



Hemicryptophane as a supramolecular host for the selective recognition and potential removal of halogenated pollutants

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ARTICLE INFO

Keywords:

Hemicryptophane
Decontamination
Non-covalent interactions
Toxic pollutants
Host-guest

ABSTRACT

Chloro- and fluorocarbon compounds are toxic environmental pollutants that pose serious risks to both human health and ecosystems, highlighting the need for their efficient detection and removal. Although macrocyclic hemicryptophane (Hm) systems are well known for their role in catalysis and energy-related applications, their potential as host materials for pollutant capture remains insufficiently explored. In this study, the sensing capability and selectivity of hemicryptophane macrocycles toward various freon-type molecules, including CCl₄, CCl₃F, CHCl₃, CH₂Cl₂, CF₃Br, C₂F₆, and CF₄, are investigated using computational methods. The host-guest complexes are analyzed through interaction energy calculations, natural bond orbital (NBO) analysis, frontier molecular orbital (FMO) studies, and interaction region indicator (IRI) analysis. The results demonstrate that the central cavity of selected hemicryptophane platform provides a favorable binding site for the studied freon-type molecules. The calculated interaction energies confirm the thermodynamic stability of the resulting complexes, while the HOMO–LUMO energy gaps (E_{H-L}) provide insight into their electronic stability and reactivity. Among the studied compounds, chlorinated species, particularly CCl₄, CCl₃F, and CHCl₃, show the strongest interactions with the Hm platform, with interaction energies of -128.32 , -109.37 , and -92.65 kJ mol⁻¹, respectively. These interactions are predominantly governed by non-covalent forces. Overall, this study suggests that hemicryptophane-based systems have strong potential as host materials for the capture and removal of hazardous chloro- and fluorocarbon pollutants.

1. Introduction

Air pollution has become a pressing global issue, attracting widespread scientific attention [1,2]. Both natural and anthropogenic pollutants contribute to damage infrastructure [3], acid rain [4], threaten human health, and disrupt ecological balance [5]. The pollutants are classified as primary, directly emitted from natural or industrial sources, or secondary, formed via atmospheric reactions of primary species [6]. Freons, among the most prevalent environmental pollutants, were identified as key contributors to stratospheric ozone depletion, prompting their phase-out under the Montreal Protocol for industrialized nations [7]. The Montreal Protocol allowed developing countries a grace period, exempting them from the 1993 chlorofluorocarbon phase-out required of developed nations until 2003 [8]. Nevertheless, freon production persisted in many developing regions, and with their

ongoing use in industry as propellants and refrigerants, urgent development of efficient removal and degradation methods after use remains essential for complete elimination [9].

Freons belong to a group of environmentally persistent compounds notorious for their resistance to degradation. Their destructive interaction with stratospheric ozone poses severe risks [7]. Extensive efforts have targeted the neutralization of toxic, often carcinogenic halogenated organics, especially those bearing fluorine and chlorine [10,11]. Various synthetic hosts including organic macrocycles and metal complexes can capture halocarbon guests like halogenated aromatics or common solvents such as CH₂Cl₂, CHCl₃, and CCl₄ [12–14]. Miljanic *et al.* developed a porous organic system for the capture of fluorocarbons and chlorofluorocarbons [15]. Similarly, Atwood *et al.* explored various freon encapsulation strategies [16]. Additionally, it has been explored that the host-guest complexation of chlorofluorocarbons within calix [4]

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<https://doi.org/10.1016/j.jece.2026.123557>

Received 17 April 2026; Received in revised form 2 June 2026; Accepted 9 June 2026

Available online 10 June 2026

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arene macrocycles and found that chlorinated halocarbons display enhanced binding affinity toward the calix [4]arene cavity [17].

Hemicryptophanes (Hm) are C₃-symmetric ditopic molecular systems built from chiral cyclotriphenylene (CTB) derivatives [18]. Unlike cryptophanes, which rely mainly on van der Waals and cation- π interactions for substrate binding, hemicryptophanes enable diverse molecular recognition contacts [19]. Hosts incorporating motifs like tris (2-aminoethyl)amine (TREN), triacetamidoamine, benzenetricarboxamide, cyclopeptides, or calixarenes excel at anion complexation via ion-pair binding, stereoselective glucopyranoside recognition [20,21], and capture of bioactive ammoniums including zwitterions [22–25]. These cages also support confined-space catalysis. Recently, R. Mao *et al.* investigated the distinctive catalytic activation of methane in an iron-loaded hemicryptophane cage (FeO-TPA@Hm), elucidating key roles of its architecture and electronic effects [26]. In another study, F. Br  gier *et al.* experimentally examined a chiral hemicryptophane cavity formed by capping permethylated α -cyclodextrin (α -CD) with a C₃-chiral cyclotriphenylene derivative for solvent sensing through ECD and NMR spectroscopy. The α -CD methoxy protons respond to solvent size (e.g., greater shielding in C₂D₂Cl₄ than CDCl₃), with MD simulations revealing selective binding of CHCl₃ (–32.7 kJ/mol) and C₂H₂Cl₄ (–21.1 kJ/mol) in the α -CD cavity alone [27]. Additionally, L. Miton *et al.* designed an electron-poor hemicryptophane featuring tetra-fluoroxylene arms and a benzene triimide core to boost anion- π interactions, achieving 10-fold greater chloride binding ($K_a = 207\text{ M}^{-1}$) and novel triiodide affinity ($K_a = 416\text{ M}^{-1}$) relative to less deficient counterparts [28].

Despite extensive studies on hemicryptophane systems, their application in sensing freon-type pollutants has not been previously explored. Investigating Hm/freon interactions is therefore important to understand how encapsulation influences the structural, electronic, and polarity characteristics of the host, as well as its potential for selective recognition of halogenated contaminants.

This work offers insights into the applicability of an eco-friendly macrocyclic hemicryptophane platform as freon-specific host, describing selective binding mechanisms and thus, offering potential environmental remediation strategies. The inclusion complexes of hemicryptophane with chlorocarbons (CCl₄, CHCl₃, CH₂Cl₂, CCl₃F) and fluorocarbons (CF₄, C₂F₆, CF₃Br) were described to facilitate material innovations for hazardous pollutant remediation.

2. Computational methodology

Pristine hemicryptophane, hemicryptophane along with chlorocarbons and fluorocarbons and the corresponding host-guest complexes were optimized using the B3LYP-D3/6–311 + G(d,p) level of theory, with full atomic relaxation under unrestricted conditions. Accurate and reliable optimized geometries were obtained as all calculated convergence parameters, including maximum force, RMS force, maximum displacement, and RMS displacement, remained below their respective threshold limits of 0.000450, 0.000300, 0.001800, and 0.001200 a.u. The B3LYP hybrid functional is commonly applied in quantum chemistry to evaluate thermodynamic stability and electronic properties of diverse molecular systems [29]. B3LYP is widely utilized for mechanistic studies and geometry optimizations across diverse systems [30,31]. Grimme's D3 dispersion correction was incorporated here to accurately model non-covalent interactions [32]. Frequency calculations were carried out at the same level of theory to confirm that the optimized geometries correspond to stable minima on the potential energy surface, as evidenced by the absence of imaginary frequencies. From all feasible interactions, only the most stable systems were selected for in-depth analysis. Interaction energies between hemicryptophane and targeted analytes such as CHCl₃, CCl₄, CH₂Cl₂, CCl₃F, CF₃Br, C₂F₆, and CF₄, were computed in gas phase and in water as given in Eq. 1:

$$E_{\text{int}} = E_{\text{Hm/freon}} - (E_{\text{freon}} + E_{\text{Hm}}) \quad (1)$$

The interaction energy (E_{int}) is defined in Eq. (1) as the difference between the energies of the Hm/freon complex ($E_{\text{Hm/freon}}$), the isolated Hm macrocycle (E_{Hm}), and the freon guest (E_{freon}). Furthermore, the basis set superposition error (BSSE), arising from the overlap of finite basis sets, was corrected using the counterpoise method. The counterpoise-corrected interaction energies (E_{CP}) were calculated according to Eq. (2).

$$E_{\text{CP}} = E_{\text{int}} + E_{\text{BSSE}} \quad (2)$$

Additionally, the change in enthalpies and Gibbs free energies for all Hm/freons complexes have been calculated.

To mimic the effect of water, the CPCM and SMD implicit solvation model was employed [33]. The coulombic interactions drive electrostatic forces between interacting molecules. Sensor sensitivity primarily depends on the extent of charge transfer. Natural bond orbital (NBO) analysis was employed to quantify electron transfer from hemicryptophane to bound analytes during complexation. Density of states (DOS) spectra, generated via Multiwfn [34] for pristine and complexed Hm, assess shifts in electronic conductivity and HOMO-LUMO gaps. The variations in HOMO and LUMO density and their energy gaps upon complexation have a significant effect on a material's conductivity [35].

The nature of intra- and intermolecular interactions can be more effectively analyzed using the interaction region indicator (IRI) approach [36]. IRI is a relatively new real-space function that enables the simultaneous identification of multiple types of interactions within chemical systems. To properly balance the description of both covalent and non-covalent interactions, a constant scaling factor is introduced between IRI and the reduced density gradient (RDG). The IRI can be expressed as [36];

$$IRI(r) = \frac{|\nabla\rho(r)|}{[\rho(r)]^\alpha} \quad (3)$$

Here, α represents an adjustable parameter. In the standard formulation of the IRI method, a value of $\alpha = 1.1$ is commonly adopted as appropriate. The reduced density gradient is a dimensionless quantity that reflects a normalized form of the electron density gradient, essentially representing a scaled magnitude of the density gradient. The RDG is defined as follows:

$$RDG(r) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla\rho(r)|}{[\rho(r)]^{4/3}} \quad (4)$$

In this expression, ρ denotes the electron density, while r represents the position (coordinate) vector. On the three-dimensional IRI isosurfaces, different colors indicate the nature of interactions: red corresponds to repulsive regions, green highlights weak non-covalent interactions, and blue signifies attractive interactions. By projecting the $\text{sign}(\lambda_2)\rho$ function onto two-dimensional IRI plots, the characteristics of the interaction regions identified by IRI can be interpreted more clearly. Regions where $\text{sign}(\lambda_2)\rho$ is close to zero and the electron density is low typically indicate the absence of significant interactions or, at most, weak van der Waals (vdW) forces. In contrast, areas with larger absolute values of $\text{sign}(\lambda_2)\rho$ combined with higher electron density are associated with stronger interactions, such as hydrogen bonding or halogen bonding. The scattered plots and isosurfaces for all resulting compounds were generated using Multiwfn [37] and Visual Molecular Dynamics (VMD) [38] software. All calculations utilized Gaussian 16 [39], with results visualized via GaussView 6.1.1 [40].

3. Results and discussions

3.1. Geometrical parameters

The objective of this study is to investigate the nature of interactions formed during the complexation of a hemicryptophane platform with seven freon molecules (CHCl₃, CCl₄, CH₂Cl₂, CCl₃F, CF₃Br, C₂F₆, and CF₄).

To identify the most stable host-guest complexes, several initial orientations of the guest molecules relative to the hemicyrptophane cavity are constructed and fully optimized at the selected level of theory. Four representative configurations (conformer I–IV) are examined for Hm/freons systems to explore different possible binding modes based on steric accessibility and potential intermolecular interaction sites. The optimized structure exhibiting the lowest total electronic energy is considered the most stable configuration. Although exhaustive conformational sampling of large supramolecular systems is computationally demanding, the selected conformers are designed to represent the most chemically reasonable host-guest arrangements. The investigated configurations for Hm/ CCl_4 system are presented in Figure S2. It is found that the inclusion complexes between Hm and the studied analytes are stable since the initial frequencies are positive, which reveals that these actually correspond to local minima on the potential energy surface (Table 1). The optimized structures of Hm/freon complexes and pure hemicyrptophane are displayed in Fig. 1.

The results show that the hemicyrptophane host molecule's cavity size and structure are significantly altered upon complexation with different types of chlorinated and fluorinated compounds. The relatively symmetrical framework of Hm in the original state, with radius, diameter, and volume ($2.74 \text{ \AA}$, $5.48 \text{ \AA}$, $86.58 \text{ \AA}^3$ respectively using Multiwfn), indicates a well-defined, stable cavity. The volume calculations are also performed using MolVol software and similar trends have been observed for Hm/freons systems. However, when guest molecules are inserted, these dimensions become asymmetrical, revealing how the different sizes, shapes, and interactions of the guests alter the host geometry. The variations in the cavity can be seen in all Hm/freon systems (see Fig. 2).

Fig. 2 illustrates the cavity region of the hemicyrptophane host to qualitatively demonstrate the spatial accessibility available for guest encapsulation. The highlighted yellow region represents an approximate internal cavity surface generated using molecular visualization software and is intended solely as a graphical aid to visualize the accessible void within the host framework. There are observable variations in these properties during complex formation. For Hm/ CCl_4 and Hm/ CHCl_3 complexes, there is a notable decrease in cavity size, with volumes falling to $53.61 \text{ \AA}^3$ and $57.72 \text{ \AA}^3$, respectively, along with comparable reductions in diameter and radius. This suggests that when these guests are included, the host cavity undergoes significant structural compression.

For Hm/ CCl_3F and Hm/ C_2F_6 systems, moderate decreases are seen, indicating that the guest molecules are partially accommodated within the cavity. On the other hand, the Hm/ CH_2Cl_2 , Hm/ CF_3Br , and Hm/ CF_4 systems, show very little structural distortion in terms of radius, diameter, and volume when compared to the free host. Overall, the findings show that the type and size of the encapsulated guest molecules have a significant impact on the degree of cavity deformation (Table 1).

3.2. Thermodynamic parameters

The stability of host-guest systems is crucial for practical applications

Table 1

The radius ($\text{\AA}$), diameter ($\text{\AA}$), volume ($\text{\AA}^3$) of the cavity of hemicyrptophane (Hm) and first frequencies ν (cm^{-1}) of optimized Hm inclusion complexes formed with different freons, CHCl_3 , CCl_4 , CH_2Cl_2 , CCl_3F , CF_3Br , C_2F_6 , and CF_4 .

Complex	Radius ($\text{\AA}$)	Diameter ($\text{\AA}$)	Volume ($\text{\AA}^3$)	Frequency (cm^{-1})
Hm	2.74	5.48	86.58	-
Hm/ CCl_4	2.33	4.67	53.61	8.39
Hm/ CCl_3F	2.57	5.15	71.65	5.65
Hm/ CHCl_3	2.39	4.79	57.72	9.15
Hm/ CH_2Cl_2	2.75	5.50	87.11	8.79
Hm/ CF_3Br	2.72	5.44	84.51	12.04
Hm/ C_2F_6	2.64	5.29	77.93	8.19
Hm/ CF_4	2.74	5.49	86.66	8.48

of eradicating dangerous pollutants from the environment. The interaction energy (E_{int}) and distance between the least interacting atoms (D_{int}) in a complex are the key components for thermodynamic stability of a system [41]. A higher negative interaction energy suggests a more stable system and a stronger contact between the substrate and analytes [42]. The investigated Hm/freon inclusion complexes exhibit enhanced thermodynamic stability, as indicated by their pronounced exothermic interaction energies in both gas phase and water. In gas phase, the interaction energies of Hm/freon systems range from $-45.21 \text{ kJ mol}^{-1}$ to $-128.32 \text{ kJ mol}^{-1}$. The stability of inclusion complexes follows a trend as: $\text{Hm}/\text{CCl}_4 > \text{Hm}/\text{CCl}_3\text{F} > \text{Hm}/\text{CHCl}_3 > \text{Hm}/\text{CH}_2\text{Cl}_2 > \text{Hm}/\text{CF}_3\text{Br} > \text{Hm}/\text{C}_2\text{F}_6 > \text{Hm}/\text{CF}_4$. The findings reveal that complexes incorporating chlorinated guest molecules (e.g., CCl_4 and CHCl_3) exhibit higher interaction energies compared to those having fluorinated compounds such as C_2F_6 and CF_4 . This behavior can be attributed to the larger atomic size and greater polarizability of chlorine atoms, which enhance intermolecular interactions. While, fluorinated molecules (except CF_3Br), characterized by the small size and high electronegativity of fluorine, show comparatively weaker interactions and thus, lower interaction energies. Among the studied complexes, the Hm/ CCl_4 complex displays the strongest interaction, with the shortest intermolecular distance ($D_{\text{int}} = 3.17 \text{ \AA}$) and the most negative interaction energy ($E_{\text{int}} = -128.32 \text{ kJ mol}^{-1}$) (see Table 2). D_{int} represents the shortest geometrical interaction distance between the interacting atoms involved in the dominant host-guest contacts identified from the optimized structures. For systems exhibiting multiple halogen interactions, the reported D_{int} values correspond to the shortest and most significant intermolecular contacts contributing to the stabilization of the inclusion complexes, while additional weaker interactions are discussed qualitatively as part of the overall non-covalent interaction network. The Hm/freon complexes were further analyzed using the counterpoise correction method to eliminate the basis set superposition error (BSSE). The counterpoise-corrected interaction energies (E_{CP}) for the investigated systems range from -31.88 to $-101.29 \text{ kcal mol}^{-1}$ (Table 2). These values differ only slightly from the calculated interaction energies (E_{int}), indicating that BSSE has a negligible influence on the host-guest interactions and the freon-capturing ability of hemicyrptophane. Therefore, the B3LYP-D3/6–311 G(d,p) computational level can be considered a reliable and suitable method for the present study.

A consistent trend in interaction energies is observed for Hm/freon complexes in both gas and solvent phases (Fig. 3).

The dipole moments of all Hm/freon complexes are computed in both gas phase and aqueous medium (Table 2). The dipole moment is increased in water, which can be attributed to solvation effects. This enhancement is due to the ability of guest species to interact with the surrounding water molecules, through hydrogen bonding, leading to greater polarization of the complexes. Additionally, various thermodynamic parameters, such as the change in enthalpies (ΔH) and Gibbs free energies (ΔG) of the respective Hm/freon systems, are also computed for both gas phase and water (Table 3). The results showed the formation of these Hm/freon inclusion complexes is exothermic ($\Delta H < 0 \text{ kJ/mol}$). Additionally, in both phases, the ΔG is also negative in all Hm/freon complexes which shows the spontaneous nature of complex formation. Overall, the thermodynamic properties indicate that Hm is more suitable to capture chlorinated pollutants than the fluorinated species.

It should be noted that both CPCM and SMD are continuum solvation models and therefore do not explicitly account for specific solvent-solute interactions. Consequently, effects such as direct water-guest or water-host hydrogen-bonding/halogen-bonding interactions, competitive hydration of the hemicyrptophane cavity, and hydrophobic desolvation phenomena are not fully captured. These factors may contribute significantly to host-guest selectivity under experimental aqueous conditions. Therefore, the calculated thermodynamic parameters should be interpreted as providing qualitative trends rather than quantitative predictions of aqueous binding selectivity. Future investigations employing explicit-solvent molecular dynamics simulations would be

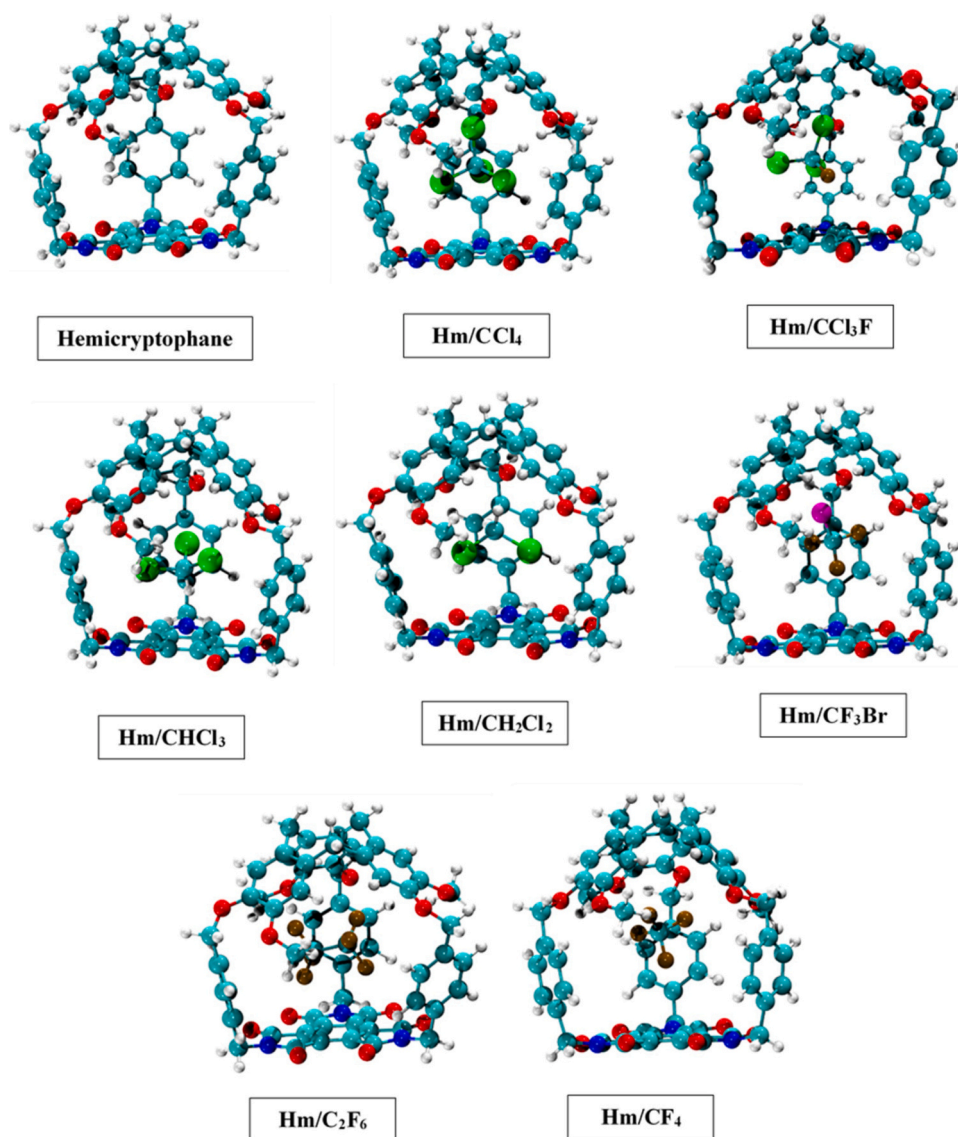


Fig. 1. Optimized structures of pristine Hm and Hm/freon complexes.

valuable for capturing these effects more realistically.

3.3. NBO analysis

Charge transfer analysis is necessary for a comprehensive understanding of the behavior and interaction mechanisms within the studied Hm/analyte complexes. Natural bond orbital (NBO) analysis was employed to quantify and elucidate the extent of charge transfer among the freon molecules and the studied hemicryptophane undergoing complex formation [43]. The calculated NBO charges for all systems are summarized in Table 4. A positive total charge on the analytes indicates charge transfer from the analytes to the substrate, whereas a negative value signifies charge transfer from the substrate to the analytes. The overall charge is positive in case of CCl_4 [0.019 e-], CCl_3F [0.006 e-], CH_2Cl_2 [0.022 e-], C_2F_6 [0.003 e-] and CF_4 [0.003 e-] analytes which confirms that the charge has been transferred from hemicryptophane (substrate) towards the analytes. While in CHCl_3 [-0.011 e-] and CF_3Br [-0.006 e-] analytes, the total charge is negative which indicate that the charge has been accepted by the respective freon molecules. This observation further confirms that the direction of charge transfer is governed by the intrinsic properties of both the hemicryptophane host and the freon guests. A comparative investigation reported in the

literature, examining interaction energies, NBO charge distributions, and energy gaps across different complexes, supports this conclusion [44]. The results indicate that both the nature of the substrate and the physicochemical characteristics of the target pollutants play a decisive role in defining the interaction mechanism, direction and magnitude of charge transfer between the surface and the adsorbed species [44].

3.4. Frontier molecular orbital analysis

Frontier molecular orbital (FMO) analysis is widely employed to evaluate the optical properties, chemical reactivity, and electronic characteristics of compounds [45]. In this study, the FMO energies of Hm/freons complexes were calculated using the B3LYP functional with the 6-31 + G(d,p) basis set. The spatial distributions of the HOMO and LUMO densities and the corresponding energy gaps ($E_{\text{H-L}}$) are illustrated in Fig. 4 and Table 4.

The isosurfaces for all the Hm/freon complexes show that HOMO in hemicryptophane is predominantly concentrated over the π -rich aromatic framework, while the LUMO is localized on the nitrogen-containing side, indicating pronounced electronic asymmetry. This orbital distribution favors the encapsulation of electron-deficient chloro-fluorocarbon pollutants within the cavity via π -halogen and van der

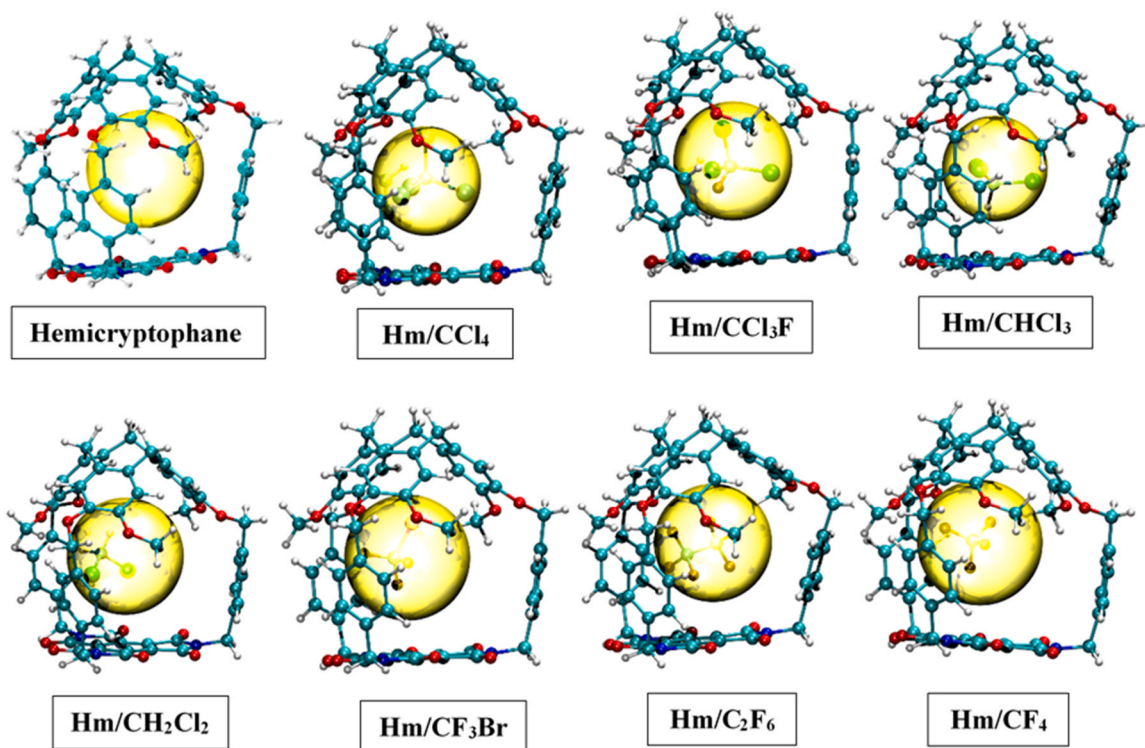


Fig. 2. Pictorial representation of the cavity volume (yellow hole) of pure hemicryptophane and Hm/freon complexes.

Table 2

Distance between the least interacting atoms (D_{int} , Å), interaction energies (E_{int} , in kJ mol^{-1}) (in gas and solvent phase), and dipole moments (μ_D) of all studied Hm/freons complexes.

Complex	E_{CP} (kJ mol^{-1})	D_{int} (Å)	E_{int} (kJ mol^{-1})				μ_D (Debye)	
			Gas	Water (SMD)	Water (CPCM)	Gas	Water	
Hm/ CCl_4	-101.29	3.17	-128.32	-118.25	-110.17	1.025	0.88	
Hm/ CCl_3F	-85.98	3.19	-109.37	-102.09	-94.08	1.25	1.65	
Hm/ CHCl_3	-74.26	3.24	-92.65	-91.96	-79.36	0.23	0.72	
Hm/ CH_2Cl_2	-73.42	3.24	-85.39	-78.75	-71.28	2.37	3.47	
Hm/ CF_3Br	-62.84	3.26	-70.42	-78.42	-68.37	1.88	2.55	
Hm/ C_2F_6	-49.66	3.33	-68.45	-76.85	-64.68	0.80	0.43	
Hm/ CF_4	-31.88	3.36	-45.21	-73.00	-39.70	1.10	1.45	

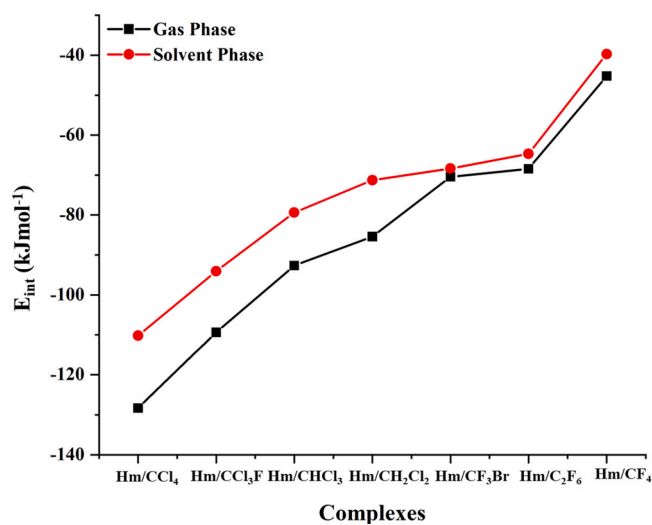


Fig. 3. Graphical representation of interaction energies of Hm/freon complexes (gas and solvent phase).

Table 3

The difference in enthalpies (ΔH , kJ mol^{-1}) and Gibbs free energies (ΔG , kJ mol^{-1}) (solvent and gas-phase) of optimized Hm/freon complexes.

Complex	ΔH (kJ mol^{-1})			ΔG (kJ mol^{-1})		
	Gas	Water (SMD)	Water (CPCM)	Gas	Water (SMD)	Water (CPCM)
Hm/ CCl_4	-124.98	-115.87	-107.01	-79.33	-62.40	-61.70
Hm/ CCl_3F	-106.13	-102.09	-91.02	-60.96	-45.98	-42.68
Hm/ CHCl_3	-89.80	-89.91	-76.55	-36.82	-32.57	-25.58
Hm/ CH_2Cl_2	-83.09	-78.75	-68.91	-36.42	-19.21	-21.38
Hm/ CF_3Br	-67.71	-78.42	-65.17	-15.29	-24.94	-16.94
Hm/ C_2F_6	-65.19	-74.06	-61.25	-19.51	-32.03	-15.55
Hm/ CF_4	-41.88	-69.77	-35.91	-0.97	-26.86	-0.01

Waals interactions. The separation of frontier orbitals also facilitates intramolecular charge transfer (ICT) upon the guest inclusion [46]. Therefore, this enhances host-guest binding stability and supports

Table 4

Energies of HOMO (E_{HOMO} , eV) and LUMO (E_{LUMO} , eV) orbitals, HOMO-LUMO gap energies ($E_{\text{H-L}}$, eV), energy gap change ($\%E_{\text{H-L}}$), and NBO charges (Q_{NBO} , e⁻) of the studied Hm/freon complexes.

Complex	HOMO (eV)	LUMO (eV)	$E_{\text{H-L}}$ (eV)	Q_{NBO} [e ⁻]
Hm	-5.58	-3.56	2.01	-
Hm/ CCl ₄	-5.67	-3.52	2.15	0.019
Hm/ CCl ₃ F	-5.65	-3.49	2.16	0.006
Hm/CHCl ₃	-5.63	-3.68	1.95	-0.011
Hm/CH ₂ Cl ₂	-5.65	-3.40	2.24	0.022
Hm/CF ₃ Br	-5.64	-3.49	2.14	-0.006
Hm/C ₂ F ₆	-5.62	-3.54	2.07	0.003
Hm/CF ₄	-5.62	-3.53	2.08	0.003

selective recognition of halogenated pollutants.

The fluctuations in the HOMO-LUMO energy gap ($E_{\text{H-L}}$) upon complexation correlate well with the Q_{NBO} charge transfer values,

reflecting the strength and nature of host-guest interactions. The systems such as Hm/CH₂Cl₂ (2.24 eV, 0.022 e⁻) and Hm/CCl₄ (2.15 eV, 0.019 e⁻) possess increased $E_{\text{H-L}}$ along with positive charge transfer, revealing stabilization of the electronic structure with limited but favorable electron donation from the guest to the host. This indicates relatively stable systems with reduced reactivity. While the Hm/CHCl₃ system shows a decreased energy gap (1.95 eV) and a negative charge value (-0.011 e⁻), implying opposite charge transfer (from host to guest) and higher orbital interaction. This results in greater electron delocalization, leading to a smaller gap and relatively higher reactivity. For other systems such as Hm/CF₄, Hm/C₂F₆, and Hm/CF₃Br, the minimal Q_{NBO} values (close to zero) and moderate energy gaps (between ~2.07–2.14 eV) indicate weak charge transfer and predominantly van der Waals interactions governing the complex stability. In short, an increase in $E_{\text{H-L}}$ is associated with enhanced electronic stability and weak charge transfer, whereas a decrease in the gap leads to stronger electronic interaction and charge delocalization between host and guest

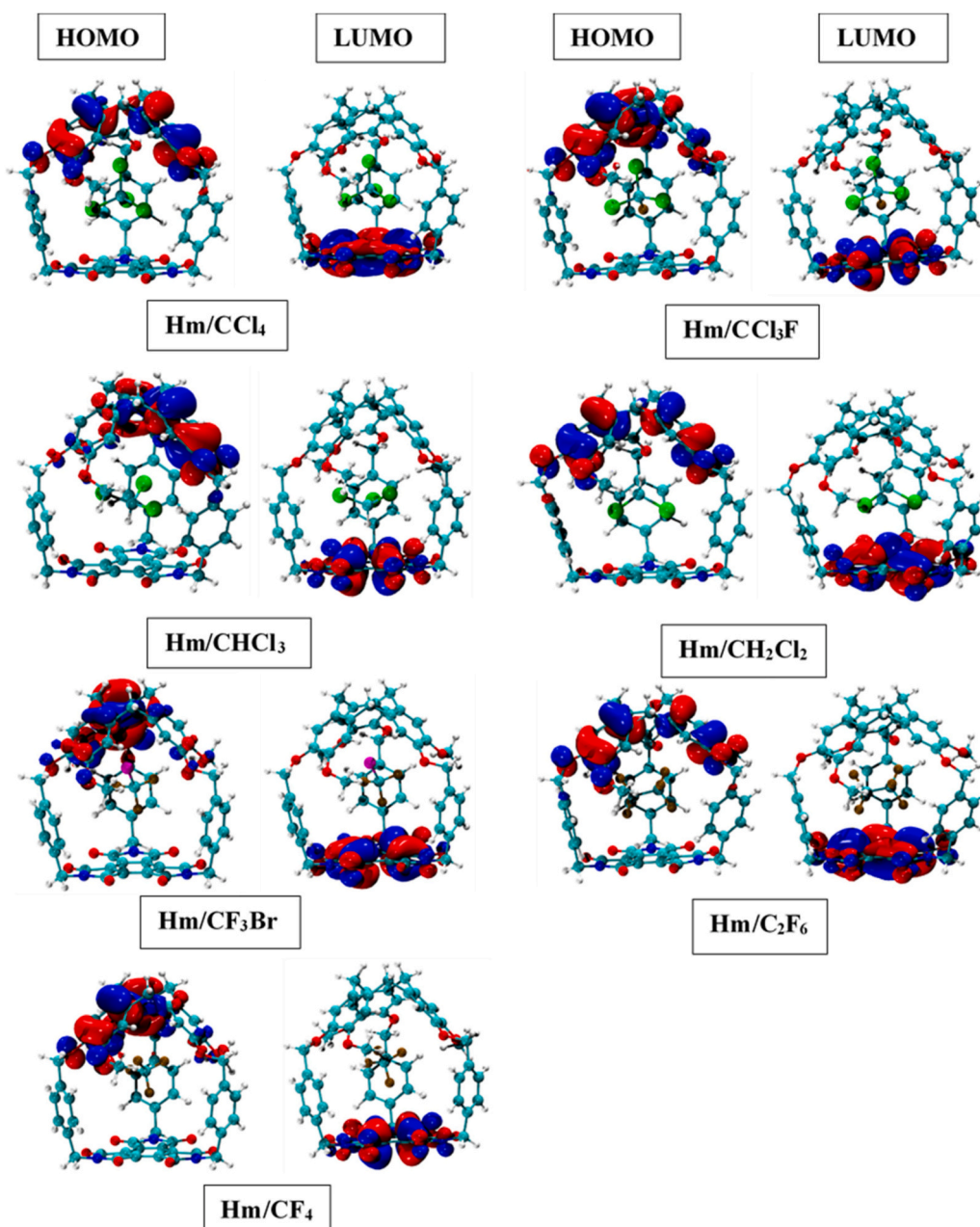


Fig. 4. HOMO-LUMO isosurfaces of the studied Hm/freon complexes.

molecules [47].

3.5. DOS analysis

The density of states (DOS) describes the number of available electronic states that can be occupied at a given energy level. To evaluate the electronic properties particularly the formation of new highest occupied

molecular orbitals (HOMOs) and the contributions of individual components in the newly designed freon-based systems. This study examines both the total density of states (TDOS) and partial density of states (PDOS) spectra. The DOS spectra of hemicyptophane and the corresponding Hm/freon complexes are presented in Fig. 5.

The TDOS profile of pristine hemicyptophane indicates that both occupied and unoccupied regions contribute to states primarily at lower

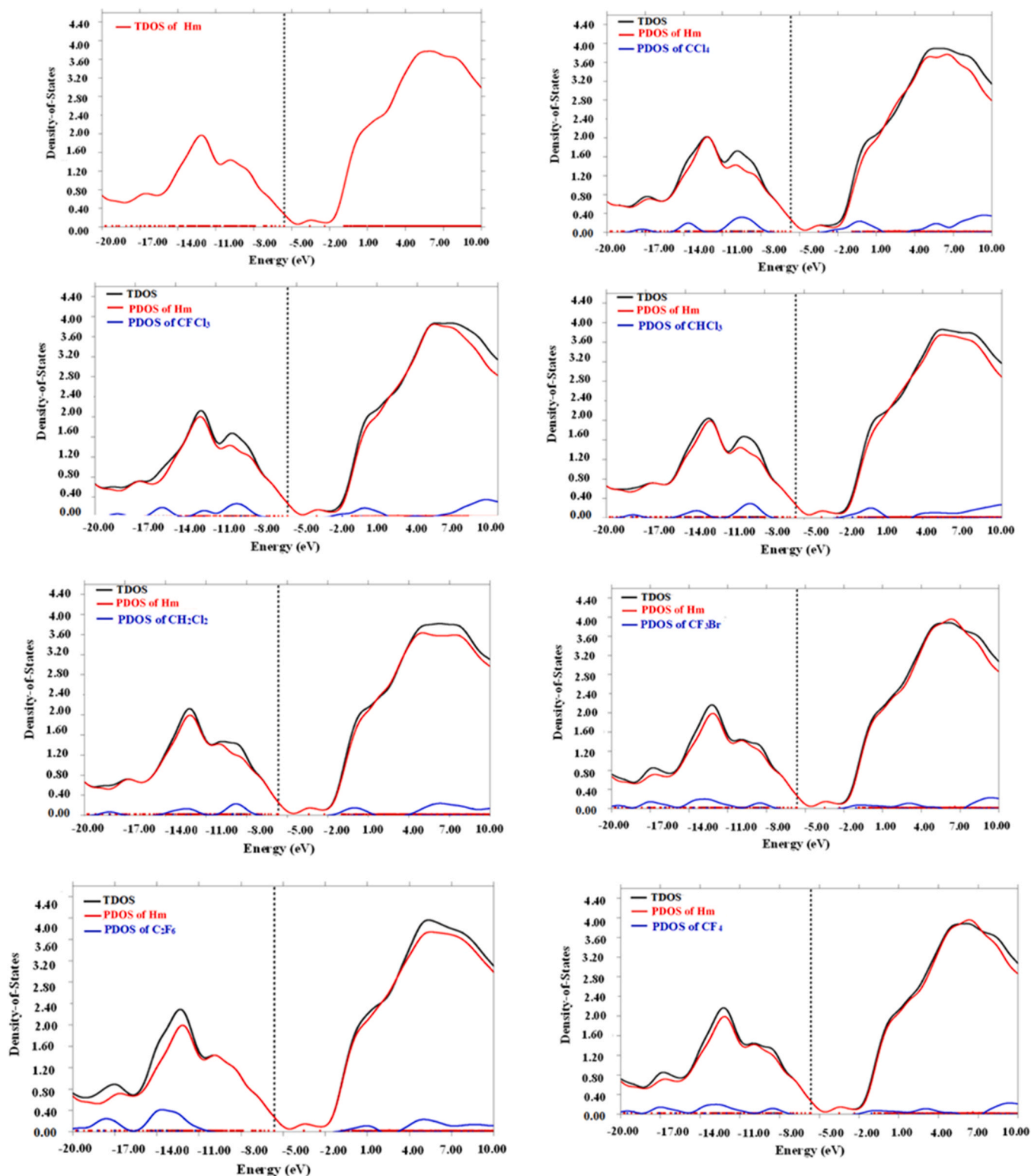


Fig. 5. Total density of states (TDOS) and partial density of states (PDOS) spectra of pure Hm and Hm/freon complexes.

energy levels. Upon encapsulation of freon molecules within the Hm cavity, a noticeable change in the PDOS peak intensities is observed. This deviation reflects the formation of new high-energy HOMO levels arising from interactions between hemicryptophane and the freons. The DOS spectra of these freon-containing complexes exhibit clear shifts in

energy levels, supporting the emergence of new HOMOs, which is highlighted by a vertical dashed line. These orbitals appear in the higher energy region, typically ranging from about -6.00 to -5.96 eV, whereas the HOMO of isolated hemicryptophane is located at -7.00 eV. As a result, the HOMO–LUMO energy gap is reduced. The contribution for

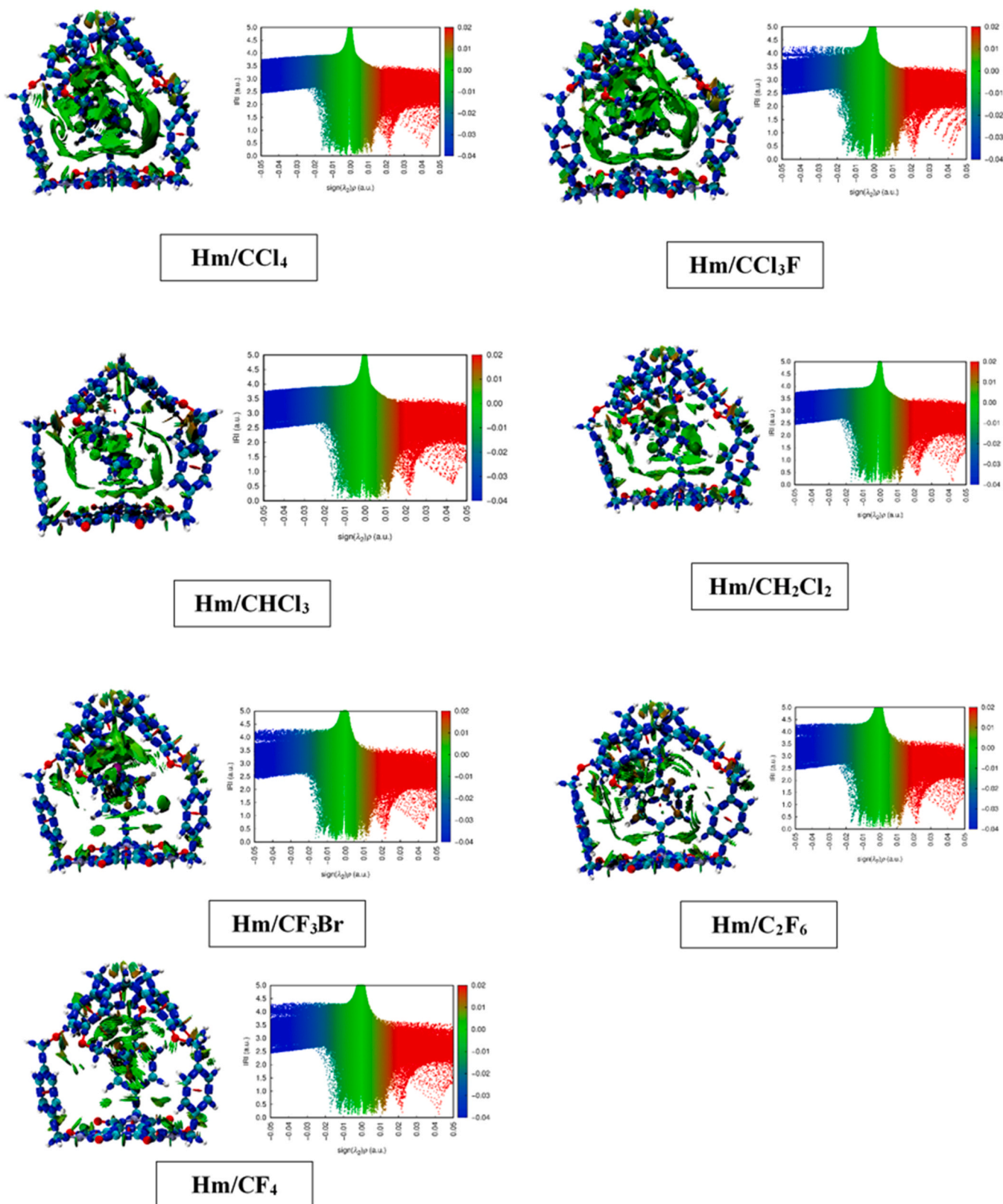


Fig. 6. 2D-isosurfaces and 3D-interaction region indicator (IRI) scatter graphs of the studied Hm/freon systems.

the formation of new HOMOs is from both hemicryptophane (red line contribution) and freons (blue line contribution) in all Hm/freons systems. Moreover, the increase in intensities of freon molecules also shows their contribution in the investigated systems. The DOS spectra of Hm/freons complexes revealed a substantial enhancement in both conductive and electronic features.

3.6. IRI analysis

The analysis of both 3D IRI-isosurfaces and 2D IRI-plots for the Hm/freons systems was performed to better understand the nature of covalent and non-covalent interactions, as illustrated in Fig. 6.

The findings indicate the occurrence of very small blue regions corresponding to hydrogen bonding, along with extensive green areas associated with weak dispersive van der Waals interactions in the studied Hm/freon inclusion complexes. Furthermore, the presence of these weak dispersive interactions is confirmed by noticeable green spikes in the 2D IRI plots, appearing within the range of -0.01 – 0.01 a.u. The combination of low electron density, small gradient values, and sharp spikes observed for the Hm/freon systems is in good agreement with results of previously reported studies *e.g.*, for removal of freon-based materials by calix [4]arene moiety [17,48,49].

3.7. Applicability of hemicryptophane compared to other platforms

A comparative evaluation of the present results with previously reported host materials for freon capture highlights the effectiveness of hemicryptophane-based platforms. In this study, the calculated adsorption energies for Hm/freon complexes range from -128 to -45 kJ mol $^{-1}$ in the gas phase and from -110 to -39 kJ mol $^{-1}$ in aqueous media, indicating strong host-guest interactions (see above and Table 5). These values are comparable to, and in several cases exceed, those reported for other host frameworks. For instance, calix [4]arene-based complexes exhibit moderate binding strengths, with adsorption energies ranging from -64 to -36 kJ mol $^{-1}$ in the gas phase and -56 to -30 kJ mol $^{-1}$ in aqueous medium (Table 5). Similarly, materials such as graphene and graphene oxide generally show weaker interactions with halomethanes, typically within the range of -19 to -39 kJ mol $^{-1}$, primarily governed by van der Waals forces and surface functionalities [50,51] (Table 5). In the case of metal-organic frameworks (MOFs), including Ni-MOF-74, reported adsorption energies vary between -27 and -70 kJ mol $^{-1}$ depending on the guest molecule and structural characteristics of the framework [52,53] (Table 5).

Table 5

Comparison of the adsorption energies reported for different host materials toward halogenated organic compounds. The listed values were obtained using different computational approaches (DFT calculations or GCMC simulations) and under different conditions; therefore, the comparison is intended primarily for qualitative evaluation of relative binding strengths and adsorption trends rather than direct quantitative benchmarking.

Base Material	Target Molecule(s)	Adsorption Energy (kJ·mol $^{-1}$)	Key Observations	Reference
Hemicryptophane (current work)	CHCl $_3$, CCl $_4$, CH $_2$ Cl $_2$, CCl $_3$ F, CF $_3$ Br, C $_2$ F $_6$, CF $_4$	-128 to -45 (gas phase) -110 to -39 (aqueous phase)	Strong binding via non-covalent interactions	Current work
Calix[4]arene	CHCl $_3$, CCl $_4$, CH $_2$ Cl $_2$, CCl $_3$ F, CF $_3$ Br, C $_2$ F $_6$, CF $_4$	-64.57 to -36.58 (gas phase) -56 to -30 (aqueous phase)	Moderate binding via non-covalent interactions; host-guest specificity	Khalil et al., [17]
Graphene	CHBr $_3$ (bromoform)	-39	Slightly stronger vdW interaction than chloroform	Akesson et al., 2012 [50]
Graphene	CHCl $_3$ (chloroform)	-34	Weak physisorption via van der Waals forces	Akesson et al., 2012 [50]
Graphene oxide	CHCl $_3$ (chloroform)	-19 to -38	Stronger binding due to surface functional groups	Kuisma et al., 2016 [51]
Ni-MOF-74 (GCMC sims)	R134a (1,1,1,2-Tetrafluoroethane)	~ -27	Stronger adsorption than Cr-MIL-101 at low loading	Barpaga et al., 2019 [52]
Metal-Organic Frameworks (MOFs)	CHCl $_3$, CCl $_4$, refrigerants	-35 to -70	Tunable pore sizes allow strong physical adsorption	Vicent-Luna et al., 2024 [53]

Compared to these systems, hemicryptophane not only demonstrates competitive or superior binding strength but also offers enhanced molecular selectivity due to its well-defined cavity and ability to facilitate specific host-guest recognition. These features underscore its strong potential as an efficient and selective adsorbent for freon-type pollutants in both gaseous and aqueous environments. The reported benchmark systems were investigated in the literature using different computational methodologies and theoretical levels, including DFT calculations employing various exchange-correlation functionals and basis sets for supramolecular and graphene-based systems, as well as Grand Canonical Monte Carlo (GCMC) simulations for MOF materials. Therefore, the adsorption energies should be considered primarily for qualitative comparison rather than direct quantitative evaluation. Nevertheless, the results indicate that hemicryptophane exhibits comparatively strong host-guest interactions, highlighting the important role of its pre-organized cavity and non-covalent interactions in selective pollutant capture.

4. Conclusion

This work provides a detailed analysis of hemicryptophane/freon inclusion complexes with emphasis on their structural, electronic, and interaction properties. The findings demonstrate that all studied complexes are thermodynamically stable, as reflected by their favorable interaction energies ranging from -45.21 to -128.32 kJ mol $^{-1}$. The strongest interaction is observed for the Hm/CCl $_4$ complex, indicating its superior stability among the studied systems. The negative Gibbs free energy values further confirm the spontaneous nature of the host-guest complexation, with enthalpy playing a dominant role in stabilizing these interactions. Electronic structure analysis reveals a significant reduction in HOMO-LUMO energy gaps, reaching values as low as 1.95 eV in case of the Hm/CHCl $_3$ complex, which suggests enhanced electronic responsiveness and potential applicability in sensing. Among the investigated complexes, Hm/CH $_2$ Cl $_2$ exhibits the highest degree of charge transfer (0.022 |e|), as determined from natural bond orbital analysis. Additionally, electron density-based approaches, including interaction region indicator analysis, confirms that the interactions are predominantly governed by non-covalent forces, primarily van der Waals interactions. The hemicryptophane framework exhibits a clear preference for chlorinated freons due to the larger size and higher polarizability of chlorine atoms, which enhance interactions within the host cavity. The associated changes in electronic properties upon guest binding indicate promising sensing capabilities, while the well-defined

cavity ensures improved selectivity compared to other adsorbents. Compared to previously reported systems such as graphene-based materials, calix [4]arene macrocycles and MOFs, hemicryptophane demonstrates superior selectivity arising from its tailored host-guest recognition. Therefore, hemicryptophane-based systems show strong potential for the selective capture and sensing of freon-based pollutants in environmental applications.

CRedit authorship contribution statement

Magdalena Malecka: Writing – review & editing, Validation, Supervision, Resources, Formal analysis, Conceptualization. **Khalida Khalil:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Project administration, Methodology, Investigation, Formal analysis, Data curation. **Fiser Bela:** Writing – review & editing, Validation, Supervision, Formal analysis, Conceptualization.

Declaration of Competing Interest

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

Acknowledgments

We gratefully acknowledge Polish high-performance computing infrastructure PLGrid (HPC Center: ACK Cyfronet AGH) for providing computer facilities and support within computational grant no. PLG/2025/018935 & PLG/2026/019341. This work is also supported by the Incentive Scholarship by NAWA STER for best foreign PhD students. BF was supported by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jece.2026.123557](https://doi.org/10.1016/j.jece.2026.123557).

Data availability

Data will be made available on request.

References

- [1] C.-C. Jung, H.-J. Su, H.-H. Liang, Association between indoor air pollutant exposure and blood pressure and heart rate in subjects according to body mass index, *Sci. Total. Environ.* 539 (2016) 271–276, <https://doi.org/10.1016/j.scitotenv.2015.08.158>.
- [2] J.-H. Kwak, et al., Temperature and air pollution affected tree ring $\delta^{13}\text{C}$ and water-use efficiency of pine and oak trees under rising CO_2 in a humid temperate forest, *Chem. Geol.* 420 (2016) 127–138, <https://doi.org/10.1016/j.chemgeo.2015.11.015>.
- [3] Y. Fan, S. Zhang, Q. Wang, S.P. Shah, The effects of nano-calcined kaolinite clay on cement mortar exposed to acid deposits, *Constr. Build. Mater.* 102 (2016) 486–495, <https://doi.org/10.1016/j.conbuildmat.2015.11.016>.
- [4] J. Wu, et al., Prolonged acid rain facilitates soil organic carbon accumulation in a mature forest in Southern China, *Sci. Total. Environ.* 544 (2016) 94–102, <https://doi.org/10.1016/j.scitotenv.2015.11.025>.
- [5] M. Franchini, C. Mengoli, M. Cruciani, C. Bonfanti, P.M. Mannucci, Association between particulate air pollution and venous thromboembolism: A systematic literature review, *Eur. J. Intern. Med.* 27 (2016) 10–13, <https://doi.org/10.1016/j.ejim.2015.11.012>.
- [6] Q. Wang, et al., Evolution of particulate sulfate and nitrate along the Asian dust pathway: Secondary transformation and primary pollutants via long-range transport, *Atmos. Res.* 169 (2016) 86–95, <https://doi.org/10.1016/j.atmosres.2015.09.013>.
- [7] M. Ghanbari Ghazikali, et al., Evaluation of chronic obstructive pulmonary disease (COPD) attributed to atmospheric O_3 , NO_2 , and SO_2 using Air Q Model (2011–2012 year), *Environ. Res.* 144 (2016) 99–105, <https://doi.org/10.1016/j.envres.2015.10.030>.
- [8] M.H. Abraham, J.M.R. Gola, J.E. Cometto-Muñiz, An assessment of air quality reflecting the chemosensory irritation impact of mixtures of volatile organic compounds, *Environ. Int.* 86 (2016) 84–91, <https://doi.org/10.1016/j.envint.2015.07.012>.
- [9] S. Okazaki, A. Kurosaki, Decomposition of chlorofluorocarbons by the reaction with water vapor catalyzed by iron oxide supported on activated carbon, *Chem. Lett.* (11) (1989) 1901–1904, <https://doi.org/10.1246/cl.1989.1901>.
- [10] M. Bonarowska, B. Burda, W. Juszczak, J. Pielaszek, Z. Kowalczyk, Z. Karpiński, Hydrodechlorination of CCl_2F_2 (CFC-12) over Pd-Au/C catalysts, *Appl. Catal. B Environ.* 35 (1) (2001) 13–20, [https://doi.org/10.1016/S0926-3373\(01\)00227-2](https://doi.org/10.1016/S0926-3373(01)00227-2).
- [11] M. Bonarowska, J. Pielaszek, V.A. Semikolenov, Z. Karpiński, Pd-Au/Sibunit carbon catalysts: characterization and catalytic activity in hydrodechlorination of dichlorodifluoromethane (CFC-12), *J. Catal.* 209 (2) (2002) 528–538, <https://doi.org/10.1006/jcat.2002.3650>.
- [12] H.J. Schneider, U. Schneider, The host-guest chemistry of resorcinarenes, *J. Incl. Phenom. Mol. Recognit. Chem.* 19 (1–4) (Mar. 1994) 67–83, <https://doi.org/10.1007/BF00708975/METRICS>.
- [13] R.A. Bilbeisi, et al., Subcomponent self-assembly and guest-binding properties of face-capped Fe_4L_4 8+ capsules, *J. Am. Chem. Soc.* 134 (11) (2011) 5110–5119.
- [14] H. Takezawa, T. Murase, G. Resnati, P. Metrangola, M. Fujita, Recognition of polyfluorinated compounds through self-aggregation in a cavity, *J. Am. Chem. Soc.* 136 (5) (2014) 1786–1788, <https://doi.org/10.1021/ja412893c>.
- [15] T.-H. Chen, et al., Thermally robust and porous noncovalent organic framework with high affinity for fluorocarbons and CFCs, *Nat. Commun.* 5 (1) (2014) 5131, <https://doi.org/10.1038/ncomms6131>.
- [16] J.L. Atwood, L.J. Barbour, A. Jerga, Storage of methane and freon by interstitial van der Waals confinement, *Science* 296 (5577) (2002) 2367–2369, <https://doi.org/10.1126/science.1072252>.
- [17] K. Khalil, B. Fiser, M. Mał, ecka, “Calix [4] arene as an efficient framework for environmental remediation of water bodies from chloro- and fluorocarbons, *Chemosphere* 390 (2025) 144711.
- [18] A. Collet, Cyclotrimeratrylenes and cryptophanes, *Tetrahedron* 43 (24) (1987) 5725–5759, [https://doi.org/10.1016/S0040-4020\(01\)87780-2](https://doi.org/10.1016/S0040-4020(01)87780-2).
- [19] T. Brotin, J.-P. Dutasta, Cryptophanes and their complexes-present and future, *Chem. Rev.* 109 (1) (2009) 88–130, <https://doi.org/10.1021/cr0680437>.
- [20] O. Perraud, A. Martinez, J.-P. Dutasta, Exclusive enantioselective recognition of glucopyranosides by inherently chiral hemicryptophanes, *Chem. Commun.* 47 (20) (2011) 5861–5863, <https://doi.org/10.1039/C1CC10964B>.
- [21] A. Schmitt, et al., Improved hemicryptophane hosts for the stereoselective recognition of glucopyranosides, *Org. & Biomol. Chem.* 12 (24) (2014) 4211–4217, <https://doi.org/10.1039/C4OB00156G>.
- [22] A. Schmitt, V. Robert, J.-P. Dutasta, A. Martinez, Synthesis of the first water-soluble hemicryptophane host: selective recognition of choline in aqueous medium, *Org. Lett.* 16 (9) (2014) 2374–2377, <https://doi.org/10.1021/ol500706z>.
- [23] O. Perraud, S. Lefevre, V. Robert, A. Martinez, J.-P. Dutasta, Hemicryptophane host as efficient primary alkylammonium ion receptor, *Organic & Biomolecular Chemistry* 10 (5) (2012) 1056–1059, <https://doi.org/10.1039/C1OB06657A>.
- [24] J. Boekhoven, W.E. Hendriksen, G.J.M. Koper, R. Eelkema, J.H. van Esch, Transient assembly of active materials fueled by a chemical reaction, *Science* 349 (6252) (2015) 1075–1079, <https://doi.org/10.1126/science.aac6103>.
- [25] O. Perraud, V. Robert, A. Martinez, J.-P. Dutasta, A designed cavity for zwitterionic species: selective recognition of taurine in aqueous media, *Chem. A Eur. J.* 17 (48) (2011) 13405–13408, <https://doi.org/10.1002/chem.201101522>.
- [26] X.-R. Mao, C.-Y. Zhao, Y.-Z. Gong, K.-X. Xing, G.-S. Zhu, C.-Y. Geng, Unraveling the distinct catalytic features of methane activation in an iron-containing hemicryptophane cage FeO-TPA@Hm : insights from molecular cage architecture and electronic interactions, *J. Catal.* 456 (2026) 116731, <https://doi.org/10.1016/j.jcat.2026.116731>.
- [27] F. Brégier, E. Aubert, E. Espinosa, J.-C. Chambron, An optically-pure hemicryptophane as NMR and ECD responsive probe for chloroform, *ChemistrySelect* 1 (10) (2016) 2389–2395, <https://doi.org/10.1002/slct.201600312>.
- [28] L. Miton, et al., Electron-deficient hemicryptophanes for the recognition of anions through anion- π interactions, *Org. & Biomol. Chem.* 23 (18) (2025) 4360–4364, <https://doi.org/10.1039/D5OB00245A>.
- [29] H. Tahir, N. Kosar, K. Ayub, T. Mahmood, Outstanding NLO response of thermodynamically stable single and multiple alkaline earth metals doped C20 fullerene, *J. Mol. Liq.* 305 (2020) 112875, <https://doi.org/10.1016/J.MOLLIQ.2020.112875>.
- [30] T.Q. Hung, et al., Synthesis and properties of 5,7-Dihydropyrido[3,2-b:5,6-b'] diindoles, *Eur. J. Org. Chem.* 2015 (5) (2015) 1007–1019, <https://doi.org/10.1002/EJOC.201403035>.
- [31] K.A. Maria, Aromaticities of five membered heterocycles through dimethyldihydropyrenes probe by magnetic and geometric criteria, *J. Chem.* 2015 (2015), <https://doi.org/10.1155/2015/456961>.
- [32] S. Grimme, S. Ehrlich, L. Goerigk, Effect of the damping function in dispersion corrected density functional theory, *J. Comput. Chem.* 32 (7) (2011) 1456–1465, <https://doi.org/10.1002/jcc.21759>.
- [33] V. Barone, M. Cossi, Quantum calculation of molecular energies and energy gradients in solution by a conductor solvent model, *J. Phys. Chem. A* 102 (11) (1998) 1995–2001, <https://doi.org/10.1021/JP9716997/ASSET/IMAGES/LARGE/JP9716997F00004.JPEG>.
- [34] T. Lu, F. C. Multiwfn: A multifunctional wavefunction analyzer, *J. Comput. Chem.* 2012 33 (5) (2012) 580–592, <https://doi.org/10.1002/jcc.22885>.
- [35] H. Sajid, T. Mahmood, A DFT study on M30 (M = Li & Na) doped triphenylene and its amino-, hydroxy- and thiol-functionalized quantum dots for triggering

- remarkable nonlinear optical properties and ultra-deep transparency in ultraviolet region, *Phys. E Low-dimens. Syst. Nanostruct.* 134 (2021) 114905, <https://doi.org/10.1016/j.physe.2021.114905>.
- [36] T. Lu, Q. Chen, Interaction region indicator: a simple real space function clearly revealing both chemical bonds and weak interactions, *Chem. - Methods* 1 (5) (2021) 231–239, <https://doi.org/10.1002/CMTD.202100007>.
- [37] T. Lu, F. C. Multiwfn: A multifunctional wavefunction analyzer, *J. Comput. Chem.* 2012 33 (5) (2012) 580–592, <https://doi.org/10.1002/jcc.22885>.
- [38] W. Humphrey, A. Dalke, K. S.-J., of molecular graphics, and undefined. *VMD: Visual Molecular Dynamics*, Elsevier, 1996.
- [39] M.J. ea Frisch, et al., *Gaussian 16*. Gaussian, Inc, Wallingford, CT, 2016.
- [40] R. Dennington, T. Keith, J. Millam, *GaussView, Version 6.1. 1*, Release notes, Semichem Inc, Shawnee Mission, KS, 2019.
- [41] H. Sajid, T. Mahmood, K. Ayub, An accurate comparative theoretical study of the interaction of furan, pyrrole, and thiophene with various gaseous analytes, *J. Mol. Model.* 23 (10) (2017) 295, <https://doi.org/10.1007/s00894-017-3458-x>.
- [42] R. Bano, et al., Superalkali (Li2F, Li3F) doped Al12N12 electrides with enhanced static, dynamic nonlinear optical responses and refractive indices, *Mater. Sci. Semicond. Process.* 143 (2022) 106518, <https://doi.org/10.1016/j.mssp.2022.106518>.
- [43] J.P. Foster, F. Weinhold, Natural hybrid orbitals, *J. Am. Chem. Soc.* 102 (24) (1980) 7211–7218, <https://doi.org/10.1021/ja00544a007>.
- [44] V. Nagarajan, R. Bhuvaneswari, R. Chandiramouli, Novel arsenborane as a sensing material for dichlorofluoromethane and dichlorodifluoromethane vapours – a first-principles study, *Mater. Today Commun.* 39 (2024) 109212, <https://doi.org/10.1016/j.mtcomm.2024.109212>.
- [45] S. Bibi, et al., Molecular and electronic structure elucidation of polypyrrole gas sensors, *J. Phys. Chem. C* 119 (28) (2015) 15994–16003, <https://doi.org/10.1021/acs.jpcc.5b03242>.
- [46] R.G. Pearson, Absolute electronegativity and hardness: application to inorganic chemistry, *Inorg. Chem.* 27 (4) (1988) 734–740, <https://doi.org/10.1021/ic00277a030>.
- [47] R.G. Parr, Density functional theory of atoms and molecules. *Horizons of Quantum Chemistry: Proceedings of the Third International Congress of Quantum Chemistry Held at Kyoto, Japan, October 29–November 3, 1979*, Springer, 1979, pp. 5–15, https://doi.org/10.1007/978-3-319-14045-2_37.
- [48] K. Khalil, B. Fiser, M. Malecka, Computational insights into solvent encapsulation and host–guest recognition by calix [4] arene, *Sci. Rep.* 15 (1) (2025) 36216, <https://doi.org/10.1038/s41598-025-20260-x>.
- [49] K. Khalil, et al., Unraveling the role of superalkalis in modulating the static and dynamic hyperpolarizabilities of emerging calix[4]arenes, *Phys. Chem. Chem. Phys.* 26 (8) (2024) 6794–6805, <https://doi.org/10.1039/D3CP04825J>.
- [50] J. Åkesson, O. Sundborg, O. Wahlström, and E. Schröder, “A van der Waals density functional study of chloroform and bromoform on graphene,” *arXiv preprint arXiv: 1206.1972*, 2012, doi: [10.1103/PhysRevB.86.195436](https://doi.org/10.1103/PhysRevB.86.195436).
- [51] E. Kuisma, C.F. Hansson, T.B. Lindberg, C.A. Gillberg, S. Idh, E. Schröder, Graphene oxide and adsorption of chloroform: a density functional study, *J. Chem. Phys.* 144 (18) (2016), <https://doi.org/10.1063/1.4948321>.
- [52] D. Barpaga, et al., Insight into fluorocarbon adsorption in metal-organic frameworks via experiments and molecular simulations, *Sci. Rep.* 9 (1) (2019) 10289, <https://doi.org/10.1038/s41598-019-46269-7>.
- [53] J.M. Vicent-Luna, A. Luna-Triguero, Adsorption characteristics of refrigerants for thermochemical energy storage in metal–organic frameworks, *ACS Appl. Eng. Mater.* 2 (3) (2024) 542–552, <https://doi.org/10.1021/acsaenm.3c00474>.