Electronic Supplementary Material (ESI) for Nanoscale.

The Role of the Secondary Structure of Helical Poly(phenylacetylene)s in the Formation of Nanostructures from Polymer-Metal Complexes (HPMCs)

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Electronic Supporting Information

Contents:

Materials and Methods

CD measurements were done in a Jasco-720. The amount of polymer used for CD measurements was 0.3 mg/mL.

VT-CD measurements were done in a Jasco-1100. The amount of polymer used for CD measurements was 0.3 mg/mL.

UV spectra were registered in a Jasco V-630. The amount of polymers used for CD measurements were 0.3 mg/mL.

Raman spectra were carried out in a Renishaw confocal Raman spectrometer (Invia Reflex model), equipped with two laser (diode laser 785 nm and Ar laser 514 nm).

DSC traces were obtained in a DSC Q200 Tzero Technology (TA Instruments, New Castle, UK), equipped with a refrigerated cooling system RCS90 (TA Instruments, New Castle, UK), using a Tzero low-mass aluminium pan.

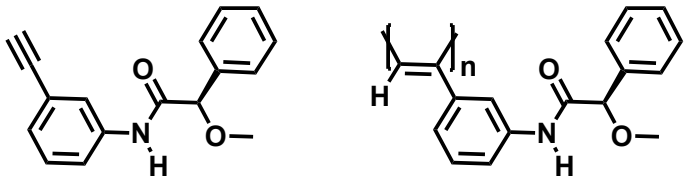
TGA traces were obtained in a TGA Q5000 (TA Instruments, New Castle, UK) using a platinum pan.

GPC studies were carried out in a Waters Alliance equipped with Phenomenex GPC columns. The amount of polymer used for GPC measurements was 0.3 mg/mL.

AFM measurements were performed in a Park NX10 (Park Systems) in air at rt with standard silicon cantilevers in non contact mode. XEI software (Park Systems) was used for image analysis.

Spartan 10 (MMFF94) was used for molecular modelling and PyMOL as molecular visualization system.

Synthesis of *m*-(*R*)-1 and *m*-poly-(*R*)-1



m-(*R*)-**1** *m*-poly-(*R*)-**1**

m-(*R*)-**1** and *m*-poly-(*R*)-**1** were prepared following our previously reported method. See Ref. **S1**

VT-CD studies of *m*-poly-(*R*)-1/$LiClO_4$ complex

We previously report how the temperature affects the equilibrium between compressed and stretched helices in *m*-poly-(*R*)-**1**. VT-CD experiments were carried out in order to demonstrate that this equilibrium could be even more biased towards the stretched structure in a synergistic way (e.g., metal complexation and thermal effects). These experiments clearly show how increasing temperatures favour the equilibrium process towards the stretched scaffold (increase in the intensity and red shift in the band related to the polyene backbone, see graph below) (for further information of thermal effects in *m*-poly-**1** see ref. **S1**).

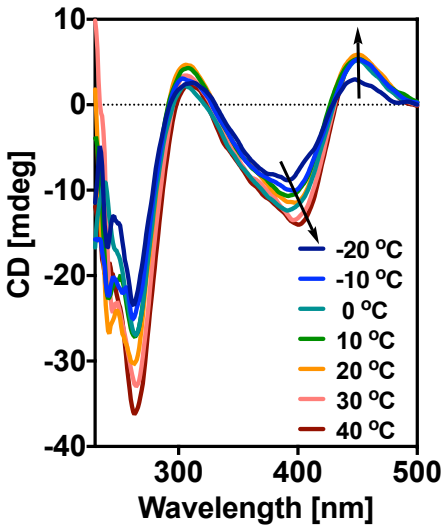


Figure S1. VT-CD spectra of *m*-poly-(*R*)-**1**/Li^+ (1:1 mol/mol) at different temperatures.

Interaction of *m*-poly-(*R*)-1 with $AgClO_4$

Titration of *m*-poly-(*R*)-**1** (0.3 mg·mL^{-1}, $CHCl_3$) with $AgClO_4$ (10 mg·mL^{-1}, THF) show an amplification —analogous process that the one reported along the manuscript with $LiClO_4$— towards the stretched helix of *m*-poly-(*R*)-**1**, as demonstrated by CD and UV measurements (bathochromic shift at the vinylic region).

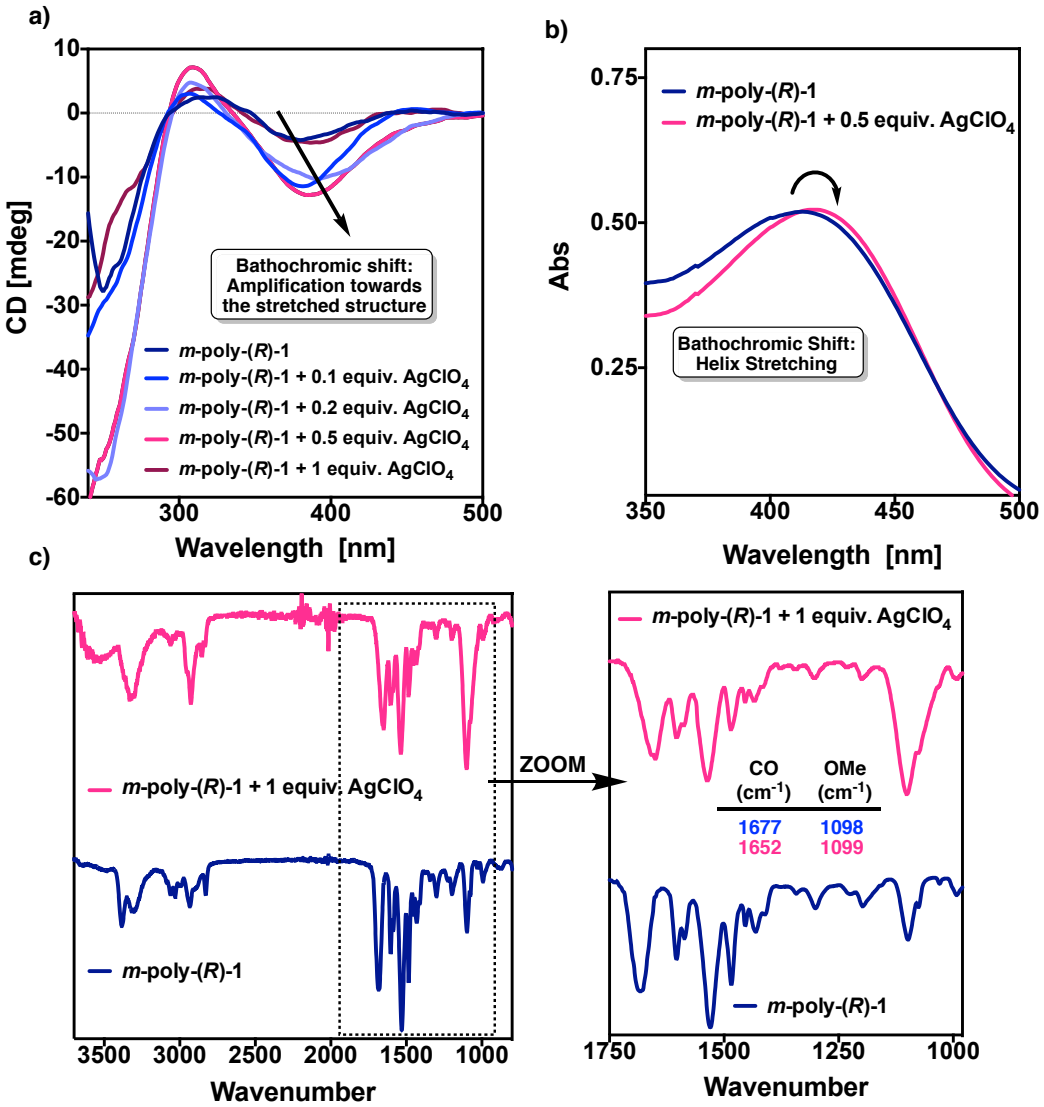


Figure S2. a) CD titration of *m*-poly-(*R*)-**1** with $AgClO_4$ and b) UV titration of *m*-poly-(*R*)-**1** with $AgClO_4$ (only one point of the titration is shown for the sake of clarity). c) IR data of *m*-poly-(*R*)-**1** and of *m*-poly-(*R*)-**1**/ $AgClO_4$ (1:1 mol/mol) extracted from the IR spectra shown in the image.

Interaction of *m*-poly-(*R*)-1 with $NaClO_4$

Titration of *m*-poly-(*R*)-**1** (0.3 mg·mL^{-1}, $CHCl_3$) with $NaClO_4$ (10 mg·mL^{-1}, MeCN) shows similar results than the ones reported above for lithium and silver. Moreover, sodium is now able to generate nanospheres with controlled size and low polydispersity.

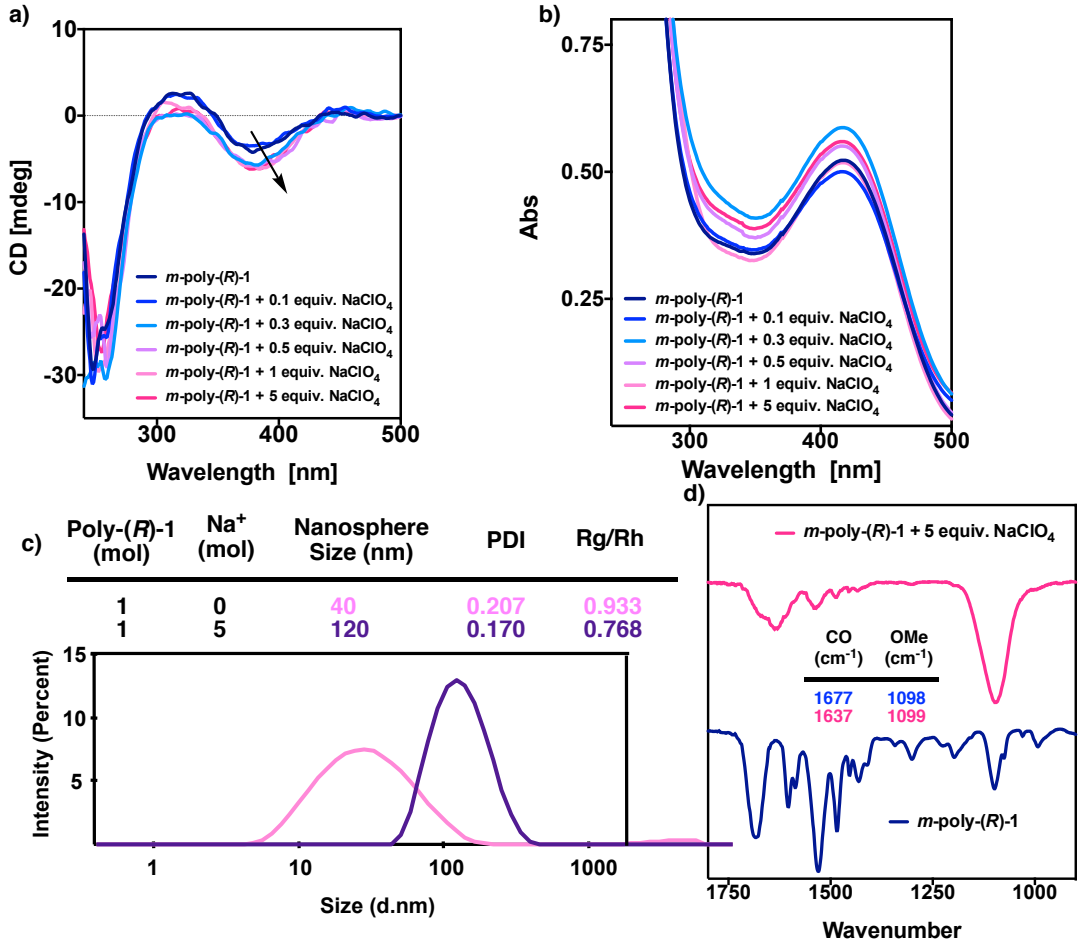


Figure S3. a) CD titration of *m*-poly-(*R*)-**1** with $AgClO_4$ and b) UV titration of *m*-poly-(*R*)-**1** with $NaClO_4$. c) DLS trace of the *m*-poly-(*R*)-**1**/$NaClO_4$ (1:1 mol/mol) metal complex showing the formation of nanospheres in solution. d) IR data of *m*-poly-(*R*)-**1** and *m*-poly-(*R*)-**1**/$NaClO_4$ (1:5 mol/mol) extracted from the IR spectra shown in the figure.

Interaction of *m*-poly-(*R*)-1 with salts in MeOH

Titration of *m*-poly-(*R*)-**1** (0.3 mg·mL^{-1}, $CHCl_3$) with $M(ClO_4)_n$ (n=1,2) (10 mg·mL^{-1}, MeOH) shows similar results than the ones aforementioned for THF. Moreover, these systems generate nanospheres with lower polydispersity than the ones from THF. In all cases, the metal ion coordinates only the carbonyl group, while the OMe group remains uncoordinated (see IR experiments below).

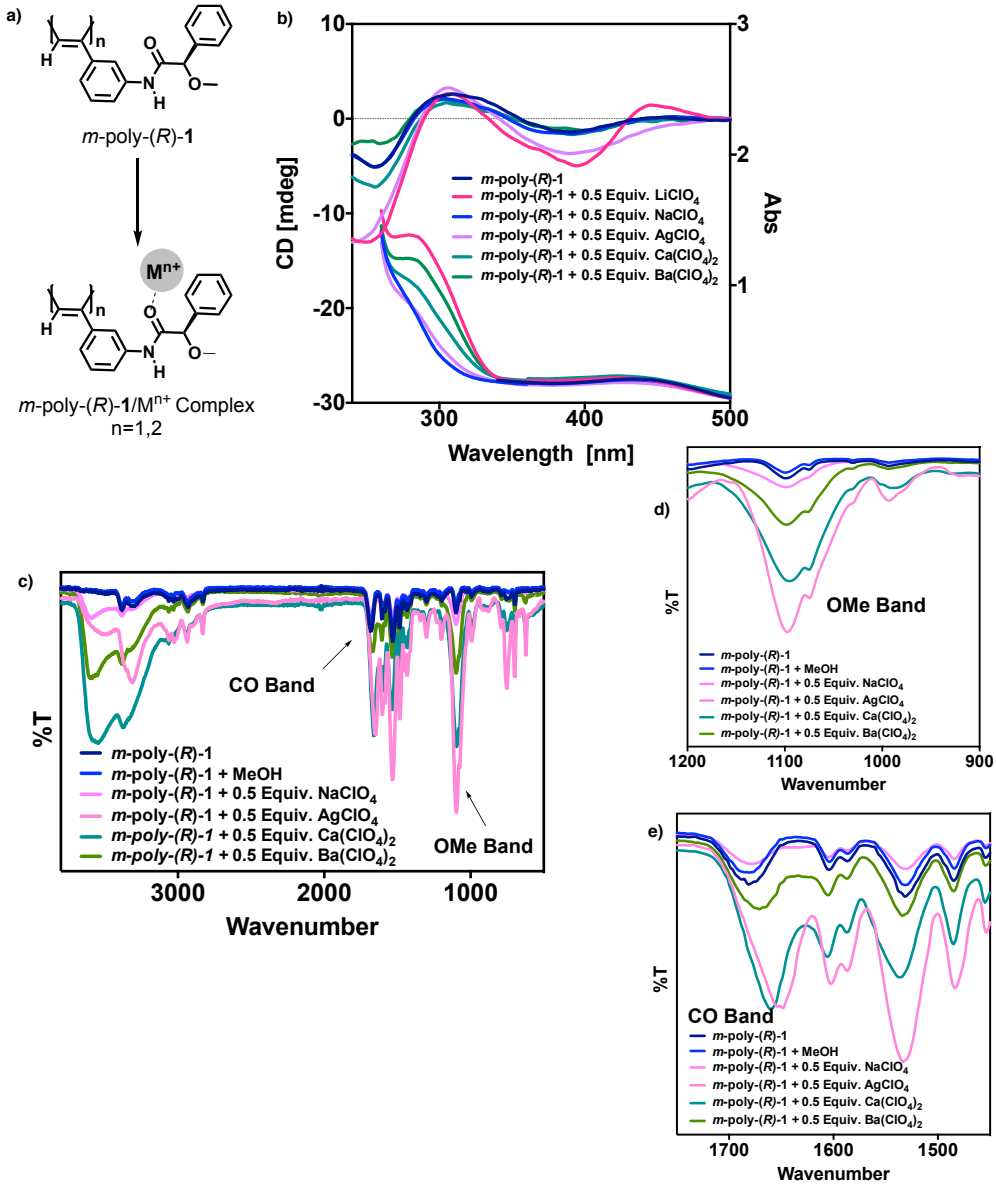


Figure S4. a) Schematic illustration of the coordination process. b) CD titration of *m*-poly-(*R*)-**1** (0.3 mg·mL^{-1}, $CHCl_3$) with $M(ClO_4)_n$ (n=1,2) (10 mg·mL^{-1}, MeOH). c) IR data of *m*-poly-(*R*)-**1** (0.3 mg·mL^{-1}, $CHCl_3$) with $M(ClO_4)_n$ (n=1,2) (10 mg·mL^{-1}, MeOH). d) Zoom of the OMe band showing the absence of coordination. e) Zoom of the CO band showing in all cases coordination with the metal cation.

Microscopy Studies

Microscopy studies (AFM and SEM) were performed in order to visualize the nanostructures formed by *m*-poly-(*R*)-**1**/M^{n+} (n= 1, 2) complexes. Samples were prepared by drop-casting 10μL of the corresponding solution of the HPMC onto a silicon wafer chip. The samples were allowed to dry at rt for 2h and submitted to the corresponding analysis.

AFM Studies of *m*-poly-(*R*)-1/$LiClO_4$ complexes

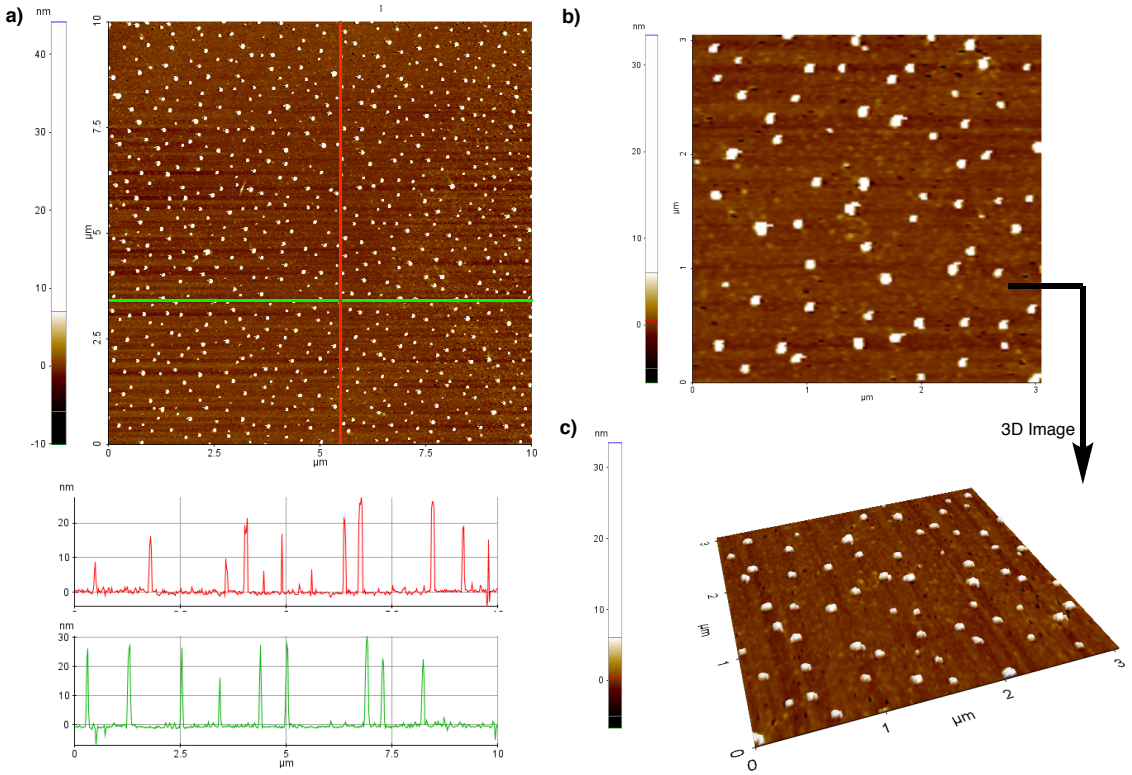


Figure S5. a) AFM image of *m*-poly-(*R*)-**1**/$LiClO_4$ (1:1 mol/mol) and cross-section height profiles. b) Magnification of image a). c) 3D-projection of image b).

AFM Studies of *m*-poly-(*R*)-1/$AgClO_4$ complexes

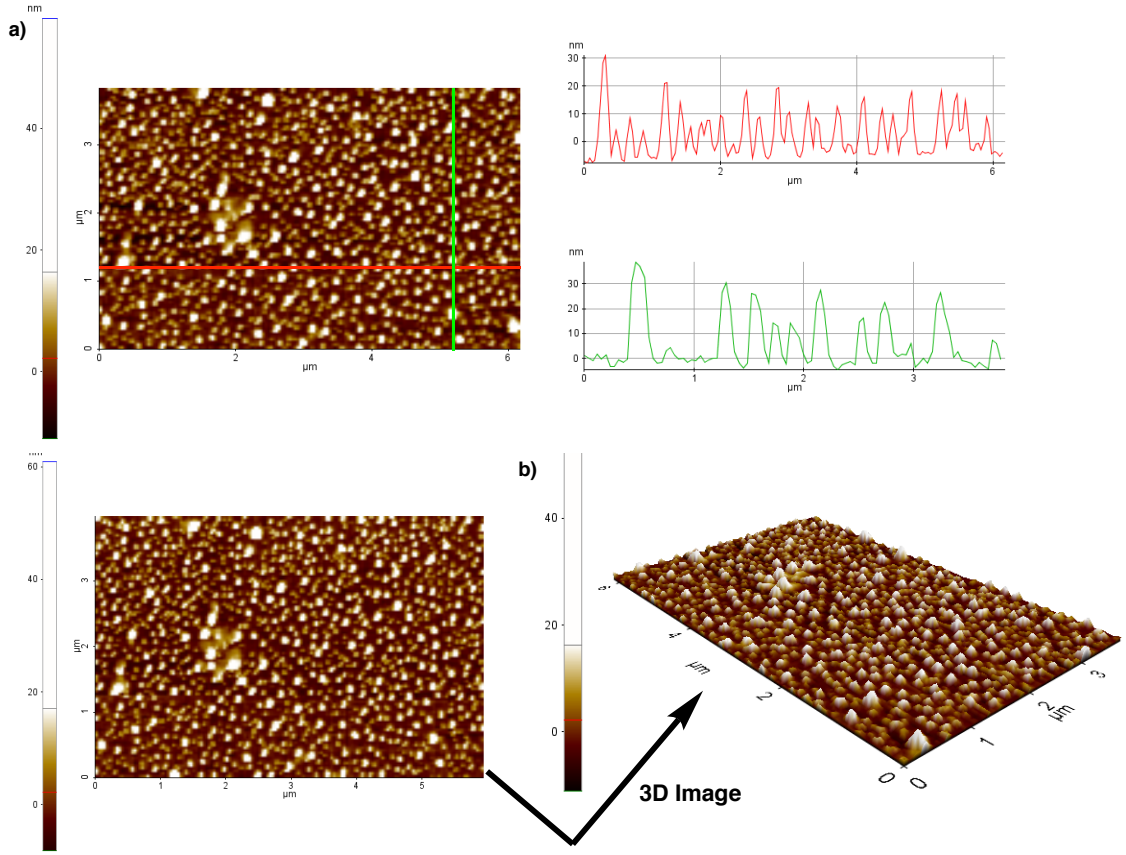


Figure S6. a) AFM image of *m*-poly-(*R*)-**1**/$AgClO_4$ (1:1 mol/mol) and cross-section height profiles. b) 3D-projection of image a).

AFM Studies of *m*-poly-(*R*)-1/$Ba(ClO_4)_2$ complexes

Toroidal Structures

During the AFM, studies toroidal structures generated by the assembly of *m*-poly-(*R*)-**1**/$Ba(ClO_4)_2$ HMPCs were found. The dimension of the torus wall is in good agreement with the size of the nanospheres in solution. For other examples of toroidal nanostructures formed during the drop casting and drying process see ref. **S2**

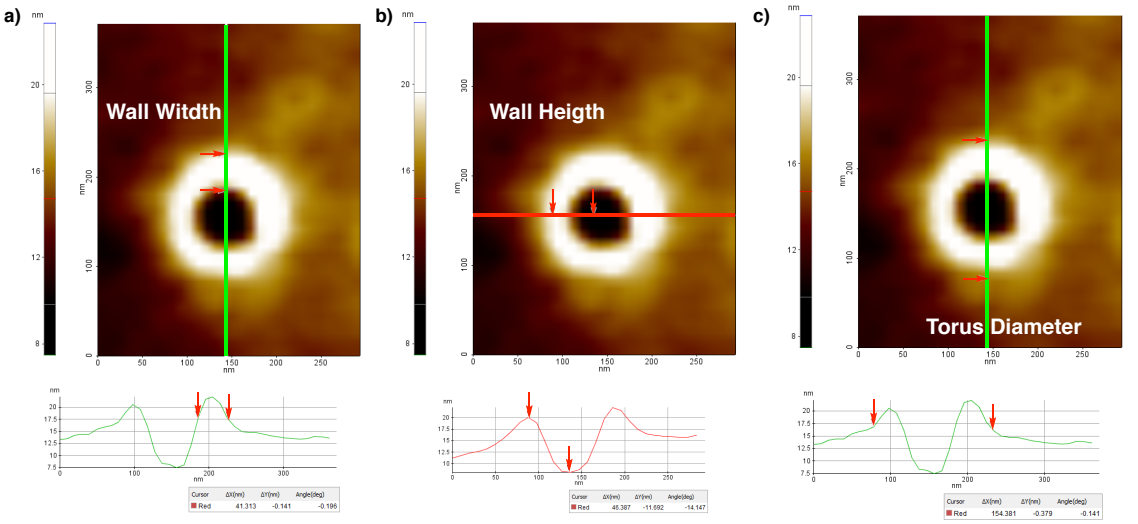


Figure S8. AFM studies of toroidal structures: a) Wall width b) Wall height and c) torus diameter.

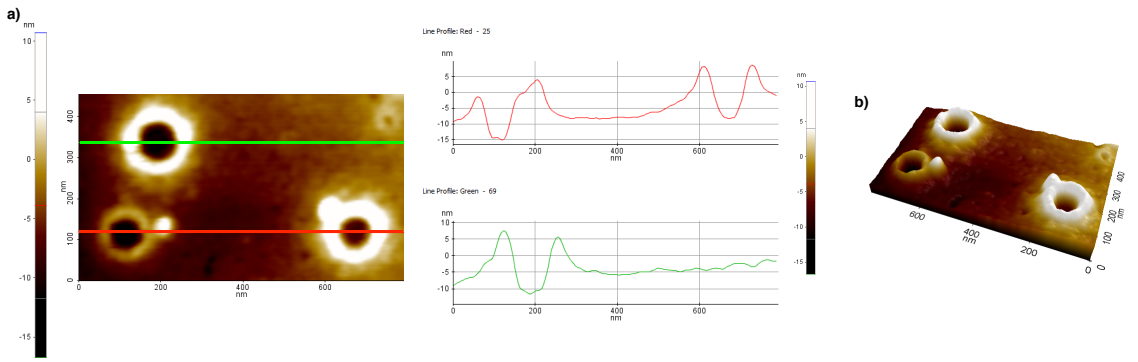


Figure S9. AFM studies of toroidal structures: a) AFM of toroidal structures and height profiles. b) 3D-projection of a).

Nanospheres

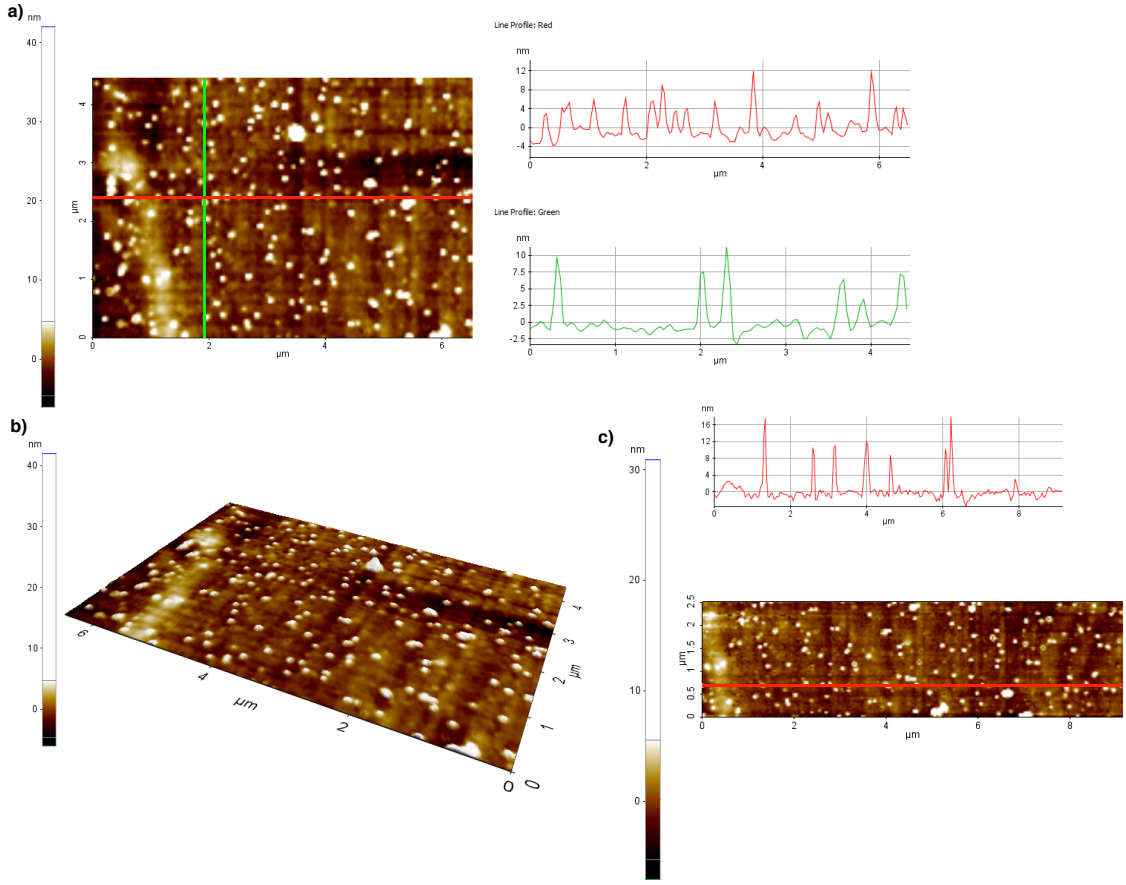


Figure S7. a) AFM image of *m*-poly-(*R*)-**1**/$Ba(ClO_4)_2$ (1:1 mol/mol) and cross-section height profiles. b) 3D-projection of image a).

SEM Studies of *m*-poly-(*R*)-1/$LiClO_4$ complexes

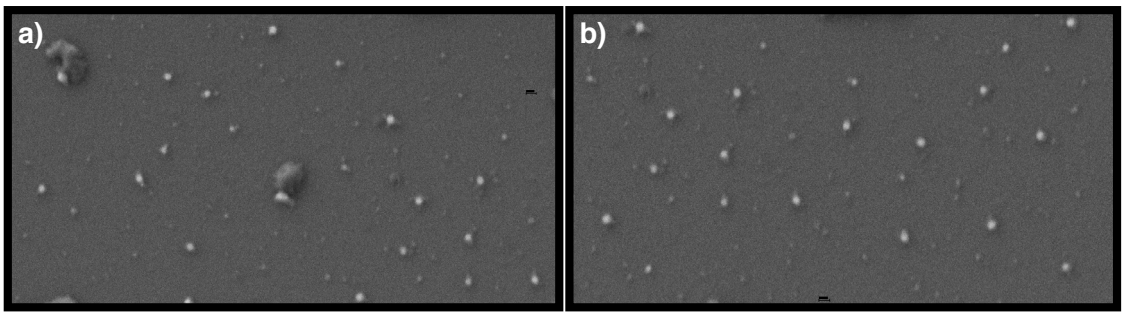


Figure S10. a) to c) SEM images of *m*-poly-(*R*)-**1**/$LiClO_4$ (1:1 mol/mol).

SEM Studies of *m*-poly-(*R*)-1/$AgClO_4$ complexes

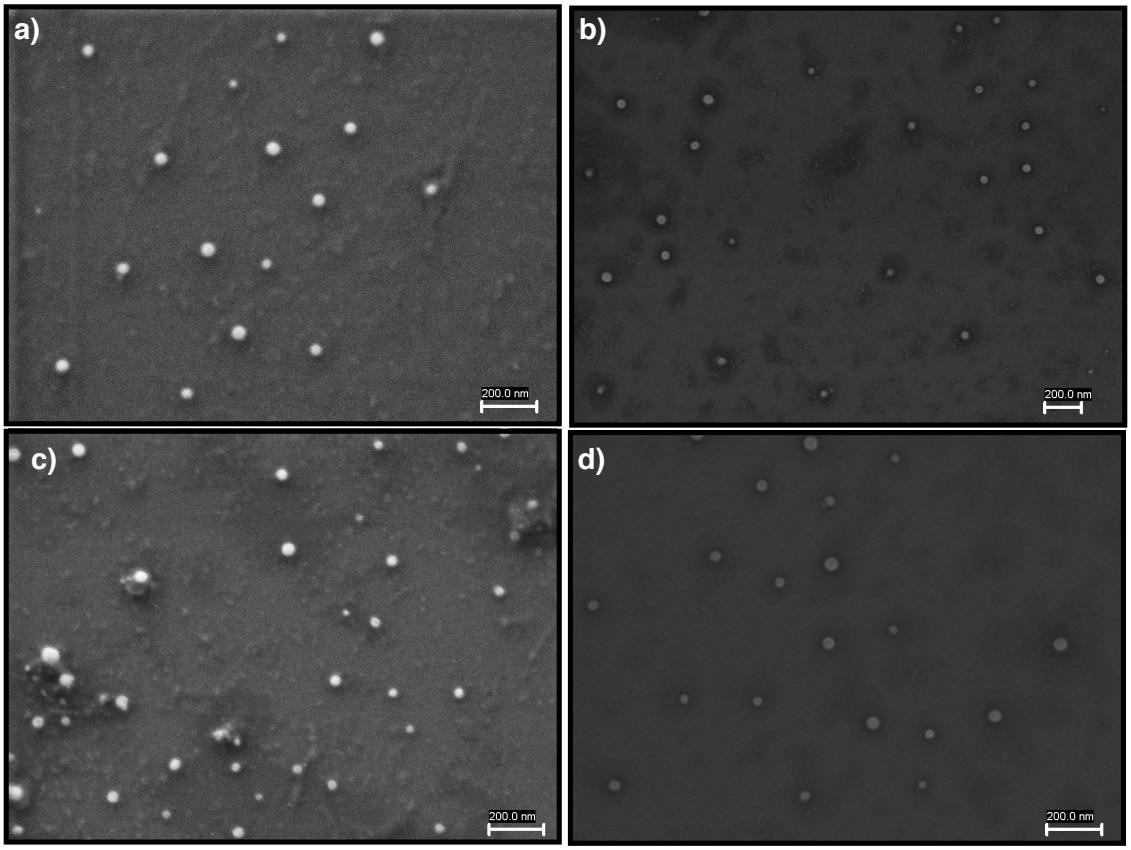


Figure S11. a) to d) SEM images of *m*-poly-(*R*)-**1**/$AgClO_4$ (1:1 mol/mol).

SEM Studies of *m*-poly-(*R*)-1/$NaClO_4$ complexes

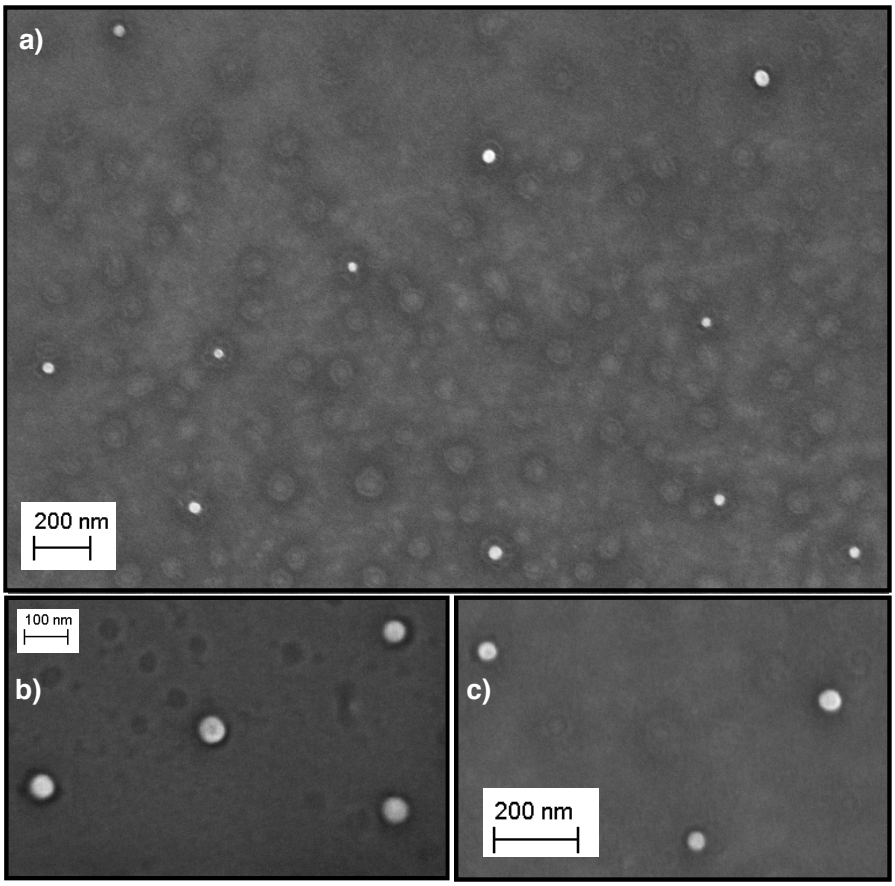


Figure S12. a) to d) SEM images of *m*-poly-(*R*)-**1**/$NaClO_4$ (1:1 mol/mol).

SEM Studies of *m*-poly-(*R*)-1/$M(ClO_4)_2$ complexes (M^{2+}= Ca^{2+} and Ba^{2+})

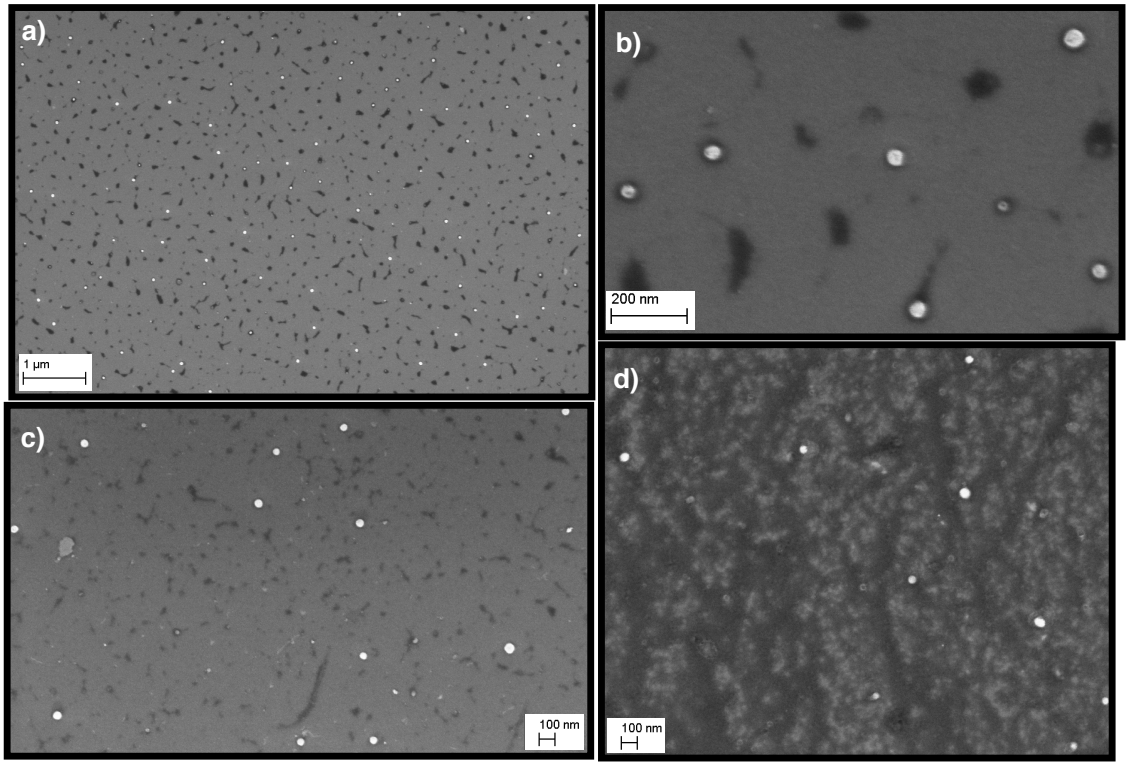


Figure S13. a) to c) SEM images of *m*-poly-(*R*)-**1**/$Ba(ClO_4)_2$ (1:0.5 mol/mol). d) SEM image of *m*-poly-(*R*)-**1**/$Ca(ClO_4)_2$ (1:0.5 mol/mol).

Supporting References

S1. R. Rodríguez, E. Quiñoá, R. Riguera, F. Freire, *J. Am. Chem. Soc.* 2016, **138**, 9620.

S1. S. Arias, F. Freire, E. Quiñoá, R. Riguera, *Angew. Chem. Int. Ed.* 2014, **53**, 13720.