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Enhanced ZIF-8-enabled colorimetric CO₂ sensing through dye-precursor synthesis

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ABSTRACT

The accumulation of carbon dioxide (CO₂) within enclosed spaces, along with volatile organic compounds, under certain humidity, temperature, and ventilation conditions is associated with detrimental human health symptoms such as fatigue. Color-based chemical sensing is a promising approach to detect CO₂ levels relevant to indoor air quality through producing fast, quantifiable output visible to the naked eye. In a prior work, a colorimetric gas sensor was fabricated through synthesizing the metal-organic framework, ZIF-8, as the adsorbent, followed by post-synthetic mixing with a dye, phenol red (PSP), and primary amine, ethylenediamine (ED). While this sensor (termed PSP-ED/ZIF-8) maintained its structural integrity in atmospheric conditions and exhibited an increasing fuchsia-to-yellow color change with increasing CO₂ levels in dry environment, the colorimetric response greatly suffered in the presence of humid CO₂. In this work, a significantly improved colorimetric CO₂ sensor (referred to as ED/PSP:ZIF-8) is accomplished through *directly* incorporating phenol red in the ZIF-8 metal and linker precursor solutions and then blending with ethylenediamine. MATLAB-generated color distributions and in-situ ultraviolet-visible (UV-Vis) spectroscopic studies quantitatively demonstrate an enhanced colorimetric gas response of ED/PSP:ZIF-8 compared to that of PSP-ED/ZIF-8 across an important range of CO₂ for indoor air quality monitoring (500 - 3500 ppm) and across a range of humidity. The new sensor also exhibits high selectivity to CO₂ compared to select volatile organic compounds, such as acetone and ethanol, which contribute to human health symptoms experienced indoors. The enhanced performance is attributed to the proposed incorporation of phenol red within ZIF-8, while maintaining the chemical stability of the MOF.

1. Introduction

While global industrial operations continue to account for scores of pollutants emitted into the atmosphere, the associated consequences for human and environmental health remain a major concern in the 21st century [1,2]. These burgeoning emissions—consisting of various species such as particulate matter, nitrogen dioxide, and carbon dioxide (CO_2)—impose deleterious conditions on the human cardiovascular and respiratory systems, which can develop into acute diseases resulting in shortened life expectancy [1,2]. Of these airborne molecules, CO_2 has been a target gas of particular interest to scientists whose various studies

in such areas as chemical sensing [3] and separation and capture [4] elucidate chemical and physical processes that inform relationships between CO_2 and the collective wellness of life on the planet [1].

Given that humans spend most their lives in enclosed spaces, such as homes [5] and commercial buildings [6], indoor air quality should be optimized for their overall wellbeing. As a natural product of human metabolism [5], CO_2 is a common species existent within indoor settings. However, the accumulation of certain levels of CO_2 indoors introduces specific harms to occupants [5,6]. While indoor CO_2 levels have been as low as ~400 parts per million (ppm) in certain environments, prior research has linked prolonged exposure to concentrations

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in the range of 1000 and 2500 ppm with reduced decision-making performance [7]. Since indoor CO₂ concentrations can feasibly reach 3000 ppm [8] (depending on the number of occupants and ventilation rate), the U.S. Occupational Health and Safety Administration (OSHA) recommends a maximum of 5000 ppm CO₂ as a time-weight average (TWA) for an 8 hr workday [7]. However, discrepancies exist in the literature on whether pure CO_2 (or its airborne coexistence with other bioeffluents, such as volatile organic compounds, VOCs) is responsible for compromised human cognitive function indoors [8-10]. Despite these contentions, previous studies attribute indoor CO2, VOCs, temperature, humidity, and improper ventilation collectively to sick building syndrome (SBS), which defines a group of symptoms including headaches and decreased productivity [11,12]. In recent decades, efforts to minimize energy consumption have led to decreased ventilation rates in some indoor spaces, resulting in the accumulation of CO₂ and associated pollutants linked to SBS [7,9]. Moreover, rising atmospheric CO₂ levels (reported to have approached near 420 ppm in 2021) from industrial activities vented indoors could further contribute to SBS symptoms for building occupants [13].

The ongoing coronavirus disease 2019 (COVID-19) pandemic has necessitated increased periods indoors to prevent the spread of the virus [14–16]. In certain cities with lockdown measures, residents experienced prolonged exposure to CO₂, VOCs, and other indoor pollutants, which is ascribed to the heightened use of cleaning agents and insufficient ventilation from civic strategies to conserve energy [7,9,14]. Of those who contracted and recovered from COVID-19, some have developed "Long-COVID," which describes the persistence of symptoms post-initial infection, such as fatigue, loss of smell, shortness of breath, confusion, and chest pain [17,18]. As more COVID-19 variants emerge and scientists ascertain their long-term effects on human sensory capabilities, the design and operation of optimal indoor pollutant sensors is imperative for the improvement of human wellness in enclosed spaces [17,18].

This paper focuses on CO_2 as a purported indoor air pollutant. Toward detecting indoor CO_2 levels, the desired sensor should be low-cost, simple to operate, non-responsive to other indoor pollutants, and capable of exhibiting a signal clear to the naked eye [19]. The common indoor CO_2 monitor is based on the nondispersive infrared (NDIR) technique, which screens wavelength absorption in the infrared region of the electromagnetic spectrum resonant with the IR-active vibrational modes of target gases [20]. While NDIR technologies demonstrate longevity, these devices characteristically have been limited by their bulky dimensions and high cost [20,21]. Colorimetry, however, offers simple and scalable fabrication, low-cost operation, quick response times, and obvious signal to the human eye [22,23].

In a previous paper [24], we introduced a colorimetric CO_2 sensor composed of a porous adsorbent, a dye, and a primary amine (in methanol) drop-cast on cellulose filter paper. The adsorbent was based on a metal-organic framework (MOF), which constitutes a class of porous, crystalline materials composed of metal nodes coordinated by organic linkers with large surface areas and tunable pore chemistries suitable for applications in chemical sensing [24,25]. For this application, we selected a zeolitic imidazolate framework (ZIF), which is a class of MOFs consisting of metal cations tetrahedrally-coordinated to imidazolate linkers structured with "zeolite-like" topologies [24,26,27]. The specific ZIF, ZIF-8, is composed of zinc (Zn^{2+}) cations coordinated to 2-methylimidazolate (mIm⁻) linkers with 3.4 Å six-member pore windows and 11.6 Å pore cages accessible to small molecules such as CO₂ [24,26,27]. In addition to its simple room temperature synthesis and chemical stability, ZIF-8 was selected because of its documented selectivity to CO_2 in binary gas mixtures [26,27], as well as prior simulations associating preferential CO2 adsorption sites with positions near the imidazolate linker [24,28]. In addition to the ZIF-8 adsorbent, the colorimetric gas sensor consisted of (a) the dye, phenol red (PSP), whose color transitioned from fuchsia ($\lambda_{max}\sim 570$ nm) in basic environment to yellow ($\lambda_{max} \sim 443$ nm) in acidic environment [24,29,30], as well (b) the primary amine, ethylenediamine [ED], which has been used in other studies toward enhanced CO_2 absorption and adsorption [24,31].

The first-generation colorimetric CO₂ sensor, termed PSP-ED/ZIF-8, demonstrated several feats. Upon post-synthetically mixing ZIF-8 with PSP and ED, the structural integrity of ZIF-8 was maintained for four weeks [24]. Colorimetric assays demonstrated a sensitivity to dry CO₂ levels as low as 700 ppm, with increasing purple-to-yellow color intensity as CO₂ levels were increased to 7500 ppm [24]. Moreover, in the absence of ZIF-8, no color change was observed on cellulose filter paper [24]. The change in color intensity was quantified as a function of CO₂ concentration using an *ex-situ* ultraviolet-visible (UV-Vis) spectroscopic technique, which used the 443 and 570 nm reflectance (% R) peaks attributed to phenol red [24]. However, in the presence of humidity, both colorimetric assays and *ex-situ* UV-Vis spectroscopic analyses exhibited a largely diminished colorimetric CO₂ response [24].

In this paper, we present a second-generation sensor (referred to as ED/PSP:ZIF-8) based on dye-precursor synthesis, which involves directly mixing phenol red with the ZIF-8 metal and linker precursor solutions to form dye-loaded ZIF-8 (called PSP:ZIF-8), and then incorporating ethvlenediamine to complete the sensor. Given the realistic concentrations of CO₂ that can develop in enclosed spaces with varied occupants and ventilation [8], the sensors are exposed to $540-3500 \text{ ppm } \text{CO}_2$ (in both dry and humid conditions). Furthermore, in contrast to the ex-situ UV-Vis spectroscopic technique shown in the prior work [24], here we employ an in-situ UV-Vis spectroscopic method toward a more accurate and efficient colorimetric gas sensing. In-situ UV-Vis spectroscopy and MATLAB-generated color parsing quantitatively reveal an improved colorimetric CO2 response (across humidity) of the ED/PSP:ZIF-8 material compared to that of the PSP-ED/ZIF-8. To quantitatively assess the colorimetric CO₂ sensing fitness of ED/PSP:ZIF-8 in the presence of other indoor air pollutants, in-situ UV-Vis spectroscopy and optical measurements are also conducted using acetone and ethanol, which illustrate the negligible impact of VOCs on the sensor's affinity for CO₂.

2. Experimental section

2.1. Sensing material synthesis

PSP-ED/ZIF-8 synthesis follows the process described previously [24]. 1.04 g of zinc nitrate hexahydrate $[Zn(NO_3)_20.6 H_2O;$ Fischer Scientific] and 1.04 g of 2-methylimidazole (Hmim, 99%, Sigma-Aldrich) are sonicated in 60 ml of methanol (Fischer Chemical) in separate beakers [24]. Then, the 2-methylimidazole methanolic solution is slowly poured into the zinc nitrate hexahydrate solution and allowed to react overnight in an unstirred environment [24]. The resulting ZIF-8 crystals are obtained *via* centrifugation (12,000 rpm for 5-min) and washed three times in methanol [24]. Once the ZIF-8 crystals are collected, 400 µl of ethylenediamine (Sigma-Aldrich) are poured into 19.6 ml of methanol, and 10 mg of phenolsulfonpthalein (Acros Organics) are dissolved into this solution [24]. Pristine ZIF-8 crystals are then dissolved into this mixture to form an 80 mg/ml solution of PSP-ED/ZIF-8 [24]. The fabrication process is shown in Fig. S1.

For the synthesis of ED/PSP:ZIF-8, 2.08 g of zinc nitrate hexahydrate $(Zn(NO_3)_2.6H_2O;$ Fischer Scientific) and 2.08 g of 2-methylimidazole (Hmim, 99%, Sigma-Aldrich) are dissolved in 120 ml of methanol (Fischer Chemical) in separate beakers through prolonged sonication (Crest Ultrasonics). Then, 60 mg of phenol red are added to the zinc precursor solution and 60 mg of phenol red are added to the imidazolate precursor solution. After sonicating these solutions, the phenol red/imidazolate precursor solution is poured into the phenol red/zinc precursor solution and allowed to react at room temperature for 48 h (with no stirring). The resulting crystals, termed PSP:ZIF-8, are separated from the methanolic supernatant through slowly pouring into a disposable scintillation vial (Trident technology (Jiangsu)Co., Ltd.). Then, a 2% ethylenediamine (99%, Sigma-Aldrich) solution (% v/v) in methanol is produced by adding 100 µl of ethylenediamine to 4.9 ml of methanol.

This solution is then blended with the PSP:ZIF-8 crystals to form an 80 mg PSP:ZIF-8/ml solvent mixture. This fabrication process is displayed in Fig. S2.

2.2. Materials characterization methods

Powder X-ray diffraction (PXRD) patterns are accomplished using a Bruker diffractometer (Cu *K*- α radiation, $\lambda = 1.54$ Å, 40 kV, 40 mA) [24]. Morphological information about the synthesized materials is acquired using scanning electron microscopy, SEM (Zeiss Gemini Ultra55 Field Emission SEM) at an operating voltage of 5 kV. Samples are drop-cast on silicon chips, and sputter coated with Au (10.0 nm) for 7-min to provide appreciable electrical conductivity prior to collecting SEM imaging data. ZIF-8-based sensors are dispersed in isopropyl alcohol by bath sonication for 15 min and drop-cast onto copper/lacey carbon grids for transmission electron microscopy (TEM) imaging. TEM imaging is carried out on a JEOL-2010 microscope operated at 80 keV. Particle size distributions are completed using Fiji imaging software. Fourier transform infrared (FTIR) transmittance data are collected (spectral range: 4000–400 cm⁻¹; resolution: 4 cm⁻¹) using a Bruker Vertex80 FTIR instrument. Brunaeur-Emmett-Teller (BET) surface analysis and pore size distribution measurements (N2 at 77 K) are accomplished using a Micromeritics Gemini VII Surface Area and Porosity instrument. Prior to BET measurements, 80 mg/ml solutions of ZIF-8-based samples are centrifuged, separated from the supernatant, and dried at room temperature (21.5 \pm 0.3 °C at 49.8 \pm 1% RH). The resulting powders are then degassed at 150 °C overnight using a Micromeritics VacPrep 061 Sample Degas System.

2.3. Gas sensing characterization

In-situ ultraviolet-visible diffuse reflectance spectroscopy with an Evolution 300 UV-Vis (Thermo Scientific) spectrophotometer (spectral range: 400–600 nm; bandwidth: 1.0 nm; scan speed: 60 nm/min) is used to quantify the color change upon controlled exposure to CO₂. Sample deposition onto cellulose filter paper (VWR North American) and insertion into the spectrophotometer closely follows the procedure reported in the prior work [24]. Specifically, a 0.7 cm \times 0.7 cm piece of cellulose filter paper is attached to the UV-Vis sample enclosure *via* double-sided carbon black tape (Ted Pella, Inc.), inserted into the UV-Vis chamber, and used as a reflectance (% R) background [24]. Then, 20 ul of PSP-ED/ZIF-8 or ED/PSP:ZIF-8 is drop-cast on another piece of 0.7 cm \times 0.7 cm cellulose filter paper, dried for 120 s, and placed into the UV-Vis spectrophotometer for *in-situ* target gas exposure [24].

The in-situ UV-Vis measurements under controlled CO2 exposures proceed as illustrated in Fig. S3. A CO₂ cylinder (Airgas; 0.995 mol% CO2 in N2), dry air cylinder (Praxair; 79 mol% N2; 21 mol% O2), and acetone cylinder (Airgas; 0.1001 mol% (CH₃)₂CO in N₂) are attached to a gas line. To achieve the desired CO₂ levels, the gas valves (shown in red) are opened and needle valves particular to the inlet CO₂ and dry air flows are adjusted to attain desired flowrates (plotted in Fig. S4). Once the gases are mixed, they are channeled through either (a) a continuous stream that maintains dry conditions (indicated in Fig. S3 with a downward yellow arrow) or (b) a bubbler to adjust the relative humidity (indicated in Fig. S3 with an upward blue arrow). The resulting mixture is fed into the UV-Vis chamber until steady-state is reached after about 7 min (Fig. S5). The total gas flow rate (set at 300 ml/min) composed of a given concentration of CO2 and air flow rates is measured using an Agilent Technologies ADM2000 Universal Gas Flowmeter. As shown in Fig. S3, each CO₂ concentration (and corresponding humidity value) is calibrated with a wireless GasLab Plus CM-501 NDIR sensor (contained within a sealed plastic vessel). Dry and humid conditions are taken to be $0.133\pm0.8\%$ RH and 45.4 \pm 3% RH, respectively, at 23.5 \pm 1 °C.

Once the sensor-coated filter paper is placed inside the UV-Vis spectrophotometer, the sensor is exposed to a specific CO_2 concentration and humidity using the methods described above [24]. After

steady-state is reached, a reflectance (% R) vs. wavelength (nm) profile is collected [24]. Each diffuse reflectance value is then converted into a Kubelka-Munk value, F(R) (shown as Eq. 1), consisting of the absorption coefficient (K) and scattering coefficient (S) [24,32].

$$F(R) = \frac{(1-R)^2}{2R} = \frac{K}{S}$$
(1)

In the diffuse reflectance UV-Vis spectra, phenol red changes color from violet ($\lambda_{max} \sim 570$ nm) under basic conditions to yellow ($\lambda_{max} \sim 443$ nm) under acidic conditions [24,29,30]. For each CO₂ exposure, the ratios of the respective 443 and 570 nm F(R) values are depicted as scatter plots as a function of CO₂ concentration (ppm) [24].

Toward probing the long-term gas sensing performance and sensor stability in variable humidity, additional *in-situ* UV-Vis spectra are collected in which sensors (25 μ l drop-cast on cellulose filter paper) are exposed to 3500 \pm 300 ppm CO₂ (total gas flow rate: 300 ml/min). All trials are collected at room temperature (23.0 \pm 0.8 °C) and in dry (0% RH) and humid (82.0 \pm 5% RH) environments. Colorimetric 443/ 570 nm F(R) ratios are tabulated for up to 120 min of exposure to CO₂. After that, the sensor is exposed to 300 ml/min dry air for 20 min. Subsequently, the dry air is turned off for an additional 20 min. At this time, another "0-min" spectrum is obtained, and the sensor is exposed to 3500 ppm CO₂ again at different times for 120 min. For this experiment, three cycles are collected (in dry and humid environment). Following multiple hours of repeated *in-situ* UV-Vis spectroscopic measurements, ZIF-8 stability on cellulose filter paper is analyzed using FTIR spectroscopy.

To evaluate the effect of VOCs on colorimetric CO₂ sensing, the same *in-situ* UV-Vis dosing experiments (described in Fig. S3) are performed using acetone (Airgas; 0.1001 mol% (CH₃)₂CO in N₂). Given the emergence of nasal, throat, and optic irritation from acetone exposure, the U. S. National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit/time weight average (REL/TWA) for this gas is 250 ppm [33]. In this study, the acetone concentration up to 314 ppm is probed. The acetone flow rate is varied while maintaining a set CO₂ concentration (in 450–3600 ppm range) and a total gas flow rate of 350 ml/min. Eq. 2 demonstrates how these selected acetone flow rates are converted to respective concentrations in ppm.

$$[Ac]_{UV-Vis} = \frac{[Ac]_{cylinder} * Ac_{flowrate}}{TG_{flowrate}}$$
(2)

where:

[Ac]_{UV-Vis} = concentration of acetone in the *in-situ* UV-Vis chamber (ppm)

 $\begin{array}{l} \mbox{[Ac]}_{cylinder} = \mbox{concentration of acetone in the cylinder (1000 ppm)} \\ \mbox{Ac}_{flowrate} = \mbox{flow rate of acetone/nitrogen stream (ml/min)} \\ \mbox{TG}_{flowrate} = \mbox{total gas flow rate entering the UV-Vis chamber (350 ml/min)} \\ \end{array}$

In addition to the *in-situ* UV-Vis spectroscopic technique, optical images of both sensors (in variable CO₂ and humid environments) are obtained and then read into a MATLAB script for subsequent analysis [24]. First, 20 µl of the sensing solutions are drop-cast on cellulose filter paper and allowed to dry in ambient air (453 ± 2 ppm CO₂; $40.6 \pm 2\%$ RH; 27.7 ± 0.7 °C) for 120 s [24]. The same LabView-controlled gas manifold system described in prior work is used for qualitative color change studies, consisting of house air, an evaporator system, pressure swing adsorption dryers, mass flow controllers (Bronkhorst), and target gases [24]. A cylinder of 50,380 ppm CO₂ balanced in nitrogen (Praxair) is used for colorimetric imaging [24]. Toward qualitatively assessing the role of select VOCs on the observed color change (in dry conditions), a 978 ppm ethanol cylinder (Praxair; balanced in nitrogen) and 400 ppm acetone (Praxair; balanced in nitrogen) cylinder are used. Similar to the human health symptoms borne from acetone exposure [33], ethanol is

associated with nasal and optic irritation, resulting in a NIOSH REL/TWA of 1000 ppm [34]. For these colorimetric imaging assays, the total gas flow rate is kept constant at 300 standard cubic centimeters per minute (sccm) and the corresponding humidity values are measured at ambient temperature (27.7 \pm 0.7 °C). Select CO₂ and humidity levels are validated using a wireless GasLab Plus CM-501 NDIR sensor [24].

For a given CO_2 concentration and humidity (or VOC exposure), each sensor is directly exposed for 20 s. Progressive color changes are recorded using a Google Pixel 4 XL smartphone [24]. From these videos, "Before controlled exposure" and "Exposed" images are prepared and downloaded into a MATLAB script as 1.7" x 1.7" squares [24]. Color output is produced as a 162×162 -pixel red-green-blue (RGB) distribution [24]. RGB values are obtained with the Y-axis held constant at pixel 81, with the X-axis sweeping from pixels 60–100 [24].

3. Results and discussion

3.1. Material characterization

Fig. 1 shows the collected PXRD patterns from the simulated pristine ZIF-8 (refcode: VELVOY) [35], synthesized pristine ZIF-8, PSP-ED post synthetically added to ZIF-8 (PSP-ED/ZIF-8), PSP added to ZIF-8 precursor solution (PSP:ZIF-8), and ED added to PSP:ZIF-8 (ED/PSP:ZIF-8). In all samples, the diffraction peaks are consistent with the expected sodalite structure of ZIF-8 reported in the literature [24,36]. However, small peak shifts are observed with the PSP:ZIF-8 and ED/PSP:ZIF-8 materials compared to the pristine ZIF-8 and PSP-ED/ZIF-8 materials. Computational methods examining the structure and stability of ZIF-8 suggest that this observation could be ascribed to emergent defects within the lattice [37], such as from linker vacancies and dangling linkers, which could result in strain of the ZIF-8 lattice when synthesized with PSP. Moreover, the addition of ethylenediamine to form PSP-ED/ZIF-8 and ED/PSP:ZIF-8 produces a change in relative XRD peak intensities compared to those of pristine ZIF-8 and PSP:ZIF-8. As has been observed with metal-organic frameworks loaded with C₆₀ fullerenes [38] and with adsorbed benzene [39], the changes in relative XRD peak intensities between the first- and second-generation sensors may be attributed to the changes in electron density along crystallographic planes upon ethylenediamine incorporation onto the MOF.

SEM images of pristine ZIF-8, PSP-ED/ZIF-8, PSP:ZIF-8, and ED/PSP: ZIF-8 are depicted in Fig. 2. For the pristine ZIF-8 and PSP-ED/ZIF-8, \sim 100 nm nanocrystals are obtained, which is in agreement with



Fig. 1. Powder X-ray diffraction patterns (Cu K- α radiation, $\lambda = 1.54$ Å) of simulated ZIF-8 (VELVOY), pristine ZIF-8, PSP-ED/ZIF-8, PSP:ZIF-8, and ED/PSP:ZIF-8.

reported room temperature methanolic ZIF-8 synthesis with similar metal: linker: precursor molar ratios [24,40]. Upon incorporation of phenol red into the ZIF-8 precursor mixture, however, the PSP:ZIF-8 (and ED/PSP:ZIF-8) crystals formed are significantly larger in size (~400 nm). In addition to the role of the modified duration of MOF synthesis [41], the change in reaction solution composition (with phenol red now mixed with ZIF-8 precursors in methanol) may result in a ZIF-8 growth favoring larger crystals [42]. TEM images for PSP-ED/ZIF-8 and ED/PSP:ZIF-8 are shown in Fig. 3. Whereas the average particle size for PSP-ED/ZIF-8 is 0.11 \pm 0.03 μ m, the ED/PSP:ZIF-8 particles are 0.43 \pm 0.07 μ m.

FTIR transmittance spectra for the gas sensing materials and their constituents are shown in Fig. S6. As listed in Table S1, the observed 421 cm⁻¹ vibrational band in pristine ZIF-8, PSP-ED/ZIF-8, PSP:ZIF-8, and ED/PSP:ZIF-8 is associated with the Zn-N stretch of the ZIF-8. In addition, the bands at 2931 and 3135 $\rm cm^{-1}$ observed in PSP-ED/ZIF-8 and ED/PSP:ZIF-8 samples are ascribed to the aliphatic and aromatic C-H stretches of the imidazolate ligand, respectively [42-44]. The broad band positioned at 3310 cm⁻¹ is assigned to an -OH stretching mode from the methanol solvent [45]. Finally, the bands observed at 3280 and 3355 cm⁻¹ are attributed to N-H stretching modes of ethylenediamine [45,46]. Consistent with the PXRD patterns, these FTIR spectra confirm the formation of ZIF-8, as well as its chemical stability in the presence of phenol red and ethylenediamine for both sensors, PSP-ED/ZIF-8 and ED/PSP:ZIF-8. Moreover, as evidenced via the preserved Zn-N 421 cm⁻¹ mode shown in Fig. S7, both PSP-ED/ZIF-8 and ED/PSP:ZIF-8 remain stable in basic environment over multiple weeks. This chemical stability of ZIF-8 in basic environment is attributed to the linkage of soft imidazolate anions with soft Zn²⁺ cations, which hard-soft acid-base theory predicts an excellent metal-ligand bond strength toward good metal-organic framework stability [24,47].

3.2. Colorimetric analyses in dry environment

Colorimetric responses of PSP-ED/ZIF-8 and ED/PSP:ZIF-8 exposed to 300 sccm dry CO₂ are displayed in Fig. 4. With increasing CO₂ levels, both sensors exhibit an increased yellow intensity. However, compared to the modest responses of the first-generation PSP-ED/ZIF-8 material at 600 ppm CO_2 and above, those of the second-generation ED/PSP:ZIF-8 material indicate a stronger yellow color. Mean RGB intensities for these exposures are provided in Tables 1 and 2 for PSP/ED-ZIF-8 and ED/PSP: ZIF-8, respectively. For the first-generation PSP/ED-ZIF-8 sensor, the average G-values increase and the average B-values decrease with increasing dry CO2 exposure, demonstrating a stronger fuchsia-toyellow colorimetric transition. For the second-generation ED/PSP:ZIF-8 material, the mean R-values and mean G-values both increase with rising dry CO₂ exposures. In alignment with the colorimetric assays depicted in Fig. 4, the mean R- and G-values for the new ED/PSP:ZIF-8 material exposed to 600 ppm CO₂ and above, respectively, are significantly larger than those for the PSP-ED/ZIF-8 material, indicating a stronger color response.

Transient and repeated exposures to 2500 ppm CO₂ are displayed in Fig. S8. Similar to the results of Fig. 4, the ED/PSP:ZIF-8 exhibits a vibrant yellow color compared to that of PSP-ED/ZIF-8, indicating a stronger colorimetric gas response. Both sensors respond to CO₂ within 1 s, and achieve a full color change within 20–30 s. The quick response times, as well as sensitivity to < 1000 ppm dry CO₂ displayed in Fig. 4, are consistent with reported ambient colorimetric CO₂ detection using dye- and tertiary amino alcohol-loaded porous adsorbents [19]. However, whereas the latter sensors are reversible [19], PSP-ED/ZIF-8 and ED/PSP:ZIF-8 only partially recover upon CO₂ removal (as shown in Figs. S4-C and S4-D) and sustain a residual yellow tinge compared to their pre-exposed states.

In addition to the color-based assays, quantitative results from the *insitu* UV-Vis spectra for various CO_2 exposures are presented in Fig. 5. As the CO_2 level increases from 540 to 3350 ppm, the 443 nm F(R) peak



Fig. 2. SEM images for (A) Pristine ZIF-8, (B) PSP-ED/ZIF-8, (C) PSP:ZIF-8, and (D) ED/PSP:ZIF-8. Size bar: 0.2 µm.



Fig. 3. TEM images for (A) PSP-ED/ZIF-8 (size bar: 0.2 µm) and (B) ED/PSP:ZIF-8 (size bar: 0.5 µm).

intensity rises relative to that at 570 nm for the PSP-ED/ZIF-8 material. However, for the new ED/PSP:ZIF-8 material, the 570 nm F(R) peak decreases relative to the 443 nm F(R) peak with increasing CO₂ levels. Colorimetric ratios of the 443 and 570 nm F(R) values *versus* CO₂ level (in ppm) are shown in Fig. 6. For both sensors, the ratios expectedly increase with rising CO₂ concentrations as the fuchsia-to-yellow color transition intensifies. However, as anticipated from the imaged exposures and RGB color distributions, the 443/570 nm F(R) ratios for the ED/PSP:ZIF-8 material are much larger than those of the PSP-ED/ZIF-8 material, similarly revealing a stronger colorimetric response to CO₂ in dry environment.

3.3. Colorimetric analyses in humid environment

Colorimetric profiles of PSP-ED/ZIF-8 and ED/PSP:ZIF-8 exposed to 1500 ppm CO₂ in 0%, 40%, and 80% relative humidity are depicted in Fig. 7. With increasing humidity, while the first-generation sensor scarcely provides a colorimetric CO₂ response at 40% RH and above, the second-generation sensor still exhibits a visible fuchsia-to-yellow transition compared to its "Before controlled exposure" at higher humidity. The effect of humidity on the colorimetric sensitivity to CO₂ is also portrayed in Tables 3 and 4. For the PSP-ED/ZIF-8 material, the R- and G-values both decrease with increasing humidity, with a significantly larger drop observed in the G-values. The ED/PSP:ZIF-8 material also exhibits reduced R- and G-values with increased humidity; however, these R- and G-values are markedly more intense than those of the PSP-



Fig. 4. Colorimetric images of sensors before controlled exposure under 0% relative humidity, exposed to 600 ppm CO₂, and 3500 ppm CO₂. Top row: PSP-ED/ZIF-8 (first-generation sensor). Bottom row: ED/PSP:ZIF-8 (second-generation sensor). Images are taken after 30 s of exposure.

 Table 1

 Mean RGB values for PSP-ED/ZIF-8 exposed to dry CO₂.

Exposure	Mean R-value	Mean G-value	Mean B-value
Before exposure 600 ppm CO ₂ 3500 ppm CO ₂	$205 \pm 0.7 \\ 203 \pm 1.0 \\ 209 \pm 1.0$	$egin{array}{c} 145\pm2.0\ 163\pm1.0\ 169\pm1.0 \end{array}$	209 ± 1.0 187 ± 2.0 183 ± 1.0

Table 2	
Mean RGB values ED/PSP:ZIF-8 exposed to dr	y CO ₂ .

Exposure	Mean R-value	Mean G-value	Mean B-value
Before exposure 600 ppm CO ₂ 3500 ppm CO ₂	$\begin{array}{c} 209 \pm 0.7 \\ 215 \pm 0.3 \\ 218 \pm 0.5 \end{array}$	$\begin{array}{c} 158 \pm 0.7 \\ 188 \pm 0.8 \\ 194 \pm 0.3 \end{array}$	$\begin{array}{c} 191 \pm 1.0 \\ 182 \pm 0.9 \\ 187 \pm 1.0 \end{array}$

ED/ZIF-8 sensor at the same CO_2 concentration and humidity. Similarly, the B-values in dry and humid CO_2 conditions for the second-generation sensor are smaller than those for the first-generation sensor, indicating a stronger fuchsia-to-yellow color change.

Transient and repeated colorimetric imaging assays for PSP-ED/ZIF-8 and ED/PSP:ZIF-8 exposed to 2500 ppm CO_2 in 35% and 60% RH are shown in Figs. S9 and S10, respectively. Similar to their dry exposures, both sensors respond to humid CO_2 within seconds. However, with increased humidity, the colorimetric gas response is suppressed in both sensors (with that of ED/PSP:ZIF-8 outperforming that of PSP-ED/ZIF-8 at both moderate and elevated humidity). Finally, neither sensor completely recovers upon release from humid CO_2 environment, maintaining a slightly different color from its original state following four cycles of humid gas exposure.

Normalized F(R) profiles *versus* wavelength (in nm) are plotted in Fig. 8 as a function of CO₂ concentration under RH of $45.4 \pm 3\%$. As the CO₂ exposures rise from 540 to 3350 ppm, the 443 nm F(R) peak intensity increases relative to that of the 570 nm F(R) peak for both first-and second-generation materials. Fig. 9 depicts these ratios as a function of humid CO₂ level. At any humid CO₂ concentration in this span, the colorimetric response is enhanced for the second-generation ED/PSP: ZIF-8 material relative to the first-generation PSP/ED-ZIF-8 material, with a sharp increase in the yellow intensity at higher CO₂ exposures.

However, compared to colorimetric ratios achieved from the dry gas exposures displayed in Fig. 6, the 443/570 nm F(R) ratios in humid environment are smaller for both first- and second-generation sensors, establishing water as a sustained interferant in the colorimetric gas sensing mechanism [24].

Cyclic in-situ UV-Vis measurements of PSP-ED/ZIF-8 and ED/PSP: ZIF-8 exposed to 3500 ppm CO₂ (in 0% and 80% RH, respectively) are tabulated in Tables S2, S3, S4, and S5. As observed qualitatively from the colorimetric imaging assays, neither sensor fully recovers the 443/ 570 nm F(R) ratio ascribed to its pre-exposed state. The irreversible nature of both sensors upon gas exposure (across humidity) is largely attributed to the gradual evaporation of methanol upon deposition onto cellulose filter paper, which prevents either sensor from fully recovering its original color [24]. As shown in Table S2, PSP-ED/ZIF-8 maintains achieves similar quantitative color change responses to dry CO₂ in the first and second cycle. However, the colorimetric response comparatively decreases upon the third cycle. While PSP-ED/ZIF-8 exhibits a stronger quantitative color change to dry CO2 (as evidenced in Table S3), the colorimetric response noticeably decreases with increased cycles. Upon prolonged exposure to humid CO₂ (in Table S4), PSP-ED/ZIF-8 exhibits an increase in its 443/570 nm F(R) ratio from the first to the second cycle, with a small increase from the second cycle to the third cycle. Finally, as depicted in Table S5, the ED/PSP:ZIF-8 similarly shows an increase in 443/570 nm F(R) ratios with increased cycling in humidity.

Following cyclic exposure to both dry and humid gas conditions, both sensors are scanned *via* FTIR spectroscopy to probe the stability of ZIF-8. Recent studies in the literature have illustrated how the structural integrity of ZIF-8 is compromised when submerged in pure water under specific mass ratios and ambient conditions for 24 h [48]. ZIF-8 hydrolysis has similarly been reported in water at higher temperatures [49]. In addition to structural degradation from prolonged immersion in water, ZIF-8 has also been shown to be vulnerable to structural degradation under prolonged exposure to acidic gases (such as CO₂) at elevated humidity [50]. Fig. S11 shows FTIR spectra of recovered PSP-ED/ZIF-8 and ED/PSP:ZIF-8 samples following cyclic exposure to dry and humid CO₂. The preserved 421 cm⁻¹ Zn-N stretch in both the first- and second-generation sensors subsequent gas exposure indicates the stability of ZIF-8 to prolonged dry and humid CO₂ exposure.



Fig. 5. Normalized F(R) values *versus* wavelength (nm) for dry CO_2 exposures. 540 ppm (black); 620 ppm CO_2 (red); 830 ppm (blue); 1630 ppm (wine); and 3350 ppm (magenta). **(A)** PSP-ED/ZIF-8 (first-generation sensor). **(B)** ED/PSP: ZIF-8 (second-generation sensor).

Compared to prior studies on ZIF-8 degradation, it is possible that the dilute CO_2 atmospheres exposed (resembling indoor air conditions), as well as the length of time exposed and mass of sensor deposited on the cellulose filter paper, do not readily induce a measurable collapse of the crystalline MOF network.

3.4. Sensors' responses to volatile organic compounds (VOCs)

To assess the role of other airborne pollutants (such as VOCs) as possible interferants in the colorimetric CO₂ sensing mechanism, colorimetric assays and *in-situ* UV-Vis spectra are collected in response to acetone and ethanol. Fig. S12 shows colorimetric images of the PSP-ED/ ZIF-8 and ED/PSP:ZIF-8 materials exposed to dry house air (458 \pm 3 ppm CO₂), as well as dry house air mixed with 200 ppm ethanol and 200 ppm acetone. Compared to humid CO₂ exposures, the presence of these select VOCs demonstrates a relatively negligible effect on the observed color change achieved in dry atmosphere. In addition to the colorimetric imaging results, Fig. S13 demonstrates the results of *in-situ* UV-Vis experiments with CO₂ (450–3600 ppm) mixed with dry air and acetone (0, 20, and 314 ppm) at a total gas flow rate of 350 ml/min. Unlike the spectra observed in a humid atmosphere, both sensors exhibit a high selectivity to CO₂ with rising acetone levels, with the ED/PSP:ZIF-8 material displaying a significantly stronger color change than the PSP-



Fig. 6. 443/570 nm F(R) ratios for PSP-ED/ZIF-8 (blue) and ED/PSP:ZIF-8 (red) as a function of dry CO_2 exposure (in ppm). Standard deviation values are plotted as error bars which are smaller than the symbol size for PSP-ED/ZIF-8 sensor. For the ED/PSP:ZIF-8 material, the larger error bars observed at higher CO_2 concentrations are attributed to the high reflectance values achieved with increasing CO_2 levels (87% and up) as the sensor becomes more yellow.

ED/ZIF-8 material.

3.5. Discussions of the sensing mechanism and differences between the two sensors

To understand the colorimetric CO_2 sensing behavior observed in dry and humid conditions, as well as in the presence of select VOCs, the zwitterion mechanism is described in this section. In the previous work [24], the zwitterion mechanism (characteristically used to evaluate the reaction chemistries involving CO_2 absorbed into aqueous primary and secondary amine solutions) was proposed to comprehend the color change dynamics involving ZIF-8, phenol red, and ethylenediamine in response to CO_2 and humidity in methanolic solvent [31,51,52]. Once adsorbed by ZIF-8, CO_2 is posited to first react with ethylenediamine (shown in Eq. 3 as RNH₂) to produce a zwitterion species [24,31,51,52].

$$CO_2 + RNH_2 \leftrightarrow RN^+H_2CO_2^-$$
 (3)

Upon formation of the zwitterion, the second step of the reaction (shown as Eq. 4) ensues in which a base in the system, B, deprotonates the zwitterion to form a protonated species and carbamate species [24, 31,51,52].

$$RN^{+}H_{2}CO_{2}^{-} + B \leftrightarrow RNHCO_{2}^{-} + BH^{+}$$
(4)

At low humidity, the pH indicator, phenol red, is expected to function as the primary base and abstract the proton from the zwitterion species, thus modifying its conjugation and triggering a clear fuchsia-toyellow color transition dependent on CO₂ concentration [24,29,30]. However, in humid conditions, water can participate in Eq. 4 as a free base to deprotonate the zwitterion [24,53]. Thus, it is hypothesized that adsorbed phenol red molecules might compete with water for access to the proton of the zwitterion, resulting in colorimetric suppression with increased humidity [24,53]. In addition, the intrinsic hydrophilicity of ethylenediamine [54] could promote water adsorption to the detriment of CO₂ adsorption, inhibiting formation of the zwitterion and thus disrupting the colorimetric gas response accomplished in dry environment [24].

Related to the cyclic in-situ UV-Vis results shown in Tables S2 and S3,



Fig. 7. Colorimetric images of sensors before controlled exposure, exposed to 600 ppm CO₂, under varied relative humidity. Top row: PSP-ED/ZIF-8 (first-generation sensor). Bottom row: ED/PSP:ZIF-8 (second-generation sensor). Images are taken after 30 s of exposure.

Table 3 Mean RGB values for PSP-ED/ZIF-8 exposed to 1500 ppm CO_2 in variable humidity.

Relative humidity (%)	Mean R-value	Mean G-value	Mean B-value
0	213 ± 2	171 ± 1	192 ± 1
40	208 ± 1	164 ± 1	196 ± 1
80	203 ± 1	148 ± 1	191 ± 1

Table 4

Mean RGB values for ED/PSP:ZIF-8 exposed to 1500 ppm CO_2 in variable humidity.

Relative humidity (%)	Mean R-value	Mean G-value	Mean B-value
0 40	216.0 ± 0.5 212.0 ± 0.4	$\begin{array}{c} 192.0 \pm 0.7 \\ 180.0 \pm 0.5 \end{array}$	$\begin{array}{c} 186.0 \pm 0.3 \\ 181.0 \pm 0.5 \end{array}$
80	205.0 ± 0.3	168.0 ± 0.5	178.0 ± 0.5

it is possible that the reduced colorimetric gas response observed with increased cycling can be ascribed to both the transient loss of methanol and formation of stable carbamates, which both age the sensor and limit the regeneration of ethylenediamine for subsequent CO₂ chemisorption [24,51–54]. However, as observed in Tables S4 and S5, it is possible that the dry air purge streams between cycles disrupt hydrogen bonding interactions between ethylenediamine and water in a humid gas environment, freeing more ethylenediamine molecules for subsequent CO₂ chemisorption and generating higher 443/570 nm F(R) ratios [54]. In contrast with these colorimetric studies using dye- and amine-modified ZIF-8 species, other amine-based systems exhibit an increased sensitivity to indoor levels of CO₂ in humid environment [55]. For example, a polymer blend of poly(ethylene oxide) and poly(ethyleneimine) coated onto a resonant mass sensor was proposed to demonstrate an enhanced indoor CO2 detection in humid environment due to the availability of water molecules to convert carbamate species into stable bicarbonates, which provides free amines to bind additional CO₂ [55]. Given these differences, it is imperative to establish the specific interaction between ethylenediamine and water in these ZIF-8-based sensors, as well as possible competition between water and phenol red in the zwitterion deprotonation step during humid gas delivery [24,51-54]. However,

with respect to mixed CO₂/VOC studies reported in Figs. S12 and S13, it is possible that neither acetone nor ethanol disturbs the chemisorptive interaction between CO₂ and ethylenediamine, nor functions as a competitive base for adsorbed phenol red species [24,51–53].

To understand the enhanced response to CO₂ observed in the second generation (ED/PSP:ZIF-8) sensor, the nature of phenol red and ethylenediamine adsorption onto ZIF-8 need to be evaluated between both sensors. While both sensors incorporate ethylenediamine through postsynthetic mixing with the MOF, the ED/PSP:ZIF-8 material involves the direct inclusion of phenol red into the ZIF-8 precursor broth, which results in the formation of nanocrystals more than triple the size of the pristine ZIF-8. In addition to understanding the role of synthetic phenol red mixing on ZIF-8 growth [42], the location of phenol red with respect to ZIF-8 between both sensors must be established. The structural flexibility of ZIF-8-associated with the "gate-opening" phenomenon describing a rotational swing of the imidazolate linkers to expand the 6-member ring pore aperture beyond its nominal 3.4 Å size-has been observed with penetrating liquids at high-pressure [56], as well as both computational and experimental studies involving the adsorption of gases with kinetic diameters exceeding 3.4 Å [57,58]. However, the ambient-pressure, room-temperature mixing of phenol red molecules with pristine ZIF-8 nanoparticles in methanol that produces the first-generation sensor is not anticipated to result in phenol red penetration through the ZIF-8 nominal pore aperture via the gate-opening phenomenon. Rather, it is expected that phenol red remains adsorbed on the external surface of the ZIF-8 adsorbent. However, in the case of the second-generation sensor, it is hypothesized that phenol red molecules, mixed with the ZIF-8 ligand and metal precursor solution in methanol, might become incorporated within the 11.6 Å pore cavities as ZIF-8 grows [26,27]. Prior studies on ZIF-8 have attributed preferential gas adsorption sites with regions proximate to the imidazolate linkers [28,59]. Given how ZIF-8 crystals grow in a phenol red-incorporated methanolic MOF precursor solution in the second-generation sensing approach, it is possible that dye molecules are well-distributed throughout the MOF and more proximate to CO2-affinative regions of the linker than the first-generation sensor, triggering stronger colorimetric gas responses across humidity [28,59]. To test this hypothesis on comparative phenol red location on ZIF-8 between both sensors, the following set of experiments are conducted.

Fig. S14 shows the PSP-ED/ZIF-8 and ED/PSP:ZIF-8 materials after



Fig. 8. Normalized F(R) values *versus* wavelength (nm) for humid CO₂ exposures (RH: $45.4 \pm 3\%$). 540 ppm (black); 620 ppm CO₂ (red); 830 ppm (blue); 1630 ppm (wine); and 3350 ppm (magenta). (A) PSP-ED/ZIF-8 (first-generation sensor). (B) ED/PSP:ZIF-8 (second-generation sensor).



Fig. 9. 443/570 nm F(R) ratios for PSP-ED/ZIF-8 (blue) and ED/PSP:ZIF-8 (red) as function of CO₂ concentration (in ppm) under relative humidity of 45.4 \pm 3%. Standard deviation values are plotted as error bars.

successive washes in methanol. Whereas the PSP-ED/ZIF-8 sensor becomes much lighter with increased washes, the ED/PSP:ZIF-8 sensor does not. The structural integrity of ZIF-8 is maintained upon washing, as displayed from the sustained 421 cm⁻¹ Zn-N stretches shown in Fig. S15-A. With increased washes, the 1028 cm⁻¹ C-O stretch associated with methanol emerges for both sensors [43]. Though the ZIF-8 structure is maintained, ethylenediamine is lost with successive washes. Figs. S15-B and S15-C show the disappearance of the 3280 and 3355 N-H stretches associated with ethylenediamine upon washing, which suggests that ethylenediamine is adsorbed to the external surface of the ZIF-8 adsorbent.

Toward estimating phenol red adsorption onto ZIF-8 between both materials, three samples (each) of PSP-ED/ZIF-8 and ED/PSP:ZIF-8 are (i) centrifuged, (ii) separated from their supernatant, (iii) rinsed with methanol for 60-min (in a sonication bath), (iv) centrifuged again, (v) separated again from their supernatant, and (vi) blended with methanol, a 2% ethylenediamine (by volume) methanolic solution, or a 0.5 mg/ml solution of phenol red dissolved in a 2% ethylenediamine (by volume) methanolic solution. Fig. S16 shows the response of these washed sensors to 800 ppm CO_2 (in dry conditions). When re-mixed with only methanol, neither sensor responds to CO₂. However, when re-mixed with ethylenediamine in methanol, the washed second-generation ED/ PSP:ZIF-8 material demonstrates a strong fuchsia-to-yellow color change. On the other hand, the first-generation PSP-ED/ZIF-8 material turns white-yellow and shows minimal response to CO2. When re-mixed with phenol red and ethylenediamine in methanol, though, the original PSP/ED-ZIF-8 material demonstrates a CO2 response similar to that of its unwashed, fresh state. In other words, whereas the rinsed ED/PSP:ZIF-8 material only requires ethylenediamine (in methanol) to recover its colorimetric sensitivity to CO2, the rinsed PSP-ED/ZIF-8 material requires both phenol red and ethylenediamine (in methanol). These results support that ethylenediamine is bound to the external MOF surface for both sensors, whereas phenol red is incorporated within the internal surfaces of ZIF-8 in the second-generation sensor but on the external surface of ZIF-8 for the first-generation sensor.

To further test the location of phenol red within ZIF-8 between the two sensors, an 80 mg/ml ZIF-8 solution is prepared by blending ZIF-8 with a 0.5 mg/ml phenol red solution (in methanol). Similar to the processes described above, this material-termed PSP/ZIF-8-is washed several times in methanol (for 30-min). The same process is performed using an 80 mg/ml PSP:ZIF-8 solution (in methanol). Fig. S17 shows how the PSP/ZIF-8 material becomes lighter with successive washes, transitioning from orange to light pink. In contrast, as shown in Fig. S18, the PSP:ZIF-8 material does not exhibit such a large color change with continued washing. Upon washing several times, the PSP/ZIF-8 and PSP: ZIF-8 materials are placed into the UV-Vis spectrophotometer and the reflectance (%R) at 570 nm is evaluated. As displayed in Table S6, the rinsed PSP/ZIF-8 material exhibits large increases in 570 nm reflectance values upon successive washes, suggesting loss of phenol red. However, the PSP:ZIF-8 material does not demonstrate such pronounced changes in its 570 nm reflectance value with continued washing, implying the retention of phenol red molecules and their incorporation within the internal surfaces of MOF.

Comparative surface area and micropore volume are shown for pristine ZIF-8 and PSP:ZIF-8 in Table 5. The reported BET surface area and micropore volume of pristine ZIF-8 are consistent with those in the literature [26,60,61]. BET surface area plots for the respective materials are displayed in Fig. S19. Relative to pristine ZIF-8, the formation of PSP:ZIF-8 results in crystals with a reduced BET surface area, Langmuir surface area, and micropore surface area, which could be ascribed to the incorporation of phenol red molecules into the micropores of ZIF-8. As shown in Fig. S20, the two micropores near 10 Å and 12 Å of PSP-ED/ZIF-8 and ED/PSP:ZIF-8 are consistent with reported ZIF-8 micropore widths [62,63]. However, as shown in Table 6, ED/PSP: ZIF-8 exhibits a decreased BET surface area compared to that of PSP-ED/ZIF-8, which could similarly be ascribed to phenol red

Table 5

BET surface area, Langmuir surface area, Dubinin-Astakhov micropore surface area, and Horvath-Kawazoe maximum pore volume for Pristine ZIF-8 and PSP:ZIF-8.

Material	BET surface area (m ² /g)	Langmuir surface area (m ² /g)	Dubinin-Astakhov micropore surface area (m ² /g)	Horvath-Kawazoe maximum pore volume at $p/p^\circ=0.981~(\text{cm}^3/\text{g})$
Pristine ZIF-8	1778.6	1933.0	1710.5	0.72
PSP:ZIF-8	1700.7	1794.6	1693.1	0.64

Table 6

BET surface area for PSP-ED/ZIF-8 and ED/PSP:ZIF-8.

Material	BET surface area (m ² /g)
PSP-ED/ZIF-8	1698.9
ED/PSP:ZIF-8	1631.6

Table 7

T-plot external surface area of Pristine ZIF-8, PSP-ED/ZIF-8, PSP:ZIF-8, and ED/PSP:ZIF-8.

Material	t-plot external surface area (m^2/g)
Pristine ZIF-8	177.4
PSP-ED/ZIF-8	58.5
PSP:ZIF-8	66.4
ED/PSP:ZIF-8	43.4

adsorption within the pore cage of ZIF-8. Finally, as shown in Table 7, the significant reduction of external surface area between the pristine ZIF-8 and PSP-ED/ZIF-8 could be assigned to the binding of phenol red to the external surface of ZIF-8 in this synthetic approach (rather than within the internal pores).

To expand on these experiments, the nature of interactions that inform phenol red and ethylenediamine adsorption onto ZIF-8 [64–67] will need to be studied in the future. Several spectroscopies, including second harmonic scattering techniques [68–71], nuclear magnetic resonance, X-ray-based, and vibrational techniques, will be pursued to elucidate the complex reaction mechanism involving ZIF-8, phenol red, ethylenediamine, CO_2 , and humidity in methanol [72–74]. Through these experiments, the reaction products of the colorimetric gas sensing can be established, as well as the role of water as an interferant.

4. Conclusions

In this work, we successfully synthesized a second-generation, ZIF-8based colorimetric CO₂ sensor from the direct mixing of the pH indicator, phenol red, with ZIF-8 precursors in a room temperature methanolic solvent. While PXRD patterns and FTIR spectra confirmed the chemical stability of this new sensor, ED/PSP:ZIF-8, MATLAB-generated RGB distributions and in-situ UV-Vis spectroscopy demonstrated an improved colorimetric CO2 response in variable humidity and in presence of acetone and ethanol interferents, compared to that of the firstgeneration sensor, PSP-ED/ZIF-8. Additional experiments suggested that in the ED/PSP:ZIF-8 sensor, phenol red molecules were most likely incorporated in the interior of ZIF-8, while they resided on its external surface in the first-generation sensor, PSP-ED/ZIF-8. Future work will employ both vibrational and X-ray spectroscopies to understand colorimetric sensing differences between both PSP-ED/ZIF-8 and ED/PSP: ZIF-8, with emphasis on identifying differences in phenol red adsorption onto ZIF-8 and the role of water as an inhibitor for colorimetric gas sensing.

CRediT authorship contribution statement

Adrian K. Davey: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Software, Validation, Writing – original draft. Zhou Li: Investigation, Writing – review & editing. Natalie Lefton: Investigation, Resources. Branden E. Leonhardt: Investigation, Resources. Alireza Pourghaderi: Investigation. Stuart McElhany: Investigation. Derek Popple: Resources, Software. Chunhui Dai: Investigation. Salman Kahn: Resources. Matthew N. Dods: Investigation, Resources, Writing – review & editing. Alex Zettl: Resources. Carlo Carraro: Writing – review & editing. Roya Maboudian: Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.snb.2022.132783.

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