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Chiral Water-Soluble Perylenediimides

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For the first time the synthesis of covalently linked very water-soluble chiral perylenediimides (PDIs) is presented. The PDIs carry the amino acids alanine or lysine as imide substituents, respectively, which are coupled to Newkome-type dendrimers acting as hydrophilic groups. The *tert*-butyl-protected precursors **5** as well as its water-soluble free acid compounds **6** were investigated by absorption, fluorescence and circular dichroism (CD) spectroscopy. Except for the sterically most crowded 2nd generation alanine compounds **5f** and **6f** all chiral dyes show bisignate CD effects which indicate helical aggregation. The 1st generation alanine compound **6b** shows the greatest CD effects in buffer solution and its aggregation behaviour was also directly proven by the use of cryogenic transmission electron microscopy. Furthermore, the formation of chiral superstructures of **6b** was found to be pH- and concentration-dependent.

Introduction

Perylenediimide (PDI) derivatives are thermally-, chemically- and photo-stable fluorescent dyes and in the last decades they gained more and more interest for electronic devices due to their good n-type semiconductivity.[1,2] PDIs without bay-substituents easily form aggregates with other molecules like nanotubes[3,4] or with themselves via π-π stacking.[1] The control of this self-aggregation process is an important requirement for constructing electronic devices like dye-sensitized solar cells or organic field-effect transistors. It is assumed that bay-unsubstituted PDIs prefer to form columnar π-stacks due to rotational displacements of neighbouring molecules.[5,6] Whereas achiral PDIs cause the formation of racemic mixtures of helical assemblies, PDIs with chiral substituents show a diastereoselective self-assembly to a preferred helicity. Meijer and co-workers[7] and Würthner and co-workers[8] have demonstrated that helical aggregation in organic solvents and obtained *M*- and *P*-helices dependent on the absolute configuration of the chiral side chains. In water the self-aggregation of perylenediimides should be much stronger than in organic solvents due to the additional hydrophobic effect. However, to the best of our knowledge no example of water-soluble covalently linked chiral PDIs exists in literature. Faul and co-workers[9] described the formation of chiral complexes between an achiral perylene sulfonic acid diimide salt and chiral cationic ligands by ionic self-assembly and Sun et al.[10] created PDIs with amino acids as substituents, but the corresponding chiral PDIs showed only very low solubility in water. Former studies in our group showed that Newkome dendrimers[11–13] are very versatile building blocks for solubilizing hydrophobic moieties like fullerenes,[14] calixarenes,[15] porphyrins[16] or perylenes[17] in water. Therefore we decided to use amino-acid-linked Newkome-type dendrimers as hydrophilic substituents for the construction of chiral water-soluble PDIs.

Results and Discussion

For the synthesis of chiral water-soluble PDIs the dendritic Newkome amines **1** of 1st (1G) or 2nd (2G) generation, respectively were first condensed via DCC-coupling with the Cbz-protected alanine and lysine (**2**, see Scheme 1). Lysine was taken, because the distance between its ε-amino and acid group is the same as in ε-aminocaproic acid which was taken as spacer for the achiral water-soluble PDIs that we reported previously.[17] In case of the unnatural D-lysine-based spacer (2-chloro)-Cbz-protected derivative was used as starting material. As an alternative amino acid we employed alanine, because in this case the stereogenic center is brought into closer contact with the chromophoric unit. The Cbz-protected alanine was also coupled with the elongated dendritic amines 1G-C_6 and 2G-C_6 used for the achiral PDIs described before[17] to reduce steric hindrance. The Cbz- or (2-chloro)-Cbz groups of **3** were removed by catalytic hydrogenation leading to the free amines **4** (Scheme 1). Two equivalents of these chiral dendritic amines **4** were then condensed with one equivalent of 3,4,9,10-perylenetetra-

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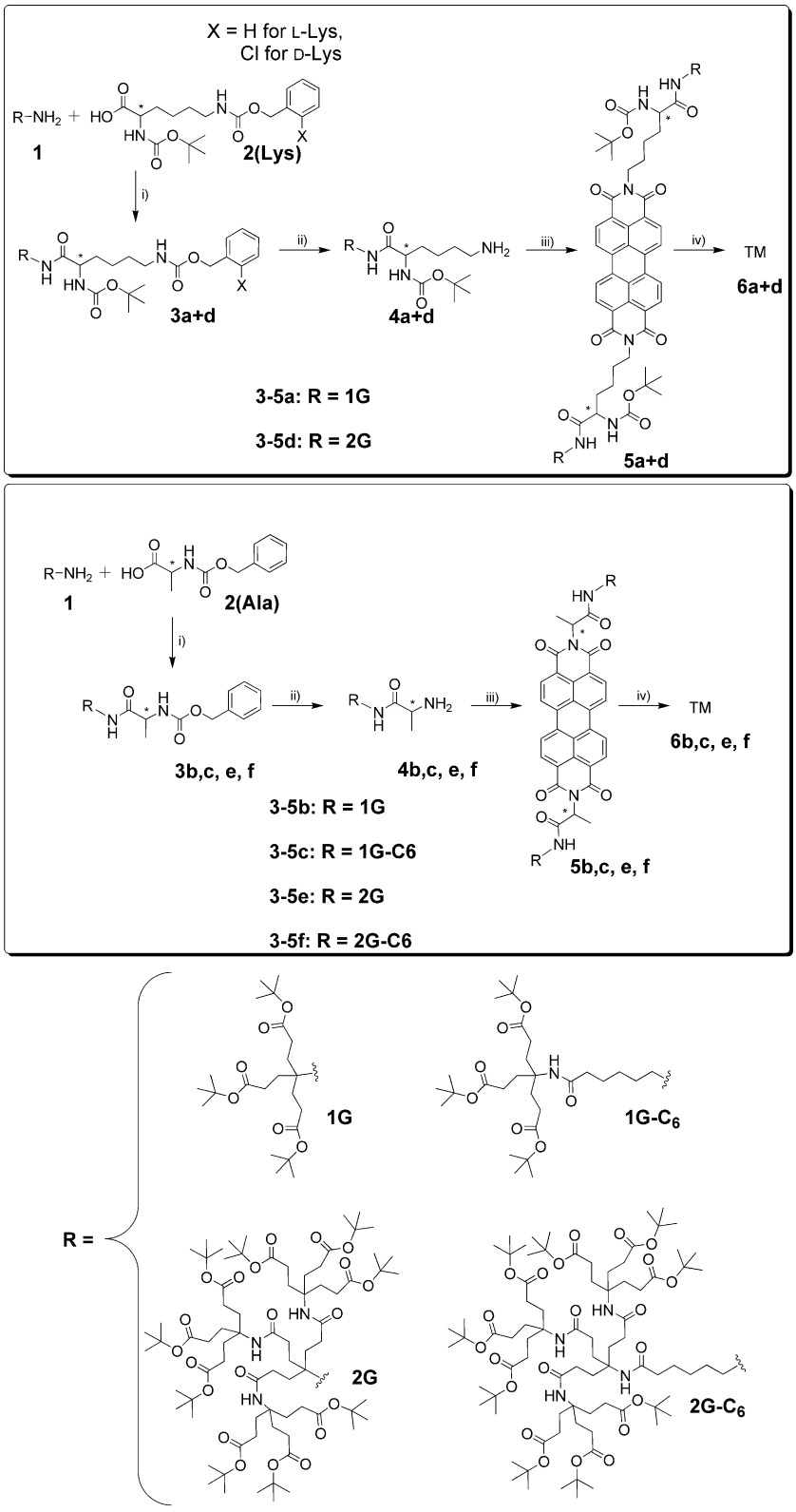
carboxylic dianhydride (PTCDA) under conditions developed by Langhals[18] with imidazole as base and zinc acetate as catalyst to yield the chiral PDIs **5**. After acidic hydrolysis of the *tert*-butyl esters the water-soluble chiral PDIs **6** were obtained (Scheme 1). The target molecules (TM) are shown in Figure 1.



Scheme 1. Synthesis of chiral water-soluble PDIs; i) DCC, DMAP, HOBt, DMF, 0 °C → r.t., 7 d; ii) H_2, Pd/C, EtOH, r.t., 5–15 h; iii) 0.5 equiv. PTCDA, imidazole, $Zn(OAc)_2$, 90 °C, 2 h; iv) CF_3COOH, $CHCl_3$, r.t. 24 h.

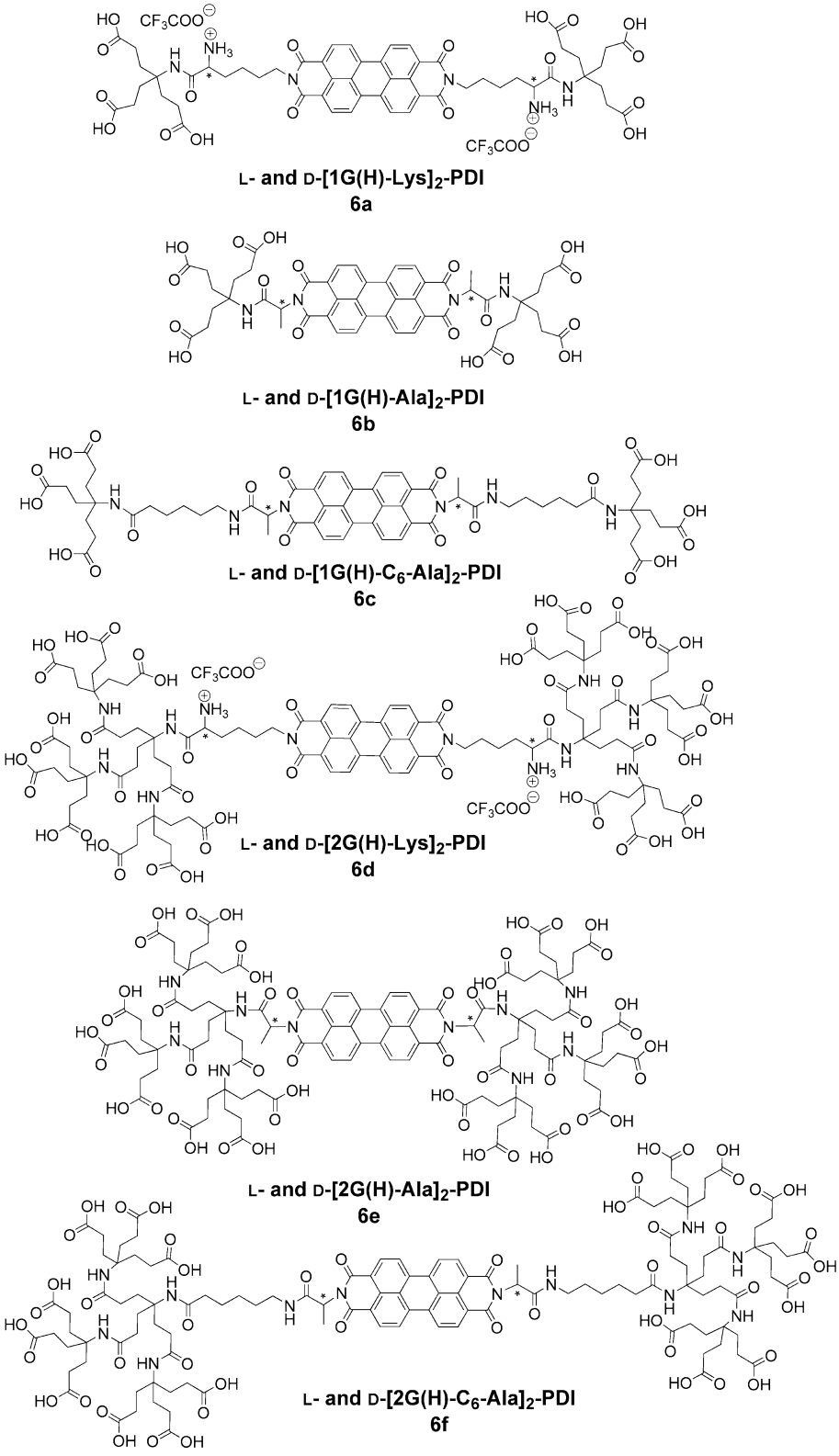


Figure 1. Target molecules (TM): highly water-soluble chiral PDIs.

All new molecules were completely characterized by NMR and IR spectroscopy as well as by mass spectrometry and elemental analysis. Additionally, the *tert*-butyl-protected chiral PDIs **5** as well as the water-soluble target molecules **6** were investigated by absorption-, fluorescence- and circular dichroism spectroscopy.

In Figure 2 the absorption spectra of the *tert*-butyl-protected PDIs **5** are shown. The PDI monomer UV/Vis spec-

tra show absorption bands between 400 and 550 nm for the S_0–S_1 transition of the perylene chromophore, with a well-resolved vibronic structure that can be attributed to breathing vibrations of the perylene skeleton which strongly couples with the S_0–S_1 transition polarized along the long axis of the molecules.[6,19,20] However, changes in the absorption ratio between the 0→0 (around 550 nm) and 0→1 (around 500 nm) transition indicate aggregation which can be quantified from the absorption ratios: while monomeric PDIs exhibit normal Franck–Condon progression with $A^{0\rightarrow0}/A^{0\rightarrow1} \approx 1.6$, aggregated PDIs display an inverted intensity distribution among their vibronic states with $A^{0\rightarrow0}/A^{0\rightarrow1} \leq 0.7$.[21–23] In Table 1 the $A^{0\rightarrow0}/A^{0\rightarrow1}$ ratios of the chiral PDIs **5** are depicted. Figure 2 and Table 1 show that compounds **5a**, **5b**, **5d** are only very weakly aggregated at a concentration of 1×10^{-4} M ($A^{0\rightarrow0}/A^{0\rightarrow1} \approx 1.4$) in toluene and **5e** is aggregated not at all ($A^{0\rightarrow0}/A^{0\rightarrow1} = 1.58$). The corresponding absorption spectra show each three bands between 460 and 531 nm with increasing intensity at higher wavelengths. For **5a**, **5b** and **5d** the absorption maximum is at 528 nm, 531 nm is observed for the most crowded 2G-alanine derivative **5e**. It was impossible to investigate concentrations larger than 1×10^{-4} M as the solutions became intransparent.

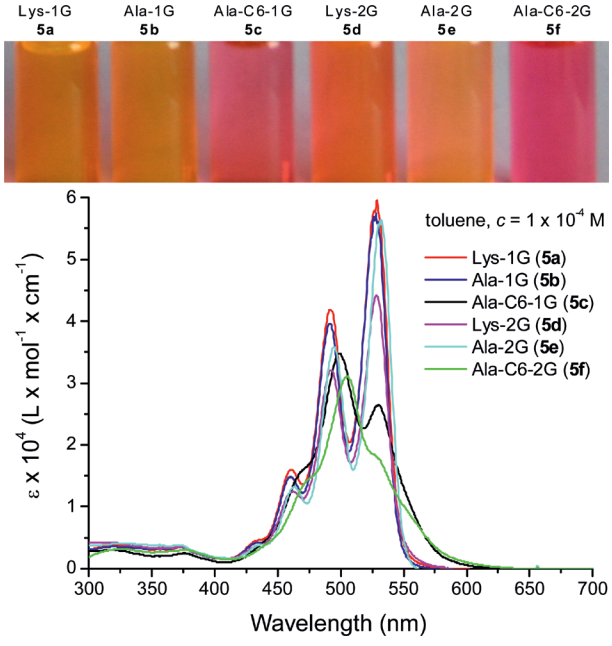


Figure 2. Top: 1×10^{-4} M solutions of **5** in toluene. Bottom: absorption spectra of the *tert*-butyl-protected PDIs **5** recorded in toluene at a concentration of 1×10^{-4} M.

Table 1. Absorption ratios $A^{0\rightarrow0}/A^{0\rightarrow1}$ of PDIs **5**.

	5a	5b	5c	5d	5e	5f
$A^{0\rightarrow0}/A^{0\rightarrow1}$	1.42	1.45	0.76	1.38	1.58	0.59[a]

[a] For compound **5f** the shoulder at 526 nm was taken as $A^{0\rightarrow0}$.

As the PDI-aggregation is due to extending π–π stacking typical spectral changes such as the decrease of the extinction coefficients and the broadening of the spectrum can be observed. The spectral features for compounds **5c** and **5f** are highly indicative of the formation of densely packed face-to-face H-type π-π stacked aggregates.[5,6,19,24] The less structured spectrum reflects the electronic coupling between the chromophoric units.[6,19] It is obvious that the alanine derivatives with a C_6-spacer (**5c** and **5f**) aggregate in toluene (Figure 2) at a concentration of 1×10^{-4} M. The extinction coefficients of **5c** and **5f** have lower intensity and the spectra show only two (**5c**) or one (**5f**) absorption band(s) instead of three compared to compounds **5a**, **5b**, **5d** and **5e**. Also the absorption maxima are shifted hypsochromically from 528 nm (**5a**, **5b**, **5d**) or 531 nm (**5e**) to 500 nm (**5c**) or 505 nm (**5f**), respectively. In addition, the ratios of $A^{0\rightarrow0}/A^{0\rightarrow1} = 0.76$ for **5c** and 0.59 for **5f** indicate that both compounds are strongly aggregated (Table 1).

Upon dilution disaggregation of the assemblies takes place and eventually at a concentration of less than 1×10^{-5} M (**5c**) or 1×10^{-6} M (**5f**), respectively, the typical monomeric PDI absorption spectrum is obtained (see Figures S1, S2 in the Supporting Information). Surprisingly, the more sterically demanding 2nd generation compound **5f** is stronger aggregated than **5c** (indicated by a monomeric spectra at lower concentration) as is reasonable by steric effects: with the 1st generation compound **5c** aggregation and disaggregation rates are faster, whereas with the 2nd generation compound **5f** self-aggregation is slow but in return stable aggregates are obtained here. That the spacer-elongated alanine compounds **5c** and **5f** behave differently than the lysine (**5a** and **5d**) or alanine compounds without spacer (**5b** and **5e**) can also been seen when looking at the colour of the corresponding solutions: in daylight the 1×10^{-4} M toluene solutions of **5c** and **5f** are pink (Figure 2, top) and non-fluorescent at 366 nm (Figure 3, top), whereas compounds **5a**, **5b**, **5d** and **5e** are yellow or orange in daylight (Figure 2, top) and show fluorescence at 366 nm (Figure 3, top). The fluorescence spectra (Figure 3, bottom) correspond to these observations: besides the lower intensity the spacer derivatives **5c** and **5f** reveal different band ratios, relating to the maximum around 580 nm the band at about 550 nm is decreased and the maximum at about 630 nm is increased.

The fact, that the insertion of a C_6-spacer triggers aggregation in toluene is further confirmed by CD-spectroscopy (Figure 4). (The spectra of the L-compounds **5a**–**f** are shown in Figure S5.) Compounds **5c** and **5f** which show characteristic aggregate absorption spectra also exhibit the highest CD effects ($\Delta\varepsilon$ = –35 and +30 for **5c** and –30 and +20 for **5f**). These $\Delta\varepsilon$ values are in the same range of magnitude as those observed by Würthner and co-workers for other types of chiral PDIs ($\Delta\varepsilon$ ca. ±20)[8] or for chiral hydrogen-bonded PDI-melamine complexes ($\Delta\varepsilon \approx$ +30 and –70),[25] determined from methylcyclohexane solutions. All other compounds show only small CD effects with $\Delta\varepsilon$ values around –5 and +5. Except for the most sterically crowded 2nd generation alanine compound **5e** all D-compounds show bisign-

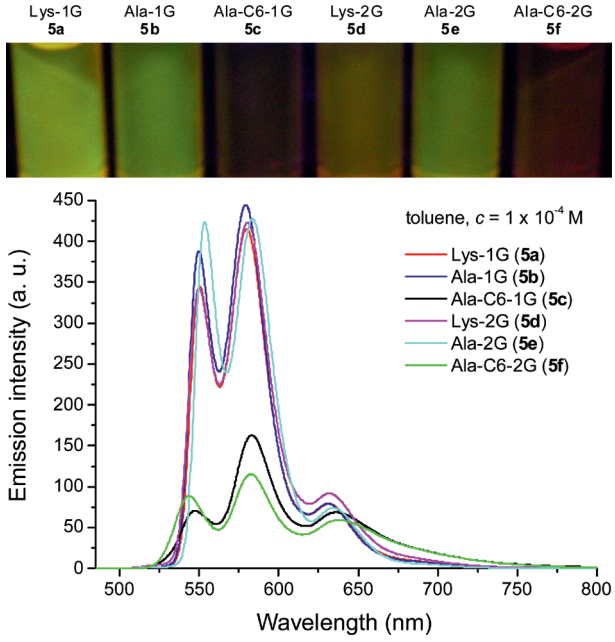


Figure 3. Top: 1×10^{-4} M solutions of **5** in toluene at 366 nm. Bottom: fluorescence spectra of *tert*-butyl-protected PDIs **5** recorded in toluene at a concentration of 1×10^{-4} M.

ate CD-effects. Bisignate CD-effects indicate aggregation via π-π stacking in a helical fashion.[9,25] From the sign of the CD-couplet the sense of the helix can be determined.[9,25] Enantiomers with D-configuration give rise to a positive sign of the couplet (change from negative to positive $\Delta\varepsilon$ values with increasing wavelength) indicating right-handedness. In the case of compounds **5a**, **5b** and **5d**, which show weak bisignate CD-effects and a typical monomer absorption spectra it is assumed that only a small amount of molecules is aggregated, probably to dimers or small oligomers. In contrast to the other D-**5** compounds, compound **5e** shows no zero-crossing in the absorption region but gives three minima localized at wavelengths where the absorption maxima are. This molecule represents the most sterically crowded system in this series, as the 2nd generation dendrimers are in close proximity to the perylene chromophore. Therefore, it is assumed that aggregation via π-π stacking is hindered by the voluminous dendrimers, which efficiently shield the π-systems.

Unlike for the *tert*-butyl-protected precursors **5**, the spacer has a much less pronounced influence on the aggregation properties of the corresponding deprotected water-soluble products **6**. Instead the size of the dendrimers plays the major role here. As can be seen in the spectra depicted in Figures 5 and 6, respectively, all 1st generation PDIs (**6a**–**c**) are strongly aggregated. Their water solutions are pink and non-fluorescent. The absorptions maxima at 500 nm are hypsochromically shifted and a second smaller maximum at 540 nm appears, which is characteristic for H-aggregation as outlined above for compounds **5c** and **5f**.

Table 2 shows $A^{0\rightarrow0}/A^{0\rightarrow1}$ ratios for the 1st generation compounds **6a**–**c** in the range of 0.47 and 0.70, which also provides evidence for strongly aggregated PDIs. In contrast

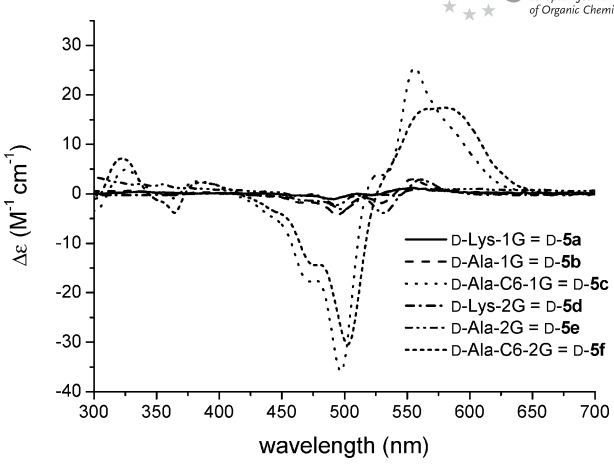


Figure 4. Circular dichroism (CD) spectra of the D-enantiomers of the *tert*-butyl-protected PDIs **5** recorded in toluene at a concentration of 1×10^{-4} M.

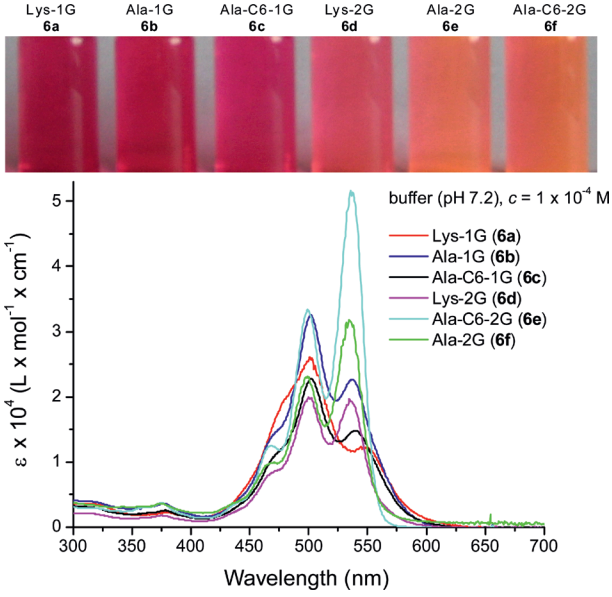


Figure 5. Top: 1×10^{-4} M solutions of **6** in phosphate buffer solution at pH 7.2. Bottom: absorption spectra of the water-soluble PDIs **6** recorded in phosphate buffer solution (pH 7.2) at a concentration of 1×10^{-4} M.

solutions of 2nd generation alanine compounds **6e** and **6f** appear orange in colour, show fluorescence and the typical fine structure for monomeric PDI absorption spectra[26] with three maxima at 468, 500 and 537 nm (Figure 5). The absorption ratios (Table 2) amount to 1.55 for **6e** (predominantly monomeric dye) and 1.37 for **6f** (almost completely monomeric dye). However, the 2nd generation lysine PDI **6d** represents an intermediate case indicating both aggregated as well as monomeric molecules at this concentration. This can be deduced from the weakly fluorescent water solutions and absorption spectra (Figure 5 and Table 2, respectively) where the maxima at 501 and 535 nm have nearly the same intensity ($A^{0\rightarrow0}/A^{0\rightarrow1}$ = 0.97). The fact that the 2nd generation lysine compound **6d** tends to aggregate more than the 2nd generation alanine derivative **6f** can be explained by the

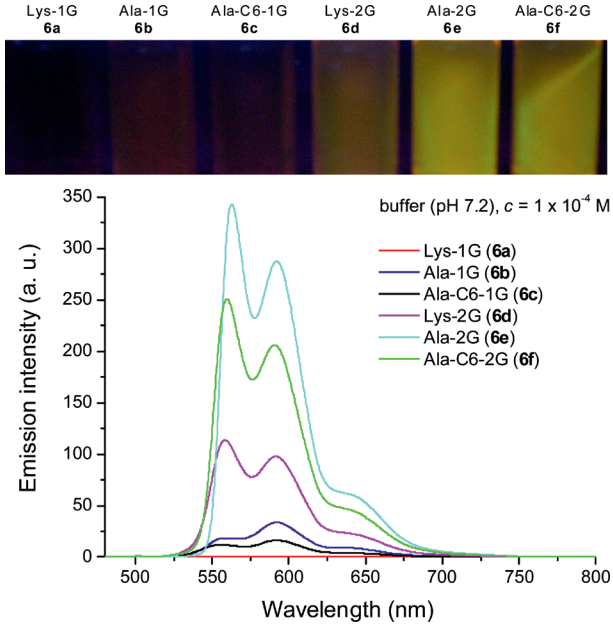


Figure 6. Top: 1×10^{-4} M solutions of **6** in phosphate buffer solution at pH7.2 at 366 nm. Bottom: fluorescence spectra of water-soluble PDIs **6** recorded in phosphate buffer at pH 7.2 at a concentration of 1×10^{-4} M.

position of the first branching unit: **6d** has the first branch (the quaternary amine) at the ε-position related to the PDI core, whereas **6f** has a methyl group in α-position. In accordance with the behaviour of the sterically crowded molecule **5e** the 2nd generation alanine compound **6e** (without spacer) does also not aggregate.

Table 2. Absorption ratios $A^{0\rightarrow0}/A^{0\rightarrow1}$ of PDIs **6**.

	6a	**6b**	**6c**	**6d**	**6e**	**6f**
$A^{0\rightarrow0}/A^{0\rightarrow1}$	0.47	0.70	0.65	0.97	1.55	1.37

Quantitative absorption measurements (Figure 10, S3, S4) of the 1G-PDIs **6a**–**c** demonstrate that the lysine **6a** derivative aggregates strongest: even upon dilution to 10^{-7} M no disaggregation of the assemblies was observed. The 1G-C6-alanine compound **6c** exists as monomer at concentrations of 10^{-6} M and below and the 1G-alanine PDI **6b** disaggregates already at 0.5×10^{-5} M.

These findings are confirmed by the corresponding fluorescence behaviour: **6a** fluoresces very weak, **6c** and **6b** more intensive (Figure 6) at 1×10^{-4} M. Considering the fluorescence spectra the following disposition for aggregation is obtained: **6a** > **6c** > **6b** > **6d** > **6f** > **6e** (Figure 6).

However, the 1st generation alanine derivative **6b** without spacer reveals the most pronounced Cotton effects in the CD-spectra (Figure 7) with Δε values above ±32. This observation can be explained by the fact that here the stereogenic center is located very close to the perylene chromophore, thus facilitating efficient chirality transfer, e.g., sense of helicity. The Cotton effects of the 1st generation PDIs **6a** and **6c** represent an intermediate case with Δε values of up to ±5. In these cases the stereocenters are located in a more remote position and as a consequence are less effective with respect to the formation of homogeneous chiral assemblies. The alanine compound with spacer **6c** has opposite Δε signs compared to the other 1st generation compounds **6a** and **6b**. Therefore it is assumed that **6c** is able to form other kinds of superstructures at this concentration due to the higher flexibility of the spacer. All 2nd generation PDIs **6d**–**f** give rise to only weak Cotton effects. In the case of the most crowded compound **6e** only one-sided (not bisignate) Cotton effects are observed which is in analogy to the corresponding *tert*-butyl-protected derivative **5e**. The spectra of the L-compounds **6a**–**f** are shown in Figure S7, Supporting Information.

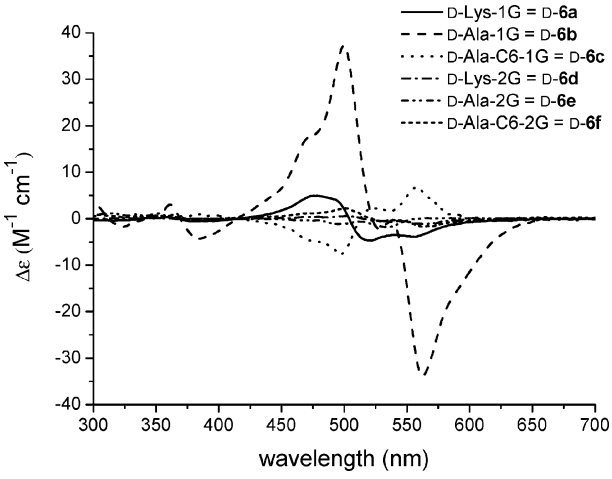


Figure 7. Circular dichroism (CD) spectra of the D-enantiomers of the water-soluble PDIs **6** recorded in phosphate buffer solution at pH7.2 at a concentration of 1×10^{-4} M.

As an example for the mirror image behaviour of PDIs enantiomers the CD-spectra of D- and L-**6b** are shown in Figure 8 recorded at a concentration of 1×10^{-4} M and a pH of 7.2. (The CD-spectra of the other enantiomer pairs **6a** and **6c**–**f** are shown in figures S9–13.) The L-enantiomer of **6b** shows a minimum at 500 nm (Δε = –36) and a maximum at 563 nm (Δε = +32) whereas the D-enantiomer gives rise to a maximum at 500 nm (Δε = +37) and minimum at 563 (Δε = –34). The strong bisignate Cotton effects have a zero-crossing at 523 nm corresponding to the minimum in the absorption spectrum at 1×10^{-4} M and the peak positions of the CD couplet almost coincides with the absorption maxima of the aggregated species at a concentration of 1×10^{-4} M. Upon dilution the CD effects diminish without a shift of the maxima or minima. From these observations a helical arrangement of two or more dyes can be assumed.[25] Furthermore, unambiguous assignment of the sense of the helicities deduced from the sign of the CD couplet can be made: a positive sign of the couplet (change from negative to positive Δε values with increasing wavelength) observed for the L-enantiomer indicates a right-handed (*P*-helical) arrangement, whereas the mirror-imaged negative CD couplet indicates a left-handed (*M*)-helicity for the D-enantiomer.[25]

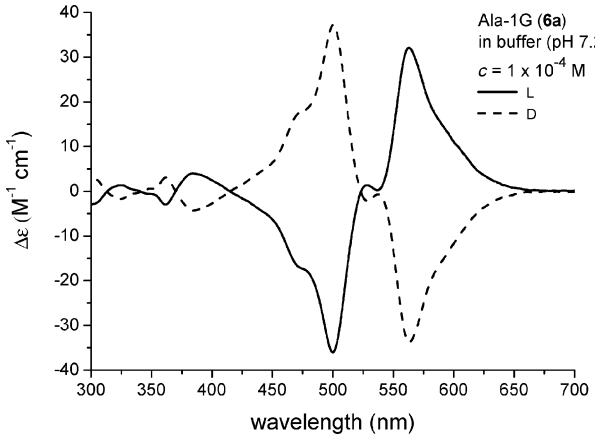


Figure 8. CD spectra of Ala-1G (**6b**) in toluene.

Concentration- and pH-dependent UV/Vis spectra of Ala-1G (**6b**) (Figures 9 and 10) measured in phosphate-buffered solution show that at 1×10^{-4} M and pH 5 the molecules are strongly aggregated, as characteristic shoulders and maxima at 483, 504.5 and 573 nm are observed. By increasing the pH to 7.2 aggregation is still observed. However, the maxima and shoulders are hypsochromically shifted to 471, 502 and 537 nm (Figure 9).

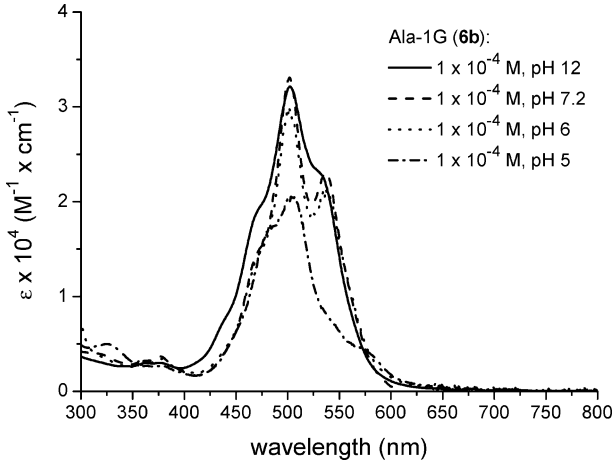


Figure 9. pH-Dependent absorption spectra of Ala-1G (**6b**) in buffer solution.

During dilution while keeping pH 7.2 constant disaggregation takes place. This is demonstrated by the fact that the absorption maximum at 537 nm increases and becomes more intensive than the maximum at 502 nm. In addition, both maxima are shifted hypsochromically to 534 and 498 nm, respectively. At a concentration of 1×10^{-6} M mostly monomeric chiral dye is present (Figure 10).

Since the 1st generation alanine compound **6b** shows the most pronounced CD-effects, its aggregation behaviour was studied in more detail and pH- and concentration-dependent CD-spectra were recorded (Figures 11 and 12).

For the pH-dependency (Figure 11) solutions of L-**6b** in the range between pH 5–12 with $c = 1 \times 10^{-3}$ M were desirable. However, for pH 5, dilution to 1.1×10^{-4} M was required due to the comparatively low solubility under these

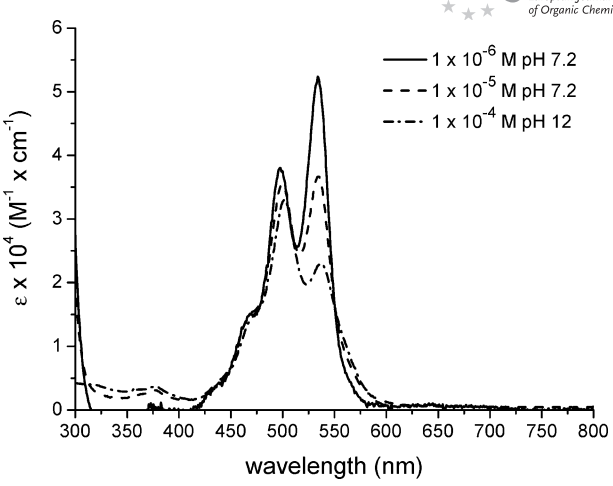


Figure 10. Concentration dependent absorption spectra of Ala-1G (**6b**) in buffer solution at a concentration of 1×10^{-4} M.

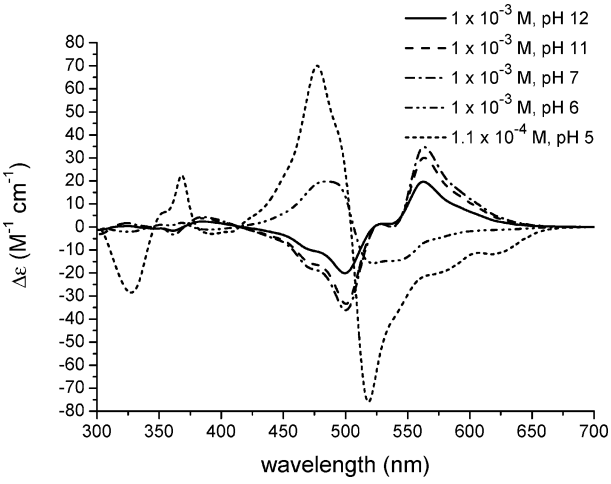


Figure 11. pH-Dependent CD spectra of L-Ala-1G (**6b**).

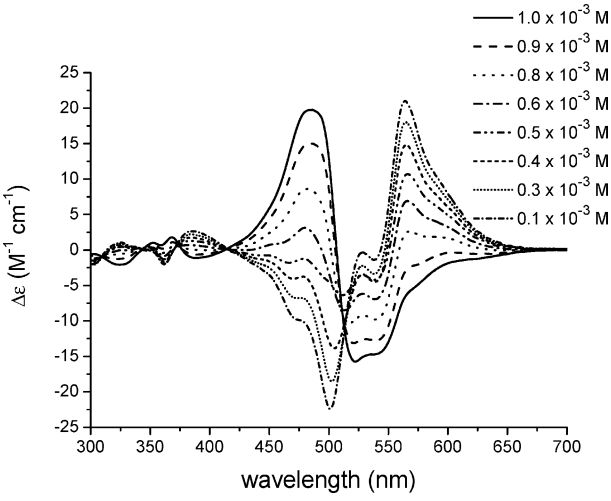


Figure 12. Concentration-dependent CD spectra of L-Ala-1G (**6b**).

conditions. Nevertheless, it can be seen that at pH 5 and 6 negative CD couplets corresponding to an *M*-helical aggregation occurs, whereas positive CD couplets and therefore

P-helical arrangements are observed for higher pH values. At pH 12 the CD couplet is less intensive than at pH 7. At pH 5 the most pronounced effects are obtained ($\Delta\varepsilon \geq \pm 70$) although the concentration is one magnitude lower than those applied for the higher pH values. The intensity dependence of the Cotton effects can be explained by the solubility: the better the solubility of the chiral compound, the lower is the corresponding the CD effect. At pH 12 all carboxylic acid groups are deprotonated. Upon lowering of the pH value the degree of protonated carboxylic acid groups increases where most carboxylic groups are protonated at pH 5.

At pH 6 concentration dependent CD spectra were recorded. The transition between *M*- and *P*-helical aggregation is shown in Figure 12. A similar concentration-dependent transition in organic solvents was observed by Würthner and co-workers:[8] At low concentration the presence of predominantly dimers was assumed, which exhibit opposite helicity than the polymeric stacks formed at higher concentration.[8] This suggests that similar effects might play a role for our water-soluble chiral PDI **6b**. To further corroborate this assumption cryo-TEM investigations were carried out at pH 6 to get a direct information about the aggregation state solutions at concentrations of 1×10^{-3} and 1×10^{-4} M, respectively (Figure 13).

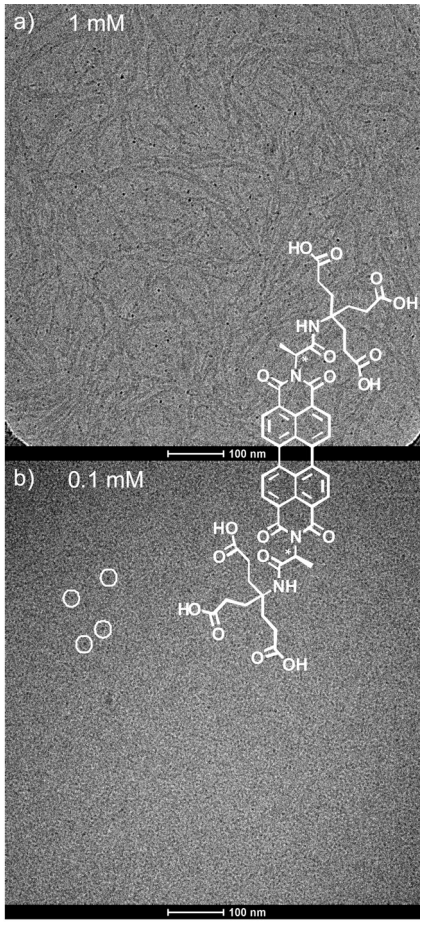


Figure 13. cryo-TEM micrographs of L-Ala-1G (**6b**) in phosphate buffer at pH 6, a) $c = 1 \times 10^{-3}$ M, b) $c = 1 \times 10^{-4}$ M (selected particles are encircled).

At a concentration of 1×10^{-3} M (Figure 13a and S14) micellar fibres with diameters of ≈ 2 nm and a length ranging from a few up to several hundred nanometers are observed. These fibers also tend to form larger twisted bundles of 15 nm diameter. Dark spots might indicate different spatial views of the fibers deviating from the orthogonal side view orientation thereby increasing the assembly contrast due to the accumulation of molecules towards the electron beam direction. At the lower concentration (1×10^{-4} M at 0.1 mM) only small particles with a diameter of about 2–3 nm are observed (highlighted in Figure 13, b), which could be assigned to small dimeric aggregates.

Conclusions

For the first time the synthesis of covalently linked water-soluble chiral PDIs and the investigation of their aggregation behaviour are reported. The aggregation properties of the *tert*-butyl-protected precursors **5** dissolved in toluene sensibly depends on the distance between chromophoric and dendritic unit. The spacer-elongated 1st and 2nd generation alanine compounds **5c** and **5f** are found to show strong aggregation and have the greatest CD-effects. In contrast, the steric bulk of dendritic termini as well as the position of the first branching unit relating to the imide positions plays the major role in the case of the water-soluble PDIs **6** and therefore the lysine 1st generation compound **6a** is aggregated strongest. Except for the most sterically hindered 2nd generation alanine compounds **5f** and **6f** all chiral PDIs show bisignate Cotton effects, which indicates helical arrangements of the perylene cores via π-π stacking. If aggregation is possible, the alanine compounds show greater CD-effects than the corresponding lysine compounds, because in the case of the alanine linkage the stereo centre is directly located at the PDI core and therefore the chirality transfer from the chiral substituents to the perylene unit is most efficient. At the same time the direct influence to the stereoselectivity of the helical aggregation is more pronounced. The 1st generation alanine compound **6b** shows the largest CD-effects with $\Delta\varepsilon > \pm 30$ associated with the highest stereoselectivity of aggregate formation. The formation of the chiral superstructures is also dependent on the pH value and the concentration. For L-**6b** at a concentration of 1×10^{-4} M at pH 5 the sign of the CD couplet is negative, whereas at pH 7.2 it is positive. This demonstrates a transition between *M*-helical polymers and *P*-helical dimers or small oligomers. Also at higher concentration (in the range between 1×10^{-3} M to 1×10^{-4} M) a concentration dependent transition at pH 6 is observed. Corroborated by TEM investigations at concentrations of 1×10^{-3} M *M*-helical polymers are found and at 10^{-4} M small *P*-helical oligomers or dimers prevail. Such a switching of the helicity by changing the pH value or the concentration is of interest for the controlled assembly of supramolecular perylene aggregates in water in order to design new electronic devices.

Experimental Section

Materials and Methods: ^1H and ^{13}C NMR spectra were recorded with a Jeol JNM EX 400, Jeol JNM GX (each 400 MHz for ^1H and 100 MHz for ^{13}C) and a Jeol Bruker Avance 300 (300 MHz for ^1H and 75 MHz for ^{13}C) spectrometer. Chemical shifts are reported in ppm at room temperature (r.t.) using $CDCl_3$ as solvent and internal standard unless otherwise indicated. Abbreviations used for splitting patterns are s = singlet, d = doublet, t = triplet, m = multiplet. IR spectra were recorded with an ASI React IR™ 1000 spectrometer. For UV/Vis spectra a Specord S 600 was used. Fluorescence was measured with a Shimadzu RF-5301 PC spectrometer. FAB-Mass spectrometry was carried out on a Micromass Zabspec (Cs+) spectrometer with 3-Nitrobenzyl alcohol as matrix for other samples a MALDI Time of Flight (TOF) mass spectrometer from Shimadzu (AXIMA Confidence) was used. The measuring mode was reflectron, used matrices were: sin (sinapinic acid) or dctb (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile). For elemental analyses a CE instrument EA 1110 CHNS was used. Circular dichroism (CD) measurements were carried out at r.t. on a Jasco J 810 spectrometer with optical grade solvents and quartz glass cuvettes with 2 mm path length.

Cryo-Transmission Electronmicroscopy. (a) Sample Preparation: Droplets of the corresponding buffered perylene solution (5 μL) were applied to perforated carbon film covered 200 mesh grids (R1/4 batch of Quantifoil Micro Tools GmbH, Jena, Germany), which had been hydrophilized before use by 60 s plasma treatment at 8 W in a BALTEC MED 020 device. The supernatant fluid was removed with a filterpaper until an ultrathin layer of the sample solution was obtained spanning the holes of the carbon film. The samples were immediately vitrified by propelling the grids into liquid ethane at its freezing point (90 K) operating a guillotine-like plunging device.

(b) Microscopy: The vitrified samples were transferred under liquid nitrogen into a Tecnai F20 FEG transmission electron microscope (FEI Company, Oregon, USA) using the Gatan (Gatan Inc., California, USA) cryoholder and -stage (Model 626). Microscopy was carried out at 94 K sample temperature using the microscopes' low dose protocol at a calibrated primary magnification of 62,000× and an accelerating voltage of 160 kV (FEG illumination). Images were recorded using an EAGLE 2k-CCD camera device (FEI Company, Oregon, USA) at full 2048 by 2048 pixel size. The defocus was chosen in all cases to be 980 nm.

General Description of DCC-Coupling Reactions. Procedure a: 1 equiv. of the Cbz-protected amino acid, 1.5 equiv. DCC, 1.5 equiv. HOBT and 1.5 equiv. DMAP were solved (under nitrogen) in DMF (abs.) and cooled down to 0 °C. Afterwards 1 equiv. of the Newkome-type dendritic amine was added. The solution was stirred at r.t. for 7 d. Then the formed DCU was filtered off, DMF was removed in vacuo and the solid was solved in ethyl acetate. The organic phase was washed with each 100 mL solutions of 10% HCl, 10% $NaHCO_3$, saturated NaCl and water. Then the organic phase was dried with $MgSO_4$. The products were purified by column chromatography as described below.

L-1G(*t*Bu)-Lys-NH-Cbz (L-3a): Purification: SiO_2, ethyl acetate:hexanes 1:1; yield 0.878 g (1.129 mmol, 43.0%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.40 (s, 27 H, CH_3), 1.42 (s, 9 H, CH_3), 1.51 (m, 5 H, CH_2), 1.75 (m, 1 H, CH_2), 1.92 (m, 6 H, CH_2), 2.17 (m, 6 H, CH_2), 3.17 (m, 2 H, CH_2), 3.88 (m, 1 H, CH), 5.06 (m, 1 H, NH), 5.11 (s, 2 H, CH_2), 6.42 (br. s, 1 H, NH), 7.29 (m, 5 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.60 (1 C, CH_2), 28.03 (9 C, CH_3), 28.29 (3 C, CH_3), 29.42 (1 C, CH_2), 29.66 (3 C, CH_2), 29.84 (3 C, CH_2), 31.55 (1 C, CH_2), 40.39 (1 C, CH_2), 54.92 (1 C, CH), 57.48 (1 C, C_{quat}), 66.61 (1 C, CH_2), 80.11 (1 C, C_{quat}), 80.66 (3 C, C_{quat}), 128.03, 128.09, 128.47 (5 C, Ar-CH), 136.59 (1 C, Ar-C_{quat}), 155.86, 155.62 (2 C, NHCOOR), 171.49 (1 C, NHCO), 172.74 (3 C, COOR) ppm. MS (FAB, NBA): *m*/*z* = 778 [M^+]. IR (ATR): $\tilde{\nu}$ = 3333, 2977, 2937, 1724, 1528, 1456, 1392, 1367, 1314, 1249, 1152, 1101, 1027, 955, 849, 776, 757 cm^{-1}. $C_{41}H_{67}N_3O_{11}$ (777.98): calcd. C 63.30, H 8.68, N 5.40; found C 63.38, H 8.86, N 5.48.

D-1G(*t*Bu)-Lys-NH-(2-Cl)Cbz (D-3a): Purification: SiO_2, ethyl acetate:hexanes, 1:1; yield 1.21 g (1.489 mmol, 61.8%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.42 (s, 27 H, CH_3), 1.45 (s, 9 H, CH_3), 1.56 (m, 5 H, CH_2), 1.79 (m, 1 H, CH_2), 1.95 (m, 6 H, CH_2), 2.20 (m, 6 H, CH_2), 3.21 (m, 2 H, CH_2), 3.91 (m, 1 H, CH), 5.09 (m, 1 H, NH), 5.21 (s, 2 H, CH_2), 6.38 (br. s, 1 H, NH), 7.17 (m, 1 H, Ar-H), 7.25 (m, 1 H, Ar-H), 7.37 (m, 1 H, Ar-H), 7.42 (m, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.60 (1 C, CH_2), 28.04 (9 C, CH_3), 28.29 (3 C, CH_3), 29.40 (1 C, CH_2), 29.64 (3 C, CH_2), 29.80 (3 C, CH_2), 31.59 (1 C, CH_2), 40.44 (1 C, CH_2), 54.87 (1 C, CH), 57.39 (1 C, C_{quat}), 63.83 (1 C, CH_2), 80.02 (1 C, C_{quat}), 80.63 (3 C, C_{quat}), 126.79, 129.22, 129.41, 129.68, 133.45, 134.35 (6 C, Ar-C), 155.82, 156.31 (2 C, NHCOOR), 171.20 (1 C, NHCO), 172.73 (3 C, COOR) ppm. MS (MALDI, dctb): *m*/*z* = 835 [M + Na^+], 851 [M + K^+]. IR (ATR): $\tilde{\nu}$ = 3349, 2981, 1726, 1528, 1456, 1392, 1367, 1316, 1247, 1152, 1100, 1037, 946, 847, 826, 773, 754 cm^{-1}. $C_{41}H_{66}ClN_3O_{11}$ (812.43): calcd. C 60.61, H 8.19, N 5.17; found C 60.69, H 8.35, N 5.12.

L- and D-1G(*t*Bu)-Ala-NH-Cbz (3b): Purification: column chromatography (SiO_2, ethyl acetate/hexanes, 1:2); yield L 1.459 g (2.35 mmol, 31.0%), D 0.860 g (1.385 mmol, 30.9%). ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.34 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.40 (s, 27 H, CH_3), 1.92 (m, 6 H, CH_2) ppm. 2.17 (m, 6 H, CH_2), 4.09 (m, 1 H, CH), 5.08 (s, 2 H, CH_2), 5.43 (d, $^3J_{H,H}$ = 6.6 Hz, 1 H, NH), 6.60 (s, 1 H, NH), 7.29 (m, 5 H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.73 (1 C, CH_3), 28.02 (9 C, CH_3), 29.66 (3 C, CH_2), 29.90 (3 C, CH_2), 50.94 (1 C, CH), 57.54 (1 C, C_{quat}), 67.00 (1 C, CH_2), 80.80 (3 C, C_{quat}), 128.09, 128.15, 128.50 (5 C, Ar-CH), 136.19 (1 C, Ar-C_{quat}), 155.94 (1 C, NHCOOR), 171.81 (1 C, NHCO), 172.90 (3 C, COOR) ppm. MS (FAB, NBA): *m*/*z* = 621 [M^+]. IR (ATR): $\tilde{\nu}$ = 3375, 3275, 2981, 2935, 1722, 1653, 1529, 1460, 1367, 1321, 1244, 1151, 1104, 1066, 1027, 958, 850, 757, 695 cm^{-1}. $C_{33}H_{52}N_2O_9$ (620.77): calcd. C 63.85, H 8.44, N 4.51; found C 64.04, H 8.71, N 4.27.

L- and D-1G(*t*Bu)-C_6-Ala-NH-Cbz (3c): Purification: column chromatography (SiO_2, ethyl acetate: hexanes 1:2); yield L 0.445 g (0.607 mmol, 76.2%), D 0.361 g (0.492 mmol, 60.7%). ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.29 (m, 2 H, CH_2), 1.35 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 1.40 (s, 27 H, CH_3), 1.46 (m, 2 H, CH_2), 1.56 (m, 2 H, CH_2), 1.92 (m, 6 H, CH_2), 2.06 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2), 2.18 (m, 6 H, CH_2), 3.19 (m, 2 H, CH_2), 4.18 (m, 1 H, CH), 5.07 (m, 2 H, CH_2), 5.60 (d, $^3J_{H,H}$ = 6.4 Hz, 1 H, NH), 5.94 (s, 1 H, NH), 6.41 (t, $^3J_{H,H}$ = 5.2 Hz, 1 H, NH), 7.31 (m, 5 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.80 (1 C, CH_3), 24.90 (1 C, CH_2), 26.24 (1 C, CH_2), 28.02 (9 C, CH_3), 28.82 (1 C, CH_2), 29.82 (3 C, CH_2), 29.92 (3 C, CH_2), 36.97 (1 C, CH_2), 39.21 (1 C, CH_2), 50.57 (1 C, CH), 57.30 (1 C, C_{quat}), 66.85 (1 C, CH_2), 80.72 (3 C, C_{quat}), 128.00, 128.12, 128.48 (5 C, Ar-CH), 136.26 (1 C, Ar-C_{quat}), 155.94 (1 C, NHCOOR), 172.25 (1 C, NHCO), 172.33 (1 C, NHCO), 172.95 (3 C, COOR) ppm. MS (MALDI, sin): *m*/*z* = 734 [M^+]; 756 [M + Na^+], 772 [M + K^+]. IR (ATR): $\tilde{\nu}$ = 3295, 2972, 2936, 1729, 1694, 1650, 1556, 1539, 1456, 1366, 1322, 1301, 1247, 1217, 1152, 1105, 1069, 955, 849, 755, 736 cm^{-1}.

$C_{39}H_{63}N_3O_{10}$ (733.93): calcd. C 63.82, H 8.65, N 5.73; found C 63.81, H 8.66, N 5.70.

L-2G(*t*Bu)-Lys-NH-Cbz (L-3d): Purification: column chromatography (SiO_2, ethyl acetate); yield 4.193 g (2.326 mmol, 91.8%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.40 (s, 81 H, CH_3), 1.42 (s, 9 H, CH_3), 1.55 (m, 2 H, CH_2), 1.77 (m, 4 H, CH_2), 1.92 (m, 24 H, CH_2), 2.16 (m, 24 H, CH_2), 3.16 (m, 2 H, CH_2), 3.81 (m, 1 H, CH), 5.05 (s, 2 H, CH_2), 5.26 (br. s, 1 H, NH), 5.75 (d, $^3J_{H,H}$ = 4.4 Hz, 1 H, NH), 6.03 (s, 1 H, NH), 6.11 (s, 3 H, NH), 7.30 (m, 5 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.92 (1 C, CH_2), 28.05 (27 C, CH_3), 28.39 (3 C, CH_3), 29.32 (1 C, CH_2), 29.79 (9 C, CH_2), 29.94 (9 C, CH_2), 30.93 (1 C, CH_2), 31.35 (6 C, CH_2), 40.51 (1 C, CH_2), 56.22 (1 C, CH), 57.26 (3 C, $C_{quat.}$), 57.88 (1 C, $C_{quat.}$), 66.43 (1 C, CH_2), 79.66 (1 C, $C_{quat.}$), 80.49 (9 C, $C_{quat.}$), 127.93, 128.09, 128.40 (5 C, Ar-CH), 136.77 (1 C, Ar-$C_{quat.}$), 156.28, 156.59 (2 C, NHCOOR), 172.66 (1 C, NHCOOR), 172.77 (9 C, COOR), 172.91 (3 C, NHCO) ppm. MS (FAB, NBA): *m*/*z* = 1802 [M^+]. IR (ATR): $\tilde{\nu}$ = 3352, 2981, 2943, 1730, 1661, 1537, 1460, 1367, 1313, 1251, 1151, 1104, 1043, 958, 850, 757, 703 cm^{-1}. $C_{95}H_{160}N_6O_{26}$ (1802.31): calcd. C 63.31, H 8.95, N 4.66; found C 62.99, H 8.89, N 4.52.

D-2G(*t*Bu)-Lys-NH-(2Cl)Cbz (D-3d): Purification: column chromatography (SiO_2, ethyl acetate); yield 0.870 g (0.474 mmol, 45.5%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.40 (s, 81 H, CH_3), 1.43 (s, 9 H, CH_3), 1.53 (m, 2 H, CH_2), 1.84 (m, 4 H, CH_2), 1.94 (m, 24 H, CH_2), 2.17 (m, 24 H, CH_2), 3.18 (m, 2 H, CH_2), 3.81 (m, 1 H, CH), 5.17 (s, 2 H, CH_2), 5.36 (br. s, 1 H, NH), 5.77 (br. s, 1 H, NH), 6.13 (s, 4 H, NH), 7.17 (m, 1 H, Ar-H), 7.21 (m, 1 H, Ar-H), 7.34 (m, 1 H, Ar-H), 7.41 (m, 1 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.89 (1 C, CH_2), 28.02 (27 C, CH_3), 28.35 (3 C, CH_3), 29.30 (1 C, CH_2), 29.72 (9 C, CH_2), 29.83 (9 C, CH_2), 30.80 (1 C, CH_2), 31.28 (3 C, CH_2), 31.86 (3 C, CH_2), 40.53 (1 C, CH_2), 56.18 (1 C, CH), 57.18 (3 C, $C_{quat.}$), 57.85 (1 C, $C_{quat.}$), 63.60 (1 C, CH_2), 79.61 (1 C, $C_{quat.}$), 80.48 (9 C, $C_{quat.}$), 126.76, 129.13, 129.34, 129.64, 133.34, 134.47 (6 C, Ar-C), 156.26 (1 C, NHCOOR), 158.31 (1 C, NHCOOR), 172.75 (9 C, COOR), 172.82 (1 C, NHCO), 172.89 (3 C, NHCO) ppm. MS (MALDI, sin): *m*/*z* = 1858 [M + Na^+]. IR (ATR): $\tilde{\nu}$ = 3328, 2978, 2937, 1726, 1673, 1529, 1457, 1392, 1367, 1315, 1257, 1152, 1101, 1035, 958, 920, 849, 800, 758, 732 cm^{-1}. $C_{95}H_{159}ClN_6O_{26}{\cdot}1CHCl_3$ (1836.78 + 119.38): calcd. C 58.94, H 8.24, N 4.30; found C 59.25, H 7.93, N 4.27.

L- and D-2G(*t*Bu)-Ala-NH-Cbz (3e): Purification: column chromatography (SiO_2, ethyl acetate/hexanes, 1:1); yield L 1.128 g (0.686 mmol, 60.6%), D 0.715 g (0.434 mmol, 51.7%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.31 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 1.39 (s, 81 H, CH_3), 1.91 (m, 24 H, CH_2), 2.15 (m, 24 H, CH_2), 3.96 (t, $^3J_{H,H}$ = 6.6 Hz, 1 H, CH), 5.12 (m, 2 H, CH_2), 6.03 (br. s, 3 H, NH), 6.09 (d, $^3J_{H,H}$ = 5.6 Hz, 1 H, NH), 7.29 (t, $^3J_{H,H}$ = 7.5 Hz, 2 H, Ar-H), 7.38 (m, 3 H, Ar-H), 8.00 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.28 (1 C, CH_3), 28.02 (27 C, CH_3), 29.73, 29.86 (18 C, CH_2), 30.89, 31.31 (6 C, CH_2), 52.15 (1 C, CH), 57.23 (3 C, C_{quat}), 57.66 (1 C, C_{quat}), 66.65 (1 C, CH_2), 80.50 (9 C, C_{quat}), 127.60, 127.73, 128.31 (5 C, ArC-H), 136.83 (1 C, ArC_{quat}), 156.38 (1 C, NHCOOR), 172.74 (9 C, COOR), 172.92 (4 C, NHCO) ppm. MS (FAB, NBA): *m*/*z* = 1645 [M^+]. IR (ATR): $\tilde{\nu}$ = 3334, 2981, 2939, 1727, 1672, 1540, 1456, 1367, 1317, 1251, 1230, 1217, 1152, 1104, 956, 849, 759 cm^{-1}. $C_{87}H_{135}N_5O_{24}$ (1645.10): calcd. C 63.52, H 8.88, N 4.26; found C 63.02, H 9.05, N 4.25.

L- and D-2G(*t*Bu)-C6-Ala-NH-Cbz (3f): Purification: column chromatography (SiO_2, ethyl acetate 100%); yield L 1.506 g (0.856 mmol, 62.1%), D 0.819 g (0.466 mmol, 72.3%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.28 (m, 2 H, CH_2), 1.35 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 1.39 (s, 81 H, CH_3), 1.55 (m, 2 H, CH_2), 1.90 (m, 26 H, CH_2), 2.07 (t, $^3J_{H,H}$ = 6.8 Hz, 2 H, CH_2), 2.15 (m, 24 H, CH_2), 3.22 (m, 2 H, CH_2), 4.20 (m, 1 H, CH), 5.07 (m, 2 H, CH_2), 6.00 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, NH), 6.17 (s, 3 H, NH), 6.70 (m 1 H, NH), 7.28 (m, 5 H, Ar-H), 7.53 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.65 (1 C, CH_3), 24.90 (1 C, CH_2), 25.99 (1 C, CH_2), 28.05 (27 C, CH_3), 28.87 (1 C, CH_2), 29.75 (18 C, CH_2), 31.59 (3 C, CH_2), 31.66 (3 C, CH_2), 36.97 (1 C, CH_2), 39.15 (1 C, CH_2), 50.43 (1 C, CH), 57.38 (3 C, C_{quat}), 57.46 (1 C, C_{quat}), 66.77 (1 C, CH_2), 80.58 (9 C, C_{quat}), 128.06, 128.46 (5 C, Ar-CH), 136.42 (1 C, Ar-C_{quat}), 156.22 (1 C, NHCOOR), 172.32 (1 C, NHCO), 172.71 (9 C, COOR), 172.92 (3 C, NHCO), 173.26 (1 C, NHCO) ppm. MS (FAB, NBA): *m*/*z* = 1757 [M^+]. IR (ATR): $\tilde{\nu}$ = 3312, 2976, 2937, 1725, 1652, 1536, 1455, 1420, 1390, 1366, 1312, 1251, 1216, 1146, 1104, 1069, 953, 849, 757, 699 cm^{-1}. $C_{93}H_{156}N_6O_{25}$ (1758.26): calcd. C 63.53, H 8.94, N 4.78; found C 63.73, H 8.97, N 4.62.

General Description of Hydrogenation Reactions. Procedure b: Compound from **Procedure a** (see above) was solved in ethanol and Pd/C catalyst was added. Hydrogen was flushed through for 5–15 h. Afterwards the Pd-catalyst was removed by filtering the solution over Celite 500. The solvent was evaporated and without further purification a white solid was obtained as product.

L- and D-1G(*t*Bu)-Lys-NH_2 (4a): Yield L 655 mg (1.018 mmol, 92.96%), D 887 mg (1.38 mmol, 98.7%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.21 (m, 1 H, CH_2), 1.38 (s, 9 H, CH_3), 1.39 (s, 27 H, CH_3), 1.50 (m, 4 H, CH_2), 1.73 (m, 1 H, CH_2), 1.90 (m, 6 H, CH_2), 2.14 (m, 6 H, CH_2), 2.72 (t, $^3J_{H,H}$ = 6.8 Hz, 2 H, CH_2), 3.15 (br. s, 2 H, NH_2), 3.89 (1 H, CH), 5.14 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, NH), 6.47 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.71 (1 C, CH_2), 28.04 (9 C, CH_3), 28.30 (3 C, CH_3), 29.63 (3 C, CH_2), 29.68 (1 C, CH_2), 29.79 (3 C, CH_2), 31.82 (1 C, CH_2), 41.19 (1 C, CH_2), 54.92 (1 C, CH), 57.50 (1 C, C_{quat}), 80.01 (1 C, C_{quat}), 80.59 (3 C, C_{quat}), 155.85 (1 C, NHCOOR), 171.38 (1 C, NHCO), 172.72 (3 C, COOR) ppm. MS (FAB, NBA): *m*/*z* = 644 [M^+]. IR (ATR): $\tilde{\nu}$ = 3280, 2981, 2940, 1721, 1509, 1458, 1392, 1367, 1317, 1253, 1155, 1101, 1055, 951, 849, 762, 652, 634, 614 cm^{-1}. $C_{33}H_{61}N_3O_9{\cdot}1CH_3CH_2OH$ (643.86 + 46.07): calcd. C 60.93, H 9.79, N 6.09; found C 60.67, H 9.34, N 6.24.

L- and D-1G(*t*Bu)-Ala-NH_2 (4b): Yield L 221 mg (0.454 mmol, 85.15%), D 651 mg (1.338 mmol, 97.7%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.31 (d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3), 1.39 (s, 27 H, CH_3), 1.93 (m, 6 H, CH_2), 2.16 (m, 6 H, CH_2), 2.46 (br. s, 2 H, NH_2), 3.47 (m, 1 H, CH), 7.20 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.37 (1 C, CH_3), 28.04 (9 C, CH_3), 29.69 (3 C, CH_2), 29.72 (3 C, CH_2), 51.05 (1 C, CH), 56.68 (1 C, C_{quat}), 80.54 (3 C, C_{quat}), 172.66 (3 C, COOR), 172.86 (1 C, NHCO) ppm. MS (FAB, NBA): *m*/*z* = 488 [M^+]. IR (ATR): $\tilde{\nu}$ = 2981, 2927, 1722, 1668, 1529, 1460, 1367, 1321, 1220, 1151, 1043, 950, 919, 749, 664 cm^{-1}. $C_{25}H_{46}N_2O_7$ (486.64): calcd. C 61.70, H 9.53, N 5.76; found C 61.35, H 9.19, N 5.66.

L- and D-1G(*t*Bu)-C6-Ala-NH_2 (4c): Yield L 342 mg (0.570 mmol, 97.9%), D 261 mg (0.435 mmol, 98.9%). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.32 (m, 5 H, CH_3 + CH_2), 1.40 (s, 27 H, CH_3), 1.49 (m, 2 H, CH_2), 1.59 (m, 2 H, CH_2), 1.92 (t, $^3J_{H,H}$ = 7.8 Hz, 6 H, CH_2), 2.09 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, CH_2), 2.18 (t, $^3J_{H,H}$ = 7.8 Hz, 6 H,CH_2), 2.33 (br. s, 2 H, NH_2), 3.21 (m, 2 H, CH_2), 3.51 (m, 1 H, CH), 5.96 (br. s, 1 H, NH), 7.38 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.43 (1 C, CH_3), 25.21 (1 C, CH_2), 26.41 (1 C, CH_2), 28.04 (9 C, CH_3), 29.14 (1 C, CH_2), 29.81 (3 C, CH_2), 29.90 (3 C, CH_2), 37.19 (1 C, CH_2), 38.74 (1 C, CH_2), 50.62 (1 C, CH), 57.29 (1 C, C_{quat}), 80.69 (3 C, C_{quat}), 172.40 (1 C, NHCO),

172.86 (1 C, NHCO), 172.96 (3 C, COOR) ppm. MS (MALDI, sin): *m*/*z* = 600 [M$^+$]; 622 [M + Na$^+$]. IR (ATR): $\tilde{\nu}$ = 3327, 2978, 2936, 1727, 1653, 1541, 1508, 1457, 1392, 1367, 1317, 1256, 1153, 1104, 1054, 957, 849, 822, 758 cm^{-1}. $C_{31}H_{57}N_3O_8$·1CH_3CH_2OH (599.81 + 46.07): calcd. C 61.37, H 9.83, N 6.51; found C 61.37, H 10.11, N 6.46.

L- and D-2G(*t*Bu)-Lys-NH$_2$ (4d): Yield L 900 mg (0.540 mmol, 97.0%), D 550 mg (0.330 mmol, 90.1%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, NH_2), 1.40 (s, 81 H, CH_3), 1.43 (s, 9 H, CH_3), 1.59 (m, 2 H, CH_2), 1.81 (m, 4 H, CH_2), 1.93 (m, 24 H, CH_2), 2.17 (m, 24 H, CH_2), 2.72 (m, 2 H, CH_2), 3.86 (m, 1 H, CH), 5.99 (d, $^3J_{H,H}$ = 6.0 Hz, 1 H, NH), 6.29 (br. s, 3 H, NH), 7.70 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.46 (1 C, CH_2), 27.85 (1 C, CH_2), 28.08 (27 C, CH_3), 28.29 (1 C, CH_2), 28.40 (3 C, CH_3), 29.70 (9 C, CH_2), 29.86 (9 C, CH_2), 31.73 (6 C, CH_2), 39.78 (1 C, CH_2), 56.25 (1 C, CH), 57.26 (3 C, C_{quat}), 57.42 (1 C, C_{quat}), 79.66 (1 C, C_{quat}), 80.52 (3 C, C_{quat}), 156.20 (1 C, NHCOOR), 172.67 (3 C, NHCO), 172.80 (9 C, COOR), 172.90 (1 C, NHCO) ppm. MS (FAB, NBA): *m*/*z* = 1668 [M$^+$]. IR (ATR): $\tilde{\nu}$ = 2981, 2932, 1730, 1661, 1537, 1460, 1367, 1313, 1251, 1151, 1104, 1043, 950, 850, 757 cm^{-1}. $C_{87}H_{154}N_6O_{24}$·1CH_3CH_2OH (1668.20+46.07): calcd. C 61.85, H 9.21, N 4.86; found C 61.82, H 9.16, N 4.85.

L- and D-2G(*t*Bu)-Ala-NH$_2$ (4e): Yield L 351 mg (0.232 mmol, 90.1%), D 255 mg (1.688 mmol, 98.8%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (m, 3 H, CH_3), 1.39 (s, 81 H, CH_3), 1.91 (m, 24 H, CH_2), 2.11 (m, 6 H, CH_2), 2.16 (m, 18 H, CH_2), 2.62 (br. s, 2 H, NH_2), 4.18 (m, 1 H, CH), 6.09 (br. s, 4 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.57 (1 C, CH_3), 28.04 (27 C, CH_3), 29.77 (9 C, CH_2), 29.83 (9 C, CH_2), 31.64 (3 C, CH_2), 31.96 (3 C, CH_2), 51.28 (1 C, CH), 57.33 (1 C, C_{quat}), 57.37 (3 C, C_{quat}), 80.49 (9 C, C_{quat}), 171.89 (1 C, NHCO), 172.46 (3 C, NHCO), 172.72 (9 C, COOR) ppm. MS (FAB, NBA): *m*/*z* = 1511 [M$^+$]. IR (ATR): $\tilde{\nu}$ = 3316, 2980, 2934, 2880, 1729, 1652, 1536, 1455, 1420, 1393, 1366, 1312, 1251, 1216, 1150, 1104, 1034, 953, 923, 849, 757, 718 cm^{-1}. $C_{79}H_{139}N_5O_{22}$ (1510.97): calcd. C 62.80, H 9.27, N 4.64; found C 62.72, H 9.35, N 4.74.

L- and D-2G(*t*Bu)-C6-Ala-NH$_2$ (4f): Yield L 461 mg (0.284 mmol, 99.6%), D 671 mg (0.413 mmol, 98.1%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (m, 5 H, CH_2 + CH_3), 1.39 (s, 81 H, CH_3), 1.50 (m, 2 H, CH_2), 1.58 (m, 2 H, CH_2), 1.90 (m, 24 H, CH_2), 2.14 (m, 26 H, CH_2), 3.23 (m, 2 H, CH_2), 6.21 (m, 1 H, CH), 6.34 (br. s, 2 H, NH), 6.46 (br. s, 3 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.42 (1 C, CH_3), 24.84 (1 C, CH_2), 25.51 (1 C, CH_2), 26.33 (1 C, CH_2), 28.03 (27 C, CH_3), 29.69 (9 C, CH_2), 29.74 (9 C, CH_2), 31.69 (6 C, CH_2), 37.10 (1 C, CH_2), 38.57 (1 C, CH_2), 50.41 (1 C, CH), 57.41 (3 C, C_{quat}), 57.69 (1 C, C_{quat}), 80.56 (9 C, C_{quat}), 172.72 (3 C, NHCO), 172.80 (9 C, COOR), 173.09 (1 C, NHCO), 173.45 (1 C, NHCO) ppm. MS (FAB, NBA): *m*/*z* = 1624 [M$^+$]. IR (ATR): $\tilde{\nu}$ = 3316, 2976, 1725, 1648, 1540, 1455, 1390, 1366, 1312, 1251, 1216, 1146, 1104, 1034, 953, 849, 757 cm^{-1}. $C_{85}H_{150}N_6O_{23}$ (1624.13): calcd. C 62.86, H 9.31, N 5.17; found C 62.88, H 9.37, N 5.24.

General Description of Condensation Reactions. Procedure c: In a small round-bottomed flask 2 equiv. of compound from **Procedure b**, 1 equiv. PTCDA, 20 equiv. imidazole and 0.3 equiv. $Zn(OAc)_2$ were heated to 90 °C for 2 h. After cooling down to r.t. the red product was purified by flash chromatography as described below.

L- and D-*N*,*N*′-[1G(*t*Bu)-Lys]$_2$-perylene-3,4,9,10-tetracarboxylic Acid Diimide (5a): Purification: flash chromatography (SiO_2, ethyl acetate); yield L 86.5 mg (0.053 mmol, 66.4%), D 78.5 mg (0.048 mmol, 20.7%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.40 (s, 72 H, CH_3) 1.51 (m, 4 H, CH_2), 1.74 (m, 4 H, CH_2), 1.98 (m, 16 H, CH_2), 2.21 (m, 12 H, CH_2), 3.98 (br. s, 2 H, CH), 4.18 (m, 4 H, CH_2), 5.25 (d, $^3J_{H,H}$ = 7.3 Hz, 2 H, NH), 6.44 (br. s, 2 H, NH), 8.30, 8.47 (m, 8 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.83 (2 C, CH_2), 27.07 (2 C, CH_2), 28.03 (18 C, CH_3), 28.29 (6 C, CH_3), 29.60 (6 C, CH_2), 29.75 (6 C, CH_2), 31.32 (2 C, CH_2), 39.60 (2 C, CH_2), 54.75 (2 C, CH), 57.42 (2 C, C_{quat}), 79.88 (2 C, C_{quat}), 80.48 (6 C, C_{quat}), 122.91, 125.81, 128.90, 131.18 134.11 (6 C, Ar-C), 156.00 (2 C, NHCOOR), 163.19 (4 C, C_{imide}), 171.83 (2 C, NHCO), 172.68 (6 C, COOR) ppm. IR (ATR): $\tilde{\nu}$ = 3355, 2921, 2851, 1728, 1700, 1653, 1595, 1577, 1559, 1541, 1508, 1458, 1403, 1366, 1345, 1258, 1217, 1153, 1099, 1033, 961, 850, 810, 746, 720 cm^{-1}. UV/Vis (toluene, 1×10^{-4} M): λ_{max} = 461 nm, 492, 528; fluorescence (toluene, 1×10^{-4} M): λ_{max} = 550 nm, 580, 631. MS (FAB, NBA): *m*/*z* = 1643 [M$^+$]. $C_{90}H_{126}N_6O_{22}$·0.5$CHCl_3$ (1643.99+59.69): calcd. C 63.80, H 7.48, N 4.93; found C 63.81, H 7.41, N 4.70.

L- and D-*N*,*N*′-[1G(*t*Bu)-Ala]$_2$-perylene-3,4,9,10-tetracarboxylic Acid Diimide (5b): Purification: column chromatography (SiO_2, $CHCl_3$); yield L 148.1 mg (0.111 mmol, 49.3%), D 110 mg (0.083 mmol, 23.4%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (s, 54 H, CH_3), 1.72 (d, $^3J_{H,H}$ = 7.1 Hz, 6 H, CH_3), 1.99 (m, 12 H, CH_2), 2.28 (m, 12 H, CH_2), 5.65 (m, 2 H, CH), 6.73 (s, 2 H, NH), 8.53 (m, 8 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.60 (2 C, CH_3), 27.99 (18 C, CH_3), 29.73 (6 C, CH_2), 30.18 (6 C, CH_2), 50.94 (2 C, CH), 57.61 (2 C, C_{quat}), 80.50 (6 C, C_{quat}), 122.98, 123.36, 126.22, 129.42, 131.50, 134.45 (20 C, Ar-C), 162.86 (4 C, C_{imide}), 168.82 (2 C, NHCO), 173.31 (6 C, COOR) ppm. UV/Vis (toluene, 1×10^{-4} M): λ_{max} = 460.5 nm, 491, 528; fluorescence (toluene, 1×10^{-4} M): λ_{max} = 550 nm, 579, 631. MS (FAB, NBA): *m*/*z* = 1330 [M$^+$]. IR (ATR): $\tilde{\nu}$ = 3375, 2981, 2943, 1707, 1661, 1591, 1529, 1460, 1367, 1313, 1251, 1151, 1035, 958, 850, 811, 749 cm^{-1}. $C_{74}H_{96}N_4O_{18}$·1$CHCl_3$ (1329.59+119.38): calcd. C 62.17, H 6.75, N 3.87; found C 62.67, H 6.93, N 3.71.

L- and D-*N*,*N*′-[1G(*t*Bu)-C$_6$-Ala-]$_2$-perylene-3,4,9,10-tetracarboxylic Acid Diimide (5c): Purification: column chromatography (SiO_2, $CHCl_3$: EtOH 19:1); yield L 84.5 mg (0.054 mmol, 38.2%), D 80.8 mg (0.052 mmol, 52.5%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.38 (s, 54 H, CH_3), 1.46 (m 4 H, CH_2), 1.66 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH_3), 1.69 (m, 4 H, CH_2), 1.89 (m, 4 H, CH_2), 1.97 (m, 12 H, CH_2), 2.20 (m, 16 H, CH_2), 3.45 (m, 4 H, CH_2), 5.63 (m, 2 H, CH), 6.02 (s, 2 H, NH), 7.04 (s, 2 H, NH), 8.27 (m, 8 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.59 (2 C, CH_3), 25.59 (2 C, CH_2), 26.56 (2 C, CH_2), 28.02 (18 C, CH_3), 29.42 (2 C, CH_2), 29.81 (6 C, CH_2), 29.92 (6 C, CH_2), 37.37 (2 C, CH_2), 39.78 (2 C, CH_2), 50.65 (2 C, CH), 57.30 (2 C, C_{quat}), 80.65 (6 C, C_{quat}), 122.50, 123.29, 125.20, 128.38, 131.07, 133.91 (20 C, Ar-C), 162.69 (4 C, C_{imide}), 169.45 (2 C, NHCO), 172.56 (2 C, NHCO), 173.31 (6 C, COOR) ppm. MS (MALDI, dhb): *m*/*z* = 1578 [M + Na$^+$]. UV/Vis (toluene, 1×10^{-4} M): λ_{max} (ε) = 499 nm (34728), 530 (26438); fluorescence (toluene, 1×10^{-4} M): λ_{max} = 548 nm, 583, 636. IR (ATR): $\tilde{\nu}$ = 3364, 2977, 2937, 1727, 1700, 1659, 1594, 1533, 1457, 1392, 1367, 1343, 1315, 1254, 1152, 1104, 1038, 972, 958, 849, 811, 747 cm^{-1}. $C_{86}H_{118}N_6O_{20}$·0.4$CHCl_3$ (1555.89+47.75): calcd. C 64.71, H 7.44, N 5.24; found C 64.48, H 7.81, N 5.18.

L- and D-*N*,*N*′-[2G(*t*Bu)-Lys]$_2$-perylene-3,4,9,10-tetracarboxylic Acid Diimide (5d): Purification: column chromatography (SiO_2, ethyl acetate); yield L 386 mg (0.105 mmol, 76.2%), D 115 mg (0.031 mmol, 48.3%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (s, 162 H, CH_3), 1.41 (m, 4 H, CH_2), 1.43 (s, 9 H, CH_3), 1.78 (m, 4 H, CH_2), 1.91 (m, 54 H, CH_2), 2.10 (m, 4 H, CH_2), 2.16 (t, $^3J_{H,H}$ = 8.1 Hz, 54 H, CH_2), 3.82 (m, 2 H, CH), 4.18 (m, 4 H, CH_2), 5.81 (d, $^3J_{H,H}$ = 5.5 Hz, 2 H, NH), 6.10 (s, 2 H, NH), 6.17 (s, 6 H, NH),

8.66 (m, 8 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.32 (2 C, CH_2), 27.51 (2 C, CH_2), 28.02 (54 C, CH_3), 28.38 (2 C, CH_3), 29.76 (18 C, CH_2), 29.88 (18 C, CH_2), 30.97 (6 C, CH_2), 31.34 (6 C, CH_2), 31.74 (2 C, CH_2), 40.47 (2 C, CH_2), 56.33 (2 C, CH), 57.26 (6 C, C_{quat}), 57.90 (2 C, C_{quat}), 79.74 (2 C, C_{quat}), 80.41 (18 C, C_{quat}), 123.23, 126.47, 128.38, 129.38, 131.63, 134.76 (20 C, Ar-C), 156.29 (2 C, NHCOOR), 163.54 (4 C, C_{imide}), 172.72 (18 C, COOR), 172.77 (6 C, NHCO), 172.81 (2 C, NHCO) ppm. IR (ATR): $\tilde{\nu}$ = 3352, 2981, 2943, 1730, 1661, 1599, 1529, 1460, 1367, 1313, 1251, 1151, 1043, 958, 850, 811, 757, 695 cm^{-1}. UV/Vis (toluene, 1×10^{-4} M): λ_{max} = 462 nm, 492, 528; fluorescence (toluene, 1×10^{-4} M): λ_{max} = 550 nm, 581, 632. MS (FAB, NBA): *m*/*z* = 3694 [M$^+$]. $C_{193}H_{312}N_{12}O_{52}$ (3692.65): calcd. C 64.40, H 8.52, N 4.55; found C 64.08, H 8.62, N 4.29.

L- and D-*N*,*N*′-[2G(*t*Bu)-Ala-]$_2$-perylene-3,4,9,10-tetracarboxylic Acid Diimide (5e): Purification: column chromatography (SiO_2, EtOH/$CHCl_3$, 1:19); yield L 52.1 mg (0.015 mmol, 14.8%), D 115.8 mg (0.034 mmol, 48.2%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.39 (s, 162 H, CH_3), 1.63 (m, 6 H, CH_3), 1.80 (m, 12 H, CH_2), 1.92 (m, 36 H, CH_2), 2.14 (m, 48 H, CH_2), 5.68 (m, 2 H, CH), 6.00 (s, 2 H, NH), 6.10 (s, 6 H, NH), 8.68 (m, 8 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.31 (2 C, CH_3), 28.02 (81 C, CH_3), 29.60 (18 C, CH_2), 29.67 (18 C, CH_2), 31.66 (6 C, CH_2), 31.82 (6 C, CH_2), 50.61 (2 C, CH), 57.15 (3 C, C_{quat}), 57.95 (1 C, C_{quat}), 80.41 (18 C, C_{quat}), 123.31, 123.58, 126.63, 129.49, 131.63, 135.06 (20 C, Ar-C), 163.33 (4 C, C_{imide}), 169.70 (2 C, NHCO), 172.59 (18 C, COOR), 173.29 (6 C, NHCO) ppm. MS (FAB, NBA): *m*/*z* = 3400 [M + Na$^+$]. UV/Vis (toluene, 1×10^{-4}): λ_{max} = 463 nm, 494, 531; fluorescence (toluene, 1×10^{-4} M): λ_{max} = 553 nm, 584, 634. IR (ATR): $\tilde{\nu}$ = 3327, 2976, 2934, 2856, 1725, 1625, 1594, 1536, 1455, 1393, 1366, 1312, 1254, 1216, 1146, 1100, 1034, 953, 923, 849, 811, 757 cm^{-1}. $C_{182}H_{282}N_{10}O_{48}$ (3378.22): calcd. C 64.71, H 8.41, N 4.15; found C 64.37, H 8.72, N 4.28.

L- and D-*N*,*N*′-[2G(*t*Bu)-C_6-Ala-]$_2$-perylene-3,4,9,10-tetracarboxylic Acid Diimide (5f): Purification: column chromatography (SiO_2, ethyl acetate:$CHCl_3$ 2:1); yield L 52.4 mg (0.015 mmol, 10.8%), D 51 mg (0.014 mmol, 13.5%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.38 (s, 162 H, CH_3), 1.58 (m, 12 H, CH_2), 1.71 (d, $^3J_{H,H}$ = 6.84 Hz, 6 H, CH_3), 1.92 (m, 58 H, CH_2), 2.15 (m, 54 H, CH_2), 3.33 (m, 4 H, CH_2), 5.70 (quat, $^3J_{H,H}$ = 6.8 Hz, 2 H, CH), 6.14 (br. s, 6 H, NH), 6.53 (br. s, 2 H, NH), 7.46 (s, 2 H, NH), 8.52 (m, 8 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.56 (2 C, CH_3), 25.17 (2 C, CH_2), 26.33 (2 C, CH_2), 27.96 (81 C, CH_3), 29.06 (2 C, CH_2), 29.68 (36 C, CH_2), 31.59 (6 C, CH_2), 31.73 (6 C, CH_2), 37.10 (2 C, CH_2), 39.58 (2 C, CH_2), 50.48 (2 C, CH), 57.32 (3 C, C_{quat}), 57.45 (1 C, C_{quat}), 80.52 (18 C, C_{quat}), 123.14, 123.30, 126.17, 129.28, 131.59, 134.56 (20 C, Ar-C), 163.04 (4 C, C_{imide}), 169.57 (2 C, NHCO), 172.77 (18 C, COOR), 172.97 (6 C, NHCO), 173.44 (2 C, NHCO) ppm. UV/Vis (toluene, 1×10^{-4} M): λ_{max} = 505.5 nm; fluorescence (toluene, 1×10^{-4} M): λ_{max} = 544 nm, 583, 637. MS (FAB, NBA): *m*/*z* = 3606 [M$^+$]. IR (ATR): $\tilde{\nu}$ = 3356, 2978, 2933, 1727, 1658, 1595, 1536, 1456, 1392, 1367, 1343, 1315, 1255, 1152, 1104, 1039, 957, 849, 811, 758, 682, 671, 640 cm^{-1}. $C_{194}H_{304}N_{12}O_{50}$·0.5$CHCl_3$ (3604.54+59.69): calcd. C 63.75, H 8.38, N 4.59; found C 63.60, H 8.51, N 4.53.

General Description of Deprotection Reactions. Procedure d: Compound from **Procedure c**, was solved in $CHCl_3$/TFA, 2:1 and stirred for 24 h at room temperature. After drying in vacuo the product was obtained without purification.

L- and D-*N*,*N*′-{[1G(H)-Lys]$^+$$CF_3COO^-$}$_2$-perylene-3,4,9,10-tetracarboxylic Acid Diimide (6a): Yield L 26.5 mg (0.020 mmol, 98.9%), D 23.0 mg (0.017 mmol, 96.6%). ^{1}H NMR (400 MHz, $CDCl_3$/CF_3COOH 2:1): δ = 1.72 (4 H, CH_2), 1.96 (4 H, CH_2), 2.22 (m, 16 H, CH_2), 2.55 (m, 12 H, CH_2), 4.31 (m, 2 H, CH), 4.36 (m, 4 H, CH_2), 7.38 (s, 2 H, NH), 7.42 (br. s, 6 H, NH_3), 8.16 (s, 2 H, 21), 8.84 (m, 8 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$/CF_3COOH, 2:1): δ = 22.62 (2 C, CH_2), 27.28 (2 C, CH_2), 28.50 (6 C, CH_2), 29.64 (6 C, CH_2), 31.51 (2 C, CH_2), 40.96 (2 C, CH_2), 55.83 (2 C, CH), 60.44 (2 C, C_{quat}), 122.58, 124.90, 127.04, 129.91, 133.58, 136.71 (20 C, Ar-C), 166.41 (4 C, C_{imide}), 167.85 (21, 2 C), 180.35 (2 C, NHCO), 180.67 (6 C, COOR) ppm. MS (MALDI, sin, MeOH): *m*/*z* = 1109 [M$^+$ –H$^+$ – 2 CF_3COO^-]. IR (ATR): $\tilde{\nu}$ = 2922, 2853, 1686, 1594, 1596, 1578, 1447, 1405, 1347, 1196, 1140, 844, 810, 799, 748, 724, 668, 650 cm^{-1}. UV/Vis (phosphate buffer, pH 7.2, 1×10^{-4} M): λ_{max} = 501.5 nm, 546.5; fluorescence (phosphate buffer, pH 7.2, 1×10^{-4} M): λ_{max} = 552 nm, 595. $C_{60}H_{64}F_6N_6O_{24}$·2.5CF_3COOH (1367.18 + 285.06): calcd. C 8.18, H 4.14, N 5.19; found C 47.93, H 4.05, N 5.13.

L- and D-*N*,*N*′-[1G(H)-Ala]$_2$-perylene-3,4,9,10-tetracarboxylic Acid Diimide (6b): Yield L 57.2 mg (0.058 mmol, 89.6%), D 59.5 mg (0.060 mmol, 99.6%). ^{1}H NMR (400 MHz, $CDCl_3$/CF_3COOH, 2:1): δ = 1.85 (d, $^3J_{H,H}$ = 6.6 Hz, 6 H, CH_3), 2.29 (t, $^3J_{H,H}$ = 7.6 Hz, 12 H, CH_2), 2.67 (m, 12 H, CH_2), 5.99 (m, 2 H, CH), 6.80 (s, 2 H, NH), 8.84 (m, 8 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$/CF_3COOH, 2:1): δ = 14.17 (2 C, CH_3), 28.50, 29.51 (12 C, CH_2), 52.00 (2 C, CH), 60.14 (2 C, C_{quat}), 122.48, 124.95, 127.04, 129.99, 133.74, 136.69 (20 C, Ar-C), 165.50 (4 C, C_{imide}), 173.73 (2 C, NHCO), 181.35 (6 C, COOH) ppm. MS (MALDI, sin, MeOH): *m*/*z* = 994 [M$^+$], 1017 [M + Na$^+$]. IR (ATR): $\tilde{\nu}$ = 3321, 3174, 3066, 2943, 1699, 1645, 1591, 1537, 1437, 1344, 1251, 1182, 1104, 973, 865, 811, 749 cm^{-1}. UV/Vis (phosphate buffer, pH 7.2, 1×10^{-4} M): λ_{max} = 502 nm, 537; fluorescence (phosphate buffer, pH 7.2, 1×10^{-4} M): λ_{max} = 559 nm, 592. $C_{50}H_{48}N_4O_{18}$·0.75CF_3COOH (992.93+85.52): calcd. C 57.36, H 4.56, N 5.20; found C 57.02, H 4.64, N 5.17.

L- and D-*N*,*N*′-[1G(H)-C_6-Ala-]$_2$-perylene-3,4,9,10-tetracarboxylic Acid Diimide (6c): Yield L 25.9 mg (0.021 mmol, 94.4%), D 17.2 mg (0.014 mmol, 94.1%). ^{1}H NMR (400 MHz, $CDCl_3$/CF_3COOH, 2:1): δ = 1.43 (m, 4 H, CH_2), 1.67 (m, 8 H, CH_2), 1.79 (d, $^3J_{H,H}$ = 6.59 Hz, 6 H, CH_3), 2.14 (m, 12 H, CH_2), 2.45 (m, 16 H, CH_2), 3.45 (br. s, 4 H, CH_2), 5.95 (m, 2 H, CH), 6.98 (br. s, 1 H, NH), 7.13 (br. s, 1 H, NH), 8.78 (m, 8 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$/CF_3COOH, 2:1): δ = 13.73 (2 C, CH_3), 25.63 (2 C, CH_2), 26.02 (2 C, CH_2), 28.00 (2 C, CH_2), 28.18 (6 C, CH_2), 29.12 (6 C, CH_2), 36.30 (2 C, CH_2), 40.93 (2 C, CH_2), 50.90 (2 C, CH), 59.77 (2 C, C_{quat}), 122.14, 124.63, 126.71, 129.68, 133.42, 136.32 (20 C, Ar-C), 165.02 (4 C, C_{imide}), 174.18 (2 C, NHCO), 178.80 (2 C, NHCO), 180.35 (6 C, COOH) ppm. MS (MALDI, sin, MeOH): *m*/*z* = 1220 [M$^+$], 1242 [M + Na$^+$]. IR (ATR): $\tilde{\nu}$ = 3335, 2970, 2921, 2851, 1737, 1699, 1652, 1594, 1577, 1542, 1457, 1437, 1404, 1366, 1348, 1228, 1216, 1204, 1105, 977, 898, 863, 810, 811, 747 cm^{-1}. UV/Vis (phosphate buffer, pH 7.2, 1×10^{-4} M): λ_{max} = 502 nm, 539; fluorescence (phosphate buffer, pH 7.2, 1×10^{-4} M): λ_{max} = 556 nm, 592. $C_{62}H_{70}N_6O_{20}$·4CF_3COOH (1219.26+456.09): calcd. C 50.18, H 4.45, N 5.02; found C 50.31, H 4.89, N 5.11.

L- and D-*N*,*N*′-{[2G(H)-Lys]$^+$$CF_3COO^-$}$_2$-perylene-3,4,9,10-tetracarboxylic Acid Diimide (6d): Yield L 30.4 mg (0.011 mmol, 92.0%), D 29.2 mg (0.011 mmol, 95.9%). ^{1}H NMR (400 MHz, $CDCl_3$/CF_3COOH, 2:1): δ = 1.72 (m, 4 H, CH_2), 1.97 (m, 4 H, CH_2), 2.22 (m, 52 H, CH_2), 2.53 (m, 48 H, CH_2), 4.37 (m, 6 H, CH_2 + CH), 7.33 (br. s, 6 H, NH), 7.49 (br. s, 6 H, NH_3^+), 7.63 (br. s, 2 H, NH), 8.87 (m, 8 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$/CF_3COOH, 2:1): δ = 22.92 (2 C, CH_2), 27.45 (2 C, CH_2), 28.64 (18 C, CH_2), 29.36 (18 C, CH_2), 30.09 (2 C, CH_2), 31.36 (6 C, CH_2),

32.02 (6 C, CH_2), 41.17 (2 C, CH_2), 55.26 (2 C, CH), 60.10 (6 C, C_{quat}), 60.31 (2 C, C_{quat}), 122.60, 124.99, 127.10, 129.95, 133.78, 136.81 (20 C, Ar-C), 166.60 (4 C, C_{imide}), 169.96 (2 C, NHCO), 176.98 (6 C, NHCO), 181.32 (18 C, COOH) ppm. UV/Vis (phosphate buffer, pH 7.2, 1×10^{-4} M): λ_{max} = 500 nm, 541; fluorescence (phosphate buffer, pH 7.2, 1×10^{-4} M): λ_{max} = 558 nm, 592. MS (MALDI, sin, MeOH): *m/z* = 2485 [$M^+ - H^+ - 2\ CF_3COO^-$], 2506 [$M^+ - 2\ H^+ - 2\ CF_3COO^- + Na^+$]. IR (ATR): $\tilde{\nu}$ = 2927, 1735, 1717, 1699, 1685, 1671, 1653, 1637, 1595, 1569, 1559, 1541, 1523, 1508, 1498, 1490, 1473, 1457, 1419, 1397, 1364, 1264, 1216, 1206, 1134, 1108, 1042, 997, 974, 897, 852, 811, 768 cm^{-1}. $C_{120}H_{154}F_6N_{12}O_{52}$·4$CF_3COOH$ (2710.57 + 456.09): calcd. C 48.55, H 5.03, N 5.31; found C 48.85, H 5.28, N 4.81.

L- and D-*N*,*N*′-[2G(H)-Ala-]$_2$-perylene-3,4,9,10-tetracarboxylic Acid Diimide (6e): Yield L 10.7 mg (0.005 mmol, 94.2%), D 29.0 mg (0.012 mmol, 96.7%). ^1H NMR (400 MHz, $CDCl_3/CF_3COOH$, 2:1): δ = 1.75 (d, $^3J_{H,H}$ = 6.1 Hz, 6 H, CH_3), 2.15 (m, 48 H, CH_2), 2.46 (m, 48 H, CH_2), 6.02 (m, 2 H, CH), 6.92 (br. s, 2 H, NH), 7.19 (br. s, 6 H, NH), 8.79 (m, 8 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3/CF_3COOH$, 2:1): δ = 14.00 (2 C, CH_3), 28.25 (18 C, CH_2), 29.05 (18 C, CH_2), 29.92 (6 C, CH_2), 30.77 (6 C, CH_2), 51.34 (2 C, CH), 59.58 (6C, C_{quat}), 60.01 (2C, C_{quat}), 122.39, 124.67, 126.85, 129.74, 133.21, 136.40 (20 C, Ar-C), 165.09 (4 C, C_{imide}), 173.82 (2 C, NHCO), 176.98 (6 C, NHCO), 180.63 (18 C, COOH) ppm. MS (MALDI, sin, MeOH): *m/z* = 2433 [$M^+ - 2\ H^+ + 3\ Na^+$]. UV/Vis (phosphate buffer, pH 7.2, 1×10^{-4} M): λ_{max} = 468 nm, 499.5, 537; fluorescence (phosphate buffer, pH 7.2, 1×10^{-4} M): λ_{max} = 563 nm, 592. IR (ATR): $\tilde{\nu}$ = 3333, 3201, 3033, 2949, 2932, 1697, 1652, 1594, 1577, 1542, 1458, 1438, 1404, 1370, 1343, 1295, 1180, 1104, 979, 961, 948, 920, 871, 857, 811, 757, 735, 704, 688, 668, 650, 629, 612 cm^{-1}. $C_{111}H_{139}N_9O_{48}$·5$CHCl_3$ (2367.35 + 596.89): calcd. C 46.58, H 4.86, N 4.72; found C 46.86, H 5.15, N 4.72.

L- and D-*N*,*N*′-[2G(H)-C_6-Ala-]$_2$-perylene-3,4,9,10-tetracarboxylic Acid Diimide (6f): Yield L 36.0 mg (0.014 mmol, 99.3%), D 13 mg (0.005 mmol, 97.5%). ^1H NMR (300 MHz, $CDCl_3/CF_3COOH$, 2:1): δ = 1.41 (m, 4 H, CH_2), 1.65 (m, 8 H, CH_2), 1.79 (d, $^3J_{H,H}$ = 6.6 Hz, 6 H, CH_3), 2.14 (m, 48 H, CH_2), 2.45 (m, 52 H, CH_2), 3.43 (m, 4 H, CH_2), 5.95 (m, 2 H, CH), 7.04 (br. s, 6 H, NH), 7.12 (br. s, 2 H, NH), 7.19 (br. s, 2 H, NH), 8.79 (m, 8 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3/CF_3COOH$, 2:1): δ = 13.68 (2 C, CH_3), 25.77 (2 C, CH_2), 26.26 (2 C, CH_2), 27.21 (2 C, CH_2), 28.20 (18 C, CH_2), 29.00 (18 C, CH_2), 31.13 (6 C, CH_2), 31.75 (6 C, CH_2), 41.16 (2 C, CH_2), 50.99 (2 C, CH), 59.25 (2 C, C_{quat}), 59.53 (6 C, C_{quat}), 122.15, 124.71, 126.76, 129.73, 133.55, 136.43 (20 C, Ar-C), 165.15 (4 C, C_{imide}), 173.98 (2 C, NHCO), 176.59 (6 C, NHCO), 178.85 (2 C, NHCO), 180.55 (18 C, COOH) ppm. UV/Vis (phosphate buffer, pH 7.2, 1×10^{-4} M): λ_{max} = 539 nm, 501.5; fluorescence (phosphate buffer, pH 7.2, 1×10^{-4} M): λ_{max} = 560 nm, 591. MS (MALDI, sin, MeOH): *m/z* = 2616 [M + Na^+]. IR (ATR): $\tilde{\nu}$ = 3296, 3287, 2960, 2927, 2916, 2869, 2851, 1727, 1697, 1640, 1594, 1577, 1537, 1498, 1461, 1402, 1370, 1338, 1317, 1287, 1242, 1180, 1168, 1098, 1026, 1001, 985, 975, 931, 894, 876, 860, 834, 808, 746, 722, 694, 637, 627, 611 cm^{-1}. $C_{122}H_{160}N_{12}O_{50}$·8$CF_3COOH$ (2594.63+912.19): calcd. C 47.26, H 4.86, N 4.79; found C 47.33, H 5.15, N 4.52.

Supporting Information (see also the footnote on the first page of this article): UV/Vis and CD spectra of compounds **5** and **6** and an additional cryo-TEM micrograph of **6b** are provided.

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