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

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Materials and Methods

All reagents were obtained from commercial sources and used without purification, unless stated otherwise. 1,4,8,11,15,18,22,25-Octafluoro-2,3,9,10,16,17,23,24-octakis-perfluoro-isopropyl Zinc and Cobalt(II) Phthalocyanines, F₆₄PcZn and F₆₄PcCo, respectively were prepared as per the literature by treating perfluoro-(4,5-di-isopropyl)phthalonitrile (Gorun, S. M.; Bench, B. A.; Carpenter, G.; Beggs, M. W.; Mague, J. T.; Ensley, H. E. J. Fluorine Chem. 1998, 91, 37) with the metal acetate and crystallizing the product from acetone.³b Their UV-Vis, IR, ¹⁹F NMR properties matched those reported. ¹H and ¹⁹F NMR spectra were recorded using a Bruker 300 MHz instrument. Variable temperature ESR spectra were obtained with a Bruker EMX spectrometer. Cyclic voltammetry measurements were performed with a EG&G 175/179 (Princeton Applied Research) instrument. Tetrahydrofuran, 99.5% purity was kept under N₂ over molecular sieves and used fresh for catalytic studies. The PcCo catalysts were dried to constant weight at 150 °C. Oxidations were performed at 25±0.2 °C under O₂ atmosphere (99.998% purity) in a closed system. Oxygen was dosed with a Dosimat 665 dispenser (Metrohm, Switzerland) and its consumption was measured manometrically. Reaction mixtures consisted of 50 mL 11±1 μM catalyst solution in THF, 1 mL NaOH 0.25% (aq) and 500 μL 2-mercaptoethanol.

![Figure S1. ESR spectrum of F₆₄PcCo in acetone](image1.png)

![Figure S2. ESR spectrum of F₆₄PcCo in acetone/N-methylimidazole](image2.png)
Table S1. ESR parameters of selected phthalocyanines

<table>
<thead>
<tr>
<th>Complex</th>
<th>$g_\perp$</th>
<th>$g_\parallel$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$_{64}$PcCo, in acetone</td>
<td>2.276</td>
<td>2.0026</td>
<td>This work</td>
</tr>
<tr>
<td>F$_{64}$PcCo, powder</td>
<td>2.282</td>
<td>2.0063</td>
<td>This work</td>
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</tbody>
</table>

Figure S3. UV-Vis titration of F$_{64}$PcCo with aqueous NaOH in THF. The reduction appears complete at 1:10 Pc/HO$^-$ ratio as the spectrum no longer changes at higher concentrations. Addition of HCl restores the original spectrum.
Figure S4. Ratio of Q-bands intensities after 24 h/initial intensities, taken as a measure of catalysts stability. For F_{16}PcCo the Q-band shifts gradually in both position and width as the reaction proceeds, mainly due to its increasing de-aggregation.

Figure S5. UV-Vis monitored stability of F_{16}PcCo during the catalytic oxidation of 2-mercaptoethanol.
Figure S6. UV-Vis monitored stability of F64PcCo during the catalytic oxidation of 2-mercaptoethanol.

Figure S7. UV-Vis monitored stability of H16PcCo during the catalytic oxidation of 2-mercaptoethanol.
Figure S8. O$_2$ consumption in the oxidation of perfluorobenzethiol. Inset: the parallel reaction of thioether-thiol formation via nucleophilic attack in the absence of the catalyst.