Robust, fluorescent, and nanoscale freestanding conjugated films†

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The fabrication of *purely polymeric* free-standing structures of nanoscale thickness is technically challenging because of the poor mechanical stability of conventional polymers. Conjugated polymers (CP) composed of rod-like chains with much stronger mechanical properties are exploited here for layer-by-layer assembly. We successfully fabricated ultrathin freestanding layer-by-layer conjugated films (under 20 nm thick) which are flexible, easily fabricated, and demonstrated excellent mechanical properties combined with high fluorescence. This unique combination of properties can be considered for new applications such as flexible, lightweight displays and large luminescent panels.

Ultrathin polymeric films with well-defined nanoscale structures have great potential to be integrated in microdevices with fast response times and high sensitivity as a new generation of sensors and microactuators.[1] The ultrathin planar freestanding layer-by-layer (LbL) films, with versatile multilayer architectures composed of alternating layers of magnetite nanoparticles, clay palletes, and polyelectrolytes, have showed extraordinary mechanical properties.[2] With novel spin-assisted LbL (SA-LbL) assembly, a series of robust free-standing nanoscale film from polyelectrolytes reinforced by nanofillers (gold nanoparticles, carbon nanotubes, or silver nanorods) have recently been fabricated and studied.[3] These exceptionally stable (albeit flexible) films demonstrated interesting micromechanical and optical properties and were suggested as promising candidates for prospective sensing elements for acoustic, thermal, magnetic, and pressure sensors.[4]

The freestanding LbL films fabricated to date are truly self-supporting structures (preserving their shape and dimensions under their own weight and under significant mechanical loads) which survive under normal laboratory conditions (humid air, capillary forces, vibrations, temperature fluctuations) and possess a truly long shelf-life (years). However, to achieve this mechanical robustness, they are either reinforced with high-strength nanoscale fillers (*e.g.*, metal nanoparticles or carbon nanotubes) or are made relatively thick (microns), which limits their applications as flexible nanoscale films. The successful fabrication of *purely polymeric robust* free-standing nanoscale structures is technically challenging. This is due to the poor mechanical stability of non-reinforced chains within ultrathin films with thickness comparable to their molecule dimensions.[5] Thus, a minimum thickness for sustainable freely suspended LbL polymeric films achieved today is around 50 nm.[3]

On the other hand, conjugated polymers have several unique physical properties such as strong inter-chain interaction, light weight, semiconducting properties, high strength, strong fluorescence and low-voltage actuation, which make them attractive for various electro-optical applications.[1,6] Controlling the solid state organization of such conjugated polymers within nanoscale films is critical for tuning their macroscopic optical and electrical properties and, therefore, should be intensively studied for the applications of light emitting diodes, photovoltaic cell, electrochromic switchers and optical sensors. In fact, LbL films from various conjugated polymers have already been fabricated and their interesting electrochemical, photoluminescence and non-linear optical properties have been explored.[7] The most commonly-used water soluble conjugated polymer is poly(2,5-methoxypropyloxy sulfonate phenylene vinylene) (MPS-PPV).[8] The stable conjugated films offer the possibility for impact in the areas of photovoltaic cells,[9] light emitting diodes (LED),[10] thin-film transistors[11] and bio-sensors[12] due to their intriguing opto-electronic properties.[13] However, all these films studied to date have been assembled on the supporting solid substrates and the questions of their mechanical integrity and stability as well as fluorescent properties in the free standing state have not even been addressed.

In this communication, we report on the fabrication of freely suspended polymeric LbL films *without any nanofillers with a truly nanoscale thickness* (below 20 nm) which demonstrate very robust mechanical properties combined with fluorescence. For this fabrication, we selected a water soluble conjugated polymer MPS-PPV, which is essentially a rod-like chain with much stronger mechanical properties than usual flexible-chain polyelectrolyte exploited for previous LbL assembly of free-standing films. Moreover, the conjugated nature of the MPS-PPV chains brings an intense fluorescent response, which is extremely stable even under large mechanical deformations. The morphology as well as mechanical and optical properties of these ultra-thin LbL films are investigated and discussed.

The polymer films with different thicknesses were fabricated using spin-assisted LbL (SA-LbL) method and characterization techniques as described in detail in previous publications.[3,14] Briefly, a sacrificial cellulose acetate (CA) layer was spin coated on the freshly cleaned (100) silicon substrate. A droplet (150 μL) of 0.2% (w/w) cationic polyelectrolyte (poly(allylamine hydrochloride), PAH) solution was spun coated on the sacrificial layer (3000 rpm) and followed by thorough rinsing with nanopure water. After that, aqueous anionic MPS-PPV solution was spun coated and rinsed in a similar manner. This procedure was

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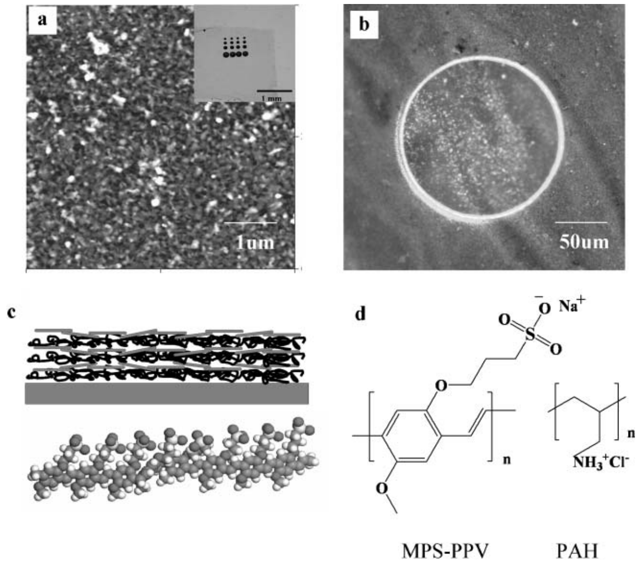

Fig. 1 (a) AFM topographical image of (MPS-PPV/PAH)$_5$ film (*z* range is 80 nm) and an optical image of a whole free standing film on an array of holes (inset). (b) Fluorescence image of freely suspended film on a 150 um diameter hole. (c) The cartoon of multilayered structure and a molecular model of MPS-PPV chain; (d) Chemical structure of polymers.

repeated until the required number of polymer bilayers, *n*, was achieved. Acetone solution was used to dissolve the sacrificial CA layer in order to release the LbL films. The LbL films were transferred to Nanopure water where they could then be picked up with different substrates. The morphology of the films and their micromechanical and optical properties have been characterized in accordance with published procedures:[3,14,15] atomic force microscopy, fluorescent optical microscopy, fluorescent spectroscopy, the bulging test and buckling instability, as described in the ESI.†

SA-LbL films with different thicknesses have been prepared on a sacrificial support in accordance with the known procedure.[14] These films could be transferred in large pieces to cover an array of holes with different diameters and showed relatively uniform optical appearance (Fig. 1a, b). The surface of SA-LbL films was relatively uniform, with a developed grainy morphology and a microroughness (within a 1 μm^2 surface area) below 5 nm which is a typical value for LbL films from conjugated polymers (Fig. 1a). The thickness of LbL films increased linearly with the number of bilayers with an increment of about 3.5 nm per bilayer, which is a common value for PPV-based LbL films.[9] This thickness corresponds to the transversal dimension of two rod-like chains packed side-to-side (2.6 nm) combined with the thickness of PAH [poly(allylamine hydrochloride)] layer (about 1 nm) (Fig. 1c). The average thickness of (MPS-PPV/PAH)$_5$, the thinnest film discussed here in great detail, was 18 $\pm$ 2 nm.

The major absorption maxima in UV-vis spectra at 295 and 425 nm correspond to the longitudinal π–π* transitions of the MPS-PPV backbones (Fig. 2a), as reported in the literature.[16] The broad absorption band at 355 nm corresponds to the pendant groups (sulfur trioxide)[17] and transversal transitions of delocalized states of rigid backbones.[16] The steady linear increase in absorbance intensities at both 295 and 425 nm with a number of deposited layers (n = 5–30) indicates a progressive LbL assembly growth (Fig. 2).[18]

Fig. 2b shows the emission spectra of (MPS-PPV/PAH)$_5$ LbL film as well as the spin-cast MPS-PPV film and dilute solution normalized to the same peak intensity. The emission profiles are very similar for all states, with an emission maximum at 530 nm (Fig. 2b). The presence of a single poorly resolved broad (half-width about 120 nm) peak can be also associated with the fact that MPS-PPV cast film shows predominantly single-chain emission in solid state with significant overlap of the individual vibronic bands.[19] This is usually observed for LbL and LB films based on PPV-derivatives as well as corresponding spin-cast films and blends.[20]

The emission peak of MPS-PPV is blue-shifted significantly as compared to bulk PPV films (at 583 nm for as spin-cast and at 610–630 nm for annealed films).[16,21] A significant blue shift of the emission band for PPV-based molecules embedded into multilayered LbL films is a common phenomenon.[22,23] This behavior is caused by coupling of the longitudinal packing of rod-like molecules combined with their loose lateral packing both caused by the confinement of rod-like MPS-PPV molecules between PAH

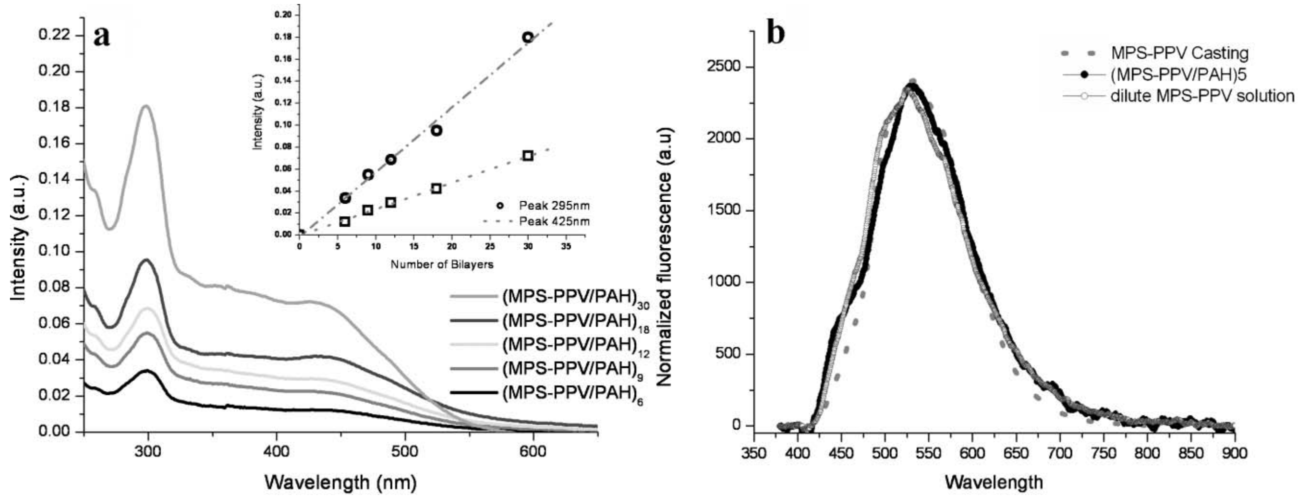

Fig. 2 (a) UV/Vis spectra for LbL films with different numbers of bilayers, inset shows absorbance at 425 nm *vs.* the number of deposited bilayers. (b) Fluorescent spectra (normalized) of the spin-cast MPS-PPV film, dilute MPS-PPV solution, and (MPS-PPV/PAH)$_5$ LbL film.

layers (Fig. 1c). In such a structure, the presence of PAH interlayers significantly disturbs transversal interchain interactions typical for crystalline packing which, in turn, should result in blue-shift of the corresponding emission band due to decoupling side-by-side interactions, in fact observed here. On the other hand, this significant blue shift can be an indication of the formation of strong H-aggregates within the MPS-PPV layer with predominant parallel side-by-side packing of rod-like segments.[24]

The emission spectra collected in resting and deformed states have very similar shapes with an insignificant blue shift of the peak position close to the experimental uncertainty (from 528 to 525 nm) (Fig. 3a). Fitting of the emission band with five Lorentzian peaks (as suggested before for PAH-PPV composites[25]) with different contributing peaks, attributed to longitudinal intrachain transitions (shorter wavelength), transversal interchain transitions, and side-by-side interactions, was conducted to test the consistency of photoemission.[21,26,27] Under mechanical deformation, the fluorescent emission is quite stable and there is no simple, clear correlation. As we observed, the characteristics of all peaks but last one remain virtually unchanged (within experimental accuracy) indicating stable state of PPV backbones under these deformation conditions (strain reaching 0.8% and film deflection reaching 7 μm). Apparently, this result indicates the highly stable local ordering and conformation of the PPV chain under level of tensile elastic deformation tested here which results in very stable photoemission signature even under significant mechanical deformations. The highly stable photoemission can be originated from strong intermolecular interactions between the MPS-PPV and PAH in the multilayer structures. By using PAH layer as a spacer layer, we were able to construct assemblies which lead to a reduction of the interpenetration of each photoemission PPV layer thus reducing self-quenching effect and preventing easy changes in physical aggregation under stresses responsible for changes in interchain energy transfer. It is worth noting that reduced intermolecular quenching and stable fluorescence was reported for the fluorescent labelled polyelectrolyte LbL multilayers.[28]

The micromechanical properties of these LbL films under tensile and compression stresses were studied using two independent experiments. For tensile properties, a bulging test was used and compressive properties were tested with a buckling instability test (see the ESI†). Fig. 4(a) shows the deflection of the freely-suspended (MPS-PPV/PAH)$_5$ film under an increasing hydrostatic pressure applied from one side. The deflection of the LbL film with pressure applied demonstrated a nonlinear response. Experimental data in the small deformation region (below 7 μm) are well fit with the theoretical prediction for the elastic deformation of a circular plate clamped to a stiff edge.[14] The 18 nm thick (MPS-PPV/PAH)$_5$ films freely suspended across 150 μm opening showed extremely robust but flexible behavior: multiple elastic deformations were

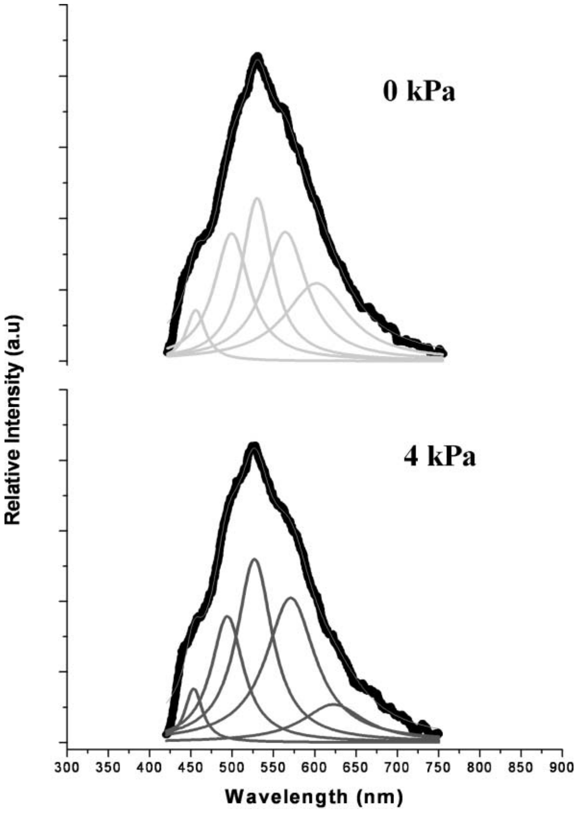

Fig. 3 Fluorescence spectra of (MPS-PPV/PAH)$_5$ LbL film in the rest state and under elastic deformation (0.8% strain) and corresponding fit with five bands.

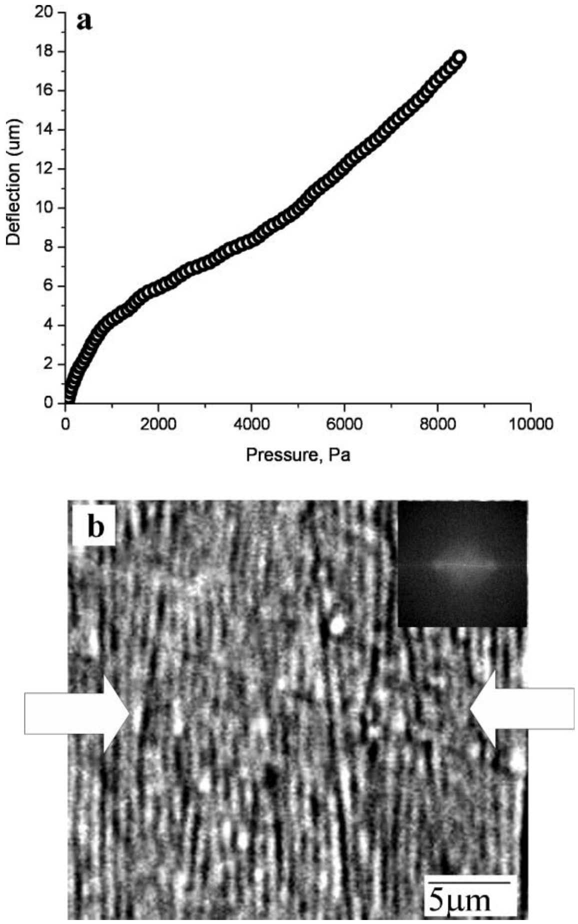

Fig. 4 (a) Pressure-induced deflection of the freely suspended (MPS-PPV/PAH)$_5$ LbL film in both elastic deformation (<2500 Pa) and plastic deformation regions. (b) Optical image of the buckling pattern of the compressed LbL film (compression direction is shown by arrows), Inset: the Fourier transform image of the buckling pattern.

observed for pressures reaching 4 kPa which corresponds to the tensile strain 0.8% at stress reaching 35 MPa, a high value for polymers. A full pressure *versus* deflection curve can be converted into a stress *versus* strain curve (not shown), from which the elastic and plastic region can be deduced and the toughness of the film can be estimated.[29] The necking region from the stress–strain curve is apparent at a pressure of 2.5 kPa (close to the deflection value of 7 μm) and indicates the occurring of plastic deformation. The toughness of the $(MPS\text{-}PPV/PAH)_5$ film estimated from film fracture was determined to be 118 kJ m^{-3} which is very high value for nanoscale polymeric films and indicates their exceptional long-term durability. The film deflection can reach up to 20 μm for the highest pressure applied which is close to failure point in the permanent plastic deformation region. However, only deformations below 7 μm (in elastic deformation) were completely reversible with higher deflection leading to plastic deformation. The average elastic modulus obtained from the data analysis by fitting the experimental data in the elastic region using the theory of the elastic deformation of the freely suspended membranes was calculated to be 2.4 ± 0.3 GPa.

On the other hand, in-plane compression of LbL film deposited on the PDMS substrate resulted in uniform buckling pattern with microscopic spacing (obtained from the spacing of distinctive spots on 2D FFT images), which can be used in the estimation of the elastic modulus (Fig. 4b).[29,30] The elastic modulus of 2.6 ± 0.3 GPa calculated from the buckling spacing is remarkably close to that evaluated from budging experiments as expected for uniform elastic solids.

The Young's moduli of the ultra-thin LbL films determined here is two-fold higher than typical values obtained for conventional polymeric LbL films in dry state (usually within 1–2 GPa).[4] For example, LbL films of PAH/PSS [poly(sodium-4-styrene sulfonate)] usually shows the modulus of 1.5 GPa.[3] By comparing the molecular structure of PSS and MPS-PPV, we can clearly realize that the presence of rigid rod-like conjugated backbones with stronger inter-chain interactions can enhance the mechanical properties of the multilayer films.

In conclusion, we demonstrated successful fabrication of record thin (below 20 nm), robust, free-standing purely polymeric LbL films which incorporated polyelectrolyte MPS-PPV molecules as an important reinforcing and electro-optically active component. These LbL films of nanoscale thickness can be significantly deformed and show elastic behavior for strain reaching 0.8% with the elastic modulus of 2.6 GPa. Moreover these robust LbL films in the free-standing state possess strong photoemission in a green range which can be easily detected and stable under the elastic regimes applied here. This optical-quality freely standing conjugated film offers the possibility for prospective applications such as flexible, lightweight displays and ultrathin luminescent panels with strong and stable emission properties.

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