SUPPORTING INFORMATION

Reducing Zirconium(IV) Phthalocyanines and the structure of a $Pc^{4-}Zr$ complex

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General procedure for the Reduction of $PcZrCl_2$ (1) with KC_8 and subsequent re-oxidation

A suspension of KC_8 (1.1, 2.2, 3.3 or 4.4 equiv) was prepared in DME (10 mL). $PcZrCl_2$ (**1**) (0.169 g, 0.25 mmol) was added to the KC_8 suspension as a solid, with stirring. The reaction was left to stir for 24 h. The mixture was filtered through celite and the solvent removed *in vacuo*. The products were recrystallized from a 1:1 mixture of DME/hexanes and UV-vis spectra collected (Figure S2). For each sample, a DME solution of the recrystallized material (0.010 g, 0.017 mmol in 3 mL DME) was added to ferrocenium tetrafluoroborate (0.005 g, 0.017 mmol for mono-reduced species; stoichiometric amounts adjusted accordingly for re-oxidation of more highly reduced compounds) and the mixture stirred overnight. A turquoise reaction mixture was formed and the UV-vis spectra collected (Figure S2). The solvents were removed *in vacuo* and the residue analyzed by MALDI-TOF mass spectrometry.

For one equiv. KC_8 with **1**: UV-vis: (THF) λ_{max} 326, 526, 580, 618, 686 nm; MALDI-TOF MS of oxidized material, *m/z*: 1114.5 (37% $[(Pc_2Zr)]^+$), 674.2 (53% $[(PcZrCl)K]^+$), 640.2 (100% $[(PcZr)K]^+$), 621.2 (16% $[PcZrOH_2]^+$).

For two equiv. KC_8 with **1**: UV-vis: (THF) λ_{max} 326, 526, 576 (sh, due to oxidation in UV-vis cell), 616 (sh, due to oxidation in UV-vis cell) nm; MALDI-TOF MS of oxidized material, *m/z*: 1114.5 (16% $[(Pc_2Zr)]^+$), 674.2 (9% $[(PcZrCl)K]^+$), 640.2 (100% $[(PcZr)K]^+$), 621.2 (25% $[PcZrOH_2]^+$).

For three equiv. KC_8 with **1**: UV-vis: (THF) λ_{max} 322, 526 nm; MALDI-TOF MS of oxidized material, *m/z*: 1114.5 (16% $[(Pc_2Zr)]^+$), 640.2 (100% $[(PcZr)K]^+$), 621.2 (13% $[PcZrOH_2]^+$).

Reaction of **1** with 1 equiv NaCp

NaCp (0.05 mL of a 2.0 M solution in THF, 0.100 mmol) was added *via* syringe to a suspension of $PcZrCl_2$ (67.5 mg, 0.100 mmol) in THF (10 mL). After approximately 15 min the reaction mixture turned a plum purple colour. The reaction mixture was stirred at room temperature for 48 hours, before filtering through celite and removing the solvent *in vacuo*. X-ray quality crystals could not be obtained from the product mixture.

UV-vis: (THF) λ_{max} 466(sh), 570, 587, 679 nm.

Reaction of **1** with 2 eq NaCp

NaCp (0.013 mL of a 2.0 M solution in THF, 0.25 mmol) was added *via* syringe to a suspension of $PcZrCl_2$ (0.169 g, 0.25 mmol) in THF (10 mL). After approximately 15 min the reaction mixture turned a plum purple colour. The reaction mixture was stirred at room temperature for 48 h, before filtering through celite and removing the solvent *in vacuo* to give quantitative recovery of material, which however could not be induced to yield single crystalline products. UV-vis: (THF) λ_{max} 467(sh) 535, 589, 667 nm.

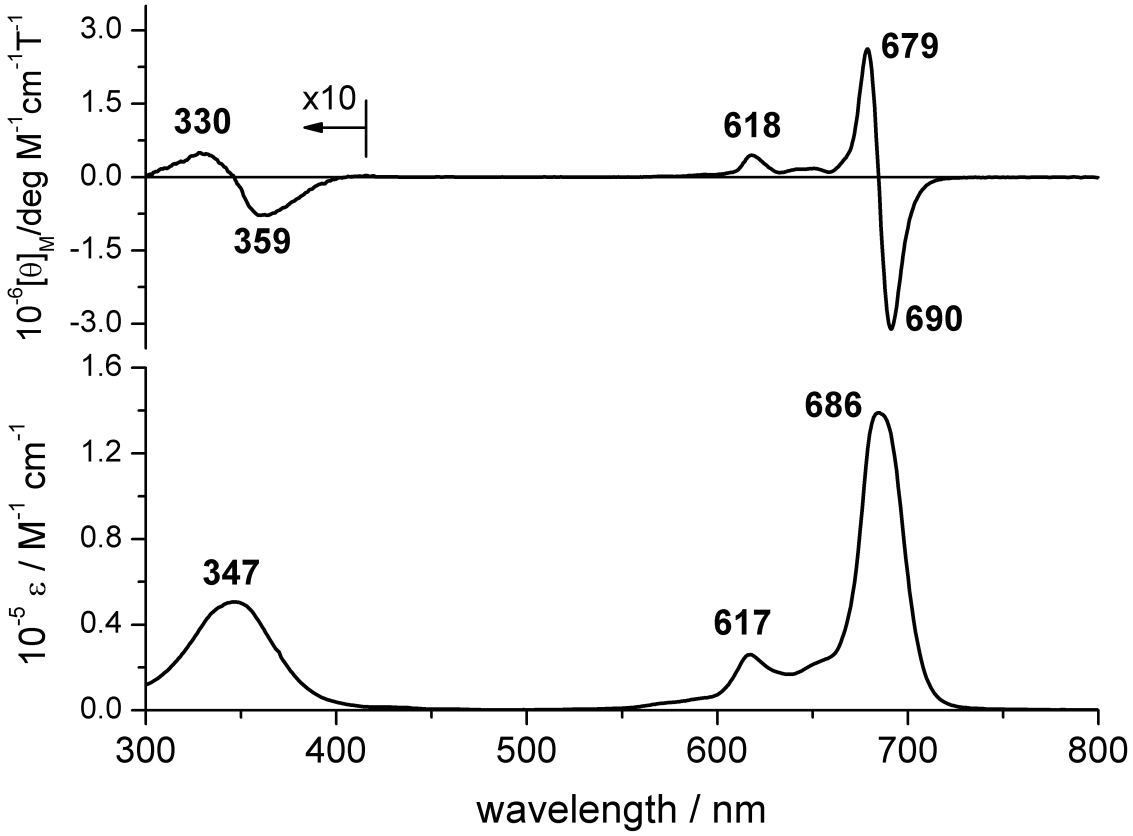

Figure S1. Electronic absorption (bottom) and magnetic circular dichroism (top) spectra of **1** in DMSO (concentration = 5.6 x 10^{-6} M).

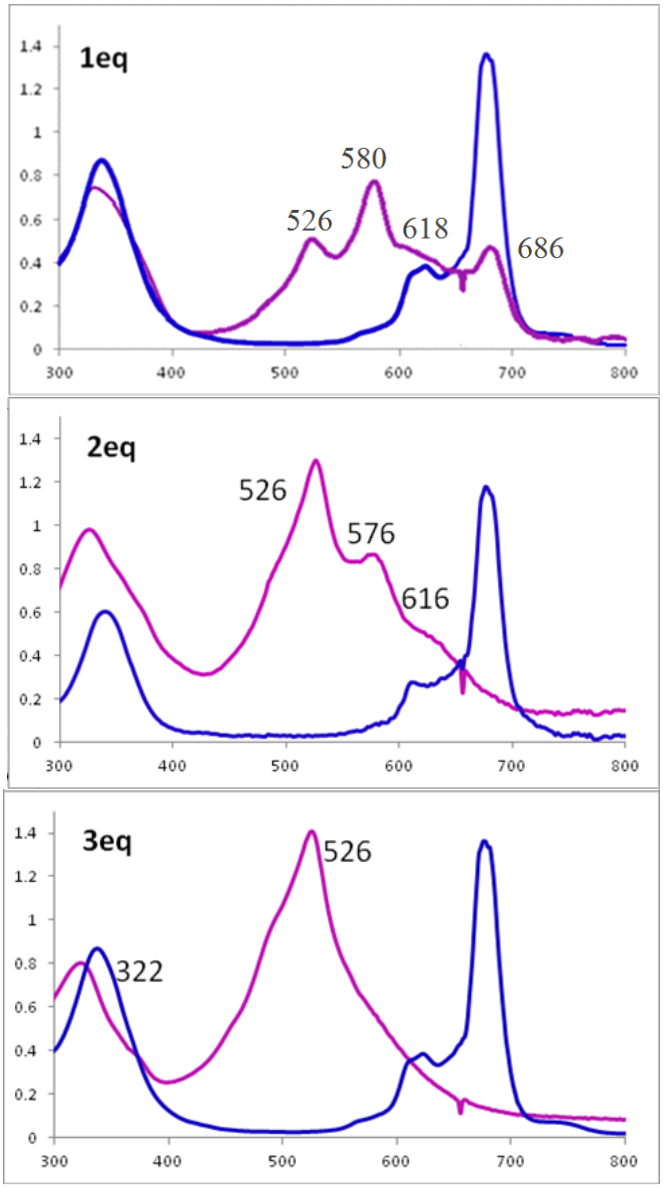

Figure S2. Absorption spectra of the products of reduction of **1** with one, two or three equivalents of KC_8 (pink lines) and the re-oxidized products (blue lines). The spectrum for the 2 equiv. reaction is contaminated with some Pc^{3-} species, likely due to slight oxidation during the UV-vis data collection.

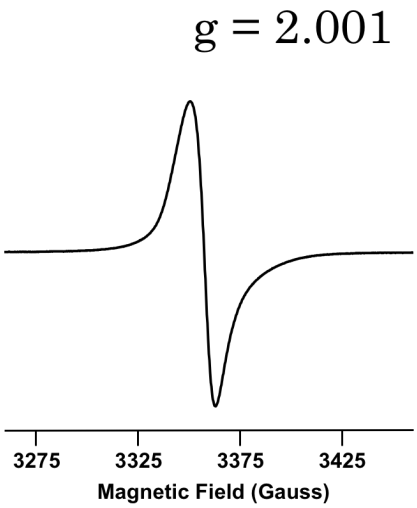

Figure S3. EPR spectrum of **2-K** in THF at 77 K.

Table S1. X-ray crystallographic data for complexes **1** and **3-Li**.

	1	**3-Li**
Compound reference	$PcZrCl_2$	$PcZr(LiCl)_{1.5}(DME)_3$
Chemical formula	$C_{64}H_{32}Cl_4N_{16}Zr_2$	$C_{88}H_{77}Cl_3Li_3N_{16}O_{12}Zr_2$
Formula Mass	1349.29	1860.26
Crystal system		
a/Å	9.7144(3)	13.5859(4)
b/Å	11.9970(3)	24.4074(7)
c/Å	12.1652(3)	32.2986(9)
α/°	80.502(2)	90
β/°	76.732(2)	90.1560(18)
γ/°	81.249(2)	90
Unit cell volume/Å^3	1351.34(6)	10710.1(5)
Temperature/K	299(2)	150(2)
Space group	$P\bar{1}$	$P21/c$
No. of formula units per unit cell, *Z*	1	4
Radiation type	Mo Kα	CuKα
Absorption coefficient, μ/mm^{-1}	0.645	2.753
No. of reflections measured	14246	207765
No. of independent reflections	4697	18907
R_{int}	0.0555	0.0621
Final R_1 values ($I > 2\sigma(I)$)	0.0528	0.0757
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1227	0.2312
Final R_1 values (all data)	0.0953	0.0844
Final $wR(F^2)$ values (all data)	0.1447	0.2417
Goodness of fit on F^2	1.022	1.066