An Organocobalt-Carbon Nanotube Chemiresistive Carbon Monoxide Detector

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Supporting Information

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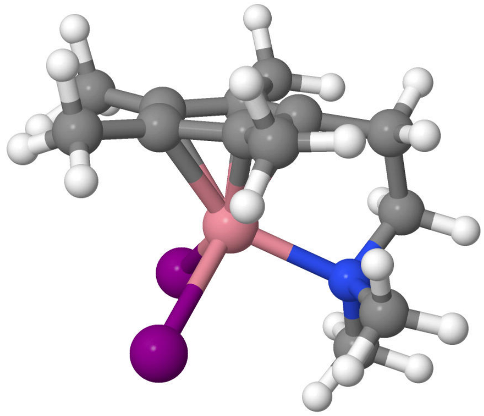
General Methods and Instrumentation

(6,5) chirality-enriched SWNTs (SG65) and halocarbon oil 27 were purchased from Sigma-Aldrich. Carbon monoxide (99.3%), carbon dioxide (99.9%), acetylene (99.6%), and ethylene (99.9%) were purchased from Airgas. 2-Bromo-2-butene (98%) was purchased as a mixture of *cis* and *trans* isomers from Sigma-Aldrich. Lithium wire (99.8%), ethyl 3-dimethylaminopropionate (97%), and 1,3-cyclohexadiene (96%, stabilized with 0.1% BHT) were purchased from Alfa Aesar. Dicobalt octacarbonyl stabilized with 1-5% hexanes was purchased from Strem. Solvents were purchased from Sigma-Aldrich and dried over activated 4 Å molecular sieves (diethyl ether, dichloromethane) or used as received (chloroform, 1,2-dichlorobenzene).

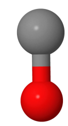
UV-Vis spectra were recorded on an Agilent 8453 UV-visible spectrometer. Samples for Raman spectroscopy were prepared by drop-casting from a suspension in a solution of 80:20:5 DCB:$CHCl_3$:HC27 onto Si/SiO_2 wafers with subsequent removal of volatile organics in vacuo; spectra were recorded on a Horiba LabRAM Raman spectrometer (0.4 cm^{-1} resolution) with a 532 nm wavelength laser and internally referenced to the first-order silicon peak at 519 cm^{-1}. Scanning electron microscopy (SEM) images were recorded on a JEOL 6010LA scanning electron microscope; samples were prepared by drop-casting from a suspension in a solution of 80:20 DCB:$CHCl_3$ onto Si/SiO_2 wafers with subsequent removal of volatile organics in vacuo. ^{1}H NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer and were referenced to the proton resonances resulting from incomplete deuteration of the NMR solvent.

Computational Details

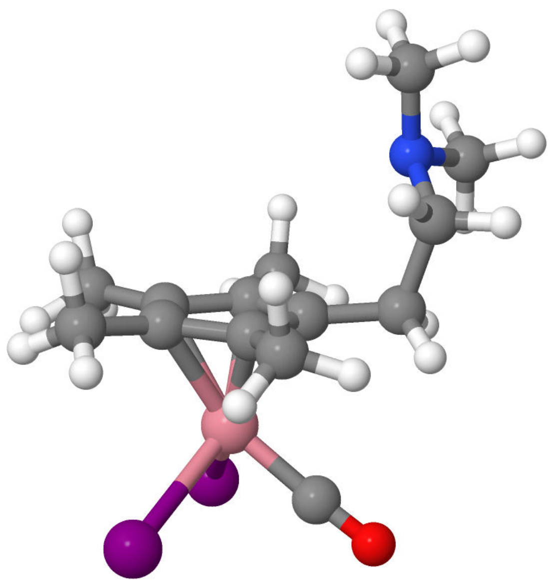
All DFT calculations were performed with Orca[1] version 3.0.3 using the Becke B3LYP hybrid functional,[2,3] the Hay-Wadt LANL effective core potential and basis sets[4,5] for cobalt, and the def2-TZVP(-f) basis set.[6,7] To efficiently run calculations, the resolution-of-identity chain-of-spheres ("RIJCOSX") approximation[8] was utilized. Geometry-optimized molecular structures were verified to be local minima with frequency calculations, which showed no imaginary frequency vibrations greater than 20 cm^{-1} in absolute magnitude. The optimized structures were also used for single-point calculations including the conductor-like screening model ("COSMO")[9] with a dielectric constant of 2.0 to approximate halocarbon oil 27 (c.f. 2.0 for Teflon at 23 °C).[10] The solution-phase Gibbs free energies were determined by adding the gas-phase Gibbs free energy from the frequency calculations and the solvation energy (i.e., the difference in electronic energy between the COSMO-treated and plain single-point calculations). All thermodynamics were calculated at 298.15 K and 1.00 atm.



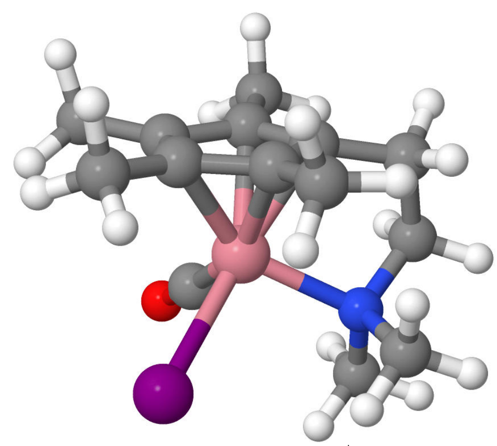
[Cp^CoI_2]



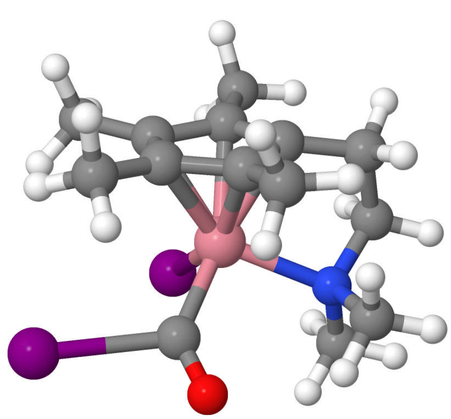
CO



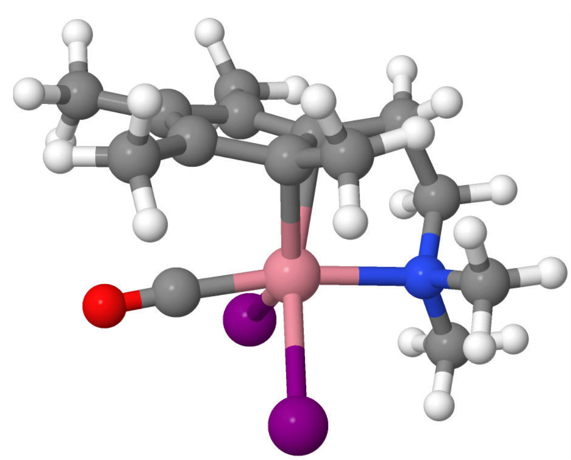
[Cp^CoI_2(CO)]



[Cp^CoI(CO)]$^+$



[Cp^CoI(COI)]



[Cp^CoI_2(CO)]’

Figure S-1. Pictures and names of optimized structures.

Table S-1. Cartesian coordinates for [Cp^CoI$_2$].

Co	2.06971258935551	2.41123114363425	2.76181829636438
I	0.47263509804261	2.68625106662613	0.66891557786415
I	0.09913532812762	1.99700875061572	4.45644954731065
N	2.52730479363279	0.33992493735983	2.53638682846047
C	3.66750704149151	3.47800527388707	1.83212776786041
C	2.83153746437541	4.45795527574339	2.47975424000507
C	2.80534959744012	4.17150653094036	3.86046131004704
C	3.60258154919364	3.00018183908018	4.10106149659757
C	4.14084842541864	2.58999714620094	2.83748908577455
C	4.09017573838537	3.52984968769444	0.39893291262009
C	2.23920735465370	5.66889170519019	1.83488697283408
C	2.15900758402635	5.00710903620710	4.91394837310342
C	3.94464976529942	2.50643310476285	5.47254074081266
C	4.83251696551367	1.28619765664176	2.53937889774949
C	3.84473948778500	0.35064391669550	1.83234106685297
C	1.56202684250763	-0.45736683511836	1.73674838944750
C	2.67839005278238	-0.36237697929644	3.83844161174234
H	4.78455804788226	4.36280420319904	0.24863797163746
H	4.60453950427679	2.62104456706813	0.08835032727215
H	3.23574372534926	3.67486755903412	-0.26151942684878
H	2.91738726282673	6.51927354180845	1.97183491533546
H	2.07735732910964	5.52122255454908	0.76953245450194
H	1.28105300144093	5.93046801775913	2.28032718804290
H	2.89320174512961	5.71142152496863	5.32271212734698
H	1.33091424494106	5.58645384893758	4.50953338727541
H	1.77331944242979	4.39958732160198	5.72987424990829
H	4.44581186267286	3.30110342556785	6.03337341719722
H	3.05112509299718	2.22048594519800	6.03048160112315
H	4.62682322848012	1.65730716469657	5.45004759702543
H	5.20673799863834	0.83069093878937	3.45597390814140
H	5.70045203441133	1.44139265574073	1.89425577631998
H	3.65731851685602	0.70110747176997	0.81890583583554
H	4.23836675402863	-0.67183706696274	1.76821254036771
H	1.91783740080364	-1.49121971267476	1.66172730113474
H	0.59472456434654	-0.43630209164753	2.23272797035205
H	1.45080106446618	-0.02738318445735	0.74710871372557
H	3.11449845621127	-1.35394175851160	3.66933586350161
H	3.31323301211892	0.19808414262561	4.51353272324644
H	1.70287003255153	-0.46107432592516	4.30335044211052

Table S-2. Cartesian coordinates for CO.

C	0.00000000000000	0.00000000000000	-0.64304817610388
O	0.00000000000000	0.00000000000000	0.48275847170534

Table S-3. Cartesian coordinates for [Cp^CoI$_2$(CO)].

Co	1.90431523409472	2.46656570896913	2.69366189851085
I	0.80585273029875	2.51109426788900	0.30173898988250
I	-0.39473140385037	2.41528727234891	3.95072553001392
N	7.04410814094589	2.61705002490294	2.43411533382942
C	3.68071672686865	3.44680893263535	2.02526427898280
C	2.82136911386492	4.41853817124699	2.65868299848511
C	2.64547637877187	4.03169174034011	4.01025205412249
C	3.31352434910536	2.77821230527468	4.21081717505406
C	3.99792731360530	2.44845221652582	2.98753960120297
C	4.24454338085304	3.56486506508083	0.64892944762227
C	2.31522147318934	5.68490031891795	2.04627012897199
C	1.96711176418968	4.83106546021362	5.06999714866417
C	3.42611004527921	2.06939418605809	5.52298647351487
C	4.94327997905156	1.29581311747768	2.81374887964391
C	6.36920754796386	1.63746323411073	3.28029664641362
C	8.09071076647209	3.32098464245742	3.16395147342182
C	7.57321302651083	2.02048607265559	1.21357823952166
H	5.18805498198306	4.11395445574962	0.69958957685692
H	4.44994947417159	2.59100332972932	0.20943729602402
H	3.56372036574567	4.08868503484037	-0.01702327133127
H	3.06001764482138	6.47997765323815	2.15940840114324
H	2.10143957551469	5.56221588860671	0.98569303269601
H	1.39959708704533	6.01767668947852	2.53201670545311
H	2.70179128176271	5.50062920774263	5.53245839774288
H	1.16437790310983	5.44271784477473	4.66397268383305
H	1.54394204651191	4.20071381769477	5.84849776701289
H	4.14182178421077	2.58156096141330	6.17385015443195
H	2.46664729978091	2.04879819618246	6.03963330727294
H	3.76451429466022	1.04090558375171	5.40478441346635
H	4.95678640966276	0.96557545481802	1.77479356299906
H	4.60078149697569	0.44040459016625	3.39871281872694
H	6.31183607815720	2.05039079444507	4.28932960590589
H	6.94910366873607	0.70177805731856	3.35465495382610
H	8.88993494594307	2.65087922452501	3.52553371217848
H	8.54912913630097	4.07219299062584	2.51848555634152
H	7.65794510936050	3.83266636382668	4.02515453553676
H	8.35829163278025	1.27220373725336	1.41617223221207
H	6.78020597057851	1.52993127790875	0.64923901399746
H	8.00121224040595	2.79868402578331	0.57964354538920
C	1.74886095401205	0.67894576486014	2.61547383868503
O	1.71108205055422	-0.45516368183820	2.58593186174099

Table S-4. Cartesian coordinates for [Cp^CoI(CO)]$^{+}$.

Co	2.13927290606903	2.29709087923430	2.66416874859073
I	-0.09651259568655	2.01688312455813	3.96765896370745
N	2.66339999322126	0.26854257111781	2.60750530492150
C	3.69125423006568	3.41590616380106	1.81999445310729
C	2.74662739124705	4.33665724085520	2.41741792838221
C	2.70514762236607	4.08078994762978	3.81682844582811
C	3.57017312755147	2.97789315754138	4.10263583319382
C	4.17328378939960	2.57034906674390	2.86289821060441
C	4.16639330543176	3.46278434502050	0.40247497469244
C	2.06555245155269	5.47706277136204	1.73285069569824
C	1.96921071210770	4.88298392350442	4.83223112294981
C	3.89845208556654	2.51749198686535	5.48809601722960
C	4.95233891049619	1.29967343064597	2.65169064212077
C	4.03780316792197	0.25688686697971	1.99824553100785
C	1.76291507403801	-0.56451844788718	1.76039270151430
C	2.70635296092584	-0.37682264171336	3.95046583509837
H	4.96490219905491	4.20525641755771	0.31456998550516
H	4.57418096565926	2.51103634988435	0.06597381520278
H	3.37771020790355	3.75894006779833	-0.28809625573532
H	2.66555568511070	6.38352629467388	1.85877218554770
H	1.94425948915752	5.30741467297951	0.66409666475708
H	1.08388059123616	5.67332716338311	2.16094060970758
H	2.64597780596631	5.64842143133237	5.22831888489677
H	1.10617917706030	5.38905698046878	4.40670049141885
H	1.62908299561146	4.27304163640397	5.66588718596866
H	4.36412137587897	3.33945215226512	6.03833275343785
H	3.00763152747598	2.21893644807448	6.04176202860795
H	4.60614651585978	1.69099829350000	5.49634063231313
H	5.34521274723179	0.93518860714795	3.59921855005601
H	5.81512492842331	1.47095219191228	2.00509583287432
H	3.91738664612221	0.48234877347523	0.93994760187901
H	4.45943751653325	-0.75056331344015	2.07399472961684
H	2.12902185841065	-1.59408723261669	1.73412139179070
H	0.76169238808446	-0.55173333103444	2.18386960283568
H	1.73662190516767	-0.17734043751611	0.74460508326651
H	3.09009787612944	-1.39644993542266	3.85044210308272
H	3.34725058913052	0.17529461460556	4.62652663550388
H	1.70434732917220	-0.40195510351816	4.36808969857923
C	1.08365868130795	2.33759857524213	1.17467971270320
O	0.45485386603734	2.43168429658438	0.23925466753679

Table S-5. Cartesian coordinates for [Cp^CoI(COI)].

Co	2.13943332027758	2.42056653483369	2.66102793591337
I	0.84351377066420	2.85536804990418	0.41593257544166
I	-1.13212940272785	4.00479992726268	3.86381029463399
N	2.56371134039329	0.32939406270648	2.28804986161416
C	3.88886816149907	3.52428326218000	1.99745337315438
C	3.01475696696723	4.43321976633061	2.70457377287444
C	2.88275213756585	3.97266239336201	4.03497938483507
C	3.59846994072708	2.74058988831055	4.16231678120656
C	4.23560858115485	2.48684674902635	2.89258204594436
C	4.42027314040272	3.74423761573695	0.61654697439119
C	2.49626382820017	5.73693281085259	2.18892293397181
C	2.22999351318119	4.70526376699184	5.15636505926670
C	3.86397935269993	2.07822145267181	5.48377100228631
C	4.89943544889695	1.20120317582739	2.48223783084658
C	3.91374524290058	0.37762751209784	1.64546312271283
C	1.64018322783219	-0.39504274025392	1.37523587247884
C	2.64192091837173	-0.48425914386100	3.52908280313777
H	5.13195244176996	4.57614906490134	0.62400139072045
H	4.94802451311633	2.86938194538697	0.23834187990456
H	3.62446927469024	3.98496426334193	-0.08662244087253
H	3.06502471731770	6.55979702008785	2.63358711783801
H	2.58872990830833	5.80308715144440	1.10672666609576
H	1.44605387574276	5.87397659141898	2.44674031222136
H	2.99686531573414	5.25838799870457	5.71221174237075
H	1.48781330054758	5.41380896628413	4.79953258323810
H	1.73016564252214	4.03545956588294	5.85487447006018
H	4.35754823016307	2.78824203621189	6.15364645030691
H	2.94929101322196	1.75005308534964	5.97967560306347
H	4.52596120600351	1.21844413666211	5.39340784400588
H	5.23686482398544	0.64063437846305	3.35415585695371
H	5.79007023466382	1.39736643211156	1.88169580898293
H	3.78040622350538	0.84380759381520	0.67039911669568
H	4.27958994818588	-0.64449826665409	1.48434475629201
H	2.00913704814180	-1.41548997724619	1.22222219951467
H	0.65041132653205	-0.43444438791622	1.82283200870342
H	1.57403347718648	0.12283335622593	0.42552785990836
H	3.04303831788091	-1.47567943754898	3.28962054244680
H	3.28149118064048	-0.01592149456626	4.26562286083647
H	1.64827719033537	-0.58983434596746	3.95220663135542
C	0.47539484768159	2.08267008916628	3.60166456013618
O	0.03460645311625	1.12688915046034	4.09523255451144

Table S-6. Cartesian Coordinates for [Cp^CoI$_2$(CO)]$^{\cdot}$.

Co	1.67797461552133	2.00129356130432	2.52495816334447
I	0.84610134336691	2.23423743632161	-0.04110356591858
I	-0.42688128529992	1.07634336716813	3.81242011563202
N	2.50830909914267	0.03835561516335	2.29560664794709
C	3.72361465367538	3.74988183134034	2.05184355711198
C	3.17998464225793	4.80115299550818	2.88400642349940
C	2.82904029735589	4.23733870033539	4.08364033171326
C	3.16077864935208	2.79115199384169	4.06020322807995
C	3.79217413726796	2.54748842895575	2.80160047247559
C	4.22515417386513	3.96891824995192	0.66895613493596
C	2.93801622837476	6.19911183535326	2.40335811031325
C	2.16688154674059	4.88261372561207	5.25447129373906
C	3.41611892783259	2.08973528340027	5.37149693172142
C	4.61863393405113	1.33794744432813	2.43575999720334
C	3.82787945321944	0.29175436406584	1.65690673643310
C	1.71616568502957	-0.86364710696561	1.41485836002607
C	2.69543811400832	-0.70690425749426	3.56850317454531
H	4.95047781454081	4.78889742589114	0.65667302228222
H	4.70227626345834	3.08322513155454	0.25287924723267
H	3.41052615590805	4.25010845988954	-0.00509241513361
H	3.85150236750823	6.65361242838540	2.00907293603050
H	2.19844644228779	6.22535652926151	1.59613167191519
H	2.56890160572666	6.84064766565024	3.20267101910927
H	2.87086595943029	5.00780313919807	6.08412045682940
H	1.76356981441000	5.86421218769644	5.00914636398832
H	1.34918172938546	4.26280902410221	5.62996705924835
H	3.85199410617445	2.79317328311645	6.08618558318154
H	2.50633922468150	1.69176420431116	5.82448637200019
H	4.12978005177473	1.27303928576003	5.27518871760637
H	5.04168771095441	0.89634120913651	3.34049209588491
H	5.47446945480370	1.64109062459498	1.82914845286011
H	3.62435877140375	0.65361790984795	0.64927767874768
H	4.38512775266783	-0.64962423702839	1.57613198107605
H	2.24191154768064	-1.81828969451339	1.30859386979649
H	0.74182964794190	-1.03513235268283	1.86514492177216
H	1.57707401309293	-0.40954647700409	0.44081642097316
H	3.26209616357387	-1.62409767604679	3.37548995517922
H	3.22348773868959	-0.11315595111159	4.29982184065656
H	1.72235759289947	-0.96315497990095	3.97668019250617
C	0.70220409975412	3.55357110078244	2.59220100181760
O	0.06314975548973	4.48995829091909	2.64728544163685

Device Preparation

Devices were prepared on microscope glass slides (VWR) cleaned by water bath ultrasonication in acetone. The glass slides were fitted with a custom-made aluminum mask, and using a thermal evaporator (Angstrom Engineering), a 10 nm adlayer of chromium (99.99%, R.D. Mathis) was deposited onto the glass, followed by 100 nm of gold (99.99%, R.D. Mathis).

In a typical device, 0.25 mg (21 µmol C) of SWNTs and 1.0 mg [Cp^CoI_2] (2.0 µmol) were suspended in 0.80 mL 1,2-dichlorobenzene (DCB), 0.20 mL $CHCl_3$, and 50 µL halocarbon oil 27 (HC27) and treated in an ultrasonic water bath at room temperature for several minutes. The resulting dispersion was drop-casted using a micropipette onto the glass slide in between the gold electrodes. The volatile organics were removed in vacuo at room temperature. The application of the dispersion followed by the removal of the solvent was repeated until the resistance across the SWNT network reached a resistance of 10-100 kΩ as measured by a multimeter.

Gas Detection Measurements

Gas detection measurements were acquired by using a test clip (3M) fitted with a PTFE spacer to connect the gold electrodes of the device to a PalmSens EmStat potentiostat equipped with a MUX16 multiplexer. The chemiresistive device was enclosed in a PTFE chamber, and a gas mixer system was used to deliver to the chamber various concentrations of analyte gas diluted by the carrier gas (nitrogen or air). The gas mixer was comprised of two digital mass flow controllers (MFCs) purchased from Alicat Scientific. One was used to deliver up to 12.0 mL/min of analyte gas into the carrier gas stream delivered by the other MFC set at a constant 1.00 L/min. The potentiostat was used to apply a constant potential of 0.100 V across the electrodes, and the current was recorded using PSTrace software (v. 3.0) as the device was exposed to the diluted analyte for 60 s at a time. Data for gas detection measurements were corrected to a linear fit of the baseline current that was measured prior to gas exposures.

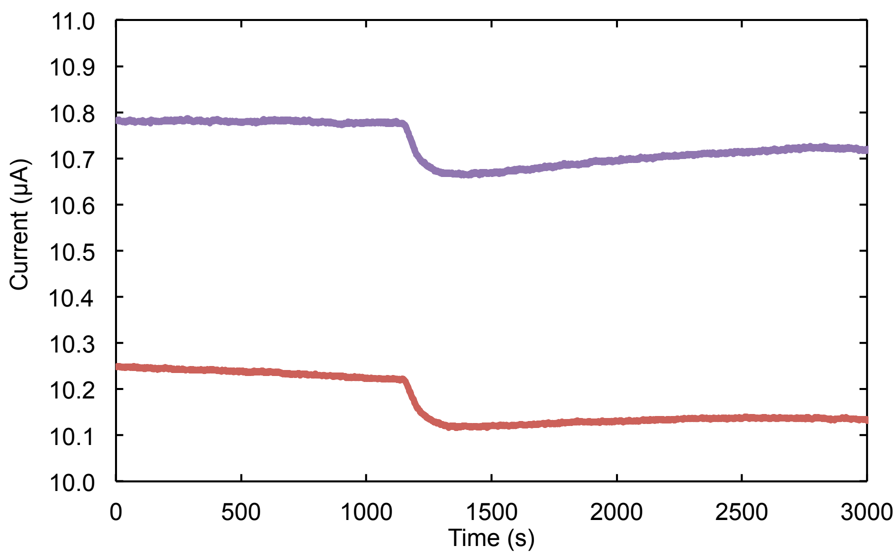


Figure S-2. Raw current traces of two [Cp^CoI_2]-SWCNT devices exposed to 3000 ppm CO.

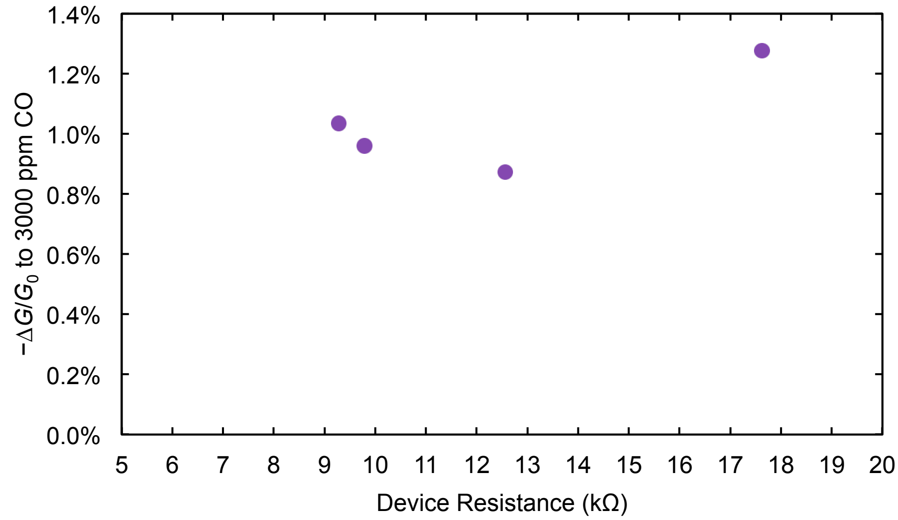


Figure S-3. Responses of [Cp^CoI$_2$]-SWCNT devices to 3000 ppm CO vs. resistance.

Raman Spectroscopic Characterization of [Cp^CoI$_2$]-SWCNT Composite

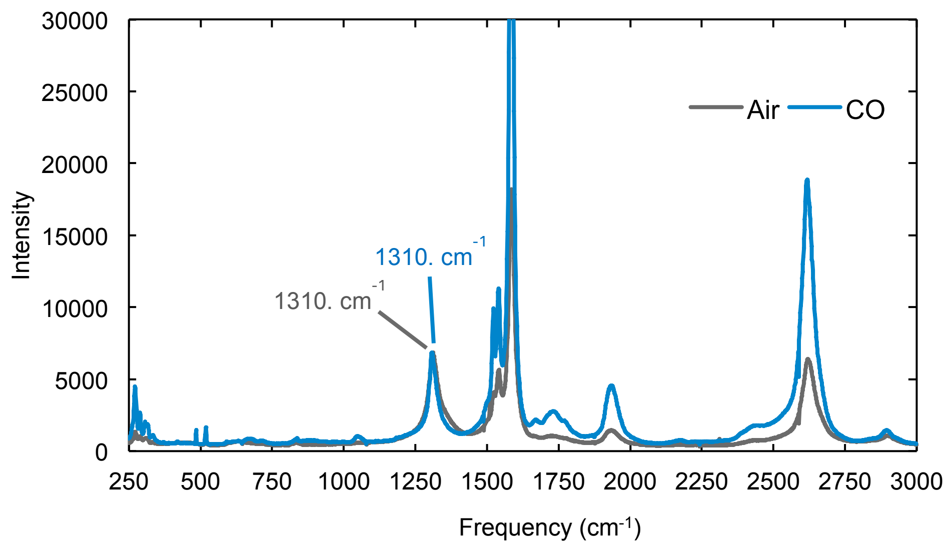


Figure S-4. Raman spectra of SWCNTs recorded under air and under 1 atm CO.

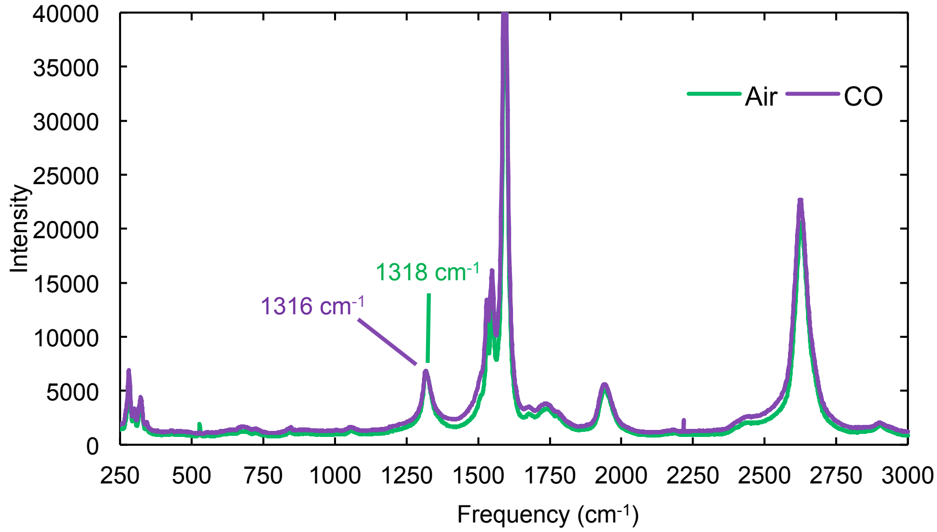


Figure S-5. Raman spectra of [Cp^CoI$_2$]-SWCNT composite recorded under air and under 1 atm CO.

Scanning Electron Microscopic Characterization of [Cp^CoI$_2$]-SWCNT Composite

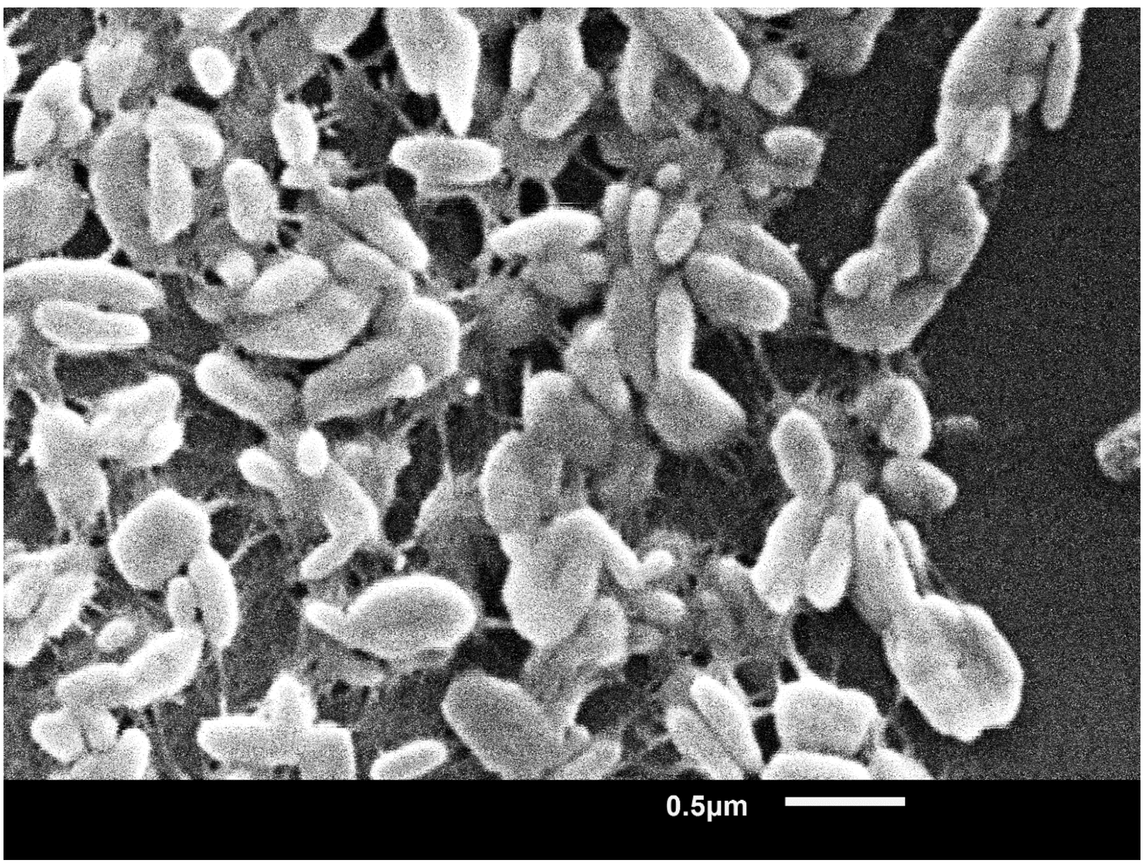


Figure S-6. SEM image of [Cp^CoI$_2$]-SWCNT.

[1]H NMR Spectroscopic Characterization of [Cp^CoI$_2$]

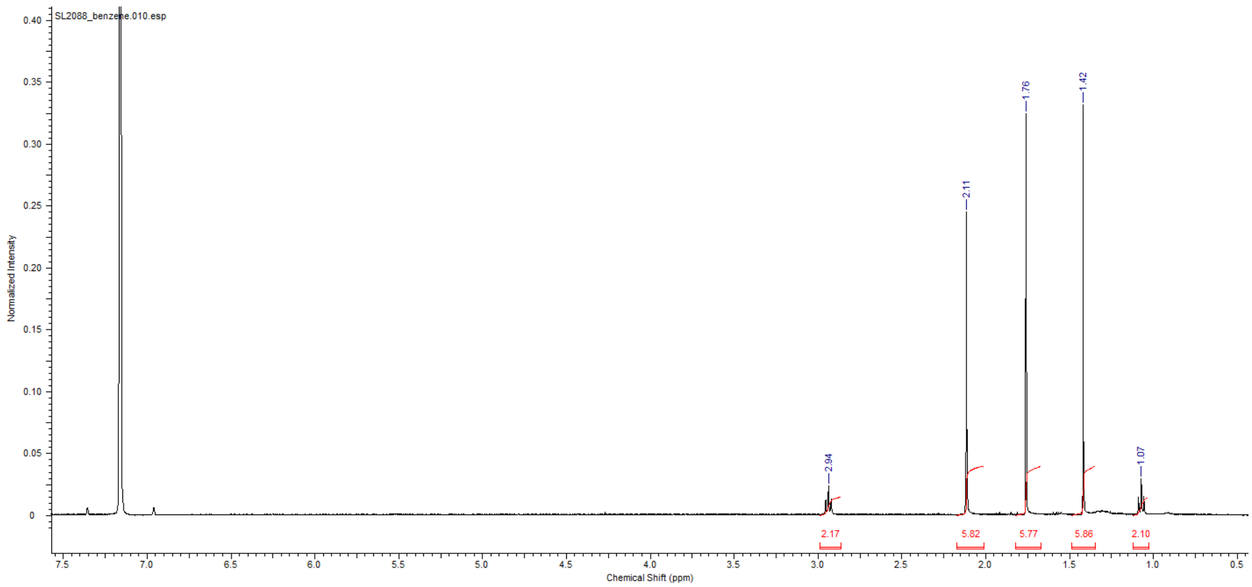


Figure S-7. [1]H NMR spectrum of [Cp^CoI$_2$] in C_6D_6.

References

(1) Neese, F. The ORCA program system. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2*, 73–78.

(2) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(3) Stephens, P.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. *J. Phys. Chem.* **1994**, *98*, 11623–11627.

(4) Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. *J. Chem. Phys.* **1985**, *82*, 299–310.

(5) Roy, L. E.; Hay, P. J.; Martin, R. L. Revised basis sets for the LANL effective core potentials. *J. Chem. Theory Comput.* **2008**, *4*, 1029–1031.

(6) Schäfer, A.; Horn, H.; Ahlrichs, R. Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr. *J. Chem. Phys.* **1992**, *97*, 2571–2577.

(7) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

(8) Kossmann, S.; Neese, F. Comparison of two efficient approximate Hartee-Fock approaches. *Chem. Phys. Lett.* **2009**, *481*, 240–243.

(9) Klamt, A.; Schüürmann, G. COSMO: a new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient. *J. Chem. Soc., Perkin Trans. 2* **1993**, No. 5, 799–805.

(10) Ehrlich, P. Dielectric properties of Teflon from room temperature to 314 °C and from frequencies of 10^2 to 10^5 c/s. *J. Res. Natl. Bur. Stand. (U. S.)* **1953**, *51*, 185–188.