# Ultrasound-promoted hydrogelation of terpyridine derivatives†

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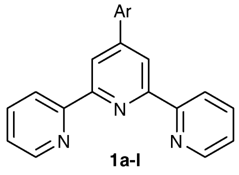
**Terpyridine derivatives proved to be versatile hydrogelators when subjected to ultrasound irradiation in their bis-protonated form. The chelating ability of the terpyridine ligands allows for the capture of metal cations resulting in stable gels with tunable emissive properties.**

Low molecular weight gelators (LMWGs), which form supramolecular gels, have attracted much attention over the last years[1] since they represent a new class of materials with various potential applications,[1,2] such as electronic devices,[3,4] smart materials,[2a] confined reaction media,[5] light harvesting systems,[4] and sensors.[6] In particular the study of hydrogelators is an expanding area of research[7] owing to their possible applications in bio-materials,[2a] drug delivery[8] and pollutant capture and removal.[9]

In addition, LMWGs caught the interest of scientists since their properties can be tuned by external stimuli,[10] such as temperature,[1,2b] light,[11] pH,[12] ultrasounds[13,14] and so on.

During our studies on the synthesis of transition metal complexes, we serendipitously found that compound **1a** (Scheme 1), when centrifuged in the presence of water, formed a yellow gel. Since the ability of an organic molecule to gel water is nowadays extremely interesting, we decided to investigate in detail this behaviour.

When a hot solution of **1a** in water was cooled to room temperature, a precipitate was formed. On the other hand, the **1a**-aqueous solution obtained by ultrasound irradiation (0.18 W cm$^{-2}$, 40 kHz) for 5 min resulted in clear gel after standing for 30 min at room temperature (Fig. 1). A solution is again obtained by simply subjecting the vial to ultrasounds for a few minutes. The reversibility of the gelation process was tested by performing six sonication cycles and a gel was again formed by allowing the solution to stand. The critical gel concentration (CGC) was established to be 6.0 × 10$^{-3}$ M and the soft material turned out to be transparent and highly resistant, being stable for 6 months at least.



**1a-l**

**1a** : Ar=4-COOH-$C_6H_4$ · 2HBr
**1b** : Ar=4-COOH-$C_6H_4$
**1c** : Ar=4-COOH-$C_6H_4$ · 2HCl
**1d** : Ar=4-COOH-$C_6H_4$ · $H_2SO_4$
**1e**: Ar=4-COONa-$C_6H_4$
**1f**: Ar=4-COOMe-$C_6H_4$
**1g**: Ar=4-COOMe-$C_6H_4$ · 2HBr
**1h**: Ar=4-CN-$C_6H_4$ · 2HBr
**1i**: Ar=4-OMe-$C_6H_4$ · 2HBr
**1j**: Ar=2,4,6-$Me_3$-$C_6H_2$ · 2HBr
**1k**: Ar=4-Br-$C_6H_4$ · 2HBr
**1l**: Ar=4-OH-$C_6H_4$ · 2HBr

**Scheme 1** Structures of the terpyridine derivatives **1a–l**.

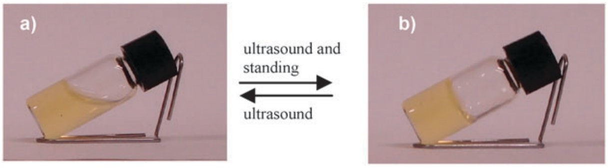


**Fig. 1** Reversible gelation of a solution (6.0 × 10$^{-3}$ M) of **1a** in water: (a) solution after ultrasound irradiation and (b) gel after 30 min standing at 20 °C.

Since the pioneer work of Naota and Koori in 2005,[14b] ultrasound promoted gelation has received much interest.[13,14] A gelation process initiated by ultrasounds could be nonsensical at first sight, sonication being generally used to disrupt intermolecular interactions. On the contrary, if ultrasound irradiation provides sufficient energy to induce cavitation of the solvent, a new set of specific interactions can dominate the system and ultimately triggers its gelation. For example H-bonds, π–π-stacking and Van der Waals forces were found to be activated by sonication.[2,13,14]

It is important to underline that the ultrasonic effect is always unpredictable, and it is only possible to speculate on the mechanism of the gel formation. In our case, probably the energy provided by the sonication is sufficient to dissolve the salts and to promote the formation of H-bonding between water and protonated terpyridine derivatives.

Various examples of gelators containing the 2,2′:6′,2″-terpyridine (terpy) moiety are present in the literature.[15] In particular, terpy-derivatives bearing a carboxylic group were reported to form gels in their anionic form.[16] On the contrary, we have found that the presence of the terpyridine in its bisprotonated form proved to be essential ( **1a**, Table 1). In fact in our experimental conditions the neutral substrate **1b** did not form any gel in water, neither under sonication nor under heating (Table 1). Thus, the gelation occurs in a range of pH varying from 2.2 to 4. At pH = 6 precipitation takes place, while at pH > 7.5 a completely soluble product was obtained.

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**Table 1** Ability of hydrogelation of compounds **1a–1l** varying the Ar–terpyridine substituent[a]

| Compound | State | CGC[b] (× $10^{-2}$ M) |
|---|---|---|
| **1a** | G(T)[c] | 0.6 |
| **1b** | I[d] | — |
| **1c** | G(T) | 1.0 |
| **1d** | I | — |
| **1e** | S[e] | — |
| **1f** | I | — |
| **1g** | I | — |
| **1h** | G (O)[f] | 1.9 |
| **1i** | G (O) | 2.0 |
| **1j** | PG[g] | — |
| **1k** | I | — |
| **1l** | I | — |

[a] 5 mg of each compound in 0.5 ml of water was subjected to ultrasound irradiation (0.18 W $cm^{-2}$, 40 kHz, 5 min) and the resulting state was checked after 1 h. [b] CGC = critical gel concentration. [c] G(T) = transparent gel. [d] I = insoluble. [e] S = soluble. [f] G(O) = opaque gel. [g] PG = partial gel.

**Table 2** Effect on the gelation after the addition of 1 equiv. of metal salt to the hydrogel of **1a**

| Entry | Metal salt | State (colour) |
|---|---|---|
| 1 | $EuCl_3 \cdot 6H_2O$ | G(O)[a] (yellow) |
| 2 | $CuCl_2 \cdot 6H_2O$ | G(O) (green) |
| 3 | $CeCl_3 \cdot 7H_2O$ | G(T)[b] (yellow) |
| 4 | $Ce(ClO_4)_3 \cdot nH_2O$ | P[c] |
| 5 | $PtCl_2 \cdot 2PhCN$ | G(O) (beige) |
| 6 | $K_2PtCl_4$ | P |
| 7 | $Zn(ClO_4)_2 \cdot 7H_2O$ | P |
| 8 | $IrCl_3 \cdot nH_2O$ | G(O) (dark red) |
| 9 | $PdCl_2$ | G(O) (orange) |
| 10 | $NiCl_2 \cdot 6H_2O$ | G(O) (yellow) |

[a] G(O) = opaque gel. [b] G(T) = transparent gel. [c] P = precipitate.

We have investigated how the gelation process was influenced by the presence of different counterions and substituents on the phenyl ring of the terpyridine unit. The results are summarized in Table 1. No notable changes to the gelation were noted when the counterion[10,15c,17] was changed from $Br^-$ to $Cl^-$ ( **1c**), while the gel formation did not occur in the presence of a doubly charged counterion such as the sulfate ( **1d**) obtaining a precipitate. Also, under basic conditions the sodium salt **1e** was not able to gel water since it resulted in an isotropic solution, both before and after ultrasound irradiation.

The conversion of the –COOH group into the corresponding methyl ester (compound **1f)** makes the substrate insoluble in water and no gelation was observed (Table 1). The same behaviour is displayed by the Br or OH substituted derivatives, compounds **1k** and **1l**, respectively.

When a CN or OMe group is present in the 4-position of the phenyl ring, compounds **1h** and **1i**, respectively, an opaque gel was formed, even if the CGC values are higher (1.9 × $10^{-2}$ M and 2.0 × $10^{-2}$ M, respectively) than for **1a** (0.6 × $10^{-2}$ M). Finally for compound **1j**, when Ar = mesityl, a transparent partial gel was observed (Table 1).

Therefore, the results summarized in Table 1 suggest that, in addition to the bisprotonated terpy-core, the presence of a highly polar substituent is essential for promoting the formation of gels.

Owing to the importance of including/incorporating metals in supramolecular gels,[10,15,18] and considering the ability of the terpyridine unit to coordinate metal ions, the effect of different cations on the gel was tested. Various metal salts (1 equivalent) were directly added to the formed hydrogel of **1a** (pH = 2.3). Then sonication of the resulting mixtures was performed in order to obtain a solution and the formation of a new gel was checked after 1 h.

As reported in Table 2 in entries 1–3 and 5, after the addition of $EuCl_3 \cdot 6H_2O$, $CuCl_2 \cdot 6H_2O$, $CeCl_3 \cdot 7H_2O$, and $PtCl_2(PhCN)_2$, very stable gels were obtained. On the contrary, insoluble precipitates were recovered after the treatment of the **1a**-based gel with metal salts containing different counterions,[10,17] such as $Ce(ClO_4)_3 \cdot nH_2O$ and $K_2PtCl_4$ (Table 2, entries 4 and 6). The same behaviour is observed when the gel is treated with $Zn(ClO_4)_2 \cdot 7H_2O$ (Table 2, entry 7). The addition of other cations, such as Ir(III), Pd(II) and Ni(II) (Table 2, entries 8–10) gave rise to the formation of less stable gels, as they collapsed within a few hours.

To investigate the morphology of the gels, dried samples were analyzed by scanning electron microscopy (SEM). In each case, well developed retiform structures were observed. As shown in the two representative examples in Fig. 2, the fibers are bundled and have a general length of several micrometres, with diameters approximately less than one micrometre.

Further images of the gels are reported in the ESI.† It can be observed that both hydrogels **1a** (Fig. 2a) and **1c** display a

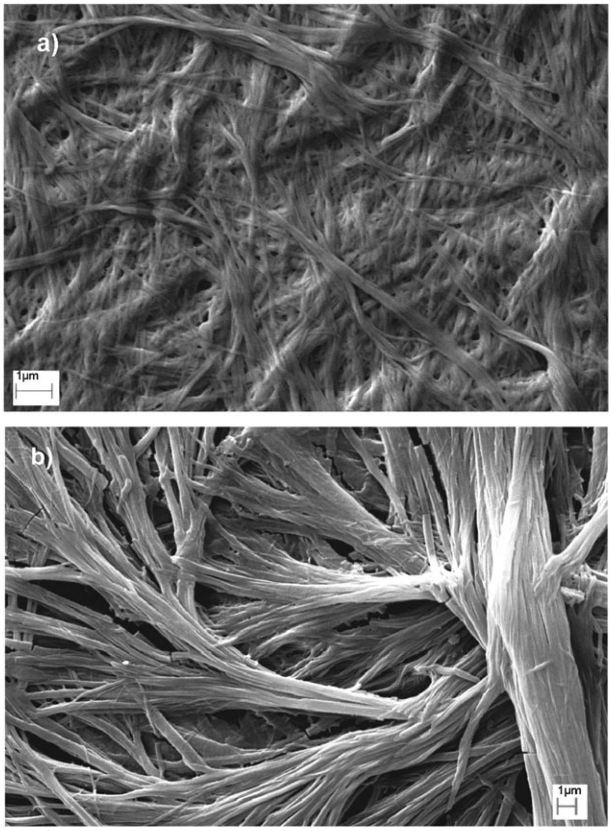

**Fig. 2** SEM image of a dried film of: (a) **1a**-hydrogel and (b) $CeCl_3 \cdot 7H_2O$– **1a**-hydrogel.

flattened fiber-like structure, with only a small size difference between the fiber morphologies of the gel forming counter-anions Br$^-$ and Cl$^-$. The presence of metal cations such as Eu(III) and Ce(III) (Fig. 2b) seems to influence the gel structure towards the formation of branched fibers, whereas upon addition of Pt(II) and Cu(II) salts no significant changes are observed in the morphology of the corresponding gels.

The stable **1a**-gels containing the metal salts were characterized by UV/Vis absorption and emission spectroscopy, performed on xerogel solid substrates. For this purpose the gel samples were drop casted onto a microscope slide and let dry before measuring.

Even though the photophysical characterization is not complete and it will require further investigations, the preliminary measurements indicate that in most cases the metal ions interact with the ligand **1a**. The UV/Vis absorption spectra are very similar for all the gels and the presence of a metal seemed to affect only slightly the absorption of the **1a**-xerogel, as the recorded spectra of the metal-containing films resemble the absorption profile of the metal-free film (Fig. 3). The latter one displays a band in the UV region (up to 380 nm) due to the $\pi^* \leftarrow \pi$ transition centered on the terpyridine moiety. This band broadens for the metal-containing films. As shown in Fig. 3 (see also ESI† for the corresponding diluted solutions), the incorporation of copper(II) broadens the band in the UV portion of the spectrum, while the other metal-containing films display new features at long wavelengths. These spectral changes in the light absorption are likely due to any interaction occurring between the metals and **1a** within the supramolecular gel network.

The emission spectrum of the gel containing **1a** shows two bands centered at 430 and 530 nm. The high energy emission is due to the non aggregate terpyridine derivative and is attributed to $\pi^* \leftarrow \pi$ transitions.[19] The excited state lifetime is also in good agreement with such assignment. The lower energy band is due to the aggregate form of **1a** in the gel.

The emission features of the gels depend on the nature of the metal (Fig. 4).[20] For example, in the case of the **1a**-gel containing 1 equivalent of $EuCl_3 \cdot 6H_2O$, exciting at 350 nm, the emission of **1a**, in the aggregate form, at 530 nm is completely quenched in favour of the characteristic Eu(III)-based radiative processes. The detected red luminescence upon excitation of **1a** within the soft material along with a lifetime value of 159.64 μs indicates that a sensitization of the lanthanide ion takes place (antenna effect).[21]

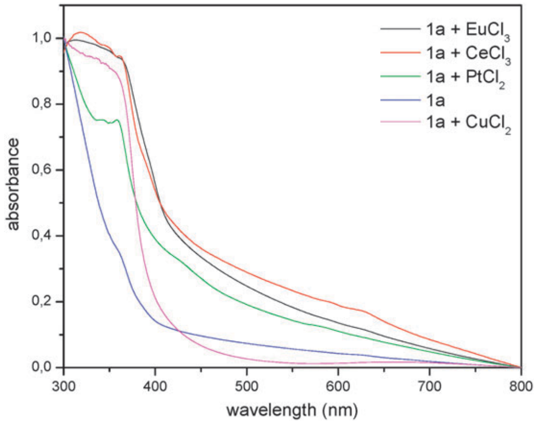

**Fig. 3** Normalized UV/vis absorption spectra of films of **1a**-hydrogels containing different metal salts.

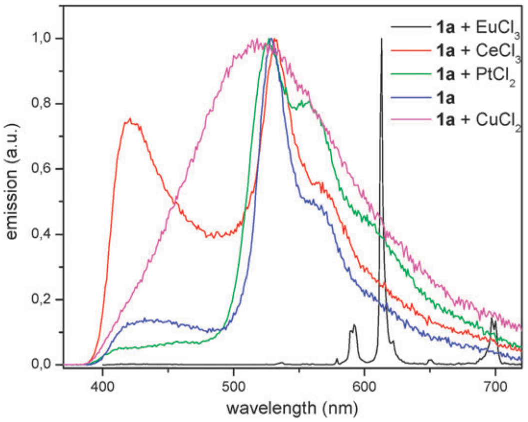

**Fig. 4** Normalized emission spectra of films of **1a**-hydrogels containing different metal salts ($\lambda_{exc}$ = 350 nm).

On the other hand, the gel emission spectrum is slightly modified by the presence of $CeCl_3 \cdot 7H_2O$. In particular, even though the emission band of the ligand at approximately 440 nm increased in intensity in relation to the band at 530 nm, the luminescence lifetimes do not change significantly when compared to those of **1a** (see also Table 3).

An even less pronounced effect in the emission spectrum is observed in the case of the gel obtained by doping with $PtCl_2(PhCN)_2$, whose emission band recalls the one of **1a**, showing the same vibronic progression (within the range 100–1200 cm$^{-1}$). However, the elongation of the lifetime to the microsecond scale which is observed in the presence of the metal suggests the probable triplet nature of the emitting excited state (Table 3).

Conversely, the gel containing the $CuCl_2 \cdot 6H_2O$ salt shows a structureless broad emission band, ranging from 400 to 700 nm, and a decay very similar to that of **1a**.

In conclusion, we reported the formation of stable hydrogels with small organic molecules, such as terpyridine derivatives. The gelation occurs only under acidic conditions and in the presence of a highly polarized substituent. The ability of **1a**-hydrogel to coordinate metal cations was tested and various examples are reported in which the gelation still occurs.

**Table 3** Emission lifetimes of the studied hydrogels, at 440 and 530 nm unless otherwise mentioned, recorded on films

| | Lifetimes | |
|---|---|---|
| Hydrogel | $\lambda_{em}$ = 440 nm | $\lambda_{em}$ = 530 nm |
| **1a** | 0.92 ns (60%)<br>6.63 ns (40%) | 0.87 ns (55%)<br>5.76 ns (45%) |
| **1a** + $CeCl_3$ | 0.88 ns (43%)<br>2.27 ns (57%) | 0.83 ns (40%)<br>2.96 ns (60%) |
| **1a** + $PtCl_2$ | 1.50 μs (29%)<br>7.44 μs (71%) | 1.77 μs (16%)<br>8.18 μs (84%) |
| **1a** + $CuCl_2$ | 1.34 ns (42%)<br>5.35 ns (58%) | 0.98 ns (31%)<br>4.80 ns (69%) |
| **1a** + $EuCl_3$ | 159.64 μs[a] | — |

[a] Detected at $\lambda_{em}$ = 612 nm.

Studies are in progress in our laboratories in order to optimize the gelation process and, in particular, to further understand whether the photophysical behavior of various metal complexes can be influenced by the formation of corresponding terpyridine-based gels.

## Experimental

### General procedure for the synthesis of terpyridine derivatives 1a–l

Compounds **1a**[22] and **1b**[23] were synthesized according to previously reported procedures. Compound **1f** was obtained by treating **1b** with $TMSCH_2N_2$. The corresponding neutral forms of compounds **1h–l** were synthesized starting from the suitable aromatic aldehydes, according to a previously reported procedure.[24] Compounds **1c–e** and **1g–l** were obtained by treatment of the neutral forms with an excess of the desired concentrated acid (HBr, HCl or $H_2SO_4$) or NaOH. Detailed experimental descriptions and NMR analysis of the compounds are reported in ESI.†

### General procedure for the 1a-gel preparation

In a 5 ml vial, 1.3 ml of water was added to 4 mg ($7.8 \times 10^{-3}$ mmol) of **1a**. The suspension was put in the ultrasound bath (Branson 2200, 0.18 W $cm^{-2}$, 40 kHz) for 5 min. A transparent solution was obtained. After 30 min standing at room temperature the formation of the gel occurred.

### General procedure for the preparation of 1a-gels containing a metal salt

After the preparation of a **1a**-hydrogel sample, the desired metal salt (1 equiv.) was added. The mixture was submitted to ultrasound irradiation (Branson 2200, 0.18 W $cm^{-2}$, 40 kHz) for 5 min. The resulting solution was left at room temperature for at least 1 h and then the formation of the gel was checked.

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