

Supporting Information

Rapid, facile synthesis of conjugated polymer zwitterions in ionic liquids

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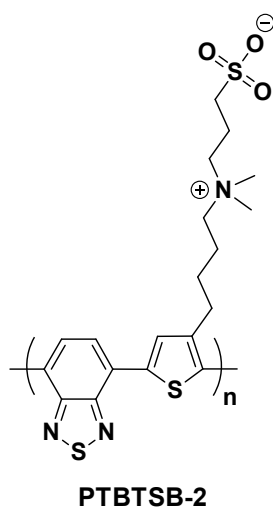
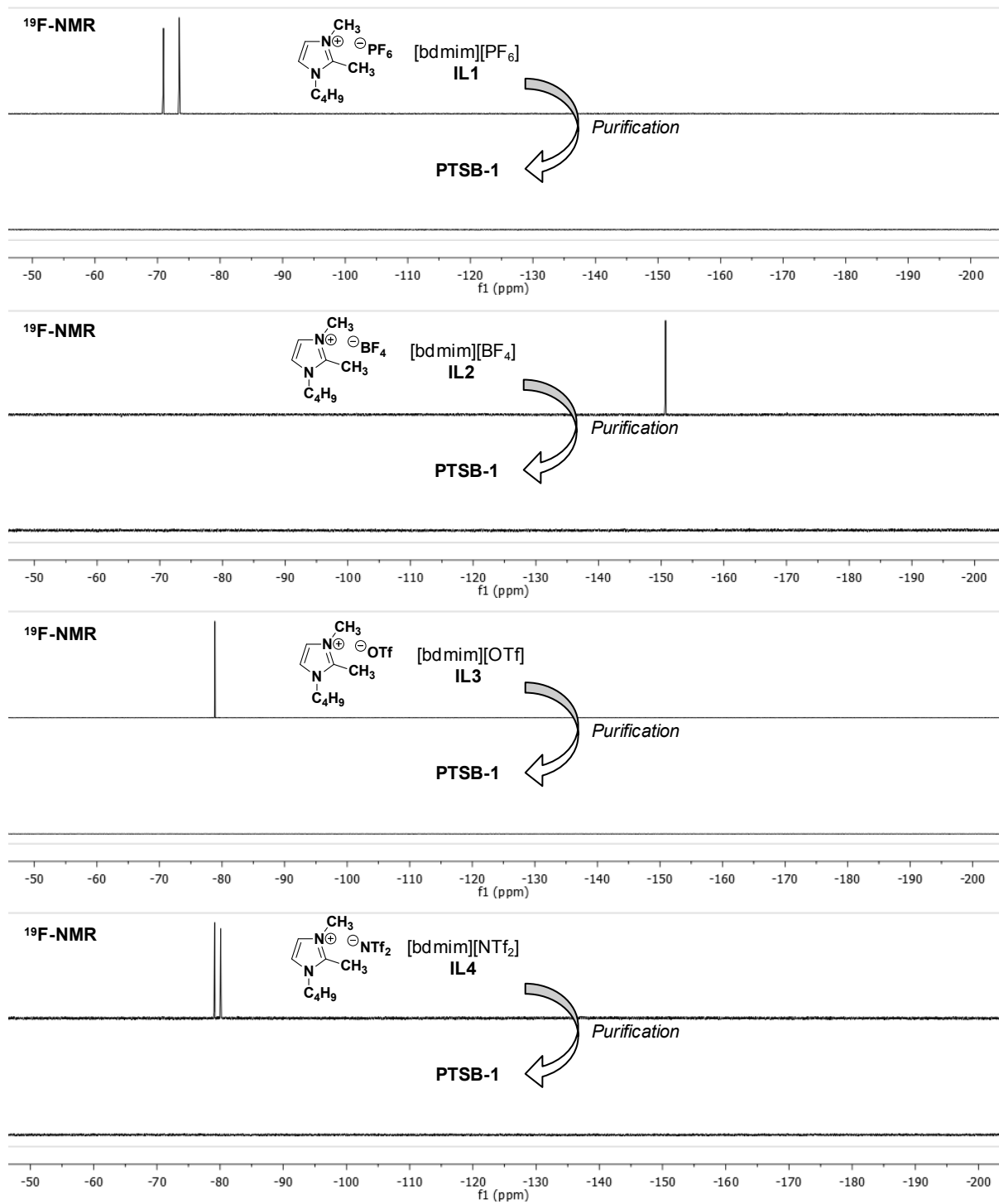
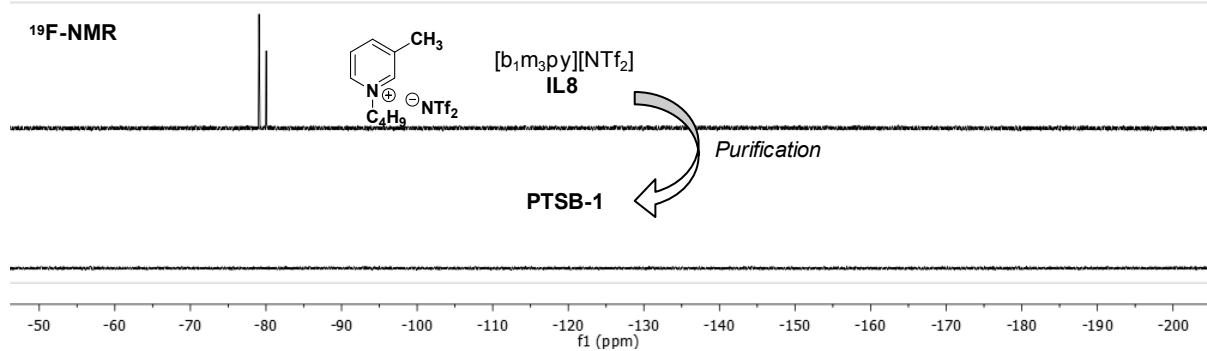
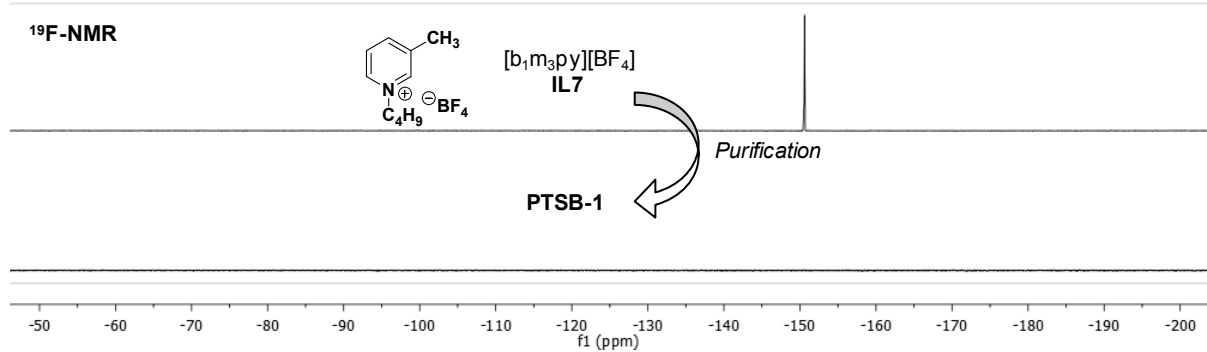
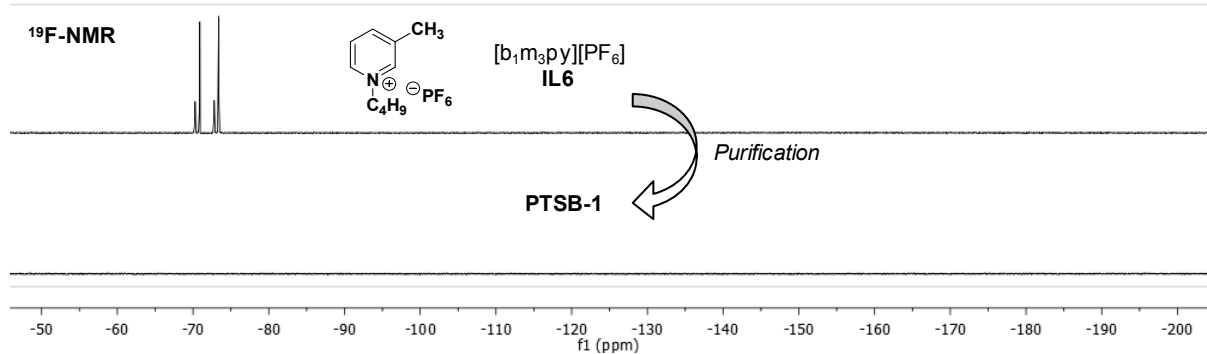
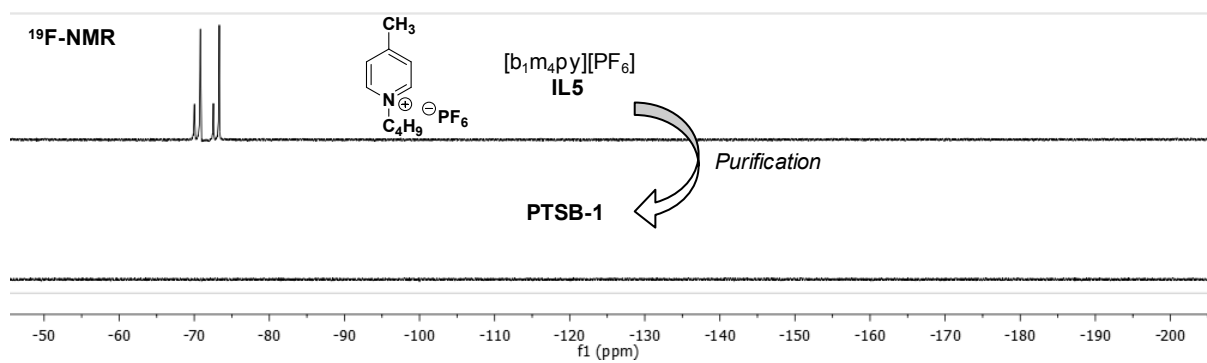


Figure S1. Chemical structure of **PTBTSB-2** used in OPV devices.





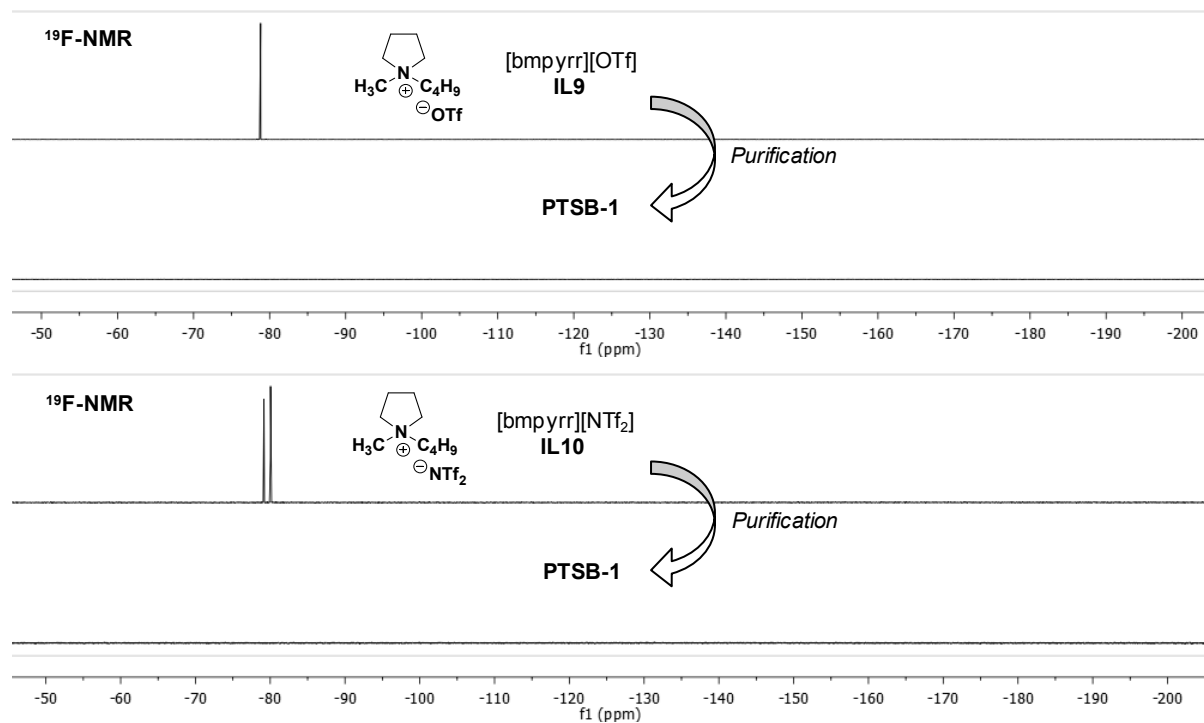


Figure S2. ^{19}F -NMR spectra of ILs (top spectra) and of the polymers (corresponding bottom spectra) in D_2O containing 0.2 M NaCl. The absence of fluorine signal confirms IL removal following purification.

The ILs used here containing either $[\text{PF}_6]$ or $[\text{NTf}_2]$ anions are not readily miscible with salt water (0.2 M NaCl), but do fully mix when heated ($\sim 40^\circ\text{C}$), which was noticed when preparing IL1, IL4, IL5, IL6, IL8 and IL10 for NMR analysis in D_2O (0.2 M NaCl). ILs containing $[\text{BF}_4]$ and $[\text{OTf}]$ (IL2, IL3, IL7 and IL9) are fully miscible with salt water (0.2 M NaCl). **PTSB-1** has the greatest solubility in ILs containing $[\text{OTf}]$ (IL3 and IL9), as shown in the fluorescence images in **Figure S3**, where a substantial red-shift and attenuation (typical of aggregated semiconducting polymers) was noted for all the ILs except IL3 and IL9. The high solubility of **PTSB-1** in IL9 may have contributed to the higher molecular weight obtained when using it as a cosolvent compared to the other ILs. Higher molecular weight polymers typically form more uniform thin films, an important factor for consideration when using these materials as interlayers in optoelectronic applications.

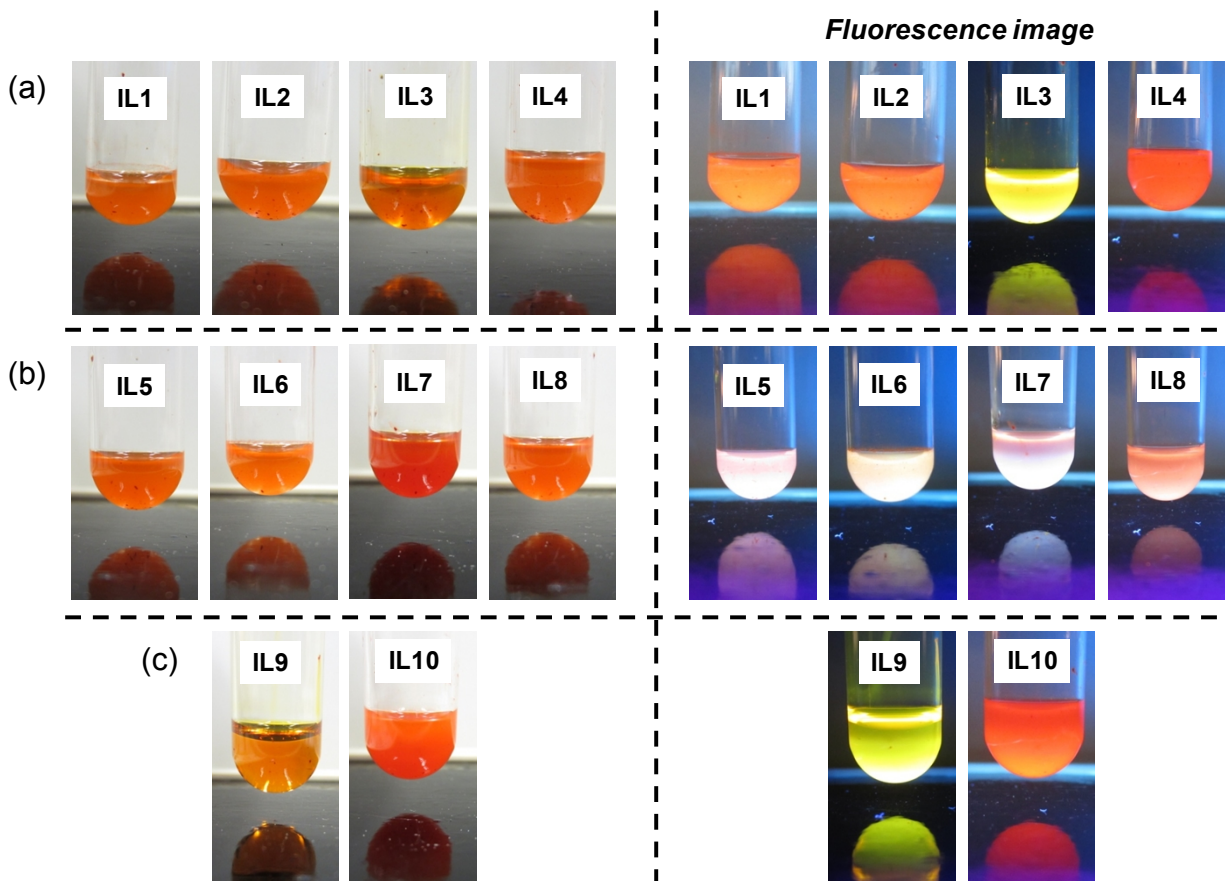


Figure S3. Non-UV-irradiated (left) and UV-irradiated (fluorescent) (right) images of a common, average molecular weight (~ 15 kDa) **PTSEB-1** sample dissolved in the ten different ionic liquids; (a) Imidazolium; (b) pyridinium*; (c) pyrrolidinium. The polymer/IL mixture was heated at 100°C for 5 minutes prior to taking the pictures. *The fluorescent images of the pyrrolidinium's appear different from the imidazolium and pyrrolidinium due to the ILs weak blue fluorescence.

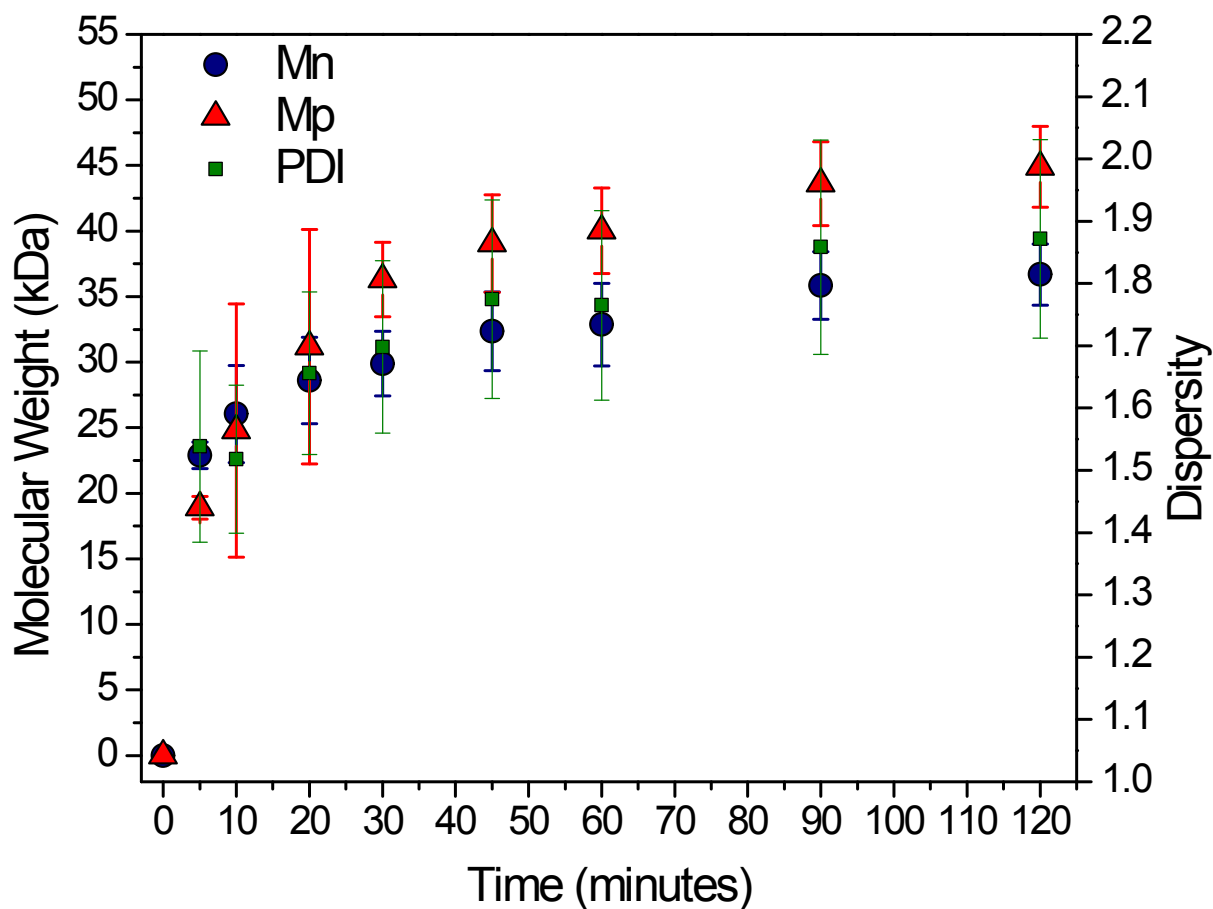


Figure S4. Polymerization of **PTBTSB-2** in IL9. Aliquots from three separate reactions were removed at the denoted time points and the polymer was precipitated into MeOH and washed with MeOH to remove residual ionic liquid and prior to running SEC in TFE. Averages of the three reactions are given with error bars representing ± 1 standard deviation. At $t = 5$ minutes, polymers with molecular weights exceeding 20 kDa were obtained, showing that the Suzuki coupling is very rapid, with a steady increase in molecular weight up to two hours, beyond which molecular weight does not appear to increase further.

Ultraviolet photoelectron spectroscopy (UPS) of CPZs

Sample Preparation and measurement for UPS. Silicon wafers (n-doped with arsenic) were cut ($\sim 10 \times 10$ mm) and cleaned with detergent, water, acetone and isopropanol. The substrates were dried in an oven at 150°C for 12 hours, cooled to room temperature, treated with UV-ozone for 15 minutes, transferred to a nitrogen filled glove-box, and placed in a vacuum deposition chamber (2×10^{-6} mbar). A ~ 40 nm thick layer of silver or gold was deposited. Immediately after deposition the substrates were removed and the polymers spun from a 1 mg / mL solution of trifluoroethanol at 4000 rpm for 60 seconds. The samples were brought into the UPS analysis chamber, under ultrahigh vacuum (1×10^{-9} mbar). The ionization potentials were determined through two steps: first the intersection of a line tangent to the low kinetic energy onset of the spectrum with the abscissa axis was ascertained and subtracted from 21.2 eV (the UV-source energy), followed by the addition of the intersection of high kinetic energy onset with the abscissa axis. All measurements were done at a -3 V sample bias, allowing for facile collection of low kinetic energy electrons. The resolution of the UPS instrument was 0.1 eV as determined from the width of the Fermi level of silver. All samples were < 10 nm thick as determined by the surface profiler (KLA Tencor, model Alpha-Step IQ).

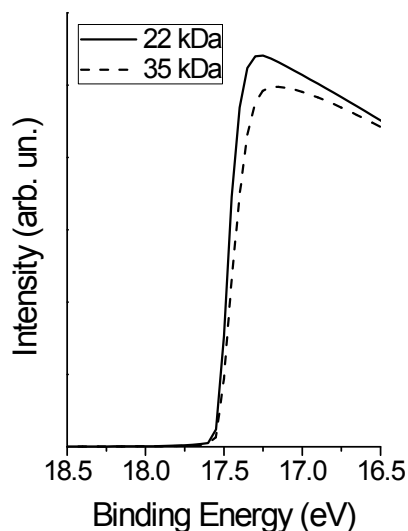


Figure S5. High binding energy region of the UPS spectra for **PTBTSB-2** on Ag showing no significant difference in Δ ; 22 kDa (solid line); 35 kDa (dashed line).

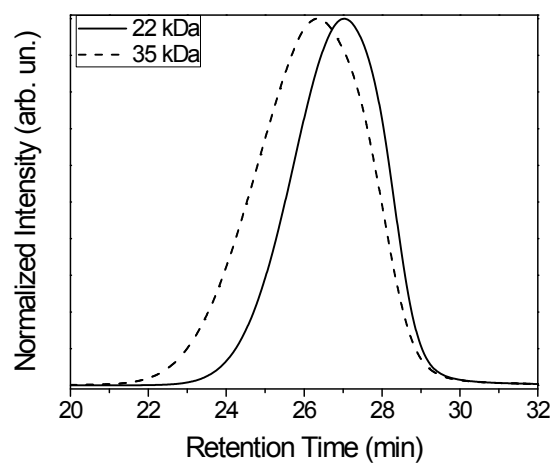


Figure S6. SEC of **PTBTSB-2** in TFE, monitoring with a UV-detector at 600 nm; 22 kDa (solid line); 35 kDa (dashed line).