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Modeling Adsorption and Optical Properties for the Design of CO₂ Photocatalytic Metal-Organic Frameworks

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Abstract: Four Metal-Organic Frameworks (MOFs) were modeled (IRMOF-C-BF₂, IRMOF-C-(2)-BF₂, IRMOF-C-BF₂, and IRMOF-C-CH₂BF₂) based on IRMOF-1. A series of linkers, based on Frustrated Lewis Pairs and coumarin moieties, were attached to IRMOF-1 to obtain MOFs with photocatalytic properties. Four different linkers were used: (a) a BF₂ attached to a coumarin moiety at position 3, (b) two BF₂ attached to a coumarin moiety in positions 3 and 7, (c) a BF₂ attached in the coumarin moiety at position 7, and (d) a CH₂BF₂ attached at position 3. An analysis of the adsorption properties of H₂, CO₂, H₂O and possible CO₂ photocatalytic capabilities was performed by means of computational modeling using Density Functional Theory (DFT), Time-Dependent Density Functional (TD-DFT) methods, and periodic quantum chemical wave function approach. The results show that the proposed linkers are good enough to improve the CO₂ adsorption, to hold better bulk properties, and obtain satisfactory optical properties in comparison with IRMOF-1 by itself.

Keywords: MOFs; photocatalysis; CO₂ reduction; environmental-remediation; bonding; QTAIM

1. Introduction

Metal-Organic Frameworks (MOFs), also known as porous coordination polymers, are crystalline materials with a bi- or tri-dimensional structure. They constitute the bridge between micro- and mesoporous materials. Among its properties, MOFs can be used for gas storage, energy conversion, chemical sensors, drug delivery and catalysis [1]. In particular, MOFs have recently been studied for their photocatalytic properties, primarily focused on H₂ production from water [1–6], degradation of organic pollutants [2,7], and CO₂ photo-reduction [2,8]. IRMOF-1 (MOF-5) is a crystalline and stable MOF, reported in 2005 by Li and co-workers [9]. Even at relatively high temperatures (300 °C), IRMOF-1 displays the desired thermo-stability for a material to be used for real-life applications. Because of its wide superficial area and fixed pore volume, IRMOF-1 was purposed for gas storage. These two properties make IRMOF-1 attractive as catalytic platform for the design of new MOFs for CO₂ photo-reduction. IRMOF-1 is reported as support for an active photo-catalyst [8], as precursor of a catalyst [10–12] or as part of composites [13] or post modified structures [14] with photocatalytic activity. It is known that IRMOF-1 is capable of performing charge transfer by means of its organic linkers [2,15,16] through a process called Metal Ligand Charge Transfer (MLCT). Such MOF has proved its efficiency in phenol photo-degradation [3].

In other hand, coumarin has been widely used in the construction of optical devices because of its high optical efficiency. Photo sensors, molecular markers for both qualitative and quantitative studies, among others hold a coumarin moiety as the basic chromophore unit [17,18]. Coumarin and its derivatives display a remarkable behavior in photon capture in the UV-visible region [17]. Nevertheless, using coumarin as linker in MOFs to be the source of energy for a chemical transformation of adsorbates remained unexplored until now. Considering the potential advantages of using coumarin, we propose it as starting...
material in the design of aggregate value linkers for the central cluster \((\text{Zn}_4\text{O}(\text{CO}_2)_6)\) of IRMOF-1-based-MOFs.

A further modification to obtain a catalytic MOF, addressed in the present contribution, is based on the recent finding that Frustrated Lewis Pairs (FLPs) activate the hydrogenation of \(\text{CO}_2\) for the production of hydrogen-rich fuels \([19–22]\). FLPs are formed by a Lewis acid-base pair hindered to form an adduct, either sterically or geometrically. However, voluminous substituents—commonly used to avoid adduct formation—tend to increase the activation energy required for the FLPs catalysis \([19]\). To overcome this problem, Ye Jingyun and Karl Johnson proposed in 2015 to stabilize FLPs by anchoring them to MOFs in the linker’s structure, thus, using the macromolecule as a catalytic platform \([23]\). Among the advantages of FLPs-functionalized-MOFs are the potentially efficient recuperation of the catalyst, potentially good capture and conversion of \(\text{CO}_2\) processes using the same material, thermal stability of the catalyst and low activation barriers. Such characteristics suggest that \(\text{CO}_2\) photo-reduction is possible under mild conditions.

In the present contribution, we address the design of a multipurpose linker. Such linker must have a combination of cooperative effects to obtain the desired \(\text{CO}_2\) catalytic properties: efficient UV-VIS absorption properties, capability of \(\text{CO}_2\) hydrogenation and subsequent reduction, and the expected structural spacing for obtaining a stable MOF. Our hypothesis is that hybrid organic coumarin-FLP linker (C-BF\(_2\)) connected with the central metallic cluster displayed in the IRMOF-1 will achieve \(\text{CO}_2\) photo-reduction in the presence of \(\text{H}_2\) and \(\text{H}_2\text{O}\). With these considerations, we aim to improve the photocatalytic activity of IRMOF-1 central cluster by reducing the energy required for photon absorption and providing a catalytic-active site for the guest molecules in the MOF. This work considers the boron atom of the BF\(_2\) substituent in the coumarin moiety as the acidic counterpart of the FLP, whereas the basic counterpart is either the carbonyl oxygen of the coumarin moiety or oxygen of the closest OCO bridge in the central cluster of the IRMOF-1 derivative. In both cases, the FLP is restricted by coumarin’s rigid ring and MOF rigid and stable structure, without the need for steric hindrance. In this way, once \(\text{CO}_2\), \(\text{H}_2\), and \(\text{H}_2\text{O}\) molecules are adsorbed, they could interact through the captured energy from the photon absorption and consequently, the \(\text{CO}_2\) could be photo catalytically transformed into a less contaminant molecules and hopefully in useful products.

2. Methods

IRMOF-C-BF\(_2\) was constructed using the central cluster of IRMOF-1 \((\text{Zn}_4\text{O}(\text{CO}_2)_6)\), under the assumption that both IRMOF-C-BF\(_2\) and IRMOF-1 crystallize in a cubic arrangement. For this purpose, 3-BF\(_2\)-coumarin derivatives (C-BF\(_2\)) were linked by their C8 to the C atom of the OCO bridges. Only three ligands were added in the direction of the three Cartesian axes (primitive cell, Figure 1). Both C5 and C8 of C-BF\(_2\) were connected to vicinal central clusters. Periodic replication of the primitive cell for unit cell construction used the BAND-ADF software \([24, 25]\). The parameters of the cell were fixed as \(a = b = c = 12.941\ \text{Å}\) and \(\alpha = \beta = \gamma = 90^\circ\), as reported for IRMOF-1 \([9]\) (unit cell, Figure 1). In addition, IRMOF-C’-BF\(_2\) was built from IRMOF-C-BF\(_2\), by changing the location of the BF\(_2\) group to the C7 of the coumarin moiety. In a similar way, it was assumed that this MOF crystallized on a cubic arrangement with the same cell parameters of IRMOF-C-BF\(_2\). IRMOF-C-CH\(_2\)BF\(_2\) was built from IRMOF-C-BF\(_2\), by adding a methylene moiety in C3, between the coumarin linker and the BF\(_2\) group.

Finite models of adsorbed \(\text{CO}_2\), \(\text{H}_2\), and \(\text{H}_2\text{O}\) molecules were analyzed to characterize optical and catalytic properties. All molecular DFT calculations used the 2014 version of Amsterdam Density Functional (ADF) program \([26, 27]\). A Double-zeta polarized basis (DZP) and a Generalized Gradient Approximation with a Perdew–Burke–Ernzerhof functional (GGA: PBE), for the Exchange and Correlation estimation were employed in all calculations (in exception of Zn atoms, for which Triple-zeta polarized basis (TZP) was used). Calculations that included IRMOF central cluster, where consideration of relativistic
effects was needed, were done with a scalar approximation—ZORA scalar [27–29]. The Self-Consistency Field convergence criterion was fixed to $10^{-7}$.

Figure 1. Unit cell of IRMOF-C-BF$_2$ purposed in this work. The cell’s parameters considered are $a = b = c = 12.941$ Å and $\alpha = \beta = \gamma = 90^\circ$. At the left superior corner, primitive cell of IRMOF-C-BF$_2$. Coordinates in xyz format are available in the Supplementary Materials (Table S2).

Calculations of IRMOF-C-BF$_2$, IRMOF-C’-BF$_2$, and IRMOF-C-CH$_2$BF$_2$ with guest molecules adsorbed considered the primitive cell. To warrant the proper filling of the valence orbitals, H atoms were added in the coumarin ring and CH$_3$ groups to C atoms in OCO bridges (Figure 2). In addition, the MOF’s structure was frozen, making the guests move freely; this approach has proven to be effective by Jingyun in a prior report [23]. For the modeling of adsorption of more than one guest molecule, the atoms of the MOF structure were feezed, such guest molecules were added successively. As a comparison, similar calculations were performed for IRMOF-1 and the correspondent linker (C-BF$_2$ for IRMOF-C-BF$_2$, C’-BF$_2$ for IRMOF-C’-BF$_2$, and C-CH$_2$BF$_2$ for IRMOF-C-CH$_2$BF$_2$), to evaluate the effects of the change of linker and the bond of the coumarin derivative to the metal cluster, respectively. Excited states were obtained using TD-DFT Davidson’s method. Geometry optimizations were done for the brightest states —those with higher oscillator strength ($f$)—using symmetry restriction [30–32].
Figure 2. Structure of the primitive cell of IRMOF-C-BF$_2$, after the proper filling with CH$_3$ and H groups for OCO bridges and C5 position of the coumarin ring, respectively. Coordinates in xyz format available in the Supplementary Materials).

The modeling for the unit cell employed the BAND-ADF software 2014 [25], and the same theory level considered for the primitive cells. The PBE functional was used, to be consistent with the primitive cell’s calculations and because of the good agreement with experimental data reported for band properties’ calculations of IRMOF-1, in particular the band gap and Density of States (DOS) [33]. Geometry optimizations were performed by freezing the MOF structure. Band structure calculations considered an interpolation level of 4 and the effective mass. A K-space vector of (3-3-3) was employed for the Brillouin-zone integration in DOS calculations. In addition, 1801 equidistant energy points—energy grid—for adequate observation of the band’s population were used, as reported previously for IRMOF-1 [33].

QTAIM has been successfully and widely used to understand the properties of shared-shell and closed-shell bonding [34–40]. Relevant characteristics of a bond can be well evaluated by some criteria, (i) the presence of a bond critical point (BCP), (ii) values of electron density ($\rho$) and Laplacian ($\nabla^2\rho$) at BCP, (iii) change of charge or electron population ($\Delta N$), (iv) change of energy, ($\Delta E$), and (v) delocalization index DI(X,Y) [41–46]. QTAIM analysis was performed at M06-2X/6-311 + +G(d,p) level of theory [47] of single points for finite models to study the intermolecular interactions between IRMOF’s and guest molecules adsorbed, using AIMAll program for properties calculation [48], Multifwn [49] and VMD [50] suites of program for a visual purpose.
3. Results and Discussion

3.1. IRMOF-C-BF2

3.1.1. Primitive Cell of IRMOF-C-BF2

Previous studies [23] limit the modeling of the CO$_2$ photo-reduction properties to the organic linker to model a new MOF, thus, ignoring the effects of the metallic cluster in its core. To evaluate if such approximation is reliable, we compared the optimized geometries of H$_2$ and CO$_2$ adsorption for the most affordable excited state of the primitive cell with the correspondent isolated coumarin derivative linker. Intermolecular distances were mostly inferior for the linker modeled in the absence of the metallic cluster (See Supplementary Materials, Figure S1).

Distances between the two guests and C-BF$_2$ linker imply that their absorption is performed on the linker structure in absence of the metallic cluster; the observed distance between the oxygen atom of CO$_2$ and the B atom is 3.29 Å, H atoms of H$_2$ and the oxygen atom of the carbonyl group are at 2.65 Å. These data lead us to confirm that H$_2$ is susceptible to interact with the basic part of the FLP (O), whereas CO$_2$ prefers the acidic counterpart (B). As mentioned above, the intermolecular distances are larger for the IRMOF-C-BF$_2$ finite model which considers the metallic cluster. An O atom of the CO$_2$ shows a distance of 4.971 Å with the closest hydrogen of the H$_2$ molecule. Moreover, it is evident that H$_2$ is too far from the MOF’s structure, and CO$_2$ is adsorbed close to one of the OCO bridges instead of the nearest linker (the observed distances of each O atom to the O of the closest OCO bridge are 3.867 Å and 4.319 Å). Two hypotheses to explain this particular behavior are: (1) there is a competition between the ligands for the association with the guest molecules; and (2) this behavior is caused by the antagonism of the two electron-rich sites of the MOF, the carbonyl oxygen and the oxygen atoms of the OCO bridges for the absorption of the guest molecules. This situation is more evident for the case of CO$_2$ absorption.

To explain the preference of the guests for the OCO bridges for absorption we have performed an analysis of the Quantum Chemical Topology of the adsorption process using the Quantum Theory of Atoms in Molecules to obtain a quantitative insight from the quantitative binding analysis. We used the absorption geometries reported in the Figure S1. As mentioned previously, some criteria help to evaluate bond characteristics. IRMOF-C-BF$_2$ complex properties are shown in Table 1. All intermolecular interactions that present bond path and BCP with guest molecules adsorbed are shown in molecular graphs in Figures S2–S7. There are several intermolecular interactions with guest molecules, most of them show values for Van der Waals interactions ($\rho = \sim10^{-3}$ au, $\nabla^2\rho > 0$ au) [45,51,52]. Delocalization index is a measure of polarity bond, pairs of atoms in closed-shell interactions show delocalization indices close to zero meanwhile in covalent bond tend to 1 [44]. Most of the interactions in these systems agree with weakly bound interactions (Di(X,Y) < 0.05) [53–56]. Moreover, each interaction represents a positive contribution (destabilization) for guest molecules ($\Delta E > 0$) and some of them are involved in a loss of electronic population ($\Delta N(X) < 0$) [54]. In the next lines, interactions are quantitatively analyzed.

Adsorbed CO$_2$ establish interaction with MOF’s oxygens (69.23%), MOF’s carbons (15.4%), or even MOF’s hydrogens (15.4%), all bond paths and BCP are shown in molecular graphs Figures S2 and S5–S7. CO$_2$ preference for OCO bridges is backed up for BCP. Moreover, Laplacian isosurface shows an electron density concentration at OCO oxygens (Figures S2–S7). That explains how CO$_2$ carbon is attracted to these domains. In this domain, CO$_2$ oxygens are close to other oxygens and interacting with them (Figures S2 and S5). Moreover, CO$_2$ can interact with H$_2$ and H$_2$O, some of such interactions agree with hydrogen bond criteria [57–60] (i.e., 0.002–0.034 au for electron density and 0.024–0.139 au for Laplacian, 140–180°, $\Delta E(X) > 0$, $\Delta N < 0$, Di(X,Y) < 0.05). Then, CO$_2$ maintains its ability to establish diverse interactions in this domain, especially with MOF’s oxygen. Additionally, guest intermolecular interactions have a stabilizing effect over CO$_2$. 
Table 1. Topological parameters of the BCP of bond in adsorption configurations of guest molecules (CO₂, H₂O and H₂) on IRMOF-C-BF₂.

| Structure       | Guest      | Bond **X—Y** | Distance (Å) | ρ        | ν²ρ      | DI(X,Y) | ΔE(X) kcal/mol | ΔN(X) |
|-----------------|------------|--------------|--------------|----------|----------|---------|----------------|-------|
| IRMOF-C-BF₂-CO₂ | CO₂        | O—O         | 3.07         | 0.00771  | 0.02996  | 0.03868 | 91.27          | −0.00446 |
|                 | CO₂        | O—O         | 3.26         | 0.00381  | 0.01612  | 0.02143 | 92.83          | −0.02477 |
|                 | C—O        | C—O         | 3.16         | 0.00528  | 0.02320  | 0.00999 | 37.41          | 0.03874 |
| IRMOF-C-BF₂-H₂O | H₂O        | O—H         | 2.32         | 0.01168  | 0.04255  | 0.04561 | 71.77          | −0.00224 b |
|                 | H₂         | H—C         | 3.03         | 0.00456  | 0.01150  | 0.01614 | 12.24          | −0.00126 |
|                 | H₂O        | O—O         | 3.01         | 0.00823  | 0.03263  | 0.04285 | 69.81          | 0.02101 |
|                 | H₂O        | O—O         | 3.22         | 0.00593  | 0.02241  | 0.03059 | 69.81          | 0.02101 |
| IRMOF-C-BF₂-CO₂| CO₂        | O—O         | 3.55         | 0.00250  | 0.01147  | 0.00836 | 89.88          | 0.01492 |
|                 | CO₂        | O—O         | 2.99         | 0.00373  | 0.01351  | 0.01197 | 91.68          | −0.03609 |
|                 | C—O        | C—O         | 2.95         | 0.00798  | 0.03175  | 0.01660 | 43.12          | 0.03087 |
|                 | C—O        | C—O         | 3.02         | 0.00725  | 0.03000  | 0.01374 | 43.12          | 0.03087 |
| IRMOF-C-BF₂-CO₂| H₂         | H—H         | 2.70         | 0.00302  | 0.01053  | 0.00854 | 14.47          | −0.01376 |
|                 | C—C        | C—C         | 3.26         | 0.00559  | 0.01996  | 0.00869 | 29.53          | 0.04988 |
|                 | C—O        | C—O         | 3.49         | 0.00264  | 0.01230  | 0.01181 | 29.53          | 0.04988 |
| IRMOF-C-BF₂-H₂ | H₂         | H—H         | 3.14         | 0.00105  | 0.00417  | 0.00314 | 14.95          | −0.01398 |
| IRMOF-C-BF₂-CO₂| H₂O        | O—O         | 2.03         | 0.01879  | 0.07680  | 0.05326 | 16.71          | −0.03286 b |
|                 | CO₂        | C—C         | 3.27         | 0.00539  | 0.01927  | 0.00828 | 36.07          | 0.04204 |

* In bond column, X represents guest atom and Y MOF atom; b ΔE(X) and ΔN(X) in hydrogen bond are reported for H.

Regarding to the water adsorption, water interact with MOF’s oxygens (75%) and MOF’s hydrogens (25%), all bond paths and BCP are shown in molecular graphs (Figures S4, S5 and S7). Hydrogen bonds were found in the presence of a water molecule (IRMOF-C-BF₂-H₂O and IRMOF-C-BF₂-H₂ CO₂ H₂O) and values of ρ and ν²ρ (Table 1) are within the expected range (i.e., 0.002–0.034 au for electron density and 0.024–0.139 au for Laplacian). Angles were corroborated (140°–180°) and distance is consistent with a strong hydrogen bond = 2.5–3.0 Å [57–60]; however, one of them is a non-classical hydrogen bond (IRMOF-C-BF₂-H₂O).

Regarding adsorbed H₂, there are interactions displayed by H₂ with MOF’s carbon, MOF’s hydrogens, but not with MOF’s oxygens (Figures S3, S6 and S7). Additionally, dihydrogen bonds that are present in IRMOF-C-BF₂–H₂ CO₂ and IRMOF-C-BF₂–H₂ CO₂ H₂O agree with topological criteria (i.e., angle= 90–171°, distance < 2.4–2.6, ρ = 10⁻²–10⁻³, ν²ρ > 0 ua) [55,56].

Guest intermolecular interactions were calculated using the AIMAll program. For each system, intermolecular interactions between H₂, CO₂, and H₂O were detected (see BCP’s in Figures S2–S7). Most of the intermolecular interactions between guest molecules agree with hydrogen bond criteria (Table 2) [57–60]. Additionally, water and carbon dioxide show an intermolecular BCP (O—C) (Figure S7), whose properties are consistent with Van der Waals interactions [51,52].

Optical Properties of Primitive Cell of IRMOF-C-BF₂ during Adsorption Process

To contrast the optical properties of IRMOF-C-BF₂, C-BF₂, and IRMOF-1, a calculation of the most affordable excited states was performed, considering CO₂ and H₂ as guest molecules. The brightest transition for the coumarin derivative is 25 times more probable when it is isolated (C-BF₂, Table 3) than when it is bonded at C8 to the metallic cluster (IRMOF-C-BF₂, Table 3). The energy of the transition, on the other hand, is 1.48 times greater for C-BF₂ (4.0 eV) than for IRMOF-C-BF₂ (2.7 eV). The optical properties of coumarin are appreciably decreased when it is attached to a MOF, considering the oscillator strength (f) of vertical photo-excitations. Nevertheless, there is a probable improvement of the optical properties displayed by IRMOF-C-BF₂ compared with IRMOF. IRMOF-C-BF₂ shows a smaller energy of excitation, which was localized in the visible part of the electromagnetic
spectra (Figure S8a), such behavior is desirable for photocatalytic devices. Comparing the observed transitions in IRMOF-1 and IRMOF-C-BF$_2$, it is clear that the change in the ligand’s nature has positive effects both in the energy of the brightest transition and its probability (given by a higher $f$) (Figure S8a), Table 3). IRMOF-C-BF$_2$ shows a transition 14.7 times brighter than for IRMOF-1, whose respective energies are 2.7 eV and 4.2 eV. This implies a noticeable improvement of the optical properties to activate photocatalysis when a coumarin-like replaces the benzenoid linker in IRMOF-1.

Table 3. Energies and oscillator strengths of the brightest transitions of IRMOF-C-BF$_2$ and C-BF$_2$ in the presence of H$_2$ and CO$_2$ as probe guest molecules.

| Structure Name | Energy/eV | $f$ $10^{-3}$ |
|----------------|-----------|---------------|
| IRMOF-1        | 4.2       | 0.57          |
| IRMOF-C-BF2    | 5.4       | 8.4           |
| C-BF2          | 4.0       | 210           |
| IRMOF-C’-BF2   | 5.4       | 6.3           |
| C’-BF2         | 3.0       | 305           |
| IRMOF-C-CH2BF2 | 2.5       | 5.02          |
| C-CH2BF2       | 4.0       | 331           |

Table 4 and Figure 3 show the optimized geometries of the brightest excited states of the adsorption of H$_2$, CO$_2$, and H$_2$O in IRMOF-C-BF$_2$. Structure of Figure 3a) shows the adsorption of CO$_2$ close to an OCO bridge (4.028 Å between the C of the bridge and the nearest O of CO$_2$) and to one of the coumarin-derivative-linkers (with a distance of 5.007 Å between the B and an O of the guest). Regarding the adsorption of H$_2$ (Figure 3b) and H$_2$O (Figure 3c), the distances between the guests and IRMOF-C-BF$_2$ are larger than 6.00 Å. On the other hand, Figure 3d–f displays geometry optimizations that imply more than one guest molecule. The closest proximity of adsorbed molecules to the MOF structure and among them are shown in Figure 3d) for adsorption of H$_2$ followed by CO$_2$ and Figure 3e) for adsorption of CO$_2$ and then H$_2$O. In the case of H$_2$ and CO$_2$ adsorption (Figure 3d), the oxygen atoms of CO$_2$ are located at 4.148 Å and 4.123 Å of the carbon of an OCO bridge of MOF; H$_2$ molecule is located at 2.899 Å of adsorbed CO$_2$. In the case of CO$_2$ and H$_2$O as guest molecules (Figure 3e), CO$_2$ is localized near a carbon atom of a OCO bridge, at 4.388 Å; the water molecule is localized at 3.608 Å of one oxygen of the same OCO bridge. The bond angles and interatomic distances of adsorbed molecules are not affected in any of the structures. Regarding the adsorption of H$_2$ followed by CO$_2$ and then H$_2$O (Figure 3f), the places where H$_2$, CO$_2$, and H$_2$O adsorb are similar to those observed for the two guest molecules. Thus, the results involving more than one guest molecule suggest a reaction between the guest molecules, mediated by the MOF structure.
Table 4. Primitive cell’s bonding energies of IRMOF-C-BF$_2$ in the presence and absence of guest molecules.

| Structure Name         | Guest Molecule(s) | Relative Energy/eV |
|------------------------|-------------------|--------------------|
| IRMOF-C-BF2            | -                 | 0.000              |
| IRMOF-C-BF2-CO$_2$     | CO$_2$            | -22.912            |
| IRMOF-C-BF2-H$_2$      | H$_2$             | -6.803             |
| IRMOF-C-BF2-H$_2$O     | H$_2$O            | -14.096            |
| IRMOF-C-BF2-CO$_2$-H$_2$ | CO$_2$ + H$_2$   | -29.661            |
| IRMOF-C-BF2-CO$_2$-H$_2$O | CO$_2$ + H$_2$O | -37.117            |

Figure 3. Optimized geometries of bright excited states reported in Table 5 for the interaction between IRMOF-C-BF$_2$ and guest molecules. The energies for these are shown in Table 4. The structures presented are, considering the guest, as (a) IRMOF-C-BF$_2$-CO$_2$, (b) IRMOF-C-BF$_2$-H$_2$, (c) IRMOF-C-BF$_2$-H$_2$O, (d) IRMOF-C-BF$_2$-H$_2$-CO$_2$, (e) IRMOF-C-BF$_2$-CO$_2$-H$_2$O, (f) IRMOF-C-BF$_2$-H$_2$-CO$_2$-H$_2$O. The specified distances and angles are shown in Angstrom (Å) and degrees. Coordinates in xyz format available in the Supplementary Materials (Table S2).

Table 5. Optimized energies and oscillator strengths of the brightest transitions of IRMOF-C-BF$_2$, in the presence and absence of guest molecules. A column including the results for IRMOF-1 is included as a comparison.

| Guest Molecules | IRMOF-C-BF$_2$ Energy/eV | f $\cdot 10^5$ | IRMOF-1 Energy/eV | f $10^{-3}$ |
|-----------------|--------------------------|--------------|------------------|--------------|
| -               | 2.7                      | 8.3          | 4.1              | 0.64         |
| CO$_2$          | 2.7                      | 5.6          | 4.1              | 0.42         |
| H$_2$           | 2.7                      | 8.3          | 4.1              | 0.69         |
| H$_2$O          | 2.7                      | 8.3          | 4.2              | 0.56         |
| CO$_2$ H$_2$    | 2.7                      | 8.4          | 4.2              | 0.57         |
| CO$_2$ H$_2$O   | 2.5                      | 4.3          | 4.2              | 0.43         |

Regarding the vertical excitations, the ones with higher f value are singlet-singlet transitions. The brightest ones are shown in Table 5. As showed, f values for IRMOF-C-BF$_2$ with and without guest molecules are, despite their magnitudes, 10 times greater than the respective ones for IRMOF-1. Furthermore, the energy required for electron excitation is
150% smaller for IRMOF-C-BF₂ than for IRMOF-1 (the optimized geometries in the absence of guest molecules are taken as reference).

The information related to the photocatalytic capability of the IRMOF-C-BF₂ can be obtained from the characterization of the Potential Energy Surface (PES), such study is in progress. With this regard, a characterization of some candidate transition states and maximums found along the optimization process of the excited states, are presented in the Supplementary Materials (Figures S9 and S10). A relevant observation is that at such maximums, the absorbed guest molecules display large distortions of their geometry.

Change in Order of the Guests’ Adsorption for Geometry Optimization in IRMOF-C-BF₂

We performed the adsorption of the guest molecules adding CO₂ and then H₂ to IRMOF-C-BF₂, to compare the optimized absorption geometries at the brilliant excited states. Figure S11 shows the resultant geometry, for which a slight difference can be perceived when compared to Figure S1, in which the guest molecules are added in the opposite order. CO₂ is near three different atoms in the MOF structure (Figure S11): its carbon atom is placed in the middle of two oxygen atoms of different kind, the first one located at 3.721 Å is the carbonyl oxygen of a linker; the second one is located at 3.157 Å and forms part of the OCO bridge located just next to the C-BF₂ linker. Regarding the oxygen atom of CO₂, it is placed farthest to the central cluster and it is also near the OCO bridge, at 4.826 Å. In contrast with the original adsorption order, H₂ then CO₂, in this experiment adsorbed H₂ is located between the adsorbed CO₂ molecule and the central cluster of the primitive cell. The distance among both guests is 3.161 Å. It is remarkable that when CO₂ is added first, both guests are absorbed closer to the C-BF₂ linker. Finally, the energies of both geometries are similar, −608.917 eV when H₂ is added first and −608.753 eV when CO₂ is added first.

Regarding the binding displayed for these systems, AIM properties of BCP were obtained and intermolecular interactions were analyzed (Tables 1 and 6). BCP and bond paths are shown in the molecular graph (Figures S6 and S12). Change in order addition results in different behavior in guest localization and intermolecular interactions. In the case of IRMOF-C-BF₂—H₂ CO₂, molecular hydrogen is adsorbed first; it prefers to interact with the aromatic framework of coumarin (it is consistent with its behavior in IRMOF-C-BF₂—H₂, see Figure S3, where it interacts with aromatic ring). Then CO₂ is added, it is attracted to OCO framework (Figure S6), CO₂ is near H₂ and they form an interaction that agrees with hydrogen bond criteria (Table 2). In the case of IRMOF-C-BF₂—CO₂ H₂, carbon dioxide is adsorbed first; it is attracted to the OCO region and carbonyl of coumarin (this agrees with IRMOF-C-BF₂—CO₂, see Figure S2, where CO₂ interacts with carbonyl groups and OCO region). Then H₂ is added, and it interacts with the aromatic ring of coumarin and forms an O—H interaction that agrees with hydrogen bond criteria (Table 7) with CO₂ (Figure S12). The number of intermolecular interactions of guest and IRMOF-C-BF₂ is larger when CO₂ is added first (Table 6) because the dioxide interacts with OCO and carbonyl frameworks. This behavior is present in IRMOF-C-BF₂—CO₂ H₂O and IRMOF-C’-BF₂—H₂ CO₂. In IRMOF-C-BF₂—CO₂ H₂, most of intermolecular interactions are consistent with Van der Waals interactions (ρ = −10⁻³ au, ∇²ρ > 0 au and DI(X,Y) < 0.05) (Table 7) [51,52].

3.1.2. Unit Cell of IRMOF-C-BF₂

Unit cell geometries with H₂ and CO₂ as guest molecules were optimized and evaluated using BAND-ADF to confirm the changes in the properties of the primitive cell. We have special interest on the geometries adopted by the guests and the structure of the valence and conduction bands of the semiconductor cluster in the center of each node.

As can be seen in Figure 4, when the geometry optimization is performed considering the bulk structure of the unit cell, the guest molecules are located slightly more distant to the Lewis acid and base moieties of the FLP. When CO₂ is the only guest molecule (a), the distances between the CO₂ molecules and one of the linkers are: 5.692 Å from one
oxygen atom of CO$_2$ and the closest boron of the linker (BO distance), and 4.642 Å for the carbon-oxygen distance (CO) between the CO$_2$ carbon and the carbonyl oxygen. The OCO bridge and the guest are located at 4.795 Å (CO distance between the carbon of CO$_2$ and the closest oxygen of the indicated bridge). In addition, there is no change in bond angles or distances in CO$_2$. When both H$_2$ and CO$_2$ are present (b), the distances between CO$_2$ and the MOF structure are slightly increased: the CO distance between the carbon atom of CO$_2$ and the closest oxygen atom in the OCO bridges is 5.722 Å, whereas the OB distance to the closest BF$_2$ group is 6.568 Å. The guest molecules are located at 3.403 Å from each other, a value similar to the one obtained for calculations on the primitive cell. As in the case of the single guest adsorption, there are no significant changes in the bond distances and bond angles in the guest’s structures.

| Table 6. Topological parameters of the BCP of bond in adsorption configurations of guest molecules (CO$_2$ and H$_2$) on IRMOF-C-BF$_2$—CO$_2$ H$_2$. |
| --- |
| Name | Guest | Bond | Distance (Å) | $\rho$ | $\nabla^2 \rho$ | DI(X,Y) | $\Delta E(X)$ kcal/mol | $\Delta N(X)$ |
| IRMOF-C-BF$_2$—CO$_2$ H$_2$ | H$_2$ | H–C | 2.92 | 0.00624 | 0.01902 | 0.01642 | 7.96 | 0.01584 |
| | C–O | 3.16 | 0.00526 | 0.02315 | 0.00998 | 37.96 | 0.03723 |
| | O–H | 2.97 | 0.00378 | 0.01325 | 0.01322 | 1.34 | −0.00624 |
| | O–O | 3.26 | 0.00379 | 0.01606 | 0.02123 | 92.68 | −0.02581 |
| | O–O | 3.08 | 0.00768 | 0.02994 | 0.03838 | 91.29 | −0.00058 |

$^a$ In bond column X represents guest atom and Y MOF atom; $^b \Delta E(X)$ and $\Delta N(X)$ in hydrogen bond are reported for H.

| Table 7. Topological parameters of the BCP of bond in adsorption configurations of guest molecules (CO$_2$ and H$_2$) on IRMOF-C-BF$_2$—CO$_2$ H$_2$. Guest intermolecular interactions. |
| --- |
| Name | Guest | Angle | Distance (Å) | $\rho$ | $\nabla^2 \rho$ | DI(X,Y) | $\Delta E(X)$ kcal/mol | $\Delta N(X)$ | $\Delta E(Y)$ kcal/mol | $\Delta N(Y)$ |
| IRMOF-C-BF$_2$—CO$_2$ H$_2$ | HH$_2$O–OCO$_2$ | 157.24 | 3.16 | 0.00163 | 0.00708 | 0.00766 | 15.89 | −0.01790 | 91.29 | −0.00058 |

**Figure 4.** Minimum energy geometry for IRMOF-C-BF$_2$ unit cell in the presence of (a) CO$_2$ and (b) H$_2$ and CO$_2$ as guest molecules. The specified distances are shown in Angstrom (Å). Coordinates in xyz format available in the SI. According to previous theoretical works, the band gap of IRMOF-1 is decreased when halogens are added to the linkers [61] or when the linkers are longer containing more conjugated carbon atoms [62]. Consequently, the band gap of IRMOF-C-BF$_2$ is expected to decrease in a similar way, resulting in an improvement of the conduction properties of the MOF. The band properties of the isolated unit cell and the unit cell in the presence of guests are reported in Table 8. For the isolated unit cells, the band gap is considerably decreased from 3.4 eV to 0.403 eV (88.2 %); this is consistent with a previous report for linkers with more conjugated carbon atoms [62]. Such result implies a semiconductor behavior, with an increased facility for electronic conduction. The DOS of IRMOF-C-BF$_2$ shows the
contribution of the different atoms in both the valence and conduction bands (Figure S11). The major contribution to the valence band comes from the most electronegative atoms located in both the central MOF cluster and linkers (O atoms), whereas Zn and C atoms in the MOF cluster have both major contributions to energies surrounding the Fermi level (Figure S11b)). This can be explained as a result of the influence of the electronegativity and the atomic effective charge on the shielding of the valence orbitals, the latter holds for the case of the Zn atom. The C atoms in the linker c) show a similar pattern to the C atoms in the cluster, with an appreciable contribution to both the valence and conduction bands, majorly due to their electronegativity and the amount of them in the MOF’s structure. The FLP proposed behaves according to the assumption that the B atoms would act as Lewis acids (with greater contribution to the conduction band) and the O atoms as Lewis bases (with greater contribution to the valence band) d). Considering the proximity of the energy levels generated by O atoms, it seems reasonable that the C atoms of CO$_2$ associate to both the carbonyl and OCO bridge’s oxygen atoms.

Table 8. Band properties for IRMOF-C-BF$_2$ unit cell with and without the guest molecules H$_2$ and CO$_2$, and IRMOF-C'-BF$_2$ without guest molecules. The values for IRMOF-1 are cited as reference [33,34].

| Structure          | Guest Molecules | Band Gap/eV | Valence Electrons | Valence Band Index | Conduction Band Index | Bottom of Valence Band/eV | Top of Conduction Band/eV |
|--------------------|----------------|-------------|-------------------|--------------------|------------------------|---------------------------|--------------------------|
| IRMOF-1            | -              | 3.4         | -                 | -                  | -                      | -                         | -                        |
| IRMOF-C-BF$_2$     | -              | 0.403       | 548               | 274                | 275                    | -4.789                    | -4.408                   |
| IRMOF-C-BF$_2$     | CO$_2$         | 0.378       | 570               | 285                | 286                    | -4.789                    | -4.408                   |
| IRMOF-C-BF$_2$     | CO$_2$, H$_2$  | 0.714       | 572               | 286                | -                      | -5.089                    | -4.354                   |
| IRMOF-C'-BF$_2$    | -              | 2.413       | 548               | 274                | -                      | -6.476                    | -4.082                   |

Comparing the energy parameters for the conduction and valence bands (Table 8), addition of a CO$_2$ guest decreases the band gap (6.2% of decrease, from 0.403 eV to 0.378 eV) keeping the limits of both bands almost intact (-4.789 to -4.408 eV). The major changes take place when both guest molecules, H$_2$ and CO$_2$, are introduced to the MOF: an augument in the band gap (77.2% of augment, from 0.403 eV to 0.714 eV) resulting from a decrease in the bottom limit of the valence band (to -5.089 eV) and growth in the top of the conduction band (to -4.354 eV).

To analyze intermolecular interactions, QTAIM properties were calculated. However, to use less computing resources, only rigid fragments were evaluated. Molecular graphs show bond paths and BCP of intermolecular interactions in each system (Figures S13 and S14). Comparing bulks and isolated frameworks (IRMOF-C-BF$_2$ unit cell CO$_2$ with IRMOF-C-BF$_2$—CO$_2$ and IRMOF-C-BF$_2$ unit cell CO$_2$ H$_2$ with IRMOF-C-BF$_2$—H$_2$ CO$_2$), it was found that some interactions changed, then some BCP properties. One clear example of this is observed in O—O interaction with CO$_2$ and carbonyl oxygen (see Tables 1 and 9) where a decrease in $\rho$, $\nabla^2 \rho$ and DI(X,Y) is observed in bulk structure when is compared with the isolated framework, which means less bonding strength. This behavior is consistent with an increase in distance [44]. Additionally, in the presence of H$_2$ and CO$_2$, there are more intermolecular interactions in bulk system than in isolated framework (Tables 1 and 9). These new intermolecular interactions come from H$_2$ and bulk atoms, with OCO region, coumarin carbon (H—$\pi$), and carbonyl region. Moreover, one of its two H—O interactions (Table 9 and Figure S14) agrees with hydrogen bond criteria [57–60]. On the other hand, CO$_2$ has two Van der Waals interactions [51,52].

Guest intermolecular interactions were obtained using the AIMAll program. Intermolecular interactions were detected between H$_2$ and CO$_2$ (Figure S14). Such interaction is formed between H—O; however, it does not agree with hydrogen bond criteria, mainly because of its angle (89.15°) (Table 10, it corresponds to a Van der Waals-like interaction [51,52]. This assumption is supported by topological properties. For example, if we compare the interactions with those for the isolated unit cell, Table 10 vs. Table 2, it is evident that binding properties of H—O such as electron density, Laplacian, and delocalization index are larger in magnitude.
Table 9. Topological parameters of the BCP of bond in adsorption configurations of guest molecules (CO$_2$ and H$_2$) on fragments of unit cells.

| Structure                  | Guest | Bond  | Distance (Å) | $\rho$  | $\nabla^2 \rho$ | DI(X,Y) | $\Delta E(X)$ kcal/mol | $\Delta N(X)$ kcal/mol | $\Delta N(Y)$ kcal/mol |
|----------------------------|-------|-------|--------------|--------|--------------|---------|--------------------------|--------------------------|------------------------|
| IRMOF-C-BF2 unit cell CO$_2$ | CO$_2$ | O−C   | 3.62         | 0.00282 | 0.01015      | 0.01167 | 98.13                    | −0.02245                 |                        |
| IRMOF-C-BF2 unit cell CO$_2$ | CO$_2$ | O−O   | 3.67         | 0.00118 | 0.00666      | 0.00844 | 101.69                   | −0.04197                 |                        |
| IRMOF-C-BF2 unit cell CO$_2$ | H$_2$  | H−O   | 2.93         | 0.00298 | 0.01044      | 0.01512 | 18.43 b                  | −0.02876 b               | 0.02471 b               |

*a In bond column X represents guest atom and Y MOF atom; b $\Delta E(X)$ and $\Delta N(X)$ in hydrogen bond are reported for H...”

Table 10. Topological parameters of the BCP of bond in adsorption configurations of guest molecules (CO$_2$, H$_2$O, and H$_2$) on unit cell IRMOF-C-BF$_2$. Guest intermolecular interactions.

| Name                      | Guest | Angle | Distance (Å) | $\rho$  | $\nabla^2 \rho$ | DI(X,Y) | $\Delta E(X)$ kcal/mol | $\Delta N(X)$ kcal/mol | $\Delta N(Y)$ kcal/mol |
|---------------------------|-------|-------|--------------|--------|--------------|---------|--------------------------|--------------------------|------------------------|
| IRMOF-C-BF2 unit cell CO$_2$ | H$_2$O-OCO$_2$ | 89.14 | 3.40         | 0.00171 | 0.00742      | 0.00738 | 18.43                    | −0.02876                 | 76.99                  | −0.02534               |

3.2. IRMOF-C’-BF$_2$

3.2.1. Primitive Cells of IRMOF-C-(2)-BF$_2$ and IRMOF-C’-BF$_2$

Based on the previous observations that both H$_2$ and CO$_2$ adsorb preferentially close to the central cluster of IRMOF-C-BF$_2$, a new linker was designed. Figure S1 shows that CO$_2$ adsorbs near one of the OCO bridges of IRMOF-C-BF$_2$. With this regard, a BF$_2$ group added on carbon C7 of the coumarin moieties will form a new FLP (formed by one oxygen atom of one OCO bridge and the boron on the coumarin moiety). Such FLP could be more suitable for guest adsorption over the pair formed by the carbonylic oxygen and the BF$_2$ group C3 carbon of the linker.

To prove this hypothesis, a MOF structure with BF$_2$ groups on carbons C3 and C7 is modeled (IRMOF-C-(2)-BF$_2$). Geometry optimizations for H$_2$ and CO$_2$ adsorbed in IRMOF-C-(2)-BF$_2$ were carried out. Figure 5b) shows the results of the competition for guest molecule’s absorption in the MOF structure. The BF$_2$ group placed closer to the OCO bridges of the central cluster is preferred over the one in the $\alpha$-position to the carbonyl groups. The OB distance between CO$_2$ and the closest B (BF$_2$ group) is 4.462 Å. The carbon of adsorbed CO$_2$ is located at 3.793 Å of one of the oxygen atoms of the OCO bridge connected to the same linker as BF$_2$, which the molecule is interacting with. This indicates that CO$_2$ is being absorbed by the FLP built to include the OCO bridge. In addition, the guests are at 2.807 Å from each other (measuring the distance between the closest atoms of each guest, CO$_2$ oxygen and H$_2$ hydrogen); notice that the oxygen atom of CO$_2$ that is located closest to H$_2$ is not involved with the new FLP mentioned above. The hydrogen in H$_2$ that is farthest of CO$_2$ is observed almost in the middle of both oxygen atoms of the ester of another linker (3.363 Å from the O in the ring and 4.203 Å of the carbonylic oxygen).

An important question to be solved is: is the adsorption near OCO bridges improved by the BF$_2$ groups not directly involved in it? To give an answer to this question, the MOF structure IRMOF-C’-BF$_2$ was built (Figure 5c), maintaining the BF$_2$ groups on C7 of the coumarin moieties but eliminating the other ones. Geometry optimizations for the IRMOF-C’-BF$_2$ were performed, maintaining the addition order of the guest molecules (H$_2$ followed by CO$_2$). Figure 5c shows the guests as close to each other as when adsorbed on IRMOF-C-BF$_2$. The distances among them are 3.193 Å for the HO interaction (measured between H$_2$ and the closest oxygen of CO$_2$) and 3.364 Å for the HC interaction (measured between H$_2$ and the carbon atom of CO$_2$). These values are smaller than the ones observed for IRMOF-C-BF$_2$ (a), 4.971 Å for the HO distance) and larger than those observed for IRMOF-C-(2)-BF$_2$ (b), 2.807 Å for the HO distance). Nevertheless, H$_2$ is adsorbed in such...
place in IRMOF-C’-BF\textsubscript{2} not just because of its proximity to CO\textsubscript{2}, but in response to the presence of the carbonyl oxygen atom in the closest linker (displaying a HO distance of 2.709 Å). Moreover, the proximity of H\textsubscript{2} to atoms other than those in CO\textsubscript{2} is not as remarkable as for IRMOF-C-(2)-BF\textsubscript{2}. In addition, there is a distance of 4.241 Å between an oxygen atom of CO\textsubscript{2} and the carbon atom of the closest OCO bridge. It is noticeable that when a BF\textsubscript{2} group is placed near the OCO bridges (b,c)) the guest molecules are adsorbed in the middle of two linkers.

![Figure 5](image-url)

**Figure 5.** Comparison between the optimized geometries for the calculation of the excited states of the primitive cells (a) IRMOF-C-BF\textsubscript{2}, (b) IRMOF-C-(2)-BF\textsubscript{2} y (c) IRMOF-C’-BF\textsubscript{2}, in the presence of H\textsubscript{2} and CO\textsubscript{2}. The distances specified are shown in Angstroms (Å). Coordinates in xyz format available in the the Supplementary Materials (Table S2).

Until this point, the proximity of the guests-MOF is comparable for both IRMOF-C-(2)-BF\textsubscript{2} and IRMOF-C’-BF\textsubscript{2}. In addition, their absorption is apparently better (at closer proximity with the MOF structure) than in IRMOF-C-BF\textsubscript{2}. To discern the most suitable MOF for H\textsubscript{2} and CO\textsubscript{2} absorption, the excited states that could lead to electronic vertical excitations were obtained (Table 11). For the brightest transition, the probability estimated for the three MOF has the same magnitude order (10\textsuperscript{−3}), although the probability calculated for IRMOF-C-BF\textsubscript{2} is slightly greater than the one for IRMOF-C-(2)-BF\textsubscript{2} and IRMOF-C’-BF\textsubscript{2} (2.5 \times 10\textsuperscript{−3} and 6.3 \times 10\textsuperscript{−3}, respectively). The energies of the optimized transitions show an interesting behavior (Table 11): for IRMOF-C-(2)-BF\textsubscript{2}, the energy of the brightest transition is decreased (to 1.96 eV, 27.4\% of decrement). In contrast, the energy of such transition in IRMOF-C’-BF\textsubscript{2} is augmented (to 3.0 eV, 11.1\% of increment). This implies that the gap between the ground and the excited state is bigger when there is just one B atom per linker than when there is more than one. This is caused by an augment of the ground state’s energy in the case of two BF\textsubscript{2} groups on the coumarin moiety. Furthermore, the electrons on the HOMO are more stabilized if the boron atoms are located closer to the central cluster of the MOF (Table 8). The energies of the bottom of the valence band are – 5.089 eV for IRMOF-C-BF\textsubscript{2} (B on C3) and – 6.476 eV for IRMOF-C’-BF\textsubscript{2} (B on C7). This observation could be explained by the increased contribution of fluorine atoms to the valence band when they are closer to the metallic cluster (Figures S11 and S15). If the valence and conduction bands are more separated in IRMOF-C’-BF\textsubscript{2}, it is evident that the energy of its brightest transition will be larger.

Intermolecular interactions of both systems (IRMOF-C’-BF\textsubscript{2} and IRMOF-C-(2)-BF\textsubscript{2}) were analyzed; AIM properties of BCP were obtained (Table 12). BCP and bond paths are showed in molecular graphs (Figures S16 and S17). Energy contribution, E(X), points out to destabilization contribution from guest molecules, especially in CO\textsubscript{2} molecule. The delocalization index agrees with noncovalent interactions (<0.05) [53,54], Laplacian, and electron density agree with Van der Waals interactions [51,52].
Table 11. Energies and oscillator strengths of the brightest transitions of the optimized excited states for the absorption of CO$_2$ and H$_2$, in the cited order, into the primitive cells IRMOF-C-BF$_2$, IRMOF-C-(2)-BF$_2$ and IRMOF-C'-BF$_2$.

| Structure Name    | Energy/eV | $f \cdot 10^3$ |
|-------------------|-----------|----------------|
| IRMOF-C-BF$_2$    | 2.7       | 8.4            |
| IRMOF-C-(2)-BF$_2$| 1.96      | 2.5            |
| IRMOF-C'-BF$_2$   | 3.0       | 6.3            |

Table 12. Topological parameters of the BCP of bond in adsorption configurations of guest molecules (CO$_2$ and H$_2$) on IRMOF-C-(2)-BF$_2$ and IRMOF-C'-BF$_2$.

| Structure          | Guest | Bond $^a$ X—Y | Distance (Å) | $\rho$ | $\nabla^2 \rho$ | DI(X,Y) | $\Delta E(X)$ kcal/mol | $\Delta N(X)$ |
|--------------------|-------|---------------|--------------|--------|----------------|---------|------------------------|--------------|
| IRMOF-C-(2)-BF$_2$ | H$_2$ | H—C          | 3.07         | 0.00529 | 0.01608        | 0.01332 | 13.98                  | −0.01306     |
|                    | O—C  | 3.36          | 0.00443      | 0.01573 | 0.01788        | 87.19   | −0.01574               |              |
|                    | O—C  | 3.18          | 0.00481      | 0.02022 | 0.01158        | 84.24   | −0.00994               |              |
|                    | C—O  | 3.01          | 0.00703      | 0.02939 | 0.01498        | 34.01   | 0.03829                |              |
| IRMOF-C'-BF$_2$    | H$_2$ | H—O          | 2.71         | 0.00524 | 0.01680        | 0.02629 | 19.67 $^b$             | −0.03312 $^b$|
|                    | O—C  | 3.12          | 0.00610      | 0.02394 | 0.02616        | 86.48   | −0.01103               |              |

$^a$ In bond column X represents guest atom and Y MOF atom; $^b$ $\Delta E(X)$ and $\Delta N(X)$ in hydrogen bond are reported for H.

Absorbed CO$_2$ shows interactions with MOF’s oxygens, MOF’s carbon, and even with H$_2$ (Figures S16 and S17). BCP pointed out the interaction between CO$_2$ and H$_2$, in agreement with hydrogen bond criteria in IRMOF-C'-BF$_2$ [57–60]. CO$_2$ is attracted to the carbonyl domain and can interact with coumarin oxygens in IRMOF-C'-BF$_2$, but this attraction is weaker in IRMOF-C-(2)-BF$_2$. Additionally, parameters are similar to those observed in CO$_2$ in a previous system (Table 1, IRMOF-C-BF$_2$—CO$_2$H$_2$O), but the number of interactions is fewer, because in IRMOF-C'-BF$_2$—CO$_2$H$_2$O carbon dioxide access more easily to OCO and coumarin frameworks than CO$_2$ in IRMOF-C'-BF$_2$ and IRMOF-C-(2)-BF$_2$. Laplacian isosurface shows electron density concentration in OCO and coumarin oxygens, where guest molecules are attracted.

As CO$_2$, molecular hydrogen is attracted to the OCO framework too, it shows interactions with MOF’s carbon and one hydrogen bond interaction with coumarin oxygen in IRMOF-C'-BF$_2$. Such hydrogen bond fully agrees with the common hydrogen bond criteria (Table 12) [57–60]. Furthermore, there are H—π interactions between H$_2$ and coumarin in both systems.

Guest intermolecular interactions were analyzed using AIM descriptors. Intermolecular interactions were detected between H$_2$ and CO$_2$, see BCP in Figures S16 and S17. There are O—H interactions; however, one of these interactions in IRMOF-C'-BF$_2$ does not agree with hydrogen bond criteria [57–60] because of its angle (112.87°) (Table 13).

Table 13. Topological parameters of the BCP of bond in adsorption configurations of guest molecules (CO$_2$ and H$_2$) on IRMOF-C-(2)-BF$_2$ and IRMOF-C'-BF$_2$. Guest intermolecular interactions.

| Name               | Guest         | Angle   | Distance (Å) | $\rho$     | $\nabla^2 \rho$ | DI(X,Y) | $\Delta E(X)$ kcal/mol | $\Delta N(X)$ | $\Delta E(Y)$ kcal/mol | $\Delta N(Y)$ |
|--------------------|---------------|---------|--------------|------------|----------------|---------|------------------------|---------------|------------------------|---------------|
| IRMOF-C-(2)-BF$_2$ | H/H2—O/OCO2  | 141.45  | 2.81         | 0.00429    | 0.01474       | 0.02012 | 13.98                  | −0.01306      | 84.24                  | −0.00994      |
| IRMOF-C'-BF$_2$   | H/H2—O/OCO2  | 112.87  | 3.12         | 0.00270    | 0.01030       | 0.01307 | 5.33                   | 0.02927       | 86.48                  | −0.01103      |

To compare the differences in the optical properties of the purposed MOF (IRMOF-C'-BF$_2$) and its isolated linker (C'-BF$_2$), a calculation of the excited states in UV and Visible regions was performed, using optimized geometries (Figure S8b). Once again, it is clear
the isolated linker structure (C'-BF$_2$) shows brighter transitions (Table 3). Comparing the linker’s transitions (C'-BF$_2$ and C-BF$_2$), their energies are 5.4 eV for C'-BF$_2$ with an $f$ value of 0.305, and 4.0 eV for C-BF$_2$ with an $f$ value of 0.210. Although the energy is increased when changing the BF$_2$ moiety from C3 to C7, it is weighted by a transition 1.4 times brighter. The different MOF structures are similar in energy (2.7 eV for IRMOF-C-BF$_2$ and 3.0 eV for IRMOF-C'-BF$_2$) and similar in $f$ values ($8.4 \times 10^{-3}$ for IRMOF-C-BF$_2$ and $6.3 \times 10^{-3}$ for IRMOF-C'-BF$_2$).

3.2.2. Unit Cells of IRMOF-C'-BF$_2$

Regarding the bulk properties, the band gap of the unit cell of IRMOF-C'-BF$_2$ is decreased with respect to IRMOF-1 [30,32] (Table 8), such behavior is similar to the displayed by IRMOF-C-BF$_2$. The calculated value of 2.413 eV implies a decrease of 29.0% with respect to IRMOF-1, which is much smaller than the one obtained for IRMOF-C-BF$_2$ (IRMOF-C-BF$_2$ displays 88.1% of decrement and a band gap of 0.403 eV). The energy of the bottom of the valence band and the top of the conduction band are 6.476 and 4.082 eV, respectively. Although the structure of the linkers in both proposed MOFs is similar, the placement of the boron atom closer to the OCO bridges and far from the carbonyl moiety in the coumarin ring causes an increase in the band gap.

The information of the contributions of the different atoms that compose the MOF in its valence and conduction bands are placed in the DOS (Figure S15). The major contribution to the valence band comes from the most electronegative atoms both in the central cluster and linkers (oxygen atoms and fluorine atoms), whereas zinc atoms in the cluster have important contributions to the states surrounding the Fermi level (Figure S15b)); this can be understood as the influence of the electronegativity for non-metal atoms, and in the case of the zinc atom by the effect of the atomic effective charge on the shielding of the valence orbitals. The carbon atoms in the central cluster exhibit a contribution oriented to the conduction band (b), nevertheless, there is an appreciable contribution of such carbon atoms to the valence band. The carbon atoms in the linker (c) follow a different pattern, they have an appreciable contribution to both the valence and conduction bands, majorly due to their electronegativity and their location on the electron-rich coumarin rings. The FLP behaves with the boron atoms as Lewis acids; they have a greater contribution to the conduction band. In addition, the oxygen atoms of the OCO bridges play as Lewis bases; they have a greater contribution to the valence band (d). Considering the proximity of the energy levels generated by oxygen atoms, it seems reasonable that the C atoms of CO$_2$ prefer the association with the OCO bridge’s oxygen atoms. In addition, oxygen atoms of CO$_2$ prefer to interact with carbon atoms from the OCO bridges and with the boron atoms of BF$_2$, both with major contributions to the conduction band.

DOS of IRMOF-C-BF$_2$ (Figure S11) and IRMOF-C'-BF$_2$ (Figure S15), have more populated valence bands; this difference in population is bigger for IRMOF-C'-BF$_2$. Fluorine atoms of the linkers and carbon atoms of the OCO bridges show an appreciable difference when present in the two MOFs. Fluorine atoms contribute to both valence and conduction bands over a wide range of energies in IRMOF-C-BF$_2$ but show a localized role in a few states of remarkable population density in IRMOF-C'-BF$_2$. This might be related to a redistribution of the fluorine electron density when these atoms are located closer to the central cluster. Carbon atoms of the OCO bridges display an active role on the conduction band of IRMOF-C'-BF$_2$, this is not observed in IRMOF-C-BF$_2$. It is possible that the proximity of the fluorine atoms (electron-rich entities) of the linkers increase the energy of frontier orbitals due to electronic repulsion.

3.3. IRMOF-C-CH$_2$BF$_2$

Primitive Cells of IRMOF-C-CH$_2$BF$_2$

IRMOF-C-CH$_2$BF$_2$ was purposed as a MOF whose organic linker could be more suitable to be synthesized than the displayed by IRMOF-C-BF$_2$. The optimized geometry when H$_2$ and CO$_2$ are added is shown in Figure 6. The proximity of the guest molecules to
the MOF is comparable to that obtained for a similar treatment with the MOF purposed herein (IRMOF-C-BF$_2$, Figure S1; IRMOF-C’-BF$_2$, Figure 5c)). The proximity of both guests is of 3.317 Å (OH closest distance); each guest adsorption is influenced by two groups on the MOF. In addition, the hydrogen atom of H$_2$, farthest of the CO$_2$ molecule, is adsorbed close to two OCO bridges; the OH distances among them are 4.381 Å and 4.791 Å. Moreover, CO$_2$ is located near a FLP in one of the linkers, its oxygen atom that is not in proximity of H$_2$ is at 4.493 Å of boron. In addition, the C of CO$_2$ is located at 3.332 Å of the carbonyl oxygen of the coumarin moiety.

![Figure 6. Optimized geometry for the absorption of H$_2$ and CO$_2$, in the primitive cell IRMOF-C-CH$_2$BF$_2$. The cited distances and bond angles are shown in Angstroms (Å) and degrees, respectively. Coordinates in xyz format available in the the Supplementary Materials).](image)

BCP’s in IRMOF-C-CH$_2$BF$_2$ were calculated to analyze intermolecular interactions with guest molecules (CO$_2$ and H$_2$), AIM properties of BCP were obtained (Table 14) and in the following lines, interactions are analyzed.

Table 14. Topological parameters of the BCP of bond in adsorption configurations of guest molecules (CO$_2$ and H$_2$) on IRMOF-C-CH$_2$BF$_2$.

| Structure     | Guest | Bond $^a$ X—Y | Distance (Å) | $\rho$  | $\nabla^2 \rho$ | DI(X,Y) | $\Delta E(X)$ kcal/mol | $\Delta N(X)$ |
|---------------|-------|---------------|--------------|---------|----------------|---------|------------------------|---------------|
| IRMOF-C-CH$_2$BF$_2$ | H$_2$ | H—O          | 3.13         | 0.00216 | 0.00855        | 0.01077 | 13.40 $^b$             | -0.00557 $^b$ |
|               | H$_2$ | H—O          | 2.92         | 0.00432 | 0.01430        | 0.01754 | 11.98                  | -0.00067      |
|               | CO$_2$| O—O          | 3.47         | 0.00128 | 0.00549        | 0.00566 | 11.98                  | -0.00067      |
| H$_2$         | CO$_2$| O—C          | 3.19         | 0.00516 | 0.01941        | 0.02875 | 92.17                  | -0.01350      |
|               | CO$_2$| O—C          | 3.43         | 0.00477 | 0.01459        | 0.01971 | 91.03                  | -0.01823      |

$^a$ In bond column X represents guest atom and Y MOF atom; $^b$ $\Delta E(X)$ and $\Delta N(X)$ in hydrogen bond are reported for H.
As was observed in a similar system (i.e., IRMOF-C’-BF$_2$—H$_2$ CO$_2$), in IRMOF-C-CH$_2$BF$_2$ CO$_2$ and H$_2$ are attracted to OCO domain (Figure S18). Interaction properties (Table 14) agree with no covalent interactions [51,52]. Molecular graph (Figure S18) shows the BCP’s and bond paths for some intermolecular interactions. CO$_2$ interacts with coumarin oxygen and coumarin carbon, but with H$_2$. On the other hand, H$_2$ has direct contact with oxygens in OCO and coumarin oxygen. This last interaction agrees with hydrogen bond criteria [57–60].

Additionally, an intermolecular interaction between H$_2$ and CO$_2$ was found, and its topological properties are shown in Table 15. There is an O—H interaction, it does not agree with hydrogen bond criteria because its angle (90.48°), but its properties are consistent with noncovalent interactions [51,52].

Table 15. Topological parameters of the BCP of bond in adsorption configurations of guest molecules (CO$_2$ and H$_2$) on IRMOF-C-CH$_2$BF$_2$—H$_2$ CO$_2$. Guest intermolecular interactions.

| Name               | Guest     | Angle  | Distance (Å) | ρ   | ϕ$^2$ρ | DΩ(X,Y) | ΔE(X) kcal/mol | ΔN(X) | ΔE(Y) kcal/mol | ΔN(Y) |
|--------------------|-----------|--------|--------------|-----|--------|---------|----------------|-------|----------------|-------|
| IRMOF-C-CH$_2$ BF$_2$ H$_2$ CO$_2$ | HH$_2$—OCO$_2$ | 90.48  | 3.32         | 0.00204 | 0.00855 | 0.00873 | 13.40           | −0.00557 | 91.03           | −0.01823 |

The excited states of IRMOF-C-CH$_2$BF$_2$ in the presence of H$_2$ and CO$_2$ as guest molecules were calculated (Table 3, Figure S4c)). In comparison to the previous linkers, the brighter excited state of C-CH$_2$BF$_2$ has a greater f value (0.331); its energy of 4.0 eV is similar to that of C-BF$_2$, which implies that the inclusion of an electron deficient substituent, regardless of its nature (BF$_2$ or CH$_2$BF$_2$), leads to a brighter state at 4.0 eV. It is remarkable, however, that the addition of a CH$_2$ group increases the probability of the mentioned transition. With this regard, similar characteristics of the brighter states of C-CH$_2$BF$_2$ and C’-BF$_2$ are observed, although it is clear that C’-BF$_2$ requires less energy for the mentioned transition. The IRMOF-C-CH$_2$BF$_2$ has an important improvement in energy, comparing the energy needed for the transition, it is just 0.59 times the value reported for IRMOF-1. Such situation is not possible with IRMOF-C-BF$_2$ or IRMOF-C’-BF$_2$ (Table 3). In addition, the probability to reach the brighter transition is 8.8 times greater than the reported value for IRMOF-1, belonging to the same magnitude to the MOF purposed in this paper.

3.4. Further Topological Analysis of All Possible Intermolecular Hydrogen Bond

In the framework of QTAIM a decrement of the kinetic energy density (G) at BCP is related to a depletion of the electron density, because this situation implies less repulsion among electrons. Moreover, this behavior is observed at the hydrogen bond BCP when the hydrogen bond distance is increased, d(H—O) [62–64]. In addition, the positive curvature of ρ at the BCP, $\lambda^3_{CP}$, shows a good correlation with d(H—O), at variance with $\rho$ and $\nabla^2\rho$ displaying large data dispersion. With this regard, Espinosa and co-workers proposed a formula to calculate G at the bond critical point $G_{CP}$ using $\lambda^3_{CP}$ as a variable in a linear fitting, $G_{CP} = 15.3(1) \lambda^3_{CP}$. [63] Then, the strength of a hydrogen bond is unambiguously characterized by $G_{CP}$, the stronger the hydrogen bond the stronger repulsive among electron at BCP, increasing $\lambda^3_{CP}$ and therefore $G_{CP}$. To clarify hydrogen bond interactions between MOFs and molecular guest, additional kinetic energy ($G_{CP}$) and positive curvature ($\lambda^3_{CP}$) analyses were performed (Table S1), all possible intermolecular hydrogen bonds were considered. Graphical plot of $\lambda^3_{CP}$ vs. d(H—O) exhibits a similar behavior reported by Espinosa [63,64], (see Figure S19). Furthermore, G vs. d(H—O), Figure 7, displays the expected behavior reported by Espinosa. In base of $G_{CP}$ values the complete set of hydrogen bonds observed for guest molecules adsorbed in our modeled MOFs are consistent with a closed-shell interaction. Moreover, three strong hydrogen bonds are displayed related with water adsorption, which $\lambda^3$ values (6.6, 4.9, and 12.2) highlight over the rest.
Figure 7. Behavior of $G^{\text{CP}}$ versus $d(H-O)$. Black dots are for hydrogen bonds between MOF’s and guest molecules. Triangles are for hydrogen bonds between guest molecules.

4. Conclusions

We modeled four MOFs (IRMOF-C-BF$_2$, IRMOF-C-(2)-BF$_2$, IRMOF-C’-BF$_2$ and IRMOF-C-CH$_2$BF$_2$) based on IRMOF-1 and a linker based on Frustrated Lewis Pairs and coumarin moieties to confer photocatalytic properties to the MOFs. The four different linkers used: (a) a BF$_2$ attached to a coumarin moiety at position 3, (b) two BF$_2$ attached in the coumarin moiety at positions 3 and 7 C-(2)-BF$_2$, (c) one BF$_2$ attached to the coumarin moiety at position 7, and (d) one CH$_2$BF$_2$ attached to the coumarin moiety at 3 position. We observe that the adsorption of H$_2$, CO$_2$, and H$_2$O is possible and that it is probable that the systems will display CO$_2$ photocatalytic properties.

In addition, we find that the hydrogen molecule is susceptible to interact with the basic part of the FLP (O), whereas carbon dioxide prefers the acidic counterpart (B). Moreover, for the MOFs primitive cells modeled, adsorbed H$_2$ is far from the MOF’s structure and CO$_2$ is adsorbed near one of the OCO bridges instead of the nearest linker. Moreover, BF$_2$ attached to the coumarin reduces the vertical transition probabilities of such chromophore. Isolated Coumarin-BF$_2$ moieties display larger optical properties than when being linkers in a MOF. Nevertheless, C-BF$_2$-like linkers improve optical properties of IRMOF-1 by itself, thus an opportunity in this direction is evinced. The characterization of the binding properties by means of AIM shows that the adsorption of the guest molecules is the consequence of the formation of relevant binding interactions, as hydrogen bonds, Van der Waals forces, and electron localization and delocalization interactions.

Structure and adsorption properties of synthesized MOFs could be different to the expected ones, for instance, displaying lower adsorption efficiency to the calculated [65]. For this reason, an important question to be solved is: have this Coumarin-BF$_2$ linkers produce MOF defects that negatively affect the stability, adsorption, and catalytic properties, beyond the predictive computational capability? Whit this regard, we have an encouraging clue: similar linkers display common MOFs structures as was reported by Hendon et al. [66]. In addition, the same study presents modeling results in agreement with experimental structures of synthesized MOFs. Moreover, the characterization of changes of electron density during guest (CO$_2$, H$_2$, H$_2$O) adsorption is relevant to the understanding of the interactions responsible for the stability of guest-MOF complexes. Whit this regard, G(CP) and $\lambda_3$ results are used to classify the strength of the displayed hydrogen bonds of adsorbed molecules, finding 3 relevant hydrogen bond interactions related with water adsorption. Currently, we focused on the analysis of behavior of $\rho(r)$ positive curvature ($\lambda_3$) and
G(GP) at the bond critical point versus the topological distance, [63,64,66] along the guest adsorption reaction path.

The relevance of our present work relies on the plausibility of the improvement of photocatalytic properties of IRMOF using Coumarin-BF₂ linkers. Nevertheless, future computational and experimental work is needed to study the changes of the interactions along the adsorption process and to test the photocatalytic efficiency of such new MOFs.

Supplementary Materials: The following are available online. Figure S1. Optimized geometries for the calculation of the brightest excited states of the primitive cell (IRMOF-C-BF₂) and the linker (C-BF₂) in the presence of H₂ and CO₂. Figure S2. (a) Electron density topologies for IRMOF-C-BF₂—CO₂. Figure S3. (a) Electron density topologies for IRMOF-C-BF₂—H₂. Figure S4. (a) Electron density topologies for IRMOF-C-BF₂—H₂O. Figure S5. (a) Electron density topologies for IRMOF-C-BF₂—CO₂ H₂O. Figure S6. (a) Electron density topologies for IRMOF-C-BF₂—H₂ CO₂. Figure S7. (a) Electron density topologies for IRMOF-C-BF₂—H₂ CO₂ H₂O. Figure S8. Calculated UV and Visible spectra of MOF and its parent linkers in the presence of H₂ and CO₂ as guest molecules. Figure S9. Energetic maximums obtained during excited states optimizations for IRMOF-C-BF₂—H₂—CO₂. Figure S10. Energetic maximums obtained during excited states optimizations for IRMOF-C-BF₂—CO₂ H₂O. Figure S11. Density of States of IRMOF-C-BF₂, as a function of energy (eV). Figure S12. (a) Electron density topologies for IRMOF-C-BF₂—CO₂ H₂. Figure S13. (a) Electron density topologies for IRMOF-C-BF₂ unit cell CO₂. Figure S14. (a) Electron density topologies for IRMOF-C-BF₂ unit cell CO₂ and H₂. Figure S15. Density of States of IRMOF-C-BF₂, as a function of energy (eV). Figure S16. (a) Electron density topologies for IRMOF-C-(2)-BF₂ unit cell CO₂ and H₂. Figure S17. (a) Electron density topologies for IRMOF-C'-BF₂—H₂ CO₂. Figure S18. (a) Electron density topologies for IRMOF-C-CH₃BF₂—CO₂ H₂. Figure S19. Behavior of λ₃CP versus d(H—O). Table S1. Analysis of Quantum Theory Atoms in Molecules for hydrogen bonds. Table S2. xyz-coordinates of the geometries for the optimized molecules.

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