Optimized CO$_2$ Capture of the Zeolitic Imidazolate Framework ZIF-8 Modified by Solvent-Assisted Ligand Exchange

Yuel W. Abraha, Chih-Wei Tsai, J. W. Hans Niemantsverdriet, and Ernst H. G. Langner

ABSTRACT: Zeolitic imidazolate frameworks, like ZIF-8 and related structures, have shown great potential for the capture of carbon dioxide. Modifying their structure by exchanging part of the constituent organic ligands is a proven method for enhancing the capacity to absorb CO$_2$. In this work, we performed solvent-assisted ligand exchange (SALE) on nanosized ZIF-8 (nZIF-8) with a series of functionalized imidazole derivatives (exchange percentages, after 24 h): 2-bromoimidazole (19%), 2-chloroimidazole (29%), 2-trifluoromethylbenzimidazole (4%), 2-mercaptobenzimidazole (4%), and 2-nitroimidazole (54%). The sodalite topology and porosity of nZIF-8 were maintained with all SALE modifications. Low-pressure CO$_2$ adsorption of nZIF-8 (38.5 cm$^3$ g$^{-1}$) at STP was appreciably enhanced with all mixed-linker SALE products. Using halogenated (−Cl, −Br, and −CF$_3$) imidazole derivatives in a 24 h SALE treatment resulted in increases between 11 and 22% in CO$_2$ adsorption, while the thiol (−SH)- and nitro (−NO$_2$)-functionalized SALE products led to 32 and 100% increases in CO$_2$ uptakes, respectively. These CO$_2$ uptakes were further optimized by varying the SALE treatment time. The SHbIm- and NO$_2$Im-exchanged SALE products of nZIF-8 show 87 and 98 cm$^3$ g$^{-1}$ of CO$_2$ uptakes after 60 and 120 h of SALE, respectively. These are record high CO$_2$ adsorptions for all reported ZIF derivatives at low-pressure conditions.

1. INTRODUCTION

The removal of carbon dioxide (CO$_2$), a major greenhouse gas from the atmosphere, has become one of the greatest environmental challenges faced by the human race in the 21st century. At the time of writing, the level of CO$_2$ amounted to 415 ppm, which is about 100 ppm higher than in 1960 and predicted to grow further in the next 20 years due to the persistent usage of fossil fuels as the main source of energy. CO$_2$ capture and storage/sequestration (CCS) technologies are considered essential as a short to mid-term solution to minimize the impact of global warming, up until renewable technologies reach the required maturity.

Porous materials such as zeolites, bituminous coal-based activated carbon (BFL carbon), and metal–organic frameworks (MOFs) are being investigated for their high CO$_2$ adsorption capacities. In the last two decades, MOFs have attracted extensive attention for CCS applications owing to their high surface area, tunable pore size, high CO$_2$ selectivity, capacity, porosity, and thermal and chemical stabilities. Zeolitic imidazolate frameworks (ZIFs) are a subclass of MOFs made of bivalent metal centers, tetrahedrally coordinated to imidazolate organic linkers. ZIFs have shown a high affinity for CO$_2$ over other components in flue gas resulting from fossil fuel combustion. This, coupled with independence on regeneration temperature, makes ZIFs ideal for industrial CO$_2$ uptake.

Direct synthesis (de novo) of ZIFs with the desired linker (functionalized imidazole) and metal center combination suffers from many limitations such as low solubility of linkers or metal salts, catenation, loss of porosity, formation of undesired topologies, and loss of sensitivity. Solvent-assisted ligand/linker exchange (SALE) can be used to overcome these limitations. SALE, also known as a bridging-linker replacement, is a type of postsynthetic modification (PSM) where the organic linkers of a MOF are exchanged with another suitable linker in an appropriate solvent medium. This is a heterogeneous reaction, where the parent MOF crystals are reacted with an excess of the new linkers. SALE occurs via single-crystal to single-crystal transformations as opposed to the dissolution of the framework and recrystallization.

The term SALE was established by Karagiari et al., who used the method to replace the 2-ethylimidazole linkers of cadmium-based ZIF (CdIF-4) with 2-nitroimidazole (NO$_2$Im) and 2-methylimidazole (mIm) in dimethylformamide (DMF), dimethylacetamide, and n-butanol solvents, resulting in the formation of CdIF-9 and SALEM-1, respectively. The RHO topology of the parent CdIF-4 was maintained in both SALE products. Furthermore, the particle size of the MOF remained...
the same, while a high Brunauer–Emmett–Teller (BET) surface area was maintained. The required molar ratio of imidazole linker to ZIF-8 was found to be 6.7:1, while the ratio 3:1 was adequate for performing SALE on CdIF-4. Higher molar ratios (>6.7:1) resulted in degradation of the framework, while lower molar ratios (<3:1) did not result in any ligand exchange.

SALE can be selective when applied to mixed-linker MOFs. Lalonde et al. reported selective SALE of ZIF-69 (NO2Im and 5-ClbIm linkers), ZIF-78 (NO2Im and NO2bIm linkers), and ZIF-76 (Im and 5-ClbIm linkers) with 5-trifluorobenzimidazole. The SALE was selective to the bulky linkers (5-ClbIm and NO2bIm), while the imidazole linkers remained unchanged. Linker exchanges of over 90% was achieved for all three ZIFs as determined by digestive 1H nuclear magnetic resonance (NMR). Powder X-ray diffraction (PXRD) and N2 adsorptions showed that the topology and permanent porosity of the ZIFs were retained during the ligand exchange.

Similarly, Tuleushov and Attfield have shown that Zn(Im) (bIm) can be formed via selective SALE of 5-chlorobenzimidazole (5-ClbIm) linkers of ZIF-76 with benzimidazole at 100 °C over 5 days. The selectivity was due to the similar pKₐ of 5-ClbIm (~5.74) and bIm (~5.74) compared to 14.5 of Im. The SALE product maintained the LTA topology of the mother MOF according to PXRD analysis as well as scanning electron microscopy images.

The electronic and chemical properties of a MOF can be modified by SALE, introducing linkers with desired functional groups. SALE of ZIF-71 (Zn(dcIm)₂) and ZIF-8 with 4-bromoimidazole and 2-ethyl-imidazole, respectively, resulted in the formation of ZIF-71(4-BrIm/dClIm) and ZIF-8 (mIm/eIm), both retaining the RHO and sodalite (SOD) topology of the parent MOFs, respectively. Ban et al. have reported SALE of ZIF-108, Zn(NO2Im), with an exchange percentage for mIm (56%), eIm (40%), Im (12.5%), NO2bIm (50%), and dMebIm (20%) to form ZIF-108-mIm, ZIF-108-eIm, ZIF-70, ZIF-78, and ZIF-74, respectively. ZIF-108-mIm and ZIF-108-eIm maintained the SOD topology of ZIF-108, while ZIF 70 & 78 resulted in GME topology, and ZIF-74 formed in GIS topology. The formation of different topologies is possible due to the heterogeneous nucleation process that takes place during SALE, where the parent ZIF acts as a seed.

During solvent-assisted ligand incorporation (SALI), another route for PSM of MOFs, the desired functionalities are incorporated into the MOF nodes. The CO2 uptake of NU-1000 was enhanced by incorporating a perfluoroalkane functionality via SALI. The SALI-1 product with...
CF₃COO⁻ functionality resulted in a 68% increase in CO₂ uptake at low pressure (0.15 bar) over the parent NU-1000. Dual-linker ZIFs have shown enhanced selectivity for CO₂ than for other gases (CH₄, O₂, and N₂) commonly found in flue gas. Additionally, ZIFs with electron-withdrawing linkers exhibit improved CO₂ uptakes as a result of the enhanced interaction with CO₂. Yaghi and co-workers synthesized a series of ZIF 68–70 and ZIF 78–82 using de novo (conventional direct) method starting with a mixed-linker system. The ZIFs showed GME topology with a pore diameter of 16 Å. Increasing CO₂ adsorptions (at 1 bar) were observed with increasing electronegativity of the imidazole/benzimidazole linker’s functionalities: ZIF-78 (–NO₂, –NO₂) > ZIF-69 (–NO₂, –Cl), ZIF-81 (–NO₂, –Br), ZIF-82 (–CN, –Cl) > ZIF-68 (–NO₂, –H) > ZIF-70 (NO₂, –H) > ZIF-79 (–NO₂, –Me) (Table 2). This is due to the high quadrupole moment of CO₂. ZIFs with high quadrupole moments (ZIF-78 & 82) resulted in high adsorption as a result.

Figure 1. ¹H digestive NMR spectra of (a) nZIF8, (b) LeZIF8-ClIm₂₄h, (c) LeZIF8-BrIm₂₄h, (d) LeZIF8-NO₂Im₂₄h, (e) LeZIF8-CF₃bIm₂₄h, and (f) LeZIF8-SHbIm₆₀h.
of the increased interaction between CO₂ and the polar functional groups of the MOFs. No relations were found between the pore diameter and CO₂ adsorptions, which indicate that CO₂ adsorption is predominantly influenced by the functionalities of the linkers rather than the pore properties of the MOFs. Furthermore, ZIF-68, -69, -70, -78, -81, and -82 gave better CO₂ uptake (≥55 cm³ g⁻¹) than the industrially used BPL carbon (46.8 cm³ g⁻¹).20

SALE can also be used to synthesize single-linker MOFs by complete exchange of the original linker with the linker of choice. TMU-4-SALE-L6 and TMU-4-SALE-L6 was obtained after SALE of TMU-4 and TMU-6, respectively. In both cases, complete linker exchange was achieved by an extended SALE time of 5 days at 80 and 100 °C, respectively.21 The SALE products showed 10 and 30x increases in porosity over their de novo synthesized counterparts (TMU-4 and TMU-6). The CO₂ uptake (at 273 K and 1 bar) of TMU-4-SALE-L6 was doubled compared to that of the directly synthesized TMU-6.

In 2018, we reported a series of SALE products of nanosized ZIF-8 (abbreviated as nZIF-8) with 2-mercaptopenimidazole (SHbIm), 2-aminobenzimidazole (NH₂bIm), 2-phenylimidazole (PhIm), and 2-nitroimidazole (NO₂Im) with 12.5, 16, 10, and 67% linker exchanges, respectively.22 SALE generally resulted in a decrease in the BET surface area of the ZIF, especially with the 2-nitroimidazole-exchanged ZIF, which has a BET surface area of 633 m² g⁻¹ compared to the 1605 m² g⁻¹ of parent nZIF-8. All of the nZIF-8 derivatives maintained the SOD topology of ZIF-8, while the NO₂Im-exchanged SALE products developed an FRL topology. All SALE-modified ZIFs resulted in improved low-pressure CO₂ adsorptions at 0 °C, and ZIFs with electron-withdrawing (−NO₂ and −SH) functionalities showed the highest CO₂ adsorptions of 76 and 77 cm³ g⁻¹, respectively. NO₂Im-exchanged ZIF-8 showed considerably higher CO₂ adsorptions with half the BET surface area of its SH-functionalized (1416 cm³ g⁻¹) counterpart. Furthermore, an increase in CO₂ adsorption was observed with increasing electronegativity of the functional groups (NO₂ > SH > NH₂ > phenyl).22

Herein, we further explore the usefulness of the SALE method applied to nZIF-8 with 2-bromomimidazole (BrIm), 2-chloromimidazole (ClIm), and 2-trifluoromethylbenzimidazole (CF₃bIm) linkers. We also aim to optimize the CO₂ uptake capacity under ambient conditions of the high-performing SALE products (with NO₂Im and SHbIm linkers) of nZIF-8 by performing time-resolved SALE reactions.22 We found that the SHbIm and NO₂Im exchanged materials have CO₂ uptakes that are up to 2.5 times that of the parent ZIF-8, which are record high CO₂ adsorptions of all reported ZIF derivatives under ambient conditions.

2. RESULTS AND DISCUSSION

2.1. Synthesis. SALE was performed by isothermal heating of nZIF-8 suspended in methanol with ~3X excess of imidazolate-based linkers (ClIm, BrIm, or NO₂Im) and ~8X excess of benzimidazole-based linkers (SHbIm or CF₃bIm) for the above stated reaction temperature and time (Scheme 1, Table 3). The mixed-linker ZIF products are denoted with a “Le” (ligand exchange) prefix, followed by “ZIF8” and a new linker name with SALE time and linker exchange percentages (as determined by ¹H NMR) as a subscript.

The ClIm, BrIm, and CF₃bIm linkers were all dissolved in methanol prior to mixing with the suspended nZIF-8, while SHbIm was dissolved in 1-butanol and NO₂Im in DMF due to their low solubility in methanol. A minimum yield of 79% was achieved for all SALE reactions, with the exception of the LeZIF8-SHbIm products, which resulted in ~30% yields due to partial digestion of the nZIF-8 structure by the acidic thiol substituent.25

All SALE products were activated at 150 °C (in a vacuum oven overnight) to remove any solvents and unreacted linkers from the pores of the MOF. The mixed-linker SALE products were all stable under atmospheric conditions and thermally stable up to 264 °C in the N₂ atmosphere according to thermal gravimetric analysis (TGA) (Supporting Information Figure S10).

2.2. Characterization. 2.2.1. Digestive ¹H NMR. Digestive ¹H NMR using the D₂O/D₂SO₄ (9:1) solvent system was used for quantitative determination of exchange percentages for the SALE products from the ratio of the integrals (or intensities) of CH==CH peaks of mIm and CH==CH or benzylic peaks (i–iv) of the new linkers (Figure 1, Table 3). The NO₂Im, ClIm, and BrIm nZIF8-SALE products all have a singlet at ~1.82 ppm representing −CH₃ and another singlet at ~6.48 ppm corresponding to CH==CH of mIm protons. Additional peaks corresponding to CH==CH and benzylic protons of the new imidazole-based linkers are also observed between 6.6 and 7.4 ppm. The SHbIm and CF₃bIm nZIF8-SALE products both lead to a downfield shift of the −CH₃ (mIm) peak to resonate at 1.92 and 1.98 ppm and CH==CH peak shift to 6.59 and 6.66 ppm, respectively. The shift is induced by the electron-withdrawing substituents (−CF₃ and −SH) forming intermolecular interactions with mIm protons in solution, for example, −H−S− or −H−F−. The benzylic ring could add a stabilizing effect to the intermolecular interactions in these two cases.

Nitro-functionalized SALE products (LeZIF8-NO₂Im) were the least soluble in the used digestive system and required heating to achieve complete solubility. Thus, digestive NMR was only used as a preliminary method for linker exchange determination for the nitro-functionalized SALE products. LeZIF8-NO₂Im shows the highest linker exchange (~55%) after 24 h compared to LeZIF8-ClIm24h (29%), LeZIF8-BrIm24h (19%), LeZIF8-CF₃bIm24h (4%), and LeZIF8-SHbIm24h (2%). CF₃bIm and SHbIm SALE products gave low exchange percentages (<10%) due to their bulky size, limiting the exchange to only the surface of nZIF-8. Thus, NO₂Im is the most suited ligand for SALE of ZIF-8.

The linker exchanges of LeZIF8-SHbIm and LeZIF8-NO₂Im products were further increased by time-resolved SALE reactions of 24–60 and 24–120 h, respectively. The effect of increasing the reaction time on the linker exchange of nZIF-8 with SHIm and NO₂Im is observed as a relative decrease in the amount of mIm protons and an increase in the number of SHIm and NO₂Im (Supporting Information Figures S7 and S8). The linker exchange rates for 2-mercaptopenimidazole and 2-nitroimidazole both increased with time, reaching a maximum exchange of 7.2 and 81% after 60 and 120 h, respectively.

The digestive ¹H NMR spectrum of LeZIF8-SHbIm (Figure 1f; Supporting Information Figure S8) shows an overlap of the benzylic protons of the SHbIm linker (marked i) with the spinning sidebands of the CH==CH singlet of mIm. This overlap could cause the calculated exchange percentages to be lower than expected. Thus, the exchange percentages of the LeZIF8-SHbIm products were further verified using inductively coupled plasma (ICP), which indeed showed a higher
SHIm content of 4.25, 6.82, and 9.93% for the 24, 48, and 60 h SALE reactions, respectively (Table 3).

2.2.2. Solid-State $^{13}$C NMR. Solid-state $^{13}$C NMR for LeZIF8-BrIm$_{24h}$ (19%), LeZIF8-ClIm$_{24h}$ (29%), and LeZIF8-CF$_3$Im$_{24h}$ (4%) (Supporting Information Figure S9) was not useful for quantitative analysis due to their low exchange percentages. The high linker exchange observed for LeZIF8-NO$_2$Im from digestive NMR led to the use of solid-state $^{13}$C NMR to confirm the exchange percentages.

The solid-state $^{13}$C NMR of LeZIF8-NO$_2$Im (Figure 2) have five distinct peaks at 16.8, 127.2, 134.1, 154.2, and 165.5 ppm corresponding to CH$_3$ (mIm), CH═CH (mIm), CH═CH (NO$_2$Im), C=N−C (mIm), and C=N−C (NO$_2$Im) carbon atoms, respectively. The exchange percentages were determined from the ratio of CH═CH (mIm) and CH═CH (NO$_2$Im) peak intensities/integrals. These exchange percentages are lower by about 10% at low exchange ratios and are similar to those determined from digestive NMR after 72 h of SALE. As with the digestive NMR results, the exchange ratios begin to stabilize after 3 days, reaching a maximum of 81% after 5 days, slightly lower than the 85% determined from digestive $^1$H NMR (Figure 3). Thus, digestive $^1$H NMR is suited for determining low linker exchange rates (<60%), while solid-state $^{13}$C NMR is apt with high linker exchanges.

2.2.3. PXRD. The PXRD pattern of all SALE products are identical to the SOD pattern of the synthesized nZIF-8 (Supporting Information Figure S3) Thus, the SOD topology of nZIF-8 is maintained during all SALE reactions, as confirmed by the presence of the main peaks of the SOD pattern at $2\theta$ = 7.26, 10.18, 12.65, and 17.93° for all SALE products. The PXRD patterns also show that the mixed ligand nZIF-8 derivatives are highly crystalline and structurally similar to the mother nZIF-8. The extended SALE time of LeZIF8-SHIm led to a decrease in crystallinity as indicated with the weakening of the peak intensity with increasing SALE time (Supporting Information, Figure S4), confirming the structural
Figure 4. TEM images and particle size distribution of (a) LeZIF8-BrIm$_{24h}$ (19%), (b) LeZIF8-SHIm$_{40h}$ (7%), (c) LeZIF8-ClIm$_{24h}$ (29%), and (d) LeZIF8-NO$_2$Im$_{24h}$ (54%).

Figure 5. N$_2$ isotherms at 77 K of (a) nZIF-8, (b) LeZIF8-SHbIm$_{24h}$ (2%), (c) LeZIF8-CF$_3$bIm$_{168h}$ (8%), (d) LeZIF8-ClIm$_{24h}$ (29%), (e) LeZIF8-BrIm$_{24h}$ (19%), and (f) LeZIF8-NO$_2$Im$_{24h}$ (54%). (● = adsorption and × = desorption cycle).
degradation of the MOF due to the acidic thiol substituent. SALE times longer than 60 h was thus not pursued in the case of 2-mercaptobenzimidazole. PXRD patterns of LeZIF8-NO2Im SALE products with up to 80% (or 4 days of SALE) linker exchanges showed similar intensities and thus crystallinity to that of nZIF-8 (Supporting Information, Figure S5a−d). Longer (5 days) SALE with NO2Im resulted in stronger PXRD peak intensities indicating an improved product crystallinity (Supporting Information, Figure S5e).

2.2.4. Transmission Electron Microscopy. The average size of the synthesized ZIF-8 starting material was determined to be 25 nm with a range of 15−34 nm from transmission electron microscopy (TEM) images. TEM images of all SALE products show that the spherical shape of nZIF-8 is maintained, consistent with the SOD topology of the mixed-linker ZIFs (Supporting Information, Figure S2). TEM images of SALE products with ClIm, BrIm, CF3bIm, and SHbIm linkers showed a slight increase in the particle size, with average sizes between 38 and 51 nm (Figure 4a−c). The bulky CF3bIm- and SHbIm-exchanged SALE products did not result in a noticeable increase due to low linker exchange percentages attained. The nitro-functionalized SALE products showed a dramatic size increase, with an average of 148 nm after 24 h of SALE (Figure 4d). The large particle size can be attributed to the high linker exchange (55%), determined from solid-state 13C NMR. The general increase in the particle size of the mixed-linker ZIFs can be attributed to the formation of core−shell morphologies, where the SALE starts from the external surface of the MOF.23

2.2.5. Porosity Analyses. Porosity studies on all activated mixed-linker SALE products with N2 at 77 K gave typical type-1 isotherms, retaining the microporosity of nZIF-8 (Table 1, Figure 5). Application of SALE generally resulted in decreased porosity compared to that of nZIF-8. LeSHbIm SALE products resulted in the highest BET surface areas (1625−1693 m2 g−1), despite the low yields (Table 1, Supporting Information Figure S11). Moreover, increased SALE time with SHbIm led to improved porosity and external surface area, attaining slightly lower BET surface area (1693 m2 g−1) than that of nZIF-8 after 60 h of exchange (9.93%). The BrIm, ClIm, and CF3bIm exchanged SALE products indicated relatively low BET surface areas of 1405, 1450, and 1525 m2 g−1, respectively, compared to that of nZIF-8 starting material. The t-plot external surface area of the halogenated SALE products increased with decreasing particle size as determined from TEM images (Table 1, Figure 5c−e). LeZIF8-CF3bIm168h (8%) with an average size of 38 nm attained an external surface area of 221 m2 g−1. Noticeable hysteresis

Table 1. Porosity Analysis (BET, t-plot, and Micropore Surface Areas as Well as Micropore Volume by N2 Adsorption at 77 K) and Low-Pressure CO2 Uptake at 273 K of all ZIF-8 Derivatives

| compound (exchange %) | BET SA (m2 g−1) | t-plot external SA (m2 g−1) | micropore SA (m2 g−1) | micropore volume (cm3 g−1) | CO2 quantity adsorbed (cm3 g−1) |
|------------------------|----------------|-----------------------------|---------------------|---------------------------|--------------------------------|
| nZIF-8                 | 1777           | 268                         | 1504                | 0.56                      | 38.3                           |
| LeZIF8-BrIm12h (19%)   | 1405           | 144                         | 1261                | 0.47                      | 46.8                           |
| LeZIF8-ClIm12h (29%)   | 1550           | 121                         | 1428                | 0.48                      | 47.1                           |
| LeZIF8-CF3bIm12h (8%)  | 1562           | 221                         | 1340                | 0.49                      | 43.3                           |
| LeZIF8-SHbIm14h (4.5%) | 1655           | 147                         | 1478                | 0.49                      | 50.5                           |
| LeZIF8-SHbIm48h (8.5%) | 1655           | 190                         | 1464                | 0.53                      | 61.3                           |
| LeZIF8-SHbIm60h (9.9%) | 1693           | 214                         | 1479                | 0.58                      | 87.3                           |
| LeZIF8-NO2Im12h (54%)  | 1161           | 107                         | 1054                | 0.37                      | 76.9                           |
| LeZIF8-NO2Im48h (64%)  | 1285           | 101                         | 1184                | 0.45                      | 78.7                           |
| LeZIF8-NO2Im72h (77%)  | 860            | 92                          | 768                 | 0.30                      | 86.0                           |
| LeZIF8-NO2Im96h (70%)  | 897            | 84                          | 812                 | 0.31                      | 88.8                           |
| LeZIF8-NO2Im120h (81%) | 1228           | 83                          | 1145                | 0.43                      | 97.6                           |

aExchange percentages from ICP-OES measurements.
Loops are observed with the desorption cycle of LeZIF8-ClIm24h (29%) and LeZIF8-CF3bIm168h (8%) due to capillary condensation.

LeNO2Im SALE products resulted in the most drastic drop in porosity due to the high (54−81%) linker exchange with NO2Im (Table 1, Supporting Information Figure S12). Time-resolved SALE study showed a drop in porosity for the first 3 days of SALE reactions, with LeNO2Im72h (77%) reaching a low BET surface area of 860 m2 g−1 with a micropore volume of 0.3 cm3 g−1. Longer SALE reactions led to improved porosity results, with LeNO2Im120h (81%) recording the highest porosity of the NO2Im SALE series with a BET surface area of 1228 m2 g−1 and a micropore volume of 0.43 cm3 g−1, respectively. This is consistent with the observed improvements in the crystallinity of LeNO2Im120h (81%) (Supporting Information, Figure S5e). LeNO2Im SALE products also showed the least external surface area, in line with the large particle size observed in TEM images (Figure 4).

2.2.6. CO2 Adsorption. Carbon dioxide adsorption of mixed-linker ZIFs (SALE products) were measured at 273 K under low-pressure conditions (0−1 bar) and compared to the CO2 capacity of synthesized nZIF-8 (38.3 cm3 g−1) (Figure 6 and Table 1). The −Cl- and −Br-functionlized SALE products showed slight improvements with CO2 adsorptions of 46.8 and 47.1 cm3 g−1, respectively. This corresponds well with the marginally higher electronegativity of the Cl substituent, along with the higher linker exchange of 29% attained compared to 19% of LeZIF8-BrIm24h (19%). LeZIF8-CF3bIm24h (4%) showed the least improvement of all SALE products with regard to CO2 uptake, despite the high electronegativity of the CF3 group. This was initially ascribed to the low linker exchange (4%) since exchange of the bulky CF3bIm linker was limited to the external surface of nZIF-8. However, extended (168 h) SALE with CF3bIm resulted in nearly double the exchange percentage achieved after 24 h, but it did not yield any significant improvement of CO2 uptake. Thus, the application of SALE with electron-withdrawing CF3bIm is not effective in increasing the CO2 uptake of nZIF-8.

LeZIF8-SHBzIm24h with only 4.25% linker exchange attained a high CO2 uptake of 51.5 cm3 g−1. A time study (24−60 h) of this SALE resulted in a nearly linear increase of CO2 adsorption with increasing SALE time (Figure 7). A maximum CO2 uptake of 87.3 cm3 g−1 was achieved after 60 h of SALE with a low linker exchange of 9.93%. Longer SALE reactions products showed slight improvements with CO2 adsorptions of 46.8 and 47.1 cm3 g−1, respectively. This corresponds well with the marginally higher electronegativity of the Cl substituent, along with the higher linker exchange of 29% attained compared to 19% of LeZIF8-BrIm24h (19%). LeZIF8-CF3bIm24h (4%) showed the least improvement of all SALE products with regard to CO2 uptake, despite the high electronegativity of the CF3 group. This was initially ascribed to the low linker exchange (4%) since exchange of the bulky CF3bIm linker was limited to the external surface of nZIF-8. However, extended (168 h) SALE with CF3bIm resulted in nearly double the exchange percentage achieved after 24 h, but it did not yield any significant improvement of CO2 uptake. Thus, the application of SALE with electron-withdrawing CF3bIm is not effective in increasing the CO2 uptake of nZIF-8.

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Figure 7. CO2 adsorption as a function of the linker exchange percentage for NO2Im- and SHbIm-exchanged SALE products.

Table 2. CO2 Uptake of Selected ZIFs and ZIF-8 Derivatives

| name               | formula                   | topology | CO2 uptake (cm3 g−1) | analysis condition | refs   |
|--------------------|---------------------------|----------|----------------------|--------------------|--------|
| ZIF-8              | Zn(mIm)2                  | SOD      | 38.5                 | 1.2 bar, 273K      | 22     |
| ZIF-68             | Zn(bIm)(NO2Im)            | GME      | 65.0                 | 1 bar, 273 K       | 19     |
| ZIF-69             | Zn(5-ClbIm)(NO2Im)        | GME      | 69.0                 | 1 bar, 273 K       | 19     |
| ZIF-70             | Zn(Im)13(NO2Im)0.67       | GME      | 55.0                 | 1 bar, 273 K       | 20     |
| ZIF-78             | Zn(NO2bIm)(NO2Im)         | GME      | 68.1                 | 1 bar, 273 K       | 17     |
| ZIF-79             | Zn(mblIm)(NO2Im)          | GME      | 34.0                 | 1 bar, 273 K       | 17     |
| ZIF-81             | Zn(brbIm)(NO2Im)          | GME      | 66.7                 | 1 bar, 273 K       | 17     |
| ZIF-82             | Zn(CNIm)(NO2Im)           | GME      | 85.1                 | 1 bar, 273 K       | 17     |
| ZIF-108            | Zn(NO2Im)2                | SOD      | 53.0                 | 1 bar, 273 K       | 25     |
| LeZIF8-NO2Im168h   | Zn(mIm)0.67(NO2Im)0.33    | FRL      | 76.0                 | 1.2 bar, 273K      | 22     |
| LeZIF8-SHBzIm32h   | Zn(mIm)0.73(SHbIm)0.24    | SOD      | 77.2                 | 1.2 bar, 273K      | 22     |
| LeZIF8-PhIm       | Zn(mIm)0.37(PhIm)0.62    | SOD      | 49.9                 | 1.2 bar, 273K      | 22     |
| LeZIF8-NH4bIm2h    | Zn(mIm)0.4(NH4)0.62      | SOD      | 48.2                 | 1.2 bar, 273K      | 22     |
| LeZIF8-ClIm24h(29%)| Zn(mIm)0.5(ClIm)0.5      | SOD      | 47.1                 | 1.2 bar, 273K      | 22     |
| LeZIF8-BrIm24h(4%) | Zn(mIm)0.26(BrIm)0.74    | SOD      | 46.8                 | 1.2 bar, 273K      | 22     |
| LeZIF8-CF3bIm24h   | Zn(mIm)0.26(CF3bIm)0.74  | SOD      | 43.3                 | 1.2 bar, 273K      | 22     |
| LeZIF8-SHBzIm24h   | Zn(mIm)0.73(SHbIm)0.24   | SOD      | 87.3                 | 1.2 bar, 273K      | 22     |
| LeZIF8-NO2Im120h(81%) | Zn(mIm)0.38(NO2Im)1.62 | SOD      | 97.6                 | 1.2 bar, 273K      | 22     |

*This work.*
were not ideal since the acidic nature of the SHbIm linker resulted in structural degradation of the MOF and low yields.  

LeZIF-8: NO2Im,sh shows the highest improvement of all SALE products after 24 h of SALE, with a CO2 uptake of 76.9 cm3 g−1. This is even more remarkable, given its lower BET surface area (1161 m2 g−1) and external surface area (107 m2 g−1) compared to all other SALE products. A time-resolved study (24−120 h) SALE of nZIF-8 with NO2Im shows that CO2 uptake increases linearly with reaction time and linker exchange percentage, reaching a maximum of 97.6 cm3 g−1 after 120 h (Figure 6, Table 1). This is almost a threefold increase in CO2 adsorptions of the unmodified nZIF-8 and the highest CO2 uptake of all reported ZIF derivatives at low-pressure conditions, surpassing the 85 cm3 g−1 attained by ZIF-82 with NO2Im and CNIm linkers (Figure 6 and Table 2).  

The CO2 uptakes of the mixed-linker products show that enhanced adsorptions are more dependent on the functionality of the linker rather than the surface area (BET and t-plot external surface area) of the MOF. The enhanced CO2 uptakes of the SALE products can be attributed to the electron-withdrawing groups (EWGs)/functionality of the newly introduced linkers. EWG increases the electrostatic/Van der Waal interactions between the ZIF and CO2 molecules, where the locally diminished electron density causes the slightly polar CO2 molecules to be attracted by the MOF.  

LeZIF-8: NO2Im results in an additional Lewis acid−base interaction between CO2 and the nitro group, leading to further enhancement in CO2 uptakes. The dramatic CO2 uptakes of LeZIF-8: SHbIm is due to the enhanced binding of CO2 molecules to the thiol functional groups and lower adsorption energies of SH containing ZIF unit cells, as shown by the theoretical work done by Bolotov et al. and Tsai et al., respectively.  

4. CONCLUSIONS

ZIF-8 is a potent CO2 absorbent, whose absorption capacity for CO2 can be increased by a factor of up to 2.5 by postsynthetically replacing more than 80% of its 2-methylimidazolate ligands by 2-nitromidazolate using a method called SALE.  

Functionality imidazoles such as 2-nitromidazole (NO2Im), 2-chloroimidazole (ClIm), 2-bromomidazole (BrIm), 2-trifluoromethylbenzimidazole (CF3-bIm), and 2-mercaptobenzimidazole (SHbIm) were successfully incorporated in the nZIF-8 structure via SALE while maintaining the SOD topology of nZIF-8. Linker exchange percentages were controlled by the synthesis time and determined via digestive 1H NMR and solid-state 13C NMR.  

All mixed-linker nZIF-8 SALE products had improved CO2 uptake when compared to nZIF-8. The halogenated (−Cl, −Br, and −CF3) imidazolate linkers resulted in moderate (11−22%) improvement in CO2 uptake, while SALE with 2-mercapto-benzimidazole (SHbIm) and 2-nitromidazole (NO2Im) improved the CO2 uptake with up to 128 and 155%. The latter is so far the highest of all reported low pressure CO2 uptakes by a ZIF derivative.  

5. EXPERIMENTAL SECTION

5.1. Materials and Equipment. All chemical reagents were purchased from Sigma-Aldrich, with the exception of 2-nitromidazole, which was obtained from Ambeed, USA. All solvents were purchased from Merck. Chemicals and solvents were used without further purification, unless stated otherwise.

PXRD patterns were collected on a Bruker D2 PHASER powder X-ray diffractometer at room temperature, employing a flat plate sample holder and Cu radiation (λ = 1.54 Å). Diffraction patterns were collected in the range 5−50° for 2θ, with a step size of 0.1° and a counting time of 2 s per step. 1H NMR spectra were measured on a 300 MHz Bruker Fourier NMR spectrometer with a 5 mm 13C/1H high-resolution NMR probe equipped with a Z gradient coil. The 1H chemical shifts are reported relative to SiMe4 at 0.0 ppm as the internal standard, where applicable. Soluble compounds were dissolved in dimethyl sulfoxide, unless stated otherwise. 13C Solid-state NMR spectra were measured on a Bruker 400 MHz AVANCE III NMR spectrometer with a 4 mm VTN multinuclear double-resonance-magic-angle spinning probe operating at 25 °C having a 13C frequency of 100.61 MHz. All infrared spectra were measured on a Thermo Scientific Nicolet iS50 ATR infrared spectrometer with OMNIC v9.2.86 software from 500−4000 cm−1. Shimadzu ICP−MS 7100 ICP−optical emission spectrometry (ICP−OES) with a radial-sequential plasma spectrometer was used for the wet chemical analysis. TGA were performed on a METTLER TOLEDO TGA/SDTA851 analyzer under an N2 atmosphere, and the data were analyzed with METTLER STARe Evaluation software.  

All porosity and surface area measurements were performed on a Micromeritics ASAP 2020 surface area and porosity analyzer, and the data were analyzed with ASAP 2020 V2.0 for physisorption with nitrogen and carbon dioxide. Nitrogen adsorption was measured with a relative pressure at 77 K, and carbon dioxide was measured with an absolute pressure at 273 K. A typical amount of ~40 mg was used for each analysis with the warm and cold free space determined separately with helium. Porosity results were refined by MicroActive V1.01 software. TEM was performed with a Philips (FEI) CM100 equipped with a MegaView III digital camera. TEM pictures were analyzed utilizing Soft Imaging System (analySIS) software.  

5.2. Synthesis of ZIF-8 Nanoparticles. nZIF-8 was synthesized using an adopted procedure from the literature.  

Zn(NO3)2·4H2O (1.3050 g, 5 mmol) was dissolved in methanol (150 cm3) and heated to 60 °C with stirring. This solution was rapidly added to a solution of 2-methylimidazole (3.284 g, 40 mmol) that was dissolved in methanol (150 cm3) and heated to 60 °C. The formed nZIF-8 microcrystals were then isolated by centrifugation (8500 rpm, 30 min, 15 °C), washed with methanol (3 × 100 cm3), and DMF (2 × 100 cm3) and dried overnight and activated in vacuum at 150 °C to yield nano-ZIF-8 as a white powder (0.5715 g, 44.7%).

5.3. SALE of ZIF-8. A general SALE procedure was adopted from the literature.  

nZIF-8 (0.300 g, 1.306 mmol) was suspended in solvent I (30 cm3) with an ultrasonic probe for 3 min and transferred into a Teflon cup in a stainless steel reactor. Consequently, the functionalized imidazoles was then dissolved in solvent II (30 cm3) and mixed with the nZIF-8 suspension. The reactor was sealed and heated to the desired temperature for a set time. After cooling, the nanocrystals were isolated by centrifugation (8500 rpm, 30 min, 15 °C), washed with methanol (3 × 150 cm3), and DMF (2 × 100 cm3) for 2-nitromidazole SALE products. The mixed-linker nZIF-8 derivative was then air dried overnight and activated in vacuum at 150 °C. Yields and reaction conditions for the SALE
Table 3. SALE Reaction Conditions, Product Yields, and Linker Exchange Percentages (Determined by Digestive ¹H NMR and ICP-OES® for the SHbIm Linker)

| imidazole derivative | reaction time (h) | temp (°C) | solvent I         | solvent II        | yield (%) | linker exchange (%) |
|----------------------|-------------------|-----------|-------------------|-------------------|-----------|---------------------|
| 2-mercapto-benzimidazole (SHbIm) | 24                | 100       | n-butanol         | n-butanol         | 32        | 2 (4.25*)           |
|                      | 48                |           |                   |                   | 27        | 6 (6.82*)           |
|                      | 60                |           |                   |                   | 30        | 7 (9.93*)           |
| 2-chloroimidazole (ClIm) | 24                | 60        | methanol          | methanol          | 97        | 29                  |
| 2-bromoimidazole (BrIm) | 24                | 60        | methanol          | methanol          | 95        | 19                  |
| 2-trifluoromethyl-benzimidazole (CF3BIm) | 24            | 60        | methanol          | methanol          | 82        | 4                   |
|                      | 168               |           |                   |                   | 84        | 7                   |
| 2-nitroimidazole (NO2Im) | 24                | 60        | methanol          | DMF               | 83        | 54                  |
|                      | 48                |           |                   |                   | 83        | 64                  |
|                      | 72                |           |                   |                   | 90        | 77                  |
|                      | 96                |           |                   |                   | 79        | 78                  |
|                      | 120               |           |                   |                   | 80        | 81                  |

procedures are summarized in Table 3, and Scheme 1 presents an overview of all systems prepared.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c01130.

List of all reported CO₂ uptakes of ZIF derivatives to date; FTIR spectra; PXRD patterns; digestive ¹H NMR; solid-state ¹³C NMR; TGA thermograms; N₂ and CO₂ isotherms of nZIF-8; and SALE products (PDF)

■ AUTHOR INFORMATION

Corresponding Author
Ernst H. G. Langner — Department of Chemistry, University of the Free State, Bloemfontein 9300, South Africa; orcid.org/0000-0002-3633-1835; Email: langneeh@ufs.ac.za

Authors
Yuel W. Abraha — Department of Chemistry, University of the Free State, Bloemfontein 9300, South Africa; orcid.org/0000-0002-4667-3396; Email: langneeh@ufs.ac.za
Chih-Wei Tsai — Department of Chemistry, University of the Free State, Bloemfontein 9300, South Africa; Department of Physics, University of the Free State, Bloemfontein 9300, South Africa
J. W. Hans Niemantsverdriet — Department of Chemical Engineering and Chemistry, Schuit Institute of Catalysis, Technische Universiteit Eindhoven, Eindhoven 5600 MB, Netherlands

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c01130

Notes
The authors declare no competing financial interest.

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