Electronic Supplementary Information

S-Mg₂(dobpdc): A metal-organic framework for determining chirality in amino acids

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Experimental

General Considerations

All chemicals and solvents were used as obtained and without further purification. 4,4'dioxidobiphenyl-3,3'-dicarboxylic acid (H₄dobpdc),^[16] Pd(PPh₃)₄^[32] and *S*-Mg₂dobpdc^[31] were made according to literature procedures. Fourier Transform Infrared spectra were measured on an ATR Bruker Alpha spectrometer between 4000 – 400 cm⁻¹ with 4 cm⁻¹ resolution and 32 scans and normalised as absorbance spectra. Thermal gravimetric analysis was conducted on a Mettler Toledo TGA/SDTA851 instrument using aluminium crucibles as sample holders under high purity nitrogen. Typical analysis involved heating the sample up to 450 °C with a temperature increment of 10 °C min⁻¹. Microanalysis was carried out at the Chemical Analysis Facility – Elemental Analysis Service in the Department of Chemistry and Biomolecular Science at Macquarie University, Australia. Powder diffraction data were collected on an XtaLAB Synergy diffractometer employing CuK α at λ = 1.5418 Å. Samples were loaded as powder into Lindemann glass capillary tubes and patterns were collected at 100 K. PXRD patterns from single crystal structures were calculated using Mercury v.4.0.

Synthesis of BOC Protected Amino Acid Appended Frameworks (S-Mg₂dobpdc@BOC-Xxx, Xxx = Ala, Val, Pro)

The as synthesised S-Mg₂dobpdc framework in N, N-dimethylformamide was initially solvent exchanged for dichloromethane according to the following procedure. S-Mg₂dobpdc in DMF was filtered (without allowing the solid to dry out) before being redispersed in dichloromethane and allowed to sit at room temperature overnight. The suspension was centrifuged and the supernatant was decanted. Fresh dichloromethane was added and the suspension allowed to sit at room temperature overnight. This was repeated once more before the white solid was filtered and quickly air dried.

S-Mg₂dobpdc (200 mg, 0.623 mmol) was suspended in a solution of the BOC protected amino acid (1.56 mmol) in dichloromethane (2 mL). These suspensions were shaken to ensure the S-Mg₂dobpdc solid was well dispersed before being left to sit at room temperature for 44 hours. The suspension was then centrifuged, the supernatant removed and the solid washed with dichloromethane (3 \times 6 mL) before being air dried.

S-Mg₂dobpdc@BOC-L-Ala [Mg₂dobpdc(BOC-L-Ala)_{1.14}]. Obtained as a white powder. Yield = 154 mg, 40%. Found C, 44.98; H, 5.540 and N, 3.59%; Calculated for $Mg_2C_{14}O_6H_6(C_8H_{14}NO_4)_{1.14} \cdot 0.58(C_3H_7NO) \cdot 4.83H_2O$: C, 44.98; H, 5.40; N, 3.59%.

S-Mg₂dobpdc@BOC-D-Ala [Mg₂dobpdc(BOC-D-Ala)_{1.1}]. Obtained as a white powder. Yield = 153 mg, 40%. Found C, 44.20; H, 5.728 and N, 3.58%; Calculated for $Mg_2C_{14}O_6H_6(C_8H_{14}NO_4)_{1.14} \cdot 0.61(C_3H_7NO) \cdot 5.49H_2O$: C, 44.20; H, 5.52; N, 3.58%.

S-Mg₂dobpdc@BOC-DL-Ala [Mg₂dobpdc(BOC-DL-Ala)_{1.0}]. Obtained as a white powder. Yield = 150 mg, 38%. Found C, 43.46; H, 5.666 and N, 4.05%; Calculated for $Mg_2C_{14}O_6H_6(C_8H_{14}NO_4) \cdot 1.0(C_3H_7NO) \cdot 6.15H_2O$: C, 43.46; H, 5.73; N, 4.05%.

S-Mg₂dobpdc@BOC-L-Val. Obtained as a white powder. Yield = 160 mg, 46%. Found C, 46.78; H, 5.71 and N, 3.33%; Calculated for $Mg_2C_{14}O_6H_6(C_{10}H_{18}NO_4)_{0.75} \cdot 0.69(C_3H_7NO) \cdot 4.09(H_2O)$: C, 46.78; H, 5.41; N, 3.33%.

S-Mg₂dobpdc@BOC-D-Val. Obtained as a white powder. Yield = 168 mg, 48%. Found C, 46.82; H, 5.664 and N, 3.34%; Calculated for $Mg_2C_{14}O_6H_6(C_{10}H_{18}NO_4)_{0.78} \cdot 0.68(C_3H_7NO) \cdot 4.13(H_2O)$: C, 46.82; H, 5.45; N, 3.34%.

S-Mg₂dobpdc@BOC-L-Pro. Obtained as a light grey powder. Yield = 190 mg, 47%. Found C, 48.11; H, 5.481 and N, 4.13%; Calculated for $Mg_2C_{14}O_6H_6(C_{10}H_{16}NO_4)_{1.1} \cdot 0.95(C_3H_7NO) \cdot 3.96(H_2O)$: C, 48.11; H, 5.53; N, 4.13%.

S-Mg₂dobpdc@BOC-D-Pro. Obtained as a light grey powder. Yield = 183 mg, 45%. Found C, 47.82; H, 5.846 and N, 4.18%; Calculated for $Mg_2C_{14}O_6H_6(C_{10}H_{16}NO_4)_{1.1}\cdot 1.00(C_3H_7NO)\cdot 4.40(H_2O)$: C, 47.82; H, 5.59; N, 4.18%.

Solution State NMR – Digestion of S-Mg₂dobpdc

The amino acid appended S-Mg₂dobpdc (10 mg) (for all samples except *S*-Mg₂dobpdc@BOC-L-Pro) was digested by adding three drops of concentrated HCl (10 M) and DMSO- d_6 (~ 0.6 mL). The solution was gently heated on a hotplate until no particulates remained. ¹H NMR spectra were recorded on a Varian MR400 spectrometer operating at 400 MHz. ¹H chemical shifts were referenced internally to the DMSO residual solvent resonance at 2.5 ppm.

For *S*-Mg₂dobpdc@BOC-L-Pro, the sample was digested in an equal volume mixture of DMSO- d_6 and concentrated HCl for a period of 1 week. The ¹H spectrum was acquired using a Bruker Avance III 600 spectrometer (¹H, 600.13 MHz) with a BBFO probe, with a 18028 Hz sweep width, 1.8 s acquisition time and 5 s recycle delay. The excitation sculpting pulse program was used for suppression of the H₂O signal. The ¹H chemical shifts stated in ppm (δ) were referenced to tetramethylsilane ($\delta = 0$ ppm).

Synthesis of BOC Amino Acid Appended Frameworks (S-Mg₂dobpdc@ Xxx, Xxx = Ala, Val, Pro)

General Procedure (Small scale < 10 mg)

The S-Mg₂dobpdc@BOC-Xxx, Xxx = Ala, Val, Pro materials were heated to 200 °C in the Mettler Toledo TGA/SDTA851 using a ramp rate of 10 °C/min before the temperature was held at 200 °C for

30 mins. The temperature was then lowered to room temperature before the materials were characterised by FT-IR and PXRD. The same process was carried out to determine the identity of the mass loss between 200 and 290 °C by heating the sample up to 290 °C at a rate of 10 °C/min before the sample was held at 290 °C for 30 mins.

Large Scale Procedure for Solid state NMR measurements (50 mg to 100 mg)

The *S*-Mg₂dobpdc@BOC-L-Ala, *S*-Mg₂dobpdc@BOC-D-Ala and *S*-Mg₂dobpdc@BOC-DL-Ala materials were heated to 200 °C in an oven for 30 mins upon which a slight darkening of the solid from white to light grey was observed. The thermal deprotection of the BOC group was confirmed by FT-IR by the disappearance of the carbonyl peak at 1672 cm⁻¹ before the ¹³C CP MAS experiments were performed.

Solid-state NMR

The solid-state nuclear magnetic resonance (NMR) spectra were acquired using a Bruker Biospin Avance III solids-700 spectrometer or using a Bruker Biospin Avance III solids-300 spectrometer. The Bruker Biospin Avance III solids-700 spectrometer had a 16.4 T superconducting magnet operating at frequency of 175 MHz and 700 MHz for the ¹³C and ¹H nuclei, respectively. Approximately 30 mg of powder was packed into 4 mm zirconia rotors fitted with Kel-f® caps and spun in a double resonance H-X probe head at 8 kHz MAS. The ¹³C CPMAS spectra were acquired with the Total Suppression of Spinning sidebands (TOSS) scheme, to prevent overlap of the isotropic peaks by the spinning sidebands, a 1 ms ramped cross polarization to transfer signal from the ¹H to the ¹³C and recycle delays of 2 s. 3 µs and 8 µs pulse lengths were used for the ¹H 90° and ¹³C 180° pulses respectively. For suppression of non-quaternary signals, a 40 µs gated decoupling period was inserted in the TOSS scheme where the ¹H decoupling was turned off. The Spinal-64 scheme was used for the ¹H decoupling with a field strength of 83 kHz. 2k to 4k signal transients were co-added to yield spectra with sufficient signal to noise ratio. The spectra were referenced to tetramethylsilane (TMS) using solid adamantane with peaks at 38.48 and 29.42 ppm as the secondary reference. The probe was shimmed on the adamantane sample to yield linewidths of less than 3 Hz. The adamantane sample was run immediately before and after the MOF samples which ensured that the error in the measurement of the ppm due to field drift was <0.03 ppm.

The solid-state nuclear magnetic resonance (NMR) spectra were acquired using a Bruker Biospin Avance III solids-300 spectrometer with a 7 T superconducting magnet operating at frequency of 75 MHz and 300 MHz for the ¹³C and ¹H nuclei, respectively. Approximately 60 mg of powder was packed into 4 mm zirconia rotors fitted with Kel-f® caps and spun in a double resonance H-X probe head at 6.5 kHz MAS. The ¹³C CPMAS spectra were acquired with the Total Suppression of Spinning sidebands (TOSS) scheme, to prevent overlap of the isotropic peaks by the spinning sidebands, a 1 ms

ramped cross polarization to transfer signal from the ¹H to the ¹³C and recycle delays of 1.5 s. 3.5 µs and 8 µs pulse lengths were used for the ¹H 90° and ¹³C 180° pulses respectively. For suppression of non-quaternary signals, a 40 µs gated decoupling period was inserted in the TOSS scheme where the ¹H decoupling was turned off. The Spinal-64 scheme was used for the ¹H decoupling with a field strength of 72 kHz. 1k signal transients were co-added to yield spectra with sufficient signal to noise ratio. The spectra were referenced to tetramethylsilane (TMS) using solid adamantane with peaks at 38.48 and 29.42 ppm as the secondary reference. The probe was shimmed on the adamantane sample to yield linewidths of less than 3 Hz.



Figure S1. The PXRD of the as synthesised, solvent exchanged and amino acid appended S-Mg₂dobpdc variants graphed against the calculated powder pattern for $Zn_2(dobpdc)$ from $3 - 50^{\circ}$ 20.



Figure S2. The PXRD of *S*-Mg₂dobpdc in dichloromethane and with BOC-L-Ala and BOC-D-Ala grafted onto the framework against the calculated powder pattern for $Zn_2(dobpdc)$ from 3 – 50° 20.



Figure S3. The PXRD of *S*-Mg₂dobpdc in dichloromethane and with BOC-L-Val and BOC-D-Val grafted onto the framework against the calculated powder pattern for $Zn_2(dobpdc)$ from $3 - 50^{\circ} 2\theta$.



Figure S4. The PXRD of *S*-Mg₂dobpdc in dichloromethane and with BOC-L-Pro and BOC-D-Pro grafted onto the framework against the calculated powder pattern for $Zn_2(dobpdc)$ from $3 - 50^{\circ} 2\theta$.



Figure S5. ATR infrared spectra (normalised) of *S*-Mg₂dobpdc and *S*-Mg₂dobpdc@BOC-Ala grafted materials from $4000 - 400 \text{ cm}^{-1}$. The asterisk indicates the carbonyl peak at 1670 cm⁻¹ corresponding to the BOC group in the appended BOC-Ala guest.



Figure S6. ATR infrared spectra (normalised) of *S*-Mg₂dobpdc and *S*-Mg₂dobpdc@BOC-Val grafted materials from $4000 - 400 \text{ cm}^{-1}$. The asterisk indicates the carbonyl peak at 1670 cm⁻¹ corresponding to the BOC group in the appended BOC-Val guest.



Figure S7. ATR infrared spectra (normalised) of *S*-Mg₂dobpdc and *S*-Mg₂dobpdc@BOC-Pro grafted materials from $4000 - 400 \text{ cm}^{-1}$. The asterisk indicates the carbonyl peak at 1670 cm⁻¹ corresponding to the BOC group in the appended BOC-Pro guest.



Figure S8. Solution state ¹H NMR of *S*-Mg₂dobpdc@BOC-L-Ala digested with concentrated HCl (10 M) and DMSO- d_6 at 400 MHz. The multiple peaks for BOC-L-Ala and BOC are due to partial BOC deprotection of the NH₂ group under strongly acidic conditions.



Figure S9. Solution state ¹H NMR of *S*-Mg₂dobpdc@BOC-D-Ala digested with concentrated HCl (10 M) and DMSO- d_6 at 400 MHz. The multiple peaks for BOC-D-Ala and BOC are due to partial BOC deprotection of the NH₂ group under strongly acidic conditions.



Figure S10. Solution state ¹H NMR of *S*-Mg₂dobpdc@BOC-L-Val digested with concentrated HCl (10 M) and DMSO- d_6 at 400 MHz. The multiple peaks for BOC-L-Val and BOC are due to partial BOC deprotection of the NH₂ group under strongly acidic conditions.



Figure S11. Solution state ¹H NMR of *S*-Mg₂dobpdc@BOC-D-Val digested with concentrated HCl (10 M) and DMSO- d_6 at 400 MHz. The multiple peaks for BOC-D-Val and BOC are due to partial BOC deprotection of the NH₂ group under strongly acidic conditions.



Figure S12. Solution state ¹H NMR of *S*-Mg₂dobpdc@BOC-L-Pro digested with concentrated HCl (10 M) and DMSO- d_6 at 600 MHz. The multiple peaks for BOC-L-Pro and BOC are due to partial BOC deprotection of the NH₂ group under strongly acidic conditions. A note that this sample was left to digest in concentrated HCl for 1 week, which resulted in some ligand decomposition.



Figure S13. Solution state ¹H NMR of *S*-Mg₂dobpdc@BOC-D-Pro digested with concentrated HCl (10 M) and DMSO- d_6 at 400 MHz. The multiple peaks for BOC-D-Pro and BOC are due to partial BOC deprotection of the NH₂ group under strongly acidic conditions.



Figure S14. Thermal gravimetric analysis (TGA) of *S*-Mg₂dobpdc@BOC-L-Ala between 25 and 450 °C heated at a rate of 5 °C/min under a flow of nitrogen. The percentage mass loss is shown in black and the first derivative, the rate of mass change, shown in blue.



Figure S15. Thermal gravimetric analysis (TGA) of *S*-Mg₂dobpdc@BOC-D-Ala between 25 and 450 °C heated at a rate of 5 °C/min under a flow of nitrogen. The percentage mass loss is shown in black and the first derivative, the rate of mass change, shown in blue.



Figure S16. Thermal gravimetric analysis (TGA) of *S*-Mg₂dobpdc@BOC-L-Val between 25 and 450 °C heated at a rate of 5 °C/min under a flow of nitrogen. The percentage mass loss is shown in black and the first derivative, the rate of mass change, shown in blue.



Figure S17. Thermal gravimetric analysis (TGA) of *S*-Mg₂dobpdc@BOC-D-Val between 25 and 450 °C heated at a rate of 5 °C/min under a flow of nitrogen. The percentage mass loss is shown in black and the first derivative, the rate of mass change, shown in blue.



Figure S18. Thermal gravimetric analysis (TGA) of *S*-Mg₂dobpdc@BOC-L-Pro between 25 and 450 °C heated at a rate of 5 °C/min under a flow of nitrogen. The percentage mass loss is shown in black and the first derivative, the rate of mass change, shown in blue.



Figure S19. Thermal gravimetric analysis (TGA) of *S*-Mg₂dobpdc@BOC-D-Pro between 25 and 450 °C heated at a rate of 5 °C/min under a flow of nitrogen. The percentage mass loss is shown in black and the first derivative, the rate of mass change, shown in blue.



Figure S20. Thermal gravimetric analysis (TGA) of *S*-Mg₂dobpdc@BOC-DL-Ala between 25 and 450 °C heated at a rate of 5 °C/min under a flow of nitrogen. The percentage mass loss is shown in black and the first derivative, the rate of mass change, shown in blue.



Figure S21. Thermal gravimetric analysis (TGA) of *S*-Mg₂dobpdc@BOC-DL-Val between 25 and 450 °C heated at a rate of 5 °C/min under a flow of nitrogen. The percentage mass loss is shown in black and the first derivative, the rate of mass change, shown in blue.



Figure S22. Thermal gravimetric analysis (TGA) of *S*-Mg₂dobpdc@BOC-DL-Pro between 25 and 450 °C heated at a rate of 5 °C/min under a flow of nitrogen. The percentage mass loss is shown in black and the first derivative, the rate of mass change, shown in blue.



Figure S23. ATR infrared spectra (normalised) of *S*-Mg₂dobpdc@BOC-DL-Ala grafted materials from $4000 - 400 \text{ cm}^{-1}$ as synthesised (black) and after heating at 200 °C (red) and 290 °C (blue). The asterisk indicates the carbonyl peak at 1670 cm⁻¹ corresponding to the BOC group in BOC-DL-Ala.



Figure S24. ATR infrared spectra (normalised) of *S*-Mg₂dobpdc@BOC-DL-Val grafted materials from $4000 - 400 \text{ cm}^{-1}$ as synthesised (black) and after heating at 200 °C (red) and 290 °C (blue). The asterisk indicates the carbonyl peak at 1670 cm⁻¹ corresponding to the BOC group in BOC-DL-Val.



Figure S25. ATR infrared spectra (normalised) of *S*-Mg₂dobpdc@BOC-DL-Pro grafted materials from $4000 - 400 \text{ cm}^{-1}$ as synthesised (black) and after heating at 200 °C (red) and 290 °C (blue). The asterisk indicates the carbonyl peak at 1670 cm⁻¹ corresponding to the BOC group in BOC-DL-Pro.



Figure S26. The PXRD of *S*-Mg₂dobpdc@BOC-DL-Ala as synthesised (black) and heated at 200 °C (red) and 290 °C (blue) from $4 - 50^{\circ} 2\theta$.



Figure S27. The PXRD of *S*-Mg₂dobpdc@BOC-DL-Val as synthesised (black) and heated at 200 °C (red) and 290 °C (blue) from $4 - 50^{\circ} 2\theta$.



Figure S28. The PXRD of *S*-Mg₂dobpdc@BOC-DL-Pro as synthesised (black) and heated at 200 °C (red) and 290 °C (blue) from $4 - 50^{\circ} 2\theta$.



Figure S29. Thermal gravimetric analysis (TGA) of *S*-Mg₂dobpdc@L-Ala between 25 and 450 °C heated at a rate of 5 °C/min under a flow of nitrogen. The percentage mass loss is shown in black and the first derivative, the rate of mass change, shown in blue.



Figure S30. Thermal gravimetric analysis (TGA) of *S*-Mg₂dobpdc@D-Ala between 25 and 450 °C heated at a rate of 5 °C/min under a flow of nitrogen. The percentage mass loss is shown in black and the first derivative, the rate of mass change, shown in blue.



Figure S31. Thermal gravimetric analysis (TGA) of *S*-Mg₂dobpdc@DL-Ala between 25 and 450 °C heated at a rate of 5 °C/min under a flow of nitrogen. The percentage mass loss is shown in black and the first derivative, the rate of mass change, shown in blue.



Figure S32. Thermal gravimetric analysis (TGA) of *S*-Mg₂dobpdc between 25 and 450 °C heated at a rate of 5 °C/min under a flow of nitrogen. The percentage mass loss is shown in black and the first derivative, the rate of mass change, shown in blue.



Figure S33. Solid state ¹³C CPMAS (cross polarisation magic angle spinning) spectra (black) and ¹³C NQS (non-quaternary suppression) spectra of *S*-Mg₂dobpdc at 75 MHz.



Figure S34. Solid state ¹³C CPMAS (cross polarisation magic angle spinning) spectra (black) and ¹³C NQS (non-quaternary suppression) spectra of *S*-Mg₂dobpdc@BOC-L-Ala at 75 MHz.



Figure S35. Solid state ¹³C CPMAS (cross polarisation magic angle spinning) spectra (black) and ¹³C NQS (non-quaternary suppression) spectra (red) of *S*-Mg₂dobpdc@BOC-L-Val at 75 MHz.



Figure S36. Solid state ¹³C CPMAS (cross polarisation magic angle spinning) spectra (black) and ¹³C NQS (non-quaternary suppression) spectra of *S*-Mg₂dobpdc@BOC-L-Pro at 75 MHz.



Figure S37. The assigned ¹³C CPMAS NMR spectra of *S*-Mg₂dobpdc@BOC-L-Pro (black) and *S*-Mg₂dobpdc@BOC-D-Pro (red) at 175 MHz between 200 and 0 ppm.



Figure S38. The ¹³C CPMAS NMR spectra of *S*-Mg₂dobpdc@BOC-L-Pro (black) and *S*-Mg₂dobpdc@BOC-D-Pro (red) at 175 MHz zoomed in between 145 and 105 ppm. The vertical lines are to guide the reader for the differences in chemical shift between the L and D enantiomers.



Figure S39. The ¹³C CPMAS NMR spectra of *S*-Mg₂dobpdc@BOC-L-Pro (black) and *S*-Mg₂dobpdc@BOC-D-Pro (red) recorded at 175 MHz zoomed in between 70 and 10 ppm. The vertical lines are to guide the reader for the differences in chemical shift between the L and D enantiomers.



Figure S40. The assigned ¹³C CPMAS NMR spectra of *S*-Mg₂dobpdc@BOC-L-Val (black) and *S*-Mg₂dobpdc@BOC-D-Val (red) at 175 MHz between 200 and 0 ppm.



Figure S41. The ¹³C CPMAS NMR spectra of *S*-Mg₂dobpdc@BOC-L-Val (black) and *S*-Mg₂dobpdc@BOC-D-Val (red) at 175 MHz zoomed in between 145 and 105 ppm. The vertical lines are to guide the reader for the differences in chemical shift between the L and D enantiomers.



Figure S42. The ¹³C CPMAS NMR spectra of *S*-Mg₂dobpdc@BOC-L-Val (black) and *S*-Mg₂dobpdc@BOC-D-Val (red) at 175 MHz zoomed in between 70 and 10 ppm. The vertical lines are to guide the reader for the differences in chemical shift between the L and D enantiomers.