Spiropyran-based polymers for photo-responsive layer-by-layer coatings capable of photo-induced disassembly

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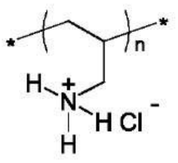
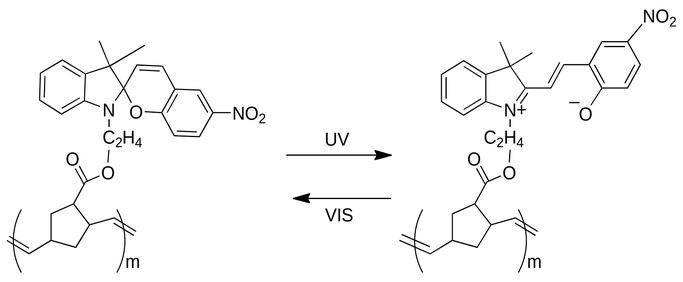
Spiropyrans (SP) constitute one of the most popular classes of photochromic compounds. The photochromism of SP is due to the photo-cleavage of the C-O bond upon irradiation with ultraviolet light (UV), given rise to the planar, conjugated merocyanine (MC) isomer. Irradiation with white light triggers the ring-closing reaction, and regeneration of the colourless SP isomer[1-3]. As MC contains the anionic nitrophenolate group, it is possible to use MC-functionalised polymers as polyanions in the formation of layer-by-layer (LbL) coatings. Photo-switching of the MC back to the uncharged SP isomer upon white light irradiation could be used for on-demand LbL disassembly.

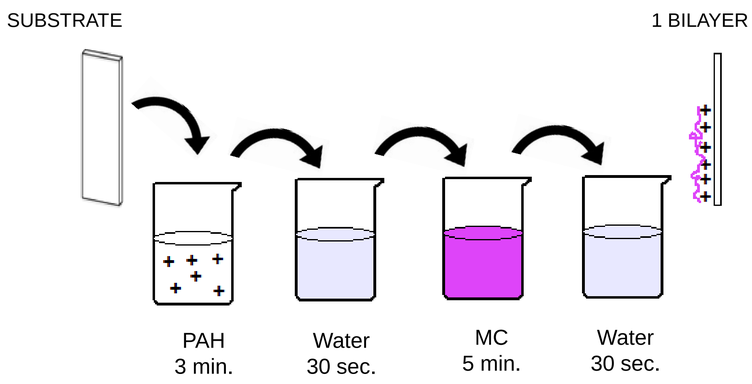
MATERIALS AND METHODS



Chemical structure of poly(allylamine hydrochloride) (PAH) polycation



Light-induced reversible switching of the photochromic polymer between the spiropyran form (poly(SP)) and the open merocyanine form (poly(MC))



Layer-by-layer deposition of PAH and poly(MC-R) on a substrate slide by dip coating, forming (PAH/poly(MC)) bilayer

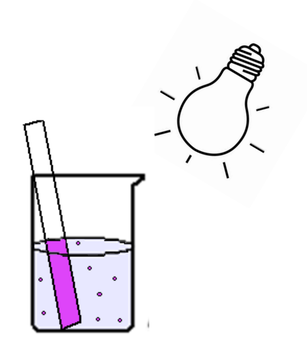
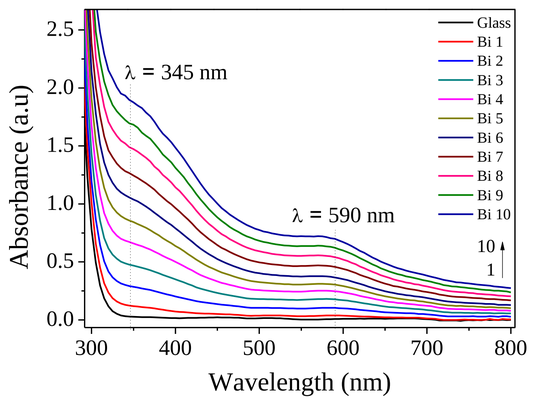


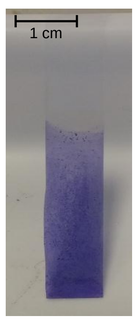
Photo-induced disassembly of (PAH/poly(MC)) LbL film upon exposure to white light

RESULTS AND DISCUSSION

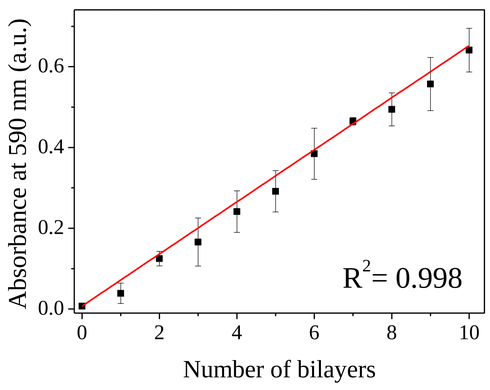
The UV-Vis spectra of the LbL films show the typical absorption bands of SP (λ_{max}=360 nm) and MC (λ_{max}=590 nm) assigned to the π-π* electronic excitation of the benzopyran part of the molecule and the conjugated merocyanine form, respectively. These absorbance bands increase linearly with the number of bilayers, showing effective deposition of the material on the glass substrate. The photochromic behaviour of poly(SP-R) solution and LbL films was investigated under UV and white light irradiation cycles and showed similar response.

✓ LbL assembly



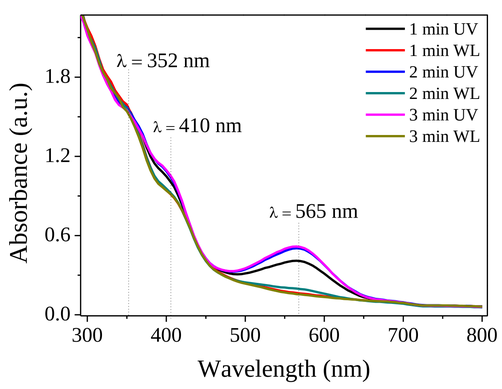


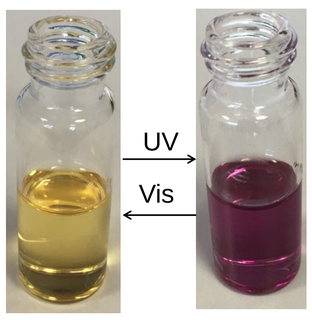
UV-Vis spectra of each bilayer of the $(PAH/poly(MC))_{10}$ film and photo of the corresponding $(PAH/poly(MC))_{10}$ coated glass slide.



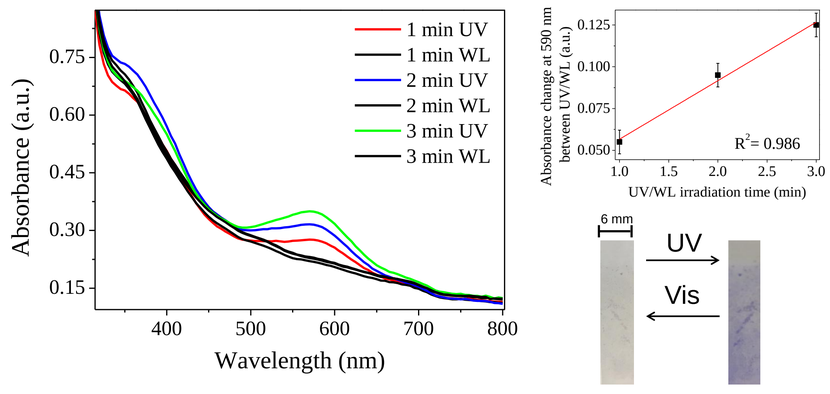
Plot of the absorbance at 590 nm of $(poly(MC\text{-}R))_{10}$ *versus* the bilayer number. The error bars represent the standard deviation of the absorbance at 590 nm for each bilayer (n=3).

✓ Photo-switching





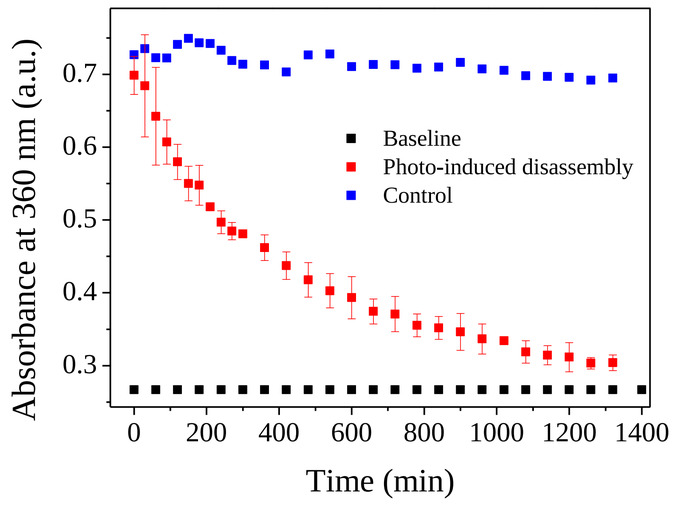
UV-Vis spectra of poly(SP-R) ⇔ poly(MC-R) solution in DMF:Water (3:1, V:V) after 1, 2 and 3 min irradiation with UV and white light, respectively, and photo of the solution.



UV-Vis spectra of a 5 bilayer film upon 3 successive UV/WL irradiation cycles of increased duration. Change in the absorbance at 590nm between $(PAH/poly(SP))_5$ and $(PAH/poly(MC))_5$ *vs* time and photo of the respective film.

✓ Photo-induced disassembly

It was observed that the absorbance band centred at 360 nm of the film exposed to white light decreased by 90.4% ±1.7% (n=3) relative to the baseline, during 20 hours of white light exposure. In the case of the control film (in the absence of white light irradiation) the absorbance band at 360 nm remained relatively constant during the course of the experiment.



Absorbance at 360 nm of the $(PAH/poly(MC\text{-}R))_5$ film during white light exposure (red) and in the dark (blue). The black line represents the absorbance of the bare glass substrate at 360 nm.

CONCLUSION

$(PAH/poly(MC))_n$ films were successfully deposited by LbL assembly and subsequently disassembled upon exposure to white light. Such LbL coatings have the potential to be used for the encapsulation of drugs to be released upon photo-stimulation.

REFERENCES

1. Florea, L., McKeon, A., Diamond, D., Benito-Lopez, F. *Langmuir* **29** (2013) 2790.
2. Florea, L., Hennart, A., Diamond, D., Benito-Lopez, F. *Sens. Act. B* **175** (2012) 92.
3. Florea, L., Diamond, D., Benito-Lopez, F. Macromolec. Mat. Eng. **297** (2012) 1148.

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