Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary information

Electrochemical water oxidation by cobalt-Prussian blue coordination polymer and theoretical studies of the electronic structure of the active species

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Table S1. Onset potentials for j = 0.5 mA cm^{-2} for the water oxidation reaction using the different modified FTO electrodes. Potentials in V vs SCE

pH	E_{onset} CoHCF	E_{onset} CoFeisn
3.0	1.794	1.739
5.0	1.633	1.528
7.0	1.421	1.309
9.0	1.396	1.199
11.0	1.126	0.888

Electrochemical Impedance Spectroscopy – Equivalent circuits

Equivalent circuits were obtained for each of the electrodes used in the water oxidation experiments after impedance analysis. The circuits were generated using the Equivalent Circuit Tool of the Software NOVA® 1.10.1 and fitted based on the corresponding Nyquist plots by adding circuit elements in agreement with the properties of the modified FTOs and the electrode/electrolyte interface. Furthermore, the values of χ^2 obtained by the fitting were as low as possible in order to obtain a trustworthy analysis.

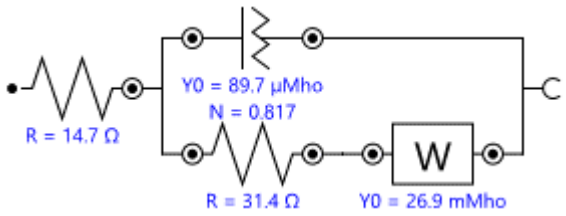

Figure S1. Equivalent circuit obtained for bare FTO electrode

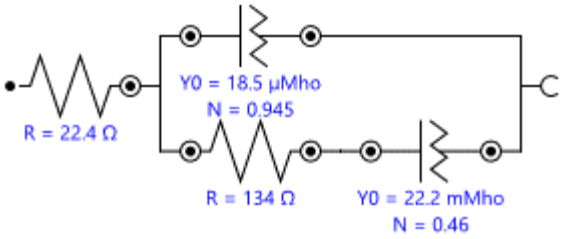

Figure S2. Equivalent circuit obtained for FTO/CoHCF electrode

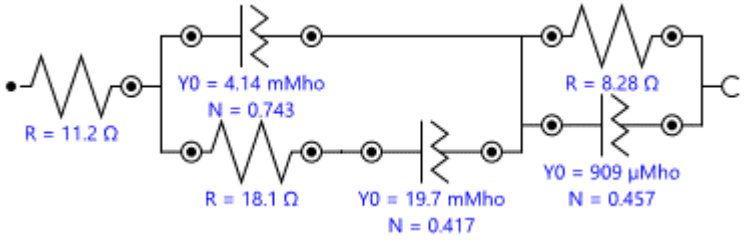

Figure S3. Equivalent circuit obtained for FTO/CoFeisn electrode

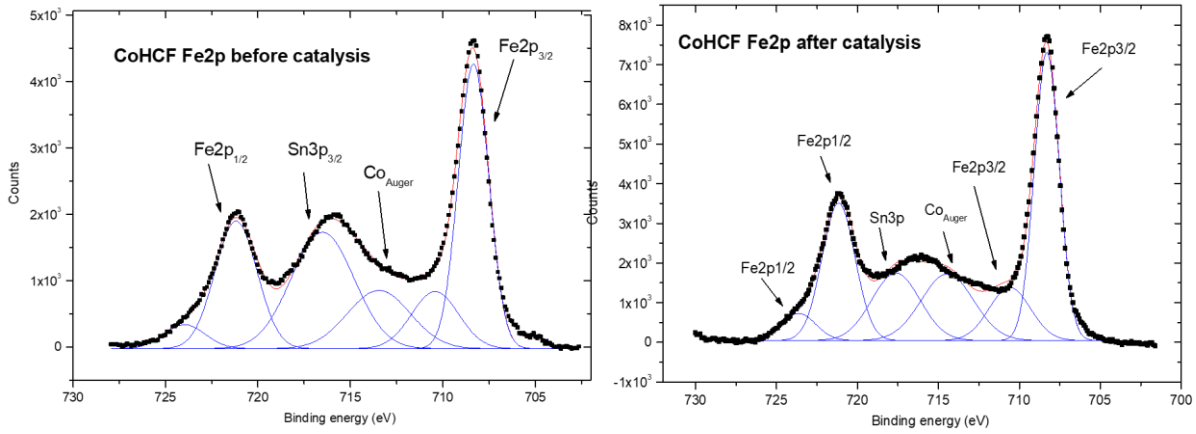

Figure S4. XPS spectrum of the Fe 2p range of FTO/CoHCF electrode before and after water electrolysis.

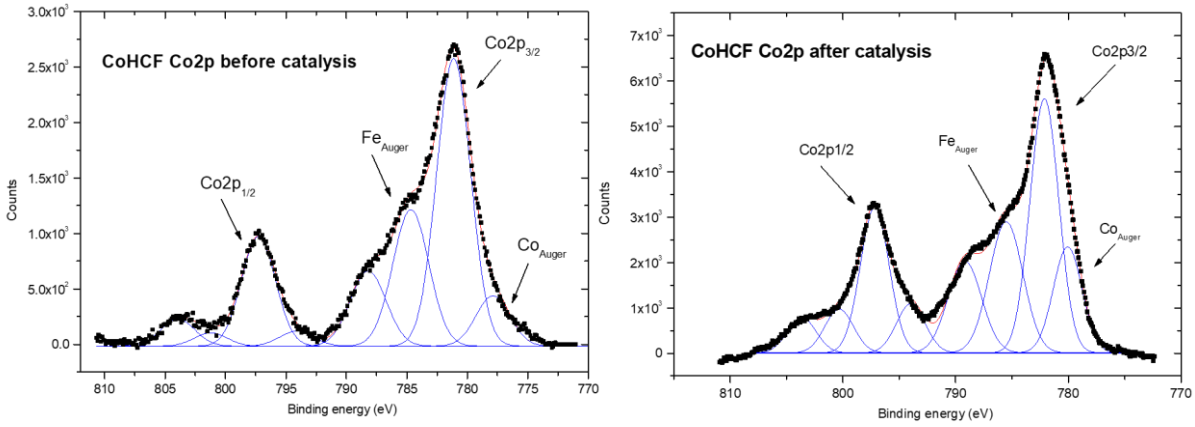

Figure S5. XPS spectrum of the Co 2p range of FTO/CoHCF electrode before and after water electrolysis.

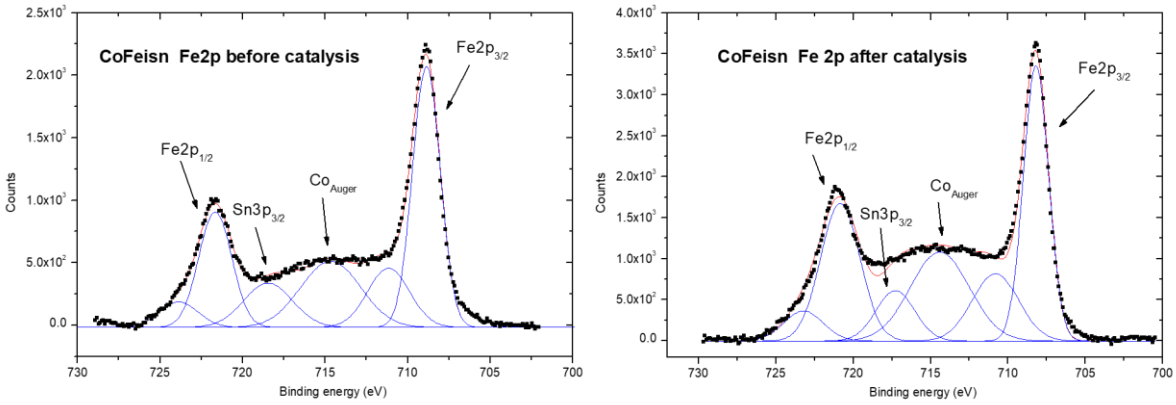

Figure S6. XPS spectrum of the Fe 2p range of FTO/CoFeisn electrode

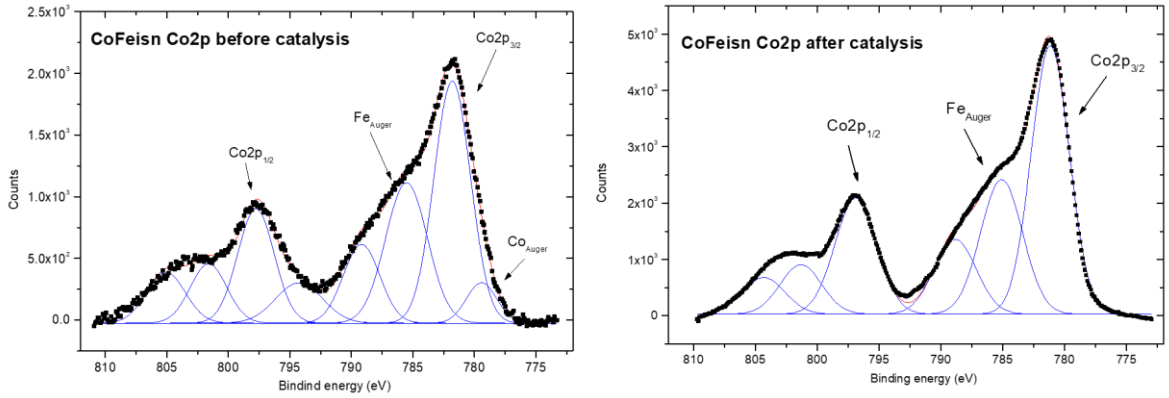

Figure S7. XPS spectrum of the Co 2p range of FTO/CoFeisn electrode before and after water electrolysis.

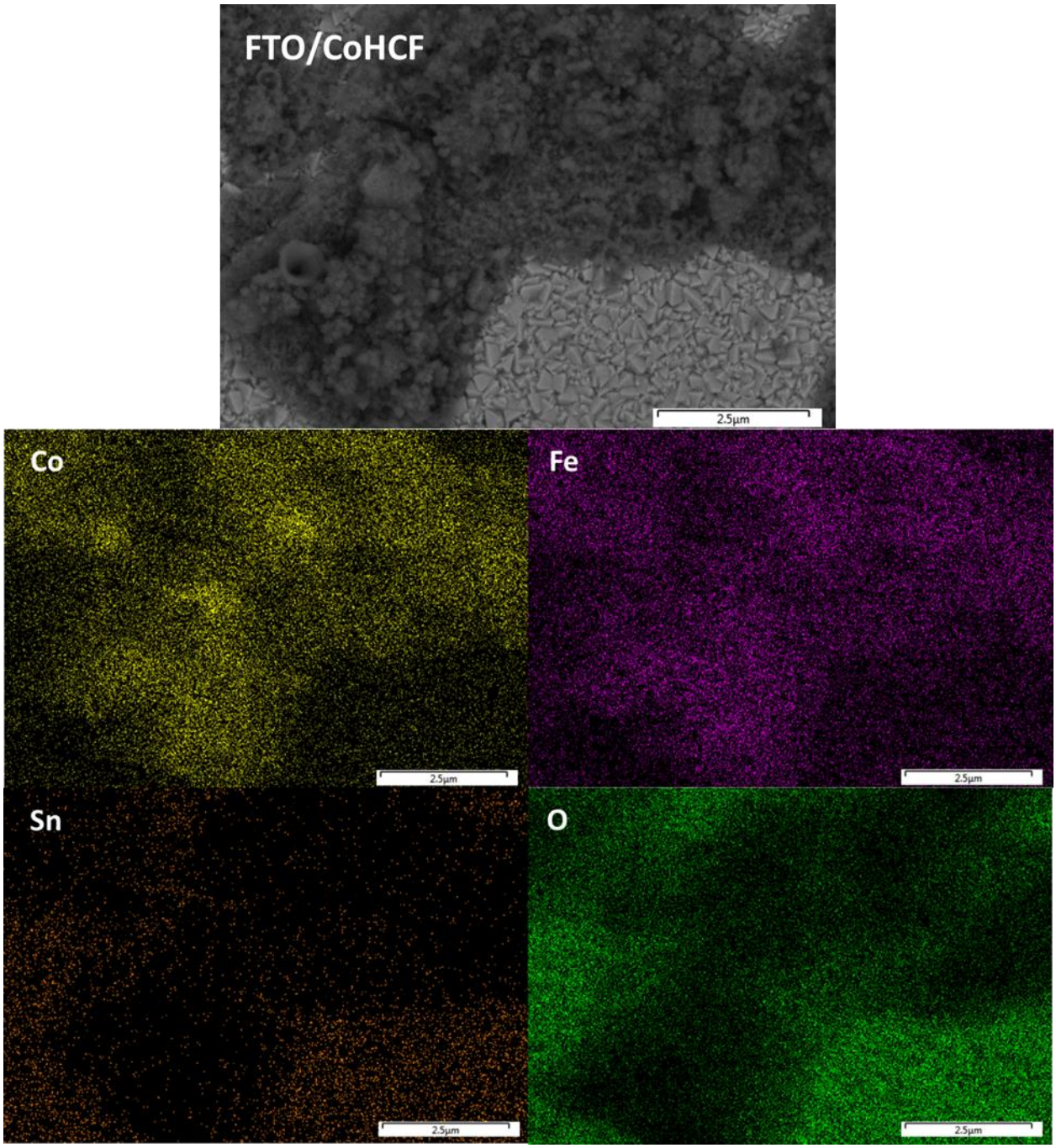

Figure S8. SEM micrographs and EDS analysis of FTO/CoHCF electrode.

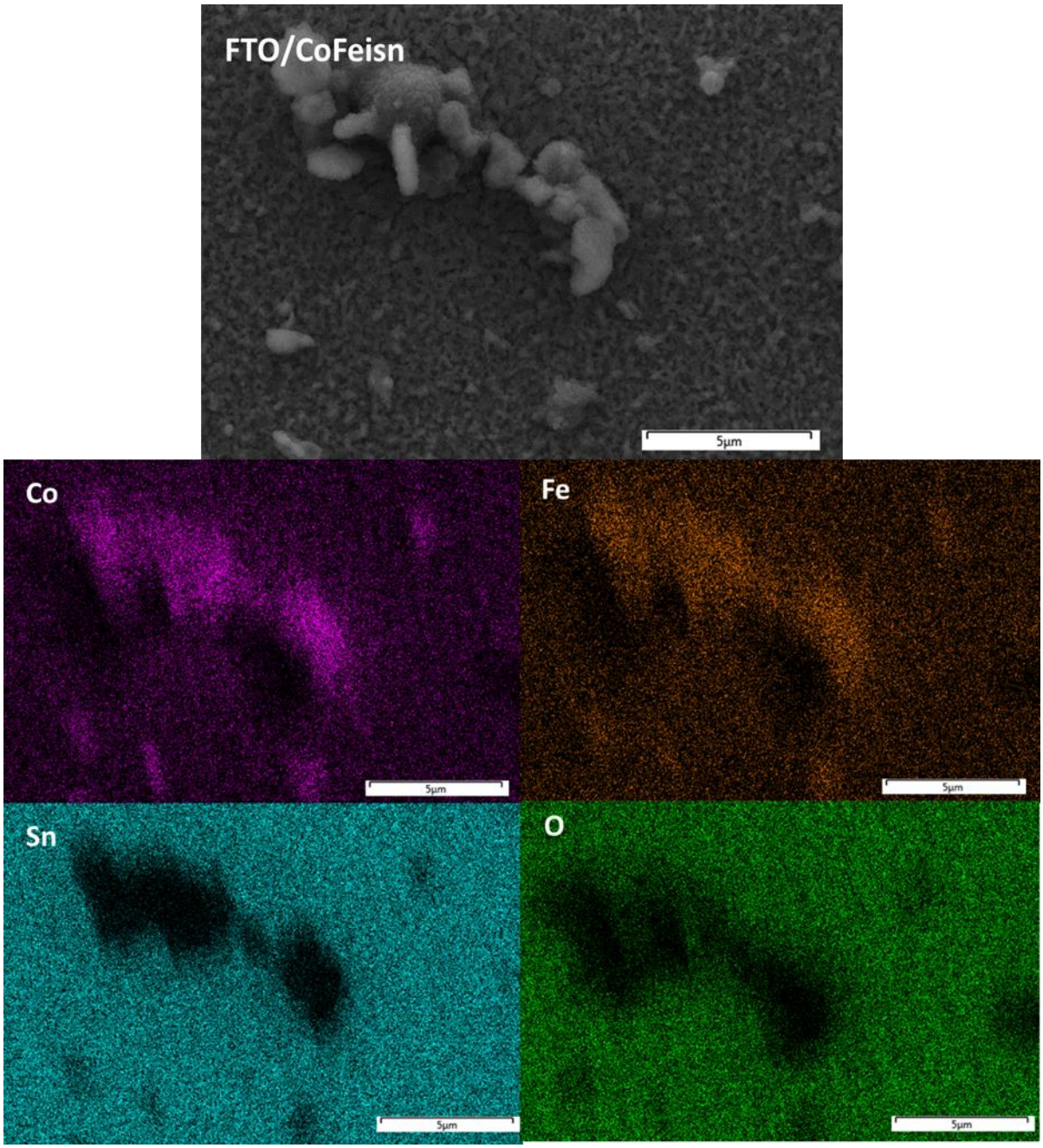

Figure S9. SEM micrographs and EDS analysis of FTO/CoFeisn electrode.

Table S2. Spin states and spin populations calculated for the $\{[Co(O)(NC)_4](\mu_2\text{-}NC)[Fe(CN)_6]\}^{5-}$ cluster embedded in the array of point-charges using U-M06L/Def2-TZVP.

		Spin population			
	Rel. En. (kcal mol^{-1})	**Co**	**O**	**Fe**	**Total**
Singlet (*BS*)	0.20	-0.01	1.00	-1.19	0.00
Triplet	0.00	-0.01	1.03	1.15	2.00
Triplet (*BS*)	18.9	1.63	1.15	-1.18	2.00
Quintet	18.4	1.64	1.15	1.19	4.00
Quintet (*BS*)	*unstable*				4.00
Septet	33.9	2.98	1.47	1.21	6.00

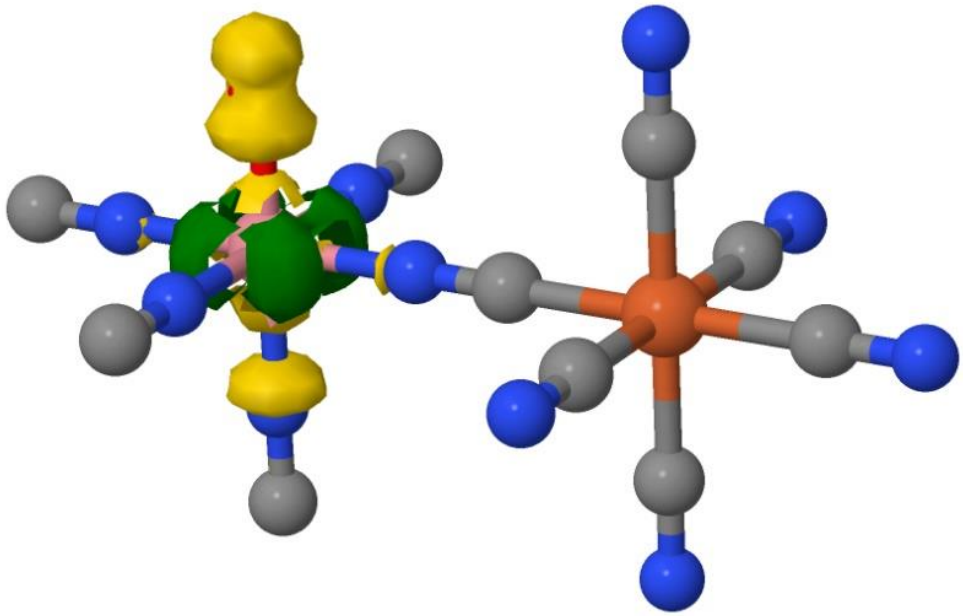

Figure S10. Difference density for the lowest Co(III)-$O^{-\bullet}$ charge transfer for the cluster $\{[Co(O)(NC)_4](\mu_2\text{-}NC)[Fe(CN)_6]\}^{5-}$ calculated by TD-DFT U-PBE0/Def2-TZVP. The array of point-charges is not shown for clarity. Positive (green) and negative (yellow) regions show that an electron is transferred from Co to O to generate a Co(IV)-O^{2-} excited state. This state lies 64 kcal mol^{-1} above the ground state in this level of theory.

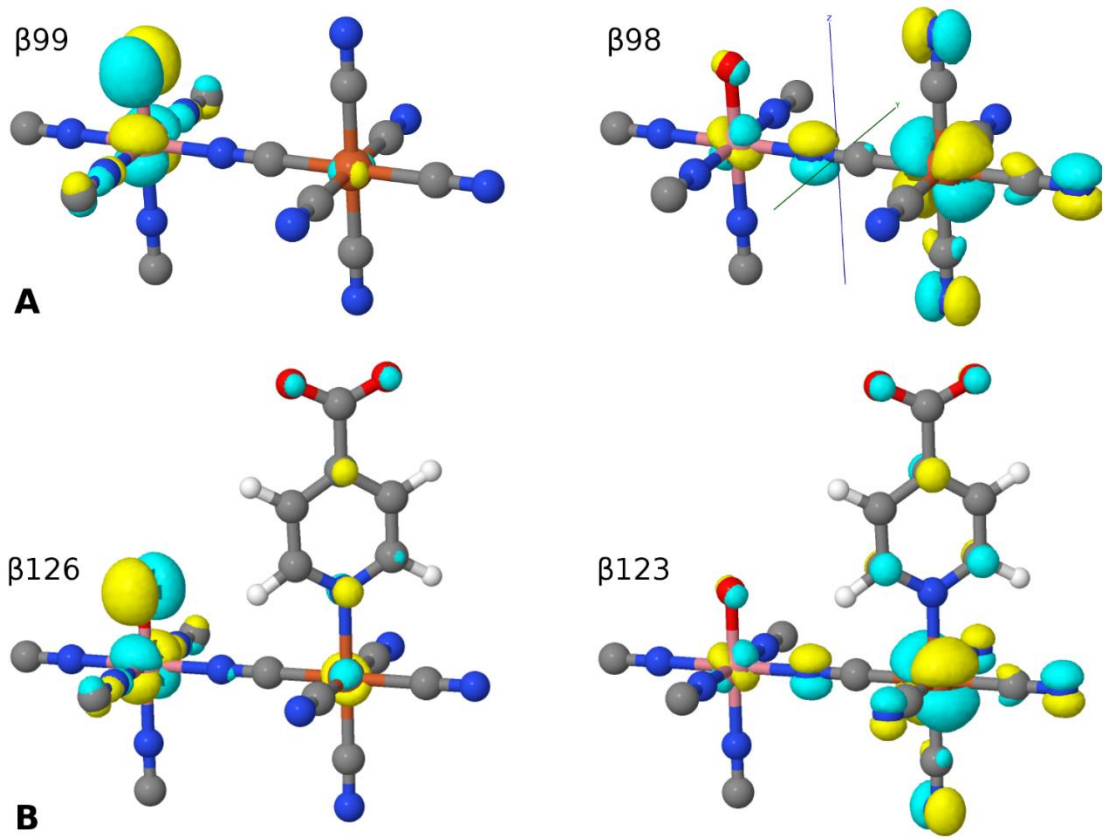

Figure S11. Plots of virtual β Kohn-Sham orbitals obtained with U-PBE0/Def2-TZVP for the clusters $\{[Co(O)(NC)_4](\mu_2\text{-}NC)[Fe(CN)_5(L)]\}^{5-}$ A) L=CN^- and B) L=isn. The array of point-charges is not shown for clarity.

Table S3. Kohn-Sham orbital composition (%) based on the UPBE0/Def2-TZVP calculations for $\{[Co(O)(NC)_4](\mu_2\text{-}NC)[Fe(CN)_6]\}^{5-}$ cluster embedded in the array of point-charges. Frontier orbitals for each set are shown in bold face.

	Alpha set					Beta set					
#	**E/a.u.**	**Fe**	**Co**	**O**	**CN**	**#**	**E/a.u.**	**Fe**	**Co**	**O**	**CN**
87	-0.190	14.6	0.8	0.3	84.2	87	-0.186	11.8	1.3	0.1	86.9
88	-0.189	0.0	10.8	6.7	82.5	88	-0.177	5.3	7.3	3.0	84.4
89	-0.187	0.9	12.4	32.7	54.0	89	-0.176	5.0	32.7	0.0	62.3
90	-0.186	14.0	1.2	2.0	82.8	90	-0.172	7.4	10.0	2.0	80.7
91	-0.178	3.5	11.1	6.4	79.0	91	-0.171	6.1	23.1	0.0	70.8
92	-0.177	11.6	28.2	0.0	60.1	92	-0.168	0.0	57.7	1.1	41.1
93	-0.173	15.9	21.9	0.0	62.2	93	-0.166	6.2	15.2	17.6	61.0
94	-0.168	17.5	2.1	0.6	79.8	94	-0.158	4.5	13.9	16.0	65.7
95	-0.165	8.6	11.1	2.5	77.8	95	-0.133	73.1	2.3	0.0	24.6
96	-0.160	0.0	56.9	23.5	19.7	96	-0.129	72.9	0.0	0.0	27.1
97	-0.153	59.1	8.5	0.0	32.4	**97**	**-0.092**	**3.7**	**14.0**	**58.2**	24.1
98	-0.148	60.4	0.1	0.0	39.6	**98**	**0.020**	**66.4**	**0.7**	**0.3**	32.6
99	**-0.116**	**2.7**	**20.3**	**57.3**	**19.8**	99	0.072	0.0	7.4	58.6	33.9
100	**0.073**	**2.3**	**56.3**	**0.0**	**41.4**	100	0.072	1.0	61.3	0.2	37.4
101	0.095	2.6	47.3	9.0	41.1	101	0.092	2.3	46.8	11.5	39.4
102	0.117	12.6	0.8	0.1	86.5	102	0.132	12.5	0.3	0.0	87.1
103	0.129	12.5	0.1	0.0	87.5	103	0.155	12.2	0.0	0.0	87.9
104	0.160	5.7	3.4	0.0	90.8	104	0.161	2.2	5.2	0.0	92.6
105	0.161	5.3	1.9	1.4	91.4	105	0.164	0.4	3.2	3.4	93.0
106	0.163	4.3	1.4	0.0	94.3	106	0.165	7.8	0.3	0.0	92.0
107	0.164	2.5	1.8	1.7	94.0	107	0.169	4.5	1.4	0.1	94.0
108	0.168	3.2	1.5	0.1	95.3	108	0.171	0.6	2.3	1.0	96.1
109	0.169	0.3	3.3	0.3	96.1	109	0.173	10.3	0.1	0.0	89.6
110	0.170	9.1	0.0	0.0	90.9	110	0.175	1.7	1.6	0.3	96.4

Table S4. Kohn-Sham orbital composition (%) based on the UPBE0/Def2-TZVP calculations for $\{[Co(O)(NC)_4](\mu_2\text{-}NC)[Fe(CN)_5(isn)]\}^{5-}$ cluster embedded in the array of point-charges. Frontier orbitals for each set are shown in bold face.

Alpha set

#	E/a.u.	Fe	Co	O	CN	isn
112	-0.211	0.5	13.4	5.5	80.1	0.5
113	-0.209	18.0	13.1	19.6	45.6	3.7
114	-0.209	22.9	16.2	14.7	45.4	0.8
115	-0.207	6.5	4.6	0.2	32.4	56.3
116	-0.204	22.0	1.3	4.1	49.9	22.7
117	-0.198	6.0	31.2	7.4	45.4	10.0
118	-0.195	18.0	46.5	0.0	34.2	1.3
119	-0.194	2.2	2.3	1.1	8.6	85.8
120	-0.184	0.3	56.0	21.2	21.6	0.9
121	-0.141	0.8	16.5	48.6	10.6	23.5
122	-0.141	0.3	0.1	0.4	1.0	98.2
123	-0.136	2.1	0.0	0.0	5.7	92.2
124	**-0.125**	**0.1**	**0.0**	**0.0**	**0.2**	**99.7**
125	**0.037**	**23.2**	**3.6**	**0.0**	**41.7**	**31.5**
126	0.040	2.2	0.5	0.1	8.8	88.4
127	0.049	9.6	23.3	0.0	62.5	4.6
128	0.063	10.9	1.9	0.3	76.3	10.6
129	0.071	0.5	41.5	8.3	27.4	22.3
130	0.082	11.9	0.7	0.1	84.2	3.1
131	0.115	4.5	0.1	0.0	42.9	52.5
132	0.121	12.6	0.1	0.0	80.7	6.6
133	0.126	9.2	0.0	0.0	71.9	18.9
134	0.133	11.8	0.3	0.2	77.1	10.6

Beta set

#	E/a.u.	Fe	Co	O	CN	isn
112	-0.202	8.3	58.1	0.0	32.8	0.8
113	-0.198	6.7	31.0	4.2	55.6	2.5
114	-0.194	1.8	2.2	1.1	6.4	88.5
115	-0.192	8.9	45.6	1.7	40.5	3.3
116	-0.188	23.6	20.3	20.9	30.2	5.0
117	-0.183	29.7	13.5	20.7	30.1	6.0
118	-0.182	59.6	7.6	0.2	30.3	2.3
119	-0.141	0.4	0.0	0.0	0.9	98.7
120	-0.136	2.1	0.0	0.0	5.4	92.5
121	-0.125	0.1	0.0	0.0	0.3	99.6
122	**-0.118**	**1.2**	**15.5**	**66.6**	**15.6**	**1.1**
123	**-0.028**	**64.2**	**0.2**	**0.3**	**26.0**	**9.3**
124	0.045	3.7	4.7	1.3	16.3	74.0
125	0.046	5.4	44.2	0.2	32.8	17.4
126	0.048	5.2	5.5	41.2	33.8	14.3
127	0.059	23.1	4.3	0.7	40.7	31.2
128	0.067	3.4	39.8	10.4	37.0	9.4
129	0.069	3.9	3.0	0.7	26.1	66.3
130	0.100	12.2	0.1	0.0	87.1	0.6
131	0.118	5.6	0.1	0.0	40.6	53.7
132	0.127	12.0	0.1	0.0	76.9	11.0
133	0.133	12.1	0.3	0.1	77.7	9.8
134	0.140	6.5	1.0	0.0	85.4	7.1