Supporting information to accompany:

Considering a Possible Role for $[H\text{-}Fe_4N(CO)_{12}]^{2-}$ in Selective Electrocatalytic CO_2 Reduction to Formate by $[Fe_4N(CO)_{12}]^-$

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Table S1. Crystallographic data for $[(\text{diglyme})_2(\text{THF})_{4.5})\text{Na}_3][\text{Fe}_4(\text{N})(\text{CO})_{11}]$ (Na_3-**2**).

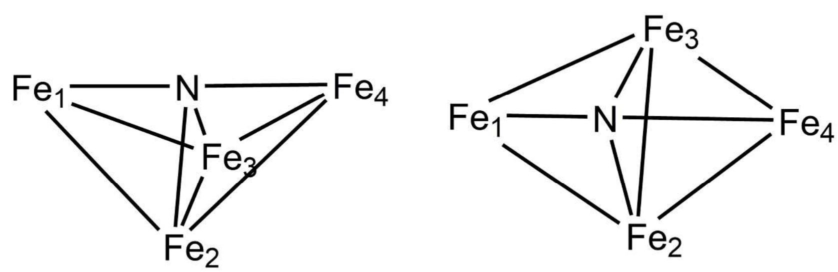
	$[\text{Na}]_3[\text{Fe}_4(\text{N})(\text{CO})_{11}]\bullet 4.5\text{C}_4\text{H}_8\text{O}\bullet 2\text{C}_6\text{H}_{14}\text{O}_3$
Formula	$\text{C}_{11}\text{Fe}_4\text{NNa}_3\text{O}_{11}\bullet 4.5\text{C}_4\text{H}_8\text{O}\bullet 2\text{C}_6\text{H}_{14}\text{O}_3$
Crystal size	0.354 × 0.261 × 0.136
Formula weight, g mol^{-1}	2414.6
Space group	*I* 2/*a*
a, Å	19.240(2)
b, Å	14.308(1)
c, Å	38.854(3)
α, deg	90
β, deg	93.133(1)
γ, deg	90
V, Å^3	10679(1)
Z	4
T, K	90 (2)
ρ, calcd, g cm^{-3}	1.502
Refl. collected/2θ_{max}	47672/50.484
Unique refl./ $I > 2\sigma(I)$	8506/7559
No. parameters/restrains	668/39
λ, Å/μ (Kα), cm^{-1}	0.71073
R_1/GOF	0.0465/1.016
wR_2 ($I > 2\sigma(I)$)[a]	0.1207
Residual density, e Å^{-3}	+1.549/-0.696

[a] $R_1 = \Sigma||F_o|-F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma [w(F_o^2-F_c^2)^2]/ \Sigma [w(F_o^2)^2]\}^{0.5}$.

Table S2. Selected average interatomic distances (Å) and selected average angles (deg) for $[(\text{diglyme})_2(\text{THF})_{4.5})\text{Na}_3][\text{Fe}_4(\text{N})(\text{CO})_{11}]$ (Na_3-**2**). View Chart S1 for numbering scheme.

	Na_3-**2**
Fe_1-N	1.813(3)
Fe_2-N	1.991(3)
Fe_3-N	1.926(3)
Fe_4-N	1.824(2)
Fe_1-Fe_2	2.5420(6)
Fe_1-Fe_3	2.5943(7)
Fe_2-Fe_3	2.5449(6)
Fe_2-Fe_4	2.5356(6)
Fe_3-Fe_4	2.5760(7)
Fe_2-Fe_1-Fe_3	59.39(2)
Fe_1-Fe_2-Fe_4	90.68(2)
Fe_1-Fe_3-Fe_4	88.61(2)
Fe_2- Fe_4-Fe_3	59.71(2)

Chart S1. Numbering scheme for Na_3-**2**.



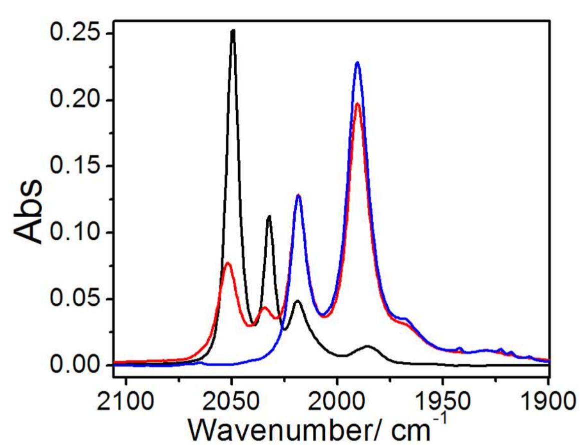


Figure S1. IR spectra of $[HFe_4N(CO)_{12}]$ in toluene (black), $[HFe_4N(CO)_{12}]$ in MeCN (red), and $[Fe_4N(CO)_{12}]^-$ in MeCN (blue).

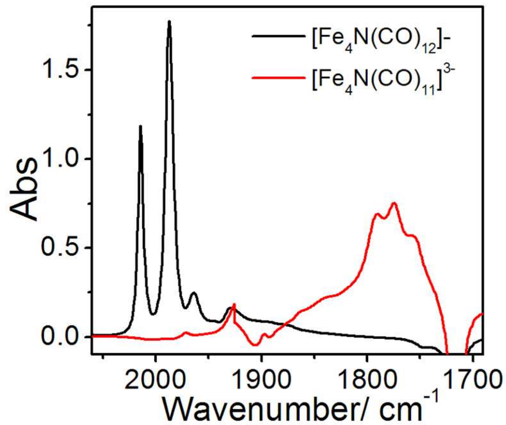


Figure S2. IR spectra of $[Fe_4N(CO)_{12}]^-$ (black) and $[Fe_4N(CO)_{11}]^{3-}$ (red) in MeCN.

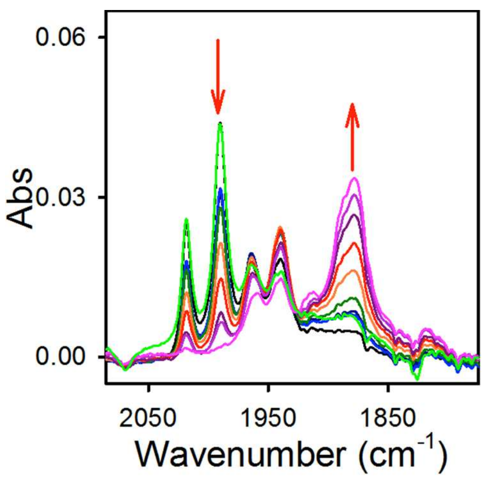


Figure S3. IR Absorption spectra showing the conversion of $\mathbf{1}^-$ to $\mathbf{1}^{3-}$ at -1.9 V vs. SCE, performed over 3 min, passing through the $\mathbf{1}^{2-}$ intermediate (red arrows indicate decrease or increase of bands). The final trace (lime green) was taken after re-oxidation of $\mathbf{1}^{3-}$ to $\mathbf{1}^-$ performed at -1.2 V vs. SCE.