A Homochiral Vanadium-Salen-Cadmium bpdc MOF with Permanent Porosity as Asymmetric Catalyst in Solvent-Free Cyanosilylation

Asamanjoy Bhunia,a Subarna Dey,b José María Moreno,c Urbano Diaz,c Patricia Concepcion,c Kristof Van Hecke,d Christoph Janiakb and Pascal Van Der Voort* a

a Dept. of Inorganic and Physical Chemistry, Center for Ordered Materials, Organometallics and Catalysis, Ghent University, Krijgslaan 281-S3, 9000 Ghent, Belgium
b Institut für Anorganische Chemie und Strukturchemie, Universität Düsseldorf, 40204 Düsseldorf, Germany
c Instituto de Tecnología Química (UPV-CSIC), Avenida de los Naranjos s/n, 46022 Valencia, Spain
d Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281-S3, 9000 Ghent, Belgium

* To whom correspondence should be addressed. E-mail: pascal.vandervoort@ugent.be; Tel: (+)32-92644442; Fax: (+)32-92644983.

Supporting information
13 pages

Table of contents
1. Experimental section ..............................................................................................................................................S2
2. Synthesis of V-salen Cd-bpdc MOF and VO-salen complex ..................................................................................S3
3. FT-IR spectrum ..................................................................................................................................................S3
4. Powder X-ray diffraction patterns ....................................................................................................................S4
5. Thermogravimetric analysis (TGA) ..................................................................................................................S4
6. Isosteric heats of adsorption of CO₂ ..................................................................................................................S4-S5
7. Pore size distribution .......................................................................................................................................S5
8. BET surface area and gas uptake capacities (H₂, CO₂ and CH₄) of reported salen-based MOFs..........................S6
9. Catalysis: Cyanosilylation of aromatic aldehyde ............................................................................................S7-S9
10. Cyanosilylation of benzaldehyde by using chloroform and acetonitrile as solvent ........................................S10-S11
11. Chiral GC spectra .......................................................................................................................................S11-S14
12. Framework topology .....................................................................................................................................S14-S17
13. X-ray crystallography .....................................................................................................................................S18
14. References .......................................................................................................................................................S19

Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2015
1. **Experimental Section**

**Materials and methods**

All chemicals were purchased from commercial suppliers (Sigma-Aldrich and TCI Europe) and used without further purification, unless stated otherwise. Ligands (R,R)-(-)-1,2-cyclohexanediamino-N,N’-bis(3-tert-butyl-5-(4-pyridyl)salicylidene (H$_2$L) was synthesized according to the reported procedures.$^1$

Diffuse-reflectance infrared Fourier transform (DRIFT) spectra were obtained with a Thermo Nicolet 6700 FTIR spectrometer equipped with a nitrogen-cooled MCT detector and a KBr beam splitter. Elemental analyses (C, H, N) were carried out with a Thermo Scientific Flash 2000 CHNS-O analyzer equipped with a TCD detector. Thermogravimetric analysis (TGA) was performed with a Netzsch STA-409CD thermal analyzer in a temperature range of 25–600 °C under an air atmosphere at a heating rate of 2 °C min$^{-1}$. Powder X-ray diffraction (PXRD) data were recorded with a Thermo Scientific ARL X’Tra diffractometer operated at 40 kV, 40 mA with Cu-K$_\alpha$ ($\lambda = 1.5406$ Å) radiation. Sorption isotherms were measured using a Micromeritics ASAP 2020 automatic gas sorption analyzer equipped with oil-free vacuum pumps (ultimate vacuum $<10^{-8}$ mbar) and valves, which guaranteed contamination free measurements. The sample was connected to the preparation port of the sorption analyzer and degassed under vacuum until the outgassing rate, i.e., the rate of pressure rise in the temporarily closed manifold with the connected sample tube, was less than 2 μTorr/min at the specified temperature 80 °C. After weighing, the sample tube was then transferred to the analysis port of the sorption analyzer. All used gases (H$_2$, He, N$_2$, CO$_2$, CH$_4$) were of ultra-high purity (UHP, grade 5.0, 99.999%) and the STP volumes are given according to the NIST standards (293.15 K, 101.325 kPa). Helium gas was used for the determination of the cold and warm free space of the sample tubes. H$_2$ and N$_2$ sorption isotherms were measured at 77 K (liquid nitrogen bath), whereas CO$_2$ and CH$_4$ sorption isotherms were measured at 293±1 K (passive thermostating) and 273.15 K (ice/deionized water bath). The heat of adsorption values and the DFT pore size distributions (‘N$_2$ DFT slit pore’ model) were calculated out using the ASAP 2020 v3.05 software. The yield of the cayanosilylations were determined by capillary gas chromatography. They were carried out in a Varian 3900 equipped with a Sapiens 5MS column (30m*0.25mm*0.25μm) and was operated at 280 °C in the injector temperature and 300 °C in the detector temperature (FID). Moreover, the ee was determined by chiral chromatography in a Varian 3900 with a Chiraldex γ-TA column (30m*0.25mm*0.25μm) and was operated at 230°C both in the injector temperature and the detector temperature (FID).
2. **a. Synthesis of V-salen Cd-bpdc MOF**

A mixture of H$_2$L (16 mg, 0.027 mmol), VOSO$_4$·(H$_2$O)$_x$ (8 mg, 0.05 mmol), Cd(NO$_3$)$_2$·(H$_2$O)$_4$ (15 mg, 0.05 mmol) and biphenyl-4,4′-dicarboxylic acid (6 mg, 0.025 mmol) were combined in 1.5 mL of DMF with stirring for 3 h at room temperature followed by addition of 1.5 mL ethanol and 15 µL H$_2$O. The resulting solution was then sealed in a 10 mL glass vial. The glass vial was heated at 100 °C for 2 d in an oven and cooled to room temperature. The green needle shaped crystals were collected and washed three times with DMF followed by MeOH and dried in air. Yield: 16 mg, 32% (based on vanadium salt).

![Scheme S1: Synthesis of V-salen Cd-bpdc MOF. The structure of MOF is heavily simplified. The exact connectivity are not shown.](image_url)

2. **b. Synthesis of VO-salen complex:** A solution of ligand H$_2$L (0.088g, 1 mmol) was dissolved in 20 mL of MeOH. The reaction mixture was stirring for 5 min and then VO(acac)$_2$ (0.040g, 1 mmol) was added. The mixture was refluxed for 4 h at 70 °C and then mixture was filtered and washed with 10 mL cold MeOH and dried in vacuo. Yield: 76 mg, 77% for VO(acac)$_2$. ESI-MS m/z: 654.8 (Calcd m/z 654.28 for [M+H$^+$]). IR (KBr pellet): $\nu$ = 3493 (w), 2943 (s), 2863 (m), 1601 (s), 1543 (m), 1432 (w), 1394 (s), 1349 (m), 1308 (s), 1264 (m), 1172 (s), 1081 (m), 1032 (w), 985 (s), 930 (m), 898 (w), 820 (s), 782 (m), 727 (w), 634 (m), 571 (s), 495 (s), 455 (w) cm$^{-1}$. 
3. FT-IR Spectrum

![FT-IR Spectrum](image)

**Fig. S1:** IR spectrum of V-salen Cd-bpdc MOF.

4. Powder X-ray diffraction patterns

![Powder X-ray Diffraction](image)

**Fig. S2:** Powder X-ray pattern of V-salen Cd-bpdc MOF (simulated and activated).

5. Thermogravimetric analysis (TGA)

![TGA Plot](image)

**Fig. S3:** TGA plot for V-salen Cd-bpdc MOF.
6. **Isosteric heats of adsorption of CO$_2$**

From two adsorption isotherms acquired at different temperatures $T_1$ and $T_2$, the differential heat of adsorption $\Delta H_{ads,\text{diff}}$, that is isosteric heat of adsorption $Q_{st}$ can be calculated for any amount of adsorbed substance after determining the required relative pressures $p_1$ and $p_2$. A modified form of the Clausius-Clapeyron equation is used (eq (1)) $\Delta H_{ads,\text{diff}}$ was calculated over the whole adsorption range from the 273 K and 298 K isotherms for CO$_2$.

$$\Delta H_{ads,\text{diff}} = Q_{st} = -R \ln \left( \frac{p_2}{p_1} \right) \frac{T_1 T_2}{T_2 - T_1}$$

(1)

Fig. S4: Isosteric differential heat of adsorption (adsorption enthalpy, $Q_{ads,\text{diff}}$) as a function of CO$_2$ uptake for V-salen Cd-bpdc MOF.

7. **Pore size distribution from a CO$_2$ adsorption isotherm**

Fig. S5. The pore size distribution from a CO$_2$ adsorption isotherm at 273 K, calculated by the NL-DFT with a “CO$_2$ on carbon based slit-pore” model at 273 K.
8. BET surface area and gas uptake capacities (H\textsubscript{2}, CO\textsubscript{2} and CH\textsubscript{4}) of reported salen-based MOFs.

a. Table S1. BET surface area and gas uptake capacities (H\textsubscript{2}, CO\textsubscript{2} and CH\textsubscript{4}) of reported salen-based MOFs.

<table>
<thead>
<tr>
<th>Compound</th>
<th>BET (m\textsuperscript{2}/g), from N\textsubscript{2} at 77 K</th>
<th>BET (m\textsuperscript{2}/g), from CO\textsubscript{2} at 195K</th>
<th>H\textsubscript{2} (mmol/g)</th>
<th>CO\textsubscript{2} (cm\textsuperscript{3}/g) at 273K, 1 bar</th>
<th>CH\textsubscript{4} (cm\textsuperscript{3}/g) at 273K, 1 bar</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-salen Cd-bpdc MOF</td>
<td>574</td>
<td>Not measured</td>
<td>5.35 (1.05 wt%)</td>
<td>51</td>
<td>17</td>
<td>Present work</td>
</tr>
<tr>
<td>M’MOF 1</td>
<td>Not measured</td>
<td>Not measured</td>
<td>4.78</td>
<td>Not measured</td>
<td>Not measured</td>
<td>J. Am. Chem. Soc. 2008, 130, 6411–6423</td>
</tr>
<tr>
<td>M’MOF-2</td>
<td>Not measured</td>
<td>388</td>
<td>Not measured</td>
<td>~36</td>
<td>Not measured</td>
<td>Nat. Commun. 2011, 2, 204</td>
</tr>
<tr>
<td>M’MOF-3</td>
<td>Not measured</td>
<td>110</td>
<td>Not measured</td>
<td>~18</td>
<td>Not measured</td>
<td>Nat. Commun. 2011, 2, 204</td>
</tr>
<tr>
<td>M’MOF-4a</td>
<td>Not measured</td>
<td>602</td>
<td>Not measured</td>
<td>Not measured</td>
<td>Not measured</td>
<td>J. Am. Chem. Soc. 2012, 134, 8703–8710</td>
</tr>
<tr>
<td>M’MOF-5a</td>
<td>Not measured</td>
<td>202</td>
<td>Not measured</td>
<td>Not measured</td>
<td>Not measured</td>
<td>J. Am. Chem. Soc. 2012, 134, 8703–8710</td>
</tr>
<tr>
<td>M’MOF-6a</td>
<td>Not measured</td>
<td>369</td>
<td>Not measured</td>
<td>Not measured</td>
<td>Not measured</td>
<td>J. Am. Chem. Soc. 2012, 134, 8703–8710</td>
</tr>
<tr>
<td>M’MOF-7a</td>
<td>Not measured</td>
<td>90</td>
<td>Not measured</td>
<td>Not measured</td>
<td>Not measured</td>
<td>J. Am. Chem. Soc. 2012, 134, 8703–8710</td>
</tr>
</tbody>
</table>
9. **Catalysis: Cyanosilylation of benzaldehyde**

![Catalysis Reaction](image)

**a. Cyanosilylation of benzaldehyde under solvent-free condition, catalyzed by vanadium-salen Cd-bpdc MOF:**

![Graph](image)

**Fig. S6:** Yield of the leaching test for cyanosilylation of benzaldehyde under solvent-free condition. The catalyst was separated by centrifugation at 1.5 h of the reaction. Reaction conditions: Catalyst (0.25 mol %), benzaldehyde (0.87 mmol), TSMCN (2.61 mmol), Temperature (30°C), N₂ atmosphere. Yield of blank of reaction 14 % (14 h), without catalyst.

The enantiomeric excess (ee) was determined by chiral GC, being obtained negative values from optical parameters. It was concluded that the higher enantiomeric product was the compound (S).³

**Table S2:** Asymmetric cyanosilylation of benzaldehyde catalyzed by V-salen Cd-bpdc MOF.

<table>
<thead>
<tr>
<th>Run</th>
<th>Substrate</th>
<th>Yielda (%)</th>
<th>eea (%)</th>
<th>TONb</th>
<th>TOFb (h⁻¹)</th>
<th>r0,b (moles·L⁻¹·h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>95</td>
<td>78</td>
<td>23</td>
<td>46</td>
<td>0.8</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>90</td>
<td>76</td>
<td>12</td>
<td>24</td>
<td>0.4</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>77</td>
<td>70</td>
<td>5</td>
<td>11</td>
<td>0.2</td>
</tr>
</tbody>
</table>

³ee at 14 h of reaction. bValues at 0.5 h of reaction and considering all vanadium sites as actives (4.16 wt%).
b. Recyclability of the catalyst:

![Recyclability of the catalyst. Left: powder X-ray diffraction patterns of the catalyst before and after. Right: UV-vis spectrum of fresh catalyst and after 3rd run.]

**Fig. S7:** Recyclability of the catalyst. Left: powder X-ray diffraction patterns of the catalyst before and after. Right: UV-vis spectrum of fresh catalyst and after 3rd run.

c. Catalysis: Cyanosilylation of aromatic aldehyde

\[
\begin{align*}
\text{Catalyst (0.25 mol\%)} & \quad \text{30°C, N}_2 \\
\text{(CH}_3\text{)}_3\text{SiCN} & \quad \text{NOSi(CH}_3\text{)}_3\text{CN}
\end{align*}
\]

**Fig. S8:** Asymmetric cyanosilylation of aldehydes catalyzed by V-salen Cd-bpdc MOF.
c. Comparison of the catalytic activity between the homogeneous catalyst and the MOF

The comparison between homogeneous VO-salen complex and the solid V-salen Cd-bpdc MOF was performed in the same reaction conditions (Table 1 and Fig. S9) and the results obtained showed that yield of 91% was obtained after 9 hours, although the achieved ee (57%) was lower compared with heterogeneous catalytic tests using V-salen Cd-bpdc MOF recyclable solid (Fig. S9).

![Graph](image_url)

**Fig. S9:** Asymmetric cyanosilylation of benzaldehydes catalyzed by VO-Salen complex and V-salen Cd-bpdc MOF. Condition: Catalyst (0.25 mol %), benzaldehyde (0.87 mmol), TSMCN (2.61 mmol), Temperature (30°C), N₂ atmosphere.
10. Cyanosilylation of benzaldehyde by using chloroform and acetonitrile as solvent

we studied the catalytic activity for cyanosilylation reactions of aromatic aldehydes in dry acetonitrile and chloroform under N₂ atmosphere at 30 °C. By using dry chloroform as solvent, the yield of the reaction reached up to 95 % (Fig. S10a, ESI). Similarly, a value of 80 % was achieved in the presence of acetonitrile (Fig. S10b, ESI). The obtained results suggested that chloroform is a better solvent compared to acetonitrile, but we anticipated significant leaching of vanadium atoms (Fig. S10a-S10b, in ESI). To confirm the leaching, the solid catalyst was separated by filtration or centrifugation when the yield had reached 35 % and the reaction was continued (hot filtration test) (Fig. S10a-S10b, in ESI). We observed that the reaction did indeed continue further in the filtrate for both solvents chloroform and acetonitrile, at similar rate as for the reaction without solid catalyst separation. Therefore, we investigated the catalytic reaction in the absence of any solvent.

![Graph](image)

**Fig. S10a:** Yield of the leaching test for cyanosilylation of benzaldehyde using chloroform as solvent. For the leaching test the catalyst was separated by centrifugation when the yield was 35%, that is, after ~6 h. Reaction conditions: Catalyst (0.25 mol %), benzaldehyde (0.87 mmol), TSMCN (2.61 mmol), Temperature (30°C), N₂ atmosphere.
Fig. S10b: Yield of the leaching test for cyanosilylation of benzaldehyde using acetonitrile as solvent. For the leaching test the catalyst was separated by centrifugation when the yield was 35%, that is after ~3 h. Reaction conditions: Catalyst (0.25 mol %), benzaldehyde (0.87 mmol), TSMCN (2.61 mmol), Temperature (30°C), N₂ atmosphere.

11. Chiral GC spectra

![Chiral GC spectra](image)
ee = 57%, Catalyzed by VO-salen in the homogeneous phase

12. Framework topology

Analysis was performed with the ToposPro program package. The structure is interpenetrated 2-fold (Fig. S11), each of the two equivalent frameworks can be simplified to its underlying net in two ways: (1) standard (2) cluster representation. Four oxygen and four vanadium atoms of the structure are disordered over two positions, we will consider the structure with maximum occupation. The disorder does not affect the underlying topologies.

Fig. S11: Views along the cell axes for the two interpenetrated frameworks of the structure.
(1) Standard representation

The underlying net of the framework (Fig. S12) in the standard representations is 2-nodal 3,5-coordinated net with stoichiometry of nodes (3-c)(5-c). The net has a fet topology (Fig. S13). See also http://rcsr.net/nets/fet

Fig. S12: A single framework of the structure.

Fig. S13: Illustration of the underlying net fet in the standard representation (left) and the net merged with the corresponding fragment of the framework (right).
Each node of the underlying net corresponds to a ligand or an atom in the structure. In our case, the 5-coordinated nodes of the underlying net fet correspond to the Cd atoms in the structure (Fig. S14).

Fig. S14: 5-coordinated node of the underlying net fet and the corresponding fragment of the structure.

The 3-coordinated nodes of the underlying net fet correspond to the 4-(4-carboxyphenyl)benzoic acid ligand (Fig. S15). The trans long edges of the underlying net fet that connect the 5-coordinated nodes correspond to chelated vanadium atoms (Fig. S14).

Fig. S15: 3-coordinated node of the underlying net fet and the corresponding fragment of the structure.
(2) Cluster representation

The underlying net of the framework in the cluster representations is a uninodal 6-coordinated net with the **pcu** topology (Fig. S16) with 4 edges short (16.8 Å) and two long (24.0 Å) opposite (trans) edges double bridged (running down b axis [010]). Fig. S17 shows the conformity of the underlying net elements and fragments of the structure.

![Fig. S16](image1)

**Fig. S16:** The **pcu** underlying net in the cluster representation (left) and the net merged with the corresponding fragment of the framework (right).

![Fig. S17](image2)

**Fig. S17:** The nodes and edges of the underlying 6-coordinated net **pcu** and the corresponding fragment of the structure.

**Symmetry interpenetration of V-salen Cd-bpdc MOF**

There are two identical interpenetrating nets related by the 2-fold axis as full interpenetration symmetry (non-translating) element. So, it belongs to class of interpenetration IIa.

**Summary of the framework topology:**

In the ToposPro TTO collection there are 97 MOF structures, whose underlying nets in the standard representation have the **fet** topology as well as 2025 MOF structures, whose underlying nets in the cluster representation have the **pcu** topology. Six structures have the same pattern of interpenetration (2-fold interpenetrated related by the 2-fold axis as full interpenetration symmetry, Class IIa) and the same topology in the cluster and standard representations as the $\text{C}_{104}\text{H}_{100}\text{Cd}_2\text{N}_8\text{O}_{13.63}\text{V}_2$ structure.
13. **X-ray Crystallography:**

For the structure of compound the V-salen Cd-bpdc MOF, X-ray intensity data were collected on an Agilent Supernova Dual Source (Cu at zero) diffractometer equipped with an Atlas CCD detector using CuKα radiation (λ = 1.54178 Å) and ω scans. The images were interpreted and integrated with the program CrysAlisPro (Agilent Technologies)⁸. Using Olex2⁹, the structures were solved by direct methods using the ShelXS structure solution program and refined by full-matrix least-squares on F² using the ShelXL program package¹⁰. Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode and isotropic temperature factors fixed at 1.2 times U(eq) of the parent atoms (1.5 times for methyl groups). The contribution of heavily disordered solvent molecules was taken into account and suppressed using the SQUEEZE procedure in PLATON¹¹.

CCDC-1422004 contains the supplementary crystallographic data for this paper and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or deposit@ccdc.cam.ac.uk).

Crystal data. C₁₀₄H₁₀₀Cd₂N₈O₁₃.₆₃V₂, M = 2006.69, orthorhombic, space group P2₂2₁ (No. 17), a = 17.0460(5), b = 24.0462(6) Å, c = 28.8442(6) Å, V = 11823.0(5) Å³, Z = 4, T = 100 K, ρ(calc) = 1.127 g cm⁻³, μ(Cu-Kα) = 4.565 mm⁻¹, F(000) = 4124.1, 68492 reflections measured, 24063 unique (R(int) = 0.0926) which were used in all calculations. The final R₁ was 0.0564 (I > 2σ(I)) and wR₂ was 0.1393 (all data).

![View of the structure of the V-salen Cd-bpdc MOF (Left: along a-axis; right: along b-axis).](image)
14. References