

# Peptoid-phthalocyanine architectures with different grafting positions: Synthetic strategy and photoproperties

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- 3
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# 16 Graphical abstract



17 18

# 19 Abstract

A monoazido Zn phthalocyanine has been grafted onto three different alkynyl-functionalized peptoid helices using copper-catalyzed azide–alkyne cycloaddition, demonstrating the feasibility of such conjugates. Their photoproperties have been examined relatively to the spatial geometry induced by the peptoid helix.

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# 25 Keywords

26 Peptoid, phthalocyanine, helix, conjugate.

27	Highl	ights
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29	•	Peptoid chains with one and two alkynyl moieties on different residues have been
30		prepared.
31	•	A monoazido Zn phthalocyanine has been grafted using copper-catalyzed azide-
32		alkyne cycloaddition
33	•	The absorption and fluorescence of these conjugates have been recorded
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# 35 **1. Introduction**

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Porphyrinoids are aromatic macrocycles with an extended electronic delocalization, 37 conferring sought-after electronic and spectroscopic properties, amongst others.<sup>1</sup> Many 38 biomolecules such as chlorophylls,<sup>2</sup> hemes<sup>3</sup> and vitamin B12<sup>4</sup> are natural porphyrinoid 39 derivatives. The most common porphyrinoids are porphyrins and phthalocyanines, used in 40 several applications fitting the preoccupations of our modern world, such as artificial 41 photosynthesis,<sup>5</sup> catalysis<sup>6</sup> and photocatalysis,<sup>7</sup> photosensitisers for photodynamic therapy,<sup>8</sup> 42 conversion of light into electric current,<sup>9</sup> amongst others. Many of these applications require 43 multi-porphyrinoids arrays, often to promote photoinduced electron<sup>10</sup> or energy<sup>11</sup> transfers or 44 also mimick the antennas in the photosynthetic reaction center of photosystems.<sup>12</sup> Several 45 strategies have been developed to prepare multi-porphyrinoids arrays, either by using covalent 46 (possibly conjugated) bonds,<sup>13,14</sup> self-assemblies<sup>15,16,17</sup> or supramolecular edifices<sup>18</sup>. Peptoid 47 backbones have been used recently to prepare cofacial arrays of two porphyrins.<sup>19</sup> 48

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Peptoids (N-substituted glycine oligomers)<sup>20</sup> are a special class of peptide mimics 50 with desirable pharmacokinetic characteristics,<sup>21</sup> including resistance against enzymatic 51 degradation.<sup>22</sup> They can be synthesized in a sequence-specific manner with hundreds of 52 different side chains, thanks to the submonomer method<sup>23</sup> which uses primary amines as a 53 source of side chains diversity.<sup>24</sup> For these reasons, they have been investigated for numerous 54 biological applications.<sup>25</sup> The supramolecular assembly properties of peptoids also lead 55 researchers to envisage their application as biomaterials.<sup>26</sup> The side chains of peptoids are 56 appended to the amide nitrogen atoms rather than to the  $\alpha$ -carbons, resulting in tertiary amide 57 bonds. Unlike the peptide secondary amide bonds that are trans, with the exception of the 58 prolyl-amide bonds, the peptoid tertiary amide bonds can adopt both the *cis* and *trans* 59 conformations, one of the major cause of peptoid chain conformational flexibility.<sup>27</sup> Great 60 efforts have been devoted to controlling the *cis/trans* isomerization of peptoid amides.<sup>28</sup> This 61 allowed the identification of predictable discrete secondary structures, *i.e.* peptoid 62 foldamers.<sup>29</sup> Some foldamers are based on a defined combination of backbone *cis* and *trans* 63 amides,<sup>30</sup> whereas others comprise only *trans*<sup>31</sup> or *cis*-amides.<sup>32</sup> It is now well established that 64 peptoids with bulky  $\alpha$ -chiral side chains adopt a helical conformation resembling the all-cis 65 polyproline I (PPI) helix, with a 3-fold periodicity and a pitch of approximately 6 Å. The 66 handedness of a peptoid PPI-type helix is governed by the side chains stereochemistries. (S)-67  $\alpha$ -chiral side chains induce right-handed helices while the R configuration induces the left-68

handed one. The most widely-used  $\alpha$ -chiral side chains are aromatic, especially the 69 phenylethyl  $(pe)^{33}$  and 1-naphthylethyl (Inpe) side chains.<sup>32a</sup> Beside their bulkiness, it has 70 been reported that local  $n \rightarrow \pi^*$  interactions between backbone carbonyls and the aromatic 71 groups might be operative for stabilizing the *cis*-amides required for peptoid helix 72 formation.<sup>28a-c</sup> The presence of one or several aromatic helical faces may also contribute to the 73 conformational stability of peptoids.<sup>33a</sup> By contrast, very few studies have so far been 74 75 undertaken to achieve conformationally stable peptoid PPI-type helices from non-aromatic monomers.<sup>32b,34</sup> Recently, we demonstrated that the very bulky *tert*-butyl (*t*Bu) and  $\alpha$ -gem-76 dimethyl groups do provide exclusively the *cis*-amide geometry.<sup>35</sup> Another side chain 77 proposed by us with structure-inducing properties is the  $\alpha$ -chiral 1-tert-butylethyl group 78 79 (1tbe). An octamer sequence consisting of NtBu and Ns1tbe monomers in equal proportion provided a very stable PPI-type helix, the longest linear peptoid ever solved by X-ray 80 crystallography.<sup>32b</sup> 81

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83 So far, the insertion of one or several porphyrins on peptoid scaffolds has been 84 performed to optimize the cellular uptake efficiency of photosensitising porphyrins<sup>36</sup>,<sup>37</sup> or 85 mimic the protein–chlorophyll ensemble found in photosynthetic antenna.<sup>38</sup> Jiwon Seo and his 86 team beautifully used peptoid scaffolds to control porphyrin interactions, in the case of pure 87 <sup>19,39</sup> or mixed<sup>40,41,42</sup> porphyrinic arrays.

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In this work, the construction of conformationally stable PPI-type helices is sought after as topological templates to display phthalocyanine arrays. As such architectures are entirely new, this exploratory work aims at demonstrating the synthetic feasibility of such hybrids, at investigating the effect of the peptoid on the photoproperties of the phthalocyanine core, and at assessing the efficiency of the peptoid backbone in controlling the topology of dimeric phthalocyanine arrays.

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- 96
- 97 2. Results and discussion
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# 99 **2.1. Molecular design.**

All the hybrid structures designed in the framework of these investigations are represented in Fig. 1. The first conjugate **1** made of a single phthalocyanine on a pentapeptoid scaffold was prepared to evaluate the effect of the presence of a peptoid scaffold on the photoproperties of the phthalocyanine core. Hybrids 2 and 3 have each 2 phthalocyanines grafted on a nonameric peptoid scaffold, with two residues between the two phthalocyanines in hybrid 2, and only residue between the two phthalocyanines in hybrid 3. Phthalocyanine 4 will be used as the pristine reference phthalocyanine macrocycle.

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Fig. 1. Structures of the peptoid-phthalocyanine architectures 1-3 (with their expected topology) and of reference phthalocyanine 4. For each phthalocyanine, only one of the existing isomers is shown.

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113 The phthalocyanine core was chosen taking into account several considerations: Zn 114 phthalocyanines have interesting photophysical and photochemical properties which can be 115 tailored by their substitution pattern,<sup>43</sup> and *O*-hexyl non-peripheral substitution is known to 116 ensure of a satisfying solubility in common organic solvents.<sup>44</sup>

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The sequence design of the oligomers lies on the 3-fold periodicity of the PPI-like helix. The aliphatic *N*s1tbe monomers have been chosen as helical structure inducers (Fig. 2). Rather than aromatic side chains likely to interact with the phthalocyanine moieties, aliphatic side chains have been chosen, also because among all the aliphatic side chains tested so far the chiral bulky s1tbe side chain have achieved the best performance as helical structure inducer. Three peptoid oligomers have been selected: one pentamer (**5**) and two nonamers (**6** 

and 7), each with an acetamide and a carboxamide group at the N- and C-termini (Table 1). 124 The pentamer 5 comprises a (propargyl side chain as the central residue, flanked on each side 125 by two Ns1tbe residues. Both nonamers are composed of seven Ns1tbe and two Nem (N-126 ethynylmethyl glycine) residues. In the sequence of 6, the propargyl side chains are appended 127 on residues 4 and 7 (*i* and i+3), thus the two functional side chains are expected to be on the 128 same face of the helix. For the nonamer 7, the two Nem residues correspond to the residues 5 129 and 7 of the sequence. Consequently, based on the three-fold periodicity, the propargyl side 130 chains are expected to form a 120° degree angle. 131

The synthetic strategy was conceived as detailed on Fig. 2. To anchor the phthalocyanines onto the peptoid scaffold, the copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC) was chosen for its great versatility<sup>45,46,47</sup> and the easy access to azide-functionalized phthalocyanines. This implied the introduction of peptoid side chains containing an alkyne function, which we have demonstrated to be achievable.<sup>48</sup> Another expected advantage is that the formed 1,2,3-triazole linker is also, at least to some extent, a *cis*-amide inducer,<sup>28c</sup> which may help folding the peptoid chain of the conjugate compounds.

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- Fig. 2. Retrosynthetic strategy for the preparation of the targeted peptoid-phthalocyanineconjugates
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2.2.1. Propargyl-functionalized peptoid scaffold. Peptoids are commonly synthesized on 150 solid support by the submonomer method pioneered by Zuckermann.<sup>23</sup> In this method, each 151 new monomer is constructed in two iterative steps: (1) bromoacetylation of the N-terminus of 152 the growing chain, (2) introduction of the side chain by bromine atom displacement of the 153 formed bromoacetamide by a primary amine. This process is most often very efficient, 154 yielding to pure peptoids in high yields. The major limitation may originate from the steric 155 hindrance of the formed N-terminus secondary amine which may impair chain elongation 156 157 efficiency. In this work, the solid-phase synthesis of peptoid oligomers comprising Ns1tbe monomers was evaluated for the first time. The optimized conditions for the synthesis of 158 159 peptoids 5-7 are depicted in Scheme 1.

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Scheme 1. Solid-phase submonomer synthesis of peptoids 5-7 (optimized conditions).
Acylation step: BrCH<sub>2</sub>CO<sub>2</sub>H (6 equiv., 0.4 M/DMF), diisopropylcarbodiimide (DIC, 8 equiv.,
2 M/DMF), 2 x 5 min at 40 °C. Substitution step: 25 equiv. of HC≡CCH<sub>2</sub>NH<sub>2</sub>, 2M/DMF, 1h
at 40 °C or 15 equiv. of *t*BuCH(CH<sub>3</sub>)NH<sub>2</sub>), 2 M/DMF, 2 x 1h at 40 °C. Cleavage: TFA/DCM
(95/5), RT, 10 min. Acetylation: Ac<sub>2</sub>O (4 equiv.), Et<sub>3</sub>N (2 equiv.), EtOAc (0.2 M), 18h, RT.

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169 The syntheses were performed manually using a Fmoc-protected Rink amide MBHA resin as 170 the support, leading to *C*-terminus carboxamides upon cleavage. After several round of 171 optimizations, we found that conducting the two steps of the submonomer protocol under 172 gentle warming (40  $^{\circ}$ C) had a beneficial effect on the purity of the peptoids. Other important 173 improvements concern the acylation step and the substitution reactions with the bulky (2*S*)- 174 3,3-dimethylbutan-2-amine (*s1tbe* amine) which were systematically repeated with new 175 amount of reagents. The final acetylation of the peptoids was carried out in solution (Ac<sub>2</sub>O, 176 Et<sub>3</sub>N), after cleavage from the resin, and the compounds were purified by flash 177 chromatograpghy on silica gel. We have indeed observed that the cleavage of the acetylated 178 resin-bound peptoids under acidic conditions led to the loss of one residue at the *N*-extremity 179 of the oligomers (Table 1).

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n antai d		overall	%	expected	observed
peptoid	monomer sequence	yield <sup>b</sup>	purity <sup>c</sup>	mass	mass
5	$Ac-Ns1tbe-Ns1tbe-Ns1tbe-Ns1tbe-NH_2$	57	96	718.54	719.54 [M+H] <sup>+</sup>
6	$\begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} $	46	94	1236.92	1237.92 [M+H] <sup>+</sup>
7	$\begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} $	56	94	1236.92	1237.92 [M+H] <sup>+</sup>

**Table 1**. Sequence, purity, and mass spectra data of the peptoids **5**-7

<sup>a</sup>The peptoids were drawn with amides in the *trans* conformation by ease of drawing.

<sup>b</sup>Based on the resin loading (0.52 mmol.g<sup>-1</sup>), include all the solid-phase steps and the final
acetylation in solution.

<sup>c</sup>Determined by integration of the high-performance liquid chromatography (HPLC) UV trace
at 214 nm.

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2.2.2. Conformational studies. The helical character of the three peptoids 5-7 was assessed by
 Circular Dichroism (CD) in methanol (Fig. 3). The three peptoids display the typical signature
 associated with the PPI-type helical conformation of peptoid oligomers bearing aliphatic side

chains. It is worth noting that peptoids with  $\alpha$ -chiral aromatic side chains exhibit a completely 193 different profile resembling that of the peptide  $\alpha$ -helix. In our case, the S configuration of the 194 sltbe side chains produces CD curves with the same right-handed helicity as those of poly-(L-195 prolines) in alcohol solvents. The curves are characterized by a positive maximum at around 196 197 210 nm and two minima at 190 and 225 nm. The strong intensities of ellipticity on a perresidue molar basis, at 210 nm for the two nonamers, as compared to literature data, are 198 indicative of well-structured compounds and likely also reflect a cooperative folding process. 199 Unsurprisingly, the short length pentamer is less structurally stable; protohelical structures are 200 201 generally observed from the tetramer length. Measurements at the Q band wavelength were not expected to be meaningful due to the high concentrations used to record CD and the 202 subsequent aggregation affecting their absorption at this wavelength, unlike porphyrins that 203 are much less prone to agregation<sup>19</sup>. 204

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**Fig. 3**. CD spectra of peptoid oligomers 5-7 in MeOH at 500  $\mu$ M

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As the degree of PPI helical conformational order depends on the population of *cis*-amide bonds, we also estimated overall backbone amide  $K_{cis/trans}$  values. As recently described by us, the calculations were made on the basis of the NMR integration (2D-HSQCAD experiments, Fig. 4) of the methyne protons of the s1tbe side chains, which show distinct resonances depending on the *cis* or *trans* conformation of the amides (Supporting information). This calculation does not take into account the amide bonds connecting the *N*em residues with their

preceding residues, which corresponds to one in five amide bonds in the case of the pentamer 216 5, and two in nine amides in the case of the nonamers 6 and 7. The overall proportion of *cis*-217 amide determined for the amide bonds connecting the Ns1tbe residues with their preceding 218 residu was found to be 93% for the pentamer 5 ( $K_{cis/trans} = 13.2$ ), and 95% for the nonamer 6 219  $(K_{cis/trans} = 21.5)$ . The trans-amide rotamers were no longer detectable in the case of nonamer 220 7, it can be confidently considered that the proportion of cis-amides >98% ( $K_{cis/trans}$  > 49.0) in 221 this case. These results confirm the high helical character of the nonamer peptoids, the lower 222 223 degree of structuration of the pentamer, as seen from CD, appears to be correlated to a 224 substantial conformational heterogeneity arising from *cis/trans* amide bond isomerization.

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Fig. 4.  ${}^{1}\text{H}{}^{-13}\text{C}$  HSQCAD NMR spectra of peptoids 5-7. Panels display side chains *N*s1tbe methyne protons. Peptoid concentration was ~ 10 mM in CD<sub>3</sub>OD.

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2.2.3. Synthesis of azidophthalocyanine. Azidophthalocyanines, especially when an 233 asymmetric substitution pattern, are often prepared from corresponding hydroxylated 234 phthalocyanines, via successive mesylation then azidation. Hence monohydroxylated 235 phthalocyanine 10 was first prepared from phthalonitriles 8 and 9, reference phthalocyanine 4 236 being produced concomitantly. The significant difference in polarity of both phthalocyanines 237 allowed the quite easy separation by silica gel chromatography. Monohydroxylated 238 phthalocyanine 10 was first mesylated, and the crude product was immediately reengaged 239 without further purification in the nucleophilic substitution by sodium azide, yielding 240 241 phthalocyanine **11** (Scheme 2).



Scheme 2. Synthesis of azidophthalocyanine 11 and of the reference phthalocyanine 4. Foreach phthalocyanine, only one of the existing isomers is shown.

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2.2.4. Peptoid-phthalocyanine conjugates 1-3. Access to the three conjugates 1-3 by copper-247 catalysed azide-alkyne cycloadditions (CuAAC) was successfully achieved using ligand-free 248 conditions. The azidophthalocyanine 11 and alkyne-functionalized peptoids were simply 249 combined in presence of CuSO<sub>4</sub> and ascorbic acid in a biphasic CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O solvent system 250 known to increase CuAAC reaction rates (Scheme 3).<sup>49</sup> The azidophthalocyanine 11 was used 251 in a 1.5-fold excess per alkyne functional group to facilitate peptoid conversion. The three 252 conjugates were first purified on silica gel to remove excess azidophthalocyanine 11, and then 253 254 by size-exclusion chromatography, using THF or dichloromethane as eluent, to eliminate residual amount of starting peptoids. 255

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Scheme 3. Synthesis of the peptoid-phthalocyanine conjugates 1-3. For each phthalocyanine,
only one of the existing isomers is shown.

CD analysis of peptoid backbone is based on the amide chromophore in the far UV region
(240-180 nm), which necessitates the use of UV-transparent solvents, typically, acetonitrile,
methanol and water. Unfortunately, the poor solubility of peptoid-phthalocyanine conjugates
1-3 in these solvents prevented their CD analysis.

Interestingly, we were able to determine the peptoid amide  $K_{cis/trans}$  for the three conjugates, 265 from <sup>1</sup>H-<sup>13</sup>C-HSQCAD experiments in deuterated dichloromethane (Fig. 5). As previously, 266 the methyne cis and trans peaks of the s1tbe side chains were integrated for Kcis/trans 267 determination. We observed a dramatic decrease (84%) in average  $^{Ns1tbe}K_{cis/trans}$  value for the 268 shorter peptoid oligomer conjugate 1 (cis/trans ratio ~2:1), relative to its parent peptoid 5 269 270 (>13:1). By contrast, peptoid amide isomerism was not significantly affected in the conjugates 271 2 and 3 relative to peptoid nonamers 6 and 7, respectively. Interestingly, the conformational 272 homogeneity is even increased for the conjugate 2, for which the *trans* rotamers are no longer 273 detectable. The opposite is observed for the conjugate 3 relative to 7. A small proportion of *trans*-amide rotamers (4%) are observed for **3**, while the parent nonamer **7** was completely 274 275 homogeneous in term of amide rotamerism. Overall, the conformational homogeneity of the two peptoid-phthalocyanine conjugates 2 and 3 is remarkable, especially considering the size 276 277 of the phthalocyanine moieties relative to the peptoid templates, and also, the potential intraand inter-molecular interactions they can establish. The unique conformation known for 278 peptoids displaying all-cis amides is the PPI helix, the most likely outcome for the two 279 280 nonameric conjugates.

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Fig. 5. <sup>1</sup>H-<sup>13</sup>C HSQCAD NMR spectra of peptoids 1-3. Panels display side chains *N*s1tbe
methyne protons. Peptoid concentration was ~ 5 mM in deuterated dichloromethane.

#### 286 **2.3.** UV-vis spectroscopy.

The photoproperties of phthalocyanines are depending on structural factors (metal, 287 nature, number and position of substituents) as well as on external parameters such as the 288 solvent, concentration and temperature. As all compounds 1-4 have the same phthalocyanine 289 core, and for the sake of comparisons, UV-vis spectra of 1-4 have been first recorded in 290 different solvents. As derivatives 2 and 3 have twice the amount of phthalocyanines, 2 µM 291 concentrations were used for 2 and 3 whereas 4 µM concentrations were used for 1 and 4 292 (Fig. 6). The maximum absorption for the Q band in each solvent is summarized in Table 2, 293 together with the extinction coefficient values. Spectra used to determine these values are 294 295 displayed in the supplementary material (Figs S1-16).







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Figure 6. Superimposed UV-vis spectra of 1 (green, 4 μM), 2 (red, 2 μM), 3 (blue, 2 μM) and
4 (black, 4 μM) in dichloromethane (top left), chloroforme (top right), tetrahydrofurane
(bottom left) and dimethylformamide (bottom right)

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The first observation is that the presence of a peptoid helix and of the triazole ring does not affect by itself the photoproperties of the phthalocyanine macrocycle, as can be deduced when comparing spectra of **1** and **4**, whose spectra have roughly the same shape and intensity in all solvents, with the presence of H-aggregates in chlorinated solvents characterised by the

apparition of a red-shifted second Q band in THF and DMF. Conjugates 2 and 3 are very 307 aggregated in dichloromethane and in chloroform, as evidenced by their large and potato-308 shaped Q band. In THF and DMF, their Q band is sharper but the absorption is much less 309 intense than for 1 and 4. As the overall concentration of phthalocyanines is the same in all the 310 311 samples, one can infer that it is due to their spatial proximity induced by the grafting of two phthalocyanine units on a same peptoid backbone, who therefore interact with each other. The 312 position of the phthalocyanine on the peptoid backbone does not affect significantly this 313 phenomenon. Even though the helix retains its conformation after the grafting, the flexibility 314 315 of the C6 spacer between the peptoid backbone and the phthalocyanine core provide enough freedom of movement to the two macrocycles whose  $\pi$ - $\pi$  stacking occurs similarly for both 316 conjugates 2 and 3 in dichloromethane and chloroforme. Tetrahydrofuran and N,N-317 dimethylformamide both appear to inhibit this intramolecular aggregation, in line with 318 319 previous general observations on phthalocyanines.

320

# 321 Table 2

Compound	Solvent	$\lambda_{max} Q \text{ band } (nm)$	log E
	CH <sub>2</sub> Cl <sub>2</sub>	752	5.1
1	CHCl <sub>3</sub>	704	5.1
1	THF	698	5.2
	DMF	700	5.1
	CH <sub>2</sub> Cl <sub>2</sub>	683	4.9
2	CHCl <sub>3</sub>	704	5.0
2	THF	698	5.0
	DMF	700	5.4
	CH <sub>2</sub> Cl <sub>2</sub>	682	5.0
3	CHCl <sub>3</sub>	704	5.1
5	THF	698	5.2
	DMF	698	5.5
	CH <sub>2</sub> Cl <sub>2</sub>	751	5.2
4	CHCl <sub>3</sub>	705	5.1
-	THF	697	5.3
	DMF	700	5.3

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#### 323 **2.3. Fluorescence**

Fluorescence has been recorded in THF to explore more in detail the behaviour of the set of compounds, as it known to be a more sensitive technique. Spectra are displayed on Fig. 7 and data are gathered in Table 3.

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## 329 **Table 3**.

	Excitation	Emission	Stokes shift		
	$\lambda_{Ex}(nm)$	$\lambda_{Em}\left(nm\right)$	$\Delta_{\text{Stokes}} (\text{nm})$	$\Phi_{\rm L}$	
1	698	705	7	0.168	
2	698	705	7	0.098	
3	698	705	7	0.074	
4	700	707	10	0.270	

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At the working concentrations (normalized at absorption 0.2), a significant effect of the sole 332 presence of the peptoid helix is observed when comparing 1 and 2. The fluorescence quantum 333 yield ( $\Phi_F$ ) of **1** is indeed only 2/3 of those of the reference phthalocyanine **4**. When comparing 334 the data for **3** and **4**,  $\Phi_F$  value is significantly lower than for the monomeric derivatives, and is 335 interestingly slightly higher for 2 than for 3, even though the helix of conjugate 2 is more 336 likely to promote intramolecular interactions as it would promote co-facial geometry. It 337 338 confirms the fact the phthalocyanines have enough freedom of movement and hence that their relative configuration is not much affected by the helix configuration but rather by being 339 340 maintained close to each other by the grafting on the same peptoid backbone.

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oxide via a solvent purification system. EtOAc, CH<sub>2</sub>Cl<sub>2</sub>, cyclohexane, and MeOH for column chromatography were obtained from commercial sources and were used as received. All other solvents and chemicals obtained from commercial sources were used as received. NMR spectra were recorded on a 400 MHz Bruker Avance III HD spectrometer. Chemical shifts are referenced to the residual solvent peak and J values are given in Hertz. The following multiplicity abbreviations are used: (s) singlet, (bs) broad singlet, (d) doublet, (t) triplet, (q) quartet, (m) massif, and (br) broad. TLC was performed on Merck TLC aluminum sheets, silica gel 60, F254. Visualizing of spots was effected with UV-light and vanillin in EtOH/H<sub>2</sub>SO<sub>4</sub>, or ninhidrin or phosphomolybdic acid in EtOH. Flash chromatography was performed with Merck 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. LC-MS was recorded a Q Exactive Quadrupole-Orbitrap mass spectrometer coupled to a UPLC 

363 Ultimate 3000 (Kinetex EVO C18; 1.7  $\mu$ m; 100 mm × 2.1 mm column with a flow rate of 364 0.45 mL min–1 with the following gradient: a linear gradient of solvent B from 5% to 95% 365 over 7.5 min (solvent A = H<sub>2</sub>O + 0.1% formic acid, solvent B = acetonitrile + 0.1% formic 366 acid) equipped with a DAD UV/vis 3000 RS detector.

367 Synthesis of compounds 4 and 8-11: All solvents and reagents were of reagent grade quality and obtained commercially from Aldrich, Fluka or Merck. Phthalonitrile 9<sup>44</sup> and 3-368 nitrophthalonitrile<sup>50</sup> were prepared as previously reported. Previously reported procedure for 369 phthalonitrile 8 was slightly modified<sup>51</sup>. IR spectra were recorded between 4000 and 650 cm<sup>-1</sup> 370 using a PerkinElmer Spectrum 100 FT-IR spectrometer. Mass spectra were recorded on a 371 MALDI (matrix assisted laser desorption ionization) BRUKER Microflex LT using dithranol 372 (DIT) or 2,5-dihydroxybenzoic acid (DHB) as the matrix. High resolution mass spectra were 373 measured on an Agilent 6530 Accurate-Mass Q-TOF LC/MS spectrometer equipped with 374 375 electrospray ionization (ESI) source. NMR spectra of 4, 8, 10 and 11 were recorded in deuterated solvents (CDCl<sub>3</sub>) on a Varian 500 MHz spectrometer at 298 K. Electronic 376 377 absorption spectra were measured with a Shimadzu UV-2600 UV-vis spectrophotometer, and a Varian Cary Eclipse spectrofluorometer is used to record steady-state fluorescence emission 378 379 spectra were recorded by using at room temperature, using 10 mm path length cuvettes. Details about the determination of the fluorescence quantum yields are provided in the 380 supplementary material. 381

382

### **383 3.2. Synthesis of peptoid oligomers.**

Peptoid oligomers 5-7 were prepared by solid-phase submonomer synthesis. All steps were 384 carried out manually in 5 mL plastic fritted syringes fitted with a stopcock. The syringes were 385 placed on a benchtop orbital shaker for reaction incubations. Peptoids were synthesized on 386 polystyrene resin with an Fmoc-protected Rink amide MBHA linker (Novabiochem 100-200 387 mesh; 0.52 mmol g<sup>-1</sup>). The Fmoc-protected resin (0.150 g, 0.078 mmol) was swollen in DMF 388 (2 mL) for 10 min. The swelling was repeated (2x). The Fmoc group was removed by soaking 389 390 the resin in a 20% piperidine/DMF solution for 15 min at rt after which time the resin was washed with DMF (5×2 ml) and drained. The deprotection reaction was repeated (1x). A 391 solution of bromoacetic acid (65 mg, 0.46 mmol, 6 equiv) in DMF (1.2 mL) was added to the 392 deprotected resin, followed by a solution of diisopropylcarbodiimide (DIC) (0.1 mL, 0.63 393 mmol, 8 equiv) in DMF (0.3 mL). The reaction was heated at 40 °C under stirring for 10 min. 394 This acylation step was repeated (1x) when the growing chain was ended by a bulky N-395 tertbutylethyl group. The resin was filtered, washed with DMF (5×2 ml) and drained. A 396

solution of amine (for s1tbe 0.16 mL / 0.6 mL DMF 1.17 mmol, 15 equiv; for em 0.124 mL/ 397 0.6 mL DMF, 1.95 mmol, 25 equiv) added to the resin, and the reaction mixture was agitated 398 at 40 °C for 1 h.. This step was repeated (1x) in the case of a substitution by the (2S)-3,3-399 dimethylbutan-2amine. The resin was filtered, washed with DMF (5×2 mL) and drained. This 400 2-steps sequence of acylation and substitution was repeated until the target oligomer was 401 obtained. After the elongation steps, the resin was washed with CH<sub>2</sub>Cl<sub>2</sub> (5 x 2 mL) and 402 drained. The peptoid was cleaved from the resin by stirring in 95% trifluoroacetic 403 acid/CH<sub>2</sub>Cl<sub>2</sub> (2 mL) for 10 min at rt. This cleavage procedure was repeated (1x). The resin 404 was washed with CH<sub>2</sub>Cl<sub>2</sub> (2 x 2 mL) and the filtrate evaporated under reduced pressure. The 405 residual TFA was eliminated by adding CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and evaporation. Identity of the 406 peptoids was controlled by LC-MS (UV detection at 220 nm). The crude oligomers were 407 acetylated in solution. The peptoid was dissolved in EtOAc (0.2 M) and cooled to 0 °C under 408 409 Ar.  $Et_3N$  (2.0 equiv) was added to the stirring solution of amine, followed by addition of acetic anhydride (4 equiv) under Ar. After 2 h at 0 °C, the mixture was allowed to stand 410 411 overnight at room temperature. The mixture was filtered, and the solids washed with EtOAc. The filtrate was then concentrated in vacuo, yielding the crude N-acetylated compound which 412 413 was purified by flash column chromatography on silica gel. Purity was determined by HPLC (UV detection at 220 nm), and the product identity was confirmed by HRMS before CD and 414 415 NMR analyses.

416 *Peptoid 5 (Ac-Ns1tbe-Ns1tbe-Nem-Ns1tbe-Ns1tbe-NH*<sub>2</sub>). Pentamer **5** was isolated as a white 417 solid after purification by flash column chromatography on silica gel. 32.8 mg (0.045 mmol) 418 were obtained.  $R_f = 0.63$  (9:1 CH<sub>2</sub>Cl<sub>2</sub>/MeOH). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 0.76-419 1.41 (m, 48 H, CH(CH<sub>3</sub>)C(CH<sub>3</sub>)<sub>3</sub>), 1.92-2.26 (m, 4 H, COCH<sub>3</sub> and C=CH), 3.33-5.10 (m, 16 420 H, 5×NCH<sub>2</sub>CO, NCH<sub>2</sub>C=C and 4×CH(CH<sub>3</sub>)C(CH<sub>3</sub>)<sub>3</sub>), 5.52-7.95 (m, 2 H, CONH<sub>2</sub>). HRMS 421 (TOF MS ES+) m/z calcd for C<sub>39</sub>H<sub>71</sub>N<sub>6</sub>O<sub>6</sub>+ [M+H]<sup>+</sup> 719.5429; found 719.5417.

422 **Peptoid** 6 (Ac-Ns1tbe-Ns1tbe-Ns1tbe-Ns1tbe-Ns1tbe-Ns1tbe-Ns1tbe-Nh2). Peptoid 6 was isolated as a white solid after purification by flash column chromatography on 423 silica gel. 25.17 mg (0.020 mmol) were obtained.  $R_f = 0.65$  (9:1 CH<sub>2</sub>Cl<sub>2</sub>/MeOH). <sup>1</sup>H NMR 424 (400 MHz, CDCl<sub>3</sub>) δ (ppm): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 0.71-1.36 (m, 84 H, 425 CH(CH<sub>3</sub>)C(CH<sub>3</sub>)<sub>3</sub>), 1.92-2.17 (m, 3 H, COCH<sub>3</sub>), 2.26-2.49 (m, 2 H, C=CH), 3.47-4.88 (m, 29 426 H, 9×NCH<sub>2</sub>CO, 2×NCH<sub>2</sub>C=C and 7×CH(CH<sub>3</sub>)C(CH<sub>3</sub>)<sub>3</sub>), 5.97-7.92 (m, 2 H, CONH<sub>2</sub>). HRMS 427 (TOF MS ES+) m/z calcd for  $C_{68}H_{121}N_{10}O_{10}^+$  [M+H]<sup>+</sup> 1237.9262; found 1237.9267. 428

429 Peptoid 7 (Ac-Ns1tbe-Ns1tb

430 Peptoid 7 was isolated as a white solid after purification by flash column chromatography on

silica gel. 54.2 mg (0.043 mmol) were obtained.  $R_f = 0.65$  (9:1 CH<sub>2</sub>Cl<sub>2</sub>/MeOH). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 0.62-1.37 (m, 84 H, CH(CH<sub>3</sub>)C(CH<sub>3</sub>)<sub>3</sub>), 2.00-2.07 (m, 3 H, COCH<sub>3</sub>), 2.26-2.39 (m, 2 H, C≡CH), 3.39-4.88 (m, 29 H, 9×NCH<sub>2</sub>CO, 2×NCH<sub>2</sub>C≡C and 7×CH(CH<sub>3</sub>)C(CH<sub>3</sub>)<sub>3</sub>), 5.97-7.92 (m, 2 H, CONH<sub>2</sub>). HRMS (TOF MS ES+) m/z calcd for C<sub>68</sub>H<sub>121</sub>N<sub>10</sub>O<sub>10<sup>+</sup></sub> [M+H]<sup>+</sup> 1237.9262; found 1237.9247.

436

# 437 **3.3. Synthesis of azidophthalocyanine 11**

- Phthalonitrile 8. 3-nitrophthalonitrile (3.46 g, 20 mmol), 1,6 hexanediol (100 mmol, 12.0 g) 438 439 and K<sub>2</sub>CO<sub>3</sub> (500 mmol, 69 g) were stirred overnight at 60 °C in DMF (150 mL), then the reaction mixture was poured into water. The resulting white precipitate was filtrated and 440 441 purified by column chromatography (silica gel) using CH<sub>2</sub>Cl<sub>2</sub>/EtOH (50/1) as the eluent. Yield: 53% (2.6 g). C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>, MW: 244.29 g/mol. FT-IR (v, cm<sup>-1</sup>): 3315, 3088, 2935, 442 443 2861, 2238, 2226, 1978, 1580, 1473, 1453, 1399, 1291, 1177, 1033, 923, 844, 795, 729, 684. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 1.47 (2 H), 1.56 (m, 3 H), 1.90 (2 H), 3.67 (t, 2 H), 444 4.14 (t, 2 H), 7.21 (d, 1 H), 7.33 (d, 1 H), 7.62 (t, 1 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>), δ 445 (ppm): 25.58, 25.84, 28.81, 32.68, 62.91, 70.03, 110.01, 116.69, 117.37, 125.02, 134.57, 446 447 161.63.
- Hydroxyphthalocyanine 10 and phthalocyanine 4. Phthalonitrile 8 (300 mg, 1.23 mmol), phthalonitrile 9 (1.4 g, 6.15 mmol), and zinc acetate (0.13 g, 0.61 mmol) were stirred at 140 °C for 18 h under argon atmosphere in dry dimethylaminoethanol (6 mL). After evaporation of the solvent, the residue was dissolved in dichloromethane and purified by column chromatography (silica gel) using CH<sub>2</sub>Cl<sub>2</sub>/EtOH (20/1) as the eluent. Symmetrically substituted phthalocyanine 4 was first eluted, followed by the monohydroxylated AB<sub>3</sub> derivative 10.
- 455 *Symmetric phthalocyanine 4.* Dark-blue waxy solid. 50 mg.  $C_{56}H_{64}N_8O_4Zn$ , MW 978.56. 456 ATR-IR:  $v_{max}$  (cm<sup>-1</sup>) 2924, 2853 (aliph. C-H), 1594 (C=N).<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$
- 457 ppm: 0.89-1.06 (m, 12 H, CH<sub>3</sub>), 1.25-2.58 (m, 32 H, CH<sub>2</sub>), 3.95-4.89 (m, 8 H, CH<sub>2</sub>), 6.71-
- 458 9.04 (m, 12 H, ArCH). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ ppm: 14.36, 22.98-32.44, 68.73-69.56,
- 459 68.55, 70.59, 110.31-157.47. Anal. calc. for C<sub>56</sub>H<sub>64</sub>N<sub>8</sub>O<sub>4</sub>Zn: 68.74 C, 6.59; H, 11.45; N %,
- 460 Found: C, 68.50; H, 6.40; N, 11.20. MALDI-TOF: *m/z* 979.12 [MH]<sup>+</sup>. HR-ESI-MS *m/z*:
- 461 Calcd for  $C_{56}H_{65}N_8O_5Zn: 977.4420$ , Found 977.4331.
- 462 *Monohydroxyphthalocyanine 10.* Dark-blue waxy solid. 20 mg. C<sub>56</sub>H<sub>64</sub>N<sub>8</sub>O<sub>5</sub>Zn, MW 994.56.
- 463 ATR-IR: υ<sub>max</sub> (cm<sup>-1</sup>) 3410 (OH), 2924, 2853 (aliph. C-H), 1594 (C=N). <sup>1</sup>H NMR (500 MHz,
- 464 DMSO-*d*<sub>6</sub>) δ ppm: 0.81-1.01 (m, 9 H, CH<sub>3</sub>), 1.26-1.78 (m, 24 H, CH<sub>2</sub>), 1.85-2.31 (m, 10 H,

CH<sub>2</sub>), 3.50-3.58 (m, 1 H, OH), 4.07-4.94 (m, 8H, CH<sub>2</sub>O), 7.27-8.25 (m, 12 H, ArCH). <sup>13</sup>C
NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ ppm: 14.65, 22.73-33.40, 61.12, 61.44, 68.55, 70.59, 113.16156.50. Anal. calc. for C<sub>56</sub>H<sub>64</sub>N<sub>8</sub>O<sub>5</sub>Zn: 67.63 C, 6.49; H, 11.27; N %, Found: C, 67.50; H,
6.55; N, 11.35. MALDI-TOF: *m/z* 992.52 [M]<sup>+</sup>. HR-ESI-MS *m/z*: Calcd for C<sub>56</sub>H<sub>65</sub>N<sub>8</sub>O<sub>5</sub>Zn:
993.4369, Found 993.4282.

Azido-phthalocyanine (11). Monohydroxlated 10 (50 mg, 0.05 mmol) and triethylamine (0.50 470 mL) were stirred in dichloromethane (2 mL) in an ice bath, then mesyl chloride (0.20 mL) 471 was added drop by drop over 10 min. The stirring continues overnight at room temperature, 472 473 then the reaction mixture was washed by a dilute solution of potassium carbonate then by water. The organic phase was dried on sodium sulfate. The resulting crude mesylated 474 derivative and NaN<sub>3</sub> (0.5 mmol) are stirred in DMF at 80 °C overnight. CAUTION: NaN<sub>3</sub> 475 476 must be kept away from acid medium and be handled with care. Water is then added to the 477 cooled reaction mixture and the resulting precipitate is filtrated, recovered in dichloromethane and purified by column chromatography (silica gel) using CH<sub>2</sub>Cl<sub>2</sub>:EtOH (20:1) as the mobile 478 phase. Yield 90% (46 mg). C<sub>56</sub>H<sub>63</sub>N<sub>11</sub>O<sub>4</sub>Zn, MW 1019.57. ATR-IR: v<sub>max</sub> (cm<sup>-1</sup>) 2924, 2854 479 (aliph. C-H), 2092 (N<sub>3</sub>), 1590 (C=N). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ ppm: 0.77-1.05 (m, 480 481 9H, CH<sub>3</sub>), 1.20-2.37 (m, 34H, CH<sub>2</sub>), 4.65, 4.90 (b, 8H, CH<sub>2</sub>–O), 7.62-9.08 (m, 12H, ArCH). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ ppm: 14.21, 22.52-32.21, 51.29, 55.44, 68.83, 70.76, 482 113.30-156.38. Anal. calc. for C<sub>56</sub>H<sub>63</sub>N<sub>11</sub>O<sub>4</sub>Zn: 65.97 C, 6.23; H, 15.11; N %, Found: C, 483 65.40; H, 6.35; N, 15.45. MALDI-TOF: m/z 1020.50 [MH]<sup>+</sup>. HR-ESI-MS m/z: Calcd for 484 485 C<sub>56</sub>H<sub>64</sub>N<sub>11</sub>O<sub>4</sub>Zn: 1018.4434, Found 1018.4331.

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#### 487 **3.4.** Synthesis of peptoid-phthalocyanine conjugate

Synthesis of peptoid-phthalocyanine conjugate 1. To a solution of peptoid 5 (13 mg, 0.0180 488 mmol) and phthalocyanine 11 (20 mg, 0.0216 mmol, 1.2 equiv) dissolved in a biphasic 489 490 CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O (1:1) solvent system (0.5 mL) were added freshly prepared 0.1 M aq. ascorbic acid (0.3 equiv.), and 0.1 M aq. CuSO<sub>4</sub> (0.1 equiv.). After vigorous stirring for 24 h, the 491 mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (6 mL), washed with water (2 x1 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, 492 and concentrated in vacuo. The crude residue was purified first by flash column 493 chromatography (SiO<sub>2</sub>, 0.1 % EtOH in CH<sub>2</sub>Cl<sub>2</sub>) and then on Bio-Beads S3 stationary phase 494 (CH<sub>2</sub>Cl<sub>2</sub>), to yield the peptoid-phthalocyanine conjugates 1 (12.4 mg, 40%) as a green 495 powder. TLC : Rf = 0.63 (9:1 CH<sub>2</sub>Cl<sub>2</sub>/MeOH). <sup>1</sup>H NMR (400 MHz, DMF- $d_7$ )  $\delta$  (ppm): 0.56-496 2.32 (m, 91 H, 4×CH(CH<sub>3</sub>)C(CH<sub>3</sub>)<sub>3</sub>, 3×OCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>, and OCH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>), 2.40 (bs, 3 H, 497 COCH<sub>3</sub>), 3.63-4.86 (m, 20 H, 4×OCH<sub>2</sub>, 5×NCH<sub>2</sub>CO, and NCH<sub>2</sub>-triazole), 4.88-5.19 (m, 4 H, 498

- 499  $4 \times CH(CH_3)C(CH_3)_3$ , 7.09-9.24 (m, 13 H,  $4 \times Ar(CH)_3$ , and C=CHN-triazole). HRMS (TOF 500 MS ES+) *m/z* calcd for C<sub>95</sub>H<sub>134</sub>N<sub>17</sub>O<sub>10</sub><sup>64</sup>Zn [M+H]<sup>+</sup> 1736.9785; found 1736.9771. MALDI-501 TOF: *m/z* 1735.9712 (calcd. for C<sub>95</sub>H<sub>133</sub>N<sub>17</sub>O<sub>10</sub><sup>64</sup>Zn; [M]<sup>+</sup>; found 1735.171).
- Synthesis of peptoid-phthalocyanine conjugate 2. To a solution of peptoid 6 (10.5 mg, 502 503 0.0084 mmol) and phthalocyanine 11 (25.1 mg, 0.025 mmol, 3 equiv) dissolved in a biphasic CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O (1:1) solvent system (0.66 mL) were added freshly prepared 0.1 M aq. ascorbic 504 acid (0.9 equiv.), and 0.1 M aq. CuSO<sub>4</sub> (0.3 equiv.). After vigorous stirring for 24 h, the 505 mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL), washed with water (2 x2 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, 506 507 and concentrated in vacuo. The crude residue was purified first by column chromatography (SiO<sub>2</sub>, 0.1 % EtOH in CH<sub>2</sub>Cl<sub>2</sub>) and then by Bio-Beads S3 (THF), to yield the peptoid-508 phthalocyanine conjugates 2 (17.2 mg, 62 %) as a green powder. TLC:  $R_f = 0.65$  (9:1 509 CH<sub>2</sub>Cl<sub>2</sub>/MeOH). <sup>1</sup>H NMR (400 MHz, DMF-*d*<sub>7</sub>) δ (ppm): 0.64-2.62 (m, 173 H, 510 511 7×CH(CH<sub>3</sub>)C(CH<sub>3</sub>)<sub>3</sub>, 6×OCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>, 2×OCH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub> and COCH<sub>3</sub>), 3.53-5.33 (m, 45 H, 8×OCH<sub>2</sub>, 9×NCH<sub>2</sub>CO, 2×NCH<sub>2</sub>-triazole and 7×CH(CH<sub>3</sub>)C(CH<sub>3</sub>)<sub>3</sub>), 6.34-9.30 (m, 26 H, 512 513  $8 \times Ar(CH)_3$ , and  $2 \times C = CHN$ -triazole). HRMS (TOF MS ES+) m/z calcd for C<sub>180</sub>H<sub>248</sub>N<sub>32</sub>O<sub>18</sub><sup>64</sup>Zn<sub>2</sub> [M+2H]<sup>2+</sup> 1636.9023; found 1636.9044. MALDI-TOF: *m/z* 3271.790 514 (calcd. for  $C_{180}H_{246}N_{32}O_{18}^{64}Zn_2$ ; [M]<sup>+</sup> 3271.7901). 515
- Synthesis of peptoid-phthalocyanine conjugate 3. The same protocol as for the synthesis of 516 compound 2 was applied to the synthesis of conjugate 3, which was isolated in 83% yield (22 517 mg), starting from 10 mg of peptoid 7. TLC:  $R_f = 0.65$  (9:1 CH<sub>2</sub>Cl<sub>2</sub>/MeOH). <sup>1</sup>H NMR (400 518 519 MHz, DMF-*d*<sub>7</sub>) δ (ppm): 0.56-2.65 (m, 173 H, 7×CH(CH<sub>3</sub>)C(CH<sub>3</sub>)<sub>3</sub>, 6×OCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>, 2×OCH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub> and COCH<sub>3</sub>), 3.54-5.39 (m, 45 H, 8×OCH<sub>2</sub>, 9×NCH<sub>2</sub>CO, 2×NCH<sub>2</sub>-triazole 520 and 7×CH(CH<sub>3</sub>)C(CH<sub>3</sub>)<sub>3</sub>), 6.82-9.30 (m, 26 H, 8×Ar(CH)<sub>3</sub>, and 2×C=CHN-triazole). HRMS 521 (TOF MS ES+) m/z calcd. for C<sub>180</sub>H<sub>249</sub>N<sub>32</sub>O<sub>18</sub><sup>64</sup>Zn<sub>2</sub> [M+3H]<sup>3+</sup> 1091.6039; found 1091.6047. 522 523 MALDI-TOF: m/z 3271.790 (calcd. for C<sub>180</sub>H<sub>246</sub>N<sub>32</sub>O<sub>18</sub><sup>64</sup>Zn<sub>2</sub>; [M]<sup>+</sup> 3271.7901).
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### 525 **4. Conclusions**

In this work, peptoid oligomers have been used as scaffolds to display phthalocyanines dyes. In this way, the first synthesis and analysis of the photoproperties of peptoid-phthalocyanine conjugates has been achieved. The peptoid oligomers with aliphatic side chains to prevent aromatic interactions were designed to adopt the PolyProline type I conformation characterized by *cis*-amide bonds and the phthalocyanines were grafted by CuAAC reactions. Very importantly, the helix content of the peptoids is conserved upon phthalocyanine grafting, allowing for an accurate comparison of the photoproperties of the conjugates. Measurements

of the electronic absorption and fluorescence spectra of the conjugates and of a monomeric 533 reference phthalocyanine showed that the presence of the peptoid backbone has no effect on 534 the photoproperties of the phthalocyanines. Conjugates in which two phthalocyanine units are 535 grafted on a same peptoid backbone exhibit intramolecular aggregation behaviour, due to the 536 fact that the two phthalocyanines are kept close to each other, quite independently of their 537 relative position on the peptoid backbone, probably due to the important flexibility of the 538 spacer used. Further works with more rigid spacers between the phthalocyanine and the helix 539 backbone should allow to better control the interactions between the macrocycles. 540

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