DOI: 10.1002/ejoc.200601044

Supramolecular Dendrimers Self-Assembled from Dendritic Fullerene Ligands and a Homotritopic Hamilton Receptor

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Keywords: Cooperativity / Dendrimers / Depsipeptides / Fullerenes / Hydrogen bonding / Self-assembly

Supramolecular dendrimers resulting from the self-assembly of a series of dendrofullerens **2a**–**4b** containing a cyanuric acid building block at their focal point with the homotritopic Hamilton receptor **1** were prepared. The 1:3 compositions of the supramolecular dendrimers as well as the association constants K_n and the cooperativity of binding expressed by Scatchard plots and Hill coefficients n_H were determined by NMR titration experiments. The most pronounced positive cooperativity was observed for the **1**:$\mathbf{L_3}$ complexes with **L** being first generation dendrons. With the bulky second generation dendrons less stable complexes are formed.

Introduction

Recently, we reported on the self-assembly of chiral depsipeptide dendrimers consisting both of a tritopic Hamilton receptor **1**[1] and chiral depsipeptide cyanurates as ligands.[2] We also used a porphyrin substituted with four Hamilton receptor units for the supramolecular binding of the same depsipeptide cyanurates.[3] The depsipeptide dendrons represent a new type of chiral building blocks and were developed recently in our laboratories.[2–7] They consist of tartaric and amino acids connected through ester and amide linkages. Self assembly of these chiral depsipeptide dendrons with the complementary Hamilton receptor represent the first cases of chiral supramolecular dendrimers whose construction was provided by complementary hydrogen bonding motifs (Figure 1).[2]

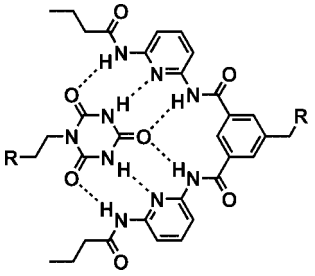

Figure 1. Schematic representation of the complementary hydrogen bonding motif of a cyanuric acid derivative and a Hamilton receptor.

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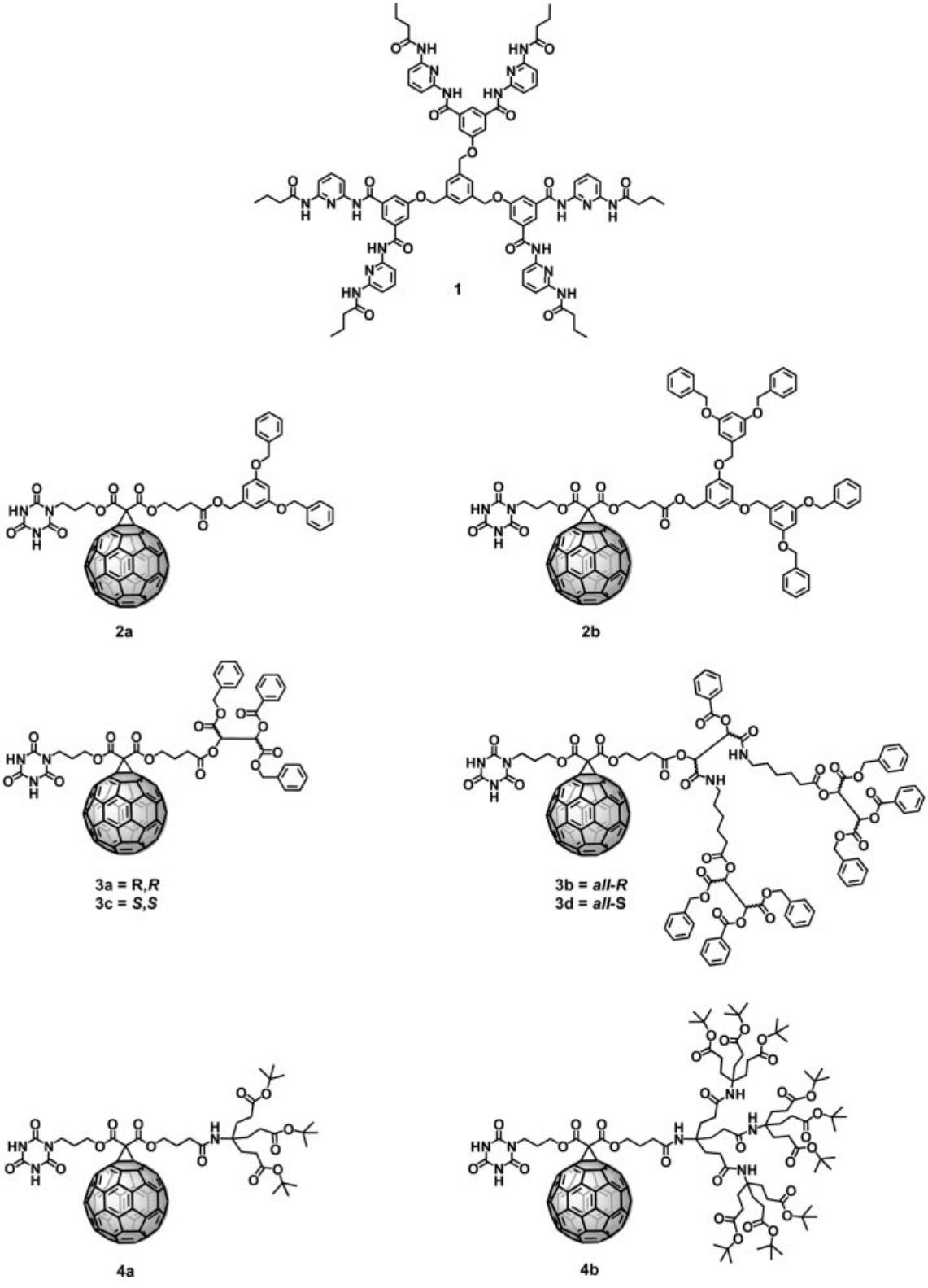
These investigations showed that the association constants as well as the cooperativity of the subsequent ligand binding depend on the steric requirement of the dendritic ligands. The highest association constants were determined for the third binding step of the corresponding second generation dendrons. The pronounced cooperativity of the threefold binding is a result of the conformational reorganization induced by the complexation of the first and second ligand. In the case of the first generation dendrons this induced reorganisation of the Hamilton receptor **1** is much less pronounced. On the other hand the steric requirement of the third generation dendrons causes the third binding step to be less favourable.

In recent years, extensive research has been dedicated to the preparation of fullerene-functionalized dendrimers, so called fullero dendrimers.[8] If fullerenes are functionalized with dendritic branches their solubility increases considerably.[9] In general, fullero dendrimers are attractive targets for various applications in supramolecular chemistry and material science.[10] In the past years Nierengarten et al. established a research theme devoted to the synthesis of fullerene rich dendrimers.[11] Next to the synthesis of such covalent dendrimers supramolecular approaches for the assembly of poly-fullerene architectures using hydrogen bonding motifs have been developed.[12] In general, the use of hydrogen bonding motifs represents an emerging approach in fullerene chemistry.[13] We now report on the self-assembly of a series of dendrofullerenes containing Fréchet-,[14] Newkome-,[15–16] and Depsipeptide-type cyanurates **2a**–**4b** of different generations through complementary hydrogen bonding with the homotritopic Hamilton receptor **1**.[1]

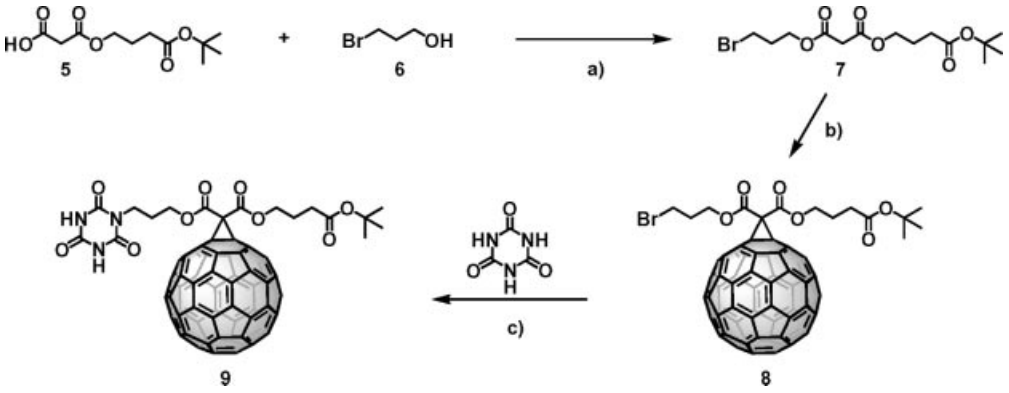


Results and Discussion

Syntheses

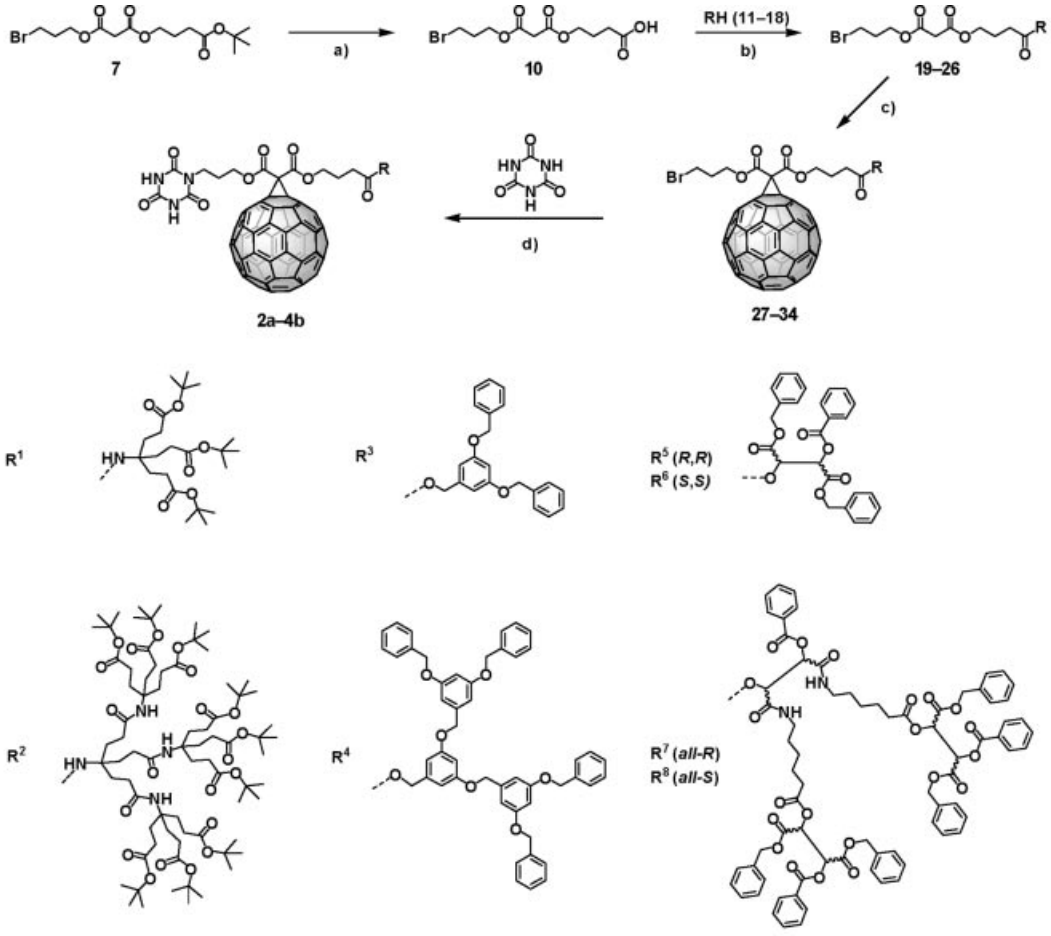
The synthesis of the homotritopic Hamilton receptor **1** was carried out according to the procedure of Berl et al.[1] For the synthesis of the dendrofullerenes **2a**–**4b** we first prepared the malonate **7** as a versatile building block for the preparation of non-symmetrical malonates (Scheme 1).

This precursor addend was easily obtained by the esterification of **5**[17] with 3-bromo-1-propanol (**6**) using dicyclo-



Scheme 1. Synthesis of a non dendritic fullerene ligand **9**. a) DMAP, HOBt, DCC, CH_2Cl_2, room temp., 24 h, 63%; b) C_{60}, I_2, DBU, toluene, room temp., 3–5 h, 45%; c) DBU, DMF, 40 °C, 4–6 h, 52%.

hexylcarbodiimide (DCC) as coupling reagent. After cyclopropanation under modified Bingel conditions[18] the fullerene monoadduct **8** was obtained in 45% yield. The initial approach for the attachment of the dendrons **11**–**18** (for assignment of the dendrons see Scheme 2) was to use a modified Steglich coupling with the deprotected carboxyl deriva-



R	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8
compound	**11, 19, 27**	**12, 20, 28**	**13, 21, 29**	**14, 22, 30**	**15, 23, 31**	**16, 24, 32**	**17, 25, 33**	**18, 26, 34**

Scheme 2. Synthesis of the dendritic fullerene ligands **2a**–**4b**. a) TFA, CH_2Cl_2, room temp., 20 h, 99%; b) DMAP, HOBt, DCC, CH_2Cl_2, room temp., 24 h, 40–73%; c) C_{60}, I_2, DBU, toluene, room temp., 3–5 h, 21–49%; d) cyanuric acid, DBU, DMF, 40 °C, 4–6 h, 19–52%.

tive of **8** generated by acid-promoted removal of the *tert*-butyl group. Unfortunately, the obtained yields were not satisfactory and also purification was too laborious. Similar problems arose when using the deprotected free acid of **9** for coupling of the dendrons **11**–**18**.

Because theses approaches turned out to be unsuccessful we decided to develop an alternative route (Scheme 2). The idea was to couple the dendrons **11**–**18** with the deprotected acid **10** prior to the addition to C_{60} and the connection with cyanuric acid. Compound **10** was obtained by the acidic cleavage of the *tert*-butyl groups of **7**. The ester coupling of the dendrons **11**–**18** was carried out using Steglich conditions. The yields of the resulting malonates **19**–**26** were about 40–73% depending on the size of the dendrons. The subsequent cyclopropanation of C_{60} with the malonates **19**–**26** afforded the monoadducts **27**–**34** in yields between 21–49%. Purification was accomplished by flash chromatography on silica gel. Finally, the target molecules **2a**–**4b** were obtained after base-promoted nucleophilic substitution of the bromo monoadducts **27**–**34** with cyanuric acid. In fact, this reaction step turned out to be the key step in the synthesis of the compounds **2a**–**4b**, which required the use of very dry solvents and glassware. Also the cyanuric acid itself needed to be dried for at least 24 h in vacuo at 100 °C. The final purification of the dendrofullerenes **2a**–**4b** was done by column chromatography. In case of the first-generation depsipeptidefullerenes **3a**,**c** additional purification by HPLC was required.

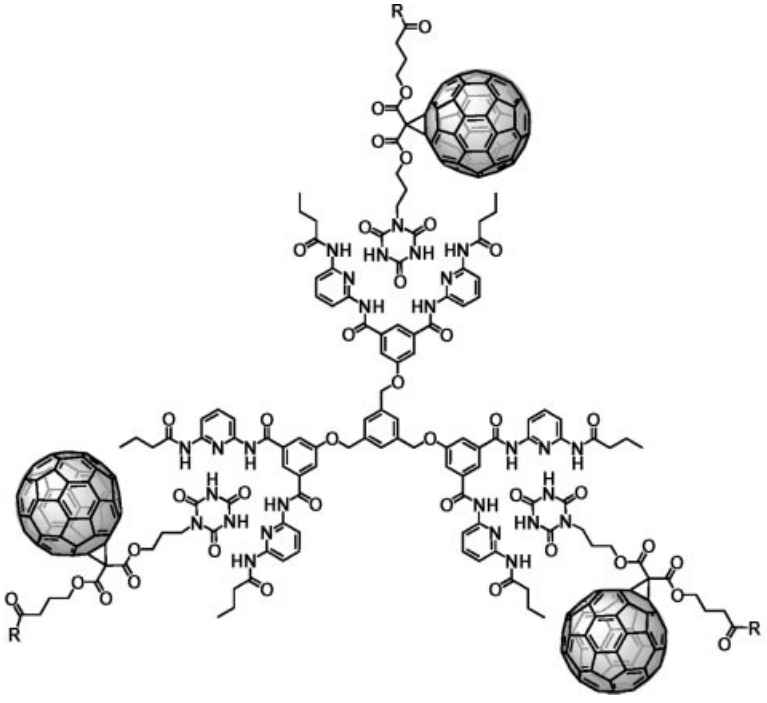
Determination of Association Constants and Cooperativity of Binding

For the investigation of the targeted complexes **1**:$\mathbf{L_3}$, (L = **2a**–**4b**) between the Hamilton receptor **1** and the cyanuric acid dendrofullerenes **2a**–**4b** we carried out a series of quantitative as well as temperature-dependent NMR binding studies.

In $CDCl_3$ the ^{1}H NMR spectrum of **1** shows rather broad and unresolved signals due to the formation of a variety of inter- and intramolecular hydrogen bonds.[1] However, in analogy to our previous studies on the binding of dendritic cyanurates,[2] the successive addition of **2a**–**4b** leads to sharpening of the proton signals of **1** (Figure 2). This is accompanied by a continuous downfield shift of the resonances of the amide protons NH^1 and NH^2 until the point when the 1:3 complexes are the predominant aggregates (Figure 2). In analogy to our previous observations[2] no signal for the imide protons of free cyanurates, which in the absence of **1** appears at about 9 ppm, can be detected. In the presence of 0.5 to 2 equiv. of **2a**–**4b** a broad averaged signal for NH^3 at about 13 ppm is observed that is due to both bound and free ligands being in a fast exchange process with respect to the NMR time scale. After further addition of **2a**–**4b** this averaged signal disappears again.

The formation of complexes with 1:3 stoichiometry is confirmed by a Jobs plot analysis. As an example the Job plot of **1:3b$_3$** is shown in Figure 3. The determined maximum appears close to the expected mol fraction of 0.75 consistent with a 1:3 stoichiometry.

The dynamic character of the association of the complexes **1:(2a**–**4b)$_3$** is further revealed by temperature-dependent NMR spectroscopy. As an example, the ^{1}H NMR spectra of a 1:10 mixture of **1** and **4a** are shown in Figure 4. At 40 °C only the signals for the two amide protons of the receptor **1** are detected. Neither the NH signals for the free (NH_{free}) nor for the bound (NH_{bound}) cyanuric acid derivative appear. However, lowering the temperature to –20 °C causes the resonances for the NH_{free} and NH_{bound} protons to appear as broad signals at about 9.0 and 13.5 ppm,



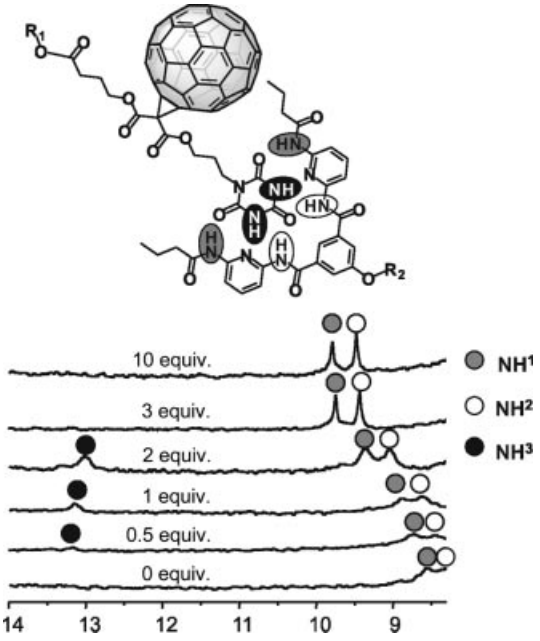


Figure 2. Binding motif between **1** and **2a**–**4b** with indication of the NH protons NH^1, NH^2 and NH^3 and 300-MHz ^1H NMR spectra of **1** at a concentration of 0.5 mM in $CDCl_3$ and different equivalents of **2a**.

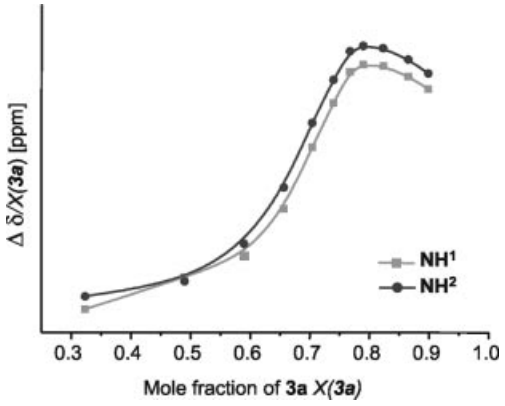


Figure 3. Determination of the 1:3 stoichiometry of the system **1:3b** at a total concentration of 2.75 mM by a Job plot analysis. The *y* axis has been normalized.

respectively. Further cooling results in line sharpening as well as successive shifting to lower field. Simultaneously, a moderate downfield shift of the resonances of the amide protons of the receptor **1** takes place. These investigations clearly show, that at low temperatures the association-dissociation equilibrium is slow on the NMR time scale.

Moreover, it can be concluded that by lowering the temperature the thermodynamic equilibrium is shifted towards the complexed species. The remarkable shift to lower field proofed this assumption. The temperature range between 0–40 °C represents the coalescence regime, where the signals of the NH_{bound} and NH_{free} protons are very broad and cannot be detected anymore. Further increase in temperature causes the development of one averaged signal, demonstrating fast exchange processes between free and bound ligands.

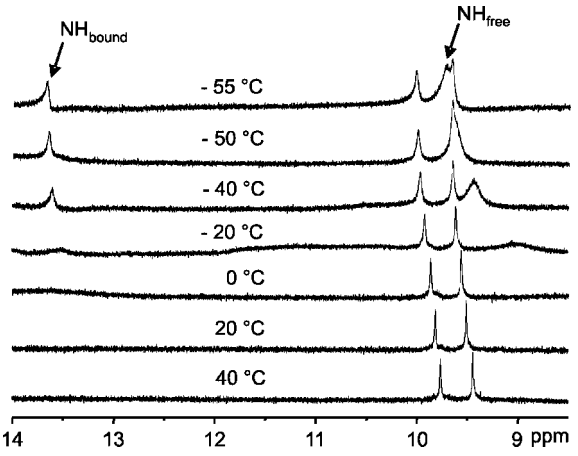


Figure 4. 400-MHz ^1H NMR spectra of a 1:10 mixture of **1** and **3a** at a concentration of 2.75 mM in $CDCl_3$ at –55 °C, –50 °C, –40 °C, –20 °C, 0 °C, 20 °C, and 40 °C, respectively.

Systematic titration experiments have been carried out in order to determine the association constants for the subsequent binding steps. The downfield shift of the NH protons of **1** was determined as a function of the dendron concentration. In a typical experiment 0.5 mL of a 0.5 mM solution of the Hamilton receptor **1** was titrated with 50 μL portions of a 2.5 mM solution of **2a**–**4b**. The ^1H NMR spectra were measured 45 min after the components were mixed together in order to enable the adjustment of the equilibrium. The titration experiments were accomplished in a quantitative manner and allow both the determination of the association constants for each individual complexation step and the evaluation of cooperative effects. Typical examples of titration curves are shown in Figure 5.

The titration curves show a sigmoidal shape with an inflection point at about 2 equiv. of added dendrofullerene. A sigmoidal titration curve represents an indication for a positive cooperative effect for the subsequent binding of guest molecules.[19–21] Comparison of the titration curves obtained for first-and second-generation systems **1:3a** and **1:3b** reveals more pronounced downfield shifts for the binding of the first generation ligands. In this case saturation is almost complete after the addition of three equivalents of the ligands. However, higher concentrations of the second generation ligand **3b** are required in order to cause a comparable saturation behaviour. Obviously, the threefold ligand binding is less efficient for the bulkier second-generation dendron **3b** because of steric hindrance. A similar trend is seen for all types of dendrons **2a**–**4b**. The determination of the association constants for complexation of the individual dendrofullerene derivatives with **1** was accomplished with the help of the program Chem-Equili.[22–23] The determined *K* values are summarized in Table 1. The calculations were based on the assumption of the following three equilibria (1), (2), and (3) (L = **2**, **3** or **4**).

In general, the association constants K_n are in good agreement with those reported by Lehn and co-workers for a **1:L$_3$** system with **L** being a non-dendritic cyanuric acid derivative[1] and with those reported by ourselves with **L**

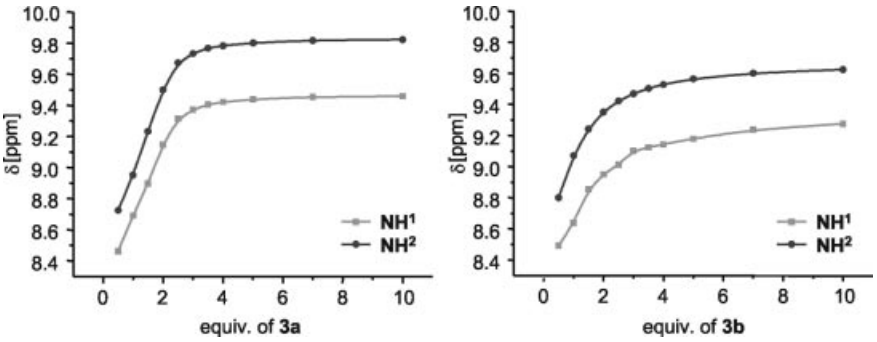


Figure 5. ^{1}H NMR titration plots of the chemical shifts of the NH^1 and NH^2 protons as a function of the amount of added dendrons **3a** and **3b**.

K_1: **1** + **L** ⇋ **1:L** (1)

K_2: **L** + **1:L** ⇋ **1:L$_2$** (2)

K_3: **L** + **1:L** ⇋ **1:L$_3$** (3)

being a non-fullerene-containing dendritic cyanurate ligand.[2] The association constant for the first complexation step (K_1) is to a first approximation rather independent of the nature of the ligand. However, major differences are observed for the second and particularly the third binding step. In general, within one family of ligands the smaller first-generation addends lead to higher K_2 and K_3 values than their second-generation counterparts.

The relatively flat and flexible Frechét ligands **2a**,**b** give rise to the most stable supramolecular architectures in this series, which is especially reflected by the largest K_3 values. In this case both the K_1 and the K_3 values of the first and second generation systems do not differ very much. On the other hands the Newkome-type systems **1:4a**,**b** show relatively small association constants K_3 even for the first generation ligand **4a**. This is a result of the steric demand of the comparatively rigid Newkome dendrons (amide linkages, branching multiplicity of three), who in contrast to the Frechét dendrons have a much more globular and bulky structure.[24–25] The association constant K_3 of the second-generation ligand **4b** is comparable with the value of the second-generation depsipeptide ligand **3b**, which according to molecular modelling studies (Figure 6), presents also a comparatively globular and rigid structure. These results clearly demonstrate that the rigidity as well as the steric demand of the dendritic ligands are the main factors determining the stability of the supramolecular dendrimers.

The assembly of all supramolecular dendrimers **1:2a**–**4b$_3$** is accompanied by positive cooperativity. For the case of a statistical binding Equation (4) must be fulfilled,[19–20] whereby t is the total number of binding sites (in this case $t = 3$).

$$\frac{K_{n+1}}{K_n} = \frac{n(t-n)}{(n+1)(t-n+1)} \quad (4)$$

However, the experimental values for K_{n+1}/K_n are much higher than those obtained from Equation 4, which clearly demonstrates the presence of pronounced positive cooperativity. The free binding energy of the dendritic ligands increases by going from the monocomplex **1:L** to bis- and triscomplexes **1:L$_2$** and **1:L$_3$**, respectively. This is also reflected by the sigmoidal shape of the corresponding titration curves (Figure 5).

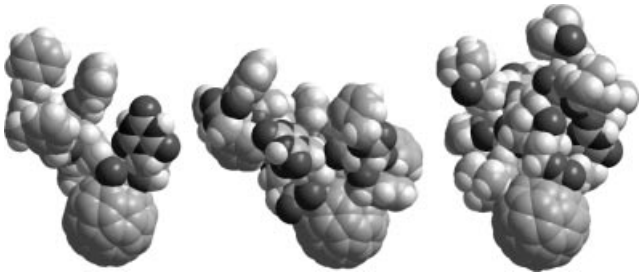


Figure 6. Molecular structure of **2b** (left), **3b** (middle) and **4b** (right) obtained from a molecular dynamics simulation (in vacuo; starting temperature: 0 K, simulation temperature: 550 K, final temperature: 0 K; heat time: 1 ps, run time: 3 ps, cool time: 1 ps; step size: 0.001 ps) followed by a force field minimization (MM$^+$) (HyperChem. 7.5, Hypercube, Inc.).

The preferred formation of **1:L$_3$** (L = **2a**–**4b**) compared to the corresponding **1:L$_2$** complexes becomes also apparent upon analysing the distribution of **1** as free core and as part of the complexes **1:L$_n$** (n = 1–3) as a function of added dendron equivalents (Figure 7). For example, the amount of **1:L$_3$** (**L** = **3a**) complexes prevails already at low concentrations of added dendronfullerene **3a**.

After the addition of three equivalents of **3a** the amount of **1:L$_3$** complexes ranges between 80 and 90%. After the addition of 4 equiv. of **3a** the whole amount of **1** is bound in the corresponding **1:L$_3$** complex. On the other hand the formation of **1:L$_3$** complexes involving the second generation dendron **3b** is much less pronounced (Figure 7). The **1:L$_3$** fraction becomes not predominant until three or more equivalents of **3b** are added. After the addition of 10 equiv. only about 80% of **1** is bound in the corresponding **1:L$_3$** complex.

The cooperativity phenomenon can be described with the help of the "cooperative association theory".[19,26] Therefore, the determination of the occupancy r is necessary, which is the average number of ligands bound to the receptor, see Equation (5).

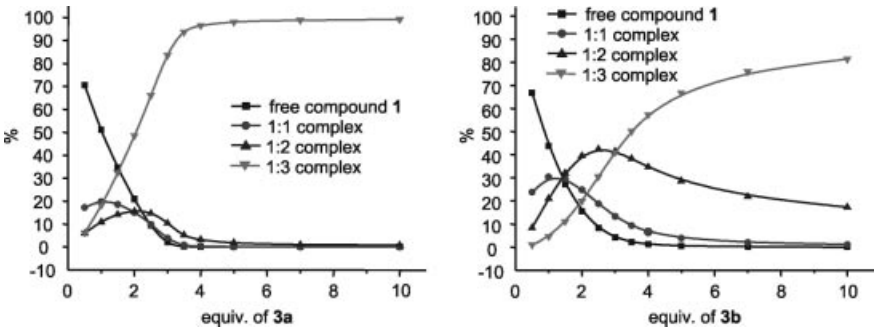


Figure 7. Distribution in percent of **1** as free core and within the complexes **1:L**$_n$ (n = 1–3) as a function of the amount of added dendrons **3a** and **3b** obtained from analysis of the titration plots using the computer program Chem-Equili.[21–22] The total concentration of **1** within the mixtures is 0.5 mM.

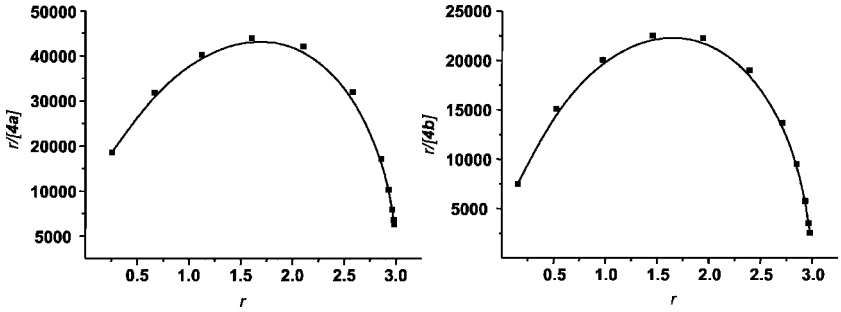


Figure 8. Scatchard plots for the systems **1:L** (**L** = **3a**, **3b**).

$$r = \frac{[1 \circ L] + 2[1 \circ L_2] + 3[1 \circ L_3]}{[1] + [1 \circ L] + [1 \circ L_2] + [1 \circ L_3]} \quad (5)$$

For statistical binding r can be described by the Scatchard Equation (6) with Q being the site binding constant and x the concentration of the added ligands.

$$r = \frac{t \cdot Q \cdot x}{1 + Q \cdot x} \quad (6)$$

For a graphic illustration of this relationship r/x was monitored as a function of x. In case of a statistic, independent binding of the dendrofullerenes a straight line would be received. In case of a positive cooperativity the Scatchard plot exhibits a convex curve. The Scatchard plots of all investigated systems show a very pronounced convex behaviour. The Scatchared plots of the first (**3a**) and second (**3b**) generation depsipeptide ligands are shown in Figure 8.

The quantification of the amount of cooperativity of a given system is usually expressed by the Hill coefficient n_H, which can be obtained from the maximum of the Scatchard plot according to Equation (7).

$$n_H = \frac{r_{max}}{t - r_{max}} \quad (7)$$

The amount of cooperativity is directly correlated to the value of n_H. For an infinitely high cooperativity n_H becomes equal to t (here t = 3). However, this has never been observed in real systems. The larger n_H values are always found for the systems with the corresponding first generation dendrons (Table 1).

Table 1. Association constants, R-factor (R), r_{max} and Hill coefficients of the systems **1:2**, **1:3** and **1:4**.

	$\log K_1$ [L mol^{-1}]	$\log K_2$ [L mol^{-1}]	$\log K_3$ [L mol^{-1}]	R [%]	r_{max}	n_H
2a	4.13	4.24	5.26	±0.40	1.74	1.38
2b	4.28	3.50	5.16	±0.18	1.66	1.24
3a	4.39	4.54	5.02	±0.29	1.53	1.05
3b	4.09	4.09	3.60	±0.18	0.99	0.49
4a	4.74	3.35	4.10	±0.36	1.33	0.79
4b	4.22	3.70	3.54	±0.14	0.96	0.47

Conclusions

The observed association properties of **1** with the dendritic ligands **2a**–**4b** can be explained by having a closer look to the planar rotamers of the Hamilton receptor **1**.[2] As already reported by Vögtle and De Cola et al.,[27] an open-chain Hamilton receptor can in principle adopt three distinct planar conformations, namely *cis-cis*, *cis-trans* and *trans-trans*. Rotation about the two central aryl–CO bonds is not frozen at room temperature, and as a consequence all planar rotamers are in an equilibrium. Complexation of the free receptor with complementary guest molecules, like barbiturate or cyanurate derivatives, causes the remaining free binding sites to preferably adopt the planar *cis-cis* conformation, which is the most favourable conformation for the

ligand binding. This behaviour explains the observed association phenomena such as the positive cooperativity of the second and third binding steps. These results are also in full agreement with our previous studies using depsipeptide ligands in the absence of fullerenes.[2] In this case the highest positive cooperativity was found for the second-generation dendrons. These values are in the range of the first-generation systems presented in this publication. Obviously, the second-generation depsipeptide dendrons used previously[2] are not as bulky as the corresponding fullerene-containing ligands **3b** and **4b** involving depsipeptide and Newcome dendrons. The results of the binding of the second-generation dendrons **3b** and **4b** are comparable to those observed for third-generation depsipentide dendrons without fullerene substitutents.[2] These results show clearly that the positive cooperativity is determined by two opposite effects. The remaining free sites of **1** are increasingly forced to adopt the *cis*-*cis* conformation after the initial binding steps, and therefore the subsequent binding of ligands is preferred. Very bulky ligands on the other hand disfavour this subsequent binding steps because of their steric demand. The most pronounced positive cooperativity is achieved when these factors are well balanced. We are currently extending this new type of supramolecular dendrimers which contain redoxactive elements with respect to the development of new opto-electronic properties.

Experimental Section

General Remarks: All chemicals were obtained from Sigma–Aldrich and Acros Organics or were prepared according to known literature procedures. The preparation of the depsipeptide dendrons **14**–**18** was described previously.[6] All reactions were performed using standard glassware under nitrogen. The solvents were purified by distillation. Dry solvents were prepared using customary literature procedures. Reactions were monitored by thin-layer chromatography (TLC) using Riedel de-Haën silica gel 60 F_{254} aluminium foils, detection by UV lamp. ^{1}H and ^{13}C NMR spectra were recorded with Bruker Avance 300, JEOL JNM EX 400, JEOL JNM GX 400 and JEOL A 500. The chemical shifts are given in ppm relative to TMS or the solvent peak as a standard reference. The resonance multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet), unresolved signals as br. C*H** indicates the stereogenic centres. Mass Spectra were measured with a Micromass Lab Spec (FAB) with a Finnigan MAT 900 spectrometer with 3-nitrobenzyl alcohol as the matrix. IR spectra were recorded with React IR®-1000 ASI Applied Systems (ATR-DiComp detector) on a diamond crystal. UV spectroscopy was performed using a Shimadzu UV-3102 spectrophotometer. Elementary analysis succeeded by combustion and gas chromatographical analysis with an EA 1110 CHNS analyser (CE Instruments). Products were isolated by flash column chromatography (FC) (silica gel 60, particle size 0.04–0.063 nm, Merck). Analytical HPLC was performed with a Shimadzu LC-10 AT HPLC system (Nucleosil 200 × 4, particle size 5 μm, Machery–Nagel), detection by photo diode array (SPD-M 10). Compound **3a** and **3c** were purified by preparative HPLC with a Shimadzu LC-8A HPLC system (Nucleosil 250 × 21, particle size 5 μm, Machery–Nagel) detection by UV/Vis (SPD-10A).

General Procedure I for the Preparation of Esters or Amides: The carboxylic acid (1.6 mmol), 4-(dimethylamino)pyridine (DMAP) (1.6 mmol) and 1-hydroxybenzotriazole (HOBt) (1.6 mmol) were added to a solution of the alcohol or amine (1.6 mmol) in CH_2Cl_2 (100 mL). Dicyclohexylurea (DCC) (1.6 mmol) was added all at once at room temperature and the suspension was stirred for 24 h. The solution was washed with 10% aqueous HCl (1 × 100 mL) and with saturated aqueous $NaHCO_3$ (3 × 150 mL) and then dried with $MgSO_4$. After evaporation of the solvent the crude product was purified by column chromatography.

General Procedure II for the Synthesis of the C_{60} Monoadducts: DBU (694 μmol) was added dropwise to a solution of C_{60} (694 μmol), the malonate derivative (463 μmol) and I_2 (486 μmol) in dry toluene under nitrogen. The reaction mixture was stirred at room temperature for 3–5 h and the progress of the reaction was monitored by TLC. The product was isolated by flash chromatography and dried in vacuo affording a red brownish solid.

General Procedure III for the Preparation of Cyanurate Compounds: Cyanuric acid (4.61 mmol) was dissolved in dry DMF (50 mL) and DBU (461 μmol) was added under vigorous stirring. After ten minutes the bromide compound (461 μmol) was added and the mixture was heated to 40 °C. The progress of the reaction was monitored by TLC and the product was isolated by flash chromatography or by HPLC. The product fractions were evaporated, precipitated from CH_2Cl_2/pentane and dried in vacuo to afford a red brownish solid.

3-(*tert*-Butoxycarbonyl)propyl 3-Bromopropyl Malonate (7): Compound **7** was synthesised according to the general procedure **I** with 2-{[3-(*tert*-butoxycarbonyl)propoxy]carbonyl}acetic acid (**5**) (1.00 g, 4.06 mmol), 3-bromopropan-1-ol (**6**) (0.46 mL, 5.08 mmol), HOBt (603 mg, 4.47 mmol), DMAP (496 mg, 4.06 mmol) and DCC (1.09 g, 5.28 mmol) in CH_2Cl_2 (75 mL). The crude product was purified by column chromatography (SiO_2, gradient hexane/ethyl acetate, 75:25→50:50). Yield 939 mg (2.56 mmol, 63%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz, room temp.): δ = 4.20 (t, ^3J = 6.0 Hz, 2 H, OCH_2), 4.07 (t, ^3J = 6.4 Hz, 2 H, OCH_2), 3.37 (t, ^3J = 6.1 Hz, 2 H, BrCH_2), 3.30 (s, 2 H, O_2CCH_2CO_2), 2.21 (t, ^3J = 7.4 Hz, 2 H, CH_2CO), 2.10 (q, ^3J = 6.2 Hz, 2 H, BrCH$_2$CH_2), 1.83 (q, ^3J = 6.9 Hz, 2 H, CH_2CH$_2$CO), 1.35 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz, room temp.): δ = 171.72 (1 C, *C*=O), 166.15, 166.08 (2 C, *C*=O), 80.28 [1 C, *C*(CH$_3$)$_3$] 64.43 (1 C, OCH$_2$), 62.92 (1 C, OCH$_2$), 41.19 (1 C, O_2C*C*H$_2$CO_2), 31.54 (1 C, BrCH$_2$*C*H$_2$), 31.25 (1 C, *C*H$_2$CO), 28.97 (1 C, Br*C*H$_2$), 27.87 [3 C, C(*C*H$_3$)$_3$], 23.79 (1 C, *C*H$_2$CH$_2$CO) ppm. MS (FAB, NBA): *m*/*z* = 389 [M + Na]$^+$, 367 [M]$^+$, 311 [M – *t*Bu]$^+$; *MW* = 367.23 g/mol. IR (ATR): $\tilde{\nu}$ = 2972, 2928, 2191, 1723, 1459, 1416, 1390, 1367, 1229, 1146, 1111, 1058, 997, 961, 880, 842, 791, 741, 702 cm^{-1}. $C_{14}H_{23}BrO_6$ (367.23): calcd. C 45.79, H 6.31; found C 45.87, H 6.34.

4-{2-[(3-Bromopropoxy)carbonyl]acetoyloxy}butanoic Acid (10): Trifluoroacetic acid (3.0 mL, 39.0 mmol) was added to a solution of 7 (500 mg, 1.36 mmol) in CH_2Cl_2 (25 mL). The reaction mixture was stirred at room temperature for 20 h and the progress of the reaction monitored by TLC. The mixture was concentrated and dried in vacuo. Yield 420 mg (1.35 mmol, 99%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz, room temp.): δ = 10.24 (br., 1 H, COO*H*), 4.25 (t, ^3J = 6.1 Hz, 2 H, OCH_2), 4.17 (t, ^3J = 6.3 Hz, 2 H, OCH_2), 3.42 (t, ^3J = 6.5 Hz, 2 H, BrCH_2), 3.36 (s, 2 H, O_2CCH_2CO_2), 2.42 (t, ^3J = 7.3 Hz, 2 H, CH_2CO), 2.14 (q, ^3J = 6.3 Hz, 2 H, BrCH$_2$CH_2), 1.95 (q, ^3J = 6.8 Hz, 2 H, CH_2CH$_2$CO) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz, room temp.): δ = 178.66 (1 C, *C*OOH), 166.33, 166.27 (2 C, *C*=O), 64.29 (1 C, OCH$_2$), 63.16 (1 C, OCH$_2$), 41.25 (1 C, O_2C*C*H$_2$CO_2), 31.30 (1 C, BrCH$_2$*C*H$_2$), 30.23 (1 C, *C*H$_2$COOH), 29.05 (1 C, Br*C*H$_2$), 23.47 (1 C,

CH_2CH_2CO) ppm. MS (FAB, NBA): *m/z* = 333 [M + Na]$^+$, 311 [M]$^+$; *MW* = 311.13 g/mol. IR (ATR): $\tilde{\nu}$ = 2981, 2920, 2192, 1720, 1457, 1428, 1390, 1367, 1229, 1146, 1113, 1058, 997, 961, 882, 845, 791, 741, 702 cm^{-1}. $C_{10}H_{15}BrO_6$ (311.13): calcd. C 38.60, H 4.86; found C 38.76, H 4.95.

Newkome-Type [G-1]-3-Bromopropyl Malonate 19: Compound **19** was synthesised according to the general procedure **I** with compound **11** (521 mg, 1.254 mmol), 4-{2-[(3-bromopropoxy)carbonyl] acetoyloxy}butanoic acid (**10**) (300 mg, 0.965 mmol), HOBt (143 mg, 1.061 mmol), DMAP (118 mg, 0.965 mmol) and DCC (258 mg, 1.254 mmol) in CH_2Cl_2 (100 mL). The crude product was purified by column chromatography (SiO_2, gradient hexane/ethyl acetate, 50:50→35:65). Yield 403 mg (0.57 mmol, 59%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz, room temp.): δ = 5.97 (br., 1 H, N*H*), 4.22 (t, ^3J = 6.0 Hz, 2 H, OCH_2), 4.09 (t, ^3J = 6.2 Hz, 2 H, OCH_2), 3.38 (t, ^3J = 6.4 Hz, 2 H, BrCH_2), 3.31 (s, 2 H, $O_2CCH_2CO_2$), 2.21 (m, 10 H, $BrCH_2CH_2$, CH_2CONH, CH_2COO), 1.87 (m, 8 H, CH_2CH_2CONH, CH_2CH_2COO), 1.33 [s, 27 H, C(CH_3)$_3$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, room temp.): δ = 172.62 (3 C, *C*=O), 171.04 (1 C, *C*ONH), 166.46 (1 C, *C*=O), 166.12 (1 C, *C*=O), 80.40 [3 C, *C*(CH$_3$)$_3$], 64.44 (1 C, OCH_2), 63.08 (1 C, OCH_2), 57.28 (1 C, NHC_{quat}), 41.19 (1C $O_2CCH_2CO_2$), 33.07 (1 C, CH_2CONH), 31.27 (1 C, BrCH_2), 29.75 (3 C, CH_2COO), 29.61 (3 C, $C_{quat}CH_2$), 28.96 (1 C, $BrCH_2CH_2$), 27.89 [9 C,C(CH_3)$_3$], 24.45 (1 C, CH_2CH_2CONH) ppm. MS (FAB, NBA): *m/z* = 708 [M]$^+$; *MW* = 708.68 g/mol. IR (ATR): $\tilde{\nu}$ = 2970, 2934, 1722, 1526, 1455, 1428, 1390, 1361, 1231, 1147, 1096, 1058, 1001, 953, 845, 760, 730, 703 cm^{-1}. $C_{32}H_{54}BrNO_{11}$ (708.68): calcd. C 54.23, H 7.68, N 1.98; found C 54.31, H 7.71, N 1.92.

Monoadduct 27: Compound **27** was synthesised according to the general procedure **II** with malonate **19** (1.70 g, 2.40 mmol), C_{60} (2.59 g, 3.60 mmol), I_2 (670 mg, 2.64 mmol) and DBU (467 µL, 3.12 mmol) in toluene (2.0 L). The crude product was purified by column chromatography (SiO_2, toluene/ethyl acetate, 90:10). Yield 1.16 g (816 µmol, 34%) as a red brownish solid. ^{1}H NMR ($CDCl_3$, 400 MHz, room temp.): δ = 6.03 (br., 1 H, N*H*), 4.63 (t, ^3J = 5.9 Hz, 2 H, OCH_2), 4.49 (t, ^3J = 6.3 Hz, 2 H, OCH_2), 3.54 (t, ^3J = 6.3 Hz, 2 H, BrCH_2), 2.35 (q, ^3J = 6.1 Hz, 2 H, $BrCH_2CH_2$), 2.28 (t, ^3J = 7.2 Hz, 2 H, CH_2CONH), 2.20 (m, 6 H, CH_2COO), 2.13 (m, 2 H, CH_2CH_2CONH), 1.95 (m, 6 H, CH_2CH_2COO), 1.40 [s, 27 H, C(CH_3)$_3$] ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz, room temp.): δ = 172.87 (3 C, *C*=O), 170.81 (1 C, *C*ONH), 163.58 (1 C, *C*=O), 163.47 (1 C, *C*=O), 145.30, 145.21, 145.14, 145.10, 145.04, 145.00, 144.92, 144.69, 144.68, 144.62, 143.89, 143.10, 143.03, 143.00, 142.20, 141.91, 141.85, 141.01, 140.99, 139.18, 138.84, (58 C, sp^2-C_{60}), 80.65 [3 C, *C*(CH$_3$)$_3$], 71.31 (2 C, sp^3-C_{60}), 66.61 (1 C, OCH_2), 64.85 (1 C, OCH_2), 57.46 (1 C, NHC_{quat}), 51.85 (1C O_2CCCO_2), 33.97 (1 C, CH_2CONH), 31.22 (1 C, BrCH_2), 29.89 (3 C, CH_2COO), 29.71 (3 C, $C_{quat}CH_2$), 29.05 (1 C, $BrCH_2CH_2$), 27.96 [9 C, C(CH_3)$_3$], 24.47 (1 C, CH_2CH_2CONH) ppm. MS (FAB, NBA): *m/z* = 1427 [M]$^+$; *MW* = 1427.30 g/mol. IR (ATR): $\tilde{\nu}$ = 2972, 2934, 1725, 1679, 1525, 1455, 1428, 1390, 1366, 1231, 1146, 1100, 1058, 996, 953, 845, 757, 730, 703, 676, 637 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 258, 324, 424 nm.

Monoadduct 4a: Compound **4a** was synthesised according to the general procedure **III** with monoadduct **27** (400 mg, 280 µmol), cyanuric acid (361 mg, 2.80 mmol) and DBU (42 µL, 280 µmol) in DMF (70 mL). The crude product was purified by column chromatography (SiO_2, dichloromethane/ethyl acetate, 60:40). Yield 215 mg (146 µmol, 52%) as a red brownish solid. ^{1}H NMR ($CDCl_3$, 400 MHz, room temp.): δ = 9.75 (br., 2 H, N*H*), 6.26 (br., 1 H, N*H*), 4.56 (t, ^3J = 5.7 Hz, 2 H, OCH_2), 4.52 (t, ^3J = 6.3 Hz, 2 H, OCH_2), 3.54 (t, ^3J = 6.4 Hz, 2 H, NCH_2), 2.36 (t, ^3J = 7.0 Hz, 2 H, CH_2CONH), 2.23 (m, 8 H, CH_2COO, NCH_2CH_2), 2.16 (m, 2 H, CH_2CH_2CONH), 2.00 (m, 6 H, CH_2CH_2COO), 1.42 [s, 27 H, C(CH_3)$_3$] ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz, room temp.): δ = 173.42 (3 C, *C*=O), 171.76 (1 C, *C*ONH), 163.52 (1 C, *C*=O), 163.44 (1 C, *C*=O), 149.49 (2 C, NH*C*ON), 147.97 (1 C, NH*C*ONH), 145.34, 145.25, 145.16, 145.12, 144.95, 144.74, 144.69, 143.92, 143.14, 143.08, 143.03, 142.24, 141.95, 141.02, 139.10, 139.00 (58 C, sp^2-C_{60}), 81.04 [3 C, *C*(CH$_3$)$_3$], 71.47 (2 C, sp^3-C_{60}), 66.80 (1 C, OCH_2), 64.96 (1 C, OCH_2), 57.59 (1 C, NHC_{quat}), 51.97 (1 C, O_2CCCO_2), 39.04 (1 C, NCH_2), 34.02 (1 C, CH_2CONH), 29.97 (3 C, CH_2COO), 29.82 (3 C, $C_{quat}CH_2$), 28.00 [9 C, C(CH_3)$_3$], 27.05 (1 C, NCH_2CH_2), 24.53 (1 C, CH_2CH_2CONH) ppm. MS (FAB, NBA): *m/z* = 1476 [M]$^+$; *MW* = 1475.46 g/mol. IR (ATR): $\tilde{\nu}$ = 3246, 2976, 2818, 1702, 1455, 1424, 1366, 1150, 1100, 1058, 957, 845, 760, 703 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 257, 325, 425 nm.

Newkome-Type [G-2]-3-Bromopropyl Malonate 20: Compound **20** was synthesised according to the general procedure **I** with compound **12** (1000 mg, 0.694 mmol), 4-{2-[(3-bromopropoxy)carbonyl]acetoyloxy}butanoic acid (**10**) (188 mg, 0.603 mmol), HOBt (90 mg, 0.603 mmol), DMAP (74 mg, 0.603 mmol) and DCC (162 mg, 0.784 mmol) in CH_2Cl_2 (100 mL). The crude product was purified by column chromatography (SiO_2, hexane/ethyl acetate, 50:50). Yield 580 mg (0.335 mmol, 56%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz, room temp.): δ = 7.36 (br., 1 H, N*H*), 6.04 (br., 3 H, N*H*), 4.26 (t, ^3J = 6.0 Hz, 2 H, OCH_2), 4.16 (t, ^3J = 6.1 Hz, 2 H, OCH_2), 3.42 (t, ^3J = 6.5 Hz, 2 H, BrCH_2), 3.39 (s, 2 H, $O_2CCH_2CO_2$), 2.12 (m, 28 H, $BrCH_2CH_2$, CH_2CONH, CH_2-dendronCONH, CH_2-dendronCOO), 1.88 (m, 26 H, CH_2CH_2CONH, CH_2CH_2-dendronCONH, CH_2CH_2-dendronCOO), 1.37 [s, 81 H, C(CH_3)$_3$] ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz, room temp.): δ = 172.78 (3 C, *C*ONH), 172.69 (9 C, *C*=O), 171.72 (1 C, *C*ONH), 166.91 (1 C, *C*=O), 166.73 (1 C, *C*=O), 80.44 [9 C, *C*(CH$_3$)$_3$], 64.43 (1 C, OCH_2), 63.24 (1 C, OCH_2), 57.53 (1 C, $C_{quat\text{-}inner}$), 57.27 (3 C, $C_{quat\text{-}outer}$), 41.28 (1 C, $O_2CH_2CO_2$), 32.51 (1 C, CH_2CONH), 31.44, 31.39 (6 C, inner-CH_2-dendron), 31.33 (1 C, BrCH_2), 29.67, 29.60 (18 C, outer-CH_2-dendron), 29.08 (1 C, CH_2CH_2Br), 27.93 [27 C, C(CH_3)$_3$], 24.19 (1 C, CH_2CH_2CONH) ppm. MS (FAB, NBA): *m/z* = 1755 [M + Na]$^+$, 1733 [M]$^+$; *MW* = 1733.00 g/mol. IR (ATR): $\tilde{\nu}$ = 3335, 2980, 2937, 1729, 1656, 1536, 1459, 1420, 1366, 1316, 1254, 1216, 1150, 1104, 1034, 953, 849, 760, 614 cm^{-1}. $C_{86}H_{147}BrN_4O_{26}$ (1733.00): calcd. C 59.60, H 8.55, N 3.23; found C 59.48, H 8.56, N 3.30.

Monoadduct 28: Compound **28** was synthesised according to the general procedure **II** with malonate **20** (417 mg, 241 µmol), C_{60} (270 mg, 375 µmol), I_2 (67 mg, 265 µmol) and DBU (47 µL, 312 µmol) in toluene (300 mL). The crude product was purified by column chromatography (SiO_2, gradient toluene/ethyl acetate, 90:10→50:50). Yield 287 mg (117 µmol, 49%) as a red brownish solid. ^{1}H NMR ($CDCl_3$, 400 MHz, room temp.): δ = 7.69 (br., 1 H, N*H*), 6.01 (br., 3 H, N*H*), 4.64 (t, ^3J = 6.0 Hz, 2 H, OCH_2), 4.52 (t, ^3J = 6.5 Hz, 2 H, OCH_2), 3.54 (t, ^3J = 6.4 Hz, 2 H, BrCH_2), 2.36 (m, 2 H, CH_2CONH), 2.30 (m, 2 H, $BrCH_2CH_2$), 2.14 (m, 24 H, CH_2-dendronCONH, CH_2-dendronCOO), 1.94 (2 m, 26 H, CH_2CH_2CONH, CH_2CH_2-dendronCONH, CH_2CH_2-dendronCOO), 1.38 [s, 81 H, C(CH_3)$_3$] ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz, room temp.): δ = 172.79 (3 C, *C*ONH), 172.66 (9 C, *C*=O), 171.47 (1 C, *C*ONH), 163.63 (1 C, *C*=O), 163.56 (1 C, *C*=O), 145.27, 145.19, 145.17, 145.14, 145.08, 144.89, 144.69, 144.64, 143.88, 143.05, 143.01, 142.97, 142.20, 141.95, 141.910, 141.88, 140.98, 139.20, 139.18, 138.87, 138.84 (58 C, sp^2-*C*), 80.49 [9 C, *C*(CH$_3$)$_3$], 71.36 (2 C, sp^3-*C*), 66.78 (1 C, OCH_2), 64.98 (1 C,

O*C*H$_2$), 57.48 (1 C, $C_{quat\text{-}inner}$), 57.37 (3 C, $C_{quat\text{-}outer}$), 51.96 (1 C, O$_2$*C*CO$_2$), 32.59 (1 C, *C*H$_2$CONH), 31.53, 31.39 (6 C, inner-*C*H$_2$-dendron), 31.28 (1 C, Br*C*H$_2$), 29.67, 29.63 (18 C, outer-*C*H$_2$-dendron), 29.10 (1 C, *C*H$_2$CH$_2$Br), 27.97 [27 C, C(*C*H$_3$)$_3$], 24.30 (1 C, *C*H$_2$CH$_2$CONH) ppm. MS (FAB, NBA): *m*/*z* = 2451 [M]$^+$, 720 [C$_{60}$]$^+$; *MW* = 2451.63 g/mol. IR (ATR): $\tilde{\nu}$ = 3246, 2976, 2930, 1725, 1540, 1458, 1428, 1390, 1366, 1262, 1204, 1150, 1112, 1058, 1004, 845, 753, 703 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ_{max} = 256, 326, 425 nm.

Monoadduct 4b: Compound **4b** was synthesised according to the general procedure **III** with monoadduct **28** (287 mg, 117 μmol), cyanuric acid (151 mg, 1.17 mmol) and DBU (18 μL, 117 μmol) in DMF (70 mL). The crude product was purified by column chromatography (SiO$_2$, 1. toluene/ethyl acetate, 70:30; 2. dichloromethane 100). Yield 85 mg (34 μmol, 29%) as a red brownish solid. ^{1}H NMR (CDCl$_3$, 400 MHz, room temp.): δ = 10.69 (br., 2 H, N*H*), 7.94 (br., 1 H, N*H*), 6.35 (br., 3 H, N*H*), 4.56 (t, ^3J = 5.2 Hz, 2 H, OC*H*$_2$), 4.51 (t, ^3J = 6.5 Hz, 2 H, OC*H*$_2$), 4.07 (t, ^3J = 5.6 Hz, 2 H, NC*H*$_2$), 2.38 (m, 4 H, C*H*$_2$CONH, NCH$_2$C*H*$_2$), 2.16 (m, 24 H, C*H*$_2$-dendronCONH, C*H*$_2$-dendronCOO), 1.95 (2 m, 26 H, C*H*$_2$CH$_2$CONH, C*H*$_2$CH$_2$-dendronCONH, C*H*$_2$CH$_2$-dendronCOO), 1.40 [s, 81 H, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR (CDCl$_3$, 100.5 MHz, room temp.): δ = 173.37 (3 C, *C*ONH), 173.05 (9 C, *C*=O), 172.89 (1 C, *C*ONH), 163.81 (1 C, *C*=O), 163.30 (1 C, *C*=O), 149.96 (2 C, NH*C*ON), 149.06 (1 C, NH*C*ONH), 145.47, 145.46, 145.30, 145.28, 145.23, 145.21, 144.89, 144.72, 144.69, 144.66, 144.63, 143.91, 143.88, 143.08, 143.07, 143.02, 142.99, 142.97, 142.23, 142.19, 141.99, 141.90, 140.98, 140.92, 138.84, 138.82 (58 C, sp^2-*C*), 80.70 [9 C, *C*(CH$_3$)$_3$], 71.60 (2 C, sp^3-*C*), 66.49 (1 C, O*C*H$_2$), 65.34 (1 C, O*C*H$_2$), 57.57 (1 C, $C_{quat\text{-}inner}$), 57.36 (3 C, $C_{quat\text{-}outer}$), 52.57 (1 C, O$_2$*C*CO$_2$), 38.78 (1 C, N*C*H$_2$), 32.83 (1 C, *C*H$_2$CONH), 31.79 (6 C, inner-*C*H$_2$-dendron), 29.91, 29.73 (18 C, outer-*C*H$_2$-dendron), 27.99 [27 C, C(*C*H$_3$)$_3$], 26.68 (1 C, *C*H$_2$CH$_2$N), 24.44 (1 C, *C*H$_2$CH$_2$CONH) ppm. MS (FAB, NBA): *m*/*z* = 2522 [M + Na]$^+$, 2500 [M]$^+$, 720 [C$_{60}$]$^+$; *MW* = 2499.79 g/mol. IR (ATR): $\tilde{\nu}$ = 3358, 3273, 2980, 2934, 2872, 1725, 1656, 1540, 1459, 1366, 1150, 1100, 953, 845, 799, 764, 737, 703 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ_{max} = 258, 325, 425 nm.

Fréchet-Type [G-1]-3-Bromopropyl Malonate 21: Compound **21** was synthesised according to the general procedure **I** with compound **13** (401 mg, 1.061 mmol), 4-{2-[(3-bromopropoxy)carbonyl] acetoyloxy}butanoic acid (**10**) (300 mg, 0.965 mmol), HOBt (143 mg, 1.061 mmol), DMAP (118 mg, 0.965 mmol) and DCC (258 mg, 1.254 mmol) in CH$_2$Cl$_2$ (100 mL). The crude product was purified by column chromatography (SiO$_2$, hexane/ethyl acetate, 5:2). Yield 379 mg (0.618 mmol, 64%) as a colorless oil. ^{1}H NMR (CDCl$_3$, 300 MHz, room temp.): δ = 7.37 (m, 10 H, Ph*H*), 6.60 (m, 3 H, Ar*H*), 5.06 (s, 2 H, OC*H*$_2$), 5.03 (s, 4 H, OC*H*$_2$), 4.27 (t, ^3J = 6.1 Hz, 2 H, OC*H*$_2$), 4.20 (t, ^3J = 6.3 Hz, 2 H, OC*H*$_2$), 3.42 (t, ^3J = 6.5 Hz, 2 H, BrC*H*$_2$), 3.37 (s, 2 H, O$_2$CC*H*$_2$CO$_2$), 2.46 (t, ^3J = 7.4 Hz, 2 H, COC*H*$_2$), 2.15 (q, ^3J = 6.3 Hz, 2 H, BrCH$_2$C*H*$_2$), 2.00 (q, ^3J = 6.9 Hz, 2 H, COCH$_2$C*H*$_2$) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz, room temp.): δ = 172.21 (1 C, *C*=O), 166.16 (1 C, *C*=O), 166.08 (1 C, *C*=O), 159.94 (2 C, Ar*C*O), 137.98 (1 C, Ar*C*H$_2$), 136.57 (2 C, Ph*C*CH$_2$), 128.43 (4 C, *m*-Ph*C*H), 127.87 (2 C, *p*-Ph*C*H), 127.37 (4 C, *o*-Ph*C*H), 106.94 (2 C, Ar*C*H), 101.58 (1 C, Ar*C*H), 69.93 (2 C, PhC*C*H$_2$O), 66.04 (1 C, ArC*C*H$_2$O), 64.32 (1 C, *C*H$_2$O), 63.01 (1 C, *C*H$_2$O), 41.19 (O$_2$C*C*H$_2$CO$_2$), 31.26 (1 C, *C*H$_2$CH$_2$Br), 30.41 (1 C, *C*H$_2$COO), 29.01 (1 C, *C*H$_2$Br), 23.69 (1 C, *C*H$_2$CH$_2$COO) ppm. MS (FAB, NBA): *m*/*z* = 655 [M + K]$^+$, 614 [M]$^+$; *MW* = 613.49 g/mol. IR (ATR): $\tilde{\nu}$ = 3242, 2926, 1733, 1648, 1598, 1563, 1451, 1378, 1293, 1262, 1212, 1158, 1089, 1058, 1031, 957, 907, 807, 749, 699, 637 cm^{-1}. C$_{31}$H$_{33}$BrO$_8$ (613.49): calcd. C 60.69, H 5.42; found C 60.81, H 5.45.

Monoadduct 29: Compound **29** was synthesised according to the general procedure **II** with malonate **21** (200 mg, 326 μmol), C$_{60}$ (350 mg, 489 μmol), I$_2$ (91 mg, 359 μmol) and DBU (66 μL, 440 μmol) in toluene (300 mL). The crude product was purified by column chromatography (SiO$_2$, gradient toluene/ethyl acetate, 90:10→50:50). Yield 214 mg (160 μmol, 49%) as a red brownish solid. ^{1}H NMR (CDCl$_3$, 400 MHz, room temp.): δ = 7.39 (m, 10 H, Ph*H*), 6.58 (d, ^4J = 2.1 Hz, 2 H, Ar*H*), 6.56 (d, ^4J = 2.1 Hz, 1 H, Ar*H*), 5.07 (s, 2 H, OC*H*$_2$), 5.01 (s, 4 H, OC*H*$_2$), 4.62 (t, ^3J = 6.0 Hz, 2 H, OC*H*$_2$), 4.55 (t, ^3J = 6.2 Hz, 2 H, OC*H*$_2$), 3.51 (t, ^3J = 6.4 Hz, 2 H, BrC*H*$_2$), 2.57 (t, ^3J = 7.3 Hz, 2 H, COC*H*$_2$), 2.33 (q, ^3J = 6.2 Hz, 2 H, BrCH$_2$C*H*$_2$), 2.19 (q, ^3J = 6.8 Hz, 2 H, COCH$_2$C*H*$_2$) ppm. ^{13}C NMR (CDCl$_3$, 100.5 MHz, room temp.): δ = 172.26 (1 C, *C*=O), 163.47 (1 C, *C*=O), 163.39 (1 C, *C*=O), 160.14 (2 C, Ar*C*O), 145.27, 145.244, 145.21, 145.19, 145.17, 145.03, 145.01, 144.95, 144.90, 144.68, 144.67, 144.66, 144.64, 144.59, 144.57, 143.87, 143.86, 143.07, 143.03, 143.01, 142.99, 142.95, 142.17, 141.88, 141.82, 140.98, 139.05, 138.91 (58 C, sp^2-*C*), 137.98 (1 C, Ar*C*H$_2$), 136.65 (2 C, Ph*C*CH$_2$), 128.62 (4 C, *m*-Ph*C*H), 128.07 (2 C, *p*-Ph*C*H), 127.58 (4 C, *o*-Ph*C*H), 107.17 (2 C, Ar*C*H), 101.72 (1 C, Ar*C*H), 71.28 (2 C, sp^3-*C*), 70.05 (2 C, PhC*C*H$_2$O), 66.35 (1 C, ArC*C*H$_2$O), 66.19 (1 C, *C*H$_2$O), 64.84 (1 C, *C*H$_2$O), 51.79 (O$_2$C*C*CO$_2$), 31.18 (1 C, *C*H$_2$CH$_2$Br), 30.45 (1 C, *C*H$_2$COO), 28.97 (1 C, *C*H$_2$Br), 22.21 (1 C, *C*H$_2$CH$_2$COO) ppm. MS (FAB, NBA): *m*/*z* = 1331 [M]$^+$, 720 [C$_{60}$]$^+$; *MW* = 1332.12 g/mol. IR (ATR): $\tilde{\nu}$ = 3253, 3212, 2961, 2930, 2856, 1733, 1594, 1509, 1451, 1428, 1370, 1266, 1227, 1154, 1061, 1000, 961, 942, 907, 838, 733, 699, 637 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ_{max} = 256, 320, 425 nm.

Monoadduct 2a: Compound **2a** was synthesised according to the general procedure **III** with monoadduct **29** (220 mg, 165 μmol), cyanuric acid (213 mg, 1.65 mmol) and DBU (25 μL, 165 μmol) in DMF (50 mL). The crude product was purified by column chromatography (SiO$_2$, toluene/ethyl acetate, 70:30). Yield 79 mg (57 μmol, 35%) as a red brownish solid. ^{1}H NMR (CDCl$_3$, 300 MHz, room temp.): δ = 8.93 (br., 2 H, N*H*), 7.39 (m, 10 H, Ph*H*), 6.60 (d, ^4J = 2.0 Hz, 2 H, Ar*H*), 6.58 (d, ^4J = 2.0 Hz, 1 H, Ar*H*), 5.09 (s, 2 H, OC*H*$_2$), 5.02 (s, 4 H, OC*H*$_2$), 4.55 (m, 4 H, OC*H*$_2$), 4.04 (t, ^3J = 6.4 Hz, 2 H, NC*H*$_2$), 2.59 (t, ^3J = 7.2 Hz, 2 H, COC*H*$_2$), 2.17 (m, 4 H, NCH$_2$C*H*$_2$, COCH$_2$C*H*$_2$) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz, room temp.): δ = 172.96 (1 C, *C*=O), 163.46 (1 C, *C*=O), 163.36 (1 C, *C*=O), 160.12 (2 C, Ar*C*O), 149.23 (2 C, NH*C*ON), 148.50 (1 C, NH*C*ONH), 145.24, 145.16, 145.10, 145.02, 144.99, 144.95, 144.91, 144.86, 144.65, 144.60, 144.59, 144.54, 143.83, 143.81, 143.02, 143.00, 142.99, 142.94, 142.90, 142.14, 141.84, 140.92, 140.90, 139.25, 138.68, 138.02 (58 C, sp^2-*C*), 136.66 (3 C, Ar*C*H$_2$, Ph*C*CH$_2$), 128.64 (4 C, *m*-Ph*C*H), 128.09 (2 C, *p*-Ph*C*H), 127.61 (4 C, *o*-Ph*C*H), 107.16 (2 C, Ar*C*H), 101.67 (1 C, Ar*C*H), 71.37 (2 C, sp^3-*C*), 70.06 (2 C, PhC*C*H$_2$O), 66.43 (1 C, ArC*C*H$_2$O), 66.35 (1 C, *C*H$_2$O), 64.95 (1 C, *C*H$_2$O), 51.91 (1 C, O$_2$C*C*CO$_2$), 39.11 (1 C, *C*H$_2$N), 30.45 (1 C, *C*H$_2$COO), 26.95 (1 C, *C*H$_2$CH$_2$N), 23.84 (1 C, *C*H$_2$CH$_2$COO) ppm. MS (FAB, NBA): *m*/*z* = 1380 [M]$^+$, 720 [C$_{60}$]$^+$; *MW* = 1380.28 g/mol. IR (ATR): $\tilde{\nu}$ = 3221, 3088, 2964, 1733, 1702, 1594, 1455, 1424, 1378, 1266, 1231, 1154, 1096, 1058, 1027, 961, 907, 833, 730, 699 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ_{max} = 258, 326, 426 nm.

Fréchet-Type [G-2]-3-Bromopropyl Malonate 22: Compound **22** was synthesised according to the general procedure **I** with compound **14** (790 mg, 1.061 mmol), 4-{2-[(3-bromopropoxy)carbonyl]-acetoyloxy}butanoic acid (**10**) (300 mg, 0.965 mmol), HOBt (143 mg, 1.061 mmol), DMAP (118 mg, 0.965 mmol) and DCC

(258 mg, 1.254 mmol) in CH_2Cl_2 (100 mL). The crude product was purified by column chromatography (SiO_2, hexane/ethyl acetate, 2:1). Yield 490 mg (0.618 mmol, 49%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz, room temp.): δ = 7.31 (m, 20 H, Ph*H*), 6.63 (d, ^4J = 2.0 Hz, 4 H, Ar*H*), 6.53 (d, ^4J = 2.1 Hz, 2 H, Ar*H*), 6.51 (d, ^4J = 2.1 Hz, 2 H, Ar*H*), 6.49 (t, ^4J = 2.2 Hz, 1 H, Ar*H*), 4.99 (s, 2 H, OCH_2), 4.94 (s, 8 H, OCH_2), 4.89 (s, 4 H, OCH_2), 4.17 (t, ^3J = 6.0 Hz, 2 H, OCH_2), 4.11 (t, ^3J = 6.2 Hz, 2 H, OCH_2), 3.32 (t, ^3J = 6.5 Hz, 2 H, BrCH_2), 3.28 (s, 2 H, $O_2CCH_2CO_2$) 2.38 (t, ^3J = 7.3 Hz, 2 H, CH_2CO), 2.05 (q, ^3J = 6.0 Hz, 2 H, $BrCH_2CH_2$), 1.92 (q, ^3J = 6.8 Hz, 2 H, CH_2CH_2CO) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz, room temp.): δ = 172.30 (1 C, *C*=O), 166.24 (1 C, *C*=O), 166.16 (1 C, *C*=O), 160.06 (4 C, Ar*C*O), 159.90 (2 C, Ar*C*O), 139.04 (2 C, Ar*C*CH_2), 138.03 (1 C, Ar*C*CH_2), 136.64 (4 C, Ar*C*CH_2), 128.44 (8 C, *m*-Ph*C*), 127.87 (4 C, *p*-Ph*C*), 127.42 (8 C, *o*-Ph*C*), 106.95 (2 C, Ar*C*CCH_2), 106.22 (4 C, Ar*C*CCH_2), 101.55 (1 C, Ar*C*H), 101.35 (2 C, Ar*C*H), 69.83 (4 C, PhC*C*H_2O), 69.72 (2 C, ArC*C*H_2O), 65.97 (1 C, ArC*C*H_2O), 64.24 (1 C, *C*H_2O), 62.92 (1 C, *C*H_2O), 41.05 (1 C, $O_2CCH_2CO_2$), 31.11 (1 C, $BrCH_2CH_2$), 30.27 (1 C, *C*H_2COO), 28.96 (1 C, Br*C*H_2), 23.56 (1 C, *C*H_2CH_2COO) ppm. MS (FAB, NBA): *m*/*z* = 1038 $[M]^+$, 720 $[C_{60}]^+$; *MW* = 1037.98 g/mol. IR (ATR): $\tilde{\nu}$ = 3250, 3069, 3034, 2876, 1733, 1594, 1498, 1451, 1374, 1320, 1293, 1146, 1047, 957, 911, 830, 737, 695, 633 cm^{-1}. $C_{59}H_{57}BrO_{12}$ (1037.98): calcd. C 68.27, H 5.54; found C 68.38, H 5.60.

Monoadduct 30: Compound **30** was synthesised according to the general procedure **II** with malonate **22** (397 mg, 383 µmol), C_{60} (415 mg, 576 µmol), I_2 (107 mg, 421 µmol) and DBU (77 µL, 517 µmol) in toluene (300 mL). The crude product was purified by column chromatography (SiO_2, toluene/ethyl acetate, 98:2). Yield 141 mg (80 µmol, 21%) as a red brownish solid. ^{1}H NMR ($CDCl_3$, 400 MHz, room temp.): δ = 7.36 (m, 20 H, Ph*H*), 6.67 (d, ^4J = 2.3 Hz, 4 H, Ar*H*), 6.58 (d, ^4J = 2.2 Hz, 2 H, Ar*H*), 6.57 (d, ^4J = 2.3 Hz, 2 H, Ar*H*), 6.54 (t, ^4J = 2.2 Hz, 1 H, Ar*H*), 5.08 (s, 2 H, OCH_2), 5.02 (s, 8 H, OCH_2), 4.95 (s, 4 H, OCH_2), 4.61 (t, ^3J = 6.0 Hz, 2 H, OCH_2), 4.55 (t, ^3J = 6.2 Hz, 2 H, OCH_2), 3.50 (t, ^3J = 6.4 Hz, 2 H, BrCH_2), 2.58 (t, ^3J = 7.2 Hz, 2 H, CH_2CO), 2.33 (m, 2 H, $BrCH_2CH_2$), 2.19 (m, 2 H, CH_2CH_2CO) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz, room temp.): δ = 172.32 (1 C, *C*=O), 163.47 (1 C, *C*=O), 163.36 (1 C, *C*=O), 160.19 (4 C, Ar*C*O), 160.04 (2 C, Ar*C*O), 145.23, 145.19, 145.15, 145.14, 145.13, 144.97, 144.96, 144.86, 144.64, 144.63, 144.59, 144.56, 144.51, 143.83, 143.81, 143.03, 142.98, 142.96, 142.94, 142.91, 142.13, 141.84, 141.78, 140.94, 139.05, 138.95, 138.93 (60 C, sp^2-*C*, Ar*C*CH_2), 137.97 (1 C, Ar*C*CH_2), 136.71 (4 C, Ph*C*CH_2), 128.59 (8 C, *m*-Ph*C*), 128.02 (4 C, *p*-Ph*C*), 127.57 (8 C, *o*-Ph*C*), 107.17 (2 C, Ar*C*CCH_2), 106.48 (4 C, Ar*C*CCH_2), 101.75 (1 C, Ar*C*H), 101.52 (2 C, Ar*C*H), 71.26 (2 C, sp^3-*C*) 70.02 (4 C, PhC*C*H_2O), 69.93 (2 C, ArC*C*H_2O), 66.35 (1 C, ArC*C*H_2O), 66.17 (1 C, *C*H_2O), 64.83 (1 C, *C*H_2O), 51.81 (1 C, O_2CCCO_2), 31.15 (1 C, $BrCH_2CH_2$), 30.45 (1 C, *C*H_2COO), 28.96 (1 C, Br*C*H_2), 23.82 (1 C, *C*H_2CH_2COO) ppm. MS (FAB, NBA): *m*/*z* = 1756 $[M]^+$, 720 $[C_{60}]^+$; *MW* = 1756.61 g/mol. IR (ATR): $\tilde{\nu}$ = 3252, 3212, 2926, 2895, 1737, 1590, 1444, 1370, 1343, 1293, 1266, 1231, 1204, 1143, 1042, 1004, 957, 907, 826, 730, 691, 637 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 257, 324, 425 nm.

Monoadduct 2b: Compound **2b** was synthesised according to the general procedure **III** with monoadduct **30** (151 mg, 86.1 µmol), cyanuric acid (111 mg, 861.0 µmol) and DBU (12.9 µL, 86.1 µmol) in DMF (25 mL). The crude product was purified by column chromatography (SiO_2, toluene/ethyl acetate, 80:20). Yield 39 mg (22.0 µmol, 25%) as a red brownish solid. ^{1}H NMR ($CDCl_3$, 400 MHz, room temp.): δ = 7.37 (m, 20 H, Ph*H*), 6.65 (d, ^4J = 2.0 Hz, 4 H, Ar*H*), 6.56 (d, ^4J = 1.9 Hz, 2 H, Ar*H*), 6.54 (d, ^4J = 2.1 Hz, 2 H, Ar*H*), 6.51 (m, 1 H, Ar*H*), 5.05 (s, 2 H, OCH_2), 5.00 (s, 8 H, OCH_2), 4.91 (s, 4 H, OCH_2), 4.54 (t, ^3J = 5.9 Hz, 2 H, OCH_2), 4.47 (m, 2 H, OCH_2), 3.96 (m, 2 H, NCH_2), 2.53 (t, ^3J = 7.0 Hz, 2 H, CH_2CO), 2.13 (m, 4 H, NCH_2CH_2, CH_2CH_2CO) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz, room temp.): δ = 172.97 (1 C, *C*=O), 163.43 (1 C, *C*=O), 163.32 (1 C, *C*=O), 160.18 (4 C, Ar*C*O), 160.02 (2 C, Ar*C*O), 149.04 (2 C, NH*C*ON), 148.11 (1 C, NH*C*ONH), 145.22, 145.20, 145.13, 145.09, 145.07, 144.94, 144.88, 144.84, 144.64, 144.63, 144.58, 144.56, 144.51, 143.81, 143.78, 143.00, 142.98, 142.97, 142.95, 142.91, 142.88, 142.12, 141.82, 140.91, 140.88, 139.22, 139.08 (58 C, sp^2-*C*), 138.63 (2 C, Ar*C*CH_2), 138.02 (1 C, Ar*C*CH_2), 136.73 (4 C, Ph*C*CH_2), 128.61 (8 C, *m*-Ph*C*), 128.05 (4 C, *p*-Ph*C*), 127.60 (8 C, *o*-Ph*C*), 107.13 (2 C, Ar*C*CCH_2), 106.56 (4 C, Ar*C*CCH_2), 101.73 (1 C, Ar*C*H), 101.51 (2 C, Ar*C*H), 71.36 (2 C, sp^3-*C*) 70.04 (4 C, PhC*C*H_2O), 69.93 (2 C, ArC*C*H_2O), 66.44 (1 C, ArC*C*H_2O), 66.32 (1 C, *C*H_2O), 64.89 (1 C, *C*H_2O), 51.94 (1 C, O_2CCCO_2), 39.12 (1 C, N*C*H_2), 30.54 (1 C, *C*H_2COO), 26.94 (1 C, NCH_2CH_2), 23.82 (1 C, *C*H_2CH_2COO) ppm. MS (FAB, NBA): *m*/*z* = 1803 $[M]^+$, 720 $[C_{60}]^+$; *MW* = 1804.77 g/mol. IR (ATR): $\tilde{\nu}$ = 3246, 2926, 2856, 138, 1733, 1702, 1594, 1451, 1374, 1262, 1231, 1150, 1046, 826, 807, 749, 695, 633 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 257, 326, 425 nm.

(*R*,*R*)-Depsipeptide-[G-1]-3-bromopropyl Malonate 23: Compound **23** was synthesised according to the general procedure **I** with compound **15** (722 mg, 1.66 mmol), 4-{2-[(3-bromopropoxy)carbonyl]-acetoyloxy}butanoic acid (**10**) (516 mg, 1.66 mmol), HOBt (223 mg, 1.83 mmol), DMAP (224 mg, 1.66 mmol) and DCC (445 mg, 2.16 mmol) in CH_2Cl_2 (100 mL). The crude product was purified by column chromatography (SiO_2, hexane/ethyl acetate, 3:1). Yield 688 mg (0.946 mmol, 57%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz, room temp.): δ = 7.93 (dd, ^3J = 8.2 Hz, ^4J = 1.3 Hz, 2 H, 2 H, *o*-Bz*H*), 7.57 (dd, ^3J = 7.5 Hz, 1 H, *p*-Bz*H*), 7.40 (dd, ^3J = 7.9 Hz, 2 H, *m*-Bz*H*), 7.31 (m, 5 H, Bn*H*), 7.16 (m, 2 H, Bn*H*), 7.09 (m, 3 H, Bn*H*), 5.92 (d, ^3J = 2.8 Hz, 1 H, C*H**), 5.82 (d, ^3J = 2.8 Hz, 1 H, C*H**), 5.26 (d, ^3J = 12.0 Hz, 1 H, PhCH_2), 5.18 (d, ^3J = 12.0 Hz, 1 H, PhCH_2), 5.12 (d, ^3J = 12.0 Hz, 1 H, PhCH_2), 5.04 (d, ^3J = 12.0 Hz, 1 H, PhCH_2), 4.27 (t, ^3J = 6.0 Hz, 2 H, OCH_2), 4.13 (t, ^3J = 6.3 Hz, 2 H, OCH_2), 3.42 (t, ^3J = 6.5 Hz, CH_2Br), 3.37 (s, 2 H, $O_2CCH_2CO_2$), 2.39 (m, 1 H, CH_2COO) 2.20 (m, 2 H + 1 H, CH_2CH_2Br, CH_2COO), 1.87 (q, ^3J = 7.2 Hz, *C*H_2CH_2COO) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz, room temp.): δ = 171.36 (1 C, *C*=O), 166.36 (1 C, *C*=O), 166.31 (1 C, *C*=O), 165.55 (2 C, *C*OOBn), 165.04 (1 C, *C*OPh), 134.85 (1 C, Ph*C*CH_2), 134.47 (1 C, Ph*C*CH_2), 133.69 (1 C, *p*-Ph*C*CO), 130.06 (2 C, *o*-Ph*C*CH_2), 128.63, 128.53, 128.49, 128.46, 128.37, 128.33 (13 C, Ph*C*), 71.06 (1 C, **C*H), 70.88 (1 C, **C*H), 67.85 (1 C, Ph*C*H_2O), 67.69 (1 C, Ph*C*H_2O), 64.11 (1 C, *C*H_2O), 63.10 (1 C, *C*H_2O), 41.23 ($O_2CCH_2CO_2$), 31.28 (1 C, *C*H_2CH_2Br), 29.72 (1 C, *C*H_2COO), 29.03 (1 C, *C*H_2Br), 23.44 (1 C, *C*H_2CH_2COO) ppm. MS (FAB, NBA): *m*/*z* = 729 $[M]^+$; *MW* = 727.55 g/mol. IR (ATR): $\tilde{\nu}$ = 3223, 2964, 1729, 1455, 1413, 1382, 1336, 1258, 1193, 1131, 1092, 1069, 1023, 957, 907, 807, 753, 714, 637 cm^{-1}. $C_{35}H_{35}BrO_{12}$ (727.55): calcd. C 57.78, H 4.85; found C 57.85, H 4.87.

(*S*,*S*)-Depsipeptide-[G-1]-3-bromopropyl Malonate 24: Compound **24** was synthesised according to the general procedure **I** with compound **16** (1.452 g, 3.34 mmol), 4-[2-[(3-bromopropoxy)carbonyl]-acetoyloxy]butanoic acid (**10**) (800 mg, 2.57 mmol), HOBt (347 mg, 2.57 mmol), DMAP (314 mg, 2.57 mmol) and DCC (689 mg, 3.34 mmol) in CH_2Cl_2 (200 mL). The crude product was purified by column chromatography (SiO_2, hexane/ethyl acetate, 3:1). Yield 748 mg (1.028 mmol, 40%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz, room temp.): δ = 7.92 (dd, ^3J = 8.2 Hz, ^4J = 1.3 Hz, 2 H, 2 H, *o*-Bz*H*), 7.56 (dd, ^3J = 7.6 Hz, 1 H, *p*-Bz*H*), 7.40 (dd, ^3J

= 7.9 Hz, 2 H, *m*-BzH), 7.30 (m, 5 H, BnH), 7.14 (m, 2 H, BnH), 7.09 (m, 3 H, BnH), 5.91 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.82 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.26 (d, ^3J = 12.0 Hz, 1 H, PhCH$_2$), 5.17 (d, ^3J = 12.0 Hz, 1 H, PhCH$_2$), 5.10 (d, ^3J = 12.0 Hz, 1 H, PhCH$_2$), 5.02 (d, ^3J = 12.0 Hz, 1 H, PhCH$_2$), 4.25 (t, ^3J = 6.0 Hz, 2 H, OCH$_2$), 4.12 (t, ^3J = 6.3 Hz, 2 H, OCH$_2$), 3.41 (t, ^3J = 6.4 Hz, CH$_2$Br), 3.36 (s, 2 H, O$_2$CCH$_2$CO$_2$), 2.39 (m, 1 H, CH$_2$COO) 2.18 (m, 2 H + 1 H, CH$_2$CH$_2$Br, CH$_2$COO), 1.86 (q, ^3J = 7.2 Hz, CH$_2$CH$_2$COO) ppm. ^{13}C NMR (CDCl$_3$, 100.5 MHz, room temp.): δ = 171.34 (1 C, C=O), 166.33 (1 C, C=O), 166.29 (1 C, C=O), 165.54 (2 C, COOBn), 165.02 (1 C, COPh), 134.83 (1 C, PhCCH$_2$), 134.48 (1 C, PhCCH$_2$), 133.68 (1 C, *p*-PhCCO), 130.04 (2 C, *o*-PhCCH$_2$), 128.64, 128.54, 128.50, 128.46, 128.38, 128.34 (13 C, PhC), 71.06 (1 C, *CH), 70.88 (1 C, *CH), 67.86 (1 C, PhCH$_2$O), 67.68 (1 C, PhCH$_2$O), 64.09 (1 C, CH$_2$O), 63.07 (1 C, CH$_2$O), 41.22 (O$_2$CCH$_2$CO$_2$), 31.27 (1 C, CH$_2$CH$_2$Br), 29.70 (1 C, CH$_2$COO), 29.00 (1 C, CH$_2$Br), 23.43 (1 C, CH$_2$CH$_2$COO) ppm. MS (FAB, NBA): *m*/*z* = 729 [M]$^+$; *MW* = 727.55 g/mol. IR (ATR): $\tilde{\nu}$ = 3223, 2966, 1729, 1455, 1412, 1382, 1336, 1258, 1193, 1131, 1091, 1069, 1023, 957, 907, 807, 752, 714, 638 cm^{-1}. $C_{35}H_{35}BrO_{12}$ (727.55): calcd. C 57.78, H 4.85; found C 57.92, H 4.91.

Monoadduct 31: Compound **31** was synthesized according to the general procedure **II** with malonate **23** (253 mg, 347 μmol), C_{60} (375 mg, 521 μmol), I_2 (97 mg, 382 μmol) and DBU (63 μL, 417 μmol) in toluene (400 mL). The crude product was purified by column chromatography (SiO_2, toluene/ethyl acetate, 98:2). Yield 216 mg (149 μmol, 43%) as a red brownish solid. ^{1}H NMR (CDCl$_3$, 400 MHz, room temp.): δ = 7.93 (dd, ^3J = 8.3 Hz, ^4J = 1.3 Hz, 2 H, 2 H, *o*-BzH), 7.57 (dd, ^3J = 7.5 Hz, 1 H, *p*-BzH), 7.41 (dd, ^3J = 7.7 Hz, 2 H, *m*-BzH), 7.33 (m, 5 H, BnH), 7.15 (m, 2 H, BnH), 7.10 (m, 3 H, BnH), 5.93 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.86 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.30 (d, ^3J = 12.0 Hz, 1 H, PhCH$_2$), 5.22 (d, ^3J = 12.0 Hz, 1 H, PhCH$_2$), 5.12 (d, ^3J = 12.0 Hz, 1 H, PhCH$_2$), 5.06 (d, ^3J = 12.0 Hz, 1 H, PhCH$_2$), 4.62 (t, ^3J = 6.0 Hz, 2 H, OCH$_2$), 4.49 (t, ^3J = 6.4 Hz, 2 H, OCH$_2$), 3.49 (t, ^3J = 6.4 Hz, CH$_2$Br), 2.51 (m, 1 H, CH$_2$COO), 2.32 (m, 2 H + 1 H, CH$_2$CH$_2$Br, CH$_2$COO), 2.07 (q, ^3J = 6.8 Hz, 2 H, CH$_2$CH$_2$COO) ppm. ^{13}C NMR (CDCl$_3$, 100.5 MHz, room temp.): δ = 171.12 (1 C, C=O), 165.47 (1 C, COOBn), 165.45 (1 C, COOBn), 165.00 (1 C, COPh), 163.40 (1 C, C=O), 163.38 (1 C, C=O), 145.28, 145.26, 145.19, 145.17, 145.07, 144.99, 144.90, 144.88, 144.87, 144.69, 144.66, 144.61, 144.59, 143.87, 143.06, 143.00, 142.95, 142.17, 141.89, 141.84, 140.99, 139.20, 138.84 (58 C, sp^2-C), 134.85 (1 C, PhCCH$_2$), 134.42 (1 C, PhCCH$_2$), 133.71 (1 C, *p*-PhCCO), 130.03 (2 C, *o*-PhCCH$_2$), 128.68, 128.67, 128.55, 128.51, 128.31 (13 C, PhC), 71.27 (2 C, sp^3-C), 71.03 (1 C, *CH), 70.94 (1 C, *CH), 67.88 (1 C, PhCH$_2$O), 67.71 (1 C, PhCH$_2$O), 65.89 (1 C, CH$_2$O), 64.87 (1 C, CH$_2$O), 51.72 (O$_2$CCCO$_2$), 31.16 (1 C, CH$_2$CH$_2$Br), 29.73 (1 C, CH$_2$COO), 29.02 (1 C, CH$_2$Br), 23.61 (1 C, CH$_2$CH$_2$COO) ppm. MS (FAB, NBA): *m*/*z* = 1446 [M]$^+$, 720 [C$_{60}$]$^+$; *MW* = 1446.18 g/mol. IR (ATR): $\tilde{\nu}$ = 3065, 3034, 2961, 2895, 1733, 1602, 1540, 1498, 1455, 1429, 1378, 1351, 1231, 1158, 1092, 1004, 957, 737, 699, 637 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ_{max} = 254, 322, 424 nm.

Monoadduct 32: Compound **32** was synthesized according to the general procedure **II** with malonate **24** (292 mg, 400 μmol), C_{60} (432 mg, 600 μmol), I_2 (101 mg, 440 μmol) and DBU (78 μL, 520 μmol) in toluene (450 mL). The crude product was purified by column chromatography (SiO_2, toluene/ethyl acetate, 98:2). Yield 226 mg (156 μmol, 39%) as a red brownish solid. ^{1}H NMR (CDCl$_3$, 400 MHz, room temp.): δ = 7.92 (dd, ^3J = 8.3 Hz, ^4J = 1.3 Hz, 2 H, 2 H, *o*-BzH), 7.56 (dd, ^3J = 7.5 Hz, 1 H, *p*-BzH), 7.41 (dd, ^3J = 7.7 Hz, 2 H, *m*-BzH), 7.33 (m, 5 H, BnH), 7.15 (m, 2 H, BnH), 7.08 (m, 3 H, BnH), 5.93 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.86 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.30 (d, ^3J = 12.0 Hz, 1 H, PhCH$_2$), 5.20 (d, ^3J = 12.0 Hz, 1 H, PhCH$_2$), 5.11 (d, ^3J = 12.0 Hz, 1 H, PhCH$_2$), 5.07 (d, ^3J = 12.0 Hz, 1 H, PhCH$_2$), 4.61 (t, ^3J = 6.0 Hz, 2 H, OCH$_2$), 4.49 (t, ^3J = 6.4 Hz, 2 H, OCH$_2$), 3.48 (t, ^3J = 6.4 Hz, CH$_2$Br), 2.49 (m, 1 H, CH$_2$COO), 2.33 (m, 2 H + 1 H, CH$_2$CH$_2$Br, CH$_2$COO), 2.08 (q, ^3J = 6.8 Hz, 2 H, CH$_2$CH$_2$COO) ppm. ^{13}C NMR (CDCl$_3$, 100.5 MHz, room temp.): δ = 171.10 (1 C, C=O), 165.45 (1 C, COOBn), 165.43 (1 C, COOBn), 165.00 (1 C, COPh), 163.40 (1 C, C=O), 163.37 (1 C, C=O), 145.27, 145.26, 145.19, 145.17, 145.08, 144.99, 144.91, 144.88, 144.87, 144.68, 144.64, 144.59, 144.59, 143.86, 143.06, 143.01, 142.94, 142.17, 141.87, 141.84, 140.99, 139.21, 138.83 (58 C, sp^2-C), 134.85 (1 C, PhCCH$_2$), 134.40 (1 C, PhCCH$_2$), 133.71 (1 C, *p*-PhCCO), 130.01 (2 C, *o*-PhCCH$_2$), 128.68, 128.65, 128.55, 128.49, 128.31 (13 C, PhC), 71.28 (2 C, sp^3-C), 71.03 (1 C, *CH), 70.92 (1 C, *CH), 67.86 (1 C, PhCH$_2$O), 67.68 (1 C, PhCH$_2$O), 65.90 (1 C, CH$_2$O), 64.87 (1 C, CH$_2$O), 51.71 (O$_2$CCCO$_2$), 31.16 (1 C, CH$_2$CH$_2$Br), 29.72 (1 C, CH$_2$COO), 29.02 (1 C, CH$_2$Br), 23.62 (1 C, CH$_2$CH$_2$COO) ppm. MS (FAB, NBA): *m*/*z* =1446 [M]$^+$, 720 [C$_{60}$]$^+$; *MW* = 1446.18 g/mol. IR (ATR): $\tilde{\nu}$ = 3065, 3033, 2961, 2895, 1730, 1602, 1540, 1499, 1455, 1429, 1376, 1351, 1231, 1158, 1091, 1004, 957, 737, 637 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ_{max} = 254, 324, 424 nm.

Monoadduct 3a: Compound **3a** was synthesized according to the general procedure **III** with monoadduct **31** (320 mg, 221 μmol), cyanuric acid (570 mg, 4.42 mmol) and DBU (33 μL, 221 μmol) in DMF (125 mL). The crude product was purified by column chromatography (SiO_2, dichloromethane/ethyl acetate, 2:1 followed by preparative HPLC, dichloromethane/ethyl acetate, 85:15). Yield 102 mg (69 μmol, 31%) as a red brownish solid. ^{1}H NMR (CDCl$_3$, 400 MHz, room temp.): δ = 9.26 (br., 2 H, NH), 7.91 (d, ^3J = 7.3 Hz, 2 H, 2 H, *o*-BzH), 7.56 (dd, ^3J = 7.4 Hz, 1 H, *p*-BzH), 7.39 (dd, ^3J = 7.8 Hz, 2 H, *m*-BzH), 7.31 (m, 5 H, BnH), 7.16 (m, 2 H, BnH), 7.08 (m, 3 H, BnH), 5.94 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.89 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.27 (d, ^3J = 12.0 Hz, 1 H, PhCH$_2$), 5.23 (d, ^3J = 12.0 Hz, 1 H, PhCH$_2$), 5.13 (d, ^3J = 12.0 Hz, 1 H, PhCH$_2$), 5.04 (d, ^3J = 12.0 Hz, 1 H, PhCH$_2$), 4.50 (m, 4 H, OCH$_2$), 4.00 (t, ^3J = 6.1 Hz, 2 H, NCH$_2$), 2.53 (m, 1 H, CH$_2$COO), 2.35 (m, 1 H, CH$_2$COO), 2.10 (m, 4 H, CH$_2$CH$_2$N, CH$_2$CH$_2$COO) ppm. ^{13}C NMR (CDCl$_3$, 100.5 MHz, room temp.): δ = 171.60 (1 C, C=O), 165.80 (1 C, COOBn), 165.78 (1 C, COOBn), 165.02 (1 C, COPh), 163.41 (1 C, C=O), 163.37 (1 C, C=O), 149.02 (2 C, NHCON), 148.00 (1 C, NHCONH), 145.28, 145.19, 145.12, 145.04, 144.95, 144.90, 144.68, 144.64, 144.61, 143.86, 143.07, 143.03, 142.98, 142.95, 142.18, 141.89, 141.88, 140.95, 139.22 138.81 (58 C, sp^2-C), 134.81 (1 C, PhCCH$_2$), 134.42 (1 C, PhCCH$_2$), 133.74 (1 C, *p*-PhCCO), 130.06 (2 C, *o*-PhCCH$_2$), 128.70, 128.62, 128.52, 128.37, 128.33 (13 C, PhC), 71.37 (2 C, sp^3-C), 71.11 (1 C, *CH), 70.99 (1 C, *CH), 68.06 (1 C, PhCH$_2$O), 67.85 (1 C, PhCH$_2$O), 66.15 (1 C, CH$_2$O), 64.79 (1 C, CH$_2$O), 51.85 (O$_2$CCCO$_2$), 39.06 (1 C, NCH$_2$), 29.86 (1 C, CH$_2$COO), 27.02 (1 C, NCH$_2$CH$_2$), 23.58 (1 C, CH$_2$CH$_2$COO) ppm. MS (FAB, NBA): *m*/*z* = 1494 [M]$^+$, 720 [C$_{60}$]$^+$; *MW* = 1494.34 g/mol. IR (ATR): $\tilde{\nu}$ = 3240, 3065, 2964, 1741, 1705, 1602, 1455, 1382, 1231, 1128, 1069, 1023, 957, 907, 733, 699, 630 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ_{max} = 254, 325, 425 nm.

Monoadduct 3c: Compound **3c** was synthesized according to the general procedure **III** with monoadduct **32** (450 mg, 316 μmol), cyanuric acid (408 mg, 3.16 mmol) and DBU (47 μL, 316 μmol) in DMF (80 mL). The crude product was purified by column chromatography (SiO_2, dichloromethane/ethyl acetate, 2:1 followed by preparative HPLC, dichloromethane/ethyl acetate, 85:15). Yield 102 mg (60 μmol, 19%) as a red brownish solid. ^{1}H NMR (CDCl$_3$, 400 MHz, room temp.): δ = 9.27 (br., 2 H, NH), 7.93 (d, ^3J =

7.3 Hz, 2 H, 2 H, *o*-BzH), 7.57 (dd, ^3J = 7.4 Hz, 1 H, *p*-BzH), 7.38 (dd, ^3J = 7.8 Hz, 2 H, *m*-BzH), 7.30 (m, 5 H, BnH), 7.17 (m, 2 H, BnH), 7.08 (m, 3 H, BnH), 5.95 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.89 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.28 (d, ^3J = 12.0 Hz, 1 H, PhCH_2), 5.23 (d, ^3J = 12.0 Hz, 1 H, PhCH_2), 5.13 (d, ^3J = 12.0 Hz, 1 H, PhCH_2), 5.06 (d, ^3J = 12.0 Hz, 1 H, PhCH_2), 4.51 (m, 4 H, OCH_2), 4.02 (t, ^3J = 6.1 Hz, 2 H, NCH_2), 2.55 (m, 1 H, CH_2COO), 2.35 (m, 1 H, CH_2COO), 2.12 (m, 4 H, CH_2CH$_2$N, CH_2CH$_2$COO) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz, room temp.): δ = 171.62 (1 C, *C*=O), 165.83 1C, (*C*OOBn), 165.79 (1 C, *C*OOBn), 165.04 (1 C, *C*OPh), 163.43 (1 C, *C*=O), 163.39 (1 C, *C*=O), 149.04 (2 C, NH*C*ON), 148.01 (1 C, NH*C*ONH), 145.29, 145.18, 145.14, 145.04, 144.93, 144.90, 144.66, 144.64, 144.62, 143.86, 143.07, 143.03, 142.99, 142.95, 142.19, 141.91, 141.88, 140.95, 139.23 138.81 (58 C, sp^2-*C*), 134.81 (1 C, Ph*C*CH$_2$), 134.43 (1 C, Ph*C*CH$_2$), 133.74 (1 C, *p*-Ph*C*CO), 130.06 (2 C, *o*-Ph*C*CH$_2$), 128.70, 128.62, 128.54, 128.37, 128.33 (13 C, Ph*C*), 71.39 (2 C, sp^3-*C*), 71.12 (1 C, **C*H), 71.02 (1 C, **C*H), 68.06 (1 C, Ph*C*H$_2$O), 67.87 (1 C, Ph*C*H$_2$O), 66.15 (1 C, *C*H$_2$O), 64.79 (1 C, *C*H$_2$O), 51.86 (O$_2$C*C*CO$_2$), 39.06 (1 C, N*C*H$_2$), 29.86 (1 C, *C*H$_2$COO), 27.01 (1 C, NCH$_2$*C*H$_2$), 23.59 (1 C, *C*H$_2$CH$_2$COO) ppm. MS (FAB, NBA): *m*/*z* = 144 [M]$^+$, 720 [C_{60}]$^+$; *MW* = 1494.34 g/mol. IR (ATR): $\tilde{\nu}$ = 3242, 3065, 2964, 1741, 1706, 1602, 1455, 1428, 1382, 1231, 1127, 1069, 1023, 957, 907, 733, 699, 629 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 255, 324, 426 nm.

(*all-R*)-Depsipeptide-[G-2]-3-bromopropyl Malonate 25: Compound **25** was synthesized according to the general procedure **I** with compound **17** (675 mg, 514 μmol), 4-[2-[(3-bromopropoxy)carbonyl]-acetoyloxy]butanoic acid (**10**) (160 mg, 514 μmol), HOBt (70 mg, 514 μmol), DMAP (32 mg, 256 μmol) and DCC (137 mg, 668 μmol) in CH_2Cl_2 (100 mL). The crude product was purified by column chromatography (SiO_2, gradient hexane/ethyl acetate, 1:1→1:2). Yield 619 mg (385 μmol, 73%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz, room temp.): δ = 8.06 (d, ^3J = 8.3 Hz, 2 H, 2 H, *o*-BzH_{inner}), 7.91 (m, 4 H, *o*-BzH_{outer}), 7.55 (m, 3 H, *p*-BzH), 7.40 (m, 6 H, *m*-BzH), 7.29 (m, 10 H, BnH), 7.17 (m, 4 H, BnH), 7.08 (m, 6 H, BnH), 6.72 (t, ^3J = 5.8 Hz, 1 H, NH), 6.51 (t, ^3J = 5.8 Hz, 1 H, NH), 5.92 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.89 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.88 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.82 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.80 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.78 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.23 (d, ^3J = 3.8 Hz, 1 H, PhCH_2), 5.21 (d, ^3J = 4.5 Hz, 1 H, PhCH_2), 5.19 (d, ^3J = 3.8 Hz, 1 H, PhCH_2), 5.17 (d, ^3J = 4.5 Hz, 1 H, PhCH_2), 5.11 (d, ^3J = 4.7 Hz, 1 H, PhCH_2), 5.08 (d, ^3J = 4.4 Hz, 1 H, PhCH_2), 5.04 (d, ^3J = 4.4 Hz, 1 H, PhCH_2), 5.02 (d, ^3J = 4.5 Hz, 1 H, PhCH_2), 4.24 (m, 4 H, OCH_2), 3.39 (t, ^3J = 6.5 Hz, 2 H, CH_2Br), 3.36 (s, 2 H, O$_2$CCH_2CO$_2$), 3.17 (m, 4 H, NCH_2), 2.51 (m, 2 H, CH_2COO), 2.05 (3 m, 8 H, CH_2), 1.33 (m, 12 H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz, room temp.): δ = 172.04 (1 C, *C*ONH), 172.03 (1 C, *C*ONH), 171.05 (1 C, *C*=O), 166.65 (1 C, *C*=O), 166.42 (1 C, *C*=O), 166.12 (1 C, *C*=O), 166.01 (1 C, *C*=O), 165.68 (1 C, *C*=O), 165.66 (1 C, *C*=O), 165.57 (1 C, *C*=O), 165.53 (1 C, *C*=O), 164.99 (1 C, *C*=O), 164.96 (1 C, *C*=O), 164.90 (1 C, *C*=O), 134.74 (1 C, Ph*C*CH$_2$), 134.74 (1 C, Ph*C*CH$_2$), 134.45 (2 C, Ph*C*CH$_2$), 133.86 (1 C, *p*-Ph*C*CO), 133.61 (1 C, *p*-Ph*C*CO), 133.59 (1 C, *p*-Ph*C*CO), 129.93 (8 C, *o*-Ph*C*CH$_2$), 128.57, 128.53, 128.53, 128.51, 128.42, 128.40, 128.39, 128.38, 128.37, 128.36, 128.35, 128.32, 128.24, 128.20 (27 C, Ph*C*), 72.80 (1 C, **C*H$_{inner}$), 72.51 (1 C, **C*H$_{inner}$), 71.08 (1 C, **C*H$_{outer}$), 71.04 (1 C, **C*H$_{outer}$), 70.59 (1 C, **C*H$_{outer}$), 70.58 (1 C, **C*H$_{outer}$), 67.69 (2 C, Ph*C*H$_2$O), 67.56 (1 C, Ph*C*H$_2$O), 67.55 (1 C, Ph*C*H$_2$O), 63.88 (1 C, *C*H$_2$O), 63.05 (1 C, *C*H$_2$O), 41.17 (1 C, O$_2$C*C*H$_2$CO$_2$), 39.09 (2 C, *C*H$_2$N), 32.98 (1 C, *C*H$_2$COO), 32.86 (1 C, *C*H$_2$COO), 31.14, 29.84, 29.00, 28.75, 28.69, 25.73, 25.73, 23.85, 23.82, 23.71 (10 C, *C*H$_2$) ppm. MS (FAB, NBA): *m*/*z* = 1606 [M]$^+$; *MW* = 1606.46 g/mol. IR (ATR): $\tilde{\nu}$ = 3395, 3065, 2941, 2864, 1732, 1668, 1602, 1536, 1454, 1262, 1235, 1150, 1092, 1069, 1030, 957, 907, 733, 700 cm^{-1}. $C_{83}H_{85}BrN_2O_{26}$ (1606.46): calcd. C 62.05, H 5.33, N 1.74; found C 62.19, H 5.37, N 1.70.

(*all-S*)-Depsipeptide-[G-2]-3-bromopropyl Malonate 26: Compound **26** was synthesized according to the general procedure **I** with compound **18** (900 mg, 685 μmol), 4-{2-[(3-bromopropoxy)carbonyl]-acetoyloxy}butanoic acid (**10**) (213 mg, 685 μmol), HOBt (93 mg, 685 μmol), DMAP (42 mg, 341 μmol) and DCC (183 mg, 891 μmol) in CH_2Cl_2 (100 mL). The crude product was purified by column chromatography (SiO_2, gradient hexane/ethyl acetate, 1:1→1:2). Yield 682 mg (425 μmol, 62%) as a colorless oil.^{1}H NMR ($CDCl_3$, 400 MHz, room temp.): δ = 8.05 (d, ^3J = 8.3 Hz, 2 H, 2 H, *o*-BzH_{inner}), 7.91 (m, 4 H, *o*-BzH_{outer}), 7.54 (m, 3 H, *p*-BzH), 7.40 (m, 6 H, *m*-BzH), 7.28 (m, 10 H, BnH), 7.15 (m, 4 H, BnH), 7.08 (m, 6 H, BnH), 6.70 (t, ^3J = 5.8 Hz, 1 H, NH), 6.49 (t, ^3J = 5.8 Hz, 1 H, NH), 5.92 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.90 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.88 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.81 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.79 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.78 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.23 (d, ^3J = 3.8 Hz, 1 H, PhCH_2), 5.21 (d, ^3J = 4.5 Hz, 1 H, PhCH_2), 5.19 (d, ^3J = 3.8 Hz, 1 H, PhCH_2), 5.16 (d, ^3J = 4.5 Hz, 1 H, PhCH_2), 5.11 (d, ^3J = 4.7 Hz, 1 H, PhCH_2), 5.08 (d, ^3J = 4.4 Hz, 1 H, PhCH_2), 5.05 (d, ^3J = 4.4 Hz, 1 H, PhCH_2), 5.02 (d, ^3J = 4.5 Hz, 1 H, PhCH_2), 4.22 (m, 4 H, OCH_2), 3.39 (t, ^3J = 6.5 Hz, 2 H, CH_2Br), 3.36 (s, 2 H, O$_2$CCH_2CO$_2$), 3.17 (m, 4 H, NCH_2), 2.49 (m, 2 H, CH_2COO), 2.05 (3 m, 8 H, CH_2), 1.33 (m, 12 H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz, room temp.): δ = 172.04 (1 C, *C*ONH), 172.02 (1 C, *C*ONH), 171.05 (1 C, *C*=O), 166.65 (1 C, *C*=O), 166.42 (1 C, *C*=O), 166.12 (1 C, *C*=O), 166.01 (1 C, *C*=O), 165.68 (1 C, *C*=O), 165.66 (1 C, *C*=O), 165.55 (1 C, *C*=O), 165.53 (1 C, *C*=O), 164.98 (1 C, *C*=O), 164.96 (1 C, *C*=O), 164.92 (1 C, *C*=O), 134.74 (1 C, Ph*C*CH$_2$), 134.73 (1 C, Ph*C*CH$_2$), 134.45 (2 C, Ph*C*CH$_2$), 133.84 (1 C, *p*-Ph*C*CO), 133.61 (1 C, *p*-Ph*C*CO), 133.59 (1 C, *p*-Ph*C*CO), 129.93 (8 C, *o*-Ph*C*CH$_2$), 128.57, 128.53, 128.53, 128.51, 128.41, 128.40, 128.39, 128.38, 128.37, 128.36, 128.33, 128.32, 128.20, 128.19 (27 C, Ph*C*), 72.80 (1 C, **C*H$_{inner}$), 72.50 (1 C, **C*H$_{inner}$), 71.08 (1 C, **C*H$_{outer}$), 71.04 (1 C, **C*H$_{outer}$), 70.59 (1 C, **C*H$_{outer}$), 70.58 (1 C, **C*H$_{outer}$), 67.69 (2 C, Ph*C*H$_2$O), 67.56 (1 C, Ph*C*H$_2$O), 67.54 (1 C, Ph*C*H$_2$O), 63.88 (1 C, *C*H$_2$O), 63.05 (1 C, *C*H$_2$O), 41.17 (1 C, O$_2$C*C*H$_2$CO$_2$), 39.09 (2 C, *C*H$_2$N), 32.96 (1 C, *C*H$_2$COO), 32.86 (1 C, *C*H$_2$COO), 31.12, 29.84, 28.98, 28.75, 28.67, 25.73, 25.71, 23.84, 23.82, 23.70 (10 C, *C*H$_2$) ppm. MS (FAB, NBA): *m*/*z* = 1606 [M]$^+$; *MW* = 1606.46 g/mol. IR (ATR): $\tilde{\nu}$ = 3389, 3065, 2941, 2864, 1733, 1668, 1602, 1536, 1455, 1262, 1231, 1150, 1092, 1069, 1027, 957, 907, 733, 699 cm^{-1}. $C_{83}H_{85}BrN_2O_{26}$ (1606.46): calcd. C 62.05, H 5.33, N 1.74; found C 62.21, H 5.40, N 1.66.

Monoadduct 33: Compound **33** was synthesized according to the general procedure **II** with malonate **25** (710 mg, 442 μmol), C_{60} (550 mg, 764 μmol), I_2 (123 mg, 486 μmol) and DBU (83 μL, 553 μmol) in toluene (600 mL). The crude product was purified by column chromatography (SiO_2, toluene/ethyl acetate, 80:20). Yield 432 mg (186 μmol, 42%) as a red brownish solid. ^{1}H NMR ($CDCl_3$, 400 MHz, room temp.): δ = 8.03 (dd, ^4J = 1.3 Hz, ^3J = 8.3 Hz, 2 H, 2 H, *o*-BzH_{inner}), 7.90 (m, 4 H, *o*-BzH_{outer}), 7.54 (m, 3 H, *p*-BzH), 7.41 (m, 6 H, *m*-BzH), 7.29 (m, 10 H, BnH), 7.16 (m, 4 H, BnH), 7.09 (m, 6 H, BnH), 6.50 (t, ^3J = 5.8 Hz, 1 H, NH), 6.37 (t, ^3J = 5.8 Hz, 1 H, NH), 5.91 (d, ^3J = 2.9 Hz, 1 H, CH*), 5.87 (d, ^3J = 2.9 Hz, 1 H, CH*), 5.85 (d, ^3J = 3.5 Hz, 1 H, CH*), 5.82 (d, ^3J = 3.5 Hz, 1 H, CH*), 5.80 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.77 (d, ^3J = 2.8 Hz, 1 H, CH*), 5.24 (d, ^3J = 3.9 Hz, 1 H, PhCH_2), 5.20 (m, 2 H, PhCH_2), 5.16 (d, ^3J = 3.9 Hz, 1 H, PhCH_2), 5.12 (d,

^3J = 3.9 Hz, 1 H, PhCH_2), 5.09 (d, ^3J = 3.6 Hz, 1 H, PhCH_2), 5.06 (d, ^3J = 3.6 Hz, 1 H, PhCH_2), 5.02 (d, ^3J = 3.6 Hz, 1 H, PhCH_2), 4.61 (m, 4 H, OCH_2), 3.51 (t, ^3J = 6.4 Hz, 2 H, CH_2Br), 3.20 (m, 4 H, NCH_2), 2.62 (m, 2 H, CH_2COO), 2.15 (3 m, 8 H, CH_2), 1.31 (m, 12 H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz, room temp.): δ = 172.08 (1 C, *C*ONH), 172.06 (1 C, *C*ONH), 171.01 (1 C, *C*=O), 166.14 (1 C, *C*=O), 165.95 (1 C, *C*=O), 165.7 *C*=O, 1 C, (), 165.73 (1 C, *C*=O), 165.61 (1 C, *C*=O), 165.59 (1 C, *C*=O), 165.09 (1 C, *C*=O), 165.04 (1 C, *C*=O), 165.04 (1 C, *C*=O), 163.64 (1 C, *C*=O), 163.48 (1 C, *C*=O), 145.31, 145.28, 145.23, 145.01, 144.93, 144.92, 144.91, 144.92, 144.73, 144.68, 144.65, 144.58, 144.53, 143.88, 143.86, 143.12, 143.12, 143.05, 142.99, 142.18, 142.16, 141.91, 141.78, 141.78, 141.03, 140.96, 139.06, 139.05, 138.86, 138.86 (58 C, sp^2-*C*), 134.80 (1 C, Ph*C*CH$_2$), 134.80 (1 C, Ph*C*CH$_2$), 134.51 (2 C, Ph*C*CH$_2$), 134.00 (1 C, *p*-Ph*C*CO), 133.67 (1 C, *p*-Ph*C*CO), 133.65 (1 C, *p*-Ph*C*CO), 130.02, 129.97 (8 C, *o*-Ph*C*CH$_2$), 128.72, 128.60, 128.58, 128.49, 128.48, 128.47, 128.46, 128.45, 128.44, 128.43, 128.40, 128.39, 128.29, 128.28 (27 C, Ph*C*), 72.71 (1 C, **C*H$_{inner}$), 72.50 (1 C, **C*H$_{inner}$), 71.26 (2 C, sp^3-*C*), 71.16 (1 C, **C*H$_{outer}$), 71.11 (1 C, **C*H$_{outer}$), 70.66 (1 C, **C*H$_{outer}$), 70.65 (1 C, **C*H$_{outer}$), 67.81 (1 C, Ph*C*H$_2$O), 67.79 (1 C, Ph*C*H$_2$O), 67.65 (1 C, Ph*C*H$_2$O), 67.63 (1 C, Ph*C*H$_2$O), 65.98 (1 C, *C*H$_2$O), 64.92 (1 C, *C*H$_2$O), 51.83 (1 C, O$_2$C*C*CO$_2$), 39.26 (1 C, *C*H$_2$N), 39.23 (1 C, *C*H$_2$N), 33.04 (1 C, *C*H$_2$COO), 32.96 (1 C, *C*H$_2$COO), 31.19, 30.09, 29.07, 28.96, 28.76, 25.84, 25.82, 23.94, 23.91, 23.82 (10 C, *C*H$_2$) ppm. MS (FAB, NBA): *m*/*z* = 2323 [M]$^+$; *MW* = 2325.09 g/mol. IR (ATR): $\tilde{\nu}$ = 2978, 2934, 1729, 1656, 1536, 1454, 1393, 1366, 1251, 1150, 1104, 954, 849, 760, 706 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 257, 325, 425 nm.

Monoadduct 34: Compound **34** was synthesized according to the general procedure **II** with malonate **26** (220 mg, 137 μmol), C_{60} (150 mg, 208 μmol), I_2 (38 mg, 151 μmol) and DBU (27 μL, 178 μmol) in toluene (150 mL). The crude product was purified by column chromatography (SiO_2, toluene/ethyl acetate, 80:20). Yield 111 mg (48 μmol, 35%) as a red brownish solid. ^{1}H NMR ($CDCl_3$, 400 MHz, room temp.): δ = 8.04 (dd, ^4J = 1.3 Hz, ^3J = 8.3 Hz, 2 H, 2 H, *o*-BzH_{inner}), 7.91 (m, 4 H, *o*-BzH_{outer}), 7.55 (m, 3 H, *p*-Bz*H*), 7.41 (m, 6 H, *m*-Bz*H*), 7.29 (m, 10 H, Bn*H*), 7.16 (m, 4 H, Bn*H*), 7.09 (m, 6 H, Bn*H*), 6.51 (t, ^3J = 5.8 Hz, 1 H, N*H*), 6.37 (t, ^3J = 5.8 Hz, 1 H, N*H*), 5.91 (d, ^3J = 2.9 Hz, 1 H, C*H**), 5.89 (d, ^3J = 2.9 Hz, 1 H, C*H**), 5.85 (d, ^3J = 3.5 Hz, 1 H, C*H**), 5.82 (d, ^3J = 3.5 Hz, 1 H, C*H**), 5.80 (d, ^3J = 2.8 Hz, 1 H, C*H**), 5.78 (d, ^3J = 2.8 Hz, 1 H, C*H**), 5.24 (d, ^3J = 3.9 Hz, 1 H, PhCH_2), 5.20 (m, 2 H, PhCH_2), 5.17 (d, ^3J = 3.9 Hz, 1 H, PhCH_2), 5.12 (d, ^3J = 3.9 Hz, 1 H, PhCH_2), 5.09 (d, ^3J = 3.6 Hz, 1 H, PhCH_2), 5.06 (d, ^3J = 3.6 Hz, 1 H, PhCH_2), 5.03 (d, ^3J = 3.6 Hz, 1 H, PhCH_2), 4.61 (m, 4 H, OCH_2), 3.51 (t, ^3J = 6.4 Hz, 2 H, CH_2Br), 3.21 (m, 4 H, NCH_2), 2.62 (m, 2 H, CH_2COO), 2.18 (3 m, 8 H, CH_2), 1.32 (m, 12 H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz, room temp.): δ = 172.07 (1 C, *C*ONH), 172.06 (1 C, *C*ONH), 171.01 (1 C, *C*=O), 166.13 (1 C, *C*=O), 165.95 (1 C, *C*=O), 165.7 *C*=O, 1 C, (), 165.73 (1 C, *C*=O), 165.61 (1 C, *C*=O), 165.59 (1 C, *C*=O), 165.08 (1 C, *C*=O), 165.04 (1 C, *C*=O), 165.03 (1 C, *C*=O), 163.64 (1 C, *C*=O), 163.48 (1 C, *C*=O), 145.30, 145.28, 145.21, 145.01, 144.94, 144.92, 144.91, 144.90, 144.71, 144.68, 144.66, 144.58, 144.53, 143.87, 143.86, 143.12, 143.10, 143.05, 142.98, 142.18, 142.16, 141.89, 141.78, 141.77, 141.03, 140.97, 139.06, 139.05, 138.86, 138.85 (58 C, sp^2-*C*), 134.80 (1 C, Ph*C*CH$_2$), 134.79 (1 C, Ph*C*CH$_2$), 134.51 (2 C, Ph*C*CH$_2$), 134.00 (1 C, *p*-Ph*C*CO), 133.67 (1 C, *p*-Ph*C*CO), 133.65 (1 C, *p*-Ph*C*CO), 130.02, 129.97 (8 C, *o*-Ph*C*CH$_2$), 128.72, 128.60, 128.59, 128.49, 128.48, 128.47, 128.46, 128.45, 128.44, 128.43, 128.40, 128.39, 128.29, 128.28 (27 C, Ph*C*), 72.71 (1 C, **C*H$_{inner}$), 72.51 (1 C, **C*H$_{inner}$), 71.26 (2 C, sp^3-*C*), 71.15 (1 C, **C*H$_{outer}$), 71.11 (1 C, **C*H$_{outer}$), 70.66 (1 C, **C*H$_{outer}$), 70.65 (1 C, **C*H$_{outer}$), 67.80 (1 C, Ph*C*H$_2$O), 67.79 (1 C, Ph*C*H$_2$O), 67.65 (1 C, Ph*C*H$_2$O), 67.63 (1 C, Ph*C*H$_2$O), 65.98 (1 C, *C*H$_2$O), 64.92 (1 C, *C*H$_2$O), 51.82 (1 C, O$_2$C*C*CO$_2$), 39.25 (1 C, *C*H$_2$N), 39.23 (1 C, *C*H$_2$N), 33.04 (1 C, *C*H$_2$COO), 32.96 (1 C, *C*H$_2$COO), 31.16, 30.09, 29.07, 28.93, 28.76, 25.84, 25.79, 23.92, 23.91, 23.83 (10 C, *C*H$_2$) ppm. MS (FAB, NBA): *m*/*z* = 2323 [M]$^+$; *MW* = 2325.09 g/mol. IR (ATR): $\tilde{\nu}$ = 2976, 2934, 1729, 1656, 1536, 1455, 1393, 1366, 1251, 1150, 1104, 953, 849, 757, 706 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 258, 325, 426 nm.

Monoadduct 3b: Compound **3b** was synthesized according to the general procedure **III** with monoadduct **33** (160 mg, 68.8 μmol), cyanuric acid (150 mg, 1.16 mmol) and DBU (10 μL, 68.8 μmol) in DMF (60 mL). The crude product was purified by column chromatography (SiO_2, gradient dichloromethane/ethyl acetate, 70:30 →50:50). Yield 44 mg (19 μmol, 27%) as a red brownish solid. ^{1}H NMR ($CDCl_3$, 400 MHz, room temp.): δ = 9.82 (br., 2 H, N*H*), 8.02 (dd, ^3J = 8.0 Hz, 2 H, 2 H, *o*-BzH_{inner}), 7.91 (m, 4 H, *o*-BzH_{outer}), 7.54 (m, 3 H, *p*-Bz*H*), 7.40 (m, 6 H, *m*-Bz*H*), 7.28 (m, 10 H, Bn*H*), 7.17 (m, 4 H, Bn*H*), 7.08 (m, 6 H, Bn*H*), 6.84 (br., 2 H, N*H*), 5.92 (d, ^3J = 2.9 Hz, 1 H, C*H**), 5.90 (d, ^3J = 2.9 Hz, 1 H, C*H**), 5.86 (d, ^3J = 4.8 Hz, 1 H, C*H**), 5.82 (d, ^3J = 2.9 Hz, 1 H, C*H**), 5.81 (d, ^3J = 2.9 Hz, 1 H, C*H**), 5.77 (d, ^3J = 4.8 Hz, 1 H, C*H**), 5.23 (d, ^3J = 3.8 Hz, 1 H, PhCH_2), 5.21 (m, 2 H, PhCH_2), 5.18 (t, ^3J = 7.0 Hz, 1 H, PhCH_2), 5.14 (d, ^3J = 3.9 Hz, 1 H, PhCH_2), 5.09 (d, ^3J = 4.1 Hz, 1 H, PhCH_2), 5.06 (d, ^3J = 7.7 Hz, 1 H, PhCH_2), 5.01 (d, ^3J = 7.8 Hz, 1 H, PhCH_2), 4.54 (m, 4 H, OCH_2), 4.03 (m, 2 H, CH_2NCO), 3.23 (m, 4 H, HNCH_2), 2.64 (m, 2 H, CH_2COO), 2.23 (2 m, 8 H, CH_2), 1.45 (m, 8 H, CH_2), 1.32 (m, 4 H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz, room temp.): δ = 172.30 (1 C, *C*ONH), 172.26 (1 C, *C*ONH), 171.62 (1 C, *C*=O), 166.60 (1 C, *C*=O), 166.37 (1 C, *C*=O), 165.83 (1 C, *C*=O), 165.78 (1 C, *C*=O), 165.71 (1 C, *C*=O), 165.67 (1 C, *C*=O), 165.14 (1 C, *C*=O), 165.06 (1 C, *C*=O), 165.03 (1 C, *C*=O), 163.44 (1 C, *C*=O), 163.39 (1 C, *C*=O), 149.21 (2 C, NH*C*ON), 148.31 (1 C, NH*C*ONH), 145.27, 145.21, 145.18, 145.15, 145.12, 145.06, 145.04, 145.01, 144.90, 144.69, 144.66, 144.63, 144.61, 144.58, 143.87, 143.86, 143.09, 143.03, 143.01, 142.95, 142.19, 142.18, 141.91, 141.87, 140.96, 140.96, 140.95, 139.16, 139.14, 138.82 (58 C, sp^2-*C*), 134.81 (1 C, Ph*C*CH$_2$), 134.79 (1 C, Ph*C*CH$_2$), 134.51 (1 C, Ph*C*CH$_2$), 134.49 (1 C, Ph*C*CH$_2$), 133.99 (1 C, *p*-Ph*C*CO), 133.69 (1 C, *p*-Ph*C*CO), 133.66 (1 C, *p*-Ph*C*CO), 130.03, 130.00 (8 C, *o*-Ph*C*CH$_2$), 128.63, 128.62, 128.50, 128.48, 128.46, 128.45, 128.32 (27 C, Ph*C*), 72.78 (1 C, **C*H$_{inner}$), 72.67 (1 C, **C*H$_{inner}$), 71.38 (1 C, sp^3-*C*), 71.37 (1 C, sp^3-*C*), 71.18 (1 C, **C*H$_{outer}$), 71.14 (1 C, **C*H$_{outer}$), 70.72 (2 C, **C*H$_{outer}$), 67.86 (2 C, Ph*C*H$_2$O), 67.70 (2 C, Ph*C*H$_2$O), 66.23 (1 C, *C*H$_2$O), 64.62 (1 C, *C*H$_2$O), 51.84 (1 C, O$_2$C*C*CO$_2$), 39.36 (2 C, *C*H$_2$N), 38.55 (1 C, *C*H$_2$N), 33.05 (1 C, *C*H$_2$COO), 33.00 (1 C, *C*H$_2$COO), 30.16, 30.12, 28.67, 28.48, 27.12, 25.79, 25.74, 23.90, 23.87, 23.63 (10 C, *C*H$_2$) ppm. MS (FAB, NBA): *m*/*z* = 2374 [M]$^+$; *MW* = 2373.25 g/mol. IR (ATR): $\tilde{\nu}$ = 3268, 2945, 2864, 1732, 1540, 1455, 1418, 1382, 1262, 1150, 1092, 1027, 957, 908, 733, 701 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 256, 325, 425 nm.

Monoadduct 3d: Compound **3d** was synthesized according to the general procedure **III** with monoadduct **34** (340 mg, 146 μmol), cyanuric acid (189 mg, 1.46 mmol) and DBU (22 μL, 146 μmol) in DMF (60 mL). The crude product was purified by column chromatography (SiO_2, gradient dichloromethane/ethyl acetate, 70:30→50:50). Yield 69 mg (29 μmol, 20%) as a red brownish solid. ^{1}H NMR ($CDCl_3$, 400 MHz, room temp.): δ = 9.81 (br., 2 H, N*H*), 8.03 (dd, ^3J = 8.0 Hz, 2 H, 2 H, *o*-BzH_{inner}), 7.91 (m, 4 H, *o*-BzH_{outer}), 7.54 (m, 3 H, *p*-Bz*H*), 7.39 (m, 6 H, *m*-Bz*H*), 7.28 (m,

10 H, BnH), 7.16 (m, 4 H, BnH), 7.08 (m, 6 H, BnH), 6.85 (br., 2 H, NH), 5.92 (d, ^3J = 2.9 Hz, 1 H, CH*), 5.90 (d, ^3J = 2.9 Hz, 1 H, CH*), 5.85 (d, ^3J = 4.8 Hz, 1 H, CH*), 5.82 (d, ^3J = 2.9 Hz, 1 H, CH*), 5.79 (d, ^3J = 2.9 Hz, 1 H, CH*), 5.75 (d, ^3J = 4.8 Hz, 1 H, CH*), 5.23 (d, ^3J = 3.8 Hz, 1 H, PhCH_2), 5.21 (m, 2 H, PhCH_2), 5.18 (t, ^3J = 7.0 Hz, 1 H, PhCH_2), 5.12 (d, ^3J = 3.9 Hz, 1 H, PhCH_2), 5.09 (d, ^3J = 4.1 Hz, 1 H, PhCH_2), 5.06 (d, ^3J = 7.7 Hz, 1 H, PhCH_2), 5.02 (d, ^3J = 7.8 Hz, 1 H, PhCH_2), 4.51 (m, 4 H, OCH_2), 4.00 (m, 2 H, CH_2NCO), 3.23 (m, 4 H, HNCH_2), 2.61 (m, 2 H, CH_2COO), 2.25 (2 m, 8 H, CH_2), 1.43 (m, 8 H, CH_2), 1.32 (m, 4 H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100.5 MHz, room temp.): δ = 172.29 (1 C, CONH), 172.25 (1 C, CONH), 171.62 (1 C, C=O), 166.58 (1 C, C=O), 166.37 (1 C, C=O), 165.81 (1 C, C=O), 165.78 (1 C, C=O), 165.71 (1 C, C=O), 165.68 (1 C, C=O), 165.14 (1 C, C=O), 165.06 (1 C, C=O), 165.03 (1 C, C=O), 163.43 (1 C, C=O), 163.39 (1 C, C=O), 149.19 (2 C, NHCON), 148.31 (1 C, NHCONH), 145.27, 145.19, 145.18, 145.15, 145.09, 145.08, 145.04, 144.97, 144.90, 144.69, 144.64, 144.63, 144.61, 144.57, 143.87, 143.86, 143.09, 143.03, 142.99, 142.95, 142.19, 142.18, 141.88, 141.87, 140.97, 140.96, 140.95, 139.15, 139.14, 3138.84 (58 C, sp^2-C), 134.80 (1 C, PhCCH$_2$), 134.79 (1 C, PhCCH$_2$), 134.51 (1 C, PhCCH$_2$), 134.50 (1 C, PhCCH$_2$), 133.99 (1 C, *p*-PhCCO), 133.69 (1 C, *p*-PhCCO), 133.68 (1 C, *p*-PhCCO), 130.03, 130.01 (8 C, *o*-PhCCH$_2$), 128.63, 128.62, 128.50, 128.48, 128.46, 128.45, 128.32 (27 C, PhC), 72.78 (1 C, *CH$_{inner}$), 72.66 (1 C, *CH$_{inner}$), 71.38 (1 C, sp^3-C), 71.37 (1 C, sp^3-C), 71.17 (1 C, *CH$_{outer}$), 71.13 (1 C, *CH$_{outer}$), 70.70 (2 C, *CH$_{outer}$), 67.86 (2 C, PhCH$_2$O), 67.70 (2 C, PhCH$_2$O), 66.21 (1 C, CH$_2$O), 64.60 (1 C, CH$_2$O), 51.83 (1 C, O$_2$CCCO$_2$), 39.37 (2 C, CH$_2$N), 38.55 (1 C, CH$_2$N), 33.05 (1 C, CH$_2$COO), 33.00 (1 C, CH$_2$COO), 30.14, 30.13, 28.67, 28.48, 27.10, 25.79, 25.75, 23.90, 23.86, 23.61 (10 C, CH$_2$) ppm. MS (FAB,NBA): *m*/*z* = 2374 [M]$^+$; *MW* = 2373.25 g/mol. IR (ATR): $\tilde{\nu}$ = 3266, 2945, 2864, 1733, 1540, 1455, 1420, 1382, 1262, 1150, 1092, 1027, 957, 907, 733, 699 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 256, 324, 425 nm.

Acknowledgments

This work was supported by the Bundesministerium für Bildung und Forschung (BMBF) and the Deutsche Forschungsgemeinschaft (DFG) (SFB 583).

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Received: December 1, 2006
Published Online: February 23, 2007

