Monitoring Layer-by-layer Self-assembling Processes of Natural Polyelectrolytes by Fluorescent Bio-probe with Aggregation-induced Emission Characteristics

Jingwei Jia, Zhengke Wang, Qingwen Wu, Wei Qin, Qiaoling Hu, Benzhong Tang

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

Introduction

Surface properties of biomaterials play a crucial role in their applications in numerous biomedical fields. One promising way to functionalize or constitute biointerfaces in a controllable and versatile manner can be achieved with the layer-by-layer (LbL) self-assembly technique.

CS and ALG are all natural polyelectrolytes with chemical flexibility and typically good biological performance. CS/ALG layer-by-layer self-assembly system has been studied a lot.

Here we synthesize the AIE-active TPE−CS bioconjugate and study the layer-by-layer self-assembly process of TPE-CS and ALG, trying to prove its capacity to be used directly to monitor self-assemblies of polycations and polyanions.

Method

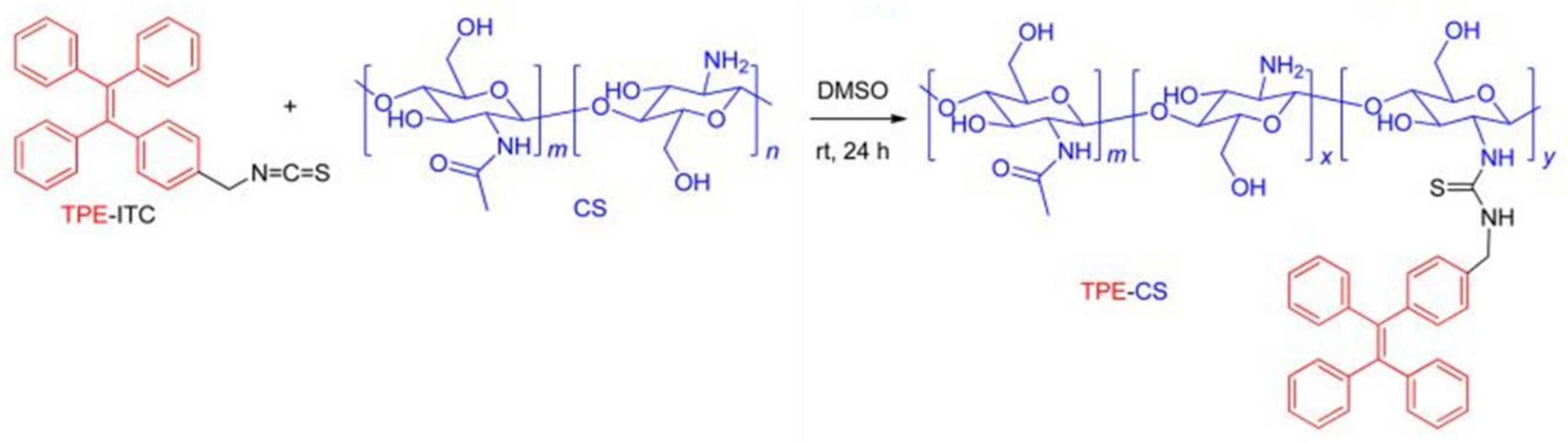

Figure 1. Synthesis of a Bioconjugate of Tetraphenylethene (TPE) and Chitosan (CS)

1. **TPE-CS was synthesized by the addition reaction of the isothiocyanate (ITC) group in TPE−ITC with the amino group in CS.**
2. **TPE-CS and ALG were deposited on the substrate successively through layer-by-layer self-assembly process. The properties of multilayer films were investigated by QCM, contact angle analyzer, spectroscopic ellipsometer and FL spectra.**
3. **At last, the cell adhesive properties of TPE-CS/ALG multilayer films were investigate.**

Results and Discussions

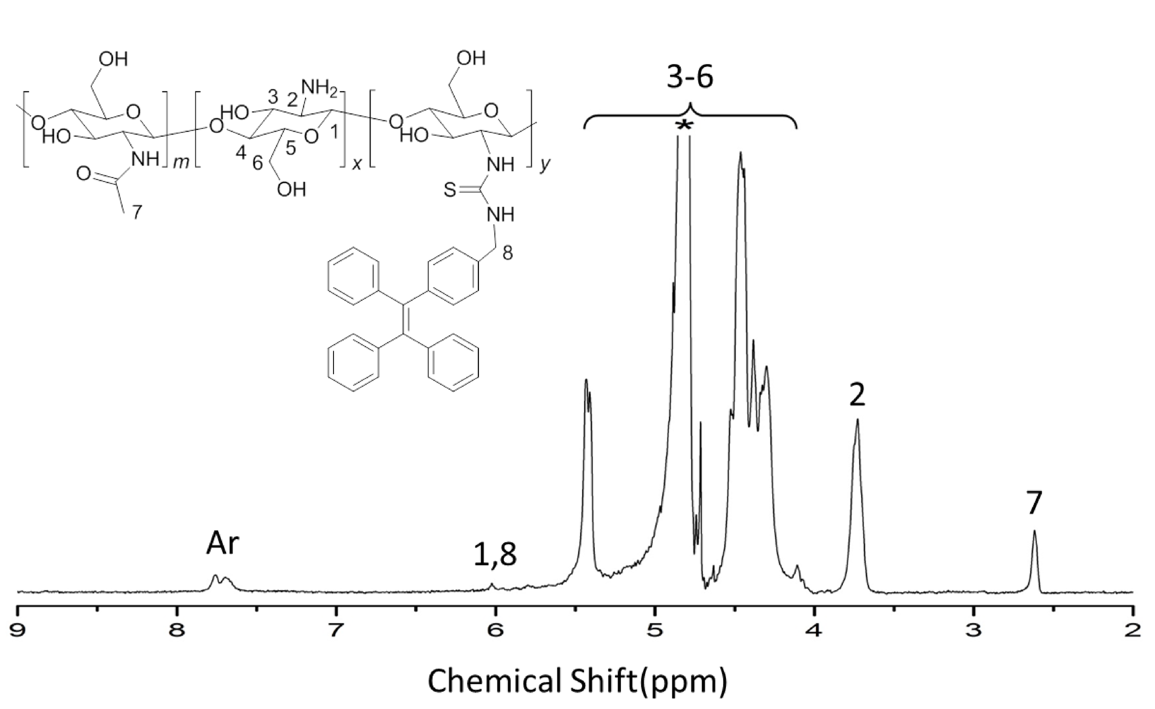

Figure 2. ^{1}H NMR spectra of CS-TPE. The solvent peaks are marked with asterisks.

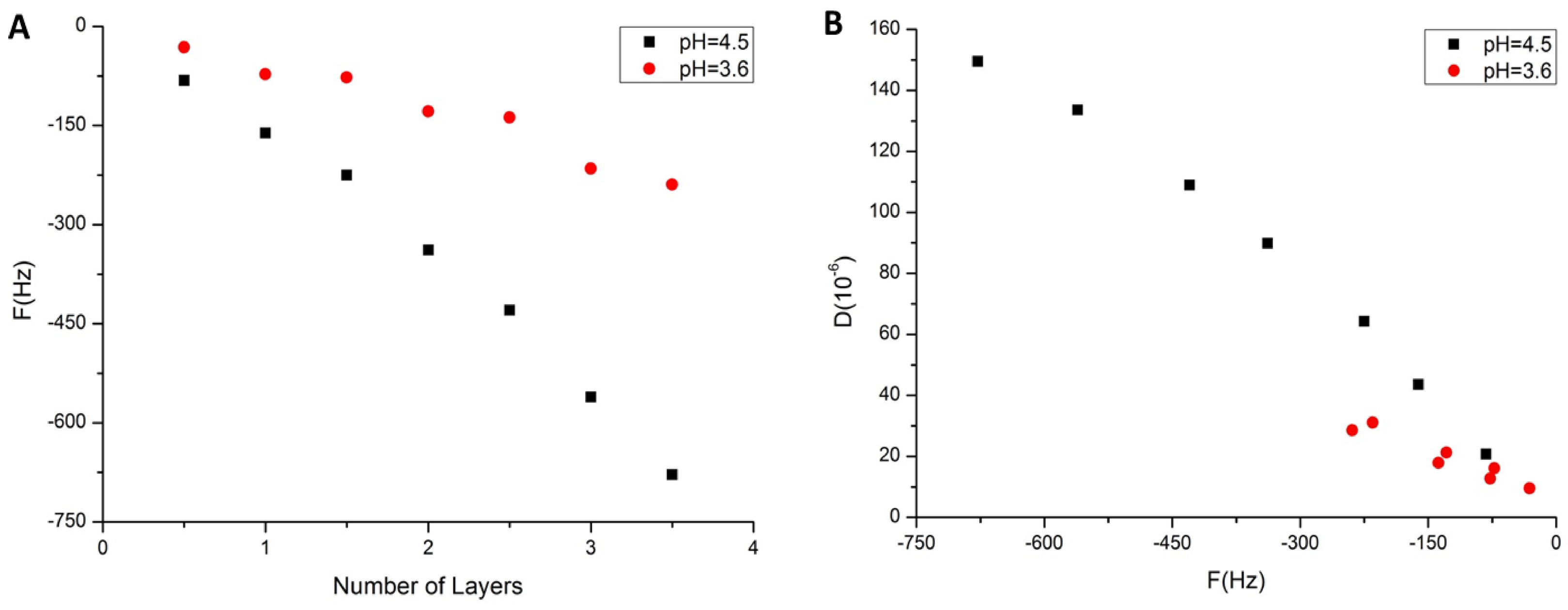

Figure 3. QCM-D results: (A) variation in frequency F during the build-up of multilayers. (B) variation in the dissipation factor D with frequency F

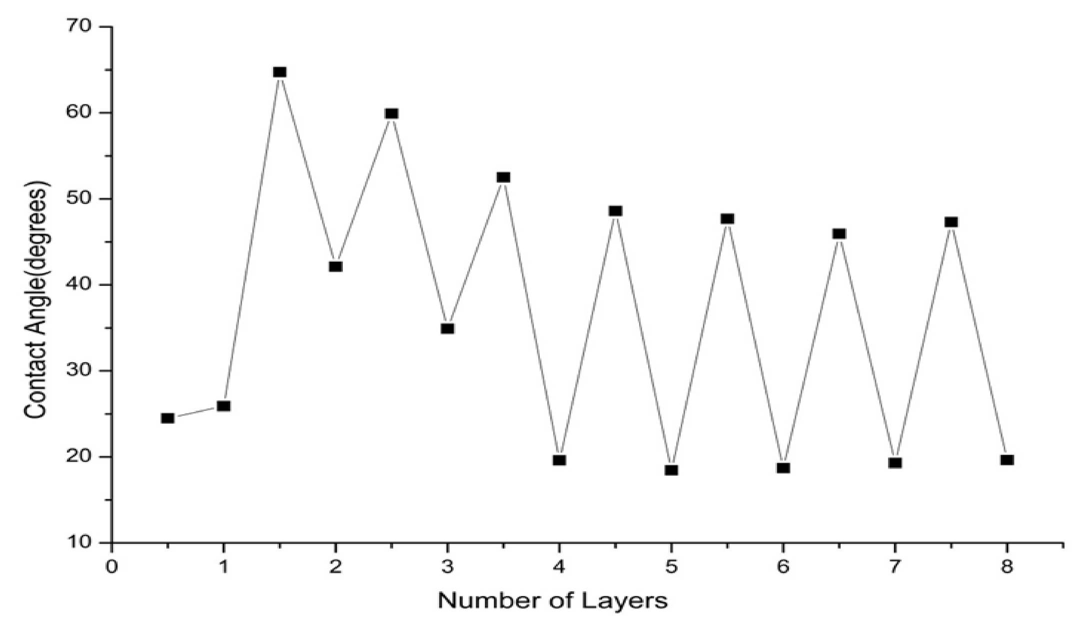

Figure 4. Contact angle of TPE−CS /ALG multilayer films with certain numbers of layers. Even numbers represent films with ALG as the outermost layer whereas odd number films have TPE−CS as the outermost layer.

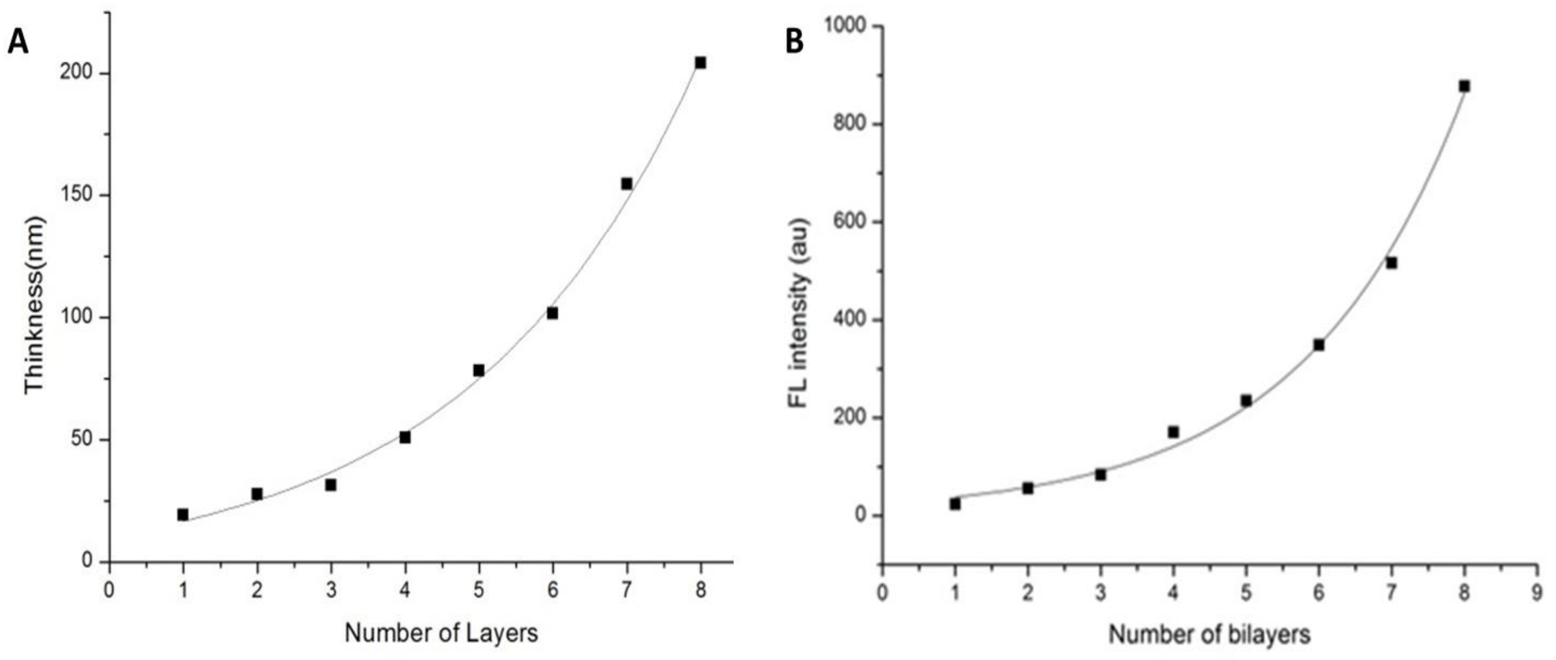

Figure 5. Exponential growth of the TPE−CS /ALG multilayer films: variation in thickness measured by ellipsometry (A) and FL intensity (B) with number of layers.

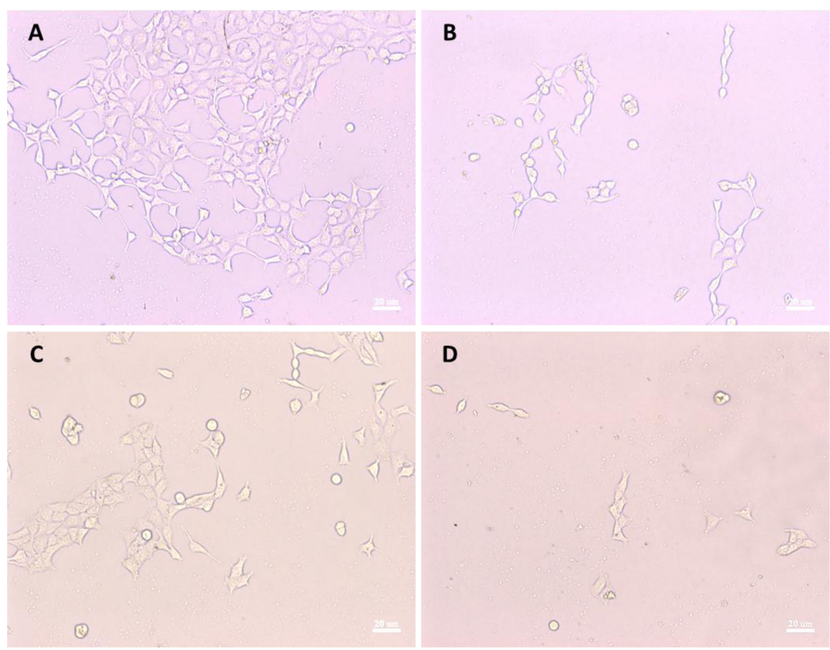

Figure 6. Microscopic observation of 293T cells cultured on (A) (TPE-CS /ALG)$_3$ /TPE-CS, (B) (TPE-CS /ALG)$_4$, (C) (TPE-CS /ALG)$_5$/TPE-CS, (D) (TPE-CS /ALG)$_6$ multilayer films after 3 d incubation.

Conclusion

In this work, we have successfully synthesized the AIE-active TPE−CS bioconjugate as a FL probe (and also a polycation itself) to monitor its layer-by-layer self-assembling process with ALG. Compared with the conventional dyes, TPE−CS with AIE characteristic shows neither FL quenching nor spectral shift. The FL intensity of the TPE−CS in the deposit films follows an excellent exponential relationship with the number of layers in accordance with variation in thickness. This novel CS-based AIE-active FL probe can be directly used to monitor multilayer deposition process on UV-absorbing and opaque substrates, thus providing a new simple and convenient way for probing the layer-by-layer self-assemblies of polycations and polyanions.

Acknowledgements

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