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1. Experimental details

1.1. Chemicals: Tris(4-bromophenyl)amine (98%), \( p \)-phenylenediamine (99%), \( o \)-tolidine (97%), 4,4′-diaminostilbene (95%), 4,4′-ethylenediamine (95%), bis(dibenzylideneacetone)palladium(0) (Pd(dba)_2, 63.9 - 78.1% carbon, 16.6 - 20.4% palladium), 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (XPhos, 97%), sodium tert-butoxide (NaOtBu, 97%) and all the solvents with A.R and C.R. grades were purchased from Sigma-Aldrich and used as received.

1.2. Synthesis of PTPA-1, 2, 3 and 4: A Schlenk tube was charged with tris(4-bromophenyl)amine (0.5 mmol), diamine (0.75 mmol, \( p \)-phenylenediamine, \( o \)-tolidine, 4,4′-diaminostilbene, or 4,4′-ethylenediamine), Pd(dba)_2 (dba=dibenzylideneacetone, 17.3 mg, 0.03 mmol, 4mol%), 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (XPhos, 21.5 mg, 0.045 mmol), and sodium tert-butoxide (NaOtBu, 192.2 mg, 2 mmol) and placed under an nitrogen atmosphere. Anhydrous toluene (50 mL) was added and the reaction mixture was heated under stirring to 110 °C. After 24h, TLC analyses were carried out indicating complete consumption of the starting tris(4-bromophenyl)amine. The reaction was cooled to room temperature and solvents were then removed by centrifugation. The remaining solids were washed by chloroform, hot MQ water, and methanol (200 mL each), and then dried 72 h in a vacuum oven to yield corresponding amine networks as black blue, brown, and yellow powders (see Figure S1) with purities of >95% and yields of 65-80%, respectively (based on elemental analyses). Anal. Calcd. for PTPA-1: C, 77.1; N, 17.5; H, 5.4. Found: C, 76.5; N, 16.1; H, 5.4. Anal. Calcd. for PTPA-2: C, 82.5; N, 11.2; H, 6.2. Found: C, 83.1; N, 10.3; H, 6.2. Anal. Calcd. for PTPA-3: C, 83.1; N, 11.3; H, 5.6. Found: C, 81.8; N, 10.9; H, 5.6. Anal. Calcd. for PTPA-4: C, 82.6; N, 11.2; H, 6.2. Found: C, 83.3; N, 11.0; H, 6.1.

![Figure S1](image-url) Appearance of PTPA powders.
1.3. Synthesis of a model molecular analogue of PTPAs, 4,4,’4’’-tri(phenylamino)triphenyl amine: A Schlenk tube was charged with tris(4-bromophenyl)amine (241 mg, 0.5 mmol), aniline (200 mg, 2 mmol), Pd(dbca)₂ (17.3 mg, 0.03 mmol), XPhos (21.5 mg, 0.045 mmol), and NaOtBu (192.2 mg, 2 mmol) and placed under a nitrogen atmosphere. Anhydrous toluene (50 mL) was added and the reaction mixture was heated under stirring to 110 °C. After 24 h, TLC analyses were carried out indicating complete assumption of the starting tris(4-bromophenyl)amine. The reaction was cooled to room temperature and solvents were then removed by centrifugation. The remaining solid was further washed by toluene (200 mL) to remove the excess and unreacted aniline and then dissolved in chloroform (100 mL). A large volume of MQ water (200 mL) was then added to extract the formed bromide salts. Final purification was achieved dissolving the materials in ethanol (20 mL) and then precipitating from an excess of hot water. The purified product, 4,4,’4’’-tri(phenylamino)triphenylamine with a yield of 75% in dark green color was obtained after removal of residual solvents (drying at 50°C for 48h): \(^1\text{H NMR}\) (400 MHz, DMSO-
\textit{d}_6, 25°C): \(\delta=7.96\) (s, 3H), 7.15 (t, 6H), 6.98 (dd, 12H), 6.88 (d, 6H), 6.71(t, 3H) ppm; \(\text{IR}\) (neat): 3387, 1595, 1490, 1402, 1303, 1173, 1026, 801 cm\(^{-1}\); \textit{Anal. Calcd for C}_{36}H_{30}N_4: C, 83.37; H, 5.83; N, 10.80. \textit{Found}: C, 82.91; H, 5.76; N, 10.53; \textit{Calcd M}_w for C}_{36}H_{30}N_4: 518.25, \textit{MALDI/TOF MS Found (M-1): 517.14.}

![Scheme S1 Synthetic route to molecular analogue of PTPAs.](image)

2. Characterization and measurements

2.1. Elemental analyses, ultra-violet (UV/Vis-NIR), mass, proton nuclear magnetic resonance (\(^1\text{H NMR}\)) spectra and scanning electron microscope (SEM) microscope. The elemental analyses were carried out using a Euro Vector EuroEA3000 Elemental Analyzer. The solid-state UV/Vis-NIR spectra were recorded on a Shimadzu UV-2600 Spectrometer. The MALDI/TOF mass spectra were obtained on an Applied Biosystems 4700 Proteomics Analyzer MALDI-TOF mass spectrometer. The \(^1\text{H NMR}\) spectra were recorded on a JEOL Eclipse-400 (400 MHz) using
DMSO-$d_6$ as a solvent.

2.2. **Fourier transform infrared (FT-IR) and solid-state $^{13}$C cross-polarization magic angle spinning nuclear magnetic resonance (CP/MAS NMR) spectra.** The FT-IR spectra were taken on a Perkin Elmer Spectrum 100 spectrometer. The $^{13}$C CP/MAS NMR spectra were taken at Solid state NMR Service, Durham University on a Varian VNMRS-600 spectrometer using a spin-rate of 6800 Hz. The FT-IR spectra indicated the bands which can be attributed to the primary amine group of diamine at 3470 and 3420 (–NH$_2$ stretching) and 1650 cm$^{-1}$ (–NH$_2$ deformation) as well as to the aromatic C–Br groups of the tri(4-bromophenylamine) at 1178 cm$^{-1}$ (aromatic C–Br stretching) are absent or strongly attenuated in the spectra of the PTPAs (Figure S2). The distinct bands corresponding to the –NH– (3382 cm$^{-1}$), 1598 and 1498 cm$^{-1}$ of the benzenoid rings and quinoid rings and 820 cm$^{-1}$ of the aromatic C–H are present in the spectra of the resulted materials. Solid-state $^{13}$C CP/MAS NMR spectra of all polymers show three main resonances at ~ 141, ~ 127 and ~ 118 ppm originated from the aryl carbons of the both building blocks (Figure S3). Note that, three additional resonances at 17, 116 and 35 ppm attributed to the methyl, alkenyl and methylene groups of PTPA-2, 3 and 4, respectively. Both FT-IR and NMR information signify the successful formation of the conjugated polymer networks consisting of amine linkages.

![Figure S2](image)

**Figure S2** FT-IR spectra of PTPAs (Left) and the starting molecules tris(4-bromophenyl) amine core and aryl diamine linkers (right) are shown for comparison.
2.3. **Powder X-ray diffraction (XRD).** XRD patterns were obtained on a Bruker D8 Advance diffractometer (40 kV, 30 Ma) using Cu Kα radiation ($2\theta = 5–45^\circ$). As expected, PTPAs display a nonordered, amorphous structure determined by the XRD measurements which show only broad peaks at $2\theta \approx 12.2^\circ$ (see Figure S4). No indication of π-stacking was evident at $2\theta \approx 26^\circ$ from these investigations.
2.4. High resolution transmission electron microscope (TEM). The TEM images were obtained on JEOL 2010 TEM microscope. The TEM images are indicative of microporous structures of PTPA nanoparticles (see Figure S5), which are normally found in amorphous CMPs.

![Figure S5 TEM images of PTPA-3.](image)

2.5. Thermal gravimetric analysis (TGA). TGA was carried out on a TGA Q500 apparatus in nitrogen atmosphere (flow rate 30 mL min\(^{-1}\)) in the temperature range 30–1000 °C (heating rate 10 °C/min). Scanning electron microscope (SEM) images were obtained on a JEO 5600LV. The materials are thermally stable in N\(_2\) up to 500 °C, as revealed by thermal gravimetric analysis (TGA) (see Figure S6). In particular, for PTPA-3 and PTPA-4, ~60 wt% remained after heating to 1000 °C. The excellent thermal stability of PTPAs is mostly owing to the nature of their cross-linking networks.

![Figure S6 TGA scans of PTPAs.](image)
3. N₂ and CO₂ interaction measurements

3.1. N₂ and CO₂ adsorption/desorption measurements. Nitrogen adsorption/desorption measurements at 77.4 K were performed after degassing the samples under high vacuum at 70 °C for at least 20 hours using a Quantachrome Quadrasorb SI-MP machine. CO₂ and N₂ adsorption/desorption isotherms at 273 and 303 K were conducted on a Quantachrome Autosorb-1MP instrument after prior degassing under high vacuum (turbomolecular pump) and 70 °C. The specific surface areas were calculated by applying the Brunauer–Emmett–Teller (BET) model to adsorption or desorption branches of the isotherms (N₂ at 77.4 K) using the QuadraWin 5.05 software package. Analysis of the isotherms by commercialized Quenched Solid Density Functional Theory (QSDFT)² and Grand-canonical Monte-Carlo (GCMC)³,⁴ methodologies were also done using the QuadraWin 5.05 package. The pore size distribution (PSD) profiles of the PTPAs were calculated from the adsorption branch of the isotherms with the Grand-canonical Monte-Carlo (GCMC) approach. The main fraction of pores have sizes between 0.5 and 1 nm (Figure S7).

![Figure S7 Pore size distribution of PTPAs, derived from GCMC analysis of the CO₂ adsorption isotherm at 273 K.](image)

3.2. Ideal adsorption solution theory (IAST) calculations. Selectivity was calculated using the common IAST equation:
where $\alpha$ is the selectivity, $x$ the adsorbed amount and $y$ represents the gas phase composition. The amount adsorbed from the mixed-gas phase $x_{\text{CO}_2}$ is determined following the known protocols based on a Ref.\(^5\) via a Newton-Raphson method implemented within a MatLab® (R2011a) script or an octave (open source software) script, these scripts are available for download at: http://f-n.hs-zg.de/fakultaet/hochschullehrerinnen/jens-weber/jens-weber/vermischtsem.html or upon request via e-mail. The fit parameters shown in Figure S8 were used as basis for the analytical description of the single-gas adsorption isotherms. The gas phase composition was set 15 vol.-% CO\(_2\) and 85 vol.-% N\(_2\), i.e. $y_{\text{CO}_2} = 0.15$ and $y_{\text{N}_2} = 0.85$.

Figure S8 Dual-site Langmuir fit of CO\(_2\) adsorption/desorption (303 K) on PTPA-3 (left-hand side) and Langmuir fit of N\(_2\) adsorption/desorption (303 K) on PTPA-3 (right-hand side).

References