Supporting Information

for

*Thermodynamics of Various F420 Coenzyme Models as Sources of Electrons, Hydride Ions, Hydrogen Atoms and Protons in Acetonitrile*

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SI–1. General Methods

Solvents and reagents were obtained from commercial sources and used as received. $^1$HNMR spectra were recorded in CDCl$_3$ and CD$_3$CN on 400 MHz or 300 MHz NMR spectrometer. The chemical shifts (δ) were described in parts per million (ppm) downfield from tetramethylsilane (TMS, 0.00 ppm) as an internal standard.

All reagents of commercial quality were from freshly opened containers or were purified according to the standard methods before use. Reagent grade acetonitrile was refluxed over KMnO$_4$ and K$_2$CO$_3$ for several hours and was distilled over P$_2$O$_5$ under argon twice before use. The commercial tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$, Aldrich) was recrystallized from CH$_2$Cl$_2$/Et$_2$O and dried in vacuo at 110 °C overnight before preparation of a supporting electrolyte solution.

Acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) was used as solvent in electrochemical measurements. Ferrocene/ferrocenium redox couple (Fc/Fc$^+$) was used as an internal reference for all measurements. All electrochemical measurements were performed under dry nitrogen atmosphere using 0.1 V/s scan rate, unless otherwise specified, the concentration of samples was 10$^{-3}$ M.

SI-2. Synthesis Route of 6FH$^-$ and 6F:

Solvents and reagents used here are all commercial available and were used as received. $^1$H NMR spectra were recorded on 400 MHz or 300 MHz spectrometer using CD$_3$Cl as a solvent for XFH$_2$ and CD$_3$CN as a solvent for XF respectively. The chemical shifts (δ) are given relative to
internal SiMe₄ standard.

Substituted N-methylanilines (1) and 6-chloro-5-formyl-1,3-dimethyluracil (2) can be purchased from the Alfa Company or be synthesized easily according to literature.\[S1-S3]\n
**Preparation of 3a-i:**

5 Mmol 6-chloro-5-formyl-1,3-dimethyluracil (2) was solved in CH₂Cl₂ in a round-bottomed flask, add 5 mmol substituenced N-methylanilines (1) into the flask, then 0.7ml of dried Et₃N was added, stirred the solution for 10 h at room temperature. Then the reaction mixture was evaporated in vacuo and will get yellow products. The yellow residues are pure enough for the next step, so they do not need any purification, although they can be purified easily through column chromatography by using a mixture of petroleum ether and ethyl acetate (PE : EA = 5 :1) as eluate, for example, the intermediate 3c.

6-((4-methoxyphenyl)(methyl)amino)-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidine-5-carbaldehyde (3c): \(^1\)H NMR (CDCl₃, 300M): δ 10.05 (s, 1H), 6.85 (d, 4H), 3.79 (s, 3H), 3.41 (s, 3H), 3.37 (s, 3H), 3.06 (s, 3H).

**Preparation of 4a-i**

Compounds 3(a-i) without purification are placed in a 50ml flask, then add polyphosphoric acid (PPA) to cover the yellow compounds, the mixture was stirring at room temperature for 12h by using a mechanical stirrer. Then, 30 ml of cold methanol was added into the flask slowly to prevent violent exothermic. When the mixture became liquid from viscous, the mixture was poured into a 500 ml flask which contains 200ml water in it. Add sodium hydroxide to adjust pH to 7 under ice bath, adding sodium perchlorate (NaClO₄) slowly while adjusting the pH, and precipitate of the models’ salt will appear, add sodium perchlorate until the precipitate stop to increase. The precipitate was filtered. The pale yellow powder collected was then dissolved in acetonitrile directly. Monitored by TLC, the salt has a bright fluorescence under UV lamp. Then add NaBH₄ into the solution, monitored by TLC until the bright fluorescence disappeared. The solution was removed by a rotary evaporator, and the white reduced F420 model will be got. Purification through column chromatography will get pure target products (4a-i). The eluate used for 4b-e is PE:EA = 20:1 to separate the by-products 4’b-e, and for 4f-i, the eluate can be pure EA.
to remove the inorganic compounds produced during reduction.

1,3,10-Trimethyl-5,10-dihydropyrimido[4,5-b]quinoline-2,4(1H,3H)-dione (4a): \(^1\)H NMR (CD\(_3\)Cl, 400M): \(\delta\) 7.03~7.26 (m, 4H), 3.76 (s, 2H), 3.47 (s, 3H), 3.37(s, 3H), 3.34(s, 3H); ESI-MS/M\(^+\) = 257.

1,3,8,10-Tetramethyl-5,10-dihydropyrimido[4,5-b]quinoline-2,4(1H,3H)-dione (4b): \(^1\)H NMR (CD\(_3\)Cl,400M): \(\delta\) 7.05 (d, 1H), 6.90 (d, 1H), 6.86 (s, 1H), 3.71 (s, 2H), 3.49 (s, 3H), 3.37(s, 3H), 3.33(s, 3H),2.34(s, 3H); ESI-MS/M\(^+\) = 272.27.

8-Methoxy-1,3,10-trimethyl-5,10-dihydropyrimido[4,5-b]quinoline-2,4(1H,3H)-dione (4c): \(^1\)H NMR (CD\(_3\)Cl, 400M): \(\delta\) 7.02~6.96 (m, 3H), 3.64 (s, 2H), 3.49 (s, 3H), 3.37(s, 3H), 3.30(s, 3H), 2.32 (s, 3H); ESI-MS/M\(^+\) = 288.33.

8-Chloro-1,3,10-trimethyl-5,10-dihydropyrimido[4,5-b]quinoline-2,4(1H,3H)-dione (4d): \(^1\)H NMR (CD\(_3\)Cl, 400M): \(\delta\) 7.02~6.96 (m, 3H), 3.64 (s, 2H), 3.37(s, 3H), 3.30(s, 3H), 2.32 (s, 3H); ESI-MS/M\(^+\) = 292.20.

8-Fluoro-1,3,10-trimethyl-5,10-dihydropyrimido[4,5-b]quinoline-2,4(1H,3H)-dione (4e): \(^1\)H NMR (CD\(_3\)Cl, 400M): \(\delta\) 7.10 (t, 1H), 6.84~6.73 (m, 2H), 3.71 (s, 2H), 3.46 (s, 3H), 3.37 (s, 3H), 3.33 (s, 3H); ESI-MS/M\(^+\) = 276.27.

1,3,7,10-Tetramethyl-5,10-dihydropyrimido[4,5-b]quinoline-2,4(1H,3H)-dione (4f): \(^1\)H NMR (CD\(_3\)Cl, 400M): \(\delta\) 7.72 (d, 1H), 7.01~6.91 (m, 2H), 3.71 (s, 2H), 3.49 (s, 3H), 3.37 (s, 3H), 3.30 (s, 3H), 2.32 (s, 3H); ESI-MS/M\(^+\) = 272.27.

7-Methoxy-1,3,10-trimethyl-5,10-dihydropyrimido[4,5-b]quinoline-2,4(1H,3H)-dione (4g): \(^1\)H NMR (CD\(_3\)Cl, 400M): \(\delta\) 6.91 (d, 1H), 6.71~6.68 (m, 1H), 6.62 (d, 1H), 3.72 (s, 3H), 3.66 (s, 2H), 3.40 (s, 3H), 3.30 (s, 3H), 3.21 (s, 3H); ESI-MS/M\(^+\) = 288.20.

7-Chloro-1,3,10-trimethyl-5,10-dihydropyrimido[4,5-b]quinoline-2,4(1H,3H)-dione (4h): \(^1\)H NMR (CD\(_3\)Cl, 400M): \(\delta\) 7.11 (d, 1H), 7.09 (s, 1H), 6.90 (d, 1H), 3.64 (s, 2H), 3.39 (s, 3H), 3.29(s, 3H), 3.24(s, 3H); ESI-MS/M\(^+\) = 292.20.

7-Fluoro-1,3,10-trimethyl-5,10-dihydropyrimido[4,5-b]quinoline-2,4(1H,3H)-dione (4i): \(^1\)H NMR (CD\(_3\)Cl,400M): \(\delta\) 6.94~6.92 (m, 1H), 6.87~6.78 (m, 2H), 3.66 (s, 2H), 3.40 (s, 3H), 3.29(s, 3H), 3.23(s, 3H); ESI-MS/M\(^+\) = 276.20.
Preparation of 5a-i

1 Mmol of 4a-i was dissolved in acetonitrile, and 2 mmol of NO\textsuperscript{+}ClO\textsubscript{4}\textsuperscript{-} was added, the solution became deep red under stirring, and the yellow perchlorate salt precipitated, filter to get pure perchlorate salt of target models XFH\textsuperscript{+}ClO\textsubscript{4}\textsuperscript{-}.

1,3,10-Trimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimido[4,5-b]quinolin-10-ium (5a): \textsuperscript{1}H NMR (CD\textsubscript{3}CN,400M): δ 9.50 (s, 1H), 8.36(d, 1H), 8.20~8.29(m, 2H), 7.93(t, 1H), 4.31(s, 3H), 3.75(s, 3H), 3.41(s, 3H);

1,3,8,10-Tetramethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimido[4,5-b]quinolin-10-ium (5b): \textsuperscript{1}H NMR (CD\textsubscript{3}CN,400M): δ 9.68 (s, 1H), 9.10 (d, 1H), 8.56~8.04(m, 2H), 4.41(s, 3H), 3.88(s, 3H), 3.55(s, 3H) , 2.80(s, 3H);

8-Methoxy-1,3,10-trimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimido[4,5-b]quinolin-10-ium (5c): \textsuperscript{1}H NMR (CD\textsubscript{3}CN,400M): δ 9.45 (s, 1H), 8.54 (d, 1H), 7.86~7.83(m, 2H), 4.24(s, 3H), 3.99(s, 3H), 3.70(s, 3H) , 3.48(s, 3H);

8-Chloro-1,3,10-trimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimido[4,5-b]quinolin-10-ium (5d): \textsuperscript{1}H NMR (CD\textsubscript{3}CN,400M): δ 9.49 (s, 1H), 8.37 (d, 1H), 8.31 (s, 1H), 7.95~7.92(m, 1H), 4.29(s, 3H), 3.77(s, 3H), 3.44(s, 3H);

8-Fluoro-1,3,10-trimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimido[4,5-b]quinolin-10-ium (5e): \textsuperscript{1}H NMR (CD\textsubscript{3}CN,400M): δ 9.60 (s, 1H), 8.58~8.54(m, 1H), 8.10 (d, 1H), 7.88 (d, 1H), 4.37(s, 3H), 3.87(s, 3H), 3.54(s, 3H);

1,3,7,10-Tetramethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimido[4,5-b]quinolin-10-ium (5f): \textsuperscript{1}H NMR (CD\textsubscript{3}CN,400M): δ 9.42 (s, 1H), 8.16(d, 3H), 4.33(s, 3H), 3.77(s, 3H), 3.43(s, 3H) , 2.64 (s, 3H);

7-Methoxy-1,3,10-trimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimido[4,5-b]quinolin-10-ium (5g): \textsuperscript{1}H NMR (CD\textsubscript{3}CN,400M): δ 9.60 (s, 1H), 8.48~8.11(m, 3H), 4.36(s, 3H), 4.18(s, 3H), 3.78(s, 3H) , 3.44(s, 3H);

7-Chloro-1,3,10-trimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimido[4,5-b]quinolin-10-ium (5h): \textsuperscript{1}H NMR (CD\textsubscript{3}CN,400M): δ 9.52 (s, 1H), 8.50 (s, 1H), 8.33 (s, 2H), 4.42(s, 3H), 3.87(s, 3H), 3.53(s, 3H);

7-Fluoro-1,3,10-trimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimido[4,5-b]quinolin-10-ium (5i): \textsuperscript{1}H NMR (CD\textsubscript{3}CN,400M): δ 9.56 (s, 1H), 8.40~8.38(m, 1H), 8.20 (t, 2H), 4.43(s, 3H), 3.41(s, 3H);
3.87(s, 3H), 3.54(s, 3H);

**Preparation of 4j, 4k and 5j**

The single and double deuterated 4j and 4k, and one deuterated 5j were achieved by circulations of reduction of 8a by NaBD₄ and oxidation again by NO⁻ClO₄⁻. Details are the same as that described above.

**One deuterated 4j:** ¹H NMR (CD₃Cl, 400M): δ 7.21~7.26 (m, 1H), 7.17 (d, 1H), 7.03~7.09 (m, 2H), 3.73 (s, 1H), 3.47 (s, 3H), 3.37(s, 3H), 3.34(s, 3H).

**Double deuterated 4k:** ¹H NMR (CD₃Cl, 400M): δ 7.21~7.24 (m, 1H), 7.15(d, 1H), 7.03~7.09 (m, 2H), 3.47 (s, 3H), 3.37(s, 3H), 3.34(s, 3H).

**One deuterated 5j:** ¹H NMR (CD₃CN, 400M): δ 8.39~8.41 (d, 1H), 8.24~8.31(m, 2H), 7.95~7.98(t, 1H), 4.35(s, 3H), 3.79(s, 3H), 3.45(s, 3H).

SI-3. References


SI-4. Plots of \( E_{\text{ox}}(\text{XFH}) \) and \( E_{\text{red}}(\text{XF}) \) as well as \( \Delta H_{\text{red}}(\text{XFH}) \), \( \Delta H_{\text{HD}}(\text{XFH}) \), and \( \Delta H_{\text{PD}}(\text{XFH}) \) against the Sum of Hammett Substituent Parameters \( \sigma_p \) and \( \sigma_m \)
Figure S1. Plots of redox potentials of XFH\textsuperscript{-} and XF against the sum of Hammett substituent parameters $\sigma_p$ and $\sigma_m$. 
\[ \Delta H_{\text{PD}}(2\text{F}) : \]
\[ \text{slope} = -34.644 \quad \text{intercept} = 59.9 \quad R = 0.999 \]

\[ \Delta H_{\text{PD}}(3\text{F}) : \]
\[ \text{slope} = -21.613 \quad \text{intercept} = 50.2 \quad R = 0.999 \]

\[ \Delta H_{\text{PD}}(3\text{F}) : \]
\[ \text{slope} = -27.032 \quad \text{intercept} = 19.0 \quad R = 0.999 \]

\[ \Delta H_{\text{PD}}(3\text{F}) : \]
\[ \text{slope} = -40.105 \quad \text{intercept} = 1.7 \quad R = 0.999 \]

\[ \Delta H_{\text{PD}}(3\text{F}) : \]
\[ \text{slope} = 9.652 \quad \text{intercept} = 48.3 \quad R = 0.981 \]

\[ \Delta H_{\text{PD}}(3\text{F}) : \]
\[ \text{slope} = 16.175 \quad \text{intercept} = 32.1 \quad R = 0.995 \]

\[ \Delta H_{\text{PD}}(3\text{F}) : \]
\[ \text{slope} = 12.726 \quad \text{intercept} = 2.8 \quad R = 0.990 \]

\[ \Delta H_{\text{PD}}(3\text{F}) : \]
\[ \text{slope} = 6.135 \quad \text{intercept} = -7.9 \quad R = 0.942 \]
\( \Delta H_D(4FH) \):
slope = -31.944  intercept = 63.5  R = 0.997

\( \Delta H_D(4FH) \):
slope = -24.547  intercept = 53.2  R = 0.998

\( \Delta H_D(4FH) \):
slope = -25.738  intercept = 22.6  R = 0.999

\( \Delta H_{1o}(4FH) \):
slope = -33.094  intercept = 5.8  R = 0.997

\( \Delta H_{1o}(5FH) \):
slope = 10.799  intercept = 54.6  R = 0.976

\( \Delta H_{1o}(5FH) \):
slope = 18.790  intercept = 36.4  R = 0.995

\( \Delta H_{1o}(5FH) \):
slope = 16.302  intercept = 6.6  R = 0.997

\( \Delta H_{1o}(5FH) \):
slope = 8.341  intercept = -2.2  R = 0.967
Figure S2. Plots of $\Delta H_{IP}(XF^-)$, $\Delta H_{ID}(XF^-)$, $\Delta H_{ID}(XF^-)$ and $\Delta H_{PD}(XF^-)$ against the sum of Hammett substituent parameters $\sigma_p$ and $\sigma_m$. 