# Ion Mobility Mass Spectrometry Coupled with Molecular Dynamics Simulations: In-depth Structural Analysis of Polystyrene-based Au-Containing Copolymers

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## **1D NMR Spectroscopy Measurements**

<sup>1</sup>H and <sup>31</sup>P spectra were recorded on a Bruker Avance III HD 600 MHz spectrometer, equipped with a BBO-Probe (5 mm) with z-gradient (<sup>1</sup>H 600.13 MHz). All measurements were carried out in deuterated solvents. The chemical shift ( $\delta$ ) is reported in parts per million (ppm) relative to the residual solvent protons. The measured coupling constants were calculated in Hertz (Hz). MESTRENOVA 11.0 software was used to analyze the spectra.

# Size Exclusion Chromatography

The SEC measurements were conducted on a PSS SECurity2 system consisting of a PSS SECurity Degasser, PSS SECurity TCC6000 Column Oven  $(35 \,^{\circ}C)$ , PSS SDV Column Set  $(8x150 \text{ mm } 5 \mu\text{m} \text{ Precolumn}, 8x300 \text{ mm } 5 \mu\text{m} \text{ Analytical Columns}, 100000 Å, 1000 Å and 100 Å) and an Agilent 1260 Infinity Isocratic Pump, Agilent 1260 Infinity Standard Autosampler, Agilent 1260 Infinity Diode Array and Multiple Wavelength Detector (A: 254 nm, B: 360 nm), Agilent 1260 Infinity Refractive Index 5 Detector (35 °C). HPLC grade THF, stabilized with BHT, is used as eluent at a flow rate of 1 mL·min<sup>-1</sup>. Narrow disperse linear poly(styrene) (<math>M_n$  266 g·mol<sup>-1</sup> to 2.52·10<sup>6</sup> g·mol<sup>-1</sup>) standards (PSS ReadyCal) were used as calibrants. All samples were passed over 0.22 µm PTFE membrane filters. Molecular weight and dispersity analysis was performed in PSS WinGPC UniChrom software (version 8.2).

# General Procedure for NMP of Styrene Based Monomers

Styrene (1.27 g, 12.21 mmol, 133 eqv), styryl alcohol (0.25 g, 1.84 mmol, 20 eqv) and NMP initiator, 2,2,6,6-Tetramethyl-1-(1-phenylethoxy)piperidine, (0.024 g, 0.092 mmol, 1 eqv) were added to a Schlenk tube. Dry toluene was added (0.8 mL) and the combined solution was subjected to four freeze pump thaw cycles. The Schlenk tube was subsequently placed into an oil bath heated to 135 °C and left to stir for 90 minutes. The reaction mixture was quenched upon exposure to atmosphere and cooling in liquid nitrogen and concentrated under reduced pressure, redissolved in a minimal amount of dichloromethane and precipitated three times into cold methanol. The precipitate was centrifuged and dried at 40 °C in a vacuum oven affording TEMPO-(styrene)<sub>x</sub>-(styrene-CH<sub>2</sub>-OH)<sub>y</sub> as an off white powder.

A styrene based, triphenylphosphine containing polymer was synthesized according to the same general NMP procedure<sup>1,2</sup> to synthesize TEMPO-(styrene)<sub>x</sub>-(styrene-CH<sub>2</sub>-OH), with modified stoichiometry and a reaction duration of 45 minutes. Styrene (0.18 g, 1.77 mmol, 66 eqv), styryl alcohol (0.035 g, 0.27 mmol, 10 eqv), 4-(diphenylphosphino) styrene (0.039 g, 0.13 mmol, 5 eqv) and nitroxide initiator (0.007 g, 0.027 mmol, 1 eqv) combined in dry toluene (0.4 mL).

The resulting phosphine polymer (0.025 g, 0.012 mmol) was dissolved in dry dichloromethane (0.2 mL) and ethanol (0.4 mL), and HAuCl<sub>4</sub> •  $3H_2O$  (0.006 g, 0.015 mmol) was dissolved separately in ethanol (0.4 mL) and added dropwise to the first solution. The combined reaction mixture was subsequently stirred at room temperature for 1.5 h. After stirring the solvent was removed under reduced pressure and the resulting light-yellow solid was redissolved in a minimal amount of dichloromethane and precipitated once into ice cold methanol and then dried at 40 °C in a vacuum oven affording TEMPO-(styrene)<sub>x</sub>-(styrene-CH<sub>2</sub>-OH)<sub>v</sub>-(styrene-P-Ph<sub>2</sub>-AuCl)<sub>z</sub>.

#### TEMPO-(styrene)<sub>x</sub>-(styrene-CH<sub>2</sub>-OH)<sub>v</sub> Copolymer analysis by SEC and <sup>1</sup>H NMR



**Figure S1:** SEC and <sup>1</sup>H NMR spectrum of TEMPO-(styrene)<sub>x</sub>-(styrene-CH<sub>2</sub>-OH)<sub>y</sub>, ( $D = 1.2 - Mn = 3,200 \text{ g mol}^{-1}$ )

<sup>1</sup>H-NMR Spectroscopy was used to characterize the TEMPO-(styrene)<sub>x</sub>-(styrene-CH<sub>2</sub>-OH)<sub>y</sub> (Figure S1). Characteristics resonances between ( $\delta$  = 7.23 – 6.28 ppm) are attributed to the aromatic hydrogen atoms of the styryl groups. Benzylic hydrogens belonging to the alcohol containing styryl units are characterized by a distinct resonance at ( $\delta$  = 4.69 – 4.45 ppm). The resonances between ( $\delta$  = 2.47 – 0.81 ppm) represent the aliphatic hydrogens belonging to the backbone of the polymer. The number average molecular weight of the polymer was determined using Size Exclusion Chromatography (SEC) and found to be 3,200 g mol<sup>-1</sup> with a low dispersity of 1.26.





**Figure S2:** SEC and <sup>1</sup>H NMR analysis of TEMPO-(styrene)<sub>x</sub>-(styrene-CH<sub>2</sub>-OH)<sub>y</sub>-(styrene-PPh<sub>2</sub>-AuCl)<sub>z</sub>, ( $\mathcal{D} = 1.15 - Mn = 2,400 \text{ g mol}^{-1}$ ).

<sup>1</sup>H-NMR Spectroscopy was used to characterize the TEMPO-(styrene)<sub>x</sub>-(styrene-CH<sub>2</sub>-OH)<sub>y</sub>-(styrene-P-Ph<sub>2</sub>-AuCl)<sub>z</sub> (Figure S2). Resonances between ( $\delta$  = 7.85 – 7.34 ppm) are attributed to the aromatic hydrogens of gold complexed triphenylphosphine. The <sup>31</sup>P-NMR spectrum further corroborated the complexation of gold to phosphine showing a resonance at ( $\delta$  = 32.36 ppm). Characteristics resonances between ( $\delta$  = 7.2 – 6.22 ppm) are attributed to the aromatic hydrogen atoms of the styryl groups. Benzylic hydrogens belonging to the alcohol containing styryl units are characterized by a distinct resonance at ( $\delta$  = 4.73 – 4.42 ppm). The resonances between ( $\delta$  = 2.59 – 0.77 ppm) represent the aliphatic hydrogens belonging to the backbone of the polymer. The number average molecular weight of the polymer was determined using Size Exclusion Chromatography (SEC) and found to be close to 2,400 g mol<sup>-1</sup> with a low dispersity of D = 1.15.

## Ion mobility experiments

Tetrahydrofuran and acetonitrile (20:80, v/v) were used to prepare copolymer stock solutions containing 1.0 mg mL<sup>-1</sup>. Without the use of a cationizing agent, the copolymers were examined. Before ESI analysis, the copolymer solutions were diluted 100 times with tetrahydrofuran and acetonitrile (20:80, v/v).

Using a Waters Synapt G2-Si mass spectrometer, MS spectra and *CCS* measurements were taken. The solutions were infused at a rate of 5  $\mu$ L min<sup>-1</sup>, with a source temperature of 100°C and a desolvation temperature of 150°C, and a capillary voltage of 3.1 kV. The standard IMS-MS parameters were as follows: trap bias = 45.0 V, N<sub>2</sub> flow rate = 60 mL min<sup>-1</sup>, He flow rate = 180 mL min<sup>-1</sup>, mass range = *m*/*z* (50-4,000), wave height = 40 V and wave velocities = 350, 600, or 800 m s<sup>-1</sup>. A pre-recognized calibration procedure<sup>3</sup> was used to transform the experimentally determined arrival time distributions to <sup>TW</sup>CCS<sub>N2→He</sub>,<sup>4</sup> which will be represented to as *CCS*<sub>exp</sub>.

## Molecular dynamics simulations

a) Details procedure of CCS calculations:

All calculations were performed with the Materials Studio software (BIOVIA, San Diego, CA).<sup>5</sup> For TEMPO-(styrene)<sub>x</sub>-(styrene-CH<sub>2</sub>-OH)<sub>y</sub> copolymer, PCFF force field was used and validated by the fact that the calculated effective density of TEMPO-polystyrene (0.62-0.66 Da/Å<sup>3</sup>) is in good agreement with the reported density of bulk polystyrene (0.57-0.62 Da/Å<sup>3</sup>).<sup>6</sup> For the TEMPO-(styrene)<sub>x</sub>-(styrene-CH2-OH)<sub>y</sub>-(styrene-PPh<sub>2</sub>-AuCl)<sub>z</sub> copolymer, we switched to the UFF force field since the parameters for gold are not available in PCFF (see specific section in SI "Universal Force Field (UFF) Validation" and Figure S13).Force field assigned atomic charges were used for the simulations with the PCFF force field, while Gasteiger charges<sup>7</sup> were used in combination with the UFF force field. At first, geometry optimization was performed starting from a linear polymer chain (without charge). After adding a charge (H<sup>+</sup>) to the optimized polymer chain, the geometry underwent additional optimization; the TEMPO group is chosen as the proton carrier due to the presence of the basic nitrogen atom. Next, a quenched dynamics (frames quenched every 5ps) was run for 20 ns at 300K, with a 1 fs timestep, and a cutoff of 100 Å for the van der Waals and

electrostatic interactions. The most stable structure obtained from the quenched dynamics was then used as the starting point for a 25ns-long MD run (NVT ensemble; constant number of particles, N, volume, V, and temperature (T = 300 K) and using a 1 fs time step). From this MD trajectory, 500 structures were extracted and used to obtained an average theoretical  $CCS_{th}$  computed by using the trajectory method (TM)<sup>8</sup> model implemented within Collidoscope software.<sup>9</sup>

b) Details procedure for the investigation of the folding process:

Since the folding process occurs in short timescale, to visualize it, one must save snapshots very frequently. In practice, instead of running a 25 ns-long MD with frames saved every 5 ps, we performed shorter MDs (2 ns-long) with snapshots saved every 0.5 ps; keeping all the other MD parameters constant.



**Figure S3:** ESI-MS mass spectra of TEMPO-(styrene)<sub>x</sub>-(styrene-CH<sub>2</sub>-OH)<sub>y</sub> (0.01 mg mL<sup>-1</sup>) in acetonitrile/ tetrahydrofuran (80/20) (v/v); Comparison between experimental and simulated isotope patterns: (a) [TEMPO-(styrene)<sub>5</sub>-(styrene-CH<sub>2</sub>-OH)<sub>1</sub> + H]<sup>+</sup> (DP = 6) and (b) [TEMPO-(styrene)<sub>7</sub>-(styrene-CH<sub>2</sub>-OH)<sub>3</sub> + H]<sup>+</sup> (DP = 10) ions, as selected examples.



**Figure S4:** ESI-MS mass spectra of TEMPO-(styrene)<sub>x</sub>-(styrene-CH<sub>2</sub>-OH)<sub>y</sub>-(styrene-PPh<sub>2</sub>)<sub>w</sub>-(styrene-PPh<sub>2</sub>-AuCl)<sub>z</sub> (0.01 mg mL<sup>-1</sup>) in acetonitrile/ tetrahydrofuran (80/20) (v/v); Comparison between experimental and simulated isotope patterns.



**Figure S5:** ESI-MS mass spectra of TEMPO-(styrene)<sub>x</sub>-(styrene-CH<sub>2</sub>-OH)<sub>y</sub>-(styrene-PPh<sub>2</sub>-AuCl)<sub>z</sub> (0.01 mg mL<sup>-1</sup>) in acetonitrile/ tetrahydrofuran (80/20) (v/v); Comparison between experimental and simulated isotope patterns and structure of the ion.



**Figure S6:** Ion mobility mass spectrometry analysis of the copolymer (0.01 mg mL<sup>-1</sup>) in acetonitrile/ tetrahydrofuran (80/20) (v/v) using Waters Synapt G2-Si mass spectrometer; arrival time distribution (ATD) of selected [TEMPO-(styrene)<sub>x</sub>-(styrene-CH<sub>2</sub>-OH)<sub>y</sub> + H]<sup>+</sup> ions: (a) x = 9, y = 0; (b) x = 8, y = 1; (c) x = 7, y = 2; (d) x = 6, y = 3; (e) x = 5, y = 4; (f) x = 4, y = 5; here total DP = 9 in every case.



**Figure S7:** Ion mobility mass spectrometry analysis of copolymer (0.01 mg mL<sup>-1</sup>) in acetonitrile/ tetrahydrofuran (80/20) (v/v); (a) TEMPO-(styrene)<sub>x</sub>-(styrene-CH<sub>2</sub>-OH)<sub>y</sub> (styrene-CH<sub>2</sub>-OH)<sub>y</sub> (styrene-PPh<sub>2</sub>)<sub>w</sub>-(styrene-PPh<sub>2</sub>-AuCl)<sub>0</sub> ions, (a) and (b) are represent by the blue-green-yellow palette, (c) TEMPO-(styrene)<sub>x</sub>-(styrene-CH<sub>2</sub>-OH)<sub>2</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>-AuCl)<sub>0</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>-AuCl)<sub>0</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene)<sub>x</sub>-(styrene-CH<sub>2</sub>-OH)<sub>2</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene)<sub>x</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene)<sub>x</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene)<sub>x</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene)<sub>x</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styrene-PPh<sub>2</sub>)<sub>0</sub>-(styre





Sequence of S6B6	CCS (Å <sup>2</sup> )	SD
EB2S6B4	366	7
EB3S6B3	369	7
EB6S6	371	5
EB1S1B1S1B2S2B1S2B1	373	6
EB4S6B2	376	9
ES6B6	376	6
EB1S6B5	376	6
ES3B6S3	377	6
ES2B3S2B3S2	378	8
EB5S6B1	380	7
ES2B2S1B2S1B2S2	383	6
ES1B1S1B1S1B1S1B1S1B1S1B1	386	6

Sequence of S12B6	CCS (A <sup>2</sup> )	SD
ES6B4S6B2	457	6
ES2B1S2B1S2B1S2B1S2B1S2B1	466	6
ES4B2S2B3S2B1S4	468	6
EB1S12B5	470	10
ES6B6S6	473	6
EB4S12B2	475	6
ES4B1S2B3S2B2S4	476	9
EB2S12B4	476	8
ES2B1S2B1S2B1S2B1S2B2S2	477	7
ES6B2S6B4	477	8
ES6B5S2B1S4	479	8
EB5S12B1	480	7
ES4B3S4B3S4	481	8
EB6S12	481	7
EB3S12B3	482	7
ES12B6	484	7
ES6B5S6B1	485	5
ES4B1S2B5S6	485	8
ES6B1S6B5	489	9
ES4B1S2B4S2B1S4	490	6
ES4B2S2B2S2B2S4	491	8

**Figure S8:** Theoretical CCS estimation using molecular dynamics simulation of the H-(styrene)<sub>x</sub>-(styrene-CH<sub>2</sub>-OH)<sub>y</sub>-TEMPO : (a) Theoretical CCS evolution for different sequences of S6B6 and (b) Theoretical CCS evolution for different sequences of S12B6.

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**Figure S9:** Molecular Dynamics simulations (PCFF force field, 298K, 25 ns) of  $[TEMPO-(styrene)_x-(styrene-CH_2-OH)_y + H]^+$  ions, snapshot of the last frame of the MD that represent the hydrogen bond by red colour : (a) DP = 18 (x = 17, y = 1), (b) DP = 15 (x = 13, y = 2), (c) DP = 21 (x = 18, y = 3), (d) DP = 21 (x = 17, y = 4), (e) DP = 19 (x = 14, y = 5) and (f) DP = 20 (x = 14, y = 6).



**Figure S10:** Molecular Dynamics simulations (PCFF force field, 300K, 25 ns) of [TEMPO-(styrene)<sub>22</sub>-(styrene-CH<sub>2</sub>-OH)<sub>1</sub> + H]<sup>+</sup> ions (DP = 23, x = 22, y = 1). Snapshot of the last frame of the MD with enlarged views of the charged centers : H-bonding interaction between the protonated TEMPO end group and hydroxyl group of the styrene-CH<sub>2</sub>-OH unit. Here in the zoom section, the light blue represents the styrene-CH<sub>2</sub> unit of styrene-CH<sub>2</sub>-OH, while the conventional color represents the remaining portion.



**Figure S11:** Ion mobility mass spectrometry analysis and Molecular Dynamics simulations of  $[TEMPO-(styrene)_x-(styrene-CH_2-OH)_1 + H]^+$  ions: comparison between the  $CCS_{exp}$  and  $CCS_{th}$  over the full mass range.



**Figure S12:** Molecular Dynamics simulations (PCFF force field, 300K, 2 ns) of (a)  $[E-S_{11}-B_1-S_{11} + H]^+$  ions and (b)  $[E-B_1-S_{22} + H]^+$  ions (DP = 23): snapshots at different times of the trajectory revealing that the folding process is mostly initiated by  $\pi$ - $\pi$  interactions between phenyl rings (a) with the H-bonded protonated TEMPO and styrene-CH<sub>2</sub>-OH for the E-S<sub>11</sub>-B<sub>1</sub>-S<sub>11</sub> ions ultimately being incorporated in the core of the equilibrated structure and (b) the TEMPO / styrene-CH<sub>2</sub>-OH sequence remaining at the surface of the globular ion. The styrene-CH<sub>2</sub>-OH and the TEMPO residues are highlighted in blue and grey for visualisation.

#### Universal Force Field (UFF) and PCFF comparison

Since the gold parameters are not incorporated into the PCFF force field used successfully in our first study,<sup>10</sup> we turned to UFF (Universal Force Field) with charges assigned on the different atoms using the Gasteiger method for the Au-containing copolymer ions. We calculated, using both UFF and PCFF, the  $CCS_{th}$  for TEMPO-initiated polystyrene homopolymer ions (DP = 8-17) and TEMPO-initiated styrene/styrene-CH<sub>2</sub>-OH copolymer ions (DP = 8-19) in order to check whether PCFF will reproduce the UFF data without further parametrization/validation. The UFF and PCFF-computed  $CCS_{th}$  were further compared with the  $CCS_{exp}$  (refer to Figure S13). Since the three different CCS are nearly identical over the investigated DP-ranges, we will consider that both force fields are able to generate reliable molecular structures.



**Figure S13:** Ion mobility mass spectrometry and molecular dynamics simulations using (PCFF and UFF) force fields for TEMPO-initiated styrene homopolymer ions and TEMPO-initiated styrene- $CH_2$ -OH copolymer ions : (a) CCS evolution with DP for [TEMPO-PS + H]<sup>+</sup> and (b) CCS evolution with DP for [TEMPO-(styrene)<sub>x</sub>-(styrene-CH<sub>2</sub>-OH)<sub>1</sub> + H]<sup>+</sup> ions.



*gure S14:* Molecular Dynamics simulations (UFF force field, 298K, 25 ns) of  $[TEMPO-(styrene)_x-(styrene-CH_2-OH)_y-(styrene-PPh_2)_w-(styrene-PPh_2-AuCl)_z + H]^+ions, snapshot of the last frame of the MD that represent the hydrogen bond by red colour : (a) DP = 16 (x = 11, y = 4, w = 1, z = 0), (b) DP = 15 (x = 11, y = 2, w = 2, z = 0), (c) DP = 13 (x = 7, y = 4, w = 1, z = 1), (d) DP = 14 (x = 13, y = 0, w = 0, z = 1), (e) DP = 15 (x = 13, y = 1, w = 0, z = 1) and (f) DP = 10 (x = 7, y = 2, w = 0, z = 1).$ 



**Figure S15:** Molecular Dynamics simulations (UFF force field, 298K, 25 ns) of  $[TEMPO-(styrene)_{13}-(styrene-CH_2-OH)_1-(styrene-PPh_2-AuCl)_1 + H]^+ions (DP = 15, x = 13, y = 1, z = 1).$  Snapshot of the last frame of the MD with enlarged views of the charged center : H-bonding interaction between the protonated TEMPO end group and chloride group of the styrene-PPh\_2-AuCl unit. Here, the styrene monomer unit is indicated by dark green, the styrene-CH\_2-OH is indicated by light blue, styrene-PPh\_2 represent by the plum and the end group is indicated by grey.

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