

Electronic Supporting Information
for

Reversible binding and quantification of heparin and chondroitin sulfate in water using redoxstable biferrocenylene SAMs

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Chemicals

Chondroitin sulfate (mixture of 4- and 6-sulfate), hyaluronic acid, phytic acid sodium salt and bovine blood plasma (3.8% trisodium citrate as anticoagulant) were obtained from Sigma-Aldrich. Heparin (IU \geq 100/mg), H₂AMP and Na₂H₂ATP were purchased from Alfa Aesar.

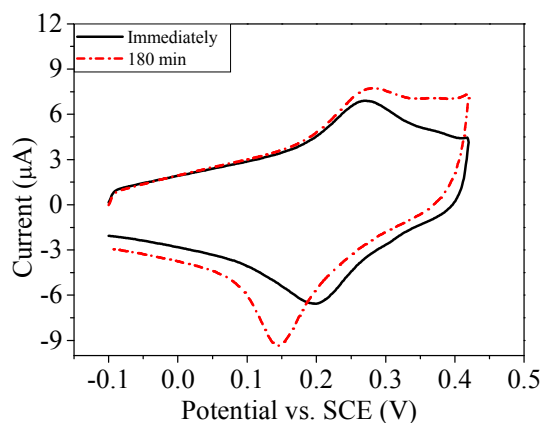


Fig. S1 CV curves of β -(11-mercaptoundecyl)-BFD SAMs in Tris-Cl buffered solution ($\text{pH} = 7.24 \pm 0.10$, 0.01 M Tris-Cl, 0.1 M NaCl) immediately (black) after immersion and after 180 min of immersion (red). Scan rate = 100 mV/s.

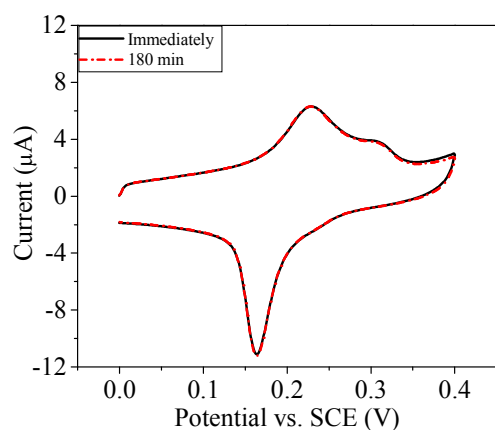


Fig. S2 CV curves of β -(11-mercaptoundecyl)-BFD SAMs immersion in Tris-NO₃ buffered solution ($\text{pH} = 7.24 \pm 0.10$, 0.01 M Tris-NO₃, 0.1 M NaNO₃) immediately (black) after immersion and after 180 min of immersion (red). Scan rate = 100 mV/s.

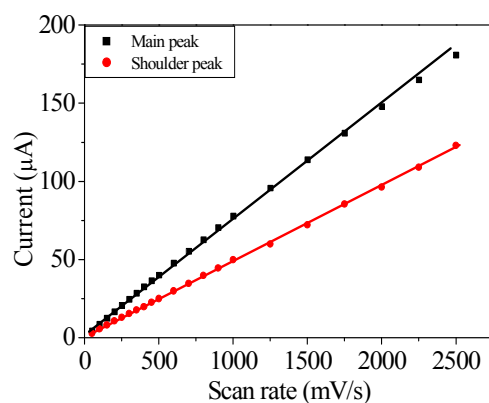


Fig. S3 Linear relationship of the main anodic peak current (■) and shoulder anodic peak current (●) with scan rates of β -(11-mercaptoundecyl)-BFD SAMs in Tris-NO₃ buffer ($\text{pH} = 7.24 \pm 0.10$, 0.01 M Tris-NO₃, 0.1 M NaNO₃) from 25 mV/s to 2500 mV/s.

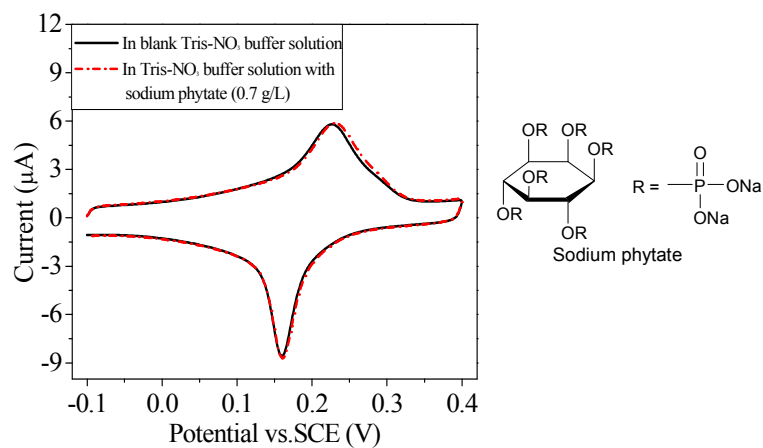


Fig. S4 CV curves of β -(11-mercaptoundecyl)-BFD SAMs in absence (black) and presence of 0.7 g/L sodium phytate (red) in Tris-NO₃ buffer (pH = 7.24 ± 0.10, 0.01 M Tris-NO₃, 0.1 M NaNO₃). Scan rate = 100 mV/s

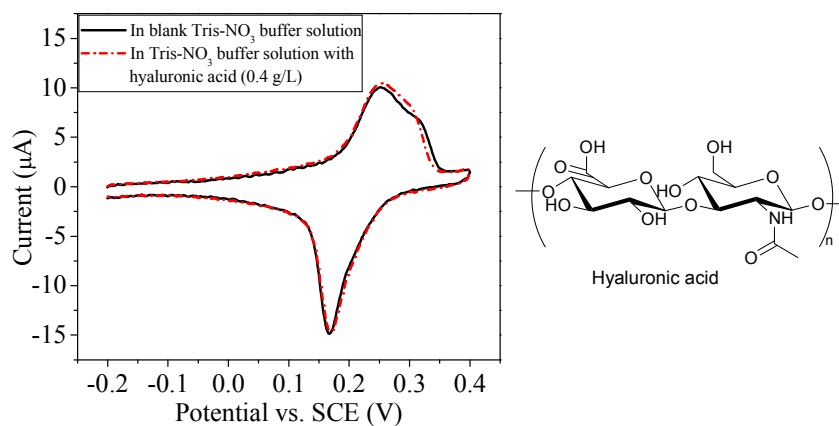


Fig. S5 CV curves of β -(11-mercaptoundecyl)-BFD SAMs in absence (black) and presence of 0.4 g/L hyaluronic acid (red) in the Tris-NO₃ buffer (pH = 7.24 ± 0.10, 0.01 M Tris-NO₃, 0.1 M NaNO₃). Scan rate = 100 mV/s.

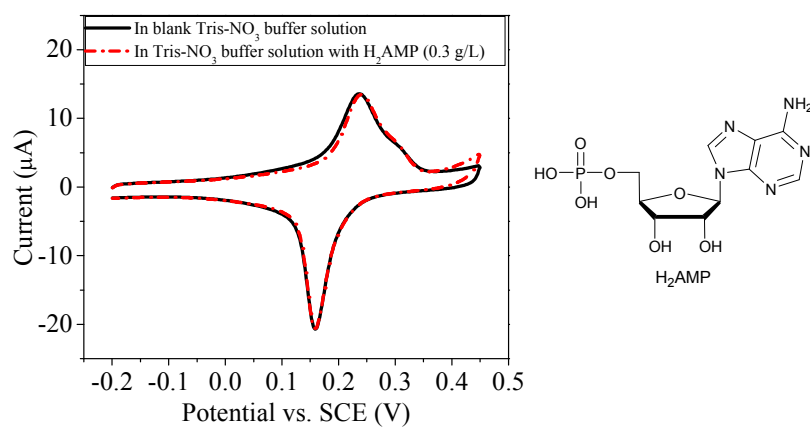


Fig. S6 CV curves of β -(11-mercaptoundecyl)-BFD SAMs in absence (black) and presence of 0.3 g/L H_2AMP (red) in $Tris-NO_3$ buffer ($pH = 7.24 \pm 0.10$, 0.01 M $Tris-NO_3$, 0.1 M $NaNO_3$). Scan rate = 100 mV/s.

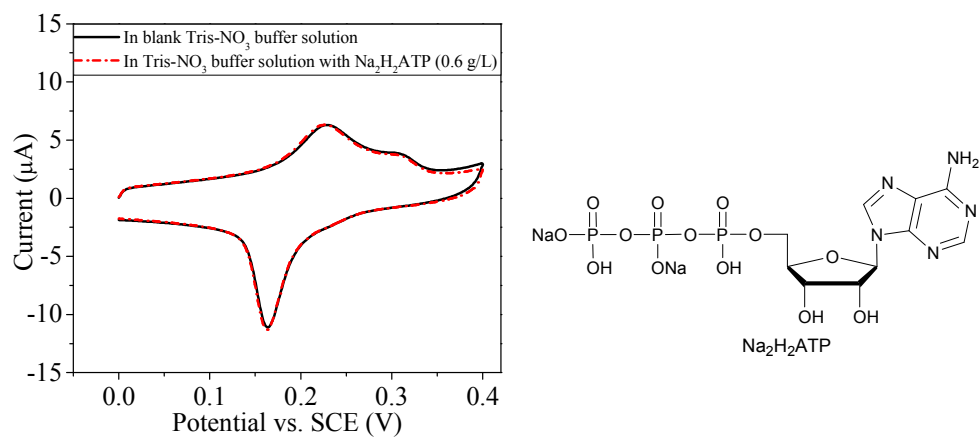


Fig. S7 CV curves of β -(11-mercaptoundecyl)-BFD SAMs in absence (black) and presence of 0.6 g/L Na_2H_2ATP (red) in $Tris-NO_3$ buffer ($pH = 7.24 \pm 0.10$, 0.01 M $Tris-NO_3$, 0.1 M $NaNO_3$). Scan rate = 100 mV/s.

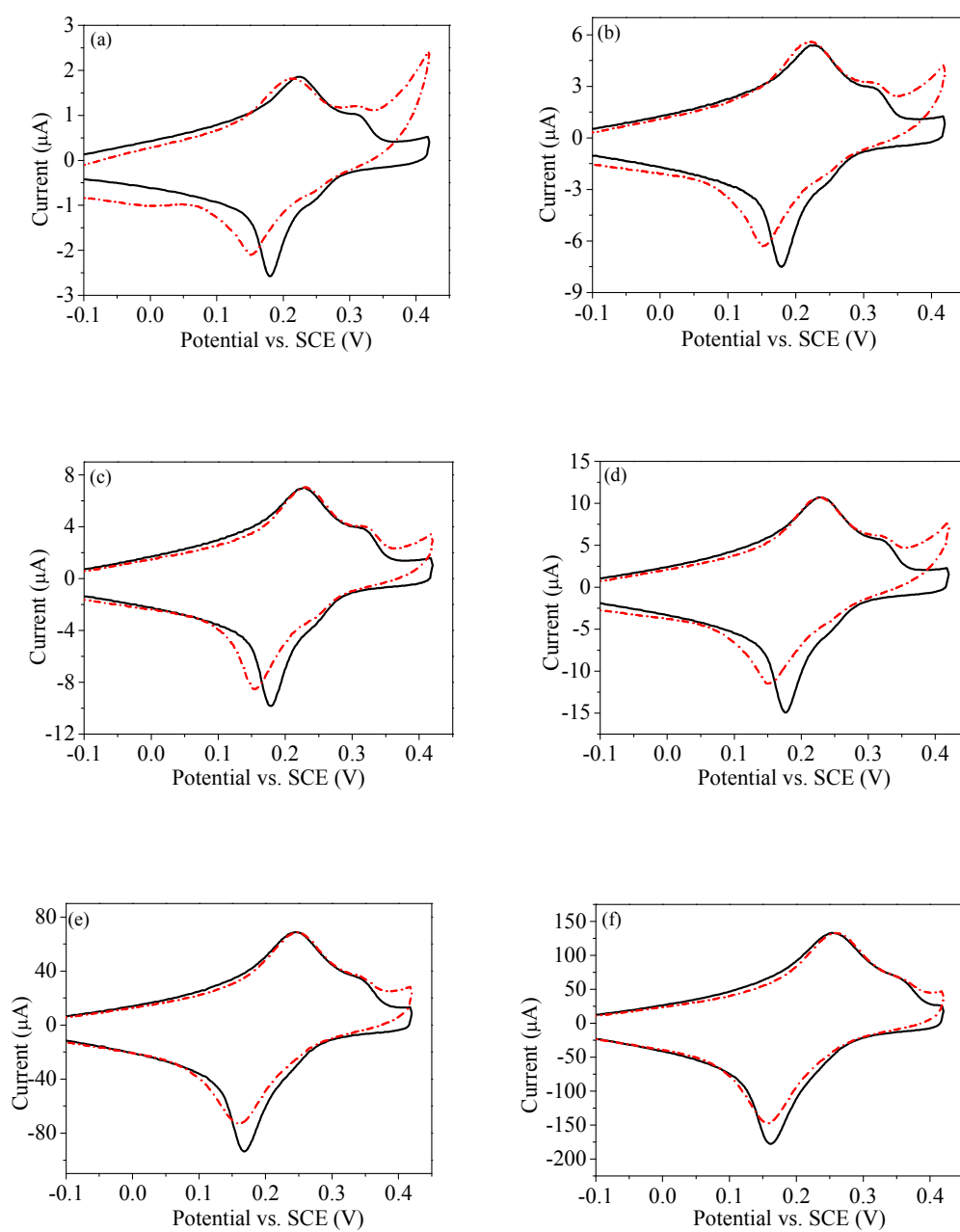


Fig. S8 CVs of β -(11-mercaptoundecyl)-BFD SAMs in blank Tris-NO₃ buffer (black) and in Tris-NO₃ buffer + 6.4×10^{-3} g/L heparin (red) at different scan rates: (a) 25 mV/s; (b) 75 mV/s; (c) 100 mV/s; (d) 150 mV/s; (e) 1000 mV/s and (f) 2000 mV/s (pH = 7.24 ± 0.10 , 0.01 M Tris-NO₃, 0.1 M NaNO₃).

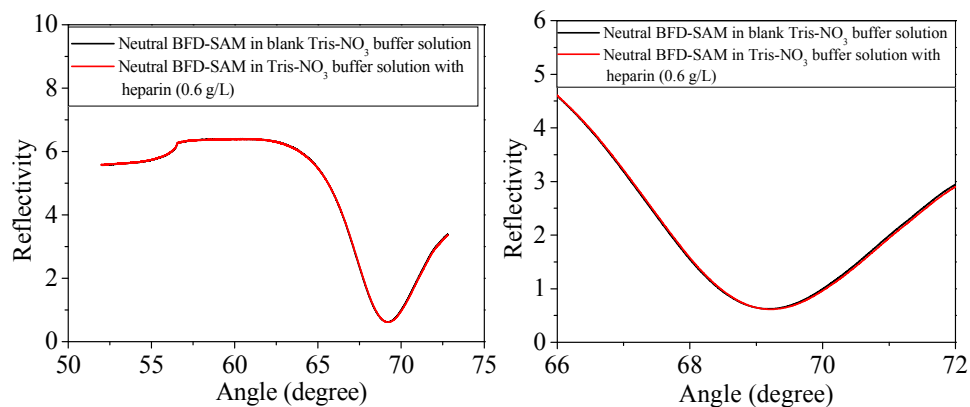


Fig. S9 Left: SPR measurements of neutral of β -(11-mercaptoundecyl)-BFD SAMs in Tris-NO₃ buffer (pH = 7.24 \pm 0.10, 0.01 M Tris-NO₃, 0.1 M NaNO₃) with 0.6 g/L heparin (red) and without (black). Right: Enlarged picture of SPR measurements (Incident angle from 66° to 72°).

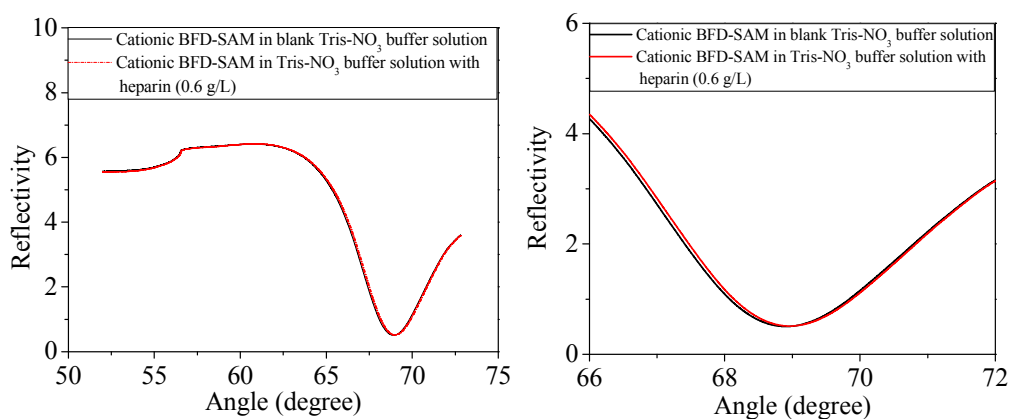


Fig. S10 Left: SPR measurements of monooxidised β -(11-mercaptoundecyl)-BFD SAMs in Tris-NO₃ buffer (pH = 7.24 \pm 0.10, 0.01 M Tris-NO₃, 0.1 M NaNO₃) with 0.6 g/L heparin (red) and without (black). Right: Enlarged picture of SPR measurements (Incident angle from 66° to 72°).

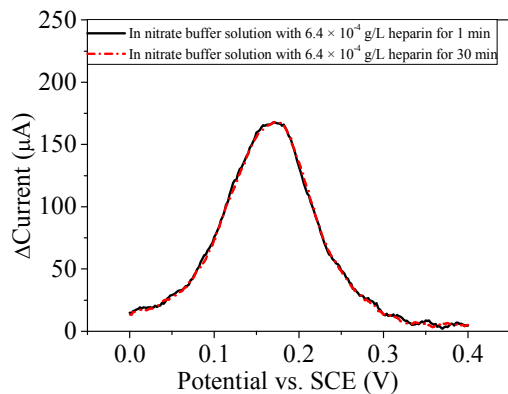


Fig. S11 SWV curves of β -(11-mercaptopoundecyl)-BFD SAMs in Tris-NO₃ buffer (pH = 7.24 ± 0.10, 0.01 M Tris-NO₃, 0.1 M NaNO₃) in presence of heparin (6.4×10^{-4} g/L) after 1 min (black) and 30 min of immersion (red).

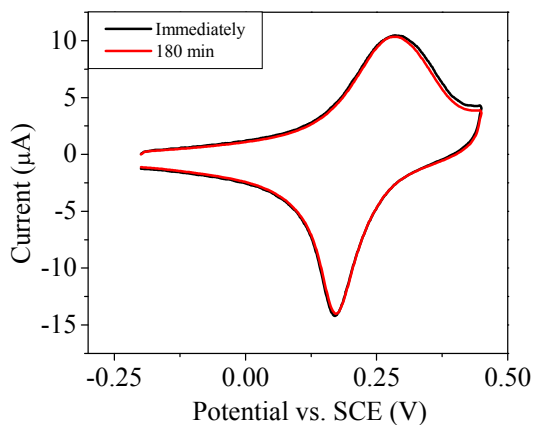


Fig. S12 CV curves of a β -(11-mercaptopoundecyl)-BFD SAM immersed into a bovine plasma sample (diluted 50x by adding a Tris-NO₃ buffered solution): Scan rate = 100 mV/s; the black trace was recorded immediately after immersion and the red trace after 180 min of immersion. Buffer: pH = 7.24 ± 0.10, 0.01 M Tris-NO₃, 0.1 M NaNO₃.

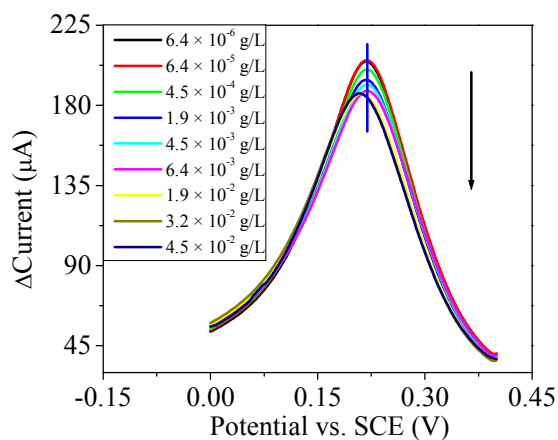


Fig. S13 Cathodic SWV curves of a β -(11-mercaptopoundecyl)-BFD SAM upon generating defined concentrations of heparin in the diluted bovine plasma sample (for details, see caption of Fig. S12).

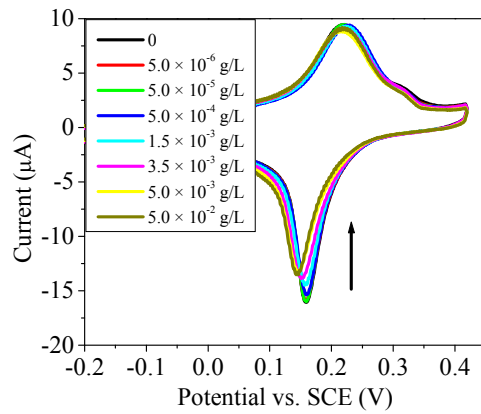


Fig. S14 CV curves of β -(11-mercaptopundecyl)-BFD SAMs upon addition of various amounts of chondroitin sulfate in Tris- NO_3 buffer solution ($\text{pH} = 7.24 \pm 0.10$, 0.01 M Tris- NO_3 , 0.1 M NaNO_3). Scan rate = 100 mV/s.

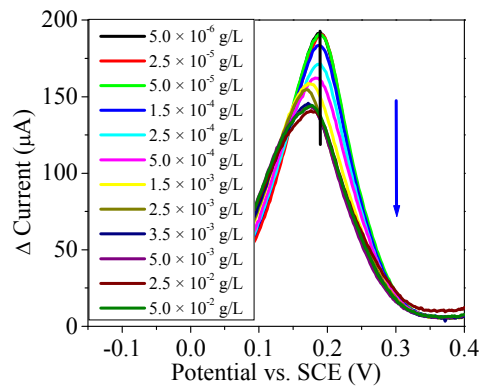


Fig. S15 Cathodic SWV curves of β -(11-mercaptopundecyl)-BFD SAMs after addition of various amounts of chondroitin sulfate in the Tris- NO_3 buffer ($\text{pH} = 7.24 \pm 0.10$, 0.01 M Tris- NO_3 , 0.1 M NaNO_3).

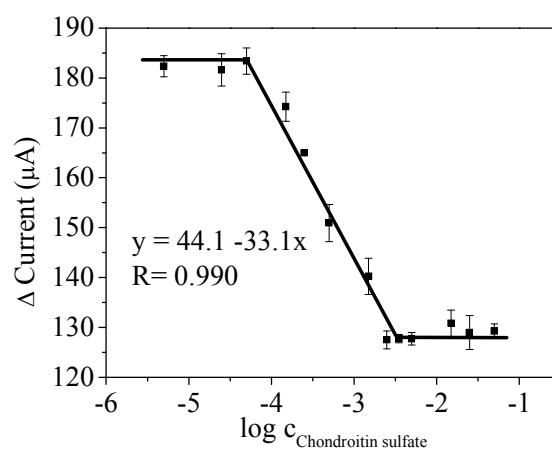


Fig. S16 Titration curve for β -(11-mercaptopundecyl)-BFD SAMs and concentration of chondroitin sulfate in Tris- NO_3 buffer ($\text{pH} = 7.24 \pm 0.10$, 0.01 M Tris- NO_3 , 0.1 M NaNO_3). Δ Current vs. logarithm of $c_{\text{Chondroitin}}$ (g/L) shows a good linear relationship from 5.0×10^{-5} g/L to 2.5×10^{-3} g/L.

Table S1 The buffer solutions used for potential measurement in presence of different anions

Buffer system	Concentration of Tris	Acid	pH	Concentration of electrolyte
Tris-PF ₆	0.01 M	HPF ₆	7.24 ± 0.10	0.1M NaPF ₆
Tris-BF ₄	0.01 M	HBF ₄		0.1M NaBF ₄
Tris-ClO ₄	0.01 M	HClO ₄		0.1M NaClO ₄
Tris-NO ₃	0.01 M	HNO ₃		0.1M NaNO ₃
Tris-Cl	0.01 M	HCl		0.1M NaCl