

**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, $F_{64}PcZn$ and $F_{64}PcCo$, 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, ^{19}F NMR properties matched those reported. 1H and ^{19}F 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 N_2 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 O_2 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.

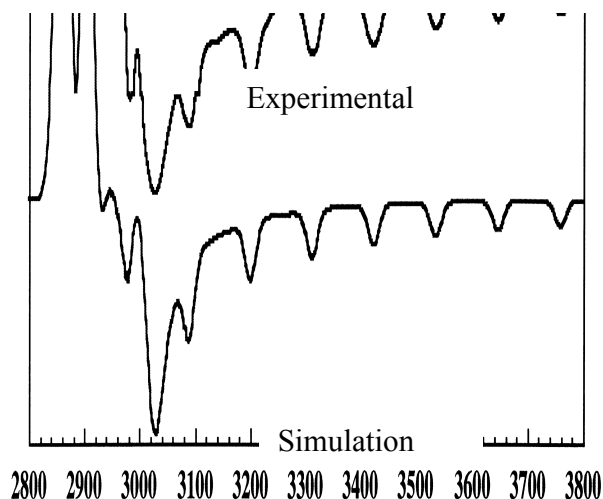


Figure S1. ESR spectrum of $F_{64}PcCo$ in acetone

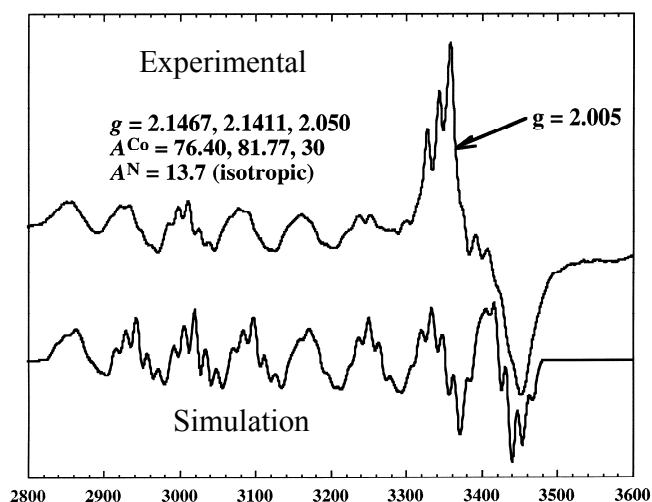


Figure S2. ESR spectrum of $F_{64}PcCo$ in acetone/N-methylimidazole

Table S1. ESR parameters of selected phthalocyanines

Complex	$g_{\perp}$	$g_{\parallel}$	Reference
H ₁₆ PcCo, in acetone	2.60	1.99	Cariati, F.; Galizzioli, D.; Morazzoni, F. <i>J. Chem. Soc., Dalton Trans.</i> 1975 , 556
F ₆₄ PcCo, in acetone	2.276	2.0026	This work
F ₆₄ PcCo, powder	2.282	2.0063	This work
(SO ₃ H) ₄ PcCo, in DMF	2.26	2.006	Zwart, J.; Van Wolput, J. H. M. C. <i>J. Mol. Catal.</i> 1979 , 5, 51.

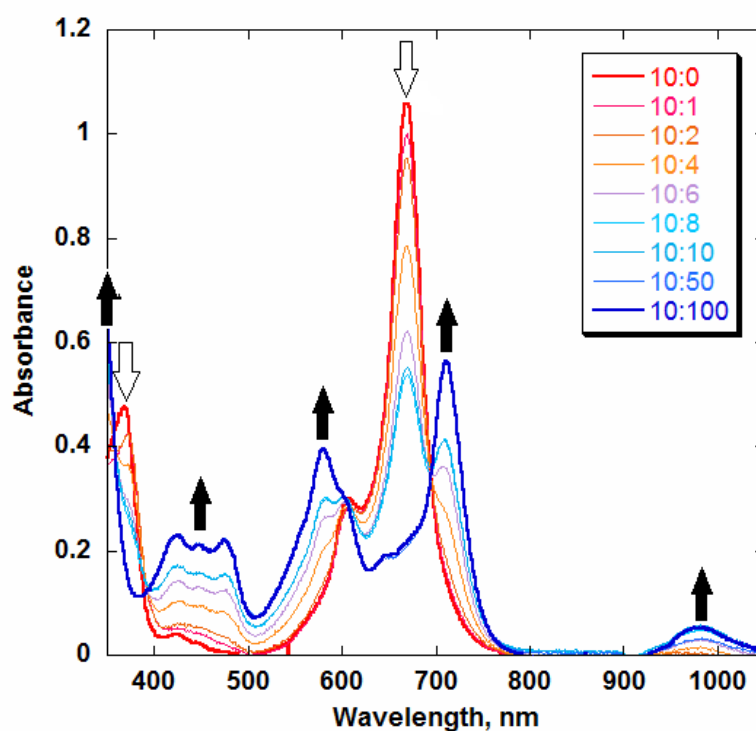


Figure S3. UV-Vis titration of F₆₄PcCo with aqueous NaOH in THF. The reduction appears complete at 1:10 Pc/HO⁻ ratio as the spectrum no longer changes at higher concentrations. Addition of HCl restores the original spectrum.

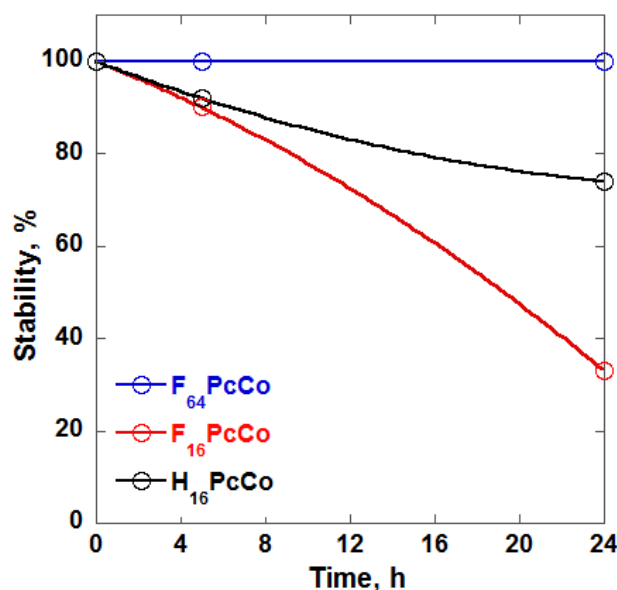


Figure S4. Ratio of Q-bands intensities after 24 h/initial intensities, taken as a measure of catalysts stability For $F_{16}PcCo$ the Q-band shifts gradually in both position and width as the reaction proceeds, mainly due to its increasing de-aggregation.

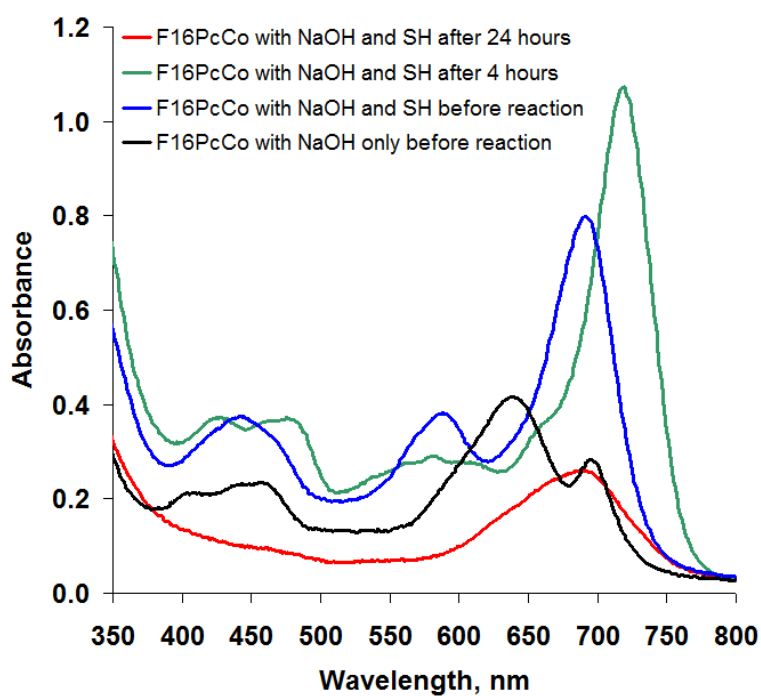


Figure S5. UV-Vis monitored stability of $F_{16}PcCo$ during the catalytic oxidation of 2-mercaptoethanol.

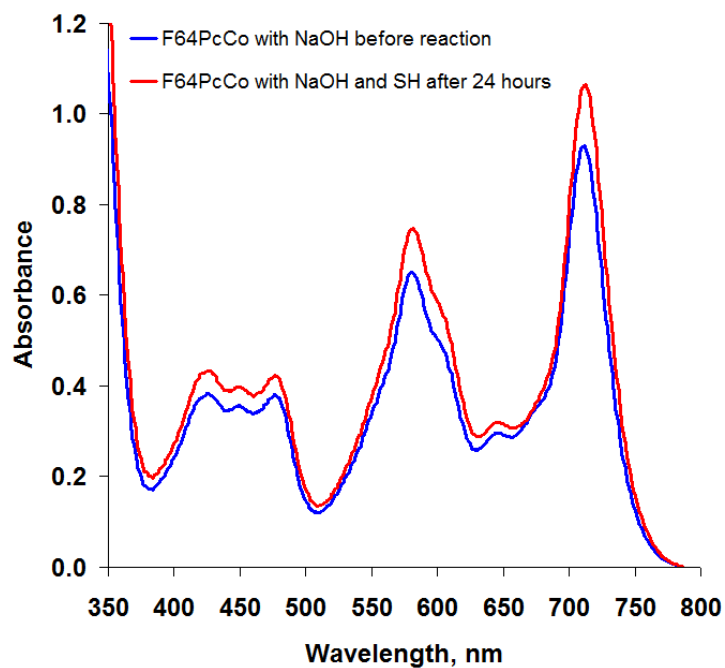


Figure S6. UV-Vis monitored stability of F₆₄PcCo during the catalytic oxidation of 2-mercaptoethanol.

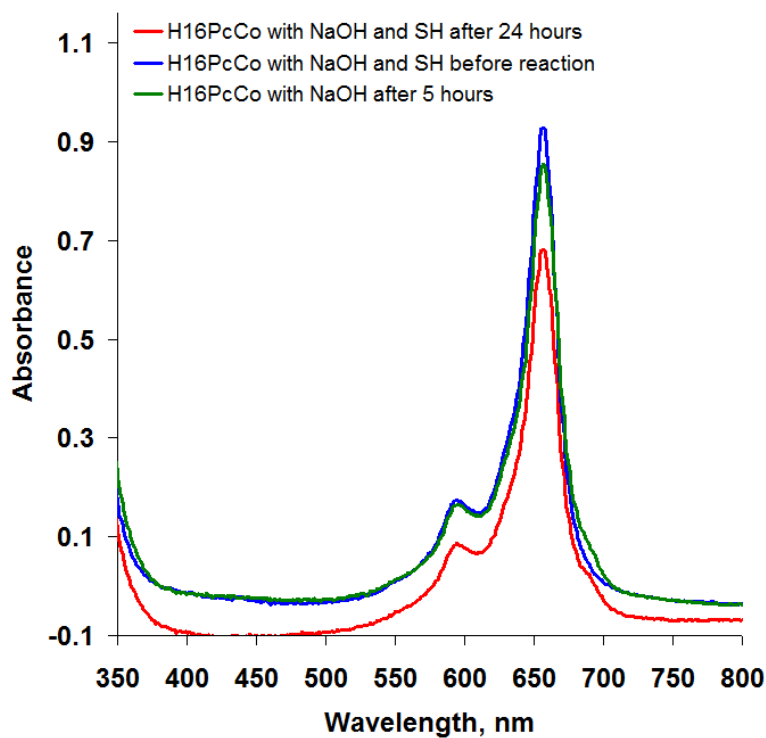


Figure S7. UV-Vis monitored stability of H₁₆PcCo during the catalytic oxidation of 2-mercaptoethanol.

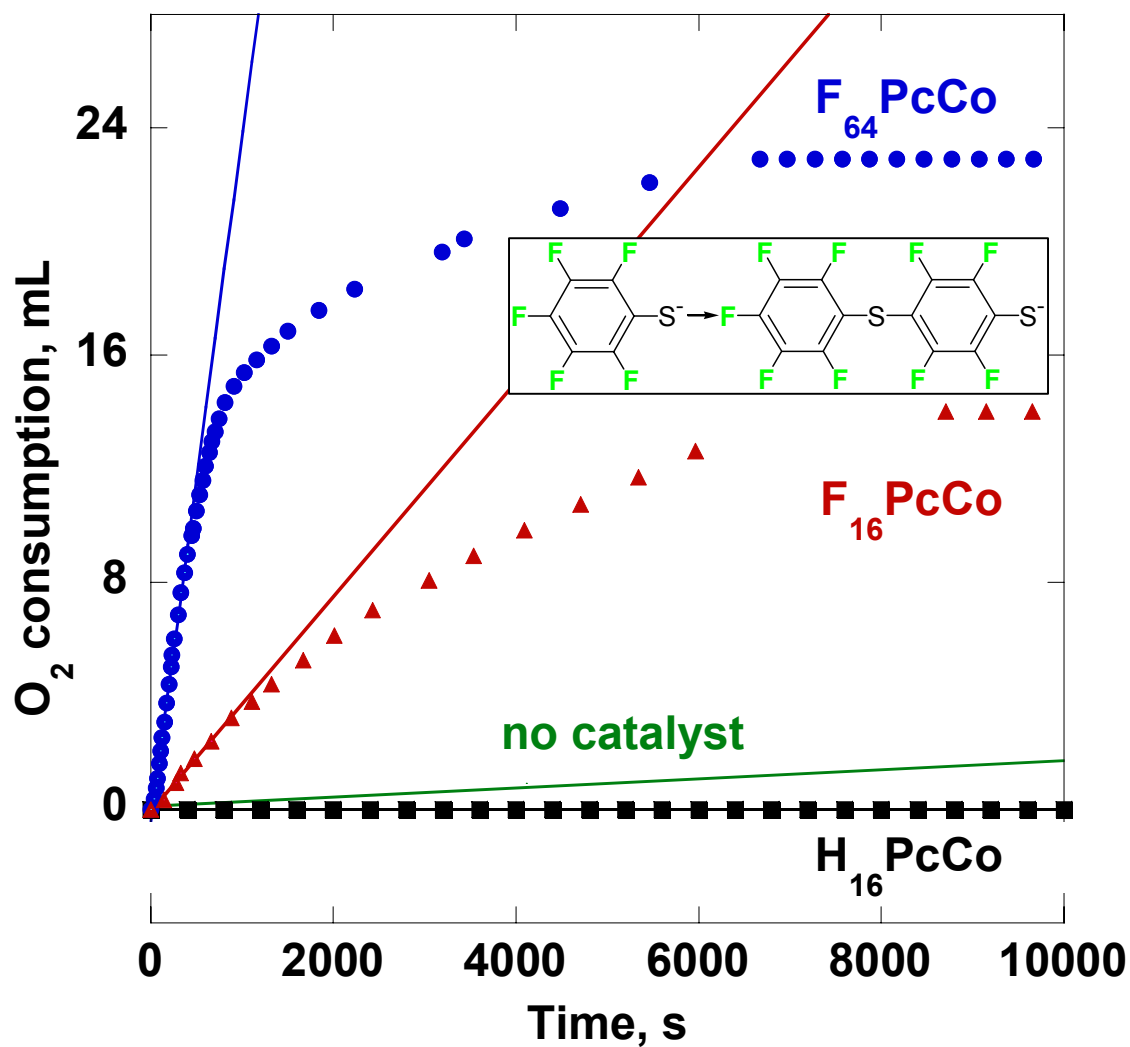


Figure S8. O₂ consumption in the oxidation of perfluorobenzenethiol. Inset: the parallel reaction of thioether-thiol formation via nucleophilic attack in the absence of the catalyst.