Supporting Information for:

Effect of Protons on the Redox Chemistry of Colloidal Zinc Oxide Nanocrystals

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General Considerations. Tetramethylammonium hydroxide (TMAOH), zinc acetate dihydrate, dodecylamine (DDA), 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phos-phoranylidenamino]-$2\lambda^5,4\lambda^5$-catenadi(phosphazene) (P4 phosphazene base, 1.0 M in hexanes), isopropylmagnesium chloride, and 1,3-bis(trifluoromethyl)-5-bromobenzene were purchased from Aldrich and used as received. Sodium tetrafluoroborate, bis(pentamethylcyclopentadienyl) cobalt (decamethylcobaltocene, $Cp*_2Co$) and 2,4,6-tri-*tert*-butylphenol ($^tBu_3ArOH$) were obtained from Aldrich and were dried in a vacuum oven, recrystallized from pentane or ethanol, respectively, before use. The oxidation purity of $Cp*_2Co$ was confirmed using ^{1}H NMR. The corresponding phenoxyl radical $^tBu_3ArO^\bullet$ was prepared according to the literature procedure.[1] $[H(Et_2O)_2^+][BAr^F_4^-]$ was synthesized using reported literature procedures[2] from $[Na^+][BAr^F_4^-]$[3] (dried in a vacuum oven for at least 24 hours) and HCl. Bis(pentamethylcyclopentadienyl)iron ($Cp*_2Fe$), bis(cyclopentadienyl)cobalticinium hexafluoro-phosphate ($[Cp_2Co][PF_6]$), and bis(pentamethylcyclopentadienyl)chromium ($Cp*_2Cr$) were purchased from Strem and used as received, except for $Cp*_2Cr$ which was purified by sublimation or recrystallization from pentane before use. The oxidized product $[Cp*_2Fe^+][BAr^F_4^-]$ ($BAr^F_4^- = [B(C_6H_3(CF_3)_4)]^-$) was prepared via adapted literature procedures.[4] Toluene-d_8 and THF-d_8 were purchased from Cambridge Isotope and dried by three freeze-pump-thaw cycles and (in the case of THF) storage over sieves for two days. All other solvents were purchased from Fischer Scientific and were dried using a Seca Solvent System installed by Glass Contour. Fluka TraceCERT® High Purity brand Zn standard (1000 μg/L in 2% HCl) was used as the standard for ICP-OES (inductively coupled plasma-optical emission spectrometry).

All samples were prepared under N_2. UV-vis spectra were recorded in an N_2-filled glovebox using an Ocean Optics USB4000 spectrometer configured with an XR1 grating for extended range, and a DT-Mini-2-GS lightsource. The data were processed using Ocean Optics SpectraSuite© and Igor Pro Version 6.22A. Other UV-vis spectra were obtained on a Hewlett Packard 8453 diode array spectrophotometer. Continuous wave EPR spectra were obtained at room temperature on a Bruker E580 X-band spectrometer (perpendicular mode detection). Electrochemical data were obtained using a CH Instruments 600D potentiostat (see below for procedure).

^{1}H NMR spectra were obtained on Bruker AV300, AV301, DRX499, or AV500 spectrometers and data were processed using MestReNova©. Chemical shifts were reported relative to TMS by referencing the residual solvent. Inductively-coupled plasma optical-emission spectroscopy (ICP-OES) was carried out using a Perkin Elmer Optima 8300.

ZnO Nanocrystal Preparation. Nanocrystals (NCs) were prepared following reported procedures with minor modifications.[5,6] For small NCs, at 0 °C under air, a solution of $Me_4NOH \cdot 5H_2O$ (TMAOH, 13.3 g, 7.3 mmol) in 140 mL of ethanol was added to a stirring solution of zinc acetate ($Zn(OAc)_2 \cdot 2H_2O$, 10.0 g, 4.6 mmol) in 300 mL DMSO and 150 mL ethanol, at a rate of ~5 mL/minute. For larger NCs, the solution was heated to 50 °C. After 60

(1) Manner, V. W.; Markle, T. F.; Freudenthal, J. H.; Roth, J. P.; Mayer, J. M. *Chem. Commun.* **2008**, 256.
(2) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.
(3) Yakelis, N. A.; Bergman, R. G. *Organometallics* **2005**, *24*, 3579.
(4) Le Bras, J.; Jiao, H.; Meyer, W. E.; Hampel, F.; Gladysz, J. A. *J. Organomet. Chem.* **2000**, *616*, 54.
(5) Schwartz, D. A.; Norberg, N. S.; Nguyen, Q. P.; Parker, J. M.; Gamelin, D. R. *J. Am. Chem. Soc.* **2003**, *125*, 13205.
(6) Hayoun, R.; Whitaker, K. M.; Gamelin, D. R.; Mayer, J. M. *J. Am. Chem. Soc.* **2011**, *133*, 4228.

minutes of stirring, NCs were precipitated from the clear solution with the addition of ~800 mL ethyl acetate until the solution was cloudy and white. The NCs were isolated from the solution by centrifugation in six separate tubes followed by decantation. The resulting white pellets were washed twice to remove excess starting material by iterative dissolution of each pellet in 2 mL of ethanol and precipitation with 10 mL *n*-heptane. The NCs were then capped by dissolving each of the six pellets in 1 mL molten DDA (120 - 160 °C), consolidated in one test tube, and allowed to rest for 5 – 10 minutes. After cooling, NCs were precipitated from solution with the addition of ~5 mL ethanol. The white solid was collected by centrifugation and decantation and dried under vacuum for one hour. The white solid was brought into an N_2 glovebox, dissolved in ~20 mL of toluene to give a colorless solution and stored in the freezer (-35 °C). The average NC diameter was calculated from the UV-visible absorption spectrum using the experimentally derived relationship between diameter and the energy of the band gap absorbance.[7]

Calculation of Nanocrystal Concentration. An aliquot (0.5 mL) of room temperature ZnO NCs in toluene was dried under vacuum, and the sample was calcined at 500 °C for at least 2 hours to remove residual organic matter. After calcination, samples were digested in EMD Omni*Trace*® HNO_3 and diluted to a volume of 5 mL with deionized water in a volumetric flask. Five samples were then prepared for ICP analysis and the concentration determined by the method of standard additions. Each of the five samples contained a 100 μL aliquot of the 5 mL calcined ZnO sample and 0, 50, 150, 300, and 500 μL of Zn standard (1000 μg/mL in 2% HCl), and were diluted with deionized water in 10 mL volumetric flasks. The intensity of the atomic emission spectrum for Zn was recorded by ICP for each sample and used to extrapolate the concentration of Zn in the original sample, using the x-intercept for the linear fit of a plot of Zn intensity *vs.* [Zn added]. The average volume of each ZnO NC was calculated assuming a spherical NC with $^4/_3\pi r^3$, where r is the radius determined from the optical spectra (see above). Crystalline Wurtzite ZnO has a unit cell volume of 47.66 $Å^3$ with two formula units per unit cell. Thus the average number of Zn atoms per NC is $(2 \times {}^4/_3\pi r^3) \div 47.66$ $Å^3$. The concentration of NCs is given by dividing the total Zn concentration (determined by ICP) by the number of Zn atoms per NC.

Photochemical Reduction of ZnO Nanocrystals. Photochemical reduction was carried out by photoexcitation of anaerobic ZnO NC solutions using an Oriel 200 W Hg/Xe lamp. In a typical titration or photochemical charging experiment, an anaerobic solution of NCs $(10^{-3}\text{-}10^{-5}$ M) was prepared in a quartz Kontes cuvette equipped with a stir bar, and irradiated while stirring for 1-60 minutes, approximately 10 cm from the lamp aperture. In other experiments, NC solutions were stirred in a Unisoku sample holder to prevent large concentration gradients, and irradiation of the solutions was carried out orthogonally to UV-vis detection. The reduced solutions were taken into a N_2 glovebox where titrations were carried out using the Ocean Optics spectrometer described above. In a typical titration, twenty 10 μL aliquots of reagent (e.g. ~0.1 M solution of $^tBu_3ArO^{\bullet}$ in toluene) were added to 2 mL of a 5×10^{-4} M solution of reduced ZnO NCs in a cuvette, while stirring. The optical spectra were recorded 30 seconds after each addition.

Chemical Reduction of ZnO Nanocrystals. In a typical experiment, a $\sim 2 \times 10^{-4}$ M solution of NCs in 50/50 (v/v) toluene/THF in the glovebox was prepared in a cuvette equipped with a stirbar. Ten to twenty 10 μL aliquots of a ~0.1 M solution of Cp^*_2Co was added. Spectra were recorded 30 seconds after each addition, to allow the solution to stir and become homogeneous. Each aliquot was one to five equivalents of metallocene per nanocrystal. The concentration of

(7) Meulenkamp, E. A. *J. Phys. Chem. B* **1998**, *102*, 5566.

electrons in solution was calculated using the previously reported extinction coefficient per electron at 850 nm ($\varepsilon = 1000 \pm 200$ M^{-1}cm^{-1}),[8] and is plotted *vs.* the equivalents of Cp*$_2$Co added per NC. Addition of Cp$_2$Co or Cp*$_2$Cr (without acid) did not result in reduced NCs.[9] For the addition of acid, 10 μL aliquots of a stock solution of [H(Et$_2$O)$_2^+$][BAr$^F_4{}^-$] in THF was added to the mixed solution of NCs and Cp*$_2$Co. This solution is stable for a few hours, but decomposes at longer times. If the acid is added to a solution of Cp*$_2$Co without NCs present, the Cp*$_2$Co decomposes, likely due to the absence of a base (DDA or NCs).

Other Acids Attempted for ZnO Nanocrystal Protonation. In addition to [H(Et$_2$O)$_2^+$][BAr$^F_4{}^-$], other acids were prepared in an attempt to protonate the ZnO NCs, including pyridinium triflate [py-H][OTf], protonated DMF triflate [DMF-H][OTf], protonated DBU triflate [DBU-H][OTf] and [P1-^{t}Bu phosphazene][BF$_4$] prepared according to reported procedures.[10] However, these acids were insoluble in toluene and toluene/THF mixtures, and thus were unsuitable for protonating the NCs.

Attempts to Deprotonate ZnO NCs Using Phosphazene Bases and ^{31}P NMR. In an attempt to identify a base strong enough to remove the protons native to as-prepared ZnO NCs and/or generated using photoreduction and oxidation with [Cp*$_2$Fe$^+$][BAr$^F_4{}^-$] (ZnO-H$^+$), phosphazene bases and ^{31}P NMR were used. The bases were P1-^{t}Bu [*tert*-butylimino-tri(pyrrolidino)phosphorane] pK_{BH} = 28.35 in MeCN,[11] P2-^{t}Bu [1-*tert*-butyl-2,2,4,4,4-pentakis (dimethylamino)-2λ^5,4λ^5-catenadi(phosphazene)] pK_{BH} = 33.5 in MeCN,[12] and the P4 base pK_{BH} = 42.7 in MeCN[12] described earlier. Approximately 40 equiv of P1-^{t}Bu was added to a solution of ZnO and ZnO-H$^+$, and no evidence of the protonated P1-^{t}Bu was observed. With the stronger P2-^{t}Bu base, the ^{31}P NMR signal broadens, complicating our ability to determine if the protonated base is formed. However, addition of the P4 base to a solution of the NCs in toluene-*d$_8$* gives a ^{31}P NMR spectrum where both protonated and unprotonated forms of the base are observable. The protonated chemical shifts at −22.7 (q, 1P) and 12.6 ppm (d, 3P) are similar to the literature values (see Figure S1).[12]

(8) Schrauben, J. N.; Hayoun, R.; Valdez, C. N.; Braten, M.; Fridley, L.; Mayer, J. M. *Science* **2012**, *336*, 1298.

(9) (a) *E*°(Cp$_2$Co) = -1.36 V (ref 13) and *E*°(Cp*$_2$Cr) = -1.46 V (ref 14) both vs. Fc/Fc$^+$ in MeCN. (b) The previous report of chemical reduction of ZnO NCs in heptamethylnonane by sodium biphenyl (Shim, M.; Guyot-Sionnest, P. *Nature* **2000**, *407*, 981) was not reproducible in our hands due to apparent reaction of the reductant with the DDA capping groups.

(10) Saouma, C. T.; Kaminsky, W.; Mayer, J. M. *J. Am. Chem. Soc.* **2012**, *134*, 7293.

(11) R. Schwesinger, J. Willaredt, H. Schlemper, M. Keller, D. Schmitt, H. Fritz, *Chem. Ber.* 1994, **127**, 2435–2454.

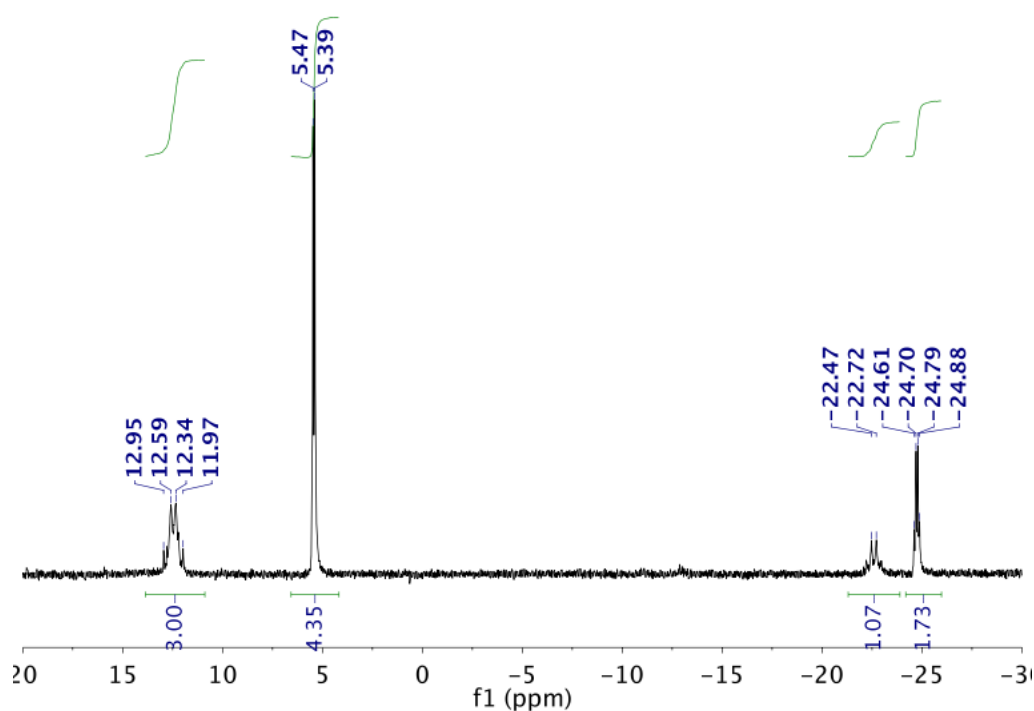(12) Boileau, S.; Illy, N. *Prog. Polym. Sci.* **2011**, *36*, 1132.

Figure S1: ^{31}P NMR spectrum of ZnO NCs (1.1×10^{-4} M, $d = 6.4$ nm) and P4 base (50 mM) in toluene-d_8. The signals at -22.7 (q, 1P) and 12.6 ppm (d, 3P) correspond to protonated P4 (P4-H$^+$), and -24.7 (q, 1P) and 5.4 (d, 3P) ppm correspond to the unprotonated P4 base.

Electrochemistry of Cp*$*_2$*Co and Cp*$*_2$*Cr in THF/toluene. The reduction potentials of Cp*$_2$Co (-1.94 V vs. Fc/Fc$^+$ in CH$_2$Cl$_2$)[13] and Cp*$_2$Cr (-1.46 V vs. Fc/Fc$^+$ in MeCN)[14] are reported in solvents typical for electrochemistry. To determine the reduction potentials under our conditions, cyclic voltammetry (CV) was performed in a N$_2$ glovebox with THF and toluene mixtures. These experiments used a glassy carbon working electrode, Ag wire pseudo-reference, a platinum wire counter electrode, and a scan rate of 0.1 V/s. CVs were internally referenced to Fc/Fc$^+$ (0 V) by addition of Fc to the solution of analyte. Figure S2 shows the CV of a THF solution of Cp*$_2$Co and Cp*$_2$Cr (~5 mM each) with 0.4 M ^{n}Bu$_4$NPF$_6$ supporting electrolyte. The Figure also shows CVs of the same solution after the addition of solid DDA (~50 mM), and then after the addition of 1 mL toluene (to 25% by volume), to make the solution more similar to the conditions used for all other experiments. When more than ~25% toluene was added, the electrolyte precipitated. The measured reduction potentials, E$_{1/2}$[Cp*$_2$Co]= -1.95 V vs. Fc/Fc$^+$ and E$_{1/2}$[Cp*$_2$Cr]= -1.56 V vs. Fc/Fc$^+$), and the ΔE$_{1/2}$ = ~400 mV are the same in all three cases (see Figure S2).
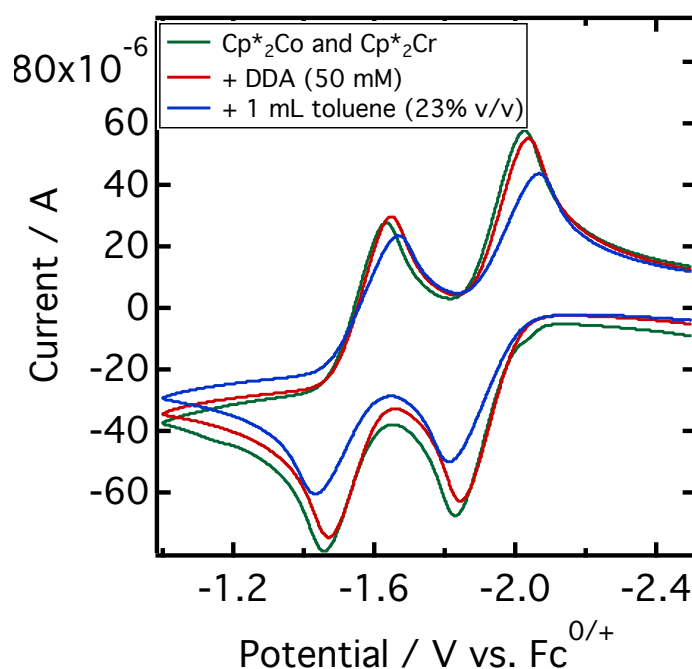

Figure S2: Overlaid CVs of Cp*$_2$Co and Cp*$_2$Cr in THF (green), with added DDA (red), and with added toluene (blue).

(13) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.
(14) Astruc, D. *Electron Transfer and Radical Processes in Transition-Metal Chemistry*; John Wiley & Sons, Inc.: New York, 1995.

Absorption Spectra of Recharging ZnO-H$^+$ with Cp*$_2$Cr. In one experiment, a solution of NCs in 50/50 toluene/THF (6.4×10^{-4} M, $d = 3.5$ nm) was photoreduced up to $n_{e^-} = 3.3$, and then split into two separate cuvettes. In Figure S3, only selected spectra from the titration are shown for clarity. To each cuvette was added an oxidant in 10 μL aliquots, either the ET acceptor [Cp*$_2$Fe$^+$][BAr$^F_4^-$] (up to 4.0 equiv), or with an H-atom oxidant, ^{t}Bu$_3$ArO$^\bullet$ (up to 4.8 equiv). After all of the NCs were oxidized, Cp*$_2$Cr was added in 10 μL aliquots (each aliquot was 1.6 equiv), and then excess (> 20 equiv). The NCs that were oxidized by the ET-only acceptor are recharged by the Cp*$_2$Cr, as determined from the absorbance at greater than 600 nm, to $n_{e^-} = 0.8$. The NCs oxidized with the H-atom acceptor could not be recharged by Cp*$_2$Cr, as would be expected given that the extra proton that comes from oxidation of ethanol is removed as ^{t}Bu$_3$ArO**H**. This latter case is analogous to the reaction of Cp*$_2$Cr with as-prepared ZnO.
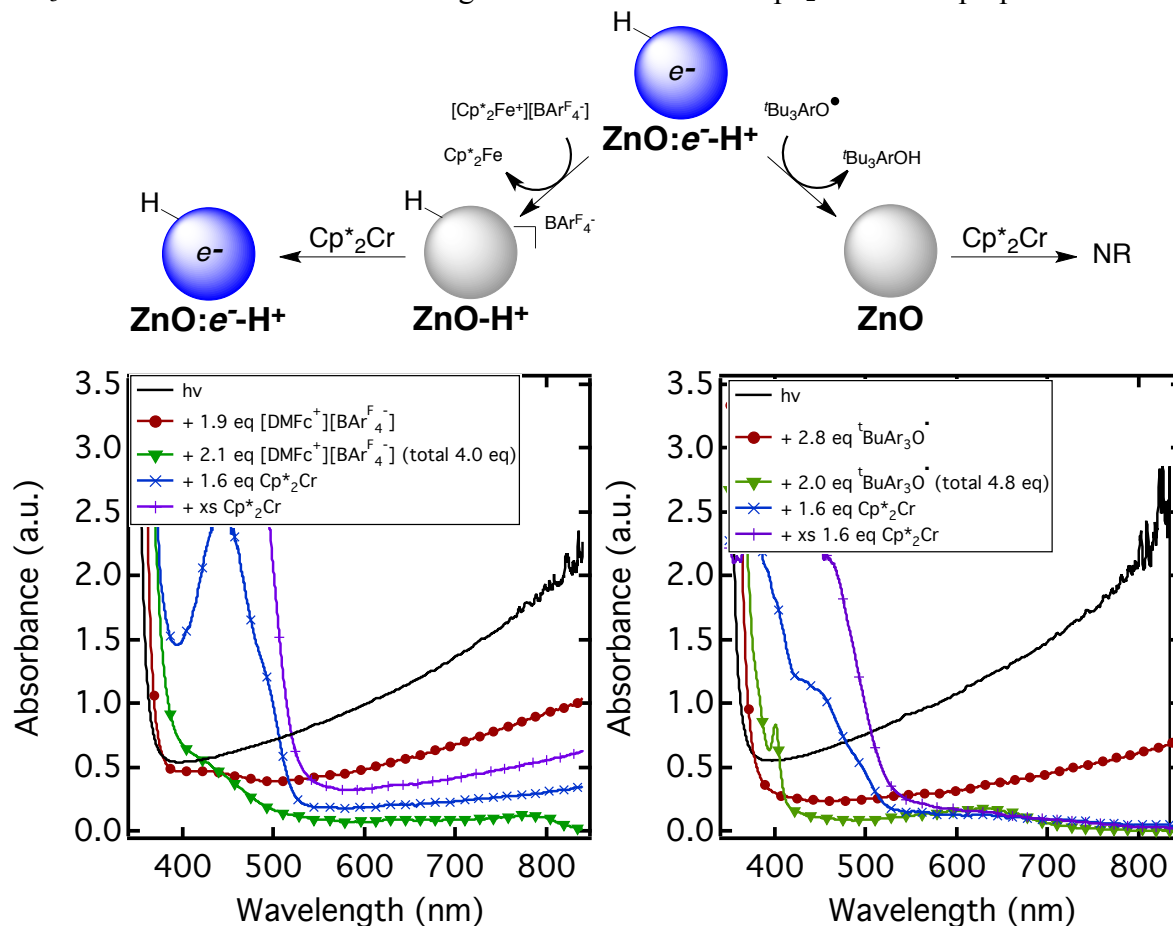

Figure S3: Titration of photoreduced ZnO NCs (6.4×10^{-4} M, $d = 3.5$ nm, black lines). Left: NCs oxidized by 1.9 equiv [Cp*$_2$Fe$^+$][BAr$^F_4^-$] (●) and fully oxidized with 4.0 equiv (▼). The features at 620 and 790 nm are from slight excess of [Cp*$_2$Fe$^+$][BAr$^F_4^-$]. Addition of Cp*$_2$Cr (1.6 equiv, ×) and (excess, +) results in reduced NCs at wavelengths greater than 600 nm, and excess unreacted Cp*$_2$Cr at wavelengths less than 500 nm. Right: NCs oxidized by 2.8 equiv ^{t}Bu$_3$ArO$^\bullet$ (●) and fully oxidized with 4.8 equiv (▼). The feature at 625 nm is due to slight excess of ^{t}Bu$_3$ArO$^\bullet$. Addition of Cp*$_2$Cr (1.6 equiv, ×) and (excess, +) results in no change in the spectra besides unreacted Cp*$_2$Cr at wavelengths less than 500 nm.

Correlation of EPR Spectra and Absorbance at 850 nm. EPR and absorption spectra of d = 5.6 nm ZnO NCs capped with DDA and suspended in toluene were recorded at room temperature. The NCs were either photoreduced (10-30 minutes) in Kontes quartz cuvettes, chemically reduced with Cp*$_2$Co alone or with [H(Et$_2$O)$_2$$^+$][BAr$^F_4$$^-$], or chemically reduced with Cp*$_2$Co/acid and diluted with as-prepared NCs. The data were collected on three separate days using the same batch of NCs, but with freshly prepared reductant and acid. Absorption spectra were recorded in cuvettes, and samples were then transferred to quartz EPR tubes. Samples were referenced to the external standard DPPH (g = 2.0036). The absorbance at 850 nm was normalized to the same concentration of NCs (1.1 × 10^{-4} M), and the ε(850 nm) was used to calculate the number of electrons per NC. Examples of the absorption data and the parallel EPR data are shown below in Figures S4 and S5.

Previous studies of photoreduced ZnO:e^--H$^+$ NCs have shown that EPR g values correlate with n_{e-} from titrations,[15] and that the A(850) is linear with n_{e-}.[8] There is thus a characteristic relationship between g and A(850) for photoreduced NCs, plotted as blue diamonds in Figure S6. The g and A(850) values for seven different solutions of chemically reduced and protonated NCs are also plotted in Figure S7, as red circles. Within the scatter of the data, the g/A(850) relationship is the same for the two charging methods. Therefore it is likely, though not certain, that the underlying g/n_{e-} and A(850)/n_{e-} relationships are also independent of charging method. This supports the use of the same ε(850 nm) for photochemically and chemically reduced NCs. Absorbance at 850 nm (11,765 cm^{-1}) is the very high energy tail of the peak maximum (centered between 1500 – 3500 cm^{-1} depending on NC size and n_{e-}), and this tail does not appear to be dramatically affected (within error) by reduction method, NC size, or n_{e-}. A more complete spectroscopic analysis of this transition, including its peak shape in the IR, is in progress.

(15) Liu, W. K.; Whitaker, K. M.; Smith, A. L.; Kittilstved, K. R.; Robinson, B. H.; Gamelin, D. R. *Phys. Rev. Lett.* **2007**, *98*, 186804.
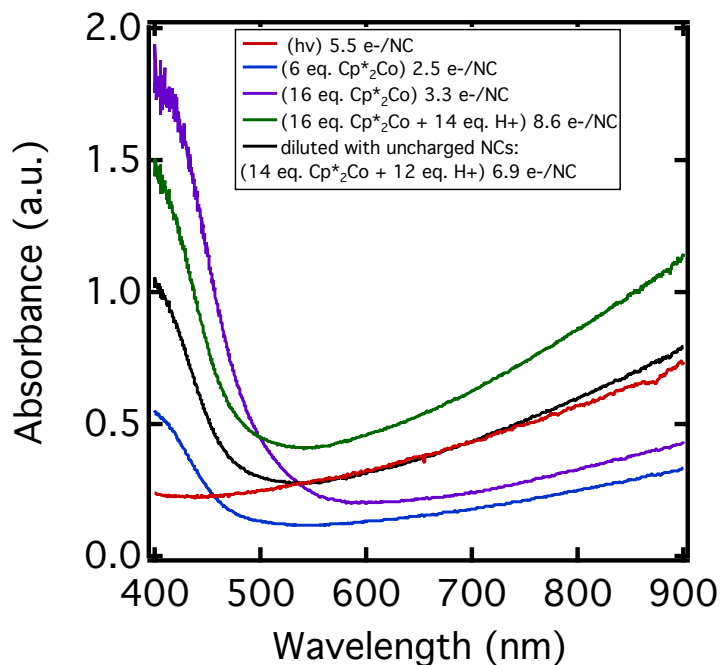
Figure S4: Absorption spectra of photoreduced (normalized to concentration of other samples), Cp^*_2Co-reduced, and Cp^*_2Co/acid-reduced ZnO NCs (2.3×10^{-4} M, $d = 5.6$ nm).
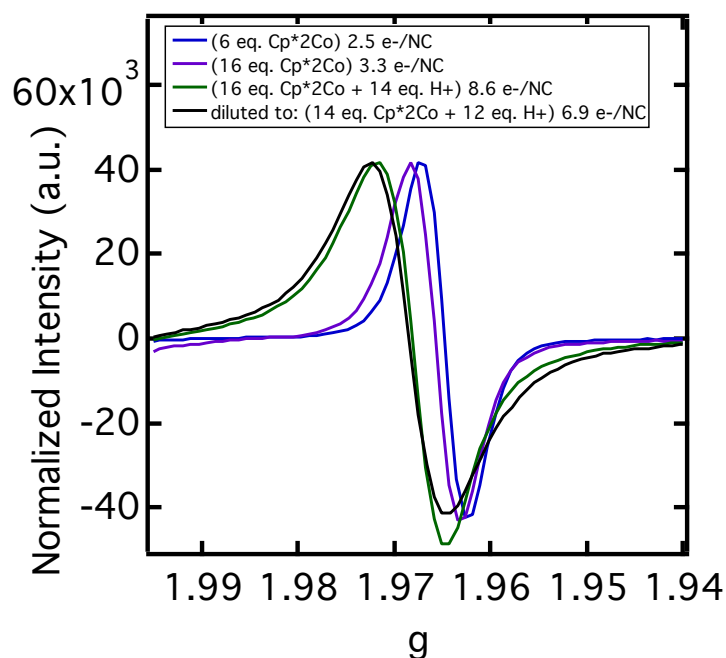

Figure S5: EPR spectra of photoreduced, Cp^*_2Co-reduced, and Cp^*_2Co/acid-reduced ZnO NCs (2.3×10^{-4} M, $d = 5.6$ nm).
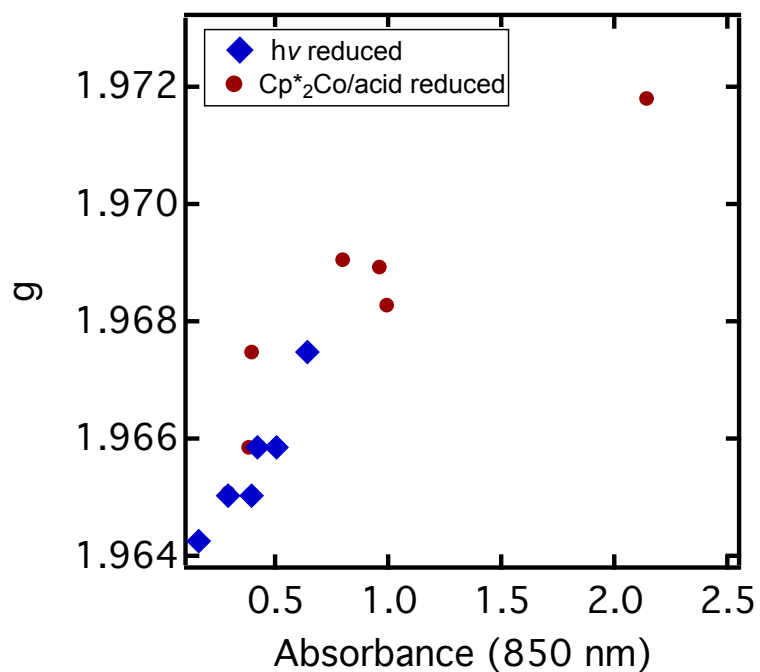
Figure S6: The g value of reduced ZnO NCs (d = 5.6 nm) as a function of the normalized absorbance at 850 nm of reduced NCs. Photochemically reduced and chemically reduced ZnO NCs follow the same trend of higher g value with more electrons per NC.
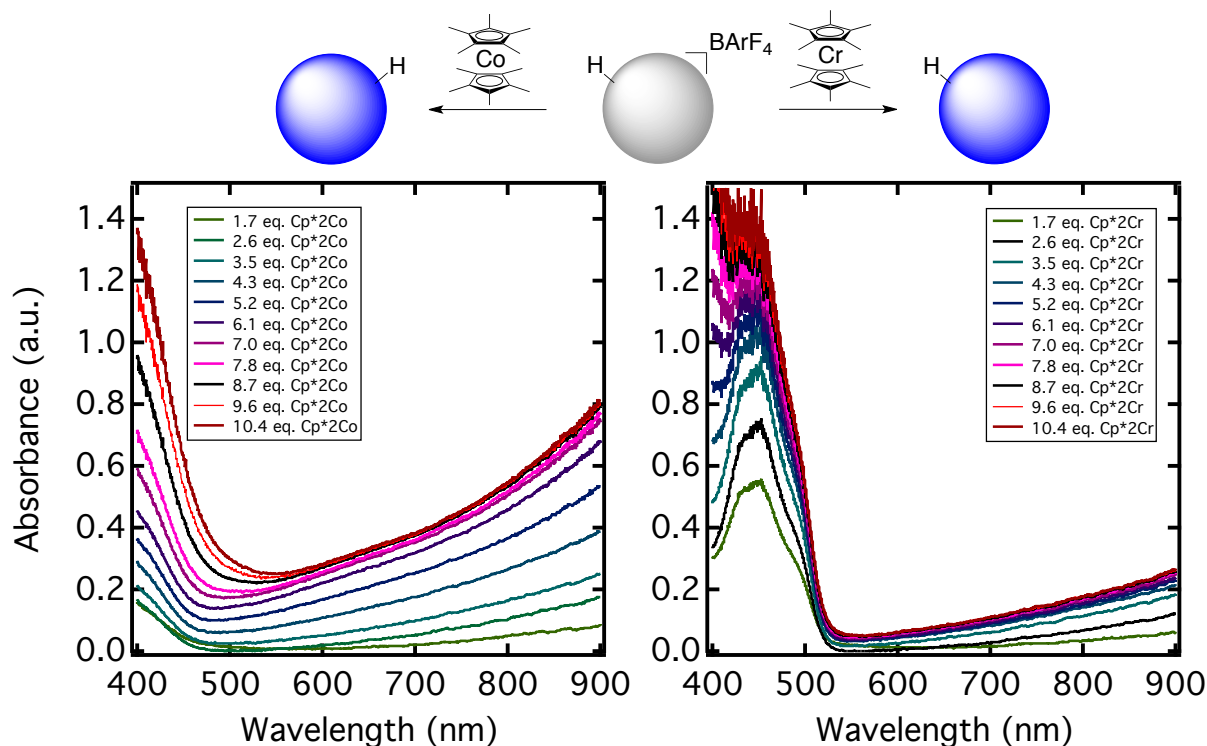
Figure S7: A solution of ZnO NCs (1.6×10^{-4} M, d = 4.3 nm) in 50/50 toluene and THF was acidified with solid $[H(Et_2O)_2^+][BAr^F_4{}^-]$ to make a solution with 10 equiv of acid per NC. Cp*$_2$Co (left) and Cp*$_2$Cr (right) were added in 10 μL aliquots (stock solutions of 3 x 10^{-2} M in toluene) with stirring, until the maximum equilibrium value of electrons per NC was reached (1.4 e^- per NC for Cp*$_2$Cr; 4.4 e^- per NC for Cp*$_2$Co), see Figure S8.
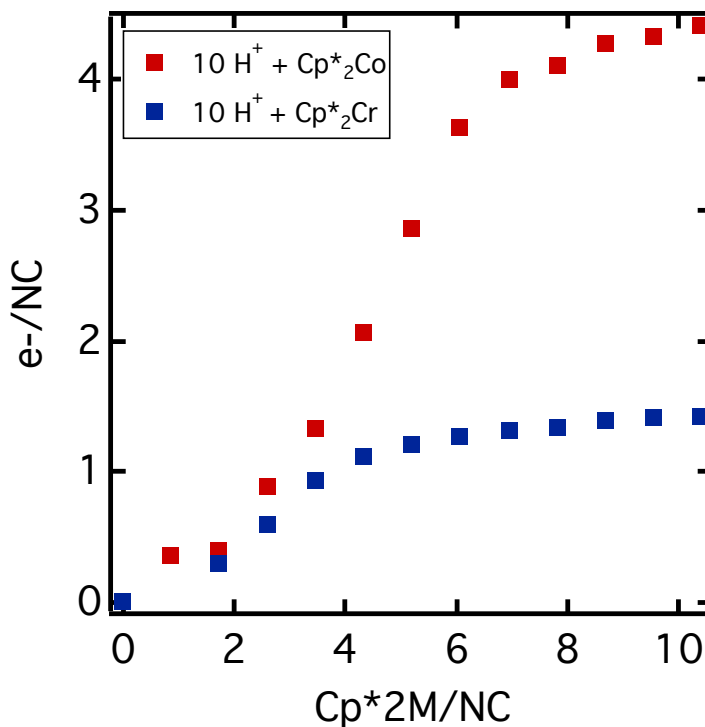
Figure S8: Plot of equiv of metallocene per d = 4.3 nm ZnO NC versus electrons injected per NC as calculated using ε(850 nm) per electron, for the experiment shown in Figure S7. Cp*$_2$Cr and Cp*$_2$Co (stock solutions of 3×10^{-2} M in toluene) were added by 10 µL aliquots to NC solutions (1.6×10^{-4} M) with 10 equiv [H(Et$_2$O)$_2$][BAr$^F_4$] per NC, until the maximum equilibrium value of electrons per NC was reached (4.4 e^- per NC for Cp*$_2$Co and 1.4 e^- per NC for Cp*$_2$Cr).