(Electronic Supplementary Information)

Direct Cation Exchange of CdSe Nanocrystals into ZnSe Enabled by Controlled Binding between Guest Cations and Organic Ligands

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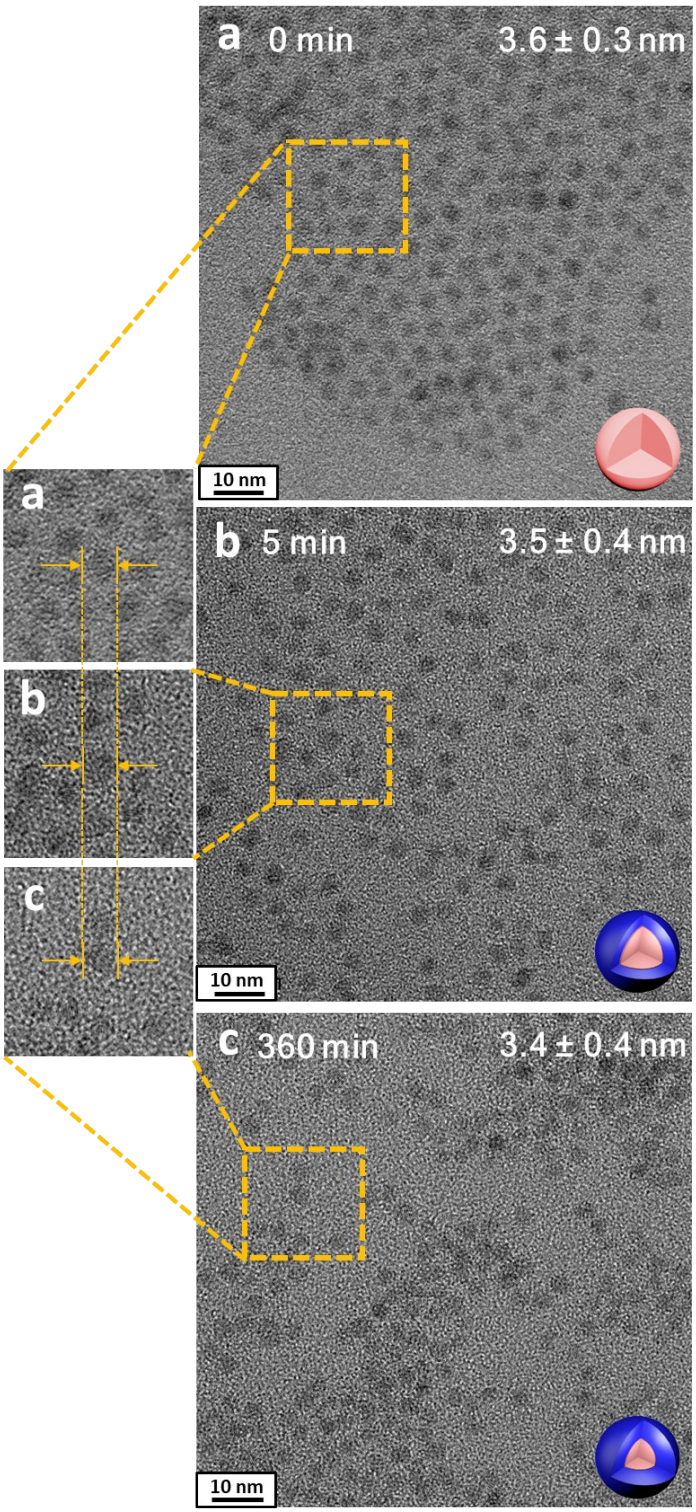

Figure S1. TEM images of (a) CdSe (0 min) and cation-exchanged CdSe/ZnSe ((b) 5 min and (c) 360 min) NCs using 0.694 M ZnI_2 and TOPO at 230 °C.

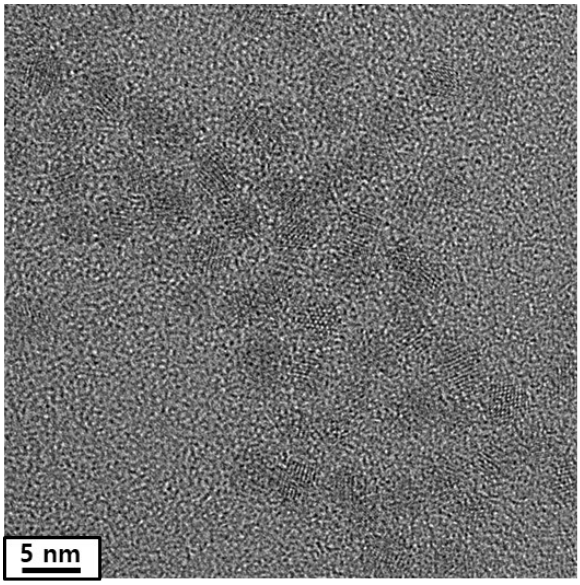

Figure S2. High-magnification TEM image of CdSe/ZnSe HNCs that were produced *via* cation exchange using 0.694 M ZnI_2 and TOPO for 360 min at 230 °C.

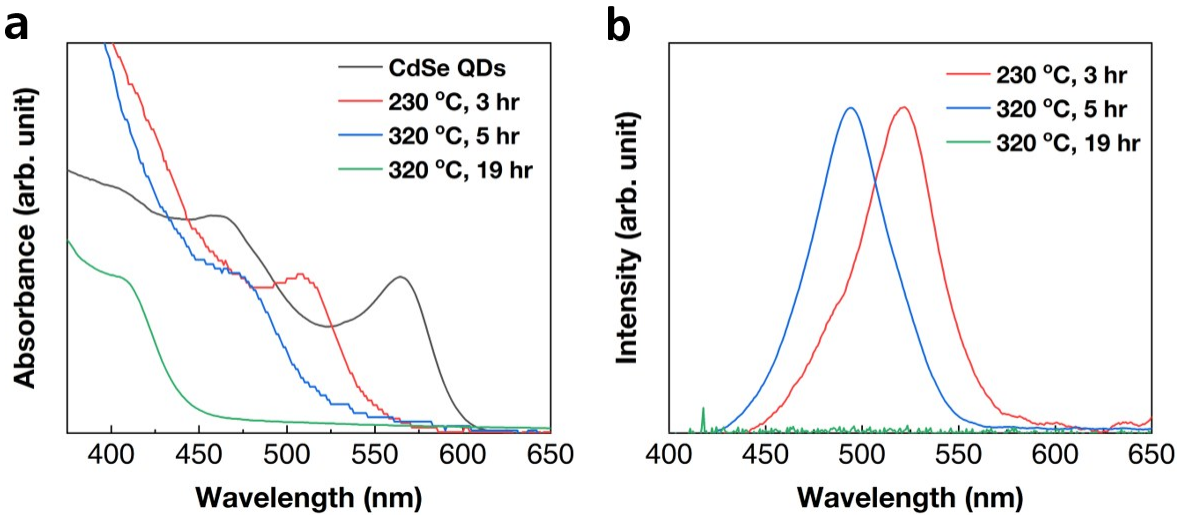

Figure S3. (a) UV-vis absorption spectra and (b) PL spectra of CdSe QDs before and after cation exchange reaction using 0.694 M ZnI_2 and TOPO.

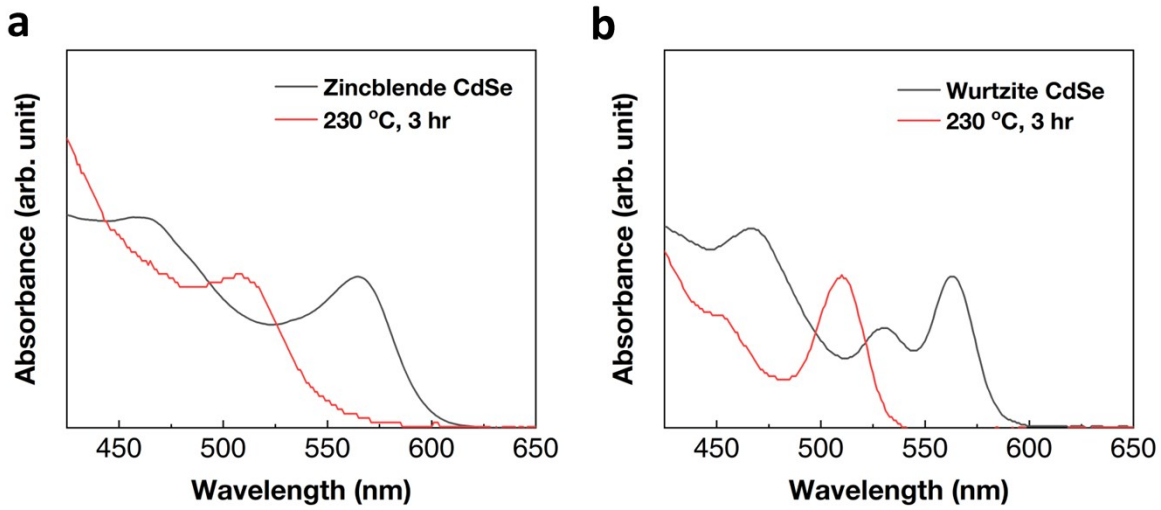

Figure S4. Absorption spectra of QDs with (a) zinc blende and (b) wurtzite crystal structure before and after cation exchange reaction using 0.694 M ZnI_2 and TOPO at 230 °C.

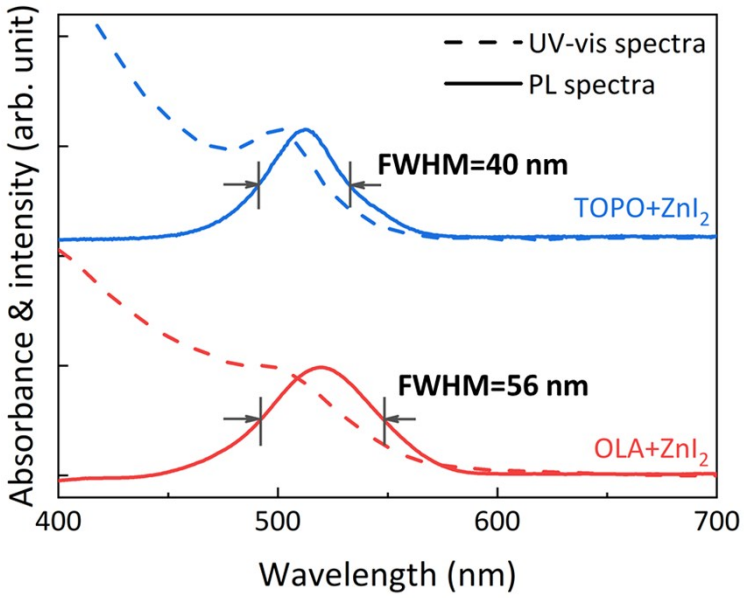

Figure S5. UV-vis and PL spectra of CdSe/ZnSe HNCs cation-exchanged with different precursors at 230 °C: blue and red lines are when 0.694 M TOPO or OLAm with 0.694 M ZnI_2 were used, respectively. Reaction time was 360 min with TOPO and 30 min with OLAm, respectively.

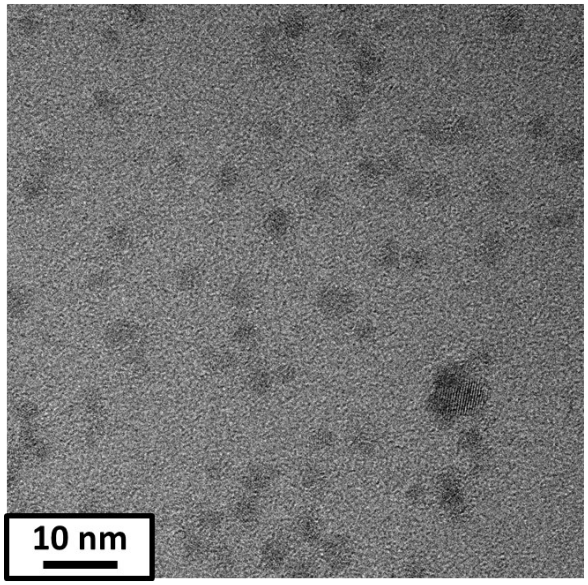

Figure S6. TEM images of CdSe/ZnSe NCs reacted with 0.694 M OLAm and ZnI_2 for 6 h at 230 °C. The size of CdSe/ZnSe NCs decreased from 3.6 nm (size of original CdSe NCs) to 3.1 nm.

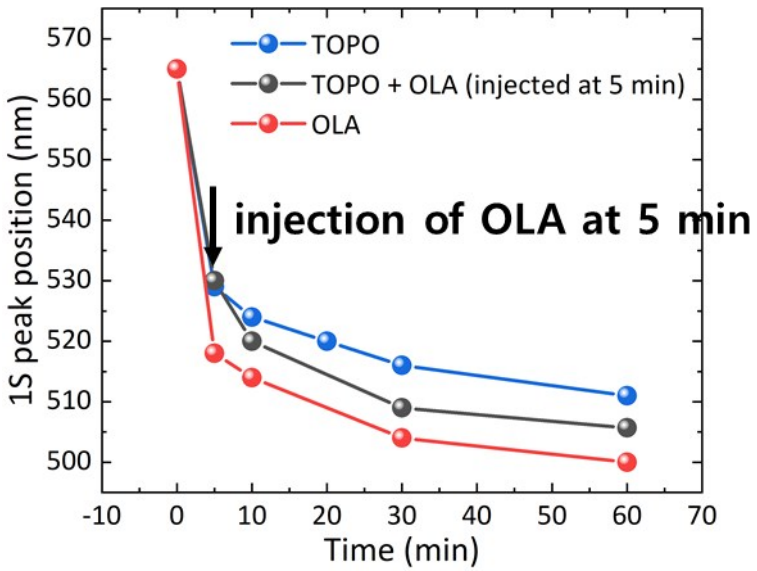

Figure S7. 1S exciton peak position changes of NCs mixed with 0.694 M of TOPO and ZnI_2 or 0.694 M of OLAm and ZnI_2. For red line, 0.694 M OLAm was additionally injected at 5 min into the reaction flask containing 0.694 M TOPO and ZnI_2.

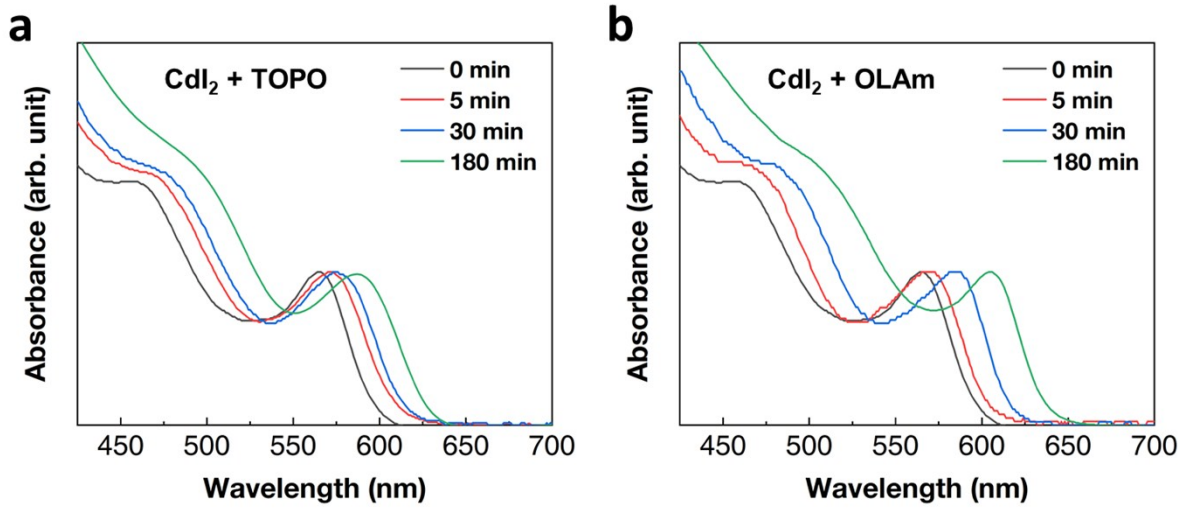

Figure S8. UV-vis absorption spectra of CdSe NCs after reaction using 0.694 M CdI_2 with TOPO or OLAm at 230 °C.

Table S1. Enthalpy changes of bulk transformation from CdSe(s) + ZnX_2(s) to ZnSe(s) + CdX_2(s), where X = Cl, Br, and I (unit: eV/formula unit)

	$ZnCl_2$	$ZnBr_2$	ZnI_2
zb-CdSe	0.00	–0.08	–0.09
wz-CdSe	–0.01	–0.08	–0.09

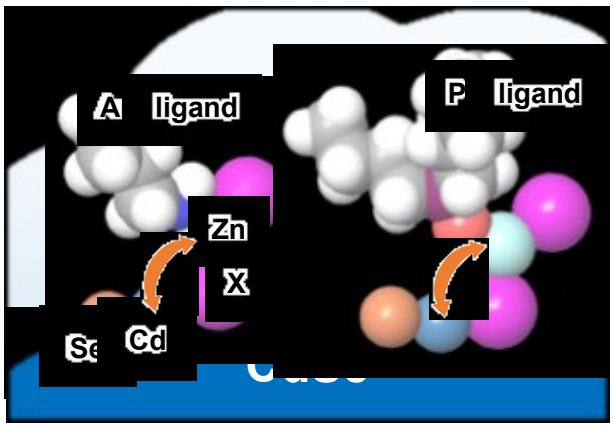

Figure S9. Simplified molecular model and schematic for cation exchange reaction between CdSe and ZnX2-ligand complex.

Table S2. Electrostatic potential (ESP) derived partial charge @ halogen species in ZnX_2-ligand complexes

	ZnCl2	ZnBr2	ZnI2
No-ligand	–0.57	–0.52	–0.46
Am-ligand	–0.61	–0.56	–0.50
PO-ligand	–0.65	–0.60	–0.55

Table S3. PL QY and FWHM of CdSe/ZnSe NCs reacted with ZnI_2+OLAm, ZnI_2+TOPO, and ZnI_2+TOPO+OLAm

	PL QY	FWHM
OLAm-ZnI2	55%	56 nm
TOPO-ZnI2	35%	40 nm
TOPO-ZnI2+OLAm	60%	41 nm

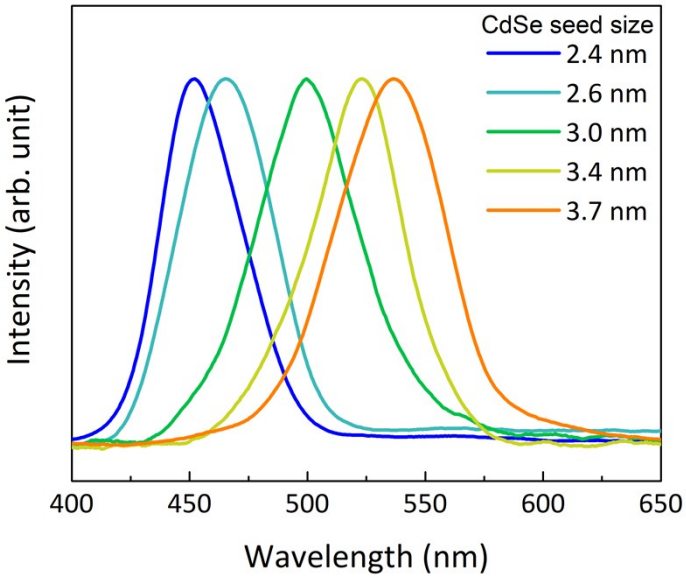

Figure S10. PL spectra of CdSe/ZnSe NCs cation-exchanged with different sizes of CdSe NCs. PL intensity was normalized at the points of the respective photoluminescence peak positions.

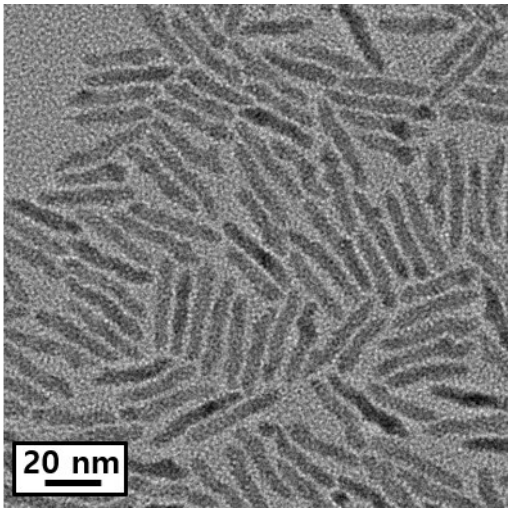

Figure S11. TEM image of CdSe NRs before cation exchange reaction

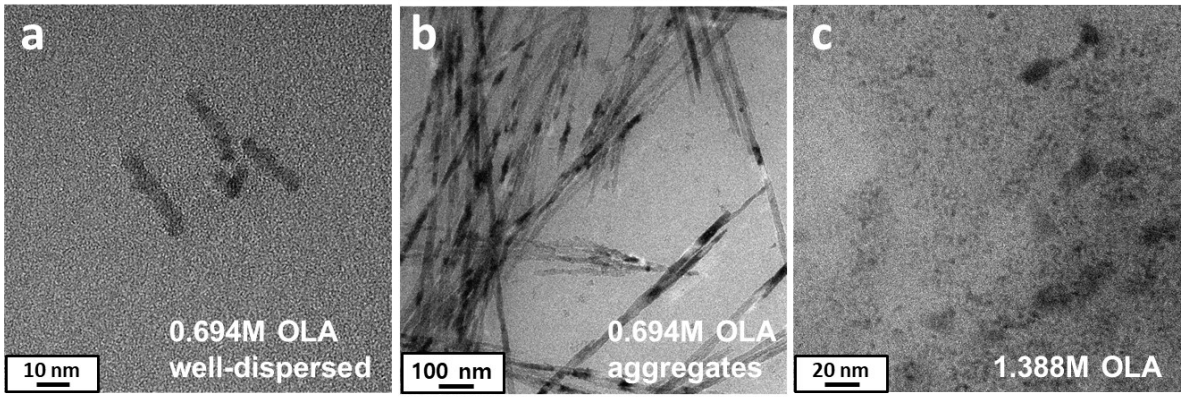

Figure S12. TEM images when (a, b) 0.694 M or (c) 1.388 M OLAm with 0.694 M ZnI_2 were used for cation exchange of CdSe NRs. (a) and (b) images are well-dispersed products that were obtained *via* arrested precipitation and aggregates that were produced during cation exchange reaction, respectively.

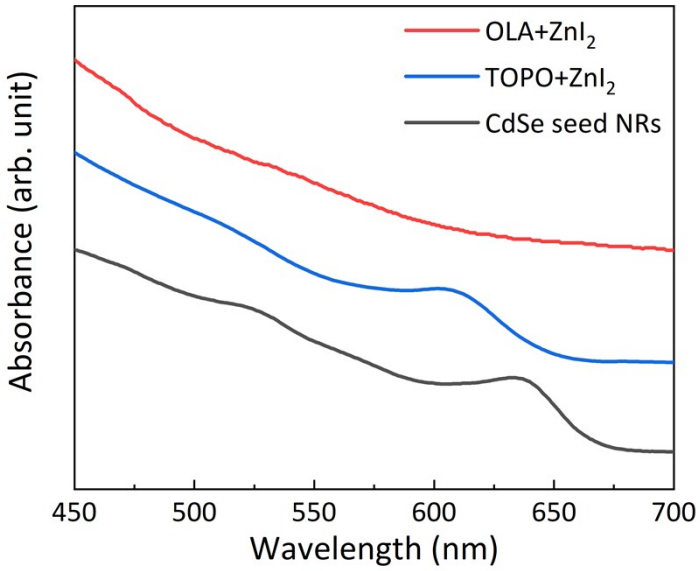

Figure S13. UV-vis spectra of CdSe NRs, CdSe/ZnSe cation-exchanged with 0.694 M TOPO+ZnI_2 or OLAm+ZnI_2 for 3 h at 300 °C.

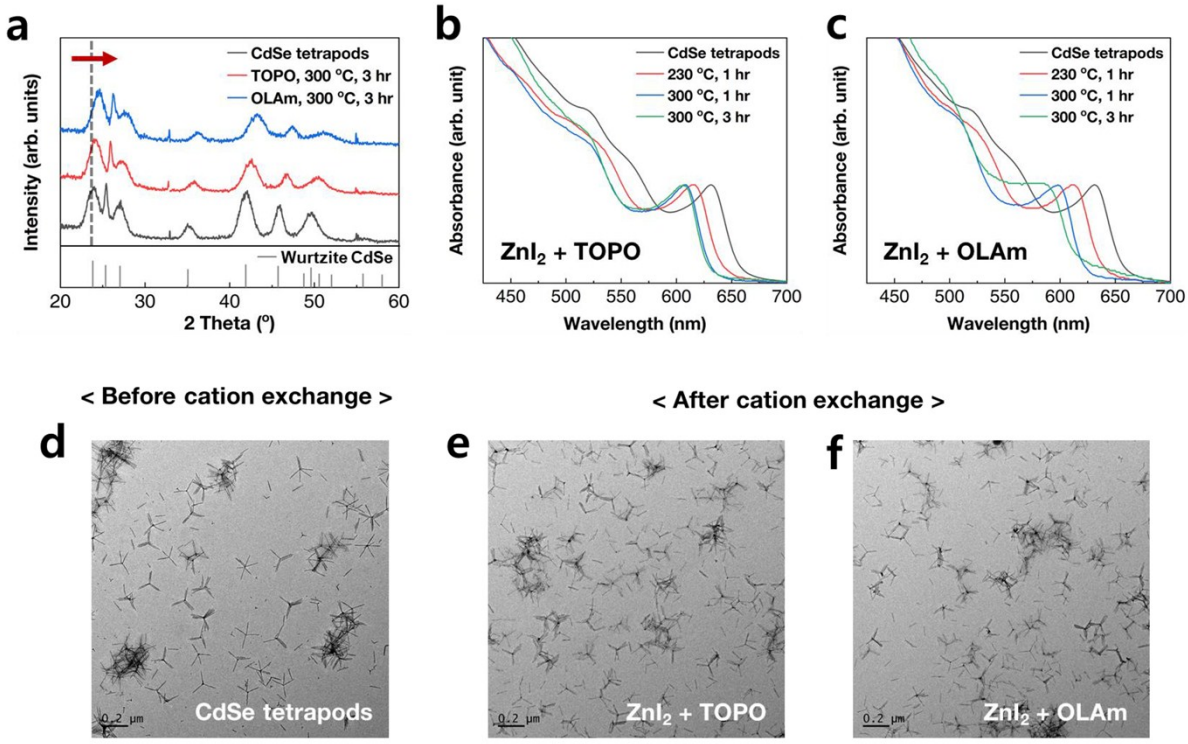

Figure S14. (a) XRD patterns and (b)-(c) UV-vis absorption spectra of CdSe tetrapods before and after cation exchange reaction using 0.694 M TOPO or OLAm with ZnI_2. (d)-(f) TEM images of CdSe tetrapods before and after cation exchange reaction.

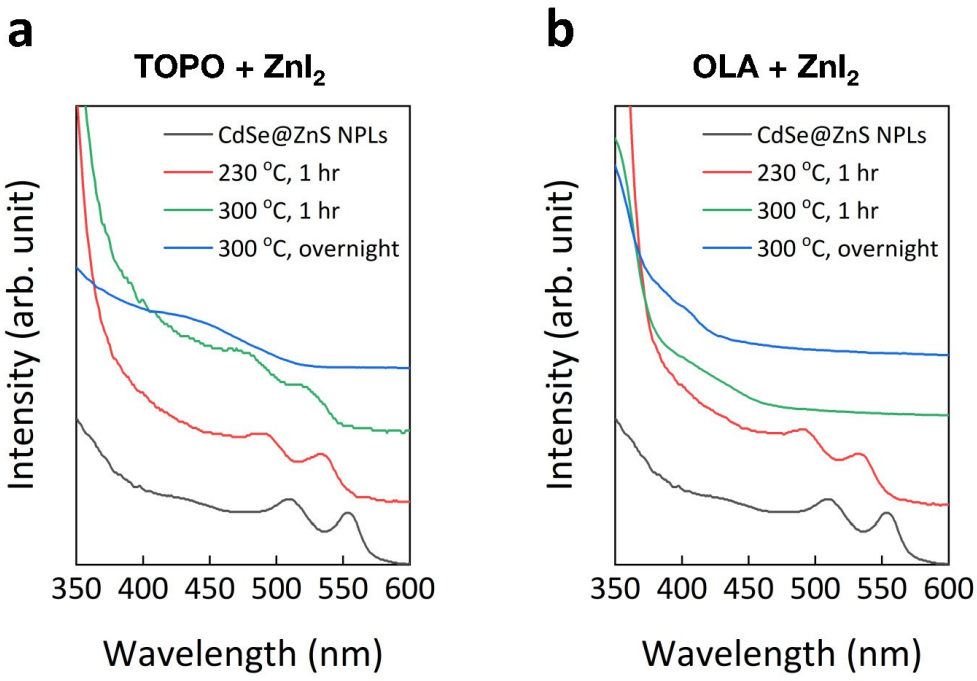

Figure S15. UV-vis spectra of CdSe/ZnS core/shell NPLs cation-exchanged using 0.694 M ZnI_2 with (a) TOPO or (b) OLAm.

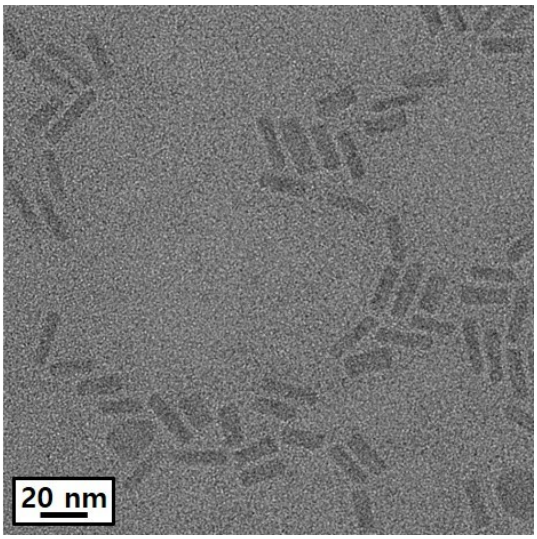

Figure S16. TEM image of CdSe/ZnS core/shell NPLs before cation exchange reaction