## Supporting Information

## for

# Synthesis of tripodal catecholates and their immobilization on zinc oxide nanoparticles 

Franziska Klitsche ${ }^{1}$, Julian Ramcke ${ }^{1}$, Julia Migenda ${ }^{2}$, Andreas Hensel ${ }^{3}$, Tobias Vossmeyer ${ }^{3}$, Horst Weller ${ }^{3}$, Silvia Gross*2 ${ }^{* 2}$ and Wolfgang Maison*1

Address: ${ }^{1}$ Department of Chemistry, University of Hamburg, Institute of Pharmaceutical and Medicinal Chemistry, Bundesstr. 45, 20146 Hamburg, Germany, ${ }^{2}$ IENI-CNR, Department of Chemical Sciences, University of Padova, INSTM, Via Marzolo 1, 35131 Padova, Italy and ${ }^{3}$ Department of Chemistry, University of Hamburg, Institute of Physical Chemistry, Grindelallee 117, 20146 Hamburg, Germany

Email: Silvia Gross - silvia.gross@unipd.it; Wolfgang Maison - maison@chemie.uni-hamburg.de *Corresponding author

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## Experimental procedures and analytical data for compounds 4, 5, 7-11, 13

General methods: Infrared spectra (IR) of the substances were measured with a Bruker Tensor 37 ATR-FTIR-spectrophotometer. Spectra were recorded from 400 to $4000 \mathrm{~cm}^{-1}$ at room temperature. Mass spectra were obtained with a Micro-TOF-Q instrument equipped with an ESI-source. Measurements were conducted in positive or negative mode. NMR spectra were recorded on a Bruker FOURIER 300 at 300 $\mathrm{MHz}\left({ }^{1} \mathrm{H}\right)$, and $75 \mathrm{MHz}\left({ }^{13} \mathrm{C}\right)$. The spectra were referenced to residual non-deuterated solvent signal. The chemical shifts $\delta$ are noted in ppm and the multiplicity of the signals is designated as s (singlet), d (doublet), dd (doublet of doublet), t (triplet), q (quartet), sext (sextet) and $m$ (multiplet). Signal identification was carried out with adequate 1D and 2D-NMR experiments (e.g., HSQC, HMBC and COSY). The applied solvents were distilled prior to use and all reagents were reagent grade and used without further purification unless otherwise specified. Column chromatography was carried out in glass columns with the use of silica $(60-200 \mu \mathrm{~m})$ purchased by Macherey-Nagel GmbH \& Co KG with the appropriate mentioned solvent. The determination of the $R_{\mathrm{f}}$-values was performed with thin-layer chromatography on aluminium sheets (ALUGRAM Xtra SIL G/UV 254) purchased by Macherey-Nagel GmbH \& Co KG. The detection of the UV active substances was conducted at a wavelength of 254 nm whereas UV inactive substances were detected with cerium sulfate solution. The poly(ethylene glycol) derivatives were stained with ethanolic sulfuric acid prior to analysis. Melting points were measured with the Büchi M-560 device. The elementary analyses have been performed at an EA 1108 CHNS-O of the manufacturer Carlo Erba through the service devision of the Department of Chemistry at the University of Hamburg.

Acrylamide 4: Triester 1 [1] ( $1.15 \mathrm{~g} ; 2.60 \mathrm{mmol}$ ) was dissolved in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(40 \mathrm{~mL})$ and $\mathrm{NEt}_{3}(4.00 \mathrm{~mL} ; 28.6 \mathrm{mmol})$ were added at $0{ }^{\circ} \mathrm{C}$. The solution was treated with acryloyl chloride ( 0.53 mL ; 6.5 mmol ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(20 \mathrm{~mL})$ over 30 minutes and stirred for 17 h at r . The solution was washed with 2 m aqueous $\mathrm{HCl}(50 \mathrm{~mL})$ dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and the solvent was evaporated. The title compound was obtained as an orange oil ( $1.17 \mathrm{~g} ; 2.52 \mathrm{mmol} ; 97 \%$ ). ${ }^{1} \mathrm{H}-\mathrm{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=6.17$ (dd, $1 \mathrm{H},{ }^{2} J_{\mathrm{H}, \mathrm{H}}=1.9 \mathrm{~Hz},{ }^{3} J_{\mathrm{H}, \mathrm{H}}=17.1 \mathrm{~Hz}, 11[\mathrm{E}$ to 10$\left.]-\mathrm{H}\right) ; 5.98\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=10.2 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}\right.$ $=17.1 \mathrm{~Hz}, 10-\mathrm{H}) ; 5.53\left(\mathrm{dd}, 1 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=1.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=10.2 \mathrm{~Hz}, 11[\mathrm{Z}\right.$ to 10$\left.]-\mathrm{H}\right) ; 3.61(\mathrm{~s}$, $9 \mathrm{H}, 8-\mathrm{H}) ; 2.22\left(\mathrm{t}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=8.1 \mathrm{~Hz}, 6-\mathrm{H}\right) ; 1.63(\mathrm{~s}, 6 \mathrm{H}, 2-\mathrm{H}) ; 1.49\left(\mathrm{t}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=8.1\right.$ $\mathrm{Hz}, 5-\mathrm{H}) ; 1.13\left(\mathrm{~d}, 3 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=12.0 \mathrm{~Hz} 4 \mathrm{a}-\mathrm{H}\right) ; 1.02\left(\mathrm{~d}, 3 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=12.0 \mathrm{~Hz} 4 \mathrm{~b}-\mathrm{H}\right) .{ }^{13} \mathrm{C}-$ NMR (75 MHz, $\mathrm{CDCl}_{3}$ ): $\delta=174.5$ (C7); 164.8 (C9); 131.7 (C11); 126.0 (C10); 53.9 (C8); 51.7 (C1); 45.1 (C4); 44.6 (C2); 37.4 (C5); 34.8 (C3); 28.1 (C6). HRMS-ESI: $m / z \quad[\mathrm{M}+\mathrm{Na}]^{+}=$calc. $\mathrm{C}_{25} \mathrm{H}_{37} \mathrm{NO}_{7} \mathrm{Na}^{+}, 486.2468 ;$ found 486.2468. $R_{\mathrm{f}}: 0.80$ $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{MeOH} ; 9: 1 ; \mathrm{v} / \mathrm{v}\right)$.

Triacid 5: Acrylamide 4 ( 250 mg ; 0.539 mmol ) were dissolved in water ( 50 mL ). Dimethylammonium chloride ( $88.0 \mathrm{mg} ; 1.08 \mathrm{mmol}$ ), KOH ( $305 \mathrm{mg} ; 5.40 \mathrm{mmol}$ ) and CsF ( 8.0 mg ; $54 \mu \mathrm{~mol}$ ) were added and stirred for 17 h at rt . The solution was treated with 1 m aqueous HCl to adjust a pH -value of 1 . After freeze-drying the crude product was dissolved in THF ( 50 mL ), stirred for 5 minutes at $40^{\circ} \mathrm{C}$, filtered and the solvent was evaporated. The title compound was obtained as a yellow solid (204 mg; 437 $\mu \mathrm{mol} ; 81 \%$ ). ${ }^{1} \mathrm{H}-\mathrm{NMR}\left(300 \mathrm{MHz}\right.$, Methanol- $d_{4}$ ): $\delta=3.35\left(\mathrm{t}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=6.7 \mathrm{~Hz}, 9-\mathrm{H}\right.$ ); $2.89(\mathrm{~s}, 6 \mathrm{H}, 11-\mathrm{H}) ; 2.66\left(\mathrm{t}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=6.7 \mathrm{~Hz}, 10-\mathrm{H}\right) ; 2.30\left(\mathrm{t}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=8.1 \mathrm{~Hz}, 6-\mathrm{H}\right)$; $1.64(\mathrm{~s}, 6 \mathrm{H}, 2-\mathrm{H}) ; 1.52\left(\mathrm{t}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=8.1 \mathrm{~Hz}, 5-\mathrm{H}\right) ; 1.18-1.07(\mathrm{~m}, 6 \mathrm{H}, 4-\mathrm{H}) .{ }^{13} \mathrm{C}-\mathrm{NMR}$ (75 MHz, Methanol-d4): $\delta=176.3$ (C7); 171.1 (C8); 55.4 (C1); 55.1 (C10); 46.0 (C4); 45.4 (C2); 43.5 (C11); 38.8 (C5); 35.9 (C3); 30.9 (C9); 28.9 (C6). HRMS-ESI: m/z
$[\mathrm{M}+\mathrm{H}]^{+}=$calc. $\mathrm{C}_{24} \mathrm{H}_{38} \mathrm{~N}_{2} \mathrm{O}_{7} \mathrm{H}^{+}, 467.2752$; found 467.2753. $\mathrm{R}_{\mathrm{f}}: 0.10$ (EtOAc/EtOH; 9:1; $\mathrm{v} / \mathrm{v}$ ).

Protected triscatecholate 7: Triacid 5 ( 160 mg ; $343 \mu \mathrm{~mol}$ ) was dissolved in 20 mL DMF and DIEA ( $N, N$-diisopropylethylamine, $0.10 \mathrm{~mL}, 548 \mu \mathrm{~mol}$ ) were added at $0^{\circ} \mathrm{C}$. The solution was treated with EDC•HCl (217 mg; 1.13 mmol ) and HOBt (153 mg; 1.13 mmol ) in DMF ( 5 mL each). The resulting solution was stirred for 30 min at $0^{\circ} \mathrm{C}$ and 2-(2,2-dimethylbenzo[d][1,3]dioxol-5-yl)ethanamine hydrochloride (6) [2] (260 $\mathrm{mg} ; 1.13 \mathrm{mmol}$ ) in DMF ( 5 mL ) were added. The mixture was stirred for 72 h at rt and the solvent was removed in vacuo. The resulting residue was dissolved in 2 m aqueous $\mathrm{HCl}(50 \mathrm{~mL})$ and extracted three times with EtOAc ( 50 mL each). The combined organics were washed three times with sat. aqueous $\mathrm{KHSO}_{4}$ ( 15 mL each), dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and the solvent was evaporated. The remaining solid was purified by flash chromatography on silica ( $\mathrm{EtOAc} / \mathrm{EtOH}^{2} / \mathrm{NEt}_{3}, 90: 10: 2 \mathrm{v} / \mathrm{v} / \mathrm{v}$ ) to give the title compound ( $266 \mathrm{mg} ; 268 \mu \mathrm{~mol} ; 78 \%$ ) as a yellow solid. ${ }^{1} \mathrm{H}-\mathrm{NMR}(300 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right): \delta=7.77(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}) ; 6.66-6.56(\mathrm{~m}, 9 \mathrm{H}, 15-\mathrm{H}, 18-\mathrm{H}, 19-\mathrm{H}) ; 5.90(\mathrm{~m}, 3 \mathrm{H}$, $\mathrm{NH}) ; 3.45-3.38(\mathrm{~m}, 6 \mathrm{H}, 12-\mathrm{H}) ; 2.77-2.66(\mathrm{~m}, 8 \mathrm{H}, 9-\mathrm{H}, 13-\mathrm{H}) ; 2.41-2.39(\mathrm{~m}, 8 \mathrm{H}$, $10-\mathrm{H}, 11-\mathrm{H}) ; 2.07\left(\mathrm{t}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=7.1 \mathrm{~Hz}, 6-\mathrm{H}\right) ; 1.65(\mathrm{~s}, 18 \mathrm{H}, 21-\mathrm{H}) ; 1.57(\mathrm{~s}, 6 \mathrm{H}, 2-\mathrm{H})$; 1.51-1.45 (m, 6H, 5-H); 1.16-0.99 (m, 6H, 4-H). ${ }^{13} \mathrm{C}-\mathrm{NMR}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ : $\delta=173.5$ (C7); 170.8 (C8); 147.7 (C16); 146.1 (C17); 132.0 (C14); 121.0 (C15); 117.9 (C20); 108.9 (C18); 108.2 (C19); 53.5 (C1); 45.9 (C4); 45.5 (C9); 44.8 (C10); 44.2 (C2); 41.0 (C12); 38.5 (C5); 35.5 (C13); 34.9 (C3); 30.5 (C6); 25.9 (C21). HRMS-ESI: $m / z[M+H]^{+}=$calc. $\mathrm{C}_{57} \mathrm{H}_{77} \mathrm{~N}_{5} \mathrm{O}_{10} \mathrm{H}^{+}$, 992.5743; found 992.5743. HRMSESI: $m / z[\mathrm{M}+\mathrm{Na}]^{+}=$calc. $\mathrm{C}_{57} \mathrm{H}_{77} \mathrm{~N}_{5} \mathrm{O}_{10} \mathrm{Na}^{+}$, 1014.5563; found 1014.5555. Melting point: $126{ }^{\circ} \mathrm{C}$. $R_{\mathrm{f}}: 0.20\left(\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{MeOH}, 9: 1 \mathrm{v} / \mathrm{v}\right)$.

Zwitterionic triscatecholate 8: Protected triscatecholate 7 (100 mg; $102 \mu \mathrm{~mol}$ ) was dissolved in toluene ( 50 mL ), $\mathrm{K}_{2} \mathrm{CO}_{3}(6.9 \mathrm{mg} ; 50 \mu \mathrm{~mol})$, 1,3-propanesultone ( 24 mg ;
0.20 mmol ) and 18 -crown-6 ( $26 \mathrm{mg} ; 0.10 \mathrm{mmol}$ ) were added and stirred for 72 h at $120^{\circ} \mathrm{C}$. The suspension was filtered, the solid dried and dissolved in THF. The suspension was filtered and the solvent was evaporated. The intermediate protected zwitterionic triscatecholate was obtained as a yellow solid (111 mg; $99.6 \mu \mathrm{~mol} ; 98 \%$ ). ${ }^{1} \mathrm{H}-$ NMR (300 MHz, THF-d $): \delta=6.62-6.57(\mathrm{~m}, 9 \mathrm{H}, 18-\mathrm{H}, 21-\mathrm{H}, 22-\mathrm{H}) ; 3.55-3.53$ $(\mathrm{m}, 2 \mathrm{H}, 9-\mathrm{H}) ; 3.24\left(\mathrm{t}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=7.4 \mathrm{~Hz}, 15-\mathrm{H}\right) ; 3.14(\mathrm{~s}, 6 \mathrm{H}, 11-\mathrm{H}) ; 2.86\left(\mathrm{t}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=\right.$ $6.9 \mathrm{~Hz}, 12-\mathrm{H}) ; 2.74-2.69(\mathrm{~m}, 2 \mathrm{H}, 10-\mathrm{H}) ; 2.62\left(\mathrm{t}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=7.4 \mathrm{~Hz}, 16-\mathrm{H}\right) ; 2.54(\mathrm{t}$, $\left.2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=6.7 \mathrm{~Hz}, 14-\mathrm{H}\right) ; 2.24-2.18(\mathrm{~m}, 2 \mathrm{H}, 13-\mathrm{H}) ; 2.14-2.08(\mathrm{~m}, 6 \mathrm{H}, 6-\mathrm{H}) ; 1.64(\mathrm{~s}$, $6 \mathrm{H}, 2-\mathrm{H}) ; 1.57(\mathrm{~s}, 18 \mathrm{H}, 24-\mathrm{H}) ; 1.48-1.42(\mathrm{~m}, 6 \mathrm{H}, 5-\mathrm{H}) ; 1.19\left(\mathrm{~d}, 3 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=11.8 \mathrm{~Hz}\right.$ $4 \mathrm{a}-\mathrm{H}) ; 1.03\left(\mathrm{~d}, 3 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=11.8 \mathrm{~Hz} 4 \mathrm{~b}-\mathrm{H}\right) .{ }^{13} \mathrm{C}-\mathrm{NMR}\left(75 \mathrm{MHz}, \mathrm{THF}-\mathrm{d}_{8}\right): \delta=175.9$ (C7); 170.1 (C8); 148.4 (C19); 146.7 (C20); 133.9 (C17); 122.1 (C18); 118.4 (C23); 109.9 (C21); 108.5 (C22); 71.4 (C10); 71.3 (C12); 54.8 (C1); 51.8 (C11); 48.5 (C9); 46.3 (C4); 44.9 (C2); 42.1 (C15); 39.9 (C5); 36.3 (C16); 35.8 (C3); 31.0 (C6); 30.0 (C24); 24.7 (C14); 19.6 (C13). HRMS-ESI: $m / z[\mathrm{M}+\mathrm{H}]^{+}=$calc. $\mathrm{C}_{60} \mathrm{H}_{83} \mathrm{~N}_{5} \mathrm{O}_{13} \mathrm{SH}^{+}$, 1114.5768; found 1114.5760. HRMS-ESI: $\mathrm{m} / \mathrm{z}[\mathrm{M}+2 \mathrm{H}]^{2+}=$ calc. $\mathrm{C}_{60} \mathrm{H}_{83} \mathrm{~N}_{5} \mathrm{O}_{13} \mathrm{SH}_{2}{ }^{2+}$, 557.7932; found 557.7931. Melting point: $281^{\circ} \mathrm{C}$ (dec.). $R_{\mathrm{f}}: 0.30\left(\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{MeOH}, 9: 1\right.$ $\mathrm{v} / \mathrm{v}$ ).

This intermediate (20 mg; $18 \mu \mathrm{~mol}$ ) was suspended in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$, TFA ( 1.0 mL ) was added and stirred for 24 h at rt . The solvent was evaporated under reduced pressure. The title compound 8 was obtained as a yellow solid ( $18 \mathrm{mg} ; 18 \mu \mathrm{~mol}$; $100 \%$ ). ${ }^{1} \mathrm{H}-\mathrm{NMR}\left(300 \mathrm{MHz}, \mathrm{DMSO}-d_{6}\right): \delta=8.73(\mathrm{~s}, 6 \mathrm{H}, \mathrm{OH}) ; 7.87-7.83(\mathrm{~m}, 3 \mathrm{H}, \mathrm{NH})$; $7.72-7.68(\mathrm{~m}, 1 \mathrm{H}, \mathrm{NH}) ; 6.63\left(\mathrm{~d}, 3 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=7.9 \mathrm{~Hz}, 21-\mathrm{H}\right) ; 6.42\left(\mathrm{~d}, 3 \mathrm{H},{ }^{4} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=1.8 \mathrm{~Hz}\right.$, $18-\mathrm{H}) ; 6.40\left(\mathrm{dd}, 3 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=7.9 \mathrm{~Hz},{ }^{4} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=1.8 \mathrm{~Hz}, 22-\mathrm{H}\right) ; 3.50\left(\mathrm{t}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=6.5 \mathrm{~Hz}\right.$, 9-H); 3.16-3.10(m, 6H, 15-H); 3.00-2.95 (m, 6H, 11-H); 2.50-2.46 (m, 6H, 16-H); 2.04-1.90(m, 8H, 6-H, 14-H); 1.58-1.47 (m, 6H, 10-H, 12-H, 13-H); 1.37-1.23(m,
$12 \mathrm{H}, 2-\mathrm{H}, 5-\mathrm{H}) ; 1.08-0.97(\mathrm{~m}, 6 \mathrm{H}, 4-\mathrm{H}) .{ }^{13} \mathrm{C}-\mathrm{NMR}\left(75 \mathrm{MHz}, \mathrm{DMSO}-\mathrm{d}_{6}\right): \delta=172.4$ (C7); 168.8 (C8); 145.0 (C19); 143.4 (C20); 130.2 (C17); 119.1 (C18); 115.9 (C21); 115.4 (C22); 69.8 (C10); 67.0 (C12); 53.2 (C1); 50.7 (C11); 49.8 (C9); 46.7 (C4); 45.0 (C2); 40.5 (C15); 34.6 (C5); 34.4 (C16); 29.8 (C3); 29.5 (C6); 22.4 (C14); 13.9 (C13). HRMS-ESI: $m / z[\mathrm{M}+\mathrm{H}]^{+}=$calc. $\mathrm{C}_{51} \mathrm{H}_{71} \mathrm{~N}_{5} \mathrm{O}_{13} \mathrm{SH}^{+}$, 994.4847; found 994.4822. MS-ESI $m / z$ (\%): 994.47 (14) $[\mathrm{M}+\mathrm{H}]^{+} ; 1016.45$ (8) $[\mathrm{M}+\mathrm{Na}]^{+}$. Melting point: $296{ }^{\circ} \mathrm{C}$ (dec.). $R_{\mathrm{f}}: 0.15\left(\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{MeOH}, 9: 1 \mathrm{v} / \mathrm{v}\right)$.

Adamantyl triacid 9: Triester 1 [1] ( $1.00 \mathrm{~g} ; 2.24 \mathrm{mmol}$ ) was dissolved in THF ( 400 mL ) and treated with EDC $\cdot \mathrm{HCl}$ ( $865 \mathrm{mg} ; 4.52 \mathrm{mmol}$ ), DMAP ( $55 \mathrm{mg} ; 45 \mu \mathrm{~mol}$ ) and 1-(2-carboxyethyl)adamantane [3] ( $416 \mathrm{mg} ; 1.99 \mathrm{mmol}$ ). The resulting solution was stirred for 72 h at rt and the solvent was evaporated under reduced pressure. The resulting residue was dissolved in 2 m aqueous $\mathrm{HCl}(50 \mathrm{~mL})$ and extracted three times with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ( 50 mL each). The combined organics were washed two times with sat. aqueous $\mathrm{KHSO}_{4}$ ( 50 mL each) and water ( 50 mL ). The organic layer was dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and the solvent was evaporated in vacuo. The remaining solid was purified by flash chromatography on silica $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$ to give the intermediate adamantyl triester ( $1.15 \mathrm{~g} ; 1.92 \mathrm{mmol} ; 96 \%$ ) as a colorless solid. ${ }^{1} \mathrm{H}-\mathrm{NMR}(300 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right): \delta=5.16(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}) ; 3.64(\mathrm{~s}, 9 \mathrm{H}, 15-\mathrm{H}) ; 2.24\left(\mathrm{t}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=8.0 \mathrm{~Hz}, 6-\mathrm{H}\right) ; 2.03$ - 1.98 (m, 2H, 9-H); $1.92(\mathrm{~s}, 3 \mathrm{H} ; 13-\mathrm{H}) ; 1.74\left(\mathrm{~d}, 3 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=12.1 \mathrm{~Hz}, 12 \mathrm{a}-\mathrm{H}\right) ; 1.63-$ $1.56(\mathrm{~m}, 9 \mathrm{H}, 2-\mathrm{H}, 12 \mathrm{~b}-\mathrm{H}) ; 1.54\left(\mathrm{t}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=8.0 \mathrm{~Hz}, 5-\mathrm{H}\right) ; 1.43(\mathrm{~s}, 6 \mathrm{H}, 14-\mathrm{H}) ; 1.36-$ $1.30(\mathrm{~m}, 2 \mathrm{H}, 10-\mathrm{H}) ; 1.13\left(\mathrm{~d}, 3 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=11.9 \mathrm{~Hz}, 4 \mathrm{a}-\mathrm{H}\right) ; 1.02\left(\mathrm{~d}, 3 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=11.9 \mathrm{~Hz}\right.$, 4b-H). ${ }^{13} \mathrm{C}-$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=174.5$ (C7); 173.6 (C8); 53.7 (C1); 51.7 (C11); 45.1 (C4); 44.8 (C2); 42.2 (C13); 39.9 (C3); 37.5 (C12); 37.1 (C14); 34.9 (C15); 32.0 (C5); 31.2 (C10); 28.7 (C6); 28.1 (C9). HRMS-ESI: $m / z[\mathrm{M}+\mathrm{H}]^{+}=$calc. $\mathrm{C}_{35} \mathrm{H}_{53} \mathrm{NO}_{7} \mathrm{H}^{+}$, 600.3900; found 600.3904. HRMS-ESI: $\mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{Na}]^{+}=$calc. $\mathrm{C}_{35} \mathrm{H}_{53} \mathrm{NO}_{7} \mathrm{Na}^{+}$,
622.3720; found 622.3722. CHN: calc. $\mathrm{C}_{35} \mathrm{H}_{53} \mathrm{NO}_{7} \mathrm{C}: 70.09, \mathrm{H}: 8.91, \mathrm{~N}: 2.34$; found $\mathrm{C}: 69.30, \mathrm{H}: 8.85, \mathrm{~N}: 1.94$. Melting point: $101^{\circ} \mathrm{C}$. $R_{\mathrm{f}}: 0.20\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$.

This intermediate ( 552 mg ; 0.921 mmol ) was dissolved in THF $(80 \mathrm{~mL}$ ), treated with KOTMS (potassium trimethylsilanolate; $1.06 \mathrm{~g} ; 8.29 \mathrm{mmol}$ ) and stirred for 20 h at rt . The solvent was evaporated in vacuo and the residue was dissolved in 2 M aqueous HCl and extracted four times with EtOAc ( 50 mL each). The combined organics were dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and the solvent was evaporated. The title compound 9 was obtained as a colorless solid ( $483 \mathrm{mg} ; 867 \mu \mathrm{~mol} ; 94 \%$ ). ${ }^{1} \mathrm{H}-\mathrm{NMR}(300 \mathrm{MHz}$, Methanol- $d_{4}$ ): $\delta=7.46(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}) ; 2.27\left(\mathrm{t}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=8.0 \mathrm{~Hz}, 6-\mathrm{H}\right) ; 2.10-2.05(\mathrm{~m}$, $2 \mathrm{H}, 9-\mathrm{H}) ; 1.95(\mathrm{~s}, 3 \mathrm{H} ; 13-\mathrm{H}) ; 1.75\left(\mathrm{~d}, 3 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=12.3 \mathrm{~Hz}, 12 \mathrm{a}-\mathrm{H}\right) ; 1.69-1.64(\mathrm{~m}, 9 \mathrm{H}$, 2-H, 12b-H); 1.55-1.51 (m, 12H, 5-H, 14-H); 1.37-1.31 (m, 2H, 10-H); 1.19 (d, 3H, $\left.{ }^{2} J_{\mathrm{H}, \mathrm{H}}=12.2 \mathrm{~Hz}, 4 \mathrm{a}-\mathrm{H}\right) ; 1.12\left(\mathrm{~d}, 3 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=12.2 \mathrm{~Hz}, 4 \mathrm{~b}-\mathrm{H}\right) .{ }^{13} \mathbf{C}-\mathbf{N M R}(75 \mathrm{MHz}$, Methanol- $d_{4}$ ): $\delta=178.1$ (C7); 176.9 (C8); 54.6 (C1); 46.2 (C4); 45.5 (C2); 43.2 (C12); 41.5 (C11); 39.0 (C3); 38.2 (C13); 35.8 (C14); 33.1 (C5); 31.7 (C10); 30.1 (C9); 29.0 (C6). HRMS-ESI: $m / z[M+H]^{+}=$calc. $\mathrm{C}_{32} \mathrm{H}_{47} \mathrm{NO}_{7} \mathrm{H}^{+}, 558.3431$; found 558.3424 . HRMS-ESI: $m / z[M+N a]^{+}=$calc. $\mathrm{C}_{32} \mathrm{H}_{47} \mathrm{NO}_{7} \mathrm{Na}^{+}, 580.3250$; found 580.3242. CHN: calc. $\mathrm{C}_{32} \mathrm{H}_{47} \mathrm{NO}_{7} \mathrm{C}: 68.91, \mathrm{H}: 8.49, \mathrm{~N}: 2.51$; found $\mathrm{C}: 69.00, \mathrm{H}: 8.44, \mathrm{~N}: 2.47$. Melting point: $123{ }^{\circ} \mathrm{C}$. $R_{\mathrm{f}}: 0.25\left(\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{MeOH}, 9: 1 \mathrm{v} / \mathrm{v}\right)$.

Adamantyl triscatecholate 10: Adamantyl triacid ( $100 \mathrm{mg} ; 179 \mu \mathrm{~mol}$ ) was dissolved in DMF ( 30 mL ) and DIEA ( $N, N$-diisopropylethylamine, $49.0 \mu \mathrm{~L}, 286 \mu \mathrm{~mol}$ ) were added at $0^{\circ} \mathrm{C}$. The solution was treated with EDC. $\mathrm{HCl}(113 \mathrm{mg} ; 591 \mu \mathrm{~mol})$ and HOBt ( $80.0 \mathrm{mg} ; 591 \mu \mathrm{~mol}$ ) in DMF ( 5 mL each). The resulting solution was stirred for 30 min at $0^{\circ} \mathrm{C}$ and dopamine hydrochloride ( $112 \mathrm{mg} ; 591 \mu \mathrm{~mol}$ ) in DMF ( 10 mL ) were added. The solution was stirred for 72 h at rt and the solvent was evaporated under reduced pressure. The resulting residue was washed two times with 2 m aqueous HCl ( 50 mL each) and two times with EtOAc ( 50 mL each). Freeze drying
gave the title compound ( $161 \mathrm{mg} ; 167 \mu \mathrm{~mol} ; 93 \%$ ) as a colorless solid. ${ }^{1} \mathrm{H}$-NMR (300 MHz , Methanol- $d_{4}$ ): $\delta=6.68\left(\mathrm{~d}, 3 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=8.0 \mathrm{~Hz}, 21-\mathrm{H}\right) ; 6.64\left(\mathrm{~d}, 3 \mathrm{H},{ }^{4} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=1.9 \mathrm{~Hz}\right.$, $18-\mathrm{H}) ; 6.52\left(\mathrm{dd}, 3 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=8.0 \mathrm{~Hz},{ }^{4} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=1.9 \mathrm{~Hz}, 22-\mathrm{H}\right) ; 3.37-3.30(\mathrm{~m}, 6 \mathrm{H}, 15-\mathrm{H})$; $2.64\left(\mathrm{t}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=7.1 \mathrm{~Hz}, 16-\mathrm{H}\right) ; 2.18-2.06(\mathrm{~m}, 8 \mathrm{H}, 6-\mathrm{H}, 9-\mathrm{H}) ; 1.93(\mathrm{~s}, 3 \mathrm{H}, 13-\mathrm{H})$; $1.74\left(\mathrm{~d}, 3 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=12.5 \mathrm{~Hz}, 12 \mathrm{a}-\mathrm{H}\right) ; 1.67-1.61(\mathrm{~m}, 9 \mathrm{H}, 2-\mathrm{H}, 12 \mathrm{~b}-\mathrm{H}) ; 1.47-1.41(\mathrm{~m}$, $12 \mathrm{H}, 4-\mathrm{H}, 14-\mathrm{H}) ; 1.34-1.29(\mathrm{~m}, 2 \mathrm{H}, 10-\mathrm{H}) ; 1.15\left(\mathrm{~d}, 3 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=12.6 \mathrm{~Hz} 4 \mathrm{a}-\mathrm{H}\right) ; 1.05$ (d, 3H, $\left.{ }^{2} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=12.6 \mathrm{~Hz} 4 \mathrm{~b}-\mathrm{H}\right) .{ }^{13} \mathrm{C}-\mathrm{NMR}\left(75 \mathrm{MHz}\right.$, Methanol- $\left.\mathrm{d}_{4}\right): \delta=177.0(\mathrm{C} 7) ; 176.9$ (C8); 146.2 (C19); 144.8 (C20); 131.8 (C17); 121.0 (C18); 116.9 (C21); 116.3 (C22); 55.1 (C1); 46.2 (C4); 45.4 (C2); 43.2 (C12); 42.4 (C14); 41.6 (C13); 40.1 (C15); 38.1 (C5); 36.1 (C11); 35.7 (C16); 34.5 (C3); 31.6 (C10); 30.9 (C9); 30.1 (C6). HRMS-ESI: $\mathrm{m} / \mathrm{z}[\mathrm{M}+\mathrm{H}]^{+}=$calc. $\mathrm{C}_{56} \mathrm{H}_{74} \mathrm{~N}_{4} \mathrm{O}_{10} \mathrm{H}^{+}, 963.5483$; found 963.5499. Melting point: $143{ }^{\circ} \mathrm{C}$. $R_{\mathrm{f}}: 0.10\left(\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{MeOH}, 9: 1 \mathrm{v} / \mathrm{v}\right)$.

Acrylamido triscatecholate 11: Acrylamide 4 ( $1.17 \mathrm{~g} ; 2.52 \mathrm{mmol}$ ) was dissolved in THF ( 80 mL ), treated with KOTMS (potassium trimethylsilanolate; $4.85 \mathrm{~g} ; 37.8 \mathrm{mmol}$ ) and stirred for 17 h at rt . The solvent was evaporated in vacuo and the residue was dissolved in 1 m aqueous HCl and extracted four times with EtOAc ( 50 mL each). The combined organics were dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and the solvent was evaporated. The intermediate triacid was obtained as an orange solid (1.02 g; $2.42 \mathrm{mmol} ; 96 \%$ ). ${ }^{1} \mathrm{H}-$ NMR (300 MHz, DMSO-d $\mathrm{d}_{6}$ ): $\delta=12.02$ (s, $3 \mathrm{H}, \mathrm{COOH}$ ); 7.61 (s, 1H, NH); 6.23 (dd, $\left.1 \mathrm{H},{ }^{3} J_{\mathrm{H}, \mathrm{H}}=10.0 \mathrm{~Hz},{ }^{3} J_{\mathrm{H}, \mathrm{H}}=16.9 \mathrm{~Hz}, 9-\mathrm{H}\right) ; 5.99\left(\mathrm{dd}, 1 \mathrm{H},{ }^{2} J_{\mathrm{H}, \mathrm{H}}=2.2 \mathrm{~Hz},{ }^{3} J_{\mathrm{H}, \mathrm{H}}=16.9\right.$ $\mathrm{Hz}, 10[\mathrm{E}$ to 9$]-\mathrm{H}) ; 5.48\left(\mathrm{dd}, 1 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=2.2 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=10.0 \mathrm{~Hz}, 10[\mathrm{Z}\right.$ to 9$\left.]-\mathrm{H}\right) ; 2.15(\mathrm{t}$, $\left.6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=7.8 \mathrm{~Hz}, 6-\mathrm{H}\right) ; 1.55(\mathrm{~s}, 6 \mathrm{H}, 2-\mathrm{H}) ; 1.39\left(\mathrm{t}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=7.8 \mathrm{~Hz}, 5-\mathrm{H}\right) ; 1.10-$ 0.99 (m, 6H, 4-H). ${ }^{13} \mathrm{C}-\mathrm{NMR}\left(75 \mathrm{MHz}, \mathrm{DMSO}-d_{6}\right): \delta=175.0$ (C7); 163.8 (C8); 132.8 (C10); 124.3 (C9); 52.9 (C1); 44.6 (C4); 44.3 (C2); 37.4 (C5); 34.3 (C3); 27.9 (C6). HRMS-ESI: $m / z[M+H]^{+}=$calc. $\mathrm{C}_{22} \mathrm{H}_{31} \mathrm{NO}_{7} \mathrm{H}^{+}, 422.2173$; found 422.2162. CHN: calc.
$\mathrm{C}_{22} \mathrm{H}_{31} \mathrm{NO}_{7} \mathrm{C}: 62.69, \mathrm{H}: 7.41, \mathrm{~N}: 3.32$; found $\mathrm{C}: 61.42, \mathrm{H}: 7.22, \mathrm{~N}: 3.19$. Melting point: $129^{\circ} \mathrm{C} . R_{\mathrm{f}}: 0.10\left(\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{MeOH} ; 9: 1 ; \mathrm{v} / \mathrm{v}\right)$.

This intermediate ( 240 mg ; $570 \mu \mathrm{~mol}$ ) was dissolved in DMF $(20 \mathrm{~mL})$ and DIEA ( $\mathrm{N}, \mathrm{N}$ diisopropylethylamine, $0.16 \mathrm{~mL}, 0.91 \mathrm{mmol}$ ) were added at $0^{\circ} \mathrm{C}$. The solution was treated with EDC $\cdot \mathrm{HCl}(360 \mathrm{mg} ; 1.88 \mathrm{mmol})$ and $\mathrm{HOBt}(250 \mathrm{mg} ; 1.88 \mathrm{mmol})$ in DMF ( 5 mL each). The resulting solution was stirred for 30 min at $0^{\circ} \mathrm{C}$ and dopamine hydrochloride ( 360 mg ; 1.88 mmol ) in DMF ( 5 mL ) were added. The mixture was stirred for 72 h at rt and the solvent was removed in vacuo. The resulting residue was dissolved in 2 m aqueous $\mathrm{HCl}(50 \mathrm{~mL})$ and extracted three times with EtOAc ( 50 mL each). The combined organics were washed three times with sat. aqueous $\mathrm{KHSO}_{4}$ (20 mL each), dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and the solvent was evaporated. The crude product was suspended in $50 \mathrm{~mL} \mathrm{Et}_{2} \mathrm{O}$ and stirred at $30^{\circ} \mathrm{C}$ for 30 min . The resulting slurry was filtered and the procedure repeated five times to give the title compound 11 ( $344 \mathrm{mg} ; 416 \mu \mathrm{~mol} ; 73 \%$ ) as a colorless solid. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ ( 300 MHz , Methanol- $\mathrm{d}_{4}$ ): $\delta=6.68\left(\mathrm{~d}, 3 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=8.4 \mathrm{~Hz}, 17-\mathrm{H}\right) ; 6.65\left(\mathrm{~d}, 3 \mathrm{H},{ }^{4} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=1.9 \mathrm{~Hz}, 14-\mathrm{H}\right) ; 6.52(\mathrm{dd}, 3 \mathrm{H}$, $\left.{ }^{3} J_{\mathrm{H}, \mathrm{H}}=8.4 \mathrm{~Hz},{ }^{4} J_{\mathrm{H}, \mathrm{H}}=1.9 \mathrm{~Hz}, 18-\mathrm{H}\right) ; 6.25\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{H}, \mathrm{H}}=10.5 \mathrm{~Hz},{ }^{3} \mathrm{~J}=16.9 \mathrm{~Hz}, 9-\right.$ H); 6.13 (dd, $1 \mathrm{H},{ }^{2} J_{\mathrm{H}, \mathrm{H}}=2.2 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=16.9 \mathrm{~Hz}, 10[\mathrm{E}$ to 9$\left.]-\mathrm{H}\right) ; 5.56\left(\mathrm{dd}, 1 \mathrm{H},{ }^{2} J_{\mathrm{H}, \mathrm{H}}=\right.$ $2.2 \mathrm{~Hz},{ }^{3} J_{\mathrm{H}, \mathrm{H}}=10.5 \mathrm{~Hz}, 10[\mathrm{Z}$ to 9$\left.]-\mathrm{H}\right) ; 3.37-3.32(\mathrm{~m}, 6 \mathrm{H}, 11-\mathrm{H}) ; 2.64\left(\mathrm{t}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=\right.$ $7.4 \mathrm{~Hz}, 10-\mathrm{H}) ; 2.17-2.12(\mathrm{~m}, 6 \mathrm{H}, 6-\mathrm{H}) ; 1.64(\mathrm{~s}, 6 \mathrm{H}, 2-\mathrm{H}) ; 1.51-1.44(\mathrm{~m}, 6 \mathrm{H}, 5-\mathrm{H})$; 1.15-1.06 (m, 6H, 4-H). ${ }^{13} \mathbf{C}-$ NMR ( 75 MHz , Methanol- $d_{4}$ ): $\delta=177.0$ (C7); 167.3 (C8); 146.1 (C15); 144.7 (C16); 133.1 (C10); 131.8 (C13); 125.9 (C9); 121.0 (C14); 116.9 (C17); 116.3 (C18); 55.0 (C1); 46.1 (C4); 45.4 (C2); 42.0 (C11); 40.0 (C5); 36.0 (C12); 35.7 (C3); 31.0 (C6). HRMS-ESI: $m / z[M+H]^{+}=$calc. $\mathrm{C}_{46} \mathrm{H}_{58} \mathrm{~N}_{4} \mathrm{O}_{10} \mathrm{H}^{+}, 827.4231$; found 827.4226. HRMS-ESI: $m / z[\mathrm{M}+\mathrm{Na}]^{+}=$calc. $\mathrm{C}_{46} \mathrm{H}_{58} \mathrm{~N}_{4} \mathrm{O}_{10} \mathrm{Na}^{+}$, 849.4051; found 849.4045. Melting point: $97^{\circ} \mathrm{C} . R_{\mathrm{f}}$ : 0.15 (EtOAc/EtOH; 9:1; v/v).

Bromo triscatecholate 13: Bromo triacid 12 [4] (552 mg; 1.28 mmol ) was dissolved in DMF ( 50 mL ) and DIEA ( $N, N$-diisopropylethylamine, $350 \mu \mathrm{~L}$, 2.05 mmol ) was added at $0^{\circ} \mathrm{C}$. The solution was treated with EDC $\cdot \mathrm{HCl}(809 \mathrm{mg} ; 4.22 \mathrm{mmol})$ and HOBt ( $570 \mathrm{mg} ; 4.22 \mathrm{mmol}$ ) in DMF ( 10 mL each). The resulting solution was stirred for 30 min at $0^{\circ} \mathrm{C}$ and dopamine hydrochloride ( $800 \mathrm{mg} ; 4.22 \mathrm{mmol}$ ), in DMF ( 10 mL ) was added. The mixture was stirred for 72 h at rt and the solvent was removed in vacuo. The resulting residue was dissolved in EtOAc ( 200 mL ) and washed three times with 1 m aqueous $\mathrm{HCl}\left(40 \mathrm{~mL}\right.$ each), three times with sat. aqueous $\mathrm{KHSO}_{4}$ ( 100 mL each) and brine ( 50 mL ). The organic layer was dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and the solvent was evaporated in vacuo. The crude product was suspended in 50 $\mathrm{mL} \mathrm{Et} \mathrm{E}_{2} \mathrm{O}$ and stirred at $30^{\circ} \mathrm{C}$ for 30 min . The resulting slurry was filtered and the procedure repeated five times to give the title compound ( $761 \mathrm{mg} ; 909 \mu \mathrm{~mol} ; 71 \%$ ) as a colorless solid. ${ }^{1} \mathrm{H}-\mathrm{NMR}\left(300 \mathrm{MHz}\right.$, Methanol- $\left.\mathrm{d}_{4}\right): \delta=6.68\left(\mathrm{~d}, 3 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=8.1 \mathrm{~Hz}\right.$, $14-\mathrm{H}) ; 6.64\left(\mathrm{~d}, 3 \mathrm{H},{ }^{4} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=1.9 \mathrm{~Hz}, 11-\mathrm{H}\right) ; 6.52\left(\mathrm{dd}, 3 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=8.1 \mathrm{~Hz},{ }^{4} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=1.9 \mathrm{~Hz}\right.$, $15-\mathrm{H}) ; 3.35(\mathrm{~s}, 6 \mathrm{H}, 8-\mathrm{H}) ; 2.63\left(\mathrm{t}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=7.3 \mathrm{~Hz}, 9-\mathrm{H}\right) ; 2.11\left(\mathrm{t}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=8.1 \mathrm{~Hz}\right.$, $6-\mathrm{H}) ; 1.93(\mathrm{~s}, 6 \mathrm{H}, 2-\mathrm{H}) ; 1.45\left(\mathrm{t}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=8.1 \mathrm{~Hz}, 5-\mathrm{H}\right) ; 1.19\left(\mathrm{~d}, 3 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=12.6 \mathrm{~Hz}\right.$, $4 \mathrm{a}-\mathrm{H}) ; 1.10\left(\mathrm{~d}, 3 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=12.6 \mathrm{~Hz}, 4 \mathrm{~b}-\mathrm{H}\right) .{ }^{13} \mathrm{C}-\mathrm{NMR}\left(75 \mathrm{MHz}\right.$, Methanol- $\left.d_{4}\right): \delta=176.5$ (C7); 146.2 (C12); 144.7 (C13); 131.9 (C10); 121.0 (C11); 116.9 (C14); 116.3 (C15); 66.9 (C4); 66.1 (C2); 53.5 (C1); 42.2 (C5); 39.7 (C6); 38.9 (C8); 35.8 (C9); 31.0 (C3). HRMS-ESI: $\mathrm{m} / \mathrm{z}[\mathrm{MH}]^{+}=$calc. $\mathrm{C}_{43} \mathrm{H}_{55} \mathrm{BrN}_{3} \mathrm{O}_{9}{ }^{+}$, 838.3101; found 838.3096. IR: $\mathrm{v} / \mathrm{cm}^{-1}=$ $3276 ; 2926 ; 2848 ; 1625 ; 1520 ; 1444 ; 1247 ; 1193 ; 959 ; 813 . \mathrm{CHN}$ : calc. $\mathrm{C}_{43} \mathrm{H}_{54} \mathrm{BrN}_{3} \mathrm{O}_{9} \mathrm{C}: 61.72, \mathrm{H}: 6.50, \mathrm{~N}: 5.02$; found $\mathrm{C}: 60.96, \mathrm{H}: 6.61, \mathrm{~N}: 4.94$. Melting point: $154{ }^{\circ} \mathrm{C} . \mathrm{R}_{\mathrm{f}}: 0.25$ (EtOAc/EtOH; 9:1; v/v).

NMR spectra



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## Supplementary data and general notices of the immobilization experiments

Immobilization of monomeric PEG-catecholate: 16 mg zinc oxide nanoparticles (NPs) (calculated surface area according to TEM is $2.85 \cdot 10^{18} \mathrm{~nm}^{2}$ ) and 500 mg 1-( $N$-PEG)-dopamine $(0.098 \mathrm{mmol})$ which corresponds to a five-fold excess of molecules (when taking into account that 4 molecules cover $1 \mathrm{~nm}^{2}$ ) were dissolved in 0.3 mL methanol, 0.3 mL water and 6.6 mL MOPS buffer ( pH 10 ), stirred for 12 hours at $40^{\circ} \mathrm{C}$ with sonification, separated by centrifugation and washed one time with methanol ( 5 mL ), water ( 5 mL ) and freeze-dried for 72 h . The data were obtained at different steps of centrifugation and washing according to the notification in the appropriate plot.

Immobilization of tripodal PEG-catecholate: 50 mg zinc oxide nanoparticles (NPs) (calculated surface area according to TEM is $8.91 \cdot 10^{18} \mathrm{~nm}^{2}$ ) and 431 mg PEGTriscatechol ( $74.1 \mu \mathrm{~mol}$ ) which corresponds to a five-fold excess of molecules (when taking into account that 1 molecule covers $1 \mathrm{~nm}^{2}$ ) were dissolved in 1 mL methanol, 1 mL water and 20 mL MOPS buffer $(\mathrm{pH} 10)$, stirred for 12 hours at $40^{\circ} \mathrm{C}$ with sonification, separated by centrifugation and washed one time with methanol ( 5 mL ), water ( 5 mL ) and freeze-dried for 72 h . The data were obtained at different steps of centrifugation and washing according to the notification in the appropriate plot.

Immobilization of bromotriscatecholate: 50 mg zinc oxide nanoparticles (NPs) (calculated surface area according to TEM is $8.91 \cdot 10^{18} \mathrm{~nm}^{2}$ ) and 50 mg of bromotriscatecholate $(59.7 \mu \mathrm{~mol})$ which corresponds to a four-fold excess of molecules (when taking into account that 1 molecule covers $1 \mathrm{~nm}^{2}$ ) were dissolved in 1 mL methanol, 1 mL water and 20 mL MOPS buffer ( pH 10 ), stirred for 12 hours at
$40^{\circ} \mathrm{C}$ with sonification, separated by centrifugation and washed three times with methanol ( 5 mL ), water ( 5 mL ) and freeze-dried for 72 h .

## Preparation of MOPS-buffer (pH 10):

2.09 g 3-morpholinopropanesulfonic acid sodium salt (MOPS), 3.50 g NaCl and $10.46 \mathrm{~g} \mathrm{~K}_{2} \mathrm{SO}_{4}$ were dissolved in 100 mL deionized water.

SEM-EDX data of the pure ZnO particles:



SEM and EDX Analysis: For SEM and energy-dispersive X-ray analysis (EDX), the dried particles were transferred to a carbon conductive tab and fixed on an Al specimen stub. The samples were analyzed using a Zeiss Leo 1550 Gemini microscope with field emission gun (FEG) and an Oxford EDX-System.

## Data for pure molecules:

## For 3-morpholinopropanesulfonate sodium:

XRD pattern:


IR spectra:


TGA:


TGA curves of the pure PEG-triscatecholate:


TGA curves of the pure PEG-dopamine:


TGA curves of the pure bromotriscatecholate:


## Further analytical data of the immobilized samples:

Pure particles in MOPS buffer without any catecholate:
XRD pattern:


TGA


HRTEM and EDX:

kV:200.0 X Tilt:0.0 Y Tilt:20.0 Det: XLT Windowless
Res:137 Amp.T:1.92 FS:5552 Lsec:127 11-Feb-2015 11:38:53


## Bromotriscatecholate 13 immobilized on ZnO in MOPS buffer:



IR spectra


## XRD pattern



## EDX data

kV:200.0 X Tilt:0.0 Y Tilt:20.0 Det: XLT Windowless
Res:128 Amp.T:7.68 FS: 5286 Lsec:119 17-Nov-2014 09:20:28


## Washing experiments

## PEG-dopamine 14 immobilized on ZnO

TGA of the sample centrifuged directly after immobilization:


TGA of the sample after washing with water and methanol:


EDX of the sample after washing with water and methanol:

## kV:200.0 X Tilt:0.0 Y Tilt:20.0 Det: XLT Windowless

Res:137 Amp.T:1.92 FS: 8038 Lsec:150 11-Feb-2015 09:03:03


XRD pattern of the sample after washing with water and methanol:


## PEG-triscatecholate 3 immobilized on ZnO :

TGA of the sample centrifuged directly after immobilization:


TGA of the sample after washing with water and methanol:


EDX of the sample after washing with water and methanol:


XRD pattern of the sample after washing with water and methanol:


The XRD pattern shown above displays next to the signals of ZnO also signals of PEG.

IR spectra after washing with MeOH and water three times:


## References:

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