Tetrahedron 69 (2013) 3656–3663

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis of multifunctional coupling agents and their selective reactions with hydroxy and amino groups in the melt

Haiping Zhang [a,b], Lothar Jakisch [a], Hartmut Komber [a], Brigitte Voit [a,b], Frank Böhme [a,*]

[a] Leibniz Institute of Polymer Research Dresden, Hohe Straße 6, 01069 Dresden, Germany
[b] Organic Chemistry of Polymers, Technische Universität Dresden, 01062 Dresden, Germany

ARTICLE INFO

Article history:
Received 4 January 2013
Received in revised form 21 February 2013
Accepted 5 March 2013
Available online 13 March 2013

Keywords:
Coupling reactions
Benzoxazinone
N-Acyllactam

ABSTRACT

Three new coupling agents with different numbers of *N*-acyl lactam and 4*H*-3,1-benzoxazin-4-one groups were synthesized. A selective stepwise conversion of the coupling agents with 1-dodecanol and 1-dodecylamine was demonstrated by means of solvent-free model reactions in melt at 195 and 210 °C, respectively. These coupling agents are regarded as potential cores for the synthesis of novel star-like compounds and polymers with defined arms varying in type and lengths.

1. Introduction

Coupling reactions are widely used in organic chemistry. Besides immediate coupling, utilization of coupling agents has become more and more important especially in those cases where the reactivity of groups to be coupled is not high enough to achieve direct coupling. Equal functional groups can be linked relatively easily by using symmetric bifunctional coupling agents such as bisoxazolines,[1] bisoxazinones,[2] diisocyanates,[3] bislactams,[4,5] and bisepoxides.[6] Such coupling agents have very often been used in polymer chemistry as chain extenders and compatibilizers. However, they are only partly usable when linking different compounds or components in a defined manner. Here, coupling agents with different highly selective reacting groups are required. Under the above mentioned symmetric bifunctional coupling agents, only carbonylbiscaprolactam (CBC) meets this requirement. Loontjens et al.[7] figured out that the lactam groups of CBC possessed different reactivity. In bulk at 100 °C, the conversion of equimolar amounts of amino or hydroxy group terminated oligomers with CBC yielded *N*-carbamoyl caprolactam terminated oligomers. The remaining *N*-carbamoyl caprolactam group is on disposal for further reactions. At higher temperatures, this selectivity is lost. We have introduced a new bifunctional coupling agent with one oxazoline and one 4*H*-1,3-benzoxazin-4-one (hereinafter referred to as benzoxazinone) group for the simultaneous conversion of carboxylic and amino groups, respectively.[8–11] These reactions have proved to be very selective at higher temperatures up to 220 °C.

An even greater challenge is a selective linking reaction between aliphatic hydroxy and amino groups, which do not react with each other under normal conditions. As described by Milstein et al.,[12] direct coupling between both groups could be performed by a dehydrogenation reaction in the presence of a ruthenium catalyst resulting in the formation of an amide bond. Zeng and Guan[13] utilized this reaction for the preparation of polyamides. One limitation of this reaction is that it has to be performed in solvents.

Selective coupling reactions that link aliphatic hydroxy and amino groups in a defined manner in the melt are rare. Reason for this is their similar reactivity at elevated temperatures. As typical nucleophiles, both groups react with carboxylic acids, acid chlorides, acid anhydrides, epoxides, *N*-acyl lactams, isocyanates, etc. Toward benzoxazinone groups, amino groups have proved to be distinctly more reactive than hydroxy groups.[14] We utilized this behavior in developing a new selectively reacting bifunctional coupling agent for amino and hydroxy groups in melt.[14,15] Beside the benzoxazinone group, this coupling agent possesses an *N*-acyl lactam group, which serves as a potential reactant for hydroxy groups. The chemistry of benzoxazinones and *N*-acyl lactams is described in detail.[16–18]

In this article, we describe the synthesis of novel tri- and tetrafunctional coupling agents (**CA1**–**3**) containing *N*-acyl lactam and benzoxazinone groups in varying numbers. These coupling agents are designed for solvent-free coupling reactions up to 220 °C. This is especially important for polymers, which are usually processed in the melt. Their selective reactivity with amino and hydroxy groups

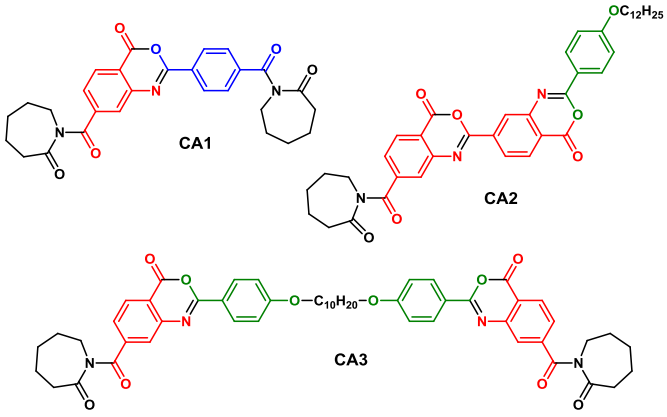
* Corresponding author. E-mail address: Boehme@ipfdd.de (F. Böhme).

0040-4020/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2013.03.024

is demonstrated by means of model reactions. These coupling agents are regarded as potential cores for the synthesis of novel star-like compounds and polymers with defined arms varying in type and lengths.

2. Results and discussion

The new compounds **CA1**–**3** were synthesized following the principles described in our earlier publication.[14] The benzoxazinone and *N*-acyl lactam functional groups contained therein are derivatives of carboxylic acids. For the preparation of **CA1**–**3** three basic compounds are used, these are terephthalic acid (**TA**), 2-aminoterephthalic acid (**ATA**), and 4-hydroxybenzoic acid (**HBA**) as illustrated by means of color enhancements in Scheme 1. The synthetic approach is very similar for all three compounds. At first, the benzoxazinone group is synthesized by conversion of the amino group of **ATA** with the acid chloride of alkoxybenzoic or monomethoxylated terephthalic acid followed by cyclization in the presence of a water withdrawing agent (acetic anhydride). After cyclization, the carboxylic groups are converted into acyl chloride groups, which after reaction with ε-caprolactam (**CL**) form the *N*-acyl lactam groups. The specific synthetic routes of **CA1**, **CA2**, and **CA3** are shown in Schemes 2–4, respectively.



Scheme 1. Multifunctional coupling agents with *N*-acyl lactam and benzoxazinone groups in varying numbers.

As shown in Scheme 2, synthesis of **CA1** starts from 4-(methoxycarbonyl)benzoyl chloride, the acyl chloride group of which is converted with the amino group of **ATA** under Schotten–Baumann conditions yielding compound **1**. After deprotection of the ester group of **1** by saponification with KOH and cyclization in presence of acetic anhydride compound **2** is obtained. The carboxylic groups of **2** are activated by $SOCl_2$ and reacted with **CL** yielding compound **3** (**CA1**). Alternatively, cyclization of deprotected **1** can also be performed in presence of $SOCl_2$ with simultaneous activation of the carboxylic groups. The latter route, however, is accompanied by the formation of side products, which makes purification of the final product more difficult.

Synthesis of **CA2** is depicted in Scheme 3. Here, **HBA** is reacted first with an alkyl bromide resulting in compound **4**. The carboxylic group of **4** is chlorinated with $SOCl_2$ and then reacted with the amino group of **ATA**. Cyclization of the resulting intermediate **5** proceeds as described above yielding compound **6** with one benzoxazinone group. To introduce a second benzoxazinone group, the whole procedure including chlorination, reaction with **ATA**, and cyclization is repeated. In the last step, the carboxylic group of **8** is converted into an *N*-acyl lactam group as described for **CA1**.

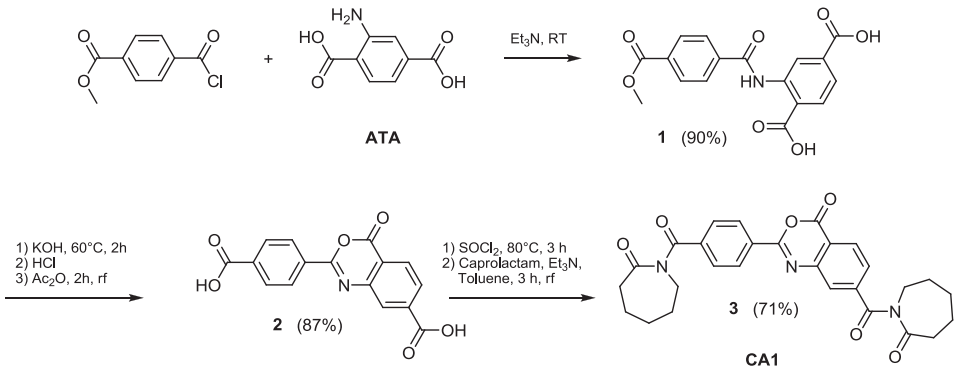
Synthesis of **CA3** follows nearly the same protocol (see Scheme 4). However, instead of an alkyl bromide, **HBA** is converted with a dibromoalkane to yield the symmetric dicarboxylic acid **10**. This is followed by a successive introduction of a benzoxazinone group and an *N*-acyl lactam group on both sides as described for **CA2**.

In the syntheses of compounds **CA1**, **CA2**, and **CA3**, we avoided laborious workup of the intermediates. The carboxylic acid intermediates are difficult to be recrystallized because of their reduced solubility in organic solvents. Therefore, only some of the acyl chloride intermediates, but all final products were recrystallized in toluene or acetone. This approach ensures acceptable overall yields at high purity of the final products.

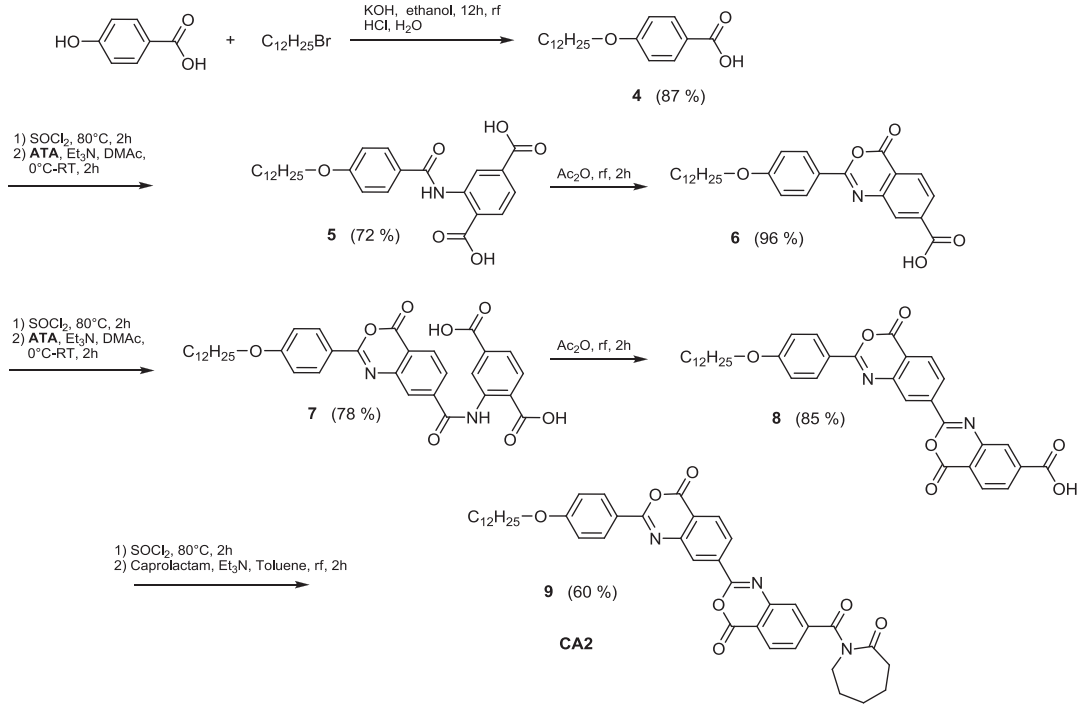
Thermal behavior and solubility of compounds **CA2** and **CA3** can be tailored by the length of their aliphatic parts. For our purposes, melting points between 170 and 220 °C are required. With T_m=185 °C, 180 °C, and 171 °C for **CA1**, **CA2**, and **CA3**, respectively, all values meet our requirements.

The reactivity of the synthesized compounds with aliphatic hydroxy and amino groups was tested at higher temperatures in melt. For this, model reactions were performed with 1-dodecanol and 1-dodecylamine. In our earlier publications[14,15] it has been shown that the reactivity of amino groups with benzoxazinone and *N*-acyl lactam groups was not selective. Both groups react in a similar extent. Therefore, the conversions of the *N*-acyl lactam groups with 1-dodecanol were performed first at 195 °C. This is an elimination reaction in the course of which **CL** is generated. In the second step, the benzoxazinone groups of intermediates **I1**–**3** were converted in an addition reaction with 1-dodecylamine at 210 °C. The reactions are depicted in Scheme 5.

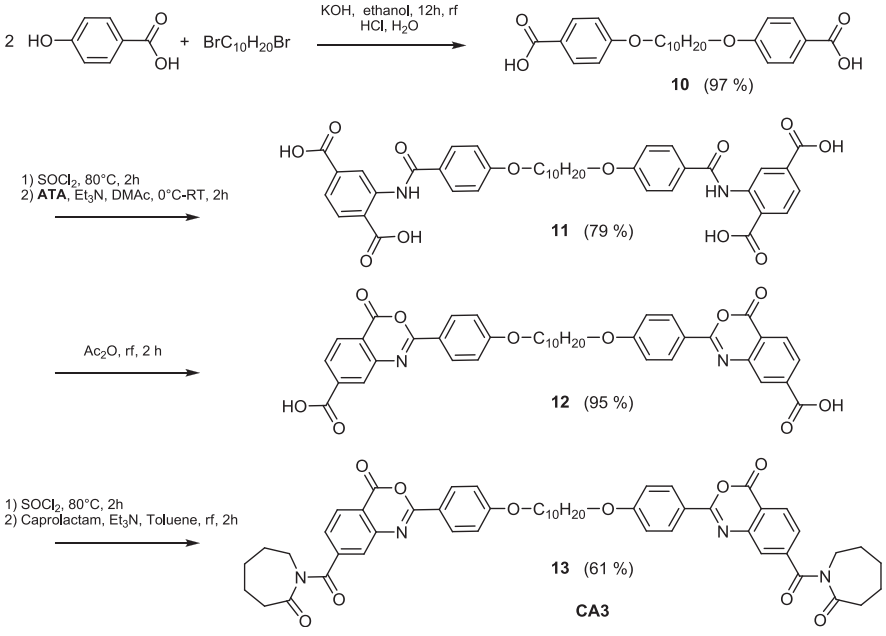
The conversion with 1-dodecanol proceeded with pronounced selectivity. However, a certain portion of the benzoxazinone groups (20, 4, and 7% for **CA1**–**3**, respectively) reacted also by ring opening as determined by ^{1}H NMR measurements. The side products could be separated by recrystallization in acetone yielding pure intermediates **I1**–**3** with unreacted benzoxazinone groups. The conditions applied (195 °C, 2 h) represent a compromise with regard to selectivity and



Scheme 2. Synthesis of coupling agent **CA1**.



Scheme 3. Synthesis of coupling agent **CA2**.

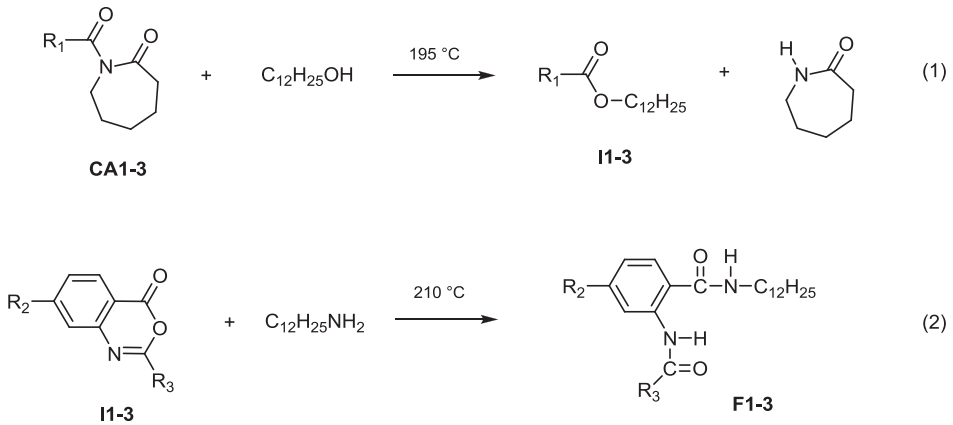


Scheme 4. Synthesis of coupling agent **CA3**.

reaction time. At higher temperatures the benzoxazinone ring opening by alcohols becomes more significant. Lower temperatures are not acceptable with regard to very long reaction times. Equimolar conversion of these purified intermediates **I1**–**3** with 1-dodecylamine at 210 °C yielded the final products **F1**–**3** quantitatively. Although compounds **F1**–**3** were not recrystallized, by-products could not be detected in significant amounts by NMR spectroscopy showing that this ring opening reaction proceeded very efficiently. Generally, this reaction delivers acceptable yields within a wide temperature range (100–220 °C). Higher temperatures lead to the formation of quinazolinone structures under elimination of water.[16] Under the conditions described here, such structures could not be detected in significant amounts by ^{1}H NMR measurements.

3. Conclusions

Our synthetic approach shows that a series of new coupling agents with varying numbers of benzoxazinone and *N*-acyl lactam functional groups are available by an appropriate combination of simple esterification, amidation, and cyclization reactions. The



Scheme 5. Sequential conversion of coupling agents **CA1**–**3** with 1-dodecanol and dodecylamine.

coupling agents synthesized are based on just a few frequently used building blocks such as terephthalic acid, 2-aminoterephthalic acid, 4-hydroxybenzoic acid, and ε-caprolactam. The principle methodology in synthesizing coupling agents as introduced here can be modified in an appropriate manner, which may increase the structural variety and the number of functional groups of targeted products. Thus, the sequence of reactions depicted in Scheme 3 illustrates the possibility to build up longer sequences of benzoxazinone groups. This approach is only limited by the solubility of the reaction products, which, however, can be influenced by the flexible substituents and bridging groups in the molecule.

The suitability of the coupling agents for reactions with aliphatic hydroxy and amino groups in melt has been demonstrated. Selectivity is ensured when the conversion proceeds according to the sequence shown in Scheme 5. That means the reaction of the *N*-acyl lactam groups with hydroxy groups has to be performed first (formation of **I1**–**3**) followed by the conversion of the benzoxazinone groups with amino groups (formation of **F1**–**3**).

Basically, intermediates **I1**–**3** are also available by conversion of the acyl chlorides of compounds **2**, **8**, and **12** with 1-dodecanol. However, these reactions have to be performed more preferably in solution. Moreover, because of their high reactivity, acyl chlorides are instable against traces of water and have to be further processed timely. Based on this, the advantages of coupling agents **CA1**–**3** are apparent. They possess high storage stability and allow synthesis of various branched and star-like compounds in melt using amino and hydroxy functionalized compounds. Handling, utilization, and reactivity of the coupling agents under discussion are very similar to the bifunctional one described earlier.[14,15] The latter, however, is more intended to be used for linear coupling as, for example, for synthesis of block copolymers or functionalization of surfaces.

4. Experimental

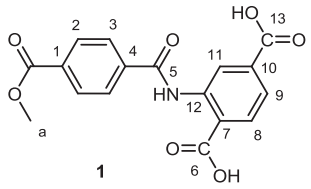
4.1. General

All chemicals and solvents (analytical grade) were received from commercial sources and used without further purification. *N*,*N*-Dimethylacetamide and toluene were dried over molecular sieves. Gaseous by-products such as HCl and SO_2 were neutralized with aqueous NaOH.

^{1}H NMR (500.13 MHz) and ^{13}C NMR spectra (125.74 MHz) were recorded on an Avance III 500 NMR spectrometer (Bruker). $CDCl_3$ ($\delta(^1H)$=7.26 ppm, $\delta(^{13}C)$=77.0 ppm) and DMSO-d_6 ($\delta(^1H)$=2.50 ppm, $\delta(^{13}C)$=39.6 ppm) were used as solvent, lock, and internal standard. The ^{1}H NMR spectra recorded from solutions in trifluoroacetic acid-d_1 (TFA-d_1) were referenced on external solution of sodium 3-(trimethylsilyl) propionate-2,2,3,3-d_4 in D_2O ($\delta(^1H)$=0 ppm). The corresponding ^{13}C NMR spectra were referenced on the center of the CF_3 quartet ($\delta(^{13}C)$=116.6 ppm). Signal assignments were verified by ^{1}H–^{1}H and ^{1}H–^{13}C correlated 2D NMR spectra. Elemental analyses were carried out on a EuroEA 3000, CHNS-O elemental analyzer.

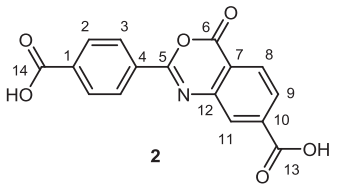
4.2. Typical procedures

*4.2.1. 2-(4-(Methoxycarbonyl)benzamido)terephthalic acid (**1**).*



To a cooled solution (ice bath) of methyl 4-(chlorocarbonyl) benzoate (19.86 g, 100 mmol) in *N*,*N*-dimethylacetamide (150 mL), 2-aminoterephthalic acid (18.11 g, 100 mmol) was added. Then, triethylamine (11.13 g, 0.11 mol) was added dropwise within 30 min. After further 1 h stirring at room temperature, the mixture was poured into water (1 L). Then, the solution was treated with aqueous HCl up to pH 1. The white precipitate was filtered off, washed several times with water, and dried in vacuo to give **1** (30.90 g, 90%), which was used without further purification for the next step. δ_H (DMSO-d_6) 13.4 (2H, br, COOH), 12.18 (1H, s, NH^5), 9.20 (1H, s, H^{11}), 8.13 (2H, d, H^2), 8.12 (1H, d, H^8), 8.06 (2H, d, H^3), 7.74 (1H, d, H^9), 3.90 (a).

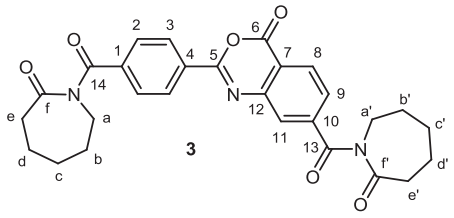
*4.2.2. 2-(4-Carboxyphenyl)-4-oxo-4H-benzo[d][1,3]oxazine-7-carboxylic acid (**2**).*



Compound **1** (27.46 g, 80 mmol) was suspended in a mixture of KOH (26.40 g, 400 mmol), methanol (150 mL), and water (50 mL) and heated up to 60 °C for 2 h. After cooling, the clear solution was treated with aqueous HCl up to pH 1. The precipitate was filtered off

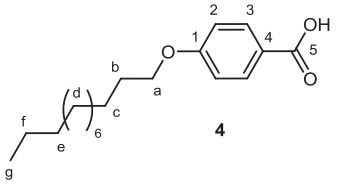
and washed several times with water. After drying in vacuo, the obtained intermediate was stirred with acetic anhydride (150 mL) for 2 h under reflux. After cooling to room temperature acetic acid (150 mL) was added. Subsequently, the white precipitate was filtered off, washed with water, and dried in vacuo to give **2** (21.66 g, 87%). Mp: no melting up to 350 °C; δ_H (DMSO-d_6) 13.4 (2H, br, COOH), 8.29 (2H, d, H^3), 8.23 (1H, d, H^8), 8.13 (1H, s, H^{11}), 8.12 (2H, d, H^2), 8.08 (1H, d, H^9). δ_C (DMSO-d_6) 166.63 (C^{14}), 166.02 (C^{13}), 158.22 (C^6), 156.20 (C^5), 146.10 (C^{12}), 138.73 (C^{10}), 134.56 (C^1), 133.41 (C^4), 129.83 (C^2), 128.76 (C^9), 128.57 (C^8), 127.68 (C^{11}), 128.09 (C^3), 120.03 (C^7).

*4.2.3. 7-(2-Oxoazepane-1-carbonyl)-2-(4-(2-oxoazepane-1-carbonyl)phenyl)-4H-benzo[d][1,3]oxazin-4-one (**3**).*



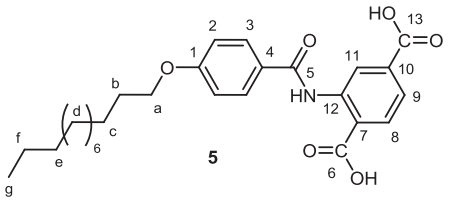
Compound **2** (15.56 g, 50 mmol) was stirred at 80 °C with thionyl chloride (150 mL) and two drops of *N*,*N*-dimethylformamide until bubble formation stopped (2–3 h). Then, the excess of thionyl chloride was distilled off in vacuo. The residue was recrystallized from toluene (100 mL) and dried in vacuo to give 14.45 g (83%) of the corresponding acid dichloride. To a mixture of this acid dichloride (14.45 g, 41.5 mmol), ε-caprolactam (9.39 g, 83 mmol) and toluene (250 mL) preheated to 80 °C, triethylamine (8.40 g, 83 mmol) was added dropwise. The mixture was then heated under reflux for 3 h. After removing the solvent on a rotary evaporator, the solid residue was washed with water, dried in vacuo, and recrystallized from acetone to give **3** (**CA1**). Overall yield of **3**, on the basis of **2**: 17.80 g (71%). Mp 185–186.5 °C; δ_H ($CDCl_3$) 8.32 (2H, d, H^3), 8.25 (1H, d, H^8), 7.72 (1H, s, H^{11}), 7.62 (2H, d, H^2), 7.56 (1H, d, H^9), 4.04 (2H, m, $H^{a'}$), 4.00 (2H, m, H^a), 2.72 (4H, $H^{e,e'}$), 1.87 (12H, $H^{b-d,b'-d'}$); δ_C ($CDCl_3$) 177.32 ($C^{f,f'}$), 172.75 (C^{14}), 171.60 (C^{13}), 158.40 (C^6), 156.53 (C^5), 146.46 (C^{10}), 144.89 (C^{12}), 140.51 (C^1), 131.79 (C^4), 128.42 (C^8), 127.98 (C^3), 127.44 (C^2), 126.40 (C^9), 125.26 (C^{11}), 117.88 (C^7), 44.71 ($C^{a'}$), 44.47 (C^a), 38.51 and 38.45 ($C^{e',e}$), 29.29 ($C^{c'}$), 29.23 (C^c), 28.93 and 28.86 ($C^{b,b',c,c'}$), 23.50 ($C^{d,d'}$). Anal. Calcd for $C_{28}H_{27}N_3O_6$: C, 67.06; H, 5.43; N, 8.38. Found C, 67.39; H, 5.54; N, 8.28.

*4.2.4. 4-(Dodecyloxy)benzoic acid (**4**).*



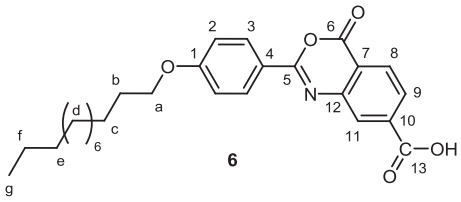
A mixture of 1-dodecylbromide (44.86 g, 180 mmol), 4-hydroxybenzoic acid (27.62 g, 200 mmol), KOH (26.40 g, 400 mmol, 85%) in ethanol (400 mL), and potassium iodide (0.50 g, 3 mmol) was heated under reflux for 12 h. After cooling to room temperature the suspension was treated with aqueous HCl up to pH 1. The white precipitation was filtered off and dried in vacuo at 40 °C to give **4** (54.06 g, 98%), which was used without further purification in the next step. δ_H (TFA-d_1) 8.07 (2H, d, H^3), 7.03 (2H, d, H^2), 4.20 (2H, t, H^a), 1.85 (2H, m, H^b), 1.47 (2H, m, H^c), 1.4–1.2 (16H, H^{d-f}), 0.83 (3H, t, H^g); δ_C (TFA-d_1) 175.42 (C^1), 166.18 (C^5), 134.86 (C^3), 122.65 (C^4), 117.21 (C^2), 71.85 (C^a), 33.73 (C^e), 31.36, 31.36, 31.20, 31.08 and 30.96 (C^d), 30.56 (C^b), 27.46 (C^c), 24.27 (C^f), 14.57 (C^g).

*4.2.5. 2-(4-Dodecyloxybenzamido)terephthalic acid (**5**).*



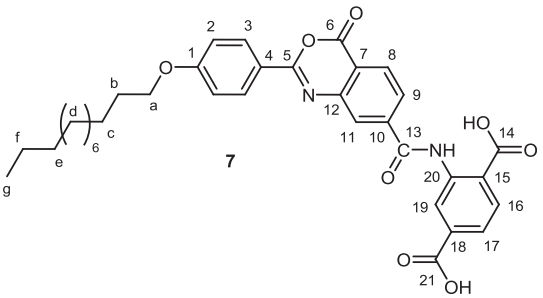
Compound **4** (45.97 g, 150 mmol) was stirred at 80 °C with 75 mL of thionyl chloride until bubble formation stopped (2 h). Then, the excess of thionyl chloride was distilled off in vacuo, and dry DMAc (200 mL) was added under cooling. The further conversion of the acid chloride with 2-aminobenzoic acid (27.17 g, 150 mmol) and triethylamine (15.18 g, 150 mmol) was performed according to the synthesis of **1**. The yellowish powder obtained **5** (50.71 g, 72%) was used without further purification for the next step. δ_H (DMSO-d_6) 13.3 (2H, br, COOH), 12.03 (1H, s, NH^5), 9.27 (1H, s, H^{11}), 8.13 (1H, d, H^8), 7.91 (2H, d, H^3), 7.70 (1H, d, H^9), 7.12 (2H, d, H^2), 4.07 (2H, t, H^a), 1.74 (2H, m, H^b), 1.42 (2H, m, H^c), 1.4–1.2 (16H, m, H^{d-f}), 0.85 (3H, t, H^g).

*4.2.6. 2-(4-(Dodecyloxy)phenyl)-4-oxo-4H-benzo[d][1,3]oxazine-7-carboxylic acid (**6**).*



Compound **6** was synthesized according to the preparation of **2** (second step) using **5** (37.57 g, 80 mmol) and acetic anhydride (200 mL). Yield: 34.68 g (96%). Mp 202–205 °C; δ_H (TFA-d_1) 8.55 (1H, s, H^{11}), 8.46 (1H, AB spin system, H^8), 8.45 (1H, AB spin system, H^9), 8.37 (2H, d, H^3), 7.23 (2H, d, H^2), 4.23 (2H, t, H^a), 1.89 (2H, m, H^b), 1.51 (2H, m, H^c), 1.4–1.2 (16H, H^{d-f}), 0.83 (3H, t, H^g); δ_C (TFA-d_1) 172.24 (C^1), 170.74 (C^{13}), 168.24 (C^5), 154.48 (C^6), 140.55 (C^{10}), 138.78 (C^{12}), 135.51 (C^3), 133.34 (C^9), 133.19 (C^8), 123.16 (C^{11}), 119.02 (C^2), 118.37 (C^7), 114.04 (C^4), 72.16 (C^a), 33.81 (C^e), 31.46, 31.37, 31.31, 31.19 and 30.04 (C^d), 30.54 (C^b), 27.53 (C^c), 24.37 (C^f), 14.70 (C^g).

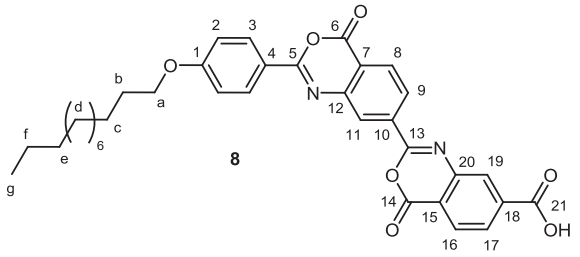
*4.2.7. 2-(2-(4-(Dodecyloxy)phenyl)-4-oxo-4H-benzo[d][1,3]oxazine-7-carboxamido)terephthalic acid (**7**).*



The synthesis of compound **7** was performed according to the preparation of **1** and **5**, respectively, using **6** (27.20 g, 60 mmol) and $SOCl_2$ (80 mL) for the first step. The obtained acid chloride was

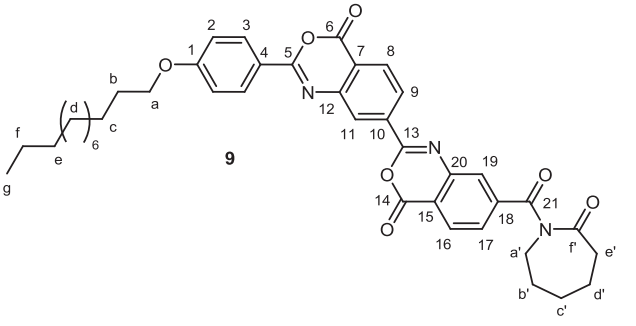
recrystallized from toluene (150 mL) with a yield of 23.41 g (83%). Overall yield of **7**, on the basis of **6**: (24.58 g, 78%). δ_H (DMSO-d_6) 13.4 (2H, br, COOH), 12.26 (1H, s, NH^{13}), 9.19 (1H, s, H^{19}), 8.31 (1H, s, H^{11}), 8.17 (2H, d, H^3), 8.15 (1H, AB spin system, H^9), 8.14 (1H, AB spin system, H^8), 8.06 (1H, m, H^{16}), 7.78 (1H, d, H^{17}), 7.13 (2H, d, H^2), 4.09 (2H, t, H^a), 1.75 (2H, m, H^b), 1.43 (2H, m, H^c), 1.4–1.2 (16H, H^{d-f}), 0.85 (3H, t, H^g).

*4.2.8. 2′-(4-(Dodecyloxy)phenyl)-4,4′-dioxo-4H,4′H-[2,7′-bibenzo[d][1,3]oxazine]-7-carboxylic acid (**8**).*



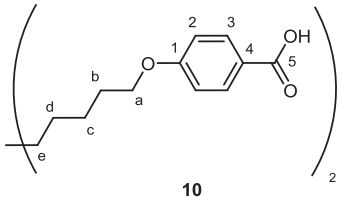
Compound **7** (24.39 g, 40 mmol) was converted into **8** according to the procedure described for compound **2** (second step) using 120 mL of acetic anhydride. Yield: 20.30 g (85%). Mp 260–264 °C; δ_H (TFA-d_1) 8.81 (1H, s, H^{11}), 8.64 (1H, d, H^9), 8.61 (1H, s, H^{19}), 8.51 (2H, d, H^8), 8.47 (1H, d, H^{16}), 8.40 (1H, s, H^3), 8.39 (1H, s, H^{17}), 7.24 (2H, d, H^2), 4.23 (2H, t, H^a), 1.89 (2H, m, H^b), 1.51 (2H, m, H^c), 1.4–1.2 (6H, H^{d-f}), 0.83 (3H, t, H^g); δ_C (TFA-d_1) 172.37 (C^{21}), 172.31 (C^1), 168.27 (C^5), 163.26 (C^{14}), 156.37 (C^{13}), 154.71 (C^6), 148.39 (C^{20}), 141.67 (C^{12}), 139.53 (C^{18}), 139.02 (C^{10}), 135.52 (C^3), 133.45 (C^8), 133.05 (C^{17}), 132.21 (C^{19}), 131.60 (C^{16}), 131.47 (C^9), 122.45 (C^{15}), 121.23 (C^{11}), 119.08 (C^2), 117.32 (C^7), 114.07 (C^4), 72.21 (C^a), 33.78 (C^e), 31.43, 31.34, 31.28, 31.16, 31.01 and 30.52 ($C^{b,d}$), 27.51 (C^c), 24.34 (C^f), 14.62 (C^g).

*4.2.9. 2′-(4-(Dodecyloxy)phenyl)-7-(2-oxoazepane-1-carbonyl)-4H,4′H-[2,7′-bibenzo[d][1,3]oxazine]-4,4′-dione (**9**).*



The synthesis of compound **9** was performed according to the preparation of **3** using **8** (19.62 g, 33 mmol) and thionyl chloride (80 mL) for the chlorination step. The obtained acid chloride was recrystallized from toluene with a yield of 14.41 g (71%). For further reaction with equimolar amounts of ε-caprolactam and triethylamine 200 mL of toluene was used. The recrystallization of **9** (**CA2**) was performed in toluene. Overall yield of **9**, on the basis of **8**: 12.53 g (60%). Mp 180–183 °C; δ_H (TFA-d_1) 8.81 (1H, s, H^{11}), 8.61 (1H, d, H^9), 8.51 (1H, d, H^8), 8.42 (1H, d, H^{16}), 8.41 (2H, d, H^3), 7.95 (1H, s, H^{19}), 7.79 (1H, d, H^{17}), 7.25 (2H, d, H^2), 4.24 (2H, t, H^a), 4.22 (2H, m, $H^{a'}$), 2.90 (2H, m, $H^{e'}$), 1.97 (6H, $H^{b'-d'}$), 1.90 (2H, m, H^b), 1.51 (2H, m, H^c), 1.45–1.2 (16H, H^{d-f}), 0.83 (3H, t, H^g); δ_C (TFA-d_1) 185.33 (C^f), 176.46 (C^{21}), 172.28 (C^1), 168.27 (C^5), 163.14 (C^{14}), 156.69 (C^{13}), 154.68 (C^6), 148.42 (C^{18}), 147.26 (C^{20}), 141.61 (C^{12}), 138.96 (C^{10}), 135.54 (C^3), 133.47 (C^8), 131.82 (C^{16}), 131.46 (C^9), 130.32 (C^{17}), 128.07 (C^{19}), 121.30 (C^{11}), 120.32 (C^{15}), 119.07 (C^2), 117.35 (C^7), 114.09 (C^4), 72.20 (C^a), 48.29 ($C^{a'}$), 40.24 ($C^{e'}$), 33.80 (C^e), 31.45, 31.36, 31.29, 31.18, 31.02, 30.80, 30.53 and 30.22 ($C^{b,d,b',c'}$), 27.52 (C^c), 25.28 ($C^{d'}$), 24.35 (C^f), 14.66 (C^g). Anal. Calcd for $C_{41}H_{45}N_3O_7$: C, 71.18; H, 6.56; N, 6.07. Found: C, 71.55; H, 6.82; N, 6.09.

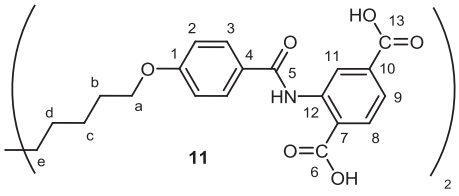
*4.2.10. 4,4′-(Decane-1,10-diylbis(oxy))dibenzoic acid (**10**).*



The preparation of compound **10** was performed according to the synthesis of **4** using 1,10-dibromdecane (27.84 g, 90 mmol), 4-hydroxybenzoic acid (27.90 g, 200 mmol), KOH (26.40 g, 400 mmol, 85%) in ethanol (300 mL), and potassium iodide (0.50 g, 3 mmol).

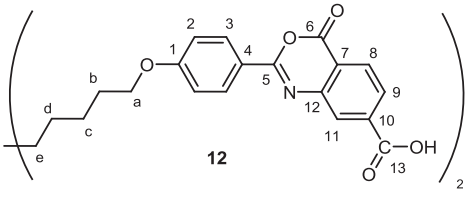
Yield: 36.19 g (97%). δ_H (DMSO-d_6) 12.5 (2H, br, COOH), 7.87 (4H, d, H^3), 6.98 (4H, d, H^2), 4.02 (4H, t, H^a), 1.72 (4H, m, H^b), 1.45–1.25 (12H, H^{c-e}).

*4.2.11. Compound **11**.*



The synthesis of compound **11** was performed according to the preparation of **5** using **10** (20.72 g, 50 mmol) and thionyl chloride (80 mL). The acid dichloride was washed with *n*-hexane and dried in vacuo at 40 °C (20.76 g, 92%). For further conversion with 2 equiv of 2-aminoterephthalic acid, triethylamine and 250 mL of DMAc were used. Overall yield of **11**, on the basis of **10**: 29.26 g (79%). Compound **11** was used without further purification for the next step. δ_H (DMSO-d_6) 13.3 (4H, br, COOH), 12.08 (2H, s, NH^5), 9.27 (2H, s, H^{11}), 8.12 (2H, d, H^8), 7.91 (4H, d, H^3), 7.70 (2H, d, H^9), 7.11 (4H, d, H^2), 4.06 (4H, t, H^a), 1.74 (4H, m, H^b), 1.45–11.2 (12H, H^{c-e}).

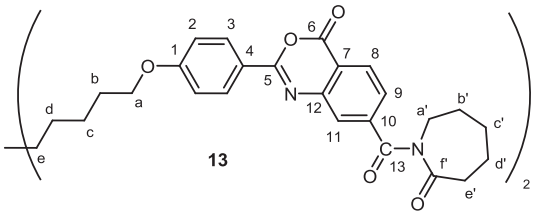
*4.2.12. Compound **12**.*



Compound **12** was synthesized according to the preparation of **2** (second step) using **11** (25.93 g, 35 mmol) and acetic anhydride (150 mL). Yield: 23.43 g (95%). Mp 295–303 °C; δ_H (TFA-d_1) 8.54 (2H, s, H^{11}), 8.46 (2H, AB spin system, H^8), 8.45 (2H, AB spin system, H^9), 8.37 (4, d, H^3), 7.23 (4H, d, H^2), 4.23 (4H, t, H^a), 1.89 (4, m, H^b), 1.52 (4H, m, H^c), 1.39 (8H, H^{d-e}); δ_C (TFA-d_1)

172.25 (C^1), 170.75 (C^{13}), 168.28 (C^5), 154.52 (C^6), 140.60 (C^{10}), 138.77 (C^{12}), 135.52 (C^3), 133.38 (C^9), 133.22 (C^8), 123.13 (C^{11}), 119.03 (C^2), 118.37 (C^7), 114.05 (C^4), 72.11 (C^a), 31.20 and 31.00 ($C^{d,e}$), 30.51 (C^b), 27.51 (C^c).

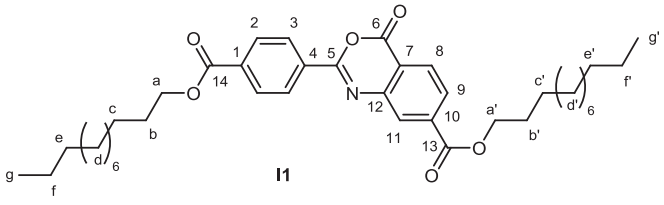
*4.2.13. Compound **13**.*



The synthesis of compound **13** was performed according to the preparation of **3** using **12** (21.14 g, 30 mmol) and thionyl chloride (80 mL). The obtained acid chloride was recrystallized from toluene (150 mL) with a yield of 15.57 g (70%). For further reaction with 2 equiv of ε-caprolactam, triethylamine and 150 mL of toluene were used. The recrystallization of **13** (**CA3**) was performed in toluene. Overall yield of **13**, on the basis of **12**: 16.38 g (61%). Mp: 171–174 °C; δ_H (TFA-d_1) 8.41 (2H, d, H^8), 8.40 (4H, d, H^3), 7.99 (2H, s, H^{11}), 7.82 (2H, d, H^9), 7.27 (4H, d, H^2), 4.27 (4H, t, H^a), 4.23 (4H, m, $H^{a'}$), 2.90 (4H, m, $H^{e'}$), 2.1–1.9 (16H, $H^{b,b'-d'}$), 1.56 (4H, m, H^c), 1.43 (8H, $H^{d,e}$); δ_C (TFA-d_1) 185.18 ($C^{f'}$), 174.67 (C^{13}), 172.14 (C^1), 168.22 (C^5), 154.74(C^6), 148.67 (C^{10}), 138.91 (C^{12}), 135.49 (C^3), 133.02(C^8), 130.18 (C^9), 119.70 (C^{11}), 118.98 (C^2), 115.96 (C^7), 114.13 (C^4), 72.07 (C^a), 48.15 ($C^{a'}$), 40.09 ($C^{e'}$), 31.20, 31.00, 30.64, 30.52 and 30.06 ($C^{b,d-e,b',c'}$), 27.52 (C^c), 25.26 ($C^{d'}$). Anal. Calcd for $C_{52}H_{54}N_4O_{10}$: C, 69.78; H, 6.08; N, 6.26. Found: C, 69.78; H, 6.29; N, 5.97.

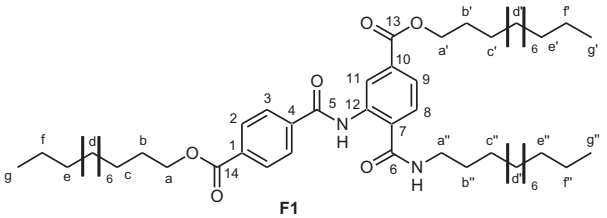
*4.2.14. Model reactions of compounds **3**, **9**, and **13** (**CA1**–**3**) with 1-dodecanol and 1-dodecylamine.* Model reactions of the coupling agents **CA1**–**3** with equimolar amounts of 1-dodecanol were performed in the melt in a 50 mL two-necked flask under argon at 195 °C for 2 h. In order to evaluate the selectivity of the reactions, the raw products obtained after cooling to room temperature were analyzed by NMR spectroscopy. The major parts of the raw products were recrystallized from acetone yielding the respective intermediates **I1**–**3**. In a second model reaction, these intermediates were converted with equimolar amounts of 1-dodecylamine in the melt in a 50 mL two-necked flask under argon at 210 °C for 15 min giving the final products **F1**–**3**, respectively.

*4.2.15. Intermediate **I1**.*



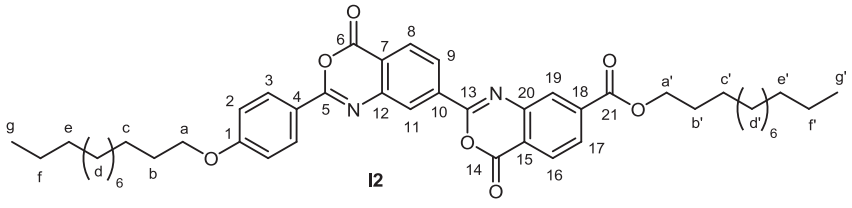
Conversion of **CA1** (2.01 g, 4 mmol) with 1-dodecanol (1.44 g, 8 mmol). Recrystallization from acetone, yield: 64%. δ_H ($CDCl_3$) 8.39 (2H,d, H^3), 8.37 (1H, s, H^{11}), 8.31 (1H, d, H^8), 8.18 (2H, d, H^2), 8.16 (1H, d, H^9), 4.40 (2H, t, $H^{a'}$), 4.36 (2H, t, H^a), 1.81 (4H, $H^{b,b'}$), 1.5–1.2 (36H, $H^{c-f,c'-f'}$), 0.88 (6H, $H^{g,g'}$); δ_C ($CDCl_3$) 165.74 (C^{14}), 164.92 (C^{13}), 158.50 (C^6), 156.79 (C^5), 146.70 (C^{12}), 138.04 (C^{10}), 134.26 (C^1), 133.67 (C^4), 129.87 (C^2), 128.92 (C^9), 128.88 (C^8), 128.76 (C^{11}), 128.34 (C^3), 120.03 (C^7), 66.18 ($C^{a'}$), 65.68 (C^a), 31.90 ($C^{e,e'}$), 29.63, 29.62, 29.57, 29.51, 29.33 and 29.27 ($C^{d,d'}$), 28.69, 28.64 ($C^{b,b'}$), 26.01 ($C^{c,c'}$), 22.67 ($C^{f,f'}$), 14.08 ($C^{g,g'}$). Anal. Calcd for $C_{40}H_{57}NO_6$: C, 74.15; H, 8.87; N, 2.16. Found: C, 74.34; H, 9.06; N, 2.13.

*4.2.16. Final product **F1**.*



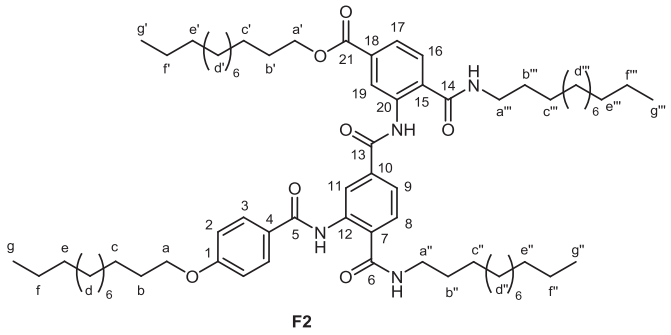
Conversion of **I1** (1.00 g, 1.54 mmol) with 1-aminododecan (0.286 g, 1.54 mmol). δ_H ($CDCl_3$) 12.18 (1H, s, NH^5), 9.39 (1H, s, H^{11}), 8.18 (2H, d, H^2), 8.10 (2H, d, H^3), 7.75 (1H, d, H^9), 7.55 (1H, d, H^8), 6.43 (1H, t, NH^6), 4.35 (4H, t, $H^{a,a'}$), 3.48 (2H, q, $H^{a''}$), 1.79 (4H, $H^{b,b'}$), 1.66 (2H, m, $H^{b''}$), 1.5–1.2 (54H, $H^{c-f,c'-f',c''-f''}$), 0.88 (9H, $H^{g,g',g''}$); δ_C ($CDCl_3$) 168.39 (C^6), 165.76 and 165.66 ($C^{13,14}$), 164.56 (C^5), 139.24 (C^{12}), 138.12 (C^4), 133.68 (C^{10}), 133.48 (C^1), 129.93 (C^2), 127.35 (C^3), 126.84 (C^8), 124.45 (C^7), 123.87 (C^9), 122.24 (C^{11}), 65.66 and 65.47 ($C^{a,a'}$), 40.30 ($C^{a''}$), 31.85 ($C^{e,e',e''}$), 29.7–29.0 ($C^{b'',d,d',d''}$), 28.66 and 28.59 ($C^{b,b'}$), 27.01 ($C^{c''}$), 25.99 and 25.86 ($C^{c,c'}$), 22.60 ($C^{f,f',f''}$), 14.02 ($C^{g,g',g''}$). Anal. Calcd for $C_{52}H_{84}N_2O_6$: C, 74.96; H, 10.16; N, 3.36. Found: C, 75.06; H, 10.34; N, 3.35.

*4.2.17. Intermediate **I2**.*



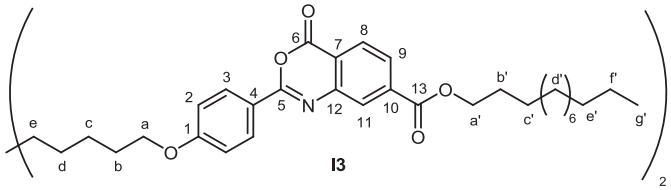
Conversion of **CA2** (1.38 g, 2 mmol) with 1-dodecanol (0.373 g, 2 mmol). Recrystallization from acetone, yield: 20%. δ_H ($CDCl_3$) 8.52 (1H, s, H^{11}), 8.36 (1H, H^{19}), 8.34 (1H, d, H^9), 8.31 (1H, d, H^{16}), 8.30 (1H, d, H^8), 8.23 (2H, d, H^3), 8.17 (1H, d, H^{17}), 6.97 (2H, d, H^2), 4.40 (2H, t, $H^{a'}$), 4.04 (2H, t, H^a), 1.82 (4H, $H^{b,b'}$), 1.48 (4H, $H^{c,c'}$), 1.4–1.2 (36H, $H^{d-f,d'-f'}$), 0.89 (6H, $H^{g,g'}$); δ_C ($CDCl_3$) 164.80 (C^{21}), 163.28 (C^1), 158.95 (C^6), 158.08 (C^{14}), 157.95 (C^5), 155.95 (C^{13}), 147.73 (C^{12}), 146.38 (C^{20}), 138.10 (C^{18}), 137.16 (C^{10}), 130.46 (C^3), 129.30 (C^{17}), 129.02 and 128.94 ($C^{8,16}$), 128.92 (C^{19}), 127.00 (C^{11}), 126.40 (C^9), 121.75 (C^4), 120.11 (C^{15}), 119.45 (^7C), 114.71 (C^2), 68.38 ($C^{a'}$), 66.23 (C^a), 31.91 ($C^{e,e'}$), 29.7–29.0 ($C^{d,d'}$), 28.64 ($C^{b,b'}$), 26.00 ($C^{c,c'}$), 22.67 ($C^{f,f'}$), 14.08 ($C^{g,g'}$). Anal. Calcd for $C_{47}H_{60}N_2O_7$: C 73.79, H 7.91, N 3.66. Found: C 73.88, H 8.07, N 3.68.

*4.2.18. Final product **F2**.*



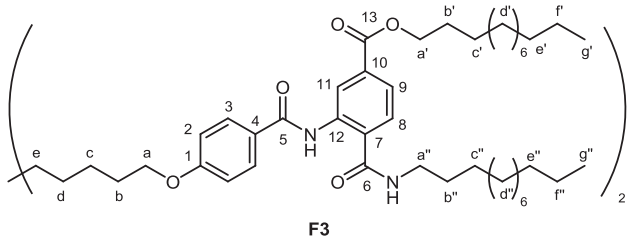
Conversion of **I2** (0.182 g, 0.238 mmol) with 1-aminododecan (0.0883 g, 0.476 mmol). δ_H ($CDCl_3$) 12.17 (1H, s, NH^{13}), 11.44 (1H, s, NH^5), 9.31 (1H, s, H^{19}), 9.01 (1H, s, H^{11}), 8.02 (2H, d, H^3), 7.66 (1H, t, NH^6), 7.36 (3H, $H^{8,9,16}$), 7.21 (1H, d, H^{17}), 7.20 (1H, t, NH^{14}), 7.02 (2H, d, H^2), 4.38(2H, t, $H^{a'}$), 4.05 (2H, t, H^a), 3.63 (2H, q, $H^{a''}$), 3.52 (2H, q, $H^{a'''}$), 1.85 (6H, $H^{b,b',b''}$), 1.73 (2H, m, $H^{b'''}$), 1.5–1.2 (72H, $H^{c-f,c'-f',c''-f'',c'''-f'''}$), 0.87 (12H, $H^{g,g',g'',g'''}$); δ_C ($CDCl_3$) 169.00 (C^6), 168.66 (C^{14}), 167.45 (C^{21}), 164.91 (C^5), 162.87 (C^{13}), 162.46 (C^1), 139.30 (C^{20}), 138.28 (C^{12}), 136.39 (C^{10}), 132.95 (C^{18}), 129.43 (C^3), 128.00 (C^8), 126.89 (C^{16}), 126.16 and 126.11 ($C^{4,7}$), 123.92 (C^{15}), 122.80 (C^{17}), 122.44 (C^{11}), 121.17 (C^{19}), 120.84 (C^9), 114.53 (C^2), 68.30 ($C^{a'}$), 65.83 (C^a), 40.68 ($C^{a''}$), 40.29 ($C^{a'''}$), 31.91($C^{e,e',e'',e'''}$), 30.0–28.7 ($C^{b,d,b',d',b'',d'',b''',d'''}$), 27.45 and 27.12 ($C^{c'',c'''}$), 25.93 and 26.02 ($C^{c,c'}$), 22.67 ($C^{f,f',f'',f'''}$), 14.08 ($C^{g,g',g'',g'''}$). Anal. Calcd for $C_{71}H_{114}N_4O_7$: C 75.09, H 10.12, N 4.93. Found: C 75.36, H 10.35, N 4.93.

*4.2.19. Intermediate **I3**.*



Conversion of **CA3** (2.900 g, 3.24 mmol) with 1-dodecanol (1.208 g, 6.48 mmol). Dissolved in chloroform, precipitated with acetone, yield: 66%. δ_H ($CDCl_3$) 8.29 (2H, s, H^{11}), 8.27 (2H, d, H^8), 8.26 (4H, d, H^3), 8.07 (2H, d, H^9), 7.00 (4H, d, H^2), 4.38 (4H, t, $H^{a'}$), 4.05 (4H, t, H^a), 1.82 (8H, $H^{b,b'}$), 1.49 (8H, $H^{c,c'}$), 1.4–1.2 (40H, $H^{d,e,d'-f'}$), 0.88 (6H, $H^{g'}$); δ_C ($CDCl_3$) 165.12 (C^{13}), 163.17 (C^1), 159.08 (C^6), 157.73 (C^5), 147.41 (C^{12}), 137.75 (C^{10}), 130.41 (C^3), 128.68 (C^8), 128.25 (C^{11}), 127.72 (C^9), 121.89 (C^4), 119.61 (C^7), 114.67 (C^2), 68.31 (C^a), 66.01 ($C^{a'}$), 31.89 ($C^{e'}$), 30.0–29.0 ($C^{b,d-e,d'}$), 28.63 ($C^{b'}$), 26.00 and 25.96 ($C^{c,c'}$), 22.65 ($C^{f'}$), 14.07 ($C^{g'}$). Anal. Calcd for $C_{64}H_{84}N_2O_{10}$: C 73.82, H 8.13, N 2.69. Found: C 74.56, H 8.38, N 2.72.

*4.2.20. Final product **F3**.*



Conversion of **I3** (0.562 g, 0.54 mmol) with 1-aminododecan (0.201 g, 1.08 mmol). δ_H ($CDCl_3$) 11.84 (2H, s, NH^5), 9.37 (2H, H^{11}), 7.98 (4H, d, H^3), 7.71 (2H, d, H^9), 7.51 (2H, d, H^8), 6.98 (4H, d, H^2), 6.37 (2H, t, NH^6), 4.34 (4H, t, $H^{a'}$), 4.02 (4H, t, H^a), 3.47 (4H, q, $H^{a''}$), 1.80 (8H, $H^{b,b'}$), 1.65 (4H, $H^{b''}$), 1.5–1.2 (72H, $H^{c-e,c'-f',c''-f''}$), 0.88 (12H, $H^{g',g''}$); δ_C ($CDCl_3$) 168.58 (C^6), 165.87 (C^{21}), 165.20 (C^5), 162.28 (C^1), 139.87 (C^{12}), 133.85 (C^{10}), 129.30 (C^3), 126.55 ($C^{4,8}$), 124.33 (C^7), 123.43 (C^9), 122.46 (C^{11}), 114.49 (C^2), 68.21 (C^a), 65.64 ($C^{a'}$), 40.28 ($C^{a''}$), 31.89 ($C^{e',e''}$), 30.0–28.6 ($C^{b,d,e,b',d',b'',d''}$), 27.02 ($C^{c''}$), 25.98 and 25.91 ($C^{c,c'}$), 22.66 ($C^{f',f''}$), 14.07 ($C^{g',g''}$). Anal. Calcd for $C_{88}H_{138}N_4O_{10}$: C 74.85, H 9.85, N 3.97. Found: C 76.11, H 10.71, N 3.92.

Acknowledgements

We would like to thank the Deutsche Forschungsgemeinschaft for financial support (BO 1121/6-1)

Supplementary data

^1H and ^{13}C NMR of compounds **CA1–3**, **I1–3**, and **F1–3**. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.03.024. These data include MOL files and InChiKeys of the most important compounds described in this article.

References and notes

1. Inata, H.; Matsumura, S. *J. Appl. Polym. Sci.* **1986**, *32*, 5193.
2. Inata, H.; Matsumura, S. *J. Appl. Polym. Sci.* **1987**, *34*, 2609.
3. Leistner, D.; Stephan, M.; Häußler, L.; Vogel, R.; Rätzsch, M. *Angew. Makromol. Chem.* **1993**, *206*, 141.
4. Maier, S.; Loontjens, T.; Scholtens, B.; Mülhaupt, R. *Angew. Chem.* **2003**, *115*, 5248.
5. Stier, U.; Schweizer, M. *J. Appl. Polym. Sci.* **2007**, *106*, 425.
6. Pena, G.; Eceiza, A.; Valea, A.; Remiro, P.; Oyanguren, P.; Mondragon, I. *Polym. Int.* **2003**, *52*, 1444.
7. Maier, S.; Loontjens, T.; Scholtens, B.; Mülhaupt, R. *Macromolecules* **2003**, *36*, 4727.
8. Böhme, F.; Jakisch, L.; Komber, H.; Wursche, R. *Polym. Degrad. Stab.* **2007**, *92*, 2270.
9. Dung, B. T.; Jakisch, L.; Komber, H.; Häußler, L.; Voit, B.; Nghia, N. D.; Böhme, F. *Macromol. Chem. Phys.* **2006**, *207*, 1953.
10. Jakisch, L.; Komber, H.; Böhme, F. *J. Polym. Sci. Polym. Chem.* **2003**, *41*, 655.
11. Jakisch, L.; Komber, H.; Wursche, R.; Böhme, F. *J. Appl. Polym. Sci.* **2004**, *94*, 2170.
12. Gunanathan, C.; Ben-David, Y.; Milstein, D. *Science* **2007**, *317*, 790.
13. Zeng, H. X.; Guan, Z. B. *J. Am. Chem. Soc.* **2011**, *133*, 1159.
14. Jakisch, L.; Komber, H.; Böhme, F. *Macromol. Mater. Eng.* **2007**, *292*, 557.
15. Gube, A.; Jakisch, L.; Häußler, L.; Schneider, K.; Voit, B.; Böhme, F. *Polym. Int.* **2012**, *61*, 157.
16. Coppola, G. M. *J. Heterocycl. Chem.* **1999**, *36*, 563.
17. Donaruma, L. G.; Scelia, R. P.; Schonfeld, S. E. *J. Heterocycl. Chem.* **1964**, *1*, 48.
18. Boyd, G. V. In *Acid Derivatives*; Patai, S., Ed.; Wiley: Chichester, UK, 1979; Vol. 1, p 491.