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Ligand Mediated Metal Cations Exchanges within Metallo-Dynameric Solid Films

Yan Zhang^[a] and Mihail Barboiu*^[b]

Dedicated to Jean-Marie Lehn for his 80th birthday

Dynameric solid films may be generated via the adequate imine-bond connection between bis(pyridine-2,6-diimine) core centres, coordinated with different metal cations and diamino-PEG connectors. The adequate selection of metal cations leads to cross-linked metallo-dynameric films, allowing the fine modulation of their colour and mechanical property. The coordination of the metal cations and bis(pyridine-2,6-diimine), results in the formation of interlocked structures, leading to the most probably formation of interweaved structures with better

mechanical properties than those formed in the absence of the metallic cations. Removal and addition of metal cations from solid films can be achieved via tris(2-aminoethyl)amine (TREN) complexing agent, which strongly binds the metal cations, followed by subsequent insertion of other metallic cations. It allows a ligand-modulated dynamic release of the metal cations from the solid films, together with colour transfer and change of mechanical strength at the interfaces between various solid films.

1. Introduction

As a rapidly growing research topic in recent years, the design of stimuli-responsive dynamic materials is a major facet of constitutional chemistry, expanding their applications to various fields, including drug delivery,^[1] biosensing,^[2] luminescent devices^[3] and pollutant removal,^[4] through different external stimuli, such as pH, light, temperature, pressure, etc.^[5] Inherently featured with responsive character, dynamic polymers – *dynamers* have emerged as a new class of polymer materials for applications of all scales,^[6] from self-healing materials^[7] to directional water transport membranes,^[8] to microscale enzyme activation^[9] and even nanoscale DNA recognition.^[10] The dynamic character has featured them of new emerging properties, along with advantages such as facile synthetic routes, best optimised structures in equilibrium and fast adaptive functions.

Imine chemistry is one of the most reliable reversible reactions have been used in constructing dynamers, mostly because of its mild reaction conditions and good stability in solvents including water.^[11] The metal cation hexacoordination by two iminopyridine ligands relies on the catenation behaviours of the involved ligands and the modification of the

conjugation of imino-aromatic groups, leading to the various absorption behaviors and thus to different optical properties. Dynameric materials possessing optical properties have attracted considerable attention for their potential as molecular sensors or photoactive devices.^[12] Within this context, changes in the optical properties of the dynamers have been induced by imine-bond exchanges of the ligand molecular connectors and component migration through the interface of two systems in contact.

Within this context, we are pursuing our efforts to construct functional metallo-dynameric species, combining imine bond chemistry and metal coordination of bis(pyridine-2,6-diimine) scaffold resulting in the formation of double dynamic frameworks. Until now several supramolecular architectures of this type showed interesting applications in gas transport,^[12] charge-transfer^[13] and double helix biomimetic structures.^[14] For this specific scaffolds, most of the reported work was focused on the ligand exchange, while replacement of the coordinated metal ions, despite its simplicity, is still rare, although the change of chelating metal did significantly alter the property of whole dynamers.^[12,15]

By extending the concept to solid metallo-dynameric films, herein, we envisioned the possibility of *in situ* metal exchanges within the scaffold of bis(pyridine-2,6-diimine) on the interfaces of solid films and solution, leading to smart membranes for adaptive capture of a variety of metal cations (Figure 1).

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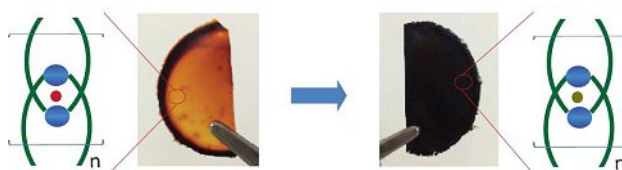


Figure 1. Schematic representation of metal ions exchanges within metallo-dynameric films of different metal cations.

2. Results and Discussion

The chemical synthesis of metallo-dynamers was initiated by mixing 2,6-pyridinedicarboxaldehyde (1), 2,2-(ethylenedioxy)bis(ethylamine) (2) and different metallic cations in methanol at 60 °C for 1 h, resulting in the formation of metal-coordinated/imine double dynameric scaffolds of hexacoordinated bis(pyridine-2,6-diimine) PEG network (Scheme 1). Without the presence of any metallic cations, there was no formation of any solid film. After the addition of different acetate salts such as Zn(OAc)₂, Cu(OAc)₂·H₂O, AgOAc and Co(OAc)₂·4H₂O, membranes of red colour of different intensities could be formed. The obvious colour change and the ¹H NMR spectra indicated the coordination of the metal cations by bis(pyridine-2,6-diimine) centres, results in the formation of the interlocked solid self-standing membrane films with good mechanical properties.

Interestingly, the colour of Zn²⁺ coordinated membrane turns red due to the strong delocalized charge transfer of two ligands around hexacoordinated Zn²⁺ metal ions and due to highly compact catenated superstructures that keep the coordinating centres in the close proximity.

To remove the coordinated metal ion from the prepared films, different methods were tested, by using a strong chelating ligand which has higher affinity toward the targeted metal and different solvents. For this tris(2-aminoethyl)amine (TREN) was reported to have strong coordination strength toward a few metal cations^[16] and it was previously used for modulation of coordination behaviours for ion-triggered mechanical molecular motions.^[17] Since connecting through the highly cross-linked structures, the obtained membranes showed generally good stability at neutral to mild basic conditions at room temperature in water, but decomposed at acidic conditions at pH < 2. However, due to the issue of solvent compatibility, only the membrane containing Zn(OAc)₂, showed resistance for organic solvents, for example, CH₃CN, while membranes with other metal cations could be slowly dissolved in CH₃CN, MeOH or H₂O. Thus Zn²⁺ coordinated membrane was

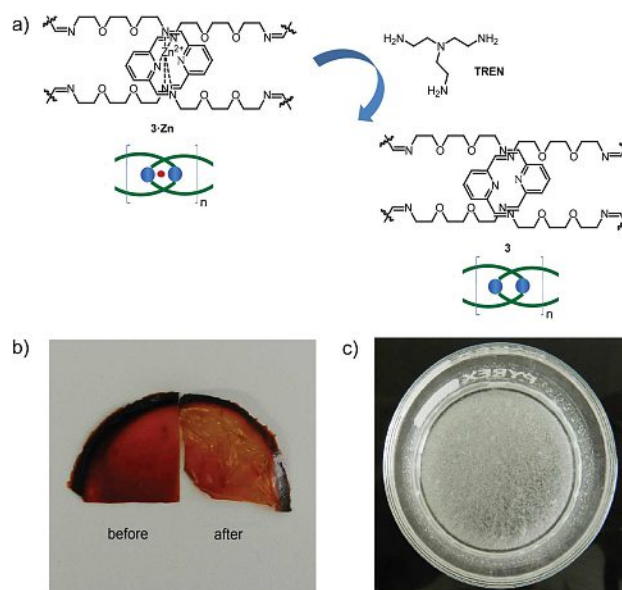
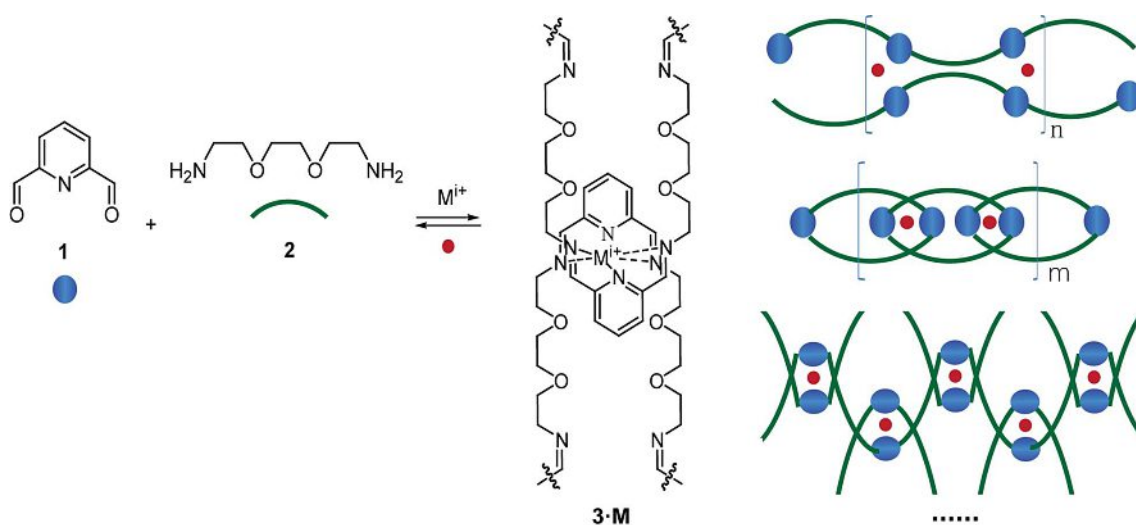


Figure 2. a) Schematic representation of TREN induced demetallation of Zn²⁺ coordinated membrane film; b) membrane image of before (left) and after (right) removal of Zn²⁺; c) white precipitation into the CH₃CN residual washing solution of Zn²⁺ coordinated membrane after demetallation process.

chosen for demetallation experiments with TREN (Figure 2a). After submerging the membrane film in CH₃CN with excess amount of TREN for twice of 20 minutes, the red colour of the membrane started to fade away, leaving less intensive red colour (Figure 2b). Meanwhile there were white powders precipitated on the bottom of the residual washing solution (Figure 2c), suggesting the removal of Zn(OAc)₂ from the membrane and the formation of TREN-Zn²⁺ coordination complexes. Furthermore, direct evidence of elemental distribution on membrane surface can be collected by energy dispersive X-ray (EDX) analysis. As a result, the Zn²⁺ atom



Scheme 1. Synthesis of metallo-dynamers via aldehyde/amine imino chemistry and metal ion coordination

percentage was decreased from 1.8% to 0.4% after TREN induced demetallation.

So far, the metal-removal strategy has successfully prepared a free interconnected membrane film that could not be achieved by direct synthesis. A catenation process is occurring in the presence of metal ions leading to the most probably formation of interweaved structures as previously reported^[18] and reminiscent to the template synthesis of molecular rotaxanes, catenanes or interlocked rings.^[19] The removal of metal ions should maintain several interlocked rings in the structure combined with interlaced molecular organic threads, similar to a woven fabric, conferring it supplementary mechanical stability when compare with linear chains obtained during the polymerization in the absence of the metal templating cations.

Re-inserting Zn^{2+} into the membrane was the next step to check the reversibility of the process. The procedure started by immersing the membrane into H_2O solution with excess amount $Zn(OAc)_2$ for 20 minutes and EDX analysis was used to measure the changes of metallic cation composition within the membrane. The results showed the increase of Zn^{2+} atom percentage back to 2.3%, confirming the re-coordination of Zn^{2+} to the cavity of bis(pyridine-2,6-diimine) inside the membrane.

Moreover, the whole demetallation-remetallation processes were recorded by Fourier-transform infrared spectroscopy (FTIR) spectroscopy, displaying with the differences between coordinated and non-coordinated imine bonds (Figure 3). Thus, the appearance of peak at the wavenumbers of 1645 cm^{-1} for demetallated membrane film demonstrated the presence of non-coordinated $C=N$ double bonds, and the shift of the peak at 1400 cm^{-1} to 1450 cm^{-1} indicated the changes of $N-H$ stretches.

The effective demetallation-remetallation of Zn^{2+} coordinated membrane films at the solid-liquid membrane-solution interface, encouraged us to test if other metal cations could fit the bis-pseudoterpyridine coordinating centres, left from Zn^{2+} metal ions in the membrane. Therefore, the free metal

membrane **3** after removal of Zn^{2+} was subjected to accommodate other cations, including Cu^{2+} , Ag^+ and Co^{2+} , of the format of acetate salts, and subsequently examined by EDX analysis. Table 1 shows the elemental distribution of different membrane surfaces, where the numbers inside are the calculated percentages of the specific atom among all the tested elements, in order to illustrate the demetallation-remetallation processes. Interestingly, no Zn^{2+} atom was detected in all three membranes after remetallation process in H_2O . On the other hand, the percentages of other metal atom distributions were recorded as even higher numbers than the membranes originally made from these cations (Table 1). The reason can be the incompletely washed cation water solutions left on membrane surfaces, or higher chelation strengths between bis(pyridine-2,6-diimine) scaffold and other metals of Cu^{2+} , Ag^+ and Co^{2+} .

The coordination of other metal cations into the membrane cavity left from Zn^{2+} was unexpected and prompted us to study the competitive insertion of different cations compared to Zn^{2+} . When Zn^{2+} and Cu^{2+} presented together in the H_2O solution, only Cu^{2+} was detected by EDX analysis, while no indication of Zn^{2+} in the membrane. The combination of Zn^{2+} and Ag^+ gave atom distribution of 0.5% of Zn^{2+} and 2.2% of Ag^+ . Meanwhile, the competition between Zn^{2+} and Co^{2+} provided more Zn^{2+} than Co^{2+} , 1.4% compared to 1.0% for atom percentages (Table 1). Therefore, the lack of exclusiveness for Zn^{2+} coordination inside the membranes showed adaptivity of the imine dynamers for hosting different metal guests, and the potential for a broad range of metal extractions.

In order to test the competitive binding between bis(pyridine-2,6-diimine) and different metal cations in solution, 1H NMR spectroscopy was used to analysis their behaviour in deuterated water. However, due to the paramagnetic property of Cu^{2+} and Co^{2+} , only the performances of Zn^{2+} and Ag^+ were recorded (Figure 4).

From the spectra, the original chemical shifts of aromatic and imine protons changed a lot after addition of Zn^{2+} and Ag^+ , indicating different coordination modes in respect of Zn^{2+} and Ag^+ . Furthermore, with the mutual presence of Zn^{2+} and Ag^+ in solution, 1H NMR peaks from both Zn^{2+} and Ag^+ coordinated products were observed, which is in consistence

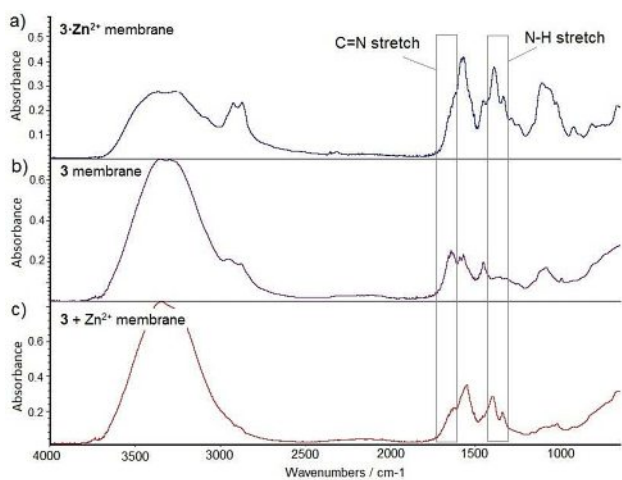


Figure 3. FTIR spectra of a) original $3 \cdot Zn^{2+}$ membrane; b) demetallated **3** membrane and c) remetallated $3 + Zn^{2+}$ membrane.

Table 1. Elemental analysis and distribution on membrane surfaces determined by EDX.

Membranes	C %	N%	O%	Zn%	Cu%	Ag%	Co%
$3 \cdot Zn^{2+}$	67.3 ^a	12.2	18.6	1.8	–	–	–
$3 \cdot Cu^{2+}$	60.1	16.7	21.6	–	1.9	–	–
$3 \cdot Ag^+$	63.4	18.7	15.5	–	–	2.4	–
$3 \cdot Co^{2+}$	65.4	10.9	21.3	–	–	–	2.4
3	55.2	24.8	19.7	0.4	–	–	–
$3 + Zn^{2+}$	64.5	16.0	17.2	2.3	–	–	–
$3 + Cu^{2+}$	63.0	15.5	17.6	–	3.9	–	–
$3 + Ag^+$	56.5	23.2	16.9	–	–	3.5	–
$3 + Co^{2+}$	65.0	16.5	16.4	–	–	–	2.1
$3 + Cu^{2+}/Zn^{2+}$	62.5	15.5	18.0	–	3.9	–	–
$3 + Ag^+/Zn^{2+}$	58.0	22.0	17.1	0.5	–	2.2	–
$3 + Co^{2+}/Zn^{2+}$	62.3	17.0	18.2	1.4	–	–	1.0

^a Atom percentage (%) of different elements.

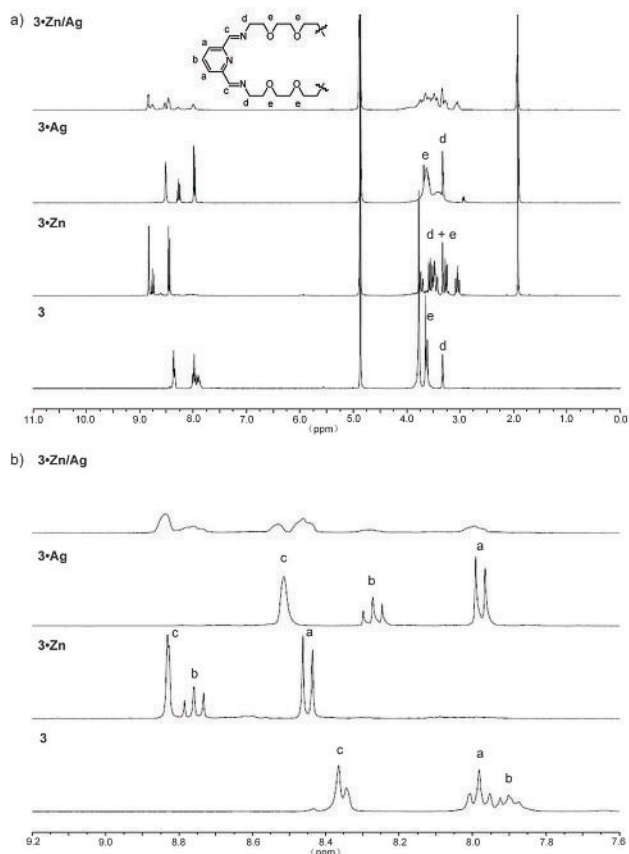


Figure 4. ^1H NMR spectra (top, a) and enlarged part (bottom, b) of the aromatic region of metallo-dynamers **3**, $3 \cdot \text{Zn}^{2+}$ and $3 \cdot \text{Ag}^+$ in solution and competitive coordination between Zn^{2+} and Ag^+ .

with the trend of EDX result for membranes. The only difference is that more Zn^{2+} coordinated peaks were observed in solution by ^1H NMR, while more Ag^+ atom was detected in solid membranes by EDX.

To further explore the differences between these metallo-dynameric films and the impacts of demetallation procedure, the films $3 \cdot \text{Zn}^{2+}$, $3 \cdot \text{Co}^{2+}$ and the demetallated **3** were subjected to mechanical analysis (Figure 5). From the obtained stress-strain curves, the film $3 \cdot \text{Co}^{2+}$ showed higher fracture strength (38.3 MPa) than the film $3 \cdot \text{Zn}^{2+}$ (26.0 MPa), probably owing to the stronger coordination of Co^{2+} with the pyridine group. Moreover, the fracture strength dramatically decreased after the removal of Zn^{2+} from the film, indicating the importance of the presence of metal cations and the role of double cross-linking structure inside the films. These results demonstrated the tunable mechanical properties through above mentioned demetallation and metal cations exchange strategies.

3. Conclusions

In the current study, we prepared a series of dynameric films via imine/coordination chemistries, that further were subjected to demetallation of Zn^{2+} and remetallation of Zn^{2+} and other

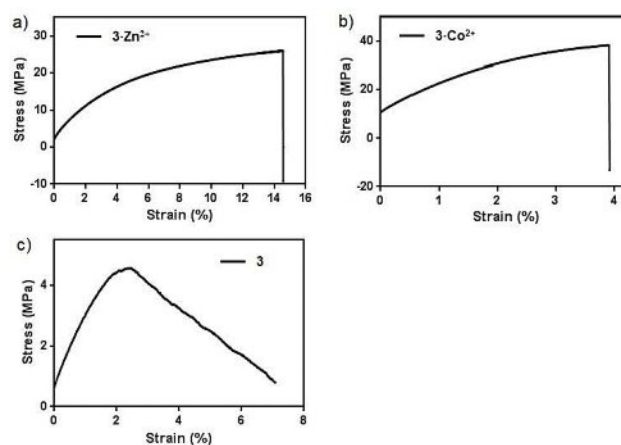


Figure 5. Stress-strain curves of the films a) $3 \cdot \text{Zn}^{2+}$; b) $3 \cdot \text{Co}^{2+}$ and c) demetallated **3**.

metal cations in membranes. With the scaffold of bis(pyridine-2,6-diimine) in dynamer materials, different metal cations can be embedded into the membranes. TREN, possessing higher Zn^{2+} chelation strength, was adopted to remove Zn^{2+} from the membrane, leading to metal free membrane that could not be directly prepared by its own components. Remetallation of Zn^{2+} and other metal cations was subsequently achieved. Thereafter, the competitive coordination between Zn^{2+} and other cations was also tested, in both solid and solution states. To monitor the whole processes, EDX analysis and FTIR were used to follow the changes of atom distribution and imine bond stretches. Furthermore, the change of the mechanical strength of the obtained membranes were also observed between the membranes of different metals and before/after demetallation, showing great potentials of this strategy in tuning membrane mechanical properties. In conclusion, for the first time, metal cations exchange was realized in the solid state of membrane, and we can foresee the potential applications for broader type of smart materials with metal cations extraction.

Experimental Section

General methods: Reagents were obtained from Sigma Aldrich and used as received. ^1H NMR spectra were recorded on an ARX 300 MHz Bruker. Chemical shifts are reported as δ values (ppm) with D_2O (^1H -NMR δ 4.79) as an internal standard. EDX were obtained with a Hitachi S-4500 apparatus, under a tension of 0.5–30 kV. FTIR measurements were performed with a Nicolet Nexus FT-IR spectrometer equipped with an ATR Diamant Golden Gate. Tensile experiments were performed on an Instron 5967 tensile tester.

Typical preparation of the membrane films : 0.4 mmol 2,6-pyridinedicarboxaldehyde (**1**, 54.0 mg) and 0.4 mmol dialdehyde 2,2'-(ethylenedioxy)bis(ethylamine) (**2**) were added together with 0.5 equivalent of each metal cation acetate salt and 5 mL methanol, and the resulted solution was stirred at 60°C with reflux for 1 h. The solution mixture was then cooled to r.t. and poured to a Teflon template, and the solvent was subsequently evaporated at r.t. inside the hood until solid membrane was formed.

Typical procedure of removing Zn²⁺ from membrane 3·Zn²⁺: 400 μL of tris(2-aminoethyl)amine (TREN) was added to 4 mL CH₃CN solution, and half of the 3·Zn²⁺ membrane was immersed into it for 20 min. The same procedure was repeated for another time with fresh TREN in CH₃CN solution. The membrane piece was picked out and washed with mini-Q water for three times, and dried in air.

Typical procedure of remetalation for membrane 3: A half piece of demetalated membrane 3 was put into 0.5 mL mini-Q water with 10 mg of Zn(OAc)₂, Cu(OAc)₂·H₂O, AgOAc or Co(OAc)₂·4H₂O respectively or combined, and was kept there for 20 min. The membrane piece was then picked up and washed with mini-Q water for three times, and dried in air.

Typical procedure of mechanical tests: Cut the membranes to a size of approximately 80×30 mm. Put the membranes in the device with two end fixed, leaving an effective measuring range of 40 mm height. The experiments were operated at 25 °C and 65% humidity. The stress-strain curves were obtained with a stretch rate of 5 mm/min and a frequency of 20 Hz.

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Keywords: dynamers · adaptive chemistry · metal cations exchanges · membranes

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