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Polymethacrylic zinc porphyrin: A new approach to chiral recognition

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ABSTRACT

A methacrylic homopolymer bearing in the side-chain achiral zinc tetraarylporphyrin moieties, has been studied as macromolecular chromophoric host to determine the absolute configuration of α,ω-diamines. The polymeric material resulted able to bind the chiral guest through amine nitrogen/zinc coordination to form a complex which exhibits exciton-coupled bisignate circular dichroism (CD) spectra, due to stereodifferentiation leading to a preferred porphyrin helicity. The sign of CD signal reflects the absolute configuration of diamine and the method turns out very sensitive, requiring only few microgram quantities of guest compound.

To our knowledge this is the first example of absolute configuration assignment to chiral molecular compounds by means of a polymeric derivative containing in the side-chain metallo-porphyrins moieties.

1. Introduction

In recent years there has been a widespread interest in the study of porphyrins and their derivatives which are characterized by an intense and red-shifted *Soret band*, propensity to undergo π–π stacking and easy incorporation of metals. In fact, such attributes, besides the vital role played in biological processes, make these materials available to a wide range of practical applications in areas such as catalytic asymmetric synthesis [1–3], nonlinear optics [4,5], and molecular devices [6,7].

In addition, the literature reports the possibility to enhance the circular dichroism (CD) sensitivity of chiral compounds through their derivatization with 5-(4-methylcarboxy-phenyl)-10,15,20-triphenylporphyrin and/or its zinc analog [8–10]. Thus, resulting powerful, versatile and multifaced chromophores for CD studies, porphyrins have been employed also in the field of molecular and chiral recognition [11,12], as well as absolute configuration assignment [13–21].

In the last few years, indeed, the so-called CD exciton chirality method was developed [14,15], a nonempirical microscale approach for absolute stereochemical determinations, which has been applied to discriminate between enantiomeric forms of a wide variety of compounds, such as diamines, carbohydrates and amino acids [15–21]. All that is essential because these substrates exhibit important biological activities but often are available only in limited amounts.

The method is based on the through-space exciton coupling between two or more chirally oriented chromophores, which are usually introduced through derivatization of functional groups present in the substrates [14,15].

However, it was recently demonstrated that the absolute configuration assignment may be performed through reversible complexation of the chiral guest with achiral porphyrin hosts, which can then be recovered after the spectroscopic measurements, thus bypassing the chromophoric derivatization [15–23]. In particular, linker bridged bisporphyrin derivatives (zinc porphyrin tweezers) resulted capable of binding various chiral guests (acyclic α,ω-diamines, amino alcohols, etc.) to form 1:1 host/guest complexes, giving rise to exciton-coupled CD spectra. The sign of the dichroic bands reflects the absolute configuration of the optically active compound [13,22–24], while their intensity depends on several other factors such as solvent, temperature, and the relative steric bulkiness of the guest molecule [25].

In this context, we envisaged the possibility to use a macromolecular system binding achiral tetraarylporphyrin moieties in the side-chain for the absolute configuration assignment to optically active acyclic α,ω-diamines. To this purpose, we have synthesized the new homopolymeric porphyrin–zinc derivative poly{{5-[4-(methacryloyloxy)phenyl]-10,15,20-triphenylporphyrin}zinc(II)} {poly[Zn–**M-TPP**]} (Fig. 1), which shows high thermal stability and should easily coordinate amines with a squared pyramidal ligand arrangement of the metal atom, as reported by Buchler for low molecular weight porphyrin compounds [26].

The chiral recognition ability of this macromolecular compound has been verified in the presence of two well known and thoroughly studied 1,2-diaminopropane enantiomers and investigated by UV–Vis and CD spectroscopy.

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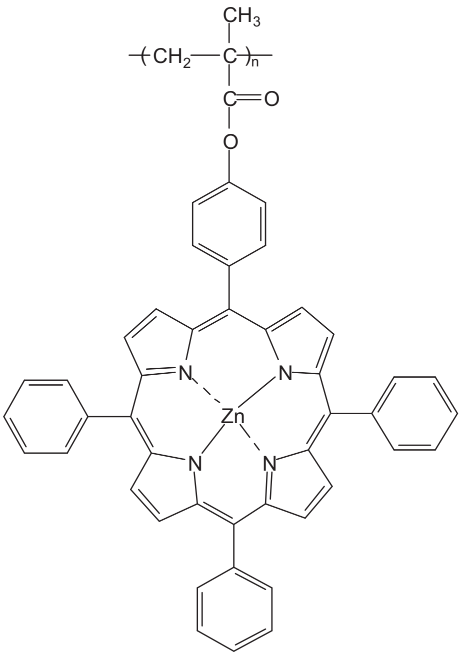

Fig. 1. Structure of poly[Zn–**M-TPP**].

2. Experimental

2.1. Physico-chemical measurements l

^{1}H and ^{13}C NMR spectra were obtained at room temperature, in 5–10% $CDCl_3$ solutions, using a Varian NMR Gemini 300 spectrometer. Chemical shifts are given in ppm relative to tetramethylsilane (TMS). ^{1}H NMR spectra were run at 300 MHz by using the following experimental conditions: 24,000 data points, 4.5 kHz spectral width, 2.6 s acquisition time, 128 transients. ^{13}C NMR spectra were recorded at 75.5 MHz, under full proton decoupling, by using the following experimental conditions: 24,000 data points, 20 kHz spectral width, 0.6 s acquisition time, 64,000 transients.

FT-IR spectra were recorded with a Perkin–Elmer 1750 spectrophotometer, equipped with an Epson Endeavour II data station, on sample prepared as KBr pellets.

Number average molecular weights of the polymer ($\overline{M}_n$) and their polydispersity indexes ($\overline{M}_w/\overline{M}_n$) were determined in THF solution by SEC using a HPLC Lab Flow 2000 apparatus, equipped with an injector Rheodyne 7725i, a Phenomenex Phenogel 5 μm MXM column and a UV–Vis detector Linear Instrument model UVIS-200, working at 254 nm. The calibration curve for the MXM column was obtained by using monodisperse polystyrene standards in the range 2700–200,000.

The glass transition temperatures of the polymer (T_g) were determined by differential scanning calorimetry (DSC) on a TA Instruments DSC 2920 Modulated apparatus, adopting a temperature program consisting of three heating and two cooling ramps starting from room temperature (heating/cooling rate 10 °C/min under a nitrogen atmosphere). Each sample (5–9 mg) was heated up to only 250 °C in order to avoid thermal decomposition.

The initial thermal decomposition temperature (T_d) was determined on the polymeric samples with a Perkin–Elmer TGA-7 thermogravimetric analyzer by heating the samples in air at a rate of 20 °C/min.

UV–Vis absorption spectra in solution were recorded at 25 °C in $CHCl_3$ with a Perkin–Elmer Lambda 19 spectrophotometer by using cell path lengths of 0.1 cm and concentrations of porphyrin chromophore of about 3.5×10^{-5} mol L^{-1}.

Circular dichroism (CD) spectra were recorded at 25 °C in chloroform solutions on a Jasco 810 A dichrograph, using the same path length and solution concentrations as for the UV–Vis measurements. $\Delta\varepsilon$ values, expressed as L mol^{-1} cm^{-1}, were calculated from the following expression: $\Delta\varepsilon = [\Theta]/3300$, where the molar ellipticity $[\Theta]$ in deg cm^2 dmol^{-1} refers to one porphyrin chromophore.

Measurement of chiral recognition have been performed by adding an aliquot (175 μL) of chiral diamine solution (0.02 mol L^{-1}) to porphyrin solution (3.5×10^{-5} mol L^{-1}) in $CHCl_3$.

2.2. Materials

5-(4-Hydroxyphenyl)-10,15,20-triphenylporphyrin (**HOTPP**) was synthesized from benzaldehyde, p-hydroxybenzaldehyde and pyrrole as previously reported by Little et al. [27].

Methacryloyl chloride (Aldrich) was distilled (bp 95 °C) under dry nitrogen in the presence of traces of 2,6-di-*tert*-butyl-*p*-cresol, as polymerization inhibitor, before use. Triethylamine (Aldrich) was refluxed over dry $CaCl_2$ for 8 h and then distilled (bp 89 °C). 2,2′-Azobisisobutyronitrile (AIBN) (Aldrich) was crystallized from abs. ethanol before use.

Chloroform ($CHCl_3$), methylene dichloride (CH_2Cl_2), and tetrahydrofuran (THF), were purified and dried according to reported procedures [28] and stored over molecular sieves (4 Å) under nitrogen. All other reagents and solvents (Aldrich) were used as received.

2.2.1. 5-[4-(Methacryloyloxy)phenyl]-10,15,20-triphenylporphyrin (*M-TPP*) [29]

Methacryloyl chloride (0.1 mL, 0.9 mmol) in dry methylene dichloride (3 mL) and triethylamine (0.13 mL, 0.9 mmol) in dry methylene dichloride (3 mL) were simultaneously added dropwise to an ice cooled, vigorously stirred solution of the porphyrin alcohol **HOTPP** (0.50 g, 0.73 mmol), dimethylamino pyridine (0.03 g, 0.25 mmol) as catalyst, and 2,6-di-*tert*-butyl-4-methyl phenol (0.02 g) as polymerization inhibitor, in dry methylene dichloride (30 mL), under nitrogen flow.

The mixture was kept ice cooled for 2 h, then left at room temperature for one night, washed with 0.1 M HCl, 5% Na_2CO_3 and finally with water, in that order. The organic layer was dried (Na_2SO_4) and the solvent was evaporated under reduced pressure. The solid residue was purified by column chromatography (SiO_2, CH_2Cl_2 as eluent) (84% yield).

^{1}H NMR ($CDCl_3$): 8.53 (m, 8H, 2, 3, 7, 8, 12, 13, 17, 18-H **TPP**), 7.70 (m, 8H, 2H arom. *metha* to ester group and 6H arom. *ortho* to monosubst. phenyl groups), 7.25 (m, 9H, arom. *metha* and para to monosubst. phenyl groups), 7.00 (d, 2H, arom. *ortho* to ester group), 6.05 and 5.35 (2d, 2H, CH_2=), 1.7 (s, 3H, CH_3) ppm.

FT-IR: 3059 (ν_{C-H} arom.), 1718 ($\nu_{C=O}$, ester), 1633 ($\nu_{C=C}$ methacr.), 1602 and 1515 ($\nu_{C=C}$ arom.) 1222 (ν_{C-O}, ester), 818 (δ_{CH} 1,4-disubst. arom. ring), 760 and 687 (δ_{CH} monosubst. arom. ring) cm^{-1}.

2.2.2. Poly{5-[4-(methacryloyloxy)phenyl]-10,15,20-triphenylporphy rin} {Poly[*M-TPP*]} [29]

The homopolymerization of **M-TPP** was carried out in a glass vial using 2,2′-azobisisobutyronitrile (AIBN) as thermal initiator (2 wt.% with respect to the monomers) and dry THF as solvent (1 g of monomer in 15 mL of THF). The reaction mixture was prepared and introduced into the vial under nitrogen atmosphere, submitted to several freeze–thaw cycles, and allowed to polymerize at 60 °C for 72 h. The polymerization was then stopped by pouring the mixture into a large excess of methanol and the polymeric product purified by repeated precipitations in methanol. The material was finally dried at 80 °C for 4 days under high vacuum to constant weight (68% yield). $(\overline{M}_n)$ = 9200 g mol^{-1}, $(\overline{M}_w/\overline{M}_n = 1.6)$, T_g = 210 °C, T_d = 358 °C.

The monomer conversion was determined gravimetrically and the product characterized by FT-IR, ^{1}H- and ^{13}C NMR.

^{1}H NMR ($CDCl_3$): 8.88–8.15 (8H, 2, 3, 7, 8, 12, 13, 17, 18-H **TPP**), 7.80–7.42 (8H, 2H arom. *metha* to ester group and 6H arom. *ortho* monosubst. phenyl groups), 7.20–6.65 (11H, 2H arom. *ortho* to ester group and 9H arom. *metha* and *para* to monosubst. phenyl groups), 5.60–5.10 (1H, CH), 2.72–2.20 (main chain CH_2), 2.10–1.05 (main chain CH_3) ppm.

^{13}C NMR ($CDCl_3$) (ppm): 169.3 (CO), 150.1 (arom. α to phenyl group), 141.9 (C–N), 140.0 (arom. α to ester group of disubst. phenyl group), 135.2 (arom. *ortho* to ester group of disubst. phenyl group), 134.5 (arom. *ortho* to monosubst. phenyl groups), 131.2 (β-**TPP**), 127.8 (arom. *para* to monosubst. phenyl groups), 126.6 (arom. *metha* to monosubst. phenyl groups), 119.6 and 120.0 (*meso*-**TPP**), 70.1 (CH), 54.6 (main chain CH_2—C), 46.0 (main chain CH_2—C), 17.7 (main chain CH_3—C) ppm.

FT-IR: 3062 (ν_{C-H} arom.), 1729 ($\nu_{C=O}$, ester), 1606 and 1507 ($\nu_{C=C}$ arom.), 1219 (ν_{C-O}, ester), 816 (δ_{CH} 1,4-disubst. arom. ring), 762 and 684 (δ_{CH} monosubst. arom. ring) cm^{-1}.

2.2.3. Poly{{5-[4-(methacryloyloxy)phenyl]-10,15,20-triphenylporphyrin}zinc(II)} {Poly[Zn–*M-TPP*]}

Poly[**M-TPP**] (0.041 mmol) and $Zn(OAc)_2$ (0.082 mmol) were dissolved in chloroform (30 mL) and MeOH (6 mL). The solution was kept at room temperature under nitrogen flow for 2 h, then washed with a NaCl saturated solution, 5% aq. Na_2CO_3 and water in that order. After drying the organic layer on anhydrous Na_2SO_4 and evaporation of the solvent under vacuum, the desired pure product is quantitatively obtained.

2.2.4. Preparation of diamine solutions

A solution of (*R*)-(+)- or (*S*)-(−)-1,2-diaminopropane dihydrochloride (0.102 mmol) in MeOH (2 mL) was allowed to react in the presence of Na_2CO_3 (28 mmol) at room temperature for one night. The solvent was evaporated and the residue dried under high vacuum for 1 h. Then chloroform (5 mL) was added to yield a solution of (*R*)-(+)- or (*S*)-(−)-1,2-diaminopropane (0.02 mol L^{-1}).

3. Results and discussion

3.1. Synthesis and characterization of the polymer

5-[4-(Methacryloyloxy)phenyl]-10,15,20-triphenylporphyrin (**M-TPP**) and poly{5-[4-(methacryloyloxy)phenyl]-10,15,20-triphenylporphyrin} {Poly[**M-TPP**]}, were synthesized by a slightly different procedure with respect to that one previously reported by Kamachi et al. [29].

The methacrylic monomer **M-TPP** was obtained starting from porphyrin alcohol **HOTPP** and methacryloyl chloride in the presence of triethylamine (**TEA**) and dimethylamino pyridine (**DMAP**) as catalyst.

The structure of the above mentioned product was confirmed by ^{1}H NMR analysis, which displays the resonances of the vinylic protons of monomeric methacrylate (around 5.35 and 6.05 ppm) and the aromatic protons of the porphyrin moiety.

The radical homopolymerization of **M-TPP** in THF solution and in the presence of AIBN as thermal initiator, afforded a polymeric product in high yield (68%), average molecular weight $(\overline{M}_n)$ of 9200 g mol^{-1} and polydispersity index $(\overline{M}_w/\overline{M}_n)$ of 1.6.

The occurrence of polymerization, involving the methacrylic double bond, was confirmed by FT-IR, showing the disappearance of the band around 1630 cm^{-1}, which corresponds to the stretching vibration of the monomer double bond, and the shift of the carbonyl stretching to higher frequencies, as a result of the reduced electron delocalization caused by the reaction of the methacrylic double bond.

Accordingly, in the ^{1}H NMR spectrum of the polymer, the resonances of the vinylic protons of monomeric methacrylate are absent and the methyl resonances are shifted to higher field.

The thermal stability of Poly[**M-TPP**], as determined by thermogravimetric analysis (TGA), resulted high, with decomposition temperature value of 358 °C, indicative of a remarkable presence of strong dipolar interactions in the solid state between the chromophores located in the macromolecular side-chains. Such a behavior makes this material interesting by the applicative point of view.

The DSC thermogram revealed only one second-order transition, originated by glass transition, with no melting peaks, thus suggesting that this polymeric material is substantially amorphous in the solid state. Furthermore, the T_g value appears to be quite high, around 210 °C.

Poly[**M-TPP**] was fully metallated with $Zn(OAc)_2$ to give poly[Zn–**M-TPP**] (Fig. 1). The formation of this new porphyrin–zinc polymeric derivative was confirmed by UV–Vis analysis and comparison with the metallated monomer Zn–**M-TTP** obtained from **M-TPP** with similar procedure.

3.2. UV–Vis analysis

As previously reported for other porphyrin derivatives [30,31], the absorption spectra of the synthesized monomer and corresponding polymer (Table 1 and Fig. 2) show an intense *Soret band* at 418 nm related to $\pi \rightarrow \pi^*$ transitions, and four *Q bands* at 515, 550, 590 and 645 nm of lower intensity.

A remarkable hypochromism is observed for the *Soret band* when passing from the low molecular weight compound, where the lack of structural restraints originates a random distribution of the chromophores in dilute solution, to the corresponding homopolymer (Table 1 and Fig. 2). Such a behavior was previously observed for porphyrin dimers [32,33] and polymers [29], and explained in terms of an exciton coupling model due to the close approach of two porphyrin rings which are forced to interact. Assuming that no aggregates of monomer nor intermolecular interactions are present in dilute solution, and that the nature of the chromophoric moieties is the same for the monomer and the corresponding polymer, although the chromophores are anchored to the polymer backbone, it therefore appears that intramolecular electrostatic dipolar interactions between porphyrin moieties are present in the macromolecules, evidently as a consequence of close proximity of the side-chain chromophores located along the macromolecular backbone. The extinction coefficient of *Q bands*, instead, does not exhibit any relevant change.

The addition of increasing amounts of trifluoroacetic acid (TFA) to the solutions of these porphyrin derivatives alters significantly their electronic spectra (Fig. 3), as previously reported for low molecular weight systems [34–36] and demonstrated by sudden color change: the acid immediately turns the reddish solution to a brilliant green.

As reported in Fig. 3 for Poly[**M-TPP**], it can be noticed that, by increasing the amount of acid in solution (5 → 60 eq.), the intensity of the *Soret band* at around 418 nm fades, with a progressive growth of a new absorption band centered at 439 nm and attributed to the formation of the protonated species. At the same time, the *Q bands* at 515 and 550 nm progressively decrease of intensity, while those at 590 and 645 nm increase. As suggested by Gouterman and subsequently proved by means of semiempirical calculations [34,37,38], the observed red-shift of the *Soret band* of 21 nm reflects the occurrence of phenyl-to-porphyrin charge transfer transitions.

Table 1
UV–Vis spectra of the investigated compounds in chloroform solution at 25 °C.

Sample	*Soret band*		1st *Q band*		2nd *Q band*		3rd *Q band*		4th *Q band*	
	λ_{max}[a]	ε_{max}[b] (10^{-3})	λ_{max}[a]	ε_{max}[b] (10^{-3})	λ_{max}[a]	ε_{max}[b] (10^{-3})	λ_{max}[a]	ε_{max}[b] (10^{-3})	λ_{max}[a]	ε_{max}[b] (10^{-3})
TPP[c]	417	478.6	514	20.0	549	9.1	592	6.9	647	6.3
HOTPP	419	505.2	516	18.8	552	8.8	590	5.7	646	4.3
M-TPP	418	486.0	515	19.1	550	7.9	590	5.7	645	3.8
Zn–**M-TTP**	422	417.3	–	–	550	16.7	594	4.4	–	–
Poly[**M-TPP**]	417	261.1	516	17.0	551	7.2	591	5.2	647	3.5
Poly[Zn–**M-TPP**]	422	265.5	–	–	552	16.3	594	4.1	–	–

[a] Wavelength of maximum absorbance, expressed in nm.
[b] Expressed in L mol^{-1} cm^{-1} and calculated for one single chromophore.
[c] **TPP**: tetraphenylporphyrin from Ref. [34].

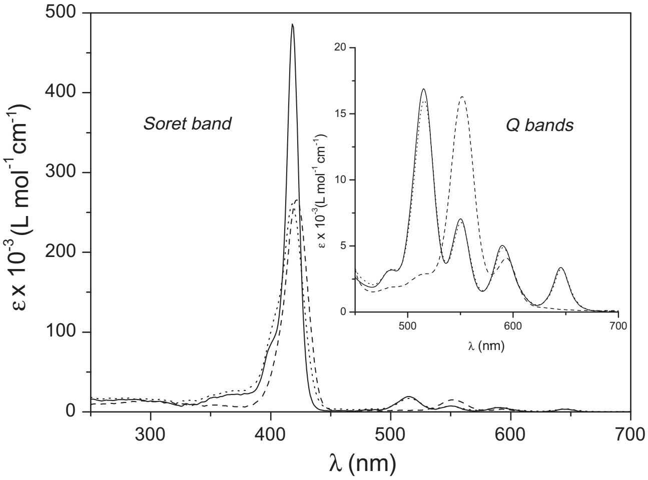

Fig. 2. UV–Vis spectra of **M-TPP** (—), Poly[**M-TPP**] (···), and poly[Zn–**M-TPP**] (- - -) in chloroform solution.

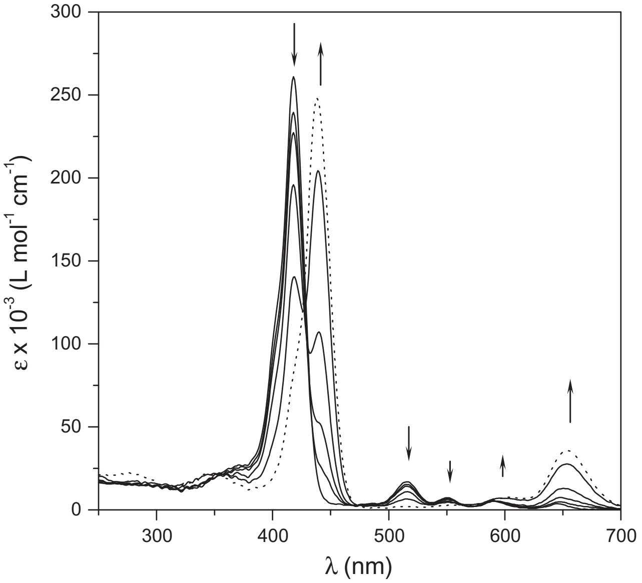

Fig. 3. UV–Vis spectra of Poly[**M-TPP**] in chloroform after addition of increasing amounts of TFA (5–60 equivalents per porphyrin unit).

Such a behavior is due to the gradual protonation of the pyrrolic moieties and the process is reversible: by adding an equivalent amount of base (for example triethylamine), it is possible to restore the original spectra, as shown in Fig. 4. In the inset of this figure we report the absorbance variation at 420 nm after 10 subsequent protonations and deprotonations in order to verify the chemical stability of the polymeric substrate (the absorbance values are corrected as a function of volume changes due to the subsequent addition of acid and base). These results suggest the possibility to obtain a two-state molecular switch whose interconversion can be monitored by UV–Vis spectroscopy, which seems promising also for its application as acid responsive organic material.

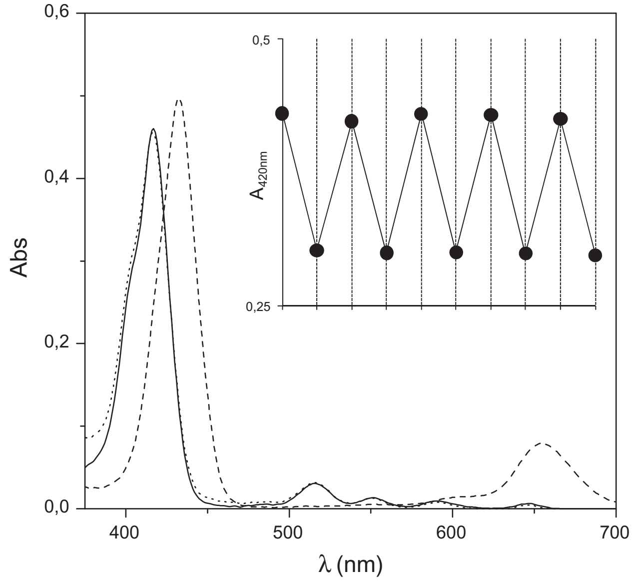

Fig. 4. UV–Vis spectra of poly[Zn–**M-TPP**] in chloroform before (—) and after (- - -) addition of TFA and after subsequent addition of TEA (···). Inset: relative intensity at 420 nm of the UV–Vis spectra of the same solution, measured after each subsequent addition of TFA and TEA.

A similar behavior is shown by the monomer, but the protonation, under the same experimental conditions, takes place with lower amount of TFA (0.5 → 10 eq.). This occurrence can be due to the presence, in the polymer, of π–π dipolar interactions between adjacent chromophores which reduce the electronic density at the pyrrolic nitrogen atoms and the free volume necessary to the acid to give protonation, thus requiring a larger amount of acid.

The macromolecular Zn-derivative poly[Zn–**M-TPP**] displays with respect to Poly[**M-TPP**] a red-shift of the *Soret band* from 418 to 422 nm and, in the spectral region of the *Q bands*, the disappearance of two bands with a shift of the remaining signals to around 552 and 594 nm (Fig. 2). This effect was previously reported for similar compounds [39–41].

3.3. Assignment of absolute configuration

As reported in the Introduction, the stereoselective complexation of metal–porphyrin derivatives with chiral diamines gives rise to one preferred porphyrin helicity, disclosed by the exciton-coupled CD spectra with the signs reflecting the absolute configurations of the guest molecule [13,22–24].

To assess whether the same process can take place between the above porphyrin polymer and an acyclic α,ω-diamine, solutions of poly[Zn–**M-TPP**] containing a known aliquot of a solution of (*R*)-(+)- or (*S*)-(−)-1,2-diaminopropane (10 equivalents with respect to the porphyrin unit) were prepared. Thus, formation of the host/guest complex via coordination of the amine nitrogens to the zinc atoms of porphyrin moieties in the side-chain, was revealed by the solution color change which turns from reddish to teal blue and confirmed by UV–Vis and CD spectroscopy.

As reported in Fig. 5, in fact, after addition of the diamine to the achiral zinc–porphyrin polymer, the two *Q bands* shift from 552 and 594 nm to 560 and 600 nm (red-shift) and a new band rises at 635 nm.

It is noteworthy that no red-shift of the *Soret band* is observed after addition of the diamine to the zinc polymer, contrary to what reported by other authors [24,42]. Such a behavior could be due to the use of a polar solvent, required because of the low solubility of the macromolecular system.

Nevertheless, the CD spectra, initially silent, display two signals of opposite sign, with a crossover point in correspondence of the maximum absorption. Such a behavior suggests that chiral diamine complexation leads to a unique twisted arrangement of the effective electric transition moments of zinc porphyrins. By using dilute solutions, intermolecular interactions should be prevented, thus the excitonic CD couplet can be ascribed to interactions between adjacent chromophores bound to the same macromolecular chain. The absolute sense of the twist can be correlated with the sign of the couplet and hence with the diamine configuration.

By adding (*R*)-(+)-1,2-diaminopropane, a negative CD couplet is obtained (Fig. 5) which, accordingly to the CD exciton chirality method [14,15], suggests the presence of cooperative interactions between side-chain porphyrin chromophores disposed in a mutual chiral geometry of anticlockwise prevailing handedness. Similar results have been previously obtained by Nakanishi et al. [22] who reported the possibility to bind a pentanediol-linked bis zinc porphyrin molecule (porphyrin tweezer) with various diamines to form macrocyclic host/guest complexes.

The dependence of the observed UV–Vis and chiroptical properties on sample concentration have also been investigated in the range 10^{-6}–10^{-4} mol L^{-1}, based on porphyrin repeating unit, by using variable cell pathlength. In these conditions, the UV–Vis and CD spectra result, within the limit of experimental errors, practically unchanged, thus confirming that the observed spectroscopic behavior is related to individual polymeric chains and originated by chromophoric intrachain interactions.

As expected, the achiral porphyrin polymer gives a CD spectrum which is the mirror image of the previous one (positive couplet) in the presence of (*S*)-(−)-1,2-diaminopropane (Fig. 5), thus revealing a clockwise orientation of the porphyrin moieties, at least for chain sections.

The couplet intensity, normalized for two porphyrin moieties in order to allow a comparison with the data reported in the literature, in presence of 10 equivalents of (*R*)-(+)-1,2-diaminopropane, is about four times lower than that one for porphyrin tweezer ($\Delta\varepsilon$ = 24.40 and +15.32 L mol^{-1} cm^{-1} vs. −93 and +76 L mol^{-1} cm^{-1}, respectively) [22] and could be attributed to the reduced mobility of

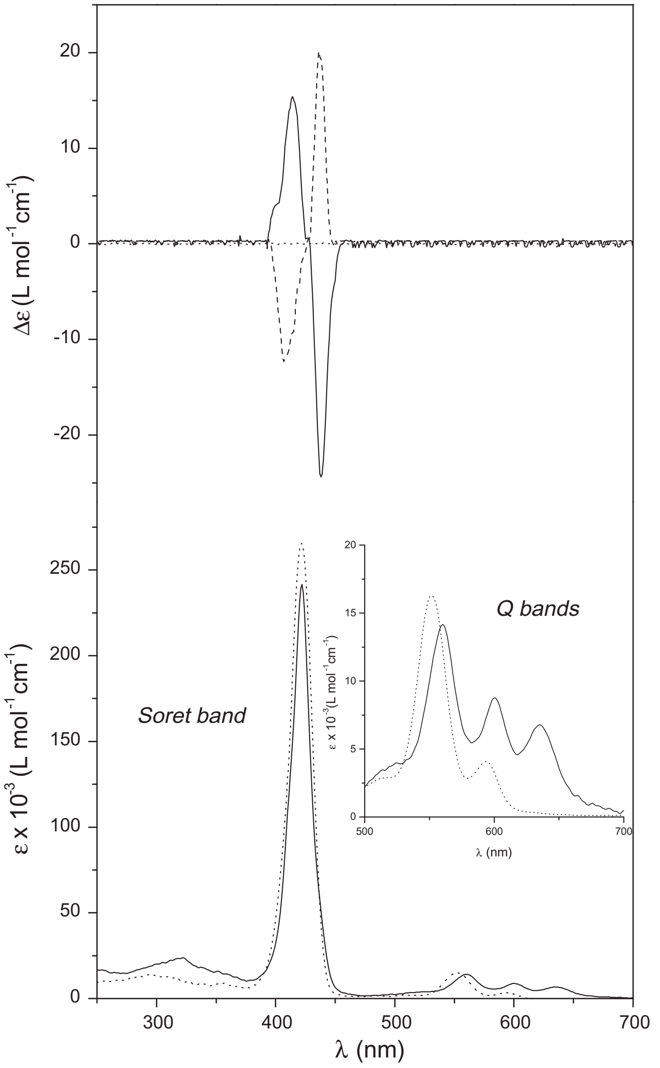

Fig. 5. UV–Vis spectra (bottom) in chloroform solution of poly[Zn–**M-TPP**] before (···) and after addition of (*S*)-(−)- or (*R*)-(+)-1,2-diaminopropane (—). CD spectra (top) of poly[Zn–**M-TPP**] after addition of (*S*)-(−)- (- - -) or (*R*)-(+)-1,2-diaminopropane (—).

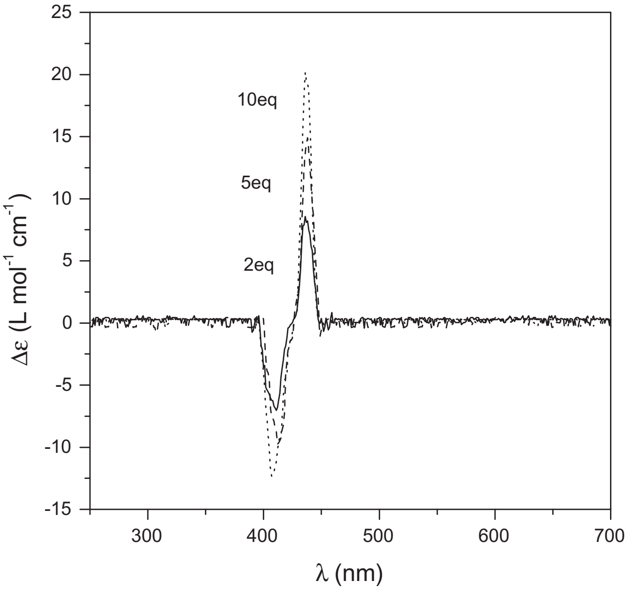

Fig. 6. CD spectra of poly[Zn–**M-TPP**] after the addition of 2 (—), 5 (- - -) and 10 (···) equivalents of (*S*)-(−)-1,2-diaminopropane.

porphyrin chromophores in the polymer with consequent reduced availability to diamine complexation.

However, as reported in Fig. 6, the presence of only two equivalents of α,ω-diamine is sufficient to achieve a slight signal still detectable by CD.

Thus, the method results very sensitive for the absolute configuration assignment to α,ω-diamine, requiring only few microgram quantities of the guest compound. In addition, being the amine complexation reversible, it advantageously allows to repeatedly use the polymeric Zn–porphyrin system for further chiral recognition. Work is in progress to assess the applicability of this system to other classes of chiral compounds.

4. Conclusions

A new homopolymeric polymethacrylate bearing in the side-chain the tetraarylporphyrin chromophore as well as its zinc-complex, were synthesized. Displaying remarkable changes of UV–Vis spectrum in response to pH, these materials seem to be promising for application as acid responsive organic materials.

Furthermore, the polymeric zinc derivative resulted capable to complex a chiral α,ω-diamine (1,2-diaminopropane) as demonstrated by color variation and spectroscopic analysis. In particular, the CD spectra, initially silent, upon addition of optically active diamine, show dichroic signals related to the electronic transitions of the porphyrin chromophores, with a behavior typical of exciton splitting determined by cooperative interactions between side-chain porphyrin chromophores disposed in a mutual chiral geometry of one prevailing handedness. Being the observed couplet sign a direct consequence of the chirality of the diamine, which is transmitted to a prevailing helical handedness of the interacting chromophores, the assignment of chirality is nonempirical.

Although the CD signals displayed by this polymeric system resulted four times lower in intensity with respect to low molecular weight porphyrin tweezers previously reported in the literature, it appears however very sensitive and convenient for chiral recognition, being the material easy to synthesize, thermally stable, and requiring only few microgram quantities of the guest compound.

This example may open a new route for a general approach to the design of polymeric systems to be applied in the field of chiral recognition and absolute configuration assignment and could be extendable to a large variety of chiral substrates.

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