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

Supporting information for

Visible-Light-Driven Reduction of CO_2 to CO in Fully Aqueous Media using a Water-soluble Cobalt Porphyrin

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Materials and reagents. All solvents were of the highest quality available and were used as received. All other reagents were purchased from Tokyo Chemical Industry Co., and used without further purification. Purification of water (0.055 µS) was performed with an Advantec RFD250RB water distillation apparatus.

Instrumentation. UV-Visible absorption spectra were recorded on a Shimadzu UV2450SIM spectrophotometer. All the sample solutions were maintained at 25 ºC during the spectrophotometric measurements. ESI-TOF mass spectra were recorded on a JEOL JMS-T100LC mass spectrometer in positive or negative ion mode. ^{1}H NMR spectra were acquired on a JEOL JNM-ESA 600 spectrometer. Cyclic voltammetry experiments were recorded on a BAS ALS Model 602DKM electrochemical analyzer using a three electrode system consisting of a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE). The quantification of gases was done using Shimadzu GC-8A equipped with a molecular sieve 5 Å column of 2 m x 3 mm *i.d.*, at 30 ºC. The injection of the sample gas (200 µL) was performed manually using a gas-tight syringe and the output signal from the thermal conductivity detector of the gas chromatograph was analyzed using a Shimadzu C-R8A integrator. The CO and H_2 peaks were determined using a calibrated curve which had been previously obtained using standard CO and H_2 gas. Photoirradiation experiments were carried out by an ILC Technology CERMAX LX-300 Xe lamp (179 mW·cm^{-2}) equipped with a CM-1 cold mirror which reflects light in the range of $400 < \lambda < 800$ nm. The photolysis vial (21 mL) was immersed in a 25 ºC water bath to remove IR radiation and to eliminate the temperature fluctuations.

Photocatalytic experiments and chromatographic detection of gases. In a typical photocatalytic run, a 10 mL aqueous solution containing **CoTCPP** (10 µM), $[Ru(bpy)_3]Cl_2$ (500 µM), sodium ascorbate (0.1 M), and $NaHCO_3$ (0.1 M), was purged with CO_2 (purity ≥ 99.995 %) for 15 min prior to irradiation. The temperature was held constant at 25 ºC throughout the experiment. The gases generated from the reaction during the photolysis were quantified by GC-TCD measurements of 200 µL aliquots from the reaction vial headspace. It was found in this study that the purity of the **CoTCPP** catalyst is very important for the reproducibility of the photocatalytic experiments.

Quantification of formate. The amount of formate in the liquid phase was determined by the following method. After 4 hours of irradiation, the reaction solvent was removed by a freeze-drying method. The resulting residue was dissolved in 0.8 mL D_2O and 3-(trimethylsilyl)propionic-2,2,3,3-*d*$_4$ acid sodium salt (TSP-*d*$_4$, 2 µmol) was added as internal standard. After filtering the solution through Celite, ^{1}H NMR spectrum was measured and the amount of formate was determined using relative integral values compared to that of TSP-*d*$_4$.

Determination of the quantum yield (Φ_{CO}). Since the reduction of CO_2 to CO is a two-electron reduction process, the quantum yield of the process has been estimated using the following equation:

$$\Phi_{CO} = \frac{\text{number of CO molecules x 2}}{number\ of\ photons\ absorbed} \times 100$$

The number of CO molecules generated can be determined from the moles of CO measured in the headspace and using the Avogadro's number. The number of photons absorbed (1.81 x 10^{18} photons·s^{-1}) was estimated by measuring the incident light power inside the reaction vessel (140 mW·cm^{-2}) (an Optical Power Meter TQ8210 with Optical Sensor Q82017A from Advantest was used), taking the photon wavelength equal to 428

nm (a set of interference filters L39 + SV490) (380 < λ < 490 nm) was used) and considering an illuminated area of 6 cm^2. Under the photolysis conditions, the complete absorption of photons is satisfied due to the high absorbance of the solution at the wavelength adopted. The quantum yield at 1 h irradiation is 0.24%.

Synthesis of CoTCPP

CoTCPP [[*meso*-tetra(4-carboxyphenyl)porphyrinato]cobalt(III)]Cl·$3H_2O$. It was prepared following the previous reported procedures.[1] $CoCl_2·6H_2O$ (0.090 g, 6 mmol), and TCPP (0.090 g, 1 mmol) were dissolved in DMSO (25 mL), followed by refluxing for 24 h. After the solution was cooled to room temperature, 1 M HCl (ca. 75 mL) was added to the solution to cause deposition of the crude product as a purple solid, which was collected by filtration, washed with water, and dried in vacuo. This was redissolved in 0.1 M NaOH (ca. 20 mL) followed by addition of 1 M HCl (ca. 40 mL), which caused deposition of the product as a purple solid. This was collected by filtration and dried in vacuo. Yield 92%. MS (ESI – MeOH, positive mode) (m/z): 847.12 $[C_{48}H_{28}CoN_4O_8]^+$ ([***CoTCPP***-$3H_2O$-Cl]$^+$) (100%) (calcd: 847.09). Elemental analysis of **CoTCPP** calcd: (%) for $C_{48}H_{28}N_4O_8ClCo·3H_2O$ (936.1): C 61.52, H 3.66, N 5.98; found: C 61.18, H 3.97, N 5.99.

Table S1. Relevant selected reported systems for photocatalytic CO_2-to-CO conversion conducted *in aqueous media*.

Photosensitizer	Catalyst	Electron donor	Solvent	TON_{CO}	TON_{H2}	Φ (%)	Sel_{CO2} [%][a]	Reference
A-QDs	CoTPPS	AscHNa	H_2O	84000	-	0.96-3.39	99	*J. Am. Chem. Soc.* **2021**, 143, 18131
Water-soluble Cu PS	CoTMPyP	AscHNa	H_2O	2680	820	1.6	77	*ACS Catal.* ***2019,*** **9**, 11263.
$[Ru(bpy)_3]^{2+}$	CoTPPS	AscHNa	H_2O	926	197	0.81	82	*ACS Catal.* ***2019,*** **9**, 4867.
CdS-MPA	dinuclear cobalt complex	TEOA	H_2O	1380	n.r.	n.r.	95	*ACS Catal.* **2018**, 8, 11815.
$CuInS_2$/ZnS	Fe-tetraphenylporphyrin	TEOA	H_2O	450	n.r.	n.r.	99	*ACS Nano.* **2018**, 12, 568.
ZnSe	$Ni(cyclam)Cl_2$	MEDA	H_2O	283	n.r.	3.4	34	*Chem. Sci.* **2018**, *9*, 2501.
CdS	$[Ni(terpy)_2]^{2+}$	TEOA	H_2O	20	n.r.	0.28	> 90	*J. Am. Chem. Soc.* **2017**, 139, 7217
purpurin	Fe-p-TMA	TEA	CH_3CN: H_2O = 1:9	63	3		95	*ChemSusChem* **2017**, 10, 4447.
$[Ru(dmb)_2–(BL)–Re(CO)_3Cl]^{2+}$ (BL = bridging ligand)		$BI(CO_2H)H$	H_2O	130	n.r.	13	81	*Green Chem.* **2016**, 18, 139.
RuP/ZrO_2	Ni^{II}CycP ((CycP = [(1,4,8,11-tetraaza-cyclotetradecan-1-yl)methylene]phosphonic acid))	AscHNa	H_2O	4.8	n.r.	n.r.	19	*Chem. Commun.* **2016**, *52*, 14200.
$[Ru(bpy)_3]^{2+}$	Ni(cyclam)@Cu-azurin	AscHNa	H_2O	38		n.r.	<10	*Chem. Commun.* **2016**, 52, 9889.
Ru–cyclam–$NiCl_2$		AscHNa	CH_3CN: H_2O = 1:1	5.2	2	n.r.	72	*Chem. Chem. Phys.* **2014**, *16*, 12067.
$[Ru(dtb)(bpy)_2]^{2+}$	$Re(dtb)(CO)_3Cl$ (dtb=4,4'-ditridecyl-2,2'-bipyridyl)	AscHNa	H_2O	190	n.r.	n.r.	98	*Photochem. Photobiol. Sci.* **2014**, *13*, 691.
$[Ru(bpy)_3]^{2+}$	Ni^{II}cyclam	AscHNa	H_2O	2.1	n.r.	0.14	87	*Angew. Chem. Int. Ed.* **2011**, *50*, 7391.
$[Ru(bpy)_3]^{2+}$	[6,6'-bi(5,7-dimethyl-1,4,8,11-tetraazacyclotet-radecane)]dinickel(II) triflate	$AscH_2$	H_2O	2.2	n.r.	n.r.	94	*Inorg. Chem.* **1996**, 35, 5132.
$[Ru(bpy)_3]^{2+}$	$[Ni(cyclam)]^{2+}$	AscHNa	H_2O	n.r.	n.r.	0.06	80	*J. Chem. Soc., Dalton Trans*. **1987**, 9, 2105.

[a] Sel_{CO2} = mol (CO)/(mol(CO) + mol(H_2)). n.r. = not reported.

Table S2. Control experiments and other photocatalytic runs to characterize the performance of the $[Ru(bpy)_3]^{2+}$/AscHNa/**CoTCPP** system for the photocatalytic reduction of CO_2.

Entry[a]	Atm	Catalyst	CO [µmol][b]	CO (TON)	H_2 [µmol][b]	Sel_{CO2} [%][c]
1[d]	CO_2	**CoTCPP**	61	610	20.9	74
2[e]	CO_2	-	4.2	-	36.8	10
3[f]	N_2	**CoTCPP**	5.2	52	37.2	12
4[f]	N_2	-	*n. d.*	-	*n. d.*	-
5[g]	CO_2	**CoTCPP**	*n. d.*	-	*n. d.*	-
6[h]	CO_2	**CoTCPP**	*n. d.*	-	*n. d.*	-
7[i]	CO_2	**CoTCPP**	*n. d.*	-	*n. d.*	-
8[j]	CO_2	$CoCl_2$	5.3	53	22.7	19
9[k]	CO_2	**CoTCPP**	49.3	493	16.7	75

[a] Photolysis carried out in a 10 mL CO_2-saturated solution containing catalyst (10 µM), $[Ru(bpy)_3]Cl_2$ (500 µM), 0.1 M $NaHCO_3$ and 0.1 M AscHNa (pH = 6.7), at T = 25 ºC, for 4 h, using Xe lamp irradiation (λ > 400 nm, 179 $mW \cdot cm^{-2}$). Yields of H_2 and CO determined by GC analysis. *n. d.* = not detected. The amount of formate in solution was determined by ^1H NMR (see section *Quantification of formate* for detailed information). [b] Experiments performed at least in duplicate (error 1-15%). [c] Apparent Sel_{CO2} = mol (CO)/(mol (H_2) + mol (CO)). The determination of Sel_{CO2} was done without considering the amount of formate as it was formed in trace amounts in both the presence and absence of **CoTCPP**. [d] 5.6 µmol of formate was produced. [e] 5.0 µmol of formate was produced. [f] In the absence of CO_2, the photolysis was performed under N_2 in a 0.1 M phosphate buffer (pH = 6.9). [g] In the absence of $[Ru(bpy)_3]Cl_2$. [h] In the absence of AscHNa or when using TEOA (0.1 M) or EDTA (0.1 M) as a sacrificial electron donor. [i] Reaction done in the dark. [j] Using $CoCl_2$ as catalyst (10 µM). [k] In the presence of Hg^0 (1 g, 50000 eq. *vs.* **CoTCPP**).

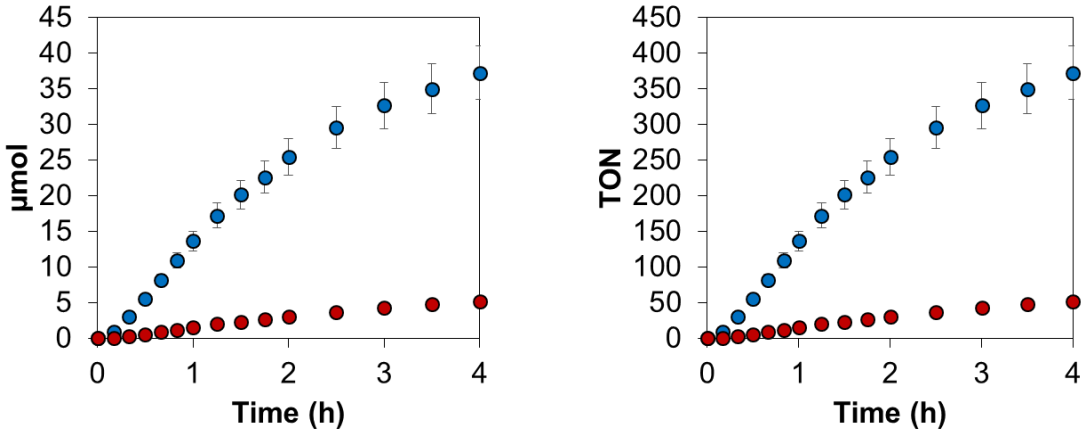


Fig. S1 Time courses of CO (red) and H_2 (blue) produced using **CoTCPP** (10 µM) $[Ru(bpy)_3]Cl_2$ (500 µM) and 0.1 M AscHNa, in a N_2-saturated 0.1 M phosphate buffer (pH 6.9) under visible light irradiation (λ > 400 nm, 179 mW·cm^{-2}). The pH was measured after addition of AscHNa and gas bubbling.

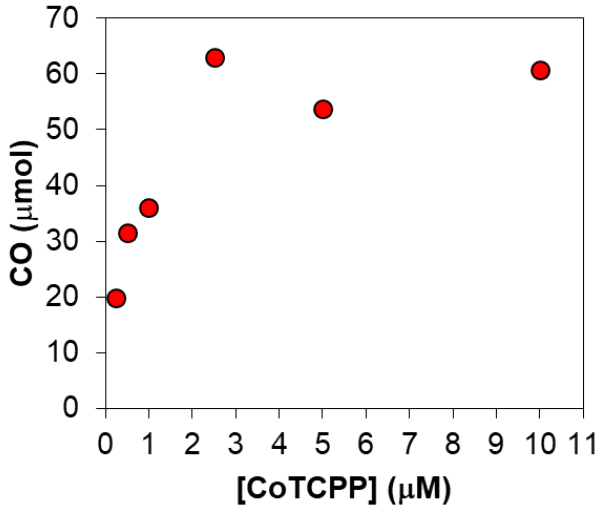


Fig. S2 Plot of the amount of CO produced after 4 h irradiation versus the **CoTCPP** concentration. Conditions: photolysis carried out in a 10 mL CO_2-saturated solution (pH = 6.7) containing **CoTCPP** (10 µM) $[Ru(bpy)_3]Cl_2$ (500 µM), AscHNa (0.1 M) and $NaHCO_3$ (0.1 M) at 298 K using Xe lamp irradiation (λ > 400 nm, 179 mW·cm^{-2}). Experiments performed at least in duplicate (error 1-15%).

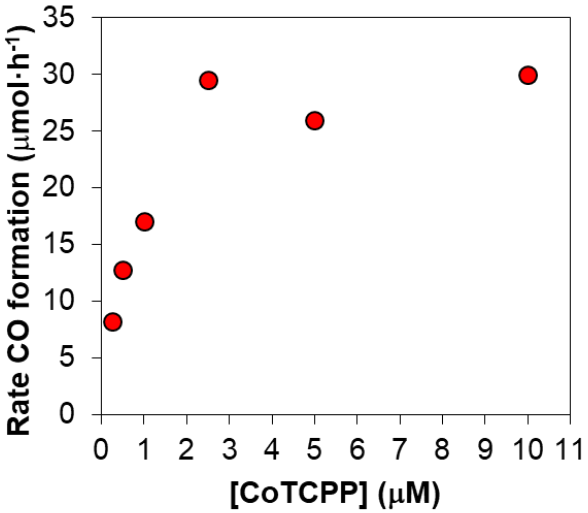


Fig. S3 Plot of the initial rates in CO formation versus the **CoTCPP** concentration. Conditions: photolysis carried out in a 10 mL CO_2-saturated solution (pH = 6.7) containing **CoTCPP** (10 µM) $[Ru(bpy)_3]Cl_2$ (500 µM), AscHNa (0.1 M) and $NaHCO_3$ (0.1 M) at 298 K using Xe lamp irradiation (λ > 400 nm, 179 mW·cm^{-2}). Experiments performed at least in duplicate (error 1-15%).

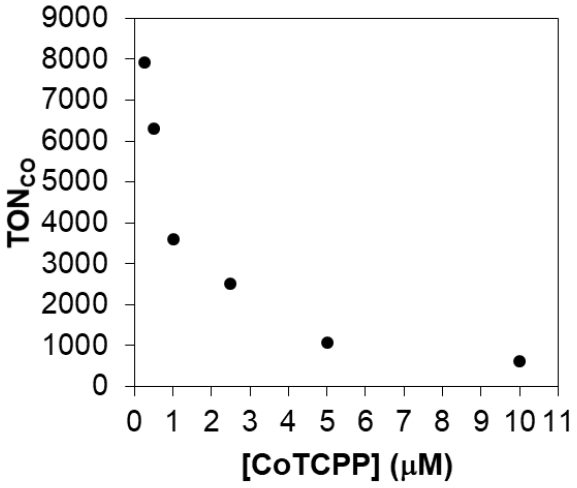


Fig. S4 Plot of the TON_{CO} measured after 4 h irradiation versus the **CoTCPP** concentration. Conditions: photolysis carried out in a 10 mL CO_2-saturated solution (pH = 6.7) containing **CoTCPP** (10 µM) $[Ru(bpy)_3]Cl_2$ (500 µM), AscHNa (0.1 M) and $NaHCO_3$ (0.1 M) at 298 K using Xe lamp irradiation (λ > 400 nm, 179 mW·cm^{-2}). Experiments performed at least in duplicate (error 1-15%).

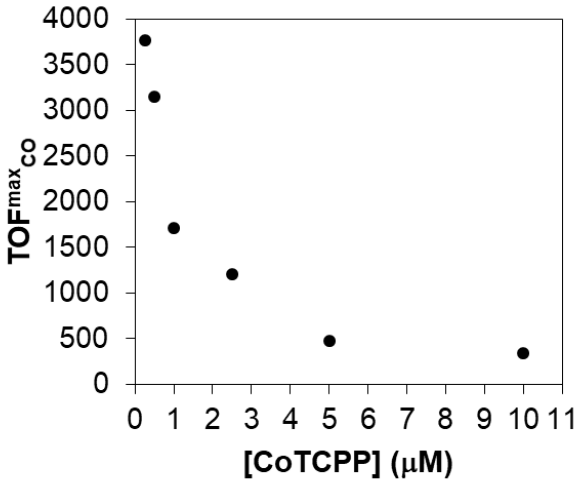


Fig. S5 Plot of the TOF^{max}_{CO} measured after 4 h irradiation versus the **CoTCPP** concentration. Conditions: photolysis carried out in a 10 mL CO_2-saturated solution (pH = 6.7) containing **CoTCPP** (10 μM) $[Ru(bpy)_3]Cl_2$ (500 μM), AscHNa (0.1 M) and $NaHCO_3$ (0.1 M) at 298 K using Xe lamp irradiation (λ > 400 nm, 179 mW·cm^{-2}). Experiments performed at least in duplicate (error 1-15%).

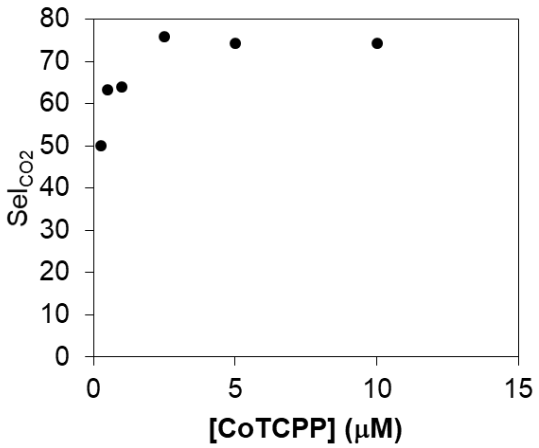


Fig. S6 Plot of the Sel_{CO2} values measured after 4 h irradiation versus the **CoTCPP** concentration. Conditions: photolysis carried out in a 10 mL CO_2-saturated solution (pH = 6.7) containing CoTCPP (10 μM) $[Ru(bpy)_3]Cl_2$ (500 μM), AscHNa (0.1 M) and $NaHCO_3$ (0.1 M) at 298 K using Xe lamp irradiation (λ > 400 nm, 179 mW·cm^{-2}). Experiments performed at least in duplicate (error 1-15%).

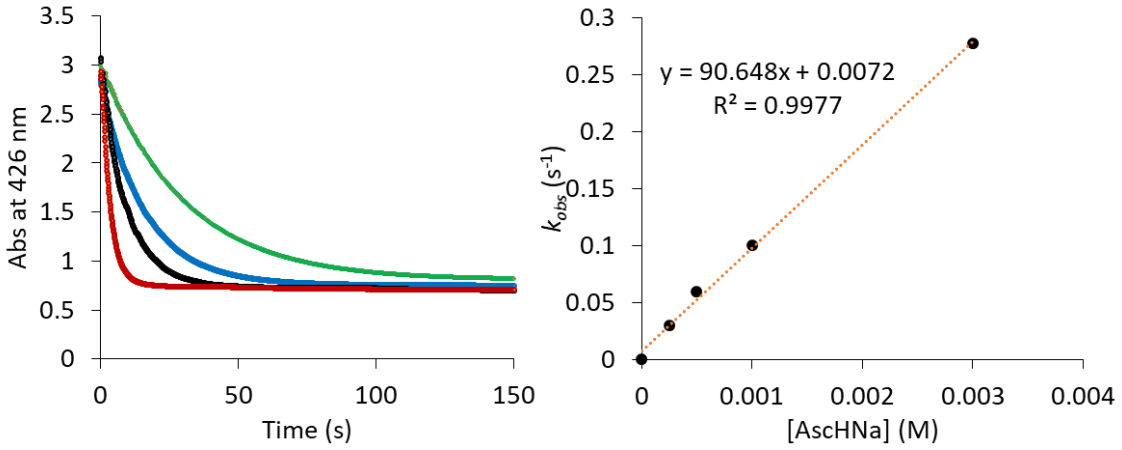
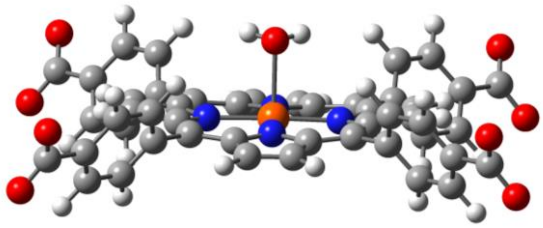


Fig. S7 Left: Decay time profiles at 426 nm due to $Co^{III}TCPP$ (the initial concentration was 10 μM) in the presence of various concentrations of AscHNa in a CO_2-saturated 0.1 M $NaHCO_3$ solution (pH = 6.7) at 298 K. Right: Plot of k_{obs} for the electron transfer from AscHNa to $Co^{III}TCPP$ *vs.* [AscHNa].

DFT calculations. Density functional theory (DFT) calculations were performed using the Gaussian 16 package[2] to better understand the electronic structures of the cobalt porphyrin intermediates that are supposed to be involved in the reaction. The structures were fully optimized using the M06 density functional with the effect of solvation in water taken into consideration using the conductor-like polarizable continuum model (C-PCM) method.[3] Calculations for all the possible intermediates were performed by applying the SDD and 6-31G* basis sets for the cobalt ion and other elements, respectively. The graphical representations of geometry and Mulliken spin distribution were generated using GaussView 5.0.9.[4]

The isodesmic reaction methods were used to calculate the redox potentials,[5] which were benchmarked by employing the experimentally observable redox couple of $[Co^{II}(TCPP)(H_2O)]^{4-}$/{$[Co^{I}(TCPP)]^{5-}$ + H_2O} (E = -0.94 V vs. SCE). The free energies of all chemical species in solution were considered to be in a 1 M standard state except for water supposed to have a 55.6 M standard state.

Table S3. DFT-optimized geometry of $[Co^{II}TCPP(H_2O)]^{4-}$ (doublet), computed at the M06 level with SDD(Co) and 6-31G*(HCNO) basis sets, using CPCM.[a]



atom	x	y	z	Mulliken Charge	Spin density
Co1	0.008547	-0.000023	0.004773	0.413859	1.084853
N2	0.018083	-1.984957	-0.032873	-0.570016	-0.012894
C3	1.115953	-2.810883	0.035461	0.254189	-0.006314
C4	2.448409	-2.412851	-0.071255	-0.037405	0.002114
C5	0.710492	-4.175382	0.2196	-0.215073	-0.002585
H6	1.38611	-5.015097	0.330408	0.180821	0.000091
C7	3.506664	-3.456347	-0.080672	0.010398	-0.000349
C8	3.578396	-4.396171	-1.116295	-0.19181	0.000213
H9	2.846163	-4.351921	-1.923672	0.164204	-0.000002
C10	5.518312	-5.436395	-0.100193	0.049494	0.00012
C11	6.61038	-6.508298	-0.111572	0.464607	-0.000008
C12	4.571792	-5.367927	-1.123282	-0.21914	-0.000059
H13	4.635808	-6.097135	-1.929088	0.153301	0.000004
O14	6.599037	-7.297818	-1.086393	-0.65647	0.000006
C15	-1.069379	-2.823918	0.053686	0.245768	-0.006442
C16	-2.407854	-2.44249	-0.041726	-0.036692	0.002868
C17	-0.644945	-4.18321	0.23379	-0.21669	-0.002675
H18	-1.30822	-5.030814	0.357915	0.180943	0.000094
C19	-3.453985	-3.498127	-0.029964	0.010861	-0.000423
C20	-4.393058	-3.565474	1.006583	-0.191971	0.000209
H21	-4.344821	-2.833083	1.813601	0.164375	0.000014
C22	-5.443277	-5.500577	-0.008519	0.049496	0.000156
C23	-6.520273	-6.587732	0.004185	0.464665	-0.000011
C24	-5.369237	-4.55453	1.014607	-0.218923	-0.000085

H25	-6.097905	-4.615384	1.821156	0.153332	0.000005
O26	-7.309128	-6.571978	0.979475	-0.656428	0.00001
N27	1.988895	0.011917	-0.082086	-0.570569	-0.011639
C28	2.827045	-1.074408	-0.172663	0.255075	-0.006558
C29	4.185126	-0.650359	-0.366713	-0.216906	-0.002679
H30	5.030709	-1.314141	-0.50174	0.180493	0.000116
C31	4.45686	-3.52351	0.945479	-0.191632	0.000164
H32	4.409228	-2.799372	1.759991	0.16413	0.000015
C33	5.44418	-4.501531	0.933345	-0.219225	-0.000066
H34	6.18257	-4.561802	1.73102	0.153356	0.000004
O35	7.410355	-6.492125	0.854649	-0.656484	0.000007
C36	-3.527129	-4.447502	-1.056516	-0.191653	0.00026
H37	-2.804524	-4.402619	-1.872531	0.164257	-0.000006
C38	-4.509686	-5.430257	-1.043471	-0.219302	-0.00008
H39	-4.574376	-6.167968	-1.841412	0.153467	0.000006
O40	-6.509772	-7.387257	-0.962498	-0.656442	0.000008
C41	2.813886	1.109523	-0.155775	0.255114	-0.006628
C42	2.418442	2.442174	-0.042758	-0.03763	0.002211
C43	4.17726	0.704783	-0.353935	-0.216543	-0.00265
H44	5.014791	1.381072	-0.476728	0.180402	0.000112
C45	3.464731	3.497621	-0.029109	0.01037	-0.000357
C46	3.539631	4.447964	-1.054657	-0.191947	0.000217
H47	2.818999	4.403316	-1.872416	0.164225	-0.000002
C48	5.452316	5.501715	-0.000828	0.049485	0.000123
C49	6.528678	6.589442	0.01545	0.464596	-0.000008
C50	4.521267	5.431615	-1.038131	-0.219361	-0.000061
H51	4.587431	6.170155	-1.835192	0.153374	0.000004
O52	6.520005	7.39003	-0.95037	-0.656491	0.000006
N53	-1.978329	-0.012082	-0.086821	-0.564063	-0.011147
C54	-2.803806	-1.110163	-0.159439	0.252587	-0.006663
C55	-4.166153	-0.705449	-0.360959	-0.215956	-0.002704
H56	-5.00363	-1.381673	-0.484428	0.180633	0.000126
C57	-2.817119	1.074451	-0.178586	0.252033	-0.006618
C58	-2.437818	2.41272	-0.074843	-0.036472	0.002801
C59	-4.174175	0.649945	-0.374711	-0.216292	-0.002716
H60	-5.019813	1.313316	-0.511375	0.180762	0.000128
C61	-3.496096	3.456214	-0.084722	0.011025	-0.00042
C62	-4.44735	3.523333	0.940375	-0.192052	0.000207
H63	-4.400468	2.799446	1.755157	0.164337	0.000014
C64	-5.508213	5.435634	-0.106963	0.049499	0.000155
C65	-6.600304	6.507533	-0.11942	0.46468	-0.000011
C66	-5.434959	4.50107	0.926883	-0.219143	-0.000085
H67	-6.174205	4.561421	1.723736	0.153401	0.000005
O68	-7.399976	6.49247	0.847066	-0.656451	0.00001
C69	-3.567067	4.395587	-1.120836	-0.191613	0.000258
H70	-2.833965	4.351236	-1.927412	0.164254	-0.000006
C71	-4.560738	5.367028	-1.129187	-0.219124	-0.00008
H72	-4.624058	6.096016	-1.935251	0.153395	0.000006
O73	-6.588929	7.296019	-1.09504	-0.656394	0.000008
C74	4.401187	3.564827	1.009799	-0.191464	0.000169
H75	4.351348	2.831694	1.816063	0.164127	0.000014
C76	5.376514	4.554675	1.021213	-0.218999	-0.000068
H77	6.103127	4.615311	1.829622	0.153284	0.000004

O78	7.314523	6.574021	0.99321	-0.656485	0.000007
N79	-0.006477	1.984841	-0.036242	-0.569683	-0.012895
C80	-1.105119	2.810635	0.032448	0.245909	-0.006421
C81	-0.699889	4.175309	0.216514	-0.216523	-0.002677
H82	-1.375641	5.014837	0.327773	0.180855	0.000094
C83	1.080027	2.823766	0.04976	0.254568	-0.006356
C84	0.65554	4.183193	0.229007	-0.215354	-0.002589
H85	1.318827	5.030868	0.352653	0.180848	0.000091
O86	-0.109903	0.005118	2.308655	-0.792477	0.026337
H87	-0.734537	0.740639	2.409761	0.484554	-0.000202
H88	-0.657355	-0.787159	2.426705	0.483941	-0.000204

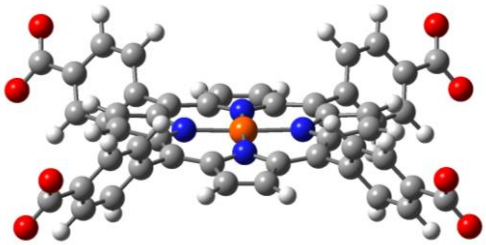
[a]part of the Gaussian output file:

	1	2	3
	A	A	A
Frequencies --	10.9149	19.0224	21.9503
Red. masses --	10.2384	12.8024	12.3931

Zero-point correction= 0.630292 (Hartree/Particle)
Thermal correction to Energy= 0.680897
Thermal correction to Enthalpy= 0.681841
Thermal correction to Gibbs Free Energy= 0.539980
Sum of electronic and zero-point Energies= -2884.896645
Sum of electronic and thermal Energies= -2884.846040
Sum of electronic and thermal Enthalpies= -2884.845096
Sum of electronic and thermal Free Energies= -2884.986957

Item	Value	Threshold	Converged?
Maximum Force	0.000229	0.000450	YES
RMS Force	0.000045	0.000300	YES

Table S4. DFT-optimized geometry of $[Co^{I}TCPP]^{5-}$ (singlet), computed at the M06 level with SDD(Co) and 6-31G*(HCNO) basis sets, using CPCM.[a]



atom	x	y	z	Mulliken Charge
Co1	0	0	0	0.010284
N2	0	1.966452	0.040124	-0.546485
C3	1.090554	2.809364	0.117575	0.234748
C4	2.423527	2.423527	0	-0.049748
C5	0.677387	4.17159	0.313611	-0.226919
H6	1.348066	5.014119	0.437257	0.165269
C7	3.475165	3.475165	0	0.015671
C8	4.416496	3.551594	1.033825	-0.1931
H9	4.36809	2.825631	1.846822	0.158439

C10	5.473723	5.473723	0	0.048179
C11	6.555225	6.555225	0	0.462039
C12	5.396888	4.536998	1.031718	-0.220908
H13	6.127177	4.602079	1.836667	0.149655
O14	7.346243	6.547264	0.97417	-0.658298
C15	-1.090554	2.809364	0.117575	0.234748
C16	-2.423527	2.423527	0	-0.049748
C17	-0.677387	4.17159	0.313611	-0.226919
H18	-1.348066	5.014119	0.437257	0.165269
C19	-3.475165	3.475165	0	0.015671
C20	-4.416496	3.551594	1.033825	-0.1931
H21	-4.36809	2.825631	1.846822	0.158439
C22	-5.473723	5.473723	0	0.048179
C23	-6.555225	6.555225	0	0.462039
C24	-5.396888	4.536998	1.031718	-0.220908
H25	-6.127177	4.602079	1.836667	0.149655
O26	-7.346243	6.547264	0.97417	-0.658298
N27	1.966452	0	-0.040124	-0.546485
C28	2.809364	1.090554	-0.117575	0.234748
C29	4.17159	0.677387	-0.313611	-0.226919
H30	5.014119	1.348066	-0.437257	0.165269
C31	3.551594	4.416496	-1.033825	-0.1931
H32	2.825631	4.36809	-1.846822	0.158439
C33	4.536998	5.396888	-1.031718	-0.220908
H34	4.602079	6.127177	-1.836667	0.149655
O35	6.547264	7.346243	-0.97417	-0.658298
C36	-3.551594	4.416496	-1.033825	-0.1931
H37	-2.825631	4.36809	-1.846822	0.158439
C38	-4.536998	5.396888	-1.031718	-0.220908
H39	-4.602079	6.127177	-1.836667	0.149655
O40	-6.547264	7.346243	-0.97417	-0.658298
C41	2.809364	-1.090554	-0.117575	0.234748
C42	2.423527	-2.423527	0	-0.049748
C43	4.17159	-0.677387	-0.313611	-0.226919
H44	5.014119	-1.348066	-0.437257	0.165269
C45	3.475165	-3.475165	0	0.015671
C46	3.551594	-4.416496	-1.033825	-0.1931
H47	2.825631	-4.36809	-1.846822	0.158439
C48	5.473723	-5.473723	0	0.048179
C49	6.555225	-6.555225	0	0.462039
C50	4.536998	-5.396888	-1.031718	-0.220908
H51	4.602079	-6.127177	-1.836667	0.149655
O52	6.547264	-7.346243	-0.97417	-0.658298
N53	-1.966452	0	-0.040124	-0.546485
C54	-2.809364	1.090554	-0.117575	0.234748
C55	-4.17159	0.677387	-0.313611	-0.226919
H56	-5.014119	1.348066	-0.437257	0.165269
C57	-2.809364	-1.090554	-0.117575	0.234748
C58	-2.423527	-2.423527	0	-0.049748
C59	-4.17159	-0.677387	-0.313611	-0.226919
H60	-5.014119	-1.348066	-0.437257	0.165269
C61	-3.475165	-3.475165	0	0.015671
C62	-3.551594	-4.416496	-1.033825	-0.1931

H63	-2.825631	-4.36809	-1.846822	0.158439
C64	-5.473723	-5.473723	0	0.048179
C65	-6.555225	-6.555225	0	0.462039
C66	-4.536998	-5.396888	-1.031718	-0.220908
H67	-4.602079	-6.127177	-1.836667	0.149655
O68	-6.547264	-7.346243	-0.97417	-0.658298
C69	-4.416496	-3.551594	1.033825	-0.1931
H70	-4.36809	-2.825631	1.846822	0.158439
C71	-5.396888	-4.536998	1.031718	-0.220908
H72	-6.127177	-4.602079	1.836667	0.149655
O73	-7.346243	-6.547264	0.97417	-0.658298
C74	4.416496	-3.551594	1.033825	-0.1931
H75	4.36809	-2.825631	1.846822	0.158439
C76	5.396888	-4.536998	1.031718	-0.220908
H77	6.127177	-4.602079	1.836667	0.149655
O78	7.346243	-6.547264	0.97417	-0.658298
N79	0	-1.966452	0.040124	-0.546485
C80	-1.090554	-2.809364	0.117575	0.234748
C81	-0.677387	-4.17159	0.313611	-0.226919
H82	-1.348066	-5.014119	0.437257	0.165269
C83	1.090554	-2.809364	0.117575	0.234748
C84	0.677387	-4.17159	0.313611	-0.226919
H85	1.348066	-5.014119	0.437257	0.165269

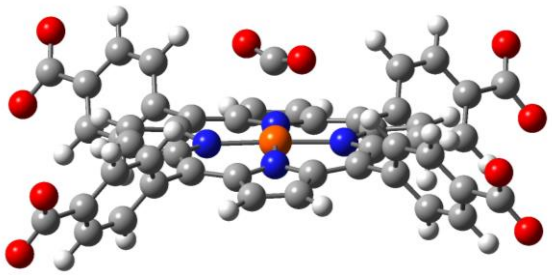
[a]part of the Gaussian output file:

	1	2	3
	A2	B2	E
Frequencies --	11.8027	17.8315	20.9726
Red. masses --	10.2853	12.8802	12.4952

Zero-point correction= 0.604875 (Hartree/Particle)
Thermal correction to Energy= 0.652266
Thermal correction to Enthalpy= 0.653211
Thermal correction to Gibbs Free Energy= 0.519813
Sum of electronic and zero-point Energies= -2808.623176
Sum of electronic and thermal Energies= -2808.575785
Sum of electronic and thermal Enthalpies= -2808.574840
Sum of electronic and thermal Free Energies= -2808.708238

Item	Value	Threshold	Converged?
Maximum Force	0.000008	0.000450	YES
RMS Force	0.000002	0.000300	YES

Table S5. The transition state (TS) geometry computed for for the CO_2 binding process of $[Co^{I}TCPP]^{5-}$ (singlet), at the M06 level with SDD(Co) and 6-31G*(HCNO) basis sets, using CPCM.[a]



atom	x	y	z	Mulliken Charge
Co1	0.000031	-0.000006	-0.062531	0.021605
N2	-1.962796	-0.166084	-0.161493	-0.535756
C3	-2.700638	-1.327418	-0.203597	0.242565
C4	-2.197666	-2.620026	-0.070501	-0.049272
C5	-4.095741	-1.044543	-0.407405	-0.225337
H6	-4.874254	-1.791844	-0.509673	0.166659
C7	-3.159615	-3.753098	-0.021532	0.01335
C8	-3.199128	-4.715553	-1.037702	-0.19396
H9	-2.506908	-4.627523	-1.876402	0.159357
C10	-5.004551	-5.891598	0.075842	0.048034
C11	-6.00664	-7.04598	0.124925	0.462106
C12	-4.109007	-5.765339	-0.98719	-0.221178
H13	-4.147475	-6.511023	-1.779691	0.150311
O14	-5.978068	-7.844987	-0.842317	-0.658126
C15	-2.895403	0.841631	-0.274857	0.229029
C16	-2.629361	2.206793	-0.193775	-0.046272
C17	-4.216133	0.303741	-0.457421	-0.225524
H18	-5.113702	0.893062	-0.605829	0.167018
C19	-3.76492	3.165119	-0.245226	0.015728
C20	-3.888816	4.071486	-1.305597	-0.193421
H21	-3.140996	4.060274	-2.099909	0.159381
C22	-5.911094	5.001339	-0.343643	0.048248
C23	-7.069258	5.999112	-0.392727	0.462178
C24	-4.947063	4.971447	-1.352329	-0.220675
H25	-5.049355	5.673243	-2.178555	0.150207
O26	-7.102471	6.760769	-1.389357	-0.657965
N27	0.177788	-1.965162	-0.098864	-0.539284
C28	-0.833864	-2.893073	0.003867	0.254478
C29	-0.302513	-4.21842	0.169301	-0.226285
H30	-0.896021	-5.115807	0.301223	0.166992
C31	-4.058189	-3.880401	1.044914	-0.192911
H32	-4.037384	-3.137682	1.843884	0.159069
C33	-4.96246	-4.935042	1.091206	-0.220312
H34	-5.658425	-5.040159	1.921996	0.150073
O35	-6.761881	-7.081826	1.12635	-0.65801
C36	-4.735428	3.191941	0.763808	-0.193557
H37	-4.650606	2.493248	1.597435	0.159624
C38	-5.788707	4.097702	0.712951	-0.221112
H39	-6.540372	4.126427	1.500169	0.150426
O40	-7.873416	5.960968	0.56988	-0.658028
C41	1.336054	-2.709042	-0.062838	0.229045
C42	2.629453	-2.206799	-0.193257	-0.046275
C43	1.046815	-4.104852	0.122722	-0.224518

H44	1.790041	-4.88891	0.2109	0.166987
C45	3.765015	-3.16513	-0.244549	0.015725
C46	4.73526	-3.192137	0.764733	-0.193559
H47	4.650237	-2.493576	1.59845	0.159624
C48	5.91117	-5.001385	-0.342706	0.048247
C49	7.069322	-5.999179	-0.391654	0.462178
C50	5.788536	-4.09791	0.713998	-0.221112
H51	6.540007	-4.126769	1.501397	0.150426
O52	7.873308	-5.961122	0.5711	-0.658028
N53	-0.177722	1.965148	-0.098752	-0.539282
C54	-1.335999	2.709023	-0.062954	0.229045
C55	-1.046808	4.104813	0.122828	-0.224519
H56	-1.790058	4.888861	0.210895	0.166988
C57	0.833902	2.893047	0.004336	0.25448
C58	2.197725	2.62001	-0.069693	-0.049271
C59	0.302507	4.218378	0.169762	-0.226284
H60	0.89598	5.115752	0.301928	0.166992
C61	3.159641	3.753099	-0.020446	0.013349
C62	4.057961	3.880411	1.046213	-0.192915
H63	4.037001	3.137672	1.84516	0.15907
C64	5.004456	5.89168	0.077414	0.048033
C65	6.00647	7.046114	0.12678	0.462106
C66	4.962172	4.935095	1.092742	-0.220313
H67	5.65793	5.040232	1.923703	0.150074
O68	6.761447	7.08198	1.128404	-0.65801
C69	3.199352	4.71558	-1.036583	-0.193958
H70	2.507327	4.627541	-1.875443	0.159357
C71	4.109172	5.765405	-0.985835	-0.221177
H72	4.147801	6.511103	-1.778317	0.150312
O73	5.978108	7.845138	-0.840453	-0.658125
C74	3.889166	-4.071329	-1.305034	-0.193418
H75	3.141554	-4.059969	-2.09954	0.159381
C76	4.9474	-4.971311	-1.351635	-0.220675
H77	5.049881	-5.672985	-2.177941	0.150206
O78	7.102702	-6.760762	-1.388335	-0.657965
N79	1.962886	0.166077	-0.160935	-0.535757
C80	2.70074	1.327414	-0.202739	0.242571
C81	4.095901	1.044553	-0.406169	-0.225338
H82	4.874446	1.791861	-0.508149	0.166659
C83	2.895521	-0.841631	-0.274122	0.229035
C84	4.216305	-0.303727	-0.456259	-0.225524
H85	5.113916	-0.893039	-0.604457	0.167017
C86	-0.000264	-0.000041	2.344396	0.74333
O87	-0.766431	-0.867593	2.621547	-0.431832
O88	0.765828	0.8675	2.621785	-0.431833

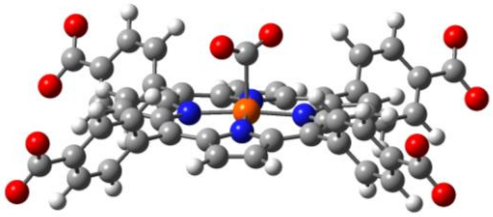
[a]part of the Gaussian output file:

	1	2	3
	A	A	A
Frequencies --	-241.5686	11.4561	16.3221
Red. masses --	15.0000	10.4169	7.0801

Zero-point correction= 0.616581 (Hartree/Particle)
Thermal correction to Energy= 0.667408
Thermal correction to Enthalpy= 0.668352
Thermal correction to Gibbs Free Energy= 0.524922
Sum of electronic and zero-point Energies= -2997.112992
Sum of electronic and thermal Energies= -2997.062166
Sum of electronic and thermal Enthalpies= -2997.061221
Sum of electronic and thermal Free Energies= -2997.204652

Item	Value	Threshold	Converged?
Maximum Force	0.000029	0.000450	YES
RMS Force	0.000004	0.000300	YES

Table S6. DFT-optimized geometry of $[Co^{III}TCPP(CO_2^{2-})]^{5-}$ (singlet), computed at the M06 level with SDD(Co) and 6-31G*(HCNO) basis sets, using CPCM.[a]



atom	x	y	z	Mulliken Charge
Co1	-0.000233	0.003587	-0.000494	-0.006763
N2	-1.97208	-0.017595	-0.166561	-0.528732
C3	-2.80507	-1.109176	-0.237389	0.235108
C4	-2.416023	-2.441518	-0.109203	-0.04218
C5	-4.166778	-0.702548	-0.452767	-0.221592
H6	-5.005365	-1.376945	-0.58113	0.171585
C7	-3.464984	-3.49446	-0.097331	0.01466
C8	-3.538058	-4.447908	-1.120426	-0.192639
H9	-2.810536	-4.409239	-1.932421	0.160891
C10	-5.466749	-5.487782	-0.081979	0.048882
C11	-6.552208	-6.565729	-0.074482	0.463132
C12	-4.525538	-5.425862	-1.110539	-0.220432
H13	-4.589419	-6.165111	-1.907288	0.151174
O14	-6.543083	-7.366637	-1.040286	-0.657549
C15	-2.808053	1.069416	-0.2654	0.251821
C16	-2.429946	2.406273	-0.1573	-0.045589
C17	-4.168105	0.651855	-0.473047	-0.223323
H18	-5.008749	1.319334	-0.622279	0.171608
C19	-3.489391	3.449566	-0.173578	0.010769
C20	-3.564314	4.38507	-1.212719	-0.193078
H21	-2.832175	4.338392	-2.020233	0.160931
C22	-5.50289	5.430725	-0.198201	0.048635
C23	-6.593105	6.503756	-0.211395	0.46301
C24	-4.558051	5.356917	-1.22265	-0.220142
H25	-4.623477	6.082833	-2.031442	0.150994
O26	-6.583861	7.289847	-1.189333	-0.657647

N27	0.002722	-1.973932	-0.104786	-0.533946
C28	-1.078255	-2.819615	-0.013618	0.237156
C29	-0.65087	-4.180596	0.15889	-0.222097
H30	-1.311472	-5.03089	0.281492	0.172158
C31	-4.410996	-3.555145	0.933333	-0.192984
H32	-4.364813	-2.819204	1.737381	0.161603
C33	-5.39277	-4.53902	0.938794	-0.220111
H34	-6.127074	-4.592892	1.74081	0.151198
O35	-7.346602	-6.543799	0.896497	-0.657537
C36	-4.438847	3.522241	0.853025	-0.192327
H37	-4.390121	2.800781	1.669925	0.161286
C38	-5.426767	4.499758	0.838699	-0.220026
H39	-6.16347	4.56307	1.637843	0.151125
O40	-7.390566	6.493959	0.757304	-0.657605
C41	1.10036	-2.798563	-0.049952	0.26645
C42	2.429449	-2.398048	-0.170824	-0.045521
C43	0.703922	-4.16763	0.133144	-0.222604
H44	1.384009	-5.005882	0.230026	0.171704
C45	3.489285	-3.440868	-0.190531	0.010777
C46	4.438047	-3.516435	0.836532	-0.192244
H47	4.388256	-2.797745	1.655803	0.161273
C48	5.503943	-5.420813	-0.220152	0.048615
C49	6.594648	-6.493303	-0.236008	0.463007
C50	5.426569	-4.493271	0.819723	-0.220044
H51	6.162674	-4.558804	1.619245	0.151145
O52	7.391677	-6.486	0.733074	-0.657602
N53	-0.003244	1.981628	-0.093437	-0.533973
C54	-1.100839	2.806015	-0.034131	0.266315
C55	-0.70434	4.174099	0.155973	-0.222572
H56	-1.384388	5.011839	0.257418	0.171699
C57	1.07776	2.826863	0.001511	0.237078
C58	2.415458	2.449394	-0.097343	-0.04221
C59	0.650462	4.186919	0.181334	-0.222083
H60	1.311128	5.036553	0.308093	0.172153
C61	3.464135	3.502588	-0.082061	0.01463
C62	4.411261	3.559756	0.947759	-0.193022
H63	4.366392	2.820662	1.74899	0.161601
C64	5.46487	5.496857	-0.061343	0.048904
C65	6.549948	6.575166	-0.050952	0.463133
C66	5.392492	4.544182	0.955888	-0.22009
H67	6.127691	4.595417	1.757257	0.151181
O68	7.345173	6.550036	0.919266	-0.657539
C69	3.535558	4.460004	-1.101557	-0.192568
H70	2.807075	4.424102	-1.912815	0.160889
C71	4.522538	5.438414	-1.089078	-0.220437
H72	4.58511	6.180734	-1.883075	0.151171
O73	6.539779	7.379421	-1.013952	-0.657546
C74	3.565507	-4.372888	-1.232704	-0.193176
H75	2.833991	-4.323952	-2.040648	0.160931
C76	4.559814	-5.344153	-1.245047	-0.220141
H77	4.626275	-6.067386	-2.056156	0.150996
O78	6.586144	-7.276599	-1.216196	-0.657646
N79	1.971531	0.025842	-0.16734	-0.528767

C80	2.804477	1.117807	-0.232886	0.235195
C81	4.166067	0.712359	-0.451085	-0.2216
H82	5.004556	1.387465	-0.576358	0.171589
C83	2.807463	-1.060612	-0.272196	0.25171
C84	4.167426	-0.641929	-0.47826	-0.223307
H85	5.008023	-1.308597	-0.631332	0.171608
C86	0.00014	-0.002886	2.05403	0.724871
O87	0.849274	-0.765522	2.485353	-0.512697
O88	-0.84895	0.7571	2.490106	-0.512665

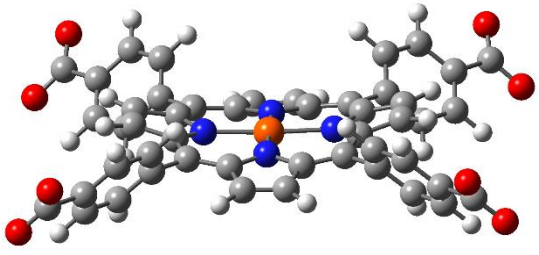
[a]part of the Gaussian output file:

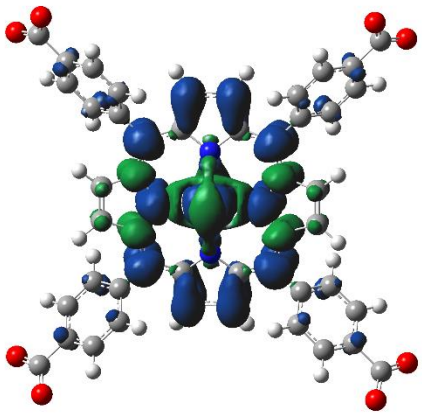
	1	2	3
	A	A	A
Frequencies --	12.0707	18.4667	18.5784
Red. masses --	10.3505	8.2572	9.0666

Zero-point correction= 0.617311 (Hartree/Particle)
Thermal correction to Energy= 0.668347
Thermal correction to Enthalpy= 0.669291
Thermal correction to Gibbs Free Energy= 0.525913
Sum of electronic and zero-point Energies= -2997.115053
Sum of electronic and thermal Energies= -2997.064017
Sum of electronic and thermal Enthalpies= -2997.063073
Sum of electronic and thermal Free Energies= -2997.206451

	Item	Value	Threshold	Converged?
Maximum	Force	0.000004	0.000450	YES
RMS	Force	0.000001	0.000300	YES

Table S7. DFT-optimized geometry of $[Co^{I}(TCPP^{\cdot-})]]^{6-}$ (doublet), computed at the M06 level with SDD(Co) and 6-31G*(HCNO) basis sets, using CPCM.[a]





Mulliken spin distribution

atom	x	y	z	Mulliken Charge	Spin density
Co1	-0.000015	-0.000033	-0.001576	0.110408	0.729134
N2	-0.000347	-2.011155	-0.059009	-0.549184	-0.005163
C3	1.098151	-2.835858	-0.227097	0.221979	-0.000507
C4	2.454222	-2.425362	-0.022073	-0.081401	0.04897

C5	0.69454	-4.138796	-0.562191	-0.286249	0.027215
H6	1.360084	-4.973069	-0.759552	0.119934	-0.002017
C7	3.501667	-3.475539	-0.004588	0.033753	-0.005904
C8	4.578206	-3.446795	-0.903707	-0.205328	0.006598
H9	4.630143	-2.635176	-1.631165	0.143851	-0.000241
C10	5.512629	-5.483369	0.026883	0.044122	0.005614
C11	6.591868	-6.563014	0.043675	0.45536	-0.00028
C12	5.564288	-4.427184	-0.883282	-0.224756	-0.002858
H13	6.396323	-4.397256	-1.58573	0.140668	0.000142
O14	7.529772	-6.427231	-0.780728	-0.663229	0.000446
C15	-1.099148	-2.835506	-0.226964	0.221961	0.000153
C16	-2.455044	-2.424569	-0.021777	-0.081335	0.047431
C17	-0.696026	-4.138562	-0.56213	-0.28622	0.026618
H18	-1.361878	-4.972608	-0.759426	0.119944	-0.00199
C19	-3.502834	-3.474404	-0.004321	0.033733	-0.005731
C20	-4.579304	-3.44529	-0.903504	-0.205309	0.006471
H21	-4.630938	-2.633635	-1.630942	0.143863	-0.000231
C22	-5.514409	-5.481602	0.026962	0.04413	0.005474
C23	-6.593978	-6.56092	0.043645	0.455367	-0.000272
C24	-5.565691	-4.425372	-0.883168	-0.224753	-0.002779
H25	-6.397673	-4.395162	-1.585668	0.140676	0.000138
O26	-7.531388	-6.425222	-0.781333	-0.663225	0.000437
N27	1.962987	-0.000346	0.044122	-0.611495	0.052844
C28	2.808966	-1.111489	0.149279	0.23308	-0.031546
C29	4.156461	-0.674299	0.450906	-0.228241	-0.003643
H30	4.992205	-1.339359	0.640329	0.150314	0.000394
C31	3.453232	-4.544056	0.904836	-0.195382	0.0034
H32	2.622579	-4.593575	1.610264	0.143824	-0.000212
C33	4.43867	-5.52282	0.920332	-0.226909	-0.001379
H34	4.399524	-6.343684	1.635413	0.14031	0.000095
O35	6.442813	-7.487329	0.880973	-0.663043	0.000319
C36	-3.454764	-4.542968	0.905062	-0.195377	0.003273
H37	-2.624153	-4.592779	1.610518	0.143837	-0.000201
C38	-4.440517	-5.521419	0.920475	-0.226908	-0.001302
H39	-4.401669	-6.342324	1.635523	0.140318	0.00009
O40	-6.444882	-7.48569	0.880432	-0.663037	0.00031
C41	2.809332	1.110556	0.14927	0.233055	-0.030634
C42	2.455009	2.424507	-0.022152	-0.081337	0.047429
C43	4.156691	0.672956	0.450872	-0.228221	-0.004542
H44	4.992654	1.33775	0.640263	0.150321	0.000436
C45	3.502789	3.474353	-0.004811	0.033735	-0.005731
C46	3.45478	4.542922	0.904569	-0.195375	0.003273
H47	2.62423	4.59272	1.610099	0.143837	-0.000201
C48	5.514329	5.481589	0.026284	0.044131	0.005474
C49	6.593885	6.560922	0.042875	0.455367	-0.000272
C50	4.440513	5.521392	0.919889	-0.226908	-0.001302
H51	4.401711	6.342303	1.634934	0.140317	0.00009
O52	6.444808	7.485729	0.879625	-0.663037	0.00031
N53	-1.963012	0.000284	0.044352	-0.611494	0.052844
C54	-2.809346	-1.110612	0.149639	0.233052	-0.030635
C55	-4.156672	-0.673001	0.451372	-0.228221	-0.004541
H56	-4.992614	-1.337789	0.640879	0.150321	0.000436
C57	-2.80898	1.111431	0.149565	0.23308	-0.031546

C58	-2.454255	2.425296	-0.021879	-0.081403	0.04897
C59	-4.156442	0.674254	0.451355	-0.228241	-0.003643
H60	-4.992164	1.339323	0.640843	0.150314	0.000394
C61	-3.5017	3.475472	-0.004332	0.033751	-0.005904
C62	-3.453191	4.544017	0.905053	-0.195382	0.0034
H63	-2.62248	4.593561	1.61041	0.143825	-0.000212
C64	-5.512664	5.483297	0.02724	0.044121	0.005613
C65	-6.591907	6.562936	0.04409	0.45536	-0.000281
C66	-4.438633	5.522777	0.920602	-0.226912	-0.001378
H67	-4.399432	6.343662	1.635656	0.140309	0.000095
O68	-6.442123	7.487953	0.880483	-0.663042	0.000319
C69	-4.578313	3.446695	-0.903362	-0.205326	0.006598
H70	-4.630309	2.63505	-1.630787	0.143851	-0.000241
C71	-5.564394	4.427085	-0.882889	-0.224753	-0.002857
H72	-6.396486	4.397133	-1.585269	0.140669	0.000142
O73	-7.529193	6.427824	-0.781126	-0.66323	0.000445
C74	4.57918	3.445254	-0.904089	-0.205311	0.006471
H75	4.630765	2.633597	-1.631529	0.143863	-0.000231
C76	5.56555	4.425356	-0.883846	-0.224753	-0.002779
H77	6.397471	4.395159	-1.586418	0.140676	0.000138
O78	7.531188	6.425276	-0.782232	-0.663225	0.000437
N79	0.000308	2.011088	-0.059085	-0.549184	-0.005163
C80	-1.09821	2.835784	-0.227076	0.221982	-0.000508
C81	-0.694641	4.138709	-0.562271	-0.286249	0.027215
H82	-1.360211	4.972972	-0.759586	0.119934	-0.002017
C83	1.099088	2.835433	-0.227202	0.221958	0.000153
C84	0.695925	4.138476	-0.562376	-0.28622	0.026617
H85	1.361753	4.972514	-0.759784	0.119944	-0.00199

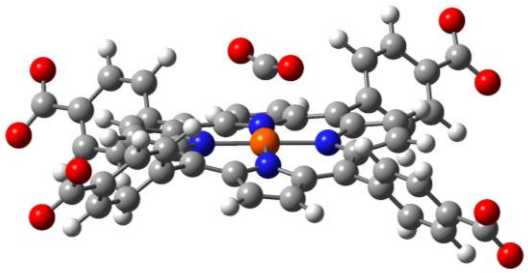
[a]part of the Gaussian output file:

	1	2	3
	A	A	A
Frequencies --	11.7702	21.2278	24.7311
Red. masses --	10.2128	12.7064	12.1504

Zero-point correction= 0.603740 (Hartree/Particle)
Thermal correction to Energy= 0.651177
Thermal correction to Enthalpy= 0.652121
Thermal correction to Gibbs Free Energy= 0.519004
Sum of electronic and zero-point Energies= -2808.705619
Sum of electronic and thermal Energies= -2808.658183
Sum of electronic and thermal Enthalpies= -2808.657239
Sum of electronic and thermal Free Energies= -2808.790355

	Item	Value	Threshold	Converged?
Maximum	Force	0.000077	0.000450	YES
RMS	Force	0.000010	0.000300	YES

Table S8. The TS geometry computed for the CO_2 binding process of $[Co^{I}(TCPP^{\cdot-})]^{6-}$ (doublet), at the M06 level with SDD(Co) and 6-31G*(HCNO) basis sets, using CPCM.[a]



atom	x	y	z	Mulliken Charge	Spin density
Co1	-0.000004	-0.000004	-0.072768	-0.072993	0.180382
N2	0.198507	-1.982478	-0.086302	-0.534054	-0.010608
C3	-0.816149	-2.917176	-0.066033	0.234798	0.032382
C4	-2.189636	-2.637107	-0.288472	-0.080661	0.111234
C5	-0.30606	-4.209126	0.217848	-0.270093	0.074721
H6	-0.900258	-5.112077	0.312566	0.128418	-0.005218
C7	-3.114113	-3.790577	-0.429299	0.030036	-0.012885
C8	-4.179937	-3.994617	0.458712	-0.204053	0.012944
H9	-4.325477	-3.285556	1.275168	0.147002	-0.000626
C10	-4.865988	-6.006212	-0.712267	0.04493	0.010253
C11	-5.805733	-7.20065	-0.862428	0.456341	-0.000558
C12	-5.039308	-5.078905	0.315988	-0.224367	-0.005165
H13	-5.86439	-5.232946	1.010408	0.1427	0.000261
O14	-6.734477	-7.287524	-0.021364	-0.66235	0.000831
C15	1.356797	-2.708213	0.122974	0.216825	0.034215
C16	2.66829	-2.174348	0.042043	-0.074665	0.108514
C17	1.059393	-4.076033	0.348459	-0.270931	0.071656
H18	1.787187	-4.852166	0.559879	0.129881	-0.005103
C19	3.82122	-3.101386	0.165075	0.030033	-0.012366
C20	4.77455	-2.931222	1.179612	-0.201254	0.012237
H21	4.646194	-2.108458	1.884823	0.146819	-0.000512
C22	6.045162	-4.848651	0.409667	0.045212	0.009413
C23	7.243458	-5.786606	0.538307	0.45648	-0.000505
C24	5.864377	-3.786538	1.296559	-0.22405	-0.004726
H25	6.599696	-3.650319	2.088495	0.142754	0.000249
O26	8.044977	-5.541473	1.473527	-0.662018	0.000759
N27	-1.970998	-0.183099	-0.177275	-0.549643	0.101489
C28	-2.693598	-1.351145	-0.355053	0.231224	-0.041043
C29	-4.091496	-1.046803	-0.571002	-0.235064	-0.008178
H30	-4.861668	-1.779166	-0.787479	0.15021	0.000749
C31	-2.942658	-4.728616	-1.45855	-0.195129	0.006623
H32	-2.116166	-4.592932	-2.157855	0.146712	-0.000503
C33	-3.802375	-5.810961	-1.596799	-0.225486	-0.00253
H34	-3.6693	-6.531283	-2.402862	0.142295	0.000213
O35	-5.562168	-7.985668	-1.811947	-0.662053	0.000552
C36	4.006896	-4.172405	-0.722007	-0.196773	0.006255
H37	3.279482	-4.324634	-1.520628	0.14696	-0.000397
C38	5.096912	-5.025783	-0.600762	-0.22626	-0.002585
H39	5.240637	-5.850889	-1.297332	0.142526	0.000222
O40	7.316277	-6.715577	-0.303867	-0.662251	0.000515
C41	-2.91473	0.829146	-0.17043	0.216666	-0.03965

C42	-2.668297	2.174344	0.042067	-0.074665	0.108512
C43	-4.229945	0.290539	-0.439511	-0.230929	-0.009641
H44	-5.135653	0.88063	-0.530371	0.149328	0.000781
C45	-3.821223	3.101388	0.165088	0.030032	-0.012365
C46	-4.006896	4.172392	-0.722013	-0.196772	0.006254
H47	-3.279485	4.324601	-1.520641	0.14696	-0.000397
C48	-6.045147	4.848678	0.409663	0.045212	0.009413
C49	-7.243427	5.786654	0.5383	0.45648	-0.000505
C50	-5.096904	5.025782	-0.600777	-0.22626	-0.002585
H51	-5.240627	5.850875	-1.297363	0.142526	0.000222
O52	-7.31627	6.715579	-0.303925	-0.662251	0.000515
N53	1.970987	0.183091	-0.177313	-0.549642	0.10149
C54	2.914719	-0.829153	-0.170473	0.216665	-0.039651
C55	4.229929	-0.290548	-0.439583	-0.230929	-0.00964
H56	5.135635	-0.88064	-0.530459	0.149328	0.000781
C57	2.693584	1.351137	-0.355105	0.23122	-0.041043
C58	2.189626	2.637099	-0.288498	-0.080659	0.111233
C59	4.091477	1.046793	-0.571083	-0.235064	-0.008179
H60	4.861645	1.779153	-0.787584	0.15021	0.000749
C61	3.114105	3.79057	-0.429313	0.030035	-0.012885
C62	2.942627	4.728638	-1.458534	-0.195129	0.006623
H63	2.116122	4.592974	-2.157825	0.146712	-0.000503
C64	4.865976	6.006211	-0.712259	0.04493	0.010253
C65	5.805714	7.200656	-0.862406	0.45634	-0.000558
C66	3.80234	5.810988	-1.59677	-0.225486	-0.00253
H67	3.669241	6.531339	-2.402803	0.142295	0.000213
O68	5.562057	7.985761	-1.811829	-0.662053	0.000552
C69	4.179952	3.994581	0.458677	-0.204052	0.012944
H70	4.325509	3.285499	1.275111	0.147002	-0.000626
C71	5.039322	5.078872	0.315962	-0.224368	-0.005165
H72	5.864426	5.232886	1.010362	0.1427	0.000261
O73	6.734542	7.28745	-0.021427	-0.66235	0.000831
C74	-4.774549	2.93125	1.179632	-0.201254	0.012237
H75	-4.646196	2.108497	1.884858	0.146819	-0.000512
C76	-5.864366	3.786579	1.296573	-0.22405	-0.004725
H77	-6.599681	3.650383	2.088517	0.142754	0.000249
O78	-8.04491	5.541583	1.473566	-0.662018	0.000758
N79	-0.198513	1.98247	-0.086286	-0.534055	-0.01061
C80	0.816145	2.917167	-0.066027	0.234798	0.032382
C81	0.306056	4.209119	0.217849	-0.270093	0.074722
H82	0.900254	5.112071	0.312561	0.128418	-0.005218
C83	-1.356802	2.708208	0.122984	0.216824	0.034217
C84	-1.059396	4.076029	0.34846	-0.270931	0.071656
H85	-1.78719	4.852164	0.559878	0.129881	-0.005103
C86	0.000028	-0.00005	2.431896	0.746318	-0.030353
O87	0.817958	0.821292	2.68386	-0.422725	-0.009284
O88	-0.817892	-0.821389	2.683898	-0.422729	-0.009284

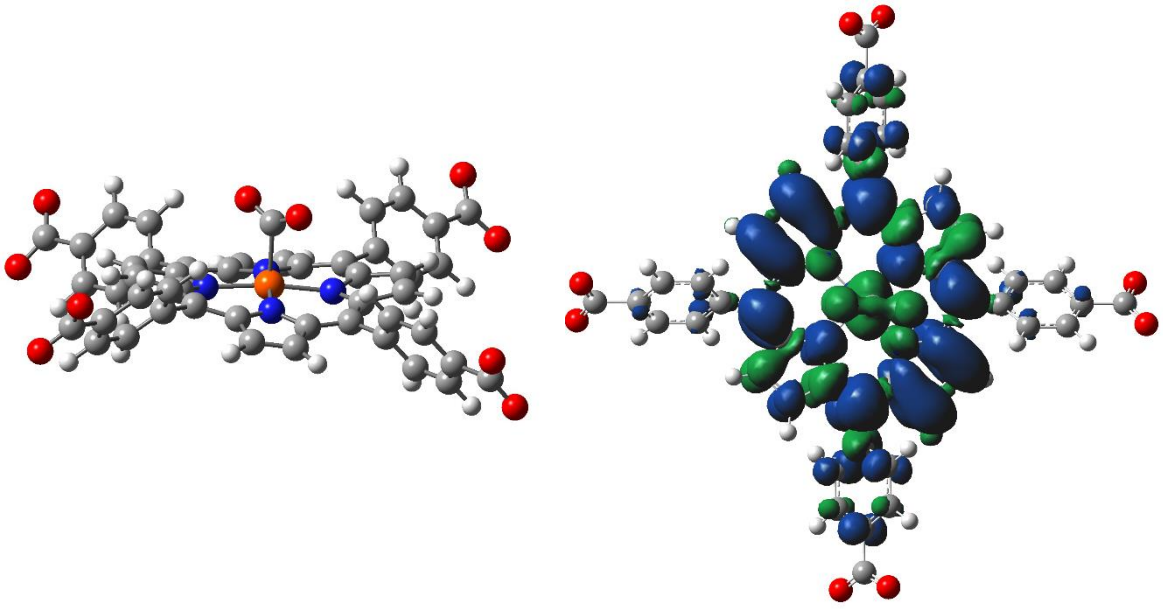
[a]part of the Gaussian output file:

	1	2	3
	A	A	A
Frequencies --	-352.8468	11.7521	22.3621
Red. masses --	13.6508	10.2419	14.1639

Zero-point correction= 0.611699 (Hartree/Particle)
Thermal correction to Energy= 0.663170
Thermal correction to Enthalpy= 0.664114
Thermal correction to Gibbs Free Energy= 0.519248
Sum of electronic and zero-point Energies= -2997.194563
Sum of electronic and thermal Energies= -2997.143093
Sum of electronic and thermal Enthalpies= -2997.142149
Sum of electronic and thermal Free Energies= -2997.287015

Item	Value	Threshold	Converged?
Maximum Force	0.000003	0.000450	YES
RMS Force	0.000000	0.000300	YES

Table S9. DFT-optimized geometry of $[Co^{III}(TCPP^{\cdot-})(CO_2^{2-})]^{6-}$ (doublet), computed at the M06 level with SDD(Co) and 6-31G*(HCNO) basis sets, using CPCM.[a]



Mulliken spin distribution

atom	x	y	z	Mulliken Charge	Spin density
Co1	0.000026	0.000139	0.029848	-0.108126	0.10934
N2	1.971986	-0.195519	-0.178717	-0.519288	-0.016231
C3	2.889233	0.81303	-0.41578	0.227262	0.069506
C4	2.618311	2.196687	-0.31839	-0.062695	0.05313
C5	4.17223	0.27019	-0.681623	-0.261703	0.049557
H6	5.057498	0.844889	-0.931167	0.139554	-0.004064
C7	3.754981	3.146876	-0.42398	0.024241	-0.006608
C8	3.791677	4.120838	-1.431134	-0.200016	0.007848
H9	2.971847	4.163881	-2.149868	0.150652	-0.000177
C10	5.910251	4.977458	-0.61705	0.046207	0.004852
C11	7.072342	5.963993	-0.724164	0.458391	-0.000269
C12	4.849791	5.01846	-1.522898	-0.223376	-0.001877
H13	4.878102	5.772053	-2.308648	0.145079	0.000073

O14	7.010229	6.794351	-1.663751	-0.660539	0.000477
C15	2.704411	-1.359487	-0.214762	0.224071	0.019189
C16	2.191554	-2.657604	0.037445	-0.076656	0.17184
C17	4.059649	-1.093608	-0.54656	-0.263654	0.098258
H18	4.832311	-1.844591	-0.671394	0.136769	-0.00626
C19	3.154356	-3.778153	0.161645	0.033469	-0.020872
C20	3.10962	-4.883458	-0.701446	-0.204203	0.01906
H21	2.348491	-4.909332	-1.482591	0.14861	-0.001182
C22	5.012841	-5.911949	0.39677	0.045069	0.0173
C23	6.009755	-7.061536	0.528929	0.456968	-0.001012
C24	4.018451	-5.928773	-0.582028	-0.224465	-0.009096
H25	3.979998	-6.782096	-1.257882	0.143481	0.000492
O26	5.897743	-7.995069	-0.303436	-0.661749	0.001251
N27	0.169895	1.977363	-0.107168	-0.548065	0.091748
C28	1.3495	2.70063	-0.101207	0.252126	0.00428
C29	1.081802	4.088884	0.180543	-0.225986	-0.032298
H30	1.837357	4.862043	0.267986	0.156376	0.001618
C31	4.82342	3.108112	0.483364	-0.194248	0.002328
H32	4.81275	2.358641	1.275841	0.151509	-0.000092
C33	5.877571	4.008285	0.388044	-0.224496	-0.000016
H34	6.701302	3.981847	1.100042	0.144902	0.000069
O35	7.97998	5.850376	0.135687	-0.66059	0.000216
C36	4.162289	-3.762991	1.138344	-0.19741	0.01333
H37	4.222177	-2.910243	1.816372	0.148913	-0.000958
C38	5.068678	-4.809457	1.25296	-0.224798	-0.006927
H39	5.842658	-4.79682	2.019254	0.143196	0.000445
O40	6.847463	-6.966414	1.459631	-0.661672	0.000969
C41	-0.829022	2.9067	0.098137	0.236047	-0.053897
C42	-2.191536	2.657862	0.037724	-0.076648	0.171852
C43	-0.257377	4.214344	0.32288	-0.234152	0.023847
H44	-0.823239	5.111279	0.548464	0.156006	-0.00089
C45	-3.154343	3.778397	0.161987	0.033476	-0.020877
C46	-4.16244	3.763075	1.138515	-0.197415	0.013336
H47	-4.222447	2.910213	1.81639	0.148911	-0.000958
C48	-5.01287	5.912158	0.397158	0.045069	0.017307
C49	-6.009818	7.061715	0.529321	0.456967	-0.001013
C50	-5.068848	4.809523	1.253155	-0.224799	-0.006932
H51	-5.842956	4.796753	2.019318	0.143195	0.000446
O52	-6.84763	6.966488	1.459918	-0.661673	0.000969
N53	-0.169871	-1.977078	-0.107431	-0.548074	0.091749
C54	0.829038	-2.906453	0.097752	0.236055	-0.053892
C55	0.257388	-4.214142	0.322219	-0.234152	0.023841
H56	0.823244	-5.111116	0.547662	0.156006	-0.000889
C57	-1.349473	-2.700358	-0.101688	0.252091	0.004275
C58	-2.618274	-2.196392	-0.318889	-0.062697	0.053133
C59	-1.081782	-4.088664	0.179822	-0.225987	-0.032294
H60	-1.837338	-4.861844	0.267069	0.156377	0.001617
C61	-3.754948	-3.146546	-0.424721	0.024247	-0.006609
C62	-4.823487	-3.107852	0.48251	-0.194246	0.002329
H63	-4.812857	-2.358499	1.275098	0.151509	-0.000092
C64	-5.91034	-4.97693	-0.618333	0.046207	0.004854
C65	-7.072538	-5.9633	-0.725799	0.458391	-0.000269
C66	-5.877697	-4.007926	0.386925	-0.224495	-0.000017

H67	-6.701515	-3.981532	1.098826	0.144903	0.000069
O68	-7.980268	-5.849754	0.133965	-0.660589	0.000216
C69	-3.791585	-4.120368	-1.432014	-0.200016	0.007849
H70	-2.971673	-4.163364	-2.150658	0.150652	-0.000177
C71	-4.849759	-5.017893	-1.524041	-0.223378	-0.001878
H72	-4.878029	-5.771368	-2.309906	0.145078	0.000073
O73	-7.010423	-6.793456	-1.665566	-0.660541	0.000477
C74	-3.109456	4.883857	-0.700901	-0.204204	0.019066
H75	-2.348197	4.909865	-1.481915	0.14861	-0.001183
C76	-4.018303	5.929153	-0.581458	-0.224466	-0.0091
H77	-3.979726	6.782596	-1.257152	0.14348	0.000492
O78	-5.897732	7.995329	-0.302943	-0.66175	0.001252
N79	-1.971952	0.195799	-0.178745	-0.519302	-0.016231
C80	-2.889182	-0.812712	-0.416065	0.227249	0.069509
C81	-4.172147	-0.269826	-0.68196	-0.261702	0.049556
H82	-5.05739	-0.844481	-0.93169	0.139555	-0.004064
C83	-2.704373	1.359776	-0.214697	0.22407	0.019188
C84	-4.059575	1.09395	-0.546677	-0.263655	0.09826
H85	-4.832222	1.844953	-0.671486	0.136769	-0.00626
C86	0.000159	0.000169	2.039509	0.71613	-0.044254
O87	0.915727	0.668786	2.515301	-0.543105	-0.021512
O88	-0.915363	-0.668445	2.515405	-0.543115	-0.021514

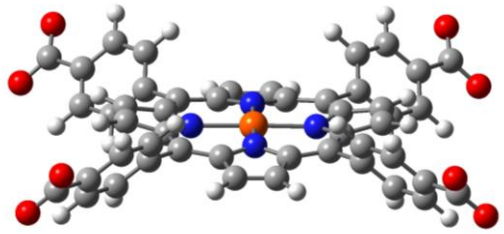
[a]part of the Gaussian output file:

	1	2	3
	A	A	A
Frequencies --	7.8044	15.0610	21.8825
Red. masses --	10.7291	11.1958	11.2583

Zero-point correction= 0.613568 (Hartree/Particle)
Thermal correction to Energy= 0.664894
Thermal correction to Enthalpy= 0.665838
Thermal correction to Gibbs Free Energy= 0.521219
Sum of electronic and zero-point Energies= -2997.201602
Sum of electronic and thermal Energies= -2997.150276
Sum of electronic and thermal Enthalpies= -2997.149331
Sum of electronic and thermal Free Energies= -2997.293951

Item	Value	Threshold	Converged?
Maximum Force	0.000004	0.000450	YES
RMS Force	0.000001	0.000300	YES

Table S10. DFT-optimized geometry of $[Co^{I}(TCPP^{2-})]^{7-}$ (quintet), computed at the M06 level with SDD(Co) and 6-31G*(HCNO) basis sets, using CPCM.[a]



atom	x	y	z	Mulliken Charge	Spin density
Co1	0	0	0	-0.07236	2.188571
N2	2.066565	0	-0.021499	-0.589768	0.099541
C3	2.886464	-1.114105	0.098676	0.216093	-0.000126
C4	2.463562	-2.463562	0	-0.103383	0.196867
C5	4.224156	-0.688043	0.355582	-0.275059	0.064435
H6	5.072808	-1.343647	0.5256	0.112158	-0.00379
C7	3.510597	-3.510597	0	0.041793	-0.023889
C8	3.487134	-4.582137	0.911538	-0.206398	0.024736
H9	2.674265	-4.628757	1.637832	0.132557	-0.001116
C10	5.529821	-5.529821	0	0.039614	0.030829
C11	6.607155	-6.607155	0	0.449237	-0.001333
C12	4.468589	-5.565374	0.908391	-0.229039	-0.0115
H13	4.438146	-6.384867	1.626083	0.132803	0.000603
O14	6.470611	-7.537246	0.834807	-0.667817	0.002179
C15	2.886464	1.114105	0.098676	0.216093	-0.000126
C16	2.463562	2.463562	0	-0.103383	0.196867
C17	4.224156	0.688043	0.355582	-0.275059	0.064435
H18	5.072808	1.343647	0.5256	0.112158	-0.00379
C19	3.510597	3.510597	0	0.041793	-0.023889
C20	3.487134	4.582137	0.911538	-0.206398	0.024736
H21	2.674265	4.628757	1.637832	0.132557	-0.001116
C22	5.529821	5.529821	0	0.039614	0.030829
C23	6.607155	6.607155	0	0.449237	-0.001333
C24	4.468589	5.565374	0.908391	-0.229039	-0.0115
H25	4.438146	6.384867	1.626083	0.132803	0.000603
O26	6.470611	7.537246	0.834807	-0.667817	0.002179
N27	0	-2.066565	0.021499	-0.589768	0.099541
C28	1.114105	-2.886464	-0.098676	0.216093	-0.000126
C29	0.688043	-4.224156	-0.355582	-0.275059	0.064435
H30	1.343647	-5.072808	-0.5256	0.112158	-0.00379
C31	4.582137	-3.487134	-0.911538	-0.206398	0.024736
H32	4.628757	-2.674265	-1.637832	0.132557	-0.001116
C33	5.565374	-4.468589	-0.908391	-0.229039	-0.0115
H34	6.384867	-4.438146	-1.626083	0.132803	0.000603
O35	7.537246	-6.470611	-0.834807	-0.667817	0.002179
C36	4.582137	3.487134	-0.911538	-0.206398	0.024736
H37	4.628757	2.674265	-1.637832	0.132557	-0.001116
C38	5.565374	4.468589	-0.908391	-0.229039	-0.0115
H39	6.384867	4.438146	-1.626083	0.132803	0.000603
O40	7.537246	6.470611	-0.834807	-0.667817	0.002179
C41	-1.114105	-2.886464	-0.098676	0.216093	-0.000126

C42	-2.463562	-2.463562	0	-0.103383	0.196867
C43	-0.688043	-4.224156	-0.355582	-0.275059	0.064435
H44	-1.343647	-5.072808	-0.5256	0.112158	-0.00379
C45	-3.510597	-3.510597	0	0.041793	-0.023889
C46	-4.582137	-3.487134	-0.911538	-0.206398	0.024736
H47	-4.628757	-2.674265	-1.637832	0.132557	-0.001116
C48	-5.529821	-5.529821	0	0.039614	0.030829
C49	-6.607155	-6.607155	0	0.449237	-0.001333
C50	-5.565374	-4.468589	-0.908391	-0.229039	-0.0115
H51	-6.384867	-4.438146	-1.626083	0.132803	0.000603
O52	-7.537246	-6.470611	-0.834807	-0.667817	0.002179
N53	0	2.066565	0.021499	-0.589768	0.099541
C54	1.114105	2.886464	-0.098676	0.216093	-0.000126
C55	0.688043	4.224156	-0.355582	-0.275059	0.064435
H56	1.343647	5.072808	-0.5256	0.112158	-0.00379
C57	-1.114105	2.886464	-0.098676	0.216093	-0.000126
C58	-2.463562	2.463562	0	-0.103383	0.196867
C59	-0.688043	4.224156	-0.355582	-0.275059	0.064435
H60	-1.343647	5.072808	-0.5256	0.112158	-0.00379
C61	-3.510597	3.510597	0	0.041793	-0.023889
C62	-4.582137	3.487134	-0.911538	-0.206398	0.024736
H63	-4.628757	2.674265	-1.637832	0.132557	-0.001116
C64	-5.529821	5.529821	0	0.039614	0.030829
C65	-6.607155	6.607155	0	0.449237	-0.001333
C66	-5.565374	4.468589	-0.908391	-0.229039	-0.0115
H67	-6.384867	4.438146	-1.626083	0.132803	0.000603
O68	-7.537246	6.470611	-0.834807	-0.667817	0.002179
C69	-3.487134	4.582137	0.911538	-0.206398	0.024736
H70	-2.674265	4.628757	1.637832	0.132557	-0.001116
C71	-4.468589	5.565374	0.908391	-0.229039	-0.0115
H72	-4.438146	6.384867	1.626083	0.132803	0.000603
O73	-6.470611	7.537246	0.834807	-0.667817	0.002179
C74	-3.487134	-4.582137	0.911538	-0.206398	0.024736
H75	-2.674265	-4.628757	1.637832	0.132557	-0.001116
C76	-4.468589	-5.565374	0.908391	-0.229039	-0.0115
H77	-4.438146	-6.384867	1.626083	0.132803	0.000603
O78	-6.470611	-7.537246	0.834807	-0.667817	0.002179
N79	-2.066565	0	-0.021499	-0.589768	0.099541
C80	-2.886464	1.114105	0.098676	0.216093	-0.000126
C81	-4.224156	0.688043	0.355582	-0.275059	0.064435
H82	-5.072808	1.343647	0.5256	0.112158	-0.00379
C83	-2.886464	-1.114105	0.098676	0.216093	-0.000126
C84	-4.224156	-0.688043	0.355582	-0.275059	0.064435
H85	-5.072808	-1.343647	0.5256	0.112158	-0.00379

[a]part of the Gaussian output file:

	1	2	3
	B2	A	B
Frequencies --	13.5256	22.1922	25.9060
Red. masses --	10.3089	12.8026	12.1966

Zero-point correction= 0.597218 (Hartree/Particle)
Thermal correction to Energy= 0.645199

Thermal correction to Enthalpy= 0.646143
Thermal correction to Gibbs Free Energy= 0.513120
Sum of electronic and zero-point Energies= -2808.777656
Sum of electronic and thermal Energies= -2808.729675
Sum of electronic and thermal Enthalpies= -2808.728731
Sum of electronic and thermal Free Energies= -2808.861754

	Item	Value	Threshold	Converged?
Maximum	Force	0.000011	0.000450	YES
RMS	Force	0.000003	0.000300	YES

Table S11. DFT-optimized geometry of H_2O (singlet), computed at the M06 level with 6-31G* basis set, using CPCM.[a]

atom	x	y	z	Mulliken Charge
O1	0	0	0.119961	-0.86146
H2	0	0.756805	-0.47984	0.430732
H3	0	-0.75681	-0.47984	0.430732

[a]part of the Gaussian output file:

	1	2	3
	A1	A1	B2
Frequencies --	1694.8685	3812.1514	3930.0110
Red. masses --	1.0808	1.0470	1.0806

Zero-point correction= 0.021499 (Hartree/Particle)
Thermal correction to Energy= 0.024334
Thermal correction to Enthalpy= 0.025278
Thermal correction to Gibbs Free Energy= 0.003839
Sum of electronic and zero-point Energies= -76.362173
Sum of electronic and thermal Energies= -76.359339
Sum of electronic and thermal Enthalpies= -76.358394
Sum of electronic and thermal Free Energies= -76.379833

	Item	Value	Threshold	Converged?
Maximum	Force	0.000064	0.000450	YES
RMS	Force	0.000052	0.000300	YES

Table S12. DFT-optimized geometry of CO_2 (singlet), computed at the M06 level with 6-31G* basis set, using CPCM.[a]

atom	x	y	z	Mulliken Charge
C1	0	0	0	0.851713
O2	0	0	1.163984	-0.42586
O3	0	0	-1.16398	-0.42586

[a]part of the Gaussian output file:

1	2	3
PIU	PIU	SGG

Frequencies --	662.2188	662.2188	1405.5958
Red. masses --	12.8774	12.8774	15.9949

Zero-point correction= 0.011874 (Hartree/Particle)
Thermal correction to Energy= 0.014500
Thermal correction to Enthalpy= 0.01544
Thermal correction to Gibbs Free Energy= -0.008827
Sum of electronic and zero-point Energies= -188.492840
Sum of electronic and thermal Energies= -188.490215
Sum of electronic and thermal Enthalpies= -188.489270
Sum of electronic and thermal Free Energies= -188.513541

	Item	Value	Threshold	Converged?
Maximum	Force	0.000040	0.000450	YES
RMS	Force	0.000028	0.000300	YES

References

1. a) G. Granados-Oliveros, F. M. Ortega, E. Páez-Mozo, C. Ferronato and J.-M. Chovelon, *Open Mater. Sci. J.*, 2010, **4**, 15-22; b) T. Nakazono, A. R. Parent and K. Sakai, *Chem. Commun.*, 2013, **49**, 6325-6327.
2. M. J. Frisch, et al., Gaussian 16 (Revision C.01), Gaussian Inc., Wallingford, CT, 2016.
3. a) V. Barone, M. Cossi and J. Tomasi, *J. Comput. Chem.*, 1998, **19**, 404-417; b) M. Cossi, G. Scalmani, N. Rega and V. Barone, *J. Chem. Phys.*, 2002, **117**, 43-54; c) J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999-3094.
4. R. Dennington and T. Keith and J. Millam, GaussView (Version 5), Semichem Inc., Shawnee Mission, KS, 2009.
5. a) B. H. Solis and S. Hammes-Schiffer, *Inorg. Chem.*, 2011, **50**, 11252-11262; b) K. Koshiba, K. Yamauchi and K. Sakai, *Dalton Trans.*, 2019, **48**, 635-640; c) Y. Sakaguchi, A. Call, K. Yamauchi and K. Sakai, *Dalton Trans*, 2021, **50**, 15983-15995.