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Leading Role of Cation-π Interactions in Polymer Chemistry: the Control of the Helical Sense in Solution †

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Cation-π interactions determine the helical sense adopted by a polyphenylacetylene bearing (*R*)-α-methoxy-α-phenylacetamide as pendant group (poly-**1**). These interactions take place when small amounts of Li^+, Na^+ and Ag^+ salts dissolved in donor cosolvents, are added to the polymer dissolved in a non-donor solvent and the corresponding helical polymer-metal complexes (HPMCs) are formed. Extensive spectroscopic studies (i.e., ^{7}Li, ^{23}Na, ^{1}H NMR and IR among others) indicate that the pendants act as dipodal receptors for metal cations, where cation-π interactions play a major role in controlling the *M* or *P* helicity of the polymer. Although all the cations tested generate cation-π binding, each metal presents its own particular and distinctive behaviour, based on polymer/cosolvent ratios and the type of cosolvent. Manipulation of these variables allows the selective disruption or activation of the cation-π interactions (i.e., a controlled switch on/off mechanism) and the selection of the helical sense on à la carte basis. The 3/1 helical structure of poly-**1** can originate a novel “triple cascade effect” of cooperative cation-$(\pi)_n$-π interactions, which further induce the high chiral amplification response found in these HPMCs. These non-covalent interactions are not found when divalent cations are used instead.

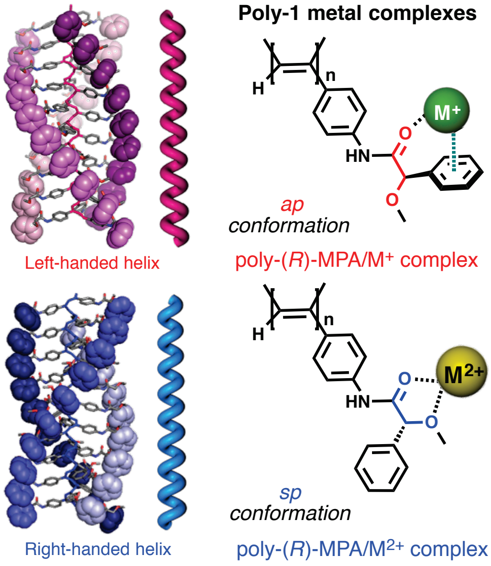
Introduction

The non-covalent binding between certain cations (e.g., alkali, silver or ammonium) and a nearby π-system[1] (aromatic ring,[2] alkene[3] or alkyne[4]) —known as cation-π interaction—, have been identified to play a central role in supramolecular[5] and biological chemistry[6] with applications in the fields of molecular sensors[7] and functional materials.[8] Several studies have reported on the structures of metal cation-π complexes in solid[9] and solution states[10] and suggest that their stability may be sufficiently strong to have a significant impact at molecular and supramolecular level.

In a previous work we have shown that a polyphenylacetylene[11] (poly-**1**) bearing (*R*)-α-methoxyphenylacetic acid (MPA) as chiral pendant (Scheme 1) presents in solution a 1:1 equilibrium of both helical senses[12] (M and P; null CD; *cis-cisoidal* conformation[13]) and that addition of metal salts shifts this equilibrium towards a predominant helical sense (forming helical polymer-metal complexes, HPMCs).

This helical induction requires a very low amount of metal ion —a chiral amplification phenomenon is operative— and the final helical sense obtained is determined by the valence of the metals due to their different mode of complexation to the alkoxy and carbonyl groups at the pendants.[12]

Thus, monovalent metal ions coordinate with the carbonyl and fix the pendant in the *ap* conformation (i.e., antiperiplanar carbonyl and methoxy groups, Scheme 1), while divalent metal ions coordinate to both the carbonyl and methoxy groups, fixing the pendant in the *sp* conformation (i.e., synperiplanar carbonyl and methoxy groups, Scheme 1). These two conformations place the phenyl ring in orientations with different steric requirements. So, monovalent complexes (*ap* conformation) force the polyene chain to adopt a left-handed helical structure. On the other hand, the right-handed form is adopted when divalent metal complexes are formed (*sp* conformation).



Scheme 1. Structure of poly-**1** and its mono- and divalent metal cation complexes. The *M* and *P* helicities generated in both cases are also shown.

Herein we report the central role played by M^+-π interactions in the stabilization of the pendant conformations of HPMCs in the helical sense response of poly-**1** to the addition of Li^+, Na^+ and Ag^+ ions, and how this interaction can be controlled by the presence/absence of small amounts of appropriate donor cosolvents. In this way, the adjustment of the poly-**1**/cosolvent ratio induces the HPMC to adopt the left- or the right-handed helix.

It is noteworthy to point out that to the best of our knowledge, no records on cation- π interactions operative on polymers in non-aqueous media are found in the scientific literature.[14]

Results and discussion

The structural characteristics of MPA, with two donor oxygens (OMe, C=O) and a Ph group, seem perfect for this pendant to behave as a dipodal receptor for metal cations via a donor atom (i.e., oxygen) and the Ph (i.e., cation-π interaction). Furthermore, the 3/1 helical structure of poly-**1** suggested that novel types of cooperative cation-π/π–π interactions could be in operation.

Analysis of the behaviour of the HPMCs originated from the interaction between poly-**1** and Li^+, Na^+ and Ag^+ ions, which confirmed these hypotheses, follows.

Poly-1/Li^+ HPMC: cation-π stabilization.

A solution of poly-**1** in $CHCl_3$ (0.3 mg mL^{-1}; null CD) was titrated with solutions of $LiClO_4$ (10 mg mL^{-1}) in different cosolvents (i.e., THF, DMF, DMSO, MeOH, MeCN, acetone, butanone, methyl isobutyl ketone, acetophenone, pyridine, piperidine). CD monitoring indicated that in all cases, the addition of those Li^+ solutions induces on the poly-**1** a left-handed helix (negative CD, $g_{384nm}<0$) (Figure 1b).

The process goes through a chiral amplification phenomenon —just a few Li^+ ions are necessary to obtain the maximum CD response from the polymer [poly-**1** (mru)/Li^+ mole ratio= 1.0/<0.1]—, being independent of the cosolvent used to deliver the salt to the poly-**1** solution (Figure 1b). This means that solutions of Li^+ at different concentrations and in different cosolvents induce the same helical sense (*M*) when added to poly-**1** in $CHCl_3$.

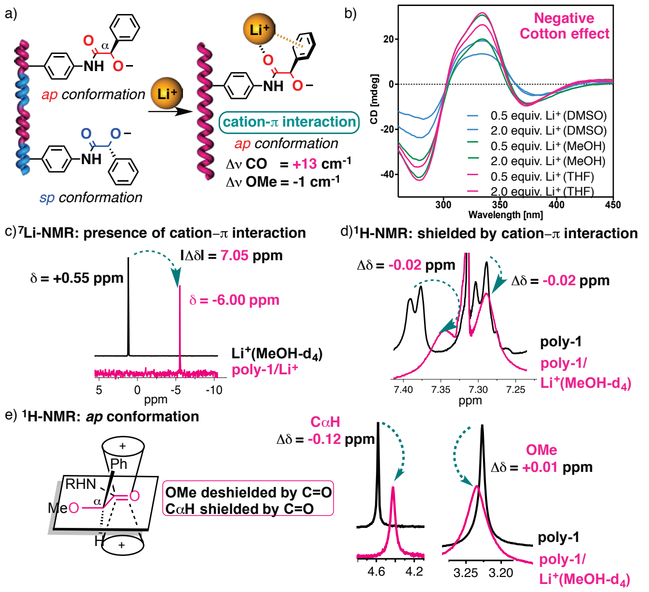


Figure 1. Chiral amplification of poly-**1** with Li^+. a) *ap* conformation stabilized by cation-π interactions and determined by IR. b) CD spectra of different poly-**1**/Li^+ HPMCs; Li^+ equiv per mru equiv are indicated; cosolvents in parentheses; [poly-**1**]= 0.3 mg mL^{-1} in $CHCl_3$, [$LiClO_4$]= 10 mg mL^{-1} in DMSO, MeOH and THF. c) ^7Li NMR and d) ^1H NMR spectra showing the cation-π interactions. e) Partial ^1H NMR spectra showing the conformational change at the pendant moiety prior and after the addition of Li^+; [poly-**1**]= 3.0 mg mL^{-1} in $CDCl_3$, [$LiClO_4$] = 10 mg mL^{-1} in CD_3OD; polymer (mru)/Li^+ mole ratio= 1.0/2.0.

^7Li NMR, ^1H NMR and IR studies of the aforementioned poly-**1**/Li^+ solutions provided very useful information about the structure of the HPMCs generated and informed about the existence (or not) of cation–π interaction.

So, the ^7Li signal, once the complexation of the alkali cation with poly-**1** took place, was found strongly shielded. It showed d= -6.5 ppm, which is the expected value for Li^+ ions involved in cation-π interactions[13] (Figure 1c). This chemical shift also indicates that the Li^+ ion interacts with only one phenyl ring, discarding structures where the ion could act as a template between two close phenyl rings [e.g., δ(^7Li)= -12 ppm in Cp_2].[15a] The presence of this cation-π interaction was corroborated by ^1H NMR that showed the hydrogens at the MPA phenyl ring shifted upfield when compared to those in poly-**1** (Figures 1d, e).

Moreover, IR studies confirmed the coordination of Li^+ to the carbonyl group (Δν= +13 cm^{-1}) (Figure 1a), and ^1H NMR showed that the addition of Li^+ deshields the OMe and shields the CαH groups of the pendant, in full agreement with the existence —in the MPA part of the polymer— of an *ap* conformation (Figure 1e).

In summary, the experimental data proves that Li^+ efficiently interacts not only with the carbonyl group but also with the phenyl ring of MPA through a Li^+–π interaction that stabilizes the *ap* conformation of the pendant and, as a consequence, the left-handed helix (Figure 1a). This interaction seems to be strong enough to resists the presence of strong donor cosolvents such as DMSO and DMF.[16]

Poly-1/Na$^+$ HPMC: cation-π vs. chelate effect.

Only a few examples of Na^+-π complexes have been published and although is known that cation-π interactions with Na^+ are weaker than with Li^+,[17] we investigated if this kind of non-covalent bonding was also involved in the helical induction on poly-**1** by Na^+ salts.

Thus, a solution of poly-**1** in $CHCl_3$ (0.3 mg mL^{-1}; null CD) was titrated with solutions of $NaClO_4$ at different concentrations (100, 50, 30, 10 and 5 mg mL^{-1}) on different cosolvents (THF, DMF, DMSO, MeOH, MeCN, acetone, butanone, methyl isobutyl ketone, acetophenone, pyridine, piperidine) and monitored by CD.

In contrast to the Li^+ case, which induced a left-handed helix in all cosolvents tested, we found that addition of Na^+ to poly-**1** could induce both helical senses depending on two variables: namely the amount and type of the cosolvent used to deliver the metal ion. Analysis of these two factors follows.

a) The helical induction depends, not on the amount of Na^+ ion added —a minimum of polymer (mru)/Na^+ ratio= 1.0/0.05 (mol/mol) is necessary to induce a helical response in all cosolvents—, but on the amount of cosolvent (e.g., MeOH) used to deliver the Na^+ salt. So, a left-handed helix results when a MeOH solution of $NaClO_4$ is added to the $CHCl_3$ solution of poly-**1** at a poly-**1** (mru)/MeOH ratio= 1/<100 (mol/mol) (Figure 2a), while if the ratio is 1/>100 (mol/mol), the polymer adopts a right-handed helix (Figure 2d). Analogous results —left-handed sense helix at 1/<100 poly-**1** (mru)/solvent ratio and right-handed at 1/>100 ratio— were obtained when, instead of MeOH, the Na^+ salt was delivered in THF, MeCN, acetone, butanone, methyl isobutyl ketone, acetophenone, pyridine and piperidine (see SI).

b) When DMF or DMSO are used as cosolvents, the polymer adopts always a right-handed helix (positive CD), independently of the poly-**1** (mru)/cosolvent ratio employed. Therefore, with Na^+, the selection of the cosolvent is a key for determining the helical sense. With Li^+, this is not the case (see above).

In order to detect the presence and role of Na^+–π interactions,[17] and to determine the structures of the complexes, ^{23}Na NMR, ^{1}H NMR and IR studies were carried out on the solutions that produced the left- and right-handed helices (Figure 2).

Thus, the left-handed helix solutions [negative CD; poly-**1** (mru)/MeOH ratio= 1/<100 (mol/mol)], showed a ^{23}Na NMR resonance peak at δ= -16.08 ppm, typical for a Na^+–π interaction[17] and the phenyl ring protons shifted upfield with regard to those in poly-**1** as a result of the complexation (Figures 2b and 2c).

IR studies, in its turn, showed that the Na^+ ion was coordinated to the carbonyl (Δν= +10 cm^{-1}; Figure 2a) and not with the OMe (Δν= 0 cm^{-1}; Figure 2a). This information, together with that obtained from ^{1}H NMR (deshielding of OMe and shielding of CαH) suggests the presence of an *ap* conformation at the pendant moiety (see SI).

In sum, these data indicates that, at poly-**1** (mru)/MeOH ratio= 1/<100 (mol/mol), a Na^+ HPMC is produced where the metal ion is coordinated to both the carbonyl and to the phenyl ring by Na^+-π interaction forming an *ap* conformation and therefore, inducing a left-handed helix at the main backbone (Figure 2a).

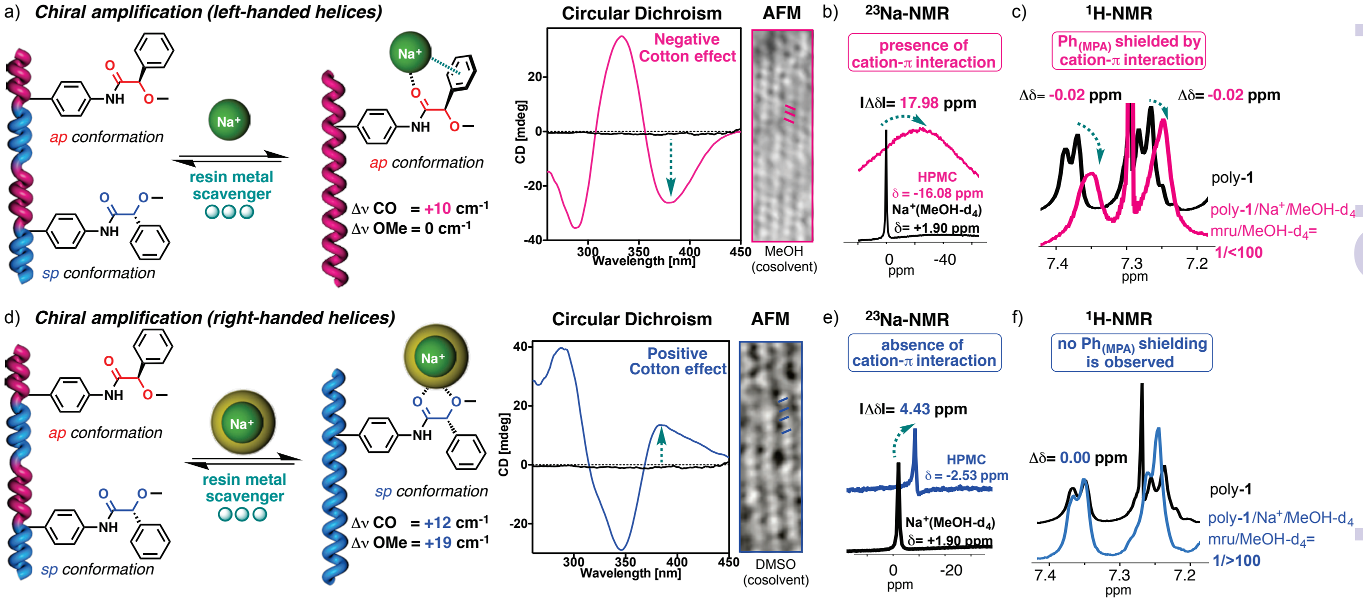


Figure 2. Chiral amplification of poly-**1** with Na^+. a) *ap* conformation stabilized by cation-π interactions and determined by IR, CD and AFM; CD: [poly-**1**]= 0.3 mg mL^{-1} in $CHCl_3$, [$NaClO_4$]= 100 mg mL^{-1} in MeOH; CD, IR and AFM: polymer (mru)/Na^+/MeOH mole ratio= 1.0/0.3/30.0. b) ^{23}Na NMR and c) ^1H NMR spectra showing the cation–π interactions; [poly-**1**]= 3.0 mg mL^{-1} in $CHCl_3$, [$NaClO_4$]= 100 mg mL^{-1} in MeOH; polymer (mru)/Na^+/MeOH mole ratio= 1.0/0.3/30.0 [i.e., poly-1 (mru)/MeOH ratio= 1/<100 (mol/mol)]. d) *sp* conformation stabilized by cation-π interactions and determined by IR, CD and AFM; CD: [poly-**1**]= 0.3 mg mL^{-1} in $CHCl_3$, [$NaClO_4$]= 100 mg mL^{-1} in MeOH; CD: polymer (mru)/Na^+/MeOH mole ratio= 1.0/0.3/151.0; AFM: polymer (mru)/Na^+/DMSO mole ratio= 1.0/0.3/30.0. e) ^{23}Na NMR and f) ^1H NMR spectra showing the absence of cation-p; [poly-**1**]= 3.0 mg mL^{-1} in $CHCl_3$, [$NaClO_4$]= 100 mg mL^{-1} in MeOH; polymer (mru)/Na^+/MeOH mole ratio= 1.0/0.3/151.0 [i.e., poly-**1** (mru)/MeOH ratio= 1/>100 (mol/mol)](these values also valid for IR).

Similar experiments, carried out on the right-handed helical solutions —obtained at poly-**1** (mru)/MeOH ratio= 1/>100 (mol/mol) (Figures 2d-f) or using DMF or DMSO as cosolvents for the salt—, showed substantial structural differences: absence of cation-π interaction[17] [^{23}Na NMR, δ(^{23}Na)= -2.53 ppm (Figure 2e); ^1H NMR, no shielding of the phenyl protons (Figure 2f)] and coordination of the Na^+ to both the carbonyl and the methoxy groups (IR, Δν= +12 and +19 cm^{-1} respectively; Figure 2b). These studies denote the absence of cation-π interaction[17a] and the presence of a *sp* structure for the complex (Figures 2d) that now forces the right-handed helicity in poly-**1**. The reversibility of the process was demonstrated by the use of resin metal scavengers (see SI).

Moreover, AFM studies on highly oriented pyrolitic graphite (HOPG) of HPMC (M= Na^+) obtained by the addition of a solution of $NaClO_4$ in MeOH to a solution of poly-**1** in $CHCl_3$ at polymer (mru)/Na^+/MeOH mole ratio= 1.0/0.3/30.0 [i.e., poly-**1** (mru)/MeOH ratio= 1/<100 (mol/mol); negative CD], show 2D-crystals where the polymer chains are packed parallel one another adopting a left-handed helical structure defined by the pendant groups (Figure 2a).[12c]

On the other hand, AFM studies (HOPG) of HPMC (M= Na^+) obtained by the addition of a solution of $NaClO_4$ in DMSO to a solution of poly-**1** in $CHCl_3$ at polymer (mru)/Na^+/DMSO mole ratio= 1.0/0.3/30.0 —as stated before, positive CD at any poly-**1** (mru)/DMSO ratio)— show 2D crystals also packed in a parallel fashion, but now the polymer chains adopt a right-handed helical structure. It is interesting to point out that in this case, helical pitch and packing angles are similar to those previously reported for poly-**1** when a divalent, instead of monovalent, metal ion is used to generate the HPMC (Figure 2d).[12c]

As the left- and right-handed helices obtained from Na^+ HPMCs depend on the poly-**1** (mru)/cosolvent ratio when MeOH (or any other cosolvent with similar behaviour listed previously) is used as cosolvent, it is very easy to induce helical inversion by manipulation of that ratio (for instance, by addition of either a small volume of cosolvent or more poly-**1** to the Na^+ HPMC).

Thus, the addition of more MeOH to a left-handed HMPC (M= Na^+) shifts the helical sense to the right (positive CD, Figure 3a), with effective disruption of the Na^+-π interaction (verified by ^{23}Na NMR, ^1H NMR and IR) and the shift of the conformation of the pendant from *ap* to *sp* (Figure 3c and 3d). Conversely, addition of more poly-**1** to a right-handed Na^+ HPMC (positive CD) inverts the helical sense to the left (Figure 3b) and restores both the Na^+-π interaction and the *sp* conformation.

To summarize, the addition of Na^+ to poly-**1** produces a HPMC where cation-π interaction is crucial for structural stabilization. The weaker nature of the Na^+-π interaction as compared with Li^+, allows its selective formation/disruption by manipulation of the polymer/cosolvent ratio, producing at demand the left-or right- handed helices.

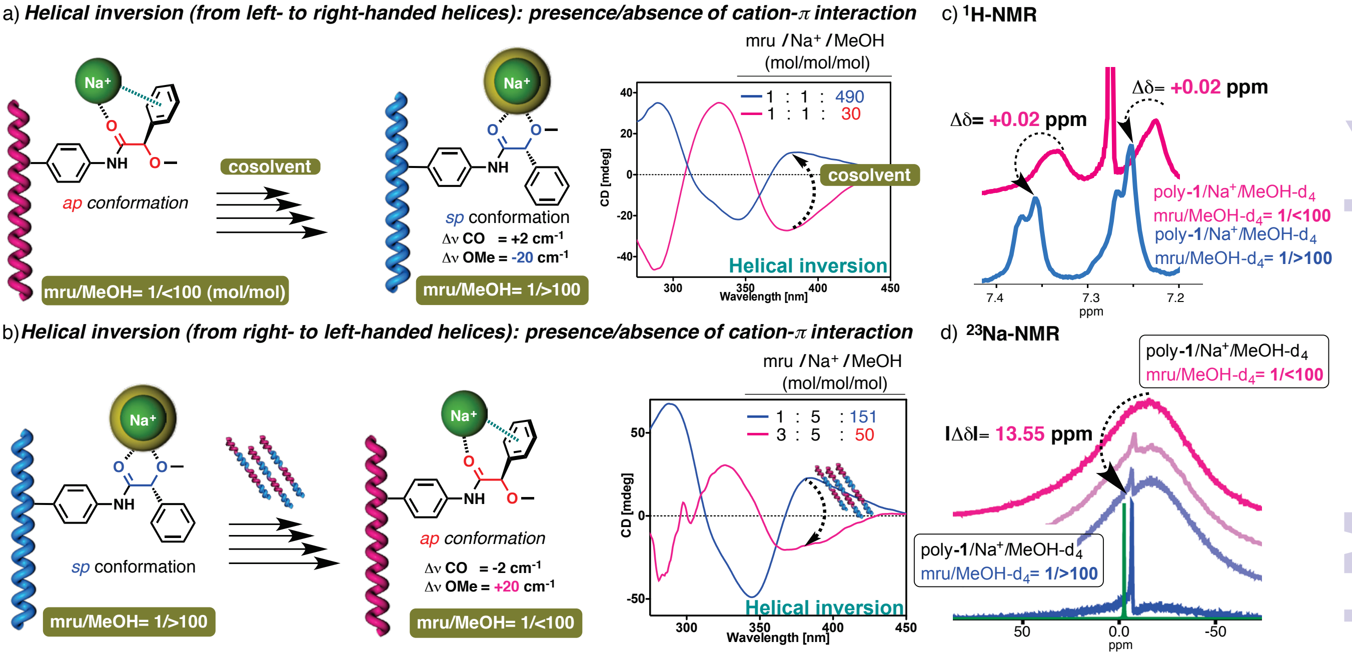


Figure 3. Helical inversion of poly-**1** with Na$^+$. a) From left- to right-handed helices with poly-**1** (mru)/MeOH ratio= 1/<100 (mol/mol); [poly-**1**]= 0.3 mg mL^{-1} in CHCl$_3$, [NaClO$_4$]= 100 mg mL^{-1} in MeOH; IR and CD determination. b) From right- to left-handed helices with poly-**1** (mru)/MeOH ratio= 1/>100 (mol/mol); [poly-**1**]= 0.3 mg mL^{-1} in CHCl$_3$, [NaClO$_4$]= 100 mg mL^{-1} in MeOH; IR and CD determination. c) ^{1}H NMR showing the cation-π interactions (MPA Ph shifts) and d) ^{23}Na NMR showing the shift of Na$^+$ peak when going from presence to absence of cation-π interaction.

Poly-1/Ag$^+$ HPMC: cation-π.

Addition of AgClO$_4$ solutions to poly-**1** in CHCl$_3$ (0.3 mg mL^{-1}) produced a left-handed helix (negative CD, Figure 4a) in all the cosolvents tested with the exception of MeCN. With this cosolvent, the two helical senses can be obtained (Figure 4b) depending on the poly-**1** (mru)/MeCN ratio but not on the amount of Ag$^+$ added —a minimum of polymer (mru)/Ag$^+$ ratio= 1.00/0.05 (mol/mol) is necessary to induce a helical response in all cosolvents; see SI)—. At a poly-**1** (mru)/MeCN ratio= 1/<450 (mol/mol), a left-handed helix results, while at a 1/>450 ratio, the right-handed sense is originated.

The left-handed Ag$^+$ HPMC is characterized by the presence of Ag$^+$-π interaction[18] similar to those found with Li$^+$ and Na$^+$ ions. This interaction stabilizes the *ap* conformation as shown by spectroscopic evidences. In ^{1}H NMR, upfield shifting of the MPA phenyl protons, deshielding of the OMe group and shielding of CαH after addition of Ag$^+$ is observed (Figure 4c). As for IR, it shows coordination just to the carbonyl group and not to the OMe (Δν CO= +32 cm^{-1}) (Figure 4c).

For its part, ^{1}H-NMR studies[18b] on the right-handed Ag$^+$ HPMC obtained at poly-**1** (mru)/MeCN ratio= 1/>450 (mol/mol) show no evidence of cation-π interaction (MPA Ph shifts) but they do about the presence of a *sp* conformation (Figures 4c and 4d). IR confirms the chelation of Ag$^+$ to both carbonyl and methoxy groups of MPA through significant shifts of the carbonyl and methoxy bands (Δν CO= +52 cm^{-1}, Δν OMe= +29 cm^{-1}) (Figure 4d).

As shown before with Na$^+$, the left- and right-handed helical structures can be easily interconverted by manipulation of the poly-**1**/MeCN ratio. More precisely, transformation from a left- to a right-handed sense is achieved by addition, to the original Ag$^+$ HPMC solution, of extra amount of MeCN until a poly-**1** (mru)/MeCN ratio= 1/<450 (mol/mol) is reached (see SI). The opposite inversion of helicity is produced when poly-**1** is added to the Ag$^+$ HPMC solution until a final poly-**1** (mru)/MeCN ratio= 1/>450 (mol/mol) (see SI).

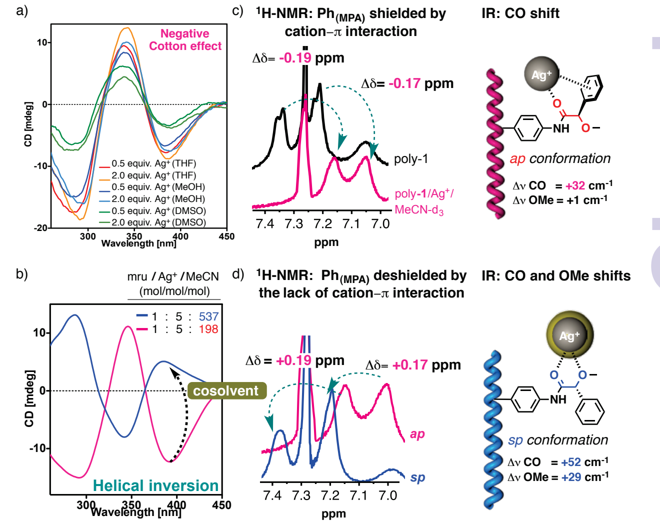


Figure 4. Chiral amplification of poly-**1** with Ag$^+$. a) CD spectra of different poly-**1**/Ag$^+$ HPMCs; Ag$^+$ equiv per mru equiv are indicated; cosolvents in parentheses;

[poly-**1**]= 0.3 mg mL^{-1} in $CHCl_3$, [$AgClO_4$]= 10 mg mL^{-1} in DMSO, MeOH and THF. b) Helical inversion of poly-**1** controlled by the (mru)/MeCN ratio. c) *ap* conformation stabilized by cation-π interactions and determined by ^{1}H NMR and IR; poly-**1** (mru)/MeCN ratio= 1/<450 (mol/mol); [poly-**1**]= 0.3 mg mL^{-1} in $CHCl_3$, [$AgClO_4$]= 100 mg mL^{-1} in MeCN. d) *sp* conformation determined by ^{1}H NMR and IR showing the absence of cation-π interactions; poly-**1** (mru)/MeCN ratio= 1/>450 (mol/mol); [poly-**1**]= 0.3 mg mL^{-1} in $CHCl_3$, [$AgClO_4$]= 100 mg mL^{-1} in MeCN.

Cooperativity between cation-π and π−π interactions.

In recent years, the possible interplay (i.e., cooperativity) between metal cation-π and π-π interactions —how that pair of non-bonded interactions mutually influences each other— has been the object of a number of theoretical studies.[18] However, and to our knowledge, real experimental systems where such a cooperativity —cation-π and π-π interactions working in concert— might be in operation are not found in the literature.

Those theoretical studies on ternary complexes (i.e., M^+-π-π motifs) predict a significant increase (i.e., 2-5 kcal mol^{-1} or even higher)[19a] in the π-π interaction energy in the presence of cations and also an enhancement, although lower, for the cation-π interaction energy. Both interactions reinforce each other when they are combined. As a result, the quantum calculations[19d] indicate that the magnitude of π-π interactions, due to the strong synergic effect, may become comparable to other non-covalent interactions such as hydrogen bonding.

When monovalent metal cations interact with poly-**1**, the structural situation generated due to the characteristics of the polymer is ideal for cation-π/π-π cooperativity to take place. Even though the alignment between two adjacent MPA phenyl rings in the M^+ HPMCs of poly-**1**, does not correspond to pure "sandwich" dimer, the "parallel displaced" arrangement of the aromatic rings,[19a,d] is also highly favoured (Figure 5a).[20]

Furthermore, high-level *ab initio* (MP2) calculations demonstrate that the presence of a metal cation interacting with the π system of an aromatic ring favours the face-to-face stacking interaction with additional aromatic rings and this effect is extended in space up to five stacked aromatic rings [i.e., cation-$(\pi)_n$-π interactions (n= 1-4)].[19e]

The structural geometry of poly-**1** seems to be just the adequate for all the above theoretical interplay between non-covalent interactions in solution (Figure 5a).

Actually, these synergistic effects are probably at the origin of the high chiral amplification response obtained with M^+ HPMCs [e.g., M^+/mru ratios< 0.1/1.0 (mol/mol) give CD response in a variety of cosolvents].

As poly-**1**/M^+ complexes form 3/1 helices, cation-$(\pi)_n$-π interactions sliding down the polymer through the three components of the helix can be expected, and this non previously described "triple cascade cooperative effect" should reinforce the chiral amplification (Figure 5b).

It is important to point out that cation-π interactions are not observed by ^{7}Li and ^{23}Na NMR when the monomer [i.e., (*R*)-*N*-(4-ethynylphenyl)-2-methoxy-2-phenylacetamide] is used instead of the polymer to make the complex with the monovalent metal ions. This fact indicates the importance that the polymer structure plays in the cation-π effects.

Poly-1/M^{2+} HPMCs: absence of cation-π stabilization.

CD studies with divalent metal cations —titrations of solutions of poly-**1** in $CHCl_3$ (0.1 mg mL^{-1}) with different divalent metal ions (Ca^{2+}, CD studies with divalent metal cations —titrations of solutions of poly-**1** in $CHCl_3$ (0.1 mg mL^{-1}) with different divalent metal ions (Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Ba^{2+}, Hg^{2+}, Pb^{2+}) in different cosolvents (THF, MeOH, MeCN, DMF, DMSO, acetone, pyridine, piperidine; 10 mg mL^{-1})— show in all cases a positive Cotton effect at the vinyl region indicating the presence of a right-handed helical structure. This helicity is adopted always independently on the amount of cosolvent added (see full description at SI).

These results, together with IR studies (see SI), confirm the chelate behaviour of carbonyl and methoxy groups of the MPA pendants with the divalent cations (i.e., *sp* conformation) and the lack of M^{2+}-π interactions.

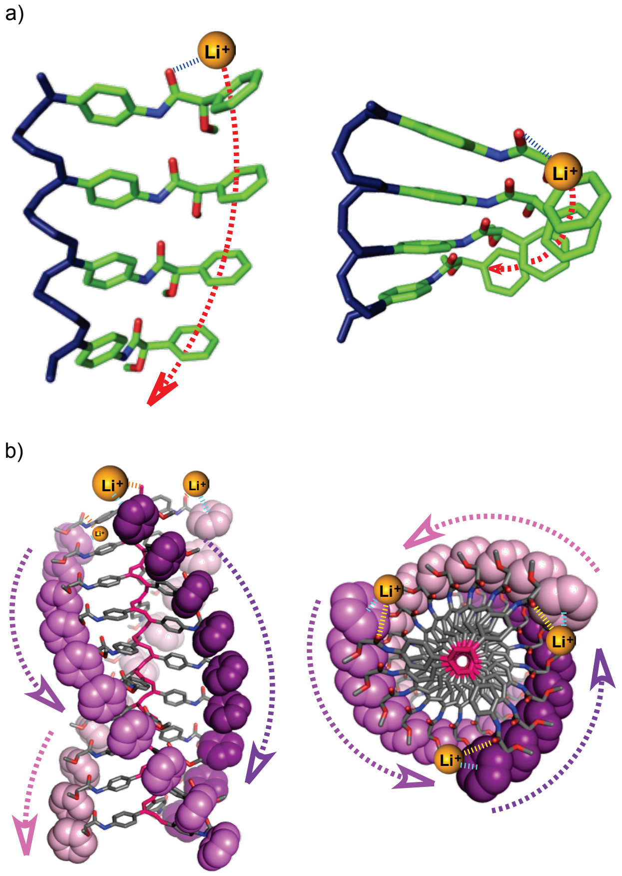


Figure 5. a) Two views showing the favourable structure for the formation of cation-$(\pi)_n$-π interactions (red broken arrows) in poly-**1**/M^+ (coordination between carbonyl and M^+ in blue). For the sake of clarity, only one crest of the polymer is shown, even though the complete polymer structure consists in a 3/1 left-handed helix. b) Conceptual representation (side and frontal views) of the "triple cascade effect" that cation-$(\pi)_n$-π interactions can cause in the complete 3/1 helical structure of poly-**1**. MPA phenyl groups are shown as space-filling models.

Conclusions.

Cation-π interactions are essential for the stabilization of the polymer metal complexes obtained by addition of Li^+, Na^+ or Ag^+ salts to a polyphenylacetylene (poly-**1**) bearing chiral pendants dissolved in a non donor solvent (i.e., $CHCl_3$). That interaction stabilizes the *ap* conformation at the pendant due to the coordination of the metal ion to both the MPA phenyl and the carbonyl group and makes the polymer chain to adopt a left-handed helical sense.

The strength of this interaction is determined by the nature of the metal cation and the cosolvent used to deliver the metal salt and its disruption favours the *sp* conformation, making a new coordination between metal ion and the methoxy group. This change provokes chelation of the metal ion to both carbonyl and methoxy groups at the pendants and forces the right-handed helicity of the polymer backbone.

With Li^+, the cation-π interaction remains in a wide variety of cosolvents and the polymer adopts the left-handed helix in all cases. By contrast, with Na^+ and Ag^+ the polymer can be forced to adopt either left- or right-handed helicities depending on the cosolvent used to deliver the salt, more precisely on the poly-**1** (mru)/cosolvent ratio.

In the HPMC obtained by addition of Na^+ dissolved in strong donor cosolvents such as DMSO or DMF, no cation-π interactions are present and the polymer adopts a right-handed helix. If the Na^+ salt is added in any other cosolvent, both the left- and right-handed helices can be obtained by modulation of the amount of cosolvent: at high poly-**1**/cosolvent ratios, Na^+-π interaction determines the left-handed helicity, and at low poly-**1**/solvent ratios, that interaction disappears and the helix inverts to right-handed sense.

Ag^+-π interaction is present when the Ag^+ salt is dissolved in most cosolvents inducing the left-handed helix. Nevertheless, when the cosolvent of the silver salt is MeCN, both left- and right- helical senses can be obtained depending, as before, on the poly-**1** (mru) /cosolvent (i.e., MeCN) ratio. At high ratios (i.e., low MeCN contain), there is Ag^+-π interaction and the polymer turns left-handed but at low ratios (i.e., high MeCN contain), the Ag^+-π interaction is disrupted and the helical backbone shifts to the right-handed helix.

On the other hand, cation-π interactions are not observed when the monomer is used instead of the polymer to make the complexes with the monovalent metal ions. These results indicate the importance that the polymer structure plays in the cation-π interaction.

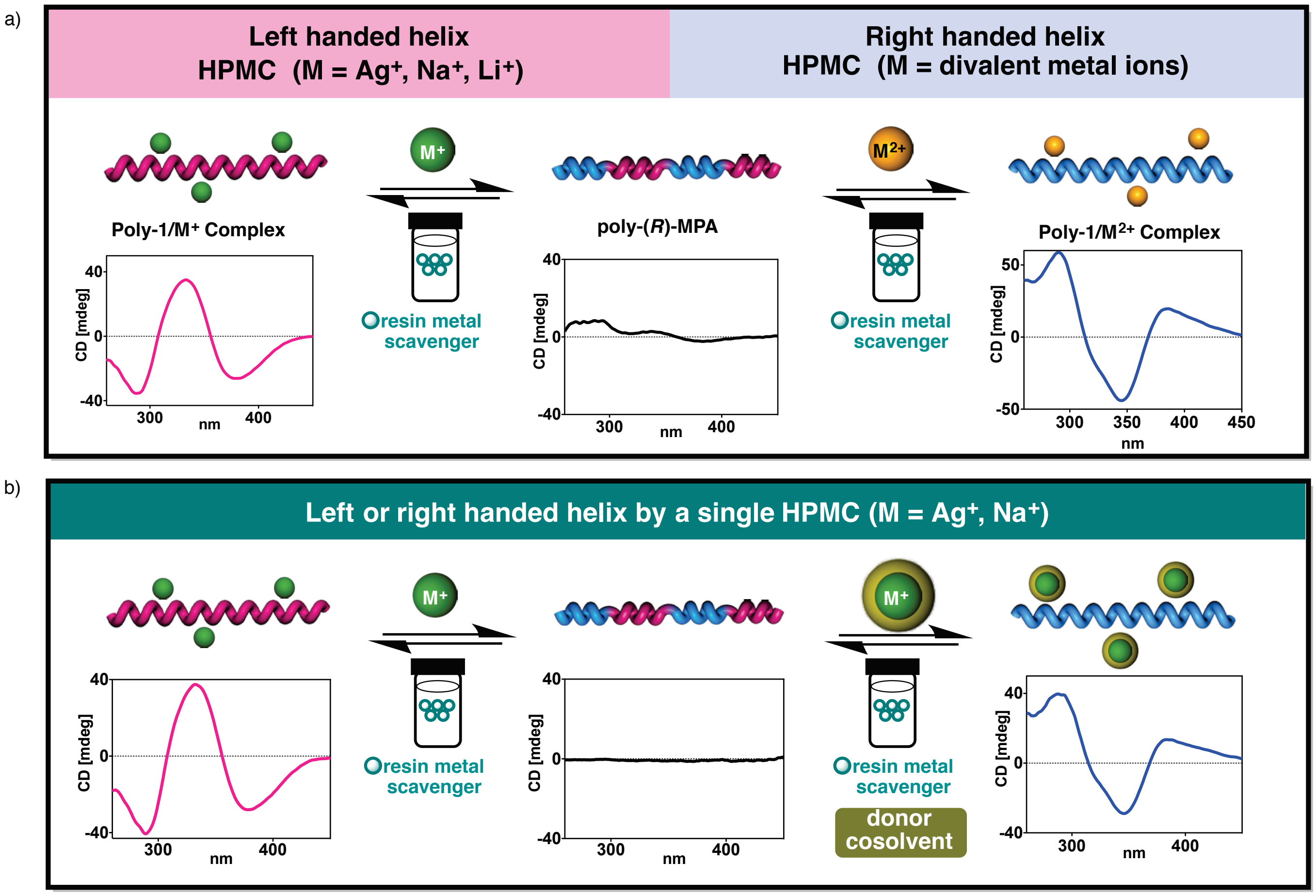


Figure 6. (a) Chiral amplification of poly-(*R*)-MPA either to the left- or right-handed helical sense induced by the presence of monovalent or divalent metal ions respectively. Two different HPMCs are required to get the two helicities. (b) Chiral amplification of poly-(*R*)-MPA either to the left- or right-handed helical sense with a single HPMC (M= Na^+, Ag^+) induced by the presence/absence of cation-π interactions.

In fact, cation-$(\pi)_n$-π interactions working in concert in a novel cooperative "triple cascade effect" can originate the high chiral amplification responses observed in HPMCs.

So, poly-**1** could be considered as a sensor to the presence/absence of M^+-π interactions indirectly detected by CD due to the sensitivity of its helical structure to conformational changes in the pendants and to the chiral amplification mechanism of this process: a small number of cations shifts the conformation of some pendants and that fact is enough to force the whole polymer to adopt a certain helical sense.

The cation-π interaction can be disrupted by high amounts of donor cosolvent, affecting to the conformational equilibrium of the pendant moiety. This effect is further transmitted from the pendants to the main polymer backbone inducing helical inversion.

In summary, a different approach to control the *M*/*P* helicity of poly-**1** has been developed based on a single HPMC using Na^+ or Ag^+ as metal cations. In this case, the helical sense is controlled by the presence/absence of cation-π interactions that depend on the action of donor solvents (Figure 6b). In previous studies, two different valence metal ions were necessary in order to produce the *M*/*P* helicity of poly-**1** in two different HPMCs (Figure 6a).

Associated content

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Abbreviations

AFM, atomic force microscopy; ap, antiperiplanar; CD, circular dichroism; DMF, dimethylformamide; DMSO, dimethyl sulfoxide; HPMC, helical polymer−metal complex; IR, infrared; M, minus; MPA, α-methoxyphenylacetic acid; mru, monomer repeating unit; NMR, nuclear magnetic resonance; P, plus; sp, synperiplanar; THF, tetrahydrofuran.

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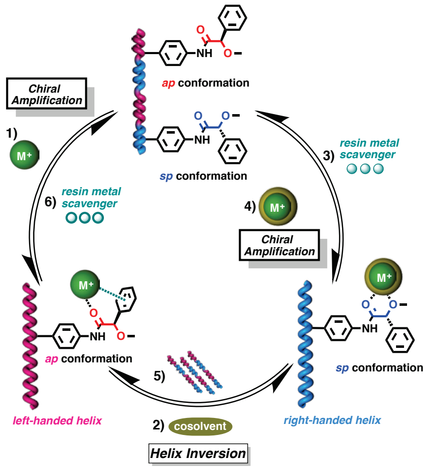
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