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L-Phe-D-Oxd: A Privileged Scaffold for the Formation of Supramolecular Materials

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Some compounds containing the L-Phe-D-Oxd [L-Phe = L-phenylalanine; D-Oxd = (4*R*,5*S*)-4-carboxy-5-methyl oxazolidin-2-one] moiety have been prepared and their properties as supramolecular material have been determined. Some derivatives of the dipeptide L-Phe-L-Phe (which usually forms nanotubes) and some long-chain derivatives that behave as low-molecular-weight gelators have been prepared. We have also replaced the D-Oxd moiety with a D-Pro (D-Pro = D-proline) moiety to check if the presence of the Oxd moiety was essential for the existence of those materials. In contrast to the D-Oxd-containing compounds, no material was ever formed with any of the D-Pro-containing molecules. This outcome suggests that the L-Phe-D-Oxd moiety may be defined as a "privileged scaffold" for the formation of supramolecular materials and it can be introduced into more complex structures to induce some selected properties in the solid state.

Introduction

A number of strategies have been envisaged recently to design and build molecular materials based on self-assembling peptides and their derivatives.[1]

In our recent interest in this field, we have demonstrated that the protected pseudo-peptide Boc-L-Phe-D-Oxd-OBn [Boc = *tert*-butoxycarbonyl; L-Phe = L-phenylalanine; D-Oxd = (4*R*,5*S*)-5-methyl-2-oxooxazolidin-4-carboxylic acid] (Figure 1) forms a fibre-like material by self-organization because it spontaneously forms infinite linear chains, in which the parallel dipeptide units are connected only by single hydrogen bonds.[2] This effect is due to the oxazolidin-2-one ring (D-Oxd), which has a nitrogen atom connected to an endocyclic carbonyl, so that, on formation of the imide bond, the exo- and endocyclic carbonyl groups lie *anti* to one another, thus adopting a *trans* rigid conformation. The presence of stacking interactions is also important for the formation of the materials.

To understand the importance of the L-Phe-D-Oxd scaffold to build new architectures and, in particular, the role of the D-Oxd group, we decided to explore how it behaved when it was included in more complex structures and if the term "privileged scaffold" could be used to define it. This term was first proposed by Evans et al. to describe selected

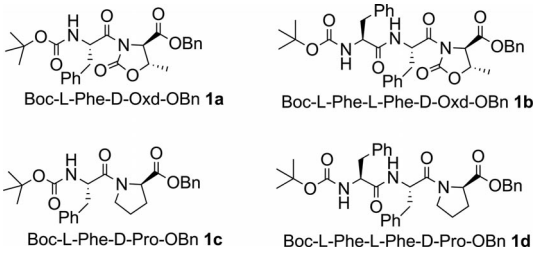

Figure 1. Di- and tripeptides analyzed in this work. Bn = benzyl.

structural types that bind to multiple, unrelated classes of protein receptors as high-affinity ligands.[3] These privileged structures are typically rigid, polycyclic heteroatomic systems capable of orienting a variety of substituent patterns in a well-defined three-dimensional space.[4]

We selected two examples for the formation of supramolecular materials: the tendency of derivatives of the dipeptide L-Phe-L-Phe to form nanotubes[5] and the formation of gels by the use of low-molecular-weight gelators (LMWGs).[6] We also replaced the D-Oxd moiety with a D-Pro (D-Pro = D-proline) moiety to check if the presence of the Oxd moiety was essential for the properties of the supramolecular material.

Thus, we prepared the tripeptide Boc-L-Phe-L-Phe-D-Oxd-OBn (**1b**) and its analogue Boc-L-Phe-L-Phe-D-Pro-OBn (**1d**) to determine their properties in the solid state.

Then, we prepared some long-chain derivatives of **1a**–**d** to determine the properties of these new compounds as LMWGs, since an intermolecular interaction of suitable strength was required for the formation of a gel. It is known that three factors can favour the formation of a gel: 1) the presence of hydrogen bonding and π–π stacking interac-

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tions, which are the principle interactions involved in gel aggregation; 2) the tendency of the molecule head to organize into a network; this influences the probability of gel formation; and 3) the presence of medium-sized aliphatic chains (4–8 methylene units) connected to a polar head.[7]

Results and Discussion

To determine the role of the D-Oxd unit in the dipeptide **1a**, we prepared three new di- and tripeptides (**1b**, **1c** and **1d**; Figure 1) that differ from **1a** by the addition of a L-Phe unit (**1b**) or by the replacement of the D-Oxd moiety with one L-Phe unit (**1c**) and with two L-Phe units (**1d**). These three compounds have been obtained by means of normal peptide synthesis in solution (see the Experimental Section).

By comparing the ^{1}H NMR spectra of **1a**–**d**, we immediately noticed that compounds **1a** and **1b** exist in solution as a single conformer, whereas **1c** and **1d** were always a mixture of conformers, as shown by ^{13}C NMR spectra (see the Supporting Information). This effect is typical of Pro-containing peptides because the peptide bond is in a *trans–cis* mixture, usually preferring the *trans* conformation.[8] This equilibrium is missing from the pseudo-peptides containing the Oxd moiety, since in this case the peptide bond is always forced in the *trans* conformation owing to the effect of the exocyclic carbonyl.[9] Several macroscopic effects depend on this rigid conformation: the two pseudo-peptides **1a** and **1b** are crystalline compounds that tend to aggregate into fibre-like materials. While **1a** has been already extensive described,[2a] we report herein optical microscopy (OM) and SEM images of **1b** (Figure 2).

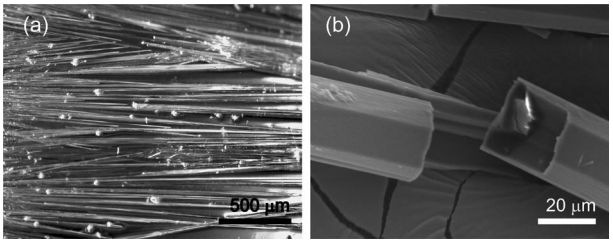


Figure 2. a) OM and b) SEM images of **1b**.

It is possible to observe how **1b** precipitates to form elongated crystals (up to a few millimeters) locally iso-oriented. Each single crystal (about 20 mm thick) has a well-defined crystalline habit and shows faces that are probably parallel to the crystallographic *a* axis. The pseudo-hexagonal cross-section is also shown.

The conformational analysis of **1b** in the solid state was further elucidated by a single-crystal X-ray diffraction study.

The molecular conformation of **1b** is shown in part a of Figure 3 and relevant torsion angles are reported in Table 1. The backbone torsion angles for the two L-Phe units correspond approximately to those in peptide β strands, as previously reported for Boc-L-Phe-D-Oxd-OBn.[2a] In the crystal packing of **1b** (Figure 3, b) each molecule is connected through four intermolecular NH···OC hydrogen bonds [N2H2N···O6′ 2.204 Å, N2···O6′ 3.005(4) Å, N2–H2N···O6′ 163°, symmetry code (I): *x*–1,*y*,*z*; N3H3N···O7′′ 2.137 Å, N3···O7′′ 2.941 Å, N3–H3N···O7′′ 168°, symmetry code (II): *x* + 1,*y*,*z*] to two neighbours, thus generating an infinite parallel β-sheet structure running along the crystallographic *a* axis. Interestingly, this arrangement is similar to that observed in Boc-L-Phe-D-Oxd-OBn, in which one unit is connected to the adjacent ones through single NH···OC hydrogen bonds and other related compounds.[10]

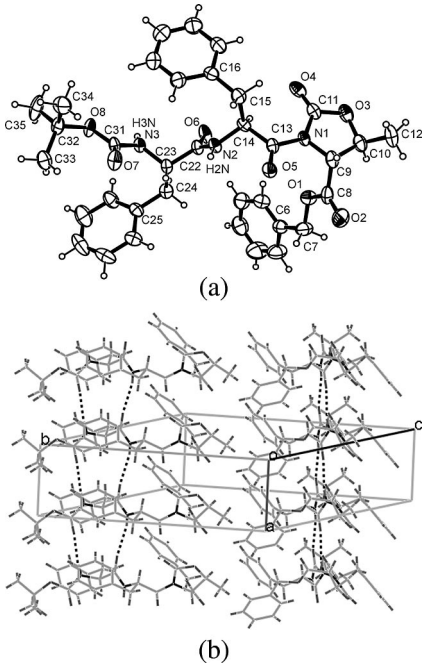


Figure 3. a) X-ray molecular structure and b) crystal packing of **1b**.

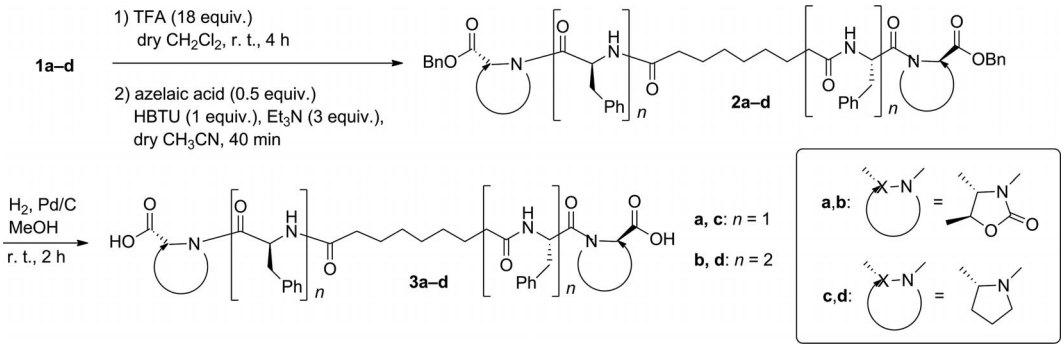
Table 1. Selected backbone torsional angles [°] for **1b**.

L-Phe1	C31–N3–C23–C22	ϕ_1	–127.3(3)
	N3–C23–C22–N2	ψ_1	109.5(3)
L-Phe2	C22–N2–C14–C13	ϕ_2	–126.4(3)
	N2–C14–C13–N1	ψ_2	147.9(3)
Oxd	C13–N1–C9–C8	ϕ_3	56.2(4)
	N1–C9–C8–O1	ψ_3	32.4(4)

On the contrary, compounds **1c** and **1d** do not show any propensity to form fibre-like materials because they hardly become solids (**1c** is a liquid[11]). The powder X-ray diffraction of **1d** shows that it is an amorphous solid (see the Supporting Information).

To check the propensity of the derivatives of these four compounds to behave as LMWGs, after several attempts we synthesized **2a**–**d** and **3a**–**d**, which were eight derivatives of a dicarboxylic, medium-sized aliphatic acid [azelaic acid = HOOC-$(CH_2)_7$-COOH] that fulfil this requirement. Interestingly, no derivative of monocarboxylic acids, such as hexonoic or undecanoic acids, form any kind of gel.

Compounds **2a**–**d** and **3a**–**d** may be defined as synthetic bolaamphiphiles.[12] In general, these compounds reproduce the unusual architecture of monolayered membranes found in archaebacteria.



Scheme 1. Preparation of compounds **2a**–**d** and **3a**–**d**.

Compounds **1a**–**d** were deprotected with trifluoroacetic acid (TFA) in dichloromethane to obtain the corresponding trifluoroacetate salt in quantitative yield; this was coupled with azelaic acid, using *O*-benzotriazole-*N*,*N*,*N*′,*N*′-tetramethyluronium hexafluorophosphate (HBTU) and triethylamine as coupling agents (Scheme 1). Compounds **2a**–**d** were obtained pure after flash chromatography in high yields. Then, they were all deprotected by hydrogenolysis to give the free carboxy termini **3a**–**d** in quantitative yield.

Then, the propensity of all of these compounds to form gels was determined. The general method adopted to form gels was to place one compound (**2a**–**d** or **3a**–**d**) in a small test tube (8 mm in diameter) and dissolve it in pure solvent (distilled water was used) or in a solvent mixture (see Table 2) to obtain a 10 mM solution. Because ultrasound influences the aggregation properties of the molecules in the solvents,[13] the tube was sonicated for 20 min at room temperature, then it was left to stand for 2 h before gel formation was monitored. When a mixture of solvents was used, the solvent that the gelling compound was more soluble in was introduced first (i.e., dichloromethane was introduced first in entries 1, 4, 7 and 10 and methanol was first in entries 15, 18, 21 and 24 in Table 2).

The most common diagnostic test of gelation is tube inversion. In this test, a sample tube containing the mixture of compound and solvent was inverted to ascertain if the sample would flow under its own weight. A gel was assumed to be a sample that had a yield stress that prevented it from flowing down the tube. A solution was taken to be a sample that flowed down the tube. When a partial gel is formed, the compound sticks to the bottom of the test tube, while a little solvent (< 20%) flows down.

Compounds **2a**, **2b**, **3a** and **3b** form gels (Table 2, entries 1, 4, 6, 15 and 18) or partial gels (Table 2, entries 2 and 14), whereas the Pro-containing molecules **2c**, **2d**, **3c** and **3d** never form gels.

To check the structural properties of the gels formed, we carried out our studies only on the gel reported in entry 1 as an example of this class of compounds (Figure 4).

Then, the sample was left to dry in air to form the xerogel and was completely dry after 24 h at 20 °C. We recorded an FTIR spectrum (1% in dry KBr) and compared it with the spectra of **2a** in dilute solution (3 mM in dichloromethane) and as a precipitated material (1% in dry KBr) (Figure 5). The spectra of both the precipitated sample and the xerogel showed the presence of a signal at about 3310 cm^{-1}, typical of C=O···H–N hydrogen bonds, whereas the 3 mM solution had a signal at 3430 cm^{-1}, which was attributed to the presence of a free NH group.[14]

Table 2. Gelation properties of compounds **2a**–**d** and **3a**–**d** in selected solvents (concentration: 10 mM).

Entry	Solvent	Compd.	After sonication[a]	After 2 h[a]
1	CH_2Cl_2/AcOEt 1:1	**2a**	SP	G
2	CH_2Cl_2	**2a**	S	PG
3	AcOEt	**2a**	SP	PG
4	CH_2Cl_2/AcOEt 1:1	**2b**	SP	G
5	CH_2Cl_2	**2b**	S	S
6	AcOEt	**2b**	SP	G
7	CH_2Cl_2/AcOEt 1:1	**2c**	S	S
8	CH_2Cl_2	**2c**	S	S
9	AcOEt	**2c**	S	S
10	CH_2Cl_2/AcOEt 1:1	**2d**	S	S
11	CH_2Cl_2	**2d**	S	S
12	AcOEt	**2d**	S	S
13	MeOH	**3a**	SP	SP
14	H_2O	**3a**	SP	PG
15	MeOH/H_2O 1:1	**3a**	G	G
16	MeOH	**3b**	S	S
17	H_2O	**3b**	S	S
18	MeOH/H_2O 1:1	**3b**	SP	G
19	MeOH	**3c**	S	S
20	H_2O	**3c**	S	S
21	MeOH/H_2O 1:1	**3c**	S	S
22	MeOH	**3d**	S	S
23	H_2O	**3d**	SP	SP
24	MeOH/H_2O 1:1	**3d**	S	S

[a] SP = suspension; G = gel; PG = partial gel; S = solution.

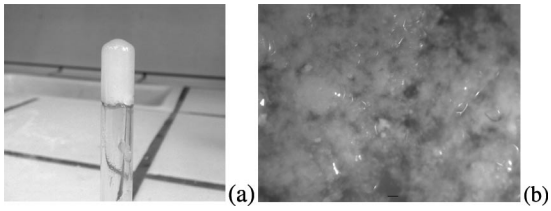


Figure 4. a) Photograph of **2a** in a 1:1 mixture of dichloromethane and ethyl acetate (10 mM solution); b) OM image of the same sample; scale bar: 500 μm.

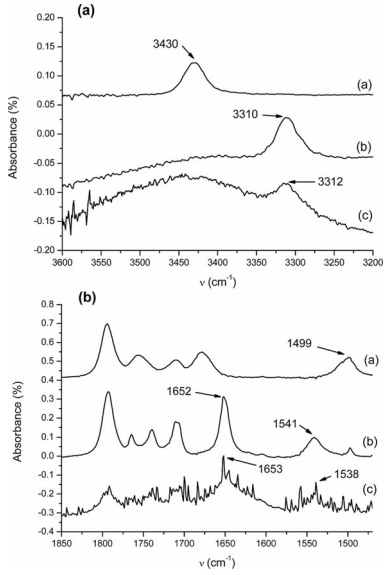


Figure 5. FTIR absorption spectra in the N–H (left) and C=O (right) stretching regions for **2a**: a) 3 mM solution in pure CH_2Cl_2; b) solid as 1% mixture with dry KBr; and c) xerogel as a 1% mixture with dry KBr.

Further investigations, using SEM, gave a better idea of the morphology of the xerogel (Figure 6): it forms long filaments highly interconnected and branched with a diameter of about 0.5 μm. They have a strong tendency to aggregate, forming a network of meshed and bundled architectural assemblies (Figure 6, a). These observations fit with the OM images and the FTIR spectral analyses. The gel appears opaque, suggesting the existence of extended molecular assemblies in the wet gel.[15] Moreover, the FTIR spectrum indicates that this molecule may assemble into an organized form by hydrogen-bonding interactions as soon as a limit concentration that favours the formation of β sheets is reached.

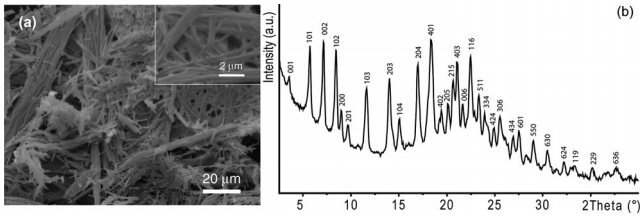


Figure 6. SEM picture (a) and XRD patterns (b) of the xerogel prepared from **2a**. In (a) the inset shows a high magnification of the wide view. The diffraction peaks have been indexed according to a tetragonal unit cell (a = 1.97 nm, c = 2.67 nm).

A further clue to the presence of an ordered assembly of molecules in the xerogels is given by XRD analysis (Figure 6, b). The XRD pattern of the xerogel of **2a** shows many sharp diffraction peaks and a broad band at around 2θ = 20°, which suggests the coexistence of amorphous and high crystalline phases. The diffraction peaks have been indexed according to a tetragonal unit cell (a = 1.97 nm, c = 2.67 nm). These unit cell parameters agree with long-range ordering and suggest that **2a** may form crystalline multilayer structures within the self-assemblies. This observation agrees with that observed for 2-glucosamide-based bolaamphiphiles.[16]

Conclusions

We have shown several examples of pseudo-peptides containing D-Oxd moieties and compared them with similar compounds, in which D-Oxd was replaced with D-Pro. With all of the D-Pro-containing molecules, no fibre-like material or gel was ever formed. Furthermore, the presence of two Phe moieties connected to one another did not affect the properties of the material, since molecules containing one or two Phe residues showed the same behaviour in the solid. This outcome is opposite to that obtained with other L-Phe-L-Phe derivatives, thus showing that L-Phe-D-Oxd is very strong and leads to the formation of solids with well-defined properties. Thus, L-Phe-D-Oxd fulfils the requirements of a privileged scaffold for the formation of supramolecular materials containing pseudo-proline moieties and it can be introduced into more complex structures to induce some selected properties in the solid state.

Experimental Section

Synthesis: The melting points of the compounds were determined in open capillaries and are uncorrected. High-quality infrared spectra (64 scans) were obtained at 2 cm^{-1} resolution using a 1 mm NaCl solution cell and a Nicolet 210 FTIR spectrometer. All spectra were obtained of 3 mM solutions in dry CH_2Cl_2 at 297 K or as a 1% solid mixture with dry KBr. All compounds were dried in vacuo and all of the sample preparations were performed in a nitrogen atmosphere. Routine NMR spectra were recorded with a Varian Mercury 400 spectrometer at 400 MHz and with a Varian Inova 300 at 300 MHz (^{1}H NMR) and at 100 or 75 MHz (^{13}C NMR). The measurements were carried out in CD_3OD and in [D_6]DMSO. The proton signals were assigned by *g*COSY spectra. Chemical shifts are reported in δ values relative to the solvent (CD_3OD or [D_6]DMSO) peak.

Boc-L-Phe-L-Phe-D-Oxd-OBn (1b): A solution of Boc-L-Phe-D-Oxd-OBn[2a] (2 mmol, 0.96 g) and TFA (36 mmol, 2.78 mL) in dry dichloromethane (20 mL) was stirred at room temperature for 4 h, then the volatile compounds were removed under reduced pressure and the corresponding amine salt was obtained in quantitative yield without the need for further purification.

A solution of Boc-L-Phe-OH (1.38 g, 0.52 mmol) and HBTU (0.4 g, 1.04 mmol) in dry acetonitrile (22 mL) was stirred under a nitrogen atmosphere for 10 min at room temperature. Then, a mixture of the previously obtained amine salt (1.04 mmol) and Et_3N (3.2 mmol, 0.47 mL) in dry acetonitrile (15 mL) was added dropwise at room temperature. The solution was stirred for 40 min under a nitrogen atmosphere, then acetonitrile was removed under reduced pressure and replaced with ethyl acetate. The mixture was washed with brine, 1 N aqueous HCl (3 × 30 mL), and with 5% (w/v) aqueous $NaHCO_3$ (1 × 30 mL), dried with sodium sulfate and concentrated in vacuo. The pure product was obtained after silica gel chromatography [CH_2Cl_2 100% → CH_2Cl_2/ethyl acetate (80:20) as eluent] in 78% (0.98 g) overall yield; m.p. 68 °C. $[\alpha]_D^{20}$ = +34 (c = 1.0, CH_2Cl_2). IR (CH_2Cl_2, 3 mM): $\tilde{\nu}$ = 3415, 1798, 1753, 1713,

1688 cm^{-1}. IR (1% in dry KBr): $\tilde{\nu}$ = 3327, 3307, 1794, 1746, 1714, 1686, 1658 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.52–1.56 (m, 12 H, Me + *t*Bu), 2.87–3.05 (m, 4 H, 2× CHN-CH_2-Ph), 3.11 (dd, J = 5.2, 12.4 Hz, 1 H, C*H*N-CH_2-Ph), 4.20–4.35 (m, 2 H, C*H*N-Oxd + C*H*N-CH_2-Ph), 4.45–4.52 (m, 1 H, CHO-Oxd), 4.95 (br. s, 1 H, NH-Boc), 5.2, 2 H, J = 111 (AB system, 6 Hz, CH_2OBn), 5.80–6.03 (m, 1 H, NH-Boc), 6.42 (br. s, 1 H, NH-Phe), 7.05–7.36 (m, 15 H, 3× Phe) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.4, 21.3, 28.5, 38.5, 38.6, 53.1, 55.8, 60.7, 62.0, 68.3, 70.7, 73.9, 126.7, 127.5, 128.6, 128.8, 128.9, 129.0, 129.6, 135.6, 167.5, 170.4, 170.6 ppm. $C_{35}H_{39}N_3O_8$ (629.3): calcd. C 67.76, H 6.24, N 6.67; found C 67.79, H 6.21, N 6.68.

Boc-L-Phe-D-Pro-OBn (1c): For the synthetic details, see ref.[7]

Boc-L-Phe-L-Phe-D-Pro-OBn (1d): The synthetic procedure was the same as that of **1b**, starting from **1c**; yield 79%; m.p. 55 °C. $[\alpha]_D^{20}$ = +35 (c = 1.0, $CHCl_3$). IR (CH_2Cl_2, 3 mM): $\tilde{\nu}$ = 3418, 1742, 1711, 1673, 1645 cm^{-1}. IR (1% in dry KBr): $\tilde{\nu}$ = 3419, 3285, 1747, 1712, 1633 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.41 (s, 9 H, *t*Bu), 1.77–1.95 (m, 4 H, $NCH_2CH_2CH_2CH$-CO), 2.80–3.18 (m, 6 H, $NCH_2CH_2CH_2CH$-CO + 2× CH-CH_2-Ph), 4.31–4.43 (m, 2 H, 2× C*H*-CH_2-Ph), 4.83–5.00 (m, 2 H, $NCH_2CH_2CH_2CH$-CO + NH), 6.72 and 6.96 (d, J = 8 Hz, 1 H, NH, mixture of conformers), 7.18–7.38 (m, 15 H, 3× Ph) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, mixture of conformers): δ = 22.4 and 24.3 , 26.9 and 28.3, 28.9 and 31.0, 37.5 and 38.3, 39.7, 46.6 and 46.8, 51.9 and 52.4, 55.4, 58.8 and 59.5, 66.7 and 67.3, 79.9, 126.7, 126.8, 127.0, 128.1, 128.2, 128.4, 128.5, 128.7, 129.2, 129.5, 135.2 and 135.6, 136.2 and 136.6, 155.2, 169.5, 170.5, 171.4, 172.0 ppm. $C_{35}H_{41}N_3O_6$ (599.3): calcd. C 70.10, H 6.89, N 7.01; found C 70.05, H 6.85, N 6.99.

CH_2(C_3H_6CO-L-Phe-D-Oxd-OBn)$_2$ (2a): A solution of Boc-L-Phe-D-Oxd-OBn (2 mmol, 0.96 g) and TFA (36 mmol, 2.78 mL) in dry dichloromethane (20 mL) was stirred at room temperature for 4 h, then the volatile compounds were removed under reduced pressure and the corresponding amine salt was obtained pure in quantitative yield without further purification.

A solution of azelaic acid (0.98 g, 0.52 mmol) and HBTU (0.4 g, 1.04 mmol) in dry acetonitrile (22 mL) was stirred under nitrogen atmosphere for 10 min at room temperature. Then, a mixture of the previously obtained amine salt (1.04 mmol) and Et_3N (3.2 mmol, 0.47 mL) in dry acetonitrile (15 mL) was added dropwise at room temperature. The solution was stirred for 40 min under a nitrogen atmosphere then acetonitrile was removed under reduced pressure and replaced with ethyl acetate. The mixture was washed with brine, 1 N aqueous HCl (3 × 30 mL), and 5% (w/v) aqueous $NaHCO_3$ (1 × 30 mL), dried with sodium sulfate and concentrated in vacuo. The pure product was obtained after silica gel chromatography [CH_2Cl_2 100% → CH_2Cl_2/ethyl acetate (80:20) as eluent] in 64% (1.17 g) overall yield; m.p. 207 °C. $[\alpha]_D^{20}$ = 45.0 (c = 0.1, $CHCl_3$). IR (CH_2Cl_2, 3 mM): $\tilde{\nu}$ = 3428, 1789, 1754, 1707, 1672 cm^{-1}. IR (1% in dry KBr): $\tilde{\nu}$ = 3309, 1793, 1765, 1736, 1708, 1650 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 0.95–1.18 [m, 10 H, $CH_2(CH_2)_5CH_2$], 1.20–1.40 [m, 4 H, $CH_2(CH_2)_5CH_2$], 1.50 (d, J = 6.3 Hz, 6 H, OCHCH_3), 2.00 (m, 4 H, CH_2CO), 2.70 (dd, J = 10.8, 13.5 Hz, 2 H, CHN-C*H*H-Ph), 3.10–3.20 (dd, J = 3.3, 13.5 Hz, 2 H, CHN-CH*H*-Ph), 4.65 (d, J = 4.2 Hz, 2 H, C*H*N), 4.80–4.90 (m, 2 H, OC*H*), 5.18 (d, J = 12.3 Hz, 2 H, OC*H*HPh), 5.25 (d, J = 12.6 Hz, 2 H, OCH*H*Ph), 5.8 (m, 2 H, C*H*N-CH_2Ph), 7.20–7.40 (m, 20 H, 4× Ph), 8.25 (d, J = 8.7 Hz, 2 H, N*H*) ppm. ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 14.8, 15.3, 21.1, 25.9, 29.0, 35.7, 37.7, 38.5, 51.0, 53.1, 55.4, 62.0, 67.7, 74.3, 127.2, 128.6, 128.8, 128.9, 129.2, 129.8, 136.0, 138.0, 152.5, 168.6, 172.7, 173.2 ppm. $C_{51}H_{56}N_4O_{12}$ (916.4): calcd. C 66.80, H 6.16, N 6.11; found C 66.75, H 6.19, N 6.07.

CH_2(C_3H_6CO-L-Phe-L-Phe-D-Oxd-OBn)$_2$ (2b): The synthetic procedure was the same as that of **2a**, starting from **1a**; yield 57%; m.p. 175 °C. $[\alpha]_D^{20}$ = +19 (c = 0.9, $CHCl_3$). IR (CH_2Cl_2, 3 mM): $\tilde{\nu}$ = 3440, 3358, 3309, 1773, 1748, 1716, 1655 cm^{-1}. IR (1% in dry KBr): $\tilde{\nu}$ = 3297, 1644, 1795, 1740, 1710 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.16–1.21 [m, 10 H, $CH_2(CH_2)_5CH_2$], 1.48 (d, J = 6.4 Hz, 6 H, 2× CH_3Oxd), 2.10–2.18 [m, 4 H, $CH_2(CH_2)_5CH_2$], 2.52–3.04 (m, 8 H, 4× CHN-CH_2-Ph), 3.93 (d, J = 4.8 Hz, 1 H, CHN-Oxd), 4.40 (m, 1 H, CHO-Oxd), 4.46 (m, 1 H, CHN-Oxd), 4.67 (m, 1 H, CHO-Oxd), 5.15 (m, 4 H, 2× CH_2OBn), 5.32 (br. s, 2 H, 2× NH), 5.92 (br. s, 1 H, NH), 7.08–7.36 (m, 30 H, 6× Phe) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, mixture of conformers): δ = 21.0, 21.2, 24.6, 25.3, 25.4, 28.6, 28.8, 29.6, 30.9, 33.9, 36.2, 36.3, 37.8, 38.0, 38.3, 38.6, 52.9, 53.0, 54.0, 54.2, 61.7, 61.8, 67.3, 68.0, 73.7, 126.9, 128.2, 128.5, 128.7, 129.4, 130.0, 134.6, 135.3, 136.3, 136.4, 150.3, 151.2, 167.3, 170.4, 170.5, 170.7, 170.8, 171.3, 171.8, 177.6, 177.7, 177.8 ppm. $C_{69}H_{74}N_6O_{14}$ (1210.5): calcd. C 68.41, H 6.16, N 6.94; found C 68.38, H 6.18, N 6.94.

BnO-D-Pro-L-Phe-CO-(CH_2)$_7$-CO-L-Phe-D-Pro-OBn (2c): The synthetic procedure was the same as that of **2a**, starting from **1c**; yield 83%; m.p. 63 °C. $[\alpha]_D^{20}$ = +76 (c = 1.0, $CHCl_3$). IR (CH_2Cl_2, 3 mM): $\tilde{\nu}$ = 3419, 3304, 1746, 1717 cm^{-1}. IR (1% in dry KBr): $\tilde{\nu}$ = 3404, 1736, 1629 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.07–1.19 [m, 10 H, $CH_2(CH_2)_5CH_2$], 1.31–1.53 (m, 8 H, 2× $NCH_2CH_2CH_2CH$), 1.60–1.80 [m, 4 H, $CH_2(CH_2)_5CH_2$], 1.94–2.04 (m, 4 H, 2× $NCH_2CH_2CH_2CH$), 2.71–2.98 (m, 4 H, 2× CHN-CH_2Ph), 4.21 (dd, J = 3.6, 8.4 Hz, 2 H, 2× $NCH_2CH_2CH_2CH$), 4.78–4.88 (m, 2 H, C*H*N-CH_2Ph), 4.91–4.98 (m, 1 H, C*H*N-CH_2Ph), 4.99–5.04 (m, 4 H, 2× OCH_2Ph), 6.53 (d, J = 8.0 Hz, 1 H, NH), 7.02–7.22 (m, 20 H, 4× Phe) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, mixture of conformers): δ = 24.2, 24.9, 25.0, 25.1, 25.2, 28.5, 28.6, 28.8, 30.9, 36.0, 38.5, 39.4, 46.8, 52.1, 58.7, 66.6, 67.2, 126.9, 127.8, 128.1, 128.1, 128.3, 128.4, 128.5, 129.0, 129.3, 135.4, 136.2, 136.9, 151.6, 170.2, 170.3, 171.5, 172.5, 172.6 ppm. $C_{51}H_{60}N_4O_8$ (856.4): calcd. C 71.47, H 7.06, N 6.54; found C 71.44, H 7.10, N 6.52.

BnO-D-Pro-(L-Phe)$_2$-CO-(CH_2)$_7$-CO-(L-Phe)$_2$-D-Pro-OBn (2d): The synthetic procedure was the same as that of **2a**, starting from **1d**; yield 82%; m.p. 59 °C. $[\alpha]_D^{20}$ = +40 (c = 1.0, $CHCl_3$). IR (CH_2Cl_2, 3 mM): $\tilde{\nu}$ = 3412, 3293, 1749, 1643 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.17–1.50 [m, 10 H, $CH_2(CH_2)_5CH_2$], 1.80–1.89 (m, 8 H, 2× $NCH_2CH_2CH_2CH$), 2.05 [m, 4 H, CH_2-$(CH_2)_5CH_2$], 2.81–3.03 (m, 4 H, 2× CHN-CH_2Ph), 3.39–3.53 (m, 4 H, 2× $NCH_2CH_2CH_2CH$), 4.33 (dd, J = 3.6, 7.6 Hz, 2 H, $NCH_2CH_2CH_2CH$), 4.62 (q, J = 6.8 Hz, 1 H, NCH-CH_2Ph), 4.81 (dt, J = 6.0, 9.2 Hz, 1 H, 2× CHN-CH_2Ph), 5.08 (AB, J = 12.4 Hz, 2 H, OCH_2Ph), 6.04 (d, J = 7.2 Hz, 2 H, NH), 6.57 (d, J = 7.6 Hz, 2 H, NH), 7.06–7.30 (m, 30 H, 6× Phe) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, mixture of conformers): δ = 24.3, 25.3, 28.8, 28.9, 36.3, 38.2, 39.5, 46.8, 52.4, 53.8, 58.8, 66.7, 126.9, 127.0, 128.0, 128.3, 128.4, 128.5, 129.2, 129.4, 129.5, 135.6, 136.1, 136.3, 169.3, 170.3, 171.4, 172.8 ppm. $C_{69}H_{78}N_6O_{10}$ (1150.6): calcd. C 71.98, H 6.83, N 7.30; found C 72.01, H 6.80, N 7.28.

CH_2(C_3H_6CO-L-Phe-D-Oxd-OH)$_2$ (3a): Compound **2a** (1 mmol, 0.92 g) was dissolved in MeOH (35 mL) under nitrogen. Pd/C (50 mg, 10% w/w) was added under nitrogen. Vacuum was created inside the flask by using the vacuum line. The flask was then filled with hydrogen by using a balloon (1 atm). The solution was stirred for 2 h under a hydrogen atmosphere. The pure product was obtained in quantitative yield (0.73 g) after the solution was filtered

through a Celite pad using ethyl acetate and concentrated in vacuo; m.p. 201 °C. $[\alpha]_D^{20}$ = –36.0 (*c* = 1.2, MeOH). ^{1}H NMR (CD_3OD, 400 MHz): δ = 1.06–1.47 [m, 10 H, $CH_2(CH_2)_5CH_2$], 1.58 (d, *J* = 6.4 Hz, 6 H, $OCHCH_3$), 2.03–2.15 [m, 4 H, $CH_2(CH_2)_5CH_2$], 2.91 (dd, *J* = 9.6, 13.6 Hz, 2 H, CHN-CHHPh), 3.14 (dd, *J* = 5.2, 13.6 Hz, 2 H, CHN-CHHPh), 4.00 (d, *J* = 5.6 Hz, 2 H, CHN-CHHPh), 4.62–4.87 (m, 2 H, OCH), 5.80 (m, 2 H, CHN-CH_2Ph), 7.20–7.40 (m, 20 H, 4× Ph) ppm. ^{13}C NMR (CD_3OD, 100 MHz): δ = 19.8, 25.3, 28.3, 28.5, 35.2, 37.6, 52.7, 61.7, 74.4, 126.5, 128.0, 129.1, 136.6, 151.1, 153.3, 169.7, 172.7, 174.4 ppm. $C_{37}H_{44}N_4O_{12}$ (736.3): calcd. C 60.32, H 6.02, N 7.60; found C 60.36, H 6.04, N 7.55.

$CH_2(C_3H_6CO$-L-Phe-L-Phe-D-Oxd-OH)$_2$ (3b): The synthetic procedure was the same as that of **3a**, starting from **2b**; yield 92%; m.p. 52 °C. $[\alpha]_D^{20}$ = +2 (*c* = 0.49, MeOH). ^{1}H NMR (CD_3OD, 400 MHz): δ = 1.14–1.25 [m, 10 H, $CH_2(CH_2)_5CH_2$], 1.43–1.57 (m, 6 H, 2× CH_3Oxd), 2.12–2.25 [m, 4 H, $CH_2(CH_2)_5CH_2$], 2.71–2.88 (m, 8 H, 4× CHN-CH_2-Ph), 3.06–3.25 (m, 2 H, 2× CHN-CH_2-Ph), 4.29–4.65 (m, 4 H, 2× CHO-Oxd + 2× CHN-Oxd), 5.50–5.62 (m, 2 H, 2× CHN-CH_2-Ph), 6.98–7.33 (m, 20 H, 6× Phe) ppm. ^{13}C NMR (CD_3OD, 100 MHz): δ = 14.0, 19.8, 24.6, 25.3, 28.6, 33.5, 35.3, 37.0, 37.3, 37.4, 52.9, 53.4, 54.0, 65.5, 74.6, 126.2, 126.3, 126.5, 128.0, 128.5, 128.9, 129.2, 129.8, 136.3, 137.0, 137.1, 171.6, 171.8, 173.4, 174.5, 174.7, 176.2 ppm. $C_{55}H_{62}N_6O_{14}$ (1030.4): calcd. C 64.07, H 6.06, N 8.15; found C 64.03, H 6.05, N 8.17.

HO-D-Pro-L-Phe-CO-$(CH_2)_7$-CO-L-Phe-D-Pro-OH (3c): The synthetic procedure was the same as that of **3a**, starting from **2c**; yield 96%; m.p. 103 °C. $[\alpha]_D^{20}$ = +30 (*c* = 1.04, MeOH). IR (1% in dry KBr): $\tilde{\nu}$ = 3408, 3291, 1733, 1630 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.92–1.39 [m, 10 H, $CH_2(CH_2)_5CH_2$], 1.80–1.89 (m, 8 H, 2× $NCH_2CH_2CH_2CH$), 2.05 [m, 4 H, $CH_2(CH_2)_5CH_2$], 2.80–3.40 (m, 12 H, 2× $NCH_2CH_2CH_2CH$-CO + 4× CH-CH_2Ph), 3.40–3.78 (m, 4 H, 2× CH-CH_2Ph), 4.83–5.00 (m, 2 H, 2× $NCH_2CH_2CH_2CH$-CO), 7.18–7.38 (m, 10 H, 2× Ph) ppm. ^{13}C NMR (CD_3OD, 50 MHz, mixture of conformers): δ = 23.6, 25.4, 26.0, 26.7, 29.8, 30.1, 32.1, 34.9, 36.4, 36.6, 37.9, 38.8, 39.4, 53.6, 54.2, 60.4, 61.1, 127.7, 128.0, 129.4, 129.5, 130.3, 130.5, 138.1, 138.9, 172.0, 173.3, 175.2, 175.6, 176.1 ppm. $C_{37}H_{48}N_4O_8$ (676.3): calcd. C 65.66, H 7.15, N 8.28; found C 65.70, H 7.18, N 8.31.

HO-D-Pro-(L-Phe)$_2$-CO-$(CH_2)_7$-CO-(L-Phe)$_2$-D-Pro-OH (3d): The synthetic procedure was the same as that of **3a**, starting from **2d**; yield 97%; m.p. 98 °C. $[\alpha]_D^{20}$ = +5 (*c* = 1.1, MeOH). IR (1% in dry KBr): $\tilde{\nu}$ = 3493, 3407, 3282, 1734, 1630 cm^{-1}. ^{1}H NMR (CD_3OD, 400 MHz): δ = 0.97–1.48 [m, 10 H, $CH_2(CH_2)_5CH_2$], 1.60–1.88 (m, 8 H, 2× $NCH_2CH_2CH_2CH$), 2.05 [m, 4 H, $CH_2(CH_2)_5CH_2$], 2.82–2.95 (m, 8 H, 4× NHCH-CH_2Ph), 3.36–3.53 (m, 2 H, 2× $NCH_2CH_2CH_2CH$), 4.48–4.70 (m, 4 H, 4× CHN-CH_2Ph), 6.93–7.30 (m, 20 H, 4× Ph) ppm. ^{13}C NMR (CD_3OD, 100 MHz, mixture of conformers): δ = 22.1, 24.0, 25.3, 28.4, 28.6, 28.6, 28.7, 30.7, 35.4, 36.7, 37.5, 38.0, 52.4, 52.6, 54.1, 59.0, 126.2, 126.3, 126.6, 127.9, 128.0, 128.1, 128.9, 128.9, 129.1, 136.5, 136.9, 137.1, 137.3, 170.0, 171.2, 171.7, 171.8173.6, 174.3, 174.5 ppm. $C_{55}H_{66}N_6O_{10}$ (971.1): calcd. C 68.02, H 6.85, N 8.65; found C 68.00, H 6.87, N 8.70.

Conditions for Gel Formation: Compounds **2a**–**d** or **3a**–**d** (5 μmol) and the solvent reported in Table 1 (500 μL) were placed in a test tube (8 mm wide). The mixture was sonicated for 20 min until the solid was totally dissolved and then it was left stand for 2 h for gel formation.

The xerogel was obtained from **2a** after solvent evaporation at room temperature.

Microscopy: The gel and xerogel of **2a** were systematically observed by OM and SEM. The OM images were collected by using a Leica optical microscope equipped with a CCD camera. SEM images were obtained from samples on glass cover slips after being coated with gold and observed by using a Philips XL20 scanning electron microscope. The images were recorded by using a CCD digital camera.

Single-Crystal X-ray Diffraction for 1b: The X-ray intensity data for **1b** were measured on a Bruker SMART Apex II CCD area detector diffractometer. Cell dimensions and the orientation matrix were initially determined from a least-squares refinement on reflections measured in three sets of 20 exposures, collected in three different ω regions and eventually refined against all data. A full sphere of reciprocal space was scanned by 0.3° ω steps. The software SMART[8] was used for collecting frames of data, indexing reflections and determining of lattice parameters. The collected frames were then processed for integration by the SAINT program[9] and an empirical absorption correction was applied by using SADABS.[11] The structure was solved by direct methods (SIR 97)[10] and subsequent Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXTL)[11] by using anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms, except the amidic protons and methine hydrogen atoms, were added in calculated positions, included in the final stage of refinement with isotropic thermal parameters, U(H) = 1.2 U_{eq}(C) [U(H) = 1.5 U_{eq}(C-Me)], and allowed to ride on their carrier carbons. The absolute structure configuration was not determined from X-ray data, but was known from the synthetic route. Crystal data and details of the data collection for **1b** are reported in Table S1 in the Supporting Information.

XRD Analysis: XRD patterns were collected by using a PanAnalytical X'Pert Pro system equipped with an X'Celerator detector powder diffractometer using $Cu_{K\alpha}$ radiation generated at 40 kV and 40 mA. The instrument was configured with 1/32° divergence and 1/32° antiscattering slits. A standard quartz sample holder 1 mm deep, 20 mm high and 15 mm wide was used. The diffraction patterns were collected within the 2θ range from 2.5 to 40° with a step size ($\Delta 2\theta$) of 0.02° and a counting time of 1200 s. The diffraction pattern was analysed by means of the software X'Pert High Score Plus.

CCDC-803709 contains the supplementary crystallographic data for **1b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ^{13}C NMR spectra of compounds **1c** and **1d**, XRD patterns of Boc-L-Phe-L-Phe-D-Pro-OBn (**1d**), and crystal data and structure refinement for **1b**.

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[1] a) G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **1991**, *254*, 1312–1319; b) L. L. del Mercato, P. P. Pompa, G. Maruccio, A. D. Torre, S. Sabella, A. M. Tamburro, R. Cingolani, R.

Rinaldi, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 18019–18024; c) F. W. Kotch, R. T. Raines, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 3028–3033; d) J. D. Hartgerink, E. Beniash, S. I. Stupp, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 5133–5138; e) L. Ziserman, H.-Y. Lee, S. R. Raghavan, A. Mor, D. Danino, *J. Am. Chem. Soc.* **2011**, *133*, 2511–2517.

[2] a) G. Angelici, G. Falini, H.-J. Hofmann, D. Huster, M. Monari, C. Tomasini, *Angew. Chem.* **2008**, *120*, 8195; *Angew. Chem. Int. Ed.* **2008**, *47*, 8075–8078; b) G. Angelici, G. Falini, H.-J. Hofmann, D. Huster, M. Monari, C. Tomasini, *Chem. Eur. J.* **2009**, *15*, 8037–8048.

[3] B. E. Evans, K. E. Rittle, M. G. Bock, R. M. DiPardo, R. M. Freidinger, W. L. Whitter, G. F. Lundell, D. F. Veber, P. S. Anderson, R. S. L. Chang, V. J. Lotti, D. J. Cerino, T. B. Chen, P. J. Kling, K. A. Kunkel, J. P. Springer, J. Hirshfield, *J. Med. Chem.* **1988**, *31*, 2235–2246.

[4] a) J. S. Mason, I. Morize, P. R. Menard, D. L. Cheney, C. Hulme, R. F. Labaudiniere, *J. Med. Chem.* **1999**, *42*, 3251–3264; b) K. C. Nicolaou, J. A. Pfefferkorn, A. J. Roecker, G.-Q. Cao, S. Barluenga, H. J. Mitchell, *J. Am. Chem. Soc.* **2000**, *122*, 9939–9953.

[5] For a review on diphenylalanine-based nanostructures, see: a) X. Yan, P. Zhu, J. Li, *Chem. Soc. Rev.* **2010**, *39*, 1887–1890; see also: b) A. Banerjee, G. Palui, A. Banerjee, *Soft Matter* **2008**, *4*, 1430–1437; c) L. Adler-Abramovich, M. Reches, V. L. Sedman, S. Allen, S. J. B. Tendler, E. Gazit, *Langmuir* **2006**, *22*, 1313–1320; d) J. Ryu, S.-W. Kim, K. Kang, C. B. Park, *ACS Nano* **2010**, *4*, 159–164.

[6] a) L. Frkanec, M. Žinić, *Chem. Commun.* **2010**, *46*, 522–537; b) A. Dawn, N. Fujita, S. Haraguchi, K. Sada, S.-I. Tamaru, S. Shinkai, *Org. Biomol. Chem.* **2009**, *7*, 4378–4385; c) P. Terech, R. G. Weiss, *Chem. Rev.* **1997**, *97*, 3133–3159; d) J. H. van Esch, B. L. Feringa, *Angew. Chem.* **2000**, *112*, 2351; *Angew. Chem. Int. Ed.* **2000**, *39*, 2263–2266; e) D. J. Abdallah, R. G. Weiss, *Adv. Mater.* **2000**, *12*, 1237–1247; f) M. George, R. G. Weiss, *Acc. Chem. Res.* **2006**, *39*, 489–497; g) K. Yoza, N. Amanokura, Y. Ono, T. Akao, H. Shinmori, M. Takeuchi, S. Shinkai, D. N. Reinhoudt, *Chem. Eur. J.* **1999**, *5*, 2722–2729; h) P. Babu, N. M. Sangeetha, P. Vijaykumar, U. Maitra, K. Rissanen, A. R. Raju, *Chem. Eur. J.* **2003**, *9*, 1922–1932; i) F. S. Schoonbeek, J. van Esch, R. Hulst, R. M. Kellogg, B. L. Feringa, *Chem. Eur. J.* **2000**, *6*, 2633–2643; j) P. Gao, C. Zhan, L. Liu, Y. Zhou, M. Liu, *Chem. Commun.* **2004**, 1174–1175; k) M. Yamanaka, K. Sada, M. Miyata, K. Hanabusa, K. Nakano, *Chem. Commun.* **2006**, 2248–2250; l) B. Bai, H. Wang, H. Xin, F. Zhang, B. Long, X. Zhang, S. Qu, M. Li, *New J. Chem.* **2007**, *31*, 401–408; m) S. Cicchi, G. Ghini, L. Lascialfari, A. Brandi, F. Betti, D. Berti, S. Ferraiti, P. Baglioni, *Chem. Commun.* **2007**, 1424–1426; n) G. John, G. Zhu, J. Li, J. S. Dordick, *Angew. Chem.* **2006**, *118*, 4890; *Angew. Chem. Int. Ed.* **2006**, *45*, 4772–4775; o) A. R. Hirst, J. F. Miravet, B. Escuder, L. Noirez, V. Castelletto, I. W. Hamley, D. K. Smith, *Chem. Eur. J.* **2009**, *15*, 372–379; p) B. Escuder, J. F. Miravet, J. A. Sáez, *Org. Biomol. Chem.* **2008**, *6*, 4378–4383; q) J. R. Moffat, D. K. Smith, *Chem. Commun.* **2009**, 316–318.

[7] a) J. Becerril, M. I. Burguete, B. Escuder, F. Galindo, R. Gavara, J. F. Miravet, S. V. Luis, G. Peris, *Chem. Eur. J.* **2004**, *10*, 3879–3890; b) J. Becerril, B. Escuder, J. F. Miravet, R. Gavara, S. V. Luis, *Eur. J. Org. Chem.* **2005**, 481–485.

[8] a) A. E. Aliev, S. Bhandal, D. Courtier-Murias, *J. Phys. Chem. A* **2009**, *113*, 10858–10865; b) Y. K. Kang, *J. Phys. Chem. B* **2002**, *106*, 2074–2082; c) T. Shi, S. M. Spain, D. L. Rabenstein, *J. Am. Chem. Soc.* **2004**, *126*, 790–796.

[9] a) F. Bernardi, M. Garavelli, M. Scatizzi, C. Tomasini, V. Trigari, M. Crisma, F. Formaggio, C. Peggion, C. Toniolo, *Chem. Eur. J.* **2002**, *8*, 2516–2525; b) C. Tomasini, V. Trigari, S. Lucarini, F. Bernardi, M. Garavelli, C. Peggion, F. Formaggio, C. Toniolo, *Eur. J. Org. Chem.* **2003**, 259–267.

[10] a) S. Guha, M. G. B. Drew, A. Banerjee, *Cryst. Growth Des.* **2010**, *10*, 4716–4721; b) A. Banerjee, S. K. Maji, M. G. B. Drew, D. Haldar, A. Banerjee, *Tetrahedron Lett.* **2003**, *44*, 6741–6744; c) A. Banerjee, S. K. Maji, M. G. B. Drew, D. Haldar, A. K. Das, A. Banerjee, *Tetrahedron* **2004**, *60*, 5935–5944; d) A. K. Das, A. Banerjee, M. G. B. Drew, D. Haldar, A. Banerjee, *Supramol. Chem.* **2004**, *16*, 331–335.

[11] V. Madison, C. M. Deber, E. R. Blou, *J. Am. Chem. Soc.* **1977**, *99*, 4788–4798.

[12] a) T. Shimizu, *Macromol. Rapid Commun.* **2002**, *23*, 311–331; b) J.-H. Fuhrhop, T. Wang, *Chem. Rev.* **2004**, *104*, 2901–2937.

[13] a) Y. Y. Choi, Y. Jeong, M. K. Joo, B. Jeong, *Macromol. Biosci.* **2009**, *9*, 869–874; b) Y. Y. Choi, M. K. Joo, Y. S. Sohn, B. Jeong, *Soft Matter* **2008**, *4*, 2383–2387; c) K. Isozaki, H. Takaya, T. Naota, *Angew. Chem.* **2007**, *119*, 2913; *Angew. Chem. Int. Ed.* **2007**, *46*, 2855–2857.

[14] a) L. J. Bellamy, in: *The Infrared Spectra of Complex Molecules*, Methuen, London, **1966**; b) W. L. Driessen, P. L. A. Everstijn, *J. Coord. Chem.* **1980**, *10*, 155–158.

[15] a) L. A. Estroff, A. D. Hamilton, *Chem. Rev.* **2004**, *104*, 1201–1217; R. N. Mitra, D. Das, S. Roy, P. K. Das, *J. Phys. Chem. B* **2007**, *111*, 14107–14113; b) N. Mahmoudi, S. Mehalebi, T. Nicolai, D. Durand, A. Riaublank, *J. Agric. Food Chem.* **2007**, *55*, 3104–3111.

[16] I. Nakazawa, M. Masuda, Y. Okada, T. Hanada, K. Yase, M. Asai, T. Shimizu, *Langmuir* **1999**, *15*, 4757–4764.

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