Macromolecules

ARTICLE

pubs.acs.org/Macromolecules

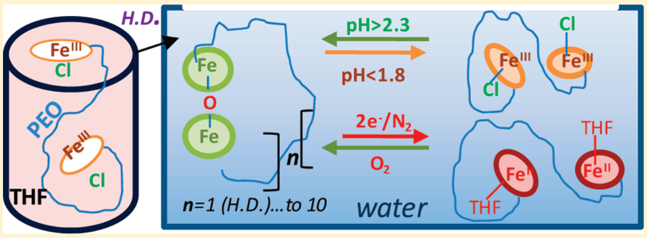
Reversible Switching between Linear and Ring Poly(EO)s Bearing Iron Tetraphenylporphyrin Ends Triggered by Solvent, pH, or Redox Stimuli

Michel Schappacher and Alain Deffieux*

Laboratoire de Chimie des Polymères Organiques ENSCBP, CNRS and Université Bordeaux, 16, Avenue Pey Berland, 33607 Pessac Cedex

S Supporting Information

ABSTRACT: The action of various external stimuli on telechelic poly(ethylene oxide) bearing iron(III) tetraphenylporphyrin chloride or iron(II) tetraphenylporphyrin derivatives at their ends has been investigated in organic and water media. Fully reversible chain end coupling processes were shown to take place yielding bis-iron(III) μ-oxo-tetraphenylporphyrin poly(ethylene oxide) under changes in acido-basic conditions, solvent nature, or the action of redox additives. At low concentration macrocyclic poly(ethylene oxide)s of same molar mass as the linear poly(ethylene oxide) precursors are almost exclusively formed via intramolecular coupling whereas increasing the poly(ethylene oxide) concentration yields both intra- and intermolecular chain coupling and formation of large macrocycles with [bis-iron(III) μ-oxo-tetraphenylporphyrin poly(ethylene oxide)] repeating units. The mechanisms involved are discussed.



INTRODUCTION

The design of polymers that are able to rapidly and reversibly change their physical properties under the action of an external stimulus is an area of rapidly increasing interest in functional material research.[1,2] One way to change the polymer properties consists in the modification of the chain architecture, going for instance from linear to cyclic or branched conformations or to vary the polymer dimensions via chain coupling or cross-linking. Reversibility of these processes can be achieved by introduction of covalent or noncovalent linkages that can be open and close under the action of external stimuli such as the variation of concentration, temperature, light, pH, and redox. Supramolecular chemistry involving hydrogen bonding, metal chelation or ionic interactions has been thoroughly investigated to generate dynamic polymer systems capable of undergoing constitutional variation and physical properties changes in response to stimuli.[3−9] The use of reversibly breakable covalent bonds has also been utilized within this context for creating stimuli responsive polymer materials. This includes for instance photoreversible olefin cycloadditions,[10] thiol-driven sulfide coupling,[11,12] carbene dimerization,[13] nucleophilic addition of isocyanates with imidazoles,[14] thermally cleavable alkoxyamines.[15] One of the most studied approach deals with the temperature reversibility of Diels−Alder reactions,[1,16−21] which was recently used as modular polymer color switch.[22]

Among reversible covalent bonding processes the monomer-to-dimer conversion of iron(III)tetraphenylporphyrin derivatives (Fe^{III}TPPX) into bis-iron(III) μ-oxo-tertaphenylporphyrin dimer (bis-Fe^{III} μ-oxo-TPP) has been thoroughly investigated and reported in literature.[23−25]

We have recently applied this reversible reaction to porphyrin end-functionalized polystyrene chains allowing them to switch from linear to cyclic conformation.[26] The reversible chain end coupling process involved the acid−base driven conversion of the two iron(III) tetraphenylporphyrin chloride (Fe^{III}TPPCl) termini into a bis-iron(III) μ-oxo-tertaphenylporphyrin dimer (bis-Fe^{III} μ-oxo-TPP).[24,27−29] In organic media, under high dilution telechelic α,ω-Fe^{III}TPPCl polystyrene were readily and reversibly converted into the corresponding macrocycle by intramolecular end-to-end chain coupling, whereas at higher concentration intermolecular chain coupling yielded much larger rings. This macrocyclization process was found to be reversible simply by switching the “basicity”/“acidity” of the organic polystyrene solution.

In this work this process has been applied to poly(ethylene oxide) a polymer soluble both in organic media and in water, with the aim to further investigate the various stimuli that can be used to trigger the reversible chain coupling. The influence of solvent polarity, acid/base in organic media, pH in water and oxidizing and reducing agents on the end-to-end coupling of poly(ethylene oxide) chains bearing iron(II) or iron(III) tetraphenylporphyrin derivatives, is studied .

Received: March 7, 2011
Revised: April 18, 2011
Published: May 05, 2011

■ EXPERIMENTAL SECTION

Materials. THF (>99.5%, J. T. Baker, The Netherlands), was purified by distillation from calcium hydride and stored in glass vessels over sodium benzophenone.

N,N-dimethylformamide (DMF) (99%, Sigma-Aldrich France), iron(II) chloride, (99%, Sigma-Aldrich France), potassium hydride (30 wt %, dispersion in mineral oil, Sigma-Adrich France), α,α-dichloro-*m*-xylene (98%, Fluka), poly(ethylene glycol) (**1A**) $M_w = 4600$ and (**1B**) $M_w = 8000$ (Sigma-Aldrich France), were characterized by SEC before use.

PEG di-OH 4600: $M_n = 4450$ g/mol, $M_w = 4530$ g/mol, $M_p = 4600$ g/mol, $I_p = 1.02$.

Poly(EO) 4600 di-H_2TPP: $M_n = 4400$ g/mol, $M_w = 4500$ g/mol, $M_p = 4400$ g/mol, $I_p = 1.02$.

Cyclized poly(EO) 4600 FeOFe: $M_n = 3430$ g/mol, $M_w = 3490$ g/mol, $M_p = 3550$ g/mol, $I_p = 1.02$ G ($M_{p,cyclic}/M_{p,linear}$) = 0.8.

PEG di−OH 8000: $M_n = 7870$ g/mol, $M_w = 8000$ g/mol, $M_p = 8140$ g/mol, $I_p = 1.02$.

Cyclized poly(EO) 8000 FeOFe: $M_n = 6340$ g/mol, $M_w = 6880$ g/mol, $M_p = 6350$ g/mol, $I_p = 1.08$.

G ($M_{p,cyclic}/M_{p,linear}$) = 0.78.

Characterization. 1H NMR spectra were recorded in $CDCl_3$ on a Bruker 400 MHz apparatus.

SEC analysis was performed in *N,N*-dimethylformamide (DMF) (elution rate 0.5 mL/min) at 60 °C on a Waters apparatus equipped with a refractive index/photodiode array 2996 dual detection and fitted with four TSK columns (250, 1500, 10^4, 10^5 Å).

The polymer molar masses were determined using linear poly(ethylene oxide)s as calibration standards. A trace of trichlorobenzene added to the sample was used as the internal flow marker reference.

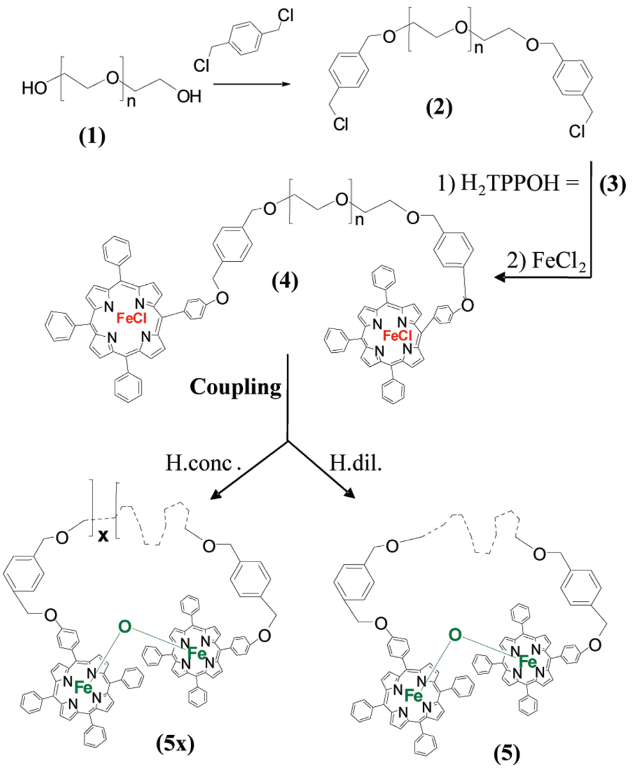
UV−vis spectra were recorded on a Varian Cary 3E spectrophotometer. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI−TOF MS) of functionalized poly(EO) was performed using a voyager-DE STR (Applied Biosystems) spectrometer equipped with a nitrogen laser (337 nm), a delay extraction, and a reflector. The instrument operated at an accelerating potential of 20 kV. Polymer (2 μL) and matrix (20 μL, dithranol) solutions in CH_2Cl_2 (10 g·L^{-1}) were mixed with 2 μL of a sodium iodide solution (10 g·L^{-1} in methanol), which favors ionization. The final solution (1 μL) was deposited onto the sample target and dried in air at room temperature. The MALDI−TOF mass spectra represent averages over 100 laser shots.

Synthesis. *5-(4-Hydroxyphenyl)-10,15,20-triphenylporphyrin.* This compound was synthesized according to the literature.[30] ^{1}H NMR (400 MHz, CD_2Cl_2), δ, ppm: −2.9 (br s, 2H, NH), 1.2 (t, 6H, CH_3), 2.17 (br, 2H, CH_2), 3.56 (br, 2H, OCH_2), 3.69 (br, 2H, OCH_2), 4.26 (t, 2H, $PhOCH_2$), 4.83 (t, 1H, acetal), 7.22 (d, 2H, $H_{3,5}$ Ar), 7.69 (d, 6H, $H_{3,5}$ Ar), 8.04 (d, 2H, $H_{2,6}$ Ar), 8.14 (d, 6H, H2,6 Ar), 8.77 (bd, 6H, H_β, pyr), 8.82 (d, 2H, H_β,pyr).

Telechelic α,ω-Chlorobenzyl Functionalized Poly(ethylene oxide) ***(2)***. For example, α,ω-dihydroxy-terminated poly(EO) (**1A**) (10 g, $M_w = 4600$) was dissolved in anhydrous THF (100 mL). Potassium hydride (0.2 g, 5 mmol), was added in small portions under nitrogen. The mixture was vigorously stirred for 24 h at room temperature under vacuum before addition of α,α-dichloro-*m*-xylene (8 g, 46 mmol). The temperature was increased at 50 °C and the mixture was vigorously stirred for 24 h under vacuum.

After addition of methyl alcohol (3 mL), the solution was evaporated to dryness. The polymer was dissolved in dichloromethane (100 mL) and the organic phase was washed with water (3 × 100 mL), dried with magnesium sulfate, filtered, and concentrated under vacuum. The product (**2A**) was finally recovered and purified twice by precipitation in diethyl ether. After filtration the product was dried under vacuum. Yield: 10 g.

Scheme 1. Strategy of Synthesis of Telechelic α,ω-Diiron(III)tetraphenylporphyrin Chloride Poly(EO) and of Cyclic Bis-Iron(III) μ-Oxo-Tetraphenylporphyrin Poly(EO)



Preparation of Telechelic α,ω-Di(meso-tetraphenyl porphyrinato)-Functionalized Poly(ethylene oxide) ***(3)***. For instance, compound **2A** (0.5 g, 0.1 mmol) was dissolved in dry DMF (20 mL) with 5-(4-Hydroxyphenyl)-10,15,20-triphenylporphyrin (0.2 g, 0.3 mmol) and K_2CO_3 (0.1 g, 7 mmol) was added. After 48 H at room temperature, dichloromethane (100 mL) was added. The organic phase was washed with water, dried with magnesium sulfate, filtered, and concentrated under vacuum. The recovered polymer (**3A**) was purified twice by precipitation in diethyl ether. After filtration the product was dried under vacuum Yield: 0.5 g.

UV/visible (THF), λ (nm): 417; 614; 549; 592; 652.

Preparation of Telechelic α,ω-Di(Fe^{III} meso-tetraphenyl porphyrinato)-Functionalized Poly(ethylene oxide) ***(4)***. For example, to telechelic α,ω-di(iron(III) *meso*-tetraphenyl porphyrinato)-functionalized poly(EO) (**3A**) (250 mg) in dry DMF (40 mL) was added a large excess of anhydrous $FeCl_2$ (150 mg), and the mixture was stirred at 100 °C under N_2 atmosphere until complete insertion of the metal was confirmed by UV/vis spectroscopy, see the corresponding spectra of **3A** and **4A** (Figure S3, Supporting Information). The resulting solution was diluted with 50 mL of dichloromethane and washed with water several times and concentrated. The product **4A** was finally recovered and purified by precipitation in diethyl ether. Yield: 0.25 g (95%).

UV/visible (THF), λ (nm): 370; 419; 509.

Cyclization. *Solvent Effect.* The linear precursor, for instance (**4A**) (100 mg, 2.05 × 10^{-5} mol.) was dissolved in 10 mL THF and the solution was added slowly under stirring into a large volume of pure water or DMF (100 mL). A color change from brown to green was immediately observed and the formation of bis-Fe^{III} μ-oxo-TPP poly(EO) was confirmed by UV/vis spectroscopy titration. After partial evaporation of the solvent, macrocyclic poly(EO) (**5A**) was dissolved in dichloromethane (10 mL) and recovered by precipitation in diethyl ether to give 95 mg of a green solid.

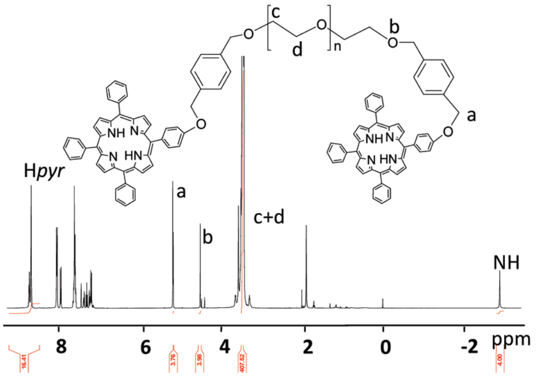


Figure 1. 400 Mz ^{1}H NMR of α,ω-di(*meso*-TPP) poly(EO) (**3A**) in $CDCl_3$ at 20 °C.

UV/visible (THF), λ (nm): 409; 571; 611.

Redox Process. Telechelic α,ω-$Fe^{II}(THF)_2TPP$ poly(EO) (**7**) was prepared by reduction of macrocyclic poly(EO) (**5**) under vacuum atmosphere in a glass flask equipped with a PTFE stopcock. Typically, macrocyclic poly(EO) (**5A**) (5 mg, 8.3 × 10^{-7} mol.) was dissolved in 2 mL of THF and diluted by addition of 8 mL of water. The solution was degassed under vacuum before adding 3 mg of sodium dithionite dissolved in 50 μL of water. The temperature of the solution was then increased to 40 °C. UV/vis spectra were recorded at increasing time until complete disappearance after 1 h of the characteristic μ-oxo Soret band at 409 nm of (**5A**) and formation of pure $Fe^{II}(THF)_2$ TPP poly(EO) (**6A**) (UV/vis, λ(nm): 427; 539; 562; 607.

Oxidation of **7** to re-form macrocyclic bis-Fe^{III} μ-oxo-TPP poly(EO) (**5**) was readily achieved by introducing air in the glass flask. Rapid color change from red to green as well as UV/vis spectroscopy confirmed the quantitative reformation of **5**. UV/visible (THF), λ (nm): 408; 571; 611.

RESULTS AND DISCUSSION

Synthesis of Linear α,ω-H_2TPP Poly(EO) Precursors (3). Linear end-functional poly(EO) precursors, *l*-H_2TPP-poly(EO), were prepared by end-group transformation reaction of two commercially available HO−poly(EO)−OH (**1A**): M_w = 4600 g/mol and (**1B**): 8000 g/mol) in three steps, see Scheme 1. Telechelic α,ω−dichloro benzyl poly(EO) (**2A**) and (**2B**) were first prepared by Williamson reaction between HO−poly(EO)−OH and a large excess of α,α-dichloro-*m*-xylene in the presence of potassium hydride. The polymers were purified by repeated selective precipitation in diethyl ether until no trace of unreacted α,α-dichloro-*m*-xylene was detected by SEC. The ^{1}H NMR spectrum of (**2A**) given as Supporting Information (Figure S1) shows characteristic methylene signals of the oxybenzyl and chlorobenzyl methylene groups at 4.48 and 4.53 ppm respectively, with an intensity in good agreement with quantitative chain-ends functionalization. SEC chromatograms indicate the presence of a small fraction of poly(EO) dimer (about 5%) corresponding to the coupling of two HO−poly(EO)−OH chains with an α,α-dichloro-*m*-xylene molecule, despite its use in large excess.

α,ω-Di(H_2TPP) poly(EO)s (**3A** and **3B**) were prepared in a second step by reaction of telechelic α,ω-dichlorobenzyl-poly(EO)s (**2**) with 1.5 equiv of 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin (**1**), in DMF in presence of potassium carbonate. The ^{1}H NMR spectrum of (**3 A**) given Figure 1, shows the characteristic peaks of the *meso*-tetraphenylporphyrin moieties as well as the signals of the phenylethoxy methylene and the porphyrin phenylphenoxy methylene end groups at 4.5 and 5.2 ppm, respectively. The relative number of tetraphenylporphyrin end groups per chain, was determined in two ways: (i) from the relative integration of the phenylethoxy methylene groups of poly(EO) and of the NH porphyrin protons and (ii) from the poly(EO) methylene units and of the NH porphyrin protons; see Figure 1.

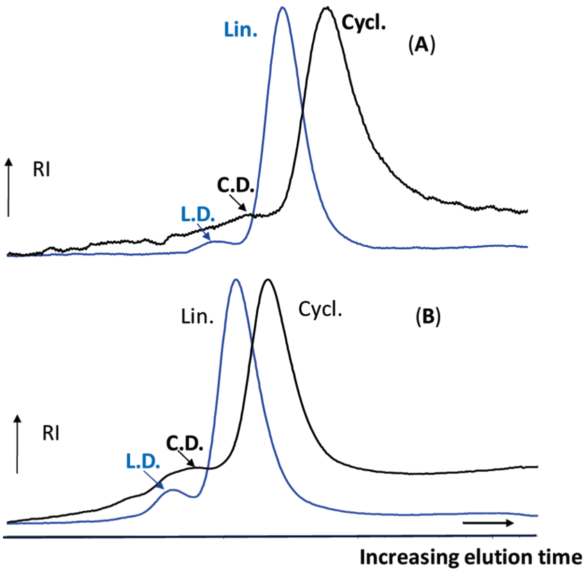


Figure 2. SEC chromatograms of α,ω-di(H_2TPP) poly(EO) (**3A** and **3B**) (blue traces) and cyclized μ-oxo−*bis*(Fe^{III}TPP) poly(EO) (**5A** and **5B**) (black traces) using a refractive index detector. **A** (top) and **B** (bottom) samples. L.D. and C.D. correspond respectively to linear and cyclic poly(EO) dimers.

Results are in agreement with poly(EO) end chain functionalization close to 100%. The MALDI−TOF MS spectrum of α,ω-di(H_2TPP) poly(EO) (**3A**), see Figure S2 in the Supporting Information, shows a single peak series corresponding to experimental molar masses in agreement with calculated ones by the following equation:

$$\begin{aligned} M_n = {} & n44.02 + 16(\text{poly(EO)} - \text{O} -) \\ & + 2x[104, 12(\text{xylen moiety}) \\ & + 630.84(\text{H}_2\text{TPP} - \text{O} -)] + 23.0(\text{sodium}) \end{aligned}$$

where *n* is the number of EO units. For example, for α,ω-di(H_2TPP) poly(EO) with *n* = 100, the MALDI−TOF MS spectrum yields an experimental molar mass of 5911 that corresponds exactly to the theoretical value.

The linear α,ω-di(Fe^{III}TPPCl) poly(EO) linear precursors (**4**) were finally obtained by reacting $FeCl_2$ with the free-base porphyrin ended poly(EO)s (**3**) according to a standard procedure .[31] Formation of telechelic α,ω-di(Fe^{III}TPPCl) end-capped poly(EO)s was confirmed by UV−vis spectroscopy, see Figure S3, Supporting Information, by the presence of the characteristic Soret band at 418 nm ($\varepsilon^{418\text{ nm}}$ Fe^{III}TPPCl = 10.8 × 10^4)[28] with a smaller band at 372 nm and Q-band at 509 nm as well as by the total disappearance of the free-base porphyrin characteristic signals in particular at λ = 549 nm.

Stimuli-Induced α,ω-Di(Fe^{III}TPPCl) Poly(EO) Coupling and Application to Poly(EO) Cyclization and Chain Extension. *Organic Media.* The effect of the solvent nature and polarity on

Table 1. Characteristics of Linear α,ω-Di(Fe$^{\text{III}}$TPPCl) Poly(EO) (4) and Cyclized μ-Oxo−Bis(Fe$^{\text{III}}$TPP) Poly(EO) (5)

PEO	$M_n{}^a \times 10^{-3}$	$M_p{}^a \times 10^{-3}$	$M_w{}^a \times 10^{-3}$	M_w/M_n	M_{p_c}/M_{pl} apparent
4A	4.60	4.60	4.53	1.02	
5A	3.43	3.55	3.49	1.02	0.8
4B	7.87	8.14	8.00	1.02	
5B	6.34	6.35	6.88	1.09	0.78

[a] Determined by SEC using PEO standards.

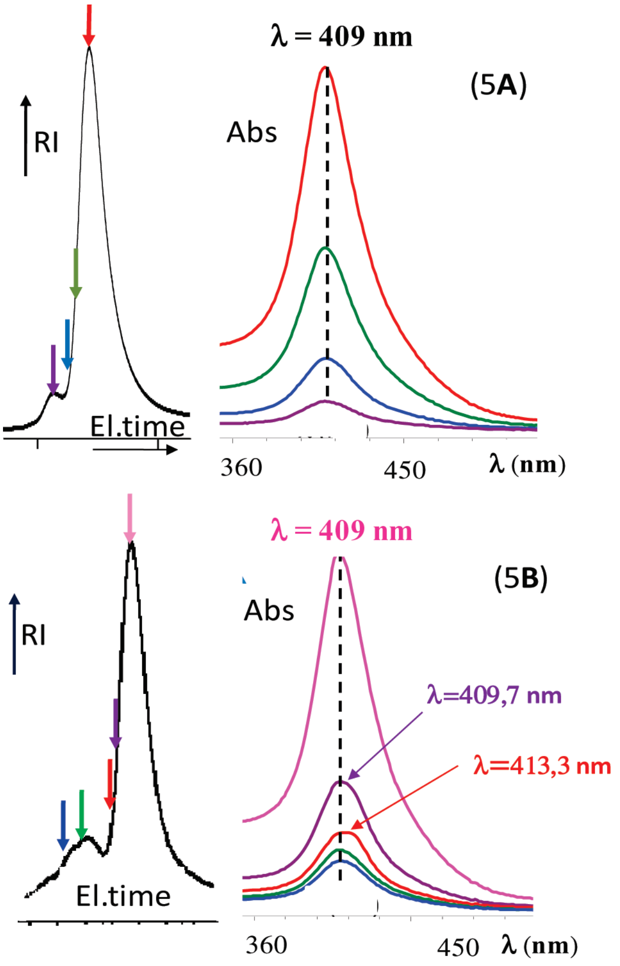


Figure 3. SEC chromatograms (left) of cyclized poly(EO) (**5A**) (top) and (**5B**) (bottom) recovered from diluted DMF solutions. Concentration at cyclization: 2 × 10^{-5} M. Arrows indicates the polymer fractions taken at different SEC elution volumes and analyzed using a UV−vis diode array detector. The corresponding Soret bands (same color as the arrow) and the position of their maximum position are indicated (right).

the spontaneous chain end coupling process of linear telechelic α,ω-di(Fe$^{\text{III}}$TPPCl) poly(EO)s (**4**) has been investigated in pure THF, in DMF, and in their mixtures, in absence of any additional catalyst or base. In pure THF the UV−visible spectra of telechelic α,ω-di(Fe$^{\text{III}}$TPPCl) poly(EO)s remains unchanged over several days without any detectable new signals corresponding to the formation of the μ-oxo-bis(Fe$^{\text{III}}$TPP) dimer. In contrast when a **4A** and **4B** THF solution is added to a large volume of DMF (THF/DMF: 10/100 v/v, poly(EO) concentration 5 × 10^{-5} mol L^{-1}) the color of the solution immediately changes from red brown to green, accompanied by a blue shift of the Soret band on the UV−vis spectra. The new absorption bands (Soret band at 409 nm and Q bands centered at 571 and 612 nm) are characteristic of the μ-oxo-bis(Fe$^{\text{III}}$TPP) complex,[24] ($\varepsilon^{409\text{ nm}}$ μ-oxo-Fe$^{\text{III}}$TPP = 12.0 × 10^{4})[28] whereas the total disappearance of the Fe$^{\text{III}}$TPPCl bands (Soret at 419 nm and other

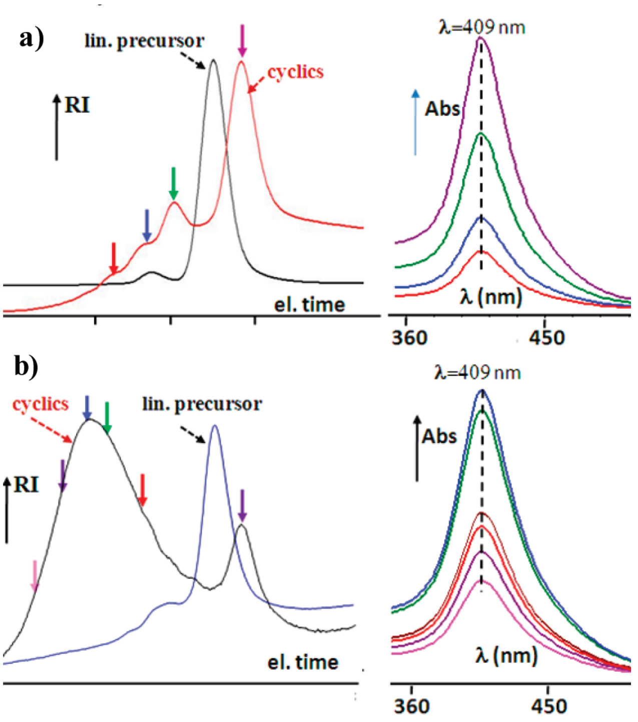


Figure 4. SEC chromatograms (refractive index detection) (left) of linear poly(EO) (**4A**) and cyclized (**5A** + **5Ax**) obtained by adding DMF to concentrated THF solution. Concentrations at cyclization: (a) 10^{-3} M; (b) 10^{-2} M. Arrows refer to polymer fractions taken at different SEC elution times, and analyzed using a UV−vis diode array detector to determine the position of their Soret band (right).

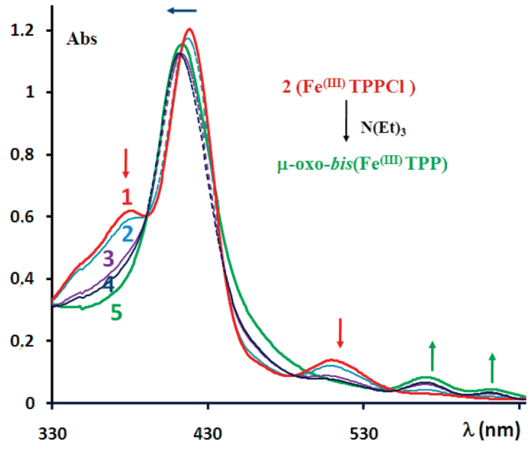


Figure 5. Spectral changes of telechelic α,ω-di(Fe$^{\text{III}}$TPPCl) poly(EO) (**4B**) in THF upon addition of increasing amounts of triethyl amine (TEA). Poly(EO) starting solution (red trace): 2.0 × 10^{-5} M. TEA concentrations (mol L^{-1}): (1) 0; (2) 2.0 × 10^{-4}; (3) 2.0 × 10^{-3}; (4) 3.0 × 10^{-3}; (5) 4.0 × 10^{-3} (green trace).

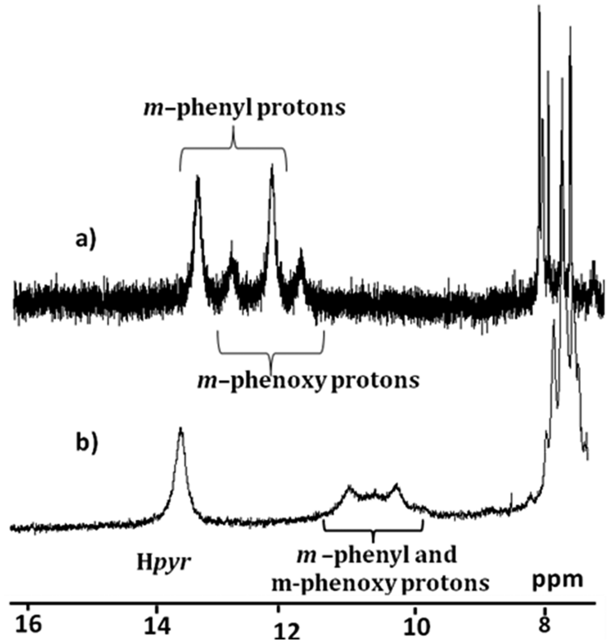


Figure 6. 400 MHz ^{1}H NMR spectra (zoom of the region 7−16 ppm) at room temperature of (a) α,ω-di(Fe^{III}TPPCl) poly(EO) precursor in acetone-d_6 and (b) of macrocyclic μ-oxo-bis(Fe^{III}TPP) poly(EO) obtained by adding 5 mol % CD_3ONa at room temperature.

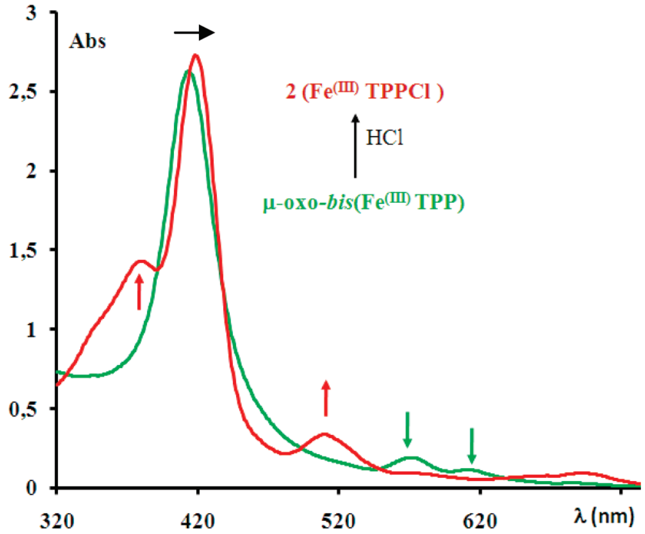


Figure 7. Reversed spectral changes of μ-oxo-bis(Fe^{III}TPP) poly(EO) (**5B**), upon addition of HCl (6N). Initial poly(EO) concentration in DMF: 4.0×10^{-5} mol L^{-1} (green trace). HCl concentrations (mol L^{-1}): 4.0×10^{-3} (red trace).

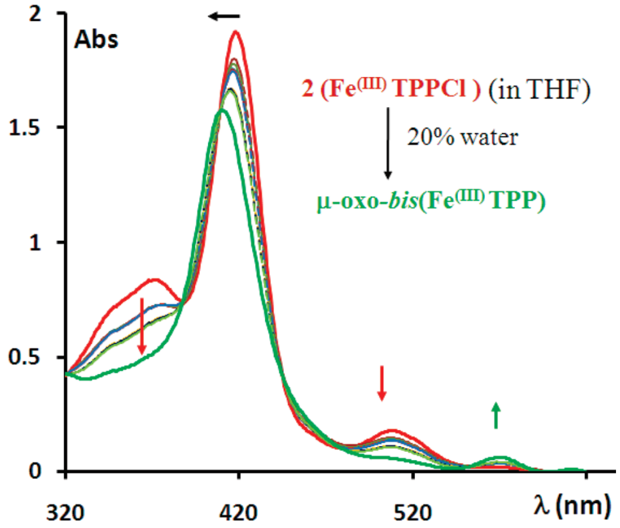


Figure 8. Spectral changes of Fe^{III}TPPCl poly(EO) (**4B**) in THF upon addition of H_2O. Concentration of initial solution of Fe^{III}TPPCl poly(EO): 3.0×10^{-5} mol L^{-1} (red trace). THF/H_2O proportions (vol %): (1) 0; (2) 95; (3) 90; (4) 85; (5) 80; (6) 75 (green trace).

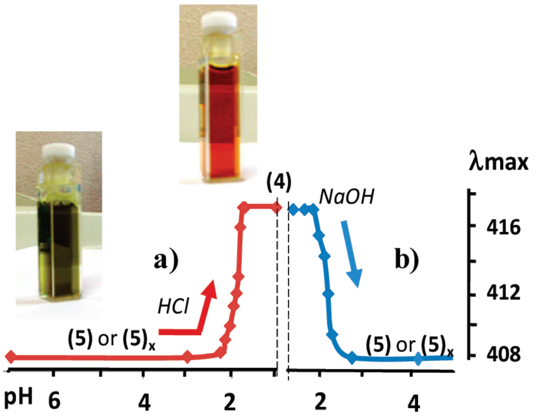


Figure 9. Evolution of the Soret band maximum of a solution of μ-oxo-bis(Fe^{III}TPP) poly(EO) (**5B**) as a function of the pH. (a) addition of HCl (red curve) and then (b) addition of NaOH (blue curve). Concentration of the initial poly(EO) water solution 1.2×10^{-5} mol L^{-1} (pH = 7).

characteristic bands at 380 and 508 nm) indicates their almost quantitative dimerization in DMF. The SEC chromatograms of poly(EO) precursors (**3A** and **3B**) and of the corresponding poly(EO)s, recovered from highly diluted DMF solutions are shown Figure 2. Shift of the polymer signals to higher elution times indicates a reduction of the hydrodynamic volume of the polymer, fully consistent with the formation of cyclic μ-oxo bis (Fe^{III}TPP) poly(EO)s (**5A** and **5B**) by end-to-end intramolecular coupling. The small peaks observed at lower elution volumes (noted L.D, C.D Figure 2) likely corresponds to small amount of linear α,ω-di(Fe^{III}TPPCl) poly(EO)s dimer formed as indicated before and of the corresponding cyclic μ-oxo bis (Fe^{III}TPP) poly(EO).

The G factor ($M_{p,c}/M_{p,l}$) corresponding to the ratio of the apparent peak molar mass (M_p) of cyclic and linear polymers observed by SEC are close to 0.8, which agree well with data reported for polymer cyclization in literature[26,32,33] (see Table1).

Thanks to the differences in the UV/visible absorbance spectra of di(Fe^{III}TPPCl) ended linear poly(EO) chains and of coupled μ-oxo-bis(Fe^{III}TPP) poly(EO) chains, the extent of the coupling/cyclization reaction could be analyzed for polymer fractions eluting at different volumes, using a UV/vis diode array detector coupled to the SEC. The almost complete disappearance of initial Fe^{III}ClTPP bands for all polymer fractions (unimer, dimer, trimer, ...) recovered from experiments performed in dilute DMF solutions indicates that conversion into μ-oxo bis(Fe^{III}TPP) poly(EO), see Figure 3, is close to quantitative for all fractions.

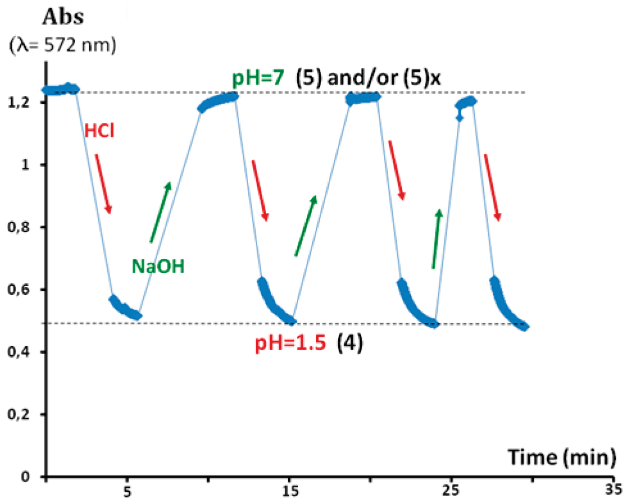
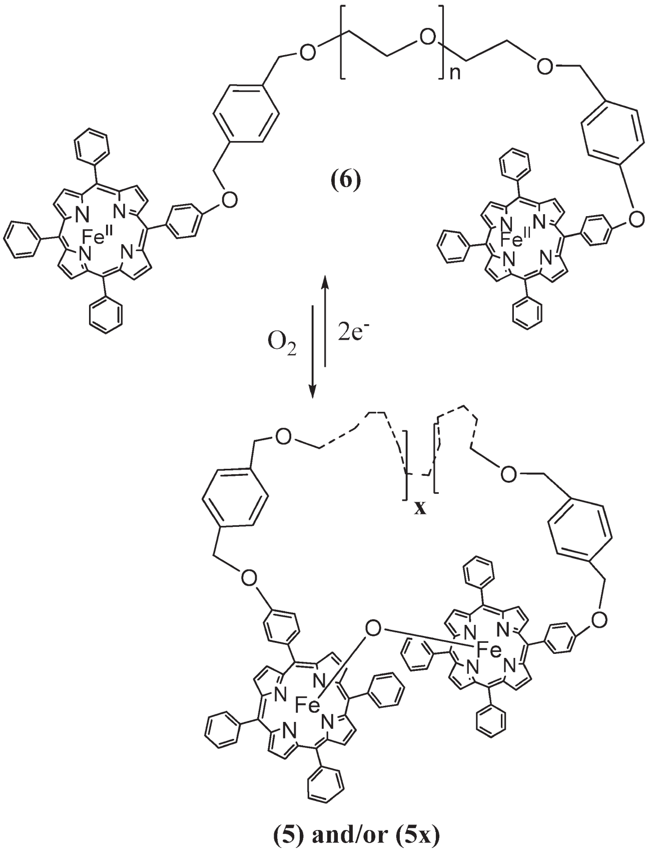


Figure 10. Plot of absorbance at 572 nm as a function of time and pH (4 pH cycles between 7 and 1.5) performed on the same polymer sample **4B** (initial concentration in water: 3.0 × 10^{-3} M). HCl and NaOH solution (6 N) were used for titration.

Scheme 2. Reversible Interconversion of $Fe^{II}(THF)_2TPP$ Poly(EO) (6) into μ-Oxo-bis(Fe^{III}TPP) Poly(EO) (5) by Oxido-Reduction



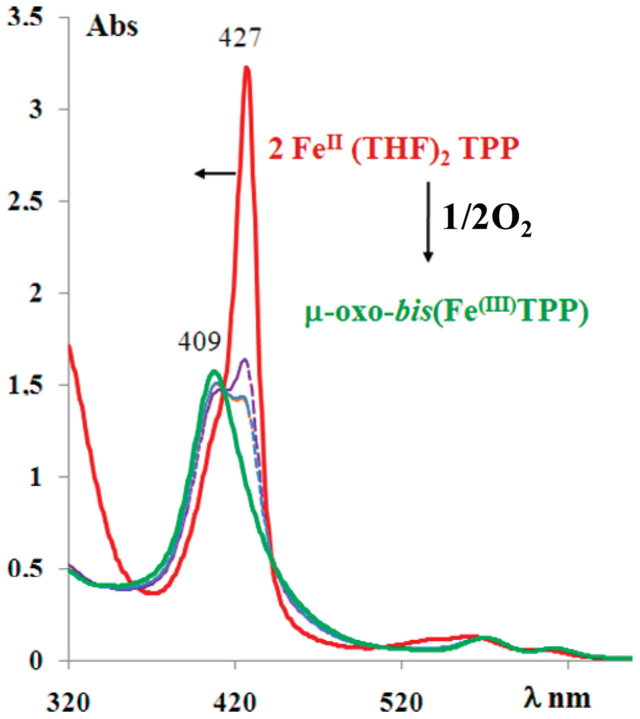


Figure 11. Spectral changes in THF/H_2O of $Fe^{II}TPP(THF)_2$ poly(EO) (**6A**) (red trace) corresponding to the formation of poly(EO) (**5A**) (green trace) by addition of oxygen from air. Initial spectrum of (**6A**) recorded under vacuum. Concentration of initial solution: 3.0 × 10^{-5} mol L^{-1}.

Although not observed by SEC using RI detection, Figure 2, the presence of traces of uncyclized linear precursor can be deduced from the slight shift of the Soret band to higher wavelength (fraction corresponding to red arrow), characteristics of Fe^{III}TPPCl, (Soret band at 418), in minute fractions corresponding to the foot of the main peak (**5B**). No traces of linear chains are detected in **5A**. Dimer and trimer fractions show also a maximum of their Soret band centered around 409 nm, in agreement with an almost exclusive formation of macrocyclic structures.

Increasing the Fe^{III}TPPCl end group concentration by adding DMF to a concentrated THF solution of poly(EO) (**4A**) from 5 mmol (Figure 4a) to 10 mmol (Figure 4b) results in an increase of the oligomer and high polymer fractions. All the fractions, from the one corresponding to cyclic poly(EO) unimer to those centered on poly(EO) oligomers and polymers, show a Soret band at 409 nm corresponding precisely to μ-oxo-bis(Fe^{III}TPP) species. These results are is in agreement with the almost quantitative formation of macrocyclic poly(EO) dimer, trimer, tetramer (Figure 4a) as well as a majority of very large poly(EO) rings (Figure 4b). The main poly(EO) polycondensate population exhibits an apparent SEC peak molar mass of 56000 g mol^{-1} in equivalent linear poly(EO). This corresponds to the covalent assembly of more than 10 telechelic di(Fe^{III}TPPCl) poly(EO) linear precursors before cyclization.

Influence of Added Bases. Besides the effect of solvent nature a similar coupling process was observed when adding triethylamine (TEA) to the linear precursor (**4B**) into THF. Upon adding small amounts of concentrated TEA incremental conversion of Fe^{III}TPPCl into μ-oxo-bis(Fe^{III}TPP) poly(EO) was observed until full conversion was reached at a TEA concentration of about 4.0 × 10^{-3} mol L^{-1} which is about 2 hundred times than that of Fe^{III}TPPCl endgoups. The corresponding UV−vis spectral changes are shown Figure 5.

Table 2. Influence of Conditions on the Iron−Porphyrin Structure and Poly(ethylene oxide) Architecture[a]

($Fe^{III}TPPCl$)/ linear telechelic poly(EO)	μ-oxo-bis($Fe^{III}TPP$) macrocyclized poly(EO)
THF	THF/TEA THF/DMF (1:10) THF/H_2O (5:1)
DMF/HCl	DMF
CH_2Cl_2	
H_2O pH< 1.9	H_2O pH > 2.3
($Fe^{II}TPP(THF)_2$)/ linear telechelic poly(EO)	same
$THF/H_2O + O_2 \rightleftarrows THF/H_2O$ + dithionite	

[a] TEA: triethylamine.

Addition of strong bases such as sodium hydroxide or sodium methanolate to $Fe^{III}TPP$ poly(EO) in THF yields to the same quantitative coupling process.

Formation of the μ-oxo-bis($Fe^{III}TPP$) dimer was checked by ^1H NMR while the large predominance of end-to-end cyclization was confirmed by SEC. The ^1H NMR spectrum of α,ω-di-($Fe^{III}TPPCl$) poly(EO) (**4A**) recorded before and after addition of $NaOCD_3$ in acetone-d_6 is shown in Figure 6. The characteristic signal assigned to the pyrrole groups of the μ-oxo-bis-($Fe^{III}TPP$) function is observed at δ= 13.6 ppm whereas the two doublets between 11.7 and 13.4 ppm corresponding to the *m*-phenyl protons and *m*-phenoxy of $Fe^{III}TPPCl$ moieties are shifted upfield in the 10.1−11.2 ppm range.[34]

Addition of Brönsted Acids. Macrocycles (**5**) were converted reversibly into linear precursor (**4**) by adding protonic acids to their DMF solution. The corresponding changes in the color of the solution from green to red brown and in the UV−visible spectra upon incrementally adding a HCl solution (6 N) are shown in Figure 7. In the presence of about 100 HCl equivalents with respect to **5**, the maximum of the Soret band is shifted to 418 nm, in agreement with reformation of **4**

Investigation in Aqueous Solution. Addition of a solution of **4** in THF to a large volume of water (5/95 v/v) yields an immediate color change from red brown to green accompanied by a blue shift of the Soret band in the UV−vis spectra. The new spectrum (Soret band at 409 nm and Q bands centered at 571 and 612 nm) indicates that the $Fe^{III}TPPCl$ moieties have been spontaneously converted into μ-oxo-bis($Fe^{III}TPP$). The SEC analysis of the polymer shows a peak maximum at lower elution volume indicating a reduction of the apparent poly(EO) molar mass consistent with the formation of cyclic poly(EO) (**5**). Incremental addition of water aliquots to the THF solutions of **4** followed by UV−vis spectroscopy indicates that macrocycles **5A** or **5B** are completely formed at a final composition 20/80 H_2O/THF (v/v), Figure 8.

As already shown above in organic media, addition of HCl to a solution of **5** in water (THF > 1%) results in a reverse process and reformation of **4**. These changes and their reversibility were monitored by following the λ max of the Soret band as a function of the pH (addition of HCl and then of NaOH), Figure 9. The ring-opening process was shown to proceed readily and completely within a narrow pH range between 2.3 and 1.7, both for the poly(EO) samples (A and B). No further change in the UV−visible spectrum was noticed in pH ranges lower than 1.7 and higher than 2.3, indicating the stability domain of the open $Fe^{III}TPPCl)_2$ poly(EO) and closed μ-oxo-*di*($Fe^{III}TPP$) poly-(EO) forms in water.

The repeatability of this process was further checked by performing a series of opening/closing cycles by varying the pH of the solution and monitoring both the color change and the intensity of a signal specific to μ-oxo-bis($Fe^{III}TPP$) poly(EO) with λ max Q-band at 572 nm, see Figure 7.

The absorbance at 572 nm was then measured repeatedly and successively at pH 7 and 1.5 corresponding respectively to closed and open poly(EO) architectures, Figure 10. Results clearly indicate that interchange between the ring and linear polymer architectures proceeds without any significant variation of the maximum and minimum of absorbance at 572 nm. The SEC chromatogram of the μ-oxo-bis($Fe^{III}TPP$) poly(EO) after several opening/closing cycles is shown Figure S4 given as Supporting Information.

The reversible monomer-to-dimer conversion of iron−porphyrin ends involves in the present system exchange of labile chloride ligands by hydroxyl ones followed by dimerization as schematized in eqs Ia and Ib while regeneration of porphyrin monomer requires acidic conditions, eq II. Relatively similar processes may occurs in organic media in acido/basic situations

$$Fe^{III}TPPCl + Na^+OH^- \rightleftarrows Fe^{III}TPPOH + Na^+Cl^- \qquad (Ia)$$

$$2Fe^{III}TPPOH \rightleftarrows (Fe^{III}TPP)_2O + H_2O \qquad (Ib)$$

and

$$(Fe^{III}TPP)_2O + 2H^+Cl^- \rightleftarrows 2Fe^{III}TPPCl + H_2O \qquad (II)$$

Opening/Closing by a Redox Process. Dissociation of μ-oxo-bis($Fe^{III}TPP$) poly(EO) (**5**) in a THF/H_2O mixture (20/80% v/v), could also be achieved quantitatively by a reduction process using aqueous sodium dithionite as a reducing agent under vacuum. The equivalent linear poly(EO) precursor (**6**) with $Fe^{II}(THF)_2TPP$ chain ends, ($\varepsilon^{427\,nm}$ $Fe^{II}TPP$) = 20.8 × 10^4),[35] Scheme 2, was quantitatively produced under vacuum or inert atmosphere at 50 °C.

Introduction of dioxygen to the above system (**6**) resulted in the rapid autoxidation of the six-coordinate $Fe^{II}TPP(THF)_2$ complex, into μ-oxo-bis($Fe^{III}TPP$) poly(EO) (**5**). ($\varepsilon^{409\,nm}$ μ-oxo-$Fe^{III}TPP$ = 12.0 × 10^4),[28,36] see Figure11.

The effect of the different stimuli and conditions on the iron−porphyrin and polymer structures are summarized in Table 2.

CONCLUSIONS

Reversible commutation between linear telechelic poly(EO) bearing either iron(III) TPPCl or iron(II) TPP at their ends and μ-oxo-bis($Fe^{III}TPP$) poly(EO) has been shown to proceed both in organic and water media under the action of various stimuli. At low concentration macrocyclic poly(ethylene oxide)s of same molar mass as the linear precursors are selectively formed via intramolecular coupling whereas increasing the poly(ethylene oxide) concentration induces a competition between intra- and intermolecular coupling and results in the formation of large macrocycles with [bis-iron(III) μ-oxo-TPP poly(EO)] repeating units.

Architecture changes between α,ω-di(Fe^{III}TPPCl) poly(EO) and μ-oxo-bis(Fe^{III}TPP) poly(EO) in water proceeds in a narrow and quite acidic pH range, approximately between 1.7 to 2.3, where the two porphyrin derivatives coexit in equilibrium. At lower pH di(Fe^{III}TPPCl) poly(EO) is the only species present. At higher pH (>2.3) or in organic media such as DMF or in THF in presence of water (20%) or of a base such as $N(Et)_3$ di(Fe^{III}TPPCl) end groups readily dimerize into cyclic μ-oxo-bis(Fe^{III}TPP) poly(EO).[24]

A quite similar reversible on/off switching between linear and cyclic poly(EO) can be also achieved by repeated α,ω-di-(Fe^{II}TPP) poly(EO) oxidation/μ-oxo-bis(Fe^{III}TPP) poly(EO) reduction in water using for instance air as oxidizing agent and sodium dithionite as reductor in aerobic conditions.

Applications of these features to design polymer systems with switchable properties are under study.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. ^{1}H NMR spectrum of poly(EO) (**2A**), MALDI−TOF spectrum of **3A**, UV/visible spectra of **3A** and **4A**, SEC chromatograms several commutation cycles, and reversed spectral change for the reduction of **5B**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: deffieux@ipb.fr.

■ REFERENCES

(1) Inglis, A. J.; Nebhani, L.; Altintas, O.; Schmidt, F. G.; Barner-Kowollik, C. *Macromolecules* **2010**, *43*, 5515–5520.

(2) Wojtecki, R. J.; Meador, M. A.; Rowan, S. J. *Nat. Mater.* **2011**, *10*, 14–27.

(3) Rowan, S. J.; Cantrill, S. J.; Cousins, G. R. L.; Sanders, J. K. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 899–952.

(4) Ulrich, S.; Buhler, E.; Lehn, J. M. *New J. Chem.* **2009**, 33, 271–292.

(5) Lehn, J. M. *Chem. Soc. Rev.* **2007**, *36*, 151–160.

(6) Lehn, J. M. *Prog. Polym. Sci. (Oxford)* **2005**, *30*, 814–831.

(7) Cordier, P.; Tournilhac, F.; Soulié-Ziakovic, C.; Leibler, L. *Nature* **2008**, *451*, 977–980.

(8) Bouteiller, L. *Adv. Polym. Sci.* **2007**, *207*, 79–112.

(9) De Greef, T. F. A.; Meijer, E. W. *Nature* **2008**, *453*, 171–173.

(10) Chen, Y.; Chen, K.-H. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 613–624.

(11) Whittaker, M. R.; Goh, Y. K.; Gemici, H.; Legge, T. M.; Perrier, S.; Monteiro, M. J. *Macromolecules* **2006**, *39*, 9028–9034.

(12) Furusho, Y.; Oku, T.; Hasegawa, T.; Tsuboi, A.; Kihara, N.; Takata, T. *Chemistry − A European Journal* **2003**, *9*, 2895–2903.

(13) Kamplain, J. W.; Bielawski, C. W. *Chem. Commun.* **2006**, 1727–1729.

(14) Chang, J. Y.; Do, S. K.; Han, M. J. *Polymer* **2001**, *42*, 7589–7594.

(15) Themistou, E.; Patrickios, C. S. *Macromolecules* **2005**, *39*, 73–80.

(16) Reinecke, M.; Ritter, H. *Makromol. Chem.* **1993**, *194*, 2385–2393.

(17) Chen, X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F. *Science* **2002**, *295*, 1698–1702.

(18) Gandini, A.; Silvestre, A. J. D.; Coelho, D. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 2053–2056.

(19) Gheneim, R.; Perez-Berumen, C.; Gandini, A. *Macromolecules* **2002**, *35*, 7246–7253.

(20) Imai, Y.; Itoh, H.; Naka, K.; Chujo, Y. *Macromolecules* **2000**, *33*, 4343–4346.

(21) Jones, J. R.; Liotta, C. L.; Collard, D. M.; Schiraldi, D. A. *Macromolecules* **1999**, *32*, 5786–5792.

(22) Paulöhrl, T.; Inglis, A. J.; Barner-Kowollik, C. *Adv. Mater.* **2010**, *22*, 2788–2791.

(23) Sutter, J. R.; Hambright, P.; Chock, P. B.; Krishnamurthy, M. *Inorg. Chem.* **1974**, *13*, 2764–2765.

(24) Fielding, L.; Eaton, G. R.; Eaton, S. S. *Inorg. Chem.* **1985**, *24*, 2309–2312.

(25) Fleischer, E. B.; Palmer, J. M.; Srivastava, T. S.; Chatterjee, A. *J. Am. Chem. Soc.* **1971**, *93*, 3162–3167.

(26) Schappacher, M.; Deffieux, A. *J. Am. Chem. Soc.* **2011**, *133* (6), 1630–1633.

(27) Liu, Q.; Gong, Y. Z.; Gong, C. J.; Li, Q. H.; Guo, C. C. *J Porphyrins Phthalocyanines* **2009**, *13*, 854–858.

(28) Fleischer, E. B.; Srivastava, T. S. *J. Am. Chem. Soc.* **1969**, *91*, 2403–2405.

(29) Ghosh, S. K.; Patra, R.; Rath, S. P. *Inorg. Chem.* **2010**, *49*, 3449–3460.

(30) Bakleh, M. E.; Sol, V.; Estieu-Gionnet, K.; Granet, R.; Déléris, G.; Krausz, P. *Tetrahedron* **2009**, *65*, 7385–7392.

(31) Manso, C. M. C. P.; Neri, C. R.; Vidoto, E. A.; Sacco, H. C.; Ciuffi, K. J.; Iwamoto, L. S.; Iamamoto, Y.; Nascimento, O. R.; Serra, O. A. *J. Inorg. Biochem.* **1999**, *73*, 85–92.

(32) Hadziioannou, G.; Cotts, P. M.; Ten Brinke, G.; Han, C. C.; Lutz, P.; Strazielle, C.; Rempp, P.; Kovacs, A. J. *Macromolecules* **1987**, *20*, 493–497.

(33) Roovers, J. *J. Polym, Sci., Part A-2: Polym. Phys.* **1985**, *23*, 1117–1126.

(34) Ikezaki, A.; Nakamura, M. *J. Inorg. Biochem.* **2001**, *84*, 137–144.

(35) Collman, J. P.; Gagne, R. R.; Reed, C. A.; Halbert, T. R.; Lang, G.; Robinson, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 1427–1439.

(36) Collman, J. P.; Brauman, J. I.; Suslick, K. S. *J. Am. Chem. Soc.* **1975**, *97*, 7185–7186.