

# Microporous polymer networks for heterogeneous organocatalysis assembled by Tröger's base formation.

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## References.

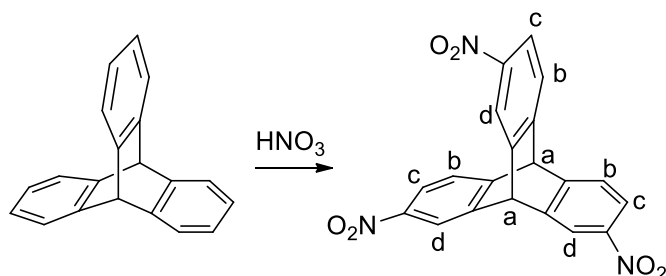
### 1. Experimental techniques

Commercially available reagents were used without further purification. Anhydrous dichloromethane was obtained by distillation over calcium hydride under nitrogen atmosphere. Anhydrous *N,N*-dimethylformamide was bought from Aldrich. All reactions using air/moisture sensitive reagents were performed in oven-dried or flame-dried apparatus, under a nitrogen atmosphere. TLC analysis refers to analytical thin layer chromatography, using aluminium-backed plates coated with Merck Kieselgel 60 GF254. Product spots were viewed either by the quenching of UV fluorescence, or by staining with a solution of Cerium Sulfate in aqueous  $\text{H}_2\text{SO}_4$ . Flash chromatography was performed on silica gel 60Å (35-70 micron) chromatography grade (Fisher Scientific). Melting points were recorded using a Gallenkamp Melting Point Apparatus and are uncorrected. Infra-red spectra were recorded in the range

4000-600  $\text{cm}^{-1}$  using a Perkin-Elmer 1600 series FTIR instrument either as a thin film or as a nujol mull between sodium chloride plates. All absorptions are quoted in  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra were recorded in the solvent stated using an Avance Bruker DPX 400 (400 MHz) or DPX 500 (500 MHz) instruments, with  $^{13}\text{C}$  NMR spectra recorded at 100 MHz or 125 MHz respectively. Low-resolution mass spectrometric data were determined using a Fisons VG Platform II quadrupole instrument using electron impact ionization (EI) unless otherwise stated. High-resolution mass spectrometric data were obtained in electron impact ionization (EI) mode unless otherwise reported, on a Waters Q-TOF micromass spectrometer. Low-temperature (77 K)  $\text{N}_2$  adsorption/desorption measurements of PIM powders were made using a Coulter SA3100. Samples were degassed for 800 min at 120  $^\circ\text{C}$  under high vacuum prior to analysis. The TGA was performed using the device Thermal Analysis SDT Q600 at a heating rate of 10  $^\circ\text{C}/\text{min}$  from room temperature to 1000  $^\circ\text{C}$ . Elemental analysis has been performed by MEDAC LTD. Solid state  $^{13}\text{C}$  NMR was measured at EPSRC National Solid-state NMR Service at Durham using a Varian VNMRS 400.

## 2. Synthetic methods

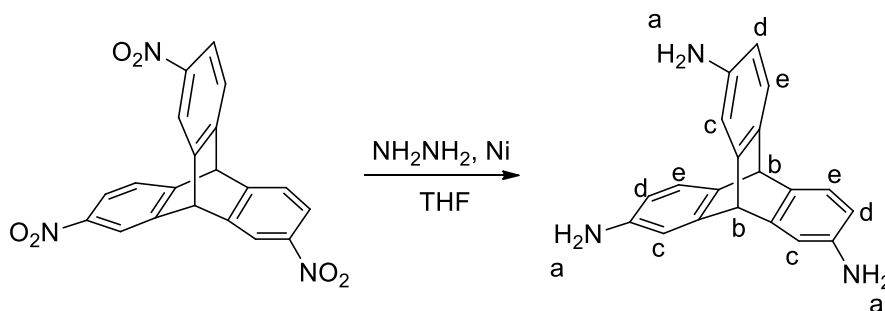
### 2.1. 2, 6(7), 14-Trinitrotritycene



Triptycene (5.00 g, 19.69 mmol) was added to a mixture of concentrated nitric acid (70%, 200 mL) and concentrated sulphuric acid (95%, 15 mL). The mixture was heated to 80 $^\circ\text{C}$  and stirred for 16 hours, before the temperature was increased to 100 $^\circ\text{C}$  for 2 hours, until all remaining solid had dissolved. The reaction was then quenched in water (1000 ml) and stirred for an hour. The crude product was extracted with chloroform (3 x 150 ml) and the chloroform removed under reduced pressure. The crude material was purified by column chromatography (4:1 DCM:Hexane), giving the product as a light yellow powder (4.97 g, 64.9%). Mp 172-174 $^\circ\text{C}$  (Lit mp 178-180 $^\circ\text{C}$ )<sup>1</sup>;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 5.83 (2H, m,  $\text{H}_a$ ), 7.64 (3H, m,  $\text{H}_b$ ), 8.05 (3H, m,  $\text{H}_c$ ), 8.34 (3H, m,  $\text{H}_d$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 53.1, 53.2,

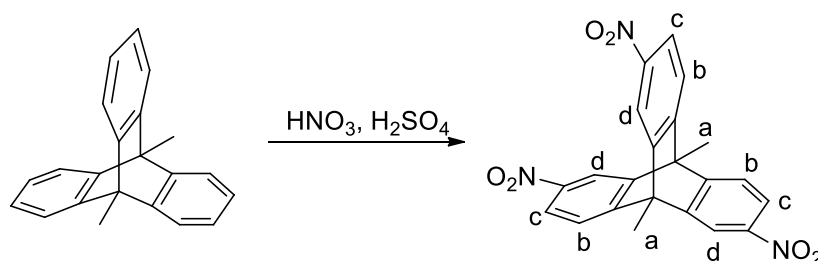
53.4, 53.5, 119.6, 121.0, 122.5, 122.6, 125.0, 143.9, 144.3, 144.7, 146.3, 148.9, 149.2, 149.6; LRMS  $m/z$  (EI,  $M^+$ ) = 389.07; IR (NaCl): 3092, 1591, 1521, 1459.9, 1346.1, 1197.6, 794.5, 735.7  $\text{cm}^{-1}$ .

## 2.2. 2, 6(7), 14-triaminotriptycene



2,6(7),14-Trinitrotriptycene (1.00 g, 2.64 mmol) was dissolved in THF (40 mL) with stirring under nitrogen. Raney nickel (catalytic amount) and hydrazine monohydrate (1.2 ml, 23.8 mmol) were added slowly to the solution before the temperature was increased to 60 °C. This was stirred under nitrogen for 16 hours, then filtered and the solvent removed under reduced pressure. The resulting oil was added to water (50 ml), the product extracted with chloroform (3 x 10 mL) and the solvent removed under reduced pressure, giving the product as a cream-white powder (0.80 g, 98.8%). Mp 160-162 °C (Lit mp 152-154 °C)<sup>1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 3.48 (6H, br. s, H<sub>a</sub>), 5.03 (2H, m, H<sub>b</sub>), 6.25 (3H, m, H<sub>c</sub>), 6.72 (3H, m, H<sub>d</sub>), 7.06 (3H, m, H<sub>e</sub>); <sup>13</sup>C NMR (100 MHz, *d6*-acetone)  $\delta$  ppm 52.2, 53.3, 54.4, 55.5, 110.3, 110.5, 110.9, 111.3, 111.5, 111.9, 123.6, 124.0, 124.2, 135.5, 136.4, 137.3, 145.9, 146.3, 146.5, 147.6, 148.4, 149.2; LRMS  $m/z$  (ES,  $M^+$ ) = 299.14; IR (NaCl): 3341, 3209, 3007, 2957, 1620, 1479, 1329, 1188, 819, 730  $\text{cm}^{-1}$ .

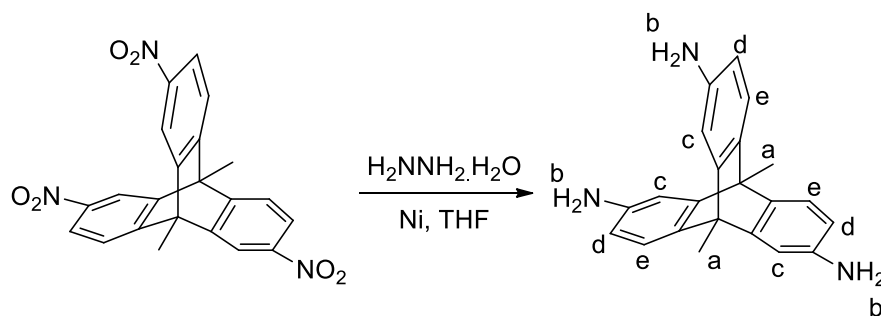
## 2.3. 2,6(7),14-trinitro-9,10-dimethyltriptycene



To a mixture of concentrated nitric acid (70 %, 50 mL) and concentrated sulphuric acid (95 %, 2.5 mL) was added 9,10-dimethyltriptycene<sup>2</sup> (1.50 g, 5.32 mmol). The reaction mixture was

heated to 80 °C for 40 hours, after which time all of the solid had dissolved. The reaction was then quenched in water (250 mL) and stirred for an hour. The product was then extracted with chloroform (3 x 50 mL) and the chloroform then removed under reduced pressure. This gave the crude product as a yellow powder, which was loaded onto silica and eluted through a silica column (4:1, DCM:hexane) to give the product as a pale yellow powder (2.14 g, 96.5%). Mp > 350 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm 2.62 (6H, m, H<sub>a</sub>), 7.58 (3H, m, H<sub>b</sub>), 8.06 (3H, m, H<sub>c</sub>), 8.26 (3H, m, H<sub>d</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ ppm 13.4, 49.5, 116.6, 122.1, 122.2, 146.2, 147.5, 147.8, 148.1, 152.1, 152.4, 152.8; HRMS [C<sub>22</sub>H<sub>15</sub>N<sub>3</sub>O<sub>6</sub>]<sup>+</sup> calculated 417.0961, found 417.0966 g mol<sup>-1</sup>; IR (NaCl): 3092, 2925, 2854, 1595, 1525, 1450, 1383, 1344, 1288, 1268, 1216, 1145, 1097, 1044 cm<sup>-1</sup>.

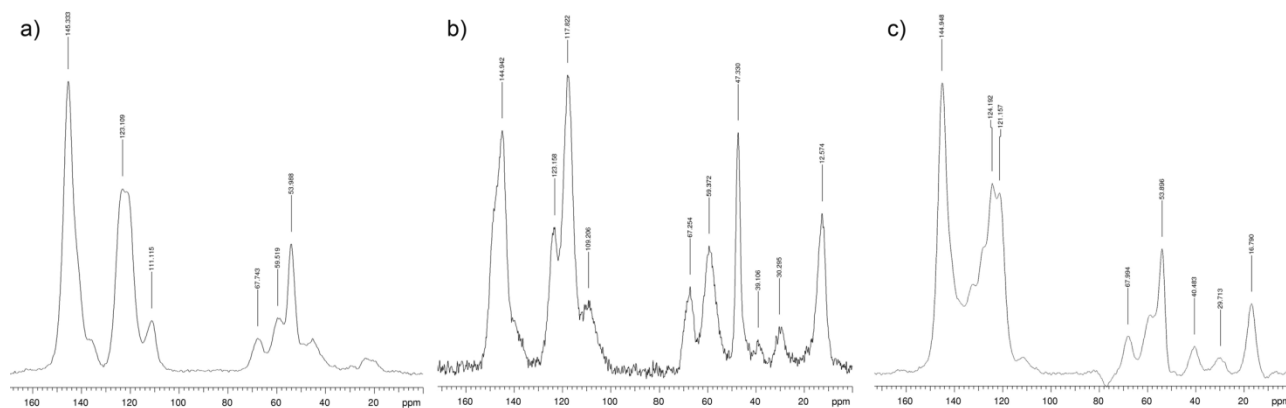
#### 2.4. 2,6(7),14-triamino-9,10-dimethyltriptycene.



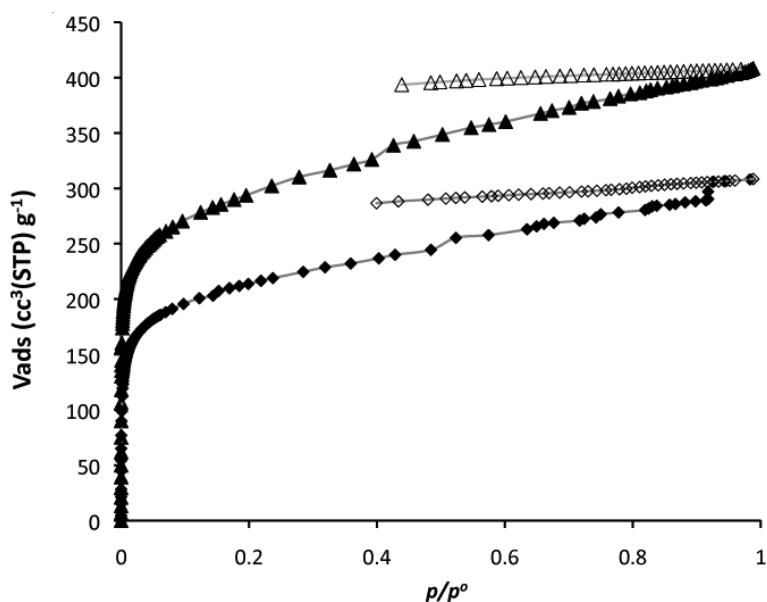
To a solution of 2,6(7),14-trinitro-9,10-dimethyltriptycene (3.00 g, 7.19 mmol) in THF (100 mL) was added hydrazine monohydrate (8.44 ml, 107.91 mmol) and Raney nickel (catalytic amount). The reaction mixture was heated to 60 °C and stirred for 16 hours under a nitrogen atmosphere, cooled to room temperature and filtered to remove the nickel before the solution was concentrated to an oil under reduced pressure. The oil was added to water (200 mL) and the product extracted with chloroform (3 x 80 mL). The chloroform was removed under reduced pressure to give the product as a peach coloured powder (2.27 g, 96.5%). Mp 298 – 300 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm 2.23 (6H, m, H<sub>a</sub>), 3.50 (6H, br. s, H<sub>b</sub>), 6.28 (3H, m, H<sub>c</sub>), 6.67 (3H, m, H<sub>d</sub>), 7.03 (3H, d, *J* = 8 Hz, H<sub>e</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ ppm 13.6, 47.0, 108.5, 108.8, 109.1, 110.0, 110.3, 110.5, 120.3, 120.6, 120.9, 125.5, 138.7, 139.4, 140.2, 143.1, 143.3, 143.5, 149.4, 150.0, 150.6; HRMS [C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>]<sup>+</sup> 327.1735, found 327.1734 g mol<sup>-1</sup>; IR (NaCl): 3338, 3213, 3006, 2968, 2877, 1619, 1502, 1476, 1454, 1378, 1321, 1287, 1249, 1215, 1147, 1083 cm<sup>-1</sup>.

	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore Volume (mL/g)	Amine content (mmol g <sup>-1</sup> )	%N (calculated)
TB	-	-	8.0	11.2
HXLPP-WAX-EDA <sup>3</sup>	1000	-	0.8	-
PPN-6 <sup>4</sup>	1014	0.44	5.4	7.5 (20.4)
DMAP-NCP <sup>5</sup>	508	0.46	4.0	5.65 (12.85)
TB-polymer 3 <sup>6</sup>	750	0.74	5.0	7.21 (8.81)
Si-TB-50-F <sup>7</sup>	816	0.85	3.1	4.4
PIM-TB-Trip-1	1035	0.63	8.5	12.1 (11.9)
PIM-TB-Trip-2	752	0.48	6.8	9.6 (11.0)
P-TB-Trip-3	1.5	0.01	6.5	9.1 (10.9)

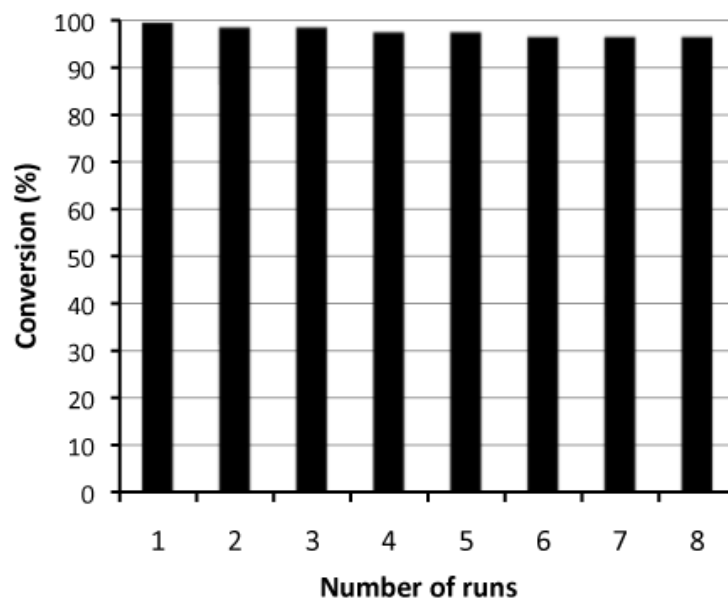
**SI Table 1.** A comparison of the physical properties of TB-network polymers with other nanoporous materials used as basic heterogeneous catalysts.



**SI Figure 1.** Solid state  $^{13}\text{C}$  NMR spectra for a) PIM-TB-Trip-1; b) PIM-TB-Trip-2; and P-TB-Trip-3.



**SI Figure 2.** Nitrogen adsorption isotherms collected at 77 K with  $\blacktriangle$  representing data points for PIM-TB-Trip-1 (apparent BET surface area =  $1035\text{ m}^2\text{ g}^{-1}$ ) and  $\blacklozenge$  data points for PIM-TB-Trip-2 (apparent BET surface area =  $752\text{ m}^2\text{ g}^{-1}$ ). Empty symbols are desorption data.



**SI Figure 3.** Plot of conversion of malononitrile after repeated use of PIM-TB-Trip-1 as heterogeneous catalyst. After eight repeated reactions the conversion is 96%.

## References

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