Helical Polymer-Anchored Porphyrin Nanorods

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Abstract: Well-defined arrays of porphyrins attached to a rigid polyisocyanide backbone have been synthesized and their physical and optical properties studied. The helical polymers are rigidified by an inter-side chain hydrogen-bonded network and have an average mass of 1.1×10^6 Daltons and a polydispersity index of 1.3. Each of the polymer strands contains four columns of around 200 stacked porphyrins and has an overall length of 87 nm. The chromophores are arranged in a left-handed helical fashion along the polymer backbone. Photophysical studies show that at least 25 porphyrins within one column are excitationally coupled.

Introduction

Well-defined arrays of chromophoric molecules are of great interest not only as mimics of natural antenna systems but also because they can display unique optical and physical properties.[1] The beautiful examples found in nature, for example the photosynthetic light-harvesting antenna complexes and reaction centers in bacteria and green plants, contain organized assemblies of bacteriochlorophyll molecules held together by protein scaffolds.[2] The precise organization and orientation of the chromophores results in efficient absorption and transportation of light energy and its conversion into chemical energy.[3]

Inspired by these naturally occurring architectures, much attention is currently focused on the design of nanometer-sized chromophoric assemblies, which may find application in the fields of molecular photonics and electronics. In order to construct such assemblies several methods have been tried. Stepwise covalent coupling is one of the most commonly used approaches.[4] This approach is, however, limited, because large structures can only be obtained by multi-step synthetic

routes which usually lead to low yields, although more recently an elegant procedure has been developed by Osuka et al. which allows the covalent synthesis of porphyrin arrays through a Ag^I-promoted *meso–meso*-coupling, resulting in linear arrays of up to 128 porphyrins (ca. 106 nm).[5]

The introduction of molecular recognition motifs into the porphyrin building blocks, such as hydrogen bonding, $\pi-\pi$ stacking, electrostatic interactions, and metal-ligand bonds and the use of self-assembly, offers an easy way to access well-defined arrays such as fibers, sheets, grids, cubes and rings.[6]

In this paper we describe an alternative approach to obtain well-defined nanometer-sized arrays of porphyrins by anchoring these molecules to precisely defined polymers, for example polymers of isocyanides. Many porphyrin pendant polymers and porphyrin coordination polymers have been synthesized, but they possessed limited structural definition.[7] We previously attempted to graft porphyrins onto polyisocyanides but obtained only incomplete substitution of the polymeric backbone and an ill-defined arrangement of the chromophores.[8] To overcome this problem we decided to synthesize monomeric isocyano peptide porphyrins, which can be subsequently polymerized to give highly organized architectures. Recently, we reported that polyisocyanides prepared from isocyanodipeptides form exceptionally stable β-helical architectures due to the presence of hydrogen-bonding arrays along the helical polymer backbone.[9] This secondary hydrogen-bonding network rigidifies the helix and prevents unwinding, a problem previously encountered with polyisocyanides.[10] The chiral centers in the side chains control the handedness of the polymeric backbone, which allows one in principle to tune the architectures and consequently the macromolecular properties. The resulting helical polymers are very rigid, have a precise architecture

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and a persistence length of the order of 70 nm. Using improved polymerization procedures, the isocyanopeptides can be polymerized to reach single polymer lengths of up to 12 μm.[11] It was therefore decided to decorate these rigid peptido polyisocyanides with porphyrins and synthesize nanometer-long porphyrin wires.

In this paper we describe the synthesis of porphyrin monomer **1** and its polymerization with a nickel(II) catalyst to give polymers in which the chromophores are arranged in precisely defined stacks that run parallel to the polymer axis.[12]

Results and Discussion

Synthesis: The preparation of porphyrin **1** is shown in Scheme 1. The monomer is derived from the amino acid L-alanine in order to provide a peptide bond, which leads to the β-helical structure of the polymer. In addition the porphyrin is functionalized with aliphatic tails to increase the solubility of the resulting polymer. Monohydroxyporphyrin **4** having three

dodecyloxy tails was synthesized according to standard procedures and coupled to 3-bromopropylamine. The resulting amino compound **5** was coupled to N-formyl-L-alanine using dicyclohexylcarbodiimide and N,N-dimethylaminopyridine, and the product **6** was converted into the isocyanide using diphosgene as dehydrating agent and N-methylmorpholine as base. Polymerization of **1** was carried out in CH$_2$Cl$_2$ under air in a reaction vessel protected from light using 3×10^{-3} equivalents of Ni(ClO$_4$)$_2 \cdot$6H$_2$O as catalyst. The yield of polymer **2** was 68%. The IR spectrum showed an N−H stretching vibration at 3265 cm^{-1}, which implies a structure in which the side chains are in a hydrogen-bonding arrangement, in agreement with previous studies on polyisocyanides prepared from isocyanodipeptides.[13] Additionally, the position of the amide carbonyl vibration (1655 cm^{-1}) was proof of its participation in a hydrogen-bonding array.

Photophysical studies: The UV/Vis absorption spectra of monomer **1** and polymer **2** are depicted in Figure 1. The observed spectra are identical in chloroform and in aromatic
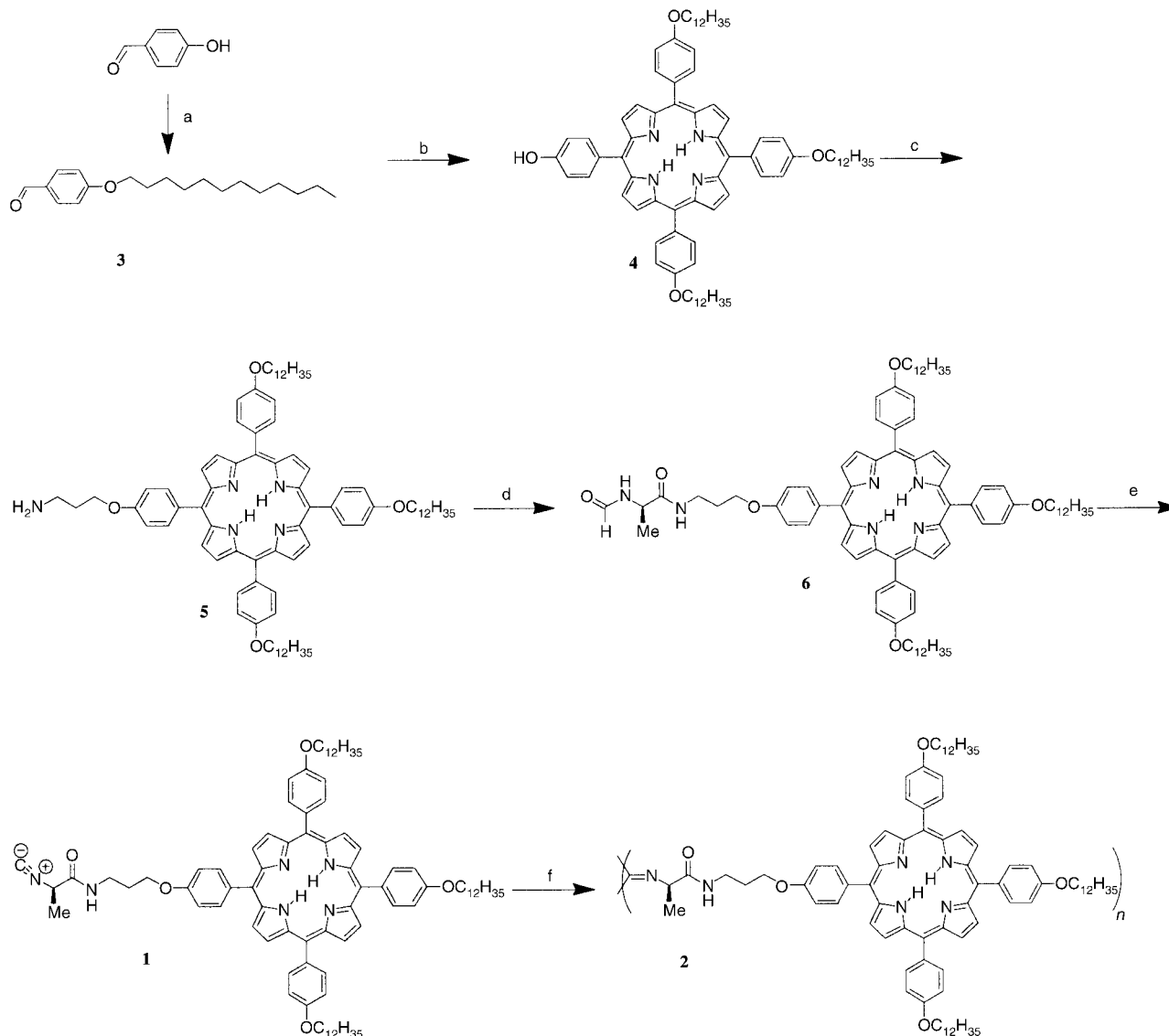
Scheme 1. a) C$_{12}$H$_{25}$Br/K$_2$CO$_3$, cyclohexanone; b) p-hydroxybenzaldehyde/pyrrole, propionic acid, reflux 1 h; c) bromopropylamine hydrobromide/NaOH, DMF; d) N-formyl-L-alanine, DCC/DMAP, CH$_2$Cl$_2$; e) N-methylmorpholine/diphosgene, CH$_2$Cl$_2$; f) Ni(ClO$_4$)$_2 \cdot$6H$_2$O (2 × 10^{-3} equiv), CH$_2$Cl$_2$.
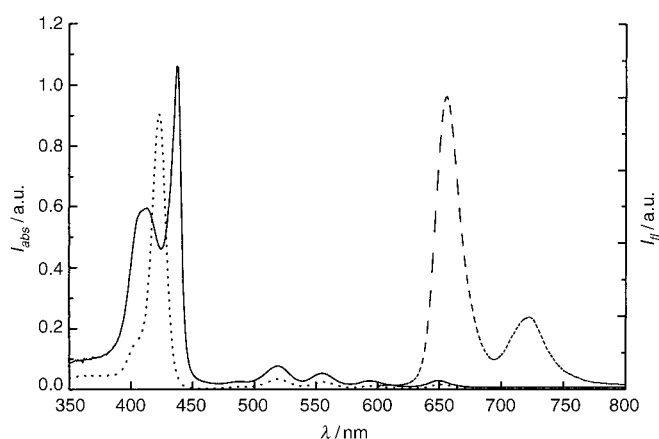
Figure 1. Absorption spectrum of monomer **1** (••••, solvent CHCl₃, 2.4 × 10^{-6} M) and polymer **2** (——, CHCl₃, 4.3 × 10^{-6} M), and emission spectrum (– – –, CHCl₃, 4.3 × 10^{-6} M) of polymer **2**.

solvents such as toluene. Dramatic changes are observed upon going from the monomer spectrum to that of the polymer. The monomer displays a Soret band at 421 nm, whereas, in the polymer this band has disappeared and two new Soret bands are present at 413 and 437 nm. The splitting of the bands and the very sharp absorption observed at 437 nm are indicative of the presence of well-defined and excitationally-coupled stacks of porphyrin molecules. We attribute the red-shifted Soret band to an offset stacking of the 1st and 5th porphyrin and the blue shift is attributed to a combination of interactions between the 1st and 4th porphyrin and the 1st and 2nd porphyrin.

The emission spectrum of monomer **1** showed a typical two-band profile of a free-base porphyrin. Polymer **2** displayed essentially the same two bands (Figure 1), but the maxima were hypsochromically shifted by 3 nm and the intensity had decreased significantly. This is attributed to quenching by neighboring porphyrins.

The circular dichroism spectrum of a solution of **2** in CHCl₃ (Figure 2) showed a strong bisignate Cotton effect originating from the porphyrin Soret band at 437 nm and smaller bisignate signals with lower intensities corresponding to the
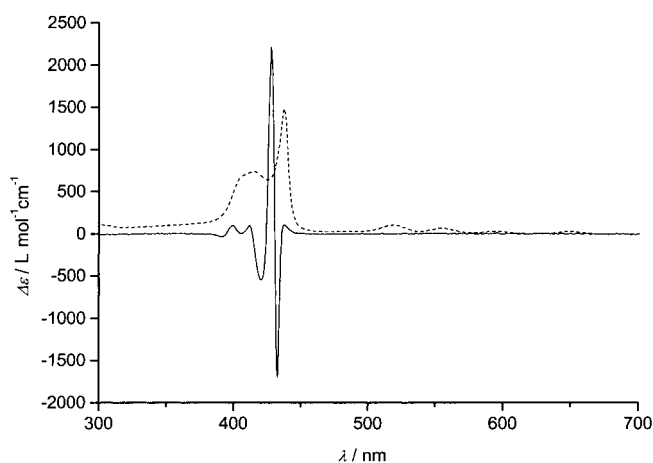
blue-shifted Soret bands. No CD signal was observed for the porphyrin monomer **1**. The intense bisignate signal at 431 nm is slightly asymmetric and blue-shifted by 6 nm due to overlap of other transitions. It stems from coupling interactions between the 1st and the 5th porphyrin molecule in the polymer backbone, which are located on top of each other (see Figure 6). From the negative sign of this couplet a left-handed helical arrangement of the porphyrins can be inferred, according to the exciton chirality method for porphyrins.[14] The smaller bisignate signals are due to other intramolecular couplings, as mentioned above. The positive couplet at 400 nm is assigned to an exciton coupling between the 1st and 4th porphyrin, which have a right-handed orientation with respect to each other in the stack (see Takahashi et al.)[12]

Atomic force microscopy: Single molecules of polymer **2** were visualized by atomic force microscopy (AFM) using spin-coated solutions of **2** on mica. The results are presented in Figure 3. At high concentration (10^{-5} M) monolayer islands of aggregated polymers are visible (Figure 3a) as is often seen for rigid rod polymers. Upon dilution, isolated single polymer strands can be observed (10^{-6} M, Figure 3b). Further dilution did not result in any change of the features. The images reveal that polymer **2** has a rod-like character as was expected for polyisocyanides with hydrogen-bonding amino acid side chains.[11] The measured height of the single molecules was 4.2(±0.3) nm and of the islands was 4.7(±0.2) nm. CPK models show that the diameter of a polymer chain with stretched side groups is 8.6 nm, and without tails the diameter

Figure 2. CD spectrum of polymer **2** (solvent CHCl₃, conc. 4.0 × 10^{-6} M) and the corresponding absorption spectrum (– – –).
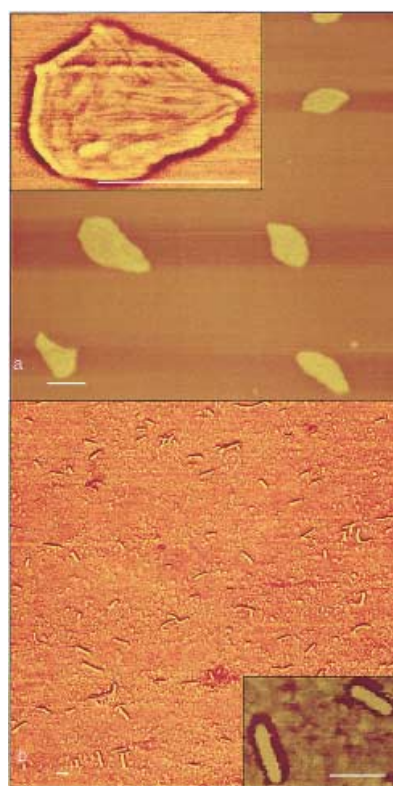

Figure 3. AFM images of polymer **2**: a) monolayer islands at 10^{-5} M (inset: enlargement of island); b) isolated single polymer fibers at 10^{-6} M (inset: enlargement of fibers). (bar = 100 nm).

amounts to 5.6 nm. It is known that, due to the indentation of the tip, the measured height can be less than the real height.[15] The measured values are in good agreement with the calculated heights and further confirm the presence of single molecules.

Molecular weight determination: Since it was not possible to determine the molecular weight and polydispersity of **2** by MALDI-MS or GPC due to the rod-like nature of the polymers we turned to the AFM images to calculate these parameters. Several images of the type shown in Figure 3b were used to evaluate the polymer contour lengths. The results are shown in Figure 4. From this histogram the weight-average and number-average apparent length (L_w and L_n) and the length polydispersity PD were calculated using the Equations (1) and (2).[16]

$$L_w = \frac{\sum_i N_i \cdot L_i^2}{\sum_i N_i \cdot L_i}, \quad L_n = \frac{\sum_i N_i \cdot L}{\sum_i N_i} \tag{1}$$

$$PD = \frac{L_w}{L_n} \tag{2}$$

These values amounted to: $L_w = (87 \pm 7)$ nm and $L_n = (69 \pm 5)$ nm, giving PD $= 1.27 \pm 0.14$. Assuming that every monomer segment adds 1.05 Å to the polymer chain,[9] a weight-average length of 87 nm corresponds to a degree of polymerization of about 830 and a weight-average molecular mass of 1.1×10^6 Daltons. Therefore these porphyrin polyisocyanides are probably the longest well-defined porphyrin pendant polymers described to date.
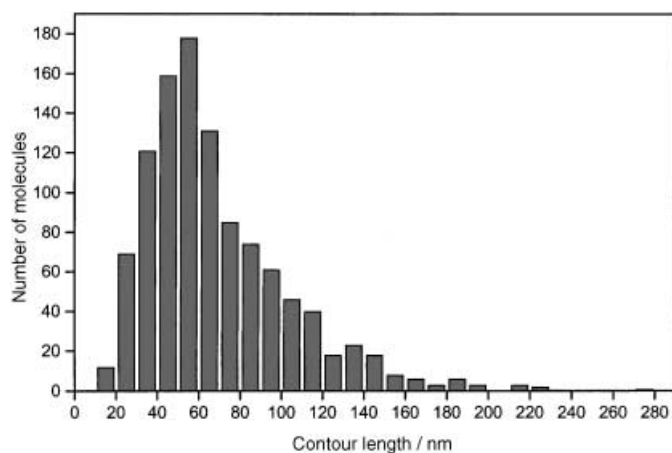

Figure 4. Histogram of the length distribution of **2**, as calculated from the AFM images.

Resonance light scattering: In order to obtain more insight into the precise geometry of the porphyrins in these long rigid polymers we used the technique of resonance light scattering (RLS). This technique has proven to be a sensitive and selective tool for the investigation of electronic and geometrical properties of aggregated chromophores, such as synthetic porphyrins[17] and natural chlorophyll *a* arrays.[18] In particular, depolarized RLS measurements can give further

information about the relative orientation of the stacked porphyrin molecules.[19]

The RLS effect is an enhancement of the scattered light intensity in the red edge of an absorption band. In turn this is related to an electronic coupling between adjacent chromophores, to the size and the geometry of the aggregates in which the chromophores are present, and to the molar absorbance of the individual chromophores.[17] This phenomenon allows identification of the precise orientation of the chromophores in an aggregate and their interactions even when they are present in complex matrices. A simple quantum mechanical model for RLS, based on exciton-coupling theory, has recently been developed, addressing the relationship between the intensities of the observed RLS features and the electronic and geometrical properties of the aggregates.[19]

The RLS spectrum of **2** (Figure 5) showed the presence of an intense peak (at least two orders of magnitude larger than the peak of the neat solvent) in the region of the Soret band (444 nm), accompanied by a deep well in the region 408 – 438 nm, due to photon absorption. The enhancement observed for the scattered light intensity of the polymer is consistent with the presence of large domains of more than 25 (n ≫ 25) interacting chromophores.
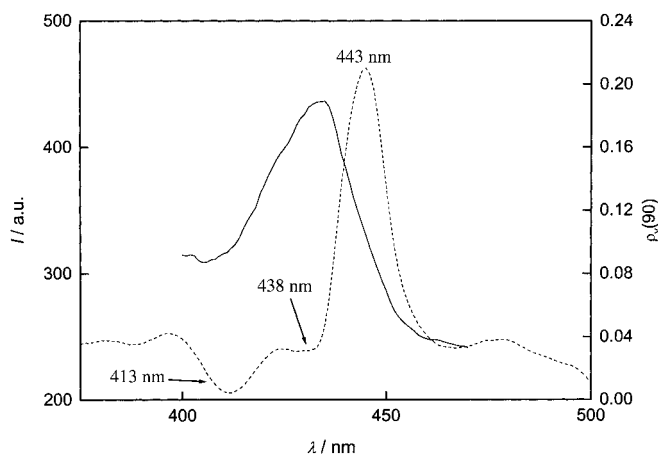

Figure 5. RLS spectrum of **2** (– – –). The dispersion profile of the RLS depolarization ratio $\rho_v(90)$ is reported as a full line.

In addition to obtaining information concerning the number of interacting chromophores, depolarized RLS studies can also give details about the precise orientation of the chromophores in the polymeric nanorods. Figure 5 shows the dispersion profile of the depolarization ratio $\rho_V(90)$ at the absorption feature for polymer **2**. The value of $\rho_V(90)$ provides information about the geometry of the excited state of an aggregated species.[19] The absorption feature at 437 nm has the appearance of a J band and the corresponding $\rho_V(90)$ is 0.185. From this an angle $\alpha \cong 30°$ is calculated[20] between porphyrin molecules 1 and 5 which are stacked 4.2 Å apart (see below).[9] From this value the twist angle β (Figure 6c) is calculated to be 22°.[21] This angle β is in complete agreement with that predicted using previous experimental results. Crystal structures of the monomeric peptido isocyanides indicate that the hydrogen-bonding network places the dipeptides 4.7 Å apart. In contrast, studies on simpler poly-

isocyanides predict an imine C_1 – C_5 length of 4.2 Å. In order to accommodate this difference, the helix has to twist by a calculated angle β of 20°. This value is in good agreement with the value of 22° that is derived from the RLS experiments. In addition, it is known that porphyrins have a preference for an off-set stacking.[22]

Conclusions

The combined results presented in this paper indicate that nanometer-long, well-defined arrays of porphyrin molecules can be constructed using peptido isocyanide polymers as scaffolds. These polymers have a rigid chiral core to which the porphyrin chromophores are attached in four parallel stacks. In one stack the porphyrins are precisely 4.2 Å apart with a slip angle of 30° (see Figure 6). Resonance light scattering shows that the arrays contain at least 25 interacting porphyrin molecules in one stack, with the overall stack having an average length of 87 nm.

To the best of our knowledge the present polymer system is the only system displaying a unique well-defined face-to-face porphyrin architecture involving hundreds of chromophores arranged over tens of nanometers.[12]
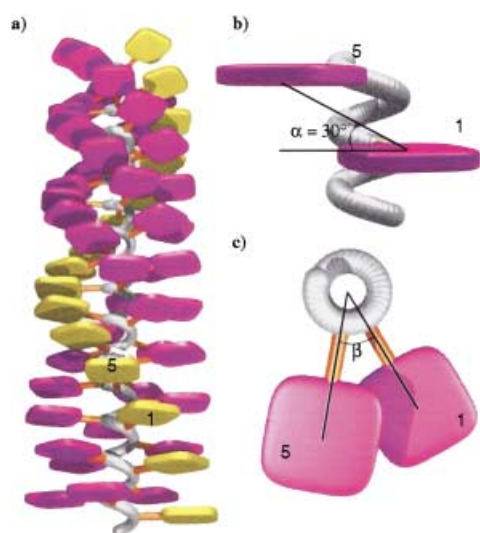

Figure 6. a) Schematic drawing of a molecule of polymer **2**, one column is shown in yellow; b) side view of a detail of the stack showing that the fifth porphyrin has a slip angle of 30° with respect to the first porphyrin; c) top view showing a twist angle β of 22°.

These rigid rod-like porphyrin polymers may be of interest as a synthetic antenna system, which will be further optimized and equipped with an energy gradient to measure energy transfer properties. Work along this line is in progress.

Experimental Section

Atomic force microscopy: AFM experiments were performed using a Nanoscope IIIa instrument from Digital Instruments. A solution of **2** in CHCl₃ was spincoated onto freshly cleaved Muscovite mica. All images were taken in tapping mode in air at room temperature. Commercial

tapping-mode tips (Digital Instruments) were used with a typical resonance frequency of around 300 kHz.

Light scattering: Resonance light scattering experiments were performed on a Jasco mod. FP-750 spectrofluorimeter, using a synchronous scan protocol with a right angle geometry.[17] Depolarized resonance light scattering measurements were carried out on the same spectrofluorimeter equipped with linear polarizers (Sterling Optics 105 UV). The depolarization ratio is defined as $\rho_V(90) = I_{VH}/I_{VV}$, where I_{VH} and I_{VV} are the scattered light intensities with horizontal and vertical polarization, respectively. In order to correct the value of I_{VH} for the difference in transmission efficiency of polarized light from both excitation and emission monochromators, we used Equation (3) where $G = I_{HV}/I_{HH}$ is a correction factor.[19]

$$\rho_V(90) = G \times \frac{I_{VH}}{I_{VV}} \tag{3}$$

Depolarized dynamic light scattering measurements were made with a Malvern 4700 submicron particle analyzer. Elastic light scattering experiments were performed with a home-built goniometer apparatus in the range 20 – 150° (5.8 – 32.5 μm⁻¹ in the scattered wavevector range). The exciting light source was a 50 mW polarized Nd/YAG laser (532 nm). A Glan-Thompson polarizer was placed before the photomultiplier.

Molecular weight determination with AFM: For the analysis of the polymer several images were evaluated, taken from different samples and different places on the mica substrate. Only molecules that were separated and had a consistent height and phase appearance were measured. In total 1058 molecules were analyzed. It was assumed that the overestimation of the length due to the shape of the AFM tip was equal to the overestimation of the width.

Synthesis

4-(Dodecyloxy)benzaldehyde (3): This compound was synthesized using a modified literature procedure, that is dodecyl bromide was used instead of hexadecyl bromide in cyclohexanone.[23] ¹H NMR (CDCl₃, 300.13 MHz): $\delta = 9.88$ (s, 1H; HC(O)), 7.82 (d, 2H; ArH *ortho* to formyl), 6.98 (d, 2H; ArH *ortho* to formyl), 4.04 (t, 2H; OCH₂), 1.81 (p(pentet), 2H; OCH₂CH₂), 1.46 (p, 2H; OCH₂CH₂OCH₂), 1.27 (m, 16H; aliphatic), 0.88 (t, 3H; CH₃).

Porphyrin 4: A suspension of **3** (15 g, 51.7 mmol) and 4-hydroxybenzaldehyde (2.09 g, 17.3 mmol) in propionic acid was heated until the compounds were dissolved. As soon as the temperature had reached 110 °C freshly distilled pyrrole (4.66 g, 69.2 mmol) was added at once to the solution, whereupon the mixture was refluxed for 1 h. After cooling, the obtained slurry was filtered and washed with ethanol until most of the polypyrrole side product was removed. After column chromatography (2 ×) (silica gel, 0 – 2 % MeOH in CHCl₃) compound **3** was isolated as a purple solid (0.95 g, 4.6 %). ¹H NMR (CDCl₃, 300.13 MHz): $\delta = 8.86$ (m, 8H; β-pyrrole), 8.10 (d, 6H; ArH *meta* to OR), 8.06 (d, 2H; ArH *meta* to *O*-aminopropyloxy), 7.28 (d, 6H; ArH, *ortho* to OR), 7.19 (d, 2H; ArH *ortho* to *O*-aminopropyloxy), 5.01 (br s, 1H; OH), 4.25 (t, 6H; OCH₂), 1.98 (p, 6H; OCH₂CH₂), 1.63 (p, 6H; OCH₂CH₂CH₂), 1.37 (m, 48H; aliphatic), 0.89 (t, 9H; CH₃), −2.77 (s, 2H; NH).

Porphyrin 5: For the synthesis of this compound a modified literature procedure was followed.[24] To a solution of **4** (350 mg, 0.30 mmol) in DMF (10 mL) and toluene (15 mL) was added crushed sodium hydroxide (0.245 g). After stirring for 20 min at room temperature, 3-bromopropylamine hydrobromide (74 mg, 0.34 mmol) was added and the reaction was continued for 3 h, upon which another 50 mg (0.23 mmol) of 3-bromopropylamine hydrobromide was added. The suspension was stirred for an additional 1 h and the reaction mixture was poured into water and extracted with dichloromethane (2 ×). The combined organic layers were washed with water, dried (MgSO₄) and evaporated to dryness. The resulting purple solid was subjected to column chromatography (silica gel, 5 % MeOH in CHCl₃) to yield **5** as a purple solid (276 mg, 74.2 %). ¹H NMR (CDCl₃, 300.13 MHz): $\delta = 8.86$ (m, 8H; β-pyrrole), 8.09 (d, 8H; ArH *meta* to OR), 7.26 (d, 8H; ArH *ortho* to OR), 4.35 (t, 2H; OCH₂), 4.24 (t, 6H; OCH₂), 3.10 (t, 6H; NHCH₂), 2.16 (p, 2H; NHCH₂CH₂), 1.96 (p, 6H; OCH₂CH₂), 1.61 (m, 6H; OCH₂CH₂CH₂), 1.30 (m, 48H; aliphatic), 0.90 (t, 9H; CH₃), −2.75 (s, 2H; NH); ¹³C NMR (CDCl₃, 75.47 MHz): $\delta = 158.9$ (Ar*C* ipso to OCH₃), 158.7, 135.6, 134.7, 134.4 (all Ar*C*), 130.9 (br; Ar*C* next to ArN), 119.8, 119.6, 113.8, 112.7 (all Ar*C*), 68.3, 66.2 (ArO*C*H₂),

39.4 (CH_2NH_2), 31.9 ($CH_2CH_2CH_3$), 29.6 (m; CH_2), 26.2 ($CH_2CH_2NH_2$), 22.7 (CH_2CH_3), 14.2 (CH_3); FAB-MS: m/z: 1240 $[M]^+$.

Porphyrin 6: *N*-Formyl-L-alanine (31.8 mg, 0.168 mmol) was suspended in a solution of **5** (190 mg, 0.153 mmol) in dichloromethane (10 mL) and the mixture was cooled with an ice bath. To this mixture was added dicyclohexylcarbodiimide (34.9 mg, 0.168 mmol) and a catalytic amount of dimethylaminopyridine. The reaction mixture was stirred for 1 h at 0°C under a nitrogen atmosphere and stirred overnight at room temperature. The mixture was concentrated and subjected to column chromatography (silica gel, 2 % MeOH in CHCl$_3$). The collected purple solid was dissolved in CHCl$_3$ and precipitated by addition of MeOH. The compound was filtered, washed with MeOH and dried to give **6** as a purple solid (142 mg, 69.3 %). ^{1}H NMR (CDCl$_3$, 300.13 MHz): $\delta = 8.86$ (m, 8H; β-pyrrole), 8.22 (s, 1H; formyl), 8.12 (d, 2H; ArH *meta* to O-propyl), 8.10 (d, 2H; ArH *meta* to OC$_{12}$H$_{25}$), 7.26 (d, 8H; ArH *ortho* to OR), 6.50 (t, 1H; NHCH$_2$), 6.36 (d, 1H; HC(O)NH), 4.62 (p, 1H; CH), 4.33 (t, 2H; OCH$_2$), 4.24 (t, 6H; OCH$_2$), 3.65 (q, 2H; NHCH$_2$), 2.22 (p, 2H; NHCH$_2$CH$_2$), 1.97 (p, 6H; OCH$_2$CH$_2$), 1.63 (p, 6H; OCH$_2$CH$_2$CH$_2$), 1.50 (d, 3H; alanine CH$_3$), 1.30 (m, 48H; aliphatic), 0.89 (t, 9H; CH$_3$), −2.75 (s, 2H; NH); ^{13}C NMR (CDCl$_3$, 75.47 MHz): $\delta = 171.2$ (CO; alanine), 160.3 (HCO; formyl), 158.5 (Ar*C* ipso to OC$_{12}$H$_{25}$), 157.9 (idem), 135.2 (Ar*C* meta to OC$_{12}$H$_{25}$ and *O*-propyl), 134.7 (CH; β-pyrrole), 134.0 (C; meso), 130.6 (br; Ar*C* next to ArN), 119.5 (Ar*C* ipso to meso C), 119.0 (idem), 112.3 (Ar*C* ortho to OR), 67.9 (OCH$_2$), 66.1 (OCH$_2$), 47.3 (CH; alanine), 37.4 (H$_2$NCH$_2$), 31.5 – 22.3 (CH$_2$; aliphatic), 25.8 (CH$_2$; propyl), 18.1 (CH$_3$; alanine), 13.7 (CH$_3$); MS (HR-MALDI-TOF, dithranol): m/z: calcd for C$_{87}$H$_{114}$N$_6$O$_6$: 1338.880; found: 1338.882 $[M]^+$.

Isocyanoporphyrin 1: *N*-Methylmorpholine (5.3 μL, 47.4 μmol) was added to a solution of the formamide **6** (30 mg, 22.4 μmol) in CH$_2$Cl$_2$ (6 mL). The mixture was cooled on an ice bath at 0°C and over a period of 30 min diphosgene (1.4 mL, 11.3 mmol in 1 mL CH$_2$Cl$_2$) was added. After 10 min the ice bath was removed and the mixture was dropped into a vigorously stirred saturated aqueous NaHCO$_3$ solution (100 mL). The resulting mixture was extracted with CH$_2$Cl$_2$ (2 ×), and the combined organic layers were washed with water (2 ×), dried (MgSO$_4$), and concentrated. The resulting solid was purified by preparative HPLC (reversed phase, 1 % MeOH in CHCl$_3$) to yield the title compound as a purple solid (20 mg, 67.6 %). ^{1}H NMR (CDCl$_3$, 300.13 MHz): $\delta = 8.86$ (m, 8H; β-pyrrole), 8.13 (d, 2H; *meta* to O-propyl), 8.10 (d, 6H; *meta* to OC$_{12}$H$_{25}$), 7.34 (d, 2H; *ortho* to O-propyl), 7.27 (d, 6H; *ortho* to OC$_{12}$H$_{25}$), 7.15 (t, 1H; NHCH$_2$), 4.39 (t, 2H; OCH$_2$), 4.25 (t, 6H; OCH$_2$), 4.34 (q, 1H; CH), 3.71 (q, 2H; NHCH$_2$), 2.26 (p, 2H; NHCH$_2$CH$_2$), 1.98 (p, 6H; OCH$_2$CH$_2$), 1.74 (d, 3H; alanine CH$_3$), 1.63 (p, 6H; OCH$_2$CH$_2$CH$_2$), 1.31 (m, 48H; aliphatic), 0.90 (t, 9H; CH$_3$), −2.75 (s, 2H; NH); ^{13}C NMR (CDCl$_3$, 75.47 MHz): $\delta = 166.2$ (CO; alanine), 158.9 (Ar*C* ipso to OC$_{12}$H$_{25}$), 158.3 (idem), 135.7 (Ar*C* meta to OC$_{12}$H$_{25}$ and O-propyl), 135.1 (CH; β-pyrrole), 134.1 (C; meso), 131.0 (br; Ar*C* next to ArN), 120.0 (Ar*C* ipso to meso C), 119.5 (idem), 112.8 (Ar*C* ortho to OR), 68.2 (OCH$_2$), 67.1 (OCH$_2$), 53.8 (CH; alanine), 38.7 (H$_2$NCH$_2$), 32.0 – 22.5 (CH$_2$; aliphatic), 26.1 (CH$_2$; propyl), 20.0 (CH$_3$; alanine), 14.2 (CH$_3$); FTIR (KBR): $\tilde{v} = 3313$ (NH), 2134 (NC), 1685 cm^{-1} (amide); MS (HR-MALDI-TOF, dithranol) m/z: calcd for C$_{87}$H$_{112}$N$_6$O$_5$: 1320.869; found: 1320.876 $[M]^+$.

Polymer 2: In a vessel protected from light monomer **1** (19 mg, 14 μmol) was dissolved in CH$_2$Cl$_2$ (1.5 mL). To this solution was added 0.003 equiv Ni^{2+} catalyst (0.35 mL of a solution of Ni(ClO$_4$)$_2$ · 6H$_2$O (2.5 mg) in 97 mL CH$_2$Cl$_2$ and 3 mL EtOH). The mixture was stirred for 1 h, after which it was poured into methanol/water 1:1 v/v (50 mL). The precipitate was filtered and the residue washed with acetone until the filtrate was colorless, followed by washing with dichloromethane. The residue was dissolved in CHCl$_3$ and precipitated in EtOAc filtered and dried, resulting in a purple/red solid (13 mg, 68 %). ^{1}H NMR (CDCl$_3$, 400.15 MHz): $\delta = 9.0 – 6.7$ (br with maxima at 8.7, 8.0, 7.2), 4.1 (br; OCH$_2$), 2.5 – 1.0 (br with maxima at 1.6, 1.5, 1.3, 0.9, 0.7, 0.6, 0.3); ^{13}C NMR (CDCl$_3$, 100.62 MHz): $\delta = 32.2$, 30.1, 23.1, 14.5 (aliphatic tails); FTIR (KBR): $\tilde{v} = 3265$ (NH), 1655 (amide), 1605 cm^{-1} (C=N).

For further characterization see text. It was not possible to determine the molecular weight of polymer **2** by GPC due to severe tailing on the column. MALDI-TOF MS experiments were also unsuccessful. AFM was used instead (see text).

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