Supplementary Information for:

Electronic and Vibrational Structure of Complexes of Tetracyanoquinodimethane with Cadmium Chalcogenide Quantum Dots

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EXPERIMENTAL METHODS

Synthesis of Cd-enriched CdSe QDs. All reagents were used as-received from Sigma Aldrich, except for cadmium stearate, which was used as-received from MP Biomedicals, and *n*-octadecylphosphonic acid (ODPA), which was used as-received from Alfa Aesar. Chloroform and methanol were used as-received from VWR. Adapting a procedure from Qu, *et al.*,¹ we added 90% trioctylphosphine oxide (TOPO) (1.94 g, 5.02 mmol), hexadecylamine (HDA) (1.94 g, 8.03 mmol), and cadmium stearate (CdSt₂) (0.112 g, 0.165 mmol) to a dry 50-mL three-neck round bottom flask, and heated the mixture to 140 °C while stirring under a stream of dry N_{2(g)} to remove water from the reagents. After 1 hour, we sealed the flask under a positive, dry N_{2(g)} atmosphere and raised the temperature to 260 °C. We removed the heating mantle and then rapidly injected 1 mL of a 1 M stock solution of trioctylphosphine selenide (TOPSe) in trioctylphosphine (TOP), which had been prepared in advance and stored in a glovebox. Once the temperature of the reaction mixture reached 200 °C we unsealed the reaction vessel and applied a strong flow of N_{2(g)} to quench the growth of the QDs.

Synthesis of Nearly-Stoichiometric CdSe QDs. Adapting a procedure from Chen, *et al.*,² we added 99% TOPO (3 g, 7.76 mmol), cadmium oxide (CdO) (66 mg, 0.5 mmol), and 97% ODPA (340 mg, 1 mmol) to a dry 50-mL three-neck round bottom flask, and sealed and heated the mixture to 300 °C while stirring under a positive, dry N_2 atmosphere. After 1 hour, the maroon color of the reaction mixture turned clear as result of the consumption of CdO to generate cadmium n-octadecylphosphonate, and we

decreased the temperature to 140 °C, unsealed the reaction vessel, and applied a stream of $N_{2(g)}$ to remove water from the reaction vessel. After 30 minutes, we sealed the reaction vessel under a positive, dry N₂ atmosphere and increased the temperature to 390 °C. We removed the heating mantle and then rapidly injected 0.75 mL of a 1 M stock solution of TOPSe in TOP, which had been prepared in advance and stored in a glovebox. Two seconds later we injected 0.75 mL of TOP to decrease the rate of growth of the QDs. Once the temperature of the reaction mixture reached 220 °C we unsealed the reaction vessel and applied a strong flow of N_{2(g)} to fully quench the growth of the QDs.

Purification of CdSe QDs. The crude reaction mixtures of all QD samples were dissolved in 10-15 mL of hexanes and allowed to sit overnight so that the un-reacted surfactants, which are not soluble in hexanes, would precipitate as a white solid. We kept the supernatant and discarded this white precipitate. To isolate the QDs from excess Cd and Se precursors and remaining surfactants, we precipitated the QDs, dispersed in ~ 10 mL of hexanes, added 20 mL of methanol (ACS grade), and isolated a pellet containing the QDs through centrifugation (at 3500 rpm for five minutes) and decantation of the clear supernatant. We then redispersed the QD pellet in ~8 mL of hexane and centrifuged the solution to produce a white pellet of unreacted surfactant and a colored supernatant containing the QDs. We decanted the supernatant into a clean centrifuge tube and discarded the white pellet. We repeated this precipitation/redispersion procedure a total of three times to obtain the final purified samples of QDs. Three was the fewest number of purification rounds required to eliminate all of the unreacted surfactants from the QD sample: no white solid precipitated out of solution during the last redispersion and centrifugation step. We then evaporated the hexane solvent with a gentle flow of $N_{2(g)}$ and redispersed the QDs in CHCl₃.

ICP-AES. We added between 20-40 drops of each QD solution in CHCl₃ to a clean, 20-mL glass vial such that each sample contained ~10 ppm Cd upon dilution to 10 mL in aqueous acid solution. We evaporated the solvent using a gentle flow of $N_{2(g)}$, added 0.5 mL of aqua regia (concentrated HCl/concentrated HNO₃, 3:1 v/v) to each vial, allowed the samples to digest for 30 minutes, and subsequently diluted the solutions in milli-porefiltered water to 10 mL. NOTE: AQUA REGIA IS A STRONG OXIDIZING AGENT AND IS HIGHLY CORROSIVE. DO NOT USE AQUA REGIA WITHOUT PROPER TRAINING OR SAFETY PRECAUTIONS. The ICP-AES instrument was calibrated with samples prepared from stock solutions of Cd (1,000 mg/L Cd in 3% HNO₃, Aldrich) and Se (1000 mg/L Se in 3% HNO₃, Aldrich). We acquired and analyzed the data using Varian's ICP-expert II software, and calculated the elemental concentrations using the calibrated intensities of the second-most intense Cd (228.802 nm) and most intense Se (196.026 nm) atomic emission peaks. The 361.051-nm peak of Cd was the most intense emission peak, but the error for the calibration curve of this emission peak exceeded 5% and consequently was not used.

Synthesis of Cd(OPA)₂. We produced Cd-octylphosphonate (OPA) molecules from Cd-stearate (St) by mixing 2:1 OPA:CdSt₂ in CHCl₃ and letting the mixture stir for 4 hours. CdSt₂ is insoluble in CHCl₃, so the sample to appeared cloudy upon addition of CdSt₂. After 4 hours the mixture was nearly optically clear, which was a result of the OPA replacing the stearate as the ligand for the Cd²⁺ ion. OPA binds much more strongly to Cd²⁺ ions than stearate and other carboxylates. We added TCNQ directly to this solution of Cd(OPA)₂ in CHCl₃ to determine whether or not Cd(OPA)₂ could produce the reduced TCNQ we observe in the absorbance and FT-IR spectra of Cd-enriched CdSe QDs and TCNQ. It does not reduce TCNQ, see Figures **S7 and S8**.

Binding Energies of TCNQ and TOP to Surface Se Atoms. To estimate the relative binding energies of TCNQ and Se vs. TOP and Se, we optimized the geometries of TOP and TCNQ on the surface of a model Cd_6Se_6 cluster. Separately for Cd_6Se_6 -TOP and Cd_6Se_6 -TCNQ, we calculated the difference in total DFT energy between the bound complex and the sum of the energies of isolated components, where one component is the ligand (TCNQ or TOP, in the optimized bound geometry), and the other component is the Cd_6Se_6 cluster. We performed the proper correction for basis set superposition error (BSSE) using the Counterpoise method. We found that the 1.08 eV needed to separate TOP-Cd_6Se_6 into Cd_6Se_6 and TOP so that the Se is available to the neutral TCNQ cannot be overcome by the -0.56 eV of stabilization energy resulting from the complex formed by the Cd_6Se_6 and TCNQ.

³¹**P NMR.** We followed the sample preparation and experimental procedures used by Morris-Cohen *et al.* to determine the bound and free phosphorous-containing species in samples of CdSe QDs.³ The limit of detection is much higher for ³¹P NMR than for ¹H

NMR, so we prepared our samples by synthesizing and purifying double batches of Cdenriched and nearly-stoichiometric CdSe QDs, using the procedures described above, and we dissolved each double-batch of QDs in 1.2 mL of CDCl₃. We added 0.01 g of triphenylphosphate (TPP) to each sample as a calibration standard so that we could compare the intensities of peaks between spectra. We used an Agilent 400-MHz instrument to acquire the NMR spectra. We collected 1024 scans, each for 1 second, and used a 90° pulse angle. All spectra were normalized to the intensity of the peak at -18.8 ppm (TPP). Bound ligands manifest as broad peaks in NMR and these peaks are often so broad that they are not observable. We performed an exchange with propionate ligands,³ which allowed us to determine the identities of the bound ligands by the frequencies of the sharp peaks they produce in the post-exchange spectrum. The post-exchange QD samples were prepared by adding the necessary volume of a 0.95 M solution of propionic acid and benzyl(trimethyl)ammonium hydroxide (Triton B) in methanol to the QD solution to achieve a propionate:QD ratio of 4000 and stirring overnight. We then evaporated the methanol and CDCl₃ and redispersed the propionate-exchanged QDs in 1.2 mL of CDCl₃.

Absorbance Spectra of Solutions of TCNQ CT Complexes Over Time.



Figure S1. Absorbance spectra of mixtures of TCNQ and the electron donor after different amounts of time, where the electron donors are (**A**) TMS₂S, (**B**) TOPSe, and (**C**) DFe. The concentration of TCNQ is 0.7 mM in CHCl₃ and the concentrations of each of the electron donors are 7 mM in CHCl₃ in all spectra. In (**A**) the integrated area of the CT band at 620 nm grows by a factor of 1.7 on going from 7 to 11 days while the sum of the areas of the 840 and 850-nm peaks (TCNQ¹⁻) grow by a factor of 2.4 on going from 7 to 11 days.



Figure S2. Absorbance spectra of samples of CdSe QDs (red), mixtures of TCNQ and the QDs after 3 days (blue), and mixtures of TCNQ and the QDs after 7 days (green) where the QDs are Cd-enriched CdSe QDs (**A**), (**C**) and nearly-stoichiometric CdSe QDs (**B**), (**D**). We show the fits the 850 and 840-nm peaks of TCNQ¹⁻ and the 620-nm peak of the CT band of TCNQ in (**C**) and (**D**). All samples are in CHCl₃. The concentrations of TCNQ, with and without the electron donors, are 0.2 mM, and the concentrations of each of the electron donors, with and without TCNQ, are 8 μ M.

Peak Fits of the FT-IR Spectra of Mixtures of Cd-Enriched and Nearly-Stoichiometric CdSe QDs with TCNQ.



Figure S3. FT-IR spectra of mixtures of TCNQ and QDs after 3 days where the QDs are Cd-enriched CdSe QDs (**A**) and nearly-stoichiometric CdSe QDs (**B**). We also show the fits of the peaks in these spectra. All samples are in CHCl₃. These samples are identical to those corresponding to the absorbance spectra of **Figure S2** and all concentrations are the same as those listed in the caption of **Figure S2**. These spectra are also shown in the main text.

Absorbance and FT-IR Spectra of Oxidized Forms of Molecular Reducing Agents.



Figure S4. Absorbance spectra of an electron donor only (red), mixtures of electron donors with silver nitrate (black), and mixtures of the electron donor and TCNQ (blue), where the electron donors are (A) TMS₂S, (B) TOPSe, and (C) DFe. The samples of the electron donors oxidized by silver nitrate, black traces, are the same concentration as TCNQ in the blue traces, and therefore the same concentration as the maximum amount of electron donor oxidized by TCNQ, which is 0.7 mM. The concentration of AgNO₃ in all samples is 3.5 mM.



Figure S5. FT-IR spectra electron donors only (red), mixtures of electron donors with silver nitrate (black), and mixtures of TCNQ and the electron donor (blue) where the electron donors are (A) TMS₂S, (B) TOPSe, and (C) DFe. These samples are identical to those for which the visible-NIR absorbance spectra are presented Figure S4, and all concentrations are the same as those listed in the caption of Figure S4.



³¹P NMR Spectra of Cd-Enriched and Nearly-Stoichiometric CdSe QDs.

Figure S6. Phosphorus NMR spectra of Cd-enriched (A,C) and nearly-stoichiometric (B,D) CdSe QDs before (A,B) and after (C,D) exchange of the original ligands with an excess of propionate, in CDCl₃.

³¹P NMR shows that the Cd-enriched CdSe QDs (**Figure S6A**) have a small amount of free TOPO (51.3 ppm)³⁻⁵ and free TOPSe (36.1 ppm),³⁻⁵ 500 μ M (3.5 free TOPO molecules per QD) and 250 μ M (1.8 free TOPSe molecules per QD), respectively, as well as bound phosphorus-containing ligands (10 ppm, broad).³⁻⁵ The TPP standard is at -18.8 ppm.^{3,4} We also observe free TOPO (48.8 ppm), 1.8 mM or 6.4 free TOPO molecules per QD, free TOPSe (36.6 ppm), 0.16 mM or 1 free TOPSe molecule for every 2 QDs, and bound phosphorus-containing ligands (20-35 ppm, broad) in the spectrum of nearlystoichiometric CdSe QDs (**Figure S6B**). There are typically hundreds of ligands per QD that are bound to the surface of the QD,³ so these ratios of free TOPO:QD and free TOPSe:QD show that less than ten percent of the ligands are free in solution. The absence of a sharp peak at -30 ppm indicates that there is no free TOP in either sample.⁵ It is difficult to determine the identity of the bound ligands from these spectra because the signals of different phosphorus-containing, bound ligands are not differentiable: broad peaks between 10 and 35 ppm have previously been assigned to alkylphosphonates bound to the surface of the QD,^{3,4} but TOPO and TOPSe bound to the QD surface also produce broad peaks near 20-30 ppm, and very small, broad peaks near -20 ppm have been tentatively assigned to TOP that is loosely-bound to surface selenide ions.⁵ We therefore exchanged the native ligands with a large excess of propionate, 4000 propionate:QD, following previously-published procedures,^{3,4} and acquired ³¹P NMR spectra of the post-exchange samples. The exchange of native ligands with propionate is usually not quantitative – it occurs with an estimated yield of 60% for phosphonates native ligands^{3,4} – so we do not attempt to use this method quantitatively, but rather to determine what type of ligands were originally bound the QD.

After the propionate displaces the native ligands, the broad signals to due to bound, native ligands disappear and we observe sharp peaks attributed to the now-free, native ligands. The ligand exchange with propionate also oxidizes TOP and TOPSe, so the displacement of TOP or TOPSe from the QD surface manifests as an increase in the signal of free TOPO. The spectrum of post-exchange, Cd-enriched QDs has a large, sharp peak at 26.1 ppm, which shows that bound signal in the pre-exchange spectra was due to octylphosphonate (Figure S6C), in agreement with previous results.^{3,4} The peak due to free TOPO does not change after the exchange with propionate, which shows that there is no TOPO, TOPSe, and/or TOP free in solution that was bound to the surface of the QD and displaced by the propionate. The post-exchange spectrum of the nearlystoichiometric CdSe QDs (Figure S6D) exhibits new, sharp peaks at 26.2 ppm and 18.6 ppm due to the displacement of ODPA^{3,4} and P,P'-(di-n-octadecyl)dihydrogen pyrophosphonic acid, a condensation product of octadecylphosphonic acid^{3,4} from the OD surface as well as a very large peak at 52.2 ppm, which is due to free TOPO.^{3,4} This new peak at 52.2 ppm reveals that TOPSe, TOPO, and/or TOP were strongly-bound to the surface selenide ions of nearly-stoichiometric CdSe QDs.

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Absorbance and FT-IR Spectra of Mixtures of TCNQ and QD Reaction Precursors.



Figure S7. Absorbance spectra of mixtures of TCNQ and reaction precursors of the Cdenriched (**A**) and nearly-stoichiometric (**B**) CdSe QDs. The spectra of the mixtures of TCNQ and Cd-enriched (**A**) and stoichiometric (**B**) CdSe QD products are shown for reference. Only TOPSe reduces TCNQ (also shown in the main text), as evidenced by the decrease in the neutral TCNQ peak at 400 nm and by the appearance of the 555-nm CT band. The wavelength of this band is approximately 65 nm shifted from that of the band in the spectra of the TCNQ reduced by both types of CdSe QDs, and this difference in peak position shows that residual TOPSe is clearly not the dominant reducing agent of TCNQ in either sample of CdSe QDs and TCNQ. We multiplied the TCNQ/QD spectra by a factor of five for clarity.



Figure S8. FT-IR spectra of mixtures of TCNQ and precursors of the Cd-enriched (**A**) and stoichiometric (**B**) CdSe QD syntheses. The spectra of the mixtures of TCNQ and Cd-enriched (**A**) and nearly-stoichiometric (**B**) CdSe QDs are shown for reference.



Figure S9. Simulated IR spectra of complexes of Cd^{2+} (**A**), a neutral Cd atom (**B**), and triethylphosphine selenide (TEPSe) (**C**) with TCNQ. The interaction between Cd^{0} and TCNQ is more symmetric than that of Cd^{2+} and TCNQ, so there is significantly less distortion of the TCNQ when it forms of a complex with Cd^{0} than with Cd^{2+} . Only three peaks are present in (**B**) because the decreased distortion of the TCNQ molecule by Cd^{0} leads one of its four nitrile modes, the totally asymmetric mode at 2204 cm⁻¹, to be nearly IR-silent: this mode is two orders of magnitude less intense than the other three modes.

Table S1. Bond lengths and bond angles of the free TCNQ molecule in its three redox states, and a diagram of the TCNQ molecule with atom labels for reference. Numbers computed with the B3LYP functional and 6-311+G(d,p) basis set.

	TCNQ Redox State ^a		
	0	-1	-2
Bond Length (Å)			
C ₁ -N ₁ , C ₃ -N ₂ , C ₁₁ -N ₃ , C ₁₂ -N ₄	1.15587	1.16206	1.17102
C ₂ -C ₁ , C ₂ -C ₃ , C ₁₀ -C ₁₁ , C ₁₀ -C ₁₂	1.42442	1.41257	1.41257
C_4 - C_2 , C_9 - C_{10}	1.38543	1.42934	1.47368
C ₄ -C ₅ , C ₄ -C ₇ , C ₉ -C ₆ , C ₉ -C ₈	1.44622	1.42399	1.40950
C ₅ -C ₆ , C ₇ -C ₈	1.35268	1.37293	1.39248
C ₅ -H ₁ , C ₆ -H ₂ , C ₇ -H ₃ , C ₈ -H ₄	1.08396	1.08507	1.08705
Bond Angle (°)			
C_1 - C_2 - C_3 , C_{11} - C_{10} - C_{12}	116.2943	116.7360	116.8585
C ₂ -C ₄ -C ₅ , C ₂ -C ₄ -C ₇ , C ₁₀ -C ₉ -C ₈ , C ₁₀ -C ₉ -C ₆	121.1919	121.6693	122.2156
C ₅ -C ₄ -C ₇ , C ₆ -C ₉ -C ₈	117.6163	116.6614	115.5692
C ₆ -C ₅ -C ₄ , C ₅ -C ₆ -C ₉ , C ₄ -C ₇ -C ₈ , C ₉ -C ₈ -C ₇	121.1920	121.6694	122.2158
C ₄ -C ₅ -H ₁ , C ₄ -C ₇ -H ₃ , C ₉ -C ₆ -H ₂ , C ₉ -C ₈ -H ₄	118.8689	119.0212	119.0631

^{*a*}The molecule is planar, and charge is distributed symmetrically with respect to all three mirror planes of the molecule.



Scheme S1.

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