Expanding the Scope of Metastable Species in Hydrogen Bonding-
Directed Supramolecular Polymerization

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Nucleation-Elongation Model for cooperative supramolecular Polymerizations

The equilibrium between the monomeric and supramolecular polymer species can be described in a cooperative process with the Nucleation-Elongation model which was developed by Ten Eikelder, Markvoort and Meijer. This model is used to describe the aggregation of 1 which exhibits a non-sigmoidal cooling curve as shown in temperature-dependent UV/Vis experiments. The model extends nucleation-elongation based equilibrium models for growth of supramolecular homopolymers to the case of two monomer and aggregate types and can be applied to symmetric supramolecular copolymerizations, as well as to the more general case of nonsymmetric supramolecular copolymerizations.

In a cooperative process, the polymerization occurs via two steps: a nucleation step, where a nucleus, which is assumed to have a size of two molecules, is formed and a following elongation step. The values $T_e$, $\Delta H_{nucl}$, $\Delta H^*$ and $\Delta S^*$ can be found by a non-linear least-squares analysis of the experimental cooling curves. The equilibrium constants associated with the nucleation and elongation phases can be calculated using the following equations:

- **Nucleation step:**
  $$K_{nucl} = e^{-\frac{(\Delta H_{nucl} - \Delta H^* - T_e \Delta S^*)}{RT}}$$

- **Elongation step:**
  $$K_e = e^{-\frac{\Delta H^* - T_e \Delta S^*}{RT}}$$

Furthermore, the cooperativity factor ($\sigma$) is given by:

$$\sigma = \frac{K_{nucl}}{K_e} = e^{\frac{\Delta H_{nucl} - \Delta H^*}{RT}}$$

Figure S1. a) Plot of the absorbance ($\lambda = 290$ nm) against temperature obtained upon cooling a hot solution of 1 at a rate of 0.1 Kmin$^{-1}$. b) Magnification of the area in the red box in (a), showing the slight, linear increase of absorbance in the high-temperature regime (process A in Fig. 2a). c) Aggregation plots and cooperative curves obtained by the nucleation-elongation fit applied to the data shown in (a).

| $c$ [µM] | $\Delta H^*$ [kJmol$^{-1}$] | $\Delta S^*$ [JK$^{-1}$mol$^{-1}$] | $T_e$ [K] | $\Delta G_{298K}$ [kJmol$^{-1}$] | $K_{nucl}$ $^{\dagger}$ | $K_e$ $^{\dagger}$ | $\sigma$ $^{\dagger}$ |
|---------|-----------------|-----------------|---------|---------------------|-----------------|-----------------|---------|
| 20-60   | -126.4          | -350.6          | -16.8   | 286.9 (20 µM)       | 5.00 $\times$ 10$^4$ | 4.43 $\times$ 10$^2$ | 8.86 $\times$ 10$^4$ |
|         |                 |                 |         | 290.7 (40 µM)       | 2.50 $\times$ 10$^4$ | 2.43 $\times$ 10$^2$ | 9.72 $\times$ 10$^4$ |
|         |                 |                 |         | 293.0 (60 µM)       | 1.67 $\times$ 10$^4$ | 1.71 $\times$ 10$^2$ | 1.03 $\times$ 10$^3$ |

$^{\dagger}$ in µM; $^{\ddagger}$ in kJmol$^{-1}$; $^{\S}$ in JK$^{-1}$mol$^{-1}$; $^{\dagger}$ in K, $^{\ddagger}$ in M; the value in parentheses correspond to the utilized concentration.

Due to the fact that even at the slowest possible cooling rate (0.1 Kmin$^{-1}$), still a pronounced thermal hysteresis is observed between cooling and heating curves, a bias of the cooling curves through kinetic effects has to be assumed. Therefore, we assume that the thermodynamic parameters derived from the cooperative nucleation-elongation model do not precisely describe the energetics of the system. As the elongation temperature shifts to higher temperatures, at slower cooling rates, i.e. at conditions which exhibit a higher degree of thermodynamic control, we assume that the values of $\Delta H$ and $\Delta G$ are overestimated under the given conditions and the actual values are expected to be lower.
Figure S2. Comparison of the UV/Vis spectra of 1 (a) and ref-1 (b) in different solvents (c = 20 µM, T = 298 K).

Figure S3. AFM images and height profile analyses of supramolecular polymers of 1 on drop-casted onto HOPG. a) Gel state (c = 2 mM), b) gel diluted with MCH, c) fibers formed after equilibration of a rapidly cooled solution (368 K to 278 K, c = 40 µM), d) fibers in a diluted solution of the one used for (c) (c = 20 µM). The height of a single fiber determined in c) and d) was ~5 nm.
The images demonstrate that both compounds form the same fibrous aggregates with a strong tendency to form macroscopic, clustered bundles.

Applying a slower cooling rate shifts $T_c$ towards higher temperatures, which is typical for systems with an intermediate kinetic species. Even at the slowest cooling rate ($0.1$ Kmin$^{-1}$), a pronounced thermal hysteresis is observed between cooling (royal blue) and heating cycle (red, $1$ Kmin$^{-1}$). Note that the kink at about $40^\circ$C in the heating curve is an artifact and does not originate from the self-assembly.
Figure S6. Kinetic profiles of aggregate formation of ref-1 over time ($\lambda = 296$ nm) after rapidly cooling a hot monomer solution at different concentrations (a) and different temperatures (b).

Figure S7. Morphologic analysis of the kinetic experiments of 1. Top panel: SEM (a), AFM (b,c) and DLS (d) studies during the initial lag phase in which the metastable species is present. Bottom panel: SEM (e), AFM (f) and DLS (g,h) studies of the equilibrated solutions at the endpoint of the kinetic experiments ($c = 20 \, \mu M, T = 298$ K, samples were drop-casted onto the substrate, HOPG for AFM, silicon-wafer for SEM).

The structures visualized in the imaging studies in the metastable regime (a,b) clearly lack any order and thus arise from surface and solvent evaporation effects upon drying of the solution of the metastable species on HOPG. The undefined correlation function obtained from the corresponding solution in the metastable regime (d) cannot be fitted adequately to give a size distribution, whereas the one obtained after aggregate formation yields a size distribution which agrees with the formation of large, clustered nanostructures (g+h).
Figure S8. a) Fluorescence emission spectra of 1: monomer in CHCl$_3$ (red), metastable species in a freshly quenched solution (pink, $c = 20 \mu$M, $\lambda_{exc} = 292$ nm), metastable species after ageing of the quenched solution (purple, $c = 20 \mu$M, $\lambda_{exc} = 292$ nm) and of an aggregated solution in MCH (royal blue, $c = 1$ mM, $\lambda_{exc} = 292$ nm). b) VT-emission spectra of 1, obtained at a rate of 0.1 Kmin$^{-1}$ ($c = 1$ mM, $\lambda_{exc} = 296$ nm, corresponds to transformation of the metastable species to the aggregates). c) Fluorescence emission spectra of ref-1: monomer in CHCl$_3$ (red, $c = 20 \mu$M, $\lambda_{exc} = 296$ nm), and of an aggregated solution in MCH (royal blue, $c = 1$ mM, $\lambda_{exc} = 296$ nm). d) VT-emission spectra of ref-1, obtained at a rate of 0.1 Kmin$^{-1}$ ($c = 1$ mM, $\lambda_{exc} = 296$ nm, corresponds to transformation of the metastable species to the aggregates).

In the freshly quenched solution, apart from the broad emission around 450 nm (metastable species), the emission characteristics of the monomer are still observed ($\lambda_{max} \sim 350$ nm). Ageing this solution overnight (yet no polymers are formed) results in a decreased emission intensity in the monomer region and a slightly increased intensity of the band of the metastable species. Consequently, besides the metastable monomer, a second metastable species seems to be present, which has the same emission characteristics as the aggregated state. The VT-studies at high concentration do not show any signs of the monomer emission, indicating that the observed spectral changes correspond to the transition from the metastable regime to the aggregated state.
Figure S9. Spectra of the filtration experiment of 1 (initial concentration of c = 40 µM prior to filtration, T = 298 K). a) UV/Vis absorption spectra (purple: solution of the metastable species, blue: solution of the aggregates, red: spectrum of 1 in the monomer state in MCH at 95 °C as a reference for the absorbance values, which are neither affected by aggregation/dimerization nor filtration). b) Normalized UV/Vis absorption spectra of both solutions (dimers and aggregates) after filtration. c) Emission spectra of the metastable species (λexc = 292 nm). d) Emission spectra of the solution of the aggregates (λexc = 292 nm).

For the experiment, a solution of 1 in the aggregated state and in the metastable regime (five minutes after thermal quenching from 368 K to 298 K) was characterized before and after filtration through a syringe filter with 0.2 µm pore size.

The solution containing the metastable species shows only minor changes during filtration, both in the absorption and emission studies. Thus, the metastable species passes through the filter unaffected. In contrast, the non-normalized absorption spectrum of the solution containing aggregate fibers (blue in (a)) changes upon filtration: before filtration, the shape of the band is less defined, and a shoulder is observed at higher wavelengths. After filtration, the absorption band is more finely structured, with sharper maxima, similar to the spectra of metastable species. Furthermore, the low-energy shoulder is no longer present, indicating a removal of the aggregates. Also, the absorbance of the solution containing the aggregates is significantly diminished after filtration (dashed blue in (a)) when compared to the solution containing the metastable dimers after filtration (dashed purple in (a)) and/or compared to the reference spectra of an unfiltered monomer solution (dashed red in (a)). Note that the absorbance of a solution is also diminished upon aggregation (hypochromicity, solid blue in (a) see also Fig. 2a). Therefore, comparison of the absorbance of the aggregate solution after filtration with those of monomers and/or dimers should be made, rather than comparing the absorbance of the same solution before and after filtration.

Comparison of the normalized absorption spectra after filtration shows that in both cases the same (metastable) species is present. This could in part be due to the fact that a small portion of the metastable species coexists in the original aggregate solutions and passes through the filter. It is also possible that a small portion of the aggregates are fragmented and converted to the metastable species during filtration. However, it is not the case that all aggregates are fragmented into the smaller, metastable structures during filtration, since the absorbance of the aggregate solution after filtration is lower than that of the metastable species, even though the concentration of both solutions was identical before filtration. Since the filtered solutions exhibit the same emission profiles as an aggregate solution in the gel state, the experiment suggests that the metastable species exhibits similar exciton coupling to the aggregates but does not form elongated polymers.
Figure S10. a) VT-$^1$H NMR of 1 in CDCl$_3$ showing the development of the aromatic resonances upon decreasing the temperature from 55 °C to 5 °C ($c = 2$ mM). b) Corresponding UV/Vis spectra ($c = 2$ mM) and illustration of the pseudo-cyclic formation driven by intramolecular H-bonding. c) VT-fluorescence emission spectra in CHCl$_3$ and corresponding VT-UV/Vis absorption spectra (d) at low concentrations ($c = 40$ µM, $\lambda_{exc.} = 292$ nm). e) $^1$H NMR dilution experiments of 1 in CDCl$_3$ ($c = 2$ mM to $c = 0.25$ mM, $T = 298$ K), showing a negligible shift of the amide resonances ($\Delta \delta = 0.02$ ppm). f) Corresponding FTIR spectra in the carbonyl region of the solutions used in (e).

In the VT-experiments, only the resonances of the amide protons are shifted to lower fields, whereas all other resonances are unaffected, indicating that the direct chemical environment of only these protons is affected by the changes in temperature. This behavior is characteristic for the formation of seven-membered pseudo-cycles through intramolecular H-bonding,[2] which are in equilibrium with the extended open conformation (without H-bonds). The shift of the N-H resonance to higher fields is in accordance with a shift of the equilibrium between H-bonded and non-H-bonded conformation towards the latter. In contrast, upon dilution of the monomer solution in CDCl$_3$ (e), only a negligible shift of the amide resonances is observed. This agrees with the intramolecular H-bonds being stable towards dilution/the equilibrium between open and pseudo-cyclic monomer conformers being virtually unaffected by concentration. The corresponding FTIR spectra (f) furthermore show that wavenumber of the amide I carbonyl stretching is unaffected and that despite the equilibrium between open and pseudo-cyclic conformers, only a single band is observed. The emission and absorption spectra recorded at low concentration (c,d) demonstrate that the same process occurs at low concentrations.
Figure S11. VT-$^1$H NMR of ref-1 in CDCl$_3$ showing the development of the aromatic resonances upon decreasing the temperature from 55 °C to 5 °C (c = 2 mM).

b) Corresponding UV/Vis spectra (c = 2 mM) and illustration of the pseudo-cycle formation driven by intramolecular H-bonding.

c) $^1$H NMR dilution experiments of ref-1 in CDCl$_3$ (c = 2 mM to c = 0.25 mM, T = 298 K), showing a negligible shift of the amide resonances ($\Delta \delta = 0.02$ - 0.03 ppm)
Figure S12. Packing mode studies of 1 (c ~ 2 mM, T = 298 K). a) UV/Vis spectra of the solutions used for the $^1$H NMR studies at different CDCl$_3$:MCH$_{d14}$ ratios in Fig. 3a. b) Corresponding FTIR spectra in the N-H stretching region of those solutions, in which monomers (100 % CDCl$_3$, red), metastable dimers (20 % CDCl$_3$, 80 % MCH, cyan) and SPs (100 % MCH, blue), respectively, are the dominant species. c) Corresponding emission spectra upon decreasing the CHCl$_3$:MCH$_{d14}$ ratio ($\lambda_{exc.} = 292$ nm). d) Plot of the emission intensities of monomers (345 nm) and dimers/SPs (456 nm) against MCH volume fraction, extracted from the spectra in (c).

The absorption spectra corroborate that no SPs are formed up to a fraction of 80 % MCH$_{d14}$. At higher MCH volume fractions, polymerization occurs, as also indicated in the strong signal broadening in the NMR studies in Fig. 3a.

The FTIR spectra in the region of the amide N-H stretching gave further insights into the H-bonding properties in regimes ①, ② and ③: In pure chloroform (→ monomer solutions), a sharp band at 3453 cm$^{-1}$ and a broad band at 3348 cm$^{-1}$, which are characteristic for the equilibrium between open (free N-H: ~3450 – 3460 cm$^{-1}$) and pseudo-cyclic (intramolecularly H-bonded, ~3300 – 3350 cm$^{-1}$) conformers can be appreciated.[3] At 80 % MCH, just before SP is initiated, metastable dimers should be the dominant species in the solution. In this solution, the band corresponding to intramolecular H-bonding dominates and a shoulder at lower wavenumbers is observed. This shoulder appears in the region where typically the N-H stretching of secondary amides involved in intermolecular H-bonds appear. This matches with the proposed concomitant intra- and intermolecular H-bonds in the metastable dimers. Notably, a band of minor intensity corresponding to the free monomers is also observed, reflecting the dynamic equilibria between the different supramolecular species in solution, prior to polymerization. However, the minor intensity when compared to the band of the intramolecular H-bonded N-H, indicates that the dimers are indeed the dominant species. The solution in pure MCH, which should exclusively contain aggregated SPs, exhibits a single band at 3278 cm$^{-1}$, diagnostic of strong intramolecular H-bonds, in agreement with the formation of arrays of extended intermolecular H-bonds in the SPs.

In the emission studies, the initial solutions with a high excess of chloroform exhibit a pronounced monomer band ($\lambda$ ~ 350 nm). Upon increasing the volume fraction of MCH, this band is gradually diminished and a weak emission at ~450 nm arises, which is ascribed to the metastable dimers. The occurrence of both monomer and dimer emission indicates that both species are in equilibrium in the solutions. At high MCH contents, the intensity of the emission at ~450 nm suddenly starts to increase drastically, whereas the monomer emission band is depleted, diagnostic of the formation of elongated SPs. The fact that the transition from the monomer to SP emission does not exhibit isosbestic points further underlines that polymerization does not occur directly from the monomer to the SP, supporting the intermediate formation of metastable dimers.
Figure S13. a) $^1$H NMR studies of ref-1 upon stepwise increasing the volume fraction of MCH-d$_{14}$, starting from 100 % CDCl$_3$ ($T = 298$ K, $c = 2$ mM). Corresponding UV/Vis (b) and FTIR spectra in the carbonyl stretching region (c). d) Schematic illustration of the multi-step polymerization mechanism.
No signal broadening is observed in (a). The resonances shift linearly with temperature, but the changes are rather small. This suggests the existence of a small supramolecular species, which we suggest to be the metastable dimers.
SUPPORTING INFORMATION

Figure S15. VT-1H NMR of 1 in a mixture of MCH-d_{14}:CDCl_{3} 7:3 showing the development of the aromatic resonances upon decreasing the temperature (c = 2 mM). Corresponding UV/Vis (b) and emission spectra (c, \lambda_{exc} = 292 nm). d) Plot of emission intensity vs. T monitored at 450 nm.

The self-assembly of 1 in pure MCH was also studied in VT-NMR experiments (c = 2 mM). Due to the increase in concentration by one to two orders of magnitude when compared to many studies shown in the main text, UV/Vis absorption and emission studies were recorded in parallel to correlate the occurring processes. At high temperatures, the well resolved proton resonances and the absorption spectra indicate that small, discrete, non-polymeric species are present under the given conditions. The emission spectra on the other hand, do not show signs of the monomer emission at high temperatures. Instead, a low-intensity emission centered around 450 nm, which has previously been ascribed to the metastable dimers, is observed (see also studies in Fig. S12). These metastable dimers were further characterized by DOSY NMR under the same conditions (main text Fig. 3c). When the temperature of the solution is lowered, initially the NMR resonances remain sharp, albeit the chemical shift of some protons changes gradually, especially the amide resonances. Absorption and emission studies do not yet exhibit any significant changes, which is also reflected in the plateau between 90 – 30 °C in the secondary plot of emission intensity at 450 nm vs. temperature (d). Hence, no elongation of the SPs occurs yet and short, discrete structures, likely dimers and possibly short oligomers, are present in the solution. After surpassing the critical temperature of ~30 °C drastic changes take place in all three spectroscopic measurements: The emission band at 450 rapidly grows, the absorption spectra experience a hypsochromic shift and a diminishing intensity and the NMR resonances suddenly broaden, to the point that they can no longer be distinguished from the baseline. The combined experimental findings match well with the elongation of the SPs from the dimers in a cooperative process, as also reflected in the non-sigmoidal shape of the aggregation-curve derived from the emission studies.

Analogous observations are made in the VT-UV/Vis absorption and NMR studies for the SP of ref-1 (Figure S16).
Figure S16. a) VT-^1^H NMR of ref-1 in pure MCH-d_{14} showing the development of the aromatic resonances upon decreasing the temperature (c = 2 mM). b) VT-UV/Vis spectra under identical conditions as in (a).
The small difference in length between the open and closed monomer conformation is not detected. Possibly this is also due to the fact that at both temperatures both species exist in equilibrium and only the relative population of the two states is shifted. In MCH at high temperature, where VT-NMR (Figure S13b) could be related to the presence of the metastable dimers, the calculated Stokes radius is within the same order of magnitude as in the monomer state, corroborating the similar size regime of the structures found in the metastable (i.e., dimer) and monomer regime. Considering that the calculation of the Stokes radius assumes a spherical particle, the relative sizes should be considered rather than the exact values. The comparison of the sizes determined for dimer and open/closed monomer based on the DOSY experiments supports the absence of large elongated polymers in and thus reasonably supports dimer formation.4

Figure S17. a-c) DOSY-NMR spectra and extracted Diffusion coefficients + Stokes radii (c = 2 mM) of 1 at different stages of the self-assembly. d-f) Corresponding species present in the analyzed solutions.

Figure S18. Seed-induced SP of 1. a) AFM image of polymer seeds of 1 (obtained through sonication of SPs for 30 min, drop-casted onto HOPG). b) Corresponding size distribution (based on the manual length analysis of 50 seeds). c) Development of the absorbance (λ = 292 nm) upon abrupt cooling of a hot monomer solution and subsequent seeding of the formed metastable dimers. d) Elongated polymer fibers formed after seeding with a seed/metastable dimer ratio of 1:10 (c = 20 µM, T = 298 K, drop-casted onto HOPG).
Figure S19. AFM images showing the LSP of 1 through controlling the [metastable]:[seed] ratio. a-d) Height images. e-h) Corresponding phase images. The red bars highlight the length of one of the clearly distinguishable fibers that was used for length analyses and determination of size distributions. i-l) Corresponding size distributions (based on the manual length analysis of 25 (i,j), 20 (k), or 10 (l) fibers). m) Plot of fiber length against the [metastable]:[seed] ratio and linear fit. Solution conditions prior to drop-casting the samples onto HOPG: $c = 20 \mu M$, $T = 298 K$; ratios [seed]:[metastable]: a,e) 1:1, b,f) 1:2, c,g) 1:5, d,h) 1:10.

Note: The cuvettes used for some of these experiments were bought shortly before these studies were performed. Despite cleaning/rinsing the cuvettes several times, cuvettes from this specific commercial supplier continuously release some nanosized glass-particles, especially during the first weeks of usage. These nanoscopic glass particles most probably originate from the joints for the cuvette caps, where the glass was cut and polished. We have observed this with several batches of those cuvettes. Nevertheless, the particles do not have any effect on the SSP behavior. This is clearly visible from the lack of polymer growth at the particles, which are unaltered in size and shape in each of the images (a)-(c) as well as the phase images (e)-(g). This LSP experiment with different [feedstock]:[seed] ratios was performed using four different cuvettes in parallel (one for each ratio), in order to have exactly the same timely evolution for all solutions and thus be able to attribute any differences in size only to the different ratios. This explains, why not all images contain the glass particles: whereas the solutions for the ratios 1:1, 1:2 and 1:5 were apparently prepared in new cuvettes, the cuvette used for the 1:10 ratio must have been from another batch bought a longer time ago.
Figure S20. AFM images showing the LSP of 1 upon repeated cycles of adding metastable dimers to an invariant amount of SP seeds. a-d) AFM images recorded after completion of each cycle. e-h) Magnifications of the areas labelled in a-d. a+i) Seeds, f+j) cycle I, g+k) cycle II, h+l) cycle III. (c = 20 µM, T = 298 K, drop-casted onto HOPG).

In repeated cycle of adding 1 in the metastable state to an invariant amount of SP seeds allowed to gradually increase the size of the nanostructures in a stepwise manner. However, in this experiment, the determination of the exact length of individual fibers was hampered by the strong lateral association of fibers, regardless of the size.
Theoretical Calculations

Spartan 10 was used for molecular modelling and PyMOL was employed as a molecular visualization system. Gaussian-16 (G16RevC.01) was used to compute the different supramolecular species (monomers, dimers, trimers, tetramers). The DFT-B3LYP method together with the 6-31(+)G(d,p) basis set was used to perform the geometry optimization. In all cases, solvent correction (MCH) was implemented. To reduce computational costs, the long alkoxy chains were replaced by methoxy groups ($\rightarrow$ 1-OMe).

Frequency calculations on the optimized geometries revealed no imaginary frequencies, indicating that the calculated structures correspond, at least, to local minima on the potential energy surface.

The stabilization energy per monomer ($\Delta E_{avg}$) was calculated as the difference in energies of an oligomer of $n$ molecular units ($H_n$) and $n$ corresponding monomers ($n \cdot H_{mon}$) divided by the term (n-1) (Equation S1).

$$\Delta E_{avg} = \frac{(H_n - n \cdot H_{mon})}{n-1} \quad (S1)$$

| structure | $H$ (kJ/mol) | $\Delta E_{avg}$ (kJ/mol) | intermolecular N-H···O=C (Å) | intramolecular N-H···O=C (Å)$^b$ | $\mu$ (D) |
|-----------|--------------|---------------------------|-------------------------------|----------------------------------|----------|
| closed monomer conformation 1a | -4058339.6007285 | - | 2.04 | 3.269 |
| closed monomer conformation 1b | -4058344.4368995 | - | 1.97 | 7.234 |
| open monomer conformation | -4058335.4655660 | - | - | 4.147 |
| parallel dimer | -8116703.1512680 | 2.02/1.97 ($\Theta = 1.99$) | - | 8.257 |
| pseudocyclic dimer | -8116703.1512680 | -26.226119 | 2.05/2.05 ($\Theta = 2.05$) | 2.29/2.29 ($\Theta = 2.29$) | 3.180 |
| antiparallel dimer | -8116708.9063640 | -20.032565 | 2.00/2.00 ($\Theta = 2.00$) | - | 0.387 |
| antiparallel trimer | -1217508.5407165 | -27.615009 | 1.92/1.93/1.94/2.05 ($\Theta = 1.97$) | - | 5.879 |
| parallel trimer | -12175073.9042 | -20.29675075 | 1.96/1.96/1.96/2.01 ($\Theta = 1.97$) | - | 10.897 |
| antiparallel tetramer | -16233465.4970590 | -29.249820 | 2.04/1.91/1.93/1.93/1.90/2.02 ($\Theta = 1.96$) | - | 2.291 |
| parallel tetramer | -16233448.2449 | -23.4991 | 1.97/1.93/1.98/1.96/2.00 ($\Theta = 1.96$) | - | 13.579 |

Figure S21. Geometry-optimized structures of the different conformational states of the monomer of 1-OMe. a) Closed conformation 1a with an intramolecular H-bond between the OPE-centered carbonyl as acceptor and the 3,4,5-trialkoxybenzamide-centered N-H as donor. b) Closed conformation 1b with an intramolecular H-bond between the OPE-centered N-H as donor and the 3,4,5-trialkoxybenzamide-centered carbonyl as acceptor. c) Open conformation without intramolecular H-bonds.
Figure S22. Geometry-optimized structures of the different possible dimer arrangements of 1-OMe. a) Dimer with a parallel arrangement of the molecules. b) Dimer with an antiparallel arrangement of the molecules. c-e) Different views of the closed dimer with all H-bonding sites saturated either by intra- or intermolecular H-bonds. The dimer was constructed from two monomers in the more stable intramolecularly H-bonded state 1b.
Figure S23. a-d) Geometry-optimized structures and enthalpy differences of the antiparallel and parallel trimers (a,b) and tetramers (c,d) of 1-OMe. e,f) Different view of the optimized antiparallel (e) and parallel (f) tetramers with illustrations of the vector of the dipole moment of the corresponding stack.
Experimental Part

Materials and Methods

General Procedures
All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon or nitrogen atmosphere.

For all spectroscopic measurements, spectroscopic grade solvents were used.

Colum Chromatography
Preparative column chromatography was conducted in self-packed glass columns of different sizes with silica gel (Merck Silica 60, particle size 0.04 - 0.063 nm).

NMR measurements
$^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance II 300 ($^1$H: 300 MHz, $^{13}$C: 75 MHz), and a Bruker Avance II 400 ($^1$H: 400 MHz, $^{13}$C: 101 MHz). Additional 1D $^1$H as well as 2D spectra were recorded on an Agilent DD2 500 ($^1$H: 500 MHz, $^{13}$C: 126 MHz) and an Agilent DD2 600 ($^1$H: 600 MHz, $^{13}$C: 151 MHz) at a standard temperature of 298 K in deuterated solvents. The recorded spectra were referenced to the remaining resonance signals of the deuterated solvents. The coupling constant J of the measured spin multiplets is given in Hertz (Hz) and the chemical shift $\delta$ is given in reference to the chemical shift of trimethylsilane (0 ppm). Multiplicities for proton signals are abbreviated as s, d, t, q, quint and m for singlet, doublet, triplet, quadruplet, quintet and multiplet, respectively.

Mass spectrometry (MS)
MALDI mass spectra were recorded on a Bruker Daltronics Ultraflex ToF/ToF or a Bruker Daltronics Autoflex Speed with a SmartBeamTM NdYAF-Laser with a wavelength of 335 nm. ESI mass spectra were measured on a Bruker MicrOTOF system. The signals are described by their mass/charge ratio (m/z) in u.

UV-Vis absorption spectroscopy
UV-Vis absorption spectra were recorded on a JASCO V-770 or a JASCO V-750 with a spectral bandwidth of 1.0 nm and a scan rate of 1000 nm min$^{-1}$ or on an Agilent Cary 4000 with a spectral bandwidth of 2 nm at a scan rate of 600 nm min$^{-1}$. Glass cuvettes with an optical length of 1 cm, 1 mm and 0.1 mm and 0.01 mm were used. All measurements were conducted in commercially available solvents of spectroscopic grade.

Emission spectroscopy
Fluorescence emission and excitation spectra were recorded on a JASCO Spectrofluorometer FP-8500 with an excitation and emission bandwidth of 5.0 nm at a scan rate of 1000 nm min$^{-1}$ in quartz cuvettes with an optical length of 1 cm.

FTIR spectroscopy
Solution and solid-state measurements were carried out using a JASCO-FTIR-6800 equipped with a CaF$_2$ cell with a path length of 0.1 mm or with a JASCO Pro One single-reflection ATR accessory.

Atomic force microscopy (AFM)
The AFM images were recorded on a Bruker AXS Multimode®8 SPM System. The used cantilevers were AC200TS by Oxford Instruments with an average spring constant of 9 N m$^{-1}$, an average frequency of 150 kHz, an average length of 200 µm, an average width of 40 µm and an average tip radius of 7 nm. All samples were drop casted or spin-coated at a spin velocity between 2000 and 4000 rpm from freshly prepared solutions onto an HOPG surface. Length analysis was conducted on fibers whose length was clearly distinguishable (see marked example fibers in phase images) using the built-in section analysis of the NanoScope Analysis program.

Dynamic Light Scattering (DLS)
DLS spectra were recorded on an ALV GmbH CGS-3 Compact Goniometer System, equipped with a HeNe laser with a wavelength of 632.8 nm (22 mW) and an ALV GmbH ALV/LSE-5004 Digital Correlator.

Gel permeation chromatography (GPC)
Gel permeation chromatography was performed on a Shimadzu prominence GPC system equipped with a Japan Analytical Industry Co., Ltd. JAIJEL-2HR (20 mm I.D. x 600 mm) with CHCl$_3$ as eluent. The solvent flow was set to be 4 mL/min. Detection was carried out via a Shimadzu prominence SPD-M20A diode array detector (DAD).

Scanning Electron Microscopy (SEM)
SEM images were recorded on a Thermo Fisher Scientific Phenom ProX Desktop SEM. The individual images were recorded with an acceleration voltage between 5 to 15 kV. A backscattered-electron detector (BSD) or a secondary-electron detector (SED) were used. All samples were prepared by drop casting the sample onto Si-wafer surfaces which were then dried under ambient conditions.
Synthesis and Characterization

Scheme S1. Synthesis route to obtain bisamide ligand 1 and reference compound ref-1.

3,4,5-Tris(dodecyl)benzoic acid (2)\(^{[10]}\) and tert-butyl (2-aminoethyl)carbamate (3)\(^{[11]}\) were prepared according to known literature protocols and showed spectroscopic properties similar to the ones published.

**Tert-butyl (2-(3,4,5-tris(dodecyl)benzamido)ethyl)carbamate (4)**

3,4,5-tris(dodecyl)benzoic acid 2 (1.0 g, 1.48 mmol, 1.0 eq), and 1-hydroxybenzotriazole hydrate (1-HOBt, 0.25 g, 1.63 mmol, 1.1 eq) were suspended in DCM. Subsequently, \(\text{N-}(3\text{-dimethylaminopropyl})\text{-N-ethylcarbodiimide hydrochloride (EDC-HCl, 0.31 g, 1.63 mmol, 1.1 eq)}\) was added. The solution was stirred at RT for 30 min and subsequently, tert-butyl (2-aminoethyl)carbamate 5 (0.26 g, 1.63 mmol, 1.1 eq) was added and the reaction mixture was stirred at room temperature for 4 hours. The solids were filtered off and the solvent was removed in vacuo. The resulting crude product was purified by column chromatography (DCM +1 % MeOH+ 1 % NEt\(_3\) and n-pentane:EtOAc 10:1 → 3:1), giving the product as a colorless solid (1.05 g, 1.28 mmol, 87 %).

\(^1\)H NMR (CDCl\(_3\), 600 MHz) \(\delta\) (ppm) = 7.52 (s, 1H, NH\(_8\)), 7.06 (s, 2H, H\(_9\)), 5.26 (m, 1H, NH\(_5\)), 3.96 (m, 6H, OC\(_2\)H\(_2\)), 3.49 (m, 2H, H\(_7\)), 3.35 (m, 2H, H\(_6\)), 1.76 (m, 4H, CH\(_2\)), 1.71 (m, 2H, CH\(_{2}\)), 1.44 (m, 6H, CH\(_3\)), 1.39 (s, 9H, t-Bu-CH\(_3\)), 1.27 (m, 48H, C\(_4\)H\(_2\)-C\(_{11}\)H\(_2\)), 0.87 (t, J = 6.9 Hz, 9H, C\(_{12}\)H\(_3\)).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\)(ppm) = 167.61, 157.76, 153.08, 141.04, 129.01, 105.71, 79.84, 73.51, 69.25, 42.34, 40.33, 32.03, 32.02, 30.42, 29.84, 29.83, 29.82, 29.80, 29.78, 29.76, 29.74, 29.74, 29.69, 29.51, 29.48, 29.46, 28.43, 26.20, 26.18, 22.77, 14.18.

HR-MS (ESI-Orbitrap, toluene/MeOH): calculated for C\(_{50}\)H\(_{92}\)N\(_2\)O\(_6\)Na\(^{+}\) [M+Na]\(^{+}\): 839.6848
found: 839.6846
Figure S20. $^1$H NMR (600 MHz, CDCl$_3$) spectrum of tert-butyl (2-(3,4,5-tris(dodecyloxy)benzamido)ethyl)carbamate (4).

Figure S21. $^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of tert-butyl (2-(3,4,5-tris(dodecyloxy)benzamido)ethyl)carbamate (4).

N-(2-aminoethyl)-3,4,5-tris(dodecyloxy)benzamide (5)

Tert-butyl (2-(3,4,5-tris(dodecyloxy)benzamido)ethyl)carbamate 4 (870 mg, 1.06 mmol, 1 eq) was dissolved in 10 mL DCM and gradually trifluoroacetic acid (~800 µL, ~10.6 mmol, ~10 eq) was added. The mixture was stirred at room temperature for two hours. The solvent and TFA were removed in vacuo, the residue was dissolved in DCM and was washed with saturated NaHCO$_3$ and brine. The combined organic phases were dried over Na$_2$SO$_4$ and the solvent was removed in vacuo, giving the product as a colorless solid (695 mg, 0.97 mmol, 91%).
**Supporting Information**

**$^1$H NMR** (CDCl$_3$, 500 MHz) $\delta$ (ppm) = 6.99 (s, 2H, H$^9$), 6.90 (t, $J = 5.6$ Hz, 1H, NH$^8$), 3.94 (m, 6H, OCH$_2$), 3.43 (q, $J = 5.8$ Hz, 2H, H$^3$), 2.88 (t, $J = 5.9$ Hz, 2H, H$^7$), 1.75 (m, 4H, C$^2$H$_2$), 1.71 (m, 2H, C$^2$H$_2$), 1.42 (m, 6H, C$^3$H$_2$), 1.25 (m, 48H, C$^4$H$_2$-C$^{11}$H$_2$), 0.87 (t, $J = 7.0$ Hz, 9H, C$^{12}$H$_3$).

**$^{13}$C NMR** (126 MHz, CDCl$_3$) $\delta$ (ppm) = 167.74, 153.10, 141.15, 129.55, 105.83, 73.53, 69.37, 42.62, 41.41, 32.01, 32.00, 30.40, 29.82, 29.81, 29.80, 29.78, 29.76, 29.74, 29.72, 29.66, 29.49, 29.46, 29.44, 26.17, 26.16, 22.75, 14.16.

**HR-MS** (ESI-Orbitrap, CHCl$_3$/MeOH): Calculated for C$_{45}$H$_{85}$N$_2$O$_4$ [M+H]$^+$: 717.6503, Found: 717.6498.

Figure S22. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of N-(2-aminoethyl)-3,4,5-tris(dodecyloxy)benzamide (5).

Figure S23. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of N-(2-aminoethyl)-3,4,5-tris(dodecyloxy)benzamide (5).
4-iodobenzoic acid, (239 mg, 0.96 mmol, 1.0 eq), and 1-hydroxybenzotriazole hydrate (1-HOBt, 162 mg, 1.06 mmol, 1.1 eq) were suspended in DCM. Subsequently, N-(3-dimethylaminopropyl)-N-ethylcarbodiimide hydrochloride (EDC-HCl, 203 mg, 1.06 mmol, 1.1 eq) was added. The solution was stirred at RT for 30 min and subsequently, N-(2-aminoethyl)-3,4,5-tris(dodecyloxy)benzamide 5 (690 mg, 0.96 mmol, 1.0 eq) was added and the reaction mixture was stirred at room temperature for six hours. The solids were filtered off and the solvent was removed in vacuo. The resulting crude product was purified by column chromatography (n-pentane:EtOAc 2:1 → 1:1), giving the product as a colorless solid (821 mg, 0.87 mmol, 90%).

**1H NMR** (CDCl₃, 500 MHz) δ (ppm) = 7.72 (d, J = 8.4, 2H, H₄), 7.62 (m, br, 1H, NHᵭ), 7.54 (d, J = 8.4 Hz, H₃), 7.33 (m, br, 1H, NHᵭ), 7.00 (s, 2H, H₉), 3.96 (m, 6H, OCH₂), 3.63 (m, br, 4H, H₆+7), 1.77 (m, 4H, C₂H₂a), 1.44 (m, 6H, C₃H₂), 1.27 (m, 48H, C₄H₂-C₁₁H₂), 0.88 (t, J = 6.9 Hz, 9H, C₁₂H₃).

**13C NMR** (126 MHz, CDCl₃) δ (ppm) = 169.08, 167.99, 153.23, 141.30, 137.89, 133.35, 128.85, 128.76, 105.70, 98.83, 73.67, 69.35, 41.22, 40.94, 32.08, 32.07, 30.47, 29.89, 29.88, 29.87, 29.86, 29.85, 29.81, 29.81, 29.73, 29.58, 29.53, 29.51, 29.51, 26.26, 26.22, 22.83, 14.25.

**HR-MS** (ESI-Orbitrap, MeOH/CHCl₃): calculated for C₅₂H₈₈N₂O₅⁺ [M+H]⁺: 947.5732 found: 947.5740

Figure S24. ¹H NMR (500 MHz, CDCl₃) spectrum of 3,4,5-tris(dodecyloxy)-N-(2-(4-iodobenzamido)ethyl)benzamide (6).
3,4,5-tris(dodecyloxy)-N-(2-(4-iodobenzamido)ethyl)benzamide (1)

3,4,5-tris(dodecyloxy)-N-(2-(4-iodobenzamido)ethyl)benzamide 6 (500 mg, 0.53 mmol, 1.0 eq), copper(I) iodide (3 mg, 0.02 mmol, 0.03 eq) and Pd(PPh₃)₄ (31 mg, 0.03 mmol, 0.05 eq) were placed in a Schlenk tube and exposed to three vacuum/argon cycles. 5 mL of a degassed 9:1 mixture of THF/NEt₃ was added and the suspension was stirred at room temperature for 15 minutes. Subsequently, a solution of 4-ethynylpyridine (65 mg, 0.63 mmol, 1.2 eq) in 3 mL of a degassed 9:1 mixture of THF/NEt₃ was added and the reaction solution was stirred at 50 °C for 18 hours. The solvents were removed in vacuo and the remaining crude product was purified by column chromatography (DCM → DCM+3 % MeOH). The product was obtained as an off-white solid (429 mg, 0.47 mmol, 88 %).

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 8.63 (AA’XX’, 2H, H¹), 7.84 (d, 2H, J = 8.5 Hz, H⁴), 7.60 (d, J = 8.4 Hz, 2H, H⁷), 7.40 (m, 3H, NH²⁺H²), 7.05 (m, 1H, NH³), 6.99 (s, 2H, H⁹), 3.99 (m, 6H, OCH₂), 3.70 (m, br, 4H, H⁶+⁷), 1.80 (quint, J = 7.5 Hz, 4H, C²H₂), 1.73 (quint, J = 7.5 Hz, 2H, C²H₂), 1.46 (quint, J = 7.0 Hz, 6H, C⁴H₂), 1.28 (m, 48H, C⁴H₂-C¹¹H₂), 0.87 (t, J = 6.9 Hz, 9H, C¹²H₃).

¹³C NMR (126 MHz, CDCl₃) δ (ppm) = δ 169.16, 167.76, 153.28, 149.97, 141.41, 134.26, 132.18, 131.10, 128.80, 127.36, 125.59, 105.72, 92.99, 88.92, 73.67, 69.42, 41.54, 40.99, 32.07, 30.47, 29.86, 29.81, 29.73, 29.57, 29.51, 26.25, 22.84, 14.26.

HR-MS (ESI-Orbitrap, MeOH): calculated for C₅₉H₉₁N₃O₅Na⁺ [M+Na]⁺: 944.6851
found: 944.6852
3,4,5-tris(dodecyloxy)-N-(2-(phenylethynyl)benzamido)ethyl]benzamide ref-1

3,4,5-tris(dodecyloxy)-N-(2-(4-iodobenzamido)ethyl]benzamide 6 (100 mg, 106 µmol, 1.0 eq), copper(I) iodide (0.6 mg, 3 µmol, 0.03 eq) and Pd(PPh₃)₄ (6 mg, 5 µmol, 0.05 eq) were placed in a Schlenk tube and exposed to three vacuum/argon cycles. 3 mL of a degassed 9:1 mixture of THF/NEt₃ was added and the suspension was stirred at room temperature for 15 minutes. Subsequently, phenylacetylene (15 µL, 14 mg, 0.14 mmol, 1.3 eq) was added and the reaction solution was stirred at 40 °C for 18 hours. The solvents were removed in vacuo and the remaining crude product was purified by column chromatography (n-pentane/EtOAc 1:1 → n-pentane/EtOAc 2:3). The product was obtained as an off-white solid (95 mg, 103 µmol, 98%).
\[ \text{\(^1H\) NMR} \text{ (CDCl}_3\text{, 500 MHz) } \delta \text{ (ppm) } = 7.84 \text{ (d, 2H, } J = 8.0 \text{ Hz, H}^4\text{), 7.74 (s, 1H, NH}^8\text{), 7.69 (s, 1H, NH}^8\text{), 7.53 (m, 4H, H}_3\text{H}_2\text{, 7.35 (m, 3H, H}_3\text{H}_2\text{), 7.05 (s, 2H, H}^8\text{), 3.97 (m, 6H, OCH}_2\text{), 3.68 (m, 4H, N-CH}_2\text{-CH}_2\text{-N), 1.74 (m, 6H, C}_2\text{H}_4\text{), 1.44 (m, 6H, C}_3\text{H}_6\text{), 1.26 (m, 48H, C}_4\text{H}_2\text{-C}^{13}\text{H}_2\text{), 0.87 (m, 9H, CH}_3\text{).} \]

\[ \text{\(^{13}C\) NMR} \text{ (126 MHz, CDCl}_3\text{) } \delta \text{ (ppm) } = 169.10, 168.29, 153.23, 141.37, 132.99, 131.84, 131.82, 128.82, 128.53, 128.39, 127.33, 127.05, 122.88, 105.79, 92.10, 88.63, 73.65, 69.35, 41.30, 41.02, 32.07, 32.06, 30.47, 29.89, 29.88, 29.87, 29.86, 29.83, 29.81, 29.73, 29.59, 29.53, 29.51, 26.26, 26.22, 22.83, 14.24. \]

\[ \text{HR-MS (ESI-Orbitrap, MeCN/CHCl}_3\text{): calculated for C}_60\text{H}_93\text{N}_2\text{O}_5\text{ } [M+H]^+ : 921.7090 \text{ found: 921.7086} \]

Figure S28. \(^1H\) NMR (CDCl\textsubscript{3}, 500 MHz) spectrum of compound ref-1.
Figure S29. $^{13}$C NMR (CDCl$_3$, 126 MHz) spectrum of compound ref-1.
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Author Contributions
J.M. and G.F. conceived the project. J.M. synthesized the compounds, performed the self-assembly studies, wrote and designed the first draft of the manuscript. Z.F. carried out theoretical calculations and was involved in editing the figures and the description of the theoretical part. N.B. recorded AFM images. G.F. supervised the project and was involved in the manuscript writing, design and figure elaboration. All authors were involved in the scientific discussion, the revision and finalization of the manuscript.