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# Soluble Oligoaramide Precursors—A Novel Class of Building Blocks for Rod–Coil Architectures

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**Abstract:** A new synthetic route is described that allows the reversible conversion of the inherently insoluble oligo-*p*-benzamides into soluble materials through the formation of imidoyl chlorides. Syntheses of the corresponding dimer, trimer, and tetramer are reported; these compounds can easily be purified by crystallization and are accessible on the multigram scale. Structural proof was obtained by single-crystal X-ray structures of the trimer and tetramer precursors. They can be selectively functionalized into amides or esters at the terminal carboxylic acid group followed by hydrolysis of the imidoyl chlorides to the parent amides. This new class of compounds gives access to strongly aggregating rigid rodlike materials in few synthetic steps, as is demonstrated by the preparation of poly(ethylene glycol)-*co*-oligo(*p*-benzamide) rod–coil block copolymers.

**Keywords:** aggregation · aramides · block copolymers · oligomers · rod–coil copolymers

## Introduction

Polyaramides are amongst the toughest synthetic materials known today. Their excellent thermal and mechanical properties arise from the ability of the amide-containing polymer chains to form hydrogen bonds between each other.[1] The rigidity of the chains in combination with the interchain hydrogen bonds render the polymer virtually insoluble in most organic solvents. For processing purposes, strong hydrogen-bond-disrupting solvents like concentrated sulfuric acid or DMAc/LiCl are typically employed.[2]

Despite the broad synthetic expertise concerning the synthesis of polyaramides,[3] surprisingly few reports describe the preparation of the corresponding monodisperse aromatic amide oligomers. Oligoaramides are central building units for novel rod–coil block-copolymer architectures and unusual liquid crystals, and are essential models for a fundamental understanding of hydrogen bonding in polymeric aramides.

Oligo-*p*-benzamides (OPBA) up to the tetramer have been reported by Bredereck.[4] However, a full characterization of the compounds according to today's analytical standards have not yet been reported. König et al. reported the synthesis of OPBA up to the trimer on a solubilising poly(ethylene glycol) support.[5] In the method they use, the OPBA is formed from 4-nitrobenzoyl chloride by means of a successive amide coupling and nitro-group reduction sequence. Two reaction steps are therefore necessary for the attachment of each monomer unit.

Due to the high chain rigidity, the hydrogen-bond donors/acceptors in OPBA are expected to align perfectly and make these materials intriguing supramolecular synthons for solution or solid-state organization in rod–coil block-copolymer architectures. Here we report a new synthetic route that allows a significantly faster formation of OPBA by using oligomers of three or four units at a time.

## Results and Discussion

As outlined in Scheme 1, reaction of *p*-nitrobenzoyl chloride with *p*-aminobenzoic acid gave the amide **2** in 95% yield.[4] Following a procedure by Julia et al.,[6] we attempted to convert dimer **2** into the corresponding acid chloride using thionyl chloride. However, this reaction failed in our hands and we obtained **4**, in which the amide and carboxylic acid had been converted to an imidoyl chloride and acid chloride, respectively, in 65% isolated yield.

While the report by Julia et al. described the product as an insoluble yellow solid, we obtained a yellow solid which exhibited excellent solubility in diethyl ether, acetone, di-

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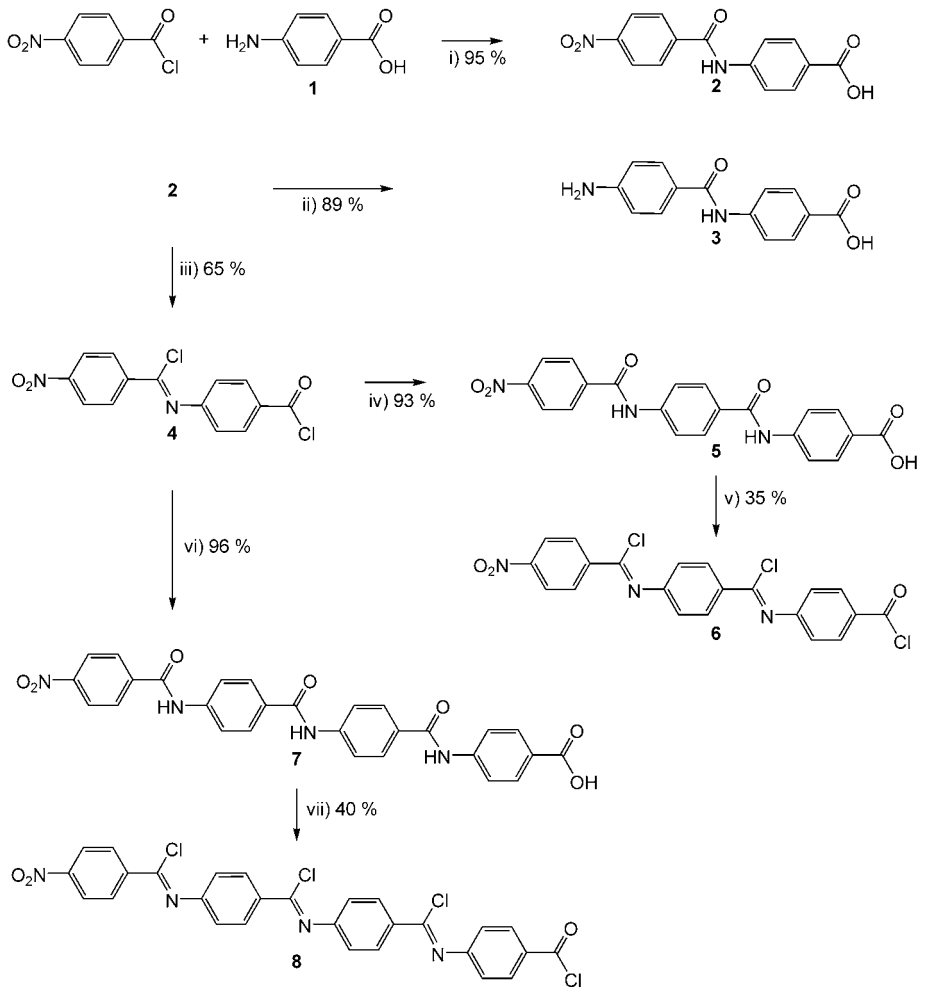



Scheme 1. Synthesis of soluble OPBA precursors: i) acetone, dimethyl aniline; ii) methanol, ammonium formate, Pd/C; iii) thionyl chloride; iv) 1. acetone, **1**, dimethyl aniline, 2. water; v) thionyl chloride; vi) 1. acetone, *N*-methyl pyrolidinone, **3**, dimethyl aniline, 2. water; vii) thionyl chloride.

chloromethane, and chloroform. The melting point of **4** (157 °C) was greatly reduced compared to the parent amide **2** (> 300 °C). While the conversion of aromatic amides into imidoyl chlorides by using thionyl chloride is a well-known reaction,[7] it has, to the best of our knowledge, never been employed as a supramolecular protecting group, improving the solubility of otherwise insoluble materials.

The reaction of **2** with thionyl chloride gave **4** as the main product, which was crystallized from toluene. In order to improve the yield of 65 % we analyzed the toluene insoluble fraction. $^{1}$H and $^{13}$C NMR spectroscopy as well as field desorption (FD) mass spectrometry unambiguously showed the formation of 4-(*N*′-formylamino)-*N*,*N*-dimethylbenzamide as the main side product, explaining the difficulties in increasing the yield of **4**. This side product was presumably formed by cleavage of the amide bond of **2** and subsequent reaction with fragments of the DMF solvent molecules present in the crystal lattice of **2**. Further investigations will be carried out to elucidate the exact mechanism of this side reaction.

Reaction of **4** with **1** gave trimer **5** in 93 % yield after hydrolysis, which could be converted into the corresponding compound **6** (35 %), in which both amide groups were transformed into imidoyl chlorides and the carboxylic acid into an acid chloride. The composition of the reaction residue could not successfully be analyzed for this reaction.

However, encouraged by the ease of these transformations we prepared tetramer **7** (96 %) from **4** and **3** and successfully converted it to the corresponding imidoyl chloride and acid chloride containing compound **8** (40 %). The analysis of the insoluble residue by $^{1}$H and $^{13}$C NMR spectroscopy as well as FD mass spectrometry showed that the *N*,*N*-dimethylamido-*N*′-formamide of **3**, $(H_3C)_2N$-CO-$C_6H_4$-NH-CO-$C_6H_4$-NH-CHO, was the main side product. For the formation of this compound, tetramer **7** had to cleaved at the central C–N bond. Interestingly, neither of the two alternative reaction products obtained by cleavage of the other two amide bonds in **7** could be observed.

The imidoyl chloride protected compounds **4**, **6**, and **8** are unusual precursors for the corresponding oligomides in that they have to be prepared from those amides to begin with. However, OPBA are virtually insoluble in most organic solvents and therefore inaccessible for chemical transformations. Thionyl chloride not only dissolves the OPBA, but also converts them into very soluble and reactive intermediates that can be hydrolyzed back to the parent amide structure after reaction. In this respect we feel confident in describing this approach as a precursor route.

Importantly, compounds **4**, **6**, and **8** can easily prepared on the multigram scale and crystallize readily from toluene. They show greatly improved solubility over the parent amides due to the fact that all amide groups responsible for hydrogen-bond formation are replaced by imidoyl chlorides. The single-crystal X-ray structures of **6**[8] and **8**[9] (Figure 1, top and bottom, respectively) show that the phenyl rings in the solid state are twisted by approximately 90° with respect to each other (**6**: 1/2:72.9(1)°, 2/3:74.0(1)°; **8**: 1/2:89.9(4)°, 2/3:74.2(4)°, 3/4:61.9(4)°), which also contributes to the enhanced solubility of these compounds.[10]

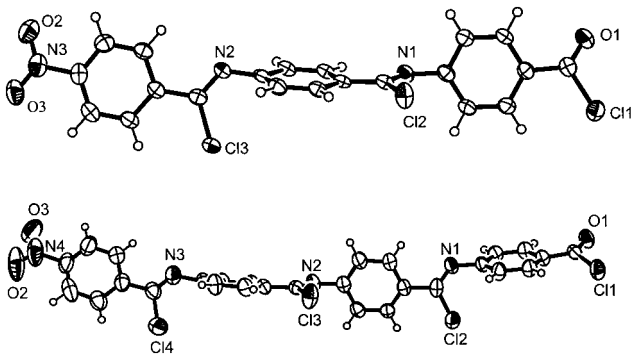



Figure 1. Single crystal X-ray structures of **6**[8] (top) and **8**[9] (bottom).

To provide evidence that a twist of the phenyl rings with respect to each other is also present in solution, UV spectra of compounds **4**, **6**, and **8** were recorded in chloroform (Figure 2, top). It can be seen that the shift of the absorption maximum with increasing oligomer length is much less ($\Delta\lambda_{max}=18$ nm, difference between **4** and **8**) than that of the parent amides ($\Delta\lambda_{max}=47$ nm, difference between **2** and **7**, Figure 2, bottom), indicating reduced conjugation due to a twist of the phenyl rings.

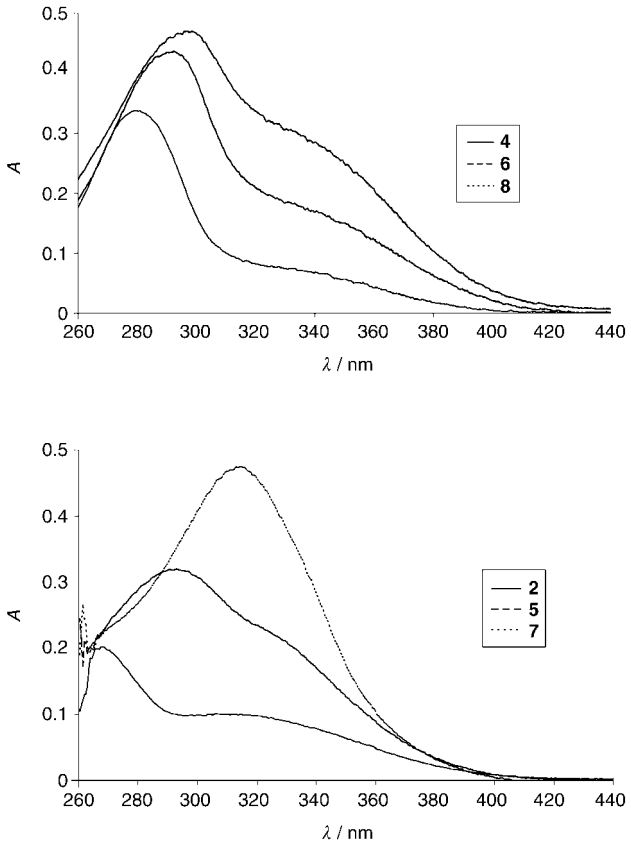



Figure 2. Top: UV-visible spectra of compounds **4**, **6** and **8** (in $CHCl_3$, $c=0.01$ mM). Bottom: UV-visible spectra of compounds **2**, **5** and **7** (in DMAc+1% LiCl, $c=0.01$ mM).

The synthesis of **5** and **7** showed that nucleophilic substitution with aromatic amines takes place selectively at the acid chloride to form the corresponding amides. Substitution of the imidoyl chlorides to give amidines was not observed under our reaction conditions.

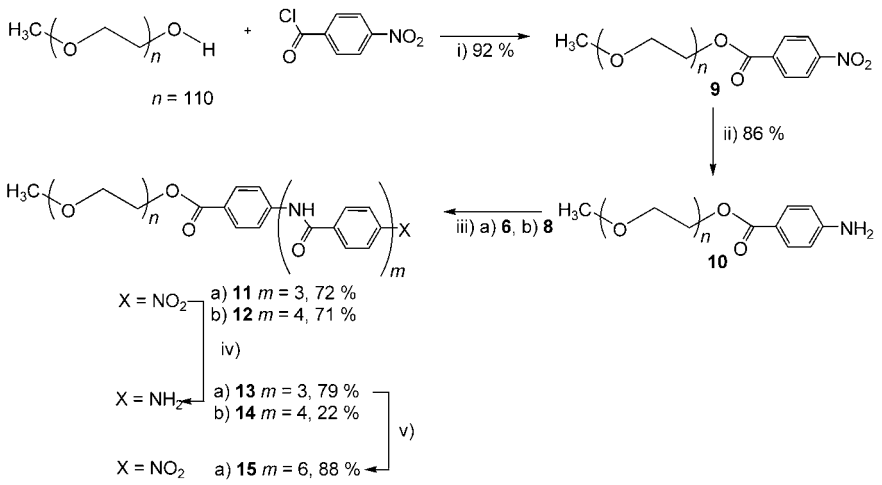
To show the preparative usefulness of these soluble oligoaramide precursors, we prepared rod–coil block copolymers from commercially available monomethyl-poly(ethylene glycol) (MPEG). In most rod–coil block copolymers,[11] the rod-segment gains its stiffness through helical structures. Examples for helical structures used in rod–coil architectures are polypeptides,[12] polyisocyanates,[13] polyisocyanides,[14] and polycarbodiimides.[15] Examples for nonhelical rods are poly(*p*-phenylene)s,[16,17] poly(thiophene)s,[18] poly(phenylquinoline)s,[19] and so forth. Ciferri et al. have exploited the strong hydrogen bonding ability of poly(*p*-benzamide)s (PPBA) in block copolymers formed from PPBA and poly(ethylene glycol) (PEG).[20] Yokozawa et al. developed a chain-growth polymerization route to PPBAs[21] and have reported triblock architectures with an outer PEG and an inner PPBA block.[22] Rod–coil block copolymers with well-defined, that is, monodisperse, OPBA as the rigid block have, to the best of our knowledge, not yet been reported. Here we describe the first synthesis of such materials using the soluble OPBA precursors.

As outlined in Scheme 2, MPEG was treated with *p*-nitrobenzoyl chloride to give the ester **9**. Nitro-terminated polymer **9** was subsequently reduced by using ammonium formate-Pd/C to give the primary amine **10**.[5] Figure 3 shows the doubly charged mass distribution of the ESI mass spectrum of polymer **10**. All peaks are isotopically resolved and can be assigned to the product structure. To emphasize this, the polymer with 104 ethylene oxide repeat units is marked as an example.

Polymer **10** was treated with soluble OPBA precursors **6** and **8** to give **11** (72%) and **12** (71%) respectively. These polymers were again reduced with ammonium formate-Pd/C to give primary amine terminated polymers **13** (79%) and **14** (22%). The low yield for the reduction of **12** was attributed to strong aggregation in solution of the block copolymer, rendering the terminal nitro group of **12** inaccessible for a heterogeneous reduction protocol. Investigations into homogeneous reductions are currently being carried out.

The triply charged mass distribution of the ESI mass spectrum of polymer **13** is shown in Figure 4. All mass peaks are isotopically resolved and can be assigned to the product structure. To illustrate this fact, the polymer with 104 ethylene oxide repeat units is marked in the spectrum.

Polymer **13** was again treated with soluble OPBA precursor **6** to give nitro-terminated polymer **15** (88%). Although the rigid hepta(*p*-benzamide) rod in this block copolymer is relatively short, the effect it has on the physical properties of the copolymer are quite dramatic. While the PEG homopolymer is miscible with water in all ratios, solid **15** does not dissolve in water unless sonicated. Additionally, the solubility in solvents like chloroform, methanol, or dioxane is greatly reduced. Also, melt enthalpies showed a systematic de-




Scheme 2. Synthesis of rod–coil block copolymers: i) dichloromethane, triethyl amine; ii) methanol, ammonium formate, Pd/C; iii) chloroform, dimethyl aniline, iv) methanol, ammonium formate, Pd/C; v) **6**, chloroform, dimethyl aniline.

(+1% LiBr) showed only the nonaggregated species. First AFM data show the existence of vesicle-like spheres in chloroform. Further investigations into the supramolecular structures formed using AFM and light scattering techniques are currently being carried out in our group.

## Conclusion

We have developed a new route to soluble OPBA in which the aromatic amides were converted to imidoyl chlorides. The imidoyl chlorides act as supramolecular protecting groups preventing hydrogen bonding and aggregation. Oligomers up to the tetramer were prepared and converted to the soluble and reactive precursor form. These could be obtained in very high purity and their structures were confirmed by single-crystal X-ray analysis.

As high reagent reactivity and few reaction steps are crucial for modifying polymer end-groups in a well-defined manner, we demonstrated the synthetic value of these novel precursors by preparing MPEG-oligoaramide block copolymers with oligomer lengths up to the heptamer in only five reaction steps and no detectable side reactions. These block-copolymers exhibit strong solution aggregation as determined by gel permeation chromatography. First AFM data shows the existence of vesicle-like structures in chloroform.

These new synthetic precursors open the door to the synthesis of novel supramolecular polymers and unusual liquid

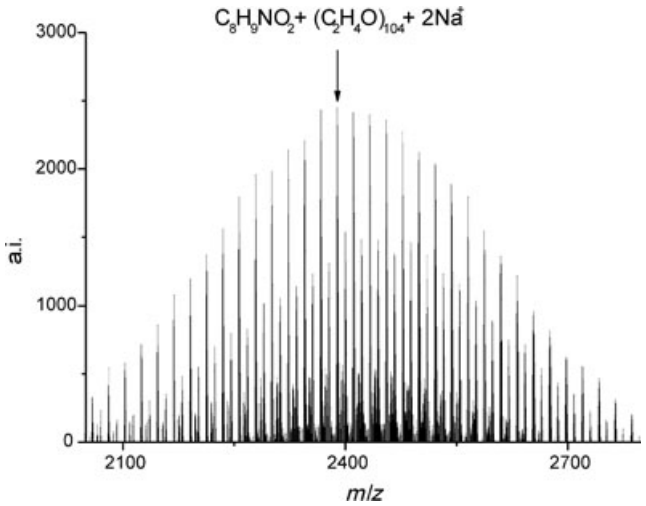



Figure 3. Mass spectrum (ESI) of **10**. The two mass distributions of lower intensity can be assigned to the mixed $Na^+$-$K^+$ adduct and the $Na^+$-$H^+$ adduct of **10**.

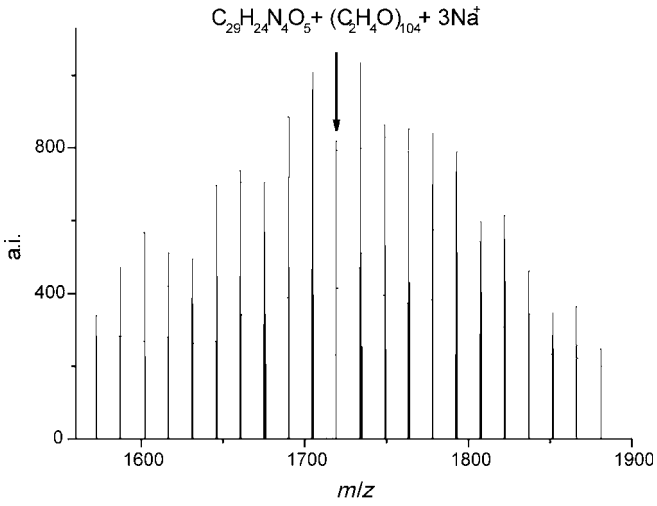



Figure 4. Mass spectrum (ESI) of **13**.

crease with increasing chain length of the OPBA. These phenomena are explained by strong intermolecular interactions of the oligo aramide blocks.

To further investigate the interaction of the aramide oligomers, gel permeation chromatography (GPC) traces were recorded in chloroform for polymers **11**, **12**, and **15**, each at different concentrations varying from 0.5 to 3.5 $g\,L^{-1}$. For polymer **11**, only the nonaggregated block copolymer could be observed at all concentrations. The elution curve for polymer **12** exhibited two peaks, one corresponding to the nonaggregated and one to the aggregated form of the material, with the latter increasing in intensity as concentration was increased.

For polymer **15**, the GPC traces showed that the aggregated form was predominant even at the lowest concentration. Polymers **11**, **12**, and **15** recorded on a GPC run in DMF

crystals as well as the study of molecular recognition based on hydrogen bonding in synthetic materials.

## Experimental Section

**Materials**: Solvents (p. a. quality) were purchased from Fisher Scientific, those for spectrometric measurements and all chemical reagents from Acros Organics. Toluene was dried by azeotropic removal of water and subsequent storage over molecular sieves (4 Å). All other chemicals were used as received without further purification. Recycling of used thionyl chloride was performed by reflux over flowers of sulfur followed by two successive distillations. Deuterated solvents ([D$_6$]DMSO and CDCl$_3$) were purchased from Deutero GmbH and used as received. Celite was purchased from Fluka. *p*-Aminobenzoic acid (**1**) (Acros) was used as received.

**Physical and analytical methods**: Standard $^1$H and $^{13}$C NMR spectra were recorded at 300 MHz (75 MHz for $^{13}$C) on a Bruker AC300 spectrometer. For high-temperature measurements a Bruker DRX400 spectrometer was used, working at 400 MHz (100 MHz for $^{13}$C). FD mass spectra were measured on a Finnigan MAT 95 and ESI mass spectra on a Micromass Q-TOF Ultima 3. Infrared spectra were recorded on a Nicolet 5DXC FT-IR spectrometer, and UV-visible spectra on a Shimadzu UV-210 2 PC scanning spectrophotometer. DSC curves were obtained from a Perkin–Elmer DSC7 and a Perkin–Elmer Thermal Analysis Controler TAC 7/DX. For elemental analyses, an Elementar Vario EL2 was used. X-ray crystal structures were obtained on a Turbo CAD4. For polymeric compounds **9**–**15** only $^1$H NMR data corresponding to the modified OPBA end-group are reported.

**4-(4-Nitrobenzamido)benzoic acid (2)**: Compound **1** (80 g, 0.584 mol) and *N,N*-dimethylaniline (100 mL) were dissolved in dry acetone (530 mL). A solution of 4-nitrobenzoyl chloride (108 g, 0.582 mol) in acetone (130 mL) was added dropwise to this mixture under stirring and cooling with an ice bath. The reaction mixture was allowed to warm to room temperature and was stirred for one further hour. The resulting yellow precipitate was collected by filtration and washed with hydrochloric acid (2 N, 400 mL) and then water until the filtrate was neutral. The resulting solid was dried under vacuum and recrystallized from DMF to give **2** (158.2 g, 95%). M.p. >300°C; elemental analysis calcd (%) for $C_{14}H_{10}N_2O_5$: C 58.73, H 3.52, N, 9.79; found: C 58.23, H 3.28, N 9.84; MS (FD): *m/z* calcd: 286.1; found: 286.5 (100) $[M]^+$; $^1$H NMR ([D$_6$]DMSO): $\delta$=7.93 (m, 4H), 8.18 (d, $J$=8.5 Hz, 2H), 8.36 (d, $J$=8.5 Hz, 2H), 10.82 (s, 1H), 12.75 ppm (br s, <1H); $^{13}$C NMR and DEPT ([D$_6$]DMSO): $\delta$= 119.8 (+), 123.7 (+), 126.2, 129.5 (+), 130.4 (+), 140.4, 142.9, 149.4, 164.4, 167.0 ppm; UV/Vis (DMAc + 1% LiCl): $\lambda_{max}$ (log $\varepsilon$)=268 nm (4.55);. IR: $\tilde{\nu}$=3319, 3108, 3075, 1669, 1645, 1524, 1342 cm$^{-1}$.

**4-(4-Aminobenzamido)benzoic acid (3)**: Compound **2** (15 g, 0.052 mol) was suspended in DMF (50 mL). Methanol (400 mL) and ammonium formate (33 g, 0.523 mol) were added while stirring and cooling with an ice bath. Under an N$_2$ atmosphere Pd/C (10%, 1 g) was added, and the resulting suspension was allowed to warm to room temperature and stirred for 12 h. It was passed through Celite (Aldrich) and the solvent was evaporated to near dryness. The residue was neutralized with HCl (conc.), resulting in a white precipitate, which was recovered by filtration. Further product could be obtained from the filtrate by addition of water. This precipitate was combined with the first, stirred in water, recovered by filtration, washed neutral with water and dried under vacuum to give **3** (11.8 g, 89%). M.p. >300°C; MS (FD): *m/z* calcd for $C_{14}H_{12}N_2O_3$: 256.1; found: 256.2 (100) $[M]^+$; $^1$H NMR ([D$_6$]DMSO): $\delta$=6.66 (d, $J$= 8.8 Hz, 2H), 7.76 (d, $J$=8.8 Hz, 2H), 7.90 (s, 4H), 10.08 ppm (s, 1H); $^{13}$C NMR and DEPT ([D$_6$]DMSO): $\delta$=112.7(+), 119.2 (+), 120.7, 124.8, 129.7 (+), 130.3 (+), 144.1, 152.6, 165.7, 167.2 ppm; UV/Vis (DMAc + 1% LiCl): $\lambda_{max}$ (log $\varepsilon$)=317 nm (4.76); IR: $\tilde{\nu}$=3384, 3350, 3275, 1683, 1653, 1604 cm$^{-1}$.

**Compound 4**: Compound **2** (120 g, 0.42 mol) was refluxed in thionyl chloride (600 mL). After 3 h complete dissolution of **2** was achieved, after 8 h a turbid suspension was obtained. The thionyl chloride was distilled off, and the residue was extracted with dry boiling toluene, which was filtered, giving a clear yellow filtrate and a white solid residue. The white solid was refluxed in thionyl chloride (600 mL) for 8 h and treated the same way as described above. The combined filtrates were cooled to room temperature, then to −20°C. A yellow solid crystallized out, which was recovered by filtration, washed with petroleum ether and dried under vacuum to give **4** (87.8 g, 65%). From the filtrate more yellow crystals were obtained by addition of petroleum ether and cooling to −20°C. M.p. 157°C; elemental analysis calcd (%) for $C_{14}H_8Cl_2N_2O_3$: C 52.18, H 2.50, N 8.67; found: C 51.81, H 2.62, N 8.76; MS (FD): *m/z* (%) calcd: 322.0 (100). 324.0 (63.9). 326.0 (10.2); found: 322.5 (100), 324.5 (65.7), 326.4 (10.3); $^1$H NMR (CDCl$_3$): $\delta$=7.08 (d, $J$=8.8 Hz, 2H), 8.19 (d, $J$=8.8 Hz, 2H), 8.33 (s, 4H); $^{13}$C NMR and DEPT: $\delta$=120.4 (+), 123.7 (+), 130.2, 130.5 (+), 132.9 (+), 139.9, 143.7, 150.2, 153.1, 167.5 ppm; UV/Vis (CHCl$_3$): $\lambda_{max}$ (log $\varepsilon$)=280 nm (4.51); IR: $\tilde{\nu}$=3109, 3065, 3043, 1741, 1662, 1518, 1343 cm$^{-1}$.

**Compound 5**: Compound **1** (21.2 g, 0.155 mol) and *N,N*-dimethylaniline (25 mL) were dissolved in dry acetone (140 mL). A solution of **4** (50 g, 0.155 mol) in of acetone (330 mL) was added dropwise to this solution under stirring and cooling in an ice bath. The reaction mixture was allowed to warm to room temperature and was stirred for a further 30 min. Water (20 mL) was added to the resulting yellow suspension and the reaction mixture was stirred for 30 min. The yellow precipitate was collected by filtration, washed with hydrochloric acid (2 N, 300 mL), then washed neutral with water and dried under vacuum. The resulting solid was recrystallized from DMF to give **5** (58.3 g, 93%). M.p. >300°C; elemental analysis calcd (%) for $C_{21}H_{15}N_3O_6$: C 62.21, H 3.73, N 10.37; found: C 61.59, H 3.58, N 10.42; MS (FD): *m/z* calcd: 405.1; found: 405.4 (100) $[M]^+$; $^1$H NMR ([D$_6$]DMSO): $\delta$=7.92–8.03 (m, 8H), 8.20 (d, $J$= 8.8 Hz, 2H), 8.38 (d, $J$=8.8 Hz, 2H), 10.46 (s, 1H), 10.83 (s, 1H), 12.73 ppm (br s, <1H); $^{13}$C NMR and DEPT: $\delta$ 119.6 (+), 119.8 (+), 123.7 (+), 125.5, 128.9 (+), 129.5 (+), 129.9, 130.3 (+), 140.4, 142.1, 143.5, 149.4, 164.4, 165.4, 167.1 ppm; UV/Vis (DMAc + 1% LiCl): $\lambda_{max}$ (log $\varepsilon$)=294 nm (4.31); IR: $\tilde{\nu}$=3337, 3112, 3070, 1725, 1654, 1347 cm$^{-1}$.

**Compound 6**: Compound **5** (56.8 g, 0.14 mol) was refluxed in thionyl chloride (400 mL) for 90 min. Total dissolution of **5** was achieved after 30 min. The $SOCl_2$ was distilled off and petroleum ether was added to give a yellow precipitate, which was collected by filtration and recrystallized from dry toluene to give **6** (22.7 g, 35%). From the filtrate of the recrystallization further product was obtained by addition of petroleum ether. M.p. 169°C; elemental analysis calcd (%) for $C_{21}H_{12}N_3Cl_3O_3$: C 54.90, H 2.63, N 9.15; found: C 54.71, H 2.77, N 9.09; MS (FD): *m/z* (%) calcd: 459.0 (100.0), 461.0 (95.8), 463.0 (30.6); found: 459.4 (100.0) $[M]^+$, 461.4 (91.1), 463.4 (35.1); $^1$H NMR (CDCl$_3$): $\delta$=7.06 (d, $J$=8.8 Hz, 2H), 7.12 (d, $J$=8.8 Hz, 2H), 8.17 (d, $J$=8.8 Hz, 2H), 8.25 (d, $J$=8.8 Hz, 2H), 8.34 ppm (s, 4 Hz); $^{13}$C NMR and DEPT (CDCl$_3$): $\delta$=120.3 (+), 120.7 (+), 123.7 (+), 129.6, 130.5 (+), 130.7 (+), 131.9, 132.8 (+), 140.2, 143.0, 144.8, 150.1, 150.8, 154.0, 167.6 ppm; UV/Vis (CHCl$_3$): $\lambda_{max}$ (log $\varepsilon$)= 292 nm (4.31); IR: $\tilde{\nu}$=3109, 3083, 1764, 1641, 1517, 1344 cm$^{-1}$.

**Compound 7**: Compound **3** (6 g, 23.4 mmol) and *N,N*-dimethylaniline (6 mL) were dissolved in a mixture of dry acetone (15 mL) and dry *N*-methylpyrrolidinone (20 mL). A solution of **2** (7.55 g, 23.4 mmol) in dry acetone (25 mL) was added dropwise to this solution under stirring at room temperature. After one hour water (15 mL) was added, and the reaction mixture was stirred for about 6 h. The resulting solid was collected by filtration, stirred with HCl (1 M), washed neutral with water, and filtered, and the filtrate evaporated to dryness under vacuum. Recrystallization from DMF or a DMF/NMP mixture was not possible, but by stirring in refluxing DMF for several hours colored impurities dissolved, while the product remained insoluble. After cooling, the solid was filtered, washed with water and acetone, and was dried under vacuum to give **7** (11.76 g, 96%). M.p. >300°C; MS (FD)*m/z* calcd for $C_{28}H_{20}N_4O_7$: 524.1; found: 524.5 (100) $[M]^+$; $^1$H NMR ([D$_6$]DMSO): $\delta$=7.92–8.05 (m, 12H), 8.20 (d, $J$=8.8 Hz, 2H), 8.38 (d, $J$=8.8 Hz, 2H), 10.43 (s, 1H), 10.46 (s, 1H), 10.83 (s, 1H), 12.72 ppm (br s, <1H); $^{13}$C NMR and DEPT ([D$_6$]DMSO, $T$=130°C, 100 MHz): $\delta$=120.05 (+), 120.11 (+), 120.42 (+), 123.56 (+), 126.26, 128.65 (+), 128.72 (+), 129.43 (+), 129.96, 130.22 (+), 130.66, 140.83, 142.14, 142.83, 143.66, 150.03, 164.51, 165.50, 165.61,

167.01 ppm. UV/Vis (DMAc + 1% LiCl): $\lambda_{max}$ (log $\varepsilon$) = 316 nm (4.19); IR: $\tilde{\nu}$ = 3339, 3103, 3064, 1653, 1349 $cm^{-1}$.

**Compound 8**: Compound **7** (11.76 g, 22.4 mmol) was dissolved in $SOCl_2$ (150 mL) and refluxed for 12 h. After that almost all solid was dissolved, the $SOCl_2$ was distilled off and the residue extracted with boiling dry toluene and passed through a paper filter. Cooling of the filtrate to −20°C gave orange crystals, which were collected by filtration, washed with petroleum ether and dried under vacuum to give **8** (5.3 g, 40%). M.p. >250°C (decomp); elemental analysis calcd (%) for $C_{28}H_{16}N_4O_3Cl_4$: C 56.38, H 2.70, N 9.40; found: C 57.24, H 2.84, N 9.31; MS (FD): *m/z* (%) calcd: 596.0 (78.3), 598.0 (100), 600.0 (47.9), 602.0 (10.2); found: 596.6 (71.5) $[M]^+$, 598.6 (100), 600.6 (49.5), 602.6 (8.3); $^1$H NMR ($CDCl_3$): $\delta$ = 7.04–7.14 (m, 6H), 8.15–8.28 (m, 6H), 8.34 ppm (s, 4H); $^{13}$C NMR and DEPT ($CDCl_3$): 120.3(+), 120.6 (+), 120.8 (+), 123.7 (+), 129.5, 103.5 (+), 130.7 (+), 131.1, 132.1, 132.9 (+), 140.2, 142.9, 144.2, 145.0, 150.1, 150.6, 151.7, 154.1, 167.6 ppm; UV/Vis ($CHCl_3$): $\lambda_{max}$ (log $\varepsilon$) = 297 nm (4.11); IR: $\tilde{\nu}$ = 3095, 1767, 1641, 1524, 1349 $cm^{-1}$.

**Compound 9**: Poly(ethylene glycol) monomethyl ether ($M_W$ = 5000, 150 g, 30 mmol) and pyridine (15 mL) were dissolved in dichloromethane (600 mL). *p*-Nitrobenzoyl chloride (28 g, 151 mmol) was added, and the resulting mixture was refluxed for two days and then stirred for one day at room temperature under exclusion of water. Upon evaporation of most of the solvent needles crystallized, which were separated by filtration. The filtrate was added dropwise into 2 L of diethyl ether and cooled to −20°C, but hardly any precipitation was observed. After most of the solvent was removed by distillation, a second precipitation into diethyl ether yielded a white solid, which was collected by filtration, washed with diethyl ether and dried under vacuum to give **9** (138.6 g, 92%). $^1$H NMR ([D$_6$]DMSO): $\delta$ = 8.18 (d, *J* = 8.8 Hz), 8.36 ppm (d, *J* = 8.8 Hz).

**Compound 10**: Compound **9** (138.6 g, 27.7 mmol) was dissolved in a mixture of methanol (1.2 L) and dichloromethane (50 mL). Ammonium formate (170 g, 2.70 mol) and Pd/C (10%, 5.5 g) were added under an $N_2$ atmosphere. After evolution of gas had started, the mixture was allowed to stir at room temperature for 12 h. After filtration through Celite (Aldrich) the filtrate was evaporated completely, and the residue extracted three times with $CHCl_3$. The combined organic extracts were washed with water, dried over $MgSO_4$ over night, and concentrated by evaporation. By precipitation into the tenfold amount of diethyl ether, a white solid was obtained, which was removed by filtration, washed with diethyl ether, and dried under vacuum to give **10** (119.5 g, 86%). $^1$H NMR ([D$_6$]DMSO): $\delta$ = 5.94 (s), 6.55 (d, *J* = 8.8 Hz), 7.62 ppm (d, *J* = 8.8 Hz).

**General procedure for the synthesis of compounds 11, 12, and 15**: Five equivalents of the corresponding acid chloride were dissolved in dry methylene chloride. A solution of one equivalent of **10** and five equivalents of *N,N*-dimethylaniline in methylene chloride was then added dropwise under stirring, cooling with an ice bath, and exclusion of water. The reaction mixture was allowed to warm to room temperature and was stirred for at least 30 min. Then the mixture was concentrated by evaporation of solvent and precipitated into dry diethyl ether. The solid obtained was collected and redissolved in a homogenous mixture of chloroform, acetone, and water. Excess acid chloride was hydrolyzed by stirring for at least 2 h. Afterwards the organic solvents were evaporated, the water was removed by azeotropic distillation with toluene, and the residue was stirred with chloroform until a solution of finely dispersed free acid was obtained. The unreacted acid was removed by filtration, the filtrate was washed with HCl (1 M), aqueous $NaHCO_3$ (conc), and then with water (when necessary for phase separation, with aqueous NaCl (conc)), and dried with sodium sulfate. After filtration of the drying agent, the clear solution was concentrated by evaporation of the solvent under vacuum and added dropwise into diethyl ether. The resulting precipitate was collected by filtration and dried under vacuum.

**Compound 11**: Reaction of **10** (30 g) gave **11** (21.5 g,72%). $^1$H NMR ([D$_6$]DMSO): $\delta$ = 7.96–8.06 (m), 8.22 (d, *J* = 8.8 Hz), 8.40 (d, *J* = 8.8 Hz), 10.46 (br s), 10.83 ppm (s).

**Compound 12**: Reaction of compound **10** (1 g) gave **12** (710 mg, 71%). Alternatively, **12** (0.92 g) could be obtained from the reaction of **11** (1.5 g) with 4-nitrobenzoyl chloride. $^1$H NMR ([D$_6$]DMSO): $\delta$ = 7.95–8.10 (m), 8.21 (d, *J* = 8.5 Hz), 8.39 (d, *J* = 8.5 Hz), 10.43 (s), 10.47 (br s), 10.84 ppm (s).

**Compound 13**: Compound **11** (14.25 g) was dissolved in methanol and some additional $CH_2Cl_2$ and a large excess of ammonium formate (15 g) and Pd/C (10%, 1 g) were added, the latter under an $N_2$ atmosphere. After stirring for 12 h at room temperature, the reaction mixture was filtered through Celite (Aldrich), and the filtrate was evaporated to dryness. The residue was stirred with chloroform, sonicated, and filtered through Celite (Aldrich). The filtrate was washed with NaCl solution (conc) and then with water, dried over $Na_2SO_4$, and concentrated under vacuum. Upon precipitation into diethyl ether **13** was obtained as a white solid, which was collected by filtration and dried under vacuum (11.3 g, 79%). $^1$H NMR ([D$_6$]DMSO): $\delta$ = 6.62 (d, *J* = 8.8 Hz), 7.75 (d, *J* = 8.8 Hz), 7.95–8.05 (m), 10.04 (s), 10.39 (s), 10.46 ppm (s).

**Compound 14**: Compound **12** (1.5 g) could not be reduced successfully by using the methods described for **10** or **13** giving a mixture of amino and nitro compound (460 mg). The reduction was completed by using the following procedure:

The mixture was dissolved in methanol and DMF. Ammonium formate (3 g) and Pd/C (10%, 300 mg) were added (the latter under an $N_2$ atmosphere), and the resulting mixture was refluxed for 12 h. After cooling to room temperature, it was filtered through Celite (Aldrich), methanol was distilled off, and the remaining DMF solution was precipitated into the tenfold amount of diethyl ether. After filtration, the collected solid was dissolved in chloroform and treated according to the procedure described for **13**, resulting in **14** (330 mg, 22%). $^1$H NMR ([D$_6$]DMSO): $\delta$ = 5.82 (br s), 6.60 (d, *J* = 8.8 Hz), 7.72 (d, *J* = 8.8 Hz), 7.90–8.05 (m), 10.04 (s), 10.40 (s), 10.43 (s), 10.46 ppm (s).

**Compound 15**: Compound **13** (4 g) and **6** (1.84 g) gave **15** (3.5 g, 88%) after additional precipitation from a DMF solution into diethyl ether. $^1$H NMR ([D$_6$]DMSO): $\delta$ = 7.92–8.06 (m), 8.21 (d, *J* = 8.8 Hz), 8.40 (d, *J* = 8.8 Hz), 10.45 (m), 10.86 ppm (s).

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[8] Crystal data for **6**: $C_{21}H_{12}N_3O_3Cl_3$; $M_r$ = 460.7; 0.05 × 0.1 × 0.7 mm; yellow; triclinic; space group $P\bar{1}$, $Z$ = 2; $a$ = 8.023(3), $b$ = 9.192(3), $c$ = 14.442(6) Å, $\alpha$ = 86.94(3), $\beta$ = 78.94(3), $\gamma$ = 70.14(3)°; $V$ = 983.0(6) Å$^3$; $\rho_{calcd}$ = 1.556 g cm$^{-3}$; $Cu_{K\alpha}$ radiation ($\lambda$ = 1.54056 Å); $2\theta_{max}$ = 146.4°; $\omega/2\theta$ scans on a Turbo-CAD4; $T$ = 150 K; 4200 reflections measured (all 3940 unique used); $-9 \le h \le 9$, $0 \le k \le 11$, $-17 \le l \le 17$; Lorentz factor and absorption correction with $\psi$ scans ($\mu$ = 4.49 mm$^{-1}$) applied; structure solved with direct methods and refined with full-matrix least-squares on $F^2$ with SHELXL 97;[23] 3940 data and 283 parameters; $R$[3067 reflections $>2\sigma(I)$/all data] = 0.0712/0.0896; $wR2$(all data) = 0.2053; $S$ = 1.034; hydrogen atoms were riding; greatest final electron density difference excursions of +0.48, −0.90 e Å$^{-3}$.[24]

  

[9] Crystal data for **8**: $C_{28}H_{16}N_4O_3Cl_4$; $M_r = 598.2$; $0.06 \times 0.16 \times 0.48$ mm; yellow; triclinic; space group $P\bar{1}$, $Z = 2$; $a = 8.295(2)$, $b = 8.9524(10)$, $c = 18.884(6)$ Å, $\alpha = 80.61(2)$, $\beta = 82.90(2)$, $\gamma = 68.53(1)°$; $V = 1284.4(5)$ Å$^3$; $\rho_{calcd} = 1.547$ g cm$^{-3}$; $Cu_{K\alpha}$ radiation ($\lambda = 1.54056$ Å); $2\theta_{max} = 146.8°$; $\omega/2\theta$ scans on a Turbo-CAD4; $T = 150$ K; 5528 reflections measured (all 5149 unique used); $-10 \le h \le 0$, $-11 \le k \le 10$, $-23 \le l \le 23$; Lorentz factor and absorption correction with $\psi$ scans ($\mu = 4.53$ mm$^{-1}$) applied; structure solved with direct methods and refined with full-matrix least-squares on $F^2$ with SHELXL 97;[23] 5149 data and 352 parameters; $R$[4173 reflections $> 2\sigma(I)$/all data] = 0.1389/0.1576; $wR2$ (all data) = 0.4264; $S = 1.058$; hydrogen atoms were riding; greatest final electron density difference excursions of 1.02, −0.76 e Å$^{-3}$.[24]

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[24] CCDC-248092 (**6**) and −248093 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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