Supporting Information

Electrochemistry and Electrogenerared Chemiluminescence of π-Stacked Poly(fluorene methylene) Oligomers. Multiple, Interacting Electron Transfers

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Figure S1. Continuous cyclic voltammograms of 0.72 mM of the F1 monomer at 0.5 V/s.

Solvent: MeCN:Bz, supporting electrolyte: 0.1 M TBAPF$_6$; Pt electrode area: 0.043cm$^2$. 
Figure S2. Comparison between simulated and experimental oxidation waves for 1.3 mM F1 at different scan rates. The model for these oxidation simulations: ECE, \( k_1^0 = 0.5 \text{ cm/s} \), \( k_2^0 = 0.1 \text{ cm/s} \), \( k_f = 40000 \text{ M/s} \). Simulated data: \( E_1 = 1.65 \), \( E_2 = 1.35 \); Diffusion coefficient: \( 2.4 \times 10^{-5} \text{ cm}^2/\text{s} \), uncompensated resistance 500 \( \Omega \), capacitance \( 4 \times 10^{-10} \text{ F} \). Experimental conditions: solvent: MeCN:Bz (1:1), supporting electrolyte: 0.1 M TBAPF\(_6\), Pt UME \( r = 12.5 \mu \text{m} \).
Figure S3. Comparison between simulated and experimental oxidation waves for 1.1 mM F2 at different scan rates. The model for these oxidation simulations: EE, $k_1^0=1$ cm/s, $k_2^0=10$ cm/s. Simulated data: $E_1=1.35$ V, $E_2=1.58$ V; Diffusion coefficient: $2 \times 10^{-5}$ cm$^2$/s, uncompensated resistance 600 $\Omega$, capacitance $2 \times 10^{-10}$ F. Experimental conditions: solvent: MeCN:Bz (1:1), supporting electrolyte: 0.1 M TBAPF$_6$, Pt UME $r = 12.5$ $\mu$m.
Figure S4. Comparison between simulated and experimental oxidation waves for 0.5 mM F3 at different scan rates. The model for these oxidation simulations: EE, $k_f^0=0.5$ cm/s, $k_r^0=10000$ cm/s. Simulated data: $E_1=1.26$, $E_2=1.43$; Diffusion coefficient: $1 \times 10^{-5}$ cm$^2$/s, uncompensated resistance 662 Ω, capacitance $3 \times 10^{-7}$ F. Experimental conditions solvent: MeCN:Bz (1:1); supporting electrolyte: 0.1 M TBAPF$_6$, Pt electrode area 0.043 cm$^2$. 
Figure S5. Comparison between simulated and experimental oxidation waves for 0.3 mM F4 at different scan rates. The model for these oxidation simulations: EEE, $k_1^0=0.1$ cm/s, $k_2^0=0.1$ cm/s, $k_3^0=0.1$ cm/s. Simulated data: $E_1=1.62$ V, $E_2=1.34$ V, $E_3=1.2$ V; Diffusion coefficient: $8 \times 10^{-6}$ cm$^2$/s, uncompensated resistance 621 $\Omega$, capacitance $6 \times 10^{-8}$ F. Experimental conditions: solvent: MeCN:Bz (1:1), supporting electrolyte: 0.1 M TBAPF$_6$, Pt electrode area 0.043 cm$^2$. 
Figure S6. Comparison between simulated and experimental oxidation waves for 0.5 mM F4 at different scan rates. The model for these oxidation simulations: EEE, $k_1^0 = 0.1$ cm/s, $k_2^0 = 0.1$ cm/s, $k_3^0 = 0.1$ cm/s. Simulated data: $E_1 = 1.62$ V, $E_2 = 1.34$ V, $E_3 = 1.2$ V. Diffusion coefficient: $8 \times 10^{-6}$ cm$^2$/s, uncompensated resistance 621 $\Omega$, capacitance $2 \times 10^{-10}$ F. Experimental conditions: solvent: MeCN:Bz (1:1), supporting electrolyte: 0.1 M TBAPF$_6$, Pt UME $r = 12.5$ $\mu$m.
Figure S7. Comparison between simulated and experimental oxidation waves for 0.4 mM F5 at different scan rates. The model for these oxidation simulations: $k_1^0=10000$ cm/s, $k_2^0=10000$ cm/s, $k_3^0=10000$ cm/s. Simulated data: $E_1 = 1.19$ V, $E_2 = 1.31$ V, $E_3 = 1.45$ V vs SCE; diffusion coefficient: $4 \times 10^{-6}$ cm$^2$/s, uncompensated resistance 700 $\Omega$, capacitance $1 \times 10^{-8}$ F.

Experimental conditions: solvent: MeCN:Bz (1:1); supporting electrolyte: 0.1 M TBAPF$_6$; Pt electrode area 0.043 cm$^2$. 
Figure S8. Comparison between simulated and experimental oxidation waves for 0.7 mM F6 at different scan rates. The model for these oxidation simulations: $k_1^0 = 10000$ cm/s, $k_2^0 = 10000$ cm/s, $k_3^0 = 10000$ cm/s, $k_4^0 = 10000$ cm/s, simulated data: $E_1 = 1.17$ V, $E_2 = 1.24$ V, $E_3 = 1.34$ V, $E_4 = 1.46$ V; diffusion coefficient: $2 \times 10^{-6}$ cm$^2$/s, uncompensated resistance 740 $\Omega$, capacitance $6 \times 10^{-7}$ F. Experimental data: solvent: MeCN:Bz (1:1), supporting electrolyte: 0.1 M TBAPF$_6$, Pt electrode area 0.043 cm$^2$. 
Figure S9. Negative scan for 2 mM monomer (a), 1.2 mM dimer (b), 1 mM trimer (c), 0.9 mM tetramer (d), 0.17 mM pentamer (e) and 0.5 mM hexamer (f). Experimental conditions; solvent: THF, supporting electrolyte: 0.1 M TBAPF$_6$, Pt electrode area: 0.043 cm$^2$, scan rate: 0.5 V/s.
Figure S10. (a) Cyclic voltammogram of 0.4 mM F1 in 1:1 acetonitrile/benzene and 0.1 M TBAPF$_6$ on Pt UME, radius $a = 12.5$ µm. Scan rate = 100 mV/s. (b) Plot of the experimental ratio $i(t)/i_{ss}$ against the inverse square root of time of 0.5 mM F1 in 0.1 M TBAPF$_6$ with 12.5 µm radius Pt UME in 1:1 MeCN/Bz. First oxidation at step potential $E_{SP} = +1.85$ V vs Ag.
Figure S11. Bulk oxidation electrolysis of 0.57 mM F6 in the presence of 20 mM C\textsubscript{2}O\textsubscript{4}\textsuperscript{2-} and 0.1 mM TBAPF\textsubscript{6} in MeCN:Bz (1:1). (a) Current versus time, (b) charge versus time.

Figure S12. UV-Vis spectra of F6 before (red) and after (blue) oxidation bulk electrolysis. Inset, the amplification figure.
Figure S13. Fluorescence spectra of F6 before (a blue, c green) and after (b red, d purple) oxidation bulk electrolysis. Blue and red (a, b, 306 nm excitation), green and purple (c, d, 520 nm excitation).
Mass Spectral data following bulk electrolysis (oxidation) of F6 in an attempt to identify the species that emits in ECL experiments

Figure S14. Electrospray ionization mass spectra (ESI-MS) of F6 in the presence of $\text{C}_2\text{O}_4^{2-}$ before (a, b) and after (c, d) bulk electrolysis.
Figure S15. Chemical ionization mass spectra (CI-MS) of F6 in the presence of $C_2O_4^{2-}$ before (a, b) and after (c, d) bulk electrolysis.
Figure S16. Matrix assisted laser desorption ionization mass spectra (MALDI-MS) of F6 in the presence of C$_2$O$_4^{2-}$ before (a) and after (b) bulk electrolysis.
**Figure S17.** Current (black) and ECL (red) transients for 0.5 mM F6 in the presence of 20 mM C$_2$O$_4^{2-}$ generated by pulsing the potential from 0 to 1.60 V vs Ag in MeCN:Bz (1:1) containing 0.1 M TBAPF$_6$. Pulse width is 0.1 s.
Figure S18. The observation of electrochemical behavior/photoelectron spectroscopy/X-ray crystallography is consistent with pi-stacked structures (Ref 1: JACS 2003)