



## The Environmental Effect of MCM-41 Mesoporous Silica on Solid Thermochromic *N*-(5-Chlorosalicylidene)aniline

E. HADJOU DIS<sup>1,\*</sup>, A.B. BOURLINOS<sup>2</sup> and D. PETRIDIS<sup>2</sup>

<sup>1</sup>Institute of Physical Chemistry. E-mail: hadjoudi@mail.demokritos.gr; <sup>2</sup>Institute of Material Science, N.C.S.R “Demokritos”, 15310 Aghia Paraskevi, Attiki, Athens, Greece

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### Abstract

Thermochromic *N*-(5-chlorosalicylidene)aniline was entrapped in a mesoporous silica designated as MCM-41 by grinding the two components in the solid state. In the composite material the title compound lost its thermochromic properties and transformed to a photochromic tautomer with dramatic differences in the forward and backward ground state reactions with temperature. The observed change in colour with light is attributed to the *cis*-keto form of the title anil stabilized in the environment of the mesoporous MCM-41 material.

### Introduction

Thermochromism and photochromism have been found to be mutually exclusive properties in *N*-salicylideneanilines (anils) [1]. Structural studies of these compounds have shown that in thermochromic crystals, the molecules are essentially planar and packed in stacks of parallel molecules with short interplanar distances, while in photochromic crystals, the aniline ring is twisted about the exocyclic N—C bond and the molecular packing is consequently much more open with no close face-to-face contacts between molecules [2]. There are two consequences of the above. First, in the planar structures the lone electron pair of the nitrogen atom does not overlap with the p electrons of the aniline ring whereas in the “twisted” structure such overlap is possible making the nitrogen basicity weaker. Accordingly, H···N interactions are stronger in the planar geometry, i.e., in the thermochromic *cis*-keto form. Second, provided that the photochromism is associated with the *trans*-keto species, the required *cis*-*trans* conversion is improbable in the plane-to-plane packing of the thermochromic molecules but possible in the “open structure” of the photochromic crystals (Figure 1) [1, 2]. The possibility that thermochromic crystals photo-isomerize enol to *cis*-keto is also likely, but reformation of enol is so rapid that colour changes are not observable [3]. If the hypothesis, that photochromism in this class of compounds arises from geometrical isomerization is correct, then the development and rate of colouration and decolouration must be sensitive to the environment of the surrounding matrices [4]. Indeed, inclusion complexes of thermochromic anils in cyclodextrins [5] and in deoxycholic acid crystal lattice cavities have been found to be photochromic [6].

In this work, we report the effect of the environment of MCM-41 mesoporous silica on the thermochromic properties of *N*-(5-chlorosalicylidene)aniline, shown in Figure 2 and referred to as 5-Cl-anil below [7]. Mesoporous silica is a high surface area porous material ( $\sim 1000 \text{ m}^2 \text{ g}^{-1}$ ) that consists of a hexagonal arrangement of cylindrical pores (pore diameter  $> 15 \text{ \AA}$ , uniform sized) between which an amorphous silicon oxide network is interposed [8]. The present mesoporous silica-5-Cl-anil system adds to the molecular and/or structural engineering strategies for the purpose of finding new ways to produce photochromic systems which, apart for their scientific interest, are of great importance for many potential applications [1].

### Experimental

#### Materials

##### *N*-(5-chlorosalicylidene)aniline

The title anil was synthesized by direct condensation of 5-chlorosalicylaldehyde with aniline in ethanol, followed by repeated recrystallizations from the same solvent. Elemental analysis, IR and melting point (110 °C, [7b]) information were utilized to establish the purity of the compound.

##### MCM-41 mesoporous silica

The MCM-41 material was synthesized according to a known procedure [9, 10]. The synthesis comprised alkaline hydrolysis of a silicon alkoxide [Si(OCH<sub>3</sub>)<sub>4</sub>] in the presence of surfactant molecules [C<sub>16</sub>H<sub>33</sub>N(CH<sub>3</sub>)<sub>3</sub>Cl] in a water/methanol mixture to afford a white precipitate. The as-formed solid after repeating washing with de-ionized water and drying, was finally calcined at 550 °C for 7 h under air and with steps of 1 °C min<sup>-1</sup>, in order to remove the organic

\* Author for correspondence.

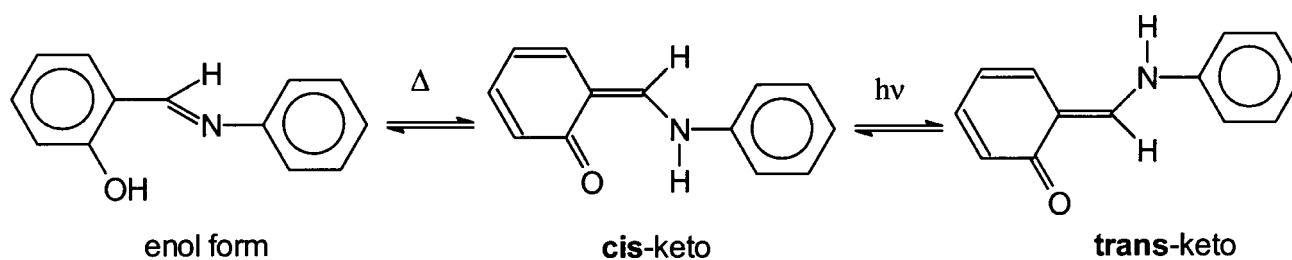


Figure 1. Thermochromic and photochromic reversible processes in anils.

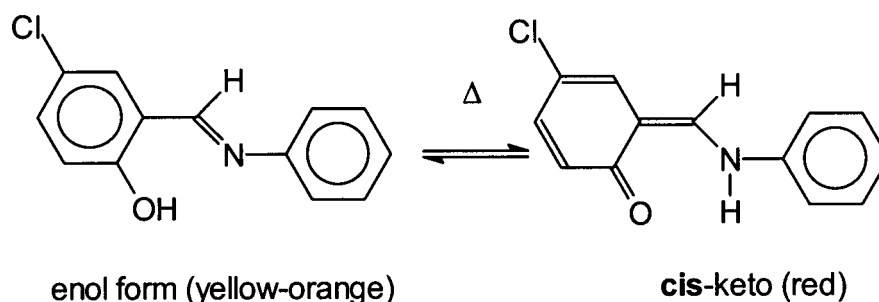


Figure 2. Thermochromic reversible process of *N*-(5-chlorosalicylidene)aniline.

matter occupying the cylindrical pores of the as-synthesized material. The BET surface area and mean pore diameter structural parameters of the final solid were extracted from the nitrogen isotherm and XRD analysis of the sample and found to be  $1200 \text{ m}^2 \text{ g}^{-1}$  and  $20 \text{ \AA}$ , respectively.

#### Entrapment of *N*-(5-chlorosalicylidene)aniline

The entrapment of anil into the MCM-41 material was carried out in the solid state by grinding a 1:1 mixture of 5-Cl-anil and MCM-41 in an agitating mortar. The resulting 5-Cl-anil/MCM-41 yellow powder was used as such without further treatment.

#### Instrumentation and characterization

X-ray powder diffraction (XRD) patterns were recorded on a Siemens XD-500 diffractometer using  $\text{CuK}\alpha$  radiation. The IR spectra were taken in the form of KBr pellets with a Bruker FT-IR spectrometer, Equinox 55/S model.

The absorption spectra were recorded with a Varian Techtron 635 spectrophotometer equipped with a diffuse reflectance accessory. Powdered samples were measured in the reflection mode using  $\text{BaSO}_4$  as the reference and the Kubelka–Munk function  $F(R_\infty)$  was plotted versus the wavelength exhibiting an analogous behavior to absorption [11].

For investigation of the colouring, the samples were measured, then irradiated with a 200W high pressure mercury lamp at a distance of 10 cm for 2.30 hours using a Corning 365 nm filter and finally the spectrum recorded again. Fading was followed with time.

## Results and discussion

#### The nature of the 5-Cl-anil/MCM-41 material

The XRD pattern of 5-Cl-anil/MCM-41 shows that the crystal structure of 5-Cl-anil is maintained in the composite, since the  $2\theta$  angles of the reflection peaks did not change position (Figure 3). However, two features are noticed: (a) the crystallinity is reduced as indicated from the decreased intensity of the relevant reflections and (b) the relative peak heights of the low  $2\theta$  peaks were changed with respect to those of crystalline 5-Cl-anil. Both features might arise from minute crystallites hosted in the porous material which retain the overall lattice but lose their long-range order. 5-Cl-anil molecules at the surface of the crystallites, that probably interact with polar Si—OH groups, constitute a high fraction of the crystalline 5-Cl-anil and could change the relative height of the XRD peaks. In addition, hydrogen bonding interactions between 5-Cl-anil and MCM-41 in the composite could cause analogous changes in the XRD patterns. An indication for hydrogen bonding is a small shift in the  $963 \text{ cm}^{-1}$  infrared band (Figure 4) of the Si—OH bonds present in the compact silica framework [10]. Similar hydrogen bonding interactions have been observed in zeolites with framework Si—OH groups acting as hydrogen bond donors and the oxygen atoms in the Si—O—Si as acceptors in stabilizing the zwitterionic form of the *N*-salicylideneaniline [12]. In the present case, because the internal surface area of the MCM-41 silica (surface area within the pores) is much greater than the external area (surface area outside the pore channels:  $\sim 50 \text{ m}^2 \text{ g}^{-1}$  [10]), it is safe to assume that the majority of the Si—OH groups involved in hydrogen bonding are located on the internal surfaces. However, the XRD and infrared results do not provide convincing evidence for a definite conclusion on the way the anil molecules are stabilized in the environment of MCM-41 mesoporous silica.

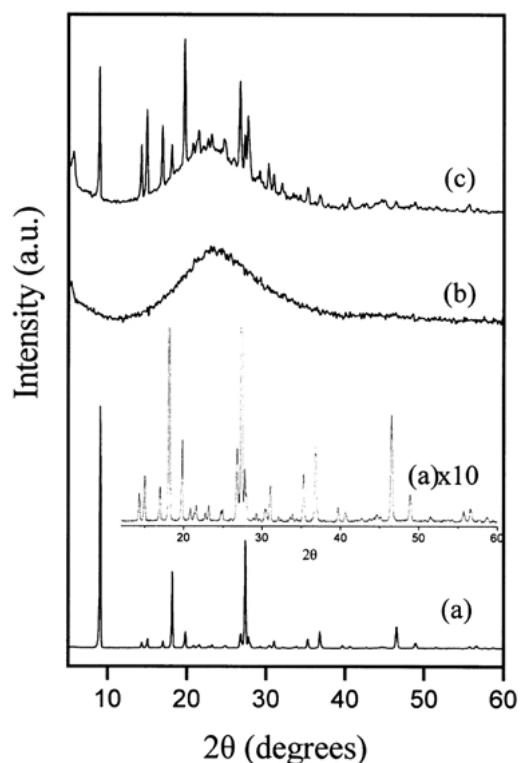


Figure 3. XRD patterns of (a) 5-Cl-anil, (b) MCM-41 and (c) 5-Cl-anil/MCM-41 composite.

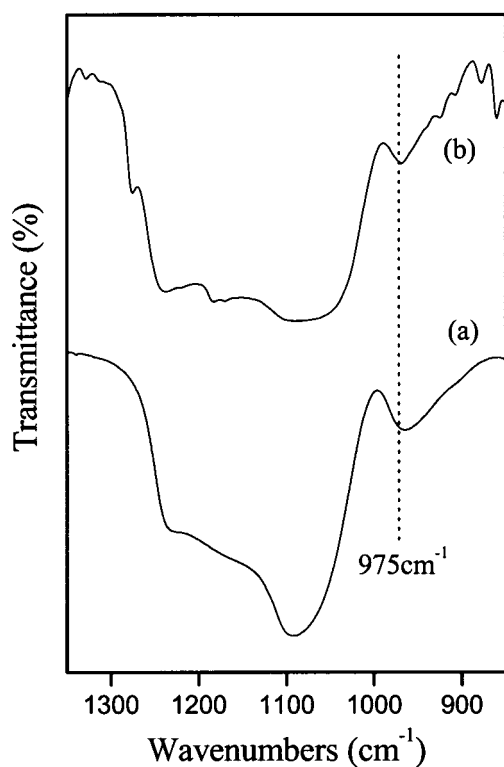


Figure 4. IR spectra for MCM-41 (a) and 5-Cl-anil/MCM-41 (b) in KBr.

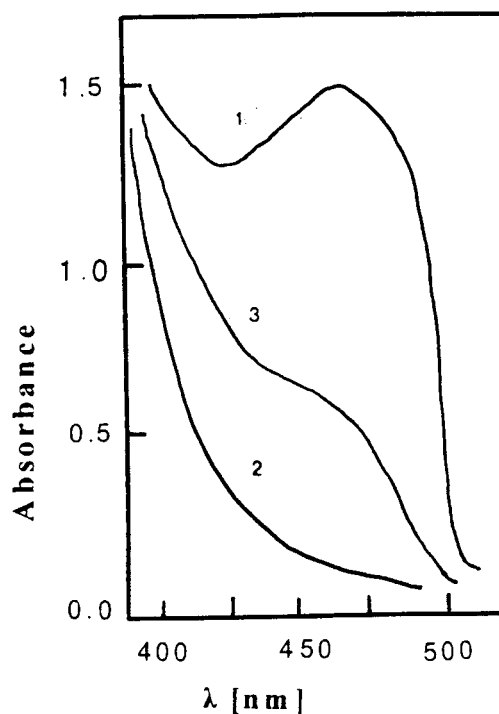


Figure 5. Absorption spectra of a thin polycrystalline film of 5-Cl-anil at room temperature (1) and at liquid nitrogen temperature (2) and of the 5-Cl-anil/MCM-41 material at room temperature (3).

#### Thermochromism

Figure 5 shows the absorption spectra of a thin polycrystalline film of 5-Cl-anil at room temperature (1) and at liquid nitrogen temperature (2) together with the diffuse reflectance spectrum of the 5-Cl-anil/MCM-41 material (3) for comparison reasons. The yellow-orange colour at room temperature of 5-Cl-anil (spectrum 1) turns to a white-yellow colour at liquid nitrogen temperature (spectrum 2). The reversibility of the process verifies the thermochromic behavior. On the contrary, the yellow colour of the 5-Cl-anil/MCM-41 composite at room temperature (spectrum 3) remains unchanged when a powdered sample was cooled to liquid nitrogen temperature or heated near to the melting point (110 °C) of the 5-Cl-anil implying no thermochromic behavior.

#### Photochromism

Although, the thermochromic properties of 5-Cl-anil were not retained in the 5-Cl-anil/MCM-41 composite, the material exhibited photochromism with considerable stability at room temperature. For instance, the yellow colour of this material turned to red upon irradiation with 365 nm light for 2.30 h. The half-life of this photo-product is about 80 days which is by far the largest observed for such material, being approximately 800 times that of the photochromic crystalline powder of *N*-salicylideneaniline [13]. Figure 6 shows the colouration and the fading process of the photochromic composite at room temperature. The results show that photochromism exists even after 120 days in the dark. Figure 7 shows the IR spectral changes in the carbonyl stretching

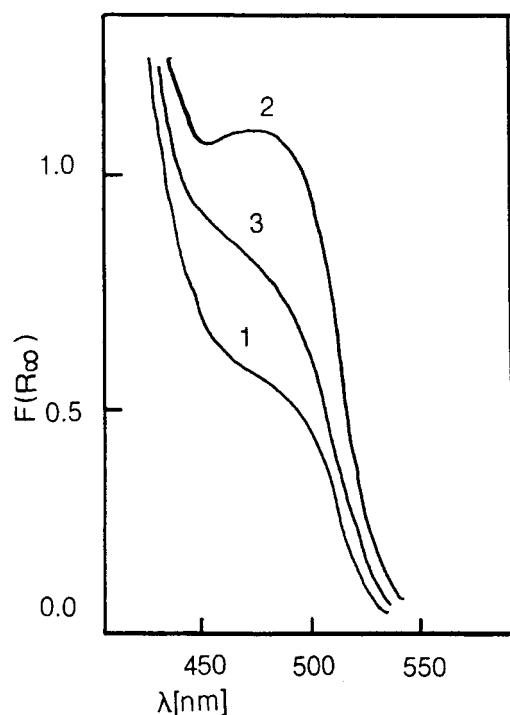


Figure 6. Diffuse reflectance spectra for 5-Cl-anil/MCM-41 material (1) before irradiation, (2) after 2.30 h irradiation with 365 nm light and (3) after 120 days in the dark.

region of the 5-Cl-anil/MCM-41 material before and after uv-irradiation.

A final important observation refers to the dramatic effect of temperature upon the forward and backward rates of colour formation and disappearance. Thus, irradiation of the 5-Cl-anil/MCM-41 solid at liquid nitrogen temperature with 365 nm light yielded within 5 to 10 min a photo-product with an intensity much stronger than that produced at room temperature after 2.30 hours irradiation. This high intensity disappeared almost *instantaneously* when the material was brought from liquid nitrogen to room temperature. The strong orange-red colour can be retained as long as it is kept at liquid nitrogen temperature. The process is reversible and can be repeated many times without losing its efficiency.

## Conclusions

In the present study, the transformation of a thermochromic anil hosted in the mesoporous MCM-41 silica to a photochromic tautomer is observed for the first time. The anil adsorbed in the inner walls of this inorganic matrix loses its thermochromic property and, although it retains its overall planar packing, appears photochromic without *cis-trans* isomerization, unlike the "open structure" photochromic *N*-silylideneanilines. This implies that the photo-product in the present case is the *cis*-keto form, as shown in Figure 2. This result is supported by a recent femtosecond fluorescence study on proton transfer in thermochromic anil crystals including *N*-(5-chlorosalicylidene)aniline, which showed that the photoexcitation causes proton transfer lead-

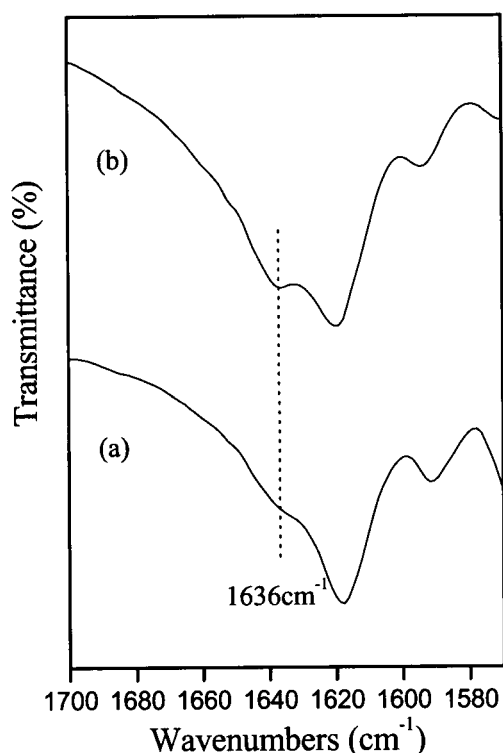


Figure 7. IR spectra for 5-Cl-anil/MCM-41 material in KBr before (a) and after 2.30 h irradiation with 365 nm light at room temperature (b).

ing to the *cis*-keto form [14]. The enol *cis*-keto tautomerization is further supported by the appearance of the carbonyl stretching frequency ( $\nu_{C=O}$ ) at about  $1640\text{ cm}^{-1}$ . The generation of the *cis*-keto form by light becomes possible through the environmental effect of MCM-41 mesoporous silica. However, the present results do not allow an operative mechanism to be proposed and more work is needed in order to elucidate this problem.

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