Fullerene in a Metal-Organic Matrix: Design of the Electronic Structure

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We present a theoretical study of a new hybrid compound, where the C_{60} molecules are encapsulated in a recently discovered metal-organic framework (MOF). Being placed in a rigid skeleton, the fullerene molecules form a cubic crystal, while the intermolecular distance of the fullerenes is tuned by the choice of appropriate organic linkers of the MOF structure. The resulting C_{60} crystal shows a density of conduction states considerably higher than any of the fullerene crystals considered so far, which is a key factor influencing the transition temperature of the superconducting state. This constitutes a new approach of tuning the density of states of a fullerene crystal.

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For over a decade, there has been significant effort directed towards exploring the physical and chemical properties of fullerenes like C_{60} [1], C_{36} [2], and even C_{28} [3]. Of particular interest are reports of superconductivity in potassium- and rubidium-doped C_{60} crystals and films [4,5]. The transition temperatures T_c for K-doped C_{60} (18 K) and Rb-doped C_{60} (28 K) are significantly higher than those reported previously for other molecular superconductors. There is also experimental evidence suggesting transition temperatures from 30 to 40 K for the Cs-doped C_{60} compound [6–8].

For systems, where the superconductivity originates from electron-phonon interaction, the transition temperature can be estimated from McMillan's formula [9]:

$$T_c = \frac{\omega_{\log}}{1.2} \exp\left[\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right], \tag{1}$$

where $\omega_{\log}$ is a typical (logarithmic average) phonon energy, μ^* is the effective electron-electron repulsive interaction, and $\lambda = N_F V_{\mathrm{ep}}$ is the electron-phonon coupling constant [10]. The value of λ is directly proportional to the electron-phonon interaction potential V_{ep}, as well as to the density of states at the Fermi level N_F. The density of states in a particular band increases with a reduction of a dispersion of the band, and so the ideal superconducting system should have the weakest possible band dispersion, while still allowing the overlap of the wave functions of the neighboring molecules to ensure the possibility of the electronic transport. One way to achieve this effect is to enlarge a lattice parameter of the system. This can be performed, for example, by introducing large alkali ions in the interfullerene spaces of the fcc C_{60} crystals [1,4–8] or haloform molecules in a hcp C_{60} crystal [11,12].

Other ways to force a bigger lattice parameter of a C_{60} crystal can be envisioned, for example, by using any external skeleton structure, which, being of a microporous type, can accommodate the C_{60} molecules. However, several strict conditions should be fulfilled in order to obtain a crystal with good superconducting properties using this type of approach. First, this framework structure should form a perfect crystal in order to obtain a periodic arrangement of the fullerene molecules, as well as it should provide a reasonable distance between the fullerenes. Second, the skeleton itself should not interact significantly with the C_{60} molecules to ensure minimum changes in the first conduction states of the fullerene crystal. And third, the resulting hybrid compound should provide possibilities to be effectively doped to populate the conduction states of the C_{60} crystal.

In this Letter we present an *ab initio* study of this type of hybrid compound, where the fullerene molecules are encapsulated in an external matrix structure. We demonstrate that the recently discovered metal-organic framework (MOF) are ideal candidates for such a kind of a skeleton structure. After being slightly modified, the MOF structure can accommodate the C_{60} molecules with a desired intermolecular distance. The resulting system is stable and after being doped will show a density of states at the Fermi level considerably higher than any of the fullerene crystals known so far.

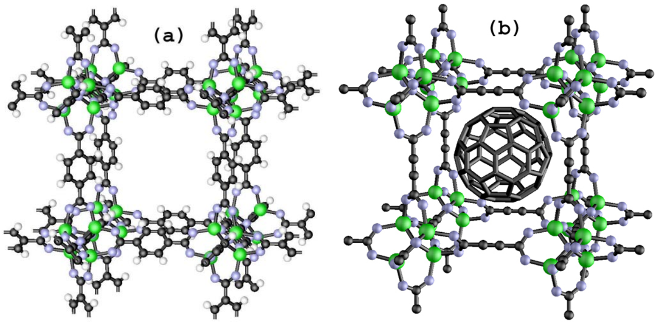

FIG. 1 (color online). (a) The cubic unit cell of the MOF-5 crystal structure. (b) Modified MOF structure, where the 1,4-benzenedicarboxylate linker was replaced by a 2-butynediodate molecule. The small black spheres are the carbon atoms. The large and small gray spheres are the zinc and oxygen atoms, respectively. The white spheres in panel (a) correspond to the hydrogen atoms of the benzene molecule.

The idea of a microporous MOF was put forth by Li *et al.* [13] as a promising material for gas storage, in particular, hydrogen. One of these structures, MOF-5 [chemical formula $Zn_4O(1,4\text{-benzenedicarboxylate})_3$] is presented in Fig. 1(a). This system was synthesized in 1999 by the group of Yaghi, and was actively studied experimentally as a potential hydrogen storage material [14]. One of the particularly interesting properties of the MOF is the possibility of tuning its lattice parameter (and thus the cage sizes) by changing the type of the organic intercage linkers and the *ab initio* approach is an effective tool to explore the properties of existing or possible structures.

Our calculations were performed within the generalized gradient approximation (GGA) [15] to the density-functional theory (DFT) [16]. The valence electrons were treated explicitly, while the interactions of the core electrons with atomic nuclei were described by norm-conserving pseudopotentials [17]. We used the SIESTA program package [18], which is a self-consistent DFT code employing numerical atomic orbitals as a basis set. A well-converged basis set, consisting of doubled $\{s, p_x, p_y, p_z\}$ orbitals plus polarization orbitals of d type was used. In order to verify the quality of the local basis set, some test calculations were also performed using the ABINIT [19] code, which uses plane waves as a basis set. All systems under study were fully relaxed both with respect to the cell size and atomic positions. A $2 \times 2 \times 2$ special **k**-point sampling [20] of the Brillouin zone showed good results for structural relaxations, while a finer $4 \times 4 \times 4$ grid was used for calculation of electronic properties.

The MOF-5 crystal [Fig. 1(a)] has an fcc structure with the center-to-center intercage distance of 12.72 Å. Our calculations demonstrated that this distance is too large to ensure the overlap of the C_{60} wave functions. The reason for this is the length of the intercage linkers, which are the 1,4-benzenedicarboxylate molecules in case of the MOF-5 structure [Fig. 1(a)]. Our study shows that replacing this linker by a 2-butynediodate molecule significantly reduces the intercage distance. The resulting crystal [Fig. 1(b)] has a simple cubic structure with a lattice parameter of 11.4 Å, and, consequently, the same distance between the centers of the neighboring cages. This distance is more than 1 Å larger than the interfullerene distance in the Cs_3C_{60} crystal (10.3 Å). If the fullerene molecules are introduced in this structure, we may still expect to have an overlap between the C_{60} wave functions, while the large intermolecular distance should give us a high density of electronic states. We should note here that this empty modified MOF-5 structure is in progress and the experimental results will be given in a forthcoming publication [21].

The cohesive energy of the C_{60}@MOF system, taking as a reference the energy of the empty MOF structure and the isolated C_{60} molecule, is calculated to be 0.3 eV per fullerene molecule, which demonstrates that the system is stable [22]. We plot in Fig. 2(a) the band structure of C_{60}@MOF along the high-symmetry directions of the Brillouin zone. The introduction of the C_{60} molecules leads to the formation of new fullerene-induced bands in the band gap of the host structure [shown by the dashed lines in Fig. 2(a)]. These fullerene bands do not hybridize with the bands of the MOF structure, and hardly change the topology of the bands of the host compound. For example, the band gap of the empty MOF structure is 4.1 eV (DFT-GGA value), and is left practically unchanged by the presence of the C_{60} molecules. This demonstrates that the fullerene-host interaction is of pure van der Waals type.

To get further insight, we present in Fig. 2 the calculated total density of electronic states (DOS) for C_{60}@MOF as well as the DOS, projected on certain atomic orbitals (PDOS) of the fullerene molecule and the host compound. We observe that the bands, originating from the valence band maximum (VBM) and conduction band minimum (CBM) or the empty MOF hardly contain any admixture of the C_{60} orbitals. As previously noted, the introduction of the C_{60} in the MOF structure leads to the formation of three groups of bands, which fit in the band gap of the host structure, and are formed only by the C-$2p$ states of the fullerene molecule [Fig. 2(c)]. As a result, the VBM and CBM of the resulting C_{60}@MOF compound are formed only by the fullerene-induced bands, which originate, respectively, from h_u and t_{1u} orbitals of the fullerene molecules. The band gap of the C_{60}@MOF system is calculated to be 1.5 eV and is very close to the energy separation of the h_u and t_{1u} orbitals in the C_{60} molecule (1.6 eV DFT-GGA value). At the same time the observed dispersion of the

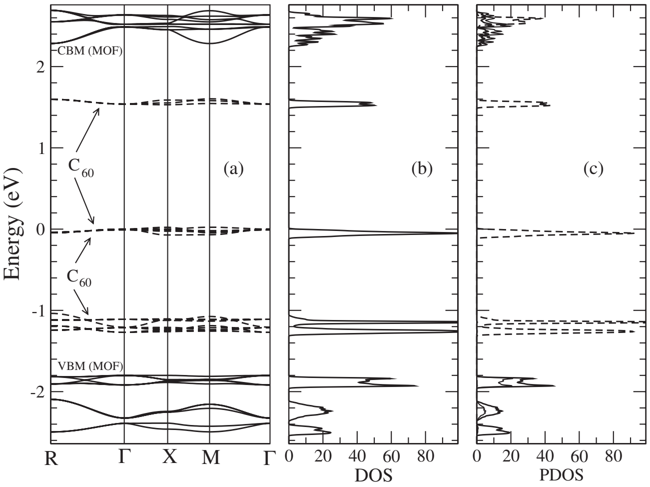

FIG. 2. (a) Electronic band structure of the C_{60}@MOF system. The dashed lines show the fullerene-induced bands in the band gap of the host framework. (b) Total density of electronic states. (c) Density of electronic states, projected on certain atomic orbitals. The solid thick and thin lines show a contribution of O-$2p$ and C-$2p$ orbitals, respectively, which belong to the atoms of the host structure. The dashed line corresponds to the fullerene C-$2p$ orbitals. DOS and PDOS values are given in states/eV/spin.

energy bands is of the order of 0.1 eV, which is considerably smaller than in solid C_{60} crystal with the fcc structure (~ 0.5 eV) [1]. This is due to a considerably larger interfullerene distance in the C_{60}@MOF structure. While in the solid C_{60} crystal the center-to-center interfullerene distance is 10 Å, in the C_{60}@MOF structure this distance increases up to 11.4 Å.

The reduction of the energy band dispersion, caused by the increase of the distance between the C_{60} molecules, leads to a significant increase of the density of electronic states of the fullerene network. This effect is especially important for t_{1u}-originating conduction bands, which being populated will determine the superconducting properties of the system. Figure 3 shows a wave function of the first conduction band of the system, calculated at the Γ point. As expected, this wave function is localized on the C_{60} subsystem, and the intermolecular overlap ensures the possibility of charge transfer through the fullerene network. This directly confirms our earlier predictions based on the band structure analysis. To complete our study, we performed high precision calculations of the density of electronic states of the first conduction bands of the C_{60}@MOF compound, originating from the t_{1u} fullerene orbitals. A dense $10 \times 10 \times 10$ **k**-point grid was used for Brillouin zone integration, and the Gaussian smearing of 7 meV was applied, which is reasonable due to a small band width (70 meV). Figure 4 shows the density of electronic states, calculated with the smearing of 7 meV, corresponding to a temperature of 81 K. The DOS structure shows two peaks with the amplitudes of about 50 states/eV/spin, which is considerably higher than 10 states/eV/spin, calculated for the fcc C_{60} crystal within the same approach. The obtained DOS amplitude is also about twice higher than 20–24 states/eV/spin obtained theoretically for the $K_xRb_yC_{60}$ system [5], suggesting that the C_{60}@MOF system can be more efficient in yielding a larger increase in DOS at the Fermi level than the doped fullerene crystals considered so far. However, we should note here that a direct prediction of a transition temperature in this system is subject to caution due to a presence of a counteracting Coulomb repulsion μ^* in Eq. (1). This parameter may increase with a reduction of a band dispersion due to a decrease of a metallic screening [23], thus counteracting the expected enhancement of the transition temperature. However, the exact behavior of this parameter depends on specific properties of the compound, and its evaluation cannot be performed within the present theory [23].

The possibility of simple and effective doping of the C_{60}@MOF system is essential in achieving the superconducting properties, and it should be a subject of a separate investigation. However, several suggestions can be made on the basis of the results obtained in the present study. The integrating of the density of electronic states with respect to the energy allows us to determine the amount of charge that is necessary to transfer to the C_{60} molecule to obtain the highest possible DOS on the Fermi level. The results show that the transfer of only one electron per C_{60} to the conduction band of the system leads to the Fermi level, located near the maximum of the density of states (dotted line in Fig. 4). Field-effect doping can be one of the possible ways to achieve this charge transfer [24]. A rough estimate shows that the external field of the order of 1 V/Å should be sufficient for the charge transfer of one electron

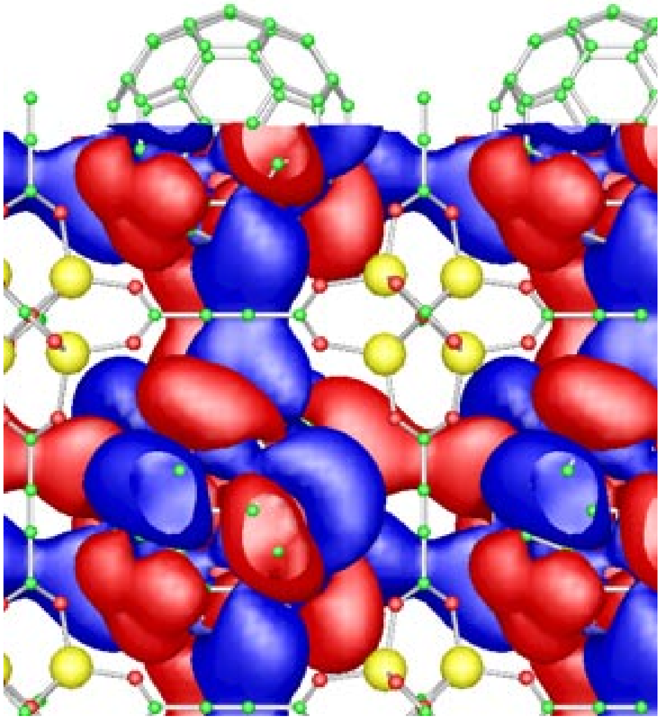

FIG. 3 (color online). Electronic wave function of the first conduction band of the C_{60}@MOF system, calculated at the Γ point.

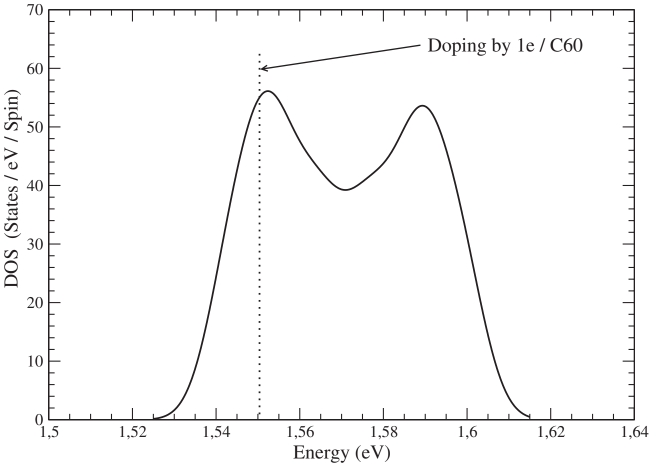

FIG. 4. Calculated density of electronic states of the first group of conduction bands of the C_{60}@MOF system. The Gaussian smearing of 7 meV is applied. The dotted line shows the position of the Fermi level under the doping condition of 1 electron per C_{60} molecule.

per C_{60} [25]. Further, the required external field can be even smaller, due to a high polarizability of a C_{60} molecule. However, the field doping may lead to a significant modification of the electronic structure caused by the Stark splitting [25], and the system will not follow a rigid-band model behavior.

Chemical doping by the alkali metals can be another effective way of populating the fullerene states in the C_{60}@MOF structure. The topology of the MOF structure provides natural spaces for the alkali atoms, which can be accommodated in the corners of the MOF cell. To verify this assumption, test calculations have been performed by placing one potassium atom in the corner of the C_{60}@MOF cage. Its coordinates were completely relaxed, and the DOS on the Fermi level was calculated. The obtained value of 40 states/eV/spin is very close to 50 states/eV/spin, obtained for the undoped C_{60}@MOF system using a rigid-band-model approach. However, we should note again, that the question of doping of the C_{60}@MOF structure should be a subject of a separate detailed investigation.

The fact that the fullerene states are practically uncoupled with the states of the host compound allows us to apply a simple tight-binding (TB) model to describe the first three conduction bands, originating from the t_{1u} orbitals of the C_{60} molecule. These bands are formed by three molecular orbitals, which transform like the *XYZ* axis, much like the p_x, p_y, and p_z atomic orbitals but without the azimuthal symmetry of the latter. Our TB model thus has three parameters and the analytical solutions for these bands are

$$\begin{aligned}\epsilon_1(\mathbf{k}) &= \gamma_1 \cos(k_x a) + \gamma_2 \cos(k_y a) + \gamma_3 \cos(k_z a) + c,\\ \epsilon_2(\mathbf{k}) &= \gamma_1 \cos(k_y a) + \gamma_2 \cos(k_z a) + \gamma_3 \cos(k_x a) + c,\\ \epsilon_3(\mathbf{k}) &= \gamma_1 \cos(k_z a) + \gamma_2 \cos(k_x a) + \gamma_3 \cos(k_y a) + c,\end{aligned} \tag{2}$$

where the parameters $\gamma_1 = 0.0034$ eV, $\gamma_2 = -0.0066$ eV, and $\gamma_3 = -0.026$ eV were obtained by fitting to our *ab initio* band structure calculations, and the constant c depends on the choice of zero of the energy scale.

In conclusion, we have presented a theoretical study of the electronic properties of a new hybrid system, where the C_{60} molecules are forced to form a simple cubic crystal, by means of an external metal-organic skeleton. The calculations, performed using the *ab initio* approach, show that the system is stable, and after being doped will show a large DOS at the Fermi level. The calculated DOS value is considerably higher than the one of any of the known C_{60} crystals, which makes a proposed C_{60}@MOF structure a promising system to study the superconducting state in the fullerene-based materials. The electric field doping is proposed as a possible technique for the doping of the system.

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