

有机 - 无机纳米复合材料光谱与电子性质研究进展

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有机 - 无机纳米复合材料的研究在当前纳米科学技术的发展中占有重要地位, 开创了材料与催化科学研究的新纪元。自从10年前首次合成纳米孔无机材料 MCM-41 至今, 该领域研究不断深入, 已展现出广阔的应用前景。当客体有机分子分散于纳米孔道内部时, 其分子性质将产生明显变化。本文结合作者近期研究成果, 力图从实验与理论两方面阐明在纳米复合体系中客体分子性质变化的原因。

关键词: 纳米复合材料 主 - 客体体系 电子限域
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Recent Advances in the Study of the Optical and Electronic Properties of Organic-Inorganic Nanocomposite Materials

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Organic-inorganic nanocomposite materials give enormous stimulus to the field of nano-science and technology, opening new horizons for materials science and catalytic science. Since the first synthesis of nanoporous inorganic material MCM-41 ten years ago, research in this field has expanded at a breathtaking pace. From the preparation of novel nanocomposite materials to the recent studies of their optical and electronic behaviors, organic-inorganic nanocomposite materials have found their way into an ever-broadening range of applications. Encapsulation of organic molecules in the inorganic host may produce significant changes of the molecular properties of the guest species. The present feature article focuses on explaining these changes in such nanocomposite systems, with particular emphasis on both experimental and theoretical evaluations.

Keywords: nanocomposite material host-guest system electronic confinement

0 Introduction

All of us, physicists, chemists, and materials scientists think and talk about organic-inorganic nanocomposite

materials when we refer to the recent trends in nano-science and technology. Nowadays, the research field of organic-inorganic nanocomposite materials has been widely recognized as one of the most promising

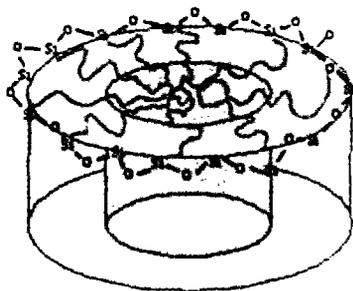
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and rapidly emerging research areas in materials science^[1-3]. A new era in confining close-packed, functionalized organic molecules within inorganic host has been opened since the discovery of the periodic nanoporous inorganic material known as Mobil Catalytic Material 41 (MCM-41) that possessing large surface areas and narrow pore-size distributions in 1992^[4]. Since then, a wide range of host nanoporous materials has been prepared, including alumina, zirconia, titania, niobia, tantalum oxide, manganese oxide, and even metals^[5]. Meanwhile, numerous papers have then been published on the preparation of nanocomposite materials of novel chemical compositions and on the fundamental understanding of physics of materials at the nanometer scale^[6,7].



MCM-41

We can perhaps best describe these systems as being organized into spatially identifiable domains of an organic and an inorganic component. A general classification has been proposed distinguishing “class I materials”, in which the inorganic and organic components interact only weakly through hydrogen bonding, van der Waals contacts, or electrostatic forces, from “class II materials”, in which the constituents are more strongly linked through ionic/covalent bond formation^[8]. Following this classification, the organic-inorganic nanocomposite materials involved in this article can be best sorted into the former class. Further harnessing the potential of these materials requires fine-tuning of the sizes, topologies, and spatial assembly of individual domains and their interfaces. This, in turn, relies on the improved understanding of the intermolecular interactions in these nanocomposite systems, especially those involving weak electron in-

teractions.

1 Concept Definition

During the past few years, scientists in this field have shown a growing interest in the variations of the molecular properties of the guest organic species^[9]. Encapsulation of organic molecules in the nanoporous channels host produces significant changes of the molecular properties of the guest species. Some of these changes such as the variations in the optical band gaps and excited-state lifetimes of the guest molecules in these nanocomposite materials, have been mentioned in previous studies^[10,11]. These variations observed in cation exchanged aluminosilicate sieves are even significant, which is related to the exchanged cations and associated fields in the pores^[12-14]. In this article, it is our intention to showcase a new concept, which can contribute to explain these significant changes in the organic-inorganic nanocomposite materials. This new concept, electronic confinement effect, which was first introduced by A. Corma and his co-workers^[15], is indeed realized in larger cavities, such as nanoporous MCM-41.

It is generally accepted that the structures of channels and cavities with molecular sizes in a few nanometers have a strong influence on diffusion and solvation effects of reactant molecules, and they can become determinant for the catalytic activity of these materials. Diffusion, which involves the dynamics of the molecules into the channels, is described by a statistic mechanical model which correlates well with experimental results^[16]. Solvation or cavity effects that involve physiochemical interactions between the host inorganic pore and the guest organic molecules are not well qualified and are still a matter of discussion^[17-19]. These types of interactions normally considered are Coulombic effects, coordination effects, and weak electron interactions. This last kind of interactions accounts for forces of the van der Waals type, which could produce the “docking” of molecules into the cavities of the molecular sieve. In this sense, it has been proposed that sorbate molecules in the nanoporous

solids, such as MCM-41, tend to optimize their van der Waals interaction with the surroundings. These van der Waals interactions are amplified by the surface curvature of the pore walls, which interact with the sorbed molecules.

Considering the partial covalent character of the aluminosilicate crystals, electrons are not localized on the framework atoms, but they are partially delocalized through the bulk. This causes the density of the electrons (i. e., the probability for finding the electrons) of the guest molecules to suddenly drop to nearly zero when reaching the walls of the cavity as a consequence of the short-range repulsion with the delocalized electronic clouds of the lattice. This implies that a contradiction of the orbitals of the guest molecules will occur, with the consequent changes in its energy levels (Fig. 1). This was the electronic confinement. It can be easily understood that this effect should be more important when the sizes of the cavity and the guest molecule are closer.

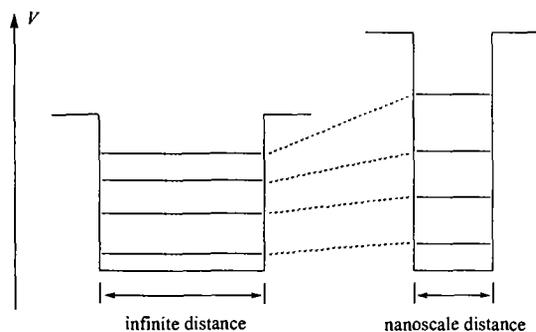


Fig. 1 Change of the energy levels of the particle when confining the microscopic particle

On the left-hand side the energy levels for the unconfined system are depicted and on the right-hand side, the corresponding levels for the confined one.

2 Model Study

For the sake of a better understanding of the electronic confinement, we present here a model study by using the aromatic compounds as the guest organic molecules^[20]. HMO theory is a method that allows one to obtain a chemical characterization of conjugated π systems without need of involved quantum chemical calculations. Its goal is to give an adequate description

of π molecular orbitals (their energy and atomic orbital composition) by only two empirical parameters, namely, the Coulomb integral α and the resonance integral β .

A confined model system can be built by locating the conjugated molecules parallel to two surfaces, for simplicity, may be simulated by two infinite planes located at a certain distance. In this case, the atomic orbitals can still have as the normal $2p_z$ orbitals a node at the molecular plane but they are adapted to the confinement, which makes them vanish beyond the limit of the plane. The schematic representation of the ψ function of an aromatic molecule in unconfined and confined spaces is shown in Fig. 2. It is evident from the figure that the density of the confined $2p_z$ orbitals (i. e., the probability for finding the electrons) suddenly drop to nearly zero when reaching the infinite plane as a consequence of the short-range repulsion with the delocalized electronic clouds. This implies that a contradiction of the molecular orbitals of the guest molecules will occur, with the consequent changes in its energy levels. Hence, the energy changes of an aromatic compound may be expressed as

$$\begin{aligned}\Delta E_{\text{HOMO}} &= E'_{\text{HOMO}} - E_{\text{HOMO}} = (\alpha' + n\beta') - (\alpha + n\beta) \\ &= \Delta\alpha + \Delta\beta\end{aligned}$$

$$\begin{aligned}\Delta E_{\text{LUMO}} &= E'_{\text{LUMO}} - E_{\text{LUMO}} = (\alpha' - n\beta') - (\alpha - n\beta) \\ &= \Delta\alpha - \Delta\beta\end{aligned}$$

where $\Delta\alpha$ and $\Delta\beta$ are (in atomic units)

$$\Delta\alpha = -\frac{1}{2} \frac{\int_{-\infty}^{\infty} dydz \partial_x a'(d, y, z) a(d, y, z)}{\int_0^d dx \int_{-\infty}^{\infty} dydz a'(x, y, z) a(x, y, z)}$$

$$\Delta\beta = -\frac{1}{2} \frac{\int_{-\infty}^{\infty} dydz \partial_x a'(d, y, z) b(d, y, z)}{\int_0^d dx \int_{-\infty}^{\infty} dydz a'(x, y, z) a(x, y, z)}$$

In this expression $a(x, y, z)$ and $b(x, y, z)$ are the $2p_z$ atomic orbitals on the neighboring carbon atoms a and b , respectively, while $a'(x, y, z)$ and $b'(x, y, z)$ are the equivalent confined atomic orbitals. Although we do not know the actual expression of the atomic orbitals in the confined system, we can state that $\Delta\alpha$ and $\Delta\beta$ are always positive quantities. Therefore, we obtain the following conditions for the

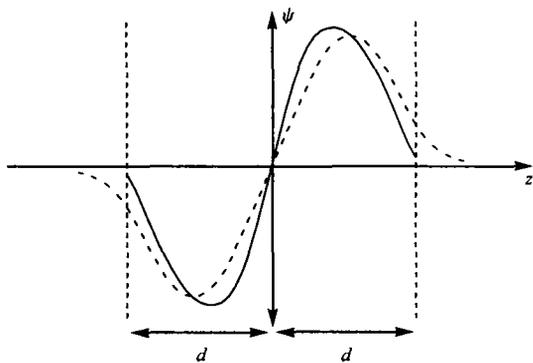


Fig. 2 Schematic representation of the ψ function of **1** in unconfined (dashed line) and confined (solid line) spaces

Coulomb and resonance integrals of the confined system

$$\alpha' = \alpha + \Delta\alpha > \alpha$$

$$n\beta' = n\beta + \Delta\beta > n\beta$$

Since α and β are both negative quantities, the above equations indicates that the values of α and β increase when confining the molecule. In Fig. 3 we have shown a qualitative correlation energy spectrum of the aromatic molecule when it is confined.

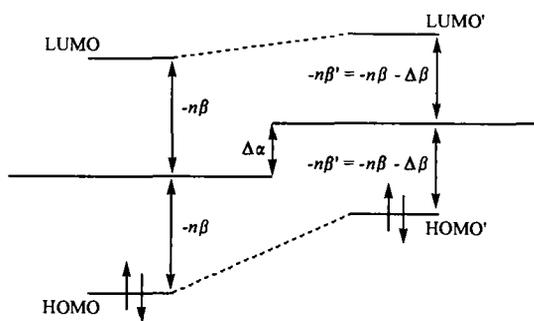


Fig. 3 Qualitative description of the frontier orbital energy spectrum for the conjugated molecule

3 Experimental Analysis

3.1 Organic Molecule

Schiff base molecule, which is one class of the most extensively studied organic molecules in molecular spectroscopy, has been found to be a suitable guest molecule for this purpose^[21]. By means of self-assembly, we have encapsulated a new Schiff base molecule N, N'-bis(2-hydroxy-5-methylbenzylidene)-1, 2-ethanediamine (**1**) in the nanoporous channels of MCM-41

host^[22]. The molecular structure diagram of **1** is shown in Fig. 4. The C(2)-O(1) bond length (1.348(9) Å) is longer than 1.30 Å indicating the ground state of **1** is enol form in the crystal. The emissions of **1** in both dimethyl sulphoxide (DMSO) and nanoporous MCM-41 result from strictures due to excited-state intramolecular proton transfer (ESIPT) reaction (Fig. 5). In DMSO the 0-0 transition of **1** appears at 23041 cm⁻¹ (2.86 eV) and is remarkably shifted to 21413 cm⁻¹ (2.66 eV) of **1** in MCM-41. Given that the main contribution to the S₀ → S₁ transition is due to the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital), this bathochromic shift can be correlated with a decreasing of the HOMO-LUMO band gap. Considering the Schiff base molecules can be treated as dispersive molecules in both DMSO solution and nanoporous MCM-41, this trend can be rationalized by the electronic confinement theory that all the energy levels of the guest Schiff base molecules increase in the nanoporous channels host as a result of the confinement. Since the increase for the HOMO has been predicted to be more sensitive than the LUMO, the overall effect is a reduction on the band gap of the frontier orbitals.

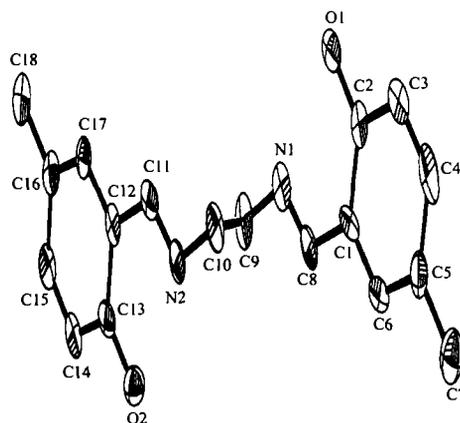


Fig. 4 Molecular structure diagram (hydrogen omitted) of **1**. Thermal ellipsoids are drawn at 30% probability level

3.2 Metal-Organic Compound

Zinc-organic compounds have attracted our attention because of their exceptional applications in the fabrication of organic-light-emitting-devices (OLEDs)^[23]. A novel compound bis[bis(N-octylsalicy-

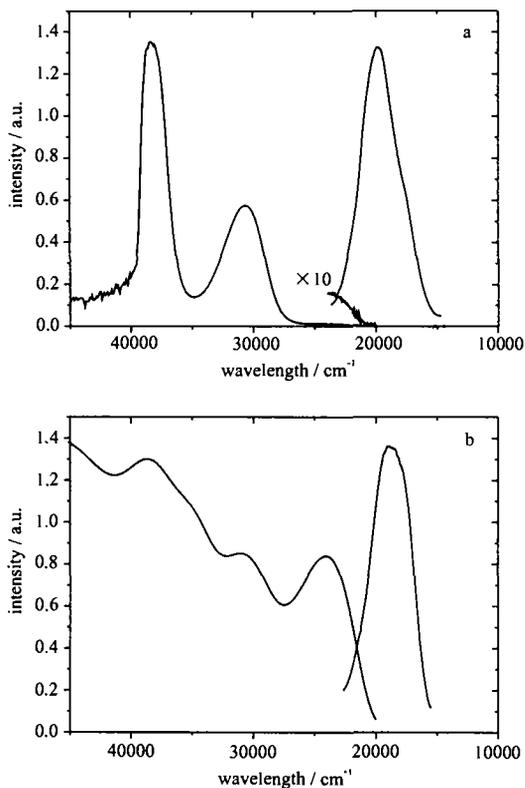


Fig. 5 Normalized absorption and emission spectra of **1** in DMSO ($\lambda_{exc} = 25000\text{cm}^{-1}$) (a) and in nanoporous MCM-41 ($\lambda_{exc} = 24100\text{cm}^{-1}$) (b) at room temperature

lideneamino)zinc(II)] (**2**) has been synthesized in this study and characterized by single crystal X-ray crystallography (Fig. 6) [24, 25]. We have also encapsulated **2** in the nanoporous channels host of MCM-41. In ethanol the 0-0 transition of **2** appears at 24450cm^{-1} (3.04eV) and is remarkably shifted to 22573cm^{-1} (2.80eV) of **2** in MCM-41 (Fig. 7). The emission kinetics of **2** fit reasonably well to single-exponential function $I = I_0 \exp(-t/\tau)$ with lifetimes decreasing from 36 ns in ethanol to 14ns in MCM-41. Considering the important decrease of the excited state lifetime, the magnitude of the radiationless decay rate induced by the confinement effect is truly remarkable. The variation of lifetime modulated by the MCM-41 host is connected with the bathochromic shift of the 0-0 transitions: the molecular orbitals of the compound **2** are confined in the nanocavities of MCM-41 and the HOMO-LUMO band gap in confined **2** should be smaller than that of **2** in ethanol. Due to this confinement ef-

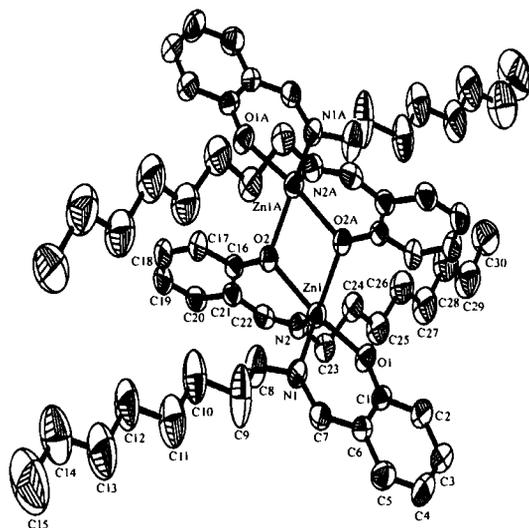


Fig. 6 Molecular structure diagram (hydrogen omitted) of **2**. Thermal ellipsoids are drawn at 30% probability level

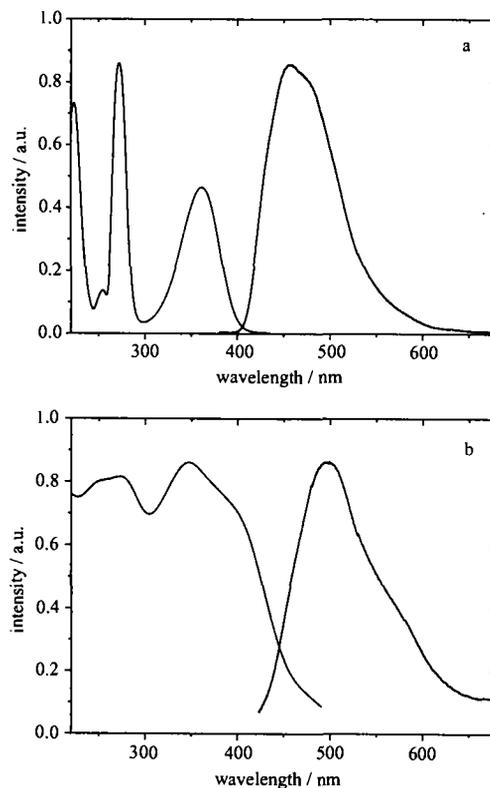


Fig. 7 Normalized absorption and emission spectra of **2** in ethanol solution (a), and nanoporous materials MCM-41 (b) at room temperature ($\lambda_{exc} = 351\text{nm}$)

fect, S_1 and S_0 electronic states can become partially degenerated through the vibronic (vibrational-electronic) coupling between both electronic states enhancing the nonradiative deactivation rate (k_{nr}) [26].

3.3 Implications of Electronic Confinement in Materials Science

In the organic-inorganic nanocomposite materials, an asymmetric confinement will exist by molecules being much closer to one "wall" than to the other one. So, the motion of electrons will be more restricted in one direction (along the wall of the nanoporous channels) than in the other directions. The results presented here may prove useful in the fabrication of optoelectronic devices, such as OLEDs using electroluminescent nanotube crystals^[27]. Since the pathways open for n/p migration-recombination are limited essentially to only one dimension, it may confer a greater degree of order on electroluminescent processes by utilizing porous, channel-type materials containing light-emitting and electronically interacting guest molecules, such as zinc-organic compounds.

4 Theoretical Evaluation

4.1 Semiempirical Calculations

To simulate the electronic confinement, a simple but effective way is to place the organic molecules parallel to a sufficiently large mica sheet at a fixed distance. Three aromatic compounds—benzene, naphthalene, and anthracene have been employed as the guest organic molecules. Fig. 8a plots the binding energies of the HOMO and LUMO orbitals of benzene, naphthalene, and anthracene in these complex systems. In general, the variation trends of HOMO and LUMO orbitals are markedly different. The HOMO orbitals increase all the time in this separation range, first gradually, then drastically; the LUMO orbitals first increase gradually up to *ca.* 2.0 Å, but then decrease obviously. As far as the HOMO orbitals are concerned, it is noteworthy that aromatic molecules with large conjugated π systems, such as anthracene, are more sensitive than those small conjugated ones. These indicate that the confinement effect is associated with not only the separation distance, but also the conjugated π system of the aromatic molecules. Considering the remarkable increase in HOMO orbitals and decrease in LUMO orbitals, the band gaps should be

decrease dramatically in the shorter separation distance (Fig. 8b). In other words, the electronic confinement effect is truly exceptional when the aromatic molecules are extremely close to the mica sheet. Seen from Fig. 8b, the band gap decrease in the order: benzene > naphthalene > anthracene, which is in agreement with their conjugated structures and spectroscopic measurements.

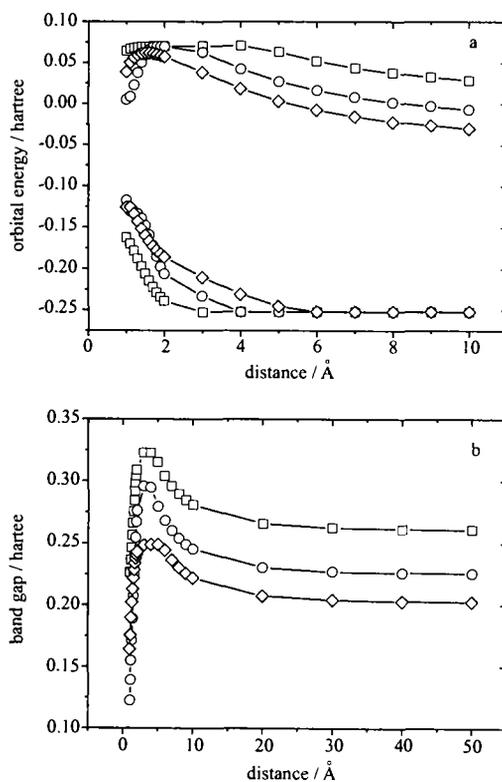


Fig. 8 (a) Plots of the binding energies of the HOMO and LUMO orbitals of confined benzene (\square), naphthalene (\circ), and anthracene (\diamond), respectively, (b) Plots of the band gap energies of confined benzene (\square), naphthalene (\circ), and anthracene (\diamond), respectively
1 Hartree = 7.21 eV

4.2 EHMO Calculations

To analyze the origin of the energy variations and acquire a better understanding of the interactions between the guest aromatic compounds and the mica host, we have performed EHMO (extended Hückel molecular orbital) calculations. Taken as an example, three-dimensional plots of the HOMO orbital surfaces of naphthalene in the gas phase and confined by the surface separated by 1.0 Å are given in Fig. 9. It should be

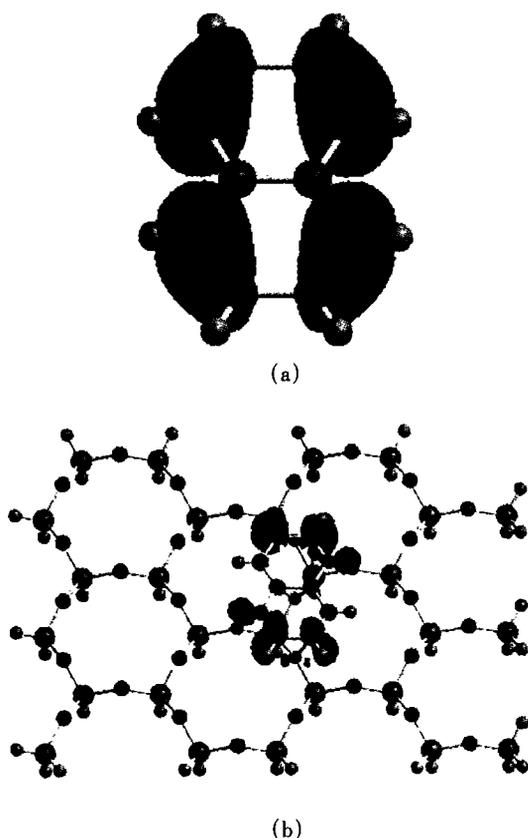


Fig. 9 Three-dimensional plots of the HOMO orbital surfaces of naphthalene in the gas phase (a) and confined by the surface separated by 1.0 Å (b), respectively

noted that the isocontours in these figures have been set using the same unit. In all the cases, the HOMO orbitals are mainly composed of $2p_z$ combinations of the aromatic carbon atoms. The main components of the HOMO orbitals are localized at the aromatic rings in these complex systems, with little contributions on the mica sheet. It is evident that the confined HOMO orbitals have been markedly contracted compared to those in the gas phase, this deformation of the electronic structure being the origin of the increase of the HOMO energy.

4.3 Implications of Electronic Confinement in Catalytic Science

As shown in Fig. 8b, the band gap between HOMO and LUMO orbitals decreases dramatically when the aromatic molecule is separated within ca. 2.0 Å from the mica sheet. Therefore, the HOMO bond becomes weaker than when unconfined. A small band gap

indicates that a quasi-degeneracy of the electronic states should occur at the ground state^[24]. A single configuration model of the many-particle wave function cannot be assumed and, at the minimal basis set level (which is implicit in HMO theory), one expects that the actual wave function can be properly represented by a multireferential function which accounts for a partially biradical character of the bond. Thus the smaller the band gap, the more the molecule with unpaired electrons on each carbon atom. So, the molecule would become intrinsically more reactive when it is confined. This means that reactions involving a loss of the π character of the molecule would be favored.

5 Conclusion and Future Opportunities

In this feature article, we have tried to elucidate the variations of molecular properties of the guest species in the organic-inorganic nanocomposite materials by the electronic confinement effect. The implication of this effect on chemical reactivity are obvious considering that changes in the energy levels of the guest molecule could imply a preactivation of the molecule when residing in the pore or cavity. The bathochromic shift of the 0-0 transitions and the shortening of the excited state lifetimes have been correlated with the reduction of the HOMO-LUMO band gap accompanying by the increased energies of the frontier orbitals.

The past ten years have demonstrated a great influence of the organic-inorganic nanocomposite materials on the development of nano-science and technology. Ultimately, the scientific and technological impact of these materials mainly depends on the molecular properties of the guest species. Hence, studies concerning the variations of these properties are of exceptionally importance. Organic-inorganic nanocomposite materials have introduced hierarchy into materials science and bode well for the further development of materials and composite with novel properties, new functions, and perceived utilities in a wide range of applications. The future looks very bright for organic-inorganic nanocomposite materials!

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