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A 'Thermodynamically Stable' 2D Ni-MOF over a Wide pH Range with Scalable Preparation for Efficient C₂s over C₁ Hydrocarbon Separations

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Abstract

Design and construction of 'thermodynamically stable' MOFs surviving in liquid water, boiling water, acidic/basic solutions over a wide pH range is highly desirable for many practical applications especially adsorption based gas separations with obvious scalable preparations. Herein, we have designed a new thermodynamically stable Ni-MOF, {[Ni(L)(1,4-NDC)(H₂O)₂]}_n, **IITKGP-20** displaying moderate porosity with 218 m²g⁻¹ BET surface area and micropores along [1 0 -1] direction. As an alternate to cost intensive cryogenic high pressure distillation process for the separation of hydrocarbons, recently MOFs have shown the promise of such separation. Thus, towards application standpoint, this MOF exhibits relatively higher uptake of C₂s hydrocarbons over the C₁ hydrocarbon at ambient conditions with one of the highest selectivities based on IAST method. Combination of two strategies (presence of stronger metal-N coordination on the spacer and the hydrophobicity on the aromatic moiety of the organic ligand) possibly makes the framework highly robust even stable in boiling water and over a wide range of pH 2-10 and representing the first example of 'thermodynamically stable' MOF displaying 2D structural network. Moreover, this material is easily scalable by refluxing the reaction mixture overnight. Because, such separations are performed in presence of water vapor and acidic gases, there is a great need to explore 'thermodynamically stable' MOFs retaining not only the structural integrity but also the porosity of frameworks.

Keywords: C₂s/C₁ separation, hydrocarbon separation, MOF, pH stable MOF, thermodynamically stable MOF

Introduction

Metal–organic frameworks (MOFs) have been documented as one of the most significant classes of porous materials due to their distinctive features and versatility.¹⁻³⁷ However, development of water stable MOFs still remains great challenge for the applications in terms of five major areas: adsorption and/or separation, sensing, catalysis, drug delivery and proton conduction where such applications are conducted in water-containing environments.³⁸⁻⁴⁷ For example, water stability of the adsorbents is the major concern for aqueous phase sensing and adsorption of pollutants in nuclear waste and industrial effluents possessing radioactive metal ions, toxic metal cations and oxyanions. Significant water vapor is also present in hydrogen fuel cell operational unit which is essential for humidifying proton conducting membranes for constant operation. While MOFs are used for those applications, integrity of frameworks must be assured to uphold their projected functionalities and features. In particular, poor stability of microporous MOFs towards water is the major barrier towards targeted adsorption-based gas separation application as water vapor is omnipresent in various industrial streams such as natural gas, flue gas and biogas.³⁸⁻⁵⁶ For example, natural gas streams are often saturated with water vapor⁵⁷ and thus during natural gas purification process by adsorption-based materials, the stability of such adsorbents at such a high level of humidity need to be taken into account. As SO₂ and CO₂ are considered as acidic gases, during natural gas sweetening process, the stability of porous adsorbents in acidic medium is again an important pre-criteria for such application. Thus, for such intended applications, the adsorbents need to be highly robust in nature and preferably be stable even over a wide pH range. While relating the traditional activated carbons and zeolites to their MOF complements, the poor hydrolytic stability is the main restraint of MOF materials for successful employments in above mentioned practical applications.

According to the criteria for water stability classification as proposed by Walton et al., a ‘thermodynamically stable’ MOF should exhibit stability after long-term exposure to aqueous solutions: week or greater in pure water, day(s) in acidic/basic or boiling conditions, however, the stability after exposure to high humid conditions but decomposition after short exposure times in liquid water is assigned to ‘high kinetic stability’ category.³⁸ On the other hand, ‘low kinetic stability’ is assigned to those MOFs showing stability in low humid condition, whereas, ‘unstable’ MOFs rapidly breaks down after any moisture exposure.³⁸ For example, the famous MOFs such as M-MOF-74 (M=Co, Zn, Ni, Mg) are assigned as ‘low kinetic stability’ while

MOF-5, MOF-177, BioMOF 11-12 are considered as 'unstable'.³⁸ For achieving ultra-stable MOFs, many efforts already have been devoted. For enhancing the stability of MOFs sometimes post-synthetic modifications are employed, however, this may lead to the reduction of their functionality or pore surface area. As a consequence, researchers are now focusing to construct MOFs directly which possess inherent stability throughout their structures and compositions. In order to enhance water stability a few strategies have been taken up.³⁸⁻⁴⁷ Generally, due to the increase in basicity, MOFs bearing stronger metal-N coordination exhibit higher stability towards moisture/water as demonstrated by Walton et al.^{38,58} Besides, steric hindrance possessed by bulky aromatic groups around the metal cluster plays an important role to enhance the hydrophobicity of MOFs.³⁸⁻⁴⁴ Except some ZIFs, MILs based on the trivalent metal ions, Zr(IV) and Hf(IV)-based MOFs, PCNs, and few more recently reported, design and development of water stable MOFs are still a great challenge to the scientific community.³⁸⁻⁴⁷ Although there are increasing reports on water stable MOFs in recent time, reports on pH stable MOFs showing high 'thermodynamically stable' nature are even rarer.⁴¹ Thus, we sought to employ a mixed ligand synthesis approach through combination of carboxylic organic ligand with appended phenyl ring on the aromatic backbone and spacer having N coordination sites for the construction of MOFs as the imposed hydrophobicity on appended phenyl ring and presence of a few relatively stronger metal-N coordination instead of having all weaker metal-carboxylate bonds around the metal center might bring the intended feature on the frameworks.

Separation of methane from other small C₂ hydrocarbons such as acetylene, ethylene, and ethane is a very important industrial practice since these small hydrocarbons are extensively utilized as energy sources and raw materials as basic feedstocks in petrochemical industries. Natural gas consisting of primarily CH₄ (~90%) is a cleaner substitute to other automobile fuels, however, the C₂s (C₂H₆, C₂H₄, C₂H₂) along with other impurities need to be removed in order to meet the standards and increase in commercial values. Thus, it is very essential to improve efficient technology for C₂s/C₁ separation. The usual practice for such separations is cryogenic distillation at high pressure which is highly energy consuming and thus, there is a cumulative demand to develop unique materials as opposed to such traditional distillation techniques. Among the several advanced separation methods, adsorptive separation is proven to be cost and energy-efficient where microporous MOFs have been briskly evolving as very promising materials for separations of small gas molecules.^{2,48-51,59-63} In fact, a diversity of microporous

MOFs were explored for their diverse gas separations such as separations of CO₂/CH₄, C₂H₂/C₂H₄, C₂H₄/C₂H₆ and C₃H₆/C₃H₈.^{2,63} Although many such types of hydrocarbons separation based on MOFs are reported, only a few MOF thus far have been employed for a systematic C₂s/C₁ separation study.⁶⁴⁻⁷⁴ Given that C₁-C₂ hydrocarbons possess kinetic diameters in the range of 3.3 to 4.4 Å, the design and synthesis of MOFs with narrow pores comparable to and/or slightly bigger than their kinetic diameters will be of distinctive importance for the separation of these small hydrocarbons.⁶⁴ The presence of open metal site or Lewis basic site or sieving effect corresponding to the pore size can act as the main trigger for selective adsorption of C₂s/C₁.⁵⁹ Besides, introducing some bulky steric hindrance group into the organic linker is also an excellent method for controlling the pore size. In particular, to justify the structure-property relationship and thus to exploit C₂s/C₁ separation ability and selectivity, Chen et al. has employed microporous MOFs UTSA-33, 34, 36 for highly selective separation of C₂s from C₁ at room temperature.⁶⁴⁻⁶⁶ Besides, Fe-MOF-74 showed excellent C₂s/C₁ separations at ambient conditions as well.⁷¹ Although, thus far there are a handful MOFs showing such systematic C₂s/C₁ separations,⁶⁴⁻⁷⁴ their stability in moisture and/or liquid water or over a pH range was never explored. Thus, development of ‘thermodynamically stable’ MOFs is eventually necessary because such separations ultimately need to be performed in presence of saturated water vapor and acidic gases as mentioned before.

Keeping all those points in mind, herein we report a microporous ‘thermodynamically stable’ Ni-MOF, {[Ni(L)(1,4-NDC)(H₂O)₂]}_n, **IITKGP-20** which can survive in drastic conditions such as in boiling water and over a wide range of pH. Besides, this material can be easily scalable by overnight refluxing treatment. Importantly, it shows a high potential for selectivity towards C₂s/C₁ separations with IAST selectivity values of 53.1, 53.9 and 40.9 for C₂H₂, C₂H₄ and C₂H₆/CH₄ mixtures respectively under 100 kPa, 295K.

Results and Discussion:

The newly synthesized MOF, **IITKGP-20** could be obtained as single crystals from solvothermal method at 110 °C for 2 days. As the ease of scalability is an important criteria for any material to successfully deploy in practical applications, we synthesized **IITKGP-20** simply by refluxing the reaction components overnight in gram scale. **IITKGP-20** is fully characterized by single crystal X-ray diffraction (SCXRD), powder X-ray diffraction (PXRD), IR

spectroscopy, elemental analysis and thermogravimetric analysis (TGA). It crystallizes in triclinic crystal system with $P\bar{1}$ space group. The asymmetric unit consists of one Ni(II) metal ion, one deprotonated 1,4-naphthalene di-carboxylic acid, one 4,4'-azbpy and two coordinated water molecules. Each Ni(II) is six-coordinated with two N atoms from two 4,4'-azbpy spacers, two oxygen atoms from two ndc^{2-} units and two oxygens from two crystallographically independent water molecules and thus resulting in a distorted octahedral configuration $\{\text{NiO}_4\text{N}_2\}$ (Figure 1a). The Ni–O bond distances range from 2.060(3) to 2.063(3) Å whereas the Ni–N bond distance ranges from 2.099(4) to 2.109(4) Å (Table S2, Supporting Information). The ndc^{2-} ligands and L spacers are connected through the Ni(II) centers to form an extended 2D square grid layer structure as shown in Figure 1b. These 2D layers are stacked over each other through AA stacking sequence (Figure S4, Supporting Information) via H-bonding interactions as shown in Figure S5 (Supporting Information). Among the two coordinated water molecules, Ow1 is H-bonded with the non-coordinated oxygen atom (O2) of the ndc^{2-} unit from the same layer and a coordinated carboxylate oxygen (O3) the ndc^{2-} unit from a different layer. In a similar fashion, the other coordinated water molecule, Ow2 makes H-bonding connections with the non-coordinated carboxylate oxygen atom (O4) from the same layer and coordinated carboxylate oxygen atom (O1) of the ndc^{2-} unit from another layer. Essentially, the coordinated waters of one layer connects the layers on its top and below through H-bonding interactions with the metal bound carboxylate oxygen atoms (O1 and O3) as listed in Table S3 (Supporting Information). The framework consists of a solvent-accessible void of 16.7% of the unit cell volume (total potential solvent area volume is 197.3 Å³ per unit cell volume of 1182.0 Å³) as estimated by PLATON.⁷⁵ Considering the van der Waals radii **IITKGP-20** possess approximate channel 3.4×5.2 Å² along [1 0 -1] direction (Figure 1c). *TOPOS* structure analysis suggested the overall framework consists of a 4-c uninodal net with point symbol $\{4^4.6^2\}$ which correlates with *sql* topology (Figure S6, Supporting Information).⁷⁶ The framework shows a thermal stability until 230°C as determined from TGA analysis (Figure S7, Supporting Information).

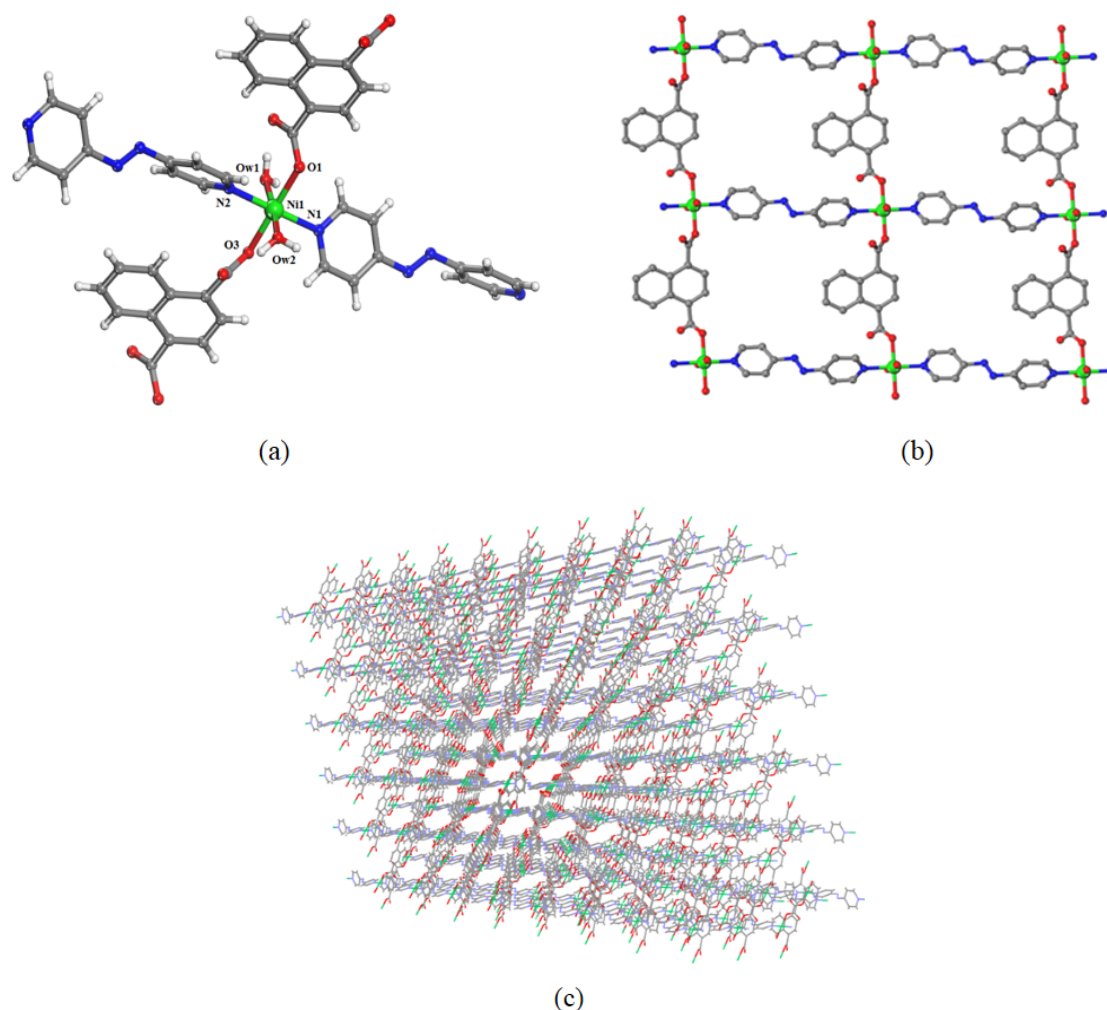


Figure 1. (a) Coordination environment around Ni1 in **IITKGP-20** (Color code: Ni, green; O, red; N, blue; C, grey; H, white). (b) A Single 2D sheet constructed of both 1,4-ndc²⁻ and 4,4'-azobis-(pyridine) ligands. H atoms are omitted for clarity. (c) Packing diagram of **IITKGP-20** showing micro-pores of approximate dimension of $3.4 \times 5.2 \text{ \AA}^2$ along [1 0 -1] direction.

The phase purity of the bulk sample of as-synthesized **IITKGP-20** was confirmed by powder X-ray diffraction (PXRD) study which clearly showed a good agreement with the corresponding simulated pattern attained from single crystal data. To check the hydrolytic stability of the sample, the MOF was immersed in water for 24 hours at room temperature. The PXRD pattern of the water exposed sample was indistinguishable from the simulated pattern (Figure 2a) confirming its hydro-stability. Continuing exposure as long as 15 days does not effect on its structural integrity as well (Figure 2a). A MOF stable in liquid water at ambient temperature, may degrade partly or completely in boiling water and/or under mild acidic or basic

aqueous solutions and thus, it is essential to comprehend the range of water stability of MOFs to classify the category and hence to expedite the proper selection of projected applications.³⁸ Thus, we have checked its stability in boiling water and over a wide range of pH (2-10). In order to further expand the scope, stability was examined upon immersing the material within a range of organic solvents (benzene, toluene, acetonitrile, 1,4-dioxane, THF and xylene). In all cases, the PXRD measurements confirm the robustness of the material as shown in Figure 2. Presence of stronger N-coordination with metal center and the existence of hydrophobic benzene moiety appended to aromatic ring shielding the $\{\text{NiO}_4\text{N}_2\}$ octahedra possibly contribute to such a high robustness to the framework. It may be noted that 1,4-ndc could be more effective proving the shielding to the metal coordination sphere than that of 2,6-ndc as the appended benzene moiety on 1,4-ndc does not take part in coordination to the metal center. This also plays important role in keeping the channel dimensions much smaller as indicated before. Furthermore, H-bonding interactions formed by both of the coordinated water molecules with non-coordinated carboxylate oxygens within the same layer and coordinated oxygens from stacked layers above and below are also accountable to some extent for the robustness of the structure.

A MOF sample with an unchanged PXRD array can still exhibit a substantial loss in porosity and surface area which can't be apprehended by PXRD technique. Thus, analysis of surface area is an imperative follow-up process to methodically conclude the MOF's stability.^{38,40} The CO_2 sorption isotherms of water exposed, pH 2 and pH 10 treated samples at 195 K/1 bar display negligible losses in BET surface area compared to the pristine sample ($196 \text{ m}^2\text{g}^{-1}$ for water, $196 \text{ m}^2\text{g}^{-1}$ for pH 2, $199 \text{ m}^2\text{g}^{-1}$ pH 10 and $218 \text{ m}^2\text{g}^{-1}$ for pristine **IITKGP-20**) (Figure 2d, Figure S8, Supporting Information). According to the criteria for water stability classification as proposed by Walton et al.³⁸ the present MOF falls under the category of 'thermodynamically stable' showing the extreme stability amongst all such categories (thermodynamically stable, high kinetic stability, low kinetic stability, unstable) and thus having strong potential for a wide range of applications including adsorption based gas separations. As pointed out before, reports on pH stable MOFs showing high 'thermodynamically stable' nature are even rarer and those are all having three dimensional networks which inherently partially favor such high robustness to the frameworks.⁴¹ To the best of our knowledge, **IITKGP-20** represents the first example of two dimensional 'thermodynamically stable' MOF. It may be noted that PXRD pattern of the as-synthesized MOF, solvent exchanged, the activated sample

and sample for post surface area measurements reveals the full retention of crystallinity as well (Figure S9, Supporting Information).

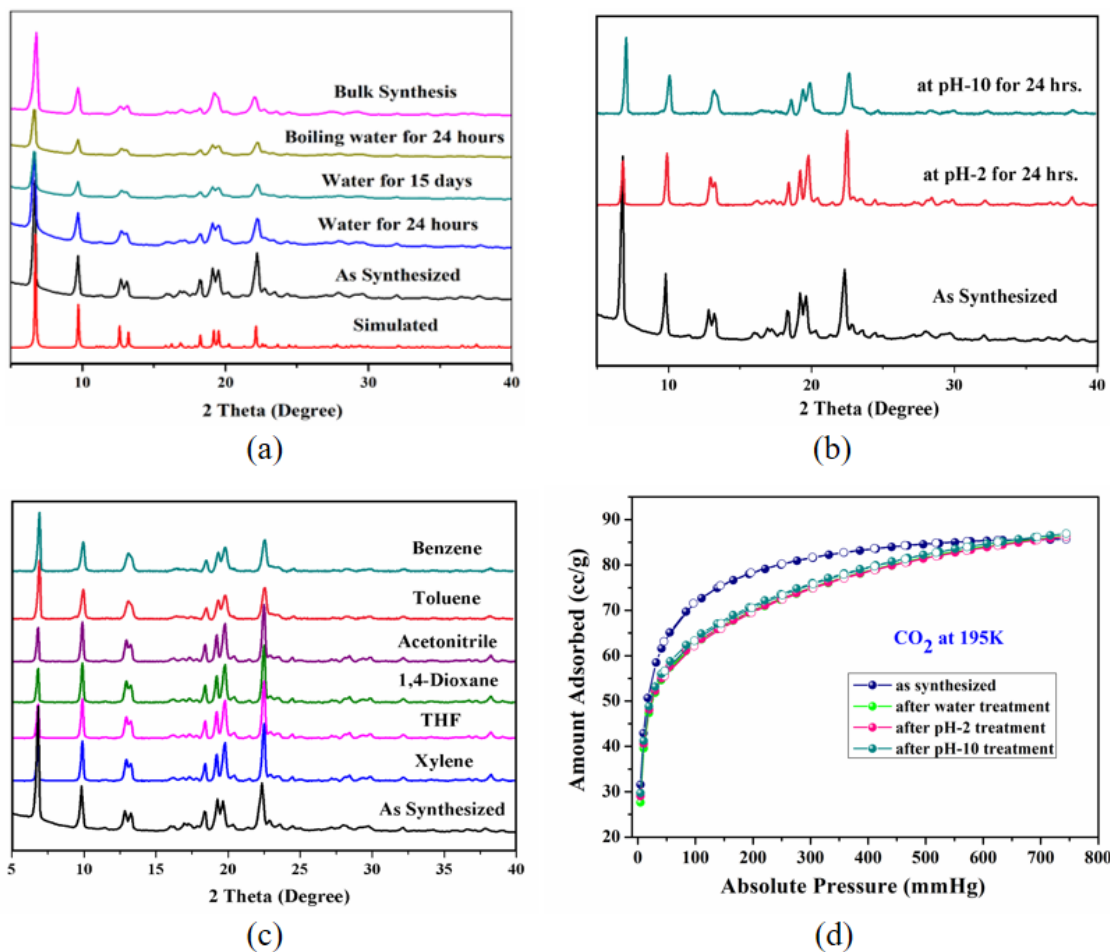


Figure 2. (a) Powder X-ray diffraction pattern (PXRD) for bulk synthesis, after boiling water treatment, after water treatment for 15 days and 24 hrs., as synthesized, simulated; (b) PXRD patterns at pH-10, pH-2 and as synthesized; (c) several solvent treated and as synthesized PXRD. (d) CO₂ sorption isotherms at 195K of **IITKGP-20** as synthesized, after water treatment and after pH treatment (filled and open circles represent adsorption and desorption respectively).

The establishment of permanent porosity with suitable pore sizes in association with high ‘thermodynamically stable’ nature of this MOF encouraged us to examine its potential as an adsorbent for industrially important C₂S/C₁ separations. Based on two different temperatures 273K and 295K, single component gas sorption experiments have been performed. Figure 3 indicates at 273K/1 bar pressure, **IITKGP-20** shows distinct uptake capacities for C₂ series hydrocarbons such as C₂H₂ (49 cc/g), C₂H₆ (47 cc/g), C₂H₄ (48 cc/g) over C₁ methane, (17 cc/g) whereas at 295K and 1 bar pressure, the uptake capacities are systematically lower as expected

(C₂H₂ (43 cc/g), C₂H₆ (40 cc/g), C₂H₄ (41 cc/g) over CH₄ (12 cc/g)). These results pointed out that **IITKGP-20** has the modest uptake capacity for all C₂ hydrocarbons than C₁ and thus may be considered as a potential sorbent for C₂s/C₁ separations.

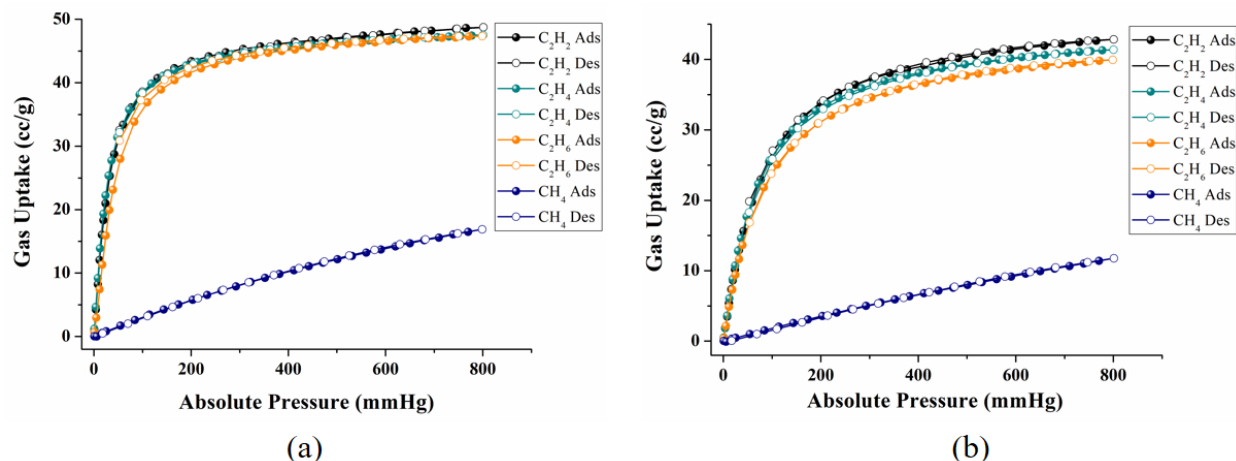


Figure 3. Adsorption and desorption isotherms for C₂H₂, C₂H₄, C₂H₆, CH₄ of **IITKGP-20a** (a) at 273 K and (b) at 295 K (adsorption and desorption isotherms are represented by filled and hollow circles, respectively).

To evaluate the separation ability of **IITKGP-20** towards C₂ hydrocarbons, the binary gas mixture selectivities of C₂s/C₁ (50:50) were calculated through IAST (Ideal Adsorbed Solution Theory) method proposed by Myers and Prausnitz with pressures up to 100 kPa, which is a very familiar method for calculation of binary gas mixture selectivity.⁷⁷ For the fitting purpose, Dual-site Langmuir-Freundlich (DSLFL) equation was used to fit the single-component adsorption isotherm data points in accordance with excellent correlation coefficients (Figure S12-15, Supporting Information). The fitting parameters (Table S5, Supporting Information) were used to calculate the binary gas sorption isotherms and selectivity via IAST method. The result showed that under 100 kPa, the selectivity of C₂H₂/CH₄ mixture is 53.4 at 273K and 53.1 at 295K (Figure 4); for C₂H₄/CH₄ mixture is 58.0 at 273K and 53.9 at 295K (Figure 5); for C₂H₆/CH₄ mixture is 35.4 at 273K and 40.9 at 295K (Figure 6) as listed in Table 1. These values are relatively higher than MOFs, UTSA-33 (C₂H₂/CH₄: 6.5/296K, C₂H₄/CH₄: 4.7/296K, C₂H₆/CH₄: 4.8/296K), UTSA-34a (C₂H₂/CH₄: 16.7/296K, C₂H₄/CH₄: 11/296K, C₂H₆/CH₄: 19.5/296K), UTSA-34b (C₂H₂/CH₄: 23.2/296K, C₂H₄/CH₄: 16.9/296K, C₂H₆/CH₄: 16.7/296K), UTSA-35 (C₂H₂/CH₄: 19.8/296K, C₂H₄/CH₄: 9.7/296K, C₂H₆/CH₄: 13.5/296K), [La(BTB)H₂O] (C₂H₄/CH₄: 12/273K, C₂H₆/CH₄: 22/273K) based on analogous calculation procedure.^{64,65,69,70}

Although, C_2H_2/CH_4 selectivity of **IITKGP-20** is higher than Fe-MOF-74, the other two mixture selectivities are lower for **IITKGP-20** compared to Fe-MOF-74 based on calculation with similar procedures (Table S4, Supporting Information).⁷¹

Table 1 Summarization of gas uptake capacities, Q_{st} values and IAST selectivity values of C_2H_2 , C_2H_4 , C_2H_6 , and CH_4 .

| Adsorbates | Gas Uptake Amount (cc/g) | | Q_{st} Values (kJ/mol) | IAST Selectivity | | |
|------------|--------------------------|------|--------------------------|------------------|------|------|
| | 273K | 295K | | (50: 50) mixture | 273K | 295K |
| C_2H_2 | 49 | 43 | 27.2 | C_2H_2/CH_4 | 53.4 | 53.1 |
| C_2H_4 | 48 | 41 | 29.5 | C_2H_4/CH_4 | 58 | 53.9 |
| C_2H_6 | 47 | 40 | 16 | C_2H_6/CH_4 | 35.4 | 40.9 |
| CH_4 | 17 | 12 | 6.5 | | | |

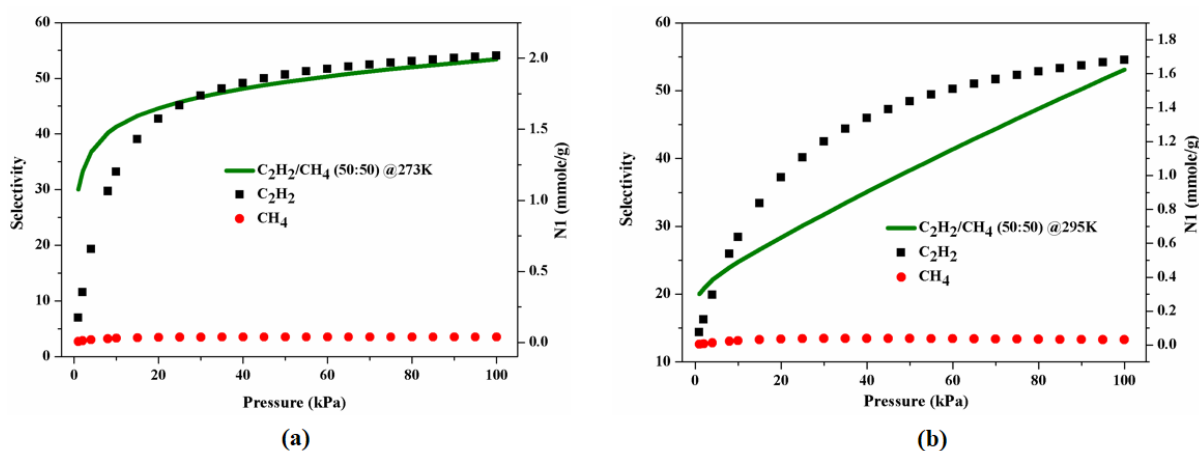


Figure 4. Loading amounts in binary gas mixture and separation selectivity for C_2H_2/CH_4 (50:50) at 273 K (a) and 295 K (b) predicted by IAST selectivity method.

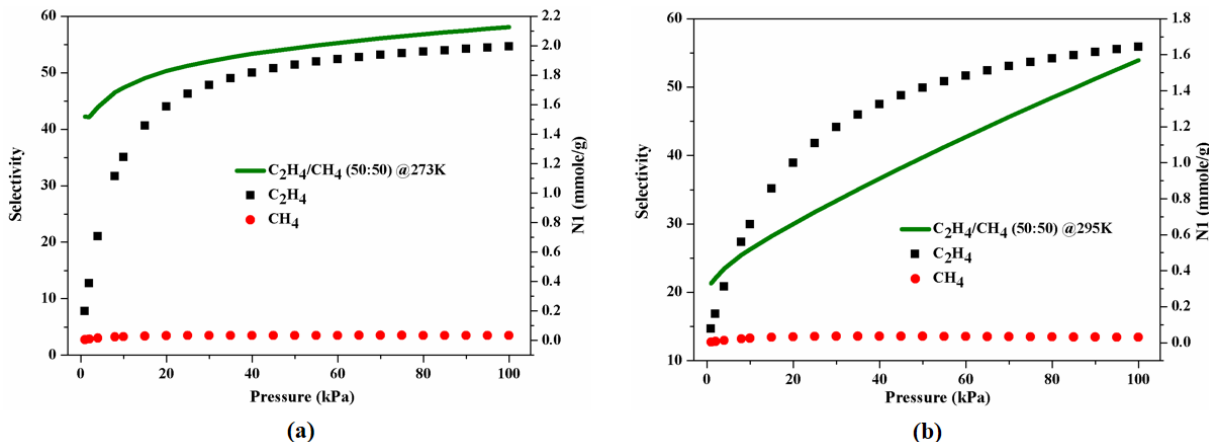


Figure 5. Loading amounts in binary gas mixture and separation selectivity for C₂H₄/CH₄ (50:50) at 273 K (a) and 295 K (b) predicted by IAST selectivity method.

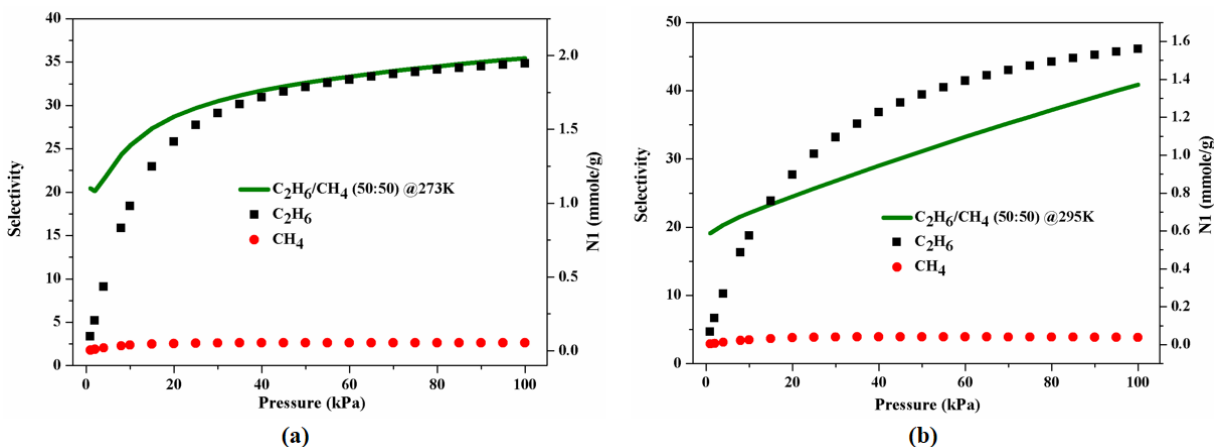


Figure 6. Loading amounts in binary gas mixture and separation selectivity for C₂H₆/CH₄ (50:50) at 273 K (a) and 295 K (b) predicted by IAST selectivity method.

For better understanding of the framework-guest interaction, the adsorption enthalpies for C₂H₂, C₂H₄, C₂H₆, CH₄ were calculated from single component isotherm at 273 and 295K by using Clausius-Clapeyron equation (Figure S16, Supporting Information) which indicates the heat of adsorption (Q_{st}) values of CH₄ at near zero coverage is significantly lower with a value of 6.5 kJ/mol than the other C₂ hydrocarbons. The Q_{st} values of C₂H₂, C₂H₄, C₂H₆, are 27.2 kJ/mol, 29.5 kJ/mol, 16 kJ/mol respectively at near zero coverage. These values indicate the gas affinity towards the framework in the decreasing order of C₂H₄ > C₂H₂ > C₂H₆ > CH₄.

Besides high separation selectivity, capacity consideration of adsorbed amount of chosen gas in mixed gas phase is essential in order to consider the performance of any given adsorbent. If the separation selectivity is high but the amount adsorbed in mixed phase is not up to the mark, then the adsorbent may not be appropriate for such intended applications. Thus, we checked the C₂s loadings calculated via IAST method under the equilibrium condition of the binary gas mixtures of C₂s/C₁ (50:50) at 273 and 295 K up to 100 kPa as presented in Figures 4-6. The predicted sorption isotherms under different C₂s/C₁ gas mixtures clearly revealed that **IITKGP-20** displays negligible uptake for CH₄ under the experimental range, whereas showing considerable uptakes for C₂s. Amounts of C₂H₂ uptake from binary gas mixture of C₂H₂/CH₄ (50:50) are 2.02 and 1.68 mmol g⁻¹ at 273 and 295 K, respectively. For case of C₂H₄/CH₄ (50:50) gas mixture, C₂H₄ uptake values are 1.99 and 1.64 mmol g⁻¹; for C₂H₆/CH₄ (50:50) gas mixture,

C₂H₆ uptake values are 1.95 and 1.56 mmol g⁻¹ at 273 and 295 K, respectively. Such high amount of loadings of C₂s in mixed gas phases indicate its potential for efficient separations of C₂s/C₁.

Conclusion:

To summarize, the first 2D ‘thermodynamically stable’ microporous MOF has been synthesized by employing a mixed ligand approach combining two strategies to impart the robustness on the framework. The material is moderately porous with the presence of a micropore along [1 0 -1] direction and showed its potential for separation of C₂ hydrocarbons over C₁ with high IAST separation selectivities. The presence of stronger metal-N coordination with the appended hydrophobic aromatic moiety of the organic ligand possibly makes the framework highly robust even stable in boiling water and over a pH range of 2-10. Besides, this MOF could be easily scalable by refluxing the components overnight as the mass scale production is an important criteria for practical applications. Given the fact that MOFs in general suffer from the disadvantage of relatively poor stability and thus limiting their practical applications in water containing media, this work might be helpful in developing ‘thermodynamically stable’ MOFs for intended applications where water and/or acidic-basic environments are necessary for improved performance without substantial loss in frameworks integrity and the porosity as well.

Supporting Information

Physical measurements, single crystal X-ray diffraction data, synthesis of spacer, NMR data, PXRD plots, TGA diagram, calculation details, related plots and tabulated data of IAST selectivity, Q_{st} plot (PDF). CCDC 1987508.

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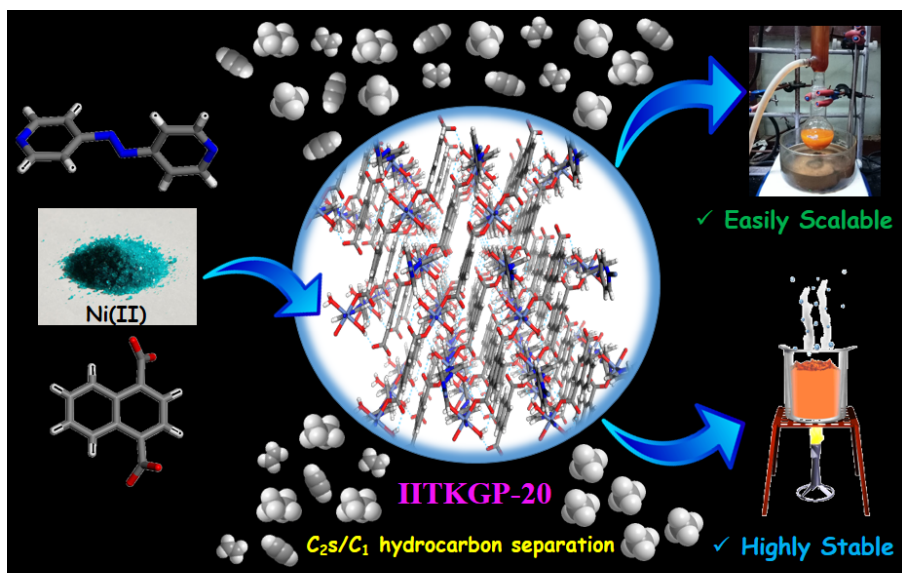
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Table of Contents:

The first 2D ‘thermodynamically stable’ microporous MOF (IITKGP-20) is reported by employing a mixed ligand strategy showing stability in liquid water, boiling water, acidic/basic solutions over a wide pH range 2-10. The material exhibits its potential for efficient separation of C₂ hydrocarbons over C₁ with high IAST separation selectivities.