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Evidence for through-framework electron transfer in intrazeolite photochemistry. Case of $Ru(bpy)_3^{2+}$ and methylviologen in novel delaminated ITQ-2 zeolite

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A sample of novel delaminated zeolite ITQ-2 containing $Ru(bpy)_3^{2+}$ on the external cups and MV^{2+} included in the independent and not connected channels has been prepared; emission and time-resolved laser flash photolysis has shown unambigously that photoinduced electron transfer from $Ru(bpy)_3^{2+}$ to MV^{2+} occurs through the zeolite framework.

In recent years there has been a continuous interest in the preparation of zeolitic materials with larger accessible surface.[1] A significant breakthrough has been the preparation of MCM aluminosilicates (pore size from 20 to 100 Å).[2,3] However, most of the initial opportunities of MCM silicates have not been brought to completion due to its poor hydrothermal stability in which the channels collapse in the presence of moisture upon storage of the solid even at room temperature.[4] A new concept in the field of zeolitic materials has appeared since the advent of ITQ2.[5] ITQ2 is a novel zeolite obtained by delamination of the layered zeolitic precursor of MCM22. The ITQ2 crystal structure is formed by layers (25 Å depth) having open cups (~7 Å diameter, 8 Å depth) along the large *xy* surface and independent, not connected sinuosoidal channels (~5.4 Å) sandwiched in the layer, running parallel to the *xy* plane. Fig. 1 shows the two morphological components (cups and channels) of the ITQ2 structure.

Conventional zeolites possess a large internal area compared to the external surface and a remarkable internal volume.[6] This is a consequence of the presence of micropores. In contrast, the novel ITQ2 has a large accessible, external surface with a minor internal surface and a reduced microporosity. For intance, the values for total BET surface area, external surface and micropore volume measured for our ITQ-2 (Si/Al ~50) are 806 $m^2\ g^{-1}$, 750 $m^2\ g^{-1}$ and 0.009 $ml\ g^{-1}$, respectively. To have some data for comparison, the related MCM22 zeolite obtained from the same precursor as the ITQ2 shows values of 400 $m^2\ g^{-1}$, 75 $m^2\ g^{-1}$ and 0.121 $ml\ g^{-1}$ for the total BET, the external area and micropore volume, respectively. Herein, we have taken advantage of the novel topology of ITQ2 and by using the welldocumented $Ru(bpy)_3^{2+}$/viologen system as a probe[7,8] we have found sound spectroscopic evidence to support that the electron transfer (ET) from a donor to an acceptor in this zeolite can take place through the framework. Up to now, most of the current models assume that ET occurs by close molecular contact or through the empty space between neighboring supercages in tridirectional faujasite.[7,8] Since zeolites are nonconducting solids, ET through the lattice has been frequently ignored.

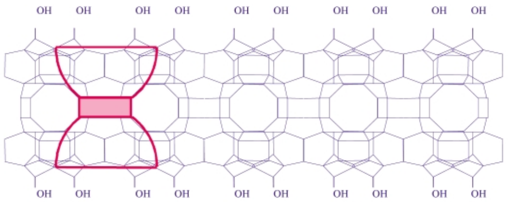
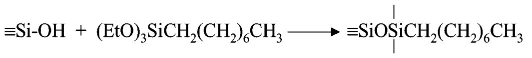


Fig. 1 Crystal structure of ITQ-2 showing the layers having external cups and 10-membered ring channels.

$Ru(bpy)_3^{2+}$ is a large metallic complex (~13 Å diameter) that is size excluded from the 10-membered ring channels of ITQ2. Deposition of $Ru(bpy)_3^{2+}$ on the external surface of the ITQ2 solid was accomplished by ion exchange using an aqueous solution of preformed $Ru(bpy)_3^{2+}$. Chemical analysis established that the $Ru(bpy)_3^{2+}$ loading after the exchange was 1 wt% that corresponds approximately to one $Ru(bpy)_3^{2+}$ every 6500 $Å^2$ or one $Ru(bpy)_3^{2+}$ every 100 cups. The presence of $Ru(bpy)_3^{2+}$ on ITQ2 was confirmed by UV–Vis and FTIR spectroscopy. Before adsorption of methyl viologen (MV^{2+}) into the micropores and to ensure that MV^{2+} will be included exclusively at the internal pores, it is necessary to devise a procedure to impede MV^{2+} from being accommodated on the external surface. Based on the ITQ2 crystal structure and considering the location of external silanol groups, (see Fig. 1) it was anticipated that silylation will impede subsequent MV^{2+} adsorption on the cups, while the channels could still host MV^{2+}. Thus, we submitted the $Ru(bpy)_3^{2+}$@ITQ2 solid to silylation using triethoxyoctylsilane (TEOS) in toluene (eqn. (1)).



$$\equiv Si\text{-}OH + (EtO)_3SiCH_2(CH_2)_6CH_3 \longrightarrow \equiv SiO\overset{|}{\underset{|}{S}}iCH_2(CH_2)_6CH_3 \qquad (1)$$

Silylation decreases considerably the population of the silanols (about 40% of the initial silanols, protecting ideally 7.2 out of 12 silanols per cup), as assessed by IR. At the same time a new band corresponding to CH_3 appeared at 2950 cm^{-1}. The fact that silylation blocks the cups while the 10membered ring channels are still accessible to organic guests of suitably small molecular dimensions (such as MV^{2+}) was proved by using 2,6-di-*tert*-butylpyridine (DTBPy) and pyridine (py) as probe molecules. Titration with py of zeolites monitored by IR spectroscopy is a standard technique to characterize acid sites;[9] py having the same kinetic diameter as MV^{2+} probes the external plus the internal surface of ITQ2, while bulky DTBPy is a specific probe molecule of the external surface. Comparison of the IR spectra of ITQ2 and silylated ITQ-2 after adsorption of DTBPy and py vapors shows a remarkable decrease in the amount of the adsorbed DTBPy (blocking of the cups by large –Si(*n*-Oct) located at the rims) while that of py remains essentially constant (channels still accessible).

Incorporation of MV^{2+} within the $Ru(bpy)_3^{2+}$@ITQ2sil sample was accomplished by ion exchange from aqueous solutions affording a $Ru(bpy)_3^{2+}/MV^{2+}$@ITQ2sil sample. According to chemical analysis the average amount introduced was one MV^{2+} cation per 20 channels. The topology of the $Ru(bpy)_3^{2+}/MV^{2+}$ at silylated ITQ2 is described by the external location of $Ru(bpy)_3^{2+}$ nested on the cups of the silylated external surface and the internal location of MV^{2+} incorporated inside the channels (Scheme 1). Therefore, the donor and acceptor are separated by interposed TO_4 framework tetrahedra (~ 3 Å minimum separation). An analogous procedure as that used for the preparation of $Ru(bpy)_3^{2+}/MV^{2+}$@ITQ-2sil, but using a size-excluded viologen namely 6,7,8,9-tetrahydrodipyr-

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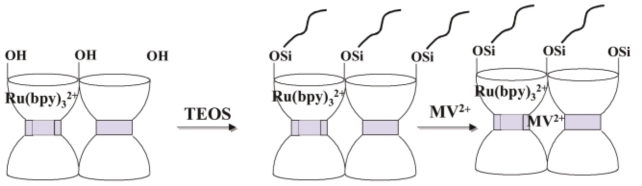

Scheme 1 Topology of Ru(bpy)$_3^{2+}$@ITQ2sil containing MV^{2+}.

ido[1,2-*a*:2,1-*c*][1,4]diazocinium dibromide (4DQ^{2+}) was followed to obtain Ru(bpy)$_3^{2+}$/4DQ^{2+}@ITQ-2.

ET quenching of the Ru(bpy)$_3^{2+*}$ excited state by viologens MV^{2+} and 4DQ^{2+} has been assessed in previous works for other zeolites by emission spectroscopy and laser flash photolysis.[7,8] Upon excitation at the λ_{max} of the metal-to-ligand charge transfer (MLCT) band of the Ru(bpy)$_3^{2+}$, an intense emission was observed for the Ru(bpy)$_3^{2+}$@ITQ2sil sample that decays in hundreds of ns. After incorporation of MV^{2+}, a significant decrease of the Ru(bpy)$_3^{2+}$ emission intensity of 56% was observed (Fig. 2). On the other hand, the decay of the emitting Ru(bpy)$_3^{2+}$ was essentially unaffected by the presence of MV^{2+} and only minor variations in the temporal profile of the emission were recorded.

These observations are typical for the predominant operation of static rather than a dynamic quenching. Both static and dynamic quenching have been reported in the literature for the Ru(bpy)$_3^{2+}$/MV^{2+} system.[7,8] In our case, the emission data can be interpreted as indicating that those Ru(bpy)$_3^{2+}$ having a MV^{2+} in close proximity (*ca.* 56%) are instantaneously quenched on the ns time scale and do not emit, while those other Ru(bpy)$_3^{2+}$ that emit are essentially unperturbed during their lifetime (hundreds of ns) by the presence of distant MV^{2+} quenchers. Since the cups and channels are independent and not connected, the interaction revealed by the static quenching has to occur through the zeolite framework. 4DQ^{2+} (exclusive external location) was used as a control to demonstrate the degree in which silylation effectively impedes any interaction between Ru(bpy)$_3^{2+}$ in silylated cups and any MV^{2+} on the external surface and not included in the channels. Although 4DQ^{2+} also quenches 10% of Ru(bpy)$_3^{2+}$ emission due to imperfections of the system, external 4DQ^{2+} shows much less influence than internal MV^{2+} (Fig. 2).

To obtain definitive evidence to support the through framework quenching, Ru(bpy)$_3^{2+}$/MV^{2+}@ITQ2sil was studied also by time resolved diffuse reflectance laser flash photolysis.

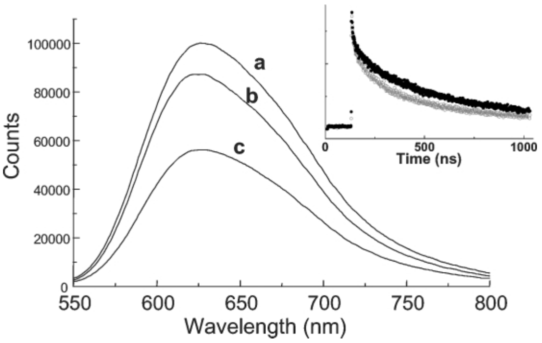

Fig. 2 Emission of Ru(bpy)$_3^{2+}$@ITQ2sil upon 466 nm excitation before (a) and after adsorption of 4DQ^{2+} (b) and MV^{2+} (c). The inset shows the decay of emission a (upper trace) and c (lower trace).

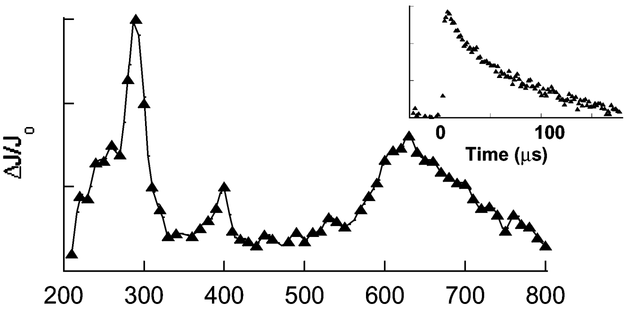

Fig. 3 Transient diffuse reflectance UV–Vis spectrum recorded 50 μs after 532 nm excitation of a sample of Ru(bpy)$_3^{2+}$/MV^{2+}@ITQ-2. The inset shows the decay monitored at 630 nm.

Upon 532 nm excitation, the transient spectrum shown in Fig. 3 was recorded. This spectrum clearly shows the formation of Ru(bpy)$_3^{3+}$ and MV$^{\cdot+}$ characterized by the absorption bands at 290 and 650 nm [Ru(bpy)$_3^{3+}$] and at 400 and 590 nm (MV$^{\cdot+}$), respectively. This conclusively proves the occurrence of photoinduced ET between Ru(bpy)$_3^{2+}$ and MV^{2+}, ruling out inorganic (Fe^{3+}) or organic (from silylation) impurities as responsible for the ET. Generation of Ru(bpy)$_3^{3+}$ and MV$^{\cdot+}$ was instantaneous on the ns time scale since no growth of the signals was observed which agrees well with the static quenching in emission spectroscopy. Ru(bpy)$_3^{3+}$ decays completely within the longest time available to our set-up (see insert in Fig. 3). In contrast, a control spectrum with the Ru(bpy)$_3^{2+}$@ITQ2sil in the absence of MV^{2+} is completely dominated by Ru(bpy)$_3^{2+}$ emission without time-resolved evidence for the formation of Ru(bpy)$_3^{3+}$.

In conclusion, the topology of novel ITQ2 comprising nonconnected external holes and channels has allowed the preparation of a geometrically well defined system in which the donor and the acceptor are separated by the zeolite framework. Using the well-studied Ru(bpy)$_3^{2+}$/MV^{2+} couple spectroscopic evidence showing that photoinduced ET within ITQ-2 can occur through the framework walls was found.

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