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Pyrene covalently anchored on a large external surface area zeolite as a selective heterogeneous sensor for iodide

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Pyrene as a fluorophore has been covalently anchored on a delaminated ITQ-2 zeolite having a large external surface area (730 m^2 g^{-1}) and the resulting solid found to have a selective response as a heterogeneous sensor for I$^-$ in the presence of other halides.

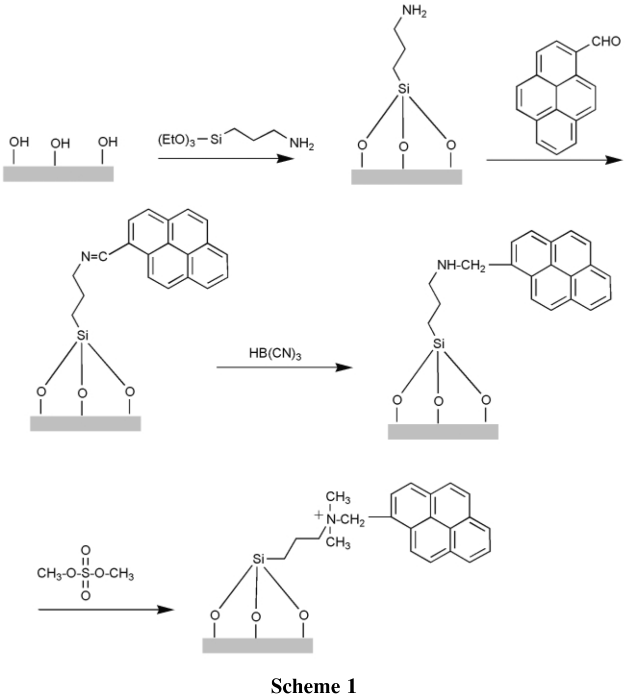
Due to the large ionic radius, low charge density and low hydrogen bonding ability, iodide is the most difficult halide to be sensed, particularly compared to fluoride or chloride for which there are numerous reported sensors.[1–3] However, the excellent electron donor ability of I$^-$ should make this anion very appropriate to devise a sensor based on fluorescence quenching. Pyrene (py) derivatives are widely used as sensors for a variety of analytes including neutral organic compounds and inorganic anions.[1,2] This use derives from their high fluorescence quantum yields.[4,5] Pyrene derivatives have not been applied to the sensing of large anions with low coordinating ability such as I$^-$.

On the other hand, most of the work up to now has been done in solution using soluble py derivatives.[1,2] In order to devise a system to monitor an analyte concentration in continuous flow it is necessary to support the active py derivative on a solid. Current strategies are the preparation of films, polymers or py–inorganic hybrid composites.[6,7] When changing a sensor from the homogeneous to the heterogeneous state, the response factor generally decreases significantly. To increase this response factor it would be, therefore, highly desirable to have a support with a very large surface area. Herein we report the preparation of a large surface area py-containing zeolite in which py has been covalently anchored. In spite of the promising opportunities of this methodology, reports describing sensing molecules anchored on inorganic oxides are very scarce. In a precedent, anthryl lumophore has been covalently anchored to aminopropyl-functionalised silica and the solid used as a pH probe.[8] Herein, we have further innovated in this methodology by using a novel support, ITQ-2, with a large surface area, and applied it to the sensing of I$^-$.

Delaminated zeolite ITQ-2 [9] has been obtained by ultrasonic delamination of the layered MCM-22 precursor. The solid is characterised by a very large external surface area (730 m^2 g^{-1}), three to four times that found for silica gels. The external ITQ-2 area is similar to that of mesoporous MCM-41 type materials, but the zeolitic crystal structure of ITQ-2 layers increases enormously the hydrothermal stability of the support as compared to MCM-41. It is known that the mesoporous structure of MCM-41 collapses upon storage at room temperature with ambient moisture[10] and much more rapidly when the solid mesoporous silicate is suspended in aqueous solutions.[11] Therefore the potential of ITQ-2 as a support is more promising than for the moisture-sensitive MCM-41 solid or a low surface area silica.

The preparation procedure followed to anchor the py fluorophore onto the surface of ITQ-2 (py$\propto$ITQ-2) is shown in Scheme 1[†] We started with pyrenecarbaldehyde (PyCHO) which was condensed with trimethoxysilylpropamine-modified ITQ-2. The aminopropylsilyl (APSi) content was maintained purposely low to minimise, after anchoring, py association on the support and the PyCHO/APSi ratio in the anchoring step was 1. The progress of imine formation was followed by the disappearance of PyCHO from the cyclohexane solution. Subsequently, the imine was reduced with NaHB(CN)$_3$ and the resulting amine exhaustively methylated with (CH$_3$O)$_2$SO$_2$. This step is necessary since it is known that amines can quench the fluorescence of polycyclic aromatic fluorophores through an electron transfer quenching mechanism. In addition, the presence of a positive nitrogen covalently anchored to the zeolite layers requires the presence of a charge compensating anion and, therefore, the solid would be especially suited for anion sensing through electrostatic fluorophore/analyte interactions. Finally the SO$_4^{2-}$ anion was ion exchanged using (NH$_4$)PF$_6$. The solid was submitted to Soxhlet extraction with acetonitrile and was vacuum dried. IR and diffuse reflectance UV-Vis spectra assessed the presence of py covalently anchored onto the solid. Both techniques show the characteristic spectra corresponding to the unaltered pyrenyl polycycle on the py$\propto$ITQ-2 sample. As expected, the py$\propto$ITQ-2 sensor exhibits strong monomer fluorescence upon excitation at 338 nm (Fig. 1). The ratio I_1/I_3 for the structure emission of py was 1.47, indicating a relatively polar environment (I_1/I_3 for water = 1.8).[12] We also observe the presence of a broad emission band between 450 and 550 nm characteristic of some excimer formation. Upon storage, the proportion of excimer emission is somewhat reduced indicating that some disaggregation and isolation of the py fluorophores has occurred at early stages upon storage. Analogous observation of py relocation in zeolite Y during ageing (reflected by a decrease of the relative excimer intensity) has been previously reported.[13]

Control experiments using the parent unsubstituted py in aqueous solution showed that fluorescence is quenched by



Scheme 1

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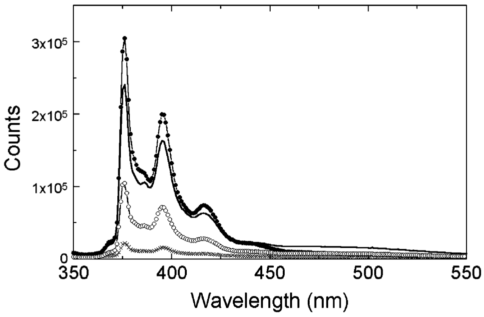

Fig. 1 Emission spectra (λ_{exc} = 338 nm) of py∝ITQ-2 as prepared (—) and after stirring the solid with an aqueous solution of 4×10^{-3} M NaI (○) or after exhaustive ion exchanges with I^- (×) and with PF_6^- (●).

iodide (k_q = 1191 M s^{-1}) and bromide (k_q = 0.023 M s^{-1}), while for practical purposes there is no quenching with chloride and fluoride. A direct comparison between the pyrene derivative in solution and when anchored in the opaque solid has to be taken with caution due the differences and photoluminescence measurements in light scattering. Nevertheless it was noted that for the same concentration of I^-, the effect on the pyrene derivative emission in solution is much higher than when pyrene is anchored on ITQ-2. The quenching rate constant (k_q) follows the oxidation potential of the halides. Thus, we suggest that after quaternisation of the amino group, the interaction of the halide with the ammonium cation favours single electron transfer to the pyrene. Additionally a heavy atom effect of pyrene fluorescence quenching by I^- can also be operative. Whatever the mechanism, it should be noted that the k_q values indicate that this sensor is very selective for I^-.

The fact that the py singlet excited state can act as electron acceptor was confirmed by diffuse reflectance UV-Vis laser flash photolysis of py∝ITQ-2. Laser excitation at 308 nm leads to two different transients that were assigned to $py^{\cdot -}$ (λ_{max} = 490 nm) and $py^{\cdot +}$ (λ_{max} = 440 nm). This assignment is supported by results of N_2 and O_2 purging as well as by previous reports in the literature about the photochemistry of py inside the voids of related zeolites.[14,15] The absorption corresponding $py^{\cdot +}$ is the only transient recorded after O_2 purging. This is consistent with the known reactivity of $py^{\cdot +}$.[14,15]

As expected, according to the results in solution, the fluorescence of the py∝ITQ-2 is almost totally quenched by exhaustive ion exchange with iodide. Magnetic stirring of py∝ITQ-2 with an aqueous solution of NaI (4×10^{-3} M) gives an emission spectrum of intermediate intensity (see Fig. 1). Back I^- to PF_6^- ion exchange allows regaining the initial fluorescence intensity, thus proving the reversibility of the py∝ITQ-2 system. This cycling I^-/PF_6^- exchange was carried out three times without noticeable variation in the response of the system, in good agreement with the covalent linkage of py to the ITQ-2 support.

Stirring a suspension of py∝ITQ-2 in aqueous solutions of NaI at different concentrations produces measurable fluorescence decreases. The intensity decrease measured at 375 nm follows a linear relationship in the mM range (100–20 mM) that can be used to calibrate the I^- concentration. The fluorescence decay is also shortened by the presence of I^-, changing from 151 ns to a biexponential decay (χ = 1.9) for an I^- concentration of 80 mM having components of 40 ns (35%) and 105 ns (65%), respectively. It is of note that not only the fluorescence intensity but also the emission temporal profile responds to the I^- concentration (Fig. 2).

Washing with distilled water reverts the fluorescence to the initial intensity and the decay returnes to the original profile. For analogous solutions of NaBr no significant fluorescence variations were observed under the conditions studied, in good agreement with the lower Br^- quenching rate constant compared to I^-. Furthermore, the emission response of py∝ITQ-2 for a 80 mmol aqueous solution of I^- is the same in the presence or absence of F^- (50 mmol). Thus, py∝ITQ-2 responds selectively to I^- as analyte.

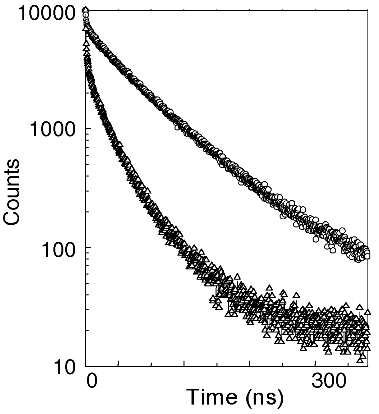

Fig. 2 Emission decay (λ_{exc} = 338 nm) measured at 375 nm of py∝ITQ-2 before (○) and after (Δ) contacting with a 80 mM solution of NaI.

The above results exemplify the vast potential of novel delaminated ITQ-2 zeolite having large external surface area and related porous silicates as supports in the design of solid sensors.

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Notes and references

† *Preparation* of py∝ITQ-2: dehydrated all silica ITQ-2 (600 mg) was stirred with a solution of APSi (12 mg) in cyclohexane (10 ml) at reflux temperature for 24 h under N_2. After, the solid was collected and stirred with a solution of pyCHO (Aldrich, recrystallized from ethanol, 8 mg) in cyclohexane (10 ml). The resulting solid was filtered off and resuspended in a solution of hexamethyldisilazane (120 mg) in cyclohexane (10 ml) and refluxed for 24 h under N_2. The resulting pyrenylimine anchored on the solid was reduced at room temperature using an excess of sodium cyanoborohydride. The sample was submitted to exhaustive methylation using dimethyl sulfate (100 mg) in acetone (10 ml) in the presence of Na_2CO_3 (1 g) and the suspension refluxed for 6 h. Finally the solid was collected and submitted to two 2 h consecutive I^- to PF_6^- ion exchanges using an aqueous solution (0.8 and 1 M, consecutively) of NH_4PF_6. Finally the solid was dried at 80 °C under vacuum.

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