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Novel Carboxylated Pyrrole- and Carbazole-Based Monomers. Synthesis and Electro-Oxidation Features

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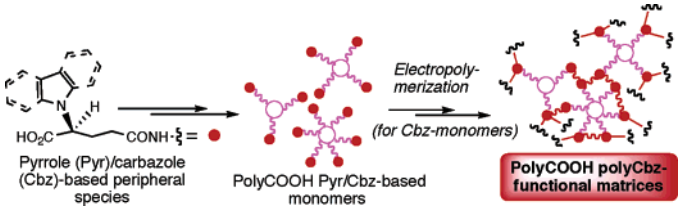

Carboxylated pyrrole (Pyr, **a** index)- and carbazole (Cbz, **b** index)-containing monomers **6**−**7a/b** and **9a/b** have been readily synthesized from the monobenzyl ester of *L*-glutamic acid and triamine **2** using Clauson−Kaas and amide coupling reactions. In contrast to Pyr-containing compounds **6**−**7a**, and **9a**, the three Cbz-containing monomers **6**−**7b**, and **9b** have been found electroactive and were successfully electropolymerized on a Pt electrode resulting in the deposition of corresponding insoluble electroconducting polyCOOH polyCbz-films poly(**6**−**7b**) and poly(**9b**).

Conducting polymer-coated micrometer-sized electrodes found multiple uses as effective biosensing transducers of variable sizes and shapes. One challenging step toward highly performant electrochemical devices remains the covalent/noncovalent mode of attachment of biomolecules (proteins, antibodies, DNA sequences, oligosaccharides) onto conductive substrates. Recently, we have reported the successful electrogeneration of amine-sensitive (polypentafluorophenyl ester) electrochemically stable chiral poly(dicarbazole) conductive films on Au microelectrodes.[1] Resulting ester-activated modified electrodes allowed the nondenaturing covalent attachment of both glucose and polyphenol oxidases toward corresponding biosensor constructs.[2] Lately, dendrimeric structures that have preorganized peripheral functionalities and size-determined internal cavities enabled the successful development of numerous important applications:[3] degradable dendrimeric prodrugs in drug delivery,[4] light-emitting diodes,[5] and redox active systems.[6]

In this context, attachment of electroactive heterocyclic species, such as pyrrole (Pyr), thiophene, carbazole (Cbz) units, at the periphery of multivalent dendrimeric and nondendrimeric organic cores is a potentially powerful approach toward new taylored potential/current-sensitive conducting films. Such films will build on the oxidative generation of periphery-localized and multivalently accessible cation radicals enabling polymer growth in a polydirectional manner. Very few examples of conducting polymeric systems generated in such a way have been reported so far.[7,8] All of them were *nonfunctional* since postpolymerization covalent grafting of biological probes was impossible because of the lack of chemical functionalization. For example, Majoral-Roncali and co-workers fabricated electroconductive poly(bithiophene) films from phosphorus-containing dendritic cores decorated by peripheral nonfunctional 2,2′-bithiophene units.[7] Electroactive composite matrices possessing a strong affinity for Pt^{2+} ions have been also synthesized from the electrocopolymerization of nonfunctional thiophene-linked poly(amido-amine) (PAMAM) dendrimers and 3-Me-thiophene.[8] Other structurally resembling nonfunctional thiophene- and Pyr-

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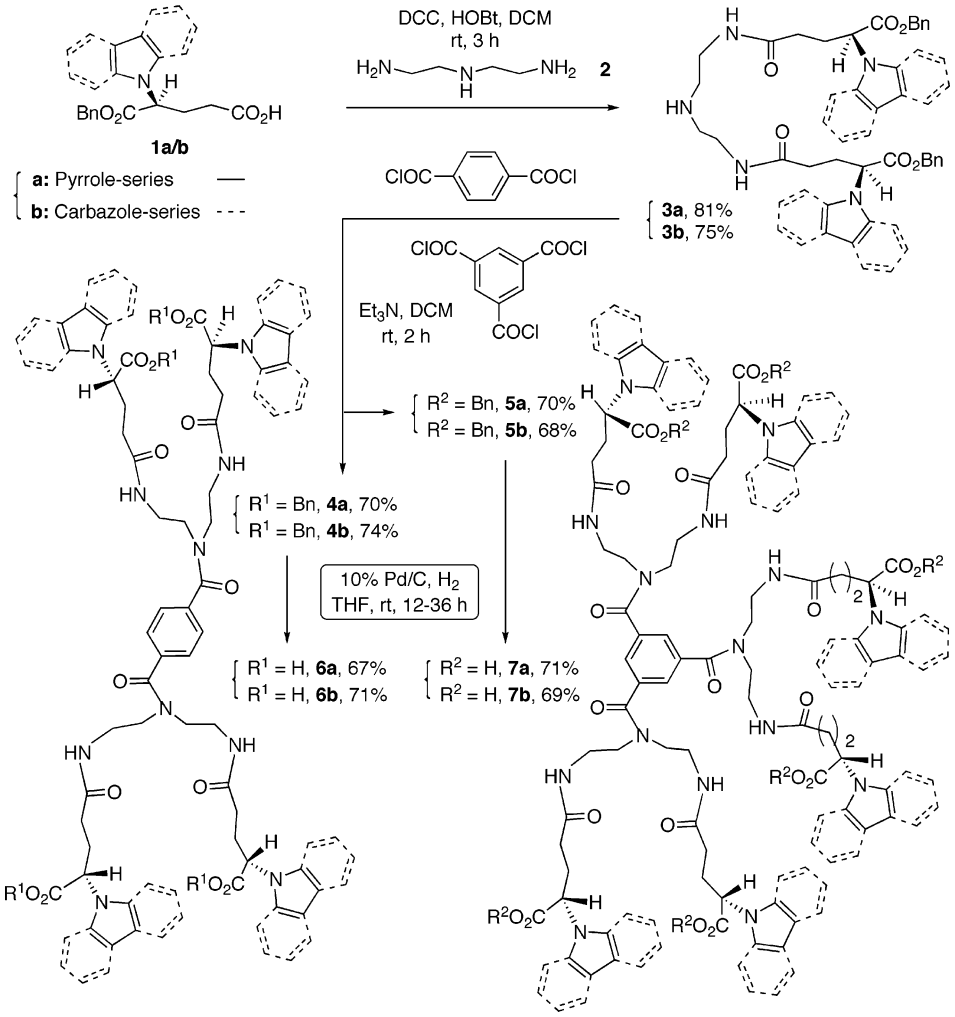
SCHEME 1. Synthesis of C2-/C3-symmetrical Pyr- and Cbz-Based Carboxylated Compounds 6−7a/b



based dendrimeric systems have been disclosed, but their electrical/electro-oxidation properties were never described.[9] McCarley and co-workers reported the intramolecular oligomerization of nonfunctional Pyr-modified diaminobutane (DAB)-Pyr$_x$ (X = 4, 8, and 16) dendrimers that were monolayered on a Au electrode.[10,11] Only adsorbed DAB-Pyr$_{16}$ layers could be electrochemically oxidized causing intramolecular oligomerizations of peripheral Pyr units. Accordingly, the capability of these monomeric multivalent electro-oxidizable species to grow conducting polypyrrole-based films/matrices remained to be established.

Clearly, none of formerly described multivalent monomers present outer pending oxidizable functionalities enabling the postpolymerization covalent grafting of biomolecules onto corresponding polymer-coated electrodes.

Herein, we report our own studies relating to the straightforward electrosynthesis of novel *polycarboxylated* conducting polyCbz-films from one unique *carboxylated* Cbz-containing building block as new electro-oxidizable peripheral species. In fact, six novel polycarboxylated homochiral monomers **6**−**7a/b**, and **9a/b** (**a** and **b** indexes: Pyr- & Cbz-based series respectively, Schemes 1 and 2) were readily synthesized from both Pyr- and Cbz-derivatives of *L*-glutamic acid (*S*)-**1a/b**. For the first time, polyCOOH *functional and stable* electroconductive polyCbz-films poly(**6**−**7b**) and poly(**9b**) have been produced by electropolymerization of corresponding carboxylated Cbz-monomers on a Pt electrode. Therefore and in agreement with former results,[1,2] the postpolymerization covalent grafting of biomolecules onto these fabricated conducting surfaces (COOH-related activation chemistry) should allow the development of numerous applications in the biosensing field for example.

Polyfunctional compounds **6**−**7a/b** presented four and six electro-oxidizable decorating peripheral Pyr-/Cbz-units and COOH groups. They included tunable acidic aromatic core linkers modified by C2-/C3-symmetrization amidations (dicyclohexylcarbodiimide (DCC)/1-hydroxybenzotriazole (HOBt)-mediated and amine-acid chloride coupling key reactions, convergent approach). On the other hand, compounds **9a/b** were produced by DCC/HOBt-mediated triamidations of triamine **2** using Pyr-/Cbz-containing compounds **1a/b**. They disclosed three Pyr-/Cbz-units and COOH groups.

These modular synthetic approaches were found economical in steps (3−4 steps maximum) mainly because of the use of synthetically advanced chiral C2-symmetrical (*S*,*S*)-bis-Pyr-/

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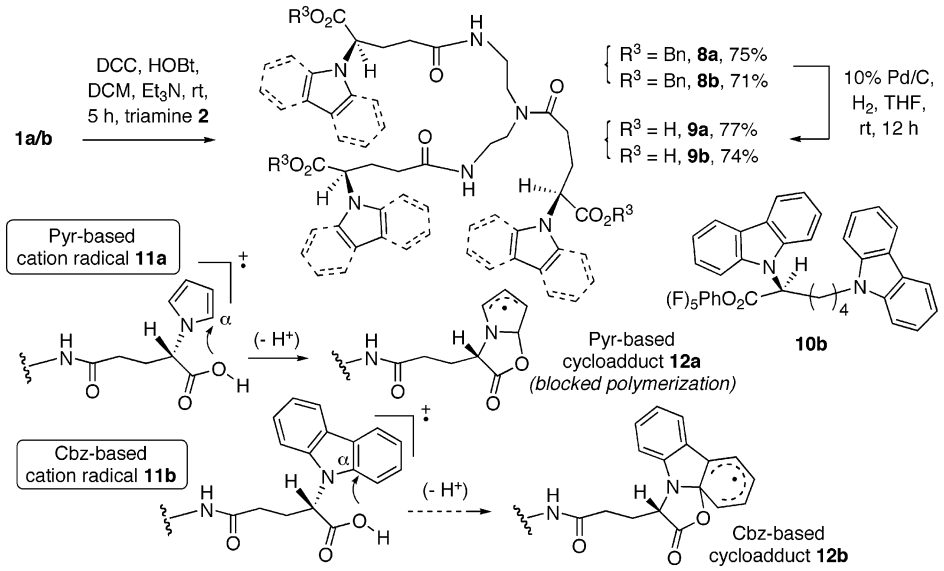
SCHEME 2. Pyr/Cbz-Based Monomers 9a/b (One-Step Triamidation of Triamine 2) and 10b. Cation Radicals 11a/b Toward Related Cycloadducts 12a/b



Cbz-building blocks **3a/b**. Clearly, this chemical design should allow a great chemical maneuverability at the core level for future monomer developments.

Starting Pyr-/Cbz-based building blocks **1a/b** have been readily prepared from benzylated H-Glu-*Z* (ee ≥ 99%) using a modified Clauson−Kaas method[12] (2,5-dimethoxytetrahydrofuran (DMT), NaOAc, AcOH, H_2O, 76 °C, 2 h, 50% yield for **1a** and DMT, dioxane, reflux, 3 h and room temperature, overnight, 30% yield for **1b**). DCC/HOBt-mediated activation of acids **1a/b** (CH_2Cl_2 (DCM), 20 °C, 3 h, Scheme 1) was followed by primary NH_2 selective condensation with triamine **2** affording corresponding benzylated bisamides **3a/b** in good yields (81 and 75%, respectively). Traces of triamide benzyl (Bn) esters **8a/b** (Scheme 2, < 5%, TLC) formed were readily eliminated during purification (flash chromatography on silica gel, 5% MeOH in DCM). Importantly, amidations did racemize neither the enantiomerically pure building blocks **1a/b** nor resulting bisamides **3a/b** as evidenced by the formation of single diastereomerically pure C_2-symmetrical amidation products (^{13}C NMR analysis of crude products, absence of meso-diastereomers).

Surprisingly, amidation yields were significantly lower (∼40%) when the water-soluble carbodiimide *N*′-(3-dimethylamino-propyl)-*N*-ethylcarbodiimide hydrochloride (EDC) was used in place of DCC although both crude workup and purification of bisamide products were easier. Carbonyl diimidazole-based coupling amidations, that were reported to be efficient and highly selective with triamine linker **2**,[13] were also inefficient under various conditions (reagent concentrations, solvents, temperatures) leading to monoamide condensation products in a 70−80% yield range (TLC).

The presence of the free internal NH group in benzylated bisamide building blocks **3a/b** allowed a further clean condensation with both di- and trifunctional acid chlorides of 1,4-di- and 1,3,5-benzene tricarboxylic acids. These amidations provided key C2-/C3-symmetrical benzyl esters **4a/b** and **5a/b**, respectively, in good yields (DCM, anhydrous Et_3N, 20 °C, 2 h; **4a/b**, 70/74% and **5a/b**, 70/68%). Monomers **4a/b** and **5a/b** presented four and six heterocyclic Pyr-/Cbz-units/Bn ester functions, respectively. On the other hand, less complex intermediates **8a/b** possessing three Pyr-/Cbz-units and Bn ester functions were prepared in one step from blocks **1a/b** and triamine **2** (Scheme 2).

Addition of anhydrous triethylamine was found necessary in key step DCC/HOBt-promoted triamidations in order to proceed beyond previously noticed 1,ω-diamidations (DCM, DCC/HOBt, anhydrous Et_3N, 20 °C, 5 h; **8a/b**, 75/71%). Resulting Pyr-/Cbz-based benzylated intermediates were thoroughly characterized using high-field ^1H-/^{13}C NMR and low-/high-resolution mass spectrometry analyses (Supporting Information).

The Bn group deprotection posed a challenge in some of the above-prepared multifunctional monomers. First trials involved transfer hydrogenation using 10% Pd/C-cyclohexene at reflux in *i*-PrOH for 2 h. Previous studies from the same laboratory indicated that this system was fully satisfactory in order to cleanly deprotect simpler C_2-symmetrical bis-carbazole bis-Bn ester monomers (30−60 min, > 95% yield). But these more complex sterically hindered polyfunctional monomers **4**−**5a/b** and **8a/b** could not undergo complete debenzylation toward corresponding polycarboxylated monomers **6**−**7a/b** and **9a/b** even after overnight reaction at reflux. ^1H NMR spectra (300 MHz, DMSO-d_6) and FAB-MS spectrometry analyses performed on partially purified reaction crudes (filtration on a silica gel column, DCM/MeOH mixtures) showed the presence of variable amounts of partially debenzylated compounds. The lone exception being the tetra-Pyr-containing compound **4a** (Bn ester) that, according to the above cleavage conditions, gave the desired tetra-Pyr tetra-acid **6a** in a good 65% yield. Alternatively, hydroxyapatite-bound Pd catalyst, reported as an efficient debenzylating agent[14] for dendrimeric polybenzylated substrates also completely failed to react. After a large screening work (various catalysts, solvent, and temperature conditions), polybenzylated Pyr-/Cbz-containing intermediate compounds **4**−**5a/b** and **8a/b** were cleanly cleaved under milder room-temperature

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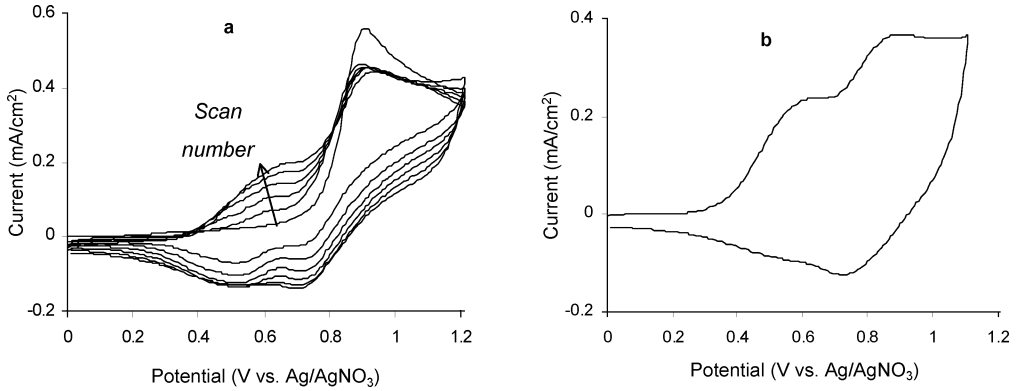

FIGURE 1. (a) Cyclic voltammograms for the electropolymerization of carboxylated hexaCbz-based monomer **7b** (5 mm ∅ Pt disk electrode); (b) voltammetric response of resulting conducting polyCbz-film poly(**7b**) in supporting electrolyte only (without monomer).

conditions in nonalcoholic THF solvent using H_2 gas affording corresponding white foamy polyCOOH monomers **6**−**7a/b** and **9a/b** (10% Pd/C, 20 °C, H_2, 12 and 36 h for Pyr- and Cbz-based monomers, respectively; **6a/6b**, 67/71%; **7a/b**, 71/69%; **9a/b**, 77/74%).

Polycarboxylated acids were unambiguously characterized by a combination of $^1H/^{13}C$ NMR (300 and 75 MHz, DMSO-d_6, disappearance of signals at δ ∼5.10 and ∼67.0 ppm, respectively, corresponding to CH_2-groups of Bn esters) and mass spectrometry analyses (presence of single molecular ion peaks). Traces of entrapped solvents were always detected by ^1H NMR although these compounds were dried under high vacuum (10^{-2} Torr, 2 days). Most likely, this resulted from their foamy nature as well as from their limited solubility in current organic solvents except DMSO. Both benzylated and free acidic intermediates/monomers showed ^1H− and ^{13}C NMR (300 and 75 MHz, $CDCl_3$, and/or DMSO-d_6) C/H-related peak broadening and magnetic asymmetry even for structurally symmetrical two-arm wedge-substituents arising from **3a/b**-related units. This may be attributed to the presence of equilibrated secondary/tertiary amide rotamers at the time scale of NMR analysis.

Electro-oxidation features of monomers **6**−**7a/b**, and **9a/b** were investigated by cyclic voltammetry (100 mV/sec) onto a 5 mm diameter Pt disk working electrode using a three-electrode cell (Pt ribbon counter-electrode, $Ag/AgNO_3$ reference electrode) operated between zero and 1.2 V (for Cbz-monomers) and −0.5 and 1.2 V (for Pyr-monomers). The background electrolyte consisted of 0.2 M *n*-Bu_4NClO_4 and 0.2 M $LiClO_4$ in a $^1/_2$ v/v ethylenecarbonate−dimethylcarbonate solution in which monomer concentrations were adjusted to 1.0 mM.

All Cbz-based acidic monomers **6**−**7b**, and **9b** were found to readily electropolymerize onto the Pt disk-working electrode toward corresponding conducting films. Following the polymerization process, the typical electrochemical behavior of so-produced polyCbz-polymers was also measured in the supporting (monomer-free) electrolyte at the same voltage range and sweep rate.

An illustrative cyclic voltammogram of the electropolymerization process of the densely functionalized polyCOOH Cbz-based monomer **7b** and its typical electrochemical behavior have been reported in Figure 1. Voltammogram analysis was based on former conclusions relating to the electropolymerization of typical 2,6-bis-carbazole-9-yl-hexanoic acid (pentafluorophenyl ester) monomer **10b** (Scheme 2) and characterization of corresponding polydicarbazole-type polymer.[15] The two reversible peaks that appeared around 0.6 and 0.85 V in the anodic scan correspond to, respectively, polymer charging (doping) and monomer oxidation to produce polyCbz polymers. During electropolymerization, peak currents around 0.6 V increased by a 20−30% factor for each scan reflecting a polymer growth—increase of the effective polymer surface area—while, excluding the first scan, peaks around 0.85 V almost did not change. In the typical behavior measurement (Figure 1b, monomer-free electrolyte), the cyclic voltammogram profile disclosed anodic peaks which appeared at the same potentials (0.6 and 0.85 V). The observed peak located around 0.85 V resulted from the oxidation of free discrete Cbz units that were not part of the polymeric network (dangling Cbz heterocycles) as demonstrated previously.[15] Accordingly, the ratio $i_{0.85V}/i_{0.6V}$ between higher and lower potential anodic peaks was closer to unit in this case rather than in polymerization voltammograms (Figure 1a). Indeed, in polymerization voltamogramms, peaks around 0.85 V indicated the oxidation of both electrolyte-contained and polymer-linked Cbz heterocycles. Similar electrochemistry-related considerations were already explained in detail for the electro-oxidation (polymerization) of the typical Cbz-based pentafluorophenyl ester **10b**.[15] Both polymerizations and characteristic electrochemical behaviors of the other two Cbz-based monomers **6b/9b** and polyCbz-matrices poly(**6b**)/poly(**9b**) much resembled the results disclosed in Figure 1.

Quite interestingly, Pyr-containing acidic monomers **6**−**7a** and **9a** neither polymerized nor oligomerized in these conditions. The formation of reversible redox peak systems, which characterized the deposition of insoluble conductive poly(*N*-alkyl Pyr)-based polymeric networks[16] via corresponding cation radicals, was never observed whatever electrochemical conditions investigated. This unexpected behavior may be tentatively explained by comparing steric and electrophilicity factors which characterize Pyr/Cbz-containing cation radicals **11a/b** generated at the initiation polymerization step (Scheme 2). Pyr-containing cation radicals **11a** may be readily trapped intramolecularly by close nucleophilic acidic hydroxyl groups toward Pyr-based cycloadducts **12a** (five-membered ring-mediated cyclo-alkoxylation onto the electrophilic nonhindered C_α position). Cycloadducts **12a** may then undergo classical radical dimerization and/or oxidation (re-aromatization) resulting in polymerization blocking.[17] In contrast, Cbz-containing cation radicals **11b** disclose a more hindered less electrophilic C_α position owing

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to the presence of additional phenyl rings (higher degree of C_α substitution and increased charge delocalization, respectively) in Cbz-units. Therefore, generation of corresponding Cbz-based cycloadducts **12b** is highly disfavored allowing polymer chain propagation from reactive peripherally localized cation radicals of type **11b**. This explanation is strongly supported by similar observations recently made during the unsuccessful electrooxidation of a range of *N*-(hydroxyalkyl) Pyr-based monomers owing to intramolecular HO-mediated cycloalkoxylations.[18]

In conclusion, we have simply designed and readily synthesized six novel functional polycarboxylated Pyr-/Cbz-based monomers that contained three, four, and six electro-oxidizable outer decorating Pyr-/Cbz-units and COOH groups. Additionally and for the first time, the three reported polycarboxylated Cbz-containing monomers **6**−**7b** and **9b** were successfully electropolymerized on a Pt electrode affording corresponding electroconductive polycarboxylated polyCbz-films poly(**6**−**7b**) and poly(**9b**), respectively. Our current efforts are now directed at the development of suitable applications of these functional (polyCOOH) electroactive chiral films[2c] for analyte sensing through the covalent attachment of a range of biological probes (DNA sequences, proteins/antibodies, oligosaccharides) onto them (COOH-related covalent grafting).

Experimental Section

A Typical DCC/HOBt-Mediated Amidation Protocol (Illustrated for Intermediate Compound 3a). 4-{2-[2-((*S*)-4-Benzyloxycarbonyl-4-pyrrol-1-yl-butyrylamino)-ethylamino]-ethylcarbamoyl}-(*S*)-2-pyrrol-1-yl-butyric Acid Benzyl Ester (3a). HOBt, (0.690 g, 5.1 mmol) was suspended in anhydrous DCM (10 mL) and added to a solution of (i) DCC (1.029 g, 5.3 mmol) and (ii) monobenzylated Pyr-acid **1a** (1.429 g, 4.98 mmol) in DCM (20 mL). The reaction mixture was stirred for 1 h at 20 °C. The precipitated dicyclohexylurea (DCU) was discarded by filtration (5 μm Büchner filter). Then, the triaminated linker **2** (0.256 g, 2.4 mmol) was dissolved in anhydrous DCM (5 mL) and then added dropwise to the resulting clear filtrate solution. The reaction mixture was gently agitated for a further 15 min and evaporated under vacuum. Purification of the crude compound has been performed on a silica gel column (40−60 mesh, eluent: 6/4 v/v DCM/MeOH mixture) in order to afford the chromatographically pure dibenzylated dipyrrole-amine **3a** (1.290 g, 81% yield) as a pale yellow mobile oil. FT-IR (neat, ν in cm^{-1}): 736 (s), 1094 (m), 1177 (s), 1269 (s), 1387 (w), 1448 (w), 1492 (w), 1547 (s), 1657 (s), 1739 (s), 2831 (w), 2890 (m), 2943−44 (m), 3065 (s), 3403 (m). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.82−1.84 (m, 2H), 2.20 (m, 2H), 3.00 (m, 2H), 3.39 (m, 2H), 4.50 (m, 1H), 5.03 (s, 2H), 6.03 (s, 2H), 6.54 (s, 2H), 7.16−7.26 (m, 3H), 7.26 (m, 3H), 7.46 (m, 1H), 7.56 (m, 1H), 7.91 (m, 2H), 8.94 (bs, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.8, 31.3, 36.5, 47.9, 60.8, 67.1, 108.7, 110.9, 118.2, 120.0, 124.7, 127.4, 127.9, 128.3, 128.45, 128.6, 135.1, 142.9, 170.1, 172.8. TOF-MS (ES, positive mode ionization): *m*/*z* 642 [MH^+, 100%], 534 (28%), 467 (12%), 136 (17%). FAB-HRMS (positive mode, *m*-nitrobenzyl alcohol matrix): *m*/*z* calcd for $C_{36}H_{43}N_5O_6$ [M], 641.3254; found, 641.3251 (5.0 mDa). $[\alpha]^{25}_D$ −4.1 (*c* 5.56, DCM).

A Typical Acylation Procedure Using Acid Chlorides. 4-{2-[[2-((*S*)-4-Benzyloxycarbonyl-4-pyrrol-1-yl-butyrylamino)-ethyl]-(4-{bis-[2-((*S*)-4-benzyloxycarbonyl-4-pyrrol-1-yl-butyrylamino)-ethyl]-carbamoyl}-benzoyl)-amino]-ethylcarbamoyl}-(*S*)-2-pyrrol-1-yl-butyric Acid Benzyl Ester (4a). Anhydrous triethylamine (1.010 g, 10.0 mmol) was added to a solution of intermediate dibenzylated dipyrrole-amine **3a** (2.600 g, 2.05 mmol) in anhydrous DCM (40 mL) followed by terephthaloyl chloride (0.406 g, 2.0 mmol, dry N_2, 20 °C) in one portion. The reaction mixture was allowed to stir until completion (∼1 h, TLC checking). Then, the reaction mixture was washed with distilled water (2 × 20 mL) and brine (1 × 20 mL), dried on dry Na_2SO_4, and filtered (5 μm Büchner filter). Following concentration of the filtrate under vacuum, the resulting crude condensation compound was purified by flash chromatography on a silica gel column (40−60 mesh) eluted by a 7/3 v/v DCM/MeOH mixture affording the pure compound **4a** (2.010 g, 70% yield) as a pale yellow viscous oil. FT-IR (KBr pellet, ν in cm^{-1}): 700 (m), 731 (s), 804 (s), 864 (w), 1024 (s), 1094 (s), 1175 (s), 1262 (s), 1379 (w), 1427 (m), 1545 (s), 1651 (s), 1741 (s), 2885 (w), 2967 (m), 3068 (w), 3299 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.87−2.30 (m, 16H), 3.10−3.19 (m, 8H), 3.42−3.59 (m, 8H), 3.56−3.65 (m, 4H), 4.62 (m, 2H), 4.73 (m, 2H), 5.11 (s, 8H), 6.14 (s, 8H), 6.50 (bs, 2H), 6.65−6.69 (s, 8H), 7.11 (bs, 2H), 7.12−7.33 (m, 26 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.3, 31.7, 37.9, 39.0, 45.9, 49.4, 60.9, 67.3, 109.0, 109.3, 120.3, 126.6, 128.1, 128.5, 128.7, 135.3, 137.1, 170.1, 170.3, 172.1, 172.5. FAB-MS (glycerol matrix, positive mode ionization): *m*/*z* 1414 [MD^+, 100%], 1145 (49%), 1132 (41%), 1038 (17%), 976 (12%). FAB-HRMS (glycerol matrix, positive mode ionization): *m*/*z* calcd for $C_{80}H_{88}N_{10}O_{14}$ [M], 1412.6481; found, 1412.6472 (3.0 mDa). $[\alpha]^{25}_D$ −16.4 (*c* 3.8, THF).

A Typical Debenzylation Procedure of Pyr-/Cbz-Containing Dendrimers. 4-(2-{(4-{Bis-[2-((*S*)-4-carbazol-9-yl-4-carboxy-butyrylamino)-ethyl]-carbamoyl}-benzoyl)-[2-((*S*)-4-carbazol-9-yl-4-carboxy-butyrylamino)-ethyl]-amino}-ethylcarbamoyl)-(*S*)-2-carbazol-9-yl-butyric Acid (6b). A suspension of 10% Pd/C (0.20 g), in THF (10 mL) containing tetracarbazole benzylester **4b** (1.00 g, 0.55 mmol) was stirred under a H_2 atmosphere for 48 h at room temperature. Removal of the Pd/C catalyst was effected by filtration through a celite bed (250 mg). Then, the filtrate was concentrated under vacuum, and the resulting crude product purified by flash chromatography on a silica gel column (40−60 mesh) eluted by a DCM/THF mixture (gradient from 80% v/v DCM/THF to 10% v/v DCM/THF). It afforded the chromatographically pure compound **6b** (0.57 g, 71%) as a pale yellow foamy solid (mp: 218−220 °C). FT-IR (neat, ν in cm^{-1}): 724 (m), 754 (s), 1079 (w), 1240 (s), 1333 (s), 1452 (s), 1483 (m), 1551 (m), 1628 (s), 1728 (s), 2943 (s), 3057 (s), 3398 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.39 (bs, 2H), 1.75 (m, 4H), 2.06 (bs, 2H), 2.34 (bs, 2H), 2.50 (bs, 4H), 2.66 (2H), 2.80 (bs, 4H), 2.90 (bs, 4H), 3.22 (bs, 4H), 3.32 (bs, 4H), 5.54 (bs, 2H), 5.69 (bs, 2H), 6.94 (bs, 4H), 7.21 (bs, 8H), 7.43−7.52 (m, 18H), 7.85 (bs, 2H), 8.16−8.33 (bs, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.2, 31.5, 36.4, 36.7, 44.3, 48.1, 55.7, 109.9, 119.1, 120.3, 122.6, 125.8, 126.1, 137.0, 139.9, 170.2, 171.2, 171.5, 171.7, 171.8. TOF-MS (ES+): *m*/*z* 1454 [MH^+, 23%], 663 (40%), 529 (23%), 342 (100%), 286 (75%). FAB-HRMS (negative mode ionization, *m*-nitrobenzyl alcohol matrix): *m*/*z* calcd for $C_{84}H_{79}N_{10}O_{14}$ [M − H], 1451.5777; found, 1451.5782 (−0.6 mDa). $[\alpha]^{25}_D$ −52.3 (*c* 2.1, THF).

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Supporting Information Available: Characterization data of compounds **1a/b**, **3**−**4b**, **5**−**6a**, **5b**, **7a/b**, **8a/b**, and **9a/b**; cyclic voltammograms for the electropolymerization of polycarboxylated tri/tetraCbz-based monomers **9b** and **6b** (5 mm ∅ Pt disk electrode) that included corresponding voltammetric responses of resulting conducting polyCbz-films Poly(**9b**) and Poly(**6b**) in supporting electrolyte (without monomer). This material is available free of charge via the Internet at http://pubs.acs.org.

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