Isomeric scandium-organic frameworks with high hydrolytic stability and selective adsorption of acetylene

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Metal-Organic Frameworks, Adsorption, Selectivity

ABSTRACT: Two solvent-controlled topological isomers of scandium-organic frameworks [Sc(Hpz)(pzc)]∙DMF∙2H2O (1∙DMF∙2H2O) and [Sc(Hpz)(pzc)]∙DMA∙4H2O (2∙DMA∙4H2O) were synthesized using 2,5-pyrazinedicarboxylate. Despite the isomeric nature of the obtained MOFs they possess different structural features and unique adsorption properties towards gases and iodine. The compound 1 has widely spread among MOF’s structures dia topology with ultra-narrow channels which together with inner surface functionalization leads to enhanced CO2 adsorption and high selectivity factors in CO2/CH4 and CO2/N2 gas mixtures (25.9 and 35.6, respectively, 1/1 v/v). Moreover, rare preferable adsorption of CO2 over C2H2 was demonstrated. The biporous isomeric framework 2 has erb topology inherent in zeolites. Remarkable adsorption affinity to C2H2 with the IAST selectivity factor of 127.1 for C2H2/C3H4 mixture (1/99 v/v) was achieved for 2. Both compounds have exceptional chemical stability in a wide range of pH from acidic to basic media.

INTRODUCTION

Nowadays, most industrial separation/purification processes are based on distillation including a series of evaporation/condensation cycles that require high energy sources.1,2 Membrane-based technologies could be energy effective alternative to traditional distillation. These technologies separate molecules according to their size or other specific property like polarity or chemical affinity. Different porous solids like activated carbon, zeolites, and MOFs could be used as bases for such membranes due to their property of size/shape selective permeability and modulated functionality of the inner surface. Such an approach to separation could seriously reduce energy costs for related industrial processes. Traditional porous materials like zeolites and activated carbons have already been used as adsorbents for many years for purification and separation of gaseous mixtures.3,4 However these materials have some disadvantages in the separation efficiency of molecules with similar physical and chemical properties due to the low modularity of porous structure. Thus there is an urgent task to develop new porous materials with wide opportunities of structural design and functionality which meet industrial demands.5

Metal–organic frameworks (MOFs) represent a unique type of material that combines high porosity with extraordinary modularity of inner surface and precise design of functional groups.6–9 An ideal MOF adsorbent for gas separation must have high selectivity and sufficient adsorption capacity, as well as many other requirements for use in real industrial processes. Most production processes pass in conditions of high temperature and harsh media. Despite numerous advantages, applications of many MOFs are ultimately limited by their chemical stability under harsh conditions.10 There are two main approaches for the synthesis of chemically stable MOFs: high-valence metal–carboxylate frameworks and low-valence metal–azolate frameworks. This practical observation is in good agreement with Pearson’s hard/soft acid/base (HSAB) principle. The carboxylate-based ligands are regarded as hard bases, which form stable MOFs together with high-valence metal ions, such as Ti4+, Zr4+, Hf4+, Ce4+, Al3+, Fe3+, and Cr3+.11–13

In our work, we employ Sc3+ cations and 2,5-pyrazinedicarboxylate anions to prepare two isomeric metal-organic frameworks with the formula [Sc(Hpz)(pzc)]∙DMF∙2H2O (1∙DMF∙2H2O) and [Sc(Hpz)(pzc)]∙DMA∙4H2O (2∙DMA∙4H2O). Both frameworks demonstrate high hydrolytic stability in a wide range of pH and great selectivity factors for adsorption of binary gas mixtures, such as C2H2/C3H4, CO2/C2H2, CO2/N2, or CO2/CH4. Also, the I2 vapor adsorption experiments reveal highly stable host-guest complexes with a promising potential for safe storage of radioactive iodine during its decay.

RESULTS AND DISCUSSION

Synthesis and crystal structures. The title compounds [Sc(Hpz)(pzc)]∙DMF∙2H2O (1∙DMF∙2H2O) and [Sc(Hpz)(pzc)]∙DMA∙4H2O (2∙DMA∙4H2O) were synthesized under solvothermal conditions using slightly differing solvent mixtures (Table S1). In the case of compound 1∙DMF∙2H2O, the best crystallinity and the highest yield were achieved in a solvent mixture consisting of DMF, THF, and water acidified with HCl. The THF could be replaced by ethanol, methanol, NMP, or additional water with some decrease of reaction yield depending on the solvent. In contrast, the compound
2·DMA·4H₂O could be obtained only in an acidified solvent mixture containing DMA, likely, because of the template effect of the larger solvent molecule (vide infra). Also, some acidification facilitates hydrolysis of DMA to acetic acid which probably modulates the crystal growth for better crystallinity of the product.

Analysis of the crystal structure of the frameworks 1 and 2 reveals that these compounds are topological isomers (Table S2).¹⁴,¹⁵ Both structures share a common mononuclear complex where Sc(III) cations are coordinated by 8 donor atoms: four O atoms and four N atoms from four chelating pyrazinedicarboxylate (pzcd⁻) ligands (Fig. 1a, 2a). The coordination geometry of this unit could be described as distorted square antiprism. In the compound 1 Sc–Ocoo bond length is 2.1136(8) Å, Sc–N₁pzc one is 2.4098(10) Å. In the case of compound 2 Sc–Ocoo bond lengths are 2.1302(11) and 2.1242(12) Å, Sc–N₁pzc ones are 2.4172(14) and 2.3986(14) Å. According to the Cambridge Structure Database, all those distances are in good agreement with the average distances for Sc–Ocoo bonds (range from 1.962 to 2.328 Å, av. 2.10(6) Å) and for Sc–N bonds (range from 2.188 to 2.600 Å, av. 2.318(7) Å).

Each pzc⁻ ligand binds two Sc(III) complexes while each Sc(III) complex coordinates to four different pzc⁻ ligands, effectively serving a four-connecting node with slightly distorted tetrahedral topology. The connectivity of such nodes in compounds 1 and 2 turned out to be completely different. The framework 1 possesses one of the most common and the simplest four-connected dia topology with ultra-small pores with a diameter of ~3 Å (Fig. 1c).¹⁶ These pores are decorated by aromatic moieties and carboxylic groups of pzc⁻ ligands. Despite relatively small pore size, the solvent-accessible volume for 1, calculated using the PLATON package,¹⁷ is 40 %.

![Figure 1](image1.png)

**Figure 1.** a) A node of compound 1 with a structure view along a axis. Scandium cations are shown in cyan, oxygen – red, nitrogen – blue, carbon – grey. Hydrogen atoms are omitted for clarity. b) A schematic representation of the pore system in 1. Independent channel systems are shown in different colors. c) The structure view with pore system along a, b and c axis. The framework is shown with dark blue, the inner surface of the pores is blue, and the outer surface of the pores is pink.

The compound 2 shows more complex and rare crb topology known for zeolites and some MOFs.¹⁸ Inherently, there are two types of pores in the structure 2 with different geometry and chemical environment. The narrower channels have an aperture of 3.5 Å and hydrophobic nature due to the aromatic moieties of the organic linkers. The wider cruciform channels feature a large central passage of 7×7 Å and four smaller side pockets of ca. 3 Å (Fig. 2b). The largest guest accessible dimension of the cross-section reaches 14 Å. The inner surface of such channels is lined mostly by polar carboxylate groups of the pzc⁻ ligands determining their hydrophilic nature. The calculated free solvent-accessible volume of 2 reaches 51%.¹⁷ Both metal-organic frameworks were prepared at the same reaction temperature, from similar starting compounds and have identical chemical formulae [Sc(Hpzc)(pzcd)]; thus 1 and 2 should be regarded topological isomers. The determination of the particular topology of the framework self-assembly during nucleation and further crystal growth apparently depends on the solvent composition. The smaller N, N-dimethylacetamide guest molecules (ca. 5.6 Å) in 1 seem to be sufficient to template the narrow-pore structure with dia topology, which is the most regular one and, therefore, most frequently observed in MOF design. The somewhat larger N, N-dimethylformamide guest molecules (ca. 5.2 Å) in 2 directs the formation of the porous host with necessarily wider channels, apparently resulting in crb topology among other possible 4-connecting structures. Such a delicate balance of solvent composition and its influence on the framework topology of the product is remarkable.

![Figure 2](image2.png)

**Figure 2.** a) A node of compound 2 with structure view along c axis. Scandium cations are shown in cyan, oxygen – red, nitrogen – blue, carbon – grey. Hydrogen atoms are omitted for clarity. b) The structure view with pore system along c axis. The framework is shown with dark blue, the inner surface of the pores is blue, and the outer surface of the pores is pink.

The phase-purity of bulk crystalline samples was established by X-ray powder diffraction (Fig. S1). The guest composition of the obtained compounds was determined based on single-
crystal X-ray diffraction data on the electron density inside the framework and confirmed by IR spectra, TG, and elemental analyses (Fig. S2, S3). According to the TGA analysis (Fig. S2), compound I loses guest water molecules while heated up to 150°C (calculated for 2 H2O molecules: 7.4%; found: 10%). The next step on the TG curve is the removal of guest DMF molecule at ca. 280°C (calculated for 1 DMF molecule: 15.0%; found: 13%). The irreversible pyrolysis of the framework takes place above 300°C. The TGA data of the compound 2 (Fig. S3) shows a continuous escape of guest H2O and high-boiling point solvent (DMA) in the range up to ca. 250°C followed by a sharper decrease of sample weight at 280°C, attributed to a loss of a majority of DMA molecules. The overall measured weight loss (ca. 30%) is consistent with the proposed guest composition of 2·DMA·4H2O (calculated for 4H2O + DMA: 30%). The presence of guest H2O molecules, DMF and DMA was also confirmed by IR spectra (Fig. S2, S3). The characteristic stretch vibrations of O–H bonds are observed in the range from 3000 to 3500 cm⁻¹ for both compounds, C=O bond vibrations of carbonyl groups of DMF and DMA are found at 1661 cm⁻¹ (for 1) and 1670 cm⁻¹ (for 2).

The pyrazinedicarboxylate bridging ligands in both metalorganic structures are semiprotonated. From the X-ray data, it was impossible to conjecture the positions of the H⁺ cations as there is no C…O distances characteristic either for single or for double bonds. The protonation was assumed from the reaction conditions (i.e. acidification by HCl), as well as from charge-neutrality of the overall frameworks [Sc(Hpz)(pz)] since no anionic species were detected in the interstitial space of both of 1 or 2. Presumably, those extra protons are dynamically disordered over non-coordinated O atoms of the carboxylate groups decorating the narrow pores of 1 and larger hydrophilic channels of 2. Such abundant protonation implies interesting proton-conducting properties of both of 1 and 2, which may be a subject of further studies.

Porosity and textural characterization. The sample activation was carried out through solvent exchange in acetone for 3 days, followed by a treatment in a vacuum. The nitrogen adsorption measurements of both compounds 1 and 2 did not show adequate results, probably due to the very slow diffusion of N2 molecules into the micropores. In such a case, the textural characterization by a smaller gas probe, such as CO2, is a viable solution (Table 1). The complete removal of guest molecules was proved by elemental analysis of samples after activation procedure.

<table>
<thead>
<tr>
<th>Specific surface area / m²·g⁻¹</th>
<th>Vₚore / cm³·g⁻¹</th>
<th>V_ads(CO₂)⁴ / cm³(STP)·g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>BET</td>
<td>DFT</td>
</tr>
<tr>
<td>1</td>
<td>712</td>
<td>652</td>
</tr>
<tr>
<td>2</td>
<td>634</td>
<td>569</td>
</tr>
</tbody>
</table>

* measured at P/P₀ = 0.95

The measured isotherms of carbon dioxide adsorption at 195 K are represented in Fig. 3. The initial region of isotherm for 1 up to relative pressure of 0.4 belongs to type I(a) according to the IUPAC classification, which is typical for microporous compounds with narrow slit pores. At relative pressures 0.4–0.6 the step on adsorption isotherm is observed, which could usually be attributed to either pressure-driven structure transformation or appearance of new adsorption sites due to guest-guest intermolecular interactions, which drastically increase the gas uptake at certain pressure. The latter example was demonstrated recently for a microporous MOF [Mn(Hpdc)₂(pdc)₂] (pdc⁻ = pyridine-2,4-dicarboxylate). The compound 2 is also possessing type I(a) isotherm up to p/p₀ = 0.5, where adsorption isotherm makes a small step. The desorption isotherm of 1 shows a large pseudo–triangular hysteresis of H2(a) type with an intermediate desorption step at p/p₀ = 0.1. The maximum CO2 adsorption capacity corresponds to ca. 3.5 CO2 and 2.5 CO2 molecules per formula units of 1 and 2, correspondingly.

In the case of 2, the adsorption-desorption hysteresis is less pronounced. Calculated parameters of the porous structure are given in Table 1. The compound 1 features Vₚore=0.433 cm³·g⁻¹ and the calculated BET surface area 652 m²·g⁻¹. The compound 2 shows a lower CO2 capacity, resulting in Vₚore=0.329 cm³·g⁻¹ and the S_BET = 569 m²·g⁻¹. The porosity of the 2 is markedly lower, compared with the expected Vₚore values based on its crystal structures (0.51 cm³·g⁻¹). Such discrepancies could be explained by the poor accessibility of narrow channels by CO2 probe during the adsorption measurements.

![Figure 3. CO2 adsorption-desorption isotherms at 195 K for 1 (blue) and 2 (red). Filled symbols are for adsorption curve and open ones are for desorption.](image-url)

Theoretical elucidations of the CO2 adsorption data

To explain the origin of the observed hysteresis in 1, we have thoroughly studied adsorption of CO2 molecules inside 1 porous framework employing a computational approach based on the dispersion-corrected density functional theory methods (SCAN+rVV10//PBE-D3(BJ) level of theory; computational details are given in Supporting Information).

A study of gradual molecule-by-molecule interaction with the framework allowed us to elucidate the CO2 adsorption pathway (Fig. 4), which includes the lowest-energy orientations and corresponding adsorption energies of (CO2)n molecules, where n = 1–4, physically adsorbed inside 1. The calculated adsorption centers inside 1 channel (Fig. S15–S18) indicate that the most energetically preferred position of single CO2 molecule is located between organic linkers along the a axis and the highest binding energy value for CO2 at adsorp-
tion site 1a (ΔE = −56.6 kJ·mol⁻¹) can be rationalized by a large number of short van der Waals interatomic contacts with the oppositely charged framework atoms (Fig. S19).²⁵

![Figure 4](image)

**Figure 4.** Calculated structures and adsorption energies (ΔE, kJ·mol⁻¹) of CO₂ molecules at the most energetically preferred adsorption sites inside 1 pores. The relative change of ΔE when introducing one additional CO₂ molecule with respect to the previous step is given in parentheses.

The introduction of subsequent CO₂ molecules into 1 framework slightly affects the position of adsorbed species up to n = 3. Dimeric CO₂ structure is formed when two guest molecules are adsorbed, whereas adsorption of three and four CO₂ molecules leads to formation of cyclic CO₂ trimer and CO₂ tetramer with hybrid structure, respectively (Fig. S20). It is necessary to note that introduction of the second and fourth CO₂ molecules leads to a typical decrease in adsorption energy with respect to the previous step, while the opposite situation is observed when three CO₂ guest molecules are inside 1 channel and form cyclic superstructure stabilized due to favorable electrostatic interactions between (i) guests and (ii) guests and host.²⁰,²⁶ The gain in the adsorption energy of the third CO₂ molecule very well corresponds to the emerged adsorption step on the isotherm plot at V_ads = 130 ml·g⁻¹.

A noticeable difference in the adsorption energies calculated at different CO₂ loadings (Fig. 4) suggests the presence of diffusion barrier inside 1 channel at low CO₂ loadings and low temperatures. Thus, a pronounced step observed in the experimental adsorption isotherm can be explained by the delay in the formation of cyclic CO₂ superstructure due to a low diffusion rate of CO₂ within the pores of 1.²⁰

**Hydrolytic stability and water adsorption.** Scandium complexes and MOFs with carboxylic ligands are known to possess high thermal and hydrolytic stability.¹²,¹³ These properties are explained by the HSAB principle that in compounds with bonds between pair of “hard” atoms or pair of “soft” atoms, higher chemical stability is observed compared to compounds based on bonds between “hard” and “soft” atoms. Therefore, the bonds between scandium and oxygen should provide 1 and 2 with increased stability. Both compounds were shown to reproducibly and reversibly adsorb water vapor without losing crystallinity and porosity (Fig. 5, S1, S5).

![Figure 5](image)

**Figure 5.** Water adsorption-desorption isotherms at 298 K for 1 (blue) and 2 (red). Filled symbols are for adsorption curve and open ones are for desorption.

Water adsorption isotherm of compound 1 at 298 K has stepped shape with a maximum of 2.9 water molecules per formula unit. Framework 2 has a small hysteresis between adsorption/desorption isotherms and adsorbs 3.4 water molecules per formula unit at maximum humidity. Full desorption of water molecules from both frameworks could be achieved only by prolonged heating, suggesting a strong interaction between the guest water molecules and the porous hosts.

Moreover, the title compounds demonstrate remarkable stability in boiling water and in a wide range of pH from 2 to 12 for 1 and from 1 to 12 for 2 during 2 weeks (Fig. 6), exciding that for widely recognizable MOFs with high stability, such as MIL-53(Cr)²⁷ and MIL-53(Al),²⁸ PCN-225,²⁹ MIL-100(Fe)³⁰ and PCN-333.³¹
The selectivity of binary gas mixtures adsorption. To evaluate the applicability of 1 and 2 for gas storage and selective gas adsorption measurements of CO\textsubscript{2}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{2}, CH\textsubscript{4} and N\textsubscript{2} isotherms at 273 and 298 K were carried out.

The isotherms obtained are shown in Fig. 7, S6, S7. Gas uptakes in different units are summarized in Table S3. Framework 1 adsorbs sufficient amounts of CO\textsubscript{2}, fewer amounts of C\textsubscript{2}H\textsubscript{2} and other gases: C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, N\textsubscript{2} and CH\textsubscript{4} due to their larger kinetic diameter (Table 2) as well as possible specific interactions between CO\textsubscript{2} and, to a certain extent, C\textsubscript{2}H\textsubscript{2} guest molecules, manifested as an additional adsorption step and large adsorption/desorption hysteresis (Fig. S6), already seen for the CO\textsubscript{2} adsorption data at 195 K.

![Figure 7. Gas sorption isotherms for 1 (upper) and 2 (bottom) at 273 and 298 K.](image)

All adsorption isotherms of compound 2 are type I(a), with a small deflection for C\textsubscript{2}H\textsubscript{4} curve (Fig. 7). Because of the different crystal structures of the title compounds, their adsorption characteristics significantly differ both in terms of total capacity and selectivity to a particular component of binary gas mixtures. For example, compound 2 absorbs close amounts of CO\textsubscript{2} and C\textsubscript{2}H\textsubscript{2} gases (STP) at both temperatures (Table S3), however, at 273 K the compound 1 adsorbs significant amounts of CO\textsubscript{2} (2.18 mmol g\textsuperscript{-1}), but the uptake of C\textsubscript{2}H\textsubscript{2} is more than three times lower (0.66 mmol g\textsuperscript{-1}). Such results are promising to potential separation of CO\textsubscript{2} and C\textsubscript{2}H\textsubscript{2} which is a difficult task since the molecular geometry and thermodynamic parameters of these gases are very similar (Table 2).

**Table 2. Zero coverage heats of adsorption, calculated according to equation S1**

<table>
<thead>
<tr>
<th>Gas</th>
<th>Q\textsubscript{st}(0), kJ/mol</th>
<th>b.p., K</th>
<th>Kinetic diameter, Å</th>
<th>ΔH\textsubscript{vap}\textsuperscript{a}</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{2}H\textsubscript{6}</td>
<td>32.4</td>
<td>298</td>
<td>184.1</td>
<td>4.4</td>
<td>14.7</td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{4}</td>
<td>19.4</td>
<td>298</td>
<td>169.4</td>
<td>4.2</td>
<td>13.54</td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{2}</td>
<td>37.5</td>
<td>298</td>
<td>189.6</td>
<td>3.3</td>
<td>16.7\textsuperscript{c}</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>37.2</td>
<td>298</td>
<td>195\textsuperscript{d}</td>
<td>3.3</td>
<td>16.4\textsuperscript{e}</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>15.2</td>
<td>298</td>
<td>111.7</td>
<td>3.75</td>
<td>8.17</td>
</tr>
</tbody>
</table>

\textsuperscript{a}At normal b.p., \textsuperscript{b}low adsorption capacity \textsuperscript{c}At 207 K \textsuperscript{d}Sublimation; \textsuperscript{e}At 258 K \textsuperscript{f}At 288 K

The heats of adsorption at zero coverage (Q\textsubscript{st}(0)) for compound 1 have similar values for CO\textsubscript{2} (37.5 kJ mol\textsuperscript{-1}) and C\textsubscript{2}H\textsubscript{2} (37.2 kJ mol\textsuperscript{-1}). The difference in the uptakes of these gases could be since molecules of CO\textsubscript{2} form supramolecular structure from guest molecules that cannot be made by C\textsubscript{2}H\textsubscript{2} molecules. Also, the compound 2 shows high value of Q\textsubscript{st}(0) = 44.4 kJ mol\textsuperscript{-1} for CO\textsubscript{2} which is comparable with the SIFSIX-3-Zn (45 kJ mol\textsuperscript{-1}),\textsuperscript{36} UPC-33 (49.92 kJ mol\textsuperscript{-1}),\textsuperscript{37} Cu\textsubscript{2}(TATB) (48 kJ mol\textsuperscript{-1}),\textsuperscript{38} SIFSIX-3-Cu (54 kJ mol\textsuperscript{-1}),\textsuperscript{39} NH\textsubscript{2}-MIL-53 (Al) (50 kJ mol\textsuperscript{-1}),\textsuperscript{40} or other MOFs with unsaturated metal centers.

We have evaluated selectivity factors for adsorption of binary gas mixtures by three different methods: i) as the ratio of amount adsorbed (Table S3, equation S4); ii) as the ratio of corresponding Henry constants (Table S5, equation S5); iii) by Ideal Adsorbed Solution Theory (IAST)\textsuperscript{41} calculations enabling the estimation of the selectivity factors at different gas mixture compositions and total pressures (equation S7). The results are summarized in Table 3. Due to the exceptional affinity of 1 to CO\textsubscript{2} molecules IAST selectivity factors for CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} have significant values of 393.4 and 97.2, respectively (1/1, 273 K and 1 bar). Both frameworks demonstrate high IAST selectivity factors for adsorption of C\textsubscript{2}H\textsubscript{2}/CH\textsubscript{4} mixture of 28.1 for 1 and 36.9 for 2 (1/1, 298 K and 1 bar). Purification of CH\textsubscript{4} from C\textsubscript{2}H\textsubscript{2} is important not only for natural gas upgrading\textsuperscript{42} but also as recovery process of C\textsubscript{2} or C\textsubscript{3} hydrocarbons for further usage.\textsuperscript{43}

**Table 3. Selectivity factors for adsorption of binary gas mixtures evaluated by different approaches for 1 and 2**

<table>
<thead>
<tr>
<th>System</th>
<th>273 K</th>
<th>298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(V_i/V_j)</td>
<td>(K_{II}/K_{II})</td>
<td>(V_i/V_j)</td>
</tr>
<tr>
<td>IAST</td>
<td>IAST</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4}</td>
<td>2.9</td>
<td>8.3</td>
</tr>
</tbody>
</table>

\textsuperscript{a}For \(V_i/V_j\) \textsuperscript{b}For \(K_{II}/K_{II}\)
the 2.70 mmol g⁻¹ uptake from MOFs. Despite much wider pore size, framework C₂CH₄ selects for trace removal of C₂H₂ molecules, such as isoreticular SIFSIX series, generation MOF materials, such as isoreticular SIFSIX series, for selective adsorption capacity and great C₂H₂/C₂H₃ adsorption selectivity puts the compound 2 among the most prominent 2nd generation materials for selective adsorption in such gas mixture. Moreover, taking into account the excellent chemical stability of 2, its potential in real industrial applications seems even sounder.

Production of ethylene goes through the cracking of ethane or other heavier hydrocarbons. Small amounts of acetylene are also generated in this process, which poisons the ethylene polymerization; therefore, the removal of acetylene from C₂H₃/C₂H₄ mixtures containing ca. 1% acetylene is a very important task. The current technological solution includes the partial hydrogenation over a noble metal catalyst and the solvent extraction of cracked olefins, both of which are cost and energy consumptiv.e, Alternately, the molecular separation could be carried out on a porous material. The structure of pores of MOFs can be rationally tuned to enforce the size-selective sieving effects, or the pore surfaces can be functionalized to induce preferential interactions with specific gas molecules. The ideal porous material for C₂H₂/C₂H₄ separation should have pronounced pore sieving effect for those gases without sacrificing the acetylene uptake. Earlier examples of MOFs with C₂H₂/C₂H₄ selectivity have either very high selectivity but low gas capacity due to the very narrow pores or low selectivity with increased capacity due to specific binding sites but also large pore size for sieving effect. The 2nd generation MOF materials, such as isoreticular SIFSIX series, stepped far forward and now represent the benchmark for trace removal of C₂H₂. For example, a flexible-robust UTSA-300-Cu (NCU – 100) with a pore size of 3.6 Å shows significant C₂H₂ uptake increase with a total capacity of 4.57 mmol g⁻¹ and has IAST selectivity factor of 7291 for C₂H₂/C₂H₄ (1/99, v/v) at 298 K and 1 bar (Fig. 8).

Figure 8. Comparison of C₂H₂ uptake at 0.01 bar and 1/99 C₂H₃/C₂H₄ selectivity in representative MOFs (Table S7). MOFs with hydrolytic stability demonstrated with PXRD and sorption analysis shown in black squares and red stars, other – in grey circles.

Apparently, strong host-guest interactions between the acidic acetylene molecule and the hydrophilic channels of 2, lined with uncoordinated carboxylic groups with their basic nature, give raise such remarkable adsorption uptake of 2 towards C₂H₂ over C₂H₄. The unique combination of appreciable C₂H₂ adsorption capacity and great C₂H₂/C₂H₃ adsorption selectivity puts the compound 2 among the most prominent 2nd generation materials for selective adsorption in such gas mixture. Moreover, taking into account the excellent chemical stability of 2, its potential in real industrial applications seems even sounder.

Along with the selective adsorption of acetylene over ethylene, an important challenge is the removal of CO₂ from C₂H₃/CO₂ mixtures since CO₂ is an unavoidable contaminant in the acetylene production process. The C₂H₂ and CO₂ molecules have the almost identical size, shape, and physical properties. A lot of porous MOFs demonstrate excellent adsorption selectivity values for C₂H₂/CO₂ mixture. The adsorption preference of most such MOFs is based towards the acetylene, yet it is the CO₂ contaminations which needs be excluded from this gas mixture, therefore, the porous materials with selective adsorption preference of CO₂ over C₂H₂ are far more desirable. There are only a few MOFs with such inverse selectivity: [Mn(bdc)(dpe)], ZIU-60 and SIFSIX-3-Ni. Remarkably, the porous framework 1 demonstrates the rare CO₂ over C₂H₂ selectivity of 3.28 (calculated as a ratio of adsorbed volumes at 273 K and 1 bar) which is higher than for ZIU-60 (1.8) and comparable with [Mn(bdc)(dpe)] (7.0). SIFSIX-3-Ni has selectivity for CO₂ only at low pressure and adsorbs more C₂H₂ than CO₂ at 1 bar.

Iodine adsorption. The I-131 isotope (t½ = 8 days, β-decay) is one of the most dangerous radioactive contaminants of known anthropogenic nuclear accidents such as Chernobyl or Fukushima. The radioactive I₂ molecules form an aerosol, extremely dangerous for inhalation; therefore, the extracting of radioactive iodine from the air is an essential step for environmental remediation. The adsorption of iodine vapors by porous MOFs becomes an increasingly requisite topic of research. The crystals of activated compounds 1 and 2 were
exposed to iodine vapors at 100°C for 24 hours to ensure saturation of the samples with iodine. A change in their color from colorless to dark brown indicated the adsorption of iodine by samples (Fig. 9). The amount of iodine adsorbed by the samples was determined gravimetrically and proved by TGA (Fig. S21, S22), elemental analyses, Raman spectroscopy (Fig. 9) and single-crystal X-ray diffraction analysis (Table S2).

Compound 1 absorbs 27 wt.% of I₂, which is corresponding to chemical formula 1·0.4I₂·1.5H₂O. Compound 2 absorbed more substantial 67 wt.% of I₂, which corresponds to formula 2·I₂·2H₂O. The PXRD pattern of the iodine loaded sample 1·0.4I₂·1.5H₂O (Fig. S21) fully coincides with that for the activated compound 1 and does not contain reflexes of the free crystalline I₂. Similarly, the PXRD data for 2·I₂·2H₂O (Fig. S22) matches that for guest-free 2, apart from some changes of intensities of reflexes. The Raman spectra for both compounds (Fig. 9) contain two bands at about 110 and 170 cm⁻¹. The peak at 170 cm⁻¹ is ascribed to iodine located in the middle of the pore channels, with a vibrational frequency close to the iodine solid.⁶¹,⁶² The peak at ca. 110 cm⁻¹ indicates the existence of I⁻ anions which could be considered as the partial formation of charge-transfer complexes bound to the internal surface of the framework.⁶³,⁶⁴ The formation of such negatively charged species could be facilitated by a presence of positively charged protons, disordered over the carboxylate groups of the channels. To visualize the iodine in the channels, single-crystal X-ray diffraction studies of the iodine-enriched samples were carried out. In the case of compound 1, the guest molecules were not refined due to low occupancy and high positional disorder. In compound 2 the quantitative content of iodine in the structure was established by a PLATON/SQUEEZE procedure as the number of unassigned electrons in the interstitial space as well as by elemental analysis. There are positions of high electron density located on the symmetry elements of the unit cell, which could only be assigned as iodine atoms with partial occupancy. The proposed positions are shown in Fig. S23. Although the individual I₂ molecules cannot be identified from these data, the formation of the inclusion compound 2·I₂·2H₂O is clearly confirmed.

The iodine can be removed from the pores of MOFs by ethanol extraction or by thermal desorption at high temperatures (310°C for 1, 290°C for 2, Fig. S21, S22). Heating at lower temperatures does not initiate the iodine release which demonstrates strong interaction of I₂ guest molecules with the host frameworks. Such high stability of the inclusion complexes secures an irreversible capture of dangerous I₂ isotopes for an as long period of time as necessary to ensure its complete decay.

**Experimental**

**Materials and methods.** All reagents and solvents were at least 99% of purity and used as supplied without further purification. The Fourier transform infrared (FTIR) spectra were recorded from KBr pellets in the range 4000–400 cm⁻¹ on a Scimitar FTS 2000 Fourier transform infrared spectrometer. Thermogravimetric analysis (TGA) was performed using TG 209 F1 Iris Thermo Microbalance (NETZSCH) instrument at temperatures between 25 and 600°C under He atmosphere at a heating rate of 10°C/min. Powder X-ray diffraction (PXRD) patterns were measured with Cu–Kα radiation on a Shimadzu XRD 7000S powder X-ray diffractometer. Elemental analyses (C, H, N) were performed on the Euro EA 3000 CHN elemental analyzer. The Raman spectra were recorded on a SPEX triple spectrometer in the range of 300–50 cm⁻¹.

**Crystallography.** Diffraction data for single-crystals 1 and 2 were obtained at 130 K on an automated Agilent Xcalibur diffractometer equipped with an area AtlasS2 detector (graphite monochromator, λ(MoKα) = 0.71073 Å, ω-scans). Integration, absorption correction, and determination of unit cell parameters were performed using the CrysAlisPro program package.⁶⁵ Diffraction data for single-crystal 2·I₂·2H₂O were collected at 100 K on the ‘Belok’ beamline (λ = 0.79313 Å, ϕ-scans) of the National Research Center ‘Kurchatov Institute’ (Moscow, Russian Federation) using a Rayonix SX165 CCD detector. The data were indexed, integrated and scaled; absorption correction was applied using the XDS program package.⁶⁶ The structures were solved by dual space algorithm (SHELXT)⁶⁷ and refined by the full-matrix least-squares technique (SHELXL)⁶⁸ in the anisotropic approximation (except hydrogen atoms). Positions of hydrogen atoms of organic ligands were calculated geometrically and refined in the riding model. The structures 1·DMF·2H₂O, 2·DMA and 2·I₂·2H₂O contain large void volumes occupied with highly disordered solvent guest molecules (DMF, DMA, H₂O and I₂), which could not be refined as a set of discrete atoms. The final compositions of the compounds were defined according to PLATON/SQUEEZE procedure (235 e⁻ in 838 Å³ for 1, 358 e⁻ in 2563 Å³ for 2, 992 e⁻ in 2805 Å³ for 2·I₂·2H₂O) and the data of elemental (C, H, N) analyses. The crystallographic data and details of the structure refinements are summarized in Table S2. CCDC 2025040–2025042 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center at https://www.ccdc.cam.ac.uk/structures/.

The synthetic procedure of compound [Sc(Hpzc)(pzc)]·DMF·2H₂O (1·DMF·2H₂O). 2.5-Pyrazinedicarboxylic acid dihydrate (70 mg, 0.34 mmol) and scandium(III) chloride hexahydrate (44 mg, 0.17 mmol) were added to the solvent mixture of DMF (2 ml), H₂O (2 ml) and THF (4 ml) and acidified with concentrated hydrochloric acid (20 drops of HCl). The reaction mixture was heated at 100°C for 4 days, and then was cooled to room temperature and filtered on air. Yield: 68 %. Elemental analysis. Calculated (%): for 1·DMF·2H₂O (C₁₀H₆N₂O₄·Se·Cl); C 37.0, H 3.3, N 14.4, Sc found (%): C 37.1, H 3.6, N 14.2. The phase purity of the crystals was confirmed by PXRD (Figure S1). For IR spectra see Figure S2.

The synthetic procedure of compound [Sc(Hpzc)(pzc)]·DMA·4H₂O (2·DMA·4H₂O). 2.5-Pyrazinedicarboxylic acid dihydrate (102 mg, 0.5 mmol) and scandium(III) chloride hexahydrate (65 mg, 0.25 mmol) were exposed to iodine vapors at 100°C for 24 hours to ensure saturation of the samples with iodine. A change in their color from colorless to dark brown indicated the adsorption of iodine by samples (Fig. 9). The amount of iodine adsorbed by the samples was determined gravimetrically and proved by TGA (Fig. S21, S22), elemental analyses, Raman spectroscopy (Fig. 9) and single-crystal X-ray diffraction analysis (Table S2).

**Figure 9.** Raman spectra and photo for activated 1 and 2 and loaded with I₂.

![Raman Spectra](image-url)
added to the solvent mixture of DMA (2.5 ml), H₂O (1.25 ml) and DMF (2.5 ml) and acidified with concentrated hydrochloric acid (25 drops of HCl). The reaction mixture was heated at 100°C for 2 days, and then the reaction mixture was cooled to room temperature. Obtained crystals were used for single crystal X-Ray analysis (2-DMAn). The brownish precipitate was filtered, washed with DMF and dried on air. Yield: 91%. Elemental analysis. Calculated (%) for 2-DMAn·4H₂O (C₃₋₅H₉₋₁₃N₆O₆₋₁₇Sc): C 35.8, H 4.1, N 13.0; found(%): C 35.5, H 4.1, N 13.4. The phase purity of the crystals was confirmed by PXRD (Figure S1). For IR spectra see Figure S3.

I₂ adsorption. For iodine sorption measurements a weighted quantity of activated compounds in a glass bottle was placed into a bigger Schlenk flask containing I₂ crystals under an argon atmosphere. Then the Schlenk flask was evacuated and heated at 100°C for 24 hours. The obtained dark-brown iodine-saturated MOF samples were collected and weighted.

Characterization of 1·0.4I₂·1.5H₂O. The weight of the activated sample is 50 mg, loaded with I₂ is 65 mg. Elemental analysis, Calculated (%) for 1·0.4I₂·1.5H₂O (C₂₋₅H₆₋₁₃N₄O₆₋₁₃Sc): C 28.4, H 1.6, N 11.1; found(%): C 27.7, H 1.5, N 11.2.

Characterization of 2·1.2H₂O. The weight of the activated sample is 50 mg, loaded with I₂ is 88 mg. Elemental analysis, Calculated (%) for 2·1.2H₂O (C₁₋₅H₇₋₁₄N₂O₆Sc): C 21.6, H 1.4, N 8.4; found(%): C 22.7, H 1.4, N 8.2.

Preactivation Procedure. Samples of as-synthesized compounds 1·DMF·2H₂O and 2·DMA·4H₂O were soaked in acetone for 3 days with changing solvent every 12 hours.

Surface Area and Porous Structure. An analysis of the porous structure was performed by a CO₂ adsorption technique using Quantochrome’s Autosorb iQ at 195 K. Initially the compounds were first activated in a dynamic vacuum using standard ‘outgas’ option of the equipment at 80°C during 6 hours. Adsorption–desorption isotherms were measured within the range of relative pressures of 10⁻³ to 0.995. The specific surface area was calculated from the data obtained based on the conventional BET, Langmuir and DFT models. Pore size distributions were calculated using DFT method.

Elemental analysis of activated compounds. Calculated (%) for 1 (C₁₋₅H₄₋₁₃N₆O₆Sc): C 38.1, H 1.3, N 14.8; found(%): C 37.7, H 1.7, N 14.7. Calculated (%) for 2 (C₁₋₅H₃₋₁₃N₄O₆Sc): C 38.1, H 1.5, N 14.8; found(%): C 38.2, H 1.4, N 14.7.

Gases Sorption Experiments at 273 and 298 K. Gases adsorption isotherm measurements were carried out volumetrically on Quantachrome’s Autosorb iQ equipped with thermostat TERMEX Cryo–VT–12 to adjust the temperature with 0.1 K accuracy. Adsorption–desorption isotherms were measured within the range of pressures of 1 to 800 torr. The database of the National Institute of Standards and Technology was used as a source of p–V–T relations at experimental pressures and temperatures.

Water vapor adsorption. Water vapor adsorption isotherm measurements were carried out on volumetric a Quantachrome’s Autosorb iQ equipment at a certain temperature. The certain temperature was maintained by a thermostat TERMEX Cryo–VT–12-1 with ±0.05 K accuracy. Adsorption–desorption isotherms were measured within the range of pressures of 1 torr and up to Pₒ at the given conditions for vapors. p–V–T relations at the experimental pressures and temperatures were taken from the database of the National Institute of Standards and Technology.

Hydrotlytic stability. For the determination of the hydrotlytic stability the samples of 1 and 2 (30 mg) were placed into water or aqueous solutions of HCl or NaOH of known pH ranging from 0 to 14 at room temperature. After a while (2 weeks) the samples were filtrated and its PXRD plot was recorded. Hydrolytic stability in boiling water was examined by soaking in water for 7 days at 100°C.

CONCLUSIONS

Two isomeric scandium-organic frameworks were obtained by judicious variation of synthesis condition. Both compounds demonstrate high hydrolytic stability in a wide range of pH and boiling water. The porous frameworks show remarkable adsorption properties in the selective adsorption in binary mixtures containing CO₂, C₂H₃, and other light hydrocarbons. Great IAST selectivity factor of 127.1 for C₂H₅/C₂H₄ (199 v/v) gas mixture at 298 K was achieved.

ASSOCIATED CONTENT

Supporting Information. The SI contains details of synthesis conditions (Table S1), data on characterization of compounds (Fig. 1–3), crystallographic data (Table S2), detailed information about sorption (Fig. S4–S8, Table S3), calculations of selectivity factors and heats of adsorption (Fig. S9–S14, Tables S4–S7), computational details of DFT calculations (Fig. S15–S20) and additional information of iodine adsorption (Fig. S21–S23). This material is available free of charge via the Internet at http://pubs.acs.org.

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Isomeric scandium-organic frameworks possess unique adsorption properties towards gases and iodine with among the best selectivity factor for \( \text{C}_2\text{H}_2\text{C}_2\text{H}_4 \) mixture.