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Polymerization/depolymerization of chiral metallo-supramolecular assembly induced by redox change.

Maya Marinova,^[a] Antoine Bonnefont,^[b] Thierry Achard,^[a] Aline Maisse-François^[a] and Stéphane Bellemin-Lapponnaz^{*[a]}

Abstract: We report on the polymerization / depolymerization of chiral metallo-supramolecular assembly by Cu^I/Cu^{II} redox change. By combining a monotopic enantiopure ligand with a ditopic ligand of opposite configuration, ML₂-type complexes are generated with chiral self-recognition or self-discrimination depending on the oxidation state of copper. In presence of Cu^I, the formation of heterochiral complexes is favored

thus generating dinuclear species whereas Cu^{II} advocates for the formation of homochiral species, namely a mixture of mononuclear species and metallo-supramolecular polymeric species. Thus, cyclic voltammetry was used to study such a chirality-induced stimulus sensitive polymerization / depolymerization process.

Keywords: chirality, coordination chemistry, metallo-polymer, polymerization/depolymerization

Introduction

Chirality is one of the fundamental properties of molecular systems that enables nature to execute life.¹ For example, protein functions depend on non-covalent intermolecular (i.e. supramolecular) interactions, which are highly controlled by chiral recognition processes. Another representative example is the chirality of nucleic acids forming the DNA backbones which is essential to store genetic information.

Chemists have constantly sought to understand molecular recognition and in particular chiral recognition mechanism, in part inspired by biological systems. Therefore, the imitation of biological self-assembly must take into account chirality as an instruction encoded in the chemical structure itself, together with the dynamical nature of non-covalent interactions. Thus, supramolecular chiral self-assembly is nowadays amongst the most appealing and promising field of supramolecular chemistry.^{2, 3, 4, 5} This undeniably leads to the constant development of new molecular materials of increasing complexity, which can evolve to generate a specific function in particular by using external stimuli such as light, heat, magnetic or electric field, etc.^{6,7,8}

In recent years, we have been studying supramolecular chiral recognition between enantiomeric molecules by means of coordination chemistry. The self-assembly of two chiral C₂-symmetric ligands around a metal may generate homochiral or heterochiral species depending on the metal salt and converting these ligands into polytopic bridging ligands may lead to the formation of metallo-supramolecular polymer with the control of the metallopolymer sequence by chirality.^{9, 10, 11} Such enantiopure metallopolymers have been successfully applied in enantioselective catalysis, as highly recyclable self-supported chiral catalysts^{12,13,14} and also in the development of suitable materials for optically active sum-frequency generation (SFG) spectroscopy and imaging.¹⁵ In addition, the chiral self-recognition or self-discrimination may be induced by the Cu^I/Cu^{II} redox change using cyclic voltammetry (CV) and this led to

metallo-supramolecular copolymers with stimuli-responsive controlled arrangement.¹⁶ Stimuli-sensitive materials that show dramatic changes in their physical properties are of interest in a large number of areas, ranging from detection to self-healing and the interest for such molecular materials has been steadily increasing over the last years.^{17,18}

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FIGURE 1 Schematic principle of the stimuli-responsive polymerization/depolymerization process.

Herein, we report a study on polymerisation/depolymerisation of chiral metallo-supramolecular assembly induced by redox change. With the help of cyclic voltammetry and mass spectrometry, we show that the Cu^I/Cu^{II} redox couple in conjunction with chirality may be used for controlling such polymerization/depolymerization process and the switching is electrochemically possible in both directions (Fig. 1).¹⁹

Materials and Methods

All syntheses were carried out under an inert atmosphere of dinitrogen or argon using standard Schlenk techniques unless stated otherwise. Reagents were purchased from commercial chemical suppliers and used without further purification. Solvents were dried and degassed according to classical procedures. All other reagents were commercially available and used as received. ¹H and ¹³C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AVANCE 300 spectrometer using the residual solvent peak as reference (CDCl₃: δ_H = 7.26 ppm; δ_C = 77.16 ppm) at 298 K. Chemical shifts are given in ppm (δ) compared to tetramethylsilane. Infrared spectra (IR) were recorded on a Nicolet 380 FT-IR spectrometer. KBr discs were made for all samples. Elemental analyses were recorded by the Institute of Chemistry at the University of Strasbourg. HRMS ESI analyses were recorded on microTOF, Bruker Daltonics by the Institute of Chemistry at the University of Strasbourg. Specific rotations were recorded at the 'Laboratoire de Stéréochimie', ECPM, Strasbourg.

Valinol was obtained by reduction of valine.²⁰ 1,1-bis[(4*S*)-4-isopropyl-4,5-dihydrooxazol-2-yl]ethane (**1**) was synthesized according to previous report.²¹ *i*Pr-Box (**2**) and *i*Pr-DiBox (**3**) were synthesized according to our general procedure. The products were obtained with identical analytical data as already reported by us.^{11,22}

FIGURE 2 General synthesis of the ligands.

The electrochemical measurements were performed in a three-electrode electrochemical cell. A 3.0 mm diameter glassy carbon disk was used as working electrode and platinum wires as counter electrode and pseudo-reference electrodes. The solvent was dichloromethane containing 0.1 M TBAPF₆ (Fluka >99.0%, for electrochemical analysis) as supporting electrolyte. The cyclic voltammetry experiments were performed at room temperature

using a PGSTAT30 Autolab potentiostat. The potential of the Ferrocene Fc⁺/Fc redox transition was used as reference of the potential scale. Before the measurements, the solutions were air degassed by argon bubbling.

General procedure for preparation of copper complexes or metallopolymers for the electrochemical measurements: The desired enantiopure ligands and Cu(BF₄)₂ were weighted and added in a vial equipped with a magnetic stir bar. Dichloromethane containing 0.1 M of tetrabutylammonium hexafluorophosphate (TBAPF₆, Fluka, electrochemical grade) was added and the solution was stirred for 15 min. at room temperature (final concentration 10⁻³ mol/L, based on copper). The solution was transferred onto the electrochemical cell and the whole system was degassed under argon prior to measurements.

Results and Discussion

It has been established that the chiral molecular 'instruction' of a ligand in combination with the prevalent coordination geometry of the metal allows a precise control of the formation of the resulting ML₂ complexes. Chiral C₂-symmetric bisoxazoline ligands (called Box) are suitable building blocks for the selective heteroformation or homoformation of such ML₂-type complexes: the combination of two chiral enantiopure C₂-symmetric Box around a metal in a tetrahedral geometry favors the heterochiral combination (*R* + *S*) whereas the homochiral combination (*S* + *S* or *R* + *R*) is thermodynamically preferred in a square planar environment. On this basis, it was possible to construct alternate or block metallo-supramolecular copolymers when using ditopic ligands and Zn^{II} or Cu^{II} salt, respectively.^{9,10,11} Moreover, the chiral self-recognition or self-discrimination may be induced by the Cu^I/Cu^{II} redox transition using cyclic voltammetry thus giving metallo-supramolecular copolymers with stimuli-responsive controlled arrangement.^{16,23,24}

The judicious combination of a monotopic enantiopure C₂-symmetric Box (such as **2**) with a ditopic enantiopure C₂-symmetric DiBox (such as **3**) of opposite chiral configuration should lead to an interesting situation: since a metallic tetrahedral environment favors heterochiral complex formation, a dinuclear species should be generated in this case (Fig. 3, *top*). On the other hand, a square planar environment favors homoleptic species, therefore the monotopic/ditopic ligand combination should lead to the mix of mononuclear complexes and metallopolymers (Fig. 3, *bottom*). Thus, a Cu^I/Cu^{II} redox change underlay a polymerization/depolymerization of the whole metallo-supramolecular assembly.

FIGURE 3 General scheme for an electrochemically-induced polymerization/depolymerization by means of a chiral information: generation of dinuclear species or metallopolymer and mononuclear species through the selective formation of heteroleptic (Cu^I, top) or homoleptic coordination complexes (Cu^{II}, down).

The preferential formation of heterotopic complexes with Cu^I and homotopic formation with Cu^{II} has been first studied by *in situ* mass spectrometry experiments by mixing the bisoxazoline ligand (R-2) with the ditopic ligand (S-3) and CuOTf or Cu(OTf)₂ (Fig. 4 and Supporting Information).

The profiles of the resulting mass spectra show clear differences: in presence of CuOTf, the mass spectrum shows a significant peaks at $m/z = 1011.57$ with accurate isotopic distribution corresponding to the heteroleptic (and therefore heterochiral) complex [Cu(2)(3)]. In opposition, in presence of Cu(OTf)₂ the mass spectrum exhibits two peaks at $m/z = 747.38$ and at $m/z = 1259.17$ with isotopic distribution coherent with the homoleptic (and therefore homochiral) complexes [Cu(2)(2)] and [Cu(3)(3)], respectively.

FIGURE 4 Formation of copper (I) and copper (II) complexes using Cu(OTf) or Cu(OTf)₂. The ligands and the copper salt were stirred in dry methanol for 30 min and the resulting solution was directly analyzed by mass spectrometry (positive ESI).

Figure 5 displays the cyclic voltammograms (CVs) using the homochiral ligands recorded at a potential sweep rate of 200 mV s⁻¹.²⁵ The black curve (top) shows the CV of the homochiral enantiopure complex [Cu(R-2)₂](BF₄)₂, the red curve (bottom) corresponds to the homochiral metallopolymer [Cu(R-3)₂](BF₄)₂ and the blue curve (middle) is a stoichiometric mixture of the two

systems. The reduction of [Cu(R-2)₂]²⁺ into [Cu(R-2)₂]⁺ occurs through a reversible electrochemical wave, revealing that no rearrangement of the coordination shell of the Cu(I) complex takes place during the duration of the CV measurement. The position of the redox peaks of the Cu(II) homochiral metallopolymer ([Cu(R-3)₂]²⁺)_n (red curve) at the same Cu(II) concentration is similar to the one of [Cu(R-2)₂]²⁺. Nevertheless it is worth noticing that the redox peaks are broader while their intensities are approximately twice lower than the one of [Cu(R-2)₂]²⁺. The lower intensity of the redox wave is due to the larger size and then smaller diffusion coefficient of the metallopolymer in solution compared to [Cu(R-2)₂]²⁺, while the broadening of the redox wave is attributed to the presence of several redox centers in the same metallopolymer chain. A stoichiometric mixture of homochiral ditopic and monotopic ligand with Cu(II), contains a mixture of homoleptic metallopolymer ([Cu(R-3)₂]²⁺)_n and the homoleptic complex [Cu(R-2)₂]²⁺. The CV obtained with such stoichiometric mixture at the same Cu(II) concentration of 1 mM (blue curve) shows also a reversible Cu(II)/Cu(I) redox process, the intensities of the redox waves being in between those of [Cu(R-2)₂]²⁺ and ([Cu(R-3)₂]²⁺)_n. This suggests again that no rearrangement of the coordination shell occurs after the reduction.

FIGURE 5 Cyclic voltammograms of the homochiral enantiopure complex Cu(R-2)₂(BF₄)₂ monotopic, (top), stoichiometric mixture of Cu(R-2)₂(BF₄)₂ - Cu(R-3)₂(BF₄)₂ monotopic-ditopic (middle), Cu(R-3)₂(BF₄)₂ ditopic (bottom) on a glassy carbon electrode at a concentration of 1 mM of Cu(II) in 0.1 M TBAPF₆ CH₂Cl₂ solution. Sweep rate 200 mV s⁻¹. The potential axis is referred to the Fc^{+/0}/Fc redox potential.

Next, the CVs obtained with racemic mixtures Cu(II) complexes at a concentration of 1 mM and measured with a potential scan rate of 200 mV.s⁻¹ are plotted in Figure 6 for [Cu(2)₂]²⁺ (black curve), ([Cu(3)₂]²⁺)_n (red curve) and the stoichiometric mixture of both [Cu(S-2)₂]²⁺ and ([Cu(R-3)₂]²⁺)_n (blue curve). For the three CVs, the Cu(II) reduction waves peak at ca. -0.05 V which is very similar to the enantiopure Cu(II) complexes. This confirms that stable homotopic Cu(II) complexes initially are formed in solution, even

in the case of racemic mixtures of the ligands. Interestingly, during the backward potential scan following the Cu(II) reduction, two oxidation waves can be observed. The first oxidation wave peaks at ca. 0.02 V and corresponds to the oxidation of metastable Cu(I) homoleptic complexes, while the one at ca. 0.35 V can be attributed to the oxidation of the Cu(I) heteroleptic complexes.

FIGURE 6 Cyclic voltammograms of the racemic mixture of homochiral complex $\text{Cu}(\mathbf{2})_2(\text{BF}_4)_2$, monotopic (*top*), stoichiometric mixture of $\text{Cu}(\mathbf{2})_2(\text{BF}_4)_2$ and $\text{Cu}(\mathbf{3})_2(\text{BF}_4)_2$ monotopic-ditopic (*middle*), $\text{Cu}(\mathbf{3})_2(\text{BF}_4)_2$ ditopic (*bottom*) on a glassy carbon electrode at a concentration of 1 mM of Cu(II) in 0.1 M TBAPF₆ CH₂Cl₂ solution. Sweep rate 200 mV s⁻¹. The potential axis is referred to the Fc⁺/Fc redox potential.

Thus, after reduction of the Cu(II), the homoleptic homochiral Cu(I) complexes rearrange to form stable Cu(I) heteroleptic complexes as evidenced by cyclic voltammetry. It is interesting to notice that this homochiral/heterochiral interconversion not only occurs in racemic mixtures of $[\text{Cu}(\mathbf{2})_2]^{2+}$ but is also observed with racemic mixtures of $[\text{Cu}(\mathbf{3})_2]^{2+}$ metallopolymer switching between homochiral Cu(II) to heterochiral Cu(I) upon redox stimulation (red curve in Fig. 6), thus generating an electrochemically-induced control of the metallopolymer arrangement (block or alternating metallopolymer).¹⁶ Furthermore, the reduction of $[\text{Cu}(\mathbf{3})_2]^{2+}$ metallopolymer in the solution containing a stoichiometric mixture of ditopic (R) and monotopic (S) ligands provokes its reversible depolymerization and the formation of dinuclear species as schematically represented in Fig. 3.

Further information on the time needed to achieve the polymerization/depolymerization process can be obtained by the analysis of the shape of the CVs as a function of the potential sweep rates (Fig. 7). When the potential scan rate is fast (ca. 5 V.s⁻¹) only one single oxidation wave is observed indicating that the characteristic time of the depolymerization is longer than the one of the CV experiments. In contrast, the emergence of the oxidation wave at 0.35V at a potential scan rate of 50 mV s⁻¹

reveals that most of the complexes could be polymerized / depolymerized in less than 30 seconds.

FIGURE 7 Cyclic voltammograms of racemic mixture of homochiral $\text{Cu}(\text{S-2})_2(\text{BF}_4)_2 - \text{Cu}(\text{R-3})_2(\text{BF}_4)_2$ monotopic-ditopic on a glassy carbon electrode at a concentration of 1 mM in 0.1 M TBAPF₆ CH₂Cl₂ solution at different sweep rates 50 mV s⁻¹ (*top*), 500 mV s⁻¹ (*middle*), 5000 mV s⁻¹ (*bottom*). The potential axis is referred to the Fc⁺/Fc redox potential.

Conclusion

In summary, molecular rearrangements of chiral copper complexes combining monotopic and ditopic ligands of chiral opposite configuration have been investigated by Cu^I/Cu^{II} redox change using cyclic voltammetry technique. The chiral self-recognition and self-discrimination properties of such ML₂-type copper complexes allowed us to generate a metallo-supramolecular polymer that can undergo reversible polymerization / depolymerization process. We believe that the concept of chirality-controlled responsive supramolecular entities will open original perspectives in the field of stimuli-responsive supramolecular materials.

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Data Availability Statement

Data available on request.

Supporting information

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