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Spectroscopic Evidence in Support of the Molecular Orbital Confinement Concept: Case of Anthracene Incorporated in Zeolites

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Incorporation of organic molecules inside the micropores of zeolites may produce significant changes on the molecular properties of the adsorbed guests.[1,2] Some of these changes such as an enhanced basicity and an apparent decrease of the oxidation potential are particularly remarkable when a host/guest tight fit occurs.[3] These variations cannot be easily rationalized by the current paradigms, one of the most widely invoked being the influence of the zeolite intense electrostatic fields on the stabilization of polar adsorbates.[4−6] An *electronic confinement concept* has been proposed based on the concept that the molecular orbitals (MO) of the adsorbates inside the zeolite pores are not extended over all the space, as they are in the gas phase, but instead are forced to limit within the zeolite walls.[7,8] This “*boxing effect*” is stronger as the size of the confined guest approaches the zeolite cage dimension, producing an energy increase of all MO particularly those which are more diffuse. The HOMO has been predicted to be more sensitive than the LUMO, and the predicted effect is a reduction on the band gap of the frontier orbitals that has been interpreted as a preactivation of the molecule inside the zeolite pores compared to gas phase.[7,9] This electronic confinement should be also reflected in the optical properties of the guest.

No experimental evidence in support of this concept has been given apart from indirect qualitative reactivity tests. In the present contribution we show convincingly that the predictions of this *electronic confinement* theory are indeed realized. Anthracene (AN) was found to be a suitable probe molecule for this purpose since it is a conformationally rigid molecule having large emission quantum yields at adequate wavelengths and similar equilibrium geometries in S_0 and S_1. Several reports on the photophysical properties of AN in zeolites have been published, but none of them have paid attention to the shifts in its electronic properties upon incorporation.[10,11]

Low loadings of AN (5 $mg \cdot g^{-1}$) were adsorbed within three zeolites in their neutral Na^+-form with different geometries and pore dimensions, that is, Y (spherical supercages of 1.3 nm diameter tetrahedrally interconnected through 0.74 nm windows), mordenite (elliptical channels 0.65×0.70 nm^2), ZSM-5 (array of straight channels 0.51×0.55 nm^2 intersecting perpendicularly with sinusoidal channels 0.52×0.56 nm^2). Incorporation of AN was carried out by stirring at room temperature a CH_2Cl_2 suspension (6×10^{-6} ML^{-1}) in the presence of dehydrated zeolites (aerated calcination at 550 °C for 6 h) for 1 h. Then, the solid was filtered and washed with fresh CH_2Cl_2. XPS analysis combined with Ar^+ sputtering indicates that the C/Si atomic ratio increases from 0.03 to 0.14, going from the external surface to ~100 Å down. The formation of aggregates or $AN^{\bullet +}$ radical cation reported using acid zeolites under other conditions was not observed here at our loadings using the neutral Na^+ form.

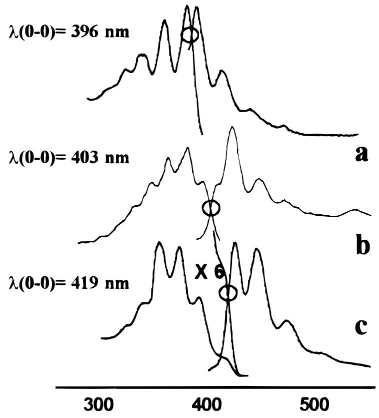

Figure 1. Excitation and emission spectra, at room temperature, of anthracene−NaY (a), anthracene−NaMor (b), and anthracene−NaZSM-5 (c).

Figure 1 shows the corresponding room temperature fluorescence and excitation spectra. These spectra are strongly structured, showing the vibronic transitions between the S_0 (1^1A_g) and S_1 (1^1B_{1u}) states. The vibronic structure of AN depends on the zeolite host and the 0−0 transition shift bathochromically from NaY to ZSM-5: the lower the pore size of the zeolite, the higher the bathochromic shift of the 0−0 transition. In 3-methylbutane the 0−0 transition of AN appears at 375 nm (not shown in Figure 1) and is shifted to 396 nm in AN included in NaY. This shift is remarkably higher in sodium mordenite (NaMor) (403 nm) and NaZSM-5 (419 nm). Given that the main contribution to the $S_0 \rightarrow S_1$ transition is due to the HOMO and LUMO, this bathochromic shift induced by the host can be correlated with a decreasing of the HOMO−LUMO band gap. The electrostatic effect could explain the shift of the 0−0 transition of AN only in zeolite Y[4−6] since the 0−0 transition measured by us in a highly polar 3 M NaCl aqueous solution is 396 nm, but not for the rest of zeolites. In fact, the polarity of the zeolites (related to their Al content) follows the order ZSM-5 (Si/Al = 30) < mordenite (Si/Al = 10) < Y (Si/Al = 2.4) that is exactly the opposite trend here observed for the 0−0 transition. To further reinforce that the observed shift of the 0−0 transition is a true reflection of the confinement effect and not due to AN−cation interaction, AN was adsorbed in three all-silica zeolites (not containing balancing cations) of varying pore dimensions, namely CIT-5 (monodirectional, 0.72×0.76 nm^2), ZSM-12 (monodirectional, 0.55×0.59 nm^2), silicalite (two orthogonal channel systems, straight 0.53×0.56 nm^2, sinusoidal 0.51×0.55 nm^2). As predicted by the confinement theory, the 0−0 transition for AN in CIT-5, ZSM-12, and silicalite was 396, 406, and 420 nm, respectively. This trend can only be rationalized by the electronic confinement theory.[7]

Figure 2 shows the fluorescence decay of pure AN and included into the three studied zeolites. The emission kinetics fit reasonably well to single-exponential functions with lifetimes decreasing from pure AN (4.5 ns) to those included within zeolite NaY (3.2 ns), this effect being more important in mordenite or ZSM-5 in which the fluorescence lifetime is in the limit of our instrument response (<100 ps). It is interesting to note that 0−0 transition and fluorescence lifetimes of AN and other aromatic compounds

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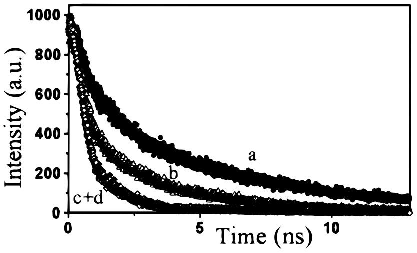

Figure 2. Normalized fluorescence decays of anthracene monitored at 425 nm after 340 nm excitation of AN (a), AN−NaY (b), AN−NaMor (c), and AN−NaZSM-5 (d). Decays c and d coincide.

adsorbed on amorphous silica−alumina at low loading (no confinement) have been reported to be similar to those from dilute methanolic solutions.

The modulation of AN fluorescence lifetime by the zeolite host is connected with the bathochromic shift of the 0−0 transition: for mordenite or ZSM-5 the dimensions of AN (0.559 × 0.979 nm^2) approach those of the zeolite pores and the $S_0 - S_1$ energy gap in confined AN should be smaller than that of pure AN. Due to this proximity effect, S_1 and S_0 states can become partially degenerated through the vibronic (vibrational−electronic) coupling between both electronic states enhancing the nonradiative deactivation rate (k_{nr}).[12] This enhanced radiationless deactivation pathways should lead to a reduced emission quantum yield but the impossibility to determine quantum yields in solids does not allow to confirm this prediction.

Considering the important decrease of the fluorescence lifetime, the magnitude of the radiationless decay rate induced by the proximity effect is truly remarkable. This effect has been described in many aromatic compounds and heterocycles.

With the aim to provide a quantum chemical prediction of the confinement effect at a reasonable computational cost, we carried out calculations at the semiempirical PM3 level. Given that the MOs of AN expand symmetrically above and below the molecular plane, the simplest way to simulate the electronic confinement is to place AN into two sufficiently large parallel sheets of mica (a layered silicate formed by an infinite array of SiO_4 tetrahedra sharing the edges) that were fixed at a distance of 7 and 0.54 nm, respectively. Even though the level of calculation is limited by the large number of atoms of the system (178 in all), the results show very clearly the general trend: the energy of the frontier MOs increases dramatically and the band gap is reduced as the distance between the sheets is reduced (Figure 3).

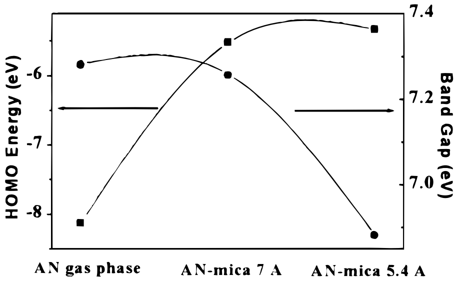

Figure 3. AN HOMO and band gap energies in gas phase and upon confinement between two mica sheets separated by 7 and 5.4 Å.

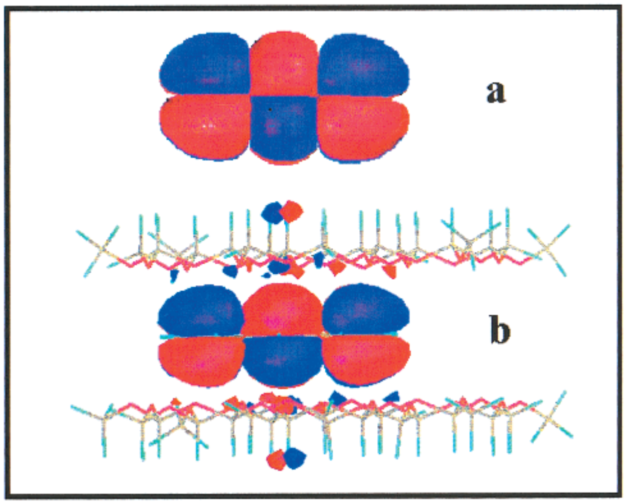

Figure 4. Plots of the AN HOMO orbital in the gas phase (a) and upon confinement inside two mica sheets separated by 5.4 Å (b).

To analyze the origin of this energy increase we have studied the composition of the HOMO orbital. Three-dimensional plots of AN HOMO orbital in gas phase and confined within two mica sheets separated by 5.4 Å are shown in Figure 4. As can be seen there the main components of the HOMO orbital of the AN−mica system (Figure 4b) are localized at the AN molecule even though very small contributions are on the mica sheets. It is noteworthy that this HOMO orbital included between the mica sheets is slightly contracted along the *z* axis compared to AN in the gas-phase being this deformation the origin of the increase in the HOMO energy. These results can rationalize the variations on the 0−0 transition observed for the AN−zeolite systems.

In summary, we have provided convincing spectroscopic evidence of the electronic confinement of AN within zeolites. The bathochromic shift of the 0−0 transition and the shortening of the fluorescence lifetime have been correlated with the increased energy of the HOMO orbital and with the reduction of the band gap. Further work is in progress to provide direct evidence of the basicity increase of probe molecules upon incorporation in zeolites.

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