Tuning the helical sense and elongation of polymers through the combined action of the two components of tetraalkylammonium-anion salts

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The helical sense and elongation of a helical polymer that bears the 4-ethynylanilide of (R)-α–methoxy-α-phenylacetic acid [m-(R)-**1**] can be tuned by the action of the two components of tetraalkylammonium-anion salts. Thus, while the supramolecular PPA-anilide/anion interaction creates a chiroptical switch, inducing either P or M helical senses in the poly(phenylacetylene) (PPA) depending on the nature of the anion —P helix: fluoride (F^-) or cyanide (CN^-); M helix: acetate (OAc^-), benzoate (OBz^-) or azide (N_3^-)—, deprotonation of the anilide group by these anions in dry conditions makes it possible to play with the elongation of the PPA, depending on the size of the tetraalkylammonium group, which results in a colorimetric switch. Thus, a color change from yellow to deep red is obtained by deprotonation of the anilide group when a tetraabutylammonium salt is used, while yellow/light-red and yellow/orange color changes are obtained when the size of the tetraalkylammonium group is reduced. Structural and mechanistic studies confirm that the color change occurs when the counterion accommodates itself close to the pendant group once the anilide hydrogen is removed. This PPA/tetraalkylammonium association is responsible of elongation changes in the PPA and therefore on the conjugation of the polyene backbone that is accompanied with color changes. Moreover, this colorimetric switch also operates in the solid state and can be switched in a vacuum/air moisture cycle.

1 Introduction

Chiral PPAs are dynamic helical polymers constituted by a flexible polyene backbone that adopts a helical scaffold stabilized by supramolecular and/or steric interactions among the pendants. [1-37] The addition of external stimuli —cations, anions, temperature, pH, polarity— to a solution or to a film of the polymer can alter those interactions and produce variations in the helical folding —chiral amplification, helical enhancement, helix inversion and/or elongation changes—. Variations on the helical sense folding can be easily monitored through changes in the ECD spectra, while elongation changes (compression/stretching) are accompanied with hypsochromic or bathochromic shifts in the UV–Vis spectra, which can also produce color changes in

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the polymer solution or film due to variations in the polyene conjugation.

Until now, the structural changes produced in a helical polymer are due to the interaction between a single stimulus and the polymer, where variations in helical sense and elongation occur at the same time by the action of the stimulus employed. In literature no examples are found about the selective manipulation of the helical sense or elongation of a helical polymer by the two counterparts of a single stimulus such as tetraalkylammonium-anion salts.

Thus, Kakuchi's research group [38-46] studied the stimuli-responsive behavior of a PPA series containing different acidic connectors —urea, sulphonamide, benzamide—. They found that the addition of anions to a PPA solution produces a supramolecular interaction between the anion and the acidic hydrogen of the PPA, which leads to structural changes easily monitored by CD or UV–Vis spectroscopies. In this case, they observed a relationship between the size of the anion and the color change of the polymer solution —larger anions produced greater red-shifts in UV–Vis— indicating that the polymer had increased conjugation. Hence, the stretching of the chains is due to the accommodation of the anions between the pendants of the helical turns, which results in an elongation of the helical scaffold. [44] As a result, the change of the helical sense and elongation of the polymer is produced just by a single stimulus, the anion.

Herein, we will demonstrate that it is possible to prepare a dual chiroptical and colorimetric switch by a two-step interaction between a PPA —with anilide linkages between pendants and the helical scaffold— and the two components of a tetraalkylammonium-anion salt. Thus, while the PPA anilide/anion interaction will produce a chiroptical switch —P or M helix induction in the polymer depending on the anion used—, a colorimetric switch will be generated by further addition of the salt, which carries out the deprotonation the polymer by the anion, and where a new PPA/tetraalkylammonium ion interaction will generate modifications in the PPA elongation associated to color changes (Scheme 1).

This color change concomitant with anilide deprotonation is achieved by all PPA/salt pairs at different temperatures, thereby functioning as colorimetric thermometers.

The mechanism of the PPA-anion recognition process responsible of the chiroptical switch and the crucial role that cation size plays in generating a color switch based on these PPA/anion salt pairs is studied in detail throughout this manuscript.

2 Results and discussion

2.1 Design and synthesis of monomers and polymers

To carry out the PPA/anion interaction studies, we chose two polymers as model compounds —poly-**1** and poly-**2**—. Thus, poly-(R)−**1** bears the 4-ethynylanilide of (R)-α–methoxy-α-phenylacetic acid (MPA) as pendant [29-35] (Fig. 1a), while poly-(R)−**2** carries the 4-ethynylanilide of (R)-α–methoxy-α-trifluoromethylphenylacetic acid (MTPA) [36-37] (Fig. 1a). These two PPAs are chiral, with well-known helical structures and stimuli-responsive properties, but with different dynamic helical behaviors. For these reasons, poly-(R)−**1** and poly-(R)−**2** were

designed to explore the chiroptical response to the presence of anions and to the anilide-anion interaction mechanism.
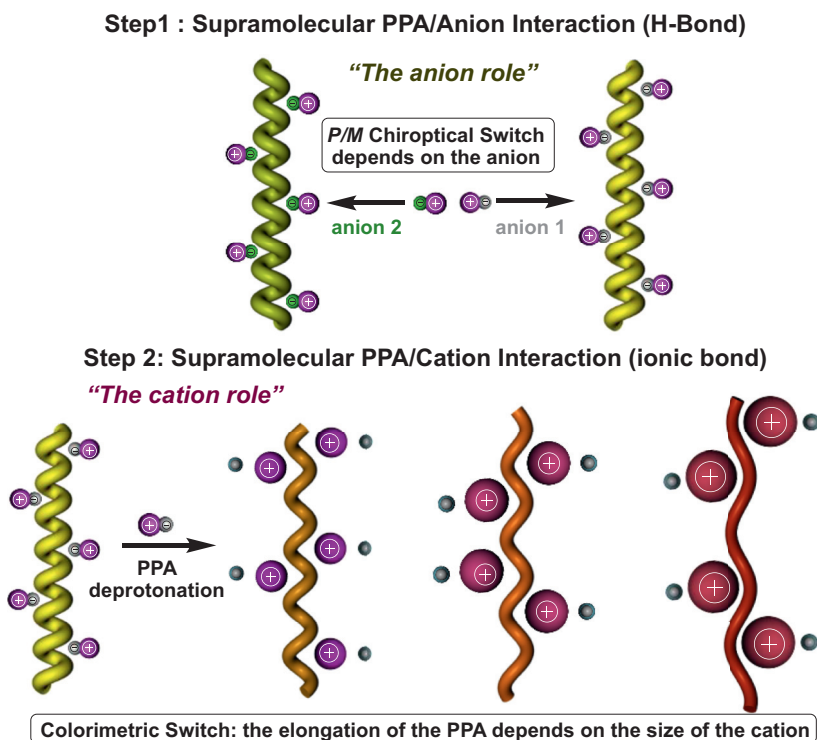
2.2 Stimuli-responsive properties of monomers with different tetra-n-butylammonium salts

Before the stimuli response properties of poly-(**1–2**) were examined, the interaction of the corresponding monomers —m-(R)−**1** and m-(R)−**2** (Fig. 1b)— with different tetra-n-butylammonium salts of different anions (TBAA) —A= $CH_3CO_2^-$ (acetate), $C_6H_5CO_2^-$ (benzoate), N_3^- (azide), CN^- (cyanide) and F^- (fluoride)— were studied by different structural techniques such as UV–Vis, Nuclear Magnetic Resonance (NMR) and Circular Dichroism (CD) to shed light on the anilide-anion interaction mechanism. All experiments were performed in dry THF to avoid interference from water (see SI for details). We will show in the main text the results obtained for the m-(R)−**1**/TBAF pair (Fig. 2a), while those of the other monomer/anion pairs are fully described in the SI (Figures S12-S15).
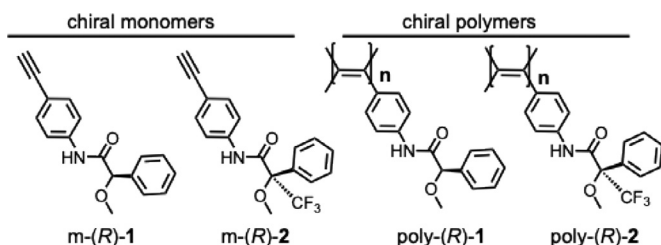
A dry THF solution of monomer m-(R)−**1** ($3.772 \cdot 10^{-4}$ M) shows a UV–Vis band centered at 270 nm (Fig. 2b), with a positive Cotton effect at the same wavelength (270 nm) in the ECD spectrum indicating that the MPA fragment has the carbonyl and methoxy group ($O = C$—C–OMe) oriented antiperiplanar (*ap* conformation). Adding 1 to 5 equivalents of a dry THF solution of TBAF (0.382 M) to the monomer solution ($3.772 \cdot 10^{-4}$ M) produced a 13 nm bathochromic shift of the UV–Vis band centered at 270 nm. This shift was accompanied by an inversion of the Cotton band in the ECD spectrum —monomer (R)−**1** CD_{270} (+); monomer (R)−**1**/TBAF CD_{283} (-)— (Fig. 2a, b). In turn, this inversion is associated with a conformational change in the MPA moiety and the formation of a hydrogen bond between the fluoride anion with the acidic hydrogen of the anilide group. Consistent with this association, a strong deshielding effect is observed for the anilide proton in the corresponding NMR spectrum (see Figure S16). This conformational change was also observed in the rest of the m-(R)−**1**/anion pairs studied (anion= N_3^-, CN^-, $CH_3CO_2^-$ and $C_6H_5CO_2^-$), confirming that the supramolecular anilide/anion interaction is accompanied in all cases by a conformational change from *antiperiplanar* (*ap*) to *synperiplanar* (*sp*) in the (O–C)—($C = O$) bond of the pendant.

This result corroborates that m-(R)−**1** can be considered as an ON/OFF chiroptical switch for this supramolecular interaction (Fig. 2d). Subsequent additions of TBAF (20 to 50 equiv) showed the disappearance of the UV–Vis band of the monomer at 283 nm and the growth of a band centered at 330 nm, which is associated with a negative Cotton band in the ECD spectrum (Fig. 2b, d). This large bathochromic shift —50 nm— is indicative of the effective deprotonation of the anilide group by the fluoride anion confirmed by NMR in the m-(R)−**2**/TBAF pair by the presence of a peak at ~16.1 ppm corresponding to the HF_2^- species (Figure S20). [47-53]

Among the different anions investigated, only fluoride (F^-) can deprotonate the anilide group of the two monomers, m-(**1–2**), although different amounts of this anion are needed in each case depending on the acidity of the anilide group (see SI). For instance, 5 equiv of F^- are enough for a complete deprotonation of m-(R)−**2**, whose anilide group is activated by the presence of a CF_3 electron

Step1 : Supramolecular PPA/Anion Interaction (H-Bond)

Step 2: Supramolecular PPA/Cation Interaction (ionic bond)

Scheme 1

Schematic illustration of a two-step chiroptical and colorimetric switch.

Fig. 1

Structures of (a) monomers m-(R)−**1**, m-(R)−**2** and (b) polymers poly-(R)-**1**, poly-(R)−**2**.

withdrawing group, while in the case of m-(R)−**1** a large excess of more than 10 equiv is necessary to fully deprotonate it (see ESI). The higher acidity of m-(R)−**2** makes its deprotonation possible by the other anions (i.e., N_3^-, CN^-, $CH_3CO_2^-$ and $C_6H_5CO_2^-$), whereas the addition of these anions to a the less acidic monomer, such as m-(R)−**1**, leads only to the supramolecular anilide/anion interaction without deprotonation (Figs. 2d and S12-S15).

2.3 Stimuli-responsive properties of poly-**1** and poly-**2** with different tetra-n-butylammonium salts

Having disclosed the two-step interaction process (complexation and deprotonation) associated with the anilide/anion pair for the monomers (m-**1** to m-**2**), we turned our attention to the behavior of the corresponding polymers in the presence of the anions. Thus, monomers m-(R)−**1** and m-(R)−**2** were polymerized using [Rh(nbd)Cl]$_2$ as catalyst (nbd= 2,5-norbornadiene), affording the corresponding PPAs [poly-(R)-(**1**–**2**)] in good yields and with high

cis double bond content (see SI for full details). UV–Vis and CD titrations of the solutions in dry THF of poly-(R)-(**1**–**2**) were carried out by adding different TBAA salts $-A = N_3^-$ (azide), CN^- (cyanide), $CH_3CO_2^-$ (acetate), $C_6H_5CO_2^-$ (benzoate) and F^- (fluoride)— prepared in the same solvent. During the titrations, a color change from yellow to red was observed in some of the PPA/TBAA pairs, but interestingly, the anion responsible for this color change was not always the fluoride anion −as could be presumed from the previous results with the monomers− (Fig. 3). For instance, a colorimetric response is produced in poly-(R)−**1** by TBAA salts containing carboxylate groups (acetate and benzoate), while in the case of poly-(R)−**2**, the TBAA salts containing fluoride or cyanide anions are those that produce a strong color change in the solution (Figs. 3 and S21-S24).

These differences in the response properties of the different PPAs —poly-(R)−**1**, poly-(R)−**2**—to stimuli of the TBAA salts, and between monomers and polymers, are a clear indication that both the polymeric character (cooperativity) and the helical structure adopted by each PPA play an important role in the PPA/anion interaction. Moreover, CD and UV–Vis titration studies also indicate the existence of the two interaction processes (association and deprotonation) described above for the interactions between the monomers and the TBAA salts. However, in the case of polymers and depending on the PPA/TBAA pair, this interaction may be limited to only the anion-anilide association or may continue until deprotonation (see Fig. 4 for the results for poly-(R)−**1** and SI for poly-(R)−**2**). These results indicate that the secondary structure adopted by the PPA plays an important role in the pendant/anion interaction, altering its strength when
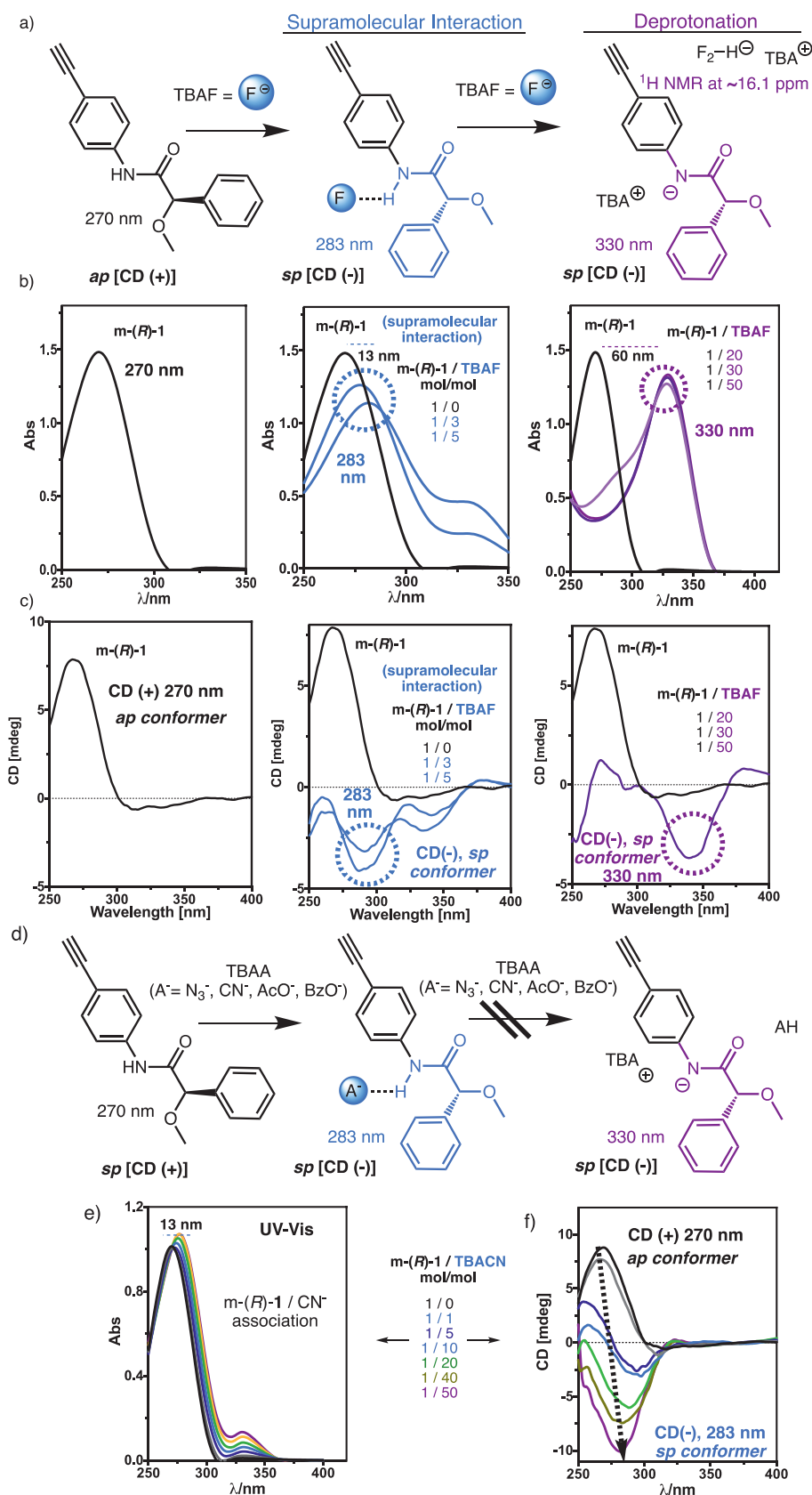
Fig. 2

(a) Schematic representation of the two-step supramolecular interaction process (association/deprotonation) for the m-(R)−**1**/TBAF pair accompanied with a conformational change at m-(R)−**1**. b) UV–Vis studies and (c) CD studies of a m-(R)−**1** solution titrated with TBAF. (d) Conformational change at m-(R)−**1** by interaction with different TBAA salts ($A = N_3{}^-$, CN^-, $CH_3CO_2{}^-$ and $C_6H_5CO_2{}^-$). (e) UV–Vis and (f) CD studies of a m-(R)−1 solution titrated with TBACN. [m-(R)−**1**] = $3.772 \cdot 10^{-4}$ M in dry THF, [TBAA] = 0.382 M in dry THF.
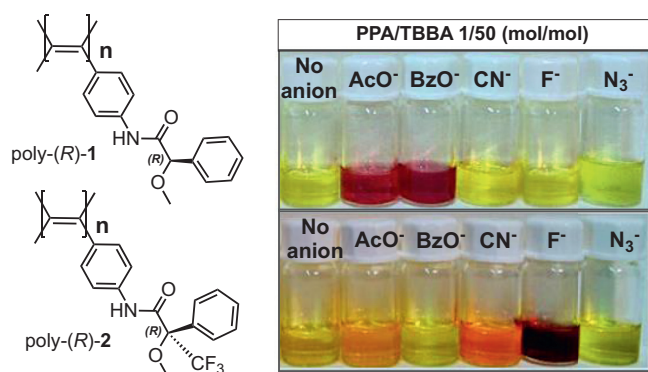
Fig. 3

Colorimetric changes associated to the different PPA/TBAA pairs [TBAA= tetrabutylammonium anion salts; A = N_3^- (azide), CN^- (cyanide), $CH_3CO_2^-$ (acetate), $C_6H_5CO_2^-$ (benzoate) and F^- (fluoride)].

compared with the parent monomer/anion interaction [54-57]. To corroborate these hypotheses, another two PPAs were prepared, poly-**3** and poly-**4**, which bear the 4-ethynylanilides of trifluoroacetic acid and tert–butyl hydrogen carbonate as pendant groups respectively and that are not chiral (Figure S3 and S15). Therefore, these PPAs are axially racemic. These monomers and polymers were designed to study both the role of electron withdrawing groups in the anion-PPA interaction and the role of the cation size in its colorimetric detection, which showed as expected the role of the PPA secondary structure in the pendant anion/interaction.

In the case of poly-(R)−**1**, different chiroptical responses are produced during the formation of the poly-(R)−**1**/TBAA supramolecular complex —association—. Thus, when fluoride

or cyanide salts were added to poly-(R)−**1** [poly-(R)−**1**/TBAF or TBACN in 1.0/5.0 (mol/mol) ratios] a 30 nm bathochromic shift was observed in the band centered at 290 nm. This shift is produced by the complexation between the anilide groups in the pendants with the F^- or CN^- anions (See Fig. 4a for poly-(R)−**1**/TBAF and SI for the other polymers). In addition, this interaction induces a P helical sense excess in poly-(R)−**1**, manifested by a positive polyene Cotton band [CD_{410} (+)] associated to the ap conformations at the pendants. Interestingly, when acetate ($CH_3CO_2^-$), benzoate ($C_6H_5CO_2^-$) and azide (N_3^-) were added as TBA salts to dry THF solutions of poly-(R)−**1** in 1.0/5.0 (mol/mol) ratios, the resulting anilide/anion association forced the polymer chain to adopt an excess of the M helical sense [CD_{410} (-)], as opposed to the P helical sense induced by fluoride and cyanide (see Fig. 4b for poly-(R)−**1**/TBAOAc and SI for the rest). The formation of this supramolecular anilide/anion aggregate was corroborated by different NMR experiments —^{1}H NMR, Diffusion Ordered Spectroscopy (DOSY), Saturation-Transfer Difference (STD) and Nuclear Overhauser Effect Spectroscopy (NOESY) (See SI for details), which confirmed that these two components —poly-(R)−**1** and TBAOAc —form a sole entity in solution. Thus, poly-(R)−**1** acts as a chiroptical switch able to distinguish not only the presence of anions in solution, but also to classify them by the helical sense excess adopted by the polymer.

This property is not observed in its parent monomer —where all the anions produced the same conformational change from ap to sp— and indicates the importance of the cooperative effects triggered on the helix of the polymer by the anions.

Increasing the amounts of TBAA salts in the poly-(R)−**1** solutions —poly-(R)−**1**/TBAA 1/>50 (mol/mol) ratio —, the deprotonation of the anilide groups occurred with all anions
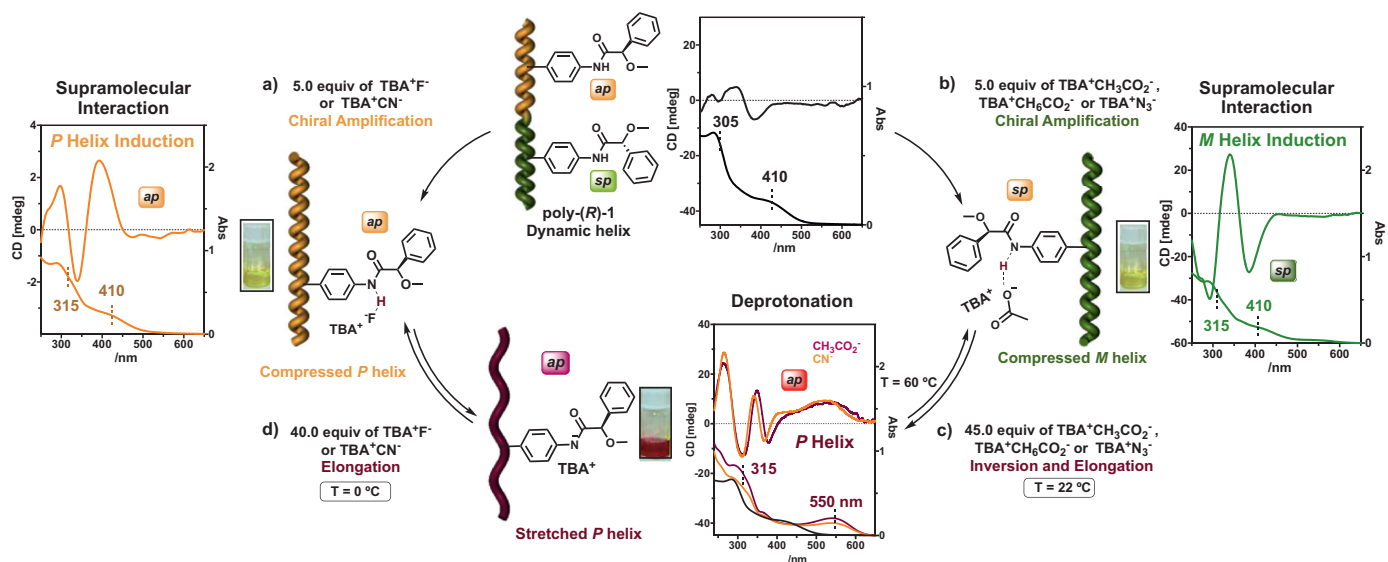

Fig. 4

(a) P helix induction in poly-(R)−**1** by addition of 5.0 equiv of TBAA (A= fluoride or cyanide). (b) M helix induction in poly-(R)−**1** by addition of 5.0 equiv of TBAA (A= acetate, benzoate or azide). (c) Elongation and P helix induction in poly-(R)−**1** by addition of 45.0 equiv of TBAA (A= acetate, benzoate or azide) at rt or (d) 40.0 equiv of TBAA (A= fluoride or cyanide) at 0 °C. [poly-(R)−**1**]= 0.1 mg/mL dry THF, [TBAA]= 100 mg/mL dry THF.
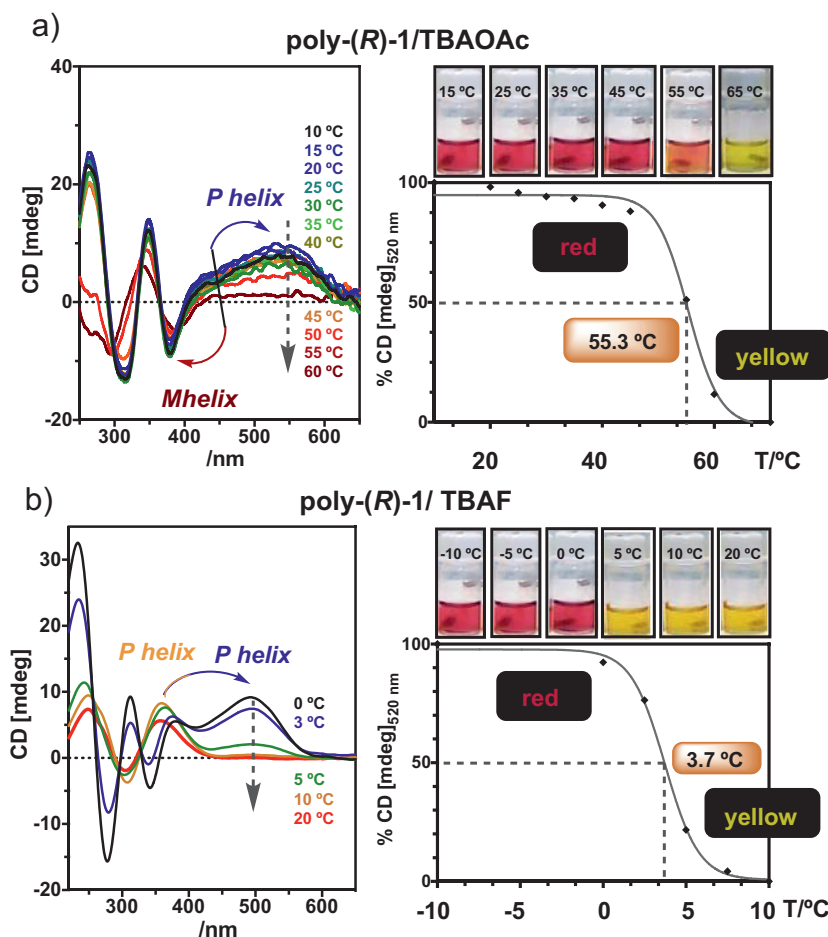
Fig. 5

Thermal protonation/deprotonation equilibrium of (a) poly-(R)−**1**/TBAOAc and (b) poly-(R)−**1**/TBAF pairs in 1/50 (mol/mol) ratio.

visualized by a strong color change from yellow to red in the polymer solution, accompanied by a large bathochromic shift (c.a. 150 nm) of the polyene band in the UV–Vis spectra that is indicative of a lengthening of the polyene backbone (Fig. 4c, d). To carry out the deprotonation of the anilide group it is necessary to work in dry conditions, otherwise the water present in the solvent will protonate the anilide, recovering the supramolecular anilide-anion interaction.

Moreover, the CD spectra of these mixtures show a first positive Cotton effect, coherent with a stretched *P* helical structure (Fig. 4 and SI) that is common to all the poly-(R)−**1**/TBAA pairs. Interestingly, this poly-(R)−**1** color change from yellow to red was found to be very sensitive to temperature.

2.4 Colorimetric thermometer based on poly-(R)−**1**/TBAA pairs
Motivated by these results, the evolution with temperature of all the poly-(R)−**1**/TBAA pairs was studied in a 1/50 (mol/mol) ratio.

For instance, in the case of the poly-(R)−**1**/TBAOAc system, the color change takes place at 25 °C, while for the poly-(R)−**1**/TBAF pair, a temperature close to 0 °C is needed to observe it (Fig. 4c-d). During these experiments, it was found that only the poly-(R)−**1**/TBAOAc and poly-(R)−**1**/TBAOBz pairs produce red (deprotonated) solutions at room temperature, while poly-

(R)−**1**/TBAN$_3$, poly-(R)−**1**/TBAF and poly-(R)−**1**/TBACN remain yellow (anilide/anion aggregate). Heating or cooling the solutions (from 60 to 10 °C) revealed that the transition temperature from red to yellow is different for each poly-(R)−**1**/TBAA pair (Figs. 5 for poly-(R)−**1**/TBAOAc, and poly-(R)−**1**/TBAF, see S36–37 for the rest).

Thus, while the color transition temperature of the poly-(R)−**1**/TBAOAc pair is 55.3 °C (Fig. 5a), the color changes in poly-(R)−**1**/TBAOBz, poly-(R)−**1**/TBAN$_3$, poly-(R)−**1**/TBAF and poly-(R)−**1**/TBACN are produced at 38.7 °C, 5.6 °C, 3.7 °C and 3.5 °C respectively (Figs. 6a and 5b for poly-(R)−**1**/TBAF). To evaluate the capabilities of these systems as colorimetric thermometers, additional TBAA salts containing (L)-t-BuO-prolinate, (L)-t-BuO-valinate, (R)−2-phenylbutanoate, (R)-α–methoxy-α-phenylacetate or (L)-t-BuO-alaninate were incorporated into the study. The results presented in Fig. 6a clearly show that each poly-(R)−**1**/TBAA system has a characteristic and easily visualized deprotonation temperature (See SI for details).

The deprotonation of the anilide group and the colorimetric response of the PPA in solid state (film) were also tested for a poly-(R)−**1**/TBAOAc pair in a 1/50 (mol/mol) ratio, obtaining that in vacuum (absence of water vapor), the film is red in color, while at atmospheric pressure the film turns yellow due to the
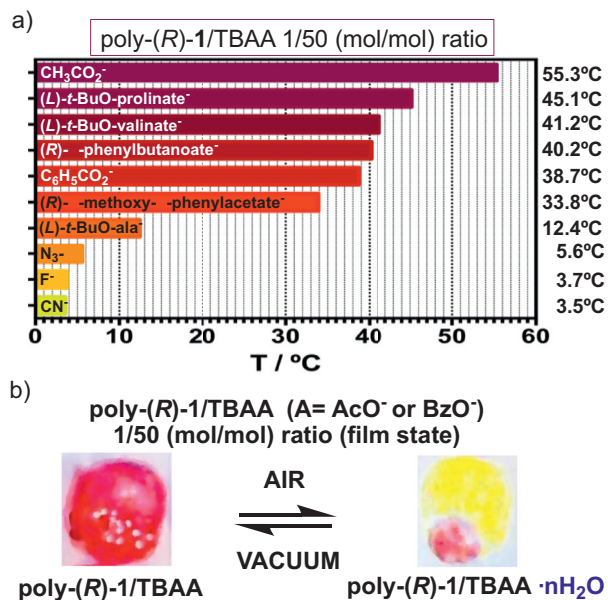
a)

poly-(R)-1/TBAA 1/50 (mol/mol) ratio

Anion	T
CH₃CO₂⁻	55.3ºC
(L)-t-BuO-prolinate⁻	45.1ºC
(L)-t-BuO-valinate⁻	41.2ºC
(R)- -phenylbutanoate⁻	40.2ºC
C₆H₅CO₂⁻	38.7ºC
(R)- -methoxy- -phenylacetate⁻	33.8ºC
(L)-t-BuO-ala⁻	12.4ºC
N₃⁻	5.6ºC
F⁻	3.7ºC
CN⁻	3.5ºC

b)

poly-(R)-1/TBAA (A= AcO⁻ or BzO⁻)
1/50 (mol/mol) ratio (film state)

poly-(R)-1/TBAA ⇌ poly-(R)-1/TBAA ·nH₂O
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Fig. 6

(a) Deprotonation temperature of the anilide group in different poly-(R)−1/TBAA pairs in 1/50 (mol/mol) ratios. (b) Deprotonation/protonation equilibrium of a poly-(R)−1/TBAA film in a 1/50 (mol/mol) ratio induced by the absence/presence of water in the atmosphere.

protonation of the anilide group by the water present in the air. This process is reversible and can be shifted to red or yellow by placing the sample under vacuum or under atmospheric pressure (Fig. 6b).

From a structural point of view, it is interesting to note that once poly-(R)−1 is deprotonated by a TBAA salt that produces a red solution, a very similar stretched P helix (positive CD_{550}) is adopted in all cases, regardless of the excess of P or M helical sense adopted by the poly-(R)−1/TBAA complex in the associated state —poly-(R)−1/TBAOAc, TBAOBz and TBAN₃ pairs present a compressed M helix while poly-(R)−1/TBAF and poly-(R)−1/TBACN adopt a compressed P helix— (Figs. 5, 6 and SI). Hence, while the nature of the anion plays an important role in the helical sense enhancement of poly-(R)−1 towards P or M helices by formation of an anilide/anion complex (yellow), the nature of the anion is no longer important once the anilide group is deprotonated (red). At this point, the helix induced by all TBAA salts is the same (stretched P helix), and different from the previous one, indicating that at this time, the anion has no relevance in the helical induction of the deprotonated poly-(R)−1.

The similar structure adopted by poly-(R)−1 independently of the TBAA salt used to deprotonate the anilide group led us to focus our attention on the mechanism of deprotonation and the resulting elongation of the polyene backbone.
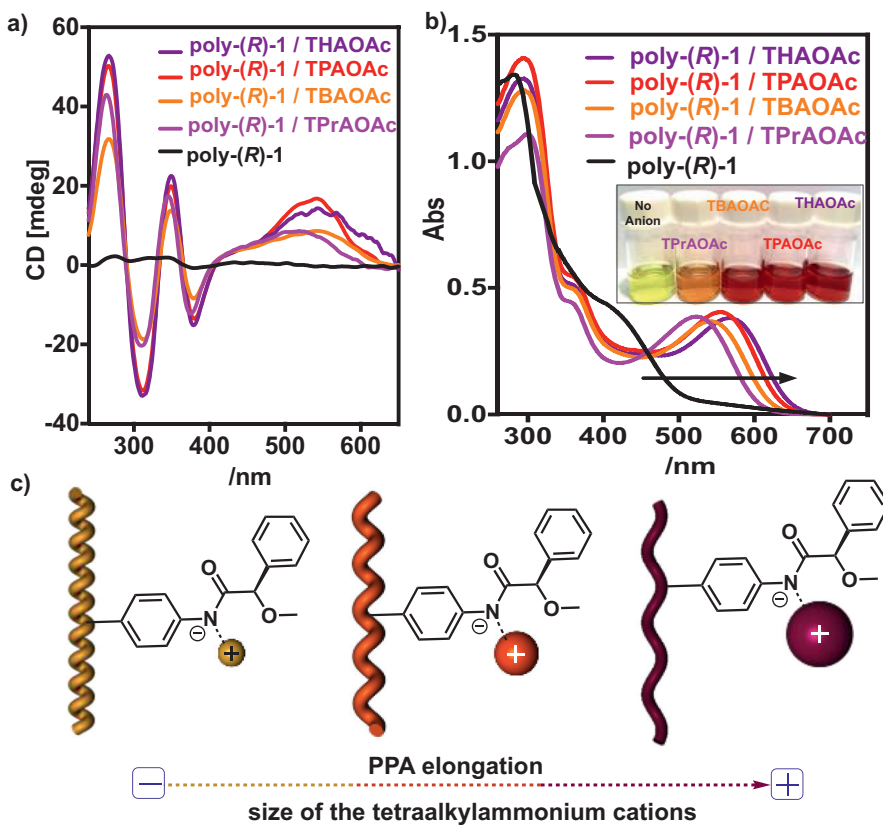

a)

CD [mdeg] vs /nm

- poly-(R)-1 / THAOAc
- poly-(R)-1 / TPAOAc
- poly-(R)-1 / TBAOAc
- poly-(R)-1 / TPrAOAc
- poly-(R)-1

b)

Abs vs /nm

- poly-(R)-1 / THAOAc
- poly-(R)-1 / TPAOAc
- poly-(R)-1 / TBAOAc
- poly-(R)-1 / TPrAOAc
- poly-(R)-1

c)

PPA elongation

size of the tetraalkylammonium cations

Fig. 7

(a) CD and (b) UV–Vis spectra showing the deprotonation of poly-(R)−1 by different TAAA salts in 1/50 (mol/mol) ratios —poly-(R)−1/ TPrAOAc, TBAOAc, TPAOAc, THAOAc —. (c) Size effect of the tetraalkylammonium counterions in the deprotonation process of a PPA bearing anilide groups.

2.5 The role of the tetralkylammonium group in the colorimetric response of poly-(R)−**1** with different tetraalkylammonium anion (TAA) salts

During deprotonation, the polymer becomes a polyanion with TBA$^+$ as the counterion, coexisting in solution with the protonated form of the anion used as base, which is now inert to the PPA. Thus, the helical stretching of the PPA backbone could only be caused either by the repulsive forces between the negative charges found within the polymer structure, or by the release of the steric hindrance in the helix scaffold during the accommodation of the TBA$^+$ groups, which are placed close to the negative charges of the polymer.

To elucidate which of these two factors affect the elongation of poly-(R)−**1** during the deprotonation process, tetraalkylammonium acetate salts (TAAOAc) of different sizes (alkyl chains with different lengths) were used to deprotonate the PPA —tetrapropylammonium (TPrAOAc), tetrabutylammoniun (TBAOAc), tetrapentylammonium (TPAOAc) and tetrahexylammonium (THAOAc)−. Dry THF solutions of these salts were added to different vials containing solutions of poly-(R)−**1** in dry THF until reaching poly-(R)−**1**/TAAOAc 1/50 (mol/mol) ratios. In these conditions, all the TAAOAc were able to deprotonate the anilide group and induce an elongated P helix in poly-(R)−**1** (Fig. 7a).

Interestingly, the stretching of the polyene band and the color of the solution depends on the TAA salt used. Thus, while the TAAOAc salt bearing the shortest alkyl chain (i.e.,TPrAOAc) induces the smallest bathochromic shift in poly-(R)−**1**, the one that has the largest alkyl chain (i.e., THAOAc) produces the highest bathochromic shift of the polyene band (Fig. 7b).

Similar results were obtained for the TAAA series containing fluoride as anion (Figure S45). Moreover, analogous experiments were carried out for poly-(R)−**2**, obtaining a similar trend for the elongation of the polyene backbone with the size of the cations (Figure S46).

These results suggest that the elongation of the polymer following anilide deprotonation is determined by the need to accommodate the cations at a short distance from the anionic centers in the helical scaffold and where the generated steric hindrance is released by elongation of the helix (Fig. 7c).

3 Conclusions

In conclusion, we have demonstrated that a multi-switch —chiroptical and colorimetric— can be obtained from the interaction of a PPA bearing the 4-ethynylanilide of the (R)-α–methoxy-α-phenylacetic acid —poly-(R)−**1**— as pendant with different TBAA salts. Thus, at low concentrations of the TBAA salts, a supramolecular interaction between the anilide group in the pendant and the anion of the salt produces a chiroptical switch that induces an excess of either a P or M screw sense in the PPA according to the nature of the anion —M helix induced by OAc$^-$, OBz$^-$ and N$_3{}^-$; P helix induced by F$^-$ and CN$^-$—.

Larger additions of TBAA salts to a dry solution of poly-(R)−**1** in THF led to deprotonation of the polymer in all cases by playing with temperature. The anions containing carboxylate groups (TBAOAc, TBAOBz), deprotonate the anilide group at room temperature. These results differ from those obtained for the corresponding monomer, where fluoride is the only one capable of deprotonating m-(R)−**1** at room temperature. This fact clearly shows the key role that the helix plays in modulating the acidity of the anilide group.

Furthermore, the different temperatures required to deprotonate poly-(R)−**1** with the different TBAA salts allow the creation of a colorimetric thermometer based on these systems. These color changes also occur in the film state for a poly (R)−**1**/TBAOAc pair when the sample is placed under either vacuum or atmospheric pressure, leading to a color change from red to yellow induced by the absence/presence of water vapor. This change in color from yellow to red, induced by the deprotonation of the anilide group, is associated in all cases with the generation of a stretched P helix, where the elongation of the polymer is due to the accommodation of the tetrabutylammonium cation in the helical structure close to the deprotonated anilide group. The degree of elongation produced in the PPA can also be controlled by playing on the size of the tetraalkylammonium group, which also affects the color produced in the polymer solution.

These studies were corroborated with three other PPAs carrying anilide groups, poly-(R)−**2**, poly-**3** and poy-**4**), confirming in all cases the two-step interaction process —association, deprotonation— between the anions and the polymer (See SI). Interestingly, while in all the monomers tested, the association/deprotonation process is favored for the fluoride, in the corresponding polymers, the pendant/anion interaction is mediated by the helical structure of the PPA. This fact makes that other anion such as OAc or OBz become more sensitive in case of poly-(R)−1/anion interactions.

Therefore, these colorimetric and chiroptical switches are dependent on the PPA, the nature of the anion, and the size of the salt cation. This work is an illustrative example of how the two components of a salt can play an important role in the helical induction of a PPA and can also shed light on how to approach stimuli-responsive studies of other systems with unknown helix induction mechanisms.

4 Methods

4.1 Chiral stwiches based on m-(R)−**1** /TBAA salts

The ability of m-(R)−**1** to recognize anions was monitored by CD and UV–Vis. Thus, solutions of 0.1 mg/mL of the corresponding monomers in anhydrous THF were measured in the presence of different concentrations of tetra-n-butylammonium (TBA) salts derived from $CH_3CO_2{}^-$, $C_6H_5CO_2{}^-$, $N_3{}^-$, CN^-, F^-, Cl^-, Br^-, $HSO_4{}^-$ and $ClO_4{}^-$ anions. TBA salts were dried for 12 h. at 50 °C under high vacuum. Then, these salts were dissolved in anhydrous THF and dried for 12 h. with molecular sieves before testing.

4.2 Preparation of chiral and colorimetric switches based on poly-(R)−1 /TBAA salts

The stimuli-responsive behavior of poly-(R)−**1** to recognize anions was monitored by CD and UV–Vis. Thus, solutions of 0.1 mg/mL of poly-(R)−**1** in anhydrous THF were measured in the presence of different concentrations of tetra-n-butylammonium (TBA) salts. TBA salts were dried for 12 h at 50 °C under high vacuum were dried for 12 h at 50 °C under high vacuum. Then, these salts were dissolved in anhydrous THF and dried for 12 h with molecular

sieves before testing. The deprotonation of the acidic proton of the anilide group and the color change take place at different temperatures depending on the poly-(R)−**1** /TBAA pair (Figures S21 and S36). CD spectra and the graphic representation of the decreasing of the Cotton Effect intensity (522 nm) were recorded at different temperatures.

4.3 Development of a colorimetric thermometers based on different poly-(R)−1 /TAAOAc and poly-(R)−1 /TAAF pairs

Solutions of poly-(R)−**1** (0.1 mg/mL, THF) in the presence of 50.0 equiv of acetate anions with different counterion sizes such as tetrapropylammonium (TPrAOAc), tetrabutylammoniun (TBAOAc), tetrapentylammonium (TPAOAc) and tetrahexylammonium (THAOAc) (100 mg/mL, THF). CD and UV–Vis studies were carried out, observing a colorimetric change from yellow (polymer solution) to dark red (polymer solution in the presence of the largest counterion) (Figure S45).

SUPPLEMENTARY MATERIALS

Supplementary material associated with this article can be found, in the online version.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.giant.2021.100068.

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