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Synthesis of alternating metallo-copolymers by chiral recognition

Maria Torres-Werlé,^[a] Benoît Heinrich,^[a] Aline Maise-François^[a] and Stéphane Bellemin-Lapponaz^{*[a]}

Abstract: We report the synthesis of chiral enantiopure polytopic bridging ligands which may lead to the formation of metallosupramolecular polymers with zinc(II) as metal linker. We show that chiral C_2 -symmetric bisoxazoline ligands are useful moieties to efficiently generate heterochiral complexes

and thus polymeric entities. The corresponding metallo-polymers were further characterized by powder X-ray diffraction (PXRD) to obtain information on the level of crystallinity of our different metallopolymers.

Keywords: chiral bisoxazoline, polytopic ligand, zinc, metallopolymer

1. Introduction

Metallo-supramolecular polymers that combine metal ions and polytopic ligands enable constructing unprecedented materials with specific properties and functions that are of interest for fundamental research but also for the development of new technologies.^{1,2} Indeed, the combination of metal ions with polytopic -organic- ligands necessarily imports the properties of the two components (organic and inorganic) into the final polymer as well as additional properties generated by the metal-ligand coordination such as luminescence for example. These metallopolymers are obtained in a straightforward manner by a process of self-assembly of metal ions with a monomer having linked units (i.e. polytopic ligands) and the resulting polymer may exhibit reversible polymerization / depolymerization characteristics due to the strength of the coordinate interactions.³⁻⁷

We have recently shown that while most of these polymers consist of a single binding motif, it may be possible to generate alternating metallopolymers with, for example, two different ligands by means of a chiral molecular instruction.⁸⁻¹⁰ The well-defined construction of such copolymers has been possible through heteroleptic coordination under chirality control at the metal center, which contains freely exchangeable ligands under thermodynamic control.

We used the complementarity of these bisoxazoline ligands to generate here alternating metallo-copolymers. Therefore, ditopic, tritopic and tetratopic chiral ligands have been synthesized for that purpose and then used to generate metallopolymers. In all cases, the metallopolymers were instantaneously formed upon addition of zinc salt to a mixture of two ligands of opposite configuration. The resulting solids were characterized including powder X-ray diffraction studies.

2. Materials and Methods

2.1 Chemicals and instruments

All manipulations were performed under an inert atmosphere of argon or nitrogen using standard Schlenk line techniques. Valinol was obtained by reduction of valine.¹¹ 1,1-bis[(4S)-4-isopropyl-4,5-dihydrooxazol-2-yl]ethane (**1**) was synthesized according to previous report.^{12,13} Solvents were purified and

degassed by standard procedures. All other reagents were commercially available and used as received. Metallopolymers were obtained using methanol as solvent (ACS reagent grade). 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 TMS (tetramethylsilane). Infrared (IR) spectra were recorded on a Nicolet 380 FT-IR spectrometer. KBr discs were made for all samples. Elemental analyses were recorded by the 'Institut de Chimie' laboratory, Université de Strasbourg. HRMS ESI analyses were recorded on microTOF, Bruker Daltonics by the 'Institut de Chimie' laboratory, Université de Strasbourg. Specific rotations were recorded at the 'Laboratoire de Stéréochimie', ECPM, Strasbourg. The XRD patterns were obtained with a linear monochromatic Cu-Kα1 beam (λ=1.5405 Å) by using a sealed-tube generator (600W) equipped with a bent quartz monochromator and recorded with a curved Inel CPS120 counter gas-filled detector linked to a data acquisition computer. Periodicities up to 70 Å can be measured, and the sample temperature controlled to within ±0.01 °C from 20 to 200 °C. In all cases, the crude powder was filled in Lindemann capillaries of 1 mm diameter and 10 μm wall-thickness.

2.2 Synthesis of polytopic bisoxazolines

2.2.1 (S)-iPr-DiBox (**2**). General procedure.¹⁴

1,1'-Bis[(4S)-4,5-dihydro-4-isopropylloxazol-2-yl]ethane (**1**, 3.96 mmol, 1g) was dissolved in dry tetrahydrofuran (25 mL). A solution of 1.6 M *n*BuLi in hexane (4.31 mmol, 2.7 mL) was

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added dropwise at -78 °C. After stirring for 15 min, the bath was removed and α,α' -dibromo-*p*-xylene (1.96 mmol, 518 mg) was added. The mixture was then stirred at room temperature for 12 h. The resulting mixture was washed with a saturated NH_4Cl solution and the aqueous phase was extracted with dichloromethane. The combined organic phases were dried over Na_2SO_4 . Evaporation of the solvent gave a colourless oil, which was purified by silica gel column chromatography (AcOEt/MeOH , 95/5) yielding a colourless viscous oil (1.56 mmol, 948 mg, 80%). $[\alpha]_D^{25}$: -0.81 (c 0.5, CHCl_3). $^1\text{H NMR}$ (300 MHz, CDCl_3): δ (ppm) = 7.03 (s, 4H; H_{arom}), 4.22 (dt, $^3J = 8.0$ Hz, $^2J = 1.3$ Hz, 4H; -NCH), 4.05-3.90 (m, 8H; - OCH_2), 3.24 (s, 4H; - CH_2), 1.84-1.67 (m, 4H; - $\text{CH}(\text{CH}_3)_2$), 1.40 (s, 6H; - $\text{C}(\text{CH}_3)_3$), 0.94-0.80 (m, 24H; - $\text{CH}(\text{CH}_3)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, CDCl_3): δ (ppm) = 167.6 (N=CO), 134.9 (- C_{arom}), 130.1 (- C_{arom}), 72.0, 71.6 (-NCH), 70.1, 69.8 (- OCH_2), 43.3 (- CCH_3), 41.8 (- CH_2), 32.5, 32.2 (- $\text{CH}(\text{CH}_3)_2$), 21.2 (- $\text{C}(\text{CH}_3)_3$), 18.8, 18.7, 17.9, 17.5 (- $\text{CH}(\text{CH}_3)_2$); IR (KBr): $\tilde{\nu} = 1658$ cm^{-1} (s, C=N); MS (ESI +): m/z : 607.42 $[\text{M}+\text{H}]^+$; elemental analysis calcd (%) for $\text{C}_{36}\text{H}_{54}\text{N}_4\text{O}_4$: C 71.25, H 8.97, N 9.23; found C 70.97, H 8.89, N 9.21. (*R*)-iPr-DiBox was obtained using the same procedure from 1,1'-Bis[(4*R*)-4,5-dihydro-4-isopropylloxazol-2-yl]ethane.

2.2.2 (S)-iPr-BP-DiBox (3)

The general procedure was followed: 2.00 mmol (51% yield). $[\alpha]_D^{25}$: -0.59. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ (ppm) = 7.42 (d, $J = 8.2$ Hz, 4H; H_{arom}), 7.21 (d, $J = 8.3$ Hz, 4H; H_{arom}), 4.30-4.23 (m, 4H; -NCH), 4.07-3.91 (m, 8H; - OCH_2), 3.33 (q, $J = 13.5$ Hz, 4H; - CH_2), 1.85-1.73 (m, 4H; - $\text{CH}(\text{CH}_3)_2$), 1.47 (s, 6H; - $\text{C}(\text{CH}_3)_3$), 0.95-0.81 (m, 24H; - $\text{CH}(\text{CH}_3)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, CDCl_3): δ (ppm) = 167.5 (N=CO), 139.5 (- C_{arom}), 135.6 (- C_{arom}), 130.8 (- C_{arom}), 126.6 (- C_{arom}), 72.0, 71.6 (-NCH), 70.1, 69.8 (- OCH_2), 43.4 (- CCH_3), 41.8 (- CH_2), 32.4, 32.3 (- $\text{CH}(\text{CH}_3)_2$), 21.3 (- $\text{C}(\text{CH}_3)_3$), 18.8, 18.7, 17.9, 17.5 (- $\text{CH}(\text{CH}_3)_2$); IR (KBr): $\tilde{\nu} = 1655$ cm^{-1} (s, C=N); MS (ESI +): m/z (%): 684.45 $[\text{M}+\text{H}]^+$; elemental analysis calcd (%) for $\text{C}_{42}\text{H}_{58}\text{N}_4\text{O}_4$ (682.93): C 73.86, H 8.56, N 8.20; found C 73.94, H 8.60, N 8.02. (*R*)-iPr-BP-DiBox was obtained using the same procedure starting from 1,1'-Bis[(4*R*)-4,5-dihydro-4-isopropylloxazol-2-yl]ethane.

2.2.3 (S)-iPr-TriBox (4)

The general procedure was followed to give the product with identical analytical data as already reported by us.¹⁴

2.2.4 (S)-iPr-TetraBox (5)

The general procedure was followed to give the product with identical analytical data as already reported by us.¹⁴

2.3 Synthesis of metallopolymers.

2.3.1 Metallopolymer (6) [Zn + (R)-iPr-DiBox + (S)-iPr-DiBox]. General procedure.

Ligands (*R*)-(2) (*R*)-iPr-DiBox and (*S*)-(2) (*S*)-iPr-DiBox (0.12 mmol, 75 mg each) were dissolved in methanol (1.0 mL). The resulting colorless solution was stirred for 10 minutes before

adding dropwise solution of $\text{Zn}(\text{BF}_4)_2$ (0.24 mmol, 57 mg) in methanol (1.0 mL). The mixture led to the instantaneous formation of an opaque gel. The polymer was then isolated by addition of diethyl ether followed by filtration, giving a white powder in quantitative yield. IR (KBr): $\tilde{\nu} = 1634$ cm^{-1} (s, C=N); elemental analysis calcd (%) for $\text{C}_{72}\text{H}_{108}\text{B}_4\text{F}_{16}\text{N}_8\text{O}_8\text{Zn}_2$: C 51.12, H 6.43, N 6.62; found C 51.53, H 6.68, N 6.75. Since the product is insoluble in most common solvents, the NMR spectrum could not be taken. Thermo-Gravimetric Analysis (TGA) revealed that the decomposition of the samples occurs above 200 °C, without crossing any phase transition.

2.3.2 Metallopolymer (7) [Zn + (S)-iPr-BP-DiBox + (R)-iPr-BP-DiBox]

The general procedure was followed (0.25 mmol of Zn, quantitative yield). Since the product is insoluble in most common solvents, the NMR spectrum could not be taken. Elemental analysis calcd (%) for $\text{C}_{84}\text{H}_{116}\text{B}_4\text{F}_{16}\text{N}_8\text{O}_8\text{Zn}_2$: C 54.72, H 6.34, N 6.06; found C 54.29, H 6.43, N 5.87.

2.3.3 Metallopolymer (8) [Zn + (S)-iPr-DiBox + (R)-iPr-BP-DiBox]

The general procedure was followed (0.25 mmol of Zn, quantitative yield). $^1\text{H NMR}$ (300 MHz, CD_3OD): δ (ppm) = 7.51 (d, $J_{\text{ortho}} = 8.2$ Hz, 4H; H_{arom}), 7.25 (d, $J_{\text{ortho}} = 7.9$ Hz, 4H; H_{arom}), 7.10 (bs, 4H, H_{arom}), 4.39-3.94 (m, 24H), 1.86-1.71 (m, 20H), 0.94-0.85 (m, 48H). Elemental analysis calcd (%) for $\text{C}_{78}\text{H}_{112}\text{B}_4\text{F}_{16}\text{N}_8\text{O}_8\text{Zn}_2$: C 52.48, H 6.41, N 6.30; found C 52.06, H 6.73, N 6.29.

2.3.4 Metallopolymer (9) [Zn + (R)-iPr-DiBox + (S)-iPr-TriBox]

The general procedure was followed (0.25 mmol of Zn, quantitative yield). $^1\text{H NMR}$ (300 MHz, CD_3OD): δ (ppm) = 7.14-6.99 (m, 7H, H_{arom}), 4.40-3.35 (m, 30H), 2.98-2.92 (m, 10H), 1.96-1.29 (m, 25H), 0.93-0.85 (m, 60H). Elemental analysis calcd (%) for $\text{C}_{210}\text{H}_{318}\text{B}_{12}\text{F}_{48}\text{N}_{24}\text{O}_{24}\text{Zn}_6$: C 50.48, H 6.41, N 6.73; found C 50.84, H 6.88, N 6.62.

2.3.3 Metallopolymer (10) [Zn + (R)-iPr-DiBox + (S)-iPr-TetraBox]

The general procedure was followed (0.25 mmol of Zn, quantitative yield). $^1\text{H NMR}$ (300 MHz, CD_3OD): δ = 7.13-6.99 (m, 6H, H_{arom}), 4.87-3.54 (m, 36H), 2.98-2.92 (m, 10H), 1.98-1.24 (m, 30H), 0.96-0.85 (m, 72H). Elemental analysis calcd (%) for $\text{C}_{138}\text{H}_{210}\text{B}_8\text{F}_{32}\text{N}_{16}\text{O}_{16}\text{Zn}_4$: C 50.15, H 6.40, N 6.78; found C 50.85, H 6.79, N 6.63.

Results and Discussion

The chiral ligands were synthesized according to the general scheme described in Figure 1. They were obtained in one step from methyl-bis(oxazoliny)methane derivative¹⁵ by deprotonation with *n*-BuLi followed by reaction with the appropriate electrophile (i.e., α,α' -dibromo-*p*-xylene, α,α' -dibromo-*p,p'*-bitolyl, 1,3,5-tris (bromomethyl)-benzene or 1,2,4,5-

tetrakis (bromomethyl)-benzene).^{16,17} All compounds were characterized by classical analytical methods. For the purpose of our studies both enantiomers of ditopic ligand (**2**) and (**3**) were synthesized whereas ligand (**4**) and (**5**) were synthesized starting from (*S*) valinol.

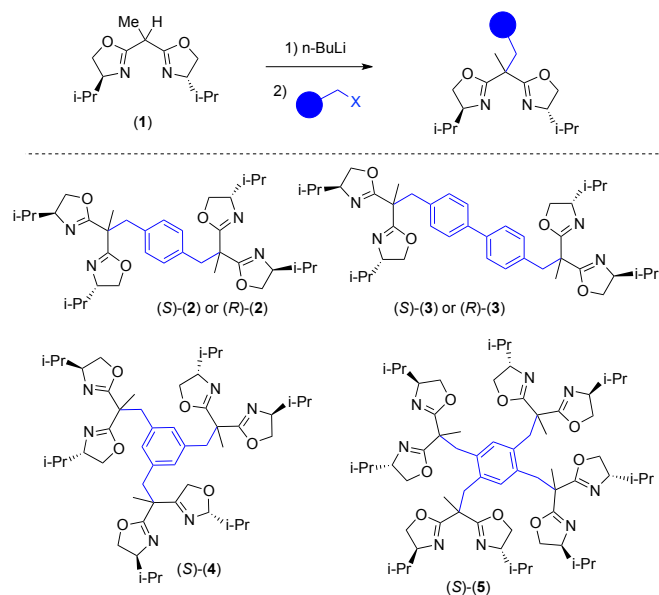


FIGURE 1 Synthesis of polytopic ligands in enantiomeric form from (*S*)-(1) or (*R*)-(1). Conditions: 1) *n*-BuLi, -78 °C, 15 min in THF; 2) Electrophile (0.5, 0.33 or 0.25 equiv.), R.T. 12 h.

On the basis of chiral molecular assemblies, the successful construction of an alternate metallo-copolymer is only possible by formation of heterochiral complexes, which has been shown to be possible using C_2 -symmetric bisoxazoline ligands. Indeed, the least sterically hindered $[ML_2]$ -type complex in a tetrahedral environment combines two chiral C_2 -symmetric bisoxazoline ligands of opposite sign, as displayed in Figure 2.^{8,9} This strategy allowed us to construct several metallopolymers with ditopic ligands. We then decided to extend this strategy to synthesize various metallopolymers in particular using units with higher topology.

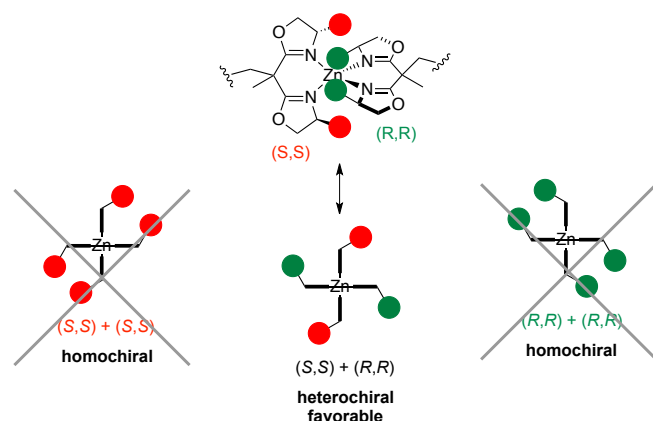


FIGURE 2 Shaping coordination spheres with chiral C_2 -symmetric bisoxazoline derivatives: favorable combination in $[Zn(\text{bisox})_2]^{2+}$ complexes in a tetrahedral environment, demonstrating the complementarity of opposite enantiomers.

Using ligands (**2**) to (**5**), we synthesized five different zinc-based metallopolymers as shown in Figure 3. In all cases, they were instantaneously formed upon addition of $Zn(\text{BF}_4)_2$ to a methanol solution containing two ligands of opposite configuration and in

the appropriate stoichiometric proportion. Metallopolymers (**6**) and (**7**) were generated from the racemic *i*Pr-DiBox ligand (**2**) and *i*Pr-BP-DiBox ligand (**3**), respectively. Metallopolymer (**8**) was obtained from the *i*Pr-DiBox ligand (*R*)-(2) and *i*Pr-BP-DiBox ligand (*S*)-(3), whereas metallopolymers (**9**) and (**10**) were obtained by combination of (*R*)-(2) with the tritopic ligand (*S*)-(4) or the tetratopic ligand (*S*)-(5), respectively. In all cases, a white gel-like material was spontaneously formed upon addition of the zinc precursor. All polymers have then been isolated as white solids in close-to-quantitative yield by addition of diethylether and elemental analyses confirmed the purity of the products. Interestingly, all attempts to generate metallopolymers using ligands with the same absolute configuration were unsuccessful thus confirming the need of heterocomplementarity to form the metal complexes. Figure 4 displays the methanol solution containing equimolar amount of ligand (*R*)-(2) and (*S*)-(3) prior to addition to the metal salt (a) and after addition (b) showing the formation of the polymer (**8**). Figure 4 (c) displays the ^1H NMR spectra of the resulting polymer that has been isolated by precipitation with diethylether and filtration. Integration of the signals confirmed the stoichiometric composition of resulting metallo-polymer.

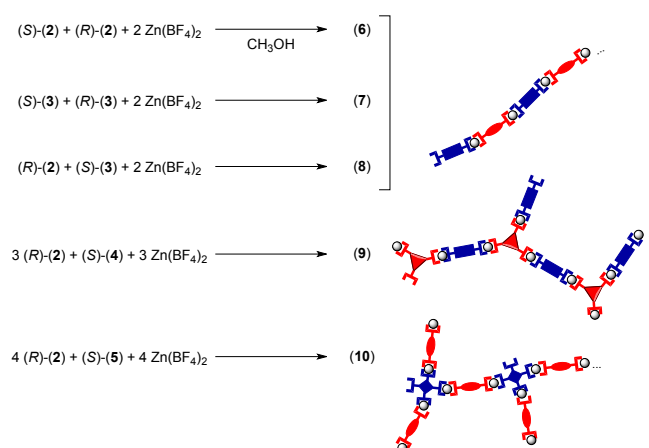


FIGURE 3 Synthesis of metallopolymers **6-10**, using ditopic, tritopic or tetratopic ligands (**2-5**). Conditions: MeOH at room temperature.

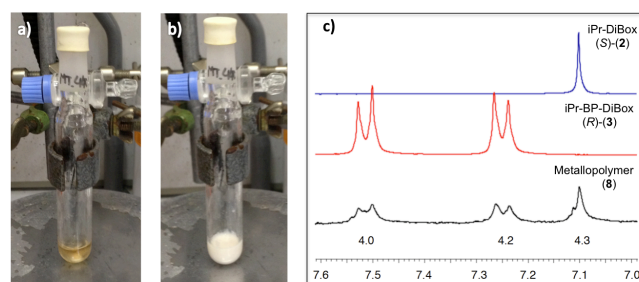


FIGURE 4 Pictures of the resulting solution before (a) and after (b) complexation of $Zn(\text{BF}_4)_2$ with an equimolar amount of (*R*)-(2) and (*S*)-(3); c) ^1H NMR spectra (CD_3OD , aromatic region) of (*S*)-*i*Pr-DiBox (top), (*R*)-*i*Pr-BP-DiBox (middle) and the corresponding copolymer (bottom) obtained from $Zn(\text{BF}_4)_2$.

We then studied our Zn (II) compounds by powder X-ray diffraction (PXRD), to obtain information on the level of crystallinity of our different products. In the case of the metallopolymer (**6**), the structure turned out to be semi-crystalline with nanometer-size crystals leading to broadened reflections, as displayed in Figure 5.

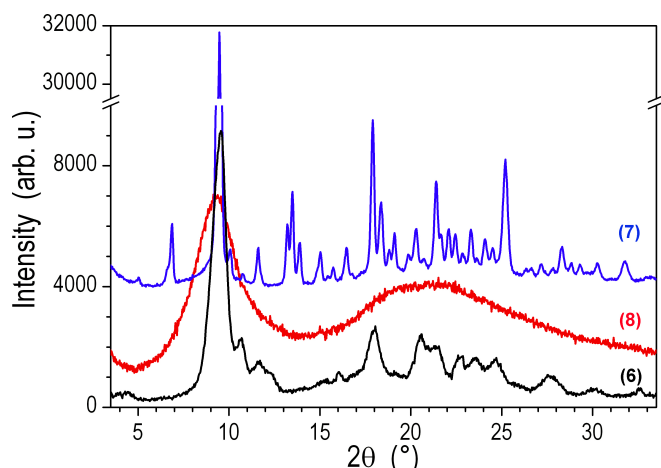


FIGURE 5 PXRD patterns of metallopolymers (6) (bottom, black), (8) (middle, red) and (7) (top, blue).

Although the overlapping and the poorly defined positions of the reflections precludes the resolution of the average crystalline structure, the information from PXRD pattern is sufficient for a general description of the material state. Specifically, the main diffracted intensity shares in two groups of unresolved reflections: one at small-angles (around the major peak at 9.5° corresponding to 9.3 Å) from the lateral arrangement of polymer chains and counter-ions, and a group at wide-angles ($18\text{--}25^\circ$ corresponding to 5–3.5 Å) from periodicities in the range of lateral distances between close-packed molecular segments. Outside these groups, diffracted signals are essentially blurred out by the structural disorder, whereupon the molecular organization could be considered as “soft-crystalline”, as meaning in a state intermediate between crystalline and amorphous solids. For metallopolymer (8), also shown in figure 5, crystallinity even totally vanished since the patterns only contains two broad scattering signals from average lateral distances between polymer chains and molecular segments. The similarity of their shapes and positions with those of the unresolved reflection groups of (6) strongly suggests close local-range arrangements for both polymers. They indeed contain the same metal ion and counter-ions, whose arrangement into ionic strata drives the self-assembly. The nature of the organic spacers and their sequence in the backbones allows however to modulate the emerging structure or here to obtain such a structure only for (6). The reason is obviously that (6) exclusively associates enantiomeric units of type (2), while (8) alternates type (2) and type (3) units: complexes from successive strata are hence connected by a phenyl spacer in (6), while they are either connected by a phenyl or a longer biphenyl spacer in (8). Prerequisite for crystallization in this latter case is that polymers self-assemble in a way that all spacers of same nature locate on the same side of ionic strata. Such an unlikely configuration is perhaps not possible for (8), which would then explain that this polymer stays in an amorphous-like state. Confirmation of this view is brought by polymer (7) in figure 5, for which both (2) units were replaced by (3), and thus all phenyl spacers by biphenyl. Constrain from spacer location was therefore removed and crystallization effectively reappeared. Ionic parts being identical for (6) and (7), structures are also quite similar, with in particular the same major periodicity at 9.3 Å from the lateral arrangement of polymers. There is nevertheless a striking difference in the regularity and correlation length of the structures: for (7), reflections are substantially sharper and appear in the whole scattering range; this material is hence in a fine-powdered crystalline state. It is unclear why the spacer nature has this

effect: tentatively, it could be related to the contribution of biphenyl to close-packing or to the higher spacing of ionic strata. Apart from modulating the emerging structure, the organic spacer offers an easy route toward higher topology and up to 4 coordinating sites could be introduced on phenyl and combined to ditopic ligands, to yield the metallopolymers (9) and (10), whose PXRD patterns are displayed in Figure 6. It was expected that ramifications would perturb the close-packing, and effectively crystallinity vanished for both copolymers. The patterns of these amorphous-like polymers display the two scattering signals from the local-range close-packing of entire polymers and molecular segments. The shapes and positions of these signals stay similar to those of the unresolved reflection groups of the linear polymer (6), indicating that ramifications have little impact on the local-range packing of complexes and counter-ions.

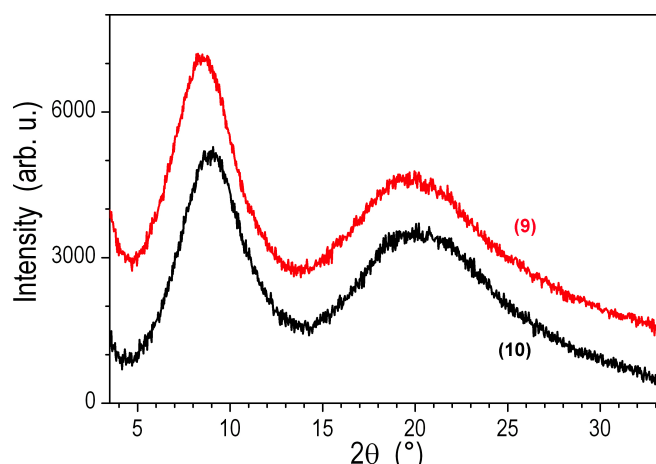


FIGURE 6 PXRD patterns for metallopolymers (9) and (10) of topology higher than 2.

4. Conclusion

In conclusion, we have shown that using zinc ions alternate metallopolymers may be easily produced through the formation of heterochiral $[ML_2]$ -type complexes. Indeed, chiral C_2 -symmetric bisoxazoline derivatives exhibit the good spatial arrangement to generate these heterochiral species. When ditopic ligands of opposite configuration were used such as (S)-(2) and (R)-(2) or (S)-(3) and (R)-(3), semi-crystalline solids were obtained. Other combination led to amorphous solids, such as pairing of (S)-(2) with (R)-(3) for example. In addition, ligands of higher topology also led to amorphous materials. Indeed, ramifications may perturb the close-packing and crystallinity disappears as soon as topology of the ligand is higher than 2. From these experiments we can further conclude that prerequisite for crystallization of linear metallopolymers from ditopic ligands is that they self-assemble in a way that all spacers of same nature locate on the same side of ionic strata.

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