A Highly Efficient Red-Emitting Luminescent Paper-Based Sensor for Hydrogen Sulfide

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Experimental Procedures

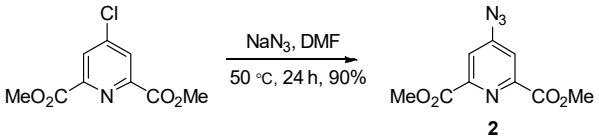
Synthetic Materials and Methods. All chemicals were purchased from Merck-Sigma-Aldrich unless otherwise specified and used without further purification. The Cu^{2+} source was $Cu(NO_3)_2.5H_2O$ (Cat. # 1027900250). $Cs[Eu(dipic)_3]$ was synthesised according to reference 1. Flash chromatography was performed using Merck 38 Silica gel 60, 230−400 mesh ASTM. Thin layer chromatography (TLC) was performed on Merck Silica Gel 60 F254 plates. TLC plates were visualised using a UV lamp at 254 nm or through the use of vanillin, $KMnO_4$ or ninhydrin staining agent. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker DRX400 spectrometer operating at 400 MHz, as solutions in deuterated solvents as specified. Each resonance was assigned according to the following convention: chemical shift; multiplicity; observed coupling constants (*J* in Hz) and number of protons, the abbreviations of s, d, t, br. and m denote singlet, doublet, triplet, broad and multiplet respectively. Chemical shifts (δ), measured in parts per million (ppm), are reported relative to the residual proton peak in the solvent used as specified. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker DRX400 spectrometer operating at 100 MHz unless otherwise stated, as solutions in deuterated solvents as specified. Chemical shifts (δ), measured in parts per million (ppm), are reported relative to the residual proton peak in the solvent used as specified. High resolution mass spectrometry (HRMS) was conducted using a Bruker BioApex 47e FTMS fitted with an analytical electrospray source using NaI for accurate mass calibration (ESI). Low resolution mass spectrometry (LRMS) was conducted using a Micromass Platform II QMS (ESI). Infrared spectra (IR) were recorded on an Agilent Technologies Cary 630 FTIR as thin films of compressed powders. The filter paper used to make the filter paper discs was ADVANTEC® Whatman filter paper Grade 2, circles 42.5 mm diameter.

The oven used to dry the filter papers was Universal Oven U by MEMMERT with a temperature range up to 300ºC.

An Advanced Calibration Designs (ACD) Cal2000 equipped with the required gas generating cell was used to generate gaseous H_2S, gaseous HCN or gaseous Cl_2. Other gases were obtained from 80% O_2/ 20% CO_2 (gas cylinder), air (in-house) and N_2 (in-house),

UV-Visible absorption spectrum was recorded at room temperature using a Varian Cary 1E UV-Visible spectrophotometer. A cell with a path length of 10 mm was used. Luminescence emission spectra of aqueous solutions were recorded at 23 °C using a Varian Cary-Eclipse fluorescence spectrophotometer set to phosphorescence mode. A quartz cell with a path length of 10 mm and a volume of 400 µL was used, the instrument excitation and emission slit widths were both set at 5 nm. The luminescence emission spectra of the paper discs were recorded in 96-well white opaque microplates at 23 °C using a Varian Cary-Eclipse fluorescence spectrophotometer equipped with the microplate reader accessory set to phosphorescence mode. In all cases the delay time used was 0.1

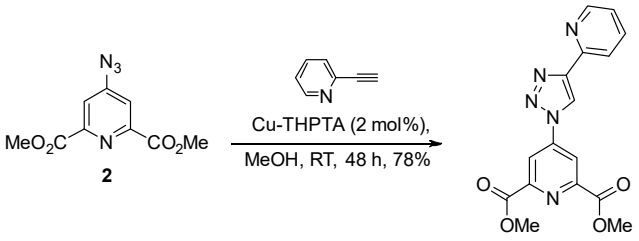
ms and the gate time was 1 ms. The paper discs were placed in the same wells for each reading to ensure that instrument variations were removed from the analysis.



2

4-Dimethylazidopyridine-2,6-dicarboxylate (2):[2]

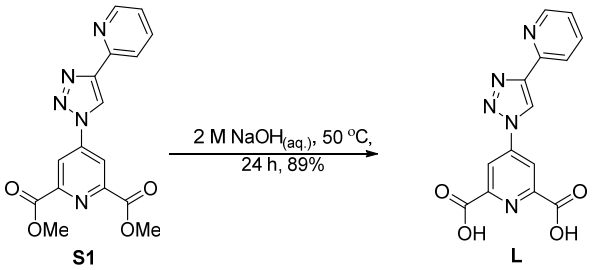
A solution of sodium azide (1.19 g, 18.30 mmol,) and dimethyl 4-chlorodipicolinate (500 mg, 2.18 mmol) in DMF (7 mL) was heated to 50 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into water (18 mL), the resulting precipitate filtered and the mother liquid was extracted with DCM (5 x 10 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed *in vacuo* to obtain a yellow oil. This oil was stirred in water (5 mL) for 30 min and then it was extracted using ethyl acetate (3 x 60 mL). The organic phases were combined, dried over $MgSO_4$, and concentration *in vacuo* to give compound **2** (463 mg, 90%).^{1}H NMR (400 MHz, DMSO-d_6): δ 7.87 (br. s, 2H), 3.92 (s, 6H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ: 164.1, 151.2, 149.1, 118.1, 52.8 ppm. HRMS (ESI): calcd. $[M+H]^+$: 237.0650, found: 237.0611.



2 **S1**

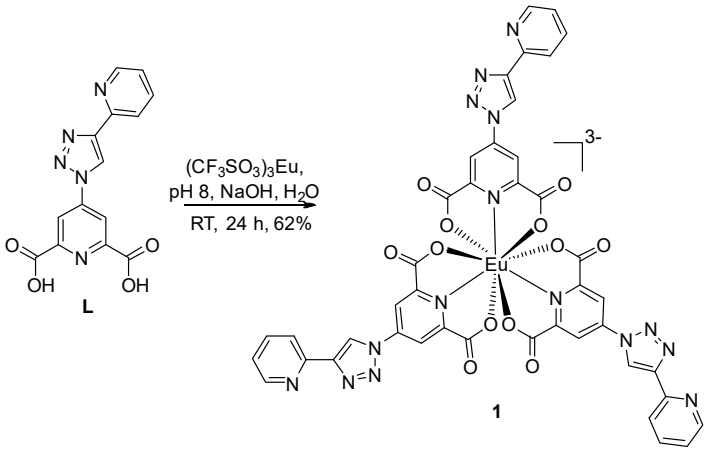
Dimethyl 4-(4-(pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)pyridine-2,6-dicarboxylate (S1):[3]

To a solution of **2** (0.73 g, 3.09 mmol) in methanol (60 mL) was added 2-ethynylpyridine (0.48 g, 4.648 mmol), followed by 0.1 M Cu-THPTA (tris(3-hydroxypropyltriazolylmethyl)amine) (1.2 mL, 2 mol%) and 0.1 M ascorbic acid (5 mL, 8 mol%). After the reaction mixture was stirred at room temperature for 48 h the resulting precipitate was filtered, washed with cold methanol (30 mL) and dried *in vacuo* to give compound **S1** (0.82 g, 78%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.87 (s, 1H), 8.90 (s, 2H), 8.68 (d, J = 3.9 Hz, 1H), 8.13 (d, J = 7.8 Hz, 1H), 7.97 (td, J = 7.8 and 1.6 Hz 1H), 7.43 (br. dd, J = 7.1 and 4.9 Hz, 1H), 3.98 (s, 6H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6) δ: 164.4, 150.3, 150.2, 149.4, 149.3, 145.4, 137.9, 122.6, 120.6, 117.9, 53.5 ppm HRMS (ESI): calcd. for $[M+H]^+$: 340.1046, found 340.1028.



4-(4-(Pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)pyridine-2,6-dicarboxylic acid (L):[3]

To a solution of **S1** (0.70 g, 4.62 mmol) in water (5 mL) was added 2 M $NaOH_{(aq)}$ (4.5 mL) and the reaction mixture was stirred for 24 h at 50 °C. After cooling to room temperature, 1 M $HCl_{(aq)}$ (2 mL) was added and the resulting precipitate was filtered, washed with cold water and dried *in vacuo*. The product **L** was obtained as a solid (0.57 g, 89%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.82 (s, 1H), 8.84 (s, 2H), 8.68 (d, *J* = 4.2 Hz, 1H), 8.13 (br. d, *J* = 7.8 Hz, 1H), 7.97 (td, *J* = 7.7 and 1.7 Hz, 1H), 7.43 (ddd, *J* = 7.5, 4.8 and 1.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 150.8, 149.9, 148.9, 148.8, 144.8, 137.4, 123.6, 122.1, 120.2, 116.9 ppm. HRMS (ESI): calcd. for $[M-H]^-$: 310.0576, found: 310.0560.



Europate(III), tris[4-(4-(pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)-2,6-pyridinedicarboxylato-*κN*^{4},*κO*^{2},*κO*^{6}], tris-sodium salt, $[EuL_3]Na_3$ 1:

To a solution of **L** (150 mg, 0.5 mmol) in water (6 mL) was added 0.5 M $NaOH_{(aq.)}$ to achieve a pH of 8. To this was added a solution of $(CF_3SO_3)_3Eu$ (100 mg, 0.166 mmol) in water (2 mL) and the resulting solution was stirred at room temperature for 24 h, ensuring that the pH was consistently at 8 by the dropwise addition of 0.5 M $NaOH_{(aq.)}$. After 24 h the resulting suspension was centrifuged, and the obtained precipitate was washed with water (20 mL). The precipitate was then freeze dried to remove residual water. The product **1** was obtained as white solid (102 mg, 62%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.56 (s, 3H), 8.48 (d, *J* = 4.8 Hz, 3H), 7.80 (m, 6H), 7.25 (t, *J* = 7.3, 3H), 5.68 (s, 6H) ppm. IR (ATR): 3367, 2289, 1592, 1415, 1047, 759 cm^{-1} HRMS (ESI): calcd. for $[M+2Na]^-$:

1124.04934, 1125.05270, 1126.05073, 1127.05408; found: 1124.04880, 1125.05092, 1126.0502, 1127.05263.

Luminescence studies – Analysis of aqueous solutions:

Cu^{2+}-dependent luminescence spectra. A solution of **1** (5 μM), in 10 mM Tris-HCl buffer (pH 7.4, containing 5% DMSO), was incrementally spiked with a standard solution of 1 M $Cu(NO_3)_2.5H_2O_{(aq.)}$ over the concentration range of 0–50 μM. The time-gated luminescence emission spectra (λ_{ex} = 250 nm) of the solution were recorded after each addition.

In situ **preparation of the $[\mathbf{1}.3Cu^{2+}]^{3+}$ sensor.** Solutions of 5 μM $[\mathbf{1}.3Cu^{2+}]^{3+}$ was prepared by combining a DMSO stock solution of **1** (100 μM) with 1 mM $Cu(NO_3)_2.5H_2O_{(aq.)}$. Solutions were then diluted with the appropriate amount of Tris-HCl buffer (final concentration 10 mM Tris-HCl buffer (pH 7.4), solutions contained 5% DMSO). Solutions were incubated at 23 °C for 5 minutes prior to use.

Sulfide-dependent luminescence spectra. A solution of $[\mathbf{1}.3Cu^{2+}]^{3+}$ (5 μM), in 10 mM Tris-HCl buffer (pH 7.4, containing 5% DMSO), was incrementally spiked with a standard solution of 1 M $Na_2S_{(aq.)}$ over the concentration range of 0–30 μM. The time-gated luminescence emission spectra (λ_{ex} = 250 nm) of the solution were recorded after each addition.

Effect of anions and sulfurous compounds. The time-delayed luminescence emission change of a solution of $[\mathbf{1}.3Cu^{2+}]^{3+}$ (5 μM), in 10 mM Tris-HCl buffer (pH 7.4, containing 5% DMSO), at 615 nm (λ_{ex} = 250 nm) was examined in the absence and presence of 1.0 to 10.0 molar equivalents of various anions. The anions in the form of 1 M aqueous solutions of; NaCl, NaI, $NaHCO_3$, Na_2CO_3, NaClO, $NaNO_2$, NaOAc, Na_2SO_3, Na_2SO_4, $Na_2S_2O_3$, $Na_2S_2O_4$, $Na_2S_2O_5$ and the sulfurous compounds in the form of 1 M aqueous solutions of lipoic acid and gutathione. The change in luminescence emission spectra (λ_{ex} = 250 nm) of the solutions were also investigated after the subsequent addition of 2.0 molar equivalents of 1 M $Na_2S_{(aq.)}$.

Quantum yield of $[\mathbf{Eu\text{-}1}]^{3-}$: The quantum yield ($\phi$) of **1** was determined to be 0.71, using $Cs[Eu(dipic)_3]$ (ϕ = 0.24)[4] as the standard, in water at pH 7.4 at 23 °C, according to the following equation:

$\phi_X = \phi_{ST}(Grad_x/Grad_{ST})\times(\eta_X/\eta_{ST})^2$

where the subscripts X and ST denote sample and standard respectively, Grad is the gradient of plotted integrated luminescence intensity vs absorbance, and η is the refractive index of the solvent.

Limit of detection. Solutions of [**1**.3Cu^{2+}]$^{3+}$ (5 μM) in 10 mM Tris-HCl buffer (pH 7.4, containing 5% DMSO),) were incrementally spiked with a standard solution of $Na_2S_{(aq.)}$ over the concentration range of 0–15 μM, with the time-resolved luminescence emission spectra at 615 nm were recorded after each addition (λ_{ex} = 250 nm). From the measured data, the limit of detection (LoD) (1.1 μM) was calculated from the linear range of the curve (0-15 μM) using 3sB/sensitivity, where sB corresponds to the standard deviation of the blank and the sensitivity is the slope of the least-squares linear fitted luminescence signal *vs* [HS^-] calibration curve (r^2 =0.973).[5]

Stability of the complex in water. The stability of parent tris-DPA lanthanide complexes has been studied by Bünzli and co-workers[4] and Andraud, Maury and co-workers,[6] utilising lifetime experiments. For Eu[$(dpa)_3$]$^{3-}$ the 1:1 species has been reported to be present at < 0.1% for concentrations between 5.6 x 10^{-6} and 1.9 x 10^{-4} M and for this reason we have assumed that the 1:1 species is present at < 0.1%.[4,7] The luminescence decay of a 5 μM solution of **1** in H_2O was obtained by monitoring the emission decay at 615 nm from the average of five independent measurements and analysed according to;

$$I(t) = A.e^{-k1t} + B.e^{-k2t} + C$$

the relative amounts of [EuL_3]$^{3-}$ and [EuL_2]$^-$ were estimated by calculating 0.66*A/(0.66*A+B) and B/(0.66*A+B) respectively,[6] with 0.66 as a correcting coefficient due to the difference of absorption of [EuL_3]$^{3-}$ and [EuL_2]$^-$; A = 61.0, B = 27.2; this equates to the solution containing 60% of [EuL_3]$^{3-}$ and 40% of [EuL_2]$^-$.

Reversibility Studies. A solution of **1** (5 μM), in 10 mM Tris-HCl buffer (pH 7.4, containing 5% DMSO), was incrementally spiked with a standard solution of $Cu(NO_3)_2.5H_2O_{(aq.)}$ (15 μM) followed by $Na_2S_{(aq.)}$ (15 μM) for five cycles. The time-gated luminescence emission spectra (λ_{ex} = 250 nm) was recorded 10 mins after each addition.

Luminescence studies – Analysis of filter paper discs:

Preparation of filter paper discs for analysis of aqueous HS^-. Three filter papers were prepared: i) filter paper doped with **1**; ii) filter paper doped **1** + $Cu^{2+}_{(aq)}$ (3 equiv) and iii) filter paper doped **1** + $Cu^{2+}_{(aq)}$ (3 equiv) + $Na_2S_{(aq)}$ (3 equiv). To filter papers (diameter 4.6 cm) was added a DMSO solution of 100 μM **1** (200 μL) using a hand-held pipette. The filter papers were allowed to air-dry for 24 h,

after which time 300 μM $Cu(NO_3)_2.5H_2O_{(aq.)}$ (200 μL) was drop cast onto the filter paper ii) and iii). After the filter papers were air-dried for 24 h, for filter paper iii) a solution of 300 μM $Na_2S_{(aq.)}$ (200 μL) was drop cast. After each drying procedure, a visual inspection of the filter paper, by illumination with a hand-held UV lamp (λ_{ex} = 254 nm), revealed even surface distribution of the solution. The time-gated luminescence emission spectra of filter paper discs (diameter 0.6 cm) of each filter paper (n=3, λ_{ex} = 250 nm) were measured using a Cary-Eclipse fluorescence spectrophotometer equipped with the microplate reader accessory.

Preparation of filter paper discs impregnated with $[1.3Cu^{2+}]^{3+}$, for analysis of hydrogen sulfide gas ($H_2S_{(g)}$). Filter papers were cut to 0.6 cm diameter discs using a hole punch. The filter paper discs were drop cast with 5 μL of a 100 μM solution of **1** (in DMSO) and 5 μL of a 300 μM solution of $Cu(NO_3)_2.5H_2O$ (in H_2O) using a hand-held pipette. A visual inspection of each filter paper, by illumination with a hand-held UV lamp (λ_{ex} = 254 nm), confirmed even distribution of the solution over the surface of the filter paper. The paper discs were then heated in an oven at 70 °C for 20 min to remove residual H_2O after which the time-gated luminescence emission spectra (λ_{ex} = 250 nm) were measured using a Cary-Eclipse fluorescence spectrophotometer equipped with the microplate reader accessory. The placement of the filter paper discs in a particular well and the orientation within a well were noted so to ensure that the same spot was read every time.

Gaseous hydrogen sulfide-dependent luminescence spectra. Hydrogen sulfide gas ($H_2S_{(g)}$) was generated using the Cal2000 gas generator equipped with a hydrogen sulfide electrochemical generating cell. A flow rate of 0.5 mL/min and 4 min exposure time was used in all cases. Filter paper discs impregnated with $[\mathbf{1}.3Cu^{2+}]^{3+}$, as described above, were exposed to $H_2S_{(g)}$ over the concentration range 0.5–8 ppm (n=3). To expedite sample testing, a "home-made" gas chamber was utilised, enabling three filter paper discs to be exposed to $H_2S_{(g)}$ in the same experiment. After exposure the time-gated luminescence emission spectra (λ_{ex} = 250 nm) were measured using a Cary-Eclipse fluorescence spectrophotometer equipped with a microplate reader.

Caution: H_2S gas is highly toxic, in this experiment the $H_2S_{(g)}$ in the outlet tube was quenched by passing the gas through a solution of sat. $CuSO_{4(aq.)}$ which results in the formation of $CuS_{(s)}$.

Construction of the "home-made" gas chamber. An 81-well cryogenic storage rack, constructed of durable polypropylene [Dimensions with lid: 1.75 x 5.125 x 5.125 inches (H x L x W)], was modified by sealing the four drain holes with glue and addition of an inlet valve (center of the top lid) and outlet valve (bottom corner) (Figure S1). Prior to the experiments the lid and base were sealed with sealing tape and the vessel tested to ensure that the gas was only liberated through the outlet

valve. Using the filter paper discs, several wells were selected and tested to ensure that the variation to their change in luminescence intensity increase was less than 1% between wells. To ensure reproducibility, the same wells were used for all experiments.

Limit of detection. Filter paper discs (diameter 0.6 cm) impregnated with [**1**.3Cu^{2+}]$^{3+}$, as described above, were exposed to varying concentrations of gaseous H_2S (0.5-8 ppm, 0.5 mL/min and 4 min exposure time) and the time-resolved luminescence emission spectra were recorded (λ_{ex} = 250 nm). From the measured data, the LoD (100 ppb) was calculated from the linear range of the curve (0-4 ppm, λ_{ex} = 615 nm) using 3sB/sensitivity, where sB corresponds to the standard deviation of the blank and the sensitivity is the slope of the least-squares linear fitted luminescence signal *vs* [H_2S] calibration curve (r^2 =0.980).[5]

Potential interferent gases. Filter paper discs (diameter 0.6 cm) impregnated with [**1**.3Cu^{2+}]$^{3+}$, as described above, were exposed to various gases (HCN, Cl_2, $NaHCO_3$, 80% O_2/ 20% CO_2, Compressed Air, N_2) and the time-resolved luminescence emission spectra were recorded (λ_{ex} = 250 nm, λ_{ex} = 615 nm). The "home-made" gas chamber was utilised, with filter paper discs exposed to gases at a concentration of 4 ppm for 4 min, at a flow rate of 0.5mL/min. For the gases 80% O_2/ 20% CO_2 (gas cylinder), air (gas cylinder) and N_2 (in-house), the filter paper discs were directly exposed to the respective gas for 4 min.

Response Cycle Studies. A filter paper disc (diameter 0.6 cm) impregnated with [**1**.3Cu^{2+}]$^{3+}$, as described above, was exposed to 4 ppm of gaseous H_2S for 2 min with the flow output placed directly above the filter paper (i.e. not using the "home-made" gas chamber). The flow rate was 0.5 mL/min. After the time-resolved luminescence emission spectrum were recorded (λ_{ex} = 250 nm, λ_{ex} = 615 nm) the filter paper was then left to stand in the fume cupboard for 60 min. The time-resolved luminescence emission spectrum was rerecorded before the same filter papers disc was exposed to gaseous H_2S. The exposure was repeated until no prominent response was observed.

Supporting Figures:

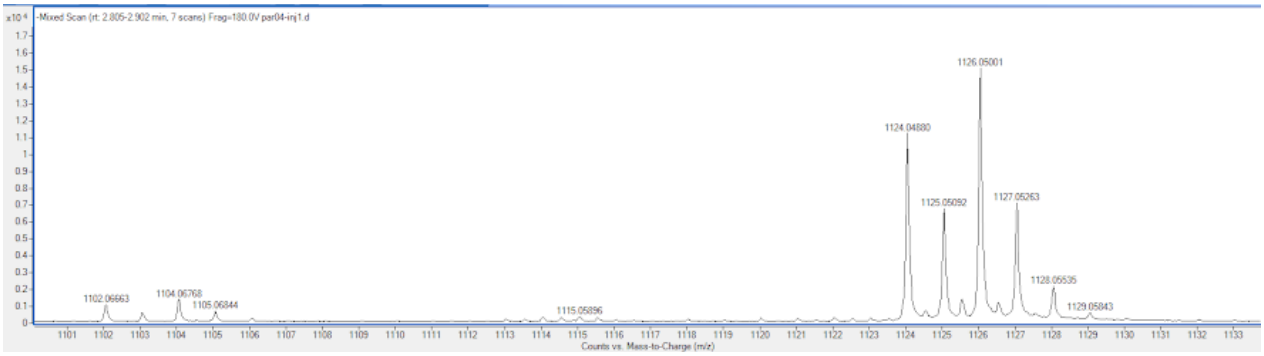


Figure S1. HRMS of [**1**.2Na^{2+}]$^{-}$.

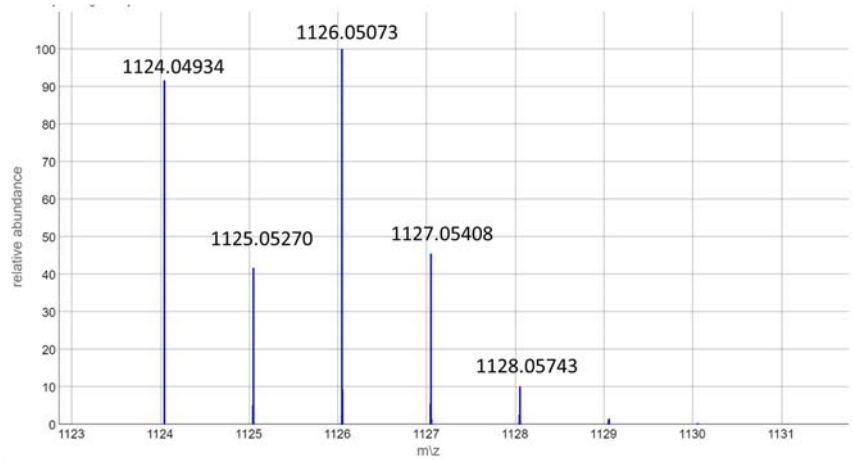


Figure S2. Simulated MS of [**1**.2Na^{2+}]$^{-}$. Determined using https://www.envipat.eawag.ch/index.php

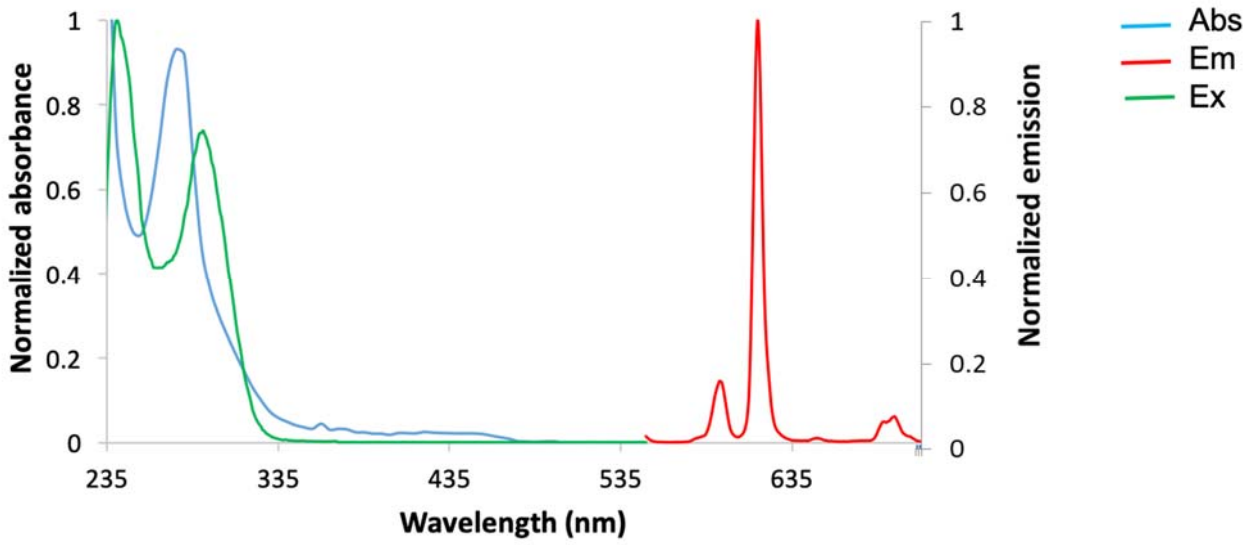


Figure S3. Absorption (blue line), excitation (green line, λ_{em} = 615 nm), and emission (red line, λ_{ex} = 250 nm) spectra of **1** (5 µM), in 10 mM Tris-HCl buffer, pH 7.4, containing 5% DMSO.

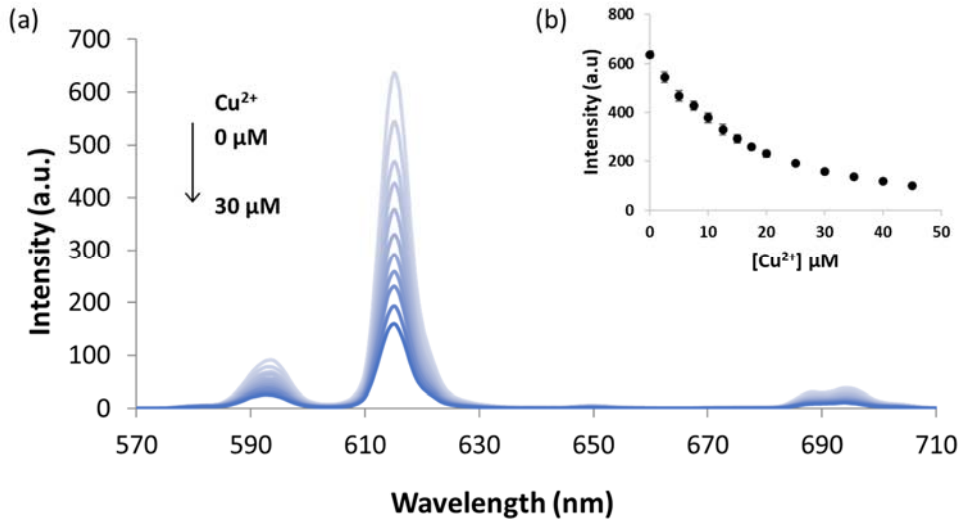


Figure S4. a) Time-delayed emission spectra of an aqueous solution of **1** (5 µM, 10 mM Tris-HCl buffer (pH 7.4) containing 5% DMSO) with the addition of various amounts of Cu^{2+} ions (0 to 30 µM), (b) Luminescent intensity changes detected at 615 nm; spectra measured in 10 mM Tris-HCl buffer (pH 7.4), containing 5% DMSO, λ_{ex} = 250 nm, and showing the average of triplicate results (n=3).

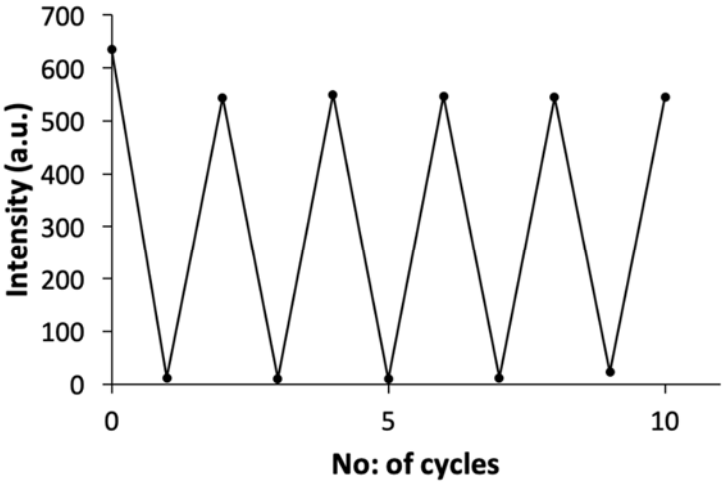


Figure S5. Luminescence intensity of **1** (5 µM) in 10 mM Tris-HCl buffer, pH 7.4, containing 5% DMSO upon the alternate addition of Cu^{2+} (15 µM) ions and Na_2S (15 µM).

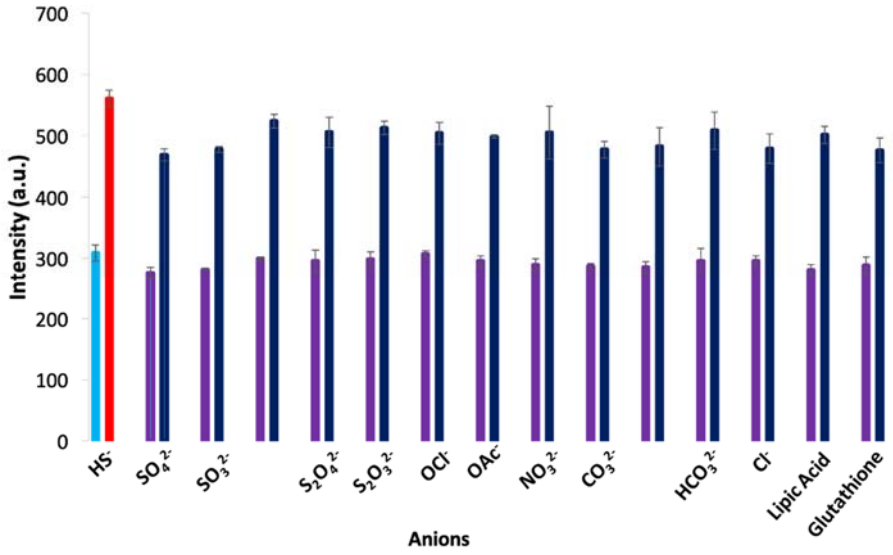


Figure S6. a) Time-delayed emission spectra [**1**.3Cu^{2+}]$^{3+}$ (5 μM) in the presence of various anions; Light blue bar: [**1**.3Cu^{2+}]$^{3+}$ (5 μM); Red bar: [**1**.3Cu^{2+}]$^{3+}$ (5 μM) + Na_2S (15 μM); (Purple bars: [**1**.3Cu^{2+}]$^{3+}$ (5 μM) + anion (50 μM); Dark blue bars: [**1**.3Cu^{2+}]$^{3+}$ (5 μM) + anion (50 μM) + Na_2S (15 μM); spectra measured in 10 mM Tris-HCl buffer (pH 7.4), containing 5% DMSO, λ_{ex} = 250 nm, λ_{em} = 615 nm and showing the average of triplicate results (n=3).

Figure S7 "Home-made" gas chamber with 81 units for the analysis of the filter paper discs impregnated with [**1**.3Cu^{2+}]$^{3+}$.

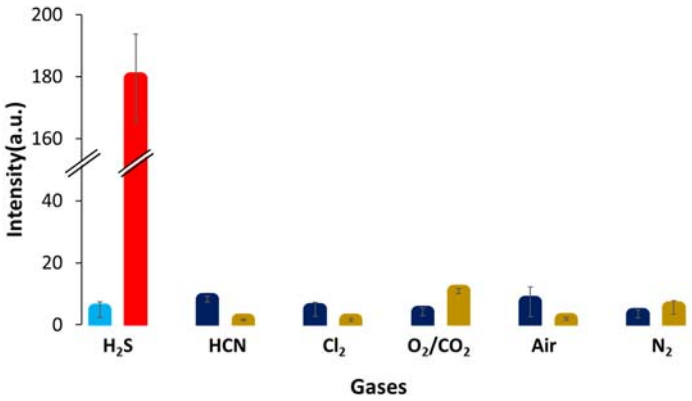


Figure S8. a) Time-delayed emission spectra of filter paper discs impregnated with [**1**.3Cu^{2+}]$^{3+}$ in the presence of various gases; Light blue bar: [**1**.3Cu^{2+}]$^{3+}$; Red bar: [**1**.3Cu^{2+}]$^{3+}$ + H_2S (4 ppm, 0.5 mL/min for 4 min); Dark blue bars: [**1**.3Cu^{2+}]$^{3+f}$ prior to exposure; Brown bars: after exposure to the respective gases [HCN (4 ppm, 0.5 mL/min for 4 min), Cl_2 (4 ppm, 0.5 mL/min for 4 min), O_2/CO_2 (4 min exposure), Air (4 min exposure), N_2 (4 min exposure); spectra measured at λ_{ex} = 250 nm, λ_{em} = 615 nm and showing the average of triplicate results (n=3).

NMR Spectra:

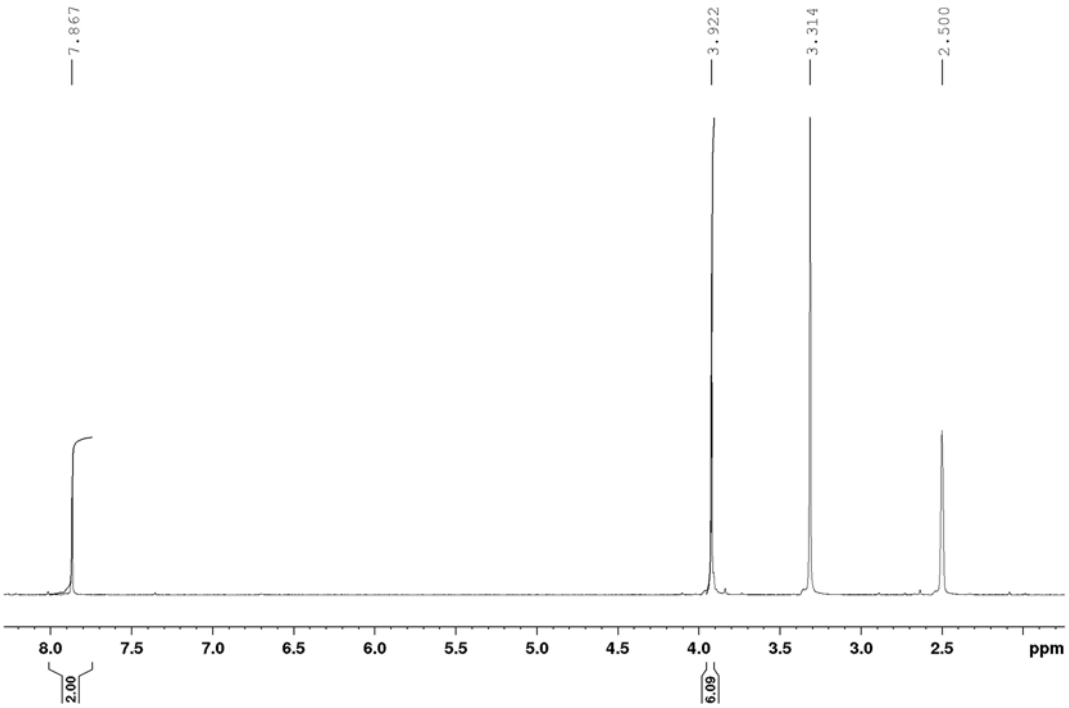


Figure S9. ^{1}H NMR spectrum of 4-dimethylazidopyridine-2,6-dicarboxylate **2** (DMSO-d_6, 400 MHz).

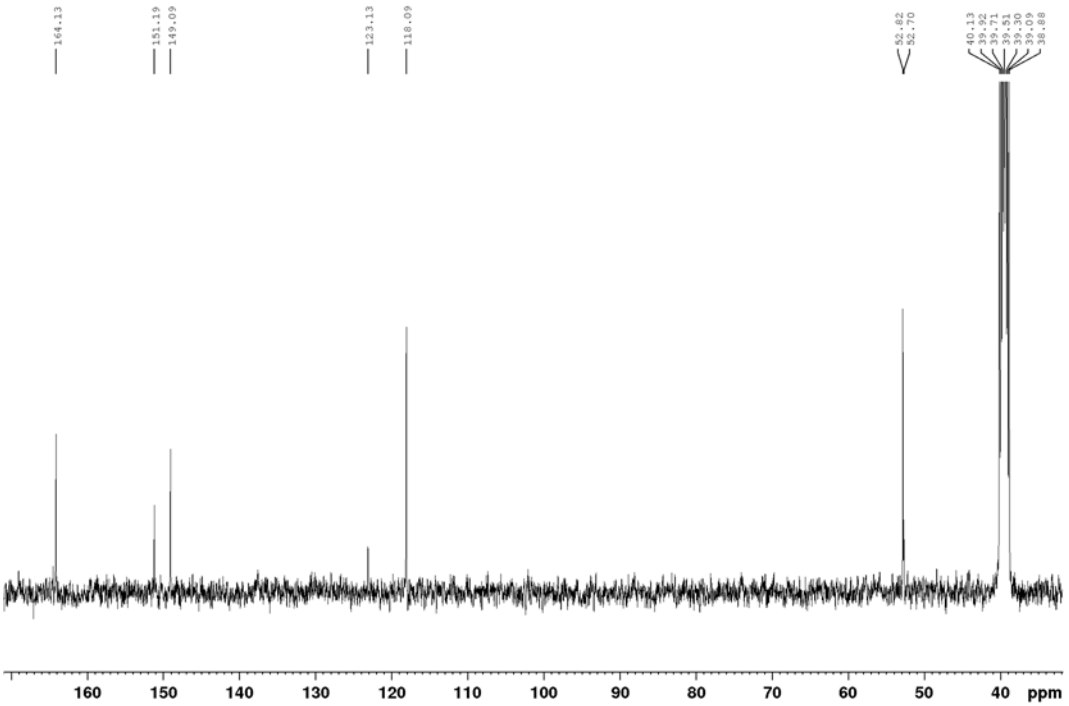


Figure S10. ^{13}C NMR spectrum of 4-dimethylazidopyridine-2,6-dicarboxylate **2** (DMSO-d_6, 100 MHz).

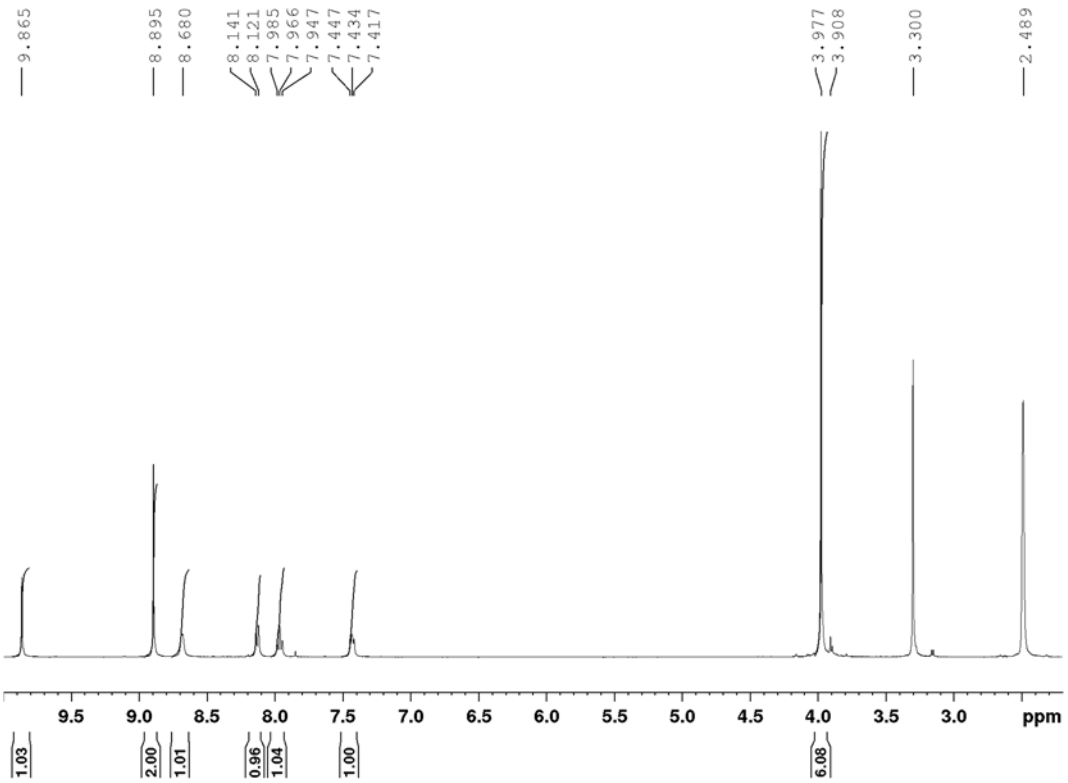


Figure S11. ^{1}H NMR spectrum of dimethyl 4-(4-(pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)pyridine-2,6-dicarboxylate (DMSO-d_6, 400 MHz).

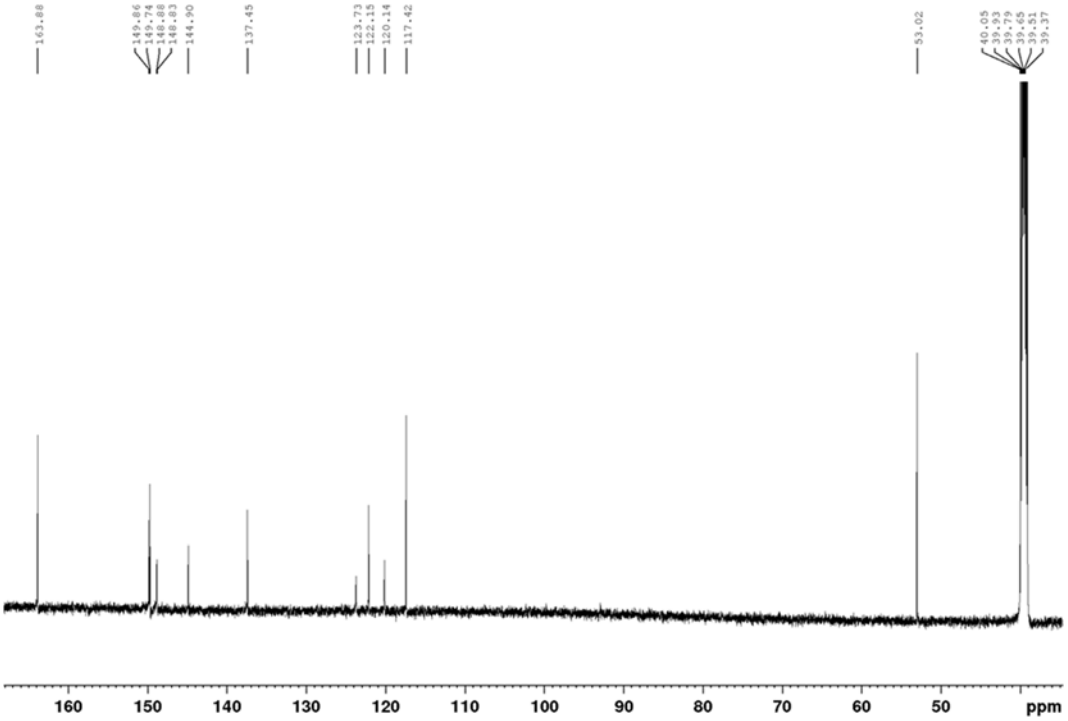


Figure S12: ^{13}C NMR spectrum of dimethyl 4-(4-(pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)pyridine-2,6-dicarboxylate (DMSO-d_6, 150 MHz).

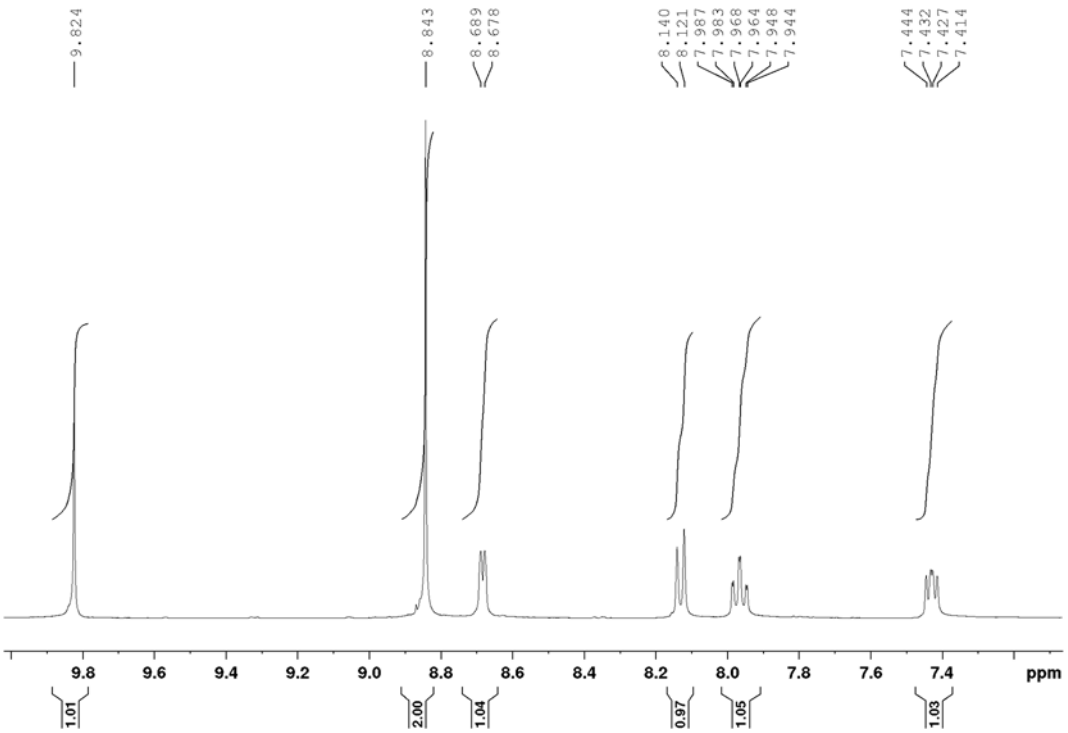


Figure S13. [1]H NMR spectrum of 4-(4-(pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)pyridine-2,6-dicarboxylic acid **L** (DMSO-d_6, 400 MHz).

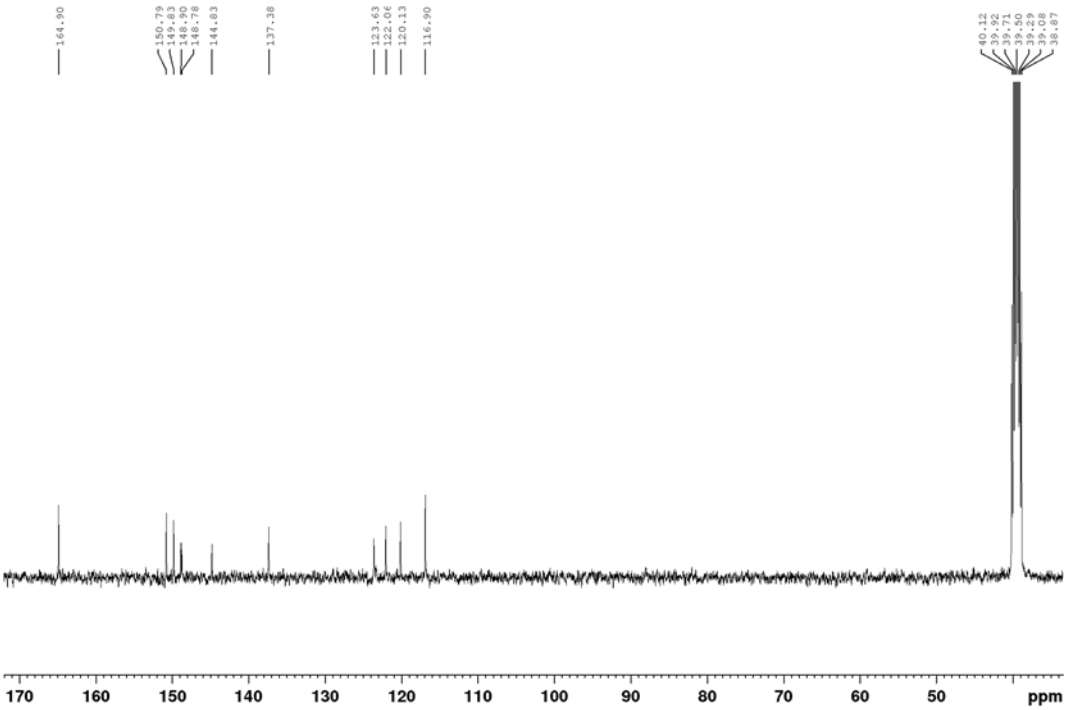


Figure S14. [13]C NMR spectrum of 4-(4-(pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)pyridine-2,6-dicarboxylic acid **L** (DMSO-d_6, 100 MHz)

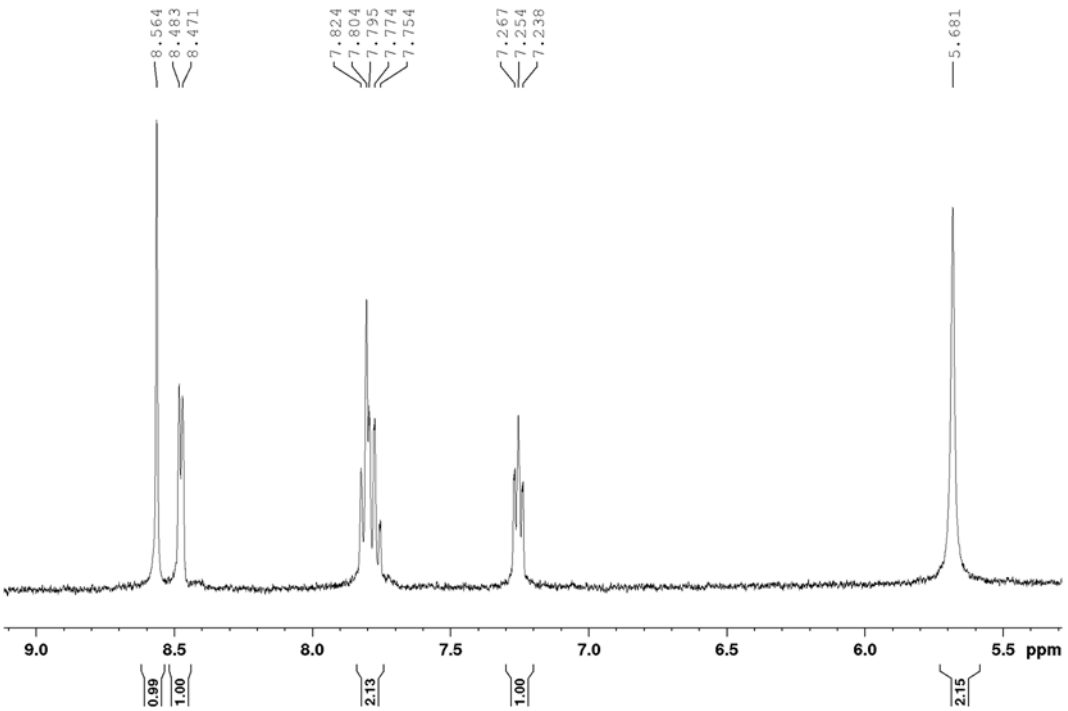


Figure S15. ^{1}H NMR spectrum of **1** (DMSO-d_6, 400 MHz)

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