Electronic Supplementary Material (ESI) for Soft Matter.

Supporting information

Polyamine-induced, chiral expression from liquid crystalline peptide nanofilaments to long-range ordered nanohelices

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1. Supporting figures

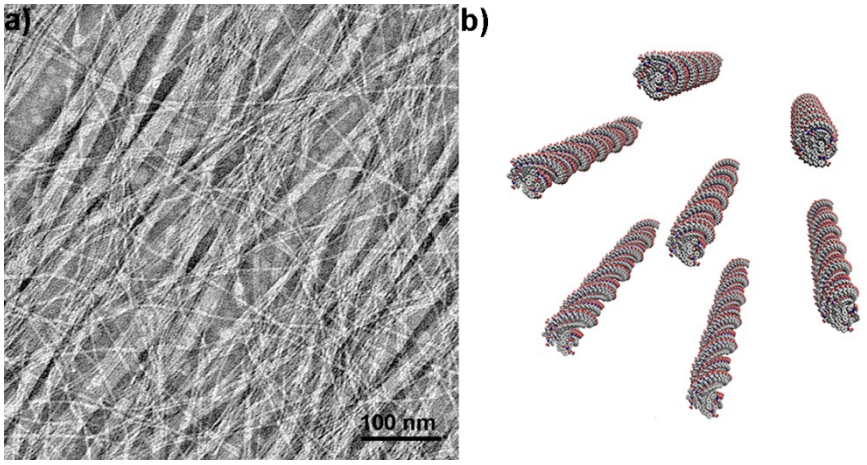

Fig. S1 a) TEM images showing the nanofilaments self-assembled by Fmoc-FF peptide in 50 mM Tris-HCl buffer at pH 8.8; b) Schematic illustration showing the columnar packing of the nanofilaments.[1]

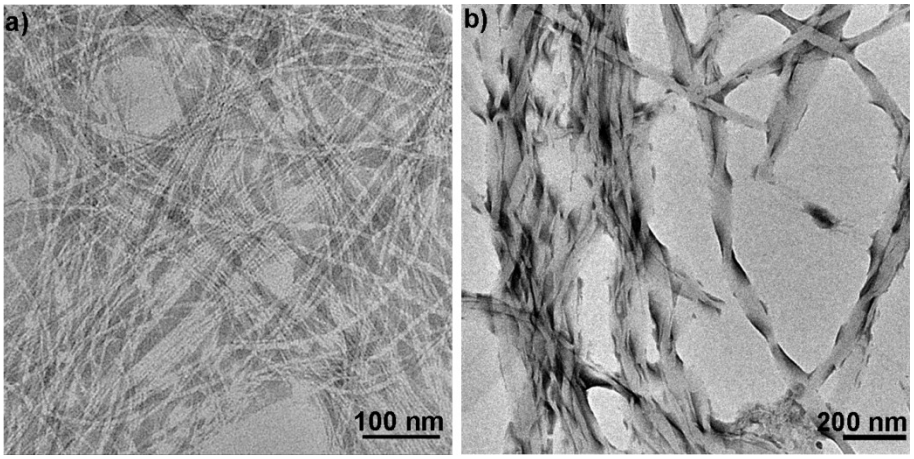

Fig. S2 TEM images showing the (a) loose-packed fibrous bundles and (b) well-defined nanohelices formed after the incubation of spermidine into the liquid-crystalline peptide solution at 60 s and 6 h, respecively.

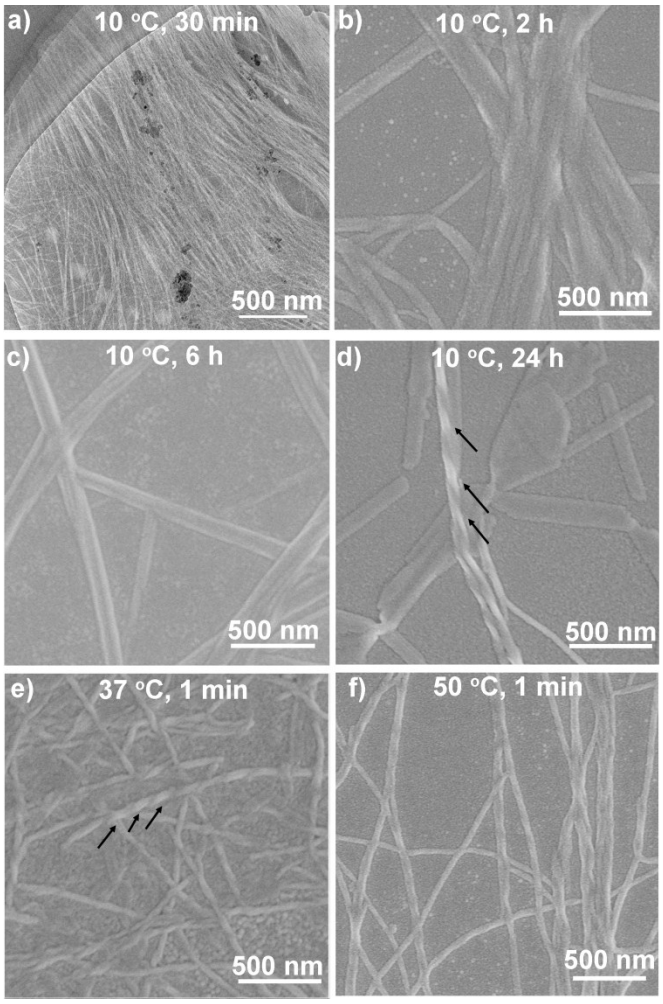

Fig. S3 a-d) TEM (a) and SEM (b-d) images showing the very slow structural transition of nanofilaments into nanoribbons after the incorporation of spermidine into the peptide solutions at 10 °C. Only a small amount of nanohelices were formed after incubation for 24 h. e-f) SEM images showing the nanohelices formed after the incorporation of spermidine into the peptide solutions at 37 and 50 °, respectively. Homogenous nanohelices could be formed just after incubation for 1 min.

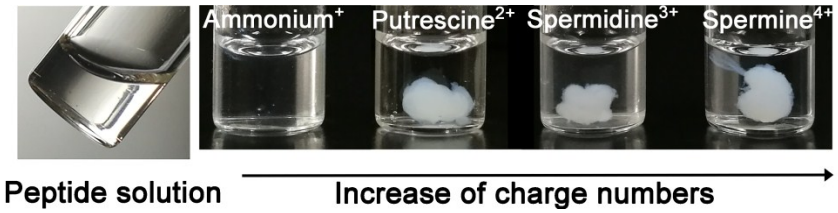

Fig. S4 Macroscopic photographic images showing the peptide solutions after the incorporation of various polyamines bearing increasing number of positive charges. The most left image is a 10 mM Fmoc-FF peptide solution (50 mM Tris-HCl, pH 8.8) incubated in a glass vial. The peptide/polyamine mixture solutions contain 5 mM Fmoc-FF, 25 mM Tris-HCl and 5 mM polyamines with a pH of 8.6 at 20 °C.

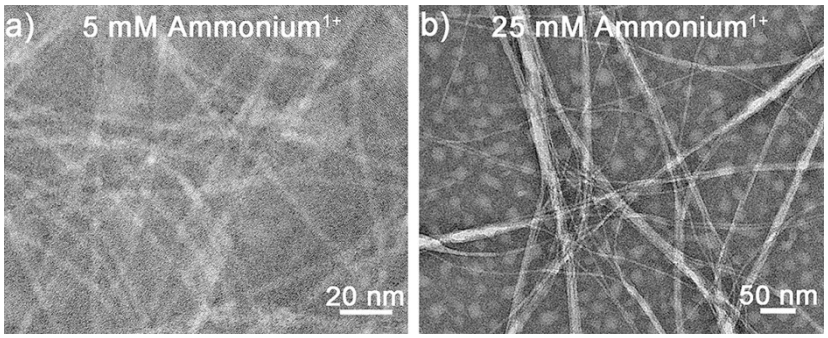

Fig. S5 Transmission electron microscopy (TEM) images showing the condensation behavior of the peptide nanofilaments by using 5 mM and 25 mM monovalent ammonium^{1+} cations, respectively. The mixture solutions contain 5 mM Fmoc-FF, 25 mM Tris-HCl with a pH of 8.6 at 20 °C.

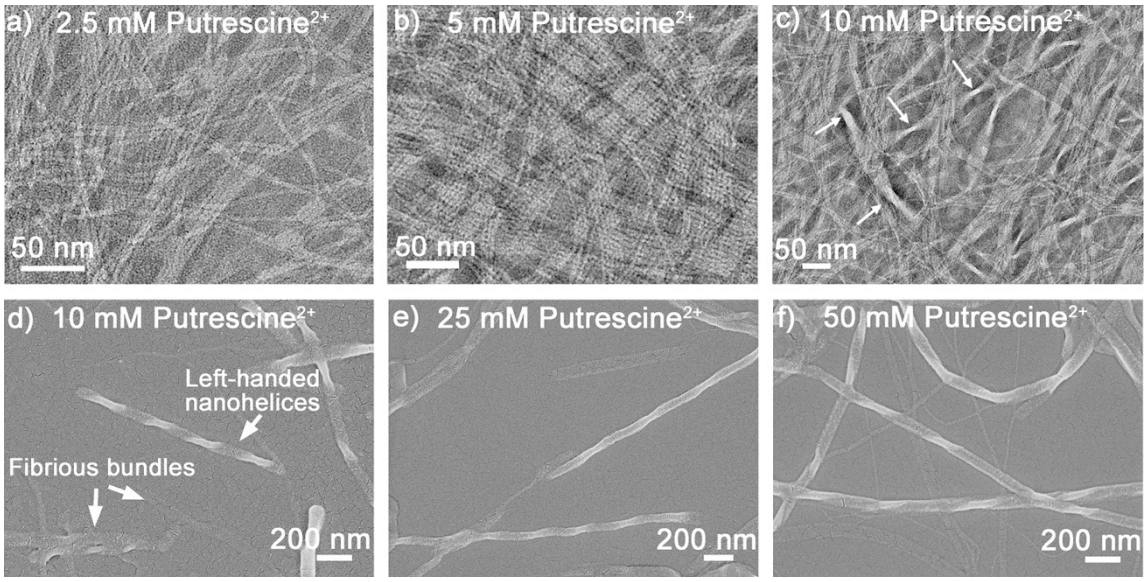

Fig. S6 TEM (a-c) and SEM (d-f) images showing the condensation of peptide nanofilaments into fibrous bundles and twisted nanoribbons by using the divalent putrecine^{2+} cations at various concentrations. The mixture solutions contain 5 mM Fmoc-FF, 25 mM Tris-HCl with a pH of 8.6 at 20 °C.

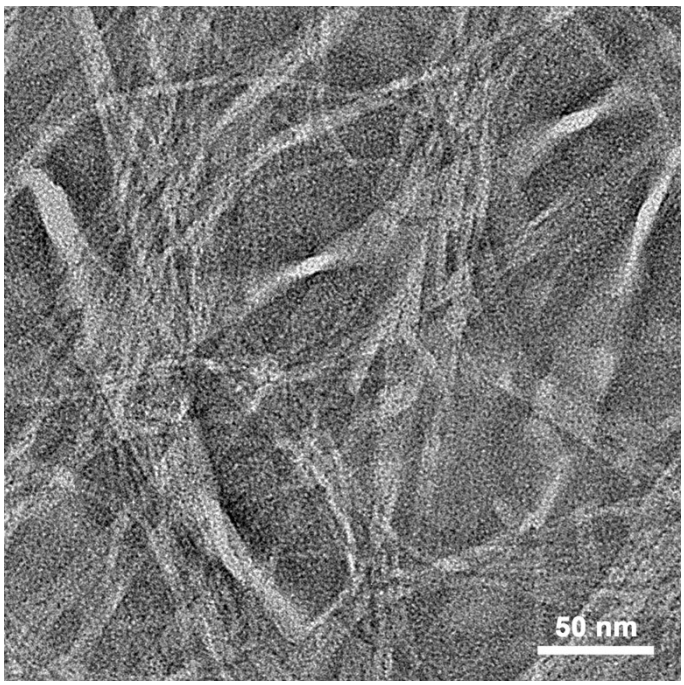

Fig. S7 A high-magnification TEM image showing the transformation of peptide nanofilaments into fibrous bundles and twisted nanoribbons by using 10 mM divalent putrecine^{2+} cations. The mixture solutions contain 5 mM Fmoc-FF, 25 mM Tris-HCl with a pH of 8.6 at 20 °C.

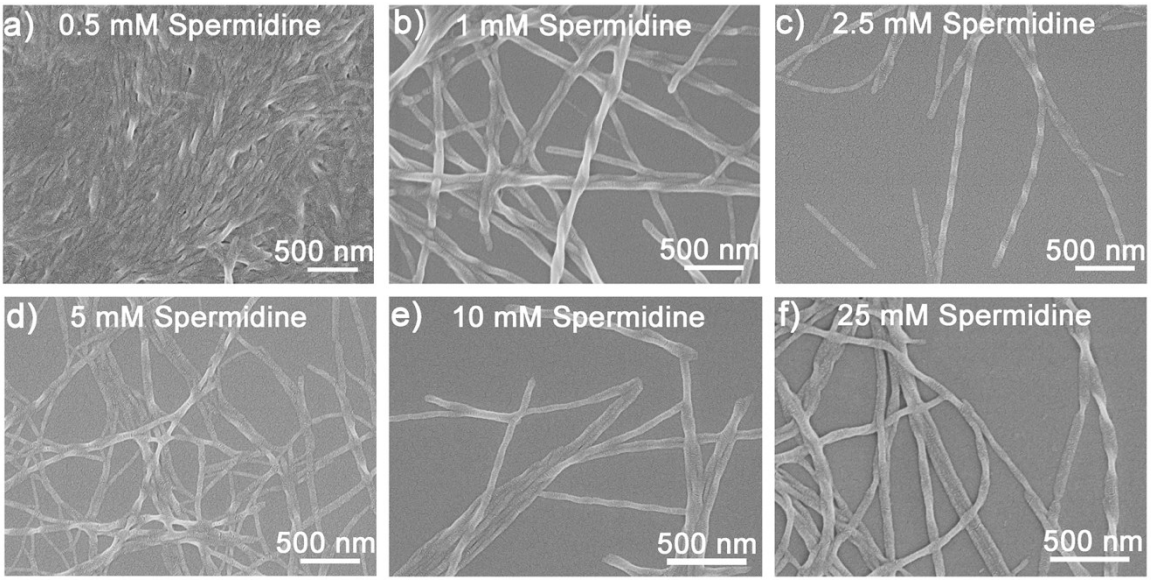

Fig. S8 SEM images showing the condensation of peptide nanofilaments into twisted nanoribbons by using the trivalent spermidine^{3+} cations at various concentrations. The mixture solutions contain 5 mM Fmoc-FF, 25 mM Tris-HCl with a pH of 8.6 at 20 °C.

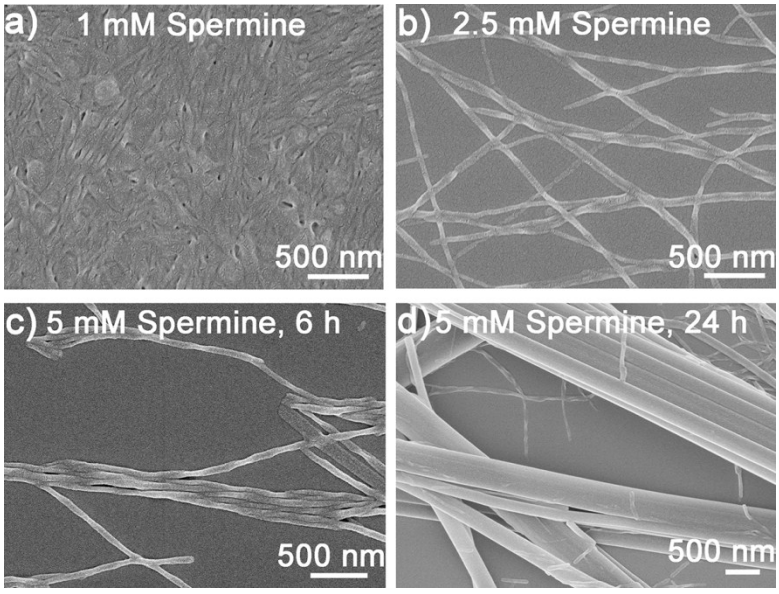

Fig. S9 SEM images showing the condensation of the peptide nanofilaments by using the tetravalent spermine^{4+} cations at various concentrations. Twisted nanoribbons can be formed using 1 or 2.5 mM spermine^{4+} cations. However, by increasing the concentration up to 5 mM, the twisted nanoribbons become unstable, which transformed spontaneously into large microcrystals after the incubation for 12 h. The mixture solutions contain 5 mM Fmoc-FF, 25 mM Tris-HCl with a pH of 8.6 at 20 °C.

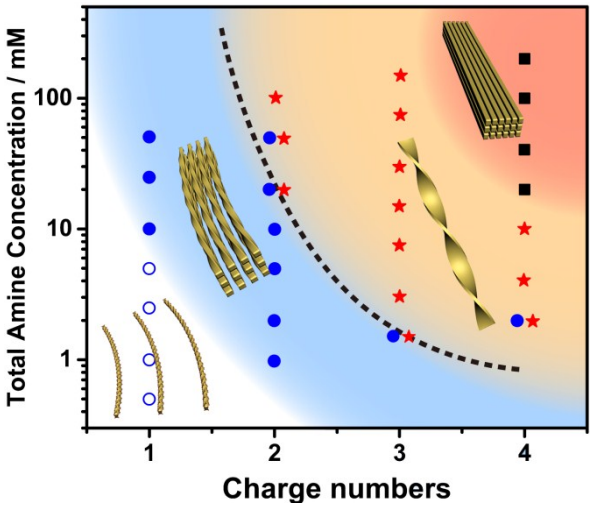

Figure S10. Phase diagram of the condensation of the peptide nanofilaments as a function of the polyamine charge number and total amine concentration. Blue circles correspond to repulsive nanofilaments; blue filled circles correspond to flat nanoribbons or giant fibrous bundles; red stars represent twisted nanoribbons; black squares represent large microcrystals. The black dashed curve denotes the critical concentration (C_c) required to induce the bundling and twisting of the nanofilaments into homogeneous twisted nanoribbons.

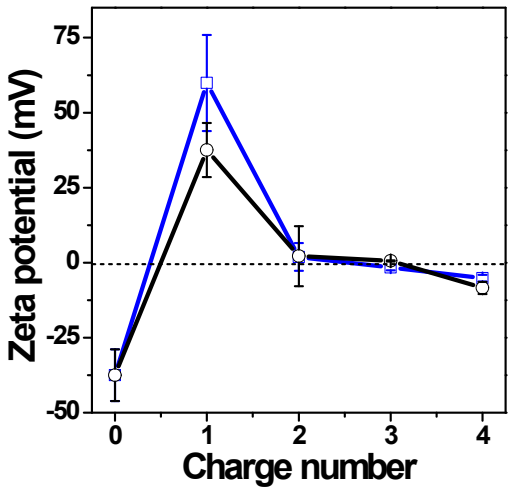

Figure S11. Zeta-potential of the peptide solutions (5 mM Fmoc-FF, 25 mM Tris-HCl, pH 8.6, 20 °C) in the presence of various polyamines as a function of the charge number of the polyamines. The concentration of the polyamines is 5 mM (black curve) and 10 mM (blue curve), respectivley.

Table S1 p*K*a values of the polyamines determined by Palmer at al. using potentiometric titration.[2]

Polyamines	p*K*a
Putrescine	10.80, 9.63
Spermidine	10.95, 9.98, 8.56
spermine	10.94, 10.12, 9.04, 7.97

2. References

(1) Wang, Y.; Qi, W.; Wang, J.; Li, Q.; Yang, X.; Zhang, J.; Liu, X.; Huang, R.; Wang, M.; Su, R. Columnar Liquid Crystals Self-Assembled by Minimalistic Peptides for Chiral Sensing and Synthesis of Ordered Mesoporous Silica. *Chem. Mater.* **2018**, *30*, 7902-7911.

(2) Palmer, B.N., Powell, H.K.J. Polyamine complexes with seven-membered chelate rings: complex formation of 3-azaheptane-1,7-diamine, 4-azaoctane-1,8-diamine (spermidine), and 4,9-diazadodecane-1,12-diamine (spermine) with copper (II) and hydrogen ions in aqueous solution. *J. Chem. Soc. Dalton* **1974**, 19, 2089–2092.