Chiral binaphthylbisbipyridine-based copper(1) coordination polymer gels as supramolecular catalysts[†]

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A novel class of chiral coordination polymer organogels, with multi-stimuli responsive properties and suitable for use as catalysts in 1,3-dipolar Huisgen cycloaddition reaction, are reported.

Recently, studies on metallogels have received much interest from chemists because the presence of the metal ions may endow the gel unusual functionalities such as spectroscopic, magnetic, redox and catalytic properties.¹ It has been reported that some discrete metal complexes may self-assemble into gel fibers by intermolecular hydrogen bonding, π -stacking, solvophobic, and metal-metal interactions.² Furthermore, the use of multidentate bridging ligands or rare earth metal ions can also result in the formation of a 3D cross–linked gel network.³ However, very few metallogels based on a 1D coordination polymer are known.⁴ For example, Kimizuka *et al.* have described that Co(II) and lipophilic 1,2,4-triazole assemble into a linear polymer structure leading to the gelation.⁵ Lee *et al.* have reported stimuli–responsive hydrogels from silver coordination polymers.⁶

As we know, 2,2'-bipyridine is one of the most important ligands in coordination chemistry.⁷ Especially, bisbipyridines have been shown to form helical complexes with a range of transition metal ions.⁸ Recently, Lützen's group testified that enantiomerically pure dinuclear double-stranded helicates may be formed by diastereoselective self-assembly of the binaphthylbisbipyridine ligands and copper(1) ion.⁹ In this communication, we report a novel self-assembly pattern between chiral binaphthyl-based bisbipyridine and copper(1) ion as a 1D metal coordination polymer organogel.

The ligands **1–6** were synthesized by a Suzuki cross-coupling reaction (Scheme 1, see ESI[†]). All of the analytical data are in full agreement with the chemical structures presented. Very interestingly, when the complexation of equimolar **1** and $Cu(CH_3CN)_4BF_4$ was performed in hot $CH_3CN-CH_2Cl_2$ (v/v, 1/1) solution, a dark red gel phase was formed on cooling to room temperature, with the minimum gel concentration (MGC) of 10 mM, which is above the upper solubility limit for the ligand in the mixed solvent. Complexation also successfully gelated $CH_3CN-THF$ and CH_3CN -dioxane mixed solvents at room temperature. The formation of the gel was dependent on

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stoichiometry. The use of less than one equivalent of Cu(CH₃CN)₄BF₄ resulted in a sol being formed. In addition, the counterions of copper(1) can influence the gelation. CuCF₃SO₃ and CuI only afforded solutions or precipitates, respectively. Slightly surprisingly, we found that gel Cu(1)·1 could also be formed *via* sonicating the suspension of 1 and Cu(CH₃CN)₄BF₄ in CH₂Cl₂-CH₃CN at room temperature. The formed gels were stable at ambient temperature and no crystallization or dissolution happened after months.

When hydrophilic methoxymethyl sidechains in 1 were replaced by hydrophobic ethyl or hexyl groups, a gel in CH₃CN-CH₂Cl₂ (v/v, 1/1) was still formed with MGC of 9.0 mM for Cu(i)·2 and 14.7 mM for Cu(i)·3, respectively. Cu(i)·4 required a longer time to produce a gel (MGC, 16.2 mM), while Cu(i)·5 completely lost the gelation ability in the mixed solvent, indicating the length of spacer unit between bipyridine and binaphthyl ring in the ligand could affect the gelation property.

All attempts to obtain single crystals of Cu(1)-1 failed. However, postulation of the polymerization of ligands and Cu(1) ions by tetrahedral coordination and the proper assembling of the 1D polymeric chains into higher-order organized fibers could easily explain the gel formation (Fig. 2). No gelation was observed when **6** was used instead of **1**, also suggesting that the formation of the 1D coordination polymer was necessary for the gelation.

The coordination behavior of 1 towards copper(1) was first investigated by ¹H NMR spectroscopy. Compared to the ¹H NMR spectrum of the free ligand, the proton signals of Cu(1)·1 in solution became broad and were significantly shifted, indicating the formation of metal coordination bonds and a very dynamic behavior on the NMR time scale.¹⁰ Lowering the temperature led to more ill-resolved signals,



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Fig. 1 Phase transition behavior of gel Cu(1)-1 triggered by sonication, temperature, chemical redox reaction and solvent.



Fig. 2 A schematic representation of the possible self-assembly processes of the coordination polymer gel $Cu(1) \cdot 1$.

presumably resulting from a slower exchange process or the formation of new species. The coordination reaction of **1** and copper(1) was further monitored through both UV-vis and circular dichroism (CD) spectroscopic titration. As depicted in Fig. 3, clear spectral changes were observed upon the addition of copper(1) aliquots to solutions of the compound **1**. The existence of unideal isosbestic points suggested the formation of oligomers or polymers in the complexation process between **1** and copper(1).¹¹ The Job plot analysis exhibited the 1:1 complexation of Cu(1) and **1**.

The CD spectra of two copper(1) complexes of 1 and its enantiomer showed they were identical mirror images, indicating the expected formation of supramolecular enantiomers. The complex Cu(1)·1 and the free ligand showed a rather dominant Cotton effect in the 235 to 275 nm region, which is caused by the (*P*)-configured chiral binaphthyl axis. More important was that the first positive Cotton effect assigned to the ligandcentered transition appeared at 375 nm (Fig. 3). Applying



Fig. 3 Titration curves of **1** solution $(2 \times 10^{-4} \text{ M} (a), 1 \times 10^{-5} \text{ M} (b))$ in CH₃CN–CH₂Cl₂ (v/v, 1/1) with Cu(CH₃CN)₄BF₄ by CD (a) and UV-vis (b) spectroscopy.

exciton coupling theory and by comparison with related literatures, ^{9,12} we assigned a Λ configuration at the copper(1) center. This led to a proposed overall *P*-helical polymeric structure for the complex Cu(1)·1 (Fig. 2).

The properties of gel $Cu(1) \cdot 1$ were characterized by various analytical techniques. Differential scanning calorimetric (DSC) analysis of gel Cu(I) 1 showed no endothermic transition when heating to 100 °C, indicating the gel was stable below this temperature. The MALDI-TOF-MS spectrum of the complex displayed the base peak at m/z = 897.24663, corresponding to $[Cu(I)\cdot 1]^+$ (calcd. 897.24966), indicating the polymer underwent severe fragmentation.13 The characteristic C-N stretching peaks of the bipyridine in ligand 1, observed at 1586, 1458 cm⁻¹ in the IR spectrum, shifted to 1593, 1468 cm⁻¹ in xerogel, suggesting the coordination of the bipyridines.¹⁴ The absorption spectra of gel $Cu(I) \cdot I$ exhibited the typical MLCT absorption band at 452 nm, which is attributable to the tetrahedrally coordinated Cu(1) (2,2'-bipyridine)₂ complex.¹⁵ In addition, the maximum absorption of gel Cu(I)·1 red-shifted 13 nm compared to diluted solution (CH₃CN-CH₂Cl₂, 2×10^{-6} M), indicating that $\pi - \pi$ stacking interactions between 1D polymeric chains could play an important role in the formation of gel-fibers (Fig. 4a). Scanning electron microscopic (SEM) images (Fig. 4b) of xerogel Cu(1) 1 revealed the existence of typical nanofibers, responsive for the observed gelation.

The redox-responsive properties of gel Cu(1)-1 were measured.¹⁶ The oxidant NOBF₄ could turn the dark red gel into the pale green solution, and afterward, ascorbic acid was used to regenerate the gel (Fig. 1, see ESI†). UV-vis spectra revealed that the MLCT absorption band at 452 nm disappeared in the oxidized solution sample and appeared again in the re-formed gel. Therefore, it is obvious that the redox state of copper ion plays a crucial role in the stability of gel system. In addition, no collapse was observed when various solvents, including CH₂Cl₂, CH₃CN, CH₃OH, THF, acetone, hexane, H₂O, DMF and HOAc, were placed over the metallogel, and no Cu(1) was leached out of the metallogel as confirmed by inductively coupled plasma-mass spectrometry (ICP-MS) analysis. However, the metallogel completely dissolved in pyridine (Fig. 1).

Using Huisgen 1,3-dipolar cycloaddition ("click" reaction) as a model reaction, we explored the catalytic ability of these metallogels (Table 1).¹⁷ Initial experiments were performed with 1 mol% xerogel Cu(1)·3 as the catalyst and with benzyl azide and ethynylbenzene as reactants in different solvents at



Fig. 4 UV-vis absorption spectra (a) of Cu(1)·1 in CH₃CN–CH₂Cl₂ (v/v, 1/1) solution $(2 \times 10^{-6} \text{ M})$ and gel $(1.6 \times 10^{-2} \text{ M})$, and the SEM image (b) of xerogel Cu(1)·1.

	∕_N ₃ +	R=== 8a-f	Xerogel (* RT, a	1 mol%) air 9a-	N∕N∕−R N≈N f	a: R = Ph b: R = <i>p</i> -Tol c: R = <i>m</i> -Tol d: R = 2-Py e: R = TMS f: R = <i>n</i> -Bu
Entry	Catalyst	Azide	Alkyne	Solvent	Time/h	Yield $(\%)^b$
1	Cu(I)·3	7	8a	CH ₂ Cl ₂	18	64
2	$Cu(I) \cdot 3$	7	8a	CH ₃ CN	18	59
3	$Cu(I) \cdot 3$	7	8a	CH ₃ CN–H ₂ O ^c	18	56
4	$Cu(I) \cdot 3$	7	8a	H_2O	18	100 (97)
5	$Cu(I) \cdot 1$	7	8a	H_2O	18	78
6	Cu(I)·2	7	8a	H_2O	18	73
7	Cu(I)·4	7	8a	H ₂ O	18	97
8	$Cu(1) \cdot 3$	7	8b	H ₂ O	18	95 (92)
9	$Cu(1) \cdot 3$	7	8c	H ₂ O	18	100 (97)
10	$Cu(1)\cdot 3$	7	8d	H ₂ O	18	100 (99)
11	$Cu(1)\cdot 3$	7	8e	H ₂ O	18	12
12	$Cu(1)\cdot 3$	7	8f	H ₂ O	18	8
13	$Cu(I)\cdot 3$	7	8a	H ₂ O	8	97
^{<i>a</i>} Reaction condition: alkyl azide (1.0 mmol), phenylacetylene (1.2 mmol), xerogel (0.01 mmol), solvent (2.0 mL), RT, air. ^{<i>b</i>} GC yield (isolated yield in parenthesis) ^{<i>c</i>} v/v , 1:1.						

room temperature in air. Using water as the solvent gave the best result. Screening the catalysts gave the excellent result for xerogel Cu(1).3. 1 mol% xerogel Cu(1).3 effectively promoted the reaction in water at room temperature in air, giving quantitative conversion (entry 4). The long lipophilic carbon chain in xerogel Cu(1).3 could provide an organic microenvironment in the aqueous phase, thus facilitating the diffusion of the substrates from surrounding media to the catalytic sites in the gel fibers.¹⁸ The xerogel Cu(I)·3 was recovered by filtration and reused in the next three cycles of the reaction of 7 with 8a without appreciable loss of reactivity, giving 9a in 100%, 100%, and 99.5% yield, respectively. No copper(I) ion was detected in aqueous phase by ICP-MS analysis, indicating the heterogenous catalysis. We also examined the reaction of various alkynes with benzyl azide catalyzed by xerogel Cu(I). Aryl alkynes gave excellent results (entry 8-10), while alkyl alkynes gave inferior outcomes (entry 11–12). Using $Cu(I) \cdot (2,2'-bipyridine)_2$ as catalyst was accompanied by a rapid color change from red to green, suggesting poor support of Cu(I) by bipyridine. However, no color change was observed for xerogel Cu(1).3 and catalytic activity remained almost unchanged on staying in air for at least one year, demonstrating significant stabilization of Cu(I) in the complex, which was further confirmed by cyclic voltammetry (CV) experiments. The redox potential of Cu(I)/Cu(II) in a $CH_3CN-CH_2Cl_2$ solution of $Cu(I)\cdot 3$ showed a dramatic increase of 1.20 V compared to that of $Cu(I) \cdot (2,2'-bipyridine)_2$.

In conclusion, we described a novel class of metal coordination polymer gels, which were not only responsive to various stimuli such as heat, sound and redox, but also well suited as self-supported stable supramolecular catalysts for "click" reaction. Further applications of the supramolecular catalysts to asymmetric reaction and atom-transfer radical polymerization are ongoing.

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