# Electronic Supporting Information

## The Structure of Polydopamine – a Never Ending Story?

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### Polydopamine obtained from TRIS buffer

Elemental analysis (found): C 56.94%, H 3.92%, N 8.52%

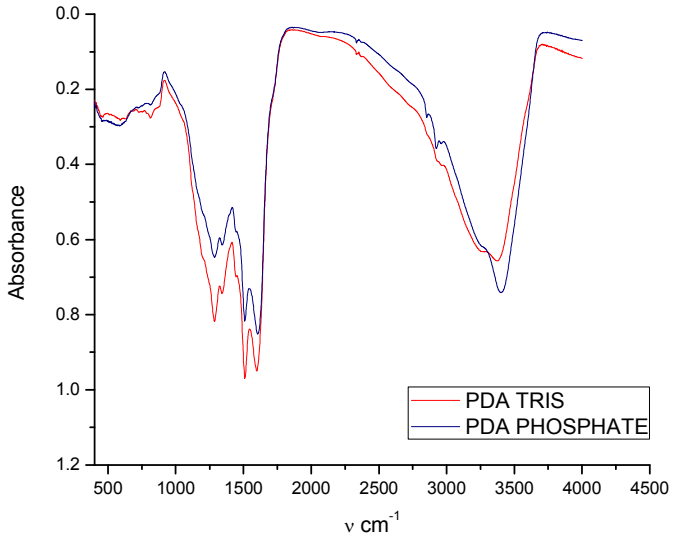


**Figure S1.** FTIR-spectra of PDA obtained in TRIS buffer (red line) and in phosphate buffer (blue line).

**Table S1**. ES (+)-HRMS peaks of PDA samples prepared in TRIS or Phosphate buffer.

| No. | *m/z* peak of PDA sample prepared in Phosphate buffer (Δ ppm) | TRIS buffer (Δ ppm) | Calculated $[M+H]^+$ mass | Oligomer |
|---|---|---|---|---|
| 1 | 438.0730 (2 ppm) | 438.0740 (4 ppm) | 438.0721 | 3Q |
| 2 | 440.0891 (3 ppm) | 440.0896 (4 ppm) | 440.0877 | 3Q+2 |
| 3 | 442.1048 (3 ppm) | 442.1052 (4 ppm) | 442.1034 | 3Q+4 |
| 4 | 444.1204 (3 ppm) | 444.1207 (4 ppm) | 444.1190 | 3Q+6 |
| 5 | 446.1360 (3 ppm) | 446.1363 (4 ppm) | 446.1347 | 3Q+8 |
| 6 | 448.1516 (3 ppm) | 448.1519 (4 ppm) | 448.1503 | 3Q+10 |
| 7 | 450.1673 (3 ppm) | 450.1676 (4 ppm) | 450.1660 | 3Q+12 |
| 8 | 452.1830 (3 ppm) | 452.1834 (4 ppm) | 452.1818 | 3Q+16 |
| 9 | 454.1987 (3 ppm) | 454.1990 (4 ppm) | 454.1973 | 3Q+18 |
| 10 | 589.1372 (3 ppm) | 589.1376 (4 ppm) | 589.1354 | 4Q+6 |
| 11 | 591.1528 (3 ppm) | 591.1534 (4 ppm) | 591.1510 | 4Q+8 |
| 12 | 593.1685 (3 ppm) | 593.1690 (4 ppm) | 593.1667 | 4Q+10 |
| 13 | 595.1841 (3 ppm) | 595.1845 (4 ppm) | 595.1823 | 4Q+12 |
| 14 | 597.1998 (3 ppm) | 597.2003 (4 ppm) | 597.1980 | 4Q+14 |
| 15 | 599.2155 (3 ppm) | 599.2159 (4 ppm) | 599.2136 | 4Q+16 |
| 16 | 601.2311 (3 ppm) | 601.2316 (4 ppm) | 601.2293 | 4Q+18 |
| 17 | 736.1699 (3 ppm) | 736.1710 (5 ppm) | 736.1674 | 5Q+8 |
| 18 | 738.1856 (3 ppm) | 738.1863 (4 ppm) | 738.1831 | 5Q+10 |
| 19 | 740.2010 (3 ppm) | 740.2019 (4 ppm) | 740.1987 | 5Q+12 |
| 20 | 742.2168 (3 ppm) | 742.2177 (4 ppm) | 742.2144 | 5Q+14 |
| 21 | 744.2325 (3 ppm) | 744.2333 (4 ppm) | 744.2300 | 5Q+16 |
| 22 | 746.2481 (3 ppm) | 746.2489 (4 ppm) | 746.2457 | 5Q+18 |
| 23 | 748.2637 (3 ppm) | 748.2646 (4 ppm) | 748.2613 | 5Q+20 |
| 24 | 750.2794 (3 ppm) | 750.2800 (4 ppm) | 750.2770 | 5Q+22 |
| 25 | 1199.4348(1ppm) | - | 1199.4362 | 8Q+36 |

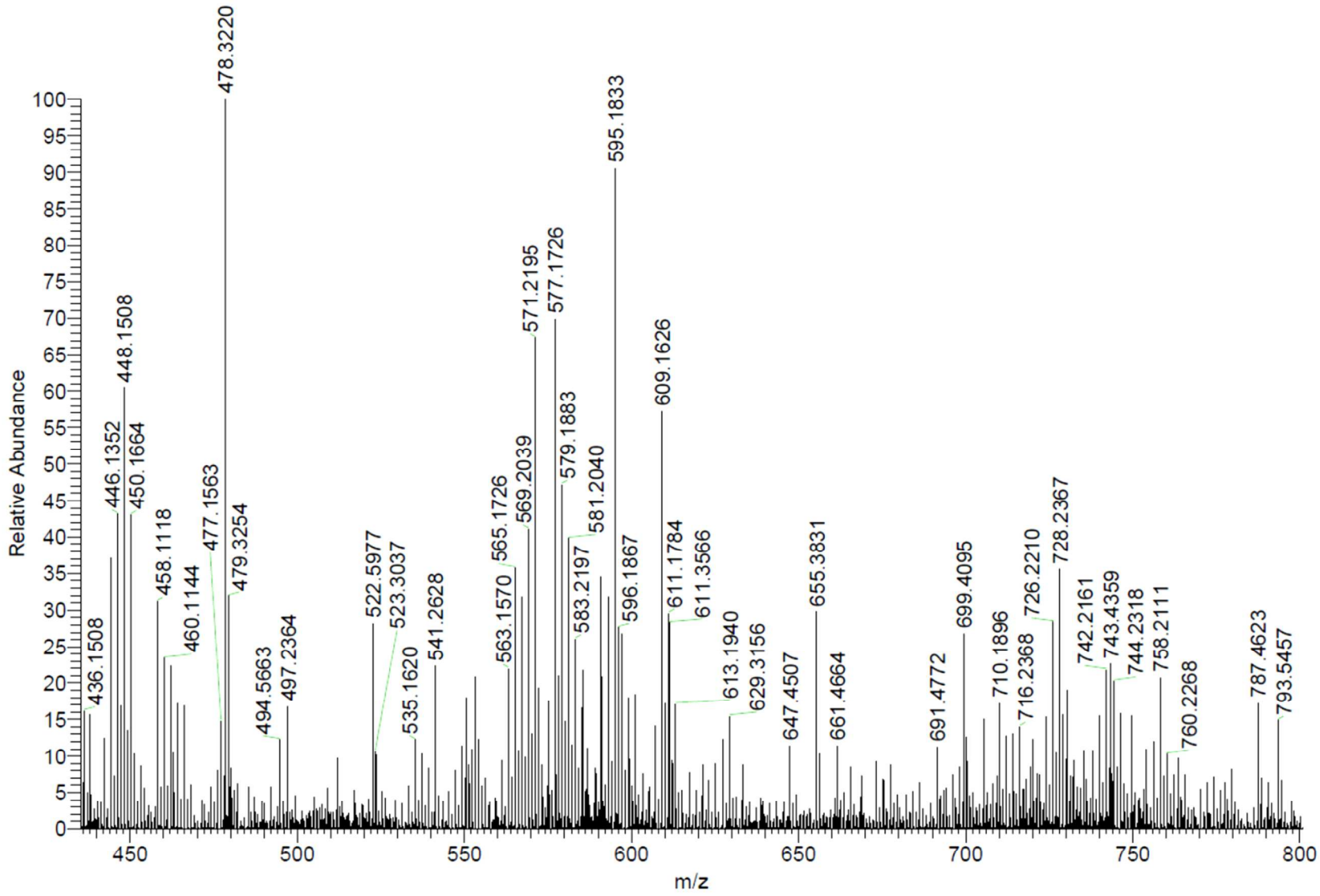


**Figure S2.** ES(+)-HRMS spectrum (oligomer peaks) of the PDA sample (0.1 mg/mL) in methanol/DMSO/TFA = 97/2/1 prepared in phosphate buffer.

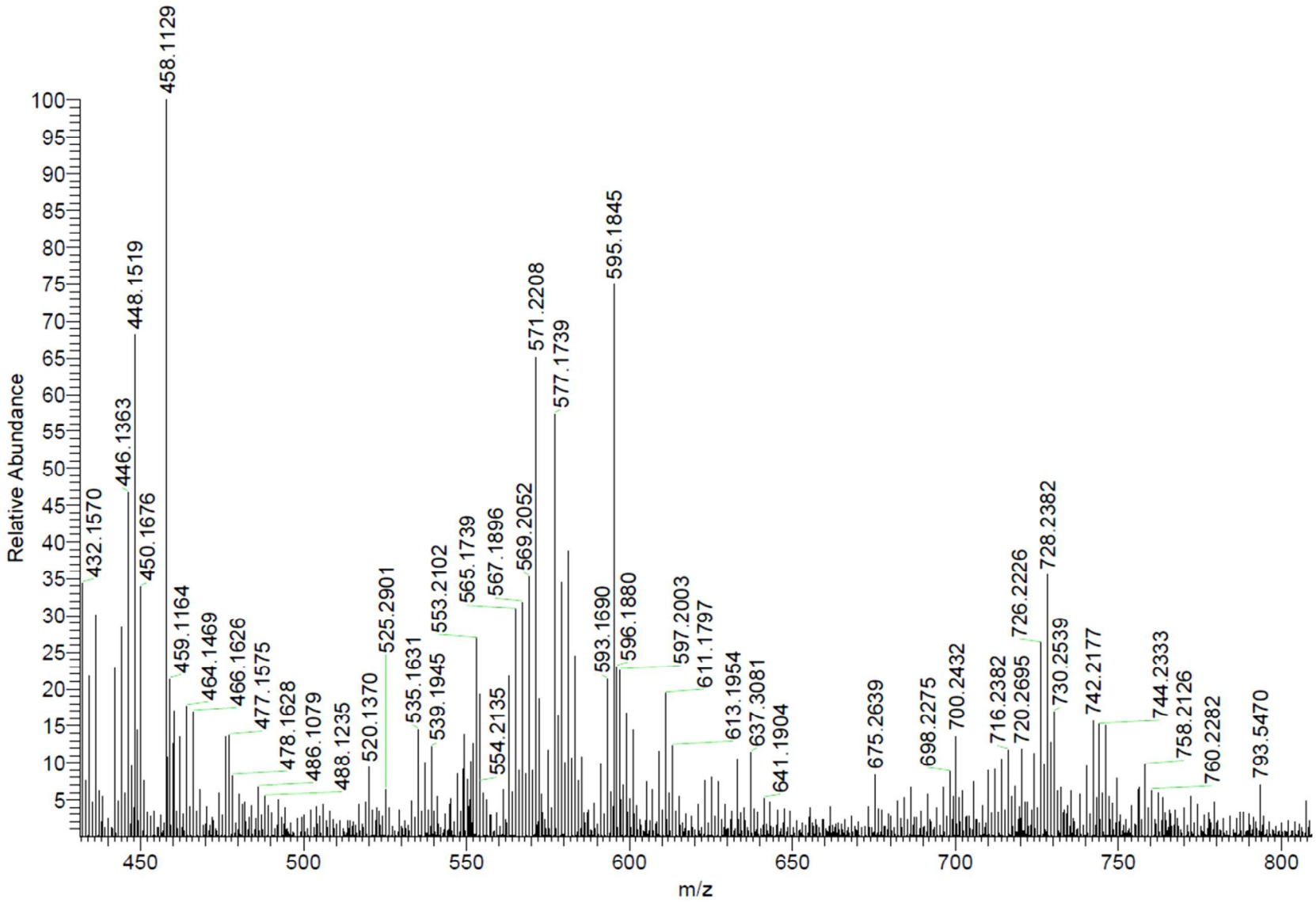


**Figure S3.** ES(+)-HRMS spectrum (oligomer peaks) of the PDA sample (0.1 mg/mL) in methanol/DMSO/TFA = 97/2/1 prepared in TRIS buffer.

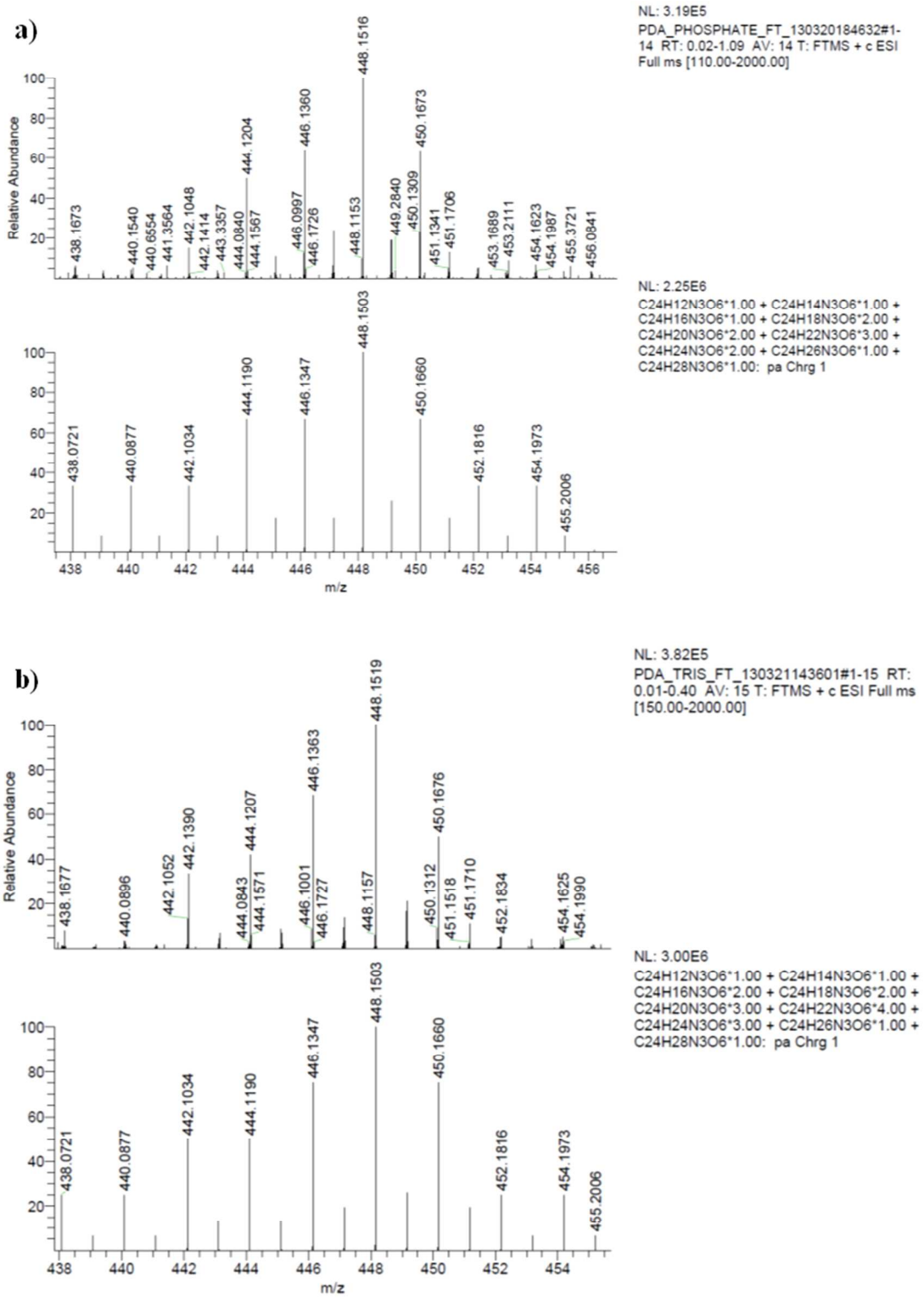


**Figure S4.** ES(+)-HRMS spectra (oligomer peaks) of the PDA samples (0.1 mg/mL) in methanol/DMSO/TFA = 97/2/1 prepared in phosphate (a) and TRIS (b) buffer. Comparison of the experimental spectra (top) and simulated isotopic patterns (bottom).

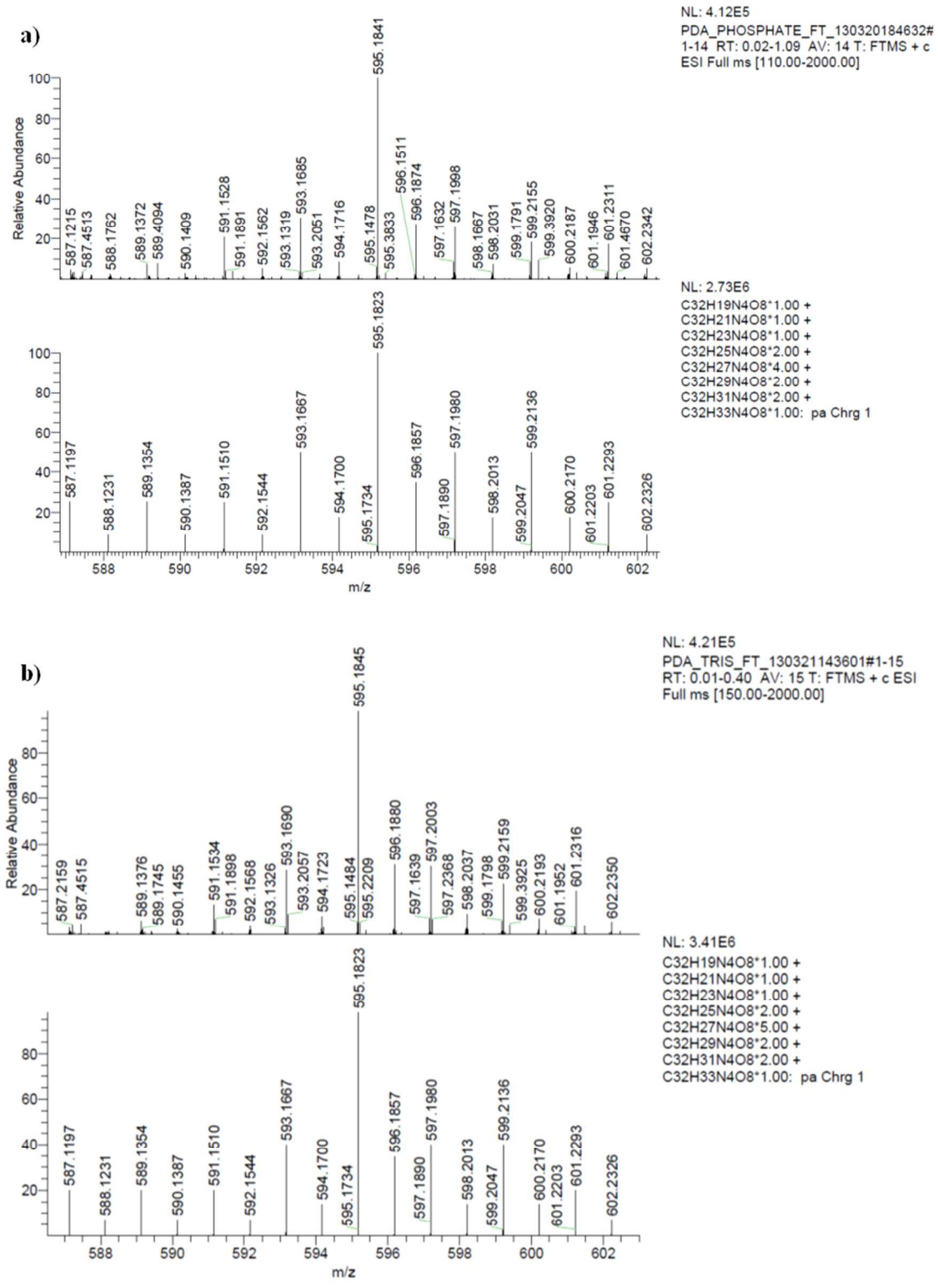


**Figure S5**. ES (+)-HRMS spectra (oligomer peaks) of the PDA samples (0.1 mg/mL) in methanol/DMSO/TFA = 97/2/1 prepared in phosphate (a) and TRIS (b) buffer. Comparison of the experimental spectra (top) and simulated isotopic patterns (bottom).

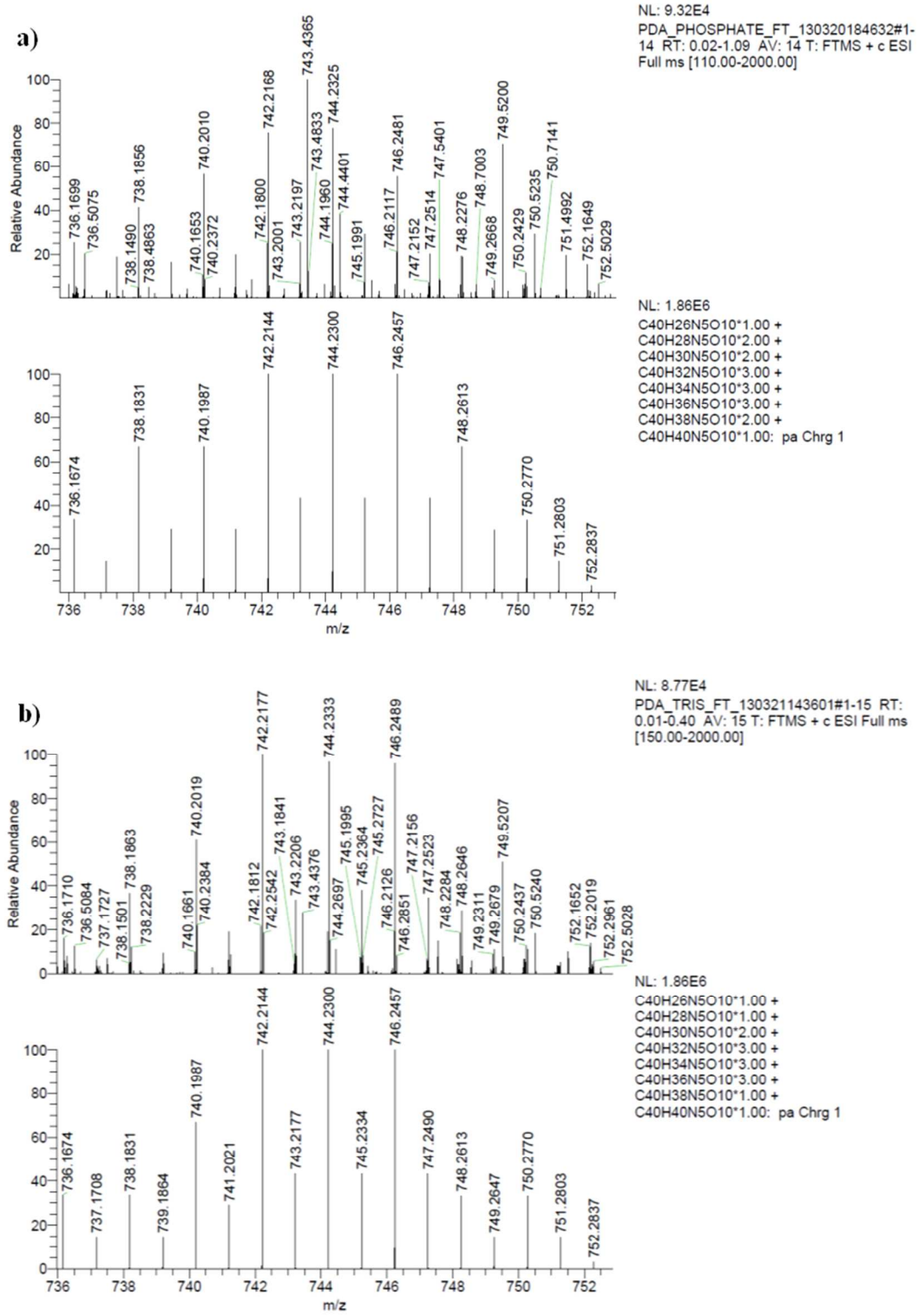


**Figure S6.** ES (+)-HRMS spectra (oligomer peaks) of the PDA samples (0.1 mg/mL) in methanol/DMSO/TFA = 97/2/1 prepared in phosphate (a) and TRIS (b) buffer. Comparison of the experimental spectra (top) and simulated isotopic patterns (bottom).

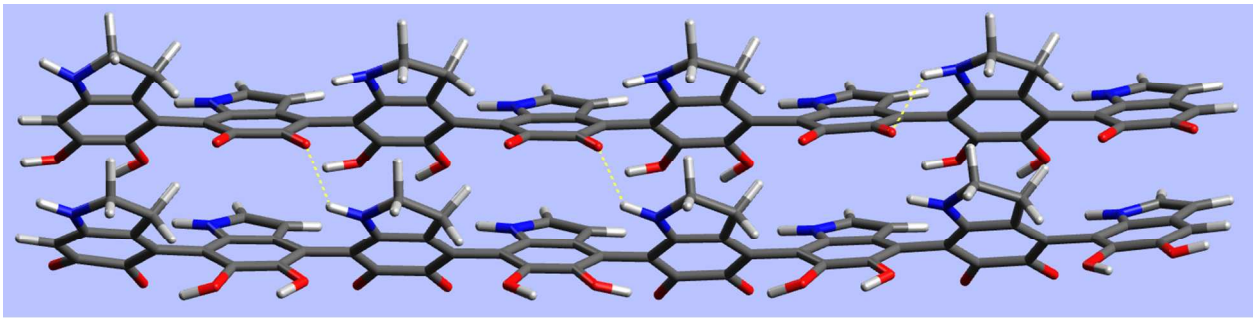

**Figure S7.** “Parallel-stacking” association pattern of the PDA octamer chains.

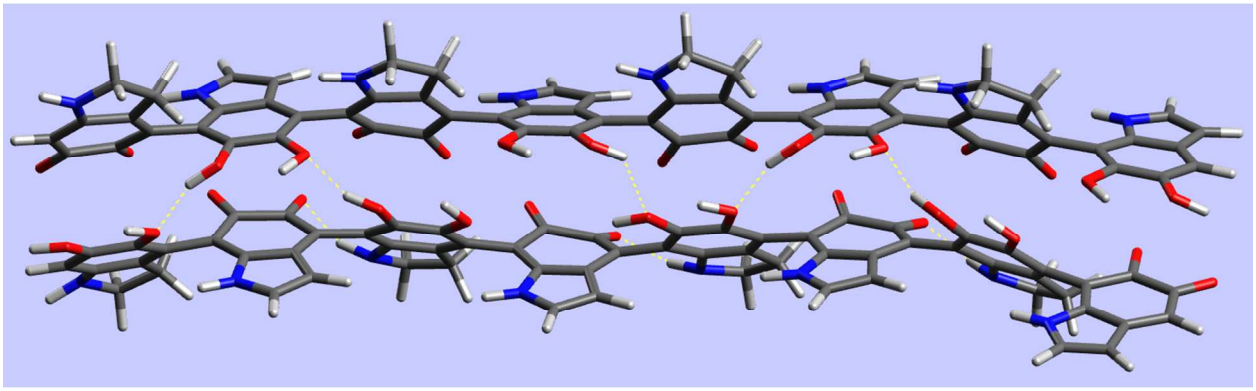

**Figure S8.** “Antiparallel-stacking” association pattern of the PDA octamer chains.

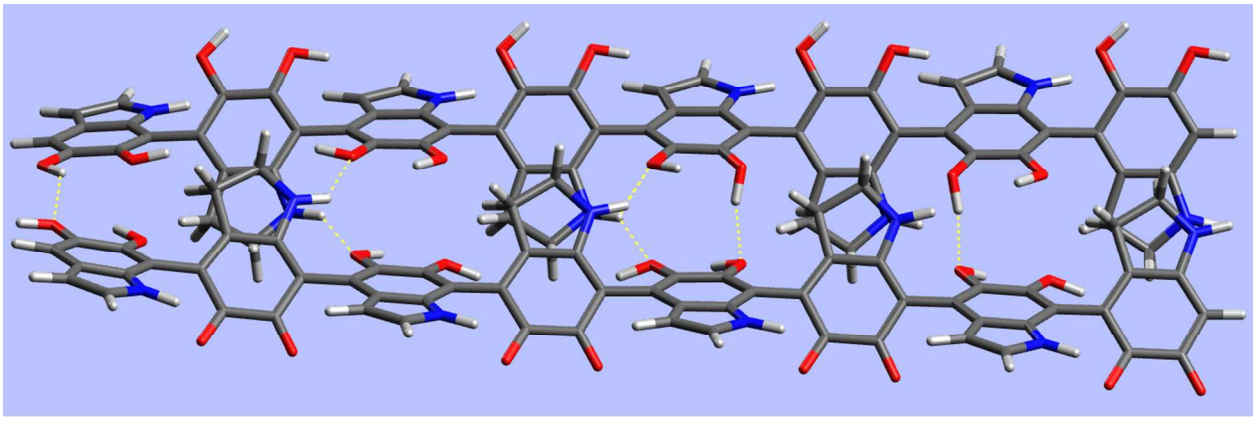

**Figure S9.** “Stacking and H-bonding” association pattern of the PDA octamer chains.

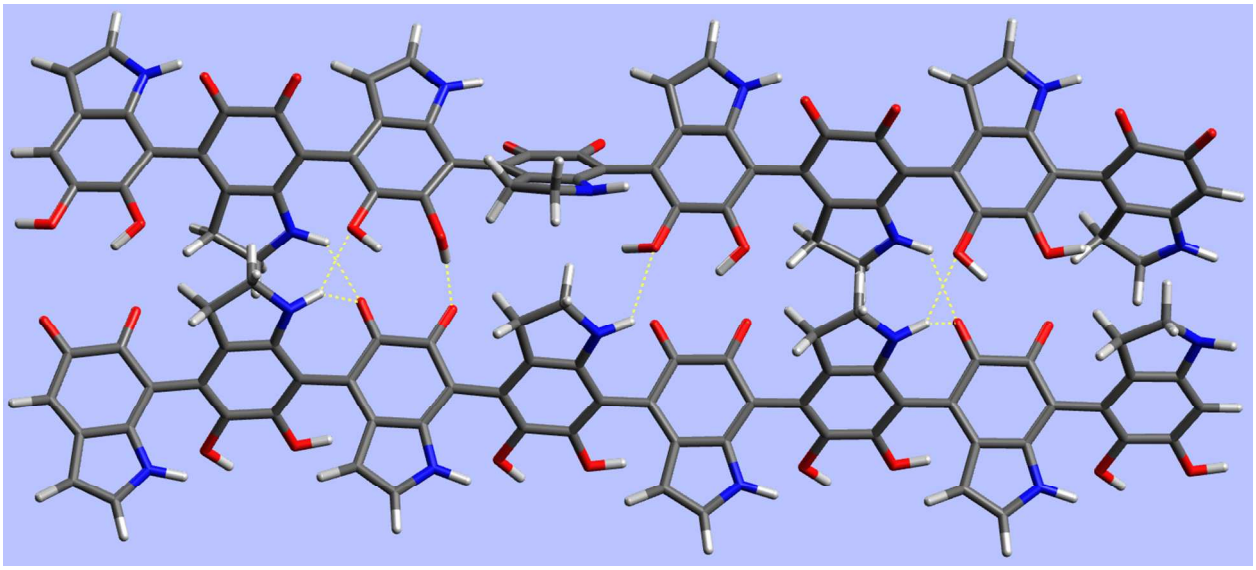

**Figure S10.** “Antiparallel-stacking and H-bonding” association pattern of the PDA octamer chains.

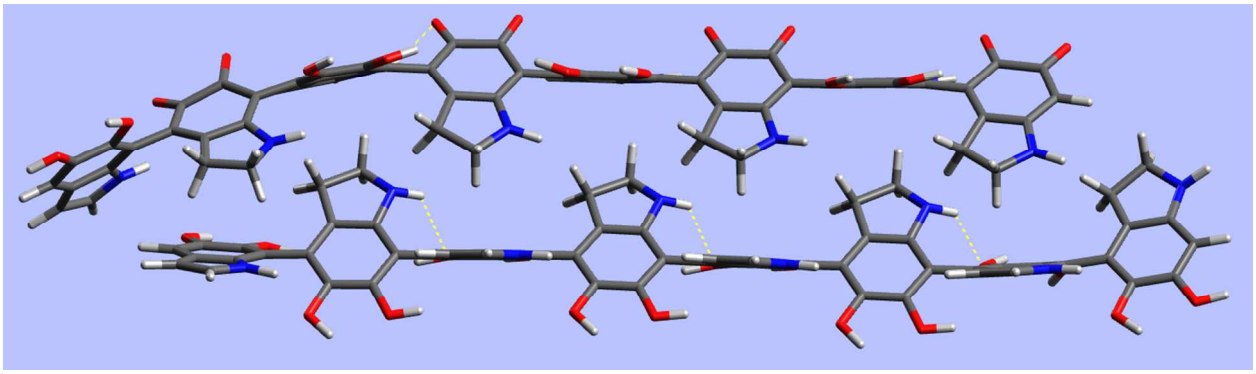

**Figure S11.** “T-shape” association pattern of the PDA octamer chains.

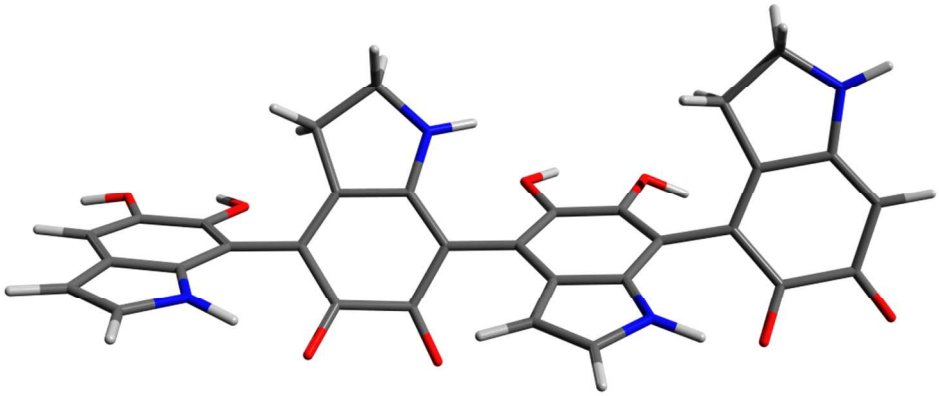

**Figure S12.** Equilibrium geometry structure of the **M3-M2-M3-M2** four units PDA chain.

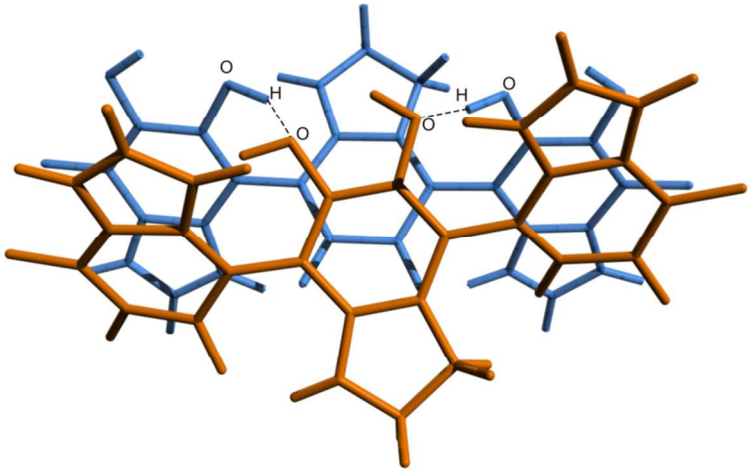


**Figure S13.** "Antiparallel-stacking" association pattern of the PDA chains.

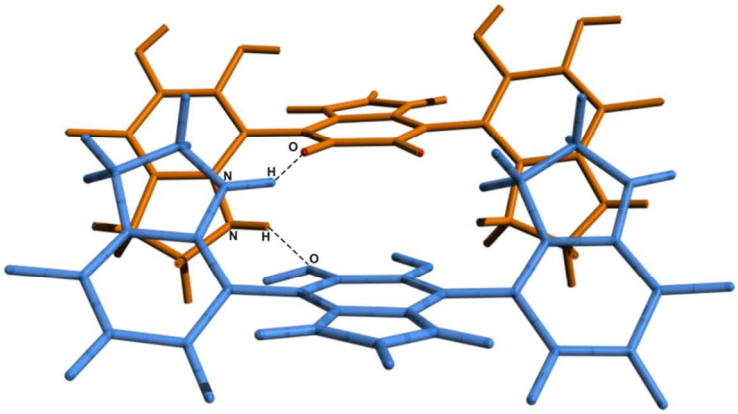


**Figure S14.** “Stacking and H-bonding” association pattern of the PDA chains.

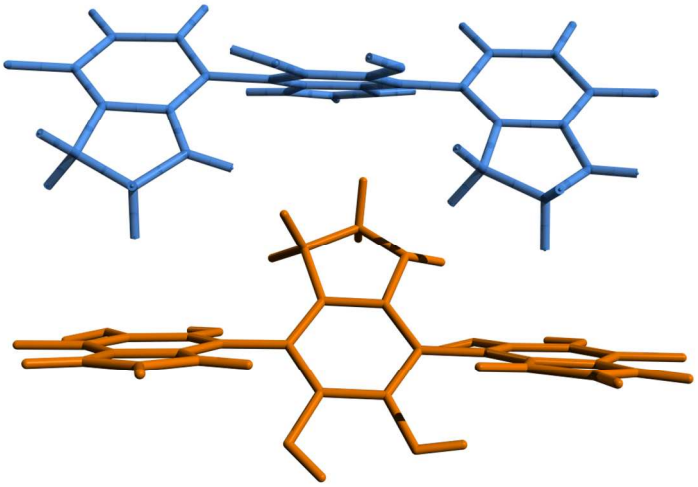

**Figure S15.** “T-shape” association pattern of the PDA chains.

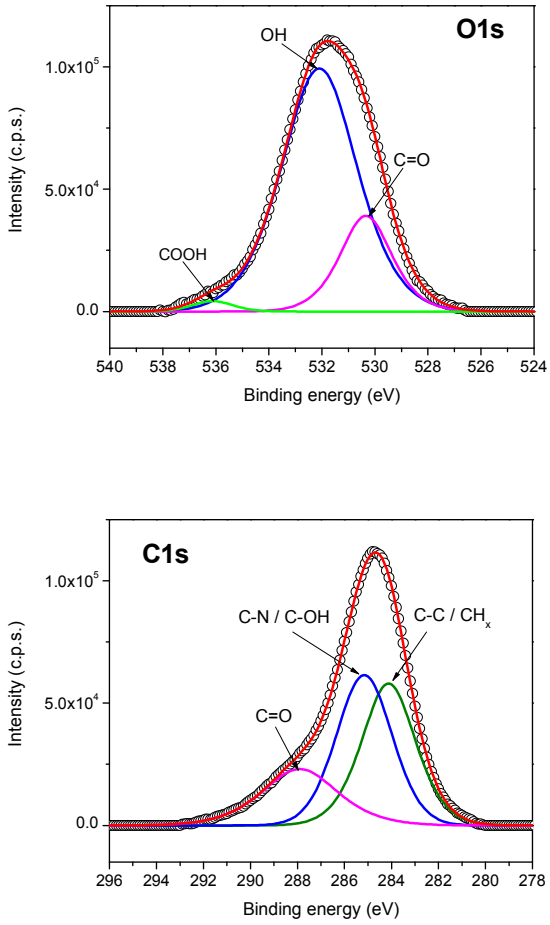


**Figure S16**. High resolution XPS spectra of O1s and C1s core-levels of PDA.

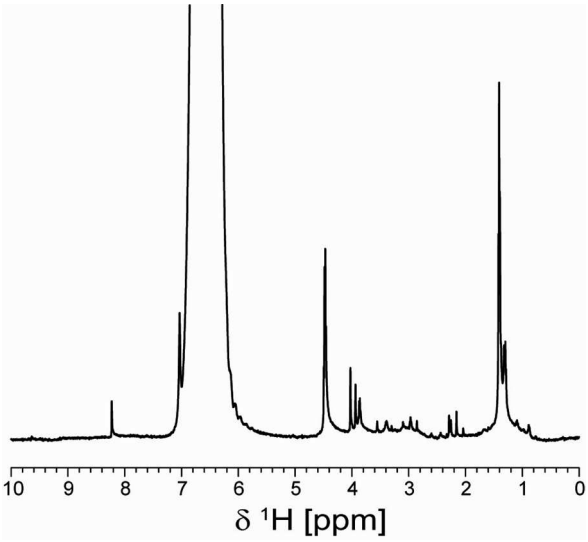


**Figure S17.** 600.1 MHz liquid state $^{1}$H NMR spectra of PDA (TRIS sample) in TFA at 303 K. A watergate W5 sequence was used for solvent suppression.

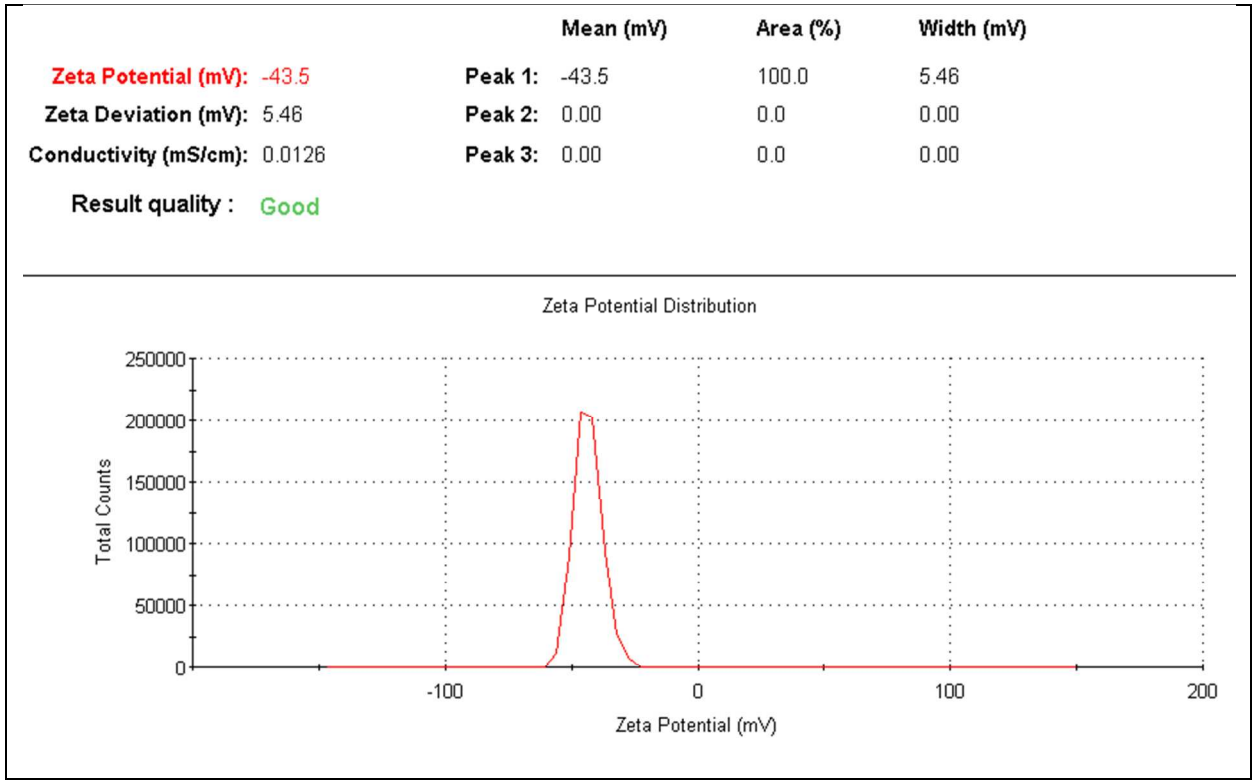


**Figure S18.** Zeta potential determination of PDA prepared in TRIS buffer.