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Chiral stimuli-responsive metallo-supramolecular assembly induced by Cu^{II}/Cu^I redox change

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We investigated the selective formation of homoleptic and heteroleptic metal complexes controlled by means of the chiral molecular instruction of the ligand and the coordination geometry of the metal. Our results showed that chiral self-recognition or self-discrimination may be induced by Cu^I/Cu^{II} redox transition using cyclic voltammetry. The further use of chiral ditopic ligands led to metallo-supramolecular copolymers with stimuli-responsive controlled arrangement.

Chirality is the molecular instruction encoded in the chemical structure itself, which allows nature to perform most biological functions essential for life.¹ Chirality enables high recognition processes, through intermolecular noncovalent interactions, that are crucial for example to create protein functions or to store genetic information. Understanding of chiral recognition encouraged synthetic chemists to develop simplified molecular systems with the purpose of mimicking biology and developing smart molecular materials. Consequently, supramolecular chiral self-assembly is now considered as the most attractive and promising area of supramolecular chemistry.²

A property of a complex biological system may be the result of the interplay of simpler integrated parts subjected to dynamic reversible interactions and that can respond to a stimulus.³ Therefore, the mimic of chirality-induced biological self-assembly should also incorporate the dynamic nature inherent in non-covalent interactions that can evolve to generate a particular function, especially under the action of an external stimulus.

Supramolecular chiral recognition between enantiomeric molecules can lead to self-discrimination or self-recognition to generate pairs of enantiomers that are homochiral or

heterochiral entities, respectively. The recognition will govern the outcome of the self-assembling process. This assembly route that links molecular and supramolecular chirality is unidirectional and occurs under thermodynamic control.⁴ Contrary to molecular chirality, supramolecular chirality can easily be influenced by external parameters (solvents, temperature, light, electrical bias, etc.) that could provide the opportunity to modulate the self-assembly and thus modify the equilibrium state of the system.⁵ We show here that the self-assembly of two chiral C₂-symmetric ligands around a metal may be electrochemically controlled. This strategy can lead to the generation of metallopolymer in which the arrangement of the structural unit of the polymer may be controlled by the oxidation state of the metal. The switching from alternating metallopolymer to block metallopolymer is electrochemically possible in both directions (Figure 1).

Figure 1 Principle of the electrochemically-induced control of the metallopolymer arrangement: generation of block or alternating metallopolymer through the selective formation of homoleptic (*top*) or heteroleptic complexes (*down*).

The heteroformation or homoformation of ML₂-type complexes may be controlled by the chiral molecular 'instruction' of the ligand in combination with the prevalent coordination geometry of the metal.^{6,7} Chiral neutral C₂-symmetric bisoxazoline **1** in its racemic form spontaneously generates heterochiral complexes with tetrahedral Zn^{II} **2** (Figure 2, *top*). Homochiral complexes **3** are formed with Cu^{II}

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precursor (Figure 2, *bottom*), as deduced from the crystallisation of solutions of these species, and resolution via X-ray diffraction studies (data available in ESI). These observations were confirmed in solution by determining the $\log \beta$ complexation values. Addition of the ligand (enantiopure or racemic) to a solution of $\text{Zn}(\text{BF}_4)_2$ or $\text{Cu}(\text{BF}_4)_2$ was analyzed by UV-vis.⁸ With Cu salt, a fitting of the experimental data to an ML_2 model allowed calculation of the overall stability $\log \beta$ being 6.0 ± 0.4 and 5.8 ± 0.4 for the enantiopure and racemic, respectively. A $\log \beta$ of 8.2 ± 0.4 was determined with Zn salt and *rac* **1**. However, the titration data for the addition of the enantiopure ligand to $\text{Zn}(\text{BF}_4)_2$ were fitted as a simple ML binding model with a $\log \beta = 3.7 \pm 0.4$ suggesting that the homochiral Zn complex could not be generated here.

Figure 2 Selective formation of heterochiral or homochiral entities as the function of the metal precursor. *Top*: Crystal and molecular structure of the heterochiral complex $[\text{Zn}(\text{R-1})(\text{S-1})](\text{BF}_4)_2$ **2** (tetrahedral geometry). *Bottom*: Crystal and molecular structure of the two enantiomeric forms of homochiral complex **3** $[\text{Cu}(\text{R-1})_2](\text{BF}_4)_2$ and $[\text{Cu}(\text{S-1})_2](\text{BF}_4)_2$ (distorted square planar geometry).[†]

We anticipated that self-recognition or self-discrimination in this system could be induced under the action of electrochemical signal akin to molecular machines induced by $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ redox transition, as described by Sauvage *et al.*^{9,10} Indeed, Cu^{I} , d^{10} , is a metal ion that adopts geometry only determined by sterics and should be isomorph to what observed here with zinc.¹¹ Thus, the homochiral/heterochiral interconversion could be triggered electrochemically by changing the oxidation state of Cu atom.¹²

The cyclic voltammogram (CV) of the homochiral enantiopure complex $[\text{Cu}(\text{R-1})_2](\text{BF}_4)_2$ is displayed in Figure 3 (blue curve). Starting from positive potential, the reduction wave of $\text{Cu}^{\text{II}}(\text{R-1})_2$ into $\text{Cu}^{\text{I}}(\text{R-1})_2$, denoted **c1**, is first observed at -0.05 V.

Upon the reverse scan, the generated $\text{Cu}^{\text{I}}(\text{R-1})_2$ species is oxidized at *ca.* 0.01 V (oxidation wave denoted **a1** in Figure 3). The $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ redox transition is reversible, suggesting that no reorganization of the coordination $\text{Cu}(\text{I})$ complex occurs on time scale of the experiment. Similar features are obtained for the CVs of the homochiral enantiopure complex $[\text{Cu}(\text{S-1})_2](\text{BF}_4)_2$ (see figure S7 in the ESI).

Next, the reduction wave of the racemic mixture of 1 mM homochiral $\text{Cu}(\text{1})_2(\text{BF}_4)_2$ **3** (red curve in Figure 3) occurs at the same potential and with approximately the same intensity as for the homochiral enantiopure Cu^{II} complexes. However, during the backward scan, two oxidation waves, separated by 350 mV are observed. The first oxidation wave at 0.01 V, denoted **a1'**, corresponds to the oxidation of the metastable homochiral $\text{Cu}^{\text{I}}(\text{R-1})_2$ and $\text{Cu}^{\text{I}}(\text{S-1})_2$ complexes and exhibits much weaker intensity compared to the **a1** peak of the homochiral enantiopure complexes. The second oxidation wave, denoted **a2**, appears at higher potential (i.e. $+0.360$ V) and is attributed to the presence of more stable heterochiral $[\text{Cu}^{\text{I}}(\text{S-1})(\text{R-1})]$ species resulting from the homochiral/heterochiral interconversion triggered by the reduction of Cu^{II} into Cu^{I} .

Figure 3 Cyclic voltammograms of the homochiral enantiopure complex $\text{Cu}(\text{R-1})_2(\text{BF}_4)_2$ (blue curve) and of the racemic mixture of homochiral $\text{Cu}(\text{1})_2(\text{BF}_4)_2$ **3** (red curve) on a glassy carbon electrode at a concentration of 1 mM in 0.1 M TBAPF₆ CH_2Cl_2 solution. Sweep rate 200 mV s^{-1} . The potential axis is referred to the Fc^+/Fc redox potential.

The rate of the reorganization of the coordination shell of the Cu^{I} species can be estimated from the evolution of the shape of the CV as a function of the potential sweep rate (Fig. 4a).¹³ Above 1000 mV s^{-1} only the peak **a1** was observed in the CV of the racemic mixture of homochiral Cu^{II} complex. This indicates that the characteristic time of the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ reduction/oxidation process at this sweep rate (less than 1 s) is too short to allow the reorganization of coordination shell and to generate detectable amount of heterochiral Cu^{I} species. The peak **a2** is clearly visible on CVs recorded at 500 mV s^{-1} . When the sweep rate was decreased from 500 to 50 mV s^{-1} , the intensity of the **a1** peak decreased concomitantly with the increase of the **a2** peak. At 20 mV s^{-1} , the time scale of the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$

reduction/oxidation experiment was of ca. 40 s and the peak **a1** was not observed anymore (cf. Fig. S8). Thus, the homochiral/heterochiral interconversion occurs on a time scale of a few seconds. This order of magnitude is confirmed by the fit of the CVs using digital simulations and assuming an EC mechanism. The homochiral/heterochiral interconversion rate was found to be $k_c = 0.20 \pm 0.05 \text{ s}^{-1}$ (see Fig. S9). Note however that the rate of the homochiral/heterochiral interconversion is expected to depend on the complex and/or ligand concentration. It should be also mentioned that the wave corresponding to the possible reduction of the heterochiral Cu^{II} complex was never observed even at high scan rate (0.5 V s^{-1}) confirming its instability and the rapid conversion to homochiral Cu^{II} complex. The full-square scheme is summarized in Fig. 4b.

Figure 4 a) Cyclic voltammograms at different sweep rates 50 mV s^{-1} (top), 500 mV s^{-1} (middle), 5000 mV s^{-1} (bottom); *Left*: with (R) enantiopure Cu complex; *Right*: with racemic Cu complex. b) Schematic representation of the electrochemically triggered rearrangement.

Stimuli-responsive polymers are promising materials because of their potential applications ranging from drug delivery to sensors.¹⁴ Among them, metallo-supramolecular polymers are ideal candidates to access new stimuli-responsive materials because they offer properties modifiable by various external stimuli including electric stimulus.¹⁵

We previously established that chiral ditopic ligand such as ligand **4** (Figure 5, a) is suitable to generate metallo-

supramolecular assemblies and thus evaluated for the possibility to implement the chiral self-sorting assembly of the metallo-polymer by $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ change.¹⁶ Figure 5b displays the typical CVs of homochiral enantiopure Cu^{II} metallopolymer obtained for a Cu^{II} concentration of 1 mM in 0.1 M TBAPF₆ CH_2Cl_2 solution at a scan rate of 50 mV s^{-1} (blue curve). The position of the reduction and oxidation waves **c1** and **a1** are almost unmodified compared to the monotopic ligand, confirming that $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ redox transition in the metallopolymer is fast. While the Cu^{II} concentrations in the solution are similar, the redox waves are broader and their intensities are approximately twice lower than the ones obtained with the monotopic ligands. This is assigned to the smaller diffusion coefficient of the metallopolymer in solution.

Figure 5 a) molecular structure of ditopic ligand **R-4**. b) Cyclic voltammograms of the homochiral enantiopure metallopolymer $[\text{Cu}(\text{R-4})_2(\text{BF}_4)_2]_n$ (blue curve) and of the racemic mixture of $[\text{Cu}(\text{4})_2(\text{BF}_4)_2]_n$ (red curve) at a concentration of 1 mM in 0.1 M TBAPF₆ CH_2Cl_2 solution on a glassy carbon electrode. Sweep rate 50 mV s^{-1} . The potential axis is referred to the Fc^+/Fc redox potential.

Finally, the homochiral/heterochiral interconversion was investigated by cyclic voltammetry starting from the racemic mixture of 1 mM homochiral Cu^{II} metallopolymer (red curve in Figure 5). The current-potential curve exhibits one reduction wave **c1** and two oxidation waves **a1** and **a2** which are typical for the case where the homochiral/heterochiral conversion of the Cu^{I} coordination shell occurs, consistent with reorganization scheme from Fig. 1. Again, the characteristic timescale for the reorganization can be extracted from the evolution of CVs with the scan rate. The peak **a2** disappears for potential scan rate above 200 mV s^{-1} suggesting that the time scale for the reorganization is of approximately 10 s. It is interesting to note that the Cu^{II} metallopolymer reorganization is only slightly slower than the racemic discrete Cu^{II} complex,

confirming the ability of Cu^{II} metallopolymer to reorganize upon electrochemical stimulation.

In summary, homoleptic homochiral copper complexes have been prepared and their ligand rearrangements have been investigated by Cu^I/Cu^{II} redox change using cyclic voltammetry. The chiral self-recognition and self-discrimination properties have been clearly established which can lead to a metallo-supramolecular copolymer that can be stimuli-responsive. This feature will now be exploited to develop more complex metallo-supramolecular systems that are able to fulfil such functions.

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Conflicts of interest

There are no conflicts to declare.

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