Metal 'Turn-off', Anion 'Turn-On' Gelation Cascade in Pyridinylmethyl Ureas

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Supplementary information

All starting materials were purchased from Aldrich or Fisher Scientific and required no purification. NMR spectra were acquired using a Bruker Avance 400 spectromerter. Electrospray ionisation mass spectrometry was performed on 1 mg mL⁻¹ methanol or acetonitrile solutions using a Walter Ltd. TQD mass spectrometer. FT-IR spectra attained for solid samples were recorded over 16 scans on a Perkin Elmer Spectrum 100 series spectrometer from 4000 cm⁻¹ to 550 cm⁻¹ at a resolution of 1 or 0.5 cm⁻¹. Elemental analysis was preformed using an Exeter CE-440 Elemental Analyser. All samples submitted were dried for four hours under vacuum in an Abderhalden drying pistol.

Synthesis of 1-Butyl-3-pyridin-3-ylmethyl-urea (L1)



3-Picolylamine (1.00 mL, 9.82 mmol) and *n*-butyl isocyanate (1.11 mL, 9.82 mmol) were added to chloroform (50 mL). The solution was put under nitrogen and refluxed at 70 °C for 4 hours. The solvent was evaporated off *in vacuo*, and the resulting white solid was washed with water and dried *in vacuo* at ~ 50 °C for 4 hours (0.70 g, 34 %).

¹H NMR (400 MHz, DMSO- d_6) δ 0.87 (3H, t, J = 7.2 Hz, C(11) H_3), 1.42 – 1.19 (4H, m, C H_2), 3.00 (2H, td, J = 6.8, 5.6 Hz, C(8) H_2), 4.21 (2H, d, J = 6.0 Hz, C(6) H_2), 5.97 (1H, t, J = 5.7 Hz, NHC(8)H₂), 6.36 (1H, t, J = 6.2 Hz, NHC(6)H₂), 7.34 (1H, ddd, J = 7.8, 4.8, 0.9 Hz, C(3)H), 7.64 (1H,dt, J = 7.9, 2.0 Hz, C(4)H), 8.49 – 8.40 (2H, m, Ar-H); ¹³C NMR (101 MHz, DMSO) δ 14.19 (C(11)H₃), 19.98, 32.59, 39.48, 41.05, 79.65, 123.81, 135.26, 136.95, 148.27, 149.05, 158.50 (C=O); Anal. Calc. C 63.74, H 8.27, N 20.27. Anal. Found. C 62.69, N 19.94, H 8.14;ES⁺-MS (m/z) 208.1 [M+H]⁺; ES⁻MS (m/z) 206.9 [M-H]⁻; FT-IR (v_{max} /cm⁻¹) 3339 (N-H stretch), 3307 (N-H stretch), 3035 (aromatic C-H stretch), 2960 (aliphatic C-H stretch), 2932 (aliphatic C-H stretch), 2874 (aliphatic C-H stretch), 2861 (aliphatic CH), 1614 (C=O stretch), 1568s (aromatic ring stretch).

Synthesis of ligands L2 - L5.

Ligands **L2 – L5** where synthesised *via* reaction of 3-picolyamine with an equimolar amount of the relevant isocyanate. 3-Picolylamine and the corresponding isocyanate were added to toluene (5 mL). The solution was sonicated for 2 minutes. The resulting solid was collected by filtration, was washed with water then dried in *vacuo* at ~ 50 °C for 4 hours.

1-Octyl-3-pyridin-3-ylmethyl-urea (L2)



Prepared using 3-picolylamine (0.50 mL, 4.91 mmol) and n-butyl isocyanate (0.87 mL, 4.91 mmol). The product is obtained is a white solid (1.19 g, 92 %).

¹H NMR (400 MHz, DMSO-*d*₆) δ 0.90 – 0.82 (3H, m, C(15)*H*₃), 1.37 – 1.20 (10H, m, *CH*₂), 1.36 (2H, s, C(9)*H*₂), 2.99 (2H, td, *J* = 6.9, 5.7 Hz, C(8)*H*₂), 4.21 (2H, d, *J* = 6.0 Hz, C(6)*H*₂), 5.97 (1H, t, *J* = 5.7 Hz, N*H*C(8)H₂), 6.36 (1H, t, *J* = 6.1 Hz, N*H*C(6)H₂), 7.33 (1H, ddd, *J* = 7.8, 4.7, 0.9 Hz, C(3)*H*), 7.63 (1H, dt, *J* = 7.8, 2.0 Hz, C(4)*H*), 8.49 – 8.40 (2H, m, Ar-H); ¹³C{¹H} NMR (101 MHz, DMSO-*d*₆) δ , 14.42 (*C*(15)H₃), 22.56, 26.84, 29.17, 29.23, 30.45, 31.70, 41.03, 123.78, 135.24, 136.94, 148.26, 149.05, 158.48 (C=O); Anal. Calc. C 68.40, H 9.57,N 15.95; Found. C 68.27, H 9.50, N 15.90; ES⁺-MS (*m*/*z*) 264.7 [M+H]⁺,248.0 [M-CH₃]⁺; ES⁻MS (*m*/*z*); 298.4 [M+Cl]⁻; FT-IR (ν_{max} /cm⁻¹) 3346 (N-H stretch), 3313 (N-H stretch), 2960w (aromatic C-H stretch), 2925 (aliphatic C-H stretch), 2874 (aliphatic C-H stretch), 2853 (aliphatic C-H stretch), 1616 (C=O stretch), 1568s (aromatic ring stretch).

1-Dodecyl-3-pyridin-3-ylmethyl-urea (L3)

 $\begin{array}{c} & & \\ & & \\ 3 & {}^{4} & {}^{5} & {}^{6} & {}^{7} & {}^{N} & {}^{8} & {}^{9} & {}^{10} & {}^{12} & {}^{14} & {}^{15} & {}^{16} & {}^{7} & {}^{18} & {}^{19} \\ \\ & \\ 1 & {}^{11} & {}^{11} & {}^{12} & {}^{13} & {}^{14} & {}^{15} & {}^{16} & {}^{17} & {}^{18} & {}^{19} \\ \\ & \\ 2 & {}^{N} & {}^{11} & {}^{11} & {}^{12} & {}^{13} & {}^{14} & {}^{15} & {}^{16} & {}^{17} & {}^{18} & {}^{19} \end{array}$

Prepared using 3-picolylamine (0.50 mL, 4.91 mmol) and dodecyl isocyanate (1.18 mL, 4.91 mmol). The product is obtained is a white solid (1.42 g, 91 %).

¹H NMR (400 MHz, DMSO-*d*₆) δ 0.86 (3H, t, *J* = 6.5 Hz, C(19)*H*₃). 1.24 (18H,s, C*H*₂), 1.35 (2H, t, *J* = 6.7 Hz, C(9)*H*₂), 2.98 (2H, q, *J* = 6.6 Hz, C(8)*H*₂), 4.21 (2H, d, *J* = 6.0 Hz, C(6)*H*₂), 5.96 (1H, t, *J* = 5.7 Hz, NHC(8)H₂), 6.35 (1H, t, *J* = 6.0 Hz, NHC(8)H₂), 7.37 – 7.29 (1H, m, C(3)*H*), 7.63 (1H, dt, *J* = 7.9, 2.0 Hz, C(4)*H*), 8.48 – 8.40 (2H, m, Ar-*H*); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 14.44 (*C*(19)H₃), 22.57, 26.84, 29.18, 29.27, 29.48, 29.52, 30.45, 31.77, 39.46, 39.89, 41.04, 123.80, 135.25, 136.95, 148.26, 149.05, 158.49 (*C*=0); Anal. Calc. C 71.43, H 10.41, N 13.15. Found C 71.46, H 10.38, N 12.98 ES⁺-MS (*m*/*z*) 320.7 [M+H]⁺; ES⁻MS (*m*/*z*) 318.3 [M-H]⁻; FT-IR (ν_{max} /cm⁻¹) 3345 (N-H stretch), 3312 (N-H stretch), 3039 (aromatic C-H stretch), 2962 (aliphatic C-H stretch), 2922s (aliphatic C-H stretch).

1-Phenyl-3-pyridin-3-ylmethyl-urea (L4)



Prepared using 3-picolylamine (1.00 mL, 9.82 mmol) and phenyl isocyanate (1.07 mL, 9.82 mmol). The product is obtained is a cream solid (1.60 g, 71 %).

¹H NMR (400 MHz, DMSO-*d*₆) δ 4.32 (2H, d, *J* = 6.0 Hz, C(6)*H*₂), 6.70 (1H, t, *J* = 6.0 Hz, N*H*C(6)H₂), 6.90 (1H, tt, *J* = 7.3, 1.2 Hz, C(11)*H*), 7.27 – 7.17 (2H, m, C(10)*H*), 7.36 (1H, dd, *J* = 7.8, 4.8, 0.9 Hz, Ar-*H*), 7.42 – 7.38 (2H, m, C(9)*H*), 7.71 (1H, ddd, *J* = 7.8, 2.4, 1.7 Hz, Ar-*H*), 8.46 (1H, dd, *J* = 4.8, 1.7 Hz, C(2)*H*), 8.53 (1H, dd, *J* = 2.3, 0.9 Hz, C(1)*H*), 8.61 (1H, s, Ar-N*H*); ¹³C{¹H} NMR (101 MHz, DMSO-*d*₆) δ 40.92 (*C*(6)H₂), 118.23, 121.64, 123.90, 129.10, 135.42, 136.35, 140.80, 148.46, 149.16, 155.71 (C=O); Anal. Calc. C 68.70, H 5.77, N 18.49. Found 68.60, H 5.72, N 18.55; ES⁺-MS (*m*/*z*) 259.4 [M+MeOH]⁺, 250.3 [M+Na]⁺ 227.5 [M+H]⁺; ES⁻MS (*m*/*z*) 225.3 [M-H]⁻; FT-IR (ν_{max} /cm⁻¹) 3343 (N-H stretch), 3306 (N-H stretch), 3095 (aromatic C-H stretch), 2963 (aliphatic C-H stretch),

2932 (aliphatic C-H stretch), 2874 (aliphatic C-H stretch), 2872 (aliphatic C-H stretch), 1612 (C=O stretch), 1571s (aromatic ring stretch).

1-Benzyl-3-pyridin-3-ylmethyl-urea (L5)

$$\begin{array}{c} & & \\ & & \\ 3 \\ 3 \\ 1 \\ 1 \\ 2 \\ N \end{array} \begin{array}{c} & & \\$$

Prepared using 3-picolylamine (1.00 mL, 9.82 mmol) and benzyl isocyanate (1.21 mL, 9.82 mmol). The is obtained is a white solid (1.52 g, 64 %).

¹H NMR (400 MHz, DMSO- d_6) δ 4.24 (4H, dd, J = 10.3, 6.0 Hz, CH_2 NH), 6.53 (2H, q, J = 6.2 Hz, NH), 7.38 – 7.18 (6H, m, Ar-H), 7.69 – 7.62 (1H, m, C(4)H), 8.44 (1H, dd, J = 4.8, 1.7 Hz, Ar-H), 8.48 (1H, dd, J = 2.3, 0.8 Hz, Ar-H); ¹³C NMR (101 MHz, DMSO- d_6) δ 40.92 (CH_2 NH), 118.23, 121.64, 123.90, 129.10, 135.42, 136.35, 140.80, 148.46, 149.16, 155.71 (C=0), Anal. Calc. C 69.69, H 6.27, N 17.41. Found C 69.56, H 6.19, N 17.44; ES⁺-MS (m/z) 246.3 [M+Na], 242.4 [M+H]⁺; ES⁻MS (m/z) 277.1 [M+Cl]⁻; FT-IR (ν_{max}/cm^{-1}) 3349 (N-H stretch), 3298 (N-H stretch), 3035 (aromatic C-H stretch), 2911 (aliphatic C-H stretch), 1623 (C=O stretch), 1563s (aromatic ring stretch).

Gelation Tests

Gelation tests on the ligands were carried out at 2.5 % by weight of gelator to volume of solvent used. 10 mg of gelator was added to 0.40 mL of solvent in a S1.75 vial (2 mL, 12 mm diameter) then sonicated for 30 seconds. The sample was then heated until a homogeneous solution was observed then left to cool for 1 hour. After cooling the contents of the vial was assigned as a gel, partial gel, crystal, precipitate or solution.

Formation of Metallogels

Gelation of metallogels was also carried out at 2.5 % by weight of gelator to volume of solvent. 10 mg of gelator was added to 0.39 mL of solvent and 0.01 mL of a metal solution composed of either 1 or 2 equivalents of metal salt dissolvent in methanol. Gelation was tested in the solvents toluene, 1,3-dichlorobenzene and nitrobenzene. The same procedure

as for ligand gelation tests previously mentioned was used for heating, cooling and characterisation.

Rheology

Oscillatory stress-sweep experiments were performed using a TA Instruments AR Rheometer 2000 or TA Instruments Discovery Hybrid rheometer HR 2 with a parallel plate set up using a 25 mm rough plate geometry. Experiments were carried out at 10 °C and a fixed frequency of 1 Hz. When preparing the sample, 2 mL of hot gelator solution was transferred to a glass cylinder sealed with vacuum grease to prevent spillage from the sol. The sol was left for 30 minutes to allow the gel to form after which the glass cylinder was removed and the gap reduced to 2500 µm before date collection.

Scanning Electron Microscopy

Samples of 1% (w/v) gels were applied to silicon plates and left to dry in air at room temperature for 24 h. The resulting xerogels were coated with 2 nm platinum using a Cressington 328 Ultra High Resolution EM Coating System. The images were obtained using an FEI Helios NanoLab DualBeam microscope in immersion mode, with beam settings of 1.5 kV and 0.17 nA. For images of less than 2500 magnification (labelled ETD) immersion mode was not used.

Fourier Transform Infrared Spectroscopy of Xerogels

Xerogels where obtained by transferring a small amount of a preformed gel to a watch glass and leaving it for a week to air-dry.

Single Crystal X-ray Diffraction

Crystals of **L5** were obtained by heating 10 mg of the ligand in 0.40 mL of methanol until homogeneous. The solution was left for a week to allow the solvent to evaporate resulting in clear needle like crystals. Crystals of the complex $[Zn(L4)_2Cl_2]$ were obtained by heating 10 mg of L4 with 2 equivalents of $ZnCl_2$ (dissolved in 0.01 mL methanol) in 0.40 mL of water for

approximately 1 minute. The solution was left for 3 weeks over which time clear square shaped crystals formed.

Crystal data for N₃OC₁₄H₁₅, *M* = 241.29 g mol⁻¹, clear colourless block, 0.316 × 0.262 × 0.124 mm³, monoclinic space group *P*2₁, a = 4.5886(16) Å, b = 24.220(7) Å, c = 5.7302(18) Å, α = 90 °, θ = 106.572(17) °, γ = 90 °, V = 610.4(5) Å³, Z = 2, Z' = 1, *D*_c = 1.312 g/cm³, *F*₀₀₀ = 256, Bruker APEX-II CCD, MoKα radiation, λ = 0.71073 Å, *T* = 120K, 2 θ _{max} = 66.6^o, 7874 reflections collected, 3670 unique (R_{int} = 0.0432). Final *GooF* = 1.023, *R1* = 0.0586, *wR2* = 0.1119, *R* indices based on 2680 reflections with I > 2σ(I) (refinement on *F*²), 163 parameters, 1 restraint. Lp and absorption corrections applied, μ = 0.086 mm⁻¹. Absolute structure parameter = 0.1(8) (Flack, H. D. *Acta Cryst.* **1983**, *A39*, 876-881).

Crystal data for C₂₆H₂₆Cl₂N₆O₂Zn, M = 590.80 g mol⁻¹, colourless block, 0.611 × 0.249 × 0.166 mm³, space group *Pnma*, V = 2574.7(3) Å³, Z = 4, $D_c = 1.524$ g/cm³, $F_{000} = 1216$, Bruker APEX-II CCD, MoK α radiation, $\lambda = 0.71073$ Å, T = 120(2)K, $2\theta_{max} = 71.2^{\circ}$, 48921 reflections collected, 5717 unique (R_{int} = 0.0737). Final *GooF* = 1.057, *R1* = 0.401, *wR2* = 0.840, *R* indices based on 4179 reflections with I > 2 σ (I) (refinement on F^2), 180 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.198$ mm⁻¹.

Rheology



Figure S1 2% w/v gel of L3 in toluene.



Figure S2 2% w/v **L2** in toluene



Figure S3 2% w/v L3 in nitrobenzene



Figure S4 2% w/v L3 in 1,3-dichlorobenzene





Figure S5 SEM image of a xerogels of **L2** obtained from (top to bottom) nitrobenzene, odichlorobenzene, toluene





Figure S6 SEM image of a xerogels of **L3** obtained from (top to bottom) nitrobenzene, odichlorobenzene and toluene.

Table S1 Free ligand gelation tests

Solvent	Results of gelation test 10 mg ligand and 0.40 mL solvent							
	L1	L2	L3	L4	L5			
acetic acid								
Acetone	S	S	PG	S	S			
Acetonitrile	S	S	S	S	S			
Butan-1-ol								
1,3-dichlorobenzene	S	G	G	Р	Р			
Chloroform	S	S	S	S	S			
DMSO	S	S	S	S	S			
Methanol	S	S	S	S	S			
Nitrobenzene	PG	PG	G	S	S			
THF			S					
Toluene	PG	G	G	Р	С			
Ethanol	Р	S	S	S	S			
Water	IS	IS	IS	IS	IS			



Figure S7 2.5 % w/v gels formed from **L3** in (left to right): toluene, 1,3-dichlorobenzene and nitrobenzene.

S = Solution

G = Gel

IS = Insoluble

C = Crystals

P = Precipitate

PG = Partial gel (not all solvent gelled)

Table S2. Elemental analysis data.

Metal	Expected formula	Calculated			Found		
		% C	% H	% N	% C	% H	% N
ZnCl ₂	Zn L3 ₂ Cl ₂	58.87	8.58	10.84	59.54	8.69	10.85
CuCl ₂	Cu L3 ₂ Cl ₂	59.01	8.60	10.87	58.62	8.49	10.76
CuCl ₂	$CuL3_2Cl_2(H_2O)_2$	56.39	8.22	10.38	56.63	8.22	10.46
Green precipitate							
formed from 1:1							
gel							



Figure S8: Metallogel (A) formed from **L2** and CuCl₂ (1:1), which gradually turns into a blue solution (B). Metallogel (C) formed from **L3** and CuCl₂ (1:0.9) which turns into a green precipitate (D).



Figure S9 Comparison of oscillatory stress sweep data for metallogels formed by ligand L3 in nitrobenzene. The ligand to metal ratio in all metallogels is 2:1. Red) CuCl₂, Purple) CoCl₂, Green) AgBF₄ and Blue) No metal added.



Figure S10. UV-Vis spectra of a 2:1 solution of **L3** and cobalt(II) nitrate in methanol before (red) and after (blue) addition of two equivalents relative to cobalt of tetrabutylammonium bromide.