Supporting Information

Investigations Into Aqueous Redox Flow Batteries Based on Ferrocene Bisulfonate

Zhiling Zhao,† Baosen Zhang, Briana R. Schrage, Christopher J. Ziegler, and Aliaksei Boika**

Department of Chemistry, The University of Akron, Akron, OH 44325

**Co-corresponding authors. E-mails: aboika@uakron.edu (A.B.), ziegler@uakron.edu (C.J.Z.)*

†Present address: Institute for Bioscience and Biotechnology Research, University of Maryland, College Park, Maryland 20742, United States.

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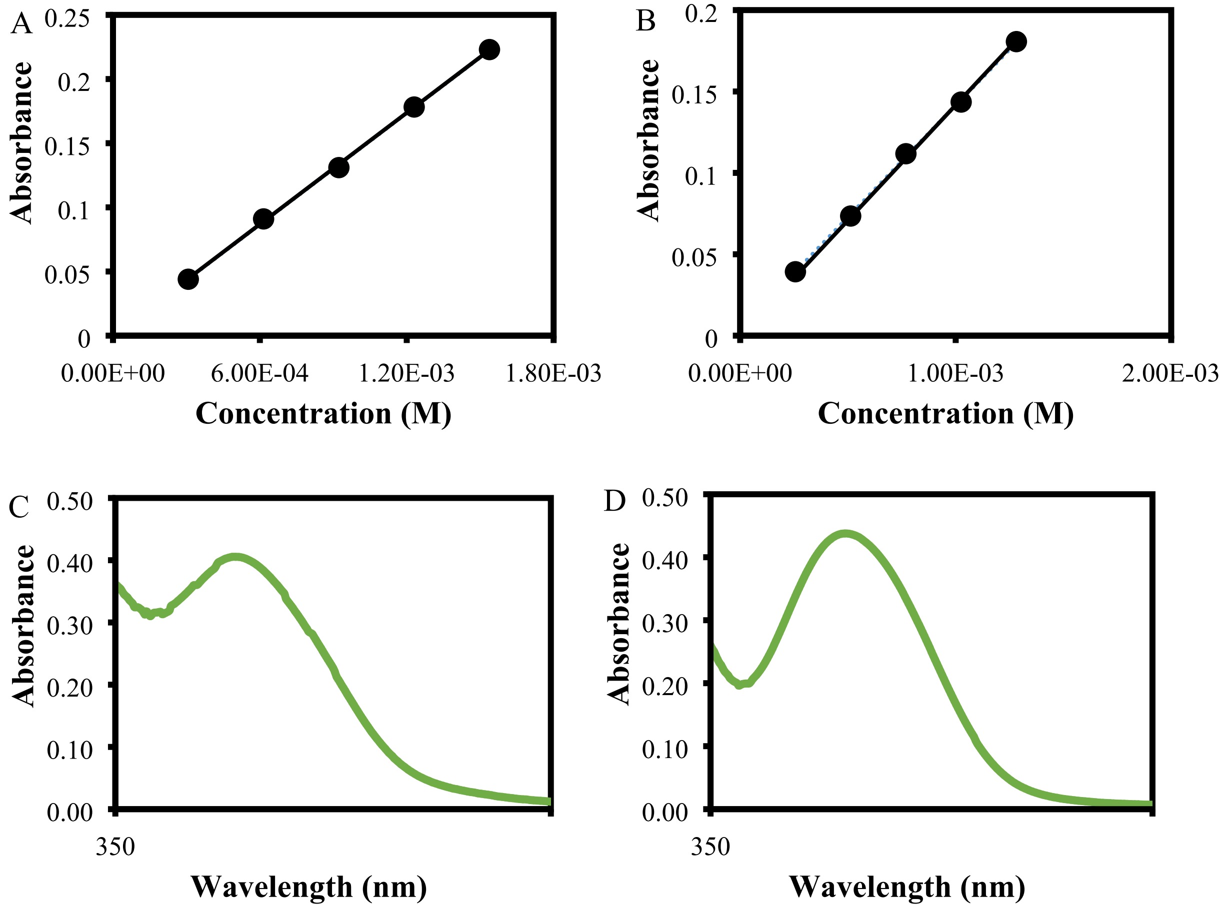


Figure S1. Solubility tests using UV–vis spectroscopy. A and B: Calibration curves for the relationship between absorbance and concentration of 1,1'-FcDS in 1 M $NaNO_3$ with (A) and without (B) the addition of 0.5 M EG. C and D: UV–vis spectra of diluted supernatant of 1,1'-FcDS supersaturated solutions prepared in 1 M $NaNO_3$ with (C: dilution 200 times) and without (D: dilution 100 times) the addition of 0.5 M EG.

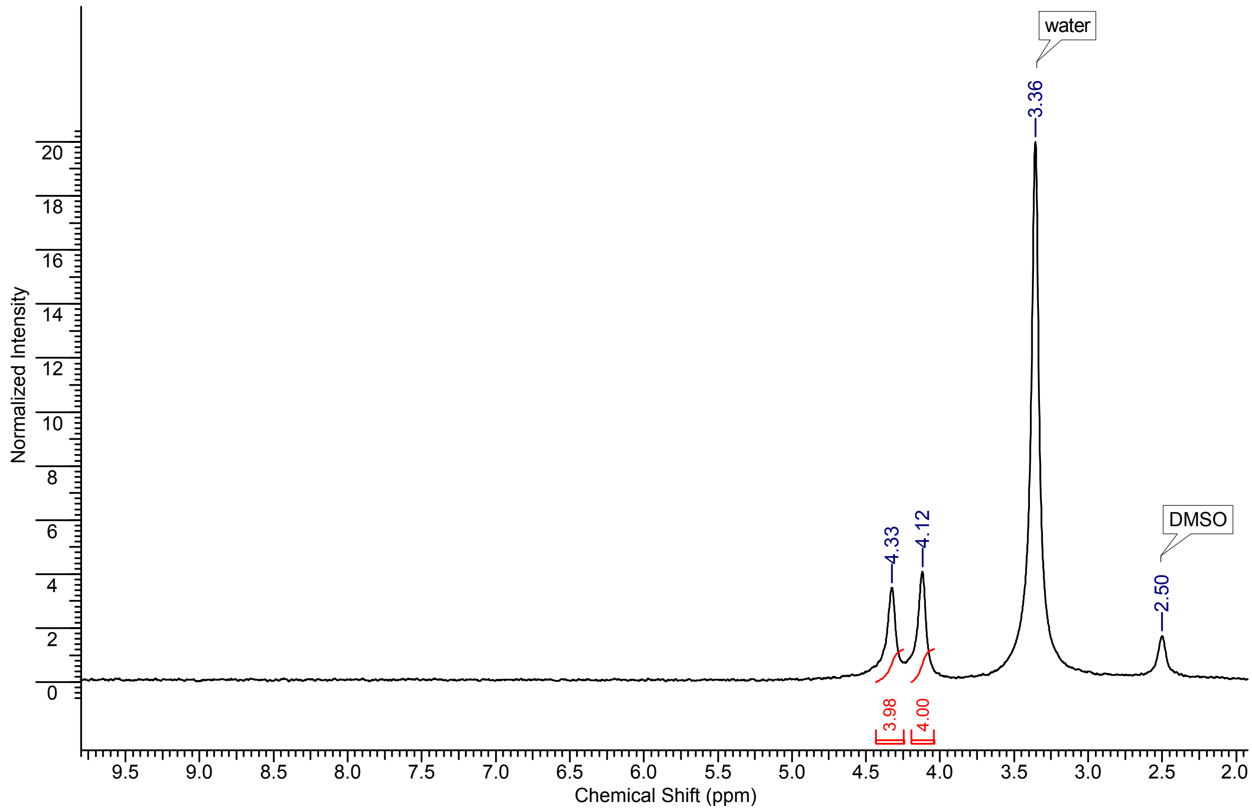


Figure S2. ^{1}H NMR (300 MHz) of **1,1'-FcDS** in d6-DMSO.

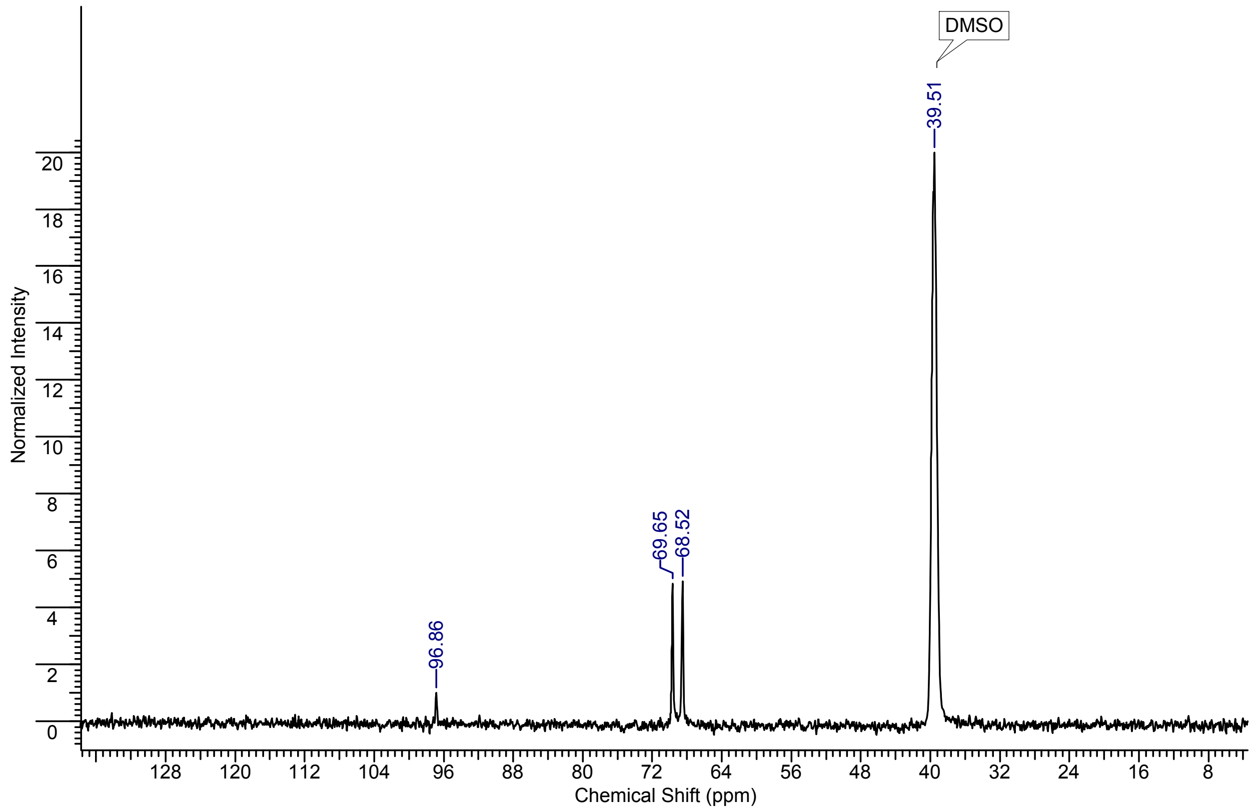
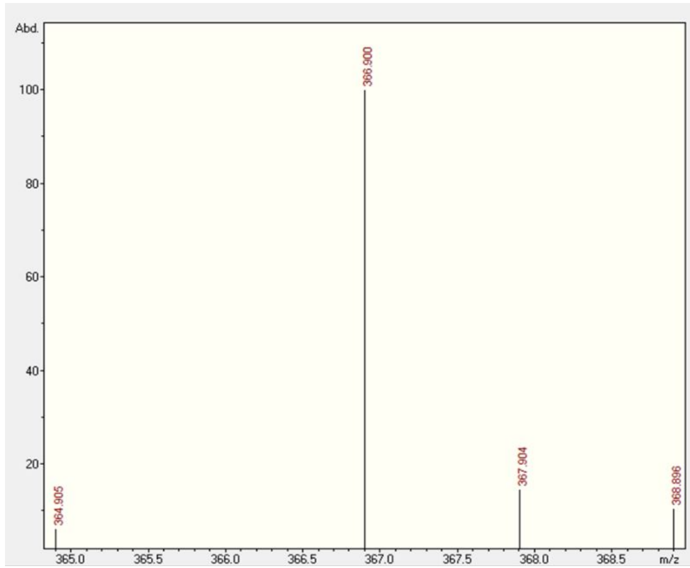


Figure S3. $^{13}C\{^{1}H\}$ NMR (125 MHz) of **1,1'-FcDS** in d6-DMSO.



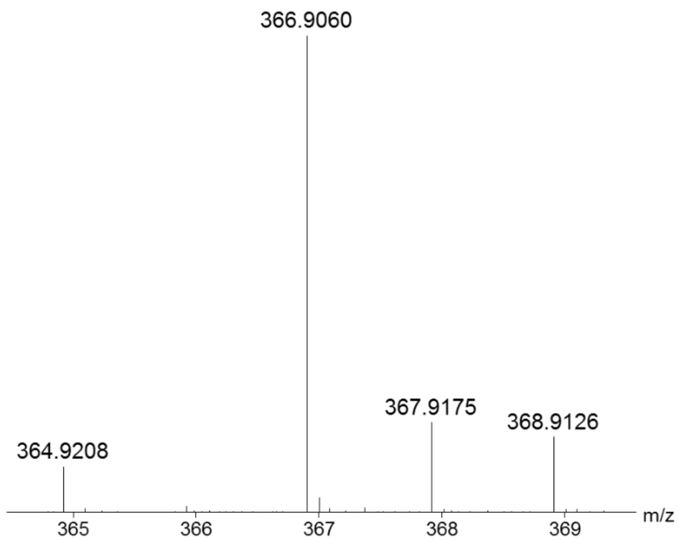


Figure S4. High-resolution ESI mass spectra of **1,1'-FcDS**. Top: calculated spectrum. Bottom: experimental spectrum.

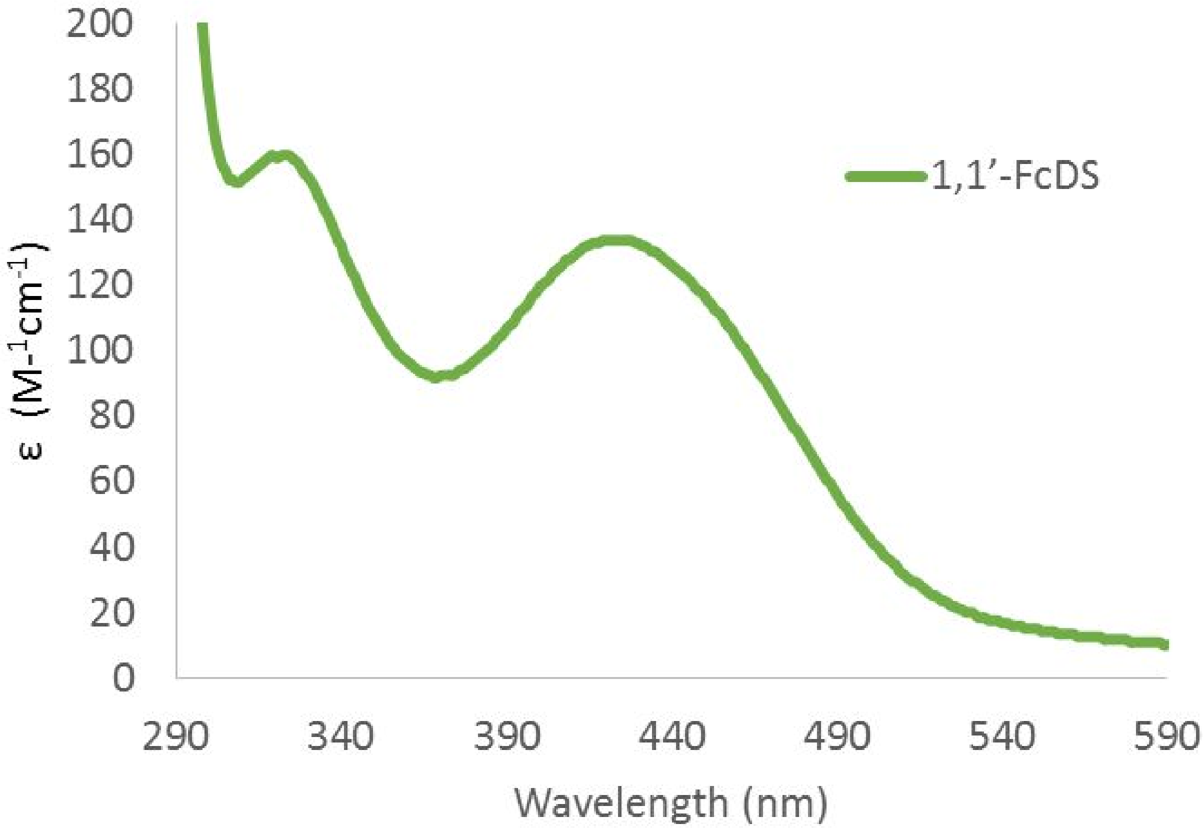


Figure S5. UV-visible spectrum for **1,1’-FcDS** in water.

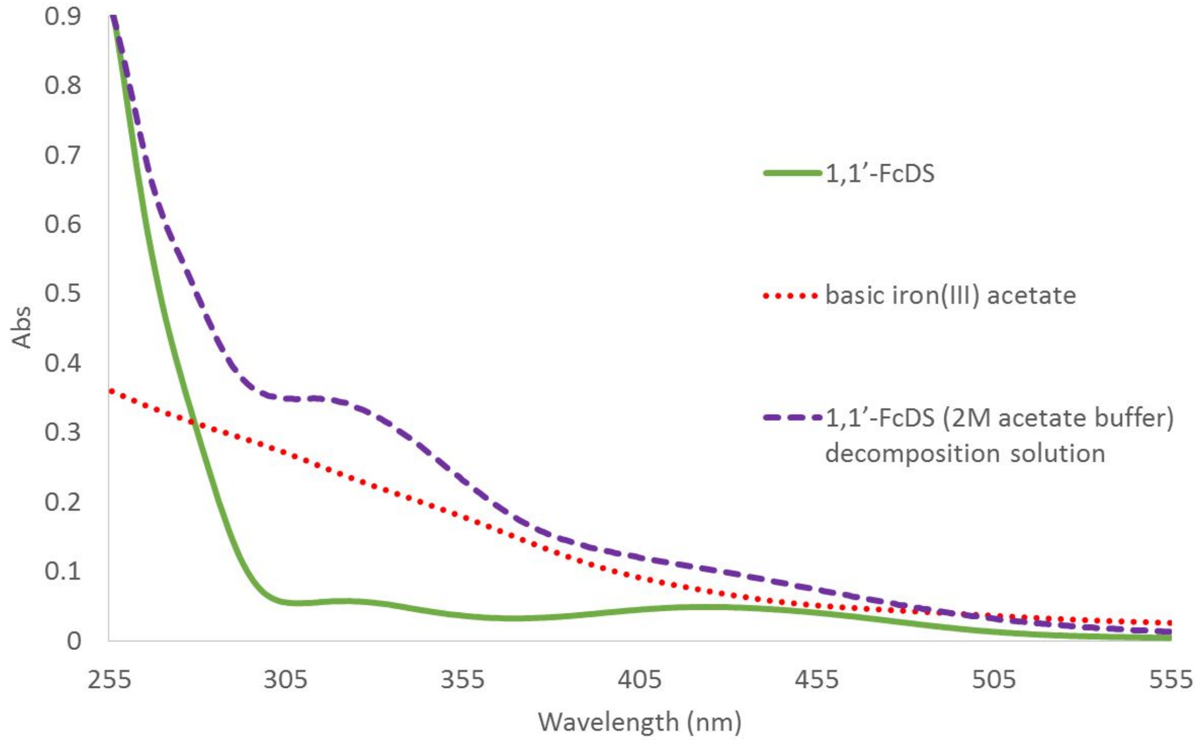


Figure S6. UV-visible spectra for **1,1’-FcDS**, basic iron(III) acetate, and the 1,1’-FcDS (2M acetate buffer) decomposition solution in water.

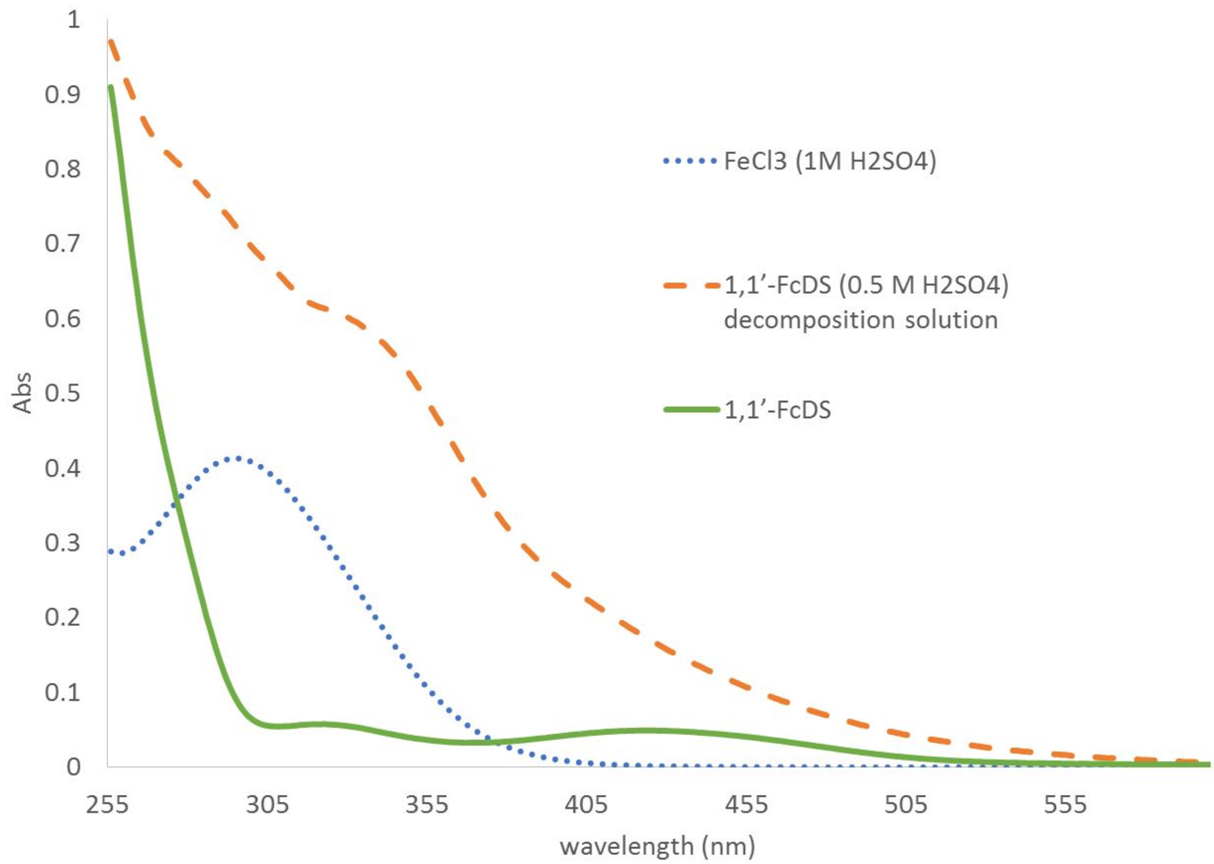


Figure S7. UV-visible spectra for **1,1’-FcDS**, $FeCl_3$ (1M H_2SO_4), and the 1,1’-FcDS (0.5 M H_2SO_4) decomposition solution in water.

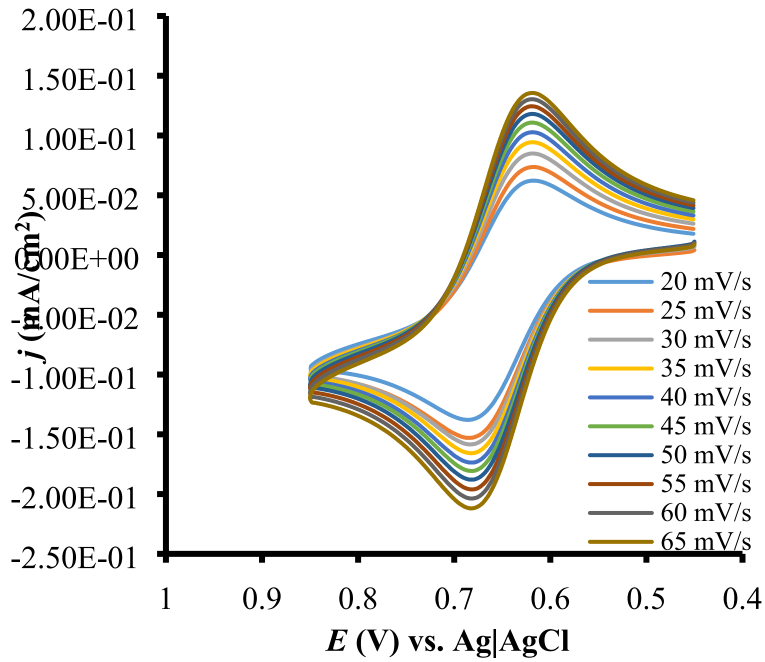


Figure S8. CVs of 2 mM 1,1'-FcDS in aqueous solution with 0.5 M EG. 1 M $NaNO_3$ was added as supporting electrolyte. Working electrode: 3 mm dia. glassy carbon, reference electrode: Ag|AgCl|KCl (2 M), counter electrode: platinum wire. From inner curve to outer one, the scan rate varies from 20 mV/s to 65 mV/s.

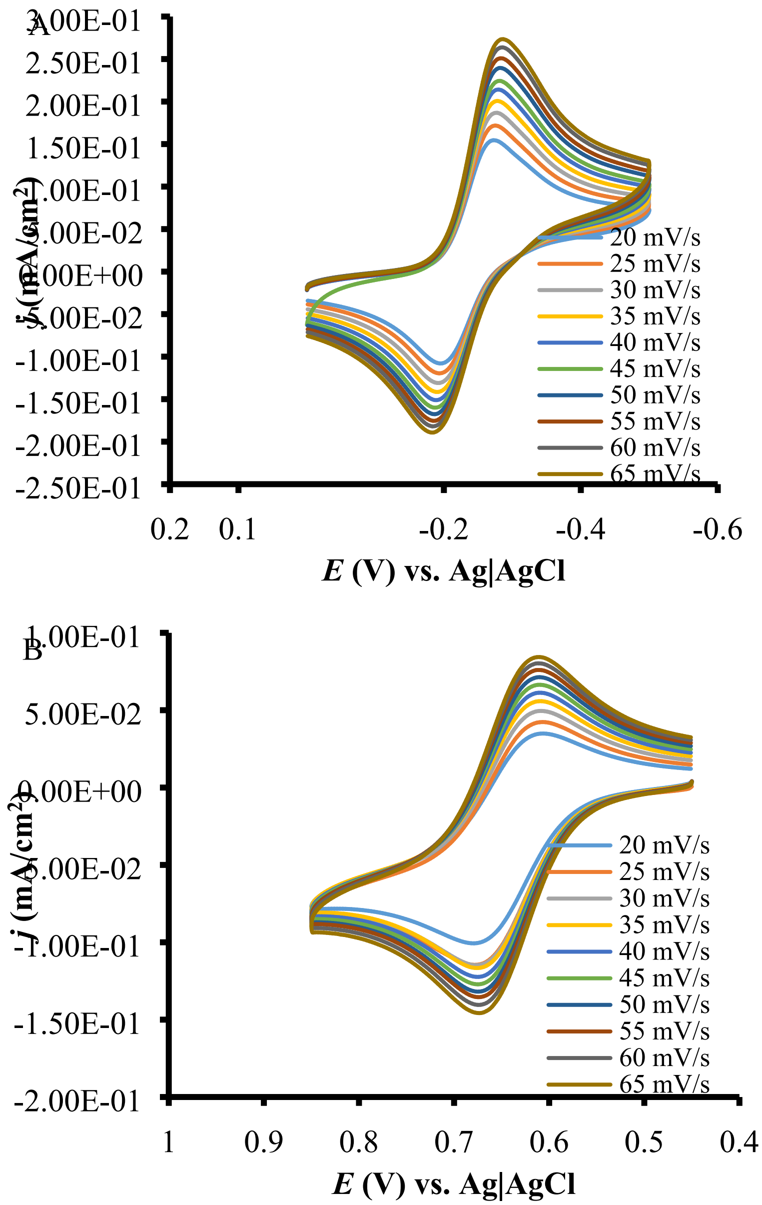


Figure S9. CVs of 2 mM 2,7-AQDS (A) or 2 mM 1,1'-FcDS (B) in aqueous solution. 2 M acetate buffer (pH:4.53) was added as supporting electrolyte. Working electrode: 3 mm dia. glassy carbon, reference electrode: Ag|AgCl|KCl (2 M), counter electrode: platinum wire. From inner curve to outer one, the scan rate varies from 20 mV/s to 65 mV/s.

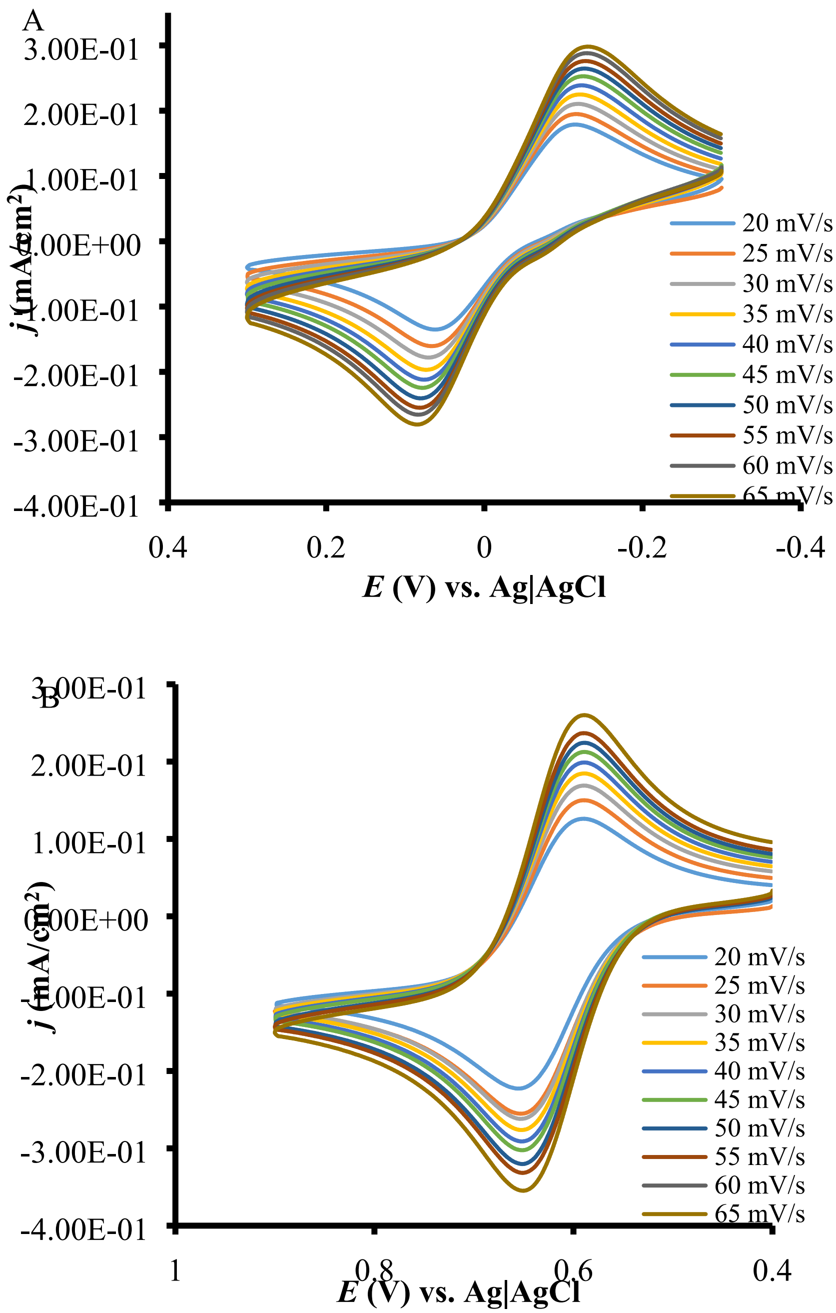


Figure S10. CVs of 3 mM 2,7-AQDS (A) or 3 mM 1,1'-FcDS (B) in aqueous solution. 0.5 M H_2SO_4 was added as supporting electrolyte. Working electrode: 3 mm dia. glassy carbon, reference electrode: Ag|AgCl|KCl (2 M), counter electrode: platinum wire. From inner curve to outer one, the scan rate varies from 20 mV/s to 65 mV/s.

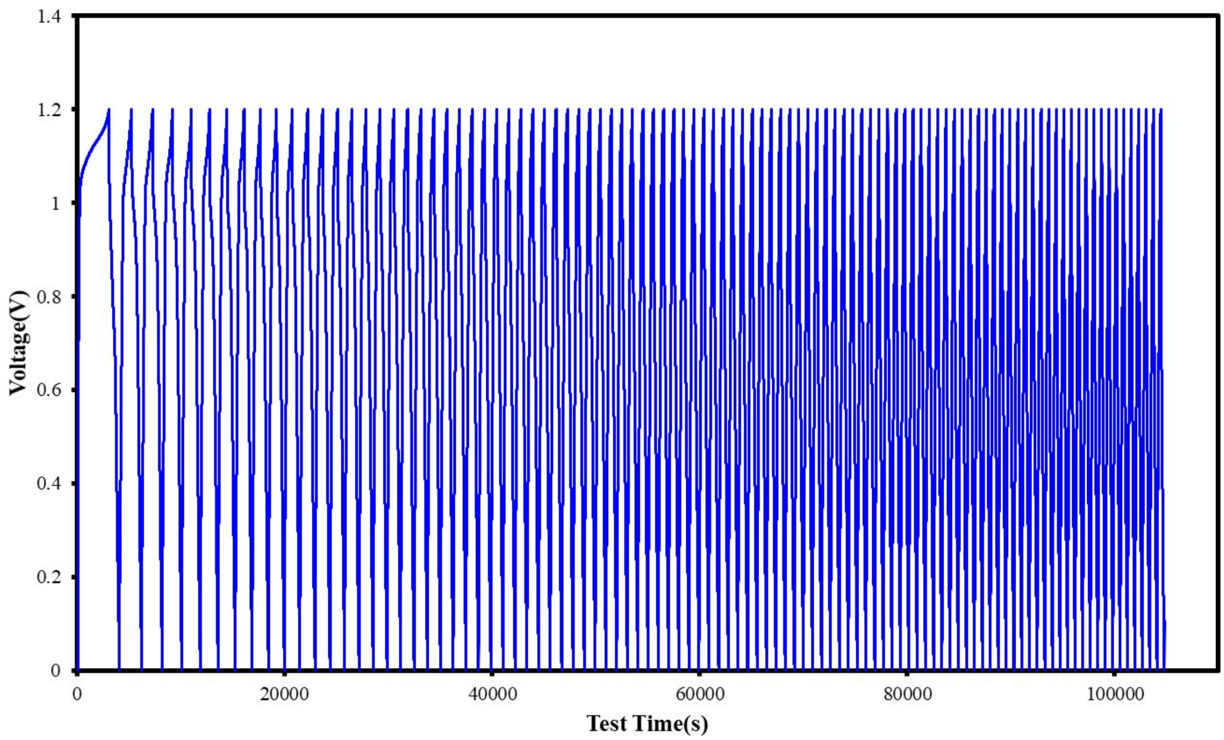


Figure S11. 100 charge and discharge cycles at constant current 25 mA for 1,1'-FcDS/2,7-AQDS RFB using 1 M $NaNO_3$ as supporting electrolyte (0.5 M EG added). Sodium ions serve as charge carriers during cell operation.

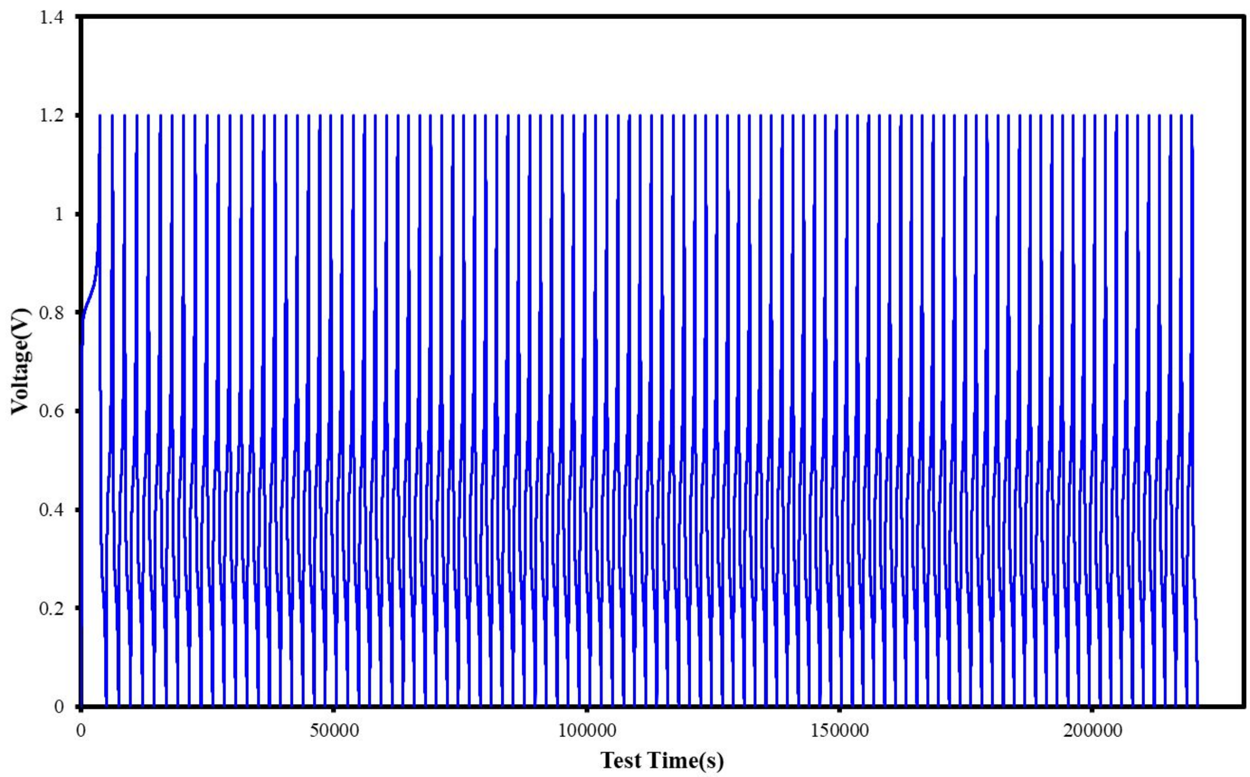


Figure S12. 100 charge and discharge cycles at constant current 25 mA for 1,1'-FcDS/2,7-AQDS RFB using 2 M acetate buffer as supporting electrolyte (0.5 M EG added). Sodium ions, as well as hydronium cations, serve as charge carriers during the cell operation.

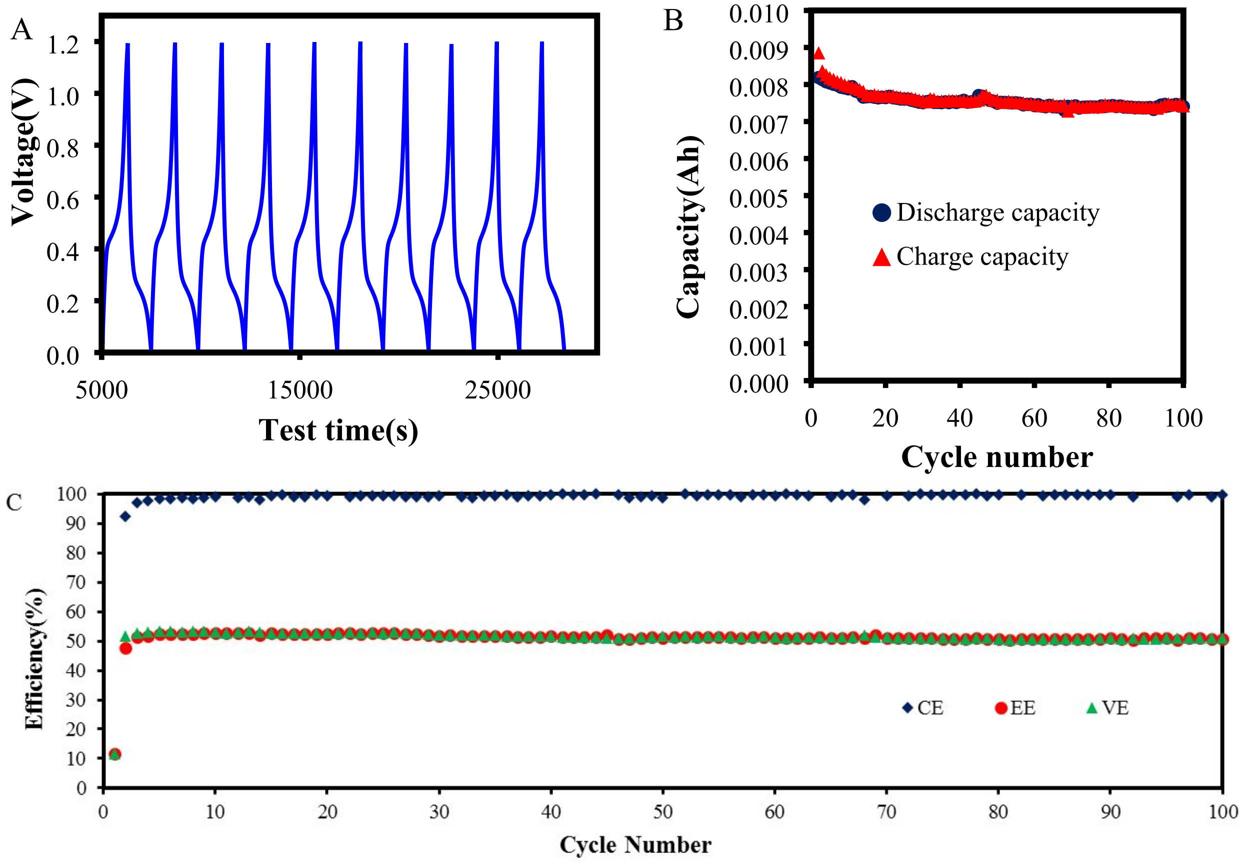


Figure S13. 1,1'-FcDS/2,7-AQDS RFB using 2 M acetate buffer as supporting electrolyte (0.5 M EG added). A: Ten charge and discharge cycles (#2 to #11 cycles) at constant current 25 mA; B: capacity vs cycling number; C: CE, EE and VE vs cycling number.

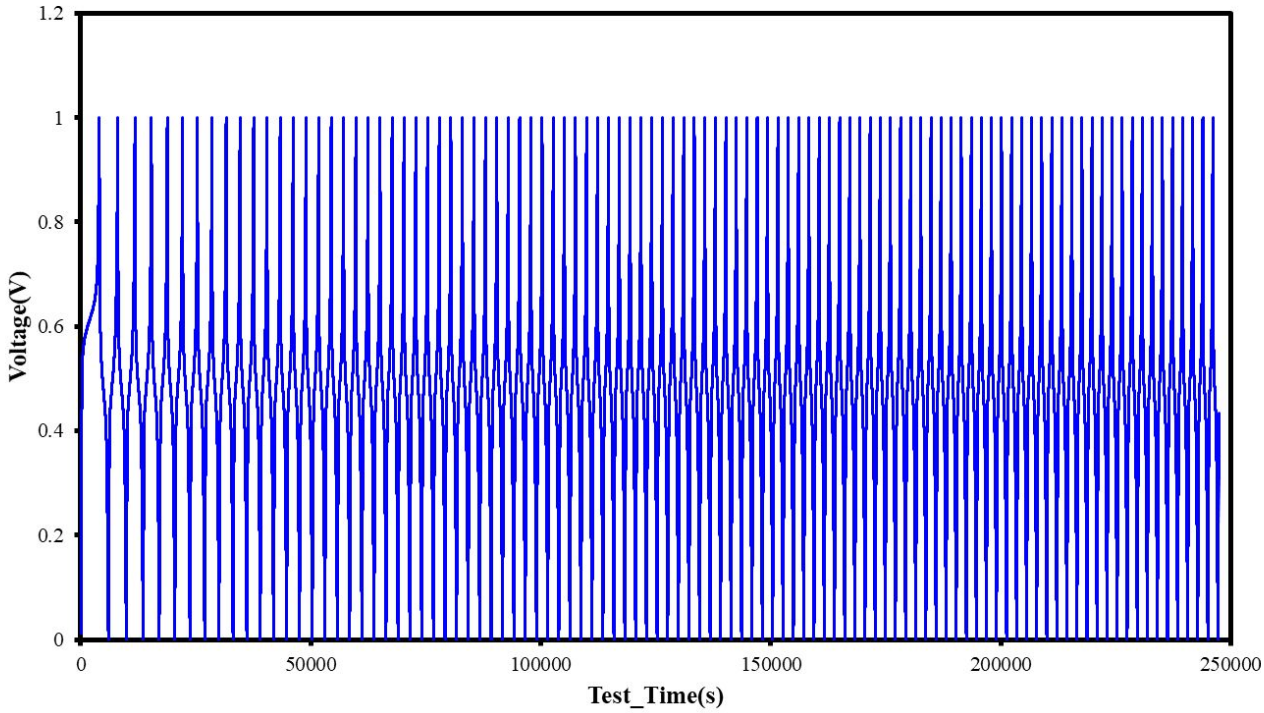


Figure S14. 100 charge and discharge cycles at constant current 25 mA for 1,1'-FcDS/2,7-AQDS RFB using 0.5 M H_2SO_4 as supporting electrolyte. Hydronium cations serve as charge carriers during the cell operation.

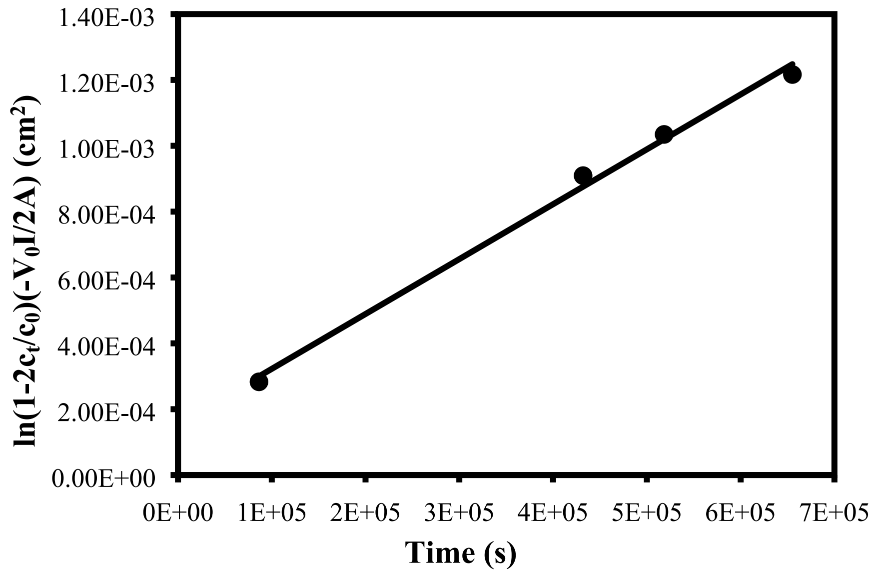


Figure S15. 1,1'-FcDS permeability calculation plot using $\boldsymbol{P} = \frac{\Delta \ln\left(1-\frac{2c_t}{c_0}\right)\left(\frac{V_0 I}{2A}\right)}{\Delta t}$, where $\boldsymbol{P}$ is permeability, $\boldsymbol{c_t}$ is the concentration of 1,1'-FcDS in the receiving side, $\boldsymbol{c_0}$ is the concentration of 1,1'-FcDS in the donating side (0.03 M), $\boldsymbol{V_0}$ is the volume of solution in reservoir (30 mL), $\boldsymbol{I}$ is the thickness of membrane (183 μm), $\boldsymbol{A}$ is the membrane effective area (9 cm^2), $\boldsymbol{t}$ is time interval. The permeability is 1.67 E-9 cm^2/s according to the slope of the trendline for plotted data.

Table S1. X-ray crystal data and structure parameters for compounds **2,7-AQDS** and **1,1'-FcDS.**

Compound	**2,7-AQDS**	**1,1'-FcDS**
CCDC	2009129	2009128
Empirical formula	$C_{96}H_{98}N_4Na_{12}O_{69}S_{12}$	$C_{10}H_{20}FeNa_2O_{12}S_2$
Formula weight	3072.38	498.21
Crystal system	Monoclinic	Triclinic
Space group	C2/m	P-1
a/ Å	20.109(2)	6.2579(4)
b/ Å	20.778(2)	6.7586(4)
c/ Å	15.8044(14)	23.6781(15)
α(°)	90	93.877(3)
β(°)	112.816(5)	96.594(3)
γ(°)	90	109.331(3)
Volume (Å^3)	6087.0(11)	932.77(10)
Z	2	2
Dc (Mg/m^3)	1.676	1.774
μ (mm^{-1})	0.370	1.137
F(000)	3156	512
reflns collected	102040	38129
indep. reflns	5544	4630
GOF on F^2	1.546	1.071
R1 (on F_o^2, $I > 2\sigma(I)$)	0.1796	0.0400
wR2 (on F_o^2, $I > 2\sigma(I)$)	0.4190	0.1284
R1 (all data)	0.2183	0.0472
wR2 (all data)	0.4383	0.1315