

## Optical Sensing in Nanopores. Encapsulation of the Solvatochromic Dye Nile Red in Zeolites

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We report on the inclusion synthesis of the solvatochromic dye nile red in the nanoscale pores of zeolites and demonstrate the optical vapor sensing capability of these systems. In recent years, chemical sensing has attracted the interest of many research groups, especially in the areas of photochemical and photophysical sensing.<sup>1</sup> Optical methods have been studied for vapor sensing,<sup>2–9</sup> however, it was not until recently that optical sensors for multiple analyte chemical detection were reported.<sup>10–12</sup> The aim of our work is to combine the shape selectivity of zeolites with the chemical sensitivity of solvatochromic dyes. By restricting a molecule such as nile red into a zeolite host, we anticipate to create a system that is highly selective to specific analytes.

Nile red, a highly fluorescent organic dye, was first introduced by Möhlau and Uhlmann in 1895.<sup>13</sup> Since then, it has been extensively used as a probe to study different homo- and heterogeneous environments.<sup>14–17</sup> Nile red is an excellent candidate for sensing applications since it is highly solvatochromic, i.e., it exhibits wavelength shifts in both absorbance and emission bands in the presence of various molecules.

Here we report the inclusion synthesis of nile red in a siliceous zeolite with faujasite structure (type FAU), in comparison to the adsorption of the dye onto several zeolites from solution. The zeolites SiY (FAU structure type with approximate unit cell composition  $\text{Na}_6(\text{Si}_{186}\text{Al}_6\text{O}_{384})$ ), NaY, ZSM-5, and LTA were used as hosts.<sup>18</sup> The cage structure of FAU can be described as assembled from sodalite cages linked by double six-rings of

oxygen-bridged (Si/Al)O<sub>4</sub> tetrahedra, thus producing large 13 Å supercages (sc) connected by 12-ring windows with 7.5 Å diameter.<sup>19</sup>

Due to the influence of the zeolite host on the dye, for the purpose of guest sensing, a low polarity hydrophobic, siliceous host is considered ideal. Minimal interaction of the dye with the zeolite host is anticipated to provide for an optimal sensing environment. The method of vapor phase exchange of Al for Si provides for a convenient method to produce highly siliceous zeolites.<sup>20</sup> After exchange with SiCl<sub>4</sub> vapor, zeolites remained highly crystalline, and their water content under ambient conditions was drastically reduced (the Si:Al ratio was increased from 2.3 to 33<sup>21</sup>). Nile red was synthesized from the reaction between 1-naphthol and 6-nitroso-3-diethylaminophenol (as a limiting reagent) in acidic environments, inspired by the original synthesis of Möhlau and Uhlmann (Scheme 1).<sup>13,22</sup> Removal of excess reagents and products was achieved by Soxhlet extraction and could be monitored by UV–vis spectroscopy. All of the samples were fully characterized.<sup>23,24</sup>

It has been reported that absorption of nile red into faujasite type zeolites is possible from solution.<sup>14</sup> However, since the pore opening is only about 1 Å greater than the rigid molecule itself (6 × 11 Å estimated from molecular models), it is not clear that effective incorporation via diffusion is feasible. Thus, the adsorption of nile red into several zeolite hosts was also explored as a synthetic route (Table 1, samples 2–5). Both inclusion synthesis and adsorption in zeolite Y result in similar average loadings of about 1 nile red molecule in 20 zeolite supercages. Soxhlet extraction of the SiY samples (1 and 2) in EtOH for 24 h reduces the loadings to 1 Nile Red in about 60 supercages, associated with a color change from pink to blue, while more dye remains in NaY. It is possible that the remaining dye is associated with acidic defect sites in the extracted samples. Adsorption experiments were also carried out with smaller pore zeolites such as ZSM-5 and LTA (Table 1, samples 4 and 5). No nile red was observed to be associated with these zeolites. From these observations we can conclude that nile red can penetrate into the cages of faujasite.

After dehydration of the zeolite/dye ensembles, those prepared by adsorption methods changed color quickly when coming into contact with ambient air. The samples prepared by inclusion synthesis could remain in atmospheric conditions for several days before any color changes were observed. This indicates that the dye remained very close to the surface when adsorbed but that, with the inclusion synthesis, incorporation deeper into the crystal was possible. The hydrophobic zeolite then leads to slow interaction with external humidity.

The hydrophobic dye/zeolite SiY ensemble prepared by inclusion synthesis (sample 1a) shows dramatic shifts in the reflectance

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(21) XRD data showed that the samples were highly crystalline and <sup>29</sup>Si MAS NMR spectra displayed only Q<sup>4</sup> resonances. Si:Al ratios were determined by ICP/AES after digestion of the host in HF.

(22) Sample 1: A solution of 1-naphthol (0.09 g, 0.62 mmol) in 5 mL of CH<sub>3</sub>COOH was added to the zeolite (0.20 g, 17 μmoles) and brought to reflux. After 30 min of refluxing, 6-nitroso 3-diethylaminophenol (0.07 g, 0.36 mmol) dissolved in 3 mL of CH<sub>3</sub>COOH and 0.25 mL of concentrated HCl was added, and reflux continued for 3 h upon which the color changed from brown to blue. The pH of the resulting solution was increased to 11 with NH<sub>4</sub>OH (aq), and the nile red/zeolite inclusion was washed with EtOH, Soxhlet-extracted with EtOH, and collected.

(23) Visible and diffuse reflectance spectra were recorded on a Hitachi U-3501 spectrophotometer with an integrating sphere. X-ray diffractograms were taken on a Scintag XDS 2000 diffractometer with Cu Kα radiation. Mass spectral analysis was carried out on a Hewlett-Packard APCI 59987A electrospray and 5989B mass spectrometer. IR spectra were recorded on a Mattson Polaris spectrometer.

(24) Two side products were observed in the extracted siliceous sample 1 (M + H = 207 and 341, 15% total), while about 10 products were detected in the solution synthesis.

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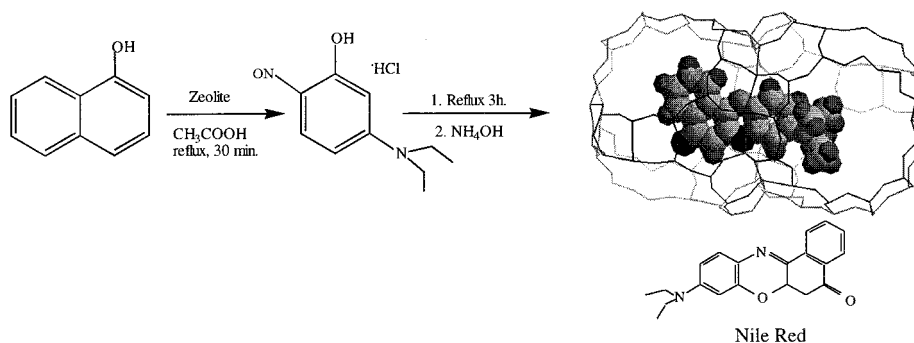
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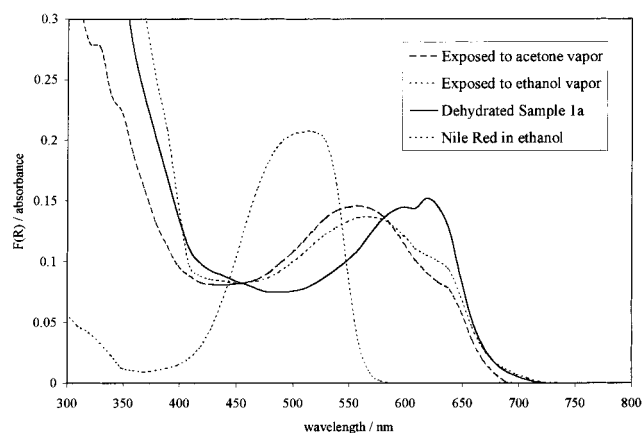
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## Scheme 1. Encapsulation of Nile Red in Faujasite

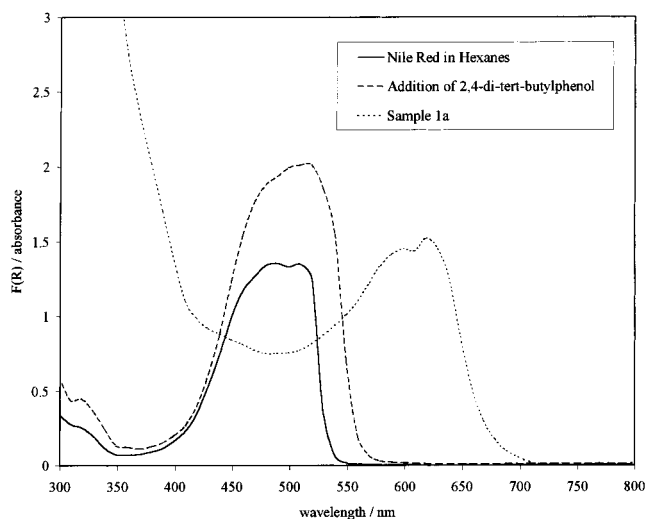
**Table 1.** Sample Preparation of Nile Red Inclusions in Zeolite Hosts<sup>a</sup>

sample	zeolite	preparation method <sup>b</sup>	Soxhlet-extracted <sup>c</sup>	dye content (dye/SC) <sup>c</sup>	color	pore opening
1a	SiY	inclusion synthesis	yes	0.017	blue	7.5 Å
1b	SiY	inclusion synthesis	no	0.05	pink	7.5 Å
2a	SiY	adsorption of dye	yes	0.015	blue	7.5 Å
2b	SiY	adsorption of dye	no	0.05	pink	7.5 Å
3a	NaY	adsorption of dye	yes	0.03	blue	7.5 Å
3b	NaY	adsorption of dye	no	0.05	blue	7.5 Å
4	ZSM-5	adsorption of dye	no	trace	white	5.5 Å
5	LTA	adsorption of dye	no	trace	white	4.1 Å

<sup>a</sup> SiY: Na<sub>6</sub>(Si<sub>186</sub>Al<sub>6</sub>O<sub>384</sub>), NaY: Na<sub>57</sub>(Si<sub>135</sub>Al<sub>57</sub>O<sub>384</sub>), ZSM-5: Na<sub>n</sub>(Al<sub>n</sub>Si<sub>96-n</sub>O<sub>192</sub>), LTA: (Na<sub>12</sub>(Al<sub>12</sub>Si<sub>12</sub>O<sub>48</sub>))<sub>8</sub>. <sup>b</sup> Inclusion synthesis: see ref 22. Adsorption method: a small amount of dry zeolite (0.20 g, 17 μmol) was dispersed in a solution of the dye (0.0040 g, 12.6 μmol) in hexane (10 mL), followed by stirring for 12 h, filtration, and washing with hexane. <sup>c</sup> Zeolites were Soxhlet-extracted with EtOH for 24 h. Determination of dye/supercage ratios was performed after the dye/zeolite ensemble was digested with HF and extracted with CHCl<sub>3</sub>. The resulting solution was analyzed by electrospray CI mass spectrometry.

**Figure 1.** Change in the visible diffuse reflectance spectra of Nile Red in SiY (sample 1a) upon equilibration with acetone vapor at 2.1 Torr and with ethanol vapor at 1.55 Torr. Also shown is Nile Red in liquid ethanol (solution phase transmission spectrum; bottom trace).

spectra when exposed to ethanol. Zeolite/dye samples were degassed ( $5 \times 10^{-4}$  Torr, 110 °C), cooled to room temperature, and exposed to ethanol vapor (equilibrated at 1.55 Torr). The color of the zeolite changed nearly instantaneously from blue to pink which can be observed with the eye (Figure 1). A similar shift is observed for Nile Red in ethanol solution ( $\lambda_{\text{max}}$  ca. 500 nm) vs Nile Red in a more polar solvent (e.g., in water/acetic acid,  $\lambda_{\text{max}}$  ca. 600 nm). The zeolite was also exposed to acetone vapors at 2.10 Torr upon which a color change to purple was observed. Exposure to hexanes at 12.9 Torr produced no shift in the visible spectrum. The above color changes are completely reversible

**Figure 2.** Absorbance spectra of Nile Red in hexanes, before and after addition of 2,4-di-*tert*-butylphenol. Diffuse reflectance spectrum of sample 1a (scaled by a factor of 10) after 2,4-di-*tert*-butylphenol addition, showing no change in the spectrum (see Figure 1).

upon removal of the vapors, and no degradation of the dye is observed. Size exclusion was explored by using a bulkier molecule: 2,4-di-*tert*-butylphenol. An excess of the phenol ( $1.87 \times 10^{-4}$  moles) was added to a Nile Red solution ( $5.65 \times 10^{-7}$  moles in 10 mL of hexanes) upon which the color changed from yellow to orange. A hexane solution of 2,4-di-*tert*-butylphenol ( $1.87 \times 10^{-4}$  moles in 10 mL of hexanes) was then added to sample 1a, resulting in no color change. The bulkier molecule could not penetrate into the zeolite cage to influence the Nile Red, demonstrating size selectivity (Figure 2). The dye/zeolite ensemble is stable in air, and color change due to very slow interaction with water takes several days. Finally, Nile Red adsorbed in SiY(2a) displays similar blue shifts on exposure to polar vapors as the samples prepared by inclusion synthesis.

In conclusion, we have demonstrated that by incorporating the solvatochromic dye Nile Red into highly siliceous zeolites, an optical sensor that is extremely sensitive to different organic molecules can be designed. Furthermore, Nile Red can serve as a sensitive probe for zeolitic environments. One can observe significant differences in both the visible spectra and fluorescence spectra (not shown here) when siliceous zeolite hosts are compared to polar aluminosilicate zeolites. Ongoing studies in this laboratory are aimed at extending the family of chemically selective intrazeolite dye based optical sensors.

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