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# Supporting Informations

# Molecular tectonics: gas adsorption and chiral uptake of (L)- and (D)tryptophan by homochiral porous coordination polymers

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# **Table of contents**

1.	Materials and methods	2
	General methods	2
	Synthetic procedures	2
2.	Characterization	7
	Thermogravimetric analysis	7
	Adsorption measurements	9
	Optical absorption spectra	9
	Heats of adsorption	10
	CO <sub>2</sub> /N <sub>2</sub> Selectivity	11
	Crystal structural data	12
	XRPD Diffraction patterns	13
	Desorption process	17
	References	19

# 1. Materials and methods.

**General methods.** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded at 25 °C on Brucker AV300 (300 MHz) Bruker AV400 (400 MHz) or Bruker AV500 (500 MHz) spectrometers in deuterated solvents with the residual solvent peak used as the internal reference. The abbreviations for specifying the multiplicity of <sup>1</sup>H-NMR signals are defined as follows: s = singlet, d = doublet, dd = doublet of doublet, ddd = doublet of doublet of doublets, t = triplet, m = multiplet, br = broad. Coupling constants are given in Hertz and chemical shifts in ppm.

Elemental analyses were performed on a Thermo Scientific Flash 2000 by the "Service Commun de Microanalyse" of the University of Strasbourg.

Polarimetric measurements were performed on a Perkin Elmer spectrometer (model 341).

Thermo gravimetric analysis (TGA) were performed on a Pyris 6 TGA Lab System apparatus (Perkin-Elmer), using a  $N_2$  flow of 20 mL/min and a heat rate of 5°/min.

Melting points were measured in capillary on Stuart Scientific Melting Point SMP-1 apparatus.

Differential Scanning Calorimetry (DSC) traces were recorded on a Mettler Toledo Star<sup>e</sup> DSC1 analysis system equipped with  $N_2$  low temperature apparatus. The experiments were run under nitrogen atmosphere in standard 40  $\mu$ l Al pans. The samples were heated from 25°C to 400°C, at 10°C/min.

#### Synthetic procedures.



1,4-dibromo-2,5-di((R)-sec-butoxy)benzene and 1,4-dibromo-2,5-bis((S)-2-methylbutoxy)benzene were synthezied as described in the litterature<sup>1</sup>.

**Synthesis of 2 and 4:** A DMF solution (50 mL) of 1,4-dibromo-2,5-di((R)-sec-butoxy)benzene (1.0 g, 2.6 mmol) or 1,4-dibromo-2,5-bis((S)-2-methylbutoxy)benzene (1.0 g, 2.4 mmol) along with 3,5-Bis(methoxycarbonyl)phenylboronic acid pinacol ester (3 eq) was degassed with Argon for 20 min. To the mixture,  $Cs_2CO_3$  (3 eq) and Pd(PPh3)4 (0.1 eq) were added under an Argon atmosphere. The reaction media was heated to 100 °C for 24 h before it was allowed to reach RT. The solvent was then evaporated to dryness and the resulting residue was purified by column chromatography (SiO<sub>2</sub>,  $CH_2Cl_2/cyclohexane$ , 1:1) to yield compounds **2** and **4** respectively 88 and 90%.

#### Compound 2:

<sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): δ (ppm) = 8.60 (t, 2H, <sup>4</sup>J = 1.7 Hz), 8.47 (d, 4H, <sup>4</sup>J = 1.7 Hz), 7.05 (s, 2H), 4.25 (m, 2H), 3.94 (s, 12H), 1.54 (m, 2H, He), 1.61 (m, 2H), 1.17 (d, 6H, <sup>3</sup>J = 6.1 Hz), 0.85 (t, 6H, <sup>3</sup>J = 7.4 Hz). <sup>13</sup>C-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz): δ (ppm) = 166.6, 149.6, 139.6, 135.2, 131.1, 130.9, 129.3, 118.3, 77.2, 52.7, 29.5, 19.2, 9.7.

**[α]20D** = - 23.1° (c = 1.00 in CHCl3).

**Elemental analysis (%) for C<sub>34</sub>H<sub>38</sub>O**<sub>10</sub> **calculated:** C 67.31, H 6.31; found: C 67.18, H 6.22. **m.p. =** 224-227 °C.



#### Compound 4:

<sup>1</sup>**H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):**  $\delta$  (ppm) = 8.61 (t, 2H, <sup>4</sup>J = 1.6 Hz), 8.48 (d, 4H, <sup>4</sup>J = 1.6 Hz), 7.05 (s, 2H), 3.94 (s, 12H), 3.85 (dd, 2H, <sup>2</sup>J = 8.8 Hz, <sup>3</sup>J = 5.7 Hz), 3.78 (dd, 2H, <sup>2</sup>J = 8.8 Hz, <sup>3</sup>J = 6.3 Hz), 1.75 (m, 2H), 1.44 (m, 2H), 1.20 (m, 2H), 0.92 (d, 6H, <sup>3</sup>J = 6.8 Hz), 0.85 (t, 6H, <sup>3</sup>J = 7.4 Hz).

<sup>13</sup>C-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz): δ (ppm) = 166.6, 150.7, 139.4, 135.1, 130.9, 129.6, 129.4, 115.6, 74.5, 52.6, 35.3, 26.4, 16.7, 11.5.
[α]20D = + 8.1° (c = 1.00 in CHCl3).
Elemental analysis (%) for C<sub>36</sub>H<sub>42</sub>O<sub>10</sub> calculated: C 68.12, H 6.67; found: C 67.41, H 6.63.

**Elemental analysis (%) for C**<sub>36</sub>H<sub>42</sub>O<sub>10</sub> **calculated:** C 68.12, H 6.67; found: C 67.41, H 6.63. **m.p.** = 205-208 °C.



**Synthesis of 1 and 3:** A solution of compound **2** (500 mg, 0.82 mmol) or **4** (500 mg, 0.79 mmol) in a mixture of THF (50 mL) and aq. KOH (2 M, 50 mL) was heated to 90 °C overnight before it was allowed to reach RT. The organic solvent was removed under reduced pressure and the resulting aqueous solution was acidified

with HCl (6 M) to pH 1. The precipitate that formed was collected by filtration, washed with  $H_2O$  (100 ml) and dried under vacuum at 50 °C for 24 h to afford compounds **1** and **3** in 96 and 97% yield respectively.

#### Compound 1:

<sup>1</sup>**H-NMR (DMSO-d<sub>6</sub>, 400 MHz):** δ (ppm) = 13.29 (br, 4H), 8.45 (t, 2H, <sup>4</sup>J = 1.6 Hz), 8.37 (d, 4H, <sup>4</sup>J = 1.6 Hz), 7.18 (s, 2H), 4.43 (m, 2H), 1.60-1.45 (m, 4H), 1.13 (d, 6H, <sup>3</sup>J = 6.0 Hz), 0.82 (t, 6H<sub>g</sub>, <sup>3</sup>J = 7.4 Hz).

<sup>13</sup>**C-NMR (DMSO-d<sub>6</sub>, 100 MHz):** δ (ppm) = 166.7, 148.5, 138.5, 134.2, 131.2, 130.0, 128.6, 117.5, 75.5, 28.5, 18.7, 9.2

 $[\alpha]^{20}_{D} = -25.0^{\circ}$  (c = 0.5 in DMF).

**Elemental analysis (%)** for C<sub>30</sub>H<sub>30</sub>O<sub>10</sub> calculated: C 65.45, H 5.49; found: C 65.73, H 5.29. **m.p.** > 300 °C.



#### Compound 3:

<sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, 400 MHz): δ (ppm) = 13.28 (br, 4H), 8.45 (t, 2H, <sup>4</sup>J = 1.6 Hz), 8.38 (d, 4H, <sup>4</sup>J = 1.6 Hz), 7.19(d, 2H), 3.89 (dd, 2H, <sup>2</sup>J = 9.1 Hz, <sup>3</sup>J = 5.7 Hz), 3.84 (dd, 2H, <sup>2</sup>J = 9.1 Hz, <sup>3</sup>J = 6.2 Hz), 1.67 (m, 2H), 1.40 (m, 2H), 1.13 (m, 2H), 0.86 (d, 6H, <sup>3</sup>J = 6.8 Hz), 0.79 (t, 6H, <sup>3</sup>J = 7.4 Hz).

<sup>13</sup>**C-NMR (DMSO-d**<sub>6</sub>, **100 MHz):** δ (ppm) = 166.6, 149.8, 138.3, 134.2, 131.1, 128.7, 128.5, 115.2, 73.5, 34.3, 25.5, 16.3, 11.1.

**Elemental analysis (%)** for C<sub>32</sub>H<sub>34</sub>O<sub>10</sub><sup>.</sup>0.5H<sub>2</sub>O calculated: C 65.41, H 6.00; found: C 65.18, H 6.22. **m.p.** > 300 °C.



## Crystallisation

### Single crystals of 1-Zn:

Under hydrothermal conditions, upon heating a DMF solution (3 mL) of  $\mathbf{1}$  (10 mg) and Zn(NO<sub>3</sub>)<sub>2</sub> (15 mg) at 100 °C for 24h, colorless crystals of  $\mathbf{1}$ -Zn were obtained.

### Single crystals of 3-Zn:

Under hydrothermal conditions, upon heating a DMF solution (3 mL) of **3** (10 mg) and  $Zn(NO_3)_2$  (15 mg) at 100 °C for 24h, colorless crystals of **3**-Zn were obtained.

## Crystalline powder of 1-Cu:

Under hydrothermal conditions, upon heating a DMF solution (5 mL) of tecton **1** (20 mg) and  $Cu(NO_3)_2$  (30 mg) and six drops of HCl (3.7 %) at 85 °C for 24h, blue crystals of **1**-Cu were obtained. The crystallization process was repeated several times in order to collect sufficient amounts of material.

#### Crystalline powder of 3-Cu:

Under hydrothermal conditions, upon heating a DMF solution (5 mL) of tecton **3** (20 mg) and  $Cu(NO_3)_2$  (30 mg) and six drops of HCl (3.7 %) at 85 °C for 24h, , blue crystals of **3**-Cu were obtained. The crystallization process was repeated several times in order to collect sufficient amounts of material.

# 2. Characterization

#### Thermogravimetric analysis.



Fig S9: Thermogravimetric analysis (TGA) of 1-Zn.



Fig S10: Thermogravimetric analysis (TGA) of 3-Zn.



Fig S11: Thermogravimetric analysis (TGA) of 1-Cu as synthetized.



Fig S12: Termogravimetric analysis (TGA) of 3-Cu.

Adsorption measurements. Nitrogen adsorption-desorption isotherms at 77 K and CO<sub>2</sub> at 195 K were obtained using a Micromeritics analyzer ASAP 2020 HD up to 1 bar, while N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> isotherms at 273 K and 298 K up to 10 bar were collected using a Micromeritics analyzer ASAP 2050. The samples were previously evacuated under vacuum at 100 °C overnight. The isosteric heat of adsorption Q<sub>st</sub> values were determined by applying the Clausius-Clapeyron equation while the selectivities of CO<sub>2</sub>/N<sub>2</sub> binary mixture were determined from the single-component isotherms using the ideal adsorbed solution theory (IAST) and a CO<sub>2</sub>/N<sub>2</sub> ratio of 15:85 (mol:mol). At 1 bar and 298K **1**-Cu adsorbs 60 and 16 cm<sup>3</sup>/g of CO<sub>2</sub> and CH<sub>4</sub> while **3**-Cu adsorbs 46 and 11 cm<sup>3</sup>/g of CO<sub>2</sub> and CH<sub>4</sub>, respectively.

**Optical absorption spectra.** All the spectra were recorded in the 220-340 nm range with a UV-visible Lambda 900 Perkin Elmer spectrophotometer, in 1 mm quartz cuvettes. Aqueous solutions of enantiopure L-tryptophan and D-tryptophan ( $3.3 \cdot 10^{-3}$  M) were prepared. The strongest absorption peak of tryptophan at 280 nm was used as the reference wavelength. 15 mg of the evacuated samples were immersed in 7 ml of the tryptophan aqueous solutions and optical absorption spectra were recorded versus time. Upon uptake of tryptophan by the porous materials, the intensity of peak measured in solution decreased until it reached a plateau. The solution absorbance showed a typical Lambert-Beer linear correlation with the concentration at different wavelengths.

Heats of adsorption.



Fig S13: CO<sub>2</sub> heat of Adsorption of 1-Cu (grey) and of 3-Cu (red).



Fig S14: CH<sub>4</sub> heat of Adsorption of 1-Cu (grey) and of 3-Cu (red).

 $CO_2/N_2$  Selectivity.



**Fig S15**: Selectivity of **1**-Cu (blue) and of **3**-Cu (red) on  $CO_2/N_2$  mixture at 273K (above). Selectivity of **1**-Cu (blue) and of **2**-Cu (red) on  $CO_2/N_2$  mixture at 298K (below).



**Fig S16**:  $CO_2$  (circles) and  $CH_4$  (triangles) adsorption isotherms at 298 K for **1**-Cu compound (full symbols) and for **3**-Cu (empty symbols) up to 1 bar.

## X-Ray diffraction.

Single-crystal data were collected on a Bruker SMART CCD diffractometer with Mo–K $\alpha$  radiation at 173 K. The structures were solved using SHELXS-97 and refined by full matrix least-squares on  $F^2$  using SHELXL-2014 with anisotropic thermal parameters for all non-hydrogen atoms.<sup>2</sup> The hydrogen atoms were introduced at calculated positions and not refined (riding model). For both structure of **1**-Zn and **3**-Zn, highly disordered solvent molecules are present, the SQUEEZE command has been employed to account for the corresponding electron density.<sup>3</sup>

CCDC 1520830 and 1520777 contain the supplementary crystallographic data for **1**-Zn and **3**-Zn. These data can be obtained free of charge *via* <u>www.ccdc.cam.ac.uk/data\_request/cif</u>.

	<b>1</b> -Zn	<b>3</b> -Zn
Fomula	$C_{30}H_{30}O_{12}Zn_2$	C <sub>32</sub> H <sub>34</sub> O <sub>12</sub> Zn <sub>2</sub>
FW	713.33	741.33
Crystal system	Rhombohedral	Rhombohedral
Space group	R3	R3
a / Å	18.9586(7)	18.8323(7)
b/Å	18.9586(7)	18.8323(7)
c/Å	38.0589(13)	38.4958(15)
α/°	90	90
$\beta/\circ$	90	90
γ/°	120	120
$V/Å^3$	11846.7(7)	11823.6(8)
Ζ	9	9
<i>T</i> / K	173(2)	173
$\mu/\text{ mm}^{-1}$	0.950	0.951
Refls. coll.	15013	14983
Ind. refls. (Rint)	15013	14983
$R_1 (I > 2\sigma(I))^a$	0.0824	0.0984
$wR_2 (I > 2\sigma(I))^a$	0.2311	0.2695
$R_1$ (all data) <sup><i>a</i></sup>	0.1327	0.1624
$wR_2$ (all data) <sup><i>a</i></sup>	0.2586	0.2968
GOF	0.905	0.917

#### Crystal structural data.

# XRPD Diffraction patterns.

Powder X-ray diffraction experiments were performed using a X-Pert Pro diffractometer at room temperature. The radiation wavelength  $\lambda$  of the incident X-rays was 1,54 Å and a 2 $\theta$  range is from 5° to 30° was investigated.



Fig S17: Simulated (a) and experimental (b) XRPD patterns for 1-Zn.



Fig S18: Simulated (a) and experimental (b) XRPD patterns for 3-Zn.



**Fig S19**: PXRD patterns of evacuated **3**-Cu (a) and **1**-Cu (b). The unit cell parameters were calculated by non linear least square fitting and the interplanar distances were indexed considering the space group R3. The cell parameters and volumes are the following: a = b = 18,7534 Å (± 0,0344), c = 38,6509 Å (± 0,0955), V = 11772,05 Å<sup>3</sup> (±0,0010) for **3**-Cu; a = b = 18,8943 Å (±0,0537), c = 38,5605 Å (± 0,1438), V = 11921,63 Å<sup>3</sup> (± 0,0013) for **1**-Cu.



Fig S20: PXRD patterns for 1-Cu after soaking in the solution containing L-Tryptophan or D-Tryptophan.



Fig S21: PXRD of 3-Cu after MOF soaking in the solution containing L-Tryptophan or D-Tryptophan.



Fig S22: PXRD for 3-Cu (a) and 1-Cu (b) after 24 hours of soaking in water.

#### **Desorption process.**

After 24 hours under magnetic stirring in water, 3 mg of **1**-Cu and **3**-Cu crystals were digested in 30  $\mu$ L of deuterated trifluoroacetic acid and then dissolved in 0.5 mL of deuterated DMSO to perform <sup>1</sup>H NMR experiments. The percentages of tryptophan release are very low, as the NMR data confirm.



**Fig S23.** <sup>1</sup>H NMR in dmso after digestion in deuterated trifluoroacetic acid of **1**-Cu and D-tryptophan after 24h release in water.



**Fig S24.** <sup>1</sup>H NMR in dmso after digestion in deuterated trifluoroacetic acid of **1**-C**u** and L-tryptophan after 24h release in water.



**Fig S25.** <sup>1</sup>H NMR in dmso after digestion in deuterated trifluoroacetic acid of **3**-C**u** and L-tryptophan after 24h release in water.



**Fig S26.** <sup>1</sup>H NMR in dmso after digestion in deuterated trifluoroacetic acid of **3**-C**u** and D-tryptophan after 24h release in water.



**Fig S27.** Desorbed Tryptophan versus time of a) 1-Cu and b) 3-Cu. D-tryptophan (circles) and L-tryptophan (squares).

#### References.

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