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Photochemical modification of the surface area and tortuosity of a *trans*-1,2-bis(4-pyridyl)ethylene periodic mesoporous MCM organosilica

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A periodic mesoporous MCM-41 organosilica containing *trans*-1,2-bis(4-pyridyl)ethylene (*t*-BE) (350 m^2 g^{-1}; 0.28 cm^3 g^{-1}) incorporated in the silica walls undergoes photochemical isomerization to the *cis* configured bis(4-pyridyl)ethylene resulting in a dramatic area (473 m^2 g^{-1}) and pore volume (0.38 cm^3 g^{-1}) increase.

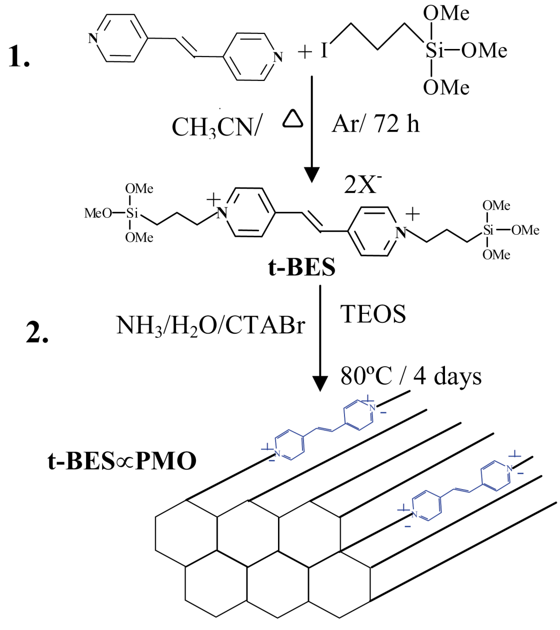
Since the initial reports on the synthesis of periodic mesoporous organosilica (PMO)[1–4] having methylene, ethylene or phenylene groups on the silica framework, there has been a considerable interest in the preparation of related PMO able to perform some action or to have a function imparted by the organic component in the walls. In this context, we recently reported the preparation and preliminary photochemical characterisation of a PMO having strong electron acceptor viologen units in the walls.[5] The as-synthesised sample having mesopores filled with a quaternary ammonium surfactant was able to generate the viologen radical cation by light excitation or even by simple heating and this radical cation lived for hours under aerobic conditions until it finally decayed.

Herein, we describe the preparation and properties of a PMO material having *trans*-1,2-bis(4-pyridyl)ethylene (*t*-BE) incorporated in the walls. Upon irradiation, the *cis*/*trans* isomerization of the C=C double bond produces a remarkable change in the textural properties of the material leading to a BET area and pore volume increase and pore size reduction.

Preparation of the *t*-BES∝PMO† was accomplished starting from tetraethylorthosilicate, TEOS, and *trans*-1,2-bis[*N*-(trimethoxysilylpropyl)pyridiumyl]ethylene (*t*-BES) as silicon sources, mimicking the synthesis of PMOs previously reported in the literature[6], as illustrated in Scheme 1.‡ The TEOS : *t*-BES molar ratio was varied from 82 : 18 to 98.5 : 1.5. Basically the procedure consisted of the slow addition of a mixture of TEOS : *t*-BES corresponding to a mole fraction in the range given above to a surfactant/base solution of cetyltrimethylammonium bromide (CTABr), NH_4OH and H_2O with slow stirring. This synthesis procedure required a mole ratio of 1.00 Si : 114 H_2O : 8.0 NH_4OH (20%) : 0.12 CTABr. After stirring for 30 min, the solutions were aged at 80 °C for 4 days in closed polyethylene bottles. The solid was washed thoroughly with water and the template was removed by exhaustive solid–liquid extraction using a diluted acid ethanol solution. Powder X-ray diffraction of the *t*-BES∝PMO before and after solid extraction showed no changes and the diffractograms correspond to a well crystallised MCM-41 like material with a d_{100} basal space of 40 Å (Fig. 1). IR spectroscopy of the as-synthesised *t*-BES∝PMO solid at different temperatures shows the removal of the peak at 1470 cm^{-1} characteristic of the long-chain of the quaternary ammonium cation, while peaks at 1520 and 1630 cm^{-1} characteristic of the pyridinium ring remain unaltered at high temperatures. The IR peaks corresponding to *t*-BES remain after exhaustive solid extraction of *t*-BES∝PMO.

The BES content of *t*-BES∝PMO was determined by combustion chemical analysis and varied between 0.067 to 0.8 mmol BES g^{-1}. This *t*-BES content indicates that there is a molar proportion varying between 100 Si(SiO_2) : 1 Si(*t*-BES) and 100 Si(SiO_2) : 31 Si(*t*-BES). Taking 3.4 Å as the length of the Si–O–Si bond and 17.2 Å as the length of an elongated *t*-BES molecule, it can be estimated that our material has 17.2 Å of organic moiety every 450 or 20 Å of silicon walls, depending on *t*-BES loading. The *t*-BES content measured by thermogravimetry agrees with combustion chemical analysis.

Steady state irradiation of *trans*-1,2-bis(4-pyridyl)ethylene in aerated CH_3CN solutions gives rise to an efficient photochemical *cis*/*trans* isomerization followed by photocyclisation of the *cis* isomer leading finally to a 3,6-diazaphenanthrene (DAP) structure in almost complete yields. This process can be followed in solution by ^{1}HNMR and also by UV-Vis spectroscopy. Formation of DAP is accompanied by a remarkable change in the UV-Vis spectrum. This photochemical cyclisation is well known to occur in stilbene and related compounds.[7] Our expectation was that *t*-BES occupying framework positions would also undergo this photochemical *cis*/*trans* isomerization. In this way a photoresponsive MCM-41 solid would be obtained



Scheme 1

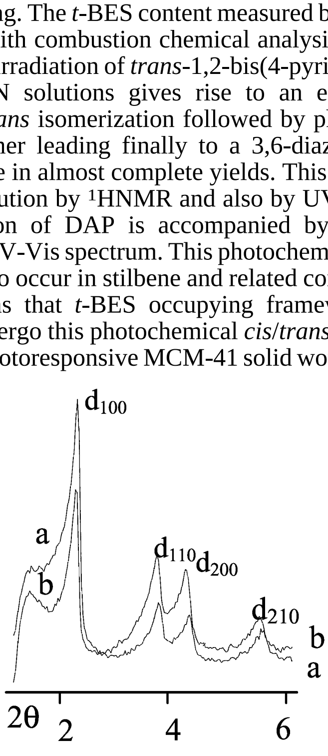


Fig. 1 Powder X-ray diffraction spectra of as-synthesised *t*-BES∝PMO (TEOS:*t*-BES 0.985:0.015) (a) and after extraction (b).

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in which changes in the porosity of the solid could be observed.

In fact, upon laser flash photolysis of *t*-BES$\propto$PMO using a 308 nm laser pulse a transient diffuse reflectance UV-Vis spectrum was recorded (Fig. 2). The differences in the transient spectrum for the as-synthesised sample and after removal of the template were minor. Both spectra corresponded basically to the same transient with somewhat different lifetimes. Three absorption peaks at 410, 510 and 710 were observed. The decay of the peak at 410 nm (τ_1 = 0.233 ms, τ_2 = 0.0127 ms) was faster and clearly different than that monitored for 510 and 710 nm. This indicates that at least two different transients are formed. Although a more detailed study is necessary to fully understand the transient spectrum, a possible explanation for these absorption bands based on the absorption maximum would be that the transients correspond to the bipyridinium radical cation (peak at 410 nm with a less intense band at 600–800 nm) and a $X_2^{\cdot -}$ (X = Br or I) radical anion (510 and 710 nm).[8] I^- is present as the *t*-BES charge balancing anion and Br^- is the counter anion of the surfactant. These species would be formed concurrently upon excitation through an electron transfer from X^- as donor to bipyridinium excited state as acceptor. Whatever the transients, Fig. 2 combined with the steady state irradiation in solution provides firm evidence of the photoactivity of the organic bipyridinium either in solution or embedded in the aluminosilicate framework. Diffuse reflectance of the photolysed *t*-BES$\propto$PMO clearly shows that DAP has not been formed.

To demonstrate that the photoactivity of the material leads to changes in surface area and porosity, we performed an experiment in which an extracted *t*-BES$\propto$PMO (98.5 : 1.5) sample was divided into two twin samples that were handled under exactly the same conditions except that one of them was maintained in the dark while the other was exposed to the UV light from a 125 W medium pressure Hg lamp for 18 h. After this time the two samples were checked for the total surface area, pore volume and pore size. The corresponding pore sizes before and after irradiation obtained from the Horvath–Kawazoe equation of the high resolution Ar adsorption isotherms are shown in Fig. 3. The results show a change in the porosity that varies upon irradiation from 350 ± 5 m^2 g^{-1} to 473 ± 5 m^2 g^{-1} for the surface area and from 0.28 ± 0.02 cm^3 g^{-1} to 0.38 ± 0.02 cm^3 g^{-1} for the pore volume. These data vary from one batch to another and also may depend on the irradiation conditions but they clearly show a response of the solid to the action of light, thus probing the principle of the photochemical modification of porosity for PMO materials. Scheme 2 shows a pictorial interpretation of the variation of the textural parameters in photoactive *t*-BES$\propto$PMO upon irradiation. Thus, initially *t*-BES$\propto$PMO has the C=C in the *trans* configuration and upon light absorption photochemical *cis*/*trans* isomerization occurs. The flexibility of the trimethylene linkers allowed these configurational changes and atomic movements. This structural reorganization is reflected in the measurements of the porosity of the material. Photocyclisation to DAP, also occurring in solution, does not take place when *c*-BES is bonded into the silicate walls, as is demonstrated by diffuse reflectance spectroscopy.

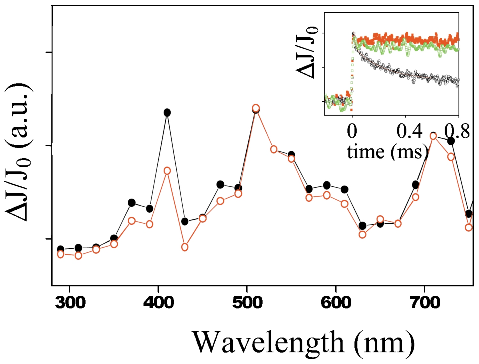


Fig. 2 Time resolved diffuse reflectance UV-Vis spectra of extracted *t*-BES$\propto$PMO (TEOS:*t*-BES 0.985 : 0.015) recorded 0.12 (●) and 0.73 (○) ms after 308 nm laser excitation. The inset shows the decays monitored at 410 (black), 510 (red) and 710 (green) nm.

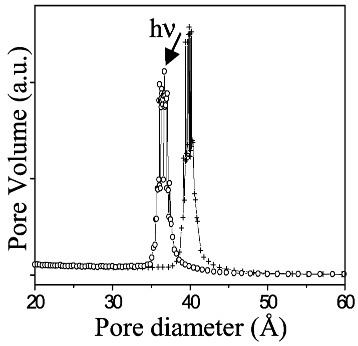
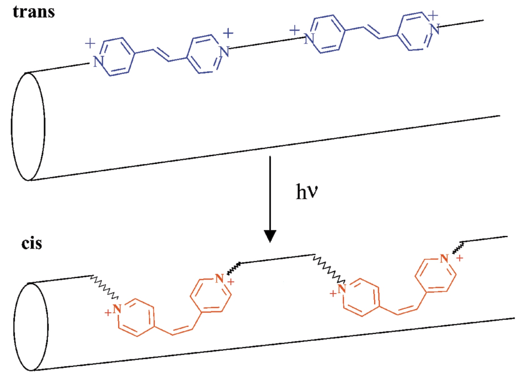


Fig. 3 Pore size distribution for *t*-BES$\propto$PMO before (+, 39.8 Å) and after (○, 36.5 Å) UV irradiation deduced by the Horvath–Kawazoe equation from the Ar adsorption isotherm.



Scheme 2

In conclusion, by using the previously reported methodology, we have taken advantage of this ability of stilbenes and related compounds to reorganize spatially the groups attached to the C=C bond to prepare a PMO solid whose porosity and internal voids can be modified by the action of light.

Notes and references

† The sign $\propto$ indicates that *t*-BES is forming part of the silica walls as indicated in Scheme 1.

‡ *trans*-1,2-bis[*N*-(trimethoxysilylpropyl)pyridiumyl]ethylene (*t*-BES) was synthesised by the slow addition of an acetonitrile solution of trimethoxysilylpropyliodide (5.81 g, 0.02 mol) to a deaerated acetonitrile solution of *trans*-1,2-bis(4-pyridyl)ethylene (*t*-BE) (0.39 g, 0.002 mol). Then, the solution was heated at reflux temperature for 72 h. The dark orange solid formed was filtered and thoroughly washed with hexane. *t*-BES was fully characterised by analytical and spectroscopic data. Combustion analysis: theoretical (%) for $C_{24}H_{40}I_2N_2O_6Si_2$: C, 37.8; N, 3.7; H, 5.3; experimental: C, 32.6; N, 3.3; H, 4.7; IR: 1473, 1522, 1541 and 1637 cm^{-1}; ^{1}H NMR (CD$_3$OD): δ_H 8.91 (4H, d), 8.31 (4H, d), 8.01 (2H, s), 4.52 (4H, t), 3.45 (18H, s), 2.03 (4H, m) 0.60 (4H, m); ^{13}C NMR (CD$_3$OD): δ_C 151.98, 145.63, 134.70, 126.84, 64.01, 50.91, 25.63, 6.19.

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