

Electronic Supplementary Information

A planar binuclear cobalt(II) phthalocyanine as a highly efficient catalyst for the oxidation of a mercaptan

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Table S1 Catalytic activities of various CoPcs for the oxidation of 2-mercaptoethanol.

Example	Catalyst	Condition	TOF (conversion mol RSH per mol CoPc per min) at RT	References
1	slurry of CoPc, R= H	insoluble CoPc, aqueous solution, pH 9	22	[S1]
2	CoPc, R= -SO ₃ ⁻	partially aggregated CoPc, aqueous solution, pH 9	846	[S1, S2]
3	CoPc, R= -H	monomolecular dissolved CoPc, in THF, 1.2 mM NaOH	180	[S3]
4	CoPc, R= -H	impregnated on charcoal, aqueous solution, pH 9	656	[S4]
5	polyCoPc	impregnated on charcoal, aqueous solution, pH 9	1074	[S4]
6	CoPc, R= -H	coordinatively bound at SiO ₂ , aqueous solution, pH 9	396	[S5]
7	CoPc, R= -COOH	covalently bound at SiO ₂ , aqueous solution, pH 9	1003	[S6]

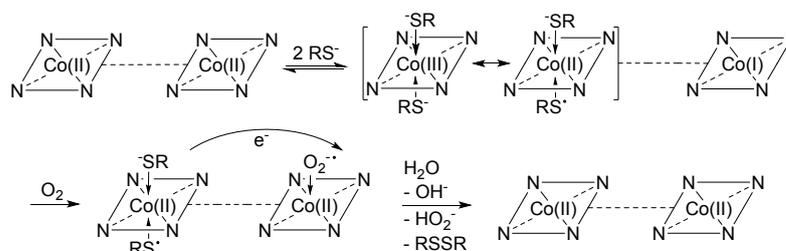
Synthesis and characterization

The preparation procedures for **1Co** and **2Co** are described elsewhere [S7, S8]. UV/Vis spectra were recorded on a Perkin-Elmer Lambda 25 spectrophotometer, ¹H NMR spectra were recorded on a Bruker Avance III 400 spectrometer, electrospray ionization mass-spectra were recorded on a Bruker Esquire LC mass-spectrometer.

1Co, ¹H NMR (DMSO-d₆ + 1 mM KCN), δ , ppm: 7.84 (br s, 8H), 7.40-7.66 (br m, 24H), 2.35 (br s, 48H), MS (ESI, CH₂Cl₂/CH₃CN 1:10), m/z : 1531 [M]⁺, UV/Vis (THF), λ , nm (10⁻⁵ ϵ): 663 (1.35), 600 (0.32), 336 (0.84); **2Co**, ¹H NMR (DMSO-d₆ + 1 mM KCN), δ , ppm: 10.92 (br, 2H), 8.96 (br, 4H), 7.88 (br, 8H), 7.34-7.64 (br, 36H), 2.57 (br, 24 H), 2.39 (br, 24 H), 2.26 (br, 24 H), MS (ESI, CH₂Cl₂/CH₃CN 1:10), m/z : 2505 [M+H]⁺, 1252.5 [M+H]²⁺, UV/Vis (THF), λ , nm (10⁻⁵ ϵ): 818 (3.16), 775 (0.62), 728 (0.82), 695 (0.91), 342 (1.81).

Measurements for the catalytic oxidations

The measurements of the catalytic activities were carried out in THF solution at 298 K similar as described previously on different water-insoluble Co(II)Pcs [S3, S9]. The equipment consists of a 100 mL reaction vessel connected with a 50 mL gas burette (hydrogenation apparatus from Marhan). The measurements were carried out at 25 °C and atmospheric pressure in the range of 746 – 764 mmHg as determined by a conventional barometer. At first 50 mL of THF (Sigma-Aldrich, stabilized with 200 ppm BHT) containing different concentrations of the mononuclear and binuclear cobalt(II) phthalocyanines as catalysts (0.05 – 0.5 μ mol **1Co**, 0.5 μ mol **1Zn**, 0.01 – 0.25 μ mol **2Co**) were prepared. Then 1 mL of 0.25 wt. % aqueous NaOH solutions was added to the THF solutions. The exact concentration of aqueous NaOH was 0.057 M. The solutions were filled into 100 mL reaction vessel. The apparatus was flushed under intensive magnetic stirring (1000 rpm) with oxygen and closed. Through a septum 500 μ L (7.13 mmol) of 2-mercaptethanol (2-ME) was added and quickly the oxygen consumption over time was measured. The volumetric oxygen consumption over time was measured and converted to molar consumption using actual atmospheric pressure. Table 1 contains the molar ratios of 2-ME to the different amounts of catalysts. Exemplarily, employing 0.5 μ mol **1Co** which contains one Co or 0.25 μ mol **2Co** which contains two Co the ratio relating to one Co as reaction centre for [2-ME]:[NaOH]:[Co(II)] is 14 260:114:1. But considering the concentration of 0.25 μ mol **2Co** the ratio is 28 520:114:1 (Table 2). For measurements at lower concentrations, the amounts of **2Co** were 0.05, 0.025 and 0.01 μ mol which corresponds to 0.1, 0.05 and 0.02 μ mol of each Co(II)-centre in this compound. All measurements were repeated at least 3 times until 2 or more plots were practically identical (TOF differences within \pm 5%).



Scheme S1 Mechanism of the mercaptan oxidation catalysed by an aggregated dissolved mononuclear Co(II) phthalocyanine.

The mechanism (Scheme S1) is based on the following observations:

- 1) higher activity of aggregated CoPcs (see Table S1);
- 2) formation of Co(I) in anaerobic process [S1, S10];
- 3) the values of reciprocal Michaelis constants for the Merox process are similar to those of the anaerobic 2:1 binding constants [S11];
- 4) binding of two thiolates per CoPc which occurs only if CoPc is aggregated and is accompanied by a greater Co(II)–Co(I) reduction [S11];
- 5) disproportionation of Co(II)Pcs induced by strong ligands [S12, S13].

The mechanism in Scheme S1 is similar to the mechanism proposed for **2Co** (Scheme 2). The first step is Co(II) disproportionation (intermolecular electron transfer) induced by thiolate anions. Then Co(III) oxidizes the thiolate, and Co(I) is quickly oxidized by oxygen. In the absence of oxygen, build-up of Co(I)Pc occurs (see Fig. S1).

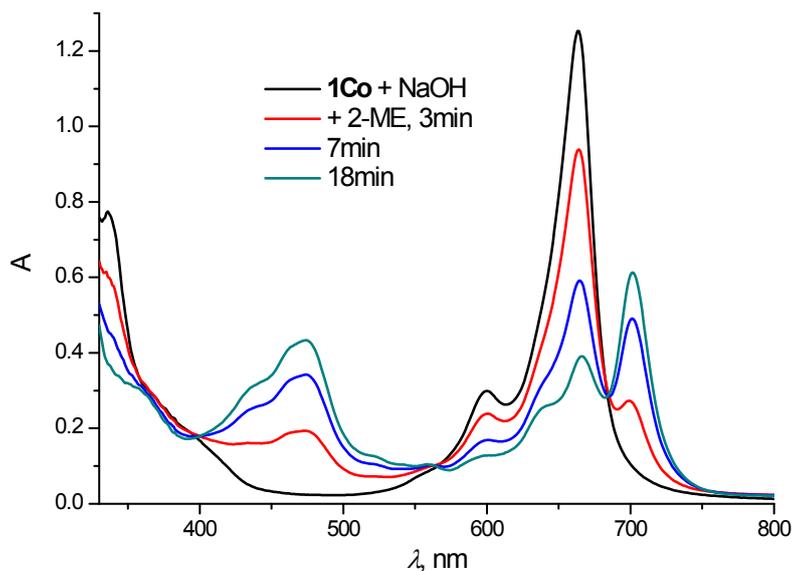


Fig. S1 UV/Vis spectra of **1Co** with NaOH under inert gas before and after addition of 2-mercaptoethanol. The concentration of **1Co** was $1.0 \cdot 10^{-5}$ M, the concentration of aq. NaOH was 4 times higher than that used for the catalytic activity measurements. The concentration of 2-ME was the same as for the catalytic activity measurement.

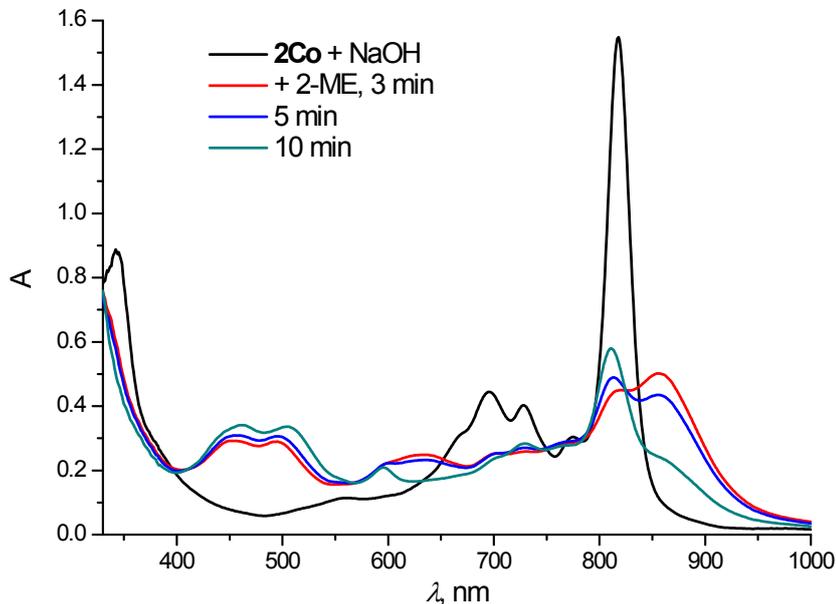


Fig. S2 UV/Vis spectra of **2Co** with NaOH under inert gas before and after addition of 2-mercaptoethanol. The concentration of **2Co** was $5.0 \cdot 10^{-6}$ M, the concentrations of aq. NaOH and 2-ME were the same as those used for the catalytic activity measurements.

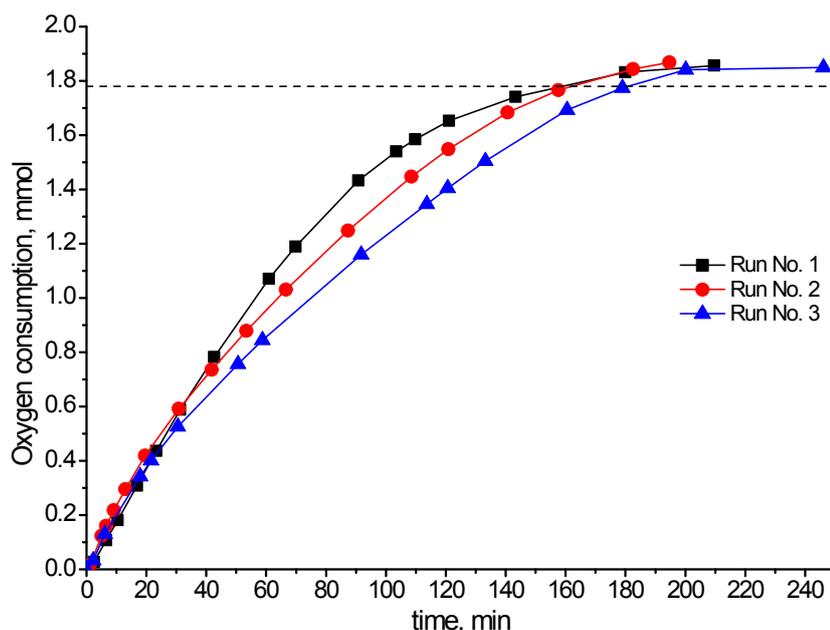


Fig. S3 Repeated measurement of the catalytic activity of **2Co**.

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