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Observation of Azo Chromophore Fluorescence and Phosphorescence Emissions from DBH by Applying Exclusively the Orbital Confinement Effect in Siliceous Zeolites Devoid of Charge-Balancing Cations

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The photochemistry of the azo functionality has been thoroughly studied and appears extensively documented in numerous reviews.[1,2] The azo chromophore ($n\pi^*$ excitation) is generally characterized by a very low intersystem crossing (ISC) yield, which makes difficult the direct population of the triplet excited state. As a consequence, the observation of phosphorescence is very unusual,[3] but recent exceptions have been documented for the direct[4] and heavy-atom-promoted[5] emissions.

In the heavy-atom effect, ISC is enhanced by more effective spin−orbital coupling.[6,7] For this purpose, solvents have been used which contain heavy atoms, for example, Br and I atoms, to increase the ISC quantum yield, as manifested by enhanced phosphorescence emission or higher amounts of products derived from the triplet state.[8] A more efficient alternative is to use zeolites as solid hosts, in which heavy-atom cations occupy the voids of the zeolite porous structure in close proximity with the absorbed guest.[5,8] By applying this well-established strategy, the phosphorescence of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) (Chart 1) has been recently observed at 77 K upon incorporation within Tl−Y zeolite.[5]

In the present contribution, we report the first direct observation of the room-temperature phosphorescence emission from DBH by using the innovative confinement effect.[9] In this novel process, the intersystem-crossing efficiency is enhanced by perturbation in the symmetry and changes in the energy of the electronic states due to spatial constraints imposed by the rigid reaction cavity. Previously, we have provided spectroscopic evidence that incorporation of organic molecules inside the micropores of zeolites significantly changes the molecular orbitals of the absorbed guests through spatial confinement.[9−11] This approach is conceptually different from the heavy-atom effect, but both have in common the use of zeolites to provide a compartmentalized rigid matrix. In the heavy-atom effect the major role is played by the nature and number of the charge-balancing metal ions, while the confinement effect is based on the host/guest tight fit and operates even with all-silica zeolites that do not contain any compensating cation. By using DBH as a test molecule, we shall show that the confinement effect influences the properties of the guest more strongly than the well-established heavy-atom effect.

DBH was incorporated in four heavy-atom-free zeolites of different pore sizes (see Supporting Information). Three of these are all-silica zeolites (cation-free) and the fourth a highly dealuminated (Si/Al = 30) theta-1 zeolite (the all-silica theta-1 zeolite has to date not been reported). The loading level was 5 mg per gram of zeolite, confirmed by thermogravimetric and combustion analysis. Direct evidence of the incorporation of DBH within the zeolite host has been additionally obtained by carrying out XPS analysis of the C-to-Si atomic ratio after different levels of sputtering with a fast Ar^+ beam (see Supporting Information).[12] In statistical terms, the DBH molecules are separated quite far from each other (at least 10 Å between van der Waals edges), and for this reason the perturbation among themselves is unlikely. The zeolites used in the present study have distinct pore sizes and morphologies.[13] Thus, SSZ24 (AFI) has cylindrical pores of 7.3 Å diameter. Ferrierite (FER) has a two-directional pore structure consisting of straight oval 10-ring channels (5.4 Å × 4.2 Å) which are intersected by channels with eight-ring windows. Silicalite (MFI) has an array of straight channels (5.1 × 5.5 Å) intersected perpendicularly with sinusoidal channels (5.2 × 5.6 Å). Theta-1 (TON) is a monodirectional zeolite with oval channels of 4.6 Å × 5.7 Å diameter.

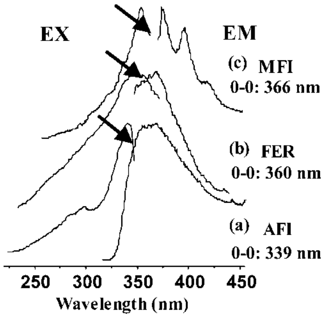

Figure 1. Excitation (EX) and emission (EM) spectra at room temperature of (a) DBH@SSZ24 (AFI), (b) DBH@Ferrierite (FER), and (c) DBH@Silicalite (MFI); the 0−0 transitions are indicated by arrows.

Chart 1

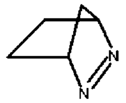

Figure 1 shows the room-temperature excitation and fluorescence spectra of DBH included within SSZ24, ferrierite and silicalite. It is interesting to note that both the excitation and emission spectra are wavelength-independent. The 0−0 transition of DBH clearly depends on the host and shifts bathochromically from SSZ24 to silicalite. The more tightly the fit of DBH inside the pores of the zeolite, that is, MFI > FER > AFI, the more pronounced the bathochromic shift of the 0−0 transition. These spectral shifts in the fluorescence emission are attributed to the orbital-confinement effect, induced by the zeolite host.[9−11] Theoretical work reveals that orbital confinement decreases the HOMO−LUMO energy gap.[9] The main contribution to the $S_0 \rightarrow S_1$ transition involves the excitation from the HOMO to the LUMO energy levels, and consequently, the bathochromic shift observed in the 0−0 transition reflects the reduction of the HOMO−LUMO energy gap.

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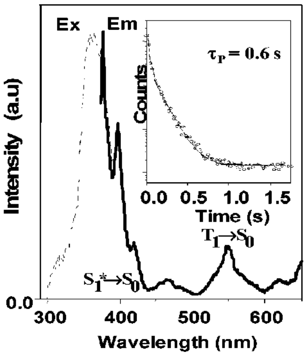

Figure 2. Excitation (EX) and emission (EM) spectra of DBH@silicalite measured at 77 K; the insert shows the phosphorescence decay monitored at 550 nm after 350-nm excitation.

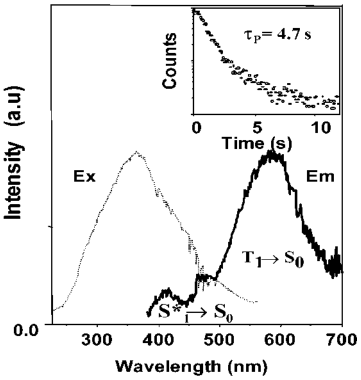

Figure 3. Room-temperature excitation (monitored at 580 nm) and emission spectra (λ_{exc} = 350 nm) of DBH@theta-1; the insert shows the phosphorescence decay monitored at 580 nm after 350-nm excitation.

The room-temperature fluorescence lifetimes for DBH included within zeolites were adjusted to single-exponential functions. These constants were significantly higher than those reported in isooctane solution (ca. 1 ns)[3] and substantially decrease from SSZ24 (5.1 ns) to ferrierite (4.8 ns) and silicalite (2.8 ns) (see Supporting Information). This kinetic behavior also validates the orbital- confinement concept, since the decrease of the HOMO−LUMO gap expectedly increases the nonradiative deactivation pathway due to the closer proximity between the S_0 and S_1 energy states.[9]

As expected, the intensity of the emission was considerably increased at 77 K, and in the case of DBH@silicalite, a new band at ca. 550 nm appeared (see Figure 2). This band was only observed at temperatures below 200 K and was assigned to the phosphorescence emission (τ_P = 0.6 s) of DBH. DBH@SSZ24 and ferrierite did not show this phosphorescence band.

In the theta-1 zeolite, the results are remarkably different (see Figure 3). DBH within theta-1 shows at room-temperature red-shifted luminescence, with two weak peaks in the 400−500 nm region and a more intense broad band at ca. 580 nm. The weak emission at 400−500 nm is assigned to fluorescence, which is bathochromically shifted with respect to that observed for DBH within all-silica zeolites (Figure 1).[14] This spectral shift is consistent with the smallest pore-size dimensions of the theta-1 zeolite, for which evidently the largest orbital-confinement effect operates. The broad band at ca. 580 nm may be safely attributed to room-temperature phosphorescence emission on the basis of the wavelength of the emission maxima.[4,5] Phosphorescence emission at room temperature has never been observed for any azoalkane and certainly not for DBH. Given the low ISC efficiency for DBH in solution, the effect responsible for phosphorescence enhancement through intersystem crossing has to be remarkably strong. Still more impressive, as shown in the insert of Figure 3, the luminescence monitored at 580 nm for the decay requires seconds (τ_P = 4.7 s), which is an exceedingly long-lived triplet excited state. Furthermore, molecular oxygen quenches significantly the intensity of this band, whose initial intensity is recovered in a nitrogen-gas atmosphere. The excitation spectrum, monitored at 580 nm, was very similar to the absorption spectrum of DBH@theta-1. Finally, on solid−liquid extraction of DBH@theta-1, unaltered DBH was recovered essentially quantitatively.

The observation of direct phosphorescence even at room temperature from DBH within theta-1 and silicalite zeolites may be rationalized on the basis of two complementary effects: (i) Decrease of the HOMO−LUMO energy gap and the orbital-symmetry perturbation, induced by the spatial confinement of the azo nπ^* chromophore through guest−host interactions, favor ISC. (ii) Inhibition of radiationless deactivation pathways by the immobilization of DBH in a rigid matrix favor long lifetimes.

Both effects (higher triplet population and less energy wastage) enhance the emission pathways.

In conclusion, the emission spectrum of DBH incorporated in zeolites is clearly modulated by the host. The direct observation of room-temperature phosphorescence from DBH without the assistance by any heavy-atom perturbations demonstrates impressively the efficiency of the orbital-confinement effect to manipulate the photophysical properties of electronically excited molecules through absorbed guest−host interactions. It must be emphasized that previous attempts to observe direct phosphorescence from DBH even in EPA glass at 77 K or in Xe matrix at 15 K have been unsuccessful; also no room-temperature phosphorescence of DBH in Tl−Y was observed.[5]

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Supporting Information Available: Structures and microphotographs of the zeolites used in this study, the normalized fluorescence decay curves of DBH included within zeolites, and an energy diagram of the HOMO and LUMO orbitals of DBH alone and within the zeolite, as well as orbital contours (PDF). This material is available free of charge via the Internet at http://pubs.acs.org

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