

The Effect of Large Electrolyte Anions on the Sequential Oxidations of
Bis(fulvalene)diiron Attached to Glassy Carbon by an Ethynyl Linkage

Matthew V. Sheridan, Paul Gamm, Severin T. Schneebeli,
Rochus Breuer, Michael Schmittel, and W.E. Geiger*

Table of Contents

(CV = cyclic voltammogram; SWV = square wave voltammogram; DPV = differential pulse voltammogram)

ΔE_{pk} values at different SW frequencies for surface-bound α E-BFD	Table S1	Page 1
CV scan of α E-BFD in $\text{CH}_2\text{Cl}_2/[\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$	Figure S1	Page 2
DPV of gce surface-modified with β E-BFD, scanned in $[\text{PF}_6]^-$	Figure S2	Page 2
SWV (60 Hz) in $[\text{PF}_6]^-$ electrolyte of surface-bound β E-BFD	Figure S3	Page 3
SWV (60 Hz) in $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ electrolyte of surface-bound β E-BFD	Figure S4	Page 3
DPV of gce surface-modified with β E-BFD, scanned in $[\text{B}(\text{C}_6\text{F}_5)_4]^-$	Figure S5	Page 4

Table S1. Values of ΔE_{pk} ($= E_{\text{fwd}} - E_{\text{rev}}$) for surface-bound α E-BFD on glassy carbon as a function of square wave frequency. The electrolyte medium was dichloromethane containing either 0.1 M $[\text{NBu}_4][\text{PF}_6]$ or 0.05 M $[\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$.

Electrolyte Anion	SW frequency (Hz)	ΔE_{pk} (mV) $[\text{E-BFD}]^{0/+}$ couple	ΔE_{pk} (mV) $[\text{E-BFD}]^{+/2+}$ couple
$[\text{PF}_6]^-$	20	26	28
$[\text{PF}_6]^-$	40	28	30
$[\text{PF}_6]^-$	60	32	32
$[\text{B}(\text{C}_6\text{F}_5)_4]^-$	40	48	44
$[\text{B}(\text{C}_6\text{F}_5)_4]^-$	60	52	50
$[\text{B}(\text{C}_6\text{F}_5)_4]^-$	150	52	50
$[\text{B}(\text{C}_6\text{F}_5)_4]^-$	300	54	32

Figure S1. Cyclic voltammogram of 1.0 mM α -EBFD in 0.10 M CH_2Cl_2 /[NBu₄][B(C₆F₅)₄], 0.2 V s⁻¹, gce.

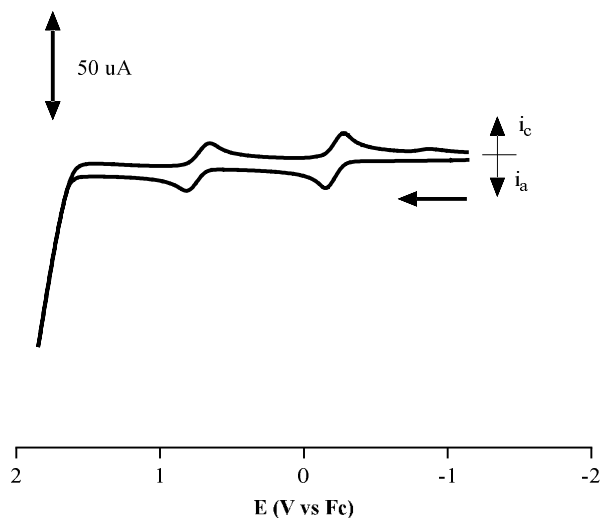


Figure S2. Differential pulse voltammogram (2 mV s⁻¹) of 2 mm glassy carbon electrode that had been modified by five CV scans at 400 mV s⁻¹ through the second oxidation wave of a 2 mM solution of β E-BFD in dichloromethane/0.05 M [Bu₄N][B(C₆F₅)₄]. The DPV scan was recorded in 0.10 M [Bu₄N][PF₆].

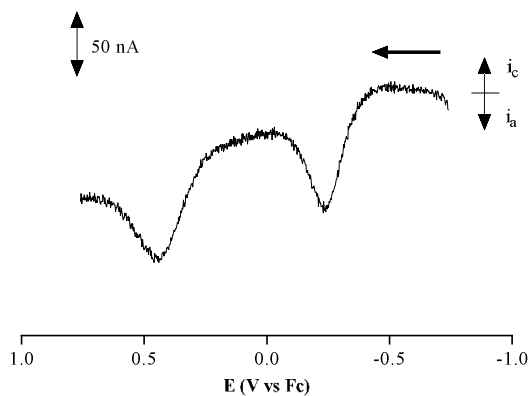


Figure S3. Square-wave voltammogram (60 Hz) of 2 mm glassy carbon electrode that had been modified by five CV scans at 400 mV s^{-1} through the second oxidation wave of a 2 mM solution of $\beta\text{E-BFD}$ in dichloromethane/0.05 M $[\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$. The SWV scan was recorded in 0.10 M $[\text{Bu}_4\text{N}][\text{PF}_6]$.

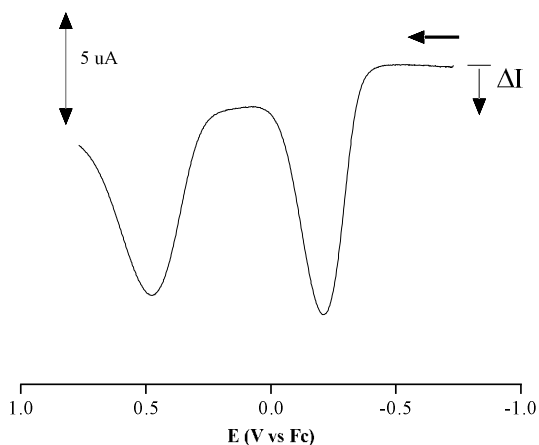


Figure S4. Square-wave voltammogram (60 Hz) of 2 mm glassy carbon electrode that had been modified by five CV scans at 400 mV s^{-1} through the second oxidation wave of a 2 mM solution of $\beta\text{E-BFD}$ in dichloromethane/0.05 M $[\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$. The SWV scan was recorded in 0.10 M $[\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$.

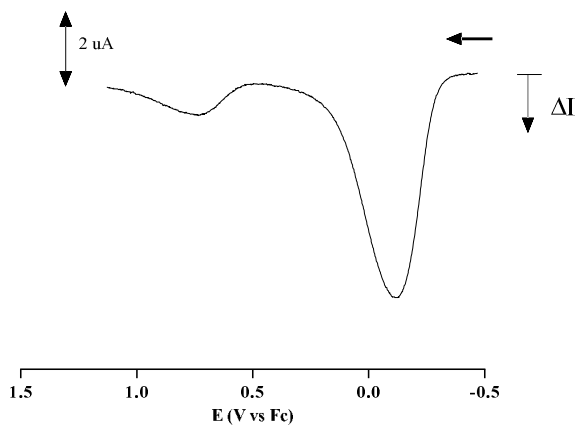


Figure S5. Differential pulse voltammogram (2 mV s^{-1}) of 2 mm glassy carbon electrode that had been modified by five CV scans at 200 mV s^{-1} through the second oxidation wave of a 2 mM solution of $\beta\text{E-BFD}$ in dichloromethane/0.05 M $[\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$. The DPV scan was recorded in 0.10 M $[\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$.

