# A novel method for encapsulation of dyes into $AlPO_4$-8 molecular sieve

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**Methylene blue and perylene are encapsulated into $AlPO_4$-8 molecular sieve utilising the structural transformation of the large-pore aluminophosphate VPI-5 into $AlPO_4$-8.**

Molecular sieve-hosted organic and inorganic materials are prospective for new uses of molecular sieves as advanced materials.[1] Especially, zeolite-hosted dyes have been investigated in recent years for uses as optical data storage systems *via* persistent spectral hole burning.[2] Methylene blue has been encapsulated into zeolites by ion exchanging the dye cation in aqueous solution or by adding the dye to the reaction mixture for the hydrothermal synthesis of the molecular sieves.[2,3] These methods have some problems such as demethylation of methylene blue in strong basic solutions for the synthesis of zeolites.

The large-pore aluminophosphate molecular sieve VPI-5 was first prepared by Davis *et al.*[4] The stability of VPI-5 is very dependent upon the preparation method; the least stable materials are those which are synthesized with di-*n*-propylamine as a template.[5] The structural transformation of VPI-5 into $AlPO_4$-8 has been investigated by many authors.[6] VPI-5 prepared with di-*n*-propylamine is known to recrystallize into the $AlPO_4$-8 molecular sieve modification under mild heating in the presence of moisture. VPI-5 contains 1D circular pores with a free diameter of 12.1 Å circumscribed by 18 tetrahedral atoms while $AlPO_4$-8 has 1D elliptical pores with free diameters of 7.9–8.7 Å circumscribed by 14 tetrahedral atoms.[7] The pore contraction, which results from the structural transformation of VPI-5 into $AlPO_4$-8, could make possible encapsulation of some molecules and ions. Organic and inorganic compounds can be encapsulated into molecular sieves by ion exchange, metal-cluster or complex formation and addition to the reaction mixture for crystallization of molecular sieves.[2,3,8] Encapsulation utilizing the structural transformation of molecular sieves has not been reported. In this work the encapsulation of methylene blue and perylene into $AlPO_4$-8 using the structural transformation of VPI-5 into $AlPO_4$-8 has been studied.

VPI-5 was prepared according to the published procedure[9] using pseudoboehmite (74.2% $Al_2O_3$, Catapal-B) and phosphoric acid (85 mass%, Junsei) as the aluminium and phosphorous sources, and di-*n*-propylamine (99 mass%, Aldrich) as a template. Methylene blue (standard stain, BDH) as chloride and perylene (ACS reagent, Sigma) were used as guest molecules. The impregnation of methylene blue was carried out using saturated aqueous solutions and perylene was impregnated using saturated chloroform solutions. The methylene blue and perylene solutions were added to VPI-5 samples and then the wet samples were dried in an oven at 60 °C. The above procedure was repeated five times. The methylene blue- and perylene-loaded VPI-5 samples were fully hydrated at saturated vapour pressure and subsequently dehydrated by heating slowly to 120 °C leading to transformation into the $AlPO_4$-8 structure. Excess molecules, which were not encapsulated into the channels of $AlPO_4$-8, were removed by Soxhlet extraction with ethanol (methylene blue) or chloroform (perylene) until the washings were colourless.

X-Ray diffraction (XRD) patterns were obtained with a Rigaku model D/MAX-3 instrument. Optical absorption spectra were measured with a Shimadzu (UV-3100S) UV–VIS–NIR spectrophotometer equipped with a Shimadzu (MPC-3100) diffuse reflectance attachment. Pure VPI-5 and $AlPO_4$-8 samples were used as diluent or reference standards. Thermogravimetric analysis (TGA) was performed on a DuPont-9900 thermogravimetric analyser in air flow at a heating rate of 10 °C $min^{-1}$.

Fig. 1 shows XRD patterns of as-synthesized VPI-5 and $AlPO_4$-8 samples obtained from as-synthesized and dye-loaded VPI-5. XRD patterns of the as-synthesized VPI-5 and $AlPO_4$-8 obtained from the as-synthesized VPI-5 are in good agreement with those in the literature.[9,10] XRD patterns of the dye-loaded $AlPO_4$-8 samples show characteristic peaks of $AlPO_4$-8 but the relative intensities of the peaks differ from pure $AlPO_4$-8. As VPI-5 prepared with di-*n*-propylamine as a template is known to be unstable thermally and hydrothermally, the transformation of VPI-5 into $AlPO_4$-8 was not impeded significantly by the impregnated dyes. The amount of dyes loaded was estimated from TGA measurements. The TGA results also suggest that VPI-5 samples contain no amine. Although VPI-5 has a smaller pore volume than faujasite,[11] more molecules can be encapsulated in the former since VPI-5 has a larger pore opening and straight channels. The amount of methylene blue encapsulated into $AlPO_4$-8 is similar to that obtained by ion exchange of methylene blue into zeolite X.[3] The optical spectra of solid and

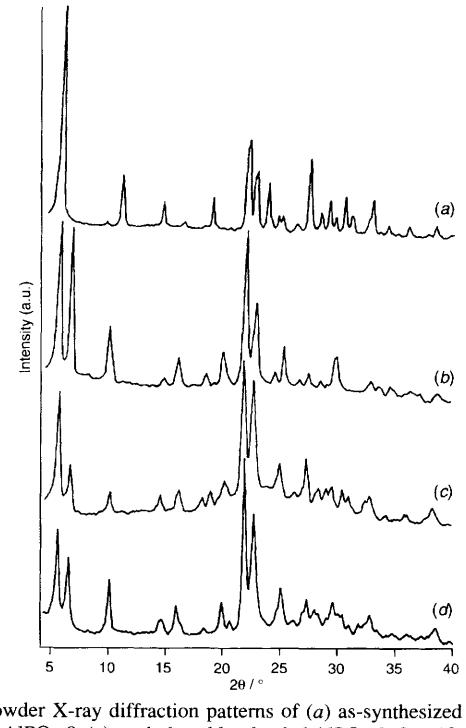


**Fig. 1** Powder X-ray diffraction patterns of (*a*) as-synthesized VPI-5, (*b*) unloaded $AlPO_4$-8, (*c*) methylene blue-loaded $AlPO_4$-8 ($3 \times 10^{-3}$ mol $g^{-1}$) and (*d*) perylene-loaded $AlPO_4$-8 ($9 \times 10^{-4}$ mol $g^{-1}$)

aluminophosphate-hosted methylene blue are shown in Fig. 2. The higher wavelength bands of aluminophosphate-hosted methylene blue are broadened relative to the solid. Optical spectra of methylene blue have been studied both in solutions of varying concentration and in systems where methylene blue is adsorbed on crystal surfaces because of metachromatic effects.[12] Methylene blue is known to exist in a monomer–oligomer equilibrium in solution. Methylene blue with dimensions of 7 × 16 Å$^3$ and its sandwich-type dimer[12] can occupy the 1D channels of $AlPO_4$-5.[3] Since VPI-5 has straight channels and a pore size of 12.1 Å, the dimer can enter the channels of VPI-5. $AlPO_4$-8 also has straight channels but a smaller pore size than VPI-5. Although the pore size of $AlPO_4$-8 can accommodate methylene blue, the mixture of methylene blue monomers and dimers encapsulated into $AlPO_4$-8 cannot be extracted because of pore contraction and blockage[13] during the

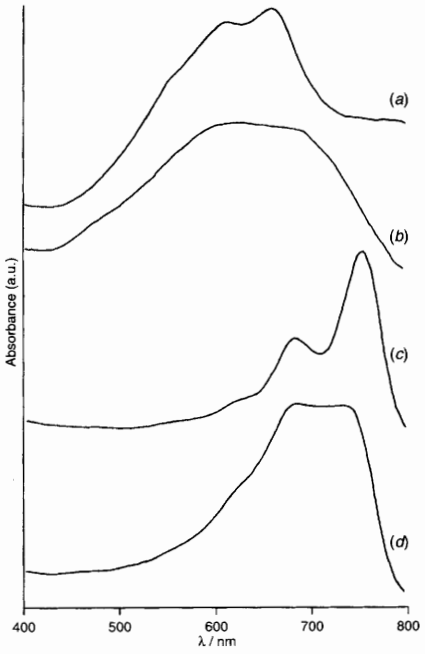


**Fig. 2** Optical spectra of (*a*) solid methylene blue, (*b*) methylene blue-loaded $AlPO_4$-8 (3 × 10$^{-3}$ mol g$^{-1}$), (*c*) methylene blue liberated from $AlPO_4$-8 in HCl and (*d*) methylene blue in HCl

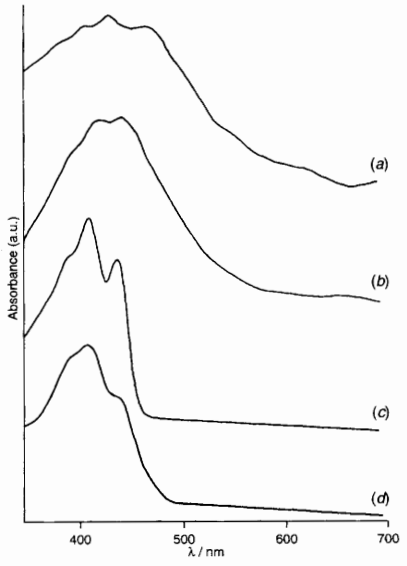


**Fig. 3** Optical spectra of (*a*) solid perylene, (*b*) perylene-loaded $AlPO_4$-8 (9 × 10$^{-4}$ mol g$^{-1}$), (*c*) perylene liberated from $AlPO_4$-8 in HCl and extracted with chloroform and (*d*) perylene in chloroform with added HCl

structural transformation. The spectra of the methylene blue encapsulated into $AlPO_4$-8 differ from those of the methylene blue ion-exchanged into zeolite Y and are similar to those of methylene blue incorporated during the hydrothermal synthesis of molecular sieves. While the ion-exchanged methylene blue gives two narrow and distinct maxima,[2] the encapsulated neutral methylene blue exhibits strongly broadened bands located in the wavelength range characteristic for a mixture of monomer and dimer. The bands of methylene blue liberated from $AlPO_4$-8 in conc. HCl show a strong red shift and are consistent with those of protonated methylene blue.[14] Fig. 3 shows optical spectra of solid and aluminophosphate-hosted perylene. Perylene was liberated from $AlPO_4$-8 in concentrated HCl and extracted with chloroform. As perylene has dimensions of *ca.* 9 × 12 Å, it can be encapsulated into the channels of $AlPO_4$-8 although it may be twisted since $AlPO_4$-8 has a smaller pore size than the dimension of perylene. However, the aluminophosphate-hosted perylene exhibits bands similar to solid perylene, indicating that most of the encapsulated perylene molecuels are not twisted severely. The spectrum of perylene liberated from $AlPO_4$-8 shows bands similar to those of a chloroform solution of perylene in HCl.

In conclusion, the structural transformation of VPI-5 into $AlPO_4$-8 can be used for encapsulation of ionic and electroneutral molecules with dimensions of *ca.* 8–12 Å and smaller species which oligomerize such as metachromatic dyes. This novel encapsulation method has some advantages over other methods[2,3] in that it is relatively simple and capable of encapsulating hydrophobic molecules.

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