

Anchoring Dyes into Multidimensional Large-Pore Zeolites: A Prospective Use as Chromogenic Sensing Materials

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Abstract: A versatile procedure for anchoring dyes into the pores of multidimensional zeolites by including organic dye precursors in the synthesis gel has been developed. To prove the concept, an aniline-functionalised zeolite Beta was obtained by reaction of triethylorthosilicate (TEOS), tetraethylammonium hydroxide, and *N*-methyl,*N*-(propyl-3-trimethoxysilyl)aniline (MPTMSA) in the presence of HF. Further extraction of the structure-directing agents resulted in a highly crystalline, white, functionalised zeolite Beta containing anchored aniline groups. Similar organic functionalised molecular sieves (OFMS) have been explored as novel catalysts, but, as far as we know, OFMS have never been used as precursors for dye-immobilisation or to design new solid-based host systems for selective molecular sensing processes as is reported here. In a

second step the solids containing dyes were prepared by reaction of the hybrid material with the appropriate reactives to obtain tricyanovinylbenzene, triphenylpyrylium, azoic, and squaraine derivatives. All these reactions are straightforward and involve electrophilic aromatic substitution or diazotisation reactions at the electron-rich aniline ring. The final dye-functionalised solid materials were isolated by simple filtration and washing procedures and have been characterised by a number of techniques. In all cases the Beta structure of the solid remains unaltered. Among the large number of areas where dye-containing zeolites might be of importance, we were inter-

ested in testing their unconventional use as heterosupramolecular hosts in chromogenic protocols. To check their potential use as chemosensors, microporous solids with anchored triphenylpyrylium and squaraine dyes were selected and used as sensors for the chromogenic discrimination of amines. It was found that the response of both solids to amines was basically governed by the three-dimensional (3D) solid architecture that tuned the intrinsic unselective reactivity of the pyrylium dye. By using new solid-state supramolecular chemistry protocols we believe that these, and similar future dye-zeolite hosts, might be promising new sensor materials allowing the visible discrimination of selected target guests by size and/or polarity within families or closely related molecules.

Keywords: chromogenic sensors • dyes/pigments • inclusion compounds • sensors • zeolites

Introduction

For years, a large amount of work has been devoted to the study of the inclusion of organic dyes into porous solids.^[1] Since solids have a large surface area, optical transparency, and mechanical stability, these organic-inorganic hybrid composites have been extensively studied for applications, such as, in second-harmonic generation,^[2] solid-state lasers,^[3] photocatalysis,^[4] and photonic antenna devices.^[5] Additionally, examples have recently been reported relating to their use in less-conventional fields such as sensing.^[6] Dyes have been extensively immobilised in amorphous silica and mesoporous materials through a sol-gel process,^[7] in contrast, the confinement of dyes in crystalline microporous solids such as zeolites has not been exhaustively explored, despite their

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well-defined structural properties, for example regular cages and channels, that make them ideal hosts for dye-inclusion compounds.^[8] In fact, as far as we know, the covalent attachment of dyes into the microporous voids of a zeolite has never been used as a method for dye-immobilisation, although dyes have been selectively anchored on the outer surface.^[9] This is probably due to the relative small openings of zeolites and the lack of abundant dangling $\equiv\text{SiOH}$ groups, which preclude immobilisation through grafting in the way that it is usually carried out in amorphous or mesoporous solids.^[10]

There are basically three strategies for dye encapsulation into silica-based microporous solids: 1) inclusion of the dye into the synthesis gel,^[11] 2) simple surface adsorption,^[12] and 3) the ship-in-the-bottle approach.^[13] The former approach is quite restrictive because of the inherent difficulties in crystallising the desired microporous phase as well as the usual low stability of the organic dyes under the synthesis conditions for microporous materials. Additionally, following this strategy it is not easy to incorporate some of the dye molecules into the crystalline framework. A possible serious drawback of the adsorption strategy is the usually uncontrollable formation of dye aggregates.^[14] This can be circumvented by selecting the appropriate host avoiding the formation of dye aggregates, for instance by using low-silica zeolites (zeolites with a large aluminium content and highly charged framework) as hosts for positively charged dyes.^[15,5] The ship-in-the-bottle approach interestingly makes use of host frameworks possessing cavities that are larger than the entrance opening; in these systems reactants are allowed to diffuse in, but the products are prevented from exiting. Following this approach, the zeolite faujasite has been used almost exclusively and beautiful examples have been reported, most of them related to the presence of transition-metal atoms.^[16] Moreover, the fact that in some cases the same reaction can occur in both within and outside of the solid makes it difficult to determine whether the product is really within the microporous voids.^[17]

However, the inclusion of dyes into microporous materials has been used in a large number of research and applied fields and therefore, new protocols for controlled dye-immobilisation in microporous solids is a field of interest. Our proposed approach widens the possibilities for dye-immobilisation through inclusion of organic dye precursors containing trialkoxysilanes in the synthesis gel. Thus, after the extraction of the pore-filling agents, the dye precursor remains covalently bonded to the microporous framework. As a proof-of-concept we show here a rather simple route to anchor selected dyes onto the inner surface of zeolite Beta. This synthesis procedure is tunable, undemanding, and versatile for ubiquitous anchoring of dyes into the pores of multidimensional zeolites. With regard to the possible large number of different applications of these solids containing anchored dyes we have tested their prospective use as molecular-selective, chromogenic sensor materials.

Results and Discussion

The protocol we have developed to anchor dyes is based on the inclusion of organic dye precursors in the synthesis gel to obtain, after the extraction of the structure-directing agents (SDA), zeolite derivatives containing covalently bonded organic groups on the pore walls.^[18] This is a general method that is operative as long as the organic moiety to be anchored is stable in the synthesis media. These organic, functionalised molecular sieves (OFMS) were formerly developed by the pioneering work of Davis.^[18] These have been explored as novel catalysts, but OFMS have never been used as precursors for dye-immobilisation or to design new solid-based host systems for selective molecular sensing processes as we will see below. The framework zeolite Beta was selected, the synthesis of which has been carried out by using tetraethylammonium (TEA) and fluoride anions as the structure-directing agents and mineralisers, following the procedure of Cámbor.^[19] One of the properties of pure silica zeolites prepared through the fluoride route is their lack of connectivity defects, related to the fact that charges arising from TEA cations are counterbalanced by fluoride anions and there is no need for the presence of the pairs $\equiv\text{SiO}^- \text{HOSi}\equiv$, giving rise to hydrophobic molecular-sieves.^[20] Zeolite Beta consists of the intergrowth of several polymorphs, all characterised by a 3D channel system with access to the microporous void that is limited by windows (ca. 6.8 Å in diameter) composed of 12 silicon atoms.^[8] Most applications require multidimensionality and no pore-blockages of the structure. As the dye precursor to be anchored to the zeolite walls we have chosen *N*-methyl,*N*-(propyl-3-trimethoxysilyl)aniline (MPTMSA).^[21]

The hybrid material was synthesised by reaction of triethylorthosilicate (TEOS), tetraethylammonium hydroxide, and the aniline derivative MPTMSA in the presence of HF. Three different amounts of the aniline derivative MPTMSA were introduced into the synthesis mixture. The starting composition was taken from that proved to be efficient for the synthesis of zeolite Beta and other pure silica polymorphs in fluoride media at near-neutral pH.^[20] Gel compositions can be expressed as $\text{SiO}_2:n\text{MPTMSA}:0.5\text{TEAF}:4\text{H}_2\text{O}$, where *n* is 0.005, 0.022, and 0.046 respectively. Each of the mixtures was allowed to react in 23-mL Teflon-lined Parr autoclave at 150°C for 12 days. After this time, the fully crystalline derivatives of zeolite Beta were obtained for all the aniline contents tested. Yields were in the range of 33–36% (higher than 90% of the silica was transformed into crystalline Beta framework). XRD patterns and SEM images of the white solids indicate high purity and a homogeneous crystal-size distribution that strongly suggests a homogeneous composition throughout every sample (i.e., all the crystals present were of the same composition). Extraction of the pore-filling agents with aqueous acetic acid was carried out twice to ensure complete removal of SDA. This resulted in a highly crystalline, white, functionalised zeolite Beta containing anchored aniline groups (see solid **I** in Scheme 1). The determination of

the amount of the organic aniline functionalisation was carried out by monitoring the aniline band of the compound in solution at 254 nm after dissolution of the sample with HF in acetonitrile/water mixtures. The values of the aniline content obtained were in agreement with those found from thermogravimetric analysis (TGA). Figure 1 shows the relationship between the amounts of the aniline derivative MPTMSA introduced into the reaction mixture and the final aniline content in solid **I**. As can be seen, when the MPTMSA-doping is small, the incorporation is near quantitative; however, there is a limit for aniline incorporation (around 1.35%) which must be related to the destabilising effect that the substitution of aniline for TEA cations has on the zeolite crystallisation.

This general behaviour has also been observed when pure silica zeolites are doped with aluminium.^[20] This destabilising effect is probably enhanced by the formation of connectivity-defects arising from the presence of the $\equiv\text{Si}-\text{C}-\text{R}$ groups, which must force the appearance of one dangling group per $\equiv\text{Si}-\text{C}$ unit substituted ($\equiv\text{Si}-\text{O}^-$ or $\equiv\text{Si}-\text{OH}$, probably dependent on the pH). On the other hand, zeolite Beta can be synthesised using about 25 different SDA^[22] when the fluoride route is employed, then, anchored aniline might be behaving as a suitable pore-filling agent and should counterbalance the above-mentioned detrimental effects. This is another reason why zeolite Beta is a good candidate for use as a host for OFMS design.

The final ideal unit cell (u.c.) composition of solid **I** (for polymorph A, $64\text{SiO}_2/\text{u.c.}$) can be described as $(\text{SiO}_2)_{64-2n}(\text{SiO}_{3/2}\text{OH})_n(\text{SiO}_{3/2}(\text{CH}_2)_3\text{CH}_3\text{N}(\text{C}_6\text{H}_5))_n$, where n can vary

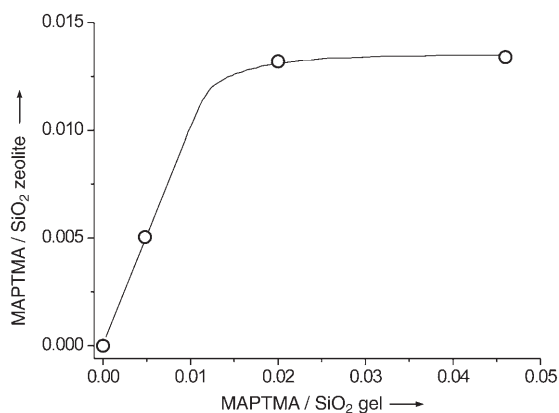


Figure 1. Aniline derivative/SiO₂ molar ratio in the zeolite as a function of that in the synthesis mixture.

up to 0.86. Thus, the amount of aniline incorporated can be readily obtained by simply controlling the MPTMSA introduced into the synthesis mixture. The ¹H and ¹³C NMR spectra of the solid dissolved in NaOH confirm the presence of the Si-C bond as well as the aromatic aniline moiety, which appears to be intact even after the demanding synthesis conditions. Figure 2 shows the XRD patterns and SEM images of the aniline-functionalised zeolite Beta as-synthesised and after the removal of the SDA (solid **I**, $n=0.0022$). The synthetic route appeared to be quite versatile and in preliminary assays we have also obtained structures based on the zeolite silicalite (2D, pore diameter ca. 5.5 Å) containing anchored aniline groups.

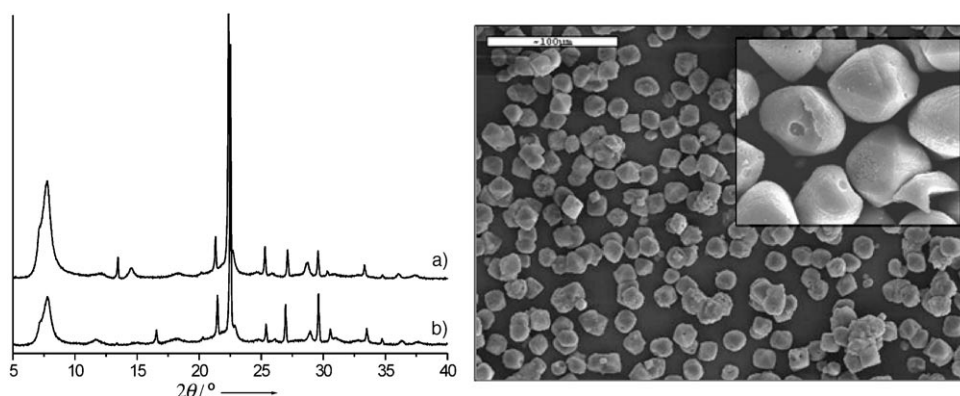
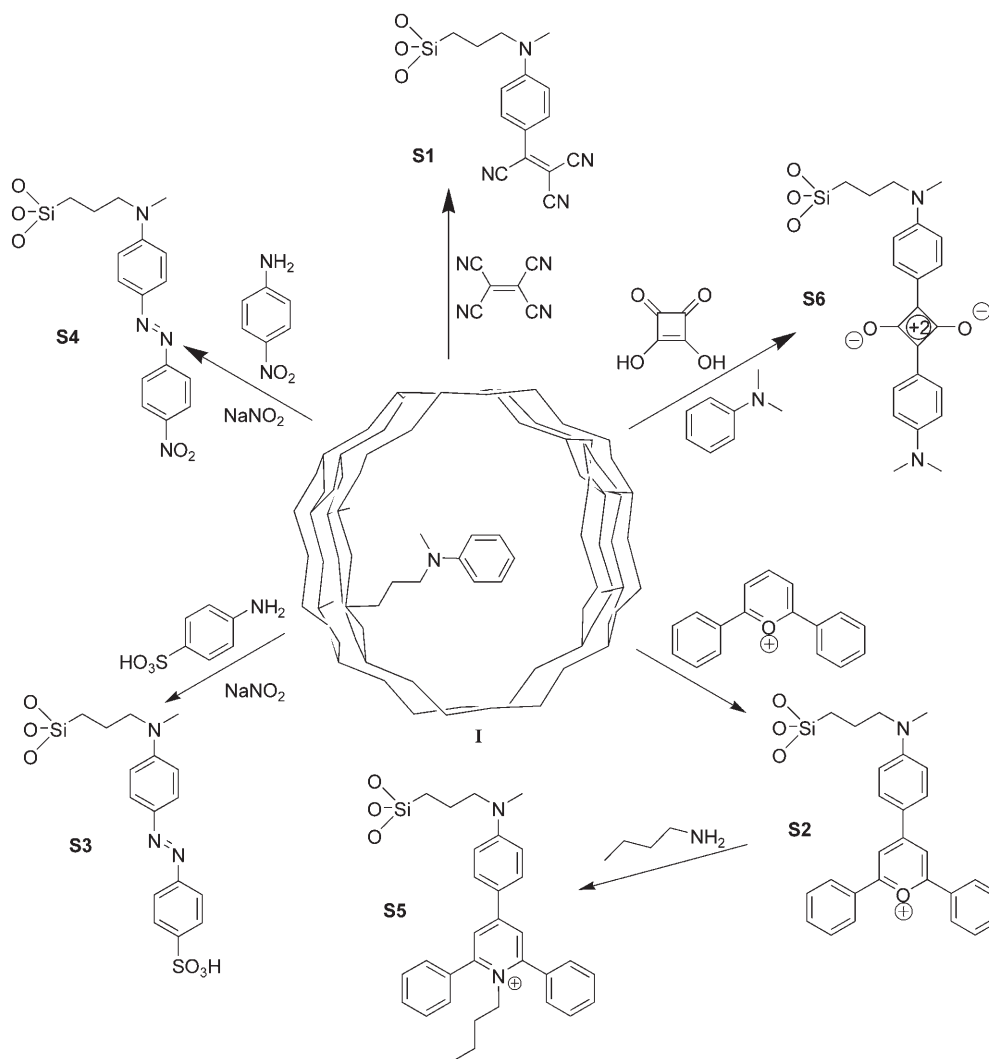
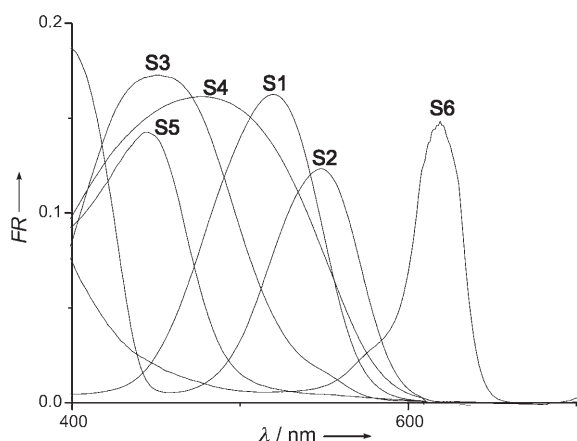


Figure 2. XRD pattern and SEM images of the aniline-functionalised Beta zeolite. a) As-synthesised; b) sample-extracted.

At this stage, the hybrid microporous material **I** containing dangling aromatic *N,N*-dialkyl-substituted aniline rings is available as a starting material to synthesise dyes of different nature. Solid **I** containing an aniline/SiO₂ ratio of 0.0135 was selected for this purpose. To show the flexibility of the approach we have prepared solids **S1-S6** by reaction of solid **I** with tetracyanoethylene (**S1**), 2,6-diphenylpyrylium (**S2** and **S5**), 4-aminobenzenesulfonic acid (**S3**), 4-nitroaniline (**S4**), or 3,4-dihydroxy-3-cyclobutene-1,2-dione (**S6**) (see Scheme 1).^[23] All these reactions are straightforward and involve electrophilic aromatic substitution or diazotisation reactions on the electron-rich aniline ring. The final dye-functionalised solid materials were isolated by simple filtration and exhaustive washing procedures. The **S1-S6** solids have been characterised by X-ray diffraction, TGA, elemental analysis, and UV/Vis spectroscopy. In all cases the Beta structure of the solid remains unaltered. The solids are brightly coloured ranging from yellow (for solid **S5**) to those absorbing at the far end of the visible window (solid **S6**). Figure 3 shows the visible spectra of the solids.

Typical final solids were obtained with dye contents ranging from 4.13×10^{-4} mol of dye/mol of SiO₂ for solid **S4** to 1.12×10^{-5} mol of dye/mol of SiO₂ for solid **S6** (see Experimental Section). Despite the partial functionalisation of the aniline in the synthesis procedure of materials **S1-S6** from solid **I**, the final solids are brightly coloured (see Graphical

Scheme 1. A schematic representation of solids **I**, **S1**–**S6**.Figure 3. Visible spectra of solids **S1**–**S6** suspended in ethylene glycol.

Abstract) and the final dye content should be adequate for many applications. More importantly, the grafting protocol through covalent bonding of organic dyes to the framework

of a zeolite shows some remarkable advantages when compared to the other strategies of inclusion of organic dyes into microporous silica-based materials. The necessary condition in the common ship-in-the-bottle approach in which the formed product has to be bulkier than the cavity to avoid leaching is not applicable in the protocol that we have followed, since the final dye is covalently bonded to the silica framework. An additional advantage is related to the enhanced chemical stability presented by the covalently anchored chromophores when compared to that in solution; that is, squaraine and tricyanovinyl derivatives are known to undergo a rapid and effective attack by nucleophiles such as $R-SH$, CN^- , and OH^- in aqueous environments, whereas the corresponding solids **S1** and **S6** that have anchored dyes do not react with these species even after weeks.^[24]

Among the large number of areas where coloured solids might be of importance, we are especially interested in their unconventional use as sensor materials in chromogenic protocols.^[25] In relation to the design of new chemical sensors, those relying on the construction of “binding structures”

using 3D solid architectures are especially appealing. Here, the selectivity is not related to the production of a complicated host but imposed by the solid structure itself that is capable of discriminating the shape-selectivity, polarity, and size of the guest.^[6] Besides, the sensor response by microporous solids might use pre-concentration effects provided by the adsorption properties of zeolites. Thus, it is unexpected that despite the number of fields where zeolites have been used, their use in chromogenic sensing procedures has been very limited.^[26] As has been suggested above, this might have been due, among other factors, to the lack of convenient routes to unambiguously anchor dyes into the pore voids.

To check their potential use as sensor materials we have selected solids **S2** and **S6** and tested their capability towards the chromogenic discrimination of amines. Preliminary experiments to find sensor properties in the rest of the solids **S1**, **S3**, **S4**, and **S5** did not show any remarkable results and will be more exhaustively studied in due course.

As has been reported, 4-(4-aminophenyl)-2,6-diphenylpyrylium dye derivatives displays a red-magenta colour that changes to yellow by reaction with primary amines due to transformation into pyridinium derivatives.^[6f] In addition to the colour change, the pyrylium derivative is not fluorescent, whereas the obtained pyridinium fluoresces at about 470 nm upon excitation to give the yellow band at approximately 440 nm.^[27] However, this chromofluorogenic pyrylium response to primary amines is rather unspecific in solution and we have found that it can be conveniently modulated when incorporated into the zeolite framework (see below). A representation of the dye anchored within the zeolite Beta pores (solid **S2**) is shown in Figure 4.

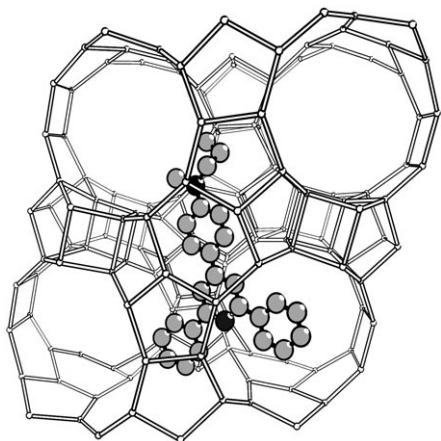


Figure 4. Representation of solid **S2** containing a pyrylium dye anchored on the zeolite Beta walls. Bridging oxygen atoms have been deleted for the sake of clarity.

The response of this dye-containing solid **S2** to a number of amines was tested and it was found that it can act as a suitable selective heterosupramolecular host in selective chromofluorogenic-sensing protocols. The response of **S2** to

amines is basically modulated by three factors: 1) the reactivity of the 4-(4-aminophenyl)-2,6-diphenylpyrylium dye, 2) the polarity, and 3) the dimensions of the openings of the zeolite Beta scaffolding. Chromogenic amine discrimination has been studied in two solvents of different polarity, ethanol and water. The results are summarised in Figure 5 that

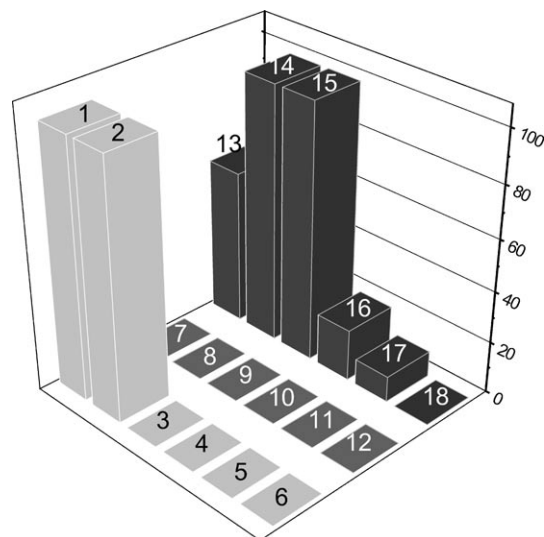


Figure 5. Schematic representation of the relative response of pyrylium-functionalised zeolite Beta (**S2**) to different amines: 3,3-Diphenylpropylamine (1), benzylamine (2), PAMAM-0 (3), dopamine (4), 1-aminomethylpyrene (5), 9-aminomethylanthracene (6), aniline (7), diethanolamine (8), tripropylamine (9), 4-(dimethylamino)benzoic acid (10), 4-bromoaniline (11), 2-aminobenzothiazole (12), 5-amino-1-pentanol (13), 6-amino-1-hexanol (14), *n*-heptylamine (15), *n*-butylamine (16), *n*-propylamine (17), and lysine (18).

shows the response to a number of amines of the functionalised-zeolite **S2**. The chromogenic sensing response was monitored in water at basic pH (pH~10) except for the amines 9-methylaminoanthracene, 1-methylaminopyrene, 3,3-diphenylpropylamine, and benzylamine, that were water-insoluble and were only tested in ethanol. In all cases the colour changes were measured after a long time to assure equilibrium conditions and minimise possible discrimination due to kinetic effects. As stated above the reactivity of the dye is governed by nucleophilic attack of primary aliphatic amines at the pyrylium ring. This response is also conserved into the zeolite framework and **S2** reacts with certain aliphatic amines (see below) but remains a magenta colour in the presence of other amines. In less-polar ethanol, the size discrimination is clearly observed and only “small” amines such as *n*-propylamine, *n*-butylamine, *n*-heptylamine, and “medium” amines such as 3,3-diphenylpropylamine, and benzylamine are capable of reaching the pyrylium signalling units in the inner pores of the zeolite inducing magenta-to-yellow colour transformations. All those amines have one longitudinal section smaller in size (at least in one direction) than the dimensions of the openings in zeolite Beta. In contrast, solid **S2** in contact with an ethanol solution of bulky primary amines such as 9-methylaminoanthracene, 1-methyl-

aminopyrene, and the amine containing the dendrimer PAMAM-0 remained completely inactive for weeks. This test also proves that the dyes are on the inner-pore surface of the microporous zeolitic framework.

We observe notable polarity discrimination in water. Thus, the increase in strength of hydrogen bonding to the solvent can cause significant decrease in the removal of highly hydrophilic amines from water to the hydrophobic zeolite pores. This effect can be observed when comparing, for instance, the reactivity of the amines *n*-propylamine, *n*-butylamine, and *n*-heptylamine (see Figure 5). Whereas the “small” but hydrophobic amine *n*-heptylamine is able to transform the pyrylium to the pyridinium group in **S2** quantitatively, other less hydrophobic amines such as *n*-propylamine and *n*-butylamine only induce a partial colour change. Additionally, the somewhat similar but highly hydrophilic amine lysine or dopamine did not induce any chromogenic response after weeks. In fact there is a clear correlation between the hydrophobicity of these amines (*n*-heptylamine > *n*-butylamine > *n*-propylamine > lysine \cong dopamine) and the ability of the amine to induce pyrylium-to-pyridinium transformation in the sensor zeolite **S2**. A similar effect can be found in the related amines, *n*-heptylamine and the less hydrophobic derivatives 6-hydroxyhexylamine and 5-hydroxypentylamine. For instance, *n*-heptylamine and 6-hydroxyhexylamine are primary amines with the same chain length but show a different polarity due to the presence of the OH group in the latter. The addition of an aqueous solution of *n*-heptylamine to **S2** resulted in a remarkable colour variation in less than four minutes. On the contrary, **S2** remained magenta for at least 30 minutes upon addition of 6-hydroxyhexylamine as expected from the hydrophobic nature of the pure silica microporous framework. This different reactivity was also observed for a longer time (see Figure 5). As an example of size and polarity discrimination, Figure 6 shows



Figure 6. Colour changes observed in solid **S2** upon addition of several amines. From left to right: no amine, 3,3-diphenylpropylamine, 1-methylaminopyrene, *n*-heptylamine, and 6-amino-1-hexanol.

the colour changes observed with solid **S2** upon addition of the amines 3,3-diphenylpropylamine, 1-methylaminopyrene in ethanol, and *n*-heptylamine and 6-hydroxyhexylamine in water after a reaction time of 20 min.

The hydrophobic effect in the inner pores of the zeolite framework is also indicated from the additional stability of the anchored dye against nucleophilic attack of OH⁻ from water. Thus, whereas basic aqueous solutions of pyrylium derivatives readily became yellow due to formation of the corresponding 1,5-dienone, the magenta colouration of solid

S2 remained unaltered for weeks even at very high pH values.

Solid **S6** was also studied as a potential sensor material for chromofluorogenic sensing of amines. Squaraine dyes have been reported to react with amines through an addition reaction with the four-membered ring leading to the rupture of the extended π system in the squaraine framework and subsequent decolouration. Studies with **S6** were carried out under the same conditions as those for solid **S2** and showed a similar reactivity. This similar response of solids **S2** and **S6** strongly indicates that the observed reactivity, and therefore the sensor ability of these materials, is governed by the 3D solid architecture that adequately tunes the reactivity of the squaraine and pyrylium dyes. This led to new solid-state, supramolecular sensor materials with enhanced sensing abilities.

Conclusion

In summary, we have reported a suitable route to anchor dyes into the inner voids of the siliceous frameworks of zeolites. The protocol developed that promotes the anchoring of dyes is based on the inclusion of organic dye precursors in the synthesis gel. This procedure is easily tuneable and versatile, and allows us to obtain novel dye-containing hybrid materials with promising applications in a number of different fields. The versatility of this approach has been demonstrated by preparing solids **S1–S6** by straightforward reaction of the organic, functionalised molecular sieve **I** with tetracyanoethylene (to give solid **S1**), 2,6-diphenylpyrylium (yielding solids **S2** and **S5**), 4-aminobenzenesulfonic acid (to give solid **S3**), 4-nitroaniline (giving solid **S4**), or 3,4-dihydroxy-3-cyclobutene-1,2-dione (resulting in solid **S6**). The anchoring of dyes through covalent bonds into the zeolite framework shows certain advantages when compared to other strategies of inclusion of organic dyes into microporous silica solids. We believe that this work might open up new possibilities for the synthesis of dye-containing microporous solids by applying similar synthesis protocols to some of the more than 150 known zeolitic topologies.^[8] Additionally, we have also shown the potential applicability of these zeolites containing dyes as sensors in chromogenic sensing protocols. By using new solid-state supramolecular chemistry protocols, we have demonstrated that employing multidimensional channel systems as solid hosts enclosing suitable binding structures and/or signalling units might lead to new sensor materials that allow to visibly discriminate selected target guests by size and polarity within families or closely related molecules.

Experimental Section

General remarks: All commercially available reagents were used without further purification. Air/water-sensitive reactions were performed in

flame-dried glassware under argon. Acetonitrile was dried with CaH_2 and distilled prior to use.

Materials characterisation: X-ray measurements were performed with a Seifert 3000TT diffractometer by using $\text{CuK}\alpha$ radiation. Thermogravimetric analysis of solids **I**, **S1**, **S2**, **S3**, **S4**, **S5**, and **S6** was carried out with a TGA/SDTA 851e Mettler–Toledo balance, by using a heating program consisting of a first heating ramp of 10°C per minute from 393–1273 K, and then a plateau at 1273 K for 30 min. UV/Vis diffuse-reflectance absorption spectra were recorded on a Perkin–Elmer Lambda35 UV/Visible spectrometer (suspension of 0.002 g of the corresponding solid in ethylene glycol (2.7 mL)). Scanning electron microscopy images were obtained with a Jeol JSM6300 microscope operated at 30 kV.

Determination of organic content: The determination of the amount of the organic functionalisation was carried out by means of UV/Vis spectroscopy by using calibration curves. These curves were obtained by dissolving increasing quantities of *N,N*-dimethylaniline or the corresponding dye (final concentrations in the range 1.0×10^{-5} to 1.0×10^{-7} mol dm $^{-3}$) with a fixed quantity of pure inorganic matrix (0.01 g) and HF (48% in water, 0.023 mL) in acetonitrile (0.5 mL) mixtures. Next, the absorbance of the aniline band (254 nm) or the visible band was plotted against organic concentration. Finally, the functionalised solids were subjected to the same treatment and the absorbances at 254 nm for solid **I**, or the visible bands in the case of solids **S1–S5**, were measured and employed to estimate organic content.

A slightly modified procedure was employed with solid **S6**. The calibration curve was obtained by dissolving increasing quantities of the squaraine dye in diethyl ether. The functionalised **S6** material was suspended in ethylene glycol and the absorbance measured. The dye content was estimated by interpolation of the calibration curve.

Synthesis procedures: The synthesis of *N*-methyl,*N*-(propyl-3-trimethoxysilyl)aniline has been previously published.^[21] Also, the synthesis of the corresponding dyes in the experiments to determine organic content were straightforward and have been published elsewhere.^[24]

Syntheses of precursor solid were carried out by reaction of triethylorthosilicate (TEOS), tetraethylammonium hydroxide, and MPTMSA (*N*-methyl,*N*-(propyl-3-trimethoxysilyl)aniline) in the presence of HF for several organosilane contents. The overall molar composition can be described as $\text{SiO}_2 : x\text{MPTMSA} : 0.5\text{TEAF} : 4\text{H}_2\text{O}$. A detailed synthesis procedure for the sample used to generate the rest of the coloured derivatives is as follows: A solution of MPTMSA (0.80 g) in TEOS (27.08 g, 0.129 mol) was added to a vessel containing a solution of tetraethylammonium hydroxide (35% wt, 28.02 g, 0.066 mol) and water (52.84 g, 2.93 mol). The alkoxides were allowed to hydrolyse at room temperature. Then, the temperature was increased to 50°C to evaporate alcohols and water until 25.27 grams of gel were obtained. HF (2.71 g, 0.065, 48%) was added to the mixture that was stirred by hand. The overall molar composition was $\text{SiO}_2 : 0.022\text{MPTMSA} : 0.5\text{TEAF} : 4\text{H}_2\text{O}$. The paste was distributed between 23-mL Teflon-lined Parr autoclaves and allowed to react at 150°C for 12 days under static conditions. After this time, the paste (pH 8.2) was recovered by filtration and washed with plenty of water, yielding (33.5 wt%) fully crystalline zeolite Beta. Extraction with aqueous acetic acid (50% wt) was carried out twice to ensure complete SDA removal (losses were kept constant from one sample to another as measured by TGA, which was used for organic content determination). This resulted in a highly crystalline, white, functionalised zeolite Beta containing anchored aniline groups (solid **I**). ^1H and ^{13}C NMR spectroscopy was carried out on samples that had been previously dissolved in NaOH (D_2O , 2.5 mol dm $^{-3}$).

S1–S6 materials were obtained by straightforward reaction of solid **I** with tetracyanoethylene (**S1**), 2,6-diphenylpyrylium perchlorate (**S2** and **S5**), 4-aminobenzenesulfonic acid (**S3**), 4-nitroaniline (**S4**), or 3,4-dihydroxy-3-cyclobutene-1,2-dione (**S6**). The **S1–S6** solids were characterised by X-ray diffraction, TGA, and UV/Vis spectra. In all cases the Beta structure of the solid remained unaltered. These were obtained as brightly coloured solids that ranged from yellow (for **S5**) to those absorbing at the far end of the visible window (**S6**).

Solid S1: Solid **I** (1.0 g containing 0.16 mmol of aniline) was suspended in acetonitrile (10 mL) and then tetracyanoethylene (0.1 g, 0.78 mmol) was

added. The mixture was allowed to react at 80°C for 16 h. The solid material was exhaustively washed with acetonitrile and acetone until no colour in the washing layers was observed and was then air-dried. The final **S1** material was an intense red colour and gave an absorption band centred at 517 nm. The amount of dye was 1.5 mmol of dye/mol of SiO_2 . **CAUTION:** HCN is evolved in the synthesis procedure.

Solid S2: Solid **I** (1.0 g containing 0.16 mmol of aniline) was suspended in ethanol (80 mL) and then 2,4-diphenylpyrylium perchlorate (0.52 g, 1.57 mmol) was added. The mixture was refluxed for 24 h and was then filtered. The solid material was exhaustively washed with ethanol and acetone until no colour in the washing layers was observed and was then air-dried. The final **S2** material was an intense magenta colour and gave an absorption band centred at 550 nm. The amount of dye was 0.06 mmol of dye/mol of SiO_2 .

Solid S3: 4-Aminobenzenesulfonic acid (0.12 g, 0.70 mmol) was dissolved in a mixture containing ethanol (7.2 mL) and hydrochloric acid (0.2 mL, 35%). Then a solution of NaNO_2 (0.05 g, 0.73 mmol) in water (0.6 mL) was added and allowed to react for 30 min. The diazonium salt solution formed was added dropwise to a cooled ($0\text{--}5^\circ\text{C}$) suspension of solid **I** (1.0 g containing 0.16 mmol of aniline) in a 1:1 (v/v) water/ethanol mixture (40 mL) and was allowed to react for 3 h at $0\text{--}5^\circ\text{C}$, and for 16 h at room temperature. The solid material was filtered, exhaustively washed with ethanol and acetone until no colour in the washing layers was observed and was then air-dried. The final **S3** material was obtained as an orange solid (absorption band centred at 521 nm). The amount of dye was 0.46 mmol of dye/mol of SiO_2 .

Solid S4: 4-Nitroaniline (0.11 g, 0.80 mmol) was dissolved in a mixture containing ethanol (7.2 mL) and hydrochloric acid (0.2 mL, 35%). Then a solution of NaNO_2 (0.055 g, 0.80 mmol) in water (0.6 mL) was added and allowed to react for 30 min. The diazonium salt solution formed was added dropwise to a cooled ($0\text{--}5^\circ\text{C}$) suspension of solid **I** (1.0 g containing 0.16 mmol of aniline) in a 1:1 (v/v) water/ethanol mixture (40 mL) and was allowed to react for 3 h at $0\text{--}5^\circ\text{C}$, and for 16 h at room temperature. The solid material was filtered, exhaustively washed with ethanol and acetone until no colour in the washing layers was observed and was then air-dried. The final **S4** material was obtained as a dark-red solid (absorption band centred at 511 nm). The amount of dye was 4.13 mmol of dye/mol of SiO_2 .

Solid S5: Solid **S2** (1.0 g, containing 9.19×10^{-4} mmol of pyrylium dye) was suspended in aqueous ammonium hydroxide (1.0 mL). The mixture was allowed to react at room temperature for 15 min. The solid material was exhaustively washed with water and with acetone and was then air-dried. The final **S5** material was obtained as a yellow solid (absorption band centred at 440 nm). The amount of dye was 0.06 mmol of dye/mol of SiO_2 .

Solid S6: In a round-bottomed flask fitted with a Dean–Stark system, solid **I** (1.0 g containing 0.16 mmol of aniline) was suspended in anhydrous toluene (100 mL) and was refluxed for 2 h. Then 3,4-dihydroxy-3-cyclobutene-1,2-dione (0.12 g, 1.07 mmol) was added and the mixture was refluxed for one more hour. After that, *N,N*-dibutylaniline (1.80 mL, 13 mmol) was added and the reflux was continued. Triethylorthoformate (15 mL, 78.16 mmol) was added 30 min later and the crude was refluxed for another 16 h. The crude reaction mixture was filtered and the solid was exhaustively washed with toluene and acetone until no colour in the washing layers was observed and was then air-dried. The final **S6** material exhibited an intense blue colour and displayed an absorption band centred at 620 nm. The amount of dye was 0.011 mmol of dye/mol of SiO_2 .

Sensing studies: Sensing studies were carried out with solid **S2** in the presence of amines with different substitution patterns, size and polarity (lysine, *n*-propylamine, *n*-butylamine, *n*-heptylamine, 6-amino-1-hexanol, 5-amino-1-pentanol, aniline, diethanolamine, tripropylamine, 4-(dimethylamino)benzoic acid, 4-bromoaniline, 2-aminobenzothiazole, 1-methylaminopyrene, 9-methylaminoanthracene, 3,3-diphenylpropylamine, benzylamine, dopamine, and PAMAM-0). Solutions of amine ($c = 0.01$ mol dm $^{-3}$) were prepared by dissolution in ethanol or water (depending on its solubility). The solution of amine (2 mL) was added to solid **S2** (0.003 g) and the mixture was allowed to react for 24 h. The liquid was separated by centrifugation and the remaining solid was suspended in

ethylene glycol. The absorbance of the final solid was measured by the diffuse reflectance technique. Upon addition of certain amines with the appropriate substitution, size, or polarity, the band at 540 nm (related to the absorption of the pyrylium moiety) disappeared and a new absorption band centred at 463 nm (related to the pyridinium moiety) was observed. This change in colour was ascribed to transformation of the pyrylium ring to the pyridinium ring by nucleophilic attack of the corresponding amine.

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