

Supporting Information

Disproportionation of Dipyrrolylquinoxaline Radical Anions via the Internal Protons of the Pyrrole Moieties

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Experimental Details

Chemicals. Acetonitrile was distilled over CaH_2 . Tetra-*n*-butylammonium perchlorate (Bu_4NClO_4) was purchased from Sigma Chemical Co. or Fluka Chemika Co., recrystallized from ethanol and dried under vacuum at 40 °C for at least one week prior to use. Cobaltocene (CoCp_2), tetrabutylammonium hydroxide (Bu_4NOH , 37% in MeOH) and quinoxaline (**6**) were purchased commercially and used as received without further purification. 2,3-Dipyrrol-2'-yl-6,7-dinitroquinoxaline (**1H₂**),^{S1} 2,3-dipyrrol-2'-yl-6-nitroquinoxaline (**2H₂**)^{S1} and 2,3-dipyrrol-2'-ylquinoxaline (**3H₂**)^{S1}, 6,7-dinitroquinoxaline (**4**)^{S2} and 6-nitroquinoxaline (**5**)^{S2} were synthesized as according literature. CD_3CN and $\text{DMSO}-d_6$ were purchased from Cambridge Isotope Laboratories, Co.Ltd.

Absorption Spectral Measurements. UV-vis absorption spectra and spectral changes were recorded on a Hewlett Packard 8453 diode array spectrophotometer using 1 cm cuvette. ^1H NMR spectra of synthesized chemicals and reaction products were recorded on a JEOL AL300 (300 MHz) spectrometer. The chemical shifts are expressed in ppm relative to tetramethylsilane (TMS).

Electrochemistry. Cyclic voltammograms were obtained with an EG&G Princeton Applied Research (PAR) 173 potentiostat/galvanostat. A homemade three-electrode cell was used and consisted of a platinum button or glassy carbon working electrode, a platinum counter electrode and a homemade saturated calomel reference electrode (SCE). The SCE was separated from the bulk of the solution by a fritted glass bridge of low porosity which contained the solvent/supporting electrolyte mixture. UV-visible spectroelectrochemical experiments were performed with a home-built thin-layer cell that had a light transparent platinum net working electrode.^{S3} Potentials were applied and monitored with an EG&G PAR Model 173 potentiostat. Time-resolved UV-visible spectra were recorded with a Hewlett-Packard Model 8453 diode array spectrophotometer.

EPR Measurements. EPR spectra of **1H₂^{•-}** and **4^{•-}** were recorded on a JEOL JES-RE1XE spectrometer. The magnitude of modulation was chosen to optimize the resolution and signal-to-noise (S/N) ratio of the observed spectra under non-saturating microwave power conditions. The *g* values and hyperfine coupling constants were

calibrated using an Mn^{2+} marker.

Calculations. Theoretical calculations of the properties of molecules were performed using Density-Functional Theory (DFT) with the UB3LYP density-functional and the 6-31G(d) basis set.^{S4} All calculations were performed using Gaussian 09, revision A.02.^{S5} Graphical outputs of the computational results were generated with the Gauss View software program (ver. 3.09) developed by Semichem, Inc.^{S6}

(S1) (a) Black, C. B.; Andrioletti, B.; Try, A. C.; Ruiperez, C.; Sessler, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 10438. (b) Anzenbacher, P. Jr., Try, A. C.; Miyaji, H.; Jursíková, K.; Lynch, V. M.; Marquez, M.; Sessler, J. L. *J. Am. Chem. Soc.* **2000**, *122*, 10268.

(S2) Fisons Pest Control Ltd. *Quinoxaline fungicides*. **1963**, 26, dpp. BE 631044 19631104.

(S3) Lin, X. Q.; Kadish, K. M. *Anal. Chem.* **1985**, *57*, 1498.

(S4) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(S5) *Gaussian 09, Revision A.02*, Gaussian, Inc.: Wallingford CT, 2004.

(S6) Dennington II, R.; Keith, T.; Millam, J.; Eppinnett, K.; Hovell, W. L.; Gilliland, R. Gaussview; Semichem, Inc.; Shawnee Mission, KS,. 2003.

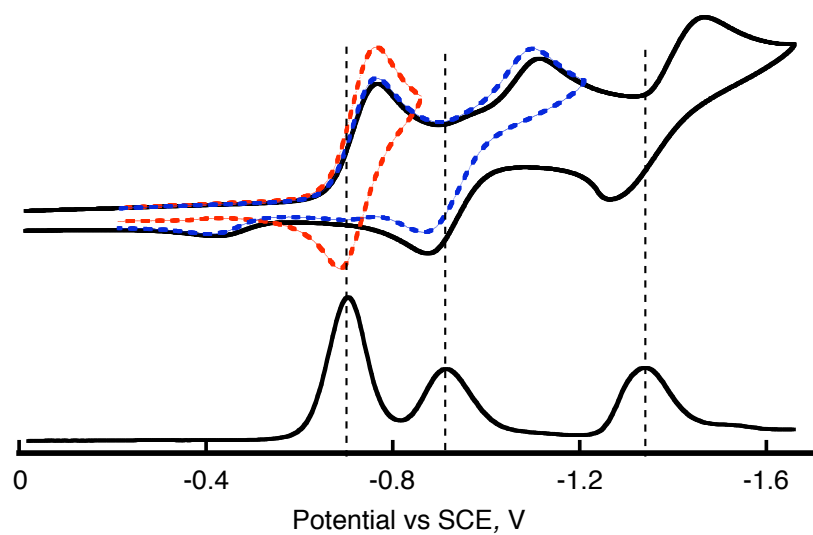


Figure S1. Cyclic voltammogram and differential pulse voltammogram of **1H₂** in deaerated MeCN containing Bu₄NPF₆ (0.10 M) at 298 K; scan rate: 0.1 V s⁻¹.

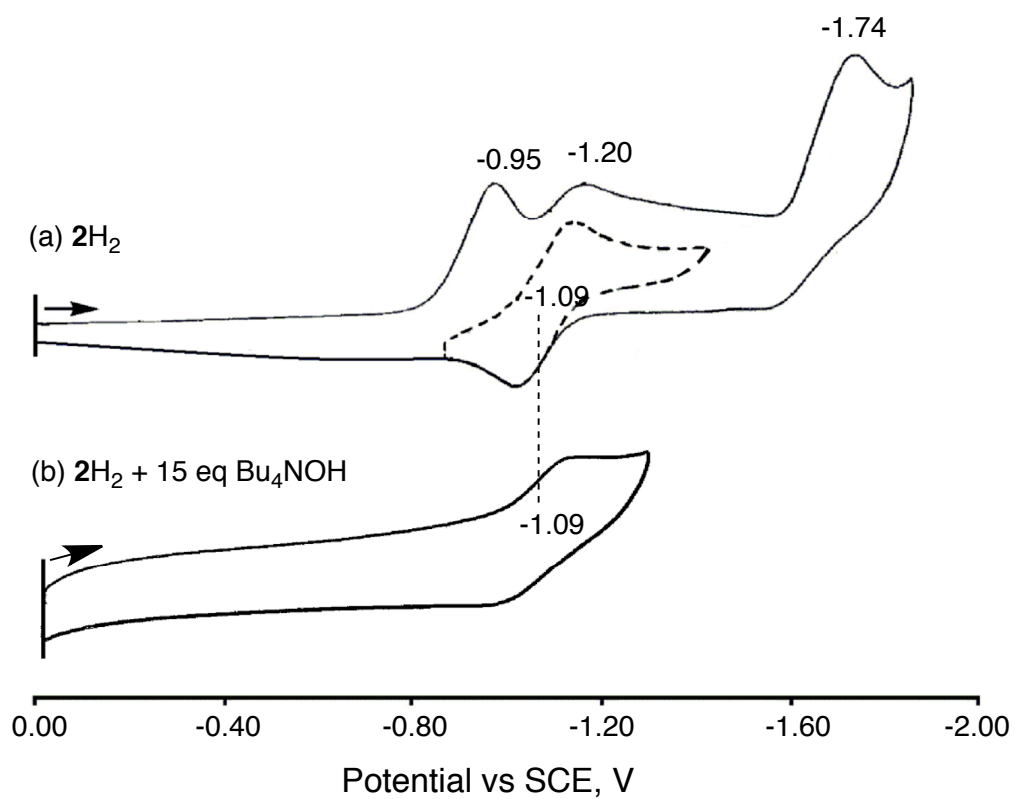
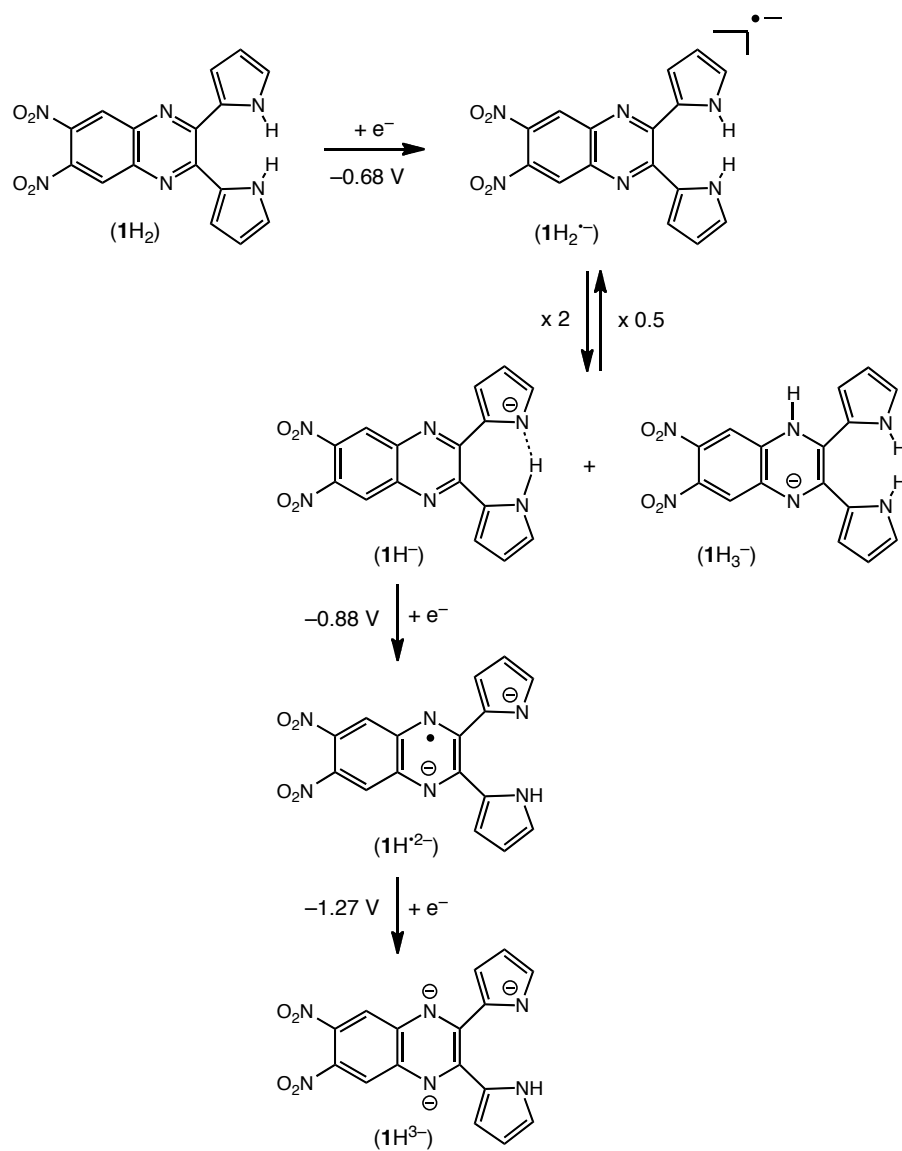


Figure S2. Cyclic voltammogram of (a) 2H_2 and (b) 2H^- produced by the reaction of 2H_2 with Bu_4NOH in MeCN containing Bu_4NClO_4 (0.10 M) at 298 K; scan rate: 100 mV s^{-1} .

Scheme S1. Reaction scheme for electrochemical reduction of **1H₂**



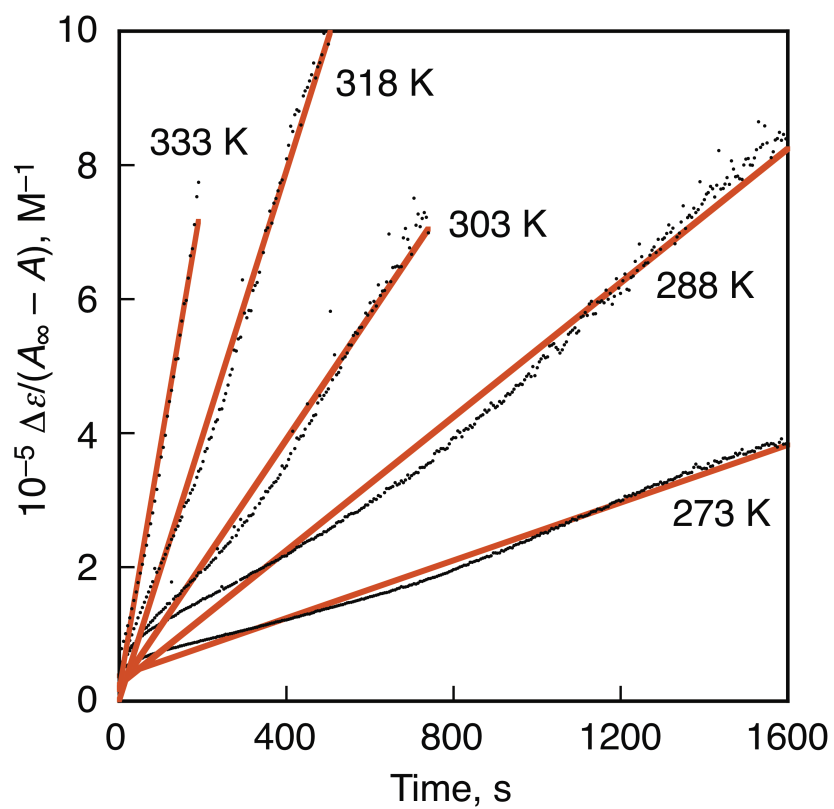


Figure S3. Second-order plots for disproportionation of $1\text{H}_2^{\bullet-}$ produced in electron transfer from CoCp_2 ($2.5 \times 10^{-5} \text{ M}$) to 1H_2 ($2.5 \times 10^{-5} \text{ M}$) in deaerated MeCN at various temperatures (273-333 K).

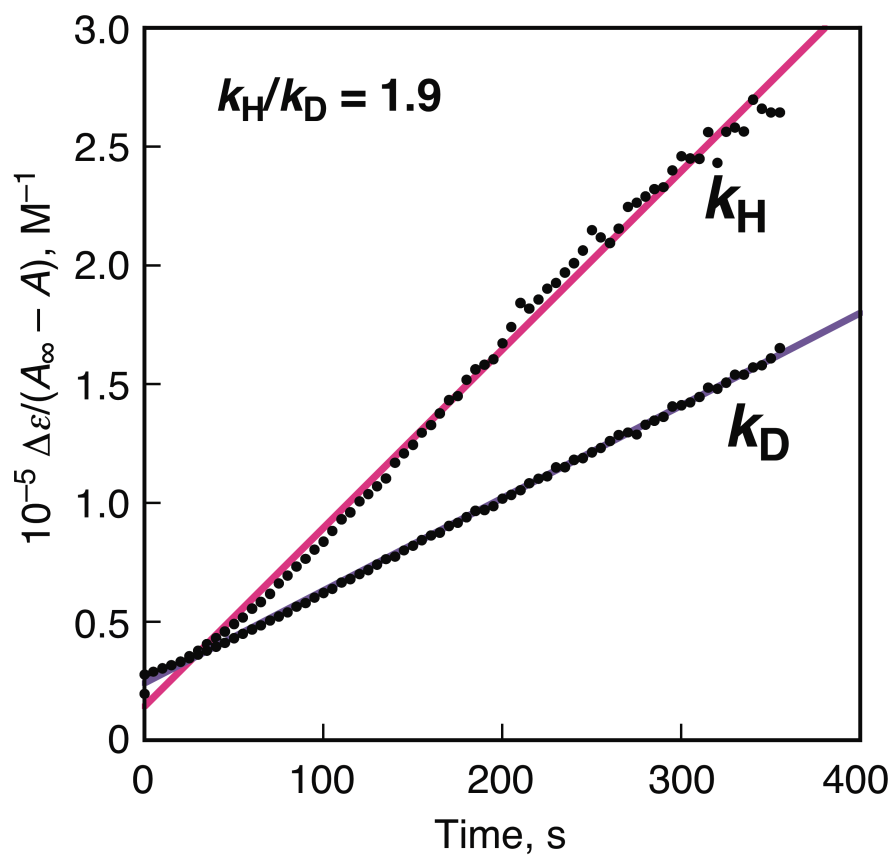


Figure S4. Second-order plots for the disproportionation of $1H_2^{\bullet-}$ (5.0×10^{-5} M) in the presence of H_2O (5.0×10^{-4} M) and D_2O (5.0×10^{-4} M) in deaerated MeCN at 298 K.

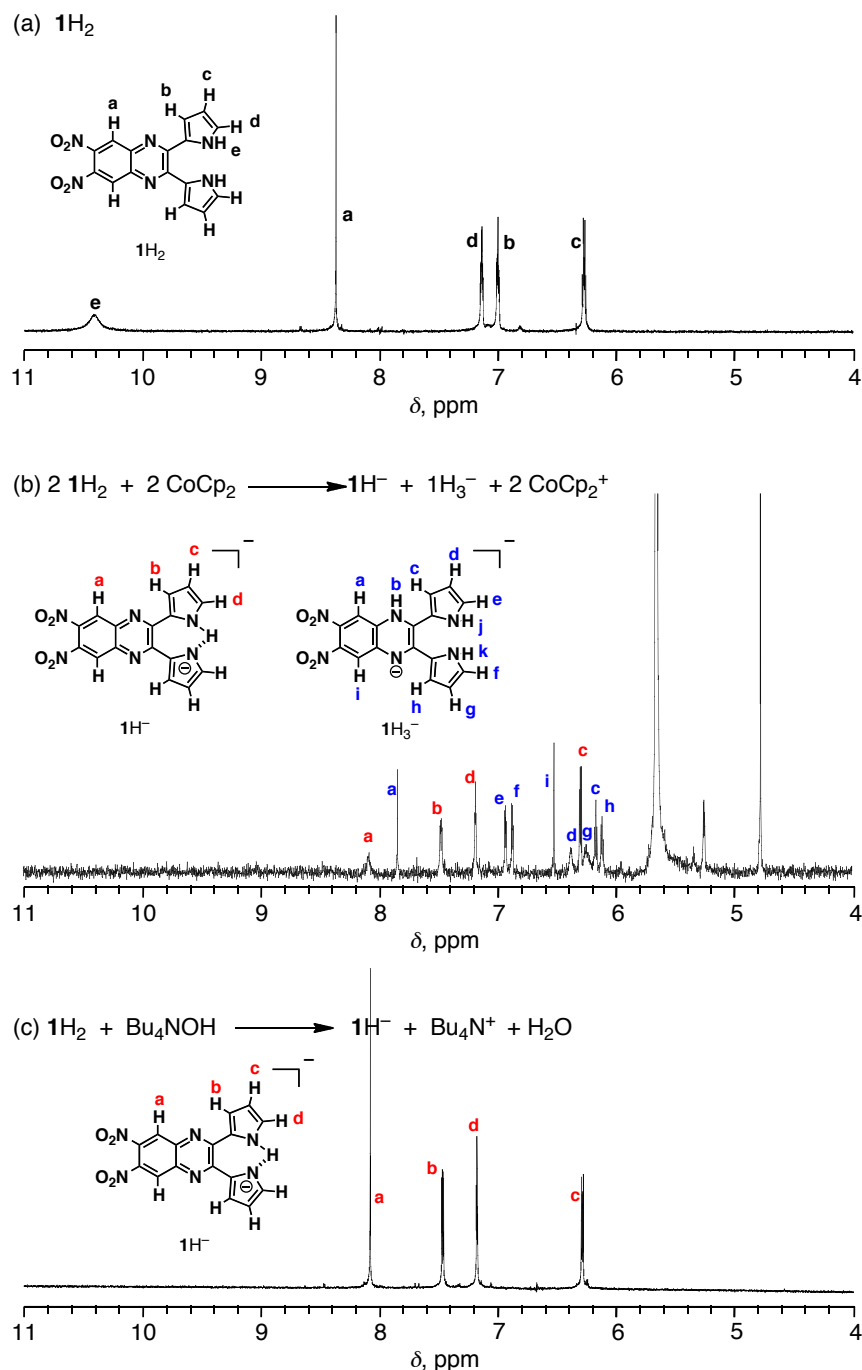


Figure S5. ^1H NMR spectra of (a) 1H_2 (a-e in black), (b) 1H^- (a-d in red) and 1H_3^- (a-i in blue) produced by electron-transfer reduction of 1H_2 (5.0 mM) with CoCp_2 (5.0 mM) and (c) 1H^- produced by deprotonation of 1H_2 (5.0 mM) with Bu_4NOH (5.0 mM) in deaerated CD_3CN . The signals of b, k and j N-H protons of 1H_3^- are too broad to observe due to the small amount of H_2O present in CD_3CN . Asterisk (*) denote the signals of CoCp^+ and decomposed products.

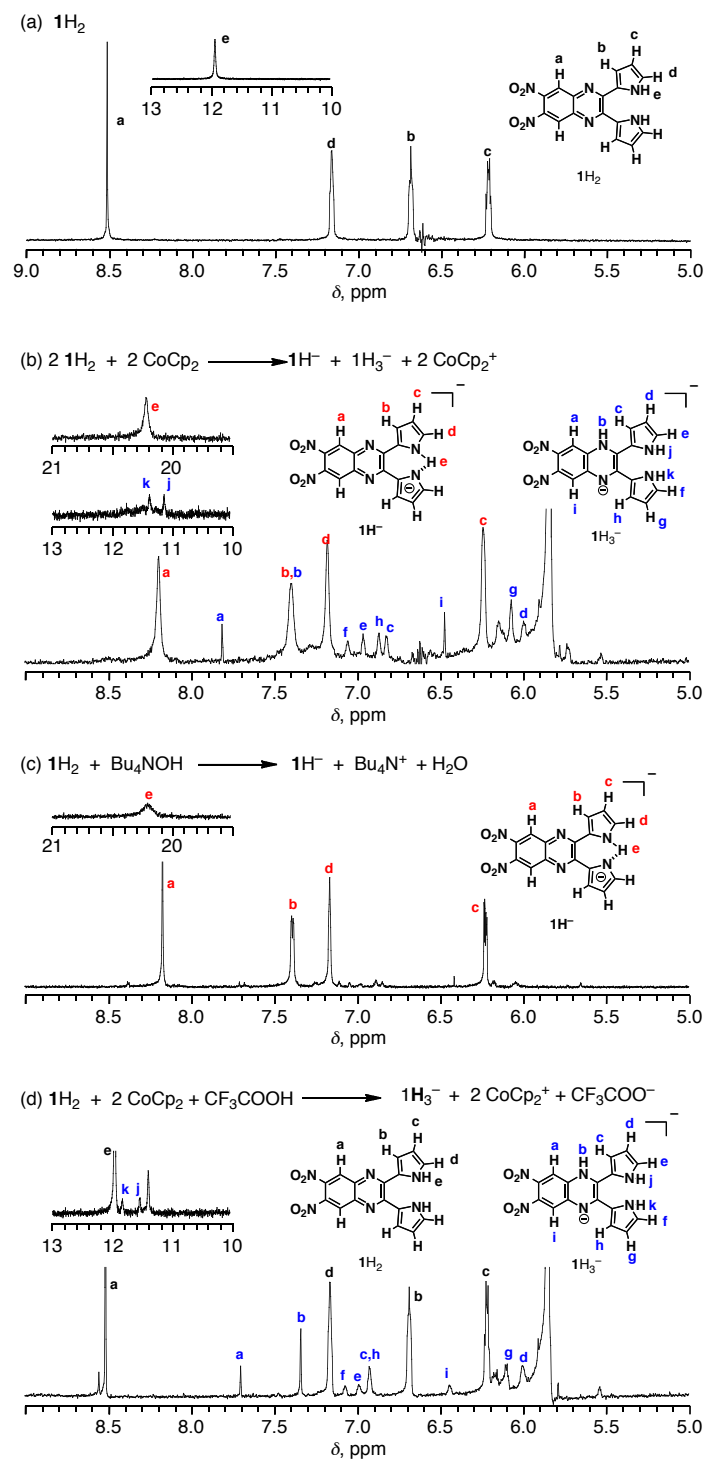


Figure S6. ^1H NMR spectra of (a) 1H_2 (a-e in black), (b) 1H^- (a-e in red) and 1H_3^- (a-k in blue) produced by the electron-transfer reduction of 1H_2 (5.0 mM) with CoCp_2 (5.0 mM) and (c) 1H^- (a-e in red) produced by deprotonation of 1H_2 (5.0 mM) with Bu_4NOH (5.0 mM) (d) 1H_3^- (a-k in blue) produced by the electron-transfer reduction of 1H_2 (5.0 mM) with CoCp_2 (4.0 mM) in the presence of trifluoroacetic acid (2.0 mM) in deaerated $\text{DMSO}-d_6$. The signals of 1H_2 as a starting material are shown with black labels. Asterisk (*) denote the signals of CoCp_2^+ and decomposed product.

^1H NMR Assignments

a) In CD_3CN

1H_2 : ^1H NMR (300 MHz, CD_3CN) δ 6.24 – 6.29 (2H, m, pyrrole H), 6.97 – 7.03 (2H, m, pyrrole H), 7.10 – 7.16 (2H, m, pyrrole H), 8.36 (2H, s, quinoxaline H), 10.40 (2H, br, s, pyrrole NH)

1H^- : ^1H NMR (300 MHz, CD_3CN) δ 6.28 – 6.32 (2H, dd, $J = 3.7, 2.2$ Hz, pyrrole H), 7.15 – 7.20 (2H, dd, $J = 2.2, 1.5$ Hz, pyrrole H), 7.44 – 7.50 (2H, dd, $J = 3.7, 1.5$ Hz, pyrrole H), 8.05 (2H, br, s, quinoxaline H)

1H_3^- : ^1H NMR (300 MHz, CD_3CN) δ 6.08 – 6.13 (1H, t, $J = 2.4$ Hz, pyrrole H), 6.15 – 6.19 (1H, t, $J = 2.4$ Hz, pyrrole H), 6.20 – 6.28 (1H, br, m, pyrrole H), 6.35 – 6.40 (1H, br, m, pyrrole H), 6.51 (1H, s, quinoxaline H), 6.86 – 6.90 (1H, dd, $J = 2.4, 1.8$ Hz, pyrrole H), 6.91 – 6.95 (1H, dd, $J = 2.4, 1.8$ Hz, pyrrole H), 7.83 (1H, s, quinoxaline H)

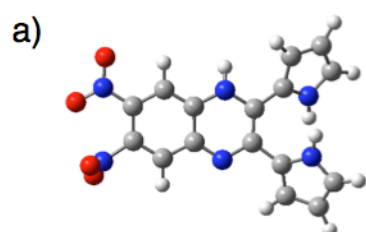
b) In $\text{DMSO}-d_6$

1H_2 : ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 6.20 – 6.28 (2H, m, pyrrole H), 6.68 – 6.77 (2H, m, pyrrole H), 7.15 – 7.22 (2H, m, pyrrole H), 8.50 (2H, s, quinoxaline H), 11.94 (2H, br, s, pyrrole NH)

1H^- : ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 6.22 (2H, m, pyrrole H), 7.17 (2H, m, pyrrole H), 7.38 (2H, m, pyrrole H), 8.17 (2H, s, quinoxaline H), 20.20 (1H, br, s, NH)

1H_3^- : ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 5.99 (1H, m, pyrrole H), 6.07 (1H, m, pyrrole H), 6.47 (1H, s, quinoxaline H), 6.82 (2H, m, pyrrole H), 6.96 (1H, m, pyrrole H), 7.06 (1H, m, pyrrole H), 7.4 (1H, br, s, quinoxaline NH), 7.81 (1H, s, quinoxaline H), 11.12 (1H, br, s, pyrrole NH), 11.36 (1H, br, s, pyrrole NH).

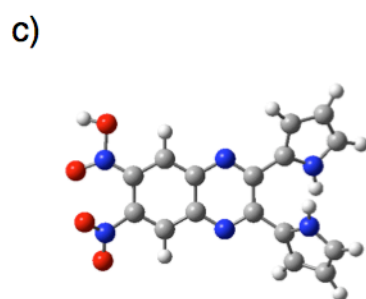
The NMR spectra of 1H_2 , 1H^- and 1H_3^- in $\text{DMSO}-d_6$ are virtually the same as those in CD_3CN although small shifts are observed due to the difference in the solvent and the hydrogen-bonded NH proton is only observed in $\text{DMSO}-d_6$. The NMR spectra of 1H_3^- produced by the electron-transfer reduction of 1H_2 with CoCp_2 in the presence of trifluoroacetic acid (Figure S6d) are also virtually the same as those of 1H_3^- produced by disproportionation of $1\text{H}_2^{\bullet-}$ (Figure S6b), although small shifts are observed due to the presence of the trifluoroacetate anion.



MOST STABLE



(+0.12 kcal mol⁻¹)



(+4.36 kcal mol⁻¹)

Figure S7. Optimized structures of 1H_3^- isomers as determined via DFT calculations carried out at the B3LYP/6-31G(d) level. Relative energies are given in parentheses.

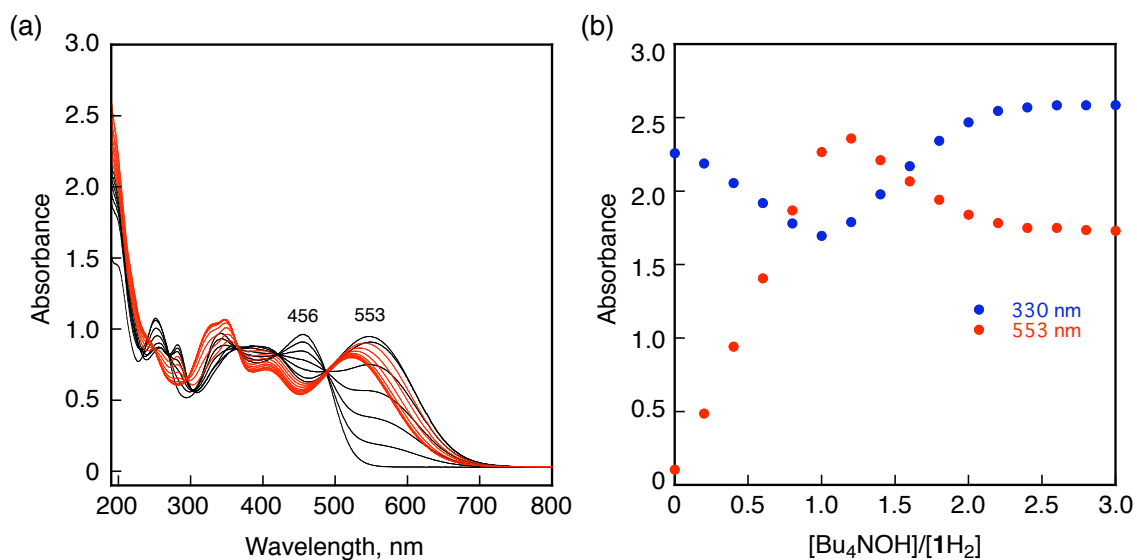


Figure S8. (a) Titration of $1H_2$ (0.50 mM) with Bu_4NOH in MeCN at 298 K. The black line shows the titration up to 1 equiv of Bu_4NOH to produce $1H^-$ and red line shows the titration from 1 equiv to 2 equiv of Bu_4NOH to produce 1^{2-} . (b) Plots of absorbance at 330 and 553 nm vs $[Bu_4NOH]/[1H_2]$.

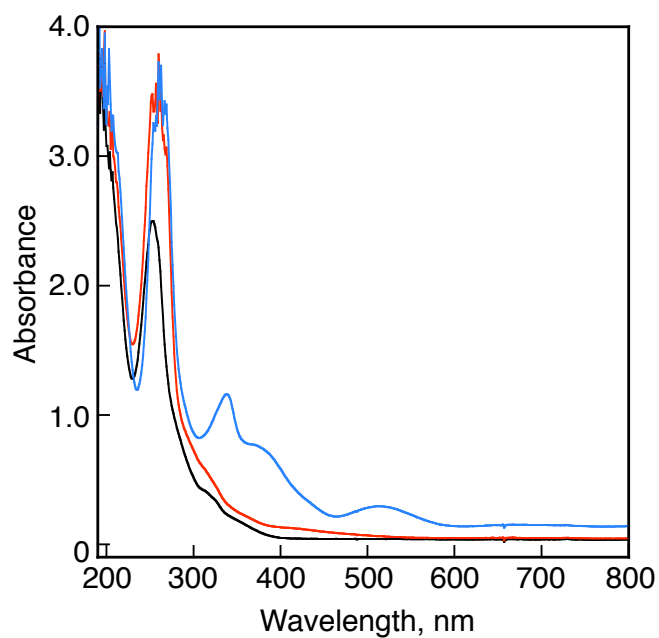


Figure S9. UV-vis absorption spectra of **4** (5.0×10^{-5} M, black), and **4**^{•-} (blue) produced by electron-transfer reduction of **4** (5.0×10^{-5} M) with CoCp₂ (5.0×10^{-5} M), and **4**^{•-} with CF₃COOH (5.0×10^{-5} M) (red) in deaerated MeCN at 298 K.

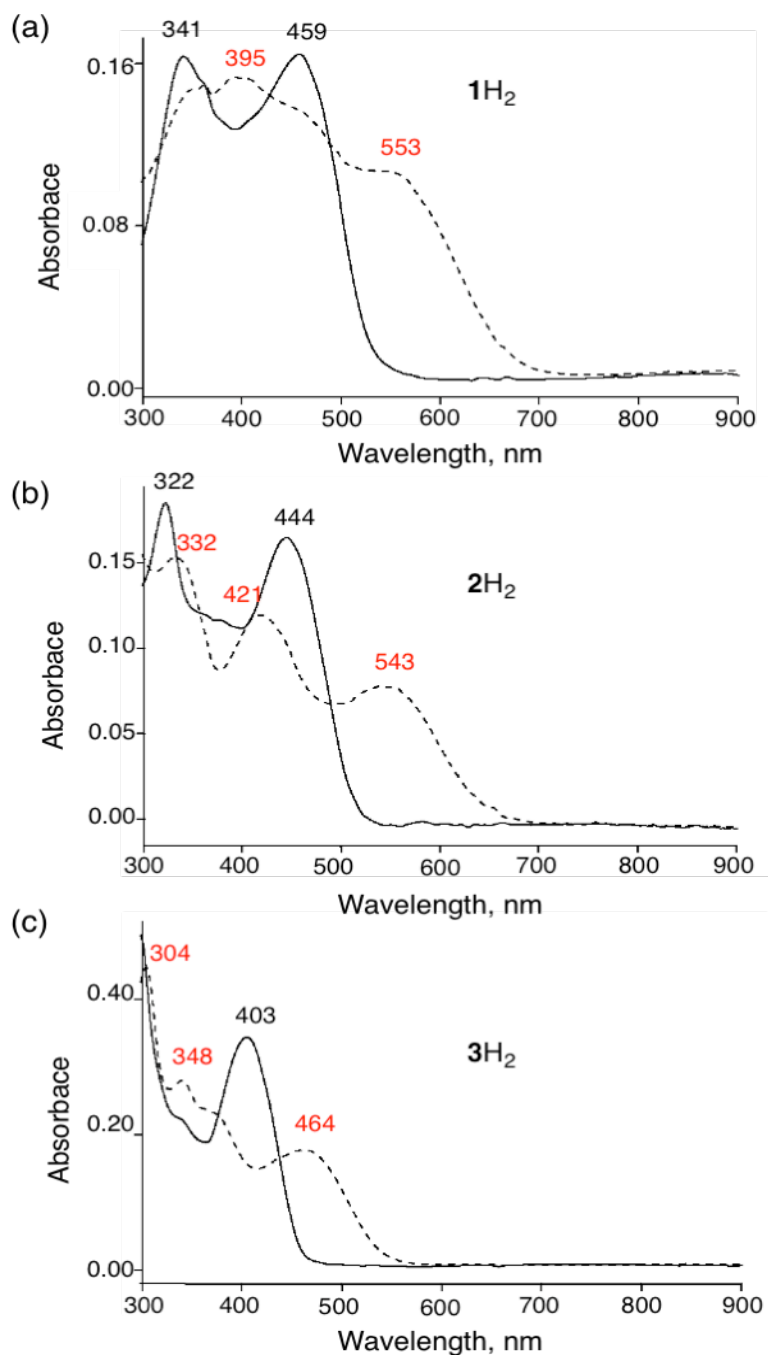


Figure S10. UV-vis absorption spectral changes in electrolysis of (a) **1H₂** (3.3×10^{-4} M), (b) **2H₂** (3.1×10^{-4} M) and (c) **3H₂** (9.2×10^{-4} M) in the presence of Bu₄NClO₄ (0.20 M) in MeCN at applied potentials of -0.80 V (vs SCE) for 347 s, -0.96 V for 310 s and -1.70 V for 180 s, respectively.

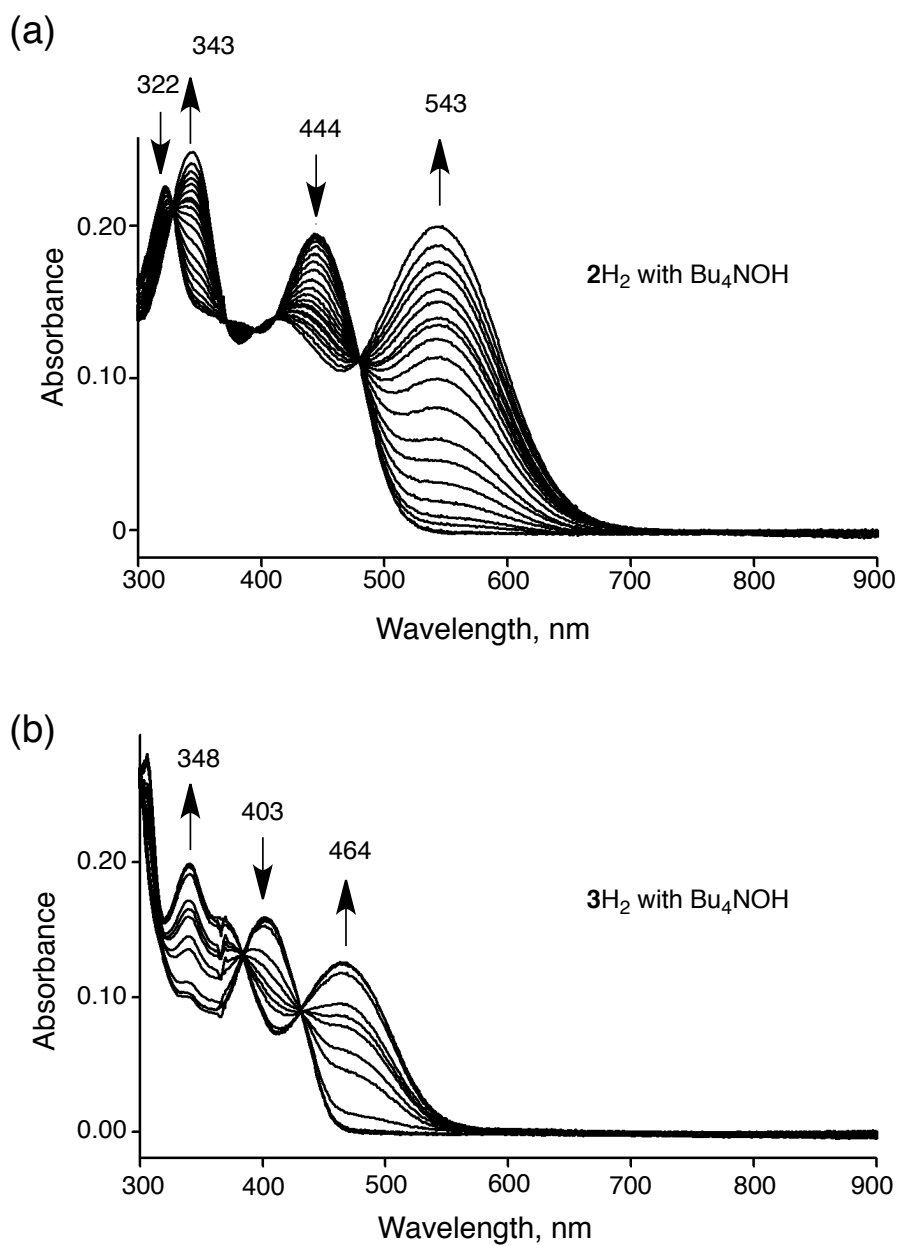


Figure S11. UV-vis absorption spectral change of (a) **2H₂** (1.7×10^{-5} M) and (b) **3H₂** (2.0×10^{-5} M) in MeCN titrated with Bu₄NOH (1.0×10^{-2} M).

Table S1. Equilibrium Constants between $1\text{H}_2^{\bullet-}$ and $1\text{H}^-/1\text{H}_3^-$ in MeCN at Various Temperatures

T , K	$[1\text{H}_2^{\bullet-}]$, mM	K
243	3.7×10^{-1}	0.48
258	3.2×10^{-1}	0.78
273	2.0×10^{-1}	2.8
288	1.0×10^{-1}	13
303	4.5×10^{-2}	87
318	1.9×10^{-2}	5.4×10^2

K values were determined by EPR spectra calibrated by DPPH.

Table S2. Rate Constants for the Disproportionation of $1\text{H}_2^{\bullet-}$ in MeCN at Various Temperatures

T , K	k , $\text{M}^{-1} \text{s}^{-1}$
273	1.1×10^2
288	2.5×10^2
303	4.6×10^2
318	1.0×10^3
333	1.8×10^3

k values were determined by using $\Delta\epsilon_{553} = 1.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.