

Supporting Information for:

**Synthesis and Surface Chemistry of Cadmium Carboxylate
Passivated CdTe Nanocrystals from Cadmium
bis(phenyltellurolate)**

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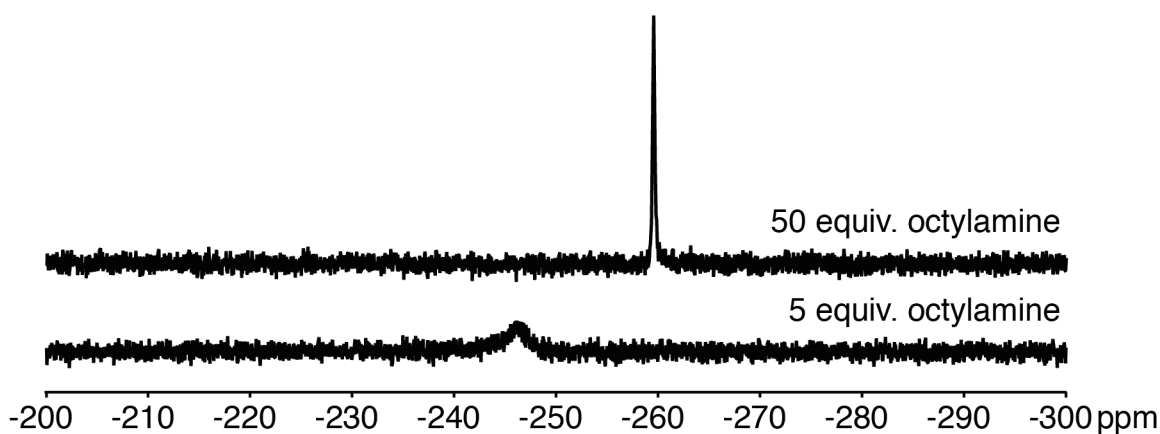


Figure S1. ^{125}Te NMR spectra of $\text{Cd}(\text{TePh})_2$ in benzene- d_6 upon addition of 5 and 50 equivalents of *n*-octylamine.

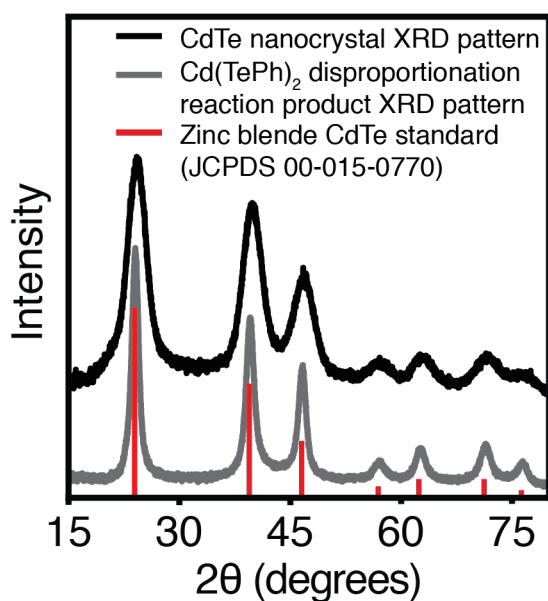


Figure S2. Powder X-ray diffraction pattern of CdTe nanocrystals (black) and polycrystalline CdTe produced by disproportionation of $\text{Cd}(\text{TePh})_2$ at 220 °C in hexadecane (gray). Exponential baseline corrections were applied to the data to remove signal from scattering. The CdTe standard (red) was obtained from the Joint Committee on Powder Diffraction Standards (JCPDS) as coll. code 00-015-0770.

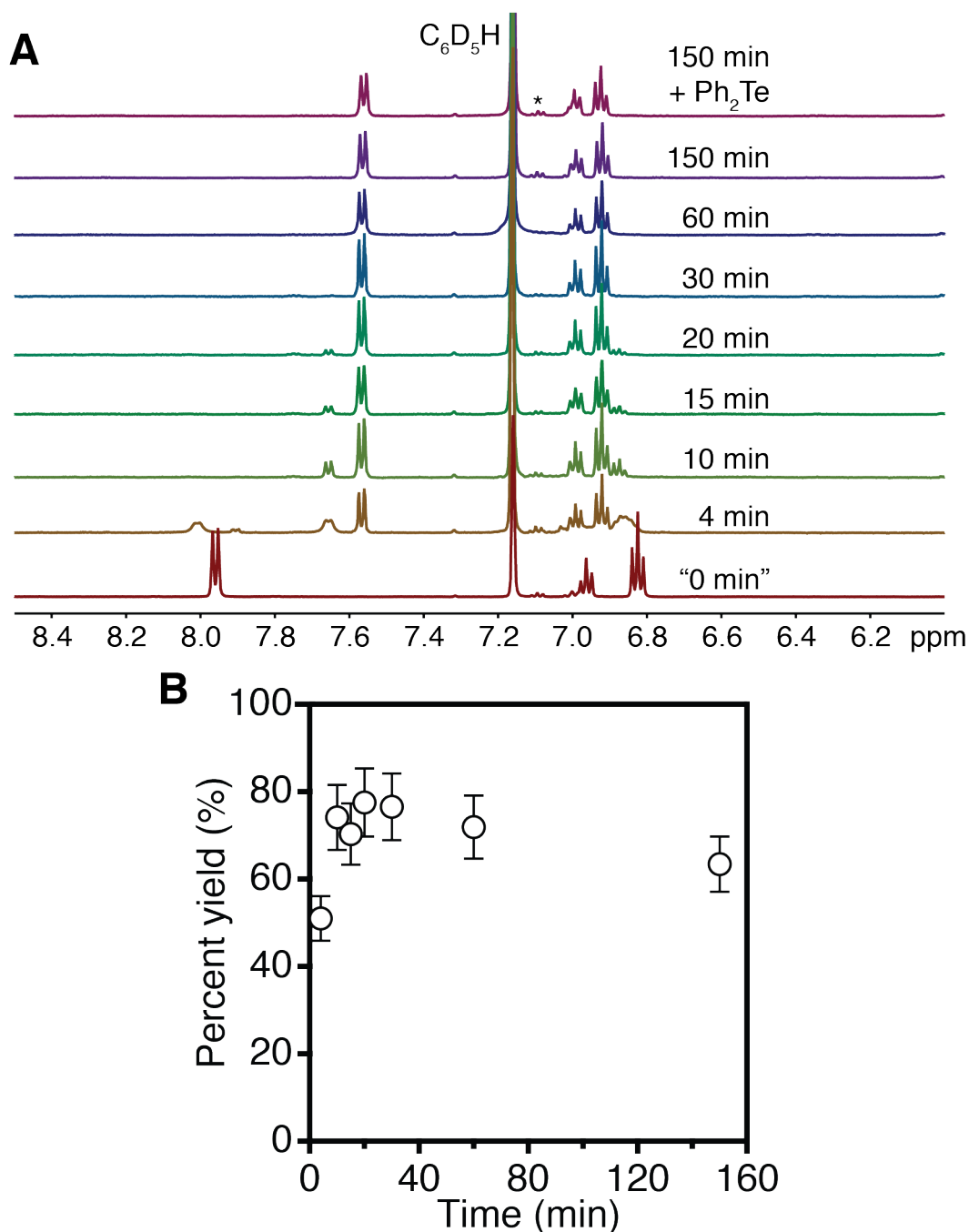


Figure S3. A) 1H NMR spectra of crude reaction mixture ("0 min"), aliquots removed during synthesis (4 min - 150 min), and the final aliquot with added diphenyl telluride prepared by the thermolysis of $Cd(TePh)_2$ in hexadecane (150 min + Ph_2Te). (*) denotes a toluene impurity. Additional signals in the $t = 4$ –20 min. aliquots may result from a complex between cadmium oleate and the diphenyl telluride, or a monocarboxylate-monotellurolate cadmium complex that results from comproportionation of the precursors. B) Ph_2Te yield as measured by 1H NMR.

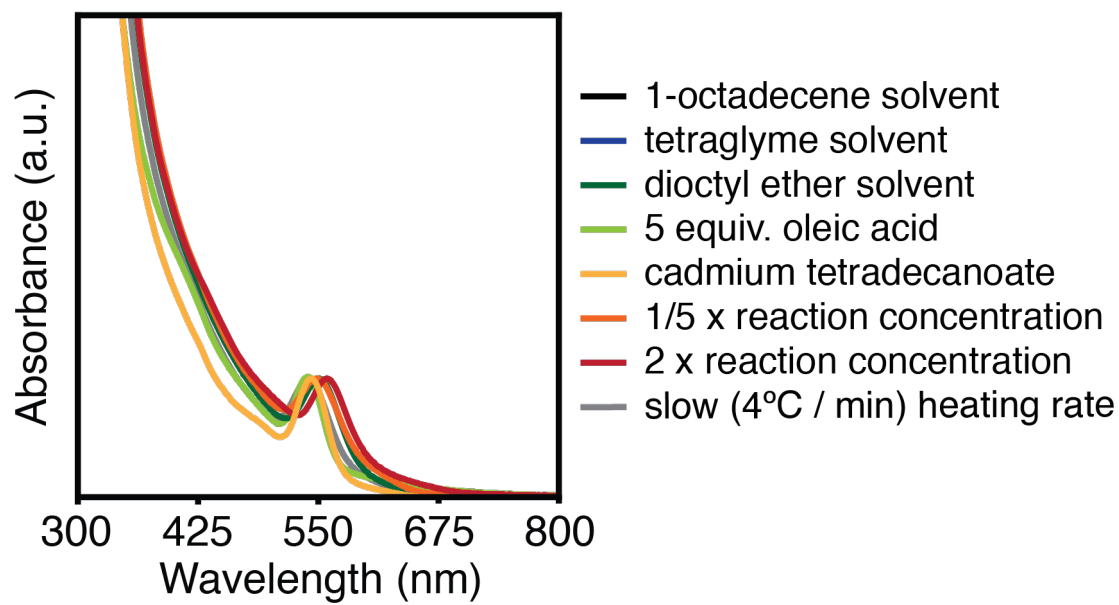


Figure S4. Absorbance spectra showing insensitivity of the final nanocrystal size to synthesis conditions. Spectra are normalized to the height of the excitonic band.

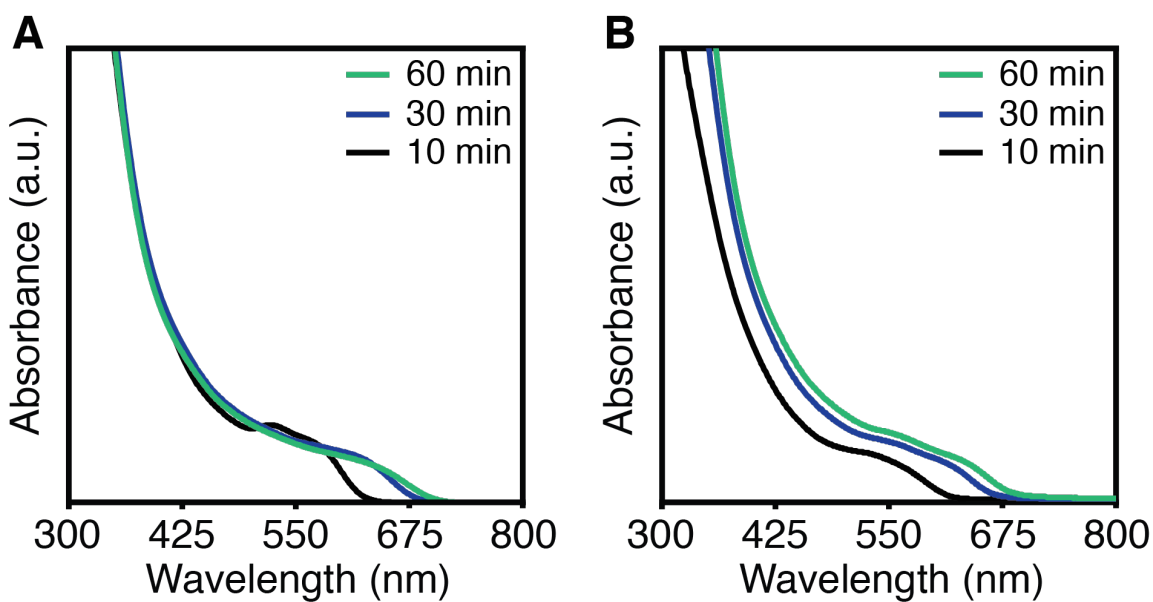


Figure S5. UV-visible absorbance spectra of nanocrystal synthesis reactions run in the presence of 5 equivalents of A) tributylphosphine and B) octadecylamine.

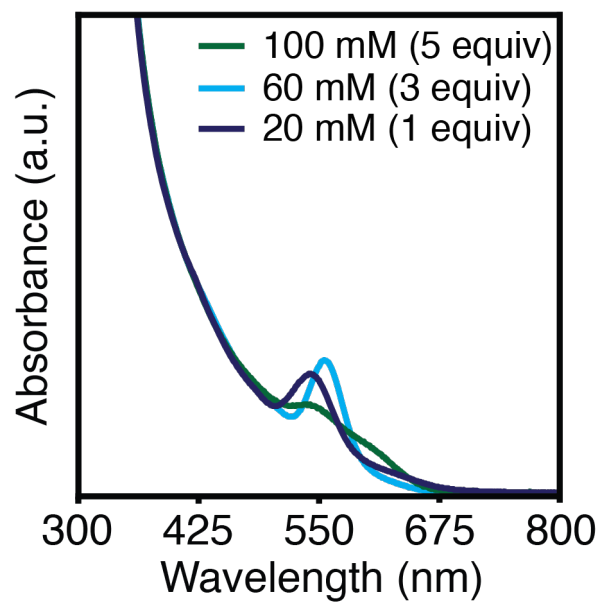


Figure S6. UV-visible absorbance spectra of nanocrystal synthesis reactions run in the presence of A) one, B) three, and C) five equivalents of cadmium oleate. Spectra are normalized to the absorbance at 410 nm.

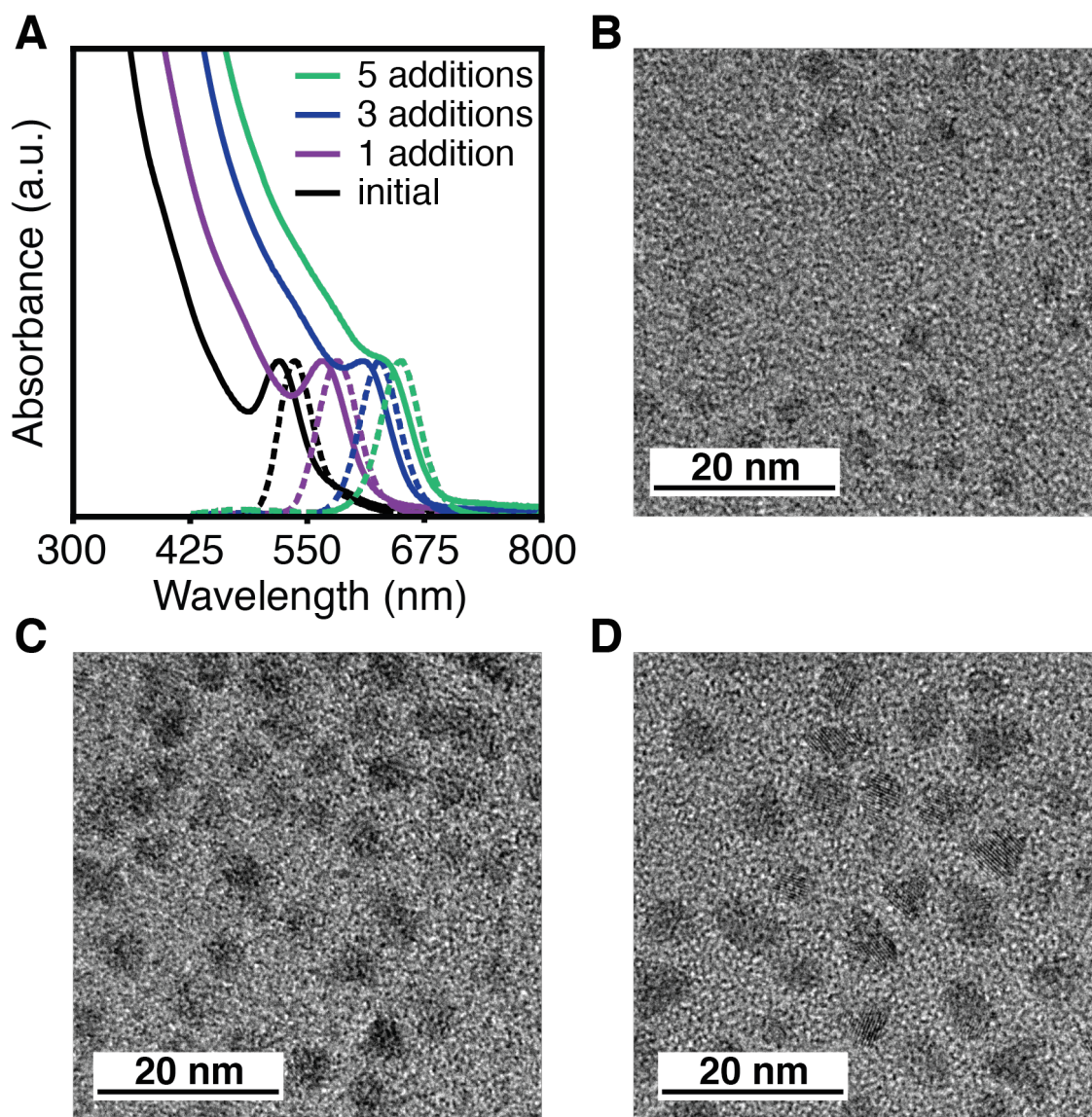


Figure S7. A) Absorbance and photoluminescence spectra of CdTe nanocrystals grown by successive additions of precursor mixture to a synthesis mixture at completion. Transmission electron micrographs of CdTe nanocrystals after A) one, B) three, and C) five additions of precursor mixture.

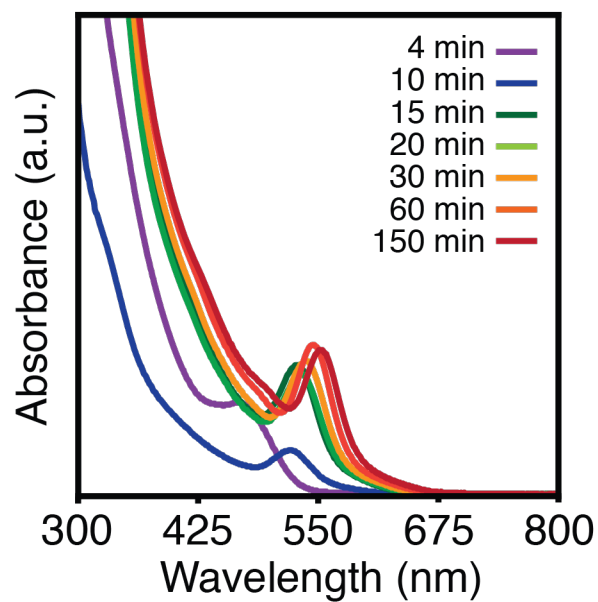


Figure S8. UV-vis absorbance spectra of aliquots removed from a nanocrystal kinetics reaction (4 min – 150 min).

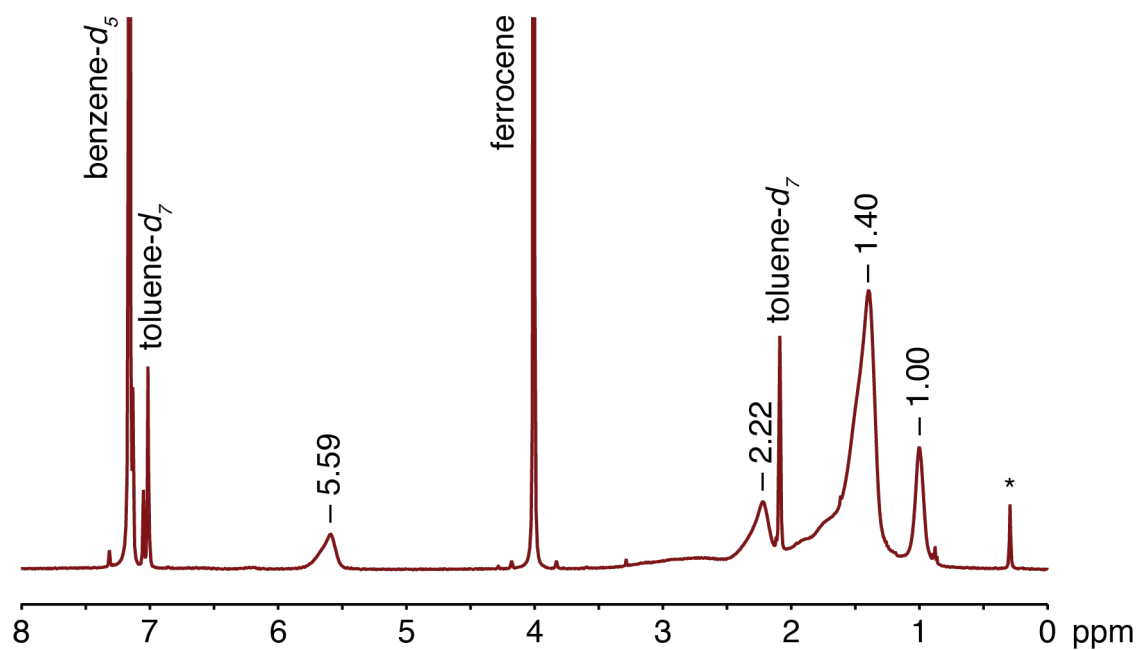


Figure S9. ^1H NMR spectrum of CdTe nanocrystals dissolved in benzene- d_6 with addition of a ferrocene internal standard dissolved in toluene- d_8 . (*) denotes a small silicone impurity leached from the silicone liner of the vial caps.

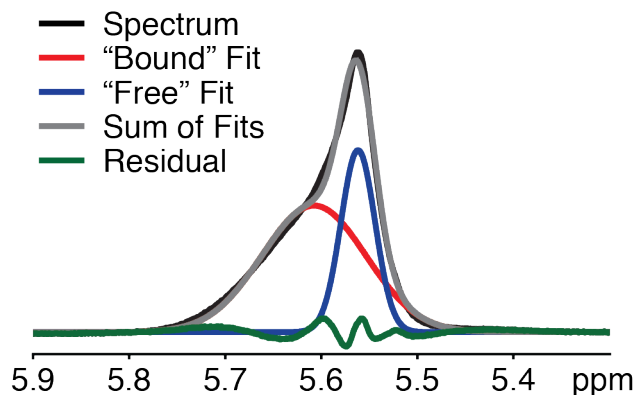


Figure S10. Vinyl region of ^1H NMR spectrum of CdTe nanocrystals with 4.7 oleates/ nm^2 shown in Figure 3B with an approximate fit to two Gaussians. The broad downfield peak represents surface-bound cadmium oleate (67.9% of total signal) and the sharper upfield peak represents free cadmium oleate (32.1% of total signal). This analysis reduces the measured surface coverage to 3.1 oleates/ nm^2 .

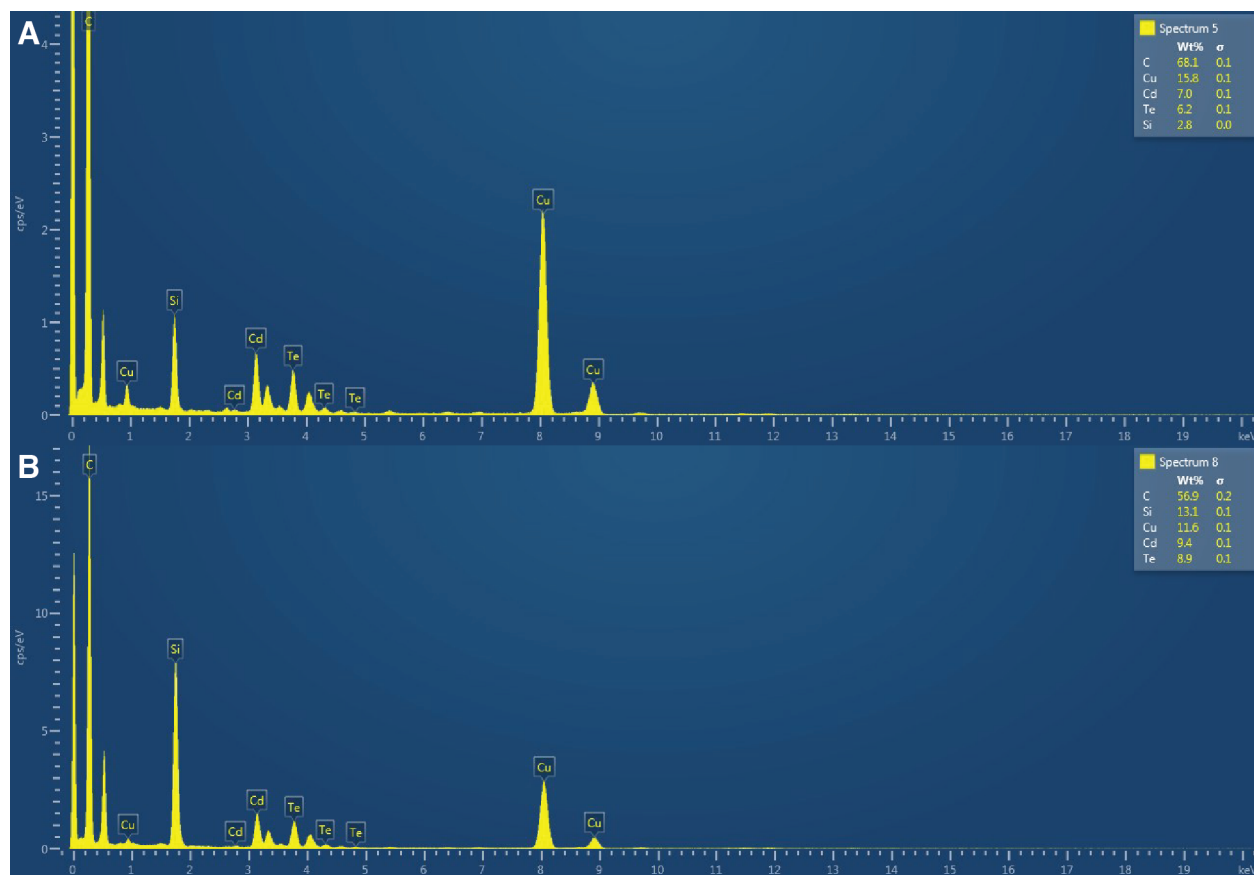


Figure S11. Energy-dispersive X-ray spectra of CdTe nanocrystal samples with A) 3.1 carboxylates/ nm^2 and B) 2.3 carboxylates/ nm^2 .

Table S1. Crystal, intensity collection, and refinement data for (TMEDA)Cd(TePh)₂ shown in Figure 1.

Crystal size	0.480 x 0.200 x 0.80 mm
Lattice	Monoclinic
Formula	C ₁₈ H ₂₆ CdN ₂ Te ₂
Formula weight	638.01
Space group	P2(1)/c
a (Å)	13.0754(8)
b (Å)	11.4619(7)
c (Å)	15.1442(10)
α (deg.)	90
β (deg.)	112.3765(8)
γ (deg.)	90
V (Å ³)	2098.7(2)
Z	4
Temperature (K)	130(2)
Radiation (λ, Å)	0.71073
ρ (calcd.) (g/cm ³)	2.019
μ (Mo Kα) (mm ⁻¹)	3.767
Θ max (deg.)	33.004
No. of data collected	36600
No. of data	7586
No. of parameters	212
R ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0184
ωR ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0424
R ₁ [all data]	0.0206
ωR ₂ [all data]	0.0432
GOF	1.105

Table S2. Cadmium-to-tellurium ratios in CdTe samples as measured by ^1H NMR/UV-visible analysis of ligand-to-semiconductor ratios and energy-dispersive X-ray spectroscopy (EDX).

Sample	Carboxylate coverage (nm^{-2})	Cd:Te ratio by NMR/UV-vis	Cd:Te ratio by EDX
1	3.7	1.25 ± 0.13	-
2	3.0	1.19 ± 0.12	1.28 ± 0.03
3	2.9	1.19 ± 0.12	-
4	2.6	1.17 ± 0.12	-
5	2.3	1.15 ± 0.12	1.20 ± 0.02

Table S3. Surface site and ligand density values calculated for $\text{Cd}(\text{O}_2\text{CR})_2$ -bound CdSe and CdTe nanocrystals. CdSe nanocrystal data is obtained from reference 29 in the main text. Lattice constants are obtained from the Joint Committee on Powder Diffraction Standards (JCPDS) as coll. codes 00-019-0191 (CdSe) and 00-015-0770 (CdTe) and atom densities are calculated geometrically from the zinc blende unit cell.

Nanocrystal sample	CdSe	CdTe
Zinc blende lattice constant (nm)	0.6077	0.6481
Atom density on {100} facet (nm^{-2})	5.42	4.76
Atom density on {111} facets (nm^{-2})	6.25	5.50
Average surface atom density (nm^{-2})	5.83	5.13
Average surface chalcogen density (nm^{-2})	2.92	2.56
Peak position (nm)	571	552
Peak position (eV)	2.17	2.25
Average nanocrystal diameter (nm)	3.57	3.25
Surface area per nanocrystal (nm^2)	39.9	33.2
Surface chalcogen sites per nanocrystal	116.5	85.0
$\text{Cd}(\text{O}_2\text{CR})_2$ per nanocrystal after isolation	64.5	50.7
Carboxylate ligand density (nm^{-2})	3.3	3.1
Percent of surface chalcogen sites occupied	55.4%	59.6%

Table S4. Electronic properties of cadmium chalcogenide semiconductors relevant to ionic/covalent character.¹ In addition to large differences in electronegativity, strong ionic character manifests in small static and optical dielectric constants (ϵ_0 , ϵ_∞ , respectively; relative to the dielectric constant of vacuum).²

Material	CdS	CdSe	CdTe
Pauling electronegativity difference	0.89	0.86	0.41
Dielectric constant ($\epsilon_0/\epsilon_\infty$)	8.28/5.23	9.3/6.2	10.4/7.1

References

- (1) He, B.; Zhang, W. II-VI Semiconductors and Their Device Applications. In *Handbook of Chalcogen Chemistry: New Perspectives in Sulfur, Selenium and Tellurium*; Devillanova, F. A.; Mont, du, W.-W., Eds.; Royal Society of Chemistry: Cambridge, 2013; Vol. 2, pp. 180–231.
- (2) R Heath, J. Covalency in Semiconductor Quantum Dots. *Chem. Soc. Rev.* **1998**, 27, 65–71.