

Indium(III) complexes: application as organic catalyst, precursor for chalcogenides nanoparticles and starting materials in the industry

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Abstract

Trivalent indium ions are not toxic like the common ions, and this implies that there are limited secondary pollution associated with their photoconversion processes. They are therefore a preferred choice for several applications. However, they are not used in their ionic form. Their salts are reacted with various organic ligands to form different trivalent complexes of indium for these applications. Herein, the use of different trivalent complexes as catalysts in organic synthesis are discussed. Their usage as a precursor of indium oxide, indium sulfide, indium tellurides and indium selenides are examined. In addition, their application as organic light-emitting diodes (OLEDs), sensor, photovoltaic and luminous materials are discussed. Finally, gaps and/or areas for future research are highlighted.

Keywords Indium · Catalyst · Nanoparticles · Inorganic complexes

Introduction

The continued study of indium(III) complexes over the years has revealed a rich tapestry of applications, which ranged from their usage as catalysts in many organic synthesis (Teo et al. 2005) to their usefulness as precursor materials in the controlled synthesis of chalcogenides nanoparticles (Masikane and Revaprasadu 2020) and their indispensable role as starting materials in various industries (Beraldo 2020). Fundamentally, indium, by itself, has garnered attention in coordination chemistry and material science due to its versatility and possibilities for application in many areas (LaFortune

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et al. 2021). This metal is considered rare on Earth (Herrera et al. 2022), with an abundance of about 0.25 ppm, and is usually found as ores with metals such as Zn (LaFortune et al. 2021). Its rarity has also contributed to its categorization as critical, heightening its economic importance and value industrially (Cho et al. 2002). Its unique chemical and physical properties have made it an asset in diverse applications. For instance, its low melting point of about 156.6 °C makes it malleable within a wide temperature range, which in turn makes it ideal for applications involving soldering and as a component to produce fusible alloys (Dennis and Such 1993; Furusawa et al. 2019). In coordination chemistry, indium can exist in different oxidation states, most notably indium(III), making it versatile in forming varying coordination compounds (Herrera et al. 2022). Its ability to behave like a Lewis acid makes the possibility for participation in various catalytic processes of different organic processes possible (LaFortune et al. 2021). Consequently, its complexes have been used in reactions involving C-C bond formation, asymmetric synthesis and other important reactions (Pérez et al. 2018; Schneider and Kobayashi 2012). Furthermore, its usage in the preparation of transparent conductive films like indium tin oxide (ITO), which are widely used in electronic devices, solar cells, touch screens and flat panel displays, due to its excellent electrical conductivity and transparency, underscores its importance in the field of material science (Kanai 1984). Thus, indium's versatile

Specifically, indium(III) complexes are a well-explored and fascinating class of compounds in coordination chemistry due to the ability of indium in its +3 state to form a variety of complexes with different ligands, which in turn contributes to its versatile applications and synthesis (Acosta-Ramírez et al. 2010; Piskunov et al. 2009; Sun et al. 1996). Hence, to understand this class of compounds, understanding their structures, boding characteristics, reactivities and usefulness in catalysis is crucial. For instance, indium(III) complexes often adopt a ligand-dependent geometry which ranges between bipyramidal and octahedral, with common donor atoms such as carboxylates, hydroxides, oxides and nitrogen donor atoms like imines and amines (Abram et al. 1997; Salsi et al. 2020). The sizes and charges of the ligands have been thought to account for the general stereochemistry of the ensuing complexes, which, in turn, lead to a variety of coordination arrangements (Adeyemi and Onwudiwe 2018). Also, the bonding in indium(III) complexes is mostly covalent, in which the indium metal acts as a Lewis acid with a partially vacant d orbital. Ligands thus easily donate electron pairs to form a coordinate covalent bond with the indium center, which is readily influenced by factors such as coordination number, the electronegativity of the donating ligand and the ensuing stereochemistry of the complexes, just as seen in other metal complexes. Several derivatives of these complexes have been involved in various chemical transformations and catalytic processes (Osten and Mehrkhodavandi 2017; Stolarov et al. 2018; Xin Zhang et al. 2007). These complexes can facilitate many reactions, including C-C bond formation, nucleophilic additions and redox reactions due to the Lewis acidity properties of the indium centers (Nan and Zhou 2013; Osten and Mehrkhodavandi 2017; Stolarov et al. 2018). Furthermore, diverse variations can be made or fine-tuned by modifying the coordinating ligands or altering the coordination environments. This propensity has allowed for the synthesis of a wide range of indium(III) complexes, which has also resulted in different applications across the fields of catalysis, biology and material science.

According to several literature reports, indium(III) complexes have been used in a wide range of applications across various scientific and industrial domains due to their versatile properties and reactivity (Beraldo 2020; Herrera et al. 2022; Masikane and Revaprasadu 2020; Pérez et al. 2018). They have been used as a catalyst in a variety of organic transformations such as the Friedel-Crafts acylation (Christopher G Frost and Lévesque 2001), hydroamination (Rajesh et al. 2014), aldol condensation (Fan Fu et al. 2006) and asymmetric alkylations (Fujimoto et al. 2008), due to the Lewis acidic nature, which enables them to activate substrates involved in critical steps of chemical reactions. Their ability to facilitate these reactions with high efficiency and selectivity has made these compounds a choice material for organic synthesis. Similarly, indium(III) complexes have become a choice precursor compound for the controlled synthesis of indium chalcogenides materials such as indium sulfides, indium selenides and indium tellurides, which are choice materials for sensing, photovoltaics and optoelectronic devices (Pahari Dutta et al. 2001; Sharma et al. 2013; Xiao et al. 2021). This controlled preparation via the use of precursor complexes allows for a precise fine-tuning ability of the material size, composition and morphology, thus underscoring their exceptional usefulness in material science. Furthermore, indium(III) complexes have become a desirable fundamental material for starting various industrial reactions, specifically for those used in the production of semiconductors and electronic devices (Gyeongbae Park et al. 2022). For instance, due to their unique transparency and conductivity, indium tin oxide has become indispensable in the production of electronic, flat panel displays, touchscreens and solar cells, which are essential in the design of many notable devices today (Heffner et al. 2023; Gyeongbae Park et al. 2022).

There are few review articles focusing on the synthesis and chemistry of indium complexes but none of them extensively discussed the various industrial applications of indium complexes (Anwar et al. 2020; Govil and Jana 2021). For instance, Pérez et al. (2001) focused on the crosscoupling reaction of indium organometallic compounds with various organic electrophiles. Also, Jung et al. (2021) focused mainly on the catalytic applications of selected cationic metal complexes including indium complexes. In our previous research (Timothy O. Ajiboye et al. 2024), we reviewed the medical and biological applications of indium complexes, but the synthesis and industrial applications of indium complexes have not been reviewed. Although other applications are continuously emerging for this group of complexes, in this current review, the focus will be limited to the recent application as a catalyst for organic reactions, usage as a single source precursor compound for the preparation of metal chalcogenides nanoparticles, as starting material for some industrial processes and their application as biological agents. As such, this review aims to explore the use of various derivatives of indium(III) complexes for the listed applications.

Application of indium(III) complexes

There are emerging industrial applications of indium(III) complexes. For instance, In(III) complex with *N*-ethyl-sulfonyl dithiocarbimate has been utilized as vulcanization accelerator. The complex was particularly useful due to its stability in aqueous media with a half-life of four hours as

revealed by the degradation studies (de Freitas et al. 2021). In this section, various applications of indium(III) complexes will be discussed. The various application are as follows; Lewis acid catalyst, catalyst, precursors for different inorganic chalcogenides, organic light-emitting diodes, photovoltaics, luminescent materials and medicine application. There are more fields to explore in the application of indium(III) complexes.

Application of indium complexes as catalyst in organic synthesis

Indium(III) complexes can serve as a catalyst in various chemical reactions. Its complexes can catalyze organic transformations such as C-C and C-N bond formation, oxidative coupling and cross-coupling reactions (Klussmann and Sureshkumar 2011). Therefore, its complexes can be used in the reaction of the following: C-C bond formation, asymmetric catalysis, carbonylation reactions, ring-opening polymerization and hydrofunctionalization reaction. These complexes can exhibit high selectivity and activity, making these complexes valuable in synthetic chemistry. Organoindium compounds are not just used as catalyst, but they are also used as Lewis acid. Although, Grignard and alkyllithiums reagents are more reactive than organo-indium compounds, indium metal reacts with organic substrate to produce an in situ species of organo-indium which prevent the application of expensive, toxic and sensitive organometallic compounds (Gopalsamuthiram 2005). Its complexes can easily promote reactions like Friedel-Craft acylation and Diels-Alder reactions by activating substrates and facilitating bond formation (Sarmah and Prajapati 2014). Therefore, Reformatsky, allylation and cyclopropanation reaction are effected via the reaction of indium metals and α -haloesters, methylene and dibromides, respectively (CG Frost and Hartley 2004).

However, there is a unique ability for indium to carry out the above listed reactions in comparison with zinc and tin. Its exceptional stability to air and water makes it useful under aqueous reactions. Water inherent benefits as a solvent have sparked a surge in interest in indium-mediated processes. As Lewis acid catalysts, indium(III) complexes have recently attracted a lot of attention. Indium(III) salts are resilient to water and reusable, while being rather weak in comparison with their aluminum and boron equivalents (Bayat and Gheidari 2022). Contrary to the reverse reactions, trans-esterification of esters to their corresponding counterparts with greater alcohol moieties is widely reported but resolved using indium iodide (Bayat and Gheidari 2022). In comparison with previously described titanium and aluminum reagents, the reaction offers a straightforward and efficient trans-esterification technique (Cotgreave 2004; Cuminet et al. 2021). This technique has been used to achieve trans-esterification to a tert-butyl ester, which is frequently difficult in acid-catalyzed processes. The same team expanded on this technology by transesterifying ethyl acetate in order to perform indium iodide-catalyzed heteroatom acylation (Cotgreave 2004; Cuminet et al. 2021). The acylation of amines and primary alcohols in the presence of secondary and phenolic alcohols is catalyzed by the use of 10 mol% InI₃ (made in situ from indium metal and iodine) (Fringuelli et al. 2003; Selas 2022).

The use of indium(III) complexes as Lewis acids can be linked to their stability when coordinated with organic substrates. In addition, they are stable in water which makes recycling in aqueous system feasible. They have been used in multicomponent coupling reactions, conjugate additions, cycloaddition reactions and aromatic functionalization (CG Frost and Hartley 2004). One of the indium complexes that has been used for different organic synthesis is indium(III) trifluoromethanesulfonate (also known as indium triflate (In(OTf)₃)). This complex has been successfully used for the ring-opening of aziridine to obtain regioselective β -arylamines as the major product as shown in Fig. 1. The reaction is even effective when the aziridine contains aryl substituent. In that case, the benzylic position of the arene is selectively attacked (Yadav et al. 2010).

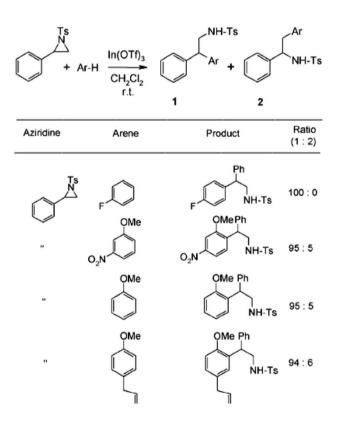


Fig. 1 The ring-opening reactions of aziridine catalyzed by indium triflate. *Reproduced with permission from* (Yadav et al. 2010). *Copyright (2010), John Wiley and Sons*

Indium triflate has also been used as catalyst for opening the ring of meso-epoxide in the presence of aniline. In this reaction, chiral β-amino alcohols are obtained when electron-donating or electron-withdrawing groups are attached to either the para- or ortho- position of the aromatic amine as shown in the Fig. 2a. Indium triflate has been utilized effectively as catalyst for converting ketones and aldehydes to 1,3-oxathiolanes (Kazahaya et al. 2002). Apart from this, indium triflate has been successfully used as catalysts for the allylation of keto-phosphonate (Fig. 2b) (Ranu et al. 2001). It has also been used to carry out Friedel-Craft reactions. For instance, the use of alkyl benzene to produce alkyl benzophenone through Friedel-Craft acylation mediated by microwave irradiation and benzoyl chloride has been made possible by using indium triflate as the catalyst in the absence of solvents (Koshima and Kubota 2003). In addition, it has been used as the catalyst for the synthesis of pyrrolidinones (Takahashi et al. 2008), phenanthridines (Yanada et al. 2008) and β -branched alpha-amino acids (Angell et al. 2007). It has also been used as catalyst for the addition of carbonyl compounds (Yamamoto and Oshima 2006) and vinylation of β -keto esters in the presence of acetylene (Nakamura et al. 2005). Others are Diels-Alder reactions, pyran and tetrahydrofuran ring formation as well as coupling of alkyne with carbonyl compounds (Rina Ghosh and Maiti 2007).

In the C–C bond formation, indium(III) complexes can be employed as catalysts such as carbon–carbon bond crosscoupling reactions (Klussmann and Sureshkumar 2011). These complexes can facilitate the coupling of different organic substrates, leading to the synthesis of important compounds such as in the case of stille coupling reaction and barbier-type reactions. Also in the asymmetric catalysis, indium(III) complexes can serve as catalysts in asymmetric

(a)

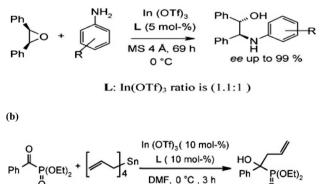


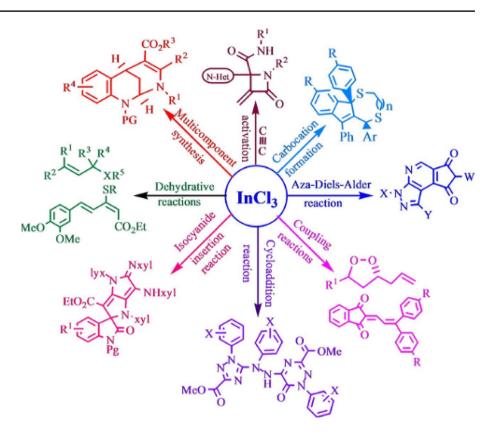
Fig. 2 a The ring-opening reaction of meso-epoxide catalyzed by indium triflate. *Reproduced with permission from* (Yadav et al. 2010). *Copyright (2010), John Wiley and Sons.* b Allylation of keto-phosphonate catalyzed by indium triflate. *Reproduced with permission from* (Ranu et al. 2001). *Copyright (2001), American Chemical Society*

reactions, enabling the production of chiral compounds with high enantioselectivity (Cao et al. 2019). These complexes have been employed in various transformations, including asymmetric allylation, aldol reactions and Michael additions. The unique coordination environment and steric properties of indium(III) complexes contribute to their ability to induce chirality in these reactions. Likewise, in the reaction of carbonylation, Indium(III) complexes have shown catalytic activity in carbonylation reactions, where carbon monoxide is incorporated into organic molecules (Artz et al. 2018). These complexes can facilitate the formation of carbon-carbon and carbon-oxygen bonds, leading to the synthesis of carboxylic acids, esters and other carbonyl-containing compounds. The mild reaction conditions and high selectivity offered by indium(III) complexes make them attractive catalysts in carbonylation processes (Yan et al. 2022). Also, in the ring-opening polymerization, Indium(III) complexes have been explored as catalysts in ring-opening polymerization reactions. These reactions involve the opening of cyclic monomers to form linear polymers (Santoro et al. 2020). Indium(III) complexes have demonstrated catalytic activity in the polymerization of cyclic esters, such as lactones, leading to the production of biodegradable polyesters. This application is particularly important in the development of sustainable materials. In the hydro functionalization reaction, indium(III) complexes have been used to catalyze the reactions, this involves the addition of functional groups (such as alkyl, aryl or heteroatom substituents) across unsaturated bonds (Juan Zhang et al. 2020). These complexes have been employed in hydroamination and hydroalkoxylation reactions, enabling the selective addition of amine or alcohol groups to carbon-carbon multiple bonds.

Another compound of indium that has been widely utilized in organic synthesis is indium(III) chlorides. Some of the reactions that has been catalyzed by indium(III) chlorides are multicomponent synthesis, alkyne activation, formation of carbocation, Aza-Diels-Alder reaction, cycloaddition reaction, isocyanide insertion reaction and dehydrative reaction (Datta 2021) (Fig. 3). Apart from the chlorides, common indium(III) compounds that have been utilized for catalyzing several reactions are the indium(III)-based ionic liquids. It has successfully been used for catalyzing reactions such as levulinic acid esterification to ethyl levulinate, biomass depolymerization to levulinic acid, condensation of aldehydes, hydrazones and 1,3-diketones, Biginelli condensation, alkylation, nucleophile additions to cyclic N-acyliminium ions, epoxides coupling, acetalization, tetrahydropyranylation of alcohols and Friedel-Crafts acylation (Więcławik and Chrobok 2023).

Cascade cycloisomerization catalyzed by indium(III) complexes have also been reported. This takes place via the reaction of pendant aryl nucleophiles with 1,5-enynes as shown in Fig. 4a. The reaction took place even when the

Fig. 3 Organic synthesis catalyzed by indium(III) chloride. *Reproduced with permission* from (Datta 2021). Copyright (2021), John Wiley and Sons



1,5-enynes reactant was furnished with phenol and phenyl groups. Further probe into the mechanism of the reaction showed that the reaction could occur through a stepwise route or concerted process as shown in Fig. 4b. If it occurs through a two-step mechanism, there will first be coordination of the alkyne moiety (C) with indium(III) halide resulting in the cyclization to give an intermediate D. This will be followed by Friedel-Crafts type alkylation reaction, aromatization and then protodemetallation with the regeneration of the catalyst (Millán et al. 2021).

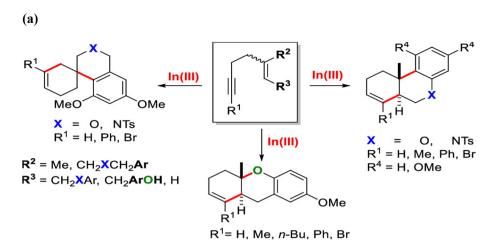
Indium(III) chloride has also been reported to be an effective catalyst for the three component coupling of amines, alkynes and aldehydes through a reaction involving C–H activation (Fig. 5). The aldehyde required for the reaction could be aliphatic or aromatic and good yields are obtained irrespective of the type used. The only byproduct of the reaction is water and the reaction required neither activator nor cocatalyst (Yicheng Zhang et al. 2009). Other reactions utilizing indium(III) species as catalysts for synthesizing different organic compounds are shown in Table 1.

Indium(III) complexes as precursors of indium chalcogenides

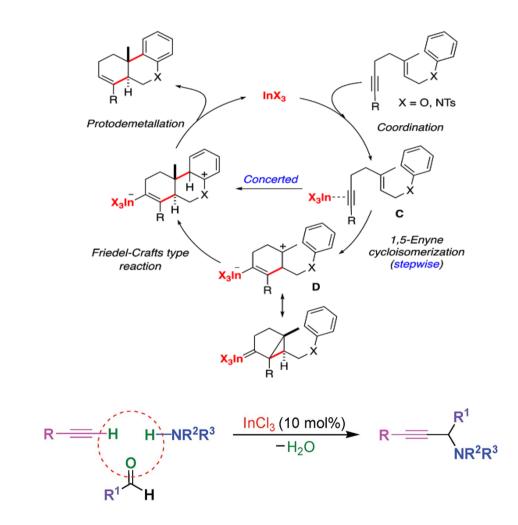
Indium chalcogenides have been produced from different single source precursors. Some of these precursors are alkoxides, dithiobiurets, thiobiurets, dithioimidodiphosphinates, dithiocarbamates, thiocarboxylates selenolates and thiolates of indium(III) complexes (Bano et al. 2023; Cheung et al. 2006; Joo-Hyun Park et al. 2020). The conversion of these single source precursors into the chalcogenides were achieved via heat-up method, chemical vapor deposition methods, spray pyrolysis, chemical bath deposition, hydrothermal, solvothermals and sol-gel methods (Ajiboye et al. 2022b; Ajiboye et al. 2022a; Kumari et al. 2023). The preparation of indium chalcogenides from these precursors is advantageous because the products obtained is characterized with pure stoichiometric phases (Joo-Hyun Park et al. 2020). The metal chalcogenides synthesized via this method have been found to be useful in electronics, optoelectronic, rectifiers, antennas, energy conversion, solar cells, magnetic storage media, batteries, medicine, gas sensors and heterogeneous catalysts (Ajiboye et al. 2023; Chavali and Nikolova 2019; de Jesus et al. 2024).

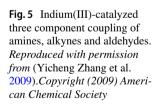
Indium(III) complexes as precursors of indium oxide

Indium oxide has several applications and some of these applications are gas sensing (Bierwagen 2015), infrared reflective and electrochromic windows, antireflection coatings in ultraviolet lasers, transparent contact, photovoltaic devices, light emission diodes, liquid crystal displays, touch screens, photodiodes and optoelectronic devices (Babu et al. 2016). Due to the numerous applications of indium oxide, its synthesis using different methods have been investigated. One of the methods involve the use of different inorganic Fig. 4 a Indium(III)-catalyzed cycloisomerization reaction. b Mechanisms of cascade cycloisomerization reaction catalyzed by indium complexes. Reproduced with permission from (Millán et al. 2021).Copyright (2021) American Chemical Society, Open Access



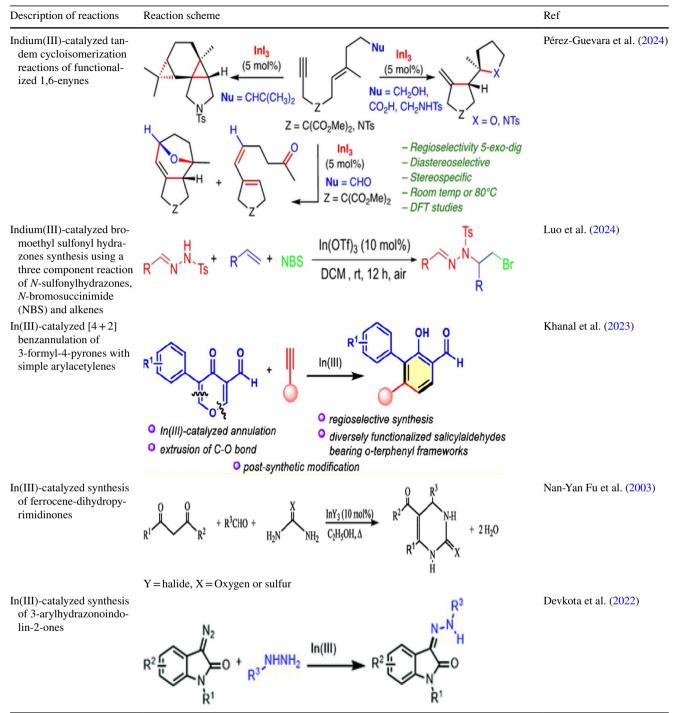
(b)





or organometallic precursors. Indium complexes containing β -diketonate ligands has attracted attention as precursors for indium oxide. They are particularly useful due to their stability in air and simpler method of synthesizing them. Indium *tris*-dipivaloylmethanate is commonly used among β -diketonate compounds because of the presence of bulky *tert*-butyl terminal groups which contributed to its high volatility compared to other similar compounds (Sliznev et al. 2015). In a particular investigation, indium *tris*dipivaloylmethanate has been used as a single source

Table 1 Indium(III)-catalyzed organic synthesis



precursor for synthesizing indium oxide. During the thermal decomposition process, it was observed that the complex was stable as condensed phase even at 250 °C. Though, between 105 and 130 °C, there was solid–solid phase transition which makes the studying of its vapor pressure feasible (Vikulova et al. 2022). Apart from this, the complex can be used to obtain the In_2S_3 as a single source precursor at a

deposition temperature that is relatively low (usually below 400 °C). It has however been observed that the growth rate of indium oxide is usually slow between 200 and 300 °C but there is a fast film growth rate of indium oxide between 300 and 350 °C (Marchand and Carmalt 2013; Vikulova et al. 2022).

Alkoxides of indium are other complexes that have been used as precursor for obtaining indium oxide nanoparticles (Marchand and Carmalt 2013). For instance, indium oxide films doped with tantalum and titanium were obtained through in situ generation of indium oxide from $M(NMe_2)_x$ (x=5, M=Ta; x=4, M=Ti), HOCH₂CH₂NMe₂ and $InMe_3$ (where Me = methyl group) at 400–450 °C in the presence of toluene. Through this method, the indium oxide obtained was the cubic phase of In_2O_3 bixbyite (Bloor et al. 2012). Yoo et al. (2021) reported the use of three different ligands bearing β -diketonate and *N*-alkoxy carboxamide to prepare novel heteroleptic indium complexes. These complexes were used as precursors for synthesizing indium oxide through atomic layer deposition technique. The novel complexes were good precursor for indium oxide due to their low vaporization temperature and high thermal stability.

Metallic-doped In₂O₃ has also been used by introducing other inorganic complexes into bismuth complexes. Nu et al. (2005) successfully prepared tin and magnesiumdoped bismuth oxide by preparing tris(2,2,6,6-tetramethyl-3,5-heptanedionato)-indium(III). The preparation of this complex involves the reaction of hydrated indium nitrate with 1-propyl amine in ethanol. The white precipitate indium complex was used along with bis(2,2,6,6-tetramethyl-3,5heptanedionato)-(N,N,N',N'-tetramethylethylenediamine) magnesium(II) and *bis*(2,4-pentanedionato)tin(II) via low-pressure metal-organic chemical vapor deposition (CMOCVD) to prepare the metallic-doped bismuth oxide (Ni et al. 2005). Relatedly, series of tin-doped indium oxide has been prepared from three different indium complexes (tert-butoxymethyl indium, indium, tris (2,2,6,6-tetramethyl-3,5-heptanedionato) and indium(III) acetylacetonate) reacted separately with either tin (II) acetylacetonate or dibutyltindiacetate and deposited at 350° using CMOCVD (Szkutnik et al. 2014). Relatedly, tert-butoxymethyl indium, indium, tris (2,2,6,6-tetramethyl-3,5-heptanedionato) and indium(III) acetylacetonate have separately been reacted with tin (II) acetylacetonate and dibutyltin diacetate to synthesize tindoped In_2O_3 having different deposition rate (275–350 °C). The one prepared by using *tert*-butoxymethyl indium as the precursor had the lowest deposition temperature while incorporation of tin doping was more efficient with the use of dibutyltin diacetate (Szkutnik et al. 2013). Other investigations involving the use of indium(III) complexes for synthesizing indium(III) oxides are shown in Table 2.

Indium (III) complexes as a precursor of indium sulfide

Indium sulfides have several unique properties, structures and composition. One of these properties is that it has three stoichiometric phases (In_6S_7 , In_2S_3 and InS) (Demir et al. 2021; Jingjing Zhang et al. 2019). Out of these three InS has the highest band gap energy (~2.44 eV) while In_6S_7 has the lowest band gap energy (~0.93 eV). Even though the band gap energy of In_2S_3 (2.0~2.3 eV) is higher than that of In_6S_7 (Gunavathy et al. 2023), it is the most popular among the three stoichiometric phases. The reason is because it has good stability, good photoelectric properties and unique crystalline structures (Jingjing Zhang et al. 2019). Indium sulfide nanoparticles have been investigated for a wide range of applications including oxygen reduction reaction, oxygen evolution reaction, hydrogen evolution reaction and photocatalysis. The need for the indium sulfide to be utilized for various applications requires the use of sulfur-containing indium complexes for their synthesis.

Different indium complexes have been subjected to high temperature to obtain indium sulfides. The change in temperature and the type of the indium complex can even affect the phase of the indium sulfide that are obtained. For instance, In₂S₃ was obtained when the dithiolate complex of indium was decomposed at 280 °C. On the other hand, InS was obtained when dibutyl-indium propylthiolates was decomposed under the same conditions (Nomura et al. 1989). Aryl thiolate also gave InS when decomposed but this was obtained at a relatively low temperature compared to the temperature required to decompose dibutyl-indium propylthiolates (Nomura et al. 1989). The polymeric precursor of 1,2-ethanedithiol and indium ether adduct has also been decomposed under inert conditions to obtain indium sulfide nanoparticles (D. P. Dutta et al. 2007). Apart from direct decomposition, indium organometallic chemical vapor deposition has also been reported for the synthesis of indium sulfide. These were carried out with or without catalyst or substrate (Afzaal et al. 2004). In an investigation, dimeric indium thiolates were subjected to different deposition temperatures. It was observed that the indium sulfide obtained varied with the temperature of decomposition. When the temperature was maintained between 290 and 350 °C, indium rich product (In/InS) was obtained. However, as the temperature was increased to 400 °C, the InS phase alone was obtained (MacInnes et al. 1993). Other thiol-indium complexes that have been used for synthesizing indium sulfides are methylindium(III) dithiolate complexes (Ghoshal et al. 2005) and Indium tris N-methylpiperazinylcarbodithioate (D Pahari Dutta et al. 2001), Generally, dithiocarbamate complexes are commonly used for synthesizing different binary, ternary and composite forms of indium sulfide nanoparticles. Examples of the investigations that utilized dithiocarbamate complexes as precursor for synthesizing sulfur-containing indium nanoparticles are shown in Table 3.

Table 2 Indium(III) complexes as precursor for indium oxide	indium oxide			
Indium precursors	Synthesis of precursors	Temperature for oxides synthesis	Temperature for Properties of the indium oxide oxides synthesis	References
Dialkylindium mono(alkoxide), $[Me_2In(OR)]_2$	HOCH ₂ CH ₂ NMe ₂ in toluene was reacted with Me ₃ In through aerosol assisted chemical vapor deposition	550 °C	Cubic crystalline In ₂ O ₃ phase; needle-like to spherical surface morphology; bandgap of 3.5-3.7 eV	Basharat et al. (2007)
Indium isopropoxide $(\ln(OC_3H_7)_3)$	Indium isopropoxide $(In(OC_3H_7)_3)$ powders was dissolved in ethanol, dropped on a sap- phire substrate then spun at 1000–3000 rpm	500 °C	Cubic structure; crystallite size of 35 nm	Cantalini et al. (2000)
Homoleptic indium alkoxide $(In(O-2,6-i-Pr_2C_6H_3)_3(H_2N-t-Bu)_2)$	Reaction of 2,6-diisopropylphenol In[N-t- Bu(SiMe ₃)] ₃	500 °C	Resistivities of 9.1 × 10^{-4} Ω;	Suh and Hoffman (2000)
Indium (III) tris(2,2,6,6-tetramethyl-3,5-hep- tanedionato)	I	230 °C	Cubic bixbyite phase of Bi_2O_3	Venkat et al. (2008)
Tris(1-phenyl-1,3-pentanedionato) In(III)	Reaction of 1-benzoylacetone with indium nitrate and aqueous ammonia under alkaline conditions	I	1.47 as [O]: [In] ratio; Cubic polycrystalline phase of In ₂ O ₃	Buono-Core et al. (2005)
Tris(2,2,6,6-tetramethyl-3,5-heptanedionato) indium(III)	I	100-400 °C	Polycrystalline cubic structure of In ₂ O ₃ ; resistivity of 2.5–3 mΩ·cm; refractive index of 2.01–2.05	Ramachandran et al. (2015)
Indium cyclopentadienyl	1	500 °C	mean size of 400 \pm 40 nm; mean diameter of 16.6 \pm 2 nm;	Soulantica et al. (2003)

Precursor	Indium sulfide syn- thesized	Reaction conditions	Properties	Applications	References
Indium(III) tris (<i>N</i> -methyl- <i>N</i> -etha- nol dithiocarbamate)	CuInS ₂	Microwave irradia- tion; ethylene glycol	Spherical grain-like shapes; minimum size of 10.3 nm; band gap of 2.87 nm	Tetracycline degrada- tion	Onwudiwe et al. (2023)
Indium(III) die- thyl dithiocarbamate	In:SnO ₂ /La ₃ InS ₆	Ultrasonication and spin-coating	Flowery flakes; band gap was 4.2 eV	Photoelectrode	Gul et al. (2023)
Indium(III) butyl dithiocarbamate	CdS/In ₂ S ₃	Addition of thiourea solution; PH 3; 400 °C	-	Solar cells	van Embden et al. (2020)
Indium(III)dithiocar- bamate	ZnIn ₂ S ₄	500 °C; argon gas for inert atmosphere	Absorb under visible region; band gap energy of 2.37 eV; photocurrent density 2.27 mA.cm ⁻²	Solar cells	Daraz et al. (2020)
Indium(III) diethyl dithiocarbamate	In_2S_3 quantum dots	Addition of 1-octa- decene, n-dode- canethiol and oleylamine; 230 °C	Average size of 6 ± 2 nm; 3.65 eV band gap energy	Photodetector devices	S. Ghosh et al. (2016)

 Table 3
 Synthesis of indium-based sulfides using indium dithiocarbamate precursors

Indium(III) complexes as a precursor of indium tellurides and selenides

Tellurides and selenides of indium are drawing attention because of their photo conducting properties and memory effects (Peranantham et al. 2007). One of the strategies that has been adopted for their synthesis is thermal decomposition of indium(III) complexes containing tellurides or selenides. For example, NaSeC₅H₃(Me-₃)N was treated with InCl₃ to obtain a novel complex of indium. Thermolysis of the indium complex at 230 °C led to the synthesis of indium selenide (In_2Se_3) . When the copper complex of NaSeC₅H₃(Me-₃)N was thermolyzed along with the obtained indium complex of NaSeC₅H₃(Me-₃)N at the ratio of 1:1, CuInSe₂ was obtained the temperature was maintained at 300 °C for 10 min. Oleylamine, tri-n-octylphosphine oxide and hexadecylamine were used as the capping agents (Sharma et al. 2013). Indium chalcogenides containing both selenium and sulfur has also been synthesized from indium complexes. The indium complex used for the investigation was made from aminothiolate ligands and indium chloride. The second complex was made from KSeCN and aminothiolate ligands. These two complexes were mixed and decomposed at high temperature which led to the formation of In₂Se₂S along with In₂S₃ (Joo-Hyun Park et al. 2020). Organic hybrid of indium tellurides has been made from telluride reactive precursors and indium(III). The organic hybrid prepared solvothermally are [Hmd] $[InTe_2]$, $[HDBU][InTe(Te_2)]$ and $[Hpip]_2$ $[In(en)_3][In_5Te_{10}]$ where md = 2-methyl-1,3-diazinane; DBU = 1,8-diazabicyclo-[5.4.0]undec-7-ene; pip=piperazine; and en=ethylenediamine (Xiao et al. 2021).

Indium(III) complexes as precursor for other indium compounds

Apart from the chalcogenides of indium(III), other compounds of indium have been synthesized by using indium(III) complexes. Example is the synthesis of highly crystalline indium arsenide by using $[((MeInAs^{t}Bu)_{3})_{2}(Me_{2}InAs(^{t}Bu))_{3})_{3}(Me_{2}InAs(^{t}Bu))_{3})_{3}(Me_{2}InAs(^{t}Bu))_{3})_{3}(Me_{2}InAs(^{t}Bu))_{3})_{3}(Me_{2}InAs(^{t}Bu))_{3})_{3}(Me_{2}InAs(^{t}Bu))_{3})_{3}(Me_{2}InAs(^{t}Bu))_{3})_{3}(Me_{2}InAs(^{t}Bu))_{3})_{3}(Me_{2}InAs(^{t}Bu))_{3})_{3}(Me_{2}InAs(^{t}Bu))_{3})_{3}(Me_{2}InAs(^{t}Bu))_{3})_{3}(Me_{2}InAs(^{t}Bu))_{3})_{3}(Me_{2}InAs(^{t}Bu))_{3})_{3}(Me_{2}InAs(^{t}Bu))_{3})_{3}(Me_{2}InAs(^{t}Bu))_{3})_{3}(Me_{2}InAs(^{t}Bu))_{3})_{3}(Me_{2}InAs(^{t}Bu))_{3}(Me_{2}InAs(^{t}Bu))_{3})_{3}(Me_{2}InAs(^{t}Bu))_{3}(Me_{2}InAs(^$ H)₂] as a single source precursor via a chemical vapor deposition assisted with aerosol. During this synthesis, it was observed that there was partial oxidation of the film surface which was no longer there when etch profiling was carried out. This synthesis was carried out at a temperature of 450 °C and the material obtained has carrier mobility and resistivity of 410 cm² V⁻¹ s⁻¹ and $3.6 \times 10^{-3} \Omega$ cm, respectively (Marchand et al. 2016). In another investigation, quantum dots of indium arsenide was successfully prepared from the dimer of [^tBu₂AsInEt₂]₂ precursor. The single source precursor was subjected to 280 °C with hexadecylamine as the capping agent. As shown by photoluminescence spectra, the indium arsenide produced had a good quantum yield (Malik et al. 2005). Nanocrystals of indium phosphide-based nanocomposite (InP/In₂O₃ core/shell) has been successfully prepared by using indium(III) carboxylates as the precursor. The preparation was carried out by using different amines(N-(4-aminophenyl)-N'-(4-nitrophenyl)benzene-1,4-diamine, ethane-1,2-diamine and hexane-1,6-diamine) as the capping agents. It was observed that the synthesis carried out with N-(4-aminophenyl)-N'-(4-nitrophenyl)benzene-1,4-diamine gave a product that the spectral magnetic and conductivity properties can be engineered easily compared to when other capping agents were used as the capping agents (Gabka et al. 2014). Asides composite of indium phosphide, pristine

indium phosphide had been made through heat-up method using indium diorganophosphide in hot 4-ethylpyridine as a precursor. As shown by the thermal studies, the process of its formation involved β -hydrogen elimination and reductive elimination (Green and O'Brien 2004).

Application of indium complexes as sensors

Indium(III) complexes have also been used for sensing different substances. One of the studies focused on the selective sensing of HSO_4^- (in the presence of PF_6^- , SCN^- , PO_4^{3-} , CH₃COO⁻ and halide ions) that is present in the blood of human. Indium(III) complex of N, N'-bis(salicylidene)ethylenediamine was used for the investigation. The selective sensing was a success without the interference of other ions except acetate. It was also observed that at increased concentration of HSO₄⁻, the fluorescence intensity of the complex was quenched (Huerta-José et al. 2019). The sensing of rutin present in the buckwheat tea has also been achieved by using reduced graphene oxide decorated with tetramine phthalocyanine indium. The material was used as the electrode material, and it showed a detection limit of 2.0 nM with 0.005-100 µM rutin concentration range. In addition, the reproducibility and selectivity of the material was very good. This shows that the presence of this non-covalent functionalized indium complex worked well as a good sensor (Shi et al. 2022).

Application of indium complexes as an organic light-emitting diodes (OLEDs)

Indium(III) complexes, such as indium(III) tris(2-phenylpyridine) (In(ppy)3), are widely used as emitting materials in OLEDs (Lan et al. 2023). These complexes exhibit high electroluminescence efficiency and can emit light in a range of colors, making them suitable for display and lighting applications (Yan et al. 2021). Indium(III) complexes have found significant application in organic light-emitting diodes (OLEDs). There are different types of OLEDs displayed technology that involves thin organic layers to emit light when an electric current passed through. These complexes play essential roles in different layers of OLED devices. For instances, in emissive layer, the emissive layer of OLEDs contains organic materials that emit light when excited by an electric current. Indium(III) complexes, such as indium(III) tris(2-phenylpyridine) (In(ppy)3), have been widely used as phosphorescent emitters in OLEDs (Dang et al. 2018). These complexes exhibit excellent electroluminescent properties, including high emission efficiency, long operational lifetime and broad color tenability (Kaur et al. 2019). Likewise, in the electron transport layer (ETL), which responsible for facilitating the efficient injection and transport of electrons from the cathode to the emissive layer. Indium(III) complexes, such as indium(III) bis(8hydroxyquinoline) (In(q)2), have been employed as electron transport materials in OLEDs (Reddy et al. 2012). These complexes possess suitable energy levels and high electron mobility, enabling efficient electron injection and transport. Also, in hole transport layer (HTL), which is responsible for facilitating the efficient injection and transport of holes from the anode to the emissive layer (Jang and Jang 2023). Although indium(III) complexes are less commonly used in this layer, they have been explored as potential HTL materials in OLEDs. Indium(III) complexes can exhibit suitable energy levels and hole transport properties, providing an alternative to traditional HTL materials. In exciton harvesting, Indium(III) complexes can also be employed in exciton harvesting layers in OLEDs. These layers are designed to capture and transfer energy from triplet excitons (formed through intersystem crossing) to the emissive layer, enhancing overall device efficiency. Indium(III) complexes, such as In(ppy)₃, have been utilized in this context due to their efficient triplet harvesting properties.

Application of indium complexes as a photovoltaics

Indium(III) complexes are employed in the fabrication of photovoltaic devices, including solar cells. These complexes can act as sensitizers or electron transport materials in dyesensitized solar cells (DSSCs) and perovskite solar cells, enhancing light absorption and charge transport properties. Indium(III) complexes have shown promising applications in photovoltaics, specifically in the field of organic photovoltaic (OPV) devices, OPVs utilize organic materials to convert sunlight into electricity (Li et al. 2023). For instance, as donor materials, Indium(III) complexes can serve as donor materials in OPVs. These complexes can be designed to have suitable energy levels and light-absorbing properties, allowing them to efficiently absorb photons from sunlight. Indium(III) complexes have been explored as light-harvesting materials in the active layer of OPVs, where they generate excitons (bound electron-hole pairs) upon light absorption (Yiu et al. 2022). As a Charge Transport Materials, Indium(III) complexes can also function as charge transport materials in OPVs. After the generation of excitons in the active layer, efficient charge separation and transport are crucial for the device's performance (Shen et al. 2021). Indium(III) complexes with appropriate energy levels and charge transport properties can facilitate the efficient movement of electrons or holes to their respective electrodes (cathode or anode) within the device. In interface engineering, Indium(III) complexes can be used to modify the interfaces between different layers in OPVs, optimizing charge extraction and reducing energy losses (Hu et al. 2022). For example, these complexes can be utilized as interfacial layers between the active layer and the electron

transport layer (ETL) or between the active layer and the hole transport layer (HTL). The presence of indium(III) complexes at these interfaces can improve charge extraction, enhance energy level alignment and minimize charge recombination losses. In tandem solar cells, Indium(III) complexes have been explored in the development of tandem solar cells, which are multijunction devices, composed of multiple subcells with different absorption characteristics (Andersen et al. 2014). By utilizing different indium(III) complexes with varying absorption properties, each subcell can harvest different regions of the solar spectrum, allowing for increased overall device efficiency. It is important to note that the development of indium(III) complex-based photovoltaic is an active area of research, and further optimization and exploration of these materials are ongoing. Additionally, indium is a relatively scarce and expensive element, which has led to the exploration of alternative materials in photovoltaics. Nevertheless, indium(III) complexes offer unique properties and have the potential to contribute to the advancement of efficient and cost-effective OPV technology.

Application of indium complexes in building luminescent materials

Indium(III) complexes are used in the development of luminescent materials, such as phosphors and scintillators. These materials find applications in lighting, display technologies, radiation detection and imaging. Indium(III) complexes have found numerous applications in the field of luminescent materials, where their unique properties enable the generation and control of light emission (Yam et al. 2020). For instance, in phosphors, Indium(III) complexes have been extensively employed as phosphors in various lighting and display technologies. These complexes can emit light efficiently when excited by an external energy source, such as ultraviolet (UV) or visible light (Kalinowski et al. 2011). They exhibit broad emission spectra, covering a wide range of colors, and can be tuned by modifying the ligands or coordination environment around the indium(III) ion. Indium(III) phosphors are commonly used in light-emitting diodes (LEDs), fluorescent lamps and plasma display panels to produce vibrant and energy-efficient light. In LED emitters, Indium(III) complexes are widely utilized as emitters in organic light-emitting diodes (OLEDs) (Pode 2020). These complexes possess excellent electroluminescent properties, including high quantum efficiency and color purity. By incorporating indium(III) complexes into the emissive layer of OLEDs, they can efficiently convert electrical energy into light emission. The unique coordination chemistry and ligand design enable the fine-tuning of their emission wavelength, facilitating the production of OLED displays with a wide range of colors. In biological imaging, Indium(III) complexes have applications in luminescent probes for biological imaging (Pashaei et al. 2019). These complexes can be functionalized with specific targeting moieties, such as peptides or antibodies, to selectively bind to biological targets of interest. When excited with light, the indium(III) complexes emit luminescence that can be detected and visualized using specialized imaging techniques. This enables the visualization and tracking of specific biomolecules or cellular processes, contributing to biomedical research and diagnostics. In security marking, Indium(III) complexes have been employed as luminescent markers in security and anti-counterfeiting applications. These complexes can exhibit unique emission properties, such as long fluorescence lifetimes or specific emission colors, making them ideal for covert marking and authentication purposes (Agrawal et al. 2022). By incorporating indium(III) complexes into inks or coatings, they can be applied to various objects or documents, providing a means of quick and reliable identification under specific lighting conditions. In sensitized solar cells, Indium(III) complexes have been investigated as sensitizers in dye-sensitized solar cells (DSSCs) (Khan et al. 2017). In DSSCs, the indium(III) complexes capture photons and transfer the energy to a semiconductor electrode, initiating the conversion of light into electricity (Khan et al. 2017). The unique electronic and optical properties of indium(III) complexes can contribute to enhancing light absorption and charge generation, leading to improved DSSC performance (Khan et al. 2017). These are just a few examples of the applications of indium(III) complexes in luminescent materials. The versatility of indium(III) complexes and their tunable properties make them valuable components in various luminescent devices and systems. Ongoing research continues to explore new ligand designs and applications, aiming to further advance the field of luminescent materials.

Application of indium complex in medicinal chemistry

Some Indium(III) complexes have shown promising biological activities and are investigated for their potential use in medicinal applications especially in medicinal chemistry and pharmaceutical research. For example, in cancer therapy, Indium(III) complexes have been investigated for their potential anticancer properties. Some indium(III) complexes have shown cytotoxic activity against cancer cells in in vitro studies (Leitao et al. 2023). These complexes can induce cell death mechanisms such as apoptosis and inhibit cancer cell proliferation. Additionally, indium(III) complexes can be designed to selectively target cancer cells while sparing normal cells, offering potential for more targeted and less toxic cancer therapies (Worm et al. 2020). Certain complexes have exhibited anticancer activity by targeting specific enzymes or pathways in cancer cells. In Imaging Agents, Indium-111 (In-111), a radioactive isotope of indium, is widely used

in nuclear medicine for diagnostic imaging. Indium(III) complexes can be chelated with various ligands, such as DTPA (diethylenetriaminepentaacetic acid) or DOTA (1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid), to form stable radiopharmaceuticals for single-photon emission computed tomography (SPECT) imaging (Blower et al. 2019). These complexes can be used to visualize and detect specific targets or tissues in the body, aiding in the diagnosis and monitoring of diseases. In targeted drug delivery, Indium(III) complexes can be utilized as targeting moieties in drug delivery systems. By conjugating indium(III) complexes to therapeutic agents or nanoparticles, targeted delivery to specific tissues or cells can be achieved. The high affinity of indium(III) for certain receptors or biomolecules allows for precise targeting, improving the therapeutic efficacy and minimizing off-target effects. In antimicrobial agents, Indium(III) complexes have also been explored as antimicrobial agents against bacteria, fungi and viruses. Certain indium(III) complexes have exhibited antimicrobial activity, inhibiting the growth or killing pathogens (Yam et al. 2020). These complexes can be further modified to enhance their efficacy and selectivity against specific pathogens, providing opportunities for the development of new antimicrobial agents. It is important to note that the development and application of indium(III) complexes in medicinal chemistry are still at a relatively early stage. Further research is required to optimize their properties, improve efficacy and assess their safety profiles. Nonetheless, indium(III) complexes hold promise as potential tools for imaging, targeted drug delivery, cancer therapy and antimicrobial applications in the field of medicinal chemistry.

Conclusion and future perspectives

In conclusion, the review has concisely explored the multifaceted applications of indium(III) complexes by highlighting their relevance in organic catalysis, synthesis of chalcogenides materials and other industrial processes. The unique properties of indium, its versatile coordination chemistry, and its scarcity on Earth have contributed to its crucial role in coordination chemistry and materials science. Specifically, the associated versatility of indium(III) complexes in catalyzing organic transformations, ranging from C-C bond formation to asymmetric synthesis, was emphasized, noting that their Lewis acid behavior and stability in aqueous systems as a stand out property, which makes them advantageous over other metals like zinc and tin. Furthermore, the detailed examination of indium triflate's catalytic activities in various reactions was noted to underscore its effectiveness in promoting diverse organic transformations. Another significant advantage which underscored the recent rise in the synthesis of these compounds is their usefulness in the

controlled synthesis of indium chalcogenides and oxide nanoparticles, which highlighted their importance in material science. This ability has been found to allow for the finetuning of size, composition and morphology of these resulting nanomaterials, showcasing their exceptional possibilities of indium complexes in preparing advanced materials for applications in sensing, photovoltaics and optoelectronics. Consequently, this review explored the role of indium complexes in the synthesis of various indium nanomaterials such as indium sulfides, selenides, tellurides and arsenides, investigating their roles and usefulness in sensors, organic light-emitting diodes (OLEDs), photovoltaics and luminescent materials, which further emphasized the wideranging impact of these complexes across different scientific and technological domains. The discussion in the medicinal chemistry realm was also explored, as certain indium(III) complexes have shown promising biological potential as therapeutic agents. Hence, their potential and usage in cancer therapy, imaging agents and targeted drug delivery proved these complexes' versatility in different fields of life, including healthcare and diagnostics.

The various examinations of indium(III) complexes presented in this review underscore their importance as versatile and indispensable compounds in coordination chemistry, materials science, catalysis and various industrial applications. Therefore, as research continues, indium(III) complexes remain poised to advance scientific knowledge and technological innovation.

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Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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