Helical Supramolecular Aggregates Based on Ureidopyrimidinone Quadruple Hydrogen Bonding

J. H. K. Ky Hirschberg, Rolf A. Koevoets, Rint P. Sijbesma,* and E. W. Meijer*[a]

Abstract: A series of mono- and bifunctional compounds **2**–**7**, based on the ureido pyrimidinone quadruple hydrogen bonding unit, was prepared to study the mode of aggregation of these compounds in the bulk and in solution. Compounds **2**–**7** exhibit thermotropic liquid crystalline properties, as evidenced by differential scanning calorimetry and optical polarization microscopy. The presence of an ordered hexagonal discotic (D_{ho}) phase of **2a** was confirmed by X-ray diffraction on an aligned sample. In chloroform, the bifunctional compounds form cyclic dimers at millimolar concentrations, and these dimers exist in equilibrium with linear species above a critical concentration, which may be from 6 mM to greater than 260 mM, depending on the structure of the spacer. Circular dichroism measurements in chloroform did not show a Cotton effect. Dodecane solutions of compounds **3**, **4b**, and **7b** display a Cotton effect at the absorption band of the phenyl-pyrimidinone unit. Amplification of chirality was observed in mixtures of **7a** and **7b**, but not in mixtures of **4a** and **4b**, indicating that **7a** and **7b** form mixed polymeric aggregates with a helical architecture in dodecane solution, whereas **4a** and **4b** do not. The Cotton effect is lost upon increasing the temperature. Half of the helicity is lost at 25 °C for **3** and at 60 °C for **4b**, suggesting that **3**, bearing the shorter spacer, forms less stable columns than **4b**. Compound **7b** loses half of its helicity at 45 °C. Compounds **2b**, **5**, and **6** do not exhibit helical organization, as evidenced by the absence of Cotton effects.

Keywords: aggregation · helical structures · hydrogen bonds · supramolecular chemistry · ureido pyrimidinone

Introduction

Supramolecular polymers[1, 2] are a fascinating class of materials, formed by the association of monomers through reversible, noncovalent interactions such as hydrogen bonding, metal coordination, or $\pi-\pi$ stacking. Linear hydrogen-bonded supramolecular polymers were first introduced by Lehn and co-workers, who used triple hydrogen bonds between monomers.[3, 4] Monomers with tartaric acid backbones were shown to form liquid-crystalline materials in which the molecules are packed in helical columns,[5] which form helically twisted fibers.[6] Stronger interactions have been obtained with single hydrogen bonds between carboxylic acids and pyridines,[7] or by use of arrays of more than three hydrogen bonds.[8–11] We have employed the high strengths of the ureidotriazine[12] and ureidopyrimidinone[13] quadruple hydrogen bonding units to obtain linear supramolecular polymers with high degrees of polymerization both in bulk and in solution from monomers containing two of these units.[14] The directionality and the selectivity of multiple hydrogen bonds allow a high degree of control over polymer architecture with respect to chain length—which can be adjusted by mixing monofunctional and bifunctional compounds—and with respect to the degree of cross-linking in reversible networks—which can be controlled by addition of trifunctional compounds. Even greater control over polymer architectures can in principle be achieved by employing additional noncovalent interactions between monomeric units that favor a specific conformation of the polymeric chain. Conformational control is the basis of the functionality of biomacromolecules such as DNA and proteins, and has become a fruitful area of research in synthetic covalent polymers. Here, the conformational preferences of monomeric units in combination with inter-residue hydrogen bonds or stacking interactions have been used to obtain macromolecules that are folded into a well-defined secondary structure ("foldamers").[15–17] Recently we have applied this concept to supramolecular polymers, by using solvophobic interactions between ureido-*s*-triazine (UTr) units connected by a spacer and provided with solubilizing trialkoxyphenyl groups to obtain supramolecular polymers with a helical columnar architecture in dodecane (Figure 1).[18] The structure of the columns was shown to be biased towards a single

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Supporting information for this article is available on the WWW under http://www.chemeuj.org or from the author. Simple model for amplification of chirality in *n*-mers.

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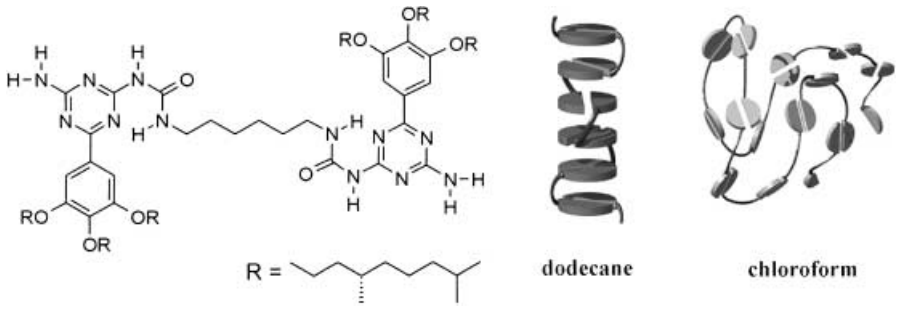


Figure 1. Ureido-*s*-triazine derivative C_6-$(UTr)_2$, and schematic representations of helical supramolecular polymers (observed in dodecane) and random coil polymers (observed in chloroform).

helicity by the use of homochiral side chains. In $CHCl_3$, a solvent in which solvophobic interactions between aromatic groups are much weaker, but the hydrogen bonding between ureidotriazine groups is still relatively strong ($K_{dim} = 2 \times 10^4\,M^{-1}$), the compounds form random coil polymers.[12] This approach was extended to defined architectures in water through the use of chiral penta(ethylene oxide) derivatives.[19]

Ureidopyrimidinones (UPy) have a much higher dimerization constant[20] ($K_{dim} = 6 \times 10^7\,M^{-1}$ in $CHCl_3$) and bifunctional compounds containing this unit should in principle allow the construction of polymers with a higher degree of polymerization in either dodecane or chloroform. Previously, we have shown that bifunctional UPy derivative **1**, which is strongly preorganized by its α,α'-tetramethyl xylylene spacer, exclusively forms cyclic dimers in $CHCl_3$ and in the crystal (Figure 2). In solution, the cyclic dimers of **1** exist as a slowly interconverting mixture of *syn* and *anti* isomers, with UPy units present in either the keto or the enol tautomeric form.[21]

To achieve highly preorganized supramolecular polymers with a columnar architecture, we studied the mode of aggregation (cyclic versus polymeric) of bifunctional ureidopyrimidinones, with less preorganized spacer units than **1**, and we provided these molecules with trialkoxyphenyl groups to promote a columnar architecture. Here we present the results of a study of compounds **2**–**7** in bulk and in solution, by differential scanning calorimetry (DSC) and X-ray crystallography in the bulk, and by ^{1}H NMR and circular dichroism in solution.

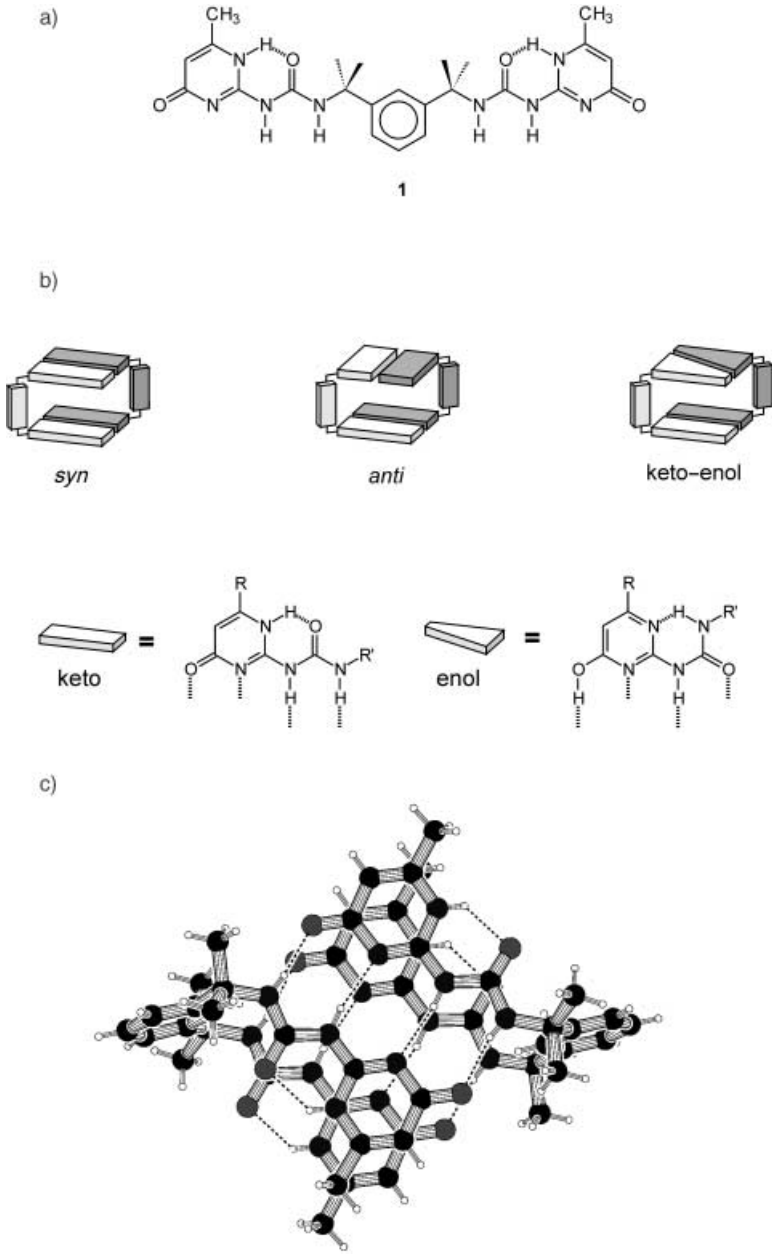
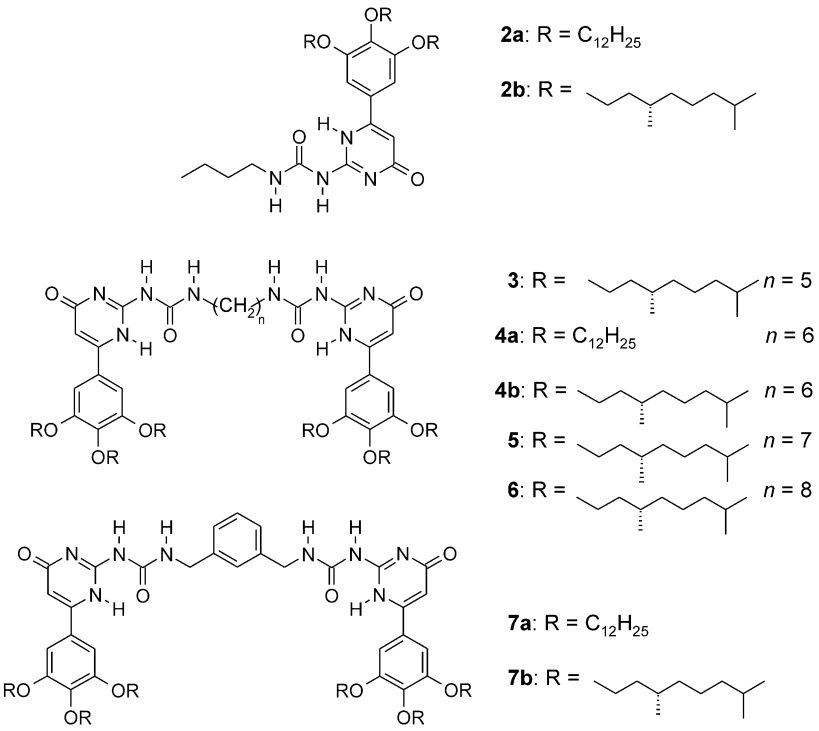
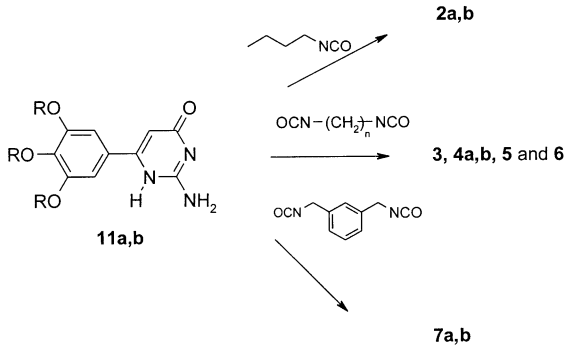


Figure 2. a) Structural formula of bifunctional UPy derivative **1**. b) Three isomeric cyclic dimers observed for this compound. c) Crystal structure of the *syn* dimer.[21]



Results

Synthesis: Monofunctional ureidopyrimidinone **2a** and **2b** and bifunctional derivatives **3**–**7** were synthesized either by acylation of isocytosines **11a** or **11b** with butyl isocyanate or the appropriate diisocyanate, when commercially available, or they were prepared by the action of di-*tert*-butyl tricarbonate on the corresponding diamine (Scheme 1). In the reported synthesis of isocytosine **2a**,[22] ethyl 3,4,5-trialkoxybenzoylacetate **9a** was obtained from the corresponding benzoyl chloride by treatment with ethyl acetoacetate **8**, followed by decarboxylation.[23] In this work a more efficient method was used for the synthesis of **9b**, in which the acid chloride was allowed to react with potassium ethyl malonate (**10**) under the action of anhydrous magnesium chloride/triethylamine as a base system.[24] By this method, β-keto ester **9b** was obtained in 86% yield. Condensation of the β-keto esters (used without further purification) with guanidinium carbonate in ethanol afforded isocytosines **11a** and **11b** in 39% and 45% yields, respectively (Scheme 2). All compounds were purified by column chromatography and were fully characterized by ^{1}H NMR, ^{13}C NMR, IR spectroscopy, MALDI-TOF mass spectrometry, and elemental analysis.

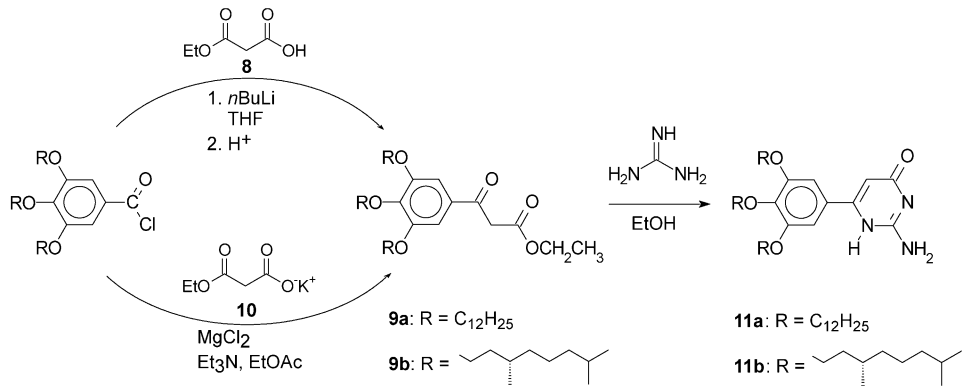


Scheme 1. Synthesis of mono- and bifunctional ureidopyrimidinones **2**–**7**.

Liquid crystallinity: Upon dimerization, the UPy derivatives **2a** and **2b** form disk-shaped dimers, with a rigid, planar core, surrounded by flexible alkyl groups. This architecture is conducive to the formation of a columnar discotic mesophase in bulk.[25] In bifunctional derivatives **3**–**7**, similar columns of UPy dimers may be formed when each spacer moiety connects two stacked disks. Depending on the arrangement of the spacers, the columns are either polymeric, or they consist of stacks of cyclic dimers of the bifunctional molecules (Figure 3).

To investigate the presence of (columnar discotic) mesophases, the thermal behavior of the compounds was studied by polarization microscopy and DSC. All compounds feature strong birefringent textures, which are liquid-like at room temperature. Monofunctional compound **2a** and bifunctional compound **3** feature fan-like textures upon slowly cooling from the isotropic phase. These focal conic textures are typical for discotic hexagonal phases. For compounds **2b** and **4**–**7**, only tiny homeotropic monodomains were present in the liquid crystalline state, probably due to the highly viscous isotropic melt. Upon heating, the DSC traces of the compounds each show a transition from the mesophase to the isotropic state at temperatures between 98 and 242 °C. The transition was also observed upon cooling, except in the case of chiral compound **3**. Sharp melting points were observed for achiral compounds **2a** (Figure 4), **4a**, and **7a**, while the chiral compounds only showed broad transitions, below -50 °C, presumably due to a glass transition. The phase transition temperatures are summarized in Table 1.

To confirm the presence of a columnar discotic arrangement of dimers, as inferred from the textures in optical polarized microscopy, the structures of the mesophases of **2a** and **3** were investigated by X-ray diffraction (Figure 5 and Table 2). The diffraction pattern of **2a** features a perpendicular orientation of the low-angle and the wide-angle reflections, indicating an orthogonal phase. The low-angle reflections at spacings of 28.9, 15.4, and 14.1 allow indexation as the 200, 120, and 400 reflections in an orthogonal lattice with lattice constants of $a = 56.4$ Å and $b = 32.6$ Å. The sharp wide-angle reflections feature a perpendicular orientation with respect to the small-angle reflections, which indicates that the phase is ordered, and the disks are stacked with an interdisc distance of 3.5 Å. For compound **3** a sharp reflection with a



Scheme 2. Synthesis of isocytosine **11a**, **b**.

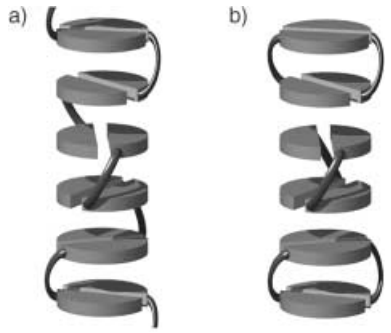


Figure 3. Schematic representation of columns of bifunctional compounds **3**–**7**, which are either polymeric (a), or consist of stacks of cyclic dimers (b).

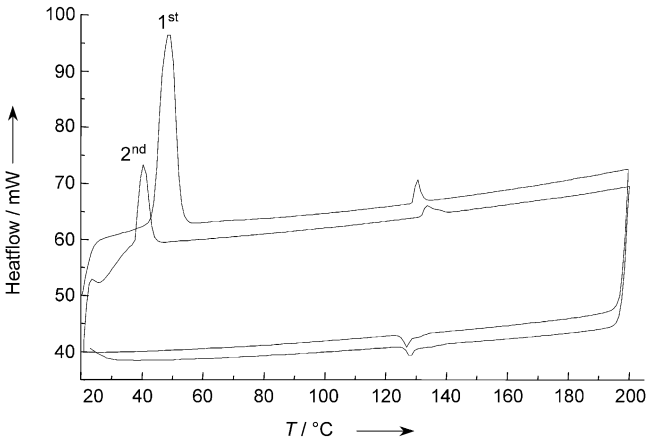


Figure 4. DSC thermogram of compound **2a**. First and second heating and cooling scans are shown.

spacing of 31.6 Å was found, but no higher order peaks were observed. In combination with a fan-like texture observed by polarization microscopy, this suggests the presence of a columnar mesophase for **3**.

Aggregation in chloroform: Ureidopyrimidinones have been shown[13] to exist in solution as mixtures of strongly dimerizing tautomers, a [1*H*]-pyrimidin-4-one (keto) tautomer and a pyrimidin-4-ol (enol) tautomer (Figure 6, inset). The position of the keto–enol equilibrium has been studied by ^{1}H NMR spectroscopy, and is substituent- and solvent-dependent. The ^{1}H NMR spectrum of monofunctional compound **2b** in $CDCl_3$ is shown in Figure 6 and shows signals of the keto and the enol tautomer in an 87:13 ratio. From the position of the NH protons (between $\delta = 10$ and 14 ppm for both tautomers) it can be concluded that hydrogen bonds are present.

^{1}H NMR spectra of dilute solutions of bifunctional compounds **3**–**7** in $CDCl_3$ are much more complex. As examples, spectra of solutions of **3** and **4b** are shown in Figure 7. Upon addition of small amounts of trifluoroacetic acid, which disrupts the hydrogen bonds between ureidopyrimidinone units, the spectra simplify dramatically (Figure 7d and 7h). Similar complex spectra have been observed for bifunctional compound **1**, which exists in

Table 1. Thermotropic properties of compounds **2**–**7b** determined by DSC.[a]

Compound	K	T [°C]	ΔH [kJ mol^{-1}]	M	T °C	ΔH [kJ mol^{-1}]	I
2a	·	45	50	·	131	2	
2b				·	98	1.5	·
3				·	173	2.2	·
4a	·	–11	14	·	164	3.7	·
4b				·[b]	160[c]		·
5				·	147	2.2	·
6				·	207	12.3	·
7a	·	–17	18	·	242	7.1	·
7b				·	239	7.5	·

[a] · The phase is observed; K = crystalline phase; M = mesophase; I = isotropic phase. [b] Only observed after precipitation in methanol. [c] This value is obtained from the first heating curve.

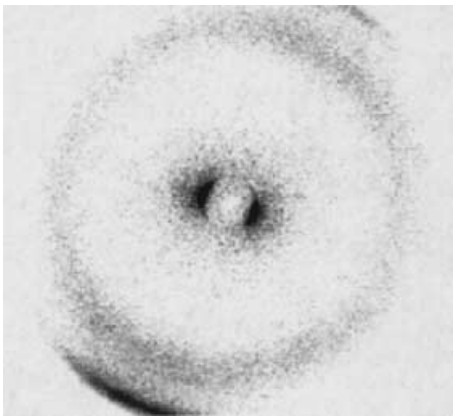


Figure 5. X-ray diffraction pattern of the mesophase of compound **2a**.

Table 2. Diffraction spacings [Å] for the D_{ho} mesophase of **2a**.

Interdisc distance		200/110	120	400/220	Alkyl halo
observed					
$a = 56.4$; $b = 32.6$	28.9	15.4	14.1	4.4	3.5
calculated	28.2	15.6	14.1		

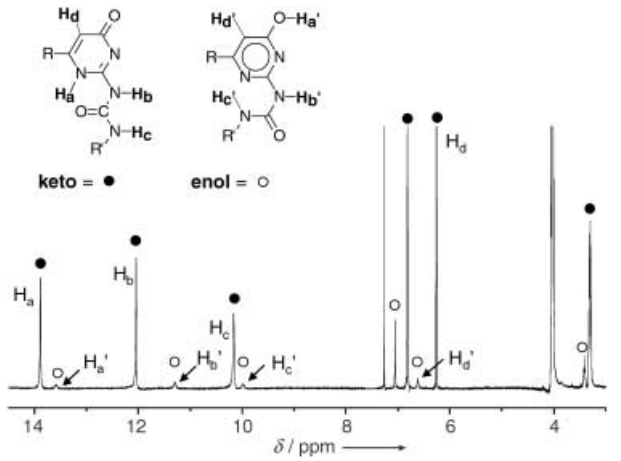


Figure 6. ^{1}H NMR spectrum of monofunctional ureidopyrimidinone **2b** in $CDCl_3$.

Table 3. Diffusion constants relative to solvent molecule of compound **3** and **4b**.

	3	**4b**
D/D_{CHCl_3} cyclic aggregates	0.095 (±0.006)	0.129 (±0.013)
D/D_{CHCl_3} polymeric aggregates	–	0.0312 (±0.003)

in keto and enol tautomeric forms. Upon increasing the concentration to 260 mM, no signals originating from polymeric aggregates were observed.

Compound **4b**, however, displays different behavior. In the ^{1}H NMR spectrum of this compound, multiple sets of signals are observed at low concentrations, with diffusion constants similar to those to the cyclic dimers of **3**, while above 10 mM, an additional set of peaks from polymeric aggregates is observed, showing a much lower diffusion constant (Table 3).

It has been predicted that equilibria between cyclic and polymeric species consisting of strongly associating bifunctional monomers should display critical concentrations, below which no polymer is present, and above which the concentration of cycles remains constant.[26], [27] Such behavior has indeed been observed by us in bifunctional UPy derivatives.[28] The lowest concentrations at which polymeric species could be observed in the ^{1}H NMR spectra were determined for compounds **3**, **4b**, **5**, and **6**. These critical concentrations are summarized in Table 4. The results show that there is a large influence of spacer structure on the critical concentration. Unfortunately, due to the extremely complex spectrum of **7b**, it was not possible to establish a critical concentration for the most preorganized compound in the series of molecules we have studied.

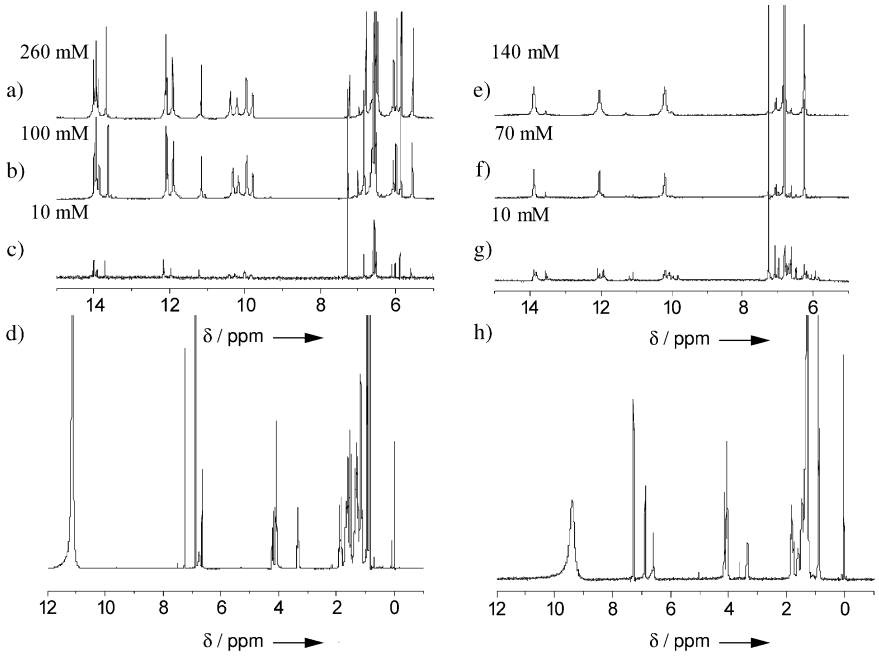


Figure 7. ^{1}H NMR spectra of bifunctional compounds **3** and **4b** in $CDCl_3$ at different concentrations (spectra a – c and e – g, respectively), and spectra after addition of small amounts of TFA (d and h).

We have investigated the chiroptical properties of the chiral bifunctional compounds **3**, **4b**, **5**, **6**, and **7b** by circular dichroism (CD) spectroscopy in chloroform, at concentrations of 1 mM, at which polymeric aggregates were shown by NMR spectroscopy to be absent. None of the compounds showed a Cotton effect, indicating that the cyclic dimers are not highly ordered in this solvent.

solution as a mixture of isomeric cyclic dimers I, II, and III, interconverting slowly on the NMR time scale, and giving rise to a set of four signals for each proton in the molecule.[21] Concentration-dependent ^{1}H NMR studies were performed on compounds **3, 4b, 5**, **6**, and **7b** in order to study the equilibrium between cycles and polymer in chloroform. Spectra of solutions of **3** show four sets of signals. To establish the relative size of the aggregates giving rise to the different sets of signals, NMR diffusion experiments were performed on a 100 mM chloroform solution of **3**. The diffusion constants relative to solvent molecules are similar for all sets of signals (Table 3) and are relatively high, indicating that at this concentration **3** is present as small, cyclic aggregates. From the similarity of the spectrum with that of **1**, we conclude that these cycles are mixtures of isomeric dimers with UPy groups

Aggregation in dodecane: ^{1}H NMR spectra of **2** and of bifunctional compounds **3** – **7** in deuterated dodecane showed

Table 4. Critical polymerization concentrations of compounds **3**, **4b**, **5**, and **6**.

3	**4b**	**5**	**6**
> 260 mM	10 mM	7 mM	30 mM

broad unresolved signals for the alkyl chains and broad signals for the phenyl-pyrimidinone cores of the molecules, indicating the formation of large aggregates in this solvent. When the temperature was increased from 20 °C to 125 °C, the intensities of the signals for the aromatic cores increased and the peaks became sharper.

CD spectra of the chiral compounds **2b**, **3**, **4b**, **5**, **6**, and **7b** were recorded in dodecane in order to examine the degree of order in aggregates of these compounds. A 1 mM solution of monofunctional compound **2b** in dodecane gave no Cotton effect. In the series of bifunctional compounds, Cotton effects at the $\pi-\pi^*$ transition of the phenyl-pyrimidinone moiety were observed in dodecane for compounds **3**, **4b**, and **7b**, while compounds **5** and **6**—with C-7 and C-8 spacers, respectively—each showed no CD signal. Although the CD effects observed are relatively small (see Figure 8a), they are

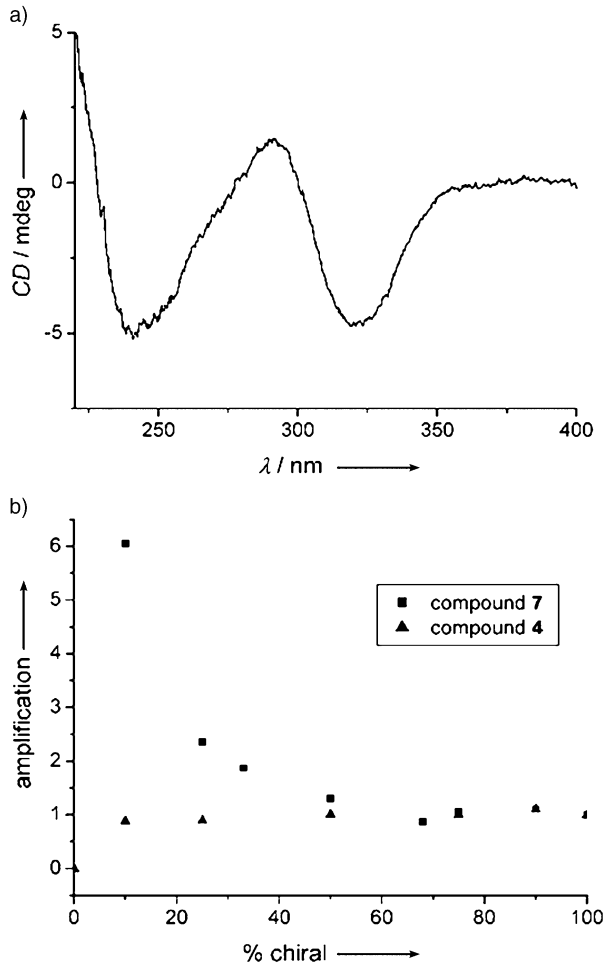


Figure 8. a) CD spectrum of a 1 mM dodecane solution of compound **7b** at −6 °C. b) "Sergeants and soldiers" experiment on mixtures of chiral and achiral compounds at fixed total concentrations of 1 mM in dodecane at −6 °C: (▲) **4a** and **4b**; (■) **7a** and **7b**. The amplification is defined as the normalized CD effect per chiral molecule versus fraction of chiral compound.

reproducible. The cooperativity of the CD effect in mixed solutions of chiral and achiral bifunctional compounds **4a,b** and **7a,b** was studied in a "sergeants and soldiers" type of experiment[29] by varying the relative amounts of chiral and achiral molecules at a constant total concentration of chromophores. The results of these measurements are plotted in Figure 9b as the Cotton effect normalized to the concentration of chiral chromophores. In this way chirality induced in achiral molecules shows up as an amplification larger than 1.

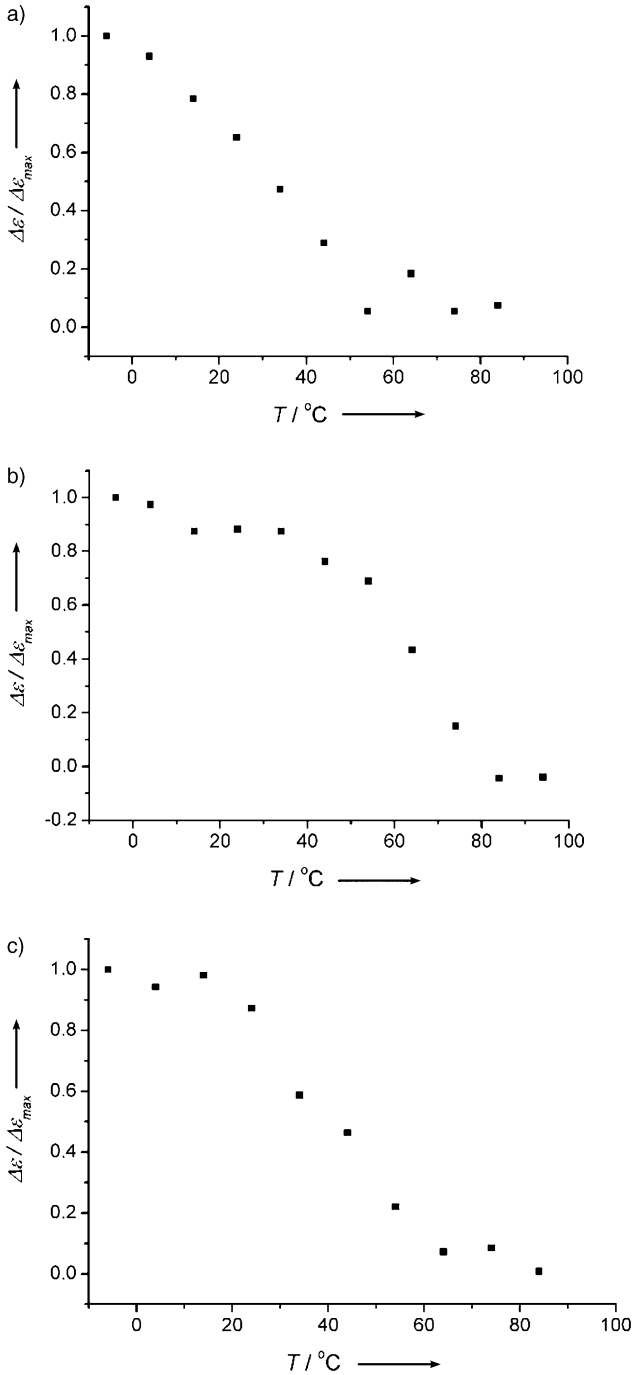


Figure 9. Temperature dependence of the CD effect in spectra of 1 mM solutions of compounds **3** (A), **4b** (B), and **7b** (C) in dodecane. The fraction of the maximum ellipticity remaining is plotted against temperature.

For mixtures of compounds **4**, no amplification of chirality was observed, even when the samples were annealed at 80 °C, or when the mixtures were prepared in $CHCl_3$, followed by

removal of this solvent and redissolution in dodecane. Therefore, only the chiral molecules **4b** contribute to the CD effect in dodecane solution. For compounds **7**, however, strong amplification of chirality was observed. At a fraction of 0.1 of chiral compound **7b**, the CD effect is amplified by a factor of 6. Since a simple model suggests that in cyclic dimers the amplification should not exceed 2 (*see* Supporting Information), this suggests that polymeric aggregates with helical order are present.

Temperature-dependent CD measurements were performed on 1 mM dodecane solutions of **3**, **4b**, and **7b** in order to establish the thermal stabilities of the aggregates (Figure 9). A plot of the molar ellipticities at $\lambda = 325$ nm (normalized against the values at $-6\,^{\circ}C$) versus temperature shows that the chiral order gradually disappears for all three compounds. The temperatures at which half of the CD effect has been lost are different for these compounds, and vary between 25 °C for **3**, 60 °C for **4b**, and 45 °C for compound **7b**.

Discussion and Conclusions

Like its ureido-*s*-triazine analogues[18], ureidopyrimidinone **2b**, provided with a trialkoxyphenyl group, forms liquid-crystalline mesophases in which dimeric units are stacked in columns with hexagonal order. This arrangement of UPy units is compatible with the presence of polymeric chains of bifunctional molecules in the mesophases of bifunctional compounds **3**–**7**, although the possibility that the columns consist of stacks of cyclic dimers in the thermotropic mesophase cannot be ruled out with the knowledge available at present. ^{1}H NMR and CD spectroscopy in $CDCl_3$ and dodecane give valuable information that sheds additional light on the mode of aggregation in solution. The ^{1}H NMR spectra of the UPy derivatives in $CDCl_3$ are much more complex than those of the corresponding triazine derivatives, due to keto–enol tautomerism. However, study of the concentration dependence of the spectra show that compounds **2**–**7** are present as small cyclic aggregates in the millimolar concentration range. A more detailed study of compounds **3** and **4b**, including measurement of the diffusion constants of the different species, shows that **3** is present as cyclic dimer even at 260 mM, while for **4b**, a critical concentration of approximately 10 mM is observed, above which polymeric aggregates are formed.

It is of interest to compare the aggregation behavior of the UPy derivatives with that of the triazine derivative $(C_6\text{-Utr})_2$.[9] The latter compound forms columnar aggregates by stacking of dimerized units induced by solvophobic interactions. Preorganization by spacer moieties is required for a helical stacked arrangement of dimerized UTr units, as no CD effect is observed for the monofunctional triazine. In the chiral monofunctional UPy derivative **2b**, the absence of a Cotton effect both in chloroform and in dodecane shows that the same requirements hold for ureidopyrimidinones. The absence of Cotton effects in cyclic dimers of bifunctional UPy derivatives **3**–**7** in chloroform shows that even when the spacers connecting the two layers enforce a stacked arrangement, there is no bias in the supramolecular chirality. In dodecane, Cotton effects are absent for compound **5** and **6**, which have longer spacers and are therefore less preorganized to form ordered helical polymers. The Cotton effects observed for compounds **3**, **4b**, and **7b**, however, show that highly ordered aggregates with supramolecular chirality are formed. The observed strength of the "sergeants and soldiers" effect in mixtures of **7a** and **7b** demonstrates that in this solvent, chirality may be transferred from **7b** to a large number of achiral molecules **7a**. This makes it improbable that **7** forms stacks of cyclic dimers in dodecane, and we conclude that helical polymeric aggregates are formed instead. A sergeants and soldiers effect is completely absent in dodecane solutions of compounds **4**. As even transfer of chirality in a cyclic dimer would lead to amplification by a factor of 2, it is probable that the formation of mixed aggregates of **4a** and **4b** is thermodynamically unfavorable. Melting experiments, analogous to thermal denaturation experiments performed on double-helical DNA, show that the stabilities of the helical arrangement of **4b** and its direct ureidotriazine analogue are quite similar (60 versus 70 °C).

The reason why **7** forms polymers in dodecane, whereas it forms cyclic dimers in chloroform, is not fully understood by us at the moment. A possible explanation would need to take account of entropic effects, which strongly disfavor polymerization in chloroform, whereas the entropic cost of polymerization in dodecane would be much smaller, because cyclic dimers would already be aggregated into columns by solvophobic interactions. Further study of the structures of the aggregates of **7** in dodecane would of great interest, because a transition from a stack of cyclic dimers to a helical polymer is analogous to the transition between a stack of disks and a polymeric helix in the self-assembly of tobacco mosaic virus (TMV),[30] which is brought about by subtle changes in conditions such as ionic strength or pH.

Experimental Section

General methods: All starting materials were obtained from commercial suppliers and were used as received. All moisture-sensitive reactions were performed under an atmosphere of dry argon. Dry and ethanol-free dichloromethane was obtained by distillation from P_2O_5; dry tetrahydrofuran (THF) was obtained by distillation from Na/K/benzophenone; dimethylformamide was dried over BaO; pyridine was dried by standing over 4 Å molecular sieves; dry toluene was obtained by distillation from Na/K/benzophenone, and triethylamine was dried over potassium hydroxide. Methyl 3,4,5-tridodecyloxybenzoate, methyl 3,4,5-tris((*S*)-3,7-dimethyloctyloxy)benzoate, 3,4,5-tri(dodecyloxy)benzoyl chloride, 3,4,5-tris((*S*)-3,7-dimethyloctyloxy)benzoyl chloride, and ethyl 3,4,5-tri(dodecyloxy)benzoylacetate (**9a**)[13] were synthesized by previously described procedures. Analytical thin layer chromatography was performed on Kieselgel F-254 precoated silica plates. Visualization was accomplished with UV light. Column chromatography was carried out on Merck silica gel 60 (70–230 mesh) or on Merck aluminium oxide 90 (70–230 mesh, activity II–III). ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz 4-nucleus NMR (Varian Mercury Vx) (400.13 MHz for ^{1}H NMR and 100.62 MHz for ^{13}C NMR). Proton chemical shifts are reported in ppm downfield from tetramethylsilane (TMS), and carbon chemical shifts in ppm downfield of TMS, with the resonance of the deuterated solvent as internal standard. Electrospray ionization mass spectrometry (ESI-MS) was carried out on a Perkin–Elmer API 300 MS/MS mass spectrometer. Matrix-assisted laser desorption/ionization mass-time of flight spectra (Maldi-TOF) were obtained by use of indole acrylic acid as the matrix on a PerSeptive

Biosystems Voyager-DE PRO spectrometer. IR spectra were measured on a Perkin–Elmer Spectrum One instrument. Optical properties and melting points were determined with a Jeneval polarization microscope equipped with a Linkam THMS 600 heating device with crossed polarizers. DSC spectra were obtained on a Perkin–Elmer Pyris 1 DSC. X-ray diffraction patterns were recorded with a multiwire area X-1000 coupled with a graphite monochromator.

Wide-angle X-ray diffraction: The X-ray diffraction pattern of an oriented sample of **2a** was recorded with a multiwire area detector X-1000 coupled with a graphite monochromator. The oriented fibers were obtained by shearing on a warm beryllium plate, and were measured by hanging in the beam at the correct focus point. Samples were screened to find suitably large monodomains. Diffraction of **3** was measured on a Bruker AXS D8 Discover, with a GADDS 2D counter.

Ethyl 3,4,5-tris((*S*)-3,7-dimethyloctyloxy)benzoylacetate (9b): Potassium ethyl malonate (**10**, 1.6 g, 9.4 mmol) and ethyl acetate (15 mL) were placed in a 25 mL flask. The mixture was stirred and cooled to 0 °C. Et_3N (2.56 g, 3.5 mL) was added to this mixture, followed by dry $MgCl_2$ (1.17 g, 12.3 mmol). The mixture was heated to 35 °C over 30 min and was then maintained at 35 °C for 6 h. The mixture was cooled to 0 °C, and 3,4,5-tris((*S*)-3,7-dimethyloctyloxy)benzoyl chloride (4.2 g, 6.9 mmol) was added dropwise over 15 min. The mixture was allowed to stir overnight at room temperature and was then cooled to 0 °C before the cautious addition of hydrochloric acid (13%, 20 mL), while the temperature was kept below 25 °C. The aqueous layer was separated and then back-extracted with toluene. The combined organic layers were washed with hydrochloric acid (12%, 2 × 10 mL) followed by H_2O (2 × 10 mL) and $NaHCO_3$ solution (5%, 20 mL), and were then concentrated under vacuum to give the product as a solid (3.9 g, 86%), which was used in the following step without further purification. ^{1}H NMR ($CDCl_3$): $\delta = 7.21$ (s, 2H; Ar–H), 4.24 (q, 2H; O–CH_2–CH_3), 4.06 (m, 6H; O–CH_2), 1.75–1.93 (m, 6H; O–CH_2–CH_2), 1.75–0.9 (multiple peaks, 54H; CH, CH_2, CH_3) ppm.

Potassium monoethyl malonate (10): Diethyl malonate (50 g, 0.312 mol) was dissolved in ethanol (200 mL). A solution of potassium hydroxide (17.5 g, 0.312 mol) in ethanol (200 mL) was added dropwise over one hour. A white precipitate was formed during the addition, and stirring was continued for another 12 h at room temperature after addition of all the hydroxide. The solution was evaporated to dryness, and the sticky residue was then taken up in ether. The salt was collected by suction filtration, washed with ether, and dried under reduced pressure at room temperature, resulting in pure **10** (45.6 g, 86%). ^{1}H NMR ($CDCl_3$): $\delta = 4.06$ (q, 2H; OCH_2), 3.15 (s, 2H; CH_2C=O), 1.12 (t, 3H; CH_3) ppm.

6-[3,4,5-Tri(dodecyloxy)phenyl]isocytosine (11a): A solution of ethyl 3,4,5-tri(dodecyloxy)benzoylacetate (**9a**, 17.6 g, 21.0 mmol) and guanidinium carbonate (4.7 g, 26.25 mmol) in absolute ethanol (200 mL) was boiled and stirred overnight at reflux temperature. The solution was then evaporated to dryness and the residue was dissolved in chloroform (400 mL). The solution was washed with water (300 mL) and the aqueous layer was back-extracted with chloroform (150 mL). The combined organic layers were washed with a saturated sodium chloride solution, dried over sodium sulfate, and filtered. Evaporation gave a white solid that was further purified by column chromatography (eluent: dichloromethane, then 2% ethanol in dichloromethane, and finally 5% ethanol in dichloromethane) (6.04 g, 39%). ^{1}H NMR ($CDCl_3$): $\delta = 12.35$ (br, 1H; NH), 7.13 (s, 2H; Ar–H), 6.19 (s, 1H; alkylidene H), 5.84 (br, 2H; NH_2) 4.02 (m, 6H; O–CH_2), 1.7–1.9 (m, 6H; O–CH_2–CH_2), 1.49 (m, 6H; O-CH_2-CH_2-CH_2), 1.28 (br, 48H; CH_2), 0.89 (t, 9H; CH_3) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 159.7$, 154.1, 153.5, 151.7, 142.4, 123.6, 106.0, 100.4, 72.0, 67.9, 32.0, 30.6, 29.7–29.3, 26.2, 26.0, 22.4, 13.9 ppm; IR: $\tilde{\nu} = 3155$, 1652, 1467, 1120 cm^{-1}; elemental analysis calcd (%) for $C_{46}H_{81}N_3O_4$ (740.35): C 74.63, H 11.03, N 5.70; found: C 74.6, H 10.7, N 5.7.

6-[3,4,5-Tris((*S*)-3,7-dimethyloctyloxy)phenyl]isocytosine (11b): A solution of ethyl 3,4,5-tris((*S*)-3,7-dimethyloctyloxy)benzoylacetate, (**9b**, 3.77 g, 5.71 mmol) and guanidinium carbonate (1.44 g, 8 mmol) in absolute ethanol (100 mL) was boiled and stirred overnight at reflux temperature. The solution was evaporated to dryness and the residue was dissolved in dichloromethane (50 mL). The solution was extracted with water (50 mL) and the water layer was extracted with dichloromethane (40 mL). The combined organic layers were washed with a saturated sodium chloride solution, dried over sodium sulfate, and filtered. Evaporation gave a white solid, which was further purified by column chromatography (eluent: ethyl acetate/hexane 1:3, and then 8% methanol in dichloromethane) (1.68 g, 45%). ^{1}H NMR ($CDCl_3$) $\delta = 12.35$ (br, 1H; C=C–N*H*–C=N), 7.13 (s, 2H; Ph–H), 6.18(s, 1H; *H*–C=C–N), 5.82(br, 2H; N=C–NH_2) 4.07m, 6H; O–CH_2), 1.7–1.9 (m, 6H; O–CH_2–CH_2), 1.7–0.8 (multiple peaks, 51H) ppm; ^{13}C NMR ($CDCl_3$) $\delta = 159.8$, 135.9, 153.5, 151.4, 142.7, 123.6, 105.7, 100.3, 71.9, 67.7, 39.6, 37.8, 37.6, 36.6, 30.1, 28.2, 24.9, 22.9, 22.8, 19.8 ppm; IR(UATR): $\tilde{\nu} = 3148$, 1649, 1120 cm^{-1}; elemental analysis calcd (%) for $C_{40}H_{69}O_4N_3$ (656.01): C 73.37, H 10.60, N 6.41; found: C 73.02, H 10.30, N 6.09.

***N*-Butylaminocarbonyl-6-[3,4,5-tri(dodecyloxy)phenyl]isocytosine (2a)**: A solution of 6-[3,4,5-tri(dodecyloxy)phenyl]isocytosine (**11a**, 1 g, 1.35 mmol) and *n*-butyl isocyanate (0.77 mL, 6.76 mmol) in dry pyridine (7 mL) was boiled and stirred overnight at reflux temperature. The solution was evaporated to dryness and the residue was co-distilled twice with toluene (5 mL). The brown residue was dissolved in chloroform and precipitated in ethanol. Thin layer chromatography showed that the product contained two minor contaminants. These were removed by precipitation from ethyl acetate, resulting in pure **2a** (0.85 g, 75%). ^{1}H NMR ($CDCl_3$): for 4[1*H*]-pyrimidinone tautomer $\delta = 13.90$ (s, 1H; NH), 12.06 (s, 1H; NH), 10.24 (s, 1H; NH), 6.83 (s, 2H; Ar–H), 6.29 (s, 1H; alkylidene H), 4.05 (m, 6H; O–CH_2), 3.29 (m, 2H; NH–CH_2), 1.86 (m, 6H; O–CH_2–CH_2), 1.77 (m, 2H; NH–CH_2–CH_2), 1.65 (m, 2H; NH-CH_2-CH_2-CH_2) 1.50 (m, 6H; O-CH_2-CH_2-CH_2), 1.29 (br, 48H; CH_2), 0.890 (t, 12H; CH_3) ppm; for pyrimidin-4-ol tautomer $\delta = 13.58$ (s, 1H; NH), 11.32 (s, 1H; NH), 10.02 (s, 1H; NH), 7.04 (s, 2H; Ar–H), 6.65 (s, 1H; alkylidene H), 3.43 (m, 2H) ppm, rest of the peaks overlap with peaks of the main tautomer; ^{13}C NMR ($CDCl_3$): $\delta =$ 4[1*H*]-pyrimidinone tautomer 173.6, 156.8, 155.1, 153.8, 149.1, 141.1, 126.0, 104.3, 103.7, 73.7, 69.4, 39.9, 32.0, 31.6, 30.4, 29.8, 29.9–29.4, 26.2, 22.8, 20.3, 14.2, 13.8 ppm; IR(UATR): $\tilde{\nu} = 3226$, 1694, 1120 cm^{-1}; elemental analysis calcd (%) for $C_{51}H_{90}N_4O_5$ (839.29): C 72.99, H 9.50, N 6.70; found: C 72.9; H 9.6; N 6.7.

***N*-Butylaminocarbonyl-6-[3,4,5-tris((*S*)-3,7-dimethyloctyloxy)phenyl]-isocytosine (2b)**: The title compound was synthesized by the same procedure as used for compound **2a** (Y = 43%). ^{1}H NMR ($CDCl_3$): for 4[1*H*]-pyrimidinone tautomer $\delta = 13.93$ (s, 1H; NH), 12.06 (s, 1H; NH), 10.17 (s, 1H; NH), 6.84 (s, 2H; Ar–H), 6.28 (s, 1H; alkylidene H), 4.05 (m, 6H; O–CH_2), 3.30 (m, 2H; NH–CH_2), 1.88–0.95 (m, CH_2), 0.890 (t, 12H; CH_3) ppm; for pyrimidin-4-ol tautomer $\delta = 13.57$ (s, 1H; OH), 11.30 (s, 1H; NH), 10.0 (s, 1H; NH), 7.07 (s, 2H; Ar–H), 6.64 (s, 1H; alkylidene H), 3.43 (m, 2H) ppm, rest of the peaks overlap with peaks of the main tautomer; ^{13}C NMR ($CDCl_3$): $\delta =$ 4[1*H*]-pyrimidinone tautomer 173.4, 156.7, 155.0, 153.8, 149.2, 141.9, 126.0, 104.1, 71.8, 67.7, 39.7–13.8 ppm; IR: $\tilde{\nu} = 3226$, 1694, 1120 cm^{-1}; elemental analysis calcd (%) for $C_{45}H_{78}N_4O_5$ (755.13): C 71.58, H 10.41, N 7.42; found: C 71.6, H 10.5, N 7.4.

***N,N'*-(1,5-Pentamethylene)-bis(2-ureido-6-[3,4,5-tris((*S*)-3,7-dimethyloctyl-oxy)phenyl]-4-pyrimidinone (3)**: Di-*tert*-butyl tricarbonate (0.20 g, 0.77 mmol) was added to a solution of 1,5-pentanediamine (38 μL, 0.32 mmol) in dichloromethane. The solution was allowed to stir for 1 h at room temperature to afford 1,5-pentane diisocyanate. The solution was evaporated to dryness and the residue was dissolved in pyridine (3 mL). 6-[3,4,5-Tris((*S*)-3,7-dimethyloctyloxy)phenyl]isocytosine (**11b**, 0.5 g, 0.76 mmol) was added to this solution, which was stirred at 90 °C for 12 h. The solution was evaporated to dryness and the residue was co-evaporated twice with toluene (2 mL). The orange/white residue was dissolved in chloroform and precipitated in ethyl acetate. The impure product was further purified by column chromatography (eluent: 2% tetrahydrofuran in chloroform, then hexane/chloroform 1:1) and precipitation in methanol, resulting in pure **3** (0.14 g, 30%). ^{1}H NMR ($CDCl_3$ + TFA): $\delta = 6.87$ (s, 4H; Ar–H), 6.64 (s, 2H; alkylidene H), 4.19 (m, 4H; O–CH_2), 4.09 (m, 8H; O–CH_2), 3.37 (m, 4H; NH–CH_2), 1.87 (m, 12H; O–CH_2–CH_2), 1.67 (m, 4H; NH–CH_2–CH_2), 1.66–0.86 (multiple peaks, 104H; CH_2, CH_3) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 173.2$, 157.5, 155.3, 153.8, 148.6, 140.9, 132.12, 126.3, 103.9, 71.9, 67.8, 39.6, 39.5, 37.8, 37.5, 36.5, 30.2, 29.9, 28.2, 25.0, 23.0, 22.0, 19.7 ppm; IR(UATR): $\tilde{\nu} = 3222$, 1694, 1114 cm^{-1}; MALDI-TOF-MS: (1465.13) *m/z*: 1466 $[M]^+$, 1489.16 $[M+Na]^+$; elemental analysis calcd (%) for $C_{87}H_{148}N_8O_{10}$ (1466.17): C 71.27, H 10.17, N 7.64; found: C 71.58; H 9.80; N 7.39.

***N,N'*-(1,6-Hexamethylene)-bis(2-ureido-6-[3,4,5-tri(dodecyloxy)phenyl]-4-pyrimidinone (4a)**: A suspension of 6-[3,4,5-tri(dodecyloxy)phenyl]isocytosine **11b** (4 g, 5.4 mmol) in dry pyridine (12 mL) and toluene (2 mL)

was heated to reflux temperature. A clear solution was obtained and some solvent was distilled off to remove traces of water. After the mixture had cooled down to room temperature, 1,6-hexane diisocyanate (0.36 mL, 2.16 mmol) was added by syringe and the solution was stirred overnight at reflux. The solution was evaporated to dryness and the residue was co-distilled twice with toluene (5 mL). The brown residue was dissolved in chloroform and precipitated in ethanol. Minor contamination was removed by precipitation in ethyl acetate resulting in pure **4a** (2.11 g, 59 %). ^{1}H NMR ($CDCl_3$ + TFA) $\delta = 6.91$ (s, 4H; Ar−H), 6.37 (s, 2H; alkylidene H), 4.04 (m, 12H; O−CH_2), 3.32 (m, 4H; NH−CH_2), 3.17, 1.81 (m, 12H; O−CH_2−CH_2, 1.75 (m, 4H; NH−CH_2−CH_2), 1.60 (m, 4H; NH-CH_2-CH_2-CH_2), 1.47 (m, 12H; O-CH_2-CH_2-CH_2), 1.26 (br, 96H; CH_2), 0.88 (t, 18H; CH_3) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 173.3$, 156.9, 155.3, 153.8, 149.5, 140.9, 126.0, 104.5, 103.8, 73.4, 69.3, 40.1, 32.1, 31.6, 30.5, 30.0, 29.9 – 29.4, 26.4, 22.5, 20.4, 14.2, 13.8 ppm; IR(UATR): $\tilde{\nu} = 3226$, 1693, 1117 cm^{-1}; elemental analysis calcd (%) for $C_{100}H_{174}N_8O_{10}$ (1648.52): C 72.86, H 10.64, N 6.80; found: C 72.54, H 9.98, N 6.71.

***N,N′*-(1,6-Hexamethylene)-bis(2-ureido-6-[3,4,5-tris((*S*)-3,7-dimethyloctyloxy)phenyl]-4-pyrimidinone (4b)**: A suspension of 6-[3,4,5-tris((*S*)-3,7-dimethyloctyloxy)phenyl]isocytosine (**11b**, 0.5 g, 0.76 mmol) in dry pyridine (4 mL) and toluene (1 mL) was heated to reflux temperature. A clear solution was obtained, and some solvent was distilled of to remove traces of water. After the mixture had cooled, 1,6-hexane diisocyanate (0.05 mL, 0.3 mmol) was added by syringe. A trace of DMAP was also added. The solution was stirred at 90 °C for 12 h. The reaction mixture was evaporated to dryness and the residue was co-evaporated twice with toluene (2 mL). The red residue was dissolved in chloroform and precipitated in methanol, ethanol, and ethyl acetate. Further purification by column chromatography (eluent: 6 % tetrahydrofuran in chloroform) and precipitation in methanol resulted in pure **4b** (0.12 g, 27 %). ^{1}H NMR ($CDCl_3$ + TFA): $\delta = 6.91$ (s, 4H; Ar−H), 6.48 (s, 2H; alkylidene H), 4.09 (m, 12H; O−CH_2), 3.33 (m, 4H; NH−CH_2), 1.87 (m, 12H; O−CH_2−CH_2), 1.71 (m, 4H; NH−CH_2−CH_2), 1.66 – 0.86 (multiple peaks, 106H; CH_2, CH_3) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 173.1$, 157.0, 155.2, 153.4, 148.2, 140.9, 126.3, 103.7, 71.5, 67.8, 39.6, 39.5, 37.8, 37.5, 36.5, 30.2, 29.9, 28.2, 25.0, 23.0, 22.0, 19.7 ppm; IR(UATR): $\tilde{\nu} = 3226$, 1692, 1115 cm^{-1}; MALDI-TOF-MS: (1479.14) *m/z*: 1480.04 $[M]^+$, 1503.01 $[M+Na]^+$; elemental analysis calcd (%) for $C_{88}H_{150}N_8O_{10}$ (1480.20): C 71.41, H 10.21, N 7.57; found: C 71.05, H 9.92, N 7.52.

***N,N′*-(1,7-Heptamethylene)-bis(2-ureido-6-[3,4,5-tris((*S*)-3,7-dimethyloctyloxy)phenyl]-4-pyrimidinone (5)**: The title compound was synthesized from 1,7-diisocyanatoheptane in the same way as compound **4**. Purification was performed by column chromatography (eluent: 2 % tetrahydrofuran in chloroform) and precipitation in methanol, resulting in pure **5** (Y = 29 %). ^{1}H NMR ($CDCl_3$ + TFA): $\delta = 6.88$ (s, 4H; Ar−H), 6.62 (s, 2H; alkylidene H), 4.19 (m, 4H; O−CH_2), 4.09 (m, 8H; O−CH_2), 3.33 (m, 4H; NH−CH_2), 1.87 (m, 12H; O−CH_2−CH_2), 1.68 (m, 4H; NH−CH_2−CH_2), 1.66 – 0.86 (multiple peaks, 108H; CH_2, CH_3) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 171.6$, 157.5, 155.3, 153.8, 148.6, 140.9, 132.1, 126.3, 103.9, 71.8, 67.8, 39.5, 37.6, 37.4, 36.5, 36.4, 30.0, 28.1, 24.8, 22.8, 22.6, 19.6 ppm; IR(UATR): $\tilde{\nu} = 3222$, 1694, 1114 cm^{-1}; MALDI-TOF-MS: (1493.16) *m/z*: 1494.22 $[M]^+$, 1517.19 $[M+Na]^+$; elemental analysis calcd (%) for $C_{89}H_{152}N_8O_{10}$ (1494.23): C 71.50, H 10.25, N 7.50; found: C 71.35, H 10.00, N 7.42.

***N,N′*-(1,8-Octamethylene)-bis(2-ureido-6-[3,4,5-tris((*S*)-3,7-dimethyloctyloxy)phenyl]-4-pyrimidinone (6)**: This compound was synthesized from 1,8-diisocyanatooctane by the procedure used for compound **3**. Purification was carried out by column chromatography (eluent: 2 % tetrahydrofuran in chloroform) and precipitation in methanol, resulting in pure **6** (Y = 28 %). ^{1}H NMR ($CDCl_3$ + TFA): $\delta = 6.88$ (s, 4H; Ar−H), 6.57 (s, 2H; alkylidene H), 4.08 (m, 12H; O−CH_2), 3.32 (m, 4H; NH−CH_2), 1.87 (m, 12H; O−CH_2−CH_2), 1.69 (m, 4H; NH−CH_2−CH_2), 1.66 – 0.86 (multiple peaks, 110H; CH_2, CH_3) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 173.0$, 157.8, 155.2, 153.8, 149.0, 141.5, 132.1, 126.3, 104.5, 72.3, 69.5, 39.4, 39.3, 37.4, 37.1, 36.3, 29.8, 29.7, 28.0, 24.8, 22.7, 22.6, 19.5 ppm; IR(UATR): $\tilde{\nu} = 3226$, 1692, 1115 cm^{-1}; MALDI-TOF-MS: (1507.18) *m/z*: 1508.18 $[M]^+$, 1530.16 $[M+Na]^+$; elemental analysis calcd (%) for $C_{90}H_{154}N_8O_{10}$ (1508.25): C 71.67, H 10.29, N 7.43; found: C 71.71, H 10.09, N 7.35.

***N*$^{\omega}$,*N*$^{\omega'}$-*m*-Xylylene-bis(2-ureido-6-[3,4,5-tri(dodecyloxy)phenyl]-4-pyrimidinone (7a)**: The title compound was obtained from *m*-xylylene diisocyanate in the same way as **3**. Column chromatography (flash silica, methanol/tetrahydrofuran/chloroform 2:4:94) gave pure **7a** (Y = 36 %). ^{1}H NMR ($CDCl_3$ + TFA): $\delta = 7.30$ (s, 2H; *m*-Ph−H), 7.10, 6.89 (s, 4H; Ar−H), 6.61 (s, 2H; alkylidene H), 4.52 (d, 4H; NH−CH_2), 4.15 (t, 4H; OCH_2), 4.06 (t, 8H; OCH_2), 1.81 (m, 12H; OCH_2−CH_2), 1.49 (m, 12H; OCH_2−CH_2−CH_2), 1.29 (br, 96H; CH_2, CH_3), 0.90 (t, 18H; CH_3) ppm; IR(UATR): $\tilde{\nu} = 3226$, 1695, 1117 cm^{-1}; elemental analysis calcd (%) for $C_{102}H_{170}N_8O_{10}$ (1668.51): C 73.43, H 10.27, N 6.72; found: C 72.54, H 9.87, N 6.71.

***N*$^{\omega}$,*N*$^{\omega'}$-*m*-Xylylene-bis(2-ureido-6-[3,4,5-tris((*S*)-3,7-dimethyloctyloxy)-phenyl]-4-pyrimidinone (7b)**: For the synthesis of the title compound see the procedure for compound **3**. Tetrahydrofuran in chloroform (2 %) was used as an eluent for column chromatography, and precipitation in methanol gave pure **7b** (Y = 14 %). ^{1}H NMR ($CDCl_3$ + TFA): $\delta = 7.34$ (s, 2H; *m*-Ph−H), 7.10, 6.87 (s, 4H; Ar−H), 6.62 (s, 2H; alkylidene H), 4.50 (m, 4H; NH−CH_2), 4.13 (m, 4H; O−CH_2 intra), 4.08 (m, 8H; O−CH_2), 1.86 (m, 12H; O−CH_2−CH_2, 1.68 – 0.86 (multiple peaks, 102H; CH_2, CH_3) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 173.2$, 157.6, 155.1, 153.8, 153.5, 148.6, 139.1, 125.4, 125.1, 124.6, 105.0, 103.6, 71.9, 67.6, 39.6, 38.4, 37.8, 37.7, 36.5, 31.5, 30.1, 29.9, 28.2. 25.0, 22.9, 19.7 ppm; IR(UATR): $\tilde{\nu} = 3226$, 1692, 1115 cm^{-1}; MALDI-TOF-MS: (MW = 1499.11) *m/z*: 1500.15 $[M]^+$, 1523.13 $[M+Na]^+$; elemental analysis calcd (%) for $C_{90}H_{146}N_8O_{10}$ (1500.19): C 72.06, H 9.81, N 7.47; found: C 71.65, H 9.97, N 7.17.

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