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Balancing Connectivity with Function in Silver(I) networks of Pyridyltriazole (tzpa) Ligands Results in the Formation of a Metallogel

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A new flexible and divergent 1,2,3-triazol-4-yl-picolinamide (**tzpa**) ligand **2** and the half-equivalent model ligand **1**, both functionalised with pendant 3-pyridyl groups, are reported and their coordination behaviour with silver(I) ions is explored, both in the crystalline phase and through the formation of a supramolecular metallogel. The self-assembly of **tzpa** ligand **1** with AgCF3SO3 resulted in the formation of a 1D coordination polymer, binding in a bidentate fashion through the pyridyl and triazole nitrogen atoms of the **tzpa** binding site and a pendant pyridyl nitrogen atom of an adjacent ligand. Doubling the number of metal binding sites in ligand **2**, while retaining the same metal binding domain, gives rise to the formation of a supramolecular metallogel on reaction with AgBF4 at 5 wt% in MeCN, possessing self-healing properties.

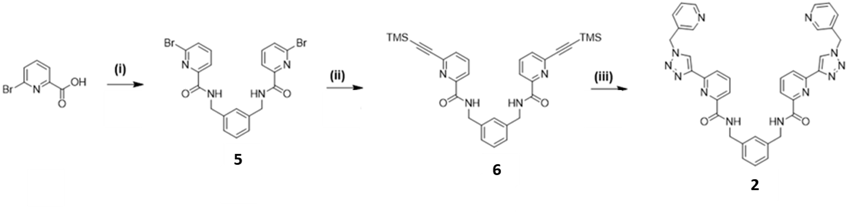
Introduction

The design of new functional materials through non-covalent interactions is an exciting and important area of research in supramolecular chemistry, where the opportunity exists to harness weak intermolecular forces, as well as, (an)ion driven and metal coordination self-assembly interactions, to engineer higher order or polynuclear assemblies.1 Metal coordination interactions are particularly useful, as metal ions can control the binding geometry and impart geometric control complementary to what is driven by the organic fragments.2 Coordination driven self-assembly also tends to be reversible in nature, and can provide metal-centred functionality, both of which being useful properties in the search for responsive materials in sensing and catalysis.3

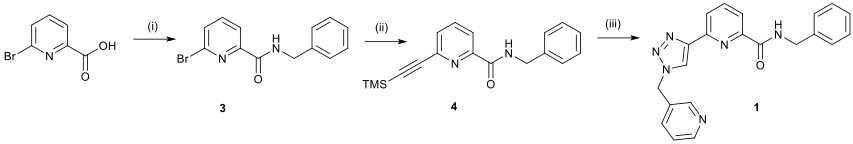
In the design and preparation of functional supramolecular materials and coordination complexes, both discrete and polymeric, effective ligand design is key.4 Modular ligand families are useful tools for deriving structure-function relationships, and allow for systematic tuning of both the metal binding properties and the subsequent material functionalities.5 The self-assembly of these ligands with silver(I) salts is frequently examined due to the extra lability and versatility of coordination geometries in monovalent d10 systems.6 Silver has long been known as an important building block in metallosupramolecular chemistry, and elegant examples of both discrete and polymeric assemblies have been reported.7 In soft materials, however, a characterisation challenge exists in coordinatively labile systems such as silver(I), given the wide range of possible coordination geometries and lack of atomically-precise characterisation methods. This is particularly vexing in the absence of optical spectroscopic fingerprints, which can otherwise help with the molecular scale characterisation of lanthanide and transition metal gelators.8 In these instances, small molecule models can be useful surrogates, allowing inspection of the possible coordination modes and geometries without the added complexity of the surrounding gel matrix.9

Recently we have reported the formation of chiral and achiral bis-tridentate (1,2,3-triazol-4-yl)-picolinamide (**tzpa**) ligands and their coordination chemistry with Cu(I), Cu(II) and Zn(II) ions, forming a variety of metallosupramolecular assemblies.10 In those cases, we consistently observed the formation of discrete tetranuclear [2×2] grid assemblies with the ligands acting in a convergent manner. Here we report on our effort to further advance this area of research by the formation of a bis-tridentate **tzpa** ligand **2**, functionalised with a 3-methylpyridine “arm” to increase the opportunities for metal-ligand interactions, and the “half-equivalent” of **2**, the tridentate ligand, **1**, designed to give further and more precise insight into the potential coordination chemistry of these systems. We demonstrate that this simple modification has not only a major effect on the coordination properties of the ligands, but also, in the case of **2**, results in the formation of metallogel, that we show is also reversibly formed.

Results and Discussion

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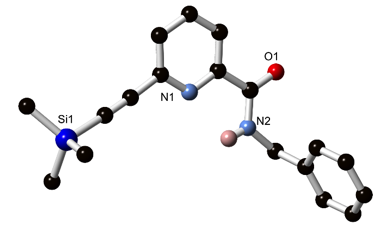
**Scheme 2** Synthesis and structure of compound **2**. Reagents and conditions: (i) *m*-xylylenediamine, HOBt, EDCI·HCl, NEt3, 4:1 DCM:DMF; (ii) Ethynyltrimethylsilane, CuI, Pd(PPh3)4, THF:NEt3; (iii) (a) 3-aminomethylpyridine, ImSO2N3·H2SO4, K2CO3, CuSO4·5H2O, CH3OH (b) sodium ascorbate, K2CO3, H2O:tBuOH **6**, DMF.

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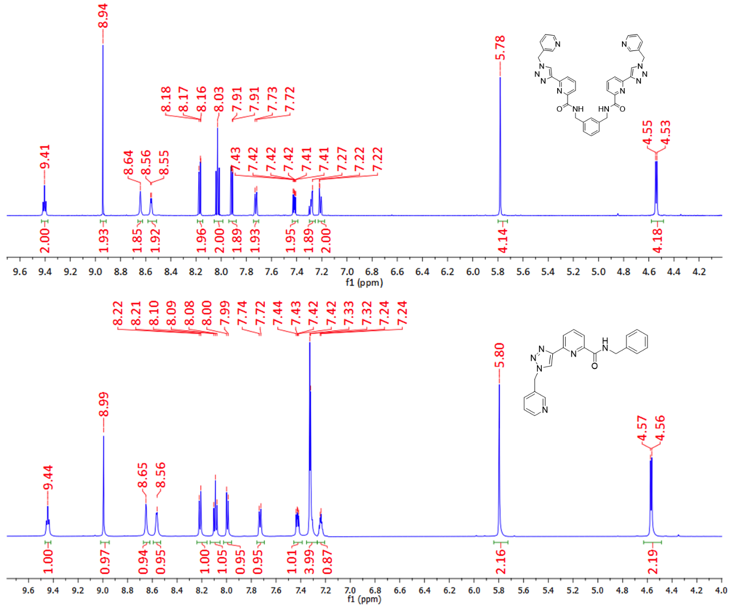
**Scheme 1** Synthesis and structure of compound **1**. Reagents and conditions: (i) *m*-xylylenediamine, HOBt, EDCI·HCl, NEt3, 4:1 DCM:DMF; (ii) Ethynyltrimethylsilane, CuI, Pd(PPh3)4, THF:NEt3; (iii) (a) 3-aminomethylpyridine, ImSO2N3·H2SO4, K2CO3, CuSO4·5H2O, CH3OH (b) sodium ascorbate, K2CO3, H2O:tBuOH **4**, DMF.

The synthetic pathways to ligands **1** and **2** are shown in Schemes 1 and 2, respectively. This synthetic procedure is related to our previously reported methodology for generating the convergent **tzpa** ligands used to generate tetranuclear grids.10  The synthesis of the model ligand **1** was achieved in a three-step synthetic pathway from 6-bromopicolinic acid which was coupled with benzylamine under peptide-coupling conditions to generate compound **3**. A Sonogashira coupling reaction with one equivalent of ethynyltrimethylsilane generated compound **4** and finally, 3-aminomethylpyridine was installed *via* a CuAAC reaction to result in compound **1**.

Ligand **2** was prepared following a similar procedure, with two equivalents of 6-bromopicolinic acid linked by amide coupling to a central *m*-xylyl spacer to give compound **5** (Scheme 2). Intermediate **5** was then subjected to a Sonogashira coupling to install two terminal trimethylsilylalkynyl substituents **6**, which were subsequently converted to the 3-picolyltriazoles *via* an equivalent CuAAC reaction described above. Both ligands were obtained in good yield and high purity as is demonstrated in the 1H NMR spectra (600 MHz, DMSO-*d6*) of compounds in Figure 1. The 1H NMR spectra **2** is shown in Figure 1 (top), with resonances corresponding to the central pyridyl protons occurring at 8.17, 8.03 and 7.91 ppm, appearing as two doublets, and a triplet. The singlet assigned to the triazole protons appears downfield at 8.94 ppm, while the amide protons occur further downfield at 9.41 ppm and as a triplet due to coupling with the adjacent CH2 protons. These CH2 protons occur at a resonance of 4.54 ppm. The *m*-xylyl protons reside at 7.27 and 7.22 ppm. Finally, the protons associated with the pyridyl “arms” are located at 8.64, 8.56, 7.72, and 7.45 ppm with the adjacent CH2 signal appearing at 5.78 ppm. The full characterisation of **1** and **2** is given in the Experimental section (See also ESI for enlarged NMR spectrum).



**Figure 2** Structure of **4** with heteroatom labelling scheme. Selected hydrogen atoms are omitted for clarity.



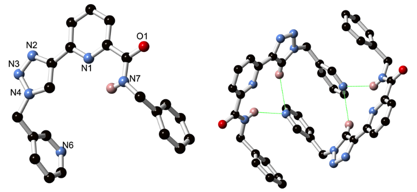
**Figure 1** 1 IH NMR spectrum (600 MHz, DMSO-d6) of (top) **2** and (bottom) **1**.

Gratifyingly, the crystal structures of both compounds **4** and **1** were obtained during the synthesis by single crystal X-ray diffraction. The structure of the intermediate **4** was analysed in the triclinic *P*-1 space group and the asymmetric unit contains one complete molecule of the compound, as shown in Figure 2, with no solvent or guest species present. Surprisingly, the expected amide-amide hydrogen bonding motif was not observed, potentially due to the unfavourable sterics of the near-orthogonally oriented aromatic groups nearby. Instead, an intramolecular hydrogen bond interaction between the amide N-H group and the pyridyl nitrogen occupies the donor. Only weak intermolecular C-H⋅⋅⋅O interactions are evident involving the amide oxygen atom O1 and benzylic methylene group of an adjacent molecule, (with an O1⋅⋅⋅C12 distance of 3.6396(17) Å and C-H⋅⋅⋅O angle of 159˚), and similar short contacts between this oxygen atom and the metal C-H groups from the trimethylsilyl substituent.



**Figure 4** (Top) Structure of the coordination polymer *poly-*{[Ag2(**1**)2](CF3SO3)2} with labelling scheme for unique heteroatoms. (Bottom) Argentophilic interactions between two equivalent Ag1 sites in the structure of *poly-*{[Ag2(**1**)2](CF3SO3)2}. Selected hydrogen atoms are omitted for clarity. Symmetry code used to generate equivalent atoms: i) x-1, +y, +z.

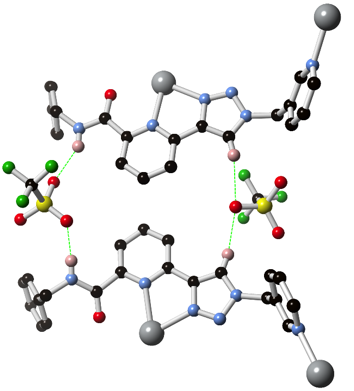
Crystals of ligand **1** were obtained by slow evaporation from hexane and the data were analysed in the chiral orthorhombic *P*21212 space group, and modelled as a two-component inversion twin. The asymmetric unit contains one molecule of the ligand and the pendant phenyl and pyridyl rings were both disordered over two orientations related by rotations about the CH2-Caryl bond. The ligand adopts a U-shaped conformation in which the triazole, pyridine, and carboxamide groups are coplanar and the pyridyl and phenyl arms are near-perpendicular to this plane, both extending in the same direction, as shown in Figure 3. Two ligands are bound together in a tight dimer by intermolecular hydrogen bonding interactions between an amide NH group and a pyridyl nitrogen atom (Figure 3). The amide nitrogen atom N7 is observed to donate a hydrogen bond to the pyridyl nitrogen atom of an adjacent molecule in the dimer, with an average N⋅⋅⋅N distance (accounting for the pyridyl group disorder) of 3.38 Å and an N-H⋅⋅⋅N angle of *ca*. 143°. Additional C-H⋅⋅⋅N interactions also exist between the pyridyl nitrogen atom and triazole ring of an adjacent molecule, with an averaged C⋅⋅⋅N distance of 3.52 Å and C-H⋅⋅⋅N angle of *ca.* 149°.



**Figure 3** (Left) Structure of ligand **1** with heteroatom labelling scheme. (Right) The interaction between adjacent molecules of **1** with hydrogen bonds (both N-H···O and C-H···O) shown as green dashed lines. Selected hydrogen atoms and aryl ring disorder are omitted for clarity.

The coordination chemistry of these two ligands was next investigated. Reaction of ligand **1** with AgCF3SO3 in a 1:1 molar ratio in THF solution, followed by slow evaporation of the organic solvent upon standing at room temperature, resulted in the formation of yellow crystals over three days. Analysis by single crystal X-ray diffraction, with data solved in the monoclinic *P*21/*n* space group, revealed a 1D polymeric structure of the form *poly-*{[Ag2(**1**)2](CF3SO3)2}. The asymmetric unit contains two whole ligand molecules with two silver atoms and two triflate ions, as shown in Figure 4, demonstrating that this **tzpa** motive behaves very different to that previously developed in our laboratory. The coordination geometry of the silver ions is best described as three-coordinate, distorted trigonal planar. Each is bound in a bidentate fashion by the N4 and N5 atoms of the pyridyl-triazole binding site, and the pyridyl nitrogen atom N7 of an adjacent pendant ligand arm completes distorted trigonal planar coordination geometry about the silver centre. Bridging of each coordination sphere by the terminal pyridyl groups gives rise to a 1-dimensional polymeric structure oriented parallel to the *a* axis. In addition, long Ag···O contacts are observed from the amide oxygen atom of each ligand, with distances for Ag2···O1 and Ag1···O2 of 2.730(4) and 2.647(4) Å, respectively. An argentophilic interaction is also evident between two symmetry equivalent Ag2 atoms, at a Ag-Ag distance of 3.0364(10) Å, significantly below the sum of the van der Waals radii of 3.44 Å. A related contact involving the Ag1-Ag1 pair exhibits an interatomic distance of 3.5627(11) Å, falling well outside the range of a genuine argentophilic interaction. While the coordination geometry of the two silver ions is essentially equivalent, this discrepancy is the most obvious desymmetrisation between the two. Each ligand molecule adopts a Z-shaped conformation, with the central pyridyltriazole group almost coplanar, and the pyridyl and phenyl arms orientated at angles of 110.9(5) and 106.1(4)˚ respectively to the mean plane of the central pyridine. As shown in Figure 5, hydrogen bonding is a key intermolecular force in the structure.

The amide groups from both unique ligand molecules act as hydrogen bond donors to the same triflate anion, with N···O distances of 2.935(7) and 2.859(7) Å for N6···O6 and N12···O7, respectively. The second triflate anion within the asymmetric unit engages in weaker C-H···O interactions with the triazolyl C-H groups of both **1** molecules. The C···O distances of 3.311(7) and 3.187(7) for C28···O5 and C7···O5 are consistent with the expectation of a moderate strength C-H···O interaction from this group, as we have seen in previous investigations of **btp** and **tzpa** ligands.10,11 The C-H···O interactions here are also supplemented by weaker contacts originating at the adjacent methylene groups, which interact with the same sulfonate group at C···O distances of 3.176(7) and 3.233(8) Å. Both types of hydrogen bonding involving the triflate anions serve to bridge the 1-dimensional polymeric strands parallel to the *c* axis, into a 2-dimensional superstructure. No solvent molecules or void space was located within the structure. Phase purity was confirmed by using powder X-ray diffraction analysis at 100K. (See Figure S1, ESI) Elemental analysis on the air-dried sample confirmed the structure of *poly*-{[Ag2(**1**)2](CF3SO3)2}.



**Figure 5** The two modes of hydrogen bonding linking adjacent chains *via* triflate anions in the structure of *poly-*{[Ag2(**1**)2](CF3SO3)2}. Selected hydrogen atoms are omitted for clarity.



**Figure 6** (a) Inversion test of the **2-**AgBF4 gel in MeCN; (b) The addition of TBACl to the sample shown in (a), results in the destruction of the metallogel network. (c) Addition of AgBF4 to the sample shown in (b) results in the re-formation the AgBF4 gel of **2**, demonstrating chemo-reversibility of the system. (d) SEM images of isolated **2-**AgBF4 gel (scale bar 20 m) showing the sheet-like structure of the material. (e) (Left) EDX energy dispersive spectrum for the **2**-AgBF4gelshowing the presence of carbon, oxygen, fluorine and silver. (Right) The area of interest of the dried gel material which was examined by EDX.

Having successfully probed the nature of the coordination bonding between **1** and silver(I) ions, the possibility of forming more complex coordination polymer structures with bis-tridentate compound **2** was then explored. Ligand **2** contains exactly equivalent coordinating functionality of ligand **1**, but being further bridged by the central xylyl unit, possesses the capability to bridge four metal ions, rather than two. Additionally, assuming a similar mode of hydrogen bonding, **2** has the ability to also act as a four-connected hydrogen bond donor species. With these design principles in mind, it was our expectation that **2** would form extended networks of much higher connectivity than its simplified model compound **1**.

Unfortunately, we were unable to generate any crystalline material from the reaction of **2** with AgCF3SO3, which gave only flocculent material. Indeed, in our screen of solvents (THF, acetone and CH3CN) we only observed amorphous precipitates on reaction of **2** with AgCF3SO3 in 1:1, 1:2 or 2:1 stoichiometries. However, the reaction of **2** with AgBF4 in CH3CN in a 1:1 molar ratio at higher concentration (4 mM), resulted not in the formation of crystalline materials, but instead the formation of a gel occurred overnight which emerged as a continuous phase from the reaction solvent. We found the formation of the gel to be reproducible over 6 preparations with equivalent formation rates and visual appearances. The ligand itself was not capable of gelation under these conditions, indicating that the metal-ligand interactions are necessary for the soft material formation, and hence in the formation of a metallogel. A crude test of the gelation behaviour, the “inversion test”, was performed and the gel supported its own weight overnight, as demonstrated in Figure 6a. Various gelation concentrations were consequently examined, and of these, the 5 wt% gel (as shown in Figure 6a) appeared the most robust to the naked eye. This metallogel was stable in a sealed vial for several months with little discolouration observed. Furthermore, thermogravimetric analysis (TGA) was utilised to determine the wt% of the gel fraction. TGA carried out from 15 to 500 ˚C showed a loss in mass of 95% below 50 ˚C indicating that the gel was formed at 5 wt%, which was consistent with the gel preparation (See Figure S2 ESI).

To investigate the robustness, and also the reversibility of the gelation, the chemoreversibility was investigated by addition of one equivalent of tetrabutylammonium chloride (TBACl) to the soft material. This resulted in destruction of the gel, which is attributed to sequestering of the silver ions by the formation of insoluble AgCl, as seen in Figure 6c. This we have previously observed with silver-containing gels of a 3-picolyl-1,8-naphthalimide ligand,12 and further confirming the necessity of the silver ions for gelation. The gel decomposition could be reversed by addition of one equivalent of AgBF4, which regenerated the gel, although with a more opaque appearance due to the dispersed AgCl (Figure 6d, and an enlarged figure in Figure S3, ESI).

The morphological nature of the **2-**AgBF4 gel was next investigated. A xerogel of the material was generated in order to examine the gel using scanning electron microscopy (SEM) by drying the gel under vacuum. The SEM images show a sheet-like structure where the gel appears like a dried fibrous film. It is likely that drying the sample under vacuum caused a compaction of the gel network. Energy dispersive X-ray (EDX) was also employed in order to examine the elemental composition of the sample under SEM analysis. This technique confirmed the presence of silver in the gel sample (Figure 6e).



**Figure 7** (Top) Amplitude (strain) sweep (f=1Hz) experiment of **2**-AgBF4 showing crossover from solid-like to liquid-like behaviour (Middle) Frequency sweep experiment and recovery test (Bottom), demonstrating the mechanical reversibility of the metallogel (Alternating strain amplitudes at and at f=1Hz).

Rheological experiments were carried out next in order to study the deformation and flow of the material under an applied mechanical stress. Strain and frequency sweeps were conducted as well as a recovery test on the compressed gel and the results of these experiments are shown in Figure 7. At low strain amplitudes, the storage modulus G′ plateau has a value of 1.62 × 103 and is an order of magnitude larger than the loss modulus G′′ at the same strain amplitude which indicates that the material behaves solid-like in the linear viscoelastic regime. A crossover of G′ and G′′ occurs at a shear strain of 30% indicating a change from solid-like to liquid-like behaviour. A frequency sweep experiment was conducted and demonstrates that the elastic response of the gel increases slightly with frequency within the linear viscoelastic regime, while G′ remained greater than G′′ over the entire frequency range. An oscillatory recovery test was also conducted to examine the mechanical reversibility of the gel. The effect on the storage and loss moduli were examined by cycling the strain amplitude between values well below and above the yield strain.. The gel returns to its original strength after shearing and this behaviour was repeated over multiple cycles, demonstrating that the metallogel has self-healing properties.

Conclusions

Herein we present our work on the synthesis of mono- and bis-terdentate **tzpa** ligands **1** and **2**, functionalised with 3-methylpyridine “arms”; ligand **1** being the half-equivalent model ligand of **2**. These two ligands have been used to investigate the formation of extended networks with silver(I) ions. Ligand **1** when reacted with AgCF3SO3 formed a 1D polymer network {[Ag2(**1**)2](CF3SO3)2}n containing three-coordinate silver ions supported by argentophilic interactions and anion-linked interstrand hydrogen bonds. This structure provides an indication of possible interactions that could occur in the gel formed upon reaction of higher connectivity ligand **2** with AgBF4 in MeCN solution, analysis of the material demonstrating the formation of a metallogel. The capability of Ag(I) ions to form complexes with a variety of different coordination numbers as well as the labile nature of these interactions is ideal for the formation of metallosupramolecular materials. The metal ligand, silver-silver and hydrogen bonding interactions observed in the 1D polymer structure give an insight into the possible interactions that cause metallogel formation. The gel-process was also shown to be reversible, as upon addition of one equivalent of TBACl to **2-**AgBF4 metallogel in MeCN, caused the gel to collapse with the formation of AgCl. However, the addition of AgBF4 resulted in the reformation of the metallogel. We are currently investigating in greater details the application of other bis-tridentate **tzpa** ligands in supramolecular coordination and soft-material chemistries.

Experimental

Materials and Methods

Compounds **5** and **6** were prepared according to our previously reported methodology.10b All reagents and solvents were purchased from Sigma-Aldrich, Merck or Fischer Scientific, were of reagent grade or better, and were used as received. All NMR spectra were recorded using either a 400 MHz Bruker Avance III or 600 MHz Bruker Avance II spectrometer, operating at 400.1/600.1 MHz for 1 H NMR and 100.2/150.2 MHz for 13C NMR. Chemical shifts are reported in ppm referenced relative to the internal residual solvent signals. Electrospray mass spectra were recorded on a Micromass LCT spectrometer or a MALDI QToF Premier, running Mass Lynx NT V 3.4 on a Waters 600 controller connected to a 996 photodiode array detector with HPLC-grade methanol or acetonitrile. High resolution mass spectra were determined by a peak matching method, using leucine enkephaline (Tyr-Gly-Gly-Phe-Leu) as the standard reference (m/z = 556.2771). All accurate masses were reported within ±5 ppm. Melting points were determined using an IA9000 digital melting point apparatus in air and are uncorrected. Infrared spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer fitted with a Universal ATR Sampling Accessory. Elemental analyses were carried out at the Microanalytical Laboratory, School of Chemistry and Chemical Biology, University College Dublin and The Department of Chemistry, Maynooth University. Thermogravimetric analysis was performed using a PerkinElmer Pyris 1 TGA instrument, with samples (1–5 mg) mounted in alumina pans and heated in the range 25–500 °C at a rate of 5 °C min−1 under a constant N2 flow of 20 mL min−1. Rheological measurements were carried out with an Anton Paar MCR 301 rheometer using a plate-plate geometry.

**X-ray Crystallography**

Data and refinement parameters are provided in Table S1, ESI. The diffraction data were collected using a Bruker APEX-II Duo dual-source instrument equipped with microfocus Cu Kα (λ = 1.54178 Å) radiation. Datasets were collected using ω and φ scans with the samples immersed in Paratone-N oil and maintained at a constant temperature of 100 K using a Cobra cryostream. The data were reduced and processed using the Bruker APEX suite of programs13 and multi-scan absorption corrections were applied using SADABS. 14 The diffraction data were solved using SHELXT and refined by full-matrix least squares procedures using SHELXL-2015 within the OLEX-2 GUI.15 The functions minimized were Σw(F2o-F2c), with w=[σ2(F2o)+aP2+bP]-1, where P=[max(Fo)2+2F2c]/3. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined with a riding model, with isotropic displacement parametersequal to either 1.2 or 1.5 times the isotropic equivalent of their carrier atoms. The structural model for compound **1** was refined as a two-component (inversion) twin, and both terminal aryl groups were split over two orientations. Specific refinement parameters are outlined in the combined crystallographic information file. CCDC 1994746-1994748.

X-ray powder diffraction patterns were measured on a Bruker APEX II Duo duel-source instrument using microfocus Cu Κα (λ = 1.54178 Å) maintained at 100 K using a cobra cryosystem. The patterns collected were compared with the patterns from the single crystal data (also collected at 100 K) to establish phase purity of each crystalline material.

Synthesis of N-benzyl-6-bromopicolinamide Compound 3

Benzylamine (1.1 mL, 10.8 mmol) was added to a solution of anhydrous DMF:DCM (4:1) (50 mL) under Ar. To this mixture HOBt (1.45 g, 10.8 mmol) and NEt3 (1.5 mL, 10.8 mmol) were added and the reaction mixture was cooled to 0 ˚C for 15 mins. Following cooling 6-bromopyridine-2-carboxylic acid (2.0 g, 9.9 mmol) was added and after stirring at 0 ˚C for a further 15 mins, EDC·HCl (3.10 g, 16.2 mmol) was added. The mixture was then stirred at room temperature for 48 hours. The product was then dried under reduced pressure and taken up in CH2Cl2, washed with 1M HCl, sat. NaHCO3 and H2O, dried over magnesium sulfate and concentrated under reduced pressure to yield an orange oil. This resulting oil was dried to a solid by repeated evaporation under reduced pressure with toluene to give compound **3** in 52% yield(1.49 g, 5.1 mmol). m.p. 167 - 174 °C; HRMS (*m/z*) (ESI+): C13H11BrN2O+ *m/z* = 291.0133 [M+H]+. Found *m/z* = 291.0127; 1H NMR (600 MHz, CDCl3): δ (ppm) = 8.20 (d, *J* = 7.7 Hz, 1H, pyridyl H), 8.14 (s, *J* = 6.2 Hz, 1H, NH), 7.72 (t, *J* = 7.7 Hz, 1H, pyridyl H), 7.61 (d, *J* = 7.7 Hz, 1H, pyridyl H), 7.36 (dd, *J* = 8.3, 5.5 Hz, 4H, Ar H × 4), 7.33 – 7.27 (m, 1H, *J* = 8.3, 5.5 Hz, Ar H × 2), 4.67 (d, *J* = 6.2 Hz, 2H, CH2); 13C NMR (150 MHz, CDCl3): δ (ppm) = 162.9, 151.1, 140.7, 139.8, 138.1, 130.9, 128.9, 128.1, 127.8, 121.6, 43.7; IR νmax (cm-1): 3354, 3318, 3166, 3033, 2942, 1736, 1639, 1603, 1568, 1527, 1502, 1451, 1374, 1278, 1247, 1222, 1161, 1089, 1049, 972, 865, 819, 764, 743, 728, 687, 631, 606.

Synthesis of N-benzyl-6-((trimethylsilyl)ethynyl)picolinamide

Compound **3** (1 g, 3.43 mmol), CuI (0.026 g, 0.14 mmol) and Pd(PPh3)4 (0.16 g, 0.14 mmol) were stirred in a solution of anhydrous THF:NEt3 (1:1 30 mL) under Ar and cooled to 0 ˚C. To this mixture ethynyltrimethylsilane (0.4 mL, 3.77 mmol) was added dropwise and the reaction was stirred overnight at room temperature. The resulting brown solution was concentrated under reduced pressure and filtered through celite with hexane. The crude product was then purified by flash column chromatography (RediSep® 24g, gradient elution 0 → 20 % EtOAc in Hexane) to yield a brown solid in 63% yield. (0.67 g, 2.16 mmol); m.p. 187 - 191 °C; HRMS (*m/z*) (ESI+): C18H21N2OSi+ *m/z* = 309.1418 [M+H]+. Found *m/z* = 309.1418; 1H NMR (600 MHz, DMSO-*d6*): δ (ppm) = 9.22 (t, 1H, *J* = 6.4 Hz, NH), 8.02 (m, *J* = 7.5, 1.1 Hz, 2H, pyr H), 7.74 (dd, *J* = 7.5, 1.1 Hz, 1H, pyr H), 7.37 – 7.25 (m, 4H, Ar H), 7.27 – 7.18 (m, 1H, Ar H), 4.49 (d, *J* = 6.4 Hz, 2H, CH2), 0.26 (s, 9H, CH3-Si); 13C NMR (150 MHz, DMSO-*d6*): δ (ppm) = 163.8, 151.0, 141.2,139.9, 139.0, 130.6, 128.7, 127.9, 127.3, 122.5, 104.0, 95.7, 43.0, 0.1; IR νmax (cm-1): 3371.0, 1674.1, 1520.7, 1442.9, 1248.4, 841.6, 762.4, 645.7, 610.3.

Synthesis of N-benzyl-6-(1-(pyridin-3-ylmethyl)-1H-1,2,3-triazol-4-yl)picolinamide 1

3-Picolylamine (0.17 mL, 1.6 mmol) was added to a solution of MeOH (20 mL) and to this mixture ImSO2N3·H2SO4 (0.46 g, 1.7 mmol) K2CO3 (0.44 g, 3.2 mmol) and CuSO4·5H2O (0.08 g, 0.32 mmol) were added. The reaction mixture was stirred for 5 hours or until the reaction mixture turned a lilac colour. Sodium ascorbate (0.16 g, 0.8 mmol) and K2CO3 (0.44 g, 3.2 mmol) were added followed by H2O:tBuOH (0.5 mL:0.75 mL) and the mixture was degassed with Ar. Compound **4** was dissolved in DMF (0.5 g, 1.6 mmol) and added to the reaction mixture under Ar. The reaction was stirred at room temperature for 18 hours, then concentrated under reduced pressure. An EDTA/NH4OH solution was added to the reaction and the product was extracted into DCM and washed with H2O (3 × 20 mL). The solution was dried over magnesium sulfate and concentrated under reduced pressure to yield a white solid in 72% yield. m.p. 156 - 163 °C; HRMS (*m/z*) (ESI+): C21H19N6O+ *m/z* = 371.1615 [M+H]+ . Found *m/z* = 371.1614; 1H NMR (600 MHz, DMSO-*d6*): δ (ppm) = 9.44 (t, 1H, *J* = 6.5 Hz, NH), 8.99 (s, 1H, triazole H), 8.65 (s, 1H, *J* = 4.8 Hz, pyridyl H), 8.56 (br d, 1H, *J* = 7.4 Hz, pyridyl H), 8.21 (d, *J* = 7.8 Hz, 1H, pyridyl H), 8.09 (t, *J* = 7.8, 1.1 Hz, 1H, pyridyl H), 7.99 (d, *J* = 7.8 Hz, 1H, pyridyl H), 7.73 (d, *J* = 7.9, 7.4 Hz, 1H, pyridyl H), 7.43 (dd, *J* = 7.9, 4.8 Hz, 1H, pyridyl H), 7.32 (d, *J* = 4.2. 3.6 Hz, 4H, Ar H × 4), 7.24 (d, *J* = 3.6 Hz, 1H, Ar H × 2), 5.80 (s, 2H, CH2-triazole), 4.57 (d, *J* = 6.5 Hz, 2H, CH2-NH). 13C NMR (150 MHz, DMSO-*d6*): δ (ppm) = 163.8, 149.7, 149.6, 149.1, 148.8, 147.2, 139.5, 138.9, 135.7, 131.6, 128.4, 127.1, 126.8, 124.5, 124.0, 121.7, 120.9, 50.8, 42.3; IR νmax (cm-1): 3350.3, 3065.8, 3030.2, 2164.5, 1977.6, 1667.4, 1599.3, 1521.9, 1478.4, 1430.1, 1361.0, 1282.0, 1255.2, 1235.9, 1168.9, 1077.3, 1046.0, 1028.6. 993.5, 849.6, 779.4, 764.8, 695.0, 627.1.

Synthesis of N,N'-(1,3-phenylenebis(methylene))bis(6-(1-(pyridin-3-ylmethyl)-1H-1,2,3-triazol-4-yl)picolinamide) 2

3-Picolylamine (0.02 mL, 0.19 mmol) was added to a solution of MeOH (20 mL) and to this mixture ImSO2N3·H2SO4 (0.06 g, 0.21 mmol) K2CO3 (0.06 g, 0.38 mmol) and CuSO4·5H2O (0.01 g, 0.04 mmol) were added. The reaction mixture was stirred for 5 hours or until the reaction mixture turned a lilac colour. Sodium ascorbate (0.018 g, 0.09 mmol) and K2CO3 (0.03 g, 0.19 mmol) were added followed by H2O:tBuOH (0.5 mL:0.75 mL) and the mixture was degassed with Ar. Compound **4** was dissolved in DMF (0.05 g, 0.09 mmol) and added to the reaction mixture under Ar. The reaction was stirred at room temperature for 18 hours, then concentrated under reduced pressure. An EDTA/NH4OH solution was added to the reaction and the product was extracted into DCM (3 × 20 mL) and washed with H2O (3 × 20 mL). The solution was dried over magnesium sulfate and concentrated under reduced pressure to yield a white solid in 81% yield. m.p. 154 – 157 °C; HRMS (*m/z*) (ESI+): C36H30N12O2+ *m/z* = 663.2615 [M+H]+. Found *m/z* = 663.2709; 1H NMR (600 MHz, DMSO-*d6*): δ (ppm) = 9.41 (t, 2H, NH), 8.94 (s, 2H, triazolyl H), 8.64 (br s, 2H, pyridyl H), 8.56 (d, 2H, *J* = 7.9 Hz, pyridyl H), 8.17 (d, 2H, *J* = 7.9, 1.0 Hz, pyridyl H), 8.03 (t, 2H, *J* = 7.9 Hz, pyridyl H), 7.91 (dd, 2H, J = 7.9, 1.0 Hz, pyridyl H), 7.72 (d, *J* = 8.1 Hz, 2H, pyridyl H), 7.45 – 7.39 (m, 2H, *J* = 7.9, 8.1 Hz, pyridyl H), 7.27 (m, 2H, Ar H), 7.22 (m, 2H, Ar H), 5.78 (s, 4H, CH2-triazole), 4.54 (d, *J* = 6.5 Hz, 4H, CH2-NH). 13C NMR (150 MHz, DMSO-*d6*): δ (ppm) = 164.2, 150.1, 150.0, 149.5, 149.1, 147.63, 140.1, 139.3, 136.2, 132.0, 128.9, 126.2, 126.1, 124.9, 124.4, 122.1, 121.3, 51.2, 42.8; IR νmax (cm-1): 3353, 2706, 2131, 1678, 1520, 1419, 1232, 1028, 767, 830, 564.

Synthesis of coordination polymer {[Ag2(1)2](CF3SO3)2}n

To a solution of AgCF3SO3 (0.0134 mmol, 3 mg) in THF (2 mL) was added a solution of **1** (0.0134mmol, 5 mg) in THF (3 mL). Upon reaction together, a colourless solution resulted and allowed to react in a closed vessel to yield yellow crystals after one week. The crystals were isolated by filtration, washed with THF and allowed to air dry. Yield; (3 mg, 48%); m.p. (decomp) >280 °C; Elemental analysis for C22H18N6O4F3SAg Calculated: C 42.12 H 2.89 N 13.39; Found: C 42.62 H 2.79 N 13.43 %; IR νmax (cm-1): 3344, 3094, 2956, 2861, 2289, 1989, 1650, 1600, 1539, 1456, 1439, 1361, 1333, 1283, 1250, 1222, 1144, 1106, 994, 833, 761, 716, 639, 600.

**Preparation of the 2·AgBF4 gel**

Solid ligand **2** (5 mg, 7.5 μmol) was combined with AgBF4 (2 mg, 7.5 μmol) in CH3CN (2 mL) in a small sample vial at room temperature. The solution was homogenized by sonication, sealed and left to stand at room temperature for 16 hours, yielding a colourless gel. Identical procedures were repeated with total mass loadings up to 5% and gave equivalent results without modification.

Conflicts of interest

There are no conflicts to declare.

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