DOI: 10.1002/ejoc.201501201

A Cu^{I}-Based Metallo-Supramolecular Gel-Like Material Built from a Library of Oligomeric Ligands Featuring Exotopic 1,10-Phenanthroline Units

José Augusto Berrocal,[a] Simone Albano,[b] Luigi Mandolini,[b] and Stefano Di Stefano*[b]

Keywords: Macrocyclic ligands / Gels / Metathesis / Dynamic covalent chemistry / Copper

A 22-membered cyclic alkene $\mathbf{C_1}$ incorporating an exotopic 1,10-phenanthroline nucleus in the ring skeleton has been synthesized and subjected to ring-opening metathesis polymerization (ROMP) in dilute dichloromethane solution at varying monomer concentrations (c_{mon}). The resultant libraries of macrocyclic oligomers were used as ligands for the generation of main-chain metal–ligand oligomeric/polymeric complexes taking advantage of the strong affinity of 1,10-phenanthroline derivatives for Cu^{I}. The formation of a gel-like material only upon addition of $[Cu(CH_3CN)_4]PF_6$ to the most concentrated library (c_{mon} = 60 mM) was explained as arising from the presence of significant amounts of trimeric and higher oligomeric macrocycles $\mathbf{C}_i$ ($i \geq 3$), acting as cross-linking components.

Introduction

Since the first templated synthesis of catenanes reported by Dietrich-Buchecker and Sauvage et al.,[1] copper(I) complexes of 1,10-phenanthroline derivatives have been extensively used to assemble catenane and rotaxane structures for use as components in a variety of discrete[2] and polymeric systems.[3]

In the course of our studies of dynamic covalent chemistry,[4] we recently reported that ring-opening metathesis polymerization (ROMP) of the macrocyclic alkene **1** in the presence of second-generation Grubbs' catalyst **G2** generates a dynamic library (DL) of cyclic oligomers under fully reversible conditions (Figure 1).[5]

These macrocycles, as well as the vast multitude of macrocyclic ligands that have found countless applications in supramolecular chemistry over many decades, possess endotopic donor sites and, consequently, undergo endocyclic coordination with metal ions. In contrast, macrocyclic ligands featuring exotopic binding sites are rare.[6] Recently, Lee and co-workers[7] showed that *exo* coordination of the sulfur donors of thiamacrocycles allows the construction of metallo-supermolecules and -supramolecular polymers not accessible by *endo*-coordination strategies.

As a contribution to the largely unexplored area of exocyclic coordination, we focused on the macrocyclic alkene $\mathbf{C_1}$ as a potential precursor of multitopic macrocyclic ligands endowed with exotopic coordination sites. In this work we report on the synthesis of $\mathbf{C_1}$, its subsequent subjection to ROMP in the presence of **G2**, and the effect of the addition of Cu^{I} to the libraries thereby obtained as a novel strategy for building a metallo-supramolecular gel-like material. The present procedure differs significantly from known procedures for synthesizing organometallic and coordination polymers[8] based on ring-opening polymerization reactions of metal-containing cyclic monomers, such as ferrocenophanes[9] and Cu^{I}–catenanes.[10] In all

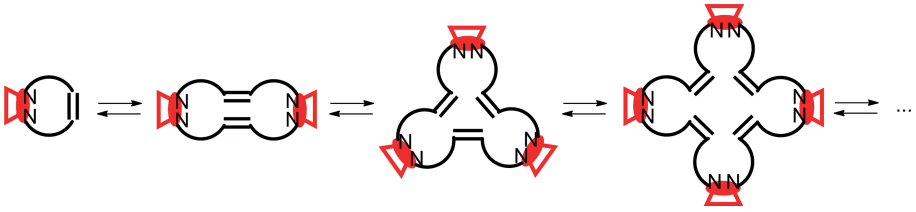
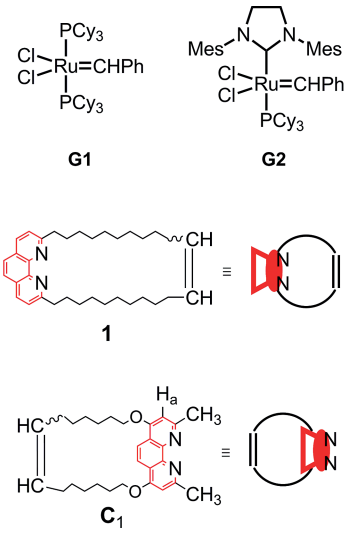


Figure 1. Dynamic library of macrocyclic oligomers generated during ROMP of **1** under dilute conditions.

[a] Institute for Complex Molecular Systems, Eindhoven University of Technology,
P. O. Box 513, 5600 MB Eindhoven, The Netherlands
[b] Dipartimento di Chimica, Sapienza Università di Roma and Istituto CNR di Metodologie Chimiche (IMC-CNR), Sezione Meccanismi di Reazione,
P.le A. Moro 5, 00185 Rome, Italy
E-mail: stefano.distefano@uniroma1.it
http://www.chem.uniroma1.it/dipartimento/persone/stefano-di-stefano

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/ejoc.201501201.



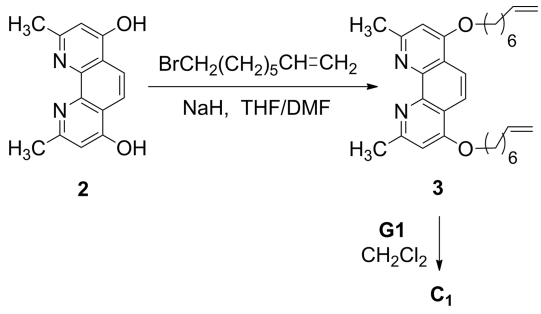
these cases the bonds involving the metal ion do not undergo any change during polymerization.

Results and Discussion

Design, Synthesis of C_1, and Equilibration Experiments

The choice to combine exocyclic coordination with Ru-catalyzed olefin metathesis demanded stringent requirements in the molecular design of $\mathbf{C_1}$, namely the presence of the two methyl groups at the 2- and 9-positions of the 1,10-phenanthroline moiety. Indeed, 1,10-phenanthroline derivatives are typically employed as Ru ligands for the generation of bioactive complexes[11] or antenna systems,[12] to name but a few. We hypothesized that the steric hindrance of the two methyl groups minimizes the displacement of the ligands bound to the Ru center of **G1** and **G2**, therefore ensuring the activity of both catalysts. Preliminary ^{1}H and ^{31}P NMR experiments in CD_2Cl_2 confirmed this hypothesis. Clear spectral variations and color change (from purple to dark brown) were observed upon treatment of a solution of **G2** with 1,10-phenanthroline, whereas neocuproine (2,9-dimethyl-1,10-phenanthroline) acted as a co-existing, but non-interacting species in solution (see Figures S1–S3 in the Supporting Information).

Macrocyclic alkene $\mathbf{C_1}$ was prepared by a two-step procedure (Scheme 1) starting from 4,7-dihydroxyneocuproine (**2**), which was synthesized according to a literature procedure[13] (see Scheme S1 in the Supporting Information). The reaction of compound **2** with 8-bromooctene in THF/DMF (1:1) at room temperature in the presence of NaH gave the doubly alkylated compound **3**. A 10 mM dichloromethane solution of **3** was then subjected to ring-closing metathesis by addition of first-generation Grubbs' catalyst **G1**. The less robust **G1** was preferred to **G2**[14] to minimize the incursion of cross-metatheses involving $\mathbf{C_1}$.[15] Column chromatography of the crude reaction product afforded macrocycle $\mathbf{C_1}$ as a mixture of *cis* and *trans* isomers, clearly detected in the ^{1}H NMR spectrum (see Figure S6). The unresolved mixture of geometrical isomers of $\mathbf{C_1}$ was subjected to ROMP (CD_2Cl_2, 30 °C) in the presence of **G2**. The initial concentration of monomer $\mathbf{C_1}$ (c_{mon}) was varied from 10 to 100 mM. Periodic monitoring of the reaction mixtures by ^{1}H NMR spectroscopy showed that equilibrium was reached in all cases after 24 h, in accordance with results obtained in the ROMP of **1** under the same conditions.[5] The expected formation of mixtures of cyclic oligomers (Figure 2) was confirmed by mass spectrometry (Figure 3).[16,17]



Scheme 1.

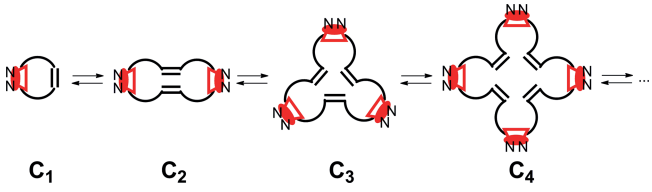


Figure 2. Dynamic library of macrocyclic oligomers generated during ROMP of $\mathbf{C_1}$.

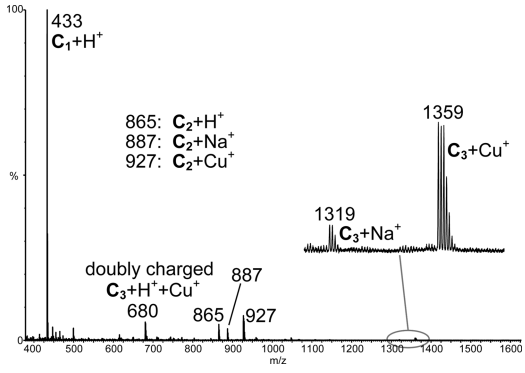


Figure 3. ROMP of $\mathbf{C_1}$ in the presence of **G2**. Typical ESI-TOF mass spectrum of a reaction mixture at equilibrium (m/z = 680 has been attributed to the doubly charged species $\mathbf{C_3}$ + H^+ + Cu^+).

The DLs obtained in the above equilibration experiments can be described as macrocyclization equilibria ruled by the Jacobson–Stockmayer (J-S) theory.[18] Theory predicts that the concentration of each oligomer $\boldsymbol{C_i}$ increases upon increasing the total monomer concentration c_{mon} until a critical value c_{mon}* is reached. Below c_{mon}* the concentration of linear polymers $\boldsymbol{P_i}$ is negligibly small and the DL is composed of cyclic oligomers only [Equation (1), which holds when $c_{mon} \leq c_{mon}$*]. Above c_{mon}* the concentration of linear species $\mathbf{P}_i$ is given by Equation (2), whereas the concentration of cyclic species $\boldsymbol{C_i}$ remains constant [Equation (3)]. The limiting value $[\boldsymbol{C_i}]$* approached by $[\boldsymbol{C_i}]$ when c_{mon} ap-

proaches c_{mon}* is a measure of the thermodynamic effective molarity EM_i of $\mathbf{C}_i$.[19]

$$\sum_i i[\mathbf{C}_i] = c_{mon} \quad (1)$$

$$\sum_i i[\mathbf{P}_i] = c_{mon} - c^*_{mon} \quad (2)$$

$$\sum_i i[\mathbf{C}_i]^* = c^*_{mon} \quad (3)$$

Figure 4 shows typical ^{1}H NMR spectra (aromatic region) of equilibrated solutions obtained from ROMP of $\mathbf{C_1}$ in the presence of 3 mol-% **G2** in CD_2Cl_2 at varying c_{mon} values. The singlets of the geometrical isomers of $\mathbf{C_1}$ appear as well-resolved signals that were easily integrated to allow the concentrations of $\mathbf{C_1}$ to be plotted as a function of c_{mon} (Figure 5). In agreement with J-S theory, the concentration profile reaches a plateau value in the high-concentration region.[20,21] Although the value of c_{mon}* cannot be precisely determined on the basis of available data, the shape of the concentration profile suggests that it should lie somewhere in the range of 0.12–0.16 M. This estimation is in line with literature data related to a large variety of macrocyclization

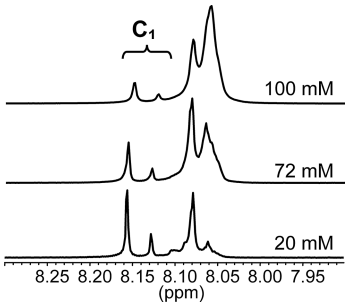


Figure 4. Aromatic portion of the ^{1}H NMR spectra of three equilibrated solutions at different c_{mon} (CD_2Cl_2, 30 °C). The two singlets at lower field are due to the aromatic protons H_a of the two *cis* and *trans* isomers.

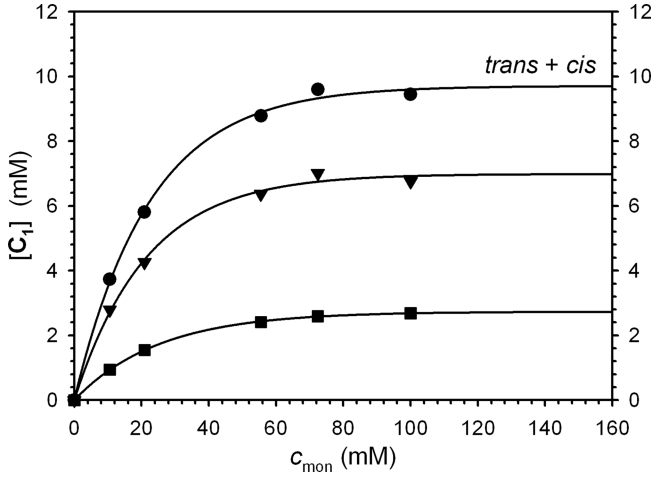


Figure 5. Concentration of total $\mathbf{C_1}$ (circles) in equilibrated reaction mixtures as a function of c_{mon}. Triangles and squares represent the contributions of the individual geometrical isomers (3 mol-% **G2**, CD_2Cl_2, 30 °C).

equilibria for which c_{mon}* values between 0.13–0.20 M have been reported.[22] The limiting value of 10 mM approached by the equilibrium concentration of $\mathbf{C_1}$ compares well with the EM of 22 mM reported for **1** and is consistent with what is expected on the basis of known EM values of large, low-strain rings of comparable size.[23]

Copper(I)-Induced Gelation Experiments

In view of the ability of the Cu^I ion to form very strong 1:2 complexes with neocuproine,[24] it was of interest to study the effect of the addition of this metal ion to the libraries obtained during the ROMP of $\mathbf{C_1}$. Linear species are virtually absent and only mono-, di-, and multitopic macrocyclic ligands are available as building blocks for the construction of main-chain metal–organic oligomeric/polymeric assemblies. Although dimeric rings $\mathbf{C_2}$ can function as binding units in the formation of linear assemblies in which monomeric rings $\mathbf{C_1}$ act as chain termini (Figure 6, a), the multitopic nature of trimers $\mathbf{C_3}$ and higher cyclic oligomers enables them to act as cross-linking agents (Figure 6, b).

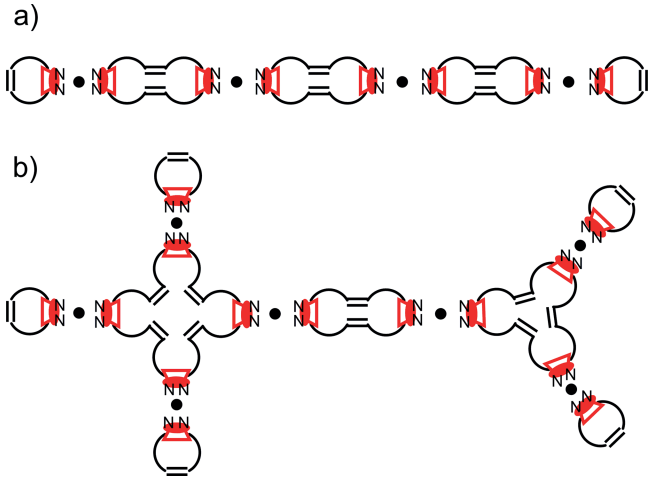


Figure 6. Schematic representation of a) linear and b) cross-linked metallo-supramolecular aggregates formed upon addition of Cu^I to a library obtained from ROMP of $\mathbf{C_1}$.

A stoichiometric amount of $[Cu(CH_3CN)_4]PF_6$ was introduced into the equilibrated solutions 4 d after the start of ROMP. This ensured that Cu^I complexation with phenanthroline units occurred when the catalyst had totally decomposed[25] and, consequently, oligomer distributions were exactly those dictated by J-S theory. For the same reasons, quenching of ROMP reactions with ethyl vinyl ether[3b] was avoided because the introduction of end-groups into a dynamic system would likely cause variations in the library composition. The results of the addition of Cu^I to the no longer dynamic, but static libraries of oligomeric macrocyclic ligands are illustrated in Figure 7. The complexation of Cu^I was revealed by the immediate appearance of a brown color. The more dilute samples (c_{mon} = 20 and 30 mM) gave free-flowing homogeneous solutions, but for c_{mon} = 60 mM, the appearance of the brown color was

followed by the formation of a gel-like material after about 3 h. As a consequence of the high stability of 2:1 complexes of neocuproine derivatives and Cu^{I},[24] we highlight the excellent thermal stability of the gel-like material. Even when heated at 65 °C[26] for prolonged periods (10–15 min), the material never turned into a solution. Such behavior is in stark contrast to typical supramolecular gels, in which a temperature increase causes disaggregation and the subsequent transformation of gels into solutions.[27] As expected, treatment of the gel-like material with Et_4NCN (ten-fold excess) restored a free-flowing solution due to the sequestration of Cu^{I} (see Figure S8 in the Supporting Information).

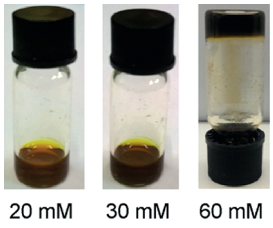


Figure 7. Appearance of static libraries obtained by ROMP of $\mathbf{C_1}$ in CH_2Cl_2 at the given monomer concentrations after the addition of a stoichiometric amount of $[Cu(CH_3CN)_4]PF_6$.

As predicted by J-S theory and actually found in real systems, the equilibrium concentration of the $\boldsymbol{C_i}$ oligomers declines progressively with increasing i. This happens not only because the limiting concentration $[\boldsymbol{C_i}]^* = EM_i$ is proportional to the –5/2 power of i,[18] but also because the rate at which each oligomer $\boldsymbol{C_i}$ approaches its limiting concentration when c_{mon} approaches c_{mon}^* varies inversely with the degree of polymerization i [Equation (4)].[18]

$$[\boldsymbol{C_i}] = ([\boldsymbol{C_1}]/EM_1)^i EM_i \quad (4)$$

As a consequence, the concentration of higher oligomers is very low in dilute solutions, that is, when $c_{mon} << c_{mon}^*$ and $[\boldsymbol{C_1}] << EM_1$, but increases rapidly with increasing c_{mon}. In line with the above arguments, it seems likely that the concentration of oligomers $\mathbf{C_i}$ with $i \geq 3$ in the library generated at c_{mon} = 30 mM is still too low and cross-links are not formed in a significant amount upon addition of Cu^{I}. However, when c_{mon} is increased to 60 mM, the concentration of oligomers with $i \geq 3$ is believed to be high enough and, consequently, the addition of Cu^{I} results in the formation of a metallo-supramolecular gel-like network. It is apparent that the exotopic orientation of the phenanthroline moiety plays a crucial role in the formation of the gel-like material. When the static library obtained from ROMP of macrocyclic monomer **1** under identical conditions (c_{mon} = 60 mM, CH_2Cl_2, 30 °C, 3 mol-% **G2**) was treated with 30 mM $[Cu(CH_3CN)_4]PF_6$, a red, free-flowing solution was obtained (see Figure S9 in the Supporting Information). It appears that in this case the conformational flexibility of the larger macrocycles is not large enough for the phenanthroline moieties to be oriented outwards for an effective cross-linking to take place.

Further Gelation Studies

Other salts of metal cations capable of forming complexes with 1,10-phenanthroline,[24,28] namely Ag^{I}, Co^{II}, Zn^{II}, and Cu^{II}, were also tested in gelation experiments in CH_2Cl_2 (Table 1). Stoichiometric amounts (0.5 mol-equiv.) of metal salts were added to c_{mon} = 60 mM static libraries, and the mixtures were kept in darkness and without stirring. With the Cu^{II} salt as the only exception, all the salts are scarcely soluble in CH_2Cl_2 and immediately after addition remained undissolved at the bottom of the vial. Eventually (1 d) an appreciable reduction of the amount of undissolved salt (Co^{II}, Zn^{II}, and Ag^{I}) was observed, most likely due to complexation. None of these metal cations caused the gelation of solutions: all of them remained free-flowing (see Figure S10 in the Supporting Information). Only Cu^{II} led to a precipitate in the dark-brown solution, but no gel was formed (see Figure S10). In addition to the metal cation, the counter anion was also varied in this series of experiments. In a previous report[10] it was shown that the substitution of PF_6^- by $CF_3SO_3^-$ did not alter the outcome of the gelation. Here, despite the pivotal role played by c_{mon} in determining the product distribution, and hence cross-linking, an influence of the counter anion on the outcome of the gelation cannot be excluded.

Table 1. Gelation studies, and related outcomes, performed at c_{mon} = 60 mM in CH_2Cl_2 with different metal cations.

Metal cation	Counter anion	Gelation
Ag^{I}	$CF_3CO_2^-$	no
Co^{II}	$CH_3CO_2^-$	no
Zn^{II}	$CH_3CO_2^-$	no
Cu^{II}	$CF_3SO_3^-$	no (precipitation)

The same strategy of adding Cu^{I} to static libraries obtained at c_{mon} = 60 mM was also used to investigate the influence of the loading of this metal cation on the generation of the gel-like material. Cu^{I} loadings of 0.25 to 5 mol-equiv. were tested (Table 2) under identical experimental conditions. Gelation was not observed, except for a partial gelation observed with a loading of 1 mol-equiv. Cu^{I}. In this case roughly 40% of the solution was gelated, with the rest free-flowing (see Figure S11 in the Supporting Information). Loadings of Cu^{I} equal to 0.25 and 0.75 gave films on the walls of the vials as minor products, together with a predominant colored free-flowing solution. A large excess of Cu^{I} (5 equiv.) provoked precipitation of dark aggregates surrounded by an even darker solution (see Figure S11). These results clearly highlight the dramatic influence of the $c_{mon}/[Cu^{I}]$ ratio on the outcome of the gelation process. Moreover, it is evident that a 2:1 stoichiometry is highly desirable for the obtainment of a homogeneous gel-like material.

Cu^{I}-induced gelation was also attempted in different organic solvents screened on the basis of polarity and boiling-point criteria. However, the selective solubility of the static libraries or $[Cu(CH_3CN)_4]PF_6$ in most of the solvents studied forced the choice towards halogenated solvents,

Table 2. Gelation studies, and related outcomes, performed at c_{mon} = 60 mM in CH_2Cl_2 with different loadings of Cu^I.

Cu^I loading [mol-equiv.]	Gelation
0.25	no
0.75	no
1	roughly 40%
5	no

namely chloroform, 1,2-dichloroethane, and tetrachloroethane (Table 3). However, halogenated aromatic solvents, for example, *o*-dichlorobenzene, could also not be used because of the insolubility of $[Cu(CH_3CN)_4]PF_6$ and the static libraries.

Table 3. Gelation studies, and related outcomes, performed at c_{mon} = 60 mM in different aliphatic halogenated solvents with 0.5 mol-equiv. of Cu^I.

Solvent	Solubility of static library	Solubility of $[Cu(CH_3CN)_4]PF_6$	Gelation
$CHCl_3$	poor	poor	no
$ClCH_2CH_2Cl$	soluble	poor	partial
$Cl_2CHCHCl_2$	poor	poor	no

However, in contrast to dichloromethane, none of the above three aliphatic halogenated solvents gave gels. Only a thin film on the walls of the vial surrounded by a colored solution was observed in $CHCl_3$ (see Figure S12 in the Supporting Information) and 1,1,2,2-tetrachloroethane gave a massive precipitate surrounded by an almost colorless solution (see Figure S12). Minor signs of gelation were observed, however, in 1,2-dichloroethane (see Figure S12). On performing a qualitative upside-down vial test, a small amount of material did not flow, but stayed attached to the bottom, but the amount of gelated solution was so small that 1,2-dichloroethane could not be used for large-scale gel preparation.

Because gelation only occurs with reliable and scalable quantities in dichloromethane, a very low-boiling point solvent, rheological studies could not be carried out: Solvent would evaporate and measurements would be performed on a dry material. On the other hand, performing plate–plate rheology directly on a pre-dried material could represent an alternative and valid approach. Thus, gels were air-dried and dark-colored films were obtained. These dry films were extremely brittle and any small mechanical deformation manually exerted caused partial fractures or breaks. Such behavior may be in contrast to the previously reported high thermal stability of the gel. However, it is in line with our previous report,[10] in which Cu^I complexation resulted in a higher thermal stability of the material, but also on an enhanced rigidity due to restriction of conformational motions. Morphological studies performed by SEM (see p. S17 in the Supporting Information) offered an explanation to this brittleness and showed that the dry, metalated material was not resistant enough to undergo plate–plate rheological studies.

Conclusions

In this paper we have introduced a simple procedure to build a metallo-supramolecular gel-like material. The key polymerization reaction was the coordination between Cu^I and 1,10-phenanthroline units. A novel feature of the procedure is the use of a library composed of a virtually infinite number of oligomeric ligands instead of a single ligand.[29] Another distinctive feature is the presence of an exotopic 1,10-phenanthroline moiety inserted into the macrocyclic frame of the monomeric olefin **C_1**, ROMP of which in dilute dichloromethane solutions afforded libraries solely composed of macrocyclic oligomers. Although the libraries were obtained under dynamic conditions, the subsequent polymerization reactions produced static libraries because treatment with $[Cu(CH_3CN)_4]PF_6$ was carried out after complete inactivation of the Ru catalyst.[30] A gel-like material was obtained from the most concentrated library (c_{mon} = 60 mM) upon addition of Cu^I. The tris-ligand macrocycle **C_3** and higher oligomers are believed to play a key role as cross-linking agents in the gel-forming process.

The presence and loading of Cu^I appears to be crucial for the obtainment of the gel-like material. Indeed, the static libraries are a powdery mixture of organic molecules in the absence of Cu^I, and only in the presence of exactly 0.5 mol-equiv. of Cu^I was a gel-like material (in the wet state) or a film (in the dry state) formed.

Experimental Section

Instruments and General Methods: NMR spectra were recorded with 300 and 400 MHz spectrometers at room temperature unless otherwise stated and were internally referenced to the residual proton solvent signal. Mass spectra were recorded with an ESI-TOF mass spectrometer. UV/Vis spectra were recorded with a single-ray spectrophotometer using a standard quartz cell (path length: 1 cm) at room temperature. Scanning electron microscopy was performed with an FEI Quanta 600F instrument under high vacuum (electron beam acceleration voltage of 1 kV) without any further treatment of the sample.

Materials: All reagents and solvents were purchased at the highest commercial quality and were used without further purification unless stated otherwise. The glassware was either flame- or oven-dried. 2,9-Dimethyl-4,7-dihydroxy-1,10-phenanthroline (**2**) was prepared according to a literature procedure[13] (see Scheme S1 in the Supporting Information). 2,9-Dimethyl-4,7-bis(oct-7-enyloxy)-1,10-phenanthroline (**3**) was synthesized as shown below, adapting a literature procedure.[31] The NaH dispersion in mineral oil was washed with hexane immediately prior to use. THF was distilled from sodium and benzophenone. The dichloromethane used in the olefin metatheses reactions was filtered through basic alumina just before use. Chloroform, 1,2-dichloroethane, and tetrachloroethane used in solvent gelation studies were flashed through basic alumina prior to use.

2,9-Dimethyl-4,7-bis(oct-7-en-1-yloxy)-1,10-phenanthroline (3): 2,9-Dimethyl-4,7-dihydroxy-1,10-phenanthroline (**2**; 2.16 g, 9 mmol) was added to a suspension of NaH (1.44 g, 60% in mineral oil, 36 mmol) in THF/DMF (1:1, 104 mL) at 0 °C and the mixture was stirred for 30 min under an inert atmosphere. Then 8-bromo-1-octene (6 mL, 36 mmol) and NaI (540 mg, 3.6 mmol) were added and

the mixture was stirred overnight at room temperature. The reaction was then quenched with water and the resulting mixture extracted three times with CH_2Cl_2. The organic phases were collected, washed with brine, dried with Na_2SO_4, and filtered. The solvent was evaporated and the crude obtained was subjected to column chromatography (basic Al_2O_3, ethyl acetate/hexane, 8:2) to afford pure **3** (1.2 g, 2.61 mmol, 29% yield), m.p. 137–140 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.48–1.59 (m, 8 H), 1.87–1.96 (m, 4 H), 2.02–2.07 (m, 4 H), 2.84 (s, 6 H), 4.16 [t, ^3J(H,H) = 6 Hz, 4 H], 4.96 (m, 4 H), 5.80 (m, 2 H), 6.81 (s, 2 H), 8.06 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.86, 26.22, 28.67, 28.69, 28.81, 33.56, 66.35, 103.29, 114.26, 117.87, 119.38, 138.18, 145.41, 160.01, 161.72 ppm. HRMS (ESI-TOF): calcd. for $C_{30}H_{41}N_2O_2$ $[M + H]^+$ 461.3168; found 461.3179. UV/Vis (CH_3OH): λ_{max} (ε) = 256 (36210), 297 (9590), 308 (9390), 325 (2070), 341 nm (1250 $dm^3 mol^{-1} cm^{-1}$).

Cyclic Monomer C_1: Compound **3** (1.06 g, 2.31 mmol) was dissolved in CH_2Cl_2 (230 mL) and the solution was degassed by freeze–pump–thaw cycles and first-generation Grubbs' catalyst **G1** (285 mg, 0.35 mmol) was added. The resulting mixture was stirred at 30 °C for 3 d under an inert atmosphere, monitoring the reaction by ESI-TOF MS. Then the solution was filtered through a short path of basic alumina, the solvent was evaporated, and the crude material was subjected to column chromatography (basic Al_2O_3, ethyl acetate/hexane, 6:4) to give $\mathbf{C_1}$ as a mixture of *cis* and *trans* isomers (150 mg, 0.35 mmol, 15% yield), m.p. 193–197 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.45–1.67 (m, 16 H), 1.93–2.11 (m, 16 H), 2.80 (s, 12 H), 4.31 (m, 8 H), 5.32 [t, ^3J(H,H) = 6 Hz, 2 H], 5.53 (m, 2 H), 6.88 (s, 2 H), 6.89 (s, 2 H), 8.13 (s, 2 H), 8.16 (s, 2 H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 25.71, 27.14, 27.35, 27.42, 27.59, 27.72, 28.83, 29.34, 29.39, 29.57, 32.66, 65.46, 69.53, 103.30, 103.65, 119.06, 119.12, 119.66, 119.81, 129.79, 130.34, 145.85, 145.92, 159.50, 161.64, 161.67 ppm. HRMS (ESI-TOF): calcd. for $C_{28}H_{37}N_2O_2$ $[M + H]^+$ 433.2834; found 433.2831. UV/Vis (CH_3OH): λ_{max} (ε) = 256 (27530), 298 (6960), 308 (6830), 325 (1470), 341 nm (975 $dm^3 mol^{-1} cm^{-1}$).

General Procedure for Ring-Opening Metathesis: Cyclic monomer $\mathbf{C_1}$ was weighed in a NMR tube and the appropriate amount of CD_2Cl_2 (500–600 μL), dried on basic alumina just before use, was added to prepare solutions of the desired concentration. Then second-generation Grubbs' catalyst **G2** (3 mol-%) was added. The reactions were run at 30 °C and monitored by ^{1}H NMR spectroscopy.

General Procedure for the Gelation Experiments: Cyclic monomer $\mathbf{C_1}$ or **1** was weighed in a screw-cap vial and the appropriate amount of CH_2Cl_2 (200–250 μL), dried on basic alumina just before use, was added to prepare solutions of the desired concentration and then second-generation Grubbs' catalyst **G2** (3 mol-%) was added. The reactions were run at 30 °C for 24 h. After cooling to room temperature, the mixture was held in the vial for additional 72 h and a weighed amount of $[Cu(CH_3CN)_4]PF_6$ (0.5 equiv. with respect to initial $\mathbf{C_1}$) was added. Gelation was observed after 3 h in the case of c_{mon} = 60 mM.

General Procedure for the Demetalation Experiments: A ten-fold excess tetraethylammonium cyanide (Et_4NCN) solution in CH_2Cl_2 (not degassed) was added to the Cu^{I}-complexed gelated material. Two phases were clearly observed immediately after mixing. Upon gentle shaking, the mixture became homogeneous, giving a clear indication of Cu^{I} sequestration by CN^-.

General Procedure for Gelation Experiments with Other Cations: Cyclic monomer $\mathbf{C_1}$ was weighed in a vial and the appropriate amount of CH_2Cl_2 (500–600 μL), dried on basic alumina just before use, was added to prepare solutions at c_{mon} = 60 mM. Then, second-generation Grubbs' catalyst **G2** (3 mol-%) was added. Reaction mixtures were left without stirring at room temperature for 4 d.

Solutions were dried under a flow of N_2 and a weighed amount of the given salt was introduced into the vial, followed by a calculated amount of the desired solvent to reach c_{mon} = 60 mM. Suspensions were sonicated and left without stirring.

General Procedure for Cu^{I} Loading Gelation Experiments: Cyclic monomer $\mathbf{C_1}$ or **1** was weighed in a screw-cap vial and the appropriate amount of CH_2Cl_2 (200–250 μL), dried on basic alumina just before use, was added to prepare solutions of the desired concentration and then second-generation Grubbs' catalyst **G2** (3 mol-%) was added. The reactions were run at 30 °C for 24 h. After cooling to room temperature, the mixture was held in the vial for an additional 72 h and a weighed amount of $[Cu(CH_3CN)_4]PF_6$ (depending on the number of mol-equiv. with respect to initial $\mathbf{C_1}$) was added.

General Procedure for the Gelation Experiments with Other Solvents: Cyclic monomer $\mathbf{C_1}$ was weighed in a vial and the appropriate amount of CH_2Cl_2 (500–600 μL), dried on basic alumina just before use, was added to prepare solutions at c_{mon} = 60 mM. Then second-generation Grubbs' catalyst **G2** (3 mol-%) was added. Reaction mixtures were left without stirring at room temperature for 4 d.

Solutions were dried under a flow of N_2 and a weighed amount of the given salt was introduced into the vial, followed by a calculated amount of the desired solvent to reach c_{mon} = 60 mM. Suspensions were sonicated and left without stirring.

Scanning Electron Microscopy: A solution collected at the bottom of a gel-containing upside-down vial was drop-cast on to a glass cover slip (12 mm diameter) and air-dried. The sample was imaged without any further treatment at an electron beam acceleration voltage of 1 kV.

Acknowledgments

Thanks are due to the Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR) (PRIN 2010CX2TLM) and Sapienza Università di Roma through the Ricerca Scientifica Anno 2014 program. The authors thank Chiara Biagini and Rachele Caruso for technical assistance in the synthetic work. Matilde Putti is acknowledged for SEM imaging.

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Received: September 16, 2015
Published Online: October 29, 2015

