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Broadening the reactivity spectrum of a phthalocyanine catalyst while suppressing its nucleophilic, electrophilic and radical degradation pathways†

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A robust molecule that resists degradation *via* nucleophilic, electrophilic and radical attacks is described. Coordinated O_2 is reduced catalytically, producing efficiently thyil radicals in spite of the extreme electronic deficiency of the catalyst.

We report an organic-based, thermally and chemically robust molecule that may suggest ways to design materials refractory to nucleophilic, electrophilic or radical attack while exhibiting useful aerobic catalytic properties. Organic-based molecules are problematic for aerobic oxidations since their C–H bonds are susceptible to radical attack. In the case of metal phthalocyanines, Fig. 1, H_{16}PcM (**1-M**),[1] Cythochrome P450 related molecules, their C–H bonds and π–π stacking limit their utility as oxidation catalysts. The replacement of H by F, to give F_{16}PcM (**2-M**) enhances the already high Pc stability to electrophilic degradation, for example by sulfuric acid, but favors nucleophilic susceptibility,[2] while promoting aggregation. Thus, even the strongest C–X bonds are insufficient to render this vast class of useful molecules completely stable. Replacing half of the F atoms of **2-M** with *iso*-perfluoropropyl (i-C_3F_7) groups gives (i-$C_3F_7)_8F_8$PcM, abbreviated to F_{64}PcM (**3-M**), enhances Pc solubility, produces the first X-ray quality crystals of a halogenated Pc and severely depresses the Pc frontier orbitals.[3] For **3-M**, π–π stacking is disfavored both in solution[4] and in the solid-state.[4,5] Diamagnetic **3-Zn** catalyzes the transfer of solar energy to $^3O_2$ to form $^1O_2$ that oxygenates quantitatively an external substrate, (*S*)-(−)-citronellol.[6]

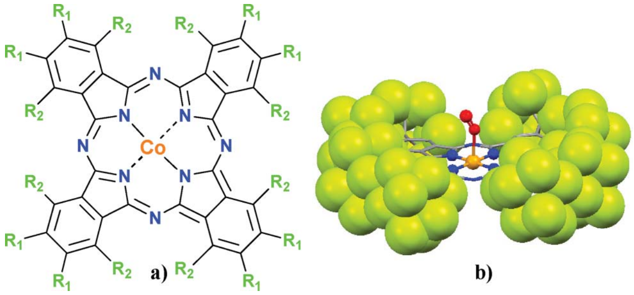

Fig. 1 Cobalt phthalocyanines. Color code: F, green; N, blue; O, red; C, gray; Co, orange. (a) **1-Co**: $R_1 = R_2 =$ H; **2-Co**: $R_1 = R_2 =$ F; **3-Co**: $R_1 = i\text{-}C_3F_7$, $R_2 =$ F. (b) $F_{64}PcCoO_2$ (**3-CoO$_2$**) reaction intermediates (O_2 stands for both $O_2^{\bullet-}$ and O_2^{2-}) drawn based on the X-ray structure of **3-Co**(acetone)$_2$ with the F groups shown as van der Waals spheres and the Co coordination sphere depicted as balls-and-sticks. The atomic coordinates of all atoms except O_2 have been determined experimentally.[3b]

Radical chemistry represents a challenge, which we have approached by examining a model reaction, *viz.* the catalyzed autooxidation of corrosive and foul smelling RSH, a process practiced industrially (MEROX), catalyzed by partly sulfonated **1-Co**.[7] The overall reaction stoichiometry is 4 RSH + O_2 → 2 RSSR + 2 H_2O. Redox reaction pathways, *via* both Co(II)/Co(III) and Co(II)/Co(I) pairs are possible. In both cases S- and O-centered radicals are intermediates. For the relevant Co(II)/Co(I) pathway (see below), the coordination of RS^- to Co(II) is followed by (i) the reduction of Co(II) to Co(I) and formation of $RS^\bullet$, (ii) oxidation of Co(I) by coordinated O_2 to regenerate Co(II) and form $O_2^{\bullet-}$ (superoxide). The cycle is repeated to form O_2^{2-} (peroxide) and $RS^\bullet$.[8–17] Reaction details are shown in eqn (1):

$$\mathrm{RS^- + PcCo(II) \rightarrow [RS^-{-}Co(II)Pc] \rightarrow [RS^\bullet{-}Co(I)Pc]} \tag{1}$$

$$\mathrm{[RS^\bullet{-}Co(I)Pc] \rightarrow RS^\bullet + PcCo(II) + e^-} \tag{2}$$

Soluble (SO_3H, $SO_3Na)_4$PcCo,[8–12] and (COOH)$_{2,4,8}$PcCo,[13] have been used to reveal mechanistic details in solution. Heterogenized systems used **1-Co,**[14] (COOH)$_4$PcCo,[14] ($NO_2)_4$PcCo,[14] ($NH_2)_4$PcCo,[15] (SO_3Na)$_{1,2}$PcCo,[16] ($SO_3^-)_4$PcCo.[17]

Polymer composites have also been used.[18,19] From a steric point of view, site-isolation in a matrix hinders the reaction of $PcCoO_2$ with another PcCo to form an inert μ-peroxo complex.[20] Turnover numbers increase, for example for $C_{10}H_{21}SH$ from 150 to 770.[17b] From an electronic point of view, since the Co(II) to Co(I) reduction is the rate determining step (r.d.s.), stabilization of Co(I) is desired. Overstabilization, however, could hinder catalyst reoxidation to Co(II), eqn 2, and thus the catalytic process. Indeed, a Sabatier (volcano) plot of the rate of electrocatalytic oxidation of RSH *vs.* the PcCo(II)/Co(I) reduction potentials exhibits a negative slope, indicating that the reoxidation to Co(II) controls the r.d.s.[21] The potentials, in turn, correlate with substituents' Hammett constants, Fig. 2. Previously, **2-Co** was the extreme low-rate point due to the strongest F-induced stabilization of Co(I). The paramagnetic **3-Co,**[3b] is electronically related to other PcCo's, all exhibiting a singly occupied d_{z^2} and equivalent d_{xz} and d_{yz} orbitals

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† Electronic supplementary information (ESI) available: Materials and methods, ESR spectra of F_{64}PcCo, ESR parameters of selected phthalocyanines, UV-Vis titration of F_{64}PcCo, stability of PcCo complexes and O_2 consumption in the oxidation of PBT. See DOI: 10.1039/c1dt10458f

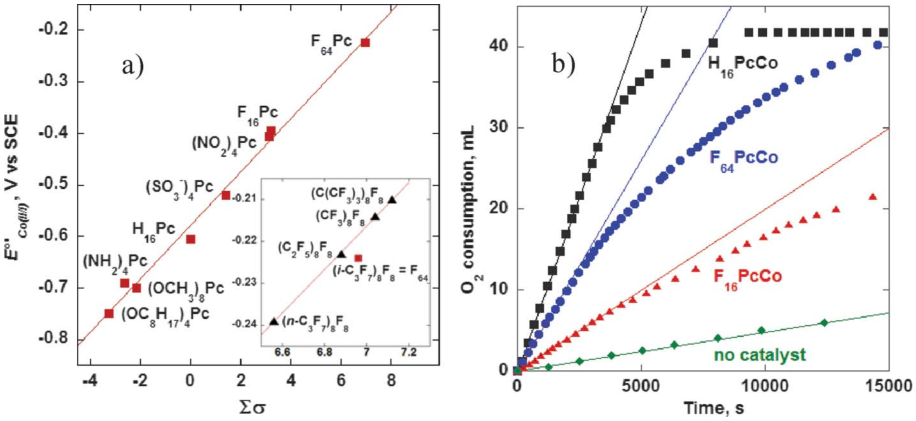

Fig. 2 (a) Plot of Pc(Co(II)/Co(I)) reduction potentials *vs.* the sum of substituents Hammett σ constants. $(SO_3^-)_4Pc$: $R_1 = SO_3^-$, H; $(NH_2)_4Pc$: $R_1 = NH_2$, H; $(NO_2)_4Pc$: $R_1 = NO_2$, H; $(OCH_3)_8Pc$: $R_1 = OCH_3$; $(OC_8H_{17})_4Pc$: $R_1 = OC_8H_{17}$, H.[21] Equation: $y = -0.579 + 0.0518x$; correlation coefficient: 0.9955. Inset: calculated reduction potentials for hypothetical $(R_f)_8F_8Pc$, using R_f substituents with known Hammett constants.[25] R_2 = F, $R_1 = R_f$ (in ascending order of the $E^{o\prime}_{Co(II)/Co(I)}$ potentials): propyl, isopropyl ($F_{64}Pc$, experimental point), ethyl, methyl, *t*-butyl. (b) O_2 consumption in the catalyzed autooxidation of 2-mercaptoethanol in aqueous THF.

(ESR in solution and solid-state, Table S1†). Axial binding by the weakly coordinating acetone is noted in solid-state.[3] Coordination of N-methylimidazole (ESR, Fig. S1, S2†) and ligand-independent site-isolation, for example for M = Zn,[6] and Cu,[4] in solution and in films[5] are characteristics imparted by the $F_{64}Pc$ scaffold. The thermal stability of **3-Co** is high; the complex sublimes in air at ~380 °C without decomposition. Interestingly, **3-Co** cannot be electrochemically oxidized to Co(III) in DMF within the solvent limits, but its reduction occurs at $E^{o\prime} = -0.22$ V (*vs.* SCE), thus justifying the choice of the Co(II)/Co(I) catalytic pathway. The **3-Zn** reduction value is –0.30 V.[22]

Do steric factors favor Co lower oxidation states? A statistical X-ray analysis of all Co porphyrins (Por) and Pcs in the Cambridge Crystallographic Database[23] indicates that Co deviates by less than 0.1 Å from the ligand N_4 coordination plane regardless of its oxidation state (I, II or III) or coordination number. For Pcs the mean Co–N distances differ by approx. 1 e.s.d. when Co(II) and Co(III) are considered, *viz.* 1.927 ± 0.003 Å on average. For the only PcCo(I) complex, Co–N distances range is 1.879–1.914 Å, mean 1.896 Å.[24] The shortening of the Co–N distances upon reduction from Co(II) to Co(I) *viz.* 0.035 Å is identical for both Por's and Pc's. Note that the mean Co(II)–N distance in **3-Co**, 1.926 Å, is typical for both Co(II) and Co(III) and thus Co(I) is not favored. Taken together, the X-ray data suggests neither a structural hindrance for oxidation of Co(II) to Co(III), nor a preference for the reduction of Co(II) to Co(I). Thus, the **3-Co**'s record electronic deficiency, Fig. 2a, beyond **2-Co**, is determined by electronic factors: aromatic F replacement by R_f groups exacerbates electronic deficiency due to loss of aromatic F π-back bonding. Relevant for catalysis, eqn (1a), the reversible chemical reduction **3-Co(II)** ↔ **3-Co(I)** occurs in the presence of HO^- ions, as indicated by isosbestic points and the increase of the 710 nm Q-band of the Co(I) complex at the expense of the 670 nm Q-band of the Co(II) one (see Fig. S3†). HCl completely reverses the reduction. In contrast, the isostructural $F_{64}Pc(2-)Zn(II) \leftrightarrow F_{64}Pc(3-)Zn(II)$ reduction is ligand centered. The actual catalytic activity of **3-Co** was far from certain given (i) the inverse correlation between electron deficiency and thiol oxidation rates,[21] (ii) strong S–Co bonds, a soft–soft type interaction and (iii) a high affinity for axial ligands. Thus, DFT frontier orbital energy calculations for **1-Co**, **2-Co** and $(C_2F_5)_8F_8PcCo$ ($F_{48}PcCo$, **3′-Co**) a surrogate for **3-Co** (too large for the calculations) reveal that the ionization potentials increase by ~1.3 eV and ~1.1 eV from **1-Co** to **2-Co** and **2-Co** to **3′-Co**, respectively. Since C_2F_5 and i-C_3F_7 have similar Hammett constants[25] (Fig. 2a, inset) **3-Co** and **3′-Co** should have similar potentials.[3d] Electron affinity varies similarly, establishing progressively more difficult oxidation/easier reduction and more favorable axial binding as the F content increases.

The results of thiol coupling studies using **1-**, **2-** and **3-Co** and 2-mercaptoethanol (2-ME) are shown in Fig. 2b. The reactions produce only the expected 2-hydroxyethyl disulfide (^1H and ^{13}C NMR). No other S-oxidized products are observed, thus allowing a 4 : 1 direct correlation between the number of moles of RSH and O_2 consumed, respectively. In the presence of a 1000-fold molar excess of thiol, but in the absence of base, **3-Co(II)** is not reduced. In contrast, the formation of the thiolate ion upon addition of NaOH, [thiol]/[NaOH] = 110/1, results in instantaneous appearance of **3-Co(I)** (UV-Vis, Fig. S6†). Immediate O_2 uptake occurs only when both RS^- and the catalyst are present. Light makes no difference indicating absence of solar energy transfer. The catalysis parameters are listed in Table 1.

3-Co is highly stable at 25 °C under the reaction conditions with nucleophiles and radicals present. Moreover, **3-Co** showed

Table 1 Parameters of the catalyzed autooxidation of 2-mercaptoethanol

Catalyst	Stability[a]	Rate[b]	TOF[c]	TON[d]
$H_{16}PcCo$	75%	23.8	3.0	12 600
$F_{16}PcCo$	35%	4.9	0.84	7700
$F_{64}PcCo$	>99%	12.8	1.74	13 000

[a] Stability, defined as the ratio of (Q-bands intensities after 24 h/initial intensities) × 100. See also Fig. S4–S7†. Pc degradation products have not been identified. [b] Initial reaction rates, µmol O_2 min^{-1}, calculated from the linear fit portion of Fig. 2a. [c] Turnover frequency, mol RSH s^{-1} mol Pc^{-1}, calculated under pseudo-first order conditions. [d] Total oxidation number after 5 h, limited by the RSH batch reaction to ~13 000.

no degradation for at least 2 days in refluxing, basic aqueous THF, or in concentrated H_2SO_4. Since the aromatic F substituents in **3-Co** should be more susceptible to nucleophilic attack relative to **2-Co**, the protective steric effect imparted by the i-C_3F_7 groups becomes apparent.

The initial oxidation rates are partly incongruent with the reduction potentials. The calculated ratio of initial reaction rates for **2-Co/1-Co** based on reduction potentials is 0.16, *vs.* the observed value of $0.84/3.0 = 0.28$. In contrast, **3-Co**, presumably less efficient than **2-Co**, has a rate twice as high, ~20 times faster than predicted based on reduction potentials. Since the reoxidation of Co(I) to Co(II) (the r.d.s.) is proceeding as expected based on free energy correlations, the discrepancy is unexplainable on electronic grounds alone. Possible reasons for the enhanced rate of **3-Co** include: (i) R_f steric crowding leading to an accelerated departure of the thyil radical (product), a classical feature of enzymatic reactions and consistent with the limited miscibility of hydrocarbons and fluorinated solvents, (ii) an R_f-induced extra loss of Co^{2+} polarizability, making it unlikely to bind soft S-radicals, (iii) hydrophobic preference for neutral (thyil radical) over charged (thiolate) species in the immediate R_f catalytic environment. Steric crowding could destabilize [RS^-–Co(II)Pc], which may exhibit an estimated ~2.2 Å Co–S bond,[26] the sp^3 hybridized S forcing the thiolate backbone too close to the R_f groups. This destabilization vanishes upon electron transfer and departure of the resulting thyil radical.

Thus, **3-Co** seems to exhibit strong RS–Co binding, a potential "deficiency", but which could be used to broaden its reactivity spectrum to include less basic thiols.

This is a testable hypothesis that could also provide a second example of thiol coupling. Perfluorobenzenethiol (PBT) is a poor nucleophile, at least one million times more acidic than 2-ME, their pK_a values being 2.68 and 9.2, respectively.[27] Thus, the critical steps of thiolate coordination and electron transfer may not occur for PBT. Indeed, to the best of our knowledge, the aerobic coupling of PBT has not been reported. We observe no oxidation with **1-Co**, unlike in the case of 2-ME. In contrast, **3-Co** produces PBT disulfide (^{19}F NMR), 6.4 times faster than **2-Co** with an yield 1.6 times as high, 53% and 32%, respectively (Fig. S8†). The low yields are due to a parallel, unrelated reaction of the PBT anion, $C_6F_5S^-$, which dimerizes *via* nucleophilic attack to yield the thioether–thiolate C_6F_5S–p–$C_6F_5S^-$;[28] glass corrosion is observed, probably due to HF. Consequently, the PBT anion concentration decreases (^{19}F NMR), consistently with the lower total O_2 uptake.

The extreme electronic deficiency of **3-Co** is actually beneficial in securing efficient binding of an acidic thiol and subsequent electron transfer, events that do not occur with the parent **1-Co**, or occur less efficiently with the sterically unhindered and electronically richer (relative to **3-Co**) **2-Co**.

Despite $F_{64}Pc$ scaffold electronic deficiency, activation of O_2 occurs within the R_f pocket of **3-Co** by two, one-electron transfer steps to form $O_2^{\bullet-}$ and O_2^{2-}. The $F_{64}Pc$ ligand is thus able to suppress electron loss from Co(II), but not from Co(I). The $1:1$ $F:R_f$ ratio appears suitable for both catalyst stability and activity. Its lowering might prevent electron loss even from the Co(I) level, thus stopping the catalysis, while its increase could lead to catalyst instability. Notably, the stepwise reduction of O_2 to O_2^{2-} without disproportionation is known for the N_4S(thiolate) chromophore of superoxide reductases, SOR, but with M = Fe. Strong *trans* thiolate binding is believed to weaken the M–O bond thus favoring the release of H_2O_2,[28] an effect relevant here since H_2O_2 released from the Co center contributes to thiol coupling.

In summary, we report the first member of a family of three-dimensional, metal–organic aerobic catalysts whose organic ligand framework is designed to stabilize it against all possible degradation pathways. Coordination and reduction of O_2 within a fluorinated active site pocket leads to both O- and S-centered radicals, the latter coupling to disulfides.

The stabilization of ligand composition, while offering labile sites for catalysis is a challenge[29] that responds to identified future technology needs.[30] The fluoro-perfluoroalkyl substituents might offer an answer within phthalocyanines and, maybe, other frameworks.

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