Efficient Synthetic Access to Cationic Dendrons and their Application for ZnO Nanoparticles Surface Functionalization: New Building Blocks for Dye Sensitized Solar Cells

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Synthesis of the Cationic Dendrons

All chemicals were purchased by chemical suppliers and used without further purification. All analytical reagent-grade solvents were purified by distillation. Thin layer chromatography (TLC): Riedel–de Haën silicagel F254 and Merck silica gel 60 F254. Detection: UV lamp and iodine chamber. Flash- chromatography (FC): Macherey–Nagel silica gel 60 M (230–400 mesh, 0.04–0.063 mm). Solvents were purified by distillation prior to use. UV/Vis spectroscopy: Shimadzu UV-3102 PC UV/Vis/NIR scanning spectrophotometer; absorption maxima λ_{max} are given in nm. Mass spectrometry: AXIMA Confidence MALDI TOF mass spectrometer, nitrogen UV laser, 50 Hz, l=337 nm wavelength, Shimadzu. 2-[(2E)–3-(4-*tert*-Butylphenyl)–2–methylprop–2-enylidene] malononitrile (DCTB), 3,5-dimethoxy-4-hydroxycinnamic acid (SIN) and 2,5-dihydroxybenzoicacid (DHB) were used as matrix or without matrix (OM). NMR spectroscopy: JEOL JNM EX 400 and JEOL JNM GX 400 and Bruker Avance 300. The chemical shifts are given in ppm relative to TMS. The resonance multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet) and m (multiplet), non-resolved and broad resonances as br. Elemental analysis (C, H, N): Succeeded by combustion and gas chromatographical analysis with an EA 1110 CHNS analyser (CE Instruments).

1,3-bis(methoxymethyl)-5-nitrobenzene. An amount of 2.23 g sodium was dissolved in 250 mL methanol under vigorous stirring. 10 g of 1,3-bis(bromomethyl)-5-nitrobenzene[48] were added and the solution was refluxed for two hours. After that period the solution was cooled down to room temperature and poured into 300 mL of water. The suspension was stirred for 5 minutes followed by extraction with Dichloromethane. The organic phase was separated, washed with saturated NaCl-solution, dried over $MgSO_4$ and finally evaporated. Yield: 6.5 g (0.03 mol, 95%). ^{1}H-NMR ($CDCl_3$, 400 MHz, RT): δ [ppm] = 3.43 (s, 6H, C*H*$_3$OCH$_2$), 4.53 (s, 4H, C*H*$_2$OCH$_3$), 7.63 (s, 1H, *p*-Ar-*H*), 8.11 (s, 2H, *o*-Ar-*H*). ^{13}C-NMR ($CDCl_3$, 100.5 MHz, RT): δ [ppm] = 58.5 (2C, *C*H$_3$OCH), 73.2 (2C, *C*H$_2$OCH$_3$), 121.2 (2C, *o*-Ar-*C*H), 131.9 (1C, *p*-Ar-*C*H), 140.6 (2C, *m*-Ar-C), 148.4 (1C, *i*-Ar-C).

3,5-bis(methoxymethyl)aniline (2). Iron powder (10 g) was suspended in 5% NaCl (50 ml) and refluxed for 30 minutes. 1,3-bis(methoxymethyl)-5-nitrobenzene (6.5 g, 30 mmol), dissolved in 30 mL of a water/THF/methanol mixture, was added over 1 hour and the reaction mixture was refluxed for additional 2 hours. After cooling the reaction mixture was filtered and the filtrate was extracted with diethyl ether, dried over $MgSO_4$ and the ether was evaporated. The residue was purified via column chromatography with EtOAc/hexane (2:1) as

eluent. Yield: 3.35 g (0.02 mol, 60%). ^{1}H-NMR ($CDCl_3$, 400 MHz, RT): δ [ppm] = 3.36 (s, 6H, C*H*$_3$OCH$_2$), 3.66 (br s, 2H, NH$_2$), 4.36 (s, 4H, C*H*$_2$OCH$_3$), 6.59 (s, 2H, *o*-Ar-*H*), 6.67 (s, 1H, *p*-Ar-*H*). ^{13}C-NMR ($CDCl_3$, 100.5 MHz, RT): δ [ppm] = 58.0 (2C, *C*H$_3$OCH), 74.5 (2C, *C*H$_2$OCH$_3$), 113.5 (2C, *o*-Ar-*C*), 117.1 (1C, *p*-Ar-*C*), 139.5 (2C, *m*-Ar-*C*), 146.8 (1C, *i*-Ar-*C*). MS (MALDI, OM): m/z: 388 $[2M+Na]^+$.

General procedure for the synthesis of the f-moc protected dendrimers 3 and 4.

An amount of 1 g (2.4 mmol) of di-*tert*-butyl-4-amino-4-[2-(*tert*-butoxycarbonyl)ethyl]heptanedioate[52] was dissolved in 100 mL of THF. 850 mg (2.5 mmol) N-(9H-fluoren-2-ylmethoxycarbonyloxy)succinimide was added and the solution was stirred over night. The solvent was evaporated and the residue purified via column chromatography with $CHCl_3$/THF (19:1) as eluent to obtain 1.47 g (2.3 mmol, 96%) f-moc protected Newkome-dendron. This dendron was dissolved in 200 mL of formic acid and stirred over night to obtain the deprotected acid. The progress of the reaction was followed via TLC. The solvent was removed on a rotary evaporator. Subsequently, the product was transferred to toluene and evaporated twice to remove any residual formic acid. The product was finally dried under vacuum. The dried acid was dissolved in 200 mL DMF at 0°C. 1.55 g EDC (8.1 mmol) and 1.1 g HOBT (8.1 mmol) were added and the solution was stirred for one hour at 0°C. After that period 1.26 g (9.2 mmol) 3-(methoxymethyl)aniline) or 1.67 g (9.2 mmol) 3,5-bis(methoxymethyl)aniline, respectively, were added to the solution and the mixture was stirred at room temperature for 48 hours. After that period, the solvent was evaporated and the residue was purified via column chromatography on silica to obtain the dendrons **3** and **4**.

(9H-fluoren-9-yl)methyl1,7-bis(3-(methoxymethyl)phenylamino)-4-(3-(3-methoxymethyl)phenylamino)-3-oxopropyl)-1, 7-dioxoheptan-4-ylcarbamate (3).

Yield: 1.12 g (1.36 mmol, 59%). ^{1}H-NMR ($CDCl_3$, 400 MHz, RT): δ [ppm] = 2.00 (m, 6H, C*H*$_2$CH$_2$C=O) 2.29 (m, 6H, C*H*$_2$CH$_2$C=O), 3.30 (s, 9H, C*H*$_3$OCH$_2$), 4.04 (t, ^{3}J = 6.4 Hz, 1H, C*H*), 4.30 (m, 8H, C*H*$_2$OCH$_3$, CHC*H*$_2$O), 5.91 (br s, 1H, N*H*(C=O)O), 6.98 (d, ^{3}J = 7.6 Hz, 3H, *p*-Ar-*H*), 7.14 (t, ^{3}J = 7.8 Hz, 3H, *m*-Ar-*H*), 7.19 (dt, 2H, ^{4}J = 1.0 Hz, ^{3}J = 7.5 Hz, fluorene-*H*), 7.29 (m 5H, fluorene-*H*, *o*-Ar-*H*), 7.46 (s, 3H, *o*-Ar-*H*), 7.53 (d, ^{3}J = 7.5 Hz, 2H, fluorene-*H*), 7.69 (d, ^{3}J = 7.6 Hz, 2H, fluorene-*H*), 8.34 (br s, 3H, N*H*). ^{13}C-NMR ($CDCl_3$, 100.5 MHz, RT): δ [ppm] = 30.8 (3C, *C*H$_2$CH$_2$C=O), 31.6 (3C, CH$_2$*C*H$_2$C=O), 47.2 (1C, *C*H), 57.2 (1C, *C*-NH), 58.1 (3C, *C*H$_3$OCH), 65.7 (1C, CH-*C*H$_2$-O), 74.4 (3C, *C*H$_2$OCH$_3$), 119.2 (3C, *o*-Ar-*C*), 119.3 (3C, *o*-Ar-*C*), 120.0 (2C, fluorene-*C*H), 123.5 (3C, *p*-Ar-*C*), 125.1 (2C, fluorene-*C*H), 127.1 (2C, fluorene-*C*H), 127.7 (2C, fluorene-*C*H), 129.0 (3C, *m*-Ar-*C*H), 138.2 (3C, *m*-Ar-*C*), 139.0 (3C, *i*-Ar-*C*), 141.4 (2C, fluorene-*C*), 143.9 (2C, fluorene-*C*),

155.0 (1 C, NH(*C*=O)O), 171.9 (3C, NH*C*=O). EA: calculated for $C_{49}H_{54}N_4O_8$ *1/2 H_2O (836): C 70.40; H 6.63; N 6.70; found: C 70.15, H 6.62, N 6.80. MS (MALDI, DCTB): m/z: 828 $[M]^+$, 851 $[M+Na]^+$, 867 $[M+K]^+$.

(9H-fluoren-9-yl)methyl1,7-bis(3,5-bis(methoxymethyl)phenylamino)-4-(3-(3,5-bis(methoxymethyl)phenylamino)-3-oxopropyl)-1,7-dioxoheptan-4-ylcarbamate (4). Yield: 1.24 g (1.29 mmol, 56%). ^{1}H-NMR ($CDCl_3$, 400 MHz, RT): δ [ppm] = 1.91 (m, 6H, CH_2CH$_2$C=O) 2.21 (m, 6H, CH_2CH$_2$C=O), 3.29 (s, 18H, CH_3OCH$_2$), 4.04 (t, ^3J = 6.4 Hz, 1H, C*H*), 4.29 (m, 14H, CH_2OCH$_3$, CHCH_2O), 6.04 (br s, 1H, N*H*(C=O)O), 6.95 (s, 3H, *p*-Ar-*H*), 7.20 (t, 2H, ^3J = 7.4 Hz, fluorene-*H*), 7.31 (t, 2H, ^3J = 7.4 Hz, fluorene-*H*), 7.39 (s, 6H, *o*-Ar-*H*), 7.54 (d, ^3J = 7.4 Hz, 2H, fluorene-*H*), 7.69 (d, ^3J = 7.6 Hz, 2H, fluorene-*H*), 8.54 (br s, 3H, N*H*) ppm. ^{13}C-NMR ($CDCl_3$, 100.5 MHz, RT): δ [ppm] = 30.7 (3C, *C*H$_2$CH$_2$C=O), 31.3 (3C, CH$_2$*C*H$_2$C=O), 47.2 (1C, *C*H), 56.9 (1C, *C*-NH), 58.1 (6C, *C*H$_3$OCH), 65.6 (1C, CH-*C*H$_2$-O), 74.2 (6C, *C*H$_2$OCH$_3$), 118.3 (6C, *o*-Ar-*C*), 119.9 (2C, fluorene-*C*H), 122.4 (3C, *p*-Ar-*C*), 125.0 (2C, fluorene-*C*H), 127.1 (2C, fluorene-*C*H), 127.6 (2C, fluorene-*C*H), 138.5 (6C, *m*-Ar-*C*), 139.2 (3C, *i*-Ar-*C*), 141.3 (2C, fluorene-*C*), 144.0 (2C, fluorene-*C*), 155.1 (1 C, NH(*C*=O)O), 171.9 (3C, NH*C*=O). MS (MALDI, DCTB): m/z: 959 $[M]^+$, 982 $[M+Na]^+$, 998 $[M+K]^+$.

General procedure for the synthesis of the nitro dendrimers 5 and 6. An amount of 1 g (2.24 mmol) of di-*tert*-butyl 4-Nitro-4-[2-*tert*-butoxycarbonyl)ethyl]-heptanedioate[52] was dissolved in 200 mL of formic acid and stirred over night to obtain the deprotected acid. The progress of the reaction was followed via TLC. The solvent was removed on a rotary evaporator. Subsequently, the product was transferred to toluene and evaporated twice to remove any residual formic acid. The product was finally dried in vacuum. The dried, deprotected acid was dissolved in 200 mL DMF at 0°C. 1.51 g (7.85 mmol) EDC and 1.06 g (7.85 mmol) HOBT were added and the solution was stirred for one hour at 0°C. After that period 1.23 g (9.0 mmol) 3-(methoxymethyl)aniline) or 1.62 g (9.0 mmol) 3,5-bis(methoxymethyl)aniline, respectively, were added to the solution and the mixture was stirred at room temperature for 48 hours. After that period, the solvent was evaporated and the residue was purified via column chromatography on silica with CH_2Cl_2/MeOH (19:1) as eluent to obtain the dendrons **5** and **6**.

N1,N7- bis (3- (methoxymethyl) phenyl)- 4- (3- (3- (methoxymethyl) phenylamino)- 3-oxopropyl)- 4-nitroheptanediamide (5). Yield: 0.93 g (1.47 mmol, 65%). ^{1}H-NMR ($CDCl_3$, 400 MHz, RT): δ [ppm] = 2.30 (m, 12H, CH_2CH_2C=O), 3.31 (s, 9H, CH_3OCH$_2$), 4.31 (s, 6H, CH_2OCH$_3$), 6.99 (d, ^3J = 7.6 Hz, 3H, *p*-Ar-*H*), 7.16 (t, ^3J = 7.8 Hz, 3H *m*-Ar-*H*), 7.32 (d,

^3J = 8.1 Hz, 3H, *o*-Ar-*H*), 7.43 (s, 3H, *o*-Ar-*H*), 8.65 (s, 3H, N*H*). ^{13}C-NMR ($CDCl_3$, 100.5 MHz, RT): δ [ppm] = 30.5 (3C, *C*H_2CH_2C=O), 31.3 (3C, CH_2*C*H_2C=O), 58.1 (3C, *C*H_3OCH), 74.3 (3C, *C*H_2OCH_3), 93.3 (1C, *C*-NO_2), 119.4 (3C, *o*-Ar-*C*), 119.5 (3C, *o*-Ar-*C*), 123.6 (3C, *p*-Ar-*C*), 129.0 (3C, *m*-Ar-*C*H), 138.0 (3C, *m*-Ar-*C*), 139.0 (3C, *i*-Ar-*C*), 170.3 (3C, NH*C*=O). MS (MALDI, DHB): m/z: 657 $[M+Na]^+$, 673 $[M+K]^+$.

N1,N7-bis(3,5-bis(methoxymethyl)phenyl)-4-(3-(3,5-bis(methoxymethyl)phenylamino)-3-oxopropyl)-4-nitroheptanediamide (6). Yield: 1.05 g (1.37 mmol, 61%). ^{1}H-NMR ($CDCl_3$, 400 MHz, RT): δ [ppm] = 2.29 (m, 12H, CH_2CH_2C=O), 3.32 (s, 18H, CH_3OCH_2), 4.31 (s, 12H, CH_2OCH_3), 6.96 (s, 3H, *p*-Ar-*H*), 7.35 (s, 6H, *o*-Ar-*H*), 8.62 (br s, 3H, N*H*). ^{13}C-NMR ($CDCl_3$, 100.5 MHz, RT): δ [ppm] = 30.5 (3C, *C*H_2CH_2C=O), 31.1 (3C, CH_2*C*H_2C=O), 58.1 (6C, *C*H_3OCH), 74.2 (6C, *C*H_2OCH_3), 93.0 (1C, *C*-NO_2), 118.3 (6C, *o*-Ar-*C*), 122.6 (3C, *p*-Ar-*C*), 138.2 (6C, *m*-Ar-*C*), 139.2 (3C, *i*-Ar-*C*), 170.1 (3C, NH*C*=O). MS (MALDI, SIN): m/z: 959 $[M]^+$, 981 $[M+Na]^+$.

General procedure for the hydrogenation of the nitro dendrimers 5 and 6. An amount of 2 g Raney-Nickel was washed six times with ethanol. A suspension of **5** (1 g, 1.58 mmol) or **6** (1 g, 1.30 mmol) and Raney-Ni (2 g) in ethanol (100 mL) was stirred vigorously under hydrogen at room temperature and ambient pressure for 12 h. The progress of the reaction could be controlled via TLC till the nitro-compound has completely vanished. The solution was decanted from the catalyst and filtered over a short celite (1-2 cm) column. The catalyst was washed with ethanol and the washing solution was filtered again. The ethanol was removed via evaporation to obtain the dendrons **7** and **8**.

4-amino-N1,N7-bis(3-(methoxymethyl)phenyl)-4-(3-(3-(methoxymethyl)phenylamino)-3-oxopropyl)heptanediamide (7). Yield: 857 mg (1.42 mmol, 90%). ^{1}H-NMR ($CDCl_3$, 400 MHz, RT): δ [ppm] = 1.66 (m, 6H, CH_2CH_2C=O), 2.31 (m, 8H, CH_2CH_2C=O, -NH_2), 3.30 (s, 9H, CH_3OCH_2), 4.30 (s, 6H, CH_2OCH_3), 6.97 (d, ^3J = 7.6 Hz, 3H, *p*-Ar-*H*), 7.15 (t, ^3J = 7.8 Hz, 3H *m*-Ar-*H*), 7.35 (d, ^3J = 8.1 Hz, 3H, *o*-Ar-*H*), 7.49 (s, 3H, *o*-Ar-*H*), 8.99 (s, 3H, N*H*) ppm. ^{13}C-NMR ($CDCl_3$, 100.5 MHz, RT): δ [ppm] = 31.5 (3C, CH_2*C*H_2C=O), 34.4 (3C, *C*H_2CH_2C=O), 53.2 (1C, *C*-NH_2), 58.1 (3C, *C*H_3OCH), 74.4 (3C, *C*H_2OCH_3), 119.3 (3C, *o*-Ar-*C*), 119.4 (3C, *o*-Ar-*C*), 123.4 (3C, *p*-Ar-*C*), 128.9 (3C, *m*-Ar-*C*H), 138.4 (3C, *i*-Ar-*C*), 139.0 (3C, *m*-Ar-*C*), 172.4 (3C, NH*C*=O). MS (MALDI, SIN): m/z: 606 $[M]^+$, 628 $[M+Na]^+$, 644 $[M+K]^+$.

4-amino-N1,N7-bis(3,5-bis(methoxymethyl)phenyl)-4-(3-(3,5-bis (methoxymethyl)phenylamino)-3-oxopropyl)heptanediamide (8). Yield: 865 mg (1.17 mmol, 90 %). ^{1}H-NMR ($CDCl_3$, 400 MHz, RT): δ [ppm] = 1.74 (m, 6H, CH_2CH_2C=O), 2.38

(m, 6H, CH_2CH_2C=O), 2.65 (br s, 2H, -NH_2), 3.33 (s, 18H, CH_3OCH_2), 4.33 (s, 12H, CH_2OCH_3), 7.00 (s, 3H, *p*-Ar-*H*), 7.44 (s, 6H, *o*-Ar-*H*), 8.97 (br s, 3H, N*H*). ^{13}C-NMR ($CDCl_3$, 100.5 MHz, RT): δ [ppm] = 31.5 (3C, CH_2CH_2C=O), 34.2 (3C, CH_2CH_2C=O), 53.2 (1C, *C*-NH_2), 58.2 (6C, CH_3OCH), 74.3 (6C, CH_2OCH_3), 118.4 (6C, *o*-Ar-*C*), 122.6 (3C, *p*-Ar-*C*), 138.5 (3C, *i*-Ar-*C*), 139.3 (6C, *m*-Ar-*C*), 172.3 (3C, NH*C*=O). MS (MALDI, DHB): m/z: 737 $[M]^+$, 760 $[M+Na]^+$.

General procedure for the Synthesis of the intermediates 9, 10, 11 and 12 via modified Steglich coupling reaction. An amount of 220 mg (0.70 mmol) 3,4-diphenylmethylenedioxyprotocatechuic acid[55] was dissolved in 100 mL DMF at 0 C. 160 mg (0.83 mmol) EDC and 112 mg (0.83 mmol) HOBT were added and the solution was stirred for one hour at 0°C. After that period 1.5 eq of the corresponding amine were added to the solution (**1**: 143 mg, 1.04 mmol; **2**: 190 mg, 1.04 mmol; **7**: 632 mg, 1.04 mmol; **8**: 770 mg, 1.04 mmol) and the mixture was stirred at room temperature for 48 hours. The solvent was evaporated and the residue was purified via column chromatography on silica with CH_2Cl_2/MeOH (19:1) as eluent to obtain the intermediates **9, 10, 11** and **12**.

N- (3- (methoxymethyl)phenyl)- 2,2- diphenylbenzo [d] [1,3] dioxole- 5-carboxamide (9). Yield: 125 mg (0.28 mmol, 41 %). ^{1}H-NMR ($CDCl_3$, 400 MHz, RT): δ [ppm] = 3.38 (s, 3H, CH_3OCH_2), 4.45 (s, 2H, CH_2OCH_3), 6.91 (d, ^3J = 8.1 Hz, 1H, Cat-*H*), 7.10 (d, ^3J = 7.8 Hz, 1H, *p*-Ar-*H*), 7.32 (t, ^3J = 8.0 Hz, 1H *m*-Ar-*H*), 7.39 (m, 8H, Ar-*H*, Cat-*H*), 7.57 (m, 6H, Ar-*H*), 7.82 (s, 1H, N*H*). ^{13}C-NMR ($CDCl_3$, 100.5 MHz, RT): δ [ppm] = 58.1 (1C, CH_3OCH), 74.3 (1C, CH_2OCH_3), 107.9 (1C, Cat-*C*H), 108.3 (1C, Cat-*C*H), 118.1 (1C, *C*-O), 119.3 (1C, *o*-Ar-*C*H), 119.4 (1C, *o*-Ar-*C*H), 121.7 (1C, Cat-*C*H), 123.5 (1C, *p*-Ar-*C*H), 126.3 (6C, Ar-*C*H), 128.4 (4C, Ar-*C*H), 129.1 (1C, *m*-Ar-*C*H), 129.4 (1C, Cat-*C*), 138.2 (1C, *i*-Ar-*C*), 139.3 (1C, *m*-Ar-*C*), 139.7 (2C, Ar-*C*), 147.8 (1C, Cat-*C*-O), 150.3 (1C, Cat-*C*-O), 165.2 (1C, NH*C*=O). MS (MALDI, DCTB): m/z: 438 $[M]^+$, 4606 $[M+Na]^+$, 476 $[M+K]^+$.

N-(3,5-bis(methoxymethyl)phenyl)-2,2-diphenylbenzo[d][1,3]dioxole-5-carboxamide (10). Yield: 135 mg (0.28 mmol, 40%). ^{1}H-NMR ($CDCl_3$, 400 MHz, RT): δ [ppm] = 3.39 (s, 6H, CH_3OCH_2), 4.45 (s, 4H, CH_2OCH_3), 6.93 (d, ^3J = 8.1 Hz, 1H, Cat-*H*), 7.10 (s, 1H, *p*-Ar-*H*), 7.39 (m, 8H, Ar-*H*, Cat-*H*), 7.53 (s, 2H, *o*-Ar-*H*), 7.57 (m, 4H, Ar-*H*), 7.75 (s, 1H, N*H*). ^{13}C-NMR ($CDCl_3$, 100.5 MHz, RT): δ [ppm] = 58.2 (2C, CH_3OCH), 74.3 (2C, CH_2OCH_3), 107.9 (1C, Cat-*C*H), 108.3 (1C, Cat-*C*H), 118.1 (1C, *C*-O), 118.3 (2C, *o*-Ar-*C*H), 121.6 (1C, Cat-*C*H), 122.6 (1C, *p*-Ar-*C*H), 126.3 (6C, Ar-*C*H), 128.4 (4C, Ar-*C*H), 129.2 (2C, *m*-Ar-*C*), 129.4 (1C, Cat-*C*), 138.3 (1C, *i*-Ar-*C*), 139.6 (2C, Ar-*C*), 147.9 (1C, Cat-*C*-O), 150.3 (1C, Cat-*C*-O), 165.0 (1C, NH*C*=O). EA: calculated for $C_{30}H_{27}NO_5$ *1/2 H_2O (491): C 73.45; H

5.75; N 2.86; found: C 73.54, H 5.71, N 2.72. MS (MALDI, DCTB): m/z: 482 $[M]^+$, 506 $[M+Na]^+$, 521 $[M+K]^+$.

4-(2,2-diphenylbenzo[d][1,3]dioxole-5-carboxamido)-N1,N7-bis(3-(methoxymethyl) phenyl)-4-(3-(3-(methoxymethyl)phenylamino)-3-oxopropyl)heptanediamide (11). Yield: 222 mg (0.25 mmol, 35 %). ^{1}H-NMR ($CDCl_3$, 400 MHz, RT): δ [ppm] = 2.22 (t, ^3J = 7.1 Hz, 6H, C*H*$_2$CH$_2$C=O), 2.41 (t, ^3J = 7.2 Hz, 6H, CH$_2$C*H*$_2$C=O), 3.29 (s, 9H, C*H*$_3$OCH$_2$), 4.28 (s, 6H, C*H*$_2$OCH$_3$), 6.71 (d, ^3J = 8.1 Hz, 1H, Cat-*H*), 6.96 (d, ^3J = 7.6 Hz, 3H, *p*-Ar-*H*), 7.13 (t, ^3J = 7.8 Hz, 3H *m*-Ar-*H*), 7.28-7.35 (m, 9H, Ar-*H*, *o*-Ar-*H*), 7.38 (dd, ^4J = 1.6 Hz, ^3J = 8.1 Hz, 1H, Cat-*H*), 7.40 (d, ^4J = 1.4 Hz, 1H, Cat-*H*), 7.42 (s, 3H, *o*-Ar-*H*), 7.49 (m, 4H, Ar-*H*), 7.55 (s, 1H, N*H*), 8.99 (s, 3H, N*H*) ppm. ^{13}C-NMR ($CDCl_3$, 100.5 MHz, RT): δ [ppm] = 31.4 (3C, *C*H$_2$CH$_2$C=O), 31.9 (3C, CH$_2$*C*H$_2$C=O), 58.1 (3C, *C*H$_3$OCH), 58.7 (1C, *C*-NH), 74.4 (3C, *C*H$_2$OCH$_3$), 107.9 (1C, Cat-*C*H), 108.0 (1C, Cat-*C*H), 117.7 (1C, *C*-O), 119.2 (3C, *o*-Ar-*C*), 119.3 (3C, *o*-Ar-*C*), 122.3 (1C, Cat-*C*H), 123.5 (3C, *p*-Ar-*C*), 126.2 (4C, Ar-*C*H), 128.4 (4C, Ar-*C*H), 129.0 (3C, *m*-Ar-*C*H), 129.3 (2C, Ar-*C*H), 138.2 (3C, *i*-Ar-*C*), 139.0 (3C, *m*-Ar-*C*), 139.8 (2C, Ar-*C*), 147.4 (1C, Cat-*C*-O), 149.9 (1C, Cat-*C*-O), 167.4 (1C, NH*C*=O), 172.4 (3C, NH*C*=O). MS (MALDI, OM): m/z: 928 $[M+Na]^+$, 944 $[M+K]^+$.

N1,N7-bis(3,5-bis(methoxymethyl)phenyl)-4-(3-(3,5-bis(methoxymethyl)phenylamino)-3-oxopropyl)-4- (2,2- diphenylbenzo[d][1,3]dioxole-5- carboxamido)heptanediamide (12). Yield: 247 mg (0.24 mmol, 34%). ^{1}H-NMR ($CDCl_3$, 400 MHz, RT): δ [ppm] = 2.20 (m, 6H, C*H*$_2$CH$_2$C=O), 2.41 (m, 6H, CH$_2$C*H*$_2$C=O), 3.24 (s, 18H, C*H*$_3$OCH$_2$), 4.25 (s, 12H, C*H*$_2$OCH$_3$), 6.70 (d, ^3J = 8.1 Hz, 1H, Cat-*H*), 6.92 (s, 3H, *p*-Ar-*H*), 7.29 (m, 6H, Ar-*H*), 7.38 (m, 8H, *o*-Ar-*H*, Cat-*H*), 7.47 (m, 4H, Ar-*H*), 7.77 (s, 1H, N*H*), 8.96 (s, 3H, N*H*) ppm. ^{13}C-NMR ($CDCl_3$, 100.5 MHz, RT): δ [ppm] = 31.0 (3C, *C*H$_2$CH$_2$C=O), 31.5 (3C, CH$_2$*C*H$_2$C=O), 57.8 (6C, *C*H$_3$OCH), 58.2 (1C, *C*-NH), 74.1 (6C, *C*H$_2$OCH$_3$), 107.7 (1C, Cat-*C*H), 107.8 (1C, Cat-*C*H), 117.4 (1C, *C*-O), 118.1 (6C, *o*-Ar-*C*H), 122.0 (1C, Cat-*C*H), 126.0 (7C, *p*-Ar-*C*H, Ar-*C*H), 128.1 (4C, Ar-*C*H), 129.1 (2C, Ar-*C*H), 138.5 (3C, *i*-Ar-*C*), 138.9 (6C, *m*-Ar-*C*), 139.6 (2C, Ar-*C*), 147.1 (1C, Cat-*C*-O), 149.5 (1C, Cat-*C*-O), 166.9 (1C, NH*C*=O), 172.1 (3C, NH*C*=O). MS (MALDI, SIN): m/z: 1038 $[M]^+$, 1060 $[M+Na]^+$, 1076 $[M+K]^+$.

General procedure for the acidic ether cleavage and the generation of the benzylic bromides.

0.2 mmol of the corresponding intermediate (**9**: 88 mg, **10**: 96 mg, **11**: 181 mg, **12**: 207 mg) was dissolved in 50 mL of CH_2Cl_2. 30 mL of a 33%-solution of HBr in glacial acetic acid was added and the mixture stirred overnight at room temperature. The reaction mixture was quenched with water and neutralized with a saturated Na_2CO_3-solution. At pH 7 the desired

product precipitated as a white solid. The precipitate was filtered and washed with water and CH_2Cl_2. It was dissolved with THF and precipitated again with pentane.

N-(3-(bromomethyl)phenyl)-3,4-dihydroxybenzamide (13). Yield: 61 mg (0.19 mmol, 95%). ^{1}H-NMR (THF-d_8, 400 MHz, RT): δ [ppm] = 4.55 (s, 2H, CH_2Br), 6.77 (d, ^3J = 8.2 Hz, 1H, Cat-*H*), 7.01 (d, ^3J = 7.7 Hz, 1H, *p*-Ar-*H*), 7.23 (t, ^3J = 7.9 Hz, 1H, *m*-Ar-*H*), 7.32 (dd, ^4J = 2.1 Hz, ^3J = 8.2 Hz, 1H, Cat-*H*), 7.40 (d, ^4J = 2.1 Hz, 1H, Cat-*H*), 7.72 (d, ^3J = 8.2 Hz, 1H, *o*-Ar-*H*), 7.88 (t, ^4J = 2.1 Hz, 1H, *o*-Ar-*H*), 8.68 (s, 1H, O*H*), 8.81 (s, 1H, O*H*), 9.30 (s, 1H, N*H*). ^{13}C-NMR (THF-d_8, 100.5 MHz, RT): δ [ppm] = 34.3 (1C, *C*H_2Br), 115.3 (1C, Cat-*C*H), 115.8 (1C, Cat-*C*H), 120.2 (1C, *o*-Ar-*C*H), 120.6 (1C, *o*-Ar-*C*H), 121.3 (1C, Cat-*C*H), 124.4 (1C, *p*-Ar-*C*H), 127.7 (1C, *m*-Ar-*C*H), 129.5 (1C, Cat-*C*), 139.5 (1C, *i*-Ar-*C*), 141.4 (1C, *m*-Ar-*C*), 146.2 (1C, Cat-*C*-O), 150.1 (1C, Cat-*C*-O), 166.1 (1C, NH*C*=O). MS (MALDI, SIN): m/z: 322 $[M]^+$, 344 $[M+Na]^+$, 362 $[M+K]^+$.

N-(3,5-bis(bromomethyl)phenyl)-3,4-dihydroxybenzamide (14). Yield: 80 mg (0.19 mmol, 96%). ^{1}H-NMR (THF-d_8, 400 MHz, RT): δ [ppm] = 4.55 (s, 4H, CH_2Br), 6.77 (d, ^3J = 8.2 Hz, 1H, Cat-*H*), 7.16 (t, ^4J = 1.5 Hz, 1H, *p*-Ar-*H*), 7.32 (dd, ^4J = 2.2 Hz, ^3J = 8.2 Hz, 1H, Cat-*H*), 7.40 (d, ^4J = 2.2 Hz, 1H, Cat-*H*), 7.82 (d, ^4J = 1.6 Hz, 2H, *o*-Ar-*H*), 8.45 (s, 1H, O*H*), 8.63 (s, 1H, O*H*), 9.27 (s, 1H, N*H*). ^{13}C-NMR (THF-d_8, 100.5 MHz, RT): δ [ppm] = 33.8 (2C, *C*H_2Br), 115.3 (1C, Cat-*C*H), 115.9 (1C, Cat-*C*H), 120.3 (1C, Cat-*C*H), 121.2 (2C, *o*-Ar-*C*H), 125.1 (1C, *p*-Ar-*C*H), 127.7 (1C, Cat-*C*), 140.1 (2C, *m*-Ar-*C*), 141.7 (1C, *i*-Ar-*C*), 146.2 (1C, Cat-*C*-O), 150.1 (1C, Cat-*C*-O), 166.0 (1C, NH*C*=O). EA: calculated for $C_{15}H_{13}Br_2NO_3$ *2/3 H_2O *1/3 THF (451): C 43.49; H 3.80; N 3.10; found: C 43.40, H 3.77, N 3.17. MS (MALDI, OM): m/z: 438 $[M+Na]^+$, 466 $[M+K]^+$.

N1,N7-bis(3-(bromomethyl)phenyl)-4-(3-(3-(bromomethyl)phenylamino)-3-oxopropyl)-4-(3,4-dihydroxybenzamido)heptanediamide (15). Yield: 169 mg (0.19 mmol, 95%). ^{1}H-NMR (THF-d_8, 400 MHz, RT): δ [ppm] = 2.27 (m, 6H, CH_2CH_2C=O), 2.47 (m, 6H, CH$_2$CH_2C=O), 4.50 (s, 6H, CH_2Br), 6.69 (d, ^3J = 8.3 Hz, 1H, Cat-*H*), 7.03 (d, ^3J = 7.6 Hz, 3H, *p*-Ar-*H*), 7.18 (t, ^3J = 7.9 Hz, 3H, *m*-Ar-*H*), 7.28 (dd, ^4J = 2.2 Hz, ^3J = 8.3 Hz, 1H, Cat-*H*), 7.38 (br s, 1H, N*H*), 7.40 (d, ^4J = 2.1 Hz, 1H, Cat-*H*), 7.54 (d, ^3J = 8.2 Hz, 3H, *o*-Ar-*H*), 7.72 (t, ^4J = 1.8 Hz, 3H, *o*-Ar-*H*), 8.37 (br s, 2H, O*H*), 9.37 (s, 3H, N*H*). ^{13}C-NMR (THF-d_8, 100.5 MHz, RT): δ [ppm] = 31.7 (3C, *C*H_2CH$_2$C=O), 32.7 (3C, CH$_2$*C*H_2C=O), 34.2 (3C, *C*H_2Br), 58.8 (*C*-NH), 115.2 (1C, Cat-*C*H), 115.8 (1C, Cat-*C*H), 119.9 (3C, *o*-Ar-*C*H), 120.2 (1C, Cat-*C*H), 120.7 (3C, *o*-Ar-*C*H), 124.5 (3C, *p*-Ar-*C*H), 128.2 (1C, Cat-*C*), 129.7 (3C, *m*-Ar-*C*H), 139.7 (3C, *i*-Ar-*C*), 141.1 (3C, *m*-Ar-*C*), 146.0 (1C, Cat-*C*-O), 149.5 (1C, Cat-*C*-O), 167.4 (1C, NH*C*=O), 172.5 (3C, NH*C*=O). MS (MALDI, DHB): m/z: 887 $[M]^+$.

N1,N7-bis(3,5-bis(bromomethyl)phenyl)-4-(3-(3,5-bis(bromomethyl) phenylamino)-3-oxopropyl)-4-(3,4-dihydroxybenzamido)heptanediamide (16). Yield: 222 mg (0.19 mmol, 96%). ^{1}H-NMR (THF-d_8, 400 MHz, RT): δ [ppm] = 2.28 (m, 6H, CH_2CH$_2$C=O), 2.48 (m, 6H, CH$_2$CH_2C=O), 4.49 (s, 12H, CH_2Br), 6.70 (d, ^{3}J = 8.2 Hz, 1H, Cat-*H*), 7.13 (s, 3H, *p*-Ar-*H*), 7.27 (dd, ^{4}J = 1.9 Hz, ^{3}J = 8.2 Hz, 1H, Cat-*H*), 7.40 (m, 2H, N*H*, Cat-*H*), 7.82 (d, ^{4}J = 1.2 Hz, 6H, *o*-Ar-*H*), 8.29 (s, 1H, O*H*), 8.46 (s, 1H, O*H*), 9.50 (s, 3H, N*H*). ^{13}C-NMR ($CDCl_3$, 100.5 MHz, RT): δ [ppm] = 31.7 (3C, *C*H$_2$CH$_2$C=O), 32.3 (3C, CH$_2$*C*H$_2$C=O), 33.7 (6C, *C*H$_2$Br), 58.8 (1C, *C*-NH), 115.2 (1C, Cat-*C*H), 115.8 (1C, Cat-*C*H), 120.2 (1C, Cat-*C*H), 120.6 (6C, *o*-Ar-*C*H), 125.2 (3C, *p*-Ar-*C*H), 128.0 (1C, Cat-*C*), 140.2 (6C, *m*-Ar-*C*), 141.3 (3C, *i*-Ar-*C*), 146.0 (1C, Cat-*C*-O), 149.5 (1C, Cat-*C*-O), 167.6 (1C, NH*C*=O), 172.7 (3C, NH*C*=O). MS (MALDI, SIN): m/z: 1189 $[M+Na]^+$.

General procedure for the quarternization reaction of the benzylic bromides with *tert*-butylpyridine. 0.16 mmol of the corresponding bromide (**13**: 52 mg, **14**: 66 mg, **15**: 142 mg, **16**: 187 mg) was dissolved either in 50 mL of dry THF (for **13** and **14**) or in 50 mL of dry DMF (for **15** and **16**). Four equivalents of 4-*tert*-butylpyridine per to be substituted bromide were added to the solution (13: 0.1 mL, 0.64 mmol; 14: 0.2 mL, 1.28 mmol; 15: 0.3 mL, 1.92 mmol; 16: 0.6 mL, 3.84 mmol). The solution was stirred at 60°C for eight hours. The solvent was evaporated and the residue was reprecipitated three times from a MeOH/Diethylether mixture to obtain a yellowish solid.

4-*tert*-butyl-1-(3-(3,4-dihydroxybenzamido)benzyl)pyridinium bromide (17). Yield: 67 mg (0.15 mmol, 92%). ^{1}H-NMR (MeOD-d_4, 400 MHz, RT): δ [ppm] = 1.44 (s, 9H, C(CH_3)$_3$), 5.80 (s, 2H, CH_2NC$_5$H$_4$), 6.85 (d, ^{3}J = 8.2 Hz, 1H, Cat-*H*), 7.26 (d, ^{3}J = 7.5 Hz, 1H, *p*-Ar-*H*), 7.36 (m, 2H, Cat-*H*), 7.45 (t, ^{3}J = 7.9 Hz, 1H, *m*-Ar-*H*), 7.62 (d, ^{3}J = 8.1 Hz, 1H, *o*-Ar-*H*), 7.94 (s, 1H, *o*-Ar-*H*), 8.16 (d, ^{3}J = 6.2 Hz, 2H, *m*-Pyr-*H*), 8.94 (d, ^{3}J = 6.3 Hz, 2H, *o*-Pyr-*H*). ^{13}C-NMR (MeOD-d_4, 100.5 MHz, RT): δ [ppm] = 30.2 (3C, C(*C*H$_3$)$_3$), 37.7 (1C, *C*(CH$_3$)$_3$), 64.8 (1C, *C*H$_2$ NC$_5$H$_4$), 116.0 (1C, Cat-*C*H), 116.2 (1C, Cat-*C*H), 121.2 (1C, *o*-Ar-*C*H), 122.5 (1C, *o*-Ar-*C*H), 123.4 (1C, Cat-*C*H), 125.6 (1C, *p*-Ar-*C*H), 127.0 (2C, *o*-Pyr-*C*H), 127.2 (1C, *m*-Ar-*C*H), 131.3 (1C, Cat-*C*), 135.4 (1C, *m*-Ar-*C*), 141.6 (1C, *i*-Ar-*C*), 145.4 (2C, *m*-Pyr-*C*H), 146.7 (1C, Cat-*C*-O), 150.9 (1C, Cat-*C*-O), 169.1 (1C, NH*C*=O), 173.6 (1C, *p*-Pyr-*C*). EA: calculated for $C_{30}H_{27}NO_5$ * H_2O *1/2 MeOH (491): C 57.44; H 5.95; N 5.70; found: C 57.27, H 5.85, N 5.66. MS (MALDI, OM): m/z: 377 $[M-Br]^+$.

1,1'-(5-(3,4-dihydroxybenzamido)-1,3-phenylene)bis(methylene)bis(4-*tert*-butylpyridinium) bromide (18). Yield: 102 mg (0.15 mmol, 93 %).^{1}H-NMR (MeOD-d_4, 400 MHz, RT): δ [ppm] = 1.39 (s, 18H, C(CH_3)$_3$), 5.80 (s, 4H, CH_2NC$_5$H$_4$), 6.79 (d, ^{3}J = 8.2 Hz,

1H, Cat-*H*), 7.29 (m, 2H, Cat-*H*), 7.49 (s, 1H, *p*-Ar-*H*), 7.81 (s, 2H, *o*-Ar-*H*), 8.13 (d, ^3J = 7.1 Hz, 4H, *m*-Pyr-*H*), 8.95 (d, ^3J = 7.0 Hz, 4H, *o*-Pyr-*H*). ^{13}C-NMR (MeOD-d_4, 100.5 MHz, RT): δ [ppm] = 30.2 (6C, C(CH$_3$)$_3$), 37.7 (1C, C(CH$_3$)$_3$), 64.2 (2C, CH$_2$NC$_5$H$_4$), 116.0 (1C, Cat-*C*H), 116.2 (1C, Cat-*C*H), 121.3 (1C, Cat-*C*H), 123.2 (2C, *o*-Ar-*C*H), 126.0 (1C, *p*-Ar-*C*H), 126.8 (1C, Cat-*C*), 127.1 (4C, *o*-Pyr-*C*H), 136.9 (2C, *m*-Ar-*C*), 142.6 (1C, *i*-Ar-*C*), 145.6 (4C, *m*-Pyr-*C*H), 146.7 (1C, Cat-*C*-O), 151.1 (1C, Cat-*C*-O), 168.0 (1C, NH*C*=O), 173.7 (2C, *p*-Pyr-*C*). EA: calculated for $C_{33}H_{39}Br_2N_3O_3$ *8/3 H_2O *MeOH (766): C 53.34; H 6.36; N 5.49; found: C 53.30, H 6.13, N 5.22. MS (MALDI, DHB): m/z: 530 $[M\text{-}2Br\text{-}2OH+K]^{2+}$.

N1,N7-bis(3-(4-*tert*-butyl-pyridium-methyl)phenyl)-4-(3-(3-(4-*tert*-butyl-pyridinium-methyl)phenylamino)-3-oxopropyl)-4-(3,4-dihydroxybenzamido)heptanediamide tribromide (19). Yield: 186 mg (0.14 mmol, 90 %). ^{1}H-NMR (MeOD-d_4, 400 MHz, RT): δ [ppm] = 1.39 (s, 27H, C(CH_3)$_3$), 2.24 (m, 6H, CH_2CH$_2$C=O), 2.47 (m, 6H, CH$_2$CH_2C=O), 5.70 (s, 6H, CH_2NC$_5$H$_4$), 6.64 (d, ^3J = 8.3 Hz, 1H, Cat-*H*), 7.14 (m, 4H, *p*-Ar-*H*, Cat-*H*), 7.21 (d, ^4J = 2.1 Hz, 1H, Cat-*H*), 7.31 (t, ^3J = 7.9 Hz, 3H, *m*-Ar-*H*), 7.49 (d, ^3J = 8.2 Hz, 3H, *o*-Ar-*H*), 7.74 (s, 3H, *o*-Ar-*H*), 8.08 (d, ^3J = 7.1 Hz, 6H, *m*-Pyr-*H*), 8.85 (d, ^3J = 7.0 Hz, 6H, *o*-Pyr-*H*). ^{13}C-NMR (MeOD-d_4, 100.5 MHz, RT): δ [ppm] = 30.2 (9C, C(CH$_3$)$_3$), 31.8 (3C, CH$_2$CH$_2$C=O), 32.5 (3C, CH$_2$$CH_2$C=O), 37.7 (3C, C(CH$_3$)$_3$), 59.6 (*C*-NH), 64.7 (3C, CH$_2$NC$_5$H$_4$), 115.8 (1C, Cat-*C*H), 116.1 (1C, Cat-*C*H), 121.2 (1C, Cat-*C*H), 121.5 (3C, *o*-Ar-*C*H), 122.4 (3C, *o*-Ar-*C*H), 125.4 (3C, *p*-Ar-*C*H), 127.1 (6C, *o*-Pyr-*C*H), 128.0 (1C, Cat-*C*), 131.3 (3C, *m*-Ar-*C*H), 135.5 (3C, *m*-Ar-*C*), 141.3 (3C, *i*-Ar-*C*), 145.4 (6C, *m*-Pyr-*C*H), 146.2 (1C, Cat-*C*-O), 150.1 (1C, Cat-*C*-O), 170.1 (1C, NH*C*=O), 173.5 (3C, *p*-Pyr-*C*), 174.6 (3C, NH*C*=O). MS (MALDI, DCTB): m/z: 1133 $[M\text{-}2Br]^{2+}$, 1057 $[M\text{-}3Br\text{-}2OH+K]^{3+}$.

N1,N7-bis(3,5-bis(4-*tert*-butyl-pyridium-methyl)phenyl)-4-(3-(3,5-bis(4-*tert*-butyl-pyridinium-methyl)phenylamino)-3-oxopropyl)-4-(3,4-dihydroxybenzamido) heptanediamide hexabromide (20). Yield: 288 mg (0.15 mmol, 91 %). ^{1}H-NMR (MeOD-d_4, 400 MHz, RT): δ [ppm] = 1.38 (s, 54H, C(CH_3)$_3$), 2.25 (m, 6H, CH_2CH$_2$C=O), 2.46 (m, 6H, CH$_2$CH_2C=O), 5.76 (s, 12H, CH_2NC$_5$H$_4$), 6.59 (m, 1H, Cat-*H*), 7.10 (m, 1H, Cat-*H*), 7.27 (s, 1H, Cat-*H*), 7.43 (s, 3H, *p*-Ar-*H*), 7.73 (s, 6H, *o*-Ar-*H*), 8.11 (d, ^3J = 6.4 Hz, 12H, *m*-Pyr-*H*), 8.93 (d, ^3J = 6.3 Hz, 12H, *o*-Pyr-*H*). ^{13}C-NMR (MeOD-d_4, 100.5 MHz, RT): δ [ppm] = 30.3 (18C, C(CH$_3$)$_3$), 31.8 (3C, CH$_2$CH$_2$C=O), 32.6 (3C, CH$_2$$CH_2$C=O), 37.7 (6C, C(CH$_3$)$_3$), 59.1 (*C*-NH), 64.1 (3C, CH$_2$NC$_5$H$_4$), 115.6 (1C, Cat-*C*H), 115.8 (1C, Cat-*C*H), 120.1 (6C, *o*-Ar-*C*H), 122.2 (1C, Cat-*C*H), 125.8 (3C, *p*-Ar-*C*H), 127.1 (6C, *o*-Pyr-*C*H), 128.2 (1C, Cat-*C*), 136.9 (6C, *m*-Ar-*C*), 142.2 (3C, *i*-Ar-*C*), 145.6 (12C, *m*-Pyr-*C*H), 147.8 (1C, Cat-*C*-O), 149.6 (1C, Cat-*C*-O), 170.7 (1C, NH*C*=O), 173.6 (6C, *p*-Pyr-*C*), 174.6 (3C, NH*C*=O).