Lanthanum- Oligopyrrole Complexes (neutral, III) for biogas capture applications by DFT

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Abstract

The structures and interactions of systems formed by the MPBCP (meta-Phenylene-Bridged Cyclic Oligopyrrole) functionalized with lanthanum atom were studied for investigating the abilities of MPBCP, [La-MPBCP]+3 and La-MPBCP to absorb biogas (CO2, N2, H2 and CH4) using density functional theory. The Eads calculated values for biogas molecules on [La-MPBCP]+3 and La-MPBCP showed that these gas molecules have favorable interactions with the lanthanum atom coordinated on the MPBCP. CO2 molecule shows strong interactions, with Eads values of -28.63 and -15.95 kcal/mol. In the case of H2 molecule, the Eads is lower with values of -7.51 and -5.28. It is easy to observe the CO2 molecule on the [La-MPBCP]+3 system has four times higher energy value than adsorption energy for the H2 molecule. The natural bond orbital analysis reveals that gas molecules are electron donator in the systems and the acceptor orbitals belong to lanthanum atom. Computational studies suggest that CO2, N2, CH4 and H2 molecules on [La-MPBCP]+3 and La-MPBCP present physisorption. Our findings divulge promising potential of the [La-MPBCP]+3 as an adsorber/separator CO2/H2.

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Abstract:

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Graphical Abstract:



Keywords : meta-Phenylene-Bridged Cyclic Oligopyrrole, Lanthanum, Adsorption, DFT

Introduction

Adsorption and gas separations are two important topics in the chemical, environmental, medical and electronic gas industries applications.¹⁻⁶ Many studies have been performed to improve the chemical activity of different materials for adsorber and separate gases. The technologies of gas separation include cryogenic separation, absorption/adsorption separation, supersonic separation, and membrane separation.⁷⁻⁹ Researchers have developed strategies to design materials to separate gas mixtures. Most of the materials used are membranes,¹⁰polymers,¹¹ zeolites,¹²carbons,¹³ and metal-organic frameworks (MOFs).¹⁴

The biogas is an effective, clean and renewable energy resource. It is obtained by process of organic matter.¹⁵⁻²¹ The biogas is composed mostly of CH_4 and CO_2 , with traces of N_2 , H_2 , H_2S , and other gases.²² The separation of CO_2 and CH_4 from biogas would enable using it for various chemicals processes. Several authors investigated materials as Co-MOF,²³ Cu-BTC,²⁴MIL-53,²⁵ UTSA-16,²⁶MOFs,²⁷ Cu-MOF, 28 Cu-TDPAT, 29 and others 30 for CO₂/CH₄ separations. Most of the studies investigate the biogas purification (CO_2/CH_4) as mentioned above. Interesting to highlight that reports of CO_2/H_2 separation are scarce. Soonchul Kwon, et al. investigated competitive CO_2 and H_2 adsorption on carbon allotropes such as graphene, which has only hexagonal rings, and graphyne. They found, graphyne provides high CO_2 selectivity for gas mixtures.³¹ In 2017 Zhou *et al* . investigated the theoretical simulation of CH_4 separation from H_2 in metal-organic frameworks CAU-17.³² Another research group reported that metal-organic frameworks containing strongly adsorbing sites are excellent candidates for CO₂/H₂separations.³³ Previous reports showed that porous graphene membrane showed high selectivity of H₂ by DFT calculation, over several other gas molecules that often accompany H₂ in industrial steam methane reforming or dehydrogenation of alkanes (such as N_2 , CO, and CH_4).³⁴ Studies in this direction, Arjmandi *et al*. have investigated the adsorption properties of H₂ and CO₂ on the organic MOF-5ligand. Their results revealed that ZnO-doped system has higher adsorption energy values than those for the pristine MOF.³⁵Recently, the graphydine like membrane was studied for separate a mixture of hydrogen (H_2) and carbon dioxide (CO_2) gases by density functional theory. The results showed that the selectivity of H_2/CO_2 is increased from 70 to 100% in the presence of 1,3,5 three amine benzene.³⁶

Synthesis and characterization of ortho-phenylene-bridged cyclic trimeric oligopyrrole has recently been reported. These molecules have cavities with electron donating atoms.³⁷⁻³⁸ Motivated by the promising properties of these materials, "MPBCP" (meta-phenylene-bridged cyclic pyrrole) was designed, to study the ability to adsorb molecules from biogas. We investigate the effect of coordinating the "MPBCP" with a lanthanum atom with neutral and +3 charge. The lanthanum systems were studied for adsorption of biogas molecules. Theoretical computations have been conducted to open up opportunities for design of materials for capture and sensing biogas.

Computational details

MPBCP, [La-MPBCP]⁺³ and La-MPBCP complexes were optimized using the density functional theory. Calculations in this paper were performed with the Perdew-Burke-Ernzerhof (PBE0-D3)³⁹⁻⁴⁰ functional and the def2-TZVP basis set,⁴¹ using the Gaussian 09 program.⁴² In order to characterize all optimized structures, we have computed their vibrational modes at the same level of theory. Geometries from local minima were used to carry out their respective NBO analysis, at the same level of theory.⁴³ The band gap of the system was calculated from the difference between HOMO and LUMO orbitals. The adsorption energy, E_{ads} , is defined as the difference between the sum of the energy of the isolated molecule gas and of [La-MPBCP]⁺³ and La-MPBCP complex and the energy of the system with a bonded gas molecule. Adsorption energy (E_{ads}) of different systems are calculated with the following equation:

 E_{ads} (gas molecule) = E ([MPBCP] -gas molecule) - (E [MPBCP] + E gas molecule)

 E_{ads} (gas molecule) = $E([\text{La-MPBCP}]^{+3}$ -gas molecule) - $(E[\text{La-MPBCP}]^{+3} + E$ gas molecule)

 E_{ads} (gas molecule) = E (La-MPBCP - gas molecule) - (E La-MPBCP + E gas molecule)

Where E (E La-MPBCP or [La-MPBCP]⁺³-gas molecule) is the total energy of the system of E [La-MPBCP]⁺³ or ELa-MPBCP and gas molecules, and E[La-MPBCP]⁺³, La-MPBCP and E gas molecule are the total energies of the functionalized structure with lanthanum and a molecule of gas present, respectively.

The quantum molecular descriptors for [La-MPBCP]⁺³, La-MPBCP consist of ionization potential (I), electron affinity (A), global hardness (η),⁴⁴ electronegativity (χ), electronic chemical potential (μ),⁴⁵ electrophilicity index (ω)⁴⁶ and chemical softness (S) are calculated according to follows equations: $I = -E_{HOMO}, A = -E_{LUMO}, \eta = (I - A)/2, \chi = I + A/2, \mu = -(I + A)/2, \omega = -\mu^2/2\eta$ and $S = 1/2\eta$

All generated files from Gaussian 09 were analyzed with the Chemcraft program v1.8

Results and discussion

The geometry and optimization of 1,3-phenylene-bridged cyclic pyrrole (MPBCP)

The geometry of the meta-phenylene-bridged cyclic pyrrole (MPBCP) structure was optimized using PBE0-D3/def2TZVP with aC_{3v} point group, adopting a non-planar geometry due to the presence of hydrogen atoms located in the cavity. The distance between the two N atoms in the middle of the pore is 4.73 Å and the pore diameter was measured as 3.84 Å. The C-N bond length of 1.37 Å is in agreement with similar bonds C-N in previous X-ray studies (1.38 Å). ³⁷ The optimized structure of MPBCP is depicted in Figure 1. The adsorption spectrum of MPBCP structure showed a band at 369 nm, slightly high compared to the experimental adsorption of ortho-phenylene-bridged cyclic pyrrole (332 nm). ³⁷

The high density of N atoms leads to the different interactions between gas molecules, due to, the adsorption of biogas molecules was studied (CO₂, H₂, N₂ and CH₄). Our results showed weak interactions between the gas and the MPBCP structure. For the case of the CO₂ and N₂ molecules, the most stable configurations adopted are a non-planar structure with Cs (CO₂) and C3v point group for N₂. Oxygen and nitrogen atoms, of both molecules, are coordinated to the hydrogens of sheet with 2.32 and 2.55 Å, respectively. These length values of coordination bonds were consistent with low E_{ads} values -7.59 and -4.62 kcal/mol, see Figure 2. On the other hand, the adsorption of CH₄and H₂ molecules exhibits adsorption energies of H₂, -1.97 and CH₄, -5.61 kcal/mol. The NBO analysis shows the CO₂ and N₂, transfers charge to the nitrogen atoms with hyperconjugative interaction energies E (2) of nO- $\sigma_{N-H} = 2.01$ kcal/mol, nN- $\sigma_{N-H} = 1.75$ kcal/mol.

To increase the coordination with the biogas molecules, MPBCP was coordinated using two strategies: a) placing a lanthanum atom in the central cavity with a covalent interaction with the nitrogen atoms. b) maintaining the interaction of the lanthanum atom with the MPBCP structure, through coordination with a total charge of +3.



Figure 1. a) Optimized structure of MPBCP. Color code for spheres: dark gray (C); blue (N); yellow (H). b Space-filling mode



Figure 2. DFT adsorption structures. a) Top and side views of gas-MPBCP system. b) NBO donor and acceptor orbitals responsible for intermolecular interactions. The adsorption energy (E_{ads}) are expressed in kcal/mol calculated with the PBE0-D3/def2-TZVP method. Color code for spheres: dark gray (C); blue (N); yellow (H); red (O).

The geometry and optimization of La-MPBCP or [La-MPBCP]⁺³ systems

The studied La-MPBCP or [La-MPBCP]⁺³ systems in this work are not planar, they belong to the C_{3V} point group. For both systems, the lanthanum atom was preferably adsorbed in the middle of the cavity. The coordination sphere about the lanthanum possesses a trigonal pyramidal geometry, with La-N bond lengths of (2.58 Å) La-MPBCP and (2.80 Å) [La-MPBCP]⁺³, these values were consistent with similar experimental bond data (2.86-2.68 Å) reported before. ⁴⁷⁻⁴⁸. The coordination is better in the neutral system as expected by the formation of stronger bonds and a N-La-N bond angle of 118°. The optimized structures are depicted in Figure 3. The La-MPBCP system undergoes a considerable distortion in order to keep the nitrogen donors close to the lanthanum center and this system shows a greater stiffness caused by the N-La interaction, allowing the lanthanum atom to lie closer to the plane of the MPBCP. Adsorption energy values, as well as some important parameters for both systems, are listed in Table 1.

The highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO are the main orbitals that participate in the chemical stability they are shown in Figure 4, and the corresponding energy levels are listed in Table 1. The HOMOs are predominantly localized on the MPBCP ligand, while the LUMOs are localized mainly on lanthanum atoms. The energy gap between HOMO and LUMO of the MPBCP is 4.22 eV and our calculated band gaps for La-systems show that the coordination of lanthanum atom on the ligand affect the non-conductor character of MPBCP. The [La-MPBCP]⁺³ system exhibits lower band gaps of 1.39 eV, indicating character de semiconductor and more excitability system. (see Table 1)

The predicted IR spectrum of MPBCP, La-MPBCP and [La-MPBCP]⁺³ system shows bands associated respectively to the stretching modes of N-H, C-H, La-N of group of pyrrole and benzene ring. The IR data calculated of the MPBCP exhibit bands at 1507 cm–1 and 3207 cm–1, due to the pyrrole ν (C=N) group and ν (C-H) bond of benzene. The band corresponding to the C=N group was considerably shifted to the lower frequency 122 cm⁻¹(1360 cm⁻¹) and 120 cm⁻¹ (1377 cm⁻¹) in their corresponding La-MPBCP and [La-MPBCP]⁺³ system indicating the involvement of the nitrogen atoms in the coordination. The presence of two bands at 1135, 323 cm⁻¹ and 917, 306 cm⁻¹attributed to ν (La–N) respectively. The calculated for assignments for the MPBCP, La-MPBCP and [La-MPBCP]⁺³ system in gas phase are collected in Table 2.

The study of natural bond orbitals shows the lone pairs from nitrogen atoms participate as donors, while the lanthanum atom as acceptor see Figure 3c and 3d. Charges on La atoms are +2.30, +2.40 in La-MPBCP and [La-MPBCP]⁺³, respectively. Charges on N atoms in the cavity are -0.79 to -0.81. The nitrogen atoms in [La-MPBCP]⁺³ system has the most negative charge, it is clear that this systems is the electron-deficient La site.



Figure 3. DFT adsorption structures. Top and side views of La-MPBCP system (a) and [La-MPBCP]⁺³ system (b). NBO donor and acceptor orbitals responsible for intermolecular interactions, lone pair (LP) (c) and (d). Bond length La-N and the adsorption energy (E_{ads}) are expressed in (Å) and kcal/mol, calculated with the PBE0-D3/def2-TZVP method. Color code for spheres: dark gray (C); blue (N); yellow (H); red (O); orange (La).



Figure 4. Frontier orbitals (HOMO–LUMO) of the of La-MPBCP and [La-MPBCP]⁺³complex calculated with the PBE0-D3/def2-TZVP method.

Table 1. N-La, N-C, N-N and La-H bond length and N-La-N bond angle, adsorption energy (E_{ads}) , energies of frontier molecular orbitals (E_{HOMO}, E_{LUMO}, eV), HOMO-LUMO energy gaps (Eg, eV), calculated dipole moment (D_M , Debye), global hardness (η , eV), chemical potential (μ , eV), and global electrophilicity index (ω , eV) of La-MPBCP and [La-MPBCP]⁺³ complex calculated with the PBE0-D3/def2-TZVP method.

	La-MPBCP	$[La-MPBCP]^{+3}$
bond length (Å)N-La	2.58	2.80
bond length (Å) N-C	1.38	1.44
bond length (Å) N-N	4.41	4.57
bond length (Å) La-H	2.57	2.62
bond angle (°) N-La-N	118	109
E_{ads} (kcal/mol)		-361.26
E_{Homo} (eV)	-5.13	-14.31
E_{Lumo} (eV)	-2.83	-12.93
Band gap (eV)	2.30	1.39
D_{M} (debye)	3.49	2.80
I	5.13	14.31
А	2.83	12.93
χ	6.55	20.78
$\eta (eV)$	1.15	0.69
μ (eV)	-3.98	-13.62
$\omega (eV)$	6.90	133.95
S	0.44	0.72

Table 2. Calculated wavenumbers (cm⁻¹) and assignments for the MPBCP, La-MPBCP and [La-MPBCP]⁺³

Assignments	MPBCP	La-MPBCP	$[La-MPBCP]^{+3}$
N1-H1	3702		3400
C5-H2	3193	3113	3051
C6=C7	1663	1661	1630
C1=C2	1647	1638	1678
C2-N1	1486	1360	1377
La-N1		$1135,\!323$	917, 306

The adsorption of molecular gases on La-MPBCP or [La-MPBCP]⁺³ systems

The study for adsorption of biogas (CO₂, H₂, N₂ and CH₄) on the La-MPBCP or [La-MPBCP]⁺³ systems, we considered that the gas molecule would interact with the lanthanum atom, because of that the gas molecule was placed directly on the top of the lanthanum atom, see Figure 4. The optimized structures shown *Cs* symmetry for interactions by CO₂, H₂, N₂ and CH₄ with neutral system. For the case of the [La-MPBCP]⁺³ system, the H₂, and CH₄ shown *Cs* symmetry and C3v symmetry for interactions by CO₂ and N₂ with perpendicular interaction gas-La (CO₂, La-O 2.50; N₂, La-N 2.77 Å) showing lower bond length than the neutral system see Table 3. On the other hand, the La-H in H₂ molecule has a similar value for both systems (neutral, La-H 2.68-2.77 and [La-MPBCP]⁺³ 2.74 Å), those interactions are significantly smaller than the sum of their van der Waals radii.⁴⁹

The calculated adsorption energies of the gas molecules adsorbed on systems are listed in Table 3. It is observed that the E_{ads} are negative, indicating adsorption was exothermic showing favorable interaction of those gas molecules. The adsorption energy for the H₂, N₂, CH₄ and CO₂ on the [La-MPBCP]⁺³ system has a values of -7.51, -16.64, -21.30 and -28.63 kcal/mol, these values are higher compared to neutral system (-5.28, -9.90, -10.79 and -15.95 kcal/mol). The calculated CO₂ adsorption energy for [La-MPBCP]⁺³ is similar to La₂O₂CO₃ systems calculate with the PBE functional.⁵⁰ The descending order of those adsorption energies is the following: CO₂>CH₄>N₂>H₂. The adsorption of lanthanum atom on MPBCP induce to increase the reactivity, causing the adsorption of gas molecule. We can clearly observe that all gas molecules (N₂, H₂, CO₂, CH₄) have coordinations with short distances with the lanthanum atom (see Figure 5). Our results predicted that these gas molecules are easy to be adsorbed on the La-MPBCP or [La-MPBCP]⁺³ systems by physisorption. It is important to highlight the computed adsorption energy for the CO₂ molecule on the [La-MPBCP]⁺³ system is four times greater than adsorption energy for the H₂ molecule. These results suggested that the [La-MPBCP]⁺³ system could serve as an adsorber-separator of CO₂/H₂.



Figure 5. DFT adsorption structures. Top and side views of the molecule gases adsorbed onto the La-MPBCP and [La-MPBCP]⁺³ optimized structures. Bond length lithium-gas molecule (Å) the adsorption energy (E_{ads}) are expressed in kcal/mol calculated with the PBE0-D3/def2-TZVP. Color code for spheres: dark gray (C); blue (N); yellow (H); red (O).

Table 3. Bond length X-La gas molecule (X:CO₂, H₂, N₂ and CH₄), N-La, N-C, N-N and La-H and bond angle N-La-N, adsorption energy (E_{ads}), energies of frontier molecular orbitals ($E_{\rm HOMO}$, $E_{\rm LUMO}$, eV), HOMO-LUMO energy gaps (Eg, eV), calculated dipole moment (D_M, Debye), global hardness (η , eV), chemical potential (μ , eV), and global electrophilicity index (ω , eV) of gaseous molecules N₂, H₂S, NH₃, SO₂, CO, H₂ and CH₄ onto La-MPBCP and [La-MPBCP]⁺³ calculated with the PBE0-D3/def2-TZVP method.

	$\rm CO_2$	H_2	N_2	CH_4
La-MPBCP	La-MPBCP	La-MPBCP	La-MPBCP	La-MPBCP
bond length (Å)X-La	2.64	2.77 - 2.68	2.86	2.92
bond length (Å)N-La	2.57 - 2.62	2.59	2.58	2.58
bond length (Å) N-C	1.38	1.38	1.38	1.38
bond length (Å) N-N	4.42-4.43	4.42	4.42	4.42
bond length (Å) La-H	2.58	2.57	2.57	2.58
bond angle (°) N-La-N	117	118	118	118
E_{ads} (Kcal/mol)	-15.95	-5.28	-9.90	-10.79

	$\rm CO_2$	H_2	N_2	CH_4
$\overline{\mathrm{E}_{\mathrm{Homo}}}$ (eV)	-5.11	-5.13	-5.11	-5.08
E_{Lumo} (eV)	-2.32	-2.65	-2.71	-2.30
Band gap (eV)	2.79	2.48	2.40	2.78
D_{M} (debye)	4.56	3.71	4.13	4.74
$[La-MPBCP]^{+3}$	$[La-MPBCP]^{+3}$	$[La-MPBCP]^{+3}$	$[La-MPBCP]^{+3}$	$[La-MPBCP]^{+3}$
bond length (Å)X-La	2.50	2.74	2.77	2.80
bond length (Å)N-La	2.82	2.2	2.81	2.80
bond length (Å) N-C	1.44	1.44	1.44	1.44
bond length (Å) N-N	4.57	4.53	4.57	4.60
bond length (Å) La-H	2.60	2.60	2.61	2.59
bond angle (°) N-La-N	108	108	109	109
E_{ads} (Kcal/mol)	-28.63	-7.51	-16.64	-21.30
E_{Homo} (eV)	-14.02	-14.17	-14.11	-14.09
E_{Lumo} (eV)	-11.83	-12.41	-12.09	-12.10
Band gap (eV)	2.19	1.75	2.02	1.99
D_M (debye)	2.72	3.39	2.56	4.11

Table 4 . Global hardness (η , eV), chemical potential (μ , eV), softness (S) and global electrophilicity index (ω , eV) of La-MPBCP and [La-MPBCP]⁺³ systems calculated with the PBE0-D3/def2-TZVP.

	CO_2	H_2	N_2	CH_4
La-MPBCP	La-MPBCP	La-MPBCP	La-MPBCP	La-MPBCP
Ι	5.11	5.13	5.11	5.08
А	2.32	2.65	2.71	2.30
χ	6.28	6.45	6.46	6.23
η (eV)	1.39	1.24	1.20	1.39
μ (eV)	-3.72	-3.89	-3.91	-3.69
$\omega (eV)$	4.95	4.10	6.36	4.90
S	0.36	0.40	0.42	0.36
$[La-MPBCP]^{+3}$	$[La-MPBCP]^{+3}$	$[La-MPBCP]^{+3}$	$[La-MPBCP]^{+3}$	[La-MPBCP] ⁺³
I	14.02	14.17	14.11	14.09
А	11.83	12.42	12.09	12.10
χ	19.94	20.38	20.15	20.13
$\eta ~(\mathrm{eV})$	1.09	0.88	1.01	0.99
μ (eV)	-12.93	-13.29	-13.09	-13.09
$\omega (eV)$	76.29	100.78	85.10	86.15
S	0.46	0.57	0.50	0.50

The chemical descriptors: (μ) , (η) , and (ω) are shown in Table 2 and 4 respectively. When the CO₂, H₂, N₂ and CH₄ are adsorbed on [La-MPBCP]⁺³, the values of η increase from 0.67 eV to 1.09, 0.88, 1.01 and 0.99 eV, respectively.. These results indicate that the interaction of gas molecule with [La-MPBCP]⁺³ the chemical stabilities of system are maintained. The difference of electrophilicity (ω) values in the system gas-[La-MPBCP]⁺³ are 76.29-CO2, 100.78-H2, 85.10-N2 and 86.15-CH4 eV.. The difference between electrophilicity values indicates the strong interactions between the donor (gas) and the acceptor (lanthanum).

NBO analysis

We investigated the most important interaction between the gas molecules with the lanthanum, through an

NBO analysis, in order to know more in detail their bond nature.

The study of natural bond orbitals shows the O, N atoms and H-H, C-H bonds, of the gas molecule participate as donors, while the lanthanum atom of La-MPBCP or [La-MPBCP]⁺³ systems as acceptor. Table 2 show stabilization energies, for donor and acceptor orbitals for all systems. The stabilization energy es mayor para [La-MPBCP]⁺³ and the order of E(2) is the following N₂ > CO₂>H₂ > CH₄.



Figure 6. NBO donor and acceptor orbitals responsible for intermolecular interactions of gas molecule onto MPBCP or [La-MPBCP]⁺³ systems. Donor orbitals are in red color, while acceptor orbitals are represented in blue color.

Table 5. Donor and acceptor orbitals for interactions from all gas molecules toward La-MPBCP or [La-

MPBCP]⁺³ systems.

Molecule	Donor	Acceptor	$E(2) (kcal/mol)^{a}$	E(j)- $E(i)$ (a.u.) ^b	$F(i, j) (a.u.)^{c}$
La-MPBCP	La-MPBCP	La-MPBCP	La-MPBCP	La-MPBCP	La-MPBCP
$\rm CO_2$	n _O	La	19.02	0.85	0.114
H_2	$\sigma_{\mathrm{H-H}}$	La	8.62	0.50	0.060
N_2	n _N	La	19.86	0.71	0.107
CH_4	$\sigma_{\text{C-H}}$	La	5.69	0.59	0.053
[La-	[La-	[La-	[La-	[La-	[La-
$MPBCP]^{+3}$	$MPBCP]^{+3}$	$MPBCP]^{+3}$	$MPBCP]^{+3}$	$MPBCP]^{+3}$	$MPBCP]^{+3}$
CO_2	n _O	La	36.65	0.86	0.158
H_2	$\sigma_{ m H-H}$	La	19.74	0.45	0.085
N_2	n _N	La	46.24	0.72	0.164
CH_4	$\sigma_{\text{C-H}}$	La	9.34	0.61	0.068

^a E(2) means energy of hyper conjugative interaction (stabilization energy)

^b Energy difference between donor and acceptor i and j BNO orbitals

c F(i, j) is the Fock matrix element between i and j NBO orbitals

Conclusions

Using DFT, we explored geometries, predicted adsorption energies, donor-acceptor natural orbitals were analyzed, and the nature of the coordination of CO_2 , H_2 , N_2 and CH_4 gas molecules on La-MPBCP and [La-MPBCP]⁺³ complexes was studied with the help of a NBO analysis. It is clear to note that by introducing the lanthanum atom into the MPBCP structure, causes better contact area, so that the gas molecules can be adsorbed. The La-MPBCP]⁺³ complex is more reactive with Eg = 1.39 eV. The results reveal that all gases are physically adsorbed with considerable adsorption energy values. Based on their adsorption energies, it can be understood that CO_2 are strongly physisorbed on La-MPBCP or [La-MPBCP]⁺³ systems. In contrast, the H₂ molecule is weakly physisorbed on both structures. The NBO analysis shows the gas molecule acts as donor through the σ and n interaction (O, N atoms and H-H, C-H) towards the lanthanum atom. Our calculations have predicted that the La-MPBCP or [La-MPBCP]⁺³ systems are a good candidates as a biogas absorbing material and as a separator for CO_2/H_2 mixtures.

Conflicts of interest

There are no conflicts to declare

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