Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting information

Novel homogeneous selective electrocatalysts for CO_2 reduction: an electrochemical and computational study of cyclopentadienyl-phenylendiamino-cobalt complexes.

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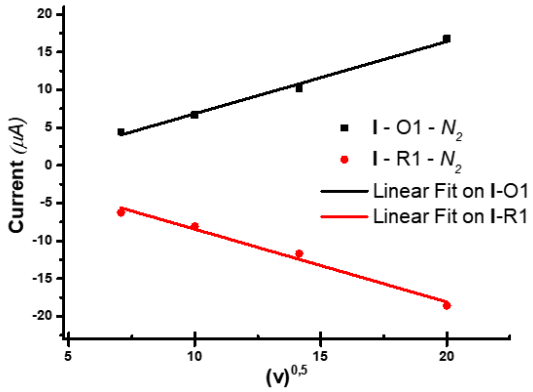
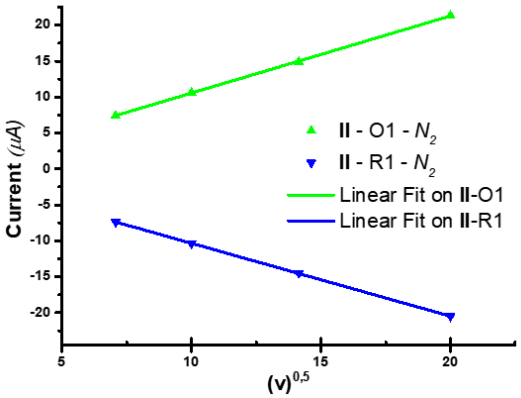
Synthesis

Complex **IV** – [CpCo(*p*-carboxy-bqdi)] – To a suspension of 0.8 g (2 mmol) of the precursor $C_5H_5Co(CO)I_2$ in 30 mL of diethyl ether is added portionwise 0.34 g (2 mmol) of p-carboxyphenylendiamine and the reaction mixture was stirred at room temperature for 1 xh. The purplish red mixture is therefore dropwise added of 0.4 g (0.56 mL, 4 mmol) of Et_3N in 10 mL of diethylether and vigourously stirred for 1.5 h and the formation of a dark precipitate is observed. A first portion of the solid is separated by centrifugation and another portion after slow evaporation of the mother liquor. The precipitate is then washed with hexane and diethyl ether to yield a dark purple bronze solid (340 mg, 66%). **IR** (ATR) cm^{-1}: 3327 (br), 3112, 1555, 1525, 1373, 1282, 1207, 1106, 1053, 1003, 780.



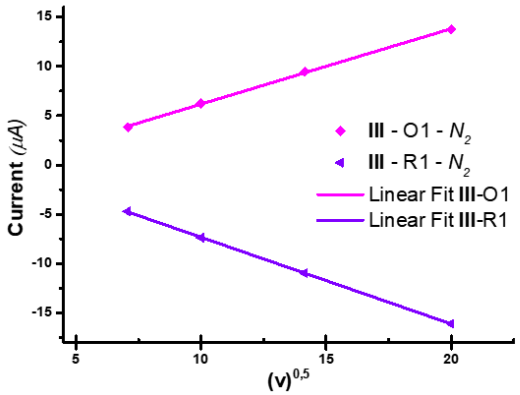
Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0,68413	1,39105	
Pearson's r	0,99606	-0,99217	
Adj. R-Square	0,98822	0,97659	
		Value	Standard Error
I-O1 (N2)	Intercept	-2,73298	0,8247
	Slope	0,95719	0,06023
I-R1 (N2)	Intercept	1,20459	1,17597
	Slope	-0,9646	0,08588

Figure S1. *Graph I vs* $(v)^{0.5}$ *of oxidation and reduction processes of complex* ***I*** *and specifics of the corresponding linear fits.*



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0,01021	0,0059	
Pearson's r	0,99995	-0,99997	
Adj. R-Square	0,99986	0,99991	
		Value	Standard Error
II-O1 (N2)	Intercept	-0,16717	0,10077
	Slope	1,07326	0,00736
II-R1 (N2)	Intercept	-0,18844	0,07659
	Slope	-1,01483	0,00559

Figure S2. *Graph I vs* $(v)^{0.5}$ *of oxidation and reduction processes of complex* ***II*** *and specifics of the corresponding linear fits.*



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0,032	0,00435	
Pearson's r	0,99971	-0,99997	
Adj. R-Square	0,99913	0,99991	
		Value	Standard Error
III-O1 (N2)	Intercept	-1,47554	0,17835
	Slope	0,76515	0,01303
III-R1 (N2)	Intercept	1,46145	0,06577
	Slope	-0,87899	0,0048

Figure S3*. Graph I vs (v)$^{0.5}$ of oxidation and reduction processes of complex* ***III*** *and specifics of the corresponding linear fits.*

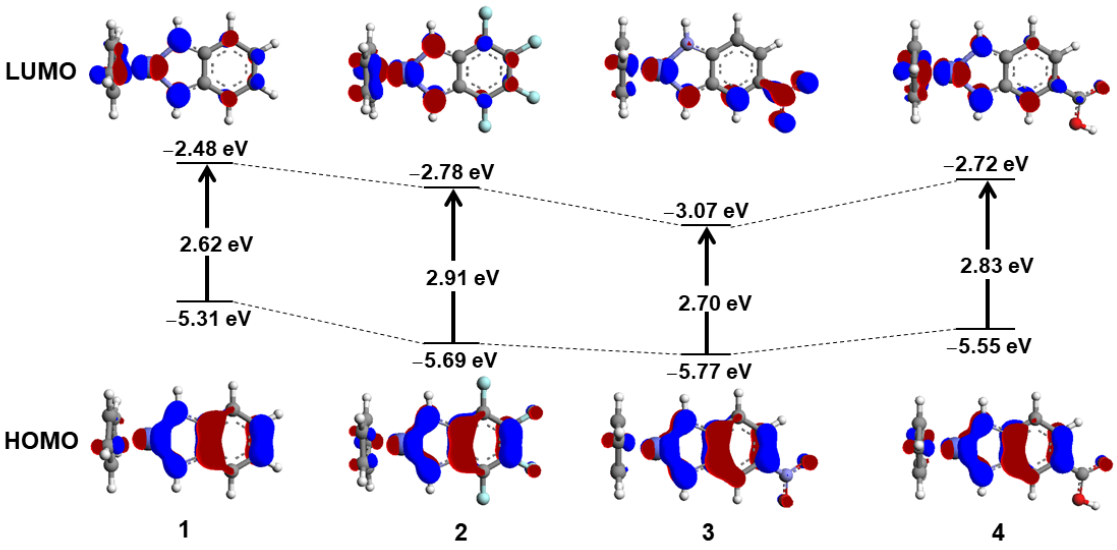


Figure S4*. Frontier orbitals of the complexes* ***I-IV*** *with the corresponding energies.*

Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	1,07717E-4		
Pearson's r	0,99895		
Adj. R-Square	**0,9958**		
		Value	Standard Error
E	Intercept	**-0,50537**	0,02943
	Slope	**0,70477**	0,03234

Figure S5*. Specifics for the linear fit on Figure 3.*

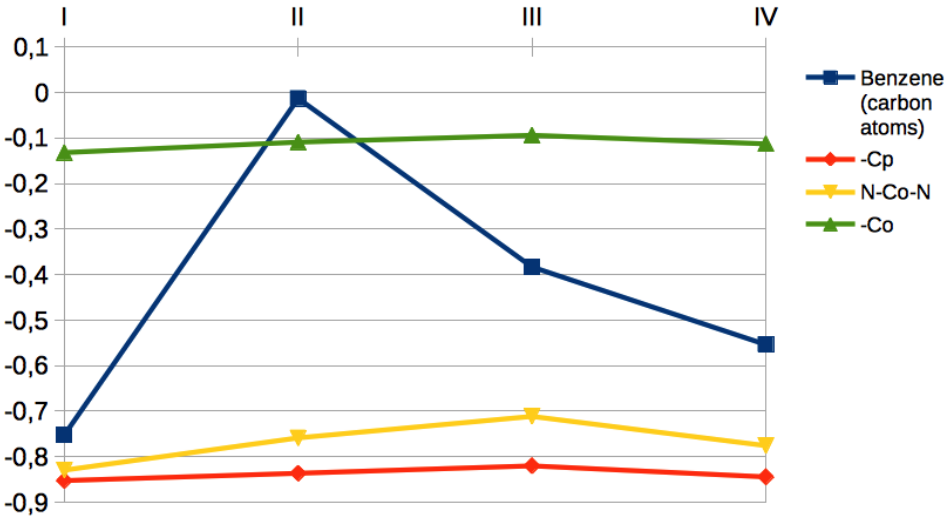


Figure S6. *ADCH partial charge on different moieties of the anionic form of the complexes. Blue: carbon atoms of the benzene; Green: Cobalt atom; Orange: carbon atoms of cyclopentadienyl; Yellow: N-Co-N moiety.*

Table S1*. Calculated enhancements (Icat/Ip) at increasing amount of water.*

	E (V)	**Catalitic enhancement (I*cat*/I*p*)**						
I	-2.09	4.12	8.24	17.15	21.20	22.55	24.40	1.09
II	-2.13	5.59	10.61	18.27	24.44	30.69	31.07	1.04
III	-1.52	4.53	4.15	3.89	3.72	4.09	3.49	1.89
	-2.13	1.11	1.61	2.37	3.656	3.665	3.25	0.76
IV	-1.74	2.78	3.44	4.84	6.16	7.58	7.13	1.78
	-1.91	3.36	5.54	7.80	9.53	9.53	9.97	2.49
	-2.13	3.78	5.30	7.57	9.13	8.73	9.00	5.01
Water content ($\%_{v/v}$)		0	1.96	3.84	5.66	7.41	9.09	9.09
Atmosphere		CO_2	CO_2	CO_2	CO_2	CO_2	CO_2	N_2

***Table S2**. Calculated TOF value using equation (4) at increasing amount of water for complexes **I-IV**.*

	E (V)	**TOF**					
I	-2.09	3.29	13.17	57.04	87.16	98.61	115.46
II	-2.13	6.06	21.83	64.73	115.84	182.66	187.21
III	-1.52	3.98	3.34	2.93	2.68	3.24	2.36
	-2.13	0.24	0.50	1.09	2.59	2.60	2.05
IV	-1.74	1.49	2.29	4.54	7.36	11.14	9.86
	-1.91	2.19	5.95	11.80	17.61	17.61	19.27
	-2.13	2.77	5.44	11.11	16.16	14.78	15.70
Water content ($\%_{v/v}$)		0	1.96	3.84	5.66	7.41	9.09

***Table S3**.* PCM//6-311++G(d,p) enthalpies of the neutral and anionic form of compounds **I-IV**

		Neutral (*Hartree*)	**Anion** (*Hartree*)	**ΔH** (*kcal/mol*)
I	DMSO	-1918.03027	-1918.15493	-0.12465
	CH_3CN	-1918.03019	-1918.15435	-0.12415
II	DMSO	-2315.10720	-2315.24401	-0.13681
	CH_3CN	-2315.10711	-2315.24352	-0.13641
III	DMSO	-2122.60192	-2122.74596	-0.14404
	CH_3CN	-2122.60176	-2122.74539	-0.14364
IV *(2a)*[a]	DMSO	-2106.65811	-2106.79257	-0.13446
	CH_3CN	-2106.65791	-2106.79190	-0.13399
IV *(2b)* [a]	DMSO	-2106.65778	-2106.79274	-0.13496
	CH_3CN	-2106.65781	-2106.79207	-0.13426

[a] **2a** and **2b** differ for the orientation of the COOH group, as shown in figure S6

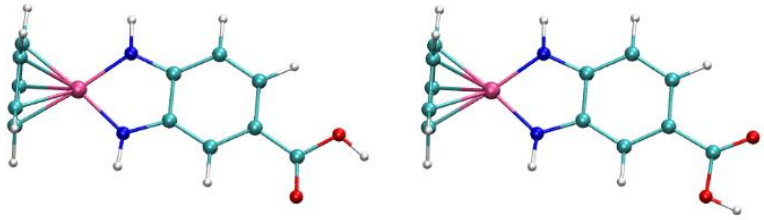
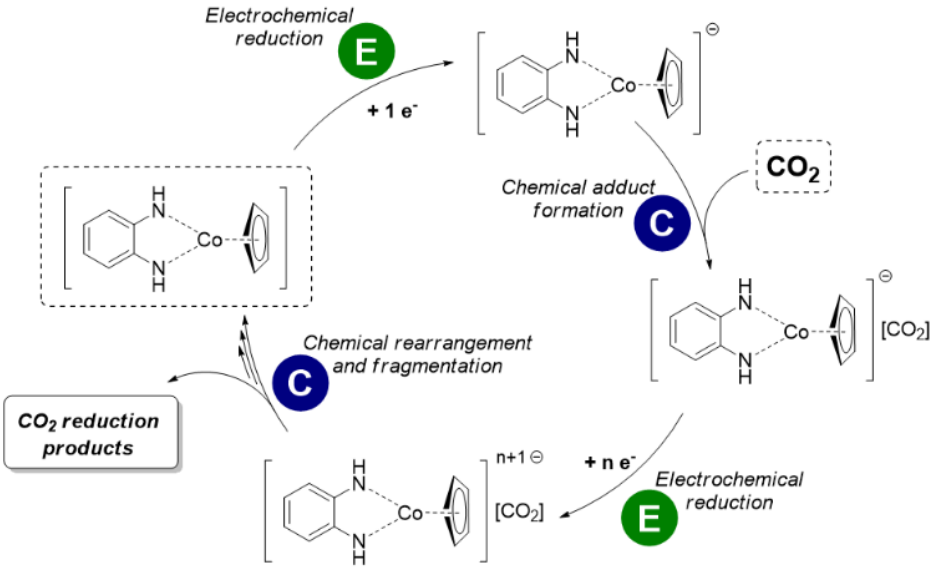


Figure S7. PCM(CH_3CN) B3LYP 6-311++g(d,p) optimized geometries of the two minima of compounds **IV** in the neutral form.

Table S4. *FMO energies for neutral and anionic (reduced) complexes **I**-**IV**.*

Complex	Orbital	Energy (Hartrees)	Energy (eV)	Energy (kJ/mol)
[I]$^{-1}$	LUMO alfa	-0.01920	-0.52246	-50.40960
	LUMO beta	-0.00828	-0.22531	-21.73914
	HOMO alfa	-0.13275	-3.61231	-348.53512
	HOMO beta	-0.15555	-4.23273	-408.39656
[**I**]	LUMO	-0.09100	-2.47624	-238.92052
	HOMO	-0.19527	-5.31357	-512.68142
[II]$^{-1}$	LUMO alfa	-0.02904	-0.79022	-76.24453
	LUMO beta	-0.02257	-0.61416	-59.25754
	HOMO alfa	-0.14561	-3.96225	-382.29908
	HOMO beta	-0.16999	-4.62566	-446.30878
[**II**]	LUMO	-0.10211	-2.77856	-268.08983
	HOMO	-0.20902	-5.68773	-548.78205
[III]$^{-1}$	LUMO alfa	-0.19851	-5.40174	-521.18804
	LUMO beta	-0.07411	-2.01664	-194.57582
	HOMO alfa	-0.15344	-4.17532	-402.85675
	HOMO beta	-0.17754	-4.83111	-466.13131
[**III**]	LUMO	-0.11276	-3.06836	-296.05140
	HOMO	-0.21211	-5.77181	-556.89485
[IV]$^{-1}$	LUMO alfa	-0.02981	-0.81117	-78.26616
	LUMO beta	-0.03228	-0.87839	-84.75115

	HOMO alfa	-0.14300	-3.89123	-375.44653
	HOMO beta	-0.16633	-4.52607	-436.69945
[**IV**]	LUMO	-0.09989	-2.71815	-262.26122
	HOMO	-0.20413	-5.55466	-535.94335



Scheme S1. *Reaction scheme for a ECEC mechanism.*