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# Journal Name

## ARTICLE

## Metallogel Formation in Aqueous DMSO by Perfluoroalkyl Decorated Terpyridine Ligands

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Terpyridine based ligands **1** and **2**, decorated with a $C_8F_{17}$ perfluorinated tag are able to form stable thermoreversible gels in the presence of several d-block metal chloride salts. The gel systems obtained have been characterized by NMR, X-ray diffraction, electron microscopies and $T_{gel}$ experiments in order to get insights on the observed different behaviour of the two similar ligands, also in terms of the effect of additional common anionic species.

## Introduction

Over the last few decades, research on gel systems based on low molecular weight gelators (LMWGs) has flourished and has nowadays become an active area of supramolecular chemistry.[1] Soft materials based on gel systems have been progressively used in a wider and wider array of applications ranging from medicine,[2] catalysis,[3] sensing,[4] and for the formation of hybrid materials.[5] Especially interesting are metallogel systems,[1,4b,6-7] where metal ions are incorporated into the soft material, thus providing a way to integrate metal specific properties into gel material. The advantages of LMWGs over their polymeric counterparts are usually constituted by a fast and enhanced responsiveness towards physical and chemical[4,7] stimuli and by the possibility to control and modulate gel properties through direct chemical modification at the molecular level. These features derive from the fact that supramolecular gels are formed by small molecules which assemble into fibrillar networks driven by weak non-covalent interactions. In this context, perfluorinated compounds (PFC) have interesting properties, being typically hydrophobic and lipophobic at the same time, and their self-assembly behavior have been extensively studied in order to assess and evaluate the peculiar features of the so called *fluorous interactions*.[8] Recently, gelator molecules comprised of perfluorinated moieties have appeared.[9] Starting from previous knowledge on metallogel systems based on the terpyridine unit,[7] we were interested in studying the effect on gelation properties of combining such classic moiety[10] with a



**Scheme 1.** Chemical formulae of ligands **1** and **2**.
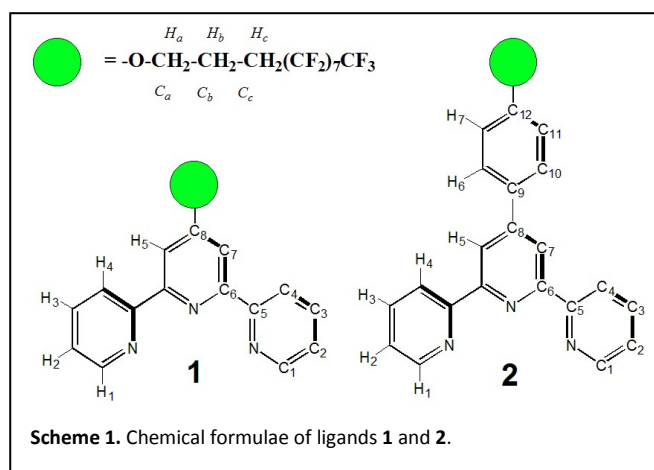
perfluorinated pendant. Aside from the interest of achieving gels in fluorous solvents,[11] *fluorous interactions* can also be employed for gelation of conventional solvents, often resulting in improved performances over their hydrocarbon counterparts.[9a]

Herein, we report on a comprehensive study of the gelation capabilities of two novel terpyridine ligands, **1** and **2**, decorated with a $C_8F_{17}$ perfluorinated tail (Scheme 1) in the presence of divalent d-block metal salts (Fe,$^{2+}$ Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$ and Hg$^{2+}$) in aqueous DMSO. Depending on the metal used, ligands **1** and **2** can form stable, thermo-reversible gels, featuring extended networks of fibrils tens of micrometers long, visible by SEM and TEM microscopy. Furthermore, we have investigated several aspects which clearly influence the gelation process of **1** and **2** up to its complete inhibition. They are: i) metal identity, ii) solvent mixture composition and iii) counteranion effect. Interestingly, the two ligands which differ only for the additional phenyl ring in **2** showed a markedly different behaviour. For example, only ligand **1** is capable to form gels with $Zn^{2+}$ and $Hg^{2+}$, while only ligand **2** can form gels with $Fe^{2+}$, under the experimental

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conditions tested. This highlights again the need of more comprehensive and systematic studies in order to reach a reliable understanding of the factors which either grant, or inhibit, gelation within LMWG systems.

## Results and discussion

Ligands **1** and **2** were synthesized by reacting 1H,1H,2H,2H,3H,3H-Perfluoroundecyl iodide with 2,2′:6′,2′′-terpyridin-4′-ol or 4′-(4-hydroxyphenyl)-2,2′:6′,2′′-terpyridine,

**Table 1.** Gelation studies for ligands **1** and **2** in the presence of 1 equivalent of different Metal (II) Chloride salts in various DMSO: water solvent mixtures (*mcg* in parenthesis expresses as % wt) [S= solution; P= precipitate; PG= partial gel; G= gel].

| | FeCl$_2$ | CoCl$_2$ | NiCl$_2$ | CuCl$_2$ | ZnCl$_2$ | CdCl$_2$ | HgCl$_2$ |
|---|---|---|---|---|---|---|---|
| | | | DMSO:water 9:1 | | | | |
| **1** | P | S | S | P | G (0.3%) | P | G (0.3%) |
| **2** | G (0.3%) | S | S | P | P | P | P |
| | | | DMSO:water 8:2 | | | | |
| **1** | P | G (0.4%) | S | P | G (0.2%) | P | G (0.2%) |
| **2** | G (0.2%) | G (0.3%) | PG | P | P | P | P |
| | | | DMSO:water 7:3 | | | | |
| **1** | P | G (0.4%) | G (0.3%) | P | G (0.2%) | P | G (0.2%) |
| **2** | G (0.2%) | G (0.3%) | G (0.3%) | P | P | P | P |

respectively, under basic conditions in acetone.[12] In a typical gelation experiment, the appropriate amount of solid ligand is placed in a test tube (length 45 mm, d 15 mm) and dissolved in DMSO upon heating, whereupon a water solution of the corresponding the metal salt is added to reach a final volume of 1mL. The mixture is then heated to obtain a clear solution which, as it cooled down to room temperature, would remain as such, or lead to a precipitate, or afford a translucent gel. In all cases presented in Table 1, a metal to ligand ratio equal to 1 was employed. The first comment concerns the tested solvents. No gels were obtained by using DMSO only (or other common solvents such as MeOH, MeCN and DMF and their aqueous mixtures), however, in 9:1 DMSO:water mixture, ligand **1** forms gel in the presence of ZnCl$_2$ and HgCl$_2$, while ligand **2** forms gel with FeCl$_2$ (Figure 1a). Minimum gelation concentrations (*mgc*) are around 0.3 % wt in all cases (Table 1). Interestingly, we were not able to obtain gels with ligand **1** and FeCl$_2$, nor gels with ligand **2** and ZnCl$_2$ or HgCl$_2$. The increase of
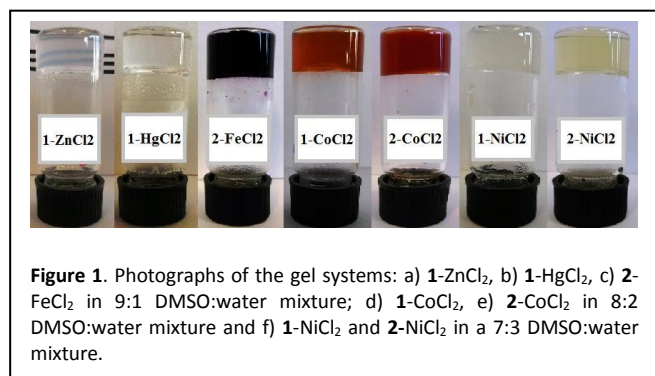


**Figure 1**. Photographs of the gel systems: a) **1**-ZnCl$_2$, b) **1**-HgCl$_2$, c) **2**-FeCl$_2$ in 9:1 DMSO:water mixture; d) **1**-CoCl$_2$, e) **2**-CoCl$_2$ in 8:2 DMSO:water mixture and f) **1**-NiCl$_2$ and **2**-NiCl$_2$ in a 7:3 DMSO:water mixture.

water content up to 20% and 30 % allowed to obtain gels with CoCl$_2$ and NiCl$_2$ with both ligands. Thus, the DMSO:water ratio is a crucial parameter that must be taken into account, in line with other studies previously published.[6b,13] Considering the effect exerted by water onto the gelation outcome and the fact that at lower water content both Co$^{2+}$ and Ni$^{2+}$ in the presence of the ligands afforded clear solutions, it seems that water renders the ligand/salt mixture less solvated and more prone to aggregation. Also, under no tested conditions we
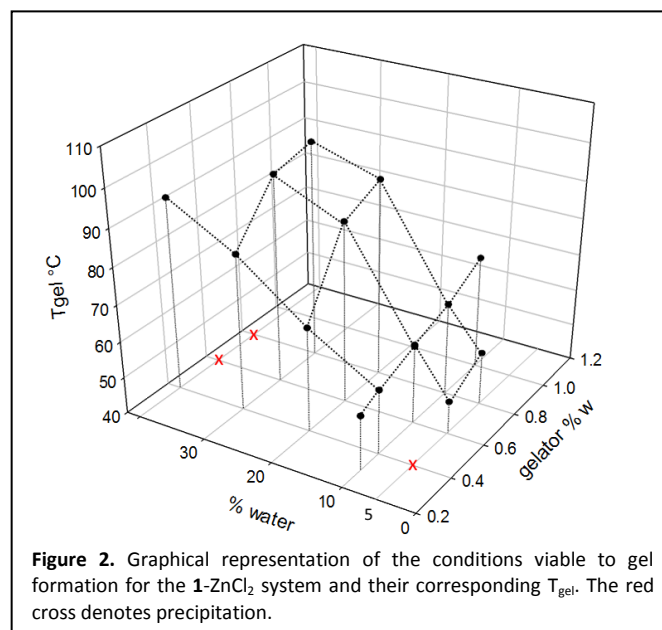


**Figure 2.** Graphical representation of the conditions viable to gel formation for the **1**-ZnCl$_2$ system and their corresponding T$_{gel}$. The red cross denotes precipitation.

were able to obtain gel with CuCl$_2$ and CdCl$_2$.

As all the gels were thermo-reversible, a series of experiments were carried out in order to determine T$_{gel}$ with the inverted test tube method. The tubes were sealed to prevent solvent evaporation. All gels present a T$_{gel}$ temperature which is directly proportional to the gelator content, in particular, increasing it from 0.4 to 0.8 % wt leads to a T$_{gel}$ increase in the range between 5 and 16 °C, the latter increment occurring in the **1**-NiCl$_2$ case (7:3 DMSO:water). In general, it seems that higher water content leads to an improved stability. In order to check this hypothesis, the **1**-ZnCl$_2$ and **2**-FeCl$_2$ gel systems were studied in more details and the water content was taken as well into consideration for the T$_{gel}$ measurements (Figure 2). The data clearly show that increasing both the gelator and the water content (up to 30%) leads to a plateau of stability, which however abruptly collapses when 40% water content is reached for the more concentrated samples. A similar behaviour was found for the **2**-FeCl$_2$ gel systems where, however, such clear plateau of stability is not observed (see Fig. S1, ESI).

Additional information on these gel systems were also acquired by electron microscopy on xerogel samples, giving insights on the gels morphology. All samples presented abundant fibrillary networks (Figure 3 and Fig. S3 ESI), however, distinct structural differences were observed depending on the given ligand/metal combination. Thinner fibres and higher aspect ratios were observed for samples

made with **2** compared to those with **1**. The typical gel fibers were cylindrical with diameter varying in the 50-100 nm range, while Zn(II) produced much larger tape-like structures. A last comment is given for the **1**-HgCl$_2$ system, which has a particular behaviour, in that, despite its initial stability, we have observed that it completely loses its gel character to yield a micro-crystalline material in few hours time. This prevented the preparation of the sample for electron microscopy analysis which showed no fibers, rather several microcrystals by SEM
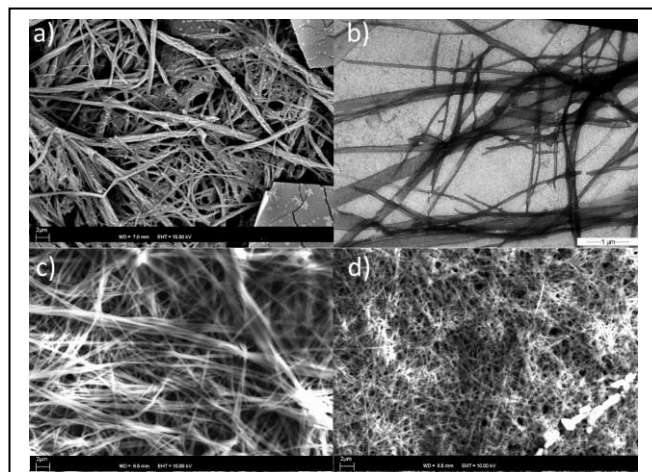


**Figure 3.** SEM and TEM images of metallogels with ligand **1**: a) SEM image of **1**-ZnCl$_2$ in 9:1 DMSO:water mixture; b) TEM image of **1**-ZnCl$_2$ in 9:1 DMSO:water mixture; c) SEM image of **1**-CoCl$_2$ in 8:2 DMSO:water mixture; d) SEM image of **1**-NiCl$_2$ in 7:3 DMSO:water mixture

(Figure 4S, ESI).
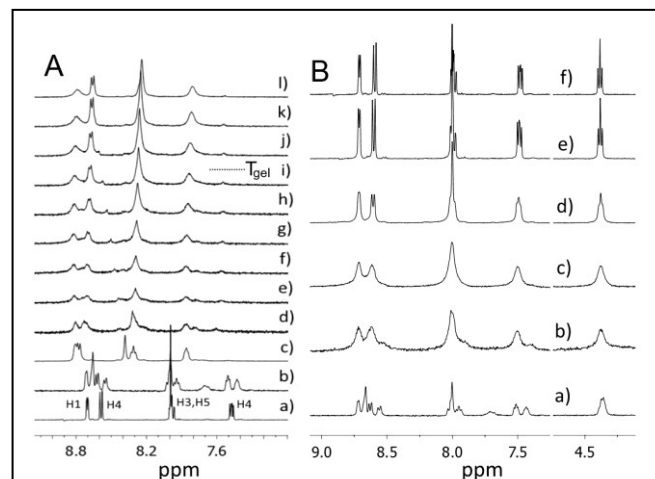
As said, the data reported so far are related to samples



**Figure 4.** <u>Panel A</u>: $^1$H-NMR spectra of a)**1** at 80°C; b) **1** at 25°C and c) after addition of 1 eq. of ZnCl$_2$; d-l) temperature dependent spectra of 1-ZnCl$_2$ gel system (from 35 °C to 75°C, 5°C step increase). <u>Panel B</u>: Temperature dependent $^1$H-NMR spectra of ligand **1** (conc. = 1.4 x 10$^{-2}$ M) in DMSO-d6 from 25° C (a) to 75°C (f) (10 °C step increase).

where a metal to ligand ratio was maintained equal to 1:1. In order to ascertain that the actual gelator unit is a 1:1 metal

complex of **1** and **2**, as strongly suggested by previous works on gel system derived from terpyridine metal complexes,[7] we have also tested the **1**-ZnCl$_2$ system using a 1:2 and a 2:1 metal to ligand ratios at 0.4% wt of ligand (which equals the *mgc* for a 1:1 sample). No gel was observed with the 1:2 ratio sample, while gel formed with 2:1 ratio. Compound **1** and **2** are strongly coordinating ligands, and thus these data lead to the straightforward conclusion of a gelating unit made of a 1:1 complex. As the sub-stoichiometric metal quantity does not allow for gelation, it means that not enough complex is formed to warrant reaching its *mgc*. We would like to point out that this behaviour can be so easily rationalized due to the high stability of terpyridine metal complexes, while more careful analyses are needed when dealing with less efficiently coordinating ligands.[6b]

Gel systems **1**-ZnCl$_2$ and **2**-FeCl$_2$ were also studied by temperature dependent $^1$H-NMR. Figure 4 (Panel A) displays the comparison between the spectra of ligand **1** in DMSO-d$_6$ at 80°C (a) and at 25°C (b), the spectrum of **1** after the addition of 1 equivalent of ZnCl$_2$ (under the *mgc*) at 25°C (c) and the spectra of the **1**-ZnCl$_2$ gel system at various temperatures from 25°C to 75°C (from d to l). First of all, ligand **1** shows significant tendency for aggregation as several additional peaks appear in its spectrum at 25°C (Fig 4, panel A, spectrum b) if compared with that at 80°C (Fig 4, panel A, spectrum a) (vide infra). More so, the addition of Zn$^{2+}$ metal ions shifts all peaks downfield in
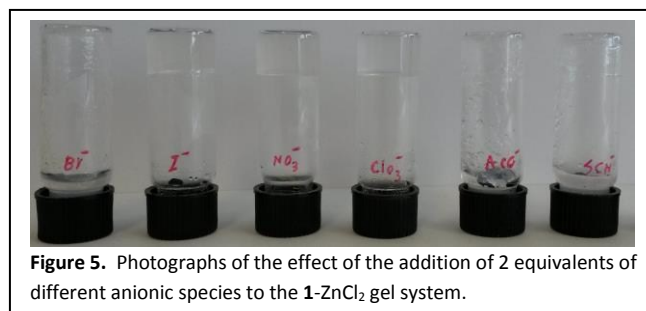


**Figure 5.** Photographs of the effect of the addition of 2 equivalents of different anionic species to the **1**-ZnCl$_2$ gel system.

the aromatic region, as expected due to metal coordination (Fig 4, panel A, spectrum c). Once the gel is formed (Fig 4, panel A, spectrum d), evident broadening and S/N decrease are observed. Such spectral appearance persists also after T$_{gel}$ (57.8 °C in this case) and that indicates a strong aggregation tendency.

Given the ample evidence of the important role of anions in gelation processes,[1g,4a,6b,14] we tested the effect of the addition of 2 equivalents of other common anions, such as Br$^-$, I$^-$, NO$_3^-$, AcO$^-$, SCN$^-$ and ClO$_3^-$ (added as sodium salts) to 4%wt 7:2 DMSO-water gel samples (see Table 2).

Figure 5 shows the outcome of such test experiments for the **1**-ZnCl$_2$ system, where the presence of Br$^-$, AcO$^-$ and SCN$^-$ anions clearly leads to complete loss of gelation attitude, while I$^-$, NO$_3^-$ and ClO$_3^-$ do not visibly alter the system. By comparison with the other gels made with ligand **1**, we observed that NO$_3^-$ and ClO$_3^-$ are the ions which do influence less the system, while SCN$^-$ is the anion which most frequently leads to gel disruption (3 out of 4 of the cases). Most interestingly, in the case of ligand **2**, it is the ClO$_3^-$ anion which induces gel collapse

(Table 2, Figs. S5 and S6). The striking difference with what observed with ligand **1** could be hardly explained if not by recalling that gelation is generated by a subtle balance between the system solvation and crystallization propensity, and small variations in the ligand structure can be significant.

| Table 2. Effect of the addition of different anionic specie to various L-MCl$_2$ gel system (L = **1**, **2**; M = Zn(II), Hg(II), Fe(II), Co(II), Ni(II)) | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | Br$^-$ | I$^-$ | NO$_3$$^-$ | AcO$^-$ | SCN$^-$ | ClO$_3$$^-$ |
| **1** | Zn | P | G | G | P | P | G |
| | Hg | P | P | G | G | P | G |
| | Co | G | G | G | G | G | G |
| | Ni | G | G | G | G | P | G |
| | | | | | | | |
| **2** | Fe | G | P | G | G | G | P |
| | Co | G | P | G | G | P | P |
| | Ni | P | P | G | G | P | P |
| | | | | | | | |
| In the case of the NiCl$_2$ gel, ratio of solvent mixture is DMSO:water 7:3, while in all other cases it is 8:2. P = precipitate, G = gel; | | | | | | | |

Data reported on Table 2 also show that **1**-CoCl$_2$ is the most stable system under the tested conditions as it can withstand all kind of anion interference, among those tested (Fig. S7, ESI). This is also confirmed by the following experiment, aimed to test the effect of additional Cl$^-$ anions to the gel system, where increasing amounts of Cl$^-$ anion (as TBA salt) were added to the gel systems (Fig. 6).[15]

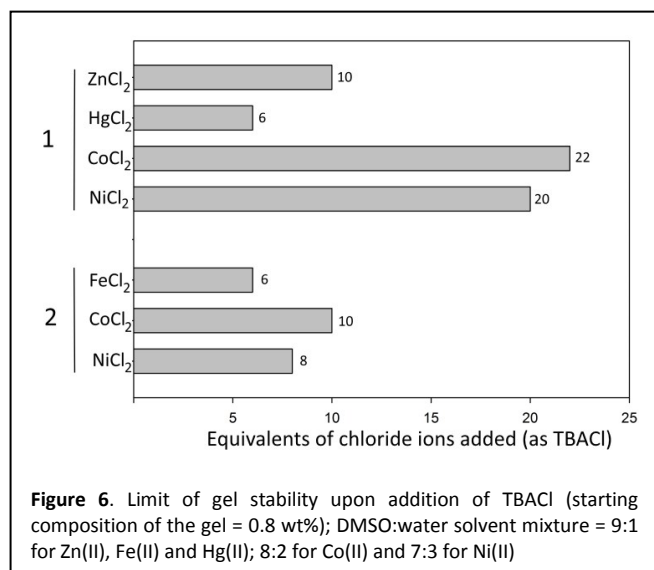For the **1**-ZnCl$_2$ gel system, the presence of additional 10



**Figure 6**. Limit of gel stability upon addition of TBACl (starting composition of the gel = 0.8 wt%); DMSO:water solvent mixture = 9:1 for Zn(II), Fe(II) and Hg(II); 8:2 for Co(II) and 7:3 for Ni(II)

equivalents of Cl$^-$ anion prevents the gel formation. Less stable than that are the **1**-HgCl$_2$ and **2**-FeCl$_2$ systems whose gelation is inhibited at 6 equivalents. On the other hand, **1**-NiCl$_2$ and, in particular, **1**-CoCl$_2$ show enhanced stability as their gels can be still obtained in the presence of additional 19 and 21 equivalents of Cl$^-$ ions, respectively. Surely, the higher water content in these two gel systems has a role in the observed stability, however, if these data are collectively analysed, they point to an intrinsic higher stability of **1**-CoCl$_2$, if compared to

the other gel systems. Also, it can be reasonably stated that ligand **1** forms more stable gels than ligand **2** (see Table 2 and Fig. 6). This could be due to a higher tendency of **1** to aggregate, as mentioned above. Temperature dependent $^1$H-NMR spectra of **1** in DMSO-d$_6$ are reported on Figure 4 (Panel B).

Indeed, the spectrum recorded at 25 °C (Fig. 4, panel B, spectrum a) clearly shows additional peaks which can be attributed to aggregated species. The temperature increase initially leads to peak broadening (Fig. 4, panel B, spectra b-c) and then to the non-aggregated species (Fig. 4, panel B,
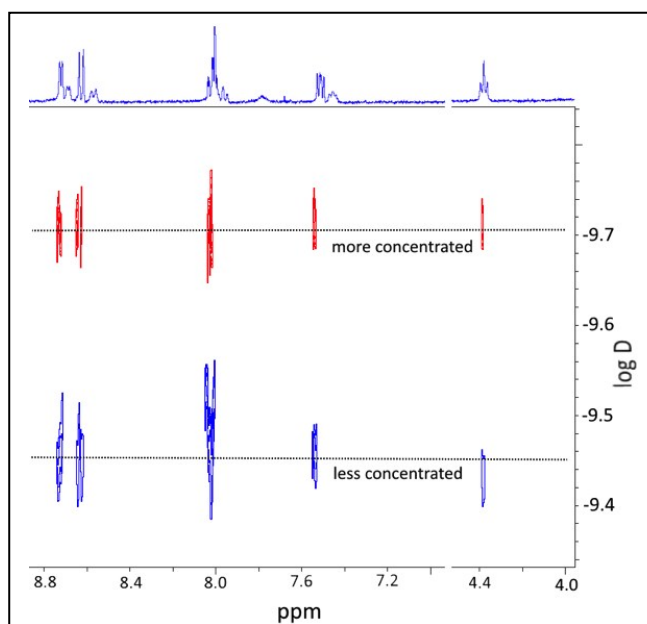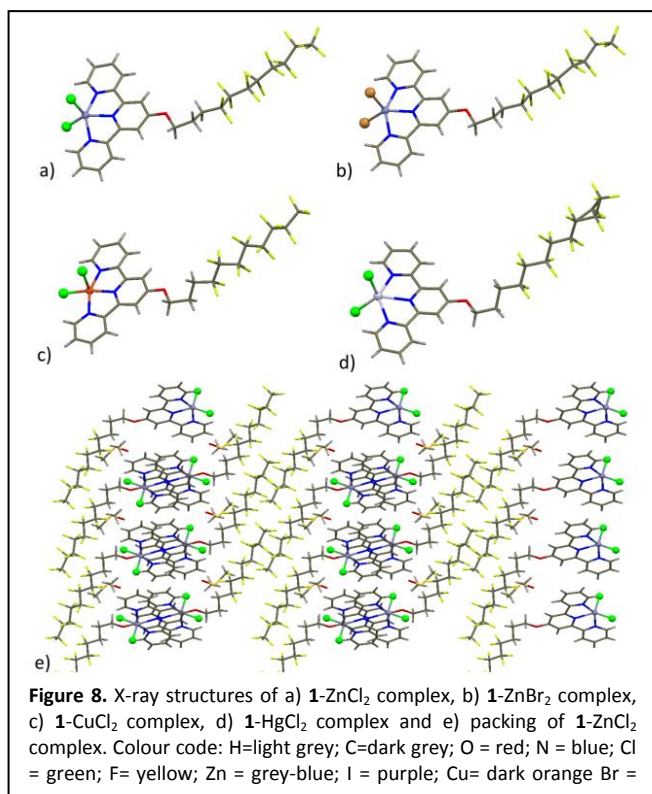


**Figure 7**. $^1$H-DOSY plot of **1** at 4.7 x 10$^{-3}$ M and 1.4 x 10$^{-2}$ M concentration. Top projection shows the more concentrated sample (pulse sequence: ledbpgp2s; T = 302 K; ns = 16; TD(f1)=16). Processed with TopSpin software.

spectra e – f), featuring well shaped and narrow peaks. Also ligand **2** shows this behaviour, but to a lesser extent (Figure S9 ESI). The high aggregation tendency of **1** is also confirmed by concentration dependent experiments (Figure S10 ESI) and by DOSY (Figure 7). The latter technique shows a fast equilibrium between free and aggregated ligand species, with a progressive reduction of the diffusion coefficient upon concentration increase (-log D from 9.47 to 9.71). An intrinsic higher tendency for aggregation for **1** could be the reason for the generally more stable gels observed with this ligand. Same conclusions could be drawn by concentration dependent $^{19}$F-NMR experiments, although the observed shifts are small (see Fig. S11 in ESI).

We were also able to obtain single crystals of good quality suitable for X-ray diffraction structural determination for complexes **1**-ZnCl$_2$ (and **1**-ZnBr$_2$), **1**-HgCl$_2$ and also for **1**-CuCl$_2$.[16] As a reminder, the **1**-ZnCl$_2$ and **1**-HgCl$_2$ systems form gel, the addition to **1**-ZnCl$_2$ of 2 equivalents of Br$^-$ leads to a precipitate, while no gel is formed with CuCl$_2$, so that if any structural elements were responsible for the behaviour observed, the analysis of the X-ray determined structures of

the above complexes should be revealing. In fact, as shown in Figure 8, the solid state characterization of both gelating (**1**-$ZnCl_2$ and **1**-$HgCl_2$) and non-gelating systems (**1**-$ZnBr_2$ and **1**-



**Figure 8.** X-ray structures of a) **1**-$ZnCl_2$ complex, b) **1**-$ZnBr_2$ complex, c) **1**-$CuCl_2$ complex, d) **1**-$HgCl_2$ complex and e) packing of **1**-$ZnCl_2$ complex. Colour code: H=light grey; C=dark grey; O = red; N = blue; Cl = green; F= yellow; Zn = grey-blue; I = purple; Cu= dark orange Br =

$CuCl_2$) gives very similar results in terms of molecular complex and packing organization as well. All four complexes, regardless of the metal identity, display pentacoordination which can be viewed as a distorted trigonal bipyramidal type.[17] That is exerted by the classical NNN chelation from the terpyridine moiety and by two additional halide ions which complete a $N_3X_2$ coordination sphere. As far as the packing of the fluorous chains is concerned, *type I* C-F···F-C inter-chains geometries are mainly observed within the lattice, with C-F···F angles in the ca. 120 – 155 deg range.[18]

Finally, the X-ray powder diffraction pattern of **1**-$ZnCl_2$ xerogel sample was compared with the simulated pattern obtained from the single crystal X-ray structure of the $ZnCl_2$ complex with ligand **1**. Indeed, this test could be very telling about the presence of similar packing patterns between the gel and the solid states.[19] As probably expected, considering the strong similarity among the solid state structures found for gelating and non-gelating systems, a modest match is found (see Fig. S13 in ESI), also due to the presence of some amount of amorphous phase. As observed in other cases,[19] this could be also due to the formation of other phases during the preparation of the xerogel sample.

## Conclusions

In conclusion, we have developed novel ligands **1** and **2**, that feature a terpyridine moiety decorated with a perfluorinated $C_8F_{17}$ tag, and tested their gelating properties in the presence

of a series of d-block metal ions. Thermo-reversible LMWG metallo-gel systems were obtained in aqueous DMSO (up to 30% v/v of water) in the case of ligand **1** with Co(II), Ni(II), Zn(II) and Hg(II), and ligand **2** with Fe(II), Co(II) and Ni(II), depending on the DMSO:water ratio employed. These gel systems were studied with a combination of electron microscopies, X-ray diffraction, $T_{gel}$ experiments and NMR spectroscopy, where not only the metal identity but also the counteranion effect and the solvent composition were taken into account. Despite the similar structure of the two ligands, **1** was not able to form gels with Fe(II) ions, while **2** was not able to form gels with either Zn(II) and Hg(II), indicating an intrinsic different selectivity pattern for the two ligands. Also, based on $T_{gel}$ experiments and its tolerance to larger amount and variety of anionic species, ligand **1** can be considered as being forming more stable gel systems. This can also be related to a more pronounced tendency to aggregate.

Given the absence of major structural characteristics that could explain the different response of **1** and **2** to metal ions in terms of gelation, the systems reported here illustrate again how subtle structural differences could lead to significantly different outcomes.

## Experimental methods

**Synthesis:** All chemicals were purchased from chemical source and used without purification. DMSO for the gelation test was ACS reagent (≥99.9%). The ligands **1** and **2** were synthesized by adopting modified literature procedure.[20] 4′-(4-hydroxyphenyl)-2,2′:6′,2′′-terpyridine was synthesized by adopting literature procedure.[21] Assignment for $^1H$- and $^{13}C$-NMR signals was carried out by 2D COSY and HMQC techniques (see ESI).

**1:** A mixture of 2,6-Bis(2-pyridyl)-4(1H)-pyridone (125 mg, 0.5 mmol), $K_2CO_3$ (207 mg, 1.5 mmol), a catalytic amount of 18-crown-6 in 30 mL of acetone was stirred at room temperature for 1h. After that, $^1H,^1H,^2H,^2H,^3H,^3H$-Perfluoroundecyl iodide (295 mg, 0.502 mmol) in 2 mL of acetone was added dropwise to the above reaction mixture at room temperature. Then, the reaction mixture was kept refluxing for 2 days. 20mL of water was added to the above reaction mixture, and extracted with $CH_2Cl_2$ (3×20 mL and dried under vacuum. Yield: 342 mg (96.5 %); $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.68 (ddd, $J_{ortho}$ = 4.8 Hz, $J_{meta}$ = 1.8 Hz, $J_{para}$ = 1.0 Hz, **$H_1$**, 2H), 8.64 (dt, $J_{ortho}$ 8.0 Hz, $J_{meta}$ = 1.0 Hz, $J_{para}$ = 1.0 Hz, **$H_4$**, 2H), 8.02 (s, **$H_5$**, 2H), 7.87 (td, $J_{ortho}$ = 8.0, $J_{ortho}$ = 8.0 Hz, $J_{meta}$ = 1.8 Hz, **$H_3$**, 2H), 7.35 (ddd, Jortho = 8.0 Hz, Jorhto= 4.8 Hz, $J_{meta}$ = 1.8 Hz, **$H_2$**, 2H), 4.32 (t, J=4.9 Hz, **$Ha$**, 2H), 2.43-2.30 (m, **$Hc$**, 2H), 2.22-2.15 (m, **$Hb$**, 2H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 166.76 (**$C8$**), 157.16, 155.88, 149.02 (**$C1$**), 136.83 (**$C3$**), 123.91 (**$C2$**), 121.34 (**$C4$**), 107.20 (**$C7$**), 66.49 (**$Ca$**), 29.70, 27.90 (t, J = 23 Hz), 20.45 (t = 3.8 Hz); $^{19}F$ NMR (282 MHz, $CDCl_3$) δ δ -81.13, -114.61, -121.99, -122.21, -123.02, -123.72, -126.41.; ESI-TOF-MS Calcd. for $[M+H]^+$ $(C_{26}H_{17}F_{17}N_3O)^+$ : 710.1100; found: 710.1080.

**2:** The synthetic procedure was similar to that of **1**, except starting material 4′-(4-hydroxyphenyl)-2,2′:6′,2′′-terpyridine was used instead of 2,2′:6′,2′′-terpyridin-4′-ol. Yield. 385 mg (~

98%); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.76 (ddd, J$_{ortho}$ = 4.8, J$_{meta}$ = 1.8, J$_{para}$ = 1.1 Hz, *H$_1$*, 2H), 8.73, (s, *H$_5$*, 2H), 8.70 (dt, J$_{ortho}$ = 8.0, J$_{meta}$ = 1.1 Hz, J$_{para}$ = 1.1, *H$_4$*, 1H), 7.90 (m, *H$_3$* and *H$_7$*, 4H), 7.38 (ddd, J$_{ortho}$ = 8.0, J$_{ortho}$ = 4.8 Hz, J$_{meta}$ = 1.1Hz, *H$_2$*, 2H), 7.08 – 7.01 (d, J= 9 Hz, *H$_6$*, 2H). 4.14 (t, J=5.9 Hz, *Ha* 2H), 2.43-2.30 (m, *Hc*, 2H), 2.20-2.12 (m, *Hb*, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.47 (*C12*), 156.35, 155.86, 149.66, 149.10 (*C1*), 136.87 (*C3*), 131.16, 128.60 (*C11*), 123.78 (*C2*), 121.38 (*C4*), 118.29 (*C7*), 114.79 (*C10*), 66.42 (*Ca*), 29.70, 28.01 (t, J=23 Hz), 20.61. ESI-TOF-MS Calcd. for [M+H]$^+$ (C$_{32}$H$_{21}$F$_{17}$N$_3$O)$^+$ : 786.1413; found: 786.1402.

**X-ray Structure Determination.** The crystals of ligand **2**, **1**-ZnCl$_2$, **1**-HgCl$_2$, **1**-ZnBr$_2$ and **1**-CuCl$_2$ were immersed in cryo-oil, mounted in a MiTeGen loop and measured at 120-123 K. The X-ray diffraction data were collected on an Agilent Technologies Supernova diffractometer using Mo Kα or Cu Kα radiation. The *CrysAlisPro*$^{22}$ program packages were used for cell refinements and data reductions. Structures were solved by charge flipping method using *SUPERFLIP*$^{23}$ program or by direct methods using *SHELXS-2008*$^{24}$ program. An analytical, Gaussian, or multi-scan (*CrysAlisPro*$^{22}$) absorption correction was applied to all data. Structural refinements were carried out using *SHELXL-2014*$^{24}$ or *SHELXL-2015*$^{24}$ software. In structure **1**-HgCl$_2$, fluorine atoms F5-F13 and F15-F17 as well as carbon atom C25 were disordered over two sites with equal occupancies. Distances C21-F5, C21-F5B, C21-F6, C21-F6B, F5-F6 and F5B-F6B were restrained to be similar. In all cases hydrogen atoms were refined using riding model. The crystallographic details of ligand **2**, **1**-ZnCl$_2$, **1**-HgCl$_2$, **1**-ZnBr$_2$ and **1**-CuCl$_2$ are summarized in Table 1 in ESI.

The NMR spectra ($^1$H, $^{13}$C and $^{19}$F) of ligands were recorded on Bruker Avance DRX 400 NMR spectrometer and chemical shifts were expressed in ppm (δ C$_6$H$_5$F internal standard = -113.6 ppm). Mass spectrum was recorded on Micromas (ESI-TOF-MS). SEM and TEM images were recorded on Bruker Quantax400 EDS (Zeiss EVO-50XVP) and JEOL JEM-1400HC respectively. X-Ray Powder Diffraction analysis was performed with PANanalytical X'pertPRO diffractometer.

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16  Single crystals of **1**-ZnX$_2$ (X=Cl or Br), **1**-CuCl$_2$ were obtained from DMSO, **1**-HgCl$_2$ was grown from acetonitrile, and ligand **2** was crystallized from chloroform. Additional details are given in ESI.

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# Graphical Abstract

## for

## Metallogel Formation in Aqueous DMSO by Perfluoroalkyl Decorated Terpyridine Ligands

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In this paper we introduce a series of stable and thermoreversible metallogels containing terpyridine based ligands with perfluorinated $C_8F_{17}$ tags and M(II) metals.