Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Oxidative Polymerization of Catecholamines: Structural Access by High-Resolution Mass Spectrometry

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Materials

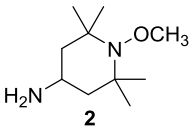
Acetonitrile (Carl Roth, LC-MS grade ≥ 99.95%, employed for ESI MS), 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (4-amino-TEMPO; abcr, 97%), chloroform-d_1 ($CDCl_3$; Sigma-Aldrich, 99.8% D), cyclohexane (VWR, p.a.), dry dichloromethane (dry DCM; Acros, 99.8% extra dry), diethyl ether (VWR, p.a.), 4-(dimethylamino)pyridine (DMAP; Acros, 99%), dimethyl sulfoxide (DMSO; Roth, 99%), ethyl acetate (VWR, p.a.), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC·HCl; Carl Roth, >99%), hydrogen chloride solution, 2 M in diethyl ether (Alfa Aesar), hydrogen peroxide solution 30% (*w/w* in water) (Carl Roth), iron(II) sulfate heptahydrate (VWR, 99%), methanol (MeOH; Carl Roth, HPLC grade, employed for ESI MS), methanol-d_4 (MeOD; Sigma-Aldrich, 99.8% D), silica gel (Merck), sodium bicarbonate (Carl Roth, ≥ 99%), sodium chloride (Carl Roth, ≥ 99%), sodium sulfate (Carl Roth, ≥ 99%), tetrahydrofuran (THF; GPC grade, Scharlau, employed for ESI MS) and tris-(hydroxymethyl)methylamine (Tris; Acros, >99%) were used as received. Type I ultrapure water was obtained from Puranity PU 15 water purification system (VWR, employed for polymerization and ESI MS). Thin layer chromatography (TLC) was performed on aluminium plates coated with silica gel 60 F_{254} (Merck).

Characterization Methods

^{1}H NMR (400 MHz)* and *^{13}C NMR (101 MHz) spectroscopy was performed on a Bruker Ascend 400 spectrometer. All samples were recorded in $CDCl_3$ or MeOD. Chemical shifts are expressed in parts per million (ppm) and coupling constants (*J* values) are reported in Hz. The *δ*-scale is referenced to characteristic solvent signals as internal standards.

Electrospray ionization mass spectrometry (ESI MS) was performed using a LTQ Orbitrap XL Q Exactive mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with an HESI II probe. The instrument was calibrated in the range of *m/z* 74 – 1822 using standard calibration solutions (Thermo Scientific). The FT resolution was set to 140 000, the capillary temperature was set to 320 °C and the S-lens RF level to 68.0. The dimensionless gas flow rates were set to 10 (sheath gas), 0 (sweep gas), 0 (aux gas) employing negative ion mode and 5 (sheath gas), 0 (sweep gas), 1 (aux gas) employing positive ion mode. A collision induced dissociation (CID) energy of 80 eV was employed. The spectra were recorded with a constant spray voltage of 3.4 ± 0.2 kV for ESI-CID MS and 4.3 kV for ESI-CID MS/MS, respectively. The samples were dissolved in water/acetonitrile (1:1, *v/v*) doped with 0.1% (*v/v*) acetic acid or in THF/MeOH (3:2, *v/v*) with a concentration of 0.05 mg·mL^{-1}. All samples were filtered prior to injection. The recorded MS spectra were evaluated using the Xcalibur software.

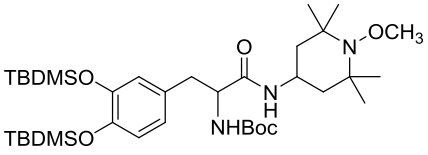
Experimental Data



2

1-Methoxy-2,2,6,6-tetramethylpiperidin-4-amine (**2**): Compound **2** was prepared by modification of a literature procedure.[1] 4-Amino-2,2,6,6-tetramethylpiperidine (1.71 g, 10.0 mmol, 1.0 eq.) was dissolved in DMSO (20 mL). After the addition of $Fe(II)SO_4 \cdot 7H_2O$ (6.95 g, 25.0 mmol, 2.5 eq.), the solution was placed in an ice bath and H_2O_2 solution (4.30 mL, 30% *w/w*, 5.0 eq.) was added dropwise to the vigorously stirring solution. The reaction mixture was stirred overnight and allowed to reach room temperature. The solution was basified using 2M NaOH (50 mL), the precipitate was filtered off and the filtrate was extracted with diethyl ether (3 × 50 mL). The organic phase was washed with deionised water (15 mL) and dried over Na_2SO_4. The solvent was carefully removed under reduced pressure yielding a yellow liquid (1.38 g, 7.4 mmol, 74%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 3.59 (s, 3H, O-C**H$_3$**), 3.04 – 2.93 (m, 1H, H_2N-C**H**), 1.69 – 1.59 (m, 2H, CH(C**H$_2$**)$_2$) , 1.33 – 1.21 (m, 2H, CH(C**H$_2$**)$_2$), 1.18 (s, 6H, C(C**H$_3$**)$_2$), 1.11 (s, 6H, C(C**H$_3$**)$_2$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ = 65.5 (O-**C**H$_3$), 60.0 (**C**(CH$_3$)$_2$), 50.0 (CH(**C**H$_2$)$_2$), 42.2 (H_2N-**C**H), 33.2 (C(**C**H$_3$)$_2$), 20.9 (C(**C**H$_3$)$_2$) ppm. HRMS (*m/z*) calculated for $C_{10}H_{23}N_2O$ $[M+H]^+$ 187.1805, found 187.1808.

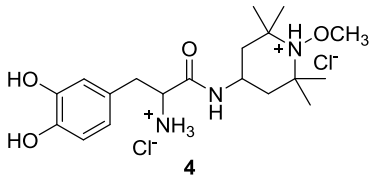


3

(TBDMS)$_2$-N-Boc-DOPA-TEMPO-CH$_3$ (**3**): 1-Methoxy-2,2,6,6-tetramethylpiperidin-4-amine (**2**) (1.12 g, 6.0 mmol, 1.0 eq.) and DMAP (1.47 g, 12.0 mmol, 2.0 eq.) were dissolved in dry DCM (25 mL). 3,4-*bis*(*tert*-Butyldimethylsilyloxy)-*N*-*tert*-butyloxycarbonyl-L-phenylalanine (**1**) (3.15 g, 6.0 mmol, 1 eq.), previously prepared according to a literature procedure,[2] was added to the solution followed by the addition of EDC·HCl (2.30 g, 12.0 mmol, 2.0 eq.). The reaction mixture was stirred at ambient temperature for 24 h followed by extraction with saturated $NaHCO_3$ solution (25 mL), water (10 mL) and brine (10 mL). The organic phase was dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography employing ethyl acetate and cyclohexane (2:7) as solvent mixture (R_f = 0.44) yielding a yellow solid (3.47 g, 5.0 mmol, 83%).

^{1}H NMR (400 MHz, MeOD, 298 K) δ = 6.77 (d, *J* = 8.0 Hz, 1H, O-C$_{Ar}$-C$_{Ar}$**H**-C$_{Ar}$H), 6.73 (d, *J* = 2.1 Hz, 1H, O-C$_{Ar}$-C$_{Ar}$**H**-C$_{Ar}$), 6.70 (dd, *J* = 8.1, 2.1 Hz, 1H, O-C$_{Ar}$-C$_{Ar}$H-C$_{Ar}$**H**), 4.18 – 4.08 (m, 1H, C$_{Ar}$-CH$_2$-C**H**), 4.06 – 3.94 (m, 1H, NH-C**H**(CH$_2$)$_2$), 3.59 (s, 3H, O-C**H$_3$**), 2.90 – 2.67 (m, 2H, C$_{Ar}$-C**H$_2$**), 1.71 – 1.22 (m, 4H,

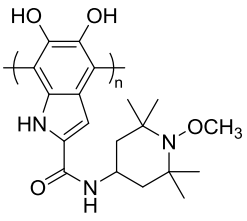
NH-CH(C**H₂**)₂), 1.40 (s, 9H, O-C(C**H₃**)₃), 1.18 (s, 3H, C(C**H₃**)₂), 1.17(s, 3H, C(C**H₃**)₂), 1.16 (s, 3H, C(C**H₃**)₂), 1.15 (s, 3H, C(C**H₃**)₂), 1.01 (s, 9H, Si-C(C**H₃**)₃), 0.99 (s, 9H, Si-C(C**H₃**)₃), 0.21 (s, 6H, Si(C**H₃**)₂), 0.20 (s, 6H, Si(C**H₃**)₂) ppm. ^{13}C NMR (101 MHz, MeOD, 298 K) δ = 178.3 (CH-**C**ONH), 157.4 (CH-NH**C**OO), 147.8 (O-**C**$_{Ar}$), 146.9 (O-**C**$_{Ar}$), 131.7 (**C**$_{Ar}$-CH$_2$), 123.7 (**C**$_{Ar}$H), 123.6 (**C**$_{Ar}$H), 122.0 (O-C$_{Ar}$-**C**$_{Ar}$H-C$_{Ar}$H), 80.6 (O-**C**(CH$_3$)$_3$), 65.9 (O-**C**H$_3$), 61.0 (**C**(CH$_3$)$_2$), 57.6 (C$_{Ar}$-CH$_2$-**C**H), 46.0 (CH-(**C**H$_2$)$_2$), 45.9 (CH-(**C**H$_2$)$_2$), 42.1 (NH-**C**H(CH$_2$)$_2$), 39.0 (C$_{Ar}$-**C**H$_2$-CH), 33.5 (C(**C**H$_3$)$_2$), 33.4 (C(**C**H$_3$)$_2$), 28.7 (O-C(**C**H$_3$)$_3$), 26.6 (Si-C(**C**H$_3$)$_3$), 26.5 (Si-C(**C**H$_3$)$_3$), 20.9 (C(**C**H$_3$)$_2$), 20.8 (C(**C**H$_3$)$_2$), 19.4 (Si-**C**(CH$_3$)$_3$), -3.7 (Si-(**C**H$_3$)$_2$), -3.7 (Si-(**C**H$_3$)$_2$) ppm. HRMS (*m/z*) calculated for $C_{36}H_{68}N_3O_6Si_2$ $[M+H]^+$ 694.4641, found 694.4648. M.p. 148 °C.



4

DOPA-TEMPO-CH₃ dihydrochloride (**4**): All solvents were purged with N_2 for 20 min prior to use. (TBDMS)$_2$-*N*-Boc-DOPA-TEMPO-CH$_3$ (**3**) (1.20 g, 1.7 mmol, 1.0 eq.) was dissolved in diethyl ether (5 mL). 2M HCl in diethyl ether (8.5 mL, 10.0 eq.) was added dropwise and the solution was stirred at room temperature overnight. The solvent was evaporated and the residue was washed with diethyl ether (25 mL). The crude product was redissolved in water (10 mL, acidified with a few drops of 1M HCl), filtered and lyophilized yielding a white-orange solid (0.61 g, 1.4 mmol, 82%).

^{1}H NMR (400 MHz, MeOD, 298 K) δ = 6.76 (d, *J* = 8.0 Hz, 1H, O-C$_{Ar}$-C$_{Ar}$**H**-C$_{Ar}$H), 6.67 (d, *J* = 2.1 Hz, 1H, O-C$_{Ar}$-C$_{Ar}$**H**-C$_{Ar}$), 6.60 (dd, *J* = 8.0, 2.1 Hz, 1H, O-C$_{Ar}$-C$_{Ar}$H-C$_{Ar}$**H**), 4.22 – 4.15 (m, 1H, NH-C**H**(CH$_2$)$_2$), 4.21 (s, 3H, O-C**H₃**), 3.94 – 3.86 (m, 1H, C$_{Ar}$-CH$_2$-C**H**), 3.04 – 2.87 (m, 2H, C$_{Ar}$-C**H₂**-CH), 2.10 – 1.65 (m, 4H, NH-CH(C**H₂**)₂), 1.62 (s, 3H, C(C**H₃**)₂), 1.61 (s, 3H, C(C**H₃**)₂), 1.51 (s, 3H, C(C**H₃**)₂), 1.50 (s, 3H, C(C**H₃**)₂) ppm. ^{13}C NMR (101 MHz, MeOD, 298 K) δ = 169.2 (**C**ONH), 146.7 (O-**C**$_{Ar}$), 146.1 (O-**C**$_{Ar}$), 126.8 (**C**$_{Ar}$-CH$_2$), 121.9 (O-C$_{Ar}$-C$_{Ar}$H-**C**$_{Ar}$H), 117.7 (O-C$_{Ar}$-**C**$_{Ar}$H-C$_{Ar}$), 116.8 (O-C$_{Ar}$-**C**$_{Ar}$H-C$_{Ar}$H), 71.7 (**C**(CH$_3$)$_2$), 71.6 (**C**(CH$_3$)$_2$), 68.5 (O-**C**H$_3$), 56.0 (C$_{Ar}$-CH$_2$-**C**H), 42.7 (NH-CH(**C**H$_2$)$_2$), 42.6 (NH-CH(**C**H$_2$)$_2$), 40.5 (NH-**C**H(CH$_2$)$_2$), 38.2 (C$_{Ar}$-**C**H$_2$-CH), 28.5 (C(**C**H$_3$)$_2$), 28.4 (C(**C**H$_3$)$_2$), 21.0 (C(**C**H$_3$)$_2$), 21.0 (C(**C**H$_3$)$_2$) ppm. HRMS (*m/z*) calculated for $C_{19}H_{32}N_3O_4$ $[M\text{-}HCl\text{-}Cl]^+$ 366.2387, found 366.2389. M.p. 138 °C (dec.).



5
(ideal structure)

Poly(DOPA-TEMPO-CH₃) (**5**): Compound **4** (548 mg, 1.25 mmol) was dissolved in 10 mM Tris buffer (151 mg, 1.25 mmol in 125 mL H_2O) previously adjusted to pH 8.5 using 1M HCl. The solution of **4** was vigorously stirred in an open glass vial. The pH value was carefully readjusted and maintained within the first 30 min of polymerization at pH 8.25 ± 0.05 using Tris. After 72 h the precipitate was isolated by centrifugation and decantation. The solid was washed with water (3 × 30 mL) followed by centrifugation and decantation. The product was lyophilized yielding a yellow-brown solid (80 mg).

NMR spectra

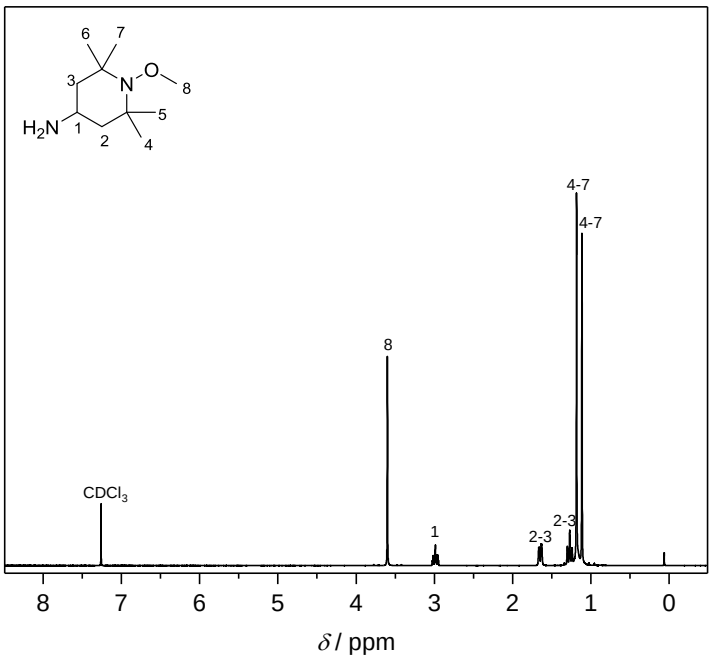


Fig. S1 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1-methoxy-2,2,6,6-tetramethylpiperidin-4-amine (**2**).

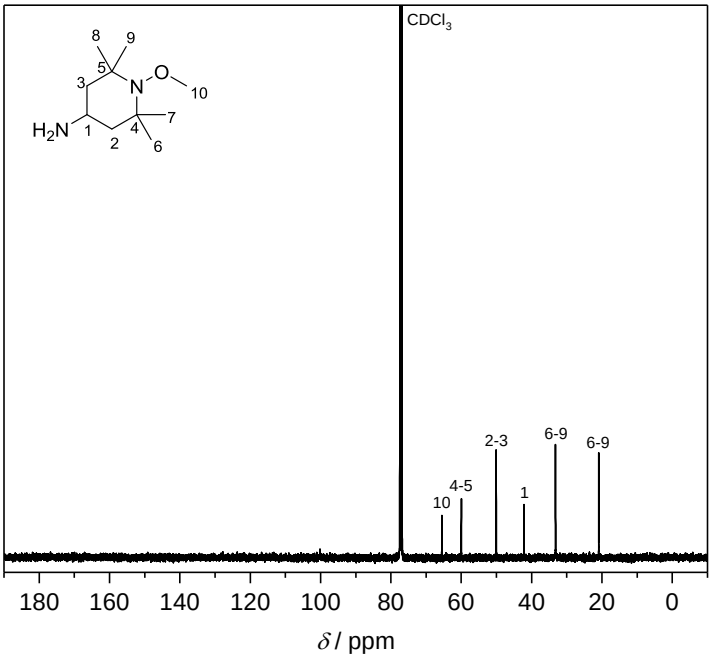


Fig. S2 ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of 1-methoxy-2,2,6,6-tetramethylpiperidin-4-amine (**2**).

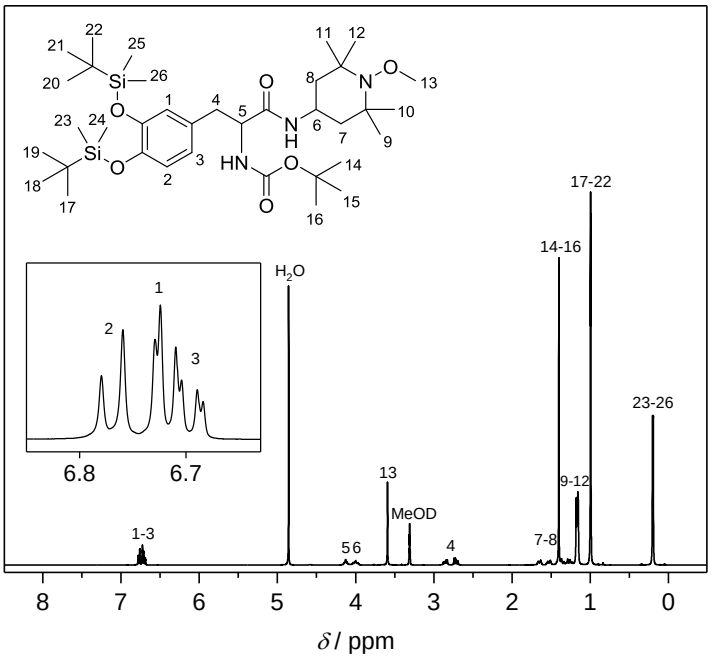


Fig. S3 ^{1}H NMR spectrum (400 MHz, MeOD, 298 K) of $(TBDMS)_2$-*N*-Boc-DOPA-TEMPO-CH_3 (**3**).

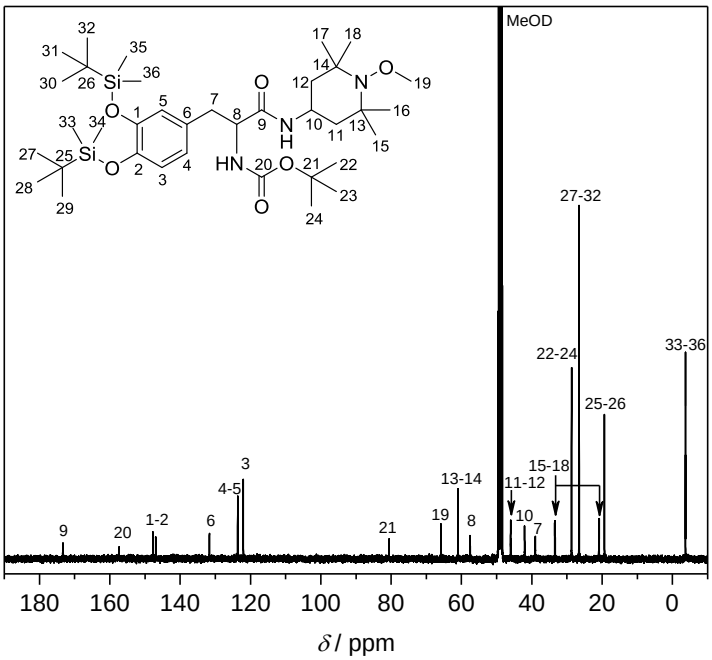


Fig. S4 ^{13}C NMR spectrum (101 MHz, MeOD, 298 K) of $(TBDMS)_2$-*N*-Boc-DOPA-TEMPO-CH_3 (**3**).

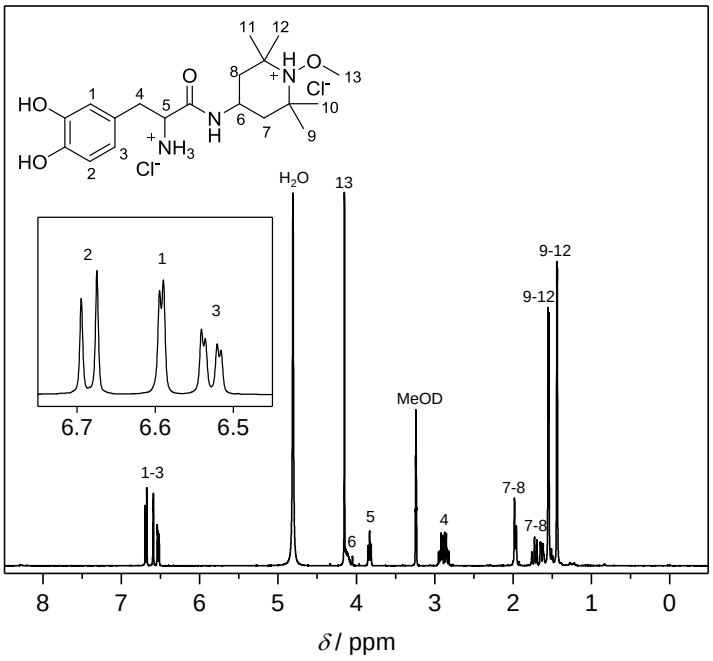


Fig. S5 ^{1}H NMR spectrum (400 MHz, MeOD, 298 K) of DOPA-TEMPO-CH_3 dihydrochloride (**4**).

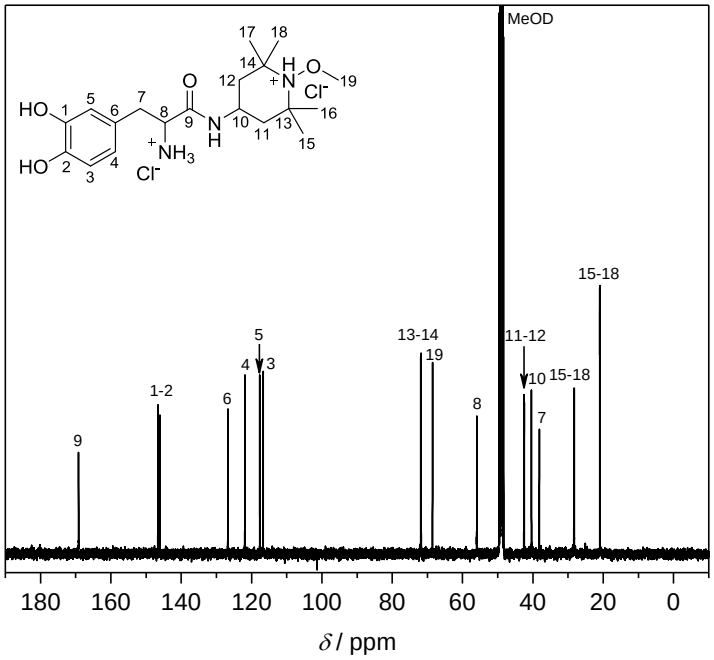


Fig. S6. ^{13}C NMR spectrum (101 MHz, MeOD, 298 K) of DOPA-TEMPO-CH_3 dihydrochloride (**4**).

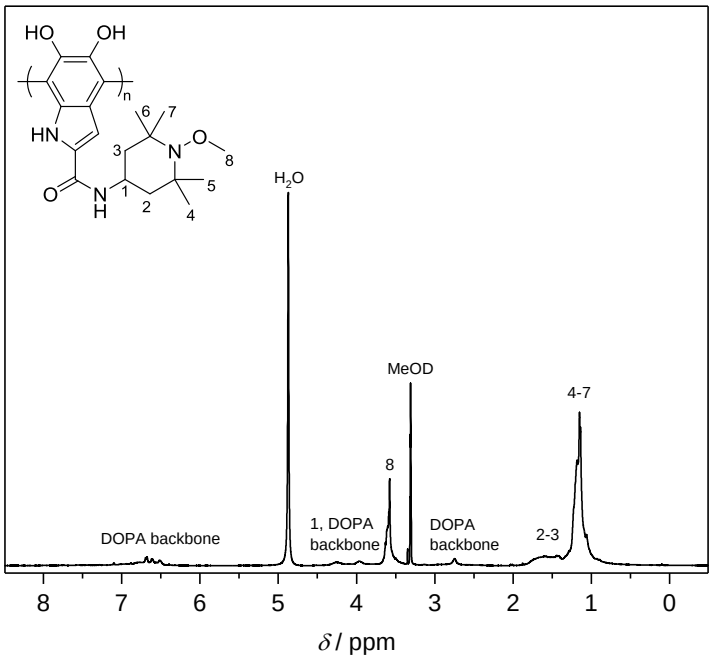


Fig. S7 ^{1}H NMR spectrum (400 MHz, MeOD, 298 K) of poly(DOPA-TEMPO-CH_3) (**5**) depicted as an ideal structure.

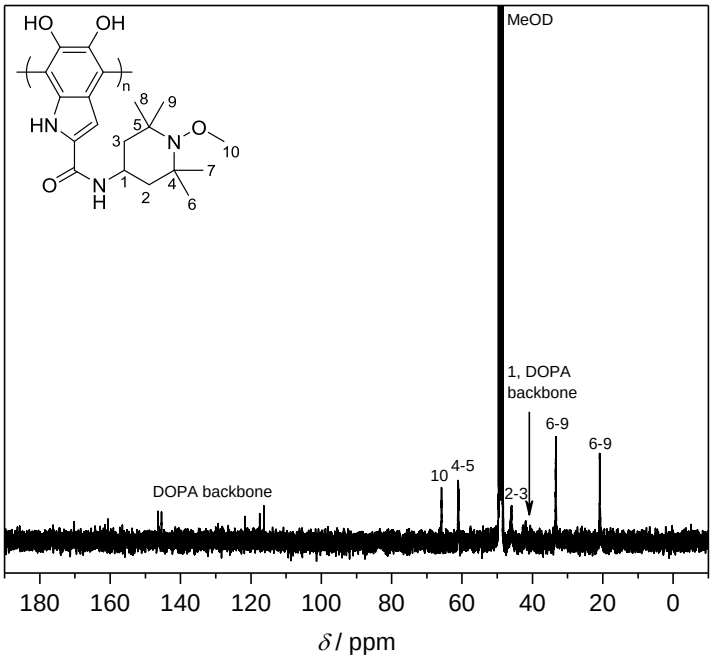


Fig. S8 ^{13}C NMR spectrum (101 MHz, MeOD, 298 K) of poly(DOPA-TEMPO-CH_3) (**5**) depicted as an ideal structure.

MS spectra and peak assignments

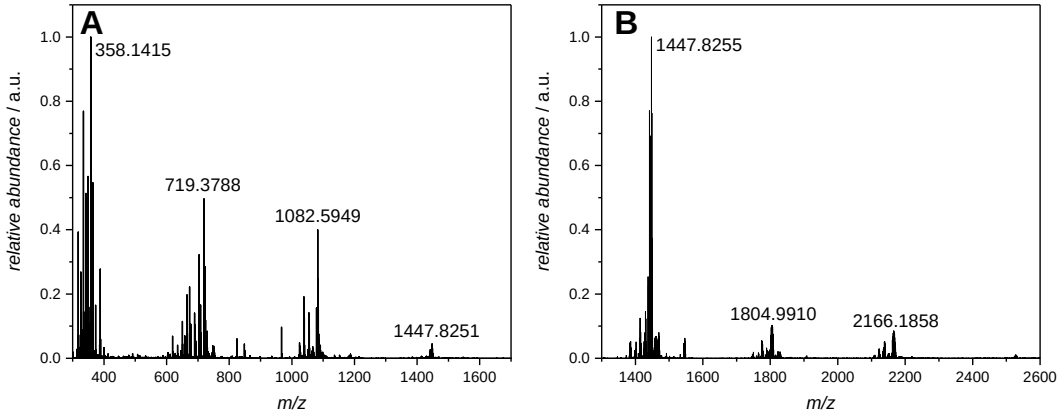


Fig. S9 ESI(-)-CID MS overview spectra of poly(DOPA-TEMPO-CH_3) (**5**) in H_2O/acetonitrile 1:1 (*v/v*) doped with 0.1% (*v/v*) acetic acid depicted from (**A**) *m/z* 300 – 1700 and (**B**) *m/z* 1300 – 2600. The most abundant peaks of each isotopic pattern are labelled with *m/z*(exp) (refer to Table S1 for structural assignments).

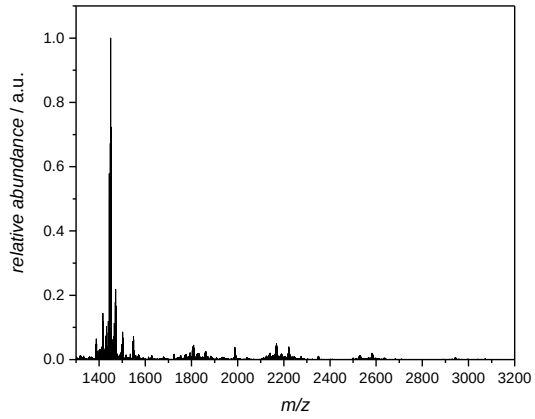


Fig. S10 ESI(+)-CID MS overview spectra of poly(DOPA-TEMPO-CH_3) (**5**) in H_2O/acetonitrile 1:1 (*v/v*) doped with 0.1% (*v/v*) acetic acid depicted from *m/z* 1300 – 3200.

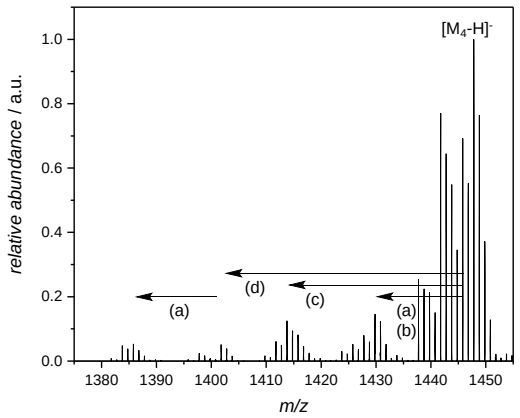


Fig. S11 Selected ESI(-)-CID MS spectrum of poly(DOPA-TEMPO-CH_3) (**5**) in H_2O/acetonitrile 1:1 (*v/v*) doped with 0.1% (*v/v*) acetic acid depicted from *m/z* 1370 – 1455 exemplarily showing typical single-charged oligomer profile of tetrameric species. The characteristic fragmentation pattern (black arrows) suggests liberation of -OH groups (a), -CH_3 groups (b), -OCH_3 groups (c), as well as C_2H_2O-fragments (d) as a portion of the phenyl ring.[3] For $[M_4\text{-}H]^-$ zoomed spectrum with simulated isotopic patterns and peak assignments refer to Fig. 3 and Table S1.

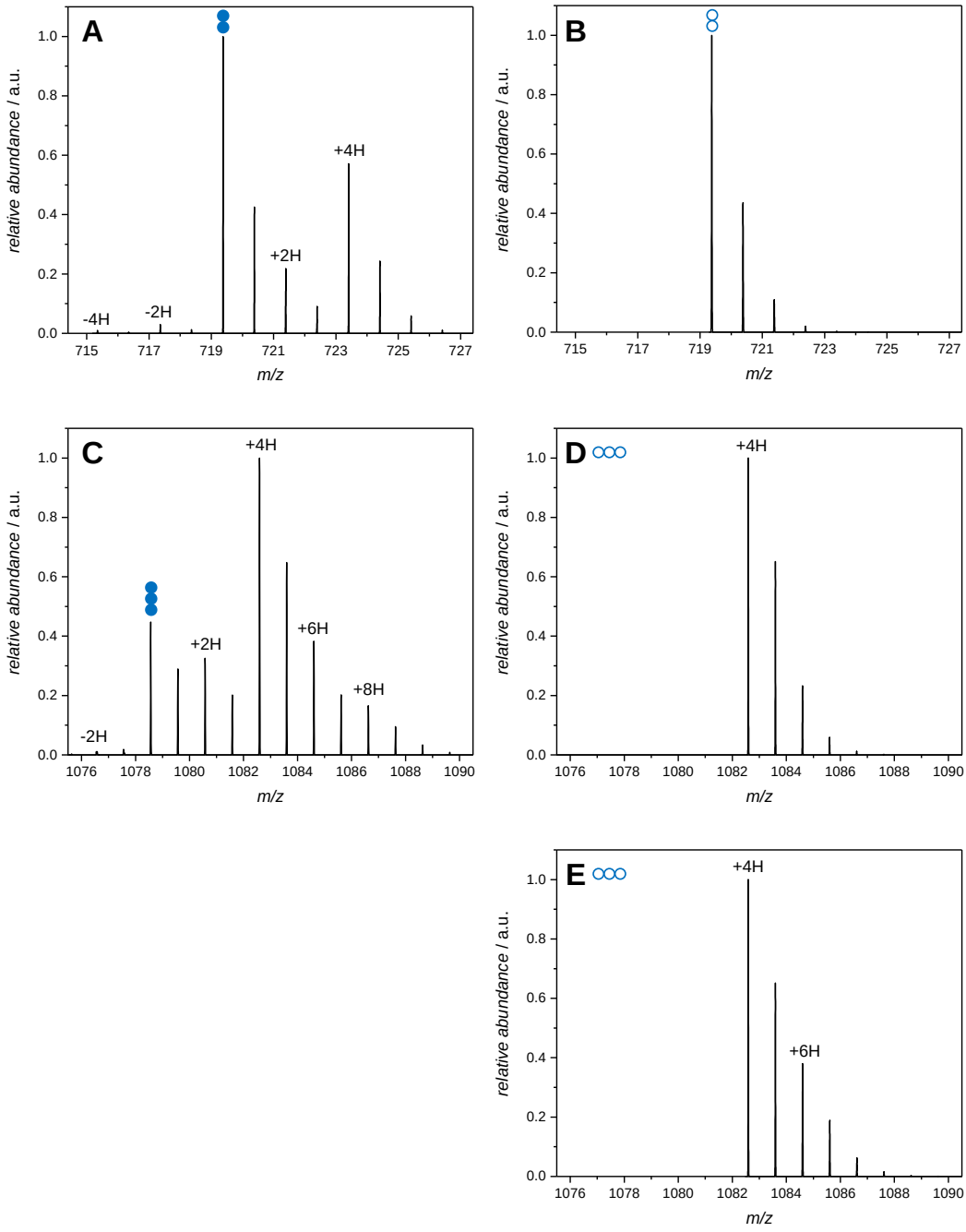
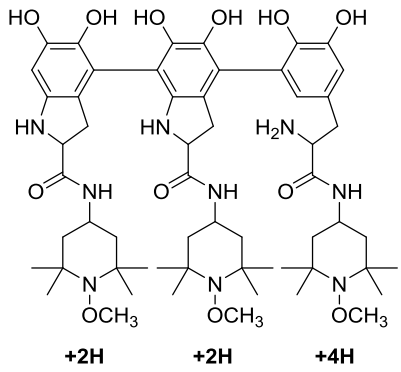
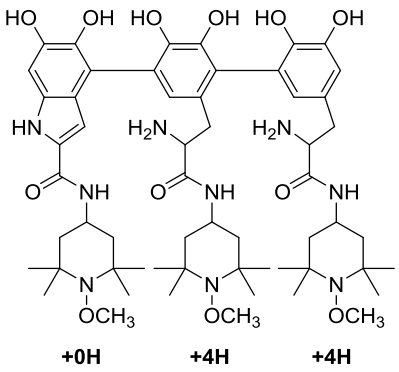


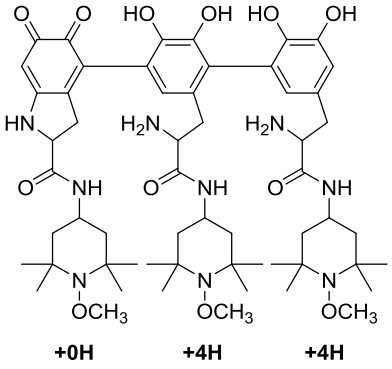
Fig. S12 Comparison of experimentally obtained spectrum of dimer region $[M_2\text{-}H]^-$ (**A**) (negative ion mode, refer to Fig. 1) and simulated isotopic pattern of most abundant peak (DHI homodimer) (**B**) indicating the presence of higher molecular weight species such as +2H and +4H dimers. The same comparison was performed for the trimer region $[M_3\text{-}H]^-$ with the experimentally obtained spectrum (**C**) (negative ion mode, refer to Fig. 1) and the simulated isotopic patterns of the most abundant species (+4H) (**D**) and additionally +6H (**E**) clearly indicating the presence of +8H dimer which correspond to incorporated open-chain dopamine units (refer to Fig S13). Blue filled circles (experimentally obtained spectra) and blue unfilled circles (simulated spectra) represent the molecular ion peak of the homodimer with DHI as the polymer backbone repeating unit. For peak assignments refer to Table S1.



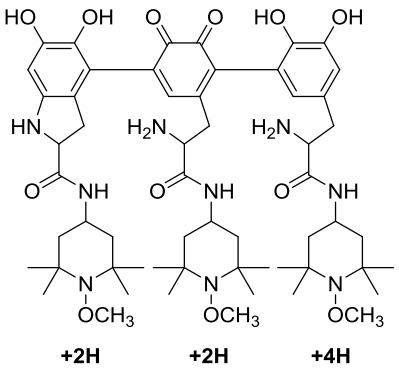
open-chain units: 1



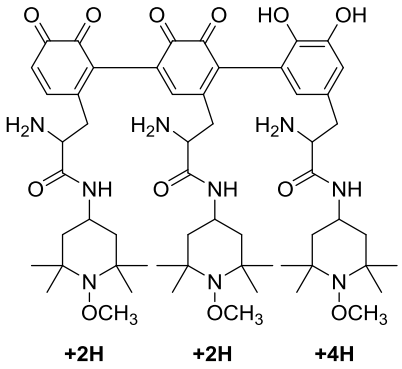
open-chain units: 2



open-chain units: 2



open-chain units: 2



open-chain units: 3

Fig. S13 Proposed structures of ●●●+8H trimeric isomers with *m/z*(theo) 1086.6192 (*m/z*(exp) 1086.6257, refer to Fig. 3 and Table S1) with different numbers of incorporated open-chain units.

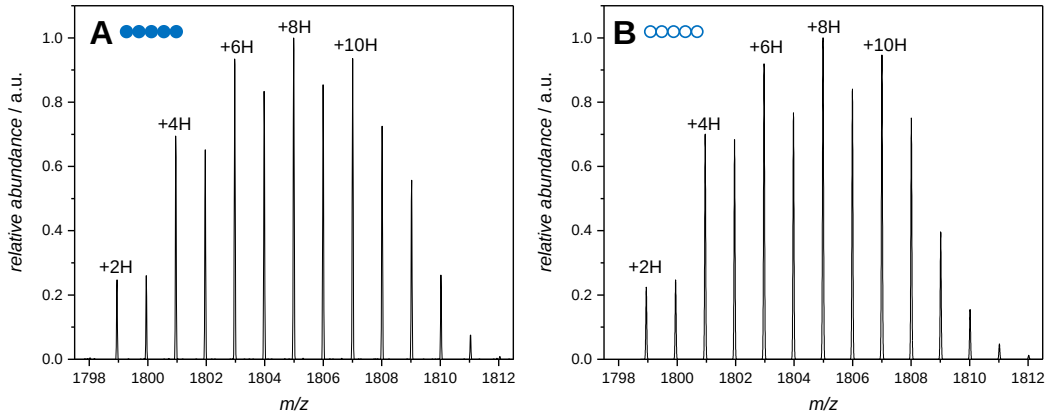


Fig. S14 Comparison of the ESI(-)-CID MS spectrum of poly(DOPA-TEMPO-CH_3) (**5**) in H_2O/acetonitrile 1:1 (*v/v*) doped with 0.1% (*v/v*) acetic acid of $[M_5\text{-}H]^-$ species (**A**) depicted from *m/z* 1798 – 1812 and (**B**) corresponding simulated isotopic patterns. For peak assignments refer to Table S1.

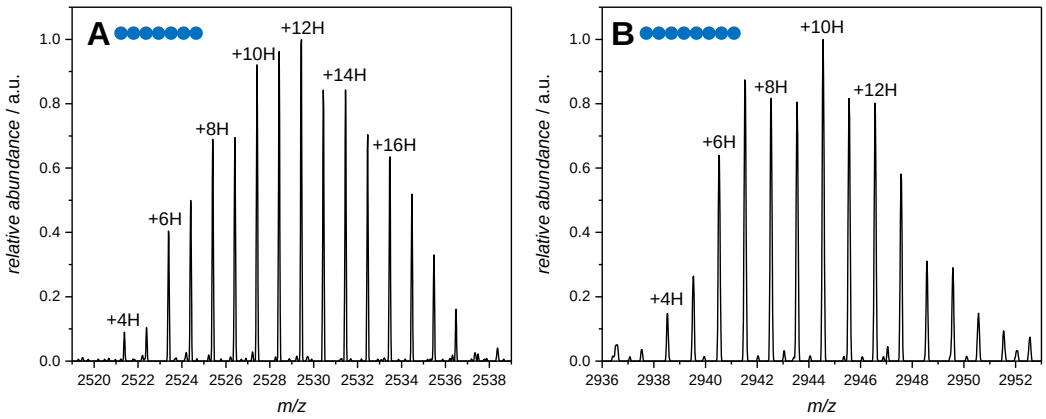


Fig. S15 ESI(+)-CID MS spectrum of poly(DOPA-TEMPO-CH_3) (**5**) in H_2O/acetonitrile 1:1 (*v/v*) doped with 0.1% (*v/v*) acetic acid. (**A**) Heptamer profile $[M_7+H]^+$ depicted from *m/z* 2519 – 2539 and (**B**) octamer profile $[M_8+H+NaCl]^+$ depicted from *m/z* 2936 – 2953. $[M_8+H]^+$ species (only detected as a minor single-charged profile) are not displayed. For peak assignments refer to Table S3.

Table S1 ESI(-)-CID MS peak assignments of $[M_n\text{-}H]^-$ oligomers with n = 2 – 6 of poly(DOPA-TEMPO-CH_3) (**5**). Isotopic pattern simulations were conducted using the Xcalibur software. The *m/z*(theo) values were obtained from simulated spectra.

$[M_2\text{-}H]^-$, DIMER ●● ±2xH (refer to Fig. 1 and Fig. S12)							
label	formula of M_2	*m/z*(exp)	*m/z*(theo)	Δ*m/z*	Δ*m/z* [ppm]	resolution	relative ratio
-4H	$C_{38}H_{48}N_6O_8$	715.3471	715.3450	0.0021	2.94	77000	0.01
-2H	$C_{38}H_{50}N_6O_8$	717.3631	717.3603	0.0028	3.90	76000	0.03
●●	$C_{38}H_{52}N_6O_8$	719.3788	719.3763	0.0025	3.48	77000	1.00
+2H	$C_{38}H_{54}N_6O_8$	721.3959	721.3885	0.0074	10.26	73300	0.21
+4H	$C_{38}H_{56}N_6O_8$	723.4102	723.4071	0.0031	4.29	77600	0.57
$[M_3\text{-}H]^-$, TRIMER ●●● ±2xH (refer to Fig. 1 and Fig. S12)							
label	formula of M_3	*m/z*(exp)	*m/z*(theo)	Δ*m/z*	Δ*m/z* [ppm]	resolution	relative ratio
-2H	$C_{57}H_{75}N_9O_{12}$	1076.5486	1076.5451	0.0034	3.16	62100	0.02
●●●	$C_{57}H_{77}N_9O_{12}$	1078.5637	1078.5607	0.0030	2.78	63500	0.46
+2H	$C_{57}H_{79}N_9O_{12}$	1080.5788	1080.5738	0.0050	4.63	60300	0.29
+4H	$C_{57}H_{81}N_9O_{12}$	1082.5949	1082.5914	0.0035	3.23	62200	1.00
+6H	$C_{57}H_{83}N_9O_{12}$	1084.6078	1084.6032	0.0046	4.24	57700	0.29
+8H	$C_{57}H_{85}N_9O_{12}$	1086.6257	1086.6192	0.0065	5.98	60400	0.14
$[M_4\text{-}H]^-$, TETRAMER ●●●● ±2xH (refer to Fig. 3)							
label	formula of M_4	*m/z*(exp)	*m/z*(theo)	Δ*m/z*	Δ*m/z* [ppm]	resolution	relative ratio
●●●●	$C_{76}H_{102}N_{12}O_{16}$	1437.7479	1437.7453	0.0026	1.81	55900	0.31
+2H	$C_{76}H_{104}N_{12}O_{16}$	1439.7605	1439.7563	0.0042	2.92	54700	0.14
+4H	$C_{76}H_{106}N_{12}O_{16}$	1441.7791	1441.7758	0.0034	2.36	56100	0.89
+6H	$C_{76}H_{108}N_{12}O_{16}$	1443.7913	1443.7874	0.0039	2.70	54100	0.38
+8H	$C_{76}H_{110}N_{12}O_{16}$	1445.8102	1445.8055	0.0047	3.25	56000	0.72
+10H	$C_{76}H_{112}N_{12}O_{16}$	1447.8255	1447.8211	0.0044	3.04	55100	1.00
$[M_5\text{-}H]^-$, PENTAMER ●●●●● ±2xH (refer to Fig. S14)							
label	formula of M_5	*m/z*(exp)	*m/z*(theo)	Δ*m/z*	Δ*m/z* [ppm]	resolution	relative ratio
+2H	$C_{95}H_{129}N_{15}O_{20}$	1798.9469	1798.9455	0.0014	0.78	54600	0.35
+4H	$C_{95}H_{131}N_{15}O_{20}$	1800.9596	1800.9592	0.0004	0.22	50300	0.90
+6H	$C_{95}H_{133}N_{15}O_{20}$	1802.9748	1802.9727	0.0021	1.16	47300	0.90
+8H	$C_{95}H_{135}N_{15}O_{20}$	1804.9910	1804.9881	0.0029	1.61	47300	1.00
+10H	$C_{95}H_{137}N_{15}O_{20}$	1807.0075	1807.0031	0.0044	2.43	48800	0.85

Table S1 continued.

$[M_6\text{-}H]^-$, HEXAMER ●●●●●● ±2xH (refer to Fig. 4)							
label	formula of M_6	*m/z*(exp)	*m/z*(theo)	Δ*m/z*	Δ*m/z* [ppm]	resolution	relative ratio
+2H	$C_{114}H_{154}N_{18}O_{24}$	2158.1271	2158.1300	0.0028	1.30	44600	0.08
+4H	$C_{114}H_{156}N_{18}O_{24}$	2160.1414	2160.1434	0.0020	0.93	46400	0.25
+6H	$C_{114}H_{158}N_{18}O_{24}$	2162.1562	2162.1591	0.0029	1.34	46500	0.88
+8H	$C_{114}H_{160}N_{18}O_{24}$	2164.1701	2164.1716	0.0015	0.69	45100	0.76
+10H	$C_{114}H_{162}N_{18}O_{24}$	2166.1858	2166.1873	0.0015	0.69	43000	1.00
+12H	$C_{114}H_{164}N_{18}O_{24}$	2168.1994	2168.2012	0.0018	0.83	45000	0.60
+14H	$C_{114}H_{166}N_{18}O_{24}$	2170.2128	2170.2156	0.0029	1.34	47200	0.35

Table S2 ESI(-)-CID MS/MS peak assignments of fragments $[F_x\text{-}H]^-$ with x = 3 – 5 of poly(DOPA-TEMPO-CH_3) (**5**) performed on hexameric species $[M_6\text{-}H]^-$ with *m/z* 2166±5 (refer to Fig. 3). Only most abundant peaks of oligomeric fragments were selected. The *m/z*(theo) values of most abundant peaks were calculated without simulation of the overlapping isotopic patterns of the remaining species.

$[F_5\text{-}H]^-$,PENTAMER FRAGMENTS -●●●●- +6H (refer to Fig. 4E)							
label	formula of F_5	*m/z*(exp)	*m/z*(theo)	Δ*m/z*	Δ*m/z* [ppm]	resolution	relative ratio
+6H	$C_{95}H_{131}N_{15}O_{20}$	1800.9606	1800.9611	0.0005	0.28	49000	1.00
$[F_4\text{-}H]^-$,TETRAMER FRAGMENTS -●●●- +6H (refer to Fig. 4D)							
label	formula of F_4	*m/z*(exp)	*m/z*(theo)	Δ*m/z*	Δ*m/z* [ppm]	resolution	relative ratio
+6H	$C_{76}H_{106}N_{12}O_{16}$	1441.7780	1441.7766	0.0014	0.97	56100	1.00
$[F_3\text{-}H]^-$,TRIMER FRAGMENTS -●●●- +6H (refer to Fig. 4C)							
label	formula of F_3	*m/z*(exp)	*m/z*(theo)	Δ*m/z*	Δ*m/z* [ppm]	resolution	relative ratio
+6H	$C_{57}H_{81}N_9O_{12}$	1082.5941	1082.5921	0.0020	1.85	65100	1.00

Table S3 ESI(+)-CID MS peak assignments of $[M_7+H]^+$ species and $[M_8+H+NaCl]^+$ species of poly(DOPA-TEMPO-CH_3) (**5**). Isotopic pattern simulations were conducted using the Xcalibur software. The *m/z(*theo) values were obtained from simulated spectra.

$[M_7+H]^+$,HEPTAMER ●●●●●●● ±2xH (refer to Fig. S15)							
label	formula of M_7	*m/z*(exp)	*m/z*(theo)	Δ*m/z*	Δ*m/z* [ppm]	resolution	relative ratio
+4H	$C_{133}H_{181}N_{21}O_{28}$	2521.3790	2521.3458	0.0332	13.17	42500	0.20
+6H	$C_{133}H_{183}N_{21}O_{28}$	2523.3941	2523.3586	0.0355	14.07	36300	0.60
+8H	$C_{133}H_{185}N_{21}O_{28}$	2525.4050	2525.3715	0.0334	13.23	38500	0.70
+10H	$C_{133}H_{187}N_{21}O_{28}$	2527.4202	2527.3869	0.0333	13.18	37800	1.00
+12H	$C_{133}H_{189}N_{21}O_{28}$	2529.4338	2529.4007	0.0330	13.05	38100	0.70
+14H	$C_{133}H_{191}N_{21}O_{28}$	2531.4493	2531.4152	0.0341	13.47	39200	0.50
+16H	$C_{133}H_{193}N_{21}O_{28}$	2533.4655	2533.4309	0.0345	13.62	38600	0.40
$[M_8+H+NaCl]^+$, OCTAMER ●●●●●●●● ±2xH (refer to Fig. S15)							
label	formula of M_8	*m/z*(exp)	*m/z*(theo)	Δ*m/z*	Δ*m/z* [ppm]	resolution	relative ratio
+4H	$C_{152}H_{206}N_{24}O_{32}$	2938.5251	2938.4889	0.0362	12.32	38500	0.40
+6H	$C_{152}H_{208}N_{24}O_{32}$	2940.5264	2940.4997	0.0266	9.05	35300	1.00
+8H	$C_{152}H_{210}N_{24}O_{32}$	2942.5366	2942.5096	0.0270	9.18	34800	0.60
+10H	$C_{152}H_{212}N_{24}O_{32}$	2944.5502	2944.5227	0.0275	9.34	34500	0.80
+12H	$C_{152}H_{214}N_{24}O_{32}$	2946.5641	2946.5371	0.0270	9.16	34600	0.40

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