Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting Information

Conjugated microporous polytriphenylamine networks

By *Yaozu Liao, Jens Weber and Charl F. J. Faul**

1. Experimental details

1.1. Chemicals: Tris(4-bromophenyl)amine (98%), *p*-phenylenediamine (99%), *o*-tolidine (97%), 4,4'-diaminostilbene (95%), 4,4'-ethylenedianiline (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'-ethylenedianiline), $Pd(dba)_2$ (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 ^{o}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.

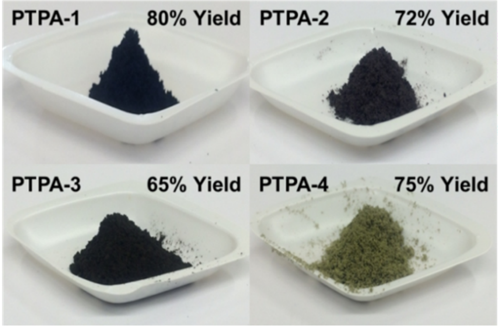
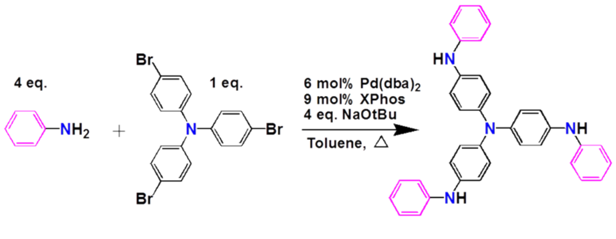


Figure S1 Appearances of PTPA powders.

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(dba)$_2$ (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 ^{o}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}H NMR* (400 MHz, DMSO-d_6, 25°C): δ=7.96 (s, 3H), 7.15 (t, 6H), 6.98 (dd, 12H), 6.88 (d, 6H), 6.71(t, 3H) ppm; *IR* (neat): 3387, 1595, 1490, 1402, 1303, 1173, 1026, 801 cm^{-1}; *Anal. Calcd* for **$C_{36}H_{30}N_4$**: C, 83.37; H, 5.83; N, 10.80. *Found*: C, 82.91; H, 5.76; N, 10.53; *Calcd M_w* for **$C_{36}H_{30}N_4$**: 518.25, *MALDI/TOF MS Found* (M-1): 517.14.



Scheme S1 Synthetic route to molecular analogue of PTPAs.

2. Characterization and measurements

2.1. Elemental analyses, ultra-violet (UV/Vis-NIR), mass, proton nuclear magnetic resonance (^{1}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}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.

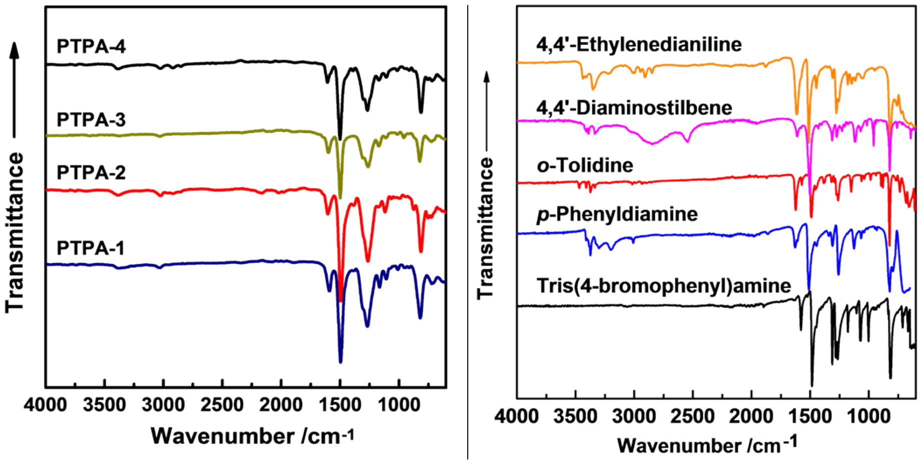


Figure S2 FT-IR spectra of PTPAs (Left) and the starting molecules tris(4-bromophenyl) amine core and aryl diamine linkers (right) are shown for comparison.

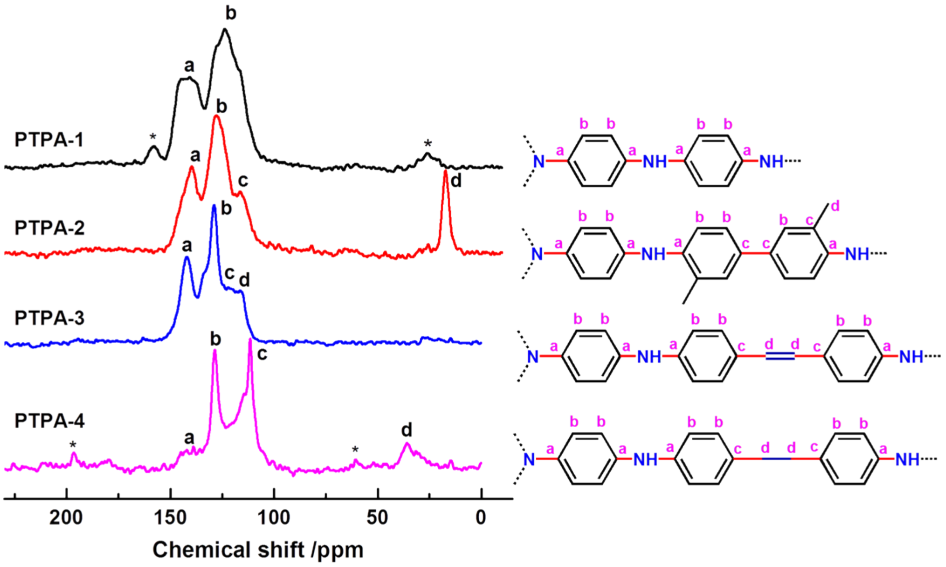


Figure S3 Solid-state ^{13}C CP/MAS NMR spectra of PTPAs (asterisk mark spinning side bands).

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 (2θ = 5–45°). As expected, PTPAs display a nonordered, amorphous structure determined by the XRD measurements which show only broad peaks at 2θ = ~12.2° (see **Figure S4**). No indication of π-stacking was evident at 2θ = ~26° from these investigations.

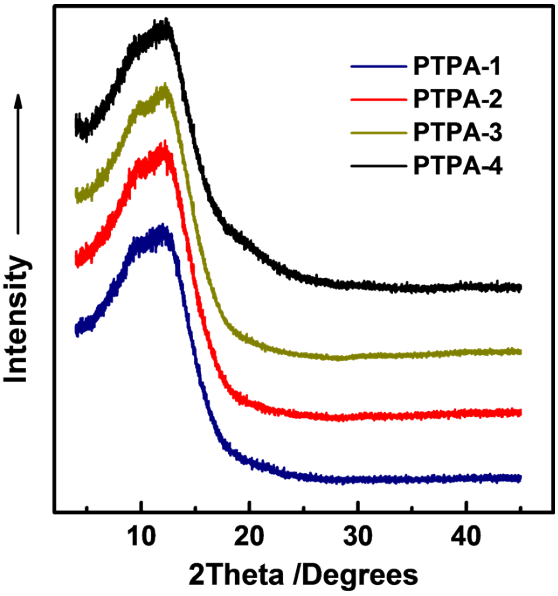


Figure S4 Powder XRD patterns of PTPAs.

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.

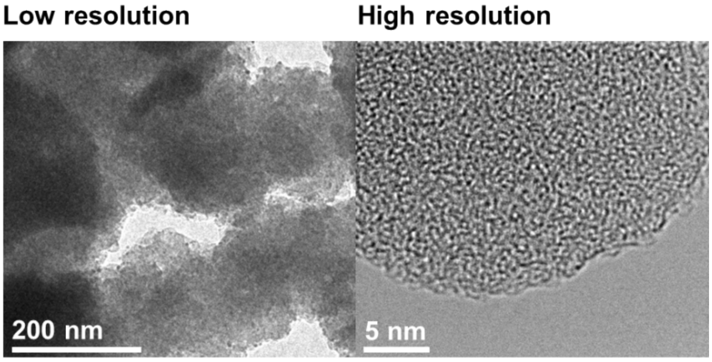


Figure S5 TEM images of PTPA-3.

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 ^{o}C (heating rate 10 ^{o}C/min). Scanning electron microscope (SEM) images were obtained on a JEO 5600LV. The materials are thermally stable in N_2 up to 500 ^{o}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 ^{o}C. The excellent thermal stability of PTPAs is mostly owing to the nature of their cross-linking networks.

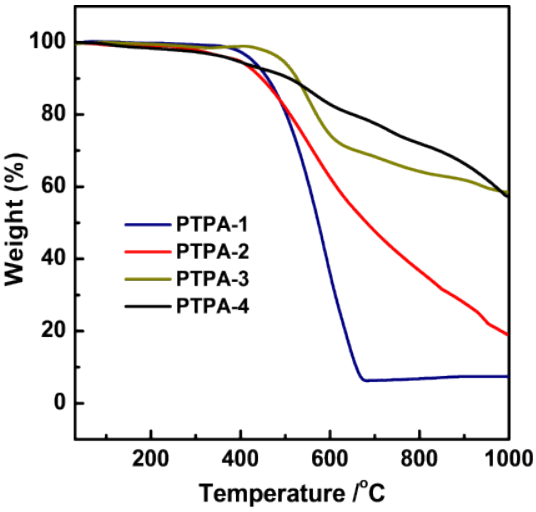


Figure S6 TGA scans of PTPAs.

3. N_2 and CO_2 interaction measurements

3.1. N_2 and CO_2 adsorption/desorption measurements. Nitrogen adsorption/desorption measurements at 77.4 K were performed after degassing the samples under high vaccum at 70 °C for at least 20 hours using a Quantachrome Quadrasorb SI-MP machine. CO_2 and N_2 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 (N_2 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**).

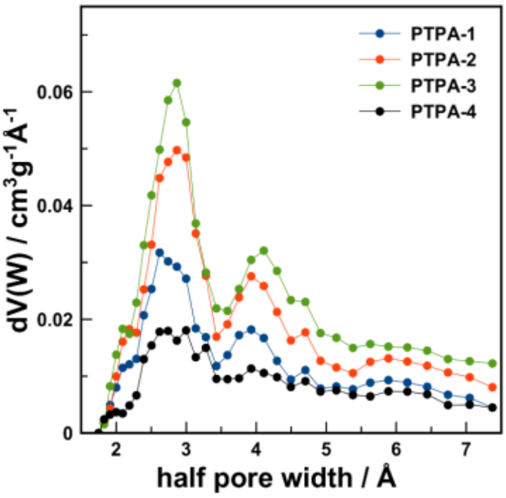
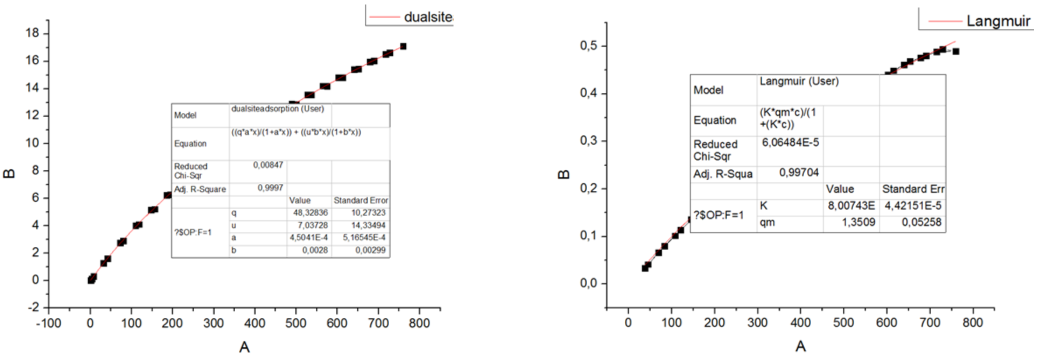


Figure S7 Pore size distribution of PTPAs, derived from GCMC analysis of the CO_2 adsorption isotherm at 273 K.

3.2. Ideal adsorption solution theory (IAST) calculations. Selectivity was calculated using the common IAST equation:

$$\alpha = \frac{x_{CO_2}/x_{N_2}}{y_{CO_2}/y_{N_2}}$$

where α is the selectivity, *x* the adsorbed amount and *y* represents the gas phase composition. The amount adsorbed from the mixed-gas phase x_{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.hszg.de/fakultaet/hochschullehrerinnen/jens-weber/jens-weber/vermischtesdownloads.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.* $y_{CO_2} = 0.15$ and $y_{N_2} = 0.85$.



Model	dualsiteadsorption (User)		
Equation	((q*a*x)/(1+a*x)) + ((u*b*x)/(1+b*x))		
Reduced Chi-Sqr	0,00847		
Adj. R-Square	0,9997		
		Value	Standard Error
?$OP:F=1	q	48,32836	10,27323
	u	7,03728	14,33494
	a	4,5041E-4	5,16545E-4
	b	0,0028	0,00299

Model	Langmuir (User)		
Equation	(K*qm*c)/(1 +(K*c))		
Reduced Chi-Sqr	6,06484E-5		
Adj. R-Squa	0,99704		
		Value	Standard Err
?$OP:F=1	K	8,00743E	4,42151E-5
	qm	1,3509	0,05258

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

1. Z. Q. Li, C. J. Lu, Z. P. Xia, Y. Zhou and Z. Luo, *Carbon*, 2007, **45**, 1686.
2. P. I. Ravikovitch and A.V. Neimark, *Langmuir*, 2006, **22**, 11171.
3. S. Samios, A. K. Stubos, N. K. Kanellopoulos, R. F. Cracknell, G. K. Papadopoulos and D. Nicholson, *Langmuir*, 1997, **13**, 2795.
4. A. Vishnyakov, P. I. Ravikovitch and A. V. Neimark, *Langmuir*, 1999, **15**, 8736.
5. A. L. Myers and J. M.Prausnitz, *AIChE J.*, 1965, **11**, 121.