reported (for exemple $K_{cis/trans}$ of 0.17 for Et side-chain in $CDCl_3$).[27] This first study shows that the efficacy of the btm$^+$ triazolium side chain in inducing the *cis* amide conformation is retained in peptoid dimers whatever the sequence pattern ($\alpha\alpha$, $\beta\beta$, $\alpha\beta$ or $\beta\alpha$). Besides no specific influence of the triazolium was observed on adjacent *N*,*N*-disubstituted amide carrying aliphatic side chain. The triazolium-type side chain could thus be incorporated in a discrete manner to lock in *cis* a selected amide in a specific peptoid sequence.

Another concern is the potential of triazolium-type side chains for building all-*cis* peptoid sequences. Access to well-defined triazolium-based peptoid homooligomers has never been reported and remains a challenging issue. In the peptoid field, the CuAAC reaction has been widely developed to access polyfunctional oligomers mainly for multivalent ligands display.[28] The efficiency of CuAAC was demonstrated in the construction of multivalent estradiol[29] or kanamycin[30] peptoid conjuguates. Up to six hormone ligands have been conjugated along the peptoid backbone but never in adjacent position. CuAAC reaction on *N*-alkynyl homooligomers was reported mainly to access glycosylated peptoids from linear[31] or cyclic[32] scaffolds up to 10 in valency. Triazole homooligomers should thus be easily accessible but their conversion into triazolium homooligomers could be challenging. Indeed well-defined triazolium clusters remain very rare architectures.[33] Tetrapeptoids from α-, β-, and α,β-series were chosen to develop synthetic access to polytriazolium peptoids. Peptoids carrying alkynyl group score high on ease of synthesis since tetrameric oligomers can be prepared at the gram scale with a single chromatographic purification at the end of the 7 steps sequence.[22] The homooligomers α-peptoid **13**, α,β-peptoid **14**

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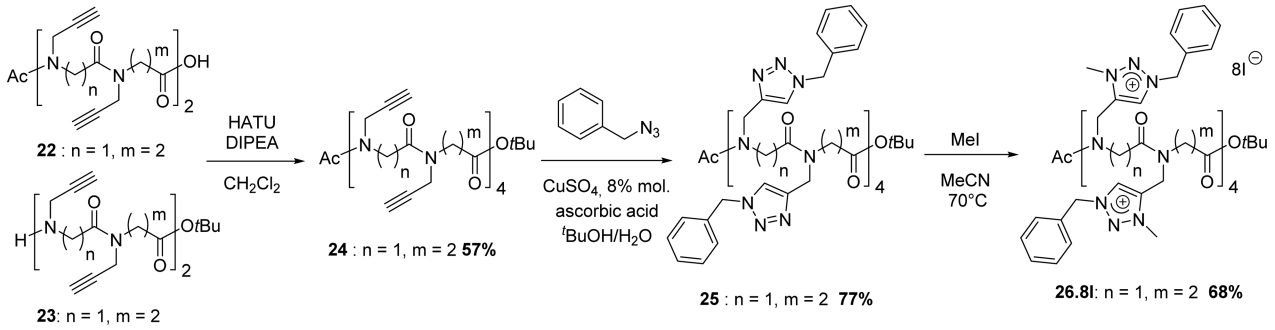
Scheme 4. Synthesis of an α,β-Octapeptoid Carrying btm^+ Side Chains



and β-peptoid **15** presenting four propargyl side chains were thus prepared in overall yields ranging from 34 to 63% starting from tertbutyl bromoacetate for **13** and tertbutyl acrylate for **14** and **15** (Scheme 3). The tetramers were then subjected to the CuAAC reaction with benzyl azide using $CuSO_4$, ascorbic acid in a *t*BuOH/water mixture.[23] The polyfunctional oligomers **16**, **17** and **18** were obtained in good yields of 75%, 98% and 54%, respectively. To generate the triazolium rings, a literature protocol using iodomethane at room temperature[3] proved inefficient in our hand. Only partial methylation occurred and separation of the formed products could not be envisaged with these polyfunctional platforms. Fortunately, the complete conversion of the triazoles into triazoliums was achieved using an excess of iodomethane in acetonitrile at reflux during 12 to 24h.[34] The 1,2,3-triazolium-based tetrapeptoids α-**19**, α,β-**20** and β-**21** were thus obtained as iodide salts in good yields.

The conformational preference of these tetrapeptoids was studied by NMR to determine the structural potential of triazolium side chains within homooligomers. The complexity of the ^{1}H NMR spectra of the propargyl and triazolyl tetrapeptoids **13**−**18** was characteristic of conformational heterogeneity mainly due to *cis*/*trans* isomerism of the *N*,*N*-disubstituted amides. Notably, a very broad massif in the 7−8 ppm region corresponding to the C−H of the triazole rings was observed (Figure 3a). Besides, two distinct and quasi equivalent populations of CH_3 corresponding to the terminal acetamide around 1.8 and 2.2 ppm, characteristic of the *trans* and *cis* rotamers, were observed.[13,15,17] The *N*-terminal acetamide was thus in ∼50:50 *cis*/*trans* proportion. By contrast, the ^{1}H NMR spectra of the polytriazolium compounds **19.4I**, **20.4I** and **21.4I** revealed a preference for one or two conformers (over the 16 possible) depending on the NMR solvent and anionic counterion (Figure 3 and see Supporting Information). For exemple, the ^{1}H NMR of α-peptoid **19.4I** shows essentially two conformers in $CDCl_3$ in unequal distribution as shown by the number of peaks corresponding to the CH of the triazolium (2 × 4 singlets) and also by the two peaks at around 2 ppm corresponding to the acetamide (Figure 3b). The very close resonance for the latter suggests a *cis* conformation of the terminal amide. In the other NMR solvents studied (CD_3CN, CD_3OD), the triazolium proton region suggests that two major conformers of **19.4I** still coexist but this time in similar proportion (Figure 3c and see Supporting Information, Figure S3). If the triazolium forces the amides in cis as demonstrated for dimeric models, the observed conformational variability could originate from different patterns of the dihedral angles Φ [$C_{(i-1)}$; N; C_α; C] as shown for achiral N*t*Bu peptoids.[35] For the α,β-peptoid **20.4I**, a limited number of conformers was also observed and that time one predominant conformer was observed in CD_3CN (see Supporting Information, Figure S4). By contrast, broad and less resolved triazolium proton signals were observed for β-peptoid **21.4I** (see Supporting Information, Figure S5). Previous studies by NMR or circular dichroism of β- and α,β-peptoid oligomers carrying (*S*)-phenylethyl side-chain (*spe*) have shown certain conformational preferences but a greater flexibility compared to α-peptoid, due to the additional methylene of the β residue.[36] However, recently thanks to the more effective *cis*-directing *1npe* side chain, the Olsen group has shown that β-peptoids can adopt a unique triangular prism-shaped helical structure.[37] Particular secondary structure has not yet been identified for linear oligomers composed of alternating α- and β-peptoid monomers.

In order to study the counteranion influence on conformational preferences, variation of the anion (I^-, PF_6^-, BF_4^-) was performed. Direct methylation of the tetramers α-**16**, α,β-**17**, β-**18** using the Meerwein salt proved inefficient for this type of multivalent quaternization.[38] Anion-exchanged of formed triazolium iodide salts was thus privileged using ammonium salts.[26a] Anion-exchanged for PF_6^- was performed on α-tetrapeptoid **19.4I** using a methanolic solution of ammonium hexafluorophosphate. Efficiency of the exchange was checked by mass spectroscopy. NMR of the PF_6^- salt in CD_3CN reveals a predominant one set of signals and an upfield shift of the triazolium CH signals compared to the iodide salt in the same solvent (Figure 3c,d,e and see Supporting Information, Table 1 and Figure S6). A variable temperature ^{1}H NMR study on **19.4PF6** in CD_3CN showed no modification of spectra upon cooling from 298 to 278 K and a coalescence phenomena above 318 K, confirming the presence of one preferential conformation at room temperature (see Supporting Information, Figure S7). The α-peptoid **19.4PF6** tend to crystallize but we were not able to grow suitable crystals for X-ray diffraction. At present, the effect of the counteranion on the conformational preference is not clear but it appears that the bulky and weakly coordinating PF_6^- counteranion promote the structuration of the peptoid into one predominant conformation, while iodide salt presented two privileged conformations in CD_3CN solution. The same trend was observed for the α,β-peptoid **20** but signals were less well resolved than for the α-peptoid series (see Supporting Information, Figure S8). We found that longer oligomers with eight triazolium pendant groups can be efficiently prepared in the same manner. The α,β-octapeptoid **24** was obtained by peptide coupling of the two tetrameric partners α,β-**22** and α,β-**23** using HATU as coupling reagent (Scheme 4). Conversion of the eight alkynes into triazoliums proceeded with 57% yield over two steps. For these longer oligomers, NMR spectra were more complex than for tetramers. Upon quaternization of triazoles, an overall change in rotameric

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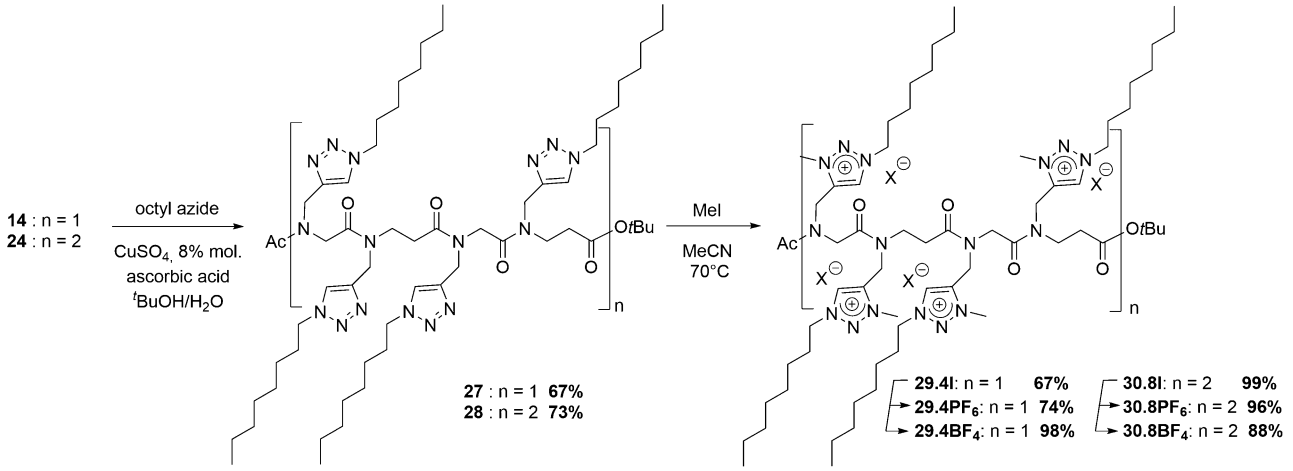
Scheme 5. Synthesis of an *α,β*-Octapeptoids Carrying *otm*$^+$ Side Chains



distribution was observed but could not be attributed to a predominant conformation in solution due to the NMR complexity (see Supporting Information, Figure S9).

Having demonstrated an easy access to polytriazolium platforms, the study of triazolium peptoid oligomers presenting long flexible aliphatic pendant groups was investigated. Indeed, these polytriazolium edifices may have interesting physicochemical properties in between ionic liquids and PILs.[39] The introduction of long flexible groups such as an octyl on triazolium has not proven difficult for tetra- and octapeptoid oligomers (Scheme 5). The CuAAc reaction using octyl azide on the *α,β*-tetrapeptoid **14** and the *α,β*-octapeptoid **24** provided the poly triazole oligomers **27** and **28** in 67% and 73% yield, respectively. Quaternization proceeded efficiently under previously optimized protocol to give the amphipathic peptoids **29.4I** and **30.8I** carrying 1-(octyltriazolium)methyl (*otm*$^+$) side chains (Figure 4 and see Supporting Information).

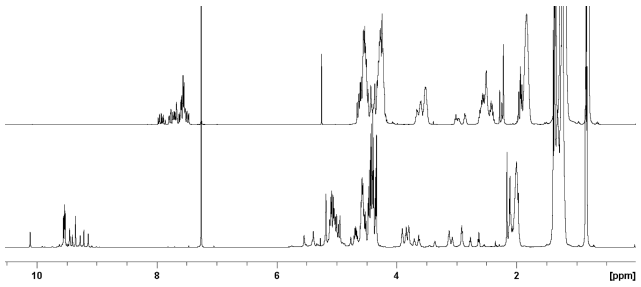


Figure 4. ^{1}H NMR spectra in $CDCl_3$ at 298 K for *α,β*-tetrapeptoid **27** carrying *otm* side chain (top curve) and for *α,β*-tetrapeptoid **29.4I** carrying *otm*$^+$ side chain (bottom curve).

Besides, different bulky hydrophobic counteranions such as PF_6^- and BF_4^- could be introduced instead of iodide by efficient anion-exchange (Scheme 5). The ^{1}H NMR spectra in $CDCl_3$ and CD_3CN shows significant and similar change upon introduction of the bulky and weakly coordinating anions (PF_6^- and BF_4^-). For **29.4PF$_6$**, **29.4BF$_4$**, **30.8PF$_6$** and **30.8BF$_4$**, an upfield shift of the triazolium CH signals were observed on ^{1}H NMR spectra compared to those of **29.4I** and **30.8I** (see Supporting Information, Figures S9, S10 and S11). This upfield shift upon I^- to PF_6^- or BF_4^- anion exchange observed for all triazolium oligomers, seems to indicate that a binding occurs between iodide anions and the triazolium CH-bond donors.[6,40]

CONCLUSION

In conclusion, we have shown that the *cis*-directing effect of the triazolium-type side chain on tertiary amide isomerism proceeds in *α-,β-* and *α,β*-peptoid oligomers as strongly as in monomeric models. An efficient access to 1,2,3-triazolium-based peptoids from *α-*, *β-* and *α,β*-series was developed combining an improved solution-phase submonomer synthesis, CuAAc reaction and efficient triazole quaternization. These poly-1,2,3-triazolium-based peptoids up to the octamer were prepared with different type of counterion such as I^-, PF_6^-, BF_4^-. The present work opens the way for the study of intrinsic properties of these new edifices for catalysis, life sciences or materials.

EXPERIMENTAL SECTION

General Information. Chemicals obtained from commercial sources were used without further purification, unless stated otherwise. THF was distilled from potassium/benzophenone and stored over 4 Å molecular sieves. CH_2Cl_2 and MeOH were distilled from CaH_2 and stored over 4 and 3 Å molecular sieves, respectively. Melting points were determined on a melting point apparatus and are uncorrected. IR spectra were recorded on a FTIR spectrometer equipped with a ATR and ν are expressed in cm^{-1}. NMR spectra were recorded on a 400 or 500 MHz spectrometer. Chemical shifts are referenced to the residual solvent peak and *J* values are given in Hz. The following multiplicity abbreviations are used: (s) singlet, (d) doublet, (t) triplet, (q) quartet, (m) multiplet, and (br) broad. Where applicable, assignments were based on COSY, HMBC, HSQC and *J*-mod-experiments. Thin layer chromatography (TLC) was performed on TLC aluminum sheets, silica gel 60, F_{254}. Flash chromatography was performed with silica gel 60, 40−63 μm. HRMS was recorded on a Micromass Q-Tof Micro (3000 V) apparatus or a Q Exactive Quadrupole-Orbitrap Mass Spectrometer.

General Procedure for *α*-Peptoid Submonomer Synthesis (Method A). To a solution of the secondary amine (1.0 equiv, 0.2 M) in EtOAc or THF at 0 °C under Ar was added Et_3N (1.2 equiv) and then bromoacetyl bromide (1.2 equiv). After stirring for 1 h at −10 °C, the resulting mixture was diluted with EtOAc and filtered, washing the solids with EtOAc. The filtrate was then concentrated and dried in vacuo, yielding the crude bromoacetyl amide. To a solution of the crude bromoacetyl amide (0.2 M) in THF or EtOAc at 0 °C under Ar was added Et_3N (2.0 equiv) followed by the chosen primary amine (4.0 equiv). After stirring overnight at rt, the resulting mixture was diluted with EtOAc and filtered, washing the solids with EtOAc. The filtrate was then concentrated under reduced pressure yielding the desired product.

General procedure for *β*-Peptoid Submonomer Synthesis (Method B). To a solution of the secondary amine (1.0 equiv, 0.2 M)

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in THF at 0 °C under Ar was added Et_3N (2.2 equiv) and then acryloyl chloride (1.2 equiv). After stirring for 1 h at 0 °C, the resulting mixture was diluted with EtOAc and filtered, washing the solids with EtOAc. The filtrate was then concentrated and dried in vacuo, yielding the crude acrylamide. To a solution of the crude acrylamide (0.4 M) in MeOH at rt under Ar was added the chosen primary amine (2.0 equiv). After stirring overnight at 50 °C, the mixture was concentrated under reduced pressure. Flash chromatography of the crude yielded the desired product.

General Procedure for Acetylation (Method C). To a solution of peptoid (1 equiv) and Et_3N (1.4 equiv) in EtOAc (0.2 M) at 0 °C under Ar, was added AcCl (1.2 equiv). After stirring for 1 h at 0 °C, the mixture was filtered washing the solids with EtOAc. The filtrate was then concentrated and dried in vacuo, yielding the crude *N*-acylated compound which was purified by flash chromatography.

General Procedure for CuAAc Reaction (Method D). To a solution of peptoid carrying n propargyl side chains ($n \times 1$ equiv) in *tert*-BuOH (0.1 M) at rt under Ar were added freshly prepared 0.1 M aq. ascorbic acid ($n \times 0.24$ equiv), 0.1 M aq. $CuSO_4$ ($n \times 0.08$ equiv) and the chosen azide ($n \times 2$ equiv). After stirring for 4 h at rt, water was added and the product was extracted with DCM (5 × 10 mL). The combined organic layer were washed twice with a basic aqueous solution of EDTA (0.1 M, pH = 9), then dried over $MgSO_4$, filtered and concentrated under reduced pressure yielding the crude triazole product.

General Procedure for Methylation (Method E). To a solution of peptoid (1 equiv) in anhydrous MeCN (0.1 M) was added MeI (15 equiv). The resulting mixture was stirred at 70 °C for 24h then evaporated under reduced pressure yielding the crude triazolium product.

General Procedure for Anion Exchange Using Ammonium Salt (Method F). To a solution of peptoid (approximately 10 μmol) in MeOH (1 mL) was added a saturated solution of NH_4PF_6 (or NH_4BF_4) in MeOH (0.5 mL). The resulting mixture was stirred at rt for 1h then evaporated under reduced pressure. The crude is dissolved in DCM (10 mL) then washed twice with water (2 × 5 mL). The organic phase is dried over $MgSO_4$ then concentrated yielding the desired triazolium salt.

α-Peptoid ***1***. Compound **1** was synthesized starting from *tert*-butylbromoacetate (200 mg, 1.03 mmol, 1.0 equiv) by application of method **A** using propargylamine as primary amine, then method A using isobutylamine as primary amine, then acetylation using method C. Flash chromatography on silica gel of the crude product using EtOAc/Cyclohexane 70:30 as solvent yielded peptoid **1** (206 mg, 0.63 mmol, 61%) as a yellowish oil: R_f (EtOAc) = 0.39; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): (4 rotamers in proprotions A/B/C/D 45:36:11:80) 76−0.90 (m, 6H, $CH_2CH(CH_3)_2$), 1.37/1.41/1.42 (3 × s, 9H, ^{t}Bu), 1.69−1.91 (m, 1H, $CH_2CH(CH_3)_2$), 1.92/1.94/2.05/2.07 (4 × s, 3H, NAc), 2.18 (t, J = 2.5 Hz, 0.45H, 0,45 × $CH_2C{\equiv}CH$, rot. A), 2.23 (t, J = 2.3 Hz, 0.11H, 0.11 × $CH_2C{\equiv}CH$, rot. C), 2.29 (t, J = 2.3 Hz, 0.36H, 0,36 × $CH_2C{\equiv}CH$, rot. B), 2.37 (t, J = 2.5 Hz, 0.08H, 0.08 × $CH_2C{\equiv}CH$, rot. D), 3.04−3.19 (m, 2H, $CH_2CH(CH_3)_2$), 3.88−4.28 (m, 6H, 2 × $NCH_2C{=}O$ and $CH_2C{\equiv}CH$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 19.9, 20.0 ($2CH_3$, $CH_2CH(CH_3)_2$), 20.7, 21.1, 21.4 (CH_3, NAc), 26.0, 26.9, 27.2, 27.4 (CH, $CH_2CH(CH_3)_2$), 27.8, 27.9 ($3CH_3$, ^{t}Bu), 35.7, 35.9, 37.5, 37.7 (CH_2, $CH_2C{\equiv}CH$), 46.5, 47.8, 48.2, 48.4, 50.2, 50.4 ($2CH_2$, 2 × $NCH_2C{=}O$), 54.3, 54.4, 56.4, 56.7 (CH_2, $CH_2CH(CH_3)_2$), 73.0, 73.4, 73.9 (CH, $CH_2C{\equiv}CH$), 77.4, 77.8 (C, $CH_2C{\equiv}CH$), 81.8, 82.2, 82.6, 83.1 (C, ^{t}Bu), 167.5, 167.8, 168.0, 168.3, 168.4 (C, $OC{=}O$), 171.1, 171.3, 171.8 (2C, 2 × $NC{=}O$); IR (ATR) ν (cm^{-1}): 3305, 3233 (≡C−H), 2962, 2935, 2872, 2118 (C≡C), 1739, 1668, 1650, 1646 (C=O amides), 1428, 1369, 1257, 1218, 1154, 1039, 967, 959, 857, 828; HRMS (TOF MS ES+): calcd for $C_{17}H_{28}N_2O_4Na$ $[M + Na]^+$ m/z 347.1947, found 347.1953.

α,β-Peptoid ***2***. Compound **2** was synthesized starting from *tert*-butyl acrylate (200 mg, 1.56 mmol, 1.0 equiv) by application of the method B using propargylamine as primary amine, then method A using isobutylamine as primary amine, then acetylation using method C. Flash chromatography on silica gel of the crude product using CH_2Cl_2 as solvent yielded peptoid **2** (460 mg, 1.36 mmol, 87%) as a yellowish oil: R_f (CH_2Cl_2)= 0.27; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): (4 rotamers in proprotions A/B/C/D 52:46:17:11) 0.86/0.90 (2 × d, J = 6.6 Hz, 6H, $CH_2CH(CH_3)_2$), 1.35−1.43 (m, 9H, ^{t}Bu), 1.75−1.94 (m, 1H, $CH_2CH(CH_3)_2$), 1.97/2.11 (2 × s, 3H, NAc), 2.18 (t, J = 2.3 Hz, 0.52H, 0.52 × $CH_2C{\equiv}CH$, rot. A), 2.21 (m, 0.17H, 0.17 × $CH_2C{\equiv}CH$, rot. C), 2.29 (t, J = 2.3 Hz, 0.46H, 0.46 × $CH_2C{\equiv}CH$, rot. B), 2.35 (m, 0.11H, 0.11 × $CH_2C{\equiv}CH$, rot. D), 2.46−2.67 (m, 2H, $NCH_2CH_2C{=}O$), 3.09−3.20 (m, 2H, $CH_2CH(CH_3)_2$), 3.56−3.72 (m, 2H, $NCH_2CH_2C{=}O$), 4.03−4.36 (m, 4H, $NCH_2C{=}O$ and $CH_2C{\equiv}CH$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 19.9, 20.0 ($2CH_3$, $CH_2CH(CH_3)_2$), 21.1, 21.5, 22.9 (CH_3, NAc), 26.8, 26.9, 27.3, 27.5 (CH, $CH_2CH(CH_3)_2$), 27.9 ($3CH_3$, ^{t}Bu), 33.3, 33.7, 33.8, 33.9, 34.2, 37.7, 37.8 ($2CH_2$, $NCH_2CH_2C{=}O$ and $CH_2C{\equiv}CH$), 41.3, 42.0, 43.4, 43.9 (CH_2, $NCH_2CH_2C{=}O$), 46.7, 46.9, 50.5 (CH_2, $NCH_2C{=}O$), 54.2, 54.4, 56.7, 57.0 (CH_2, $CH_2CH(CH_3)_2$), 72.1, 72.4, 72.8, 73.3 (CH, $CH_2C{\equiv}CH$), 78.1, 78.4 (C, $CH_2C{\equiv}CH$), 80.6, 81.2, 81.5 (C, ^{t}Bu), 167.8, 168.2 (C, $OC{=}O$), 170.3, 170.9, 171.1, 171.4 (2C, 2 × $NC{=}O$); IR (ATR) ν (cm^{-1}): 3305, 3240 (≡C−H), 2962, 2931, 2872, 2114 (C≡C), 1725, 1652, 1646 (C=O amides), 1468, 1428, 1368, 1257, 1151, 1055, 988, 845; HRMS (TOF MS ES+): calcd for $C_{18}H_{31}N_2O_4$ $[M + H]^+$ m/z 339.2284, found 339.2296.

β,α-Peptoid ***3***. Compound **3** was synthesized starting from *tert*-butylbromoacetate (200 mg, 1.03 mmol, 1.0 equiv) by application of the method A using propargylamine as primary amine, then method B using isobutylamine as primary amine, then acetylation using method C. Flash chromatography of the crude product in EtOAc yielded peptoid **3** (278 mg, 0.82 mmol, 80%) as a yellowish oil: R_f (EtOAc) = 0.44; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): (4 rotamers in proprotions A/B/C/D 40:40:10:10) 0.73−0.88 (m, 6H, $CH_2CH(CH_3)_2$), 1.37 (s, 3.6H, 0.4 × ^{t}Bu, rot. A), 1.38 (s, 0.9H, 0.1 × ^{t}Bu, rot. C), 1.39 (s, 3.6H, 0.4 × ^{t}Bu, rot. B), 1.40 (s, 0.9H, 0.10 × ^{t}Bu, rot. D), 1.78−1.93 (m, 1H, $CH_2CH(CH_3)_2$), 1.97 (s, 1.2H, 0.4 × NAc, rot. A or B), 2.00 (s, 1.2H, 0.4 × NAc, rot. A or B), 2.02 (s, 0.3H, 0.1 × NAc, rot. C or D), 2.06 (s, 0.3H, 0.1 × NAc, rot. C or D), 2.17 (t, J = 2.5 Hz, 0.4H, 0.4 × $CH_2C{\equiv}CH$, rot. A or B), 2.19 (t, J = 2.5 Hz, 0.1H, 0.1 × $CH_2C{\equiv}CH$, rot. C or D), 2.24 (t, J = 2.4 Hz, 0.4H, 0.4 × $CH_2C{\equiv}CH$, rot. A or B), 2.31 (t, J = 2.4 Hz, 0.1H, 0.1 × $CH_2C{\equiv}CH$, rot. C or D), 2.38 (t, J = 6.9 Hz, 0.2H, 0.1 × $NCH_2CH_2C{=}O$, rot. C or D), 2.50 (t, J = 6.9 Hz, 0.8H, 0.4 × $NCH_2CH_2C{=}O$, rot. A or B), 2.62 (t, J = 6.9 Hz, 0.2H, 0.1 × $NCH_2CH_2C{=}O$, rot. C or D), 2.68 (t, J = 6.9 Hz, 0.8H, 0.4 × $NCH_2CH_2C{=}O$, rot. A or B), 3.00−3.10 (m, 2H, $CH_2CH(CH_3)_2$), 3.44−3.64 (m, 2H, $NCH_2CH_2C{=}O$), 3.96−4.06 (m, 2.2H, $NCH_2C{=}O$ and 0.1 × $CH_2C{\equiv}CH$, rot. C or D), 4.14 (d, J = 2.4 Hz, 0.8H, 0.4 × $CH_2C{\equiv}CH$, rot. A or B), 4.19 (d, J = 2.5 Hz, 0.8H, 0.4 × $CH_2C{\equiv}CH$, rot. A or B), 4.20 (d, J = 2.5 Hz, 0.2H, 0.1 × $CH_2C{\equiv}CH$, rot. C or D); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 19.8. 19.9 ($2CH_3$, $CH_2CH(CH_3)_2$), 21.4, 21.5, 21.6 (CH_3, NAc), 26.6 (CH, $CH_2CH(CH_3)_2$), 27.8, 27.9 ($3CH_3$, ^{t}Bu), 31.2, 31.6, 31.7 (CH_2, $NCH_2CH_2C{=}O$), 35.1, 35.3, 38.1 (CH_2, $CH_2C{\equiv}CH$), 43.2, 43.2, 44.6, 44.8 (CH_2, $NCH_2CH_2C{=}O$), 46.9, 47.3, 48.7 (CH_2, $NCH_2C{=}O$), 52.2, 52.2, 57.0, 57.2 (CH_2, $CH_2CH(CH_3)_2$), 72.6, 72.9, 73.1, 73.5 (CH, $CH_2C{\equiv}CH$), 77.7, 78.2 (C, $CH_2C{\equiv}CH$), 81.7, 82.1, 82.5, 82.9 (C, ^{t}Bu), 167.7, 167.8, 167.9, 168.0 (C, $OC{=}O$), 170.2, 170.5, 170.9, 171.0, 171.2, 171.4 (2C, 2 × $NC{=}O$); IR (ATR) ν (cm^{-1}): 3309, 3241(≡C−H), 2964, 2937, 2872, 2117, 1739 (C=O ester), 1643 (C=O amides), 1450, 1369, 1258, 1230, 1154, 1012, 967, 852; HRMS (TOF MS ES+): calcd for $C_{18}H_{31}N_2O_4$ $[M + H]^+$ m/z 339.2284, found 339.2279.

β-Peptoid ***4***. Compound **4** was synthesized starting from *tert*-butyl acrylate (200 mg, 1.56 mmol, 1.0 equiv) by application of the method B using propargylamine as primary amine, then method B using isobutylamine as primary amine, then acetylation using method C. Flash chromatography on silica gel of the crude product using EtOAc as solvent yielded peptoid **4** (533 mg, 1.51 mmol, 97%) as a yellowish oil: R_f (EtOAc) = 0.30; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): (4 rotamers in proprotions A/B/C/D 38:38:12:12) 0.78/0.83 (2 × d, J = 6.7 Hz, 6H, $CH_2CH(CH_3)_2$), 1.34 (m, 9H, ^{t}Bu), 1.78−1.95 (m, 1H, $CH_2CH(CH_3)_2$), 1.98/2.05 (2 × s, 3H, NAc), 2.13 (t, J = 2.3 Hz, 0.38H, 0.38 × $CH_2C{\equiv}CH$, rot.A), 2.16 (t, J = 2.3 Hz, 0.12H, 0.12 × $CH_2C{\equiv}CH$, rot. C), 2.21 (t, J = 2.2 Hz, 0.38H, 0.38 × $CH_2C{\equiv}CH$, rot. B), 2.27 (t, J = 2.2 Hz, 0.12H, 0.12 × $CH_2C{\equiv}CH$, rot. D), 2.37−

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2.51 (m, 2H, $NCH_2CH_2C{=}ON$), 2.51−2.68 (m, 2H, $NCH_2CH_2C{=}OO$), 2.98−3.12 (m, 2H, $CH_2CH(CH_3)_2$), 3.41−3.67 (m, 4H, 2 × $NCH_2CH_2C{=}O$), 3.98−4.15 (m, 2H, $CH_2C{\equiv}CH$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 19.8. 19.9 ($2CH_3$, $CH_2CH(CH_3)_2$), 21.4, 21.5, 21.6 (CH_3, NAc), 26.6 (CH, $CH_2CH(CH_3)_2$), 27.8, 27.9 ($3CH_3$, ^{t}Bu), 30.9, 31.4, 31.6, 31.9 (CH_2, $NCH_2CH_2C{=}OO$), 33.7, 33.8, 33.9, 33.9, 34.0, 34.3 ($1.5CH_2$, $NCH_2CH_2C{=}ON$ and 0.5 × $CH_2C{\equiv}CH$), 38.2, 38.4 ($0.5CH_2$, 0.5 × $CH_2C{\equiv}CH$), 42.5, 42.7, 43.1, 43.2, 43.2, 44.7, 44.8 ($2CH_2$, 2 × $NCH_2CH_2C{=}O$), 52.2, 52.2, 57.0 (CH_2, $CH_2CH(CH_3)_2$), 71.6, 72.0, 72.5, 72.9 (CH, $CH_2C{\equiv}CH$), 78.23 78.4, 78.5, 78.8 (C, $CH_2C{\equiv}CH$), 80.6, 80.7, 81.1, 81.3 (C, ^{t}Bu), 170.0, 170.1, 170.2, 170.5, 170.8, 170.8, 171.0, 171.1 (3C, 3 × $C{=}O$); IR (ATR) ν (cm^{-1}): 3234 (≡C−H), 2962, 2934, 2920, 2873, 2113, 1725 (C=O ester), 1641 (C=O amides), 1468, 1443, 1421, 1368, 1257, 1152, 1014, 850; HRMS (TOF MS ES+): calcd for $C_{19}H_{33}N_2O_4$ $[M + H]^+$ m/z 353.2440, found 353.2431.

α-Peptoid ***5***. Compound **5** was synthesized starting from peptoid **1** (108 mg, 0.33 mmol, 1 equiv) by application of the method D using benzyl azide[41] (89 mg, 0.66 mmol, 2.0 equiv). Flash chromatography on silica gel of the crude product using EtOAc/MeOH 95:5 as solvent yielded **5** (128 mg, 0.28 mmol, 85%) as a colorless oil: R_f (EtOAc/MeOH 95:5) = 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): (4 rotamers in proprotions A/B/C/D 47:31:13:8) 0.76−0.92 (m, 6H, $CH_2CH(CH_3)_2$), 1.36/1.38 (2 × s, 9H, ^{t}Bu), 1.68−1.90 (m, 1H, $CH_2CH(CH_3)_2$), 1.88/2.07 (2 × s, 3H, NAc), 3.05−3.22 (m, 2H, $CH_2CH(CH_3)_2$), 3.89/3.91/3.97/4.03/4.08/4.23/4.33 (7 × s, 4H, 2 × $NCH_2C{=}O$), 4.52/4.58/4.61 (3 × s, 2H, NCH_2-triazole), 5.42/5.44/5.47 (3 × s, 2H, $NCH_2C_6H_5$), 7.16−7.37 (m, 5H, $NCH_2C_6H_5$), 7.47 (s, 0.08H, 0.08 × C=CHN, rot. D), 7.48 (s, 0.47H, 0.47 × C=CHN, rot. A), 7.50 (s, 0.13H, 0.13 × C=CHN, rot. C), 7.85 (s, 0.31H, 0.31 × C=CHN, rot. B); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 19.9, 20.0 ($2CH_3$, $CH_2CH(CH_3)_2$), 21.2, 21.5 (CH_3, NAc), 26.9, 27.5 (CH, $CH_2CH(CH_3)_2$), 27.8, 27.9 ($3CH_3$, ^{t}Bu), 42.5, 42.7, 43.3, 43.8 (CH_2, NCH_2-triazole), 46.5, 47.0, 48.0, 48.8, 49.7, 49.8, 50.3, 50.6 ($2CH_2$, 2 × $NCH_2C{=}O$), 54.1, 54.2, 54.4, 56.9, 57.1 ($2CH_2$, $NCH_2C_6H_5$ and $CH_2CH(CH_3)_2$), 81.8, 82.5, 83.0 (C, ^{t}Bu), 122.8, 123.3 (CH, C=CHN), 127.9, 128.0, 128.6, 128.7, 129.0, 129.2 (5CH, $NCH_2C_6H_5$), 134.3, 134.5 (C, $CH_2C_6H_5$), 143.7 (C, C=CHN), 166.8, 167.7, 168.1, 168.2, 168.4, 169.0 (C, OC=O), 171.3, 171.4, 171.8 (2C, NC=O); IR (ATR) ν (cm^{-1}): 2957, 2924, 2871, 2854, 1739 (C=O ester), 1663, 1646, 1640 (C=O amides), 1467, 1456, 1368, 1336, 1259, 1226, 1153, 1049, 957, 852, 800; HRMS (TOF MS ES+): calcd for $C_{24}H_{35}N_5O_4Na$ $[M + Na]^+$ m/z 480.2587, found 480.2569.

α,β-Peptoid ***6***. Compound **6** was synthesized starting from peptoid **2** (211 mg, 0.62 mmol, 1 equiv) by application of the method D using benzyl azide (124 mg, 0.93 mmol, 1.5 equiv). Flash chromatography on silica gel of the crude product using EtOAc/MeOH 95:5 as solvent yielded **6** (226 mg, 0.48 mmol, 77%) as a colorless oil: R_f (EtOAc/MeOH 95:5) = 0.26; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): (4 rotamers in proprotions A/B/C/D 53:28:13:5) 0.80−0.96 (m, 6H, $CH_2CH(CH_3)_2$), 1.36/1.39 (2 × s, 9H, ^{t}Bu), 1.79−1.93 (m, 1H, $CH_2CH(CH_3)_2$), 1.86/2.11 (2 × s, 3H, NAc), 2.46 (t, J = 7.2 Hz, 0.56H, 0.28 × $NCH_2CH_2C{=}O$, rot. B), 2.50 (t, J = 6.4 Hz, 0.1H, 0.05 × $NCH_2CH_2C{=}O$, rot. D), 2.62 (t, J = 7.0 Hz, 1.06H, 0.53 × $NCH_2CH_2C{=}O$, rot. A), 2.66 (t, J = 7.6 Hz, 0.26H, 0.13 × $NCH_2CH_2C{=}O$, rot. C), 3.08−3.20 (m, 2H, $CH_2CH(CH_3)_2$), 3.61/3.51 (2 × t, J = 7.2 Hz, 2H, $NCH_2CH_2C{=}O$), 4.19 (s, 1.06H, 0.53 × $NCH_2C{=}O$, rot. A), 4.26 (s, 0.56H, 0.28 × $NCH_2C{=}O$, rot. B), 4.28 (s, 0.26H, 0.13 × $NCH_2C{=}O$, rot. C), 4.38 (s, 0.10H, 0.05 × $NCH_2C{=}O$, rot. D), 4.51 (s, 0.26H, 0.13 × NCH_2-triazole, rot. C), 4.53 (s, 0.10H, 0.05 × NCH_2-triazole, rot. D), 4.56 (s, 1.06H, 0.53 × NCH_2-triazole, rot. A), 4.60 (s, 0.56H, 0.28 × NCH_2-triazole, rot. B), 5.45/5.50 (2 × s, 2H, $NCH_2C_6H_5$), 7.19−7.40 (m, 5H, $NCH_2C_6H_5$), 7.46 (s, 0.05H, 0.05 × C=CHN, rot. D), 7.54 (s, 0.53H, 0.53 × C=CHN, rot. A), 7.55 (s, 0.13H, 0.13 × C=CHN, rot. C), 7.75 (s, 0.28H, 0.28 × C=CHN, rot. B); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 20.1 ($2CH_3$, $CH_2CH(CH_3)_2$), 21.3, 21.6 (CH_3, NAc), 27.0, 27.6 (CH, $CH_2CH(CH_3)_2$), 27.9, 28.0 ($3CH_3$, ^{t}Bu), 33.9, 34.1, 34.2 (CH_2, $NCH_2CH_2C{=}O$), 40.8, 41.1, 42.8, 43.0, 43.2, 43.5 ($2CH_2$, $NCH_2CH_2C{=}O$ and NCH_2-triazole), 47.0, 47.4, 50.5, 51.0 (CH_2, $NCH_2C{=}O$), 54.2, 54.2, 54.4 (CH_2, $NCH_2C_6H_5$), 54.5, 57.3 (CH_2, $CH_2CH(CH_3)_2$), 80.7, 81.2, 81.4 (C, ^{t}Bu), 122.3, 123.5, 123.6 (CH, C=CHN), 128.0, 128.1, 128.6, 128.7, 128.8, 129.0, 129.1, 129.2 (5CH, $NCH_2C_6H_5$), 134.6 (C, $CH_2C_6H_5$), 144.2, 144.3, 144.5 (C, C=CHN), 168.2, 168.3, 168.4 (C, OC=O), 170.4, 170.6, 171.2, 171.4, 171.5, 171.9 (2C, NC=O); IR (ATR) ν (cm^{-1}): 2960, 2930, 2871, 2850, 1723 (C=O ester), 1653, 1646 (C=O amides), 1456, 1429, 1368, 1336, 1256, 1224, 1151, 1049, 1033, 846; HRMS (TOF MS ES+): calcd for $C_{25}H_{38}N_5O_4$ $[M + H]^+$ m/z 472.2924, found 472.2916.

β,α-Peptoid ***7***. Compound **7** was synthesized starting from peptoid **3** (117 mg, 0.35 mmol, 1 equiv) by application of the method D using benzyl azide (71 mg, 0.53 mmol, 1.5 equiv). Flash chromatography on silica gel of the crude product using EtOAc/MeOH 95:5 as solvent yielded **7** (139 mg, 0.29 mmol, 83%) as a colorless oil: R_f (EtOAc/MeOH 95:5) = 0.27; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): (4 rotamers in proprotions A/B/C/D 47:30:15:8) 0.79/0.84 (2 × d, J = 6.5 Hz, 6H, $CH_2CH(CH_3)_2$), 1.36 (s, 9H, ^{t}Bu), 1.78−1.95 (m, 1H, $CH_2CH(CH_3)_2$), 2.01 (s, 1.41H, 0.47 × NAc, rot. A), 2.04 (s, 0.90H, 0.30 × NAc, rot. B), 2.08 (s, 0.45H, 0.15 × NAc, rot. C), 2.09 (s, 0.24H, 0.08 × NAc, rot. D), 2.35 (t, J = 7.4 Hz, 0.30H, 0.15 × $NCH_2CH_2C{=}O$, rot. C), 2.45 (t, J = 6.8 Hz, 0.94H, 0.47 × $NCH_2CH_2C{=}O$, rot. A), 2.72 (t, J = 7.6 Hz, 0.16H, 0.08 × $NCH_2CH_2C{=}O$, rot. D), 2.76 (t, J = 6.9 Hz, 0.60H, 0.30 × $NCH_2CH_2C{=}O$, rot. B), 2.96−3.14 (m, 2H, $CH_2CH(CH_3)_2$), 3.37−3.56 (m, 2H, $NCH_2CH_2C{=}O$), 3.87/3.90/3.95 (3 × s, 2H, $NCH_2C{=}O$), 4.49/4.55 (2 × s, 2H, NCH_2-triazole), 5.35/5.38/5.39 (3 × s, 2H, $NCH_2C_6H_5$), 7.07−7.29 (m, 5H, $NCH_2C_6H_5$), 7.39/7.41/7.54 (3 × s, 1H, C=CHN); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 19.6, 19.7 ($2CH_3$, $CH_2CH(CH_3)_2$), 21.2, 21.3, 21.5 (CH_3, NAc), 26.4 (CH, $CH_2CH(CH_3)_2$), 27.6, 27.7 ($3CH_3$, ^{t}Bu), 30.7, 30.9, 31.4, 31.6 (CH_2, $NCH_2CH_2C{=}O$), 41.6, 42.9, 43.3, 43.7, 43.9, 44.6, 44.7 ($2CH_2$, $NCH_2CH_2C{=}O$ and NCH_2-triazole), 47.6, 48.0, 49.8 (CH_2, $NCH_2C{=}O$), 51.9, 52.0, 56.8 (CH_2, $CH_2CH(CH_3)_2$), 53.8, 53.9 (CH_2, $NCH_2C_6H_5$), 81.2, 81.6, 82.1, 82.4 (C, ^{t}Bu), 121.7, 122.1, 122.8 (CH, C=CHN), 127.7, 127.8, 128.4, 128.5, 128.7, 128.8 (5CH, $NCH_2C_6H_5$), 134.1, 134.2, 134.3 (C, $CH_2C_6H_5$), 143.3, 143.4, 143.5, 143.7 (C, C=CHN), 167.8, 167.9, 167.9 (C, OC=O), 170.2, 170.3, 170.5, 170.5, 170.7, 171.1, 171.6 (2C, NC=O); IR (ATR) ν (cm^{-1}): 3128, 3064, 2962, 2934, 2872, 1739 (C=O ester), 1641 (C=O amides), 1467, 1456, 1424, 1368, 1226, 1153, 1048, 1012, 957, 944, 797; HRMS (TOF MS ES+): calcd for $C_{25}H_{37}N_5O_4Na$ $[M + Na]^+$ m/z 494.2743, found 494.2733.

β-Peptoid ***8***. Compound **8** was synthesized starting from peptoid **4** (203 mg, 0.58 mmol, 1 equiv) by application of the method D using benzyl azide (116 mg, 0.87 mmol, 1.5 equiv). Flash chromatography on silica gel of the crude product using EtOAc to EtOAc/MeOH 95:5 as solvent yielded **8** (165 mg, 0.34 mmol, 59%) as a colorless oil: R_f (EtOAc/MeOH 95:5) = 0.42; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): (4 rotamers in proprotions A/B/C/D 42:31:17:10) 0.74/0.79 (2 × d, J = 6.8 Hz, 6H, $CH_2CH(CH_3)_2$), 1.29/1.30 (2 × s, 9H, ^{t}Bu), 1.73−1.88 (m, 1H, $CH_2CH(CH_3)_2$), 1.91 (s, 0.93H, 0.31 × NAc, rot. B), 1.92 (s, 1.26H, 0.42 × NAc, rot. A), 1.97 (s, 0.30H, 0.10 × NAc, rot. D), 2.00 (s, 0.51H, 0.17 × NAc, rot. C), 2.31−2.51 (m, 2H, $NCH_2CH_2C{=}ON$), 2.51−2.70 (m, 2H, $NCH_2CH_2C{=}OO$), 2.91−3.05 (m, 2H, $CH_2CH(CH_3)_2$), 3.38−3.60 (m, 4H, $NCH_2CH_2C{=}O$), 4.43/4.47/4.51 (3 × s, 2H, NCH_2-triazole), 5.36/5.39/5.41 (3 × s, 2H, $NCH_2C_6H_5$), 7.09−7.30 (m, 5H, $NCH_2C_6H_5$), 7.34/7.40/7.45 ((3 × s, 1H, C=CHN); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 19.7, 19.8 ($2CH_3$, $CH_2CH(CH_3)_2$), 21.3, 21.5 (CH_3, NAc), 26.4, 27.6 (CH, $CH_2CH(CH_3)_2$), 27.7, 27.8 ($3CH_3$, ^{t}Bu), 30.6, 31.2, 31.3, 31.9 (CH_2, $NCH_2CH_2C{=}OO$), 33.5, 33.7, 34.0, 34.3 (CH_2, $NCH_2CH_2C{=}ON$), 40.1, 40.4, 42.1, 42.4, 43.0, 43.2, 43.3, 43.5, 43.6, 44.7 ($3CH_2$, 2 × $NCH_2CH_2C{=}O$ and NCH_2-triazole), 51.9, 52.0, 56.6, 56.8 (CH_2, $CH_2CH(CH_3)_2$), 53.8, 53.9 (CH_2, $NCH_2C_6H_5$), 80.4, 80.5, 80.8, 81.0 (C, ^{t}Bu), 121.3, 121.6, 123.0 (CH, C=CHN), 127.7, 127.8, 128.4, 128.4, 128.6, 128.8, 128.8, 128.9 (5CH, $NCH_2C_6H_5$), 134.3 (C, $CH_2C_6H_5$), 144.0, 144.1, 144.3 (C, C=CHN), 170.0, 170.2, 170.4, 170.5, 170.6, 170.7, 171.0, 171.1 (3C, 3 × $C{=}O$); IR (ATR) ν (cm^{-1}): 2964, 2935, 2872, 1724 (C=O ester), 1640, 1635 (C=O amides), 1498, 1468, 1455, 1423, 1368, 1325, 1257, 1222, 1151, 1048, 1014, 844,

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791; HRMS (TOF MS ES+): calcd for $C_{26}H_{39}N_5O_4Na$ $[M + Na]^+$ m/z 508.2900, found 508.2878.

α-Peptoid ***9***. Compound **9** was synthesized starting from peptoid **5** (74 mg, 0.16 mmol, 1 equiv) by application of the method E. Flash chromatography on silica gel of the crude product using CH_2Cl_2/MeOH 95:5 as solvent yielded **9** (66 mg, 0.11 mmol, 69%) as a yellow foam: R_f (CH_2Cl_2/MeOH 95:5) = 0.29; ^{1}H NMR (500 MHz, CD_3CN) δ (ppm): (4 rotamers in proprotions A/B/C/D 57:28:11:4) 0.82 (d, J = 6.6 Hz, 1.92H, 0.32 × $CH_2CH(CH_3)_2$, rot. B and D), 0.90 (d, J = 6.6 Hz, 4.08H, 0.68 × $CH_2CH(CH_3)_2$, rot. A and C), 1.40/1.42/1.43 (3 × s, 9H, ^{t}Bu), 1.73−1.89 (m, 1H, $CH_2CH(CH_3)_2$), 1.82 (s, 0.96H, 0.32 × NAc, rot. B and D), 2.03 (s, 2.04H, 0.68 × NAc, rot. A and C), 3.03 (d, J = 6.0 Hz, 0.56H, 0.28 × $CH_2CH(CH_3)_2$, rot. B), 3.06 (d, J = 6.0 Hz, 0.08H, 0.04 × $CH_2CH(CH_3)_2$, rot. D), 3.11 (d, J = 6.0 Hz, 1.14H, 0.57 × $CH_2CH(CH_3)_2$, rot. A), 3.16 (d, J = 5.6 Hz, 0.22H, 0.11 × $CH_2CH(CH_3)_2$, rot. C), 3.93/3.95/3.98/4.06/4.08/4.10/4.11 (7 × s, 4H, 2 × NCH_2C=O), 4.15 (s, 2.04H, 0.68 × N^+CH_3, rot. A and C), 4.19 (s, 0.96H, 0.32 × N^+CH_3, rot. B and D), 4.70 (s, 1.14H, 0.57 × NCH_2-triazole, rot. A), 4.71 (s, 0.56H, 0.28 × NCH_2-triazole, rot. B), 4.77 (s, 0.08H, 0.04 × NCH_2-triazole, rot. D), 4.80 (s, 0.22H, 0.11 × NCH_2-triazole, rot. C), 5.69/5.70/4.71 (3 × s, 2H, $NCH_2C_6H_5$), 7.45 (bs, 5H, $NCH_2C_6H_5$), 8.43 (s, 0.57H, 0.57 × C=CHN, rotamer A), 8.45 (s, 0.28H, 0.28 × C=CHN, rot. B), 8.51 (s, 0.04H, 0.04 × C=CHN, rot. D), 8.73 (s, 0.11H, 0.11 × C=CHN, rot. C); ^{13}C NMR (100 MHz, CD_3CN) δ (ppm): 20.1, 20.3 20.4 ($2CH_3$, $CH_2CH(CH_3)_2$), 21.6, 22.2 (CH_3, NAc), 27.6, 28.4 (CH, $CH_2CH(CH_3)_2$), 28.2, 28.2 ($3CH_3$, ^{t}Bu), 39.6, 39.7, 39.9, 40.2 (CH_3, N^+CH_3), 41.3, 41.4, 43.8, 44.1 (CH_2, NCH_2-triazole), 48.1, 48.6, 50.2, 50.7, 51.1, 51.2 ($2CH_2$, 2 × NCH_2C=O), 51.6, 51.8, 54.4, 54.7, 57.6, 57.8, 58.0 ($2CH_2$, $CH_2CH(CH_3)_2$ and $NCH_2C_6H_5$), 82.5, 83.5, 83.8 (C, ^{t}Bu), 130.1, 130.5, 130.9, 131.0 (6CH, $NCH_2C_6H_5$ and C=CHN), 133.1, 133.1 (C, $CH_2C_6H_5$), 141.8, 142.0 (C, C=CHN), 169.3, 169.4 (C, OC=O), 171.0, 171.4, 171.8, 172.4 (2C, NC=O); IR (ATR) ν (cm^{-1}): 3450, 2961, 2930, 2873, 1728 (C=O ester), 1673, 1667, 1641 (C=O amides), 1633, 1479, 1446, 1368, 1234, 1155, 1038, 962, 950; HRMS (TOF MS ES+): calcd for $C_{25}H_{38}N_5O_4$ $[M - I]^+$ m/z 472.2913, found 472.2920.

α,β-Peptoid ***10***. Compound **10** was synthesized starting from peptoid **6** (145 mg, 0.31 mmol, 1 equiv) by application of the method E. Flash chromatography on silica gel of the crude product using CH_2Cl_2/MeOH 95:5 as solvent yielded **10** (140 mg, 0.23 mmol, 74%) as a white foam: R_f (CH_2Cl_2/MeOH 95:5) = 0.32; ^{1}H NMR (500 MHz, CD_3CN) δ (ppm): (3 rotamers in proprotions A/B/C 66:24:10) 0.86 (d, J = 6.5 Hz, 0.72H, 1.44 × $CH_2CH(CH_3)_2$, rot. B), 0.94 (d, J = 7.0 Hz, 4.56H, 0.76 × $CH_2CH(CH_3)_2$, rot. A and C), 1.40 (s, 6.84H, 0.76 × ^{t}Bu, rot. A and C), 1.42 (s, 2.16H, 0.24 × ^{t}Bu, rot. B), 1.80−1.99 (CH, $CH_2CH(CH_3)_2$), 1.84 (s, 0.72H, 0.24 × NAc, rot. B), 2.04 (s, 2.28H, 0.76 × NAc, rot. A and C), 2.43−2.65 (m, 2H, NCH_2CH_2C=O), 3.05 (d, J = 7.5 Hz, 0.48H, 0.24 × $CH_2CH(CH_3)_2$, rot. B), 3.17 (d, J = 7.5 Hz, 1.52H, 0.76 × $CH_2CH(CH_3)_2$, rot. A and C), 3.53 (t, J = 7.5 Hz, 0.20H, 0.10 × NCH_2CH_2C=O, rot. C), 3.58 (t, J = 6.8 Hz, 0.48H, 0.24 × NCH_2CH_2C=O, rot. B), 3.64 (t, J = 7.0 Hz, 1.32H, 0.66 × NCH_2CH_2C=O, rot. A), 3.95 (s, 0.20H, 0.10 × NCH_2C=O, rot. C), 4.08 (s, 1.32H, 0.66 × NCH_2C=O, rot. A), 4.14/4.20 (2 × s, 3H, N^+CH_3), 4.34 (s, 0.48H, 0.24 × NCH_2C=O, rot. B), 4.65 (s, 0.48H, 0.24 × NCH_2-triazole, rot. B), 4.66 (s, 1.32H, 0.66 × NCH_2-triazole, rot. A), 4.76 (s, 0.20H, 0.10 × NCH_2-triazole, rot. C), 5.66/5.70 (2 × s, 2H, $NCH_2C_6H_5$), 7.39−7.51 (m, 5H, $NCH_2C_6H_5$), 8.41 (s, 0.24H, 0.24 × C=CHN, rot. B), 8.44 (s, 0.66H, 0.66 × C=CHN, rot. A), 8.73 (s, 0.10H, 0.10 × C=CHN, rot. C); ^{13}C NMR (100 MHz, CD_3CN) δ (ppm): 20.0, 20.2, 20.3 ($2CH_3$, $CH_2CH(CH_3)_2$), 21.4, 22.2 (CH_3, NAc), 27.5 (CH, $CH_2CH(CH_3)_2$), 28.1, 28.3 ($3CH_3$, ^{t}Bu), 34.3, 34.5, 35.1 (CH_2, NCH_2CH_2C=O), 39.5, 39.6 (CH_3, N^+CH_3), 39.5, 40.7 (CH_2, NCH_2-triazole), 43.3, 43.6, 44.4 (CH_2, NCH_2CH_2C=O), 48.5, 49.0, 51.4 (CH_2, NCH_2C=O), 54.2, 57.9 (CH_2, $CH_2CH(CH_3)_2$), 57.5, 57.6 (CH_2, $NCH_2C_6H_5$), 81.5, 81.6 (C, ^{t}Bu), 129.9, 130.0, 130.3, 130.4 (6CH, $NCH_2C_6H_5$ and C=CHN), 133.0 (C, $CH_2C_6H_5$), 141.9, 142.6 (C, C=CHN), 170.5, 171.4, 171.5, 171.9, 172.5 (3 × C, C=O); IR (ATR) ν (cm^{-1}): 2960, 2933, 2872, 1720 (C=O ester), 1662, 1649, 1638 (C=O amides), 1453, 1425, 1367, 1253, 1153, 1059, 990, 957, 846; HRMS (TOF MS ES+): calcd for $C_{26}H_{40}N_5O_4$ $[M - I]^+$ m/z 486.3080, found 486.3056.

β,α-Peptoid ***11***. Compound **11** was synthesized starting from peptoid **7** (100 mg, 0.21 mmol, 1 equiv) by application of the method E. Flash chromatography on silica gel of the crude product using CH_2Cl_2/MeOH 95:5 as solvent yielded **11** (98 mg, 0.23 mmol, 76%) as a white foam: R_f (CH_2Cl_2/MeOH 90:10) = 0.33; ^{1}H NMR (500 MHz, CD_3CN) δ (ppm): (4 rotamers in proprotions A/B/C/D 57:27:11:5) 0.82 (d, J = 6.5 Hz, 1.92H, 0.32 × $CH_2CH(CH_3)_2$, rot. B and D), 0.88 (d, J = 7.0 Hz, 4.08H, 0.68 × $CH_2CH(CH_3)_2$, rot. A and C), 1.40/1.41 (2 × s, 9H, ^{t}Bu), 1.83−1.97 (CH, $CH_2CH(CH_3)_2$), 1.95 (s, 1.71H, 0.57 × NAc, rot. A), 1.96 (s, 0.33H, 0.11 × NAc, rot. C), 1.99 (s, 0.15H, 0.05 × NAc, rot. D), 2.01 (s, 0.81H, 0.27 × NAc, rot. B), 2.48 (t, J = 7.0 Hz, 1.14H, 0.57 × NCH_2CH_2C=O, rot. A), 2.52 (t, J = 7.5 Hz, 0.54H, 0.27 × NCH_2CH_2C=O, rot. B), 2.60 (t, J = 7.0 Hz, 0.22H, 0.11 × NCH_2CH_2C=O, rot. C), 2.63 (t, J = 7.5 Hz, 0.10H, 0.05 × NCH_2CH_2C=O, rot. D), 3.07/3.09 (2 × d, J = 7.7 Hz, 2H, $CH_2CH(CH_3)_2$), 3.44 (t, J = 7.5 Hz, 0.22H, 0.11 × NCH_2CH_2C=O, rot. C), 3.45 (t, J = 7.3 Hz, 1.14H, 0.57 × NCH_2CH_2C=O, rot. A), 3.54 (t, J = 7.3 Hz, 0.54H, 0.27 × NCH_2CH_2C=O, rot. B), 3.57 (t, J = 7.5 Hz, 0.10H, 0.05 × NCH_2CH_2C=O, rot. D), 3.90 (s, 0.22H, 0.11 × NCH_2C=O, rot. C), 3.93 (s, 0.10H, 0.05 × NCH_2C=O, rot. D), 4.10 (s, 1.14H, 0.57 × NCH_2C=O, rot. A), 4.11 (s, 0.54H, 0.27 × NCH_2C=O, rot. B), 4.14/4.16/4.18 (3 × s, 3H, N^+CH_3), 4.66 (s, 1.14H, 0.57 × NCH_2-triazole, rot. A), 4.68 (s, 0.54H, 0.27 × NCH_2-triazole, rot. B), 4.80 (s, 0.10H, 0.05 × NCH_2-triazole, rot. D), 4.88 (s, 0.22H, 0.11 × NCH_2-triazole, rot. C), 5.69/5.70 (2 × s, 2H, $NCH_2C_6H_5$), 7.46 (bs, 5H, $NCH_2C_6H_5$), 8.43 (s, 0.27H, 0.27 × C=CHN, rot. B), 8.45 (s, 0.57H, 0.57 × C=CHN, rot. A), 8.51 (s, 0.05H, 0.05 × C=CHN, rot. D), 8.55 (s, 0.11H, 0.11 × C=CHN, rot. C); ^{13}C NMR (100 MHz, CD_3CN) δ (ppm): 20.0, 20.2 ($2CH_3$, $CH_2CH(CH_3)_2$), 22.0 (CH_3, NAc), 27.3, 28.4 (CH, $CH_2CH(CH_3)_2$), 28.1 ($3CH_3$, ^{t}Bu), 31.5, 31.9, 32.4, 32.6 (CH_2, NCH_2CH_2C=O), 39.6, 39.6, 39.8, 40.0 (CH_3, N^+CH_3), 40.8, 44.2 (CH_2, NCH_2-triazole), 43.0, 43.3, 44.4, 45.0 (CH_2, NCH_2CH_2C=O), 50.0, 51.5, 51.6 (CH_2, NCH_2C=O), 52.3, 56.8, 56.9 0 (CH_2, $CH_2CH(CH_3)_2$), 57.6, 57.7 (CH_2, $NCH_2C_6H_5$), 82.3, 83.3 (C, ^{t}Bu), 130.0, 130.4, 130.8, 130.9 (6CH, $NCH_2C_6H_5$ and C=CHN), 133.0 (C, $CH_2C_6H_5$), 141.9, 142.0, 142.7 (C, C=CHN), 169.1, 169.4 (C, OC=O), 171.0, 171.2, 171.4 (C, NC=OCH_3), 172.4, 172.7, 173.2, 173.7 (C, NC=OCH_2); IR (ATR) ν (cm^{-1}): 3459, 3002, 2963, 2934, 2871, 1734 (C=O ester), 1635 (C=O amides), 1456, 1424, 1369, 1235, 1206, 1155, 1072, 1028, 1012, 964, 947, 837, 767; HRMS (TOF MS ES+): calcd for $C_{26}H_{40}N_5O_4$ $[M - I]^+$ m/z 486.3080, found 486.3058.

β-Peptoid ***12***. Compound **12** was synthesized starting from peptoid **8** (95 mg, 0.20 mmol, 1 equiv) by application of the method E. Flash chromatography on silica gel of the crude product using CH_2Cl_2/MeOH 95:5 as solvent yielded **12** (91 mg, 0.15 mmol, 75%) as a white foam: R_f (CH_2Cl_2/MeOH 95:5) = 0.11; ^{1}H NMR (500 MHz, CD_3CN) δ (ppm): (4 rotamers in proprotions A/B/C/D 60:28:8:4) 0.85 (d, J = 6.5 Hz, 1.92H, 0.32 × $CH_2CH(CH_3)_2$, rot. B and D), 0.90 (d, J = 7.0 Hz, 4.08H, 0.68 × $CH_2CH(CH_3)_2$, rot. B and D), 1.40 (s, 9H, ^{t}Bu), 1.86−1.98 (CH, $CH_2CH(CH_3)_2$), 1.96/2.04 (2 × s, 3H, NAc), 2.42−2.76 (m, 4H, 2 × NCH_2CH_2C=O), 3.01−3.15 (m, 2H, $CH_2CH(CH_3)_2$), 3.34−3.65 (m, 4H, 2 × NCH_2CH_2C=O), 4.19 (s, 3H, N^+CH_3), 4.61 (s, 1.20H, 0.60 × NCH_2-triazole, rot. A), 4.63 (s, 0.56H, 0.28 × NCH_2-triazole, rot. B), 4.76 (s, 0.08H, 0.04 × NCH_2-triazole, rot. D), 4.84 (s, 0.16H, 0.08 × NCH_2-triazole, rot. C), 5.68/5.70 (2 × s, 2H, $NCH_2C_6H_5$), 7.46 (bs, 5H, $NCH_2C_6H_5$), 8.40/8.46 (2 × s, 1H, C=CHN); ^{13}C NMR (100 MHz, CD_3CN) δ (ppm): 18.7, 18.9 ($2CH_3$, $CH_2CH(CH_3)_2$), 20.7 (CH_3, NAc), 26.0, 27.1 (CH, $CH_2CH(CH_3)_2$), 26.8 ($3CH_3$, ^{t}Bu), 30.3, 30.8, 31.1 (CH_2, NCH_2CH_2C=OO), 32.9, 33.8, 33.9 (CH_2, NCH_2CH_2C=ON), 38.1 (CH_3, N^+CH_3), 38.5, 38.6, 42.3 (CH_2, NCH_2-triazole), 41.8, 42.1, 42.1, 43.3, 43.4, 43.8 ($2CH_2$, 2 × NCH_2CH_2C=ON), 50.9, 55.3, 55.5 (CH_2, $CH_2CH(CH_3)_2$), 56.2, 56.2, 56.4 (CH_2, $NCH_2C_6H_5$), 80.2 (C, ^{t}Bu), 128.6, 128.7, 129.0 (6CH, $NCH_2C_6H_5$ and C=CHN), 131.8 (C, $CH_2C_6H_5$), 141.1, 141.1 (C, C=CHN), 169.7, 169.9, 170.1, 170.1, 171.3, 171.9 (3C, 3 × C=O); IR (ATR) ν (cm^{-1}): 3460, 2962, 2930, 2872, 1723 (C=O ester), 1635 (C=O amides), 1450, 1424, 1368, 1253, 1222,

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1152, 1079, 1013, 842; HRMS (TOF MS ES+): calcd for $C_{27}H_{42}N_5O_4$ $[M - I]^+$ m/z 500.3237, found 500.3213.

α-Peptoid ***13***. R_f (AcOEt/MeOH 97:3) = 0.42; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.45, 1.50, 1.53 (s, 9H, ^{t}Bu), 2.00, 2.03, 2.04, 2.06, 2.20, 2.23 (s, 3H, NAc), 2.18−2.49 (m, 4H, 4 × $CH_2C{\equiv}CH$), 4.05−4.36 (m, 13H, 4 × $CH_2C{\equiv}CH$ and 2.5 × $NCH_2C{=}O$), 4.40−4.58 (m, 3H, 1.5 × $NCH_2C{=}O$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 21.2, 21.5 (CH_3, NAc), 28.1 ($3CH_3$, ^{t}Bu), 35.2, 36.0, 36.2, 36.3, 36.6, 37.6, 37.9 ($4CH_2$, 4 × $NCH_2C{=}O$), 45.8, 46.3, 46.4, 46.6, 46.7, 47.0, 47.9, 48.1, 48.3, 48.5, 48.6 ($4CH_2$, $CH_2C{\equiv}CH$),, 72.4, 72.8, 73.2, 73.4, 73.7, 73.9, 74.1, 74.4 (4CH, 4 × $CH_2C{\equiv}CH$), 78.0, 78.1, 78.2, 79.9, 80.9, 82.1, 83.5 (5C, ^{t}Bu and 4 × $CH_2C{\equiv}CH$), 167.4, 167.7, 167.9, 168.6 (4C, 4 × $C{=}O$ amide), 170.7, 171.0, 171.5 (C, $C{=}O$ ester); IR (ATR) ν (cm^{-1}): 3273, 3253, 3242 (≡C−H), 2979, 2932, 2120 (C≡C), 1734 (C=O ester), 1668, 1661, 1653(C=O amide), 1471, 1429, 1368, 1350, 1215, 1193, 1154, 961; HRMS (TOF MS ES+): m/z calcd for $C_{26}H_{32}N_4O_6Na$ $[M + Na]^+$: 519.2220; found: 519.2207.

α,β-Peptoid ***14***. R_f (AcOEt/MeOH 95:5) = 0.54; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.36, 1.37 (2 × s, 9H, ^{t}Bu), 1.98, 1.99, 2.13, 2.15, 2.17, 2.19 (7 × s, 3H, NAc), 2.13−2.45 (m, 4H, 4 × $CH_2C{\equiv}CH$), 2.48−2.94 (m, 4H, 2 × $NCH_2CH_2C{=}O$), 3.60−3.81 (m, 4H, $NCH_2CH_2C{=}O$), 4.09−4.52 (m, 12H, 4 × $NCH_2C{\equiv}CH$ and 2 × $NCH_2C{=}O$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 21.2, 21.5, 21.8 (CH_3, NAc), 28.1 ($3CH_3$, ^{t}Bu), 30.7, 30.9, 31.4, 31.7, 32.1 (CH_2, $NCH_2CH_2C{=}O$), 33.2, 33.5, 33.7, 33.9, 34.1, 34.4, 34.5, 34.7, 34.8, 35.1, 35.3, 35.4, 35.5 ($3CH_2$, 2 × $CH_2C{\equiv}CH$ and $NCH_2CH_2C{=}O$), 37.9, 38.1, 38.3, 38.4, 38.6, 38.9, 39.0, 39.2, 39.4, 39.5, 39.9 ($2CH_2$, 2 × $CH_2C{\equiv}CH$), 41.7, 41.9, 42.3, 42.6, 43.0, 43.1, 43.6, 44.1, 44.3, 44.8 ($2CH_2$, 2 × $NCH_2CH_2C{=}O$), 46.1, 46.2, 46.3, 46.5, 46.6, 47.6, 47.7, 47.9, 48.3, 48.5 ($2CH_2$, 2 × $NCH_2C{=}O$), 72.2, 72.4, 72.5, 72.7, 72.8, 73.1, 73.2, 73.4, 73.6, 74.1 (4CH, 4 × $CH_2C{\equiv}CH$), 78.0, 78.1, 78.3, 78.4, 78.7, 78.8, 79.2 (4C, 4 × $CH_2C{\equiv}CH$), 80.9, 81.0, 81.5, 81.7 (C, ^{t}Bu), 167.2, 167.5, 167.8, 167.9, 168.1, 168.2, 168.4 (4C, 4 × $C{=}O$ amide), 170.2, 170.4, 170.7, 171.0, 171.3, 171.4, 171.6 (C, 4 × $C{=}O$ ester); IR (ATR) ν (cm^{-1}): 3288, 3257, 3250, 3236 (≡C−H), 2979, 2932, 2117 (C≡C), 1722 (C=O ester), 1652(C=O amide), 1470, 1427, 1418, 1368, 1219, 1153; HRMS (TOF MS ES+): m/z calcd for $C_{28}H_{36}N_4O_6Na$ $[M + Na]^+$: 547.2531; found: 547.2533.

β-Peptoid ***15***. Previously reported in literature.[27]

α-Peptoid ***16***. Compound **16** was synthesized starting from peptoid **13** (61 mg, 0.12 mmol, 1 equiv) by application of the method D using benzyl azide (128 mg, 0.96 mmol, 8 equiv). Flash chromatography on silica gel of the crude product using EtOAc/MeOH 90:10 as solvent yielded **16** (94 mg, 0.09 mmol, 75%) as a white foam: R_f (EtOAc/MeOH 9:1) = 0.15; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.09−1.65 (m, 9H, ^{t}Bu), 1.85/2.07/2.15/2.20 (4 × bs, 3H, NAc), 3.19−4.85 (m, 16H, 4 × $NCH_2C{=}O$ and 4 × NCH_2-triazole), 5.15−5.63 (m, 8H, 4 × $NCH_2C_6H_5$), 6.92−7.35 (m, 20H, 4 × $NCH_2C_6H_5$), 7.35−8.06 (m, 4H, 4 × C=CHN); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 21.2, 21.4 (CH_3, NAc), 27.6, 27.8 ($3CH_3$, ^{t}Bu), 41.7, 42.4, 42.9, 43.5, 44.0, 46.0, 46.3, 47.0, 48.1, 48.6, 49.3, 49.9 ($8CH_2$, 4 × $NCH_2C{=}O$ and 4 × NCH_2-triazole), 53.9 ($4CH_2$, 4 × $NCH_2C_6H_5$), 81.6, 81.7, 81.8, 81.9, 82.6, 83.0 (C, ^{t}Bu), 123.3, 128.4 (4CH, 4 × C=CHN), 127.6, 127.8, 127.9, 128.2, 128.4, 128.5, 128.6, 128.8 (20CH, 4 × $NCH_2C_6H_5$), 134.4, 135.0, 135.1 (4C, 4 × $NCH_2C_6H_5$), 167.5, 167.7, 168.2, 168.6, 169.1, 170.9, 171.6 (5C, 5 × C=O); IR (ATR) ν (cm^{-1}): 3133, 2981, 2946, 1734, 1668, 1663, 1653 (C=O), 1497, 1473, 1456, 1433, 1369, 1330, 1051, 1029, 953, 813; HRMS (TOF MS ES+): calcd for $C_{54}H_{60}N_{16}O_6Na_2$ $[M + 2Na]^{2+}$ m/z 537.2339, found 537.2326.

α,β-Peptoid ***17***. Compound **17** was synthesized starting from peptoid **14** (50 mg, 95 μmol, 1 equiv) by application of the method D using benzyl azide (101 mg, 0.76 mmol, 8 equiv). Flash chromatography on silica gel of the crude product using CH_2Cl_2/MeOH 95:5 as solvent yielded **17** (98 mg, 93 μmol, 98%) as a white foam: R_f (CH_2Cl_2/MeOH 90:10) = 0.52; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.33−1.37 (2 × s, 9H, ^{t}Bu), 1.79−2.26 (m, 3H, NAc), 2.29−3.01 (m, 4H, 2 × $NCH_2CH_2C{=}O$), 3.23−3.71 (m, 4H, 2 × $NCH_2CH_2C{=}O$), 3.92−4.72 (m, 12H, 2 × $NCH_2C{=}O$ and 4 × NCH_2-triazole), 5.11−5.62 (m, 8H, $NCH_2C_6H_5$), 6.90−7.36 (m, 20H, 4 × $NCH_2C_6H_5$), 7.36−7.96 (m, 4H, 4 × C=CHN); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 21.3, 21.5, 21.6 (CH_3, NAc), 28.0 ($3CH_3$, ^{t}Bu), 29.6, 30.9, 31.0, 31.1, 31.5, 31.8, 33.7, 34.1, 34.2 ($2CH_2$, 2 × $NCH_2CH_2C{=}O$), 40.8, 41.1, 41.3, 41.6, 41.9, 42.1, 42.2, 42.7, 43.0, 43.2, 43.4, 43.8, 44.2, 44.5, 44.9, 45.1, 46.3, 46.7, 49.4, 50.2, 50.4 ($8CH_2$, 2 × $NCH_2CH_2C{=}O$, 2 × $NCH_2C{=}O$ and 4 × NCH_2-triazole), 54.1 ($4CH_2$, $NCH_2C_6H_5$), 80.8, 81.2 (C, ^{t}Bu), 122.2, 122.3, 122.4, 122.9, 123.3, 123.5, 123.7 (4CH, 4 × C=CHN), 128.0, 128.1, 128.6, 128.6, 128.9, 129.0 (20CH, 4 × $NCH_2C_6H_5$), 134.3, 134.5, 134.6, 134.8 (4C, 4 × $NCH_2C_6H_5$), 143.2, 143.6, 143.7, 144.0, 144.3 (4C, 4 × C=CHN), 167.5, 167.6, 167.7, 167.9, 168.3, 168.4, 170.1, 170.4, 170.4, 171.0, 171.4, 171.7, 172.2 (5C, 5 × C=O); IR (ATR) ν (cm^{-1}): 3133, 3064, 3032, 2980, 2946, 2933, 1722, 1718, 1653, 1647 (C=O), 1498, 1471, 1456, 1436, 1368, 1266, 1222, 1153, 1029, 952, 821, 798; HRMS (TOF MS ES+): calcd for $C_{56}H_{66}N_{16}O_6$ $[M + 2H]^{2+}$ m/z 529.2676, found 529.2681.

β-Peptoid ***18***. Compound **18** was synthesized starting from peptoid **15** (68 mg, 123 μmol, 1 equiv) by application of the method D using benzyl azide (131 mg, 0.98 mmol, 8 equiv). Flash chromatography on silica gel of the crude product using CH_2Cl_2/MeOH 95:5 to 90:10 as solvent yielded **18** (72 mg, 66 μmol, 54%) as a white foam: R_f = 0.18 (CH_2Cl_2/MeOH 95:5); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.36 (s, 9H, ^{t}Bu), 1.89−2.18 (m, 3H, NAc), 2.32−2.96 (m, 8H, 4 × $NCH_2CH_2C{=}O$), 3.32−3.90 (m, 8H, 4 × $NCH_2CH_2C{=}O$), 4.23−4.70 (m, 8H, 4 × NCH_2-triazole), 5.21−5.60 (m, 8H, 4 × $NCH_2C_6H_5$), 7.04−7.35 (m, 20H, 4 × $NCH_2C_6H_5$), 7.35−7.81 (m, 4H, 4 × C=CHN); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 21.5, 22.0, 22.1 (CH_3, NAc), 28.0 ($3CH_3$, ^{t}Bu), 31.3, 31.6, 31.8, 32.2, 32.4, 33.8, 34.4, 34.5 ($4CH_2$, 4 × $NCH_2CH_2C{=}O$), 40.7, 41.0, 41.2, 42.4, 42.6, 43.0, 43.2, 43.7, 43.9, 44.1, 44.3, 44.4, 44.6, 45.0, 45.2, 45.5, 45.7 ($8CH_2$, 4 × $NCH_2CH_2C{=}O$ and 4 × NCH_2-triazole), 54.2 ($4CH_2$, $NCH_2C_6H_5$), 80.7, 81.2 (C, ^{t}Bu), 122.3, 123.6 (4CH, 4 × C=CHN), 128.1, 128.7, 129.1 (20CH, 4 × $NCH_2C_6H_5$), 134.5, 134.7 (4C, 4 × $NCH_2C_6H_5$), 144.2 (4C, 4 × C=CHN), 170.4, 170.6, 170.7, 171.2, 171.5 (5C, 5 × C=O); HRMS (TOF MS ES+): calcd for $C_{58}H_{68}N_{16}O_6Na_2$ $[M + 2Na]^{2+}$ m/z 565.2652, found 565.2633.

α-Peptoid ***19.4I***. Compound **19.4I** was synthesized starting from peptoid **16** (85 mg, 83 μmol, 1 equiv) by application of the method E. Flash chromatography on silica gel of the crude product using CH_2Cl_2/MeOH 90:10 as solvent yielded **19.4I** (81 mg, 51 μmol, 61%) as a white foam: R_f (CH_2Cl_2/MeOH 90:10) = 0.21; ^{1}H NMR (400 MHz, CD_3CN) δ (ppm): 1.21−1.51 (m, 9H, ^{t}Bu), 1.79−2.27 (m, 3H, NAc), 3.87−5.40 (m, 28H, 4 × $NCH_2C{=}O$, 4 × NCH_2-triazole and 4 × N^+CH_3), 5.48−5.94 (m, 8H, 4 × $NCH_2C_6H_5$), 7.15−7.69 (m, 20H, 4 × $NCH_2C_6H_5$), 8.78−9.94 (m, 4H, 4 × C=CHN); ^{13}C NMR (100 MHz, CD_3CN) δ (ppm): 22.0, 22.1 (CH_3, NAc), 28.3, 28.5 ($3CH_3$, ^{t}Bu), 40.0, 40.1, 40.2, 40.4, 40.6, 41.0 ($4CH_3$, 4 × N^+CH_3), 42.5, 42.0, 41.7, 41.4, 41.2, 40.9, 40.7, 40.4, 44.8, 50.5, 51.0, 51.1, 51.4, 51.5, 52.5, 52.7 ($8CH_2$, 4 × $NCH_2C{=}O$ and 4 × NCH_2-triazole), 57.7, 57.8 ($4CH_2$, $NCH_2C_6H_5$), 83.1, 84.2 (C, ^{t}Bu), 129.9, 130.0, 130.2, 130.3, 130.4 (20CH, 4 × $NCH_2C_6H_5$), 131.3, 131.5, 131.8 (4CH, 4 × C=CHN), 133.1, 133.2 (4C, 4 × $NCH_2C_6H_5$), 141.0, 141.1, 141.3, 141.5, 141.7, 141.9 (4C, 4 × C=CHN), 168.7, 169.1, 169.9, 170.3, 170.5, 171.2, 171.3, 171.4, 173.8, 173.9 (5C, 5 × C=O); IR (ATR) ν (cm^{-1}): 3032, 3003, 2979, 2928, 1730, 1674, 1653 (C=O), 1498, 1472, 1456, 1429, 1409, 1368, 1349, 1231, 1154, 1081, 1057, 957, 844, 768; HRMS (TOF MS ES+): calcd for $C_{58}H_{72}N_{16}O_6I_2$ $[M - 2I]^{2+}$ m/z 671.1955, found 671.1959.

α,β-Peptoid ***20.4I***. Compound **20.4I** was synthesized starting from peptoid **17** (113 mg, 107 μmol, 1 equiv) by application of the method E. Flash chromatography on silica gel of the crude product using CH_2Cl_2/MeOH 90:10 as solvent yielded **20.4I** (112 mg, 69 μmol, 64%) as a white foam: R_f (CH_2Cl_2/MeOH 80:20) = 0.29; ^{1}H NMR (400 MHz, CD_3CN) δ (ppm): 1.34/1.37/1.38 (3 × s, 9H, ^{t}Bu), 1.96−2.21 (m, 3H, NAc), 2.28−3.28 (m, 4H, 2 × $NCH_2CH_2C{=}O$), 3.31−4.84 (m, 4H, 2 × $NCH_2CH_2C{=}O$), 3.95−4.43 (m, 12H, 4 × N^+CH_3), 4.43−5.64 (12H, 2 × $NCH_2C{=}O$ and 4 × NCH_2-triazole), 5.66−6.02 (m, 8H, 4 × $NCH_2C_6H_5$), 7.16−7.73 (m, 20H, 4 × $NCH_2C_6H_5$), 8.89−9.83 (m, 4H, 4 × C=CHN); ^{13}C NMR (100 MHz, CD_3CN) δ (ppm): 22.3 (CH_3, NAc), 28.2, 28.2, 28.3 ($3CH_3$, ^{t}Bu), 33.2, 33.6, 34.3, 34.7,

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35.0, 35.3 ($2CH_2$, 2 × $NCH_2CH_2C{=}O$), 37.7, 39.8, 40.0, 40.2, 40.3 ($4CH_3$, 4 × N^+CH_3), 40.6, 40.7, 40.9, 41.0, 41.6, 51.7, 52.4, 52.6 ($4CH_2$, 4 × NCH_2-triazole), 44.0, 44.4, 44.7, 45.4, 49.5, 54.3 ($4CH_2$, 2 × $NCH_2CH_2C{=}O$ and 2 × $NCH_2C{=}O$), 57.4, 57.5 ($4CH_2$, $NCH_2C_6H_5$), 81.6 (C, ^{t}Bu), 128.89, 129.2, 129.7, 130.0, 130.1 (20CH, 4 × $NCH_2C_6H_5$), 130.3, 131.1 (4CH, 4 × C=CHN), 133.1, 133.2 (4C, 4 × $NCH_2C_6H_5$), 141.7, 141.8, 142.2, 142.3, 142.5 (4C, 4 × C=CHN), 169.8, 170.0, 170.1, 171.7, 173.7, 173.8 (5C, 5 × C=O); IR (ATR) ν (cm^{-1}): 3031, 3004, 2981, 2928, 1718, 1654 (C=O), 1472, 1456, 1429, 1420, 1395, 1348, 1256, 1208, 1153, 1079, 1057, 1030, 990, 958, 841, 766. HRMS (TOF MS ES+): calcd for $C_{60}H_{76}N_{16}O_6I_2$ $[M - 2I]^{2+}$ m/z 685.2104, found 685.2114.

β-Peptoid ***21.4I***. Compound **21.4I** was synthesized starting from peptoid **18** (54 mg, 50 μmol, 1 equiv) by application of the method E. Flash chromatography on silica gel of the crude product using CH_2Cl_2/MeOH 90:10 as solvent yielded **21.4I** (41 mg, 25 μmol, 50%) as a white foam: R_f (CH_2Cl_2/MeOH 80:20) = 0.26; ^{1}H NMR (400 MHz, CD_3CN) δ (ppm): 1.30−1.43 (m, 9H, ^{t}Bu), 2.10−2.25 (m, 3H, NAc), 2.60−3.43 (m, 8H, 4 × $NCH_2CH_2C{=}O$), 3.43−3.94 (m, 8H, 4 × $NCH_2CH_2C{=}O$), 4.10−4.39 (m, 12H, 4 × N^+CH_3), 4.52−5.32 (m, 8H, 4 × NCH_2-triazole),5.48−5.91 (m, 8H, 4 × $NCH_2C_6H_5$), 7.18−7.64 (m, 20H, 4 × $NCH_2C_6H_5$), 8.92−9.54 (m, 4H, 4 × C=CHN); ^{13}C NMR (100 MHz, CD_3CN) δ (ppm): 22.4 (CH_3, NAc), 28.4 ($3CH_3$, ^{t}Bu), 30.4, 33.0, 34.0, 34.2, 34.6, 35.5, 35.8 ($4CH_2$, 4 × $NCH_2CH_2C{=}O$), 39.5, 40.0, 40.2 ($4CH_3$, 4 × N^+CH_3), 40.6, 41.0, 41.2, 43.9, 44.3, 44.7, 45.4, 45.5, 46.1 ($8CH_2$, 4 × NCH_2-triazole and 4 × $NCH_2CH_2C{=}O$), 54.6, 57.6, 57.8 ($4CH_2$, 4 × $NCH_2C_6H_5$), 81.8 (C, ^{t}Bu), 129.2, 129.5, 130.2, 130.2, 130.3, 130.6, 131.2 (24CH, 4 × $NCH_2C_6H_5$ and 4 × C=CHN), 133.5 (4C, 4 × $NCH_2C_6H_5$), 142.7, 142.9, 143.0 (4C, 4 × C=CHN), 172.0, 172.8 (5C, 5 × C=O); IR (ATR) ν (cm^{-1}): 3059, 3003, 2956, 2925, 2853, 1715, 1637, 1634 (C=O), 1587, 1498, 1454, 1369, 1313, 1207, 1182, 1153, 1079, 1058, 1030, 841; HRMS (TOF MS ES+): calcd for $C_{62}H_{80}N_{16}O_6I_2$ $[M - 2I]^{2+}$ m/z 699.2268, found 699.2251.

α,β-Peptoid ***22***. Compound **22** was obtained starting from peptoid **14** by treatment with a solution TFA/CH_2Cl_2 (1:1 v/v, 2 mL) at 0 °C during 2 h then evaporation. The obtained acid is immediately used in the coupling step.

α,β-Peptoid ***23***. Previously reported in literature.[42]

α,β-Peptoid ***24***. To a solution of peptoid **23** (143 mg, 1.05 equiv, 0.29 mmol) and peptoid **22** (0.28 mmol, 1.0 equiv) in a CH_2Cl_2/DMF mixture (5:1, 12 mL) were added DIPEA (0.25 mL, 1.4 mmol, 5 equiv) and HATU (128 mg, 0.34 mmol, 1.2 equiv). The resulting mixture was stirred for overnight at rt then washed with a saturated solution of NH_4Cl (2 × 5 mL), a saturated solution of $NaHCO_3$ (2 × 5 mL) then brine. The organic layers were dried over MgSO4, filtered and concentrated under reduced pressure. Flash chromatography on silica gel of the crude product using AcOEt/MeOH 97:3 as solvent yielded **24** (150 mg, 0.16 mmol, 57%) as a pale yellow foam: R_f (CH_2Cl_2/MeOH 97:3) = 0.50; ^{1}H NMR (400 MHz, CD_3CN) δ (ppm): 1.41/1.43 (2 × s, 9H, ^{t}Bu), 2.01/2.16/2.18/2.20 (4 × s, 3H, NAc), 2.21−2.48 (m, 8H, 8×—C≡CH), 2.49−3.05 (m, 8H, 4× NCH_2CH_2C O), 3.46−3.81 (m, 2H,$NCH_2CH_2C{\equiv}CH$), 3.98−4.81 (m, 24H, 8×$NCH_2C{\equiv}CH$ + 4×$NCH_2C{=}O$); ^{13}C NMR (100 MHz, CD_3CN) δ (ppm): 21.2, 21.4 (CH_3, NAc), 27.98 (3CH3, ^{t}Bu), 30.9, 31.4, 31.6, 33.9, 34.0, 34.22, 34.5, 34.7, 35.2, 35.5 37.8, 38.1 38.4, 38.5. ($4CH_2$, NCH_2CH_2CO), 41.8, 42.2, 42.6 43.5, 44.0, 44.1, 44.6, ($2CH_2$, 2 × $NCH_2CH_2C{=}O$), 46.04, 46.31, 46.44, 47.70, 47.91, 48.38 53.38 ($NCH_2C{=}O$),72.3, 72.4, 72.6, 72.7, 72.9, 73, 73.1, 73.4, 73.6 (4CH, 4 × $CH_2C{\equiv}CH$),, 77.9, 78, 78.3, 78.4 (4C, 4 × $CH_2C{\equiv}CH$), 81.5, 81.7 (C, tBu), 167.1, 167.4, 167.6, 167.9, 168.1, (C=O amide), 171, 170.7, 170.9, 171.3 (C=O ester); IR (ATR) ν (cm^{-1}): 3288; 3248 (≡C−H), 3014, 2980, 2935 (C≡C), 1722 (C=O ester), 1653 (C=O amide), 1469, 1435, 1367, 1346, 1215, 1155, 1041, 964, 846, 759; HRMS (ESI +): calcd for $C_{50}H_{60}N_8O_{10}$ $[M + H]^+$ 933.45052; found: 933.4505. (0.02).

α,β-Peptoid ***25***. Compound **25** was synthesized starting from peptoid **24** (100 mg, 107 μmol, 1 equiv) by application of the method D using benzyl azide (137 mg, 1.03 mmol, 10 equiv). Flash chromatography on silica gel of the crude product using CH_2Cl_2/MeOH 95:5 then 90/10 as solvent yielded **25** (165 mg, 83 μmol, 77%) as a pale yellow foam: R_f (CH_2Cl_2/MeOH 90:10) = 0.60; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.30−1.49 (m, 9H, ^{t}Bu),1.72−2.02 (m, 3H, NAc), 2.07−3.10 (m, 8H, 4 × $NCH_2CH_2C{=}O$), 3.33−3.75 (m, 8H, 4 × $NCH_2CH_2C{=}O$), 4.03−4.74 (24H, 4 × $NCH_2C{=}O$ and 8 × NCH_2−triazole), 5.14−5.66 (m, 16H, 8 × $NCH_2C_6H_5$), 7.07−7.37 (m, 40H, 8xC_6H_5), 7.39−8.07 (m, 8H, 8 × C=CHN); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 21.5, 21.3 (CH_3, NAc), 28 ($3CH_3$, tBu), 29.6, 31.5, 31.7, 33.7 ($4CH_2$, 4 × $NCH_2CH_2C{=}O$), 41.2, 41.7, 42.0, 42.7, 43.1, 43.2, 43.4, 43.7, 46.5, 46.7, 49.3, 50.1 ($16CH_2$, 4 × $NCH_2CH_2C{=}O$, 4 × $NCH_2C{=}O$ and 8 × NCH_2-triazole), 54.0 ($8CH_2$, 8x$NCH_2C_6H_5$), 80.8, 81.2 (C, ^{t}Bu), 122.4, 122.5, 122.7, 123.0, 123.2, 123.4, 123.6, 123,7 (8CH, 8 × C=CHN), 128.0, 128.5, 129.0 (40 CH, 8 × $NCH_2C_6H_5$), 134.7 (8C, 8 × $NCH_2C_6H_5$), 143.6, 143.9, 144.1, 144.3 (8C, 8 × C=CHN), 167.6, 167.8, 168.0, 168.2, 170.1, 170.4, 171.0, 171.8 (9C, 9 × C=O); IR (ATR) ν (cm^{-1}): 3138, 3070, 3034, 3007, 2987, 2931, 1722, 1653(C=O), 1456, 1435, 1367, 1332, 1220, 1153, 1049, 756, 723. HRMS (ESI+): calcd for $C_{106}H_{118}N_{32}O_{10}$ $[M + 2H]^{2+}$ m/z 999.4849, found 999.4842.

α,β-Peptoid ***26.8I***. Compound **26.8I** was synthesized starting from peptoid **25** (101 mg, 50 μmol, 1 equiv) by application of the method E. The orange solid obtained was washed with ether to yield **26.8I** (107 mg, 34 μmol, 68%) as a pale yellow foam: R_f (CH_2Cl_2/MeOH 90:10) = 0.16; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm): 1.35−1.47 (bs, 9H, ^{t}Bu), 1.84−2.29 (m, 3H, NAc), 2.53−3.21 (m, 8H, 4 × $NCH_2CH_2C{=}O$), 3.61−4.05 (m, 8H, 4 × $NCH_2CH_2C{=}O$), 4.19−4.47 (m, 24H, 8 × N^+CH_3), 4.58−5.40 (m, 24H, 4 × $NCH_2C{=}O$ and 8xNCH_2-triazole), 5.62−6.10 (m, 16H, 8 × $NCH_2C_6H_5$), 7.23−7.78 (m, 40H, 8 × $NCH_2C_6H_5$), 8.82−9.42 (m, 8H, 8 × C=CHN); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm): 22.4 (CH_3, NAc), 28.6, 28.7 ($3CH_3$, ^{t}Bu), 30.9, 34.7, 34.8, 35.0, 35.5 ($2CH_2$, 2 × $NCH_2CH_2C{=}O$), 39.8, 40.0, 40.2, 40.3, 40.4, 40.6 ($8CH_3$, 8 × N^+CH_3), 41.2, 41.4, 41.7, 42.1, 42.4, 52.6 ($8CH_2$, 8 × NCH_2-triazole), 44.8, 45.0, 45.1, 45.1, 45.2, 45.3, 53.1, 53.7 ($8CH_2$, 4 × $NCH_2CH_2C{=}O$ and 4 × $NCH_2C{=}O$), 58.3 ($8CH_2$, 8 × $NCH_2C_6H_5$), 82.6 (C, ^{t}Bu), 130.6, 130.7, 130.9 (48CH, 8 × $NCH_2C_6H_5$, 8 × C=CHN), 133.8, (8C, 8 × $NCH_2C_6H_5$), 142.3, 142.8 (8C, 8 × C=CHN), 171.0, 171.3, 172.8, 175.0, 175.6 (9C, 9 × C=O); IR (ATR) ν (cm^{-1}): 3055, 3036, 2933, 2854, 1716, 1658 (C=O), 1585, 1496, 1473, 1456, 1408, 1367, 1346, 1257, 1207, 1207, 1153, 1080, 1058, 1030, 958, 840, 821, 758, 715. HRMS (ESI+): calcd for $C_{114}H_{140}I_4N_{32}O_{10}$ $[M - 4I]^{4+}$ m/z 656.1895, found 656.1873.

α,β-Peptoid ***27***. Compound **27** was synthesized starting from peptoid **14** (150 mg, 0.290 mmol, 1 equiv) by application of the method D using octyl azide[43] (355 mg, 2.28 mmol, 8 equiv). Flash chromatography on silica gel of the crude product using CH_2Cl_2/MeOH 95:5 as solvent yielded **27** (221 mg, 0.193 mmol, 67%) as a pale yellow oil: R_f (CH_2Cl_2/MeOH 95:5) = 0.35; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.79, 0.81, 0.82 (s, 12H, $4CH_3$octyl), 1.18−1.41 (m, 40H, $20CH_2$octyl), 1.34, 1.37 (s, 9H, ^{t}Bu), 1.83 (m, 8H, $4CH_2$octyl), 1.91, 1.92, 1.93, 1.94, 1.96, 2.21, 2.24, 2.25, 2.28 (s, 3H, NAc), 2.35−3.10 (m, 4H, 2 × $NCH_2CH_2C{=}O$), 3.48−3.71 (m, 4H, 2 × $NCH_2CH_2C{=}O$), 4.17−4.67 (20H, 2 × $NCH_2C{=}O$, 4 × NCH_2-triazole and 4 × NCH_2), 7.45−7.96 (m, 4H, 4 × C=CHN); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 14.1 ($4CH_3$, octyl), 21.5, 21.7 (CH_3, NAc), 22.6 ($4CH_2$, octyl), 26.5 ($4CH_2$, octyl), 28.0, 28.1 ($3CH_3$, tBu), 28.9 ($4CH_2$, octyl), 29.0 ($4CH_2$, octyl), 30.0, 30.2 ($4CH_2$, octyl), 31.7 ($4CH_2$, octyl), 33.8, 34.1, 34.2 ($2CH_2$, 2 × $NCH_2CH_2C{=}O$), 41.2, 41.4, 41.6, 41.9, 42.1, 42.3, 42.7, 42.9, 43.1, 43.2, 43.6, 43.8,, 44.1, 44.8, 45.4, 46.6, 49.2, 50.1, 50.2 ($8CH_2$, 2 × $NCH_2CH_2C{=}O$, 2 × $NCH_2C{=}O$ and 4 × NCH_2-triazole), 50.4, 50.5 ($4CH_2$, 4xNCH_2), 80.9, 81.2, 81.3 (C, *t*Bu), 122.1, 122.3, 122.7, 122.9, 123.2, 123.3, 123.6 (4CH, 4 × C=CHN), 142.9, 143.0, 143.1, 143.2, 143.4, 143.6, 143.7, 143.8, 143.9, 144.1, 144.2 (4C, 4× C=CHN), 167.7, 167.8, 167.9, 168.1, 168.3, 168.4, 168.6 (2C, 2 × C=O) 170.3, 170.6, 171.1, 171.4, 171.5, 171.6, 171.7, 171.8, 172.4 (3C, 3 × C=O); IR (ATR) ν (cm^{-1}): 3136, 3076, 2955, 2928, 2856, 1726, 1653, 1465, 1456, 1437, 1367, 1332, 1219, 1151, 1049, 989, 952, 846, 783, 725. HRMS (ESI+): calcd for $C_{60}H_{105}N_{16}O_6$ $[M + H]^+$ m/z 1145.8397, found 1145.8400.

α,β-Peptoid ***28***. Compound **28** was synthesized starting from peptoid **24** (98 mg, 100 μmol, 1 equiv) by application of the method D

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using octyl azide (260 mg, 1.6 mmol, 16 equiv). Flash chromatography on silica gel of the crude product using CH_2Cl_2/MeOH 95:5 as solvent yielded **28** (158 mg, 73 μmol, 73%) as a white solid: R_f (CH_2Cl_2/MeOH 95:5) = 0.49; NMR (400 MHz, $CDCl_3$) δ (ppm): 0.81, 0.82 (ls, 24H, 8CH_3octyl), 1.13−1.32 (m, 80H, 40CH_2octyl), 1.35, 1.38 (s, 9H, ^{t}Bu), 1.77−1.92 (m, 16H, 8CH_2octyl), 1.93, 1.95, 1.97, 2.23, 2.29 (s, 3H, NAc), 2.35−3.12 (m, 8H, 4 × NCH$_2$CH_2C=O), 3.49−3.70 (m, 8H, 4 × NCH_2CH$_2$C=O), 4.18−4.71 (40H, 4 × NCH_2C=O, 8 × NCH_2-triazole and 8 × NCH_2), 7.48−8.03 (m, 8H, 8 × C=C*H*N); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 14.1 (8CH_3, octyl), 21.6, 21.7, 21.8 (CH_3, NAc), 22.6 (8CH_2, octyl), 26.6 (8CH_2, octyl), 28.1 (3CH_3, *t*Bu), 29.0, 29.1 (16CH_2, octyl), 30.3 (8CH_2, octyl), 31.7 (8CH_2, octyl), 32.0, 32.1, 33.9, 34.3 (4CH_2, 4 × NCH$_2$CH_2C=O), 41.3, 41.5, 41.7, 41.8, 41.9, 42.0, 42.1, 42.2, 42.4, 42.6, 42.7, 42.8, 42.9, 43.1, 43.2, 43.3, 43.5, 43.6, 43.9, 44.0, 44.2, 44.8 45.5 (12CH_2, 4 × NCH_2CH$_2$C=O and 8 × NCH_2-triazole), 46.6, 46.8, 46.9, 49.3, 49.4 (4CH_2, 4 × NCH_2C=O), 50.4, 50.58, 50.6 (8CH_2, 8 × NCH_2), 80.9, 81.3 (C, *t*Bu), 122.4, 122.8, 123.1, 123.3, 123.6, 123.7 (8CH, 8 × C=C*H*N), 142.8, 142.9, 143.1, 143.2, 143.3, 143.4, 143.5, 143.6, 143.7, 143.8, 143.9, 144.0, 144.1, 144.2, 144.4 (8C, 8 × *C*=CHN), 167.7, 167.8, 168.0, 168.2, 168.4 (4C, 4 × C=O) 170.6, 170.7, 171.1, 171.2, 171.5, 171.6, 171.7, 171.8, 171.9 (5C, 5 × C=O); IR (ATR) ν (cm^{-1}): 3132, 3080, 2955, 2926, 2856, 1724 (C=O ester), 1649 (C=O amide), 1465, 1437, 1367, 1336, 1257, 1217, 1186, 1151, 1051, 1031, 922, 781, 723. HRMS (ESI+): calcd for $C_{114}H_{197}N_{32}O_{10}$ $[M + H]^+$ *m*/*z* 2174.5885, found 2174.5876.

α,β-Peptoid ***29.4I***. Compound **29.4I** was synthesized starting from peptoid **27** (118 mg, 0.103 mmol, 1 equiv) by application of the method E. Flash chromatography on silica gel of the crude product using CH_2Cl_2/MeOH 90:10 as solvent yielded **29.4I** (118 mg, 0.069 mmol, 67%) as a viscous pale yellow oil: R_f (CH_2Cl_2/MeOH 95:5) = 0.13; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.79, 0.80, 0.82 (s, 12H, 4CH_3octyl), 1.24, 1.28 (ls, 40H, 20CH_2octyl), 1.33, 1.35 (s, 9H, ^{t}Bu), 1.90−2.03 (m, 8H, 4CH_2octyl), 2.04, 2.05, 2.07 (s, 3H, NAc), 2.40−3.50 (m, 4H, 2 × NCH$_2$CH_2C=O), 3.53−3.92 (m, 4H, 2 × NCH_2CH$_2$C=O), 4.28−4.77 (m, 20H, 4 × N$^+$CH_3, 4 × NCH_2octyl), 4.81−5.55 (12H, 2 × NCH_2C=O, 4 × NCH_2-triazole), 9.02−10.00 (m, 4H, 4 × C=C*H*N); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 14.0, 14.1 (4CH_3, octyl), 21.9, 22.2 (CH_3, NAc), 22.5 (4CH_2, octyl), 26.1, 26.2 (4CH_2, octyl), 28.0, 28.1 (3CH_3, *t*Bu), 28.7 (4CH_2, octyl), 28.9 (4CH_2, octyl), 29.0, 29.1, 29.2, 29.3, 29.4 (4CH_2, octyl), 31.5, 31.6 (4CH_2, octyl), 32.4, 32.8, 33.6, 34.4, 35.4 (2CH_2, 2 × NCH$_2$CH_2C=O), 39.2, 39.4, 39.6, 39.7, 39.8, 39.9, 40.0, 40.1 (4CH_3, 4 × N$^+$CH_3), 40.8, 40.9, 41.2, 41.4, 41.7, 42.0, 42.7, 43.3, 43.7, 44.1, 44.4, 44.6, 44.8, 51.0, 51.5, 52.2, 52.3, 53.5, 54.3 (8CH_2, 2 × NCH_2CH$_2$C=O, 2 × NCH_2C=O and 4 × NCH_2-triazole), 54.0, 54.1 (4CH_2, 4xNCH_2), 81.2, 81.4, 81.5 (C, *t*Bu), 130.6, 130.7 (4CH, 4 × C=C*H*N), 140,7, 140.8, 140.9, 141.0, 141.1, 141.2, 141.3, 141.4, 141.5, 141.6 (4C, 4 × *C*=CHN), 168.7, 169.1, 169.2, 169.4, 169.8 (2C, 2 × C=O) 171.0, 171.2, 171.6, 171.8, 172.4, 172.7, 172.9, 173.1, 173.2, 173.3, 173.4 (3C, 3 × C=O); **IR** (ATR) ν (cm^{-1}): 3468, 2955, 2926, 2856, 1718 (C=O ester), 1662 (C=O amide), 1585, 1456, 1410, 1367, 1319, 1255, 1209, 1155, 1076, 991, 958, 840, 723. HRMS (ESI+): calcd for $C_{64}H_{116}N_{16}O_6I_2$ $[M - 2I]^{2+}$ *m*/*z* 729.3671, found 729.3679.

α,β-Peptoid ***29.4PF$_6$***. Compound **29.4PF$_6$** was synthesized starting from peptoid **29.4I** (18 mg, 10.5 μmol, 1 equiv) by application of the method F using NH_4PF_6. Compound **29.4PF$_6$** (14 mg, 7.8 μmol, 74%) was obtained as a yellow amorphous solid: IR (ATR) ν (cm^{-1}): 3140, 2956, 2928, 2856, 1718 (C=O ester), 1662 (C=O amide), 1587, 1467, 1456, 1367, 1253, 1224, 1159, 1078, 837 (P−F), 754. HRMS (ESI+): calcd for $C_{64}H_{116}N_{16}O_{6F12}P_2$ $[M - 2PF_6]^{2+}$ *m*/*z* 747.4268, found 747.4273.

α,β-Peptoid ***29.4BF$_4$***. Compound **29.4BF$_4$** was synthesized starting from peptoid **29.4I** (20 mg, 11.7 μmol, 1 equiv) by application of the method F using NH_4BF_4. Compound **29.4 BF$_4$** (18 mg, 11.5 μmol, 98%) was obtained as a pale yellow amorphous solid: IR (ATR) ν (cm^{-1}): 3130, 2956, 2928, 2856, 1720 (C=O ester), 1662 (C=O amide), 1587, 1456, 1415, 1367, 1321, 1286, 1253, 1157, 1057 (B−F), 1035, 960, 844. HRMS (ESI+): calcd for $C_{64}H_{116}N_{16}O_6B_2F_8$ $[M - 2BF_4]^{2+}$ *m*/*z* 688.4692, found 688.4703.

α,β-Peptoid ***30.8I***. Compound **30.8I** was synthesized starting from peptoid **28** (94 mg, 43 μmol, 1 equiv) by application of the method E. Flash chromatography on silica gel of the crude product using CH_2Cl_2/MeOH 90:10 as solvent yielded **30.8I** (142 mg, 42 μmol, 99%) as a pale yellow powder: R_f (CH_2Cl_2/MeOH 95:5) = 0.11; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.78, 0.80 (s, 24H, 8CH_3octyl), 1.13−1.41 (m, 89H, 40CH_2octyl, ^{t}Bu), 1.96 (ls, 16H, 8CH_2octyl), 2.06 (ls, 3H, NAc), 2.35−3.40 (m, 8H, 4 × NCH$_2$CH_2C=O), 3.56−4.00 (m, 8H, 4 × NCH_2CH$_2$C=O), 4.30, 4.37, 4.40 (s, 24H, 8 × N$^+$CH_3), 4.52 (ls, 16H, 8 × NCH_2octyl), 4.82−5.58 (24H, 4 × NCH_2C=O, 8 × NCH_2-triazole), 9.01−9.72 (m, 8H, 8 × C=C*H*N); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 14.0 (8CH_3, octyl), 22.0 (CH_3, NAc), 22.5 (8CH_2, octyl), 26.1 (8CH_2, octyl), 28.0, 28.1, 28.2 (3CH_3, *t*Bu), 28.7 (8CH_2, octyl), 28.9 (8CH_2, octyl), 29.2, 29.5 (8CH_2, octyl), 31.6 (8CH_2, octyl), 35.5, 35.6 (2CH_2, 2 × NCH$_2$CH_2C=O), 39.2, 40.0, 40.1, 40.2, 40.7 (8CH_3, 8 × N$^+$CH_3), 40.9, 41.5, 43.5, 44.7, 51.4, 52.3 (16CH_2, 4 × NCH_2CH$_2$C=O, 4 × NCH_2C=O and 8 × NCH_2-triazole), 54.1 (8CH_2, 8 × NCH_2), 81.3, 81.4, 81.5 (C, *t*Bu), 130.7, 131.0 (8CH, 8 × C=C*H*N), 140.6, 141.1, 141.2, 141.4, 141.5 (8C, 8 × *C*=CHN), 168.9, 169.0, 169.2, 169.3, 169.7 (4C, 2 × C=O), 172.0, 173.3, 173.4 (5C, 5 × C=O); IR (ATR) ν (cm^{-1}): 3462, 3045, 2955, 2926, 2856, 1716 (C=O ester), 1660 (C=O amide), 1585, 1456, 1411, 1350, 1319, 1205, 1184, 1157, 1076, 958, 837, 723. HRMS (ESI+): calcd for $C_{122}H_{220}N_{10}O_{32I4}$ $[M]^{4+}$ *m*/*z* 700.3463, found 700.34617.

α,β-Peptoid ***30.8PF$_6$***. Compound **30.8PF$_6$** was synthesized starting from peptoid **30.8I** (30 mg, 9.1 μmol, 1 equiv) by application of the method F using NH_4PF_6. Compound **30.8PF$_6$** (30 mg, 8.7 μmol, 96%) was obtained as a yellow amorphous solid: IR (ATR) ν (cm^{-1}): 3142, 2955, 2926, 2856, 1716 (C=O ester), 1662 (C=O amide), 1587, 1464, 1411, 1224, 1180, 1078, 960, 837 (P−F), 740. HRMS (ESI+): calcd for $C_{122}H_{220}N_{10}O_{32F30P5}$ $[M - 3PF_6]^{3+}$ *m*/*z* 1006.1961, found 1006.1971.

α,β-Peptoid ***30.8BF$_4$***. Compound **30.8BF$_4$** was synthesized starting from peptoid **30.8I** (24 mg, 7.3 μmol, 1 equiv) by application of the method F using NH_4BF_4. Compound **30.8 BF$_4$** (19 mg, 6.4 μmol, 88%) was obtained as a yellow amorphous solid: IR (ATR) ν (cm^{-1}): 3400, 2955, 2926, 2856, 1716 (C=O ester), 1653 (C=O amide), 1585, 1458, 1417, 1367, 1319, 1257, 1207, 1157, 1062 (B−F), 960, 844, 725. HRMS (ESI+): calcd for $C_{122}H_{220}N_{32}O_{10}B_4F_{16}$ $[M - 4BF_4]^{4+}$ *m*/*z* 660.4446, found 660.4466.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02804.

^{1}H and ^{13}C NMR spectra for all compounds and 2D NOESY spectra for dimeric peptoids (PDF)

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Notes

The authors declare no competing financial interest.

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