Supplementary Information

Immobilization of Cobalt Catalyst on Fullerene in Molecular Devices for Water Reduction

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Experimental section

General methods and chemicals used.

Solvents and reagents were ordered from Sigma-Aldrich and used without additional purification, if not especially mentioned. All the organic reactions were performed under an inert atmosphere of nitrogen using Schlenk techniques, and the prepared chemicals were dried under the traditional vacuum conditions. For electrochemical as well as photoelectrochemical testing in aqueous phase, 0.1 M acetic acid buffer solution (pH 4.5) was used and made from acetic acid and sodium acetate anhydrous in deionized water. For electrochemistry in organic phase, 0.1 M tetrabutylammonium tetrafluoroborate was acted as the supporting electrolyte, and dissolved in acetonitrile and chloroform, respectively. The carbon cloth (CC) was purchased from Shanghai HeSen Electrical Corporation. Before using, the CC (1×2 cm^2) was washed with methanol and acetone successively, and it was dried at room temperature overnight.

General characterization methods and Instrument.

The FT-IR spectra of the samples were performed on a Spectrum One FT-IR Spectrometer. UV-vis testing was proceeded with a Cary 5000 UV-Vis-NIR spectrophotometer. ^{1}H NMR spectra were recorded on the JEOL ECP-400 NMR system (400 MHz), and the chemical shifts recorded in ppm were given relative to TMS. MS were run on the Thermo Finnigan LCQ Deca XP MAX LC/MS system. SEM images were obtained from JEOL JSM-7401F operating at 2 kV. Electrochemical measurements were carried out using an AUTOLAB potentiostation and a GPES electrochemical interface (Eco Chemie) with a traditional three-electrode system, with a Pt plate electrode as the counter electrode, glass carbon (GC), CC, and CC modified electrodes as the working electrodes, and before testing, the GC electrode was polished by 0.3 μm and 0.05 μm aluminum oxide particles to a mirror finish, then sonicated in ethanol and ultrapure water in turn. When in acetonitrile testing solution, Ag/AgNO$_3$ electrode (0.01 M AgNO$_3$) acted as the reference, and its potential was calibrated after each experiment by adding ferrocene ($E^o_{Fe+/0} = 0.63$ V *vs.* NHE) in the background solution; while in aqueous testing solution, a saturated Ag/AgCl electrode (saturated KCl) worked as the reference ($E^o_{Ag/AgCl} = 0.197$ V *vs.*

NHE). Electrochemical testing in aqueous phase was performed in a two-compartment cell which was separated by a frit, and the volume of the buffer solution was 15 mL in each compartment; while in organic phase, cyclic voltammetic curves were tested in a one-compartment cell. Before measurement, the testing solution was degassed with high purity Ar atmosphere for at least 20 mins. Photoelectrochemical testing was performed using a light emitting diode array source to give a light intensity at 100 mW cm^{-2} illumination (AM 1.5 irradiation) calibrated by a silicon solar cell. For the H_2 and O_2 measurement, after adding the buffer solution and loading the electrodes, the two-compartment cell was sealed well with the polytetrafluoroethene tapes and vacuum glue carefully, in order to get rid of the leakage of the generated gases. After that, the two-compartment cell was degassed with high purified Ar at least 50 mins to make sure that there was no O_2 in the cell. After the passage of the charge for 1 h (-0.8 V *vs.* NHE), both of the gas samples (H_2 evaluated in the chamber with CC modified electrode and O_2 generated in the chamber with Pt plate electrode) in two compartments were taken using syringe, respectively, and the amount of the H_2 and O_2 was determined by sleek Clarus® 500 Gas Chromatograph from PerkinElmer. The standard curve of gas vs. integration area was made in advance. Therefore, the produced amount of H_2 or O_2 could be calculated. After carefully measuring the volume of the respective compartment, the totally generated gases could be determined.

Synthesis

N-Methyl-2-(4’-ethynyl) phenyl-3,4-fulleropyrrolidine (C_{60}-ref) was fabricated according the reference.[1] MS: *m/z* 877 [M$^+$], 720 [M-157]$^+$ and ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ = 7.77 (s, 2H), 7.54 (d, 2H, *J*= 8.6), 4.99 (d, 1H, *J*=9.5), 4.94 (s, 1H), 4.26 (d, 1H; J=9.5), 3.08 (s, 1H), 2.79 (s, 3H).

The Co catalyst (Co-N_3) was synthesized referred to the literatures.[2] MS: *m/z* 407.9 [M-H]$^-$ and ^{1}H NMR (400 MHz, ACETONE-D6) δ = 19.38 (s, 1H), 4.57 (m, 3H), 3.88 (t, 2H, *J*=13.7), 2.76 (t, *J*=1.7, 6H), 2.53 (s, 6H).

The preparation of carbon cloth-based electrode

For the preparation of the CC-C_{60}-ref modified electrode, under the optimal conditions, 0.877 mg (1 μmol) C_{60}-ref was dissolved in 50 μL $CHCl_3$, then, the homogeneous brown C_{60}-ref solution was dispersed to the CC, and the C_{60}-ref modified CC was dried with air flow at room temperature. The optimal ratio for the reaction between terminal alkynes in C_{60}-ref and the azides in Co-N_3 was as follows, C_{60}-ref (1 equiv) on CC, CuI (6 equiv), N,N-Diisopropylethylamine (DIPEA, 150 equiv), and Co-N_3 (3 equiv).[3] Before the reaction, CuI, DIPEA, and Co-N_3 were dissolved into the acetonitrile (MeCN) by ultrasonic dispersion. Then, the prepared solution was degassed with Ar atmosphere at least 10 mins. After that, the CC-C_{60}-ref electrode was immersed into the solution over night at 40 ^{o}C. Finally, before the electrochemical testing, the CC-C_{60}-Co electrode was washed with acetonitrile to get rid of the unreacted Co-N_3.

The preparation of organic photovoltaic (OPV)-based electrode

PEDOT:PSS (1.3 wt % dispersion in H_2O, Aldrich) was diluted by same volume of EtOH. 100 µL diluted PEDOT:PSS (Aldrich) ethanol solution (1:1; v/v) was placed on ITO substrate and was spin-coated at 1000 rpm 3 s and 2000 rpm 30 s. The formed ITO/PEDOT:PSS electrode was further heated on 150 °C hot plate for 3 min. Subsequently, 100 µL chlorobenzene solution of P3HT (1 mg) and C_{60}-ref (2 mg) was spin-coated on the aforementioned electrode at 1000 rpm 3 s and 2000 rpm 30 s and then was treated at 150 °C for 3 min to form the ITO/PEDOT:PSS/P3HT:C60-ref electrode. The ITO/PEDOT:PSS/P3HT:C_{60}-Co electrode was prepared by click chemistry using same condition to prepare CC-C_{60}-Co electrode and then was washed by MeCN to get rid of physically absorbed catalysts. The control electrode ITO/PEDOT:PSS/P3HT:C_{60}-ref was also treated in pure MeCN at 40 °C.

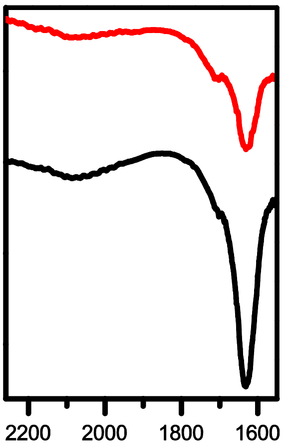

Figure S1. FTIR transmission spectra of C_{60}-ref in KBr, before (black) and after treatment (red) at 150 °C.

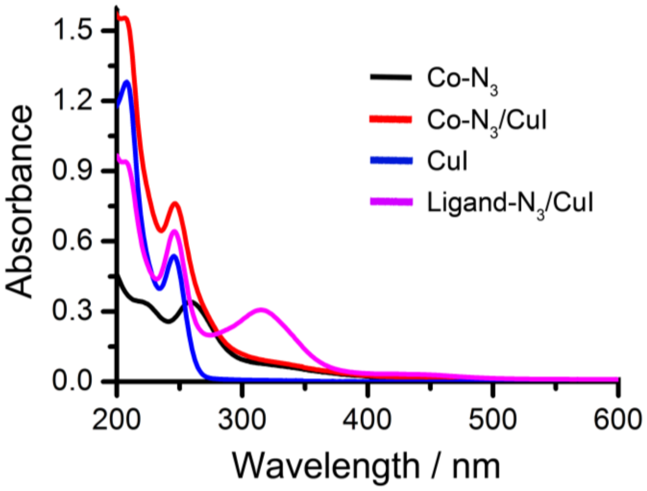

Figure S2. UV-Vis of Co-N_3, Co-N_3/CuI, CuI, and Ligand-N_3/CuI in acetonitrile (MeCN).

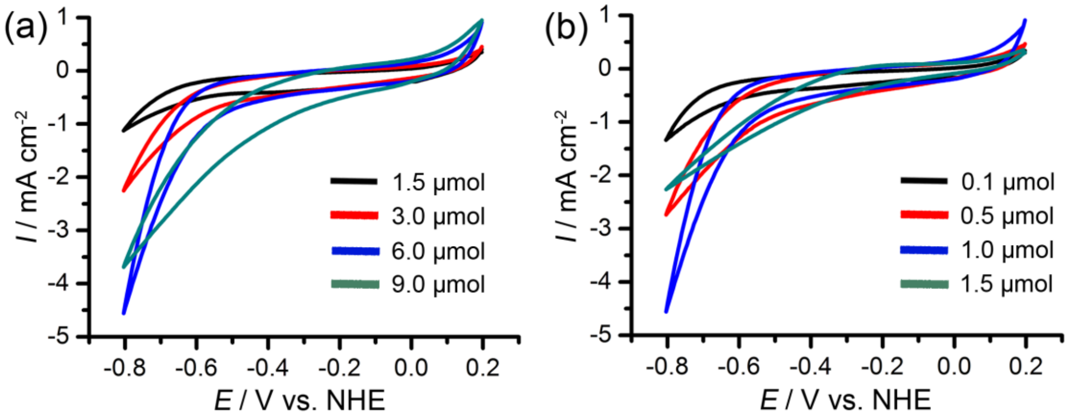

Figure S3. Cyclic voltammetry of CC-C_{60}-Co electrode modified with (a) different ratio of CuI and (b) different concentration of C_{60}-ref in 'click' reaction in acetate buffer saturated with Ar gas (0.1 M, pH 4.5) at scan rate of 50 mV s^{-1}.

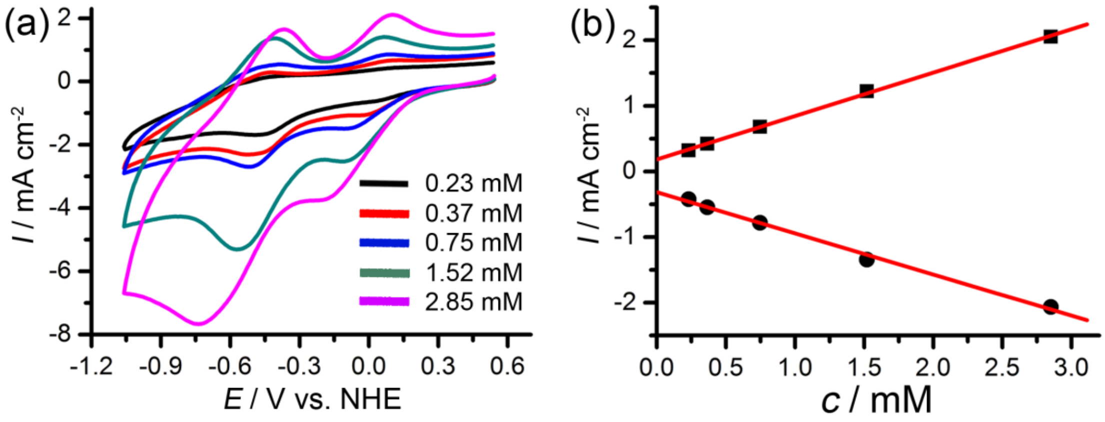

Figure S4. (a) Cyclic voltammetry of different concentrations of Co-N_3 in acetonitrile (0.1 M n-Bu_4NBF_4), and the scan rate was 50 mV s^{-1}. (b) The peak currents of Co(Ⅱ)/Co(Ⅰ) redox couple.

Figure S4a showed the CV results of Co-N_3 in acetonitrile. Two well-defined reversible peaks were discovered obviously. The reversible peaks at around -0.054 V was ascribed to the redox couple of Cu(Ⅲ)/Cu(Ⅱ), while the process exhibited at -0.464 V was ascribed to the redox performance of Co(Ⅱ)/Co(Ⅰ) couple.[2a] The redox peak currents enhanced linearly combining the concentration increase of the Co-N_3, which was shown in Figure S4b.

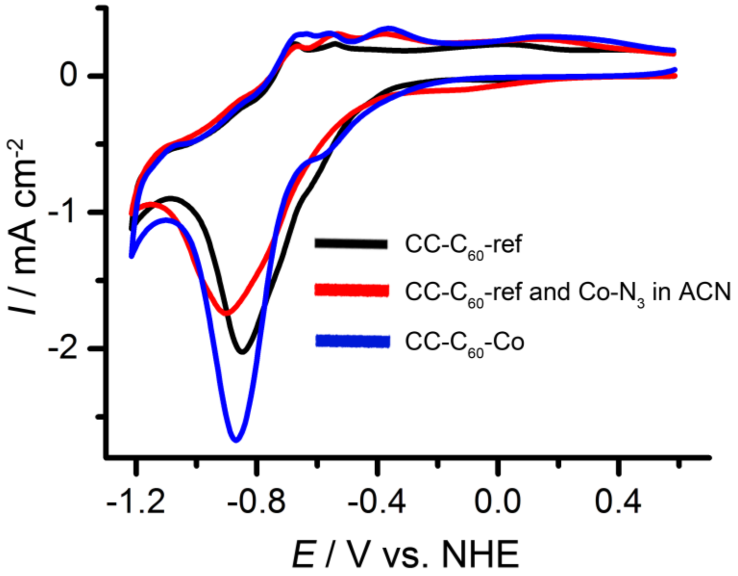

Figure S5. CV of CC-C_{60}-ref electrode in acetonitrile (0.1 M n-Bu_4NBF_4), CC-C_{60}-ref in acetonitrile (0.1 M n-Bu_4NBF_4 containing 0.2 μmol Co-N_3), and CC-C_{60}-Co in acetonitrile (0.1 M n-Bu_4NBF_4).

The electrochemistry is a conventional method to determine the amount of catalyst on the bulk electrode. However, in the aqueous solution, it is hard to detect the characteristic reduction peak of catalyst on our CC-C_{60}-Co electrode, thus it is impossible to estimate the amount of active catalyst or attached catalyst in aqueous condition. Subsequently, we found it is possible to get all compounds off from CC electrode with a negative potential scan in electrochemistry experiment in acetonitrile (MeCN), ascribing to the good solubility of reduction species in MeCN, and the reduction peak of the cobalt catalyst can be detected as a consequence, which also implies that the catalyst is still survival after electrolysis experiment. The coverage of catalyst on the CC-C_{60} electrode can be estimated according to the standard curve of the pure Co-N_3 catalyst in MeCN (Fig. S4 and Fig. S5). According to the calculation, the total amount of catalyst on CC electrode is determined to be 2.6×10^{-7} mol cm^{-2}, and the turnover number (TON) is 190 in 1 h electrolysis. Taken into account by the morphology of electrode, not all of catalysts are expected to be active for H_2 production in aqueous solution due to the poor wettability of water on electrode. Therefore, it is still difficult for us to get the real amount of active catalyst on electrode and provide a reliable turnover number. As a result, the turnover number reported here is much underestimated. However, the catalytic current of CC-C_{60}-Co electrode in this work obtained is ca. a factor of 3 greater than that reported in the cobalt catalyst modified carbon nanotube electrode[2a] under the same condition, probably owing to the increment of active catalyst loading on the electrode.

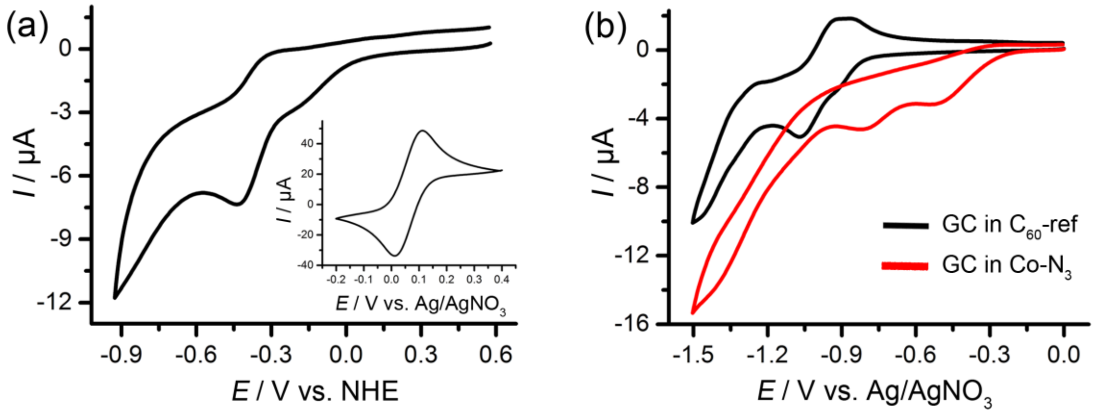

Figure S6. (a) CV of glass carbon electrode in 0.1 M n-Bu_4NBF_4 acetonitrile solution containing 0.5 mM Co-N_3. Inset: CV of glass carbon electrode in 0.1 M n-Bu_4NBF_4 containing ferrocene. (b) CVs of glass carbon electrode in 0.1 M n-Bu_4NBF_4 $CHCl_3$ solution containing 0.5 mM C_{60}-ref and 0.5 mM Co-N_3, respectively.

In order to identify the energy level of Co-N_3 and C_{60}-ref, electrochemistry method is used to determine the redox peaks of the molecular. Due to the irreversible CV behavior of ferrocene in chloroform, it has to determine the reference potential of Ag/$AgNO_3$ in acetonitrile in advance. Based on the redox potential of ferrocene/ferrocenium, which is 0.64 V *vs.* NHE, and the redox potentials of Co-N_3 in both acetonitrile and chloroform, the energy level of Co-N_3 and C_{60}-ref has been calculated depending on Figure S5. [4]

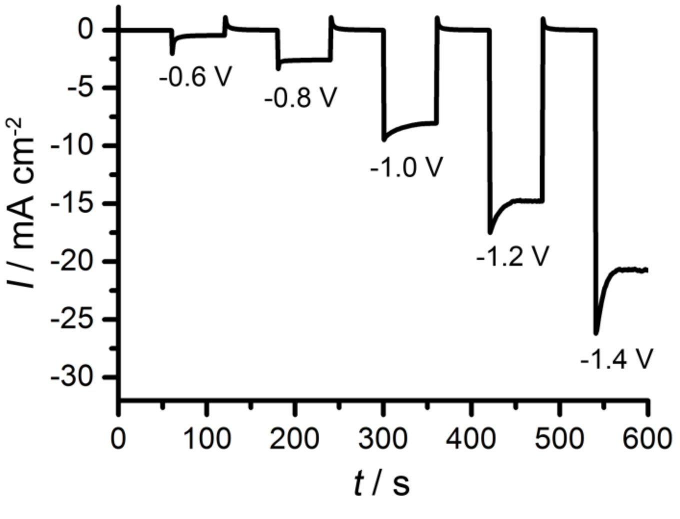

Figure S7. Chronoamperometric current density of CC-C_{60}-Co electrode measured in acetate buffer saturated with Ar gas (0.1 M, pH 4.5).

The electrocatalytic activity of the CC-C_{60}-Co electrode was further determined in 0.1 M acetic acid buffer solution (pH 4.5) by chronoamperometric experiments, and the current density of the electrode was monitored consequently under a sequence of applied electrochemical potential range from -0.6 V to -1.4 V *vs*. NHE. When the overpotential reached to about 0.1 V than the thermodynamically required reduction potential of water at pH 4.5 (E = -0.27 V *vs*. NHE), the distinguishable catalytic current was detected, and it was even conspicuous when the overpotential was at round 0.3 V. It indicated a much more effective Faradaic process at the CC-C_{60}-Co electrode for the reduction of water.[5]

Table S1. EDS data of sample CC-C_{60}-Co

Element	AN	Series	Net	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Carbon	6	K-series	20122	80.32	80.32	84.12	9.2
Nitrogen	7	K-series	319	12.14	12.14	10.90	2.6
Oxygen	8	K-series	382	5.89	5.89	4.63	1.2
Cobalt	27	K-series	129	0.98	0.98	0.21	0.1
Iodine	53	L-series	73	0.39	0.39	0.04	0.0
Chlorine	17	K-series	189	0.27	0.27	0.10	0.0
			Total:	100.00	100.00	100.00	

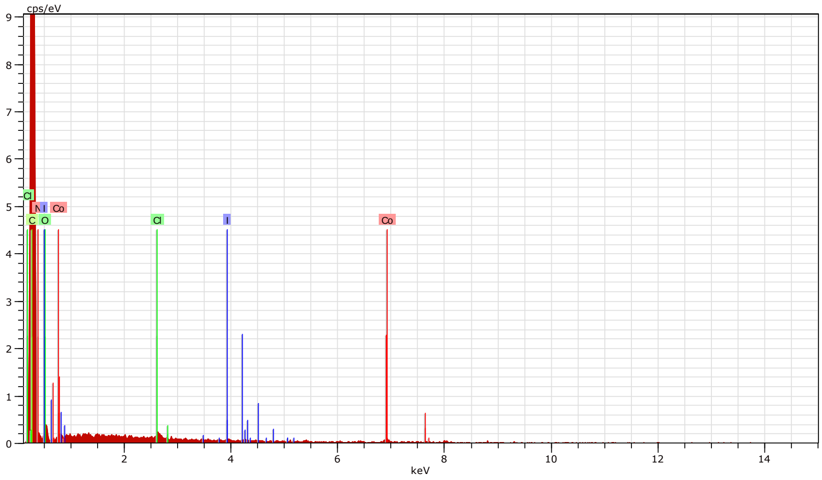

Figure S8. EDS spectrum of CC-C_{60}-Co

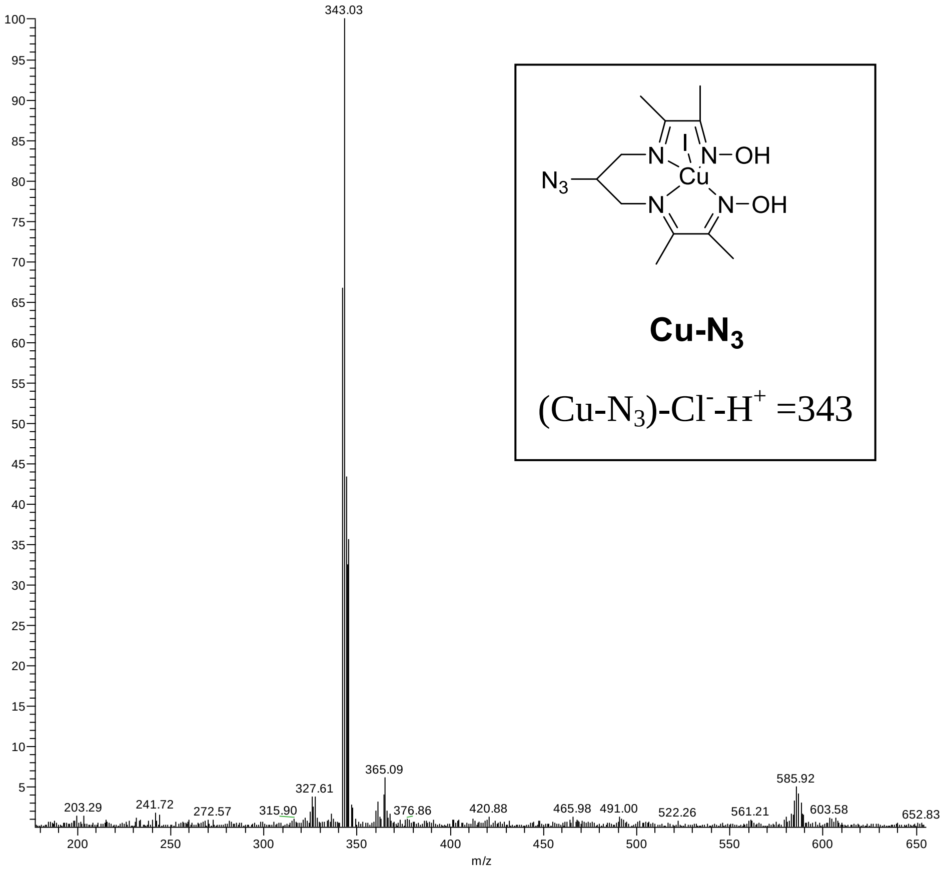

Figure S9. MS spectrum of N3-ligand mixed with CuI in acetonitrile

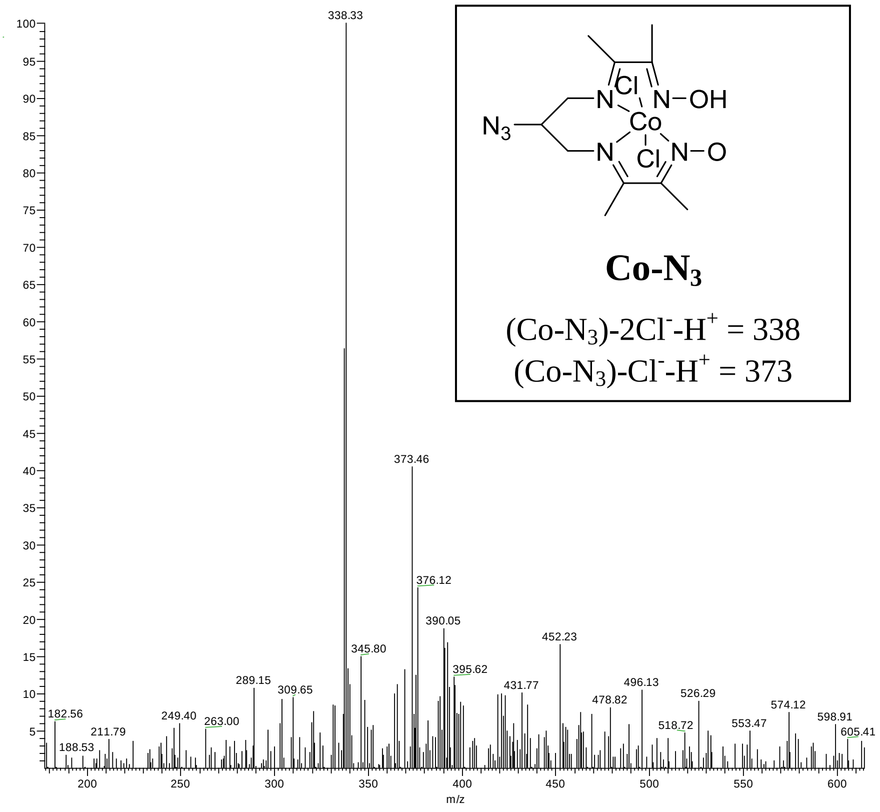

Figure S10. MS spectrum of Co-N_3 in acetonitrile

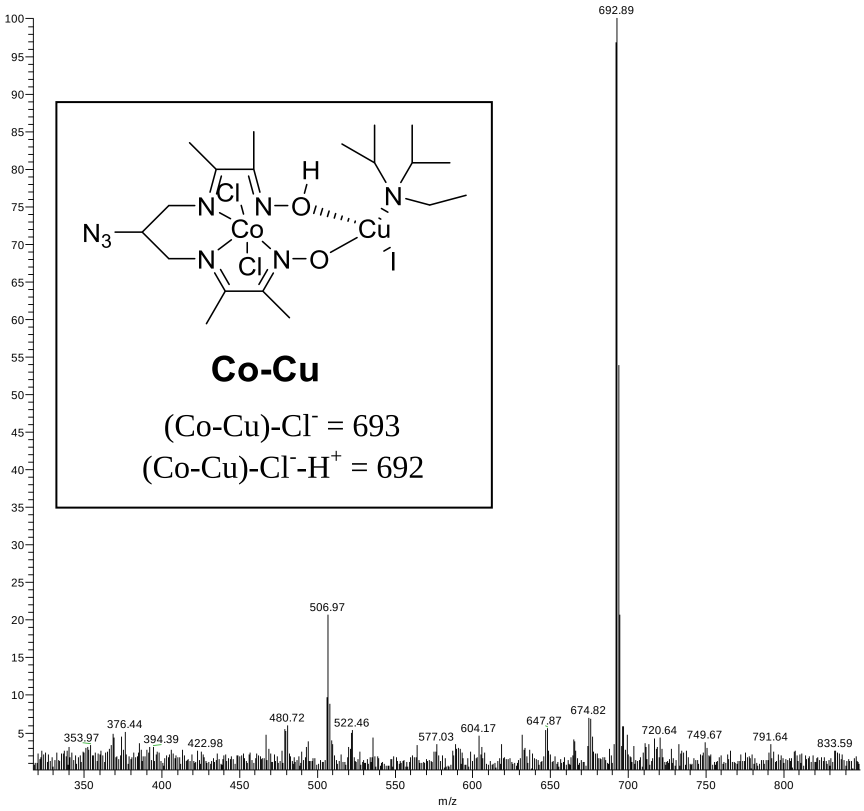

Figure S11. MS spectrum of 0.5 mM Co-N_3, 1 mM CuI and 4 mM DIPEA in acetonitrile overnight.

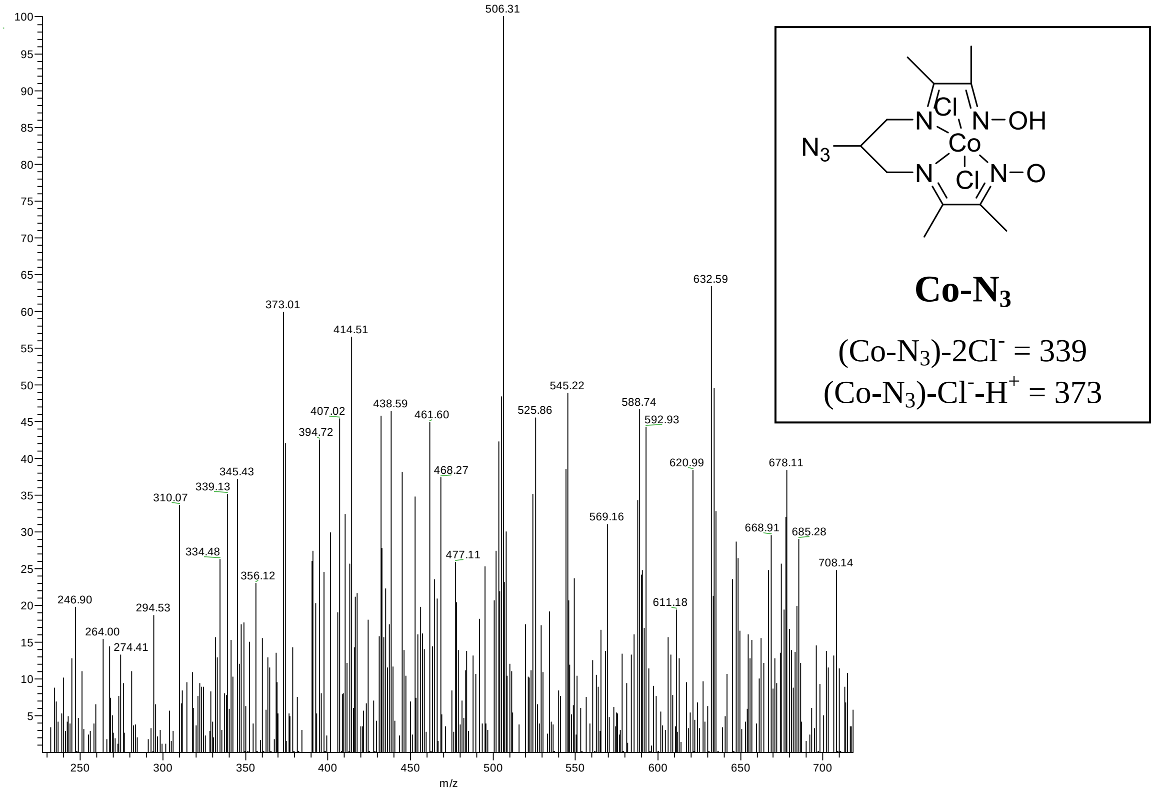

Figure S12. MS spectrum of 0.5 mM Co-N_3, 1 mM CuI and 4 mM DIPEA in acetonitrile overnight with adding acetic acid afterwards.

From the MS spectra in **Figure S9-S12**, we can see a new **Cu-Co** complex (ms: 692.9) was formed after mixing **Co-N_3 (Figure S11)**, 1mM CuI and 4 mM DIPEA overnight. No replacement of Cu in **Co-N_3** was observed since no MS signal (ms: 343) of **Cu-N_3** was appeared. The CuI and DIPEA can react with Co-N_3 to form the Cu-Co complex. However, adding acetic acid in this solution, then we can find the **Co-N_3** compound is regenerated due to the instability of **Cu-Co** complex in the acid condition. The acidic buffer solution in our experiment was used to perform final test, so we think we still have Co catalyst on surface, or not Cu catalyst.

References

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