Electronic Supplementary Information

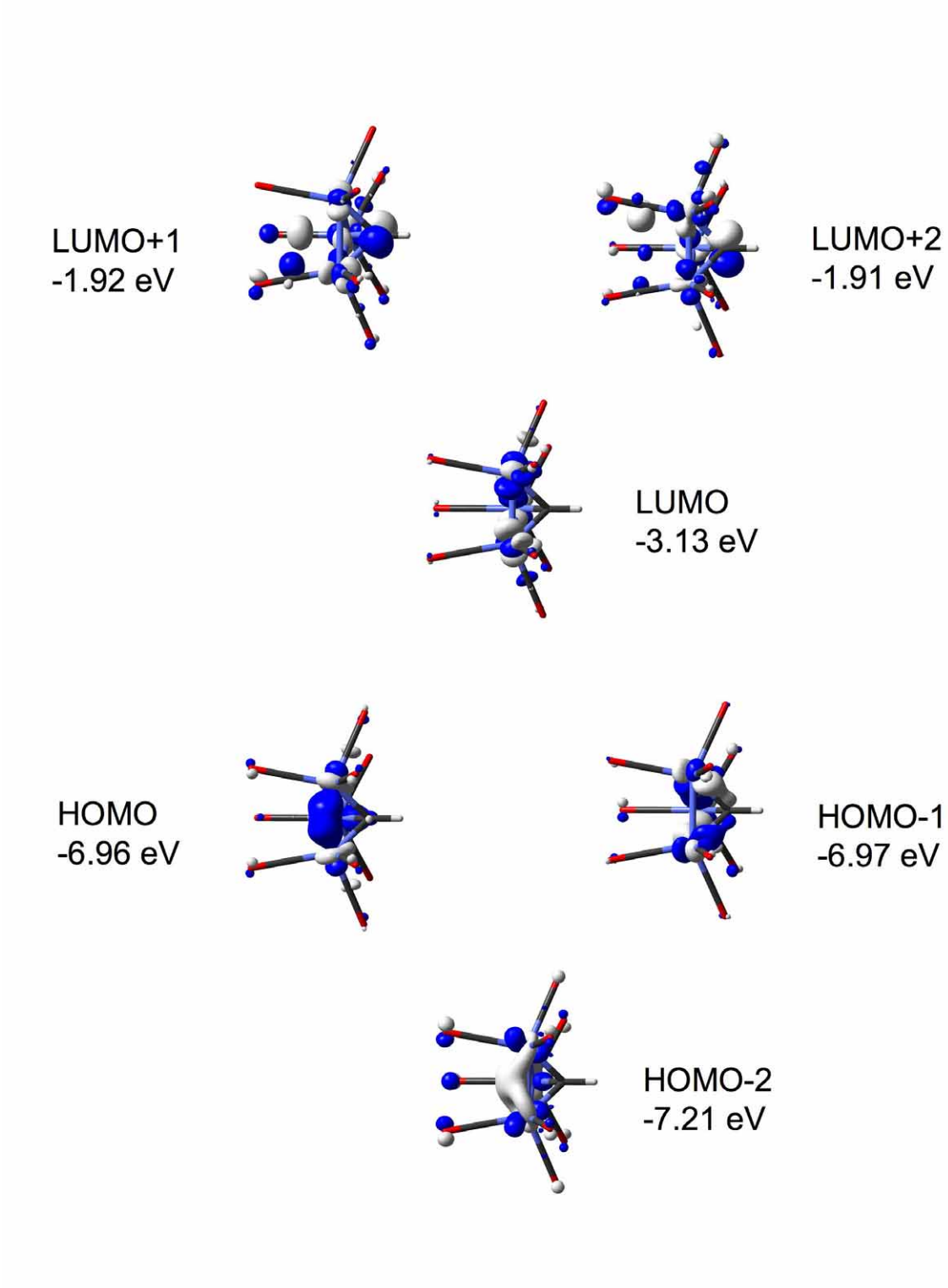

Figure S1. Plots of selected frontier orbitals and energies calculated from $Co_3(\mu_3\text{-}CH)(CO)_9$.

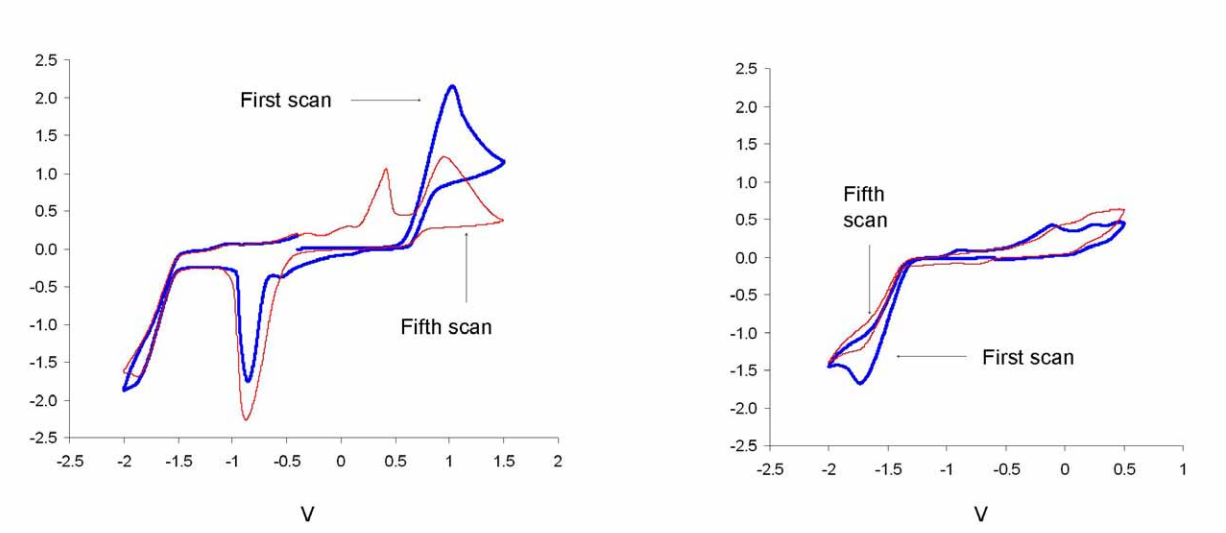

Figure S2. CV traces for **1**. Starting from initial oxidation (left) and initial reduction (right). First scan in blue and fifth cycle scan in red.

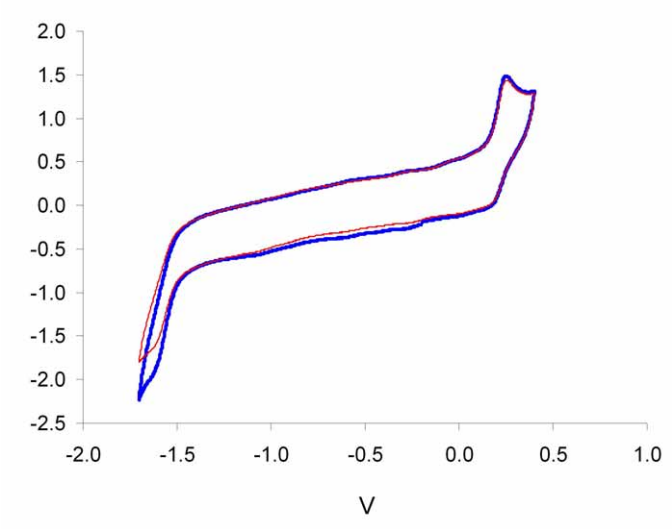

Figure S3. CV traces for **6**. Initial (blue) and fifth cycle (red) scans.

Table S1. Orbital numbers, energies and % composition for $Co_3(\mu_3\text{-}CH)(CO)_9$.

MO		eV	Co_3	CO	C	H
116	L+8	-1.14	23	77	0	0
115	L+7	-1.14	23	77	0	0
114	L+6	-1.37	30	64	3	2
113	L+5	-1.39	15	85	0	0
112	L+4	-1.40	15	85	0	0
111	L+3	-1.77	20	79	1	0
110	L+2	-1.91	45	38	17	0
109	L+1	-1.92	45	38	17	0
108	LUMO	-3.13	74	26	0	0
107	HOMO	-6.96	80	17	3	0
106	H-1	-6.97	79	17	3	0
105	H-2	-7.21	71	30	-1	0
104	H-3	-7.48	64	23	6	7
103	H-4	-7.49	63	22	15	0
102	H-5	-7.50	63	22	15	0
101	H-6	-8.06	82	18	0	0
100	H-7	-8.07	82	18	0	0
99	H-8	-8.15	84	16	0	0
98	H-9	-8.40	81	19	0	0
97	H-10	-8.41	81	19	0	0

Table S2. Orbital numbers, energies and % composition for **1-H**.

MO		eV	CH_2	S_3	Co_3	CO	C	H
131	L+8	-0.38	0	1	24	73	1	0
130	L+7	-0.38	0	1	24	73	1	0
129	L+6	-0.53	0	0	31	65	3	2
128	L+5	-1.07	3	2	36	59	0	0
127	L+4	-1.14	23	57	12	7	1	0
126	L+3	-1.14	23	57	12	7	1	0
125	L+2	-1.45	4	7	49	27	13	0
124	L+1	-1.45	4	6	49	27	13	0
123	LUMO	-1.95	1	3	75	20	0	0
122	HOMO	-5.89	2	2	84	11	1	0
121	H-1	-5.89	2	2	84	11	1	0
120	H-2	-5.96	2	2	78	20	-1	0
119	H-3	-6.25	2	7	64	18	4	6
118	H-4	-6.47	1	14	64	15	6	0
117	H-5	-6.48	1	14	64	15	6	0
116	H-6	-6.75	3	3	83	8	4	0
115	H-7	-6.75	3	3	83	8	4	0
114	H-8	-6.88	2	1	86	11	0	0
113	H-9	-7.25	0	0	78	21	0	0
112	H-10	-7.26	0	0	78	21	0	0

Table S3. Orbital numbers, energies and % composition for $\{Co_3(CO)_9\}_2(\mu\text{-}C_4)$.

MO		eV	$CO_a(1)$	$CO_e(1)$	$Co_3(1)$	C(1)	C(2)	C(3)	C(4)	$Co_3(2)$	$CO_e(2)$	$CO_a(2)$
230	L+10	-1.47	2	5	3	0	0	0	0	14	45	30
229	L+9	-1.48	34	50	15	0	0	0	0	0	0	0
228	L+8	-1.49	35	50	15	0	0	0	0	0	0	0
227	L+7	-1.79	12	11	19	6	2	1	7	20	11	12
226	L+6	-1.80	12	11	19	6	2	1	6	19	11	12
225	L+5	-1.84	1	5	1	0	0	0	1	18	66	8
224	L+4	-1.85	8	66	18	1	0	0	0	1	5	0
223	L+3	-2.85	4	5	26	8	8	8	7	25	5	4
222	L+2	-2.86	4	5	26	8	8	8	7	25	5	4
221	L+1	-3.18	0	0	0	0	0	0	0	75	19	6
220	LUMO	-3.23	6	19	75	0	0	0	0	0	0	0
219	HOMO	-6.30	3	4	25	5	13	13	5	25	4	3
218	H-1	-6.31	3	4	25	5	13	12	5	26	4	3
217	H-2	-7.07	2	4	29	1	0	0	0	52	8	4
216	H-3	-7.08	1	3	23	1	0	0	0	57	8	4
215	H-4	-7.16	5	8	50	0	1	1	0	27	4	3
214	H-5	-7.18	5	8	56	0	1	1	0	22	3	3
213	H-6	-7.27	0	0	1	0	0	0	0	69	18	12
212	H-7	-7.30	12	18	69	0	0	0	0	1	0	0
211	H-8	-7.73	2	5	20	1	1	1	4	49	12	4
210	H-9	-7.82	4	12	49	5	0	0	2	21	5	2
209	H-10	-7.85	5	4	30	7	2	3	7	32	4	5

Table S4. Orbital numbers, energies and % composition for **6-H**.

MO		eV	CH_2(1)	S_3(1)	Co_3(1)	CO(1)	C(1)	C(2)	C(3)	C(4)	Co_3(2)	CO(2)	S_3(2)	CH_2(2)
260	L+10	-0.88	2	2	26	41	0	0	0	0	10	17	1	1
259	L+9	-0.93	6	8	13	10	3	1	1	3	16	11	18	11
258	L+8	-0.93	7	9	14	11	3	1	1	3	16	11	15	10
257	L+7	-0.96	12	29	7	4	0	0	0	0	5	4	29	10
256	L+6	-0.97	12	29	6	4	0	0	0	0	5	3	30	11
255	L+5	-1.00	7	24	12	12	2	1	1	2	11	11	13	4
254	L+4	-1.00	7	23	11	11	2	1	1	2	11	10	17	5
253	L+3	-1.76	0	0	9	2	0	0	0	0	66	18	3	1
252	L+2	-1.77	1	2	67	18	0	0	0	0	9	2	0	0
251	L+1	-2.00	1	3	28	4	7	8	8	7	28	4	3	1
250	LUMO	-2.00	1	3	28	4	7	8	8	7	28	4	3	1
249	HOMO	-5.32	0	4	29	3	3	10	10	3	30	3	4	0
248	H-1	-5.33	0	4	29	3	3	10	10	3	30	3	4	0
247	H-2	-5.69	1	1	43	6	0	0	0	0	42	6	1	1
246	H-3	-5.70	1	1	35	5	0	0	0	0	50	7	1	1
245	H-4	-5.73	0	0	4	1	0	0	0	0	73	19	2	2
244	H-5	-5.75	2	2	73	19	0	0	0	0	4	1	0	0
243	H-6	-5.80	1	1	39	6	0	3	3	0	39	6	1	1
242	H-7	-5.81	1	1	46	7	0	3	2	0	31	5	1	1
241	H-8	-6.21	1	3	29	8	2	1	1	3	38	10	4	1
240	H-9	-6.28	1	4	38	10	4	0	0	3	29	8	3	1
239	H-10	-6.40	1	6	37	9	1	1	1	1	32	7	5	0