Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Flexible macrocycles as versatile supports for catalytically active metal clusters

Jason D. Ryan, Kevin J. Gagnon, Simon J. Teat and Ruaraidh D. McIntosh

General Comments

Experiments were performed under an atmosphere of dry, oxygen free N_2, using standard Schlenk techniques. Solvents were purified in an MBRAUN SPS-800 and stored over 4 Å molecular sieves. Infrared spectra were obtained on Perkin-Elmer Spectrum 100 FT-IR Universal ATR Sampling Accessory, deposited neat to a diamond/ZnSe plate. NMR spectra at 400 MHz (^1H) and 100 MHz (^{13}C) were recorded on a Bruker AVIII-400 spectrometer at 298 K. Mass spectra were obtained at the EPSRC National Mass Spectrometry Service Centre in Swansea and ESI represents electrospray ionisation. Elemental analyses (EA) were conducted using an Exeter CE-440 elemental analyser. TBC[8] was prepared following an established literature method[1], all other reagents were purchased from Sigma-Aldrich and used as received.

TBC[8]$Na_6(THF)_7$ (1)

NaH (50 mg, 1.23 mmol, 8 eq.) was added to a suspension of TBC[8]H_8 (200 mg, 0.154 mmol) in THF (30 mL). After overnight stirring, the clear, colourless liquid was concentrated under vacuum and cooled -15°C. The white crystalline solid formed after 48hrs was collected by filtration. (282 mg, 0.146 mmol, 95%.) ^1H NMR: (C_6D_6, 25.1 °C, 400 MHz) δ 7.23 (br m, 16H, Ar*H*), 4.68 (br s, 8H, ArC*H*$_2$Ar), 3.49 (br s, 8H, ArC*H*$_2$Ar), 3.19 (br s, 28H, O-C*H*$_2$ THF), 1.27 (br s, 28H, C*H*$_2$ THF), 1.12 (s, 72H, ^{t}Bu); IR: 2952, 2865, 1607, 1479, 1456, 1293 cm^{-1}. EA (%) calculated for $C_{116}H_{160}Na_6O_{15}$: C 72.1, H 8.35; Found: C 71.79, H 8.24

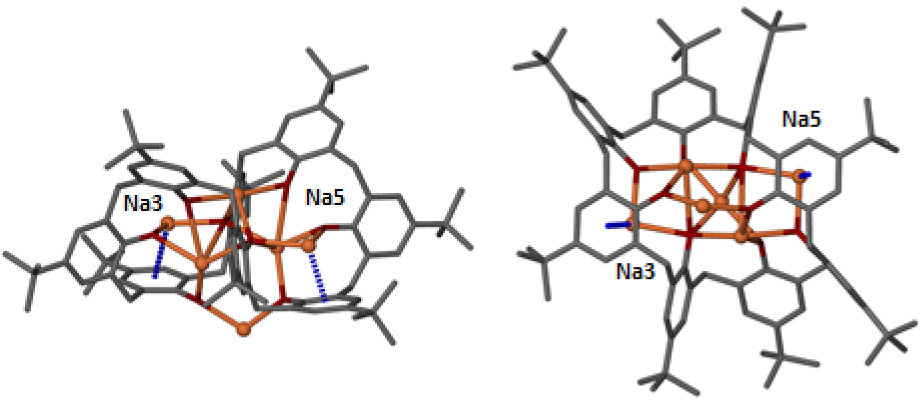

Fig. S1 Na-π interactions were observed between Na3/C34-39 and Na5/C78-83. Highlighted with dashed blue line between Na3/5 and the respective aryl centroid.

$TBC[8]Ti_4(THF)_2(OPr)_8$ (2)

$Ti(OPr)_4$ (0.17 mL, 0.616 mmol) was added to a suspension of $TBC[8]H_8$ (200 mg, 0.154 mmol) in THF (30 mL). The clear, red/orange liquid was reduced in volume under vacuum and cooled to -15°C. After several days the solution afforded deep red crystals of 2 (110 mg, 0.057 mmol, 37%, note this is a non-optimised yield based upon harvest of first crop of crystals). ^1H NMR (d^6-acetone, 25.0 °C, 300 MHz) δ, 7.26 (m, 16H, Ar*H*) 4.02 (br m, 16H, ArC*H*$_2$Ar), 3.72 (t, 8H, O-C*H*$_2$ THF), 3.49 (t, 16H, OC*H*$_2$ propoxide), 1.83 (m, 8H, C*H*$_2$ THF), 1.49 (m, 16H C*H*$_2$ propoxide), 1.25 (m, 72H, ^{t}Bu), 0.89 (t, 24H, C*H*$_3$ propoxide) ppm.

EA (%) calculated for $C_{120}H_{176}Ti_4O_{18}$: C 68.69, H 8.45; Found: C 68.04, H 8.12. MS: m/z 2120.4 (M+Na).

$Ti_8TBC[8]_2(\mu^2\text{-}O)_2(\mu^3\text{-}O)_6(OH)_2(OPr)_2(acetone)_2$ (3)

Crystals of 3 were initially grown from d^6-acetone. However, a second batch was produced, using non-deuterated acetone, to generate sufficient material for full charaterisation. An X-ray diffraction study confirmed both batches had the same unit cell dimensions.

^1H NMR ($CDCl_3$, 25.0 °C, 300 MHz) δ, 7.31 (m, 32H, Ar*H*), 4.58 (m, 32H, ArC*H*$_2$Ar), 3.47 (t, 4H, OC*H*$_2$ propoxide), 2.11 (s, 12H, C*H*$_3$ acetone), 1.54 (m, 4H, C*H*$_2$ propoxide), 1.16 (m, 144H, ^{t}Bu), 0.93 (t, 6H, C*H*$_3$ propoxide) ppm.

Elemental analysis (%) calculated for $C_{188}H_{234}Ti_8O_{28}$: C 67.92, H 7.09; Found: C 68.43, H 7.54.

MS: m/z 3345.2 (M+Na).

Polymerisation Test Reactions.

A sample of **2** (0.2 mmol) was dissolved in toluene (2 mL) along with rac-lactide (20 mmol). The solution was heated to reflux and maintained overnight. MeOH was added to terminate the reaction and precipitate the polymer. The off-white solid was collected by filtration and dried under vacuum prior to analysis.

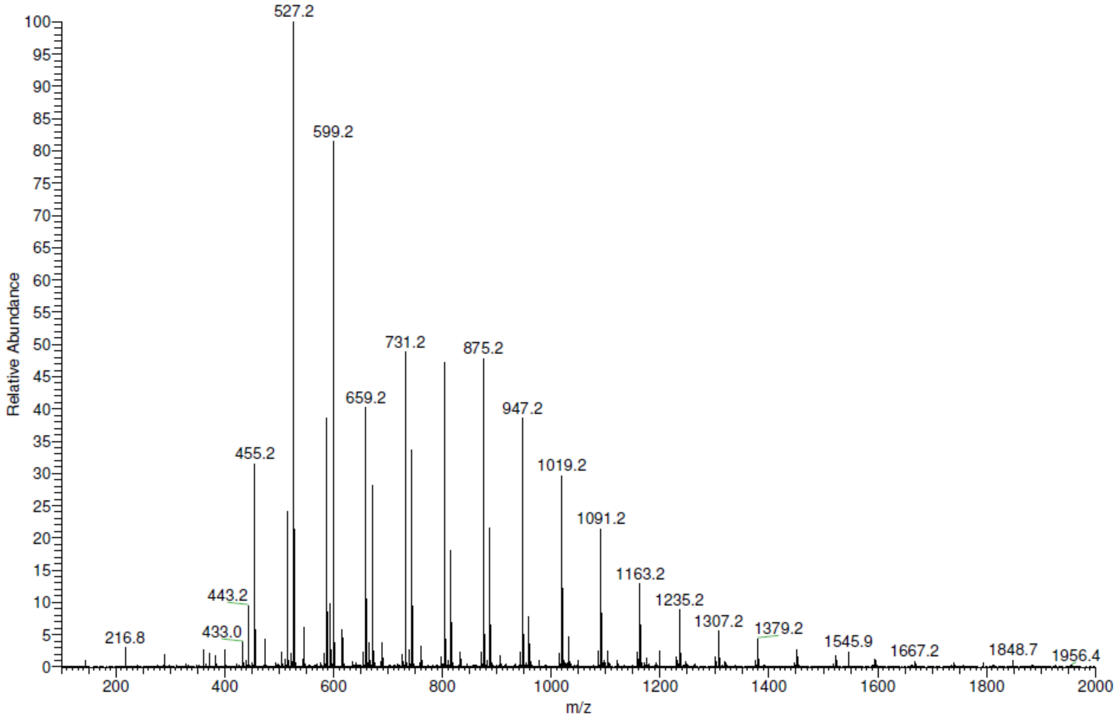

Fig. S2 ESI-MS of precipitated solid from the polymerisation reaction.

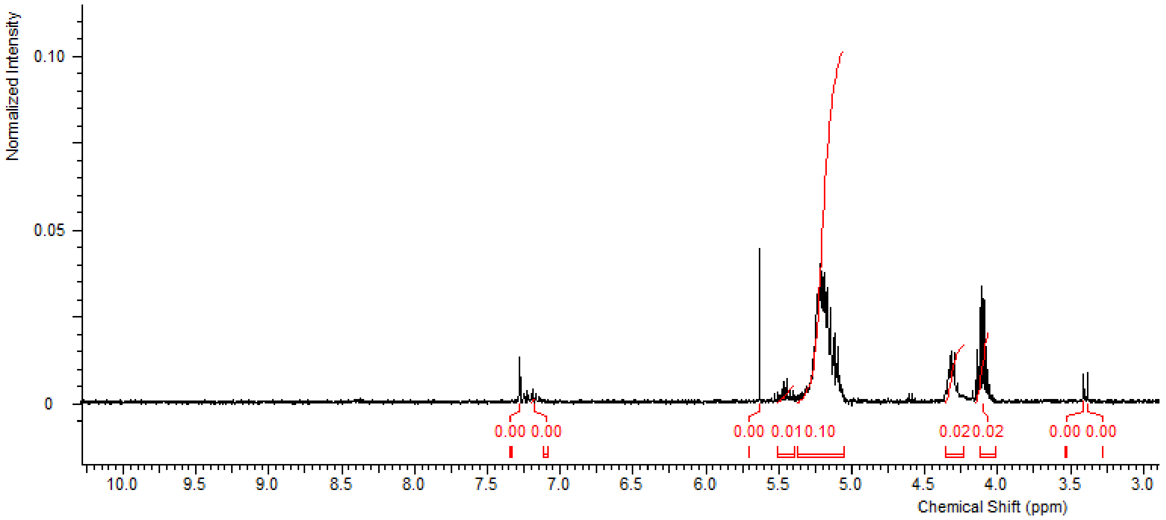

Fig. S3 ^{1}H NMR spectrum of precipitated solid from the polymerisation reaction.

References

1. C.D. Gutsche, B. Dhawan, K. No, R. Mathukrishnan, *J. Am. Chem. Soc.*, 1981, **103**, 3782.