



17.8 (d,  $^2J_{C-P} = 14.1$  Hz,  $CH_3$ - $iPr$ ), 23.5 ( $CH_2$ -piperidine), 25.3 ( $CH_2$ -piperidine), 29.3 (d,  $^1J_{C-P} = 50.2$  Hz,  $CH$ - $iPr$ ), 46.3 (N $CH_2$ -piperidine), 178.7 (CS). FTIR (KBr,  $cm^{-1}$ ):  $\nu = 3226$  v(NH), 2959, 2927, 2854 v(CH), 1487, 1443, 1297, 1123, 657 v(CN/NH/CS), 944 v(PN), 539 v(PSe). EI (m/z): 341 corresponding to  $^iPr_2P(Se)NHC(S)NC_5H_{10}$ . Microanalysis calculated for  $C_{12}H_{25}N_2SeSP$ : N = 8.26, C = 42.47, H = 7.43 %. Observed: N = 8.29, C = 42.57, H = 7.48 %.

**$^iPr_2P(Se)NHC(O)NC_5H_{10}$  (2).** Piperidine (3.95 mL, 40 mmol) and  $^iPr_2P(Se)NC(O)$  (9.52 g, 40 mmol). White solid. Yield: 10.51 g (85%). M.p. 77-79 °C.  $^{31}P\{^1H\}$  NMR ( $C_6D_6$ , 298 K, 121.65 MHz, ppm):  $\delta = 106.8$  (s) ( $^1J_{P-Se} = 751.8$  Hz).  $^{77}Se\{^1H\}$  NMR ( $C_6D_6$ , 298 K, 57.28 MHz, ppm):  $\delta = -469.4$  ( $^1J_{Se-P} = 751.8$  Hz).  $^1H$  NMR ( $C_6D_6$ , 298 K, 300 MHz, ppm):  $\delta = 1.00$  (br, 6H,  $CH_2$ -piperidine), 1.19 (2dd,  $CH_3$ - $iPr^a$   $^3J_{H-H} = 6$  Hz,  $CH_3$ - $iPr^a$   $^3J_{H-P} = 15$  Hz,  $CH_3$ - $iPr^b$   $^3J_{H-H} = 6$  Hz,  $CH_3$ - $iPr^b$   $^3J_{H-P} = 21$  Hz, 12H), 2.81 (br, 4H, N $CH_2$ -piperidine), 3.01 (dsep,  $^2J_{H-H} = 6.0$  Hz,  $^2J_{H-P} = 9$  Hz, 2H,  $CH$ - $iPr$ ), 5.11 (s, NH).  $^{13}C\{^1H\}$  NMR ( $C_6D_6$ , 298 K, 75.56 MHz, ppm):  $\delta = 17.6$  (d,  $^2J_{C-P} = 16.05$  Hz,  $CH_3$ - $iPr$ ), 24.2 ( $CH_2$ -piperidine), 24.1 ( $CH_2$ -piperidine), 25.8 ( $CH_2$ -piperidine), 29.1 (d,  $^1J_{C-P} = 50.2$  Hz,  $CH$ - $iPr$ ), 45.7 (N $CH_2$ -piperidine), 153.73 (CO). FTIR (KBr,  $cm^{-1}$ ):  $\nu = 3239$  v(NH), 2964, 2936, 2855 v(CH), 1436, 1227, 1024, 663 v(CN/NH), 1624 v(CO), 930 v(PN), 531 v(PSe). DART+ (m/z): 323 corresponding to  $^iPr_2P(Se)NHC(O)NC_5H_{10}$ . Microanalysis calculated for  $C_{12}H_{25}N_2SeOP$ : N = 8.67, C = 44.58, H = 7.79 %. Observed: N = 8.59, C = 44.49, H = 7.84 %.

**$[Zn\{^iPr_2P(Se)NC(S)NC_5H_{10-\kappa^2-Se,S}\}_2]$  (3).** 2.9 mmol of **1** and 1.45 mmol of  $ZnEt_2$ . White solid. Yield: 0.98 g (89%). M.p. 122-124 °C.  $^{31}P\{^1H\}$  NMR ( $C_6D_6$ , 298 K, 121.65 MHz, ppm):  $\delta = 61.8$  (s) ( $^1J_{P-Se} = 524.31$  Hz).  $^{77}Se\{^1H\}$  NMR ( $C_6D_6$ , 298 K, 57.28 MHz, ppm):  $\delta = -330.0$  ( $^1J_{Se-P} = 524.31$  Hz).  $^1H$  NMR ( $C_6D_6$ , 298 K, 300 MHz, ppm):  $\delta = 1.12$ -1.20 (m, 24H,  $CH_3$ - $iPr$ ), 1.23 (br, 4H,  $CH_2$ -piperidine), 1.33 (br, 8H,  $CH_2$ -piperidine), 2.21-2.40 (m, 4H,  $CH$ - $iPr$ ), 3.55 (br, 4H, N $CH_2$ -piperidine), 3.93 (br, 4H, N $CH_2$ -piperidine).  $^{13}C\{^1H\}$  ( $C_6D_6$ , 298 K, 75.56 MHz, ppm):  $\delta = 16.1$  ( $CH_3$ - $iPr$ ), 23.7 ( $CH_2$ -piperidine), 24.8 ( $CH_2$ -piperidine) 30.7 ( $CH$ - $iPr$ ), 45.6 (N $CH_2$ -piperidine), 48.9 (N $CH_2$ -piperidine), 174.3 (CS). FTIR (KBr,  $cm^{-1}$ ):  $\nu = 2961$ , 2928, 2864 v(CH), 1493, 1433, 1408, 1217 v(CN/CS), 968 v(PN), 509 v(PSe). EI (m/z): 741 corresponding to  $[Zn\{^iPr_2P(Se)NC(S)NC_5H_{10-\kappa^2-Se,S}\}_2]^+$ . Microanalysis calculated for  $C_{24}H_{48}N_4Se_2S_2P_2Zn$ : N = 7.55, C = 38.85, H = 6.52%. Observed: N = 7.62, C = 38.69, H = 6.65%.

**$[Zn\{^iPr_2P(Se)NC(O)NC_5H_{10-\kappa^2-Se,O}\}_2]$  (4).** 3.1 mmol of **2** and 1.55 mmol of  $ZnEt_2$ . White solid. Yield: 0.90 g (87%). M.p. 113-115 °C.  $^{31}P\{^1H\}$  NMR ( $C_6D_6$ , 298 K, 121.65 MHz, ppm):  $\delta = 54.58$  (s) ( $^1J_{P-Se} = 488$  Hz).  $^{77}Se\{^1H\}$  NMR ( $C_6D_6$ , 298 K, 57.28 MHz, ppm):  $\delta = -370.55$  ( $^1J_{Se-P} = 488$  Hz).  $^1H$  NMR ( $C_6D_6$ , 298 K, 300 MHz, ppm): (2d,  $\delta = 1.33$ ,  $^3J_{H-H} = 7$ ,  $CH_3$ - $iPr^b$ ;  $\delta = 1.39$ ,  $^3J_{H-H} = 7$ ,  $CH_3$ - $iPr^a$ , 24H), 2.16 (oc, ,  $^3J_{H-H} = 7$  Hz,  $^2J_{H-P} = 7$  Hz, 4H,  $CH$ - $iPr$ ), 1.52 (br, 12H,  $CH_2$ -piperidine), 3.71 (br, 8H, N $CH_2$ -piperidine).  $^{13}C\{^1H\}$  ( $C_6D_6$ , 298 K, 75.56 MHz, ppm):  $\delta = 17.5$  (d,  $^2J_{C-P} = 2$  Hz,  $CH_3$ - $iPr^b$ ), 17.23 ( $CH_3$ - $iPr^a$ ), 25.39 ( $CH_2$ -piperidine), 25.45 ( $CH_2$ -piperidine), 31.65 (d,  $^1J_{C-P} = 54$  Hz,  $CH$ - $iPr$ ), 49.52 (N $CH_2$ -piperidine), 51.89 (N $CH_2$ -piperidine), 163 (CS). FTIR (KBr,  $cm^{-1}$ ):  $\nu = 2961$ , 2926, 2849 v(CH), 1429, 1289, 1020, 649 v(CN), 1476 v(CO), 914 v(PN), 526 v(PSe). DART+ (m/z): **711** corresponding to  $[Zn\{^iPr_2P(Se)NC(O)NC_5H_{10-\kappa^2-Se,O}\}_2]^+$ . Microanalysis calculated for  $C_{24}H_{48}N_4Se_2O_2P_2Zn$ : N = 7.89, C = 40.60, H = 6.82 %. Observed: N = 7.96, C = 40.65, H = 7.0 %.

**$[Cd\{^iPr_2P(Se)NC(S)NC_5H_{10-\kappa^2-Se,S}\}_2]$  (5).** 2.9 mmol of **1** and 1.45 mmol of  $CdMe_2$ . White solid. Yield: 1.08 g (95%). M.p. 119-121 °C.  $^{31}P\{^1H\}$  NMR ( $C_6D_6$ , 298 K, 121.65 MHz, ppm):  $\delta = 60.79$  (s) ( $^1J_{P-Se} = 524.0$  Hz).  $^{77}Se\{^1H\}$  NMR ( $C_6D_6$ , 298 K, 57.28 MHz, ppm):  $\delta = -337.7$  ( $^1J_{Se-P} = 523.0$  Hz).  $^1H$  NMR ( $C_6D_6$ , 298 K, 300 MHz, ppm): (2t,  $\delta = 1.14$ ,  $^3J_{H-H} = 7$ ,  $^3J_{H-P} = 7$   $CH_3$ - $iPr^b$ ;  $\delta = 1.20$ ,  $^3J_{H-H} = 7$ ,  $^3J_{H-P} = 7$   $CH_3$ - $iPr^a$ , 24H), 1.22 (br, 4H,  $CH_2$ -piperidine), 1.35 (br, 8H,  $CH_2$ -piperidine), 2.40 (dsep,  $^3J_{H-H} = 7.0$  Hz,  $^2J_{H-P} = 11$  Hz,  $CH$ - $iPr$ , 4H), 3.55 (br, 4H, N $CH_2$ -piperidine), 3.98 (br, 4H, N $CH_2$ -piperidine).  $^{13}C\{^1H\}$  NMR ( $C_6D_6$ , 298 K, 75.56 MHz, ppm): (2d,  $\delta = 16.16$ ,  $^2J_{C-P} = 4$  Hz,  $CH_3$ - $iPr^b$ ;  $\delta = 16.42$ ,  $^2J_{C-P} = 2$  Hz,  $CH_3$ - $iPr^a$ ), 23.80 ( $CH_2$ -piperidine), 25.0

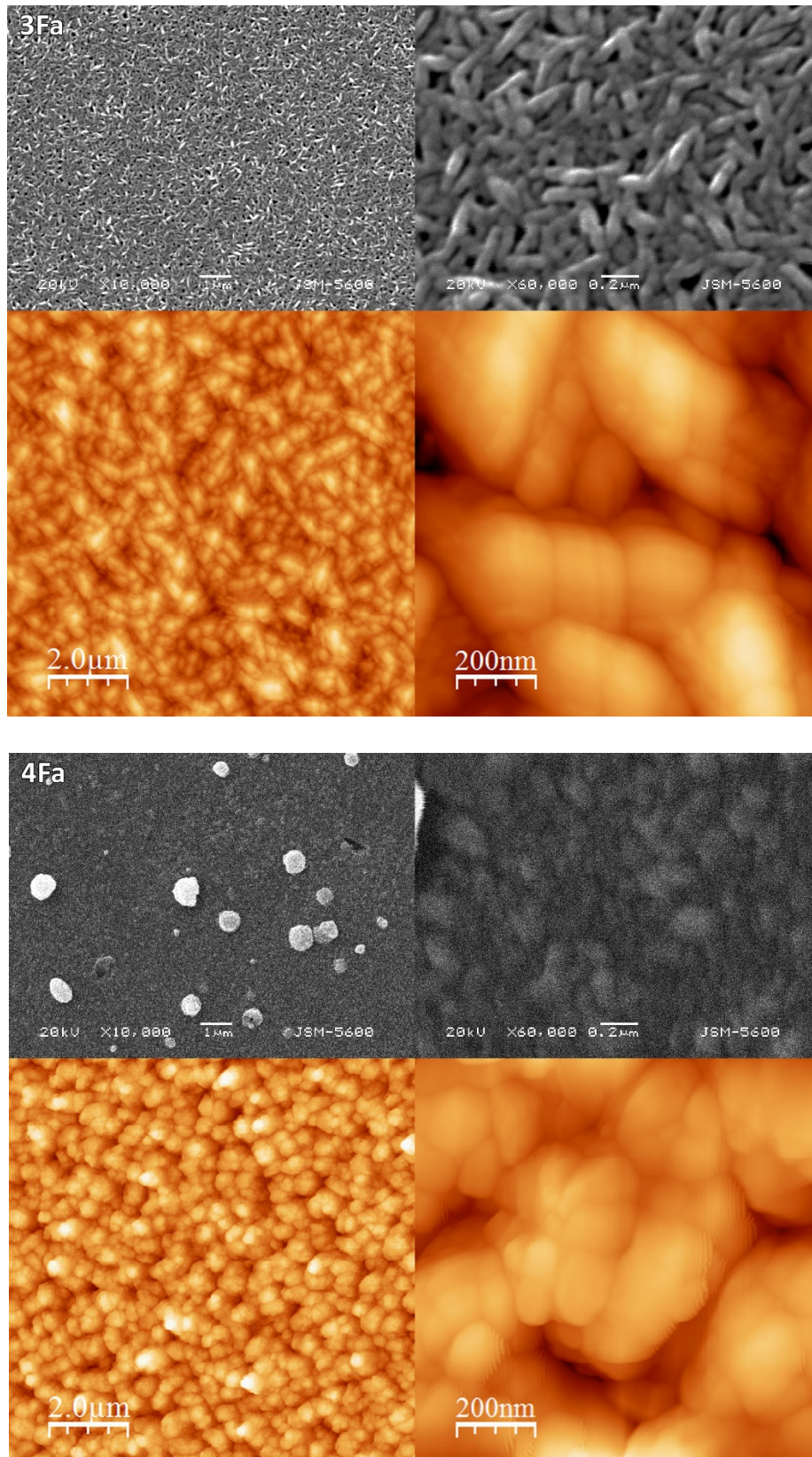
(CH<sub>2</sub>-piperidine), 31.14 (d, <sup>1</sup>J<sub>C-P</sub> = 63 Hz, CH-<sup>i</sup>Pr), 45.80 (NCH<sub>2</sub>-piperidine), 48.88 (NCH<sub>2</sub>-piperidine), 174.19 (CSe). FTIR (KBr, cm<sup>-1</sup>): ν = 2962, 2929, 2864 ν(CH), 1487, 1433, 1404, 1215 ν(CN/CS), 966 ν(PN), 511 ν(PSe). DART+ (m/z): 789 corresponding to [Cd{<sup>i</sup>Pr<sub>2</sub>P(Se)NC(S)NC<sub>5</sub>H<sub>10</sub>-κ<sup>2</sup>-Se,S}<sub>2</sub>]<sup>+</sup>. Microanalysis calculated for C<sub>24</sub>H<sub>48</sub>N<sub>4</sub>Se<sub>2</sub>S<sub>2</sub>P<sub>2</sub>Cd: N = 7.1, C = 36.53, H = 6.13 %. Observed: N = 7.19, C = 36.39, H = 6.23 %.

**[Cd{<sup>i</sup>Pr<sub>2</sub>P(Se)NC(O)NC<sub>5</sub>H<sub>10</sub>-κ<sup>2</sup>-Se,O}<sub>2</sub>] (6).** 3.1 mmol of **2** and 1.55 mmol of CdMe<sub>2</sub>. White solid. Yield: 1.09 g (93%). M.p. 120-122 °C. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K, 121.65 MHz, ppm): δ = 52.63 (s) (<sup>1</sup>J<sub>P-Se</sub> = 476.70 Hz). <sup>77</sup>Se{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K, 57.28 MHz, ppm): δ = -366.4 (<sup>1</sup>J<sub>Se-P</sub> = 475 Hz). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K, 300 MHz, ppm): (4d, δ = 1.11, <sup>3</sup>J<sub>H-H</sub> = 7, CH<sub>3</sub>-<sup>i</sup>Pr<sup>d</sup>; δ = 1.16, <sup>3</sup>J<sub>H-H</sub> = 7, CH<sub>3</sub>-<sup>i</sup>Pr<sup>c</sup>; δ = 1.27, <sup>3</sup>J<sub>H-H</sub> = 7, CH<sub>3</sub>-<sup>i</sup>Pr<sup>b</sup>; δ = 1.33, <sup>3</sup>J<sub>H-H</sub> = 7, CH<sub>3</sub>-<sup>i</sup>Pr<sup>a</sup>), 1.43 (m, 12H, CH<sub>2</sub>-piperidine), 2.16 (dsep, <sup>3</sup>J<sub>H-H</sub> = 7.0 Hz, <sup>2</sup>J<sub>H-P</sub> = 9 Hz, CH-<sup>i</sup>Pr, 4H), 3.20 (m, 8H, NCH<sub>2</sub>-piperidine). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K, 75.56 MHz, ppm): δ = 16.70 (d, <sup>2</sup>J<sub>C-P</sub> = 3 Hz, CH<sub>3</sub>-<sup>i</sup>Pr<sup>b</sup>), 17.08 (CH<sub>3</sub>-<sup>i</sup>Pr<sup>a</sup>), 25.15 (CH<sub>2</sub>-piperidine), 26.24 (CH<sub>2</sub>-piperidine), 32.12 (d, <sup>1</sup>J<sub>C-P</sub> = 66 Hz, CH-<sup>i</sup>Pr), 45.18 (NCH<sub>2</sub>-piperidine), 164.5 (CO). FTIR (KBr, cm<sup>-1</sup>): ν = 2959, 2926, 2848 ν(CH), 1429, 1280, 1026, 626 ν(CN), 1487 ν(CO), 916 ν(PN), 526 ν(PSe). DART+ (m/z): 759 corresponding to [Cd{<sup>i</sup>Pr<sub>2</sub>P(Se)NC(O)NC<sub>5</sub>H<sub>10</sub>}<sub>2</sub>]<sup>+</sup>. FAB+ (m/z): 1193 corresponding to [Cd<sub>2</sub>{<sup>i</sup>Pr<sub>2</sub>P(Se)NC(O)NC<sub>5</sub>H<sub>10</sub>}<sub>3</sub>]<sup>+</sup>. Microanalysis calculated for C<sub>48</sub>H<sub>96</sub>Cd<sub>2</sub>N<sub>8</sub>O<sub>4</sub>P<sub>4</sub>Se<sub>4</sub>: N = 7.40, C = 38.08, H = 6.39%. Observed: N = 7.33, C = 37.97, H = 6.45%.

## 2. Table S1. Crystallographic Data for compounds **4**, **5** and **6**.

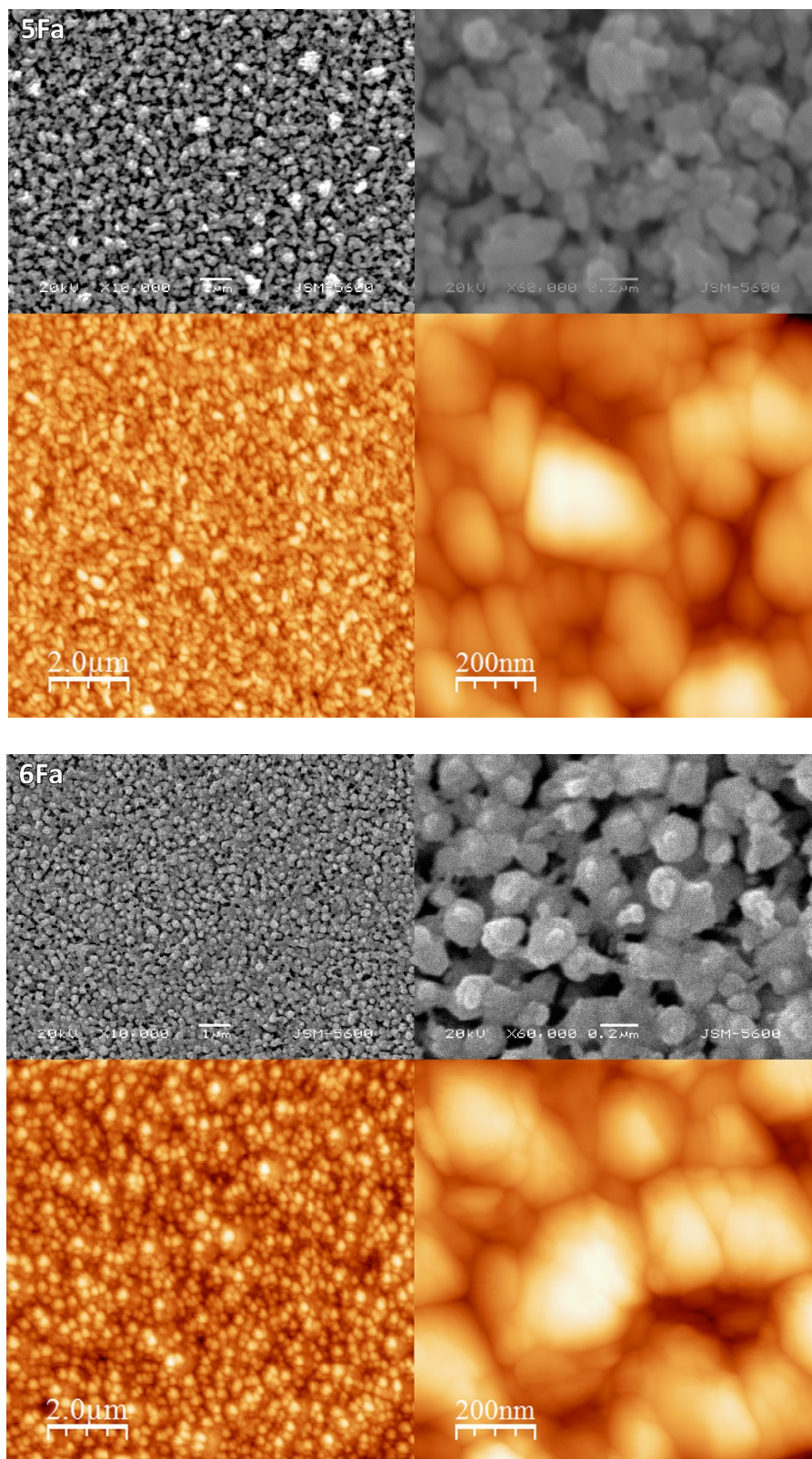
Compound	<b>4</b>	<b>5</b>	<b>6</b>
Formula	C <sub>24</sub> H <sub>48</sub> N <sub>4</sub> O <sub>2</sub> P <sub>2</sub> Se <sub>2</sub> Zn	C <sub>24</sub> H <sub>48</sub> CdN <sub>4</sub> P <sub>2</sub> S <sub>2</sub> Se <sub>2</sub>	C <sub>48</sub> H <sub>96</sub> Cd <sub>2</sub> N <sub>8</sub> O <sub>4</sub> P <sub>4</sub> Se <sub>4</sub>
M [g/mol]	709.89	789.04	1513.84
Temperature	298(2) K	298(2) K	298(2) K
Crystal size (mm)	0.402 x 0.309 x 0.156	0.437 x 0.372 x 0.114	0.287 x 0.211 x 0.140
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P -1 (2)	C 2/c (15)	P2 <sub>1</sub> /c (14)
ρ <sub>calc</sub> (g cm <sup>-3</sup> )	1.460	1.519	1.521
Z	2	4	2
a (Å)	9.0915(3)	16.1883(2)	11.8582(11)
b (Å)	11.0372(3)	17.1917(2)	13.3662(12)
c (Å)	16.6969(5)	13.48050(10)	21.3305(18)
α (°)	98.7490(10)	90.00	90.00
β (°)	91.2890(10)	113.1140(10)	102.189(5)
γ (°)	102.3670(10)	90.00	90.00
V (Å <sup>3</sup> )	1614.89(8)	3450.52(7)	3304.6(5)
μ (mm <sup>-1</sup> )	3.139	2.976	2.986
F(000)	728	1592	1528
Reflections Collected	14098	14591	18757
Unique reflections, R <sub>int</sub>	5929, 0.0222	3162, 0.0247	6020; 0.0361
R1, wR2 [I > 2σ(I)]	0.0290; 0.0664	0.0315, 0.0793	0.0359; 0.0569
R1, wR2 (all data)	0.0386; 0.0703	0.0397, 0.0840	0.0752; 0.0833
Goof	1.032	1.039	1.029

**3. Fig. S1.** Micrographs of annealed zinc thin films (**3Fa** and **4Fa**). **3Fa** SEM images (magn. 10000x and 60000x), AFM phase (1 x 1  $\mu\text{m}$ ) micrographs. **4Fa** SEM images (magn. 10000x and 60000x), and AFM phase (1 x 1  $\mu\text{m}$ ) micrographs.

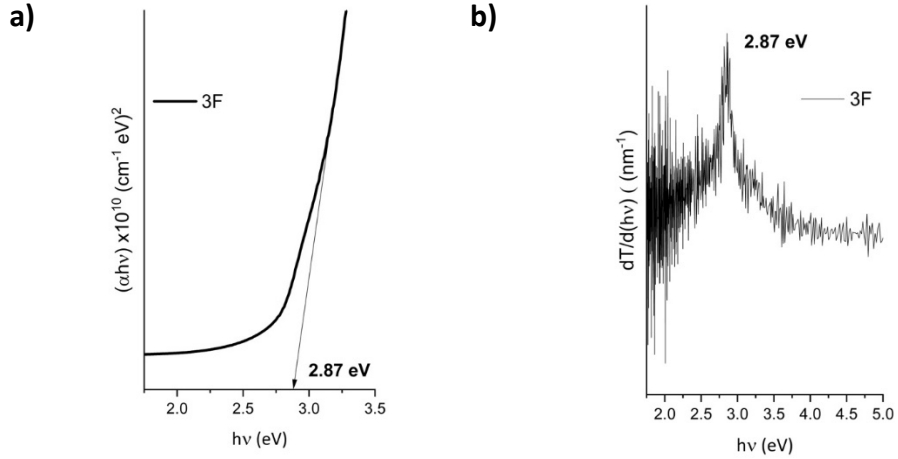




4. **Fig. S2.** Micrographs of annealed cadmium thin films (**5Fa** and **6Fa**). **5Fa** SEM images (magn. 10000x and 60000x), AFM phase (1 x 1  $\mu\text{m}$ ) micrographs. **6Fa** SEM images (magn. 10000x and 60000x), and AFM phase (1 x 1  $\mu\text{m}$ ) micrographs.



5. **Fig. S3.** Optical band gap ( $E_g$ ) estimation. Example of a)  $(\alpha hv)^2$  versus photon energy ( $hv$ ) plot for as-deposited Zn<sub>1.41</sub>So<sub>0.40</sub>Se<sub>0.60</sub> film (**3F**, as-deposited at 450°C) and b) the first derivative plot of transmittance spectra ( $dT/d(hv)$ ).



a) The optical band gap ( $E_g$ ) were estimated using Tauc's relationship:<sup>4</sup>

$$\alpha hv = B(hv - E_g)^{1/m} \quad (4)$$

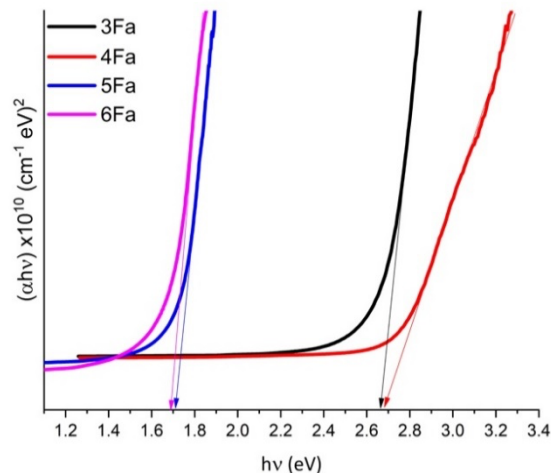
$$\alpha = -\frac{1}{t} \ln T \quad (5)$$

$$E_{\text{phonon}} = \frac{hc}{\lambda} \quad (6)$$

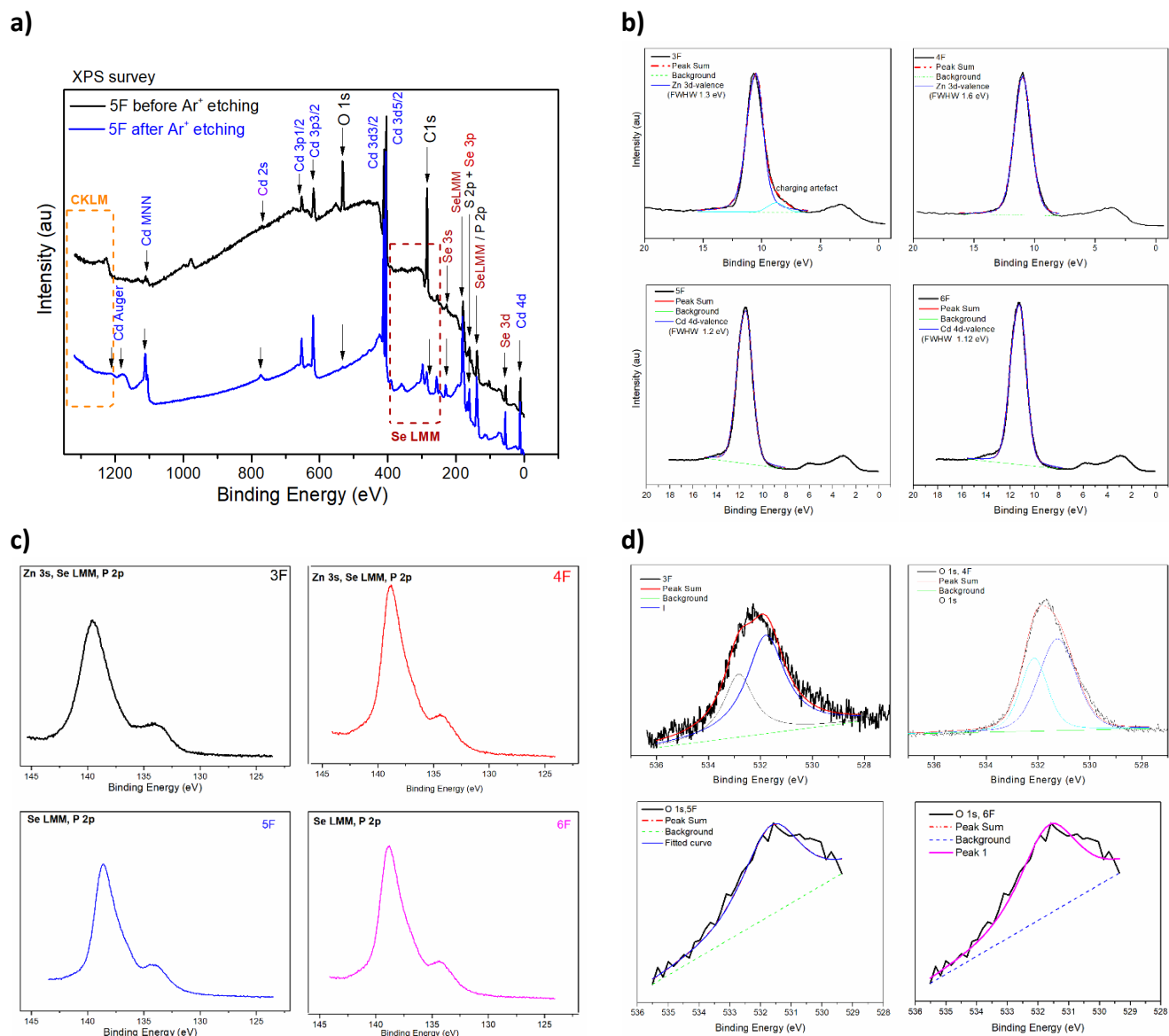
where  $\alpha$  is the absorption coefficient,  $hv$  is the incident photon energy,  $B$  is the energy-dependent constant,  $E_g$  is the optical band gap of the material, and  $m$  is the transition coefficient which can be 1/2, 3/2, 2, and 3, in this case  $m = 2$  for direct allowed transitions and  $\alpha$  was evaluated using the following relation (5) where  $t$  is the film thickness,  $T$  the transmittance. The optical energy gap,  $E_g$  of the investigated MSe thin films, were obtained from plot  $(\alpha hv)^2$  versus the photon energy ( $hv$ ) by extrapolating linear part to intersect  $(hv)$  axis at  $(\alpha hv)^2 = 0$  (Fig. S4 for annealed films).

b) Similar values were obtained by means of the first derivative plots of transmittance spectra ( $dT/d(hv)$ ).<sup>5</sup>

6. **Fig. S4.** Optical band gap ( $E_g$ ) estimation. Plot of  $(\alpha hv)^2$  versus photon energy ( $hv$ ) for annealed zinc and cadmium films(**3Fa-6Fa**, annealed at 600°C).



**7. Fig. S5 a)** XPS survey spectra of **5F** before and after Ar<sup>+</sup> etching process (as an example showing the disappearance of O-1s and C-1s features after etching process). Core-level HR-XPS spectra: **b)** Valence bands and corresponding Zn-3d (**3F** and **4F**) and Cd-4d (**5F** and **6F**), **c)** Zn 3s, Se LMM, P 2p region (**3F** and **4F**) and Se LMM, P 2p region (**5F** and **6F**), **d)** O 1s for **3F-6F**.



Experimental details. XPS spectra were performed on stored **3F-6F** (Thermo K-alpha spectrometer, Al K $\alpha$  X-ray source, 1486.68 eV). The samples were introduced into an ultra-high vacuum (UHV) chamber ( $1 \times 10^{-7}$ – $1 \times 10^{-8}$  Pa) and measured at room temperature. For every sample, survey spectra and individual core level spectra were obtained under the same conditions before and after Ar<sup>+</sup> etching (initial and final spectra). Depth profile was acquired until the intensity of core level peaks reached to constant value. The spot size in the beam was 300  $\mu$ m and the pass energy was set to 150 eV for the survey spectra (energy step 1.0 eV), 25 eV for recording C 1s and O 1s, and 50 eV for recording the individual core level spectra. 10 scans were performed for C 1s, Cd 4d, Cd 3d, O 1s, P 2p, S 2p, Se 3p, Se 3d and Zn 2p core level with an energy step size of 0.030 eV except for O 1s (0.020 eV), S 2p (0.022 eV), Se 3p (0.025 eV), Se 3d (0.021 eV) and Zn 2p (0.06 eV). The relative atomic concentrations were

determined from the primary core level XPS peak (Cd-3d, O-1s, S-2p, Se-3d and Zn-2p) and the sensitive factors provided by the XPS apparatus (SDPv4.1 software®). The high-resolution regions of interest were fitted using Tougaard or linear background with a symmetric Gauss-Lorentz sum function.

**8. Table S2.** Band gaps ( $E_g$ ) of our films\* and related MSe and MSSe thin films obtained from different precursors and/or technique.

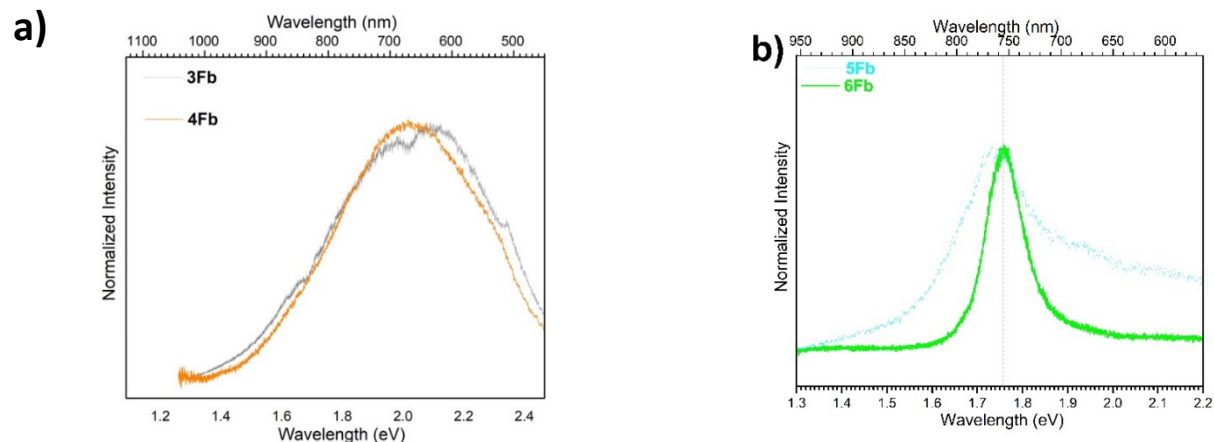
Material	Precursor	Preparation method (solvent)	T <sub>prep</sub> (°C)	E <sub>g</sub> (eV)	Ref	
ZnSSe	[Zn{Pr <sub>2</sub> P(Se)NC(S)NC <sub>5</sub> H <sub>10</sub> -K <sup>2</sup> -Se,S <sub>2</sub> }] (3)	AACVD (Toluene)	375	2.93	*	
ZnSSe	[Zn{Pr <sub>2</sub> P(Se)NC(S)NC <sub>5</sub> H <sub>10</sub> -K <sup>2</sup> -Se,S <sub>2</sub> }] (3)		450	2.87	*	
ZnSSe	[Zn{Pr <sub>2</sub> P(Se)NC(S)NC <sub>5</sub> H <sub>10</sub> -K <sup>2</sup> -Se,S <sub>2</sub> }] (3)		annealed (600)	2.67	*	
ZnSe	[Zn{Pr <sub>2</sub> P(Se)NC(O)NC <sub>5</sub> H <sub>10</sub> -K <sup>2</sup> -Se,O <sub>2</sub> }] (4)		375	2.74	*	
ZnSe	[Zn{Pr <sub>2</sub> P(Se)NC(O)NC <sub>5</sub> H <sub>10</sub> -K <sup>2</sup> -Se,O <sub>2</sub> }] (4)		450	2.71	*	
ZnSe	[Zn{Pr <sub>2</sub> P(Se)NC(O)NC <sub>5</sub> H <sub>10</sub> -K <sup>2</sup> -Se,O <sub>2</sub> }] (4)		annealed (600)	2.68	*	
ZnSe	[Zn(Se <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> ]	AACVD (THF)	350	2.25	6	
Zn <sub>x</sub> Se <sub>1-x</sub> Se <sub>rich</sub>	[Zn(Se <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> ]:[Zn(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> ] 1:0.75		350	2.55	6	
1:1 (S:Se)	[Zn(Se <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> ]: [Zn(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> ] 1:1		350	2.66	6	
ZnSe	Na <sub>2</sub> SeSO <sub>3</sub> + Zn <sup>2+</sup>	CBD	25	3.04	7	
			45	3.02		
			60	2.89		
			80	2.82		
ZnSe	[Zn{Pr <sub>2</sub> P(Se)NP(Se)Pr <sub>2</sub> }]	LP-MOCVD	425-450	2.63	8	
ZnSe	Zn(CH <sub>3</sub> COO) <sub>2</sub> ·2H <sub>2</sub> O and SeO <sub>2</sub>	Electrodeposition by three-electrode set-up (water)	27	2.7	9	
ZnSe	ZnSO <sub>4</sub> and Na <sub>2</sub> (SeSO <sub>3</sub> )	CBD (water)	80	2.65	10	
ZnSe	ZnSO <sub>4</sub> ·7H <sub>2</sub> O, SeO <sub>2</sub> Using different complexing agents:	Electrochemical deposition	50		11	
	Ammonia					2.45
	Citric acid					2.58
	EDTA					2.45
	Ethylenediamine					2.53
	Hydrazine hydrate					2.47
	Polyvinyl alcohol					2.56
	Triethanolamine	2.64				
ZnS	ZnS and ZnSe powder	Evaporation		3	12	
ZnS <sub>0.73</sub> Se <sub>0.27</sub>				2.82		
ZnS <sub>0.68</sub> Se <sub>0.32</sub>				2.77		
ZnS <sub>0.36</sub> Se <sub>0.64</sub>				2.68		
ZnSe				2.25		
ZnSe	ZnSO <sub>4</sub> , SeC(NH <sub>2</sub> ) <sub>2</sub> , NH <sub>4</sub> OH (25%), Varying (hydrazine hydrate) : (Na3-citrate)	CBD	80		13	
	Sol. A (0:10)					2.65
	Sol. B (2:8)					2.69
	Sol. C (3:7)					2.72
	Sol. D (5:5)					2.95
	Sol. E (7:3)					3.48
	Sol. F (8:2)	3.55				
ZnSe	ZnSe powder As-deposited	Pulsed laser deposition (2×10 <sup>-25</sup> Torr, Nd:YAG(λ:355 nm))		2.65	14	
	Annealed at 350 and 400			annealed (350)		2.7
				annealed (400)		2.56
ZnSe	ZnSe particles (99.99%)	Electron beam evaporation technique (2.0×10 <sup>-3</sup> Pa) and annealed at:		as-deposited	15	
				300		2.58
				400		2.52
				500		2.43
				600		2.43
ZnSe	100 mM ZnSO <sub>4</sub> and 1 mM SeO <sub>2</sub> in H <sub>2</sub> SO <sub>4</sub> and NaOH (pH=2)	Electrodeposition on Pt electrodes	RT	2.73	16	
ZnSe	ZnSO <sub>4</sub> , Se, Na <sub>2</sub> SO <sub>3</sub> , Na3-citrate, triethanolamine (TEA), hydrazine hydrate, and NaOH (pH),	Solution growth technique (SGT).	80	2.71	17	
CdSSe	[Cd{Pr <sub>2</sub> P(Se)NC(S)NC <sub>5</sub> H <sub>10</sub> -K <sup>2</sup> -Se,S <sub>2</sub> }] (5)		375	1.80	*	
CdSSe	[Cd{Pr <sub>2</sub> P(Se)NC(S)NC <sub>5</sub> H <sub>10</sub> -K <sup>2</sup> -Se,S <sub>2</sub> }] (5)		450	1.77	*	



CdS <sub>Se</sub>	[Cd{ <sup>i</sup> Pr <sub>2</sub> P(Se)NC(S)NC <sub>5</sub> H <sub>10</sub> -κ <sup>2</sup> -Se,S <sub>2</sub> }] (5)	AACVD (Toluene)	annealed (600)	1.71	*
CdSe	[Cd{ <sup>i</sup> Pr <sub>2</sub> P(Se)NC(O)NC <sub>5</sub> H <sub>10</sub> -κ <sup>2</sup> -Se,O <sub>2</sub> }] (6)		375	1.76	*
CdSe	[Cd{ <sup>i</sup> Pr <sub>2</sub> P(Se)NC(O)NC <sub>5</sub> H <sub>10</sub> -κ <sup>2</sup> -Se,O <sub>2</sub> }] (6)		450	1.74	*
CdSe	[Cd { <sup>i</sup> Pr <sub>2</sub> P(Se)NC(O)NC <sub>5</sub> H <sub>10</sub> -κ <sup>2</sup> -Se,O <sub>2</sub> }] (6)		annealed (600)	1.69	*
CdSe	[Cd( <sup>i</sup> Pr <sub>2</sub> P(Se)NP(Se) <sup>i</sup> Pr <sub>2</sub> ) <sub>2</sub> ]	LP-MOCVD	475-500	1.71	8
CdSe	[MeCd( <sup>i</sup> Pr <sub>2</sub> P(Se)NP(Se) <sup>i</sup> Pr <sub>2</sub> ) <sub>2</sub> ]	LP-MOCVD	450	1.73	18
CdSe	[Cd(Se <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub>	AACVD (THF)	300	1.75	19
Cd <sub>0.2</sub> Se <sub>0.8</sub>	[Cd(Se <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> : [Cd(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> (1:1 & 2:1)	AACVD (THF)	300	1.9	19
Cd <sub>0.4</sub> Se <sub>0.6</sub>				2.0	
n-CdSeS	CdCl <sub>2</sub> , KI, elemental Se and S)	galvanostatic method	130	2.26 - 2.48	20
CdSe	CdSe NPs		RT	2.41	21
		CBD	60	2.36	
			70	2.25	
			80	2.38	
CdS	CdS <sub>1-x</sub> Se <sub>x</sub> /ITO thin films		90	2.37	22
Cd <sub>0.75</sub> Se <sub>0.25</sub>	0.1 M CdCl <sub>2</sub> + 0.33 M CS(NH <sub>2</sub> ) <sub>2</sub> + 0.1 M Na <sub>2</sub> SeSO <sub>3</sub>	CBD during 2 h		2.18	
Cd <sub>0.5</sub> Se <sub>0.5</sub>	solutions (different proportions)			2.02	
Cd <sub>0.25</sub> Se <sub>0.75</sub>				1.92	
CdSe				1.86	
CdS	CdSO <sub>4</sub> ·8H <sub>2</sub> O,	electrochemical atomic layer		2.42-1.64	23
Cd <sub>x</sub> Se <sub>1-x</sub>	HClO <sub>4</sub> , NH <sub>4</sub> OH, CH <sub>3</sub> COONa·3H <sub>2</sub> O, CH <sub>3</sub> COOH,	epitaxy (ECALE)			
CdSe	Na <sub>2</sub> S				
Cd <sub>0.5</sub> Se <sub>0.5</sub>	Cadmium sulfide, cadmium selenide and cadmium chloride sintering process.	screen-printing method	120	2.1	24
Cd <sub>0.5</sub> Se <sub>0.5</sub>	cadmium chloride, thiourea and sodium seleno-sulphate and 8-hydroxyquinoline	CBD	70	2.2	25
Cd <sub>0.55</sub> Se <sub>0.45</sub>	CdS <sub>1-x</sub> Se <sub>x</sub> nanocrystals in a borosilicate glass matrix from commercially available samples	diffusion-limited growth (solid-state precipitation)		2.45	26
Cd <sub>0.75</sub> Se <sub>0.25</sub>	CdCl <sub>2</sub> (0.033 M), Cd(NH <sub>2</sub> ) <sub>2</sub> (0.033 M), Na <sub>2</sub> SeSO <sub>3</sub> (0.1 M). Deposition time (min):	Chemical solution deposition	75		27
				2.25	
				2.28	
				2.27	
Cd <sub>0.8</sub> Se <sub>0.2</sub>	CdS <sub>1-x</sub> Se <sub>x</sub> thin film:		80±75	2.16	28
Cd <sub>0.6</sub> Se <sub>0.4</sub>	CdSO <sub>4</sub> (0.1 M) and thiourea (0.2 M)	CBD (in air)	"	2.03	
Cd <sub>0.4</sub> Se <sub>0.6</sub>	CdSO <sub>4</sub> (20mL) + thiourea + Na <sub>2</sub> (S(Se)O <sub>3</sub> )		"	1.97	
Cd <sub>0.2</sub> Se <sub>0.8</sub>	" " "		"	1.8	
CdSe	CdSO <sub>4</sub> + Na <sub>2</sub> (S(Se)O <sub>3</sub> )		50±5 °C	1.73	
2D CdS <sub>x</sub> Se <sub>1-x</sub> alloy	CdCl <sub>2</sub> (s)+ S(s) + Se(s)	PVD	800	1.8-2.3 PL	29
CdS	CdS and CdSe (99.999%)	Thermal co-evaporation of source materials (2 x 10 <sup>-6</sup> mbar)	RT	2.43	30
Cd <sub>0.8</sub> Se <sub>0.2</sub>				2.13	
Cd <sub>0.6</sub> Se <sub>0.4</sub>				1.99	
Cd <sub>0.4</sub> Se <sub>0.6</sub>				1.83	
Cd <sub>0.2</sub> Se <sub>0.8</sub>				1.79	
CdSe				1.65	

\*This work

9. Fig. S6. PL spectra ( $\lambda_{ex} = 488$  nm) of as-deposited films at 375°C: a) 3Fb and 4Fb, and b) 5Fb and 6Fb.



## Notes and references

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