Supplementary Information

Crystal habit modification of Cu(II) isonicotinate-*N*-oxide complexes using gel phase crystallisation

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1. Concomitant crystallisation of blue and green crystals

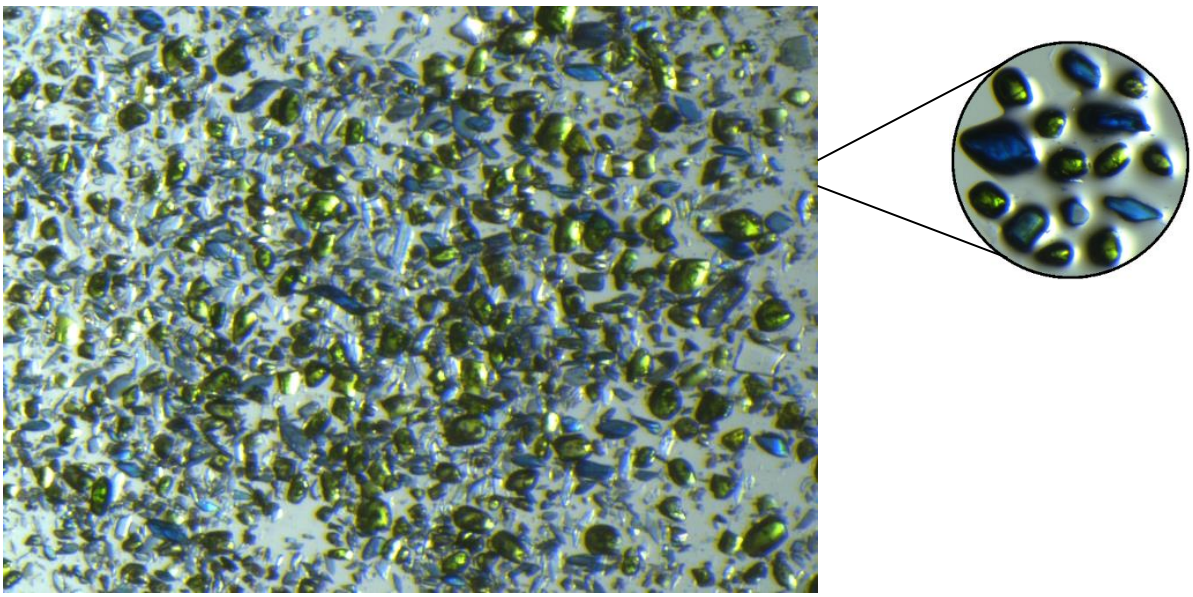


Figure S1: Concomitant crystals of copper(II) isonicotinate-*N*-oxide- form I (blue) and form II (green)

2.Crystallisation conditions for form-I and form-II

2.1. Crystals in different solvents: The crystals were isolated from the solution and dried in air. These crystals were transferred into small vials, approximately 0.5 mL of different solvent (water, methanol, ethanol, acetonitrile and THF) was added to each vail and sealed. We didn't add solvents to one of the vails to check the stability of these crystals in air.

2.1.1. Blue crystals: The crystals in ethanol changed colour to green in two hours. The crystals in methanol turned green in a couple of days and the crystals in water eventually dissolved. There was no change in colour for the crystals in THF, acetonitrile and the crystals were stable in air.

2.1.2. Green crystals: The crystals immersed in water dissolved completely after few hours. The crystals in methanol changed to darker green whereas crystals were partially soluble in ethanol. We did not observe any change with crystals in THF and acetonitrile.

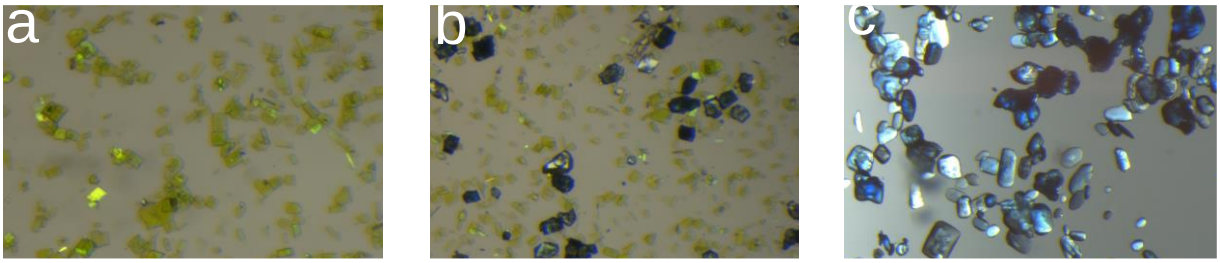


Figure S2: Crystallisation of (a) form-II (green) in (<3.5% water), (b) concomitant crystals (5-10% water) and (c) form-I (blue) (>10% water) in ethanol-water.

3. IR spectra of form-I, form-II and form-IV

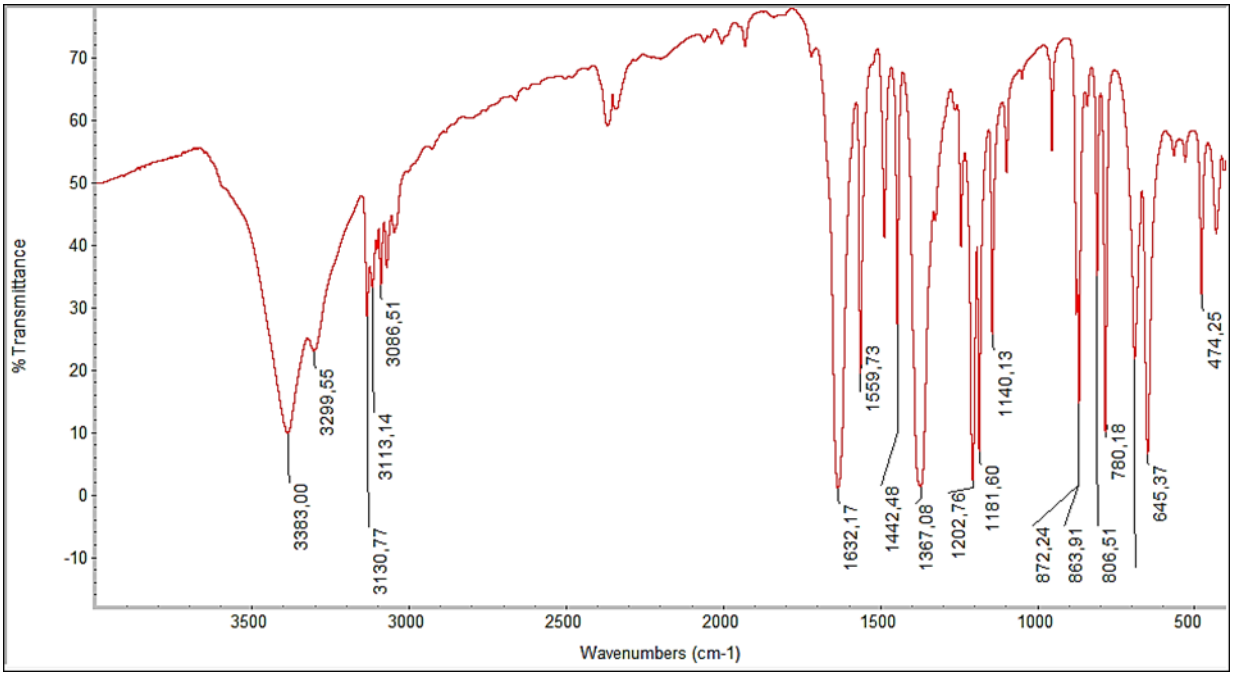


Figure S3: IR spectrum of form-I

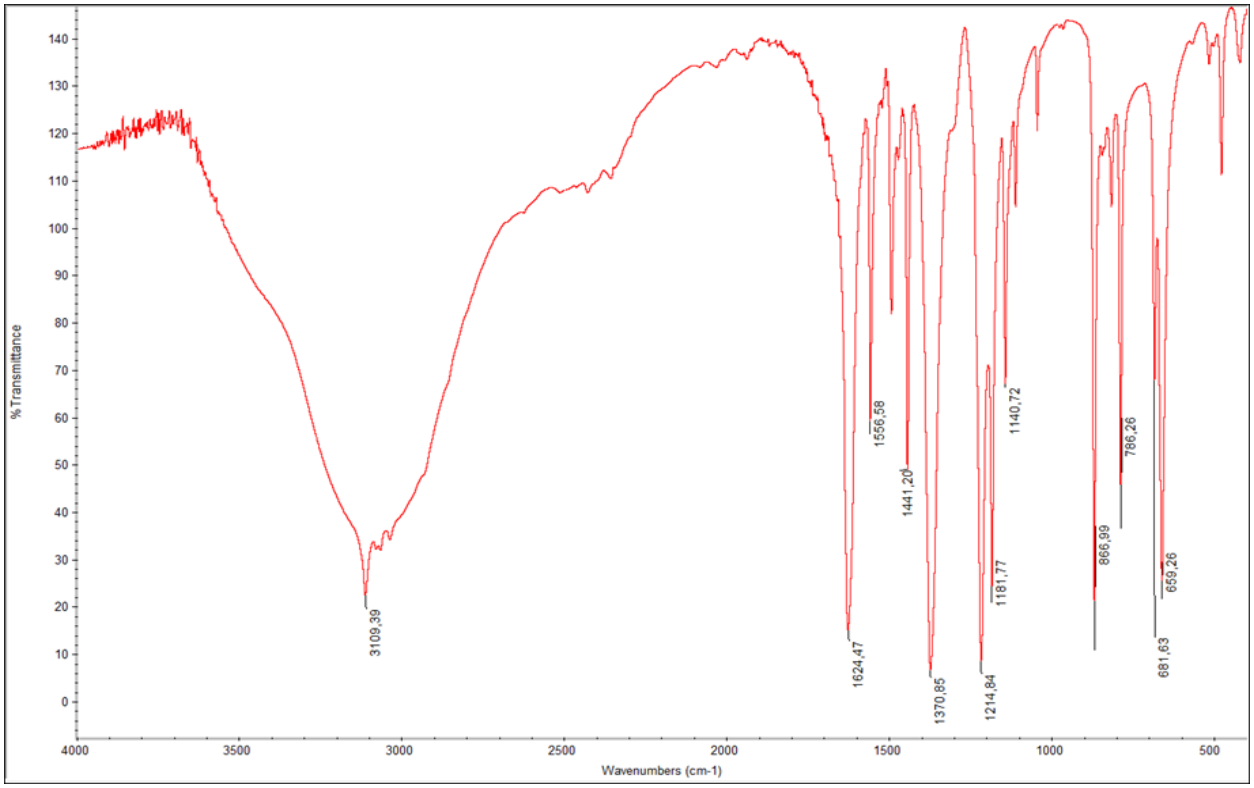


Figure S4: IR spectrum of form-II

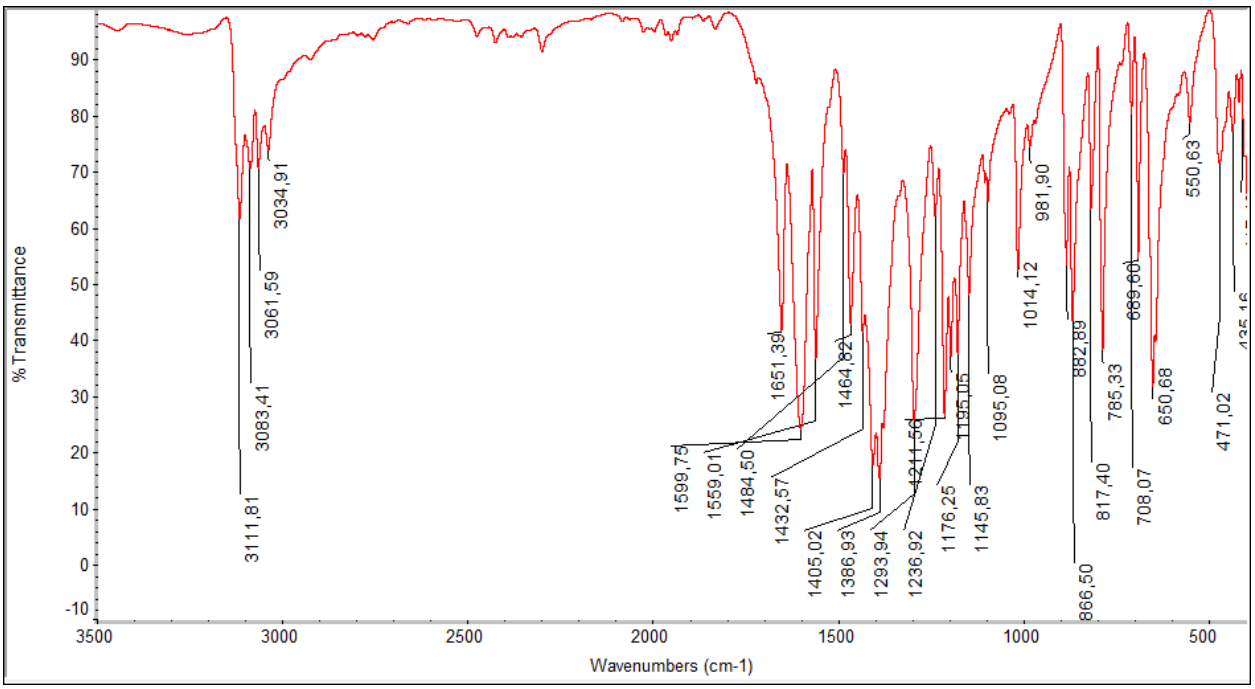


Figure S5: IR spectrum of form-IV

4. Single Crystal X-ray Diffraction: X-ray quality single crystals were obtained by heating ethanolic solution of copper(II) nitrate (24.1 mg, 0.1 mmol) and isonicotinic acid-*N*-oxide (27.8 mg, 0.2 mmol) at 85 °C in a sealed vial. The crystals were isolated from mother liquor, immediately immersed in cryogenic oil and then mounted. The X-ray single crystal data was collected using MoKα radiation (λ =0.71073Å) on a Bruker D8Venture (Photon100 CMOS detector) diffractometer equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostats at the temperature 150.0(2) K.

5. Powder X-ray Diffraction: An ethanolic solution of copper(II) nitrate (24.1 mg, 0.1 mmol) and isonicotinic acid-*N*-oxide (27.8 mg, 0.2 mmol) was heated at 85 °C in a sealed vial. Resulting green crystals obtained overnight were filtered, dried in air and XRPD was recorded. XRPD pattern of the bulk solid was then compared with simulated pattern generated from single crystal data.

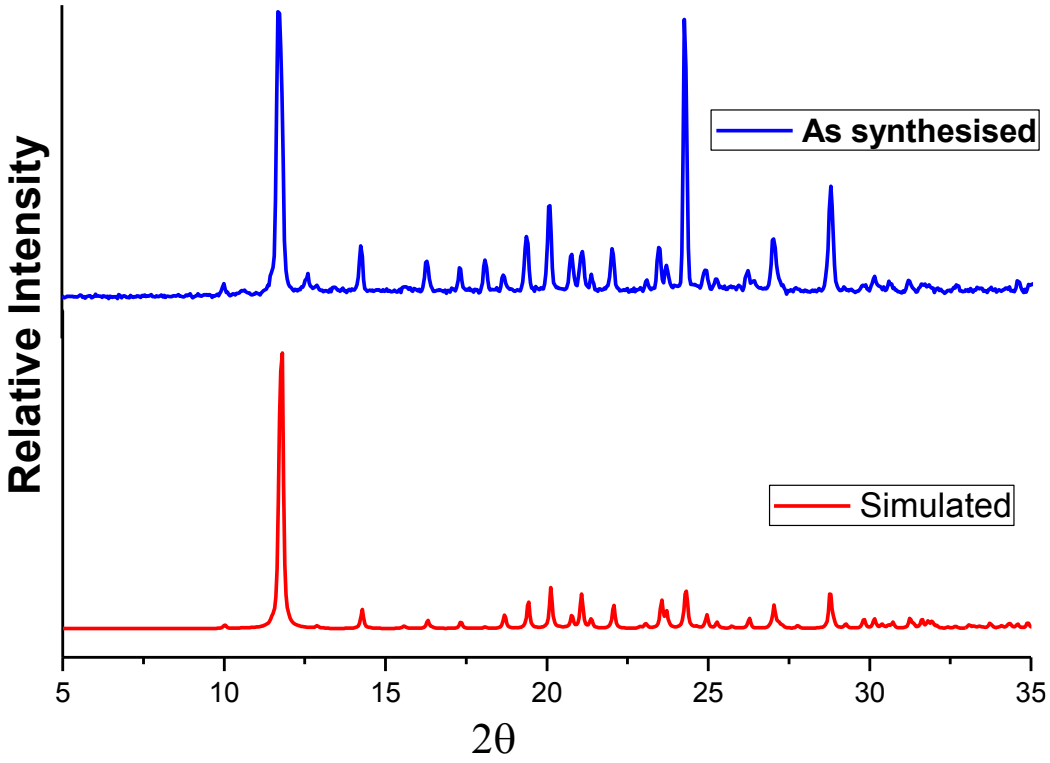
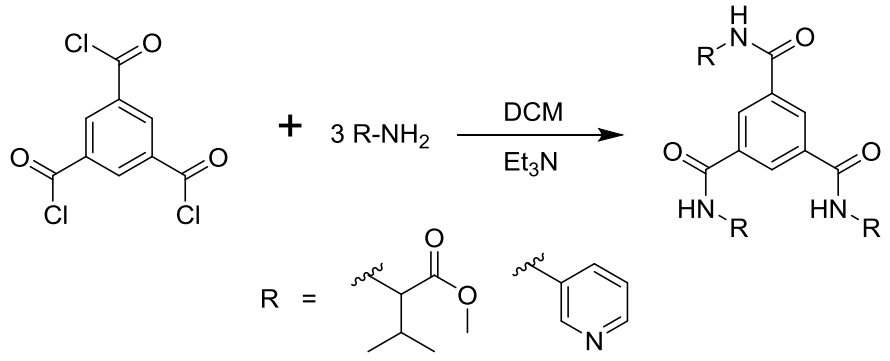


Figure S6: XRPD comparison of simulated and bulk solid of form-IV

6. Synthesis of gelators

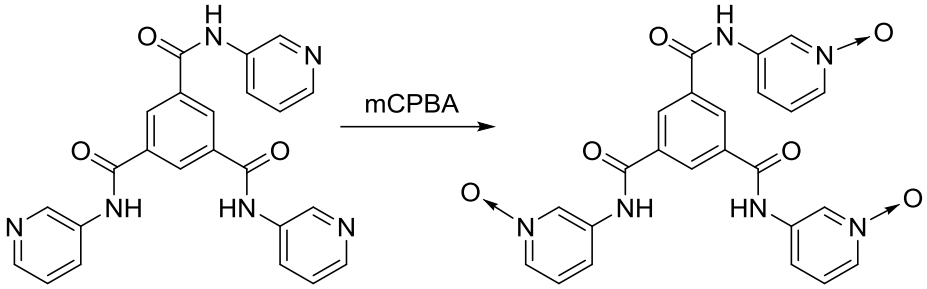
6.1 General Scheme for all gelators.

Methyl L-valinate trimesic amide[1] and 3-pyridyl trimesic amide[2] were synthesised following literature procedure. Analytical and spectroscopic data of the synthesised compounds matched with reported compounds.



Scheme S1: General synthesis of trimesic amides

6.2 Synthesis of tailored L-3Nox compound.



Scheme S2: Synthesis of *3,3',3''-((benzene-1,3,5-tricarbonyl)tris(azanediyl))tris-(pyridine 1-oxide) (**L-3Nox**)*

7. Gelation properties of tailored N-oxide compound {*3,3',3''-((benzene-1,3,5-tricarbonyl)tris-(azanediyl))tris(pyridine 1-oxide*)} (L-3Nox)

(a) Gelation test in various solvents

Gelation test for **L-3Nox** was performed in various solvent system. The gelator was soluble only in high polar solvents such as DMF, DMA, DMSO etc. In a typical experiment, **L-3Nox** was dissolved in required amount of solvent by heating and sonicating, cooled to room temperature and water was added. It was sonicated till a suspension was formed and left undisturbed.

Table S1: Gelation test of **L-3Nox** in various solvents

Amount	Solvents (mL)	Initial Observation	Final Observation
5.0 mg	DMF (0.5)/ water (0.5)	Solution	No gel
5.0 mg	DMA (0.5)/ water (0.5)	Solution	No gel
5.0 mg	DMSO (0.5)/ water (0.5)	Solution	Gel in ~1 hour
5.0 mg	DEF (0.5)/ water (0.5)	Solution	No gel
5.0 mg	DEA (0.5)/ water (0.5)	Solution	No gel

(b) Varying solvent composition

Gelation test of **L-3Nox** was performed at different DMSO/water composition. We did a solvent screening from 50% to 10% water (v/v) composition.

Table S2: Gelation of **L-3Nox** in various DMSO/water composition

Amount	DMSO	Water	Initial Observation	Final Observation
5.0 mg	500 µL	500 µL	Solution	Gel
5.0 mg	600 µL	400 µL	Solution	Gel
5.0 mg	700 µL	300 µL	Solution	Gel
5.0 mg	800 µL	200 µL	Solution	Gel
5.0 mg	900 µL	100 µL	Solution	No gel

(c) Finding minimum gelator concentration (MGC)

MGC test of **L-3Nox** gel was performed at 7:3 and 1:1 DMSO/water (v/v) composition, the gel formed at 7:3 DMSO-water ratio was most transparent. MGC was found to be 0.15 wt% at 7:3 DMSO/water and 0.3 wt% at 1:1 DMSO/water.

Table S3: Determination of MGC of **L-3Nox**

Amount	Solvents (mL)	Initial Observation	Final Observation
5.0 mg	DMSO (0.7)/ water (0.3)	Solution	Gel
4.0 mg	DMSO (0.7)/ water (0.3)	Solution	Gel
3.0 mg	DMSO (0.7)/ water (0.3)	Solution	Gel
2.0 mg	DMSO (0.7)/ water (0.3)	Solution	Gel
1.5 mg	DMSO (0.7)/ water (0.3)	Solution	Gel
1.0 mg	DMSO (0.7)/ water (0.3)	Solution	No gel
5.0 mg	DMSO (0.5)/ water (0.5)	Solution	Gel
4.0 mg	DMSO (0.5)/ water (0.5)	Solution	Gel
3.0 mg	DMSO (0.5)/ water (0.5)	Solution	Gel
2.5 mg	DMSO (0.5)/ water (0.5)	Solution	No gel

(d) Finding T_{gel}

Gel-sol transition temperature (T_{gel}) of **L-3Nox** was performed at 0.5 wt% (5 mg in 1 mL solvent) in 7:3 and 1:1 DMSO/water (v/v) composition, after 24 hours.

Table S4: Determination of T_{gel} of **L-3Nox**

Exp. no	Gelator	Solvents (mL)	Mass of glass ball	Time	T_{gel}
1	0.5 wt%	DMSO (0.5)/ water (0.5)	92.0 mg	24 hour	105 °C
2	0.5 wt%	DMSO (0.7)/ water (0.3)	92.0 mg	24 hour	106 °C

8. Gel Phase Crystallisation

8.1 In hydrogels

Crystallisation of $Cu(NO_3)_2.3H_2O$ and isonicotinic acid-*N*-oxide was performed in presence of hydrogelators like agarose, gelatin and some low molecular weight gelators (LMWGs). In a typical experiment, isonicotinic acid-*N*-oxide (2 equivalent) and the gelator were dissolved together in water (for agarose and gelatin), then $Cu(NO_3)_2.3H_2O$ (1 equivalent) was added to it and left undisturbed.

Table S5: Crystallisation of $Cu(NO_3)_2.3H_2O$ and isonicotinic acid-*N*-oxide in presence of hydrogelators

Exp no	$Cu(NO_3)_2.3H_2O$ (amount in mg)	Isonicotinic acid-*N*-oxide (amount in mg)	Gelator (amount in mg)	Solvent (in mL)	Initial Observation	Final Observation
1	25.0	28.8	agarose (12.0)	water (2.0)	Gel	No crystals
2	28.8	35.0	agarose (12.0)	water (2.0)	Gel	Blue crystals (I)
3	37.0	45.0	agarose (12.0)	water (2.0)	Gel	Blue crystals (I)
4	45.2	55.0	agarose (12.0)	water (2.0)	Gel	Precipitate
5	25.0	28.8	agarose (12.0)	EtOH (1.0)/water (1.0)	Gel	No crystals
6	28.8	35.0	agarose (12.0)	EtOH (1.0)/water (1.0)	Gel	Blue crystals (I)
7	37.0	45.0	agarose (12.0)	EtOH (1.0)/water (1.0)	Gel	Blue crystals (I)
8	45.2	55.0	agarose (12.0)	EtOH (1.0)/water (1.0)	Gel	Precipitate
9	25.0	28.8	agarose (12.0)	EtOH (2.0)	Suspension	No crystals
10	25.0	28.8	agarose (12.0)	EtOH (2.0)	Suspension	No crystals
11	25.0	28.8	Gelatin (50.0)	water (2.0)	Solution	No crystals
12	25.0	28.8	Gelatin (70.0)	water (2.0)	Gel	No crystals
13	37.0	45.0	Gelatin (70.0)	water (2.0)	Gel	Precipitate
14	25.0	28.8	Gelatin (50.0)	EtOH (1.0)/water (1.0)	Solution	No crystals
15	25.0	28.8	Gelatin (70.0)	EtOH (1.0)/water (1.0)	Solution	No crystals
16	45.2	55.0	Gelatin (70.0)	EtOH (1.0)/water (1.0)	Solution	Precipitate
17	25.0	28.8	Gelatin (50.0)	EtOH (2.0)	Suspension	No crystals
18	25.0	28.8	Gelatin (70.0)	EtOH (2.0)	Suspension	No crystals

8.2 In Low molecular weight gelators

We tried gel phase crystallisation in LMWGs based on trimesic amide of *L*-valine methyl ester.[1] In a typical experiment, isonicotinic acid-*N*-oxide and the gelator **Val-TMA** was dissolved in organic solvent, then an aqueous $Cu(NO_3)_2.3H_2O$ solution was added to it. It was sonicated and left undisturbed to form the gel. Blue crystals of form-I were obtained from these gels (characterized by SCXRD).

Table S6: Crystallization of $Cu(NO_3)_2.3H_2O$ and isonicotinic acid-*N*-oxide in presence of LMWGs

Exp. no	$Cu(NO_3)_2.3H_2O$ (mg)	Isonicotinic acid-*N*-oxide (mg)	Gelator (mg)	Solvents (mL)	Observation
1	24.1	27.8	**Val-TMA** (40.0)	DMF (0.5)/ water (0.5)	Blue crystals
2	24.1	27.8	**Val-TMA** (40.0)	DMSO (0.5)/ water (0.5)	No crystals
3	24.1	27.8	**Val-TMA** (40.0)	EtOH (0.5)/ water (0.5)	Blue crystals
4	24.1	27.8	**Val-TMA** (40.0)	EtOH (0.9)/ water (0.1)	Blue crystals

8.3 In tailored gel

Crystallisation of $Cu(NO_3)_2.3H_2O$ and isonicotinic acid-*N*-oxide was further investigated in presence of *N*-oxide gelator. In a typical experiment, isonicotinic acid-*N*-oxide (2 equivalent) and the *N*-oxide gelator were dissolved together in high polar organic solvent, and water was added. Then $Cu(NO_3)_2.3H_2O$ (1 equivalent) was added to this solution and the mixture was sonicated and left undisturbed.

Since the crystallisation depends on concentration of $Cu(NO_3)_2.3H_2O$ and isonicotinic acid-*N*-oxide, first we varied metal and ligand concentration in **L-3Nox** gel in 1:1 (v/v) DMSO-water.

Table S7: Crystallization of $Cu(NO_3)_2.3H_2O$ and isonicotinic acid-*N*-oxide in **L-3Nox** gel

L-3Nox (mg)	$Cu(NO_3)_2.3H_2O$	isonicotinic acid-*N*-oxide	Solvents (mL)	Observation after 24 h	Final observation
8.0 mg	6.0 mg	6.9 mg	DMSO (0.5)/water (0.5)	Gel	No crystal
8.0 mg	8.0 mg	9.2 mg	DMSO (0.5)/water (0.5)	Gel	No crystal
8.0 mg	10.0 mg	11.5 mg	DMSO (0.5)/water (0.5)	Gel	No crystal
8.0 mg	12.0 mg	13.8 mg	DMSO (0.5)/water (0.5)	Gel	No crystal
8.0 mg	14.0 mg	16.1 mg	DMSO (0.5)/water (0.5)	Gel	Blue crystals
8.0 mg	16.0 mg	18.4 mg	DMSO (0.5)/water (0.5)	Gel	Blue crystals
8.0 mg	18.0 mg	20.7 mg	DMSO (0.5)/water (0.5)	Gel	Blue crystals
8.0 mg	20.0 mg	23.0 mg	DMSO (0.5)/water (0.5)	Gel	Blue crystals
8.0 mg	24.0 mg	28.0 mg	DMSO (0.5)/water (0.5)	Gel	Blue crystals

We performed the crystallization of $Cu(NO_3)_2.3H_2O$ and isonicotinic acid-*N*-oxide with tailored **L-3Nox** gelator in various DMSO/water composition. Isonicotinic acid-*N*-oxide (27.8 mg, 0.2 mmol) and required amount (above MGC) of N-oxide gelator were dissolved together in DMSO, and water was added. To this mixture $Cu(NO_3)_2.3H_2O$ (24.1 mg, 0.1 mmol) was added and sonicated, left undisturbed for gel formation.

Table S8: Crystallisation of $Cu(NO_3)_2.3H_2O$ and isonicotinic acid-*N*-oxide in **L-3Nox** gel at various DMSO/water composition

N-oxide gelator	Amount	DMSO (mL)	Water (mL)	Observation after 24 h	Final observation
L-3Nox	8.0 mg	1.0	-	Clear solution	no crystal
L-3Nox	8.0 mg	0.9	0.1	Colloidal	no crystal
L-3Nox	8.0 mg	0.8	0.2	Gel	no crystal
L-3Nox	8.0 mg	0.7	0.3	Gel	blue crystal*
L-3Nox	8.0 mg	0.6	0.4	Gel	blue crystal*
L-3Nox	8.0 mg	0.5	0.5	Gel	blue crystal*

*(form-I), unit cell matched.

9. References

1. Y. Ishioka, N. Minakuchi, M. Mizuhata and T. Maruyama, *Soft Matter*, 2014, **10**, 965-971.

2. D. K. Kumar, D. A. Jose, P. Dastidar and A. Das, *Chem. Mater.*, 2004, **16**, 2332-2335.