## **Electronic Supplementary Information:**

# Solution-processed CdS thin films from a single-source precursor

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### **Experimental Details**

#### Materials

Cadmium chloride hemi(pentahydrate) (CdCl<sub>2</sub>·2.5H<sub>2</sub>O, AnalaR, 99.5 %), potassium ethylxanthate (K(EtXn), Aldrich, 96 %), pyridine (py, Aldrich, 99.9 %) and 1-propanol (1-PrOH, Aldrich, 99.7 %) were used in the preparations described here. All purchased chemicals and solvents were used without further purification. Cd(EtXn)<sub>2</sub> (**1**) was synthesised according to an adapted method described by Cusack et. al.<sup>1</sup>

#### Instrumentation

Absorption measurements were performed using a Varian Cary 5E spectrophotometer. The zero baseline for all measurements was air.

Attenuated total reflectance infrared spectroscopy (ATR-IR) was performed on a Thermo Scientific Nicolet 6700 Fourier transform infrared (FT-IR) spectrometer on a laminated diamond mounted in a stainless steel plate in the 4000–600 cm<sup>-1</sup> range with a resolution of  $4 \text{ cm}^{-1}$ .

Thermogravimetric analysis-mass spectrometry (TG-MS) was performed on a Setaram Setsys Evolution Thermal Analyser. A mass of approximately 30 mg of [Cd(EtXN)<sub>2</sub>(py)<sub>2</sub>] (**2**) was heated from ambient to 550 °C in an air atmosphere at a heating rate of 5 °C/min. A Pfeiffer - Thermostar 300 amu Mass Spectrometer was used to monitor the evolved gases emitted from the sample as it was heated.

Headspace gas chromatography-mass spectrometry (HS-GC-MS) was performed on a Agilent 6890 GC and a 5971 Mass selective detector (MSD) in full scan mode and a 30m HP PLOT Q column (id 0.32mm, film thickness 20µm).

Films were characterized by X-ray diffraction (XRD) by using a Philips PW1710 diffractometer equipped with glancing-incidence X-Ray optics. The analysis was performed at 0.5° incidence using CuKα Ni-filtered radiation at 30 kV and 40 mA. The average crystallites size of the crystalline phases has been evaluated from the diffraction patterns using the Scherrer formula: the main diffraction peaks have been fitted with Lorentzian curves, and the crystallite size has been estimated using the full width at half maximum (fwhm) of the fitting functions. Single crystal X-ray diffraction data for  $[Cd(EtXn)_2(py)_2]$  (2) unit cell determination were collected on a Bruker X8 Apex II CCD equipped with graphite monochromated Mo-K $\alpha$ radiation ( $\lambda$  = 0.71073 Å). The data collection temperature was maintained at 123 K using open flow N<sub>2</sub> cryostream. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in DMSO- $d_6$  on a Bruker BioSpin Av200 (4.70 T magnet) with a 5 mm QNP probe.

UPS and XPS measurements were carried out on a Kratos Axis-HSi instrument using He I and Al K-alpha radiation sources, respectively. Samples for these experiments were deposited on fluorine doped tin oxide/glass and were found to not exhibit any charging behaviour. For the UPS, the Fermi edge of a clean Au film was used as the 0 eV reference; while for the XPS, all the spectra were re-calibrated to a nominal C 1s binding energy of 284.5 eV

Linear i-V curves (-5 V to 5 V) revealed good ohmic contacts were achieved with 2 mm length parallel AI evaporated contacts with a 0.09 mm separation. A chopped monochromatic light illuminated the exposed area. Photoconductivity measurements were carried out using a 150W Oriel Lamp, Newport monochromator 74125 with integrated chopper (set at 11 Hz) and an Oxford DN 1704 optical cryostat. The photocurrent signal was amplified using a Stanford Research Systems (SR570) current preamplifer, which also supplied the voltage bias across the sample. Although the i-V curves in the dark and under illumation were linear, significant gain was observed at high field strengths (>100 V cm<sup>-1</sup>).

Photoconductivity data were collected at field strength of 55 V cm<sup>-1</sup> (0.5V). A Stanford Research Systems (SR830) lock-in amplifier detected the amplified signal. An in house Labview program controlled the setup and recorded the data. A calibrated silicon detector was used to determine the incident photon flux spectrum. Measurements were carried out under Nitrogen after three vacuum purged cycles to remove ambient oxygen. Very little to no difference was observed in the photoresponse under partial vacuum or under a nitrogen atmosphere. There was always a lower response (~40%) when measured under ambient conditions which is known to be caused by the chemisorption of oxygen.<sup>2</sup> CdS film thicknesses were measured on a Dektak 6M Stylus Profiler and were within the range of 130 - 140 nm.

#### References

1. J. Cusack, M. G. B. Drew and T. R. Spalding, *Polyhedron*, 2004, **23**, 2315-2321.

2. E. h. Weber, *p hys. stat. sol. (b)*, 1968, **28**, 649-662.



Fig. S1 FT-IR spectra of CdS thin films heat treated at various temperatures.



**Fig. S2** FT IR spectra of deposited  $Cd(EtXn)_2(py)_2$  thin film heat treated at 80 °C (red) and bulk  $Cd(EtXn)_2$  powder (blue).



**Fig. S3** XRD patterns of 10% CdCl<sub>2</sub> doped CdS thin films annealed for various times at 400 °C in air. Crystallite sizes calculated from the XRD patterns; 1 min, 32 nm; 2 min, 34 nm; 5 min, 35 nm; 10 min, 33 nm; 30 min, 36 nm; 60 min, 34 nm.



Fig. S4 UV-vis absorption spectra of CdS thin films (CdCl<sub>2</sub> bath dipped) annealed at various temperatures in air.

Annealing Temperature (°C)	No CdCl <sub>2</sub> treatment	CdCl <sub>2</sub> doped	CdCl <sub>2</sub> dipped
150	2.60	2.68	2.64
200	2.58	2.58	2.55
250	2.53	2.48	2.44
300	2.43	2.44	2.41
350	2.40	2.41	2.41
400	2.37	2.41	2.40

Table S1. Optical band gap (eV) as determined from the UV-vis absorption spectra shown in Fig. 2.

**Table S2.** XPS measurements of CdS thin films with CdCl<sub>2</sub> treatment (and annealing atmosphere).<sup>+</sup>

Atomic %	CdCl <sub>2</sub> Dipped (Air)	No CdCl <sub>2</sub> (Air)	CdCl <sub>2</sub> Dipped (N <sub>2</sub> )	No CdCl <sub>2</sub> (N <sub>2)</sub>	CdCl <sub>2</sub> Doped (N <sub>2)</sub>	CdCl <sub>2</sub> Doped (Air)	CBD (Air)
S 2p	20.90	21.78	21.81	24.51	26.25	25.57	14.44
Cd 3d	29.11	28.26	29.06	28.57	32.76	33.96	19.22
Cl 2p	8.58	2.34	11.02	1.81	4.62	6.30	1.09
O 1s	7.80	17.64	3.02	6.78	3.76	5.39	21.48
C 1s	33.61	29.97	35.09	38.33	32.61	28.78	43.77
Cd/S	1.40	1.32	1.33	1.17	1.25	1.33	1.41

 CdCl<sub>2</sub> dipped = CdS thin film dipped in saturated CdCl<sub>2</sub> methanol solution prior to annealing; CdCl<sub>2</sub> doped = CdS precursor solution deposited with 10 % CdCl<sub>2</sub> doped solution; CBD = CdCl<sub>2</sub>/thiourea chemical bath deposited. Unless noted Cd(EtXn)<sub>2</sub> used as CdS precursor.

**Table S3.** Mobilities  $(cm^2/Vs)$  of CdS thin films with different CdCl<sub>2</sub> treatments at various temperatures. All samples annealed in air.

Annealing Temp. (°C)	CdCl <sub>2</sub> Dipped	5 %CdCl <sub>2</sub> Doped	
200	$2.60 \times 10^{-4}$	6.10×10 <sup>-6</sup>	
250	3.40×10 <sup>-3</sup>	$1.43 \times 10^{-4}$	
300	5.00×10 <sup>-2</sup> , 1.45×10 <sup>-2</sup>	9.62×10 <sup>-3</sup> , 5.19×10 <sup>-3</sup>	
350	2.24×10 <sup>-1</sup> , 1.54×10 <sup>-2</sup>	9.54×10 <sup>-3</sup>	
400	2.11×10 <sup>-1</sup> , 1.43×10 <sup>-1</sup>	4.96×10 <sup>-2</sup> , 3.80×10 <sup>-2</sup>	