# Dalton Transactions

## PAPER

## **RSC**Publishing

View Article Online View Journal | View Issue

Cite this: Dalton Trans., 2013, 42, 10919

Received 23rd March 2013, Accepted 22nd May 2013 DOI: 10.1039/c3dt50781e www.rsc.org/dalton

## Introduction

Semiconductors with suitable band gaps and band edges are key to the development of efficient light harvesting applications such as solar cells and solar water splitting.<sup>1,2</sup> The  $\beta$ -polymorph of indium sulphide ( $\beta$ -In<sub>2</sub>S<sub>3</sub>) is known for its

## Development of molecular precursors for deposition of indium sulphide thin film electrodes for photoelectrochemical applications†

Muhammad Ali Ehsan,<sup>a</sup> T. A. Nirmal Peiris,<sup>b</sup> K. G. Upul Wijayantha,<sup>b</sup> Marilyn M. Olmstead,<sup>c</sup> Zainudin Arifin,<sup>a</sup> Muhammad Mazhar,<sup>\*a</sup> K. M. Lo<sup>a</sup> and Vickie McKee<sup>b</sup>

Symmetrical and unsymmetrical dithiocarbamato pyridine solvated and non-solvated complexes of indium(III) with the general formula  $[In(S_2CNRR')_3] \cdot n(py)$  [where py = pyridine; R,R' = Cy, n = 2 (1); R,R' = Cy, n = 2<sup>i</sup>Pr, n = 1.5 (2); NRR' = Pip, n = 0.5 (3) and R = Bz, R' = Me, n = 0 (4)] have been synthesized. The compositions, structures and properties of these complexes have been studied by means of microanalysis, IR and <sup>1</sup>H-NMR spectroscopy, X-ray single crystal and thermogravimetric (TG/DTG) analyses. The applicability of these complexes as single source precursors (SSPs) for the deposition of  $\beta$ -ln<sub>2</sub>S<sub>3</sub> thin films on fluorinedoped SnO<sub>2</sub> (FTO) coated conducting glass substrates by aerosol-assisted chemical vapour deposition (AACVD) at temperatures of 300, 350 and 400 °C is studied. All films have been characterized by powder X-ray diffraction (PXRD) and energy dispersive X-ray analysis (EDX) for the detection of phase and stoichiometry of the deposit. Scanning electron microscopy (SEM) studies reveal that precursors (1)-(4), irrespective of different metal ligand design, generate comparable morphologies of  $\beta$ -ln<sub>2</sub>S<sub>3</sub> thin films at different temperatures. Direct band gap energies of 2.2 eV have been estimated from the UV-vis spectroscopy for the  $\beta$ -ln<sub>2</sub>S<sub>3</sub> films fabricated from precursors (1) and (4). The photoelectrochemical (PEC) properties of  $\beta$ -In<sub>2</sub>S<sub>3</sub> were confirmed by recording the current–voltage plots under light and dark conditions. The plots showed anodic photocurrent densities of 1.25 and 0.65 mA cm<sup>-2</sup> at 0.23 V vs. Ag/AgCl for the  $\beta$ -In-S<sub>3</sub> films made at 400 and 350 °C from the precursors (1) and (4), respectively. The photoelectrochemical performance indicates that the newly synthesised precursors are highly useful in fabricating  $\beta$ -In<sub>2</sub>S<sub>3</sub> electrodes for solar energy harvesting and optoelectronic application.

> optoelectronic and photoelectrochemical properties and is a promising candidate for many useful applications due to its stability, moderate band gap and photoconductive behaviour.<sup>3</sup> β-Indium sulphide ( $E_g = 2.0-2.2 \text{ eV}$ ),<sup>4</sup> having a defect spinel structure, displays excellent properties of high photosensitivity and photoconductivity,<sup>5</sup> stable chemical composition and low toxicity.<sup>6</sup> Thus, it is widely applied for displays,<sup>7</sup> as a photocatalyst for dye degradation,<sup>8</sup> for water splitting<sup>6b</sup> and for solar cells.<sup>9,10</sup> Moreover, β-In<sub>2</sub>S<sub>3</sub> solar cell devices exhibit a high 16.4% power conversion efficiency,<sup>11,12</sup> which is comparable to CdS because of their equivalent band gaps and has been considered as a substitute for the highly toxic CdS.<sup>13</sup>

> Much effort has been expended to produce  $\beta$ -In<sub>2</sub>S<sub>3</sub> films and powders with a variety of structures and morphologies. These methods include chemical bath deposition,<sup>14,15</sup> sonochemical,<sup>16</sup> hydrothermal,<sup>17,18</sup> solvothermal,<sup>19</sup> solution phase synthesis,<sup>20</sup> thermal evaporation,<sup>21</sup> chemical spray,<sup>22</sup> solvent reduction route,<sup>23</sup> electrodeposition<sup>24</sup> and metal–organic chemical vapour deposition (MOCVD).<sup>25</sup> However, increasing

<sup>&</sup>lt;sup>a</sup>Department of Chemistry, Faculty of Science, University of Malaya, Lembah Pantai, 50603 Kuala Lumpur, Malaysia. E-mail: maliqau@ymail.com,

zainudin@um.edu.my, kmlo@um.edu.my, mazhar42pk@yahoo.com;

Tel: +60 (03) 79674269

<sup>&</sup>lt;sup>b</sup>Department of Chemistry, Loughborough University, Loughborough, LE11 3TU, UK. E-mail: T.A.N.Peiris@lboro.ac.uk, u.wijayantha@lboro.ac.uk, V.McKee@lboro.ac.uk; Tel: +44 (0) 1509222574

<sup>&</sup>lt;sup>c</sup>Department of Chemistry, University of California, Davis, CA 95616, USA. E-mail: marilyn\_olmstead@hotmail.com

<sup>†</sup>Electronic supplementary information (ESI) available: Microanalysis results, figures for NMR, XRD, TGA and EDX analyses. CCDC 924187-924190. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50781e

applications of semiconducting materials in optoelectronic and photovoltaic devices in the form of thin films have driven researcher's interest in CVD routes. The demand for CVD routes to a variety of materials has, in turn, generated interest in the design of single source precursors (SSP).<sup>26</sup> Historically, a variety of SSP have been investigated including dialkylindium alkanethiolate,<sup>27</sup> alkylindium bis-thiolate, tris(dialkyldithiocarbamates),<sup>28,29</sup> dialkylmonodithiocarbamate,<sup>30</sup> tris(dialkylmonothiocarbamte),<sup>31</sup> and alkyl xanthate<sup>32</sup> for the deposition of different phases of indium sulphide on a variety of substrates through CVD based techniques. However, there are restrictions imposed by the precursors on the use of this method. These issues directly affect thin film properties such as deposited phase, degree of crystallinity, crystallographic orientation, composition, morphology and possibly the structure of the deposited film. These properties are highly desirable for the fabrication of device quality films.<sup>33</sup> By developing precursors specifically for aerosol assisted chemical vapour deposition (AACVD),<sup>34</sup> the volatility and thermal sensitivity restrictions can be reduced and as a result a larger range of precursors and films can be investigated.<sup>35</sup> By carefully monitoring AACVD deposition conditions such as solution concentration, solvent, nature of the carrier gas, carrier gas flow rate, deposition time and substrate temperature, high quality nanostructured thin films can be produced that can be employed in a range of applications such as photovoltaic, gas sensors, thermoelectric, fuel cells and catalysts.36

In continuation of our efforts on the exploration of metal dithiocarbamate/dithiocarbonate pyridine adducts,<sup>37,38</sup> we have devoted our attention to the syntheses of SSPs tris(dialkyl-dithiocarbamato)indium(III),  $[In(S_2CNRR')_3] \cdot n(py)$  [where py = pyridine; R,R' = Cy, n = 2 (1); R,R' = <sup>i</sup>Pr, n = 1.5 (2); NRR' = Pip, n = 0.5 (3) and R = Me, R' = Bz, n = 0 (4)] for the deposition of  $\beta$ -In<sub>2</sub>S<sub>3</sub> films by AACVD technique. The thin films properties have been examined by PXRD, SEM, EDX and UV-vis spectroscopy, for their crystallinity, phase identification, surface morphology, stoichiometry and optical band energies, respectively. Furthermore, the photoactivities of the deposited  $\beta$ -In<sub>2</sub>S<sub>3</sub> films were observed by means of photoelectrochemical (PEC) measurements and the results confirmed that these SSPs are suited to obtain better performing thin films of  $\beta$ -In<sub>2</sub>S<sub>3</sub> for various optoelectronic applications.

#### Experimental

#### Preparation and characterization of complexes

All preparations were carried out at room temperature. All materials were obtained commercially and used as received. The dithiocarbamate ligands were prepared according to published procedures.<sup>39</sup>

The elemental analysis was performed using a Perkin Elmer CHNS/O Analyzer series II 2400. Infrared spectra were recorded with a Perkin Elmer Spectrum 400 FT-IR/FT-FIR spectrometer (4000–400 cm<sup>-1</sup>). The TGA measurements were carried out on a METTLER TOLEDO TGA/SDTA 851e Thermogravimetric

Analyzer at a heating rate of 10  $^{\circ}$ C min<sup>-1</sup> under a constant flow of nitrogen at a rate of 50 mL min<sup>-1</sup>.

#### General procedure for synthesis of $[In(S_2CNRR')_3] \cdot n(py)$ complexes, (1)-(4)

A sample of sodium dicyclohexyldithiocarbamate (0.50 g, 1.80 mmol) was dissolved in methanol (20 mL) and placed in a three-necked round bottom flask (100 mL) fitted with a dropping funnel, reflux condenser and inert gas line followed by addition of indium trichloride (0.13 g, 0.60 mmol). The resultant milky white solution was stirred for 30 min. At this point pyridine (30 mL) was added to give a clear and colourless solution and stirring was continued for another hour. Filtration and slow evaporation of the reaction mixture afforded  $[In(S_2CNCy_2)_3]$ ·2py (1) as colourless crystals; yield (0.49 g, 78%), mp. 255-260 °C (decomposition). Elemental analysis found: C, 56.73; H, 7.83; N, 6.32%; C<sub>49</sub>H<sub>76</sub>InN<sub>5</sub>S<sub>6</sub> requires: C, 56.46; H, 7.34; N 6.71%. IR ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 2925s, 2853s, 1579m, 1471w, 1440s, 1378w, 1361s, 1346m, 1332w, 1300s, 1266m, 1241s, 1166s, 1148s, 1105s, 1020w, 997s, 949s, 922s, 895s, 882w, 748w, 746m, 705s, 658s, 612s, 602m, 503w, 492w, 473s. <sup>1</sup>H-NMR  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>): 1.13–2.17 (60H, m, 3(C<sub>10</sub>H<sub>20</sub>)), 3.12 (2 H, s, (NCH)), 3.40 (2 H, s, (NCH)), 4.82 (2 H, s, (NCH)) and 7.30-8.63 ppm (10H, m, 2(NC<sub>5</sub>H<sub>5</sub>)). TGA: 55-110 °C (11.60% wt. loss); 230-400 °C (73.21% wt. loss); residual mass of 15.19%, calcd for β-In<sub>2</sub>S<sub>3</sub>: 15.64%.

Complexes (2), (3) and (4) were prepared as colourless crystals adopting the method used for the synthesis of (1).

The quantities of the reactants used for the synthesis of (2), (3) and (4) and their analytical data are as follows.

Complex (2): Sodium diisopropyldithiocarbamate (0.50 g, 2.50 mmol) and indium trichloride (0.19 g, 0.83 mmol); yield (0.51 g, 80%), mp. 265–270 °C (decomposition). Elemental analysis found: C, 43.72; H, 6.69; N, 7.94%;  $C_{28.5}H_{49.5}InN_{4.5}S_6$  requires: C, 44.90; H, 6.54; N, 8.26%. IR ( $\nu_{max}/cm^{-1}$ ): 2971m, 2931w, 1581w, 1480s, 1460w, 1444s, 1369s, 1321s, 1192s, 1142s, 1117w, 1036s, 991w, 942s, 906s, 848s, 789s, 748w, 705s, 614m, 582s, 529s, 476s. <sup>1</sup>H-NMR  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>): 1.48–1.68 (36 H, br d, 6CH(CH<sub>3</sub>)<sub>2</sub>), 3.95 (2 H, br s, CH(CH<sub>3</sub>)<sub>2</sub>), 5.16 (4H, br s, CH(CH<sub>3</sub>)<sub>2</sub>) and 7.27–8.60 (7.5 H, m, 1.5(NC<sub>5</sub>H<sub>5</sub>)) ppm. TGA: 55–115 °C (15.50% wt. loss); 230–400 °C (64.25% wt. loss); residual mass of 20.25%, Calcd for β-In<sub>2</sub>S<sub>3</sub> 21.36%).

Complex (3): Sodium piperidinedithiocarbamate (0.50 g, 2.73 mmol) and indium trichloride (0.20 g, 0.90 mmol); yield (0.48 g, 83%), mp. 280–283 °C (decomposition). Elemental analysis found: C, 37.70; H, 5.05; N, 7.40%;  $C_{20.5}H_{32.5}InN_{3.5}S_6$  requires: C, 38.76; H, 5.15; N, 7.71%. IR ( $\nu_{max}/cm^{-1}$ ): 2937s, 2853m, 1581w, 1484s, 1456w, 1436s, 1359w, 1346w, 1278m, 1258m, 1232w, 1132m, 1109s, 1069w, 1022m, 1001m, 970s, 948m, 883s, 855m, 743w, 703m, 613m, 559m, 514s, 464m. <sup>1</sup>H-NMR  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.53–1.86 (18H, m, 3(CH<sub>2</sub>)), 3.78–4.15 (12H, m, 3(NCH<sub>2</sub>)) and 7.27–8.61 (2.5H, m, 0.5 (NC<sub>5</sub>H<sub>5</sub>)) ppm. TGA: 45–110 °C (6.84% wt. loss); 230–400 °C (69.31% wt. loss); residual mass of 23.85%, calcd for  $\beta$ -In<sub>2</sub>S<sub>3</sub> 25.64%).

Complex (4): Sodium benzyl(methyl)dithiocarbamate (0.5 g, 2.28 mmol) and indium trichloride (0.17 g, 0.76 mmol); yield (0.46 g, 85%), mp. 180 °C. MW 703.69. Elemental analysis found: C, 45.70; H, 4.33; N, 6.05%;  $C_{27}H_{30}InN_3S_6$  requires: C, 46.08; H, 4.29; N, 5.96%. IR ( $\nu_{max}/cm^{-1}$ ): 3027w, 2927w, 1491s, 1453s, 1433m, 1392s, 1357w, 1348w, 1301w, 1267w, 1242s, 1196s, 1157w, 1088s, 1070w, 1029m 983m, 955s, 817w, 745s, 732s, 694s, 624s, 569s, 549s, 485s. <sup>1</sup>H-NMR  $\delta_{H}$  (400 MHz, CDCl<sub>3</sub>) 3.35 (9H, s, 3(*CH*<sub>3</sub>)), 5.10 (6H, s, 3(*CH*<sub>2</sub>)) and 7.26–7.42 (15H, m, aromatic 3(*C*<sub>6</sub>*H*<sub>5</sub>)) ppm. TGA: 230–400 °C (wt loss 74.60%); residual mass of 25.40%, calcd for  $\beta$ -In<sub>2</sub>S<sub>3</sub> 23.15%.

#### X-Ray crystallography

Single crystal X-ray diffraction data were collected on a Bruker D8 Apex II diffractometer for (1), (3) and (4) and on an Agilent SuperNova Dual for (2) with use of an Oxford low temperature apparatus. Multi-scan methods for absorption correction were applied.<sup>40</sup> The structures were solved by direct methods and difference Fourier synthesis and refined by full-matrix least-squares based on all data.<sup>41</sup> Crystal data are summarized in Table 1.

#### Deposition of thin films by AACVD

 $\beta$ -In<sub>2</sub>S<sub>3</sub> thin films were synthesised from the precursors [In(S<sub>2</sub>CNCy<sub>2</sub>)<sub>3</sub>]·2py (1), [In(S<sub>2</sub>CN(<sup>i</sup>Pr)<sub>2</sub>)<sub>3</sub>]·1.5py (2), [In(S<sub>2</sub>CPip)<sub>3</sub>]·0.5py (3) and [In(S<sub>2</sub>CNBzMe)<sub>3</sub>] (4) were deposited on FTO (1 × 2 cm<sup>2</sup>) glass substrates (TEC 15, 12–14  $\Omega$  per square) by using a self-designed ultrasonic AACVD method. The glass substrate was washed ultrasonically with distilled water, acetone and finally with ethyl alcohol before use. In a typical deposition experiment, 0.1 g of each of the precursors was dissolved in 12 mL of tetrahydrofuran and the mixture was added to a round-bottomed flask connected to a deposition assembly. Argon at a flow rate of 120 mL min<sup>-1</sup> was used as the carrier gas and the flow rate was controlled by an L1X linear flow meter. Substrate slides were placed inside the reactor tube and

View Article Online

then heated up to the desired temperature before deposition from (1)-(4). The aerosols of the precursor solution were formed by keeping the round-bottomed flask in a water bath above the piezoelectric modulator of an ultrasonic humidifier. The generated aerosol droplets of the precursor were transferred into the hot wall zone of the reactor by the carrier gas. The reactor was placed in a tube furnace. The exhaust from the reactor was vented directly into the extraction system of the fume hood where the deposition had taken place. At the end of the deposition, the aerosol line was closed and pure argon was allowed to flow over the thin films to cool them to 40 °C before the characterization.

#### Surface characterization of thin films

Film morphology and composition were determined by a fieldemission gun scanning electron microscope (FE-SEM, FEI Quanta 400) equipped with an energy dispersive X-ray spectrometer EDX (INCA Energy 200 (Oxford Inst.)) operated at an accelerating voltage of 20 kV and a working distance of 9.2 mm. The type of phase and the crystallinity of the deposited films were determined using a PANanalytical, X'Pert HighScore diffractometer with primary monochromatic high intensity Cu-K<sub>a</sub>( $\lambda = 1.54184$  Å) radiation. The data were collected by scanning from 5° to 90° in a step size of 0.026° operated at 40 kV and 40 mA to cover all possible diffraction peaks of the deposited material.

#### Optical and photoelectrochemical characterization

The optical absorbance of thin films was measured with a Lambda 35 Perkin-Elmer UV-vis spectrophotometer. The data were registered from 350 to 1000 nm using the FTO glass substrate as a reference. The photoelectrochemical (PEC) properties of  $\beta$ -In<sub>2</sub>S<sub>3</sub> films were measured using the standard three electrodes electrochemical cell fitted with a quartz window. An Ag/AgCl electrode and Pt were employed as the reference and counter electrodes, respectively. An aqueous

Table 1 Crystal data and refinement parameters for the complexes [In(S<sub>2</sub>CNCy<sub>2</sub>)<sub>3</sub>]·2py (1), [In(S<sub>2</sub>CN(<sup>i</sup>Pr)<sub>2</sub>)<sub>3</sub>]·1.5py (2), [In(S<sub>2</sub>CPip)<sub>3</sub>]·0.5py (3) and [In(S<sub>2</sub>CNBZMe)<sub>3</sub>] (4)

	(1)	(2)	(3)	(4)
Empirical formula	C49H76InN5S6	C <sub>28.5</sub> H <sub>49.5</sub> InN <sub>4.5</sub> S <sub>6</sub>	C20.5H32.5InN3.5S6	C <sub>27</sub> H <sub>30</sub> InN <sub>3</sub> S <sub>6</sub>
Formula weight	1042.33	762.40	635.18	703.72
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	<i>P</i> 1̄ (No. 2)	<i>P</i> 1̄ (No. 2)
a (Å)	10.5733(2)	11.6384(4)	9.4396(2)	9.7966(4)
b (Å)	22.1491(6)	11.9426(4)	10.7753	12.2791(8)
c (Å)	22.3726(6)	14.4945(3)	14.0452(3)	12.7790(8)
$\alpha$ (°)	90	92.781(2)	93.148(2)	96.142(4)
$\beta$ (°)	91.804(2)	102.078(2)	91.655(2)	92.353(4)
γ (°)	90	111.637(3)	107.443(3)	100.383(5)
Volume (Å <sup>3</sup> )	5236.8(2)	1813.63(9)	1359.31(6)	1500.51(15)
Ζ	4	2	2	2
F(000)	2200	794	650	716
Reflections collected	49 516	16 509	13 467	13 669
Independent reflections	$12\ 019\ (R_{\rm int} = 0.0679)$	9388 $(R_{\rm int} = 0.0209)$	$6491 (R_{int} = 0.0114)$	6504 unique ( $R_{int} = 0.0177$ )
$R_1 \left( I \ge 2\sigma(I) \right)$	0.0476	0.0219	0.0162	0.0228
$wR(F^2)$ (all data)	0.1055	0.0515	0.0403	0.0514

Na<sub>2</sub>SO<sub>4</sub> (0.01 M) and Na<sub>2</sub>S (0.10 M) electrolyte was used to measure the PEC properties of  $\beta$ -In<sub>2</sub>S<sub>3</sub> electrodes.<sup>42</sup> Steadystate current-voltage measurements of the cells were carried out using a potentiostat (Eco Chemie micro-Autolab type III), while the cells were illuminated by an AM 1.5 Class A solar simulator (Solar Light 16S-300 solar simulator), at 100 mW cm<sup>-2</sup> light intensity, calibrated by a silicon pyranometer (Solar Light Co., PMA2144 Class II). The effective area of the electrodes was 1 cm<sup>2</sup>.

## **Results and discussion**

The indium dithiocarbamates with general formula [In- $(S_2CNRR')_3$   $\cdot n(py)$  [where py = pyridine; R,R' = Cy, n = 2 (1); R,R' = <sup>i</sup>Pr, n = 1.5 (2); NRR' = Pip, n = 0.5 (3) and R = Bz, R' = Me, n =0 (4)] are conveniently prepared via metathetical reaction of the indium trichloride and sodium dithiocarbamate in methanol-pyridine solutions as shown in chemical reaction (1). Our approach in developing SSPs differs from that of previously used methods in the synthesis of indium [In(S<sub>2</sub>CNR)<sub>3</sub>] complexes, in that we used a Lewis base (pyridine) as a solvent for the crystallization of complexes (1)-(4). The dithiocarbamates with Lewis bases are a class of precursor compounds with versatile properties that include: air stability, ease of synthesis at room temperature, enhanced volatility and facile decomposition at relatively low temperatures. However, in the present case, pyridine did not coordinate with the metal centre but exists as solvate molecules in the crystal lattices (1), (2) and (3).

$$InCl_{3} + 3Na(S_{2}CNRR') \xrightarrow[MeOH]{Pyridine} [In(S_{2}CNRR')_{3}] \cdot n(py) + 3NaCl (1)$$

The synthesized complexes were characterized by microanalysis, IR, NMR, TGA and single crystal X-ray techniques. These complexes are produced in high yield and are stable in air and moisture, and highly soluble in common organic solvents such as THF, chloroform and pyridine. This makes them promising precursors for application in the deposition of indium sulphide thin films by AACVD. The CHN microanalysis found for complexes (1), (2), (3) and (4) agrees with the stoichiometry of the complex as calculated from the crystal data.

The <sup>1</sup>H-NMR studies of complexes (1), (3) and (4) reveal the usual splitting patterns for the corresponding R groups, however, an unusual splitting behaviour has been detected in the <sup>1</sup>H-NMR spectra of complex (2) where the isopropyl (CH- $(CH_3)_2$ ) group displays three broad signals. Two equally intense broad singlets appearing at 3.95 and 5.10 ppm are assigned to the methine protons of  $(NCH(CH_3)_2)$ , originating from the different positions (*syn* or *anti*) with respect to the dithiocarbamate group. The doublet signal of unequal intensities appearing at 1.48 and 1.68 ppm has been assigned to the methyl protons of the isopropyl group and has been interpreted in terms of coordination and barrier rotation about C–N, which makes the nitrogen substituents magnetically non-equivalent.<sup>43</sup>

In the IR spectra  $\nu$ (C–N) stretching vibrations for complexes (1)–(4) were detected in the range of 1471–1491 cm<sup>-1</sup>. This fact implies that the dialkyldithiocarbamate is coordinated to the metal as a bidentate ligand and indicates the partial double bond character in the C=N bond.<sup>43b,44</sup>

#### Crystal structures of (1)-(4)

The four tris-dithiocarbamate complexes have similar geometric features but the structures differ in the number of pyridine solvate molecules. The In–S distances of the bidentate dithiocarbamate ligands fall within a narrow range, as do the C–S distances, indicating full delocalization. Furthermore, the C==N distances are short, as is typical for these ligands.<sup>44</sup> To illustrate these similarities, the average complex geometry is given in Table 2, together with the average deviations from the mean.

#### Structure of [In(S<sub>2</sub>CNCy<sub>2</sub>)<sub>3</sub>]·2py (1)

The crystal structure of  $[In(S_2CNCy_2)_3]$ ·2py (1) is shown in Fig. 1. The complex (1) has non-crystallographic three-fold symmetry as viewed down the plane of C1/C14/C27 and without inclusion of the cyclohexyl conformations. All the cyclohexyl rings are connected equatorially to their parent nitrogen atoms. The two molecules of pyridine were disordered over two orientations. The two sets of atoms

**Table 2** Selected bond distances (Å) and angles (°) for the complexes  $[ln(S_2CNCy_2)_3]$ -2py (1),  $[ln(S_2CN(^iPr)_2)_3]$ -1.5py (2),  $[ln(S_2CPip)_3]$ -0.5py (3) and  $[ln(S_2CNBZMe)_3]$  (4) with average deviations from the mean given in square brackets

	(1)	(2)	(3)	(4)
In–S (Å)	2.590[4]	2.594[9]	2.592[11]	2.594[11]
S–In–S bite angle (°)	69.26[3]	69.00[2]	69.70[3]	69.70[13]
C–S (Å)	1.732[6]	1.730[2]	1.730[2]	1.726[3]
C==N (Å)	1.335[3]	1.331[2]	1.325[1]	1.332[1]



**Fig. 1** The molecular structure of complex  $[ln(S_2CNCy_2)_3]$ -2py (1). Displacement ellipsoids are shown at the 50% probability level.

comprising the pyridine molecules were refined as rigid idealized hexagonal groups with occupancies that were initially refined and then fixed at {0.50/0.50} and {0.30/0.70} for the sets involving N4 and N5, respectively. With two pyridine molecules removed from the refinement, the solvent accessible void is 1256 Å<sup>3</sup>. In the structure, one pyridine occupies a channel perpendicular to the *bc* plane. The second pyridine is sandwiched between cyclohexyl rings in an alternating fashion.

#### Structure of $[In(S_2CN(^iPr)_2)_3]$ ·1.5py (2)

In the structure of  $[In(S_2CN(^iPr)_2)_3]\cdot 1.5py$  (2), shown in Fig. 2, there is one pyridine solvent molecule in a general position and a second pyridine at half-occupancy disordered about a centre of inversion. There is also small orientational disorder (83:17) in one of the isopropyl groups (not shown). With pyridine molecules removed from the refinement, the accessible solvent volume is 438 Å<sup>3</sup>. In the structure the 1.5 pyridine solvate molecules are encaged by isopropyl groups.

#### Structure of [In(S<sub>2</sub>CPip)<sub>3</sub>]·0.5py (3)

In this complex the dithiocarbamate has a smaller footprint, as the NRR' has been replaced by piperidine as shown in Fig. 3. There is one pyridine site, which is both rotationally disordered and disordered with respect to a crystallographic center of symmetry. With pyridine removed from the refinement, the solvent accessible void is 167 Å<sup>3</sup>. In the structure the pyridine molecules occupy a channel perpendicular to the *bc* plane.

#### Structure of [In(S<sub>2</sub>CNBzMe)<sub>3</sub>] (4)

Complex (4), shown in Fig. 4, has no solvate molecules in the structure. There is a non-classical hydrogen bond between S4 and a methyl H atom of a neighbouring molecule. The S…H

S4

C15

\_\_\_\_\_

the 50% probability level.

dithiocarbamates.44

Fig. 4 Structure of [In(S<sub>2</sub>CNBzMe)<sub>3</sub>] (4). Displacement ellipsoids are shown at

distance is 2.81 Å. In this solvate-free structure the packing

index is 68.4%, and there is no solvent accessible void. The average In–S bond lengths 2.590[4], 2.594[9], 2.592[11] and 2.594[11] Å observed in complexes (1)–(4), respectively, are similar to those reported for analogues of these compounds. The average C–S distances are close to 1.72 Å indicating delocalization in the CS<sub>2</sub> skeleton. The average C=N bond distances, which are approximately 1.33 Å, are sig-

nificantly shorter than the normal single bond, suggesting considerable double bond character, as expected for metal

Fig. 2 Structure of  $[ln(S_2CN(^iPr)_2)_3]\cdot 1.5py$  (2). Displacement ellipsoids are shown at the 50% probability level.

S2



In1

S5

C27

S6



#### Thermal decomposition studies of complexes (1)-(4)

The efficacy of complexes (1)-(4) as SSPs for the deposition of indium sulphide thin films was probed by thermogravimetric experiments and their TG and DTG curves are presented in Fig. 5 and S.Fig. 5a–d (ESI†). The TG profiles of pyridine solvated (1), (2) and (3) exhibit two-steps while the non-solvated precursor (4) shows a one-step pyrolysis towards the end product. The initial weight loss at temperature range of 55–115 °C from (1) and (2) and at 45–110 °C for (3) is attributed to the loss of pyridine molecules. The observed weight losses of 11.60 (1), 15.50 (2) and 6.84% (3) show some agreement with the calculated values of 11.37, 15.54 and 6.21% for the loss of 1.5 and 0.5 molecules of pyridine from (1), (2) and (3), respectively. The TG experiment on solvent free (4) did not show any weight loss in the temperature range of 45–120 °C confirming that the initial weight loss in (1), (2) and (3) is



Fig. 5 TG curves presenting losses in weight against temperature for precursors (1)-(4).

**Dalton Transactions** 

essentially due to the loss of pyridine. The TG and DTG data reveal that the precursors (1)-(4) decompose in the temperature range 230-400 °C in a single step to produce stable residue masses of 15.19, 20.09, 23.85 and 25.40%, respectively. These mass losses agree well with the theoretical values of 15.62, 21.36, 25.64 and 23.15% for the formation of  $\beta$ -In<sub>2</sub>S<sub>3</sub> from (1)-(4). The DTG curves of the pyridine solvated complexes (1)-(3) indicate two maxima of heat intake. The first heat intake occurs at 94 °C for (1) and (3) and at 84 °C for (2), indicating the removal of pyridine, while the second maxima appeared at 340 °C for (1), 290 °C for (2) and 330 °C for (3). The DTG curve of non-solvated (4) shows maximum heat intake at 340 °C and confirms its one step decomposition (S.Fig. 5a-d, ESI<sup>†</sup>). The observed final residues upon heating to 600 °C did not undergo any change in their weight suggesting that complexes (1)-(4) decompose quantitatively to furnish  $\beta$ -In<sub>2</sub>S<sub>3</sub> as a stable end product.

# Phase and crystalline structure identification of indium sulphide thin films

Indium sulphide thin films were deposited from precursors (1)–(4) on a FTO substrate at temperatures of 300, 350 and 400 °C by AACVD. The crystalline patterns obtained for the indium sulphide thin films as a function of substrate temperature were investigated by powder X-ray diffraction (PXRD) and are displayed in Fig. 6. Interestingly, similar PXRD patterns were observed for all indium sulphide thin films prepared from precursors (1)–(4) that agree well with the standard Inorganic Crystal Structure Database ICSD = [98-002-3844]<sup>45</sup> file (S.Fig. 6, ESI<sup>†</sup>) in terms of their 2 $\theta$ , *d*-spacing and reflection planes and identify the deposited product as the  $\beta$ -In<sub>2</sub>S<sub>3</sub>



Fig. 6 PXRD patterns of  $\beta$ -ln<sub>2</sub>S<sub>3</sub> deposited from precursor [In(S<sub>2</sub>CNCy<sub>2</sub>)<sub>3</sub>]·2py (1), [In(S<sub>2</sub>CN(<sup>1</sup>Pr)<sub>2</sub>)<sub>3</sub>]·1.5py (2), [In(S<sub>2</sub>CPip)<sub>3</sub>]·0.5py (3) and [In(S<sub>2</sub>CNBzMe)<sub>3</sub>] (4) at 350 (black) and 400 °C (red) on a FTO glass substrate. All of the diffraction peaks can be matched with ICSD = [98-002-3844].

crystallizing in the tetragonal crystal system with a = b = 7.632, c = 32.36 Å. The peaks indexed by (\*) correspond to the SnO<sub>2</sub> layer of the FTO substrate. The intensity of the peaks is significantly strong, which indicates that the product is well-crystallized in all cases. All the spectra are dominated by diffraction peak (123) located at  $2\theta = 27.7^{\circ}$  (d = 3.21 Å) and there is no evidence of significant grain orientation. However, the diffraction peak intensities displayed a remarkable increase with the rise in deposition temperature, which is probably due to improved crystallinity of the films when the substrate temperature was raised from 350 to 400 °C. These PXRD peak patterns show no characteristic peaks arising from possible impurities such as InS, In<sub>2</sub>SO<sub>3</sub> and other phases of In<sub>2</sub>S<sub>3</sub>. This clearly indicates that precursors (1)–(4) are capable of producing pure crystalline tetragonal phase β-In<sub>2</sub>S<sub>3</sub> at 350 and 400 °C.

Previous studies have shown that the deposition temperature, indium sulphur contents and molecular design of precursors are major parameters in determining the nature of the deposited indium sulphide phase *i.e.* InS,  $In_6S_7$ ,  $\alpha$ -In<sub>2</sub>S<sub>3</sub> and  $\beta$ -In<sub>2</sub>S<sub>3</sub>.<sup>46</sup> For example the compound [In<sup>n</sup>Bu(S<sup>i</sup>Pr)<sub>2</sub>] yielded tetragonal β-In<sub>2</sub>S<sub>3</sub> at 400 °C, however, the sulphur deficient phase, In<sub>6</sub>S<sub>7</sub>, was also grown with the rise in temperature to 450 °C.<sup>27b</sup> This is because of the dissociation of the thiolate moiety from the precursor, resulting in deposition of In<sub>6</sub>S<sub>7</sub> at a high temperature of 450 °C. In a comparative growth study of two different alkyl thiolate precursors [InMe<sub>2</sub>(S<sup>t</sup>Bu)]<sub>2</sub> and  $[In^{t}Bu_{2}(S^{t}Bu)]_{2}$ , the methyl derivative produced a mixture of In<sub>6</sub>S<sub>7</sub> and In<sub>2</sub>S<sub>3</sub> while the butyl analogue generated only the tetragonal InS phase.27a This behaviour was explained in terms of the stronger In-C bond in the methyl substituted complex that results in fragmentation of the precursor upon decomposition to give a mixture of In<sub>6</sub>S<sub>7</sub> and In<sub>2</sub>S<sub>3</sub> phases, whereas the tert-butyl derivative exhibits a clean ligand loss to furnish InS. The bis-thiolate precursor  $[InMe(S^tBu)_2]_2$  generates an amorphous phase at 400 °C that needs further annealing to yield crystalline  $\beta$ -In<sub>2</sub>S<sub>3</sub>.<sup>27a</sup>

When indium tris-(dialkyldithiocarbamates) complexes were investigated as SSPs by LPCVD technique, their unsymmetrical forms successfully yielded cubic  $\alpha$ -In<sub>2</sub>S<sub>3</sub> thin films at 500 °C while the symmetrical derivative proved not to be volatile and no deposition occurred.<sup>28</sup> A comparison of the films deposited by LPCVD at 350 °C using two different indium tris (monothiocarbamates) [In(SOCNEt<sub>2</sub>)<sub>3</sub>] and [In(SOCN<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>] precursors, reveals that the former complex produced thin films with poor morphology while the diisopropyl derivative deposited good quality  $\beta$ -In<sub>2</sub>S<sub>3</sub> thin films.<sup>31</sup> The foregoing discussion summarizes that steric demand and coordinative flexibility of the ligand have a great influence on the aggregation, stability and volatility of the resulting complexes and therefore the choice of appropriate deposition technique is required for the growth of good quality thin films.

#### Surface characterization of $\beta\mbox{-}In_2S_3$ thin films

The morphology and architectures of  $\beta$ -In<sub>2</sub>S<sub>3</sub> thin films fabricated from precursors (1)-(4) were investigated by scanning electron microscopy (SEM).

SEM images of the thin films prepared using THF solutions of the precursors (1)-(4) on FTO glass substrates at temperatures 300, 350 and 400 °C are presented in Fig. 7. These indicate that the shape and design of  $\beta$ -In<sub>2</sub>S<sub>3</sub> films vary with the rise in substrate temperature. Thin films grown from (1)-(4) at 300 °C were too thin and were not detected by PXRD and SEM micrographs. Fig. 7(a, d, g and j) show indistinguishable designs and crystallites stacked together with poor coverage of substrate. These observations suggest that none of the four precursors is completely decomposed and the slow growth rate of the films at 300 °C is due to low deposition temperature. This observation is also confirmed by TGA where decomposition of all the complexes occurs in the temperature range 340-375 °C. With the increase in deposition temperature to 350 °C, thin film growth rates from all (1)-(4) become better and the substrate surface is fully covered with different morphologies of  $\beta$ -In<sub>2</sub>S<sub>3</sub> *i.e.* (1) granular crystallites with clear boundaries, Fig. 7b, (2) lumps, Fig. 7e, (3) agglomerates of particles along with some buds, Fig. 7h, and (4) multishaped (triangular, square and hexagonal based pyramidal) interconnected crystallites, Fig. 7k. Further increasing the deposition temperature to 400 °C, (1) showed a similar kind of morphology, Fig. 7c, as was observed for (4) at 350 °C. However, (2), (3) and (4) developed large, small and flake like architectures, Fig. 7f,i,l, respectively.

All the indium sulphide films produced from precursors (1)-(4) adhered well to the FTO substrate and passed the



**Fig. 7** SEM images of β-ln<sub>2</sub>S<sub>3</sub> films deposited using precursor [ln-(S<sub>2</sub>CNCy<sub>2</sub>)<sub>3</sub>]·2py (**1**) at (a) 300 °C, (b) 350 °C and (c) 400 °C; [ln(S<sub>2</sub>CN- $(^{1}Pr)_{2})_{3}$ ]·1.5py (**2**) at (d) 300 °C, (e) 350 °C and (f) 400 °C; [ln(S<sub>2</sub>CNPip)<sub>3</sub>]·0.5py (**3**) at (g) 300 °C (h), 350 °C and (i) 400 °C and [ln(S<sub>2</sub>CNBzMe)<sub>3</sub>] (**4**) at (j) 300 °C, (k) 350 °C and (l) 400 °C.

Table 3	Description of morphologies (Fi	g. 7) and In/S ratio in thin films fabrid	cated from precursors <b>(1)–(4)</b> at 300, 350 and 400 °
---------	---------------------------------	---	--

Type of precursor	Deposition temperature °C, morphology, In/S ratio				
	300	350	400		
(1)	(a) Flakes	(b) Irregular shaped crystallites	(c) Multi-shaped crystallites		
	1:1.69	1:1.49	1:1.48		
(2)	(d) Unstructured deposit	(e) Lumps	(f) Agglomerates		
	1:1.61	1:1.66	1:1.64		
(3)	(g) Unstructured deposit with poor coverage of substrate	(h) Lumps	(i) Deteriorated crystallites		
	1:1.68	1:1.57	1:1.58		
(4)	(i) Unstructured deposit with poor coverage of substrate	(k) Multi-shaped crystallites	(l) Flakes		
. ,	1:1.89	1:1.56	1:1.47		

scotch tape test. Visual inspection of the films revealed that dark yellow films were made at 300 and 350  $^{\circ}$ C while their colour turned to orange red at 400  $^{\circ}$ C.

The film surface composition was determined by energy dispersive X-ray analysis (EDX). Table 3 and S.Fig. 7, ESI<sup>†</sup> show that the In/S atomic ratio existing in all the films prepared from precursors (1)–(4) are close to the expected ratio of 1:1.5, indicating the formation of  $\beta$ -In<sub>2</sub>S<sub>3</sub>.

#### Optical properties and band gap of thin films

The optical band gap energies of  $\beta$ -In<sub>2</sub>S<sub>3</sub> thin films fabricated from precursor (1) at 400 °C and (4) at 350 °C were studied by spectrophotometry and are presented in Fig. 8. The UV-vis spectra of these films recorded in the wavelength range between 350–1000 nm indicate significant absorption in the ultraviolet and the early visible regions, Fig. 8a.

The optical band gap  $(E_g)$  values were obtained from eqn (2) below:

$$(\alpha h\nu) = A(h\nu - E_{\rm g})^n \dots$$
<sup>(2)</sup>

where  $\alpha$  is absorption coefficient, *A* is a constant,  $h\nu$  the photon energy and *n* is an exponent which is equal to 1/2 or 2 for direct or indirect transition, respectively. The optical band gaps were calculated from the absorbance data by plotting  $(\alpha h\nu)^2 vs.$  photonic energy  $(h\nu)$  and extrapolating the linear part of the curve on the energy axis and were found to be 2.2 eV (Fig. 8b). The thickness of the  $\beta$ -In<sub>2</sub>S<sub>3</sub> films used for the optical experiments was estimated by profilometer to be 395 and 358 nm, respectively. Our band gap value is in agreement with the band gap energies of  $\beta$ -In<sub>2</sub>S<sub>3</sub> thin films made through other synthetic routes and with the bulk material.<sup>47</sup> The band structure indicates that charge transfer upon photo excitation occurs from the sulphur 3p orbital to the indium 5p empty orbital.

#### Photoelectrochemical properties

Photoelectrochemical (PEC) characteristics obtained from the electrical and optical studies of an electrode–electrolyte interface are an important tool for identifying the stability of the deposited films for electrochemical photovoltaic applications. The PEC performance of such deposited electrodes can be improved by using desirable precursors, composition,



Fig. 8 (a) UV-vis spectra of  $\beta$ -ln<sub>2</sub>S<sub>3</sub> thin films deposited using precursor (1) at 400 °C and (4) at 350 °C on the FTO substrate. (b) Shows the direct band gaps of 2.2 eV for  $\beta$ -ln<sub>2</sub>S<sub>3</sub> films.

concentration, deposition temperature, deposition time *etc.* The PEC characteristics of as-prepared  $\beta$ -In<sub>2</sub>S<sub>3</sub> films from precursors (1) and (4) by AACVD at 400 and 350 °C under the alternative dark and illumination conditions are shown in Fig. 9 and 10, respectively. The plots indicated that under illumination a  $\beta$ -In<sub>2</sub>S<sub>3</sub> electrode exhibits an anodic photocurrent, which increases with increasing anodic bias.<sup>48</sup> The rectified *I*-*V* plot (Fig. 9) of  $\beta$ -In<sub>2</sub>S<sub>3</sub> from precursor (1) at 400 °C shows 1.25 mA cm<sup>-2</sup> of photocurrent density at 0.23 V *vs.* Ag/AgCl and rises steeply up to 1.5 mA cm<sup>-2</sup> as the applied voltage further increased without reaching the saturation point. The  $\beta$ -In<sub>2</sub>S<sub>3</sub> films prepared using precursor (1) at 400 °C displayed higher photocurrent response compared to the other



Fig. 9  $\mathit{J-V}$  plot of  $\beta\text{-In}_2S_3$  films obtained from precursor (1) by AACVD at 400 °C.



Fig. 10  $\,$  J–V plot of  $\beta\text{-In}_2S_3$  films obtained from precursor (4) by AACVD at 350 °C.

depositions, which is attributed to the good interconnections and uniform structure of the multi-shaped β-In<sub>2</sub>S<sub>3</sub> crystallites in the film. As is evident from the SEM images and XRD patterns, the film deposited using precursor (1) at 400 °C is superior to films deposited at 300 and 350 °C. For better performance of an electrode, the structural uniformity and crystallinity are highly important in acquiring a better charge transport. Films fabricated from precursor (1) at 400 °C have structural uniformity and crystallinity resulting in better PEC performance. As is evident from the SEM images, the electrodes fully covered with sharp-edged crystallites of β-In<sub>2</sub>S<sub>3</sub> films deposited at 400 °C from precursor (1) benefit in terms of improved charge transfer by avoiding electron-hole recombination. The I-V plots confirmed that precursors (1) and (4) are suited for the fabrication of good  $\beta$ -In<sub>2</sub>S<sub>3</sub> thin films by AACVD technique. The deposited  $\beta$ -In<sub>2</sub>S<sub>3</sub> films display a reasonable photosensitivity, which indicates their potential for application in optoelectronic devices.

### Conclusions

Pyridine solvated (1)-(3) and non-solvated (4) tris(N,N-dialkyldithiocarbamato)indium(III) complexes, with the general formula  $[In(S_2CNRR')_3] \cdot n(py)$ , have been prepared, characterized and implemented as AACVD precursors for the deposition of  $\beta$ -In<sub>2</sub>S<sub>3</sub> thin films. Despite of the different nature of the alkyl groups, metal ligand designs and deposition temperatures, each of the complexes exhibits only one phase and stoichiometry equivalent to  $\beta$ -In<sub>2</sub>S<sub>3</sub> as confirmed by PXRD, SEM and EDX analyses of the thin films. These studies have discovered that regardless of the attachment of different ligands to In, comparable morphologies of  $\beta$ -In<sub>2</sub>S<sub>3</sub> at different temperatures were obtained. UV-vis measurements of the  $\beta$ -In<sub>2</sub>S<sub>3</sub> films showed band gap energies ( $E_{\alpha}$ ) of 2.2 eV, making them suitable for photocatalytic activities. The  $\beta$ -In<sub>2</sub>S<sub>3</sub> films deposited from precursor (1) at 400 °C exhibited a photocurrent density of 1.25 mA cm<sup>-2</sup> vs. Ag/AgCl with an applied bias of 0.23 V. The results confirmed that the newly synthesised single source precursors are suitable to obtain promising photoactive  $\beta$ -In<sub>2</sub>S<sub>3</sub> thin films by AACVD method for application in solar cells and other optoelectronic devices.

### Acknowledgements

The authors acknowledge High-Impact Research scheme (grant numbers UM.C/625/1/HIR/131) and the UMRG scheme (grant number UM.TNC2/RC/261/1/1/RP007-13AET) for funding this research. TANP and KGUW acknowledge the support from the UK EPSRC and Johnson Matthey Plc.

#### Notes and references

- (a) A. A. Tahir and K. G. U. Wijayantha, J. Photochem. Photobiol., A, 2010, 216, 119; (b) A. A. Tahir, M. Mazhar, M. Hamid, K. G. U. Wijayantha and K. C. Molloy, Dalton Trans., 2009, 3674.
- 2 A. A. Tahir, K. G. U. Wijayantha, S. S-Yarahmadi, M. Mazhar and V. McKee, *Chem. Mater.*, 2009, 21, 3763.
- 3 L. Bhira, H. Essaidi, S. Belgacem, G. Couturier, J. Salardenne, N. Barreau and J. C. Bernede, *Phys. Status Solidi A*, 2000, 181, 427.
- 4 C. D. Lockhande, A. Ennaoui, P. S. Patil, M. Giersig,
  K. Diesner, M. Muller and H. Tributsch, *Thin Solid Films*, 1999, 340, 18.
- 5 E. Dalas and L. J. Kobotiatis, J. Mater. Sci., 1993, 28, 5456.
- 6 (a) Y. Xing, H. J. Zhang, S. Y. Song, J. Feng, Y. Q. Lei,
  L. J. Zhao and M. Y. Li, *Chem. Commun.*, 2008, 1476;
  (b) X. L. Fu, X. X. Wang, Z. X. Chen, Z. Z. Zhang, Z. H. Li,
  D. Y. C. Leung, L. Wu and X. Z. Fu, *Appl. Catal.*, *B*, 2010, 95, 393.
- 7 (a) W. Chen, J. O. Bovin, A. G. Joly, S. Wang, F. Su and G. Li, J. Phys. Chem. B, 2004, 108, 11927; (b) S. Yu, L. Shu,

Y. Qian, Y. Xie, J. Yang and L. Yang, *Mater. Res. Bull.*, 1998, 33, 717.

- 8 Y. He, H. D. Li, Z. G. C. Xiao, W. Chen, Y. B. Chen, M. Sun, H. J. Huang and X. Z. Fu, *J. Phys. Chem. C*, 2009, **113**, 5254.
- 9 (a) S. K. Sarkar, J. Y. Kim, D. N. Goldstein, N. R. Neale,
  K. Zhu, C. M. Elliott, A. J. Frank and S. M. George,
  J. Phys. Chem. C, 2010, 114, 8032; (b) J. Tabernor,
  P. Christian and P. O'Brien, J. Mater. Chem., 2006, 16, 2082.
- 10 (a) N. Naghavi, S. Spiering, M. Powalla, B. Cavana and D. Lincot, *Progr. Photovolt.: Res. Appl.*, 2003, **11**, 437;
  (b) K. Hara, K. Saya and H. Arakawa, *Sol. Energy Mater. Sol. Cells*, 2001, **62**, 441.
- 11 L.-Y. Chen, Z.-D. Zhang and W.-Z. Wang, *J. Phys. Chem. C*, 2008, **112**, 4117.
- 12 J. Sterner, J. Malmstrom and L. Stolt, *Progr. Photovolt.: Res. Appl.*, 2005, **13**, 179.
- 13 D. K. Nagesha, X. Liang, A. A. Mamedov, G. Gainer, M. A. Eastman, M. Giersig, J.-J. Song, T. Ni and N. A. Kotov, *J. Phys. Chem. B*, 2001, **105**, 7490.
- 14 I. Puspitasari, T. P. Gujar, K. D. Jung and O. S. Joo, *J. Mater. Process. Technol.*, 2008, **201**, 775.
- 15 K. Govender, D. S. Boyle and P. O'Brien, *J. Mater. Chem.*, 2003, **13**, 2242.
- 16 S. Avivi, O. Palchik, V. Palchik, M. A. Slifkin, A. M. Weiss and A. Gedanken, *Chem. Mater.*, 2001, 13, 2195.
- 17 L. Zhang, W. Zhang, H. Yang, W. Fu, M. Li, H. Zhao and J. Ma, *Appl. Surf. Sci.*, 2012, **258**, 9018.
- (a) W. Qiu, M. Xu, X. Yang, F. Chen, Y. Nan, J. Zhang, H. Iwaic and H. Chen, *J. Mater. Chem.*, 2011, 21, 13327;
  (b) H. Zhu, X. Wang, W. Yang, F. Yang and X. Yang, *Mater. Res. Bull.*, 2009, 44, 2033.
- 19 (a) S. Rengaraj, S. Venkataraj, C.-W. Tai, Y. Kim, E. Repo and M. Sillanpaa, *Langmuir*, 2011, 27, 5534; (b) L. Liu, H. Liu, H.-Z. Kou, Y. Wang, Z. Zhou, M. Ren, M. Ge and X. He, *Cryst. Growth Des.*, 2009, 9, 1.
- 20 M. A. Franzman and R. L. Brutchey, *Chem. Mater.*, 2009, 21, 1790.
- 21 N. Revathi, P. Prathap, R. W. Miles and K. T. R. Reddy, *Sol. Energy Mater. Sol. Cells*, 2010, **94**, 1487.
- 22 A. S. Cherian, M. Mathew, C. S. Kartha and K. P. Vijayakumar, *Thin Solid Films*, 2010, **518**, 1779.
- 23 S. Cingarapu, M. A. Ikenberry, D. B. Hamal, C. M. Sorensen,K. Hohn and K. J. Klabunde, *Langmuir*, 2012, 28, 3569.
- 24 T. Todorov, J. Carda, P. Escribano, A. Grimm, J. Klaer and R. Klenk, *Sol. Energy Mater. Sol. Cells*, 2008, **92**, 1274.
- 25 S. S. Lee, K. W. Seo, J. P. Park, S. K. Kim and Il-W. Shim, *Inorg. Chem.*, 2007, **46**, 1013.
- 26 M. A. Malik, M. Afzaal and P. O'Brien, *Chem. Rev.*, 2010, **110**, 4417.
- 27 (a) A. N. MacInnes, M. B. Power, A. F. Hepp and A. R. Barron, *J. Organomet. Chem.*, 1993, 449, 95;
  (b) R. Nomura, S.-J. Inzawa, K. Kanaya and H. Matsuda, *Appl. Organomet. Chem.*, 1989, 3, 195.
- 28 P. O'Brien, D. J. Otway and J. R. Walsh, *Thin Solid Films*, 1998, **315**, 57.

- 29 D. G. Hehemann, J. E. Lau, J. D. Harris, M. D. Hoops, N. V. Duffy, P. E. Fanwick, O. Khan, M. H.-C. Jin and A. F. Heppa, *Mater. Sci. Eng.*, *B*, 2005, **116**, 381.
- 30 S. W. Haggata, M. A. Malik, M. Motevalli, P. O'Brien and J. C. Knowles, *Chem. Mater.*, 1995, 7, 716.
- 31 (a) G. A. Horley, P. O'Brien, J.-H. Park, A. J. P. White and D. J. Williams, *J. Mater. Chem.*, 1999, 9, 1289;
  (b) G. A. Horley, M. Chunggaze, P. O'Brine, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1998, 4205.
- 32 V. G. Bessergenev, E. V. Ivanona, Y. A. Kovalevskaya, S. A. Gromilov, V. Kirichenko and S. V. Larionov, *Inorg. Mater.*, 1996, 6, 1639.
- 33 (a) N. L. Pickett and P. O'Brien, *Chem. Rec.*, 2001, 467;
  (b) M. Afzaal, M. A. Malik and P. O'Brien, *J. Mater. Chem.*, 2010, 20, 4031.
- 34 S. A. Bakar, S. T. Hussain and M. Mazhar, New J. Chem., 2012, 36, 1844.
- 35 M. Sultan, A. A. Tahir, M. Mazhar, K. G. U. Wijayantha and M. Zeller, *Dalton Trans.*, 2011, **40**, 7889.
- 36 M. Sultan, A. A. Tahir, M. Mazhar, M. Zeller and K. G. U. Wijayantha, *New J. Chem.*, 2012, 36, 911.
- 37 N. Alam, M. S. Hill, G. Kociok-Köhn, M. Zeller, M. Mazhar and K. C. Molloy, *Chem. Mater.*, 2008, **20**, 6157.
- 38 M. A. Ehsan, H. N. Ming, M. Misran, Z. Arifin, E. R. T. Tiekink, A. P. Safwan, M. Ebadi, W. J. Basirun and M. Mazhar, *Chem. Vap. Deposition*, 2012, **18**, 191.
- 39 M. Brewer, D. Khasnis, M. Buretea, M. Berardini, T. J. Emge and J. G. Brennan, *Inorg. Chem.*, 1994, 33, 2743.
- 40 G. M. Sheldrick, *SADABS. Program for empirical absorption correction of area detector data*, University of Göttingen, Germany, 2004.
- 41 G. M. Sheldrick, Acta Crystallogr., Sect. A: Fundam. Crystallogr., 2008, 64, 112.
- 42 I. Bedja and A. Hagfeldt, *Adv. Optoelectron.*, 2011, 6, 824927.
- 43 (a) A. F. Lindmark and R. C. Fay, *Inorg. Chem.*, 1983, 22, 2000; (b) M. M. Oliverira, G. M. Pessoa, L. C. Carvalho, C. Peppa, A. G. Souza and C. Airoldi, *Thermochim. Acta*, 1999, 328, 223.
- 44 (a) P. J. Heard, *Prog. Inorg. Chem.*, ed. K. D. Karlin, John Wiley & Sons, London, 2005, vol. 53, ch. 1, pp. 1–69;
  (b) D. P. Dutta, V. K. Jain, A. Knoedler and W. Kaim, *Polyhedron*, 2002, 21, 239;
  (c) E. B. Clark, M. L. Breen, P. E. Fanwick, A. F. Hepp and S. A. Duraj, *J. Coord. Chem.*, 2000, 52, 111.
- 45 J. Goodyear, H. H. Sutherland and G. A. Steigmann, *Acta Crystallogr.*, 1962, **15**, 512.
- 46 M. lazell, P. O'Brien, D. J. Otway and J.-H. Park, *Dalton Trans.*, 2000, 4479.
- 47 N. A. Allsop, A. Schönmann, A. Belaidi, H.-J. Muffler, B. Mertesacker, W. Bohne, E. Strub, J. Röhrich, M. C. Lux-Steiner and Ch.-H. Fischer, *Thin Solid Films*, 2006, 513, 52.
- 48 P. M. Sirimanne, S. Shiozaki, N. Sonoyama and T. Sakata, Sol. Energy Mater. Sol. Cells, 2000, **62**, 247.