

# Bound-ion Pair X-type Ligation of Cadmium and Zinc Dithiocarbamates on Cadmium Selenide Quantum Belts

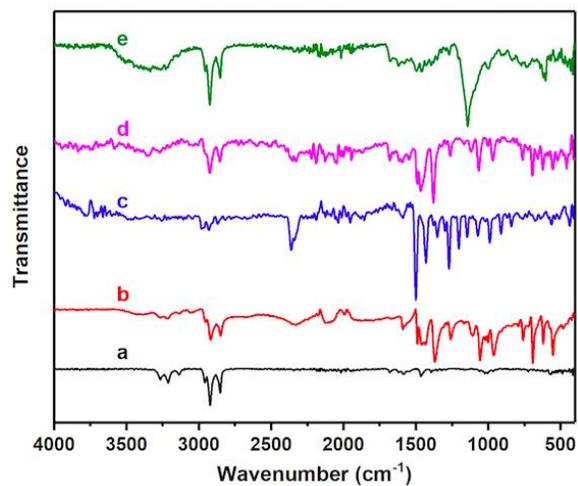
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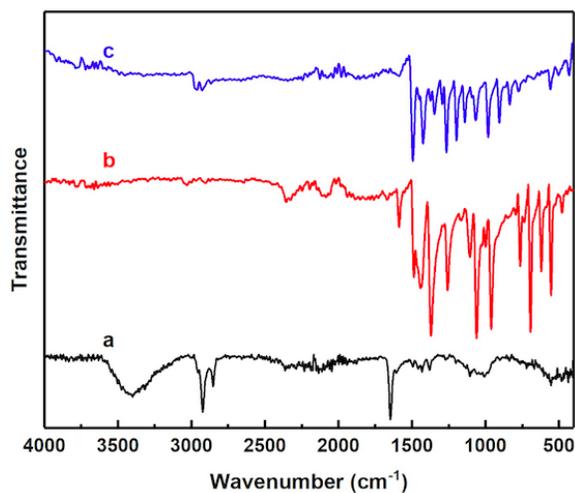
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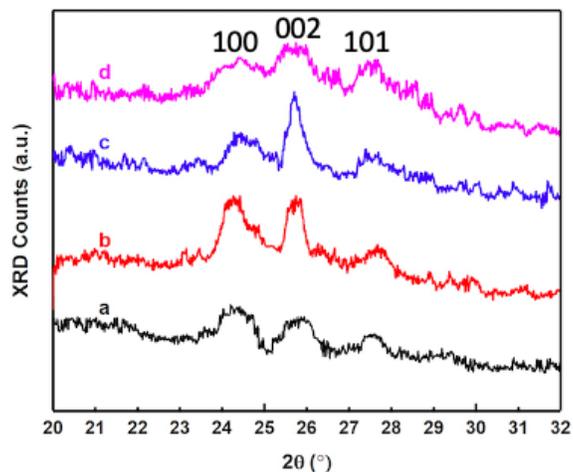
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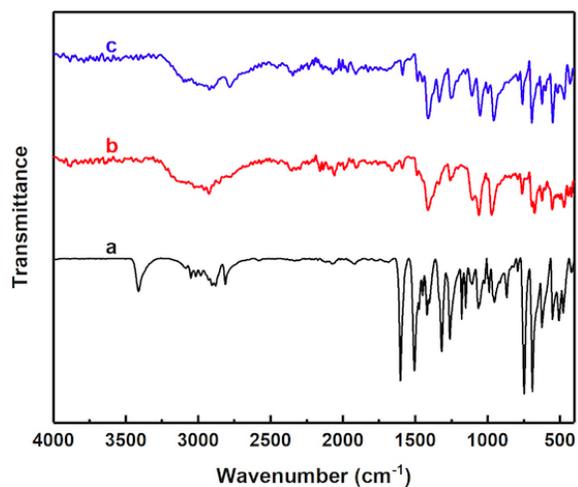
**Figure S1.** IR spectra of CdSe QBs ligated with (a) octylamine, or after ligand exchange: (b) Cd(S<sub>2</sub>CNPhMe)<sub>2</sub>; (c) Cd(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>; (d) Zn(S<sub>2</sub>CNPhMe)<sub>2</sub>; and (e) Zn(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>.



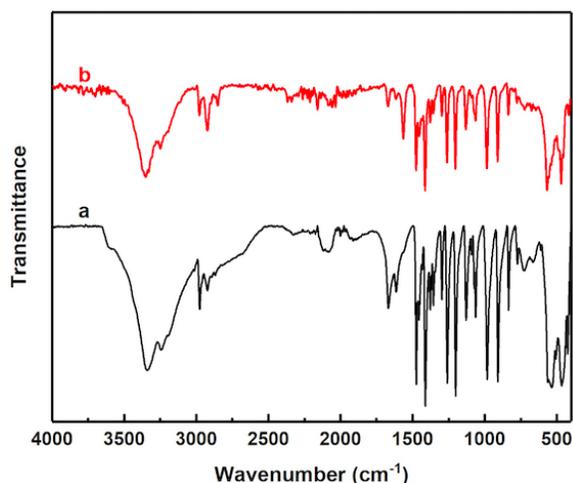
**Figure S2.** IR spectra of CdSe QBs ligated with (a) ammonia, or after ligand exchange: (b) Cd(S<sub>2</sub>CNPhMe)<sub>2</sub> and (c) Cd(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>.



**Figure S3.** XRD patterns of CdSe QDs ligated with (a)  $\text{Cd}(\text{S}_2\text{CNPhMe})_2$ ; (b)  $\text{Cd}(\text{S}_2\text{CNEt}_2)_2$ ; (c)  $\text{Zn}(\text{S}_2\text{CNPhMe})_2$ ; and (d)  $\text{Zn}(\text{S}_2\text{CNEt}_2)_2$ . The prominent low-angle features are indexed at the top of the figure.



**Figure S4.** IR spectra of (a)  $[\text{NH}_4][\text{PhMeNCS}_2]$  (b)  $\{\text{CdSe}[\textit{n}\text{-octylamine}]_{0.53}\}$  QDs after ligand exchange to  $[\text{NH}_4][\text{PhMeNCS}_2]$  ligation (c)  $\{\text{CdSe}[\text{Cd}(\text{oleate})_2]_{0.19}\}$  QDs after ligand exchange to  $[\text{NH}_4][\text{PhMeNCS}_2]$  ligation.



**Figure S5.** IR spectra of (a)  $[\text{Na}][\text{Et}_2\text{NCS}_2]$  (b)  $\{\text{CdSe}[\text{Cd}(\text{oleate})_2]_{0.19}\}$  QBs after ligand exchange to  $[\text{Na}][\text{Et}_2\text{NCS}_2]$  ligation.

**Table S1. Compressive Strain of CdSe QBs Induced by Various Ligands.**

QB Specimen	$a$ (Å)	contraction in $a$ (%)	$c$ (Å)	contraction in $c$ (%)
bulk CdSe <sup>a</sup>	4.30	-	7.02	-
CdSe[Cd(S <sub>2</sub> CNPhMe) <sub>2</sub> ] <sub>0.20</sub>	4.23	1.6	6.93	1.1
CdSe[Cd(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> ] <sub>0.19</sub>	4.25	1.1	6.93	1.1
CdSe[Zn(S <sub>2</sub> CNPhMe) <sub>2</sub> ] <sub>0.24</sub>	4.21	2.1	6.93	1.1
CdSe[Zn(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> ] <sub>0.23</sub>	4.23	1.6	6.93	1.1
octylamine/ oleylamine <sup>b</sup>	4.15	3.4	6.90	1.6
Cd(oleate) <sub>2</sub> <sup>b</sup>	4.26	0.9	7.02	0
Zn(oleate) <sub>2</sub> <sup>b</sup>	4.22	1.9	6.97	0.7
(Br) <sub>x</sub> (Na) <sub>y</sub> <sup>c</sup>		1.2		
(Cl) <sub>x</sub> (Na) <sub>y</sub> <sup>c</sup>		1.9		
(OAc) <sub>x</sub> (Na) <sub>y</sub> <sup>c</sup>		2.3		
(OBz) <sub>x</sub> (Na) <sub>y</sub> <sup>c</sup>		3.3		
(NO <sub>3</sub> ) <sub>x</sub> (Na) <sub>y</sub> <sup>c</sup>		2.3		

<sup>a</sup>This datum was taken from reference S1. <sup>b</sup>These data were taken from reference S2. <sup>c</sup>These data were taken from reference S3.

**Sample Purification for XRD and Elemental Analysis.**  $\{\text{CdSe}[\text{M}(\text{S}_2\text{CNR}_1\text{R}_2)_2]_x\}$  QB samples for characterization by XRD and elemental analysis were prepared from  $\{\text{CdSe}[\text{Cd}(\text{oleate})_2]_{0.19}\}$  QBs by the addition of the metal dithiocarbamate compound (5 mg) to the dispersion of QBs in toluene (2 mL, for  $\text{Cd}(\text{S}_2\text{CNEt}_2)_2$ ,  $\text{Zn}(\text{S}_2\text{CNPhMe})_2$ , and  $\text{Zn}(\text{S}_2\text{CNEt}_2)_2$ ) or  $\text{CH}_2\text{Cl}_2$  (2 mL, for  $\text{Cd}(\text{S}_2\text{CNPhMe})_2$ ), which were lightly shaken to dissolve the  $\text{M}(\text{S}_2\text{CNR}_1\text{R}_2)_2$ . The dispersion was centrifuged at 2000 rpm for 2 min. The supernatant was removed and placed into a new test tube. The pellet (excess  $\text{M}(\text{S}_2\text{CNR}_1\text{R}_2)_2$ ) was discarded. This process was repeated once more. Then, the solvent was removed under vacuum. If the dispersion became cloudy during the solvent evaporation, the purification process was repeated.

The purification procedure described above did not remove the  $\text{Cd}(\text{oleate})_2$  byproduct of ligand exchange. On the basis of prior experience,<sup>S3</sup> bound-ion-pair X-type ligation to CdSe QBs is comparatively weak, and readily depleted by washing. The washing (redispersion) steps required to remove the  $\text{Cd}(\text{oleate})_2$  byproduct would have removed some of the  $\text{M}(\text{S}_2\text{CNR}_1\text{R}_2)_2$  ligation, which would have given incorrect ligation stoichiometries determined by elemental analysis. Our fitting of the elemental-analysis data accounted for the  $\text{Cd}(\text{oleate})_2$  contamination (see **Fitting the Elemental Analysis Data** below).

An additional purification step was necessary to remove excess  $\text{Cd}(\text{S}_2\text{CNPhMe})_2$  from the  $\{\text{CdSe}[\text{Cd}(\text{S}_2\text{CNPhMe})_2]_x\}$  QBs. After the purification procedure described above, the QBs were redispersed in toluene (2 mL). The dispersion was centrifuged (2000 rpm for 2 min), the pellet of precipitated  $\{\text{CdSe}[\text{Cd}(\text{S}_2\text{CNPhMe})_2]_x\}$  QBs was collected, and the supernatant was discarded. The pellet was dried under vacuum.

**Table S2. Combustion-based Elemental Analysis Data.<sup>a</sup>**

<b>CdSe[Cd(S<sub>2</sub>CNPhMe)<sub>2</sub>]<sub>0.20±0.05</sub> + 0.10[Cd(oleate)<sub>2</sub>]</b>	<b>C (%)</b>	<b>H (%)</b>	<b>N (%)</b>	<b>S (%)</b>
calc'd	22.81	2.78	1.52	6.97
found	23.76	3.36	1.65	7.26
<b>CdSe[Cd(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>]<sub>0.19±0.05</sub> + 0.63[Cd(oleate)<sub>2</sub>]</b>	<b>C (%)</b>	<b>H (%)</b>	<b>N (%)</b>	<b>S (%)</b>
calc'd	42.63	6.33	0.77	3.52
found	43.98	7.72	2.33	3.72
<b>CdSe[Zn(S<sub>2</sub>CNPhMe)<sub>2</sub>]<sub>0.24±0.05</sub> + 0.71[Cd(oleate)<sub>2</sub>]</b>	<b>C (%)</b>	<b>H (%)</b>	<b>N (%)</b>	<b>S (%)</b>
calc'd	45.62	6.60	0.87	3.98
found	48.06	7.35	1.30	4.19
<b>CdSe[Zn(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>]<sub>0.23±0.05</sub> + 0.54[Cd(oleate)<sub>2</sub>]</b>	<b>C (%)</b>	<b>H (%)</b>	<b>N (%)</b>	<b>S (%)</b>
calc'd	40.99	6.00	1.01	4.63
found	42.39	7.01	2.59	4.73

<sup>a</sup>As noted in the sample-purification section above, the Cd(oleate)<sub>2</sub> byproduct was not removed from these specimens to prevent the loss of ligated M(S<sub>2</sub>CNR<sub>1</sub>R<sub>2</sub>)<sub>2</sub> and to allow a correct analysis of binding stoichiometric by elemental analysis. The fitting procedure described below explains how the amounts of M(S<sub>2</sub>CNR<sub>1</sub>R<sub>2</sub>)<sub>2</sub> and Cd(oleate)<sub>2</sub> in the specimens were separately determined.

**Fitting the Elemental Analysis Data.** The stoichiometry of  $M(S_2CNR_1R_2)_2$  ligation in each specimen was determined from the %S values in the elemental-analysis data. The excess carbon was assigned to  $Cd(oleate)_2$ , and the amount of  $Cd(oleate)_2$  byproduct in the sample was determined from this excess carbon. The mass of  $CdSe$  was taken to be that less the  $M(S_2CNR_1R_2)_2$  and  $Cd(oleate)_2$  in the specimen, which was then converted to moles of  $CdSe$ . The empirical formula for the specimen was then constructed from these values. Example calculations are given below.

**Example calculation of empirical formula from elemental-analysis data: determining the empirical formula of  $CdSe[Cd(S_2CNEt_2)_2]_{0.19 \pm 0.05} + 0.63[Cd(oleate)_2]$**

Assume the mass of the sample is 100 g.

moles of  $Cd(S_2CNEt_2)_2 = n_{X(S)} = 3.72 \text{ g} / 4(32.066 \text{ g/mol}) = 0.029 \text{ mol}$  (S1), where  $n_{X(S)}$  denotes moles of  $Cd(S_2CNEt_2)_2$  determined from the %S from the elemental-analysis data.

carbon from  $Cd(S_2CNEt_2)_2 = 0.029 \text{ mol} (16 \times 12.011 \text{ g/mol}) = 3.48 \text{ g}$  (S2)

carbon from  $Cd(oleate)_2 = 43.98 \text{ g} - 3.48 \text{ g} = 40.5 \text{ g}$  (S3)

moles of  $Cd(oleate)_2 = n_{Y(C)} = 40.5 \text{ g} / 36(12.011 \text{ g/mol}) = 0.09375 \text{ mol}$  (S4), where  $n_{Y(C)}$  denotes moles of  $Cd(oleate)_2$  extracted from the %C from the elemental-analysis data, as indicated above.

mass of Cd from  $Cd(S_2CNEt_2)_2$  and  $Cd(oleate)_2 = (0.029 + 0.09375) 112.411 \text{ g} = 13.748 \text{ g}$  (S5)

mass of  $CdSe = 100 - C - H - S - N - 13.748 = 28.502 \text{ g}$  (S6)

moles of  $CdSe = 28.502 \text{ g} / 191.371 \text{ g/mol} = 0.149 \text{ mol}$  (S7)

$0.149 / 0.149 = 1$ ;  $0.029 / 0.149 = 0.19$ ;  $0.09375 / 0.149 = 0.63$  (S8)

Thus the ratio of  $\text{Cd}(\text{S}_2\text{CNEt}_2)_2$  and  $\text{Cd}(\text{oleate})_2$  to  $\text{CdSe}$  is 0.19 and 0.63, respectively. So the empirical formula is  $\text{CdSe}[\text{Cd}(\text{S}_2\text{CNEt}_2)_2]_{0.19\pm 0.05} + 0.63[\text{Cd}(\text{oleate})_2]$ .

**Example calculation of empirical formula from elemental-analysis data: determining the empirical formula of  $\text{CdSe}[\text{Zn}(\text{S}_2\text{CNPhMe})_2]_{0.24\pm 0.05} + 0.71[\text{Cd}(\text{oleate})_2]$**

Assume the mass of the sample is 100 g.

moles of  $\text{Zn}(\text{S}_2\text{CNPhMe})_2 = n_{\text{X}(\text{s})} = 4.19 \text{ g} / 4(32.066 \text{ g/mol}) = 0.0327 \text{ mol}$  (S9), where  $n_{\text{X}(\text{s})}$  denotes moles of  $\text{Zn}(\text{S}_2\text{CNPhMe})_2$  determined from the %S from the elemental-analysis data.

carbon from  $\text{Zn}(\text{S}_2\text{CNPhMe})_2 = 0.0327 \text{ mol} (10 \times 12.011 \text{ g/mol}) = 6.2784 \text{ g}$  (S10)

carbon from  $\text{Cd}(\text{oleate})_2 = 48.06 \text{ g} - 6.2784 \text{ g} = 41.7816 \text{ g}$  (S11)

moles of  $\text{Cd}(\text{oleate})_2 = n_{\text{Y}(\text{c})} = 41.7816 \text{ g} / 36 (12.011 \text{ g/mol}) = 0.09671667 \text{ mol}$  (S12), where  $n_{\text{Y}(\text{c})}$  denotes moles of  $\text{Cd}(\text{oleate})_2$  extracted from the %C from the elemental-analysis data, as indicated above.

mass of Cd from  $\text{Cd}(\text{oleate})_2 = (0.09375) 112.411 \text{ g} = 10.83 \text{ g}$  (S13)

mass of Zn from  $\text{Zn}(\text{S}_2\text{CNPhMe})_2 = 65.39 \text{ g} (0.0327) = 2.138253 \text{ g}$  (S14)

mass of  $\text{CdSe} = 100 - \text{C} - \text{H} - \text{S} - \text{N} - 10.83 - 2.138253 = 26.132 \text{ g}$  (S15)

moles of  $\text{CdSe} = 26.132 \text{ g} / 191.371 \text{ g} = 0.137 \text{ mol}$  (S16)

$0.137 / 0.1368 = 1$ ;  $0.0327 / 0.137 = 0.24$ ;  $0.09671667 / 0.137 = 0.71$  (S17)

Thus the ratio of  $\text{Zn}(\text{S}_2\text{CNPhMe})_2$  and  $\text{Cd}(\text{oleate})_2$  to  $\text{CdSe}$  is 0.24 and 0.71, respectively. So the empirical formula is  $\text{CdSe}[\text{Zn}(\text{S}_2\text{CNPhMe})_2]_{0.24\pm 0.05} + 0.71[\text{Cd}(\text{oleate})_2]$ .

Error in the elemental analysis measurements via combustion-based analysis should have been determined from multiple analyses, which we did not have here. Prior such analyses have given errors of order  $\pm 0.05$  in the subscripts for ligation.<sup>S4,S5,S6</sup> We assumed that value here.

Error in compositional data measured by EDS were the standard deviations from multiple measurements of the same specimen.

The amount of Cd(oleate)<sub>2</sub> contaminant was excluded from the empirical formulas of the {CdSe[M(S<sub>2</sub>CNR<sub>1</sub>R<sub>2</sub>)<sub>2</sub>]<sub>x</sub>} QBs in the main text.

### **Additional References**

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