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Multipodal dynamic coordination involving cation-π interactions to control the structure of helical polymers

Mohammad Alzubi, Sandra Arias, Iria Louzao, Emilio Quiñoá, Ricardo Riguera*
and Félix Freire*

Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS) and Departamento de Química Orgánica, Universidade de Santiago de Compostela, 15782 Santiago de Compostela (Spain)

Supporting Information

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1 Synthesis of monomers

Synthesis and data of monomer M2

1 **2** **M2**

4-Ethynylbenzoic acid (2.000 g, 1.2 equiv) was dissolved in 137 mL CH_2Cl_2 dried. Then, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC.HCl, 2.622 g, 1.2 equiv),1-hydroxybenzotriazole (HOBt, 1.849 g, 1.2 equiv) and diisopropyltriethylamine (DIPEA, 2.78 mL, 1.4 equiv) were added to the solution and the reaction was stirred for 20 min to activate the acid. Next, phenylglycine methyl ester hydrochloride (Aldrich, 2.298 g, 1.0 equiv) was added to the reaction mixture. The resulting suspension was stirred and monitored by TLC. When the reaction was completed, the reaction mixture was washed with HCl 1M, a saturated solution of $NaHCO_3$ and brine. The combined organic layers were dried over anhyd Na_2SO_4, filtered and the solvent was evaporated at reduced pressure. The crude product was chromatographed on silica gel (70-230 mesh) with hexane/ethyl acetate (7/3) as eluent. After purification, 2.675 g (80%) of M**2** were obtained.

Spectroscopic data.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 3.20 (s, 1H), 3.77 (s, 3H), 5.76 (s, 1H), 7.15 (d, 1H).7.32 – 7.87 (m, 10H),

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 53.0, 56.8, 77.0, 79.7, 82.7,125.8, 127.1, 127.3, 128.7, 129.1, 132.3, 136.4, 165.8, 171.4.

$[\alpha]_D$= +68 (13.6 mg/mL, $CHCl_3$).

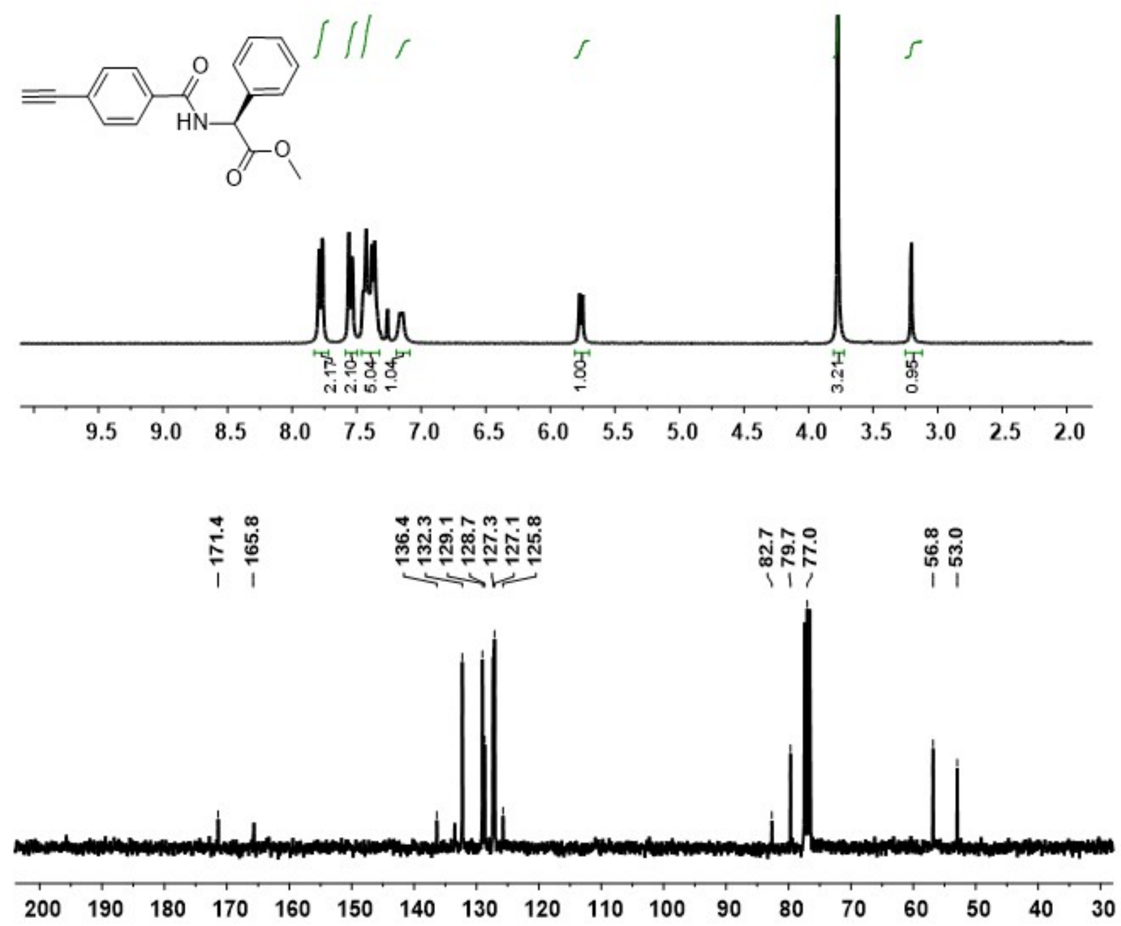
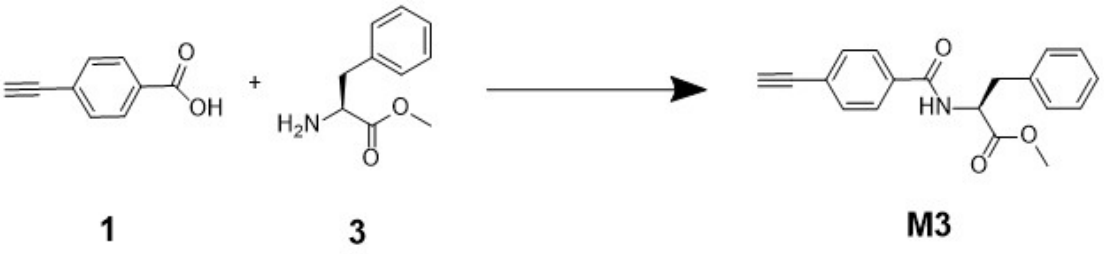


Figure S1: ^{1}H and ^{13}C NMR spectra of monomer M**2**.

- **Synthesis and data of monomer M3**



1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC, 0.656 g, 1.2 equiv), hydroxybenzotriazole (HOBt, 0.465 g, 1.2 equiv), 2-ethynylbenzoic acid (0.500 g, 1.2 equiv) and diisopropyltriethylamine (DIPEA, 0.70 mL, 2.0 equiv) were dissolved in 50 mL of CH_2Cl_2, and the mixture was stirred for 15 min to activate the acid. Then, methyl *L*-phenylalaninate, (0.500 g, 1.0 equiv) was added and the reaction mixture was stirred overnight. The organic layer was washed with HCl 1M, saturated solution of $NaHCO_3$ and brine. The combined organic layers were dried over anhyd Na_2SO_4, filtered and the solvent was evaporated at reduced pressure. The crude product was chromatographed on silica gel (70-230 mesh) with hexane/ethyl acetate (7/3) as eluent. After purification, 0.690 g (83%) of M**3** were obtained.

Spectroscopic data:

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 3.19 (s, 1H), 3.25 (m, 2H), 3.77 (s,1H), 5.08 (q, 1H), 6.56 (d, 1H), 7.12 (m, 2H), 7.28 (m, 3H), 7.53 (d, 2H), 7.68 (d, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 17.4, 52.3, 53.7, 79.8, 82.6, 125.5, 127.0, 127.1, 128.5, 129.1, 132.1, 133.6, 135.9, 166.2, 172.0.

$[\alpha]_D$= +51 (15.0 mg/mL, $CHCl_3$).

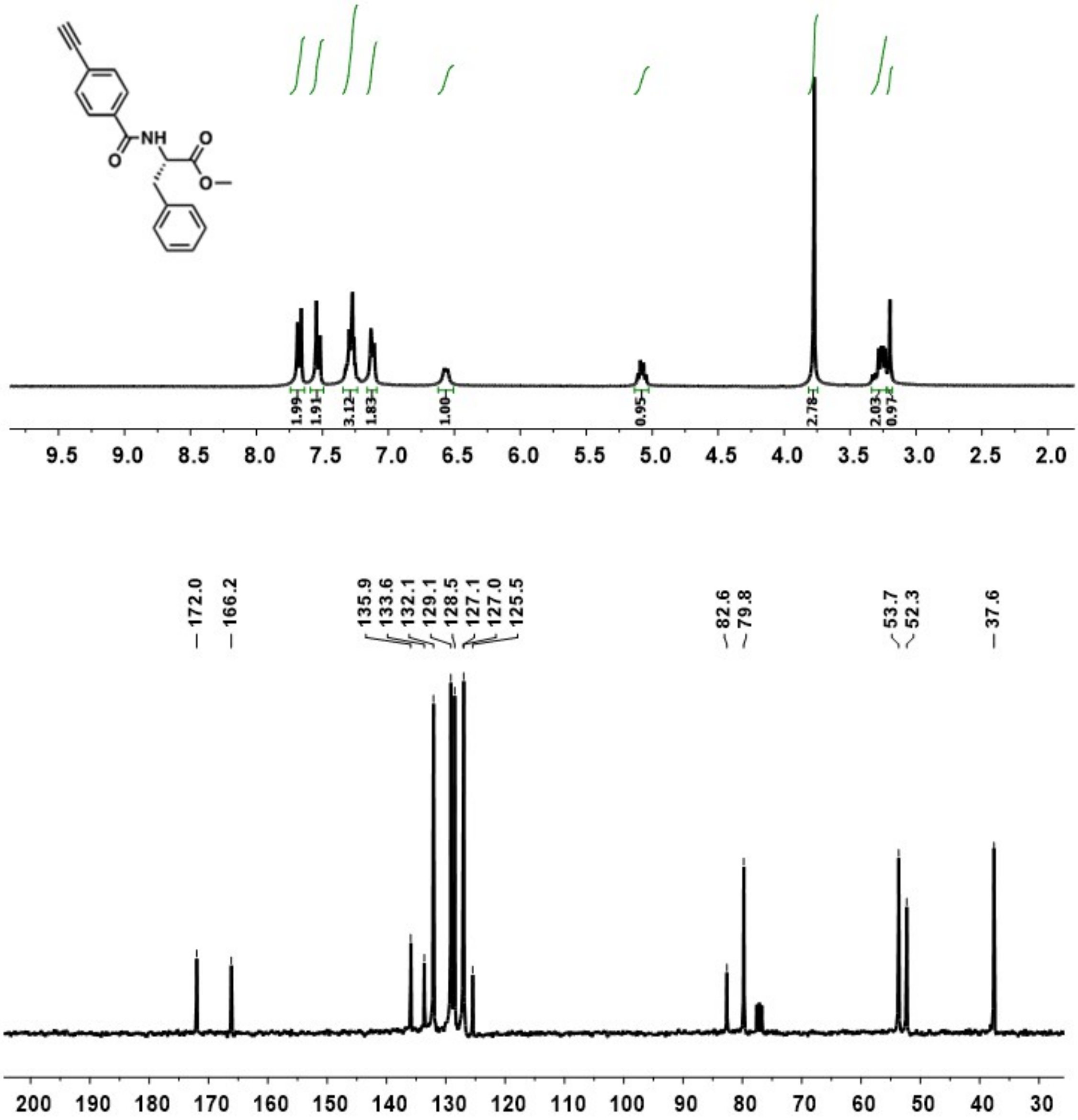
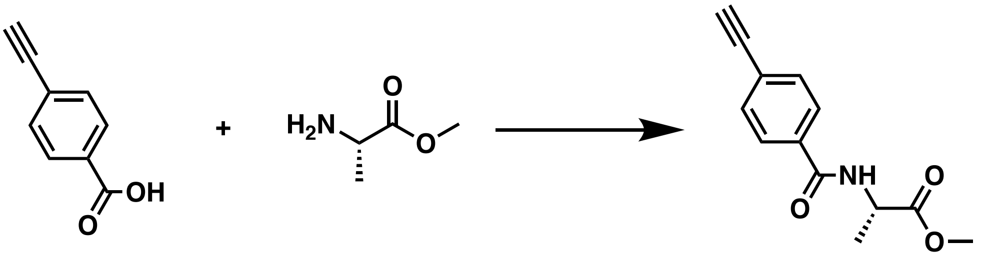


Figure S2: ^{1}H and ^{13}C NMR spectra of monomer M**3**.

- **Synthesis and data of monomer M4.**



1 **4** M**4**

1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC, 1.350 g, 1.2 equiv), hydroxybenzotriazole (HOBt, 1.400 g, 1.2 equiv), 2-ethynylbenzoic acid (1.700 g, 1.2 equiv) and diisopropyltriethylamine (DIPEA, 1 mL, 2.0 equiv) were dissolved in 70 mL of CH_2Cl_2, and the mixture was stirred for 15 min to activate the acid. Then, methyl *L*-alaninate (1.151 g, 1.0 equiv) was added, and the reaction mixture was stirred overnight. The organic layer was washed with HCl 1M, saturated solution of $NaHCO_3$ and brine. The combined organic layers were dried over anhyd Na_2SO_4, filtered and the solvent was evaporated at reduced pressure. The crude product was chromatographed on silica gel (70-230 mesh) with hexane/ethyl acetate (7/3) as eluent and 2.112 g (82%) of M**4** were obtained.

Spectroscopic data:

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.49 (d, 3H), 3.25 (s, 1H), 3.74 (s, 3H), 4.75 (q, 1H), 7.29 (d, 1H), 7.48 (d, 2H), 7.76 (d, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 18.0, 48.5, 52.4, 79.7, 82.7, 125.4, 127.1, 132.0, 133.6, 166.2, 173.5.

$[\alpha]_D$= +81 (15 mg mL^{-1}, $CHCl_3$)

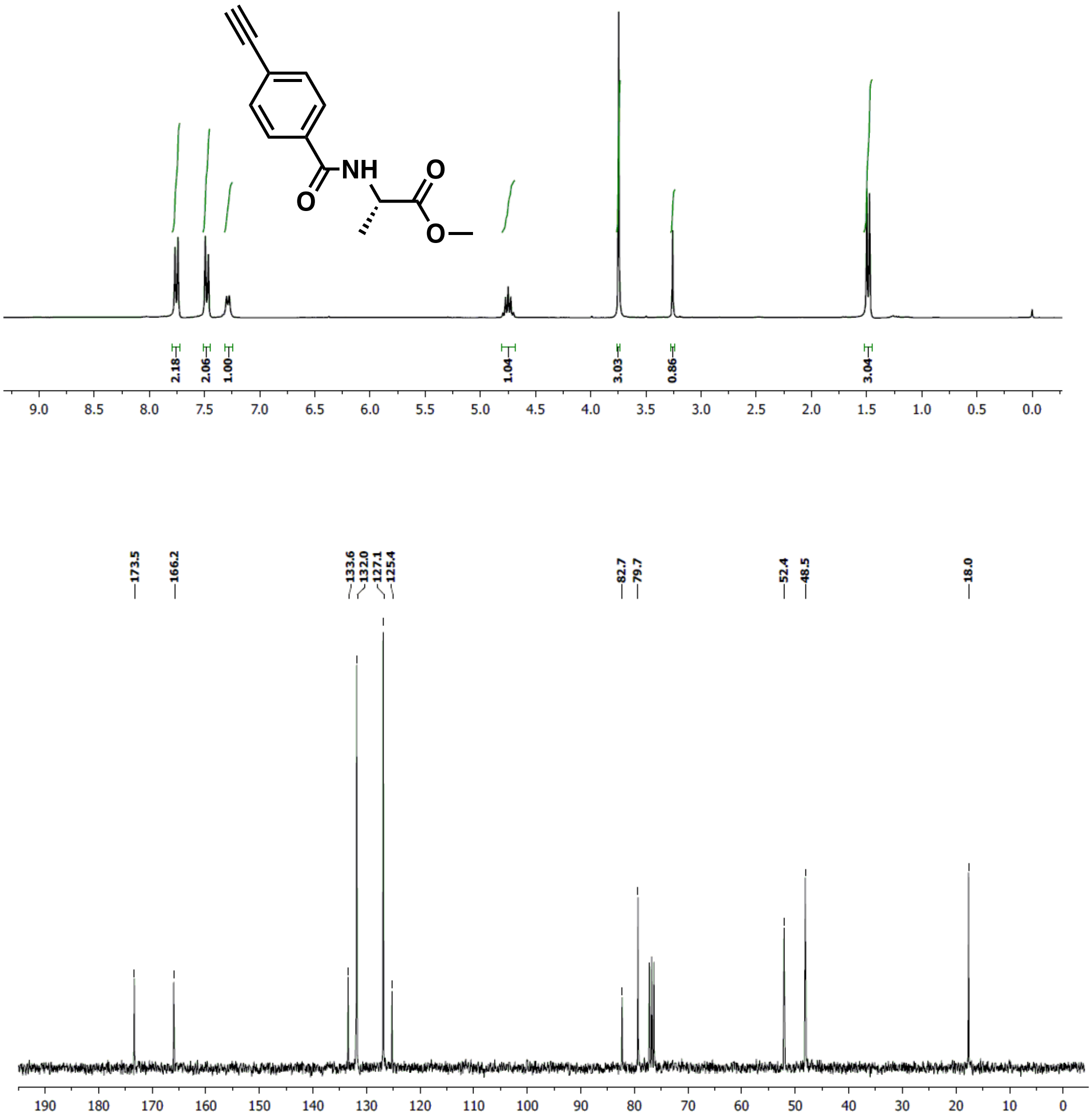


Figure S3: ^{1}H- and ^{13}C-NMR spectra of M**4**.

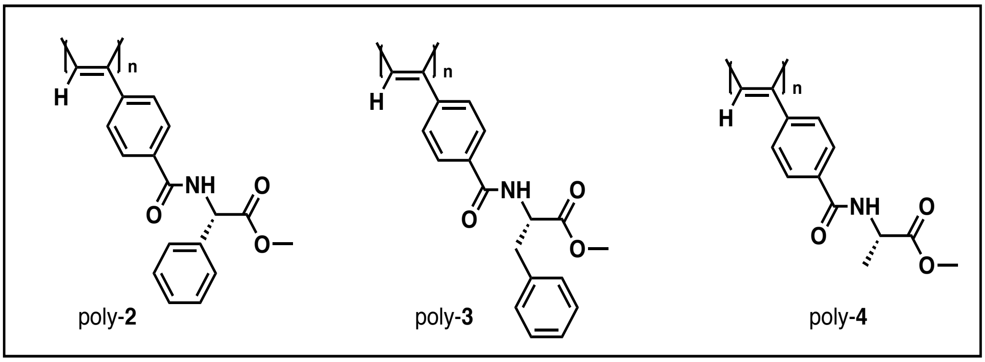
2 Synthesis of polymers

The polymers were synthesized in a reaction flask (sealed ampoule) that was dried under vacuum and argon flushed for three times before the monomers were added as a solid. Then, the flask was evacuated on a vacuum line and flushed with dry argon (three times). Dry THF was added with a syringe. A solution of rhodium norbornadiene chloride dimer, $[Rh(nbd)Cl]_2$, in THF was added at 30ºC. The concentrations of monomer and rhodium catalyst were 0.500 M and 0.005 M respectively. The reaction mixture was stirred at 30ºC for 4 hours. Next, the resulting polymers were diluted in CH_2Cl_2 and precipitated in a large amount of methanol, centrifuged (twice) and re-precipitated in hexane and centrifuged again.

The response of poly-(*S*)-**2** to the external stimuli such as solvents, metals and temperature have already been published.[1]

Monomer	**Mass(mg)**	**THF(μL)**	**Et_3N (μL)**	**Catalyst(mg)**	**Yield (%)**
Poly-(*S*)-**2**	100	1000	5	2	92
Poly-(*S*)-**3**	100	1000	5	2	93
Poly-(*S*)-**4**	100	1000	5	2	85

The *cis* stereoregularity of the polymers was determined by ^{1}H NMR spectroscopy (Figure S4a, c, e) where the vinyl proton resonates at 5.8 ppm, and by Raman resonances (Figure S4b, d, f). The peak at 1610-1570 cm^{-1} is assigned to C=C bond stretching in the *cis* poly(acetylene) and overlaps with that of the phenyl ring. The peak at 1350-1340 cm^{-1} is assigned to the *cis* C-C bond coupled with the single bond connecting the main chain and the phenyl ring. The peak at 1010-960 cm^{-1} is assigned to the C-H bond deformation of the *cis* form (Figure S4).


poly-**2** poly-**3** poly-**4**

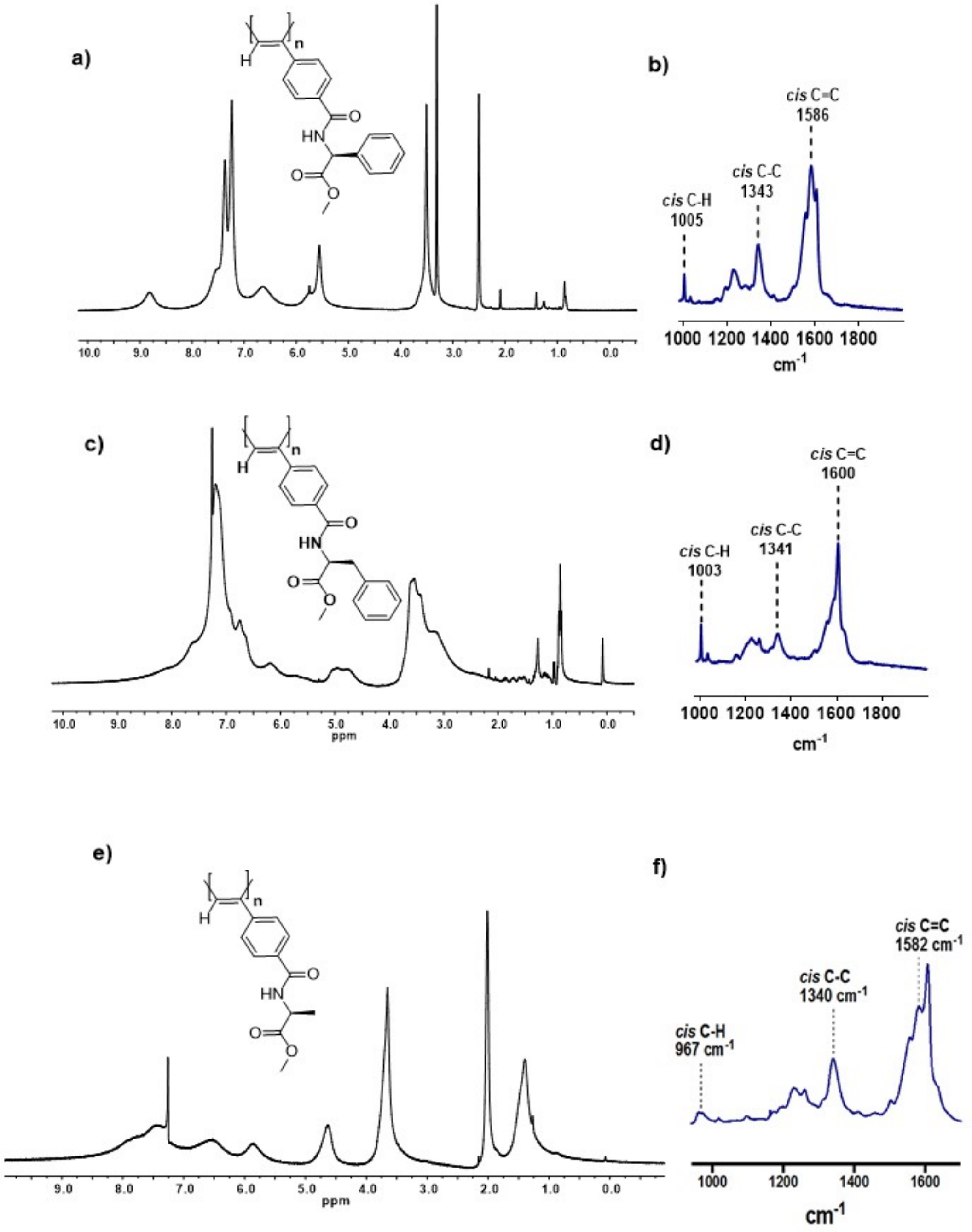


Figure S4: ^{1}H NMR and Raman spectra of: a-b) poly-**2**, c-d) poly-**3**, e-f) poly-**4**.

2.1 GPC studies

GPC data were obtained in a HPLC Alliance 2695 with a UV-2489 detector (Waters). The samples were eluted using three Phenogel columns connected to each other with stationary phases of 10^3, 10^4 and 10^5 Armstrong and packed with a solid support of a cross-linked styrene and *p*-divinylbenzene copolymer. For GPC data of the polymers in this manuscript, see Table S1.

Table S1: GPC data of poly-(*S*)-**2**, poly-(*S*)-**3**, poly-(*S*)-**4**.

Polymer	Mn	Mw	Mp	Mz	PDI
poly-(*S*)-**2**	16000	33000	37000	67000	2.1
poly-(*S*)-**3**	22000	120000	170000	340000	5.5
Poly-(*S*)-**4**	21000	54000	84000	110000	2.6

2.2 Thermal Studies. DSC

DSC measurements were performed in a DSC Q200 Tzero Technology. (TA Instruments, New Castle, UK) equipped with a refrigerated cooling system RCS90 TA Instruments.

DSC experiments were carried out for 3.0 mg of poly-(*S)*-**2**, poly-(*S)*-**3** and poly-(*S)*-**4** in all complexes with $LiClO_4$ and with different amounts of MeOH. The DSC traces of the polymer complexes were measured at a heating rate of 10.0 ºC min^{-1} and a temperature range from 0 to 340.0 ºC. The DSC traces of poly-(*S)*-**2**, poly-(*S)*-**3** and poly-(*S*)-**4** complexes show two exothermic thermal isomerizations from *cis-transoid* to *cis-cisoid* and from *cis-cisoid* to *trans-transoid*. They were observed around 100.0 ºC and 245.0 respectively (Figures S5, S6 and S7).[2]

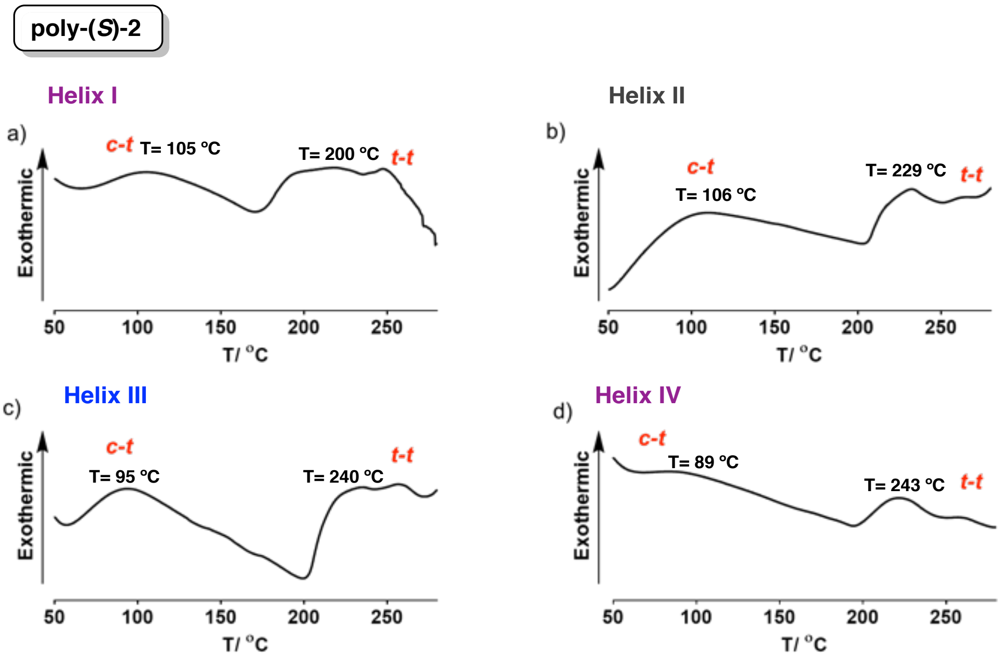


Figure S5: DSC thermograms of a) poly-(*S*)-**2**-helix I**,** b) poly-(*S*)-**2**-helix II, c) poly-(*S*)-**2**-helix III and d) poly-(*S*)-**2**-helix IV.

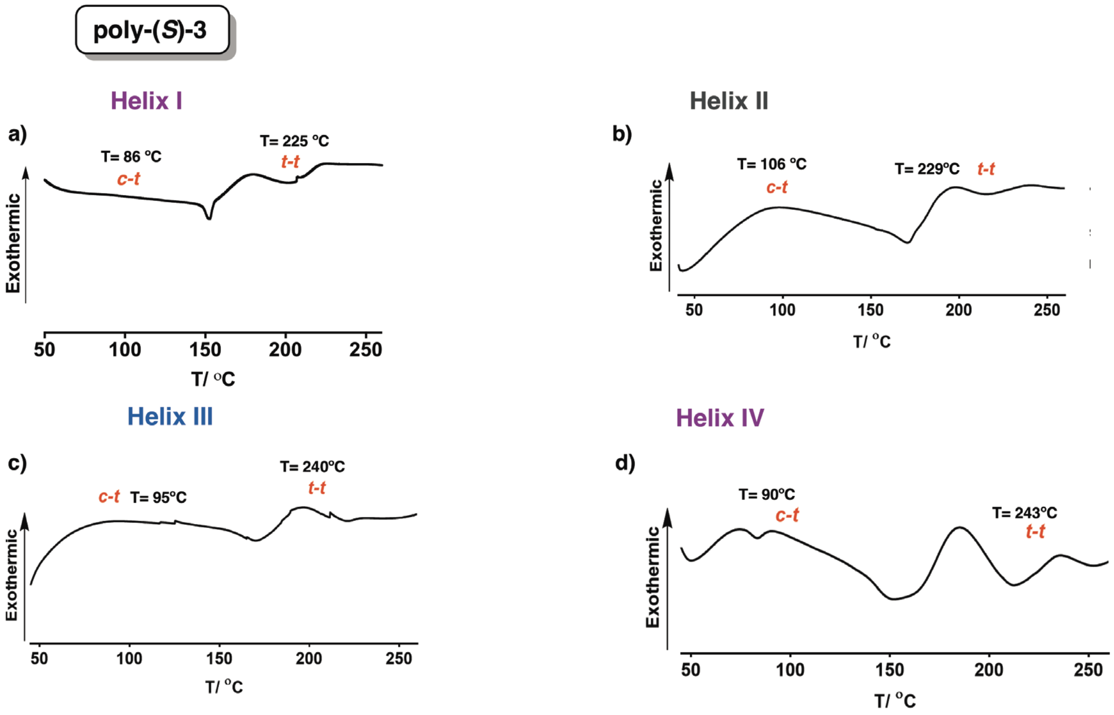


Figure S6: DSC thermograms of a) poly-(*S*)-**3**-helix I**,** b) poly-(*S*)-**3**-helix II, c) poly-(*S*)-**3**-helix III and d) poly-(*S*)-**3**-helix IV.

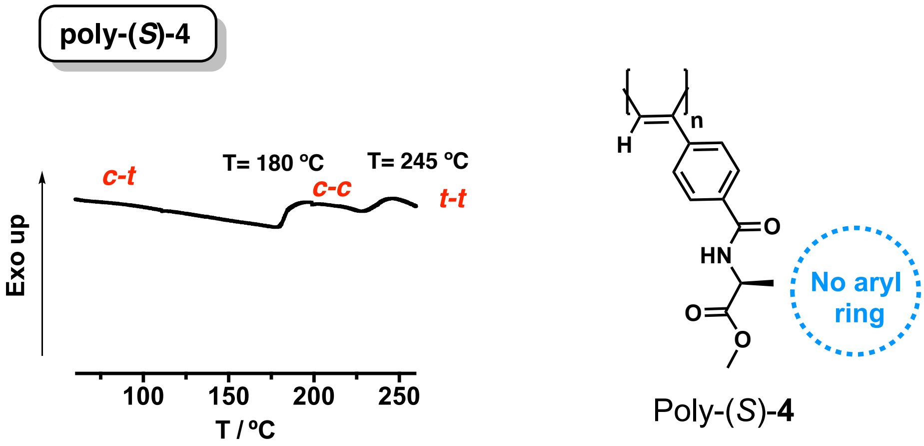


Figure S7: DSC thermograms of poly-(*S*)-**4**.

3 Helical polymer metal complexes of poly-(*S*)-2

Three different structures were obtained during these studies depending on the amount of the cosolvent. Thus, titrations of poly-(*S*)-**2** with $LiClO_4$ solutions (different concentrations and cosolvents) were performed.

3.1 Helical inversion (Helix II-Complex I)

- **CD/UV studies and ^{7}Li NMR**

CD and UV studies were carried out during a titration of a solution of poly-(*S*)-**2** in $CHCl_3$ (0.3 mg/mL) with $LiClO_4$ (10 mg/mL) in MeOH (polar donor cosolvent). These experiments aim to observe the effect of MeOH as cosolvent and to determine the response of the polymer to the cation-π interaction.

The poly-(*S*)-**2** in $CHCl_3$ shows a negative Cotton effect at the vinylic region and adopts the *sp1* conformation. After addition of $LiClO_4$ (10.0 mg/mL) in MeOH to the polymer solution, a helical inversion happens and a positive Cotton effect is obtained at the vinylic region. These results indicate that the coordination of Li^+ to the pendant group through carbonyl groups and methoxy group results in the adoption of a *sp2* conformation.

This inversion happened when poly-(*S*)-**2** (mru)/Li^+/MeOH ratio= 1/0.5/≤133 (mol/mol/mol) due to the chelation of the metal to the carbonyl groups (amide and ester) together with the presence of a cation-π interaction (Figure S8).

In order to know which factor determines the different coordination modes of Li^+ ions, a deeper conformational study was performed additionally to the IR and CD studies.

So, ^7Li-NMR experiments were carried out in a Varian Inova 500 spectrometer (11.74 T) using LiCl in D_2O (9.7 M) as internal reference.[3,4] To determine the conformation at the pendant moiety, a solution of poly-(*S*)-**2** was titrated with solutions of $LiClO_4$ in CD_3OD.

^7Li-NMR spectrum of a solution of poly-(*S*)-**2** in $CDCl_3$ (2.0 mg/mL) with $LiClO_4$ in CD_3OD (20.0 mg/mL) shows a strong shielding in the ^7Li chemical shift, which is typical when the metal ion is involved in a cation-π interaction (Figure S8).

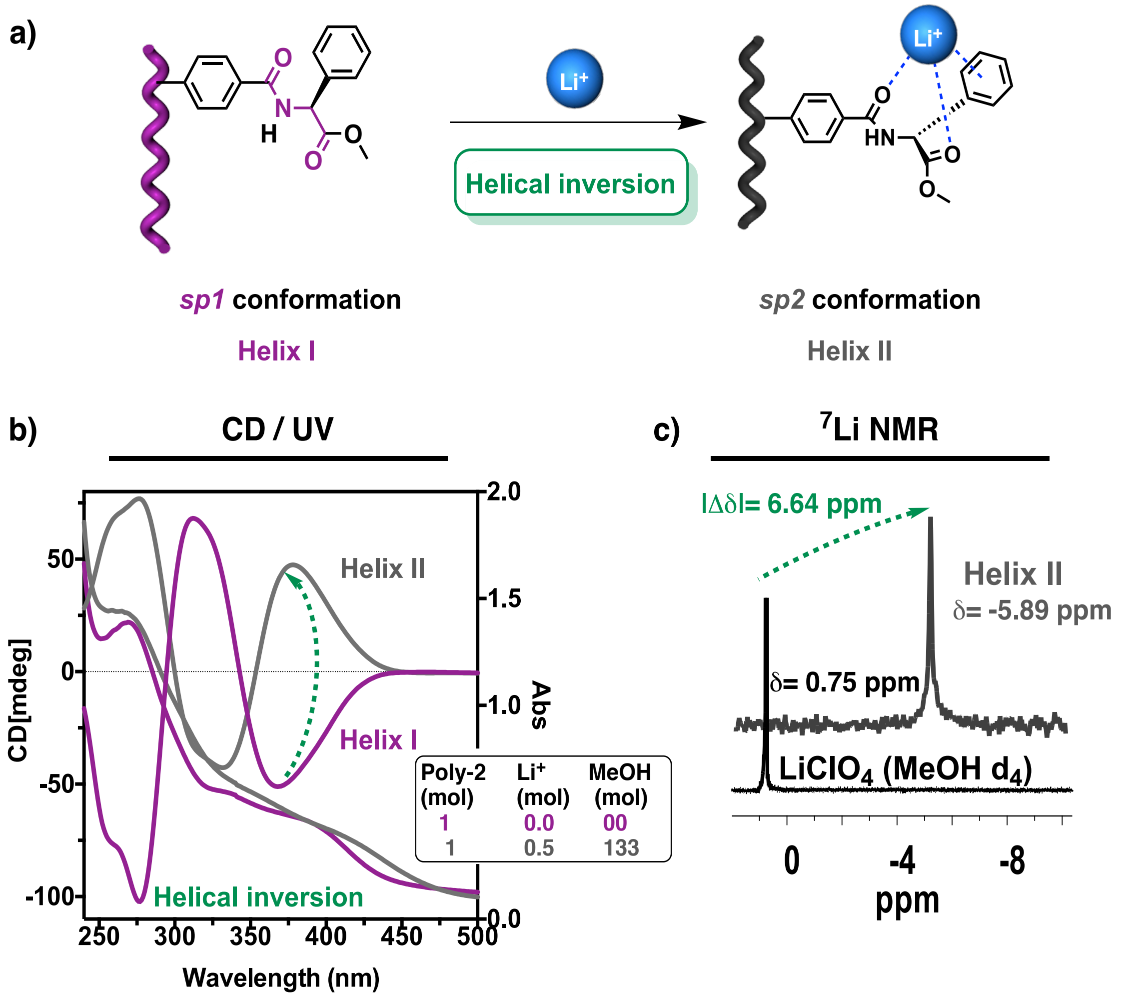


Figure S8: a) Helix inversion of poly-(*S*)-**2** from left handed –*sp1* conformation– to right handed –*sp2* conformation– after addition of Li^+, and stabilization by cation-π interactions, b) CD and UV spectra of solutions of poly-(*S*)-**2** in $CHCl_3$ (0.3 mg/mL) before and after titration with a solution of $LiClO_4$ (10.0 mg/mL) in MeOH, in a poly-(*S*)-**2** (mru)/Li^+/MeOH ratio = 1/0.5/≤133 (mol/mol/mol), and c) ^7Li NMR spectra of poly-(*S*)-**2** before and after addition of $LiClO_4$ showing the shifts due to cation-π interactions, [poly-(*S*)-**2**]= 2.0 mg/mL in $CDCl_3$, [$LiClO_4$]= 20.0 mg/mL in CD_3OD.

- **ATR/FT-IR studies**

ATR/FT-IR spectra were recorded in a BRUKER IFS-66v spectrophotometer.

A solution of $LiClO_4$ (50.0 mg/mL) in CH_3OH was added to a solution of poly-(*S*)-**2** in $CHCl_3$ (2.0 mg/mL). The mixture was allowed to react —for 5 minutes without stirring— after the addition of the Li^+ ions with a poly-(*S*)-**2** mru/Li^+/

MeOH ratio= 1/ 0.5/ ≤133 (mol/mol/mol). Both carbonyl groups, amide and ester, increase their degree of association and a helix inversion was observed by CD (Figure S9 and Table S2).

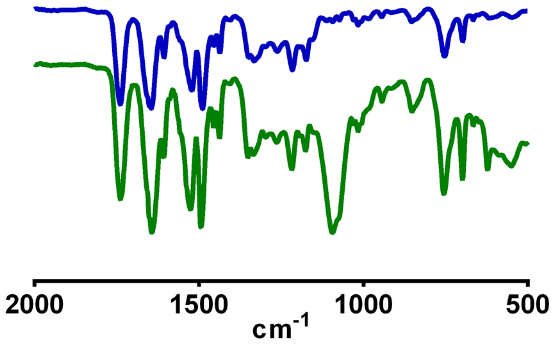


Figure S9: IR spectra of a solution of poly-(*S*)-**2** in $CHCl_3$ (2.0 mg/mL, blue) and a solution of poly-(*S*)-**2** titrated with $LiClO_4$ (50.0 mg/mL) in MeOH with a poly-(*S*)-**2** (mru)/Li^+/MeOH ratio = 1/ 0.5/ ≤130 (mol/mol/mol), green.

Table S2: FT-IR data of poly(*S*)-**2** in solution.

Polymer	υCO_{amide} (cm^{-1})	υCO_{ester} (cm^{-1})	υOMe (cm^{-1})	$\Delta\upsilon CO_{amide}$ (cm^{-1})	$\Delta\upsilon CO_{ester}$ (cm^{-1})	$\Delta\upsilon OMe$ (cm^{-1})
Poly-(*S*)-**2**($CHCl_3$)	1646	1740	1092	0	0	0
Poly-(*S*)-**2** /Li^+/MeOH 1/0.5/≤130 (mol/mol/mol)	1641	1737	1092	+5	+3	0

3.2 Helical inversion and compression (Helix III-Complex II)

- **CD/UV studies and ^7Li NMR**

During the titration of the polymer with $LiClO_4$ solution, an unexpected helical structure was observed when the amount of the cosolvent was increased with a poly(S)-**2**(mru)/MeOH ratio= 1.0/ 278-326 (mol/mol). The left-handed helical structure was recovered, but in this case the helix obtained was very compressed with *ap* conformations at the pendants (Figure S10).[5]

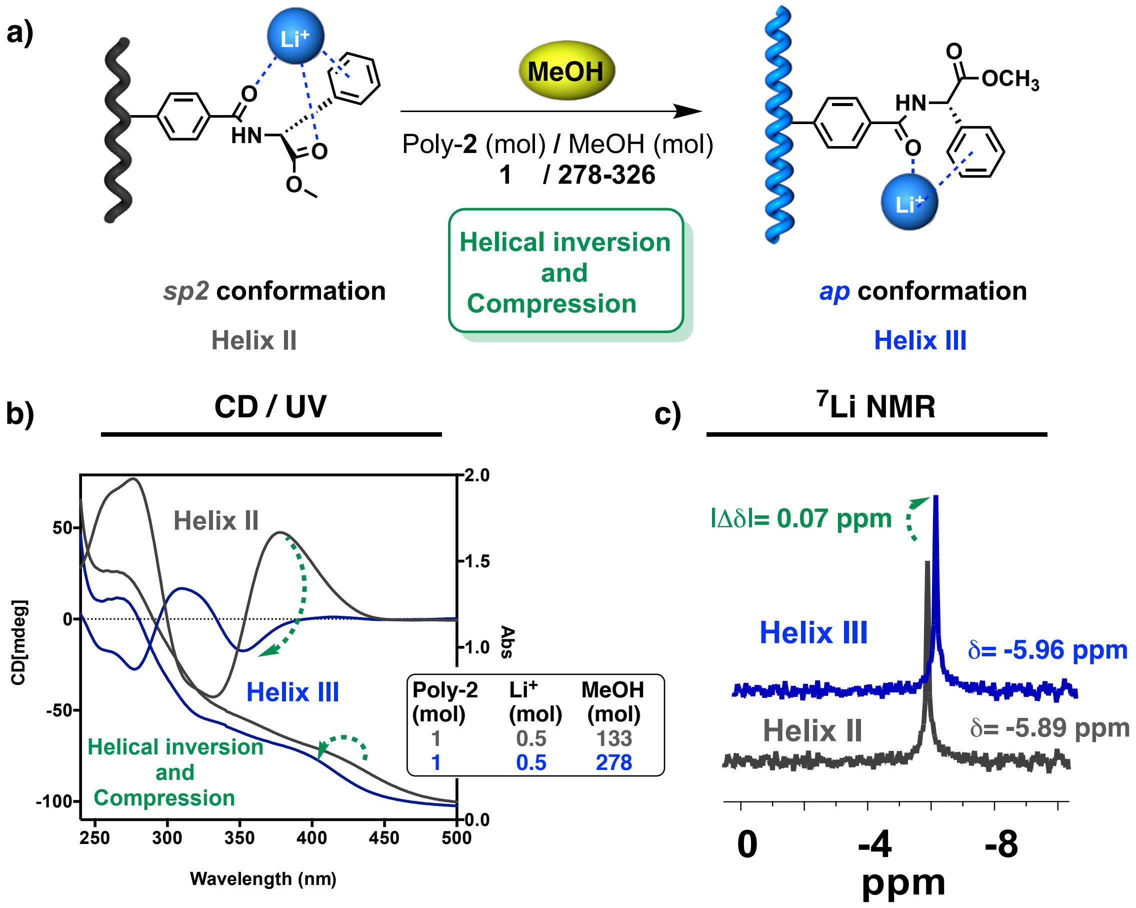


Figure S10: a) Helix inversion in the poly-(*S*)-**2**/Li$^+$ complex –*sp2* conformation– from helix II to helix III –*ap* conformation–. It was obtained after addition of a specific amount of MeOH in a poly-(S)-**2**(mru)/MeOH ratio= 1.0/ 278-326 (mol/mol), b) CD and UV spectra of helix II in a poly-(*S*)-**2**(mru)/Li$^+$/MeOH ratio= 1/0.5/≤133 (mol/mol/mol). After addition of a specific amount of MeOH, poly-(*S*)-**2**(mru)/Li$^+$/MeOH ratio= 1/0.5/278 (mol/mol/mol), helix III was obtained, and c) ^{7}Li NMR spectra showing a small shifting after addition of CD_3OD to helix II. The peak of helix III appeared at 5.96 ppm, [poly-(*S*)-**2**]= 2.0 mg/mL in $CDCl_3$ and [$LiClO_4$] = 20.0 mg/mL in CD_3OD.

ATR/ FT-IR studies

A solution of $LiClO_4$ (50.0 mg/mL) in CH_3OH was added to a solution of poly-(*S*)-**2** in $CHCl_3$ (2.0 mg/mL). The mixture was allowed to react for 5 minutes without stirring. FT-IR experiments show that, after that a specific amount of MeOH was added in a poly-(*S*)-**2**(mru)/Li^+/MeOH ratio= 1.0/ 0.5/278 (mol/mol/mol), only the amide group increases its degree of association due to the chelation with Li^+ ions. The interaction with the ester group was disrupted (Figure S11 and Table S3).

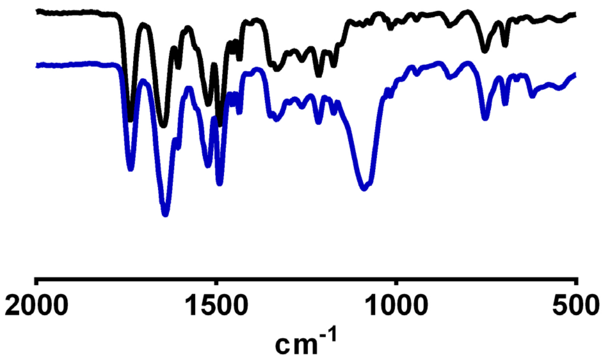


Figure S11: IR spectra of a solution of poly-(*S*)-**2** in $CHCl_3$ (2.0 mg/mL, black) and a solution of poly-(*S*)-**2** titrated with $LiClO_4$ (50.0 mg/mL) in MeOH with a poly-(*S*)-**2** (mru)/Li^+/MeOH ratio = 1.0/0.5/278 (mol/mol/mol), blue.

Table S3: FT-IR data of poly(*S*)-**2** in solution.

Polymer	υCO_{amide} cm^{-1}	υCO_{ester} cm^{-1}	υOMe cm^{-1}	$\Delta\upsilon CO_{amide}$ cm^{-1}	$\Delta\upsilon CO_{ester}$ cm^{-1}	$\Delta\upsilon OMe$ cm^{-1}
Poly-(*S*)-**2**($CHCl_3$)	1646	1740	1092	0	0	0
Poly-(*S*)-**2** /Li^+/MeOH 1 / 0.5 / 278.0 (mol/mol/mol)	1643	1740	1092	+3	0	0

3.3 Helical stretching (Helix IV-Complex III)

- <u>**CD/UV studies and ^{7}Li NMR**</u>

Finally, the addition of a larger amount of MeOH to helix III –*ap* conformation– with a poly-(*S*)-**2**/Li$^+$/MeOH ratio=1.0/0.5/>380 (mol/mol/mol) produces a structural elongation (helix IV) and recovers the starting helical conformation. The Li$^+$ ion is still coordinated to the ester group at the pendant moiety (Figure S12).

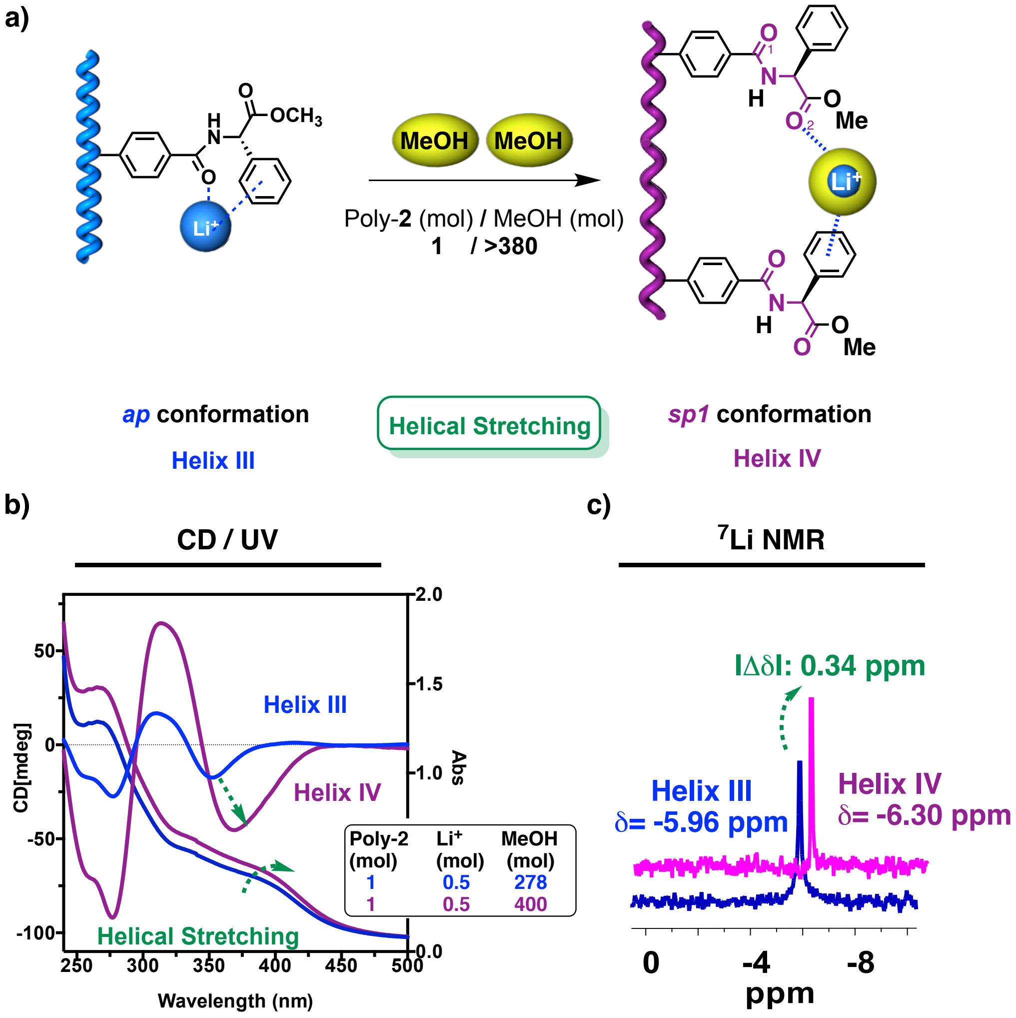


Figure S12: a) Recovery of helicity after adding —to poly-(*S*)-**2**/Li$^+$, *ap* conformation, helix III— a large amount of MeOH up to a poly-(*S*)-**2**(mru)/Li$^+$/MeOH ratio= 1/>380 (mol/mol/mol). Helix IV —*sp1* conformation— was obtained. b) CD/UV spectra of solutions of helix III after addition of a large amount of MeOH. Helix IV was obtained in a poly-(*S*)-**2**(mru)/Li$^+$/MeOH ratio=

1.0/0.5/400 (mol/mol/mol). c) ^{7}Li-NMR spectra for helix III and helix IV showing a small shifting because the cation-π interaction is still present, despite the addition of a large amount of MeOH, [poly-(*S*)-**2**] = 2.0 mg/mL in $CDCl_3$, [$LiClO_4$]= 20.0 mg /mL in CD_3OD.

- **ATR/ FT-IR studies**

A solution of $LiClO_4$ (50.0 mg/mL) in CH_3OH was added to a solution of poly-(*S*)-**2** in $CHCl_3$ (2.0 mg/mL). The mixture was allowed to react for 5 minutes without stirring. FT-IR experiments show that, after the addition of $LiClO_4$ and a large amount of MeOH with a poly-(*S*)-**2**(mru)/Li$^+$/MeOH ratio=1/0.5/>380 (mol/mol/mol), only the ester group increases its degree of association (Figure S13 and Table S4).

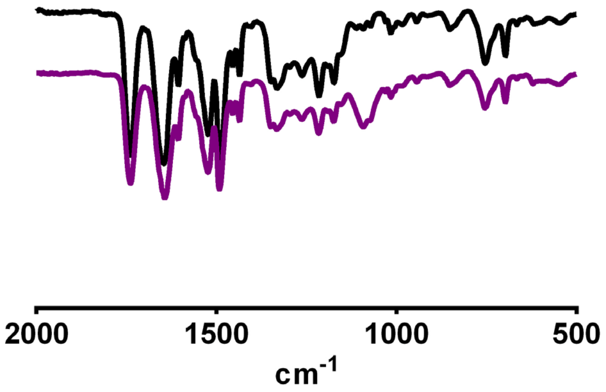


Figure S13: IR spectra of a solution of poly-(*S*)-**2** in $CHCl_3$ (2.0 mg/mL, black) and a solution of poly-(*S*)-**2** titrated with $LiClO_4$ (50.0 mg/mL) in MeOH with a poly-(*S*)-**2**(mru)/Li$^+$/MeOH mole ratio= 1/0.5/400 (mol/mol/mol), pink.

Table S4: FT-IR data of poly(*S*)-**2** in solution.

Polymer	υCO_{amide} cm^{-1}	υCO_{ester} cm^{-1}	υOMe cm^{-1}	$\Delta\upsilon CO_{amide}$ cm^{-1}	$\Delta\upsilon CO_{ester}$ cm^{-1}	$\Delta\upsilon OMe$ cm^{-1}
Poly-(*S*)-**2**($CHCl_3$)	1646	1740	1092	0	0	0
Poly-(*S*)-**2** /Li^+/MeOH 1 / 0.5 / 400.0 (mol/mol/mol)	1646	1738	1089	0	2	0

4 Helical polymer metal complexes of poly-(*S*)-3

Similar studies were carried out for poly-(*S*)-**3.** The results are analogous to those obtained with poly-(*S*)-**2**, due to the structural similarity between both polymers.

4.1 Helical inversion (Helix II-Complex I)

- **CD/UV studies and ^{7}Li NMR**

CD and UV studies were carried out during a titration of a solution of poly-(*S*)-**3** in $CHCl_3$ (0.3 mg/mL) with 10.0 mg/mL of $LiClO_4$ in MeOH. These experiments were aimed to determine the response of poly-(*S*)-**3** to cation−π interactions, and to study the effect of MeOH as a cosolvent.

Poly-(*S*)-**3** in $CHCl_3$ shows a negative Cotton effect at the vinylic region and adopts the *sp1* conformation. The addition of $LiClO_4$ (10.0 mg/mL) in MeOH to the polymer solution inverts the helicity and shows a positive Cotton effect. That outcome indicates that the coordination of Li$^+$ to the pendant group through amide and ester carbonyl groups favours the *sp2* conformation.

This inversion happened when the poly-(*S*)-**3** (mru)/Li$^+$/MeOH ratio= 1/0.5/≤130 (mol/mol/mol), due to the chelation of the metal to the carbonyl groups (amide and ester) and the presence of a cation-π interaction (Figure S14).

^{7}Li-NMR experiments were carried out in a Varian Inova 500 spectrometer (11.74 T) using LiCl in D$_2$O (9.7 M) as reference. To determine the conformation at the pendant moiety, a solution of poly-(*S*)-**3** was titrated with solutions of LiClO$_4$ in CD$_3$OD.

^{7}Li-NMR spectrum of a solution of poly-(*S*)-**3** (2.0 mg/mL) in CDCl$_3$ with LiClO$_4$ (20.0 mg/mL) in CD$_3$OD shows a strong shielding in the ^{7}Li chemical shift, which is typical when the metal ion is involved in a cation-π interaction (Figure S14).

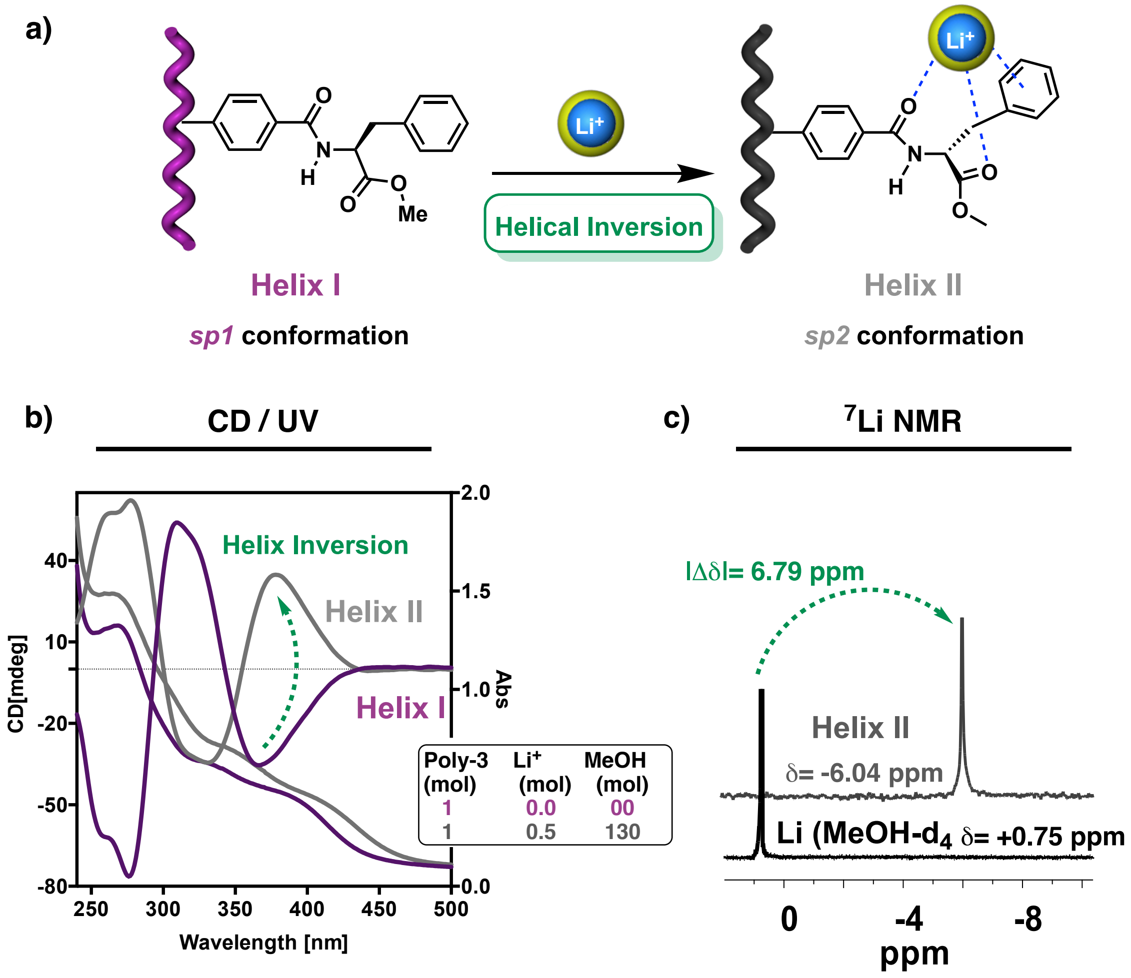


Figure S14: a) Helix inversion of poly-(*S*)-**3** from left handed –*sp1* conformation– to right handed –*sp2* conformation– after addition of Li^+, and stabilization by cation-π interactions, b) CD and UV spectra of solutions of poly-(*S*)-**3** in $CHCl_3$ (0.3 mg/mL) before and after titration with a solution of $LiClO_4$ (10.0 mg/mL) in MeOH, in a poly-(*S*)-**3**(mru)/Li^+/MeOH ratio= 1/0.5/≤130 (mol/mol/mol), and c) ^{7}Li NMR spectra of poly-(*S*)-**3** before and after addition of $LiClO_4$ showing a strong shielding in the chemical shift due to cation-π interactions, [poly-(*S*)-**3**] = 2.0 mg/mL in $CDCl_3$, [$LiClO_4$] = 20.0 mg/mL in CD_3OD.

- **ATR/ FT-IR studies**

$LiClO_4$ (50.0 mg/mL) in MeOH was added to a solution of poly-(*S*)-**3** in $CHCl_3$ (2.0 mg/mL). The mixture was allowed to react for 5 minutes without stirring. After the addition of Li^+ ions in a poly-(*S*)-**3**/Li^+/MeOH ratio= 1/0.5/130 (mol/mol/mol), the amide and ester carbonyl groups increased their degree of association and a helix inversion was observed by CD (Table S5).

Table S5: FT-IR data of poly(*S*)-**3** in solution.

Polymer	υCO_{amide} cm^{-1}	υCO_{ester} cm^{-1}	υOMe cm^{-1}	$\Delta\upsilon CO_{amide}$ cm^{-1}	$\Delta\upsilon CO_{ester}$ cm^{-1}	$\Delta\upsilon OMe$ cm^{-1}
Poly-(*S*)-**3**($CHCl_3$)	1646	1739	1095	0	0	0
Poly-(*S*)-**3** /Li^+/MeOH 1.0 / 0.5 / 130.0	1638	1735	1095	8	4	0

4.2 Helical inversion and compression (Helix III-Complex II)

- **CD/UV studies and ^{7}Li NMR**

During the titration of poly-

(S)-**3** with a solution of LiClO$_4$ in MeOH, an unexpected helical structure was observed when the amount of the cosolvent was increased in the solution up to poly(S)-**3**(mru)/MeOH ratio= 1.0/226-277 (mol/mol). The left-handed helical structure was recovered, but in this case, the helix obtained (helix III) was very compressed with *ap* conformation (Figure S15).

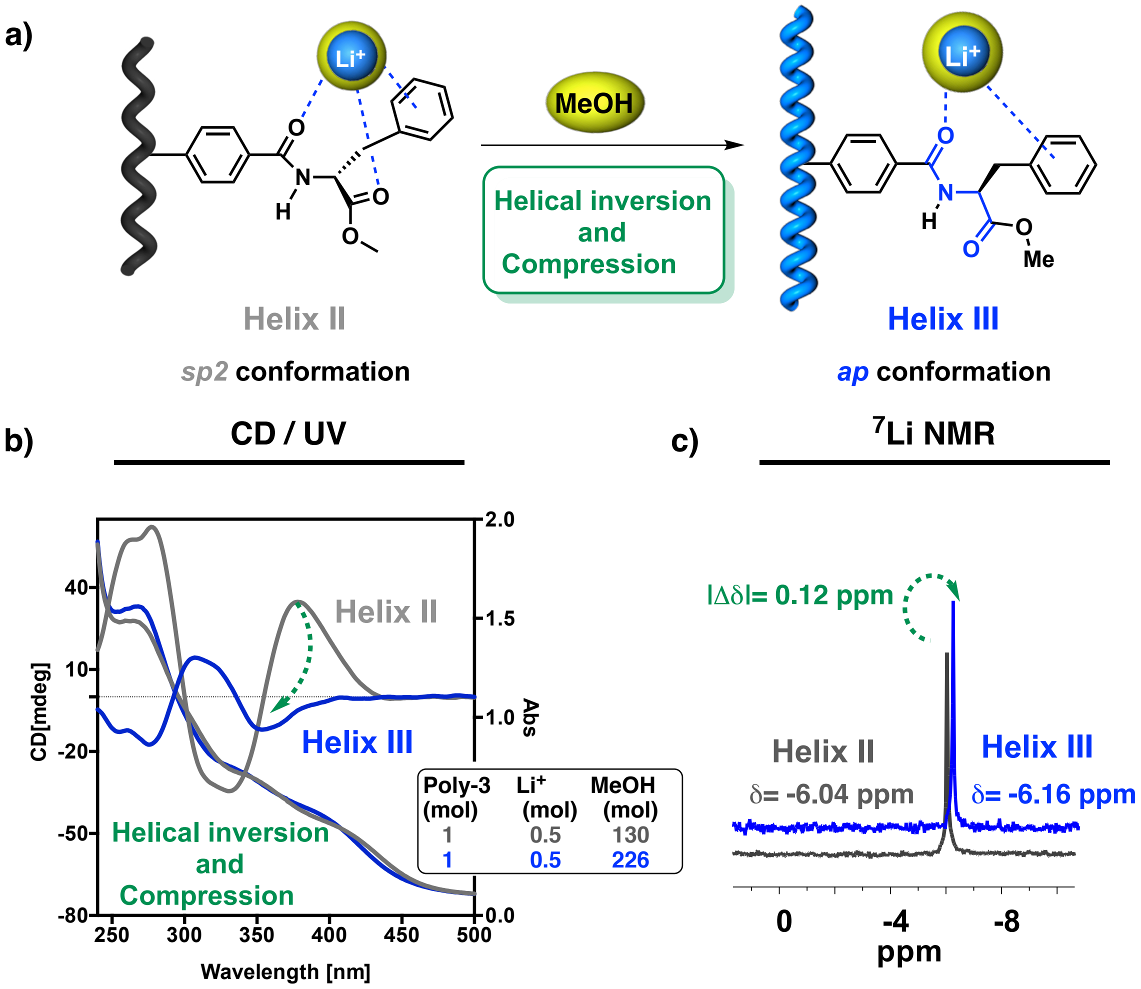


Figure S15: a) Helix inversion in a poly-(*S*)-**3**/Li$^+$ complex from helix II to helix III. The inversion took place after addition of a specific amount of MeOH in a poly-(S)-**3**(mru)/MeOH ratio= 1.0/226-277 (mol/mol), b) CD and UV spectra of helix II in a poly-(*S*)-**3**(mru)/Li^+/MeOH ratio= 1/0.5/≤130 (mol/mol/mol). After addition of a specific amount of MeOH up to poly-(*S*)-**3**(mru)/Li^+/MeOH ratio= 1/0.5/226 (mol/mol/mol), helix III was obtained, and c) ^{7}Li NMR spectra showing a small shifting after addition of CD_3OD to helix II. The peak of helix III appeared at 6.16 ppm, [poly-(*S*)-**3**]= 2.0 mg/mL in $CDCl_3$ and [$LiClO_4$]= 20.0 mg/mL in CD_3OD.

The data of ^{7}Li NMR confirmed that the cation-π is still present in the solution according to the chemical shift of ^{7}Li.

- **ATR/ FT-IR studies**

A solution of $LiClO_4$ (50.0 mg/mL) in CH_3OH was added to a solution of poly-(*S*)-**3** in $CHCl_3$ (2.0 mg/mL). The mixture was allowed to react for 5 minutes without stirring after addition of a specific amount of MeOH, with a poly-(*S*)-**3**(mru)/Li^+/MeOH ratio= 1.0/0.5/226 (mol/mol/mol). Only the amide group increases its degree of association. Li^+ coordinates to the amide group and the interaction with the ester group is disrupted (Table S6).

Table S6: FT-IR data of poly(*S*)-**3** in solution.

Polymer	υCO_{amide} cm^{-1}	υCO_{ester} cm^{-1}	υOMe cm^{-1}	$\Delta\upsilon CO_{amide}$ cm^{-1}	$\Delta\upsilon CO_{ester}$ cm^{-1}	$\Delta\upsilon OMe$ cm^{-1}
Poly-(*S*)-**3**($CHCl_3$)	1646	1739	1095	0	0	0
Poly-(*S*)-**3** /Li^+/MeOH 1/0.5/226.0 mol/mol/mol	1644	1739	1095	2	3	1

4.3 Helical stretching (Helix IV-Complex III)

- **CD/UV studies and ^{7}Li NMR**

Finally, the addition of a large amount of cosolvent (MeOH) to the solution of poly-(*S*)-**3**(mru)/Li$^+$/MeOH up to a 1.0/0.5/≥330.0 (mol/mol/mol) ratio, caused an elongation in the helical structure. Helix IV was obtained, and the initial CD signature was recovered. However, the metal ion is still coordinated to the ester group in the pendant moiety between two neighbouring pendants (Figure S16).

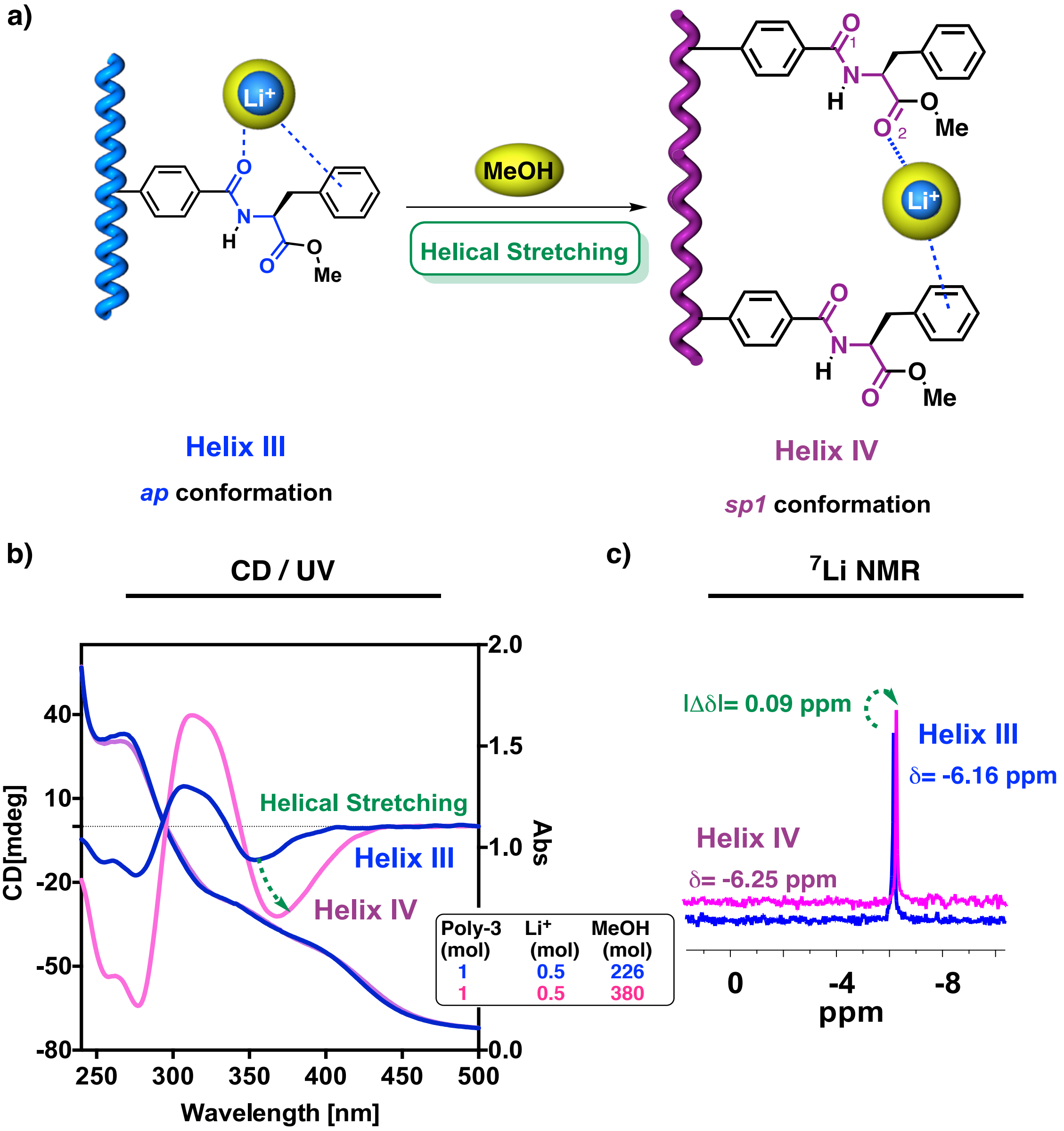


Figure S16: a) Recovery of helicity after adding —to poly-(*S*)-**3**/Li$^+$, *ap* conformation, helix III— a large amount of MeOH up to a poly-(*S*)-**3**(mru)/Li$^+$ /MeOH ratio= 1.0/0.5/≥330 (mol/mol/mol). Helix IV –*sp1* conformation– was obtained. b) CD/UV spectra of solutions of helix III after addition of a large amount of MeOH. Helix IV was obtained in a poly-(*S*)-**3**(mru)/Li$^+$/MeOH ratio = 1.0/0.5/380 (mol/mol/mol). c) ^{7}Li-NMR spectra for helix III and helix IV showing a small shifting because the cation-π interaction is still present, despite the addition of a large amount of MeOH, [poly-(*S)*-**3**]= 2.0 mg/mL in $CDCl_3$, [$LiClO_4$]= 20.0 mg/mL in CD_3OD.

- **ATR/ FT-IR studies**

A solution of $LiClO_4$ (50.0 mg/mL) in MeOH was added to a solution of poly-(*S*)-**3** in $CHCl_3$ (2.0 mg/mL). The mixture was allowed to react for 5 minutes without stirring. FT-IR experiments show that, after addition of $LiClO_4$ and a large amount of MeOH up to a poly-(*S*)-**3**(mru)/Li$^+$/MeOH ratio= 1/0.5/>330 (mol/mol/mol), only the ester group increases its degree of association (Table S7).

Table S7: FT-IR data of poly(*S*)-**3** in solution.

Polymer	υCO_{amide} cm^{-1}	υCO_{ester} cm^{-1}	υOMe cm^{-1}	$\Delta\upsilon CO_{amide}$ cm^{-1}	$\Delta\upsilon CO_{ester}$ cm^{-1}	$\Delta\upsilon OMe$ cm^{-1}
Poly-(*S*)-**3**($CHCl_3$)	1646	1739	1095	0	0	0
Poly-(*S*)-**3** /Li$^+$/MeOH 1 / 0.5 / 380 (mol/mol/mol)	1646	1736	1095	0	+3	0

5 Helical polymer metal complexes of poly-(*S*)-4

In order to demonstrate that the four states are obtained from poly-(*S*)-(**2** or **3**) by the combination of dynamic coordination chemistry and cation-π interactions, analogous studies were performed using a different and appropriate PPA. In this case, we choose 4-ethynylbenzamide L-alanine methyl ester M**4** as monomer because the pendant group in poly-(*S*)-**4**, although structurally close to those found in poly-(*S*)-(**2** or **3**), lacks their aryl groups (i.e., Ph, Bn), that have been replaced by a methyl group (Figure 17).

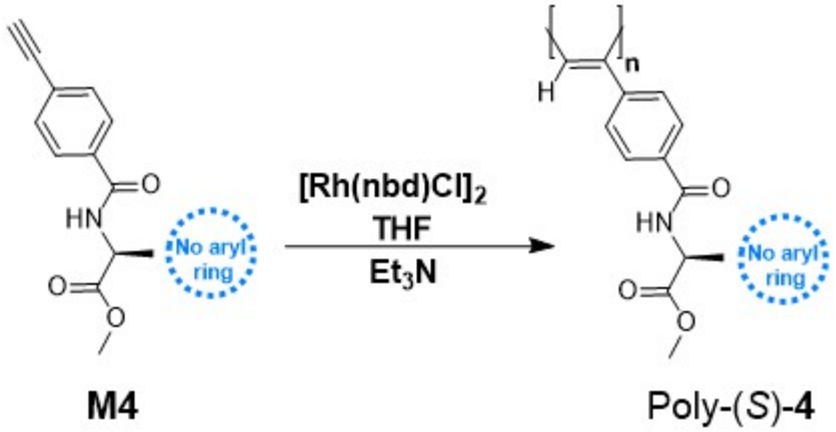


Figure S17: Structures of M**4** and poly-(*S*)-**4**.

5.1 Helical Inversion (Helix II-Complex I)

- **CD and ^{7}Li NMR studies**

Analogous experiments were performed for poly-(*S*)-**4** to confirm the absence of cation-π interaction. CD studies were carried out by titration of poly-(*S*)-**4** with $LiClO_4$ in MeOH. Only two helical structures were detected during this study.

^{7}Li-NMR experiments were performed in a Varian Inova 500 spectrometer (11.74 T) using as reference LiCl in D2O (9.7M).

The CD studies of poly-(*S*)-**4** in $CHCl_3$ (0.3 mg/mL) show a negative Cotton effect at the vinylic region with *ap* conformation (helix **II**). After addition of $LiClO_4$ (10.0 mg/mL) in MeOH with a poly-(*S*)-**4**(mru)/Li^+/MeOH ratio= 1.0/0.5/130 (mol/mol/mol), a positive Cotton effect was observed and a *sp* conformation was adopted, due to the chelation of Li^+ to the pendant by means the two carbonyl groups (Figure S18).

To determine the absence of cation-π interaction in the poly-(*S*)-**4**/Li^+ complex, experiments, similar to those performed with the other polymers, were carried out. So, a solution of poly-(*S*)-**4** in $CDCl_3$ (2.0 mg/mL) was titrated with $LiClO_4$ in CD_3OD (20.0 mg/mL) in a poly-(*S*)-**4**(mru)/Li^+/MeOH ratio= 1.0/0.3//≤130 (mol/mol/mol). The ^7Li NMR spectrum showed the ^7Li chemical shift at 2.7 ppm, which confirmed the absence of cation-π interaction as expected due to the absence of an aryl ring at the backbone moiety (Figure S18).[3, 5, 6]

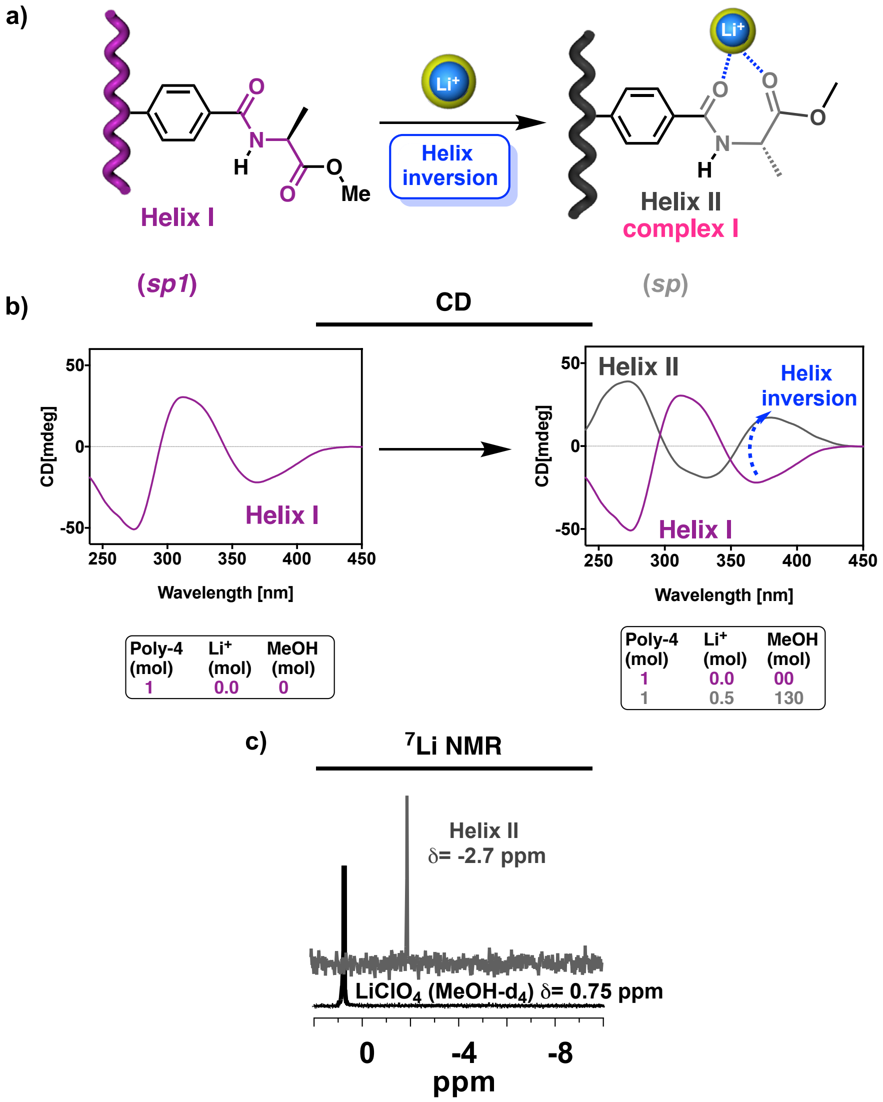


Figure S18: a) Scheme representing helical inversion of poly-(*S*)-**4** in $CHCl_3$ after addition of $LiClO_4$. b) CD spectra of poly-(*S*)-**4** in $CHCl_3$ (0.3 mg/mL) and poly-(*S*)-**4** with $LiClO_4$ in MeOH (10.0 mg/mL) with a poly-(*S*)-**4**(mru)/Li^+/MeOH ratio= 1.0/0.5/130 (mol/mol/mol). c) ^7Li NMR spectra for helix **II** showing a peak at 2.7 ppm after addition of Li^+ to poly-(*S*)-**4**, where [poly-(*S*)-**4**]= 2.0 mg/mL in $CDCl_3$, [$LiClO_4$] = 20.0 mg /mL in CD_3OD.

- **ATR/ FT-IR studies**

A solution of $LiClO_4$ in MeOH (50.0 mg/mL) was added to a solution of poly-(*S*)-**4** in $CHCl_3$ (2.0 mg/mL). The mixture was allowed to react for 5 minutes without stirring. FT-IR experiments show that, after addition of Li^+ in a poly-(*S*)-**4**(mru)/Li^+/MeOH ratio= 1/0.5/130 (mol/mol/mol), Li^+ coordinates with both amide and ester groups at the pendant moiety (Table S8).

Table S8: FT-IR data of poly-(*S*)-**4** in solution.

Polymer	υCO_{amide} cm^{-1}	υCO_{ester} cm^{-1}	υOMe cm^{-1}	$\Delta\upsilon CO_{amide}$ cm^{-1}	$\Delta\upsilon CO_{ester}$ cm^{-1}	$\Delta\upsilon OMe$ cm^{-1}
Poly-(*S*)-**4**($CHCl_3$)	1646	1738	1053	0	0	0
Poly-(*S*)-**4** /Li^+/MeOH 1 / 0.5 / 130 (mol/mol/mol)	1634	1728	1095	+12	+10	-42

5.2 Helical Inversion (Helix IV-Complex III)

- **CD and ^{7}Li NMR studies**

The addition of a large amount of MeOH to the polymer solution up to a poly-(*S*)-**4**(mru)/Li$^+$/MeOH ratio= 1.0/0.5/>300.0 (mol/mol/mol) produced another helical inversion and the recovery of the starting helical structure (adopting a *sp1* conformation). Helix IV was obtained without going previously to helix III due to the absence of the aryl ring at the pendant group and therefore, without cation-π interaction, although the metal ion is still coordinated to the ester group (Figure S19).

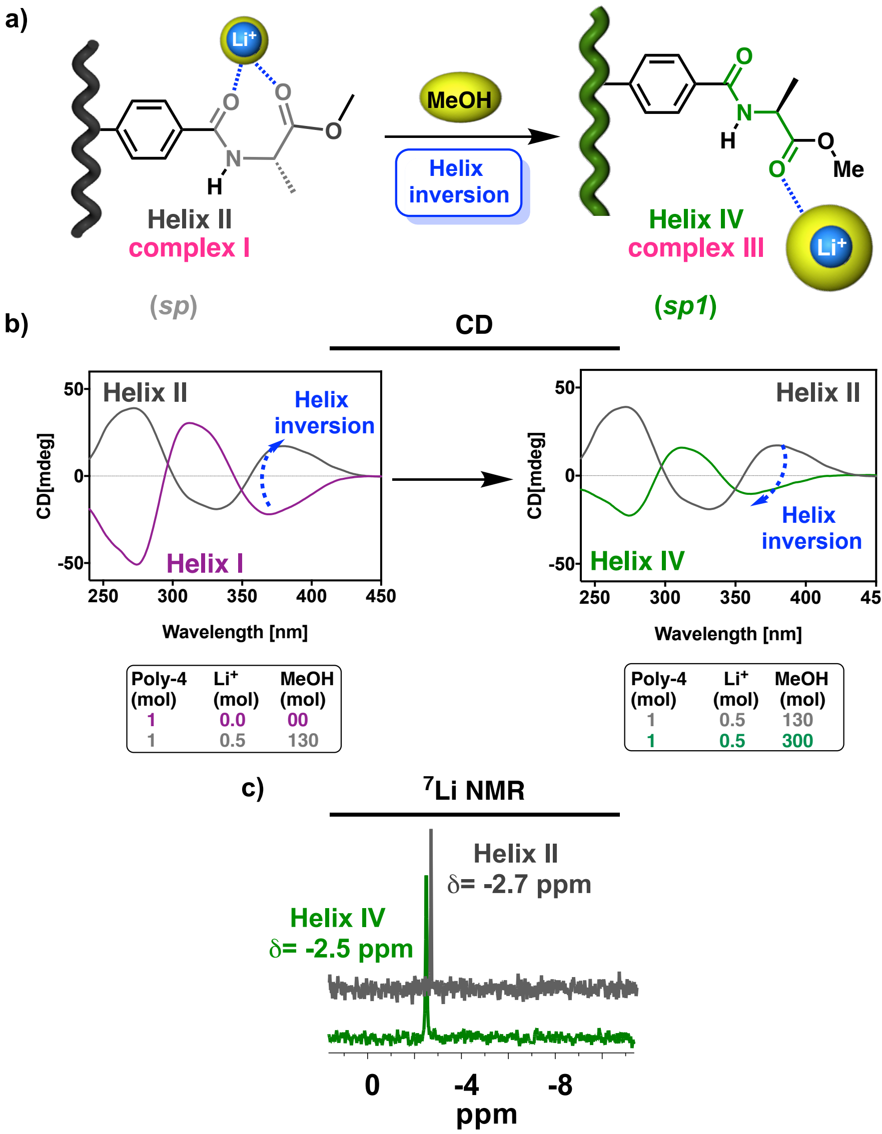


Figure S19: a) Helix inversion in the poly-(*S*)-**4**/Li$^+$ complex. A left-handed helix —*sp1* conformation— was obtained after addition of a large amount of MeOH. b) CD spectra showing the helix inversion after addition of large amount MeOH —poly-(*S*)-**4** (mru)/Li$^+$/MeOH ratio = 1/0.5/300 (mol/mol/mol)—. c) ^{7}Li NMR spectra for helix II and helix IV showing peaks at 2.7 ppm and 2.5 ppm respectively. This δ values indicate the absence of cation-π interactions, [poly-(*S*)-**4**] = 2.0 mg/mL in $CDCl_3$, [$LiClO_4$] = 20.0 mg /mL in CD_3OD.

- **ATR/ FT-IR studies**

A solution of $LiClO_4$ in MeOH (50.0 mg/mL) was added to a solution of poly-(*S*)-**4** in $CHCl_3$ (2.0 mg/mL). The mixture was allowed to react for 5 minutes without stirring. FT-IR experiments show that, after the addition of a large amount of MeOH to the polymer in a poly-(*S*)-**4**(mru)/Li$^+$/MeOH ratio= 1.0/0.5/300 (mol/mol/mol), a new helical inversion was produced and the initial CD signature was recovered. At this point, the Li$^+$ ion still makes chelation with ester group at the pendant moiety (Table S9).

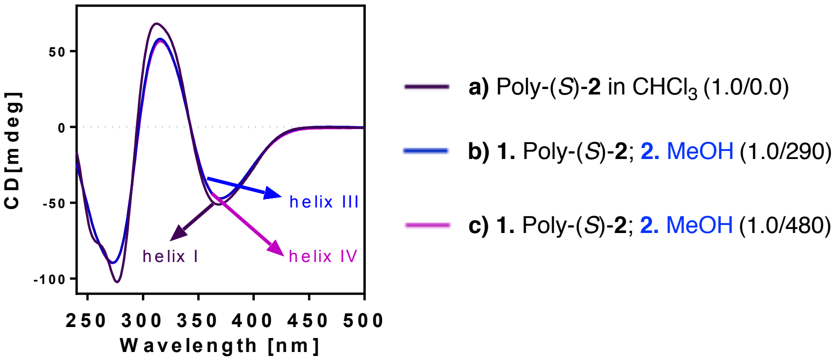
Table S9: FT-IR data of poly(*S*)-**4** in solution.

Polymer	υCO_{amide} cm^{-1}	υCO_{ester} cm^{-1}	υOMe cm^{-1}	$\Delta\upsilon CO_{amide}$ cm^{-1}	$\Delta\upsilon CO_{ester}$ cm^{-1}	$\Delta\upsilon OMe$ cm^{-1}
Poly-(*S*)-**4** ($CHCl_3$)	1646	1738	1053	0	0	0
Poly-(*S*)-**4** /Li$^+$/MeOH 1/0.5/300 (mol/mol/mol)	1640	1732	1099	+4	+6	-46

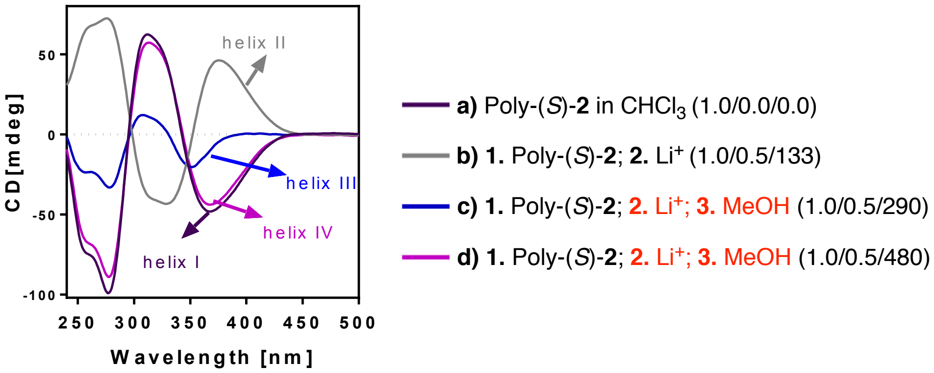
6 Control experiments

Control experiments were performed in which methanol was also added to the polymer in CHCl$_3$ both alone and before lithium (Figure S20). The latter results were similar to those obtained with the previous addition order. The experimental conditions (concentration, etc.) are as those shown in Section 3.

CD traces of: a) The polymer in CHCl$_3$. b) and c) Addition of increasing amounts of MeOH to the polymer in CHCl$_3$.
Poly-(*S*)-**2**(mru)/MeOH (mol/mol) ratios are shown between parentheses.



CD traces of: a) The polymer in CHCl$_3$. b) Addition of Li$^+$ to the polymer in CHCl$_3$. c) and d) Addition of Li$^+$ to the polymer in CHCl$_3$ followed by increasing amounts of MeOH.
Poly-(*S*)-**2**(mru)/Li$^+$/MeOH (mol/mol/mol) ratios are shown between parentheses.



CD traces of: a) The polymer in CHCl$_3$. b) Addition of Li$^+$ to the polymer in CHCl$_3$. c) and d) Addition of increasing amounts of MeOH to the polymer in CHCl$_3$ followed by addition of Li$^+$.
Poly-(*S*)-**2**(mru)/Li$^+$/MeOH (mol/mol/mol) ratios are shown between parentheses.

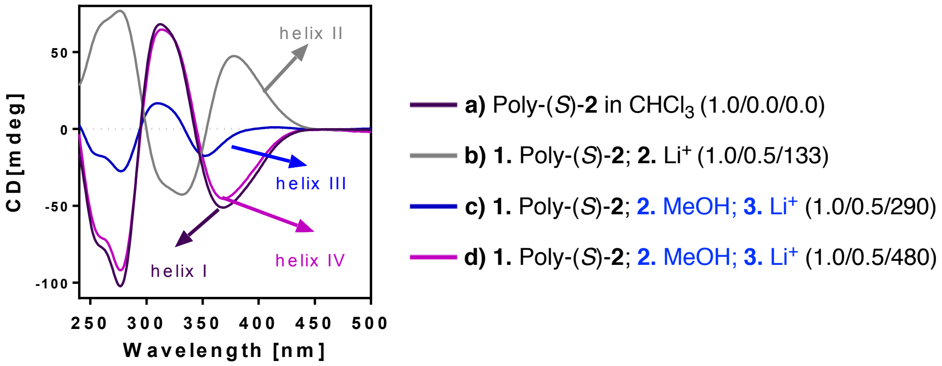


Figure S20: Control experiments.

7 Supporting References

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