Electronic Supplementary Material (ESI) for Polymer Chemistry.

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

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Electronic Supplementary Information

Contents:

1. ATR/FT-IR studies

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

$M(ClO_4)_2$ or $MClO_4$ (0.5 and 1.0 equiv) was added to a solution of poly-**1** 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 divalent metal ions, both carbonyl and methoxy groups increase their degree of association, whereas after the addition of monovalent metal ions (e.g., Li^+, Ag^+), only the carbonyl group increases its degree of association (Figure S1 and Table S1).

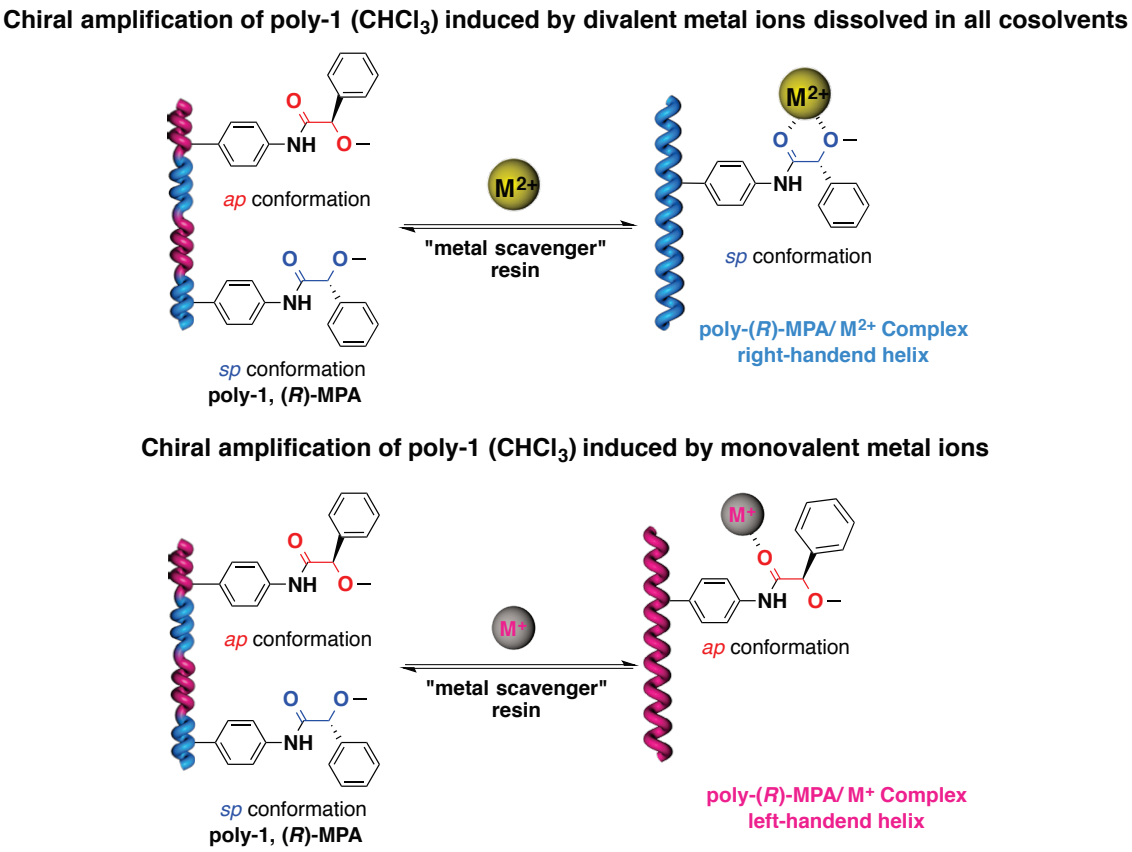


Figure S1. Coordination of divalent and some monovalent metal ions to poly-**1.**

When Ag^+ is dissolved in MeCN and when Na^+ is dissolved in acetone, THF MeOH, MeCN, pyridine, piperidine, methyl isobutyl ketone or propanone, the metal ion can chelate to the polymer in two different ways, through just the carbonyl group or to both carbonyl and methoxy groups due to the presence or the absence of cation-π interactions (Figure S2).

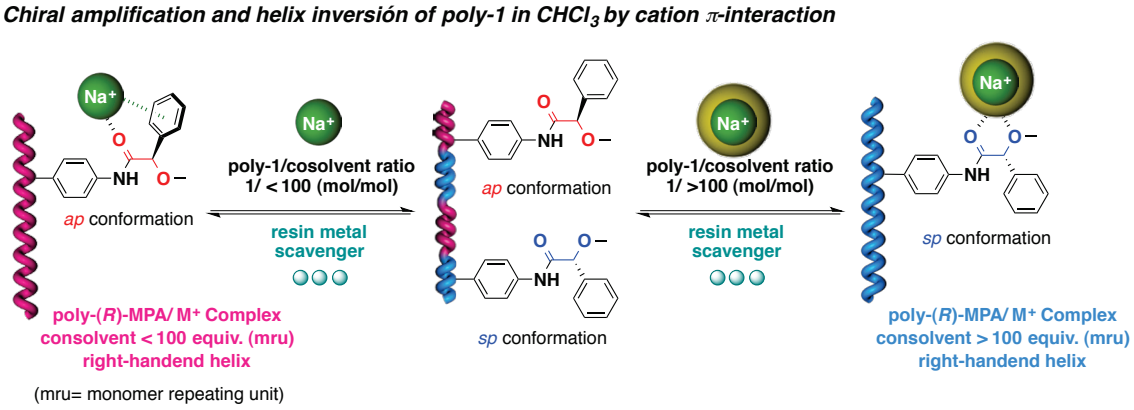
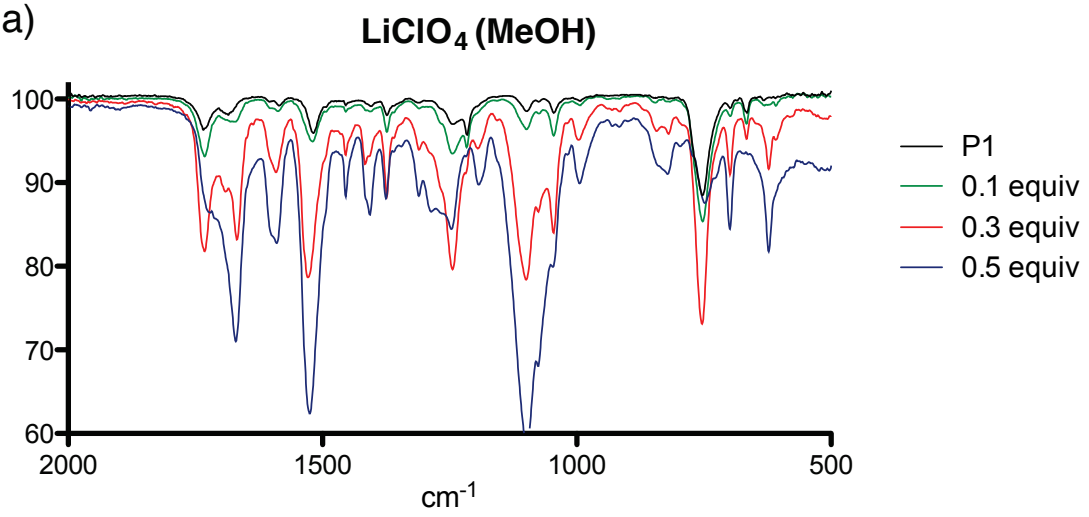


Figure S2. Different coordination modes of Na^+ and Ag^+ ions to poly-**1** depending on the polymer/cosolvent ratio.

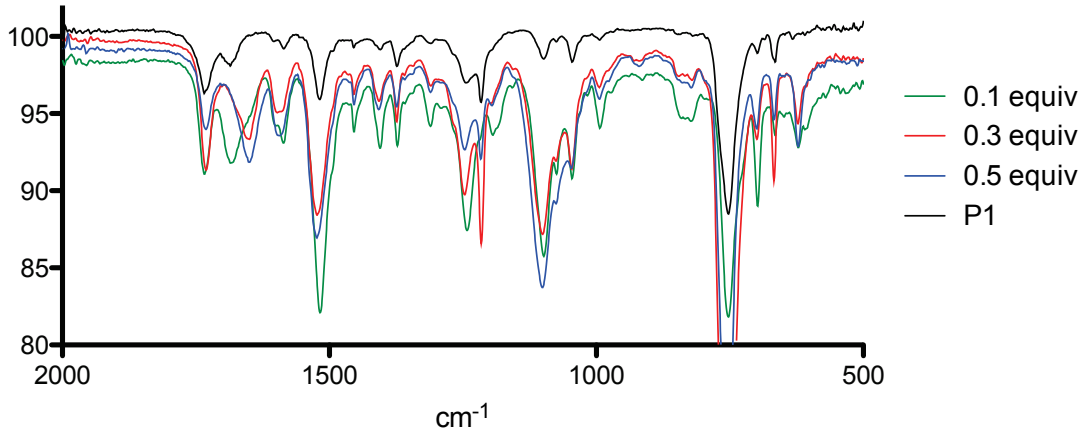
Table S1. FT-IR data of poly-(**1**) in solution (ATR/FT-IR).

POLYMER	υCO	υOMe	Δυ CO (Poly-1)- (Poly-1/M)	Δυ OMe (Poly-1)-(Poly-1/M)
Poly-**1**$_{(CHCl3)}$	1682	1099	0	0
Poly-**1**$_{(CHCl3)}$ + 0.5 equiv $Ag^+_{(THF)}$	1650	1098	+32	+1
Poly-**1**$_{(CHCl3)}$ + 0.5 equiv $Na^+_{(THF)}$	1672	1100	+10	-1
Poly-**1**$_{(CHCl3)}$ + 0.5 equiv $Li^+_{(THF)}$	1669	1100	+13	-1
Poly-**1**$_{(CHCl3)}$ + 0.05 equiv $Na^+_{(Pyridine)}$	1684	1099	+2	0
Poly-**1**$_{(CHCl3)}$ + $Na^+_{(DMSO)}$	1653	1089	+49	+10
Poly-**1**$_{(CHCl3)}$ + $Ba^{2+}_{(THF)}$	1665	1074	+17	+15
Poly-**1**$_{(CHCl3)}$ + $Ni^{2+}_{(THF)}$	1638	1074	+44	+15
Poly-**1**$_{(CHCl3)}$ + 10.0 equiv $Ag^+_{(MeCN)}$	1630	1070	+52	+29
Poly-**1**$_{(CHCl3)}$ + 2.0 equiv $Na^+_{(THF)}$	1670	1080	+12	+19
Poly-**1** + 2.0 equiv $Na^+_{(Pyridine)}$	1628	1067	+54	+32

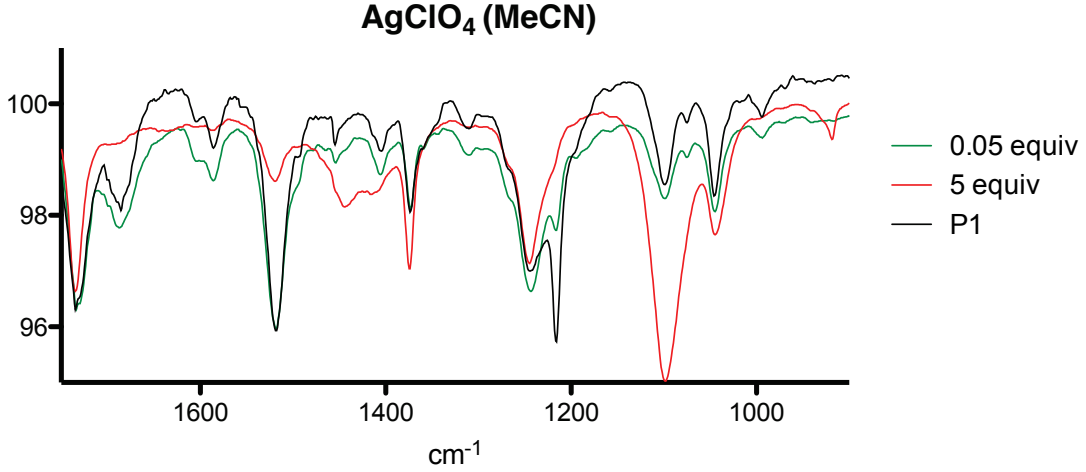
a)


LiClO4 (MeOH)
100
90
80
70
60
2000
1500
1000
500
cm-1
P1
0.1 equiv
0.3 equiv
0.5 equiv

b)


AgClO4 (MeOH)
100
95
90
85
80
2000
1500
1000
500
cm-1
0.1 equiv
0.3 equiv
0.5 equiv
P1

c)


AgClO4 (MeCN)
100
98
96
1600
1400
1200
1000
cm-1
0.05 equiv
5 equiv
P1

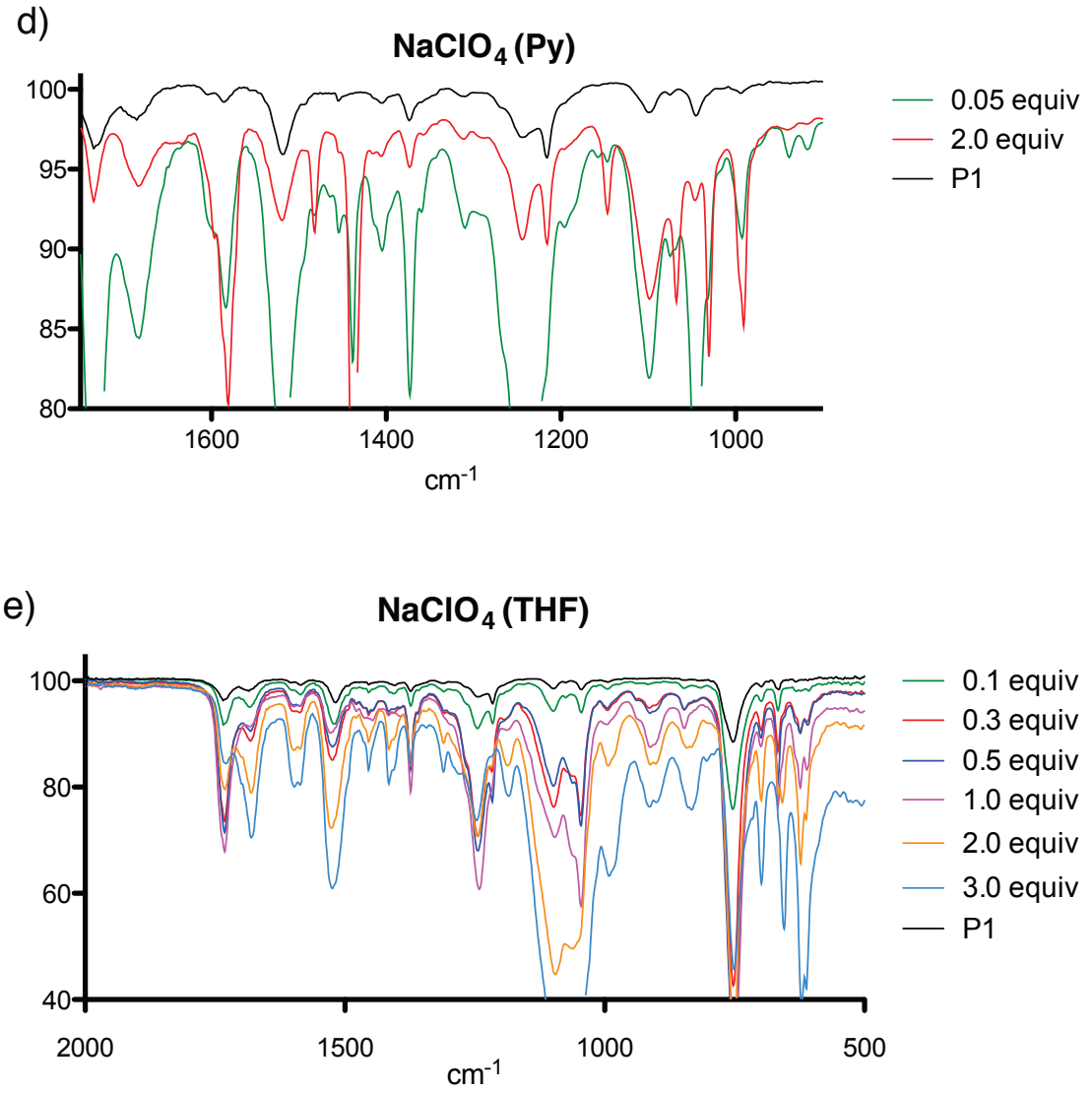


Figure S3: IR spectra of a solution of poly-**1** in $CHCl_3$ (3.0 mg/mL) titrated with different amounts of $MClO_4$ in different cosolvents: (a) $LiClO_4$ in MeOH (10 mg/mL), (b) $AgClO_4$ in MeOH, (10 mg/mL),(c) $AgClO_4$ in MeCN (10 mg/mL),(d) $NaClO_4$ in pyridine (10 mg/mL) and (e) $NaClO_4$ in THF (10 mg/mL).

2. Role of the metal ion in the helical structure of HPMCs

In order to determine the roles of the metal ion, the polymer and the cosolvent in the chiral amplification of poly-**1** towards the left- or right-handed helical structure in helical polymer-metal complexes (HPMCs), different titrations were done keeping constant two parameters and varying the third one (i.e., polymer,

metal ion, cosolvent).

All CD measures were performed in HPLC grade $CHCl_3$ filtered in basic alumina. The concentration of polymer-**1** was 0.1 and 0.3 mg/mL. The metal salts —$M(ClO_4)_2$ or $MClO_4$— were dissolved in different cosolvents (THF, MeOH, MeCN, DMF, DMSO, acetone, pyridine, piperidine…) obtaining final concentrations of 100, 50, 30, 10 and 5 mg/mL. These solutions were used to carry out titrations of poly-**1** in $CHCl_3$ to determine the response of the polymer to the metal ion.

2.1 CD/UV studies of *HPMCs (M= divalent metal ions)*

CD studies measured during a titration of a solution of poly-**1** in $CHCl_3$ (0.1 mg/mL) with different divalent metal ions (Ba^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Hg^{2+}, Pb^{2+}) in different cosolvents (THF, MeOH, MeCN, DMF, DMSO, acetone, pyridine, piperidine…) show a positive Cotton effect in the vinylic region indicating the presence of a right-handed helical structure. So, in presence of divalent metal ions, poly-**1** adopts always a right-handed helical structure independently on the amount of cosolvent added (see Figures S4-S9).

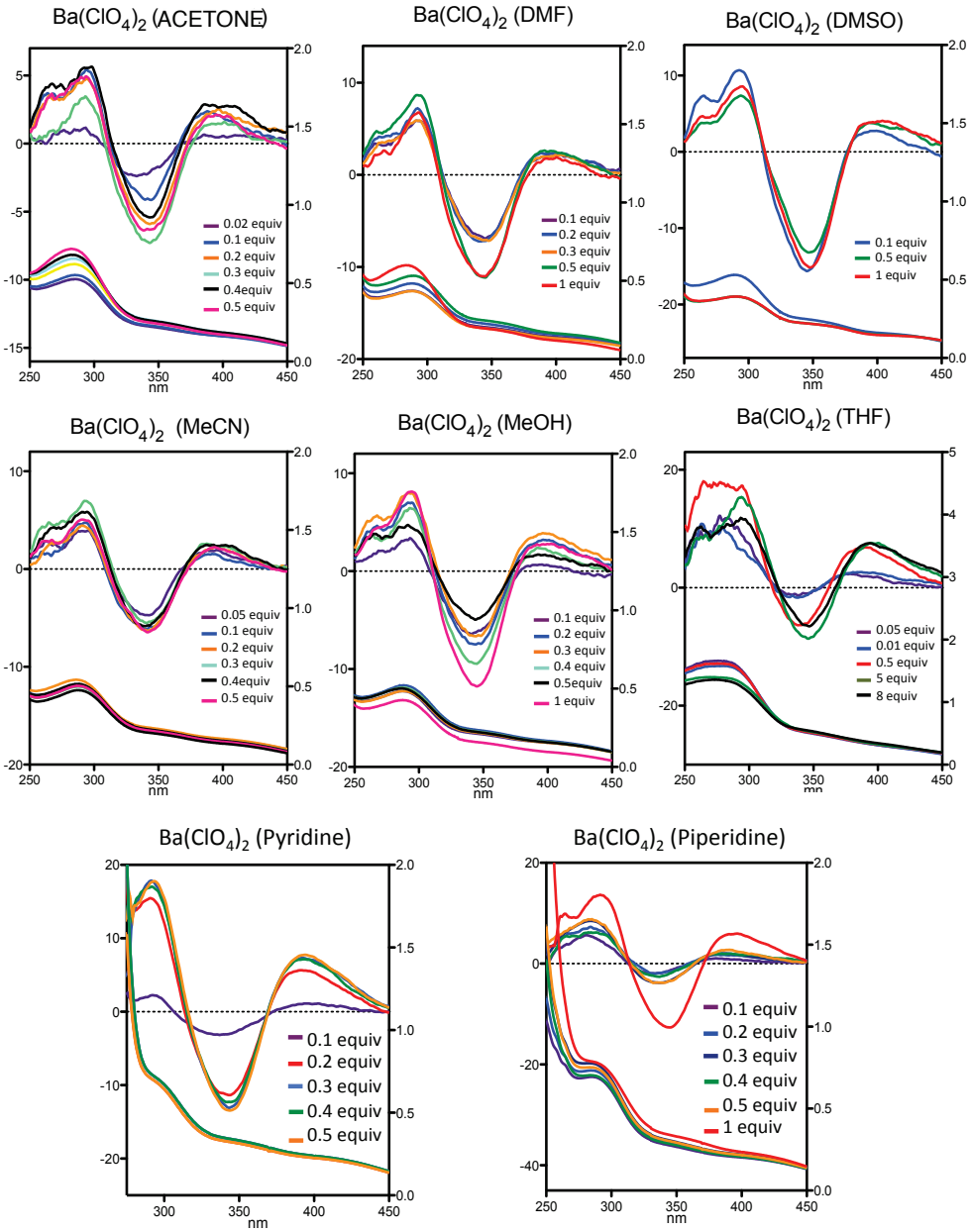


Figure S4: CD/UV spectra of a solution of poly-**1** (0.1 mg/mL in $CHCl_3$) titrated with different amounts of $Ba(ClO_4)_2$ in different cosolvents such as acetone, DMF, DMSO, MeCN, MeOH, THF, pyridine and piperidine (10 mg/mL). The mole number of poly-**1** is calculated based on the monomer repeating unit (mru).

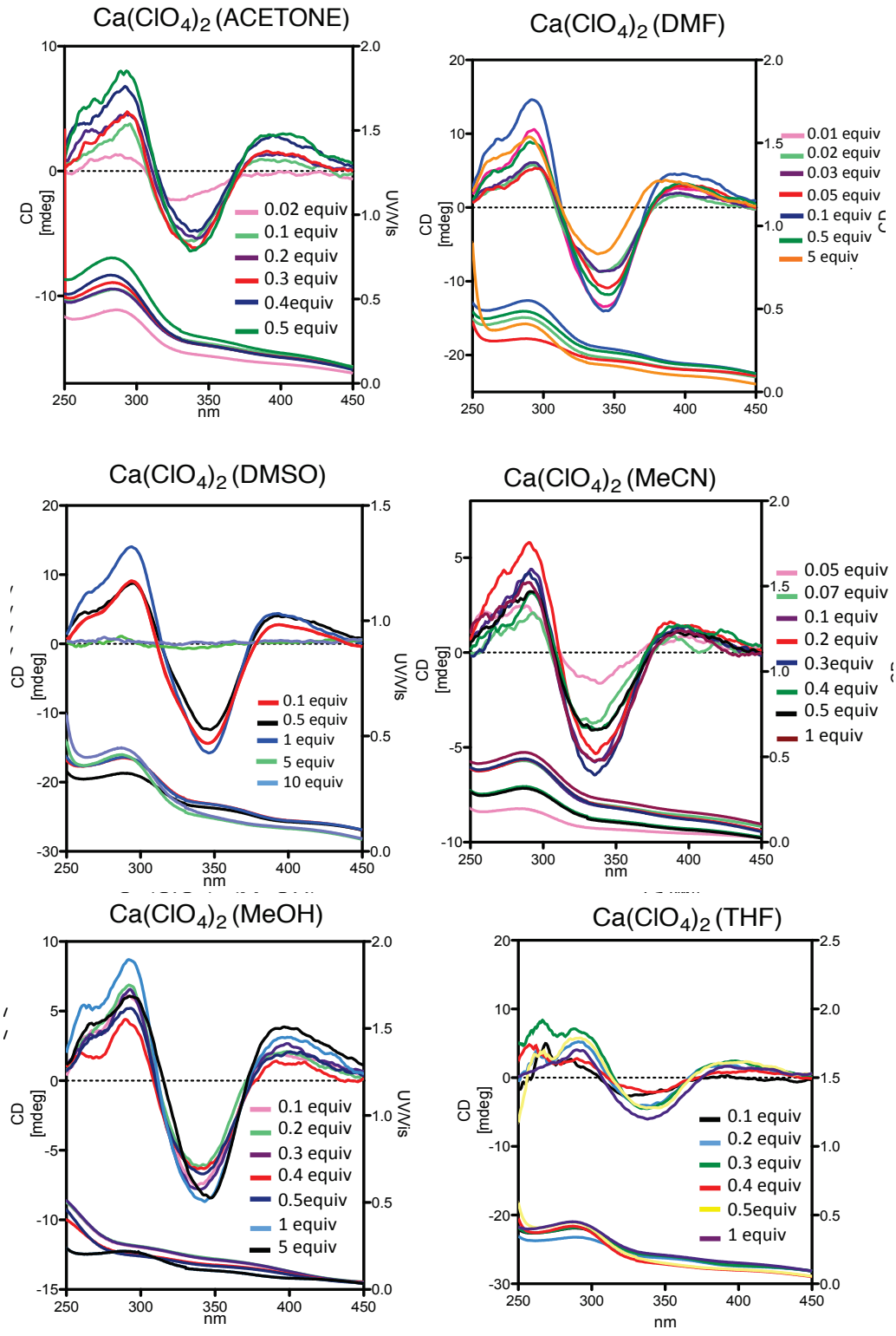


Figure S5: CD/UV spectra of a solution of poly-**1** (0.1 mg/mL in $CHCl_3$) titrated with different amounts of $Ca(ClO_4)_2$ in different cosolvents such as acetone, DMF, DMSO, MeCN, MeOH, THF, pyridine and piperidine (10 mg/mL). The mole number of poly-**1** is calculated based on the monomer repeating unit (mru).

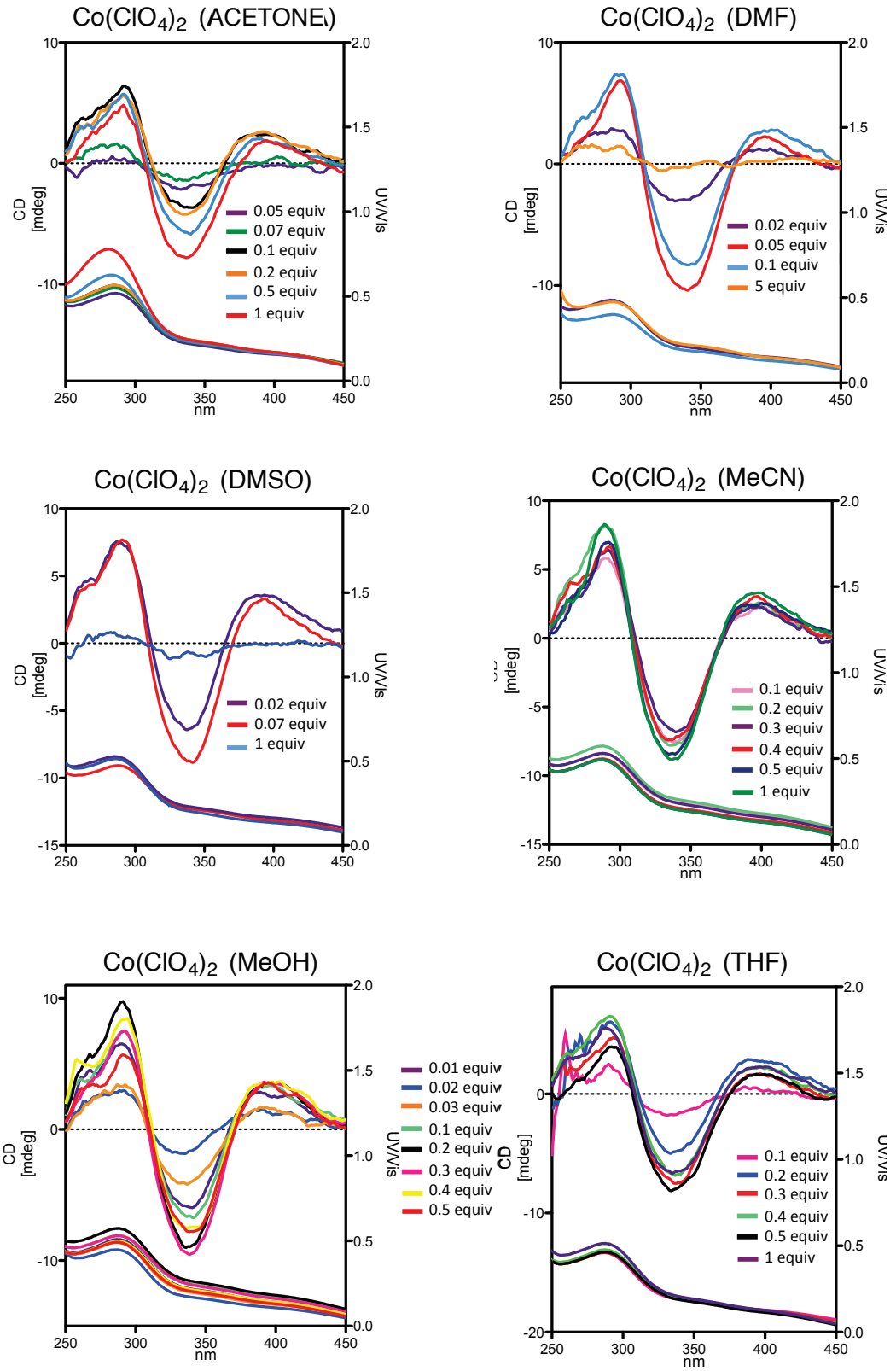


Figure S6: CD/UV spectra of a solution of poly-**1** (0.1 mg/mL in $CHCl_3$) titrated with different amounts of $Co(ClO_4)_2$ in different cosolvents such as acetone, DMF, DMSO, MeCN, MeOH, THF, pyridine and piperidine (10 mg/mL). The mole number of poly-**1** is calculated based on the monomer repeating unit (mru).

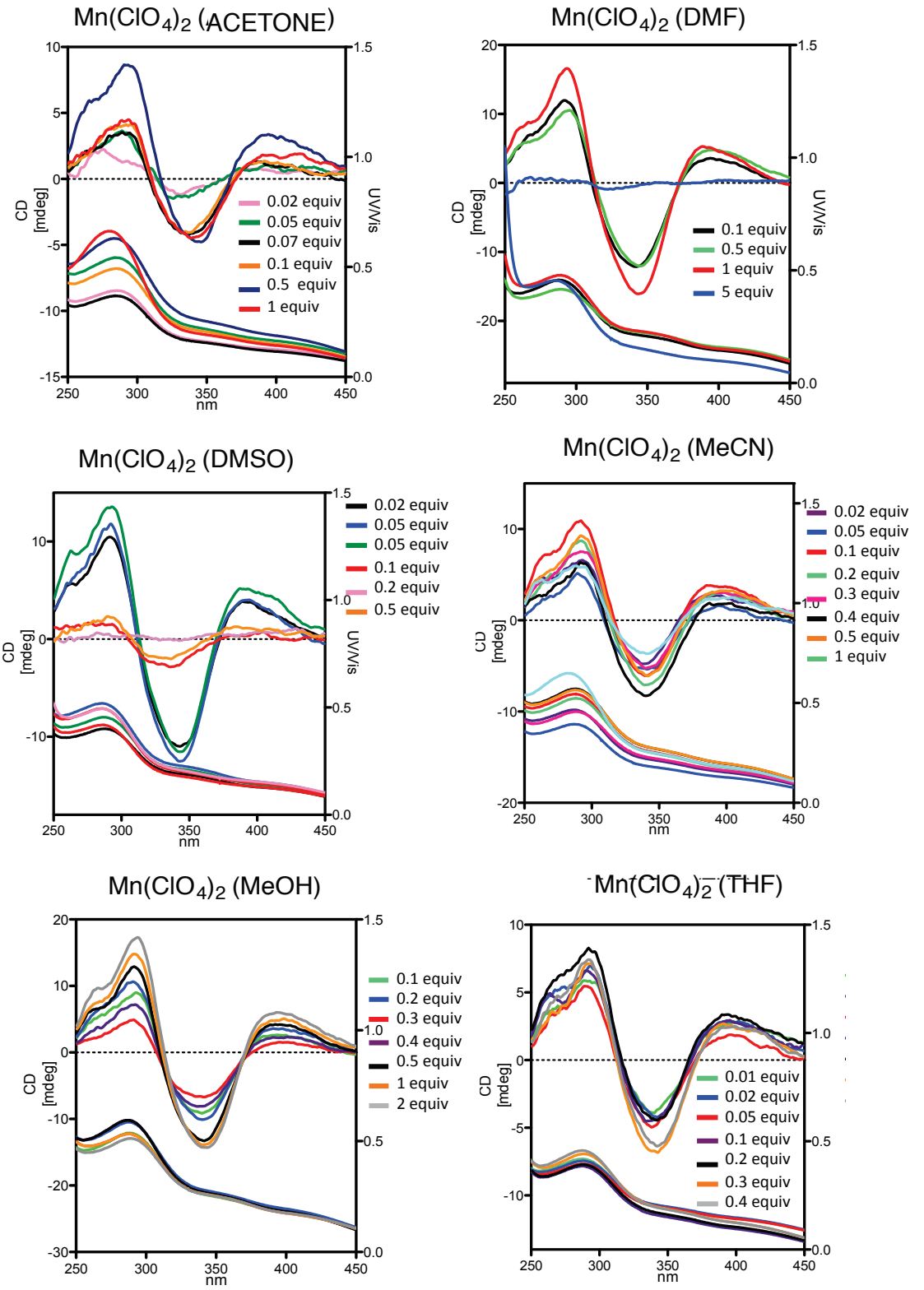


Figure S7: CD/UV spectra of a solution of poly-**1** (0.1 mg/mL in $CHCl_3$ titrated with different amounts of $Mn(ClO_4)_2$ in different cosolvents such as acetone, DMF, DMSO, MeCN, MeOH, THF, pyridine and piperidine (10 mg/mL). The mole number of poly-**1** is calculated based on the monomer repeating unit (mru).

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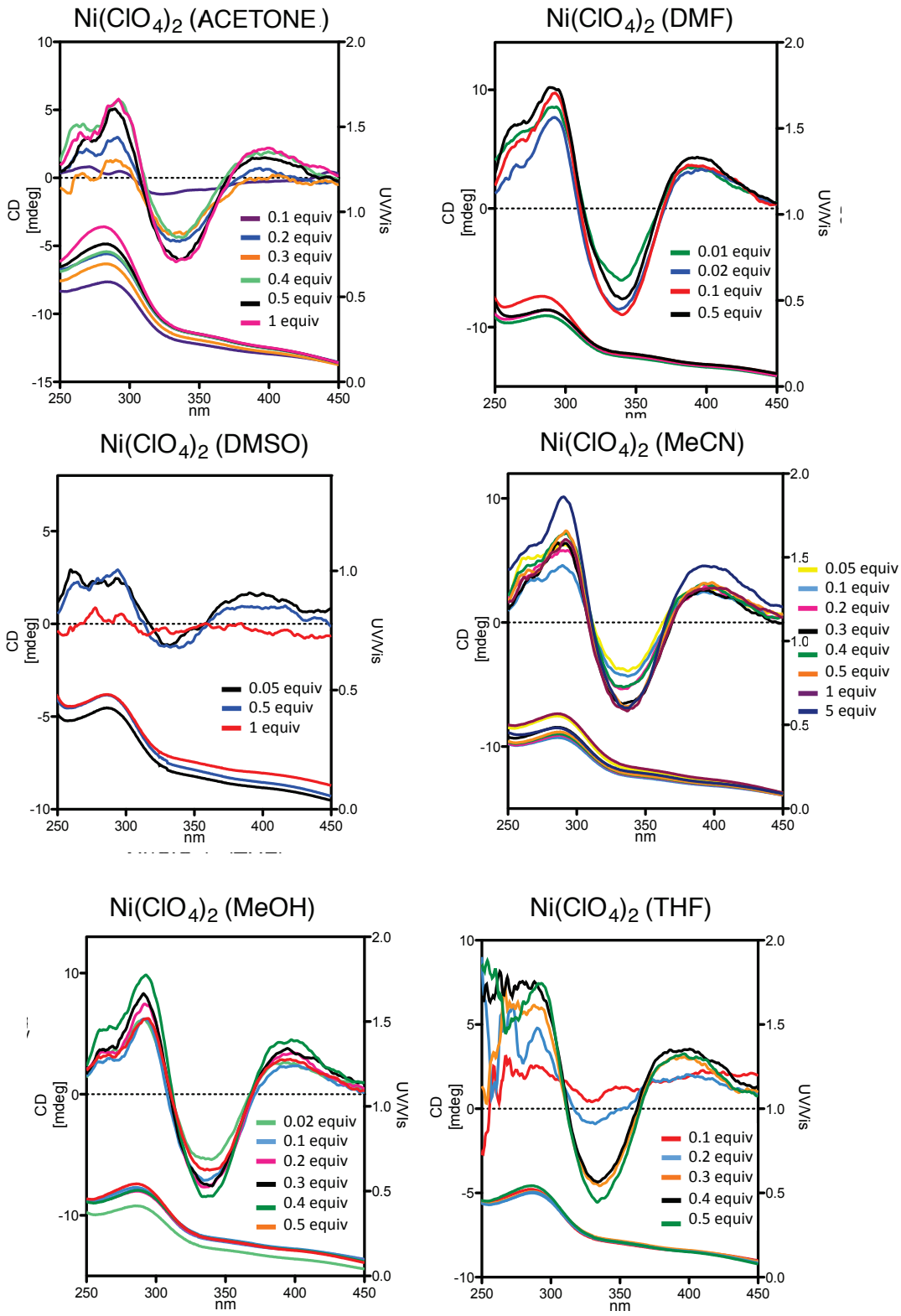


Figure S8: CD/UV spectra of a solution of poly-**1** (0.1 mg/mL in $CHCl_3$) titrated with different amounts of $Ni(ClO_4)_2$ in different cosolvents such as acetone, DMF, DMSO, MeCN, MeOH, THF, pyridine and piperidine (10 mg/mL). The mole number of poly-**1** is calculated based on the monomer repeating unit (mru).

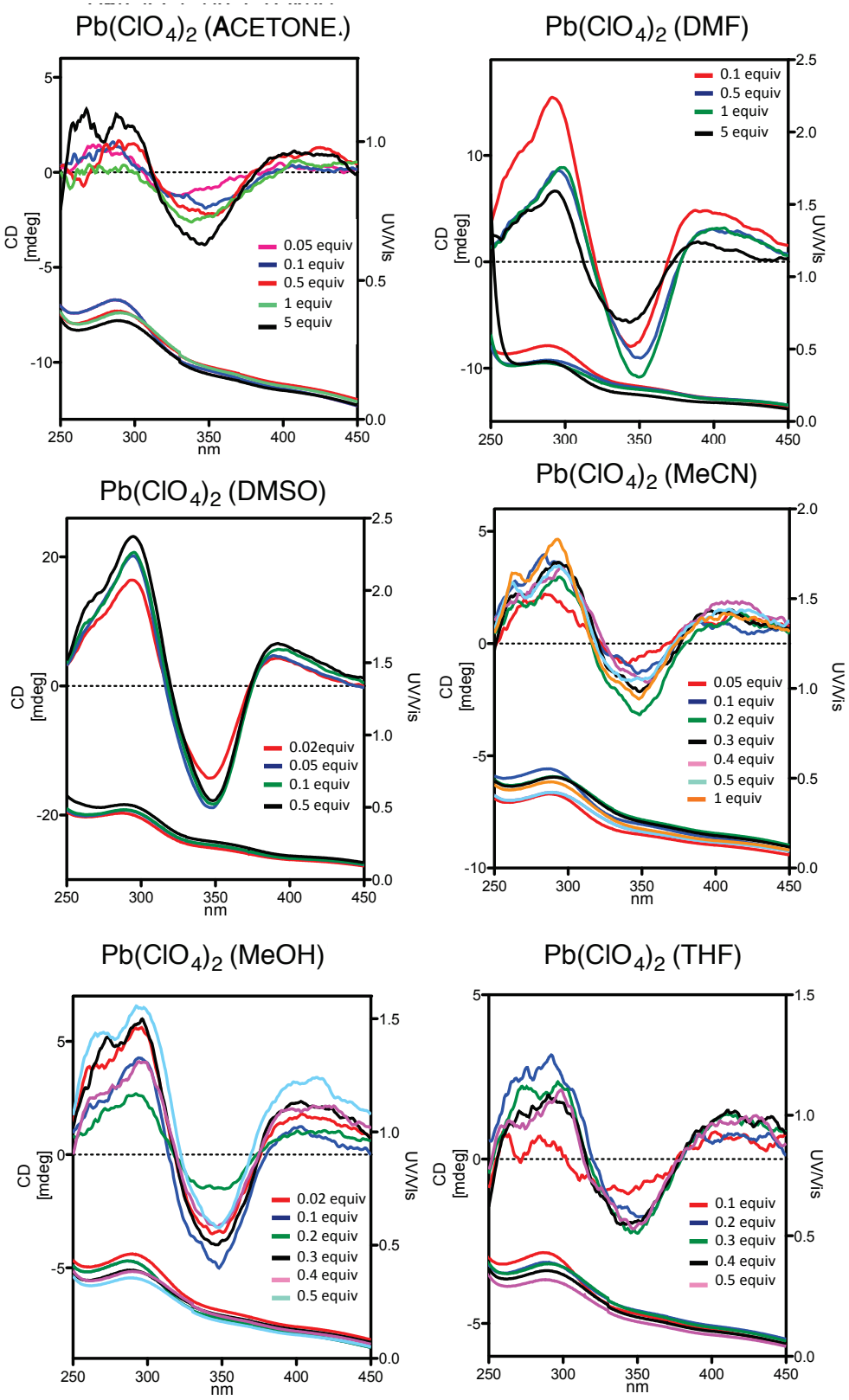


Figure S9: CD/UV spectra of a solution of poly-**1** (0.1 mg/mL in $CHCl_3$) titrated with different amounts of $Pb(ClO_4)_2$ in different cosolvents such as acetone, DMF, DMSO, MeCN, MeOH, THF, pyridine and piperidine (10 mg/mL). The mole number of poly-**1** is calculated based on the monomer repeating unit (mru).

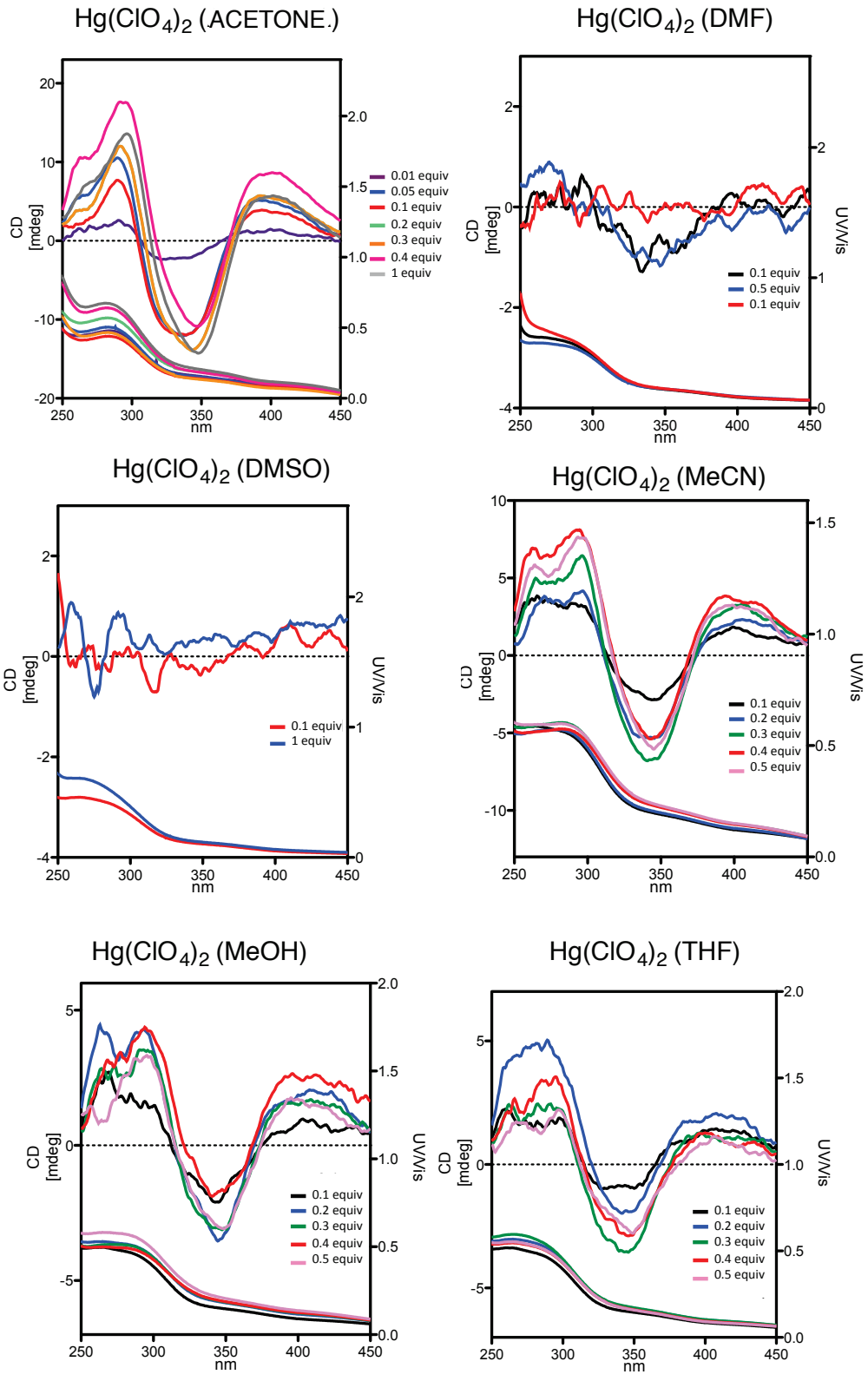


Figure S10: CD/UV spectra of a solution of poly-**1** (0.1 mg/mL in $CHCl_3$) titrated with different amounts of $Hg(ClO_4)_2$ in different cosolvents such as acetone, DMF, DMSO, MeCN, MeOH, THF, pyridine and piperidine (10 mg/mL). The mole number of poly-**1** is calculated based on the monomer repeating unit (mru).

2.2 CD/UV studies of HPMCs (M=monovalent metal ions)

Similar studies were carried out in the case of HPMCs of monovalent metal ions. Solutions of poly-**1** in $CHCl_3$ (0.1 mg/mL) were titrated with different monovalent metal ion solutions [$MClO_4$, M= Li^+, Ag^+ and Na^+, (10 mg/mL) in different cosolvents: acetone, DMF, DMSO, MeCN, MeOH, THF, pyridine and piperidine…]. The amount of metal ions added is calculated based on the monomer repeating units (mru) of poly-**1**.

2.2.1 HPMC (M= Li^+)

CD studies of a solution of poly-**1** in $CHCl_3$ (0.1 mg/mL) show a strong negative Cotton effect at the vinylic region when Li^+ is added in different cosolvents (i.e., acetone, DMF, DMSO, MeCN, MeOH, THF, pyridine and piperidine, 10 mg/mL). This fact indicates the presence of a left-handed helical structure, opposite to the one obtained with divalent metal ions. From these results it is possible to conclude that coordination of Li^+ to the pendant group is through the carbonyl group favouring the *ap* conformation and as a consequence, the left-handed helical structure.

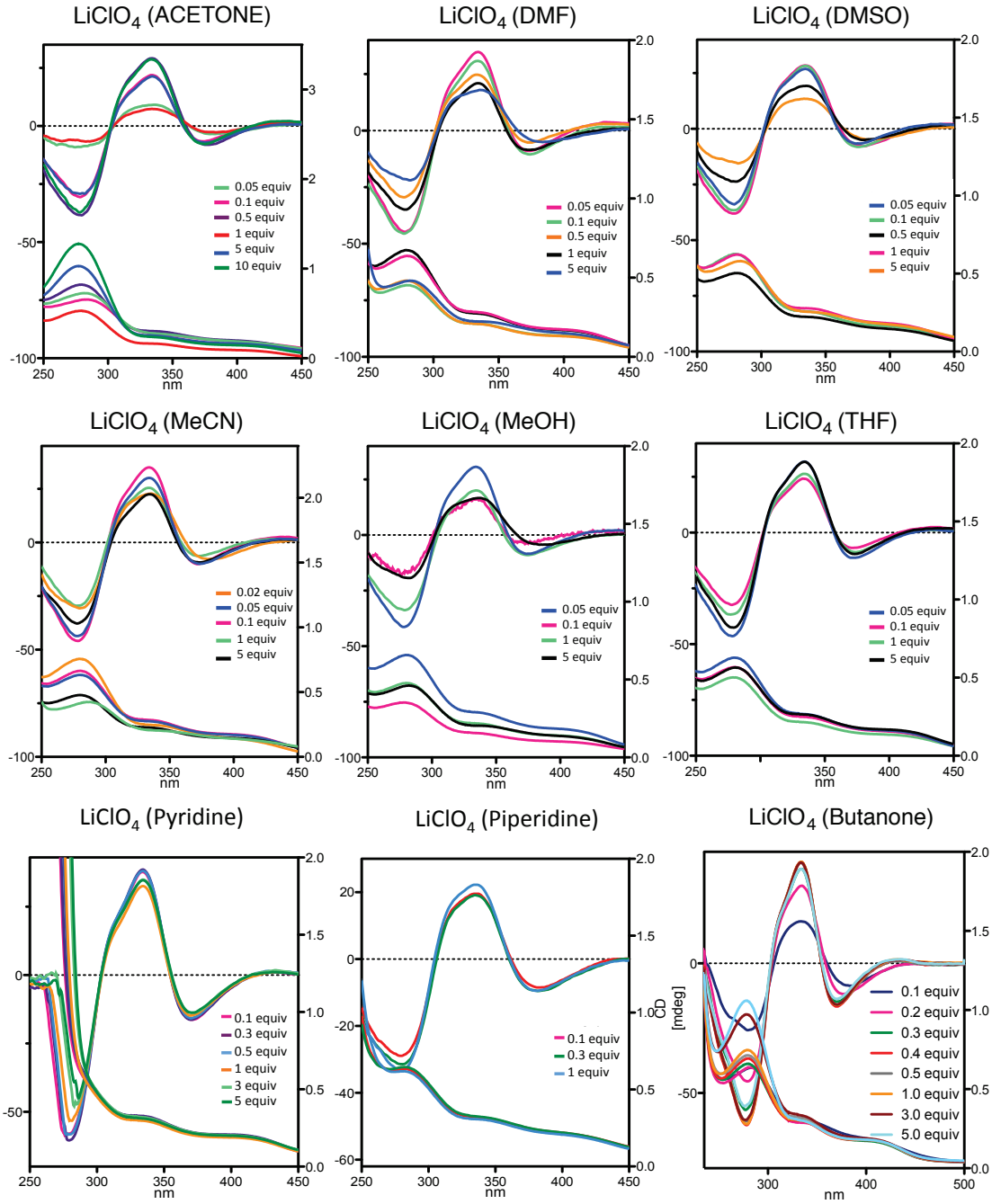


Figure S11: CD spectra of a solution of poly-**1** (0.1 mg/mL in $CHCl_3$) titrated with different amounts of $LiClO_4$, in different cosolvents (acetone, DMF, DMSO, MeCN, MeOH, THF, pyridine, piperidine and butanone); [poly-**1**] = $0.38 \cdot 10^{-3}$ M in $CHCl_3$.

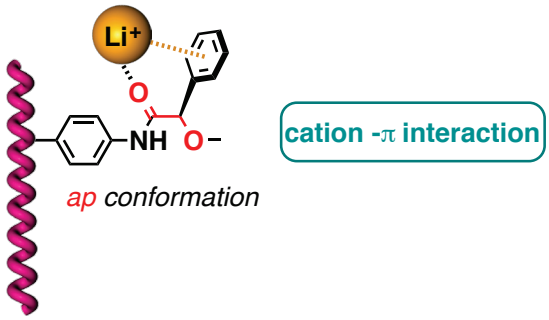
a) Cation–π interaction

In order to determine which factor determines the different coordination modes of monovalent and divalent metal ions, a deeper conformational study was performed additionally to the IR studies (see above and main manuscript text).

^{7}Li-NMR experiments were carried out in a Varian Inova 500 spectrometer (11.74 T) using as a reference LiCl in D_2O (9.7M) and for ^{1}H-NMR the Varian Mercury 300 spectrometer (7.04 T).

To determine the conformation at the pendant moiety, a solution of poly-**1** in $CDCl_3$ (3.0 mg/mL) was titrated with solutions of $LiClO_4$ in CD_3OD (10 mg/mL). ^{7}Li-NMR spectrum of a solution of poly-**1** in $CDCl_3$ (3.0 mg/mL) with 0.1 equiv. of $LiClO_4$ in CD_3OD (10 mg/mL) shows a strong shielding in the ^{7}Li chemical shift, which is typical when the metal ions is involved in cation-π interaction.[ii] From this chemical shift we can also predict that the metal ion is interacting with only one aryl ring (Figure S12). ^{1}H-NMR corroborates the presence of this interaction: the proton signals of the MPA Ph group are upfield shifted related to those without metal (Figure S13b).

a)



b) **^{7}Li-NMR: presence of cation–π interaction**

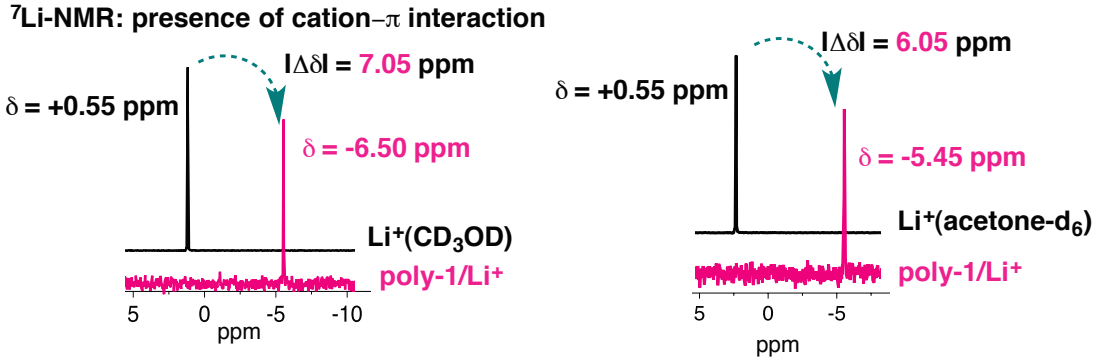


Figure S12: a) Chiral amplification of poly-**1** with Li^+ with an *ap* conformation stabilized by cation-π interactions. b) ^{7}Li-NMR showing the shifts due to cation-π interactions; [poly-**1**]= 3.0 mg/mL $CHCl_3$, [$LiClO_4$] = 10 mg /mL in CD_3OD, acetone-d_6.

The presence of *ap* conformation was corroborated also by ^{1}H NMR, that shows a deshielding at the OMe and a shielding at the CαH once the metal ion is added. These shifts are in full agreement with the adoption of an *ap* conformation at the MPA moiety (Figures S13a and S13c).

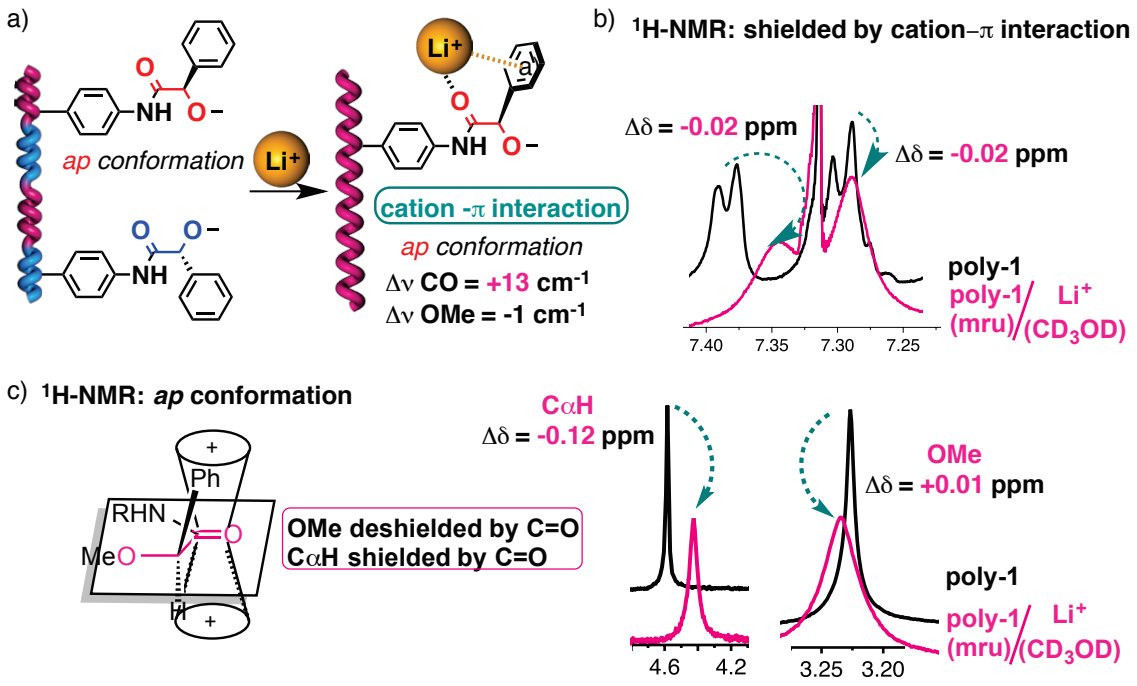


Figure S13: Chiral amplification of poly-**1** with Li^+. a) *ap* conformation stabilized by cation-π as determined by IR. b) ^{1}H NMR showing the cation-π interactions. c) ^{1}H-NMR showing the conformational change at the pendant moiety; [poly-**1**]= 3.0 mg/mL $CHCl_3$, [$LiClO_4$] = 10 mg /mL in CD_3OD.

2.2.2 HPMCs (M= Na^+)

Solutions of poly-**1** in $CHCl_3$ (0.1 mg/mL) were titrated with different solutions of $NaClO_4$ [100, 50, 30, 10 and 5 mg/mL] in different cosolvents (acetone, DMF, DMSO, MeCN, MeOH, THF, pyridine, piperidine, methyl isobutyl ketone, propanone). The amount of metal ions added is calculated based on the monomer repeating units (mru) of poly-**1**.

CD studies of poly-**1** with Na^+ in DMF and DMSO show always a positive Cotton effect at the vinylic region indicating the presence of a right-handed helical structure. So, Na^+ HPMCs adopt always a right-handed helical structure independently on the amount of those cosolvents added (Figure S14).

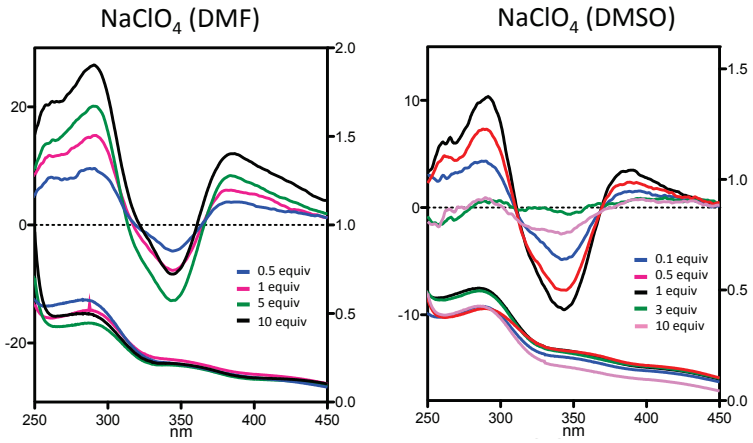


Figure S14: CD/UV spectra of a solution of poly-**1** (0.1 mg/mL in $CHCl_3$) titrated with different amounts $NaClO_4$, in DMF and DMSO as cosolvents; [poly-**1**] = $0.38 \cdot 10^{-3}$ M in $CHCl_3$.

Different results were obtained when the metal ion is dissolved in cosolvents such as pyridine, piperidine, THF, MeOH, butanone, methyl isobutyl ketone, amongst others, where a dual response of the polymer was observed. Thus, the left- or right-handed helical structures can selectively be induced by the amount of the cosolvent (e.g., pyridine) present in the chloroform solution of the HPMC due to the presence or absence of a cation-π interaction.[iii] Thus, in chloroform solutions of poly-**1**/Na^+ (0.3 mg/ml) where the poly-**1** (mru)/cosolvent ratio is 1/<100 (mol/mol), the polymer adopts a left-handed helical structure, but if the ratio is 1/>100 (mol/mol), the polymer adopts a right-handed helical structure (Figure S15).

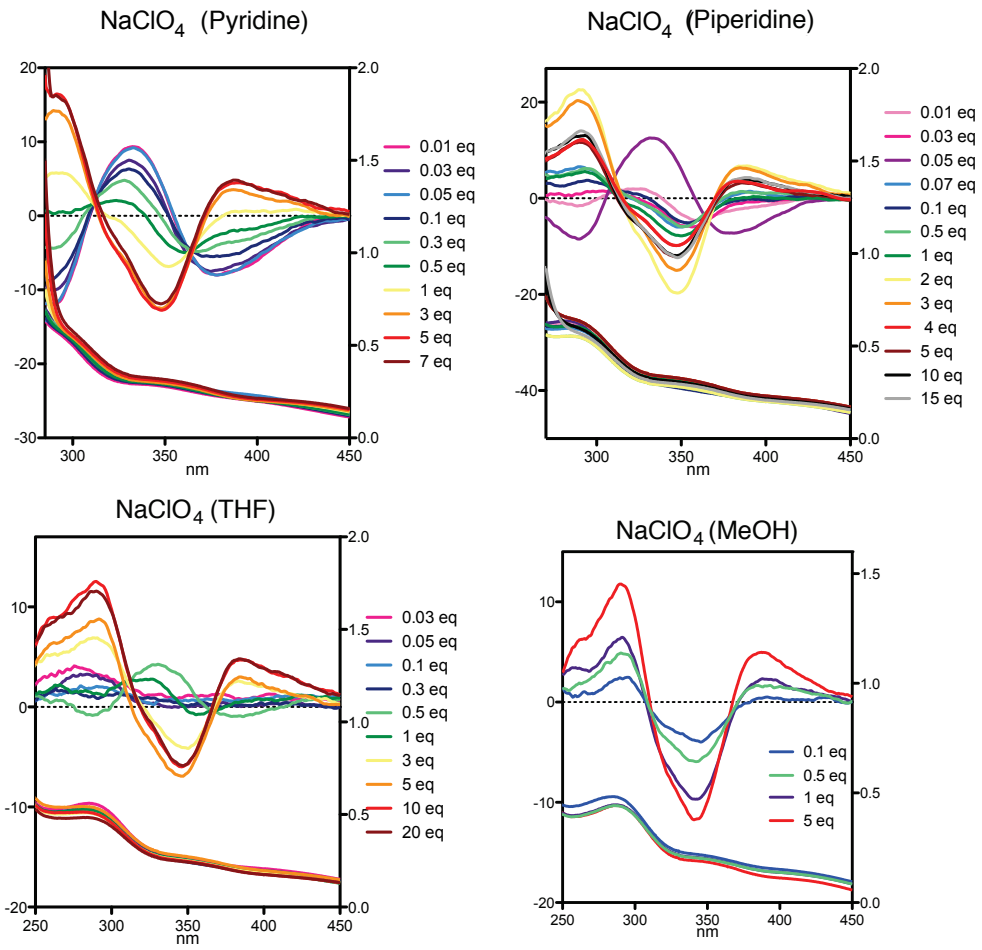


Figure S15: CD/UV spectra of a solution of poly-**1** (0.1 mg/mL in $CHCl_3$) titrated with different amounts $NaClO_4$, in different cosolvents (pyridine, piperidine, THF and MeOH); [poly-**1**] = $0.38 \cdot 10^{-3}$ M in $CHCl_3$.

Other experiments were performed to determine the role of the metal ion in the helical polymer-metal complex. So, the concentrations of both a solution of poly-**1** [0.3 mg/mL in $CHCl_3$, c_{poly}= $1.13 \cdot 10^{-3}$ M] and a solution of cosolvent [MeOH, $c_{cosolv.}$= $34.19 \cdot 10^{-3}$ M; i.e., 1,4 μL MeOH in 1 mL of $CHCl_3$] were kept constant. In order to avoid as much as possible the cosolvent effect (see below), we decided to use a minimum practical amount of cosolvent $c_{cosolv.}$= $34.19 \cdot 10^{-3}$ M, *i.e.* 1,4 μL of MeOH per 1mL of $CHCl_3$ (1.4% v/v) (Figure S16, Table S2).

During those studies, we could observe that the addition of a small amount of monovalent metal ion, [e.g. poly-**1** (mru)/Na^+ ratio= 1.00/0.01 (mol/mol)] induces a left-handed helical structure (CD signature< 0,

anisotropy factor $g_{380nm} < 0$, Figure S16a) due to the presence of cation-π interaction, whereas the addition of a small amount of a divalent metal ion [e.g. poly-**1** (mru)/Ba^{2+} ratio= 1.000/0.004 (mol/mol)] induces a right-handed helical structure in poly-**1** (CD signature> 0, anisotropy factor $g_{380nm} > 0$, Figure S16b] due to the absence of cation-π interaction. Further additions of monovalent or divalent metal ions to the polymer solutions do not produce any effect on the CD spectra indicating that in absence or small amounts of a cosolvent, monovalent metal ions fix the *ap* conformation of the pendant, while divalent metal ions fix the *sp* conformation through a chiral amplification effect (Figure S16 and Table S2), where a small amount of the inducer (less than 5%) is needed to obtain the highest response from the polymer.

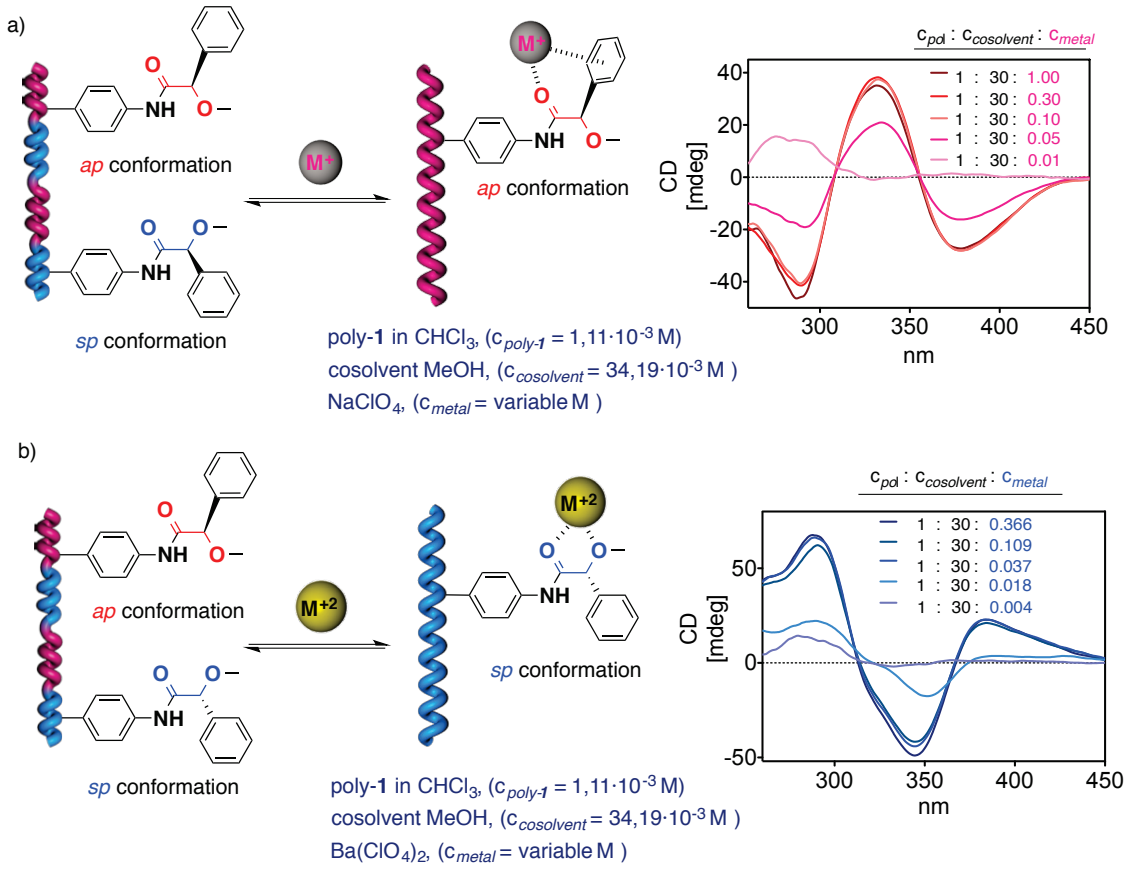


Figure S16: Effect of metal ions in the chiral amplification of poly-**1.** (a) Monovalent (Na^+) and (b) divalent (Ba^{2+}) metal ions.

Table S2: Effect of metal ions in helical polymer-metal complexes.

$C_{polymer}$[a]	$C_{cosolvent}$	C_{metal} [Ba^{2+}]	$C_{pol.}$: $C_{cosol.}$: $C_{met.}$[b]	$g_{(384nm)}$
$1.13 \cdot 10^{-3}$	$34.19 \cdot 10^{-3}$	$0.411 \cdot 10^{-3}$	1 : 30 : 0.366	+
$1.13 \cdot 10^{-3}$	$34.19 \cdot 10^{-3}$	$0.123 \cdot 10^{-3}$	1 : 30 : 0.109	+
$1.13 \cdot 10^{-3}$	$34.19 \cdot 10^{-3}$	$0.041 \cdot 10^{-3}$	1 : 30 : 0.037	+
$1.13 \cdot 10^{-3}$	$34.19 \cdot 10^{-3}$	$0.020 \cdot 10^{-3}$	1 : 30 : 0.018	+
$1.13 \cdot 10^{-3}$	$34.19 \cdot 10^{-3}$	$0.004 \cdot 10^{-3}$	1 : 30 : 0.004	+
$C_{polymer}$	$C_{cosolvent}$	C_{metal} [Na^{+}]	$C_{pol.}$: $C_{cosol.}$: $C_{met.}$	$g_{(384nm)}$
$1.13 \cdot 10^{-3}$	$34.19 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	1 : 30 : 1.0	-
$1.13 \cdot 10^{-3}$	$34.19 \cdot 10^{-3}$	$0.34 \cdot 10^{-3}$	1 : 30 : 0.3	-
$1.13 \cdot 10^{-3}$	$34.19 \cdot 10^{-3}$	$0.11 \cdot 10^{-3}$	1 : 30 : 0.1	-
$1.13 \cdot 10^{-3}$	$34.19 \cdot 10^{-3}$	$0.06 \cdot 10^{-3}$	1 : 30 : 0.05	-
$1.13 \cdot 10^{-3}$	$34.19 \cdot 10^{-3}$	$0.01 \cdot 10^{-3}$	1 : 30 : 0.01	-

[a] $c_{polymer}$ is calculated based on the molecular weight of the monomer repeating unit (mru). [b] pol. = polymer (poly-**1**), cosolv. = cosolvent (MeOH), met.= metal.

a) Role of the cosolvent in the helical structure

To evaluate the role of the cosolvent in the chiral amplification phenomenon, a titration keeping constant the concentrations of both the polymer (0.3 mg/ mL $CHCl_3$, $c_{poly}=1.13 \cdot 10^{-3}$ M) and the metal ion (c_{metal}= 0.34 M for Ba^{2+}, Li^{+} and Na^{+}) and varying the concentration of the cosolvent (MeOH, $c_{cosolv.}$= variable) was performed. During those studies, it was observed that in the case of HPMCs of divalent metal ions, the polymer adopts always a right-handed helical structure through a chiral amplification effect (CD positive at the vinylic region, $g_{384nm} > 0$), independently of the amount of cosolvent used (Figure S17, Table S3). This fact indicates that the cosolvent does not have any effect in the chiral amplification process with divalent metal ions.

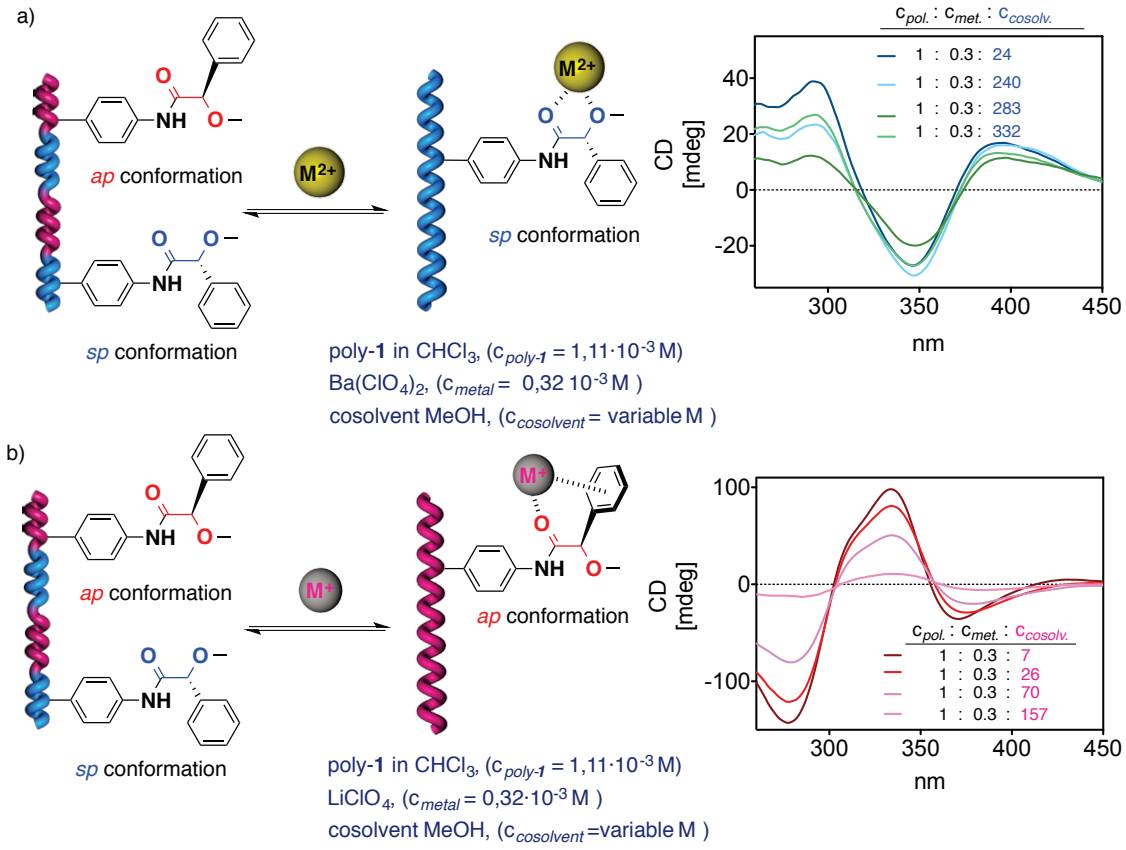


Figure S17: Cosolvent effect in the chiral amplification of poly-**1** with (a) divalent (Ba^{2+}) and (b) monovalent (Li^{+}) metal ions.

Table S3: Cosolvent effect (MeOH) in the helical structure of HPMCs.

$C_{polymer}$	C_{metal} [Ba^{2+}]	$C_{cosolvent}$	$C_{pol.}$: $C_{met.}$: $C_{cosol.}$ [a]	$g_{(384nm)}$
$1.13\cdot10^{-3}$	$0.34\cdot10^{-3}$	$28.2\cdot10^{-3}$	1 : 0.3 : 24	+
$1.13\cdot10^{-3}$	$0.34\cdot10^{-3}$	$93.9\cdot10^{-3}$	1 : 0.3 : 83	+
$1.13\cdot10^{-3}$	$0.34\cdot10^{-3}$	$281.7\cdot10^{-3}$	1 : 0.3 : 249	+
$1.13\cdot10^{-3}$	$0.34\cdot10^{-3}$	$563.5\cdot10^{-3}$	1 : 0.3 : 499	+
$1.13\cdot10^{-3}$	$0.34\cdot10^{-3}$	2.81	1 : 0.3 : 2492	+
$C_{polymer}$	C_{metal} [Li^{+}]	$C_{cosolvent}$	$C_{pol.}$: $C_{met.}$: $C_{cosol.}$ [a]	$g_{(384nm)}$
$1.13\cdot10^{-3}$	$0.34\cdot10^{-3}$	$8,91\cdot10^{-3}$	1 : 0.3 : 8	-
$1.13\cdot10^{-3}$	$0.34\cdot10^{-3}$	$29.7\cdot10^{-3}$	1 : 0.3 : 26	-
$1.13\cdot10^{-3}$	$0.34\cdot10^{-3}$	$89.12\cdot10^{-3}$	1 : 0.3 : 79	-
$1.13\cdot10^{-3}$	$0.34\cdot10^{-3}$	$170\cdot10^{-3}$	1 : 0.3 : 158	-
$1.13\cdot10^{-3}$	$0.34\cdot10^{-3}$	$891\cdot10^{-3}$	1 : 0.3 : 789	-

Another interesting effect was observed during the study of the role of cosolvents in HPMCs of monovalent metal ions. While with Li^+, the chiral amplification effect towards the left-handed helical structure is independent of the cosolvent (similarly to the behavior of divalent metal ions), this is not the case when Na^+ or Ag^+ are employed.

So, titrations of different polymer/metal solutions [poly-**1** (mru)/Na^+ ratio= 1.0/0.2; 1.0/0.3; 1.0/0.5 and 1.0/1.0 (mol/mol)] with MeOH (i.e., cosolvent) were carried out (Figure S18, Table S4). The concentration of the polymer was kept constant (c_{poly} =$1.13 \cdot 10^{-3}$ M), and the concentration of the metal ion was also kept constant for each titration [$c_{metal\ (Na+)} = 0.23 \cdot 10^{-3}$ M in the poly-**1** (mru)/Na^+ ratio= 1.0/0.2 (mol/mol), $c_{metal\ (Na+)} = 0.34 \cdot 10^{-3}$ M in the poly-**1** (mru)/Na^+ ratio= 1.0/0.3 (mol/mol), $c_{metal\ (Na+)} = 0.56 \cdot 10^{-3}$ M in the poly-**1** (mru)/Na^+ ratio = 1.0/0.5 (mol/mol) and $c_{metal\ (Na+)} = 1.13 \cdot 10^{-3}$ M in the poly-**1** (mru)/Na^+ ratio = 1.0/1.0 (mol/mol)]. During those titrations, a helical inversion from the left-handed towards the right-handed helical structure was observed. This phenomenon occurs at the same ratio between the poly-**1** (mru)/ MeOH [i.e., 1/ 100 (mol/mol)] indicating the limit where the Na^+-π interaction is broken (Figure S18, Table S4).

In the case of Ag^+, this behavior was observed just when MeCN was used as cosolvent (see below), but in the Na^+ this phenomenon was observed in almost all the cosolvents used [MeOH, THF, acetone, pyridine, piperidine amongst others] (see below).

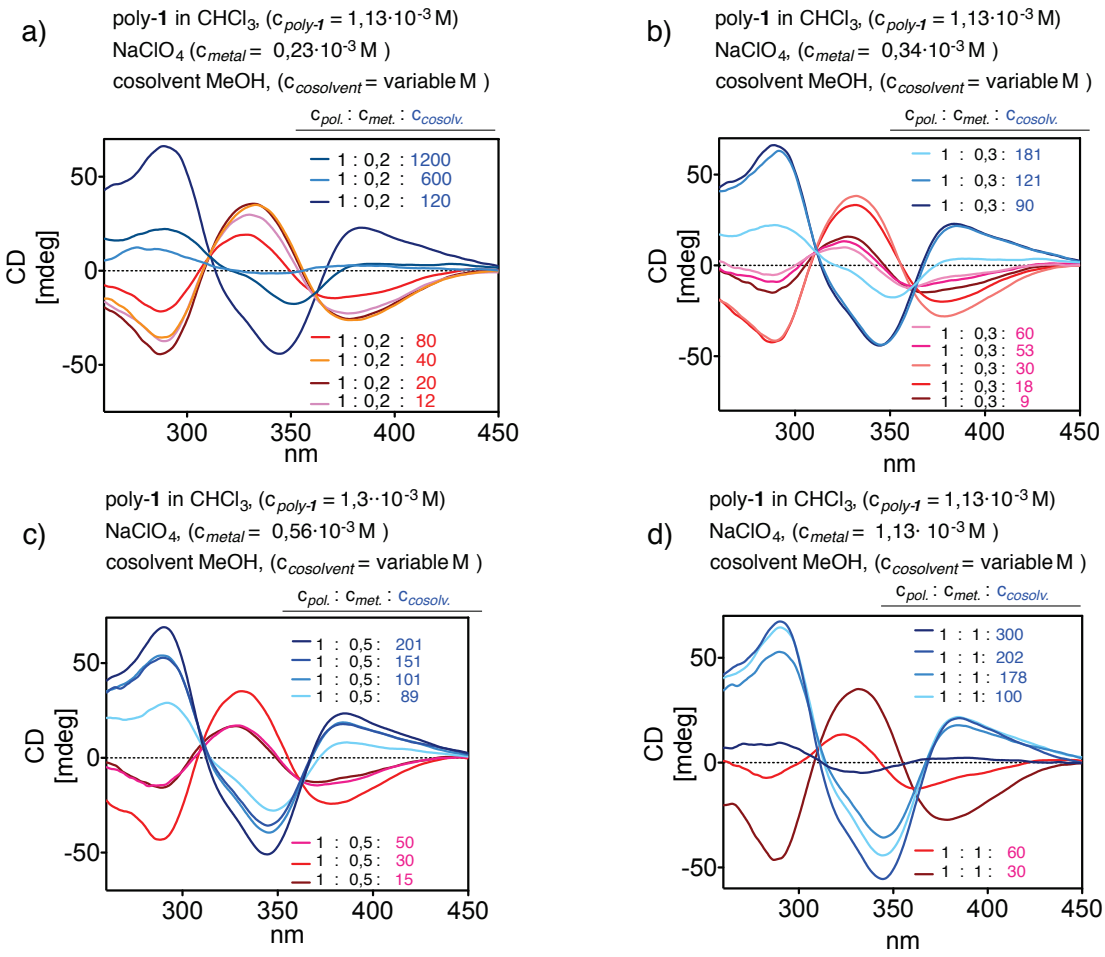


Figure S18: Cosolvent effect in Na^+ HPMCs at different poly-**1** (mru)/Na^+ ratios; (a) 1.0/0.2 (mol/mol), (b) 1.0/0.3 (mol/mol), (c) 1.0/0.5 (mol/mol) and (d) 1.0/1.0 (mol/mol).

Table S4: Cosolvent effect (MeOH) in helical polymer-metal complex structures.

Experiment	$C_{polymer}$	C_{metal} [Na^+]	$C_{cosolvent}$	$C_{pol.}$: $C_{met.}$: $C_{cosol.}$ [a]	$g_{(384nm)}$
Experiment 1	$1.13 \cdot 10^{-3}$	$0.23 \cdot 10^{-3}$	$13.67 \cdot 10^{-3}$	1 : 0.2: 12	-
Experiment 1	$1.13 \cdot 10^{-3}$	$0.23 \cdot 10^{-3}$	$22.79 \cdot 10^{-3}$	1 : 0.2: 20	-
Experiment 1	$1.13 \cdot 10^{-3}$	$0.23 \cdot 10^{-3}$	$45.59 \cdot 10^{-3}$	1 : 0.2: 40	-
Experiment 1	$1.13 \cdot 10^{-3}$	$0.23 \cdot 10^{-3}$	$91.12 \cdot 10^{-3}$	1 : 0.2: 80	-
Experiment 1	$1.13 \cdot 10^{-3}$	$0.23 \cdot 10^{-3}$	$136.6 \cdot 10^{-3}$	1 : 0.2: 120	+
Experiment 1	$1.13 \cdot 10^{-3}$	$0.23 \cdot 10^{-3}$	$683.78 \cdot 10^{-3}$	1 : 0.2: 600	+
Experiment 1	$1.13 \cdot 10^{-3}$	$0.23 \cdot 10^{-3}$	$1.367 \cdot 10^{-3}$	1 : 0.2: 1200	+

Experiment 2	$1.13 \cdot 10^{-3}$	$0.34 \cdot 10^{-3}$	$10.26 \cdot 10^{-3}$	1 : 0.3 : 9	-
Experiment 2	$1.13 \cdot 10^{-3}$	$0.34 \cdot 10^{-3}$	$20.51 \cdot 10^{-3}$	1 : 0.3 : 18	-
Experiment 2	$1.13 \cdot 10^{-3}$	$0.34 \cdot 10^{-3}$	$34.19 \cdot 10^{-3}$	1 : 0.3 : 30	-
Experiment 2	$1.13 \cdot 10^{-3}$	$0.34 \cdot 10^{-3}$	$60.33 \cdot 10^{-3}$	1 : 0.3 : 53	+
Experiment 2	$1.13 \cdot 10^{-3}$	$0.34 \cdot 10^{-3}$	$68.38 \cdot 10^{-3}$	1 : 0.3 : 60	+
Experiment 2	$1.13 \cdot 10^{-3}$	$0.34 \cdot 10^{-3}$	$102.57 \cdot 10^{-3}$	1 : 0.3 : 90	+
Experiment 2	$1.13 \cdot 10^{-3}$	$0.34 \cdot 10^{-3}$	$136.76 \cdot 10^{-3}$	1 : 0.3 : 120	+
Experiment 3	$1.13 \cdot 10^{-3}$	$0.56 \cdot 10^{-3}$	$17.10 \cdot 10^{-3}$	1 : 0.5 : 15	-
Experiment 3	$1.13 \cdot 10^{-3}$	$0.56 \cdot 10^{-3}$	$34.19 \cdot 10^{-3}$	1 : 0.5 : 30	-
Experiment 3	$1.13 \cdot 10^{-3}$	$0.56 \cdot 10^{-3}$	$56.98 \cdot 10^{-3}$	1 : 0.5 : 50	-
Experiment 3	$1.13 \cdot 10^{-3}$	$0.56 \cdot 10^{-3}$	$100.5 \cdot 10^{-3}$	1 : 0.5 : 89	+
Experiment 3	$1.13 \cdot 10^{-3}$	$0.56 \cdot 10^{-3}$	$114.0 \cdot 10^{-3}$	1 : 0.5 : 101	+
Experiment 3	$1.13 \cdot 10^{-3}$	$0.56 \cdot 10^{-3}$	$170.9 \cdot 10^{-3}$	1 : 0.5 : 151	+
Experiment 3	$1.13 \cdot 10^{-3}$	$0.56 \cdot 10^{-3}$	$224.9 \cdot 10^{-3}$	1 : 0.5 : 199	+
Experiment 4	$1.13 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$34.18.10^{-3}$	1 : 1: 30	-
Experiment 4	$1.13 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$68.38 \cdot 10^{-3}$	1 : 1: 60	-
Experiment 4	$1.13 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$113.96 \cdot 10^{-3}$	1 : 1: 100	+
Experiment 4	$1.13 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$201.11 \cdot 10^{-3}$	1 : 1: 178	+
Experiment 4	$1.13 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$227.93 \cdot 10^{-3}$	1 : 1: 202	+
Experiment 4	$1.13 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$341.89 \cdot 10^{-3}$	1 : 1: 300	+

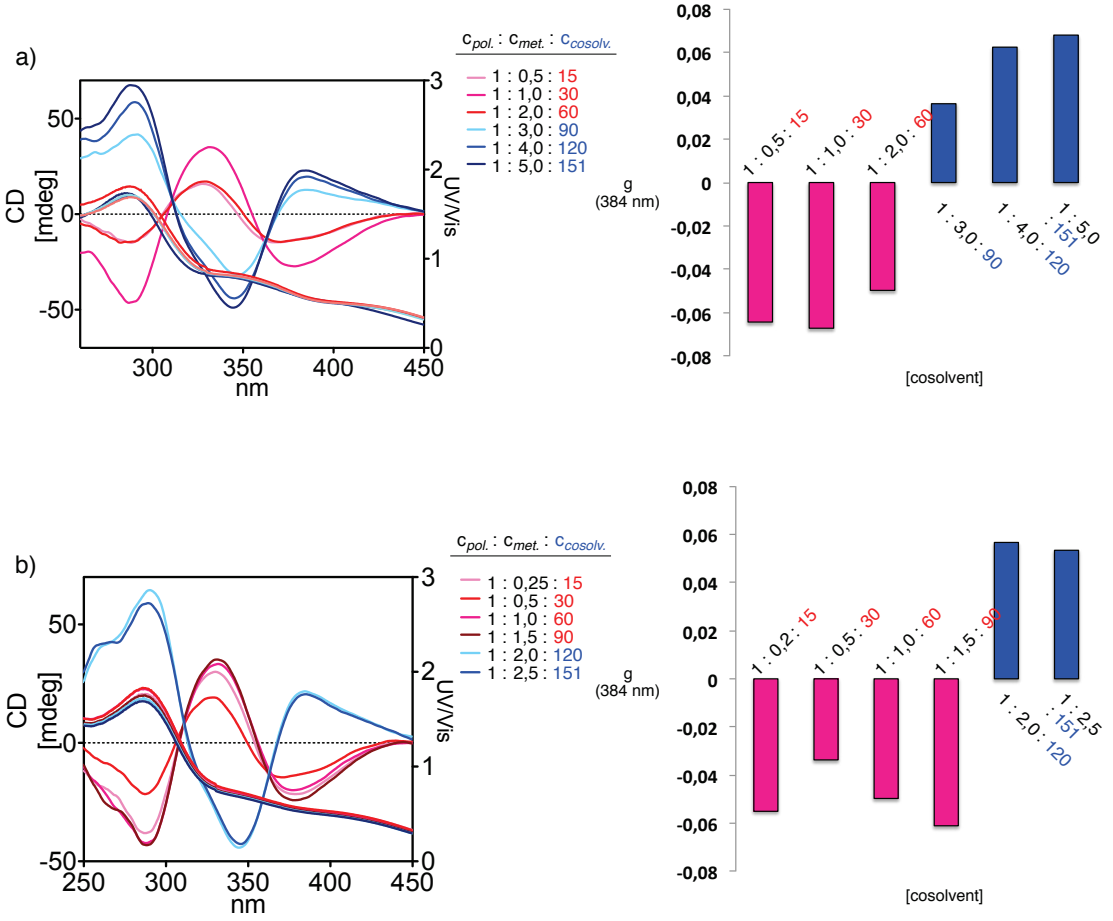
[a] $c_{polymer}$ is calculated based on the molecular weight of the monomer repeating unit (mru).

[b]pol. = polymer (poly-**1**), cosolv. = cosolvent (MeOH), met.= metal.

Interestingly, when solutions of $NaClO_4$ dissolved in different cosolvents at different concentrations (100, 50, 30, 10, and 5 mg/mL), were added to poly-**1** (0.3 and 0.1 mg/mL in $CHCl_3$), the helical sense adopted by the polymer is determined by poly-**1** (mru)/cosolvent ratio independently of the amount of Na^+ added [the minimum amount of Na ion to induce a helical structure on poly-**1** is less of 10% (mol/mol)] (from Figure S19, Table S5 to Figure S26, Table12).

During the titration of these solutions of $NaClO_4$ in different cosolvents with poly-**1**, it was observed that the polymer adopts a left-handed helical structure when poly-**1** (mru)/cosolvent ratio= 1/<100 (mol/mol), while if poly-**1** (mru)/cosolvent ratio= 1/>100 (mol/mol), the polymer adopts a right-handed helical structure (from Figure S19, Table S5 to Figure S26, Table12).

HPMC of poly-**1** and Na^+ in $CHCl_3$ using MeOH as cosolvent.



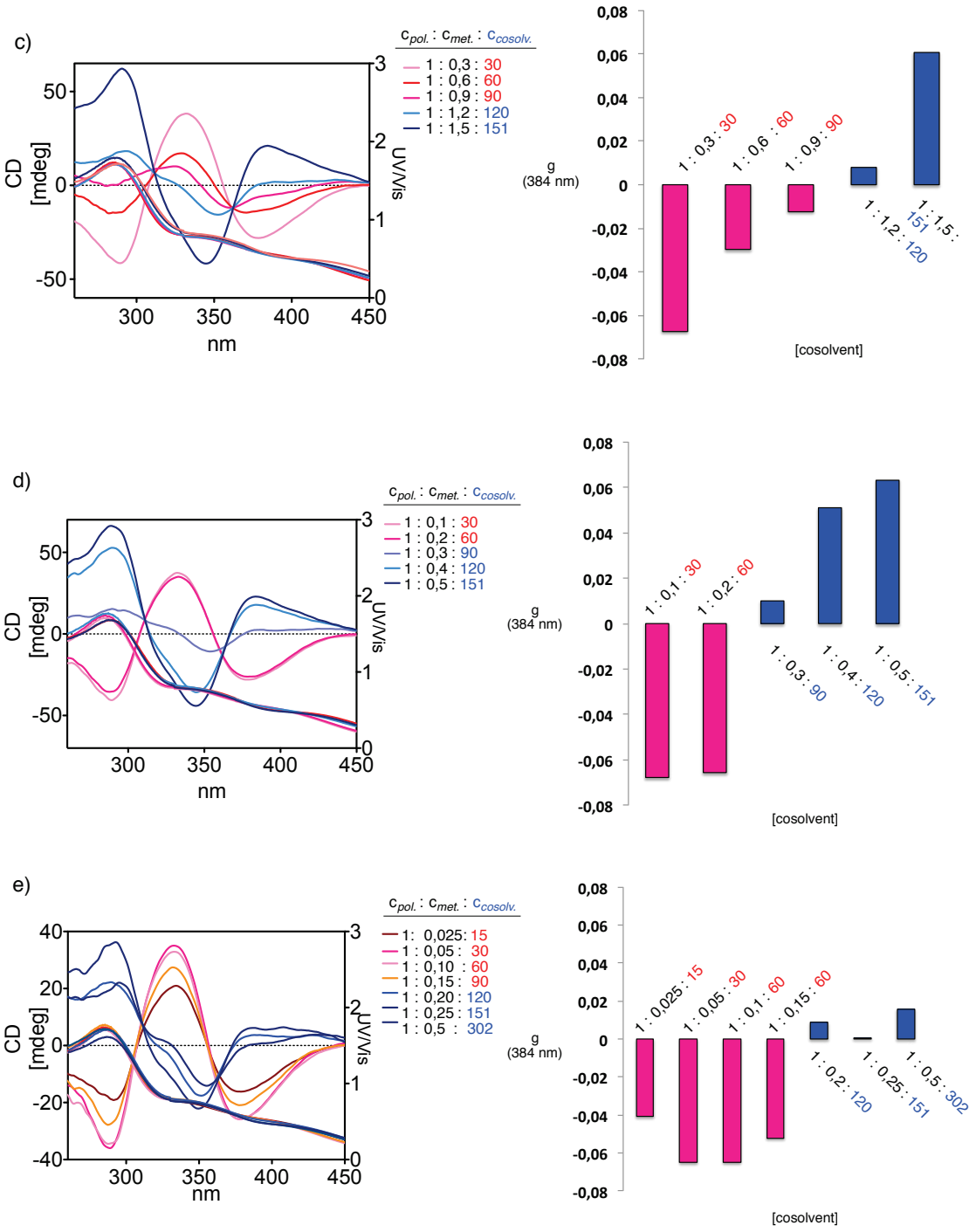


Figure S19: CD/UV spectra (left) and graphical representation of $\mathbf{C}_{cosolvet}$: g_{384nm} of a solution (right) of poly-**1** in $CHCl_3$ (0.1 mg/mL) titrated with different amounts of $NaClO_4$, in MeOH a) 100 mg/mL, b) 50 mg/mL, c) 30 mg/mL, d) 10 mg/mL, e) 5 mg/mL; [poly-**1**]= $1.13 \cdot 10^{-3}$ M in $CHCl_3$.

Table S5: Cosolvent effect (MeOH) in the helical structure of HPMCs.

Nº Experiment	$C_{polymer}$	C_{metal} [Na^+]	$C_{cosolvent}$	$C_{pol.}$: $C_{met.}$: $C_{cosol.}$ [a]	$g_{(384nm)}$
Experiment 1	$1.13 \cdot 10^{-3}$	$5.65.10^{-3}$	$17.01.10^{-3}$	1 : 0.5 : 15	-
Experiment 1	$1.13 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$34.19 \cdot 10^{-3}$	1 : 1.0 : 30	-
Experiment 1	$1.13 \cdot 10^{-3}$	$2.26 \cdot 10^{-3}$	$68.38 \cdot 10^{-3}$	1 : 2.0 : 60	-
Experiment 1	$1.13 \cdot 10^{-3}$	$3.39 \cdot 10^{-3}$	$102.57 \cdot 10^{-3}$	1 : 3.0 : 90	+
Experiment 1	$1.13 \cdot 10^{-3}$	$4.52 \cdot 10^{-3}$	$136.76 \cdot 10^{-3}$	1 : 4.0 : 120	+
Experiment 1	$1.13 \cdot 10^{-3}$	$5.65 \cdot 10^{-3}$	$170.94 \cdot 10^{-3}$	1 : 5.0 : 151	+
Experiment 2	$1.13 \cdot 10^{-3}$	$0.28 \cdot 10^{-3}$	$17.01.10^{-3}$	1 : 0.25 : 15	-
Experiment 2	$1.13 \cdot 10^{-3}$	$0.56 \cdot 10^{-3}$	$34.19 \cdot 10^{-3}$	1 : 0.5 : 30	-
Experiment 2	$1.13 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$68.38 \cdot 10^{-3}$	1 : 1.0 : 60	-
Experiment 2	$1.13 \cdot 10^{-3}$	$2.66 \cdot 10^{-3}$	$102.57 \cdot 10^{-3}$	1 : 1.5: 90	-
Experiment 2	$1.13 \cdot 10^{-3}$	$2.26 \cdot 10^{-3}$	$136.76 \cdot 10^{-3}$	1 : 2.0: 120	+
Experiment 2	$1.13 \cdot 10^{-3}$	$2.83 \cdot 10^{-3}$	$170.94 \cdot 10^{-3}$	1 : 2.5 : 151	+
Experiment 3	$1.13 \cdot 10^{-3}$	$0.34 \cdot 10^{-3}$	$34.19 \cdot 10^{-3}$	1 : 0.3 : 30	-
Experiment 3	$1.13 \cdot 10^{-3}$	$0.68 \cdot 10^{-3}$	$68.38 \cdot 10^{-3}$	1 : 0.6 : 60	-
Experiment 3	$1.13 \cdot 10^{-3}$	$1.01 \cdot 10^{-3}$	$102.57 \cdot 10^{-3}$	1 : 0.9 : 90	-
Experiment 3	$1.13 \cdot 10^{-3}$	$1.36 \cdot 10^{-3}$	$136.76 \cdot 10^{-3}$	1 : 1.2 :120	+
Experiment 3	$1.13 \cdot 10^{-3}$	$1.70 \cdot 10^{-3}$	$170.94 \cdot 10^{-3}$	1 : 1.5 : 151	+
Experiment 4	$1.13 \cdot 10^{-3}$	$0.11 \cdot 10^{-3}$	$34.19 \cdot 10^{-3}$	1 : 0.1 : 30	-
Experiment 4	$1.13 \cdot 10^{-3}$	$0.22 \cdot 10^{-3}$	$68.38 \cdot 10^{-3}$	1 : 0.2 : 60	-
Experiment 4	$1.13 \cdot 10^{-3}$	$0.34 \cdot 10^{-3}$	$102.57 \cdot 10^{-3}$	1 : 0.3 : 90	+
Experiment 4	$1.13 \cdot 10^{-3}$	$0.45 \cdot 10^{-3}$	$136.76 \cdot 10^{-3}$	1 : 0.4 : 120	+
Experiment 4	$1.13 \cdot 10^{-3}$	$0.57 \cdot 10^{-3}$	$170.94 \cdot 10^{-3}$	1 : 0.5 : 151	+
					+
Experiment 5	$1.13 \cdot 10^{-3}$	$0.03 \cdot 10^{-3}$	$17.01.10^{-3}$	1 : 0.025: 15	-
Experiment 5	$1.13 \cdot 10^{-3}$	$0.06 \cdot 10^{-3}$	$34.19 \cdot 10^{-3}$	1 : 0.05 : 30	-
Experiment 5	$1.13 \cdot 10^{-3}$	$0.11 \cdot 10^{-3}$	$68.38 \cdot 10^{-3}$	1 : 0.10 : 60	-
Experiment 5	$1.13 \cdot 10^{-3}$	$0.16 \cdot 10^{-3}$	$102.57 \cdot 10^{-3}$	1 : 0.15 : 90	-
Experiment 5	$1.13 \cdot 10^{-3}$	$0.22 \cdot 10^{-3}$	$136.76 \cdot 10^{-3}$	1 : 0.2 : 120	+

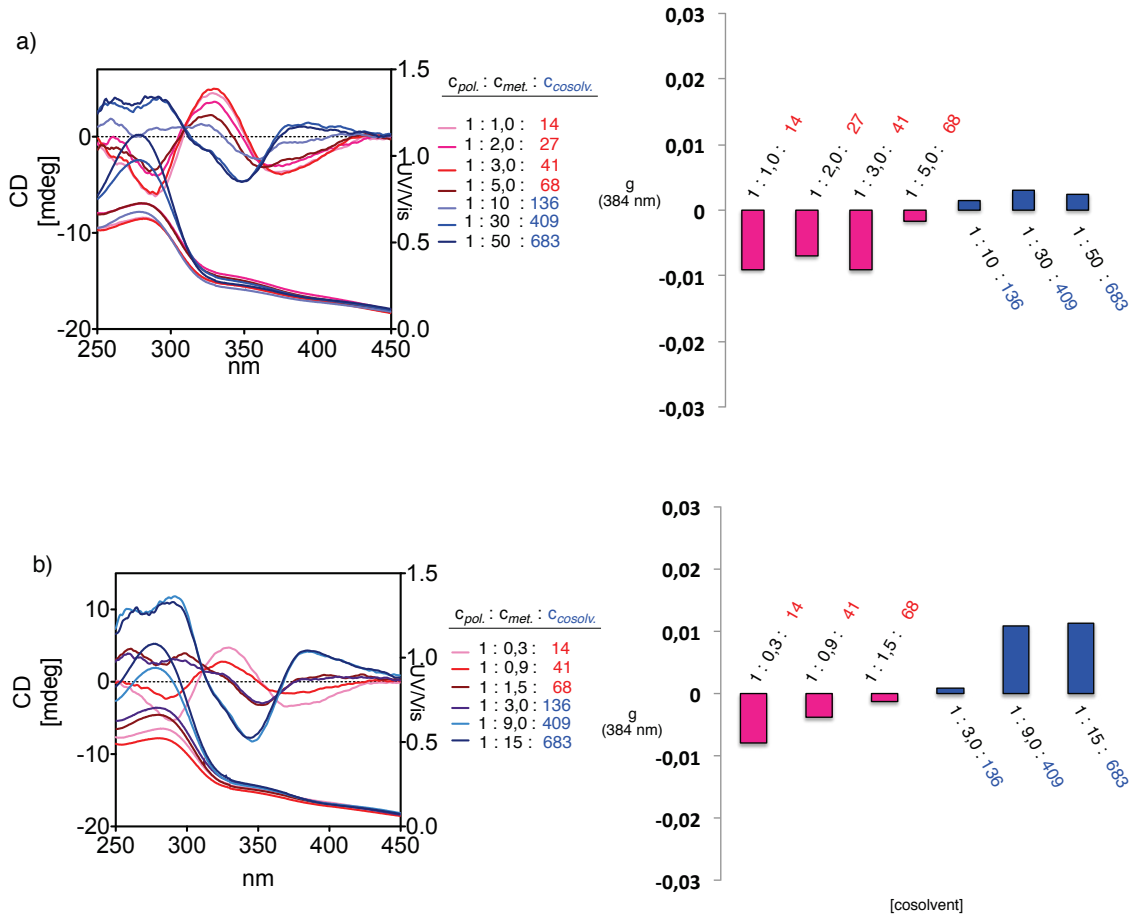
Experiment 5	$1.13 \cdot 10^{-3}$	$0.28 \cdot 10^{-3}$	$170.94 \cdot 10^{-3}$	1 : 0.25 : 151	+
Experiment 5	$1.13 \cdot 10^{-3}$	$0.56 \cdot 10^{-3}$	$341.9 \cdot 10^{-3}$	1 : 0.5 : 302	+

[a] $c_{polymer}$ is calculated based on the molecular weight of the monomer repeating unit (mru). [b]pol. = polymer (poly-**1**), cosolv. = cosolvent (MeOH), met.= metal.

The table show titrations of poly-**1** with different solutions of $NaClO_4$ in MeOH: experiment 1: 100 mg/mL; experiment 2: 50 mg/mL; experiment 3: 30 mg/mL, experiment 4: 10 mg/mL, experiment 5: 5 mg/mL.

Analogous studies were performed for other Na^+ HPMCs using other cosolvents (see below).

HPMC of poly-**1** and Na^+ in $CHCl_3$ using butanone as cosolvent.



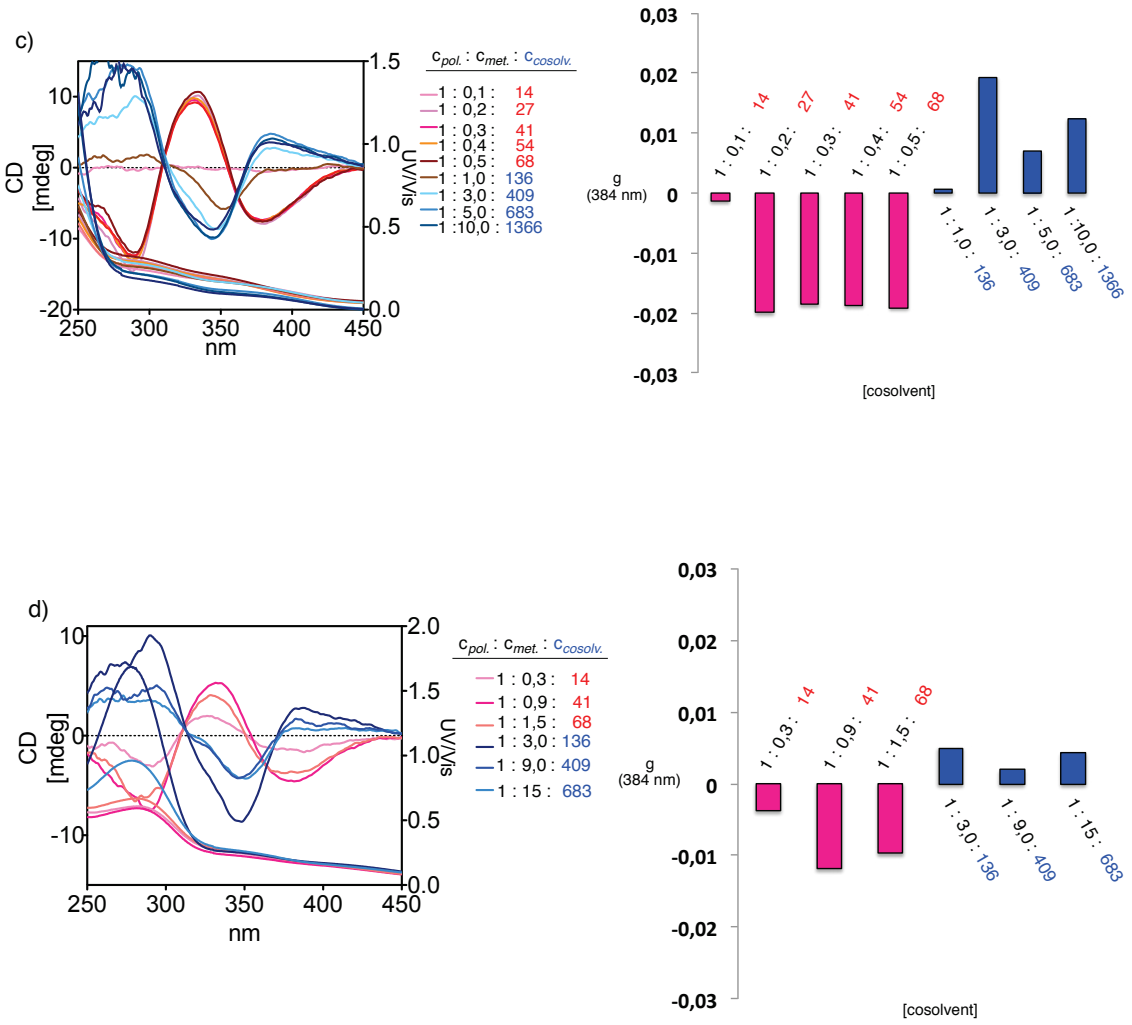


Figure S20: Left: CD/UV spectra; Right: graphical representation of $\mathbf{C}_{cosolvet}$: g_{384nm} of a solution of poly-**1** in $CHCl_3$ (0.1 mg/mL) titrated with different amounts of $NaClO_4$, in butanone a) 100 mg/mL, b) 30 mg/mL, c) 10 mg/mL, d) 5 mg/mL; [poly-**1**] = $0.38 \cdot 10^{-3}$ M in $CHCl_3$.

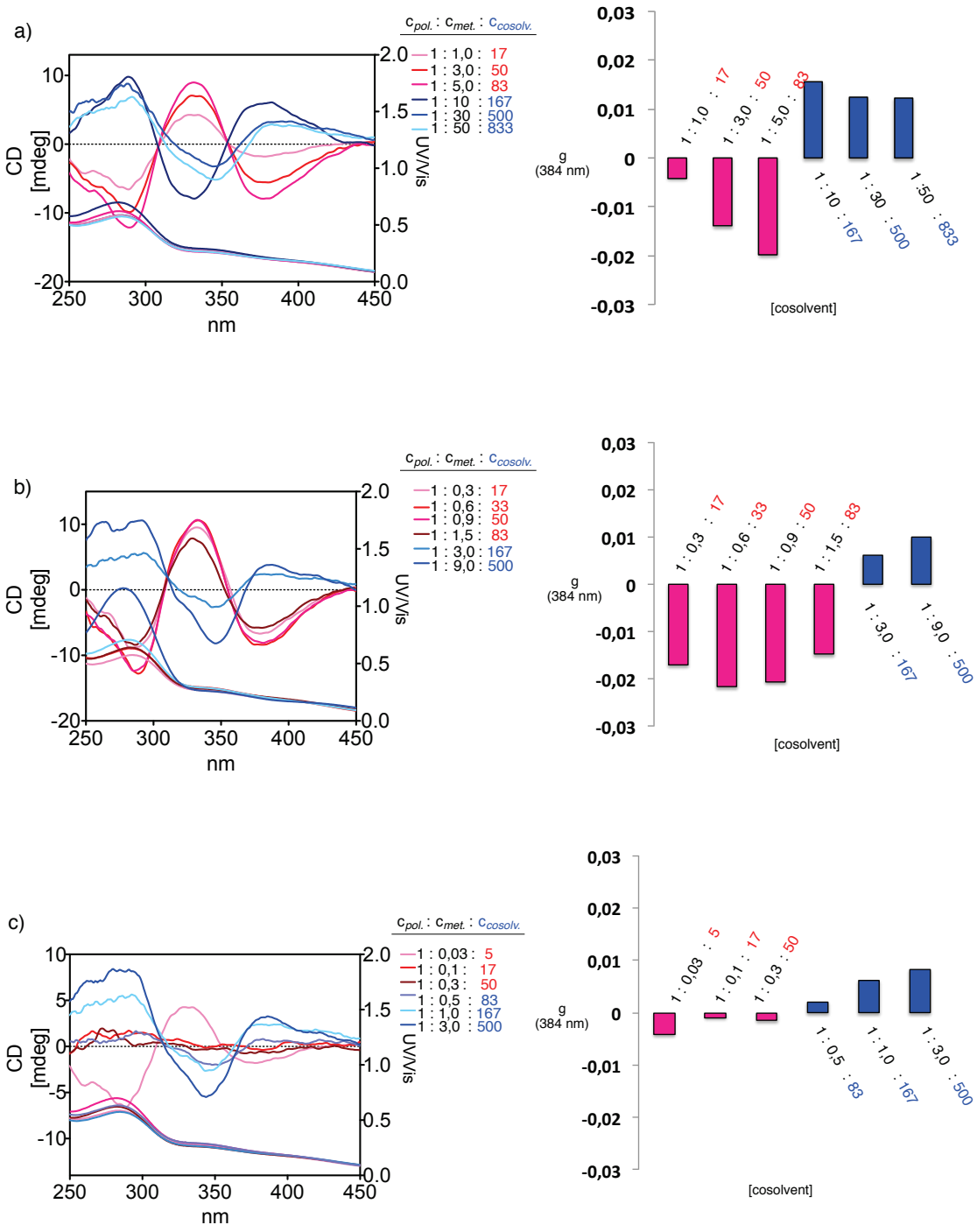
Table S6: Cosolvent effect (butanone) in the helical polymer metal complex.

N° Experiment	$\mathbf{C}_{polymer}$	$\mathbf{C}_{metal}$ **[Na$^+$]**	$\mathbf{C}_{cosolvent}$	$\mathbf{C}_{pol.}$**:** $\mathbf{C}_{met.}$**:** $\mathbf{C}_{cosol.}$ *[a]*	$\mathbf{g}_{(384nm)}$
Experiment 1	$0.38 \cdot 10^{-3}$	$0.38 \cdot 10^{-3}$	$5.15 \cdot 10^{-3}$	1 : 1.0 : 14	-
Experiment 1	$0.38 \cdot 10^{-3}$	$0.75 \cdot 10^{-3}$	$10.3 \cdot 10^{-3}$	1 : 2.0 : 27	-
Experiment 1	$0.38 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$15.4 \cdot 10^{-3}$	1 : 3.0 : 41	-
Experiment 1	$0.38 \cdot 10^{-3}$	$1.88 \cdot 10^{-3}$	$25.7 \cdot 10^{-3}$	1 : 5.0 : 68	-
Experiment 1	$0.38 \cdot 10^{-3}$	$3.77 \cdot 10^{-3}$	$51.5 \cdot 10^{-3}$	1 : 10 : 136	+
Experiment 1	$0.38 \cdot 10^{-3}$	$11.30 \cdot 10^{-3}$	$154{,}4 \cdot 10^{-3}$	1 : 30 : 409	+

Experiment 1	$0.38 \cdot 10^{-3}$	$18.80 \cdot 10^{-3}$	$257{,}4 \cdot 10^{-3}$	1 : 50 : 683	+
Experiment 2	$0.38 \cdot 10^{-3}$	$0.11 \cdot 10^{-3}$	$5.15 \cdot 10^{-3}$	1 : 0.3 : 14	-
Experiment 2	$0.38 \cdot 10^{-3}$	$0.34 \cdot 10^{-3}$	$15.4 \cdot 10^{-3}$	1 : 0.9 : 41	-
Experiment 2	$0.38 \cdot 10^{-3}$	$0.57 \cdot 10^{-3}$	$25.7 \cdot 10^{-3}$	1 : 0.5 : 68	-
Experiment 2	$0.38 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$51.5 \cdot 10^{-3}$	1 : 3.0 : 136	+
Experiment 2	$0.38 \cdot 10^{-3}$	$3.39 \cdot 10^{-3}$	$154{,}4 \cdot 10^{-3}$	1 : 9.0: 409	+
Experiment 2	$0.38 \cdot 10^{-3}$	$5{,}65 \cdot 10^{-}$	$257{,}4 \cdot 10^{-3}$	1 : 15 : 683	+
Experiment 3	$0.38 \cdot 10^{-3}$	$0.04 \cdot 10^{-3}$	$5.15 \cdot 10^{-3}$	1 : 0.1 : 14	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0.07 \cdot 10^{-3}$	$10.3 \cdot 10^{-3}$	1 : 0.2 : 27	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0.11 \cdot 10^{-3}$	$15.4 \cdot 10^{-3}$	1 : 0.3 : 41	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0.15 \cdot 10^{-3}$	$20.6 \cdot 10^{-3}$	1 : 0.4 : 55	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0.18 \cdot 10^{-3}$	$25.7 \cdot 10^{-3}$	1 : 0.5: 68	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0.38 \cdot 10^{-3}$	$51.5 \cdot 10^{-3}$	1 : 1.0 : 137	+
Experiment 3	$0.38 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$154{,}4 \cdot 10^{-3}$	1 : 3.0 : 409	+
Experiment 3	$0.38 \cdot 10^{-3}$	$1.88 \cdot 10^{-3}$	$257{,}4 \cdot 10^{-3}$	1 : 5.0 : 683	+
Experiment 3	$0.38 \cdot 10^{-3}$	$3.77 \cdot 10^{-3}$	$514.8 \cdot 10^{-3}$	1 : 10.0 : 1366	+
Experiment 4	$0.38 \cdot 10^{-3}$	$0.018 \cdot 10^{-3}$	$5.15 \cdot 10^{-3}$	1 : 0.3 : 14	-
Experiment 4	$0.38 \cdot 10^{-3}$	$0.06 \cdot 10^{-3}$	$15.4 \cdot 10^{-3}$	1 : 0.9 : 41	-
Experiment 4	$0.38 \cdot 10^{-3}$	$0.09 \cdot 10^{-3}$	$25.7 \cdot 10^{-3}$	1 : 1.5 : 68	-
Experiment 4	$0.38 \cdot 10^{-3}$	$0.18 \cdot 10^{-3}$	$51.5 \cdot 10^{-3}$	1 : 3.0 : 136	+
Experiment 4	$0.38 \cdot 10^{-3}$	$0.56 \cdot 10^{-3}$	$154.4 \cdot 10^{-3}$	1 : 9.0: 409	+
Experiment 4	$0.38 \cdot 10^{-3}$	$0.94 \cdot 10^{-3}$	$257.4 \cdot 10^{-3}$	1 : 15 : 683	+

[a] $c_{polymer}$ is calculated based on the molecular weight of the monomer repeating unit (mru). [b]pol. = polymer (poly-**1**), cosolv. = cosolvent (butanone), met.= metal.

HPMC of poly-**1** and Na^+ in $CHCl_3$ using acetone as cosolvent.



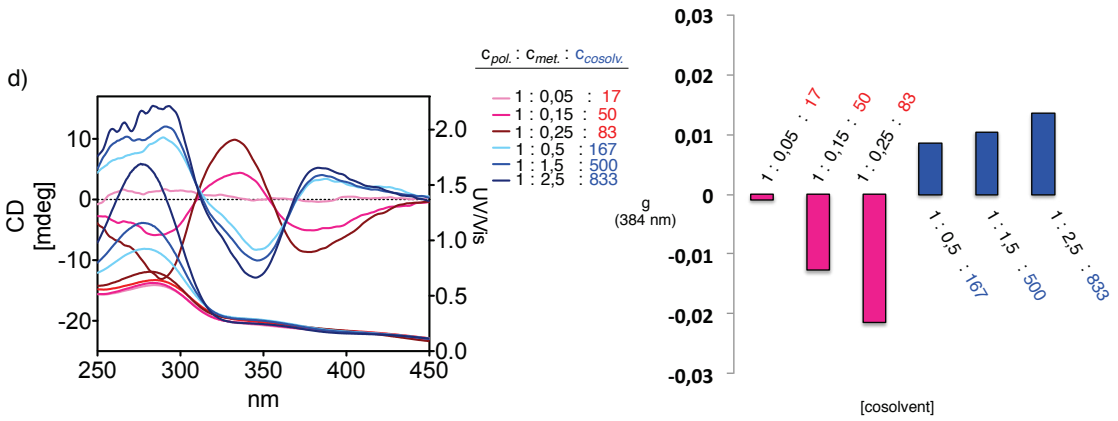


Figure S21 Left: CD/UV spectra; Right: graphical representation of $\mathbf{C}_{cosolvet}$: g_{384nm} of a solution of poly-**1** in $CHCl_3$ (0.1 mg/mL) titrated with different amounts of $NaClO_4$, in acetone a) 100 mg / mL, b) 30 mg / mL, c) 10 mg / mL, d) 5 mg / mL; [poly-**1**] = $0{,}38 \cdot 10^{-3}$ M in $CHCl_3$.

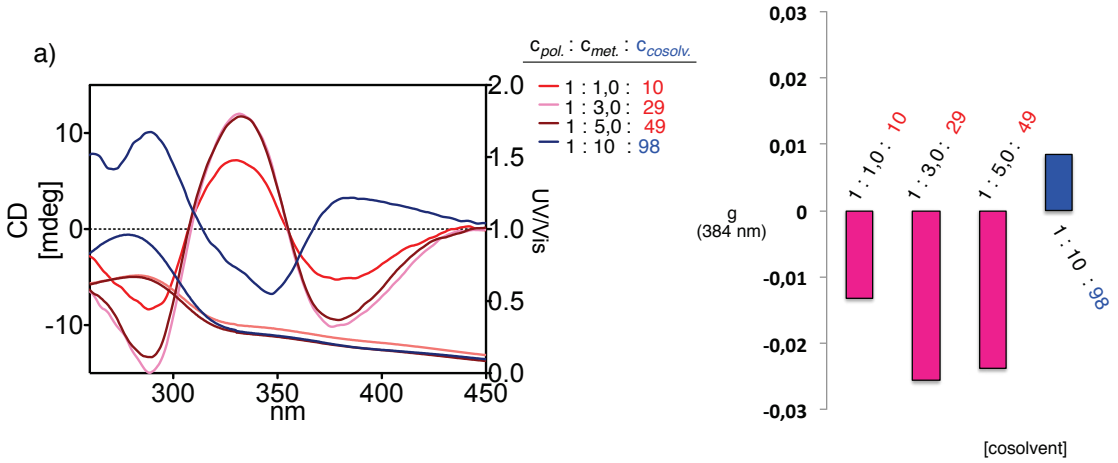
Table S7: Effect of cosolvent (acetone) in the helical polymer-metal complex.

Nº Experiment	$C_{polymer}$	C_{metal} [Na^+]	$C_{cosolvent}$	$C_{pol.}$: $C_{met.}$: $C_{cosol.}$ [a]	$g_{(384nm)}$
Experiment 1	$0.38 \cdot 10^{-3}$	$0.38 \cdot 10^{-3}$	$6.3.10^{-3}$	1 : 1,0 : 17	-
Experiment 1	$0.38 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$18.8 \cdot 10^{-3}$	1 : 3,0 : 50	-
Experiment 1	$0.38 \cdot 10^{-3}$	$1.88 \cdot 10^{-3}$	$31.4 \cdot 10^{-3}$	1 : 5,0 : 83	-
Experiment 1	$0.38 \cdot 10^{-3}$	$3.77 \cdot 10^{-3}$	$62.8 \cdot 10^{-3}$	1 : 10 : 167	+
Experiment 1	$0.38 \cdot 10^{-3}$	$11.30 \cdot 10^{-3}$	$188.4 \cdot 10^{-3}$	1 : 30 : 500	+
Experiment 1	$0.38 \cdot 10^{-3}$	$18.80 \cdot 10^{-3}$	$314.0 \cdot 10^{-3}$	1 : 50 : 833	+
Experiment 2	$0.38 \cdot 10^{-3}$	$0{,}11 \cdot 10^{-3}$	$6.3 \cdot 10^{-3}$	1 : 0.3 : 17	-
Experiment 2	$0.38 \cdot 10^{-3}$	$0.22 \cdot 10^{-3}$	$12.6 \cdot 10^{-3}$	1: 0.6 : 33	-
Experiment 2	$0.38 \cdot 10^{-33}$	$0.34 \cdot 10^{-3}$	$18.8 \cdot 10^{-3}$	1 : 0.9 : 50	-
Experiment 2	$0.38 \cdot 10^{-3}$	$0.57 \cdot 10^{-3}$	$31.4 \cdot 10^{-3}$	1 : 1,5 : 83	-
Experiment 2	$0.38 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$62.8 \cdot 10^{-3}$	1 : 3,0 : 167	+
Experiment 2	$0.38 \cdot 10^{-3}$	$3.39 \cdot 10^{-3}$	$188.4 \cdot 10^{-3}$	1 : 9,0: 500	+
Experiment 2	$0.38 \cdot 10^{-3}$	$5.65 \cdot 10^{-3}$	$314.0 \cdot 10^{-3}$	1 : 15 : 833	+
Experiment 3	$0.38 \cdot 10^{-3}$	$0.01 \cdot 10^{-3}$	$1.9 \cdot 10^{-3}$	1 : 0,03: 5	-

Experiment 3	$0.38 \cdot 10^{-3}$	$0.04 \cdot 10^{-3}$	$6.3.10^{-3}$	1 : 0,10 : 17	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0.11 \cdot 10^{-3}$	$18.8 \cdot 10^{-3}$	1 : 0,30 : 50	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0.18 \cdot 10^{-3}$	$31.4 \cdot 10^{-3}$	1 : 0.50 : 83	+
Experiment 3	$0.38 \cdot 10^{-3}$	$0.38 \cdot 10^{-3}$	$62.8 \cdot 10^{-3}$	1 : 1.00 : 167	+
Experiment 3	$0.38 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$188.4 \cdot 10^{-3}$	1 : 3.00 : 500	+
Experiment 4	$0.38 \cdot 10^{-3}$	$0.02 \cdot 10^{-3}$	$6.3 \cdot 10^{-3}$	1 : 0.05 : 17	-
Experiment 4	$0,38 \cdot 10^{-3}$	$0,06 \cdot 10^{-3}$	$18.8 \cdot 10^{-3}$	1 : 0.15 : 50	-
Experiment 4	$0.38 \cdot 10^{-3}$	$0.09 \cdot 10^{-3}$	$31.4 \cdot 10^{-3}$	1 : 0.25 : 83	+
Experiment 4	$0.38 \cdot 10^{-3}$	$0.18 \cdot 10^{-3}$	$62.8 \cdot 10^{-3}$	1 : 0.50 : 167	+
Experiment 4	$0.38 \cdot 10^{-3}$	$0.56 \cdot 10^{-3}$	$188.4 \cdot 10^{-3}$	1 : 1.25: 500	+
Experiment 4	$0.38 \cdot 10^{-3}$	$0.94 \cdot 10^{-3}$	$314.0 \cdot 10^{-3}$	1 : 2.50 : 833	+

[a] $c_{polymer}$ is calculated based on the molecular weight of the monomer repeating unit (mru). [b]pol. = polymer (poly-**1**), cosolv. = cosolvent (acetone), met.= metal.

HPMC of poly-**1** and Na^+ in $CHCl_3$ using methyl isobutyl ketone as cosolvent.



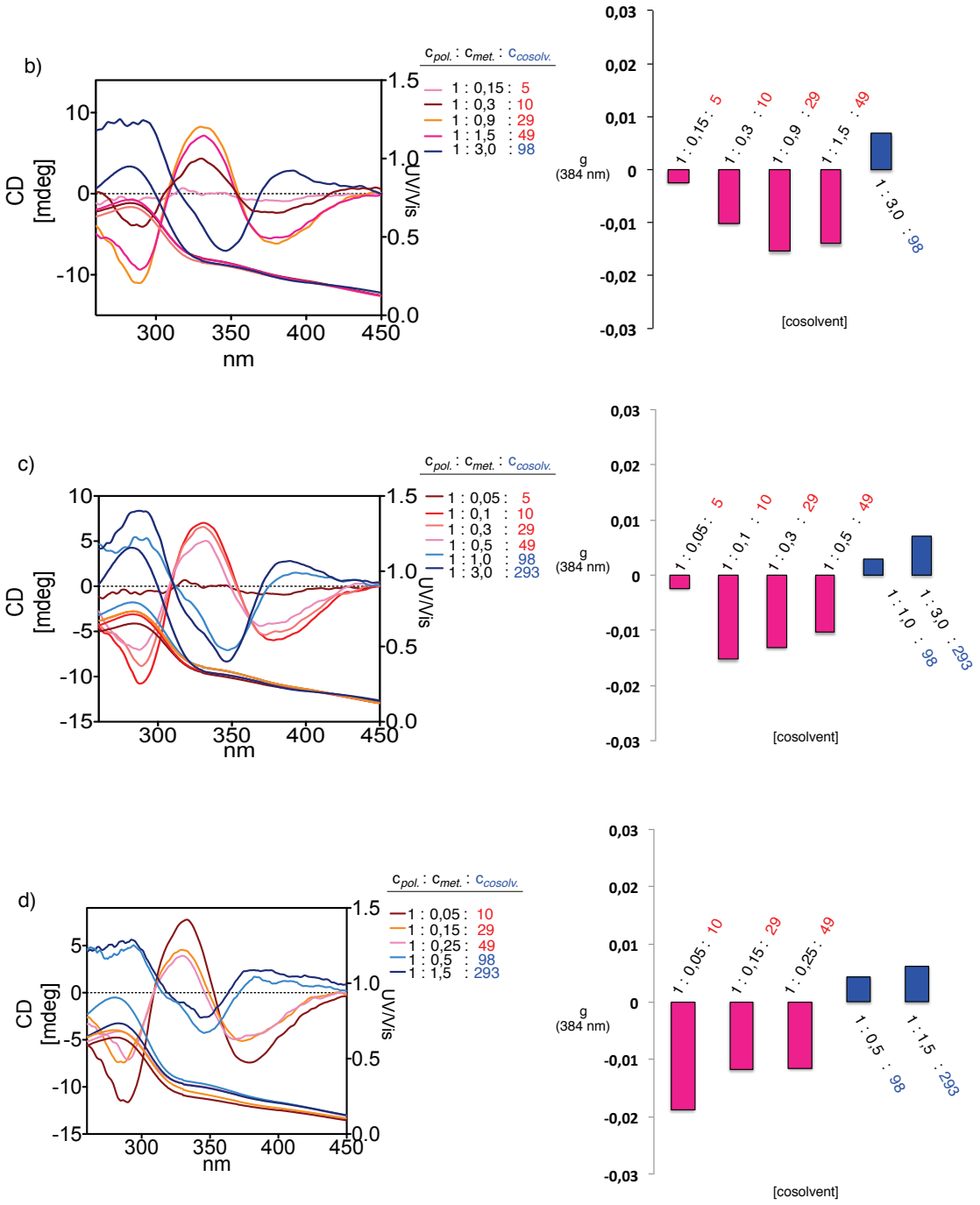


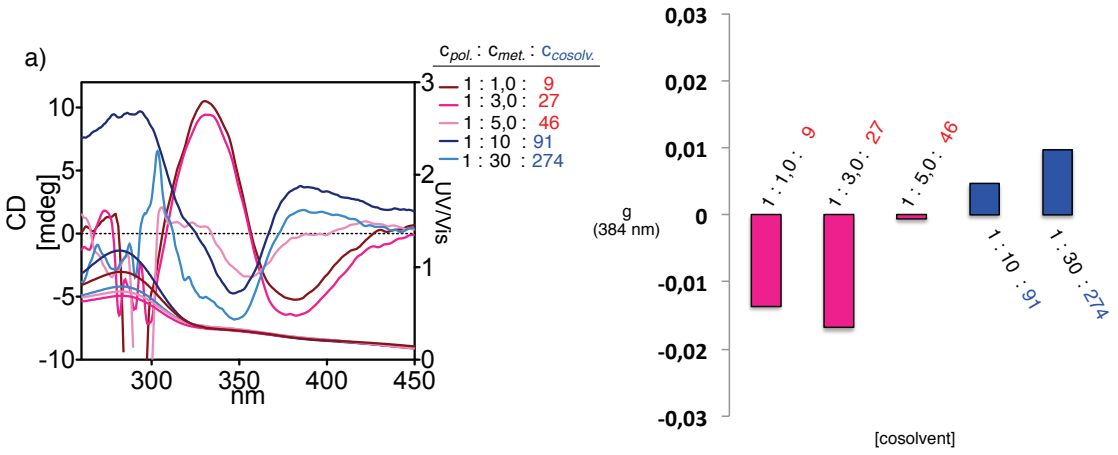
Figure S22: Left: CD/UV spectra; Right: graphical representation of $\mathbf{C}_{cosolvet}$: g_{384nm} of a solution of poly-**1** in $CHCl_3$ (0.1 mg/mL) titrated with different amounts of $NaClO_4$, in methyl isobutyl ketone a) 100 mg / mL, b) 30 mg / mL, c) 10 mg / mL, d) 5 mg / mL; [poly-**1**] = $0{,}38 \cdot 10^{-3}$ M in $CHCl_3$.

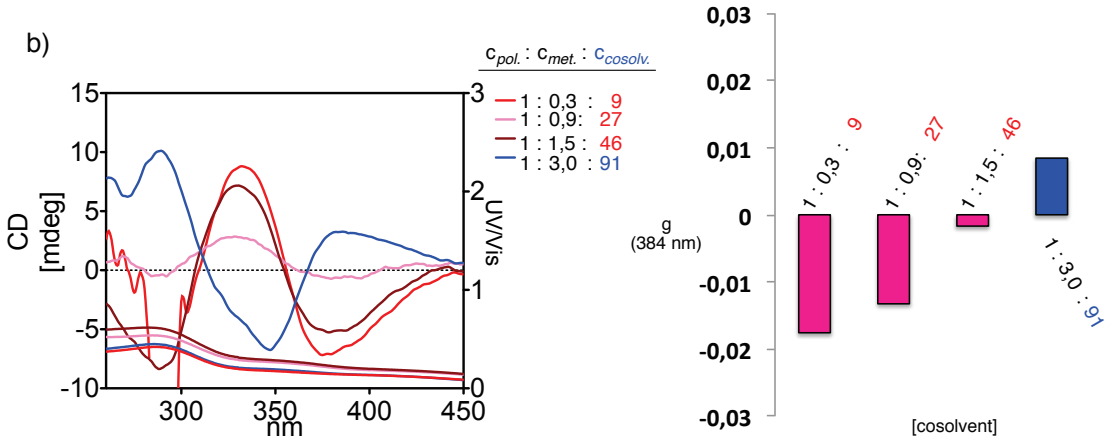
Table S8: Effect of cosolvent (methyl isobutyl ketone) in the helical polymer metal complex.

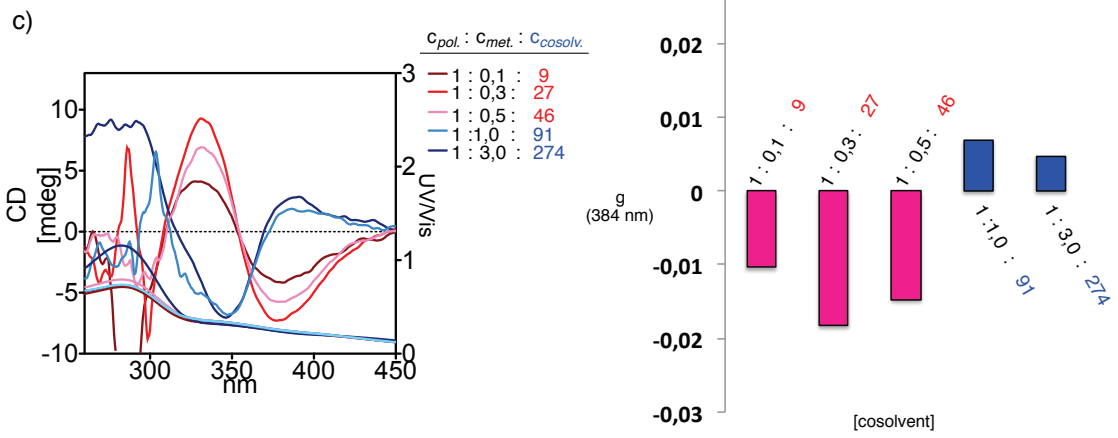
Nº Experiment	$C_{polymer}$	C_{metal} [Na^+]	$C_{cosolvent}$	$C_{pol.}$: $C_{met.}$: $C_{cosol.}$ [a]	$g_{(384nm)}$
Experiment 1	$0.38 \cdot 10^{-3}$	$0.38 \cdot 10^{-3}$	$3.7.10^{-3}$	1 : 1.0 : 10	-
Experiment 1	$0.38 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$11.0 \cdot 10^{-3}$	1 : 3.0 : 29	-
Experiment 1	$0.38 \cdot 10^{-3}$	$1.88 \cdot 10^{-3}$	$18.4 \cdot 10^{-3}$	1 : 5.0 : 49	-
Experiment 1	$0.38 \cdot 10^{-3}$	$3.77 \cdot 10^{-3}$	$36.8 \cdot 10^{-3}$	1 : 10.0 : 98	+
Experiment 2	$0.38 \cdot 10^{-3}$	$0.05 \cdot 10^{-3}$	$1.9.10^{-3}$	1 : 0.15 : 5	-
Experiment 2	$0.38 \cdot 10^{-3}$	$0.11 \cdot 10^{-3}$	$3.7.10^{-3}$	1 : 0.3 : 10	-
Experiment 2	$0.38 \cdot 10^{-3}$	$0.34 \cdot 10^{-3}$	$11.0 \cdot 10^{-3}$	1 : 0.9 : 29	-
Experiment 2	$0.38 \cdot 10^{-3}$	$0.57 \cdot 10^{-3}$	$18.4 \cdot 10^{-3}$	1 : 1.5 : 49	-
Experiment 2	$0.38 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$36.8 \cdot 10^{-3}$	1 : 3.0 :98	+
Experiment 3	$0.38 \cdot 10^{-3}$	$0.01 \cdot 10^{-3}$	$1.9 \cdot 10^{-3}$	1 : 0,05: 5	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0.04 \cdot 10^{-3}$	$3.7.10^{-3}$	1 : 0.1 : 10	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0.11 \cdot 10^{-3}$	$11.0 \cdot 10^{-3}$	1 : 0.3 : 29	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0.18 \cdot 10^{-3}$	$18.4 \cdot 10^{-3}$	1 : 0.5 : 49	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0.38 \cdot 10^{-3}$	$36.8 \cdot 10^{-3}$	1 : 1.0 : 98	+
Experiment 3	$0.38 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$110.4 \cdot 10^{-3}$	1 : 3.0 : 293	+
Experiment 4	$0.38 \cdot 10^{-3}$	$0.018 \cdot 10^{-3}$	$3.7.10^{-3}$	1 : 0.05 : 10	-
Experiment 4	$0.38 \cdot 10^{-3}$	$0.06 \cdot 10^{-3}$	$11.0 \cdot 10^{-3}$	1 : 0.15 : 29	-
Experiment 4	$0.38 \cdot 10^{-3}$	$0.09 \cdot 10^{-3}$	$18.4 \cdot 10^{-3}$	1 : 0.25 : 49	-
Experiment 4	$0.38 \cdot 10^{-3}$	$0.18 \cdot 10^{-3}$	$36.8 \cdot 10^{-3}$	1 : 0.50 : 98	+
Experiment 4	$0.38 \cdot 10^{-3}$	$0.56 \cdot 10^{-3}$	$110.4 \cdot 10^{-3}$	1 : 1.25: 293	+

[a] $c_{polymer}$ is calculated based on the molecular weight of the monomer repeating unit (mru). [b]pol. = polymer (poly-**1**), cosolv. = cosolvent (methyl isobutylketone), met.= metal.

HPMC of poly-**1** and Na^+ in $CHCl_3$ using acetophenone as cosolvent.







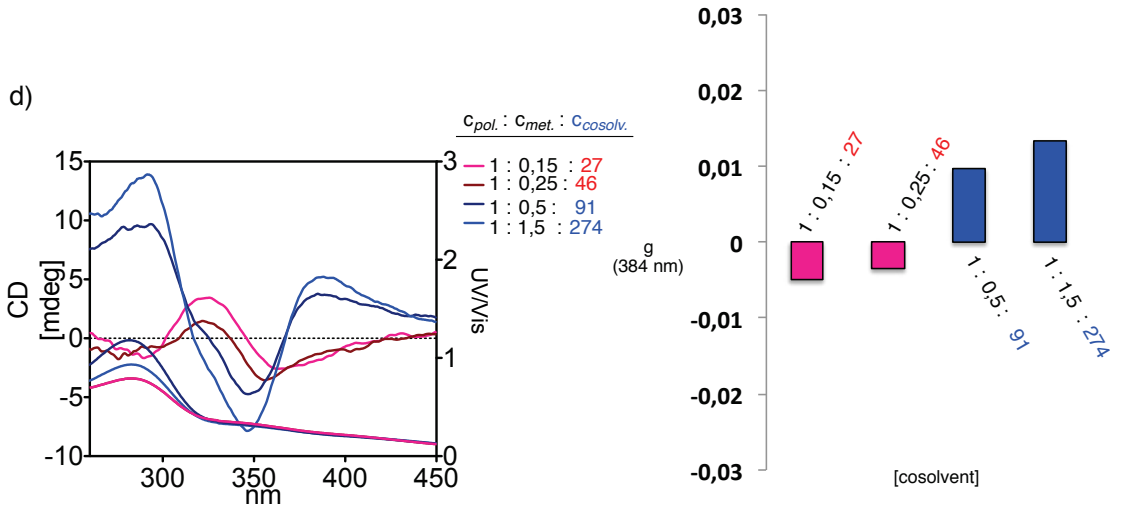


Figure S23 Left: CD/UV spectra; Right: graphical representation of $\mathbf{C}_{cosolvet}$: g_{384nm} of a solution of poly-**1** in $CHCl_3$ (0.1 mg/mL) titrated with different amounts of $NaClO_4$, in methyl acetophenone a) 100 mg / mL, b) 30 mg / mL, c) 10 mg / mL, d) 5 mg / mL; [poly-**1**] = $0{,}38 \cdot 10^{-3}$ M in $CHCl_3$.

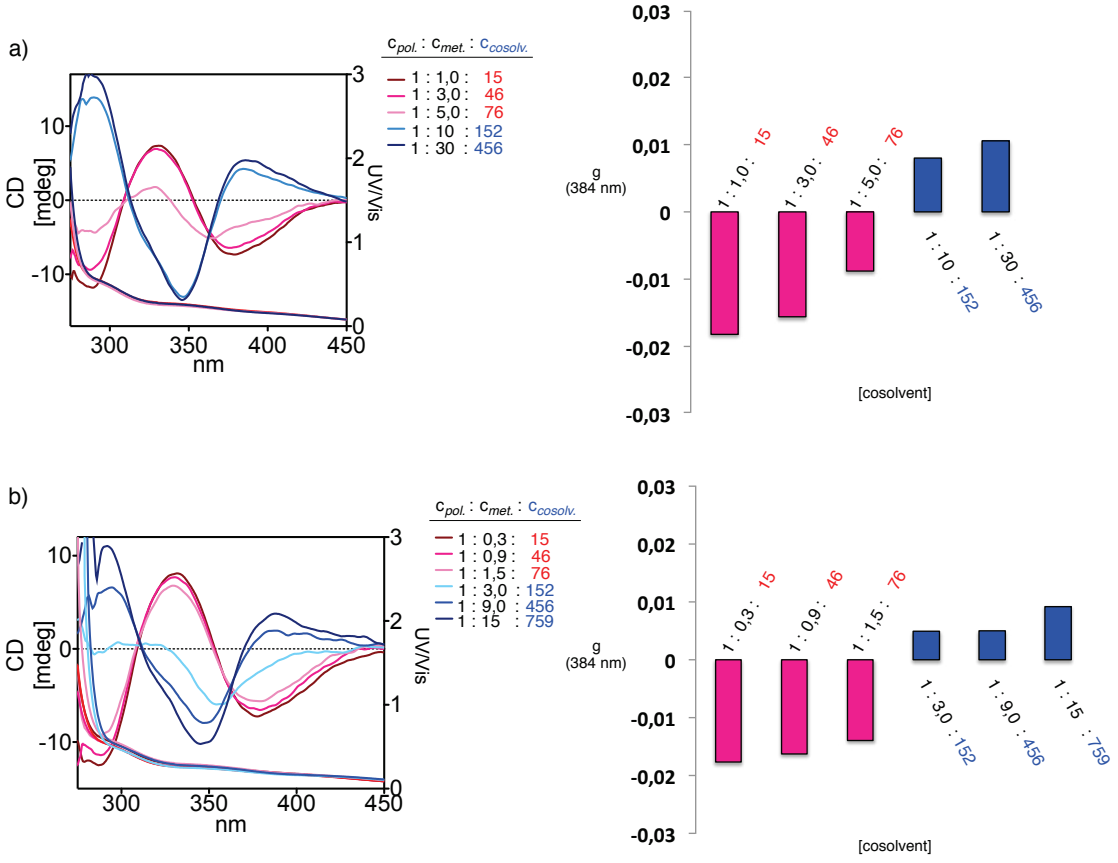
Table S9: Effect of cosolvent (methyl acetophenone) in the helical polymer metal complex.

N° Experiment	$C_{polymer}$	C_{metal} [Na^+]	$C_{cosolvent}$	$C_{pol.}$: $C_{met.}$: $C_{cosol.}$ [a]	$g_{(384nm)}$
Experiment 1	$0{,}38 \cdot 10^{-3}$	$0{,}38 \cdot 10^{-3}$	$3{,}4 \cdot 10^{-3}$	1 : 1,0 : 9	-
Experiment 1	$0{,}38 \cdot 10^{-3}$	$1{,}13 \cdot 10^{-3}$	$10{,}3 \cdot 10^{-3}$	1 : 3,0 : 27	-
Experiment 1	$0{,}38 \cdot 10^{-3}$	$1{,}88 \cdot 10^{-3}$	$17{,}2 \cdot 10^{-3}$	1 : 5,0 : 46	-
Experiment 1	$0{,}38 \cdot 10^{-3}$	$3{,}77 \cdot 10^{-3}$	$34{,}4 \cdot 10^{-3}$	1 : 10 : 91	+
Experiment 1	$0{,}38 \cdot 10^{-3}$	$11{,}3 \cdot 10^{-3}$	$103{,}3 \cdot 10^{-3}$	1 : 30 : 274	+
Experiment 2	$0{,}38 \cdot 10^{-3}$	$0{,}11 \cdot 10^{-3}$	$3{,}4 \cdot 10^{-3}$	1 : 0,3 : 9	-
Experiment 2	$0{,}38 \cdot 10^{-3}$	$0{,}34 \cdot 10^{-3}$	$10{,}3 \cdot 10^{-3}$	1 : 0,9 : 27	-
Experiment 2	$0{,}38 \cdot 10^{-3}$	$0{,}57 \cdot 10^{-3}$	$17{,}2 \cdot 10^{-3}$	1 : 1,5 : 46	-
Experiment 2	$0{,}38 \cdot 10^{-3}$	$1{,}13 \cdot 10^{-3}$	$34{,}4 \cdot 10^{-3}$	1 : 3,0 :91	+
Experiment 3	$0{,}38 \cdot 10^{-3}$	$0{,}04 \cdot 10^{-3}$	$3{,}4 \cdot 10^{-3}$	1 : 0,1 : 9	-
Experiment 3	$0{,}38 \cdot 10^{-3}$	$0{,}11 \cdot 10^{-3}$	$10{,}3 \cdot 10^{-3}$	1 : 0,3 : 27	-

Experiment 3	$0{,}38\cdot10^{-3}$	$0{,}18\cdot10^{-3}$	$17{,}2\cdot10^{-3}$	1 : 0,5 : 46	-
Experiment 3	$0{,}38\cdot10^{-3}$	$0{,}38\cdot10^{-3}$	$34{,}4\cdot10^{-3}$	1 : 1,0 : 91	+
Experiment 3	$0{,}38\cdot10^{-3}$	$1{,}13\cdot10^{-3}$	$103{,}3\cdot10^{-3}$	1 : 3,0 : 274	+
Experiment 4	$0{,}38\cdot10^{-3}$	$0{,}06\cdot10^{-3}$	$10{,}3\cdot10^{-3}$	1 : 0,15 : 27	-
Experiment 4	$0{,}38\cdot10^{-3}$	$0{,}09\cdot10^{-3}$	$17{,}2\cdot10^{-3}$	1 : 0,25 : 46	-
Experiment 4	$0{,}38\cdot10^{-3}$	$0{,}18\cdot10^{-3}$	$34{,}4\cdot10^{-3}$	1 : 0,5 : 91	+
Experiment 4	$0{,}38\cdot10^{-3}$	$0{,}56\cdot10^{-3}$	$103{,}3\cdot10^{-3}$	1 : 1,25: 274	+

[a] $c_{polymer}$ is calculated based on the molecular weight of the monomer repeating unit (mru). [b]pol. = polymer (poly-**1**), cosolv. = cosolvent (methyl acetofenone), met.= metal.

HPMC of poly-**1** and Na^+ in $CHCl_3$ using pyridine as cosolvent.



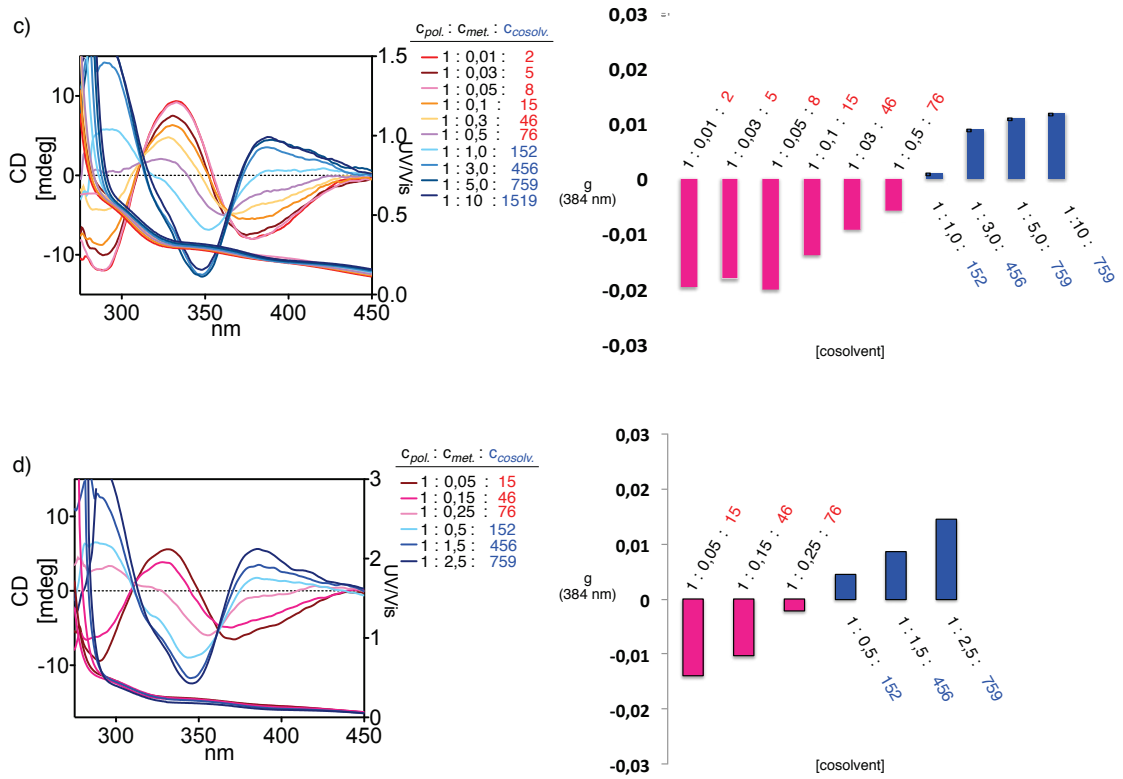


Figure S24: Left: CD/UV spectra; Right: graphical representation of $\mathbf{C}_{cosolvet}$: g_{384nm} of a solution of poly-**1** in $CHCl_3$ (0.1 mg/mL) titrated with different amounts of $NaClO_4$, in pyridine a) 100 mg / mL, b) 30 mg / mL, c) 10 mg / mL, d) 5 mg / mL; [poly-**1**] = $0{,}38 \cdot 10^{-3}$ M in $CHCl_3$.

Table S10: Effect of cosolvent (pyridine) in the helical polymer metal complex.

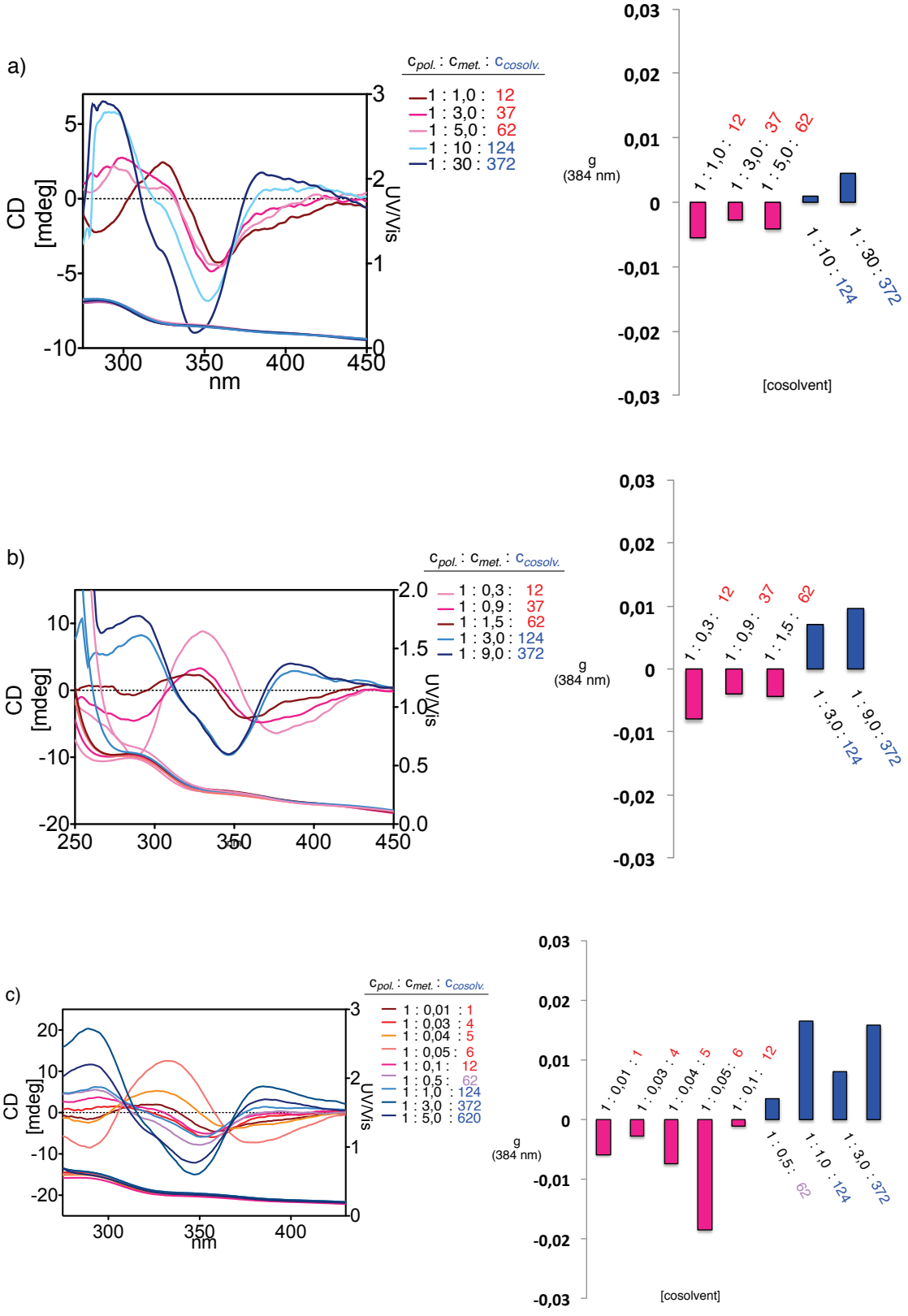
Nº Experiment	$\mathbf{C}_{polymer}$	$\mathbf{C}_{metal}$ **[Na^+]**	$\mathbf{C}_{cosolvent}$	$\mathbf{C}_{pol.}$**:** $\mathbf{C}_{met.}$**:** $\mathbf{C}_{cosol.}$ *[a]*	$\mathbf{g}_{(384nm)}$
Experiment 1	$0.38 \cdot 10^{-3}$	$0.38 \cdot 10^{-3}$	$5.7.10^{-3}$	1 : 1.0 : 15	-
Experiment 1	$0.38 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$17.2 \cdot 10^{-3}$	1 : 3.0 : 46	-
Experiment 1	$0.38 \cdot 10^{-3}$	$1.88 \cdot 10^{-3}$	$28.6 \cdot 10^{-3}$	1 : 5.0 : 76	-
Experiment 1	$0.38 \cdot 10^{-3}$	$3.77 \cdot 10^{-3}$	$57.2 \cdot 10^{-3}$	1 : 10.0 : 152	+
Experiment 1	$0.38 \cdot 10^{-3}$	$11.30 \cdot 10^{-3}$	$171.7 \cdot 10^{-3}$	1 : 30.0 : 456	+
Experiment 2	$0.38 \cdot 10^{-3}$	$0.11 \cdot 10^{-3}$	$5.7.10^{-3}$	1 : 0.3 : 15	-
Experiment 2	$0.38 \cdot 10^{-3}$	$0.34 \cdot 10^{-3}$	$17.2 \cdot 10^{-3}$	1 : 0.9 : 46	-
Experiment 2	$0.38 \cdot 10^{-3}$	$0.57 \cdot 10^{-3}$	$28.6 \cdot 10^{-3}$	1 : 1.5 : 76	-

Experiment 2	$0.38 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$57.2 \cdot 10^{-3}$	1 : 3.0 :152	+
Experiment 2	$0.38 \cdot 10^{-3}$	$3.39 \cdot 10^{-3}$	$171.7 \cdot 10^{-3}$	1 : 9.0 : 456	+
Experiment 2	$0.38 \cdot 10^{-3}$	$5.65 \cdot 10^{-3}$	$286.2 \cdot 10^{-3}$	1 : 15.0 : 759	+
Experiment 3	$0.38 \cdot 10^{-3}$	$0.004 \cdot 10^{-3}$	$0.6 \cdot 10^{-3}$	1 : 0.01: 2	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0.011 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	1 : 0.03: 5	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0,018 \cdot 10^{-.}$	$2.9 \cdot 10^{-3}$	1 : 0.05: 8	
Experiment 3	$0.38 \cdot 10^{-3}$	$0.04 \cdot 10^{-3}$	$5.7.10^{-3}$	1 : 0.10 : 15	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0.11 \cdot 10^{-3}$	$17.2 \cdot 10^{-3}$	1 : 0.30 : 46	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0.18 \cdot 10^{-3}$	$28.6 \cdot 10^{-3}$	1 : 0.50 : 76	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0.38 \cdot 10^{-3}$	$57.2 \cdot 10^{-3}$	1 : 1.00 : 152	+
Experiment 3	$0.38 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$171.7 \cdot 10^{-3}$	1 : 3.00 : 456	+
Experiment 3	$0.38 \cdot 10^{-3}$	$1.88 \cdot 10^{-3}$	$286.2 \cdot 10^{-3}$	1 : 5.00: 759	+
Experiment 3	$0.38 \cdot 10^{-3}$	$3.77 \cdot 10^{-3}$	$572,4 \cdot 10^{-3}$	1 : 10.0 : 1519	+
Experiment 4	$0.38 \cdot 10^{-3}$	$0.018 \cdot 10^{-3}$	$5.7.10^{-3}$	1 : 0.05 : 15	-
Experiment 4	$0.38 \cdot 10^{-3}$	$0.06 \cdot 10^{-3}$	$17.2 \cdot 10^{-3}$	1 : 0.15 : 46	-
Experiment 4	$0.38 \cdot 10^{-3}$	$0.09 \cdot 10^{-3}$	$28.6 \cdot 10^{-3}$	1 : 0.25 : 76	-
Experiment 4	$0.38 \cdot 10^{-3}$	$0.18 \cdot 10^{-3}$	$57.2 \cdot 10^{-3}$	1 : 0.50 : 152	+
Experiment 4	$0.38 \cdot 10^{-3}$	$0.56 \cdot 10^{-3}$	$171.7 \cdot 10^{-3}$	1 : 1.25: 456	+
Experiment 4	$0.38 \cdot 10^{-3}$	$0.56 \cdot 10^{-3}$	$286.2 \cdot 10^{-3}$	1 : 2.25 : 759	+

[a] $c_{polymer}$ is calculated based on the molecular weight of the monomer repeating unit (mru).

[b]pol. = polymer (poly-**1**), cosolv. = cosolvent (pyridine), met.= metal.

HPMC of poly-**1** and Na^+ in $CHCl_3$ using piperidine as cosolvent.



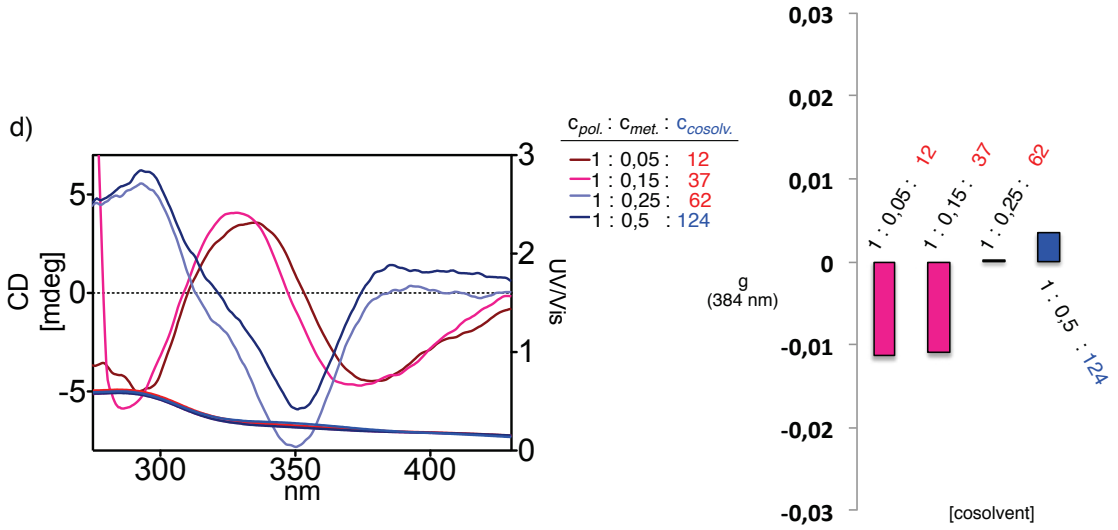


Figure S25: Left: CD/UV spectra; Right: graphical representation of $\mathbf{C}_{cosolvet}$: g_{384nm} of a solution of poly-**1** in $CHCl_3$ (0.1 mg/mL) titrated with different amounts of $NaClO_4$, in piperidine a) 100 mg / mL, b) 30 mg / mL, c) 10 mg / mL, d) 5 mg / mL; [poly-**1**] = $0{,}38 \cdot 10^{-3}$ M in $CHCl_3$.

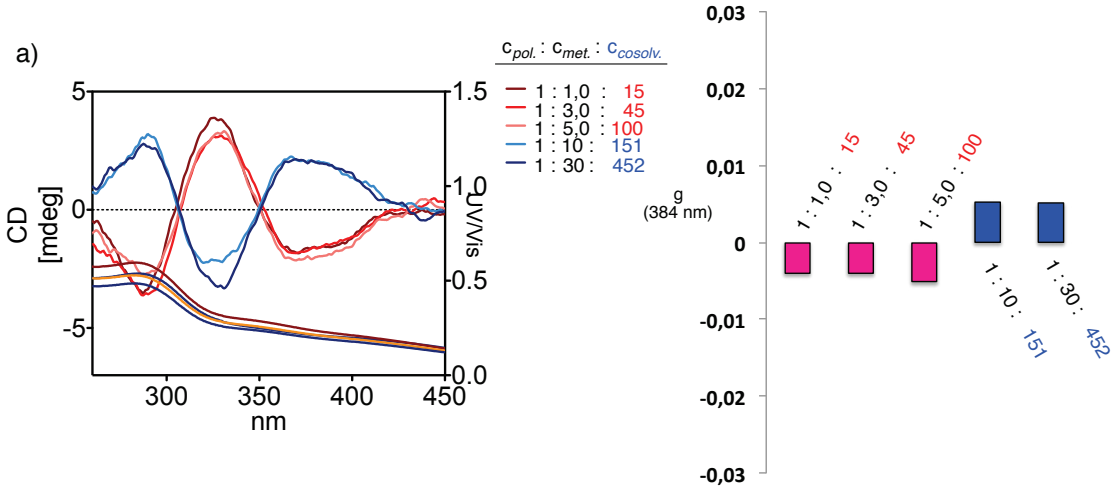
Table S11: Cosolvent effect (piperidine) in the helical polymer metal complex.

N° Experiment	$C_{polymer}$	C_{metal} [Na^+]	$C_{cosolvent}$	$C_{pol.}$: $C_{met.}$: $C_{cosol.}$ [a]	$g_{(384nm)}$
Experiment 1	$0.38 \cdot 10^{-3}$	$0.38 \cdot 10^{-3}$	$4.7.10^{-3}$	1 : 1.0 : 12	-
Experiment 1	$0.38 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$14.0 \cdot 10^{-3}$	1 : 3.0 : 37	-
Experiment 1	$0.38 \cdot 10^{-3}$	$1.88 \cdot 10^{-3}$	$23.3 \cdot 10^{-3}$	1 : 5.0 : 62	-
Experiment 1	$0.38 \cdot 10^{-3}$	$3.77 \cdot 10^{-3}$	$46.7 \cdot 10^{-3}$	1 : 10.0 : 124	+
Experiment 1	$0.38 \cdot 10^{-3}$	$11.30 \cdot 10^{-3}$	$140.0 \cdot 10^{-3}$	1 : 30.0 : 372	+
Experiment 2	$0.38 \cdot 10^{-3}$	$0.11 \cdot 10^{-3}$	$4.7.10^{-3}$	1 : 0.3 : 12	-
Experiment 2	$0.38 \cdot 10^{-3}$	$0.34 \cdot 10^{-3}$	$14.0 \cdot 10^{-3}$	1 : 0.9 : 37	-
Experiment 2	$0.38 \cdot 10^{-3}$	$0.57 \cdot 10^{-3}$	$23.3 \cdot 10^{-3}$	1 : 1.5 : 62	-
Experiment 2	$0.38 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$46.7 \cdot 10^{-3}$	1 : 3.0 :124	+
Experiment 2	$0.38 \cdot 10^{-3}$	$3.39 \cdot 10^{-3}$	$140.0 \cdot 10^{-3}$	1 : 9.0 : 372	+
Experiment 3	$0.38 \cdot 10^{-3}$	$0.0006 \cdot 10^{-3}$	$0.5 \cdot 10^{-3}$	1 : 0.01: 1	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0.011 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$	1 : 0.03: 4	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0.015 \cdot 10^{-3}$	$1.9 \cdot 10^{-3}$	1 : 0.04: 5	-

Experiment 3	$0.38 \cdot 10^{-3}$	$0.018 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$	1 : 0.05: 6	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0.04 \cdot 10^{-3}$	$4.7.10^{-3}$	1 : 0.10 : 12	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0.11 \cdot 10^{-3}$	$23.3 \cdot 10^{-3}$	1 : 0.50 : 62	+
Experiment 3	$0.38 \cdot 10^{-3}$	$0.18 \cdot 10^{-3}$	$46.7 \cdot 10^{-3}$	1 : 1.00 : 124	+
Experiment 3	$0.38 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$140.0 \cdot 10^{-3}$	1 : 3.00 : 372	+
Experiment 3	$0.38 \cdot 10^{-3}$	$1.88 \cdot 10^{-3}$	$233.3{,}0 \cdot 10^{-3}$	1 : 5.00 : 620	+
Experiment 4	$0.38 \cdot 10^{-3}$	$0.018 \cdot 10^{-3}$	$4.7.10^{-3}$	1 : 0.05 : 12	-
Experiment 4	$0.38 \cdot 10^{-3}$	$0.06 \cdot 10^{-3}$	$14.0 \cdot 10^{-3}$	1 : 0.15 : 37	-
Experiment 4	$0.38 \cdot 10^{-3}$	$0.09 \cdot 10^{-3}$	$23.3 \cdot 10^{-3}$	1 : 0.25 : 62	+
Experiment 4	$0.38 \cdot 10^{-3}$	$0.18 \cdot 10^{-3}$	$46.7 \cdot 10^{-3}$	1 : 0.50 : 124	+

[a] $c_{polymer}$ is calculated based on the molecular weight of the monomer repeating unit (mru). [b]pol. = polymer (poly-**1**), cosolv. = cosolvent (piperidine), met.= metal.

HPMC of poly-**1** and Na^+ in $CHCl_3$ using THF as cosolvent.



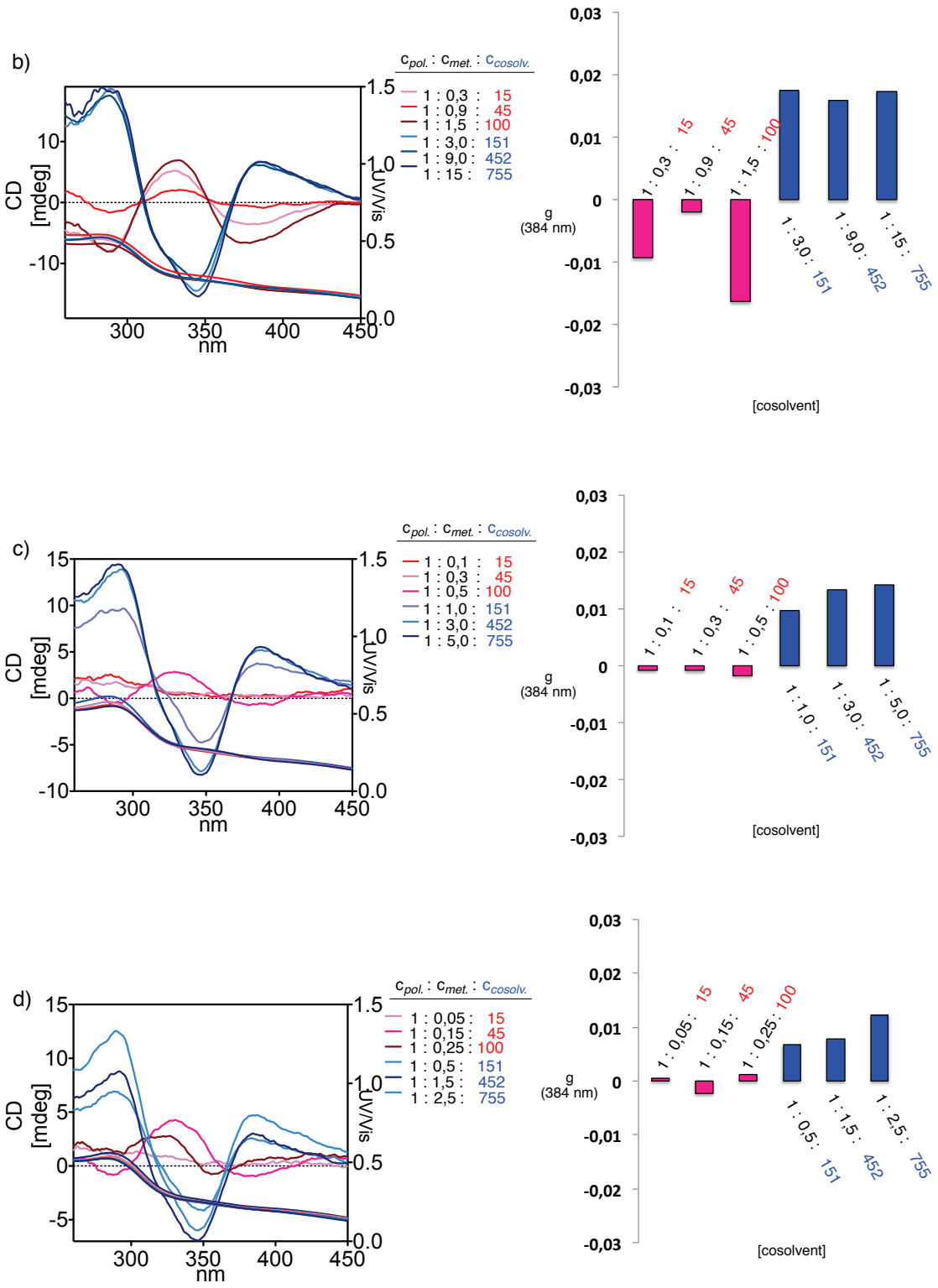


Figure S26: Left: CD/UV spectra; Right: graphical representation of $\mathbf{C}_{cosolvet}$: g_{384nm} of a solution of poly-**1** in $CHCl_3$ (0.1 mg/mL) titrated with different amounts of $NaClO_4$, in THF a) 100 mg / mL, b) 30 mg / mL, c) 10 mg / mL, d) 5 mg / mL; [poly-**1**] = $0{,}38 \cdot 10^{-3}$ M in $CHCl_3$..

Table S12: Cosolvent effect(THF) in the helical polymer metal complex.

Nº Experiment	$C_{polymer}$	C_{metal} [Na^+]	$C_{cosolvent}$	$C_{pol.}$: $C_{met.}$: $C_{cosol.}$ [a]	$g_{(384nm)}$
Experiment 1	$0.38 \cdot 10^{-3}$	$0.38 \cdot 10^{-3}$	$5.7.10^{-3}$	1 : 1.0 : 15	-
Experiment 1	$0.38 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$17.0 \cdot 10^{-3}$	1 : 3.0 : 45	-
Experiment 1	$0.38 \cdot 10^{-3}$	$1.88 \cdot 10^{-3}$	$28.4 \cdot 10^{-3}$	1 : 5.0 : 100	-
Experiment 1	$0.38 \cdot 10^{-3}$	$3.77 \cdot 10^{-3}$	$56.9 \cdot 10^{-3}$	1 : 10.0 : 151	+
Experiment 1	$0.38 \cdot 10^{-3}$	$11.30 \cdot 10^{-3}$	$170.6 \cdot 10^{-3}$	1 : 30.0 : 452	+
Experiment 2	$0.38 \cdot 10^{-3}$	$0.11 \cdot 10^{-3}$	$5.7.10^{-3}$	1 : 0.3 : 15	-
Experiment 2	$0.38 \cdot 10^{-3}$	$0.34 \cdot 10^{-3}$	$17.0 \cdot 10^{-3}$	1 : 0.9 : 45	-
Experiment 2	$0.38 \cdot 10^{-3}$	$0.57 \cdot 10^{-3}$	$28.4 \cdot 10^{-3}$	1 : 1.5 : 100	-
Experiment 2	$0.38 \cdot 10^{-3}$	$1.13 \cdot 10^{-3}$	$56.9 \cdot 10^{-3}$	1 : 3.0 :151	+
Experiment 2	$0.38 \cdot 10^{-3}$	$3.39 \cdot 10^{-3}$	$170.6 \cdot 10^{-3}$	1 : 9.0 : 452	+
Experiment 2	$0.38 \cdot 10^{-3}$	$5,65 \cdot 10^{-3}$	$284.3 \cdot 10^{-3}$	1 : 15.0 : 755	+
Experiment 3	$0.38 \cdot 10^{-3}$	$0,04 \cdot 10^{-3}$	$5.7.10^{-3}$	1 : 0.1 : 15	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0,11 \cdot 10^{-3}$	$17.0 \cdot 10^{-3}$	1 : 0.3 : 45	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0,18 \cdot 10^{-3}$	$28.4 \cdot 10^{-3}$	1 : 0.5 : 100	-
Experiment 3	$0.38 \cdot 10^{-3}$	$0,38 \cdot 10^{-3}$	$56.9 \cdot 10^{-3}$	1 : 1.0 : 151	+
Experiment 3	$0.38 \cdot 10^{-3}$	$1,13 \cdot 10^{-3}$	$170.6 \cdot 10^{-3}$	1 : 3.0 : 452	+
Experiment 3	$0.38 \cdot 10^{-3}$	$1,88 \cdot 10^{-3}$	$284.3 \cdot 10^{-3}$	1 : 5.0 : 755	+
Experiment 4	$0.38 \cdot 10^{-3}$	$0,018 \cdot 10^{-3}$	$5.7.10^{-3}$	1 : 0.05 : 15	-
Experiment 4	$0.38 \cdot 10^{-3}$	$0,06 \cdot 10^{-3}$	$17.0 \cdot 10^{-3}$	1 : 0.15 : 45	-
Experiment 4	$0.38 \cdot 10^{-3}$	$0,09 \cdot 10^{-3}$	$28.4 \cdot 10^{-3}$	1 : 0.25 : 100	-
Experiment 4	$0.38 \cdot 10^{-3}$	$0,18 \cdot 10^{-3}$	$56.9 \cdot 10^{-3}$	1 : 0.50 : 151	+
Experiment 4	$0.38 \cdot 10^{-3}$	$0,56 \cdot 10^{-3}$	$170.6 \cdot 10^{-3}$	1 : 1.50 : 452	+
Experiment 4	$0.38 \cdot 10^{-3}$	$0,94 \cdot 10^{-3}$	$284.3 \cdot 10^{-3}$	1 : 2.50 : 755	+

[a] $c_{polymer}$ is calculated based on the molecular weight of the monomer repeating unit (mru). [b]pol. = polymer (poly-**1**), cosolv. = cosolvent (THF), met.= metal.

b) ***Chiral amplification in both senses***

Circular Dichroism studies of Na^+ HPMC showed chiral amplification in both helical senses (left- and right-helicities) due to the different chelation mode of Na^+ to the pendant group provoked for the presence or absence of cation- π interaction depending on poly-**1**/MeOH ratio.

To determine that cation-π interaction producing left- and right-handed helices, ^{23}Na NMR, ^{1}H NMR and IR studies on HPMCs (M= Na^+) solutions were carried out.

^{23}Na-NMR experiments were performed in a Varian Inova 500 spectrometer (11.74 T) using as a reference NaCl in D_2O (2 M) and for ^{1}H NMR, a Varian Mercury 300 spectrometer (7.04 T).

Thus, a solution of poly-**1** in $CDCl_3$ (3.0 mg/mL) with Na^+ in CD_3OD (10 mg/mL) shows in ^{1}H-NMR an upfield shifted in the protons signals of the aryl rings of MPA when poly-**1** (mru)/CD3OD ratio= 1/<100 (mol/mol) (left-handed helix, negative CD). These ^{1}H-NMR studies also showed a deshielding on the OMe group and a shielding of the CαH proton. This fact is indicative of the presence of an *ap* conformation at the pendant moiety. IR studies shown the coordination of the metal ion to the carbonyl group ($\Delta\nu$ = +10 cm^{-1}). Overall, these studies indicate that the pendant moiety adopts a preferred *ap* conformation that induces a left handed helix in poly-**1** (Figure S27)**.**

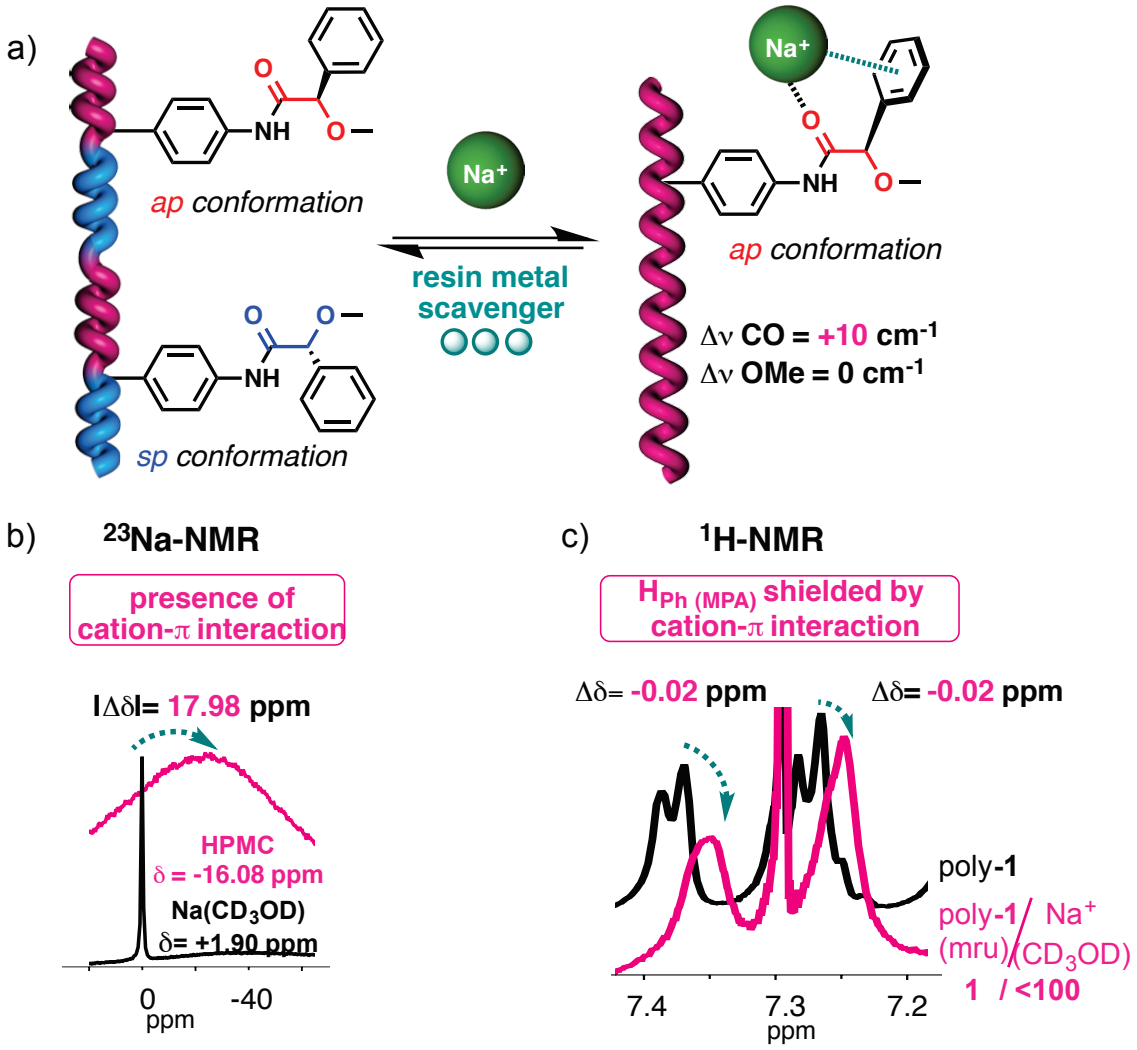


Figure S27: Chiral amplification of poly-**1** with Na^+. a) *ap* conformation stabilized by cation-π interactions and determined by IR b) ^{23}Na and c) ^{1}H NMR showing the cation-π interactions with poly-**1** (mru)/MeOH ratio of 1/<100 (mol/mol) [poly-**1**= 3.0 mg/mL $CHCl_3$, $NaClO_4$ = 100 mg /mL in MeOH]

Analogous experiments were carried out for a Na^+ HPMC solution with a positive Cotton effect, [poly-**1** (mru) / CD3OD ratio of 1/>100 (mol/mol)]. ^{23}Na NMR spectra showed a peak at -2.53 ppm indicating the absence of cation-π interaction. ^{1}H NMR spectra show no shifting in the protons signals of the Ph group of MPA when poly-**1** (mru)/CD3OD ratio= 1/>100 (mol/mol) (Figure S28). IR studies showed the coordination of the metal ion to both, carbonyl and methoxy groups, originating Δν values of +12 cm^{-1} and +19 respectively. All these studies indicate that the pendant moiety adopts a preferred *sp*

conformation that induces a right handed helix in poly-**1**, similar to the behavior of divalent metal ions.

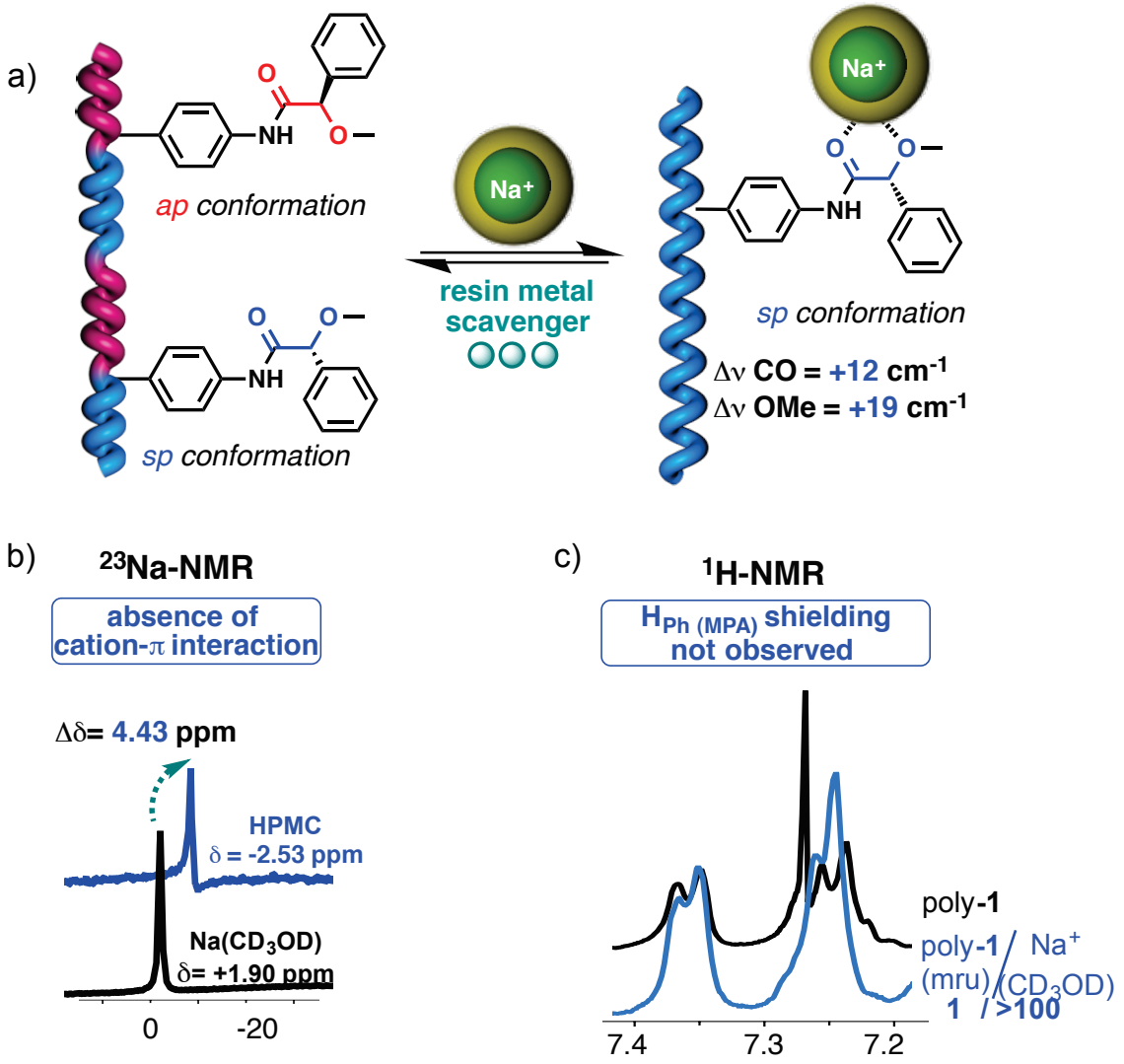


Figure S28: Chiral amplification of poly-**1** with Na^+ a) *sp* conformation stabilized by cation-π interactions and determined by IR b) ^{23}Na and c) ^{1}H NMR showing the absence of cation-π interactions with poly-**1** (mru)/MeOH ratio= 1/>100 (mol/mol) [poly-**1**= 3.0 mg/mL $CHCl_3$, $NaClO_4$ = 100 mg /mL in MeOH]

c) Helical inversion

- Helical inversion from left- to right- handed helices

Additional experiments were carried out to determine the conversion between left- and right-handed helical structures and *vice versa* by the addiction of more amount of cosolvent on poly-**1**. For example, successive

additions of cosolvent (i.e., MeOH) to a solution of HPMC (0.3 mg/mL, M= Na^+) (c_{poly} : c_{metal} : $c_{cosolv.}$ of 1 : 0.3 : 35, $g_{(384nm)} < 0$, negative CD) results in a helical inversion from left- to right-handed structure when the concentration of the cosolvent is higher than 100 equiv. due to the disruption of cation-π interaction (Figure S29, Table S13).

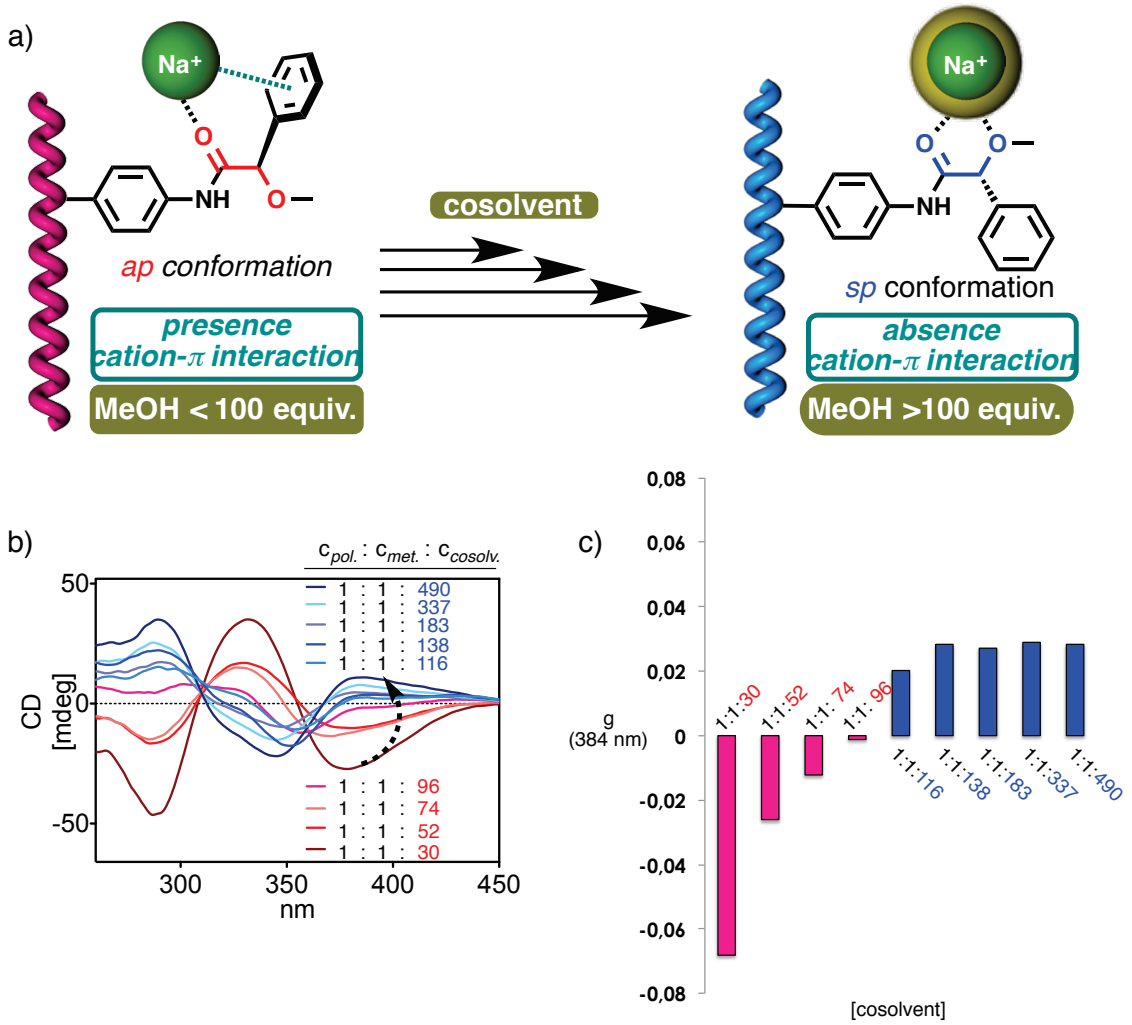


Figure S29: a) Structural effect of helical inversion of poly-**1** from left-handed to right-handed ($CHCl_3$, 0.3 mg/mL)/Na^+ (MeOH, 100 mg/mL) by the action of the cosolvent (i.e., MeOH) due to the presence/absence of cation-π interaction; b) CD spectra and c) graphical representation of $\mathbf{C}_{cosolvet}$: g_{384nm}.

Table S13: Cosolvent effect (MeOH) in the helical polymer metal complex.

$C_{polymer.}$ [a]	C_{metal} [Na^+]	$C_{cosolvent}$	$C_{pol.}$: $C_{met.}$: $C_{cosol.}$ [b]	$g_{(384nm)}$
$1.13 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	$34.19 \cdot 10^{-3}$	1 : 1 : 30	-
$1.13 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	$58.90 \cdot 10^{-3}$	1 : 1 : 52	-
$1.13 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	$83.61 \cdot 10^{-3}$	1 : 1 : 74	-
$1.13 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	$108.32 \cdot 10^{-3}$	1 : 1 : 96	-/+
$1.13 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	$130.56 \cdot 10^{-3}$	1 : 1 : 116	+
$1.13 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	$155.28 \cdot 10^{-3}$	1 : 1 : 138	+
$1.13 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	$204.70 \cdot 10^{-3}$	1 : 1 : 182	+
$1.13 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	$375.10 \cdot 10^{-3}$	1 : 1 : 337	+

[a] $c_{polymer}$ is calculated based on the molecular weight of the monomer repeating unit (mru). [b]pol. = polymer (poly-**1**), co solv. = cosolvent (MeOH), met.= metal.

NMR studies corroborate the presence of cation–π interactions. Thus, addition of extra CD_3OD to a solution of HPMC (M= Na^+) in poly-1 (mru)/CD_3OD ratio= 1/< 100 (mol/mol) (negative CD) moves the ^{23}Na signal from -16.08 ppm to -2.53 ppm which is the expected shift for $NaClO_4$ in CD_3OD (Figure 30b). This result indicates that with higher amounts of CD_3OD (positive CD), Na^+–π interactions are broken. Moreover, the disruption of the cation–π interaction produces a downfield shift at the proton signal of the MPA moiety (Figure S30).

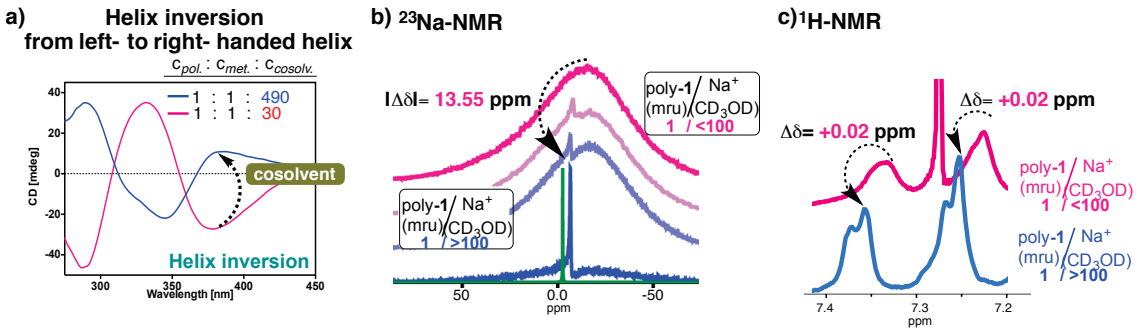


Figure S30: Helical inversion form left- to right-handed helix, a) CD, b) ^{23}Na and c) ^{1}H NMR showing the disruption of cation-π interactions [poly-**1**= 3.0 mg/mL $CHCl_3$, $NaClO_4$ = 100 mg /mL in MeOH]

- Helical inversion from right- to left-handed senses

The helical inversion of the Na^+ HPMC from right- to left-handed structures is achieved by the addition of more amount of poly-**1**. Thus, to determine the role of the polymer and the reversibility of the helical inversion process, a solution of poly-**1** in $CHCl_3$ (0.3 mg/mL) and $NaClO_4$ in MeOH (100 mg/mL) was prepared with the following ratio: c_{poly} :c_{meta} **:** $c_{cosolv.}$= 1:5:151. At this point, a right-handed helical structure ($g_{(384nm)} > 0$) was induced in poly-**1** due to the presence of a high amount of cosolvent (i.e., MeOH> 100 equiv) (Figure S31). Consecutive additions of poly-**1** increase its concentration, thus changing the polymer/cosolvent ratio (Figure S31, Table S14). If more polymers is added, the ratio between the polymer and the cosolvent is smaller than 1:100, resulting in a helical inversion from a right-handed to a left-handed helical structure (Figure 31, Table 4).
Therefore, the polymer-metal complex is involved in an equilibrium with the cosolvent, where the helical inversion is induced always at the same ratio independently of the concentration of the polymer (left-handed: C_{pol} **:** C_{met} **:** $C_{cosol.}$ ratio= 1: x : <100, and right-handed: $C_{pol.}$ **:** C_{met} **:** $C_{cosol.}$ ratio= 1: x : > 100, where x is any amount of the metal ion need to induce the chiral amplification).

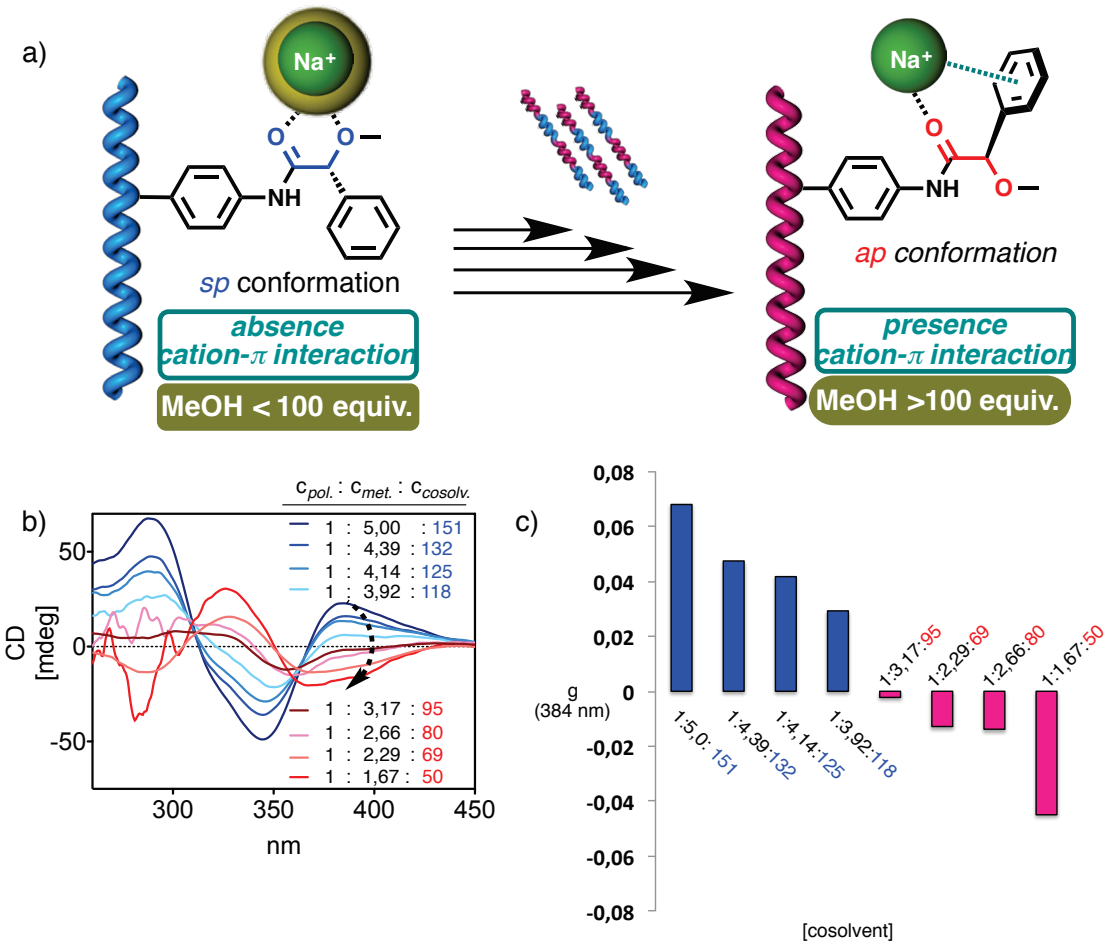


Figure S31: Helical inversion of poly-**1** from right- to left-handed senses ($CHCl_3$, 0.3 mg/mL)/Na^+ (MeOH, 100 mg/mL) by the action of poly-**1**(MeOH) (3mg/mL) due to the presence/absence of cation-π interaction; b) CD spectra and c) graphical representation of $\mathbf{C}_{cosolvet}$: $g_{384nm.}$

Table S14: Effect of the polymer in the helical polymer metal complex.

$C_{polymer}$[a]	C_{metal} [Na^+]	$C_{cosolvent}$	$C_{pol.}$: $C_{met.}$: $C_{cosol.}$[b]	$g_{(384nm)}$
$1.13\cdot10^{-3}$	$5.60\cdot10^{-3}$	$170.90\cdot10^{-3}$	1 : 5.00: 151	+
$1.26\cdot10^{-3}$	$5.57\cdot10^{-3}$	$168.60\cdot10^{-3}$	1 : 4.39 : 133	+
$1.33\cdot10^{-3}$	$5.53\cdot10^{-3}$	$167.47\cdot10^{-3}$	1 : 4.14 : 125	+
$1.40\cdot10^{-3}$	$5.49\cdot10^{-3}$	$166.34\cdot10^{-3}$	1 : 3.92 : 118	+
$1.68\cdot10^{-3}$	$5.34\cdot10^{-3}$	$161.62\cdot10^{-3}$	1 : 3.17 : 96	-/+
$1.95\cdot10^{-3}$	$5.19\cdot10^{-3}$	$157.16\cdot10^{-3}$	1 : 2.66 : 80	-
$2.20\cdot10^{-3}$	$5.05\cdot10^{-3}$	$152.94\cdot10^{-3}$	1 : 2.29 : 69	-

[a] $c_{polymer}$ is calculated based on the molecular weight of the monomer repeating unit (mru). [b]pol. = polymer (poly-**1**), cosolv. = cosolvent (MeOH), met.= metal.

This helical inversion is produced due to a conformational change from *sp* to *ap* conformer at the pendant moiety, which is stabilized by the cation-π interaction observed in ^{23}Na and ^{1}H NMR. Thus, addition of more CD_3OD to a solution of HPMC (M= Na^+) in poly-**1** (mru)/ CD_3OD ratio= 1/< 100 (mol/mol) (negative CD, Figure S32a) shifts the ^{23}Na signal from -2.53 ppm to -17 ppm which is the expected shift for $NaClO_4$ in CD_3OD (Figure S32b). This result shows that a high amount of CD_3OD (positive CD) disrupts the Na^+–π interaction. Moreover, this disruption produces a downfield shift in the proton signals of the MPA moiety.

^{23}Na NMR shows a strong shielding in the chemical shift observed when the Na^+ ion is forming part of the HPMC in a $c_{poly\text{-}1(mru)}$: c_{metal} : $c_{coslv.}$ Ratio= 1 : 0.3 : <100 . The chemical shift observed is typical when the metal ion is involved in cation-π interaction. From this chemical shift we can predict that the cation is interacting with only one aryl ring. When more methanol is added to the solution reaching a $c_{poly\text{-}1(mru)}$: c_{metal} : $c_{coslv.}$ Ratio= 1 : 0.3 : >100, the Na^+ peak shifts downfield in the NMR spectrum, resonating at a frequency typical for the perchlorate salt.

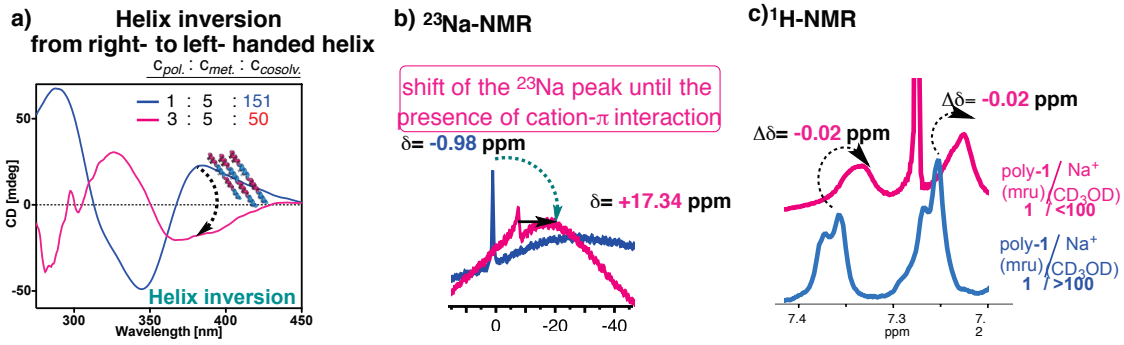


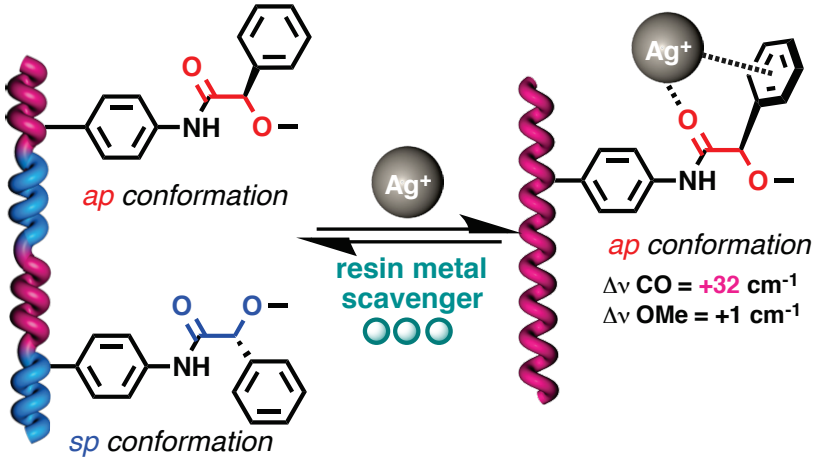
Figure S32: Helical inversion from right- to left-handed senses, a) CD, b) ^{23}Na and c) ^{1}H NMR showing the presence of cation-π interactions [poly-**1**= 3.0 mg/mL $CHCl_3$, $NaClO_4$ = 100 mg /mL in MeOH].

2.2.3 HPMCs (M= Ag^+)

Analogous experiments to the previous ones were performed. So, a solution of poly-**1** in $CHCl_3$ (0.1 mg/mL) was titrated with a solution of $AgClO_4$ in different

cosolvents such as acetone, DMF, DMSO, THF, MeOH, butanone, pyridine (10 mg/mL) (Figure S11). The results showed the presence of a left-handed helix in all of the cosolvents (negative CD) as in the case of $LiClO_4$ (see above).

Chiral amplification (left-handed helices)



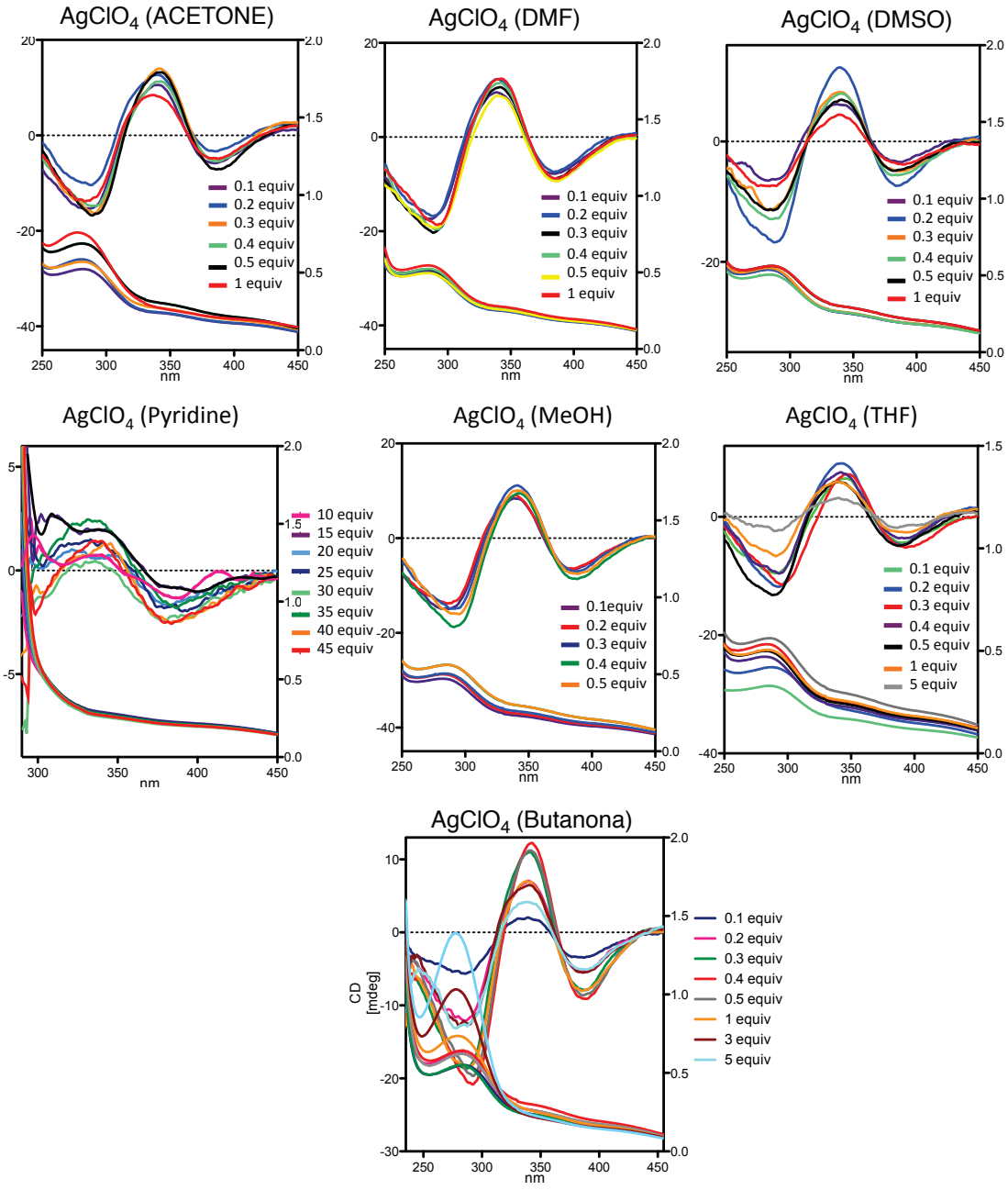


Figure S33: CD spectra of a solution of poly-**1** (0.1/mL in $CHCl_3$) titrated with different amounts of $AgClO_4$ in different solvents (acetone, DMF, DMSO, MeOH, THF and pyridine); [poly-**1**] = $0.38 \cdot 10^{-3}$ M in $CHCl_3$.

Analogously to the behavior of $NaClO_4$ in most solvents (except with DMF and DMSO), a dual behavior yielding two helical senses was observed during the study of $AgClO_4$ in MeCN. Thus, the role played by Ag^+ on the dual chiral amplification of poly-**1** was studied by titrations at different poly-**1** (mru)/Ag^+ ratios (Figure S34).

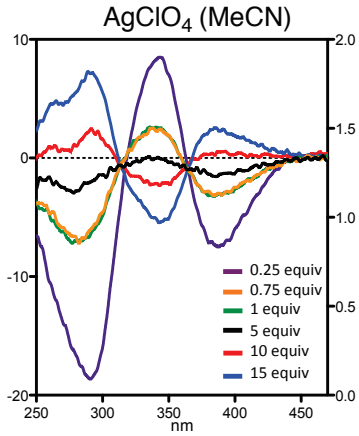


Figure S34: CD/UV spectra of a solution of poly-**1** (0.1/mL in $CHCl_3$) titrated with different amounts of $AgClO_4$ in MeCN; [poly-**1**] = $0.38 \cdot 10^{-3}$ M in $CHCl_3$.

During these titrations, it was found that the two helical senses could be obtained 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 the chiral amplification].

At a poly-**1** (mru)/MeCN ratio= 1/< 450 (mol/mol), the polymer adopts a left-handed helix, while at a poly-**1** (mru)/MeCN ratio= 1/> 450 (mol/mol) the right-handed structure is obtained.

Thus, the left-handed helix of Ag^+ HPMCs is determined by the presence of cation-π interaction. This interaction stabilizes the *ap* conformation as corroborate by spectroscopic studies. The ^1H NMR experiments on a solution of poly-**1** in $CDCl_3$ (0.3 mg/mL) with 0.1 equiv. of Ag^+ in MeCN-d_3 (10 mg/mL) at poly-**1** (mru)/MeCN ratio= 1/< 450 shows a downfield shifting of the Ph protons, deshielding of the OMe group, and shielding of CαH. IR studies of poly-**1** in $CHCl_3$ (3.0 mg/mL) with Ag^+ in MeCN (10 mg/mL) at poly-**1** (mru)/MeCN ratio= 1/< 450, show coordination of Ag^+ to the carbonyl and not to the MPA methoxy

group. (IR: $\Delta\nu$ CO= +32 cm^{-1}, $\Delta\nu$ OMe= +1 cm^{-1}) (Figure S35a and S35b). The right-handed helical structure is determined by the absence of cation-π interaction.

The presence/absence of cation-π interaction is determinated by polymer (mru)/cosolvent ratio as also happened before with Na^+ (see above).

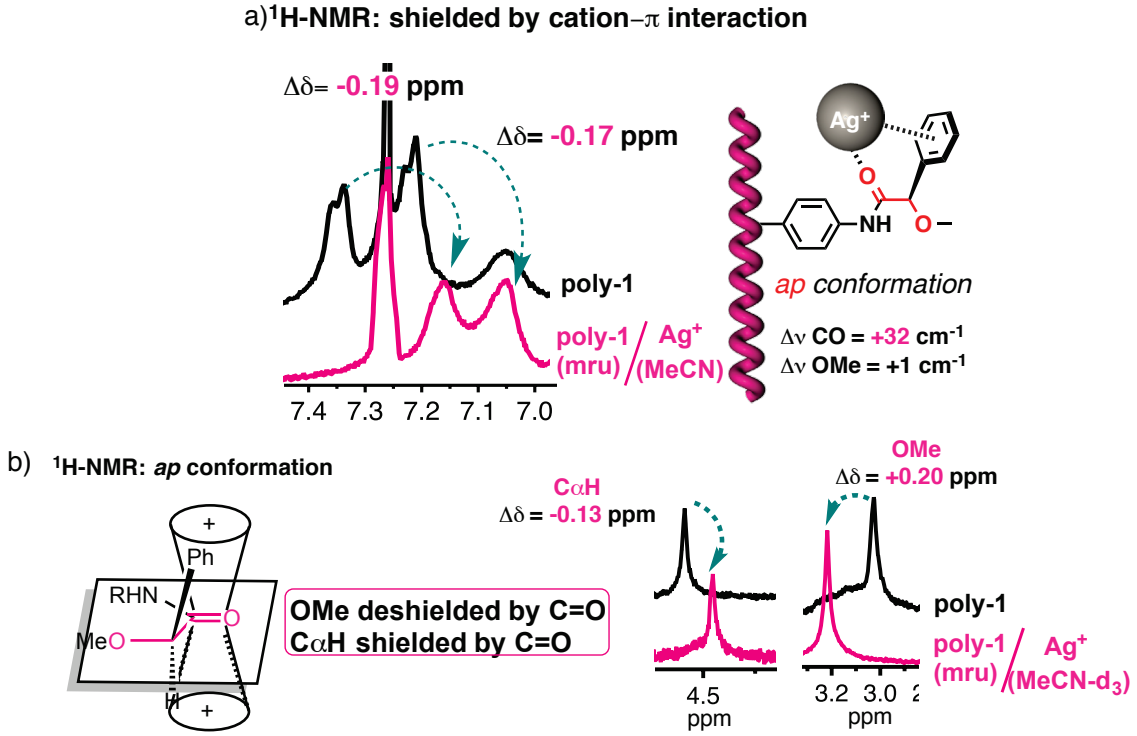


Figure S35: Chiral amplification of poly-**1** with Ag^+ a) *sp* conformation stabilized by cation-π interactions and determined by IR and ^1H NMR and b) ^1H NMR showing the *ap* conformation with poly-**1** (mru) / MeCN ratio of 1/>100 (mol/mol) [poly-**1**= 3.0 mg/mL $CHCl_3$, $AgClO_4$ = 100 mg /mL in MeCN]

a) Helical inversion

The left and right-handed helical structures are easily interconverted when MeCN is used as cosolvent. More precisely, the helical inversion form left- to right-handed helical structure is achieve by addition of more amount of MeCN to a HPMC solution at a poly-**1** (mru) /MeCN ratio= 1/<450 (mol/mol). Thus, a solution of 10 equiv. of Ag^+ in MeCN (100 mg/mL) was added to a solution of poly-**1** in $CHCl_3$ (0.3 mg/mL) [c_{poly} : c_{metal} : $c_{cosolv.}$ of 1 : 10 : 396, $g_{(384nm)} < 0$,

negative CD] followed by consecutive additions of MeCN. This titration change the poly-**1** (mru) / MeCN ratio from 1/<450 (mol/mol) to 1/>450 (mol/mol) due to the disruption of the cation-π interaction, that provokes a helical inversion from left- to right-handed sense. IR studies of poly-**1** in $CHCl_3$ (3.0 mg/mL) with Ag^+ in MeCN (10 mg/mL) and at a poly-**1** (mru) / MeCN ratio= 1/> 450, shows the coordination of Ag^+ to the carbonyl and to the methoxy groups of MPA (IR: Δν CO= +52 cm^{-1}, Δν OMe= +29 cm^{-1}) characteristic of a *sp* conformation (Figure S36). The opposite effect is observed when more amounts of poly-**1** are added to a HPMC solution at a poly-**1** (mru) / MeCN ratio of 1/ >450 (mol/mol).

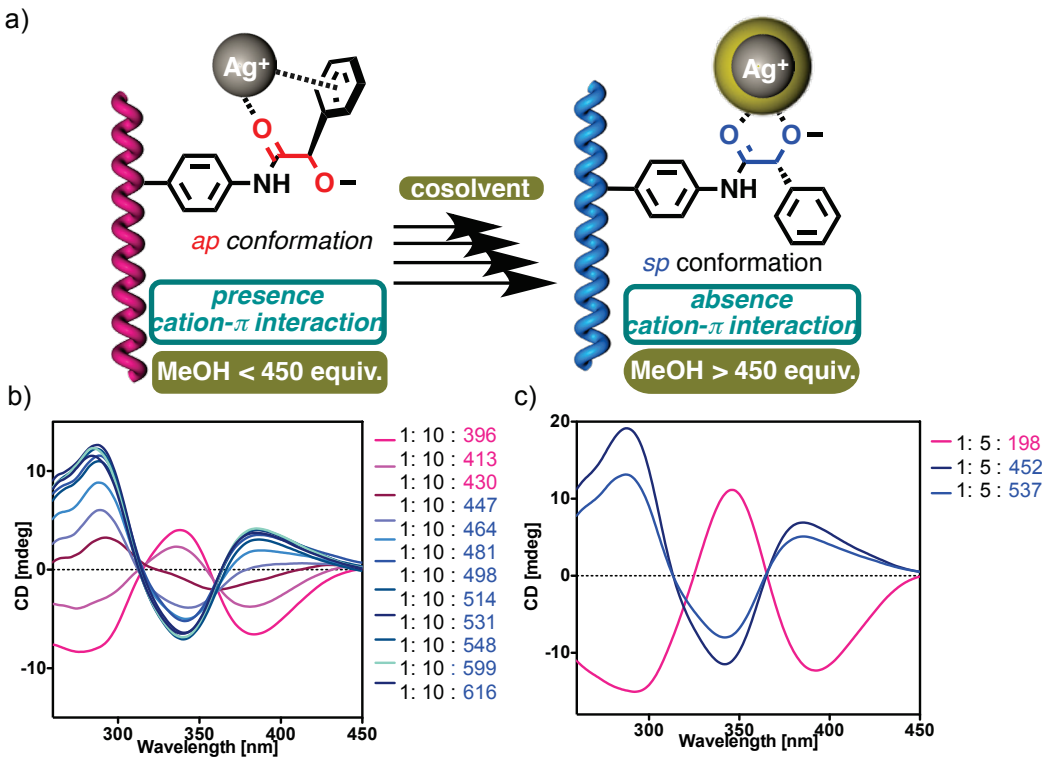
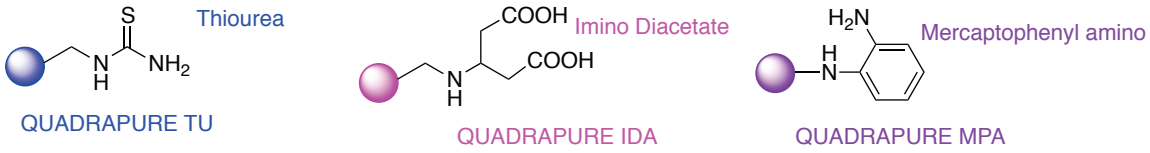


Figure S36: Helical inversion form left- to right-handed helix, a) representation of presence/absence of cation–π interaction due to the cosolvent effect, b) [poly-**1**= 0.3 mg/mL $CHCl_3$, $AgClO_4$ = 100 mg /mL in MeCN]

3. Chiral amplification and reversibility of the process by using metal scavenger resins

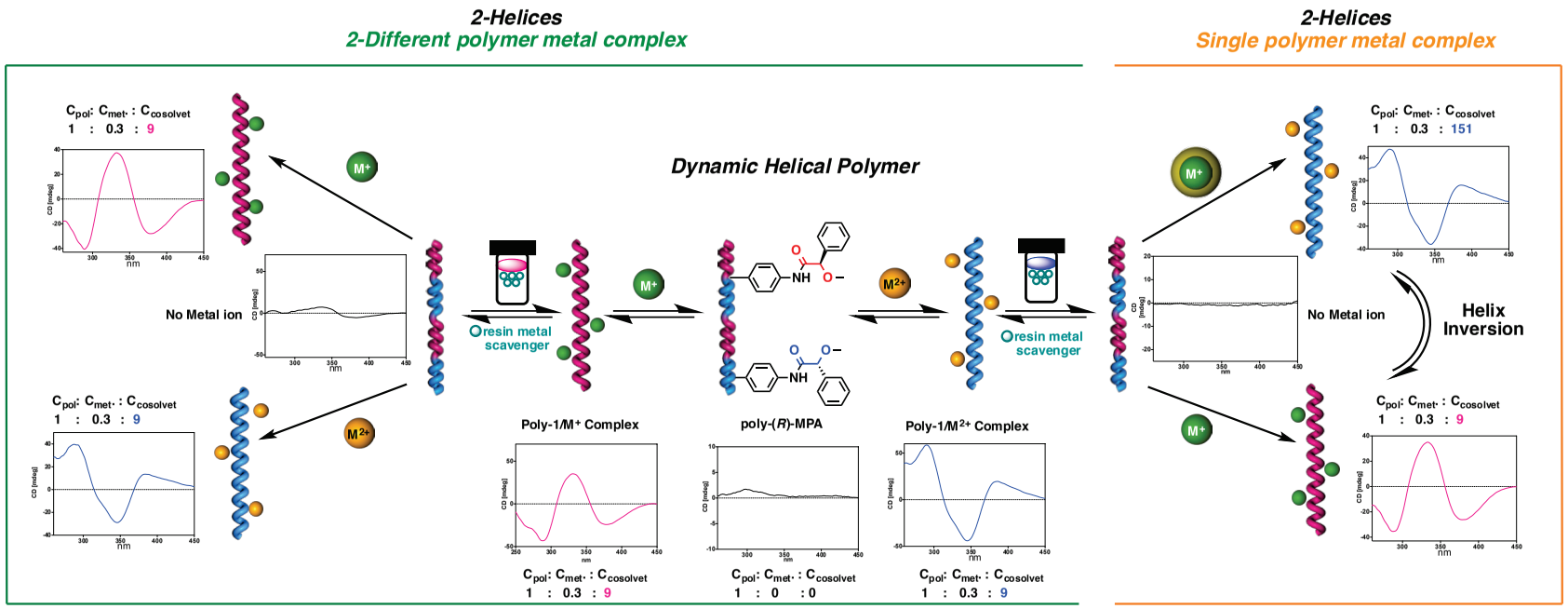
Commercial available Quadrapure™ (Aldrich) resins (IDA, MPA and TU) were used as metal scavengers. These resins contain different functionalities that trap the metal ions. The TU resin contains a thiourea functional group, the IDA resin posses an imino diacetate group and the MPA resin has a mercaptophenyl amino group.



QUADRAPURE TU QUADRAPURE IDA QUADRAPURE MPA

To perform the experiments, the resins were swollen in $CHCl_3$ for 1h (typically 5g per 100 mL of 1000 ppm solution). Then, 100 mg of the resin were added to a 1 mL solution of the polymer metal complex. After 1h, a CD spectrum was registered, showing the original signature of the free polymer in $CHCl_3$. Once the resin was removed from the solution, chiral amplification was observed when di- or monovalent metal salts were added.

Examples of the use the scavenger resins follow next:


2-Helices
2-Different polymer metal complex
2-Helices
Single polymer metal complex
Dynamic Helical Polymer
Cpol: Cmet. : Ccosolvet
1 : 0.3 : 9
No Metal ion
resin metal scavenger
Poly-1/M+ Complex
poly-(R)-MPA
Poly-1/M2+ Complex
Cpol: Cmet. : Ccosolvet
1 : 0 : 0
Cpol: Cmet. : Ccosolvet
1 : 0.3 : 151
Helix Inversion

4. Atomic Force Microscopy (AFM) and DSC measurements

Stock solutions of poly-(*R*)-**1** (0,3 mg/mL) in $CHCl_3$ were prepared and then diluted until 0.03 mg/mL. On the one hand, a solution of 10 mg/mL of $NaClO_4$ in MeOH was prepared and 0.3 equiv. of Na^+ were added to a 0,03 mg/mL solution of poly-**1** in $CHCl_3$. One drop of this mixture (10 μL) was placed on freshly cleaved HOPG and was spin coated at rt at 900 and/or 1800 rpm (Figure S37a). On the other hand, a solution of 10 mg/mL of $NaClO_4$ in DMSO was prepared and 0.3 equiv. of Na^+ were added to a 0.03 mg/mL solution of poly-**1** in $CHCl_3$. One drop of this mixture (10 μL) was placed on freshly cleaved HOPG and was spin coated at rt at 900 and/or 1800 rpm (Figure S37b).

All AFM measurements were performed at CACTI (Vigo University, Spain) in a MultiMode V Scanning Probe Microscope (Veeco Instruments) in air at rt with standard silicon cantilevers and super-sharp cantilevers in tapping mode using 12 μm and 1 μm scanners.

Nanoscope processing software and WSxM 4.0 Beta 1.0 (Nanotec Electronica, S.L.) were used for image analysis.

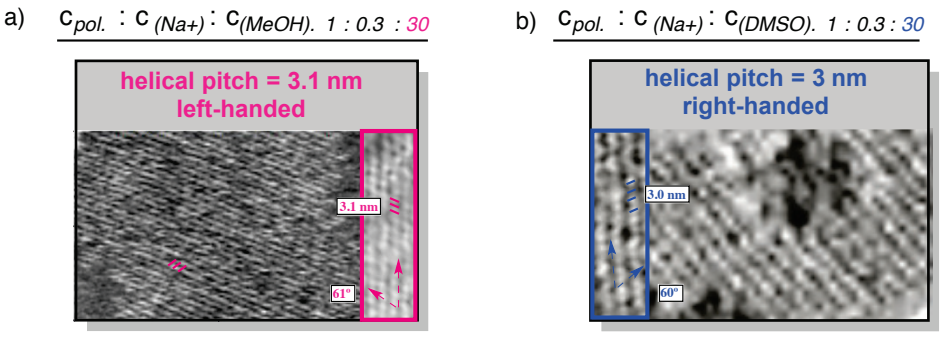


Figure S37: AFM image of a) poly-**1** + Na^+ (MeOH) with a composition $C_{pol.}$: $C_{met.}$: $C_{cosol.}$ ratio of 1 : 0.3 : 30 showing lef-handed helices and b) poly-**1** + Na^+ (MeOH) with a composition $C_{pol.}$: $C_{met.}$: $C_{cosol.}$ ratio of 1 : 0.3 : 30 showing right-handed helices.

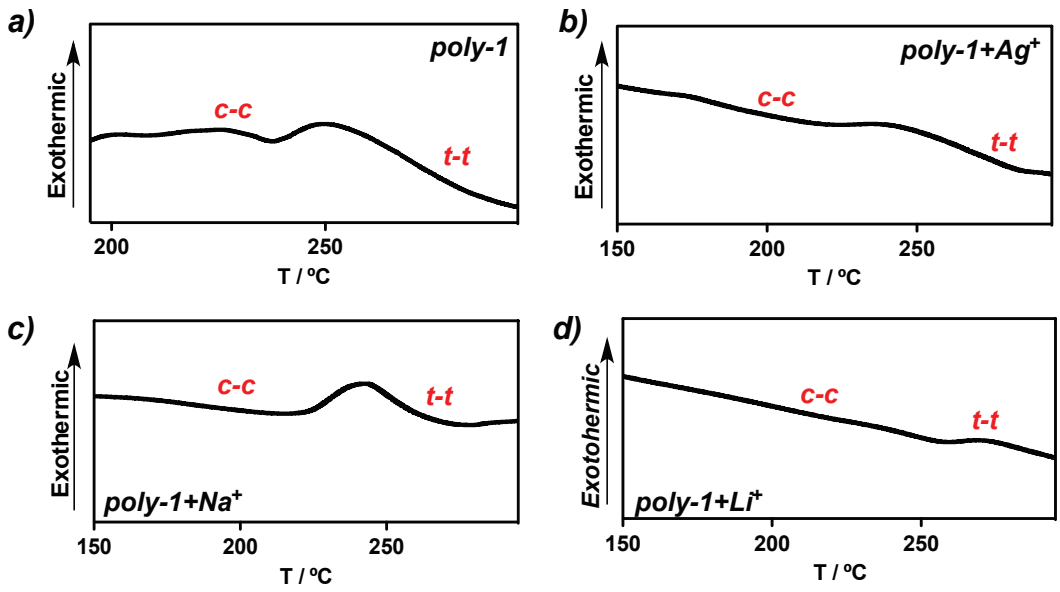


Figure S38: DSC image of a) poly-**1,** b) Poly-**1** with Ag^+, c) Poly-**1** with Na^+, d) Poly-**1** with Li^+,

5. Supporting References

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