



Hybrid compounds based on fullerene and polycyclic aromatic hydrocarbons with absorption in the near infrared region



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ABSTRACT

This manuscript reports a density functional theory (DFT) study of a series of hybrid compounds consisting of a polycyclic aromatic hydrocarbon moiety (PAH) and a buckminsterfullerene molecule. These moieties are linked through a metal atom, which allows charge transfer between both units. The PAHs employed in this work are perylene and coronene and the metal atom is iron, conforming different structural geometries. A time-dependent approach (TD-DFT) was used to get an accurate description of the photoabsorption of these hybrid compounds. The studied assemblies exhibit absorption in the infrared region.

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1. Introduction

Dye sensitized solar cells (DSSCs) are next generation solar cells, based on the use of nanostructured materials and molecular dyes, which absorb mainly in the visible region of the electromagnetic spectrum. The physical principle is the photoabsorption, consisting in photoelectron transitions directly associated to the choice of the molecular dye and the nanostructured semiconductor [1]. In general, the conversion efficiency of the DSSC are lower in comparison to other multispectrum alternatives [2]. For this reason it is really interesting to work in new molecular dyes, particularly those absorbing in the infrared region, since this would allow work to a wider range in the electromagnetic spectrum. This could be achieved through the preparation of new molecular assemblies, where molecular blocks could act as electron-donors and electron-acceptors, generating a complex set of electronic states in the HOMO–LUMO region with low energy photoelectronic transitions. This strategy has been followed for the development of organic solar cells where charge donor polymers have been used to build bulk hetero-junction devices [3]. The advantage of this approach is the capability to harvest photons in the red and even in the near infrared region of the solar spectrum.

Using a molecule as electron-donor we found more flexibility in the way to prepare these acceptor–donor systems, leading to a

possible incorporation in solar cells of different kinds. Among some candidates to be used as electron acceptors, the carbon cluster molecule C_{60} arises as an excellent option due to the empty t_{1u} electronic state [4–6].

There are many molecules that could be chosen as molecular electron donor and there are different strategies to combine it with electron acceptors. Following this procedure, some chemically modified fullerene derivatives have been studied as potential candidates as photosensitizers [7]. Wakahara et al. [8] prepared supramolecular nanoarchitectures consisting of fullerene/ferrocene nanosheets which showed interesting optical properties. This system exhibits a strong charge transfer optical transition in the near infrared region ($\lambda = 782$ nm), demonstrating the strong donor–acceptor interaction that can be achieved in such nanoarchitectures. It is important to mention that a disadvantage of this system is the thermally induced release of ferrocene, which leads to face centered cubic polymorph of C_{60} [8].

Mixed inorganic/organic assemblies as $BzTMC_{60}$ (Bz: benzene and TM: transition metal atom) were successfully synthesized through laser vaporization method [9]. But in this case the synthesis generates charged compounds, with many possibilities for generation of cationic species. This is not the case of our work, but constitutes a first approximation which shows a real possibility of preparing close related mixed inorganic/organic hybrid compounds. Zhu et al. [10] performed a comprehensive *ab initio* study on similar neutral mixed inorganic/organic assemblies, where a transition metal atom bridges one buckminsterfullerene and one benzene molecules, evaluating different connection geometries. They compared structures where the metal atom face

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the hexagonal (H) and pentagonal (P) rings, a short (S) and a long (L) C–C bond, and a single carbon atom (T) – in an apical geometry – of the buckminsterfullerene. Assemblies involving C_{60} and metal atoms have been studied in the past [11–15], and BzTMC $_{60}$ could inspire the design of new hybrid series, where benzene could be replaced by polycyclic molecules such as polycyclic aromatic hydrocarbons (PAHs).

We selected symmetric PAH, where the electron charge defect could be distributed along the geometrical plane of the molecules. These compounds can participate in charge transfer processes, with the possibility of losing charge delocalization loss in the planar π system. We selected perylene ($C_{20}H_{12}$ -D $_{2h}$) and coronene ($C_{24}H_{12}$ -D $_{6h}$) as PAH molecules due to their small size and different geometrical symmetries. In order to complete the system, and inspired in other metallocene compounds, a metal atom was chosen to bridge PAH and C_{60} allowing the charge transfer between them.

In this manuscript we present computational simulations on hybrid compounds with iron acting as a between ferrocene-like moieties and buckminsterfullerene. We focus in their geometrical structure and related optical properties, in order to evaluate its potential use as photosensitizers, particularly in the IR region of the electromagnetic spectrum.

2. Methodology

2.1. Computational method

Density functional theory (DFT) [16,17] simulations using Gaussian 09 [18] were performed using the hybrid exchange–correlation functional B3LYP [19–21]; the LAN2LTZ+/6-311+G(d,p) basis set was selected for Fe [22] and the 6-311G* for the other atoms. The tolerance in total energy was selected to 1×10^{-6} a.u. for both singlet and triplet multiplicities, applying a basis set superposition error (BSSE) correction according to the counterpoise correction [23,24]. No restrictions were applied to the point group symmetry of the molecules, allowing full degree of freedom during the geometrical optimization selecting a force tolerance of 3×10^{-4} a.u. Four different initial structures were considered according to the position of the Fe atom. This atom was positioned above the centre of the hexagonal face (H, η^6), above the pentagonal face (P, η^5), bridging the C–C atoms belonging to two hexagons (S, η^2) and bridging the C–C belonging to hexagon–pentagon (L, η^2). This procedure was repeated for the case of Fe placed at the hollow position of inner (case I) and at the edged located hexagons (case II) of the PAH. Vibrational analysis were performed in order to confirm that stable states of molecular systems correspond to global and local minima on their potential energy surfaces.

The relative stabilities of all the clusters were determined by the corresponding formation energies (E_{form}) according to:

$$E_{\text{form}}(\text{eV}) = E_{\text{Total}} - (E_{C_{60}} + E_{\text{Fe}} + E_{\text{PAH}})$$

where $E(C_{60})$, $E(\text{Fe})$ and $E(\text{PAH})$ correspond to ground states, counterpoise corrected, total energy for isolated C_{60} , Fe (triplet multiplicity) and polycyclic aromatic hydrocarbon (PAH) respectively.

Excitation energies and oscillator strengths for the most stable geometries were obtained by means of time-dependent DFT (TD-DFT) [25,26]. Thirty triplet–triplet transitions, using the hybrid exchange–correlation functional B3LYP [19–21] with the LAN2LTZ+/6-311+G(d,p) basis set for Fe [22] and 6-311G* for the other atoms. We performed further calculation using Perdew–Burke–Ernzerhof PBE [27,28] xc-functional, obtaining similar trends to B3LYP.

2.2. Validation of methodology

First of all we would like to mention that in the absence of extensive literature, particularly experimental, it is not easy to find similar hybrid molecular systems in which apply TDDFT and thus validate our methodology. Therefore we selected simple isolated PAH and C_{60} molecules for the validation of the TDDFT methodology, because there exist several theoretical and experimental work which it is possible to compare results with. In all the cases we performed TD-DFT/6-311G*/B3LYP calculations.

In the case of C_{60} the obtained energies for the first singlet (1E_1) and first triplet (3E_1) correspond to (1E_1) = 2.08 eV and (3E_1) = 1.60 eV respectively. These results agree quite well with experiments performed on C_{60} with benzene as a solvent with (1E_1) = 1.78 eV and (3E_1) = 1.65 eV [29], and with early TD-DFT results with (1E_1) = 1.83 eV and (3E_1) = 1.62 eV [30], which used a 3-21G basis set and BP86 as exchange–correlation functional. The difference between our methodology and the one reported for the first singlet 1E_1 is attributed to the differences in the GGA functional and the size of the basis set, which is more affected than the triplet 3E_1 . In the case of high energy electronic state transitions, for example up to 4 eV, differences between experiments and theory are observed, but in general they remain under to 0.4 eV in TD-DFT as presented by Bauernschmitt et al. [31]. In our work all the relevant transitions are kept down to 2.0 eV. Therefore we consider that the intrinsic error introduced by the method is restricted down to 0.4 eV.

In the case of PAH we selected free perylene as a benchmark. Halasinski et al. [32] reported on the theoretical and experimental optical properties of neutral, radical cations and anions of perylene using similar conditions for the TD-DFT methodology. According to the reference the most intense absorption bands are centred at 2.35 eV, 1.80 eV and 1.67 eV respectively. These values present very good concordance with TD-DFT being 2.02 eV, 1.93 eV and 1.76 eV at BLYP/6-31G* level [32] and 2.07 eV, 1.95 eV and 1.73 eV at B3LYP/6-311+G(d,p). Although both methods have differences in the size of the basis sets and the selected exchange correlation functional, the agreement between both levels of theory is evident. Regarding experiments there is a systematic deviation of 0.33 eV, similarly to the described deviation observed in C_{60} .

For all of these reasons we consider that the selected methodology, with TD-DFT/6-311G*/B3LYP, could be adequate for describing the photoabsorption mechanism in all the selected compounds.

3. Results and discussion

3.1. Case (I)

The first case corresponds to Fe located at the inner hexagon of the PAH, evaluating four different orientations of the fullerene.

Total energies for singlet and triplet states were determined for each configuration using the same basis set. Energy differences in favour to the triplet state correspond to 2.15 eV, 1.72 eV and 1.96 eV for H-coro, L-pery and S-pery, respectively. Having demonstrated that triplet state was the most stable configuration, the rest of the study was performed using this multiplicity for all the structural configurations (S, L, P and H).

It is important to mention that some differences may arise when comparing the formation energies with other similar works, such as Zhu et al. [10]. Our formation energies were determined using the total energy of isolated Fe in a quintet state. It is not clear to us the multiplicity used by other authors in their calculations. If we follow with our procedure the formation energy for $C_{60}/\text{Fe}/\text{Bz}$ corresponds to -1.90 eV, being quite similar to our $C_{60}/\text{Fe}/\text{PAH}$ compounds.

Total energies and geometrical information of PAH–Fe–C₆₀ systems are presented in Tables 1 and 2 and Fig. 1. Table 1 shows the geometrical distortions after the full optimization, yielding to lower coordination polyhedral between Fe and the C₆₀ carbon cage. Moreover, there is an off centre movement of the metal atom in relationship to the original PAH hollow position, in difference to its original S, L, P and H geometries.

In the case of perylene, the S and L geometries of the original η^2 Fe–C₆₀ bonds keep their symmetry. P and H cases become evidently distorted, changing their original η^5 and η^6 coordination geometries to three and two direct Fe–C₆₀ bonds as presented in Table 1. This situation is similar when considering the Fe–C_{PAH} bonds. In all the cases the original coordination geometry corresponds to η^6 , but after optimization the Fe–C_{PAH} bonds split in η^2/η^4 , η^2/η^2 , η^2/η^2 , $\eta^2/\eta^2/\eta^2$ for S, L, P and H respectively.

The situation is similar for coronene, where S and L keep the original Fe–C₆₀ bonds, but P and H changes to η^2/η^2 , $\eta^2/\eta^2/\eta^2$ splitting bonds in two and three groups. The Fe–C_{PAH} bonds become split in η^2/η^4 , η^2/η^4 , η^2/η^2 and four different bonds for S, L, P and H geometries respectively, see Table 1.

The most stable configurations correspond to P and L for coronene, and S and P for perylene, presenting similar structural geometries after the full optimization, see Fig. 1 and Table 2.

3.2. Case (II)

Another possibility consist in the location of the Fe atom over the edge hollow position of the PAH. We evaluated four different S, L, P and H- orientations for the fullerene molecule, as presented in Fig. 2. Total energy and structural information are showed in Tables 1 and 2.

Singlet and triplet spin multiplicities were evaluated for the whole set of structures, where triplet multiplicity proved to be more stable than the singlet one. For this reason triplet multiplicity where used for all the cases. All the structures were fully optimized, where original S geometry suffered major structural

changes, converging to similar final structures as obtained for the other initial L, P and H geometrical configurations. For this reason total energies and structural information, presented in Tables 1 and 2, only includes the structural details for the last three configurations. According to this the most stable configurations correspond to L and P for perylene and coronene respectively.

In the case of perylene, L and H configurations present similar formation energies, corresponding both to the actual ground state of the system. There exist a small energy barrier between both configuration corresponding to 0.1 eV. These results are quite reasonable, taking into account that both final coordinates converge to almost the same geometrical configuration. In these cases Fe presents a sixfold configuration, η^2 on the fullerene (Fe–C₆₀) and η^4 on the PAH (Fe–C_{PAH}). In the case of the P configuration, Fe adopts a sixfold configuration, with η^3 configuration on the fullerene and η^3 on the PAH. But this last geometry presented a higher formation energy, in comparison to L/H configurations, of nearly to 0.42 eV.

In the case of coronene, once again two configurations, L and P, present pretty similar formation energy and structural parameters. Iron adopts a slightly distorted square coordination polyhedron with η^2/η^2 configuration for fullerene and PAH respectively. This not a common structural configuration for Fe, and this fact is reflected in its relatively low structural stability, which proves to be unstable in comparison to the H configuration for about 0.34 eV. In the case of the H conformation, Fe presents the previously discussed sixfold configuration, η^2 on the fullerene and η^4 on the PAH, as presented for perylene.

3.3. The electronic structure of case (II) geometries

Ferrocene-like assemblies are known to follow the so called “18 electrons rule” [33]. According to this, and considering that iron contributes with eight electrons, coordination polyhedral higher than η^5 and η^6 are not expected to be the most stable. This is because PAH contributes with six electrons and C₆₀ is restricted to

Table 1
Structural information of PAH–Fe–C₆₀ for triplet spin configuration.

Perylene Fe–C distances (Å)			Coronene Fe–C distances (Å)		
Case, Site Symm.	Fe–C ₆₀	Fe–perylene	Site Symm.	Fe–C ₆₀	Fe–coronene
(I), S C _{2v}	2.055 × 2	2.463 × 2 2.491 × 4	S C _{2v}	2.067 × 2	2.329 × 2 2.332 × 4
(I), L C _s	2.263 × 2	2.423 × 2 2.491 × 2	L C _s	2.176 × 2	2.346 × 2 2.441 × 4
(I), P C _s	2.142 2.400 × 2	2.270 × 2 2.589 × 2	P C _s	2.193 × 2 2.607 × 2	2.347 × 2 2.595 × 2
(I), H C _s	2.247 × 2	2.385 × 2 2.419 × 2 2.515 × 2	H C _i	2.356 × 2 2.358 × 2 2.359 × 2	2.517 2.519 2.520 × 3 2.521
(II), L C _i	2.046 2.050	2.202 2.276 2.348 2.352	L C _i	2.115 2.214	2.135 2.143
(II), P C _i	2.123 2.367 2.367	2.048 2.177 2.359	P C _i	2.122 2.201	2.145 2.135
(II), H C _i	2.066 2.060	2.153 2.237 2.390 2.458	H C _i	2.043 2.045	2.107 2.184 2.375 2.582

Note (1): The Fe–C distance for calculated ferrocene is 2.0706 Å.

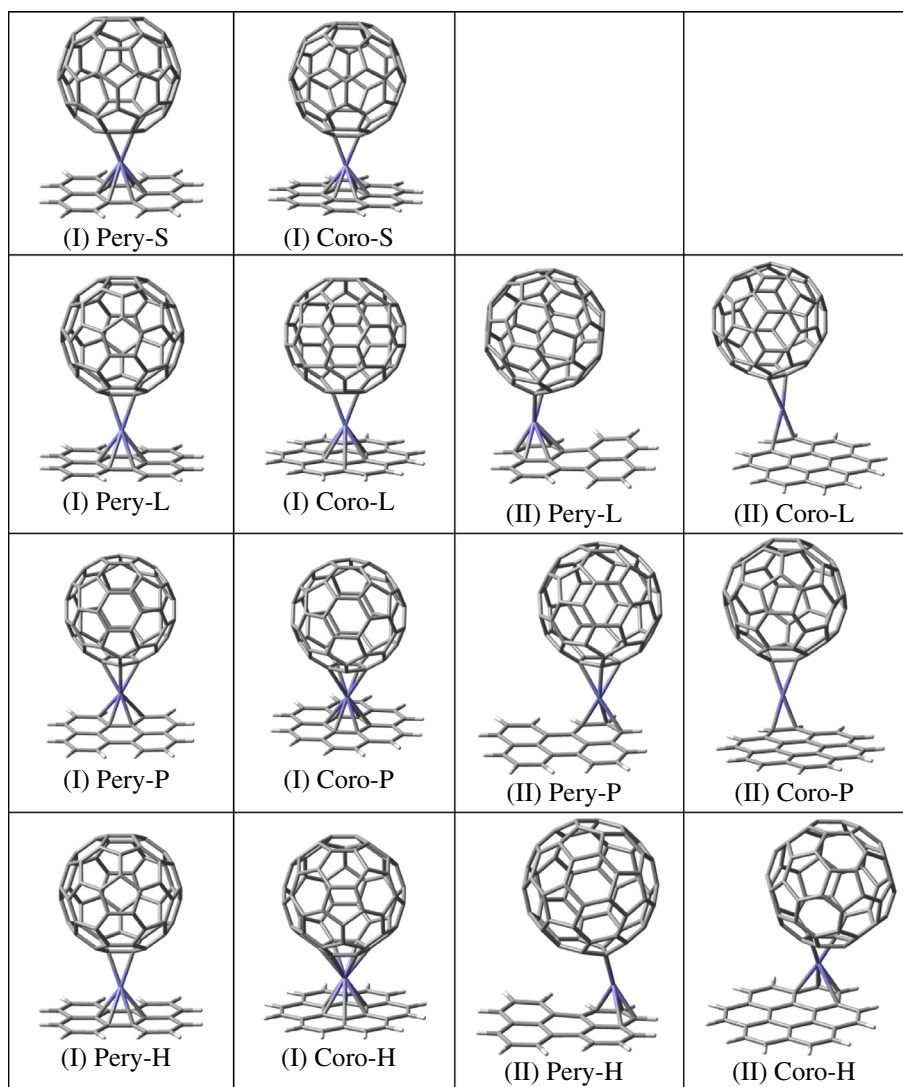
Note (2): The most stable configurations are showed with dark background.

Table 2Energetic information for triplet PAH-Fe-C₆₀.

Case, PAH	Site	Formation energy (eV)	ΔE (eV)	HOMO–LUMO TD-DFT (eV)
(I), Perylene	S	–0.736	0.000	0.168
	L	–0.251	0.485	–
	P	–0.622	0.114	–
	H	–0.251	0.485	–
(I), Coronene	S	–0.029	0.327	–
	L	–0.306	0.050	–
	P	–0.356	0.000	0.192
	H	–0.035	0.321	–
(II), Perylene	L	–1.157	0.006	–
	P	–0.746	0.417	–
	H	–1.163	0.000	0.559
(II), Coronene	L	–0.758	0.349	–
	P	–0.761	0.337	–
	H	–1.098	0.000	0.495

 ΔE : relative difference in formation energy with respect to the ground state configuration (eV).

Note: The most stable configurations are showed with dark background.

**Fig. 1.** Final optimized geometrical structures for perylene and coronene, in case (I) and case (II).

contribute with a maximum of four electrons. In order to obtain a P- η^5 stable configuration it is necessary to have a deviation from a

regular p_z states interaction. This fact can be verified confirming a shift of the iron atom from the centroid of the neighbouring rings.

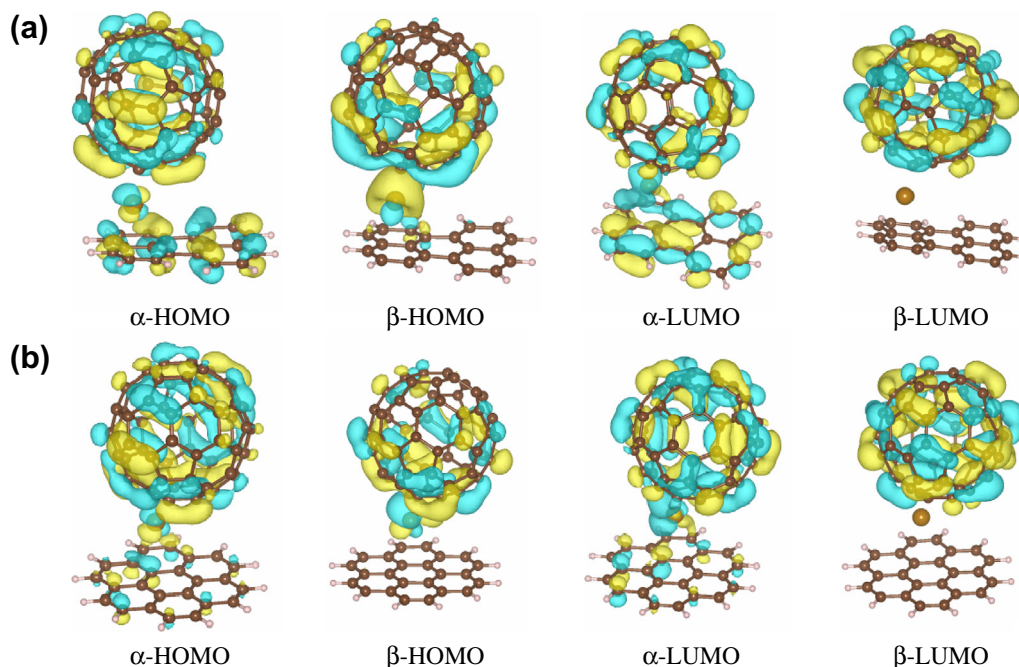


Fig. 2. Spin resolved highest occupied and lowest unoccupied molecular orbitals for the most stable perylene-H and coronene-H case (II) structures; (a and b) present the spin dependent HOMO and LUMO for each case respectively.

The Fe–C distances that constitute the 5-fold ring of the C_{60} molecule differ as much as $\Delta Fe-C_{max} = 0.57 \text{ \AA}$ and $\Delta Fe-C_{max} = 0.63 \text{ \AA}$ for perylene and coronene respectively, in agreement with this hypothesis (Table 1 shows only the shortest distances). Moreover, it is well-known that cobaltocene and nickelocene are exceptions to the “18 electrons rule”, involving 19 and 20 electrons, respectively [33]. As a consequence of the addition of these extra electrons, repulsion in the system would arise, observable through the increase of the length between the metal transition atom and the cyclopentadiene units. This fact is also verified for the hybrid PAH–Fe– C_{60} compounds, with Fe–C distances larger than in ferrocene case – being C the closest carbon atoms to iron in PAH and in C_{60} . The agreement verified in both cases could imply that for stabilization of $P-\eta^5$ configuration is achieved through some degree of symmetry breaking and repulsion, caused by the extra electrons injected from the donor. This would imply that the “18 electron rule” could be avoided for this system. As can be confirmed by inspection of Table 1, L and P-coronene configurations presents a η^2/η^2 configuration for Fe/PAH and Fe/ C_{60} pairs, which are clearly unstable in comparison to the ground state H-configuration, that presents η^2/η^{4d} geometry (*d* refers for distorted geometry). The L, P and H configurations for perylene present six fold geometrical configurations, particular P exhibits a η^{3d}/η^{3d} geometry. Distortion is enhanced for L with a η^2/η^{4d} configuration, and even more pronounced for H where the same average η^2/η^{4d} configuration presents more distortion in the Fe– C_{PAH} bonds, see Table 1.

HOMO and LUMO for α and β electrons are presented in Fig. 2 for all the configurations. There are important similarities in the HOMO/LUMO wavefunctions between coronene-H and perylene-H. In the case of α -HOMO, the d_{xz} -Fe orbital establishes an antibonding interaction with both π - C_{60} and π -PAH molecular orbitals. In the case of β -HOMO there is a bonding interaction between π - C_{60} and d_{xz} -Fe, and non-bonding interaction between π -PAH and d_{xz} -Fe. For α -LUMO the d_{xz} orbital of Fe establishes an antibonding interaction with both π - C_{60} and π -PAH. Finally the β -LUMO is clearly a π^* - C_{60} antibonding molecular orbital. Fig. 3 presents the corresponding density of states (DOS) and the equivalent crystal orbital overlap population analysis (COOP) [34] for H

configurations of perylene and coronene. The DOS allow us to determine the contribution of C_{60} , Fe and PAH to each state, while COOP allows to map the nature of the bonding between the fragments. All the early mentioned features, observed in the topology of the HOMO and LUMO wavefunctions, are consistent with COOP functions. For this purpose we selected three pair fragments: Fe/ C_{60} , Fe/PAH and C_{60} /PAH, in order to visualize the nature of the interaction between the pairs, which presents a COOP positive value for a bonding interaction while it is negative for and antibonding interaction. These features are clearly presented in Fig. 3. Moreover we can confirm that the direct interaction between C_{60} and PAH, evaluated as the COOP function in the C_{60} /PAH fragment, is negligible as observe in the null value of the function. Based on these results we present a molecular orbital diagram indicating the major contribution for each state, in terms of the early defined fragments and the main contribution to nature of the bonding, see Fig. 3. Both diagrams are qualitatively identical, with minor differences in the relative positions of the energy levels.

Table 3 shows results that confirm our hypothesis about the use of metallic centres for bridging molecules with different electrophilicity. This table shows that the Mulliken population analysis for the system, where the electronic charge-transfer from PAH to the buckminsterfullerene molecule is confirmed. This analysis allows us to compare the electronic behaviour of the systems through the electronic charge density distribution. It is worth noting that Mulliken charges are just indicative, since it is well known that they are basis set dependent. In all the cases the metallic centres present a positive net charge ranging from +0.51e to +0.66e, the C_{60} takes almost one electron, exhibiting a net charge ranging from -0.68e to -0.78e and PAH releases less than one quarter electron presenting a net charge ranging from +0.03e to +0.25e.

3.4. Optical properties from TD-DFT for case (II) geometries

First of all we performed geometrical optimization for case(II) geometries – i.e. the more stable ones-, calculating singlet and triplet solutions, confirming again that triplet multiplicity corresponds

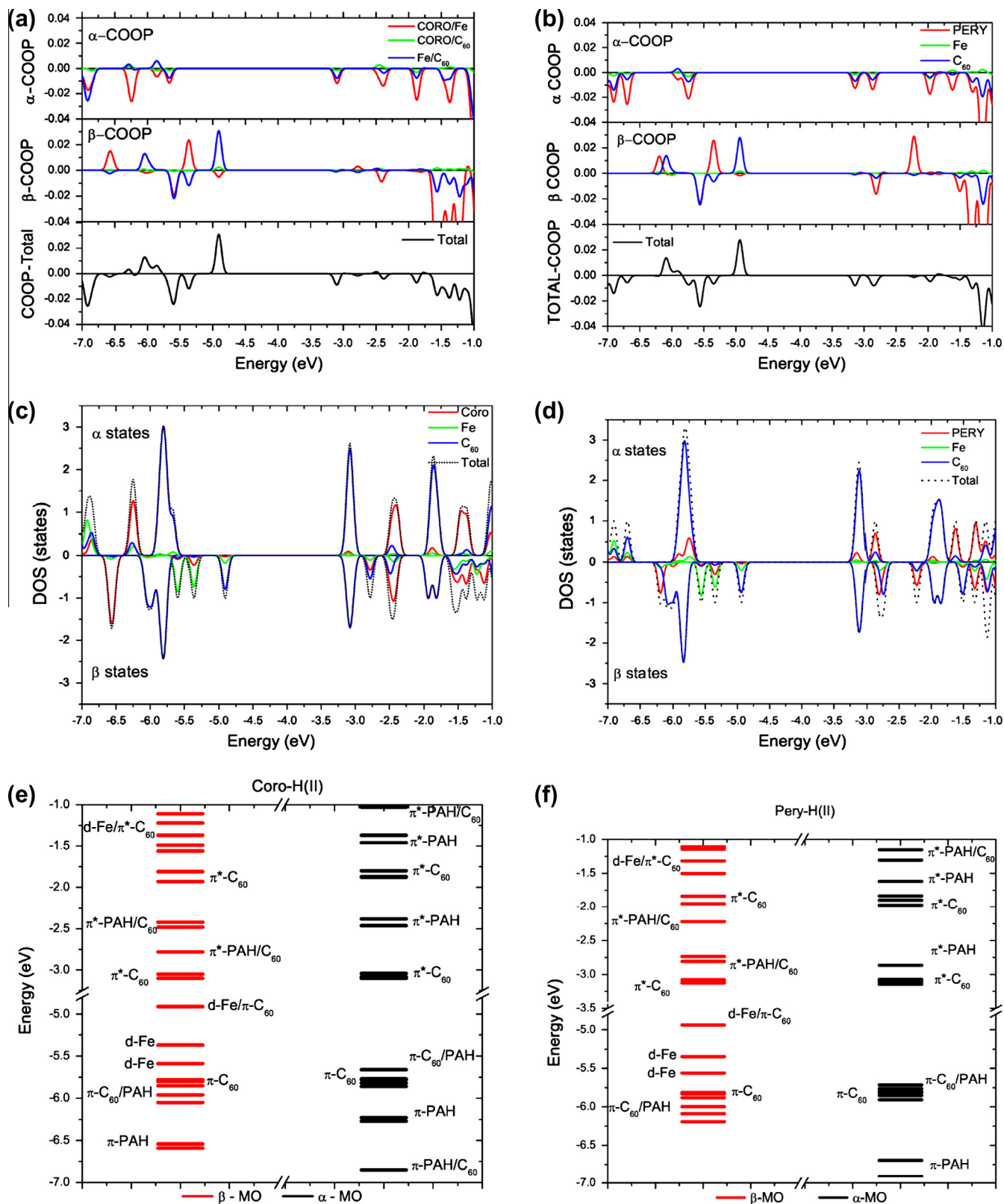


Fig. 3. Spin-resolved equivalent crystal orbital overlap population analysis (COOP) for three pair fragments Fe/C₆₀, Fe/PAH and C₆₀/PAH for coronene (a) and perylene (b). The density of states (DOS) for α (positive) and β (negative) spins of coronene-H (c) and perylene-H (d). The molecular orbital scheme for coronene-H (e) and perylene-H (f). Note: The HOMO–LUMO gap is located between -4.75 and -3.25 eV.

to the ground state. For this reason we proceeded with TD-DFT describing triplet–triplet transitions, where the spin contamination in all the calculated transitions were always located down to 25% as showed in Table 4.

Fig. 4 shows the electronic absorption spectra for coronene-H and perylene-H where the HOMO–LUMO gaps correspond to 0.50 eV and 0.56 eV respectively. It is worth noting that, for both cases, the low energy transitions present extremely low oscillator

Table 3Mulliken atomic charges for PAH, Fe and C₆₀ for the most stable configurations.

Perylene, case(I)				Coronene, case(I)			
Site	C ₆₀	Fe	PAH	Site	C ₆₀	Fe	PAH
S	−0.695	0.648	0.047	P	−0.779	0.612	0.167
Perylene, case(II)				Coronene, case(II)			
H	−0.770	0.540	0.230	H	−0.724	0.578	0.147

strength (f), indicating that single HOMO–LUMO gaps cannot be used by themselves for obtaining a direct conclusion on the optical absorption of these compounds, and further transitions should be described in order to understand the problem.

With this purpose we characterized the six most intense transitions, in terms of its oscillator strength, describing the main contribution to the corresponding configuration interaction. Transitions with oscillator strength down to $f = 0.0056$, most of them located down to 1 eV, were not included in the discussion but presented in Fig. 4. Due to the multi-configuration character of the excited states we applied electronic density differences (EDD) between the ground state and the first excited state, using GaussSum [34], in order to assign the character of the excited states unambiguously, see Table 4 and Fig. 5.

In the case of coronene-H, the most intense transition at 1.461 eV with $f = 0.0743$, is characterized as a mixed metal-to-ligand and ligand-to-ligand charge transfer (MLCT/LLCT) with a practical net contribution, 78%, from the β -HOMO(β) $\rightarrow$ β -LUMO + 2 transition, see Table 4. Here the Fe/C₆₀ interaction in HOMO and Fe/PAH in LUMO + 2 is sufficient to avoid a single metal-to-ligand charge transfer (MLCT) from metal d-to-ligand π states. The situation is similar for ligand-to-ligand charge transfer from ligand- π to ligand- π or intra-ligand charge transfer (ILCT). The following five most intense transitions are characterized by single MLCT or ILCT processes.

The situation is similar for perylene-H, the most intense transition is located at 1.438 eV with $f = 0.0624$. The contribution to the

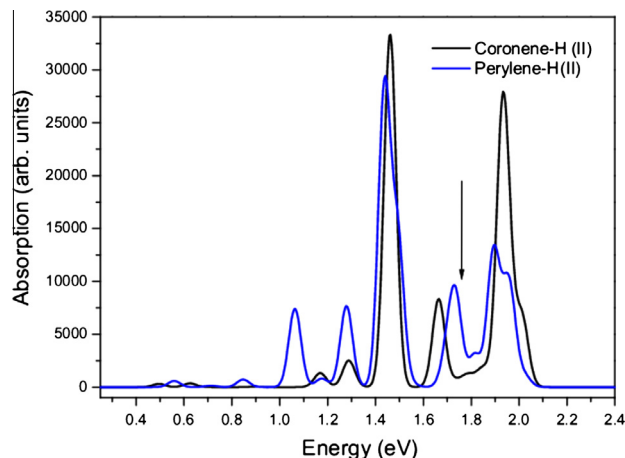


Fig. 4. Calculated optical absorption spectra for perylene-H (blue thin line) and coronene-H (black thick line) assemblies for case (II). The limit between visible and near infrared radiation is indicated by an arrow. Note: An artificial gaussian broadening was applied to the UV–VIS spectrum in order to obtain a full-width at half-maximum of FWHM = 0.03 eV. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

configuration interaction comes from 37% of H-1(β) $\rightarrow$ L + 2(β) and 19% of β -HOMO(β) $\rightarrow$ β -LUMO + 2 transitions, corresponding to

Table 4Calculated vertical transition energies (eV), oscillator strengths (f), configuration interaction, transition nature of the calculated TD-DFT triplet–triplet transitions.

System	Energy (eV)	f	Configuration interaction ^a	Transition	$\langle S^2 \rangle^b$
Coronene H (II)	1.389	0.0056	H-1(β) $\rightarrow$ L + 7(β) (24%)	MLCT	2.60
			H-1(β) $\rightarrow$ L + 10(β) (22%)		
			H-1(β) $\rightarrow$ L + 4(β) (13%)		
	1.461	0.0743	HOMO(β) $\rightarrow$ L + 2(β) (78%)	MLCT/LLCT	2.20
	1.663	0.0154	H-2(β) $\rightarrow$ L + 2(β) (15%)	MLCT	2.35
	1.931	0.0549	H-1(β) $\rightarrow$ L + 2(β) (11%)	ILCT	2.33
			HOMO(α) $\rightarrow$ LUMO(α) (47%)		
			H-4(β) $\rightarrow$ L + 1(β) (13%)		
	1.961	0.0115	H-2(α) $\rightarrow$ L + 2(α) (37%)	ILCT	2.33
	2.008	0.0056	H-4(β) $\rightarrow$ L + 1(β) (27%)	MLCT	2.52
			H-2(β) $\rightarrow$ LUMO(β) (54%)		
Perylene H (II)	1.063	0.0165	H-1(β) $\rightarrow$ L + 2(β) (20%)	MLCT	2.23
	1.279	0.0171	H-2(β) $\rightarrow$ L + 2(β) (19%)	MLCT/LLCT	2.28
			H-2(β) $\rightarrow$ L + 3(β) (15%)		
			HOMO(β) $\rightarrow$ L + 2(β) (51%)		
	1.438	0.0624	H-2(β) $\rightarrow$ L + 2(β) (15%)	MLCT/LLCT	2.38
			H-1(β) $\rightarrow$ L + 2(β) (10%)		
			H-1(β) $\rightarrow$ L + 2(β) (37%)		
	1.494	0.0306	HOMO(β) $\rightarrow$ L + 2(β) (19%)	MLCT/LLCT	2.48
	1.739	0.0135	HOMO(β) $\rightarrow$ L + 3(β) (56%)		
	1.892	0.0263	H-1(β) $\rightarrow$ LUMO(β) (15%)	MLCT	2.22
			H-4(α) $\rightarrow$ L + 2(α) (11%)		
			HOMO(β) $\rightarrow$ L + 4(β) (20%)		
			HOMO(α) $\rightarrow$ LUMO(α) (17%)	MLCT/LLCT	2.22
			H-1(β) $\rightarrow$ L + 3(β) (15%)		

^a Main contributions to the configuration interaction.

^b Total spin square mean value, which should be equal to $S(S + 1) = 2$.

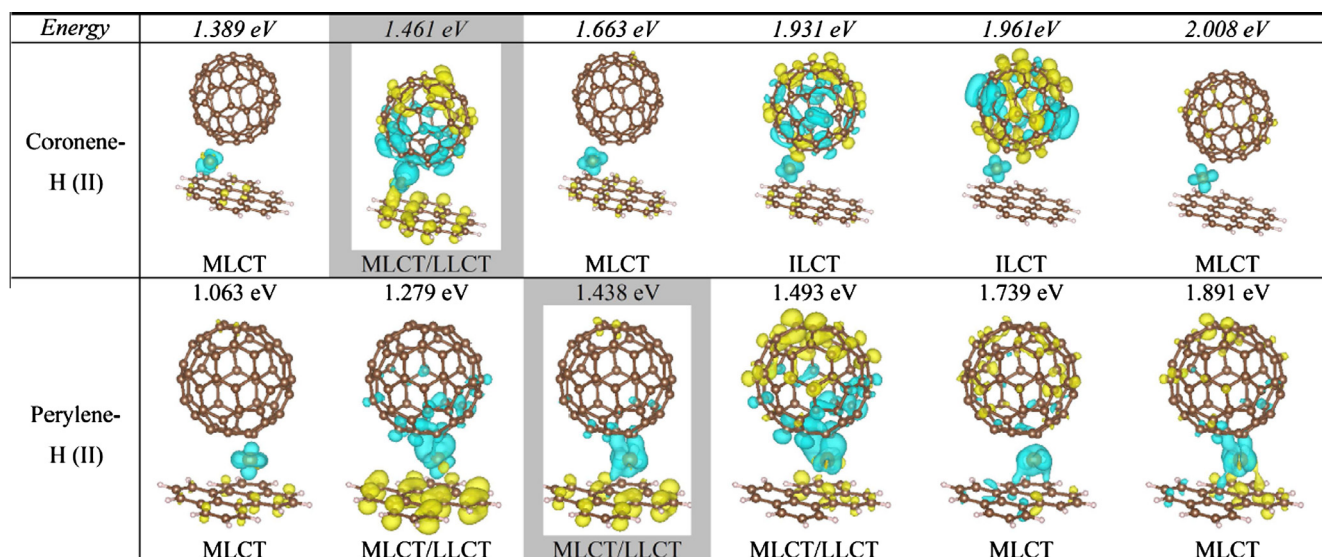


Fig. 5. Electronic density differences maps (EDDM) between the ground state and the corresponding excited state with iso-density surface at 0.0002 a.u., including its oscillator strength and transition classification. Note 1: Excited charge density is represented in cyan and the ground state density is represented in yellow. Note 2: The most intense oscillator strength is showed in dark background. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

mixed MLCT/LLCT transitions. The rest of the most intense transitions are characterized by less intense mixed MLCT/LLCT and single MLCT transitions, as presented in Table 4 and Fig. 5.

The absorption of these PAH-Fe-C₆₀ assemblies is significant in the near infrared region and the combination of both spectra covers this region in a remarkable way. Particularly the maximum oscillator strengths are located in the range of 1.25–1.75 eV confirming that an important optical absorption can be concentrated in the near infrared region of the solar spectrum.

4. Conclusions

We have demonstrated that it could be possible to prepare C₆₀-Fe-PAH hybrid compound. We presented their formation energy and corresponding geometrical configurations. The selected compounds have been analyzed in terms of their optical properties, demonstrating an interesting optical absorption in the infrared region of the solar spectrum, mediated by intense metal-to-ligand and ligand-to-ligand charge transfer.

To the best of our knowledge this behaviour is relevant since these compounds present important optical properties and therefore they could be use in technological applications. Further work is necessary in order to conclude that these assemblies could be used as infrared solar radiation absorber.

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