

SUPPLEMENTARY INFORMATION

Heavily doped *n*-type PbSe and PbS nanocrystals using ground-state charge transfer from cobaltocene

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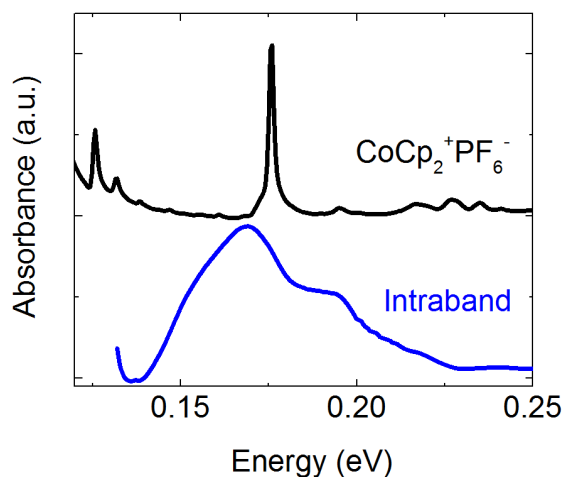


Fig. S1. Fourier-transform infrared (FT-IR) spectra of cobaltocenium hexafluorophosphate (black) and of the intraband transition of doped PbSe NCs (blue), confirming that the absorption feature in the mid-IR (Fig. 2d in the main text) is due to $1S_e-1P_e$ intra-band absorbance and not due to vibrational transitions in cobaltocene. Cobaltocenium hexafluorophosphate and cobaltocene (not shown) are not significantly different in this energy region of the FT-IR spectrum. The difference between the broad intraband feature and the sharp vibrational features of the cobaltocenium molecule is quite clear.

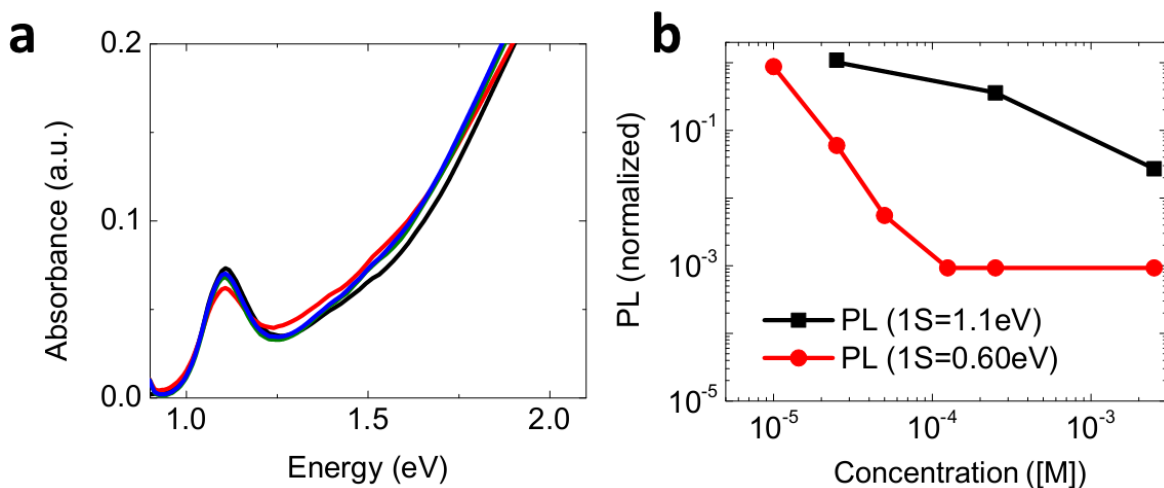


Fig. S2. (a) The absorption spectrum of a toluene solution of 3.0 nm PbSe NCs (1.5 μM , black) upon exposure to 50 μM (blue), 500 μM (green) or 5 mM (red) cobaltocene solutions shows no discernible bleaching until the very highest concentrations. The lack of 1S bleach indicates that electrons are generally not injected into the intrinsic quantum-confined states of the NCs, which is expected because the conduction band lies just above the reduction potential of cobaltocene (Fig. 1a). (b) The PL intensity of the NCs from (a) changes much less dramatically with increasing cobaltocene concentration than that of 7.9 nm PbSe NCs (red), which according to the 1S bleach (Fig. 1c, red) are readily doped by cobaltocene. In fact, at low concentrations (~ 50 μM), the PL of the smaller NCs is slightly enhanced, possibly due to passivation of surface electron traps. The slight quenching at the highest cobaltocene concentrations is similar to that seen for ~ 1 injected electron per NC. There is no evidence to suggest that other mechanisms, such as collisional quenching (*e.g.*, due to photo-induced hole-transfer to free cobaltocene in solution), can result in a discernible impact on top of the dominant effect of doping-based quenching.

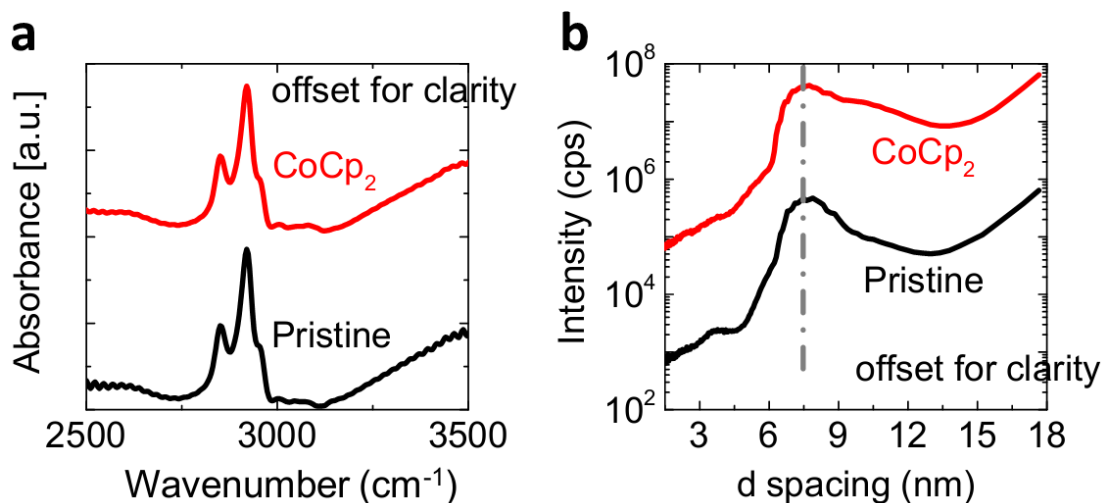


Fig. S3. (a) FT-IR spectra of pristine and cobaltocene-treated NC films. Note that C-H vibrational peaks at $\sim 2900\text{ cm}^{-1}$ from oleic acid of pristine NC film (black line) do not significantly change after cobaltocene treatment (red line). (b) Small angle X-ray scattering (SAXS, carried out with a Rigaku Ultima III diffractometer (Cu $K\alpha$ radiation) and the incident angle is typically 0.5° .) of pristine and cobaltocene-treated NC films shows that the cobaltocene treatment does not change inter-particle separation.