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Star-shaped dendritic molecules based on carboxylated carbazole and pyrrole as peripheral oxidizable units

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ABSTRACT

The synthesis and spectroscopic characterization of three tricarboxylated pyrrole (Pyr)- and carbazole (Cbz)-containing star-shaped dendritic molecules **1**–**3** have been described here. Clauson–Kaas, amide coupling and debenzylation reactions have been used as key chemical tools. Electropolymerization of these oxidizable molecules has been investigated. The carboxylated Cbz-based molecules upon oxidative electropolymerization produced stable electroactive polyCOOH polyCbz films.

1. Introduction

Electrogenerated polycarbazole (polyCbz) films have recently gained much attention due to their potential applications in light-emitting diodes [1–4], photoconductive materials [5–8], electrochemical transistors [9–11] and electrochromic materials [12–17]. Furthermore, electrogenerated functionalized conducting polyCbz films are of special interest because of their wide potential applications in the biosensing field through the post-polymerization covalent grafting of biomolecules [18,19].

Dendrimers are branched polymers and due to their multiple applications in catalysis, drug delivery, electronic materials, etc., enough efforts have been devoted for the past two decades to develop various kinds of variously shaped dendrimers [20–31]. Several trials have been attempted to use electropolymerizable heterocycles particularly carbazole, pyrrole, and thiophene either as the outer layer of dendrimer or as the dendritic backbone [32–43]. It has been well investigated that the attachment of electropolymerizable heterocycles at the periphery of a dendrimer enabled the fabrication of corresponding electroactive poly(dendrimers)-modified electrodes through electropolymerization [32,44,45]. In addition, dendrimers containing chemical functionalities attached as peripheral units are of special interest since they enabled the further covalent attachment of other chemical or biological entities through post-synthetic functional group manipulation [46–50]. The electropolymerization of carboxylated electropolymerizable heterocycle-based molecules results in the formation of polycarboxylated conducting film which could be used as biosensors coating/sensing components [51,52]. As the carboxylate functionality of the resulting polymer matrix provides attachment sites for external entities, the development of novel polycarboxylated dendrimers or of small dendritic oxidizable molecules that can undergo (electro)chemical polymerization towards carboxy-enriched polymer matrices is an important area of research.

Herein, we wish to report our design and synthesis strategy for the preparation of three novel star-shaped dendritic carboxylated Cbz-/Pyr-based monomers **1**–**3** followed by electro-oxidation investigation. The Cbz/Pyr units are connected as peripheral units to a tris(2-aminoehtyl)amine core through amide bonds in each of these star-shaped monomers (Fig. 1).

2. Experimental

2.1. Materials and characterization

Cbz- and Pyr-based building blocks **5**–**7** were synthesized by a modified Clauson–Kaas [43,45,53–56] reaction. All reagents and solvents were purchased from commercial sources and used without further purification. Spectral data of **5** and **7** were in agreement

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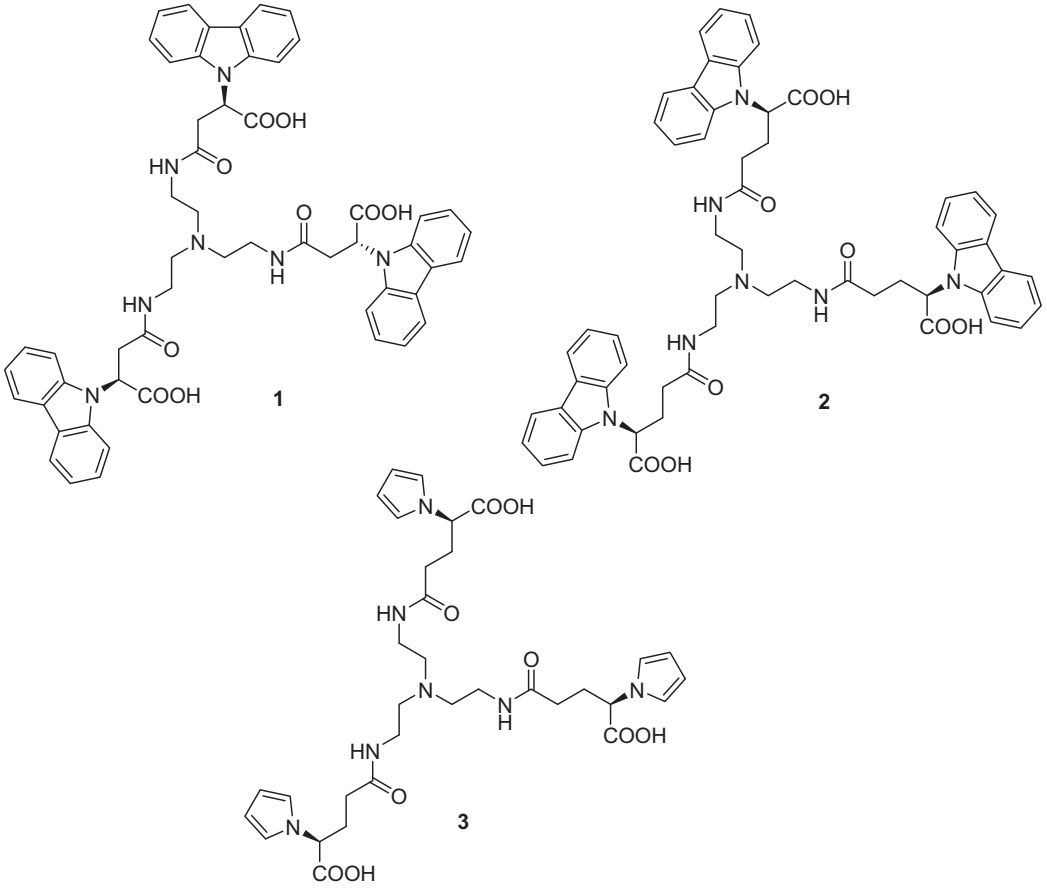


Fig. 1. Tricarboxylated Cbz-/Pyr-based dendritic oxidizable monomers.

with reported data [45]. Flash chromatography was performed on Merck silica gel (40–60 mesh). TLC was done on Merck silica gel plates ($60F_{254}$) with a fluorescent indicator. IR spectra were recorded on a FT-IR Bruker Tensor 27 spectrometer using either neat samples (KBr cell) or as 1% weight KBr dispersion pellets. Strength of each IR signal is presented as s (=strong), m (=medium) or w (=weak). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 Fourier transform spectrometer in $CDCl_3$ or DMSO-d_6 with TMS as the internal standard. NMR data are presented in the following order: chemical shift, assignment, peak multiplicity (b = broad, s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet), coupling constant, proton number(s). Mass spectra were obtained on two apparatuses, a Q-TOF MS Micro (Micromass, electrospray mode), VG AutoSpec Instrument (FAB and DCI/CH_4, Low/High Resolution Mass Spectrometer) in *m*-nitrobenzyl alcohol or glycerol matrices.

2.2. Synthesis

2.2.1. A typical DCC/HOBt-mediated amidation protocol for Cbz/Pyr-based intermediates (**9**–**11**) (illustrated for intermediate compound **9**); 4-(2-{bis-[2-((S)-4-benzyloxycarbonyl-4-pyrrol-1-yl-butyrylamino)-ethyl]-amino}-ethylcarbamoyl)-(S)-2-pyrrol-1-yl-butyric acid benzyl ester (**9**)

To a solution of monobenzylated Pyr-acid **5** (0.861 g, 3 mmol) in dry DCM was added HOBt (0.446 g, 3.3 mmol) followed by DCC (0.741 g, 3.6 mmol). The resultant mixture was stirred under N_2 for 40 min at 20 °C followed by the addition of tris-(2-aminoethyl) amine (0.145 g, 0.99 mmol) and the resultant mixture was left for stirring at room temperature under N_2 for 20 min. The reaction mixture was then filtered (5 μm Büchner filter) to remove the precipitated dicyclohexylurea (DCHU). The filtrate was concentrated by rotary evaporation and the crude product was dissolved with cold ethylacetate (EtOAc) to effect the precipitation of additional DCHU, which was removed by further filtration (5 μm Büchner filter). The organic layer was concentrated *in vacuo* and the crude product was purified by column chromatography over silica gel (40–60 mesh) using a acetone/hexane mixture as eluent (gradient from a 30% (v/v) to 80% (v/v) acetone/hexane mixture) to afford chromatographically pure compound **9** (0.878 g, 92%) as a colorless highly viscous oil. FT-IR (neat, ν in cm^{-1}): 698 (m), 730 (s), 950 (w), 1029 (m), 1093 (m), 1169 (m), 1263 (m), 1381 (w), 1453 (w), 1490 (m), 1541 (m), 1654 (m, $\nu_{C=Oamide}$), 1739 (s, $\nu_{C=Oester}$), 2940 (w), 3064 (w), 3265 (w, ν_{N-H}); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.01–2.04 (m, 6H, CH_2), 2.16–2.26 (m, 3H, COCH_2), 2.34–2.46 (m, 3H, COCH_2), 2.62 (bs, 6H, NCH_2), 3.22 (bs, 6H, NCH_2), 4.73 (dd, J = 10.2 and 5.1 Hz, 3H, NC*H*), 5.12 (s, 6H, OCH_2), 6.13 (s, 6H, Ar*H*), 6.68 (s, 6H, Ar*H*), 7.22–7.30 (m, 15H, Ar*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.13 (CH_2), 31.46 ($COCH_2$), 36.58 (NCH_2), 54.31 (NCH_2), 60.85 (NCH), 67.18 (OCH_2), 108.87 (Ar*C*), 120.23 (Ar*C*), 128.00 (Ar*C*), 128.41 (Ar*C*), 128.61 (Ar*C*), 135.22 (Ar*C*), 170.30 (*C*O), 172.44 (*C*O); TOF-MS (ES, positive mode): *m/z* 954 [MH^+]; $[\alpha]_D^{25} = -1.39^\circ$ (*C* = 0.046, DCM).

2.2.2. General debenzylation procedure for the synthesis of carboxylated Pyr-/Cbz-based molecules (**1**–**3**) (illustrated for compound **3**); 4-(2-{bis-[2-((S)-4-carboxy-4-pyrrol-1yl-butyrylamino)-ethyl]-amino}-ethylcarbamoyl)-(S)-2-pyrrol-1-yl-butyric acid (**3**)

Compound **9** (0.954 g, 1 mmol) was dissolved in a mixture of isopropanol and THF (1:1, v/v, 30 ml) followed by the addition of a

suspension of 10% Pd-C (0.6 g) in a three-necked round bottomed flask. The reaction mixture was made saturated by H_2 gas and left for stirring at room temperature under a H_2 atmosphere (H_2 balloon) for 10 h. Removal of the Pd/C was executed by filtration through a celite bed (250 mg). Then the filtrate was concentrated under vacuum to yield a residual white solid. The resulting product was washed with DCM (2 × 10 ml) followed by acetone (2 × 10 ml), and finally dried under high vacuum for 6–7 h to yield the pure compound **3** (0.560 g, 82%) as a white solid (mp: 96 °C). The product was sufficiently pure for structure confirmation by usual spectroscopic means. FT-IR (KBr, ν in cm^{-1}): 736 (s), 805 (w), 951 (w), 1092 (s), 1206 (m), 1268 (s), 1383 (m), 1451 (w), 1489 (w), 1551 (s), 1653 (s, $\nu_{C=Oamide}$), 1728 (s, $\nu_{C=Oacid}$), 2928 (m), 3095 (w), 3350 (s, $\nu_{N-H,\ O-H}$); ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.87–1.97 (m, 6H, CH_2), 2.01–2.09 (m, 3H, COCH_2), 2.24–2.28 (m, 3H, COCH_2), 2.45–2.51 (m, 6H, NCH_2), 3.04–3.05 (m, 6H, NCH_2), 4.71 (dd, J = 9.6 and 5.1 Hz, 3H, NCH), 6.00 (t, J = 2.1 Hz, 6H, ArH), 6.76 (t, J = 2.1 Hz, 6H, ArH), 7.71 (t, J = 5.4 Hz, 3H, NH); ^{13}C NMR (75 MHz, DMSO-d_6) δ 28.17 (CH_2), 31.23 (COCH_2), 36.72 (NCH_2), 53.20 (NCH_2), 60.58 (NCH), 107.72 (ArC), 120.15 (ArC), 171.03 (CO), 172.04 (CO); TOF-MS (ES, negative mode): m/z 726 [M−3H$^+$+2Na$^+$], 704 [M−2H$^+$+Na$^+$], 682 [(M−H)$^-$]; FAB-HRMS (negative mode): m/z Calcd. for $C_{33}H_{44}N_7O_9$ [(M−H)$^-$] = 682.3201, found 682.3186; $[\alpha]_D^{25} = -35.35°$ (C = 0.068, DMSO).

*2.2.3. (S)-2-Carbazol-9-yl-succinic acid 1-benzyl ester (**6**)*

Pale yellow solid (mp: 49 °C); FT-IR (KBr, ν in cm^{-1}): 696 (m), 722 (m), 749 (s), 946 (w), 1001 (w), 1028 (w), 1059 (w), 1091 (m), 1156 (m), 1173 (m), 1218 (m), 1285 (m), 1334 (m), 1454 (s), 1484 (m), 1598 (m), 1624 (w), 1712 (s, $\nu_{C=Oacid}$), 1738 (s, $\nu_{C=Oester}$), 2934 (w), 3047 (w); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.96 (dd, J = 17.4 and 6.3 Hz, 1H, CH_2), 3.68 (dd, J = 17.1 and 7.5 Hz, 1H, CH_2), 5.06 (s, 2H, OCH_2), 5.85 (t, J = 6.9 Hz, 1H, NCH), 6.92 (d, J = 7.2 Hz, 2H, ArH), 7.08–7.37 (m, 9H, ArH), 8.04 (d, J = 7.5 Hz, 2H, ArH), 9.74 (bs, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.76 (CH_2), 53.09 (NCH), 67.81 (OCH_2), 109.28 (ArC), 119.99 (ArC), 120.54 (ArC), 123.64 (ArC), 126.13 (ArC), 128.06 (ArC), 128.33 (ArC), 128.45 (ArC), 134.81 (ArC), 139.64 (ArC), 169.65 (CO), 176.54 (CO); TOF-MS (ES, positive mode): m/z 412 [MK$^+$], 396 [MNa$^+$], 374 [MH$^+$]; $[\alpha]_D^{25} = -94.98°$ (C = 0.055, DCM).

*2.2.4. N-(2-{bis-[2-((S)-3-benzyloxycarbonyl-3-carbazol-9-yl-propionylamino)-ethyl]-amino}-ethyl)-(S)-2-carbazol-9-yl-succinamic acid benzyl ester (**10**)*

White solid (mp: 79 °C); FT-IR (KBr, ν in cm^{-1}): 696 (m), 748 (s), 1053 (w), 1168 (s), 1217 (m), 1280 (m), 1339 (m), 1380 (m), 1452 (s), 1485 (m), 1545 (m), 1596 (w), 1652 (s, $\nu_{C=Oamide}$), 1737 (s, $\nu_{C=Oester}$), 2935 (m), 3059 (m), 3287 (m), 3398 (w, ν_{N-H}); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.61 (bs, 6H, CH_2), 2.26 (bs, 3H, NCH_2), 2.49 (bs, 3H, NCH_2), 2.65–2.74 (m, 3H, NCH_2), 3.22–3.29 (m, 3H, NCH_2), 4.95 (d, J = 12.3 Hz, 3H, OCH_2), 5.03 (d, J = 12.3 Hz, 3H, OCH_2), 5.89 (dd, J = 8.4 and 5.1 Hz, 3H, NCH), 6.86 (d, J = 6.9 Hz, 6H, ArH), 7.08–7.21 (m, 27H, ArH), 7.92 (d, J = 7.5 Hz, 6H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.27 (CH_2), 37.71 (NCH_2), 53.64 (NCH_2), 54.22 (NCH), 67.29 (OCH_2), 109.45 (ArC), 119.65 (ArC), 120.13 (ArC), 123.11 (ArC), 125.86 (ArC), 127.72 (ArC), 128.02 (ArC), 128.20 (ArC), 134.77 (ArC), 139.48 (ArC), 169.33 (CO), 170.01 (CO); TOF-MS (ES, positive mode): m/z 1213 [MH$^+$]; $[\alpha]_D^{25} = -110.59°$ (C = 0.037, DCM).

*2.2.5. N-(2-{bis-[2-((S)-3-carbazol-9-yl-3-carboxy-propionylamino)-ethyl]-amino}-ethyl)-(S)-2-carbazol-9-yl-succinamic acid (**1**)*

White solid (mp: 166 °C); FT-IR (KBr, ν in cm^{-1}): 723 (m), 753 (s), 940 (w), 1028 (m), 1081 (m), 1129 (m), 1165 (m), 1221 (m), 1336 (m), 1451 (m), 1485 (m), 1627 (s, $\nu_{C=Oamide}$), 1722 (s, $\nu_{C=Oacid}$), 2852 (w), 2928 (m), 3054 (w), 3326 (m, $\nu_{N-H,\ O-H}$); ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.98 (bs, 6H, CH_2), 2.67–2.77 (m, 6H, NCH_2), 2.89–2.97 (m, 6H, NCH_2), 5.91 (dd, J = 8.1 and 6.0 Hz, 3H, CH), 7.14 (t, J = 7.8 Hz, 6H, ArH), 7.31–7.43 (m, 12H, ArH), 7.74 (t, J = 5.4 Hz, 3H, NH), 8.08 (d, J = 7.8 Hz, 6H, ArH); ^{13}C NMR (75 MHz, DMSO-d_6) δ 35.85 (CH_2), 36.66 (NCH_2), 52.93 (NCH_2), 53.33 (NCH), 109.95 (ArC), 119.12 (ArC), 120.21 (ArC), 122.56 (ArC), 125.64 (ArC), 139.55 (ArC), 168.95 (CO), 171.29 (CO); TOF-MS (ES, negative mode): m/z 984 [M−3H$^+$+2Na$^+$], 962 [M−2H$^+$+Na$^+$], 940 [(M−H)$^-$]; FAB-HRMS (negative mode): m/z Calcd. for $C_{54}H_{51}N_7O_9$ [M$^-$] = 941.3748, found 941.3760; $[\alpha]_D^{25} = -117.88°$ (C = 0.094, DMSO).

*2.2.6. 4-(2-{Bis-[2-((S)-4-benzyloxycarbonyl-4-carbazol-9-yl-butyrylamino)-ethyl]-amino}-ethylcarbamoyl)-(S)-2-carbazol-9-yl-butyric acid benzyl ester (**11**)*

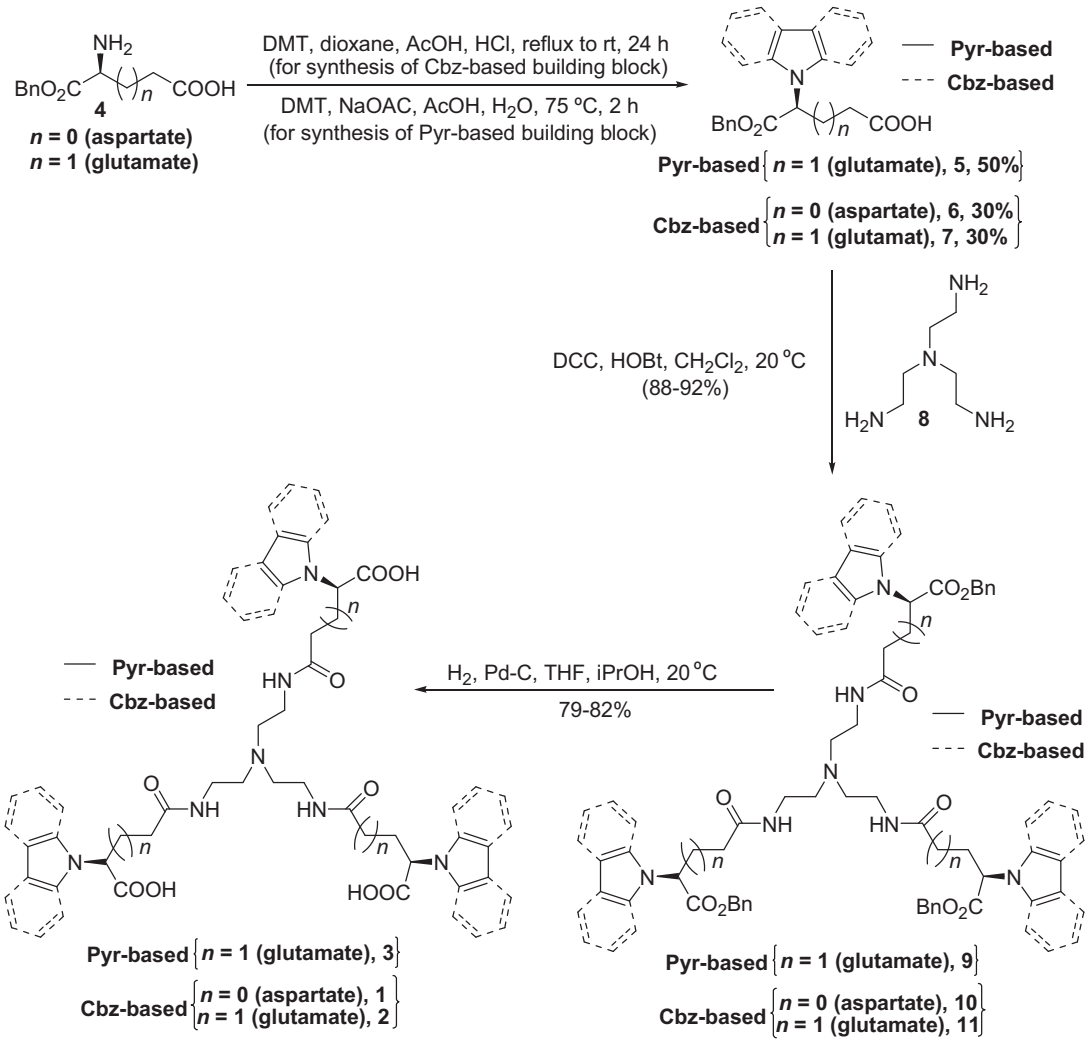
White solid (mp: 80 °C); FT-IR (KBr, ν in cm^{-1}): 749 (s), 1066 (m), 1164 (m), 1233 (m), 1337 (m), 1381 (w), 1452 (s), 1486 (m), 1539 (m), 1597 (w), 1653 (s, $\nu_{C=Oamide}$), 1737 (s, $\nu_{C=Oester}$), 2941 (w), 3057 (w), 3280 (m), 3401 (w, ν_{N-H}); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.70–2.83 (m, 24H, CH_2, COCH_2, NCH_2), 5.00 (s, 6H, OCH_2), 5.40–5.45 (m, 3H, CH), 6.94 (d, J = 6.3 Hz, 6H, ArH), 7.10–7.27 (m, 27H, ArH), 7.97 (d, J = 7.8 Hz, 6H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.86 (CH_2), 30.80 (COCH_2), 35.38 (NCH_2), 53.42 (NCH_2), 55.55 (NCH), 67.00 (OCH_2), 109.57 (ArC), 119.52 (ArC), 120.22 (ArC), 123.07 (ArC), 125.79 (ArC), 127.81 (ArC), 128.07 (ArC), 128.27 (ArC), 134.98 (ArC), 139.88 (ArC), 170.09 (CO), 172.15 (CO); TOF-MS (ES, positive mode): m/z 1293 [MK$^+$], 1277 [MNa$^+$], 1255 [MH$^+$]; $[\alpha]_D^{25} = -31.73°$ (C = 0.044, DCM).

*2.2.7. 4-(2-{Bis-[2-((S)-4-carbazol-9-yl-4-carboxy-butyrylamino)-ethyl]-amino}-ethylcarbamoyl)-(S)-2-carbazol-9-yl-butyric acid (**2**)*

White solid (mp: 172 °C); FT-IR (KBr, ν in cm^{-1}): 723 (m), 753 (s), 1026 (w), 1069 (w), 1160 (w), 1226 (s), 1331 (s), 1376 (w), 1450 (s), 1483 (m), 1540 (m), 1598 (m), 1656 (s, $\nu_{C=Oamide}$), 1725 (s, $\nu_{C=Oacid}$), 2933 (m), 3052 (m), 3389 (s, $\nu_{N-H,\ O-H}$); ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.63–1.73 (m, 3H, CH_2), 1.91–1.96 (m, 3H, CH_2), 2.23–2.39 (m, 6H, COCH_2), 2.42–2.58 (m, 6H, NCH_2), 2.80–2.87 (m, 6H, NCH_2), 5.59 (dd, J = 10.5 and 5.1 Hz, 3H, NCH), 7.18 (t, J = 7.8 Hz, 6H, ArH), 7.35–7.40 (m, 6H, ArH), 7.47–7.49 (m, 6H, ArH), 8.14 (d, J = 7.8 Hz, 6H, ArH); ^{13}C NMR (75 MHz, DMSO-d_6) δ 25.16 (CH_2), 31.20 (COCH_2), 36.65 (NCH_2), 53.06 (NCH_2), 55.60 (NCH), 109.90 (ArC), 119.03 (ArC), 120.24 (ArC), 122.47 (ArC) 125.69 (ArC), 139.78 (ArC), 170.97 (CO), 171.68 (CO); TOF-MS (ES, positive mode): m/z 984 [MH$^+$]; FAB-HRMS (negative mode): m/z Calcd. for $C_{57}H_{57}N_7O_9$ [M$^-$] = 983.4218, found 983.4257; $[\alpha]_D^{25} = -43.64°$ (C = 0.098, DMSO).

3. Results and discussion

One of the main challenges of dendrimer chemistry is to choose a suitable synthetic root in order to achieve good yields of pure desired products. We introduce here a convergent approach for the synthesis of Pyr- and Cbz-based carboxylated small dendritic molecules using tris(2-aminoethyl)amine as an aliphatic core. The synthetic procedures used for the preparation of these monomers are outlined in Scheme 1. Basically, three novel polycarboxylated homochiral *C3*-symmetrical monomers **1**–**3** were readily synthesized from Cbz-derivative of *L*-aspartic acid (*S*)-**6** and from both Pyr- and Cbz-derivatives of *L*-glutamic acid (*S*)-**5**/**7** (Scheme 1). These building blocks **5**–**7** were synthesized by a modified Clauson–Kaas [43,45,53–56] ring closure reaction using 2,5-dimethoxytetrahydrofuran (DMT) and involving the primary



Scheme 1. Synthesis of tricarboxylated *C3*-symmetrical Cbz-/Pyr-based dendritic molecules **1**–**3**.

amines of protected *L*-aspartic and *L*-glutamic acids (**4**, $n = 0$ and 1) as key materials (amino acid, DMT, NaOAC, AcOH, H_2O, 75 °C, 2 h, for **5**; amino acid, DMT, dioxane, AcOH, HCl, reflux for 3 h and then overnight stirring at rt, for **6** and **7**). *C3*-symmetrical dendritic amide intermediates **9**–**11** were synthesized by amidation of a tris(2-aminoethyl)amine linker using carboxylated Cbz-/Pyr-containing peripheral building blocks **5**–**7** in the presence of a combination of dicyclohexylcarbodiimide (DCC) and 1-hydroxybenzotriazole (HOBt) as an effective coupling system. Finally, a combination of H_2 gas and of a catalytic amount of 10% Pd/C was used as debenzylating conditions for the synthesis of desired tricarboxylated dendritic Cbz-/Pyr-based monomers (**1**–**3**). All these final tricaboxylic dendritic molecules were foamy in nature. No column purification was necessary in the final debenzylation step, since simple washing of crude desired products **1**–**3** with suitable solvents (see Section 2 for details) yielded spectroscopically grade products. The use of a suitable tetra-amine **8** as dendrimeric core and the similar one step synthesis of Cbz-/Pyr-based peripheral building blocks make this whole synthetic process cost-effective and convergent as it involves only three synthetic steps to synthesize the final oxidizable chiral monomers from readily available (commercial sources) starting materials.

All the tricarboxylated acids were fully characterized by a combination of $^1H/^{13}C$ NMR (300 and 75 MHz) and mass spectrometry analyses. In some cases, traces of entrapped solvents were detected by ^1H NMR although all these compounds were dried under high vacuum (10^{-2} Torr, 24 h) for a long time. This could be because of their foamy nature and limited solubility in most of the commonly used organic solvents. The disappearance of the benzyl proton signals at $\delta \sim 4.95$–5.12 ppm in ^1H NMR and benzyl carbon signals at $\delta \sim 67.0$–67.3 ppm in ^{13}C NMR spectra indicated the complete debenzylation of the intermediates **9**–**11** as well as the formation of desired carboxylated monomers **1**–**3**. In general, the FT-IR spectral data for all the intermediates and final carboxylated monomers are in the range of 3280–3401 ($\nu_{N-H,\,O-H}$), 2850–3064 ($\nu_{C-H\ stretching}$), 1737–1739 ($\nu_{C=Oester}$), 1712–1728 ($\nu_{C=Oacid}$), 1627–1654 ($\nu_{C=Oamide}$), 1450–1598 ($\nu_{C=C}$), 1331–1381 ($\nu_{C-H\ bending}$), 1206–1285 (ν_{C-O}), 1156–1173 (ν_{C-N}) and 722–753 ($\nu_{C=C-H}$) cm^{-1}.

When these monomers were subjected for oxidative electropolymerization, the formation of corresponding polyCOOH stable conductive films onto a Pt electrode was observed for both Cbz-based monomers **1** and **2**, whereas no electropolymerization was observed for the Pyr-based monomer **3**. The resistance of Pyr-based monomer **3** towards electropolymerization is in agreement with the literature reported results that the electropolymerization of short N-hydroxyalkyl or N-carboxyalkyl chain-based pyrroles gets blocked [45,57] due to intramolecular trapping of cation radicals by close nucleophilic hydroxyl or acidic hydroxyl groups.

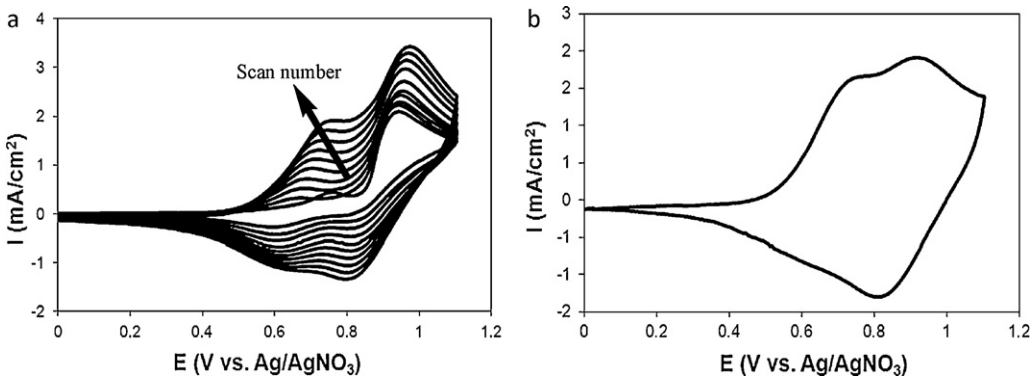


Fig. 2. (a) Ten scans oxidative electropolymerization of Cbz-monomer **2**. (b) Cyclic voltammogram of the resulting conducting poly-**2** film.

The electrochemical studies dealing with these oxidizable Cbz-/Pyr-molecules consisted of two discrete steps. First, Cbz-/Pyr-monomers synthesized previously were tentatively electropolymerized onto a Pt working electrode. Then, the corresponding modified electrodes were washed intensively by clean CH_3CN, and immersed in a monomer-free electrolyte solution (mixture of 0.2 M n-Bu_4NClO_4 and 0.2 M $LiClO_4$) in a ethylenecarbonate–dimethylcarbonate solution (1:2 molar ratio) to investigate the voltammetric response of resulting conducting films.

Accordingly, the electropolymerization of Cbz-/Pyr-monomers was investigated by cyclic voltammetry (50 mV/s) using a 1 mm diameter Pt working electrode in a three-electrode cell (Pt ribbon counter-electrode, $Ag/AgNO_3$ reference electrode) operated 10 times between 0 and 1.1 V (for Cbz-monomer polymerization), −1 V and 0.8 V (for Pyr-monomer polymerization). The background electrolyte consisted of a mixture of 0.2 M n-Bu_4NClO_4 and 0.2 M $LiClO_4$ in a ethylenecarbonate–dimethylcarbonate solutions (1:2 molar ratio) in which monomer concentrations were adjusted to 5 mM. All electrochemistry experiments were performed under a glove box atmosphere (dry Ar, <1 ppm H_2O and O_2).

An illustrative cyclic voltammogram of the electropolymerization process of monomer **2** and its typical electrochemical behavior have been reported in Fig. 2. The observed current increase during the polymerization process from one scan to another indicates the effective growth of a corresponding polyCbz conductive coating. The voltammogram analysis that can be performed is mainly based on former conclusions relating to (i) electropolymerization of a similar dicarbazole-based monomer (namely 2,6-bis-carbazole-9-yl-hexanoic acid pentafluorophenyl ester) [58,59] and (ii) the characterization of the corresponding polyCbz polymer. In brief, we noticed the presence of two main peaks in the polymerization process at ca. 0.7 and ca. 0.9 V. The first peak has been assigned to the oxidation of the deposited polymer (doping) while the second one characterized the monomer oxidation to produce the corresponding polymer [58]. We also noticed that the lower potential peak appears only from the second scan while the higher potential peak appears at the first scan. Moreover, the current of the first peak increases much faster from one scan to another than the current of the second peak. These electrochemistry-driven differences emphasized the fact that both peaks arose from different electrochemical processes. The polyCbz coating characterization in a monomer-free solution (typical CV, Fig. 2b) much resembles the polymerization voltammogram. It shows one broad peak reflecting the polymer insulator to conductor transformation via a polaron–bipolaron mechanism as referenced previously [59,60]. Tricarboxylated Cbz-monomers, **1** and **2**, were readily polymerized as reflected by the observed linear increase of the current from one scan to another (arising from an increase of the polymer surface area, i.e. polymer growth). Both cyclic votammograms relating to Cbz-monomers **1** and **2** upon oxidative elctropolymerization showed identical behaviors.

As the chiral polyCbz films act as permselective material in biosensing field for the stereoselective recognition of biomolecules [61] the present chiral polyCOOH polyCbz films produced from carboxylated chiral Cbz-monomers **1** and **2** could find wide applications in the biosensing field through post-polymerization functional group manipulation (COOH derivatization). The covalent immobilization of biomolecules mostly occurs at the functional group of the conducting film [18–19,61]. Because of the dendritic nature of present Cbz-monomers, they produce densely polycarboxy-functionalized polycarbazole films which potentially could be more effective than similar films produced by non-dendritic ones. On the other hand, these newly developed polycarboxylated chiral monomers could find wide applications as multivalent tripodal dual nature (acidic/basic) ligands in coordination chemistry/asymmetric catalysis. Moreover, the present synthetic strategy allows an easy three steps versatile synthesis of these novel carboxy-functionalized dendritic monomers that may be readily extended to the tailored combinatorial engineering of such polymeric conductive coatings [62–64], which is quite innovative in the field.

4. Conclusion

To conclude, novel tricarboxylated oxidizable Cbz-/Pyr-based dendritic molecules have successfully been synthesized in three steps thorough a convergent approach using Clauson–Kaas, amide coupling, and hydrogenation reactions. The methodology makes the synthesis of such carboxylated Cbz-/Pyr-based small dendritic molecules easy processes. All the intermediate and final products were characterized by FT-IR, ^1H and ^{13}C NMR, and mass spectrometry analyses. Resulting Cbz-containg dendritic molecules possessing peripheral carboxylated Cbz-units readily undergo electropolymerization resulting in the formation of stable electroactive polyCOOH polyCbz films.

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