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Two Closely Related Zn(II)-MOFs for Their Large Difference in CO₂ Uptake Capacities and Selective CO₂ Sorption

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IITKGP-13B (IITKGP stands for Indian Institute of Technology Kharagpur), have been constructed through the self-assembly of isomeric N,N'-donor spacers (3,3'-L = 3,3'-azobispyridine and 4,4'-L = 4,4'-azobispyridine) with organic ligand 4,4'-sulfonyldibenzoic acid (SDBH₂) and Zn(NO₃)₂·6H₂O (G represents disordered solvent molecules). Single-crystal X-ray diffraction studies reveal the 2D structure with *sql* topology for both MOFs. However, the subtle change in positions of coordinating N atoms of spacers makes IITKGP-13A noninterpenetrated, while IITKGP-13B bears a 2-fold interpenetrated structure. IITKGP-13A exhibits higher uptake of CO₂ over CH₄ and N₂ with high IAST selectivities for mixed CO₂/CH₄ (50:50, biogas) and CO₂/N₂ (15:85, flue gas) gas systems. In



contrast, IITKGP-13B takes up very low amount of CO_2 gas (0.4 mmol g⁻¹) compared to IITKGP-13A (1.65 mmol g⁻¹) at 295 K. Density functional theory (DFT)-based electronic structure calculations have been performed to explain the origin of the large differences in CO_2 uptake capacity between the two MOFs at the atomistic level. The results show that the value of the change in enthalpy (ΔH) at 298 K temperature and 1 bar pressure for the CO_2 adsorption is more negative in IITKGP-13A as compared to that in IITKGP-13B, thus indicating that CO_2 molecules are more favored to get adsorbed in IITKGP-13A than in IITKGP-13B. The computed values for the Gibbs' free energy change (ΔG) for the CO_2 adsorption are positive for both of the MOFs, but a higher value is observed for the IITKGP-13B. The noncovalent types of interactions are the main contribution toward the attractive energies between the host MOF frameworks and guest CO_2 molecules, which has been studied with the help of energy decomposition analysis (EDA).

INTRODUCTION

Metal-organic frameworks (MOFs)¹ have been broadly studied for an extensive range of applications together with gas adsorption,² separation,³ proton conductivity,⁴ heterogeneous catalysis,⁵ chemical sensors for metal ions and small organic molecules,⁶ and so on.⁷ The most widely investigated property of MOF materials is gas adsorption, gas storage, and their separations under various conditions.^{2,3} The permanent porosity, fine-tuning pore size, flexible pore surface, extra-high surface area, and thermal and chemical stability allow the realization of such intriguing properties. In recent years, MOFs are accomplished as potentially suitable porous adsorbents for CO2 uptake with reversible physical adsorption and separation.^{2b,c,e,3b} In particular, much attention has been devoted for CO₂ adsorption and separation from landfill or bio gas (50% CH_4 and 50% CO_2) and flue gas (85% N_2 and 15% CO_2) mixtures. It is important to estimate the effect of void size, functionality, and polarity on the sorption energetics of CO_2 adsorption on the pore surfaces of frameworks. Gas separation performance on MOFs usually depends on two factors. First, it depends on size-based selectivity, also known as kinetic separation, where an MOF with smaller void size may permit the gas molecules like CO_2 with a certain kinetic diameter for diffusing into the cavity with proper pore window dimensions, resulting in molecular sieving;⁸ second, it depends on altering the affinity of the network functionalities toward CO_2 for optimization of the adsorptive properties and thus preferential adsorption of CO_2 over other gases.⁹ A numerous number of functionalities, including amines, coordinated waters, exposed metal ion sites, and polarizing organic functionalities have been experimentally proven to be effective for MOF materials with increased CO_2 capture and separation performance.^{9,10} Besides, several thermodynamic parameters like adsorption

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Scheme 1. Synthesis Route for IITKGP-13A and IITKGP-13B



Figure 1. (a) Coordination environment of IITKGP-13A (color codes: violet, zinc; red, oxygen; blue, nitrogen; gray, carbon; yellow, sulfur; white, hydrogen). (b) A packing diagram showing the void space in IITKGP-13A along the crystallographic *a*-axis. (c) A representation of the *sql* topology of IITKGP-13A.

energy change (ΔE), changes in enthalpy (ΔH), and changes in Gibbs' free energy (ΔG) have played important roles in controlling CO₂ adsorption amount and the selectivity. Under similar synthesis conditions, the subtle changes in coordination position of ligating atoms for a set of isomeric spacers may allow the formation of closely related MOFs which may have significant impact on overall CO₂ gas sorption and separation performances. Thus, we sought to construct MOFs from two isomeric spacers having varying positions of the ligating coordinating atoms through a mixed ligand synthesis approach with an identical organic ligand and a metal ion by following an identical synthesis protocol (Scheme 1). The spacers contain the azo functionality and the organic acid ligand SDBH₂ (4,4'sulfonyldibenzoic acid) bears polar sulfone ($-SO_2$) group in order to impart increased CO_2 -framework binding interactions and hence separations from gas mixtures.

Along this line, two new Zn(II)-based MOFs, ({[Zn(SDB)- $(3,3'-L)_{0,5}]\cdot xG\}_n$, IITKGP-13A, and {[Zn₂(SDB)₂(4,4'-L)]· $xG\}_n$, IITKGP-13B, have been constructed through the self-assembly of isomeric N,N'-donor spacers (3,3'-L and 4,4'-L with subtle change in position of coordinating pyridyl N atom) with organic ligand SDBH₂ and Zn(NO₃)₂·6H₂O as the metal source as depicted in Scheme 1. IITKGP-13A exhibits a higher uptake of CO₂ over CH₄ and N₂. The selectivities at 273 and 295 K under 1 bar pressure were evaluated based on the IAST (ideal adsorbed solution theory)¹¹ method for mixed CO₂/CH₄ (50:50, biogas) and CO₂/N₂ (15:85, flue gas) gas systems. In contrast, IITKGP-13B captures a much lower

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Figure 2. (a) Coordination environment of IITKGP-13B (color codes: violet, zinc; red, oxygen; blue, nitrogen; gray, carbon; yellow, sulfur; white, hydrogen). (b) Interpenetration between two layers of IITKGP-13B. (c) A packing diagram showing the void space in IITKGP-13B along the crystallographic *a*-axis. (d) A representation of the *sql* topology of IITKGP-13B.

amount of CO_2 gas with respect to IITKGP-13A. Although both the MOFs are microporous and have similar framework polarity, they show marked differences in CO_2 uptake capacity. In order to understand this phenomenon at the molecular level, a computational study was performed which established that IITKGP-13A has a higher CO_2 binding affinity as compared to that in the IITKGP-13B.

EXPERIMENTAL SECTION

Materials. All reagents were used as obtained. 3,3'-Azobispyridine (3,3'-L) and 4,4'-azobispyridine (4,4'-L) were made according to a reported procedure (see SI).¹²

Synthesis of {[Zn(SDB)(3,3'-L)_{0.5}]·xG}_n: IITKGP-13A. A mixture of 30 mg of Zn(NO₃)₂·6H₂O (0.1 mmol), 9.4 mg of 3,3'-azobispyridine (3,3'-L) (0.05 mmol), 31 mg of 4,4'-sulfonyldibenzoic acid (0.1 mmol), and 4 mL of N,N'-dimethylformamide (DMF) solvent were added into a 15 mL scintillation vial followed by 30 min sonication for getting a clear red solution. The scintillation vial was then kept at room temperature for slow vaporization of the solvent. Orange rectangular crystals of IITKGP-13A were separated by filtration. The crystals were rinsed with fresh DMF (2 × 10 mL) and dried in air. FT-IR (KBr pellet, cm⁻¹): 3383(b), 1647.7(s), 1598.1(s), 1560.2(s), 1489.1(w), 1401.7(m), 1292.6(s), 1156.5(s), 1101.5(s), 1014.1(w), 872.6(w), 746.5(s), 621.2(m), 571.7(m), 485.0(m) (Figure S5).

Synthesis of $\{[Zn_2(SDB)_2(4,4'-L)]\cdot xG\}_n$: IITKGP-13B. This MOF was synthesized similarly as IITKGP-13A, except that 3,3'-L was replaced with 4,4'-L. Red block crystals of IITKGP-13B were separated by filtration. FT-IR (KBr pellet, cm⁻¹): 3443.1(b), 1647.7(s), 1565.7(m), 1489.1(w), 1407.1(s), 1298.1(m), 1226.9(w), 1167.3(m), 1096.1(m), 1014.1(w), 838.1(m), 746.5(s), 615.8(m), 506.7(m), 435.5(w) (Figure S6).

RESULTS AND DISCUSSION

The reaction between dicarboxylate ligand 4,4'-sulfonyldibenzoic acid (SDBH₂) and azo functionalized isomeric N,N'donor spacers 3,3'-azobispyridine (3,3'-L) and 4,4'-azobispyridine (4,4'-L) with $Zn(NO_3)_2$.6H₂O in DMF under room temperature slow evaporation gave crystals of IITKGP-13A and IITKGP-13B, respectively.

Crystallographic investigation reveals that IITKGP-13A crystallizes in the triclinic crystal system with the $P\overline{1}$ space group where the asymmetric unit comprises a half unit of the spacer 3,3'-L, one full unit of the SDB²⁻ ligand associated with one Zn metal center (Figure S7). In the coordination environment (Figure 1a), two Zn(II) metal centers form a paddle-wheel structure by the association of four SDB²⁻ and two 3,3'-L spacers. In this scenario, each metal center involves in pentagonal coordination geometry with four O atoms from

four different SDB²⁻ units and one N atom from one 3,3'-L. The two metal centers are situated with a separation distance of 2.96 Å. The secondary building units (SBUs) composed of paddle-wheel dinuclear carboxylates $\{Zn_2(COO)_4\}$ linking pyridyl N atoms to produce the porous 2D framework which shows the *sql* topology generated by TOPOS software package (Figure 1c).¹³ The 2D layers are further stabilized by some nonbonding interactions among the constituent elements (Table S2). When viewed down the crystallographic a-axis, a channel of dimension $3.7 \times 6.1 \text{ Å}^2$ by considering van der Waals radii could be formed as shown in Figure 1b. PLATON analysis shows a total 25.8% solvent accessible area per unit cell volume.¹⁴ The PXRD pattern of the as synthesized sample is fully in line with the simulated one which ensures the phase purity of the bulk sample (Figure S8). TGA analysis attributes 12.7% weight loss at 175 °C for the release of guest solvent molecules, and further heating revels that the framework is stable up to 290 °C after which it started to degrade (Figure **S9**).

IITKGP-13B also crystallizes in a similar crystal system and space group as IITKGP-13A. However, the asymmetric unit contains a full unit of the spacer 4,4'-L, two full units of the SDB²⁻ ligands, and two crystallographically independent Zn metal centers (Figure S10). Similar to IITKGP-13A, both the Zn centers in IITKGP-13B are five coordinated by four different O atoms from four different SDB²⁻ units and one N atom from the 4.4'-L with the formation of $\{Zn_2(COO)_{4}\}$ paddle wheel units (Figure 2a). However, contrary to IITKGP-13A, IITKGP-13B exhibits interpenetration between two layers as depicted in Figure 2b. Structural simplification reveals the porous 2D framework showing similar sql topology (Figure 2d).¹³ The 2D layers are stabilized by several nonbonding interactions among the components as listed in Table S2. Considering van der Waals radii, IITKGP-13B shows a channel dimension of 4.7 \times 7.6 Å² along the *a*-axis (Figure 2c). PLATON calculation shows a total 18.3% solvent accessible area per unit cell volume.¹⁴ Furthermore, the phase purity of the as-synthesized sample has been established by the wellmatched PXRD pattern between the simulated and assynthesized sample (Figure S11). TGA analysis attributes around 8% weight loss for the discharge of lattice solvent molecules. The framework showed stability up to 390 °C and after that started to decompose (Figure S12).

The inherent porosity of the synthesized materials IITKGP-13A and IITKGP-13B was characterized by CO₂ sorption isotherm measurements at 195 K under 1 bar. The materials were activated via solvent exchange followed by degassed under high vacuum at 363 K overnight. After activation, the PXRD patterns confirmed the retention of the frameworks (Figures S8 and S11). The activated samples IITKGP-13A' and IITKGP-13B' both displayed a typical type I reversible isotherm, indicating the microporous nature (Figure 3). The BET surface areas for IITKGP-13A' and IITKGP-13B' were calculated to be 206 and 129 $m^2~g^{-1}$, respectively. In addition, BET surface areas calculated from N_2 sorption isotherms at 77K were found to be similar (201 m^2 g^{-1} and 139 m^2 g^{-1} , respectively, Figures S13 and S14) as acquired from CO₂ sorption isotherms at 195 K/1 bar. The pore volume obtained from N₂ sorption at 77 K was calculated to be 0.12 cc/g for IITKGP-13A' and 0.08 cc/g for IITKGP-13B'. The pore size distributions for both the MOFs were obtained from the 195 K CO₂ isotherms by applying Horvath–Kawazoe analysis and are presented in Figure S15. Both materials after gas sorption



Figure 3. CO_2 sorption isotherm at 195 K/1 bar for IITKGP-13A' (red) and IITKGP-13B' (blue).

measurements retained the original crystallinity as confirmed from PXRD analysis, thus demonstrating the robustness of their frameworks (Figures S8 and S11).

To check their potential for CO_2 , CH_4 , and N_2 uptake capacity at ambient condition, single-component sorption isotherms were collected at 273 and 295 K (Figure 4). For IITKGP-13A', the uptake amounts of CO_2 are 2.01 mmol g⁻¹ at 273 K and 1.65 mmol g⁻¹ at 295 K and 1 bar. On the contrary, it takes up much less amount of CH_4 (0.87 mmol g⁻¹ at 273 K; 0.67 mmol g⁻¹ at 295 K) and N_2 (0.26 mmol g⁻¹ at 273 K; 0.18 mmol g⁻¹ at 295 K) under 1 bar. Such a systematic difference in uptake capacities illustrates the potential of IITKGP-13A' toward flue gas and bio gas separations under ambient conditions.

However, for the case of IITKGP-13B', the uptake amounts of CO_2 are 0.83 mmol g⁻¹ at 273 K and 0.40 mmol g⁻¹ at 295 K and 1 bar (Figure 5). These values are much lower than those observed for IITKGP-13A' under similar conditions (Figure 4). As the CO_2 amount uptake capacity at ambient condition is too low for IITKGP-13B', it could not be considered as potential candidate for separations of CO_2/N_2 and CO_2/CH_4 . To explain such a drastic difference in CO_2 uptake capacity between the MOFs, we have performed density functional theory (DFT)-based studies which support the observed phenomena as discussed in subsequent sections.

In order to estimate the separation capability of IITKGP-13A' for CO₂, the gas selectivities of CO_2/N_2 (15:85) and CO₂/CH₄ (50:50) were calculated by using ideal adsorbed solution theory (IAST).¹¹ The single-component adsorption isotherm data points were fitted with the single-site Langmuir-Freundlich (SSLF) equation (Figures S16-S18). Using the SSLF fitting parameters we determined the binary mixture gas sorption isotherms and selectivities under 1 bar via the IAST method as depicted in Figure 6a-d. The IAST selectivity of IITKGP-13A' for CO₂/N₂ mixture is 76 at 273 K and 47 at 295 K and for the CO_2/CH_4 mixture is 9.8 at 273 K and 6.6 at 295 K (Figure 6a-d). These selectivity values for IITKGP-13A' are comparable/higher than those of previously reported MOFs Cu-BTTri, en-Cu-BTTri, PCN-61, PCN-88, SIFSIX-1-Cu, SIFSIX-2-Cu, JUC-141, MOF-177, Zn-MOF-74, UTSA-72a, NOTT-202a, ZIFs (ZIF-68, 69, 70), and zeolites MFI under the similar conditions as presented in Table S3.^{10a,15}

It should be mentioned that besides the higher separation selectivity, capacity inspection of the chosen gas from its mixed gas system is also important while a particular adsorbent is



Figure 4. Single component sorption isotherms for CO2, CH4 and N2 of IITKGP-13A' (a) at 273 K and (b) at 295 K.



Figure 5. CO_2 sorption isotherms of IITKGP-13B' at 273 K (red) and 295 K (blue).

considered for its practical performance. If the IAST separation selectivity is high but the amount adsorbed in its mixed gas phase is poor, the given adsorbent may not be implemented for the practical applications. So, we checked the CO₂ loadings calculated via the IAST method under the equilibrium condition of the binary combinations of CO₂–N₂ and CO₂– CH₄ at 273 and 295 K up to 100 kPa as shown in Figure 6. The amount of CO₂ adsorbed from CO₂–N₂ (15:85) is 0.93 and 0.55 mmol g⁻¹ at 273 and 295 K, respectively. The CO₂ loading of 0.55 mmol g⁻¹ at 296 K, 100 kPa) and zeolite MFI (0.26 mmol g⁻¹ at 296 K, 100 kPa).^{10a} For the case of the CO₂–CH₄ (50:50) mixture, these values are 1.51 and 1.12 mmol g⁻¹ at 273 and 295 K, correspondingly, which is higher than that for IITKGP-6 (0.77 mmol g⁻¹ at 295 K, 100 kPa).^{12a} For the inspection of strength of interactions between the

For the inspection of strength of interactions between the framework and adsorbed CO_2 molecules, the isosteric heat of CO_2 adsorption (Q_{st}) of IITKGP-13A' was calculated via the Clausius–Clayperon equation based on single-component sorption isotherms obtained at 273 and 295 K. The Q_{st} value of IITKGP-13A' for CO_2 is 25 kJ mol⁻¹ (Figure S19) at near zero coverage, indicating moderately strong connections between the framework and adsorbed CO_2 molecules. The value is similar to a few well-known MOFs such as ZTF-1 (25.4 kJ mol⁻¹),^{17a} Cu-TPBTM (26 kJ mol⁻¹),^{15b} PCN-88 (27

 $kJ \ mol^{-1}), ^{15c} \ IITKGP-6 \ (23 \ kJ \ mol^{-1}), ^{16} \ IITKGP-11 \ (25 \ kJ \ mol^{-1}), ^{17b} \ SIFSIX-1-Cu \ (27 \ kJ \ mol^{-1}), ^{17c} \ NOTT-125 \ (25.35 \ kJ \ mol^{-1}), ^{17d} \ UTSA-49 \ (27 \ kJ \ mol^{-1}), ^{17e} \ HHU-3 \ (24.6 \ kJ \ mol^{-1}), ^{17d} \ HHU-5 \ (25.6 \ kJ \ mol^{-1}), ^{17d} \ ZJNU-54 \ (24.7 \ kJ \ mol^{-1}), ^{17d} \ mol^{-1}), ^{17d} \ and \ IITKGP-5 \ (22.6 \ kJ \ mol^{-1}). ^{17f}$

COMPUTATIONAL STUDY

Density functional theory (DFT)-based studies were carried out to explain the origin of the differences between the amounts of CO₂ gas adsorption in the MOFs under study. The computational details are provided in the Supporting Information. The optimized geometries of the truncated IITKGP-13A and IITKGP-13B have been presented in Figure S20. The MOF structures have been truncated and simplified for computational study from the associated experimental crystallographic data of the synthesized MOFs. These simple models for the MOFs are required to diminish the computational cost, keeping all essential relevant interactions. Due to this truncation the main structural features of the IITKGP-13A and IITKGP-13B do not change. These structures have been used throughout the computational study to check their CO₂ adsorption properties. The grand canonical Monte Carlo (GCMC) simulation and neutron scattering measurements are the well-known techniques for studying the CO₂ adsorption inside MOF cavities.^{10b,18} These studies have revealed that the open metal sites, the paddle wheel sites, the hex sites, the window sites, and the central sites are the main locations for the gas molecules to get adsorbed in the MOFs. Apart from this, a complete quantum chemical approach based on density functional theory (DFT) is equally useful to study the gas adsorption process in MOFs.^{18c,d,19} We have carefully considered and have verified the positions where the CO₂ molecules can get adsorbed inside MOF cavities. This process is employed to the MOFs as well as to ligands to find out the most favorable positions for the gas molecule to get adsorbed. First of all, one CO₂ molecule has been considered at several positions of the IITKGP-13A and IITKGP-13B. For this purpose, we have optimized one CO₂ molecule that has been considered to be adsorbed on the SBUs as 1CO2@3,3'-L, 1CO2@4,4'-L, and 1CO2@LS. The 3,3'-L, 4,4'-L, and LS represent the 3,3'-azobispyridine, 4,4'-azobispyridine, and 4,4'sulfonyldibenzoic acid, respectively. The CO₂ molecule might get adsorbed at different positions of the 3,3'-L, 4,4'-L, and LS. The optimized geometries of the conformers of 1CO₂@3,3'-L,



Figure 6. Binary mixture gas sorption isotherms and IAST selectivities (a, b) at 273 K and (c, d) at 295 K for CO_2/N_2 (15:85) and CO_2/CH_4 (50:50) of IITKGP-13A'.

1CO2@4,4'-L, and 1CO2@LS at PBE-D3/6-31G(d) level of theory have been presented in Figures S21, S22, and S23, respectively. In all of the conformations the O atoms and C atom of the CO₂ molecules are close to the H atoms of the 3,3'-L, 4,4'-L, and LS and the bridging N atoms of the azo group of the 3,3'-L and 4,4'-L and O atoms of the LS. The adsorption energy (ΔE), changes in the enthalpy (ΔH), and changes in the Gibbs' free energy (ΔG) at 298 K temperature and 1 bar pressure at the same level of theory have been computed and reported in Table S4. The ΔE values are negative in all cases, which indicates an attractive binding of CO₂ molecules in these sites. It can be noted that the presence of CO₂ molecules near the azo group of the 3,3'-L and 4,4'-L and near the $-SO_2$ - group of the LS produces the maximum negative ΔE values. These results indicate that the azo and $-SO_2$ – groups are the primary bonding sites of the CO₂ to the ligands, which act the same in the MOFs. The ΔH values for the same adsorption process are also negative. Thus, the CO₂ adsorption is exothermic in nature. The ΔG values are positive which indicates that the gas adsorption at the present temperature and pressure condition is nonspontaneous. The above results show the preferable binding sites for the CO₂ adsorption in the 3,3'-L, 4,4'-L, and LS ligands. We have considered these binding sites as the favorable CO₂ adsorption sites of the IITKGP-13A and IITKGP-13B. The next section focuses on the gas storage properties of the MOFs.

There are many gas adsorption sites present in IITKGP-13A and IITKGP-13B as identified from the previous section. We

have positioned only one CO₂ molecule at these adsorption sites. The optimized geometries of all 1CO2@IITKGP-13A and 1CO₂@IITKGP-13B at PBE-D3/6-31G(d) level of theory are presented in Figures 7 and 8, respectively. The frequency calculation results in all real frequencies which indicate the minimum energy geometries in all cases. The distance between the CO₂ molecules and different atoms of MOFs have been shown there. These distances are much higher than the corresponding covalent bond lengths. Thus, noncovalent interaction between the CO2 and MOFs is expected and will be discussed in details later. The ΔE , ΔH , and ΔG values are computed at the PBE-D3/6-311+G(d,p)//PBE-D3/6-31G(d) level of theory and have been presented in Table S5. "PBE-D3/ 6-311+G(d,p)//PBE-D3/6-31G(d)" denotes that the single point energies are computed at PBE-D3/6-311+G(d,p), taking the optimized geometries at the PBE-D3/6-31G(d) level. The thermal corrections are taken from the outputs obtained from the frequency calculation results at the PBE-D3/6-31G(d)level of theory. The negative ΔE values indicate a strong binding of the CO₂ molecules in both of the MOFs. The association of the CO_2 is exothermic in nature as shown by the negative ΔH values. The ΔG values are computed to be positive. Thus, a lower temperature is required to reach the equilibrium so that the unfavorable entropy contribution is less dominating. It may be noted that the entropy decreases during adsorption. A careful observation reveals that the ΔG values are very small for the 1CO2@IITKGP-13A(1) and 1CO2@ IITKGP-13A(4) conformers, and thus, these are the most



Figure 7. Optimized geometries of different conformers of CO_2 adsorbed IITKGP-13A ($1CO_2@IITKGP-13A$) calculated at the PBE-D3/6-31G(d) level of theory.



Figure 8. Optimized geometries of different conformers of CO_2 adsorbed IITKGP-13B ($1CO_2@IITKGP-13B$) calculated at the PBE-D3/6-31G(d) level of theory.

favorable position for the CO_2 to get adsorbed in IITKGP-13A. In general, the ΔG values are more positive for CO_2 adsorption in the IITKGP-13B as compared to that of the IITKGP-13A. This indicates that CO_2 molecules are more willing to be adsorbed in IITKGP-13A than on IITKGP-13B. The experimental CO_2 adsorption in IITKGP-13A and IITKGP-13B thus could be explained.

More CO_2 molecules (*viz.*, three CO_2 and five CO_2) are considered to be adsorbed in IITKGP-13A and IITKGP-13B, and the optimized geometries at the PBE-D3/6-31G(d) level of theory have been presented in Figures S24–S27. The CO_2



Figure 9. Plots of the NCI surfaces (isosurface = 0.5) of $5CO_2@IITKGP-13A$ (left) and $5CO_2@IITKGP-13B$ (right) calculated at PBE-D3/6-311+G(d,p)//PBE-D3/6-31G(d) level of theory.

molecules are adsorbed in such positions which have been identified from the one CO₂ adsorption study in the previous section. Similar to the previous results, the ΔE values are negative in all cases, indicating binding affinity of CO2 molecules toward both of the MOFs. But, the IITKGP-13A has a higher CO₂ binding affinity as compared to the IITKGP-13B. The ΔH values are negative, and thus, the adsorption of the CO₂ molecules in MOFs is exothermic in nature. The ΔG values are positive and gradually increase with the increase in the number of CO_2 molecules. A subtle increase in the ΔG values is observed for the three CO₂ adsorbed IITKGP-13A, but for the five CO₂ adsorbed IITKGP-13A, the ΔG values increase about 9 times as compared to one CO₂ adsorption case. For the IITKGP-13B, the ΔG values for the three CO₂ and five CO₂ adsorption processes are much higher and positive as compared to the IITKGP-13A case. This further supports that the IITKGP-13B is less capable of adsorbing CO₂ as compared to the IITKGP-13A.

The origin of the attractive forces that bind the CO_2 molecules in these MOFs has been studied with the help of energy decomposition analysis (EDA) (Table S6). The nCO2@MOFs have been fragmented in such a way that one fragment contains the MOF and another fragment holds "n" number of CO₂ molecules. Noncovalent interactions (ΔE_{el} and $\Delta E_{\rm disp}$) are major contributing factors as compared to the covalent counterparts. The contributions from ΔE_{el} and ΔE_{disp} depend on the surrounding environment of the adsorbed CO₂ molecule in the MOFs. As, for example, the contribution of ΔE_{disp} dominates over the ΔE_{el} in the case of 1CO₂@IITKGP-13A(1), whereas the opposite is true for $1CO_2@IITKGP$ -13A(2) system. The CO₂ molecule adsorbed near the bridging diazo group exhibits higher ΔE_{el} contribution in $1 \text{CO}_2 (a)$ IITKGP-13A(1). In all other cases the ΔE_{disp} is the major attractive energy that stabilizes the systems.

To shed more light into the nature of interactions between the CO_2 molecules and MOFs, Bader's atoms-in-molecules (AIM) analysis has been performed. We have considered only the 5CO₂@IITKGP-13A and 5CO₂@IITKGP-13B systems for this study. There are large number of interactions present between the CO₂ molecules and MOFs which are shown by the molecular graph of 5CO₂@IITKGP-13A and 5CO₂@ IITKGP-13B systems in Figure S28. We have considered only one of each type of interactions between the CO₂ molecules and MOFs, and the electron density descriptors at the respective bond critical points have been shown in Table S7. The electron densities $(\rho(r_c))$ at the bond critical points (BCP) are low, which suggest and support the weak interactions present in the system. The Laplacian of the electron density $(\nabla^2 \rho(r_c))$ and total energy density $(H(r_c))$ at the BCPs are positive, supporting the noncovalent interactions therein. The NCI plots are another well-known tool to visualize the noncovalent interactions of the gas storage systems. The green surfaces have been generated (in Figure 9) between CO₂ molecules and MOFs which show the weak van der Waals interactions between them. Thus, the whole computational study supports the experimental findings as well as reveals the nature of the interactions stabilizing the CO₂ molecules inside the MOFs.

SUMMARY

In summary, two Zn(II)-MOFs based on two isomeric N,N'donor linear spacers and a common organic ligand have been realized following an identical synthesis protocol. The topological studies showed that both the MOFs are of sql topology. Gas sorption measurements of activated sample IITKGP-13A' showed preferential uptake for CO₂ over N₂ and CH₄. Importantly, IITKGP-13A exhibits a high IAST selectivity for CO_2/N_2 (15:85) and CO_2/CH_4 (50:50) gas mixtures at ambient conditions which makes IITKGP-13A a good CO₂ adsorbent from biogas and flue gas mixtures. IITKGP-13B shows very low uptake of CO₂ gas with respect to IITKGP-13A. A computational study showed that the computed ΔH values at 298 K temperature and 1 bar pressure for the CO_2 adsorption are more negative for the $nCO_2@$ IITKGP-13A as compared to that in the nCO_2 @IITKGP-13B. Thus, the CO_2 molecules are more favored to get adsorbed by IITKGP-13A than by IITKGP-13B. The ΔG values are more positive for CO₂ adsorption in the IITKGP-13B as compared to that in the IITKGP-13A. Both of the ΔH and ΔG values indicate that IITKGP-13A has higher CO₂ binding affinity as compared to the IITKGP-13B which corroborate with the experimental findings. This work may be advantageous for added investigation toward designing and construction of new MOFs based on these largely unexplored spacers and various dicarboxylates for diverse gas separations and purifications while taking into account the thermodynamic parameters for controlling such important properties.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00551.

Physical measurements, single-crystal X-ray diffraction data, synthesis of spacers, NMR data, PXRD plots, TGA diagram, Q_{st} plot, calculation details, related plots and tabulated data of IAST selectivity, and computational study and related plots (PDF)

Accession Codes

CCDC 1985009–1985010 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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