

Photochemistry of a Dumbbell-Shaped Multicomponent System Hosted Inside the Mesopores of Al/MCM-41 Aluminosilicate. Generation of Long-Lived Viologen Radicals

Mercedes Álvaro, Belén Ferrer, Hermenegildo García,* and Emilio J. Palomares

Instituto de Tecnología Química CSIC-UPV y Departamento de Química, Universidad Politécnica de Valencia, Camino de Vera s/n, 46022 Valencia, Spain

Vincenzo Balzani, Alberto Credi,* and Margherita Venturi

Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via Selmi 2, 40126 Bologna, Italy

J. Fraser Stoddart* and Sabine Wenger

Department of Chemistry and Biochemistry, University of California, Los Angeles, 405 Hilgard Avenue, Los Angeles, California 90095-1569

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A dumbbell-shaped compound, 2^{6+} , comprising a Ru(II) polypyridine complex, a *p*-terphenyl, a 4,4'-bipyridinium unit, a 3,3'-dimethyl-4,4'-bipyridinium unit, and a tetraarylmethane unit, has been enclosed in the channels (3.2 nm diameter) of an Al/MCM-41 aluminosilicate. Evidence for the internal location of 2^{6+} in the Al/MCM-41 host was obtained by mapping the C/Si and N/Si atomic ratios as a function of the depth of penetration into the interior of the aluminosilicate particles. The photoluminescence of the Ru(II) polypyridine unit, when 2^{6+} is enclosed within Al/MCM-41, is red-shifted, and the excited state is considerably shorter-lived compared with the behavior of 2^{6+} in acetonitrile solution. Laser flash photolysis experiments on 2^{6+} enclosed in the aluminosilicate matrix yield different results depending on the excitation wavelength. Selective excitation (532 nm light) of the Ru polypyridine component formed, together with oxidized Ru complex moieties, long-lived (millisecond time scale) radical cations of the 4,4'-bipyridinium unit and trapped electrons. Excitation at 308 nm, with light absorption involving both the Ru complex moiety and the bipyridinium units, leads to reduction of the 4,4'-bipyridinium unit and oxidation of the Ru complex, but the two processes might not be directly related. Compound 2^{6+} is the dumbbell-shaped component of a previously investigated rotaxane, 1^{6+} , which, in acetonitrile solution, behaves as a photochemically driven molecular abacus (*Chem.—Eur. J.*, **2000**, *6*, 3558). The observation of a long-lived 4,4'-bipyridinium radical cation when 2^{6+} is incorporated in Al/MCM-41 may be relevant to the operation of molecular machines such as 1^{6+} , which are based on photoinduced electron transfer, but the occurrence of photoinduced redox processes involving the matrix would likely interfere severely with the machine-moving processes.

Introduction

Much interest is currently being devoted to the bottom-up construction of artificial machines of nanoscale dimensions, usually called molecular machines.^{1–4} Molecular machines operate via electronic and nuclear rearrangements, that is, through some kind of chemical reaction, and like macroscopic machines, they need energy to operate and signals to communicate with the operator.¹ If a molecular machine works by chemical energy inputs (i.e., by addition of a "fuel"), waste products are produced whose accumulation compromise the operation of the machine, unless they are removed from the system.⁵

Recent advances in supramolecular photochemistry^{6,7} have shown that light excitation can directly cause reactions involving extensive mechanical movements without the formation of waste products. The photoinduced isomerization of supramolecular species containing $-N=N-$ ⁸ or $-C=C-$ ⁹ double bonds have indeed been used to design molecular machines driven by light-energy inputs. In supramolecular species, photoinduced electron-transfer reactions can also cause large displacements of molec-

ular components, particularly in systems such as pseudorotaxanes, rotaxanes, and catenanes.¹⁰ Working with suitably designed systems, a sequence of cyclic molecular-level movements can indeed be performed, making use of light-energy inputs without generating waste products.^{8,9,11} The use of light as an energy input to make molecular machines work is convenient also for other reasons: (i) sunlight is a renewable and largely available energy source; (ii) light can be switched on and off easily and rapidly; (iii) lasers provide the opportunity of working in very small spaces and in short-time domains; (iv) photons, besides supplying the energy needed to make a machine work, can also be useful to "read" the state of the system and thus to control and monitor the operation of the machine.

Recently, some of us¹² have investigated a system in which, upon light excitation, a molecular ring shuttles between two "stations" along a molecular thread (1^{6+} , Figure 1). The rotaxane 1^{6+} consists of a dumbbell-shaped component, 2^{6+} , threaded by an electron-donating macrocycle, **3**. The dumbbell component is an interesting multicomponent species, which contains, in sequence, a Ru(II) polypyridine photosensitizer (**P**), a *p*-terphenyl rigid spacer (**S**), a 3,3'-dimethyl-4,4'-bipyridinium (**A**₂)

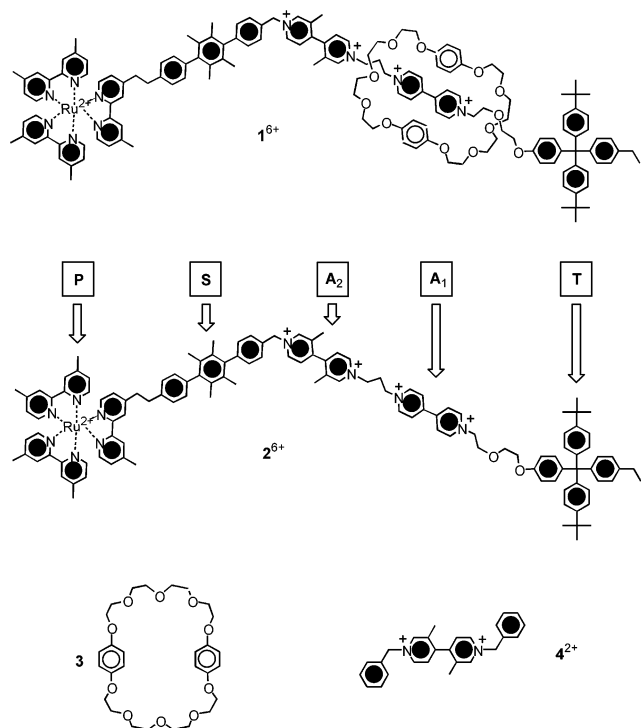


Figure 1. Structural formulas of the rotaxane 1^{6+} , the dumbbell-shaped component 2^{6+} , the macrocycle 3 , and the model compound 4^{2+} .

and a 4,4'-bipyridinium (A_1) electron-acceptor unit, and a bulky tetraarylmethane unit (T). In the 1^{6+} “machine”, P is the “light-fueled motor”, A_1 and A_2 play the role of “stations” for the electron-donating macrocycle 3 , and T , together with P , prevents the macrocycle from escaping (stoppers). The photochemical and electrochemical properties of 1^{6+} and 2^{6+} in solution have been carefully studied.¹²

Because of the presence of the two different electron-accepting bipyridinium units, A_1 and A_2 , two translational isomers are possible for 1^{6+} . The most stable co-conformation (Figure 1) is that in which the macrocycle 3 encircles the strongest electron acceptor, A_1 . Light excitation of the Ru photosensitizer unit P causes, in competition with the intrinsic excited-state decay, the transfer of an electron from P to A_1 with a consequent “deactivation” of this station. If the back electron-transfer process from reduced A_1 to oxidized P is sufficiently slow, the macrocycle moves to A_2 and then subsequently returns to A_1 when the back electron-transfer process has taken place. Such a molecular machine has been designed to produce of a full cyclic movement by light excitation without the generation of any waste product. In some ways, 1^{6+} could be considered as a “four-stroke” cyclic linear motor powered by light.¹³

A crucial point relating to the operation of this machine is the lifetime of the photoinduced electron-transfer state (oxidized P /reduced A_1), which should live long enough to allow the intrinsically slow ring shuttling. Since it is well established that photoinduced electron transfer within the pores of zeolites and related micro- and mesoporous aluminosilicates produces orders of magnitude increases in the lifetime of photogenerated electron-transfer states,^{14,15} a study of the photochemical behavior of 1^{6+} and 2^{6+} incorporated into a suitable porous host^{16–18} was thought to be a worthwhile pursuit. In particular, an extension of the lifetime of the photoinduced electron-transfer state in 1^{6+} could offer a means of increasing the efficiency of this photochemically driven machine.

We have, therefore, attempted to incorporate 1^{6+} and 2^{6+} into an aluminosilicate, but we have found that, under the severe experimental conditions required for the incorporation process, 1^{6+} undergoes dethreading by a slippage mechanism,¹⁹ so even starting from a 1^{6+} solution, only the dumbbell component 2^{6+} enters the channels of the host. Such a dumbbell is, nonetheless, a very interesting multicomponent species by itself. And so we have investigated its photophysical and photochemical behavior in the channels of an Al/MCM-41 host. We have found that the 4,4'-bipyridinium radical cation (i.e., the reduced A_1 unit) formed by light excitation is very long-lived, a result which is relevant to the operation of molecular machines such as 1^{6+} , which are based on photoinduced electron transfer. Excitation with different wavelengths has revealed the occurrence of electron-transfer processes between the excited ruthenium- or viologen-based units and the hosting matrix.

Experimental Section

Compounds 1^{6+} , 2^{6+} , and 4^{2+} as hexafluorophosphate salts were available from a previous investigation.¹²

Al/MCM-41 was prepared by hydrothermal crystallization using aerosil and alumina as Si and Al sources, respectively, and cetyltrimethylammonium bromide as a structure-directing agent, following the procedure reported in the literature.²³ The as-synthesized sample in a shallow bed was calcined in an oven by heating under a N_2 flow (5 mL min^{-1}) from room temperature up to 540°C at 3°C min^{-1} ; then the N_2 flow was gradually replaced by air in 1 h, and the temperature was maintained at 540°C for 12 h. The Si/Al ratio of the solid was obtained by chemical analysis after dissolving the aluminosilicate in concentrated hydrofluoric acid. Surface areas and pore size distributions, which were measured by isothermal gas adsorption (see Supporting Information), were $820 \text{ m}^2 \text{ g}^{-1}$ and 32 \AA , respectively. Crystallinity of the resulting Al/MCM-41 after calcinations was confirmed by powder X-ray diffraction (see Supporting Information). Combustion chemical analysis (Perkin-Elmer CHNOS analyzer) of calcined Al/MCM-41 samples established that the C and N content was below 0.05%. IR spectroscopy of calcined Al/MCM-41 recorded in KBr pellets and outgassed for 1 h at 100°C showed that the 1440 cm^{-1} peak characteristic of the cetyltrimethylammonium was completely absent, while the presence of an abundant population of silanol groups can be inferred from the 3600 cm^{-1} absorption band (see Supporting Information).

Adsorption of 2^{6+} into Al/MCM-41 was accomplished by stirring at reflux temperature under inert atmosphere a solution of $2(\text{PF}_6)_6$ (2.5 mg) in MeCN (5 mL) in the presence of thermally dehydrated Al/MCM-41 (0.5 g) for a week. Then, the solid was filtered and washed with MeCN. Controls of the supernatant solution by FAB-MS (Servicio de Espectrometría de Masas-Universidad de Valencia) revealed that 2^{6+} survives this treatment. The same adsorption procedure, when applied to a $1(\text{PF}_6)_6$ solution, showed that dethreading takes place and that the adsorbed species is again 2^{6+} . Adsorption of 1,4-dimethoxybenzene (DMB) was carried out by adding 5 mg of DMB per each 100 mg of Al/MCM-41 loaded with 2^{6+} .

Diffuse reflectance UV–vis spectra were recorded with a Shimadzu model UV 2101/3101 PC scanning spectrophotometer adapted with an integrating sphere and using BaSO_4 as reference. Combustion analysis was carried out with a Netzsch thermobalance operating under an air stream using Kaolin as standard. XPS measurements were carried out with a Vacuum Generators Escalab-210 system in the conventional mode and by using the Mg $K\alpha$ (1253.6 eV) radiation of a twin anode in the constant

analyzer energy mode with a pass energy of 40 eV. The vacuum attained during spectra acquisition was better than 5×10^{-9} mbar. Fluorescence spectra and lifetimes were recorded on an Edinburgh Analytical Instruments FL900 spectrophotometer. Laser flash photolysis studies were carried out using second (532 nm, ~ 20 mJ/pulse) and fourth (266 nm, ≤ 20 mJ/pulse) harmonic output from a Spectra Physics Nd:YAG laser and a XeCl excimer laser (Lumonics EX530) for 308 nm excitation (~ 100 mJ/pulse). An Oriel kinetic spectrometer setup, in conjunction with a Tektronix digital oscilloscope, was employed.²⁰ The ordinate units of the time-resolved diffuse reflectance spectra (Figures 4–7) correspond to $\Delta I/J_0 = (J_0 - I_t)/J_0$, where J_0 and I_t are the photomultiplier signals before the laser flash and after a time period t , respectively.

Results and Discussion

Incorporation into Al/MCM-41 Aluminosilicate. The rotaxane **1**⁶⁺ and its dumbbell component **2**⁶⁺ are long, rodlike molecules. They have roughly cylindric structures with a diameter of about 1.5 nm in the case of **2**⁶⁺, based on the reported^{21,22} size of unsubstituted [Ru(bpy)₃]²⁺ (1.2 nm). The rotaxane, which is prepared¹² by slippage of **3** over the stoppers of **2**⁶⁺, has most likely a little larger diameter than its dumbbell component. Therefore, we anticipated that an appropriate host to include these compound is a mesoporous MCM-41 silicate.²³ Taking into account that both **1**⁶⁺ and **2**⁶⁺ bear six positive charges, we thought that an aluminum-containing MCM-41 might have been even more appropriate. The isomorphic substitution of framework SiO₄⁴⁻ by AlO₄⁵⁻ introduces negative charges (one per Al) that require the presence of equivalent amounts of charge compensating cations.²⁴ In this way, the negative charges of the lattice introduced by the presence of some Al counterbalance the positive charges of the guest molecule. Thus, we synthesized an Al/MCM-41 sample with a relatively high Al content (Si/Al = 13) and hexagonal channels with 3.2 nm diameter, measured by isothermal gas adsorption. The X-ray diffraction pattern of this sample before and after template removal was the same as that previously reported for this type of mesoporous silicate. A strict calcinations protocol was followed to ensure the complete desorption/decomposition of the template. The absence of organic residues on the calcined sample was checked by combustion C and N chemical analysis and IR spectroscopy. The absence of detectable amounts of organic material is very important for the discussion of the photochemical behavior of the dumbbell rotaxane component **2**⁶⁺.

The incorporation of molecules inside the channels of an aluminosilicate host is usually performed by liquid–solid adsorption in an inert atmosphere. It was anticipated that adsorption of **1**⁶⁺ and **2**⁶⁺ would be seriously disfavored by their long dimensions. Attempts to adsorb **2**⁶⁺ from an acetonitrile solution of **2**(PF₆)₆ at room temperature with thermally dehydrated Al/MCM-41 failed: no change was observed in the UV–vis spectrum of the supernatant solution, even after several days. Adsorption was therefore carried out by refluxing an acetonitrile solution of **2**(PF₆)₆ for one week. Control by FAB-MS showed that the compound survives this treatment. In particular, peaks at 2475, 2330, and 2185 corresponding to [M – 2PF₆]⁺, [M – 3PF₆]⁺ and [M – 4PF₆]⁺ were recorded. Furthermore, the luminescence properties of **2**⁶⁺ did not change upon refluxing an acetonitrile solution of **2**(PF₆)₆ for a whole week. We have then verified that, under the drastic experimental conditions needed to obtain adsorption, the rotaxane **1**⁶⁺ undergoes substantial dethreading, since the FAB-MS of the

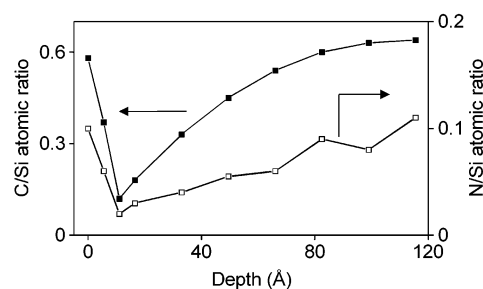


Figure 2. C/Si and N/Si atomic ratios obtained by XPS analysis as a function of the depth of penetration from the external surface of a particle after **2**⁶⁺ adsorption.

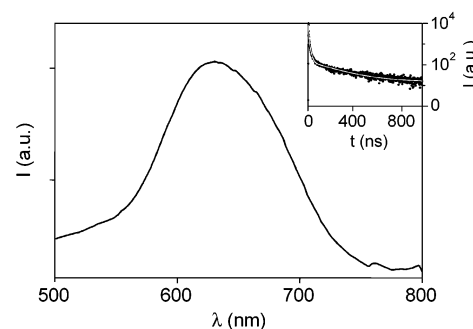


Figure 3. Emission spectrum of **2**⁶⁺ adsorbed in Al/MCM-41 upon excitation at 450 nm. The inset shows the emission decay monitored at 630 nm. The continuous line corresponds to the curve fit from which the two emission lifetimes were obtained.

solution after heating corresponds to that expected for **2**⁶⁺. Therefore, the study of **1**⁶⁺ was frustrated. To perform some control experiments, we also proceeded to incorporate 1,1'-dibenzyl-3,3'-dimethyl-4,4'-bipyridinium, **4**²⁺ (a model compound for the A₂ unit) inside Al/MCM-41.

Adsorption of **2**⁶⁺ by Al/MCM-41 yielded a pale orange powder. Elemental analyses (C and N) showed that the resulting solid contained **2**⁶⁺ (estimated loading of 5 mg of **2**⁶⁺ per gram of Al/MCM-41, 0.8 molecules per channel, 0.4 molecules per pore mouth). Evidence that compound **2**⁶⁺ partially penetrates the channels was obtained by mapping out the C/Si and N/Si atomic ratios profile versus the depth from the external surface toward the center of the particle. These profiles were obtained by combining XPS analytical data of the outermost exposed surface of the particles with extensive high-energy Ar⁺ sputtering that produces destruction of the external layers of the solid. The profile of the C/Si and N/Si atomic ratios as a function of the distance from the external surface is shown in Figure 2. Such data show that (i) the C/N ratio corresponds to that of compound **2**⁶⁺ and (ii) **2**⁶⁺ is spread throughout the particle and at least some of it has to be present inside the channels.

After adsorption of **2**⁶⁺, the diffuse reflectance UV–vis spectrum of the Al/MCM-41 powder was the same as that exhibited by **2**⁶⁺ solutions.

Luminescence. Upon excitation at 450 nm, a wavelength that corresponds to the lowest energy absorption maximum of the Ru(II)-complex moiety, the powder loaded with **2**⁶⁺ displayed the spectrum shown in Figure 3. The emission band is quite similar, but slightly red-shifted ($\lambda_{\text{max}} = 630$ nm), compared with that ($\lambda_{\text{max}} = 618$ nm) exhibited¹² by **2**⁶⁺ in acetonitrile solution. This result can be accounted for by some stabilization of the charge-transfer emitting state of the Ru(II) polypyridine unit when **2**⁶⁺ is inside the polar Al/MCM-41 channels.

The emission decay monitored at 630 nm exhibits a double exponential behavior with lifetimes of 11 and 192 ns. The decay

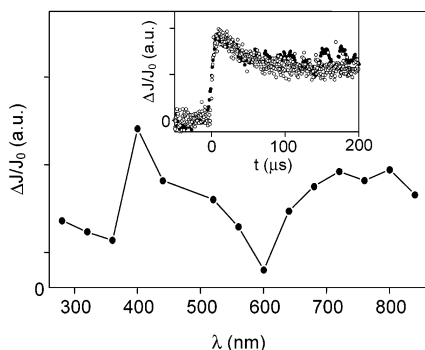


Figure 4. Time-resolved diffuse reflectance UV-vis spectrum of 4^{2+} incorporated in the aluminosilicate recorded 20 μs after 266-nm laser excitation. The inset shows the decays of the transient spectrum monitored at 400 (\circ) and 680 nm (\bullet).

and the curve fitting from which the lifetimes were obtained are shown in the inset to Figure 3. The most salient features emerging from the luminescent data are that (i) there are two different sites (or two families of slightly different sites) for the Ru-based unit (and presumably for the entire 2^{6+} dumbbell) in the aluminosilicate and (ii) the emitting excited state undergoes faster deactivation ($\tau = 730$ ns) than it does in acetonitrile solution.¹² The latter observation may arise from the interaction—possibly, quenching by electron transfer—of the Ru complex moiety of 2^{6+} with the walls of the Al/MCM-41 host; such an interpretation is in agreement with the results of laser flash photolysis experiments (vide infra).

Laser Flash Photolysis. Laser flash photolysis experiments on 2^{6+} incorporated in the Al/MCM-41 matrix were carried out with two different wavelengths (532 and 308 nm). In the case of the model compound 4^{2+} , excitation was performed with 266-nm light.

The experiments previously carried out in acetonitrile solution showed¹² that, as expected, light excitation of the Ru-complex unit **P** of 2^{6+} causes an electron transfer from **P** to the electron-accepting bipyridinium units. It should be noted that **A**₁ is more distant from **P** than **A**₂, but it is much easier to reduce ($\Delta E_{1/2} = 320$ mV). Since the absorption spectra of the one-electron reduced forms of the model compounds of **A**₁ and **A**₂ [1,1'-dibenzyl-4,4'-bipyridinium and 1,1'-dibenzyl-3,3'-dimethyl-4,4'-bipyridinium (4^{2+}), respectively] are quite different,²⁵ it was possible to demonstrate that the electron-transfer process causes, besides the oxidation of **P** (bleaching in the 450 nm spectral region), the reduction of **A**₁, either directly or via very fast transient reduction of **A**₂. The decay of the transient spectrum of the [oxidized **P**/reduced **A**₁] electron-transfer state revealed a lifetime of 1.2 μs , corresponding to a rate constant of 8.3×10^5 s⁻¹ for the back electron-transfer reaction.

We anticipated that the experiments carried out on 2^{6+} incorporated into Al/MCM-41 would have been more difficult to interpret than those in acetonitrile solution since the aluminosilicate matrix is very reactive. Particularly relevant to the present discussion are two previously reported observations.^{26,27} Excitation of viologen compounds incorporated in microporous zeolites gives rise to the corresponding radical cations even in the absence of any electron donor.²⁶ Apparently, the silicate framework is able to donate an electron to excited viologens. This result has been confirmed by our flash experiments on adsorbed 4^{2+} since the long-lived transient spectrum, obtained (Figure 4) after excitation at 266 nm of 4^{2+} incorporated in the aluminosilicate, is in agreement with that displayed by the one-electron reduced form of the same compound in acetonitrile solution.¹² It has also been reported²⁷ that excitation of [Ru-

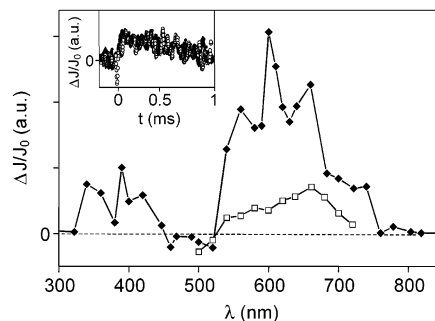


Figure 5. Time-resolved diffuse reflectance UV-vis spectra of 2^{6+} incorporated in the aluminosilicate purged with N_2 (\blacklozenge) recorded 80 μs after 532-nm laser excitation. Note that the intensity of the signal between 500 and 650 nm is much higher than that recorded at 400 nm, indicating the presence of trapped electrons. This signal decreases remarkably upon purging with CH_2Cl_2 (\square). The inset shows the decays of the residual signal after CH_2Cl_2 purging monitored at 400 (\circ) and 600 (\bullet) nm.

(bpy)₃]²⁺ incorporated in zeolites codoped with TiO_2 leads to a broad and intense absorption in the visible region, assigned to electron ejection.²⁸ In the case of [Ru(bpy)₃]²⁺ encapsulated within zeolite in the absence of TiO_2 , the recording of the diffuse reflectance absorption spectrum is difficult because of the intense photoluminescence of the metal complex.

On the basis of these observations, it was expected that excitation at different wavelengths of 2^{6+} incorporated in the aluminosilicate matrix would yield different transient spectra.

Excitation at 532 nm. At this wavelength, selective excitation of the Ru(II) polypyridine unit of 2^{6+} incorporated in the aluminosilicate is obtained. The corresponding transient reflectance spectrum is shown in Figure 5. A control experiment carried out on 4^{2+} incorporated in the aluminosilicate showed that no transient was generated upon excitation at 532 nm.

What is noteworthy in Figure 5 is that a very small bleaching in the region of the absorption band of the **P** unit is accompanied by intense positive absorption bands in the 300–400 and 550–750 nm regions. The relative intensities of these two bands do not match those expected for the reduced species of either **A**₁ or **A**₂. The remarkable intensity of the 550–750 nm band suggests the presence of trapped electrons, as already reported²⁹ for zeolites. Electron ejection by photoexcitation of guest species in zeolites had been observed^{27,28} previously. Since it is known³⁰ that very small concentrations of CH_2Cl_2 are able to scavenge completely electrons in zeolites, we purged the Al/MCM-41 powder incorporating 2^{6+} with a N_2 stream saturated with CH_2Cl_2 vapors at room temperature for 15 min. This procedure causes a strong change in the transient spectrum (Figure 5), which tends to become compatible with that of the reduced **A**₁ species. These results show that, upon light absorption by the Ru(II)-based unit of 2^{6+} , electrons are ejected and spread out through the channels of Al/MCM-41, whereas only a small fraction of the radical cation of the **A**₁ species is formed. Apparently, intramolecular electron transfer within 2^{6+} seems to be inefficient in Al/MCM-41, while site isolation, related to the inclusion of a single 2^{6+} molecule per channel, does not allow the occurrence of intermolecular electron-transfer processes.

The fate and location of ejected electrons in zeolites and related aluminosilicates is a question of much controversy and debate.^{29,31} The picture may change depending on the nature and chemical composition of the zeolite. Coadsorbed water, Brønsted or Lewis acid sites or both, and structural defects have been proposed³¹ as electron traps. Recently, Moissette and co-

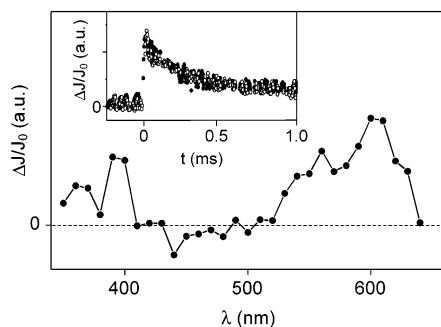


Figure 6. Time-resolved diffuse reflectance UV-vis spectra of 2^{6+} incorporated in the aluminosilicate recorded 25 μ s after 308 nm laser excitation. The inset shows the decays of the transient spectrum monitored at 390 (○) and 600 nm (●).

workers have observed³² by sophisticated electron paramagnetic resonance (EPR) techniques that the position of electrons ejected by biphenyl and anthracene within HZSM-5 are coupled with Al atoms.

Excitation at 308 nm. On excitation at this wavelength, most of the exciting light is absorbed in different fractions by the Ru complex moiety (intraligand bands), the two viologen units, the spacer group **S**, and the stopper **T**. The diffuse reflectance transient spectrum, together with the corresponding decays monitored at 390 and 600 nm, is shown in Figure 6. Two main features are evident: (i) some bleaching is observed in the 450 nm region, and (ii) positive absorption bands are observed at 390 and 600 nm. The conclusions that can be drawn, considering also the results obtained upon selective excitation of the Ru-based unit (532 nm) and of the model compound of A_2 (Figure 4), are the following: (a) the observed bleaching around 450 nm shows that some Ru complex undergoes oxidation; (b) the positive absorption bands show that the A_1 unit undergoes reduction; note that reduction of A_2 would not correspond to the presence of a maximum but rather to a minimum at 600 nm, as shown (Figure 4) by the results obtained upon excitation of 4^{2+} ; (c) the smaller than expected (in the case of A_1 reduction) ratio between the intensities of the bands at 390 and 600 nm is likely to arise from the absorption at longer wavelengths by ejected electrons, as shown (Figure 5) by the experiments performed at 532 nm. Because of the complexity of the system and the overlapping of the (positive and negative) absorption bands, quantitative data concerning the fractions of the various redox species present after photoexcitation cannot be obtained. It should also be noted that oxidation of the Ru complex and reduction of the A_1 station could be uncorrelated processes in view of the results obtained upon selective excitation of the Ru complex and the 4^{2+} model compound. In any case, the transient absorption bands decay very slowly (millisecond time scale, Figure 6, inset).

Experiments in the Presence of an Electron Donor. Since the use of sacrificial donors is a frequently employed^{5,12,13} strategy to extend the lifetime of viologen radical cations in solution, we decided to investigate the effect of an electron donor in the present system. Coadsorption of an excess of 1,4-dimethoxybenzene (DMB) onto Al/MCM-41 containing 2^{6+} was performed. DMB was chosen because its radical cation or derived species exhibit³³ distinct absorption bands. Excitation was performed at 532 nm, where light is absorbed exclusively by the Ru-based unit of 2^{6+} . The diffuse reflectance transient spectrum (Figure 7) shows the spectral features typical²⁵ of the reduced form of the A_1 unit. Furthermore, a band at around 450 nm is observed, which is attributed³³ to the formation of $DMB^{•+}$ radical cations. It should also be noted that the strong

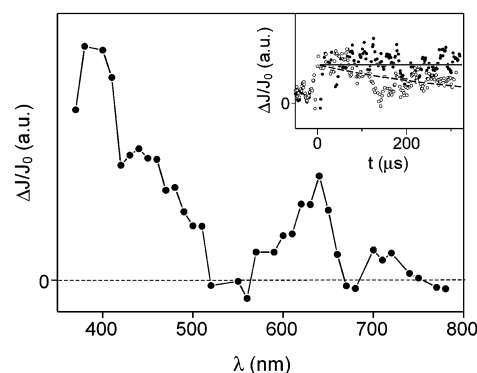


Figure 7. Time-resolved diffuse reflectance UV-vis spectrum of 2^{6+} coadsorbed with DMB in Al/MCM-41 recorded 100 μ s after 532 nm laser excitation. The inset shows the decay monitored at 390 nm before (○) and after (●) coadsorption of DMB.³⁴

positive absorption signal in the 550–750 nm region observed in the absence of DMB (Figure 5), originated by trapped electrons, can no longer be seen. The most important result, however, is that the presence of DMB causes a significant enhancement of the lifetime of the 4,4'-bipyridinium (A_1) radical cation. The inset to Figure 7 provides a comparison of the transient decay monitored at 390 nm before and after the addition of DMB.³⁴

A likely rationalization of the influence of DMB is that after the initial intramolecular electron transfer, in which the radical cation of the A_1 unit is generated (Figure 8, process a), DMB transfers one electron to the primary hole, that is, the oxidized Ru-complex moiety (Figure 8, process b). As a result of the increased distance of charge separation and because charge recombination is now a bimolecular event (Figure 8, process c), the lifetime of the reduced A_1 unit is increased. As described above, photoexcitation of the Ru moiety of 2^{6+} also causes electron ejection involving a trap site of the aluminosilicate framework (Figure 8, process d). This process is most likely followed by formation of $DMB^{•+}$ radical cations (Figure 8, process e), which could readily scavenge trapped electrons (Figure 8, process f).

Conclusions

The photochemical behavior of 2^{6+} hosted in Al/MCM-41 differs from that in acetonitrile solution. The two most important differences are (i) the longer lifetime of the reduced 4,4'-bipyridinium (A_1) unit and (ii) the occurrence of electron transfer between the aluminosilicate framework and excited units of 2^{6+} . These two factors may have opposite effects in the context of the operation of a molecular abacus such as 1^{6+} hosted in porous aluminosilicates. The longer lifetime of the reduced A_1 unit should increase the efficiency of the relatively slow shuttling movement of the macrocycle, but the occurrence of electron transfer from the excited Ru(II) complex to the matrix would decrease the efficiency of the intramolecular photoreduction of A_1 . In the case of UV excitation, the electron-transfer processes between the excited viologen units and the Al/MCM-41 matrix, whose reversibility has not been verified, could further complicate the operation of the machine. The lifetime of the photogenerated radical cation of the A_1 unit can be further increased by coadsorption of an electron donor such as 1,4-dimethoxybenzene. Under these conditions, the viologen radical cation can survive for several milliseconds.

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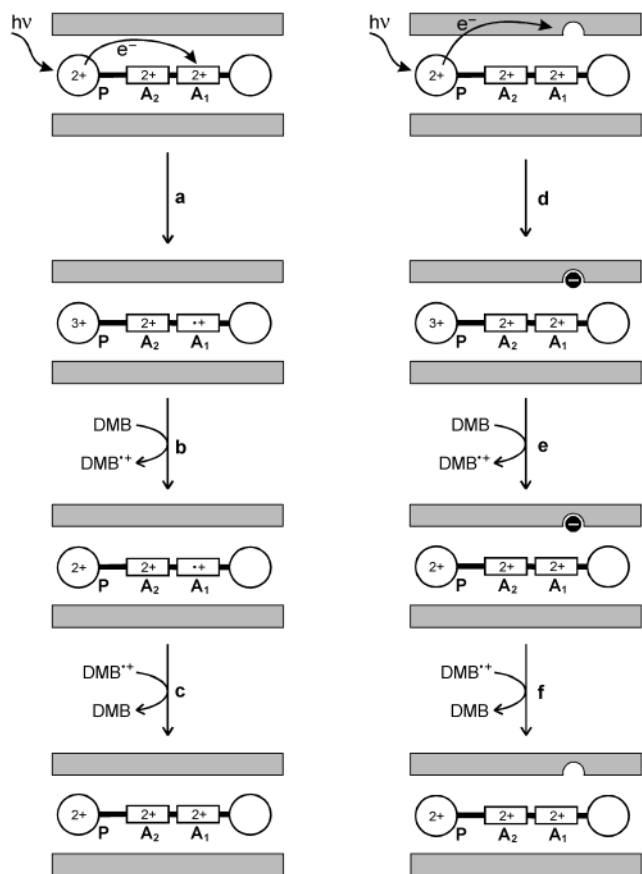


Figure 8. Pictorial illustration of the influence of DMB on the photochemistry of $2^+@Al/MCM-41$ upon 532 nm excitation: (a–c) mechanism initiated by intramolecular electron transfer; (d–f) mechanism initiated by electron ejection involving a trap site of the aluminosilicate framework.

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Supporting Information Available: Powder X-ray diffraction data, IR spectrum and isothermal gas adsorption of calcined Al/MCM-41, and additional transient absorption decay plots. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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