A Selenophene-Incorporated Metal–Organic Framework for Enhanced CO\textsubscript{2} Uptake and Adsorption Selectivity

Pavel A. Demakov\textsuperscript{1,2}, Sergey S. Volynkin\textsuperscript{1}, Denis G. Samsonenko\textsuperscript{1,2}, Vladimir P. Fedin\textsuperscript{1,2,*} and Danil N. Dybtsev\textsuperscript{1,2}

\textsuperscript{1} Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk 630090, Russia; demakov@niic.nsc.ru (P.A.D.); volynkin@niic.nsc.ru (S.S.V.); denis@niic.nsc.ru (D.G.S.); dan@niic.nsc.ru (D.N.D.)

\textsuperscript{2} Department of Natural Sciences, Novosibirsk State University, 2 Pirogova St., Novosibirsk 630090, Russia

* Correspondence: cluster@niic.nsc.ru

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Abstract: A new metal–organic coordination polymer \([\text{Zn}_2(\text{sedc})_2(\text{dabco})]\) (1se; sedc\textsuperscript{2−} = selenophene-2, 5-dicarboxylate; dabco = 1,4-diazabicyclo[2.2.2]octane) was synthesized and characterized by single-crystal X-ray diffraction analysis. This MOF is based on \([\text{Zn}_2(\text{OOCR})_4\text{N}_2]\) paddle wheels and is isoreticular to the family of \([\text{Zn}_2(\text{bdc})_2(\text{dabco})]\) derivatives (1b; bdc\textsuperscript{2−} = 1,4-benzenedicarboxylate) with \textit{pcu} topology. The gas adsorption measurements revealed that 1se shows a 15% higher CO\textsubscript{2} volumetric uptake at 273 K and 28% higher CO\textsubscript{2} uptake at 298 K (both at 1 bar) compared to the prototypic framework 1b. Methane and nitrogen adsorption at 273 K was also investigated, and IAST calculations demonstrated a pronounced increase in CO\textsubscript{2}/CH\textsubscript{4} and CO\textsubscript{2}/N\textsubscript{2} selectivity for 1se, compared with 1b. For example, the selectivity factor for the equimolar CO\textsubscript{2}/CH\textsubscript{4} gas mixture at 1 bar = 15.1 for 1se and 11.9 for 1b. The obtained results show a remarkable effect of the presence of selenium atom on the carbon dioxide affinity in the isoreticular metal–organic frameworks with very similar geometry and porosity.

Keywords: porous metal–organic frameworks; selenophene; X-ray diffraction studies; adsorption measurements; gas adsorption selectivity

1. Introduction

Carbon dioxide is a corrosive gas and a major atmospheric pollutant, causing a greenhouse effect. Selective capture and sequestration of carbon dioxide is one of the challenging problems in the modern chemical industry. Typically, a chemical sorption of CO\textsubscript{2} by amines is highly effective; however, the corrosive nature of the chemosorbents and substantial energy penalties during their regeneration demand new viable alternatives [1–4]. Porous coordination polymers or metal–organic frameworks (MOFs) are recently emerged materials with the greatest potential for adsorption of gases. Remarkable porosity, sufficient stability, as well as vast versatility of the structural and functional design make this class of porous materials among the most perspective adsorbents for selective CO\textsubscript{2} capture from natural gas or industrial flue gas [5–10]. Modular design is a widely used principle to tailor structural and/or functional properties within a certain type of isostructural MOF family, such as IRMOF-1 [11–13], MIL-53 [14–16], or UiO-66 [17–19], which are typically based on the linear 1,4-benzenedicarboxylate (bdc\textsuperscript{2−}) linker. Other than a bent shape, the striking feature of ditopic dicarboxylate linkers based on heterocyclic core (Scheme 1) is the polarity of the core and the polarizability of a heteroatom, enabling additional induced dipole interactions with a substrate. Recently, a number of research groups have shown that the incorporation of 2,5-furanedicarboxylate (fdc\textsuperscript{2−}) or
2,5-thiophenedicarboxylate (tdc$^{2-}$) into porous MOF structures imbue such materials with quite unique features such as selective ion adsorption, luminescence sensing [20–22], dielectric bistability [23], and gas/vapor uptake [24,25].

A porous coordination polymer [Zn$_2$(bdc)$_2$(dabco)] (dabco = 1,4-diazabicyclo[2.2.2]octane) is a prototypic compound of a bountiful MOF family with highly tunable structural features [26–30]. We have demonstrated that the incorporation of 2,5-thiophenedicarboxylate instead of the 1,4-benzenedicarboxylate into this MOF enhances both the CO$_2$ adsorption uptake and the CO$_2$/N$_2$ adsorption selectivity of [Zn$_2$(tdc)$_2$(dabco)] by as much as 50%, compared with the original structure [Zn$_2$(bdc)$_2$(dabco)] at the same conditions [31]. The single-crystal X-ray diffraction studies, as well as the quantum-chemical calculations unveiled the role of the thiophene moieties in the specific CO$_2$ binding via an induced dipole interaction between CO$_2$ molecules and the heterocycle. Selenium atoms possess even greater radius and higher polarizability than sulfur. Thus, an enhancement of adsorption properties owing to van der Waals intermolecular interactions between a MOF and CO$_2$ or other gaseous substrate should be expected if a selenophene moiety is incorporated into such porous material. The 2,5-selenophenedicarboxylate (sedc$^{2-}$) is the heterocyclic linker, structurally and functionally similar to the 2,5-thiophenedicarboxylate. Except for a handful of examples [32,33], sedc$^{2-}$ has mostly been ignored in MOF chemistry so far. Herein, we report the synthesis and investigation of a new selenophenedicarboxylate-based porous MOF [Zn$_2$(sedc)$_2$(dabco)] (1se), which is isoreticular to both [Zn$_2$(bdc)$_2$(dabco)] (1b) and [Zn$_2$(tdc)$_2$(dabco)] (1t). The impact of selenium heteroatom on the adsorption properties of [Zn$_2$(sedc)$_2$(dabco)] is discussed in detail.

![Scheme 1. Structural formulae of fdc$^{2-}$, tdc$^{2-}$, sedc$^{2-}$, and bdc$^{2-}$ dicarboxylate linkers.](image)

**2. Results and Discussion**

**2.1. Structure Description**

The coordination polymer 1se was synthesized by the solvothermal reaction of Zn(NO$_3$)$_2$·6H$_2$O, H$_2$sedc, and dabco in DMF at 100 °C for 24 h. According to single-crystal X-ray diffraction data, 1se crystallizes in the tetragonal space group P-421c. The asymmetric unit contains two crystallographically independent Zn(II) atoms with the same coordination environment of four O atoms of four bridging carboxylate groups and one N atom of dabco bridge. Zn–O distances lie in the range 2.015(2)–2.062(2) Å. Zn–N distances are 2.040(2) and 2.047(2) Å. Zn(1) and Zn(2) atoms form binuclear ‘paddlewheel’ blocks [Zn$_2$(OOCR)$_4$] interconnected by four sedc$^{2-}$ anions into square-grid network. The angular shape of the sedc$^{2-}$ ligands results in a considerable distortion of the binuclear blocks (Figure 1a) and corrugation of the square-grid layers (Figure 1b). These layers are bound by dabco bridges to form a three-dimensional porous framework with a primitive cubic topology (pcu)—the same as the other MOFs of the isoreticular family [Zn$_2$(bdc)$_2$(dabco)].
Figure 1. Crystal structure of 1se. A section of the structure showing dabco-bridged secondary building units [Zn₂(OOCR)₄] (a); 3D structure of the framework: view along c axis (b) and b axis (c). Zn atoms are shown green, N atoms—blue, O atoms—red, Se atoms—orange. H atoms and guest DMF molecules are not shown.

The coordination network in 1se contains a three-dimensional system of intersecting channels, with the widest channels running along the c axis, across the windows of the square-grid layers (see Figure 1b). The apertures of these channels are 5 × 8 Å. Two different types of smaller channels across the main channels of the tetragonal structure have smaller the apertures of ca. 2.5 × 5 Å or 3.5 × 4 Å, depending on the particular arrangement of arks of the sedc²⁻ ligands (Figure 1c). Importantly, all selenium atoms of the heterocycles are immediately accessible for interactions with potential substrate molecules, allowing a clear verification of the hypothesis of this work. We should also point out that the crystal structure 1se is similar to the known compound [Zn₂(tdc)₂(dabco)] (1t), based on 2,5-thiophenedicarboxylate [31] although the distortions of the binuclear blocks [Zn₂(OOCR)₄] and the square-grid layers in 1t are even more pronounced as a result of stronger bending of tdc²⁻ ligand [34], compared with that of sedc²⁻.

2.2. Characterization and Activation

To evaluate the thermal stability of 1se, thermogravimetric analysis (TGA, Figure S1) was performed. The first observed 30% weight loss step occurs between 80 °C and 200 °C, referring to the evaporation of four guest DMF molecules per formula unit (calculated: 30%). The metal–organic framework 1se itself is stable up to ca. 280 °C, after which the irreversible framework decomposition apparently takes place. Such thermal stability is comparable to other reported MOFs containing sedc²⁻ anions (T_decomp = 250 ÷ 320 °C) [32,33]. Such substantial difference between the temperature of the evaporation of guests and the temperature of the framework decomposition makes it possible direct activation of 1se by heating in a vacuum, obtaining the guest-free activated framework [Zn₂(sedc)₂(dabco)] (1se'). The infrared spectra of both 1se and 1se' (Figure S2) contain the characteristic bands of Csp²-H valence vibrations (3073 cm⁻¹), Csp³-H valence vibrations (2965 cm⁻¹ and 2935 cm⁻¹), antisymmetric (1590 cm⁻¹) and symmetric (1360 cm⁻¹) carboxylate group vibrations. Infrared spectrum of 1se also contains a characteristic band of COamide stretchings (1666 cm⁻¹), which is absent on the spectrum of 1se', confirming a complete desolvation of metal–organic framework 1se during the activation process. The PXRD data (Figure 2) suggest the phase purity of the synthesized compound 1se. The powder diffraction pattern of 1se' is generally very similar to that of 1se although there is a noticeable shift of some of the reflexes to lower angles. For example, the (2 0 0) reflection at 2θ = 8.57° (1se) is shifted to 2θ = 8.36° (1se') indicating a slight extension of the metal–organic framework upon its activation. Similar guest-assisted breathing of the framework was observed earlier for 1b and 1t [31,35]. The unit cell parameters for 1se' were refined according to the powder data using
the Powdercell program [36] and provided in Table A2. While the crystallographic parameter \( c \) is almost intact, the parameters \( a \) and \( b \) in 1se are longer by ca. 2.6\% than in 1se, likely due to certain straightening of the sec\( \text{d} \) -dicarboxylate bridges. Overall, the unit cell volume is expanded by 5.2\% during the activation of the compound.

![Figure 2. PXRD patterns of the theoretically simulated 1se (blue), as-synthesized 1se (black), activated 1se' (olive), and the theoretically simulated 1se' (red), assuming the retention of the space group P-4\_1c.](image)

### 2.3. Adsorption Measurements

The textural characteristics of the evacuated compound 1se' were studied by a nitrogen porosimetry at 77 K. The adsorption isotherm (Figure 3) corresponds to the type I with no hysteresis, typical to microporous adsorbents. The pore volume measured at \( p/p_0 = 0.95 \) is \( V_{\text{pore}} = 0.57 \text{ cm}^3 \text{ g}^{-1} \); the calculated BET surface area is \( A_{\text{BET}} = 1504 \text{ m}^2 \text{ g}^{-1} \), respectively (see other details in Table S1). The experimental \( V_{\text{pore}} \) is very much consistent with the theoretically expected value based on a solvent accessible volume of 1se', calculated using PLATON routine [37] (0.58 cm\(^3\)·cm\(^{-3}\) or 0.55 cm\(^3\)·g\(^{-1}\)). The pore-size distribution, calculated by DFT method from the N\(_2\) adsorption isotherm, gives a value of a pore size near 7 Å, which corresponds to the van der Waals diameter of the large cuboidal cages inside the pcu net. For a reference, the pore volume of the activated MOFs based on thiophenedicarboxylic acid (1t') or benzenedicarboxylic acid (1b'), reported earlier, are 0.68 cm\(^3\)·g\(^{-1}\) and 0.75 cm\(^3\)·g\(^{-1}\), respectively. The gravimetric porosity directly depends on molecular weight of a compound, which is notably higher for 1se, than for 1t and 1b. The comparison of experimental volumetric porosities for these MOFs results in a more or less comparable values: 0.60 cm\(^3\)·cm\(^{-3}\) (1se'), 0.64 cm\(^3\)·cm\(^{-3}\) (1t'), 0.62 cm\(^3\)·cm\(^{-3}\) (1b'), see also Table S2. Most importantly, the compounds 1b, 1t, and 1se represent a suitable family of porous materials where the influence of different heteroatoms on the gas adsorption properties could be systematically analyzed and assessed since the other parameters are almost identical. Being motivated by such an opportunity, we investigated the adsorption properties of 1se' towards industrially important gases (CO\(_2\) and CH\(_4\)) and compared the obtained data with the other prototypes 1b' and 1t'.
Figure 3. N\textsubscript{2} adsorption isotherm for 1se' at 77K and pose-size distribution calculated from the isotherm.

The gravimetric CO\textsubscript{2} adsorption uptakes at 1 bar for 1se' are 110 cm\textsuperscript{3}·g\textsuperscript{-1} (273 K, see Figure S3) and 46 cm\textsuperscript{3}·g\textsuperscript{-1} (298 K). Such numbers are comparable with the literature data of CO\textsubscript{2} adsorption by 1b' (122 cm\textsuperscript{3}·g\textsuperscript{-1} at 273 K, 46 cm\textsuperscript{3}·g\textsuperscript{-1} at 298 K). Taking into account the crystallographic densities, the corresponding volumetric uptakes for 1se' were calculated to be 116 cm\textsuperscript{3}·cm\textsuperscript{-3} (273 K) and 48.5 cm\textsuperscript{3}·cm\textsuperscript{-3} (298 K), which exceeds those for 1b' by 15% (101 cm\textsuperscript{3}·cm\textsuperscript{-3}) at 273 K and by 28% (38 cm\textsuperscript{3}·cm\textsuperscript{-3}) at 298 K, respectively, convincingly confirming a positive effect of the polarizable heteroatom (Se) on the absorption properties of porous materials [38–41]. Similarly, the isosteric heat of CO\textsubscript{2} adsorption at zero coverage \(Q_{st}(0)\) for 1se' (19.9 kJ·mol\textsuperscript{-1}) is greater than for 1b' (19.0 kJ·mol\textsuperscript{-1}), indicating stronger binding of CO\textsubscript{2} with the porous framework containing the selenophene heterocycle. We must mention here that the CO\textsubscript{2} adsorption by 1t' is still the highest among the MOFs discussed here, both in terms of the gravimetric uptakes (153 cm\textsuperscript{3}·g\textsuperscript{-1} at 273 K, 67.5 cm\textsuperscript{3}·g\textsuperscript{-1} at 298 K, 1 bar) and volumetric uptakes (143 cm\textsuperscript{3}·cm\textsuperscript{-3} at 273 K, 63.1 cm\textsuperscript{3}·cm\textsuperscript{-3} at 298 K, 1 bar). The isosteric heat of CO\textsubscript{2} adsorption by 1t' (23.7 kJ·mol\textsuperscript{-1}) also suggests that the thiophene moieties have greater impact on the CO\textsubscript{2} adsorption. It is probably the polarity of the aromatic ring that contributes to a stronger binding between the polar CO\textsubscript{2} guest and porous MOF host. Based on the experimental data, the following dependence of the CO\textsubscript{2} uptake on the nature of the dicarboxylate anion was established: tdc\textsuperscript{2−} > sedc\textsuperscript{2−} > bdc\textsuperscript{2−}. This dependence strengthens the earlier claim that the substitution of the common terephthalate linkers to heterocyclic ones should enhance the adsorption properties of the MOF material due to induced dipole interactions. In terms of the gas storage, the thiophene-containing tdc\textsuperscript{2−} seems to be an optimal choice for such substitution since the incorporation of heavier sedc\textsuperscript{2−} no longer improves the gas adsorption capacity of the framework.

The CH\textsubscript{4} and N\textsubscript{2} adsorption–desorption isotherms for 1se' and 1b' were measured up to \(p = 1\) bar at 273 K. The gas adsorption isotherms are shown on the Figure 5. For 1se' the gravimetric adsorption volumes at 1 bar are 16.2 cm\textsuperscript{3}·g\textsuperscript{-1} (CH\textsubscript{4}) and 6.0 cm\textsuperscript{3}·g\textsuperscript{-1} (N\textsubscript{2}) adsorption, respectively. For 1b', the corresponding uptakes are 20.0 cm\textsuperscript{3}·g\textsuperscript{-1} and 6.6 cm\textsuperscript{3}·g\textsuperscript{-1}. The gravimetric gas uptakes for 1se' are slightly lower than for 1b', mainly due to the higher density of the former. On the contrary, the volumetric assessment indicates higher gas adsorption by 1se', than by 1b', supporting the concept of stronger van der Waals interactions of methane/nitrogen with sedc\textsuperscript{2−} than with bdc\textsuperscript{2−}. 

Volumetric CO$_2$ sorption isotherms for 1se’ and 1b’ at 273 K and 298 K.

Gravimetric CO$_2$, CH$_4$, and N$_2$ sorption isotherms for 1se’ and 1b’ at 273 K. Only adsorption branches are shown.

The sequestration of CO$_2$ from N$_2$ or from CH$_4$ is a critical technology for a reduction of environmental risks and for protection of natural gas pipelines, respectively. The CO$_2$/CH$_4$ as well as CO$_2$/N$_2$ gas adsorption selectivity factors were calculated by three commonly employed approaches: (i) as the ratio of the adsorbed volumes at 1 bar ($S_V$), (ii) as the ratio of Henry constants ($S_K$), and (iii) by the ideal adsorbate solution theory ($S_{IAST}$). The calculated selectivity values are summarized in Table 1, and the details of the calculations are provided in Tables S3 and S4. By any criteria used, the incorporation of sde$_2^-$ evidently increases the adsorption selectivities of 1se’, compared with the prototypic 1b’. The calculated CO$_2$/CH$_4$ selectivity factors for 1se’ ($S_V = 6.8, S_K = 4.8, S_{IAST} = 5.6$) are comparable or even exceed those reported for other MOFs with promising application potential for separation of such small molecules [42–44]. The CO$_2$/N$_2$ adsorption selectivity factors for 1se’ are also quite remarkable $S_V = 18.6, S_K = 12.9, S_{IAST} = 15.1$ (Figure 6) for a porous MOF with no unsaturated metal centers. The results obtained for 1se’ are superior to the CO$_2$/N$_2$ selectivity factors for both 1b’ and 1t’. Particularly, the IAST CO$_2$ adsorption selectivity for the equimolar CO$_2$ + N$_2$ gas mixture for 1se’ is ca. 25% greater than for 1b’ or for 1t’ (see also Figure S4). Such remarkable increase should
apparently be attributed to the nature of the heterocyclic moiety since the pore geometry and other structural parameters of the investigated MOFs are, essentially, the same. However, the contribution of sieving effect is also possible, as the channels in 1se situated along two of three directions have the apertures smaller than 5 Å [45,46]. In terms of the CO₂/N₂ selective separation, the incorporation of the selenophene-containing anion provides the best performance in the row: sedc²⁻ > tdc²⁻ > bdc²⁻. Moreover, a rather low CO₂ adsorption enthalpy for 1se' (19.9 kJ·mol⁻¹) ensures the facile regeneration of the porous adsorbent in a cyclic CO₂ sequestration process. The unique combination of remarkable CO₂/N₂ adsorption selectivity, high CO₂ uptake, and one of the lowest CO₂ adsorption enthalpies puts the title MOF 1se' among the best porous materials for practical purification of the industrial exhausts.

Table 1. Selectivities in binary gas mixtures calculated (I) as volumes ratio at 1 bar (II) as Henry constants ratio and (III) IAST selectivity factors for equimolar mixtures at 1 bar.

| Gas Mixture                  | V₁/V₂ (273 K, 1 Bar) | Kₜ₁/Kₜ₂ (273 K) | IAST (273 K, 50:50 Ratio) |
|------------------------------|-----------------------|-----------------|--------------------------|
| CO₂/N₂ (in this work)        | 18.6 – 17.7           | 12.9 – 11.8     | 11.8 – 11.9             |
| CO₂/N₂ (from Ref. [29])      | – 10.3               | 12.5 – 8.9      | 11.2 – 9.2              |
| CO₂/CH₄ (in this work)       | 6.8 – 5.8             | 4.8 – 3.9       | 5.6 – 4.1               |

Figure 6. IAST selectivity factors on CO₂ mole fraction in binary gas mixtures: CO₂/N₂ (a) and CO₂/CH₄ (b) at 273K and P_total = 1 bar.

3. Materials and Methods

4. Reagents

Commercial starting reagents 2,5-selenophenedicarboxylic acid (Angene), 1,4-diazabicyclo[2.2.2]octane (>98.0%, TCI), terephthalic acid (>98.0%, Hidmon), N,N-dimethylformamide (reagent grade, Vekton) were used as purchased without purification.

5. Instruments

IR spectra in KBr pellets were recorded in the range 4000–400 cm⁻¹ on a VERTEX 80 spectrometer. Elemental (C, H, N) analysis was made on a varioMICROCcube analyzer. Powder X-ray diffraction (PXRD) analysis was performed at room temperature on a Shimadzu XRD-7000 diffractometer (Cu-Kα radiation, λ = 1.54178 Å). Thermogravimetric analysis was carried out on a Netzsch TG 209 F1 Iris instrument. The experiments were carried out under He flow (30 cm³·min⁻¹) at a 10 K·min⁻¹ heating rate. Adsorption experiments were performed using Quantachrome Autosorb iQ device.
Low-pressure gas adsorption isotherms at 273 K and 298 K were recorded with a thermostat TERMEX Cryo-VT-12 to adjust temperature with 0.1 K accuracy. 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. Elemental (Zn, Se) ICP-MS analysis was carried out using Agilent 8800. The samples of 1se and 1se′ were digested in the mixture of HCl 36% water solution and H₂O₂ 30% water solution, then diluted by water prior to ICP-MS.

6. X-ray Crystallography

Diffraction data for single-crystal 1se 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 with a step of 0.5°). Integration, absorption correction, and determination of unit cell parameters were performed using the CrysAlisPro program package [47]. The structures were solved by dual space algorithm (SHELXT [48]) and refined by the full-matrix least squares technique (SHELXL [49]) in the anisotropic approximation (except hydrogen atoms). Positions of hydrogen atoms were calculated geometrically and refined in the riding model. The crystallographic data and details of the structure refinement are summarized in Table A1. CCDC 2026693 contains 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/.

7. Synthetic Procedures

Synthesis of [Zn₂(sedc)₂(dabco)]-4DMF (1se) 100 mg (0.34 mmol) of Zn(NO₃)₂·6H₂O, 66 mg (0.30 mmol) of H₂sedc, 20 mg (0.18 mmol) of dabco and 5.00 mL of DMF were mixed in a glass flask. The mixture was hit in the ultrasound bath for 10 min and heated at 100°C for 24 h. After the cooling to the room temperature white-yellow precipitate was filtered off, washed thrice with DMF and dried in air. Yield: 89 mg (61%). IR spectrum (KBr, cm⁻¹) characteristic bands: 3424 (w, br, νOH); 1627 (m, νCOO as); 1356 (s, νCOO s); 1267 (m, νCOO s); 1380 (s, νCOO s). PXRD data (Figure 2) confirmed the phase purity of the product. Elemental analysis data calculated for [Zn₂(C₆H₅SeO₄)₂(C₆H₁₂N₂)]·4C₃H₇NO (%): C, 37.2; H, 4.6; N, 8.7. Found (%): C, 37.0; H, 4.6; N, 8.6. ICP-MS data. Zn:Se molar ratio: 1.02:1 (theor = 1:1). TGA: 30% weight loss step at ca.150°C (30% calculated for 4DMF).

Synthesis of [Zn₂(sedc)₂(dabco)] (1se′) The sample of 1 was activated by keeping in a primary vacuum (10⁻⁹ bar) at 50°C for 2 h, then at 70°C for 2 h, and at last 90°C for 12 h with 1°-min⁻¹ heating and cooling rates. IR spectrum (KBr, cm⁻¹) characteristic bands: 3419 (w, br, νOH); 3075 (w, νCsp²-H); 2963 and 2926 (w, νCsp³-H); 1666 (s, νCO amide); 1627 (m, νCOO as); 1356 (s, νCOO s). PXRD data (Figure 2) confirmed the phase purity of the product. Elemental analysis data calculated for [Zn₂(C₆H₂SeO₄)₂(C₆H₁₂N₂)] (%): C, 31.9; H, 2.4; N, 4.1. Found (%): C, 31.8; H, 2.5; N, 4.5. ICP-MS data. Zn:Se molar ratio: 1.07:1 (theor = 1:1).

Synthesis of [Zn₂(bdc)₂(dabco)]-4DMF·½H₂O (1b) This process carried out according to the published procedure [50]: 300 mg (1.0 mmol) of Zn(NO₃)₂·6H₂O, 165 mg (1.0 mmol) of H₂bdc, 60 mg (0.54 mmol) of dabco and 18.0 mL of DMF were mixed in a glass flask. The mixture was hit in the ultrasound bath for 10 min and heated at 120°C for 48 h. After the cooling to the room temperature white precipitate was filtered off, washed thrice with DMF and dried in air. Yield: 380 mg (88%). PXRD data (Figure S5) confirmed the phase purity of the product. Synthesis of [Zn₂(bdc)₂(dabco)] (1b′) The sample of 1b was activated by keeping in a primary vacuum (10⁻⁹ bar) at 50°C for 2 h, then at 80°C for 2 h, and at 100°C for 12 h with 1°-min⁻¹ heating and cooling rates. PXRD data (Figure S6) confirmed the phase purity of the product.

8. Conclusions

To summarize, a new porous metal–organic framework [Zn₂(sedc)₂(dabco)], based on 2,5-selenophenedicarboxylate anions (sedc²⁻) was synthesized and characterized. [Zn₂(sedc)₂(dabco)]
is based on the \([\text{Zn}_2(\text{OOCR})_2\text{N}_2]\) paddle-wheel blocks and adopts distorted primitive cubic topology, similar to other important representatives of this isoreticular family \([\text{Zn}_2(\text{bdc})_2(\text{dabco})]\) and \([\text{Zn}_2(\text{tdc})_2(\text{dabco})]\) (bdc\(^2^-\) = 1,4-benzenedicarboxylate, tdc\(^2^-\) = 2,5-thiophenedicarboxylate). The dependence of the gas adsorption properties on the nature of the bridging anion was systematically investigated. According to the experimental and literature data, the CO\(_2\) adsorption uptake increases along the following sequence: \([\text{Zn}_2(\text{bdc})_2(\text{dabco})]\) < \([\text{Zn}_2(\text{secd})_2(\text{dabco})]\) < \([\text{Zn}_2(\text{tdc})_2(\text{dabco})]\). On the other hand, the CO\(_2\)/N\(_2\) adsorption selectivity follows the trend \([\text{Zn}_2(\text{bdc})_2(\text{dabco})]\) < \([\text{Zn}_2(\text{tdc})_2(\text{dabco})]\) < \([\text{Zn}_2(\text{secd})_2(\text{dabco})]\). Such dependencies strengthen the earlier observation that the incorporation of heterocyclic moieties provides additional adsorption sites which enhances the adsorption properties of the corresponding porous frameworks. The selenophene-based anion seems to have a particular distinction towards CO\(_2\) molecules. The new porous compound \([\text{Zn}_2(\text{secd})_2(\text{dabco})]\) features a unique combination of remarkable CO\(_2\)/N\(_2\) adsorption selectivity, high CO\(_2\) uptake, and one of the lowest CO\(_2\) adsorption enthalpies, which makes it a very promising material for CO\(_2\) sequestration applications.

**Supplementary Materials:** The following are available online. Figure S1: TG plot of the synthesized 1se; Figure S2: IR spectra of the synthesized 1se and activated 1se’; Figure S3: Gravimetric CO\(_2\), CH\(_4\), and N\(_2\) sorption isotherms for 1se’ (a) and 1b’ (b) at 273 K; Figure S4: Dependences of adsorbed CO\(_2\) mole fraction in MOF on CO\(_2\) mole fraction in gas phase for binary gas mixtures: CO\(_2\)/N\(_2\) and CO\(_2\)/CH\(_4\) at 273K and P\(_{\text{total}}\) = 1 bar; Figure S5: PXRD pattern of the synthesized compound 1b compared to the theoretical one; Figure S6: PXRD pattern of the synthesized compound 1b’ compared to the theoretical one for 1b’; Table S1: Textural characteristics of 1se’; Table S2: Calculated virial coefficients for CO\(_2\) isosteric heats of adsorption and Henry constants determination; Table S3: Fit parameters of the isotherms for IAST calculations.

**Author Contributions:** P.A.D., S.S.V., and D.G.S. performed the experimental work. P.A.D. prepared the original manuscript. D.N.D. and V.P.F. reviewed and edited the manuscript. D.N.D. project administration and funding acquisition. All authors have read and agreed to the published version of the manuscript.

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**Appendix A Crystallographic data**

| Identification Code | 1se |
|---------------------|-----|
| CCDC Number         | 2026693 |
| Empirical formula   | C\(_{30}\)H\(_{44}\)N\(_4\)O\(_{12}\)Se\(_2\)Zn\(_2\) |
| M, g/mol            | 969.37 |
| Crystal system      | Tetragonal |
| Space group         | P-42_1c |
| a, b, Å             | 20.5922(17) |
| c, Å                | 19.1260(2) |
| V, Å\(^3\)          | 8110.20(16) |
| Z                   | 8 |
| D(calc.), g/cm\(^3\) | 1.588 |
| µ, mm\(^{-1}\)      | 3.040 |
| F(000)              | 3920 |
| Crystal size, mm    | 0.36 × 0.26 × 0.20 |
| θ range for data collection, deg. | 1.98–28.28 |
| Index ranges        | -27 ≤ h ≤ 19, -22 ≤ k ≤ 25, -22 ≤ l ≤ 25 |
| Reflections collected/independent | 24,964 8741 |
| R\(_{\text{int}}\)  | 0.0225 |
| Reflections with I > 2σ(I) | 8293 |
| Goodness-of-fit on F\(^2\) | 1.044 |
| Final R indices | 8293 |
| R indices (all data) | R\(_1\) = 0.0223, wR\(_2\) = 0.0492 |
| Largest diff. peak/hole, e/Å\(^3\) | 0.397(−0.271) |
Table A2. Refined unit cell parameters for 1se′.

| Identification Code | 1se′ |
|---------------------|------|
| Crystal System      | Tetragonal |
| a, b, Å             | 21.1165 |
| c, Å                | 19.1304 |
| V, Å3               | 8530.5 |
| D(calc.), g/cm³     | 1.055 |

References

1. Dutcher, B.; Fan, M.; Russell, A.G. Amine-Based CO₂ Capture Technology Development from the Beginning of 2013—A Review. ACS Appl. Mater. Interfaces 2015, 7, 2137–2148. [CrossRef] [PubMed]
2. Wang, J.; Huang, L.; Yang, R.; Zhang, Z.; Wu, J.; Gao, Y.; Wang, Q.; O’Hareb, D.; Zhong, Z. Recent advances in solid sorbents for CO₂ capture and new development trends. Energy Environ. Sci. 2014, 7, 3478–3518. [CrossRef]
3. Bhattacharyya, D.; Miller, D.C. Post-combustion CO₂ capture technologies—A review of processes for solvent-based and sorbent-based CO₂ capture. Curr. Opin. Chem. Eng. 2017, 17, 78–92. [CrossRef]
4. Leung, D.Y.C.; Caramanna, G.; Mercedes Maroto-Valer, M. An overview of current status of carbon dioxide capture and storage technologies. Renew. Sustain. Energy Rev. 2014, 39, 426–443. [CrossRef]
5. Lin, R.B.; Li, L.; Alsalme, A.; Chen, B. An Ultramicroporous Metal-Organic Framework for Sieving Separation of Carbon Dioxide from Methane. Small Struct. 2020. [CrossRef]
6. Ding, M.; Flaig, R.W.; Jiang, H.-L.; Yaghi, O.M. Carbon capture and conversion using metal–organic frameworks and MOF-based materials. Chem. Soc. Rev. 2019, 48, 2783–2828. [CrossRef] [PubMed]
7. Zhang, Z.; Yao, Z.-Z.; Xiang, S.; Chen, B. Perspective of microporous metal–organic frameworks for CO₂ capture and separation. Energy Environ. Sci. 2014, 7, 2868–2899. [CrossRef]
8. Siegelman, R.L.; Milner, P.J.; Forse, A.C.; Lee, J.-H.; Colwell, K.A.; Neaton, J.B.; Reimer, J.A.; Weston, S.C.; Long, J.R. Water Enables Efficient CO₂ Capture from Natural Gas Flue Emissions in an Oxidation-Resistant Diamine-Appended Metal–Organic Framework. J. Am. Chem. Soc. 2019, 141, 13171–13186. [CrossRef]
9. Lin, Y.; Kong, C.; Zhang, Q.; Chen, L. Metal-Organic Frameworks for Carbon Dioxide Capture and Methane Storage. Adv. Energy Mater. 2017, 7, 1601296. [CrossRef]
10. Belmabkhout, Y.; Guillerm, V.; Eddaoudi, M. Low concentration CO₂ capture using physical adsorbents: Are metal-organic frameworks becoming the new benchmark materials? Chem. Eng. J. 2016, 296, 386–397. [CrossRef]
11. Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachtler, J.; O’Keeffe, M.; Yaghi, O.M. Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application in Methane Storage. Science 2002, 295, 469–472. [CrossRef]
12. Guo, P.; Dutta, P.; Wong-Foy, A.G.; Gidley, D.W.; Matzger, A.J. Water Sensitivity in Zn₄O-Based MOFs is Structure and History Dependent. J. Am. Chem. Soc. 2015, 137, 2651–2657. [CrossRef] [PubMed]
13. Zhou, H.-F.; Liu, B.; Hou, L.; Zhang, W.-Y.; Wang, Y.-Y. Rational construction of a stable Zn₄O-based MOF for highly efficient CO₂ capture and conversion. Chem. Commun. 2018, 54, 456–459. [CrossRef] [PubMed]
14. Loiseau, T.; Serre, C.; Huguenard, C.; Fink, G.; Taulelle, F.; Henry, M.; Bataille, T.; Férey, G. A rationale for the large breathing of the porous aluminum terephthalate (MIL-53) upon hydration. Chem. Eur. J. 2004, 10, 1373–1382. [CrossRef]
15. Senkovska, I.; Hoffmann, F.; Fröba, M.; Getzschmann, J.; Böhlmann, W.; Kaskel, S. New highly porous aluminium based metal-organic frameworks: Al(OH)₊(ndc) (ndc = 2,6-naphthalene dicarboxylate) and Al(OH)(bpdc) (bpdc = 4,4’-biphenyl dicarboxylate). Microporous Mesoporous Mater. 2009, 122, 93–98. [CrossRef]
16. Rabe, T.; Fehr, H.; Reinsch, H.; Willhammar, T.; Svensson Grape, E.; Stock, N. Influence of the substitution pattern of four naphthalenedicarboxylic acids on the structures and properties of group 13 metal-organic frameworks and coordination polymers. Dalton Trans. 2020, 49, 4861–4868. [CrossRef] [PubMed]
17. Cavka, J.H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K.P. A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability. J. Am. Chem. Soc. 2008, 130, 13850–13851. [CrossRef]

18. Lammert, M.; Wharmby, M.; Smolders, S.; Bueken, B.; Lieb, A.; Lomachenko, K.A.; De Vos, D.; Stock, N. Cerium-based metal organic frameworks with UiO-66 architecture: Synthesis, properties and redox catalytic activity. Chem. Commun. 2015, 51, 12578–12581. [CrossRef]

19. Waitschat, S.; Fröhlich, D.; Reinsch, H.; Terraschke, H.; Lomachenko, K.A.; Lamberti, C.; Kummer, H.; Helling, T.; Baumgartner, M.; Henninger, S.; et al. Synthesis of M-Uio-66 (M = Zr, Ce or Hf) employing 2,5-pyridinedicarboxylic acid as a linker: Defect chemistry, framework hydrophilisation and sorption properties. Dalton Trans. 2018, 47, 1062–1070. [CrossRef]

20. Wang, H.; Wen, R.-M.; Hu, T.-L. Two Series of Lanthanide Metal-Organic Frameworks Constructed from Crown-Ether-Like Secondary Building Units. Eur. J. Inorg. Chem. 2014, 1185–1191. [CrossRef]

21. Sapchenko, S.A.; Demakov, P.A.; Samsonenko, D.G.; Dybtsev, D.N.; Schröder, M.; Fedin, V.P. A Cryptand Metal–Organic Framework as a Platform for the Selective Uptake and Detection of Group I Metal Cations. Chem. Eur. J. 2017, 23, 2286–2289. [CrossRef] [PubMed]

22. Chen, Q.; Guo, P.-C.; Zhao, S.-P.; Liu, J.-L.; Ren, X.-M. A rhombus channel metal–organic framework comprised of Sr²⁺ and thiophene-2,5-dicarboxylic acid exhibiting novel dielectric bistability. CrystEngComm 2013, 15, 1264–1270. [CrossRef]

23. Dreischarf, A.C.; Lammert, M.; Stock, N.; Reinsch, H. Green Synthesis of Zr-CAU-28: Structure and Properties of the First Zr-MOF Based on 2,5-Furandicarboxylic Acid. Inorg. Chem. 2017, 56, 2270–2277. [CrossRef]

24. Lysova, A.A.; Samsonenko, D.G.; Dorovatovskii, P.V.; Lazarenko, V.A.; Khrustalev, V.N.; Kovalenko, K.A.; Dybtsev, D.N.; Fedin, V.P. Tuning the Molecular and Cationic Affinity in a Series of Multifunctional Metal–Organic Frameworks Based on Dodecanuclear Zn(II) Carboxylate Wheels. J. Am. Chem. Soc. 2019, 141, 17260–17269. [CrossRef]

25. Lysova, A.; Samsonenko, D.G.; Dorovatovskii, P.V.; Lazarenko, V.A.; Khrustalev, V.N.; Kovalenko, K.A.; Karpov, V.M.; Platonov, V.E.; Fedin, V.P. Metal-organic frameworks based on octafluorobiphenyl-4,4′-dicarboxylic acid: Synthesis, crystal structure, and sorption properties of pillared square grid nets based on paddle-wheel motifs: Implications for hydrogen storage in porous materials. Chem. Eur. J. 2005, 11, 3521–3529. [CrossRef]

26. Chun, H.; Dybtsev, D.N.; Kim, H.; Kim, K. Synthesis, X-ray crystal structures, and gas sorption properties of pillared square grid net based on paddle-wheel motifs: Implications for hydrogen storage in porous materials. Chem. Eur. J. 2017, 23, 266–277. [CrossRef]

27. Dybtsev, D.N.; Yutkin, M.P.; Peresypkina, E.V.; Virovets, A.V.; Serre, C.; Férey, G.; Fedin, V.P. Isoreticular homochiral porous metal-organic structures with tunable pore sizes. Inorg. Chem. 2007, 46, 6843–6845. [CrossRef]

28. Khan, I.S.; Samsonenko, D.G.; Irgashev, R.A.; Kazin, N.A.; Rusinov, G.L.; Charushin, V.N.; Zavakhina, M.S.; Fedin, V.P. Synthesis, crystal structure and fluorescent properties of indolo[3,2-b]carbazole-based metal–organic coordination polymers. Polyhedron 2017, 141, 337–342. [CrossRef]

29. Cheplakova, A.M.; Kovalenko, K.A.; Samsonenko, D.G.; Lazarenko, V.A.; Khrustalev, V.N.; Vinogradov, A.S.; Karpov, V.M.; Platonov, V.E.; Fedin, V.P. Metal-organic frameworks based on octafluorobiphenyl-4,4′-dicarboxylic acid: Synthesis, crystal structure, and surface functionality. Dalton Trans. 2018, 47, 3283–3297. [CrossRef]

30. Bolotov, V.A.; Kovalenko, K.A.; Samsonenko, D.G.; Han, X.; Zhang, X.; Smith, G.L.; McCormick, L.J.; Teat, S.J.; Yang, S.; Lennox, M.J.; et al. Enhancement of CO₂ Uptake and Selectivity in a Metal–Organic Framework by the Incorporation of Thiophene Functionality. Inorg. Chem. 2018, 57, 5074–5082. [CrossRef] [PubMed]

31. Hua, C.; D’Alessandro, D.M. Systematic Tuning of Zn(II) frameworks with Furan, Thiophene and Selenophene Dipyridyl and Dicarboxylic Ligands. Cryst. Growth Des. 2017, 17, 6262–6272. [CrossRef]

32. Ding, B.; Hua, C.; Keprt, C.J.; D’Alessandro, D.M. Influence of structure–activity relationships on through-space intervalence charge transfer in metal–organic frameworks with cofacial redox-active units. Chem. Sci. 2019, 10, 1392–1400. [CrossRef] [PubMed]

33. Lysova, A.; Samsonenko, D.; Dybtsev, D.; Fedin, V. Synthesis and luminescence properties of new metal-organic frameworks based on zinc(II) ions and 2,5-thiophendicarboxylate ligands. Crystals 2018, 8, 7. [CrossRef]
35. Dybtsev, D.N.; Chun, H.; Kim, K. Rigid and Flexible: A Highly Porous Metal–Organic Framework with Unusual Guest-Dependent Dynamic Behavior. *Angew. Chem. Int. Ed.* 2004, 43, 5033–5036. [CrossRef]
36. Kraus, W.; Nolze, G. POWDER CELL–A program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powder patterns. *J. Appl. Crystallogr.* 1996, 29, 301–303. [CrossRef]
37. Spek, A.L. Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.* 2003, 36, 7–13. [CrossRef]
38. Antonio Zárate, J.; Sánchez-González, E.; Jurado-Vázquez, T.; Gutiérrez-Alejandre, A.; González-Zamora, E.; Castillo, I.; Maurin, G.; Ibarra, I.A. Outstanding reversible H2S capture by an Al(III)-based MOF. *Chem. Commun.* 2019, 55, 3049–3052. [CrossRef]
39. Georgiadis, A.G.; Charisiou, N.; Yentekakis, I.V.; Goula, M.A. Hydrogen Sulfide (H2S) Removal via MOFs. *Materials* 2020, 13, 3640. [CrossRef]
40. Dong, Q.; Guo, Y.; Cao, H.; Matsuda, R.; Duan, J. Accelerated C2H2/CO2 Separation by a Se-Functionalized Porous Coordination Polymer with Low Binding Energy. *ACS Appl. Mater. Interfaces* 2020, 12, 3764–3772. [CrossRef]
41. Díaz-Ramírez, M.L.; Vargas, B.; Raziel Álvarez, J.; Landeros-Rivera, B.; Rivera-Almazo, M.; Ramos, C.; Flores, G.; Morales, E.; Vargas, R.; Garza, J.; et al. Fluorometric detection of iodine by MIL-53(Al)-TDC. *Dalton Trans.* 2020, 49, 6572–6577. [CrossRef] [PubMed]
42. Sim, J.; Yim, H.; Ko, N.; Choi, S.B.; Oh, Y.; Park, H.J.; Park, S.Y.; Kim, J. Gas adsorption properties of highly porous metal–organic frameworks containing functionalized naphthalene dicarboxylate linkers. *Dalton Trans.* 2014, 43, 18017–18024. [CrossRef] [PubMed]
43. Yao, S.; Wang, D.; Cao, Y.; Li, G.; Huo, Q.; Liu, Y. Two stable 3D porous metal–organic frameworks with high performance for gas adsorption and separation. *J. Mater. Chem. A* 2015, 3, 16627–16632. [CrossRef]
44. Ding, Q.-R.; Wang, F. A pillared-layer framework with high uptake and selective sorption of light hydrocarbons. *Dalton Trans.* 2016, 45, 7004–7007. [CrossRef]
45. Lin, R.B.; Xiang, S.; Zhou, W.; Chen, B. Microporous Metal-Organic Framework Materials for Gas Separation. *Chem* 2020, 6, 337–363. [CrossRef]
46. Sapchenko, S.A.; Barsukova, M.O.; Belosludov, R.V.; Kovalenko, K.A.; Samsonenkov, D.G.; Poryvaev, A.S.; Sheveleva, A.M.; Fedin, M.V.; Bogomyakov, A.S.; Dybtsev, D.N.; et al. Understanding Hysteresis in Carbon Dioxide Sorption in Porous Metal–Organic Frameworks. *Inorg. Chem.* 2019, 58, 6811–6820. [CrossRef]
47. Rigaku Oxford Diffraction. *CrysAlisPro 1.171.38.46*; Rigaku Oxford Diffraction: The Woodlands, TX, USA, 2015.
48. Sheldrick, G.M. SHELXT—Integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, A71, 3–8. [CrossRef]
49. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, C71, 3–8. [CrossRef]