Supporting Information

Control of porphyrin interactions via structural changes of peptoid scaffold

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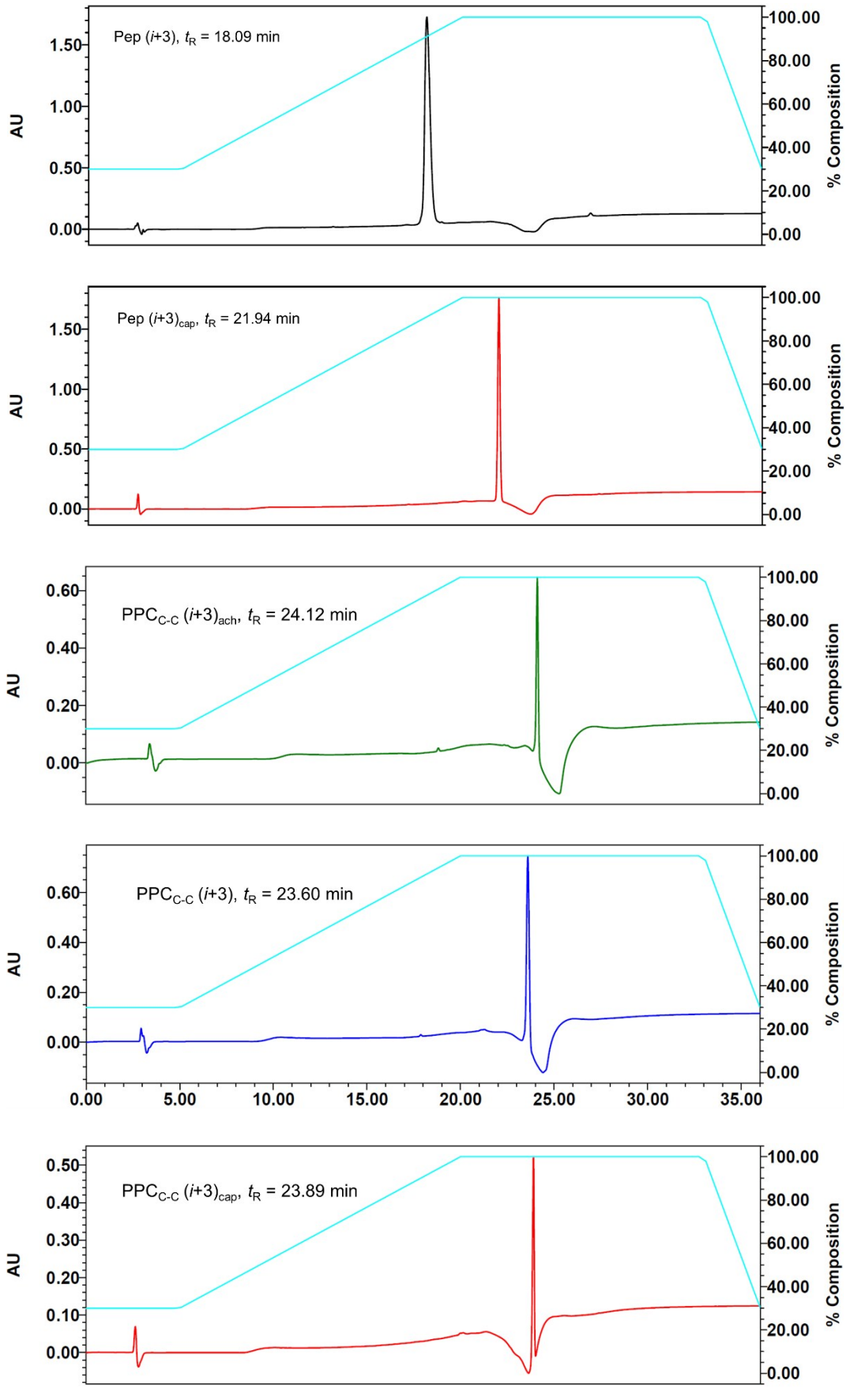
Pep (i+3), tR = 18.09 min
Pep (i+3)cap, tR = 21.94 min
PPCC-C (i+3)ach, tR = 24.12 min
PPCC-C (i+3), tR = 23.60 min
PPCC-C (i+3)cap, tR = 23.89 min
AU
% Composition
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00

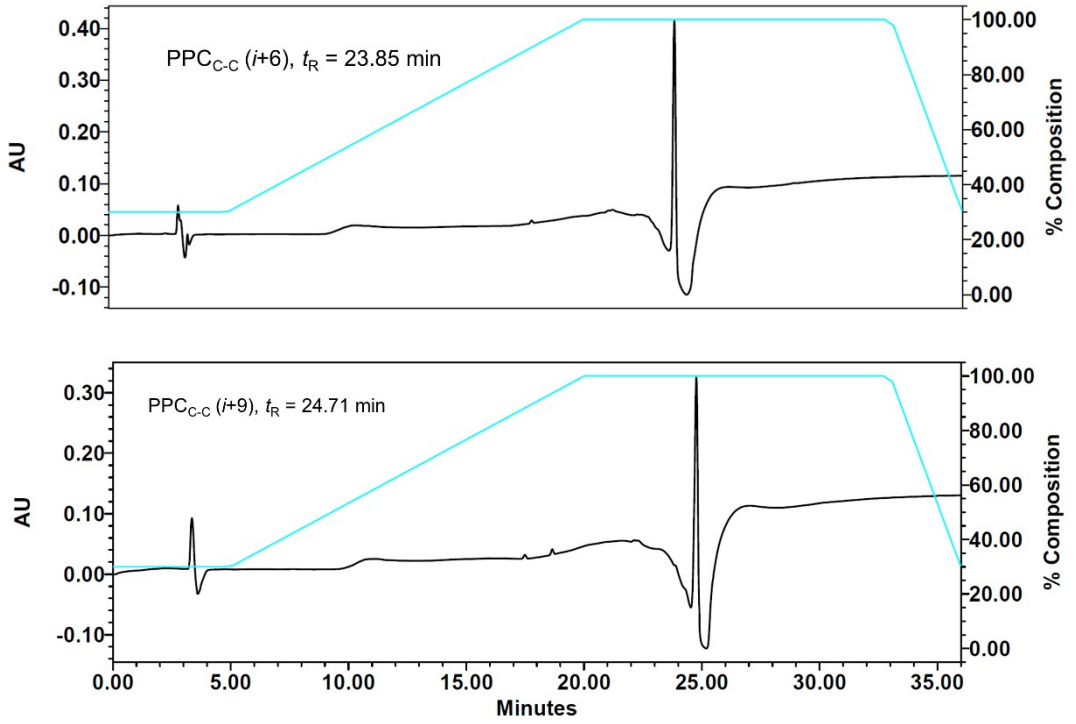

Figure S1. HPLC chromatograms of peptoids and PPCs monitored at 220 nm (>97% purity). The retention times (t_R) are shown.

Table S1. ESI-MS data of purified peptoids and PPCs.

compounds	mass calculated	mass observed[a]
Pep (*i*+3)	1438.75	1439.77 (H^+), 1461.76 (Na^+)
Pep $(i+3)_{cap}$	1480.76	1481.78 (H^+), 1503.76 (Na^+)
PPC$_{C-C}$ $(i+3)_{ach}$	2565.11	856.04 ($3H^+$), 1283.56 ($2H^+$)
PPC$_{C-C}$ (*i*+3)	2663.21	888.76 ($3H^+$), 1332.63 ($2H^+$)
PPC$_{C-C}$ $(i+3)_{cap}$	2705.23	902.75 ($3H^+$), 1353.62 ($2H^+$)
PPC$_{C-C}$ (*i*+6)	3146.47	1049.84 ($3H^+$), 1574.25 ($2H^+$)
PPC$_{C-C}$ (*i*+9)	3629.72	1210.93 ($3H^+$), 1815.88 ($2H^+$)

[a] Observed in ESI-MS. Observed masses are doubly charged or triply charged species due to the detectable mass range of instrument.

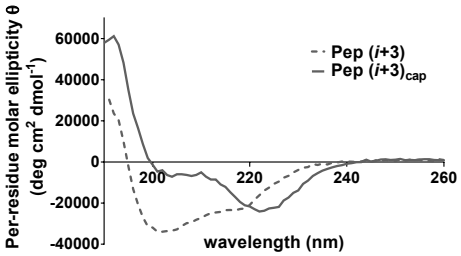

Figure S2. CD spectra of Pep (*i*+3) and Pep $(i+3)_{cap}$ in ACN (50 μM, 20 °C).

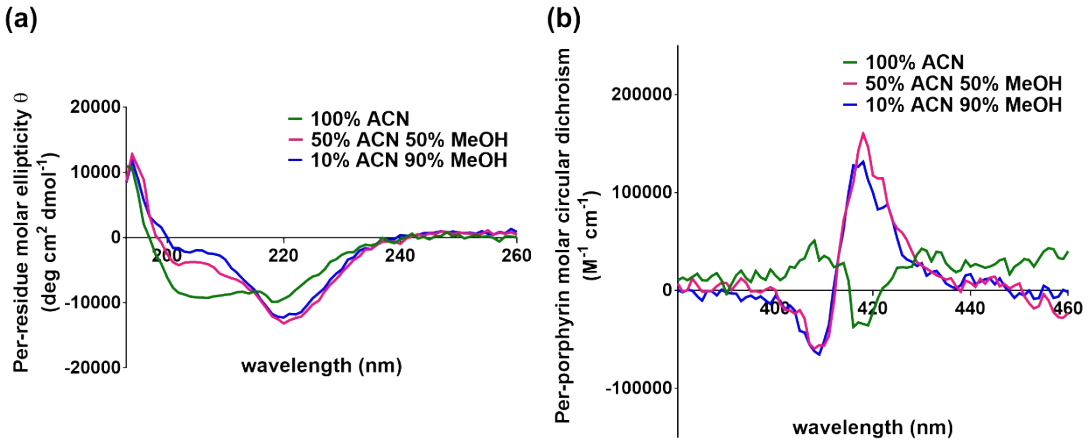

Figure S3. CD spectra of $PPC_{C\text{-}C}$ (i+3) in acetonitrile/methanol (% v/v) mixtures (50 µM, 20 °C). (a) Spectra showing the secondary structure of the peptoid (190-260 nm). (b) ECCD spectra in the porphyrin Soret absorption region (380-460 nm).

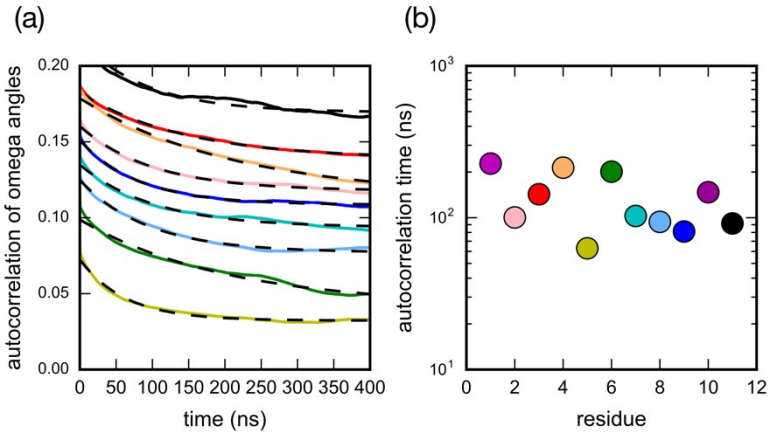

Figure S4. (a) Correlation of backbone omega angles for each residue of $PPC_{C\text{-}C}$ $(i+6)_{cap}$, sampled in 2.5 µs REMD simulations. Shown is the autocorrelation function $G(\tau) = \langle\chi(\omega(t))\chi(\omega(t+\tau))\rangle$, where $\chi(\omega) = 0$ for *cis* amides and $\chi(\omega)=1$ for *trans* amides. Black dotted lines show least-squared fits to single-exponential curves of the form $a_0 + a_1 \exp(-t/\tau_c)$, enabling estimation of the correlation time, τ_c. (b) Correlation times for all backbone amides are around 100 ns, indicating sufficient sampling is possible within 2.5 µs of simulation. Similar results are obtained from simulations of $PPC_{C\text{-}C}$ $(i+3)_{cap}$, PPC_{amide} (i+3) and PPC_{amide} (i+6).

Table S2. Average *cis*-amide population and helicity observed in REMD simulations of PPCs.

compounds	*cis*-amide population	helicity[a]
PPC_{amide} (*i*+3)*	0.62	0.55
PPC_{amide} (*i*+6)*	0.82	0.75
$PPC_{C\text{-}C}$ $(i+3)_{cap}$	0.72	0.65
$PPC_{C\text{-}C}$ $(i+6)_{cap}$	0.73	0.66

[a] A (right-handed) helical residue is one having a *cis*-amide and negative phi-angle.

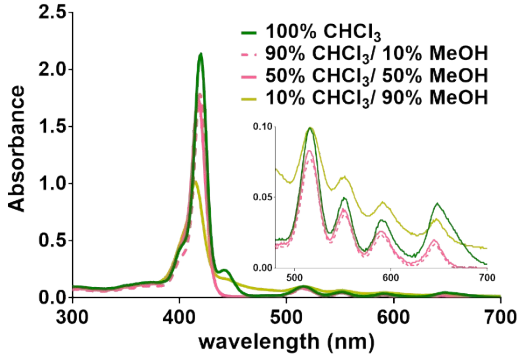

Figure S5. UV-vis absorption spectra of $PPC_{C\text{-}C}$ (*i*+3) in chloroform/methanol mixtures (50 μM).

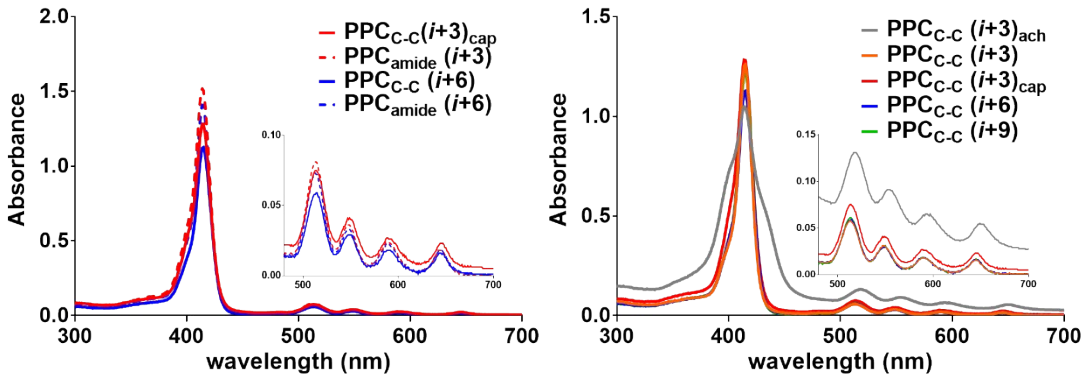

Figure S6. UV-vis absorption spectra of PPCs in ACN (50 μM).

Photophysical properties of PPCs

Photophysical properties of PPCs were measured by UV-vis absorbance and fluorescence emission spectroscopy at low molecular concentration (**Table S3**). Samples were carefully diluted from the stock solution to minimize concentration-related effects such as re-absorption, self-quenching, or intermolecular aggregation.[1] To compare the data with monomeric porphyrin, (5-(4-methoxycarbonylphenyl)-10,15,20-triphenylporphyrin (TPP-ME) was used as a reference at doubled the molecular concentration because PPCs contain two porphyrins. Generally, as in TPP-ME, maximum absorption at 419 nm and characteristic emission peaks at 648 nm and 715 nm were observed in all PPCs. The extinction coefficients of porphyrins on more structured peptoids exhibited approximately half that of the values of TPP-ME and achiral or flexible PPCs. On the other hand, the relative quantum yields of the more structure PPCs were slightly higher than those of the achiral or flexible PPCs.[2] Porphyrins on conformationally more heterogeneous peptoids are likely to have more chances for, (1) spatial interaction with peptoid side chains and vibrational energy transfer, and (2) exposure to various non-radiative pathways resulting in energy dissipation by heat.

Table S3. Photophysical properties of PPCs in chloroform.

compounds	λ_A (nm)[a]	ε_{419} ($M^{-1}cm^{-1}$)[b,e]	λ_F (nm)[c]	Φ_F[d,e]
TPP-ME	419	500,000	648	0.062
$PPC_{C\text{-}C}$ $(i+3)_{ach}$	419	500,000	649	0.074
$PPC_{C\text{-}C}$ $(i+3)$	419	260,000	649	0.086
$PPC_{C\text{-}C}$ $(i+3)_{cap}$	419	260,000	649	0.079
$PPC_{C\text{-}C}$ $(i+6)$	419	330,000	649	0.083
$PPC_{C\text{-}C}$ $(i+9)$	419	330,000	649	0.084
PPC_{amide} $(i+3)$	419	470,000	648	0.065
PPC_{amide} $(i+6)$	419	510,000	648	0.060

[a] Maximum absorption wavelength at 0.1 μM. [b] Extinction coefficient at 419 nm. [c] Maximum fluorescence emission at 0.1 μM. [d] Relative fluorescence quantum yield. [e] Rounded from the third significant digit.

References

1. M. Kaplanová, K. Čermák, *J. Photochem.*, 1981, **15**, 313.

2. (a) J. Albani, *Principles and applications of fluorescence spectroscopy*, Blackwell Publishing, Oxford, 2007. (b) J. Karolczak, D. Kowalska, A. Lukaszewicz, A. Maciejewski, R. P. Steer, *J. Phys. Chem. A*, 2004, **108**, 4570.