Accepted Manuscript

Extracting dimer structures from simulations of organic-based materials using QM/MM methods

A.J. Pérez-Jiménez, J.C. Sancho-García

PII: S0301-0104(15)00250-5

DOI: <http://dx.doi.org/10.1016/j.chemphys.2015.08.010>

Reference: CHEMPH 9392

To appear in: *Chemical Physics*

Please cite this article as: A.J. Pérez-Jiménez, J.C. Sancho-García, Extracting dimer structures from simulations of organic-based materials using QM/MM methods, *Chemical Physics* (2015), doi: <http://dx.doi.org/10.1016/j.chemphys.2015.08.010>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Extracting dimer structures from simulations of organic-based materials using QM/MM methods

A. J. Pérez-Jiménez*, J. C. Sancho-García*

*Departamento de Química Física
Universidad de Alicante, E-03080 Alicante, Spain.*

Abstract

The functionality of weakly bound organic materials, either in Nanoelectronics or in Materials Science, is known to be strongly affected by their morphology. Theoretical predictions of the underlying structure-property relationships are frequently based on calculations performed on isolated dimers, but the optimized structure of the latter may significantly differ from experimental data even when dispersion-corrected methods are used for it. Here, we address this problem on two organic crystals, namely coronene and 5,6,11,12-tetrachlorotetracene, concluding that it is caused by the absence of the surrounding monomers present in the crystal, and that it can be efficiently cured when the dimer is embedded into a general Quantum Mechanics/Molecular Mechanics (QM/MM) geometry optimization scheme. We also investigate how the size of the MM region affects the results. These findings may be helpful for the simulation of the morphology of active materials in crystalline or glassy samples.

Keywords: QM/MM, coronene, tetrachlorotetracene, dimer structure.

*Corresponding authors

Email addresses: aj.perez@ua.es (A. J. Pérez-Jiménez), jc.sancho@ua.es (J. C. Sancho-García)

1. Introduction

Calculations in materials composed of weakly interacting molecules, where the morphology of the samples and the role of molecular order affects ultimately the properties under investigation [1], are becoming key for various fields, specially for Organic Electronics and Materials Science, although in many occasions these properties are highly directional and are then governed by local environments. There is a growing need of theoretical determination of crystal structures [2–8], generally speaking, as well as finite or discrete portions of it (e.g. dimers) to disentangle their growing mechanism, to gain insight into the strength of the intermolecular interactions, or to infer how the electronic properties of isolated monomers change upon nanoaggregation [9, 10]. A step-by-step strategy might thus be envisioned to understand and rationalize the underlying structure-property relationships, which could then be extracted from calculations in a dimer of interacting molecules.

To further illustrate this issue, we list next some recent examples with polycyclic aromatic hydrocarbons (PAHs), a building block commonly used for this kind of materials [11–14], just to name a few of the large number of existing phenomena affected by specific dimer configurations: (i) the cohesive energy of crystalline (oligo)acenes, and more extended systems such as coronene, can be accurately calculated by estimating the binding energies of every unique pair of molecules found within the crystalline lattice, converging the global energy normally after considering the second coordination sphere [15–18], which can also disclosure polymorphism and growing issues; (ii) the van der Waals dispersion coefficients of PAHs can be obtained from dynamic polarizabilities computed at imaginary frequencies using time dependent density functional theory on the corresponding dimers [19]; (iii) the aggregation-induced emission of (oligo)acene molecules critically depends on the spatial separation and orientation between a pair of interacting molecules, with singlet and triplet excitation energies varying upon intermolecular interactions in an extent able to modify the efficiency of

the device built from these materials [20]; (iv) actually, the mechanism of singlet fission in (oligo)acenes, which could dramatically increase the efficiency of organic electronic devices (e.g. solar cells) after converting one singlet into two triplet states, relies on how the bright state delocalizes onto a pair of weakly interacting monomers [21], and/or how the backbone is substituted at central position (e.g. 5,6,11,12-tetraphenyltetracene) which alters the crystal packing and then concomitantly their ability to produce two triplet states from a single exciton [22]; and (v) the charge carrier migration across an active layer made on organic molecules [23], which is related to the current flowing across the device, largely depends on one hand on the intermolecular coupling between two neighbouring molecules in the crystal, and more precisely on the pattern of bonding or anti-bonding interactions between the frontier molecular orbitals of the interacting monomers, which is again completely driven by their spatial separation and orientation [24], and on the other hand on the intramolecular reorganization energy, which may also be strongly influenced by the local environment [25] beyond thermal or lattice fluctuations [26, 27].

Thus, with these antecedents in mind, our main interest here is to find out the influence of the environment when performing geometry optimizations on subunits (dimers) of the crystal using cost-effective dispersion-corrected calculations. We will achieve this goal by comparing the optimized geometries obtained on isolated dimers with those obtained from hybrid QM/MM calculations, where the Quantum Mechanics (QM) part will be the selected dimer and the Molecular Mechanics (MM) part should incorporate a sufficiently large portion of the crystal to ensure the adequate convergence of properties. We choose this route not only because of its computational efficiency, but also for the associated microscopic information that can be extracted in this way. We will also aim at disclosing what effect the size of the MM part will have on the results, by increasing the number of molecules included in it. This investigation is particularly timely since the number of potential applications relying on organic materials is rising, always needing a detailed microscopic understand-

ing of the interplaying processes, and then cost-effective multi-scale approaches might pave the way towards advanced discoveries and new technology platforms.

2. Computational details

All the calculations were done with the NWChem 6.3 quantum-chemical package [28] and with the default thresholds, unless otherwise indicated. The QM/MM expression of the energy computed by NWChem can be cast in the following form:

$$E^{QM/MM} = E^{QM}(\{\mathbf{R}_\alpha\}) + E^{MM}(\{\mathbf{R}_I\}) + E^{QM-MM}(\{\mathbf{R}_\alpha, \mathbf{R}_I\}), \quad (1)$$

where E^{QM} represents the energy of the region treated at the quantum-mechanical (QM) level, with $\mathbf{R}_\alpha$ denoting the positions of the corresponding nuclei, E^{MM} is the energy of the molecular-mechanics (MM) region, with $\mathbf{R}_I$ referring now to the atoms located in it, and finally the energy term E^{QM-MM} coupling both regions.

In the QM/MM calculations performed here the QM region always corresponds to a dimer of weakly interacting molecules surrounded by an MM region composed of a number of monomers that are initially placed at the crystal experimental geometry, as detailed in the next section. We thus avoid crossing bonds between the QM and the MM regions, and E^{QM-MM} reduces therefore to electrostatic contributions only [28]. The most relevant parameter controlling the QM-MM term is the radius of the zone where classical atoms are allowed to interact with the quantum region. We have always used a value such that the entire MM region interacts with the QM one, and therefore E^{QM-MM} is given by:

$$E^{QM-MM}(\{\mathbf{R}_\alpha, \mathbf{R}_I\}) = \sum_I q_I \sum_\alpha \frac{Z_\alpha}{|\mathbf{R}_I - \mathbf{R}_\alpha|} + \sum_I q_I \int \frac{\rho(\mathbf{r})}{|\mathbf{R}_I - \mathbf{r}|} d\mathbf{r} \quad (2)$$

where the indexes I and α run on the number of atoms in the MM and QM regions, respectively, with q and Z being, respectively, atom-centered MM point

charges (see below) and QM atomic numbers, while ρ represents the electron charge density of the QM region.

The QM/MM geometry optimizations performed will follow a sequence of decoupled partial optimizations of the QM and MM regions [28]. The algorithm starts by optimizing the geometry of the QM region, keeping the atoms in the MM region fixed, and then optimizes the geometry of the MM region while freezing the atoms of the QM part at the positions optimized in the previous step. This two-step process is then repeated until convergence is achieved. To speed-up the MM geometry optimization steps, we have exploited the capability implemented in NWChem of approximating the second member of Eq. (2) by means of point charges fitted to reproduce the QM electrostatic potential:

$$\sum_I q_I \int \frac{\rho(\mathbf{r})}{|\mathbf{R}_I - \mathbf{r}|} d\mathbf{r} \simeq \sum_I q_I \sum_i \frac{Q_i}{|\mathbf{R}_I - \mathbf{r}_i|} \quad (3)$$

considerably simplifying the evaluation of E^{QM-MM} and its derivatives [28, 29].

We choose the *General Amber Force Field* (GAFF) for the MM region, since it usually provides good estimates of crystallographic structures [30]. The GAFF energy term E^{MM} contains bond, angle, dihedral, and non-bonded terms. The van der Waals term is a 6-12 potential, and the electrostatic one is expressed as a Coulombic interaction with atom centered point charges. It can be cast in the following form [30]:

$$\begin{aligned} E^{MM} &= \sum_{bonds} k_r (r - r_{eq})^2 + \sum_{angles} k_\theta (\theta - \theta_{eq})^2 \\ &+ \sum_{dihedrals} \frac{V_n}{2} \times [1 + \cos n\phi - \gamma] \\ &+ \sum_{I < J} \varepsilon_{IJ} \left[\left(\frac{R_{IJ}^*}{R_{IJ}} \right)^{12} - 2 \left(\frac{R_{IJ}^*}{R_{IJ}} \right)^6 \right] + \sum_{I < J} \frac{q_I q_J}{R_{IJ}} \end{aligned} \quad (4)$$

where k_r , and k_θ are the force constants for bond length and angle, respectively, while r_{eq} and θ_{eq} are the equilibrium bond distances and angles. A truncated Fourier series represents the dihedral term, where V_n is the barrier height, n is

the periodicity, ϕ is the calculated dihedral angle and γ is the phase difference. The fourth term describes the steric interaction as a Lennard-Jones potential, where R_{IJ} is the distance between atoms I and J in the MM region. ε_{IJ} and R_{IJ}^* are parameters that define the shape of the potential, with $R_{IJ}^* = R_I^* + R_J^*$, R_I^* being the van der Waals radius for atom I , and $\varepsilon_{IJ} = \sqrt{\varepsilon_I \cdot \varepsilon_J}$, ε_I being the van der Waals well depth. Note that q_I are atom-centered point charges, which have been obtained from a Löwdin population analysis on an isolated molecule at the experimental geometry (see the details in the next section), and are shown in Figure 1. The atom types chosen from the GAFF definitions are “ca” for all the carbon atoms (aromatic sp^2 carbon, #5 of Table I in ref. [30]), “ha” for all the hydrogen atoms (hydrogen on aromatic carbon, #27 of Table I in ref. [30]), and “cl” for all the chlorine atoms (any chlorine, # 33 of Table I in ref. [30]). The corresponding GAFF parameters entering Eq. (4) have been collected in Table 1.

Last, not least, one should appropriately choose the method to compute the QM energies and forces on the atoms. Here we select the DFT methodology with the well-known B3LYP exchange-correlation functional [31, 32], because it gives accurate estimates of shape and volume of isolated [33] and embedded [34] medium-sized organic molecules. Admittedly, there is nowadays a plethora of available exchange-correlation functionals that could have also been used, but since our main interest here is to find out the consequences of considering (or not) the environment when performing DFT geometry optimizations on subunits (dimers) of a crystal, we limited ourselves to this extensively assessed model. However, we will perform some calculations using the non-hybrid BLYP functional [35, 36], in order to estimate the importance of the functional used. We use the -D3(ZD) scheme [37] to take into account intra- and intermolecular dispersion effects, whose impact on nanoaggregates is expected to be important. Indeed, we will address such impact by removing this dispersion correction in some of the calculations reported in the next section.

Note also that we have tried to keep the computational cost of the calculations as moderate as possible, foreseeing a potential use of this scheme on organic crystals with larger monomer units in the future, and for this reason we have chosen the cc-pVDZ basis set [38] for the trade-off between accuracy and computational cost. However, we will also carry out some calculations using the Pople-type 6-31G* basis set [39], to address the influence that the description of the hydrogens would have in the results, where both sets mainly differ ($2s1p$ set in cc-pVDZ *vs.* a $2s$ set in 6-31G*). The influence of the Basis Set Superposition Error (BSSE) in the geometries obtained will be assessed by means of complementary geometry optimizations using the larger cc-pVTZ basis set.

3. Results and discussion

We will mainly focus in the following on the structure of dimers located along the most dense-packed crystal directions. More precisely, we will consider as structural target the relative displacement of the respective centers of mass of both monomers in the X , Y , Z directions shown in Figure 1, hereafter referred to as ΔX , ΔY , and ΔZ , respectively.

3.1. Coronene

The crystal structure of coronene belongs to the $P2_1/a$ space group, with cell lengths $a=16.11\text{\AA}$, $b=4.70\text{\AA}$, $c=10.10\text{\AA}$ and angles $\alpha=90^\circ$, $\beta=110.9^\circ$, $\gamma=90^\circ$ [40]. Figure 2 shows both the unit cell and some of the molecules present in the crystal structure [41]. We will further examine dimers located along the most densely packed direction b , as it was said before.

We have first carried out a B3LYP-D3(ZD)/cc-pVDZ geometry optimization on an isolated dimer along the b direction taking the experimental structure as starting point. Both structures are displayed in Figures 3b and 3a, respectively, while the corresponding ΔX , ΔY , and ΔZ values are listed in Table 2. To ease visualizing the relative position of both monomers, we have made

use of the graphic capabilities of the *vmd* program [42], using a darker color for the monomer with higher Z . Despite the fact that the geometry optimization performed on the isolated dimer provides a good estimate of ΔZ , with a deviation as low as 0.1 Å, it is clear that both ΔX and ΔY deviate more markedly (by around 1 Å) from the experimental values. Thus, the presence of both monomers in the calculation allows for a good estimate of their interaction along the b direction. However, it seems that the absence of nearest neighbors in the remaining directions favours the two molecules to adopt a relative positioning where the center of each carbon ring in one monomer has a vertex of a carbon ring in the other monomer placed just above it (see Fig. 3b). In the experimental structure, on the other hand, the influence of the whole crystal alters the relative positioning of the monomers and, as can be seen from Fig. 3a, they place themselves in such a way that there are dense-packed regions of C-C bonds alongside the X direction.

To check out the influence of the environment on the dimer structure we have done a set of QM/MM geometry optimizations systematically varying the size of the MM region. The first one, dubbed as “small” from now on, includes the minimum amount of molecules (x34) in the MM region to guarantee that the target dimer is completely surrounded by coronene molecules (see Fig. 4). The second one, referred to as “large” in the following, includes an additional layer of coronene molecules for a total of 148 molecules in the MM region (see Fig. 7). The objective of this larger QM/MM calculation is to find out the importance (*vide infra*) of increasing the MM region in the results. In both cases, the QM part is treated at the same level of theory used for the isolated dimer calculation, namely, the B3LYP-D3(ZD)/cc-pVDZ, although several other functional-dispersion/basis set schemes have also been used to ascertain their influence in the final results and will be discussed later.

Hence, starting from the experimental geometry in Fig. 4a, we have performed the corresponding QM/MM geometry optimizations, leading to the

structure shown in Fig. 4b. It is apparent, after comparing both structures, that the QM/MM “small” optimized geometry compares quite favourably with the experimental one. This can be analyzed more in depth with the help of Figure 3 and Table 2. Fig. 3c depicts the geometry of the central QM dimer of the QM/MM “small” calculation, as well as that corresponding to the outermost MM dimer (placed at the top right corner in Fig. 4b) of the QM/MM “small” calculation (Fig. 3d), while Table 2 lists the corresponding ΔX , ΔY , and ΔZ values.

Perusing Figs. 3a–3d, and Table 2, we can infer how incorporating part of the crystal structure in the geometry optimization, albeit in an MM fashion and limited to a first neighbor layer, provides much more accurate structures than those provided by the calculation including just the isolated dimer. For both the central QM dimer and the outermost MM dimer one, the relative positioning of the monomers is much more similar to that found in the experimental one, with a large improvement in the value of ΔX , and specially in that of ΔY , with a 0.1 Å shrinking in the value of ΔZ for the QM dimer with respect to the experimental value. Overall, the QM/MM “small” geometry optimization performed is able to correctly capture the main interactions between the coronene molecules in the crystal, providing reasonable geometries at a computational cost similar to that of the isolated dimer optimization. Indeed, the percentage of the time that the code spends finding the first QM minimum (via a Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [28]), represents just the 76% of the overall calculation, which is also quite efficient because it only needs very few (4) QM-MM combined decoupled partial geometry optimizations to find the optimized geometry. The energy profile with respect to the QM/MM “small” optimized ΔX , ΔY , ΔZ values is plotted in Figure 5 [43]. Similar percentages and energy profiles are found for all the “small” QM/MM calculations performed in this work.

At this point it is worth mentioning the influence that some computational

details have in the results. We start by noticing that changing to a 6-31G* basis set has little influence in this system, with slightly worse results than those obtained with the cc-pVDZ one, and similar conclusions can be drawn with respect to using the BLYP functional instead of the B3LYP one, as Table 2 shows. However, as expected, removing the dispersion correction from the calculations leads to a noticeable worsening of both ΔY and ΔZ values. Therefore, it seems that the B3LYP-D3(ZD)/cc-pVDZ is a sound compromise to model the QM region for this kind of systems, a conclusion that will be corroborated later by the results obtained in the next section for 5,6,11,12-tetrachlorotetracene. The (small) influence of the BSSE in the geometries will be addressed also in that section by means of complementary B3LYP-D3(ZD)/cc-pVTZ calculations, which are much more computationally demanding than the B3LYP-D3(ZD)/cc-pVDZ ones, and thus will benefit from the reduced size of that system. Finally, Table 2 also shows the little influence that the MM point charges q have on the results, with a slight worsening when they are taken from a B3LYP-D3(ZD)/cc-pVDZ ESP fit on the isolated dimer at the experimental geometry, constrained to give zero total charge on each monomer: see Figure 6.

The question which still remains is whether increasing the number of coronene molecules in the MM region would lead to noticeable improvements in the structures of a QM/MM calculation. The answer is *yes*, as the results obtained from the QM/MM “large” geometry optimization, shown in Fig. 7, and in Table 2, clearly corroborate. Figure 3e depicts the central QM dimer geometry, while Fig. 3f shows the outermost MM dimer one. In both cases, the good agreement with the experimental geometry, shown in Fig. 3a, is evident, as the values of ΔX , ΔY , and ΔZ in Table 2 also confirm. This result reflects that, at least for the coronene case, a second layer of MM molecules suffices to obtain values of ΔX , ΔY , and ΔZ from QM/MM geometry optimizations which deviate less than 0.1 Å from the experimental ones. Another advantage of the QM/MM “large” calculations is their computational efficiency, since the total number of QM-MM combined decoupled partial geometry optimizations is reduced from 4

to 3, with the 82% of the computing time devoted to obtain the first QM minimum. We also want to note in passing the excellent behavior of the GAFF MM field, as the values of ΔX , ΔY , and ΔZ for the outermost MM dimer of the QM/MM “large” geometry optimization clearly indicate, supporting its choice as a good MM “partner” for the DFT description of the QM part.

The previous study indicates that to include a portion of the surrounding environment is key if one foresees to obtain reasonable estimates of dimer geometries embedded in crystal structures. To illustrate how these morphological changes affect in turn other properties, we report in Table 3 relevant orbital energies of the dimers at the optimized geometries obtained for the isolated system and from several QM/MM calculations. It is evident that, although the change in geometry does not alter the HOMO-LUMO gap (Δ_g) appreciably, it leads to important changes in the HOMO to HOMO-1 and LUMO+1 to LUMO gaps which, to a first approximation [44], are proportional to the hole and electron transfer integrals, t_h and t_e , respectively, highlighting once more the importance of structure-property interrelations.

In the next section we will consider a different crystal structure of a substance that also incorporates heteroatoms, namely that of 5,6,11,12-tetrachlorotetracene, in a first effort to analyze the general validity of all the above findings.

3.2. 5,6,11,12-Tetrachlorotetracene

The crystal structure of 5,6,11,12-Tetrachlorotetracene belongs to the monoclinic $P2_1/n$ space group, with cell lengths $a=3.80\text{\AA}$, $b=14.54\text{\AA}$, $c=13.00\text{\AA}$ and angles $\alpha=90^\circ$, $\beta=97.86^\circ$, $\gamma=90^\circ$ [45]. Figure 8 shows both the unit cell and some of the molecules present in the crystal structure. Note that the electron-active substituents substantially modify the molecular electrostatic potential [46], and then the whole through-space intermolecular interactions, so that this system complements the case previously studied. As it was formerly done with

coronene, we will pay special attention to the dimers located along the most dense-packed direction, which in this case coincides with axis a in the crystal. We will consider the relative displacements of their respective center of mass in the X , Y , Z directions shown in Figure 1b: ΔX , ΔY , and ΔZ , respectively.

We have performed geometry optimizations for the three kind of computational schemes done previously for coronene, namely: B3LYP-D3(ZD)/cc-pVDZ on an isolated dimer along the a axis, as well as QM/MM ones with “small” (x26 molecules) and “large” (x148 molecules) portions of the crystal treated classically, in addition to the central dimer of interacting molecules. The same exchange-correlation functionals and basis sets considered previously for coronene were also used here for the QM portion of the QM/MM calculations. In all cases the experimental geometry constituted the starting point. The results are collected in Figs. 9–11, and in Tables 2 and 3, leading to the same trends already found for coronene.

Considering first the results obtained with the B3LYP-D3(ZD)/cc-pVDZ scheme for the DFT description of the QM part we find, indeed, that the geometry optimization corresponding to the isolated dimer (compare Fig. 9a with Fig. 9b) yields reasonable estimates for ΔY and ΔZ , but fails completely for ΔX , pointing again towards the need of including a portion of the surrounding crystal environment to obtain reasonable results in all three directions. This is once more corroborated by the QM/MM geometry optimizations: compare Fig. 10a with Fig. 10b. The QM/MM “small” geometry optimization yields already good values for all ΔX , ΔY , ΔZ for both the central QM dimer, and the outermost MM dimer (placed at the top center of Fig. 10b): compare Fig. 9 with Figs. 9c and 9d. However, increasing the size of the MM region largely improves the value of ΔZ for both the QM and MM dimers, while keeping the already good estimates of ΔX and ΔY : see Table 2, and Figs. 9a, 9e and 9f.

Similar conclusions to those found for coronene regarding computational

details are also reached here, as it can be seen after inspecting Table 2: in summary, the B3LYP-D3(ZD)/cc-pVDZ-GAFF scheme is a sound choice for QM/MM structural optimizations on these kind of organic aggregates. The results obtained using the much larger cc-pVTZ basis set, also point towards a small influence of BSSE effects for such structural studies.

Finally, the large interrelation between structure and transport properties already found for coronene is also observed for 5,6,11,12-tetrachlorotetracene, as the values of t_h and t_e reported in Table 3 show, which emphasizes again the need for accurate theoretical structural determinations when analyzing electronic or transport properties for this type of molecular aggregates.

Therefore, the conclusions reached in the previous section for coronene can also be extended to the 5,6,11,12-tetrachlorotetracene case, and indicate that QM/MM geometry optimizations seem to be a sound approach to obtain reasonable estimates of subunits (dimers) embedded in organic molecular aggregates, being thus a good complement to calculations using periodic boundary conditions on these kind of systems [10, 18, 47]. We are also aware of the fact that we used the (known) *experimental* crystal structures as starting points for our calculations. However, the good results obtained allows us to speculate that starting from a reasonable structure of an isolated dimer, carefully achieved through some dispersion-corrected method, and replicating it via MM modelling, an initial estimate of the crystal structure may be obtained and further refined. This goes well beyond the scope of this work, but may pave the way towards the calculation and rationalization of structures for organic molecular aggregates, which would be of much interest for scientists working in the field.

4. Conclusions

The results obtained in this work confirm that, in order to obtain reasonable estimates of dimer geometries embedded in crystal structures, it is key to include

some local environment. Whereas the intermolecular separation ΔZ , which is normally in the range 3.3–3.6 Å, is reasonably predicted for an isolated dimer of weakly bound organic molecules, provided that dispersion-corrected functionals are used, the corresponding ΔX and ΔY displacements (slipped cofacial stacking) are affected by larger errors. This can be efficiently corrected by performing QM/MM geometry optimizations including, at least, a first-layer cluster of surrounding molecules. However, a second layer of molecules might be also needed, depending on the system under study, to obtain accurate results in all three X , Y , and Z directions, being also more computationally efficient. The values reported here for the hole and electron transfer integrals indicate that the aforementioned morphological changes may have a large influence in them, and should always be taken into account. Our calculations also indicate that the chosen combination of B3LYP–D3(ZD)/cc-pVDZ method for the QM part, and the GAFF force field for the MM part, performs quite reasonably for the two systems analyzed in this work, and may be thus a sound choice (largely available in common codes) for other organic molecular aggregates of the most interest, as well as for thermally activated simulations or for studying dynamic fluctuations.

Acknowledgements

This work is supported by the “Ministerio de Economía y Competitividad” of Spain and the “European Regional Development Fund” through project CTQ2014-55073-P.

References

References

- [1] M. Mas-Torrent, C. Rovira, Chem. Rev. 111 (2011) 4833.
- [2] R. Podeszwa, B. M. Rice, K. Szalewicz, Phys. Rev. Lett. 101 (2008) 115503.
- [3] J. D. Dunitz, A. Gavezzotti, Chem. Soc. Rev. 38 (2009) 2622.

- [4] K. Hongo, M. A. Watson, R. S. Sánchez-Carrera, T. Iitaka, A. Aspuru-Guzik, *J. Phys. Chem. Lett.* 1 (2010) 1789.
- [5] T. Todorova, B. Delley, *J. Phys. Chem. C* 114 (2010) 20523.
- [6] G. J. O. Beran, K. Nanda, *J. Phys. Chem. Lett.* 1 (2010) 3480.
- [7] J. G. Brandenburg, S. Grimme, *Top. Curr. Chem.* 345 (2014) 1.
- [8] J. Binns, M. R. Healy, S. Parsons, C. A. Morrison, *Acta Cryst. B* 70 (2014) 259.
- [9] J. C. Sancho-García, A. J. Pérez-Jiménez, Y. Olivier, J. Cornil, *Phys. Chem. Chem. Phys.* 12 (2010) 9381.
- [10] J. V. Climent-Medina, A. J. Pérez-Jiménez, M. Moral, E. San-Fabián, J. C. Sancho-García, *ChemPhysChem* 16 (2015) 1520.
- [11] M. Bendikov, F. Wudl, D. F. Perepichka, *Chem. Rev.* 104 (2004) 4891.
- [12] J. E. Anthony, *Chem. Rev.* 106 (2006) 5028.
- [13] M. Burghard, H. Klauk, K. Kern, *Adv. Mater.* 21 (2009) 2586.
- [14] C. Wang, H. Dong, W. Hu, Y. Liu, D. Zhu, *Chem. Rev.* 112 (2012) 2208.
- [15] A. L. Ringer, C. D. Sherrill, *Chem. Eur. J.* 14 (2008) 2542.
- [16] J. Yang, W. Hu, D. Usvyat, D. Matthews, M. Schutz, G. K.-L. Chan, *Science* 345 (2014) 640.
- [17] M. R. Kennedy, A. R. McDonald, A. E. D. III, M. S. Marshall, R. Podeszwa, C. D. Sherrill, *J. Chem. Phys.* 140 (2014) 121104.
- [18] J. C. Sancho-García, A. J. Pérez-Jiménez, Y. Olivier, *J. Chem. Phys.* 142 (2015) 054702.
- [19] M. A. L. Marques, A. Castro, G. Malloci, G. Mulas, S. Botti, *J. Chem. Phys.* 127 (2007) 014107.

- [20] D. Kim, J. Phys. Chem. C 119 (2015) 12690.
- [21] P. M. Zimmerman, F. Bell, D. Casanova, M. Head-Gordon, J. Am. Chem. Soc. 133 (2011) 19944.
- [22] D. Casanova, J. Chem. Theory Comput. 10 (2014) 324.
- [23] V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey, J.-L. Brédas, Chem. Rev. 107 (2007) 926.
- [24] J. L. Brédas, J. P. Calbert, D. A. da Silva Filho, J. Cornil, Proc. Natl. Acad. Sci. U.S.A. 99 (2002) 5804.
- [25] S. Bromley, F. Illas, M. Mas-Torrent, Phys. Chem. Chem. Phys. 10 (2008) 121.
- [26] A. Troisi, G. Orlandi, J. Phys. Chem. A 110 (2006) 4065.
- [27] N. G. Martinelli, Y. Olivier, S. Athanasopoulos, M.-C. Ruiz-Delgado, K. R. Pigg, D. A. da Silva Filho, R. S. Sánchez-Cabrera, E. Venuti, R. G. D. Valle, J.-L. Brédas, D. Beljonne, J. Cornil, Chem. Phys. Chem. 10 (2009) 2265.
- [28] M. Valiev, E. J. Bylaska, N. Govind, K. Kowalski, T. Straatsma, H. J. J. van Dam, D. Wang, J. Nieplocha, E. Apra, T. Windus, W. de Jong, Nwchem: a comprehensive and scalable open-source solution for large scale molecular simulations, Comput. Phys. Commun. 181 (2010) 1477.
- [29] M. Valiev, B. C. Garret, M.-K. Tsai, K. Kowalski, S. M. Kathmann, G. K. Schenter, M. Dupuis, J. Chem. Phys. 127 (2007) 051102.
- [30] J. Wang, R. M. Wolf, J. W. Caldwell, P. A. Kollman, D. A. Case, J. Comput. Chem. 25 (2004) 1157.
- [31] A. D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [32] P. J. Stephens, F. J. Devlin, C. F. Chabrowski, M. J. Frisch, J. Chem. Phys. 98 (1994) 11623.

- [33] S. Grimme, M. Steinmetz, *Phys. Chem. Chem. Phys.* 15 (2013) 16031.
- [34] J. Torras, S. Bromley, O. Bertán, F. Illas, *Chem. Phys. Lett.* 457 (2008) 154.
- [35] A. D. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [36] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [37] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* 132 (2010) 154104.
- [38] T. H. J. Dunning, Jr., *J. Chem. Phys.* 90 (1989) 1007.
- [39] P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* 28 (1973) 213.
- [40] J. K. Fawcett, J. Trotter, *Proc. R. Soc. A* 289 (1966) 366.
- [41] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, Mercury csd 2.0 - new features for the visualization and investigation of crystal structures, *J. Appl. Cryst.* 41 (2008) 466, figures 2 and 8 were done with the aid of the program Mercury 3.5.1: C. F. Macrae.
- [42] W. Humphrey, A. Dalke, K. Schulten, Vmd – visual molecular dynamics, *J. Mol. Graph.* 14 (1996) 33, all the figures in this paper except Figs. 1, 2, 5 and 8 were done with the aid of the program VMD 1.9.1.
- [43] Figure 5 was done with the aid of the program gnuplot 4.6.
<http://gnuplot.info>.
- [44] V. Coropceanu, J. Cornil, D. A. daSilva Filho, Y. Olivier, R. Silbey, J. L. Brédas, *Chem. Rev.* 107 (2007) 926.
- [45] X. Chi, D. Li, H. Zhang, Y. Chen, V. Garcia, C. Garcia, T. Siegrist, *Org. Electron.* 9 (2008) 234.
- [46] J. C. Sancho-García, A. J. Pérez-Jiménez, *Chem. Phys. Lett.* 499 (2010) 146.

- [47] K. Hummer, C. Ambrosch-Draxl, Phys. Rev. B 72 (2005) 205205.

ACCEPTED MANUSCRIPT

- **Table 1.** GAFF force field parameters used (see text and Ref. [30] for details).
- **Table 2.** Relative displacements between the center of mass of two consecutive monomers placed along direction b in the coronene crystal, and along direction a in the 5,6,11,12-Tetrachlorotetracene crystal. The corresponding percentile variation of each calculated value with respect to the experimental ones are shown in parenthesis at the right of each entry. The last column lists the functional, dispersion correction, and basis set used in the DFT calculations performed, either on an isolated dimer, or for the QM portion of the QM/MM scheme. See text, figures, and table notes for details.
- **Table 3.** Energies for a set of relevant orbitals, with corresponding HOMO-LUMO gaps and transport properties, of coronene and 5,6,11,12-tetrachlorotetracene dimers placed along directions b and a , respectively, of the crystal. The results correspond to geometry optimizations obtained with isolated dimers and several QM/MM schemes using B3LYP-D3(DZ)/cc-pVDZ DFT calculations for the QM part. See text and table notes for details.

Table 1:

Non bonded			
Atom	$R^*/\text{\AA}$	$\varepsilon/\text{kcal mol}^{-1}$	
ca	1.908	0.086	
ha	1.459	0.015	
cl	1.948	0.265	
Bonds			
Atoms	$r_{eq}/\text{\AA}$	$k_r/\text{kcal mol}^{-1}\text{\AA}^{-2}$	
ca-ca	1.387	478.4	
ca-ha	1.087	344.3	
ca-cl	1.729	322.8	
Angles			
Atoms	$\theta_{eq}/\text{degrees}$	$k_\theta/\text{kcal mol}^{-1}\text{rad}^{-2}$	
ca-ca-ca	119.97	67.18	
ca-ca-ha	120.01	48.46	
ca-ca-cl	119.40	62.92	
Proper dihedrals			
Atoms	$\gamma/\text{degrees}$	$V_n/\text{kcal mol}^{-1}$	n
X-ca-ca-X	180.00	14.50	2
Improper dihedrals			
Atoms	$\gamma/\text{degrees}$	$V_n/\text{kcal mol}^{-1}$	n
ca-ca-ca-ca	180.00	1.1	2
ca-ca-ca-ha	180.00	1.1	2
ca-ca-ca-cl	180.00	4.4	2

Table 2:

Coronene				
Procedure and system	$\Delta X/\text{\AA}$	$\Delta Y/\text{\AA}$	$\Delta Z/\text{\AA}$	Method
Experimental	1.88	2.55	3.47	
DFT on isolated dimer	0.85 (-54.8%)	1.20 (-52.9%)	3.40 (-2.0%)	B3LYP-D3(ZD)/cc-pVDZ
QM/MM “small” (outermost) ^a	1.20 (-36.2%)	2.74 (7.5%)	3.45 (-0.6%)	B3LYP-D3(ZD)/cc-pVDZ
QM/MM “small” (central) ^b	1.28 (-31.9%)	2.84 (11.4%)	3.37 (-2.9%)	B3LYP-D3(ZD)/cc-pVDZ
QM/MM “small” (central) ^{b,c}	1.24 (-34.0%)	2.89 (12.9%)	3.33 (-4.0%)	B3LYP-D3(ZD)/cc-pVDZ ^c
QM/MM “small” (central) ^b	1.24 (-34.0%)	2.88 (12.9%)	3.35 (-3.5%)	B3LYP-D3(ZD)/6-31G*
QM/MM “small” (central) ^b	1.24 (-34.0%)	2.84 (11.4%)	3.29 (-5.2%)	BLYP-D3(ZD)/cc-pVDZ
QM/MM “small” (central) ^b	1.25 (-33.5%)	3.16 (23.9%)	3.75 (8.1%)	B3LYP/cc-pVDZ
QM/MM “large” (outermost) ^a	1.87 (-0.5%)	2.47 (-3.1%)	3.47 (0.0%)	B3LYP-D3(ZD)/cc-pVDZ
QM/MM “large” (central) ^b	2.00 (6.4%)	2.57 (0.8%)	3.37 (-2.9%)	B3LYP-D3(ZD)/cc-pVDZ
5,6,11,12-Tetrachlorotetracene				
Procedure and system	$\Delta X/\text{\AA}$	$\Delta Y/\text{\AA}$	$\Delta Z/\text{\AA}$	Method
Experimental	-0.32	1.08	3.63	
DFT on isolated dimer	-0.04 (112.5%)	1.18 (9.3%)	3.53 (-2.8%)	B3LYP-D3(ZD)/cc-pVDZ
QM/MM “small” (outermost) ^a	-0.28 (-12.5%)	1.01 (-6.5%)	3.55 (-2.2%)	B3LYP-D3(ZD)/cc-pVDZ
QM/MM “small” (central) ^b	-0.30 (-6.3%)	1.15 (6.5%)	3.52 (-3.0%)	B3LYP-D3(ZD)/cc-pVDZ
QM/MM “small” (central) ^b	-0.29 (-9.4%)	1.15 (6.5%)	3.57 (-1.9%)	B3LYP-D3(ZD)/cc-pVTZ
QM/MM “small” (central) ^b	-0.28 (-12.5%)	1.16 (7.4%)	3.56 (-1.9%)	B3LYP-D3(DZ)/6-31G*
QM/MM “small” (central) ^b	-0.29 (-9.4%)	1.15 (6.4%)	3.55 (-2.2%)	BLYP-D3(DZ)/cc-pVDZ
QM/MM “small” (central) ^b	-0.34 (6.3%)	1.19 (10.2%)	3.90 (7.4%)	B3LYP/cc-pVDZ
QM/MM “large” (outermost) ^a	-0.32 (0.0%)	1.08 (0.0%)	3.62 (-0.3%)	B3LYP-D3(ZD)/cc-pVDZ
QM/MM “large” (central) ^b	-0.29 (-9.4%)	1.15 (6.5%)	3.61 (-0.6%)	B3LYP-D3(ZD)/cc-pVDZ

^a) Displacements for the outermost MM dimer.

^b) Displacements for the central QM dimer.

^c) Atom-centered MM point charges taken from a B3LYP-D3(ZD)/cc-pVDZ ESP fit on the isolated dimer at the experimental geometry, constrained to give zero total charge on each monomer: see Figure 6.

Table 3:

Coronene			
Property	Isolated dimer	QM/MM “small”	QM/MM “large”
$\varepsilon_{L+1}/\text{a.u.}$	-0.0569	-0.0546	-0.0421
$\varepsilon_L/\text{a.u.}$	-0.0586	-0.0566	-0.0436
$\varepsilon_H/\text{a.u.}$	-0.1945	-0.1931	-0.1801
$\varepsilon_{H-1}/\text{a.u.}$	-0.1997	-0.1993	-0.1833
Δ_g/eV^a	3.70	3.71	3.71
t_h/meV^b	70.3	84.5	43.7
t_e/meV^c	23.9	27.0	21.1

5,6,11,12-Tetrachlorotetracene			
Property	Isolated dimer	QM/MM “small”	QM/MM “large”
$\varepsilon_{L+1}/\text{a.u.}$	-0.1047	-0.1074	-0.1084
$\varepsilon_L/\text{a.u.}$	-0.1084	-0.1095	-0.1105
$\varepsilon_H/\text{a.u.}$	-0.1916	-0.1936	-0.1950
$\varepsilon_{H-1}/\text{a.u.}$	-0.1990	-0.2014	-0.2018
Δ_g/eV^a	2.26	2.29	2.30
t_h/meV^b	100.5	106.6	91.9
t_e/meV^c	51.1	28.2	28.1

^{a)} $\Delta_g = \varepsilon_L - \varepsilon_H$.

^{b)} $t_h = (\varepsilon_H - \varepsilon_{H-1})/2$.

^{c)} $t_e = (\varepsilon_{L+1} - \varepsilon_L)/2$.

- **Figure 1.** Left: In-plane X and Y directions along which the displacements of the center of mass of one monomer are measured with respect to its nearest neighbour. The Z direction is that perpendicular to the XY plane shown. The displacements ΔX , ΔY , and ΔZ mentioned in the text are the projections of the vector joining the two center of mass along each of the X , Y , and Z directions. Right: partial charges used in the MM force field from a B3LYP–D3(ZD)/cc-pVDZ calculation of the monomer at the experimental geometry (only the values for the symmetry inequivalent atoms are shown). a) Coronene; b) 5,6,11,12-Tetrachlorotetracene.
- **Figure 2.** Unit cell of the coronene crystal showing the directions a , b and c , and several molecules of the crystal structure.
- **Figure 3.** Several coronene dimer geometries along direction b of the crystal: a) Experimental; b) isolated dimer B3LYP–D3(ZD)/cc-pVDZ optimized geometry; c) QM region from QM/MM “small” geometry optimization; d) outermost dimer in the MM region from QM/MM “small” geometry optimization; e) QM region from QM/MM “large” geometry optimization; f) outermost dimer in the MM region from QM/MM “large” geometry optimization. In all cases the QM part is modelled at the B3LYP–D3(ZD)/cc-pVDZ level, while the MM part uses the GAFF force-field.
- **Figure 4.** a) Portion of the experimental crystal structure of coronene used as starting geometry for the QM/MM “small” calculation. The QM part consists of a dimer along the b direction of the crystal, and it is depicted in “ball-and-stick” format. The MM part consists of 34 coronene molecules completely surrounding the QM dimer, and it is depicted in “bond” format. b) Optimized QM/MM “small” coronene structure with the QM part modelled at the B3LYP–D3(ZD)/cc-pVDZ level, and the MM part using the GAFF force-field.

- **Figure 5.** Energy profile for the last 3 QM-MM combined steps of a coronene QM/MM “small” geometry optimization using the B3LYP–D3(ZD)/cc-pVDZ scheme for the DFT calculation of the QM part. To ease the visualization both the energy and the displacements are plotted relative to the corresponding values obtained for the optimized structure.
- **Figure 6.** Partial charges from a B3LYP–D3(ZD)/cc-pVDZ ESP fit on the coronene dimer at the experimental geometry, constrained to give zero total charge on each monomer.
- **Figure 7.** Optimized QM/MM “large” coronene structure with the QM part modelled at the B3LYP–D3(ZD)/cc-pVDZ level, and the MM part using the GAFF force-field. The QM part consists of a dimer along the b direction of the crystal, and it is depicted in “ball-and-stick” format. The MM part consists of 148 coronene molecules completely surrounding the QM dimer, and it is depicted in “bond” format.
- **Figure 8.** Unit cell of the 5,6,11,12-Tetrachlorotetracene crystal showing the directions a , b and c , and several molecules of the crystal structure.
- **Figure 9.** Several 5,6,11,12-Tetrachlorotetracene dimer geometries along direction a of the crystal: a) Experimental; b) isolated dimer B3LYP–D3(ZD)/cc-pVDZ optimized geometry; c) QM region from QM/MM “small” geometry optimization; d) outermost dimer in the MM region from QM/MM “small” geometry optimization; e) QM region from QM/MM “large” geometry optimization; f) outermost dimer in the MM region from QM/MM “large” geometry optimization. In all cases the QM part is modelled at the B3LYP–D3(ZD)/cc-pVDZ level, while the MM part uses the GAFF force-field.
- **Figure 10.** a) Portion of the experimental crystal structure of 5,6,11,12-Tetrachlorotetracene used as starting geometry for the QM/MM “small” calculation. The QM part consists of a dimer along the a direction of the crystal, and it is depicted in “ball-and-stick” format. The MM part

consists of 26 coronene molecules completely surrounding the QM dimer, and it is depicted in “bond” format. b) Optimized QM/MM “small” 5,6,11,12-Tetrachlorotetracene structure with the QM part modelled at the B3LYP–D3(ZD)/cc-pVDZ level, and the MM part using the GAFF force-field.

- **Figure 11.** Optimized QM/MM “large” 5,6,11,12-Tetrachlorotetracene structure with the QM part modelled at the B3LYP–D3(ZD)/cc-pVDZ level, and the MM part using the GAFF force-field. The QM part consists of a dimer along the a direction of the crystal, and it is depicted in “ball-and-stick” format. The MM part consists of 148 coronene molecules completely surrounding the QM dimer, and it is depicted in “bond” format.

a)

b)

Figure 1:

Figure 2:

Figure 3:

Figure 4:

Figure 5:

Figure 6:

Figure 7:

Figure 8:

a)

b)

c)

d)

e)

f)

Figure 9:

Figure 10:

Figure 11:

DFT isolated

QM/MM

Exact

Graphical Abstract

Highlights

- Geometry optimizations using dispersion-corrected DFT on isolated dimers of several organic crystals differ significantly from the experimental ones.
- This is caused by the absence of the surrounding monomers present in the crystal, because it can be corrected when the dimer is treated as the Quantum Mechanics (QM) part of a Quantum Mechanics/Molecular Mechanics (QM/MM) geometry optimization.
- The chosen combination of B3LYP–D3(ZD)/cc-pVDZ method for the QM part, and the GAFF force field for the MM part, performs quite reasonably for the systems analyzed in this work.