Selective capture and separation of potent greenhouse gases with gallium- and vanadium-based metal-organic frameworks

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ABSTRACT: Four novel metal-organic frameworks (MOFs) composed of 1,3,6,8-tetrakis(4-carboxyphenyl)pyrene (TBAPy4+) or 1,2,4,5-tetrakis(4-carboxlatephenyl)benzene (TCPB4+) linkers with gallium (Ga) or vanadium (V) were synthesized in this work. 3D electron diffraction patterns combined with high-resolution electron microscopy images were employed to
investigate the structure of these MOFs. All four MOFs were highly porous with specific Langmuir surface area ranging from ~900 to over ~1800 m$^2$ g$^{-1}$. The MOFs also showed high uptake of greenhouse gas and especially selective towards SF$_6$ (110 cm$^3$ cm$^{-3}$, 293 K 1 bar) and CO$_2$ over N$_2$ (or CH$_4$). Sorption kinetics were investigated in detail and the MOF with the highest gas uptake had pore channels with diameters of approx. 9.1 × 13.6 Å and 6.5 × 13.7 Å in dimension. These Ga- and V-MOFs are potentially interesting candidate sorbents for greenhouse gas capture and separation applications, especially for the separation of SF$_6$ and CO$_2$ from N$_2$, which are relevant in the electronics and chemical industry, respectively.

**Introduction**

The rise in global warming and climate-related issues has long been connected to the anthropogenic emission of greenhouse gases (GHGs). Six GHGs were specified in the Kyoto protocol in 1997, namely, carbon dioxide (CO$_2$), hydrofluorocarbons, methane (CH$_4$), nitrous oxide (N$_2$O), perfluorocarbons, and sulfur hexafluoride (SF$_6$) [1]. CO$_2$ is perhaps the most well-known GHG from a general public point-of-view and carbon capture and storage (CCS) technologies have garnered significant attention in the last couple of decades as a way for CO$_2$ sequestration.

The most abundant of the six known GHGs - CO$_2$, accounts for 76% of the total greenhouse gas emissions [2]. On the other hand, SF$_6$ has been found to have a global warming potential (GWP) of 22,450 times higher than CO$_2$ [3]. The excellent dielectric properties of SF$_6$, in-conjunction with it being a non-toxic, thermally stable as well as the higher density than air, has made it a commonly used gas in many electrical systems, such as high-voltage systems and circuit breakers as well as in the semiconductor industry [3]. Various methods have been employed to reduce the emission of SF$_6$ ranging from 1) disposal methods such as incineration,
2) gas treatment methods such as non-thermal plasma [4], plasma discharge, radio frequency discharge, various catalytic processes [3], and 3) recirculation of used SF₆ gas mixtures in the application process to minimize waste. However, the lack of efficient methods to selectively capture and separate SF₆ from gas mixtures remains an issue.

Capturing greenhouse gases such as CO₂ and SF₆ can be done by adsorption process through the use of solid nanoporous sorbents such as zeolites [5, 6], porous carbons [7, 8], and metal-organic frameworks (MOFs) [9, 10]. In particular MOFs, a diverse class of functional porous materials, have emerged in the last couple of decades as potential GHG sorbents [11]. There is a high number of known MOFs with large structural diversity. This structural diversity in MOFs is due to the wide range of metal cations (or metal clusters) and organic linkers that can be combined to form 2D and 3D frameworks with various topologies. As a result, MOFs can have tunable pore sizes and shapes, tailorable surface functionalities and physical properties [9, 12]. The highly adaptable nature of MOFs makes them attractive for various applications even beyond CCS technologies, such as in drug delivery, catalysis, energy conversion, gas sensing and luminescence-based sensing [13-18].

Although numerous MOF structures have been synthesized in the last couple of decades, many of them are based on common divalent transition-metals such as iron (Fe(III)), zinc (Zn(II)), nickel (Ni(II)), copper (Cu(II)), and cobalt (Co(II)). The use of metals like gallium (Ga(III)) and vanadium (V(IV)) in MOFs synthesis is, however, less common [19]. Despite that, well-known structures such as MIL-53 [20] and Ga-fumarate [21], as well as MIL-47, MIL-48, MIL-68, and MIL-101 [19] have been synthesized using Ga(III) or V(IV). The field of Ga- and V-based MOFs remains relatively unexplored and could be interesting for catalysis [22] as well as gas-separation [21].
Here we present the synthesis of four new and highly porous Ga- and V-based metal-organic frameworks composed of either 1,3,6,8-tetrakis(4-carboxyphenyl)pyrene (TBAPy\(^4\)) (referred to as UU-201 and UU-202) or 1,2,4,5-tetrakis(4-carboxylatophenyl)benzene (TCPB\(^4\)) (referred to as UU-203 and 204) linkers. For structure characterization, we combined three experimental approaches, 3-dimensional electron diffraction (3D ED), high-resolution transmission electron microscopy (HRTEM) imaging and powder X-ray diffraction. We also examined the CO\(_2\) and SF\(_6\) separation and sorption properties of these MOFs, which included a detailed analysis into sorption energetics and kinetics.

**Experimental Section**

**Materials**

\(N,N\)-dimethylformamide (DMF) and Acetic acid ≥99% were purchased from VWR International AB, Sweden. Vanadyl(IV) sulfate hydrate (VOSO\(_4\)·xH\(_2\)O), Gallium(III) nitrate hydrate (Ga(NO\(_3\))\(_3\)·xH\(_2\)O), 1,3,6,8-tetrakis(4-carboxyphenyl)pyrene (H\(_4\)TBAPy), 1,2,4,5-tetrakis(4-carboxylatophenyl)benzene (H\(_4\)TCPB), and Acetic acid ≥99% were purchased from Sigma-Aldrich, USA. All chemicals were used without further purification.

**Preparation of UU-201**

In a typical procedure, VOSO\(_4\)·xH\(_2\)O (32.60 mg, 0.20 mmol) and H\(_4\)TBAPy (136.54 mg, 0.20 mmol) were dispersed in 10 ml DMF. The yellow dispersion was thereafter transferred to a 25 ml Teflon—lined stainless steel autoclave and heated at 180 °C for 72 h. The obtained green product was collected by centrifugation at 3800 rpm for 20 min, washed once with deionized water and twice with DMF, and finally dried overnight in a ventilated oven at 70 °C.

**Preparation of UU-202**
In a typical synthesis, Ga(NO$_3$)$_3$·xH$_2$O (42.62 mg, 0.167 mmol) and H$_4$TBAPy (113.78 mg, 0.167 mmol) were dispersed in 11.5 ml DMF, followed by the addition of 1 ml acetic acid. The yellow mixture was transferred to a 25 ml Teflon—lined stainless steel autoclave and heated at 120 °C for 48 h. The obtained pale-yellow product was collected by centrifugation at 3800 rpm for 20 min, washed with DMF three times, and finally dried overnight in a ventilated oven at 70 °C.

**Preparation of UU-203**

UU-203 was synthesized in a similar procedure to UU-201, briefly, VOSO$_4$·xH$_2$O (32.60 mg, 0.20 mmol) and H$_4$TCPB (111.67 mg, 0.20 mmol) were dispersed in 10 ml DMF. The dispersion was transferred to a 25 ml Teflon—lined stainless steel autoclave and heated at 180 °C for 72 h. The obtained green product was collected by centrifugation at 3800 rpm for 20 min, washed once with deionized water and twice with DMF, and finally dried overnight in a ventilated oven at 70 °C.

**Preparation of UU-204**

UU-204 was synthesized in a similar procedure to UU-202, briefly, Ga(NO$_3$)$_3$·xH$_2$O (42.62 mg, 0.167 mmol) and H$_4$TCPB (93.06 mg, 0.167 mmol) were dispersed in 11.5 ml DMF, followed by the addition of 1 ml acetic acid. The clear mixture was transferred to a 25 ml Teflon—lined stainless steel autoclave and heated at 120 °C for 48 h. The obtained pale-yellow product was collected by centrifugation at 3800 rpm for 20 min, washed with DMF three times, and finally dried overnight in a ventilated oven at 70 °C.

**Characterization**

Powder X-ray diffraction (PXRD) diffractograms were recorded on a Bruker D8 Advanced Powder diffractometer (Bruker, Bremen, Germany) operated at 40 kV and 40 mA, using Cu K$_\alpha$
radiation ($\lambda = 1.5418 \text{ Å}$), a step-size of 0.02 ° and a time-per-step of 0.5 s. Scanning electron microscopy (SEM) images were obtained on a Zeiss Merlin Field Emission Scanning Electron Microscope (Oberkochen, Germany) using an acceleration voltage of 2.5 kV and a prove current of 80 pA. All samples were sputter coated with a thin layer of Pd/Au prior to imaging.

**Structure determination**

The structures of UU-201 – 4 were determined using 3-dimensional electron diffraction (3D ED) combined with HRTEM imaging, as well as structure modeling. The samples were dispersed in absolute ethanol and a droplet of the suspensions was transferred onto carbon-coated copper grids. The 3D ED data sets were collected on a JEM-F200 TEM (JEOL, Tokyo, Japan) operated at an accelerating voltage of 200 kV using an ASI Cheetah 1800 detector under continuous tilting mode. These data were analyzed and visualized by software EDT PROCESS [23] for determination of unit-cell parameters and reflection conditions, and processed by the X-ray Detector Software XDS [24] for extraction of reflection intensities which were subsequently used for structure solution. Using Olex2 [25], the structure was solved with the integrated space-group and crystal-structure determination program SHELXT [26] using Intrinsic Phasing and refined with the SHELXL [27] refinement package using Least Squares minimization. Selected area electron diffraction (SAED) and HRTEM images were obtained on a JEM-2100Plus TEM (JEOL, Tokyo, Japan) using a TVIPS XF416 detector.

*Le Bail* and Rietveld refinements [28, 29] of the UU-MOFs were performed using the crystallographic program JANA [30] over the full sampled angular range based on space group $P2/m$ for UU-201, 202, 204 and Pcma for UU-203. The Bragg peaks were modeled by a Pseudo-Voigt peak-shape function modified for asymmetry, with six coefficients that could be refined. The background was treated using a Legendre polynomial with six parameters that could be
refined for the samples. The starting atomic coordinates were adopted from the model obtained by 3D ED data. Because of the complexity of the structural model, constraints on V-O, Ga-O, C-O, C-C distances were applied, and their weight was totally removed in the final cycles. All materials were visualized by using the 3D visualization program VESTA [31].

**Gas sorption**

Gas sorption experiments were performed using a Micromeritics ASAP 2020 surface area analyzer (Norcross, GA, USA). All samples were pre-treated at 423 K for 3 h under dynamic vacuum (1×10^-4 Pa) prior to analysis. Brunauer-Emette-Teller (BET) and Langmuir specific surface areas were calculated from N₂ adsorption isotherms recorded at 77 K at p/p° = 0.05 - 0.15. Pore size distributions were estimated using the Density Functional Theory (DFT) function in the Micromeritics MicroActive software using the N₂ adsorption isotherms, the slit pore mode for N₂ was used for these calculations. SF₆, CO₂, CH₄, and N₂ sorption isotherms at 273 - 303 K were also recorded using the Micromeritics ASAP 2020 surface area analyzer (Norcross, GA, USA) with an insulating water bath containing either water or a water-ice slurry. The gas selectivities were calculated using the Henry’s law constants (s = K_H,gas1/K_H,gas2) and the Ideal Adsorption Solution Theory (IAST). IAST calculations were carried out for theoretical gas mixtures containing CH₄/N₂ (50:50), CO₂/CH₄ (50:50), CO₂/N₂ (85:15), and SF₆/N₂ (10:90). Single-component isotherms of SF₆, CO₂, CH₄, and N₂ recorded at 293 K were used for the IAST calculations and all isotherms were fitted with the single-site Langmuir model, dual-site Langmuir model or Toth model. Isosteric enthalpies of adsorption (-ΔH_ads) were estimated with the Clausius-Clapeyron equation for CO₂ and SF₆, using the adsorption isotherms recorded at 273, 283, 293, and 303 K fitted with the dual-site Langmuir model or Toth model.

**CO₂ and SF₆ adsorption kinetics and temperature-swing adsorption experiments**
Gravimetric gas adsorption profiles were obtained using a Mettler Toledo TGA/DSC 3+ (Schwerzenbach, Switzerland) using N₂ as purge gas and SF₆ or CO₂ as measurement gas. All experiments were carried out on 2.5 - 10 mg of material degassed at 423 K for 30 min in a N₂ atmosphere (50 ml min⁻¹ flow-rate) before the sample were subjected to SF₆ or CO₂ at 303 K for up to 30 min (50 ml min⁻¹ flow-rate). Temperature-swing adsorption experiments were carried out under the same conditions, however using a shorter degas time of 12 min in-between each cycle.

**Results and Discussion**

**Structure of UU-MOFs**

The reconstructed 3D reciprocal lattice by 3D ED data sets indicated the preliminary results of unit-cell parameters and possible space group of UU-201-204 (Figure 1 and S1-S8). These parameters were further refined through Le Bail refinement against experimental PXRD patterns (Table S1). Based on these, extracted diffraction intensities were used for ab initio structure solution. Among these four MOFs, the structure of UU-201, 203, 204 could be solved directly by 3D ED data, but not UU-202. Although resolution and completeness of diffraction data for UU-202 were good enough, the diffraction intensities were seriously disturbed by twin crystals (Figure S4), resulting in the difficulties for structure determination. However, due to the similarity of structural component, e.g., same organic linker, as well as similar cell parameters between UU-201 and UU-202, the structure model of UU-202 was built based on the solved structure of UU-201. The V metal on UU-201 was replaced by Ga for UU-202 and the entire structure was geometry optimized based on the cell parameters obtained by Le Bail refinement against PXRD data of UU-202.
**Figure 1.** Examples of electron microscopy data (UU-203) showing 3D electron diffraction as viewed along (a) the $a^*$-axis and (b) a random axis, (c) selected area electron diffraction pattern along $[100]$, and (d) a high-resolution TEM image with an inset of the structure of UU-203 as viewed along the $a$-axis.

The vanadium (UU-201, UU-203) and gallium (UU-202, UU-204) ions were found to coordinate with four oxygens from four different 1,3,6,8-tetrakis(4-carboxyphenyl)pyrene (TBAPy$^4^+$) or 1,2,4,5-tetrakis(4-carboxylatophenyl)benzene (TCPB$^4^+$) linkers with a bridging oxygen atom between every two metal ions (Figure 2). This configuration formed infinite chains of *trans* corner-sharing VO$_6$ or GaO$_6$ secondary building units (SBUs) of the structure (Figure 2e). The 1-dimensional pore channels parallel to the $a$-axis (Figure 1a-1d) were estimated to be approx. $9.1 \times 13.6 \, \text{Å}$ (hexagonally-shaped channels) and $6.5 \times 13.7 \, \text{Å}$ (lozenge-shaped channels) in diameter (taking the van der Waals radii of the atoms into account) for the TBAPy-MOF (UU-201 and UU203) and TCPB-MOF(UU-202 and UU-204), respectively. The interlayer distances (i.e., the shortest carbon-carbon distance) between the linkers were also approximate $6.7 \, \text{Å}$
(Figure 2f), which is too large to enable π-π stacking between the aromatic rings in the linkers. The large interlayer-distance meant that it would be possible for gas molecules to also diffuse in-between these layers of organic ligands. Low-dose HRTEM images were also collected to verify these structures. As shown in Figure 1, S1, S3, S5 and S7, the pore structures were exhibited clearly and matched well with structure models. The Rietveld refinement results also showed similar atomic configurations of all MOFs derived from 3D ED data (Figure S10). Before further analyses, we tested the stability of these UU-MOFs in different types of solvents as well as at extreme pH environment, more information could be found in the Supporting Information, section S7.
Figure 2. Structures of (a) UU-201, (b) UU-202, (c) UU-203, (d) UU-204 as viewed along the a-axis, (e) MO$_6$-chains along the b-axis in UU-201, and (f) the interlayers between linkers connecting the MO$_6$-chains in UU-201. Green and blue colored octahedra in the figures represent the VO$_6$ and GaO$_6$ SBUs, respectively.

Porosity and surface area

The porosities of UU-MOFs were evaluated using the nitrogen sorption isotherms recorded at 77 K (Figure 3). The calculated specific surface areas (Table 1) and the corresponding density functional theory pore size distributions (DFT-PSD) (Figure S13) for UU-MOFs show that all samples were highly microporous with a recorded Langmuir specific surface area (SA) between 1000 and 2000 m$^2$ g$^{-1}$. UU-201 and UU-202 were found to have higher porosities than UU-203 and UU-204, as was evident by the higher SAs and pore volume (Table 1) of these samples. The DFT-PSD of UU-201 and UU-202 (Figure S13) appeared to be similar to one another and three types of pores could be identified by N$_2$ sorption. The apertures of these pores were found to be in the range of around 6, 7, and 8.5 Å according to the DFT model, and similar pores could also be seen on UU-203 and UU-204 according to the DFT-PSD. The DFT pore sizes should not be taken as absolute values, but rather as range estimates, however the estimated pore apertures were found to be in good agreement with the crystallographic pore apertures.
**Figure 3.** Nitrogen sorption isotherms recorded at 77 K. Solid and open symbols represent the adsorption and desorption branches, respectively.

**Table 1.** Specific surface areas and pore volumes of UU-MOFs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{Langmuir}}^{a}$ ((\text{m}^2\text{ g}^{-1}))</th>
<th>$S_{\text{BET}}^{b}$ ((\text{m}^2\text{ g}^{-1}))</th>
<th>$V_{\text{micro}}^{c}$ ((\text{cm}^3\text{ g}^{-1}))</th>
<th>$V_{\text{tot}}^{d}$ ((\text{cm}^3\text{ g}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>UU-201</td>
<td>1884</td>
<td>1534</td>
<td>0.58</td>
<td>0.74</td>
</tr>
<tr>
<td>UU-202</td>
<td>1507</td>
<td>1218</td>
<td>0.47</td>
<td>0.60</td>
</tr>
<tr>
<td>UU-203</td>
<td>928</td>
<td>754</td>
<td>0.25</td>
<td>0.41</td>
</tr>
<tr>
<td>UU-204</td>
<td>964</td>
<td>787</td>
<td>0.32</td>
<td>0.36</td>
</tr>
</tbody>
</table>

*a*Langmuir specific surface areas ($S_{\text{Langmuir}}$) were calculated using the Langmuir equation between 4.5-16 kPa. *b*BET specific surface areas ($S_{\text{BET}}$) were calculated using the Brunauer-Emmett-Teller (BET) equation between a $p/p^*$ of 0.05–0.15. *c*Micropore volumes ($V_{\text{micro}}$) were estimated using the $t$-plot method. *d*Total pore volumes ($V_{\text{tot}}$) were determined using a single-point of the desorption branch of the isotherm at $p/p_0 = 0.98$.

**Greenhouse gas and water sorption**

The high microporosity of UU-MOFs and the seemingly suitable pore size on these MOFs make them potentially interesting sorbents for greenhouse gases such as SF$_6$ and CO$_2$. We recorded the SF$_6$, CO$_2$, CH$_4$ and N$_2$ adsorption/desorption isotherms of UU-MOFs (Figure 4). The uptake
capacities for all gases at 1 bar are listed in Table 2. All samples showed selective uptake towards the greenhouse gases over N\textsubscript{2}. This was expected as N\textsubscript{2} has the lowest boiling point of all of the gases and therefore would naturally adsorb less than the greenhouse gases with higher boiling points. Although this was not the only reason behind the differences in uptake and the details are discussed further below.

UU-201 showed the highest SF\textsubscript{6} uptake at 1 bar, 293K, of \(\sim4.00\text{ mmol g}^{-1}\) (\(\sim110\text{ cm}^3\text{ cm}^{-3}\)), followed by UU-202 with \(\sim3.28\text{ mmol g}^{-1}\) (\(\sim86.5\text{ cm}^3\text{ cm}^{-3}\)), UU-203 with \(\sim2.99\text{ mmol g}^{-1}\) (\(\sim31.2\text{ cm}^3\text{ cm}^{-3}\)) and UU-204 with \(\sim2.75\text{ mmol g}^{-1}\) (\(\sim56.2\text{ cm}^3\text{ cm}^{-3}\)). The SF\textsubscript{6} working capacities of the UU-MOFs could be represented by considering the gas uptakes at 0.1 and 1.0 bar, these values are listed in Table S2. The SF\textsubscript{6} uptake off these four MOFs can be compared with a number of other microporous sorbents in Table 3. The mmol g\textsuperscript{-1} SF\textsubscript{6} uptake of the UU-201 is comparable to those of Zn-MOF-74 (3.80 mmol g\textsuperscript{-1} at 298 K and 1 bar) \[32\], Co\textsubscript{2}-(1,4-bdc)\textsubscript{2}(dabco) (3.39 mmol g\textsuperscript{-1} at 298 K and 1 bar) \[33\], Zn\textsubscript{4}O(btbt)\textsubscript{2} (3.12 mmol g\textsuperscript{-1} at 298 K and 1 bar) \[33\], and MIL-100(Fe) (2.95 mmol g\textsuperscript{-1} at 298 K and 1 bar) \[34-36\]. As the SF\textsubscript{6} capacity of UU-201 is high, we also consider the vol./vol. gas uptake that could be relevant for real-life applications. The vol./vol. uptake of UU-201 (Table 3), although not as high as Mg-MOF-74 (\(\sim158\text{ cm}^3\text{ cm}^{-3}\) at 1 bar), is higher than most other commonly discussed potential SF\textsubscript{6} sorbents, such as Zn-MOF-74, Co-MOF-74, Co\textsubscript{2}(1,4-bdc)\textsubscript{2}(dabco), UiO-66(Zr), and zeolite 13X etc. The difference between the SF\textsubscript{6} uptake on UU-201 and UU-202 was \(\sim21\text{ mol.\% g}^{-1}\) and between UU-203 and UU-204 was \(\sim8\text{ mol.\% g}^{-1}\) (higher than the expect 6 mol.\% g\textsuperscript{-1} based on the difference in the metal alone). It was clear that the UU-201 and UU-202 structure had a higher overall SF\textsubscript{6} uptake capacity than UU-203 and UU-204, although the SF\textsubscript{6} uptake at low pressures was higher on UU-203 and UU-204. These observations could be explained with the following: 1) All four MOFs have pores
with apertures ~7-9 Å, pores in this size-range were previously observed by us on mixed-linker ZIF-7-8 to be favorable for SF$_6$ sorption. **2)** The overall pore volume related to pores in the favorable size-range may be higher on UU-201 and UU-202 than on UU-203 and UU-204, which would explain the increased SF$_6$ capacity on UU-201 and UU-202, **3)** The pores on UU-203 and UU-204 may be overall smaller than those on UU-201 and UU-202, possibly arising from the size-difference between the TBAPy$^+$- and TCPB$^+$-linkers. These smaller pores (~7 Å, Figure S13, e.g. lozenge-shaped channels) are closer in size to the kinetic diameter of SF$_6$ and have enhanced interaction with SF$_6$ compared to the larger pores found on UU-201 and UU-202 (DFT-PSD peak at around 8.7–9 Å, i.e. hexagonal channels). This is apparent according to the SF$_6$ adsorption isotherms of UU-203 and UU-204, where the isotherms showed a shape increase at the low-pressure range.

![Figure 4. CH$_4$, CO$_2$, N$_2$, and SF$_6$ sorption isotherms recorded at 293 K for (a) UU-201, (b) UU-202, (c) UU-203, and (d) UU-204. Solid and open symbols represent the adsorption and desorption branches, respectively.](image-url)
Table 2. Summary of CH$_4$, CO$_2$, N$_2$, and SF$_6$ adsorption capacities of UU-MOFs at 293 K and 1 bar.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CH$_4$ (mmol g$^{-1}$)</th>
<th>CO$_2$ (mmol g$^{-1}$)</th>
<th>N$_2$ (mmol g$^{-1}$)</th>
<th>SF$_6$ (mmol g$^{-1}$)</th>
<th>Working capacity (mmol g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CO$_2$ (0.15 – 1 bar) SF$_6$ (0 – 0.10 bar)</td>
</tr>
<tr>
<td>UU-201</td>
<td>1.03</td>
<td>3.52</td>
<td>0.34</td>
<td>4.00</td>
<td>2.43</td>
</tr>
<tr>
<td>UU-202</td>
<td>0.82</td>
<td>3.00</td>
<td>0.29</td>
<td>3.28</td>
<td>1.99</td>
</tr>
<tr>
<td>UU-203</td>
<td>1.18</td>
<td>3.22</td>
<td>0.43</td>
<td>2.99</td>
<td>0.92</td>
</tr>
<tr>
<td>UU-204</td>
<td>1.08</td>
<td>2.78</td>
<td>0.36</td>
<td>2.75</td>
<td>0.68</td>
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Table 3. SF$_6$ adsorption capacities of various porous sorbents at 298 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>0.1 bar SF$_6$</th>
<th>1.0 bar SF$_6$</th>
<th>References</th>
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<tr>
<td></td>
<td>Uptake (mmol g$^{-1}$)</td>
<td>Uptake (cm$^3$ cm$^{-3}$)</td>
<td>Uptake (mmol g$^{-1}$)</td>
</tr>
<tr>
<td>UU-203</td>
<td>2.06$^a$</td>
<td>21.50$^a$</td>
<td>2.73$^a$</td>
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<tr>
<td>UU-204</td>
<td>2.04$^a$</td>
<td>41.72$^a$</td>
<td>2.70$^a$</td>
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<tr>
<td>Mg-MOF-74</td>
<td>2.00</td>
<td>49.26</td>
<td>6.40</td>
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<tr>
<td>Co-MOF-74</td>
<td>2.00</td>
<td>37.99</td>
<td>5.34</td>
</tr>
<tr>
<td>UU-201</td>
<td>1.57$^a$</td>
<td>43.28$^a$</td>
<td>3.54$^a$</td>
</tr>
<tr>
<td>Zn-MOF-74</td>
<td>1.40</td>
<td>25.72</td>
<td>3.80</td>
</tr>
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<td>UU-202</td>
<td>1.27$^a$</td>
<td>33.42$^a$</td>
<td>3.87$^a$</td>
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<td>CAU-17</td>
<td>1.10/0.69$^a$</td>
<td>12.24/7.68$^a$</td>
<td>1.61/1.45$^a$</td>
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<td>Zeolite 13X</td>
<td>0.99</td>
<td>15.60</td>
<td>1.75</td>
</tr>
<tr>
<td>UU-200</td>
<td>0.73$^a$</td>
<td>10.33$^a$</td>
<td>1.10$^a$</td>
</tr>
<tr>
<td>Zn$_4$O(btb)$_2$</td>
<td>0.67</td>
<td>47.60</td>
<td>3.12</td>
</tr>
<tr>
<td>MOF</td>
<td>Tc (°C)</td>
<td>P (bar)</td>
<td>q (mmol g⁻¹)</td>
</tr>
<tr>
<td>-------------</td>
<td>---------</td>
<td>---------</td>
<td>--------------</td>
</tr>
<tr>
<td>DUT-9</td>
<td>30.01</td>
<td>2.32</td>
<td>52.00</td>
</tr>
<tr>
<td>MIL-101</td>
<td>21.31</td>
<td>2.01</td>
<td>45.05</td>
</tr>
<tr>
<td>Co₂(1,4-bdc)₂(dabco)</td>
<td>16.40</td>
<td>3.39</td>
<td>75.98</td>
</tr>
<tr>
<td>SU-101</td>
<td>4.56</td>
<td>0.80</td>
<td>7.02</td>
</tr>
<tr>
<td>CAU-33</td>
<td>4.29</td>
<td>1.55</td>
<td>17.49</td>
</tr>
<tr>
<td>MIL-100(Fe)</td>
<td>5.40</td>
<td>2.59</td>
<td>46.66</td>
</tr>
<tr>
<td>UiO-66(Zr)</td>
<td>5.60</td>
<td>1.45</td>
<td>27.06</td>
</tr>
<tr>
<td>ZIF-7</td>
<td>1.76</td>
<td>0.46</td>
<td>7.10</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>0.31</td>
<td>0.15</td>
<td>2.95</td>
</tr>
</tbody>
</table>

* Measured at 293 K.

The CO₂ uptake of UU-201 was the highest of the tested MOFs and reached over ~3.52 mmol g⁻¹ (~97.0 cm³ cm⁻³), followed by UU-203 with a CO₂ uptake of ~3.22 mmol g⁻¹ (~79.0 cm³ cm⁻³), UU-202 with ~3.00 mmol g⁻¹ (~33.6 cm³ cm⁻³) and UU-204 with ~2.78 mmol g⁻¹ (~56.9 cm³ cm⁻³) at 1 bar, 293 K. The working CO₂ capacity (between 0.15 and 1.0 bar) are also listed in Table S3. The CO₂ uptake of these MOFs is slightly different from other MOFs and microporous sorbents, such as HKUST-1 (4.16 mmol g⁻¹, ~105.4 cm³ cm⁻³ at 298 K and 1 bar) [40], BiMOF-11 (4.10 mmol g⁻¹, ~74.5 cm³ cm⁻³ at 298 K and 1 bar) [41] and zeolite ZK-4 (4.59 mmol g⁻¹, ~59.0 cm³ cm⁻³, 298K and 1 bar) [42], but comparable with that of NH₂-UiO-66 (3.15 mmol g⁻¹, ~55.5 cm³ cm⁻³ at 298 K and 1 bar) [43] and higher than those of MIL-125 (2.18 mmol g⁻¹, ~40.6 cm³ cm⁻³ at 298 K and 1 bar) [44], MIL-101(Cr) (1.22 mmol g⁻¹, ~44.8 cm³ cm⁻³ at 298 K and 1 bar) [43, 45]. The CO₂ vol./vol. uptake of UU-201 was comparable to the frequently discussed highly porous HKUST-1, which is a well-known MOF with high CO₂ uptake. The V-based UU-201 and UU-203 had higher CO₂ uptake than the Ga counterpart (UU-202 and UU-
204), which was partially an effect of the difference in the weight of the metal in the framework. A difference in uptake of around 6 mol.% g\(^{-1}\) was expected from this effect alone (i.e. between UU-201 and UU-202, UU-203 and UU-204). However, the CO\(_2\) uptake on the V-based MOFs was over 15 mol% g\(^{-1}\) higher than on their Ga counterparts. The enhanced uptake of CO\(_2\) on V-MOF may be related to a slight difference in pore size as compared to the Ga-based MOFs. The CO\(_2\) sorption isotherms adopted a linear shape on UU-201 and UU-202, but a slight shift toward a Langmuir isotherm was observed on UU-203 and UU-204. This indicated increase in sorbent-sorbate interaction typically means that CO\(_2\) no longer sees the pores as a flat surface (increased contact and Van der Waals interaction). The enhanced CO\(_2\)-MOF interaction suggested that the pores on UU-203 and UU-204 had an aperture (i.e. smaller) that could interact with CO\(_2\) more than those (i.e. larger) on UU-201 and UU-202. This agreed with the DFT-PSD shown in Figure S13.

The total uptake capacities of CH\(_4\) and N\(_2\) were found to be low in all samples, as compared to CO\(_2\) and SF\(_6\), ranging from 0.82 – 1.18 mmol g\(^{-1}\) and 0.29 – 0.43 mmol g\(^{-1}\) at 1 bar, respectively. The linear isotherm shapes also indicate a low molecular interaction between these gas molecules and the frameworks, and as such, the gas sorption study will focus on CO\(_2\) and SF\(_6\) going forth.

The water sorption properties of UU-MOFs were found to differ significantly between the frameworks. The H\(_2\)O sorption isotherms recorded at 293 K (Figure 5) for the MOFs show two-step isotherm shapes with low water uptake at low relative pressures. This implies a low hydrophilicity of the UU-MOFs. The water sorption isotherms of UU-201 and UU-202 exhibit a distinct step similar to what has been observed for UiO-66, PIZOF-2, MOF-804, and MOF-805 [46]. The frameworks show limited water uptake up to a relative pressure of approximately 0.60,
0.63, 0.26, and 0.32 \( p/p^* \), for UU-201 to UU-204, respectively, after which a gradual to steep increase in uptake was observed. The hydrophobicity of UU-201 and UU-202 can be assumed to be higher as compared to that of UU-203 and UU-204, since the adsorption step is located at higher relative pressures in the former two materials. However, the total adsorption capacity at \( p/p^* = 0.93 \) was found to monotonically decrease from UU-201 to UU-204, indicating that it may be strongly dependent on the total porosity of the frameworks. The low hydrophilicity of UU-MOFs implies that these sorbents can tolerate gas mixtures that contain water while keeping its greenhouse gas sorption properties.

**Figure 5.** Water sorption isotherms recorded at 293 K. Solid and open symbols represent the adsorption and desorption branches, respectively.

**Greenhouse gas selectivity**

The greenhouse gas selectivity of the tested UU-MOF using the Henry’s constants and IAST are presented in Table 4. The \( \text{CO}_2\)-over-\( \text{N}_2 \) selectivities (\( \text{CO}_2\):\( \text{N}_2 = 15:85 \)) on the UU-MOFs were in the range of 10-15, which was comparable to some other typical sorbents such as activated carbons [36, 47, 48] and some other MOFs such as PCN-88 (15 at 296 K) [49], ZJNU-44 (15 at
296 K) [50], and ZJNU-40 (18 at 296 K) [43, 51]. Note that many other CO₂ selective sorbents offer much higher selectivities than UU-MOFs including some mixed-linker ZIF-7-8s (23 – 33 at 293 K, 47 – 90% benzimidazole) [39], FJI-H14 (51 at 298 K) [52], and zeolite NaKA (60 – 271 at 273 K, ~28% K⁺) [6, 42]. The comparatively low CO₂ selectivity on UU-MOFs is partly related to the low affinity between the CO₂ molecules and the frameworks, as indicated by the linear isotherm shapes.

Table 4. Henry’s law and IAST gas selectivity of UU-MOFs at 293 K and 1 bar.

<table>
<thead>
<tr>
<th>Sample</th>
<th>IAST selectivity</th>
<th>Henry’s law selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂/CH₄ (50:50)</td>
<td>CO₂/N₂ (15:85)</td>
</tr>
<tr>
<td>UU-201</td>
<td>3.54</td>
<td>14.78</td>
</tr>
<tr>
<td>UU-202</td>
<td>3.87</td>
<td>15.16</td>
</tr>
<tr>
<td>UU-203</td>
<td>2.73</td>
<td>10.73</td>
</tr>
<tr>
<td>UU-204</td>
<td>2.70</td>
<td>11.70</td>
</tr>
</tbody>
</table>

On the other hand, the SF₆-over-N₂ (SF₆:N₂ =10:90) selectivity was observed to be high on all samples, ranging from 43–56 at 293 K and 1 bar. The high SF₆ selectivity could, as previously mentioned, be attributed to an enhanced molecular interaction between the SF₆ molecules and the pore surface of pores with suitable apertures. The SF₆/N₂ selectivities for UU-MOFs were found to be comparable to other microporous sorbents such as Zn-MOF-74 (46 at 298 K) [32], ZIF-7-8 containing 26 % benzimidazolate (40 at 293 K) [39] zeolite 13X (43 at 293 K) [34].

The CH₄-over-CO₂ (CH₄/CO₂) selectivities were found to be relatively low on all samples ranging from approx. 2.5 – 4.0 at 293 K and 1 bar. We therefore, will focus the rest of the study on SF₆ and CO₂ as the greenhouse gases of interest.

Heat of SF₆ and CO₂ adsorption and cyclic sorption
The isosteric enthalpies (-$\Delta H_{ads}$) of SF$_6$ and CO$_2$ adsorption for UU-MOFs (Figure 6 and Figure S14) were calculated using the Clausius-Clapeyron equation. The -$\Delta H_{ads}$ of SF$_6$ was observed to be comparable for UU-201 and UU-202 (approx. 30 kJ mol$^{-1}$ between 1.6–2.5 mmol g$^{-1}$). However, -$\Delta H_{ads}$ for the Ga-based MOFs was found to be significantly higher in comparison and vary greatly depending on loading (approx. 35–50 kJ mol$^{-1}$ between 1.6–2.5 mmol g$^{-1}$). Similarly, -$\Delta H_{ads}$ CO$_2$ was found to be very comparable between all UU-MOFs, ranging between 20–30 kJ mol$^{-1}$. The CO$_2$ adsorption enthalpies also appeared to be fairly consistent from low to moderate loading (0.20–2.30 mmol g$^{-1}$).

The calculated -$\Delta H_{ads}$ for both SF$_6$ and CO$_2$ adsorption in all materials fell within the range for physisorption (i.e. below 80 kJ mol$^{-1}$) [53]. The comparatively high -$\Delta H_{ads}$ of SF$_6$ for UU-203–UU-204 supports the conclusion drawn earlier that the small pores of UU-203 and UU-204 could have enhanced interaction between the MOF and the SF$_6$ molecules.

Temperature-swing adsorption experiments (Figure 6b and Figure S19-20) were carried out in order to investigate the cycling stability of UU-MOFs under relatively mild regeneration conditions (423 K and 1 bar). The CO$_2$ and SF$_6$ uptakes were found to remain stable for up to 10 cycles on UU-201, UU-203, and UU-204, however a decrease of approx. 1.5 % was observed on UU-202. The minor decrease in uptake capacity on UU-202 may be due to entrapment of the gas molecules that could be desorbed under the mild regeneration conditions used.
Figure 6. (a) isosteric enthalpies ($\Delta H_{\text{ads}}$) of SF$_6$ adsorption and (b) cyclic uptake stability of CO$_2$ (left) and SF$_6$ (right) of UU-MOFs

SF$_6$ and CO$_2$ diffusion

The adsorption of both SF$_6$ and CO$_2$ in the UU-MOFs at 303 K was found to occur rapidly in all samples (Figure 7). More than 90% of the total CO$_2$ uptake capacity was reached within the first 2 minutes for both gases. The SF$_6$ adsorption in UU-203 occurred at a slower rate, with 50% and 90% of the total uptake capacity being reached only after 3 min and 52 min, respectively. The slow diffusion of SF$_6$ in UU-203, compared to UU-201, UU-202 and UU-204, may be due to a combined effect of particle size and morphology of the sample (Figure S12).
Figure 7. Gravimetric (a) SF$_6$ and (b) CO$_2$ adsorption profiles for UU-MOFs. Measurements were performed on approximately 10 mg of sample at 303 K. The inset represents an expansion of the adsorption profile for UU-203 from 0 – 150 min.

Three diffusional models were used in order to investigate the adsorption kinetics of SF$_6$ and CO$_2$ in UU-MOFs, namely, the intraparticle (IP) diffusion model, Boyd’s film diffusion model, and the intracrystalline (IC) diffusion model. The observed multi-linearity in the IP plots, Figure 8a-b, indicates that multiple processes govern the diffusion of both SF$_6$ and CO$_2$ in UU-MOFs. Thus, showing that other mechanisms than intraparticle diffusion limit the adsorption rate of both CO$_2$ or SF$_6$ in the samples.

Similarly, the Boyd plots (Figure 8c-d and Figure S26) also show strong deviations from linearity for all samples suggesting that the external gas film surrounding the surface of the particles may have a significant effect on CO$_2$ and SF$_6$ transfer in the samples. This is in good agreement with the results obtained from the intraparticle diffusion model.

Figure 8. Intraparticle diffusion plots (a – b) and Boyd plots (c – d) for (a, c) SF$_6$ and (b, d) CO$_2$ adsorption on UU-MOFs using approx. 10 mg sample. Regions in the intraparticle diffusion
plots denoted by roman numerals I – III represent separate adsorption processes. The inset represents an expansion of the Boyd plot for UU-203 from 0 – 8000 s.

The adsorption of many small gas molecules, such as SF\textsubscript{6} and CO\textsubscript{2} in microporous materials have been found to be influenced by IC diffusional resistance [54, 55]. As such, the IC model was used to probe the SF\textsubscript{6} and CO\textsubscript{2} diffusional behavior in the UU-MOFs. IC model plots, Figure 9, show small deviations from linearity in the long-time region (i.e. when m\textsubscript{t}/m\textsubscript{e} > 0.7) for CO\textsubscript{2} (Figure 9b) while greater deviations were apparent for SF\textsubscript{6} (Figure 9a). Further, more severe deviations from linearity were observed during the initial stages of adsorption (i.e. m\textsubscript{t}/m\textsubscript{e} < 0.3) for both SF\textsubscript{6} and CO\textsubscript{2}, suggesting that IC diffusion may be the rate-limiting step for the adsorption of both gases at the end of the adsorption process. Further investigations into heat-transfer effects in the materials during SF\textsubscript{6} and CO\textsubscript{2} adsorption, using differential scanning calorimetry (DSC) (Figures S24-S25), showed that such effects were negligible for all measurements when the sample mass was below 10 mg. Thus, film diffusion or other forms of external mass transfer resistance were assumed to influence the diffusion of SF\textsubscript{6} and CO\textsubscript{2} particularly in the initial stages of adsorption while IC diffusion was found to contribute towards the end of the adsorption process.
**Figure 9.** Intracrystalline diffusion plots showing the (a – b) short time (m/m_e < 0.3) and (c – d) long time (m/m_e > 0.7) expression of the model for (a, c) SF_6 and (b, d) CO_2 adsorption on UU-MOFs using approx. 10 mg. The inset represents an expansion of the intracrystalline plot (long time region) for UU-203 from 0 – 8000 s.

The calculated Boyd and IC diffusion constants, \(D_i \cdot r^2\), (Table 5 and 6) showed comparable diffusivities for SF_6 and CO_2 in all UU-MOFs. The calculated SF_6 diffusivities on the other hand were found to be higher compared to that found in mixed-linker ZIF-7-8s (1.17 × 10^{-5} \text{ s}^{-1} to 4.20 × 10^{-5} \text{ s}^{-1}). UU-203 and UU-204 were found to have slightly lower CO_2 diffusivities as compared to UU-201 and UU-203. The CO_2 diffusion constants were found to be similar to those obtained in some zeolites (3.64 × 10^{-5} \text{ s}^{-1} to 2.20 × 10^{-2} \text{ s}^{-1}) [56-59] and MOFs such as mixed-linker ZIF-7-8s (2.98 × 10^{-3} \text{ s}^{-1} to 9.76 × 10^{-4} \text{ s}^{-1}) [39].

**Table 5.** Calculated diffusivities for SF_6 adsorption in UU-MOFs as obtained from the Boyd and intracrystalline diffusion models. Diffusion constants acquired from the Boyd model are given in brackets due to the data falling outside the application range of the model.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Approx. sample mass (mg)</th>
<th>Boyd’s film diffusion model</th>
<th>Intracrystalline diffusion model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Short time</td>
</tr>
<tr>
<td>UU-201</td>
<td>10</td>
<td>(9.44 \times 10^{-4})</td>
<td>(4.51 \times 10^{-4})</td>
</tr>
<tr>
<td>UU-202</td>
<td>10</td>
<td>(3.00 \times 10^{-3})</td>
<td>(7.61 \times 10^{-4})</td>
</tr>
<tr>
<td>UU-203</td>
<td>10</td>
<td>(1.33 \times 10^{-4})</td>
<td>(3.06 \times 10^{-4})</td>
</tr>
<tr>
<td>UU-204</td>
<td>10</td>
<td>(5.43 \times 10^{-3})</td>
<td>(5.89 \times 10^{-4})</td>
</tr>
</tbody>
</table>
Table 6. Calculated diffusivities for CO$_2$ adsorption in UU-MOFs as obtained from the Boyd and intracrystalline diffusion models. Diffusion constants acquired from the Boyd model is given in brackets due to the data falling outside the application range of the model.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Approx. sample weight (mg)</th>
<th>$D_i r^2$ (s$^{-1}$)</th>
<th>Boyd’s film diffusion model</th>
<th>Intracrystalline diffusion model</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Short time</td>
</tr>
<tr>
<td>UU-201</td>
<td>10</td>
<td>$(5.64 \times 10^{-3})$</td>
<td>$4.92 \times 10^{-4}$</td>
<td>$1.58 \times 10^{-3}$</td>
</tr>
<tr>
<td>UU-202</td>
<td>10</td>
<td>$(6.07 \times 10^{-3})$</td>
<td>$4.92 \times 10^{-4}$</td>
<td>$1.73 \times 10^{-3}$</td>
</tr>
<tr>
<td>UU-203</td>
<td>10</td>
<td>$(5.74 \times 10^{-3})$</td>
<td>$4.92 \times 10^{-4}$</td>
<td>$1.52 \times 10^{-3}$</td>
</tr>
<tr>
<td>UU-204</td>
<td>10</td>
<td>$(5.59 \times 10^{-3})$</td>
<td>$4.92 \times 10^{-4}$</td>
<td>$1.45 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Conclusions

Four highly porous and novel MOFs based on vanadium and gallium with two different organic linkers TBAPy$^+$ and TCPB$^+$ were presented in this study. 3D electron diffraction and low-dose HRTEM imaging revealed that the structures contained hexagonally- and lozenge-shaped 1-dimensional channels parallel to the $a$-direction with diameters of approx. 9.1 × 13.6 Å and 6.5 × 13.7 Å. UU-201 showed very high SF$_6$ uptake of ~4.0 mmol g$^{-1}$ (110 cm$^3$ cm$^{-3}$ 293 K, 1 bar) and also respectable SF$_6$ over N$_2$ selectivity (as calculated by IAST) over 40. The relatively high SF$_6$ uptake and selectivity were due to the pore size of these MOFs being of suitable dimensions to interact with the SF$_6$ gas molecules. Further, kinetic sorption studies revealed that the diffusion of both CO$_2$ and SF$_6$ were likely governed by film- and micropore diffusion. These MOFs have all displayed interesting sorption properties that render them possible candidate sorbents to be further developed for certain applications, including the separation of SF$_6$ from N$_2$ which is
relevant in many high voltage electronics. The pore size of these UU-MOFs may also make them suitable for the sorption of gas molecules larger than those discussed in this study, which could make them interesting sorption in the separation of compounds such as light hydrocarbons.

Acknowledgements

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Supporting Information

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