NC

R. M. Krishna and L. Kevan*

Department of Chemistry, University of Houston, Houston, TX 77204-5003, USA

Received 14th August 2001, Accepted 1st October 2001 First published as an Advance Article on the web

The photoinduced charge separation of N-alkylpyrenes in transition metal ion containing mesoporous SiMCM-41 and MeMCM-41 materials [Me = Ti(IV), V(V), Ni(II), Co(II) and Cu(II)] with ultraviolet irradiation at room temperature is investigated. N-alkylpyrene cation radicals (PvC_n^+) are generated in SiMCM-41 and MeMCM-41 mesoporous silica materials and are characterized by electron spin resonance (ESR) spectroscopy. Mesoporous SiMCM-41 and MeMCM-41 materials are shown to be effective heterogeneous hosts for the photoinduced formation and stabilization of PyC_n^+ cation radicals at room temperature indicating stable photoinduced charge separation for several hours. The long lifetimes for the cation radicals indicate the utility of the environment of these MCM-41 materials for controlling back electron transfer. A series of TiMCM-41 materials are synthesized that increase the PyC_n^+ photoionization efficiency in comparison with VMCM-41, NiMCM-41, CoMCM-41 and CuMCM-41. The photoyield efficiency is decreased significantly when the concentration of pyrene is increased above about 10^{-2} M. The photoionization efficiency depends on the type and concentration of the metal ions in the mesoporous MeMCM-41 materials which suggests that certain metal ions can act as electron acceptors. Also, as the N-alkylpyrene alkyl chain length increases from methyl to hexadecyl the photoionization yield decreases. The photoionization efficiency increases in the order TiMCM-41 > NiMCM-41 > VMCM-41 > SiMCM-41 > CoMCM-41 > CuMCM-41. The photoyield is higher by about 1.5 times at 77 K compared to room temperature. The observed photoyields of PyC_n (n = 1, 4, 8, 12, or 16) in mesoporous MeMCM-41 materials suggest that these materials are useful models for long-term photoinduced charge separation at room temperature.

Introduction

The design of artificial efficient photomolecular devices for use in energy storage and conversion has been an important goal.¹⁻⁴ A fundamental issue that limits the development of solar energy conversion is the thermal back electron transfer between the photochemically produced redox pairs prior to the accomplishment of any useful chemistry.⁵ Substantial effort is being spent in developing potential molecular assemblies that lead to stable and long-lived charge separation.⁶⁻¹¹ Systems such as micelles, vesicles, zeolites, silica gels and molecular sieves have been examined as host materials to improve the net energy conversion.¹²⁻¹⁴ Such systems provide appropriate spatial and electronic organization of the donor and acceptor molecules to retard rapid back electron transfer. Thus, one can achieve a charge-separated state for a longer period of time by appropriately tuning the spatial and electronic properties of the host system.

Pyrene and its derivatives are selected because these polycyclic hydrocarbons are known to undergo oxidative as well as reductive photoinduced electron-transfer reactions.¹⁵ These can be easily photooxidized by ultraviolet irradiation to form *N*-alkylpyrene cation radicals (PyC_n^+) which can be characterized by electron spin resonance (ESR). The design, synthesis and study of molecular models have been instrumental in advancing the knowledge of electron transfer dynamics involved in photosynthesis.¹⁶ Good heterogeneous systems which have attracted considerable attention in recent years as hosts to perform photoinduced electron transfer reactions with larger photoactive molecules are mesoporous M41S molecular sieves.¹⁷ Mesoporous SiMCM-41 materials have uniform pore sizes from 15 to 100 Å, which can be controlled during synthesis,¹⁸ are effective catalysis for oxidative reactions.^{19,20} and are promising host systems for photoredox reactions.^{21–25}

Earlier studies showed that MCM-41 materials can achieve stable photoinduced charge separation.^{21,23} Incorporation of reducible transition metal ions into porous silica materials retards back electron transfer by acting as more stable electron acceptors.^{21,23,26} Tetrahedral Si(IV) in the SiMCM-41 framework can be replaced by other transition metal ions^{27–33} such as Ti(IV), V(V), Al(III), Zr(IV), Ni(II) and Mn(II) to modify the SiMCM-41 framework to enhance the photoionization efficiency of incorporated photoactive molecules such as *N*alkylpyrenes (PyC_n), or *N*-alkylphenothiazines (PC_n).

Recently, we have reported successful photoinduced charge separation of *N*-alkylphenothiazines in SiMCM-41, AlMCM-41 and TiMCM-41 materials.²¹ The photoyield and stability of photoinduced alkylphenothiazine cation radicals (PyC_n^+) were found to be significantly increased in TiMCM-41 materials where Ti(IV) acts as an electron acceptor. In this work, we test the generality of efficient photoinduced charge separation of photoionizable molecules in metal ion containing MCM-41 materials to the alkylpyrene (PyC_n , n = 1, 4, 8, 12, or 16) class of molecules. The photoionization efficiency of PyC_n incorporated into SiMCM-41 and MeMCM-41, where Me = Ti(IV),

5348 *Phys. Chem. Chem. Phys.*, 2001, **3**, 5348–5353

V(v), Ni(II), Co(II), or Cu(II), was monitored by ESR. The experimental results show that the photoyields depend on the nature of the metal ion, with Ti(Iv) being the most efficient, and on the metal ion concentration in MeMCM-41 materials. The photoionization of PyC_n with different alkyl chain lengths is also assessed.

Experimental section

The following chemicals were used without further purification: tetramethylammonium hydroxide (TMAOH, Aldrich, 25%), tetraethylorthosilicate (TEOS, Aldrich), dodecyltrimethylammonium bromide (DTMABr, TCI). SiMCM-41 molecular sieve was prepared hydrothermally using dodecyltrimethylammonium bromide as the organic template following an earlier procedure.³²

In brief, 10.4 g of TEOS was mixed with 11.6 g of DTMABr in 2-propanol under vigorous stirring at room temperature and then 4.8 g of TMAOH and 76 mL of deionized water were added to the resultant clear solution and stirring was continued for about 2 h. The pH of the mixture was adjusted to 11.5 using 2 M H₂SO₄. After 2 h of stirring the mixture was heated at 358 K for about 4 h to remove 2-propanol and ethanol produced by the hydrolysis of tetraethylorthosilicate. The resulting gel was crystallized hydrothermally in Teflonlined autoclaves for 7 days at 373 K. After crystallization the solid product was filtered off, washed with deionized water, and dried in air at 350 K overnight. The solid powder was calcined in air at 820 K for about 6 h to remove water and organic templates.

For synthesis of TiMCM-41, initially TEOS and the required amount of tetrabutylorthotitanate (TBOT, Fluka), were vigorously mixed for 30 min and the following synthesis steps were exactly the same as described above for the synthesis of SiMCM-41. These samples are termed TiMCM-41-(x), where x is the Si/Ti ratio in the gel. Similarly for the synthesis of VMCM-41, NiMCM-41, CoMCM-41 and CuMCM-41, for each metal ion preparation, 10.4 g of TEOS was added with 11.6 g of DTMABr in 2-propanol under vigorous stirring and then 4.8 g of TMAOH with 76 mL of deionized water were added to the resultant clear solutions and stirred for 2 h. When the above solutions become cloudy, the required amounts of vanadyl sulfate, nickel sulfate, cobalt sulfate or copper sulfate dissolved in 5 mL water were added respectively and the following synthesis steps were the same as described above for the synthesis of SiMCM-41.

Commercial pyrene termed PyC_1 was received from Lancaster Chemical Co and used as received without further purification. *N*-alkylpyrene molecules termed PyC_n (where n=1, 4, 8, 12, or 16) were generous gifts from Prof. Y. S. Kang.

Characterization

Powder X-ray diffraction (XRD) patterns were collected with a Phillips 1840 diffractometer using Cu K α radiation of wavelength 1.541 Å over the range $1.5^{\circ} < 2\theta < 15^{\circ}$. Chemical analysis was measured by a JEOL JXA-8600 electron microprobe with averaging over several defocused areas to give the bulk composition. Calibration was done with known standards. The ESR spectra were recorded at room temperature and 77 K at X-band frequency using a Bruker ESP 300 spectrometer with 100 kHz field modulation and microwave power low enough to avoid saturation and distortion of the spectrum. The photoproduced PyC_n^+ , n=1, 4, 8, 12 or 16, cation radical yields were determined by double integration of the ESR spectra using the ESP 300 software. Themogravimetric analysis (TGA) of the samples were performed using a TGA 2050 analyzer from TA Instruments.

Photoionization samples

N-alkylpyrenes were incorporated into SiMCM-41 and MeMCM-41 by impregnation. For impregnation, 0.3 g of the sample was immersed in 1 mL of 10^{-2} M PyC_n in C₆H₆ overnight and the solvent was then removed by flowing nitrogen through the samples for about 1 h in the dark. Thus all samples contained the same amount of PyC_n. For ESR measurements the solid powders were introduced into 2 mm id \times 3 mm od Suprasil quartz tubes (~20 mm in height), evacuated below 1 Torr for about 5 h at room temperature and sealed. It was observed that the photoyields of all the samples subjected to evacuation to remove possible remaining traces of solvent were similar to the photoyields obtained for samples that were not evacuated. Hence, further photoionization experiments were carried out without evacuation.

Photoionization procedures

Each powder was photoirradiated at room temperature as well as at 77 K with a Cermax 300 W xenon lamp (ILC-LX 300 UV). The light was passed through a 10 cm water filter to prevent infrared light and also through a Corning glass filter 7-51 with 90% transparency at 240 and 400 nm with a maximum at 320 nm. The samples were rotated during the photoirradiation for uniform exposure to the light. ESR was used to detect the photoproduced *N*-alkylpyrene cation radicals.

Results

The XRD patterns for the synthesized SiMCM-41 and MeMCM-41 materials match well with the literature.^{21,27,32,33} The XRD patterns of as-synthesized MeMCM-41 and calcined MeMCM-41 show no significant differences. The pore sizes of the MeMCM-41 samples prepared range from 24 to 27 Å, which are bigger than the molecular dimensions of 6.9 to 19.8 Å for *N*-alkylpyrenes (PyC₁ to PyC₁₆). Fig. 1 shows the molecular dimensions of *N*-alkylpyrenes which were calculated using a PCMODEL program.³⁴ Thus, the alkylpyrenes should incorporate into these MeMCM-41 materials. But, thermal gravimetric analysis (TGA) results show that the larger PyC_n molecules do not completely penetrate into the MCM-41 channels. TGA results obtained in flowing oxygen for *N*-alkylpyrenes incorporated into SiMCM-41 are shown in Fig. 2. The curves show two or three weight loss regions. The first



Fig. 1 Structures of N-alkylpyrenes with different alkyl chain lengths.



Fig. 2 TGA curves in flowing oxygen of SiMCM-41/PyC_n (n = 1, 4, 12 and 16) materials.

near 80 °C is assigned to water desorption, the second near 200 °C is assigned to alkylpyrene desorption from the external surface of SiMCM-41 and the third peak centered around 500 °C is assigned to the oxidative decomposition of alkylpyrenes within the SiMCM-41 channels.²⁴ The peak at 500 °C assigned to decomposition of alkylpyrenes is absent when TGA is performed in flowing nitrogen. The smaller molecules of PyC_1 and PyC_4 only show peaks near $500\,^\circ C$ and not at 200 °C which indicates incorporation into the SiMCM-41 channels and no adsorption on the external surface of SiMCM-41. However, PyC₁₂ shows a small peak near 200 °C so some PyC_{12} is adsorbed on the external surface of SiMCM-41 and the peak near 500 °C for PyC_{12} shows that some PyC_{12} is also incorporated into the channels of MCM-41. PyC₁₆ shows a larger peak near 200 °C and no peak near 500 °C so most of the PyC₁₆ does not seem to penetrate into the MCM-41 channels.

Pyrene and its derivatives are known to undergo oxidative photoelectron transfer reactions.¹⁵ Photoirradiated samples of SiMCM-41 and MeMCM-41 [Me = Ti(IV), V(V), Ni(II) and Co(II)] without alkylpyrenes showed no ESR signals at room temperature. Samples of SiMCM-41 and MeMCM-41 incorporated with alkylpyrenes turn light brown before irradiation and produce very weak ESR signals of alkylpyrene cation radicals (PyC_n⁺). After being photoirradiated by 320 nm light at room temperature for 60 min, the samples turn dark brown and show strong ESR signals. The brown color is characteristic of PyC_n^+ cation radicals.³⁵ This means that some PyC_n^+ cation radicals are produced during sample preparation in a 'dark' reaction and that alkylpyrenes are the only photosensitive molecules in these systems. The relative dark reaction yields for MeMCM-41/PyC₁ are 3.8 for SiMCM-41, 3.6 for TiMCM-41, 4.1 for VMCM-41, 4.2 for CoMCM-41 and 4.4 for CuMCM-41.

Fig. 3 shows the ESR signal of pyrene cation radicals (PyC_1^+) in SiMCM-41 and TiMCM-41 samples before irradiation (a–e) and after being irradiated (A–E) by 320 nm UV light at room temperature for 60 min. The singlet ESR signal with g = 2.006 is assigned to PyC_1^+ .³⁴ This indicates photoinduced formation of relatively stable PyC_1^+ cation radicals at room temperature. From Fig. 4 and 5 it is clear that the intensities of the ESR signals of PyC_1^+ cation radical ions increase during the first 10 min and reach a plateau after about 30 min photoirradiation. CuMCM-41 and CoMCM-41 produce the highest 'dark' reaction compared to TiMCM-41, NiMCM-41 and SiMCM-41. Note that the dark reaction must be subtracted to obtain the net photoyield. The highest photoyield is obtained for TiMCM-41 followed by NiMCM-41, VMCM-41, SiMCM-41, CoMCM-41 and CuMCM-41. The photoyield in TiMCM-41 increases with increasing Ti content



Fig. 3 ESR spectra of PyC_1^+ in SiMCM-41/PyC₁ and TiMCM-41/PyC₁ at 0 (a-e) and 60 min (A-E) photoirradiation time with 320 nm light at room temperature.



Fig. 4 ESR intensity of PyC_1^+ in SiMCM-41 and TiMCM-41 *versus* 320 nm different photoirradiation times at room temperature.



Fig. 5 ESR intensity of PyC_1^+ in M-MCM-41/PyC₁ [M = Ti(IV), Ni(II), Co(II) and Cu(II)] *versus* 320 nm different photoirradiation times at room temperature.



Fig. 6 ESR intensity of PyC_1^+ in TiMCM-41-(80)/PyC₁ with different concentrations of PyC_1 .

in TiMCM-41 up to Si/Ti = 80 in the gel and then decreases for Si/Ti = 40 as shown in Fig. 4.

Fig. 6 shows the photoyield of PyC_n^+ in TiMCM-41 versus PyC_n concentration for 60 min photoirradiation times. The 0.01 M solution concentration of PyC_n corresponds to 2% coverage of the surface area of the MeMCM-41 channels. At higher solution concentrations, the photoyield decreases as shown in Fig. 6. The photoyield at 77 K is about 1.5 times higher than at room temperature.

Fig. 7 shows the ESR signal intensities of $PyC_n^+versus$ alkyl chain length for TiMCM-41/PyC₁ samples. The relative dark reaction yields become less as the alkyl chain length increases and are 3.6 for PyC₁, 3.1 for PyC₄ 2.8 for PyC₈, 2.3 for PyC₁₂ and 1.8 for PyC₁₆ As one can see from Fig. 7, the photoyields decrease with increasing alkyl chain length. The rates of formation of PyC₁⁺ cation radicals in MeMCM-41 [M = Ti(rv), V(v), Ni(II), Co(II) and Cu(II)] are evaluated from the initial slopes in Fig. 4 and 5 assuming first-order kinetics. The calculated rate constants for the formation of the PyC₁⁺ cation radicals on this basis are 5×10^{-2} s⁻¹ for TiMCM-41, 2.2×10^{-2} s⁻¹ for NiMCM-41, 1.3×10^{-2} s⁻¹ for VMCM-41, 2.8×10^{-3} s⁻¹ for CoMCM-41 and 5.3×10^{-4} s⁻¹ for CuMCM-41. This order of the rate constants is consistent with the order of the photoyields.

The stability of the photoinduced PyC_1^+ cation radical ions, as monitored by ESR, was also studied (not shown). Assuming first-order kinetics, the initial decay rates of PyC_1^+ cation radical ions for MeMMCM-41 at room temperature were evaluated to be 2.5×10^{-3} s⁻¹ for TiMCM-41, 4.2×10^{-3} s⁻¹ for NiMCM-41, 5×10^{-3} s⁻¹ for VMCM-41, 6.3×10^{-3} s⁻¹ for CoMCM -41 and 3.8×10^{-4} s⁻¹ for CuMCM-41.



Fig. 7 ESR intensity of PyC_n^+ in TiMCM-41/PyC_n (n = 1, 4, 8, 12 or 16; Si/Ti = 80) at 60 min photoirradiation time with 320 nm light at room temperature.



Fig. 8 ESR spectra of PyC_1^+ and VO^{2+} in VMCM-41/PyC₁ at 0, 3, 20 and 60 min photoirradiation time with 320 nm light at room temperature.

The ESR spectra from photoinduced PyC₁⁺ cation radicals in VCM-41 after several photoirradiation times at room temperature are shown in Fig. 8. In addition to the line at g = 2.006 due to PyC₁⁺ an eight line anisotropic spectrum due to VO²⁺ is observed with the parameters $g_{\parallel} = 2.024$, $g_{\perp} = 2.052$, $A_{\parallel} = 191 \times 10^{-4}$ cm⁻¹ and $A_{\perp} = 54 \times 10^{-4}$ cm⁻¹

Discussion

XRD and TGA experiments confirm that the pore size of MCM-41 is large enough to contain N-alkylpyrenes (PyC_n). The ESR results clearly confirm the photoionization of Nalkylpyrene molecules into N-alkylpyrene cation radical ions in SiMCM-41 and MeMCM-41 [M = Ti(IV), V(V), Ni(II), Co(II)and Cu(II)] materials by 320 nm photoirradiation at room temperature. The increase in the intensity of the ESR signal due to PyC₁⁺ radical cations with time in MeMCM-41 materials (Fig. 5) indicates that the transition metal ions enhance the photoionization of PyC_1 . Other evidence for this is the photoyield increase with Ti content up to Si/Ti=80 in TiMMC-41/PyC₁ (Fig. 4). The amount of photoyield enhancement depends on the nature of the transition metal ion. The net photoionization efficiency of MeMCM-41 decreases in the order of TiMCM-41/PyC_n > NiMCM-41/ $PyC_n > VMCM-41/PyC_n > SiMCM-41/PyC_n > CoMCM-41/$ $PyC_n > CuMCM-41/PyC_n$.

The observed higher photoyields at 77 K can be explained by less PyC_n^+ cation radical mobility at 77 K, which retards back electron transfer to PyC_n molecules. In earlier work,^{23,36,37} methylphenothiazine molecules incorporated into different host lattices also showed higher photoyields at 77 K than at room temperature.

Samples of VMCM-41 impregnated with PyC_1 show a weak ESR signal of PyC_1^+ cation radical because V(v) ions in VMCM-41 oxidise some PyC_1 to form V(v) ions, which is consistent with V(v) observation by ESR after photoirradiation, as shown in Fig. 8. This supports that V(v) ions in VMCM-41 do accept electrons from PyC_1 to enhance the photoyield of PyC_1^+ cation radicals. The ESR of the paramagnetic valence state of V(IV) in VO²⁺ in VMCM-41/PyC₁ is clearly observed (Fig. 8) as expected for capture of photoinduced electrons by V(v), but the expected ESR of Ti(III) in TiMCM-41/PyC₁ and Ni(I) in NiMCM-41/PyC₁ are not observed. The expected 'g' positions are about $g_{\parallel} = 1.91$, $g_{\perp} = 1.97$ for Ti(III) in TiMCM-41/PyC₁ and $g_{\parallel} = 2.49$, $g_{\perp} = 2.11$ for Ni(I) in TiMCM-41/PyC₁.³⁸ In general, PyC₁⁺ cation radicals occur at g = 2.006 at room temperature with a derivative peak to peak linewidth of about 10 G. Simulations indicate partial overlap of the PyC₁⁺ line with the g_{\perp} features of Ti(III) and Ni(I) and the g_{\parallel} features may be too weak to observe.

The ESR intensities of both V(IV) and PyC₁⁺ cation radical increase with irradiation time. The increase of PyC₁⁺ spin concentration ($S_{Py}C_1^+=0.98 \times 10^7$ spins cm⁻³) in VMCM-41/PyC₁ is the same as that of the V(IV) spin concentration ($S_{VO}^{2+}=0.93 \times 10^7$ spins cm⁻³) during 30 min irradiation time which supports that V(V) is an electron acceptor. At longer irradiation time (60 min), the increase of PyC₁⁺ spin concentration is ($S_{Py}C_1^+=1.02 \times 10^7$ spins cm⁻³) smaller than that of the increase in V(IV) spin concentration ($S_{VO}^{2+}=1.42 \times 10^7$ spins cm⁻³), probably due to secondary reactions of PyC₁^{+, 25,36}

The decrease of the PyC_n^+ photoyield with alkyl chain length (Fig. 7) can be partially due to size exclusion from the MCM-41 channels based on the TGA data of Fig. 2 which shows that PyC₁₂ only partially penetrates the MCM-41 channels while PyC₁₆ penetrates even less. The decrease in photoyield for larger PyC_n^+ with longer alkyl chain length may also be partly due to a lower diffusion rate of PyC_n into the MeMCM-41 channels. A longer alkyl chain length makes the molecules more bulky and more difficult to penetrate into the MeMCM-41 channels. The decrease in photoyield of PyC_n^+ with increasing alkyl chain length may also be related to molecular aggregation.^{26,39,40} Longer chain PyC_n are more likely to generate molecular aggregates. The formation of such aggregates will further lower the rate of diffusion of PyC_n into MeMCM-41 and lead to diminished photoyield. However, the stability of PyC_n^+ increases from PyC_1 to PyC_{16} due to an increased inductive effect in PyC_n^+ as a function of longer alkyl chain lengths.^{39,41,42}

A semiquantitative measure of the efficiency of the photoreaction is obtained from the amount of alkylpyrene cation radicals produced relative to the number of alkylpyrene molecules present prior to photoirradiation. The estimated photoconversion is $\sim 15\%$, which is relatively high.

Conclusions

Mesoporous transition metal ions containing SiMCM-41 materials are potential candidates for stable photoinduced charge separation of N-alkylpyrene molecules. The PyC_n^+ cation radical photoyields depend on the incorporation of metal ions into MeMCM-41. The results indicate that back electron transfer is retarded in MeMCM-41 materials and that the lifetime of photoinduced cation radical ions is increased to hours or even weeks at room temperature. It is clear that V(v)is an electron acceptor during the photoirradiation of VMCM- $41/PyC_n$ samples since V(IV) is observed. The results indicate that Ti(IV) is the most efficient electron acceptor followed by Ni(II) and V(v), all of which enhance the photoyield compared to SiMCM-41. The incorporation of Cu(II) and Cu(II) give photoyields that are less than in SiMCM-41. The PyC_n^+ photoyield and stability are also dependent on the length of the alkyl chain. The photoyield is about one and half times higher at 77 K than at room temperature. New physical insights are shown by the dependence of the photoyield on the nature and concentration of the transition metal ion present in MeMCM-41, and also on the size of the electron donor molecules.

This work shows that the photoionization with net longlived charge separation can be achieved for alkylpyrenes in TiMCM-41 materials and that the photoyield is dependent on the Ti(IV) concentration. This extends similar previous work on alkylphenothiazines in TiMCM-41 and thus demonstrates the generality of photoionization enhancement of incorporated molecules in TiMCM-41 materials. The photoyield efficency depends mainly on the electron acceptor side of the reaction and is enhanced not only by Ti(IV) but also by Ni(II) and V(V) relative to SiMCM-41.

Acknowledgement

This research was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, US Department of Energy, The Texas Advanced Research Program and the Environmental Institute of Houston.

References

- 1 V. Balzani and F. Scandola, *Supramolecular Photochemistry*, Ellis Harwood, Chichester, 1991.
- 2 D. Gust and T. A. Moore, Adv. Photochem., 1991, 16, 1.
- 3 H. Imahori and Y. Sakata, Eur. J. Org. Chem., 1999, 2445.
- 4 C. Luo, D. M. Guldi, H. Imahori, K. Tamaki and Y. Sakata, J. Am. Chem. Soc., 2000, 122, 6535.
- 5 A. J. Bard and M. A. Fox, Acc. Chem. Res., 1995, 28, 141.
- 6 D. Gust, T. A. Moore and L. A. Moore, Acc. Chem. Res., 1993, 26, 198.
- 7 Z. Chang, K. T. Ranjit, R. M. Krishna and L. Kevan, J. Phys. Chem., 2000, 26, 198.
- 8 V. Ramamurthy, P. Lakshminarasimhan, C. P. Grey and L. Johnston, *Chem. Commun.*, 1998, 2411.
- 9 J. Abraham and V. Ramamurthy, Chem. Eur. J., 2000, 6, 1287.
- 10 A. G. Panov, R. G. Larsen, N. I. Totach, S. C. Larsen and V. H. Grassian, J. Phys. Chem. B, 2000, 104, 5706.
- 11 Y.-K. Gong, T. Miyamoto and K. Nakashima, J. Phys. Chem. B, 2000, 104, 5772.
- 12 L. Kevan, in *Photoinduced Electron Transfer, Part B*, ed. M. A. Fox and M. Chanon, Elsevier, Amsterdam, 1988, p. 329.
- 13 T. Nakato, K. Kazuyuki and C. Koto, Chem. Mater, 1992, 4, 128.
- 14 L. A. Vermeulen and M. E. Thompson, Nature, 1992, 358, 656.
- 15 M. Julliard, in *Photoinduced Electron Transfer, Part B*, ed. M. A. Fox and M. Chanon, Elsevier, Amsterdam, 1988, p. 216 and references therein.
- 16 M. R. Wasielewski, Chem. Rev., 1992, 92, 435.
- 17 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
- 18 J.-Y. Ying, C. P. Mehnert and M. S. Wong, Angew. Chem., Int. Ed., 1999, 38, 873.
- 19 R. Q. Long and R. T. Yang, Ind. Eng. Chem. Res., 1999, 38, 873.
- 20 K. Kageyama, S. Ogino, T. Aida and T. Tatsumi, Macromolecules, 1998, 31, 4069.
- 21 H. M. Sung-Suh, Z. Luan and L. Kevan, J. Phys. Chem. B, 1997, 101, 10455.
- 22 A. Corma, F. L. Cozens, H. Garcia, M. A. Miranda and A. Sabater, J. Am. Chem. Soc., 1994, 116, 9767.
- 23 R. M. Krishna, A. M. Prakash and L. Kevan, J. Phys. Chem. B, 2000, 104, 1796.
- 24 V. Kurshev, A. M. Prakash, R. M. Krishna and L. Kevan, Microporous Mesoporous Mater, 2000, 34, 9.
- 25 Z. Chang, R. M. Krishna, J. Xu, R. Koodali and L. Kevan, *Phys. Chem. Chem. Phys.*, 2001, **3**, 1699.
- 26 S. Sinlapadech, R. M. Krishna, Z. Luan and L. Kevan, J. Phys. Chem. B, 2001, 105, 4350.
- 27 M. D. Alba, Z. Luan and J. Klinowski, J. Phys. Chem., 1996, 100, 2179.
- 28 M. Hartmann, S. Racouchot and C. Bischof, Microporous Mesoporous Mater., 1999, 27, 309.
- 29 W. Zhang and T. J. Pinnavaia, Catal. Lett., 1996, 38, 261.
- 30 A. A. Romero, M. D. Alba and J. Klinoski, J. Phys. Chem. B, 1998, 102, 123.
- 31 J. Xu, Z. Luan, M. Hartmann and L. Kevan, *Chem. Mater*, 1999, 11, 2928.
- 32 K. A. Koyano and T. Tatsumi, Microporous Mater., 1997, 10, 259.
- 33 Z. Chang, Z. Zhu and L. Kevan, J. Phys. Chem. B, 1999, 103, 9442.

- 34 PCMODEL, Serena Software, Box 3076, Bloomington, Indiana, 4740-3076, USA, 1993.
- J.-A. Jung, D. R. Shin, J.-S. Kim, Y. S. Kang and L. Kevan, J. Chem. Soc., Faraday Trans., 1998, 94, 1619. 35
- B. Xiang and L. Kevan, *Langmuir*, 1994, 10, 2688.
 B. Xiang and L. Kevan, *J. Phys. Chem.*, 1994, 98, 5120.
- (a) A. M. Prakash, V. Kurshev and L. Kevan, J. Phys. Chem. B, 38 1997, 101, 9794; (b) A. M. Prakash, T. Wasowicz and L. Kevan, J. Phys. Chem., 1996, 100, 15947.
- 39 R. M. Krishna, Z. Chang, H. Choo, K. T. Ranjit and L. Kevan, *Phys. Chem. Chem. Phys.*, 2000, **2**, 3335.
- 40 J. Cavanaugh, J. Am. Chem. Soc., 1959, 81, 2507.
- L. S. Levitt and H. F. Widing, in *Progress in Physical Organic Chemistry*, ed. R. W. Taft, Wiley, New York, 1976, vol. 12, 41 ch. 12.
- 42 R. M. Krishna, A. M. Prakash, V. Kurshev and L. Kevan, Phys. Chem. Chem. Phys., 1999, 1, 4119.