Supporting Information

Vapochemically and Mechanochemically Reversible Polymerization/Depolymerization of S─Fe─Cu Carbonyl Clusters

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Experimental Section. All reactions were performed under an atmosphere of pure nitrogen using standard Schlenk techniques.[1] Solvents were purified, dried and distilled under nitrogen prior to use. Dppe (ACROS) and dppm (Lancaster) were used as received. $[Et_4N]_2[SFe_3(CO)_9]$[2] and $[Cu(MeCN)_4][BF_4]$[3] were prepared by published methods. Infrared spectra were recorded on a Perkin-Elmer Paragon 500 IR spectrometer as solutions in CaF_2 cells. The ^1H, ^{13}C, and ^{31}P NMR spectra were obtained on a Bruker AV 400 at 400.13 MHz for ^1H, 100.61 MHz for ^{13}C, and 161.98 MHz for ^{31}P. ^1H and ^{13}C chemical shifts are reported in ppm and were calibrated relative to CD_2Cl_2 (^1H: δ = 5.32 ppm, ^{13}C: δ = 54.00 ppm) as the internal standard. Chemical shifts for ^{31}P NMR spectra are relative to 85% H_3PO_4 in CD_3CN at 0 ppm. Thermogravimetric analysis (TGA) was performed using a TA TGA-Q500 system with a dynamic heating rate (5 °C/ min) under flowing argon (60 mL min^{-1}) in temperatures ranging from 25 to 600 ˚C. Elemental analyses of C, H, and N were performed on a Perkin-Elmer 2400 analyzer at the NSC Regional instrumental Center at National Taiwan University, Taipei, Taiwan. ESI-mass spectra were obtained on a Thermo Finnigan LCQ

Advantage mass spectrometer. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE instrument at 40 kV and 40 mA with $Cu_{k\alpha}$ radiation (λ= 1.54050Å)

Synthesis of [{(μ_5-S)$Fe_3(CO)_9$}Cu_2(dppm)(MeCN)] (1). CH_2Cl_2 (30 mL) was added to a mixture of $[Et_4N]_2[SFe_3(CO)_9]$ (0.30 g, 0.42 mmol), $[Cu(MeCN)_4][BF_4]$ (0.27 g, 0.86 mmol), and dppm (0.16 g, 0.40 mmol), followed by stirring in an ice/water bath for 1 h to give a purplish-red solution. The resultant solution was filtered and the solvent was removed under vacuum. This residue was washed with deionized water and extracted with CH_2Cl_2 which was recrystallized with Hexanes/Et_2O/CH_2Cl_2 to give [{(μ_5-S)$Fe_3(CO)_9$}Cu_2(dppm)(MeCN)] (**1**) (0.21 g, 0.21 mmol, 53% based on $[Et_4N]_2[SFe_3(CO)_9]$). IR (υ_{CO}, CH_2Cl_2): 2036 s, 2005 w, 1976 vs, 1921 w, 1884 m cm^{-1}. Anal. Calcd for **1**: C, 43.06; H, 2.51; N, 1.39. Found: C, 42.90; H, 2.56; N, 1.39. ^{1}H NMR (400 MHz, CD_2Cl_2, 300K): δ 2.04 (s, -C*H*$_3$CN), 3.37 (t, -PC*H*$_2$P-, ^2J(H─P) = 10.69 Hz), 7.32─7.51 (m, -P(C_6H_5)$_2$). ^{13}C NMR (100 MHz, CD_2Cl_2, 300K): δ26.37 (t, -P*C*H$_2$P-, ^1J(C─P) = 18.06 Hz), 2.32, 119.36 (-*C*H$_3$*C*N), 129.12─132.87 (-P(*C*$_6$H$_5$)$_2$), 215.47 (-*C*O). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 300K): δ −4.66 (s, -*P*(C_6H_5)$_2$). Mp: 167 ^{o}C (dec). Crystals of **1** suitable for X-ray diffraction were grown from Hexanes/Et_2O/CH_2Cl_2.

Synthesis of [{(μ_3-S)$Fe_3(CO)_9$}Cu_2(dppe)] (2). CH_2Cl_2 (30 mL) was added to a mixture of $[Et_4N]_2[SFe_3(CO)_9]$ (0.60 g, 0.84 mmol), $[Cu(MeCN)_4][BF_4]$ (0.54 g, 1.72 mmol), and dppe (0.33 g, 0.83 mmol). The mixture was stirred in an ice/water bath for 3 hours to give a

purplish-brown solution. The resultant solution was filtered and the solvent was removed under vacuum. This residue was washed with deionized water and extracted with CH_2Cl_2 then recrystallized with Hexanes/Et_2O/CH_2Cl_2 to give [{(μ_3-S)$Fe_3(CO)_9$}Cu_2(dppe)] (**2**) (0.45 g, 0.46 mmol, 55% based on dppe). IR (υ_{CO}, CH_2Cl_2): 2040 m, 2008 vs, 1991 vs, 1964 s, 1904 s cm^{-1}. Anal. Calcd for **2**: C, 43.02; H, 2.48. Found: C, 42.99; H, 2.57. ^{1}H NMR (400 MHz, CD_2Cl_2, 300K): δ 2.67─2.82 (m, -PCH_2CH_2P-), 7.49─7.67 (m, -P(C_6H_5)$_2$). ^{13}C NMR (100 MHz, CD_2Cl_2, 300K): δ 21.01─21.43 (-PCH_2CH_2P-), 129.90─133.54 (-P(C_6H_5)$_2$), 212.33 (-*C*O). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 300K): δ -8.54 (s, -*P*(C_6H_5)$_2$). Mp: 160 ^{o}C (dec). Crystals of **2** suitable for X-ray diffraction were grown from Hexanes/Et_2O/CH_2Cl_2.

Synthesis of Polymer [{(μ_4-S)$Fe_3(CO)_9$}Cu_2(dppe)(MeCN)$_2$]$_n$ (3) (Conversion of 2 to 3). Method 1. MeCN (5.0 mL) was added to a sample of **2** (0.23 g, 0.24 mmol), followed by the addition of Hexanes/THF to give [{(μ_4-S)$Fe_3(CO)_9$}Cu_2(dppe)(MeCN)$_2$]$_n$ (**3**) (0.21 g, 0.20 mmol, 83% based on **2**). IR (ν_{CO}, nujol): 2026 m, 1977 s, 1963 vs, 1958 s, 1937 vs, 1917 vs, 1877 s, 1958 s cm^{-1}. ESI-MS: *m*/*z* 514.9 [(μ_3-S)$Fe_3(CO)_9Cu]^-$, 1094.1 [{$SFe_3(CO)_9$}$_2Cu_3]^-$. Anal. Calcd for **3**: C, 44.22; H, 2.85; N, 2.64. Found: C, 44.22; H, 2.92; N, 2.40. **Method 2 (vapochemical reaction).** A sample of brownish-black crystals of **2 (**0.01 g, 0.01 mmol) was prepared and exposed to MeCN vapor for 1 day. The reddish-brown product was obtained and ground into powder. The structural transformation from **2** into **3** was confirmed via a comparison of their PXRD patterns with the simulated patterns from the single-crystal X-ray

data of **2** and **3**. **Method 3 (mechanochemical reaction).** A sample of powder **2 (**0.01 g, 0.01 mmol) was ground with one drop of MeCN in a mortar and pestle. The reddish-brown product of **3** was obtained. The transformation from **2** into **3** was also confirmed by comparison of their PXRD patterns with the simulated patterns from the single-crystal X-ray data of **2** and **3**.

Conversion of 3 to 2 (mechanochemical reaction). A sample of powder **3** (0.01 g, 0.009 mmol) was ground with drops of CH_2Cl_2 or THF in a mortar and pestle. The color changed from reddish-brown to brownish-black. The structural transformation of **3** into **2** was confirmed by comparison of their PXRD patterns with the simulated patterns from the single-crystal X-ray data of **3** and **2**.

X-ray Crystallography. Some selected crystallographic data for complexes **1**─**3** are given in Table S2. Data collection for **1** and **2** was conducted using a Brucker-Nonius Kappa CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation employing the θ─2θ scan mode, and an empirical absorption correction by multiscans was applied.[4] Data for **3** were collected using a Bruker Apex II CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation in the 2θ range of 2.0 to 50°, and an empirical absorption correction by multiscans was applied.[4] The structures were solved by direct methods and refined by SHELXL packages.[5] Each of **2** and **3** contained two independent but chemically similar asymmetric structures in the unit cell where their bond distances and angles were similar and only one structure was described for

further comparison. All the non-hydrogen atoms for complexes **1─3** were refined with anisotropic temperature factors. Selected distances and angles for complexes **1─3** are shown in Table S3.

UV-vis Diffuse Reflectance Spectroscopy. For solid samples of [{(μ_3-S)$Fe_3(CO)_9$}Cu_2(dppe)] (**2**) and [{(μ_4-S)$Fe_3(CO)_9$}Cu_2(dppe)$(MeCN)_2]_n$ (**3**), the diffuse reflectance spectra were measured at room temperature between 200 and 2500 nm using a Varian Cary 5000 UV-vis-NIR spectrophotometer. Poly(tetrafluoroethylene) was used as a reference material. The reflectance spectrum was converted to the absorption by using the Kubelka-Munk function, $F = (1-R)^2/2R$.[6,7] The band gap was determined in the F-versus-E plot, by extrapolating the linear portion of starting rising curve to zero, which provided the onset of absorption.

Computational Details. Calculations reported in this study were performed via density function theory (DFT) with Becke's three-parameter (B3) exchange functional and the Lee─Yang─Parr (LYP) correlation functional (B3LYP)[8,9] using the *Gaussian 03* series of packages.[10] The geometries of **2** and 2 units of polymer **3** were taken from the X-ray diffraction data, and the single-point calculations were carried out with the LanL2DZ basis set for S, Fe, Cu, and P atoms and the 6-31G(d,p) basis set for C, O, and H atoms. Wiberg bond indices[11] and nature charges[12] were evaluated using the Weinhold NBO method.[13]

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Figure S1. ORTEP diagram showing the structure and atom labeling of [{(μ_5-S)$Fe_3(CO)_9$}Cu_2(dppm)(MeCN)] (**1**), showing 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

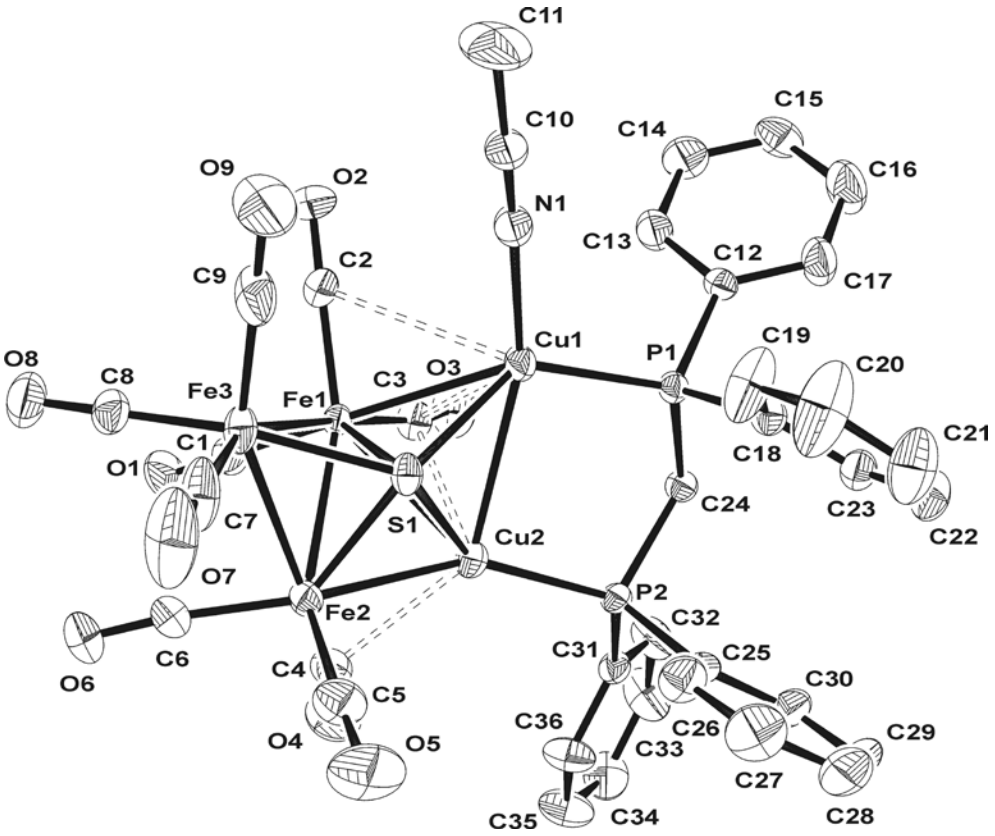

Figure S2. ORTEP diagram showing the structure and atom labeling of [{(μ_3-S)$Fe_3(CO)_9$}Cu_2(dppe)] (**2**), showing 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

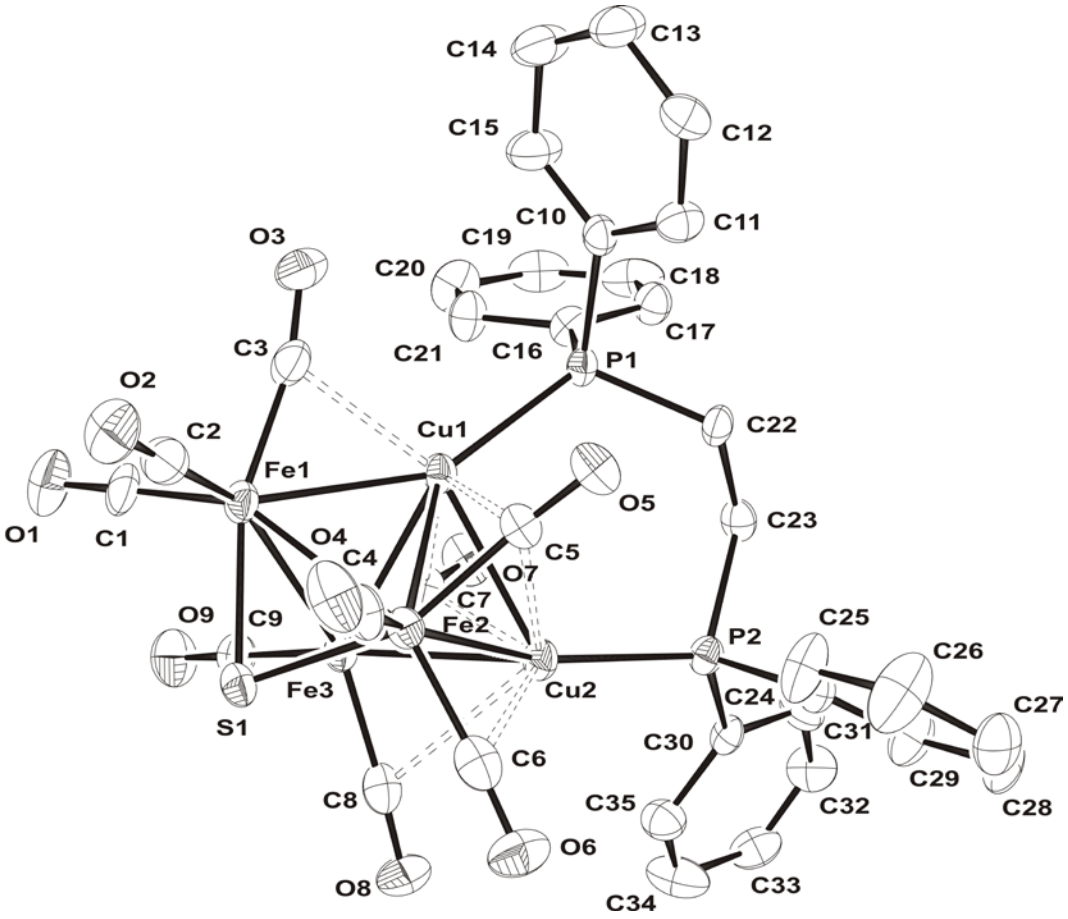

Figure S3. ORTEP diagram showing the structure and atom labeling for the segment of $[\{(\mu_4\text{-S})Fe_3(CO)_9\}Cu_2(dppe)(MeCN)_2]_n$ (**3**) showing 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

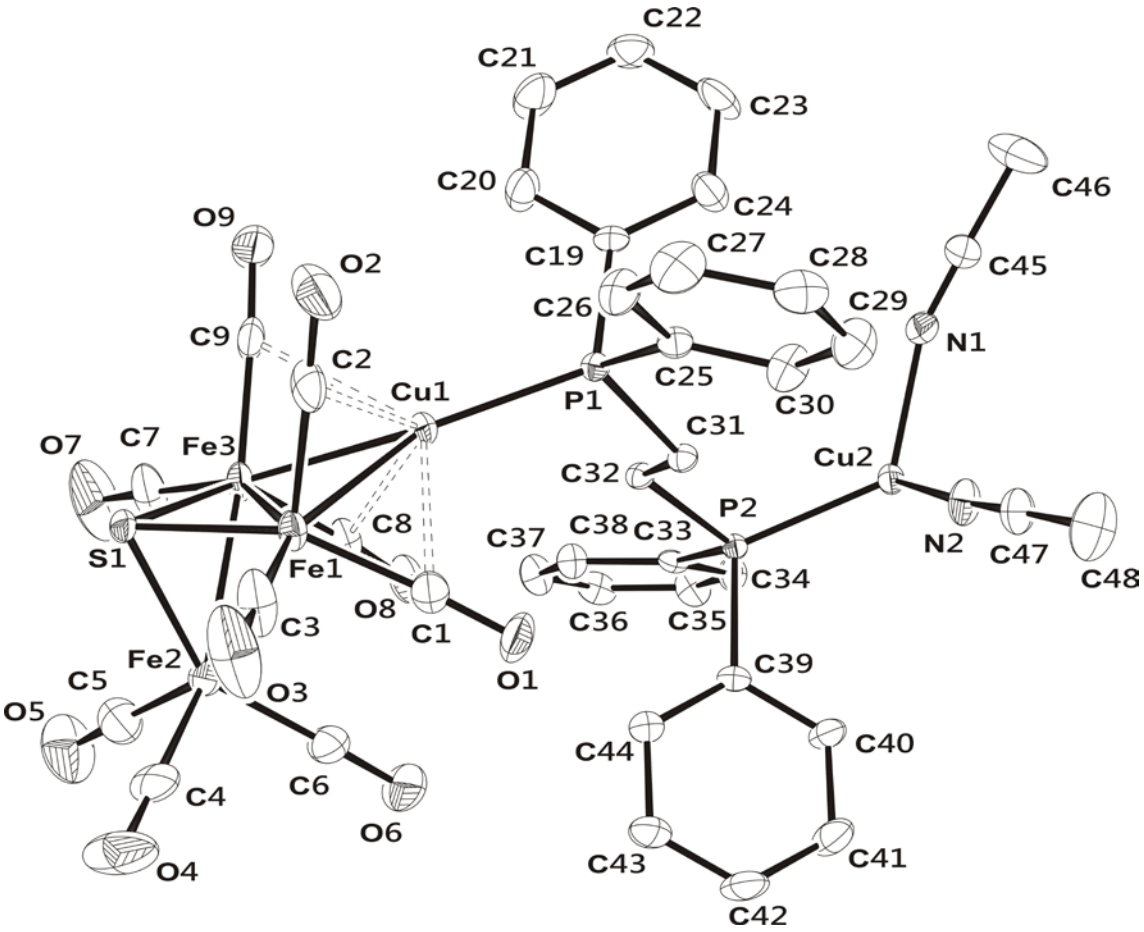

Figure S4. The TGA analysis of polymer [{(μ_4-S)$Fe_3(CO)_9$}Cu_2(dppe)$(MeCN)_2]_n$ (**3**).

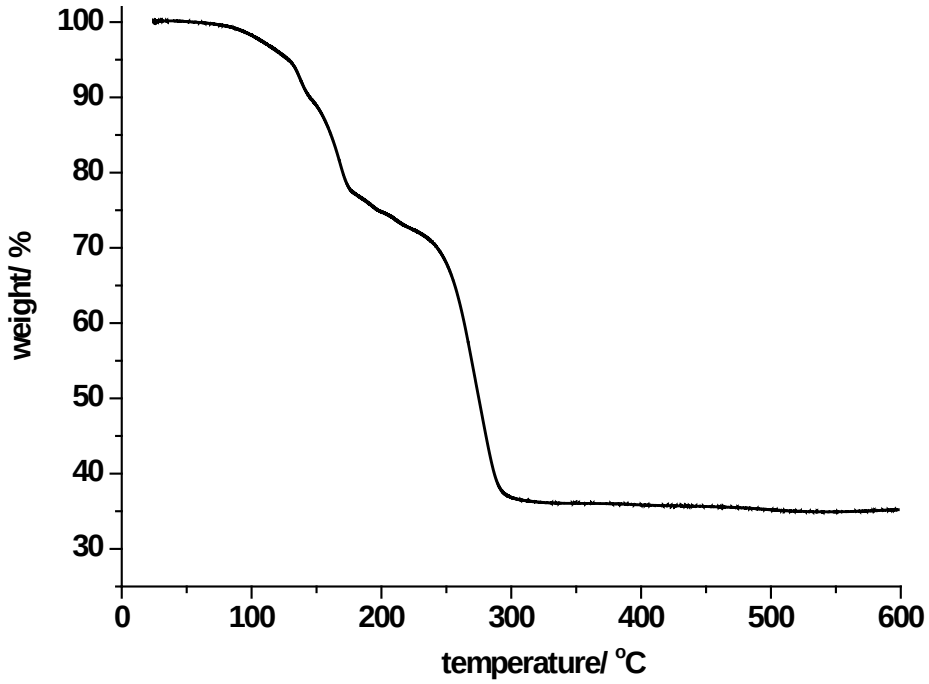

Figure S5. K-M function versus energy (eV) curve of complex [{(μ_3-S)$Fe_3(CO)_9$}Cu_2(dppe)] (**2**) (a) and polymer [{(μ_4-S)$Fe_3(CO)_9$}Cu_2(dppe)$(MeCN)_2]_n$ (**3**) (b).

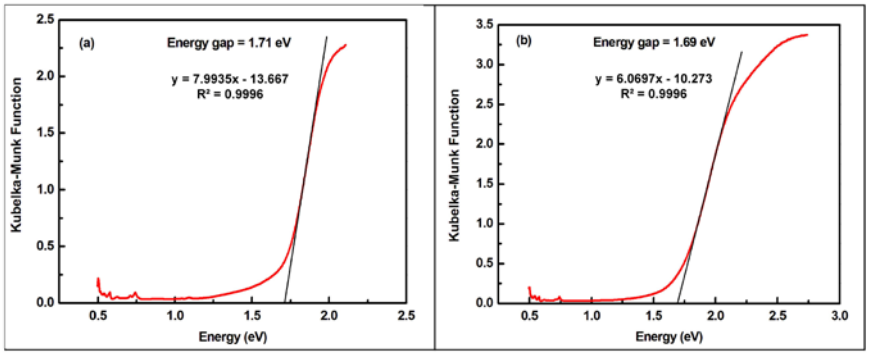

Figure S6. Spatial plot of HOMO-10 of two units of [{(μ_4-S)$Fe_3(CO)_9$}Cu_2(dppe)$(MeCN)_2]_n$ (**3**) (isovalue = 0.004).

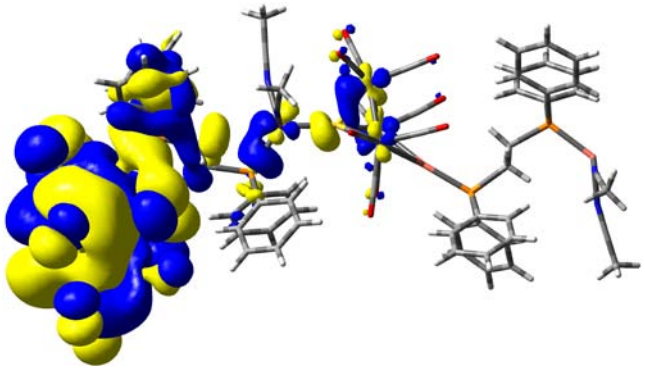

Table S1. Results of Natural Bond Order and Natural Population Analyses of {(μ_3-S)Fe_3($CO)_9$}Cu_2(dppe)] (**2**) at the Level of B3LYP/LanL2DZ/6-31G(d,p).

Complex	Wiberg bond index					Natural charge		
	S─Fe	S─Cu	Fe─Cu	Cu─Cu	Cu─P	S	Fe	Cu
2	0.780		0.200[a]	0.143	0.521	0.425	-1.441	0.272[c]
			0.214[b]					0.092[d]

[a]Associated. [b] Non-associated.[c] Cu2. [d] Cu1.

Table S2. Crystallographic Data for [{(μ_5-S)$Fe_3(CO)_9$}Cu_2(dppm)(MeCN)] (**1**), [{(μ_3-S)$Fe_3(CO)_9$}Cu_2(dppe)] (**2**), and [{(μ_4-S)$Fe_3(CO)_9$}Cu_2(dppe)$(MeCN)_2]_n$ (**3**).

	1	**2**	**3**
Empirical formula	$C_{36}H_{25}Cu_2Fe_3NO_9P_2S$	$C_{35}H_{24}Cu_2Fe_3O_9P_2S$	$C_{78}H_{60}Cu_4Fe_6N_4O_{18}P_4S_2$
Fw	1004.20	977.17	2118.56
cryst syst	triclinic	triclinic	Monoclinic
space group	*P*$\bar{1}$	*P*$\bar{1}$	*Cc*
crystal dimens, mm	0.65 × 0.60 × 0.50	0.32 × 0.30 × 0.20	0.41 × 0.32 × 0.13
a, Å	11.4929(6)	13.1357(2)	35.409(1)
b, Å	12.3565(6)	13.7196(2)	10.2025(3)
c, Å	15.8187(8)	20.6528(4)	24.5709(8)
α, deg	67.924(1)	97.810(1)	
β, deg	73.606(1)	90.021(1)	107.170(2)
γ, deg	77.975(1)	91.115(1)	
V, Å^3	1983.9(2)	3686.7(1)	8480.8(4)
Z	2	4	4
D (calcd), g cm^{-3}	1.681	1.761	1.659
μ, mm^{-1}	2.311	2.484	2.168
color, habit			
diffractometer	Nonius (Kappa CCD)	Nonius (Kappa CCD)	Apex II CCD
radiation (λ), Å	0.71073	0.71073	0.71073
temp, K	298(2)	298(2)	200(2)
θ range for data collecn, deg	1.43─25.01	2.14─25.11	2.19─25.04
T_{min}/T_{max}	0.32/0.39	0.46/0.57	0.47/0.77
no. of indep reflns	5824	10876	10175
($I > 2\ \sigma(I)$)	(R_{int} = 0.0298)	(R_{int} = 0.0878)	(R_{int} = 0.0246)
no. of parameters	488	932	1049
R1[a]/wR2[a] ($I > 2\ \sigma(I)$)	0.034/0.091	0.098/0.260	0.029/0.069
R1[a]/wR2[a] (all data)	0.045/0.118	0.113/0.272	0.032/0.072

[a] The functions minimized during least-squares cycles were $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table S3. Selected bond distances (Å) and bond angles (deg) for [{(μ_5-S)$Fe_3(CO)_9$}Cu_2(dppm)(MeCN)] (**1**), [{(μ_3-S)$Fe_3(CO)_9$}Cu_2(dppe)] (**2**), and [{(μ_4-S)$Fe_3(CO)_9$}Cu_2(dppe)$(MeCN)_2]_n$ (**3**).

1			
S(1)─Fe(1)	2.253(1)	Fe(1)─Cu(1)	2.6536(7)
S(1)─Fe(2)	2.228(1)	Fe(1)─Cu(2)	2.5790(7)
S(1)─Fe(3)	2.200(1)	Fe(2)─Cu(2)	2.4892(7)
S(1)─Cu(1)	2.345(1)	Cu(1)─Cu(2)	2.8000(7)
S(1)─Cu(2)	2.409(1)	Cu(1)─P(1)	2.231(1)
Fe(1)─Fe(2)	2.6140(7)	Cu(2)─P(2)	2.191(1)
Fe(1)─Fe(3)	2.5930(7)	Cu(1)─N(1)	2.012(4)
Fe(2)─Fe(3)	2.6046(9)		
S(1)─Fe(1)─Fe(2)	53.87(3)	Fe(1)─Fe(2)─Fe(3)	59.59(2)
S(1)─Fe(1)─Fe(3)	53.44(3)	Fe(1)─Fe(3)─Fe(2)	60.39(2)
S(1)─Fe(2)─Fe(1)	54.75(3)	Fe(2)─Fe(1)─Fe(3)	60.03(2)
S(1)─Fe(2)─Fe(3)	53.47(3)	Fe(1)─Fe(2)─Cu(2)	60.65(2)
S(1)─Fe(3)─Fe(1)	55.34(3)	Fe(2)─Fe(1)─Cu(1)	104.15(2)
S(1)─Fe(3)─Fe(2)	54.47(3)	Fe(2)─Fe(1)─Cu(2)	57.28(2)
S(1)─Fe(1)─Cu(1)	56.38(3)	Fe(3)─Fe(1)─Cu(1)	98.28(2)
S(1)─Fe(1)─Cu(2)	59.34(3)	Fe(3)─Fe(1)─Cu(2)	105.84(2)
S(1)─Fe(2)─Cu(2)	61.11(3)	Fe(3)─Fe(2)─Cu(2)	108.18(3)
S(1)─Cu(1)─Fe(1)	53.14(3)	Fe(1)─Cu(2)─Fe(2)	62.07(2)
S(1)─Cu(2)─Fe(1)	53.57(3)	Fe(1)─Cu(1)─Cu(2)	56.37(2)
S(1)─Cu(2)─Fe(2)	54.08(3)	Fe(1)─Cu(2)─Cu(1)	58.95(2)
S(1)─Cu(1)─Cu(2)	54.97(3)	Fe(2)─Cu(2)─Cu(1)	103.40(2)
S(1)─Cu(2)─Cu(1)	52.85(3)	Fe(1)─Cu(1)─P(1)	134.16(3)
S(1)─Cu(1)─P(1)	131.73(4)	Fe(1)─Cu(2)─P(2)	144.13(3)
S(1)─Cu(2)─P(2)	135.96(4)	Fe(2)─Cu(2)─P(2)	153.59(4)
S(1)─Cu(1)─N(1)	104.4(1)	Fe(1)─Cu(1)─N(1)	110.0(1)
Fe(1)─S(1)─Fe(2)	71.38(3)	Cu(1)─S(1)─Cu(2)	72.17(3)
Fe(1)─S(1)─Fe(3)	71.22(3)	Cu(1)─Fe(1)─Cu(2)	64.68(2)
Fe(2)─S(1)─Fe(3)	72.06(3)	Cu(1)─Cu(2)─P(2)	97.83(3)
Fe(1)─S(1)─Cu(1)	70.48(3)	Cu(2)─Cu(1)─P(1)	88.70(3)
Fe(1)─S(1)─Cu(2)	67.09(3)	Cu(2)─Cu(1)─N(1)	159.0(1)
Fe(2)─S(1)─Cu(1)	130.66(4)	P(1)─Cu(1)─N(1)	110.6(1)
Fe(2)─S(1)─Cu(2)	64.81(3)	P(1)─C(24)─P(2)	112.5(2)

Fe(3)─S(1)─Cu(1)	121.65(5)	N(1)─C(10)─C(11)	179.2(7)

2

S(1)─Fe(1)	2.181(4)	Fe(2)─Cu(2)	2.518(2)
S(1)─Fe(2)	2.209(3)	Fe(3)─Cu(1)	2.601(2)
S(1)─Fe(3)	2.193(3)	Fe(3)─Cu(2)	2.528(2)
Fe(1)─Fe(2)	2.639(2)	Cu(1)─Cu(2)	2.573(2)
Fe(1)─Fe(3)	2.654(2)	Cu(1)─P(1)	2.285(3)
Fe(2)─Fe(3)	2.684(2)	Cu(2)─P(2)	2.211(3)
Fe(1)─Cu(1)	2.529(2)	C(22)─C(23)	1.51(2)
Fe(2)─Cu(1)	2.612(2)		
S(1)─Fe(1)─Fe(2)	53.5(1)	Fe(2)─Fe(3)─Cu(2)	57.68(6)
S(1)─Fe(1)─Fe(3)	52.9(1)	Fe(3)─Fe(1)─Cu(1)	60.19(6)
S(1)─Fe(2)─Fe(1)	52.6(1)	Fe(3)─Fe(2)─Cu(1)	58.81(6)
S(1)─Fe(2)─Fe(3)	52.2(1)	Fe(3)─Fe(2)─Cu(2)	58.04(6)
S(1)─Fe(3)─Fe(1)	52.4(1)	Fe(1)─Cu(1)─Fe(2)	61.76(6)
S(1)─Fe(3)─Fe(2)	52.69(9)	Fe(1)─Cu(1)─Fe(3)	62.29(6)
S(1)─Fe(1)─Cu(1)	101.0(1)	Fe(2)─Cu(1)─Fe(3)	61.98(6)
S(1)─Fe(2)─Cu(2)	106.7(1)	Fe(2)─Cu(2)─Fe(3)	64.28(6)
S(1)─Fe(2)─Cu(1)	97.8(1)	Fe(1)─Cu(1)─Cu(2)	108.99(7)
S(1)─Fe(3)─Cu(1)	98.5(1)	Fe(2)─Cu(1)─Cu(2)	58.09(6)
S(1)─Fe(3)─Cu(2)	106.8(1)	Fe(2)─Cu(2)─Cu(1)	61.73(6)
Fe(1)─S(1)─Fe(3)	74.7(1)	Fe(3)─Cu(1)─Cu(2)	58.48(6)
Fe(1)─S(1)─Fe(2)	73.9(1)	Fe(3)─Cu(2)─Cu(1)	61.31(6)
Fe(3)─S(1)─Fe(2)	75.2(1)	Fe(1)─Cu(1)─P(1)	152.5(1)
Fe(1)─Fe(2)─Fe(3)	59.80(6)	Fe(2)─Cu(1)─P(1)	135.6(1)
Fe(1)─Fe(3)─Fe(2)	59.26(6)	Fe(2)─Cu(2)─P(2)	149.2(1)
Fe(2)─Fe(1)─Fe(3)	60.94(6)	Fe(3)─Cu(1)─P(1)	140.7(1)
Fe(1)─Fe(2)─Cu(1)	57.57(6)	Fe(3)─Cu(2)─P(2)	144.8(1)
Fe(1)─Fe(2)─Cu(2)	107.3(8)	Cu(1)─Fe(2)─Cu(2)	60.18(6)
Fe(1)─Fe(3)─Cu(1)	57.52(6)	Cu(1)─Fe(3)─Cu(2)	60.21(6)
Fe(1)─Fe(3)─Cu(2)	106.54(8)	Cu(1)─Cu(2)─P(2)	116.4(1)
Fe(2)─Fe(1)─Cu(1)	60.68(6)	Cu(2)─Cu(1)─P(1)	98.22(9)
Fe(2)─Fe(3)─Cu(1)	59.21(6)		

3

S(1)─Fe(1)	2.184(1)	Fe(1)─Cu(1)	2.5092(9)
S(1)─Fe(2)	2.181(1)	Fe(3)─Cu(1)	2.5113(9)

S(1)─Fe(3)	2.188(2)	Cu(1)─P(1)	2.225(1)
S(1)─Cu(2a)	2.315(1)	Cu(2)─P(2)	2.225(1)
Fe(1)─Fe(2)	2.592(1)	Cu(2)─N(1)	2.021(4)
Fe(1)─Fe(3)	2.6514(9)	Cu(2)─N(2)	2.064(4)
Fe(2)─Fe(3)	2.591(1)	C(31)─C(32)	1.519(6)

S(1)─Fe(1)─Fe(2)	53.50(4)	Fe(2)─S(1)─Cu(2a)	125.79(6)
S(1)─Fe(1)─Fe(3)	52.74(4)	Fe(3)─S(1)─Cu(2a)	147.13(6)
S(1)─Fe(2)─Fe(1)	53.63(4)	Fe(1)─Fe(2)─Fe(3)	61.54(3)
S(1)─Fe(2)─Fe(3)	53.76(4)	Fe(1)─Fe(3)─Fe(2)	59.26(3)
S(1)─Fe(3)─Fe(1)	52.60(4)	Fe(2)─Fe(1)─Fe(3)	59.20(3)
S(1)─Fe(3)─Fe(2)	53.50(4)	Fe(1)─Fe(3)─Cu(1)	58.08(2)
S(1)─Fe(1)─Cu(1)	108.83(4)	Fe(2)─Fe(3)─Cu(1)	103.05(3)
S(1)─Fe(3)─Cu(1)	108.63(4)	Fe(3)─Fe(1)─Cu(1)	58.16(3)
S(1a)─Cu(2)─P(2)	121.62(5)	Fe(2)─Fe(1)─Cu(1)	103.06(3)
S(1a)─Cu(2)─N(1)	101.1(2)	Fe(1)─Cu(1)─Fe(3)	63.76(3)
S(1a)─Cu(2)─N(2)	100.4(1)	Fe(1)─Cu(1)─P(1)	139.56(4)
Fe(1)─S(1)─Fe(2)	72.87(5)	Fe(3)─Cu(1)─P(1)	156.27(4)
Fe(1)─S(1)─Fe(3)	74.66 (5)	P(2)─Cu(2)─N(1)	125.1(1)
Fe(2)─S(1)─Fe(3)	72.74(5)	P(2)─Cu(2)─N(2)	108.3(1)
Fe(1)─S(1)─Cu(2a)	133.59(6)	N(1)─Cu(2)─N(2)	94.7(2)

Table S4. Electronic Energy and Cartesian Coordinates of [{(μ_3-S)$Fe_3(CO)_9$}Cu_2(dppe)] (**2**). E = -3480.5896518 a.u.

	x	y	z
Cu	5.14007	3.68617	5.32603
Cu	3.87522	1.66553	4.39710
Fe	3.27404	2.42838	6.71534
Fe	5.60402	1.24770	6.16289
Fe	5.51458	3.36191	7.78955
P	5.26384	4.97592	3.45384
C	2.73265	3.63615	5.53064
C	6.40573	1.67119	4.60580
C	6.04484	4.92567	6.98952
P	3.37481	1.79484	2.25482
C	2.17356	1.05400	6.34500
C	4.95250	-0.37789	5.76390
S	4.60078	1.39911	8.10875
C	2.24424	3.17282	7.98803
C	7.14194	0.62830	6.75831
C	7.07856	3.06909	8.52411
C	4.88599	4.18342	9.24025
C	6.87349	4.94842	2.59447
C	4.92888	6.75917	3.70346
C	4.00979	4.61812	2.15251
O	2.17677	4.42386	4.88816
O	6.99636	1.78097	3.62571
O	6.42246	5.94424	6.74399
C	4.13792	3.27412	1.45069
C	1.61087	1.90759	1.90289
C	4.01724	0.47481	1.16833
O	1.44717	0.20914	6.13425
O	4.51608	-1.41492	5.59407
O	1.51911	3.59260	8.76760
O	8.16093	0.18859	7.09387
O	8.12401	2.85894	9.05610
O	4.51367	4.66704	10.22443
C	8.00734	4.74934	3.35563
C	6.99233	5.19935	1.21539
C	5.96735	7.71262	3.40269

C	3.70383	7.22094	4.03698
H	3.13639	4.61687	2.55150
H	4.04998	5.29182	1.47116
H	5.08154	3.13041	1.34839
H	3.73862	3.40739	0.58928
C	0.95551	3.12305	1.86196
C	0.83723	0.80598	1.59392
C	3.90188	0.54246	-0.20461
C	4.69294	-0.58200	1.71260
H	7.91089	4.56454	4.29275
C	9.25824	4.82168	2.76839
C	8.26349	5.24147	0.63839
H	6.19744	5.35622	0.70182
H	6.82425	7.39805	3.10600
C	5.64657	9.06349	3.48453
C	3.43826	8.56598	4.14133
H	2.99302	6.59603	4.20272
H	1.45041	3.94488	1.89061
C	-0.43293	3.14712	1.70646
C	-0.54450	0.89210	1.42614
H	1.25616	-0.05410	1.51412
H	3.41206	1.27067	-0.59337
C	4.45505	-0.41792	-1.02306
C	5.23241	-1.58247	0.90643
H	4.81950	-0.61926	2.66404
H	10.05235	4.70290	3.29424
C	9.36451	5.04492	1.38113
H	8.36710	5.39666	-0.30282
H	6.32814	9.71017	3.29015
C	4.40352	9.49040	3.91217
H	2.57509	8.86574	4.43597
H	-0.85568	4.00818	1.73920
C	-1.14564	2.07182	1.49571
H	-1.04463	0.08960	1.26654
H	4.37484	-0.33238	-1.97655
C	5.10733	-1.49213	-0.44196
H	5.67938	-2.33675	1.29519
H	10.23087	5.07282	0.96781

H	4.20774	10.42817	3.97560
H	-2.10111	2.11160	1.40568
H	5.49688	-2.18811	-0.97804

Table S5. Electronic Energy and Cartesian Coordinates of $[\{(\mu_4\text{-S})Fe_3(CO)_9\}Cu_2(dppe)(MeCN)_2]_n$ (n = 2).
E = -7492.0573274 a.u.

	x	y	z
C	7.94866	10.65141	9.65796
C	7.75493	8.85883	7.39020
C	9.42782	10.94932	7.50992
C	8.40239	13.86112	7.46063
C	5.81830	14.33961	7.26343
C	6.81057	13.33773	9.56876
C	3.89510	12.05425	6.80095
C	4.65395	11.51148	9.21427
C	4.49289	9.51587	7.12727
C	4.51784	6.68162	10.78246
C	3.68136	6.69182	9.68614
H	3.77868	7.35906	9.01707
C	2.69259	5.72054	9.56406
H	2.10531	5.73789	8.81753
C	2.55897	4.74926	10.50075
H	1.90187	4.06978	10.39276
C	3.36674	4.75028	11.59942
H	3.24990	4.09426	12.27552
C	4.35264	5.70320	11.72853
H	4.92745	5.68177	12.48446
C	7.32926	6.93464	11.26841
C	8.05689	6.43982	10.20730
H	7.77053	6.63367	9.32226
C	9.18365	5.67565	10.39276
H	9.68873	5.37876	9.64623
C	9.57825	5.34101	11.67924
H	10.33071	4.77987	11.82009
C	8.87296	5.82461	12.73565
H	9.13982	5.61444	13.62304
C	7.75917	6.62856	12.51967
H	7.28772	6.97341	13.26855
C	5.47491	8.72824	12.52671
H	5.42766	8.02937	13.22629
H	6.21644	9.34039	12.75912

C	4.17161	9.50873	12.51498
H	3.44116	8.93433	12.17223
H	4.25745	10.29024	11.91399
C	2.22186	11.03604	14.03621
C	1.40955	11.16154	15.15366
H	1.65715	10.73099	15.96358
C	0.24109	11.90734	15.10201
H	-0.30807	11.99100	15.87202
C	-0.11604	12.52663	13.92118
H	-0.90612	13.05104	13.88831
C	0.65162	12.39400	12.80842
H	0.38596	12.81026	11.99851
C	1.82438	11.65228	12.85303
H	2.35698	11.56453	12.07128
C	5.02451	11.37375	14.55972
C	5.48835	11.49516	15.86733
H	5.16193	10.90851	16.53874
C	6.41758	12.46133	16.19129
H	6.71660	12.55214	17.08807
C	6.90482	13.28672	15.22174
H	7.56000	13.93764	15.44711
C	6.46387	13.19183	13.93057
H	6.79626	13.78154	13.26620
C	5.51979	12.22056	13.60426
H	5.21617	12.14506	12.70748
C	2.99217	5.46548	15.55979
C	2.82108	4.03611	15.71473
H	2.42126	3.66474	14.90012
H	2.22771	3.86063	16.47770
H	3.69238	3.61781	15.87437
C	6.77686	7.50700	16.30398
C	8.09428	7.01626	16.71011
H	8.62309	6.80099	15.91428
H	7.98793	6.21128	17.25945
H	8.55255	7.70799	17.23128
N	3.13345	6.57959	15.46354
N	5.77472	7.89469	16.02462
O	8.21007	10.72793	10.77729

O	7.78865	7.77328	7.04041
O	10.53257	11.16664	7.26812
O	9.40762	14.38349	7.22117
O	5.16902	15.19764	6.90894
O	6.76242	13.57137	10.68151
O	3.07497	12.68987	6.32674
O	4.24613	11.86653	10.23852
O	3.98872	8.54357	6.78217
P	5.83008	7.94040	10.91768
P	3.76270	10.08109	14.21885
S	6.79572	11.56290	6.19833
Fe	7.74881	10.57469	7.89704
Fe	6.88114	13.01635	7.82192
Fe	5.16704	11.08889	7.58082
Cu	5.98923	9.38855	9.23587
Cu	3.81021	8.46297	15.74478
S	3.16896	8.84210	17.93625
Fe	4.12205	9.83031	19.63497
Fe	3.25438	7.38865	19.55984
Fe	1.54028	9.31611	19.31875
C	4.32190	9.75359	21.39589
C	4.12817	11.54617	19.12812
C	5.80106	9.45568	19.24785
Cu	2.36247	11.01646	20.97379
C	4.77563	6.54388	19.19855
C	2.19154	6.06539	19.00135
C	3.18381	7.06727	21.30668
C	0.26834	8.35075	18.53888
C	1.02719	8.89352	20.95220
C	0.86613	10.88913	18.86519
O	4.58331	9.67707	22.51522
O	4.16189	12.63172	18.77833
O	6.90581	9.23836	19.00605
P	2.20332	12.46460	22.65561
O	5.78086	6.02152	18.95910
O	1.54226	5.20736	18.64687
O	3.13566	6.83364	22.41944
O	-0.55179	7.71513	18.06467

O	0.61937	8.53847	21.97645
O	0.36196	11.86143	18.52010
C	0.89108	13.72338	22.52039
C	3.70250	13.47036	23.00633
C	1.84815	11.67676	24.26464
C	0.05460	13.71318	21.42406
C	0.72588	14.70180	23.46646
C	4.43013	13.96518	21.94523
C	4.13241	13.77644	24.25760
H	1.80090	12.37563	24.96422
H	2.58968	11.06461	24.49705
C	0.54485	10.89627	24.25290
H	0.15192	13.04594	20.75500
C	-0.93417	14.68446	21.30199
C	-0.26002	15.65472	23.33734
H	1.30069	14.72323	24.22238
H	4.14377	13.77133	21.06018
C	5.55689	14.72935	22.13069
C	5.24620	14.58039	24.47358
H	3.66096	13.43159	25.00648
H	-0.18560	11.47067	23.91015
H	0.63069	10.11476	23.65192
P	0.13594	10.32391	25.95678
H	-1.52145	14.66711	20.55545
C	-1.06779	15.65574	22.23867
H	-0.37686	16.31074	24.01345
H	6.06197	15.02624	21.38415
C	5.95148	15.06399	23.41716
H	5.51306	14.79056	25.36096
C	-1.40490	9.36896	25.77414
C	1.39775	9.03125	26.29765
Cu	0.18345	11.94203	27.48271
H	-1.72489	16.33522	22.13069
H	6.70395	15.62513	23.55802
C	-2.21721	9.24347	26.89159
C	-1.80238	8.75273	24.59095
C	1.86159	8.90984	27.60525
C	1.89303	8.18445	25.34218

N	-0.49331	13.82541	27.20147
N	2.14796	12.51031	27.76254
H	-1.96961	9.67401	27.70151
C	-3.38567	8.49766	26.83994
C	-2.97514	8.01100	24.54635
H	-1.26978	8.84047	23.80921
H	1.53517	9.49649	28.27666
C	2.79082	7.94367	27.92922
C	2.83711	7.21317	25.66850
H	1.58941	8.25994	24.44541
C	-0.63459	14.93952	27.29772
C	3.15010	12.89800	28.04190
H	-3.93483	8.41400	27.60995
C	-3.74280	7.87837	25.65910
H	-3.24080	7.59474	23.73643
H	3.08984	7.85287	28.82600
C	3.27806	7.11828	26.95967
H	3.16950	6.62346	25.00413
C	-0.80568	16.36889	27.45266
C	4.46752	13.38874	28.44804
H	-4.53288	7.35396	25.62624
H	3.93324	6.46737	27.18504
H	-1.20550	16.74026	26.63805
H	-1.39905	16.54437	28.21563
H	0.06562	16.78720	27.61229
H	4.99633	13.60401	27.65221
H	4.36117	14.19372	28.99737
H	4.92579	12.69701	28.96920