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Self-Construction of Supramolecular Polyrotaxane Films by an Electrotriggered Morphogen-Driven Process

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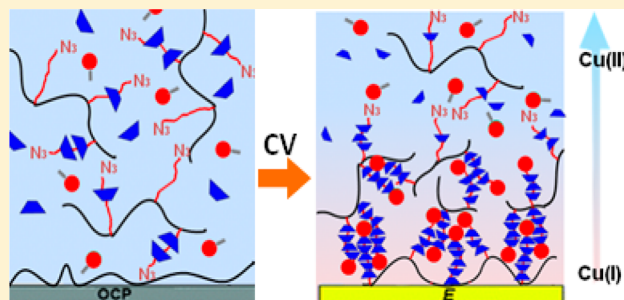
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Supporting Information

ABSTRACT: The design of films using a one-pot process has recently attracted increasing interest in the field of polymer thin film formation. Herein we describe the preparation of one-pot supramolecular polyrotaxane (PRX) films using the morphogen-driven self-construction process. This one-pot buildup strategy where the film growth is triggered by the electrochemical formation and diffusion of a catalyst in close vicinity of the substrate has recently been introduced by our group. A one-pot mixture was used that contained (i) poly(acrylic acid) (PAA) functionalized by azide groups grafted on the polymer chain through oligo(ethylene glycol) (EG) arms, leading to PAA-EG₁₃-N₃, (ii) cyclodextrins (α and β CD), as macrocycles that can be threaded along EG arms, (iii) alkyne-functionalized stoppers (ferrocene or adamantane), to cap the PRX assembly by click chemistry, and (iv) copper sulfate. The one-pot mixture solution was brought into contact with a gold electrode. Cu(I), the morphogen, was generated electrochemically from Cu(II) at the electrode/one-pot solution interface. This electrotriggered click reaction leads to the capping of polypseudorotaxane yielding to PRXs. The PRXs can self-assemble through lateral supramolecular interactions to form aggregates and ensure the cohesion of the film. The film buildup was investigated using different types of CD and alkyne functionalized stoppers. Supramolecular PRX aggregates were characterized by X-ray diffraction measurements. The film topographies were imaged by atomic force microscopy. The influence of the concentration in CD and the presence of a competitor were studied as well. The stability of the resulting film was tested in contact with 8 M urea and during the electrochemical oxidation of ferrocene.



INTRODUCTION

Supramolecular interlocked architectures have attracted a large amount of interest since their prediction in the early 1960s¹ and their first experimental discovery.^{2–6} Because the relative position of the different parts of interlocked supramolecules can be changed through external stimuli, they constitute promising candidates for molecular switches, machines, and motors.^{7–10} Among the different supramolecular structures, polyrotaxanes (PRXs) are characterized by a linear polymer chain threading multiple cyclic molecules and capped by stoppers which sterically avoid disassembly. In the early 1990s,

Harada et al. described the use of α -cyclodextrins (α -CD) and polyethylene glycol (PEG) chains for the self-assembly of pseudo-PRXs.⁵ These α -CD- and polymer-based poly(pseudo)-rotaxanes, where no stopper is used to lock the geometry, can form physical hydrogels displaying thixotropic and thermo-reversible properties based on supramolecular interactions between the α -CDs. It was shown that gels composed of PEG

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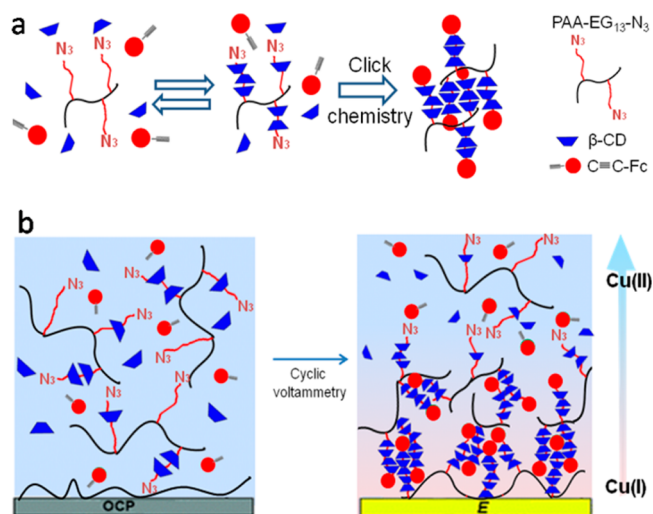
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and α -CD can be designed using a wide range of PEG^{11,12} and α -CD¹³ concentrations. Since both CD and PEG are biocompatible entities, these resulting gels, whose integrity relies on noncovalent interactions, constitute promising biomaterials.¹⁴ The first CDs based PRX film was reported by Araki et al. and its application.¹⁵ Fewer works have focused on CD-based PRX film assemblies obtained either by wet spinning¹⁶ or layer by layer deposition.¹⁷ PRX-based films composed of CD and polymer are generally synthesized with the end-capping approach which necessitates two assembling steps: a molecular threading of CD triggered by noncovalent interactions and a covalent capping of the polymer chain with bulky groups, so-called “stoppers” or “capping groups”, as adamantane (Ad) or ferrocene (Fc) groups, for instance. These steps occur successively in different solutions or using a one-pot approach.^{18–21} Yet to our knowledge, these strategies are limited to bulk or liquid–liquid²² interface reactions. Coating processes of surfaces by films made of polymers or polyelectrolytes have received considerable attention over recent years. They find many applications in areas ranging from anticorrosion, sensors, optical devices, biomaterial, and membranes up to tissue engineering. It is of interest to design buildup strategies where films construct spontaneously in a single step on the substrate by mixing the interacting species.

Very recently, in the field of polymer thin film formation, several concepts have emerged to obtain polymer films using a one-pot process.^{23–26} Our group introduced a one-pot morphogen-driven self-construction of films where the buildup is triggered by the electrochemical formation of a catalyst and its diffusion in the vicinity of the substrate. This concept has been illustrated by the one-pot self-construction of films based on a confined click reaction between azide- and alkyne-bearing polymers using electrotriggered Cu(I) as morphogen.^{23,24} Recently, we proved that such self-constructed films can be obtained using host–guest interactions through the reaction of polymer chains functionalized by azide groups with Fc and β -CD both functionalized by alkyne functions.²⁷

Herein, we describe the one-pot morphogen-driven self-construction of PRX-based films. These films were obtained by electrotriggered click reaction using a one-pot solution containing poly(acrylic acid) (PAA) functionalized through oligo(ethylene glycol) arms (EG) grafted at 5% on the polymer backbone and bearing one azide group at their free ends (PAA-EG₁₃-N₃), β -CD, alkyne bearing stoppers (HC \equiv C-Fc) and CuSO₄. In the mixture solution, spontaneous self-assembly of pseudo-PRX occurred by threading of β -CD along EG arms. In the presence of electrogenerated Cu(I) ions, alkyne-functionalized stoppers are able to lock the rotaxane architecture into PRX by click reaction with the terminal azide functions of the EG. A PRX film is thus formed at the surface of the electrode by lateral interactions between PRX (Scheme 1). All of the components are simultaneously present in the constructing mixture solution, and the morphogen driven approach allows the supramolecular interlocked architecture to take place only in the vicinity of the substrate, leading to the formation of a film. Inclusion complexes of PRX, leading to crystalline domains, are difficult to characterize on nanometric films. Thus, in this work, we focused a main part of our efforts to do many control experiments to give a strong evidence of PRX assemblies. The simultaneous presence of all the components (PAA-EG₁₃-N₃, β -CD, alkyne bearing stoppers and CuSO₄) is necessary to the film buildup. To confirm that β -CD in the PRX-based film are threaded along the PEG arms, we have done experiments to

Scheme 1. Self-Construction of a Film Based on the Interaction between Side Chain PRX (PAA-EG₁₃-N₃, β -CD, HC \equiv C-Fc) Obtained in Situ Using Electrochemically Triggered Click Chemistry^a



^a(a) PAA-EG₁₃-N₃, β -CD and HC \equiv C-Fc present in solution form reversible side chain pseudo PRX with threading of β -CD onto EG arms; PRXs are locked by reaction of HC \equiv C-Fc with PAA-EG₁₃-N₃ through click chemistry and they are able to self-assemble through lateral interactions between β -CDs; (b) Electrotriggered click-chemistry induces the formation of a PRX film at the surface of the electrode.

show that β -CD cavities are not available for another guest. Aggregate domains on the PRX based films were imaged by atomic force microscopy (AFM). The crystalline aggregates domains, resulting from the lateral interaction between threaded CDs, and responsible of the PRX-based film architecture, were characterized in the bulk by X-ray diffraction (XRD) measurements. PRX-based film buildup was studied by varying the different components and their concentration. Finally, the chemical and electrochemical stability of the resulting films is discussed in the last part of this work.

MATERIALS AND METHODS

Polymers and Functionalized Molecules. Poly(ethyleneimine) (PEI, $M = 750\,000$ g/mol, CAS 9002-98-6), ethynylferrocene (HC \equiv C-Fc, $M = 210.1$ g/mol, CAS 1271-47-2), ferrocene dimethanol (Fc(CH₂OH)₂, $M = 246.1$ g/mol, CAS 1273-86-5), 1-adamantane carboxylic acid (Ad-COOH, $M = 180.24$ g/mol, CAS 828-51-3) β -cyclodextrin (β -CD, $M = 1134.98$ g/mol, CAS 7585-39-9), α -cyclodextrin (α -CD, $M = 972.84$ g/mol, CAS 10016-20-3), sodium nitrate ($M = 84.99$ g/mol, CAS 7631-99-4), tetrakis(acetonitrile)copper(I) tetrafluoroborate salt (Cu(I), $M = 314.56$ g/mol, CAS 15418-29-8), copper sulfate pentahydrate (CuSO₄ · 5 H₂O, $M = 249.69$ g/mol, CAS 7758-99-8), and propargyl alcohol (HC \equiv C-CH₂-OH, $M = 56.06$ g/mol, CAS 107-19-7) were purchased from Aldrich and used as received. Poly(acrylic acid) (PAA) modified with 5% azide (PAA-EG₁₃-N₃) functions grafted onto the PAA backbone through ethylene glycol EG arms was synthesized according to Rydzek et al.²⁸ Ethynyladamantane (HC \equiv C-Ad) was synthesized according to Hashmi et al.²⁹ HC \equiv C-CH₂-(O-CH₂-CH₂)₂OH was synthesized according to the method of Gill et al.³⁰ All of the chemical structures are drawn in Figure S-1 of the Supporting Information (SI).

Solutions. All solutions were prepared with ultrapure water (Milli-Q Plus system, Millipore, Billerica, MA) and ethanol absolute was purchased from VWR (99.5% purity). The reactants were prepared in separated solutions and mixed together the day of the experiment.

PAA-EG₁₃-N₃ and CD solutions were prepared in water in presence of 0.6 mM CuSO₄ at pH 3.50 ± 0.05. Since they are hydrophobic molecules, HC≡C-Fc and HC≡C-Ad were dissolved in ethanol with of 0.6 mM CuSO₄. Fc(CH₂OH)₂ was also dissolved in ethanol. Building solutions, composed of 50/50 v/v water/ethanol and adjusted to pH 3.5 ± 0.05 using 0.1 M HNO₃, always contained 0.25 g/L of PAA-EG₁₃-N₃ (i.e., 10⁻⁴ M of azide functions), 10⁻³ M of alkyne-bearing stopper groups, and 10⁻³ M (respectively 10⁻² M) β-CD (respectively α-CD). When a competitive hydrophobic guest molecule (Fc(CH₂OH)₂ or Ad-COOH) was added to the building solution, its concentration was fixed to 10⁻³ M.

Electrochemical Quartz Crystal Microbalance with Dissipation Monitoring (EC-QCM-D). The electrochemical quartz crystal microbalance (EC-QCM-D) experiments were performed on a Q-Sense E1 apparatus from Q-Sense AB (Gothenburg, Sweden). Changes in the resonance frequency *f* and in the dissipation factor *D* of an oscillating quartz crystal during adsorption of a layer^{31,32} were monitored. They are due to the mass of the film deposited and the mass of the encaged water molecules, as well as to the viscoelastic characteristics of this hydrated film.³¹ The quartz crystal was excited at its fundamental frequency (5 MHz). Measurements were performed at 5, 15, 25, and 35 MHz, corresponding to the first, third, fifth, and seventh overtones. The thickness of the adsorbed layers can be estimated using the viscoelastic Voight model (see the model in the SI).³³ For this evaluation, the fluid density (1000 kg/m³), fluid viscosity (1 mPa·s), and layer density (1000 kg/m³) were kept constant. Thicknesses were estimated using the third, fifth, and seventh overtones. Simultaneous QCM and electrochemistry measurements are allowed by the Q-Sense Electrochemistry Module, QEM 401. A gold-coated QCM sensor from Q-Sense AB (Gothenburg, Sweden) and ITO-coated QCM sensor from Microvacuum (Budapest, Hungary) acted as the working electrodes. ITO-coated QCM crystals allowed us to perform UV spectroscopy on the film in order to detect trapped ferrocene. The counter-electrode is constituted by a platinum plaque on the top wall of the QCM chamber. A no-leak Ag/AgCl electrode fixed at the outlet flow channel was used as reference electrode. At the beginning of each EC-QCM-D experiment, the capacitive current and the faradic current of a 1 mM potassium hexacyanoferrate(II) (K₄[Fe(CN)₆], Sigma, CAS 14459-95-1) aqueous solution were recorded and checked to be in good agreement with the literature.³⁴ A Tris-NaNO₃ solution prepared from Tris(hydroxy-methylaminomethane) (Tris, 5 mM, Gibco BRL, cat no.: 15504-020) and sodium nitrate (NaNO₃, 0.15 M) adjusted to pH 7.4 was used as a buffer to measure the capacitive current of the EC-QCM-D cell. A 1 mM portion of potassium hexacyanoferrate(II) was solubilized in the buffer and put into contact with the crystal to monitor its cyclic voltammogram.

X-ray Diffraction Measurements (XRD). The crystalline structure of the (PAA-EG₁₃-N₃, CD, HC≡C-Fc) based materials were determined by XRD with a Bruker AXS-D8 Advanced equipment with a linear detector lynxeye and the Cu-Kα radiation (λ = 1.5404 Å). The 2θ range used was 5–35° with a 0.002° step size at a scan rate of 1 min⁻¹.

Atomic Force Microscopy (AFM). The images were obtained by AFM in contact mode in liquid and dry state conditions with the Nanoscope IV from Veeco (Santa Barbara, CA). The images were carried out with silicon nitride cantilevers, spring constant 0.03 N/m (model MSCTAUHW, Veeco, CA). Several scans were performed over a given surface area. These scans had to give reproducible images to be sure that there was no sample damage induced by the tip. Deflection and height mode images were scanned simultaneously at a fixed scan rate (2 Hz) with a resolution of 512 × 512 pixels. Data evaluation was performed with the NanoScope software version 5.31r1 (Digital Instruments, Veeco). The film thickness was determined by imaging the film after a scratch. Profilometric section analyses of a scratched film allowed us to determine its thickness by measuring the vertical distance between the top of the film and the bare substrate. The scratches were achieved with a plastic cone tip and were always imaged perpendicular to the fast scan axis. The profiles correspond to a cross section along this axis. The mean thickness of the scratched film was determined by measuring it at least on three areas.

Film Buildup Procedure. Film self-constructions were performed on either a bare gold or an ITO-coated QCM crystal. QCM crystals

were cleaned by dipping during 15 min in a 50% (v/v) 1 M sodium hydroxide/hydrogen peroxide mixture. The cleaning was followed by a rinsing step in Milli-Q water. The substrate was first put into contact during 5 min with a PEI solution (1 mg/mL in water, pH 7.0) followed by a rinsing step with a CuSO₄ solution (0.6 mM, pH 3.5). This step was performed to obtain a first electrostatic adsorption and promote further film buildup. The self-construction was obtained by injection at 0.1 mL/min of a mixture of CD, PAA-EG₁₃-N₃, and alkyne bearing molecules prepared with 0.6 mM CuSO₄ in a 50% (v/v) water-ethanol solution adjusted to pH 3.5. After the electrostatic adsorption of PAA-EG₁₃-N₃ and a stabilization of 5 min, a voltammetric cycle between -350 mV and +750 mV with a 50 mV/s scan rate was applied during 120 min. The temperature was kept at 20 °C. The Voight model allowed calculating the film thickness from QCM data. The thickness evolution was plotted after subtraction of the contribution of the electrostatic deposition of PEI and PAA-EG₁₃-N₃ on the QCM crystal

Loading of the Film with Ferrocene. In order to trap hydrophobic molecules in the coating, self-constructed films composed of β-CD, PAA-EG₁₃-N₃, and HC≡C-Ad were put in contact with an ethanol solution of 1 M Fc(CH₂OH)₂ according to Rydzek et al.²⁷ The signal of Fc(CH₂OH)₂ loaded into the film was measured by cyclic voltammetry (CV) and UV spectroscopy. CV was applied films between 0 mV and +800 mV (vs Ag/AgCl, scan rate of 10 mV/s) in the presence of 0.5 M NaNO₃ at pH 3.5. For each sample, the current intensity was recorded at 330 mV (vs Ag/AgCl) because ferrocene groups can be detected at this potential.³⁵ UV-vis spectroscopy measurements were performed with a Shimadzu 2101-PC spectrophotometer used in the single beam mode. The reference spectrum was that of the bare ITO-QCM crystal. UV-vis spectra were acquired between 190 and 600 nm with a resolution of 1 nm. The current intensity measured at 330 mV and the UV absorbance measured at 196 nm^{36,37} corresponding to a π-π* transition of the Fc(CH₂OH)₂ molecule, allow detection of ferrocene groups within the film.

Preparation of Powders for XRD Analysis. Powders from (PAA-EG₁₃-N₃, β-CD, HC≡C-Fc, Cu(I)) and (PAA-EG₁₃-N₃, α-CD, HC≡C-Fc, Cu(I)) mixtures were prepared as follows. The 1 mg/mL portions of PAA-EG₁₃-N₃, 4.10⁻³ M of HC≡C-Fc, and 4.10⁻³ M of β-CD (or 4.10⁻² M of α-CD) were mixed in 50/50 v/v water/ethanol adjusted at pH 3.5 ± 0.05. After 30 min, 10⁻² M of tetrakis(acetonitrile)copper(I) tetrafluoroborate salt was added to the solution. The resulting mixture was then evaporated at room temperature for 2 days. The samples were then suspended in ethanol for observation.

RESULTS AND DISCUSSION

Electrotriggered Self-Construction of PRX-Based Films. The buildup of a PRX-based film was first studied using the (PAA-EG₁₃-N₃, β-CD, HC≡C-Fc) system. The mixture, prepared in 50% (v/v) water-ethanol with 0.6 M CuSO₄, was composed of PAA-EG₁₃-N₃ (10⁻⁴ M in azide moieties) and an excess of β-CD (10⁻³ M) and of alkyne moieties of HC≡C-Fc (10⁻³ M). In the bulk, β-CD molecules spontaneously thread onto EG₁₃ arms worn by PAA-EG₁₃-N₃ to form pseudo-PRX structures. The interaction between β-CD and EG₁₃ chains is known to be very poor because of the EG chain short length.^{38–40} Nevertheless, favorable interactions were demonstrated allowing inclusion complexation between β-CD and PEG segments.⁴¹

To lock the pseudo-PRX architecture into PRX, alkyne-bearing stoppers (HC≡C-Fc) were used to cap azide functionalized EG₁₃ chains by Cu(I) catalyzed click chemistry. As in our previous studies,^{23,24,27} the morphogen Cu(I) was generated electrochemically by CV at the working electrode. Self-assembly of PRX structures was thus confined in the vicinity of the substrate, i.e., the working electrode. This process led to the buildup of PAA-based films where PRX self-assemblies

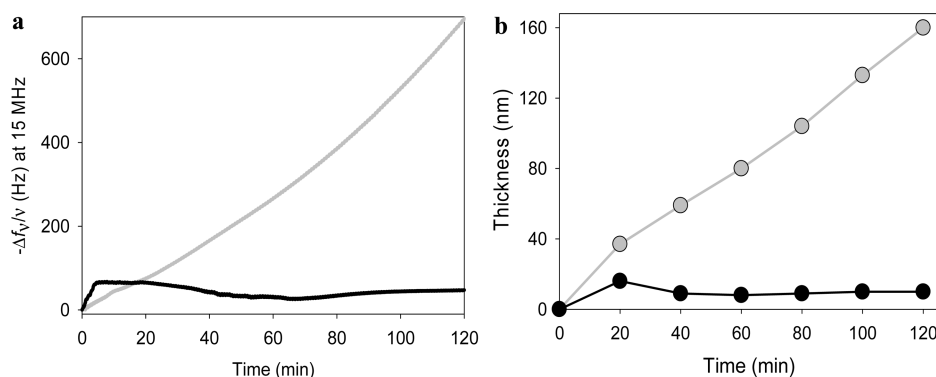


Figure 1. (a) Evolution of the normalized frequency shift, measured at 15 MHz ($\nu = 3$) by EC-QCM-D, as a function of time during the application of CV (-350 mV and $+750$ mV vs Ag/AgCl, scan rate of 50 mV/s) in the presence of (gray line) (PAA-EG₁₃-N₃, β -CD, HC≡C-Fc) mixture and (black line) (PAA-EG₁₃-N₃, β -CD, Fc(CH₂OH)₂) mixture. (b) The corresponding calculated thicknesses, using the Voight-Voinova model³³ from EC-QCM-D data. The mixture solution was prepared at 0.25 g/L of polymer (i.e., 10^{-4} M in azide moieties), 10^{-3} M of β -CD and 10^{-3} M in HC≡C-Fc (or Fc(CH₂OH)₂) in the presence of 0.6 mM CuSO₄ in 50% (v/v) water-ethanol at pH 3.5.

play the role of physical cross-link points due to lateral interactions between CDs inclusion complexes⁴² (Scheme 1). EC-QCM-D was used to follow the film buildup, which correlates with a decrease in resonance frequency and an increase of the measured dissipation. An anchoring PEI layer was adsorbed on the working electrode to allow the initial deposition of the film. At the injection of the mixture solution on a PEI precoated QCM crystal, an electrostatic adsorption of PAA-EG₁₃-N₃ is observed on the substrate. After the stabilization of the QCM signal, the application of a CV between -350 mV and $+750$ mV (vs Ag/AgCl, scan rate of 50 mV/s) induces a continuous increase of the opposite of the normalized frequency shift (Figure 1a) and of the corresponding dissipation factor (Figure S-2 of the SI). This evolution corresponds to a continuous increase of (PAA-EG₁₃-N₃, β -CD, HC≡C-Fc) film thickness that reached 160 nm after 120 min of self-construction (Figure 1b). The formation of triazole groups during this electrochemically induced click reaction between alkyne- and azide-functionalized molecules has been previously demonstrated.²³ To gain more insight into the assembling mode of the self-constructed films, control experiments were done using the same electrochemical conditions. By removing one of the components of the mixture, no film self-construction occurred for (PAA-EG₁₃-N₃, β -CD) (Figure S-3 of the SI) and (PAA-EG₁₃-N₃, HC≡C-Fc).²⁷ It is thus necessary to have the simultaneous presence of β -CD and HC≡C-Fc to obtain a film buildup. By replacing the alkyne-functionalized stopper, HC≡C-Fc, by a nonfunctionalized one, namely 1,1'-ferrocenedimethanol (Fc(CH₂OH)₂), no mass deposition was recorded. The covalent reaction between HC≡C-Fc and azide-functionalized EG₁₃ arms is required to lock the PRX structure and stabilize the film.

After 120 min of self-construction, the thickness and the topography of a PRX-based film were investigated using atomic force microscopy (AFM) in contact mode in dry state and in liquid state at pH 3.5 (Figure 2). The film thickness was determined by imaging the film after scratching. The corresponding cross-section profile indicates that the substrate is totally covered in dry and in liquid states (Figure 2a,b). The film thickness is about 60 nm in the dry state and 100 nm in water at pH 3.5. This swelling is attributed to the hydration of PAA contained in the film. The film appears homogeneous with a roughness of 35 nm in the dry state and 29 nm in liquid state (Figure 2c,d). The high surface roughness of the film induces an overestimation of the hydrodynamic thickness measured by EC-QCM-D compared to the thickness of the core determined

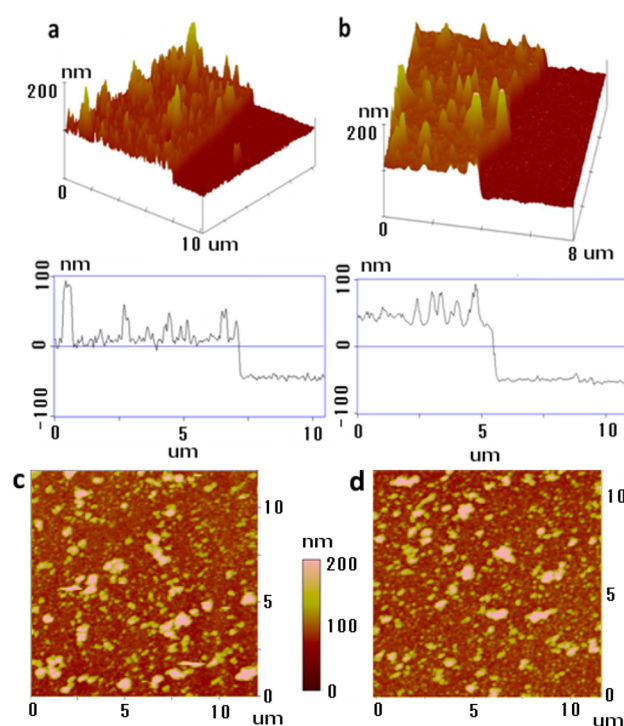


Figure 2. Typical AFM height images of (PAA-EG₁₃-N₃, β -CD, HC≡C-Fc) films obtained in contact mode: 3D images and corresponding profiles of the scratched film (a) in dry state and (b) in liquid state at pH 3.5. Topography images of the film (c) in dry state and (d) in liquid state at pH 3.5.

by AFM.⁴³ A large number of aggregates up to 405 nm in height are observed on the topography of dry (PAA-EG₁₃-N₃, β -CD, HC≡C-Fc) films. To check if these aggregates are characteristic of PRX, (PAA-EG₁₃-N₃, HC≡C-EG₃-C≡CH) films were self-constructed in the same conditions. No aggregates were observed for (PAA-EG₁₃-N₃, HC≡C-EG₃-C≡CH) film (Figure S-4a of the SI). The film roughness was of 5 nm compared to 35 nm in the case of (PAA-EG₁₃-N₃, β -CD, HC≡C-Fc) films. When β -CD was added in the building mixture, the resulting (PAA-EG₁₃-N₃, β -CD, HC≡C-EG₃-C≡CH) films exhibited a roughness of 62 nm with the presence of large aggregates (Figure S-4b of the SI). It seems that the high roughness of the film, due to aggregates, is related to the presence

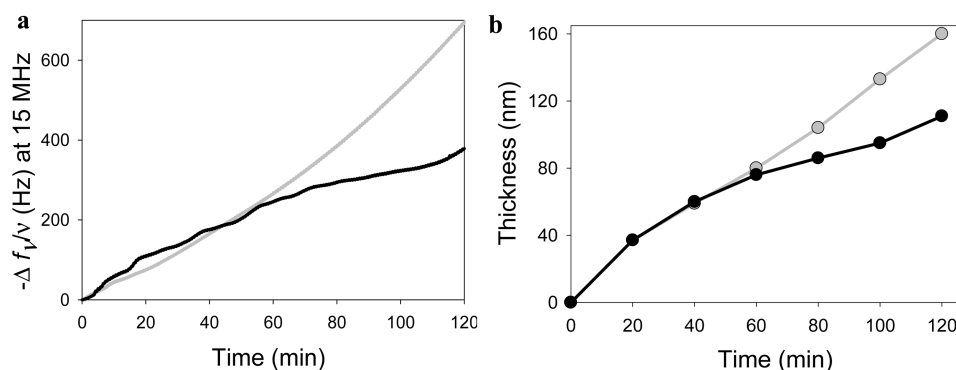


Figure 3. (a) Evolution of the normalized frequency shift, measured at 15 MHz ($\nu = 3$) by EC-QCM-D, as a function of time during the application of CV (-350 mV and $+750$ mV vs Ag/AgCl, scan rate of 50 mV/s) in the presence of (PAA-EG₁₃-N₃, HC \equiv C-Fc) mixed with (gray line) 10^{-3} M of β -CD and (black line) 10^{-2} M of α -CD. (b) The corresponding calculated thicknesses, using the Voight-Voinova model³³ from EC-QCM-D data. The mixture solution was prepared at 0.25 g/L of polymer and 10^{-3} M of HC \equiv C-Fc in the presence of 0.6 mM CuSO₄ in 50% (v/v) water-ethanol at pH 3.5 .

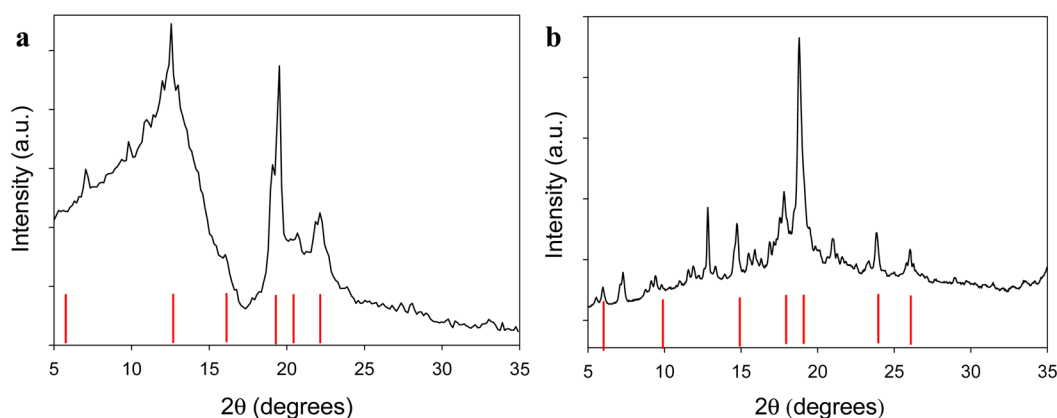


Figure 4. XRD patterns of the powders obtained for (a) (PAA-EG₁₃-N₃, α -CD, HC \equiv C-Fc) and (b) PAA-EG₁₃-N₃, β -CD, HC \equiv C-Fc mixtures brought in contact with Cu(I) salt in solution. In both diffractograms, the red peaks correspond to the main diffraction peaks described in literature for PRX-based materials.^{50,51,53,54,57–59}

of β -CD molecules during their self-construction. This result may indicate the formation of water insoluble PRX-based crystallites domains by lateral interactions between β -CDs. This behavior has been previously demonstrated for CD-based PRX.^{13,42,44,45} Besides, β -CD are known to form stable pseudo-PRX with poly(propylene oxide) chains.^{46–48} Thus even if the interaction between β -CD and EG grafted arms is not stable in the bulk, locked PRX are obtained by coupling the stopper moieties at the end of EG. This allows the self-construction of the (PAA-EG₁₃-N₃, β -CD, HC \equiv C-Fc) film via lateral interactions between CD and therefore formation of crystallites domains. The nature of the CD used to form PRX films was changed using α -CD. This class of CDs is known to form spontaneously stable pseudo-PRX with PEG chains^{49–51} inducing the formation of supramolecular structures through lateral interactions between CDs.^{52,53} It must be noted that the same behavior has been reported when using β -CD and pluronic acid.^{42,54,55} Compared to (PAA-EG₁₃-N₃, β -CD, HC \equiv C-Fc), a slower buildup was obtained using (PAA-EG₁₃-N₃, α -CD, HC \equiv C-Fc) mixture in the same conditions of self-construction (Figures 3 and S-5 of the SI). A smaller amount of β -CD than α -CD is required to obtain inclusion complexes that can interact laterally to form PRX assemblies. The α -CD containing film growth rate is probably limited due to the high amount of α -CD required to obtain aggregates domains responsible of the film cohesion. Indeed, α -CD/PEG based PRX are composed of one CD

for two EG units whereas β -CD/PEG based PRX are composed of one CD for three EG units.⁵⁶

The calculated film thickness was about 110 nm after 2 h of CV in comparison to 160 nm for (PAA-EG₁₃-N₃, β -CD, HC \equiv C-Fc). Large aggregates up to 570 nm height were observed by AFM on (PAA-EG₁₃-N₃, α -CD, HC \equiv C-Fc) films similar to those obtained for (PAA-EG₁₃-N₃, β -CD, HC \equiv C-Fc) films. When a dry (PAA-EG₁₃-N₃, α -CD, HC \equiv C-Fc) film is put in contact with water, the thickness increased from 91 to 111 nm and the roughness from 24 to 74 nm (Figures S-6 and S-7 of the SI).

XRD Characterization of the Polyrotaxane Aggregates in PRX-Based Film. Supramolecular CD crystalline structures can be detected by X-ray diffraction (XRD) for PRX materials based on α -CD^{11,50,51,53} and β -CD.^{54,55} Attempts of X-ray diffraction measurements on ~ 400 nm thick PRX-based films did not lead to any diffraction peaks probably due to the small amount of materials. PRX powder material was prepared using (PAA-EG₁₃-N₃, α -CD, HC \equiv C-Fc) and (PAA-EG₁₃-N₃, β -CD, HC \equiv C-Fc) mixture solutions in the presence of a Cu(I) salt (Cu(CH₃CN)₄.BF₄, tetrakis(acetonitrile)copper(I) tetrafluoroborate salt). The covalent capping of PRX by click chemistry was left to occur during 24 h. The obtained mixtures formed a gel that was dried and finely grinded to get a white powder for XRD analysis. (PAA-EG₁₃-N₃, α -CD, HC \equiv C-Fc, Cu(I)) powder displays diffraction peaks at 6° , 13° , 16° , 19° – 20° , and 22.5° for 2θ (Figure 4a). These diffraction peaks are in

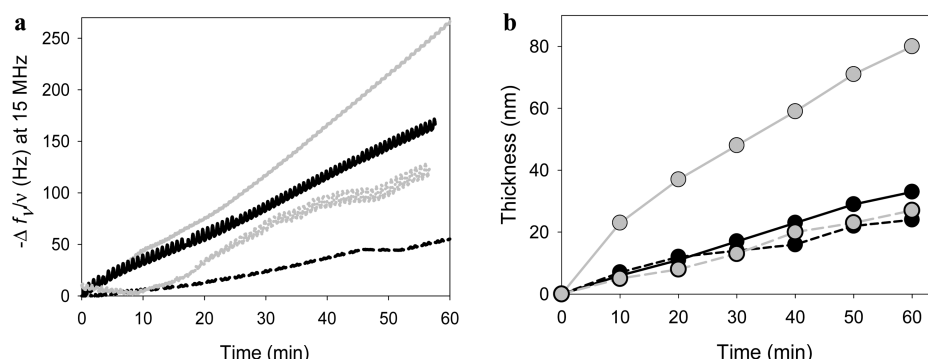


Figure 5. (a) Evolution of the normalized frequency shift, measured at 15 MHz ($\nu = 3$) by EC-QCM-D, as a function of time during the application of CV (−350 mV and +750 mV vs Ag/AgCl, scan rate of 50 mV/s) in the presence of (PAA-EG₁₃-N₃, β -CD) mixed with different alkyne bearing stoppers: (gray line) HC≡C–Fc, (black line) HC≡C–CH₂–(O–CH₂–CH₂)₂OH, (gray dashed line) HC≡C–Ad and (black dashed line) HC≡C–CH₂–OH. (b) The corresponding calculated thicknesses, using the Voight–Voinova model³³ from EC-QCM-D data. The mixture solution was prepared at 0.25 g/L of polymer (i.e., 10^{−5} M in azide moieties), 10^{−3} M of β -CD and 10^{−3} M in alkyne bearing in the presence of 0.6 mM CuSO₄ in 50% ethanol in water (v/v) at pH 3.5.

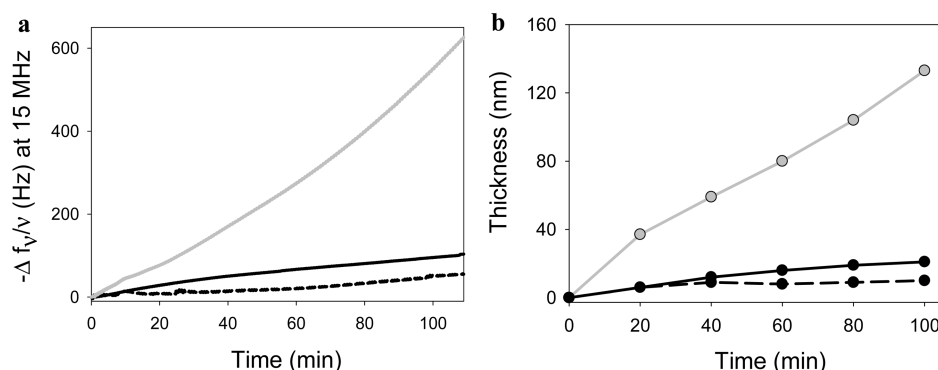


Figure 6. (a) Evolution of the normalized frequency shift, measured at 15 MHz ($\nu = 3$) by EC-QCM-D, as a function of time during the application of CV (−350 mV and +750 mV vs Ag/AgCl, scan rate of 50 mV/s) in the presence of (gray line) (PAA-EG₁₃-N₃, β -CD, HC≡C–Fc), (black line) (PAA-EG₁₃-N₃, β -CD/Fc(CH₂OH)₂, HC≡C–Fc) and (dashed line) (PAA-EG₁₃-N₃, β -CD/Ad-COOH, HC≡C–Fc) mixtures. (b) Corresponding calculated thicknesses, using the Voight–Voinova model³³ from EC-QCM-D data. The solution contains 0.25 g/L of polymer, 10^{−3} M of β -CD, 10^{−3} M HC≡C–Fc and 10^{−3} M Fc(CH₂OH)₂ or Ad-COOH in the presence of 0.6 mM CuSO₄ in 50% ethanol in water (v/v) at pH 3.5.

good agreement with those observed in the literature for cases of complexation between PEG arms and α -CD.^{50,51,53} In particular, one of the main diffraction peaks, located around 19–20°, is characteristic of the hexagonal lattice of α -CD in channel-type crystal structures.^{57–59} The main diffraction peaks of (PAA-EG₁₃-N₃, β -CD, HC≡C–Fc, Cu(I)) powder are localized for 2θ values at 6°, 10°, 15°, 18–19°, 24°, and 26° (Figure 4b). Again, these values correspond to characteristic peaks of β -CD-based PRX assemblies.^{54–56} This result is very interesting since PRX from β -CD and PEGs are rare due to weak and reversible interactions.⁵⁰ The locked assembly induced by the capping step of PEG arms with HC≡C–Fc allows stabilization of PRX-based on β -CD threaded onto PEG chains. Both XRD patterns of powders containing α -CD and β -CD were consistent with literature.

PRX-Based Films Using Different Stopper Groups.

Different alkyne bearing stoppers were used to self-construct PRX films. Ethynyl adamantane (HC≡C–Ad), propargyl-diethylene glycol (HC≡C–CH₂–(O–CH₂–CH₂)₂OH), and propargyl alcohol (HC≡C–CH₂–OH) were used instead of HC≡C–Fc. The growth speed of PRX films is decreasing with the size of the stopper, from HC≡C–Fc to HC≡C–CH₂CH₂OH and HC≡C–OH (Figures 5a,b and S-8 in SI). This effect is expected since the size of the stopper directly

influences the stability of the PRX assemblies by locking sterically the molecular geometry. To confirm that β -CD in the PRX-based film groups are threaded along the PEG arms, we have done experiments to test if β -CD cavities are free and available for another guest. In a previous study, (PAA-EG₁₃-N₃, β -CD-C≡CH, HC≡C–Ad) self-constructed films were studied. The cohesion of those films is based on host–guest interactions between Ad and β -CD that are covalently linked to PAA. With an excess of β -CD-C≡CH with respect to HC≡C–Ad in the building mixture, the obtained film can be loaded with Fc(CH₂OH)₂ molecules.²⁷

A PRX-based film using a (PAA-EG₁₃-N₃, β -CD, HC≡C–Ad) mixture was self-constructed and brought into contact with a Fc(CH₂OH)₂ solution. The absorbance of the PRX film at 196 nm, related to π – π^* transition of Fc groups,^{36,37} and the current intensity at 330 mV, related to the oxidation of Fc, were measured before and after contact with the Fc(CH₂OH)₂ solution showing almost no loading (Figure S-9 of the SI). Indeed, the absorbance is equal to 0.08 au and the current intensity equal to 3.5 μ A compared to (PAA-EG₁₃-N₃, β -CD-C≡CH, HC≡C–Ad) host–guest films loaded with Fc(CH₂OH)₂ with an absorbance of 1.36 au and a current intensity of 10 μ A.²⁷ These results confirm that β -CD groups are not empty in the self-constructed PRX films. Since the only

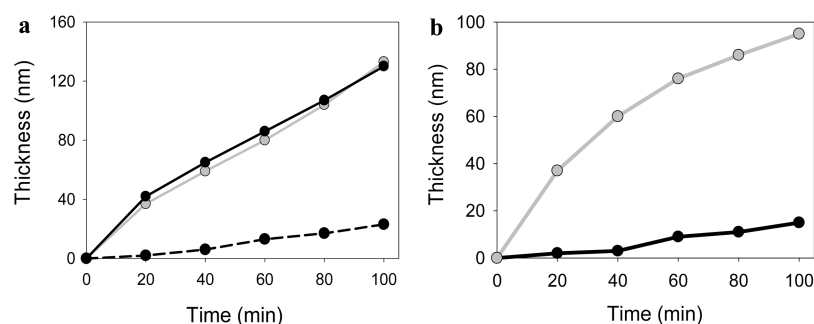


Figure 7. Evolution of the calculated film thicknesses, using the Voight–Voinova model³³ from EC-QCM-D data, as a function of time during the application of CV (−350 mV and +750 mV vs Ag/AgCl, scan rate of 50 mV/s) in the presence of (a) (PAA-EG₁₃-N₃, β-CD, HC≡C-Fc) mixture prepared with (gray line) 10^{−3} M; (black line) 10^{−4} M or (dashed line) 10^{−5} M of β-CD or (b) (PAA-EG₁₃-N₃, α-CD, HC≡C-Fc) mixture prepared with (gray line) 10^{−2} M or (black line) 10^{−3} M of α-CD. The solution contains 0.25 g/L of polymer and 10^{−3} M HC≡C-Fc in the presence of 0.6 mM CuSO₄ in 50% ethanol in water (v/v) at pH 3.5.

compounds present in solution that can interact with the β-CD cavity are PEG arms, these results are in accordance with the PRX formation.

Tunable Self-Construction of PRX Films through Guest Competition. Since the self-construction mechanism of (PAA-EG₁₃-N₃, β-CD, HC≡C-Fc) films involves the threading of β-CD by PEG arms, it could be possible to tune the self-construction by blocking the β-CD cavity with hydrophobic molecules. Indeed if a nonclickable guest is added to the (PAA-EG₁₃-N₃, β-CD, HC≡C-Fc) mixture, the efficiency of the threading of CD onto EG arms of the polymer chains should be affected. Fc(CH₂OH)₂ and carboxyadamantane (Ad-COOH) have been chosen as blocking molecules. The blocking molecules were put in solution with β-CD in an equimolar amount and then added to a (PAA-EG₁₃-N₃, HC≡C-Fc) mixture. We thus monitored the self-construction of (PAA-EG₁₃-N₃, β-CD/Fc(CH₂OH)₂, HC≡C-Fc) and (PAA-EG₁₃-N₃, β-CD/Ad-COOH, HC≡C-Fc) (Figures 6a and S-10 of the SI). The competitor guests were added in the same molar concentration as HC≡C-Fc. The presence of the competitor groups induced a strong inhibition of the self-construction of (PAA-EG₁₃-N₃, β-CD, HC≡C-Fc) PRX films. Without guest competitor, the normalized frequency shift of the PRX film was about 600 Hz after 100 min of CV application. In the presence of Fc(CH₂OH)₂ and Ad-COOH, the frequency shift reached 100 and 50 Hz, respectively. The film thickness is decreased from 133 to 21 nm in the presence of Fc(CH₂OH)₂ and 10 nm in the presence of Ad-COOH (Figure 6b). The self-construction inhibition of PRX film is higher with Ad-COOH compared to Fc(CH₂OH)₂. It can be explained by a weaker availability of empty β-CD since it is known that Ad groups interact more strongly with β-CD than Fc groups.⁶⁰

Influence of CD Concentration on Self-Construction of PRX Film. The influence of CD concentration in the (PAA-EG₁₃-N₃, α-CD or β-CD, HC≡C-Fc) building solution was studied. According to the conditions previously described, the mixtures were prepared with 10^{−4} M in azide moieties worn by PAA-EG₁₃-N₃ and 10^{−2} M α-CD or 10^{−3} M of β-CD. When the CD concentration was decreased 10-fold (10^{−4} M of β-CD), no changes in (PAA-EG₁₃-N₃, β-CD, HC≡C-Fc) film growth was observed. After a further 10-fold decrease (10^{−5} M of β-CD), a limited self-construction was observed (Figure 7a and S-11a of the SI). In the case of (PAA-EG₁₃-N₃, α-CD, HC≡C-Fc) film, the self-construction was already limited with 10^{−3} M α-CD (Figures 7b and S-11b of the SI). High concentrations

of CDs are thus required to ensure the cohesion of the self-constructed film. This is expected since the PRX assemblies constitute the physical cross-link points of the film. The difference between the critical β-CD and α-CD concentrations allowing the PRX-based film buildup can be explained by the fact that the solubility of α-CD in water is ten times higher than the solubility of β-CD (we expect the same trend in 50% ethanol in water (v/v)). The nucleation and growth of the crystalline structure of PRX assemblies require thus concentrations of α-CD and β-CD close to the saturation.

Electrochemical and Chemical Stability of PRX-Based Films. The effect of two external stimuli on PRX self-constructed films has been investigated: the application of a positive electric potential and the use of urea. Films based on (PAA-EG₁₃-N₃, β-CD, HC≡C-Fc) underwent the application of +900 mV electric potential when in contact with a 0.5 M NaNO₃ solution. The applied potential is known to switch the redox state of ferrocene group into ferrocenium, a group that has a weaker interaction with β-CD⁶¹ because of its positive charge. The application of +900 mV induces a small and reversible swelling of the film without losing material (Figure S-12a of the SI). This result is an additional proof that the cohesion of the film is not due to host–guest interaction between HC≡C-Fc and β-CD. Indeed in this case, the films would be dissolved, as was obtained in our previous study.²⁷ Moreover, when 8 M urea solution was put into contact with the (PAA-EG₁₃-N₃, β-CD, HC≡C-Fc) film to break hydrogen bonds between PRX chains, no mass decrease was measured by EC-QCM-D (Figure S-12b of the SI). It seems thus that concentrated urea is not able to simultaneously break the hydrogen bonds established between PRXs in the film. This result is expected when CDs are forming nonsoluble crystallites within the film. Indeed, the crystallites are not accessible by urea in aqueous solution.^{13,42,44,45}

CONCLUSIONS

Nanometric size films based on polyelectrolytes and PRX assemblies can be efficiently built through a one-pot morphogen-driven process. The simultaneous presence of PAA-EG₁₃-N₃, α- or β-CD, HC≡C-Fc and CuSO₄ salt, in defined concentrations, are required to get a film under an adequate cyclic voltammetry process. A molecular threading of CDs along the ethylene oxide arms followed by a capping step with a bulky group at the end of the PEG chains occurs in one-pot conditions. This process leads to PRX chains which can self-assemble through lateral interactions between the CDs and form a film with crystallites

domains. The diffusion of the Cu(I) morphogen, generated from the electrode by reduction of Cu(II), ensures the film buildup exclusively at the interface. Thus, a linear evolution of the film thickness is observed when the application time of the CV process increases. AFM images of the resulting films display a full covering of the substrate at dry and liquid states and reveal the presence of aggregates assigned to the PRX assemblies. These supramolecular architectures, responsible for the film cohesion, were identified by XRD measurements where the diffraction peaks observed are in agreement with those reported in the literature for other PRX-based materials. The film buildup can be modulated by using a guest competitor or different stopper compounds and by varying the concentration of CDs. The resulting films appear highly stable because nonsensitive to 8 M urea and electrochemical oxidation of ferrocene.

■ ASSOCIATED CONTENT

■ Supporting Information

Modeling data, additional references, and additional figures referenced in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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