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Electronic Supplementary Information

Qualitative Extension of the EC' Zone Diagram to a Molecular Catalyst for a Multi-Electron, Multi-Substrate Electrochemical Reaction

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Index *Page*

Table S1. pK_a values in acetonitrile

Acid	***para*-substituent**	**pK_a**	**pK_a ref**
4-methoxyanilinium	–OCH_3	11.86	1
4-*tert*-butylanilinium	–$C(CH_3)_3$	11.1	2
anilinium	n/a	10.62	1
4-chloroanilinium	–Cl	9.7	2
4-trifluoromethoxyanilinium	–OCF_3	9.28	3
4-(methylbenzoate)anilinium	–$COOCH_3$	8.62	3
4-trifluoromethylanilinium	–CF_3	8.03	1
4-cyanoanilinium	-CN	7	4

Table S2. Summary of variables in Equations 3–4

Variable	**Definition**	**Units**
λ	*Kinetic* dimensionless parameter	n/a
γ	*Excess* dimensionless parameter	n/a
R	Gas constant (8.3144598 J K^{-1} mol^{-1})	J K^{-1} mol^{-1}
T	Temperature	K
F	Faraday constant (96,485.33289 C mol^{-1})	C mol^{-1}
k_e	Homogeneous electron transfer rate constant	L mol^{-1} s^{-1}
υ	Scan rate	V s^{-1}
C_A^0	Initial concentration of substrate A	mol L^{-1}
C_P^0	Initial concentration of catalyst P	mol L^{-1}

Impact of k_{obs} via pK_a on waveforms

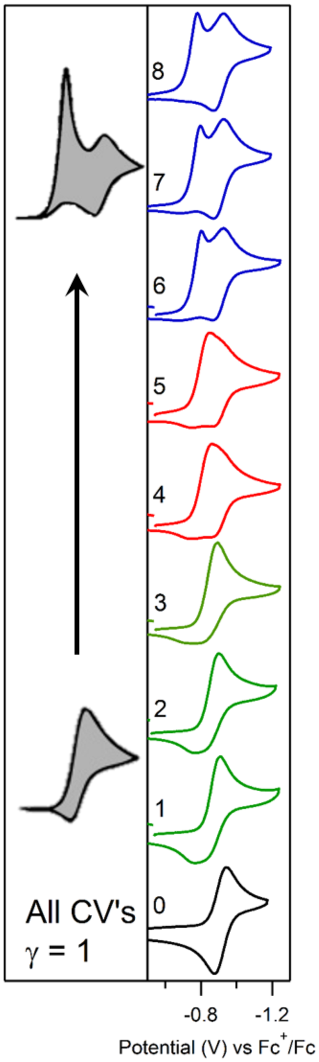

Figure S1. The left-side presents the expected waveform transformation for an ideal EC' system as k_e is increased. The right-hand side shows experimental data for an ECEC' system (**1**) reflecting changes made to k_{obs} via pK_a modification. Experimental cyclic voltammograms are of solutions containing complex **1** and 0) no substrate; 1) 4-methoxyanilinium; 2) 4-*t*-butylanilinium; 3) anilinium; 4) 4-chloroanilinium; 5) 4-trifluoromethoxyanilinium; 6) 4-(methylbenzoate)anilinium; 7) 4-trifluoromethylanilinium; 8) 4-cyanoanilinium. All solutions were at an excess factor γ = 1. All scans were performed at 100 mV/s in a 250 mM $[Bu_4N][PF_6]$ CH_3CN solution.

Calculating the rate of slow turnover

The second order rate constant k_2, describing the rate limiting step, is in the range of 3.39×10^1 to 3.28×10^2 M^{-1} s^{-1} for acids in which the broad oxidation is apparent (4-methoxyanilinium, 4-*t*-butylanilinium, anilinium). At $\gamma = 1$, 0.5 mM acid is present in solution.

$$k_2 \times [\text{substrate}] = k_{obs}$$

$$(3.39 \times 10^1\ M^{-1}\ s^{-1}) \times (0.0005\ M) \approx 0.02\ s^{-1}$$

$$(3.28 \times 10^2\ M^{-1}\ s^{-1}) \times (0.0005\ M) \approx 0.2\ s^{-1}$$

Impact of υ on waveforms

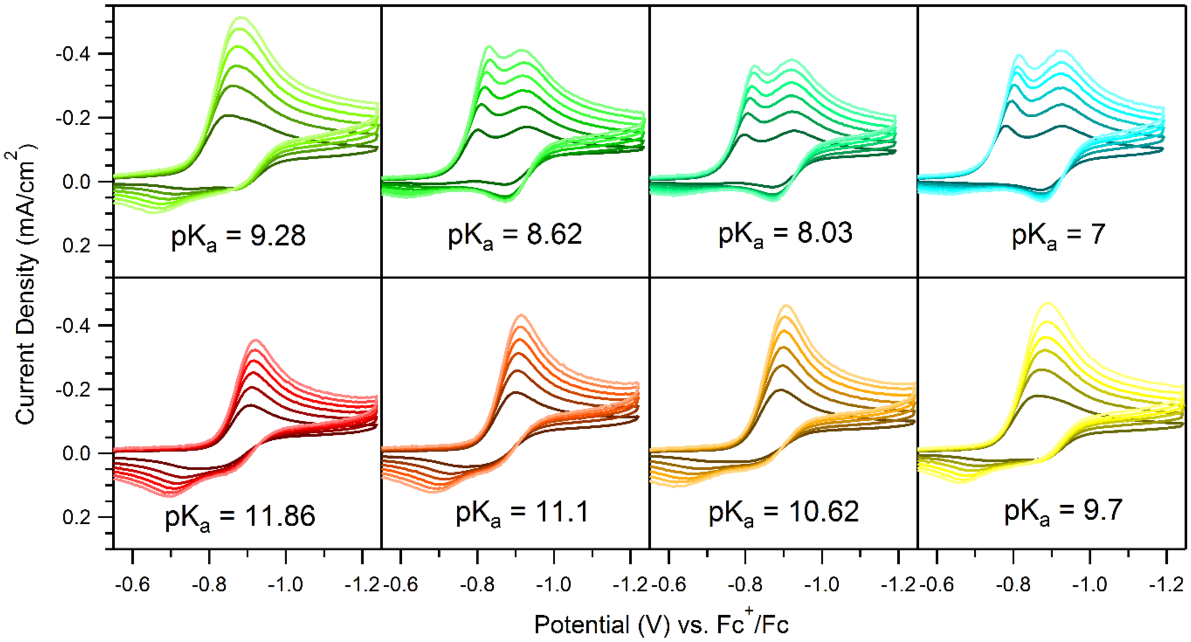

Figure S2. Each panel contains six voltammograms of solutions containing 0.5 mM **1** and 0.5 mM acid (respective pK_a values are indicated in each panel). The voltammograms in each panel were recorded at 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 V/s.

4-methoxyanilinium acid titrations

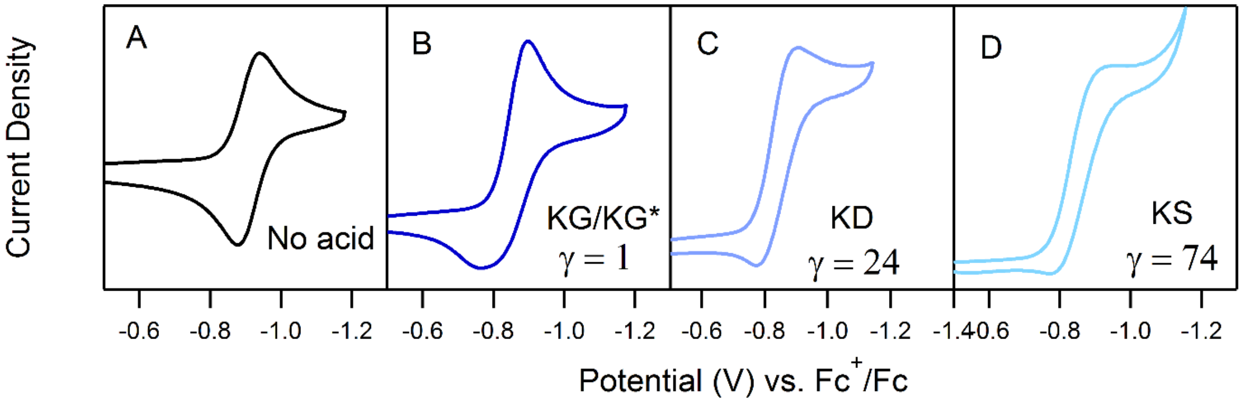

Figure S3. Cyclic voltammograms of a 0.5 mM solution of **1** with A) 0 mM; B) 0.5 mM; C) 12 mM; D) 37 mM 4-methoxyanilinium. The catalytic wave approaches a plateau-like shape, transforming from KG/KG* to KD and from KD to the boundary KS. All voltammograms recorded at 100 mV/s in a 250 mM $[Bu_4N][PF_6]$ CH_3CN solution.

4-trifluoromethoxyanilinium acid titrations

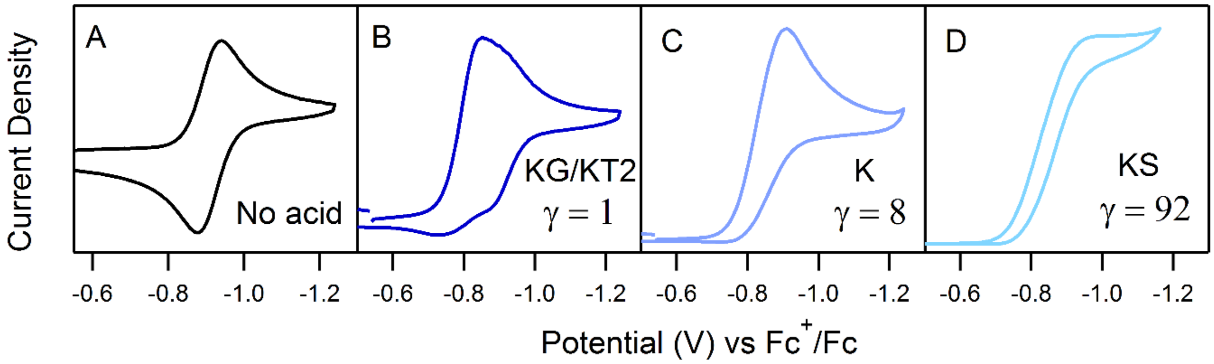

Figure S4. Cyclic voltammograms of a 0.5 mM solution of **1** with A) 0 mM; B) 0.5 mM; C) 4.0 mM; D) 46 mM 4-trifluoromethoxyanilinium. At high acid concentrations the catalytic wave approaches a plateau-like KS regime. All voltammograms produced at 100 mV/s in a 250 mM $[Bu_4N][PF_6]$ CH_3CN solution.

References

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