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Nanospheres and nanotubes with full control of their size and helical sense are obtained in chloroform from the axially racemic chiral poly(phenylacetylene) poly-(*R*)-**1** using either Ag⁺ as both chiral inducer and crosslinking agent or Na⁺ as chiral inducer and Ag⁺ as crosslinking agent. The size is tuned by the polymer/ion ratio while the helical sense is modulated by the polymer/cosolvent (i.e., MeCN) ratio. In this way, the helicity and the size of the nanoparticles can be easily interconverted by very simple experimental changes.

1. Introduction

The potential of chiral nanomaterials in fields related to sensing, chiral separation and nanoreactors among others,^[1] has attracted the attention of the scientific community towards chirality and its consequences at the nanoscale level. With this objective, the preparation of novel nanostructures (e.g., fibers, nanospheres, nanotubes) by using different families of building blocks that may range from self-assembled small molecules,^[2] to metal organic frameworks (MOFs),^[3] dendrimers,^[4] metal-peptide complexes^[5] and polymer chains,^[6] has been explored in the last decade.

Poly(phenylacetylene)s^[7] (PPAs), polysilanes^[8] and polyquinoxalines^[9] are polymers that in most cases adopt a helical scaffold instead of the fully planar one.^[10] Thanks to their conformationally mobile skeleton —dynamic helical polymers—, most of these polymers respond to interactions between the substituents of the polyene and certain external stimuli (e.g., pH, pressure, temperature, light, metal ions, etc.) shifting their *P/M* helical sense,^[11] their compressed/stretched scaffold, or their color.^[12] In addition to these sensor properties,^[13] some of these polymers have also been proposed for processes involving chiral recognition by the helix such as chiral separations^[14] or asymmetric synthesis.^[15]

In the last few years, we have been interested in the extension of those properties of PPAs from solution and film states to nanostructures, that is, the preparation from the polymer of size-controlled (chiral) nanospheres and nanotubes with selected helical sense, tunable by the action of the adequate stimulus.

One example is based on the formation of helical polymer-metal complexes (HPMCs) with mono and divalent metal ions^[16] from a PPA that bears the anilide of (*R*)- α -methoxy- α -phenylacetic acid as pendant group [i.e., poly-(*R*)-**1**].

This polymer behaves as axially racemic (null CD) in spite of the chirality of the pendants because the two helical senses (*P* and *M*) are equally populated and in a rapid equilibrium in solution.^[17]

This fact is related to the 1:1 ratio between the two main *sp/ap* conformers at the pendant MPA units: *sp* conformation, where the carbonyl and methoxy groups are synperiplanar oriented [dihedral O=C-C-OMe angle ca. 0°] and *ap* conformation, where the carbonyl and methoxy groups are antiperiplanar oriented [dihedral O=C-C-OMe angle ca. 180°].^[17]

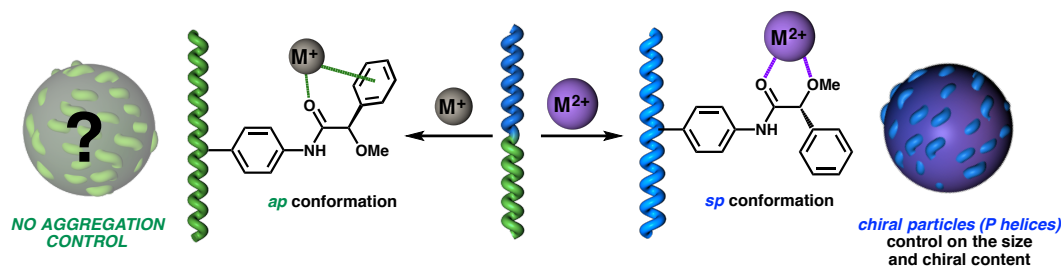
The stabilization of the *sp* conformation and therefore the induction of the *P* helical structure is possible by addition of a divalent metal ion (i.e., M^{2+}) as external stimuli, which chelates the pendant group through the carbonyl and methoxy groups.

On the other hand, monovalent metal ions (i.e., M^+) fix the *ap* conformation by coordination of the cation to the carbonyl group and to the MPA phenyl ring (the latter via cation- π interaction) inducing an *M* helical structure in the poly-(*R*)-**1** chain.^[18] This *P* or *M* helical induction occurs by means of a chiral enhancement effect where just a minute amount of the metal ion is needed (<10%). Further addition of M^{2+} as crosslinker transforms the helical HPMCs into helical nanospheres and nanotubes that conserve the original *P* sense. Unfortunately, while the size and stability of the *P* nanospheres (made from M^{2+} HPMCs) are excellent, the *M* nanospheres (made from M^+ HPMCs) are very disperse and not so stable (Scheme 1a).

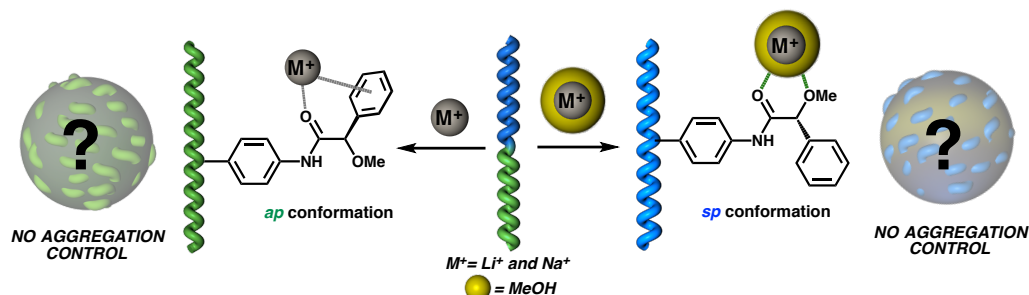
More recently, we found that the selective cleavage with an appropriate cosolvent of the cation- π interaction in M^+ HPMCs was a very efficient way to prepare helical nanospheres with either *P* or *M* helical sense (Scheme 1b). However, although the helical control was acceptable, again no good control on the size and stability of the aggregates was achieved.^[18]

In this paper we show that a combination of the selective cleavage of the cation- π interaction of M^+ HPMCs with the efficacy of Ag^+ as crosslinker solves those problems and allows the preparation of the two axially enantiomeric (*P* and *M* senses) helical nanostructures from poly-(*R*)-**1**, with good control of their size, stability and helical sense (Scheme 1c).

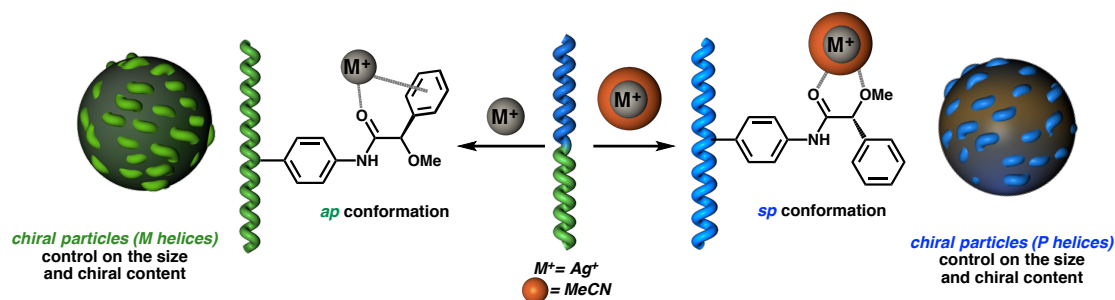
a) Helical sense control of a single PPA with different valence metal ions and aggregation control with divalent metal ions



b) Helical sense control of a single PPA with a single metal ion. NO AGGREGATION CONTROL



c) Helical sense and aggregation control of a single PPA with a single metal ion



Scheme 1. a) Helical sense control of poly-(*R*)-**1** with metal ions of different valence and aggregation control with divalent metal ions. b) Helical sense control of poly-(*R*)-**1** with a single monovalent metal ion (i.e., Li^+ and Na^+) but without aggregation control. c) Helical sense and aggregation control of poly-(*R*)-**1** with a single monovalent metal ion (i.e., Ag^+).

2. Results and Discussion

First we studied the formation of helical nanospheres from poly-(*R*)-**1** using Ag^+ ion for helical induction and aggregation and MeCN as external stimulus for the cleavage of the cation- π interaction.

Thus, titrations of a $CHCl_3$ solution of poly-(*R*)-**1** (0.3 mg mL^{-1}) with different volumes of solutions of $AgClO_4$ in MeCN at different concentrations ($10, 30, 50, 100, \text{ mg mL}^{-1}$)

were carried out. The experiments were performed in such a way that the ratio poly-(*R*)-**1**(monomer repeat unit)/Ag⁺ was kept constant [poly-(*R*)-**1**(mru)/Ag⁺ ratio= 1.0/0.5 (mol/mol)] while the amount of MeCN delivered was increased when more diluted solutions of Ag⁺/MeCN were used.

When the poly-(*R*)-**1**(mru)/MeCN ratios were in the 1/<450 (mol/mol) range, stable monodisperse left-handed (*M*) nanospheres were formed, indicating that at those ratios, the silver ions are able to induce the *M* helical sense in the polymer and to trigger the aggregation of the HPMC into good spheres.

For instance, a CHCl₃ solution containing poly-(*R*)-**1**(mru)/Ag⁺/MeCN mixture in a 1.0/0.5/70 mole ratio gives well-defined, stable and monodisperse *M* nanospheres with diameter of 76 nm [polydispersion index (PDI) = 0.071] (Figure 1). Similar particles were obtained at ratios of 1.0/0.5/150 (78 nm, PDI= 0.086) and 1.0/0.5/27 (68 nm, PDI= 0.051) (see Figure 1 and Figure S8 for details).

The size of the particles is very similar both in the solid and in solution state (Figure 1), suggesting that the nanospheres are compact, full of polymeric material and with a low solvent content.

The encapsulation properties of these nanospheres and nanotubes have been proven when the formation of the nanostructures was carried out in the presence of different guests. Thus, stable and well-formed nanostructures containing the fluorescein, the rhodamine, or inorganic species such as magnetic iron oxide nanoparticles were obtained and characterized (Figure 1e).

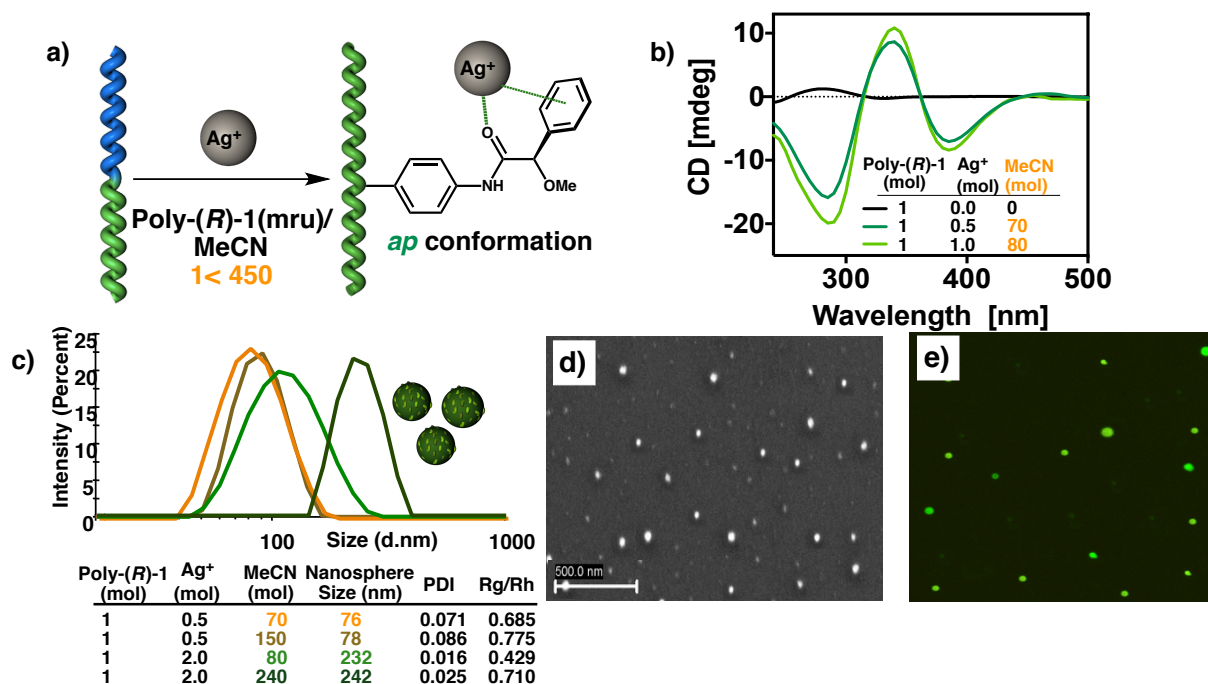


Figure 1 a) Chiral enhancement of poly-(*R*)-1 by Ag⁺ to the *M* helix. b) CD spectra of poly-(*R*)-1 and for HPMCs prepared at different poly-(*R*)-1(mru)/Ag⁺/MeCN ratios showing a *M* helical structure [poly-(*R*)-1(mru)/MeCN ratio= 1/<450 (mol/mol)]. c) DLS traces of *M* nanospheres from poly-(*R*)-1/Ag⁺ complexes in the presence of low amounts of MeCN [poly-(*R*)-1(mru)/MeCN ratio= 1/<450 (mol/mol)]. d) SEM image showing nanospheres (diameter= 65 nm ± 11, 26 particles, scale bar 500 nm) prepared in a poly-(*R*)-1(mru)/Ag⁺/MeCN ratio= 1.0/1.5/79 (mol/mol/mol). e) Confocal images of HPMC nanospheres formed by poly-(*R*)-1(mru)/Ag⁺/MeCN ratio= 1.0/1.5/79 (mol/mol/mol) with encapsulation properties (fluorescein) [poly-(*R*)-1 Mn/Mw= 93864].

Analogous experiments, varying the amount of Ag⁺ added, were also performed in order to modify the size of the nanospheres.[‡] Thus, a CHCl₃ solution containing poly-(*R*)-1(mru)/Ag⁺/MeCN in a 1.0/2.0/80 mole ratio afforded well-defined, larger, stable and monodisperse nanospheres (232 nm, PDI= 0.016). Larger or smaller, but equally homogeneous and well-formed *M* helical particles, were selectively obtained using different Ag⁺ ratios. Thus, nanospheres of 242 nm (PDI= 0.025) resulted at a 1.0/2.0/240 poly-(*R*)-

1(mru)/Ag⁺/MeCN mole ratio, while smaller ones (89 nm, PDI= 0.170) were obtained at 1.0/1.0/53 mole ratio (Figure 1, see Figure S9 for details).

Next, we studied the formation of the enantiomeric *P* nanospheres from the same polymer. To this end, the amount of MeCN present in the poly-(*R*)-**1**/Ag⁺/MeCN solutions must be increased to solvate the Ag⁺ ion to an extent that cleaves the cation- π interaction, triggering the helical inversion. This disruption consistently occurs when the poly-(*R*)-**1**(mru)/MeCN ratio is 1/>450 (mol/mol). In these conditions, the polymer that originally has the *M* sense shifts to the enantiomeric *P* helicity (Figure 2a).

Naturally, the presence of higher amounts of MeCN affects the crosslinking effectiveness of Ag⁺ and therefore, larger amounts of the metal ion are necessary to promote aggregation. Optimization of those quantities allows the efficient conversion of poly-(*R*)-**1** into stable and homogeneous *P* nanospheres of selected diameters.

For instance, poly-(*R*)-**1**(mru)/Ag⁺/MeCN in a 1.0/13.0/660 mole ratio gives *P* nanospheres with a diameter of 261 nm [PDI= 0.110] (Figure 2). If the amount of silver is increased keeping constant the amount of MeCN, the diameter of the spheres become smaller: for instance, a 1.0/20.0/660 mole ratio of reagents affords *P* nanospheres with a diameter of 235 nm [PDI= 0.191] (Figure 2).

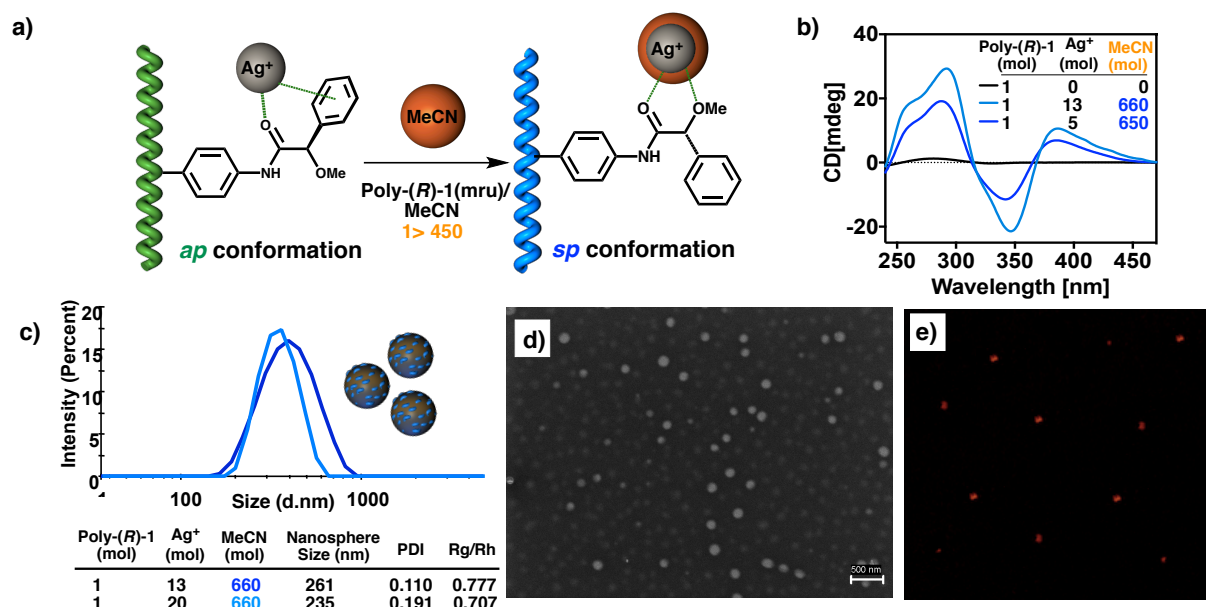


Figure 2. a) Chiral enhancement of poly-(*R*)-**1** by Ag⁺ to the *P* helix. b) CD spectra of poly-(*R*)-**1** and for HPMCs prepared at different poly-(*R*)-**1**(mru)/Ag⁺/MeCN ratios showing a *P* helical structure [poly-(*R*)-**1**(mru)/MeCN ratio= 1/>450 (mol/mol)]. c) DLS traces of *P* nanospheres from poly-(*R*)-**1**/Ag⁺ complexes in the presence of high amounts of MeCN [poly-(*R*)-**1**(mru)/MeCN ratio= 1/>450 (mol/mol)]. d) SEM image showing nanospheres (diameter= 156 nm ± 24, 44 particles, scale bar 500 nm) prepared in a poly-(*R*)-**1**(mru)/Ag⁺/MeCN ratio= 1.0/13.0/660 (mol/mol/mol). e) Confocal images of HPMC nanospheres formed by poly-(*R*)-**1**(mru)/Ag⁺/MeCN ratio= 1.0/13.0/660 (mol/mol/mol) with encapsulation properties (rhodamine) [poly-(*R*)-**1** Mn/Mw= 93864 and 102119].

As mentioned above, the helical sense of a poly-(*R*)-**1**/M⁺ complex can be inverted by selective cleavage of the cation- π interaction with an additional amount of MeCN (Figure 2a). This helical inversion of the polymer in solution can also be carried out on the helical nanospheres. Thus, when to the poly-(*R*)-**1**(mru)/Ag⁺/MeCN solution (1.0/2.0/240 mole ratio) containing *M* nanospheres, additional MeCN was added until a 1.0/13.0/660 mole ratio, *P* nanospheres (261 nm) are produced demonstrating that the poly-(*R*)-**1**/MeCN ratio is operative inverting the helicity of the nanospheres as in the polymer.

In this way, a full interconversion of *P* to *M* and vice versa nanostructures is possible by modulation of the poly-(*R*)-**1**/MeCN ratio using scavenger resins to eliminate the effect of Ag⁺ (Figure 3).

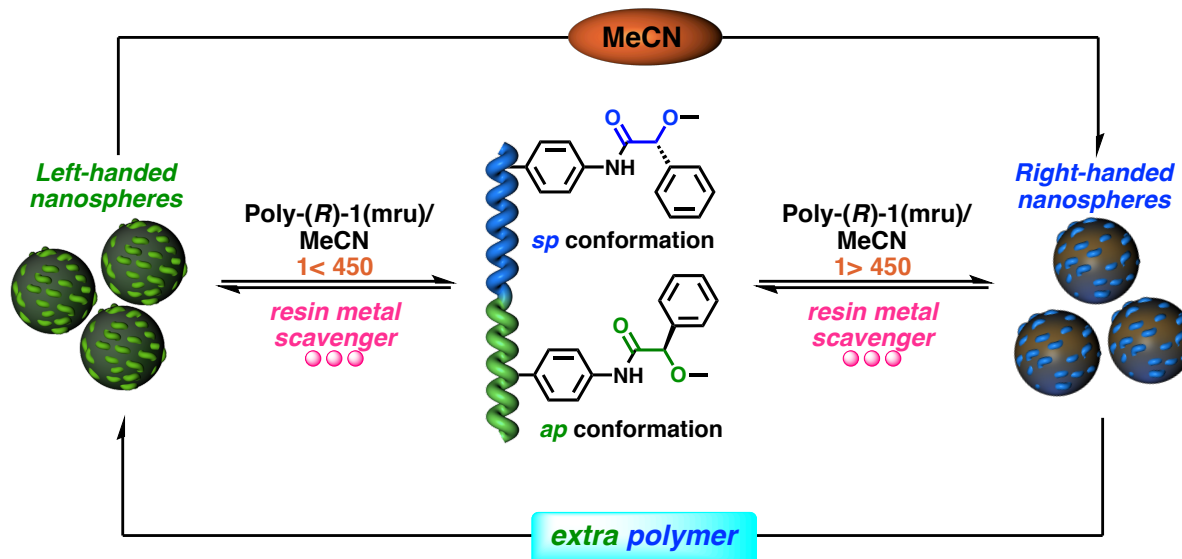


Figure 3. Formation of chiral nanospheres of poly-(*R*)-1/Ag⁺ modulated by poly-(*R*)-1/cosolvent ratio.

In a further development to produce helical and stable nanoparticles, we reasoned that it should be possible to combine the orienting ability of Na⁺—similar to that of silver—with the superior crosslinking properties of Ag⁺, if the conditions for the cleavage of the Na⁺- π interaction with MeOH were compatible with the role of Ag⁺. Thus, a CHCl₃ solution containing poly-(*R*)-1(mru)/Na⁺/Ag⁺/MeOH in 1.0/0.3/0.2/<120 mole ratio gave well-defined, stable and monodisperse nanospheres made by *M* helices (Figures 4a-d), similar to those obtained from just one single ion. Moreover, when the amount of MeOH was increased to 1.0/0.3/0.2/>120 mole ratio, stable and monodisperse nanospheres with *P* helicity were obtained (Figures 4e-h, see SI for details). This is to our knowledge the first time that a HPMC containing two different ions, each one playing a different role, is described.

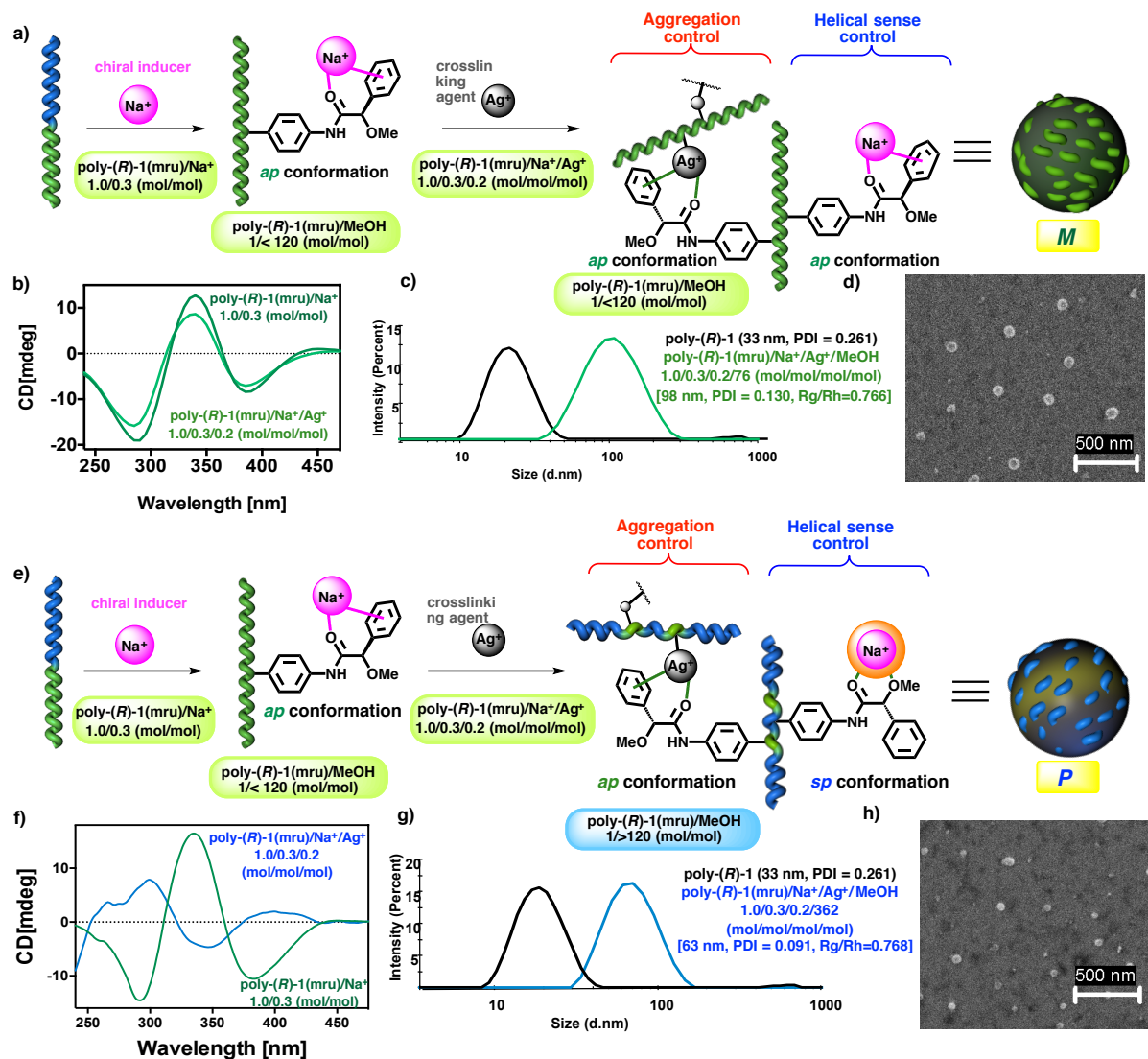


Figure 4. a) Chiral enhancement of poly-(*R*)-1 by Na⁺ to the *M* helix [formation of the poly-(*R*)-1/Na⁺ complex] followed by the aggregation to nanoparticles caused by the addition of Ag⁺. b) CD spectra for HPMCs prepared at different poly-(*R*)-1(mru)/Na⁺/Ag⁺/MeOH ratios showing an *M* helical structure [poly-(*R*)-1(mru)/MeOH ratio= 1/<120 (mol/mol)]. c) DLS traces and d) SEM images of *M* nanospheres prepared from a poly-(*R*)-1(mru)/Na⁺/Ag⁺/MeOH complex in a ratio= 1.0/0.3/0.2/76 (mol/mol/mol/mol) (diameter= 87 ± 9, 13 particles, scale bar 500 nm). e) Chiral enhancement of poly-(*R*)-1 by Na⁺ to the *P* helix and later aggregation of the poly-(*R*)-1/Na⁺ complex by the presence of Ag⁺. f) CD spectra for HPMCs prepared at different poly-(*R*)-1(mru)/Na⁺/Ag⁺/MeOH ratios showing a *P* helical structure [poly-(*R*)-1 (mru)/MeOH ratio= 1/>120 (mol/mol)]. g) DLS traces and h) SEM images of *P* nanospheres prepared from a poly-(*R*)-1(mru)/Na⁺/Ag⁺/MeOH complex in a ratio= 1.0/0.3/0.2/362 (mol/mol/mol/mol) (diameter= 63 ± 9, 13 particles, scale bar 500 nm).

SEM images of *P* nanospheres prepared from a poly-(*R*)-**1**(mru)/Na⁺/Ag⁺/MeOH complex in a ratio= 1.0/0.3/0.2/362 (mol/mol/mol/mol). h) SEM images of *P* nanospheres prepared from a poly-(*R*)-**1**(mru)/Na⁺/Ag⁺/MeOH complex in a ratio= 1.0/0.3/0.2/362 (mol/mol/mol/mol) (diameter= 52 ± 11, 22 particles, scale bar 500nm) [poly-(*R*)-**1** Mn/Mw= 102119].

Finally, we also explored the preparation of macroscopically helical nanotubes by longitudinal aggregation of the nanospheres. To that end, we added 100 μL of dioxane to a colloidal suspension of *M* nanospheres [76 nm, PDI=0.071] obtained from poly-(*R*)-**1**(mru)/Ag⁺/MeCN in a 1.0/0.5/70 mole ratio. Dioxane neither affected the stability of the particles in solution nor disrupted the cation-π interaction. However, this cosolvent with high boiling point induced the generation of *M* nanotubes during the drop-casting of the sample onto silicon wafer (Figure 5a). The longitudinal aggregation of the nanospheres was caused by the slow evaporation of the dioxane. Likewise, macroscopically enantiomeric nanotubes were obtained when dioxane was added to a colloidal suspension of *P* nanospheres [261 nm, PDI=0.110], obtained from poly-(*R*)-**1**(mru)/Ag⁺/MeCN in a 1.0/13.0/660 mole ratio (Figure 5b).

In summary, poly-(*R*)-**1**/Ag⁺ HPMC produces nanospheres with either *P* or *M* chirality in CHCl₃ by tuning the helicity of the polymer with MeCN. When this cosolvent is in very low amount [poly-(*R*)-**1**(mru)/MeCN ratio= 1/<450 (mol/mol)], it allows the formation of the cation-π interaction responsible of the *M* helix, while its cleavage when the quantity of MeCN is larger [poly-(*R*)-**1**(mru)/MeCN ratio= 1/>450 (mol/mol)], produces the *P* helix.

The combined use of two metal ions (Na⁺ as chiral inducer, Ag⁺ as crosslinking agent) and MeOH as cosolvent to produce nanospheres can also be employed to form axially

enantiomeric nanotubes when a high boiling point solvent, such as dioxane, is added before the drop-casting of the sample.

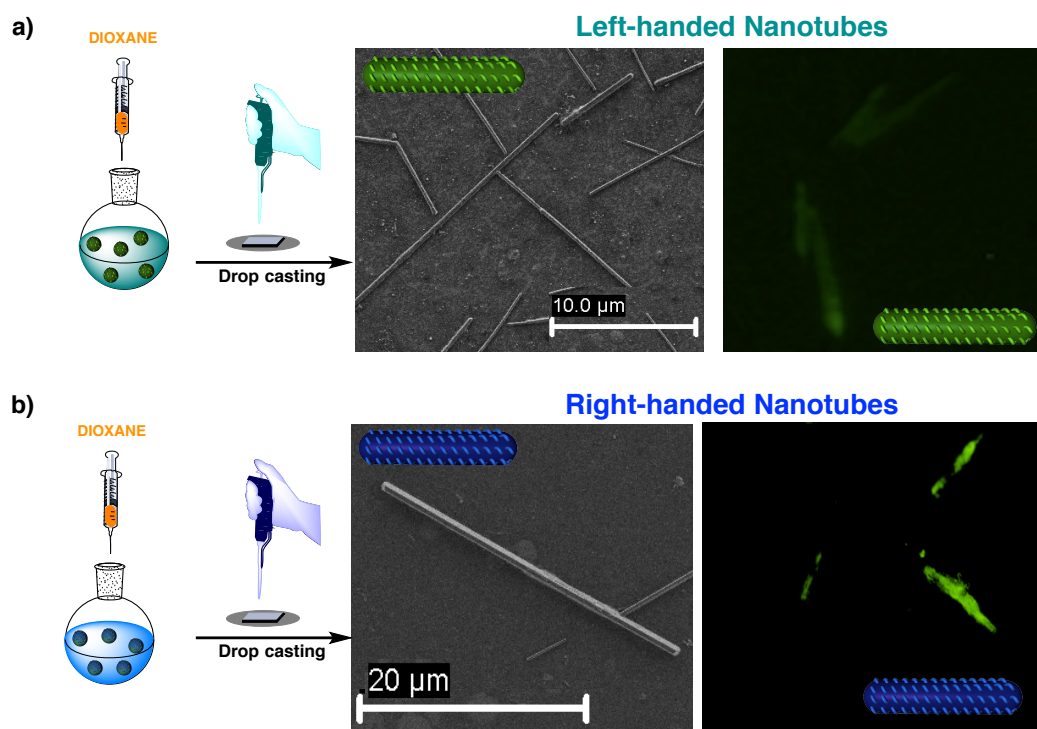


Figure 5. SEM and confocal images of: a) chiral nanotubes with encapsulation properties (fluorescein) made from a left-handed helical structure (scale bar 10 μm). b) Chiral nanotubes with encapsulation properties (fluorescein) made from a right-handed helical structure.

All the experiments described with poly-(*R*)-**1** were repeated with poly-(*S*)-**1** and, as expected, produced the enantiomeric nanospheres and nanotubes. That is, poly-(*S*)-**1** particles with *P* helical sense are obtained when cation- π interaction is operating and *M* helical particles after its cleavage (see Figure S21).

2. Conclusion

In conclusion, the work presented in this paper permit to surpass the limitations of previous methods for the preparation of optically active helical polymer particles. Those based on helical polymer metal complexes, required the use of different classes of ions for each helical sense, or the use of one specific PPA enantiomer for each helical sense. In addition, no control of the size and stability of the nanoaggregates were possible in many cases (Figures 1a and b). As for the procedures based on the precipitation of preformed PPAs with surfactants, not only are these agents difficult to remove from the particles, but size and chirality control are almost null. The method described in this paper allows the preparation “à la carte” of *P* or *M*, large or small, nanoaggregates with encapsulation properties that, in addition, are fully interconvertible.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Synthesis of monomers and polymers, helical polymer-metal complex, left-handed helix: activation of cation- π , right-handed helix: deactivation of cation- π , nanostructuration studies, microscopy studies, confocal microscopy: encapsulation studies, supporting references.

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‡ It is known that the presence/absence of cation- π interaction is independent of the amount of silver when the poly-(*R*)-**1**(mru)/MeCN ratio is 1/<450.^[16] However, the diameter of the spheres obtained can be affected by the existence of larger amounts of Ag⁺ that can interconnect more polymer chains acting as crosslinking agent.

- [1] For reviews on supramolecular chirality see: (a) F. Freire, E. Quiñoá, R. Riguera, *Chem. Rev.*, **2016**, *116*, 1242; (b) M. Liu, L. Zhang, T. Wang, *Chem. Rev.*, **2015**, *115*, 7304; (c) L. Zhang, L. Qin, X. Wang, H. Cao, M. Liu, *Adv. Mater.*, **2014**, *26*, 6959; (d) Y. Yang, Y. Zhang, Z. Wei, *Adv. Mater.*, **2013**, *25*, 6039; (e) Y. Wang, J. Xu, Y. Wang, H. Chen, *Chem. Soc. Rev.*, **2013**, *42*, 2930; (f) H. Miyake, H. Tsukube, *Chem. Soc. Rev.*, **2012**, *41*, 6977; (g) D. K. Smith, *Chem. Soc. Rev.*, **2009**, *38*, 684.
- [2] (a) C. Ren, J. Zhang, M. Chen, Z. Yang, *Chem. Soc. Rev.*, **2014**, *43*, 7257; (b) Z. Huang, S.-K. Kang, M. Lee, *J. Mater. Chem.*, **2011**, *21*, 15327; (c) I. Danila, F. Riobó, F. Piron, J. Puigmartí-Luis, J. D. Wallis, M. Linares, H. Gren, D. Beljonne, D. B. Amabilino, N. Avarvari, *J. Am. Chem. Soc.*, **2011**, *133*, 8344; (d) V. Percec, D. A. Wilson, P. Leowanawat, C. J. Wilson, A. D. Hughes, M. S. Kaucher, D. A. Hammer, D. H. Levine, A. J. Kim, F. S. Bates, K. P. Davis, T. P. Lodge, M. L. Klein, R. H. DeVane, E. Aqad, B. M. Rosen, A. O. Argintaru, M. J. Sienkowska, K. Rissanen, S. Nummelin, J. Ropponen, *Science*, **2010**, *328*, 1009; (e) T. F. A. De Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma, E. W. Meijer, *Chem. Rev.*, **2009**, *109*, 5687.
- [3] (a) Q. -Zhu, Q. Xu, *Chem. Soc. Rev.* **2014**, *43*, 5468; (b) H. Furukawa, K. E. Cordova, M. O Keeffe, O. M. Yaghi, *Science*, **2013**, *341*, 1230444; (c) A. Carnó-Sánchez, I. Imaz, M. Cano- Sarabia, D. Maspoch, *Nat. Chem.*, **2013**, *5*, 203; (d) L.

- E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp, *Chem. Rev.*, **2012**, *112*, 1105; (e) N. Stock, S. Biswas, *Chem. Rev.*, **2012**, *112*, 933.
- [4] (a) B. M. Rosen, C. J. Wilson, D. A. Wilson, M. Peterca, M. R. Imam, V. Percec, *Chem. Rev.*, **2009**, *109*, 6275; (b) V. Percec, M. R. Imam, M. Peterca, D. A. Wilson, R. Graf, H. Spiess, V. S. K. Balagurusamy, P. A. Heiney, *J. Am. Chem. Soc.*, **2009**, *131*, 7662; (c) V. Percec, M. R. Imam, M. Peterca, D. A. Wilson, P. A. Heiney, *J. Am. Chem. Soc.*, **2009**, *131*, 1294; (d) V. Percec, M. Peterca, A. E. Dulcey, M. R. Imam, S. D. Hudson, S. Nummelin, P. Adelman, P. A. Heiney, *J. Am. Chem. Soc.*, **2008**, *130*, 13079.
- [5] (a) M. Rubio-Martínez, J. Puigmartí-Luis, I. Imaz, P. S. Dittrich, D. MasPOCH, *Small*, **2013**, *9*, 4160; (b) E. Gazit, *Chem. Soc. Rev.*, **2007**, *36*, 1263; (c) X. Fu, Y. Wang, L. Huang, Y. Sha, L. Gui, L. Lai, Y. Tang, *Adv. Mater.*, **2003**, *15*, 902.
- [6] (a) J. Lin, H. Huang, M. Wang, J. Deng, *Polym. Chem.*, **2016**, *7*, 1675; (b) B. Zhao, J. Deng, J. Deng, *Macromol. Rapid Commun.*, **2016**, *37*, 568; (c) D. Liu, Y. Li, J. Deng, W. Yang, *Polymer*, **2014**, *55*, 840; (d) W. Li, H. Huang, Y. Li, J. Deng, *Polym. Chem.*, **2014**, *5*, 1107; (e) C. Song, X. Liu, D. Liu, C. Ren, W. Yang, J. Deng, *Macromol. Rapid Commun.*, **2013**, *34*, 1426; (f) V. Percec, A. E. Dulcey, V. S. K. Balagurusamy, Y. Miura, J. Smidrkal, M. Peterca, S. Nummelin, U. Edlund, S. D. Hudson, P. A. Heiney, H. Duan, S. N. Magnov, S. S. Vinogradov, *Nature*, **2004**, *430*, 764.
- [7] (a) J. Rudick, *Adv. Polym. Sci.*, **2013**, *262*, 345; (b) F. Freire, J. M. Seco, E. Quiñoá and R. Rigüera, *Adv. Polym. Sci.*, **2013**, *262*, 123; (c) B. M. Rosen, C. J. Wilson, D. A. Wilson, M. Peterca, M. R. Iman and V. Percec, *Chem. Rev.*, **2009**, *109*, 6275; (d) E. Yashima, K. Maeda, H. Iida, Y. Furusho and K. Nagai, *Chem. Rev.*, **2009**, *109*, 6102; (e) W.-S. Li and T. Aida, *Chem. Rev.*, **2009**, *109*, 6047. (f)

- J. Liu, J. W. Y. Lam and B. Z. Tang, *Chem. Rev.*, **2009**, *109*, 5799; (g) E. Yashima, K. Maeda and Y. Furusho, *Acc. Chem. Res.*, **2008**, *41*, 1166; (h) J. G. Rudick and V. Percec, *Acc. Chem. Res.*, **2008**, *41*, 1641.
- [8] (a) N. A. A. Rahim and M. Fujiki, *Polym. Chem.*, **2016**, *7*, 4618. (b) N. Suzuki, M. Fujiki, R. Kimpinde-Kalunga and J. R. Koe, *J. Am. Chem. Soc.*, **2013**, *135*, 13073.
- [9] (a) T. Yamamoto, Y. Akai, Y. Nagata, M. Sugimoto, *Angew. Chem. Int. Ed.*, **2011**, *50*, 8844; (b) Y. Nagata and M. Sugimoto, *J. Polym. Sci. Part A: Polym. Chem.*, **2011**, *49*, 4275; (c) T. Yamamoto, T. Yamada, Y. Nagata and M. Sugimoto, *J. Am. Chem. Soc.*, **2010**, *132*, 7899; (d) Y. Ito, T. Miyake, M. Sugimoto, R. Katakura, M. Mitsuishi and T. Miyashita, *Polym. J.*, **2010**, *42*, 406.
- [10] (a) T. Nakano and Y. Okamoto, *Chem. Rev.*, **2001**, *101*, 4013; (b) D. J. Hill, M. J. Mio, R. B. Prince, T. S. Hughes and J. S. Moore, *Chem. Rev.*, **2001**, *101*, 3893.
- [11] (a) R. J. M. Nolte and A. E. Rowan, *Polym. Chem.*, **2011**, *2*, 33; (b) E. Yashima and K. Maeda, in *Foldamers: Structure, Properties, and Applications*, ed. S. Hecht and I. Huc, Wiley-VCH, Weinheim, **2007**, pp. 331; (c) Y. Hu, R. Liu, F. Sanda and T. Masuda, *Polym. J.*, **2007**, *40*, 143.
- [12] (a) V. Percec, M. Peterca, J. G. Rudick, E. Aqad, M. R. Imam and P. A. Heiney, *Chem.–Eur. J.*, **2007**, *13*, 9572; (b) V. Percec, J. G. Rudick, M. Peterca, E. Aqad, M. R. Imam and P. A. Heiney, *J. Polym. Sci., Part A: Polym. Chem.*, **2007**, *45*, 4974; (c) V. Percec, E. Aqad, M. Peterca, J. G. Rudick, L. Lemon, J. C. Ronda, B. B. De, P. A. Heiney and E. W. Meijer, *J. Am. Chem. Soc.*, **2006**, *128*, 16365.
- [13] (a) E. Anger, H. Iida, T. Yamaguchi, K. Hayashi, D. Kumano, D. Crassous, N. Vanthuyne, C. Rouselc and E. Yashima, *Polym. Chem.*, **2014**, *5*, 4909; (b) H. Iida, M. Miki, S. Iwahana and E. Yashima, *Chem. – Eur. J.*, **2014**, *20*, 4257.

- [14] K. Shimomura, T. Ikai, S. Kanoh, E. Yashima and K. Maeda, *Nat. Chem.*, **2014**, *6*, 429.
- [15] (a) Y. Ke, Y. Nagata, T. Yamada and M. Sugimoto, *Angew. Chem. Int. Ed.*, **2015**, *54*, 9333. (b) H. Iida, Z. Tang and E. Yashima, *J. Polym. Sci., Part A: Polym. Chem.*, **2013**, *51*, 2869; (c) Z. Tang, H. Iida, H.-Y. Hu and E. Yashima, *ACS Macro Lett.*, **2012**, *1*, 261; (d) H. Iida, S. Iwahana, T. Mizoguchi and E. Yashima, *J. Am. Chem. Soc.*, **2012**, *134*, 15103. (e) R. P. Megens and G. Roelfes, *Chem. – Eur. J.*, **2011**, *17*, 8514; (f) T. Yamamoto and M. Sugimoto, *Angew. Chem. Int. Ed.*, **2009**, *48*, 539.
- [16] (a) J. Bergueiro, F. Freire, E. P. Wendler, J. M. Seco, E. Quiñoá, R. Riguera, *Chem. Sci.*, **2014**, *5*, 2170; (b) S. Arias, F. Freire, E. Quiñoá, R. Riguera, *Angew. Chem. Int. Ed.*, **2014**, *53*, 13720; (c) F. Freire, J. M. Seco, E. Quiñoá, R. Riguera, *J. Am. Chem. Soc.*, **2012**, *134*, 19374.
- [17] (a) R. Rodríguez, J. Ignés-Mullol, F. Sagués, E. Quiñoá, R. Riguera, F. Freire, *Nanoscale*, **2016**, *8*, 3362; (b) F. Freire, J. M. Seco, E. Quiñoá, R. Riguera, *Angew. Chem. Int. Ed.*, **2011**, *50*, 11692.
- [18] (a) S. Arias, J. Bergueiro, F. Freire, E. Quiñoá, R. Riguera, *Small*, **2016**, *12*, 238; (b) S. Arias, F. Freire, E. Quiñoá, R. Riguera, *Polym. Chem.*, **2015**, *6*, 4725.

Nanospheres and nanotubes of selected size and helical sense are obtained from an axially racemic poly(phenylacetylene) using either Ag^+ as chiral inducer and crosslinking agent or Na^+ as inducer and Ag^+ for crosslinking. In this way, the helicity and the size of the nanoparticles can be easily interconverted by very simple experimental changes.

Keyword: nanospheres, nanotubes, helices, poly(phenylacetylene)s, helical sense

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Simultaneous adjustment of size and helical sense of chiral nanospheres and nanotubes derived from an axially racemic poly(phenylacetylene)

