Molecular Modeling

Hybrid Organic–Inorganic Frameworks: Routes for Computational Design and Structure Prediction**

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The controlled synthesis of materials with very large pores is an ongoing challenge in the area of materials science. Research into large-pore materials is fueled by their use in catalysis, gas storage, and separation.[1] After intense development of inorganic frameworks in the early 1990s,[2] the subsequent discovery of hybrid porous solids, in which the connection of inorganic moieties is ensured by organic functionalized N-donor or O-donor molecules, paved the way for the rational design of hybrid frameworks.[3–11] A new class of materials has emerged at the crossroads of inorganic materials science and coordination chemistry. Among the most illustrative examples of open frameworks are the zinc carboxylate series by Yaghi, O'Keeffe, and co-workers, and the transition-metal terephtalates that have remarkable methane- and hydrogen-storage properties,[12] together with, for example, a recent series of 3d transition-metal[13a,14] and rare-earth[15]-based hybrids that exhibit interesting magnetic properties.[13a] The richness of this area lies in the diversity of topologies (from molecular to 3D) and properties, which is conveyed in the wide choice of metal atoms that are available, combined with a virtually infinite choice of organic counterparts (e.g., carboxylates, phosphonates, polyamines).

In the current search for new and interesting hybrid open frameworks, the predictability of the framework architecture and the control of its dimensionality are essential, even if one is confronted with the underlying issue of polymorphism.[6] The possibility of rational design with these types of solids has rapidly emerged through the use of topological and chemical considerations on existing networks.[7] The concept of rational design is rooted in the fact that topochemically selected reactions govern the construction process of the hybrid framework under hydrothermal conditions. Although metal-containing secondary building units (SBUs) may not be isolated, their recurrence in a large number of structures suggests that the targeted inorganic subunit already exits in solution before their condensation into the framework structure and thus may be obtained under appropriate synthetic conditions. For example, this aspect is apparent through the *iso*-reticular synthesis of IRMOFs1–16[12b] derived from the prototypic MOF-5 structure.[12a]

In this context, structural prediction is an important issue. It is crucial to consider how systematic approaches might be computationally developed for producing new hybrid frameworks, with the desire of developing virtual libraries that might be accessible by rational synthesis.

It is worth underscoring here that crystal-structure prediction is now routinely explored in organic chemistry and polymer science,[16,17] in which candidate structures may be predicted by assembling molecular entities through hydrogen-bond intermolecular interactions. In contrast, such developments have only been recently reported for inorganic crystal structures, which are extremely difficult to predict due to their infinite lattices. Pioneered by Newsam et al. in the field of zeolites,[18] crystal-structure prediction[18–28] and rational design[29–31] are now at work in the field of open frameworks. Due to their ability to cross hypersurface energy barriers and search for low-energy regions, global optimization techniques are intensively used to predict atomic-scale arrangements of infinite lattices and are able to handle the assembly of atoms, ions,[20,22–25] or predefined building units in three dimensions.[21,27,28]

We have introduced the concept of building units for the computational prediction of crystal structures with the AASBU method (automated assembly of secondary building units).[21,27,28] This method explores the possible ways of assembling predefined inorganic building units, and focuses on the topology of network-based structures.

Inspired by these recent developments, we present herein the extension of the AASBU method to the realm of hybrid organic–inorganic frameworks and demonstrate its capacity to produce hybrid candidate crystal structures that are built from predefined organic and inorganic counterparts. To our knowledge, no systematic computational strategy has been reported in this field so far.

Indeed, hybrid frameworks offer ideal features for computational developments: although the isolated metal ion, taken alone, lacks directional information, the inorganic unit derived from the metal atom and the organic ligand does (Figure 1). Once the inorganic and organic units are defined, one may assume that there are a limited number of arrangements that are compatible with periodicity and symmetry. With predefined organic and inorganic building units, AASBU simulations are used here to perform their automated assembly in three dimensions, thus exploring the possibilities of connection. The simulations yield a virtual library of candidate hybrid frameworks that are assorted by their space group, cell parameters, and atomic positions.

Our initial efforts were aimed at validating the AASBU approach in the field of hybrid frameworks by simulating existing architectures. In the second instance, we aimed at predicting structures that have not yet been synthesized, both to tackle the issue of polymorphism by limiting the domain of

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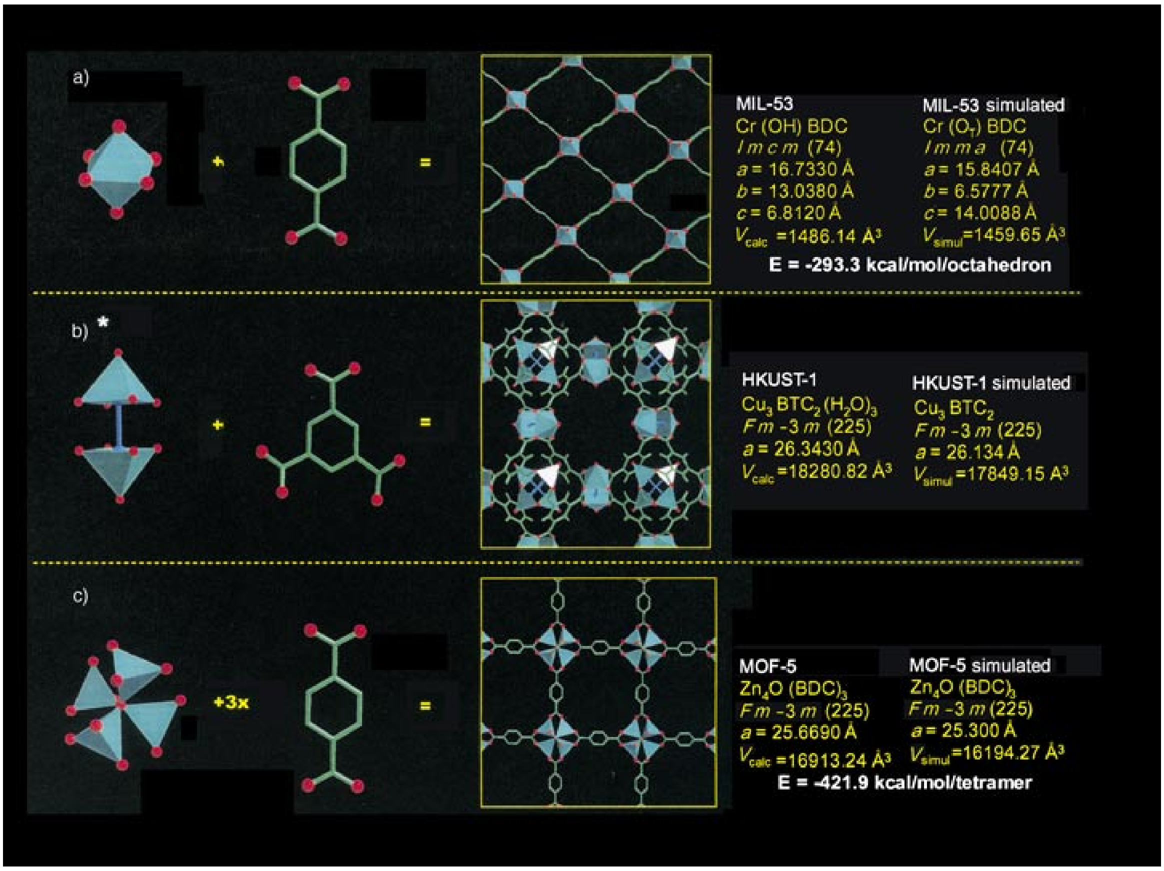

Figure 1. Left: Examples of mono-(a), di-(b), and tetrameric (c) metal clusters and organic carboxylate ligands commonly found in hybrid frameworks. Right: For each organic/inorganic combination, an example of existing very open framework is shown. (*) The lattice energy of HKUST-1 could not be easily estimated due to the Cu–Cu metal bond and therefore the difficulty of estimating partial charges on Cu atoms.

structures that are possible for a given metal–organic-ligand pair, and to aid the often-difficult task of crystal-structure determination.

In the computational approach that we have developed, the inorganic and organic counterparts may be treated as two different building units, or encapsulated in a single hybrid building block. Both approaches were explored. The preliminary step consists of the elaboration of a suitable library of SBUs, which we directly extracted from known and typical hybrid frameworks (Figure 1). The inorganic unit is modeled by a rigid body, ($\{M_xL_y^{\text{inorg}}\}$; M: metal centers; L^{inorg}: ligand atoms of the inorganic units). The organic unit is treated as a flexible body, ($C_nL_m^{\text{org}}$; C: carbon skeleton, L^{org}: ligand atoms of the organic units such as oxygen atoms of carboxylate functions). The computational assembly is further controlled through the use of predefined "sticky-atoms": all ligand atoms on both the organic and inorganic units, L^{inorg} and L^{org}, are defined as equally possible linkage points.

The rules that control the possible assembly of the organic and inorganic building units during the subsequent simulation steps are encapsulated in a forcefield that includes "sticky-atom" pairs. They are parameterized on an atom–atom basis by a simple Lennard–Jones expression for the energy of interaction between pairs of atoms i and j, as defined in Equation (1):

$$E_{ij} = \varepsilon_{ij}\,[(r^*_{ij}/r_{ij})^{12} - 2\,(r^*_{ij}/r_{ij})^{6}] \qquad (1)$$

The $L^{\text{org}}\cdots L^{\text{inorg}}$ sticky-atom pairs are those that form the organic–inorganic linkages, parameterized as a highly attractive potential well with a minimum at very short $L^{\text{org}}\cdots L^{\text{inorg}}$ separations. Similarly, $L^{\text{inorg}}\cdots L^{\text{inorg}}$ sticky-atom pairs are those that form inorganic–inorganic clusters. A repulsive potential between $L^{\text{org}}\cdots L^{\text{org}}$ pairs avoids overlapping or connections of organic molecules to one another (Table 1). This potential serves simply to "glue" together organic and inorganic units according to general criteria. The total cost or energy of a given arrangement of organic and inorganic building units in a unit cell, E_{total}, is calculated as the sum over the set of building units of the Lennard–Jones terms [Eq. (1)] that involve

Table 1: Lennard–Jones (L.–J.) parameters used in the AASBU simulations for assembling BDC and octahedral metal centres $\{ML_6\}$.[a]

Atom pairs	L.–J. potential	ε_{ij} [kcal mol^{-1}]	r_{ij} [Å]
$L^{\text{inorg}}\cdots L^{\text{org}}$	attractive	1000	0.2
$L^{\text{inorg}}\cdots L^{\text{inorg}}$	attractive	1000	0.2
$L^{\text{org}}\cdots L^{\text{org}}$	repulsive	1	2.2

[a] The potential parameters that ensure the intramolecular flexibility (bond, angle, torsions) of the organic ligand during the AASBU simulations are given in the Supporting Information.

dissimilar pairs of atoms, plus a term relating to the intramolecular energy of the flexible organic unit, as defined in Equation (2):

$$E_{\text{organic}} = \sum\nolimits_{\text{atoms}} (E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}}) \text{ with}$$
$$E_{\text{bond}} = \frac{1}{2} k_{ij} (r_{ij} - r_o)^2,\ E_{\text{angle}} = \frac{1}{2} k_{ijk} (\theta_{ijk} - \theta_{\text{O}})^2,\ E_{\text{torsion}} \tag{2}$$
$$= \frac{1}{2} \sum\nolimits_n \text{B} \left(1 - \text{d}\cos(n\, \varphi_{ijkl})\right)$$

The cost function used here is not an expression of the internal energy of the system, but simply evaluates its degree of connectivity.

Minimal amount of input data is required for a given simulation: the number of organic units per asymmetric unit, the number of inorganic units per asymmetric unit (alternatively the number of hybrid building blocks), and optionally the space group, as in the most general case simulations may be performed in $P1$. The simulations are not constrained by the cell dimensions. The number of independent entities (organic versus inorganic) is the key input parameter restricting the subsequent search within structures that have the desired metal:organic ratio. This method is therefore adequate for searching polymorphs of hybrid frameworks.

The computational steps for generating candidate periodic hybrid structures are performed by using the AASBU method.[27] The main steps are summarized below, further details may be found in reference [27]: 1) periodic trial arrangements of organic and inorganic units are generated by using a simulated annealing Monte Carlo procedure within the imposed space group and the imposed number of organic and inorganic units per asymmetric unit. At this stage, the stored configurations correspond to unconnected organic and inorganic units in 3D space. 2) Each unique arrangement is minimized with respect to the total cost function [Eqs. (1) and (2)]. This is a key step at which the assembly of inorganic and organic units (or alternatively hybrid building blocks) through the predefined linkage points is performed, which possibly leads to periodic connected hybrid arrangements. At this step, the flexibility of the organic unit is crucial to make adequate connections to the inorganic units. 4) Sticky-atom pairs, $L^{\text{org}}\cdots L^{\text{inorg}}$ and $L^{\text{inorg}}\cdots L^{\text{inorg}}$, are reduced to a single atom. Realistic predictions of crystal structures are thus produced. The symmetry of each candidate hybrid structure is redetermined by using the Find_Symmetry algorithm.[32]

The AASBU simulation steps were performed by using the Polymorph Predictor of the Cerius2 program.[33] The simulations are left with a list of candidate hybrid structures (space group, cell, atomic positions). A typical calculation requires from around 2 h for "mixing" one simple inorganic unit and one organic molecule per asymmetric unit up to more than 16 h for assembling a more-complex hybrid building block on an Octane SGI R12000 workstation operating at 300 MHz.

As a final step to estimate the stabilities of the hybrid candidates, lattice-energy minimizations were performed on each candidate crystal structure. Short-range interactions were calculated by using the UFF forcefield.[34] The electrostatic contribution was calculated with an Ewald summation by using partial charges obtained from the charge-equilibration method.[35]

With the purpose of demonstrating the viability of our approach in the area of hybrid frameworks, we first focused our efforts on the simulation of existing and well-characterized hybrid frameworks. A limited number of very-large-pore hybrids were chosen as prototypic structures, such as **MIL-53** (M(OH)(BDC), BDC = benzene-1,4-dicarboxylate, M = V^{3+},[36a] Cr^{3+}[36b] or Al^{3+}[36c]), **HKUST-1** ($Cu_3(BTC)_2(H_20)_3$; BTC = benzene, 1,3,5 tricarboxylate),[37] and MOF-5 ($Zn_4O(BDC)_3$)[12a] (Figure 1), that is, with the specific aim of predicting their full crystal structure by using the related inorganic unit (monomer, dimer, tetrameric respectively) and organic ligand.

A first possible approach consists in computationally assembling independent organic and inorganic units. This mixture approach was explored in the case of the monomeric, trimeric, and tetrameric metal clusters. In the case of the dimeric metal cluster an approach with a hybrid building block is presented below. For example, a series of AASBU simulations were performed with one single octahedron per asymmetric unit, in which the six ligand atoms were possible linkage points, together with one BDC molecule per asymmetric unit in which the four oxygen atoms were defined as possible linkage points thus ensuring a 1:1 metal:organic ratio. Various space groups were sampled: $P1$, $P\bar{1}$, Cc, $Pna2_1$, $P3$, $P\bar{3}$, $P4$, $P\bar{4}$, $P6$, and $P\bar{6}$. The **MIL-53** topology was produced in space group Cc among a list of 54 candidates, with the final high symmetry, $Imma$, in excellent agreement with that of the experimental structure, ($Imcm$)[36c](See Figure 1 a). Interestingly, **MIL-53** belongs to the class of flexible networks that exhibit a very large breathing effect upon water adsorption/removal, which results in important changes in the symmetry and cell size (hydrated:$C2/c$; calcined:$Imcm$).[36c] Interestingly, the simulations performed here in the absence of extraframework species (i.e., water) yield the **MIL-53** topology in its high symmetry form, which is indeed the symmetry of the experimental calcined (water-free) structure.

When this method was adopted for each inorganic and organic units in the required ratio, the expected metal–organic frameworks were generated (Table 2, Figure 1, and Figure 2). An illustrative example was tackled with the tetrameric units found in the prototypic **MOF-5** (Figure 1 b).[12a] AASBU simulations were performed by mixing one single tetrameric unit, $\{M_4(\mu_3\text{-}O)(L_3)_4\}$, defined with 12 possible linkage points, and 3 BDC molecules per asymmetric unit, defined with 3 × 4 possible linkage points. During the simulations steps, only connections between the inorganic unit and the BDC molecules were allowed, while preventing inorganic–inorganic connections with repulsive parameters. The **MOF-5** topology was predicted successfully and appeared in space group $Aba2$, which was ranked the lowest-energy structure among a list of 115 candidates. Indeed, only the first two candidates corresponded to plausible inorganic–organic frameworks: the framework adopts the topology in which $\{M_4(\mu_3\text{-}O)(L_3)_4\}$ tetramers are connected through twelve $L^{\text{inorg}}\cdots L^{\text{org}}$ interactions to six carboxylates in the octahedral directions to form the expected

Table 2: AASBU simulations of experimentally known hybrid frameworks.

Organic and inorganic units	Organic/inorganic ratio imposed	Initial space group[a]	Predicted structure	Final space group[a]	Ref.
BDC + $\{ML_6\}$	1:1	*Cc*	**MIL-53**	*Imma*	[36]
BDC + $\{M_4(\mu_3\text{-}O)L_{12}\}$	3:1	*Aba*2	**MOF-5**	$Fm\bar{3}m$	[12a]
Hybrid building-block	Organic/inorganic ratio imposed	Initial space group[a]	Predicted structure	Final space group[a]	Ref.
$\{M_6(BTC)_4\}$[b]	3:2	*C*2	**HKUST-1**	$Fm\bar{3}m$	[37]
$\{M_6(BTC)_4\}$[b]	3:2	$Fd\bar{3}m$	**MIL-100**	$Fd\bar{3}m$	[41]

[a] We make a distinction between the space group as imposed during the AASBU simulations themselves (initial space group) and the space group as obtained from the final symmetry analysis of the simulated structures (final space group). They may be different as arrangements of higher symmetry than that imposed may be produced. [b] The building blocks are built with 12 metal centers (4 trimeric clusters or 6 dimers). However, each dimeric (or trimeric) metal cluster is parameterized to be half-shared with another building block, hence the reported composition of 6 metal centers per building block.

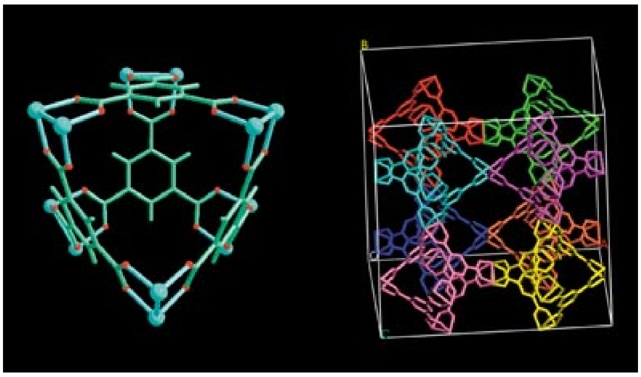

Figure 2. Left: Hybrid building blocks derived from $[\{Cu_3(BTC)_2(H_2O)_3\}_n]$.[37] This is an octahedral unit where $\{Cu_2\}$ dimers are placed at the six vertices. The four BTC molecules are placed at four of the eight triangular faces of the octahedron. Right: The expected **HKUST-1** structure was computationally generated by self-assembling the hybrid building block (different colors are used for each building block).

porous cubic structure. The lattice energy minimizations, the simulated cell parameter, and symmetry (25.3 Å, $Fm\bar{3}m$) of the first candidate are in excellent agreement with the experimental findings (25.67 Å, $Fm\bar{3}m$).

An interesting alternative to the computational mixture of independent organic and inorganic units (see above) is to consider a single hybrid building block and to allow its self-assembly during the subsequent simulation steps. This approach, which has the advantage of being directly inspired by the concept of secondary building blocks used by synthesis chemists for the design of targeted networks, was explored with a paddle-wheel cluster that is known in many complexes[38] and was involved in the synthesis of hybrid frameworks.[7a,37] We started from the SBU proposed by Williams and co-workers in the description of the 3D hybrid framework, **HKUST-1**.[37] As illustrated in Figure 2, the $\{Cu_2\}$ dimers were placed at the vertices of an octahedral unit while being interconnected through BTC molecules placed at four of the eight triangular faces of the octahedron. During the AASBU simulations, this hybrid building block was allowed to self-assembly by direct edge sharing at the Cu–Cu metal bond. By using two building blocks per asymmetric-unit, we successfully simulated and energy minimized the expected **HKUST-1** structure in the initial space group *C*2, which lead to a crystal structure with the expected symmetry $Fd\bar{3}m$ and cell parameters ($a_{\mathrm{sim}} = 26.134$ Å/$a_{\mathrm{exp}} = 26.343$ Å).

When compared to the first approach, which mixes independent organic and inorganic units, the hybrid building block inherently contains additional structural information on organic–inorganic connections. While obviously requiring an advanced knowledge of the system under study, this approach should in principle allow a more restricted (i.e., more rapid) production of viable hybrid candidates.

An attractive feature of the simulations is indeed the generation of new topologies. Typically, while assembling one $\{MO_6\}$ octahedron and one BDC molecule (section above), not only the experimentally known **MIL-53** structure was predicted but also a series of not-yet-synthesized topologies ranging from lamellar to 3D extended structures. Figure 3 shows a selection of three hypothetical structures chosen for their serendipitous topological relationships. The three structures derive from the same layer (Figure 3a) and differ only by the degree of "condensation" of the sheets: the stacking of unconnected sheets builds the first structure (Figure 3b), while the second (Figure 3c) shows stacking of dimerized-planes. The third structure has a 3D network (Figure 3d) that results from the infinite stacking of the planes. Another interesting 3D hexagonal structure was produced (Figure 4a), which exhibits large tunnels (∅ = 15,6 Å). These candidates illustrate how simulations may be a valuable tool for highlighting topological relationships.

On the other hand, the number of hybrid structures that contain trimeric metal clusters formed by the assembly of three vertex-sharing octahedra is very scarce.[7b,39] For this reason, our group has recently focused on their chemical condition of existence in hydrothermal synthesis.[40] By using our computational approach to encapsulate the trimeric metal cluster and BDC (or BTC) molecules in a hybrid building block, we simulated a whole series of plausible and very open frameworks.

Figure 4b–c show two hypothetical topologies generated by using a building block that contains BDC and trimeric metal clusters. These topologies represent cubic polymorphs with large cell volumes, 23579 Å^3 and 64524 Å^3, and have central cages with an internal diameter of 25 Å, accessible through "four rings" of trimers. A detailed study on this new family of polymorphs will be published elsewhere. [41]

Most interestingly, one of the trimeric BTC-based hybrid polymorph (Table 2) has a giant unit cell and exhibits a

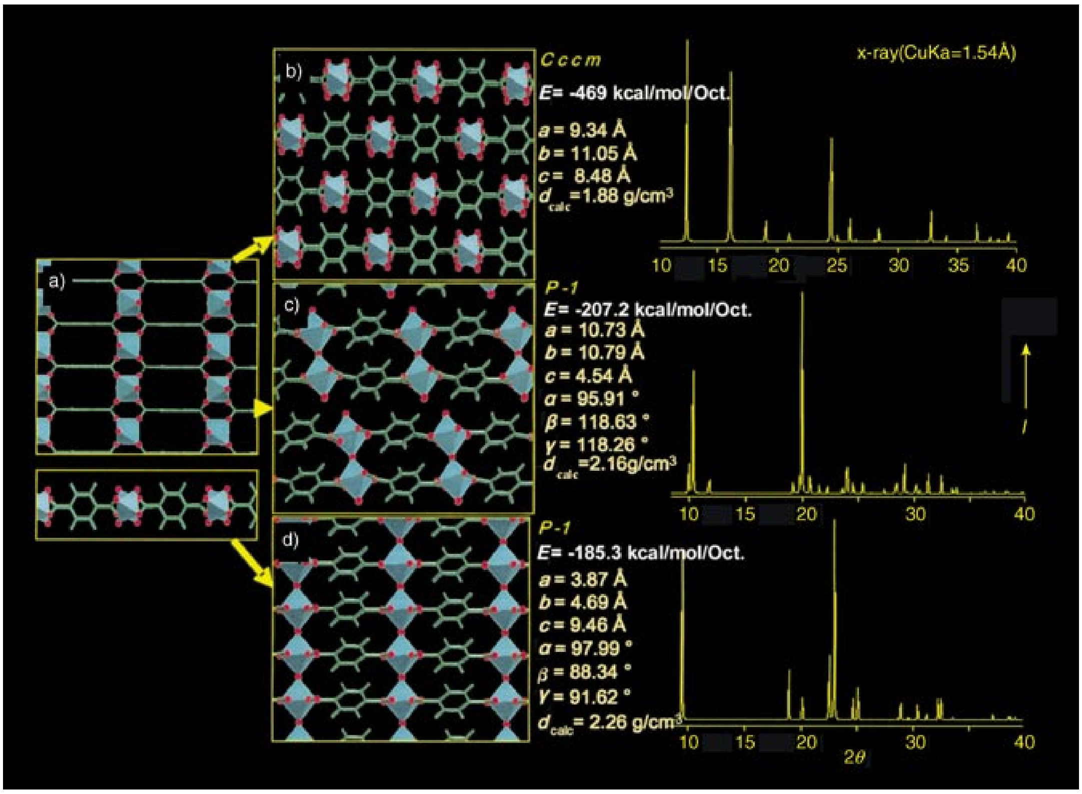

Figure 3. Topological relationships between three simulated hybrids that were obtained by assembling one BDC molecule and one octahedron per asymmetric unit. The three structures are built from the same plane (top and side view in a), which range from lamellar (b and c) to 3D networks (d). *I*: intensity (arbitrary units).

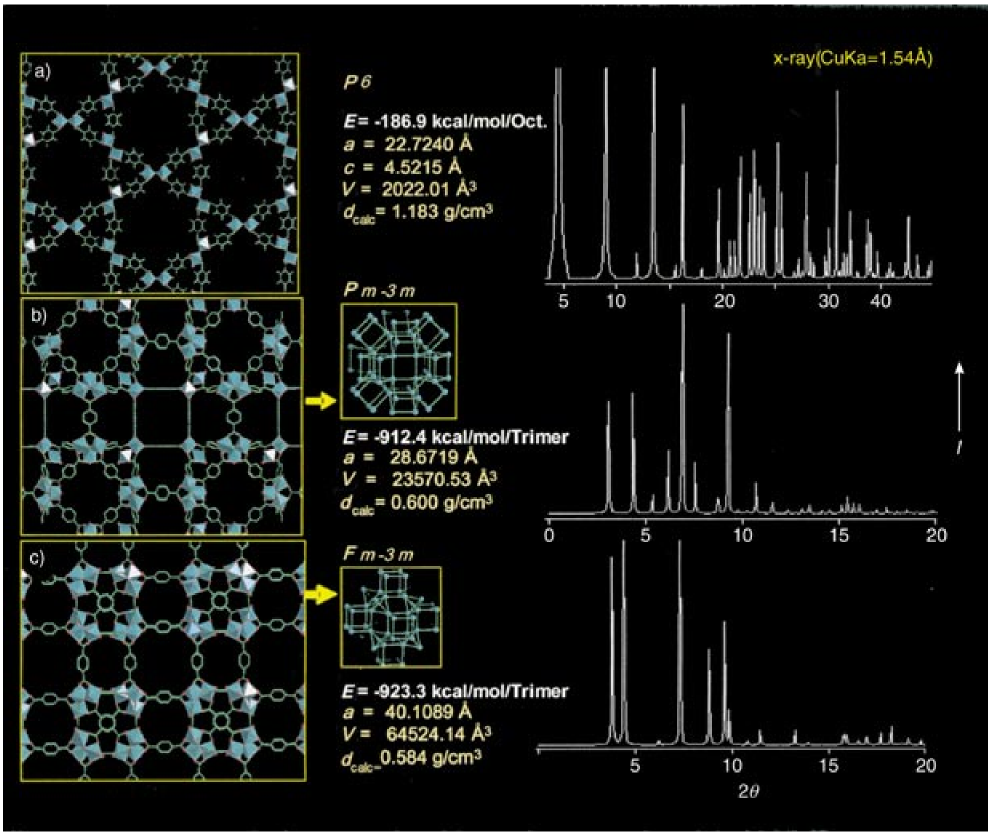

Figure 4. Hypothetical very-open hybrid frameworks, simulated by assembling BDC with a single octahedron (a), and with trimeric metal clusters (b) and (c).

simulated diffraction pattern that exactly matched the experimental pattern of a new phase synthesized in our group, MIL-100. Thus we obtained the solution of its direct-space structure and ensured a valid model for subsequent structure refinement.[42]

In conclusion, this work addresses the computational prediction of hybrid organic–inorganic extended lattices. The production of candidates of crystal structures was successfully performed by direct-space assembly of building units by the AASBU method, either through mixing independent organic and inorganic units or by assembling predefined hybrid building blocks. Hybrid candidates that are compatible with the imposed metal:organic ratios were generated with their cell parameters, space group, atomic positions, along with their simulated diffraction pattern and an estimate of their lattice energies. Since no explicit limit regarding the nature, number, and size of the inorganic and organic units, or hybrid building block is involved, the method offers boundless potential for exploring hybrid frameworks in terms of the topological diversity.

The most appealing development arises from the computer-assisted design of hybrid frameworks. Indeed, in a significant number of systems, it is well-known that controlled synthesis conditions can promote the occurrence of specific building units, which serve to "propagate" the infinite crystal structure. We believe that the computational approach presented herein is valuable to create virtual libraries of viable hybrid polymorphs. Furthermore, AASBU simulations have proven to be, for the first time in the realm of hybrids, a tangible route towards structure solution in direct space.[42] This challenging area is of crucial interest when high quality diffraction data are not available or when very large cell sizes are involved. The development of a structural model in direct space, starting with minimal knowledge such as the metal: organic ratio, is shown to be possible. With such a method in hand, formerly intractable structural problems when using methods based on conventional reciprocal space become feasible in direct space.

We believe this approach serves a step forward in the computational anticipation and structure solution of hybrid frameworks. It should allow one to tackle the issue of polymorphism, while opening up the field of synthesis of new hybrid frameworks and structure solution for compounds that have not yet been characterized.

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