Electronic Supplementary Information

A nickel complex with a biscarbene pincer-type ligand shows high electrocatalytic reduction of CO_2 over H_2O

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Materials

All synthetic procedures were carried out under N_2 unless otherwise noted. 1-methylimidazole, acetonitrile, and 2,6-dibromopyridine were purchased from Sigma-Aldrich. Chloroform (Fisher Chemical), methanol (Pharmco), nickel acetate (Alfa Aesar), tetra-butylammonium bromide (TCI), dimethyl sulfoxide (Pharmco), silver trifluoromethanesulfunoate (Alfa Aesar) were all purchased from commercial vendors and used as received. Acetonitrile was distilled over calcium hydride and stored over 4Å molecular sieves.

Synthesis of $CNCBr_2$: A mixture of 2,6-dibromipyridine (6.4 g, 26.7 mmol) and 1-methylimidazole (8.8 g, 106.9 mmol) was heated in a sealed tube at 150 ℃ for 3 h. The resulting precipitate was collected through filtration, washed with chloroform (10 mL × 3) and diethyl ether (10 mL × 3), and dried under vacuum. Quantitative yield was typically obtained.

Synthesis of $CNC(OTf)_2$: The obtained $CNCBr_2$ was mixed with two equivalents of silver trifluoromethanesulfonate in methanol and stirred for 1 h at room temperature, followed by filtration to remove the silver bromide precipitate. The filtrate was dried to obtain the desired product which was recrystallized from methanol once.

Synthesis of $[(CNC)Ni(NCCH_3)](OTf)_2$ (CNC-Ni): A mixture of $CNC(OTf)_2$ (1.6 g, 4.0 mmol), nickel acetate (0.80 g, 4.4 mmol), and tetra-butylammonium bromide (1.3 g, 4.0 mmol) in dimethyl sulfoxide (20 mL) was stirred at 50 ℃ for 12 h and then heated to 160 ℃ and stirred for 1 h. After cooling to room temperature, the resulting precipitate was collected by filtration, washed with acetonitrile (10 mL × 3) and chloroform (10 mL × 3) and dried under vacuum. Vapor diffusion of diethyl ether into the concentrated acetonitrile solution of $[(CNC)Ni(NCCH_3)](OTf)_2$ yielded the light yellow crystalline needles of $[(CNC)Ni(NCCH_3)](OTf)_2$.

X-ray crystallographic analysis

A clear light yellow prism-like specimen of $C_{17}H_{16}F_6N_6NiO_6S_2$, approximate dimensions 0.200 mm × 0.270 mm × 0.320 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on Bruker APEX-II CCD. The integration of the data using a triclinic unit cell yielded a total of 24115 reflections to a maximum θ angle of 29.81 ° (0.71 Å resolution), of which 6470 were independent (average redundancy 3.727, completeness = 96.9%, R_{int} = 2.50%, R_{sig} = 2.64%)

and 5448 (84.20%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.1515(7) Å, b = 11.4521(9) Å, c = 12.1239(9) Å, α = 75.583(3)°, β = 71.623(3)°, γ = 87.992(3) °, volume = 1166.55(16) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7180 and 0.8090. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P-1, with Z = 2 for the formula unit, $C_{17}H_{16}F_6N_6NiO_6S_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 346 variables converged at R1 = 3.00%, for the observed data and wR_2 = 8.07% for all data. The goodness-of-fit was 1.089. The largest peak in the final difference electron density synthesis was 0.664 $e^-/Å^3$ and the largest hole was -0.490 $e^-/Å^3$ with an RMS deviation of 0.062 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.814g/cm^3 and F(000), 644 e^-.

Instruments

All electrochemical measurements were performed using a Gamry Interface 1000 potentiostat. A Ag/AgCl (sat. KCl) electrode was used as the reference electrode, a platinum wire as the counter electrode, and a glassy carbon electrode as the working electrode. UV-vis spectra were collected on Agilent 8453 UV-visible spectrophotometer. Hydrogen and carbon monoxide produced during electrolysis or injected as standard gases were measured via an SRI gas chromatography system 8610C equipped with a molecular sieve 13× packed column, a HayesSep D packed column, and a thermal conductivity detector. The oven temperature was maintained at 80 °C and argon was used as the carrier gas.

Determination of turnover frequency (TOF)

TOF was determined based on a previously reported method.[1]

$$TOF = k_{cat}[Q] = \frac{Fvn_p^3}{RT}\left(\frac{0.4463}{n_{cat}}\right)^2\left(\frac{i_{cat}}{i_p}\right)^2$$

where k_{cat} is the rate constant of the catalytic reaction, [Q] is the substrate concentration, F is Faraday constant, *v* is scan rate (100 mV/s), n_p is the number of electrons in a reversible, non-catalytic reaction, R is the universal gas constant, T is temperature, n_{cat} is the number of electrons required for the catalytic reaction (n_{cat} = 2 for the reduction of CO_2 to CO), i_{cat} is the is catalytic current, and i_p is the peak current of the reversible and non-catalytic reaction. Background currents were subtracted when calculating i_{cat} and i_p.

(1) C. W. Machan, M. D. Sampson and C. P. Kubiak, *J. Am. Chem. Soc.*, 2015, **137**, 8564-8571.

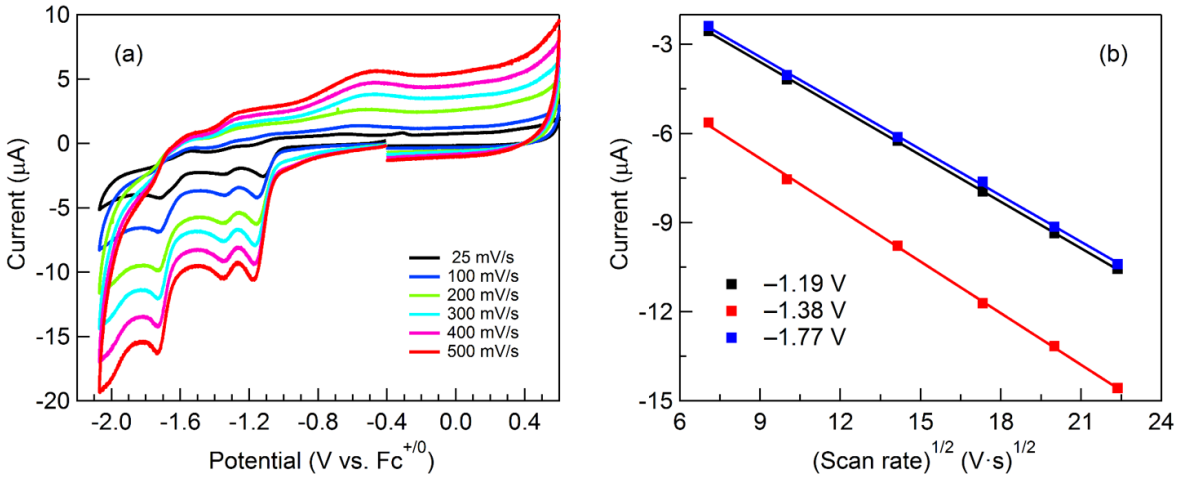


Fig. S1 (a) Cyclic voltammograms of CNC-Ni in 0.1 M NBu_4PF_6 in CH_3CN under N_2 at different scan rates and (b) current densities at three redox peaks versus the square root of scan rate.

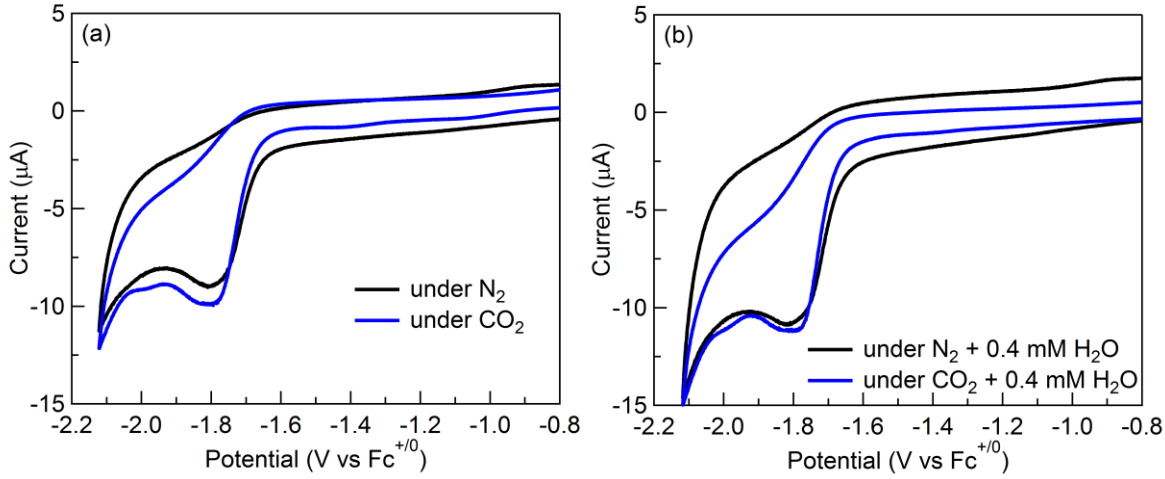


Fig. S2 (a) Cyclic voltammograms of $CNC(OTf)_2$ in 0.1 M NBu_4PF_6 in CH_3CN under N_2 (black) or CO_2 (blue). (b) Cyclic voltammograms of $CNC(OTf)_2$ in 0.1 M NBu_4PF_6 in CH_3CN in the presence of 0.4 mM H_2O under N_2 (black) or CO_2 (blue). Scan rate: 100 mV/s.

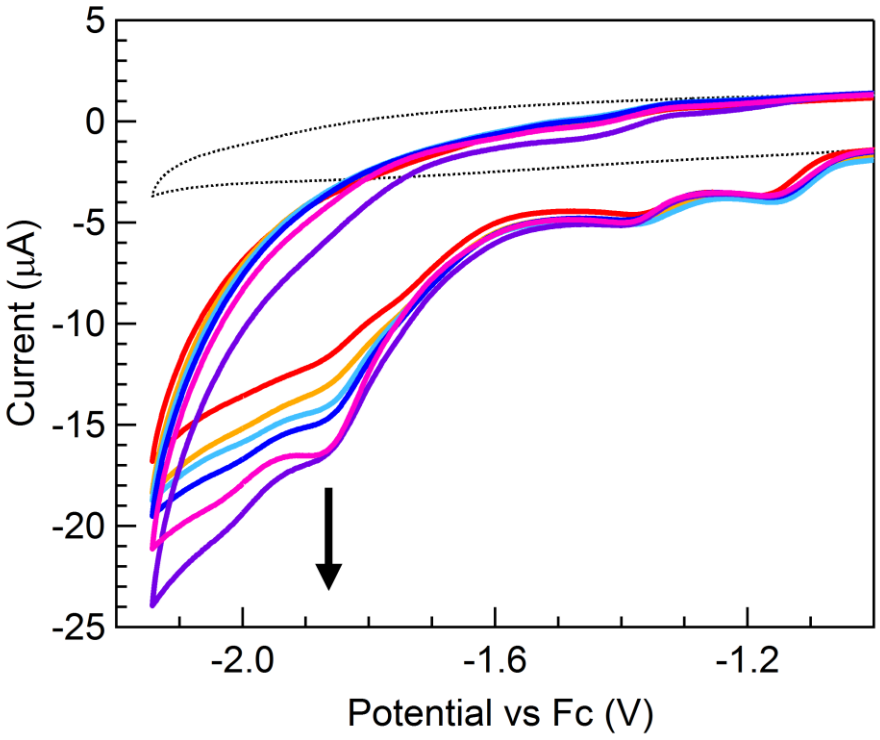


Fig. S3 Cyclic voltammograms of CNC-Ni under CO_2 with increasing addition of D_2O from 0 to 1.1 mM. Scan rate: 100 mV/s

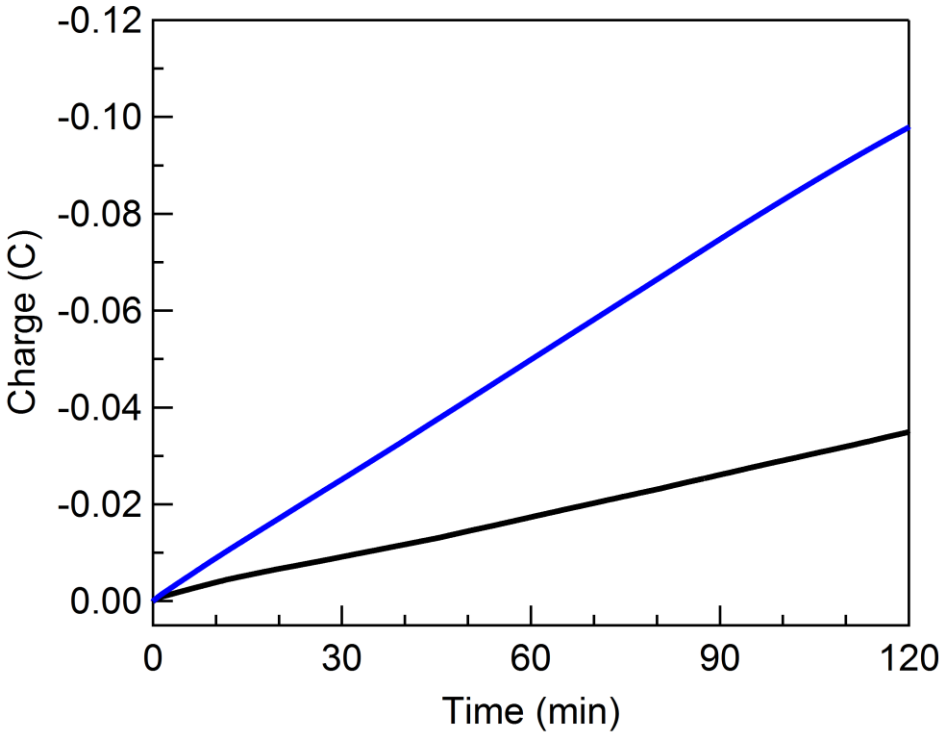


Fig. S4 Accumulated charge versus time during the 2-h controlled potential electrolysis of CNC-Ni (blue) and blank (red) in CO_2-saturated CH_3CN with 0.4 mM H_2O at an applied potential of −1.773 V vs $Fc^{+/0}$.

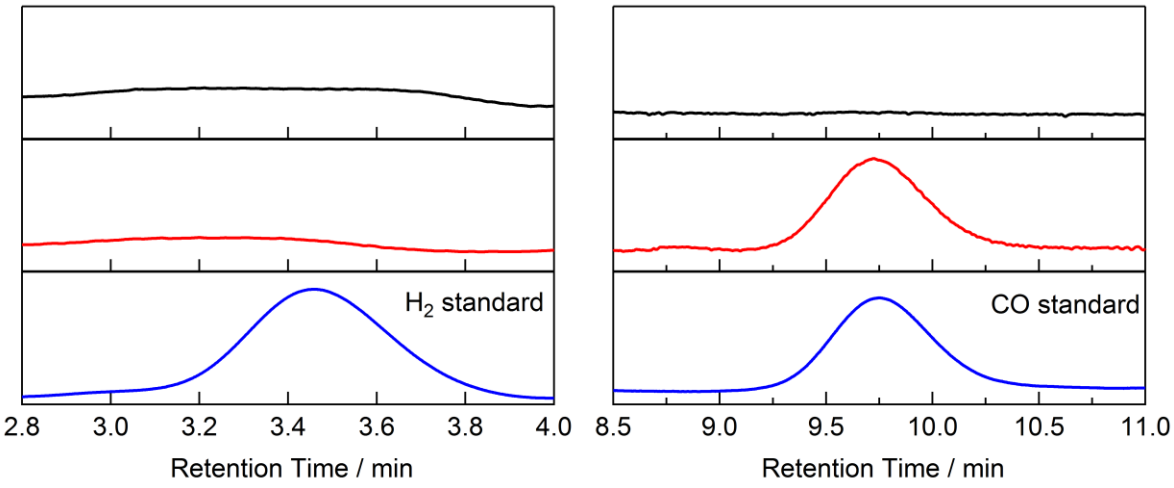
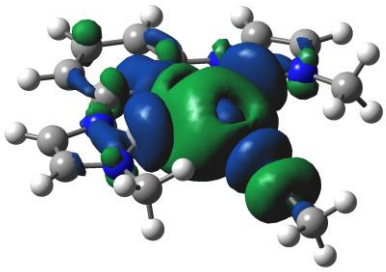


Fig. S5 Gas chromatographs after 2-h controlled potential electrolysis in CO_2-saturated CH_3CN with 0.4 mM H_2O at −1.773 V vs $Fc^{+/0}$ for blank (top, black) and CNC-Ni (middle, red). Blue curves indicate the injected H_2 (left) and CO (right) gases as standards.

Computational details

Optimized geometries were generated using the Truhlar M06 functional combined with the 6-31G(d,p) basis set for H, C, and N atoms. The LANL2DZ basis set/pseudopotential was used for Ni. All geometries correspond to stationary points and normal mode frequency analysis was carried out to confirm that all structures have zero negative vibrational frequencies. All structures were optimized using the default parameters for the SMD solvent model for acetonitrile by the keyword scrf=(smd,solvent=acetonitrile). All calculations were carried out with an ultrafine integration grid. M06/LANL2TZ(f)(6-311+G(2d,p))//M06/LANL2DZ(6-31G(d,p)) electronic energies were calculated in acetonitrile solvent. Reported free energies use this base SCF energy and the sum of zero-point, pressure-volume (1 atm), 298 K thermal, and entropic corrections based on M06/LANL2DZ(6-31G(d,p)) structures. Time dependent (TD) DFT calculations were carried out using M06/LANL2TZ(f)(6-311+G(2d,p))//M06/LANL2DZ(6-31G(d,p)) in acetonitrile solvent. The molecular orbitals reported for to the calculated excitations correspond to the largest coefficients of the TD-DFT wavefunction. For the calculated $Ni^{II/I}$ reduction free energy the $[(CNC)Ni^{I}(NCCH_3)]^+$ complex was fully optimized. The absolute $Ni^{II/I}$ reduction free energy of –87.6 kcal/mol is relative to the optimized CNC-Ni complex and an unbound electron. The M06/LANL2TZ(f)(6-311+G(2d,p))//M06/LANL2DZ(6-31G(d,p)) $Ni^{II/I}$ absolute reduction free energy corresponds to –1.19 V when compared to the experimental $Fc^{+/0}$ couple value of –114.8 kcal/mol (–4.98 V) in CH_3CN. This identical match with experimental is likely accidental. To estimate the range of what DFT values predict we also calculated the $Ni^{II/I}$ reduction free energy with ωB97X-D/LANL2TZ(f)(6-311+G(2d,p)//M06/LANL2DZ(6-31G(d,p)). This method gives a $Ni^{II/I}$ reduction potential relative to $Fc^{+/0}$ of –1.28 V. This suggests that DFT methods can calculate this $Ni^{II/I}$ reduction potential within 100 mV of experiment. Below is a plot of the M06/LANL2DZ(6-31G(d,p)) spin density polarization for $[(CNC)Ni^{I}(NCCH_3)]^+$.



M06/LANL2DZ(6-31G(d,p)/SMD xyz geometries and energies:

$[(CNC)Ni^{II}(NCCH_3)]^{2+}$
Lowest Frequency Vibration = 29.6204 cm**-1
Temperature = 298.150 K
Pressure = 1.00000 Atm
Electronic Energy = -1078.20401971
Electronic and Zero-Point Energy = -1077.905006
Enthalpy = -1077.883835
Free Energy = -1077.953873

Ni	-0.0179480	0.4592030	-0.0063740
N	-2.1649420	-1.2608860	0.0009120
N	0.0723490	-1.3966280	0.0002530
N	2.2873920	-1.0437940	-0.0015670
N	3.0442360	0.9596090	-0.0335510
N	-3.1155380	0.6576050	-0.0396520
N	-0.1156440	2.3053630	0.0239300
C	-1.9104370	0.0853800	-0.0165010
C	-1.0586990	-2.1100160	0.0136140
C	1.2675620	-1.9961040	0.0134420
C	1.9019190	0.2712090	-0.0115530
C	4.1381320	0.1001340	-0.0379330
H	5.1501570	0.4790900	-0.0560340
C	3.6662890	-1.1682060	-0.0187410
H	4.1699210	-2.1238850	-0.0184440
C	3.1539560	2.4144130	-0.0504940
H	2.6260440	2.8165220	-0.9179430
H	4.2102390	2.6772960	-0.1170860
H	2.7356950	2.8313400	0.8686380
C	1.3877300	-3.3724180	0.0393240
H	2.3627700	-3.8473260	0.0495420
C	0.2044730	-4.1092200	0.0501000
H	0.2576940	-5.1938780	0.0698240
C	-1.0452530	-3.4917790	0.0376300
H	-1.9692210	-4.0604550	0.0471250
C	-3.5239210	-1.5210500	-0.0079340
H	-3.9293490	-2.5223770	0.0021920
C	-4.1188700	-0.3059680	-0.0328900
H	-5.1634430	-0.0291910	-0.0486790
C	-3.3711800	2.0941390	-0.0623720
H	-3.0487710	2.5458740	0.8790780
H	-4.4432430	2.2506930	-0.1905500
H	-2.8380370	2.5509990	-0.8989430
C	-0.1893840	3.4582980	0.0619550

C	-0.2902030	4.8921080	0.1063790
H	-1.3448350	5.1855380	0.1111270
H	0.2033730	5.3218700	-0.7705440
H	0.1958800	5.2657950	1.0127300

$[(CNC)Ni^{I}(NCCH_3)]^{+}$
Lowest Frequency Vibration = 22.7647 cm**-1
Temperature = 298.150 K
Pressure = 1.00000 Atm
Electronic Energy = -1078.33865034
Electronic and Zero-Point Energy = -1078.043486
Enthalpy = -1078.020848
Free Energy = -1078.096466

Ni	-0.1787050	0.5979260	-0.0863320
N	-1.6692420	-1.8728890	0.0175350
N	0.5222440	-1.3395040	0.0835240
N	2.5475880	-0.3481800	0.0167610
N	2.8505530	1.7548700	-0.1561670
N	-3.2455070	-0.4535220	-0.1940700
N	-0.9388710	2.4781560	0.1272710
C	-1.9021210	-0.5215470	-0.1470050
C	-0.3433810	-2.3395360	0.0871520
C	1.8270690	-1.5551820	0.0848120
C	1.8613430	0.8435610	-0.1234220
C	4.1092470	1.1752300	-0.0442330
H	5.0145060	1.7667750	-0.0526360
C	3.9211200	-0.1584930	0.0647420
H	4.6263890	-0.9701670	0.1750980
C	2.6435230	3.1854060	-0.2983300
H	1.5700800	3.3760550	-0.3535850
H	3.1272460	3.5461680	-1.2107510
H	3.0646440	3.7120110	0.5629850
C	2.3587860	-2.8372800	0.1282270
H	3.4289230	-3.0177580	0.1294510
C	1.4427200	-3.8883050	0.1603350
H	1.8116190	-4.9099090	0.1942970
C	0.0663620	-3.6650990	0.1323980
H	-0.6419580	-4.4874420	0.1373670
C	-2.8461640	-2.6056070	0.0664450
H	-2.8697450	-3.6791030	0.1879000
C	-3.8429560	-1.7019780	-0.0636450
H	-4.9168490	-1.8274850	-0.0810200
C	-3.9979120	0.7830020	-0.3289850
H	-4.2955640	1.1598410	0.6549490

H	-4.8931360	0.5986170	-0.9278700
H	-3.3745360	1.5265120	-0.8287090
C	-1.4780060	3.4930080	0.2896250
C	-2.1664580	4.7466010	0.4849490
H	-3.2354200	4.6167710	0.2878440
H	-1.7662450	5.5035890	-0.1959780
H	-2.0326090	5.0883990	1.5155780

$[(CNC)Ni^{II}]^{2+}$
Lowest Frequency Vibration = 57.2735 cm**-1
Temperature = 298.150 K
Pressure = 1.00000 Atm
Electronic Energy = -945.477340845
Electronic and Zero-Point Energy = -945.225974
Enthalpy = -945.209221
Free Energy = -945.268875

Ni	0.0000230	-0.9715920	-0.0001290
N	2.2322260	0.6230770	-0.0000030
N	0.0000290	0.8709190	-0.0004560
N	-2.2321700	0.6230580	-0.0004120
N	-3.0655650	-1.3510420	0.0001400
N	3.0654880	-1.3510870	0.0001560
C	1.9032370	-0.7055460	0.0000240
C	1.1702290	1.5243450	-0.0001080
C	-1.1701800	1.5243160	-0.0003260
C	-1.9032600	-0.7056020	-0.0004000
C	-4.1274680	-0.4505550	0.0004460
H	-5.1532200	-0.7912980	0.0008420
C	-3.6068370	0.7986190	0.0001300
H	-4.0734410	1.7730930	0.0001640
C	-3.2230690	-2.7993000	0.0002030
H	-2.2336870	-3.2596700	0.0000410
H	-3.7730850	-3.1058830	-0.8927660
H	-3.7727960	-3.1058170	0.8933690
C	-1.2186740	2.9048480	-0.0000050
H	-2.1701200	3.4261060	0.0000860
C	0.0000070	3.5820280	0.0002400
H	-0.0000010	4.6682150	0.0005040
C	1.2187080	2.9048670	0.0002250
H	2.1701450	3.4261410	0.0004770
C	3.6069030	0.7985420	0.0001110
H	4.0735920	1.7729760	0.0001660
C	4.1274480	-0.4506690	0.0001680
H	5.1531850	-0.7914580	0.0002220

C	3.2229110	-2.7993530	0.0000390
H	3.7730430	-3.1059700	0.8929230
H	3.7724580	-3.1058920	-0.8932330
H	2.2334980	-3.2596640	0.0003480

Structure of CNC free ligand

N	2.3176760	-0.0242620	-0.0211850
N	-0.0000040	0.0778200	-0.0275640
N	-2.3176850	-0.0242420	-0.0214170
N	-4.3522510	-0.6123160	0.0450660
N	4.3522560	-0.6123250	0.0450660
C	3.5881610	0.5048830	0.0678660
C	1.1413640	0.7585560	-0.0290700
C	-1.1413660	0.7585670	-0.0292330
C	-3.5881380	0.5048740	0.0682060
C	-3.6111730	-1.7868320	-0.0514210
H	-4.0749720	-2.7638520	-0.0812330
C	-2.3148570	-1.4185620	-0.0925160
H	-1.4056990	-1.9962240	-0.1644390
C	-5.8001990	-0.6066370	0.1273610
H	-6.1397920	0.4280280	0.2003870
H	-6.1353230	-1.1594130	1.0110270
H	-6.2370720	-1.0679440	-0.7642590
C	-1.2052850	2.1498370	-0.0367880
H	-2.1633370	2.6564900	-0.0442620
C	0.0000050	2.8387640	-0.0399360
H	0.0000110	3.9260660	-0.0488810
C	1.2052880	2.1498290	-0.0365180
H	2.1633450	2.6564770	-0.0437300
C	2.3148210	-1.4186140	-0.0916580
H	1.4056440	-1.9963080	-0.1630820
C	3.6111440	-1.7868770	-0.0507370
H	4.0749270	-2.7639150	-0.0801870
C	5.8002370	-0.6066080	0.1267680
H	6.2368100	-1.0671850	-0.7653790
H	6.1357310	-1.1600380	1.0098780
H	6.1397820	0.4280260	0.2004590

TD-DFT (U) M06 Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.3608 eV 525.17 nm f=0.0000 <S**2>=0.000
HOMO-3 → LUMO+1 0.70839
HOMO-3 → LUMO+1 -0.13333
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1078.17608204

Excited State 5: Singlet-A 3.4349 eV 360.95 nm f=0.0005 <S**2>=0.000
HOMO → LUMO 0.69628

Excited State 6: Singlet-A 4.0360 eV 307.20 nm f=0.0088 <S**2>=0.000
HOMO-3 → LUMO 0.67440
HOMO-1 → LUMO -0.18058

Excited State 7: Singlet-A 4.1237 eV 300.66 nm f=0.0013 <S**2>=0.000
HOMO-4 → LUMO 83 0.38450
HOMO-3 → LUMO 83 0.19335
HOMO-1 → LUMO 83 0.53379
HOMO → LUMO+2 0.14457

Excited State 8: Singlet-A 4.3527 eV 284.84 nm f=0.2362 <S**2>=0.000
HOMO-2 → LUMO 0.67126

Excited State 9: Singlet-A 4.3648 eV 284.05 nm f=0.0572 <S**2>=0.000
HOMO-4 → LUMO 0.54991
HOMO-2 → LUMO -0.10605
HOMO-1 → LUMO -0.40868