Pyridine-functionalised ambidextrous gelators: towards catalytic gels†

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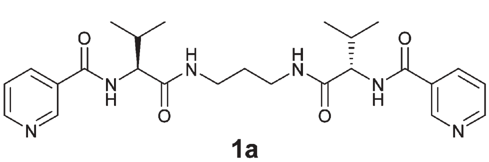
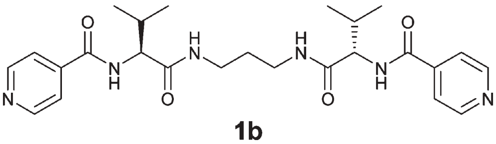
New pyridine containing gelators have been used to prepare Pd-functionalised materials with catalytic activity.

Physical gels have received increased attention in recent years because they represent an interesting case of supramolecular self-assembly to yield well-defined objects (fibers) in the nanoscale, being an example of bottom-up construction of nanostructured materials.[1] These materials are formed from the ordered aggregation of small molecules through non-covalent bonds to yield elongated supramolecules that further aggregate to fibers that percolate the solution. The nanosized fibrils formed by different organogelators have been extensively studied as templates for the preparation of mesostructured materials such as for example silica.[2] Following our previous work on the study of amino acid derived organogelators, we are currently interested in the development of functional organogelators, namely, molecules that contain binding, catalytic or reactive groups that are able to form supramolecular gels. This approach could yield nanostructured fiber-like materials which would contain well-ordered arrays of catalytic or binding units or stimuli responsive subunits with a variety of envisaged applications.

As a proof of principle, we have prepared low-molecular weight gelators containing terminal pyridine groups (see Chart 1). A few cases of organogelators containing pyridine moieties have been reported previously and recently *N*-(4-pyridyl)isonicotinamide has been shown to be a hydrogelator.[3,4] *A priori*, the pyridine unit is of interest in this type of studies for several reasons. First, the acid–base behaviour of this moiety could be of use for the preparation of pH-responsive hydrogels and, second, the donor properties of the pyridine nitrogen atom could be exploited for the coordination of transition metals of catalytic interest or in multipoint molecular recognition of H-bond donors.



1a



1b

Chart 1

The synthesis of gelators **1a** and **1b** was performed by acylation of *N*,*N*′-bis(L-valinyl) propylenediamine with nicotinoyl chloride and isonicotinoyl chloride, respectively, following a similar synthetic strategy as that used for benzoylated analogues reported recently (see ESI†).[5]

Compounds **1a** and **1b** are found to form hydrogels that are pH responsive. These compounds are soluble in acidic water (HCl, 0.1 M) and form transparent gels after exposure to concentrated ammonia vapours after a few minutes (minimum gel concentration 10.4 mM). The gelation is favored with increasing the ionic strength of the solution (NaCl, 0.1 M). Clearly, these molecules are water-soluble when the pyridine groups are protonated (pK_a *ca.* 3.5) and are able to form gels in the neutral form. This behaviour is related to that reported for anionic peptide type hydrogelators which form gels upon addition of acid although in our case the gelation results from deprotonation of a dication.[6]

Additionally, compounds **1a** and **1b** are able to form gels in a variety of organic solvents (see Table 1). As reported previously for related compounds,[5] H-bonding is the driving force for the formation of supramolecular aggregates and, as shown in Fig. 1, an energy-minimized model of a dimer with four intermolecular H-bonds can be built. Indeed, IR spectra of toluene xerogels revealed that the bands corresponding to C=O and NH stretching vibrations appeared at similar wavenumbers than those (1633 and 3283 cm^{-1}).

The microscopic aspect of the gels was studied by electron microscopy. An entangled network of fibres was found in organic solvents as well as in aqueous solution. Some representative pictures of them are collected in Fig. 2 (see ESI† for additional micrographs). For instance, TEM micrographs of **1a** organogel in CH_2Cl_2 revealed the presence of thin fibrils of a diameter of <20 nm and several micrometer length that further assemble into longer fibres of *ca.* 100 nm of diameter (Fig. 2(A)). Although

Table 1 Gelation studies of compounds **1a** and **1b** in organic solvents

Solvent	**1a**/mM	**1b**/mM
Methanol	S	S
Ethanol	S	S
Isopropanol	S	S
Butanol	S	S
$CHCl_3$	P	P
CH_2Cl_2	G (3.1)	G (10.4)
Acetone	G (5.2)	G (10.4)
DME	WG (10.4)	G (10.4)
Dioxane	G (10.4)	G (10.4)
CH_3CN	G (8.3)	G (10.4)
Ethyl acetate	G (8.3)	G (10.4)
Hexane	NS	NS
Toluene	WG + P	G (10.4)

[a] S, soluble; NS, not soluble P, precipitate; G, gel; WG, weak gel. Minimum gel concentration in parentheses.

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† Electronic supplementary information (ESI) available: Characterisation of compounds **1a** and **1b**, IR studies, detailed electron microscopy sample preparation and additional micrographs. See DOI: 10.1039/b510874h

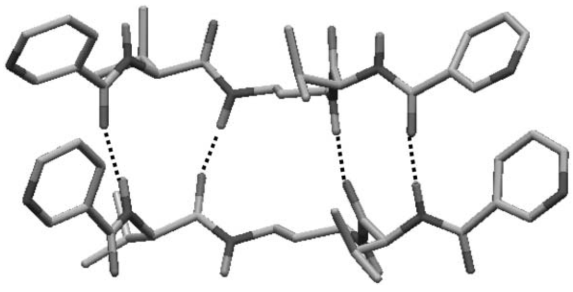


Fig. 1 Energy minimized model of compound **1a** (MACROMODEL 7.0, AMBER*).

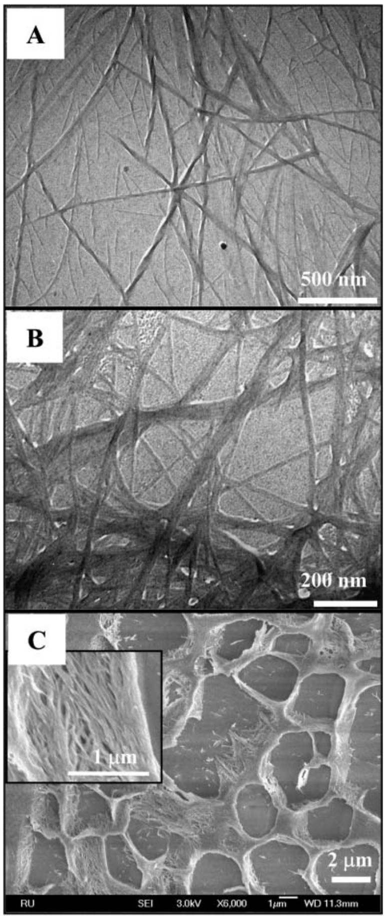


Fig. 2 TEM images of a dried CH_2Cl_2 organogel (A) and hydrogel (B) of compound **1a** (Pt-shadowing); (C) cryo-SEM image of hydrogel of compound **1b**.

some of the fibrils appeared to be helical this feature was not general and it was not present anymore at the higher assembly level. Helices could not be clearly detected by SEM (not shown). Similar results were found for compound **1b** in organic solvents (ESI†).

In the case of hydrogels, for compound **1a** TEM also reveals the presence of fibrils of less than 20 nm of diameter that further assemble and crosslink to form a crowded network (Fig. 2(B)). However, for compound **1b**, the gel is formed by a bulk of rods of *ca*. 100 nm of diameter and 500 nm to 1 µm length (see ESI†).

Cryo-SEM is a useful technique to study the three-dimensional aspect of the gel network. As can be seen in Fig. 2(C) the hydrogels are porous materials, made of fibrillar domains surrounding pools of solvent of micrometer size in a fashion that is reminiscent of, for example, crosslinked organic polymers or zeolites. In contrast with these, the dynamic nature of a supramolecular system could allow a higher mobility of solutes through the gel network.

Pd catalysts are of great interest in synthetic organic chemistry and many of them have been studied in homogeneous as well as in heterogeneous reaction media. We hypothesized that if the pyridine units in the organogel fibers are accessible to solute molecules a Pd(II) functional gel can be created by post-diffusion of palladium salts into a preformed organogel. This newly formed material could have a potential catalytic function.

In a typical experiment 0.01 mmol of $Pd(AcO)_2$ dissolved in 500 µL of toluene were poured on top of a gel made of 0.022 mmol of **1b** in 3 mL of toluene. After overnight diffusion, the over-floating solution was carefully removed and the gel was washed several times with toluene in 500 µL portions. At this point the gel showed an orange colour, whereas the originally over-floating brown solution of palladium acetate was colourless, indicating that most of the Pd(II) was retained inside the gel network. On the other hand, IR spectra of the toluene gels before and after loading of $Pd(AcO)_2$ did not show any significant difference in their C=O and NH stretching absorption bands, suggesting that no substantial changes in the H-bonding network were occurring (ESI†).

Transmission electron microscopy nicely confirmed the presence of Pd in the gel fibres. Fig. 3(A) shows the microscopic aspect (Pt shadowing) of **1b** toluene xerogel made by bundles of straight fibrils of less than 20 nm of diameter. When the xerogel obtained after Pd diffusion was analyzed with TEM similar nanoobjects were shown, however in this case they were visible without any kind of additional shadowing or staining, revealing the presence of Pd as a part of the fibres and not in the interstitial solvent (Fig. 3(B)).

After 10 days the gel remained orange and no Pd(0) particles were visible. The microscopic aspect was slightly different. Large rod-like aggregates made by the assembly of the primitive fibres could be observed without shadowing (Fig. 3(C)). The hairy aspect of the rod termini is remarkable showing probably points of assembly-disassembly and revealing the dynamic nature of the fibrous structures (Fig. 3(C), inset).

The pre-assembly of compound **1b** seems to be important for the stability of Pd(II) complexes since when compound **1b** and $Pd(AcO)_2$ were mixed before gelation no gel was formed and the suspension turned black after few minutes.

The thermal stability of the toluene gel of **1b** before and after $Pd(AcO)_2$ loading was studied. Vials containing both gels were inverted in a thermocontrolled bath and their gravitational flux was checked. In both cases, the gels were stable up to 100 °C. At this temperature, the gel without Pd showed a weaker texture than that with the metal.

A first test of the catalytic possibilities of this system was performed with a well-known reaction such as aerobic oxidation of benzyl alcohol (Scheme 1).[7] This reaction is catalysed by Pd(II) complexes, among them those with pyridine containing ligands, in organic solvents such as toluene and in the presence molecular oxygen or air. A Pd(II)-functionalised gel freshly prepared as

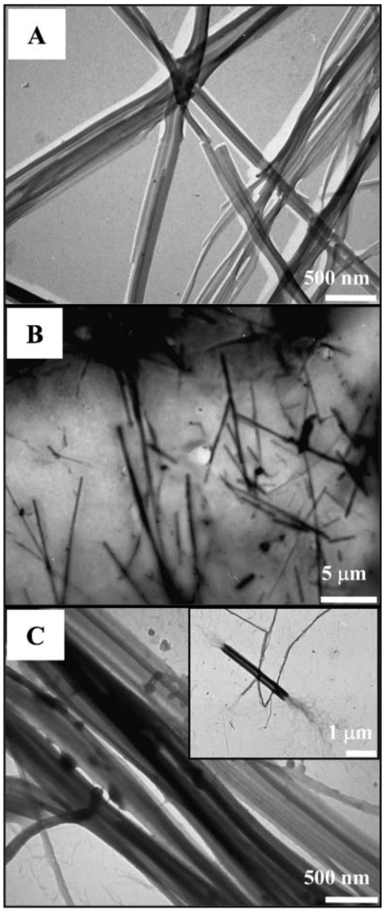
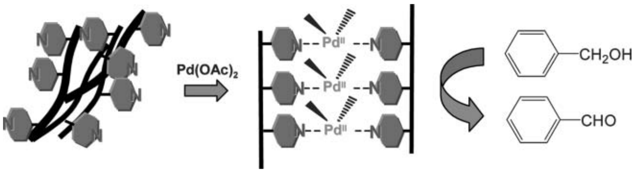


Fig. 3 TEM images of dried toluene organogels of compound **1b**: (A) without $Pd(AcO)_2$, (Pt-shadowing); (B) with $Pd(AcO)_2$ after 4 days and (C) after 10 days (no shadowing).



Scheme 1

described above, containing 0.01 mmol of Pd(II), was immersed in 3 mL of toluene containing 0.2 mmol of benzyl alcohol and heated at 65 °C under air atmosphere. The progress of the reaction was followed by NMR, and a maximum yield of *ca.* 50% could be obtained after 48 h that corresponds to a turnover number of 10 cycles.

It seems that the dynamic nature of the organogel produces after some cycles, catalytically inactive palladium complexes. Although the precipitation of Pd-black is the main mechanism of catalyst inactivation in this type of reaction, no Pd-black particles can be seen by optical microscopy. Probably, in this case another mechanistic explanation has to be found. Further research on the coordination environment of Pd in the fibres and its role in the catalysis is in progress.

In summary, we have prepared new nanostructured supramolecular catalytic materials by a pre-assembly and post-functionalisation strategy. In difference to some previously reported organometalogels, the metal is coordinated once the gel is formed.[8] Furthermore, we have shown that they offer interesting possibilities as catalysts. Interestingly, these soft materials could combine some the advantages of heterogeneous and homogeneous catalysis, as well as the special features of their supramolecular nature. Future work will be directed to their study in other important Pd-catalysed organic reactions such as C–C couplings.

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