Supporting Information

# Narrow bandgap thienothiadiazole-based conjugated porous polymers: From facile direct arylation polymerization to tunable porosities and optoelectronic properties

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## Materials and methods

1,3,5 tribromobenzene, tris-(4-bromophenyl)amine and 2,2',7,7'-tetrabromo-9,9'-spirobifluorene were purchased from Sigma Aldrich. 1-Bromo-4-hexylbenzene was purchased from Alfa aesar. 2-Bromo-9,9-dioctyl-9H-fluorene[1], 4-bromotriphenylamine[2] and 3',4'-dinitro-2,2':5',2''-terthiophene[3] were synthesized according to reported procedures. All solvents were obtained from commercial sources and used as received unless otherwise specified. $^{1}$H-NMR was performed on a Bruker AV 300 spectrometer in deuterated chloroform $CDCl_3$ at room temperature with TMS as internal reference; chemical shifts ($\delta$) are reported in parts per million. Solid state $^{13}$C magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra were collected by a JEOL ECA 400 spectrometer. FT-IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. Thermo-gravimetric analyses were performed on a Pyris Diamond TGA (Perkin Elmer) instrument, at a heating rate of 10 $^{o}$C/ min under $N_2$ atmosphere from 40 $^{o}$C to 700 $^{o}$C. SEM imaging was carried out using a JEOL JSM 6701F SEM (Scanning Electron Microscope) operating in scanning mode. Samples were prepared by depositing dry samples on aluminium stubs using an adhesive high purity carbon tape. TEM images were obtained using a Carl Zeiss Libra 120 Plus transmission electron microscope (TEM). Nitrogen sorption isotherms were obtained at 77 K using Quantachrome Instruments Autosorb-iQ (Boynton Beach, Florida USA) with extra-high pure gases. Surface areas were calculated in the relative pressure ($p/p^0$) range from 0.04 to 0.35 of the adsorption branch. UV-Vis- NIR absorption spectra were measured on a Cary 5000 UV-Vis-NIR (Varian) spectrometer. Cyclic voltammograms (CVs) were recorded on an CHI Electrochemical Analyzer Model 660D at room temperature using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) as a supporting electrolyte at a scan rate of 100 mV/s. Glassy carbon was used as working electrode, Pt wire as counter electrode and silver wire as the reference electrode. CVs of CPP-(1-3) were measured in 0.1 M TBAF6 solution in $CH_3CN$ by drop-casting a suspension of CPPs and Nafion on the glassy carbon electrode. CVs of TTD-(1-3) were measured in solution state by dissolving the small molecules in 0.1 M solution of TBAF6 in $CH_2Cl_2$ All the potentials were calibrated with the standard ferrocene/ferrocenium redox couple (Fc/Fc+). Powder X-ray diffraction patterns were obtained at 40 kV and 40 mA on a Bruker Advanced D8 XRD using Cu-K$\alpha$ radiation ($\lambda$ = 1.5418 Å) over 2$\theta$ range of 5.0° - 60° at room temperature. Elemental analysis was carried out on a Vario EL III CHNS Elemental Analyser. Mass spectroscopy was performed on a ABI 4800 Proteomics Analyzer MALDI TOF/TOF mass spectrometer (Applied Biosystems).

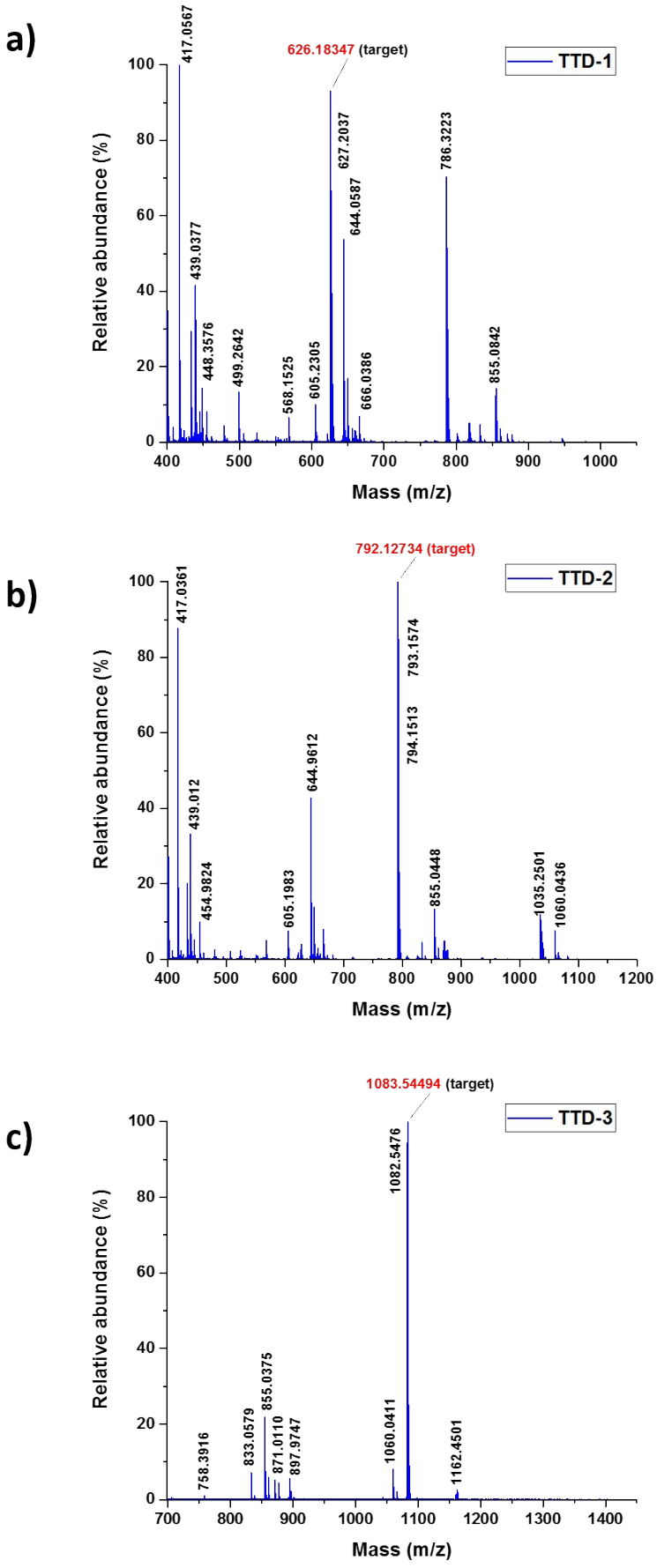



**Figure S1** Mass spectra of a) TTD-1, b) TTD-2 and c) TTD-3.

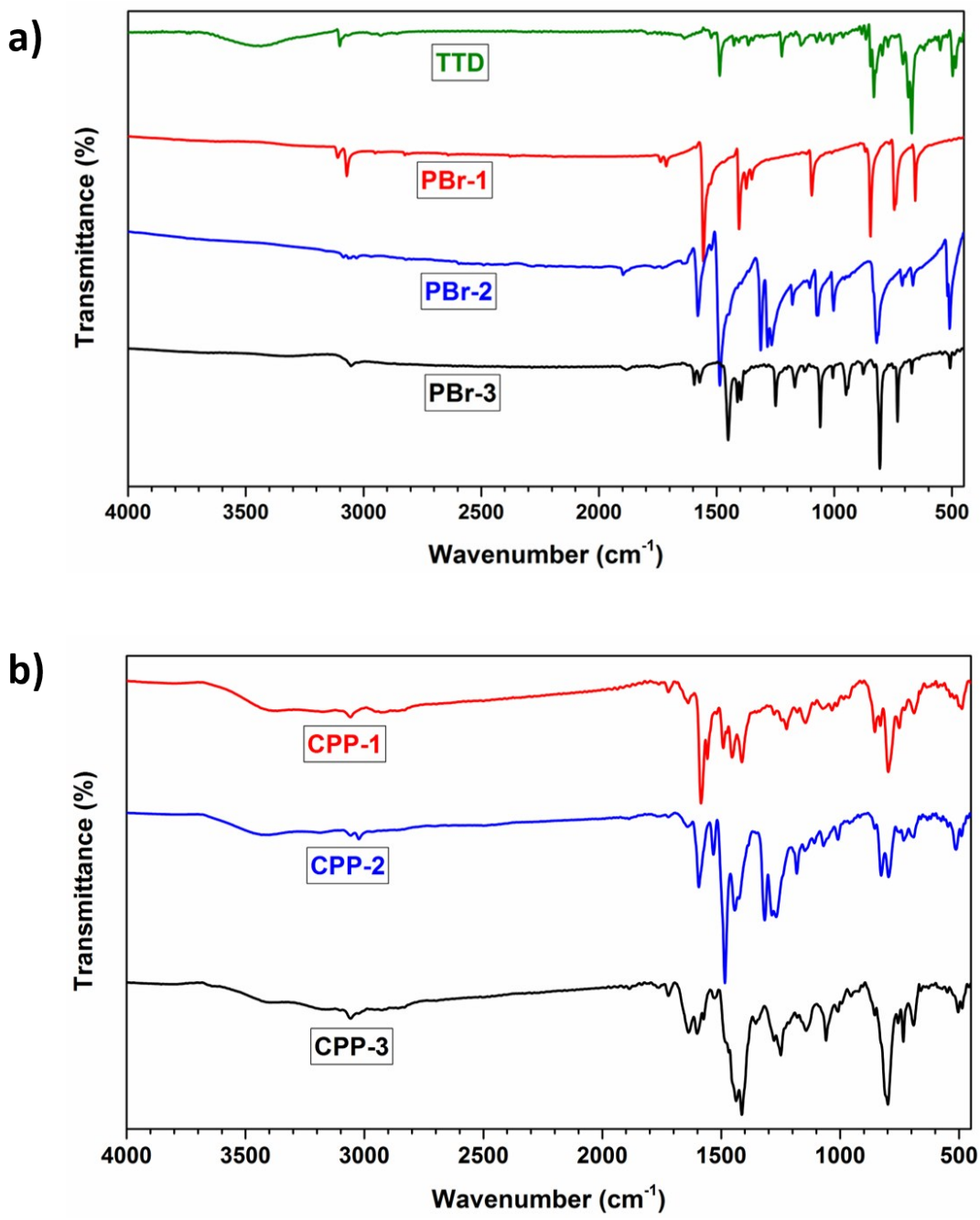



**Figure S2** Complete FT-IR spectra of CPPs (b) and their constituent monomers (a).

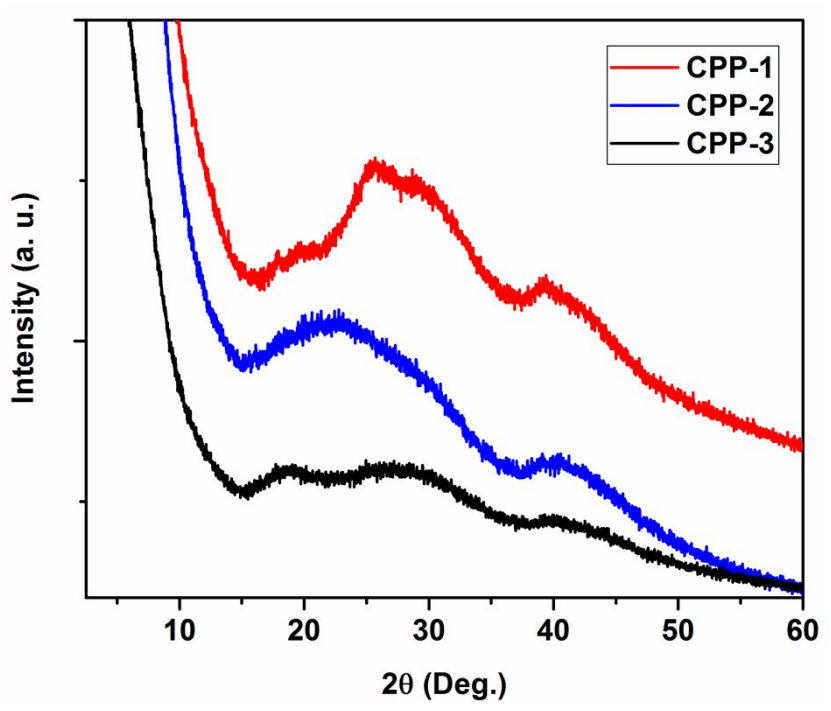



**Figure S3** Powder X-ray diffraction patterns of CPPs.

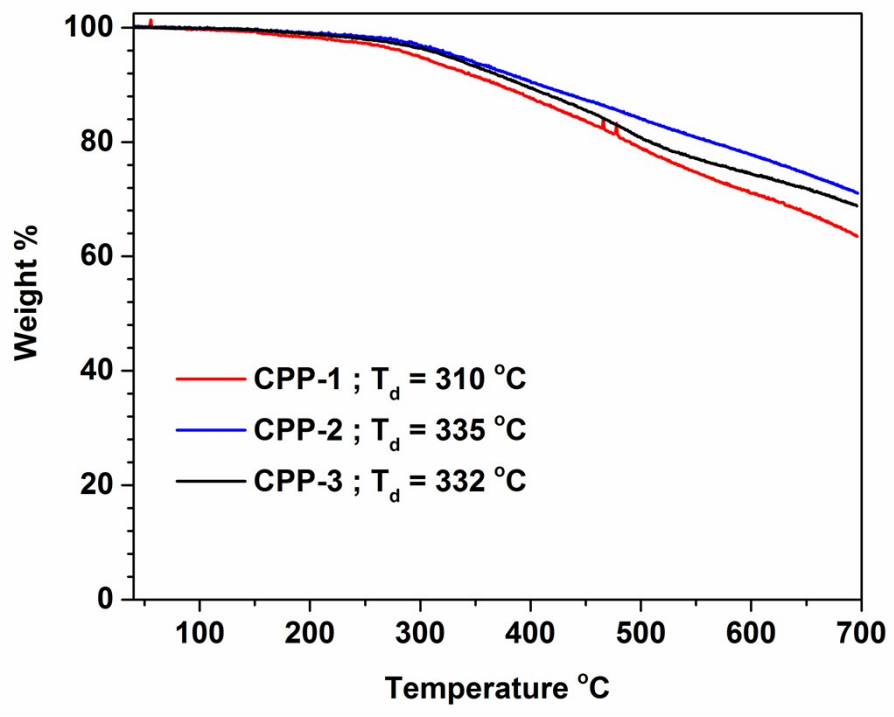



**Figure S4** TGA plots of CPPs recorded under $N_2$ atmosphere at a heating rate of 10 °C/ min.

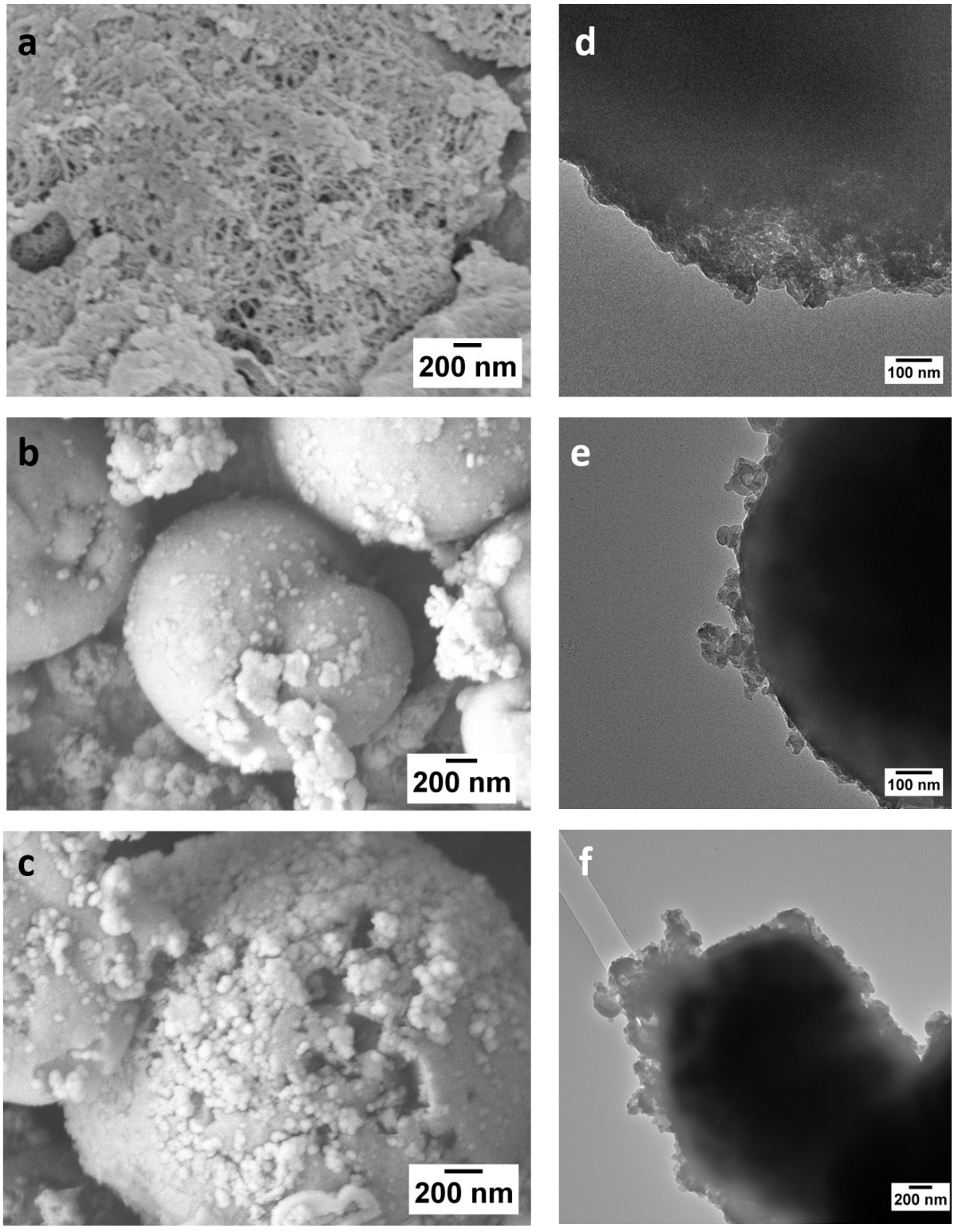
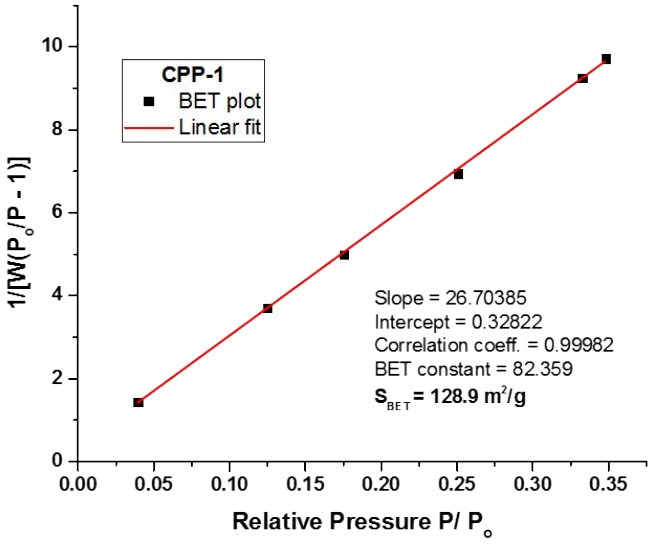
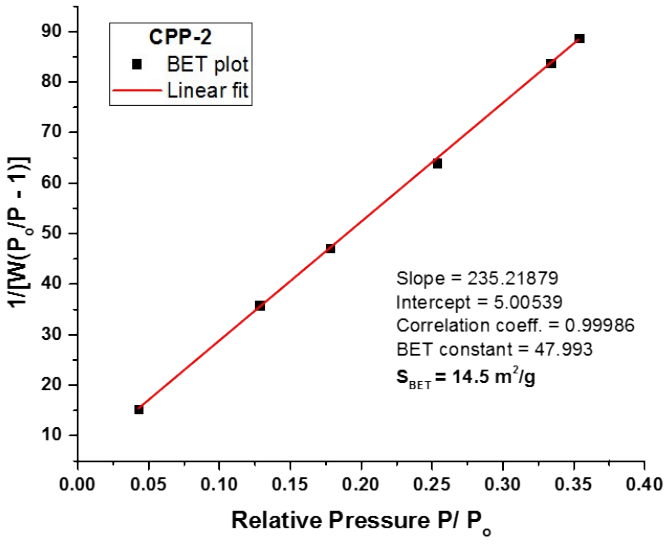



**Figure S5** Supplementary SEM (a, b, c) and TEM (d, e, f) images of CPP-1 (a,d), CPP-2 (b,e) and CPP-3 (c,f).



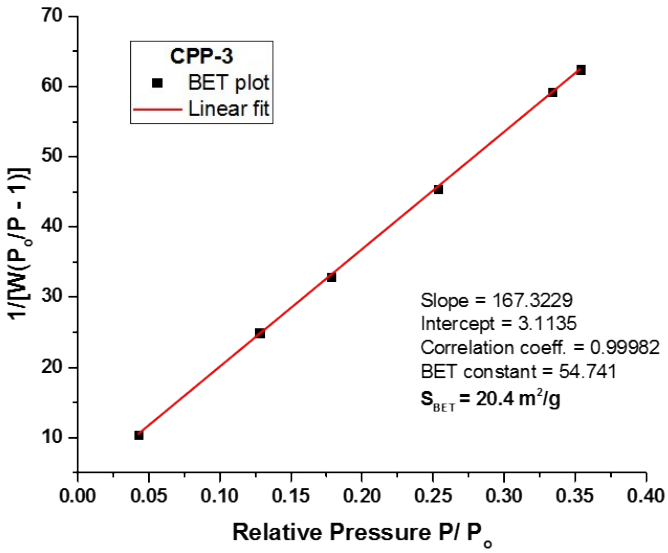




**Figure S6** BET specific surface area plots of CPPs.

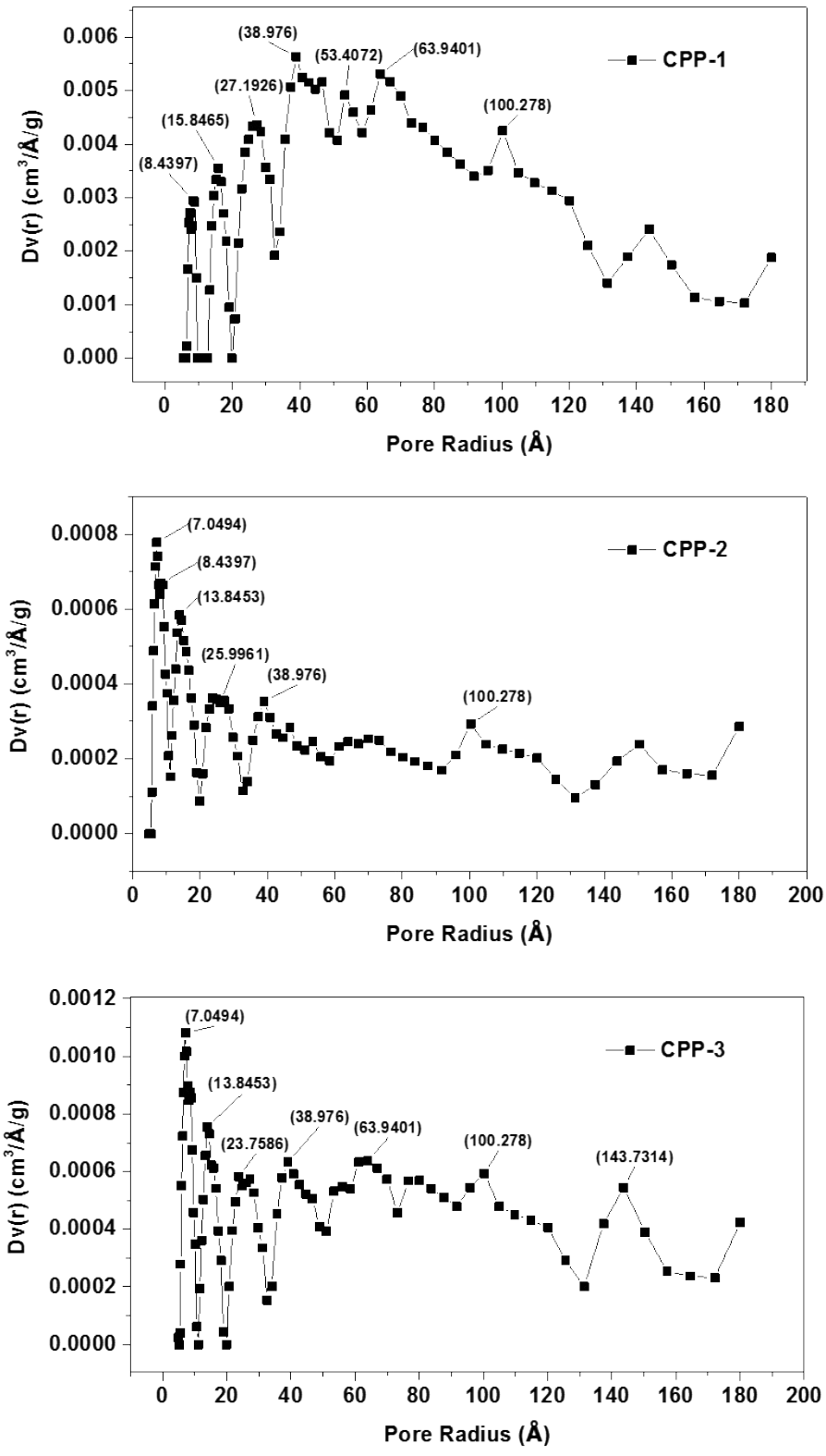



**Figure S7** Pore size distributions of CPPs calculated using the NL-DFT method.

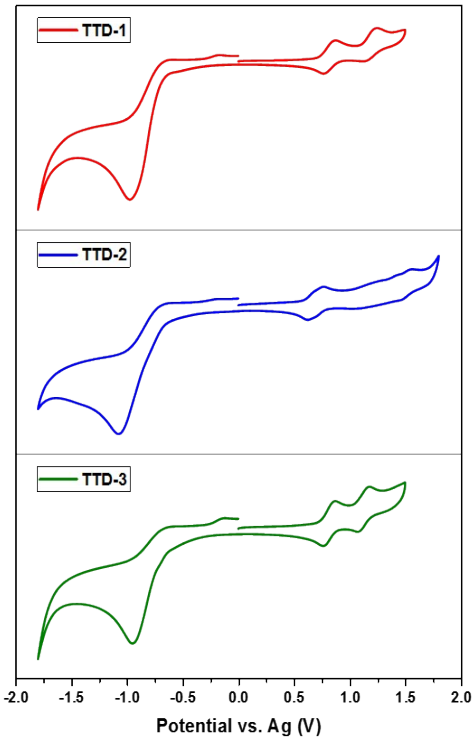



**Figure S8** Cyclic voltammograms of TTD-(1-3) with a 0.1 M solution of $Bu_4NPF_6$ as the supporting electrolyte in dry $CH_2Cl_2$.