Metallo-gels and organo-gels with tripodal cyclotriveratrylene-type and 1,3,5-substituted benzene-type ligands†

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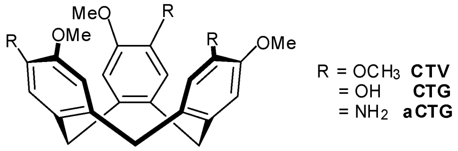
Received (in Durham, UK) 3rd November 2008, Accepted 14th January 2009
First published as an Advance Article on the web 12th February 2009
DOI: 10.1039/b819352e

The cyclotriveratrylene-type ligands tris(4-[4-methyl-2,2′-bipyridyl]methyl)cyclotriguaiacylene **1** and tris(isonicotinoyl)cyclotriguaiacylene **2** form metallo-gels with Cu(II) and Ag(I) (for **1** only), while tris(3-(3-pyridyl)-1-thiourea)cyclotriguaiacylene **3** is a low molecular weight gelator (LMWG) for 2,2,2-trifluoroethanol. Benzene-1,3,5-tricarboxylic acid tris(4-hydroxyquinoline) ester **4** is a LMWG for acetone, while 1,3,5-tris(2-quinoline-methoxyl)benzene **5** forms Cu(II) metallo-gels. All gels have fibrous structures and show different thermal behaviour. Aside from the hydrogen bonding organo-gel of **3**, an important intermolecular interaction within these gels is likely to be π–π stacking interactions. Crystal structures of a geometric isomer of **4** and of a discrete $[Ag_2(\mathbf{5})_2]^{2+}$ complex are also reported herein.

Introduction

There has been significant recent interest in the formation of gel materials from low molecular weight gelators (LMWG's).[1] Such materials are formed by the self-assembly of low molecular weight compounds into fibrous architectures, which form 3-D entangled networks, entrapping and immobilising solvent molecules. In contrast to other gel systems, the network structure formed by LMWG's is held together by non-covalent interactions such as π–π stacking, van der Waals interactions or hydrogen bonding.[1] The self-assembly of a LMWG to form an entangled network is therefore potentially reversible if coupled to a chemical or physical stimulus such as heat or pH. Organo-gels are formed by organic LMWG and have potential uses in a range of applications including templated materials,[2] drug delivery,[3] separation media[4] and electro-optical displays.[5] Transition metal containing gels, also known as metallo-gels, can be formed by the self-assembly of discrete metal complexes,[6–9] or through formation of coordination polymers linked by dative covalent bonds,[10–15] and have been reported to strengthen organo-gels through cross-linking.[16] Metallo-gels can be imparted with physio-chemical properties such as spectroscopic, magnetic, redox and catalytic properties, leading to stimuli-responsive 'smart' materials[7,12] and catalytic gels.[7]

A number of known organo- and metallo-gel systems employ tripodal molecules or ligands.[10,15,17–19] A recent paper reports new tripodal cyclotriveratrylene-related LWMGs with hydrogen bonding capabilities that form organo-gels with a range of solvents.[19] Cyclotriveratrylene (CTV) is a rigid pyramidal bowl-shaped host molecule, and C_3-symmetric extended host molecules can be synthesised *via* the chiral cyclotriguaiacylene (CTG)[20] or triaminocyclotriguaiacylene (aCTG)[21] analogues. The gels form as 1-D aggregates through columnar stacking with π–π interactions, hydrogen bonding and CH···O interactions.[19] Aligned columnar stacking of CTV-derivatives has also been reported in crystal structures.[22,23] Related bowl-shaped host molecules such as calix[4]arenes have also been shown to form both organo-gels[24] and metallo-gels.[10,11]



We have been developing a range of new tripodal CTV-related host molecules for use as ligands in coordination polymers and discrete supramolecular assemblies,[23,25–28] and report herein the gelator abilities of some of these ligands. In particular, the transition metal binding moieties of these ligands promote the formation of metallo-gels. C_3-symmetric tripodal ligands with a less pronounced pyramidal shape were also investigated. Truly planar analogues of CTV, namely substituted triphenylenes, are well known to form discotic liquid crystals;[29] hence, a more flexible 1,3,5-substituted benzene core was investigated. There have been a handful of previously reported organo-gels involving tripodal

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† Electronic supplementary information (ESI) available: ^1H NMR spectra of ligand **1** and $AgSbF_6$ with **1**. CCDC reference numbers 716036 and 716037. For ESI and crystallographic data in cif or other electronic format see DOI: 10.1039/b819352e

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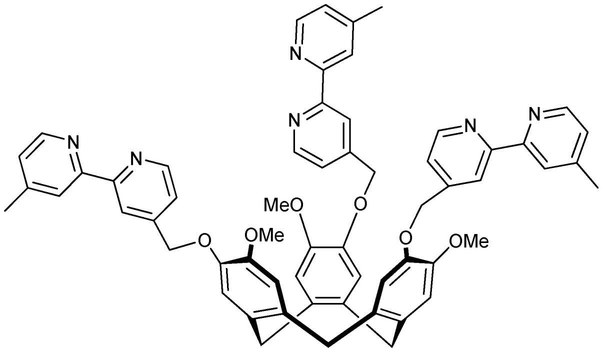
compounds with a 1,3,5-substituted benzene core,[15,30] including some metallo-gels.[15]

Results and discussion

Metallo-gels and organo-gels with cyclotriveratrylene-related ligands

While we have observed gel formation with a number of CTV-based ligands, some of these are unreliable, forming gels on some occasions and not others despite different attempts having very similar reagent mixtures. Only gels that, in our hands, reliably form under the documented conditions will be discussed in any detail. The 2,2′-bipyridine functionalised ligand tris(4-[4-methyl-2,2′-bipyridyl]methyl)cyclotriguaiacylene **1** forms metallo-gels with $CuCl_2$ and $AgSbF_6$, and has been previously reported to form discrete metallo-supramolecular catenating cages with $Zn(NO_3)_2$ and $Co(NO_3)_2$.[26] Tris-(isonicotinoyl)cyclotriguaiacylene, **2**, forms a Cu(II) metallo-gel. It has been previously shown to form head-to-head capsule-like dimers with small organic guest molecules,[27] and forms 1-D coordination chains with Ag(I)[27] and Zn(II),[31] along with discrete stella octangula $[Pd_6L_8]^{12+}$ assemblies.[28] Tris(3-(3-pyridyl)-1-thiourea)cyclotriguaiacylene, **3**, is a new ligand and forms a LMW organo-gel.



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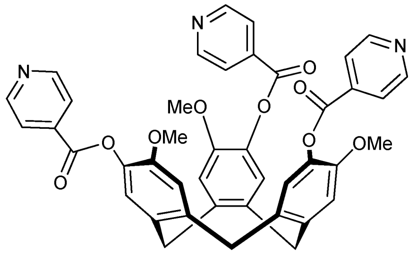

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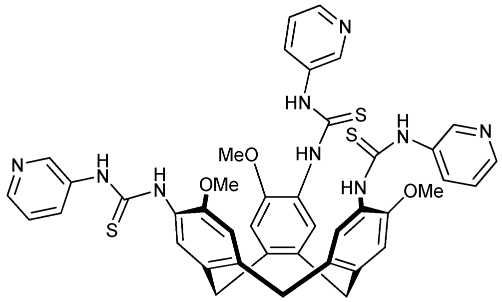

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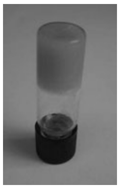


Fig. 1 Metallo-gel **A**.

In the presence of $CuCl_2$, ligand **1** is a gelator for dimethylformamide (DMF) but not for other common organic solvents. Mixing a 3 : 1 mixture of $CuCl_2$ and **1** in DMF gives an emerald green solution which forms a bright green gel **A** after 24 h if left to stand, or forms a gel on cooling to room temperature after heating the solution to 60 °C, Fig. 1. The gel is stable, showing no visible deterioration after 6 months. The formation of the gel is dependent on both stoichiometry and ligand concentration. Use of fewer than 3 equivalents of $CuCl_2$ results in a sol being formed. The gel is formed at ligand concentrations between 10 mM and 16 mM and use of higher ligand concentrations gives a precipitate.

The solid resulting from drying out the gel **A** was analysed by elemental analysis, infrared spectroscopy and mass spectrometry. IR shows the expected coordination induced shifts in C–N stretching bands of the ligand, and elemental analysis is consistent with a 3 : 1 Cu–**1** stoichiometry. ES-MS run on a dimethyl sulfoxide (DMSO) solution gives m/z values consistent with species $[Cu_3Cl_5(\mathbf{1})]^+$, $[Cu_2Cl_3(\mathbf{1})]^+$ and $[CuCl(\mathbf{1})]^+$. Metallo-gels involving 2,2′-bipyridine functionalised gelators have been previously reported.[8]

Ligand **1** also forms a metallo-gel in the presence of $AgSbF_6$ and DMSO. If a 3 : 1 mixture of $AgSbF_6$ and **1** in DMSO is heated to 50 °C it forms the colourless and translucent gel **B** on cooling. In this case heat is required to initiate the gelation. The gel forms at ligand concentrations between 12 and 21 mM (the upper solubility limit of **1** in DMSO), and using fewer than 3 equivalents of $AgSbF_6$ gives a sol. Similar experiments with other AgX salts produced either amorphous solids ($X = NO_3^-$, $CF_3SO_3^-$) or viscous solutions ($X = PF_6^-$, BF_4^-).

^{1}H NMR of a 3 : 1 $AgSbF_6$–**1** mixture in DMSO-D_6 was undertaken at concentrations marginally lower than those necessary to form a gel. On initial mixing there are small coordination induced shifts and broadening of the H5/H5′ and H6/H6′ ligand signals as would be expected on coordination of Ag(I) by the bpy moiety (ESI†). The spectrum retains its C_3 symmetry implying the formation of a symmetric $[Ag_3(\mathbf{1})]^{3+}$ species. This is supported by ES-MS where a similar mixture gives m/z values corresponding to $\{[Ag_3(\mathbf{1})](SbF_6)_2\}^+$, $\{[Ag_2(\mathbf{1})](SbF_6)\}^+$ and $[Ag(\mathbf{1})]^+$.

Ligand **2** is a gelator for acetonitrile in the presence of 3 equivalents or more of $CuBr_2$, forming the dark green opaque gel **C** on standing overnight. Gels form at a ligand concentration of 6 mM which is the upper solubility limit for **2** in acetonitrile. Using fewer than 3 equivalents of $CuBr_2$ results in a green precipitate. The IR spectrum of dried out gel shows the expected shifting of some bands, and elemental analysis is closest to a 2 : 1 Cu–**2** complex. The mass spectrum of the gel redissolved in DMSO could not be sensibly assigned. Ligand **2** did not form a gel with other common organic solvents or with other metal salts including $CuCl_2$. The 3-pyridyl isomer of **2**, tris(nicotinoyl)cyclotriguaiacylene, also gelates acetonitrile in the presence of either $CuBr_2$ or $CuCl_2$ but does not do so reliably; hence, further analysis was not carried out.

The different gelator abilities of **2** and tris(nicotinoyl)cyclotriguaiacylene may be related to the increased solubility of tris(nicotinoyl)cyclotriguaiacylene in common organic solvents.

The SEM micrograph of gel **A**, Fig. 2(a) and (b), shows large fibres that exhibit some fine structure and appear to be multi-layered. The fibres are relatively straight with only slight bending. A lack of twisting and regular shape indicates that the fibres are formed by well-ordered molecular packing. The smallest fibres present have an approximate width of 44 nm. The smallest fibres are layered together to produce thicker bundles of fibres that have an approximate width of 0.38 μm and the longest visible length is approximately 2 μm. The regular shape and the extreme ratio between width and length in this system must arise from a strong anisotropic growth process resulting in the possible presence of some 1-D structure in the system. The micrograph of gel **B** shows a very different morphology to that of gel **A**. The structure is composed of aggregated clusters with a very fine fibrous structure, Fig. 2(c) and (d). The structure is formed by fibres that are very small (width approximately 5 nm) relative to the fibres seen for gel **A**. Literature reports indicate that when solvent–gelator interactions become too strong, isotropic gelator molecular aggregation occurs resulting in the loss of fibrous structure and the favouring of clusters.[32] This may be an explanantion for the morphology of gel **B** noting that the DMSO solvent molecules may be interacting strongly with the gelator molecules. The SEM micrograph for gel **C** shows a thick, dense fibrous network, Fig. 3. The fibres are fused together to form thick clumps of fibres resulting in the dense irregular network. The fibres are not as elongated as the fibres shown for gel **A**. The fibres are approximately 25 nm in width and fuse together to form bundles that are approximately 0.13 μm in width. The longest fibre visible in the SEM micrograph is approximately 0.5 μm in length. There is some twisting of the fibres forming the network which may arise from the molecular chirality of the gelator.

Crystal structures of ligand **2** and known metal complexes of ligands **1** and **2** all show π–π stacking interactions between some or all of the phenyl faces of the CTV-framework.[25–27,30] This is likely to be an important intermolecular interaction in gels **A–C**, although the formation of coordination polymers

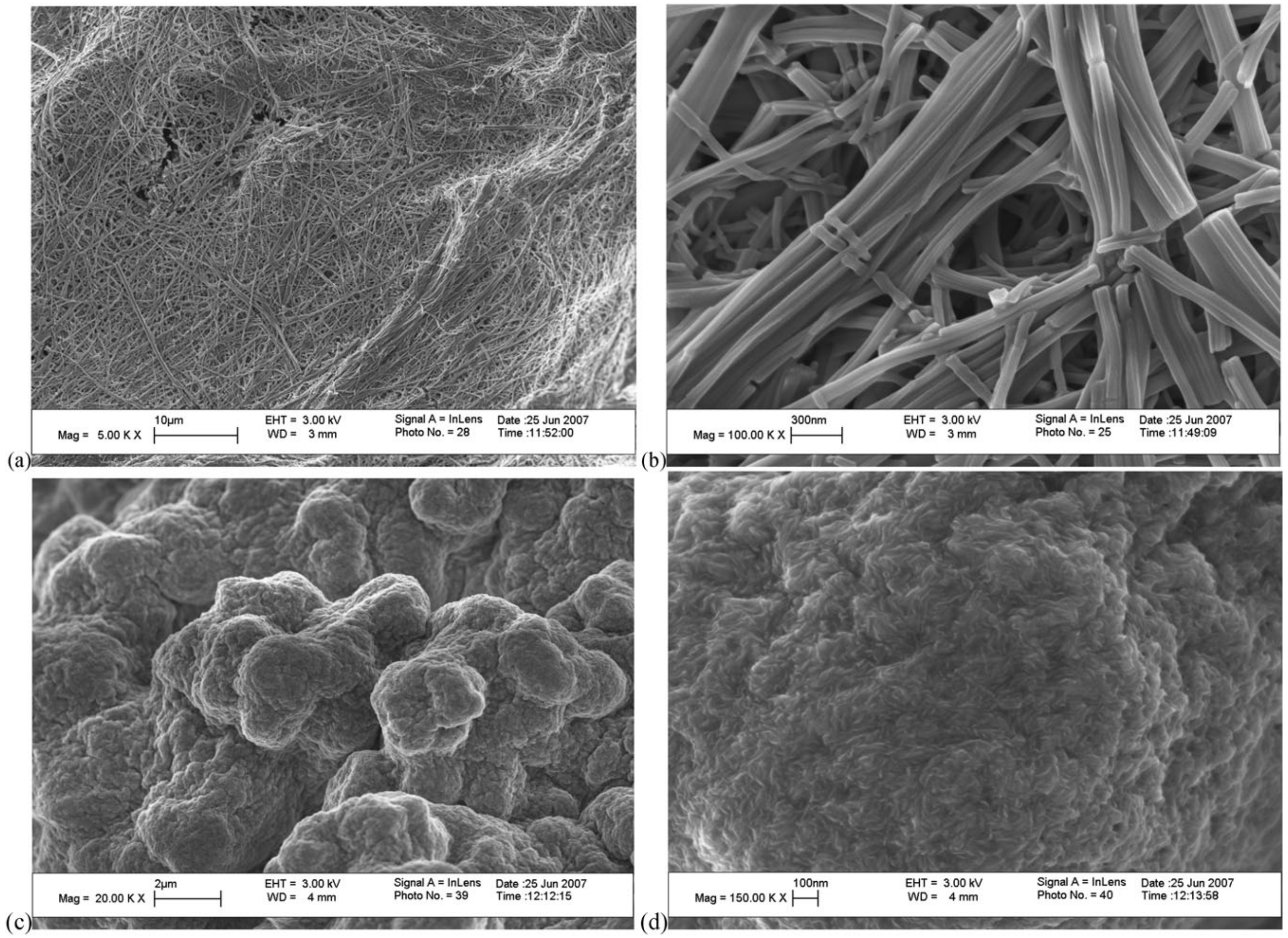


Fig. 2 SEM micrographs of metallo-gels involving ligand **1**. (a) 5000 and (b) 10^5 times magnification of gel **A** from 10 mM ligand **1** in DMF with 3 equivalents of $CuCl_2$. (c) 2×10^4 and (d) 15×10^4 times magnification of gel **B** from 12 mM ligand **1** in DMSO with 3 equivalents of $AgSbF_6$. Both gels were two days old before the images were taken.

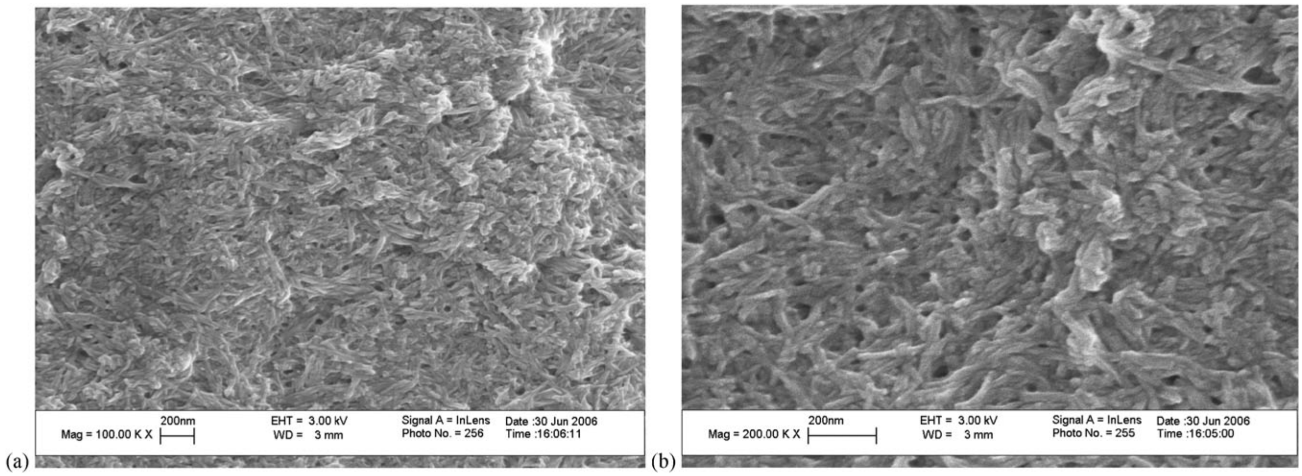


Fig. 3 SEM micrographs of gel **C** from 6 mM ligand **2** in acetonitrile with 3 equivalents $CuBr_2$. (a) 10^5 and (b) 2×10^5 times magnification. Gel was aged for one week prior to images being taken.

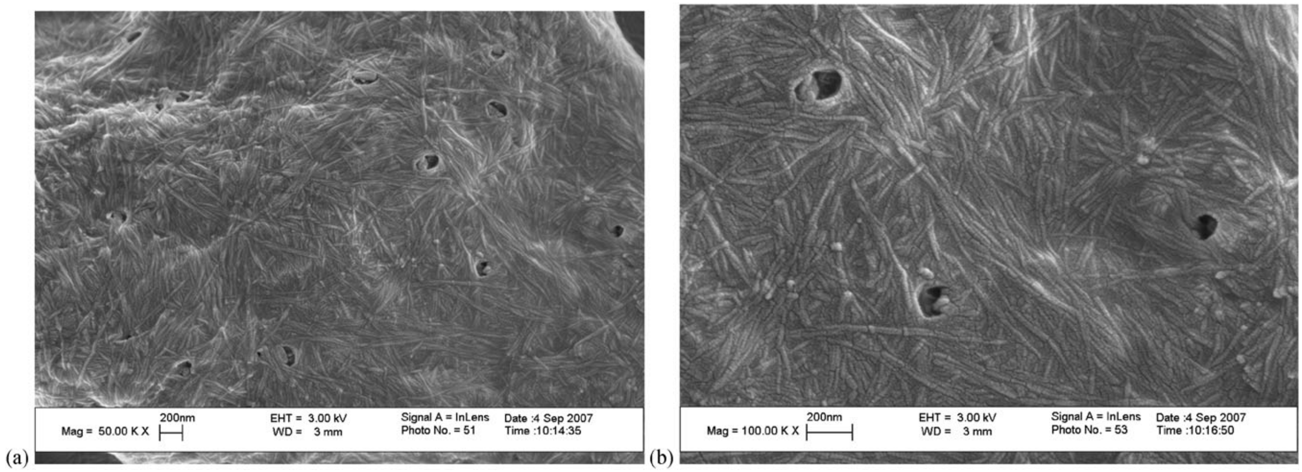


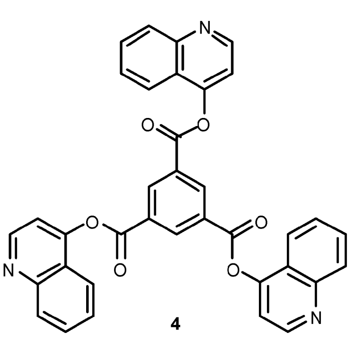
Fig. 4 SEM micrographs of gel **D** at (a) 5×10^4 and (b) 10^5 times magnification. Gel was aged for two days prior to images being taken.

cannot be discounted and lower metal content of **C** in particular is typical of this. Such π–π stacking interactions have been previously reported as the primary intermolecular interaction of some metallo-gels.[9]

The novel ligand **3** was synthesised in 86% yield by reaction of 3 equivalents of 3-pyridylisothiocyanate with aCTG. Unlike ligands **1** and **2**, it does not form a metallo-gel with transition metals but does form the organo-gel **D** with 2,2,2-trifluoroethanol. It did not act as a gelator for other common solvents, including other alcohols such as ethanol. The electronegativity of fluorine atoms means that trifluoroethanol exhibits a stronger acidic character than ethanol allowing it to form stable interactions with the pyridine donors *via* hydrogen bonds and such solvent–gelator interactions may be important in the formation of gel **D**. The optimum ligand concentration for gel formation is 12 mM. The SEM micrograph of gel **D** shows a dense entangled, fibrous structure, Fig. 4. The fibres are approximately 35–50 nm wide and the longest visible length is approximately 2 μm. The long fibre-like structure produced indicates the possible presence of a 1-D structure in the system and is most likely due to hydrogen bond formation between the thiourea groups of ligand **3**. While few organo-gels involving hydrogen bonding between thiourea groups have been previously reported,[33] bis and tris-urea molecules have been more commonly shown to act as LMW gelators in a range of solvents.[17,33,34]

Metallo- and organo-gels with tripodal quinoline functionalised ligands

The metal coordination chemistry of a series of ester-linked methylpyridyl or quinoline functionalised ligands was investigated, with quinoline ligands targeted as their ability to form intermolecular π–π stacking interactions may encourage gel formation. In the presence of transition metal cations, however, the ester-linked ligands decomposed. In the absence of metal cations, ligand **4** forms an organo-gel **E** with acetone. An ether linkage proved more robust and ligand **6** forms metallo-gels with Cu(II) cations and a discrete $[Ag_2(\mathbf{6})_2]^{2+}$ complex whose crystal structure has been determined.



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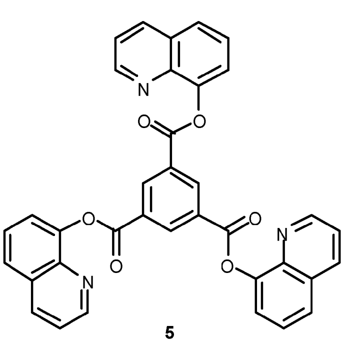

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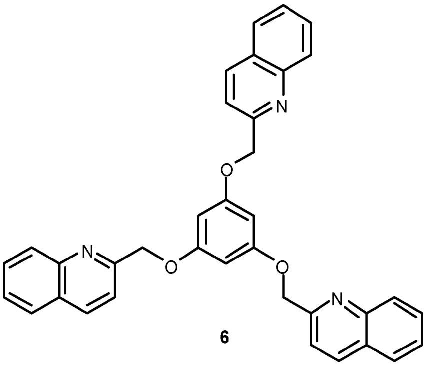

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Ligand **4** was synthesised in 76% yield by reaction of 3 equivalents of 4-hydroxyquinoline with 1,3,5-benzenetricarbonyl trichloride in the presence of base. Its geometric isomers were also synthesised from 2-hydroxyquinoline, or 8-hydroxyquinoline, to give the previously reported ligand **5**.[35] Ligand **4** acts as a gelator for acetone to form gel **E** at an optimum ligand concentration of 3 mM. Ligand **4** was not found to gelate other common solvents. Gel **E** formed on standing at room temperature for around two days. The SEM micrograph of gel **E** shows a highly entangled network of twisted fibres, Fig. 5. The network is made up of thinner fibres, width of approximately 10 nm, twisting together to produce bundles. The thicker bundles of fibres have an approximate width of 55 nm, with the longest visible length at approximately 0.8 μm. The individual fibres forming gel **E** are a lot thinner than the fibres forming organo-gel **D**; this could reflect the relative difference in size of the gelator molecules. The observation of many bends within the structure indicates that these fibres are highly flexible.

Geometric isomers of **4** did not form any gels in our hands, but single crystals were obtained by vapour diffusion of diethyl ether into an acetonitrile solution of **5**. The crystals have composition **5**$\cdot$$(C_9H_6NO)_{0.25}$ with **5** crystallising with some additional 8-hydroxyquinoline. The single crystal structure of **5**$\cdot$$(C_9H_6NO)_{0.25}$ has a molecule of **5** on general positions, along with a partially occupied 8-hydroxyquinoline sited on an inversion centre. The three quinoline groups of **5** are all approximately orthogonal to the central benzene plane and oriented with two N-containing rings above the plane and one below. There are extensive face-to-face π–π stacking interactions between molecules of **5** which create a double-layered 2-D network, Fig. 6. This is good, albeit indirect, evidence that the predominant intermolecular interaction in gel **E** is π–π stacking.

Ligand **6** was synthesised by reaction of phloroglucinol with 3 equivalents of 2-(chloromethyl)quinoline in the presence of base. Ligand **6** is a gelator for dichloromethane in the presence of $CuBr_2$ to form dark green gel **F**, and for nitromethane in the presence of $CuBr_2$ to form the dark green gel **G**. In both cases small amounts of methanol were used to dissolve the $CuBr_2$. Gel **F** only forms on standing the mixture at room temperature. The gel forms with ligand concentrations between 18 and 27 mM with 3 equivalents of $CuBr_2$. Use of fewer equivalents of $CuBr_2$ produces a precipitate. Gel **G** occurs on cooling a hot solution with much lower ligand concentrations between 5 and 11 mM with 3 equivalents of $CuBr_2$. Use of fewer equivalents of $CuBr_2$ produces a sol. The IR spectra of both gels show minor coordination induced shifts consistent with metal complex formation. Elemental analysis of the dried gels **F** and **G** indicate an overall 2 : 1 metal–ligand stoichiometry, and ES-MS of gel redissolved in DMSO gives *m*/*z* values corresponding to $[Cu(\mathbf{6})_2Br]^+$ and $[Cu(\mathbf{6})Br]^+$ species for both

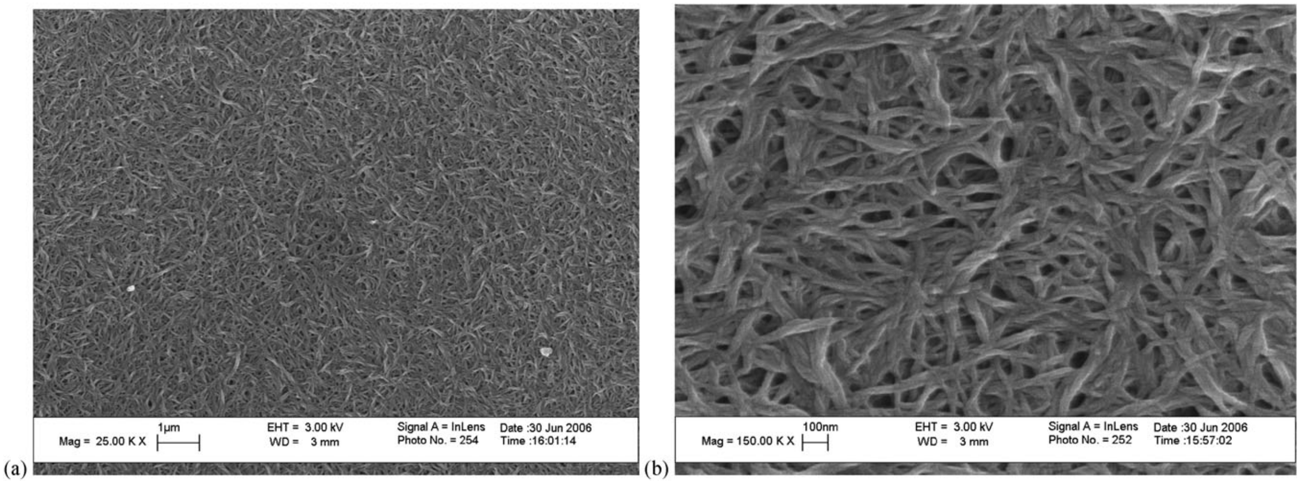

Fig. 5 SEM micrographs of gel **E** of 3 mM ligand **4** in acetone (a) at 2500 and (b) at 15 × 10^4 times magnifications. Gel was aged for two days prior to images being taken.

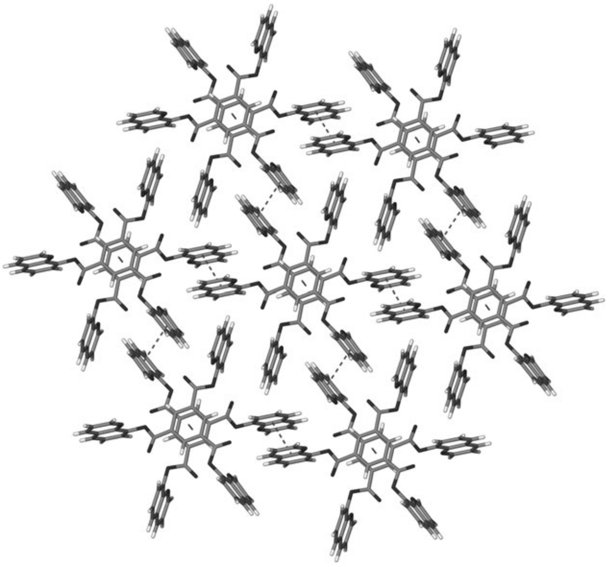

Fig. 6 Section of the X-ray structure of **5**·$(C_9H_6NO)_{0.25}$ with face-to-face π–π stacking interactions indicated by dashed lines. Centroid separations are 3.548 Å between core benzene groups, 3.898 Å between C_5N quinoline rings and 3.679 Å between C_6 quinoline rings.

gels. Evidence that two ligands bind to one metal centre and an overall M–L ratio less than 3 : 1 support the formation of coordination oligomers/polymers.

The SEM micrographs of gels **F** and **G** are shown in Fig. 7. The SEM micrograph of gel **F** shows randomly distributed, entangled fibres. The fibrous network is made up of thinner fibres twisting together to form 'rope-like' fibres and also fusing together without twisting to form flat 'tagliatelle-like' fibres. The thinnest fibres visible in the SEM micrograph are approximately 35 nm in width. These thin fibres form the 'rope-like' fibres of approximately 90 nm and the flat fibres of approximately 170 nm in width. The longest visible fibre shown has an approximate length of 9.5 μm. Gel **G** is a mass of highly flexible and entangled fibres, quite different to those of **F**. The flexibility of the fibres may arise from the flexibility of the ligand. The network is made up of fibres that are approximately 30 nm in width and orientated randomly relative to each other. The thin fibres twist together in bundles to produce rope-like thicker fibres that are approximately of width 0.2–0.5 μm, and are easily distinguished from the thinner fibres as their highly twisted nature results in a relatively greater depth/volume. The longest fibre visible has an approximate length of 15 μm. This extreme aspect ratio of

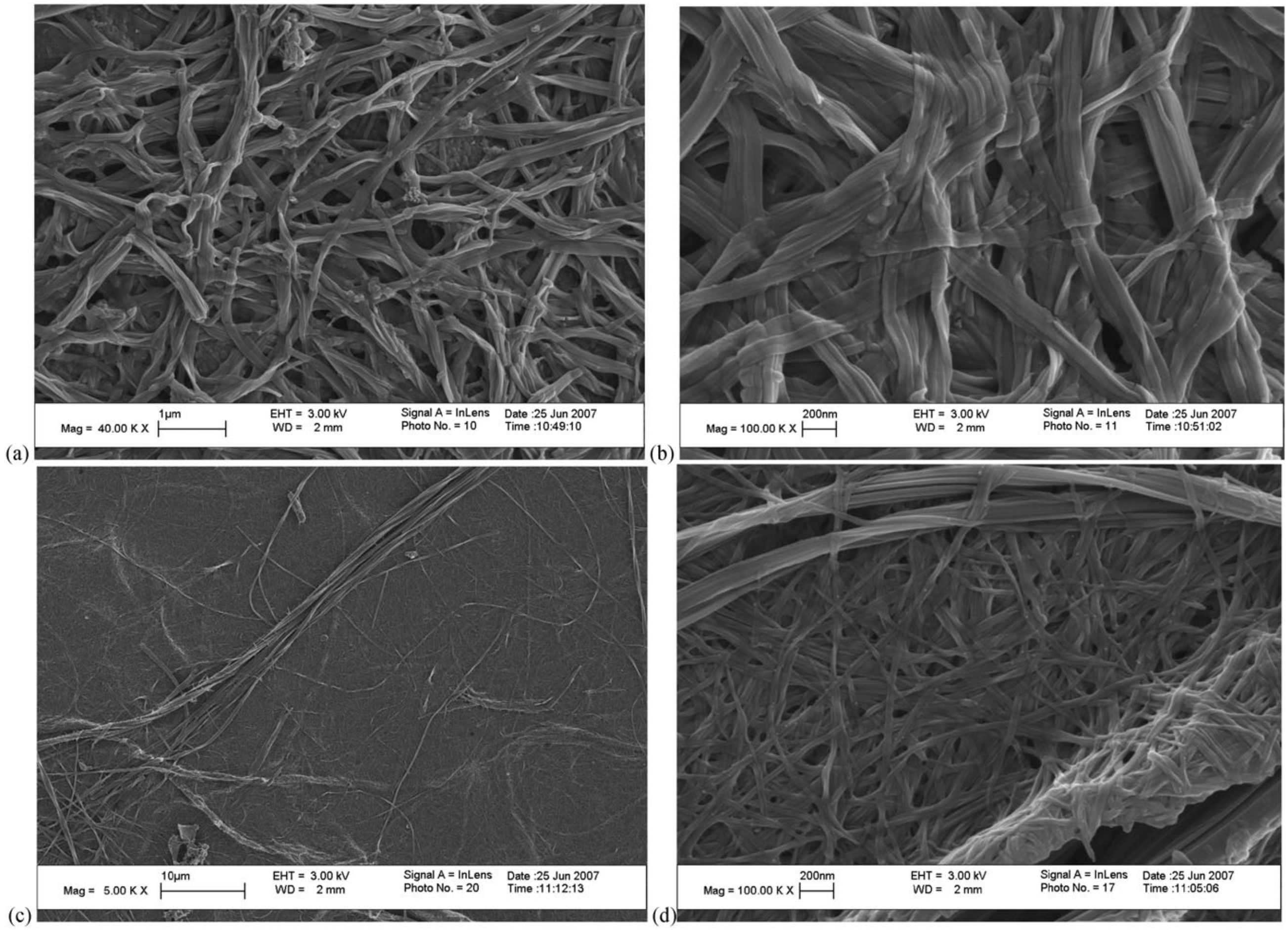

Fig. 7 SEM micrographs of metallo-gels involving ligand **6**. (a) 4 × 10^4 and (b) 105 times magnifications of gel **F** from 18 mM ligand **6** in CH_2Cl_2 with 3 equivalents of $CuBr_2$. (c) 5000 and (d) 10^5 times magnification of gel **G** from 5 mM ligand **6** in nitromethane with 3 equivalents of $CuBr_2$. Both gels were one day old before images were taken.

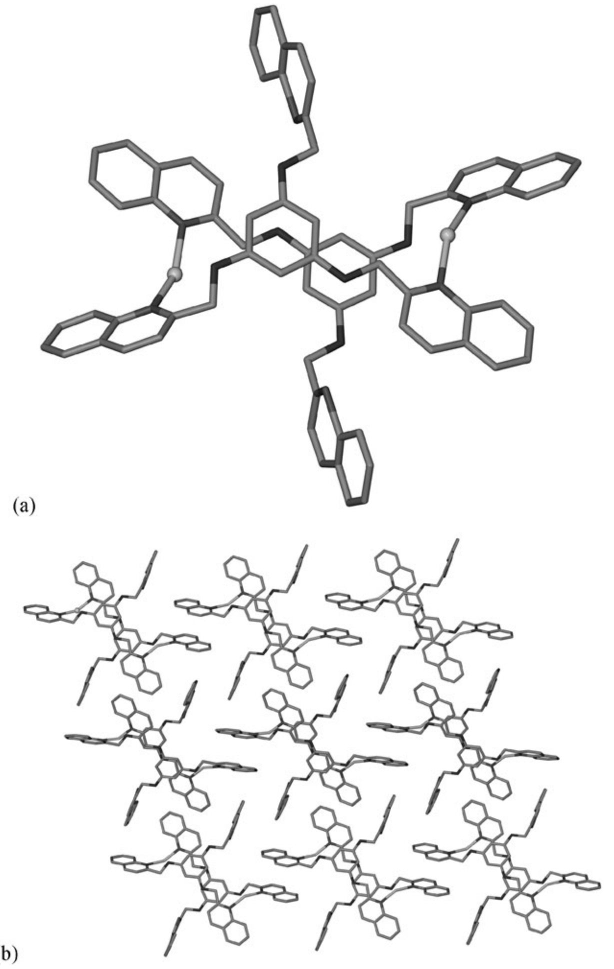

Fig. 8 From the crystal structure of complex $[Ag_2(\mathbf{6})_2](NO_3)_2$. (a) $[Ag_2(\mathbf{6})_2]^{2+}$ metallocycle; (b) 2-D layers formed through π–π stacking interactions. Hydrogen atoms and nitrate anions are excluded and only one of the three disorder positions of the unbound quinoline group is shown for the sake of clarity.

the fibres must arise from a strong anisotropic growth process, indicating that the fibres have a well-ordered molecular packing. The difference in morphology for **F** and **G** does not necessarily mean that the structures forming the gels are different, instead it highlights the effect of gelator solubility and hence gelator–solvent interactions.

Ligand **6** did not form gels with other metal salt and solvent combinations, but did form the crystalline complex $[Ag_2(\mathbf{6})_2](NO_3)_2$ from the slow evaporation of a nitromethane/acetonitrile solution of $AgNO_3$ and **6** in 1 : 1 proportions. The crystal structure reveals the complex to be a $[Ag_2(\mathbf{6})_2]^{2+}$ centrosymmetric metallocycle, Fig. 8a. Each ligand binds to two Ag(I) centres through two different quinoline groups. The third quinoline group does not coordinate to a metal and shows considerable positional disorder. The Ag(I) centres are coordinated by two ligands at Ag–N distances 2.248(4) and 2.219(4) Å with approximately linear geometry (N–Ag–N angle 156.03°). Each complex forms face-to-face π–π stacking interactions (centroid separation 3.863 Å) with a neighbouring complex molecule to form a 1-D chain. Additional C–H···π interactions link the chains into a 2-D network, Fig. 8b, with a C–H···π distance of 2.933 Å and a C–H···π angle of 147.76°. Again, the predominance of π–π stacking interactions in the crystal structure of $[Ag_2(\mathbf{6})_2](NO_3)_2$ supports similar interactions being important in gels **F** and **G**.

Properties of gels A–G

The response of all gels to mechanical, thermal and chemical external stimuli was investigated. Gels **A–C** and **E** are mechano-responsive but not mechano-reversible, with all three undergoing a gel-to-sol transition on shaking and/or sonication. Standing the sols at room temperature for a week did not result in re-gelation; hence, the intermolecular forces promoting the formation of the gels are disrupted by mechanical stimuli and do not re-form after disruption. The other gels did show some level of mechano-reversibility. Organo-gel **D** undergoes a gel-to-sol transition on sonication which re-gels at room temperature on standing for *ca.* 20 min, indicating that the hydrogen bonding interactions between the molecules are able to re-establish themselves after disruption. The metallo-gel **F** is also mechano-reversible, but not at the lowest ligand concentration for gelation (18 mM). Higher concentrations (24 and 27 mM of ligand) give a gel that re-gels after sonication.

The mechano-responsive behaviour of gel **G** is the most complicated and changes with ageing time of the gel. Shaking gel **G** for 30 min after gelation results in a gel-to-sol transition over all of the concentrations analysed. The resulting sol re-gels overnight when left to stand; however, not all of the solvent present is trapped into the re-gelation network with a very small volume (approx. <0.1 ml) of solution left over. Similar treatment of the gel one day after gelation occurred but did not result in a gel-to-sol transition. Harsher treatment by sonication does give a gel-to-sol transition over all of the concentrations analysed. As for gel **F**, the sol with the lowest ligand concentration (5 mM) did not re-gel even after one

Table 1 T_{gel} and DSC measurements for CTV-based metallo-gels

Conc./mM	%wt	T_{gel}/°C	DSC: range, maxima (cooling)/°C
Gel **A**[a]			
10	1.05	115	79–111, 101.5
13	1.32	141	115–133, 121.7
16	1.59	155	125–139, 136.4
Gel **B**[a]			
12	1.1	55	45–53,[d] (41–27)
16	1.36	62	40–55,[d] (45–27)
21	1.82	58	43–54,[d] (52–32)
Gel **C**[b]			
18	0.5	80	75.1[e]
29	0.84	116	108.3[e]
42	1.18	123	120[e]
Gel **D**[c]			
12	0.72	93	87.5,[e] (51–27)
Gel **E**[c]			
3	0.25	78	40–82.5, 65.1
Gel **F**[a]			
18	0.75	80	32–76, 67.1
24	1.02	88	36–90, 73.3

[a] Varying ligand conc. with 3 equivalents of metal salt. [b] Varying $CuBr_2$ conc. with 6 mM ligand. [c] Only one conc. studied as close to solubility limit. [d] Multiple maxima. [e] Abrupt change.

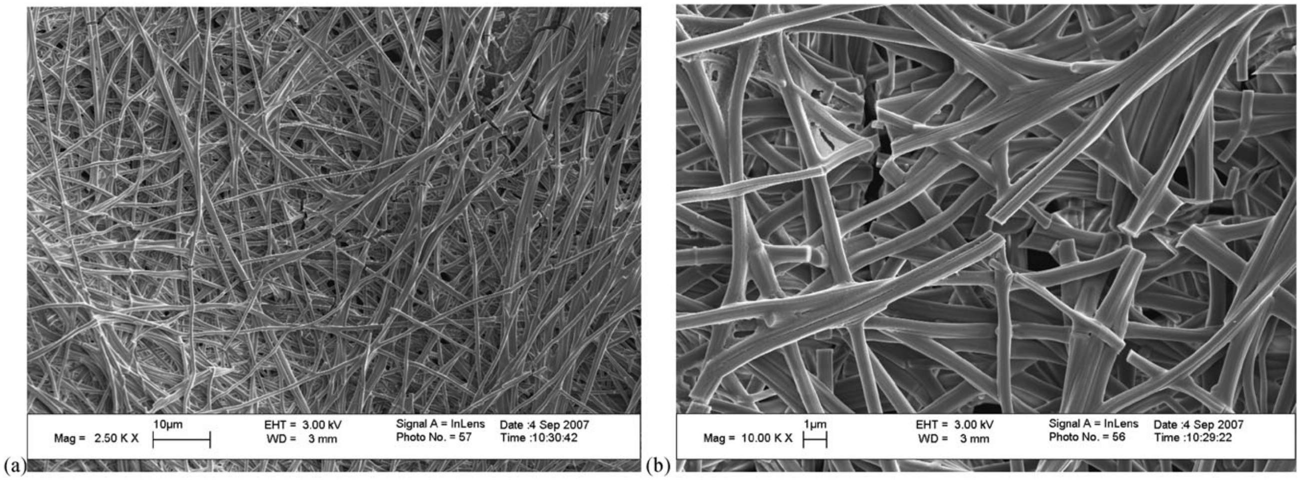

Fig. 9 SEM micrographs of gel **A2** formed on layering gel **A** with ethyl acetate. (a) 2500 and (b) 10^4 times magnification. Gel was three days old at time of images being taken.

week of standing; however, at 8 and 11 mM concentrations re-gelation did occur, though again not all of the solvent present was trapped into the re-gelation network. Gel **G** is mechano-responsive and mechano-reversible when at a certain age or concentration, indicating that structural reorganisation of gel **G** takes place upon ageing and that increasing the concentration of gel **G** increases its stability.

Gels **A–G** show differing thermal behaviour. All are thermally stable with no colour changes or visible deterioration to temperatures up to 100 °C. All aside from gel **G** are thermo-responsive, undergoing gel-to-sol transitions at elevated temperatures, but they show different abilities to re-gel (thermo-reversibility) according to identity and reactant concentration. T_{gel} and DSC measurements of the gel-to-sol transition and thermo-reversibility are given in Table 1. Broad temperature ranges, such as for **E**, indicate a weak and poorly defined gel-to-sol transition. Gels **B** and **D** are thermo-reversible at all concentrations tried, while gels **C** and **E** were not found to be thermo-reversible. Gel **A** is only thermo-reversible at higher ligand concentrations, while **F** is thermo-reversible only at 24 mM ligand concentration. For gel **F**, heating the gel made with a higher ligand concentration of 27 mM did not give a gel-to-sol transition but rather produced a solid, which is likely to be due to the low boiling point of the solvent (39 °C), meaning that the solvent was omitted before the gel-to-sol transition could occur. For gels **A**, **C** and **F** the T_{gel} temperature increases with increasing concentration of reactants, as would be expected for higher levels of interactions within the fibrous structures. This does not occur for **B** which maintains similar T_{gel} temperatures for different reactant concentrations, and has a significantly lower T_{gel} than the other gels studied here. This is likely to be due to the lack of an overtly fibrous structure for **B**, where an increase in reactant concentration will not lead to higher levels of cross-linking and hence greater T_{gel} values.

Heating gel **G** did not result in a gel-to-sol transition over all of the concentrations analysed, even up to temperatures of 145 °C. Some solvent was lost at approximately 100 °C but the gel remained intact. At approximately 135 °C gel **G** turned from green to orange, possibly due to decomposition of the system. There was no further change in the sample on heating to 145 °C and a homogeneous sol phase was not formed. Cooling the sample to room temperature did not recover gel **G** to its original state. Gel **G** is very stable at temperatures up to 130 °C, highlighting the strength of the forces holding the gel together.

The chemoresponsiveness of the metallo-gels was also tested. With the exception of gel **F**, all were disturbed by pH changes with dissolution or irreversible sol-formation occuring on shaking with aqueous 1 M NaOH or 1 M HCl. The gels showed different responses to shaking with organic solvents, with gel **B** showing no effects from methanol, acetone or ethyl acetate, and gels **C**, **D** and **G** forming an irreversible sol or dissolving when shaken with the same solvents or water. Gel **F** was impervious to shaking with water, 1 M NaOH, 1 M HCl or ethyl acetate, but formed an irreversible sol on shaking with methanol or acetone.

Gel **A** has the most interesting behaviour, giving no change on shaking with methanol or water, but producing sols when shaken with acetone or ethyl acetate. The ethyl acetate sample re-gels after *ca.* 5 min to produce a new gel, **A2**, of larger volume than the parent gel and a resulting ligand concentration of 5 mM. Re-layering gel **A2** with DMF results in an irreversible gel-to-sol transition. Curiously, ligand **1** and $CuCl_2$ were not observed to gelate ethyl acetate when mixed directly in that solvent.

The SEM micrograph of gel **A2** shows a similar fibrous entangled structure to that of parent gel **A**, Fig. 9. The fibres forming the structure are slightly different, however, as they appear thinner and longer than the original. The approximate width of the thinnest visible fibre is 0.3 μm (compared to 0.38 μm for the original) with the thicker bundles at approximately 1.2 μm and the longest visible fibre at approximately 17 μm (compared to 2 μm for the original). The fibrous network of gel **A2** appears to have stretched to accommodate the extra solvent, indicating flexibility of the network. Gel **A2** was not thermo-reversible and not as thermostable as the parent **A** with a T_{gel} of 35 °C. Gel **A2** remains unchanged for at least six months on standing at room temperature.

Experimental

Synthesis of ligands

Tris(isonicotinoyl)cyclotriguaiacylene **1**,[27] tris(4-[4-methyl-2,2′-bipyridyl]methyl)cyclotriguaiacylene **2**,[26] triaminocyclotriguaiacylene (aCTG)[21] and benzene-1,3,5-tricarboxylic acid tris(8-hydroxyquinoline) ester **5**[35] were synthesised by literature methods. All other chemicals were obtained from Sigma-Aldrich Chemical Company or Lancaster Synthesis Ltd and were used without further purification. NMR spectra were recorded by automated procedures on a Bruker DPX 300 NMR spectrometer. Electrospray mass spectra (ES-MS) were measured on a Bruker MicroTOF-Q instrument in positive ion mode. Infrared spectra were recorded as solid phase samples on a Perkin-Elmer Spectrometer.

Tris(3-(3-pyridyl)-1-thiourea)cyclotriguaiacylene 3. A solution of aCTG (0.6 g, 1.46 mmol) and 3-pyridylisothiocyanate (0.51 mL, 4.38 mmol) was heated at reflux in dichloromethane (50 mL) for six hours to give a cream precipitate. The solution was cooled to room temperature and the precipitate was collected by filtration. Washing the solid with dichloromethane (2 × 10 ml) and diethyl ether (2 × 10 ml) gave **3** as a cream solid (1.05 g, 86%). Mp: 183.4–185.1 °C; CHN Anal.: found: C, 60.25; H, 4.75; N, 14.50. Calc. for $C_{42}H_{39}O_3N_9.1.5H_2O$: C, 59.97; H, 5.04; N, 14.99%; IR: ν_{max} = 1140, 1182 (C–S double bond), 1254, 1322 (C–H alkyl), 1483 (conj, cyclic, CC), 1535, 1596 (conj, cyclic, CN), 2834 (C–H alkyl), 3420 (N–H amine) cm^{-1}; ^1H NMR (300 Hz, DMSO-D_6): δ = 3.62 (3H, d, J = 13.5 Hz, CH_2), 3.76 (9H, s, OMe), 4.83 (3H, d, J = 13.5 Hz, CH_2), 7.10 (3H, s, aryl H), 7.34 (3H, dd, J = 4.7 and 8.1 Hz, H^5), 7.97 (3H, d, J = 8 Hz, H^4), 8.07 (3H, s, aryl H), 8.28 (3H, d, J = 4.5 Hz, H^6), 8.6 (3H, s, H^2), 9.28 (3H, s, NH), 9.92 (3H, s, NH) ppm; ^{13}C NMR (300 Hz, $CDCl_3$): δ = 35.89, 56.03, 113.32, 123.35, 125.84, 127.39, 131.14, 131.60, 136.79, 138.05, 145.42, 145.65, 150.65, 180.17 ppm; TOF-MS ESI: m/z = 814.2 (M^+).

Benzene-1,3,5-tricarboxylic acid tris(4-hydroxyquinoline) ester 4. A solution of 1,3,5-benzenetricarbonyl trichloride (0.30 g, 1.13 mmol) in dry dichloromethane (15 mL) was added to a solution of 4-hydroxyquinoline (0.5 g, 3.40 mmol) and triethylamine (0.5 mL, 3.89 mmol) in dichloromethane (50 mL). The reaction mixture was heated at reflux for twenty-four hours. The solution was washed with water (2 × 30 mL) and brine (2 × 30 mL) before evaporating to dryness under reduced pressure; washing with diethyl ether (3 × 20 mL) gave **4** as a cream solid (0.51 g, 76%). Mp: 169.9–172.6 °C; CHN Anal.: found: C, 71.5; H, 3.75; N, 6.85. Calc. for $C_{36}H_{21}O_6N_3\cdot 0.5H_2O$: C, 71.87; H, 3.85; N, 6.98%; IR: ν_{max} = 1503, 1567 (conj, cyclic, CN), 1600, 1624 (conj, cyclic, CC), 1754 (aryl esters, COO), 3011, 3076 (aryl H) cm^{-1}; ^1H NMR (300 Hz, $CDCl_3$): δ = 7.53 (3H, d, J = 4.9 Hz, H^3), 7.63 (3H, t, J = 1 and 7 Hz, H^6), 7.82 (3H, t, J = 1.3 and 6.9 Hz, H^7), 8.06 (3H, d, J = 8.3 Hz, H^5), 8.23 (3H, d, J = 8.4 Hz, H^8), 9.04 (3H, d, J = 4.9 Hz, H^2), 9.54 (3H, s, arom H) ppm; ^{13}C NMR (300 Hz, $CDCl_3$): δ = 112, 120.9, 122.1, 127.4, 129.9, 130.4, 131.1, 136.8, 150.2, 150.9, 153.8, 161.9 ppm; TOF-MS ESI: m/z = 592.4 (M^+, 100%), m/z 447.4 (M − $OC_5H_2NC_4H_4^+$, 37), 302.2 (M − $(OC_5H_2NC_4H_4)_2^+$, 72).

1,3,5-Tris(2-quinoline-methoxyl)benzene 6. A solution of phloroglucinol (0.15 g, 1.19 mmol), potassium carbonate (1.3 g, 9.5 mmol), potassium iodide (1.5 g, 9 mmol) and 2-(chloromethyl)quinoline (1.1 g, 6.18 mmol) in dimethylformamide (10 mL) was heated at 70 °C under nitrogen for three days. Additional 2-(chloromethyl)quinoline (0.5 g, 3.09 mmol) was added to the suspension and the solution was allowed to stir at 70 °C for a further four days. The solution was cooled to room temperature before adding ethyl acetate (300 mL) and the organic layer was washed with water (4 × 50 mL) to remove the dimethylformamide. The organic layer was dried with magnesium sulfate before evaporating to dryness under reduced pressure to produce an oily brown solid. Purification was effected by column chromatography on silica gel using 40% ethyl acetate in dichloromethane as an eluent, to give **6** as a white solid (0.25 g, 40%). Mp: 175.3–177.3 °C; CHN Anal.: found: C, 78.5; H, 4.8; N, 7.4. Calc. for $C_{36}H_{27}O_3N_3$: C, 78.66; H, 4.96; N, 7.65%; IR: ν_{max} = 1117, 1167 (ether, CO), 1508, 1590 (conj, cyclic, CN), 1615 (conj, cyclic, CC), 3055 (aryl H) cm^{-1}; ^1H NMR (300 Hz, $CDCl_3$): δ = 5.32 (6H, s, CH_2O), 6.39 (3H, s, arom H), 7.53 (3H, t, J = 1.1 and 8.07 Hz, H^6), 7.60 (3H, d, J = 8.5 Hz, H^3), 7.73 (3H, t, J = 1.4 and 8.2 Hz, H^7), 7.81 (3H, d, J = 8.3 Hz, H^5), 8.01 (3H, d, J = 8.2 Hz, H^4), 8.11 (3H, d, J = 8.5 Hz, H^8) ppm; ^{13}C NMR (300 Hz, $CDCl_3$): δ = 71.80, 95.88, 119.50, 126.87, 127.98, 128.08, 129.41, 130.12, 137.34, 147.98, 158.01, 160.85 ppm; TOF-MS ESI: m/z = 550.2 (M^+).

$[Ag_2(\mathbf{6})_2](NO_3)_2$

A solution of **6** (8 mg, 14.5 μmol) in nitromethane (3 mL) was added to a solution of $AgNO_3$ (2.5 mg, 14.5 μmol) in acetonitrile (1 mL). The resulting colourless solution was left to slowly evaporate. After two days colourless crystals of $[Ag_2(\mathbf{6})_2](NO_3)_2$ (6.5 mg, 34%) suitable for X-ray determination were produced. CHN Anal.: found: C, 54.30; H, 3.40; N, 7.05. Calc. for $AgC_{36}H_{27}O_6N_4\cdot 3.5H_2O$: C, 55.25; H, 4.39; N, 7.16%; IR: ν_{max} = 779, 822, 1057, 1156, 1214, 1396, 1511, 1621, 1744, 1963, 2325, 2896, 3067, 3467 cm^{-1}.

Synthesis and characterisation of gels

Gelation was considered to have occurred when the sample did not exhibit any gravitational flow upon inversion of the container in which it was found. Elemental analysis, IR and SEM analysis were undertaken on the gels formed at the optimum (lowest) concentrations. Elemental analyses were run on gel samples that had been evaporated to dryness, washed with methanol and re-dried under vacuum. SEM images were obtained using a Leo 1530 Field Emission Gun SEM (FEGSEM). All gel samples were dried onto standard SEM stubs. Once mounted all samples were coated with a 3 nm layer of platinum–palladium mixture using a high resolution sputter coater. High resolution secondary electron images were acquired using a low accelerating voltage of 3 kV. The gel-to-sol and reverse transition (if relevant) for all gels were recorded on a Linkam Scientific Differential Scanning Calorimeter (DSC) 600 instrument. Sample preparation involved placing a given amount of gel in an aluminium pan, which was hermetically sealed. Heating and cooling scans were recorded at a scan rate between 2 and 5 °C per min. T_{gel} values for all gels were recorded using the 'dropping ball method' or the 'tilting tube method'.[36,37] Microanalyses and IR spectra of gels were undertaken after decanting supernatant liquid and allowing to dry out.

Gel A. Ligand **1** (10 mg, 0.010 mmol) and $CuCl_2$ (5.5 mg, 0.030 mmol) in dimethylformamide (1 mL) were heated to 60 °C. Cooling of the clear green solution to room temperature resulted in an opaque green gel almost immediately. CHN Anal.: found: C, 50.25; H, 5.10; N, 6.45. Calc. for $Cu_3C_{60}H_{54}O_6N_6Cl_6{\cdot}5H_2O$: C, 49.74; H, 4.46; N, 5.80%. IR: ν_{max} = 1264, 1444, 1615, 1651, 2928, 3479 cm^{-1}; TOF-MS ESI: m/z = 1322.1 ($[Cu_3(\mathbf{1})Cl_5]^+$), 1187.2 ($[Cu_2(\mathbf{1})Cl_3]^+$), 1052.3 ($[Cu(\mathbf{1})Cl]^+$).

Gel B. Ligand **1** (12 mg, 13 μmol) and $AgSbF_6$ (13 mg, 39 μmol) in dimethyl sulfoxide (1 mL) were heated to 50 °C. Cooling of the clear colourless solution to room temperature resulted in a translucent colourless gel after ten minutes. Analysis of solution at slightly lower ligand concentrations (11.5 mM) than required for gelation: ^1H NMR (300 Hz, DMSO-D_6): δ = 3.35, 3.47, 3.55, 4.72, 5.28, 7.01, 7.21, 7.39, 7.5, 8.20, 8.42, 8.54, 8.58 ppm. TOF-MS ESI: m/z = 1750.9 ($[Ag_3(\mathbf{1})](SbF_6)_2{}^+$), 1407.1 ($[Ag_2(\mathbf{1})](SbF_6)^+$), 1063.3 ($[Ag_3(\mathbf{1})]^+$).

Gel C. A solution of **2** (3 mg, 4.2 μmol) in acetonitrile (1 mL) was added to $CuBr_2$ (2.8 mg, 12.6 μmol). A green precipitate was formed instantaneously. Reducing the volume of the sample to 0.7 mL resulted in a green, opaque gel overnight. CHN Anal.: found: C, 43.2; H, 3.0; N, 4.35. Calc. for $Cu_2C_{44}H_{41}O_{12.5}N_4Br_4{\cdot}CH_3CN$: C, 43.62; H, 3.00; N, 4.63%. IR: ν_{max} = 732, 1072, 1141, 1178, 1268, 1439, 1475, 1508, 1611, 1736, 3568 cm^{-1}

Gel D. Ligand **3** (5 mg, 6.1 μmol) was heated in trifluoroethanol (1 mL) until a homogeneous colourless, clear solution was produced. Reducing the volume of the sample to 0.5 mL resulted in a colourless, opaque gel overnight. IR with spectrum of solvent used as background: ν_{max} = 664, 829, 947, 1022 (s, br), 1275, 1416, 3306 (br) cm^{-1}

Gel E. Ligand **4** (2 mg, 3.38 μmol) was heated in acetone (1 mL) until a homogeneous colourless, clear solution was produced. Leaving the solution to stand at room temperature for two days produced an opaque colourless gel.

Gel F. A solution of ligand **6** (10 mg, 18 μmol) in dichloromethane (1 mL) was added to a solution of $CuBr_2$ (12 mg, 55 μmol) in methanol (0.05 mL) to a produce a suspension of a dark green solid. Allowing the solution to stand at room temperature for twenty minutes resulted in an opaque dark green gel. CHN Anal.: found: C, 43.00; H, 3.20; N, 4.15. Calc. for $Cu_2C_{36}H_{27}O_3N_3Br_4$: C, 43.39; H, 2.74; N, 4.22%. IR: ν_{max} = 769, 836, 1143, 1410, 1448, 1548, 1600, 1658, 2942, 3018, 3497 cm^{-1}; TOF-MS ESI: m/z = 1241.3 ($Cu(\mathbf{6})_2Br]^+$), 692.0 ($CuLBr^+$).

Gel G. A hot solution of ligand **6** (3 mg, 5.4 μmol) in nitromethane (1 mL) was added to a solution of $CuBr_2$ (3.6 mg, 16 μmol) in methanol (0.05 mL) to produce a clear dark green solution. Allowing the solution to stand at room temperature for ten minutes resulted in an opaque dark green gel. CHN Anal.: found: C, 42.70; H, 3.15; N, 4.10. Calc. for $Cu_2C_{36}H_{27}O_3N_3Br_4$: C, 43.39; H, 2.74; N, 4.22%. IR: ν_{max} = 741, 776, 822, 1139, 1179, 1223, 1248, 1380, 1427, 1509, 1592, 1660, 2909, 3049 cm^{-1} TOF-MS ESI: m/z = 1241.3 ($Cu(\mathbf{6})_2Br]^+$), 692.0 ($CuLBr^+$).

X-Ray crystallography

Single crystals were mounted on a glass fibre under oil and X-ray data collected at 150(1) K on a Bruker X8 diffractometer with Apex II detector and Mo rotating anode source (λ = 0.71073 Å). The data were corrected for Lorentzian and polarisation effects, and absorption corrections were applied using multi-scan techniques. Structures were solved by direct methods using SHELXS-97[38] and refined by full-matrix least squares on F^2 by SHELXL-97[39] *via* the X-Seed GUI.[40] Unless otherwise stated, all non-hydrogen atoms were refined anisotropically and H atoms included at geometrically estimated positions. For $\mathbf{5}{\cdot}(C_9H_6NO)_{0.25}$ the 8-hydroxyquinoline was situated over an inversion centre and refined at half overall occupancy, with symmetry-imposed disordered C/N and OH positions. For $[Ag_2(\mathbf{6})_2](NO_3)_2$ hydrogen atoms were excluded from the disordered quinoline group which was refined isotropically and modelled over three positions and using FLAT restraints.

$\mathbf{5}{\cdot}(C_9H_6NO)_{0.25}$. $C_{38.25}H_{22.5}N_{3.25}O_{6.25}$, M_r = 627.59, triclinic, space group $P\bar{1}$, a = 11.2727(7), b = 12.8730(7), c = 12.9939(7) Å, α = 66.724(3), β = 72.538(3), γ = 71.602(3)°, V = 1609.99(16) Å^3, Z = 2, ρ_{calc} = 1.295 g cm^{-3}, μ = 0.090 mm^{-1}, crystal size 0.29 × 0.21 × 0.10 mm, θ_{max} = 33.52°, 32 482 data collected, 11 284 unique, R_{int} = 0.0213, 454 parameters, R_1 = 0.0739 (for 8106 data $I > 2\sigma(I)$), wR_2 = 0.2457 (all data), S = 1.064.

$[Ag_2(\mathbf{6})_2](NO_3)_2$. $C_{72}H_{54}Ag_2N_8O_{12}$, M_r = 1438.98, monoclinic, space group $P2_1/n$, a = 16.1964(13), b = 7.6782(6), c = 27.625(2) Å, β = 105.793(4)°, V = 3305.8(5) Å^3, Z = 2, ρ_{calc} = 1.446 g cm^{-3}, μ = 0.661 mm^{-1}, crystal size 0.42 × 0.28 × 0.10 mm, θ_{max} = 29.86°, 75 639 data collected, 9310 unique, R_{int} = 0.0505, 442 parameters, 18 restraints, R_1 = 0.0608 (for 6172 data $I > 2\sigma(I)$), wR_2 = 0.2151 (all data), S = 1.106.

Conclusions

Tripodal molecules bearing ligand functionality have been shown to form a variety of metallo- and organo-gels. While the ligands are all multi-functional and therefore capable of forming coordination polymers, there is good evidence that some of these metallo-gels are formed by discrete species rather than polymers or oligomers. With the exception of gel **D** where the gelator molecule has strongly hydrogen bonding thiourea groups, an important supramolecular interaction between gelator molecules is likely to be π–π stacking interactions between the ligands. This is supported by the crystal structures reported here and elsewhere of these and similar ligands which usually show such interactions. In the case of most of the metallo-gels, the fibrous nature of the gels is consistent with previous reports of gelating coordination polymers.[14] A notable feature of all of the examples given here is that gels were only observed to form under very specific conditions—gelator ligands with a particular metal salt, and a particular solvent. This is in marked contrast with the CTV-based gels reported by Hannon *et al.* where the host bearing a 2-dimethylacetal-5-carbonylpyridine moiety was able to gelate a wide range of organic solvents.[19] All of the ligands which formed metallo-gels will also form crystalline coordination polymers or discrete metallo-supramolecular assemblies that crystallise rather than form gels. Hence predicting whether these classes of ligands will form a metallo-gel or a more ordered complex presents itself as a significant challenge.

Acknowledgements

We thank the EPSRC and University of Leeds for supporting this research. We thank Tanya Marinko-Covell for mass spectrometry and Ian Blakeley and Martin Huscroft for elemental analysis.

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