Theoretical investigation of C1–C4 hydrocarbons adsorption and separation in a porous metalallocavitand†

Biswajit Mohanty and Gopal Avashthi

The purification of light hydrocarbons is one of the most important chemical processes globally which consumes substantial energy. Porous materials are likely to improve the efficiency of the separation process by acting as regenerative solid adsorbents. To investigate such translational systems, the underlying mechanism of adsorption in the porous materials must be taken into account. Herein we report the adsorption and selective separation of C1–C4 hydrocarbons in the coinage metal-based macromycyclic metalallocavitand Pillarplex, which exhibits excellent performance in the adsorption of CH4 at the ambient conditions with a binding energy of −17.9 kcal mol⁻¹. In addition, the endohedral adsorption of C2–C4 hydrocarbon is impressive. The CH4, C2H6, C3H8, and 1,3-butadiene have potential uptake of 2.57, 4.26, 3.60, and 2.95 mmol g⁻¹, respectively at ambient conditions are highest from their respective isomers. Selective separation of C1–C4 hydrocarbons is studied using ideal adsorption solution theory demonstrating its potential for one-step purification of C1–C3 hydrocarbons.

Molecular recognition supramolecular chemistry sets a new paradigm to study the adsorption and selective separation of guest molecules via the host–guest mechanism. The cucurbit[n]uril (n = 5,6,7,8,10) and pillar[n]arene (n = 5,6) are versatile macrocyclic molecules and ideal hosts in the supramolecular domain.3-5 Nau et al. studied the C1–C6 hydrocarbons within cucurbit[6]uril (CB[6]) for gas sensing and reveals that CB[6] is ideal for isobutene and cyclopentane adsorption.6 Coskun et al. studied the propane/methane separation using pillar[5]arene based conjugated microporous polymer via host–guest chemistry and observed the facile separation of propane from the natural gas mixture.7 Soft porous crystals of [2+3] imide based organic cage (NKPOC-1) and their HC adsorption phenomenon were investigated by Zhang et al. reveal the x-phase of NKOPC-1 selectively adsorbs propyne over propylene and propane at 298 K/1 bar condition.8

However, such organic hosts are restricted in large-scale employment due to their troublesome synthetic separation, purification, and post-synthetic modifications.9 Other than organic hosts, metal–organic frameworks (MOFs) are profound against guest binding using the supramolecular binding approach. The higher storage density of acetylene over ethylene has been studied by Schröder et al. using functionalized MOF by supramolecular binding and separation approach.10 Selective separation of C2–C4 hydrocarbons in the Zn2(sdc)2(bpe) (sdc = 4,4′-stilbenedicarboxylate, bpe = 1,2-bis(4-pyridyl)ethane) MOF has been studied by Li et al., claimed that C2 HC has higher selectivity over C3 and C4.11 Although MOFs are an attractive candidate for HCs capture and separation, their stability remains questionable. The limited stability against reactive
species such as water is a major concern as they can debase the MOF during the in-service events.\textsuperscript{15} The akin chemical properties, polarizability, and kinetic diameters of HCs (CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8}, C\textsubscript{2}H\textsubscript{2} have kinetic diameters of 3.8, 4.4, 4.9, 3.3, 4.2 Å respectively) coerce the complications for HC separations.\textsuperscript{15,16} As all the light HCs are adsorbent dependent, it is imperative to develop suitable adsorbents for effective HC separations. Early reports on metal coordinated cavitands, macrocycles, and cages are the flawless supramolecular host with exceptional guest binding effect.\textsuperscript{17,18} The coinage metal-based organometallic host has potential in the post-synthetic modification, simple synthetic pathway, tunable cavity, tailor-made pore surface, and high stability against air and water.\textsuperscript{19} Pöthig and Altmann synthesized a well-defined tubular metallocavitand with Au(1) metal center; Pillarplex (PPX) analogous to pillar[5]arenes readily accommodate linear guests with high selectivity.\textsuperscript{20} To address this challenge, we have investigated the adsorption of small HCs potentially with low carbon content (C\textsubscript{1}–C\textsubscript{4}) within the cavity of the PPX. Density functional theory (DFT) is employed to determine the electronic structure and stability of the system. The natural bond orbital (NBO) charge transfer method is used to explore the electronic transfer within the host–guest system. The nature of the interaction between HCs and PPX is analyzed using a non-covalent index (NCI). The individual components of binding energy are computed using the energy decomposition analysis (EDA). The maximum uptake of HCs is studied using the Grand canonical Monte Carlo (GCMC) simulation at various temperatures from 77–340 K and the pressure range from 0.1–10 bar. The isosteric heat of adsorption is computed to determine the thermodynamic stability of the complex. Further, the selectivity of HCs from their counterpart mixtures is studied using ideal adsorption

![The optimized geometry of PPX and HCs@PPX. The corresponding Au−H− interaction distances are shown. The distances are in Å units. The grey, white, blue and yellow colour represents the carbon, hydrogen, nitrogen and gold atom, respectively.](image-url)
solution theory (IAST) for selective separation using PPX as a separator channel.

Results and discussion

Geometries and energetic

The coherent bond properties of optimized PPX with the experimental report authenticates the befitting of the theoretical approach. The height and width of the PPX are 11.585 Å (expt. 11.700 Å) and 7.658 Å respectively measured between the distance of Au–Au positioned opposite to each other as shown in Fig. S1.† The Au–Au distance is 3.190 Å is congruent to the reported value (expt. 3.005 Å). The existing distance evidence the aurophilic interaction where the Au(i) atoms are packed at a distance that is 0.130 Å shorter than their van der Waals radii (Au: 1.66 Å).

The depth of the cavity is 3.785 Å longer than the analogous pillar[5]arene (7.800 Å). The structural resemblance with pillar[5]arene rationale PPX as a potential host and required further investigations.

The low carbon content HCs starting from CH4 to C4H8 (C1–C4) and their isomers are studied extensively using PPX to understand the adsorption behavior. The stable HC@PPX complex is discerned by swapping the position and orientation of HCs to their van der Waals radii. The Au⋯H–C interactions are impressive while in allene@PPX, the Au positioned opposite to each other as shown in Fig. 2.†

An investigation has been carried out comprising the Au⋯H–C interactions. In CH4@PPX, the CH4 resides closer to the Au atom with a distance of 3.033 Å. C2H2 was placed horizontally symmetrical fashion within the cavity with an Au⋯H–C distance of 2.937 Å. C3H4 and C4H8 molecules are in the horizontally inclined position with multiple Au⋯H–C interactions and a noticeable bond length of less than 3 Å is observed. In C3 HCs, Au⋯H–C interactions are impressive while in allene@PPX and C3H4@PPX some Au⋯H–C distances are found lesser than their van der Waals radii. C4 HCs are well buried inside the cavity of PPX and the majority of Au⋯H–C interactions are in the region of 2.721 to 3.054 Å which pronounces a weak hydrogen bond type interaction. In isobutylene and isobutane, the Au⋯H–C interactive distances are much lower compared to its isomers. The presence of such interactions influences the polarization effect by altering the bond length of HCs within the cavity. Trivial changes in bond lengths are observed for all the encapsulated HCs and details are given in Table S1.1† Upon entrapment of HCs, the structural deformation is observed in the PPX, where the Au–Au distance of HC@PPX gets reduced to some extent. Conversely, the Au–Au bond length in allene@PPX (0.019 Å) and isobutane@PPX (0.055 Å) is higher than that of PPX as shown in Table S2.†

The DE of PPX is higher than the HCs given in Table 1. The DE of PPX in allene@PPX (3.7 kcal mol−1) is the highest and C2H4@PPX (0.4 kcal mol−1) is the least among the studied system. The DE of PPX, in C2H4@PPX, is 1.1 kcal mol−1 and 0.2 kcal mol−1 higher than that of C3H6@PPX and C4H8@PPX and the ease of π electron transfer from HC to the metal center

[Image]

Fig. 2 The Au⋯H and N⋯H bond distances in the HC@PPX complex. The net binding energy values are in parenthesis inset in the figure.
Table 1. The binding energy (ΔE), basis set superposition corrected binding energy (BSSE), zero-point energy corrected binding energy (ΔE + ZPE), deformation energy (DE) of the host, change in Gibbs free energy (ΔG298) and enthalpy change (ΔH298) of the HC@PPX complex.

| Gas           | ΔE   | BSSE | ΔE + ZPE | DE       | ΔG298 | ΔH298 |
|---------------|------|------|----------|----------|-------|-------|
| CH₄           | −17.9| −18.0| −17.2    | 1.0      | −8.4  | −16.8 |
| C₂H₂          | −22.2| −19.1| −19.6    | 1.1      | −13.3 | −19.8 |
| C₂H₄          | −28.5| −23.5| −26.9    | 0.9      | −15.6 | −26.8 |
| C₂H₆          | −32.9| −27.4| −31.4    | 0.9      | −19.6 | −31.3 |
| Allene        | −30.4| −26.3| −28.1    | 3.7      | −14.9 | −28.3 |
| C₃H₆          | −31.2| −27.6| −29.3    | 3.3      | −17.1 | −29.4 |
| C₃H₄          | −37.9| −34.1| −36.1    | 2.8      | −23.9 | −36.0 |
| C₃H₈          | −43.7| −38.9| −41.8    | 1.6      | −28.6 | −41.8 |
| 1,2-Butadiene | −42.6| −38.2| −40.9    | 1.6      | −28.1 | −40.7 |
| 1,3-Butadiene | −43.8| −40.8| −41.6    | 1.0      | −28.9 | −41.5 |
| Butyne        | −42.2| −36.7| −40.6    | 0.9      | −27.8 | −40.4 |
| 2-Butyne      | −38.4| −34.0| −36.8    | 2.9      | −23.8 | −36.7 |
| C₂H₈          | −48.4| −42.9| −46.1    | 0.4      | −32.5 | −46.1 |
| (E)C₂H₄       | −48.2| −42.9| −45.9    | 3.1      | −32.6 | −46.0 |
| (Z)C₂H₄       | −48.7| −40.3| −46.6    | 3.2      | −33.4 | −46.5 |
| Isobutylene   | −47.2| −41.8| −44.3    | 3.4      | −29.7 | −44.6 |
| C₄H₁₀         | −54.7| −48.6| −52.6    | 1.5      | −38.9 | −52.6 |
| Isobutane     | −49.8| −46.9| −46.6    | 2.7      | −30.2 | −45.7 |

* All the energy units are in kcal mol⁻¹.

The ΔE value portrays the interaction of HCs within PPX as fairly high owing to its soft intertaction exerted between the Au(i) and HCs unravelled by the Pearson HSAB principle. The CH₄ molecule strongly binds to PPX with a ΔE value of −17.9 kcal mol⁻¹. The CH₄ uptake capacity of PPX is exceptionally higher than many of the reported systems such as MOF-5 (−4.51 kcal mol⁻¹), Ni-MOF-74 (−7.78 kcal mol⁻¹), Cu₂₃(m-BDC)₂₃ (−8.27 kcal mol⁻¹), TPa1 COF (−5.39 kcal mol⁻¹), Graphdiyne (−5.18 kcal mol⁻¹), etc. The ultrahigh binding energy of CH₄ in PPX is due to the strong interaction between the 6s levels of Au(i) and 2a₁ orbital of CH₄ and the charge transfer through level hybridization from CH₄ to Au(i) and not via Au(i) unoccupied orbitals.

An upraised ΔE value of C₂ HCs observed with a lowering in the percentage of s character unveils the stability of C₂H₂ over C₂H₆ and C₂H₄ with ΔE of −32.9 kcal mol⁻¹ is 10.7 and 4.4 kcal mol⁻¹ higher than C₂H₆ and C₂H₄ respectively. The higher binding energy of the C₂H₄ is due to the mixing of the occupied π*(CH₄) orbitals with the Au(i) orbitals resulting in an electron charge donation from C₂H₄ to Au(i) and a partial de-occupation of the π*(CH₄). The partial de-occupation is reflected in the lowest unoccupied molecular orbital (LUMO) that is formed by the interaction of the occupied π*(CH₄) of ethane and unoccupied s-orbitals of Au(i). The C₂H₄ stabilizes the π mode adsorption and strengthens the Au-C bond by readily balancing between donation and back-donation of electrons which strongly influence the molecular adsorption. The C₂H₂ is oriented in such a fashion that it experiences interaction with the Au(i) pₓ orbital parallel to it via dative interaction by the Dewar-Chatt-Duncanson scheme resulting donation of filled πₓ orbitals of the ligands into the vacant s orbitals of the metal atoms and the back donation. In a confined PPX region, the overlap of orbitals experiences repulsions, hence a steady decline in energy is observed. The binding energy of C₂ HCs in PPX is higher than reported benchmark study such as PCN-245 (C₂H₂ : C₂H₆: −5.5 kcal mol⁻¹; −6.5 kcal mol⁻¹), HKUST-1 (C₂H₂ : −5.5 kcal mol⁻¹), IRMOF-8 (C₂H₂ : C₂H₆: −8.4 kcal mol⁻¹; −8.4 kcal mol⁻¹), CuBTC(C₂H₆: −7.1 kcal mol⁻¹), Ni(BDC)-(TED) (C₂H₂ : C₂H₆: −6.7 kcal mol⁻¹; −7.9 kcal mol⁻¹), RPM3-2h (C₂H₂ : −12.4 kcal mol⁻¹), Fe-MOF-74(C₂H₂ : C₂H₆: −12.3 kcal mol⁻¹; −12.3 kcal mol⁻¹; −8.8 kcal mol⁻¹), MUF-15 (C₂H₂ : C₂H₆: −8.4 kcal mol⁻¹; −8.8 kcal mol⁻¹), Fe-MOF- 74(C₂H₂ : C₂H₆: −6.3 kcal mol⁻¹; −5.6 kcal mol⁻¹; −6.1 kcal mol⁻¹), etc.

The ΔE value of C₃ HCs is also remarkable where C₃H₈ possesses maximum binding energy of −43.7 kcal mol⁻¹ which is 13.3, 12.5 and 5.8 kcal mol⁻¹ higher than of allene, C₃H₄, and C₃H₆, respectively. The absence of π-electron density in C₃H₈ portrays higher ΔE value while the existence of orthogonal π-electron density in allene reduce the binding strength to −30.4 kcal mol⁻¹. The ΔE difference in allene/C₃H₈ (0.8 kcal mol⁻¹), allene/C₃H₆ (7.5 kcal mol⁻¹), C₃H₆/C₃H₄ (6.7 kcal mol⁻¹) is substantial enough for facile separation of individual C₃ HCs from their respective mixtures. The obtain ΔE is substantially higher than that of CuBTC (C₂H₂ : C₂H₆: −10.8 kcal mol⁻¹; −11.1 kcal mol⁻¹), Fe-MOF-74 (C₂H₂ : C₂H₆: −9.9 kcal mol⁻¹; −14.3 kcal mol⁻¹), pyr@Cu-BTC (C₃H₈:
C₃H₄: −8.7 kcal mol⁻¹; −11.6 kcal mol⁻¹,⁴⁴ Uio-66 (C₂H₆: 9.9 kcal mol⁻¹),⁴⁵ Cu-DTO (C₂H₆: C₃H₈: −14.0 kcal mol⁻¹; −33.5 kcal mol⁻¹),⁴⁶ tpt-Mg-MOF-74 (C₂H₆: 8.15 kcal mol⁻¹),⁴⁷ WOFOUR-1-Ni (C₃H₈: C₄H₁₀: −11.9 kcal mol⁻¹; −11.3 kcal mol⁻¹)⁴⁸ etc.

Furthermore, C₄ HCs and their ten isomers are investigated as their contributions to the natural gas mixtures cannot be ignored. C₄H₁₀ interacts strongly with an effective binding energy of −54.7 kcal mol⁻¹ whereas the binding strength of 2-butyne is least (−38.4 kcal mol⁻¹). The notable energy difference of 6.3 kcal mol⁻¹ between C₄H₁₀ and C₄H₈ is ideal for the mainstream separation of their mixture. 1,3-butadiene (−43.8 kcal mol⁻¹) exhibits higher binding strength than 1,2-butadiene (−42.6 kcal mol⁻¹) and the binding energy of 1-butyne is −42.2 kcal mol⁻¹ is 3.8 kcal mol⁻¹ higher than 2-butyne. The energy difference between E-C₄H₈/Z-C₄H₈ and isobutane/isobutylene is noteworthy. In general, the binding energy values of HC@PPX are higher than the ever-studied system. Hence, PPX can be a good material for selective adsorption and separation of light HCs. To reduce the errors associated with total binding energy, BSSE and ZPE corrected binding (∆E + ZPE) energy values are taken into account and no such perceived changes are noticed.

To explore the stability of PPX + HC → HC@PPX inclusion complex, Gibbs free energy (∆G) has been computed for HC@PPX. The ∆G value for all the studied complexes is found to be negative, proclaiming HC@PPX is exergonic. The higher ∆H reveals the stability of the system is enthalpy driven. The calculated ∆G and ∆H values are given in Table 1. The ∆G values of C₁–C₄ HCs spanned from −8.4 to −38.9 kcal mol⁻¹ while the ∆H values are in the range of −16.8 to −52.6 kcal mol⁻¹. The entropy change (ΔS) has a negligible effect on the complication given in Table S3.† Both the ∆G and ∆H values are the least for CH₄@PPX while the maximum for C₄H₁₀@PPX. Noteworthy ∆G values in C₂ and C₃ suggest PPX as a material of interest for C₂/ C₃ HCs separation. A trivial ∆G value is observed in C₄ HCs, thus the separation of C₄ HC needs an external potential.

To understand the effect of the inter-ligand and cooperativity within the cavity, for example, we have considered some of the π-bonded molecules. It is noticed that the PPX host accommodates only two HC within the cavity while the third one residing the open face of the PPX. Within the cavity C₂H₂, C₂H₄, allene, C₂H₆, 1-butylene, and 2-butyne experience π⋯π interactions at a distance of 3.189, 3.340, 3.364, 3.280, 3.506 and 3.405 Å respectively. The large size of C₂H₆, and other C₄ HC dimers exerted by CH⋯π interactions. The CH⋯π distance in C₂H₆ is 2.781 Å whereas in 1,2-butyne, 1,3-butyne, 2-butylene, C₂H₄ (E)-C₃H₈ (Z)-C₃H₈ and isobutylene, the distance is 3.022, 2.799, 2.526, 2.743, 2.517, 2.743 and 2.513 Å respectively. The π interaction impetuses the enhanced adsorption of HCs within the confined cavity.

The cooperative effect is an interesting factor in host-guest supramolecular interaction; therefore, we have computed the cooperative adsorption binding energy (CABE) and adsorption binding energy (ABE). The CABE is calculated by taking out the HC from the PPX host cavity, and single point calculations were carried out with the same orientations as obtained from the PPX cavity and the ABE is evaluated by relaxing the structure obtained from the HC@PPX complex. The ABE of HC@PPX is higher than the CABE value which suggests a cooperative interaction exists in the host-guest system. The CABE, ABE, and C–C bond distance of relax and constrained dimer is shown in Fig. S2.† The relax dimer bond distance is higher than the constrained dimer which claims the cooperative interaction engendered within PPX. C₃H₄, 1-butyne, 2-butyne, and (E)-C₄H₈ exhibit higher cooperativity interaction with an energy value of 5.1, 6.5, 6.0, and 8.4 kcal mol⁻¹. Thus, it is well observed that the HCs adsorption within the PPX is asserted by the cooperative effect.

Natural gas sweetening is another stumbling block to the industrial separation of natural gas and acidic gas such as CO₂, and H₂S. Hence we have studied CO₂ and H₂S adsorption by PPX using B97D2/LanL2DZ level of theory. The ∆E of CO₂ and H₂S is −17.6 and −21.9 kcal mol⁻¹ respectively while CH₄, C₂H₆, C₃H₈ and C₄H₁₀ is −17.9, −32.9, −43.7 and −54.7 kcal mol⁻¹ respectively. The ∆E of an alkane is higher than acidic gas, thus alkane is the superior adsorbate over CO₂ and CS₂. The ∆G⁻¹ kcal mol⁻¹ whereas CH₄, C₂H₆, C₃H₈ and C₄H₁₀ are −8.4, −19.6, −28.6 and −38.9 kcal mol⁻¹ respectively. Hence it will be difficult to separate CH₄ in presence of an excessive amount of CO₂ and CS₂ as the complexity is exergonic and the complexation will be CO₂@PPX and CS₂@PPX instead of CH₄@PPX.

The C₂–C₄ hydrocarbon separation can be easily separated in the presence of CO₂ and CS₂ as the substitution reaction undergoes endergonic.

C₃H₈@PPX + CO₂ → CO₂@PPX + CH₄ ΔG = −0.6 kcal mol⁻¹
C₃H₈@PPX + CS₂ → CS₂@PPX + CH₄ ΔG = −1.6 kcal mol⁻¹

The C₂–C₄ hydrocarbon separation can be easily separated in the presence of CO₂ and CS₂ as the substitution reaction undergoes endergonic.

C₃H₈@PPX + CO₂/CS₂ → C₃H₈@PPX + CO₂/CS₂, ΔG = 10.6/18.6 kcal mol⁻¹
C₃H₈@PPX + CO₂/CS₂ → C₃H₈@PPX + CO₂/CS₂, ΔG = 19.6/28.8 kcal mol⁻¹
C₃H₈@PPX + CO₂/CS₂ → C₃H₈@PPX + CO₂/CS₂, ΔG = 29.9/28.8 kcal mol⁻¹

The enthalpy contribution in CO₂, CS₂, CH₄, C₂H₆, C₃H₈ and C₄H₁₀ is −16.3, −21.3, −19.8, −28.3, −40.7, and −52.6 kcal mol⁻¹, respectively impacts the reaction is enthalpy driven and is ideal to use PPX for the separation of HCs except for CH₄ in presence of acidic gases.

**Electronic charge transfer**

Natural bond orbital (NBO) analysis has been performed to articulate the charge transfer between the host–guest system. An apparent charge transfer is discerned from guest HCs to PPX and the ease of charge transfer increases with the HCs size. The
significant charge transfer is observed in C4 HCs, C3H6, and C3H4 of ca. 0.10–0.13 e– while for other complexes is ca. 0.10 e–. CH4 (0.05 e–) and C2H2 (0.04 e–) experience very lower e– transfer due to their smaller size. Further illustration proclaims a metal to ligand (HCS) e– transfer (MLCT) exhibits during the complexation process. The MLCT is in the range of 0.01–0.03 e– and it’s obvious the back donation of π-electron from the bonding molecular d-orbital of metal to the empty antibonding π* orbital of ligands. The charge transfer values are given in Table S3.† In the complexation, the predominant charge transfer obtains from HCs to PPX.

Energy decomposition analysis

Energy decomposition analysis (EDA) has been accomplished by considering PPX and HC as interacting fragments are provided in Fig. 3 and their corresponding energy and percentage of contribution are given in Table S4.† The dispersion (ΔE\_disp) term is the major contributor of ca. 45.8–61.4% to the total interaction. Regardless, the electrostatic (ΔE\_elct) of ca. 22.5–34.1% and orbital (ΔE\_orb) of ca. 15.1–20.1% contribute significantly to the total binding energy of the stabilized complex. As expected, the higher ΔE\_disp of CH4@PPX is owing to its zero-field dipole and quadrupole moment, instigating the induced dipole interaction between CH4 and the charged portal of PPX. Similarly, C2 HCs exhibit zero field-dipole but unveil positive quadrupole moment and higher polarizability than the former one engenders induced dipole interaction. All C3 HCs experienced a permanent dipole moment except allene, claiming strong dipole–dipole interaction between the HCs and PPX, hence exhibiting notable ΔE\_elct interaction compared to other HCs. The presence of acidic hydrogen in allene possibly forms the hydrogen bonding interaction with the –N-centered pyrazole portal of PPX. Therefore, the contribution of ΔE\_elct (34.3%) is the highest among the studied HCs, which reflects the higher ΔE\_orb (19.9%) and lower ΔE\_disp (45.8%) term. In C4 HCs, 1,2-butadiene, 1-butyne, C3H6, (2)-C4H8, isobutylene, and isobutane interact with the PPX by dipole–dipole interaction due to permanent dipole moment, hence their ΔE\_elct term ca. 27.8–34.0% from their isomers (ca. 26.0–27.6%). Isobutane and isobutylene experienced weak hydrogen bonding resulting ΔE\_elct, of 34.0 and 32.6% and the ΔE\_disp term is 47.9 and 48.8% respectively is the lowest among the studied system. 2-Butyne, (E)-C4H8 interaction with PPX is purely dispersive like ca. 58%. All-inclusive analysis reveals the combined effect of ΔE\_disp and ΔE\_elct are major factors for HC@PPX stabilization. Although the orbital interaction is trivial but can’t be neglected and the contribution of ΔE\_orb is ca. 15.1–20.1% and stronger interactions are perceived in the complexes containing the acidic hydrogen ligands.

Noncovalent interaction

NCI index deciphered the noncovalent interaction in the HC@PPX system as shown in Fig. 4. The presence of green surfaces between HCs and PPX highlights the van der Waals type in nature. The increasing size of the green surface enhances van der Waals interaction and increasing HC size strengthens the van der Waal’s contact. The spattered red plot in the imidazole/pyrazole ring center depicts the strain produced by the ring current. The blue color surfaces claim the hydrogen bonding interaction in the stabilized system, according to the presently used color coding scheme. A significant H-bonding is visualized in the allene, isobutylene and isobutane entrapped complex. Furthermore, the plots of reduced density gradient s versus sign (λ_2)ρ elucidate better insight into the specific types of interaction present in the complex. Extremely low density, low gradient, and moderately low density and low gradient troughs with a negative sign (λ_2)ρ values indicate the presence of attractive dispersion and
hydrogen bonding interactions, respectively. Contrary, a low gradient trough appearing in the positive region of sign \((\lambda_2)\rho\) conveys the repulsive interactions produced by ring strain. The superimposed plots are shown in Fig. S3,† where PPX moieties are designated by blue color and complexes, are portrayed in red color. In every system, an additional narrow spike is observed at slightly negative sign \((\lambda_2)\rho\) values around −0.005 a.u. implies the interaction is dispersive.

**GCMC analysis**

The gravimetric uptake of C1–C4 HCs at 77–340 K/0.1–10 bar has been investigated using the PPX host. At 273, 298, and 340 K and 1 bar, CH₄ adsorption has been 3.51, 2.37, and 1.33 mmol g⁻¹ and at 10 bar the adsorption values are 5.41, 4.81, and 3.69 mmol g⁻¹, respectively. The CH₄ follows type-1 adsorption isotherm and increasing temperature reduces CH₄ uptake whereas high pressure induces higher CH₄ adsorption. At 77 K the adsorption of CH₄ is 5.60 mmol g⁻¹ at 1 bar and 7.31 mmol g⁻¹ at 10 bar pressure.

The adsorption isotherm plot of 298 K is shown in Fig. 5(a) while the 77, 273, and 340 K are shown in Fig. S4(a), S5(a), and S6(a),† respectively. The adsorption is higher at 77 K due to the lowering of intermolecular repulsion between the CH₄ molecule. 340 K results decrease in CH₄ uptake, this can be attributed to high temperature favors the CH₄ in the free gaseous state rather than adsorbed state, and also in high temperature the pore volume of the substrate decreases rendering lower adsorption.

**Fig. 4** The noncovalent interaction plot of pristine host PPX and the HC encapsulated PPX. The green, blue and red color code represents the van der Waal, hydrogen bonding attractive interaction while red color depicts repulsive interactions.
The uptake of C2H6 (3.0–4.1 mmol g⁻¹) is high compared to its isomers in the low-pressure region (298 K/0.1–1 bar). At high pressure, the C2H4 adsorption is prominent followed by C2H6 and C2H2. The gravimetric uptake of C2H2, C2H4, and C2H6 are 2.80, 4.26, and 4.22 mmol g⁻¹ respectively at ambient conditions while at 10 bar the uptake increases to 4.37, 4.74, and 4.50 mmol g⁻¹ respectively. At 77 K/1 bar the uptake varies C2H2 > C2H4 > C2H6 whereas at 273 K the adsorption strength is C2H4 > C2H6 > C2H2 up to 4 bar and thereafter C2H4 > C2H2 > C2H6. The 340 K is contrary to 273 K i.e. C2H6 > C2H4 > C2H2. This reveals at low-temperature the uptake of unsaturated HC is more effective whereas at high temperatures the C2H6 adsorption is significant. The adsorption isotherms plot of C2 HC at ambient condition is shown in Fig. 5(a) while Fig. S4(a), S5(a), and S6(a)† represents the isotherm plot of 77, 273, and 340 K respectively.

A type-IV adsorption isotherm has been observed for allene shows significant uptake of 3.76 mmol g⁻¹ at 298 K/2 bar whereas other C3 isomers exhibit type-I at 298 K. At ambient conditions, the uptake of allene, C3H4, C3H6, and C3H8 is 3.51, 3.60, 3.57 and 3.12 mmol g⁻¹, respectively are shown in Fig. 5(b), increasing pressure up to 1.5 bar results higher allene uptake followed by C3H4, C3H6, and C3H8. The gravimetric capacity of C3H4 is lower than other C3 isomers due to a larger kinetic diameter of 4.9 Å. At 77 K [Fig. S4(b)]†, the adsorption isotherm of C3H4 is moderately higher than allene with increasing pressure and C3H4 adsorption is notably higher than C3H6. At STP [Fig. S5(b)]† the allene uptake is very high and high pressure portrays the C3H4 and allene have an equal propensity for adsorption. Thus, 273 K and 0.1–4 bar could be the ideal setup for selective adsorption of C3 HCs. The adsorption of allene (3.29 mmol g⁻¹), C3H4 (3.20 mmol g⁻¹), and C3H6 (3.33 mmol g⁻¹) swing trivially at 340 K [Fig. S6(b)]†, and the uptake of C3H8 (2.90 mmol g⁻¹) is lowest. Increasing pressure reduces the C3H4 adsorption while inducing allene uptake. Unusual behavior is observed in C3H4 uptake capacity at a high-pressure and overall range of temperature which coincides with the allene adsorption isotherm. This can be explained by the activation of π-bond of allene and alkyne by Au(i) attributed to relativistic effects. Though Au(i) is coordinated with the electron-rich NHC groups which propel the π-activation more significantly with C3H4 rather than allene in high-pressure regions.

C4 HC uptake by PPX is in the ideal range, the highest adsorption is observed for 1,3-butadiene and isobutane is least at ambient condition and 1,2-butadiene follows type-IV adsorption while others are of type-I shown in Fig. 5(c). A preference analysis of C4H10, isobutane, 1,3-butadiene and isobutylene over other C4 HCs is investigated owing to its presence in the natural gas mixture. At ambient setup, the uptake capacity of C4H10, isobutane, 1,3-butadiene, and isobutylene are 2.32, 1.93, 2.95, and 2.36 mmol g⁻¹, respectively. The remaining HC adsorption is in the ideal range. Except for 1,3-butadiene (3.08 mmol g⁻¹), other HCs do not have notable uptake in cryogenic condition/1 bar as shown in Fig. S4(c).† An unrelieved uptake of HC has been observed at ambient and STP conditions [Fig. S5(c)]†. At 340 K/1 bar, the adsorption of 1,2-butadiene is high and with increasing pressure, the isobutylene shows steep growth in the adsorption as shown in Fig. S6(c).† The other C4 HC uptake strength is monotonous due to their equal kinetic diameter. Thus, the simulation study reveals that PPX might be a good candidate for the capture of C1–C4 HC under ambient conditions. Further, we have performed the density distribution of the center of mass of HC molecules in

Fig. 5 (a) Represents the adsorption isotherm of C1/C2 HCs (b) represents the adsorption isotherm of C3 HCs and (C) depicts C4 HCs at 298 K temperature and pressure 0.1–10 bar.
GCMC simulation as shown in Fig. S7.† The results from GCMC simulation at ambient condition indicate that the guest HC molecules lies at the center and also adhere to the outer open site of PPX due to the presence of the –N atom in the imidazolidine motif. C1 and C2 HC show higher density coverage than C3 and C4 due to smaller size and lower kinetic diameter. The thermodynamic view of HC adsorption using PPX at 298 K has been determined using the isosteric heat of adsorption (Q_st) and is shown in Fig. 6.

In C1/C2 HC, the Q_st of CH4 and C2H2 are constant over the entire pressure range (0.1–10 bar) whereas C2H4 and C2H6 increase slowly from 0.1–1 bar and afterward remain constant. The increasing Q_st value depicts the adsorbate interaction with the PPX and lateral interaction between the adsorbate molecules which is corroborated by the DFT and cooperative binding study. The constant Q_st portrays the adsorption that occurs in the energetically homogenous adsorbent which is due to the effect of capillary condensation in the mesoporous material. The onset of capillary condensation results in constant Q_st induced by confinement within the pore network. Akin to C2H4 and C2H6, C3 and C4 HCs exhibit the increase in Q_st value from 0.1–1 bar enunciates the adsorbate–adsorbent interaction and constant from 1–10 bar attributed by capillary condensation.

**Ideal adsorption solution theory**

The potential separation of C1–C4 HCs has been investigated using ideal adsorption solution theory (IAST) for equimolar components. At the ambient setup, the selectivity of C2H6 is higher than its counterpart C2 isomers as shown in Fig. 7(a). However, at 273 K the C2H4 separation is more facile shown in Fig. S8(a).† C2H2 selective separation is very much pronounced irrespective of temperature and pressure. The selectivity difference between allene and C3H4 is minor at 298 K and is notable at STP under high pressure shown in Fig. S8(b).† At ambient conditions the selectivity between C3H6 and C3H8 is distinguishable. However, in 273 K all C3 HCs can be easily separable by applying moderate to high pressure and the selectivity is allene > C3H4 > C3H6 > C3H8. The selectivity of C3H6 is preferred over other C3 HCs at a higher temperature of 340 K [Fig. S9(b)]. Lower temperature and high pressure will be facile for allene separation whereas high temperature leads C3H6 with effective selectivity from its isomers. The selectivity of C4 hydrocarbon is quite lower than C1–C3 HCs. At ambient conditions, the separation of 2-butyne from its isomers is a bottleneck whereas at STP [Fig. S8(c)] the separation is favorable. 2–10 bar/298 K and 0.1–2 bar/273 is the ideal range for the 2-butyne/1-butyne selective separation. The selectivity of isobutane is least in all conditions. The order of selectivity at 298 K/2–10 bar is 2-butyne > 1-butyne > 1,3-butadiene > 1,2-butadiene > (Z)-C4H8 > (E)-C4H8 ≈ C4H10 ≈ isobutylene > isobutane. The adsorption selectivity is mainly attributed to pore shape, guest size, temperature, and internal surface functionality of pores in the PPX. 298 K, 273 K, and 340 K are ideal temperature conditions for the selective separation of C2, C3, HCs. For C4 HCs more external pressure is required.

**Comparison with benchmark report**

Our results are compared with the existing benchmark reports (last three years) on the MOF-based hydrocarbon adsorption under ambient conditions and the comparison is listed in Table S5.† The CH4 adsorption in PPX is remarkable with 2.37 mmol

![Fig. 6](a) Represents the isosteric heat of adsorption (Q_st) of C1/C2 HCs (b) depicts Q_st of C3 HCs and (c) portrays Q_st of C4 HCs at 298 K temperature.
The metallocavitand PPX is a well-defined tubular cavity made up of octanuclear N-heterocyclic carbene complex of Au(i) have been explored in this study. The crystal structure obtained from ref. 20 is further investigated to understand the electronic effect and adsorption properties. The geometry of PPX and HCs entrapped PPX (HC@PPX) has been optimized at B97D2/LanL2DZ level of theory.\textsuperscript{74,75} The subsequent harmonic vibrational analysis reveals the existence of real frequency in the structure belonging to minima on the potential energy surface (PES). We have computed zero-point energy corrected binding energy (\(E + ZPE\)) and basis set superposition error (BSSE) at the same level of theory. The standard counterpoise method proposed by Boys and Bernardi has been adopted for the BSSE correction.\textsuperscript{76} The natural bond orbital (NBO) analysis has been performed at the B3LYP-D3/Def2-TZVP level of theory to determine the electronic charge transfer within the host–guest complex.\textsuperscript{77} All the calculations are computed using the Gaussian 09 program package.\textsuperscript{78}

The energy decomposition analysis (EDA) has been carried out using dispersion corrected hybrid functional B3LYP-D3 with triple-zeta two polarization function T22P implemented in the ADF (2017) program.\textsuperscript{79–82} Zeroth order relativistic approximation (ZORA) method has been incorporated for computation as gold exhibits a large relativistic effect.\textsuperscript{83} In EDA, the fragment-based computations are invoked to treat PPX as one fragment and the guest molecules are other fragments. The total energy is decomposed into four major energy components viz.
electrostatic ($E_{\text{elec}}$), dispersion ($E_{\text{disp}}$), orbital ($E_{\text{orb}}$), and the Pauli term ($E_{\text{pau}}$). The former three energy terms are attractive while the latter one is repulsive. The $E_{\text{elec}}$ term represents the classical electrostatic interaction that exists between the two charged species namely host and guest after complexation. $E_{\text{disp}}$ term arises due to the electronic fluctuation between two adjacent molecules attributed to temporary dipoles in the complex. $E_{\text{orb}}$ is the orbital interactions initiated by the overlapping of occupied and unoccupied atomic orbitals of the host-guest system. The $E_{\text{pau}}$ is the Paulis repulsive term exerted by the overlapping of an identical quantum number between the two interacting fragments.

The real-space visualization of interaction has been studied using the NCI index which identifies covalent interactions solely based on electron density and its derivatives. \textsuperscript{84} NCI index is based on the 2D plot of reduced density gradient (RDG), $s$ as a function of electron density $\rho(r)$:

$$s = \frac{1}{2(3\pi^3)^{1/3}} \frac{|\nabla \rho(r)|}{\rho(r)^{4/3}}$$

The plot where RDG value approaches zero is identified as the noncovalent region. \textsuperscript{84} Analysis of electron density determines the binding strength of interacting molecules. However, both attractive and repulsive interactions have a positive correlation with electron density in the corresponding region. \textsuperscript{85} A real space function sign ($\lambda_2$) multiplied by electron density $\rho(r)$ is indeed to define the attractive and repulsive term where the curvature $\lambda_2$ is the second eigenvalue of the Hessian density matrix. \textsuperscript{86} A negative and positive value of $\lambda_2$ is identified as strong attractive and repulsive interactions respectively while for van der Waals interaction the value of $\lambda_2$ approaches to zero. \textsuperscript{86,87} Multiwfn program has been used to compute the NCI index whereas Chemcraft for the gradient isosurface visualization, where the color codes decide the value of sign ($\lambda_2$)$\rho(r)$. \textsuperscript{88,89} Blue and green color represents the attractive hydrogen bonding and van der Waals interaction whereas red color depicts the repulsive strain ensure by steric crowding.

Grand canonical Monte Carlo (GCMC) simulation has been carried out to determine the maximum HCs uptake capacity of PPX at an adsorption temperature of 77, 273, 298, and 340 K and pressure from 0.1 to 10 bar. For each simulation $1 \times 10^5$ GCMC cycles were used for equilibration and $1 \times 10^7$ cycles were used to assess the ensemble average properties. The simulations were performed using the sorption module of Material Studio. \textsuperscript{90,91} The universal force field (UFF) parameter has been used to describe the interatomic interaction with a cut-off distance of 12.5 Å has been used for all Lennard–Jones interactions. \textsuperscript{92} Long-range electrostatic interactions were computed using the Ewald summation method. \textsuperscript{93} The simulation has been carried out in a $1 \times 1 \times 2$ supercell with imposed periodic boundary conditions in all directions.

The adsorbate uptake capacity using PPX crystal obtained from the GCMC simulation is further utilized for the computation of selective separations. Langmuir adsorption isotherm model has been used to examine the selectivity of individual gas components over multi-component using ideal adsorption solution theory (IAST). \textsuperscript{94}

$$n(P) = q \frac{KP}{1 + KP}$$

where $P$ is the pressure of the bulk gas at equilibrium, $q$ is the saturation loading The separation of the mixture is carried out at 298 K temperature and the data over the pressure range fitted more precisely with an $R^2$ value of 0.99.

**Conclusions**

In summary, Au(i) coordinated microporous metalloccavitand host, PPX has been investigated for potential HCs adsorption and separation. C1–C4 light HCs have been taken into consideration owing to their availability in the natural gas mixture. DFT study unveils facile adsorption of HCs at ambient conditions with extraordinary binding strength. All the complexes are stable at ambient conditions and the complexation is enthalpy driven. CH$_4$, C$_2$H$_6$, C$_3$H$_8$, and C$_4$H$_{10}$ are the leading adsorbents with unprecedented binding energy from their respective isomers. The energy difference between the C$_3$H$_6$/C$_2$H$_4$, C$_2$H$_5$/C$_3$H$_6$, allene/C$_3$H$_6$, C$_2$H$_4$/C$_2$H$_6$, C$_4$H$_8$/C$_4$H$_{10}$ is strong enough for selective separation from their isomers. EDA discerns the nature of interactions that are dominated by dispersion (45.8–61.4%) followed by electrostatic (22.5–34.3%) and orbital (15.1–20.1%) terms which are further corroborated by the NCI index. GCMC simulation predicts the gravimetric uptake of CH$_4$, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_8$, C$_4$H$_{10}$, and 1,3-butadiene is very high at 298 K and pressure range up to 10 bar. The magnitude of $Q_{\text{st}}$ reveals the high affinity of HCs to the pore volume of the adsorbents and the existence of adsorbate–adsorbate interaction unveils the binding cooperativity. The results of GCMC and $Q_{\text{st}}$ corroborated with the DFT and cooperative effect study. The IAST claims that 298 K, 273 K, and 340 K are ideal temperature conditions for the selective separation of C$_2$H$_6$, allene, and 1,3-butadiene from their respective isomers. This work provides an elegant example of N-heterocyclic carbene (NHC) based Au(i) metalloccavitand for the HCs separation and effectively more sophisticated porous material can be designed based on these concepts.

**Conflicts of interest**

There are no conflicts to declare.

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