Supporting Information for:

Isolation and Characterization of a Neutral Imino-Semiquinone Radical

Shawn M. Carter,[a] Allyson Sia,[a] Michael J. Shaw,[*,b] and Alan F. Heyduk[*,a]

[a]*Department of Chemistry, University of California, Irvine, California, 92697*
[b]*Department of Chemistry, Southern Illinois University, Edwardsville, IL, 62026*

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Experimental Section

General Considerations. The complexes described below are air and moisture sensitive, necessitating that manipulations be carried out under an inert atmosphere of argon or nitrogen gas using standard Schlenk, vacuum-line, and glovebox techniques. Hydrocarbon solvents were sparged with nitrogen and then deoxygenated and dried by passage through Q5 and activated alumina columns, respectively. Ethereal and halogenated solvents were sparged with nitrogen and then dried by passage through two activated alumina columns. To test for effective oxygen and water removal, nonchlorinated solvents were treated with a few drops of a purple solution of sodium benzophenone ketyl in THF. 4,6-di-tertbutyl-2(tertbutyl-amino)phenol (apH$_2$) was prepared as previously described.[1] 2,2,2-Trifluoroacetamide (97%), tetrabutyammonium acetate (97%) and tetrabutylammonium chloride (97%) were purchased from Sigma-Aldrich Co. Both the trifluoroacetamide and the tetrabutylammonium acetate were placed overnight under high-vacuum prior to use, while the tetrabutylammonium chloride was recrystalized three times from its melt under high-vacuum prior to use. Saccharin (98+%) was purchased from Acros Organics and placed overnight under high-vacuum prior to use. nBuLi (2.81 M in hexane) was purchased from Alfa Aesar and used as received. NaH (57-63 % in an oil dispersion) was purchased from Alfa Aesar and washed with heptane prior to use. PhICl$_2$ was prepared according to literature procedures and used as a solid.[2] For the electrochemical experiments, ferrocene (98%), tetrabutylammonium hexafluorophosphate (98%), and cobaltocenium hexafluorophosphate (98%), were purchased from Acros Organics and purified in the standard way prior to use, i.e., ferrocene was sublimed, tetrabutylammonium hexafluorophosphate was recrystallized from ethanol three times and dried under vacuum and cobaltocenium hexafluorophosphate was recrystallized from CH$_2$Cl$_2$/tolune.[3]

Physical Measurements. NMR spectra were collected on Bruker Avance 400 and 500 MHz spectrometers in dry, degassed benzene-d6. ^{1}H NMR spectra were referenced to TMS using the residual proteo impurities of the solvent; ^{13}C NMR spectra were referenced to TMS using the natural abundance ^{13}C impurities of the solvent. All chemical shifts are reported using the standard notation in parts per million; positive chemical shifts are to a higher frequency from the given reference. Perpendicular mode X-band electron paramagnetic resonance spectra were collected using a Bruker EMX spectrometer equipped with an ER4102ST

cavity and ER041XG microwave bridge. The instrument was previously calibrated using DPPH. EPR spectra were collected using the following spectrometer settings: attenuation, 25 dB; microwave frequency, 9.77 GHz; microwave power, 0.638 mW; sweep width, 30.000 G; modulation frequency, 100 kHz; modulation amplitude, 2.02 G; gain, 1.00×10^3; conversion time, 40.960 ms; time constant, 327.680 ms, resolution, 512 points. Infrared spectra were recorded as KBr pellets with a Perkin-Elmer Spectrum One FTIR spectrophotometer. Electronic absorption spectra were recorded with a Perkin-Elmer Lambda 800 UV/vis spectrophotometer.

Electrochemical measurements were recorded using a Gamry G300 potentiostat (Gamry Instruments, Warminster, PA, USA). For all electrochemical experiments, a 3.0 mm diameter Pt disk electrode was used as the working electrode, a silver wire acted as the reference electrode, and a platinum wire served as the auxiliary electrode. Experiments were performed at room temperature, either in a glovebox or were under an atmosphere of pre-purified Argon in a solution of the analyte in DMSO containing 1.0 M NBu_4PF_6 as supporting electrolyte. All potentials are referenced to the Fc^+/Fc couple set at 0.00 V[4], except for the electrochemical measurement of apH_2. Cobaltacenium was used as an internal reference since ferrocene's redox features obscured those of apH_2, but these potentials are referenced to the Fc^+/Fc couple. The typical solvent system window with our configuration was 0.41 V for the oxidation limit and -1.8 V for the reduction limit (vs. the Fc^+/Fc couple).

Preparation of tetrabutylammonium trifluoroacetamide, [Bu₄N][NHCOCF₃]. 2,2,2-Trifluoroacetamide (114.9 mg, 1.02 mmol) was dissolved in THF (ca. 10 mL). NaH (26.0 mg, 1.08 mmol) was slowly added to the clear, stirring solution, resulting in gas evolution. After stirring the clear solution for 2 hr, tetrabutylammonium chloride (286 mg, 1.03 mmol) was added to the solution and the mixture was further stirred overnight. A white, cloudy NaCl precipitate was observed in the mixture and was filtered. The clear filtrate was collected dried in vacuo, resulting in the isolation of [Bu₄N][NHCOCF₃] as an off-white solid.

Preparation of (*E*)-4,6-di-*tert*-butyl-2-(*tert*-butylimino)-cyclohexa-3,5-dienone (iq). apH_2 (1.0 g; 3.61 mmol) was dissolved in Et₂O (10 mL). The clear solution was chilled to just above freezing and two equivalents of *n*BuLi (2.56 ml; 7.2 mmol) were slowly syringed into the stirring mixture. The resulting clear, yellow solution was allowed to warm to room temperature with stirring. The mixture was once again chilled to

just above freezing and PhICl$_2$ (1.022 g; 3.61 mmol) was slowly added to the stirring solution. Upon addition, the solution turned dark opaque blue followed by opaque green, then a mustard yellow a few minutes later. The mixture was stirred overnight, filtered and the bright yellow solid was washed with pentane (3 x 8 mL). Soxhlet extraction of iq with pentane (150 mL) was carried out over 2 days. The resulting light brown solution was dried in vacuo and the orange-brown iq was obtained in 89% yield. ^{1}H NMR showed the presence of a major E and minor Z isomeric forms of the compound. ^{1}H NMR (500 MHz, C$_6$D$_6$, 25° C): δ 6.77 (d, 1H, J = 2.3 Hz, E isomer), 6.75 (d, 0.2H, J = 2.3 Hz, Z isomer), 6.49 (d, 1H, J = 2.3 Hz, E isomer), 6.43 (d, 0.2H, J = 2.3 Hz, Z isomer), 1.55 (s, 2H, Z isomer), 1.35 (s, 9H, E isomer), 1.24 (s, 9H, E isomer), 1.23 (s, 2H, Z isomer), 0.90 (s, 9H, E isomer), 0.89 (s, 2H, Z isomer). ^{13}C NMR (500 MHz, C$_6$D$_6$, 25° C): δ 186.86 (CO), 184.58 (CO), 158.18 (aryl C), 156.84 (aryl C), 150.76 (aryl C), 149.38 (aryl C), 148.91 (aryl C), 147.62 (aryl C), 133.07 (aryl C), 132.10 (aryl C), 115.65 (aryl C), 59.54 (C(CH$_3$)), 57.90 (C(CH$_3$)), 35.50 (C(CH$_3$)), 35.17 (C(CH$_3$)), 35.00 (C(CH$_3$)), 34.35 (C(CH$_3$)), 31.45 (C(CH_3)), 30.43 (C(CH_3)), 29.81 (C(CH_3)), 29.60 (C(CH_3)), 28.55 (C(CH_3)), 28.46 (C(CH_3)). IR (cm^{-1}): 1627, 1667, 2872, 2909, 2969, 3042. HRMS (EI) calcd for C$_{18}$H$_{29}$NO [M + Na]$^+$ 298.2147, found 298.2147.

Formation of the imino-semiquinone radical (isqH$^{\bullet}$). The isqH species is generated by the 1:1 mixture of apH$_2$ with iq in solution. In solution, isqH is a clear, bold green-blue color. IR (cm^{-1}) 1627, 1666, 2871, 2908, 2961, 3287.

X-ray Crystallography

iq. X-Ray quality crystals were grown from a saturated pentane at –30º C. An orange crystal of approximate dimensions 0.18 x 0.34 x 0.37 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART program package was used to determine the unit-cell parameters and for data collection (30 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/c$ that was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis. Hydrogen atoms were located geometrically then allowed to refined (x,y,z and U_{iso}). There were two molecules of the formula unit present (Z = 8). At convergence, wR2 = 0.1251 and Goof = 1.030 for 593 variables refined against 7231 data (0.80Å), R1 = 0.0460 for those 5239 data with I > 2.0(I).

apH$_2$ and isqH$^•$. X-Ray quality crystals were grown from a saturated CH$_3$CN at –30º C. A blue plate 0.15 x 0.10 x 0.02 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 10 seconds per frame using a scan width of 0.5°. Data collection was 99.3% complete to 67.00° in θ. A total of 25504 reflections were collected covering the indices, -12<=h<=11, -12<=k<=7, -38<=l<=38. 6176 reflections were found to be symmetry independent, with an R_{int} of 0.0260. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P2(1)/n (No. 14). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SIR-2004) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms, with the exception of hydroxyl and amino hydrogen atoms, were placed

using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. The hydroxyl and amino hydrogen atoms H1O, H1N, and H2N were located from the Fourier difference map and their positions were refined isotropically.
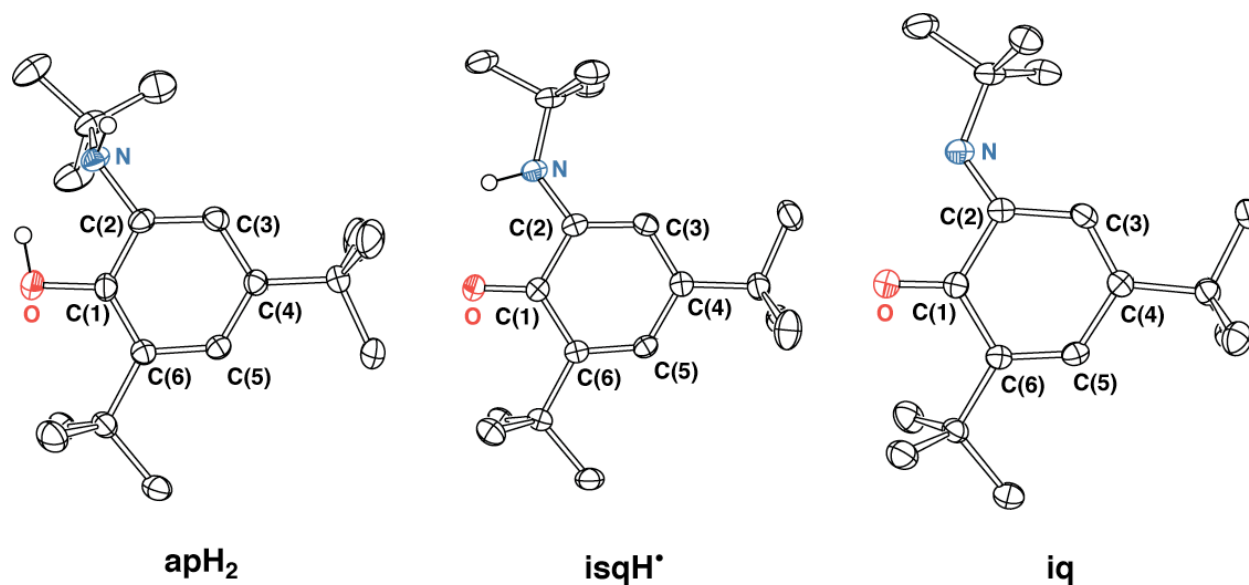

Figure S1. ORTEP diagrams of apH$_2$, isqH$^\bullet$, and iq.
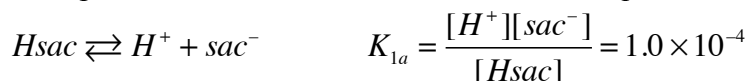
Table S1. Select bond distances (Å) for apH$_2$, isqH$^\bullet$, and iq.

	Bond Distances / Å		
	apH2	isqH$^\bullet$	iq
O–C(1)	1.3680(16)	1.2577(14)	1.215(2)
N–C(2)	1.4393(16)	1.3455(16)	1.283(2)
C(1)–C(2)	1.4025(18)	1.4716(17)	1.533(2)
C(2)–C(3)	1.3793(18)	1.4047(17)	1.456(2)
C(3)–C(4)	1.3960(18)	1.3747(18)	1.347(2)
C(4)–C(5)	1.3915(17)	1.4294(17)	1.467(2)
C(5)–C(6)	1.3977(18)	1.3644(17)	1.345(2)
C(6)–C(1)	1.3942(18)	1.4502(17)	1.485(2)

Spectrophotometric Titrations

Determination of the pKa Value for iq. The pKa value of iq in DMSO was determined through spectrophotometric titrations with saccharin (pKa = 4.0 in DMSO)[5] using UV/Vis spectroscopy. In a septum sealed, quartz cuvette, 3.0 mL of a 0.0886 mM solution of iq in DMSO was titrated with a 12.2 mM DMSO solution of saccharin, which was added in 25 µL aliquots until an absorbance plateau was reached at 467 nm in the optical spectrum (~18 total equivalence of saccharin were added) (Fig. S2). This experiment was repeated two more times, each ending with similar results. The extinction coefficient of the chromophore (iqH$^+$) at 467 nm was inferred from the plot of absorbance vs. [Titrant]. The equilibrium constant for this reaction was determined using the fitting program KaleidoGraph$^®$ 4.0 and plotting (mole iqH$^+$ vs. mole saccharin) against the quadratic equation. Weighted least-squares values of ≥0.998 were obtained in each case and the average Keq value from the three experiments was used to calculate the pKa as shown below:

$$iq + Hsac \rightleftarrows iqH^+ + sac^- \qquad K_{eq} = \frac{[iqH^+][sac^-]}{[iq][Hsac]} = 0.680$$

The above equilibrium can be expressed in terms of the acid dissociation equilibria of Hsac and iqH$^+$,

$$Hsac \rightleftarrows H^+ + sac^- \qquad K_{1a} = \frac{[H^+][sac^-]}{[Hsac]} = 1.0 \times 10^{-4}$$

$$iqH^+ \rightleftarrows H^+ + iq \qquad K_{2a} = \frac{[H^+][iq]}{[iqH^+]}$$

$$K_{eq} = \frac{[iqH^+][sac^-]}{[iq][Hsac]} = \frac{K_{1a}}{K_{2a}}$$

$$K_{2a} = \frac{K_{1a}}{K_{eq}} = \frac{1.0 \times 10^{-4}}{0.680} = 1.47 \times 10^{-4}$$
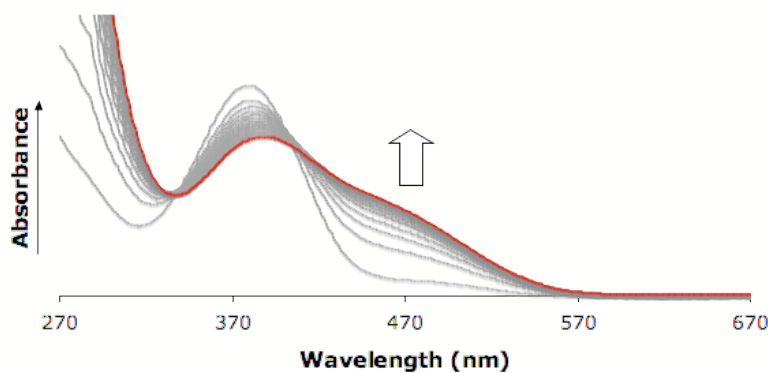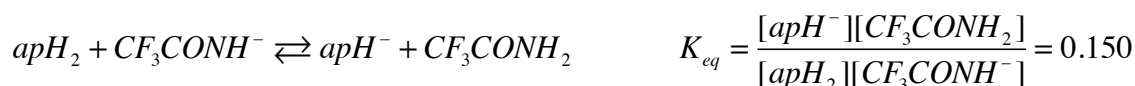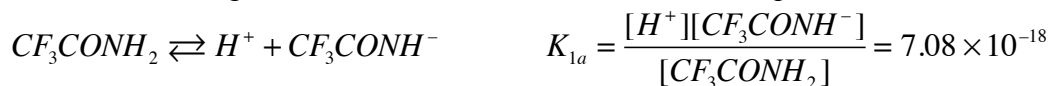
$$pK_{2a} = -\log K_{2a} = 3.83$$

Figure S2. UV/Vis spectrophotometric titration of iq with saccharin in DMSO.

Determination of the pKa value for apH$_2$. The pKa value of apH$_2$ in DMSO was determined using the spectrophotometric method described above, except the 0.119 mM DMSO solution of apH$_2$ (3.0 mL) was titrated with 1.48 mM tetrabutylammonium trifluoroacetamide, [Bu$_4$N][NHCOCF$_3$] (NH$_2$COCF$_3$ has a pKa of 17.15 in DMSO)[5]. Addition of 25 – 100 µL aliquots of the [Bu$_4$N][NHCOCF$_3$] solution to the apH$_2$ solution (~2 total equivalents of [Bu$_4$N][NHCOCF$_3$] were added) resulted in an absorbance plateau at 332 nm (Fig. S3). Data treatment similar to what was described above and the calculations follow below:

$$apH_2 + CF_3CONH^- \rightleftharpoons apH^- + CF_3CONH_2 \qquad K_{eq} = \frac{[apH^-][CF_3CONH_2]}{[apH_2][CF_3CONH^-]} = 0.150$$

The above equilibrium can be expressed in terms of the acid dissociation equilibria of CF$_3$CONH$_2$ and apH$_2$,

$$CF_3CONH_2 \rightleftharpoons H^+ + CF_3CONH^- \qquad K_{1a} = \frac{[H^+][CF_3CONH^-]}{[CF_3CONH_2]} = 7.08 \times 10^{-18}$$

$$apH_2 \rightleftharpoons H^+ + apH^- \qquad K_{2a} = \frac{[H^+][apH^-]}{[apH_2]}$$

$$K_{eq} = \frac{[apH^-][CF_3CONH_2]}{[apH_2][CF_3CONH^-]} = \frac{K_{2a}}{K_{1a}}$$

$$K_{2a} = K_{eq} \times K_{1a} = (0.150)(7.08 \times 10^{-18}) = 1.06 \times 10^{-18}$$
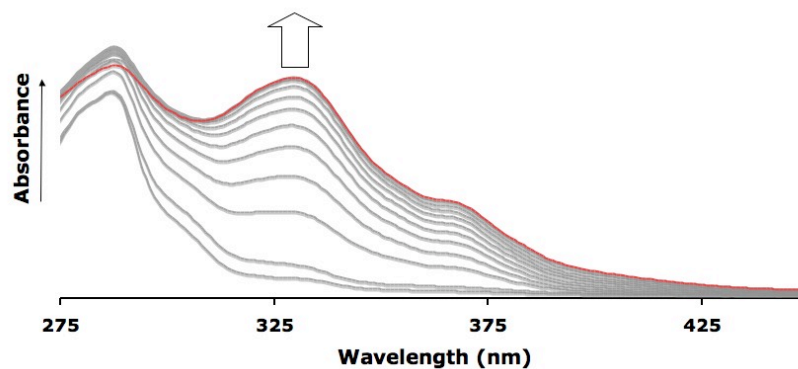
$$pK_{2a} = -\log K_{2a} = 18.0$$

Figure S3. UV/Vis spectrophotometric titration of apH$_2$ with [Bu$_4$N][NHCOCF$_3$] in DMSO.

Spectrophotometric Titration of iq with apH$_2$. Determination of the Keq of the conproportionation reaction between iq and apH$_2$ in DMSO, CH$_2$Cl$_2$, and toluene was done using spectrophotometric titrations similar to those described above (Fig S4 – S6). The following is representative: 3.0 mL of an orange 0.186 mM solution of iq in DMSO was titrated with a clear 1.59 mM DMSO solution of apH$_2$, which was added in 3 - 50 µL aliquots until an absorbance plateau was reached at 734 nm in the optical spectrum (~3 total equivalence of apH$_2$ were added) (Fig. S4). The resulting solution was green-blue. Additionally, the experiment was repeated with d-apH$_2$ (prepared by stirring apH$_2$ in d_6-MeOH for 0.5 hr, prior to drying in vacuo) in DMSO with similar results.
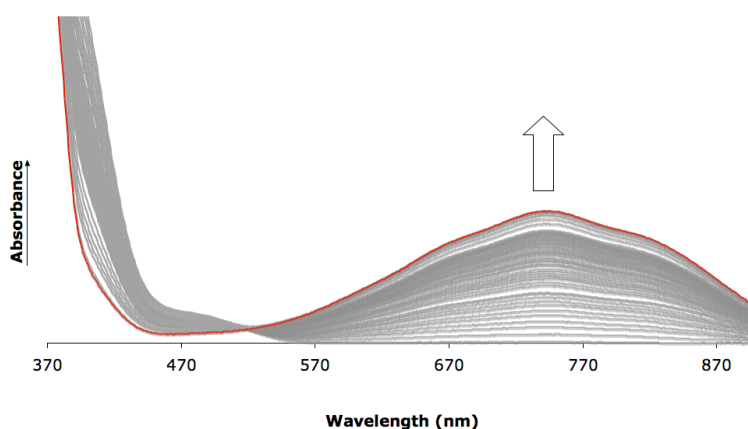

Figure S4. UV/Vis of conproportionation reaction of apH$_2$ with iq to form isqH$^•$ in DMSO.
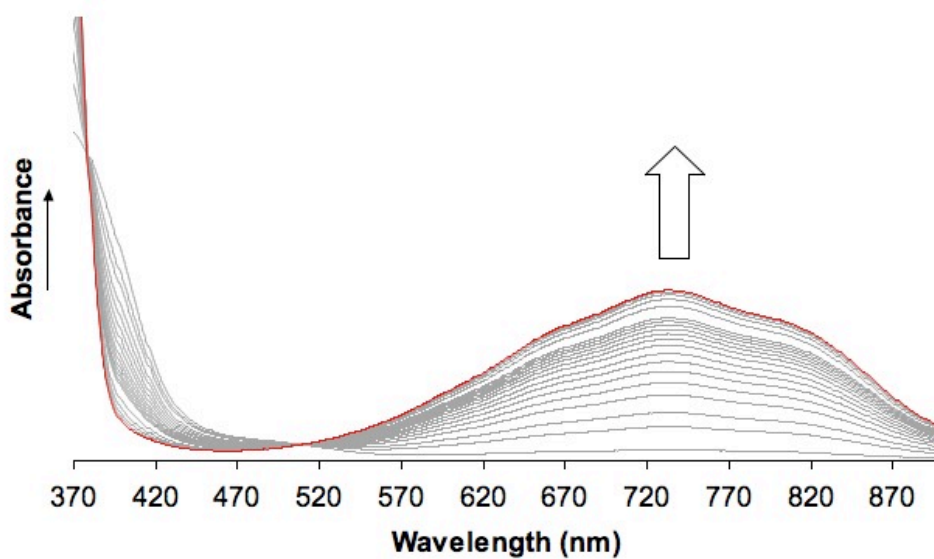
Figure S5. UV/Vis of conproportionation reaction of apH_2 with iq to form $isqH^\bullet$ in Toluene.
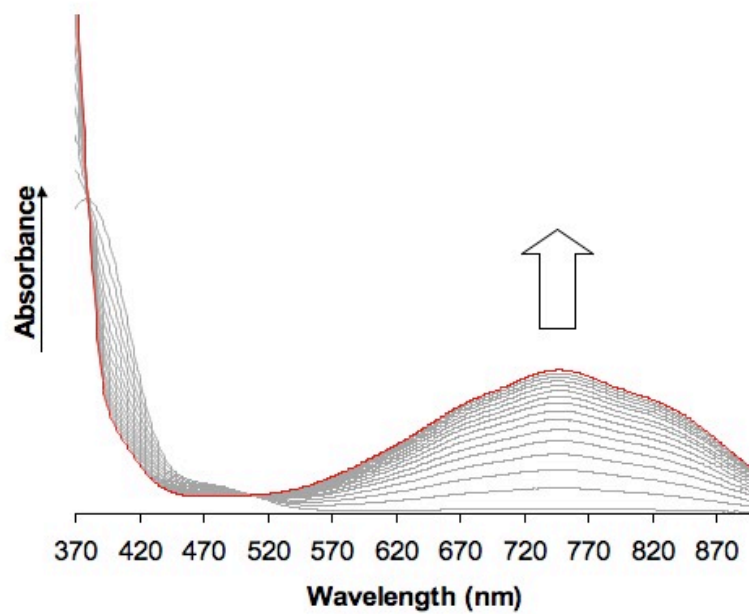

Figure S6. UV/Vis of conproportionation reaction of apH_2 with iq to form $isqH^\bullet$ in CH_2Cl_2.

Cyclic Voltammetry Experiments

apH₂. The response feature of the cyclic voltammogram for apH$_2$ shows a major oxidation couple at 0.060 V, which is partially reversible (i_{pa}/i_{pc} = 0.84; ΔE = 272 mV) at 200 mV s^{-1}, with a daughter peak at -0.810 V (Fig. S7).

iq. The response feature of the cyclic voltammogram for iq has a major reduction couple at -1.368 V which is partially reversible (i_{pc}/i_{pa} = 0.43; ΔE = 51 mV) at 200 mV s^{-1} and becomes increasingly more reversible at faster scan rates (i_{pc}/i_{pa} = 0.80; ΔE = 116 mV at 3200 mV s^{-1}). In addition to the major reduction couple observed in the voltammogram of iq, daughter peaks are observed at -0.941 and -0.205 V (Fig. S8). Keeping within the scope of this *Communication*, no further analysis of the daughter peaks observed in voltammograms of apH$_2$ and iq was carried out.

isqH•. The cyclic voltammogram of isqH• was produced by mixing 2.5 equivalents apH$_2$ with 1 equivalent iq just prior to applying a potential to the solution. The resulting green-blue isqH• solution exhibited a reduction couple at -0.924 V and an oxidation couple at -0.112 V under our conditions (Fig. S9).
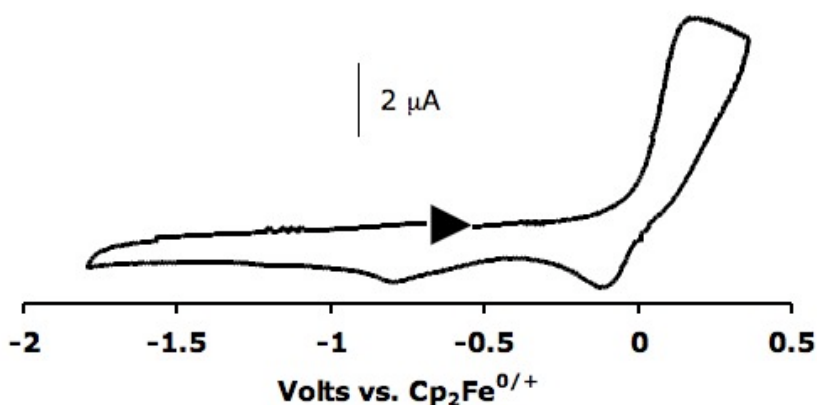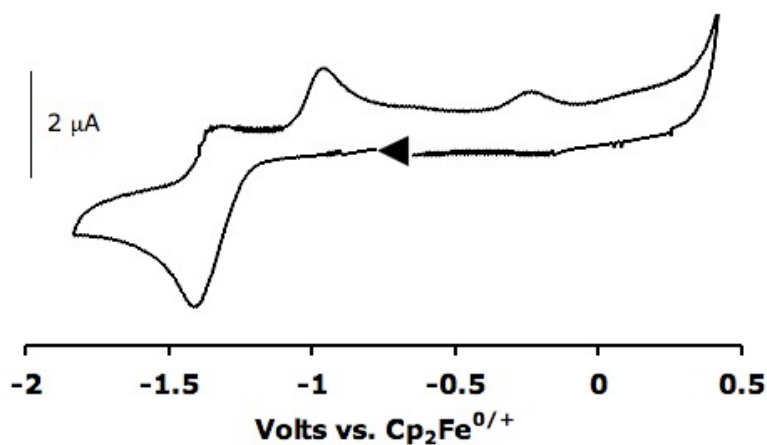

Figure S7. Cyclic voltammogram of apH$_2$.
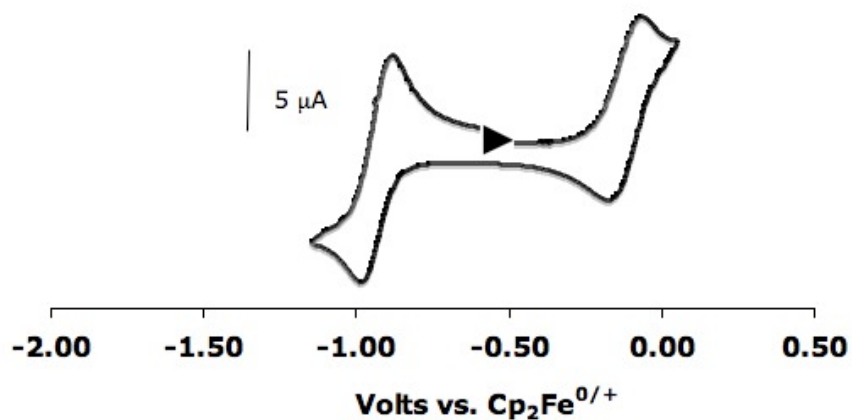
Figure S8. Cyclic voltammogram of iq.

Figure S9. Cyclic voltammogram of isqH$^{\bullet}$.

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