# Supporting Information

# Stimuli-responsive Properties of Supramolecular Gels based on Pyridyl-*N*-oxide Amides

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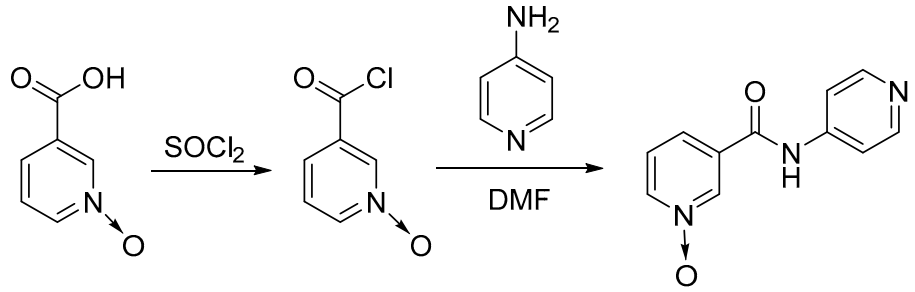
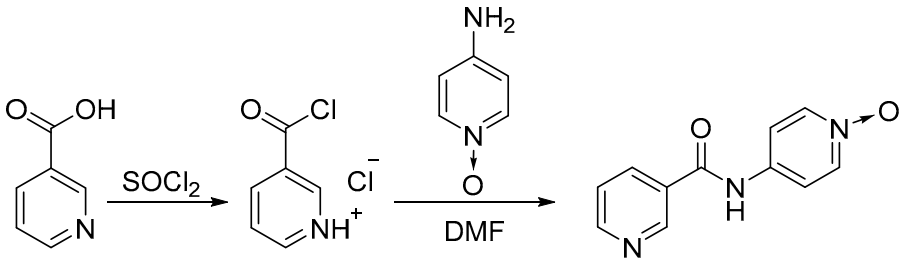
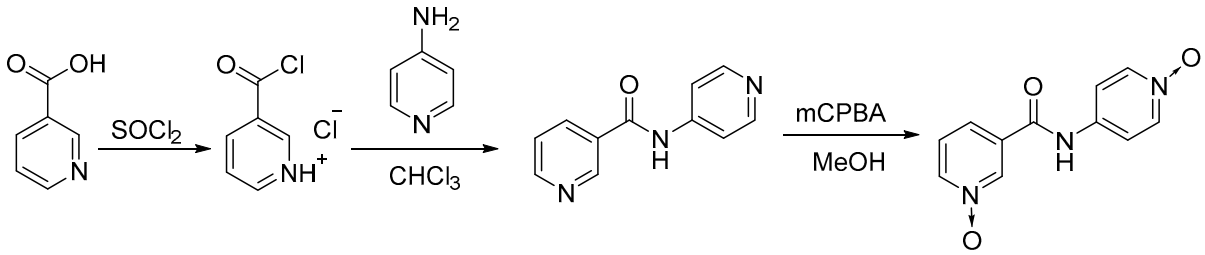
## 1. Synthetic scheme




**Scheme S1**. Synthesis of $L_1$




**Scheme S2.** Synthesis of $L_2$




**Scheme S3.** Synthesis of $L_3$

## 2. Rheology

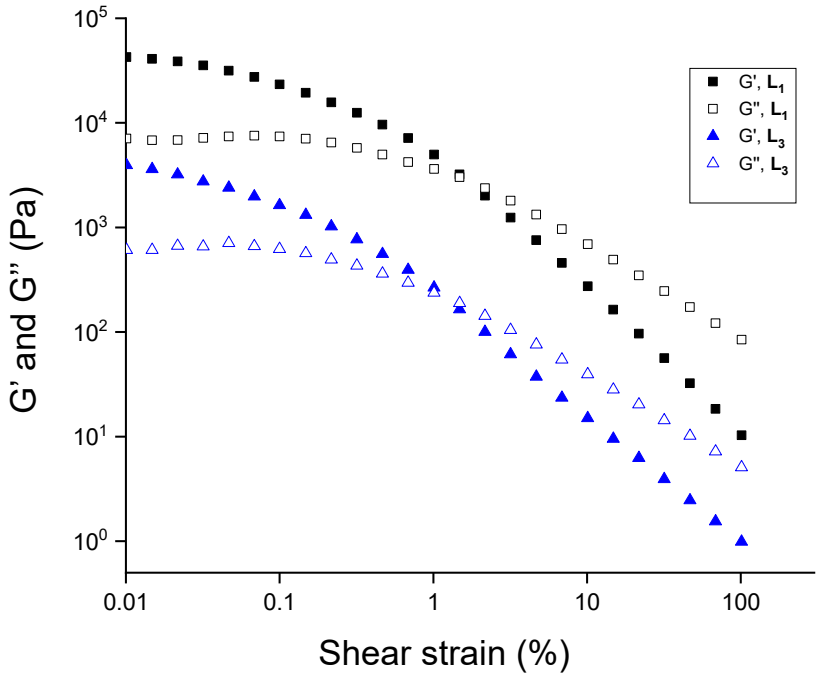



**Figure S1**. Amplitude-sweep experiments with gels of $\mathbf{L_1}$ and $\mathbf{L_2}$ (2.0 wt%) in water at 20.0 °C with a constant frequency of 1.0 Hz.

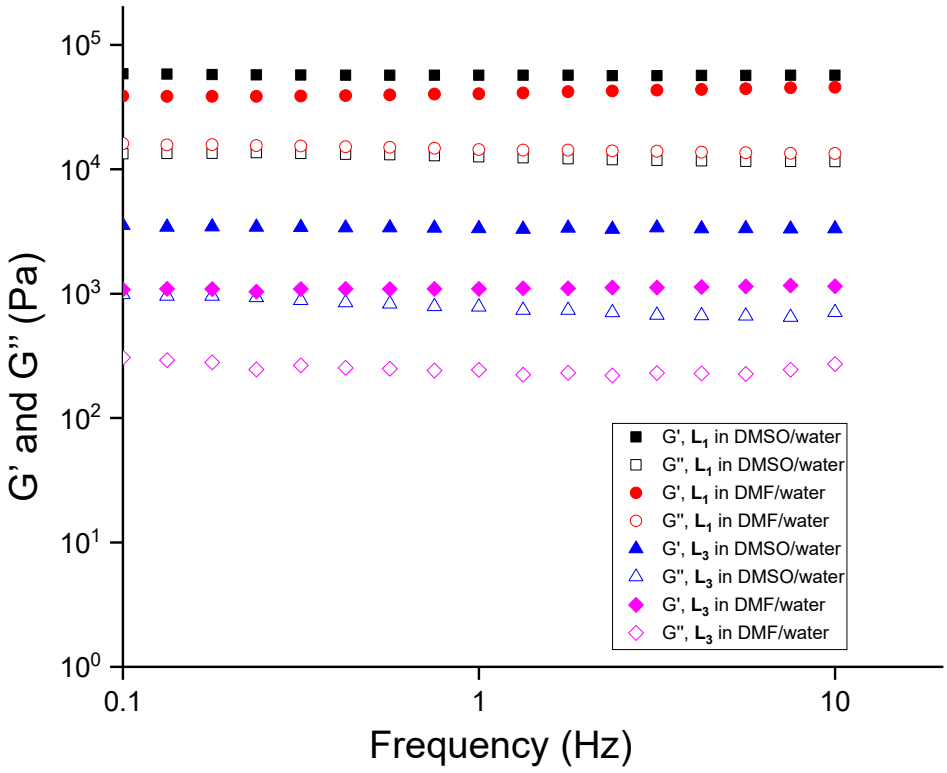



**Figure S2**. Frequency-sweep experiments with gels of $\mathbf{L_1}$ and $\mathbf{L_3}$ (2.0 wt%) in aqueous mixtures at 20.0 °C with a constant strain of 0.02%.

## 3. Scanning electron microscopy (SEM)

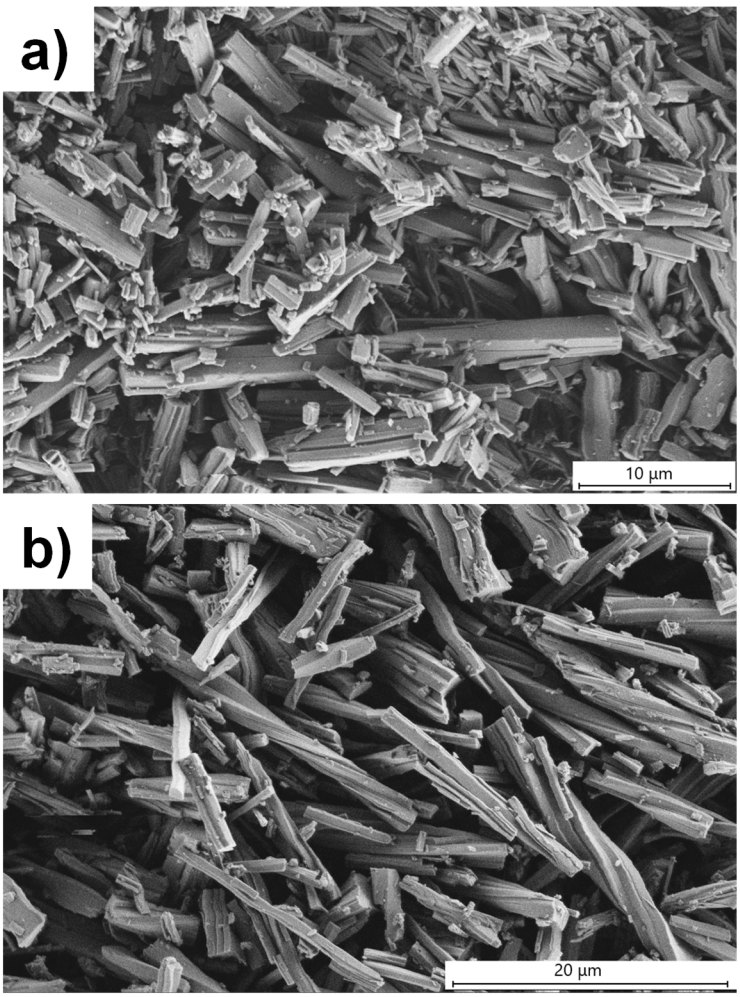



**Figure S3**. SEM images of (a) $\mathbf{L_1}$ and (b) $\mathbf{L_3}$ xerogels in water at 1.8 wt%.

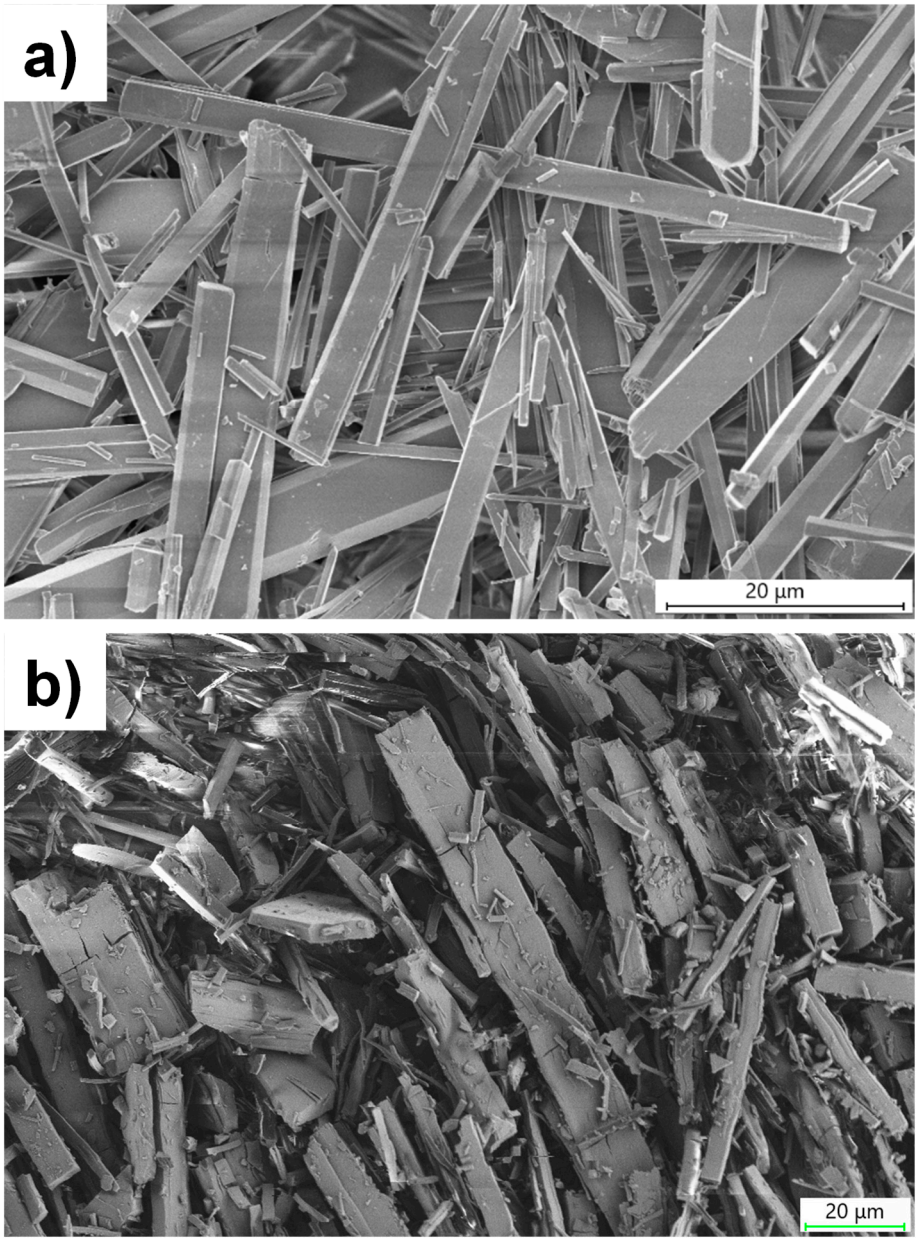



**Figure S4**. SEM images of the xerogels of (a) $\mathbf{L_3}$ and (b) **diNO** gels obtained from water at 4.0 wt%.

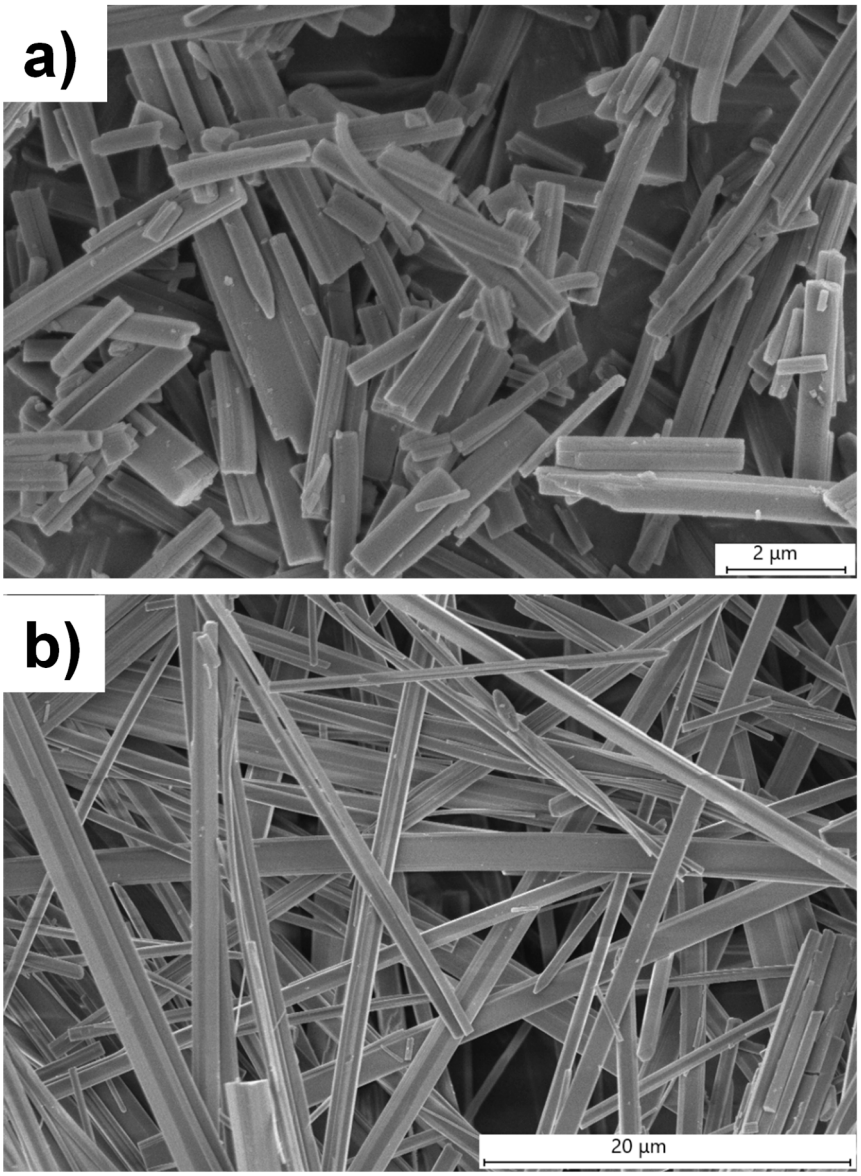



**Figure S5**. SEM images of $\mathbf{L_1}$ xerogels in (a) DMSO/water (1:1, v/v) and (b) methanol/water (1:1, *v*/*v*) at 2.0 wt/v%.

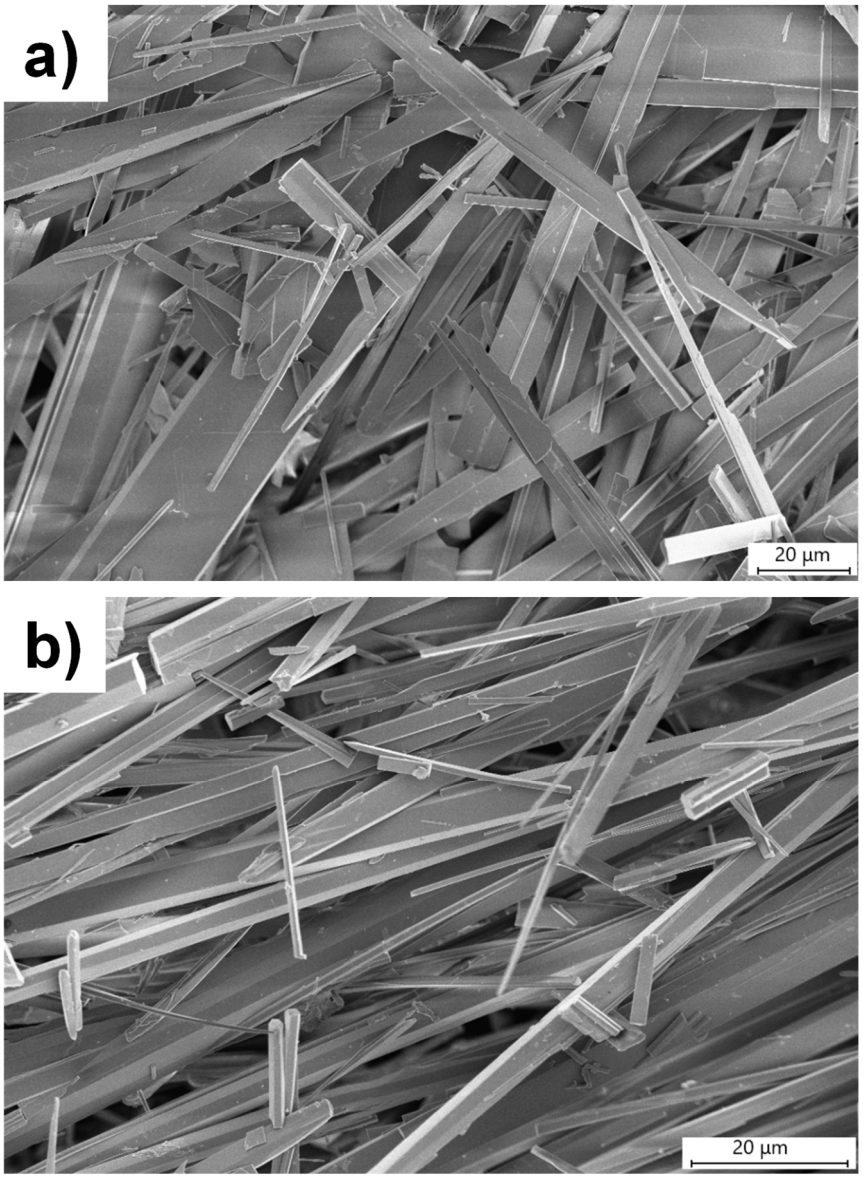



**Figure S6**. SEM images of $\mathbf{L_3}$ xerogels from (a) DMSO/water (1:1, *v*/*v*), and (b) methanol/water (1:1, *v*/*v*) at 2.0 wt/v%.

## 4. X-ray crystallography

**Table S1**: Crystal data

| **Crystal data** | **L₃**•$H_2O$ | **L₃**•$2H_2O$ |
|---|---|---|
| Empirical formula | $C_{11}H_{11}N_3O_4$ | $C_{11}H_{11}N_3O_4$ |
| Color | Colorless | Colorless |
| Formula weight | 249.23 | 249.23 |
| Crystal size (mm) | 0.19 x 0.05 x 0.03 | 0.22 x 0.16 x 0.10 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2/c$ |
| a (Å) | 3.73500(10) | 8.1758(8) |
| b (Å) | 12.7975(4) | 5.6771(5) |
| c (Å) | 22.9071(8) | 23.529(2) |
| α (°) | 90 | 90 |
| β (°) | 90.0100(14) | 97.127(2) |
| γ (°) | 90 | 90 |
| Volume (Å$^3$) | 1094.93(6) | 1083.66(18) |
| Z | 4 | 4 |
| $D_{calc.}$(g/cm$^3$) | 1.512 | 1.528 |
| F(000) | 520 | 520 |
| $\mu$ (mm$^{-1}$) | 0.998 ($CuK_\alpha$) | 0.119 ($MoK_\alpha$) |
| Temperature (K) | 302(2) | 296(2) |
| Reflections collected/ unique/observed [I>2σ(I)] | 15306/ 1730/ 1369 | 17613/ 2500/ 2071 |
| Data/restraints/parameters | 1730/0/171 | 2500/0/172 |
| Goodness of fit on $F^2$ | 1.045 | 1.062 |
| Final R indices [I>2σ(I)] | $R_1$ = 0.0457 $wR_2$ = 0.1126 | $R_1$ = 0.0409 $wR_2$ = 0.1062 |
| R indices (all data) | $R_1$ = 0.0624 $wR_2$ = 0.1227 | $R_1$ = 0.0524 $wR_2$ = 0.1144 |

**Table S2**: Hydrogen bonding parameters

| **Compound $L_3$•$H_2O$** | | | | | | |
|---|---|---|---|---|---|---|
| No. | Donor—H···Acceptor | D–H(Å) | H···A(Å) | D···A(Å) | ∠D—H···A(°) | Symmetry operation |
| 1 | O(18)—H(1)···O(15) | 1.00(3) | 1.79(3) | 2.782(3) | 170(3) | 1+x,y,z |
| 2 | O(18)—H(2)···O(15) | 0.97(5) | 1.85(5) | 2.796(3) | 165(4) | x,y,z |
| 3 | O(18)—H(2)···N(14) | 0.97(5) | 2.48(4) | 3.318(3) | 145(4)' | x,y,z |
| 4 | N(10)—H(10)···O(1) | 0.86 | 2.01 | 2.852(2) | 166 | 1-x,2-y,-z |
| 5 | C(4)—H(4)···O(15) | 0.93 | 2.58 | 3.266(3) | 131 | 1+x,3/2-y,-1/2+z |
| 6 | C(7)—H(7)···O(1) | 0.93 | 2.47 | 3.354(3) | 158 | -x,2-y,-z |
| 7 | C(13)—H(13)···O(9) | 0.93 | 2.52 | 3.166(3) | 127 | -x,1-y,-z |
| 8 | C(16)—H(16)···O(18) | 0.93 | 2.55 | 3.235(3) | 131 | 1-x,1/2+y,1/2-z |
| **Compound $L_3$•$2H_2O$** | | | | | | |
| No. | Donor—H···Acceptor | D–H(Å) | H···A(Å) | D···A(Å) | ∠D—H···A(°) | Symmetry operation |
| 1 | N(10)—H(10)···O(1) | 0.86 | 2.07 | 2.8956(16) | 161 | 1-x,-y,1-z |
| 2 | O(18)—H(18)···O(17) | 0.87(2) | 1.88(2) | 2.7447(18) | 175(2) | 1-x,2-y,1-z |
| 3 | O(19)—H(19)···O(17) | 0.91(2) | 1.91(2) | 2.8185(19) | 173(2) | x,2-y,-1/2+z |
| 4 | C(7)—H(7)···O(1) | 0.93 | 2.35 | 3.2486(18) | 163 | 1-x,-y,1-z |
| 5 | C(13)—H(13)···O(9) | 0.93 | 2.37 | 3.1134(17) | 137 | -x,2-y,1-z |
| 6 | C(15)—H(15)···O(18) | 0.93 | 2.39 | 3.129(2) | 136 | 1-x,1-y,1-z |
| 7 | C(16)—H(16)···O(1) | 0.93 | 2.39 | 3.155(2) | 139 | 1-x,-y,1-z |

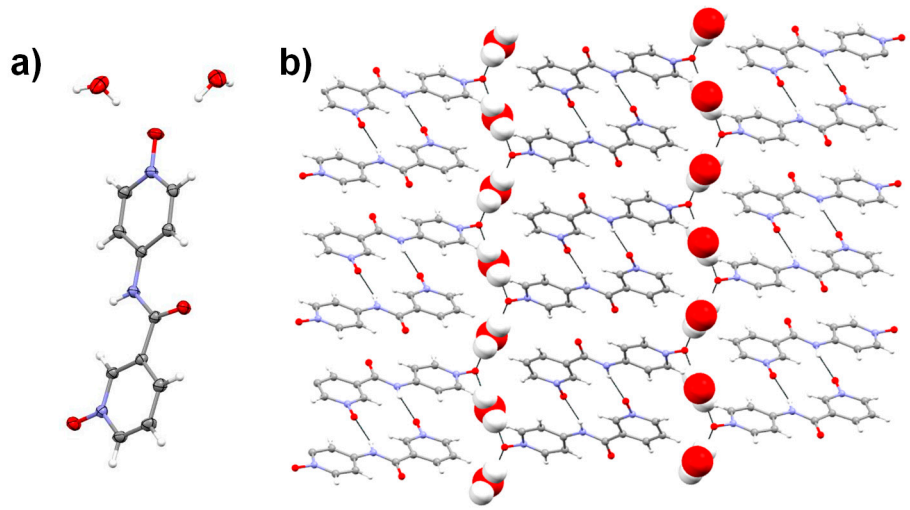



**Figure S7**. (a) Molecular structure of **L₃**•2$H_2O$ and (b) two-dimensional hydrogen-bonded network with water molecules (space fill model) located in the cavity.

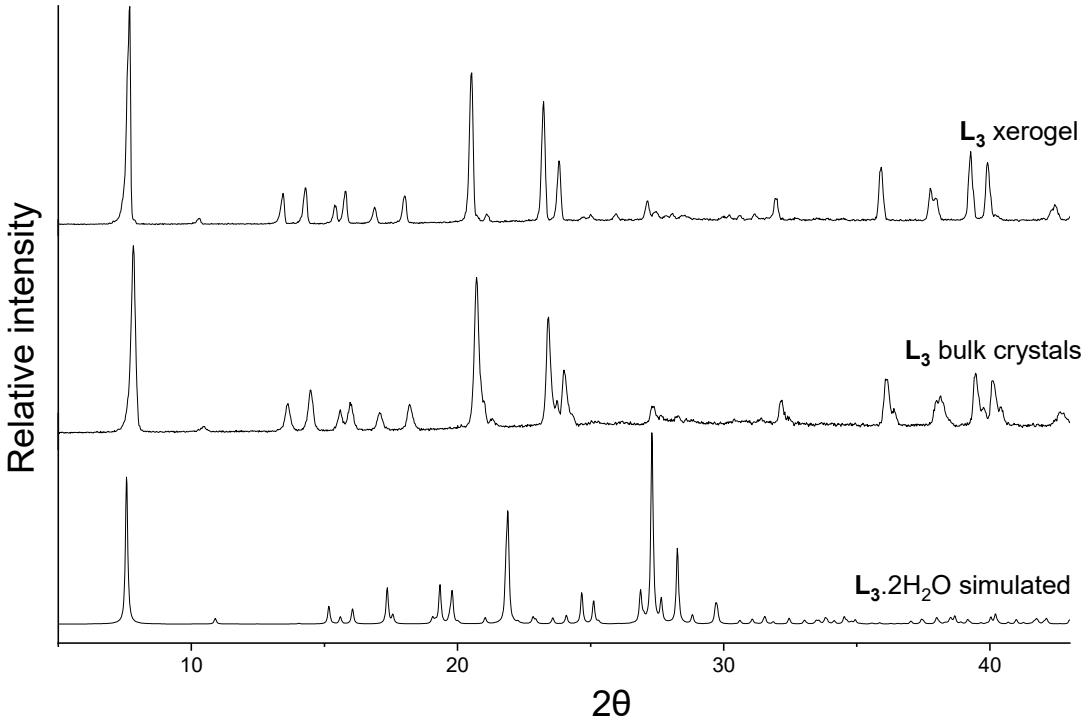



**Figure S8**. Comparison of the simulated pattern of the single-crystal X-ray structure of **L₃**.2$H_2O$ with the PXRD pattern of the bulk crystals obtained from water, and xerogel from water at 2.0 wt%.

## 5. Physical properties of the gels in the presence of salts

**Table S3**: Stimuli-responsive properties of the gelators **$L_1$** and **$L_3$**: Anion sensing in water at 1.5 wt%

| **Salts (1.0 equiv.)** | **$L_1$** | **$L_3$** |
|---|---|---|
| NaF | G | G |
| NaCl | G | G |
| NaBr | G | G |
| NaI | Ppt | PG |
| KF | G | G |
| KCl | G | G |
| KBr | G | G |
| KI | G | G |
| $NaNO_3$ | C | G |
| $NaSO_4$ | C | Ppt |
| $NaN_3$ | C | G |
| KCN | C | S |
| $KClO_4$ | Ppt | PG |
| $KPF_6$ | C | G |
| $KBF_4$ | C | G |
| KSCN | C | PG |
| $K_2C_2O_4$ | C | G |
| $KNO_3$ | C | G |

C-colloid, G-gel, PG-partial gel, Ppt-Precipitate

**Table S4**: Increase in G' values of the gelators at 1.5 wt% in the presence of various sodium and potassium salts in comparison with the hydrogels (1.8 wt%)

| **Salt added** | **Equivalence (equiv.)** | **$L_1$ 1.5%** | **$L_3$ 1.5%** |
|---|---|---|---|
| NaF | 1.0 | 2.0-fold | 2.8-fold |
| KF | 1.0 | 2.6-fold | 3.0-fold |
| NaCl | 1.0 | 1.8-fold | 4.3-fold |
| KCl | 1.0 | 3.0-fold | 5.7-fold |
| NaBr | 1.0 | 1.5-fold | 3.0-fold |
| KBr | 1.0 | 3.0-fold | 2.3-fold |
| KI | 1.0 | --- | 1.7-fold |
| $KNO_3$ | 1.0 | --- | 1.9-fold |
| $KBF_4$ | 1.0 | --- | 4.8-fold |
| $KPF_6$ | 1.0 | --- | 5.0-fold |
| $K_2C_2O_4$ | 1.0 | --- | 1.8-fold |

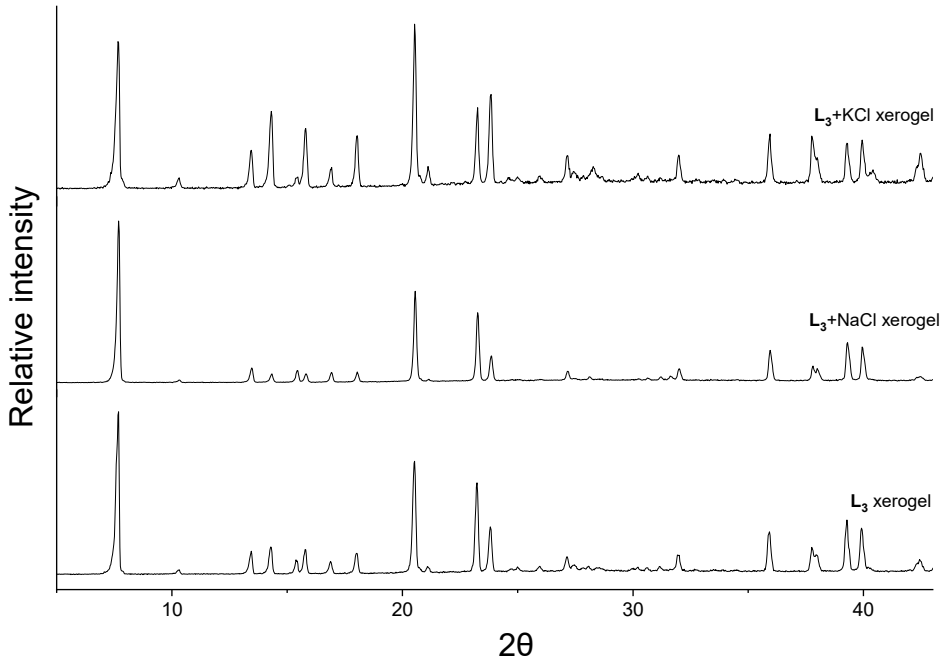



**Figure S9**. PXRD pattern of xerogels obtained from the hydrogel of $\mathbf{L_3}$ at 2.0 wt% and in the presence of 1.0 equivalence of NaCl and KCl.

**Table S5**: Stimuli-responsive properties of the gelators $\mathbf{L_1}$ and $\mathbf{L_3}$: Cation sensing in water at 1.5 wt%

| **Salts (1.0 equiv.)** | **$L_1$** | **$L_3$** |
|---|---|---|
| CsCl | G | G |
| $MgCl_2$ | G | G |
| $CaCl_2$ | G | G |
| $SrCl_2$ | G | G |
| $BaCl_2$ | G | G |
| $AlCl_3$ | S | PG |
| $NH_4Cl$ | PG | G |
| $CuCl_2$ | Ppt | PG |
| $ZnCl_2$ | Ppt | G |
| $CdCl_2$ | Ppt | G |

**Table S6**: Increase in G' values of the gelators at 1.5 wt% in the presence of chloride salts of various cations in comparison with the hydrogels (1.8 wt%)

| **Salt added** | **Equivalence** | **$L_1$** | **$L_3$** |
|---|---|---|---|
| CsCl | 1.0 | 1.1-fold | 3.8-fold |
| $MgCl_2$ | 1.0 | 1.9-fold | 4.8-fold |
| $CaCl_2$ | 1.0 | 1.7-fold | 5.0-fold |
| $SrCl_2$ | 1.0 | 1.8-fold | 2.3-fold |
| $BaCl_2$ | 1.0 | 1.5-fold | 1.8-fold |
| $NH_4Cl$ | 1.0 | --- | 1.6-fold |
| $CuCl_2$ | 1.0 | --- | ----- |
| $ZnCl_2$ | 1.0 | --- | 2.8-fold |
| $CdCl_2$ | 1.0 | --- | 24.7-fold |

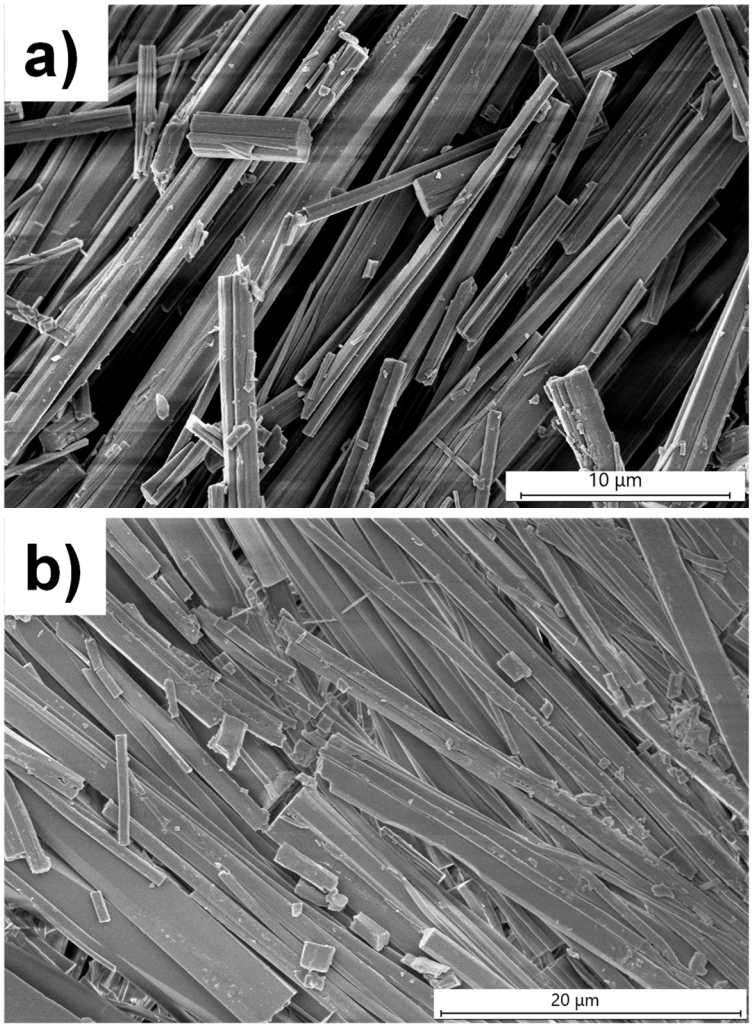



**Figure S10**. SEM images of xerogels of (a) $\mathbf{L_1}$ and (b) $\mathbf{L_3}$ at 2.0 wt% obtained from water in the presence of 1.0 equivalence of $MgCl_2$.

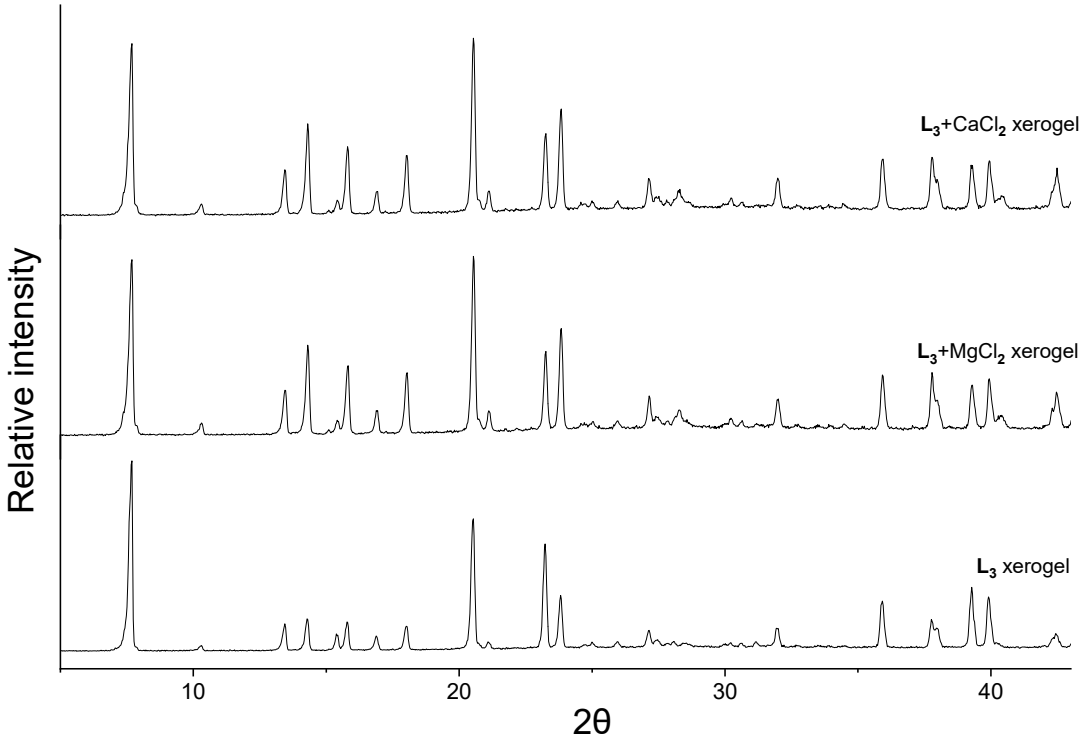



**Figure S11**. Comparison of the PXRD pattern of xerogels (2.0 wt%) of **$L_3$** hydrogels, and the gels in the presence of 1.0 equivalence of $MgCl_2$ and $CaCl_2$.

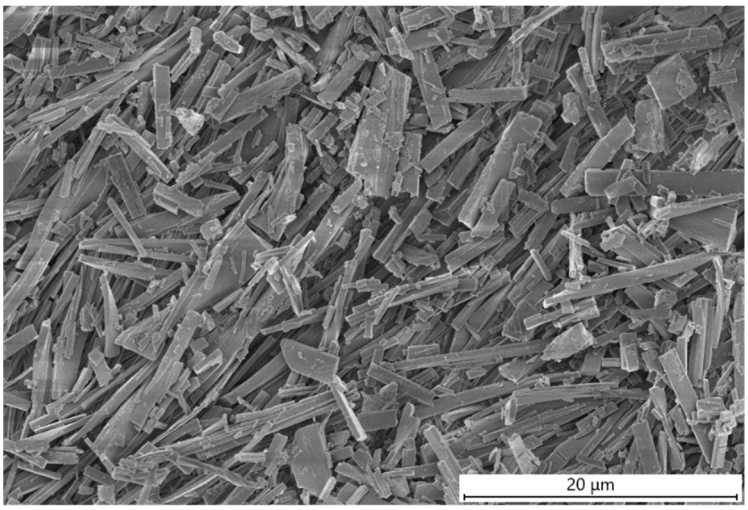



**Figure S12**. SEM images of the xerogels of **$L_3$** in the presence of 1.0 equivalence of $CdCl_2$ in water at 2.0 wt%.

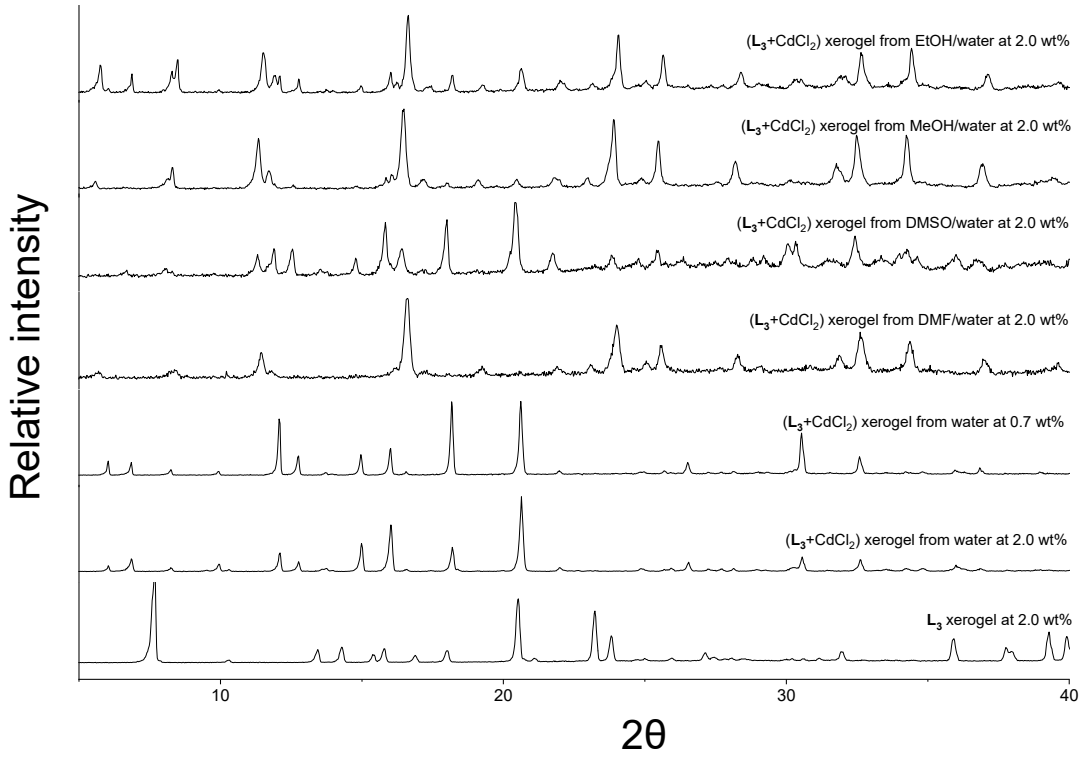



**Figure S13**. Comparison of the PXRD pattern of **$L_3$** xerogel with the PXRD pattern of the xerogels of **$L_3$**-$CdCl_2$ mixture in various solvents.

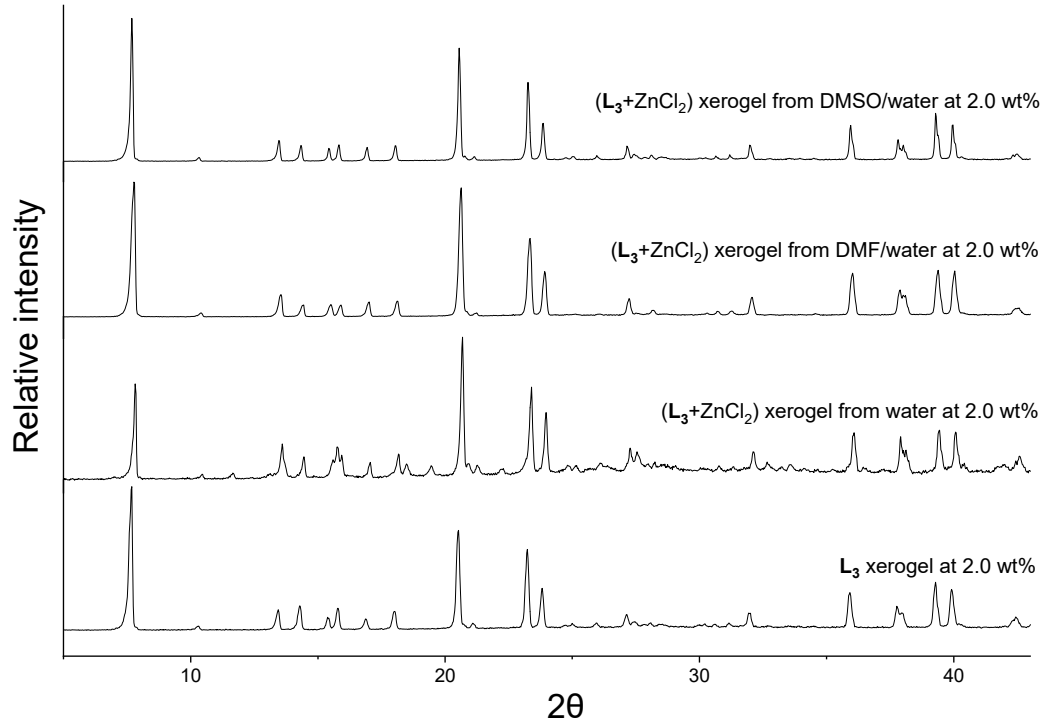



**Figure S14**. Comparison of the PXRD pattern of **$L_3$** xerogel from water with the PXRD pattern of the xerogels of the mixture (**$L_3$** + $ZnCl_2$) in various solvents.

## 6. NMR spectra

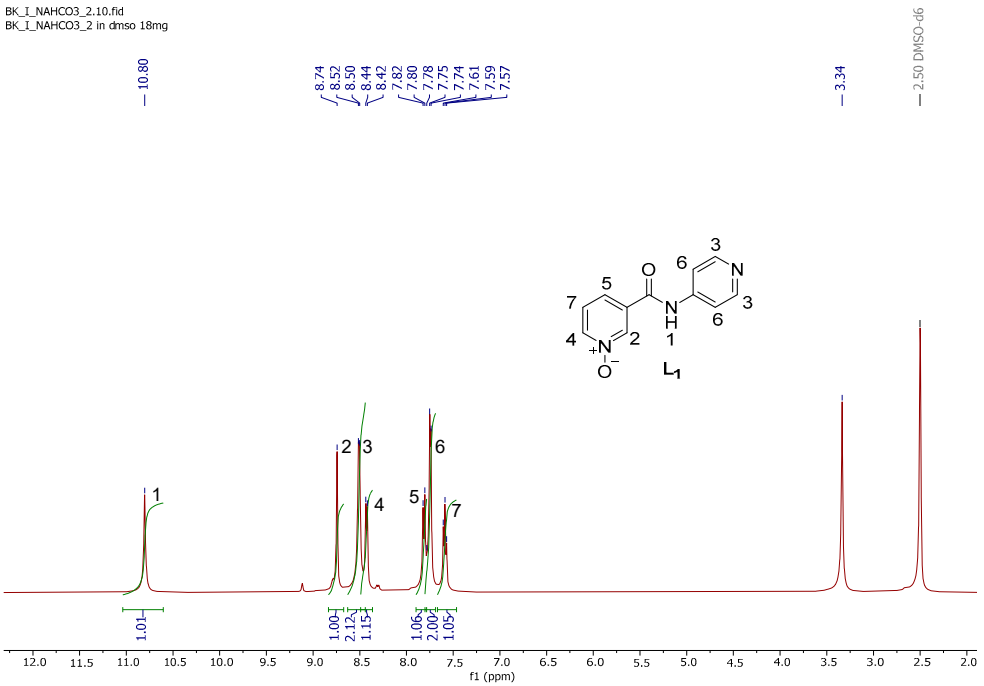



**Figure S15**. $^{1}$H NMR spectrum of compound **$L_1$**.

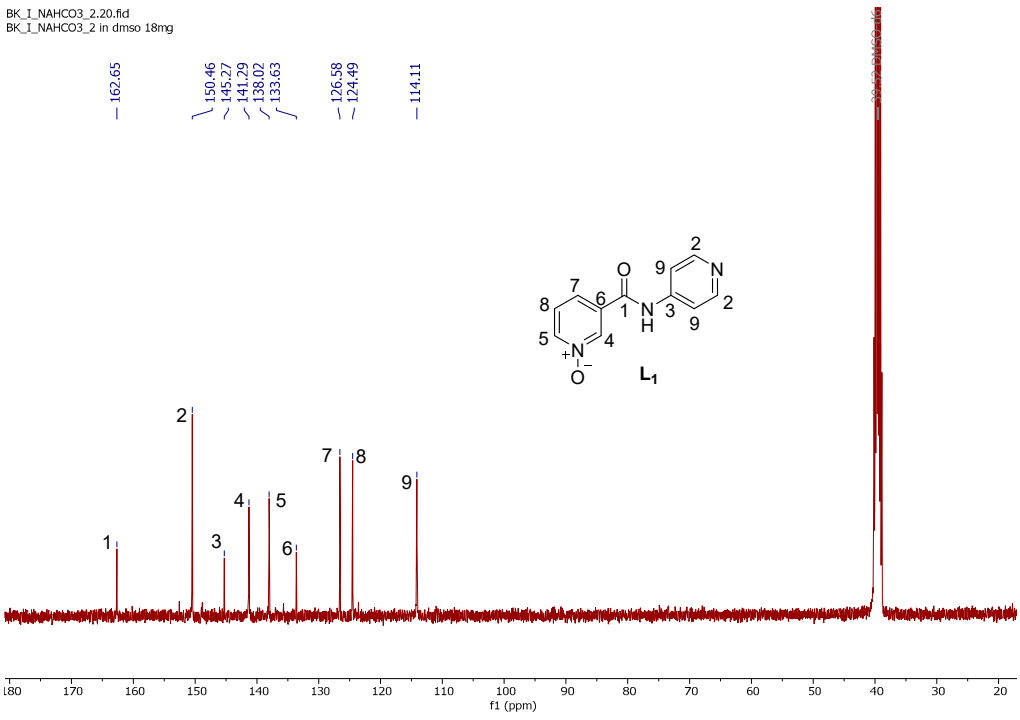



**Figure S16**. $^{13}$C NMR spectrum of compound **$L_1$**.

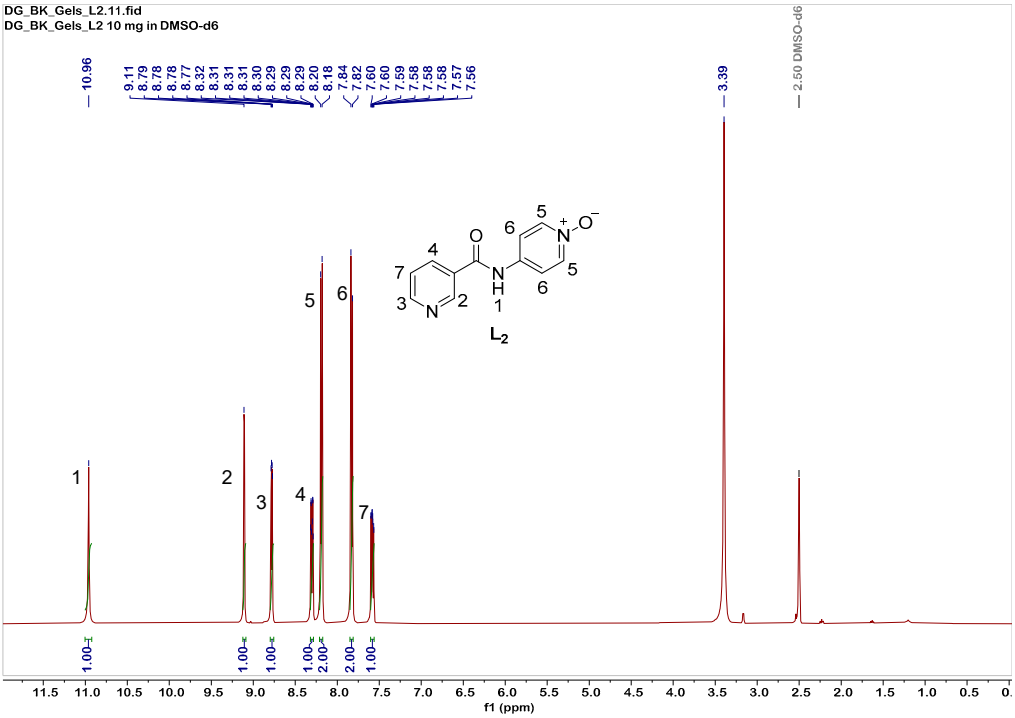



**Figure S17**. $^{1}$H NMR spectrum of compound **$L_2$**.

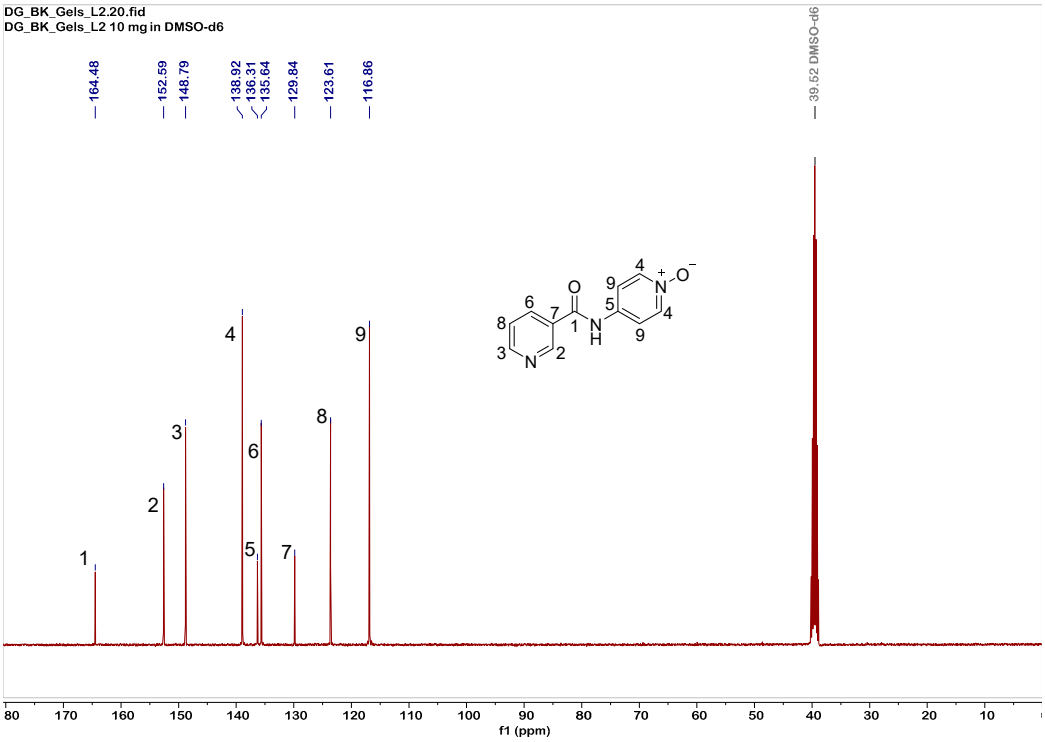



**Figure S18**. $^{13}$C NMR spectrum of compound **$L_2$**.

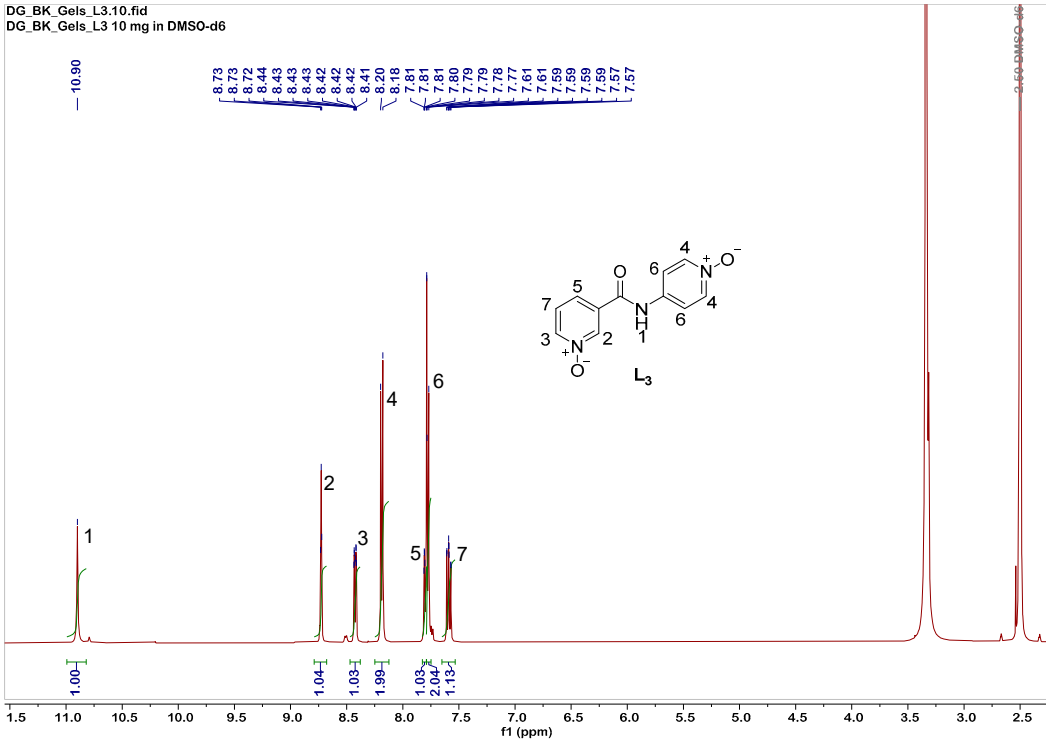



**Figure S19**. $^{1}$H NMR spectrum of compound **$L_3$**.

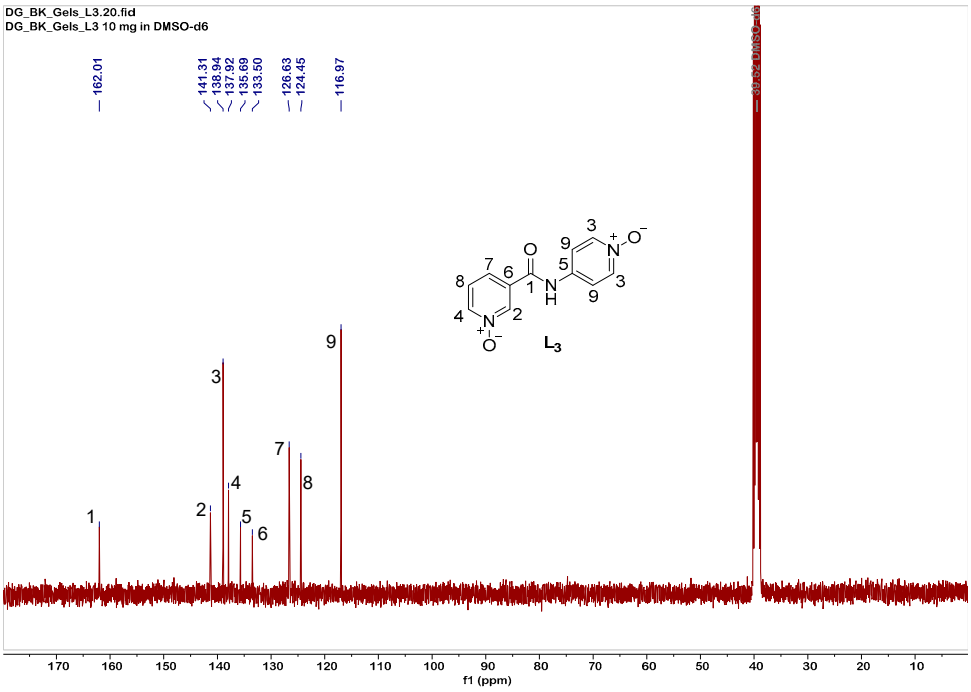



**Figure S20**. $^{13}$C NMR spectrum of compound **$L_3$**.