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Selective binding and controllable release of the anticoagulant heparin by electroactive BFD-SAMs in biological buffer solution

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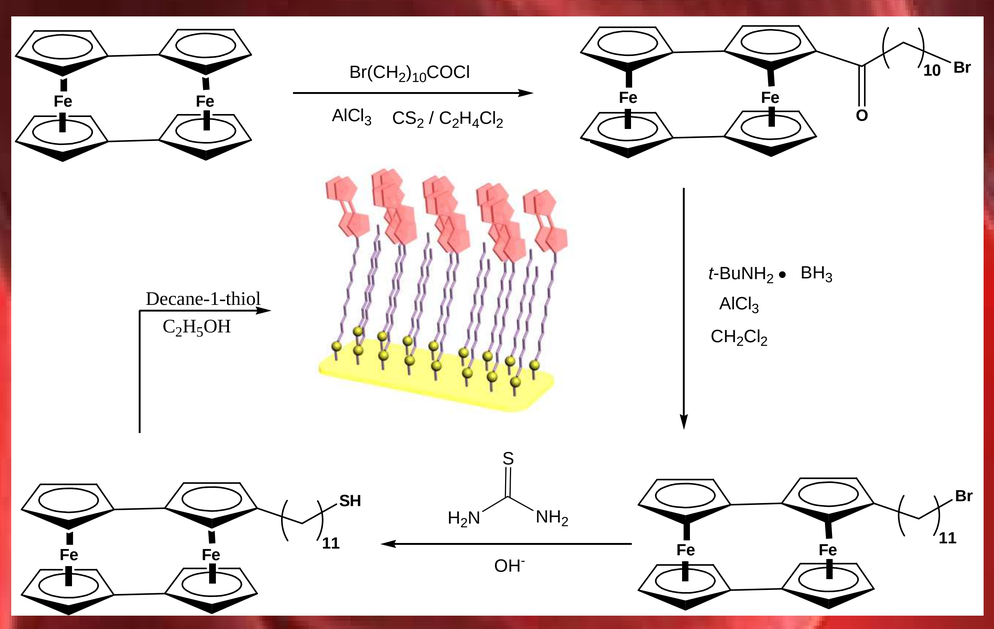
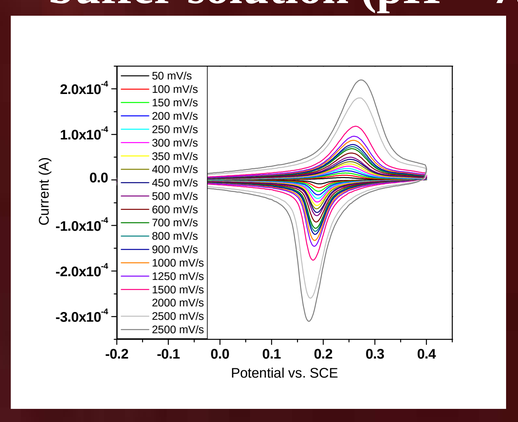
Introduction

Polyanions with a variety of biological activities are important targets for sensing.[1] Herein, we present an electroactive self-assembled monolayer (SAM) based on biferrocenylene (BFD)[2], which recognized the highly sulfated glycosaminoglycan, heparin, among several other biological anions (ATP^{4-}, AMP^{2-}, phytic acid and hyaluronic acid) in biological buffer solution. The binding process can be controlled by switching the BFD between the neutral and cationic state.

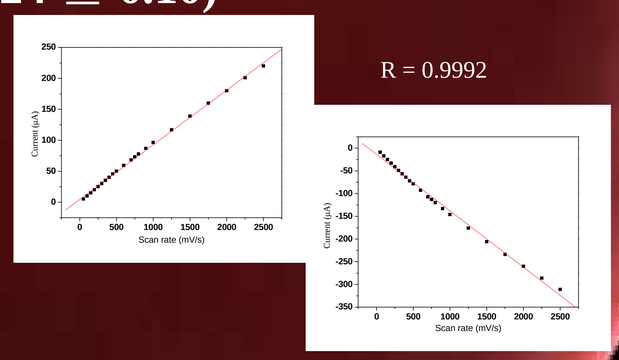
I Synthesis and general description



II Characterization and stability of the SAM in Tris-NO_3 buffer solution (pH = 7.24 ± 0.10)

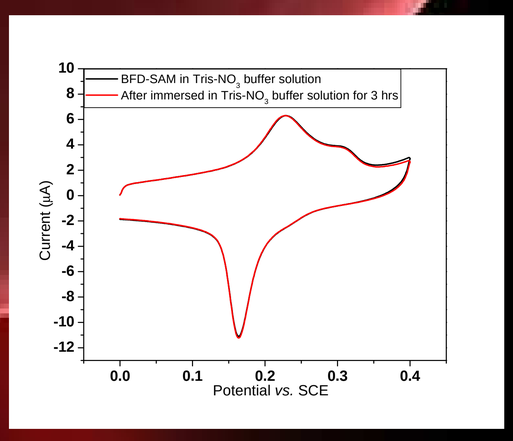


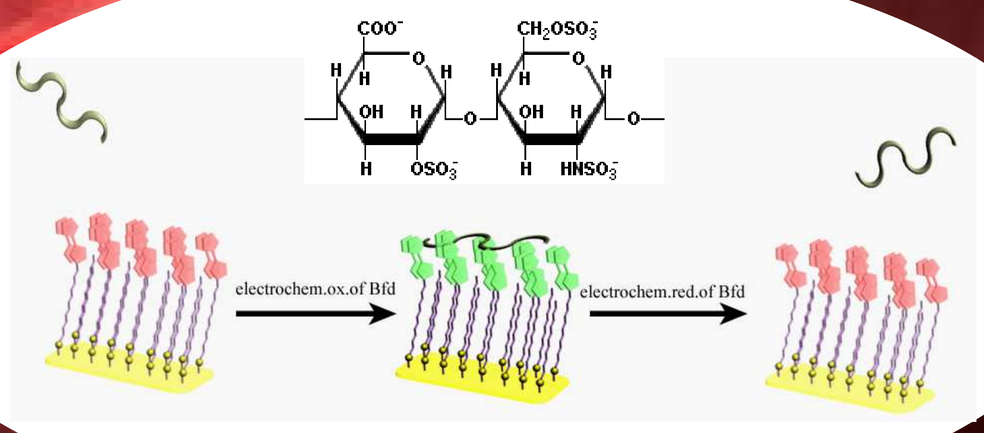
The cyclic voltammetric curves of the SAM at different scan rates (50 - 2500 mV/s)



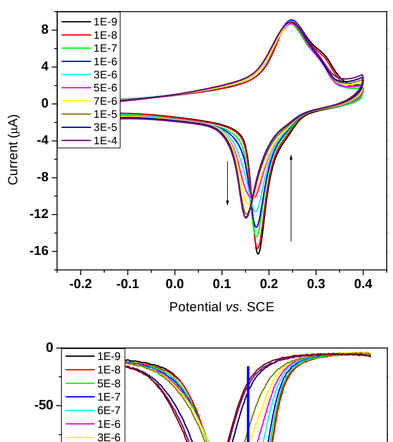
Both the cathodic (top) and anodic (bottom) peak currents showed a good linear relationship with the scan rate (R = 0.9992)

After immersion into the Tris-NO_3 buffer solution for 3 hours, the CV of the SAM did not show an obvious difference. (SR = 100 mV/s)

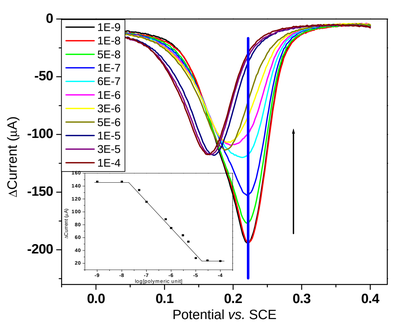




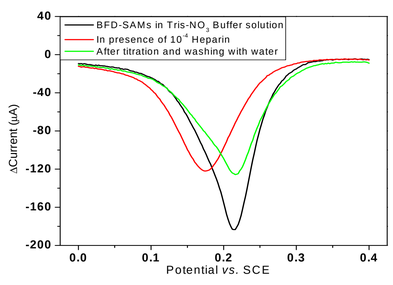
III Quantitative binding and release of heparin



Cyclic voltammetric curves of the SAM in Tris-NO_3 buffer solution (pH 7.24 ± 0.10) at different concentrations of heparin are depicted (from 1 nM to 0.4 mM). Upon addition of heparin, the anodic peak did not show response, but the cathodic peak gave a relative obvious change. (SR = 100 mV/s)

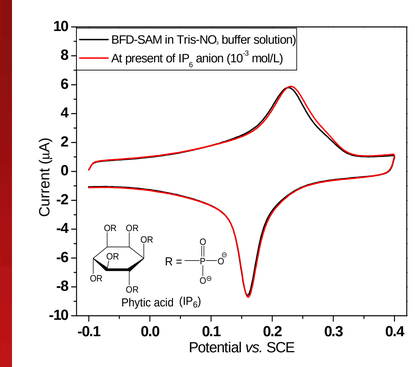


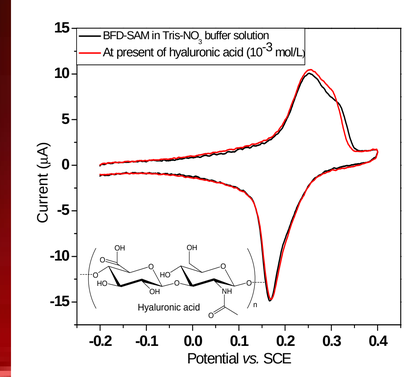
The cathodic SWV intensity of BFD-SAMs vs. concentration of heparin in Tris-NO_3 buffer solution (pH 7.24 ± 0.10) is given. (1 nM to 0.4 mM - from bottom to top). Titration curve is shown in the insert.

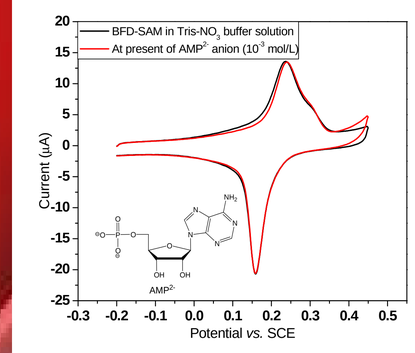


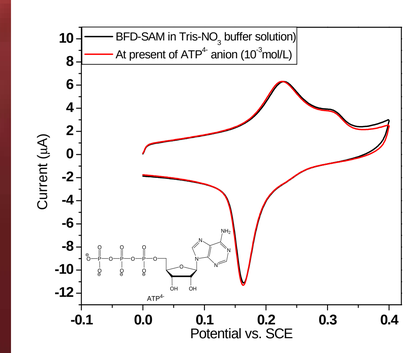
After titration the BFD-SAMs was washed with deionized water. The potential of the cathodic SWV peak is almost the same as that before titration with a lower intensity.

IV The BFD-SAM furnished no response to several other biological anions









Both the cathodic and anodic peaks of the BFD-SAMs did not respond to ATP^{4-}, AMP^{2-}, phytic acid, and hyaluronic acid in the Tris-NO_3 buffer solution, even at higher concentration (10^{-3} mol/L) of these biological anions than heparin (10^{-4} mol/L) (SR = 100 mV/s).

Conclusions

An electroactive BFD-SAMs was developed to sense selectively and quantitatively the polyanion heparin in biological buffer solution, thus furnishing an interesting potential for lab-on-chip use.

Acknowledgments

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References:

[1] a) A. Wada, S. Tamaru, M. Ikeda, I. Hamachi, *J. Am. Chem. Soc.* 2009, *131*, 5321-5330; b) R. B. C. Jagt, R. F. Gómez-Biagi, M. Nitz, *Angew. Chem. Int. Ed.* 2009, *48*, 1995-1997.

[2] C. LeVanda, et al., *J. Am. Chem. Soc.* 1976, *98*, 3181.